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DISSERTATION

SYNTHESIS AND CHARACTERIZATION OF QUATERNARY GROUP XIV AND XV RARE-EARTH CHALCOGENIDES

Submitted by

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In partial fulfillment of the requirements

for the Degree of Doctor of Philosophy

Colorado State University

Fort Collins, Colorado

Summer 2001

COLORADO STATE UNIVERSITY

June 5, 2001

WE HEREBY RECOMMEND THAT THE DISSERTATION PREPARED UNDER OUR SUPERVISION BY CARL RICHARD EVENSON IV ENTITLED "SYNTHESIS AND CHARACTERIZATION OF QUATERNARY GROUP XIV AND XV RARE-EARTH CHALCOGENIDES" BE ACCEPTED AS FULFILLING IN PART REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY.

Committee on Graduate Work

Advisor

Department Head

ABSTRACT OF DISSERTATION

Synthesis and Characterization of Quaternary Group XIV and XV Rare-Earth Chalcogenides

The reactive flux method of solid-state synthesis has been used to synthesize a variety of new rare-earth chalcogenide materials. Five selenophosphate and seven thiophosphate compounds have been synthesized including $K_2La(P_2Se_6)_{1/2}(PSe_4)$, $K_3La(PSe_4)_2$, $K_4La_{0.67}(PSe_4)_2$, $K_{9-x}La_{1+x/3}(PSe_4)_4$ (x = 0.5), $KEuPSe_4$, $KLaP_2S_6$, $K_2La(P_2S_6)_{1/2}(PS_4)$, $K_3La(PS_4)_2$, $K_4La_{0.67}(PS_4)_2$, $K_{9-x}La_{1+x/3}(PS_4)_4$ (x = 0.5), $K_4Eu(PS_4)_2$, and $KEuPS_4$. By controlling experimental conditions, these structures can be placed in quasi-quaternary phase diagrams, which show the reaction conditions necessary to obtain a particular chalcophosphate compound. This group XV chemistry has been extended to group XIV chemistry by the substitution of silicon, germanium, or tin in place of phosphorus. Three new crystal structures have been found; K_2EuTSe_5, $KEuTS_4$ (T = Si, Ge), and $Eu_8Sn_4Se_{20}$. Finally, we have synthesized a series of compounds to investigate how the size of alkali-metal and rare-earth metal cations affect a given structure type. $K_2Y(P_2S_6)_{1/2}(PS_4)$, $K_2Y(P_2Se_6)_{1/2}(PSe_4)$, $Cs_2Y(P_2S_6)_{1/2}(PS_4)$, $Cs_2Y(P_2Se_6)_{1/2}(PSe_4)$, $Cs_2La(P_2S_6)_{1/2}(PS_4)$, and $Cs_2La(P_2Se_6)_{1/2}(PSe_4)$ have been synthesized and are compared to $K_2La(P_2S_6)_{1/2}(PS_4)$ and $K_2La(P_2Se_6)_{1/2}(PSe_4)$. All compounds are characterized with single crystal x-ray diffraction and can be characterized further with Raman spectroscopy, UV-Vis optical band-gap analysis, and fluorescence spectroscopy.

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Chapter One

Introduction:

Synthesis of Solid-State Chalcogenide Compounds

The Group XVI elements sulfur, selenium and tellurium are commonly referred to as the chalcogenides. While in the same chemical group as oxygen, the chalcogenides as a group possess properties significantly different than oxygen. Table 1.1 lists some of the periodic properties of the chalcogenides. Unlike oxygen, for example, the chalcogenides tend to undergo catenation to form chalcogen-chalcogen bonds. As an example, the most stable form of sulfur is S_8, which exists as a ring with a S-S bond distance of 2.06 Å.[1] Properties of the chalcogenides vary while moving down group XVI. All three chalcogenides can be considered oxidizing agents, although their oxidizing ability is less than oxygen and decreases going down the group. Also, tellurium is slightly metallic whereas sulfur and selenium are considered non-metallic. All three chalcogenides undergo a variety of reactions with more electropositive elements including alkali and alkaline-earth metals, transition metals, and rare-earth elements.

The ability of chalcogenides to bond to themselves and to other elements is one of the reasons they have been extensively researched. Chalcogenides have been used in the solid-state synthesis of binary, ternary, and quaternary compounds. Several reviews of chalcogenide chemistry within organic, inorganic, organometallic, and solid-state synthesis shows the wide variety of oxidation states and coordination environments available for sulfur, selenium, and tellurium.[2-4] Binary compounds such as MoS_2 exist as minerals and are quite abundant. More complex ternary and quaternary solid-state compounds and materials can be synthesized in the laboratory using several different synthetic techniques. These reactions are designed to yield stable compounds with desirable properties.

Table 1.1. Properties of the chalcogens.

Element	Electronic Structure	Melting Point (°C)	Radius $(X)^{2-}$ (Å)	Covalent Radius (Å)	Electronegativity
S	$[Ne]3s^2 3p^4$	119	1.70	1.03	2.44
Se	$[Ar]3d^{10}4s^2 4p^4$	221	1.84	1.17	2.48
Te	$[Kr]4d^{10}5s^2 5p^4$	450	2.07	1.37	2.01

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Industrially important properties are some of the reasons why chalcogenide chemistry continues to be an active area of research. Novel chalcogenide compounds and materials display a wide variety of properties including unique semi-conducting properties, optical, thermoelectric, catalytic, magnetic, and superconducting properties. Transition metal sulfides are known to posses magnetic properties, but they can also be used as hydrodesulfurization catalysts.[5,6] Solar cell research includes investigation into binary materials such as CdS or CdTe [7] as well as ternary materials like $CuInSe_2$.[8] HgCdTe materials are used as photoconductive detectors.[9,10] Finally, an active area within thermoelectric research currently focuses on ternary and quaternary chalcogenides such as $CsBi_4Te_6$, $K_2Bi_8S_{13}$, and $Eu_2Pb_2Bi_6Se_{13}$.[11]

This research project has focused on the solid-state synthesis of quaternary rare-earth metal (RE) chalcogenide compounds containing anionic main-group-element chalcogenide building blocks coordinated to rare-earth metal cations. These rare-earth metal compounds are relatively scarce in the published literature and we would therefore like to develop a broader understanding of what properties are possessed by these compounds. To achieve this goal, one first needs to understand how to synthesize these complex compounds. In general, when more elements are added to a solid-state reaction mixture it is more difficult to obtain well formed crystalline products with desirable and predictable properties.

Several synthetic techniques are used to synthesize solid-state chalcogen compounds including the high temperature stoichiometric combination of reactants and reactive flux chemistry. High-temperature reactions are useful for the synthesis and simple binary and ternary compounds, but to obtain more complex products flux

reactions are more commonly used. Flux reactions utilize the combination of specific element(s) and/or compound(s) to form a "solvent" that provides an oxidizing environment for the other elements in a particular reactant mixture. In general, this "solvent" exists as a liquid only at temperatures between 350°C and 850°C. This temperature range seems relatively high, but is much lower than the high temperatures often needed in stoichiometric reactions (>1200°C). The reactive flux method of solid-state synthesis was developed by the Ibers group at Northwestern University in the synthesis of $K_4Ti_3S_{14}$,[12] and since then has been investigated extensively by the Dorhout group and others.[13-16]

The Dorhout group is interested in synthesizing quaternary compounds composed of an alkali-metal cation, a rare-earth metal cation, and anionic polychalcophosphate building blocks. Different polychalcophosphate units are stabilized within the flux and coordinate well to RE cations. Figure 1.1 shows a few of the possible polychalcophosphate units.[17] Some units such as $(P_2Q_6)^{4-}$ and $(PQ_4)^{3-}$ (Q= S, Se) seem to be very stable and are observed in many different structures while other units such as $(PQ_5)^{3-}$ and $(P_2Q_7)^{4-}$ are much rarer. The reason why one unit forms over another under certain reaction conditions has not been fully understood.

The literature on transition metal polychalcophospate compounds is quite extensive,[18-33] but lanthanide and actinide compounds have received much less attention. Only a few quaternary rare-earth metal selenophosphate structures have been reported including: $K(RE)P_2Se_6$ (RE = Y, La, Ce, Pr, Gd),[34] $K_3CeP_2S_8$,[35] $A_2(RE)P_2Se_7$ (A = Rb, Cs; RE = Ce, Gd),[36] and $K_4Eu(PSe_4)_2$.[20]

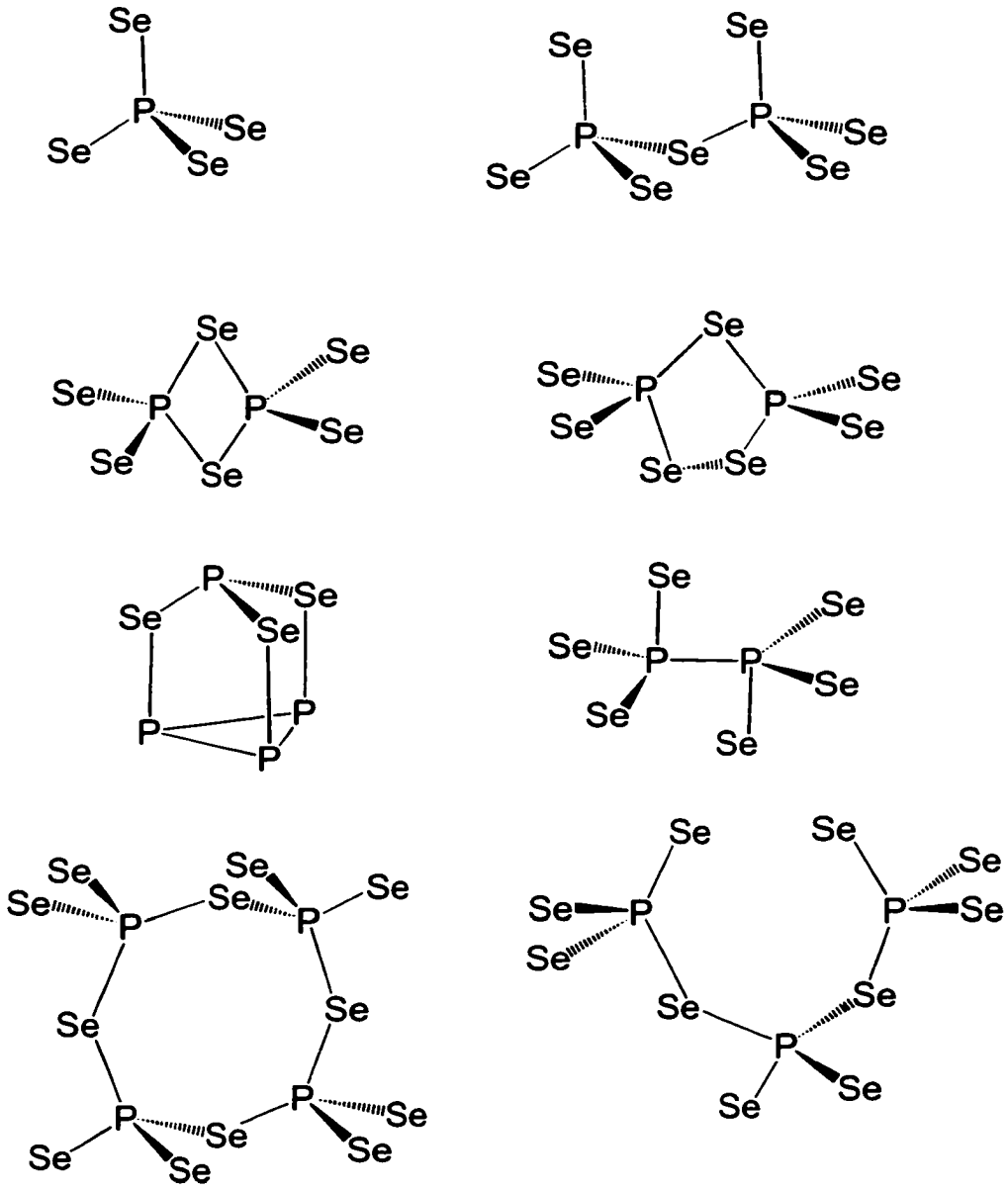


Figure 1.1. Possible $(P_xSe_y)^{z-}$ building blocks; $(PSe_4)^{3-}$, $(P_2Se_7)^{4-}$, $(P_2Se_6)^{2-}$, $(P_2Se_7)^{2-}$, $(P_4Se_3)^{6+}$, $(P_2Se_6)^{4-}$, $(P_4Se_{12})^{4-}$, and $(P_3Se_{10})^{5-}$.

The reactive flux method offers many advantages over traditional high temperature synthesis for the synthesis of the compounds listed above. It has already been mentioned that these reactions can be done at a lower temperature. Elements such as lanthanum and europium have melting points above 1000°C, but using the reactive flux method allows the same reactions to be done at 525°C to 725°C. The reactive flux provides a very oxidizing environment towards lanthanum or europium and these elements are brought into solution as they are oxidized by the flux.

A second advantage offered by the reactive flux method is increased diffusion of reactants within the flux. Just as a room temperature solvent increases the diffusion of reactants in a typical organic reaction, the solid-state flux performs the same function, albeit at a higher temperature. This allows the chemist to reduce the reaction time needed to obtain a uniform reaction product.

Finally, the reactive flux provides a highly charged medium that stabilizes the formation of ionic species within the flux. Both cationic and anionic species are stabilized until they are included into a crystalline reaction product as the reaction slowly cools back to room temperature.

As its name implies, the reactive flux involves more than simply adding a compound to a particular reaction mixture to promote crystal growth. The flux itself is also reactive, meaning that components of the flux, such as polysulfides or selenides, react to form new species that are included in the desired crystalline product.

The Dorhout group utilizes fluxes that are composed of elemental sulfur or selenium and a variety of potassium chalcogenide salts such as K_2Se, K_2Se_4, and

K_2S_2. These alkali-metal chalcogenides have melting points ranging from 205°C for K_2Se_4 to above 500°C for K_2Se.[14] The combination of chalcogen and alkali-metal chalcogenide salt provides a very oxidizing environment for the other reactants. Typically a reaction contains either lanthanum or europium as the elemental rare-earth element, and an elemental main group element. Lanthanum was chosen as a typical 3+ rare-earth element, and europium was chosen because of its optical properties and its tendency to exist as a 2+ cation.

A typical reaction is shown in Equation 1.1:

$$K_2Se_4 + 7Se + 2P + La \xrightarrow{725^\circ C} KLaP_2Se_6 + \text{excess flux} \qquad \textbf{1.1}$$

For a typical reaction, reactants are loaded into a fused silica ampoule inside an inert atmosphere glovebox. The ampoule is then flame sealed under vacuum and placed inside a computer controlled tube furnace. The furnace is ramped to 725°C and held at that temperature for 150 hours. This long reaction time ensures that the reaction reaches thermodynamic equilibrium. The furnace is then slowly cooled at 4°C/hr back to room temperature. A slow cooling time is used to allow good crystalline growth of the thermodynamic products. The desired product in these reactions is a quaternary compound such as $KLaP_2Se_6$.

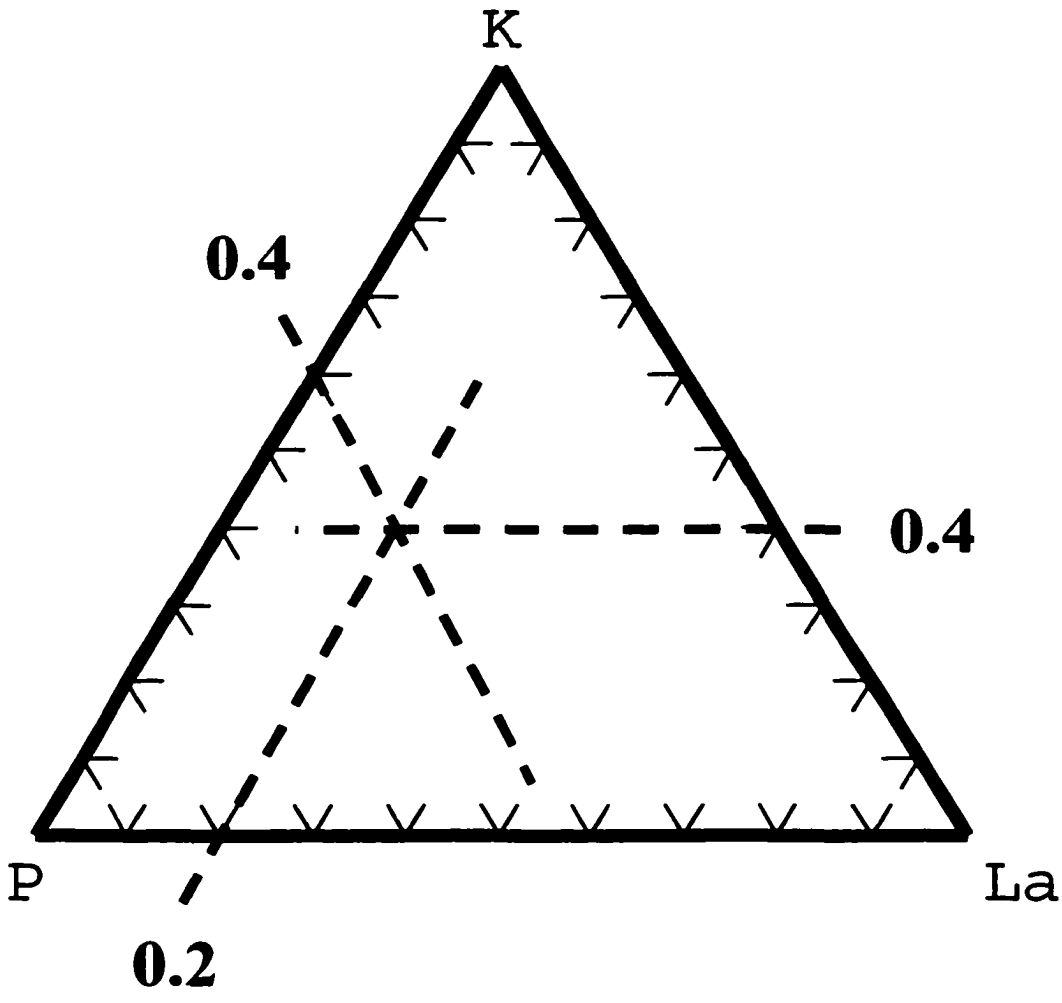
One important feature of the reactive flux is that stoichiometric products based on initial reaction stoichiometries are not found since we include the flux agent as a reactant. If this were the case, the reaction written in Equation 1.1 would give a product with the formula $K_2LaP_2Se_{11}$. Instead, the crystalline product has the formula

$KLaP_2Se_6$ and is mixed with amorphous excess flux. This excess flux can be removed from the crystalline product with an appropriate solvent. Dimethylformamide is the solvent most commonly used.

$KLaP_2Se_6$ was synthesized in the Dorhout group in 1995 [37] and was the first quaternary rare-earth polyselenophosphate reported in the literature. $KLaP_2Se_6$ is a layered structure with La(III) cations linked together by $(P_2Se_6)^{4-}$ "ethane-like" anionic units. Layers are separated from each other with potassium cations. Soon after $KLaP_2Se_6$ was reported, several research groups reported additional quaternary compounds including $K_4Eu(PSe_4)_2$,[20] $Rb_2Ce(P_2Se_6)_{1/2}(PSe_4)$,[36] $Rb_3Ce(PSe_4)_2$,[36] $Rb_9Ce(PSe_4)_4$,[38] and $K_3Ce(PS_4)_2$.[35] These six compounds were synthesized under unique reaction conditions. Some compounds contain the polychalcophosphate unit $(P_2Se_6)^{4-}$ while other compounds contain the tetrahedral unit $(PQ_4)^{3-}$ (Q = S, Se), and in $Rb_2Ce(P_2Se_6)_{1/2}(PSe_4)$, we find both of these building blocks in the same compound. There was very little explanation in the literature as to why these different polychalcophosphate units formed under different reaction conditions. One explanation put forth by the Kanatzidis group is based on Lewis basicity.[15,36] This concept looks at the ratio of alkali-metal to chalcogen in the reactant mixture and can be applied to solid-state flux reactions in the following way. High temperature (> 350°C) alkali-metal polychalcophosphate fluxes contain $(Q_x)^{2-}$ chains (Q = S, Se, Te); for example, $(Se_{11})^{2-}$. In these chains, the terminal Q atoms have a formal charge of negative one while the internal Q atoms have a formal charge of zero. Since the terminal Q atoms can act as electron pair donors, changing the ratio of terminal Q atoms relative to the internal Q atoms can be used to vary the Lewis

basicity of the flux. In other words, for a given amount of Q, a greater number of shorter chains will have more terminal Q atoms and will therefore be more Lewis basic. This can be accomplished by increasing the amount of alkali metal in the flux. For example, if more potassium is present, a greater number of shorter $(Q_x)^{2-}$ chains must be present in the flux to compensate for the additional positive charge from the extra potassium cations. Kanatzidis *et. al.* found that a more Lewis basic flux leads to $(PSe_4)^{3-}$ units whereas less Lewis basic fluxes tend to yield crystalline products containing $(P_2Se_6)^{4-}$ units.

The Lewis basicity concept partially explains the different phases observed, but it does not take into account all elements present in the reaction mixture. It is the hypothesis of this dissertation that a more rational approach would take into account the relative concentrations of all elements present. The problem is that such an approach would require a quaternary phase diagram, not including the free variables temperature and pressure. In order to reduce the complexity of this phase space problem it was necessary to run each reaction at 725°C to make temperature a constant. In addition, the relative concentration of chalcogen in every reaction was held constant at approximately 70%. Finally, it was also assumed that the pressure in every reaction was constant. The three remaining variables were the relative concentrations of alkali metal, phosphorous, and rare-earth metal in each reaction. These relative concentrations were varied and plotted within a Gibbs-type ternary phase diagram, formally, a composition diagram. In this way, the ternary phase diagram represents a slice or layer of the quaternary (K/P/RE/Q) (Q = S, Se) phase diagram. Figure 1.2 shows a typical ternary phase diagram with the reaction in



$$K_2Se_4 + 7Se + 2P + La$$

$$K / (K + P + La) = 2/5 = 0.4$$
$$P / (K + P + La) = 2/5 = 0.4$$
$$La / (K + P + La) = 1/5 = 0.2$$

Figure 1.2. Ternary phase diagram with Equation 1.1 plotted as an example.

Equation 1.1 plotted as an example. It is important to note that the amount of chalcogen in these phase diagrams was not ignored. By keeping an equivalent relative amount of chalcogenide in every reaction, each ternary phase diagram represents a layer or slice of a quaternary phase diagram, as shown in Figure 1.3.

In Chapter 2, this phase diagram approach is applied to the synthesis of new potassium rare-earth polyselenophosphates including $K_2La(P_2Se_6)_{1/2}(PSe_4)$, $K_3La(PSe_4)_2$, $K_4La_{0.67}(PSe_4)_2$, $K_{9-x}La_{1+x/3}(PSe_4)_4$ (x = 0.5), and $KEuPSe_4$. Chapter 3 describes the same approach to the synthesis of the new thiophosphates $KLaP_2S_6$, $K_2La(P_2S_6)_{1/2}(PS_4)$, $K_3La(PS_4)_2$, $K_4La_{0.67}(PS_4)_2$, $K_{9-x}La_{1+x/3}(PS_4)_4$ (x = 0.5), $K_4Eu(PS_4)_2$, and $KEuPS_4$. These compounds are characterized with single crystal X-ray diffraction, Raman spectroscopy, optical band-gap analysis, and semi-microprobe EDS analysis. Each family of compounds can thus be described by a series of fundamental empirical formulae that have been used to predict new phases.

In Chapter 4, the issue of cation size is addressed. It has been previously observed that a smaller rare-earth cation can affect the packing within a solid-state structure. This change in structure can subsequently affect important properties possessed by that particular compound. In this case, the phase diagram concept developed in Chapters 2 & 3 is used to determine the reaction conditions needed to yield specific compounds. The Dorhout Group and others have recently reported solid-state structures with the formula $A_2REP_2Q_7$ where A is an alkali-metal cation, RE is a rare-earth cation, and Q is sulfur or selenium.[35,36,39,40] The series of compounds $A_2RE(P_2Q_6)_{1/2}(PQ_4)$ (A = K, Cs; RE = Y, La; Q = S, Se) have been

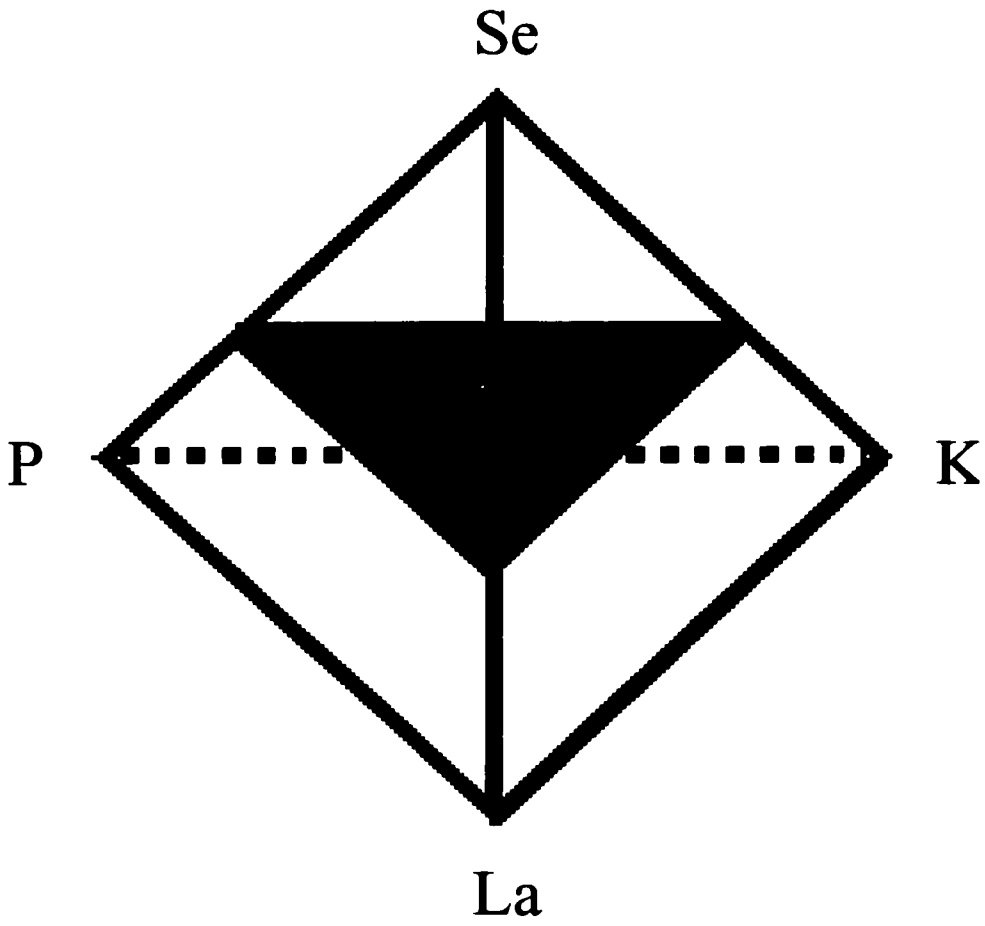


Figure 1.3. Quaternary phase diagram for K/P/La/Se system. Ternary K/P/La phase diagram is shaded.

synthesized in an effort to further investigate the effects of alkali-metal and rare-earth metal cation size on the $A_2REP_2Q_7$ structure type.

Finally, in Chapter 5, several new crystalline products are discussed in the particular context of a reaction stoichiometry, where the identity of only one element at a time was allowed to vary. Specifically we examined quaternary europium chalcogenides with the group XIV elements silicon, germanium, and tin substituted in place of phosphorus. New compound were observed with features not previously observed in chalcophosphate chemistry. In K_2EuTSe_5 (T = Si, Ge), Se-Se bonding was observed, and in $KEuTS_4$, europium was found in the 3+ oxidation state. The new ternary phase $Eu_8Sn_4Se_{20}$ is reported as the product found in the equivalent reaction with tin. These compounds were characterized with Raman spectroscopy, UV-Vis optical band-gap analysis, and fluorescence spectroscopy.

In the future, this project will continue to investigate the synthesis of these types of compounds including developing the synthetic conditions need to obtain quaternary tellurium compounds. Specific properties inherent in these types of compounds will also be addressed. Using the synthetic approaches described in the following chapters, semi-conducting, optical, thermoelectric, and magnetic properties can be developed in solid-state industrial products.

Chapter Two

Selenophosphate Phase Diagrams Developed in Conjunction with the Synthesis of the New Compounds $K_2La(P_2Se_6)_{1/2}(PSe_4)$, $K_3La(PSe_4)_2$, $K_4La_{0.67}(PSe_4)_2$, $K_{9-x}La_{1+x/3}(PSe_4)_4$ (x = 0.5), and $KEuPSe_4$

Introduction

As described in Chapter 1, ternary phase diagrams can be used to describe the composition of crystalline products in a series of similar reactions as well as providing a road map for new exploratory synthesis. Two diagrams are reported here: one containing lanthanum as a general 3+ RE element, and the second containing europium, to establish the fundamental structural differences in these types of structures when a 2+ RE element is used in place of a 3+ RE element. Phases appearing in the K-La-P-Se and K-Eu-P-Se phase diagrams reported here, are the new compounds $K_2La(P_2Se_6)_{1/2}(PSe_4)$ **I**, $K_3La(PSe_4)_2$ **II**, $K_4La_{0.67}(PSe_4)_2$ **III**, $K_{9-x}La_{1+x/3}(PSe_4)_4$ (x = 0.5) **IV**, and KEuPSe4 **V**. Most of this chapter has appeared as a full paper in Inorganic Chemistry.[39]

Experimental Section

Synthesis: Crystals of all compounds observed were obtained using the same basic procedure. The following reactants were used as received and stored in an inert atmosphere glovebox: La (99.999%, Ames Laboratory), Eu (99.95%, Ames Laboratory), P (Mallinckrodt Red), Se (99.999%, Johnson-Mathey), and SrSe (99.5%, Cerac). K_2Se and K_2Se_4 were previously made in liquid ammonia from the stoichiometric combination of the elements.[41,42] Reactants were loaded into fused silica ampoules inside an inert atmosphere glovebox. Each ampoule was flame sealed under vacuum and placed in a temperature controlled tube furnace. The furnace was ramped to 725°C where it remained for 150 hours. The furnace was then allowed to

cool back to room temperature at 4°C/hr. Crystalline products were separated from excess flux with dimethylformamide (DMF).

$K_2La(P_2Se_6)_{1/2}(PSe_4)$, I, was prepared by reacting 38.4 mg (0.486 mmol) Se, 69.7 mg (0.181 mmol) K_2Se_4, 8.22 mg (0.265 mmol) P, and 12.3 mg (0.089 mmol) La. The reaction was carried out as described above yielding dark-yellow crystals.

$K_3La(PSe_4)_2$, II, was prepared by reacting 38.9 mg (0.493 mmol) Se, 139.0 mg (0.353 mmol) K_2Se_4, 13.1 mg (0.423 mmol) P, and 19.6 mg (0.141 mmol) La. The reaction was carried out as described above producing yellow crystals.

$K_4La_{0.67}(PSe_4)_2$, III, was prepared by reacting 19.4 mg (0.246 mmol) Se, 96.8 mg (0.246 mmol) K_2Se_4, 7.6 mg (0.246 mmol) P, 34.1 mg (0.246 mmol) La, and 20.5 mg (0.123 mmol) SrSe. Reactants were combined and reacted as described above. The finished reaction revealed yellow crystals. Sr was not included in the crystalline product.

$K_{9-x}La_{1+x/3}(PSe_4)_4$ (x = 0.5), IV, was prepared from the reaction of 82.3 mg (1.04 mmol) Se, 48.2 mg (0.307 mmol) K_2Se, 7.6 mg (0.245 mmol) P, and 17.0 mg (0.122 mmol) La. The reaction product contained dark yellow crystals.

$KEuPSe_4$, V, was obtained by reacting 39.8 mg (0.504 mmol) Se, 29.4 mg (0.0746 mmol) K_2Se_4, 4.6 mg (0.149 mmol) P, and 23.5 mg (0.155 mmol) Eu. Following the reaction procedure described above yielded dark-red crystals.

Physical Measurements

Single-Crystal X-ray Diffraction. Intensity data sets for crystals **I-V** were collected using a Bruker SMART CCD diffractometer. Each intensity data set was

integrated using SAINT,[43] a SADABS correction was applied,[44] and the structure was solved by direct methods using SHELXTL.[45] Crystallographic data for compounds **I-V** are reported in Table 2.1.

Raman Spectroscopy. The solid-state Raman spectrum of compounds **II-V** were taken with a Nicolet Magna-IR Spectrometer with a FT-Raman Module attachment using a Nd:YAG excitation laser (1064 nm).

UV-Vis. Spectroscopy. A diffuse reflectance measurement for $KEuPSe_4$ was taken with a Hitachi U-3501 Spectrophotometer using a 60 mm diameter integrating sphere accessory and $BaSO_4$ sample and reference plates. UV-Vis. diffuse reflectance data was converted to optical band gap data using the Kubelka-Munk function. [46,47]

Energy Dispersive Spectroscopy. Semi-quantitative microprobe analysis of compounds **III** and **IV** was performed on a Philips 505 scanning electron microscope (SEM) equipped with a Kevex Analyst 8000 Microanalyzer.

Results and Discussion

Crystal Structures

A single crystal of **$K_2La(P_2Se_6)_{1/2}(PSe_4)$ or $K_2LaP_2Se_7$, (I),** was selected, 8862 (3365 independent) reflections were collected, and an absorption correction was applied to a monoclinic cell (R_{int} = 0.0513). The structure was solved in $P2_1/n$ by direct methods to electron density residuals of 1.285 and -1.503 $eÅ^{-3}$, and all atoms refined anisotropically with SHELXTL using full-matrix least squares refinement on F^2 for 110 variables.[45] $K_2LaP_2Se_7$ is a layered structure containing quasi-infinite layers of $^2_\infty[La(P_2Se_6)_{1/2}(PSe_4)]^{2-}$ in the (101) plane of the unit cell. These layers are

Table 2.1. Crystallographic data for $K_2La(P_2Se_6)_{1/2}(PSe_4)$, $K_3La(PSe_4)_2$, $K_4La_{0.67}(PSe_4)_2$, $K_{9-x}La_{1+x/3}(PSe_4)_4$ (x=0.5) and $KEuPSe_4$.

	$K_2LaP_2Se_7$ (I)	$K_3La(PSe_4)_2$ (II)	$K_4La_{0.67}(PSe_4)_2$ (III)	$K_{9-x}La_{1+x/3}(PSe_4)_4$ (IV)	$KEuPSe_4$ (V)
fw	831.77	949.83	943.09	1881.42	537.87
a, Å	9.42690(10)	9.5782(2)	19.0962(2)	18.2133(1)	17.5156(11)
b, Å	7.20540(10)	17.6623(4)	9.14080(10)	38.0914(4)	7.0126(5)
c, Å	21.0276(5)	9.9869(3)	10.2588(2)	10.2665(1)	6.9015(4)
α, deg	90.0	90.0	90.0	90.0	90.0
β, deg	97.4840(10)	90.1200(10)	90.0	90.0	90.0
γ, deg	90.0	90.0	90.0	90.0	90.0
V, $Å^3$	1416.12(4)	1689.51(7)	1790.72(4)	7122.59(11)	847.71(9)
Z	4	4	4	8	4
λ(Mo Kα), Å	0.71073	0.71073	0.71073	0.71073	0.71073
Space Group	$P2_1/n$ #14	$P2_1/c$ #14	Ibam #72	Ccca #68	Pnma #62
Temp., K	298(2)	170(2)	159(2)	158(2)	170(2)
$\rho_{calc.}$, Mg/m^3	3.901	3.734	3.498	3.209	4.214
μ (mm^{-1})	21.775	20.657	18.957	18.919	25.150
R1 % [a]	4.29	4.76	3.53	5.43	2.37
wR2 % [a]	8.90	10.36	7.55	11.44	5.23

[a] $R1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ $\quad wR2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]]^{1/2}$

separated by 9-coordinate potassium atoms with an average K-Se distance of 3.592(9) Å. Figure 2.1 shows that each layer is comprised of "chains" of La-Se polyhedra coordinated by $(PSe_4)^{3-}$ tetrahedra. Along each chain, each $(PSe_4)^{3-}$ tetrahedron is coordinated to three different lanthanum atoms. Two La-Se polyhedra share a common vertex and share an edge with one $(PSe_4)^{3-}$ tetrahedron. The chain propagates via another corner-shared La-Se polyhedron and a shared $(PSe_4)^{3-}$ tetrahedron. These chains are linked together by $(P_2Se_6)^{4-}$ units to form a layer. Eight selenium atoms with an average La-Se distance of 3.141(3) Å coordinate each lanthanum atom in a distorted square anti-prism. Figure 2.2 shows the coordination environment around lanthanum in $K_2La(P_2Se_6)_{1/2}(PSe_4)$. Atomic coordinates and selected bond distances and angles for $K_2La(P_2Se_6)_{1/2}(PSe_4)$ can be found in Tables 2.2 and 2.3 respectively. Several other compounds with similar structures have been reported including $Cs_2TbP_2Se_7$ [48] $K_2CeP_2S_7$, [35] and $Rb_2CeP_2Se_7$ and $Cs_2GdP_2Se_7$.[36]

A single crystal of **$K_3La(PSe_4)_2$, (II),** was selected, 10987 (4059 independent) reflections were collected, and an absorption correction was applied to a monoclinic cell (R_{int} = 0.0478). The structure was solved in $P2_1/c$ by direct methods to electron density residuals of 2.658 and -1.607 $eÅ^{-3}$, and all atoms refined anisotropically with SHELXTL using full-matrix least squares refinement on F^2 for 127 variables.[45] The structure of $K_3La(PSe_4)_2$ consists of anionic $^1_\infty[La(PSe_4)_2]^{3-}$ chains that run along the x-axis of the unit cell. These chains are separated from each other along the y and z axes by potassium cations as shown in Figure 2.3. Three different potassium coordination environments are found with K-Se bond distances greater than 3.3 Å. Along the length of the chain, eight-coordinate dodecahedral

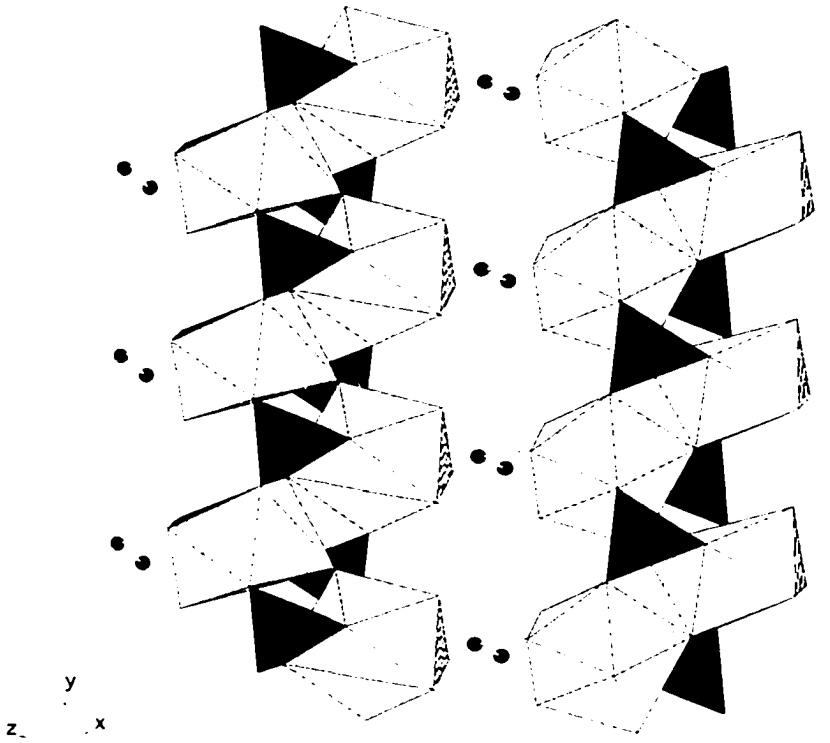


Figure 2.1. $K_2La(P_2Se_6)_{1/2}(PSe_4)$: Striped La-Se polyhedra, black $(PSe_4)^{3-}$ tetrahedra, black phosphorus atoms in $(P_2Se_6)^{4-}$, potassium atoms left out for clarity.

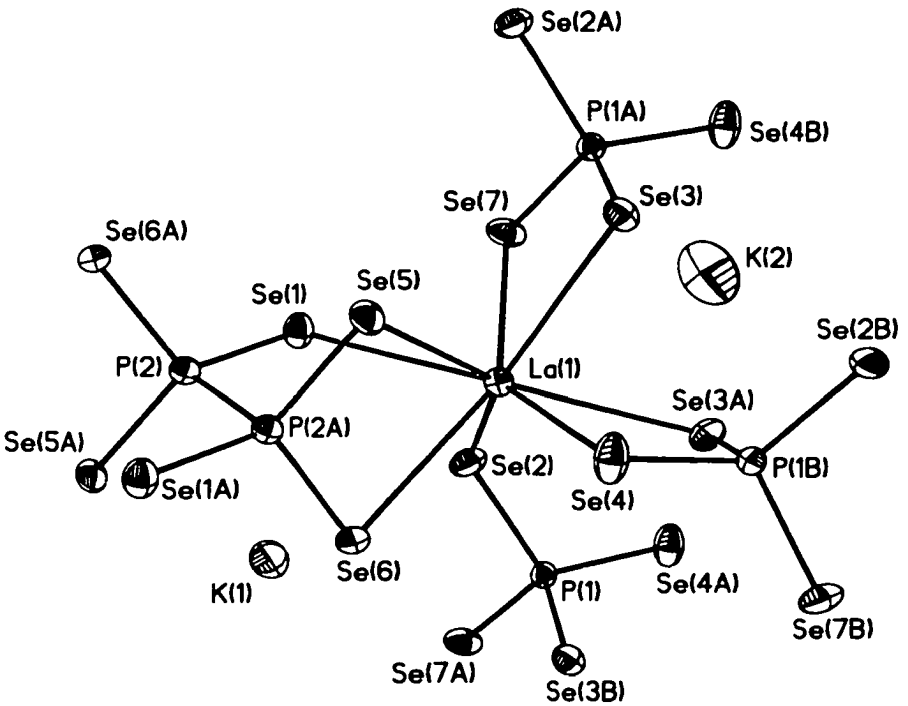


Figure 2.2. ORTEP plot of $K_2LaP_2Se_7$. Thermal ellipsoids are plotted at the 50% probability level.

Table 2.2. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($Å^2$ x 10^3)[a] for $K_2La(P_2Se_6)_{1/2}(PSe_4)$

	x	y	z	U(eq)
La(1)	0.8072(1)	0.4726(1)	0.1499(1)	19(1)
Se(1)	0.7175(1)	0.4614(1)	-0.0040(1)	26(1)
Se(2)	0.5838(1)	0.7758(1)	0.1045(1)	27(1)
Se(3)	0.8091(1)	0.0780(1)	0.2192(1)	23(1)
Se(4)	0.0527(1)	0.4794(1)	0.2592(1)	34(1)
Se(5)	0.0565(1)	0.2591(1)	0.0991(1)	26(1)
Se(6)	0.0224(1)	0.7511(1)	0.0967(1)	25(1)
Se(7)	0.5281(1)	0.2543(1)	0.1068(1)	27(1)
P(1)	0.5933(2)	0.0164(3)	0.1685(1)	18(1)
P(2)	0.9184(2)	0.4903(3)	-0.0432(1)	20(1)
K(1)	0.2576(2)	0.0075(3)	0.0091(1)	40(1)
K(2)	0.3425(3)	0.5411(4)	0.1865(1)	54(1)

[a] U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 2.3. Selected bond distances (Å) and angles (Deg.) for $K_2La(P_2Se_6)_{1/2}(PSe_4)$.

La(1)-Se(4)	3.0421(10)	La(1)-Se(7)	3.0979(10)
La(1)-Se(2)	3.0980(9)	La(1)-Se(5)	3.1127(9)
La(1)-Se(6)	3.1609(9)	La(1)-Se(3)	3.1829(9)
La(1)-Se(3)	3.1937(9)	La(1)-Se(1)	3.2380(9)
P(1)-Se(7)	2.189(2)	P(1)-Se(4)	2.195(2)
P(1)-Se(3)	2.217(2)	P(2)-Se(5)	2.184(2)
P(2)-Se(6)	2.184(2)	P(2)-Se(1)	2.171(2)
P(1)-Se(2)	2.189(2)	P(2)-P(2)	2.226(4)
Se(4)-La(1)-Se(7)	139.73(3)	Se(7)-P(1)-Se(2)	105.65(9)
Se(7)-La(1)-Se(2)	75.56(2)	Se(2)-P(1)-Se(4)	110.52(9)
Se(7)-La(1)-Se(5)	107.40(3)	Se(2)-P(1)-Se(3)	114.59(9)
Se(4)-La(1)-Se(6)	78.28(3)	Se(1)-P(2)-Se(5)	116.38(10)
Se(2)-La(1)-Se(6)	83.38(3)	Se(5)-P(2)-Se(6)	109.15(9)
Se(4)-La(1)-Se(3)	69.95(2)	Se(5)-P(2)-P(2)	105.95(13)
Se(2)-La(1)-Se(3)	78.55(2)	Se(7)-P(1)-Se(4)	110.65(9)
Se(6)-La(1)-Se(3)	117.62(3)	Se(7)-P(1)-Se(3)	107.32(9)
Se(7)-La(1)-Se(3)	68.65(2)	Se(4)-P(1)-Se(3)	108.04(9)
Se(5)-La(1)-Se(3)	75.95(2)	Se(1)-P(2)-Se(6)	114.42(9)
Se(3)-La(1)-Se(3)	78.48(2)	Se(1)-P(2)-P(2)	103.96(13)
Se(7)-La(1)-Se(1)	66.01(2)	Se(6)-P(2)-P(2)	105.95(13)
Se(5)-La(1)-Se(1)	75.80(2)	Se(5)-La(1)-Se(3)	140.85(3)
Se(3)-La(1)-Se(1)	142.69(3)	Se(4)-La(1)-Se(3)	73.20(3)
Se(4)-La(1)-Se(2)	129.90(3)	Se(3)-La(1)-Se(1)	114.79(3)
Se(4)-La(1)-Se(5)	74.53(3)	Se(6)-La(1)-Se(1)	75.99(2)
Se(2)-La(1)-Se(5)	139.09(3)	Se(2)-La(1)-Se(1)	68.32(2)
Se(7)-La(1)-Se(6)	141.14(3)	Se(4)-La(1)-Se(1)	146.03(3)
Se(5)-La(1)-Se(6)	69.13(2)	Se(6)-La(1)-Se(3)	139.55(3)
Se(7)-La(1)-Se(3)	89.96(3)	Se(2)-La(1)-Se(3)	137.05(3)

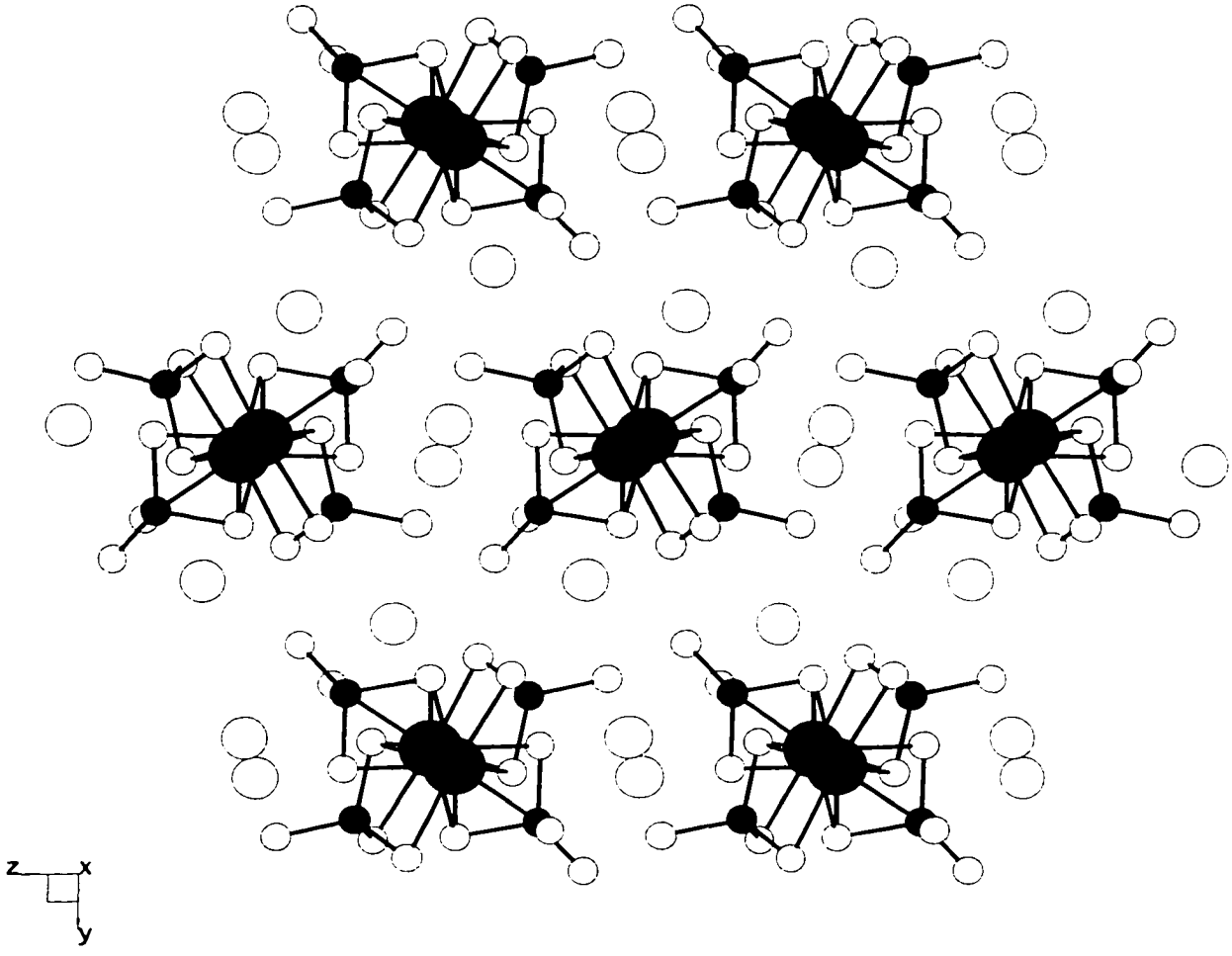


Figure 2.3. Packing plot of $K_3La(PSe_4)_2$. Large filled lanthanum atoms, small filled phosphorus atoms, small unfilled selenium atoms, and large unfilled potassium atoms.

lanthanum atoms are separated by two $(PSe_4)^{3-}$ tetrahedra in which one selenium atom on each $(PSe_4)^{3-}$ tetrahedron bridges two neighboring La atoms. Figure 2.4A shows two different long La···La distances that arise from the alternating orientation of bridging selenium atoms. Where the bridging selenium atoms and two lanthanum atoms (for example, La(1) and La(1D)) form a plane parallel to the ab plane, the La···La distance is 5.292 Å. Where the bridging selenium atoms and lanthanum atoms (for example, La(1B) and La(1C)) form a plane parallel to the bc plane, the La···La distance is 4.409 Å. The average La-Se bond distance is 3.170(3) Å. Each $(PSe_4)^{3-}$ tetrahedron has three selenium atoms bound to lanthanum atoms, while the fourth selenium atoms is terminal and points into the space between chains. The average P-Se bond distance is 2.198(8) Å. Atomic coordinates and selected bond distances and angles for $K_3La(PSe_4)_2$ can be found in Tables 2.4 and 2.5 respectively. Compounds with similar structures reported in the literature include $K_3CeP_2S_8$, [35] and $Rb_3CeP_2Se_8$ and $Cs_3GdP_2Se_8$.[36]

A single crystal of **$K_4La_{0.67}(PSe_4)_2$ or $K_6La(PSe_4)_3$, (III),** was selected, 5519 (1150 independent) reflections were collected, and an absorption correction was applied to an orthorhombic cell (R_{int} = 0.0413). The structure was solved by direct methods in Ibam to electron density residuals of 1.367 and -1.477 $eÅ^{-3}$, and all atoms refined anisotropically with SHELXTL using full-matrix least squares refinement on F^2 for 42 variables.[45] Based on its formula, one would expect $K_4La_{0.67}(PSe_4)_2$ to have a structure similar to $K_3La(PSe_4)_2$; indeed, they are related as they both contain chains of lanthanum atoms coordinated by $(PSe_4)^{3-}$ tetrahedra. In $K_4La_{0.67}(PSe_4)_2$. 8-coordinate dodecahedral lanthanum atoms are linked into $^1_\infty[La_{0.67}(PSe_4)_2]^{4-}$ chains

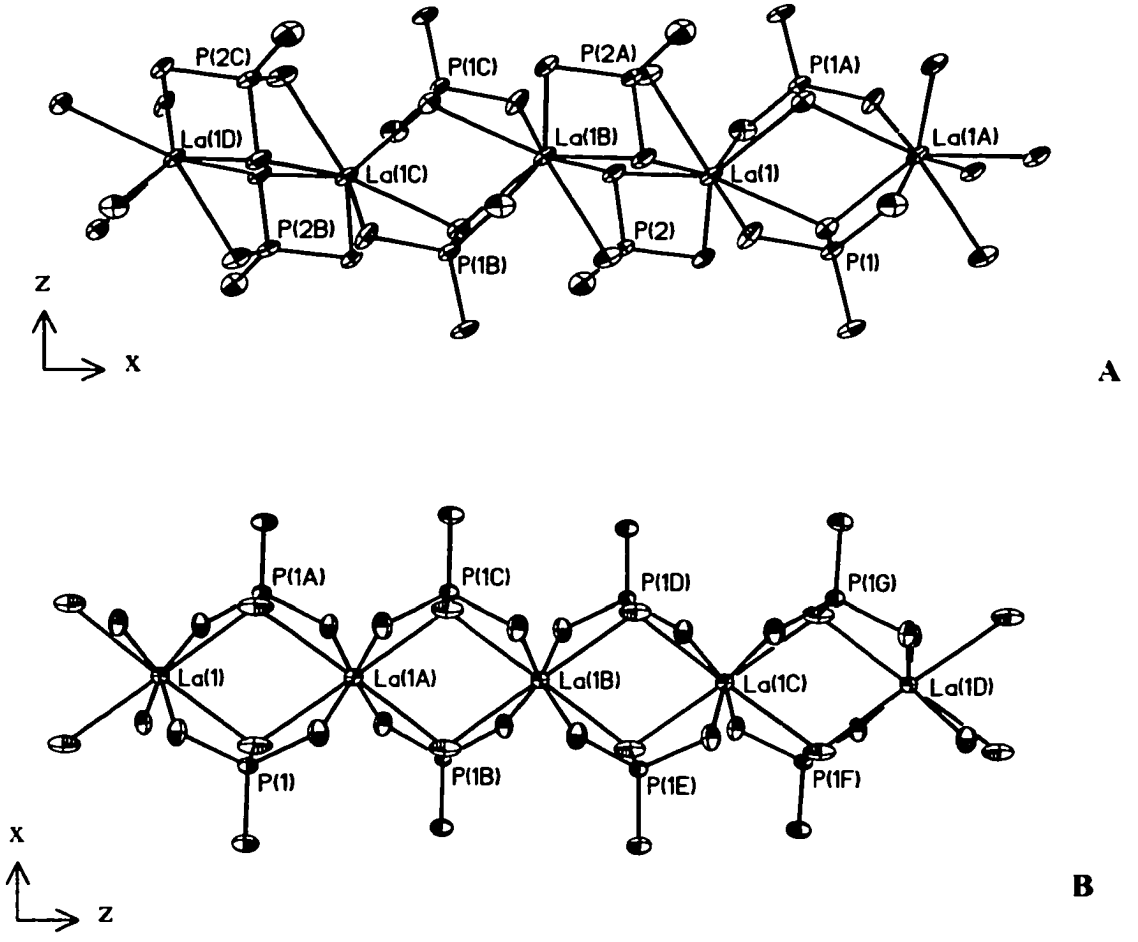


Figure 2.4. ORTEP plots of **A**: $[La(PSe_4)_2]^{3-}$ chain. **B**: $[La_{0.67}(PSe_4)_2]^{4-}$ chain. Thermal ellipsoids plotted at the 70% probability level. Unlabeled selenium atoms. Potassium atoms left out for clarity.

Table 2.4. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$)[a] for $K_3La(PSe_4)_2$.

	x	y	z	U(eq)
La(1)	0.2266(1)	0.0138(1)	0.9704(1)	17(1)
Se(1)	-0.0365(1)	0.1268(1)	0.9681(1)	22(1)
Se(2)	0.0567(1)	0.0186(1)	1.2558(1)	24(1)
Se(3)	0.5378(1)	0.0246(1)	0.8193(1)	19(1)
Se(4)	0.3088(1)	-0.1320(1)	0.8226(1)	25(1)
Se(5)	0.2172(1)	0.1166(1)	0.7183(1)	25(1)
Se(6)	-0.1278(1)	0.1815(1)	0.6308(1)	28(1)
Se(7)	0.5709(1)	-0.1259(1)	0.5680(1)	25(1)
Se(8)	0.3325(1)	0.1611(1)	1.0911(1)	24(1)
P(1)	0.5251(2)	-0.0991(1)	0.7750(2)	17(1)
P(2)	-0.0077(3)	0.1036(1)	0.7507(2)	17(1)
K(1)	0.1195(3)	0.2058(2)	1.3727(3)	43(1)
K(2)	0.3826(3)	-0.2855(2)	0.6259(3)	47(1)
K(3)	0.2699(2)	-0.0323(1)	0.5138(2)	31(1)

[a] U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 2.5. Selected bond distances (Å) and angles (Deg.) for $K_3La(PSe_4)_2$.

La(1)-Se(8)	3.0403(11)	P(1)-Se(7)	2.167(2)
La(1)-Se(5)	3.1060(11)	P(2)-Se(1)	2.228(3)
La(1)-Se(3)	3.1533(11)	P(2)-Se(2)	2.209(3)
La(1)-Se(2)	3.2856(10)	P(1)-Se(3)	2.232(3)
La(1)-Se(4)	3.0712(11)	P(1)-Se(4)	2.204(2)
La(1)-Se(1)	3.1406(11)	P(2)-Se(5)	2.191(3)
La(1)-Se(1)	3.2152(11)	P(2)-Se(6)	2.155(3)
La(1)-Se(3)	3.3496(10)	P(1)-Se(8)	2.200(3)
Se(8)-La(1)-Se(4)	145.30(3)	Se(7)-P(1)-Se(8)	110.15(11)
Se(4)-La(1)-Se(5)	96.18(3)	Se(8)-P(1)-Se(4)	108.64(11)
Se(4)-La(1)-Se(1)	65.19(3)	Se(8)-P(1)-Se(3)	109.49(11)
Se(8)-La(1)-Se(3)	71.49(3)	Se(7)-P(1)-Se(4)	109.87(11)
Se(5)-La(1)-Se(3)	133.26(3)	Se(7)-P(1)-Se(3)	113.09(11)
Se(8)-La(1)-Se(1)	74.48(3)	Se(4)-P(1)-Se(3)	105.43(10)
Se(5)-La(1)-Se(1)	67.02(3)	Se(6)-P(2)-Se(2)	119.67(12)
Se(3)-La(1)-Se(1)	134.29(3)	Se(6)-P(2)-Se(1)	110.88(11)
Se(4)-La(1)-Se(2)	124.51(3)	Se(2)-P(2)-Se(1)	100.47(10)
Se(1)-La(1)-Se(2)	64.06(3)	Se(6)-P(2)-Se(5)	111.99(11)
Se(1)-La(1)-Se(2)	66.45(3)	Se(5)-P(2)-Se(2)	107.90(11)
Se(4)-La(1)-Se(3)	66.54(2)	Se(5)-P(2)-Se(1)	104.36(11)
Se(1)-La(1)-Se(3)	130.54(3)	Se(2)-La(1)-Se(3)	146.34(3)
Se(1)-La(1)-Se(3)	131.27(3)	Se(3)-La(1)-Se(3)	71.11(3)
Se(8)-La(1)-Se(5)	80.20(3)	Se(5)-La(1)-Se(3)	68.01(3)
Se(8)-La(1)-Se(1)	142.40(3)	Se(8)-La(1)-Se(3)	80.40(3)
Se(5)-La(1)-Se(1)	127.23(3)	Se(3)-La(1)-Se(2)	77.47(3)
Se(4)-La(1)-Se(3)	87.48(3)	Se(5)-La(1)-Se(2)	132.40(3)
Se(1)-La(1)-Se(3)	96.54(3)	Se(8)-La(1)-Se(2)	78.45(3)
Se(4)-La(1)-Se(1)	135.95(3)	Se(1)-La(1)-Se(1)	92.16(3)

which propagate along the z-axis and are separated from each other along the x and y axes by potassium cations as shown in Figure 2.5. Two crystallographically distinct potassium atoms are found with K-Se bond distances ranging from 3.217(2) Å to 3.672(2) Å. Unlike in the $K_3La(PSe_4)_2$ structure, the $(PSe_4)^{3-}$ tetrahedra in $^1_\infty[La_{0.67}(PSe_4)_2]^{4-}$ are orientated with their non-bridging selenium vertices in the same direction as seen in Figure 2.4B. The average La-Se bond distance is 3.256(2) Å compared to an average La-Se bond distance of 3.170(3) Å in $K_3La(PSe_4)_2$. Another significant difference is that the lanthanum position in $K_4La_{0.67}(PSe_4)_2$ is partially occupied to satisfy the charge balancing requirements of the structure. On average, every third lanthanum atom is "missing", resulting in significantly shorter "chains" than the quasi-infinite chains found in $K_3La(PSe_4)_2$. Semi-quantitative energy dispersive spectroscopy was performed on three different crystals giving an average composition of $K_{3.86}La_{0.81}P_{2.24}Se_{7.77}$. Atomic coordinates and selected bond distances and angles for $K_4La_{0.67}(PSe_4)_2$ can be found in Tables 2.6 and 2.7 respectively. $K_4La_{0.67}(PSe_4)_2$ is isotypic with $K_4Eu(PSe_4)_2$.[20]

A single crystal of **$K_{9-x}La_{1+x/3}(PSe_4)_4$ (x = 0.5), (IV),** was selected, 21677 (4392 independent) reflections were collected, and an absorption correction was applied (R_{int} = 0.0855) for an orthorhombic solution. The structure was solved by direct methods to electron density residuals of 1.774 and -1.935 eÅ^{-3}, and all atoms refined anisotropically with SHELXTL using full-matrix least squares refinement on F^2 for 140 variables.[45] The initial monoclinic unit cell chosen by SMART [a=21.1980(1) Å, b=10.3100(1) Å, c=18.2874(1) Å, β=115.541(1)°] was very similar to the unit cell of $Rb_9Ce(PSe_4)_4$ [38] [a = 21.446(5) Å, b = 10.575(5) Å, c = 18.784(4) Å,

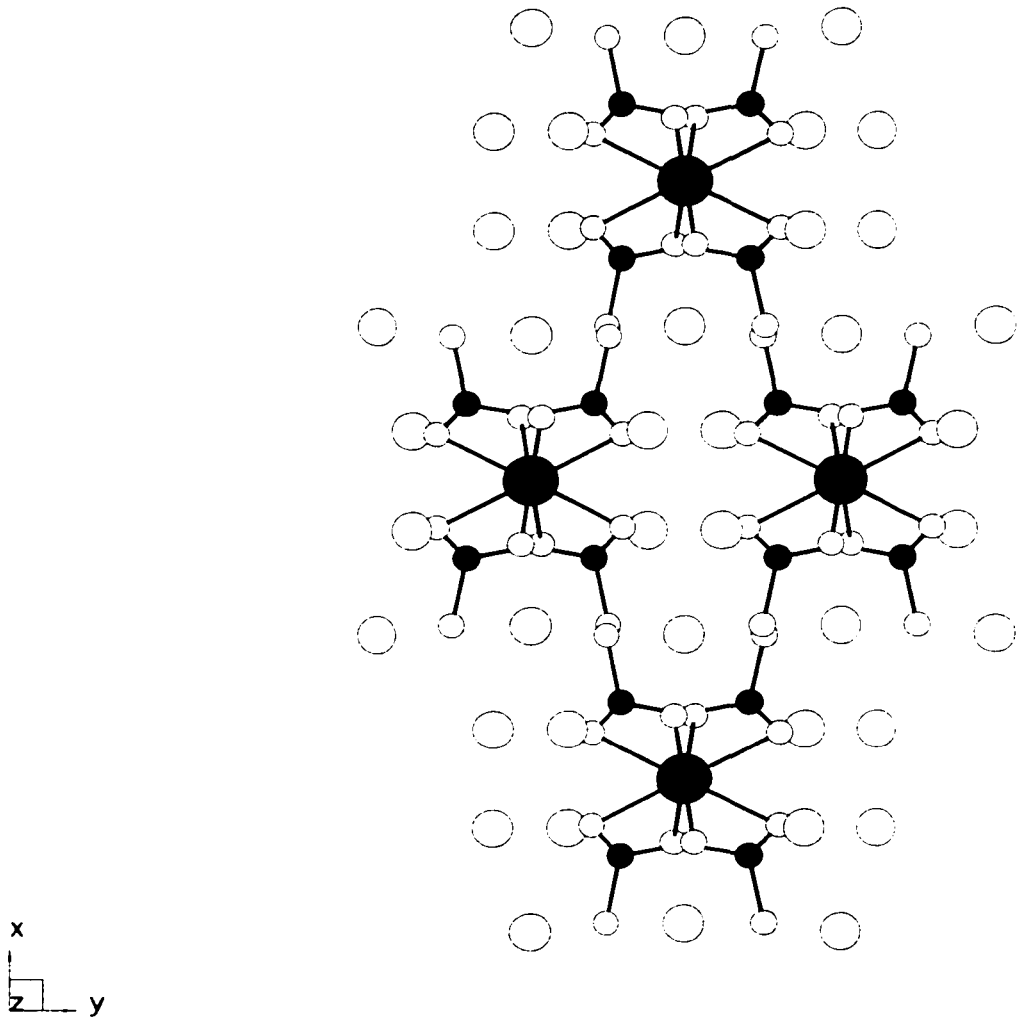


Figure 2.5. Packing plot of $K_4La_{0.67}(PSe_4)_2$. Large filled lanthanum atoms, small filled phosphorus atoms, small unfilled selenium atoms, and large unfilled potassium atoms.

Table 2.6. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($Å^2$ x 10^3)[a] for $K_4La_{0.67}(PSe_4)_2$.

	x	y	z	U(eq)
La(1)[b]	0.5000	0.0000	0.2500	14(1)
Se(1)	0.4218(1)	0.3012(1)	0.3271(1)	23(1)
Se(2)	0.3939(1)	0.0324(1)	0.0000	27(1)
Se(3)	0.2586(1)	0.2530(1)	0.5000	24(1)
P(1)	0.3710(1)	0.2054(2)	0.5000	14(1)
K(1)	0.4168(1)	0.3812(2)	0.0000	32(1)
K(2)	0.2572(1)	0.0000	0.2500	39(1)

[a] U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.
[b] The La(1) position is only 2/3 occupied.

Table 2.7. Selected bond distances (Å) and angles (Deg.) for $K_4La_{0.67}(PSe_4)_2$.

La(1)-Se(1) x 4	3.2305(6)	P(1)-Se(1)	2.2029(13)
La(1)-Se(2) x 4	3.2812(5)	P(1)-Se(1')	2.2029(13)
P(1)-Se(2)	2.218(2)	P(1)-Se(3)	2.190(2)
Se(1)-La(1)-Se(1)	124.93(2)	Se(3)-P(1)-Se(1)	110.66(6)
Se(1)-La(1)-Se(1)	63.09(2)	Se(1)-P(1)-Se(1)	107.22(9)
Se(1)-La(1)-Se(1)	151.64(2)	Se(1)-P(1)-Se(2)	107.61(6)
Se(1)-La(1)-Se(2)	80.17(2)	Se(3)-P(1)-Se(1)	110.66(6)
Se(1)-La(1)-Se(2)	123.62(2)	Se(3)-P(1)-Se(2)	112.86(9)
Se(1)-La(1)-Se(2)	66.43(2)	Se(1)-P(1)-Se(2)	107.61(6)
Se(1)-La(1)-Se(2)	90.97(2)	Se(2)-La(1)-Se(2)	103.78(2)
Se(2)-La(1)-Se(2)	103.78(2)	Se(2)-La(1)-Se(2)	169.64(3)
Se(1)-La(1)-Se(2)	90.97(2)	Se(1)-La(1)-Se(2)	66.43(2)
Se(1)-La(1)-Se(2)	66.43(2)	Se(1)-La(1)-Se(2)	90.97(2)
Se(2)-La(1)-Se(2)	169.64(3)	Se(2)-La(1)-Se(2)	77.18(2)
Se(1)-La(1)-Se(2)	123.62(2)	Se(1)-La(1)-Se(2)	80.17(2)
Se(1)-La(1)-Se(2)	80.17(2)	Se(1)-La(1)-Se(2)	123.62(2)
Se(2)-La(1)-Se(2)	77.18(2)	Se(1)-La(1)-Se(2)	123.62(2)
Se(1)-La(1)-Se(1)	151.64(2)	Se(1)-La(1)-Se(2)	80.17(2)
Se(1)-La(1)-Se(1)	63.09(2)	Se(1)-La(1)-Se(2)	90.97(2)
Se(1)-La(1)-Se(1)	124.93(2)	Se(1)-La(1)-Se(2)	66.43(2)

$\beta = 115.94(2)^{\circ}$], and we therefore predicted a structure with the formula $K_9La(PSe_4)_4$ containing isolated $^{0}_{\infty}[La(PSe_4)_4]^{9-}$ anionic clusters. However, an acceptable structure solution could not be obtained in the expected C2/c space group. It was suggested that in this monoclinic space group the structure might exist as a merohedral twin, however, a reasonable model was not found. Significant electron density was left on one of the potassium sites leading to a structure with a lanthanum ratio higher than one and a formula that could not be charge balanced. To solve this problem, a system of higher symmetry based on a unit cell transformation to an orthorhombic cell, Ccca, with lattice parameters a=18.2133(1) Å, b=38.0914(4) Å, c=10.2665(1) Å was employed. In this cell a reasonable structure solution was found with the formula $K_{9-x}La_{1+x/3}(PSe_4)_4$ (x = 0.5). The structure of $K_{9-x}La_{1+x/3}(PSe_4)_4$ (x = 0.5) contains two different crystallographically distinct lanthanum atoms. The first lanthanum exists as isolated $^{0}_{\infty}[La(PSe_4)_4]^{9-}$ clusters like those observed for the $Rb_9Ce(PSe_4)_4$ structure. These clusters alternate with potassium atoms along the z-axis of the unit cell as shown in Figure 2.6. The second lanthanum is found in chains of lanthanum atoms linked together by $(PSe_4)^{3-}$ tetrahedra along the z-axis of the unit cell. The lanthanum position along these chains is 2/3 occupied, just as in the $K_4La_{0.67}(PSe_4)_2$ structure. The two different lanthanum positions alternate throughout the structure. $^{1}_{\infty}[La_{0.67}(PSe_4)_2]^{4-}$ chains alternate with $^{0}_{\infty}[La(PSe_4)_4]^{9-}$ clusters along the x-axis and y-axis. Both lanthanum atoms exist as dodecahedra with 8 La-Se bonds. The average La-Se bond to each lanthanum illustrates the difference in environments. The average La-Se bond around each La(1) cluster is 3.125(3) Å, while the average La-Se bond length around each La(2) in a partially occupied chain

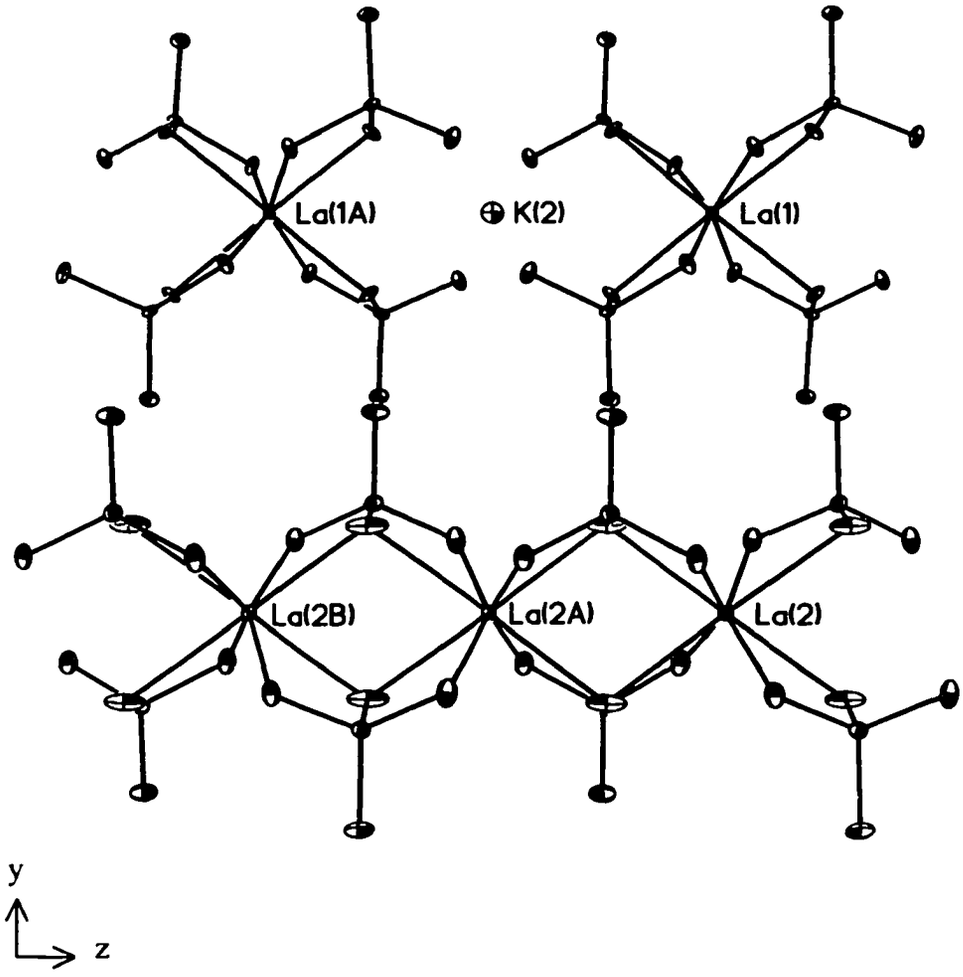


Figure 2.6. ORTEP plot of the different lanthanum coordination environments in $K_{9-x}La_{1+x/3}(PSe_4)_4$ (x=0.5). Thermal ellipsoids plotted at the 50% probability level.

is 3.256(5) Å. Semi-quantitative energy dispersive spectroscopy was performed on three different crystals giving an average composition of $K_{7.02}La_{1.06}P_{4.13}Se_{17.46}$. We have also synthesized the isostructural compounds $K_{9-x}Y_{1+x/3}(PSe_4)_4$ and $Rb_{9-x}La_{1+x/3}(PSe_4)_4$. The formation of $K_{9-x}La_{1+x/3}(PSe_4)_4$ (x = 0.5) instead of $K_9La(PSe_4)_4$ will be discussed in a later section in terms of dimensionality and the position of these quaternary structures within a ternary phase diagram. Atomic coordinates and selected bond distances and angles for $K_{9-x}La_{1+x/3}(PSe_4)_4$ (x=0.5) can be found in Tables 2.8 and 2.9 respectively.

A single crystal of **$KEuPSe_4$, (V),** was selected, 5130 (1080 independent) reflections were collected, and an absorption correction was applied to an orthorhombic cell. Systematic absence analysis and a low R_{int} (0.0368) confirmed the correct space group choice of Pnma. The structure was solved by direct methods to electron density residuals of 0.829 and -1.193 $eÅ^{-3}$, and all atoms refined anisotropically with SHELXTL using full-matrix least squares refinement on F^2 for 41 variables.[45] The structure for $KEuPSe_4$ was recently reported by Kanatzidis *et al.*, which was solved as a twinned structure in the monoclinic space group $P2_1/m$ with cell parameters a = 6.8469(6) Å, b = 6.9521(6) Å, c = 9.0436(8) Å, and β = 107.677(2)°.[49] Switching the reported a-axis and c-axis, transforming from a monoclinic cell to an orthorhombic cell, and finally doubling the new a-axis gave cell parameters similar to ours of a = 17.2338 Å, b = 6.9521 Å, and c = 6.8469 Å (see Appendix A); however, it is important to note that our reaction conditions were different from those reported by Kanatzidis *et. al.* Their reaction conditions may have led to poor quality, twinned crystals or a phase of slightly different structural

Table 2.8. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($Å^2$ x 10^3)[a] for $K_{9-x}La_{1+x/3}(PSe_4)_4$ (x=0.5).

	x	y	z	U(eq)
La(1)	0.0000	0.2500	0.7500	6(1)
La(2)[b]	-0.2500	0.0000	0.7535	9(1)
Se(1)	0.0155(1)	0.1965(1)	0.5229(1)	12(1)
Se(2)	0.1493(1)	0.2867(1)	0.6790(1)	14(1)
Se(3)	-0.1269(1)	0.1291(1)	0.5148(1)	17(1)
Se(4)	-0.1546(1)	0.2079(1)	0.3353(1)	17(1)
Se(5)	-0.4005(1)	0.0394(1)	0.3307(1)	21(1)
Se(6)	-0.4010(1)	0.0388(1)	0.6750(1)	24(1)
Se(7)	-0.3770(1)	0.1208(1)	0.5040(1)	23(1)
Se(8)	-0.2340(1)	0.0535(1)	0.5040(1)	32(1)
K(1)	0.1893(2)	0.2916(1)	1.0138(2)	23(1)
K(2)	0.0000	0.2500	0.2500	30(1)
K(3)	0.0000	0.1259(1)	0.7500	28(1)
K(4)	-0.0600(2)	0.0406(1)	0.5001(2)	30(1)
K(5)	-0.2533(1)	0.1216(1)	0.7609(2)	29(1)
K(6)	0.0000	0.1324(2)	0.2500	43(1)
P(1)	-0.1035(2)	0.1845(1)	0.5084(2)	7(1)
P(2)	-0.3531(2)	0.0636(1)	0.5039(2)	15(1)

[a] U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.
[b] The La(2) position is only 2/3 occupied.

Table 2.9. Selected bond distances (Å) and angles (Deg.) for $K_{9-x}La_{1+x/3}(PSe_4)_4$ (x=0.5).

La(1)-Se(1) x 4	3.1077(11)	P(1)-Se(2)	2.228(3)
La(1)-Se(2) x 4	3.1424(11)	P(1)-Se(3)	2.153(4)
La(2)-Se(5) x 2	3.2234(14)	P(1)-Se(4)	2.195(3)
La(2)-Se(6) x 2	3.2246(14)	P(2)-Se(5)	2.181(3)
La(2)-Se(8) x 2	3.285(2)	P(2)-Se(6)	2.176(3)
La(2)-Se(8') x 2	3.293(2)	P(2)-Se(7)	2.220(5)
P(1)-Se(1)	2.221(4)	P(2)-Se(8)	2.204(5)
Se(1')-La(1)-Se(1')	82.80(5)	Se(6')-La(2)-Se(8')	123.65(4)
Se(1')-La(1)-Se(1')	169.57(5)	Se(8)-La(2)-Se(8')	103.50(5)
Se(1')-La(1)-Se(1)	98.15(5)	Se(5')-La(2)-Se(8')	66.14(4)
Se(1')-La(1)-Se(2')	122.94(3)	Se(6')-La(2)-Se(8')	80.59(4)
Se(1)-La(1)-Se(2)	92.20(3)	Se(8)-La(2)-Se(8')	169.84(6)
Se(1')-La(1)-Se(2')	67.27(3)	Se(6)-La(2)-Se(6')	151.03(5)
Se(1')-La(1)-Se(2')	78.72(3)	Se(8')-La(2)-Se(8')	77.31(6)
Se(1')-La(1)-Se(2)	78.71(3)	Se(3)-P(1)-Se(4)	109.80(14)
Se(2')-La(1)-Se(2')	127.24(4)	Se(4)-P(1)-Se(1)	112.59(14)
Se(2')-La(1)-Se(2)	153.17(4)	Se(4)-P(1)-Se(2')	106.1(2)
Se(2')-La(1)-Se(2)	60.17(4)	Se(3)-P(1)-Se(1)	113.2(2)
Se(5')-La(2)-Se(5')	151.55(5)	Se(3)-P(1)-Se(2')	112.63(14)
Se(5')-La(2)-Se(6)	63.23(4)	Se(1)-P(1)-Se(2')	102.17(13)
Se(5')-La(2)-Se(6')	124.98(4)	Se(6)-P(2)-Se(8)	108.5(2)
Se(5')-La(2)-Se(8')	123.74(4)	Se(6)-P(2)-Se(7)	110.3(2)
Se(6)-La(2)-Se(8'	90.77(4)	Se(8)-P(2)-Se(7)	111.4(2)
Se(5')-La(2)-Se(8)	80.08(4)	Se(6)-P(2)-Se(5)	108.4(2)
Se(6)-La(2)-Se(8)	66.20(4)	Se(5)-P(2)-Se(8)	108.4(2)
Se(8')-La(2)-Se(8')	77.52(6)	Se(5)-P(2)-Se(7)	109.7(2)
Se(5')-La(2)-Se(8')	91.19(4)		

organization. Our $KEuPSe_4$ is isotypic to $CsPbPSe_4$,[20] a layered material with lead atoms intricately linked by $(PSe_4)^{3-}$ tetrahedra.

In our $KEuPSe_4$, each $^{2}_{\infty}[EuPSe_4]^{-}$ layer is formed from a zig-zag layer of europium atoms coordinated by alternating $(PSe_4)^{3-}$ units. These layers are separated by potassium cations as shown in Figure 2.7. Each potassium atoms is coordinated by eight selenium atoms with an average K-Se bond distance of 3.554(6) Å. Viewed down the x-axis, Figure 2.8, each layer contains alternating $(PSe_4)^{3-}$ tetrahedra and 8-coordinate europium atoms as bi-capped trigonal prisms. In this way, each $(PSe_4)^{3-}$ tetrahedron is coordinated to four different europium bi-capped trigonal prisms in an edge-sharing manner. The 8-coordinate europium atom contains six shorter Eu-Se bonds (3.1324(8) - 3.2259(5) Å) and two longer Eu-Se bonds (3.6374(3) Å). The long Eu-Se bonds are the capping Eu-Se bonds and result from a selenium atom bridging two alternating europium atoms. The europium coordination environment is shown in Figure 2.9. These two long bonds were not observed in the $CsPbPSe_4$ structure; however, an 8-coordinate divalent europium atom is more reasonable than a 6-coordinate divalent europium atom. Divalent europium atoms with this type of coordination have been observed before in Eu_2BiS_4[50] and $Eu_3Sb_4S_9$.[51] Atomic coordinates and selected bond distances and angles for $KEuPSe_4$ can be found in Tables 2.10 and 2.11 respectively.

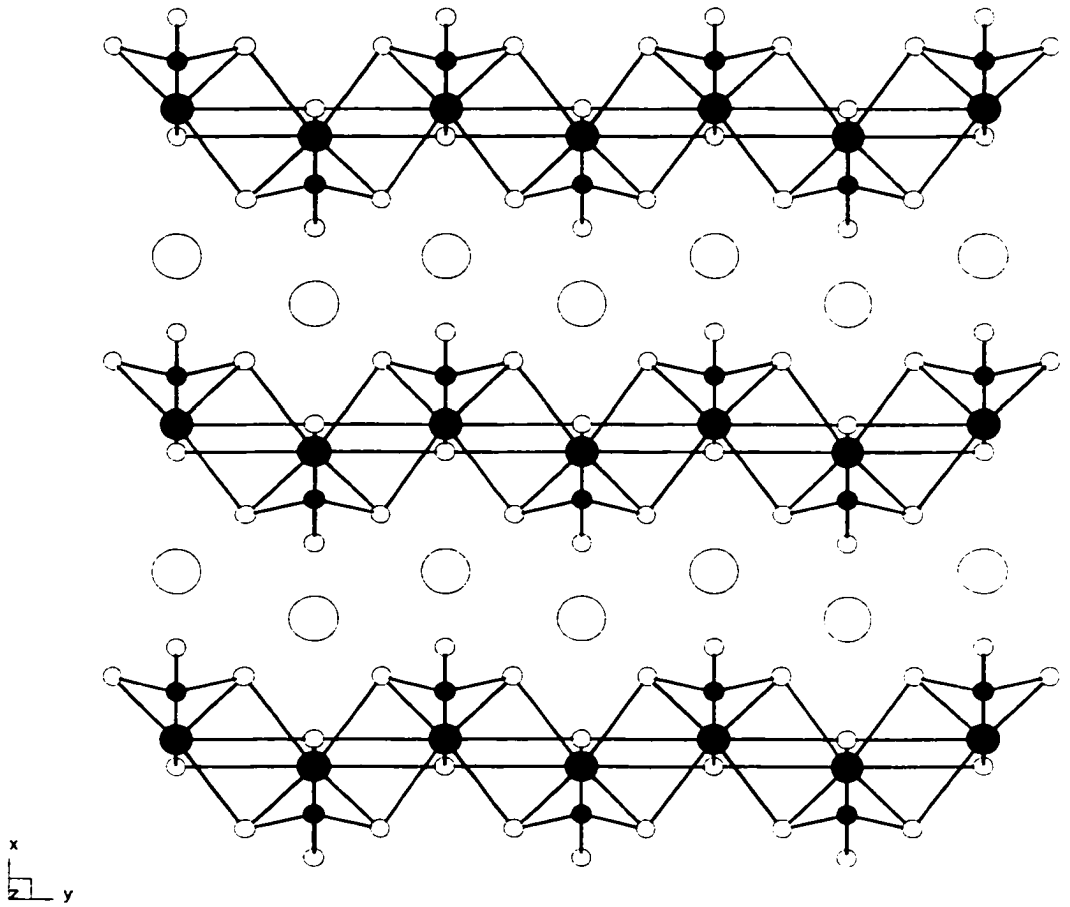


Figure 2.7. Packing plot of $KEuPSe_4$. Large filled europium atoms, small filled phosphorus atoms, small unfilled selenium atoms, large unfilled potassium atoms.

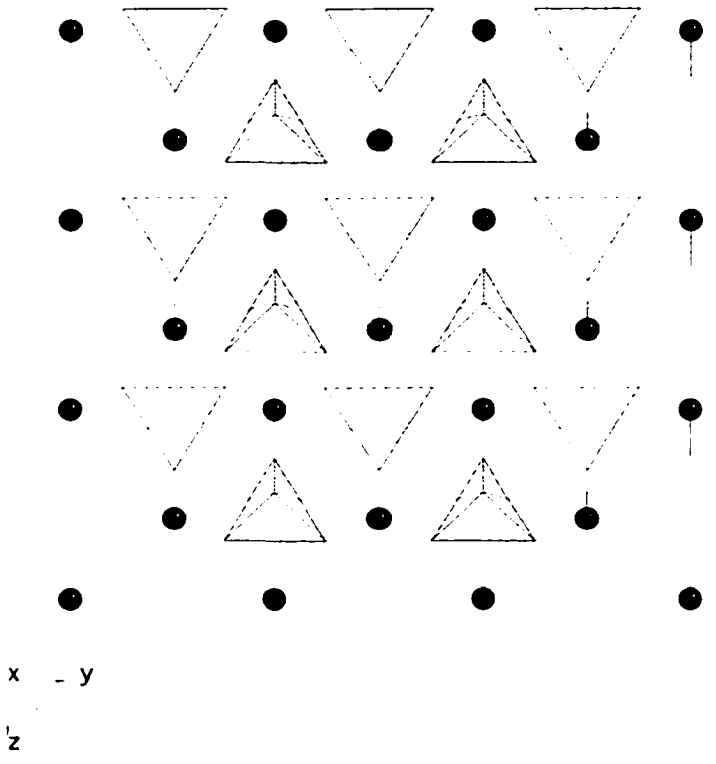


Figure 2.8. $(EuPSe_4)^-$ layer. Filled europium circles, $(PSe_4)^{3-}$ tetrahedra.

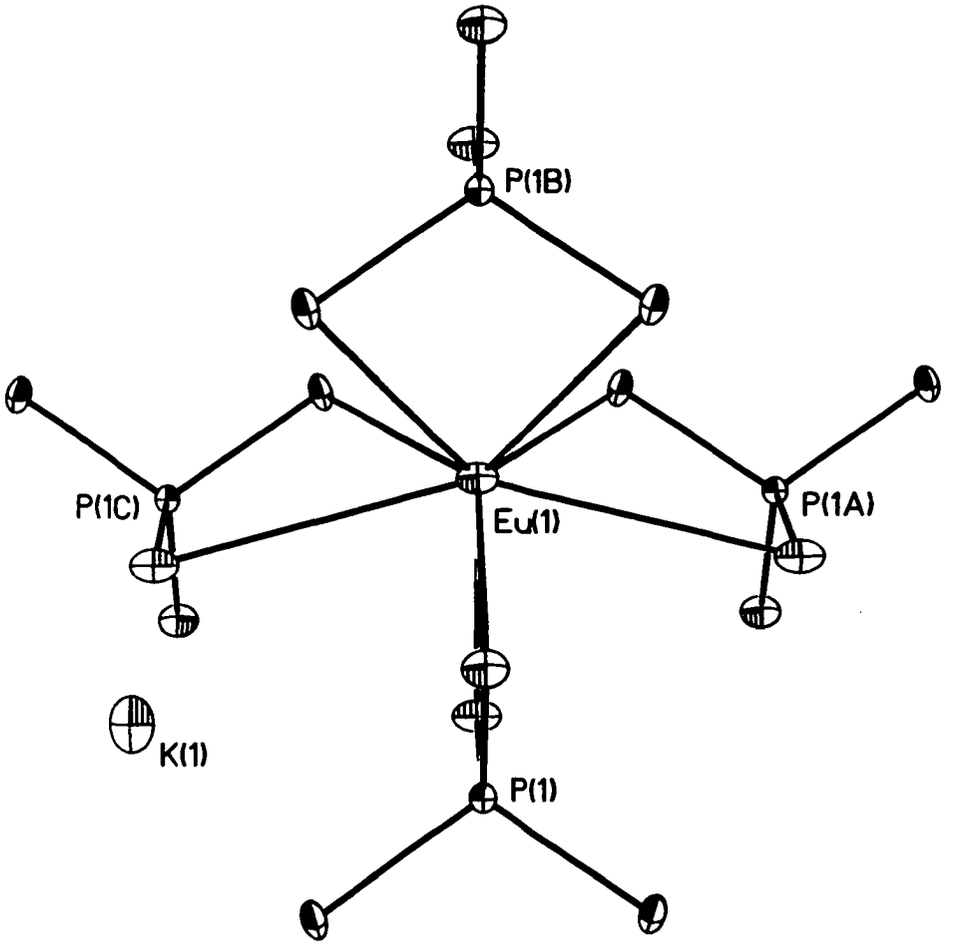


Figure 2.9. ORTEP plot of $KEuPSe_4$. Thermal ellipsoids are plotted at the 50% probability level.

Table 2.10. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$)[a] for $KEuPSe_4$.

	x	y	z	U(eq)
Eu(1)	0.4754(1)	0.2500	0.2893(1)	15(1)
Se(1)	0.3274(1)	0.2500	0.0341(1)	17(1)
Se(2)	0.4727(1)	-0.2500	0.1492(1)	18(1)
Se(3)	0.3795(1)	-0.0028(1)	0.5947(1)	15(1)
P(1)	0.4035(1)	0.2500	-0.2212(2)	10(1)
K(1)	0.2135(1)	0.2500	0.4768(2)	25(1)

[a] U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 2.11. Selected bond distances (Å) and angles (Deg.) for $KEuPSe_4$.

Eu(1)-Se(1)	3.1324(8)	Eu(1)-Se(2)	3.1598(8)
Eu(1)-Se(3)	3.1793(5)	Eu(1)-Se(3)	3.1793(5)
Eu(1)-Se(3)	3.2259(5)	Eu(1)-Se(3)	3.2259(5)
Eu(1)-Se(2)	3.6374(3)	Eu(1)-Se(2)	3.6374(3)
P(1)-Se(3)	2.2208(10)	P(1)-Se(3')	2.2208(10)
P(1)-Se(2)	2.225(2)	P(1)-Se(1)	2.209(2)
Se(1)-Eu(1)-Se(2)	72.54(2)	Se(1)-P(1)-Se(3)	110.02(5)
Se(2)-Eu(1)-Se(3)	90.62(2)	Se(1)-P(1)-Se(3)	110.02(5)
Se(2)-Eu(1)-Se(3)	90.62(2)	Se(3)-P(1)-Se(3)	105.93(7)
Se(1)-Eu(1)-Se(3)	86.39(2)	Se(1)-P(1)-Se(2)	114.16(7)
Se(3)-Eu(1)-Se(3)	123.451(12)	Se(3)-P(1)-Se(2)	108.18(5)
Se(3)-Eu(1)-Se(3)	87.246(14)	Se(3)-Eu(1)-Se(2)	68.732(13)
Se(3)-Eu(1)-Se(3)	66.67(2)	Se(3)-Eu(1)-Se(2)	127.07(2)
Se(2)-Eu(1)-Se(2)	75.474(11)	Se(2)-Eu(1)-Se(2)	75.474(11)
Se(3)-Eu(1)-Se(2)	63.359(13)	Se(3)-Eu(1)-Se(2)	134.17(2)

Phase Diagrams

La-P-K System

Figure 2.10 shows the quasi-quaternary phase diagram for La-P-K. This ternary phase diagram is used to represent quaternary phase space wherein the reactions were all performed with a constant selenium content and under a relative thermodynamic equilibrium isotherm of 725°C. In these phase diagrams, numbers represent reactions wherein various ratios of K/K+P+La, P/K+P+La, and La/K+P+La were used. Table 2.12 lists the ratio of respective components for each phase diagram point. In this way, the quasi-quaternary La-P-K phase diagrams can be thought of as an isometric selenium slice through the quaternary La-P-K-Se phase diagram.

In Figure 2.10, six different crystalline products are represented: $K_{9-x}La_{1+x/3}(PSe_4)_4$ (x = 0.5), **IV**, $K_4La_{0.67}(PSe_4)_2$, **III**, $K_3La(PSe_4)_2$, **II**, and $K_2La(P_2Se_6)_{1/2}(PSe_4)$, **I**; two additional phases, $KLaP_2Se_6$ [37] , and $K_6P_8Se_{18}$ [52] were observed as crystalline reaction products, but have been reported elsewhere. At high potassium molar ratios and low phosphorus and lanthanum molar ratios (points 1-3) compound IV was the only crystalline product observed. Increasing the molar ratio of phosphorus and decreasing the molar ratio of potassium in the reactant mixture changes what crystalline products were observed in the reactions. Compounds IV and II were observed at points 4-5 and compound III was found at point 6. Up to a phosphorus molar ratio of 35% in the phase diagram, only structures with $(PSe_4)^{3-}$ units were observed. However, as the phosphorus molar ratio was increased and the potassium molar ratio was decreased, we observed compound I at points 7-9, which contains both $(PSe_4)^{3-}$ and $(P_2Se_6)^{4-}$ units, units with P^V and P^{IV}. Continuing in a

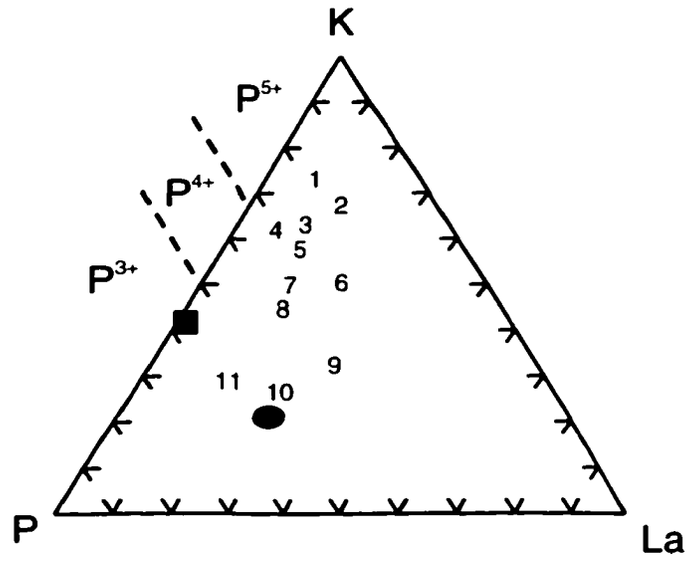


Figure 2.10. La/P/K ternary phase diagram. Numbers represent the ratio of La/P/K in a particular reaction mixture. Shapes indicate the ratio of elements in a product formula disregarding Se: **Circle** = $KLaP_2Se_6$, **Square** = $K_6P_8Se_{18}$.

Table 2.12. Reactant ratios represented in Figure 2.10.

Phase Diagram Point(s)	K/K+P+La	P/K+P+La	La/K+P+La	Reaction Product(s)
1	0.7272	0.1818	0.0909	$K_{9-x}La_{1+x/3}(PSe_4)_4$
2	0.667	0.1667	0.1667	
3	0.625	0.25	0.125	
4	0.6153	0.308	0.0769	$K_{9-x}La_{1+x/3}(PSe_4)_4$ & $K_3La(PSe_4)_2$
5	0.5714	0.2857	0.1429	
6	0.5	0.25	0.25	$K_3La_{0.67}(PSe_4)_2$
7	0.5	0.3333	0.1667	$K_3La(PSe_4)_2$ & $K_2La(P_2Se_6)_{1/2}(PSe_4)$
8	0.4545	0.3636	0.1818	$K_2La(P_2Se_6)_{1/2}(PSe_4)$
9	0.3333	0.3333	0.3333	
10	0.25	0.5	0.25	$KLaP_2Se_6$
11	0.2857	0.5714	0.1429	$KLaP_2Se_6$ & $K_6P_8Se_{18}$

similar manner and increasing the phosphorus molar ratio, there is a region of the phase diagram containing only $(P_2Se_6)^{4-}$ units as seen in $KLaP_2Se_6$ (point 12), and finally, at high phosphorus concentrations, we observed $K_6P_8Se_{18}$ as a reaction product in addition to $KLaP_2Se_6$ at point 13. The significance of the different $(P_xSe_y)^{n-}$ units observed may be attributed to the relative oxidation state of phosphorus and therefore, the relative oxidizing power of the flux. In $(PSe_4)^{3-}$ phosphorus is P^V, $(P_2Se_6)^{4-}$ contains P^{IV}, and $K_6P_8Se_{18}$ contains P^{III}. This trend is logical since the amount of material that needs to be oxidized (P, La) is increased for a given Se^0/Se^{2-} composition. Both phosphorus and lanthanum need to be oxidized, and when the $P/(Se^0/Se^{2-})$ or $La/(Se^0/Se^{2-})$ ratios are too high, there is insufficient oxidizing power in the flux to oxidize phosphorus to higher oxidation states. Based on the oxidation state of phosphorus, the phase diagram can be divided qualitatively into three regions. A line separating P^V and P^{IV} can be drawn approximately between points 6 and 7 at a 35% phosphorus molar ratio, and a line separating P^{IV} and P^{III} can be drawn approximately at a 50% phosphorus molar ratio.

There is a strong correlation between reactant ratios and the position of products on this phase diagram. For example, if a tie-line exists between $KLaP_2Se_6$ (black circle) and $K_6P_8Se_{18}$ (black square) under these reaction conditions, then a reaction with K-P-La ratios corresponding to point 13 should yield both crystalline products. This was observed experimentally. This same type of relationship was found for the other crystalline compounds. It is reasonable to conclude that, under these isometric, isothermal reaction conditions, all stable phases in this region of the phase diagram have been identified.

Eu-P-K System

The Eu-P-K phase diagram, Figure 2.11, is very similar to the lanthanum version, but with fewer stable phases found under our isometric and isothermal reaction conditions. Four crystalline products have been observed so far and are listed in Table 2.13. $KEuPSe_4$, reported here, $K_4Eu(PSe_4)_2$, [20] $K_6P_8Se_{18}$, [52] and $Eu_2P_2Se_6$, which is isostructural with $Eu_2P_2S_6$.[53]

In this phase diagram, P^V was found in $K_4Eu(PSe_4)_2$ (points 1-3) and $KEuPSe_4$ (point 4) structures. This P^V region of the phase diagram seems to extend farther into the phosphorus rich region than in the lanthanum diagram. This can be rationalized by the fact that europium was only oxidized to Eu^{2+} instead of Eu^{3+}; given the relative redox couples of lanthanum vs. europium, there is more oxidizing agent available for the oxidation of phosphorus. Structures with P^{IV} were not observed until at least a 45% phosphorus molar ratio when $Eu_2P_2Se_6$ (points 5 and 6) was found. Another difference between the two phase diagrams is that a europium structure containing both P^V in $(PSe_4)^{3-}$ and P^{IV} in $(P_2Se_6)^{4-}$ units has not yet been found. It would be expected to be found in the region of the phase diagram between 40 and 50% phosphorus. Future experiments may reveal these selenophosphate units, but not within this phase space with the selected ratio Se^0/Se^{2-}, or under these reaction conditions. We do observe the $K_6P_8Se_{18}$ structure (point 6), indicating a region of the phase diagram above 55% phosphorus where selenophosphate units containing P^{III} can be found. As was the case in the lanthanum phase diagram, tie-lines can be drawn between different products based on their element ratios. Point 6, for example, is found on a line that ties phase V to $K_6P_8Se_{18}$.

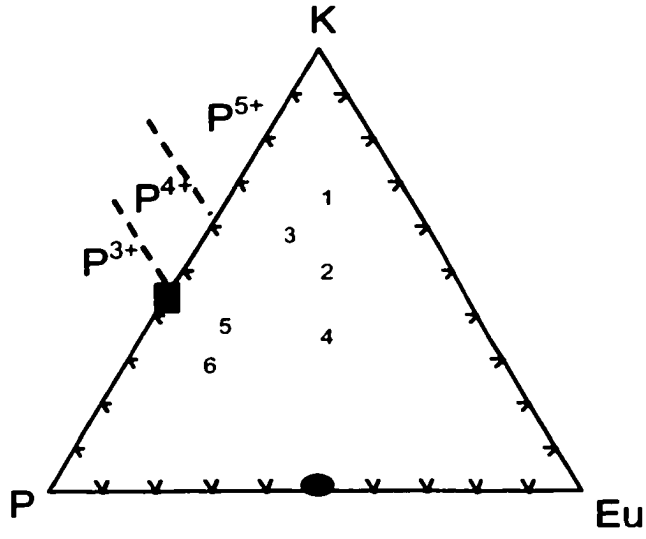


Figure 2.11. Eu/P/K phase diagram. Numbers represent the ratio of Eu/P/K in a particular reaction mixture. Shapes indicate the ratio of elements in a product formula disregarding Se: **Circle** = $Eu_2P_2Se_6$, **Square** = $K_6P_8Se_{18}$.

Table 2.13. Reactant ratios represented in Figure 2.11.

Phase Diagram Point	K/K+P+Eu	P/K+P+Eu	Eu/K+P+Eu	Reaction Product(s)
1	0.6667	0.1667	0.1667	$K_4Eu(PSe_4)_2$
2	0.5	0.25	0.25	
3	0.5714	0.2857	0.1429	
4	0.333	0.333	0.333	$KEuPSe_4$
5	0.375	0.5	0.125	$Eu_2P_2Se_6$
6	0.2857	0.5714	0.1429	$Eu_2P_2Se_6$ & $K_6P_8Se_{18}$

In general, these phase diagrams provide a more rational approach to complex solid-state reactions. The phase diagram concept is certainly not new, but the Dorhout group was the first research group to apply this concept to solid-state flux reactions. Once constructed, these phase diagrams can be used to identify the reactant ratios necessary to synthesize isotypic compounds as described in Chapter 4.

These phase diagrams can be used in conjunction with a formula developed by Kanatzidis to predict these types of structures.[36] We have modified the initial formula to include the four terms shown in Equation **2.1**.

$$(A_4P_2Se_6)_l(A_3PSe_4)_m(La_4(P_2Se_6)_3)_n(LaPSe_4)_o \qquad \textbf{2.1}$$

In this formula, $La_4(P_2Se_6)_3$ and $LaPSe_4$ are the parent structures for a RE^{3+} cation containing $(P_2Se_6)^{4-}$ and $(PSe_4)^{3-}$ building blocks, respectfully. $A_4P_2Se_6$ and A_3PSe_4 comprise each base anionic unit with the appropriate number of alkali-metal cations to balance the charge. In the case where lanthanum is the RE cation, the structures of $KLaP_2Se_6$, $K_2La(P_2Se_6)_{1/2}(PSe_4)$, $K_3La(PSe_4)_2$, $K_4La_{0.67}(PSe_4)_2$, and $K_{9-x}La_{1+x/3}(PSe_4)_4$ (x=0.5) can be derived from Equation **2.1** as seen in Table 2.14. For example, one can think of breaking up the $La_4(P_2Se_6)_3$ parent structure by adding a $(P_2Se_6)^{4-}$ anionic unit with four alkali-metal cations to charge balance the new structure whose empirical formula is the phase $KLaP_2Se_6$.

Table 2.15 contains formulae for compounds described by Equation **2.2**, which has been slightly modified from Equation **2.1** to account for the divalent Eu(II)

Table 2.14. $(A_4P_2Se_6)_l(A_3PSe_4)_m(La_4(P_2Se_6)_3)_n(LaPSe_4)_o$

l	m	n	o	Predicted Formula	Reported Structure
0	1	0	0	A_3PSe_4	
1	0	0	0	$A_4P_2Se_6$	
0	0	1	0	$La_4(P_2Se_6)_3$	
0	0	0	1	$LaPSe_4$	
1	0	1	0	$A_4La_4(P_2Se_6)_4$	$KLaP_2Se_6$ [37]
1	0	0	2	$A_4La_2(P_2Se_6)(PSe_4)_2$	$K_2La(P_2Se_6)_{1/2}(PSe_4)$
0	1	0	1	$A_3La(PSe_4)_2$	$K_3La(PSe_4)_2$
0	2	0	1	$A_6La(PSe_4)_3$	$K_4La_{0.67}(PSe_4)_2$
0	3	0	1	$A_9La(PSe_4)_4$	$K_{9-x}La_{1+x/3}(PSe_4)_4$

Table 2.15. $(A_4P_2Se_6)_l(A_3PSe_4)_m(Eu_2(P_2Se_6))_n[(Eu_3(PSe_4)_2]_o$

l	m	n	o	Predicted Formula	Reported Structure
0	0	1	0	$Eu_2P_2Se_6$	$Eu_2P_2Se_6$
0	0	0	1	$Eu_3(PSe_4)_2$	
1	0	1	0	$A_4Eu_2(P_2Se_6)_2 \equiv A_2EuP_2Se_6$	
0	1	0	1	$A_3Eu_3(PSe_4)_3$	$KEuPSe_4$
0	4	0	1	$A_{12}Eu_3(PSe_4)_6$	$K_4Eu(PSe_4)_2$ [20]
0	7	0	1	$A_{21}Eu_3(PSe_4)_9 \equiv A_7Eu(PSe_4)_3$	
0	10	0	1	$A_{30}Eu_3(PSe_4)_{12} \equiv A_{10}Eu(PSe_4)_4$	

cation. In this formula, two parent structures have changed to $Eu_2(P_2Se_6)$ and $Eu_3(PSe_4)_2$.

$$(A_4P_2Se_6)_l(A_3PSe_4)_m[Eu_2(P_2Se_6)]_n[Eu_3(PSe_4)_2]_o \qquad \textbf{2.2}$$

These formulae, combined with the appropriate phase diagram, can be used to predict new structure compositions and the reaction conditions necessary to synthesize them. For example, Equation **2.2** can be used to predict the formula $A_{10}Eu(PSe_4)_4$ which should be analogous to the homoleptic "$K_9La(PSe_4)_4$" cluster structure, and $K_7Eu(PSe_4)_3$, which should be analogous to compound III. However, these structures have eluded us to date.

The positions of the phases **II-IV** in Figure 2.10 and their low dimensionality may help explain why $K_{9-x}La_{1+x/3}(PSe_4)_4$ ($x = 0.5$) was found instead of $K_9La(PSe_4)_4$. $KLaP_2Se_6$ and $K_2La(P_2Se_6)_{1/2}(PSe_4)$ are both two-dimensional layered structures. $K_3La(PSe_4)_2$ contains one-dimensional chains. $K_4La_{0.67}(PSe_4)_2$ also contains one-dimensional chains, but one could say that its dimensionality is actually lower than $K_3La(PSe_4)_2$ since the lanthanum position is only 2/3 occupied. The $K_{9-x}La_{1+x/3}(PSe_4)_4$ structure contains these chains with a partially occupied lanthanum position, but the structure also contains isolated $[La(PSe_4)_4]$ clusters. In other words, one can imagine a relative continuum from an infinite chain structure to a relatively short chain structure when going from $K_3La(PSe_4)_2$ to $K_4La_{0.67}(PSe_4)_2$, followed by short chains and clusters in $K_{9-x}La_{1+x/3}(PSe_4)_4$, terminating at "$K_9La(PSe_4)_4$", which has no chain structure at all but only isolated $^{0}_{\infty}[La(PSe_4)_4]^{9-}$ anionic units as in

$Rb_9Ce(PSe_4)_4$.[38] Within the phase diagram, the lines separating the $K_3La(PSe_4)_2$, $K_4La_{0.67}(PSe_4)_2$, and $K_{9-x}La_{1+x/3}(PSe_4)_4$ (x = 0.5) structures are not precisely defined. Therefore, the formation of $K_9La(PSe_4)_4$, with its isolated $^{0}_{\infty}[La(PSe_4)_4]^{9-}$ clusters, might not be as thermodynamically stable under our conditions as a structure with a few short chains in addition to isolated clusters as in the $K_{9-x}La_{1+x/3}(PSe_4)_4$ (x = 0.5) structure. Figure 2.12 compares the lanthanum coordination geometry looking down the $^{1}_{\infty}[La_{0.67}(PSe_4)_2]^{4-}$ chains in $K_4La_{0.67}(PSe_4)_2$, and a $^{0}_{\infty}[La(PSe_4)_4]^{9-}$ molecular anion in "$K_9La(PSe_4)_4$". The similarity of these coordination environments shows how the difference in these compounds is only related to certain positions being occupied by lanthanum or potassium. This is supported by noting that the monoclinic unit cell of the expected stoichiometric $K_9La(PSe_4)_4$ can be related to a unit cell similar to $K_4La_{0.67}(PSe_4)_2$ by converting it [a=21.1980(1) Å, b=10.3100(1) Å, c=18.2874(1) Å, β=115.541(1)°] to an orthorhombic cell through a transposition of the b-axis and c-axis and halving the new b-axis to obtain a=19.126 Å, b=9.1437 Å, and c=10.3100 Å. In addition, the cell of $K_4La_{0.67}(PSe_4)_2$ can be transformed into the cell of $K_{9-x}La_{1+x/3}(PSe_4)_4$ (x = 0.5) by transposing and doubling the x and y axes.

Vibrational and Electronic Spectroscopy

Raman Spectroscopy

Solid-state Raman spectroscopy has been performed on compounds **II-V**. The Raman spectra, shown in Figure 2.13, clearly show the four Raman-active vibrations of the tetrahedral $(PSe_4)^{3-}$ unit when compared to the $(PS_4)^{3-}$ tetrahedral unit in K_3PS_4.[54] Table 2.16 lists the peaks observed. The intense peak near 237 cm^{-1} is

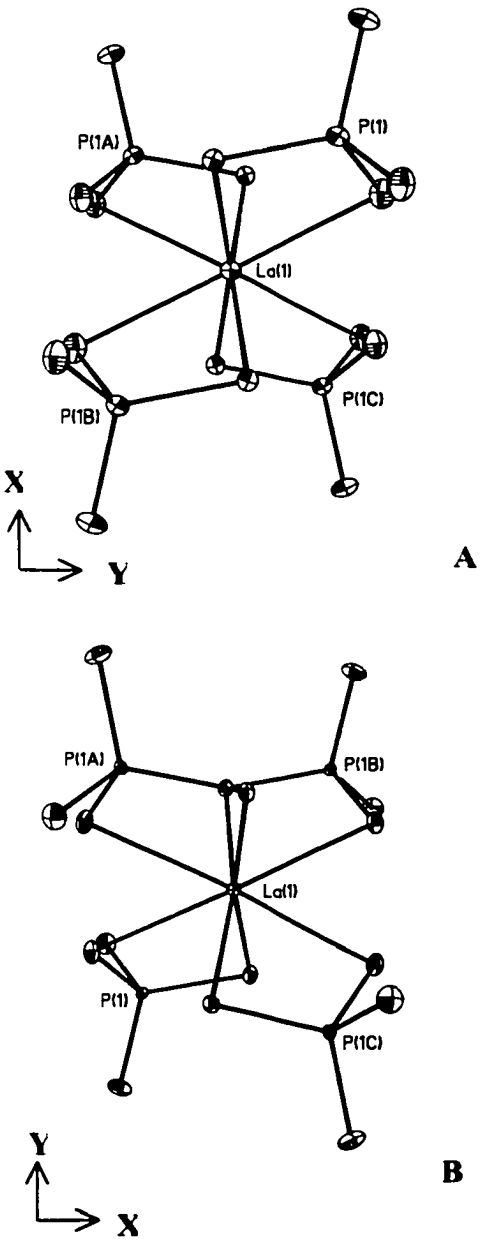


Figure 2.12. ORTEP plots of lanthanum coordination environments in $K_4La_{0.67}(PSe_4)_2$ and $K_{9-x}La_{1+x/3}(PSe_4)_4$. Thermal ellipsoids plotted at the 50% probability level. **A:** view down $[La_{0.67}(PSe_4)_2]^{4-}$ chains. **B:** $[La(PSe_4)_4]^{9-}$ isolated cluster.

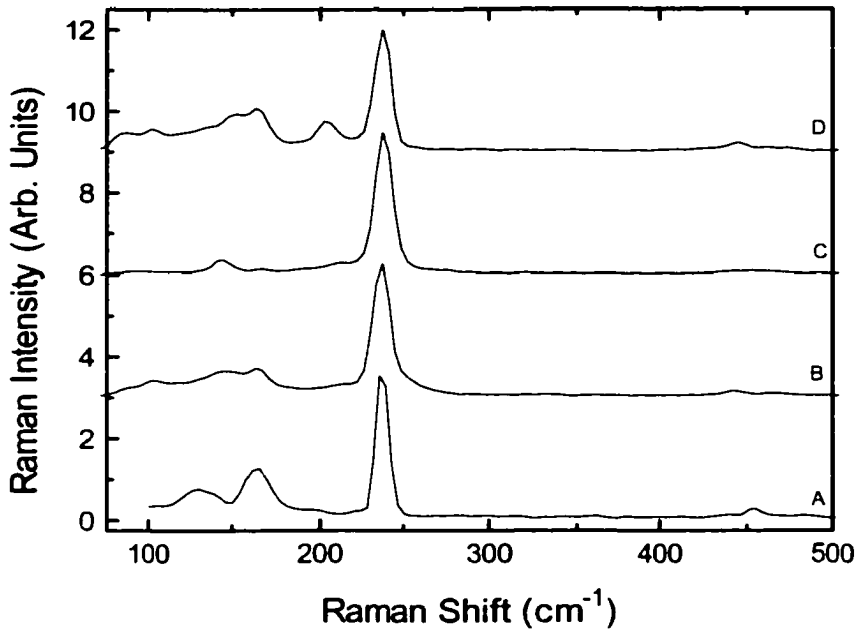


Figure 2.13. Solid-State Raman spectra: (A) $KEuPSe_4$, (B) $K_3La(PSe_4)_2$, (C) $K_4La_{0.67}(PSe_4)_2$, (D) $K_{9-x}La_{1+x/3}(PSe_4)_4$

Table 2.16. Raman peaks of compounds **II-V**.

$(PS_4)^{3-}$ (T_d) [54]	$KEuPSe_4$	$K_3La(PSe_4)_2$	$K_4La_{0.67}(PSe_4)_2$	$K_{9-x}La_{1+x/3}(PSe_4)_4$
$\nu_3(F_2)$: 548 cm^{-1}	454 cm^{-1}	443	454	446
$\nu_1(A_1)$: 416	237	237	237	237 200
$\nu_4(F_2)$: 270	165	163	166	164
$\nu_2(E)$: 215	130	145, 103	144	102

attributed to the totally symmetric stretch, and the small peak around 454 cm^{-1} is attributed to the asymmetric stretch. Bands below 200 cm^{-1} can be assigned to the bending vibrations of the $(PSe_4)^{3-}$ unit. The Raman spectrum of **IV** shows a peak at 200 cm^{-1} that is much larger than in the other three Raman spectra. The $(PSe_4)^{3-}$ tetrahedra in isolated $[La(PSe_4)_4]^{9-}$ clusters in $K_{9-x}La_{1+x/3}(PSe_4)_4$ (x = 0.5) would be expected to have much more freedom of motion which may be represent by this intense peak.

UV-Vis Spectroscopy

Diffuse reflectance optical band-gap measurements have been performed on $KEuPSe_4$. Figure 2.14 shows a plot of $(\alpha/s)^2$ vs. energy. Extrapolation shows that $KEuPSe_4$ is likely a semiconductor with an optical band gap of 1.88 eV.

Conclusions

Compounds **I-V** have been synthesized by the reactive flux method and their structures determined by single crystal X-ray diffraction. These compounds all contain $(PSe_4)^{3-}$ and/or $(P_2Se_6)^{4-}$ anionic units. The presence of these two units in many other structures reported in the literature indicates they are quite thermodynamically stable. By using a phase diagram analysis of these flux reactions, it was possible to understand what reaction conditions were necessary to form phases that comprise these units. K-P-RE phase diagrams have been constructed that indicate the molar ratios necessary to stabilize these units within phases in two

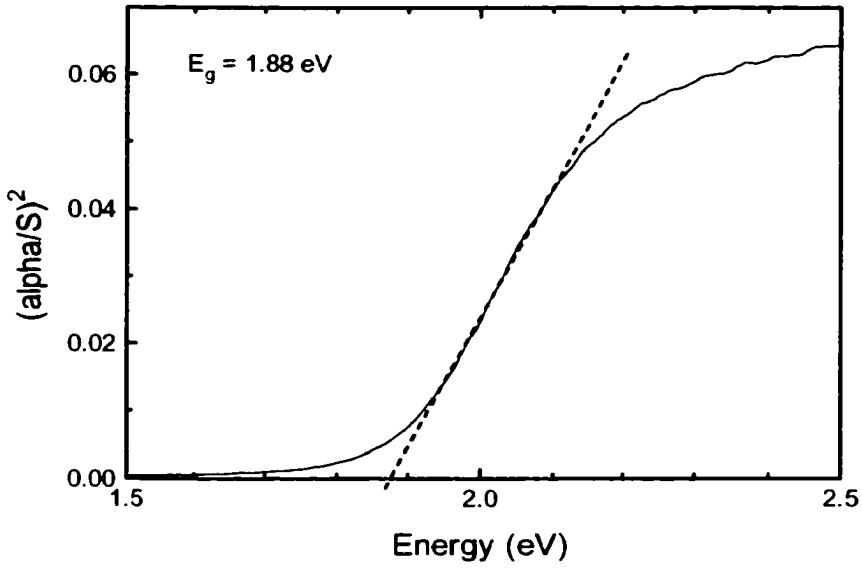


Figure 2.14. Optical Band-gap of $KEuPSe_4$

K-P-RE-Se systems. Knowing what type of anionic unit will form under various conditions allows for a rational search for new materials.

Tables of additional crystallographic details, all bond distances and angles, and anisotropic thermal parameters can be found in Appendix B, Tables B.1-B.20.

Chapter Three

Thiophosphate Phase Diagrams Developed in Conjunction with the Synthesis of the New Compounds $KLaP_2S_6$, $K_2La(P_2S_6)_{1/2}(PS_4)$, $K_3La(PS_4)_2$, $K_4La_{0.67}(PS_4)_2$, $K_{9-x}La_{1+x/3}(PS_4)_4$ (x = 0.5), $K_4Eu(PS_4)_2$, and $KEuPS_4$.

Introduction

In the preceding chapter, a detailed, directed approach to the solid-state synthesis of new quaternary rare-earth selenophosphate structures using the reactive flux method was described. By comparing reactions isometric in selenium, a series of quaternary reactions yielding different products could be plotted on a ternary phase diagram. In this chapter, that concept is extended to thiophosphate chemistry and the synthesis of $KLaP_2S_6$ **I**, $K_2La(P_2S_6)_{1/2}(PS_4)$ **II**, $K_3La(PS_4)_2$ **III**, $K_4La_{0.67}(PS_4)_2$ **IV**, $K_{9-x}La_{1+x/3}(PS_4)_4$ (x = 0.5) **V**, $K_4Eu(PS_4)_2$ **VI**, and $KEuPS_4$ **VII**. This work has been published in Inorganic Chemistry.[40]

Experimental Section

Synthesis: Crystals of all compounds observed were obtained using the same procedure. The following reactants were used as received and stored in an inert atmosphere glovebox: La (99.999%, Ames Laboratory), Eu (99.95%, Ames Laboratory), P (Mallinckrodt Red), S (99.999%, Johnson-Mathey). K_2S_2 was previously made in liquid ammonia from the stoichiometric combination of the elements.[41,42] Reactants were loaded into fused silica ampoules inside an inert atmosphere glovebox. Each ampoule was flame sealed under vacuum and placed in a temperature controlled tube furnace. The furnace was ramped to 725°C where it remained for 150 hours. The furnace was then allowed to cool back to room temperature at 4°C/hr. Crystals were separated from excess flux by washing the reaction product with dimethylformamide (DMF).

$KLaP_2S_6$, I, was synthesized by combining 58.2 mg (1.82 mmol) S, 28.7 mg (0.202 mmol) K_2S_2, 43.7 mg (1.411 mmol) P and 28.0 mg (0.202 mmol) La. The reaction yielded clear colorless crystals.

$K_2La(P_2S_6)_{1/2}(PS_4)$, II, was synthesized by combining 36.7 mg (1.13 mmol) S, 45.9 mg (0.322 mmol) K_2S_2, 20.0 mg (0.646 mmol) P and 22.4 mg (0.161 mmol) La. The reaction yielded clear colorless crystals.

$K_3La(PS_4)_2$, III, was synthesized by combining 37.0 mg (1.15 mmol) S, 46.9 mg (0.330 mmol) K_2S_2, 10.2 mg (0.330 mmol) P, and 22.9 mg (0.165 mmol) La. Clear colorless crystals were found in the reaction product.

$K_4La_{0.67}(PS_4)_2$, IV, was synthesized by combining 22.1 mg (0.689 mmol) S, 28.0 mg (0.197 mmol) K_2S_2, 6.10 mg (0.197 mmol) P, and 27.4 mg (0.197 mmol) La. Clear colorless crystals were found in the reaction product.

$K_{9-x}La_{1+x/3}(PS_4)_4$ (x = 0.5), V, was synthesized by combining 42.2 mg (1.32 mmol) S, 53.5 mg (0.375 mmol) K_2S_2, 11.6 mg (0.375 mmol) P, and 26.1 mg (0.188 mmol) La. The reactants were place in a fused silica ampoule, sealed under vacuum, and placed in a tube furnace. The tube furnace was held at 525°C for 150 hours and allowed to cool at 4°C/hour. Clear colorless crystals were separated from excess flux. The equivalent reaction at 725°C yielded crystals of $K_3La(PS_4)_2$ instead of $K_{9-x}La_{1+x/3}(PS_4)_4$ (x=0.5).

$K_4Eu(PS_4)_2$, VI, was synthesized by combining 44.0 mg (1.37 mmol) S, 55.8 mg (0.392 mmol) K_2S_2, 12.1mg (0.392 mmol) P, and 29.8 mg (0.196 mmol) Eu. The reaction yielded a binary product composed of clear colorless K_3PS_4 crystals and dark brown $K_4Eu(PS_4)_2$ crystals.

$KEuPS_4$, VII, was synthesized by combining 50.7 mg (1.58 mmol) S, 25.0 mg (0.176 mmol) K_2S_2, 10.9 mg (0.352 mmol) P and 26.7 mg (0.176 mmol) Eu in an inert atmosphere drybox. The reactants were placed in a fused silica ampoule, sealed under vacuum, and place in a tube furnace. The tube furnace was held at 525°C for 150 hours and allowed to cool at 4°C/hour. The reaction product yielded clear light brown plates of $KEuPS_4$. A second reaction with the same stoichiometries showed that $KEuPS_4$ could also be synthesized at 725°C.

Physical Measurements

Single-Crystal X-ray Diffraction. Intensity data sets for crystals **I-VII** were collected using a Bruker Smart CCD diffractometer. Each intensity data set was integrated using SAINT,[43] a SADABS absorption correction was applied,[44] and the structure was solved by direct methods using SHELXTL.[45] Crystallographic data for compounds **I-VII** are reported in Table 3.1.

Raman Spectroscopy. The solid-state Raman spectrum of compounds **I, II, VI, and VII** was taken with a Nicolet Magna-IR 760 Spectrometer with a FT-Raman Module attachment using a Nd:YAG excitation laser (1064 nm).

IR Spectroscopy. The IR spectra of compound **I** was taken on a Nicolet Magna-IR 760 Spectrometer as a KBr pellet with a pure KBr pellet subtracted with the background.

UV-Vis Spectroscopy. Diffuse reflectance measurements were taken with a Varian Cary 500 Scan UV-VIS-NIR Spectrophotometer equipped with a Praying

Table 3.1. Crystallographic data for $KLaP_2S_6$, $K_2La(P_2S_6)_{1/2}(PS_4)$, $K_3La(PS_4)_2$, $K_4La_{0.67}(PS_4)_2$, $K_{9-x}La_{1+x/3}(PS_4)_4$ (x=0.5), $K_4Eu(PS_4)_2$, and $KEuPS_4$.

	$KLaP_2S_6$ (I)	$K_2LaP_2S_7$ (II)	$K_3La(PS_4)_2$ (III)	$K_4La_{0.67}(PS_4)_2$ (IV)	$K_{9-x}La_{1+x/3}(PS_4)_4$ (V)	$K_4Eu(PS_4)_2$ (VI)	$KEuPS_4$ (VII)
fw	432.31	503.47	574.63	567.89	1131.02	626.78	350.27
a, Å	11.963(12)	9.066(6)	9.141(2)	18.202(2)	17.529(9)	18.29(5)	16.782(2)
b, Å	7.525(10)	6.793(3)	17.056(4)	8.7596(7)	36.43(3)	8.81(2)	6.6141(6)
c, Å	11.389(14)	20.112(7)	9.470(2)	9.7699(8)	9.782(4)	9.741(10)	6.5142(6)
α, deg	90.0	90.0	90.0	90.0	90.0	90.0	90.0
β, deg	109.88(4)	97.54(3)	90.29(2)	90.0	90.0	90.0	90.0
γ, deg	90.0	90.0	90.0	90.0	90.0	90.0	90.0
V, $Å^3$	964(2)	1227.9(10)	1476.5(6)	1557.7(2)	6246(6)	1570(5)	723.04(11)
Z	4	4	4	4	8	4	4
λ(Mo Kα), Å	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Space Group	$P2_1/c$ #14	$P2_1/n$ #14	$P2_1/c$ #14	Ibam #72	Ccca #68	Ibam #72	Pnma #62
Temp., K	169(2)	169(2)	168(2)	170(2)	167(2)	168(2)	168(2)
$\rho_{calc.}$, Mg/m^3	2.978	2.724	2.585	2.421	2.405	2.651	3.218
μ (mm^{-1})	6.415	5.552	5.046	4.171	3.995	6.285	10.504
R1 % [a]	5.83	4.93	3.86	4.69	6.76	4.95	3.68
wR2 % [a]	11.20	7.65	7.66	10.43	11.60	10.55	6.87

[a] $R1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ $\quad wR2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]]^{1/2}$

Mantis accessory. A polyteflon standard was used as a reference. The Kubelka-Munk function was applied to obtain band-gap information.[46,47]

Results and Discussion

Crystal Structures

A single crystal of **$KLaP_2S_6$, I,** was selected, 6077 (2307 independent) reflections were collected, and an absorption correction was applied to a monoclinic cell (R_{int} = 0.0929). The structure was solved by direct methods in $P2_1/c$ to electron density residuals of 1.563 and -1.677 $eÅ^{-3}$, and all atoms were refined anisotropically with SHELXTL using full-matrix least squares refinement on F^2 for 92 variables.[45] $KLaP_2S_6$ is isostructural to $KLaP_2Se_6$.[37] Figure 3.1 shows that $KLaP_2S_6$ is a layered structure with each $^{2}_{\infty}[La(P_2S_6)]^{1-}$ layer separated by potassium cations. Each potassium atom is coordinated by eight sulfur atoms with an average K-S bond length of 3.313(15) Å. Within each layer lanthanum atoms are intricately linked together by $(P_2S_6)^{4-}$ units. Each lanthanum atom is found as a 9-coordinate distorted tri-capped trigonal prism with an average La-S bond distance of 3.08(1) Å. The nine sulfur atoms surrounding each lanthanum atom are part of four different $(P_2S_6)^{4-}$ units. Figure 3.2 shows that each lanthanum is coordinated by two $(P_2S_6)^{4-}$ units in a face-sharing manner, edge-sharing with a third $(P_2S_6)^{4-}$ unit, and corner-sharing with a fourth $(P_2S_6)^{4-}$ unit. The P-P bond length is 2.212(5) Å, and the average P-S bond length is 2.02(1) Å. Atomic coordinates and selected bond distances and angles for $KLaP_2S_6$ are reported in Tables 3.2 and 3.3 respectively.

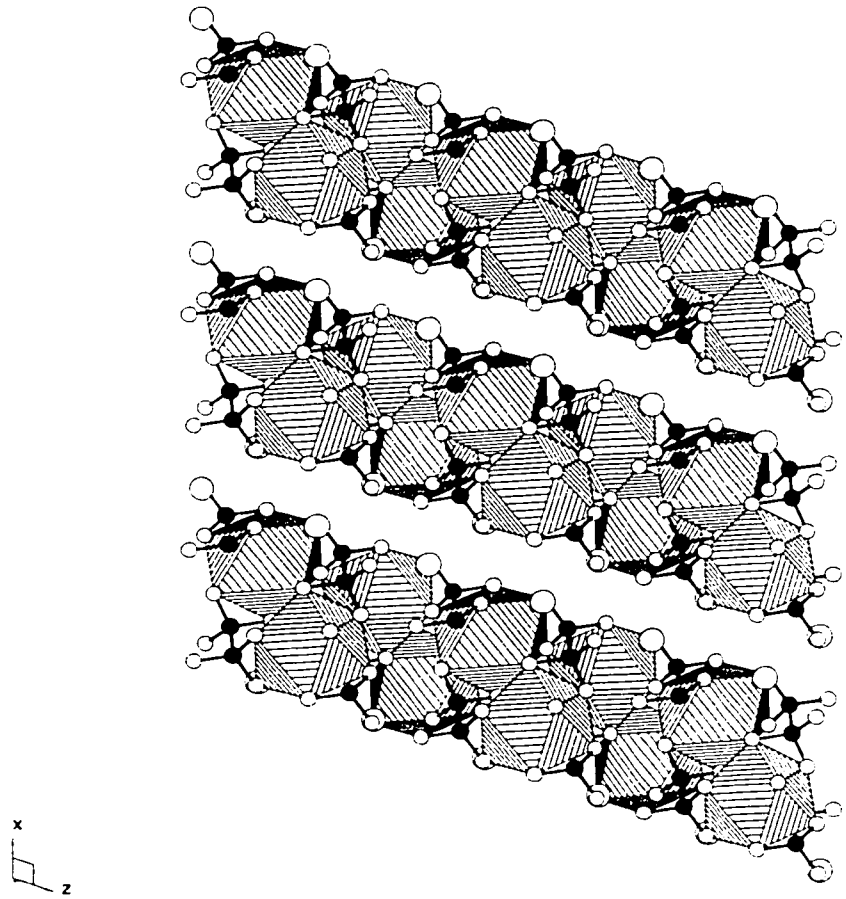


Figure 3.1. Packing plot of $KLaP_2S_6$. Striped lanthanum polyhedra, filled phosphorus atoms, small unfilled sulfur atoms, and large unfilled potassium atoms.

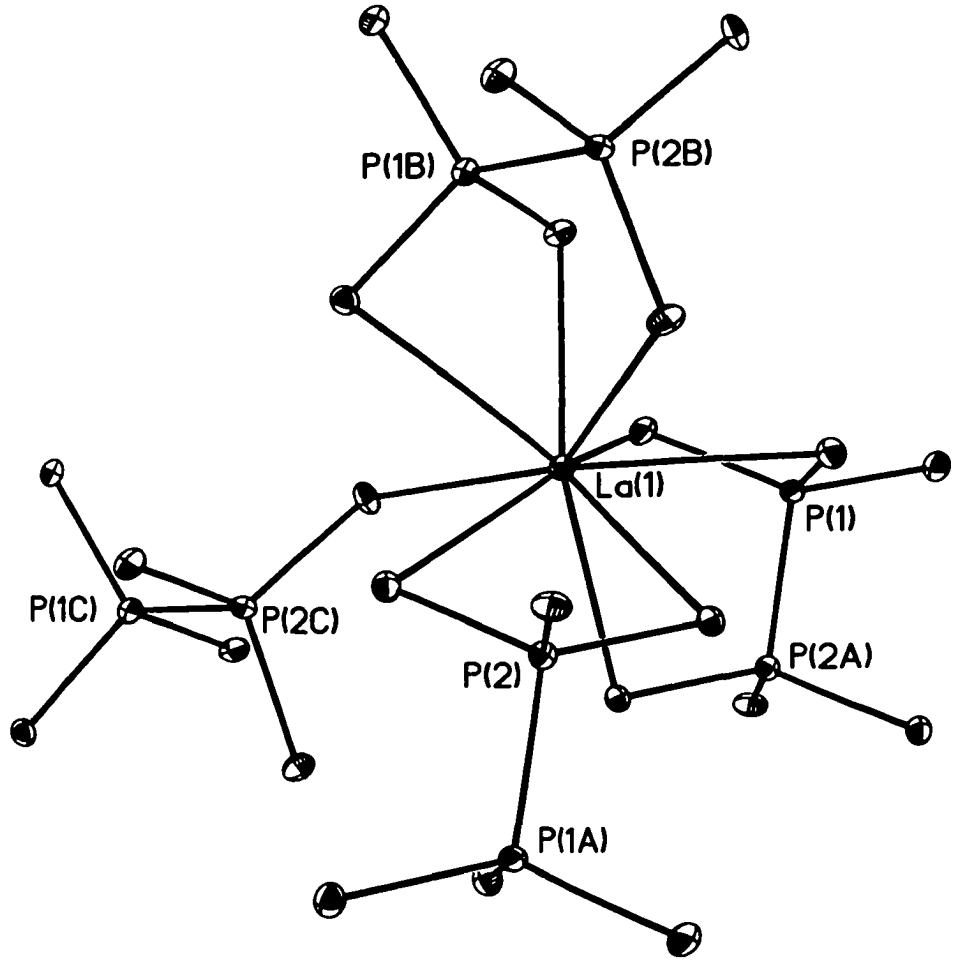


Figure 3.2. ORTEP plot of lanthanum coordination environment in $KLaP_2S_6$. Thermal ellipsoids plotted at the 50% probability level. Potassium atoms left out for clarity.

Table 3.2. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($Å^2$ x 10^3)[a] for $KLaP_2S_6$.

	x	y	z	U(eq)
La(1)	0.6505(1)	0.1060(1)	0.9037(1)	9(1)
P(1)	0.7921(3)	0.1184(4)	1.2341(3)	8(1)
P(2)	0.3258(3)	0.1015(4)	0.7530(3)	9(1)
K(1)	1.1291(2)	0.0921(4)	1.3744(3)	15(1)
S(1)	0.6765(3)	0.1927(4)	0.6396(3)	11(1)
S(2)	0.4439(3)	-0.0152(4)	0.6828(3)	12(1)
S(3)	0.8875(3)	0.0233(4)	1.1341(3)	12(1)
S(4)	0.4090(3)	0.1867(4)	0.9311(3)	10(1)
S(5)	0.8738(3)	0.2968(4)	0.9104(3)	12(1)
S(6)	0.7801(3)	-0.2131(4)	0.8570(3)	12(1)

[a] U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3.3. Selected bond distances (Å) and angles (Deg.) for $KLaP_2S_6$.

La(1)-S(6)	3.002(4)	P(1)-P(2)	2.212(5)
La(1)-S(2)	3.007(4)	P(1)-S(5)	2.016(5)
La(1)-S(4)	3.070(4)	P(1)-S(3)	1.998(5)
La(1)-S(4')	3.131(4)	P(1)-S(1)	2.019(5)
La(1)-S(3)	3.201(5)	P(2)-S(2)	2.044(5)
La(1)-S(1')	3.006(4)	P(2)-S(4)	2.035(5)
La(1)-S(5)	3.011(4)	P(2)-S(6)	2.010(5)
La(1)-S(2')	3.101(5)		
La(1)-S(1)	3.196(5)		
S(6)-La(1)-S(1')	131.19(10)	S(5)-La(1)-S(2')	78.11(11)
S(1')-La(1)-S(2)	134.97(10)	S(6)-La(1)-S(4')	77.33(12)
S(1')-La(1)-S(5)	85.16(10)	S(2)-La(1)-S(4')	89.97(12)
S(6)-La(1)-S(4)	137.46(9)	S(4)-La(1)-S(4')	70.38(11)
S(2)-La(1)-S(4)	67.12(11)	S(6)-La(1)-S(1)	76.98(10)
S(6)-La(1)-S(2')	146.41(10)	S(2)-La(1)-S(1)	65.76(11)
S(2)-La(1)-S(2')	84.61(8)	S(4)-La(1)-S(1)	116.85(9)
S(4)-La(1)-S(2')	66.22(9)	S(4')-La(1)-S(1)	145.49(9)
S(1')-La(1)-S(4')	78.08(13)	S(1')-La(1)-S(3)	64.66(11)
S(5)-La(1)-S(4')	134.51(9)	S(5)-La(1)-S(3)	62.68(11)
S(2')-La(1)-S(4')	34.82(10)	S(2')-La(1)-S(3)	124.37(9)
S(1')-La(1)-S(1)	136.43(8)	S(1)-La(1)-S(3)	117.93(11)
S(5)-La(1)-S(1)	63.68(9)	S(3)-P(1)-S(5')	120.3(2)
S(2')-La(1)-S(1)	69.80(9)	S(5')-P(1)-S(1')	108.7(2)
S(6)-La(1)-S(3)	67.85(10)	S(5')-P(1)-P(2)	105.9(2)
S(2)-La(1)-S(3)	150.87(10)	S(6')-P(2)-S(4)	113.2(2)
S(4)-La(1)-S(3)	123.85(11)	S(4)-P(2)-S(2)	110.9(2)
S(4')-La(1)-S(3)	71.93(10)	S(4)-P(2)-P(1)	106.0(2)
S(6)-La(1)-S(2)	86.33(11)	S(3)-P(1)-S(1')	111.6(2)
S(6)-La(1)-S(5)	83.02(12)	S(3)-P(1)-P(2)	105.7(2)
S(2)-La(1)-S(5)	129.45(11)	S(1')-P(1)-P(2)	103.0(2)
S(1')-La(1)-S(4)	67.97(9)	S(6')-P(2)-S(2)	115.3(2)
S(5)-La(1)-S(4)	139.52(11)	S(6')-P(2)-P(1)	106.2(2)
S(1')-La(1)-S(2')	74.73(11)	S(2)-P(2)-P(1)	104.2(2)

A single crystal of **$K_2La(P_2S_6)_{1/2}(PS_4)$ or $K_2LaP_2S_7$, II,** was selected, 7846 (2978 independent) reflections were collected, and an absorption correction was applied to a monoclinic cell (R_{int} = 0.0796). The structure was solved by direct methods in $P2_1/n$ to electron density residuals of 1.353 and -1.214 eÅ^{-3}, and all atoms were refined anisotropically with SHELXTL using full-matrix least squares refinement on F^2 for 109 variables.[45] $K_2LaP_2S_7$ is isostructural to $K_2LaP_2Se_7$. It is a layered compound with $^{2}_{\infty}[La(P_2S_6)_{1/2}(PS_4)]^{2-}$ layers lying in the (101) plane of the unit cell that are separated by potassium cations. Figure 3.3 shows that each layer is composed of lanthanum atoms coordinated by $(PS_4)^{3-}$ tetrahedra and $(P_2S_6)^{4-}$ ethane-like units. Within each layer, "chains" of lanthanum distorted square anti-prisms coordinated by $(PS_4)^{3-}$ tetrahedra are linked into a layer with ethane-like $(P_2S_6)^{4-}$ units. In this way each 8-coordinate lanthanum atom is edge-sharing with two $(PS_4)^{3-}$ tetrahedra, corner-sharing with a third $(PS_4)^{3-}$ tetrahedron, and bound in a side ways fashion to a $(P_2S_6)^{4-}$ unit. The average La-S bond distance is 3.015(6) Å. The coordination environment of lanthanum in $K_2LaP_2S_7$ is shown in Figure 3.4. Atomic coordinates and selected bond distances and angles for $K_2LaP_2S_7$ are reported in Tables 3.4 and 3.5 respectively.

A single crystal of **$K_3La(PS_4)_2$ or $K_3LaP_2S_8$, III,** was selected, 9659 (3559 independent) reflections were collected, and an absorption correction was applied to a monoclinic cell (R_{int} = 0.0499). The structure was solved by direct methods in $P2_1/c$ to electron density residuals of 1.197 and -1.974 eÅ^{-3}, and all atoms were refined anisotropically with SHELXTL using full-matrix least squares refinement on F^2 for 127 variables.[45] $K_3LaP_2S_8$ is isostructural to $K_3CeP_2S_8$[35] and isotypic to $K_3LaP_2Se_8$.

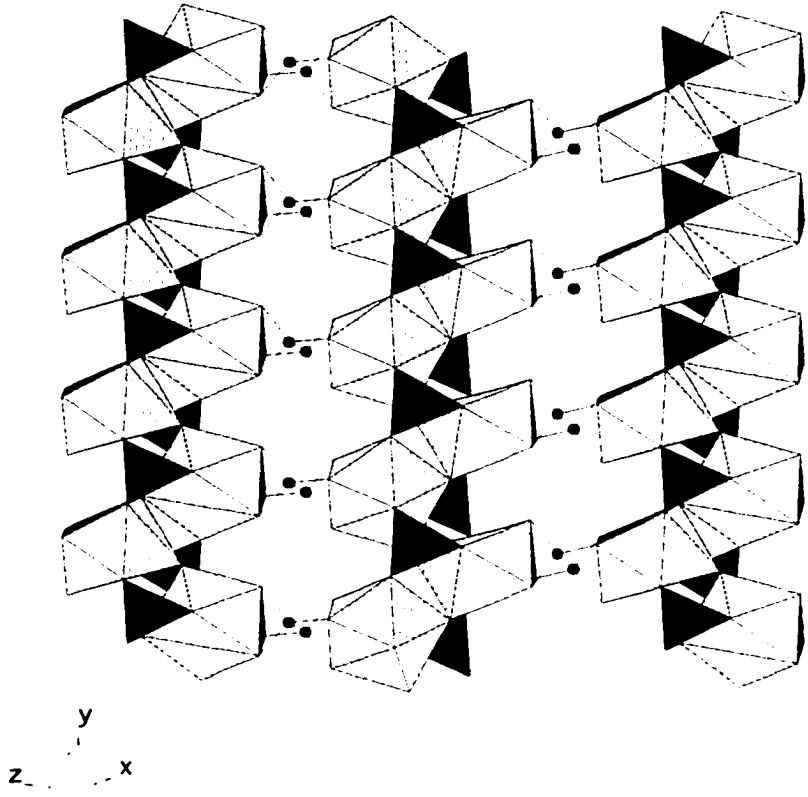


Figure 3.3. $K_2LaP_2S_7$: Striped La-S polyhedra, black $(PS_4)^{3-}$ tetrahedra, black phosphorus atoms in $(P_2S_6)^{4-}$, potassium atoms left out for clarity.

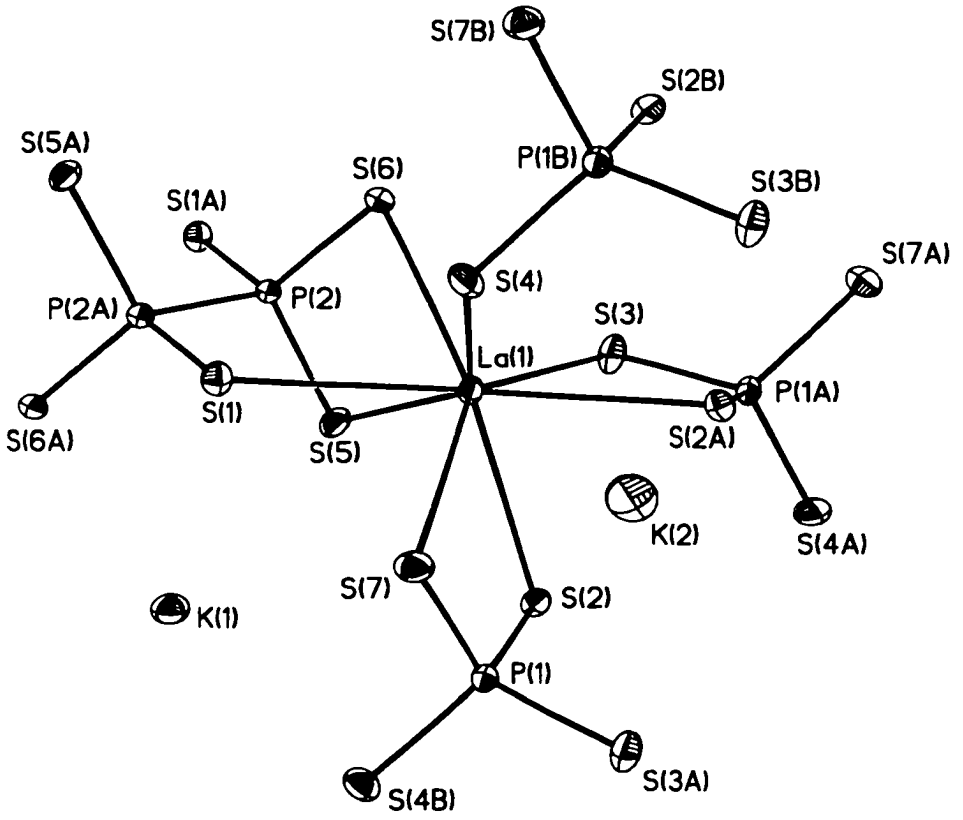


Figure 3.4. ORTEP plot of the lanthanum coordination environment in $K_2LaP_2S_7$. Thermal ellipsoids plotted at the 50% probability level.

Table 3.4. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($Å^2$ x 10^3)[a] for $K_2La(P_2S_6)_{1/2}(PS_4)$.

	x	y	z	U(eq)
La(1)	0.3109(1)	0.9770(1)	0.1505(1)	12(1)
P(1)	0.0943(2)	0.5158(3)	0.1678(1)	13(1)
P(2)	0.5847(2)	1.0101(3)	0.0442(1)	12(1)
S(1)	0.2224(2)	0.9695(3)	-0.0060(1)	16(1)
S(2)	0.3046(2)	0.5650(3)	0.2172(1)	14(1)
S(3)	0.5499(2)	0.9932(3)	0.2630(1)	19(1)
S(4)	0.0802(3)	1.2754(3)	0.1082(1)	20(1)
S(5)	0.5591(3)	0.7637(3)	0.0990(1)	16(1)
S(6)	0.5305(2)	1.2489(3)	0.0963(1)	15(1)
S(7)	0.0386(3)	0.7485(3)	0.1067(1)	18(1)
K(1)	0.7606(2)	0.5110(3)	0.0094(1)	20(1)
K(2)	-0.1508(2)	1.0262(3)	0.1918(1)	29(1)

[a] U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3.5. Selected bond distances (Å) and angles (Deg.) for $K_2La(P_2S_6)_{1/2}(PS_4)$.

La(1)-S(3)	2.922(2)	La(1)-S(7)	2.951(3)
La(1)-S(4)	2.956(2)	La(1)-S(5)	2.974(2)
La(1)-S(6)	3.022(2)	La(1)-S(2')	3.045(2)
La(1)-S(2)	3.107(2)	La(1)-S(1)	3.145(2)
P(1)-S(4')	2.021(3)	P(1)-S(7)	2.025(3)
P(1)-S(3')	2.036(3)	P(1)-S(2)	2.058(3)
P(2)-S(1')	2.005(3)	P(2)-S(6)	2.026(3)
P(2)-S(5)	2.034(3)	P(2)-P(2')	2.195(4)
S(3)-La(1)-S(7)	139.19(6)	S(3)-La(1)-S(4)	128.46(7)
S(7)-La(1)-S(4)	75.06(7)	S(3)-La(1)-S(5)	76.70(7)
S(7)-La(1)-S(5)	106.34(7)	S(4)-La(1)-S(5)	140.60(6)
S(3)-La(1)-S(6)	78.45(7)	S(7)-La(1)-S(6)	141.16(6)
S(4)-La(1)-S(6)	87.25(7)	S(5)-La(1)-S(6)	66.91(6)
S(3)-La(1)-S(2')	67.72(7)	S(7)-La(1)-S(2')	89.64(7)
S(4)-La(1)-S(2')	78.79(6)	S(5)-La(1)-S(2')	139.70(6)
S(6)-La(1)-S(2')	120.92(6)	S(3)-La(1)-S(2)	75.72(6)
S(7)-La(1)-S(2)	65.97(6)	S(4)-La(1)-S(2)	133.58(6)
S(5)-La(1)-S(2)	76.64(6)	S(6)-La(1)-S(2)	139.15(6)
S(2')-La(1)-S(2)	76.80(4)	S(3)-La(1)-S(1)	147.28(6)
S(7)-La(1)-S(1)	66.39(6)	S(4)-La(1)-S(1)	69.22(6)
S(5)-La(1)-S(1)	75.45(6)	S(6)-La(1)-S(1)	75.08(6)
S(2')-La(1)-S(1)	143.74(6)	S(2)-La(1)-S(1)	113.61(6)
S(4')-P(1)-S(3')	110.40(13)	S(4')-P(1)-S(7)	106.21(12)
S(4')-P(1)-S(2)	113.57(13)	S(7)-P(1)-S(3')	110.04(13)
S(3')-P(1)-S(2)	108.67(12)	S(7)-P(1)-S(2)	107.89(12)
S(1')-P(2)-S(5)	115.57(13)	S(1')-P(2)-S(6)	115.18(13)
S(1')-P(2)-P(2')	104.27(14)	S(6)-P(2)-S(5)	109.03(12)
S(5)-P(2)-P(2')	105.7(2)	S(6)-P(2)-P(2')	106.1(2)

The only difference between the sulfur and selenium versions of this structure is that in the selenium compound, lanthanum is 8-coordinate while the sulfur analogs contains 9-coordinate RE atoms. The average La-S bond distance is 3.076(4) Å. $K_3LaP_2S_8$ contains chains of $^1_\infty[La(PS_4)_2]^{3-}$ along the x-axis that are separated by potassium cations, shown in Figure 3.5. Along the length of each chain, distorted tri-capped trigonal prismatic lanthanum atoms are bridged by tetrahedral $(PS_4)^{3-}$ units. Figure 3.6 shows that the lanthanum atoms in $K_3La(PS_4)_2$ are coordinated by three edge-sharing $(PS_4)^{3-}$ tetrahedra and one face-sharing $(PS_4)^{3-}$ tetrahedron. In contrast, the lanthanum atom in $K_3La(PSe_4)_2$ is coordinated by four edge-sharing $(PSe_4)^{3-}$ tetrahedra. This results in a 8-coordinate lanthanum atoms versus 9-coordinate lanthanum atoms in $K_3LaP_2Se_8$ and $K_3LaP_2S_8$ respectively. Atomic coordinates and selected bond distances and angles for $K_3LaP_2S_8$ are reported in Tables 3.6 and 3.7 respectively.

A single crystal of **$K_4La_{0.67}(PS_4)_2$ or $K_6La(PS_4)_3$, IV,** was selected, 4880 (1031 independent) reflections were collected, and an absorption correction was applied to an orthorhombic cell (R_{int} = 0.0737). The structure was solved by direct methods in Ibam to electron density residuals of 1.154 and -1.064 eÅ^{-3}, and all atoms were refined anisotropically with SHELXTL using full-matrix least squares refinement on F^2 for 42 variables.[45] $K_4La_{0.67}(PS_4)_2$ is isostructural to $K_4La_{0.67}(PSe_4)_2$. One-dimensional $^1_\infty[La_{0.67}(PS_4)_2]^{4-}$ chains are found along c. Figure 3.7 shows that these chains are separated along a and b by potassium cations. Two crystallographically distinct potassium atoms are found with K-S bond distances ranging from 3.096(3) Å to 3.722(2) Å. Within these chains 8-coordinate lanthanum

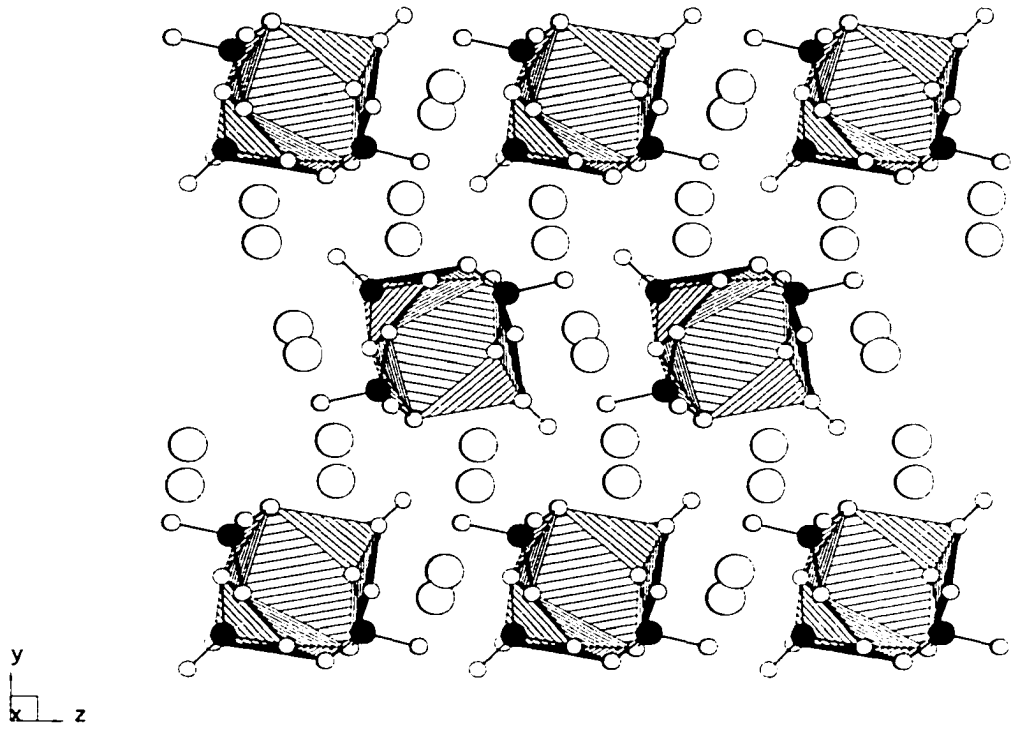


Figure 3.5. Packing plot of $K_3La(PS_4)_2$. Striped lanthanum polyhedra, filled phosphorus atoms, small unfilled sulfur atoms, and large unfilled potassium atoms.

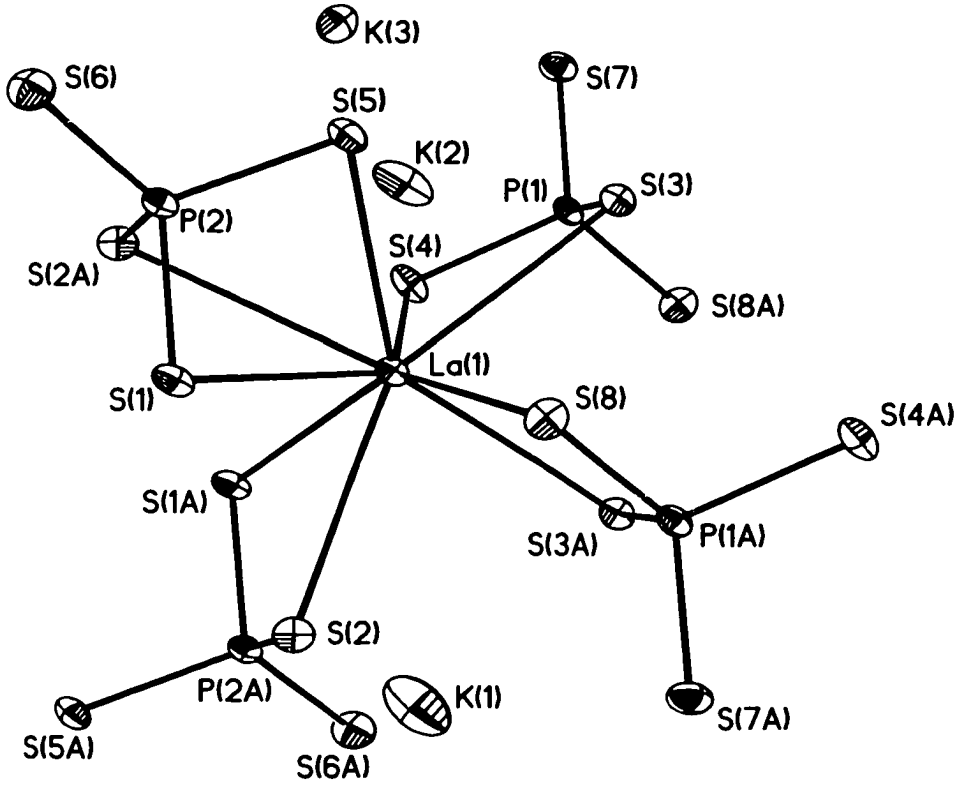


Figure 3.6. ORTEP plot of the lanthanum coordination environment in $K_3La(PS_4)_2$. Thermal ellipsoids plotted at the 50% probability level.

Table 3.6. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$)[a] for $K_3La(PS_4)_2$.

	x	y	z	U(eq)
La(1)	0.2269(1)	0.0137(1)	0.9697(1)	10(1)
S(1)	-0.0399(2)	0.1276(1)	0.9631(1)	14(1)
S(2)	0.0478(2)	0.0150(1)	1.2546(1)	15(1)
S(3)	0.5371(1)	0.0195(1)	0.8151(1)	13(1)
S(4)	0.3129(2)	-0.1312(1)	0.8225(1)	17(1)
S(5)	0.2090(2)	0.1201(1)	0.7189(1)	16(1)
S(6)	-0.1304(2)	0.1742(1)	0.6301(1)	20(1)
S(7)	0.5651(2)	-0.1270(1)	0.5745(1)	17(1)
S(8)	0.3379(2)	0.1587(1)	1.0919(1)	17(1)
P(1)	0.5231(1)	-0.1001(1)	0.7761(1)	11(1)
P(2)	-0.0084(2)	0.1040(1)	0.7528(1)	12(1)
K(1)	0.1194(2)	0.2039(1)	1.3761(2)	31(1)
K(2)	0.3843(2)	-0.2881(1)	0.6299(2)	37(1)
K(3)	0.2702(1)	-0.0272(1)	0.5146(1)	21(1)

[a] U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3.7. Selected bond distances (Å) and angles (Deg.) for $K_3La(PS_4)_2$.

La(1)-S(8)	2.9112(14)	P(1)-S(3)	2.077(2)
La(1)-S(5)	2.9929(14)	P(1)-S(4)	2.043(2)
La(1)-S(1')	3.0246(14)	P(1)-S(7)	2.003(2)
La(1)-S(2)	3.1629(14)	P(1)-S(8)	2.039(2)
La(1)-S(2')	3.317(2)	P(2)-S(1)	2.054(2)
La(1)-S(4)	2.9452(14)	P(2)-S(2)	2.062(2)
La(1)-S(3')	3.0142(14)	P(2)-S(5)	2.034(2)
La(1)-S(1)	3.119(2)	P(2)-S(6)	2.004(2)
La(1)-S(3)	3.200(2)		

S(8)-La(1)-S(4)	143.84(4)	S(5)-La (1)-S(3)	70.31(4)
S(4)-La(1)-S(5)	98.45(4)	S(1')-La (1)-S(3)	128.60(4)
S(4)-La(1)-S(3')	88.31(4)	S(1)-La (1)-S(3)	131.80(4)
S(8)-La(1)-S(1')	142.15(4)	S(8)-La (1)-S(2')	129.89(4)
S(5)-La(1)-S(1')	128.44(4)	S(5)-La (1)-S(2')	62.83(4)
S(8)-La(1)-S(1)	75.50(4)	S(1')-La (1)-S(2')	65.81(4)
S(5)-La(1)-S(1)	64.34(4)	S(2)-La (2)-S(2')	98.86(3)
S(1')-La(1)-S(1)	93.33(4)	S(2)-La (2)-S(3)	148.63(4)
S(4)-La(1)-S(2)	123.37(4)	S(4)-La (2)-S(2')	77.07(4)
S(3')-La(1)-S(2)	78.23(4)	S(3')-La (2)-S(2')	160.43(4)
S(1)-La(1)-S(2)	66.71(4)	S(1-La (2)-S(2')	59.33(4)
S(4)-La(1)-S(3)	64.53(4)	S(3)-La(2)-S(2')	112.42(4)
S(3')-La(1)-S(3)	71.48(4)	S(7)-P(1)-S(4)	109.33(8)
S(8)-La(1)-S(5)	79.51(4)	S(7)-P(1)-S(3)	112.45(8)
S(8)-La(1)-S(3')	69.13(4)	S(4)-P(1)-S(3)	105.87(8)
S(5)-La(1)-S(3')	133.35(4)	S(7)-P(1)-S(8)	110.51(8)
S(4)-La(1)-S(1')	65.38(4)	S(8)-P(1)-S(4)	108.99(8)
S(3')-La(1)-S(1')	96.39(4)	S(8)-P(1)-S(3)	109.55(8)
S(4)-La(1)-S(1)	136.38(4)	S(6)-P(2)-S(5)	111.67(8)
S(3')-La(1)-S(1)	133.42(4)	S(5)-P(2)-S(1)	105.58(8)
S(8)-La(1)-S(2)	80.54(4)	S(5)-P(2)-S(2)	107.38(8)
S(5)-La(1)-S(2)	130.27(4)	S(6)-P(2)-S(1)	111.35(8)
S(1')-La(1)-S(2)	62.02(4)	S(6)-P(2)-S(2)	118.15(9)
S(8)-La(1)-S(3)	81.24(4)	S(1)-P(2)-S(2)	101.59(7)

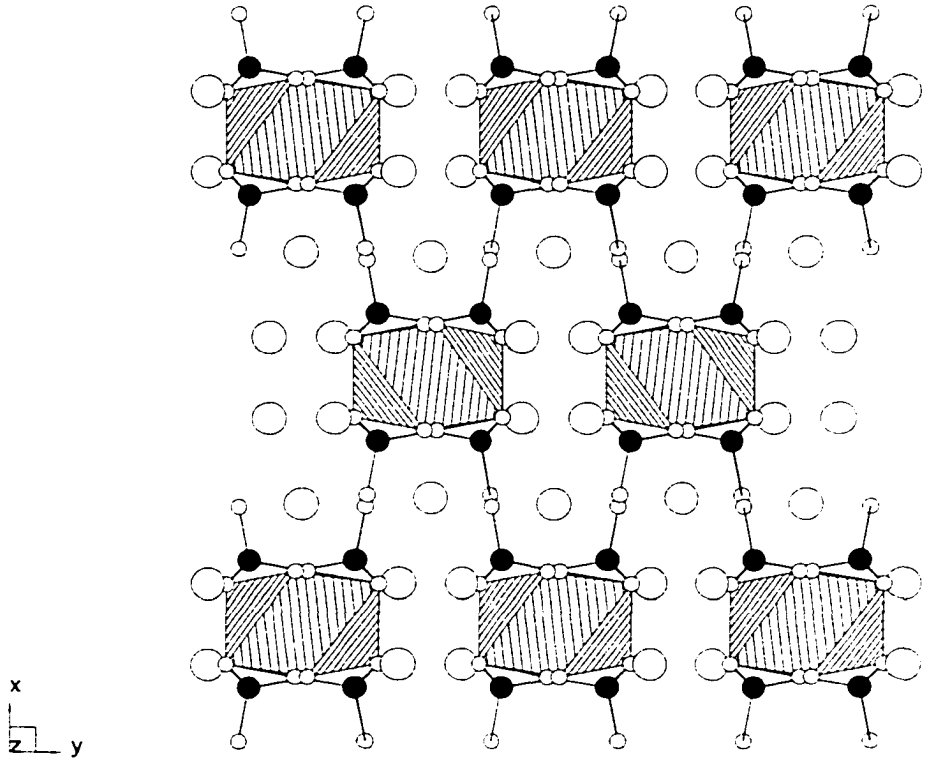


Figure 3.7. Packing plot of $K_4La_{0.67}(PS_4)_2$. Striped lanthanum dodecahedra, filled phosphorus atoms, small unfilled sulfur atoms, and large unfilled potassium atoms.

atoms are linked together by $(PS_4)^{3-}$ tetrahedra. The average La-S bond distance is 3.116(3) Å. As in the selenide structure, the lanthanum position is partially occupied to charge balance the formula. In a random fashion, every third lanthanum atom is "missing" along each chain. Figure 3.8 shows a section of these chains with La(1B) "missing". In essence, this reduces the infinite chains into shorter lanthanum dimmers, on average, containing two bridging $(PS_4)^{3-}$ units and four terminal $(PS_4)^{3-}$ units. Atomic coordinates and selected bond distances and angles for $K_4La_{0.67}(PS_4)_2$ are reported in Tables 3.8 and 3.9 respectively.

A single crystal of **$K_{9-x}La_{1+x/3}(PS_4)_4$ or $K_{9-x}La_{1+x/3}P_4S_{16}$ (x = 0.5), V,** was selected, 19212 (3880 independent) reflections were collected, and an absorption correction was applied to an orthorhombic cell (R_{int} = 0.1352). The structure was solved by direct methods in Ccca to electron density residuals of 2.153 and -1.917 eÅ^{-3}, and all atoms were refined anisotropically with SHELXTL using full-matrix least squares refinement on F^2 for 140 variables.[45] The initial unit cell found by SMART [a = 20.23(3) Å, b = 9.77(1) Å, c = 17.52(1) Å, β = 115.84(5)°] matched well with the $Rb_9Ce(PSe_4)_4$ structure,[38] and we therefore expected the solved formula to be $K_9La(PS_4)_4$ in a monoclinic system. However, just as in the isostructural selenide case, an acceptable structure solution could not obtained in the C2/c space group.[55] Significant electron density was left on one of the potassium sites leading to a structure with a lanthanum ratio higher than one and a formula that could not be charge balanced. Moving to a system of higher symmetry and a large unit cell allowed a reasonable structure solution in the orthorhombic space group Ccca with cell parameters a=17.529(9) Å, b=36.43(3) Å, and c=9.782(4) Å. The structure of

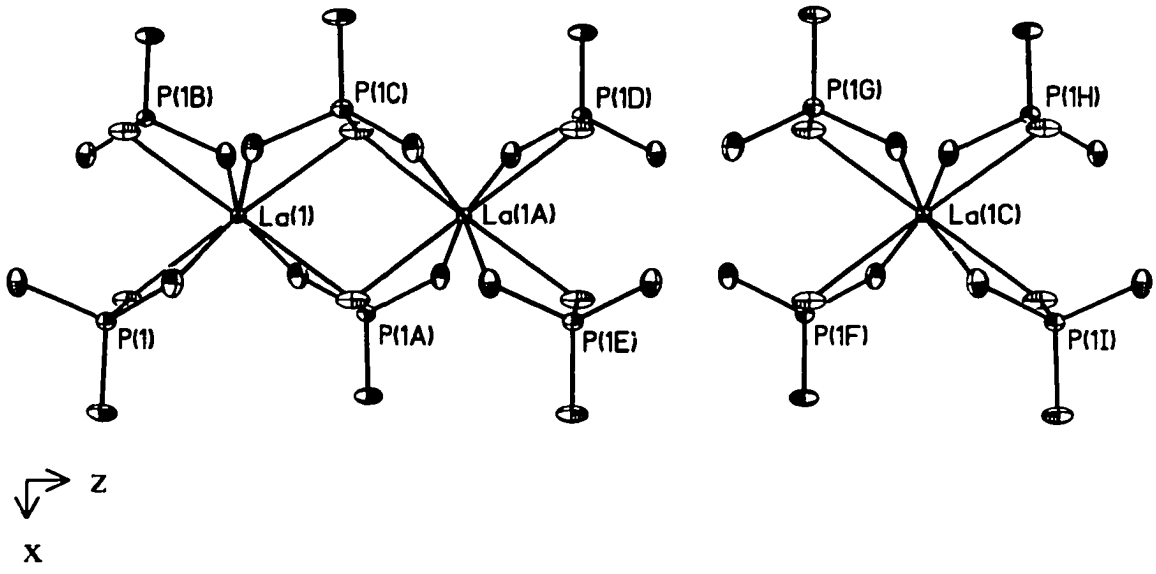


Figure 3.8. ORTEP plot of $K_4La_{0.67}P_2S_8$. Potassium atoms left out for clarity. Thermal ellipsoids plotted at the 50% probability level.

Table 3.8. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$)[a] for $K_4La_{0.67}(PS_4)_2$.

	x	y	z	U(eq)
La(1)[b]	0.0000	0.0000	0.2500	10(1)
P(1)	0.1290(1)	0.2064(2)	0.5000	15(1)
S(1)	0.0807(1)	0.2986(2)	0.3312(1)	24(1)
S(2)	0.1069(1)	0.0245(2)	0.0000	28(1)
S(3)	0.2383(1)	0.2468(2)	0.5000	27(1)
K(1)	-0.0820(1)	-0.3741(2)	0.0000	32(1)
K(2)	0.2446(1)	0.0000	0.2500	37(1)

[a] U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.
[b] The La(1) position is only 2/3 occupied.

Table 3.9. Selected bond distances (Å) and angles (Deg.) for $K_4La_{0.67}(PS_4)_2$.

La(1)-S(1) x 4	3.1024(14)	P(1)-S(3)	2.020(2)
La(1)-S(2) x 4	3.1302(12)	P(1)-S(1)	2.036(2)
P(1)-S(2)	2.062(3)	P(1)-S(1')	2.036(2)
S(1)-La(1)-S(1')	65.1(2)	S(1')-La(1)-S(2')	123.51(7)
S(1')-La(1)-S(1')	150.61(10)	S(1')-La(1)-S(2')	92.41(10)
S(1')-La(1)-S(1')	123.32(14)	S(1')-La(1)-S(2)	92.41(10)
S(1)-La(1)-S(2')	64.14(8)	S(1')-La(1)-S(2)	123.51(7)
S(1')-La(1)-S(2')	80.91(11)	S(1)-La(1)-S(2')	92.41(10)
S(1)-La(1)-S(2')	80.91(11)	S(1')-La(1)-S(2')	123.51(7)
S(1')-La(1)-S(2)	64.14(8)	S(2')-La(1)-S(2')	78.0(2)
S(2')-La(1)-S(2)	102.5(2)	S(1)-La(1)-S(2')	123.51(7)
S(1')-La(1)-S(2)	80.91(11)	S(1')-La(1)-S(2')	92.41(10)
S(1')-La(1)-S(2')	64.14(8)	S(2')-La(1)-S(2')	172.11(7)
S(2)-La(1)-S(2')	172.11(7)	S(2')-La(1)-S(2')	102.5(2)
S(1')-La(1)-S(2')	64.14(8)	S(3)-P(1)-S(1')	111.05(10)
S(1')-La(1)-S(2')	80.91(11)	S(1')-P(1)-S(1)	107.6(2)
S(2)-La(1)-S(2')	78.0(2)	S(1')-P(1)-S(2')	107.78(10)
S(1)-La(1)-S(1')	123.32(14)	S(3)-P(1)-S(1)	111.06(10)
S(1)-La(1)-S(1')	150.61(10)	S(3)-P(1)-S(2')	111.36(11)
S(1')-La(1)-S(1')	65.1(2)	S(1)-P(1)-S(2')	107.78(10)

$K_{9-x}La_{1+x/3}(PS_4)_4$ (x = 0.5), shown in Figure 3.9, contains two crystallographically distinct lanthanum atoms. The first lanthanum exists as isolated $^{0}_{\infty}[La(PS_4)_4]^{9-}$ clusters like those observed in the $Rb_9Ce(PSe_4)_4$ structure. These clusters alternate with potassium atoms along the z-axis of the unit cell. The second lanthanum is found in chains of lanthanum atoms linked together by $(PS_4)^{3-}$ tetrahedra along the z-axis of the unit cell. The lanthanum position along these chains is 2/3 occupied, just as in the $K_4La_{0.67}(PS_4)_2$ structure. The two different lanthanum positions alternate throughout the structure yielding, in effect, $^{1}_{\infty}[La_{0.67}(PS_4)_2]^{4-}$ chains alternating with $^{0}_{\infty}[La(PS_4)_4]^{9-}$ clusters along the [100] and [010] directions. Both lanthanum atoms exist as dodecahedra having 8 La-S bonds. The average La-S bond to each lanthanum shows the difference in environments. The average La-S around each La(1) cluster is 3.00(1) Å, while the average La-S bond length around each La(2) in a partially occupied chain is 3.13(1) Å. Finally, the potassium atom located between La(1) isolated clusters has a rather large thermal parameter. It was refined anisotropically, but its size suggests that perhaps a partially occupied potassium or lanthanum atom exists in this position. Efforts to incorporate this into the structure solution were unsuccessful. Atomic coordinates and selected bond distances and angles for $K_{9-x}La_{1+x/3}(PS_4)_4$ (x = 0.5) are reported in Table 3.10 and 3.11 respectively. The $K_{9-x}La_{1+x/3}(PS_4)_4$ (x = 0.5) formula fits well with the systematic dismantling of infinite $^{1}_{\infty}[La(PS_4)_2]^{3-}$ chains in $K_3La(PS_4)_2$, to shorter chains in $K_4La_{0.67}(PS_4)_2$, to short chains and isolated clusters in $K_{9-x}La_{1+x}(PS_4)_4$, and ending in isolated $^{0}_{\infty}[La(PS_4)_4]^{9-}$ clusters in the expected $K_9La(PS_4)_4$ structure. The $K_{9-x}La_{1+x}(PS_4)_4$ and $K_4La_{0.67}(PS_4)_2$ structures are very similar, differing only in the

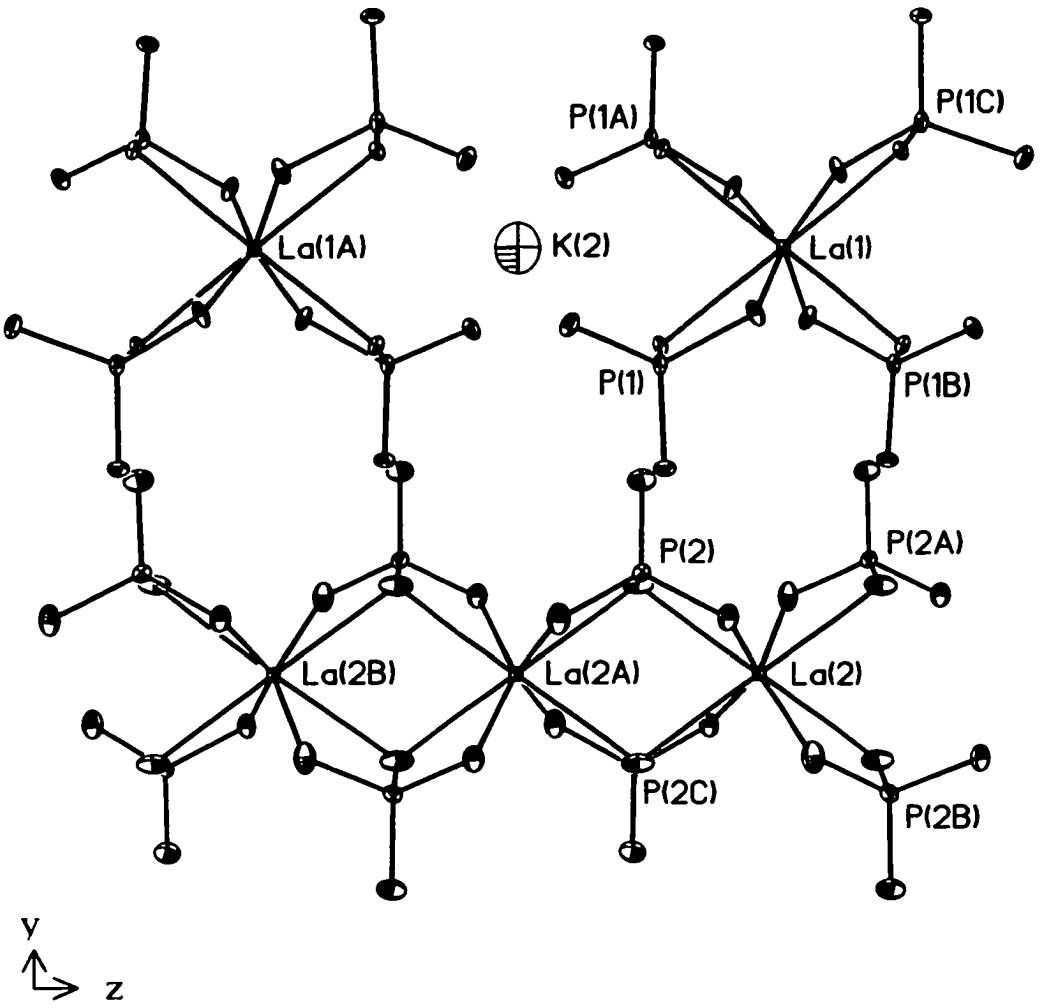


Figure 3.9. ORTEP plot of the different lanthanum coordination environments in $K_{9-x}La_{1+x/3}(PS_4)_4$. Thermal ellipsoids plotted at the 50% probability level.

Table 3.10. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$)[a] for $K_{9-x}La_{1+x/3}(PS_4)_4$ (x = 0.5).

	x	y	z	U(eq)
La(1)	0.0000	0.2500	0.7500	7(1)
La(2)[b]	0.2500	0.0000	0.7460(1)	7(1)
S(1)	0.0119(2)	0.1960(1)	0.5215(3)	9(1)
S(2)	0.1474(2)	0.2124(1)	0.8226(3)	15(1)
S(3)	-0.1531(2)	0.2064(1)	0.3405(4)	16(1)
S(4)	-0.1240(2)	0.1307(1)	0.5179(4)	16(1)
S(5)	0.0999(2)	0.0407(1)	0.6644(4)	21(1)
S(6)	0.2392(3)	0.0535(1)	0.9959(4)	28(1)
S(7)	0.4005(2)	0.0400(1)	0.8284(4)	26(1)
S(8)	0.1260(3)	0.1192(1)	0.4944(3)	24(1)
K(1)	0.1869(2)	0.2912(1)	1.0166(3)	22(1)
K(2)	0.0000	0.2500	0.2500	93(4)
K(3)	0.0000	0.1251(1)	0.7500	24(1)
K(4)	0.4364(2)	-0.0410(1)	0.9995(3)	26(1)
K(5)	-0.2463(2)	0.1218(1)	0.2632(3)	27(1)
K(6)	0.0000	0.1321(1)	0.2500	31(1)
P(1)	-0.1042(2)	0.1856(1)	0.5107(3)	11(1)
P(2)	0.1466(3)	0.0647(1)	0.4954(3)	13(1)

[a] U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.
[b] The La(2) position is only 2/3 occupied.

Table 3.11. Selected bond distances (Å) and angles (Deg.) for $K_{9-x}La_{1+x/3}(PS_4)_4$ (x = 0.5).

La(1)-S(1) x 4	2.983(3)	P(1)-S(2)	2.047(5)
La(1)-S(2) x 4	3.009(4)	P(1)-S(3)	2.021(5)
La(2)-S(7) x 2	3.119(4)	P(1)-S(4)	2.030(6)
La(2)-S(5) x 2	3.123(4)	P(2)-S(5)	2.043(5)
La(2)-S(6) x 2	3.131(4)	P(2)-S(6)	2.044(7)
La(2)-S(6) x 2	3.134(4)	P(2)-S(7)	2.040(5)
P(1)-S(1)	2.073(5)	P(2)-S(8)	2.018(7)

S(1')-La(1)-S(1')	97.59(13)	S(7')-La(2)-S(6')	122.90(12)
S(1')-La(1)-S(1)	171.98(14)	S(5')-La(2)-S(6')	92.54(12)
S(1')-La(1)-S(1')	82.97(13)	S(6')-La(2)-S(6')	173.1(2)
S(1')-La(1)-S(2')	79.46(10)	S(5')-La(2)-S(6')	81.96(12)
S(1)-La(1)-S(2')	122.44(10)	S(7')-La(2)-S(6')	63.66(12)
S(1)-La(1)-S(2')	65.40(10)	S(5)-La(2)-S(5')	150.4(2)
S(1')-La(1)-S(2)	93.61(10)	S(6)-La(2)-S(6')	103.08(12)
S(2')-La(1)-S(2)	152.70(13)	S(3)-P(1)-S(4)	109.0(2)
S(2)-La(1)-S(2')	125.9(2)	S(4)-P(1)-S(2)	112.3(2)
S(2)-La(1)-S(2')	61.65(14)	S(4)-P(1)-S(1)	110.3(2)
S(2')-La(1)-S(2')	152.71(13)	S(3)-P(1)-S(2)	108.6(3)
S(7)-La(2)-S(7')	150.1(2)	S(3)-P(1)-S(1)	112.9(2)
S(7')-La(2)-S(5)	64.85(13)	S(2)-P(1)-S(1)	103.6(2)
S(7')-La(2)-S(5')	123.85(14)	S(8)-P(2)-S(5)	110.7(2)
S(7)-La(2)-S(6)	63.84(12)	S(8)-P(2)-S(6)	111.9(3)
S(5)-La(2)-S(6)	81.57(12)	S(5)-P(2)-S(6)	107.7(2)
S(7)-La(2)-S(6')	92.17(13)	S(8)-P(2)-S(7)	111.0(2)
S(5)-La(2)-S(6')	123.07(12)	S(7)-P(2)-S(5)	107.2(3)
S(6)-La(2)-S(6')	77.4(2)	S(7)-P(2)-S(6)	108.0(2)

occupation of the rare-earth sites in the crystal lattice. It is worth noting that the unit cell of these two structures are related through a transposition and doubling of both the a-axis and b-axis going from the $K_4La_{0.67}(PS_4)_2$ to the $K_{9-x}La_{1+x}(PS_4)_4$ structure. Perhaps a smaller rare-earth cation and larger alkali-metal cation would yield the $Rb_9Ce(PSe_4)_4$ structure type with its isolated clusters.

A single crystal of **$K_4Eu(PS_4)_2$ or $K_4EuP_2S_8$, VI,** was selected, 4965 (1020 independent) reflections were collected, and an absorption correction was applied to an orthorhombic cell (R_{int} = 0.0893). The structure was solved by direct methods in Ibam to electron density residuals of 1.340 and -1.442 eÅ^{-3}, and all atoms were refined anisotropically with SHELXTL using full-matrix least squares refinement on F^2 for 42 variables.[45] $K_4Eu(PS_4)_2$ is isostructural to $K_4Eu(PSe_4)_2$.[20] Figure 3.10 shows that chains of $^1_\infty[Eu(PS_4)_2]^{4-}$ propagate along c and are separated from each other along a and b by potassium cations. Two different potassium environments are found with K-S bond distances ranging from 3.134(7) Å to 3.775(9) Å. Along the length of each chain dodecahedral europium atoms are bridged by $(PS_4)^{3-}$ tetrahedra in an edge-sharing manner as shown in Figure 3.11. The average Eu-S bond distance is 3.12(1) Å. Atomic coordinates and selected bond distances and angles for $K_4EuP_2S_8$ are reported in Tables 3.12 and 3.13 respectively.

A single crystal of **$KEuPS_4$, VII,** was selected, 4521(977 independent) reflections were collected, and an absorption correction was applied to an orthorhombic cell (R_{int} = 0.0581). The structure was solved by direct methods in Pnma to electron density residuals of 1.047 and -1.209 eÅ^{-3}, and all atoms were refined anisotropically with SHELXTL using full-matrix least squares refinement on

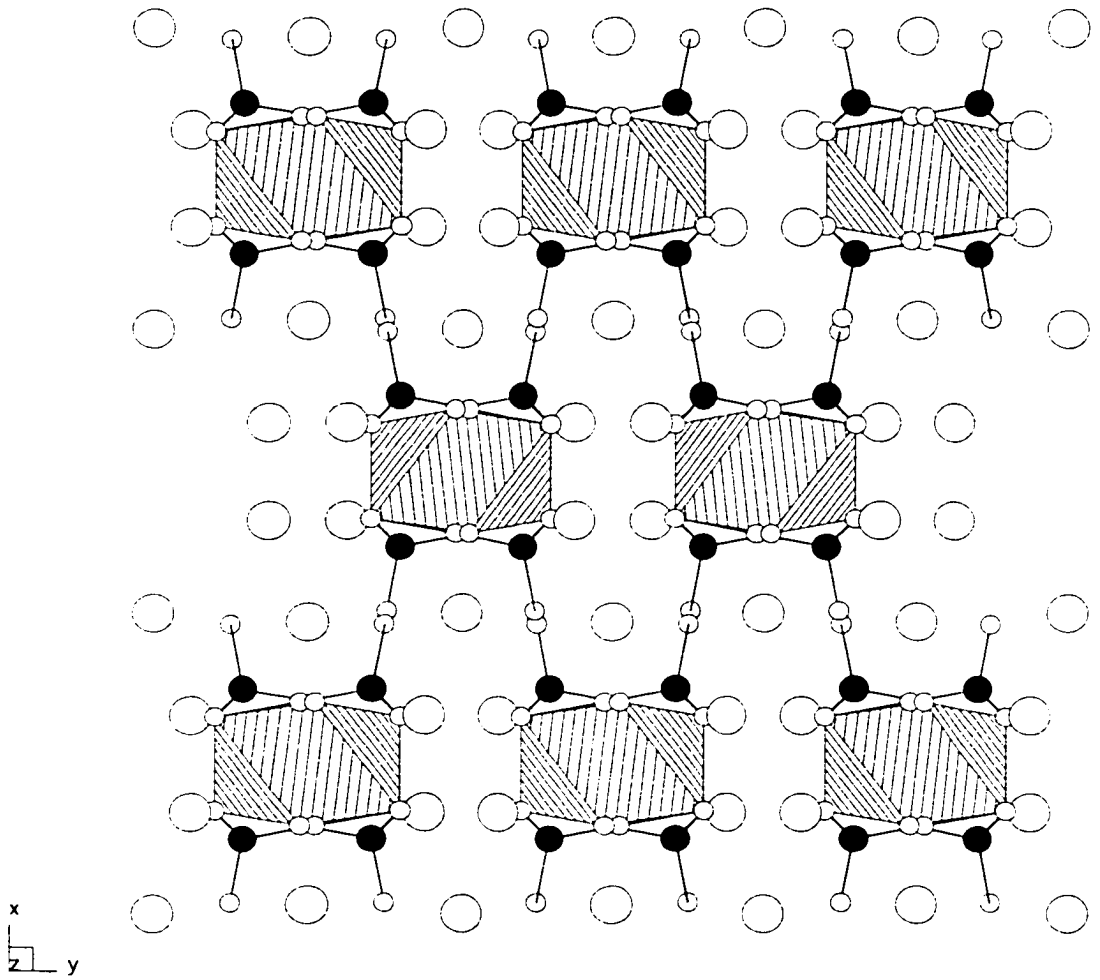


Figure 3.10. Packing plot of $K_4Eu(PS_4)_2$. Striped europium polyhedra, filled phosphorus atoms, small unfilled sulfur atoms, large unfilled potassium atoms.

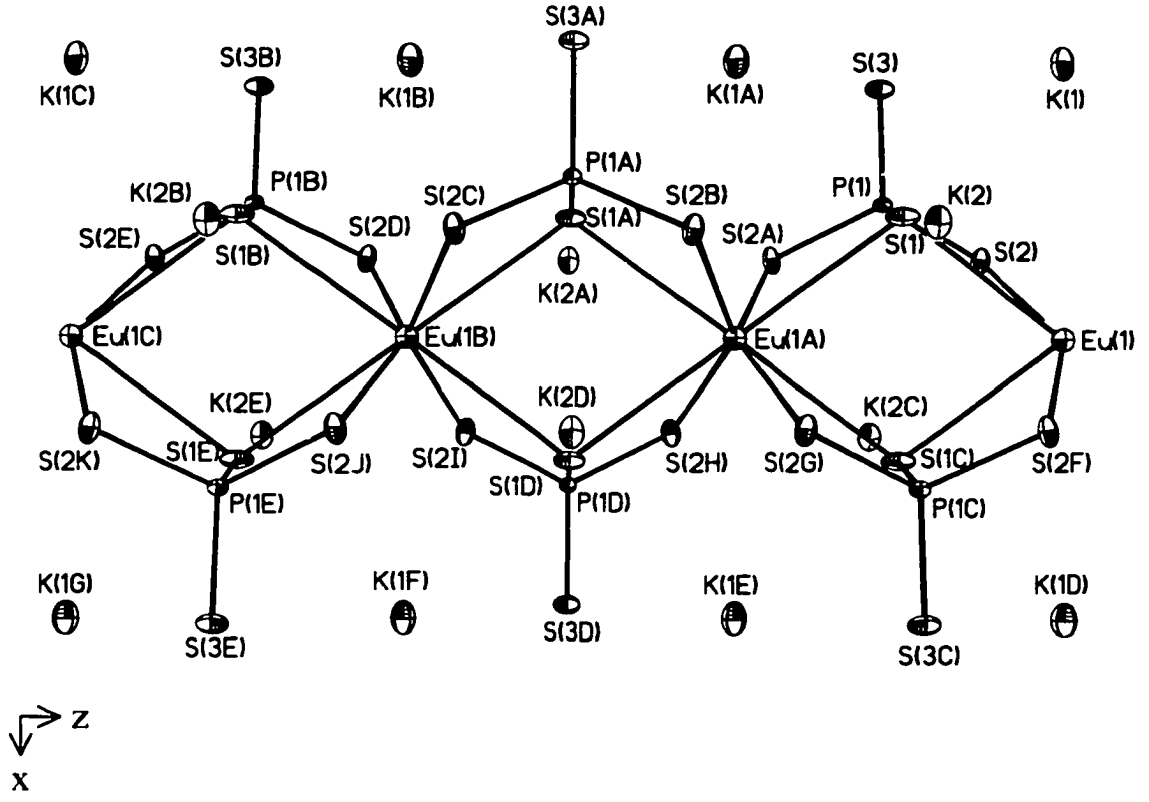


Figure 3.11. ORTEP plot of $K_4Eu(PS_4)_2$. Thermal ellipsoids plotted at the 50% probability level.

Table 3.12. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$)[a] for $K_4Eu(PS_4)_2$.

	x	y	z	U(eq)
Eu(1)	0.5000	0.0000	0.2500	12(1)
P(1)	0.3714(2)	0.2053(3)	0.0000	6(1)
S(1)	0.3941(2)	0.0238(3)	0.5000	13(1)
S(2)	0.4194(1)	0.2982(3)	0.1695(2)	13(1)
S(3)	0.2615(2)	0.2463(4)	0.0000	13(1)
K(1)	0.2575(2)	0.0000	0.2500	20(1)
K(2)	0.5833(2)	-0.3763(3)	0.5000	15(1)

[a] U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3.13. Selected bond distances (Å) and angles (Deg.) for $K_4Eu(PS_4)_2$.

Eu(1)-S(2')	3.113(5)	Eu(1)-S(2')	3.114(5)
Eu(1)-S(2)	3.114(5)	Eu(1)-S(2')	3.114(5)
Eu(1)-S(1')	3.119(4)	Eu(1)-S(1')	3.119(4)
Eu(1)-S(1)	3.119(4)	Eu(1)-S(1')	3.119(4)
P(1)-S(2)	2.041(3)	P(1)-S(2')	2.041(3)
P(1)-S(3)	2.042(7)	P(1)-S(1')	2.062(5)
S(2')-Eu(1)-S(2')	123.5(2)	S(2')-Eu(1)-S(2)	64.9(2)
S(2')-Eu(1)-S(2)	150.82(9)	S(2')-Eu(1)-S(2')	150.82(9)
S(2')-Eu(1)-S(2')	64.9(2)	S(2)-Eu(1)-S(2')	123.5(2)
S(2')-Eu(1)-S(1')	81.12(11)	S(2')-Eu(1)-S(1')	64.28(10)
S(2)-Eu(1)-S(1')	92.33(12)	S(2')-Eu(1)-S(1')	123.21(9)
S(2')-Eu(1)-S(1')	64.28(10)	S(2')-Eu(1)-S(1')	81.12(11)
S(2)-Eu(1)-S(1')	123.21(9)	S(2')-Eu(1)-S(1')	92.33(12)
S(1')-Eu(1)-S(1')	103.2(2)	S(2')-Eu(1)-S(1)	92.33(12)
S(2')-Eu(1)-S(1)	123.21(9)	S(2)-Eu(1)-S(1)	81.12(11)
S(2')-Eu(1)-S(1)	64.28(10)	S(1')-Eu(1)-S(1)	172.28(9)
S(1')-Eu(1)-S(1)	77.3(2)	S(2')-Eu(1)-S(1')	123.21(10)
S(2')-Eu(1)-S(1')	92.33(12)	S(2)-Eu(1)-S(1')	64.27(3)
S(2')-Eu(1)-S(1')	81.12(11)	S(1')-Eu(1)-S(1')	77.3(2)
S(1')-Eu(1)-S(1')	172.28(11)	S(1)-Eu(1)-S(1')	103.2(2)
S(2)-P(1)-S(2')	108.0(2)	S(2)- P(1)-S(3)	110.6(2)
S(2')- P(1)-S(3)	110.6(2)	S(2)- P(1)-S(1')	107.83(14)
S(2')- P(1)-S(1')	107.83(14)	S(3)- P(1)-S(1')	111.8(2)

F^2 for 40 variables.[45] $KEuPS_4$ is isostructural to $KEuPSe_4$ and isotypic to $CsPbPSe_4$.[20] Figure 3.12 shows that $KEuPS_4$ is a two-dimensional structure with $^2_\infty[EuPS_4]^-$ layers in the yz-plane separated by potassium cations along the x-axis. Each potassium atom is coordinated by eight sulfur atoms with an average K-S bond distance of 3.390(7) Å. Figure 3.13 shows that each layer contains eight-coordinate, bi-capped trigonal prismatic europium atoms that are linked into a layer by $(PS_4)^{3-}$ tetrahedra. Each $(PS_4)^{3-}$ tetrahedron is coordinated to four different europium atoms. Just as in $KEuPSe_4$, the europium atoms in $KEuPS_4$ have two Eu-S bonds that are longer than the other six Eu-S bonds. The two longer bonds have a Eu-S bond distance of 3.4232(7) Å while the shorter Eu-S bonds range from 2.966(2) Å to 3.086(2) Å. In Figure 3.14 these longer bonds are between Eu(1) and S(2), while the shorter bonds are to S(1), S(2A), and S(3). Eu(II) sits in a trigonal prism of sulfur atoms and is capped on each side of the prism by longer Eu-S bonds. This type of bonding has been observed before in Eu_2BiS_4[50] and $Eu_3Sb_4S_9$.[51] Atomic coordinates and selected bond distances and angles for $KEuPS_4$ are reported in Tables 3.14 and 3.15 respectively.

Phase Diagrams

Quasi-quaternary phase diagrams were constructed by plotting the reaction conditions that produced the crystal structures described above. Both the La-P-K-S and Eu-P-K-S phase diagrams are similar to their selenium counterparts. All reactions represented in Figures 3.15 and 3.16 were done under a relative thermodynamic equilibrium isotherm of 725°C and were isometric in sulfur with

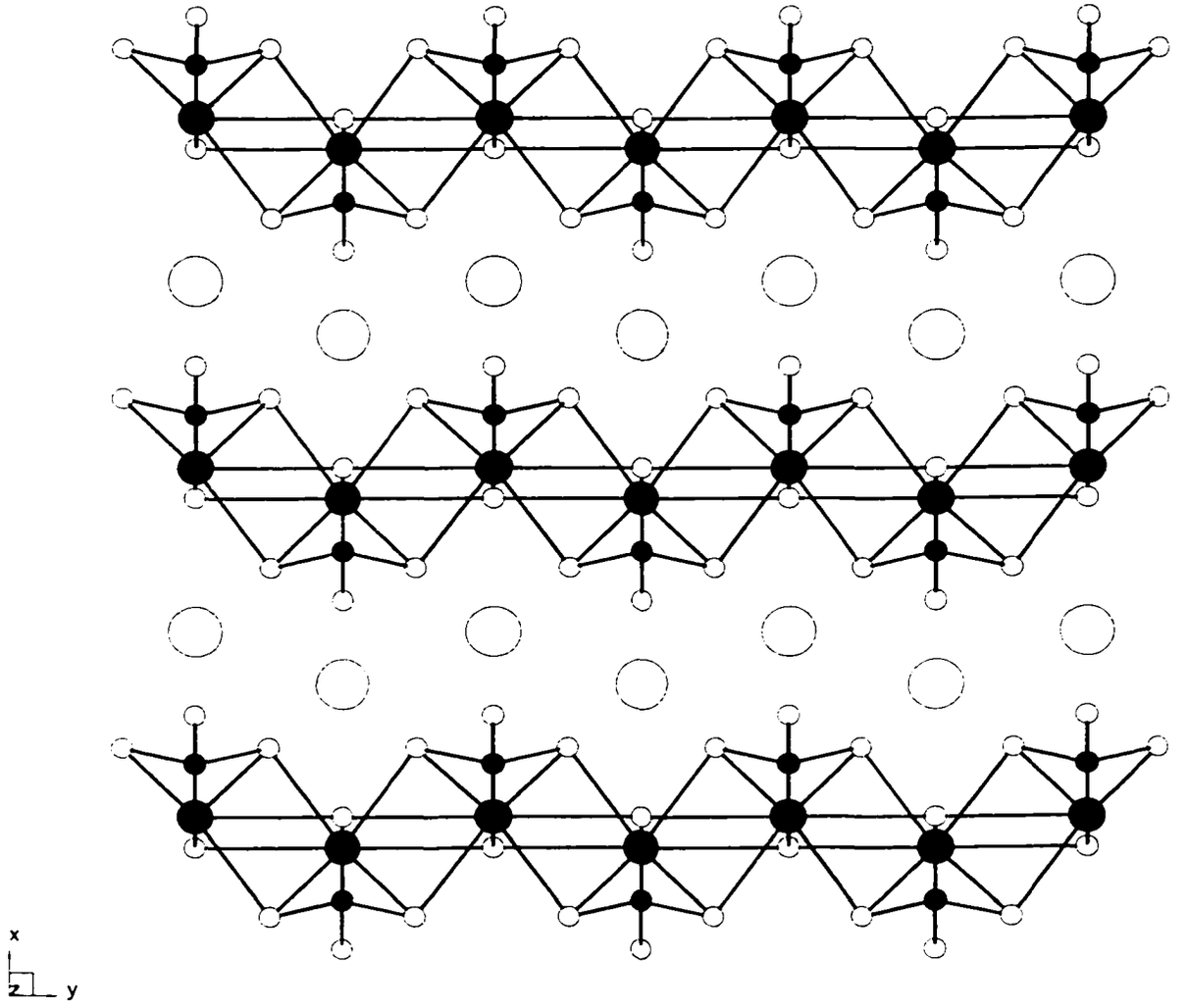


Figure 3.12. Packing plot of $KEuPS_4$. Large filled europium atoms, small filled phosphorus atoms, small unfilled sulfur atoms, large unfilled potassium atoms.

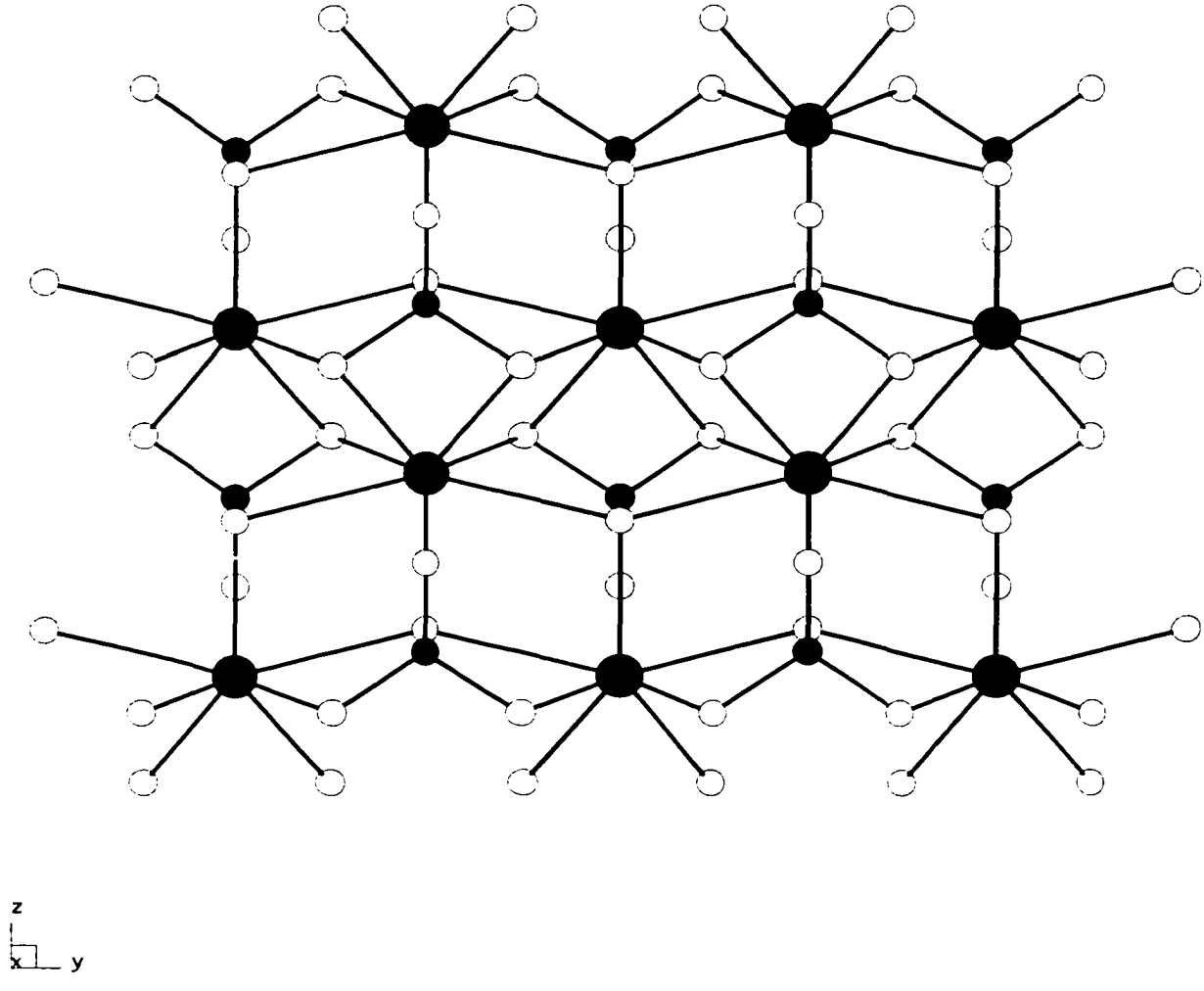


Figure 3.13. $[EuPS_4]^-$ layer in $KEuPS_4$. Large filled europium atoms, small filled phosphorus atoms, small unfilled sulfur atoms, potassium atoms removed for clarity.

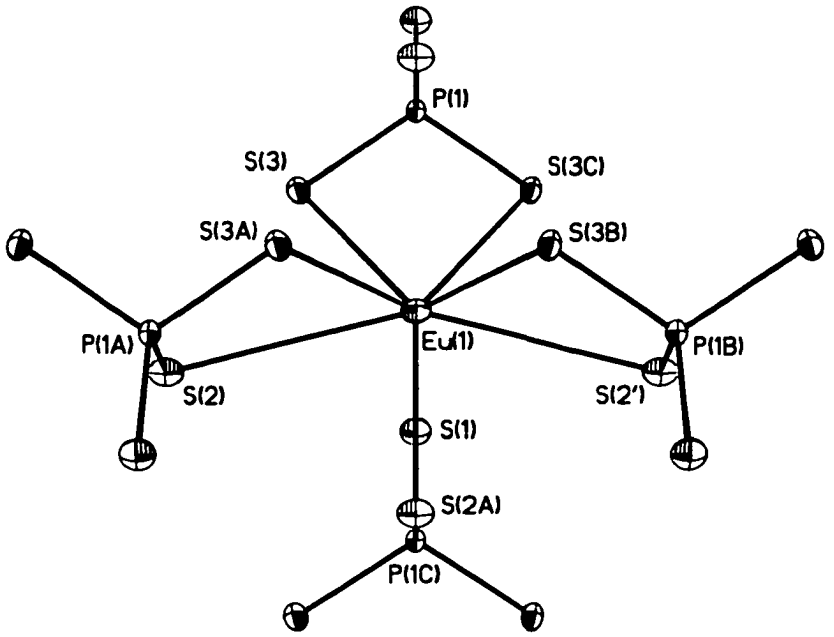


Figure 3.14. ORTEP plot of $KEuPS_4$. Thermal ellipsoids plotted at the 50% probability level. Potassium atoms left out for clarity.

Table 3.14. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$)[a] for $KEuPS_4$.

	x	y	z	U(eq)
Eu(1)	0.4780(1)	0.2500	0.2919(1)	14(1)
P(1)	0.4020(1)	0.2500	0.7786(4)	10(1)
K(1)	0.2117(1)	0.2500	0.4815(4)	24(1)
S(1)	0.3324(1)	0.2500	0.0338(4)	17(1)
S(2)	0.4785(1)	-0.2500	0.1562(4)	16(1)
S(3)	0.3786(1)	0.0027(2)	0.6013(3)	14(1)

[a] U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3.15. Selected bond distances (Å) and angles (Deg.) for $KEuPS_4$.

Eu(1)-S(1)	2.966(2)	Eu(1)-S(2')	3.009(2)
Eu(1)-S(3')	3.012(2)	Eu(1)-S(3')	3.012(2)
Eu(1)-S(3')	3.086(2)	Eu(1)-S(3)	3.086(2)
Eu(1)-S(2)	3.4232(7)	Eu(1)-S(2')	3.4232(7)
P(1)-S(1')	2.032(3)	P(1)-S(3')	2.041(2)
P(1)-S(3)	2.041(2)	P(1)-S(2')	2.050(3)
S(1)-Eu(1)-S(2')	69.51(6)	S(1)-Eu(1)-S(3')	142.12(4)
S(2')-Eu(1)-S(3')	91.73(5)	S(1)-Eu(1)-S(3')	142.12(4)
S(2')-Eu(1)-S(3')	91.73(5)	S(3')-Eu(1)-S(3')	67.42(6)
S(1)-Eu(1)-S(3')	85.68(5)	S(2')-Eu(1)-S(3')	139.89(4)
S(3')-Eu(1)-S(3')	89.26(4)	S(3')-Eu(1)-S(3')	125.13(3)
S(1)-Eu(1)-S(3)	85.68(5)	S(2')-Eu(1)-S(3)	139.89(4)
S(3')-Eu(1)-S(3)	125.13(3)	S(3')-Eu(1)-S(3)	89.26(4)
S(3')-Eu(1)-S(3)	64.03(6)	S(1)-Eu(1)-S(2')	81.70(4)
S(2')-Eu(1)-S(2')	75.45(4)	S(3')-Eu(1)-S(2')	61.42(5)
S(3')-Eu(1)-S(2')	126.43(5)	S(3')-Eu(1)-S(2')	69.99(5)
S(3)-Eu(1)-S(2')	133.01(5)	S(2')-Eu(1)-S(2)	75.45(4)
S(1)-Eu(1)-S(2)	81.70(4)	S(3')-Eu(1)-S(2)	61.42(5)
S(3')-Eu(1)-S(2)	126.43(5)	S(3)-Eu(1)-S(2)	69.99(5)
S(3')-Eu(1)-S(2)	133.01(5)	S(2')-Eu(1)-S(2)	150.06(8)
S(1')-P(1)-S(3')	110.63(9)	S(1')-P(1)-S(3)	110.63(9)
S(3')-P(1)-S(3)	106.56(14)	S(1')-P(1)-S(2')	113.13(14)
S(3')-P(1)-S(2')	107.81(9)	S(3)-P(1)-S(2')	107.81(9)

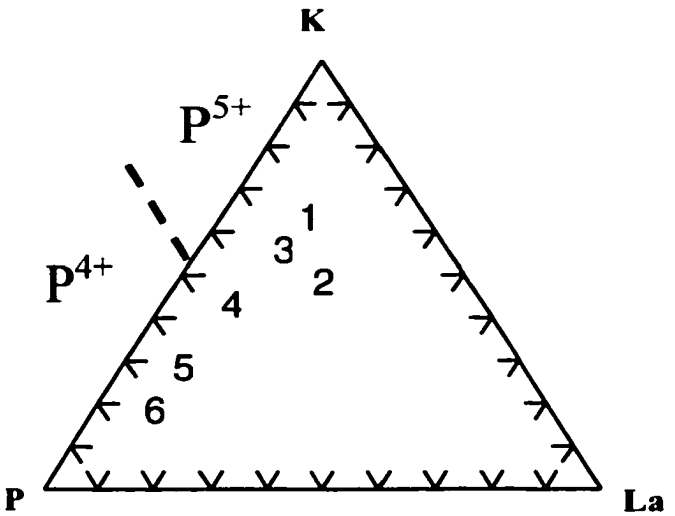


Figure 3.15. La/P/K ternary phase diagram. Numbers represent the ratio of La/P/K in a particular reaction mixture.

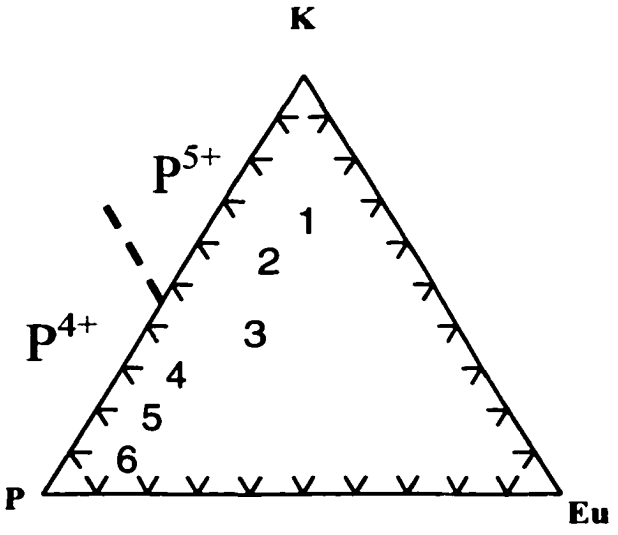


Figure 3.16. Eu/P/K ternary phase diagram. Numbers represent the ratio of Eu/P/K in a particular reaction mixture.

some expected variation. In these phase diagrams, numbers represent reactions wherein various ratios of K/K+P+RE, P/K+P+RE, RE/K+P+RE were used. Tables 3.16 and 3.17 list these ratios for each phase diagram point. In this way, the RE-P-K phase diagrams can be thought of as an isometric sulfur slice through a quaternary RE-P-K-S phase diagram.

La-P-K System

The isothermal La-P-K phase diagram in Figure 3.15 contains 5 different crystalline products: $KLaP_2S_6$, **I**, $K_2LaP_2S_7$, **II**, $K_3La(PS_4)_2$, **III**, $K_4La_{0.67}(PS_4)_2$, **IV**, and $K_{9-x}La_{1+x/3}(PS_4)_4$ (x = 0.5), **V**. At point 1, the point with the highest potassium molar ratio and lowest phosphorus and lanthanum molar ratios, only the ternary compound K_3PS_4 [56] is found as a crystalline product. This indicates the edge of where we will find quaternary compounds in this phase diagram. Decreasing the potassium molar ratio while simultaneously increasing the phosphorus molar ratio changes the observed product. Compound IV is observed at point 2 and compound III is observed at point 3. Compound V has not been observed as single crystals at 725°C as it was only found in reactions below 550°C. We would expect it to be found between points 1 and 3 on the phase diagram. Up to point 3, only P^V was found in the crystalline products as $(PS_4)^{3-}$ units. Increasing the phosphorus molar ratio to 45% finally brings us to the area of the phase diagram where P^{IV} is found. $K_2LaP_2S_7$ was observed at points 4 and 5 and contains both P^V and P^{IV}. Finally, at point 6, only P^{iV} was observed in the $KLaP_2S_6$ structure.

Table 3.16. Reactant ratios represented in Figure 3.15.

Phase Diagram Point(s)	K/K+P+La	P/K+P+La	La/K+P+La	Reaction Product
1	0.65	0.2	0.15	K_3PS_4
2	0.5	0.25	0.25	$K_4La_{0.67}(PS_4)_2$
3	0.5714	0.2857	0.1429	$K_3La(PS_4)_2$
4	0.4444	0.4444	0.1111	$K_2La(P_2S_6)_{1/2}(PS_4)$
5	0.3	0.6	0.1	
6	0.2	0.7	0.1	$KLaP_2S_6$

Table 3.17. Reactant ratios represented in Figure 3.16.

Phase Diagram Point	K/K+P+Eu	P/K+P+Eu	Eu/K+P+Eu	Reaction Product
1	0.6667	0.1667	0.1667	$K_4Eu(PS_4)_2$
2	0.5714	0.2857	0.1429	
3	0.4	0.4	0.2	$KEuPS_4$
4	0.3	0.6	0.1	
5	0.2	0.7	0.1	$Eu_2P_2S_6$
6	0.1	0.8	0.1	

Eu-P-K System

The Eu-P-K phase diagram in Figure 3.16 contains only 3 different crystalline products. $K_4Eu(PS_4)_2$ and $KEuPS_4$ have been reported here. The third compound, $Eu_2P_2S_6$, observed as a crystalline product, was previously reported.[53] $K_4Eu(PS_4)_2$ was the crystalline product observed at the highest potassium molar ratios and lowest phosphorus molar ratios (points 1 and 2). Decreasing the potassium molar ratio while increasing the phosphorus molar ratio led to the $KEuPS_4$ compound at point 3. Both $K_4Eu(PS_4)_2$ and $KEuPS_4$ contain P^V. P^{IV} was not found until very high phosphorus molar ratios at points 4-6 in the $Eu_2P_2S_6$ compound. As in the selenide case, a quaternary compound was not found containing both P^V and P^{IV}.

The major difference observed between the sulfur and selenium phase diagrams is the greater oxidizing power of the S^0/S^{2-} flux compared to the Se^0/Se^{2-} flux. Because sulfur is a better oxidizing agent, we see phosphorus in its highest oxidation state, P^V, comprising a larger area of the phase diagram. For example, in the selenide version of the europium phase diagram P^{IV} is observed for the first time at approximately a 40% mole ratio of phosphorus. In the sulfur version of the phase diagram P^{IV} is not observed until ~60% mole ratio of phosphorus. An additional effect of the oxidizing power of sulfur versus selenium is that P^{III} was not found in the sulfur phase diagrams. In both diagrams P^{IV} extends to the edge of the phase space. Perhaps ternary or quaternary structures with P^{III} can be found in a different isometric "slice" of the quaternary phase diagram.

The same formulae used in Chapter 2 can be used to describe the dismantling of rare-earth thiophosphates into two and one-dimensional structures by the addition

of $(P_2S_6)^{4-}$ and $(PS_4)^{3-}$ units. A similar set of target compounds is listed in Tables 3.18 and 3.19.

Vibrational and Electronic Spectroscopy

Raman and IR Spectroscopy

Figure 3.17 shows the Raman spectra for $KLaP_2S_6$ and $K_2La(P_2S_6)_{1/2}(PS_4)$. $KLaP_2S_6$ contains vibrations expected for the $(P_2S_6)^{4-}$ unit while $K_2La(P_2S_6)_{1/2}(PS_4)$ contains vibrations for both the $(P_2S_6)^{4-}$ unit and the $(PS_4)^{3-}$ unit. Peak assignments are based on previously known materials.[56,57] The peak at 387 cm^{-1}, observed in both spectra, is assigned to the A_{1g} symmetric stretch of the $(P_2S_6)^{4-}$ unit. The peak at 424 cm^{-1}, observed only in the $K_2La(P_2S_6)_{1/2}(PS_4)$ spectra, is assigned to the A_1 symmetric stretch of the tetrahedral $(PS_4)^{3-}$ unit. Vibrations above 500 cm^{-1} in both spectra are asymmetric stretching vibrations from $(P_2S_6)^{4-}$ and/or $(PS_4)^{3-}$ units, and peaks below 350 cm^{-1} are bending vibrations. The peak at 447 cm^{-1} is found only in the Raman spectrum of $KLaP_2S_6$. It is assigned to an A_{2u} vibrational mode of the $(P_2S_6)^{4-}$ unit. This peak is normally only IR active, but in $KLaP_2S_6$ it is observed in both the Raman and IR spectra. The IR absorbance spectrum for $KLaP_2S_6$, shown in Figure 3.18, clearly shows the same peak at 450 cm^{-1}. There is not an inversion center located between the two phosphorus atoms in $KLaP_2S_6$. Because of this, the $(P_2S_6)^{4-}$ unit does not have idealized D_{3d} symmetry, which allows the A_{2u} peak to be observed in the Raman spectrum. In $K_2La(P_2S_6)_{1/2}(PS_4)$ there is an inversion center located between the phosphorus atoms in the $(P_2S_6)^{4-}$ units, and we do not see the peak at 447 cm^{-1} in its Raman spectrum. Table 3.20 lists the Raman peaks found for $KLaP_2S_6$ and

Table 3.18. $(A_4P_2S_6)_l(A_3PS_4)_m(La_4(P_2S_6)_3)_n(LaPS_4)_o$

l	m	n	o	Predicted Formula	Reported Structure
0	1	0	0	A_3PS_4	K_3PS_4
1	0	0	0	$A_4P_2S_6$	$K_4P_2S_6$
0	0	1	0	$La_4(P_2S_6)_3$	
0	0	0	1	$LaPS_4$	
1	0	1	0	$A_4La_4(P_2S_6)_4$	$KLaP_2S_6$
1	0	0	2	$A_4La_2(P_2S_6)(PS_4)_2$	$K_2La(P_2S_6)_{1/2}(PS_4)$
0	1	0	1	$A_3La(PS_4)_2$	$K_3La(PS_4)_2$
0	2	0	1	$A_6La(PS_4)_3$	$K_4La_{0.67}(PS_4)_2$
0	3	0	1	$A_9La(PS_4)_4$	$K_{9-x}La_{1+x/3}(PS_4)_4$

Table 3.19. $(A_4P_2S_6)_l(A_3PS_4)_m(Eu_2(P_2S_6))_n[(Eu_3(PS_4)_2]_o$

l	m	n	o	Predicted Formula	Reported Structure
0	0	1	0	$Eu_2P_2S_6$	$Eu_2P_2S_6$ [53]
0	0	0	1	$Eu_3(PS_4)_2$	
1	0	1	0	$A_4Eu_2(P_2S_6)_2 \equiv A_2EuP_2S_6$	
0	1	0	1	$A_3Eu_3(PS_4)_3$	$KEuPS_4$
0	4	0	1	$A_{12}Eu_3(PS_4)_6$	$K_4Eu(PS_4)_2$
0	7	0	1	$A_{21}Eu_3(PS_4)_9 \equiv A_7Eu(PS_4)_3$	
0	10	0	1	$A_{30}Eu_3(PS_4)_{12} \equiv A_{10}Eu(PS_4)_4$	

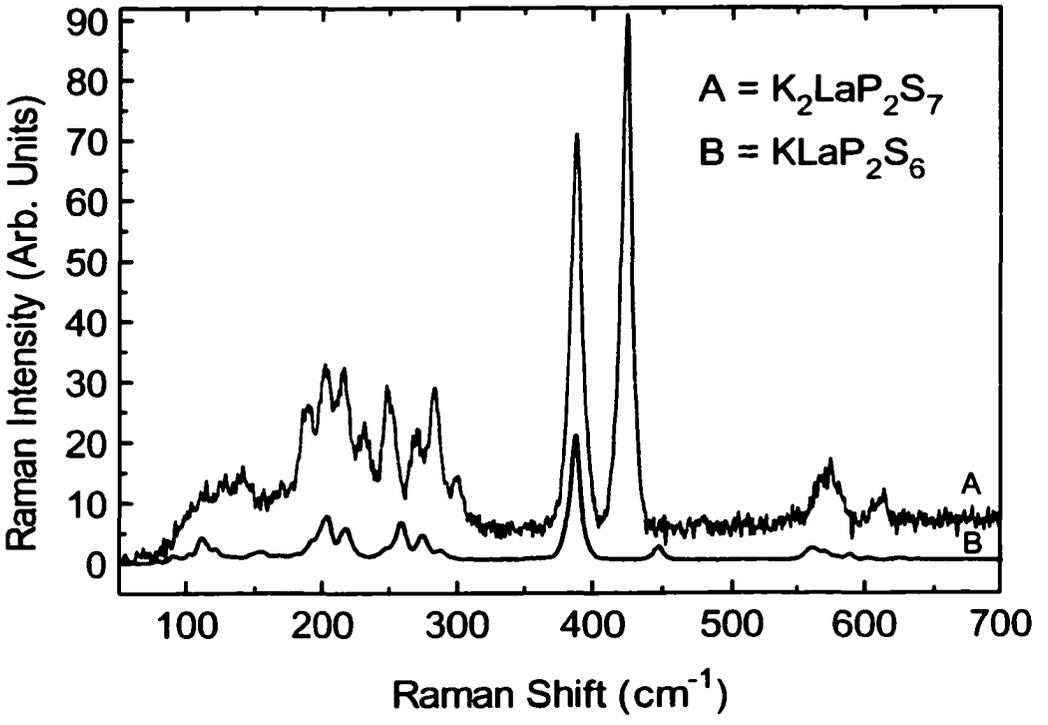


Figure 3.17. Raman spectra of $KLaP_2S_6$ and $K_2La(P_2S_6)_{1/2}(PS_4)$.

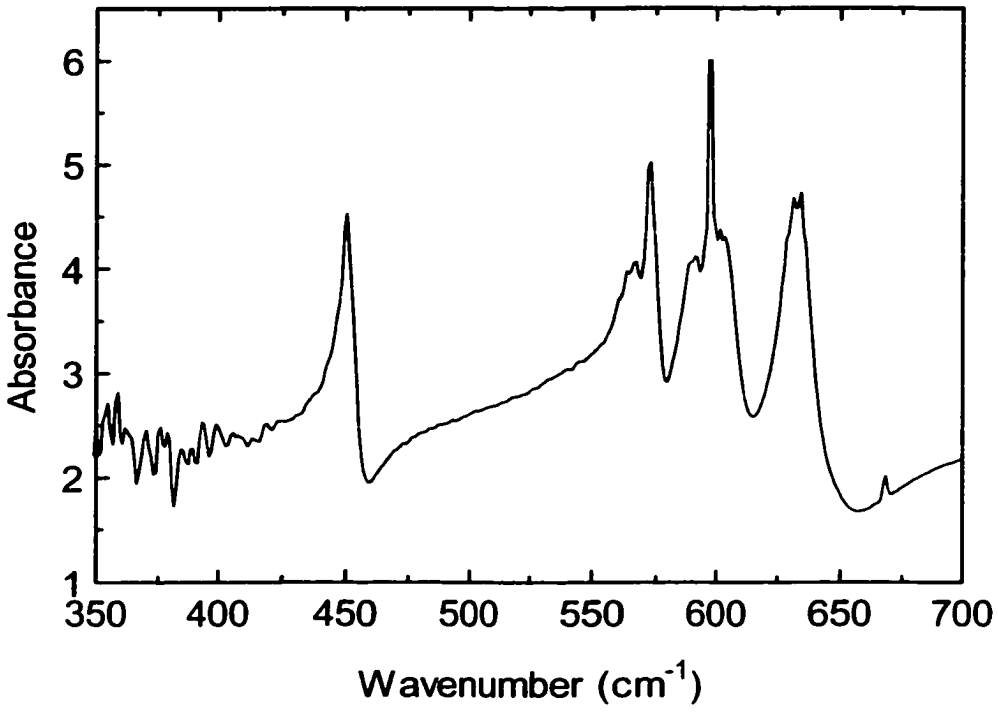


Figure 3.18. IR spectrum of $KLaP_2S_6$.

Table 3.20. Raman peaks (cm^{-1}) found in $KLaP_2S_6$, $K_2FeP_2S_6$,[58] and $K_2LaP_2S_7$.

$KLaP_2S_6$	$K_2FeP_2S_6$	$K_2LaP_2S_7$
90		
111		114
		140
153		156
	183	188
204		202
217		215
	228	231
259	245	248
275		270
288	280	283
		300
	378	
387 A_{1g}	391	387 A_{1g}
		424 A_1
447 A_{2u}*	453**	
561	565	570
589	585	574
		613

*Observed in Raman spectrum
** Observed in IR spectrum

$K_2La(P_2S_6)_{1/2}(PS_4)$. Both the Raman and IR assignments for the $(P_2S_6)^{4-}$ unit match well with those values reported for $K_2Fe(P_2S_6)$.[58]

Raman spectra were not obtained for $K_3La(PS_4)_2$, $K_4La_{0.67}(PS_4)_2$, and $K_{9-x}La_{1+x/3}(PS_4)_4$ (x = 0.5). We would expect to see four Raman vibrations corresponding to the tetrahedral $(PS_4)^{3-}$ building block.

Figure 3.19 shows the Raman spectra of $K_4Eu(PS_4)_2$ and $KEuPS_4$. Both spectra show the four vibrational modes expected for the $(PS_4)^{3-}$ unit.[54] The large peak at 424 cm^{-1} is assigned to the symmetric stretch and the peak at ~570 cm^{-1} corresponds to the asymmetric stretch. The two peaks below 300 cm^{-1} correspond to bending vibrations.

UV-Vis Spectroscopy

All four potassium lanthanum phosphorus sulfides are found as clear crystals with optical band-gaps around 3.5 eV. As an example, Figure 3.20 shows the optical band-gap curve for $K_3La(PS_4)_2$ with an optical band-gap of 3.48 eV. Figure 3.21 shows the optical band-gaps of $K_4Eu(PS_4)_2$ and $KEuPS_4$. Both were found as clear, brown crystals with optical band-gaps of 1.72 eV and 1.73 eV respectively.

Conclusions

The use of ternary phase diagrams has been extended to the synthesis of new rare-earth polythiophosphates. Compounds I-VII were synthesized using the reactive flux method and characterized using single crystal X-ray diffraction, Raman and IR spectroscopy, and optical band-gap analysis. Plotting the reactive flux conditions in a

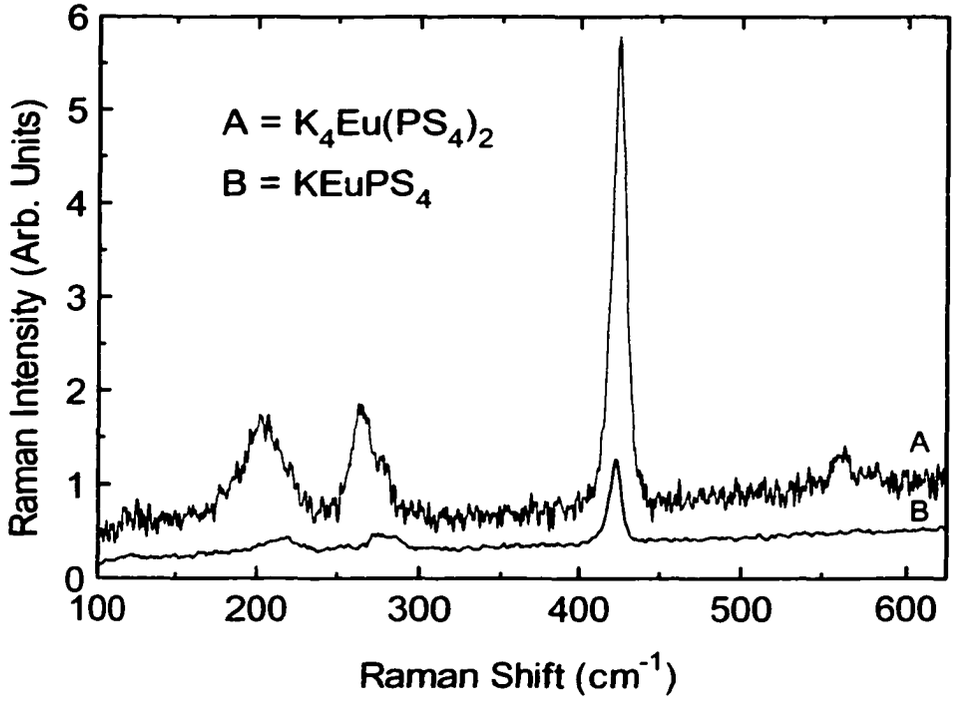


Figure 3.19. Raman spectra of $K_4Eu(PS_4)_2$ and $KEuPS_4$.

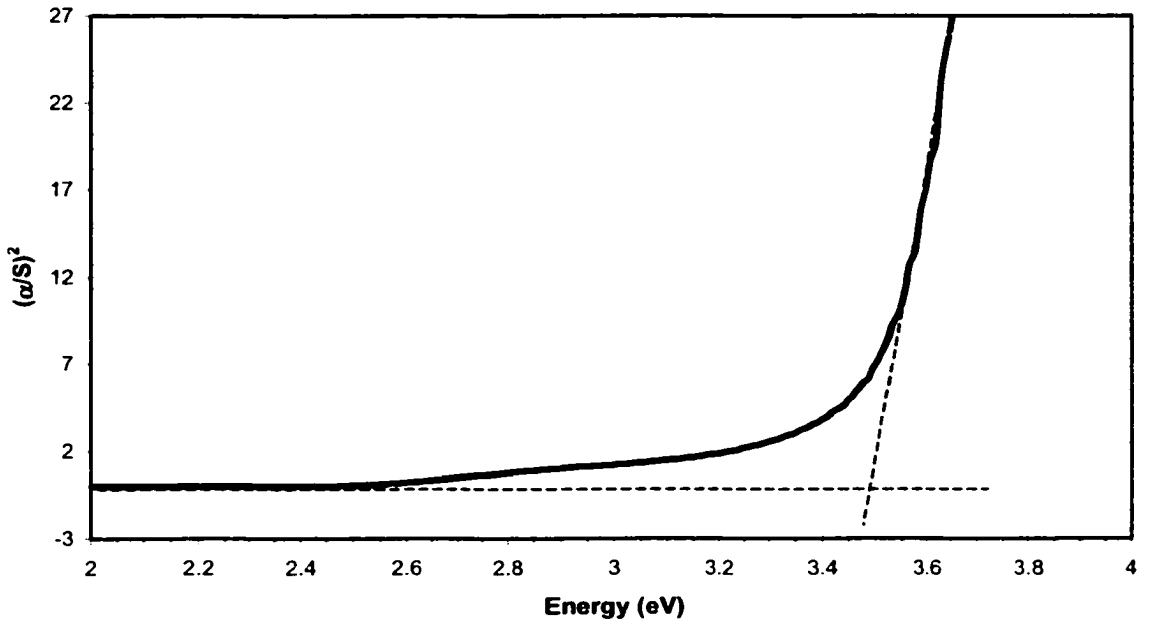


Figure 3.20. Optical band-gap of $K_3La(PS_4)_2$.

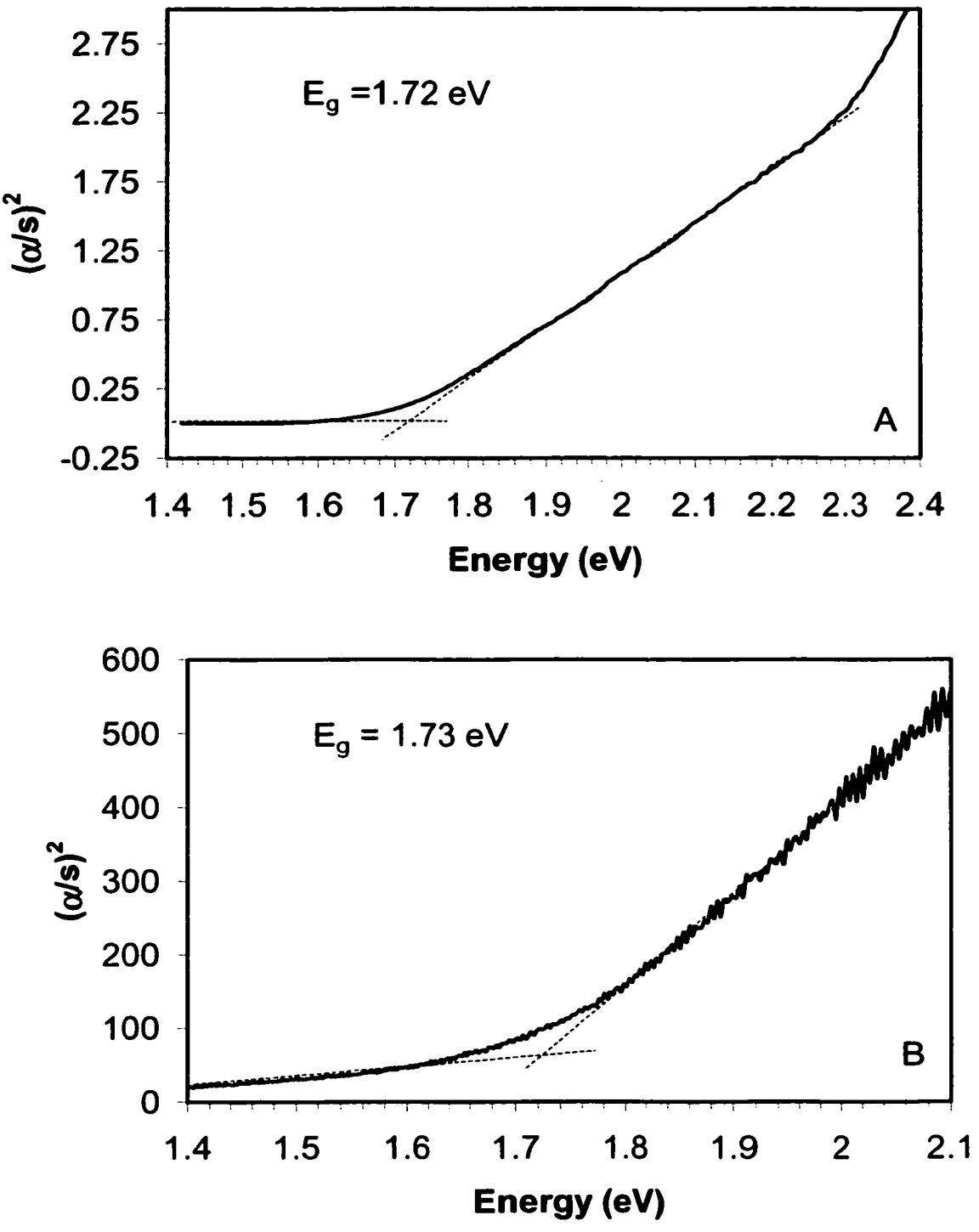


Figure 3.21. Optical band-gap spectra for (A) $K_4Eu(PS_4)_2$ and (B) $KEuPS_4$.

ternary phase diagram allows a visual understanding of the different molar ratios necessary for the synthesis of different products. These phase diagrams, constructed under the appropriate reaction conditions, offer a useful tool for understanding the conditions needed to rationally approach the synthesis of new compounds with desirable properties.

Tables of additional crystallographic details, all bond distances and angles, and anisotropic thermal parameters can be found in Appendix C, Tables C.1-C.28.

Chapter Four

Effects of Alkali-Metal and Rare-Earth Cation Size on the Crystal Structure of $A_2RE(P_2Q_6)_{1/2}(PQ_4)$ (A = K, Cs; RE = Y, La; Q = S, Se)

Introduction

The Dorhout group has previously reported the structures of $KLaP_2Se_6$ and KYP_2Se_6[34,37] as an example of how rare-earth cation size affects structure. It was found that KYP_2Se_6, with a smaller 3+ metal cation, crystallized in a different space group than $KLaP_2Se_6$. $KLaP_2Se_6$ crystallizes in the monoclinic space group $P2_1/c$ and the structure is composed of double layers of lanthanum atoms coordinated by $(P_2Se_6)^{4-}$ anionic units. KYP_2Se_6, on the other hand, crystallizes in the orthorhombic space group $P2_12_12_1$ and is composed of only a single layer of yttrium atoms linked together by $(P_2Se_6)^{4-}$ units. This difference may be subtle, but differences such as these may lead to significant differences in properties such as optical band-gap and ionic conductivity. The Dorhout group and others have recently reported solid-state structures with the formula $A_2REP_2Q_7$ where A is an alkali-metal cation, RE is a rare-earth cation, and Q is sulfur or selenium.[35,36,39,40] In an effort to further investigate the effects of alkali-metal and rare-earth metal cation size on the $A_2REP_2Q_7$ structure type, the compounds $A_2RE(P_2Q_6)_{1/2}(PQ_4)$ (A = K, Cs; RE = Y, La; Q = S, Se) have been synthesized. The crystal structures of $K_2La(P_2S_6)_{1/2}(PS_4)$ and $K_2La(P_2Se_6)_{1/2}(PSe_4)$ have been discussed in detail in Chapters 2 & 3. The structures of $K_2Y(P_2S_6)_{1/2}(PS_4)$ **I**, $K_2Y(P_2Se_6)_{1/2}(PSe_4)$ **II**, $Cs_2Y(P_2S_6)_{1/2}(PS_4)$ **III**, $Cs_2Y(P_2Se_6)_{1/2}(PSe_4)$ **IV**, $Cs_2La(P_2S_6)_{1/2}(PS_4)$ **V**, and $Cs_2La(P_2Se_6)_{1/2}(PSe_4)$ **VI** are discussed here.

Experimental Section

Synthesis: Crystals of compounds **I-VI** were obtained under similar reaction conditions. The phase diagrams described in Chapters 2 and 3 were used to accurately determine the reaction conditions necessary to synthesize these compounds. The following reactants were used as received and stored in an inert atmosphere glovebox: Y (99.999%, Ames Laboratory), La (99.999%, Ames Laboratory), P (Mallinckrodt Red), Se (99.999%, Johnson-Matthey), S (99.999% Johnson-Matthey). K_2Se, K_2S_2, Cs_2Se_3, Cs_2Se_5, and Cs_2S_5 were previously made in liquid ammonia from the stoichiometric combination of the elements.[41,42] Reactants were loaded into fused silica ampoules inside an inert atmosphere glovebox. Each ampoule was flame sealed under vacuum and placed in a temperature controlled tube furnace.

$K_2Y(P_2S_6)_{1/2}(PS_4)$, or $K_2YP_2S_7$, I, was prepared by reacting 41.7 mg (1.30 mmol) S, 34.7 mg (0.244 mmol) K_2S_2, 30.2 mg (0.975 mmol) P, and 14.5 mg (0.163 mmol) Y. The reaction was carried out 525°C for 150 hours and allowed to cool back to room temperature 4°C/hr. Washing the reaction product with dimethylformamide (DMF) yielded clear colorless crystals.

$K_2Y(P_2Se_6)_{1/2}(PSe_4)$, or $K_2YP_2Se_7$, II, was prepared by reacting 113.6 mg (1.44 mmol) Se, 35.7 mg (0.227 mmol) K_2Se, 18.8 mg (0.607 mmol) P, and 13.5 mg (0.152 mmol) Y. The reaction was carried out as described for compound I yielding clear, yellow crystals.

$Cs_2Y(P_2S_6)_{1/2}(PS_4)$, or $Cs_2YP_2S_7$, III, was prepared by reacting 9.60 mg (0.299 mmol) S, 54.7 mg (0.128 mmol) Cs_2S_5, 15.9 mg (0.513 mmol) P, and 7.60 mg

(0.086 mmol) Y. The reaction was carried out as described for compound I. The reaction was washed with DMF to give clear, colorless crystals.

$Cs_2Y(P_2Se_6)_{1/2}(PSe_4)$, or $Cs_2YP_2Se_7$, IV, was prepared by reacting 61.6 mg (0.780 mmol) Se, 73.6 mg (0.111 mmol) Cs_2Se_5, 13.8 mg (0.446 mmol) P, and 20.0 mg (0.225 mmol) Y. The reaction was allowed to react at 725°C for 100 hours and then cooled at 5°C/hour back to room temperature. The reaction looked incomplete upon visual inspection and was allowed to react further at 750°C for 72 hours and cooled back to room temperature at 5°C/hour. Washing the reaction product with DMF resulted in clear, orange crystals. $Cs_2Y(P_2Se_6)_{1/2}(PSe_4)$ was synthesized and characterized by a previous student, Dr. Pamela Van Calcar.

$Cs_2La(P_2S_6)_{1/2}(PS_4)$, or $Cs_2LaP_2S_7$, V, was prepared by reacting 10.1 mg (0.315 mmol) S, 104.4 mg (0.245 mmol) Cs_2S_5, 23.8 mg (0.768 mmol) P, and 19.4 mg (0.140 mmol) La. The reaction was allowed to react at 725°C for 150 hours and then cooled at 4°C/hour back to room temperature. The reaction was washed with DMF to give clear, colorless crystals.

$Cs_2La(P_2Se_6)_{1/2}(PSe_4)$, or $Cs_2LaP_2Se_7$, VI, was prepared by reacting 32.1 mg (0.407 mmol) Se, 146.0 mg (0.290 mmol) Cs_2Se_3, 14.4 mg (0.465 mmol) P, and 16.1 mg (0.116 mmol) La. The reaction was carried out as described for compound V. Orange crystals were found after washing the reaction product with DMF.

The syntheses of $K_2La(P_2Se_6)_{1/2}(PSe_4)$ and $K_2La(P_2S_6)_{1/2}(PS_4)$ are reported Chapters 2 and 3 respectively.

Physical Measurements

Single-Crystal X-ray Diffraction. Intensity data sets for compounds I-VI were collected using a Bruker SMART CCD diffractometer. For compounds I, II and IV intensity data sets were integrated using SAINT,[43] a SADABS correction was applied,[44] and the structure was solved by direct methods using SHELXTL.[45] For compounds III, V and VI intensity data sets were integrated using SAINT-NT,[59] a SADABS correction was applied,[44] and the structures were solved by direct methods using SHELXTL.[60] Crystallographic data for compounds I-VI are reported in Tables 4.1 and 4.2.

Crystal Structures

$K_2La(P_2Se_6)_{1/2}(PSe_4)$ was described in Chapter 2 as a two-dimensional layered structure with polyhedral chains of lanthanum and $(PSe_4)^{3-}$ tetrahedral linked into a layer with ethane-like $(P_2Se_6)^{4-}$ units. These $^{2}_{\infty}[La(P_2Se_6)_{1/2}(PSe_4)]^{2-}$ layers are separated from each other by potassium cations. The sulfur analog, $K_2La(P_2S_6)_{1/2}(PS_4)$, is completely isostructural. Compounds I-VI are all isotypic to $K_2La(P_2Q_6)_{1/2}(PQ_4)$ (Q = S, Se). The lanthanum compounds are all completely isostructural, while the yttrium compounds crystallize in different space groups and/or contain significant structural differences. The packing arrangements for all four thiophosphate and all four selenophosphate compounds are shown in Figures 4.1 and 4.2 respectively.

Table 4.1. Crystallographic data for $K_2La(P_2S_6)_{1/2}(PS_4)$, $K_2La(P_2Se_6)_{1/2}(PSe_4)$, $K_2Y(P_2S_6)_{1/2}(PS_4)$, $K_2Y(P_2Se_6)_{1/2}(PSe_4)$.

	$K_2LaP_2S_7$	$K_2LaP_2Se_7$	$K_2YP_2S_7$ (I)	$K_2YP_2Se_7$ (II)
fw	503.47	831.77	453.47	781.77
a (Å)	9.066(6)	9.4269(1)	22.739(3)	7.2394(4)
b (Å)	6.793(3)	7.2054(1)	6.7385(8)	9.0101(6)
c (Å)	20.112(7)	21.0276(5)	18.013(2)	11.3480(7)
α (degrees)	90.0	90.0	90.0	73.337(2)
β (degrees)	97.54(3)	97.484(1)	119.816(2)	74.208(2)
γ (degrees)	90.0	90.0	90.0	87.207(2)
V, Å^3	1227.9(1)	1416.12(4)	2394.8(5)	682.01(7)
Z	4	4	8	2
λ, (Mo Kα), Å	0.71073	0.71073	0.71073	0.71073
Space Group	$P2_1/n$ (#14)	$P2_1/n$ (#14)	C2/c (#15)	P-1 (#2)
Temp., K	169(2)	298(2)	170(2)	169(2)
ρ_{calc}, Mg/m^3	2.724	3.901	2.516	3.807
μ (mm^{-1})	5.552	21.775	6.997	23.750
R1%[a]	4.93	4.29	8.90	8.59
wR2%[a]	7.65	8.90	14.52	19.21

[a] $R1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$; $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]]^{1/2}$

Table 4.2. Crystallographic data for $Cs_2Y(P_2S_6)_{1/2}(PS_4)$, $Cs_2Y(P_2Se_6)_{1/2}(PSe_4)$, $Cs_2La(P_2S_6)_{1/2}(PS_4)$, $Cs_2La(P_2Se_6)_{1/2}(PSe_4)$.

	$Cs_2YP_2S_7$ (III)	$Cs_2YP_2Se_7$ (IV)	$Cs_2LaP_2S_7$ (V)	$Cs_2LaP_2Se_7$ (VI)
fw	641.09	969.39	691.09	1019.39
a (Å)	9.703(1)	10.1012(5)	9.881(2)	10.1923(18)
b (Å)	6.8543(7)	7.1845(4)	6.936(1)	7.2284(13)
c (Å)	19.504(2)	20.3145(11)	19.547(3)	20.446(3)
α (degrees)	90.0	90.0	90.0	90.0
β (degrees)	97.492(2)	97.897(1)	98.722(3)	98.796(4)
γ (degrees)	90.0	90.0	90.0	90.0
V, $Å^3$	1286.1(2)	1460.28	1324.3(3)	1488.6(4)
Z	4	4	4	4
λ, (Mo Kα), Å	0.71073	0.71073	0.71073	0.71073
Space Group	$P2_1/n$ (#14)	$P2_1/n$ (#14)	$P2_1/n$ (#14)	$P2_1/n$ (#14)
Temp., K	171(2)	298(2)	172(2)	170(2)
ρ_{calc}, Mg/m^3	3.311	4.409	3.466	4.548
μ (mm^{-1})	11.446	26.53	9.939	24.976
R1%[a]	3.27	4.83	3.50	4.19
wR2%[a]	5.20	11.63	4.89	6.82

[a] $R1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ $\quad wR2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]]^{1/2}$

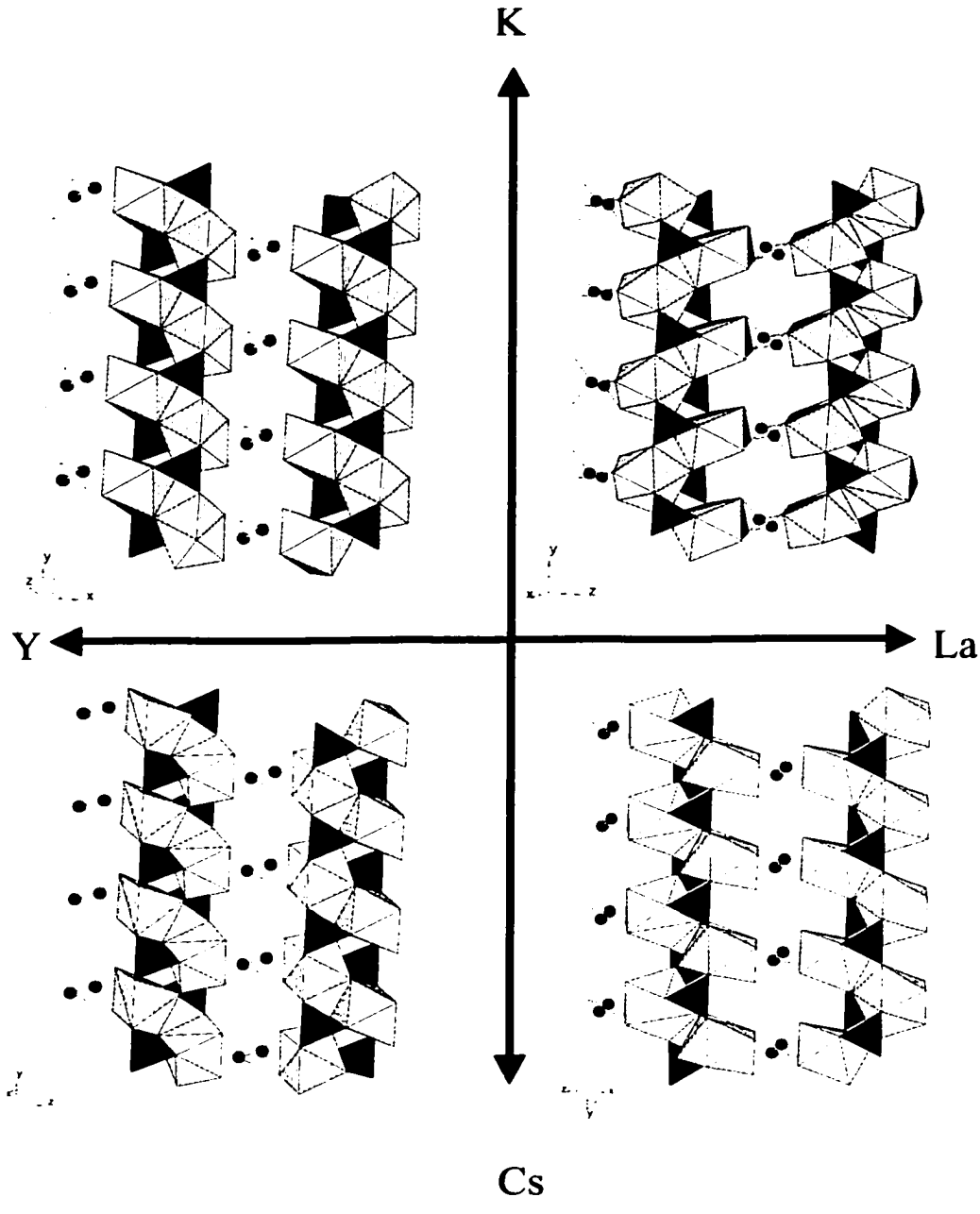


Figure 4.1. Packing plots for all four thiophosphate compounds: $K_2La(P_2S_6)_{1/2}(PS_4)$ and compounds I, III, and V. Striped rare-earth polyhedra. Filled $(PS_4)^{3-}$ tetrahedra. Filled phosphorus atoms. Alkali-metal cations removed for clarity.

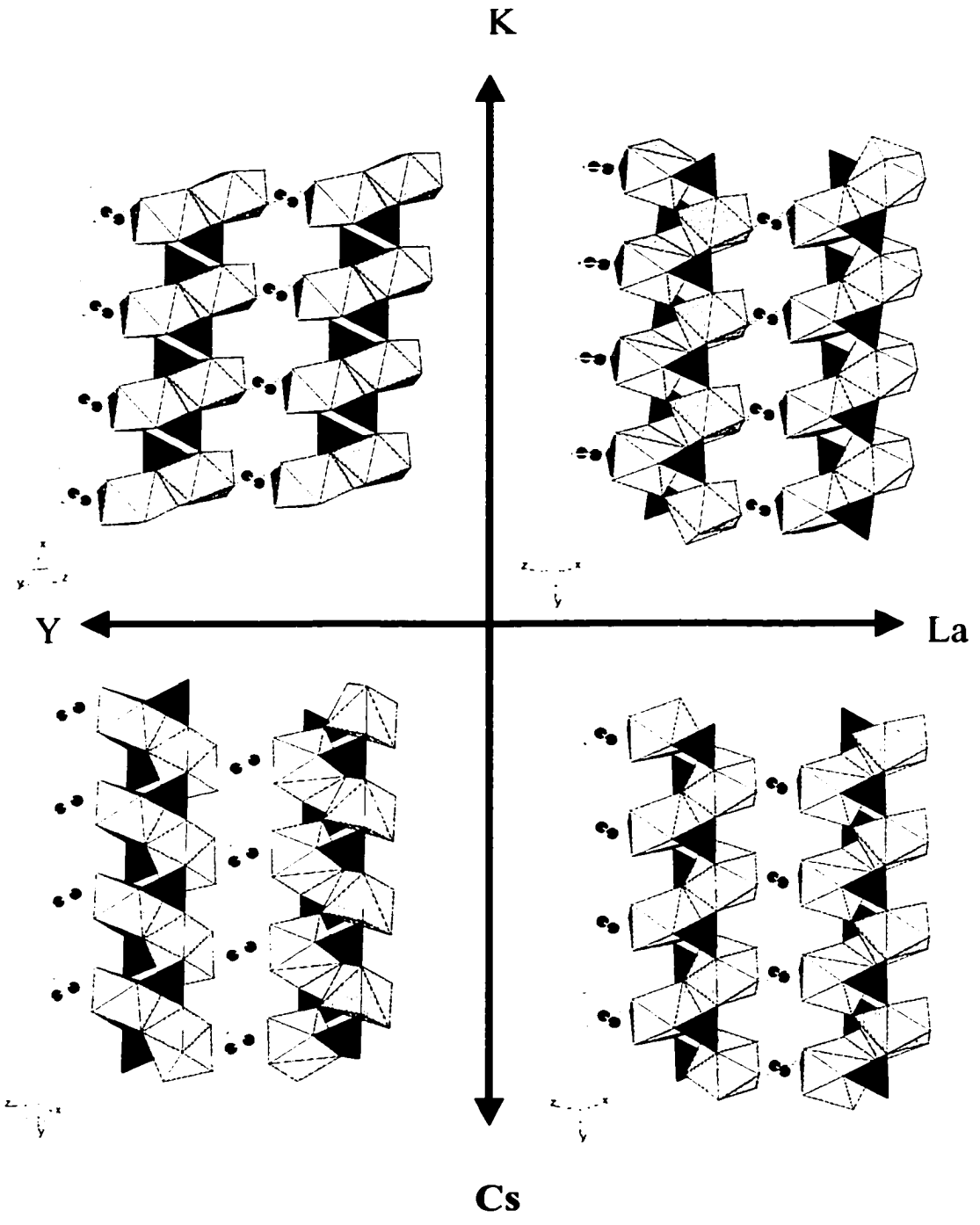


Figure 4.2. Packing plots for all four selenophosphate compounds: $K_2La(P_2Se_6)_{1/2}(PSe_4)$ and compounds II, IV, and VI. Striped rare-earth polyhedra. Filled $(PSe_4)^{3-}$ tetrahedra. Filled phosphorus atoms. Alkali-metal cations removed for clarity.

$K_2Y(P_2S_6)_{1/2}(PS_4)$ (I)

A single crystal of $K_2Y(P_2S_6)_{1/2}(PS_4)$ was selected, 7424 (2849 independent) reflections were collected, and an absorption correction was applied to a monoclinic cell (R_{int} = 0.1620). The structure was solved in C2/c by direct methods to electron density residuals of 1.261 and -1.281 eÅ^{-3}, and all atoms refined anisotropically with SHELXTL using full-matrix least squares refinement on F^2 for 109 variables.[45] $K_2YP_2S_7$ contains the same type of $^2_\infty[Y(P_2S_6)_{1/2}(PS_4)]^{2-}$ layer found in $K_2LaP_2S_7$, but one difference is observed. In $K_2LaP_2S_7$ all six sulfur atoms in the $(P_2S_6)^{4-}$ unit are bonded to lanthanum atoms. Figure 4.1 shows the packing arrangement of $K_2YP_2S_7$. Only four of the sulfur atoms on the $(P_2S_6)^{4-}$ unit are bonded to yttrium while the remaining two sulfur atoms are terminal P-S bonds pointing into the interlayer gap. The ORTEP plot in Figure 4.3 shows that a 7-coordinate yttrium atom is found in $K_2YP_2S_7$ with an average Y-S bond length of 2.85(1) Å. The longest Y-S bond is 3.015(4) Å. The closest possible Y-S bond distance involving the terminal sulfur atoms on the $(P_2S_6)^{4-}$ unit would be 3.345 Å. This is significantly longer than the other seven Y-S bonds and is therefore not included the coordination sphere for yttrium. Atomic coordinates and selected bond distances and angles for $K_2Y(P_2S_6)_{1/2}(PS_4)$ can be found in Tables 4.3 and 4.4 respectively.

$K_2Y(P_2Se_6)_{1/2}(PSe_4)$ (II)

A single crystal of $K_2Y(P_2Se_6)_{1/2}(PSe_4)$ was selected, 4554 (3141 independent) reflections were collected, and an absorption correction was applied to a triclinic cell (R_{int} = 0.0562). The structure was solved in P-1 by direct methods to

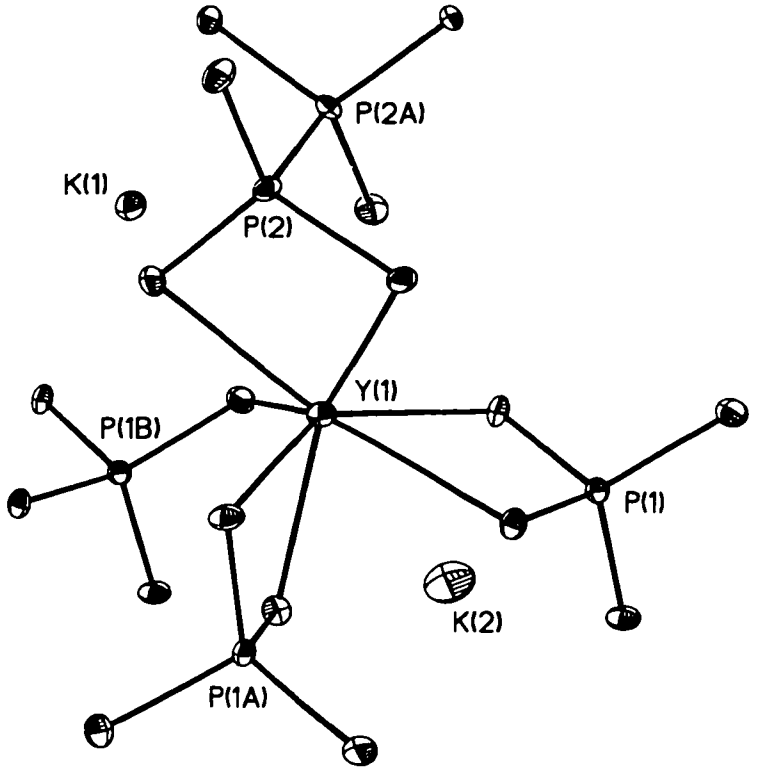


Figure 4.3. ORTEP plot of the coordination environment of yttrium in $K_2YP_2S_7$. Thermal ellipsoids plotted at the 50% probability level.

Table 4.3. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$)[a] for $K_2Y(P_2S_6)_{1/2}(PS_4)$.

	x	y	z	U(eq)
Y(1)	0.1540(1)	0.5472(2)	0.2344(1)	13(1)
S(1)	0.2243(2)	0.9432(5)	0.2671(2)	13(1)
S(2)	0.2620(2)	0.5242(5)	0.4025(2)	16(1)
S(3)	-0.0138(3)	0.5316(5)	0.1032(2)	17(1)
S(4)	0.0986(2)	0.7785(5)	0.3136(2)	15(1)
S(5)	0.1100(2)	0.2500(5)	0.1072(2)	17(1)
S(6)	0.1006(2)	0.2914(5)	0.3130(2)	14(1)
S(7)	0.1060(2)	0.7723(5)	0.0835(2)	15(1)
P(1)	0.1695(2)	0.0061(5)	0.1393(2)	12(1)
P(2)	0.0466(2)	0.5324(5)	0.3130(2)	12(1)
K(1)	-0.0111(2)	0.0271(4)	0.1173(2)	21(1)
K(2)	0.3105(2)	0.9987(5)	0.4790(2)	26(1)

[a] U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 4.4. Selected bond distances (Å) and angles (Deg.) for $K_2Y(P_2S_6)_{1/2}(PS_4)$.

Y(1)-S(2)	2.799(4)	Y(1)-S(6)	2.856(4)
Y(1)-S(4)	2.800(4)	Y(1)-S(1')	2.869(3)
Y(1)-S(7)	2.815(4)	Y(1)-S(1)	3.015(4)
Y(1)-S(5)	2.825(4)	P(2)-S(3)	1.990(4)
P(1)-S(1)	2.044(5)	P(2)-S(4)	2.032(5)
P(1)-S(2)	2.043(4)	P(2)-S(6)	2.035(5)
P(1)-S(5)	2.022(5)	P(2)-P(2')	2.204(7)
P(1)-S(7)	2.033(5)		

S(2)-Y(1)-S(4)	81.64(11)	S(2)-Y(1)-S(7)	141.66(11)
S(4)-Y(1)-S(7)	97.78(11)	S(2)-Y(1)-S(5)	127.21(11)
S(3)-Y(1)-S(5)	137.78(11)	S(7)-Y(1)-S(5)	77.77(11)
S(2)-Y(1)-S(6)	77.95(10)	S(4)-Y(1)-S(6)	70.94(10)
S(7)-Y(1)-S(6)	138.37(11)	S(5)-Y(1)-S(6)	84.74(11)
S(2)-Y(1)-S(1')	70.39(9)	S(4)-Y(1)-S(1')	145.23(11)
S(7)-Y(1)-S(1')	92.01(10)	S(5)-Y(1)-S(1')	76.89(10)
S(6)-Y(1)-S(1')	120.48(10)	S(2)-Y(1)-S(1)	75.06(10)
S(4)-Y(1)-S(1)	74.74(9)	S(7)-Y(1)-S(1)	67.97(10)
S(5)-Y(1)-S(1)	136.50(10)	S(6)-Y(1)-S(1)	138.76(11)
S(1)-Y(1)-S(1)	78.32(6)		
S(5)-P(1)-S(7)	106.2(2)	S(5)-P(1)-S(2)	111.7(2)
S(7)-P(1)-S(2)	110.4(2)	S(5)-P(1)-S(1)	116.0(2)
S(7)-P(1)-S(1)	106.4(2)	S(2)-P(1)-S(1)	106.1(2)
S(3)-P(2)-S(4)	115.7(2)	S(3)-P(2)-S(6)	116.8(2)
S(4)-P(2)-S(6)	107.6(2)	S(3)-P(2)-P(2')	104.4(2)
S(4)-P(2)-P(2')	105.4(2)	S(6)-P(2)-P(2')	105.8(2)

electron density residuals of 4.205 and -2.759 $eÅ^{-3}$, and all atoms refined anisotropically with SHELXTL using full-matrix least squares refinement on F^2 for 109 variables.[45] The program PLATON confirmed that no additional symmetry elements are present in the structure.[61] Unlike $K_2LaP_2Q_7$ (Q = S, Se), $K_2YP_2Se_7$ is not isostructural to $K_2YP_2S_7$. $K_2YP_2Se_7$ is a layered structure containing quasi-infinite layers of $^{2}_{\infty}[Y(P_2Se_6)_{1/2}(PSe_4)]^{2-}$. These layers are separated by potassium cations. Figure 4.2 shows that these layers comprise chains of Y-Se polyhedra coordinated by $(PSe_4)^{3-}$ tetrahedra. Unlike $K_2YP_2S_7$ and $K_2LaP_2Q_7$ (Q = S, Se) with their corner-sharing rare-earth polyhedra, $K_2YP_2Se_7$ contains edge-sharing yttrium dimers that are linked together by $(PSe_4)^{3-}$ tetrahedra. These "chains" of yttrium dimers and $(PSe_4)^{3-}$ tetrahedra are linked together by $(P_2Se_6)^{4-}$ units to form a layer. Figure 4.4 shows an ORTEP plot of the coordination environment around yttrium. Eight selenium atoms with an average Y-Se distance of 3.032(8) Å coordinate each yttrium atom. This coordination environment arises from each yttrium polyhedra sharing edges with two $(PSe_4)^{3-}$ units, corner sharing with a third $(PSe_4)^{3-}$ tetrahedron, and bonded through three of the six selenium atoms on the $(P_2Se_6)^{4-}$ unit. Figure 4.5 compares the coordination geometry around yttrium in $K_2Y(P_2S_6)_{1/2}(PS_4)$ and $K_2Y(P_2Se_6)_{1/2}(PSe_4)$. In $K_2Y(P_2S_6)_{1/2}(PS_4)$ yttrium is found in a 7-coordinate distorted mono-capped trigonal prismatic geometry. The capping Y-S bond is the longest Y-S bond found. In $K_2Y(P_2Se_6)_{1/2}(PSe_4)$ yttrium is found in an 8-coordinate distorted square anti-prismatic geometry. Atomic coordinates and selected bond distances and angles for $K_2Y(P_2Se_6)_{1/2}(PSe_4)$ can be found in Tables 4.5 and 4.6 respectively.

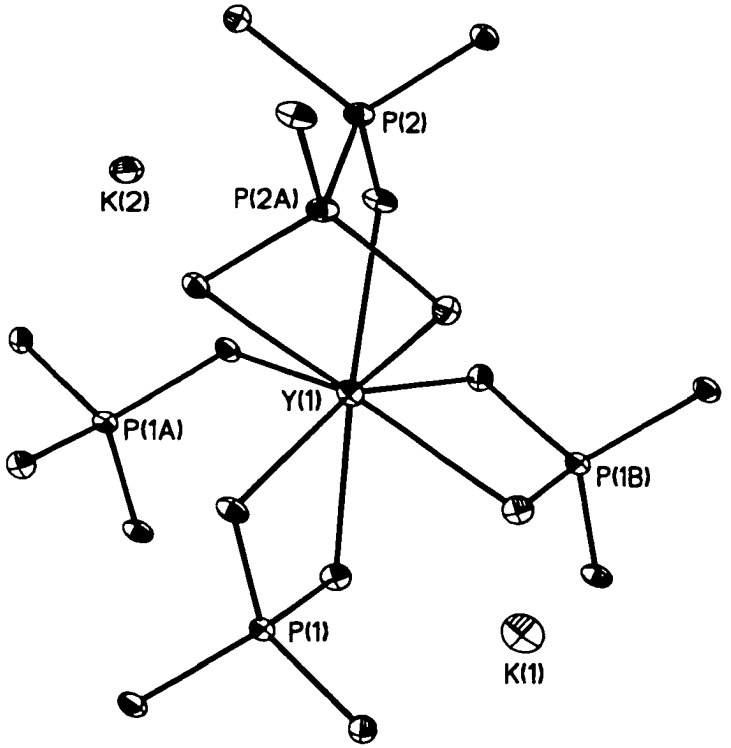
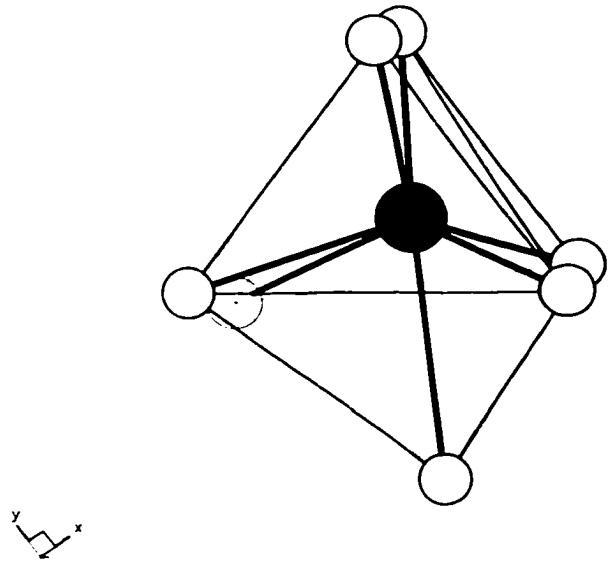
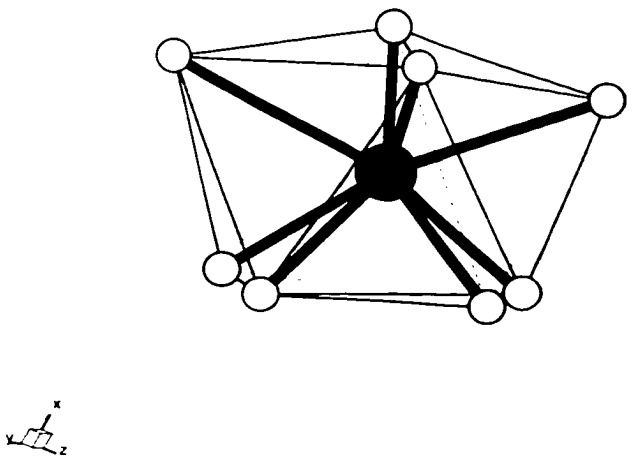


Figure 4.4. ORTEP plot of the coordination environment of yttrium in $K_2YP_2Se_7$. Thermal ellipsoids plotted at the 50% probability level.



A



B

Figure 4.5. Comparison of the coordination geometries around yttrium in (**A**) $K_2Y(P_2S_6)_{1/2}(PS_4)$ and (**B**) $K_2Y(P_2Se_6)_{1/2}(PSe_4)$. Filled yttrium atoms, open sulfur or selenium atoms.

Table 4.5. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($Å^2$ x 10^3)[a] for $K_2Y(P_2Se_6)_{1/2}(PSe_4)$.

	x	y	z	U(eq)
Y(1)	0.4089(3)	0.6589(2)	0.7967(2)	13(1)
Se(1)	0.2869(3)	0.3819(2)	0.0564(2)	15(1)
Se(2)	0.5292(3)	0.7049(2)	0.4966(2)	16(1)
Se(3)	0.1335(3)	0.4925(2)	0.7235(2)	16(1)
Se(4)	0.6642(3)	0.4172(2)	0.7246(2)	15(1)
Se(5)	0.6578(3)	0.9419(2)	0.6995(2)	14(1)
Se(6)	0.1694(3)	0.7754(2)	0.9939(2)	16(1)
Se(7)	0.1758(3)	0.9381(2)	0.6918(2)	14(1)
P(1)	0.1600(7)	0.5611(6)	0.1498(5)	12(1)
P(2)	0.5414(8)	0.9553(6)	0.4161(5)	14(1)
K(1)	0.2995(7)	0.1523(5)	0.8735(5)	23(1)
K(2)	0.0128(7)	0.7512(6)	0.4847(4)	23(1)

[a] U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 4.6. Selected bond distances (Å) and angles (Deg.)for $K_2Y(P_2Se_6)_{1/2}(PSe_4)$.

Y(1)-Se(6)	2.859(3)	Y(1)-Se(1')	3.055(3)
Y(1)-Se(4)	2.938(3)	Y(1)-Se(7)	3.091(3)
Y(1)-Se(5)	2.952(3)	Y(1)-Se(2)	3.184(3)
Y(1)-Se(3)	2.970(3)	Y(1)-Se(1)	3.206(3)
P(1)-Se(1)	2.210(6)	P(2)-Se(2)	2.174(6)
P(1)-Se(3)	2.203(5)	P(2)-Se(5)	2.205(6)
P(1)-Se(4)	2.205(6)	P(2)-Se(7)	2.183(5)
P(1)-Se(6)	2.203(5)	P(2)-P(2')	2.201(11)

Se(6)-Y(1)-Se(4)	148.66(9)	Se(6)-Y(1)-Se(5)	90.80(8)
Se(4)-Y(1)-Se(5)	104.34(8)	Se(6)-Y(1)-Se(3)	103.50(8)
Se(4)-Y(1)-Se(3)	81.87(7)	Se(5)-Y(1)-Se(3)	141.07(9)
Se(6)-Y(1)-Se(1')	86.79(8)	Se(4)-Y(1)-Se(1')	72.95(7)
Se(5)-Y(1)-Se(1')	71.08(7)	Se(3)-Y(1)-Se(1')	144.44(9)
Se(6)-Y(1)-Se(7)	67.41(7)	Se(4)-Y(1)-Se(7)	143.35(9)
Se(5)-Y(1)-Se(7)	71.12(7)	Se(3)-Y(1)-Se(7)	81.22(8)
Se(1')-Y(1)-Se(7)	133.30(8)	Se(6)-Y(1)-Se(2)	143.39(9)
Se(4)-Y(1)-Se(2)	67.63(7)	Se(5)-Y(1)-Se(2)	77.89(7)
Se(3)-Y(1)-Se(2)	69.03(7)	Se(1')-Y(1)-Se(2)	120.75(8)
Se(7)-Y(1)-Se(2)	75.99(7)	Se(6)-Y(1)-Se(1)	70.71(7)
Se(4)-Y(1)-Se(1)	79.68(7)	Se(5)-Y(1)-Se(1)	136.65(8)
Se(3)-Y(1)-Se(1)	82.19(7)	Se(1')-Y(1)-Se(1)	69.10(7)
Se(7)-Y(1)-Se(1)	129.39(8)	Se(2)-Y(1)-Se(1)	138.60(8)
Se(6)-P(1)-Se(3)	110.9(2)	Se(2)-P(2)-Se(7)	116.5(3)
Se(3)-P(1)-Se(4)	104.8(2)	Se(7)-P(2)-P(2')	104.9(3)
Se(3)-P(1)-Se(1)	115.5(2)	Se(7)-P(2)-Se(5)	106.5(2)
Se(6)-P(1)-Se(4)	112.2(2)	Se(2)-P(2)-P(2')	104.2(3)
Se(6)-P(1)-Se(1)	105.8(2)	Se(2)-P(2)-Se(5)	117.9(2)
Se(4)-P(1)-Se(1)	107.7(2)	Se(5)-P(2)-P(2')	105.6(4)

By comparing the structures of $K_2REP_2S_7$ and $K_2REP_2Se_7$ (RE = Y, La) to their cesium analogs we can see the effect of a larger alkali-metal cation on this structure type.

$Cs_2Y(P_2S_6)_{1/2}(PS_4)$ (III)

A single crystal of $Cs_2Y(P_2S_6)_{1/2}(PS_4)$ was selected, 8380 (3151 independent) reflections were collected, and an absorption correction was applied to a monoclinic cell (R_{int} = 0.0628). The structure was solved in $P2_1/n$ by direct methods to electron density residuals of 1.469 and -1.651 eÅ^{-3}, and all atoms refined anisotropically with SHELXTL using full-matrix least squares refinement on F^2 for 109 variables.[60] $Cs_2Y(P_2S_6)_{1/2}(PS_4)$ crystallizes in a different space group than $K_2Y(P_2S_6)_{1/2}(PS_4)$, but both structures contain the same two-dimensional layer; $^{2}_{\infty}[Y(P_2S_6)_{1/2}(PS_4)]^{2-}$ shown in Figure 4.1. $Cs_2Y(P_2S_6)_{1/2}(PS_4)$ contains 7-coordinate yttrium atoms with an average Y-S bond distance of 2.857(7) Å. Figure 4.6 shows an ORTEP plot of the coordination sphere around yttrium in $Cs_2Y(P_2S_6)_{1/2}(PS_4)$. Yttrium is found in the same mono-capped distorted trigonal prism as $K_2Y(P_2S_6)_{1/2}(PS_4)$. Yttrium is bonded to two $(PS_4)^{3-}$ tetrahedra in an edge-sharing fashion, a third $(PS_4)^{3-}$ tetrahedron in a corner-sharing fashion, and to two of the sulfur atoms on the $(P_2S_6)^{4-}$ unit. Atomic coordinates and selected bond distances and angles for $Cs_2Y(P_2S_6)_{1/2}(PS_4)$ can be found in Tables 4.7 and 4.8.

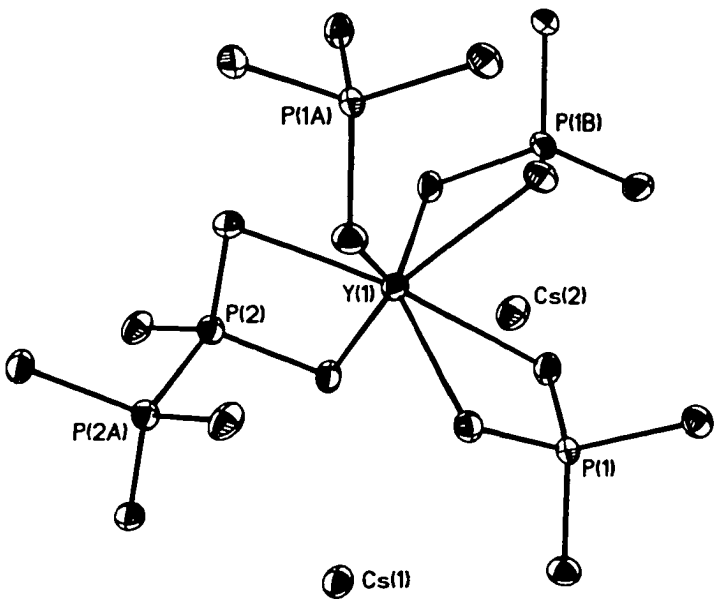


Figure 4.6. ORTEP plot of the coordination environment of yttrium in $Cs_2YP_2S_7$. Thermal ellipsoids plotted at the 70% probability level.

Table 4.7. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$)[a] for $Cs_2Y(P_2S_6)_{1/2}(PS_4)$.

	x	y	z	U(eq)
Y(1)	0.3119(1)	0.9816(2)	0.1545(1)	12(1)
S(1)	0.2402(2)	0.9981(5)	-0.0260(1)	19(1)
S(2)	0.3056(2)	0.5776(3)	0.2234(1)	15(1)
S(3)	0.5231(2)	0.0066(5)	0.2667(1)	15(1)
S(4)	0.1109(3)	0.2711(4)	0.1077(2)	16(1)
S(5)	0.5101(3)	0.7566(4)	0.1005(2)	17(1)
S(6)	0.5052(3)	0.2336(4)	0.1026(2)	16(1)
S(7)	0.0818(3)	0.7540(4)	0.1010(2)	14(1)
P(1)	0.1198(2)	0.5196(5)	0.1649(1)	12(1)
P(2)	0.5672(2)	-0.0008(5)	0.0505(1)	14(1)
Cs(1)	0.7645(1)	0.4982(1)	0.0287(1)	17(1)
Cs(2)	-0.1416(1)	0.0050(1)	0.2064(1)	22(1)

[a] U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 4.8. Selected bond distances (Å) and angles (Deg.) for $Cs_2Y(P_2S_6)_{1/2}(PS_4)$.

Y(1)-S(5)	2.777(3)	Y(1)-S(3)	2.802(2)
Y(1)-S(7)	2.810(3)	Y(1)-S(6)	2.832(3)
Y(1)-S(4)	2.848(3)	Y(1)-S(2')	2.850(2)
Y(1)-S(2)	3.082(2)	P(2)-S(1)	1.989(3)
P(1)-S(2)	2.042(3)	P(2)-S(5)	2.040(4)
P(1)-S(3)	2.048(3)	P(2)-S(6)	2.033(4)
P(1)-S(4)	2.031(4)	P(2)-P(2')	2.217(4)
P(1)-S(7)	2.037(4)		

S(5)-Y(1)-S(3)	81.85(9)	S(5)-Y(1)-S(7)	96.16(9)
S(3)-Y(1)-S(7)	142.05(9)	S(5)-Y(1)-S(6')	71.31(6)
S(3)-Y(1)-S(6')	77.93(8)	S(7)-Y(1)-S(6')	137.49(9)
S(5)-Y(1)-S(4')	138.14(9)	S(3)-Y(1)-S(4')	127.44(9)
S(7)-Y(1)-S(4')	77.89(7)	S(6')-Y(1)-S(4')	85.32(8)
S(5)-Y(1)-S(2')	144.85(9)	S(3)-Y(1)-S(2')	70.37(6)
S(7)-Y(1)-S(2')	93.05(8)	S(6')-Y(1)-S(2')	120.90(8)
S(4)-Y(1)-S(2')	76.97(8)	S(5)-Y(1)-S(2)	73.78(8)
S(3)-Y(1)-S(2)	76.61(8)	S(7)-Y(1)-S(2)	66.61(7)
S(6)-Y(1)-S(2)	139.08(8)	S(4)-Y(1)-S(2)	135.55(8)
S(2)-Y(1)-S(2)	79.05(4)		
S(4)-P(1)-S(7)	109.56(12)	S(4)-P(1)-S(2)	116.19(16)
S(7)-P(1)-S(2)	105.32(16)	S(4)-P(1)-S(3)	109.70(17)
S(7)-P(1)-S(3)	110.40(17)	S(2)-P(1)-S(3)	105.51(12)
S(1)-P(2)-S(5)	116.37(18)	S(1)-P(2)-S(6)	117.48(18)
S(1)-P(2)-P(2')	104.40(13)	S(3)-P(2)-S(5)	106.82(11)
S(5)-P(2)-P(2')	105.3(2)	S(6)-P(2)-P(2')	105.2(2)

$Cs_2Y(P_2Se_6)_{1/2}(PSe_4)$ (IV)

A single crystal of $Cs_2Y(P_2Se_6)_{1/2}(PSe_4)$ was selected, 9356 (3538 independent) reflections were collected, and an absorption correction was applied to a monoclinic cell (R_{int} = 0.0565). The structure was solved in $P2_1/n$ by direct methods to electron density residuals of 3.216 and -1.610 $eÅ^{-3}$, and all atoms refined anisotropically with SHELXTL using full-matrix least squares refinement on F^2 for 110 variables.[45] As seen in Table 4.2, $Cs_2YP_2Se_7$ crystallizes in the same space group as $K_2LaP_2Se_7$, but is structurally different than both $K_2YP_2Se_7$ and $K_2LaP_2Se_7$. Unlike $K_2YP_2Se_7$, the yttrium polyhedra in $Cs_2YP_2Se_7$ are corner sharing instead of edge sharing as seen in Figure 4.2. Another significant difference is that both $K_2LaP_2Se_7$ and $K_2YP_2Se_7$ contain 8-coordinate rare-earth cations. $Cs_2YP_2Se_7$ contains a 7-coordinate yttrium atom in a distorted mono-capped trigonal prismatic geometry. This reduced coordination number results from two terminal P-Se bonds on the $(P_2Se_6)^{4-}$ unit, just as in $K_2YP_2S_7$. One selenium atom on each side of the "ethane-like" unit is terminal and points into the gap between layers. The average Y-Se bond length is 2.986(4) Å and the longest Y-Se bond is 3.196(1) Å. The closest possible Y-Se bond for the terminal selenium atom is 3.543 Å, which is significantly longer than the other Y-Se bonds and therefore is not reported as a bond. Figure 4.7 shows an ORTEP plot of the coordination environment around yttrium in $Cs_2YP_2Se_7$. Atomic coordinates and selected bond distances and angles are reported in Tables 4.9 and 4.10.

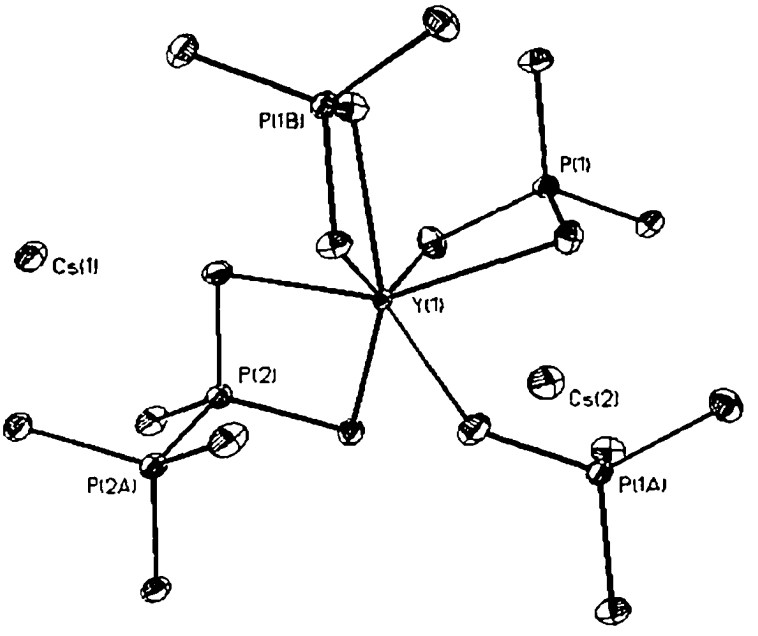


Figure 4.7. ORTEP plot of the coordination environment of yttrium in $Cs_2YP_2Se_7$. Thermal ellipsoids plotted at the 50% probability level.

Table 4.9. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$)[a] for $Cs_2Y(P_2Se_6)_{1/2}(PSe_4)$.

	x	y	z	U(eq)
Y(1)	0.8106(1)	0.4777(1)	0.1532(1)	10(1)
Se(1)	0.7350(1)	0.4969(2)	-0.0222(1)	27(1)
Se(2)	0.6074(1)	0.7610(1)	0.1038(1)	23(1)
Se(3)	0.8093(1)	0.0825(2)	0.2253(1)	23(1)
Se(4)	0.0281(1)	0.5007(2)	0.2647(1)	24(1)
Se(5)	0.0089(1)	0.2489(1)	0.1007(1)	22(1)
Se(6)	0.0030(1)	0.7392(1)	0.1035(1)	23(1)
Se(7)	0.5778(1)	0.2564(1)	0.0977(1)	22(1)
P(1)	0.6174(3)	0.0153(4)	0.1641(1)	17(1)
P(2)	0.9346(3)	0.5011(4)	-0.0486(1)	17(1)
Cs(1)	0.2622(1)	-0.0021(1)	0.0284(1)	30(1)
Cs(2)	0.3560(1)	0.4985(1)	0.2028(1)	37(1)

[a] U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 4.10. Selected bond distances (Å) and angles (Deg.) for $Cs_2Y(P_2Se_6)_{1/2}(PSe_4)$.

Y(1)-Se(5)	2.905(1)	Y(1)-Se(6)	2.978(1)
Y(1)-Se(7)	2.932(2)	Y(1)-Se(3)	2.991(1)
Y(1)-Se(4)	2.936(2)	Y(1)-Se(3')	3.196(1)
Y(1)-Se(2)	2.966(1)	P(2)-Se(1)	2.157(3)
P(1)-Se(2)	2.195(3)	P(2)-Se(5)	2.199(3)
P(1)-Se(3)	2.208(3)	P(2)-Se(6)	2.194(3)
P(1)-Se(4)	2.201(3)	P(2)-P(2')	2.218(6)
P(1)-Se(7)	2.199(3)		

Se(5')-Y(1)-Se(7)	96.26(4)	Se(7)-Y(1)-Se(3')	93.43(4)
Se(5')-Y(1)-Se(4')	80.48(4)	Se(4')-Y(1)-Se(3')	72.18(4)
Se(7)-Y(1)-Se(4')	143.40(4)	Se(2)-Y(1)-Se(3')	76.52(4)
Se(5')-Y(1)-Se(2)	138.06(4)	Se(6')-Y(1)-Se(3')	118.57(4)
Se(7)-Y(1)-Se(2)	76.17(4)	Se(5')-Y(1)-Se(3)	73.28(3)
Se(4')-Y(1)-Se(2)	129.21(4)	Se(7)-Y(1)-Se(3)	68.97(3)
Se(5')-Y(1)-Se(6')	73.56(4)	Se(4')-Y(1)-Se(3)	75.28(4)
Se(7)-Y(1)-Se(6')	137.54(4)	Se(2)-Y(1)-Se(3)	135.95(4)
Se(4')-Y(1)-Se(6')	76.83(4)	Se(6')-Y(1)-Se(3)	139.46(5)
Se(2)-Y(1)-Se(6')	84.59(4)	Se(3')-Y(1)-Se(3)	79.50(3)
Se(5')-Y(1)-Se(3')	145.41(5)		
Se(2)-P(1)-Se(7)	108.80(12)	Se(1)-P(2)-Se(6)	117.28(13)
Se(2)-P(1)-Se(4)	110.10(12)	Se(1)-P(2)-Se(5)	116.36(13)
Se(7)-P(1)-Se(4)	111.07(13)	Se(6)-P(2)-Se(5)	106.65(2)
Se(2)-P(1)-Se(3)	117.77(13)	Se(1)-P(2)-P(2')	104.0(2)
Se(7)-P(1)-Se(3)	104.18(12)	Se(6)-P(2)-P(2')	105.6(2)
Se(4)-P(1)-Se(3)	104.74(12)	Se(5)-P(2)-P(2')	105.8(2)

$Cs_2La(P_2S_6)_{1/2}(PS_4)$ (V)

A single crystal of $Cs_2La(P_2S_6)_{1/2}(PS_4)$ was selected, 8799 (3231 independent) reflections were collected, and an absorption correction was applied to a monoclinic cell (R_{int} = 0.1205). The structure was solved in $P2_1/n$ by direct methods to electron density residuals of 1.299 and -1.278 eÅ^{-3}, and all atoms refined anisotropically with SHELXTL using full-matrix least squares refinement on F^2 for 109 variables.[60] $Cs_2La(P_2S_6)_{1/2}(PS_4)$ is isostructural with the other lanthanum structures. Each lanthanum atoms is coordinated to 8 sulfur atoms with an average La-S distance of 3.025(13) Å. Figure 4.1 shows that the $^2_\infty[La(P_2S_6)_{1/2}(PS_4)]^{2-}$ layer in $Cs_2LaP_2S_7$ is completely isostructural to $K_2LaP_2S_7$. Lanthanum atoms are corner-sharing and all six sulfur atoms on the $(P_2S_6)^{4-}$ unit are bound to lanthanum atoms. Figure 4.8 shows an ORTEP plot of the coordination environment of lanthanum in $Cs_2LaP_2S_7$. Atomic coordinates and selected bond distances and angles for $Cs_2La(P_2S_6)_{1/2}(PS_4)$ can be found in Tables 4.11 and 4.12.

$Cs_2La(P_2Se_6)_{1/2}(PSe_4)$ (VI)

A single crystal of $Cs_2La(P_2Se_6)_{1/2}(PSe_4)$ was selected, 9815 (3642 independent) reflections were collected, and an absorption correction was applied to a monoclinic cell (R_{int} = 0.0966). The structure was solved in $P2_1/n$ by direct methods to electron density residuals of 1.717 and -1.466 eÅ^{-3}, and all atoms refined anisotropically with SHELXTL using full-matrix least squares refinement on F^2 for 110 variables.[60] $Cs_2LaP_2Se_7$ is isostructural to its potassium counterpart. The structure is composed of $^2_\infty[La(P_2Se_6)_{1/2}(PSe_4)]^{2-}$ layers separated by cesium

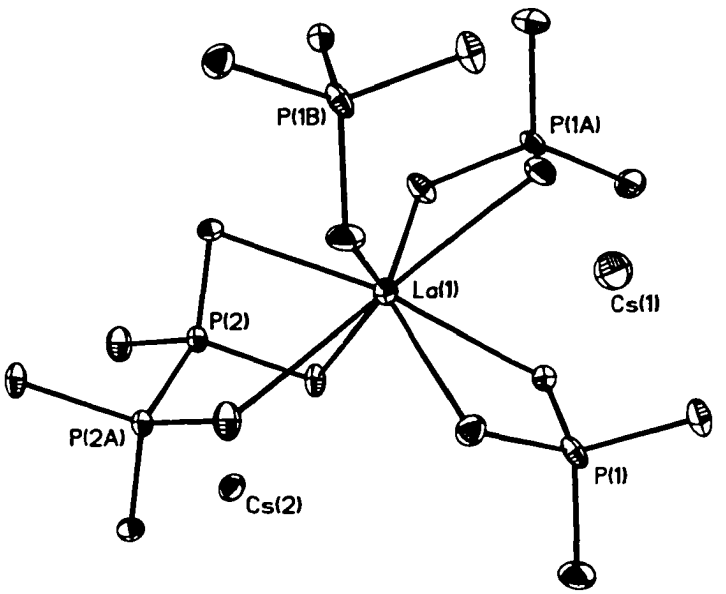


Figure 4.8. ORTEP plot of the coordination environment of lanthanum in $Cs_2LaP_2S_7$. Thermal ellipsoids plotted at the 70% probability level.

Table 4.11. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($Å^2$ x 10^3)[a] for $Cs_2La(P_2S_6)_{1/2}(PS_4)$.

	x	y	z	U(eq)
La(1)	0.3084(1)	0.9847(2)	0.1498(1)	11(1)
S(1)	0.2433(3)	0.9935(8)	-0.0184(2)	15(1)
S(2)	0.2993(4)	0.5718(5)	0.2168(2)	13(1)
S(3)	0.5272(3)	0.0115(8)	0.2683(2)	16(1)
S(4)	0.0919(6)	0.2754(6)	0.1064(3)	20(2)
S(5)	0.5295(6)	0.7634(6)	0.1006(3)	13(1)
S(6)	0.5208(7)	0.2363(6)	0.1017(3)	16(2)
S(7)	0.0654(6)	0.7521(6)	0.0988(3)	15(1)
P(1)	0.1086(4)	0.5224(8)	0.1626(2)	13(1)
P(2)	0.5726(3)	0.0024(8)	0.0485(2)	11(1)
Cs(1)	0.7607(1)	0.5008(2)	0.0225(1)	16(1)
Cs(2)	-0.1399(1)	0.0117(2)	0.2056(1)	19(1)

[a] U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 4.12. Selected bond distances (Å) and angles (Deg.) for $Cs_2La(P_2S_6)_{1/2}(PS_4)$.

La(1)-S(3)	2.924(3)	La(1)-S(6)	2.989(6)
La(1)-S(7)	2.940(6)	La(1)-S(2')	3.022(3)
La(1)-S(5)	2.949(6)	La(1)-S(2)	3.156(4)
La(1)-S(4)	2.969(6)	La(1)-S(1)	3.253(3)
P(1)-S(7)	2.028(7)	P(2)-S(1)	1.995(4)
P(1)-S(4)	2.029(7)	P(2)-S(5)	2.024(7)
P(1)-S(3)	2.046(4)	P(2)-S(6)	2.035(7)
P(1)-S(2)	2.046(5)	P(2)-P(2')	2.197(6)

S(3)-La(1)-S(7)	140.50(14)	S(3)-La(1)-S(5)	78.23(15)
S(7)-La(1)-S(4)	102.18(15)	S(3)-La(1)-S(4)	126.70(14)
S(7)-La(1)-S(5)	76.08(11)	S(5)-La(1)-S(4)	142.92(16)
S(3)-La(1)-S(6)	75.04(15)	S(7)-La(1)-S(6)	142.21(17)
S(5)-La(1)-S(6)	67.11(9)	S(4)-La(1)-S(6)	91.34(15)
S(3)-La(1)-S(2')	67.62(10)	S(7)-La(1)-S(2')	91.50(14)
S(5)-La(1)-S(2')	139.55(14)	S(4)-La(1)-S(2')	77.17(14)
S(6)-La(1)-S(2')	120.69(13)	S(3)-La(1)-S(2)	78.07(13)
S(7)-La(1)-S(2)	64.49(12)	S(5)-La(1)-S(2)	74.49(12)
S(4)-La(1)-S(2)	132.07(14)	S(6)-La(1)-S(2)	136.57(14)
S(2')-La(1)-S(2)	77.73(6)	S(3)-La(1)-S(1)	143.89(9)
S(7)-La(1)-S(1)	68.97(14)	S(5)-La(1)-S(1)	73.89(14)
S(4)-La(1)-S(1)	71.03(14)	S(6)-La(1)-S(1)	73.25(14)
S(2')-La(1)-S(1)	145.72(11)	S(2)-La(1)-S(1)	115.01(12)
S(7)-P(1)-S(3)	109.7(3)	S(7)-P(1)-S(4)	109.8(2)
S(7)-P(1)-S(2)	106.2(3)	S(4)-P(1)-S(3)	108.6(3)
S(3)-P(1)-S(2)	108.0(2)	S(4)-P(1)-S(2)	114.5(3)
S(1)-P(2)-S(5)	115.5(3)	S(1)-P(2)-S(6)	116.8(3)
S(5)-P(2)-P(6)	107.91(18)	S(1)-P(2)-P(2')	104.5(2)
S(5)-P(2)-P(2')	105.2(4)	S(6)-P(2)-P(2')	105.7(4)

cations. Figure 4.2 shows that each layer contains corner-sharing lanthanum polyhedra and $(PSe_4)^{3-}$ tetrahedra linked into a layer with $(P_2Se_6)^{4-}$ units. There are no terminal P-Se bonds. The ORTEP plot in Figure 4.9 shows an 8-coordinate lanthanum atom coordinated by three $(PSe_4)^{3-}$ tetrahedra and one $(P_2Se_6)^{4-}$ unit. The average La-Se bond length is 3.145(6) Å. By comparison to $Cs_2YP_2Se_7$ we see the effect of a smaller RE cation on this structure. The smaller yttrium atoms are 7-coordinate instead of 8-coordinate as in $Cs_2LaP_2Se_7$. Atomic coordinates and selected bond distances and angles for $Cs_2La(P_2Se_6)_{1/2}(PSe_4)$ can be found in Tables 4.13 and 4.14 respectively.

Conclusions

By looking at these eight structures as a group one can make some general statements about the effect of cation size. Based on the structures reported here, it is apparent that the size of the rare-earth metal cation has a much larger effect on structure than the size of the alkali-metal cation. This is reasonable as the alkali-metal cations are found in between the layers of each structure where there is room to accommodate a larger cation without a required change in structure. Looking at the van der Waals gap for these eight structures supports this observation. In general, the four cesium structures have slightly larger van der Waals gaps than the potassium compounds, but the difference is very small. All eight van der Waals gaps range from 3.6 to 3.8 Å. The rare-earth cation, on the other hand, is found within the two-dimensional layer of the structure. The intricate bonding within each layer is therefore much more susceptible to changes in cation size. All four structures containing lanthanum are completely isostructural. Lanthanum is always coordinated

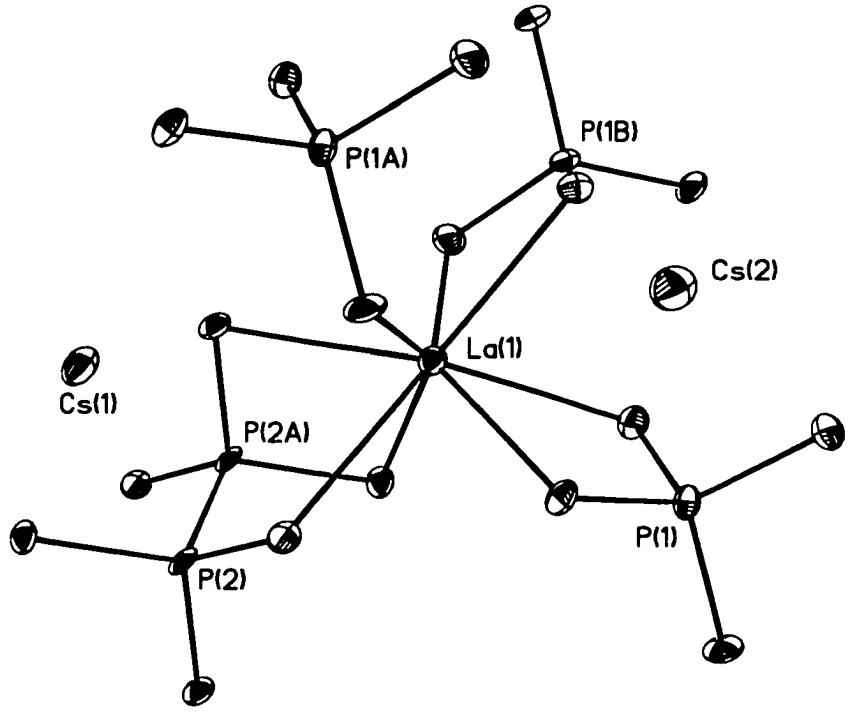


Figure 4.9. ORTEP plot of the coordination environment of lanthanum in $Cs_2LaP_2Se_7$. Thermal ellipsoids plotted at the 70% probability level.

Table 4.13. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($Å^2$ x 10^3)[a] for $Cs_2La(P_2Se_6)_{1/2}(PSe_4)$.

	x	y	z	U(eq)
La(1)	0.8082(1)	0.4802(1)	0.1499(1)	11(1)
Se(1)	0.7366(1)	0.4906(2)	-0.0151(1)	13(1)
Se(2)	0.5886(2)	0.7664(2)	0.1036(1)	15(1)
Se(3)	0.8060(2)	0.0748(2)	0.2188(1)	13(1)
Se(4)	0.0355(1)	0.5079(2)	0.2658(1)	14(1)
Se(5)	0.0282(2)	0.2526(2)	0.1006(1)	14(1)
Se(6)	0.0180(2)	0.7433(2)	0.1015(1)	14(1)
Se(7)	0.5592(2)	0.2552(2)	0.0965(1)	13(1)
P(1)	0.6061(3)	0.0197(6)	0.1630(2)	10(1)
P(2)	0.9292(3)	0.4985(6)	-0.0467(2)	11(1)
Cs(1)	0.2584(1)	0.0012(1)	0.0198(1)	17(1)
Cs(2)	0.3551(1)	0.5084(2)	0.2002(1)	20(1)

[a] U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 4.14. Selected bond distances (Å) and angles (Deg.) for $Cs_2La(P_2Se_6)_{1/2}(PSe_4)$.

La(1)-Se(4)	3.043(2)	La(1)-Se(7)	3.071(2)
La(1)-Se(5)	3.072(2)	La(1)-Se(2)	3.089(2)
La(1)-Se(6)	3.133(2)	La(1)-Se(3')	3.160(2)
La(1)-Se(3)	3.253(2)	La(1)-Se(1)	3.341(2)
P(1)-Se(2)	2.189(3)	P(2)-Se(1)	2.159(4)
P(1)-Se(3)	2.214(4)	P(2)-Se(5)	2.189(4)
P(1)-Se(4)	2.189(3)	P(2)-Se(6)	2.188(4)
P(1)-Se(7)	2.186(4)	P(2)-P(2')	2.210(7)

Se(4')-La(1)-Se(7)	142.76(5)	Se(4')-La(1)-Se(5')	77.81(5)
Se(7)-La(1)-Se(5')	101.81(5)	Se(4')-La(1)-Se(2)	128.29(5)
Se(7)-La(1)-Se(2)	74.04(5)	Se(5')-La(1)-Se(2)	142.10(5)
Se(4')-La(1)-Se(6')	74.68(5)	Se(7)-La(1)-Se(6')	140.87(5)
Se(5')-La(1)-Se(6')	69.75(4)	Se(2)-La(1)-Se(6')	89.65(5)
Se(4')-La(1)-Se(3')	69.91(4)	Se(7)-La(1)-Se(3')	91.45(5)
Se(5')-La(1)-Se(3')	140.94(5)	Se(2)-La(1)-Se(3')	76.81(5)
Se(6')-La(1)-Se(3')	119.66(5)	Se(4')-La(1)-Se(3)	77.10(5)
Se(7)-La(1)-Se(3)	67.49(4)	Se(5')-La(1)-Se(3)	73.34(5)
Se(2)-La(1)-Se(3)	133.13(5)	Se(6')-La(1)-Se(3)	137.21(5)
Se(3')-La(1)-Se(3)	78.42(3)	Se(4')-La(1)-Se(1)	143.77(4)
Se(7)-La(1)-Se(1)	67.15(4)	Se(5')-La(1)-Se(1)	74.86(4)
Se(2)-La(1)-Se(1)	68.84(4)	Se(6')-La(1)-Se(1)	73.83(4)
Se(3')-La(1)-Se(1)	143.21(5)	Se(3)-La(1)-Se(1)	116.28(5)
Se(4)-P(1)-Se(2)	109.32(18)	Se(1)-P(2)-Se(5)	115.61(18)
Se(4)-P(1)-Se(3)	107.73(15)	Se(5)-P(2)-Se(6)	108.36(15)
Se(2)-P(1)-Se(3)	115.29(17)	Se(5)-P(2)-P(2')	105.9(3)
Se(4)-P(1)-Se(7)	109.98(17)	Se(1)-P(2)-Se(6)	116.01(18)
Se(7)-P(1)-Se(2)	108.34(15)	Se(1)-P(2)-P(2')	104.2(2)
Se(7)-P(1)-Se(3)	106.09(17)	Se(6)-P(2)-P(2')	105.7(3)

by eight sulfur or selenium atoms, and these lanthanum polyhedra are corner-sharing within each two-dimensional layer. The same type of two-dimensional layer is observed in the four yttrium structures as in the lanthanum structures, but subtle differences are found within the layer itself. In compounds I, III, and IV reduced coordination numbers are found for yttrium, and in compound II edge-sharing yttrium polyhedra are observed instead of corner-sharing polyhedra. This argument can be extended to other structures as well. The structures of $Rb_{9-x}La_{1+x/3}(PSe_4)_4$ and $K_{9-x}Y_{1+x/3}(PSe_4)_4$ (x = 0.5) have also been characterized. These two structures are completely isostructural with $K_{9-x}La_{1+x/3}(PSe_4)_4$ (x = 0.5). No space group or packing differences were observed when using a smaller rare-earth element or a larger alkali-metal cation. This can be rationalized by looking at the dimensionality of the structures. $KLaP_2S_6$ and $K_2La(P_2Q_6)_{1/2}(PQ_4)$ are both 2-dimensional layered structures. As described above, these two structure types exhibited significant structural differences when substituting yttrium and/or cesium for potassium and lanthanum. The $K_{9-x}La_{1+x/3}(PSe_4)_4$ (x = 0.5) structure, on the other hand, contains zero-dimensional clusters as well as one-dimensional chains. This is a more "flexible" packing arrangement that can accommodate larger or smaller cations without a required change in space group or packing geometry. The differences in the $A_2REP_2Q_7$ structures may be subtle, but this type of synthetic approach for a given structure type offers a method of "tuning" a structure to obtain specific properties. An example of this "tuning" can be seen by looking at the color of these compounds. No specific optical band-gap data is presented here, however, it is clear that the combination of different alkali-metals and chalcogens have an effect on the

optical band-gap of a given structure type. All four sulfides are found as clear colorless crystals. Potassium selenides are clear, yellow crystals, and both cesium selenides are found as clear, orange crystals. Qualitatively, the clear crystals probably have an optical band-gap around 3.5 eV, the yellow crystals would have a smaller optical band-gap around 3.0 eV, and the orange crystals would have the smallest band-gap around 2.0 eV. In the future the concepts presented in this chapter can be extended to other structure types such as $KEuTS_4$ and K_2EuTSe_5 (T = Si, Ge).

Tables of additional crystallographic details, all bond distances and angles, and anisotropic thermal parameters can be found in Appendix D, Tables D.1-D.24.

Chapter Five

Synthesis and Characterization of Five New Europium Group XIV Chalcogenides: K_2EuTSe_5, $KEuTS_4$ (T = Si, Ge) and $Eu_8Sn_4Se_{20}$

Introduction

In the previous chapters, the use of ternary reaction phase diagrams was described as an aide in the rational synthesis of quaternary rare-earth chalcophosphate compounds. Different quaternary compounds were found by varying the stoichiometries of reactants. This allowed the determination of reaction conditions necessary to synthesize products with specific polychalcophosphate units such as $(PQ_4)^{3-}$ and $(P_2Q_6)^{4-}$ (Q = S, Se). In addition to looking at the effects of different rare-earth elements and chalcogenides on reaction products in these flux reactions one can also vary the main group metal used.

There have been a wide variety of ternary alkali-metal, group XIV chalcogenide compounds reported including $K_4Sn_3Se_8$,[62] $Cs_2Sn_3Se_7$,[63] $K_2Sn_2Se_5$,[64] $K_6Ge_2Q_6$ (Q = S, Se),[65] $K_6Sn_2Se_7$,[66] $Na_6M_2Se_7$ (M = Si, Ge),[67] $Na_6Si_2Se_8$,[68] $Na_4M_4Se_{10}$ (M = Si, Ge),[69] $Na_6M_2Se_6$ (M = Si, Ge),[70] Na_4GeSe_4,[71] $K_4Ge_4Se_{10}$,[72] and K_4SnSe_4.[73] Many of these compounds contain the stable building blocks $(MSe_4)^{4-}$ and $(M_2Se_6)^{6-}$ (M = Si, Ge, Sn) that are analogous to the $(PSe_4)^{3-}$ and $(P_2Se_6)^{4-}$ units found in selenophosphate compounds.[36,38,39] Group XIV elements also form ternary compounds with rare-earth metal (RE) chalcogenides. Several rare-earth tin sulfides including Eu_2SnS_5,[74] La_2SnS_5,[75] $Eu_5Sn_3S_{12}$,[76] $Eu_3Sn_2S_7$ and Eu_2SnS_4[77] have been reported.

Quaternary compounds containing group XIV elements include $K_2MnSnSe_4$,[78] $La_6MgGe_2S_{14}$,[79] $Dy_3CuGeSe_7$,[80] $KLnMQ_4$ (Ln = La, Nd, Gd, Y; M = Si, Ge; Q = S, Se),[81] $KInGeS_4$ and $KGaGeS_4$,[82] $Na_{0.5}Pb_{1.75}GeS_4$ and $Li_{0.5}Pb_{1.75}GeS_4$,[83] $Na_8Pb_2(M_2S_6)_2$ (M = Si, Ge) and $Na_8Sn_2(Ge_2S_6)_2$,[84] and $A_2Hg_3M_2S_8$ (A = Cs, Rb; M = Sn, Ge).[29]

Because of the ability of group XIV elements to form compounds with both RE metals and alkali-metals, silicon, germanium and tin have been substituted for

phosphorus in solid-state flux reactions with rare-earth metals. Five new europium group XIV chalcogenides are described here: $K_2EuSiSe_5$ **I**, $K_2EuGeSe_5$ **II**, $KEuSiS_4$ **III**, $KEuGeS_4$ **IV**, and $Eu_8Sn_4Se_{20}$, **V**, that we write as $Eu_8(Sn_4Se_{14})(Se_3)_2$. This work has been published in Inorganic Chemistry[85] and Zeitschrift für anorganische und allgemeine Chemie.[86]

Experimental Section

Synthesis. The following reactants were used as received and stored in an inert atmosphere glovebox: Eu (99.95%, Ames Laboratory), Si (99.999%, Johnson-Mathey), Ge (99.999% Alfa), Sn (99.999% Alfa), S (99.999%, Johnson-Mathey), and Se (99.999%, Johnson-Mathey). K_2S_2 and K_2Se_4 were previously made in liquid ammonia from the stoichiometric combination of the elements.[41,42] Reactants were loaded into fused silica ampoules inside an inert atmosphere glovebox. Each ampoule was flame sealed under vacuum and placed in temperature controlled tube furnace. Compound **I** was ramped to 525°C where it remained for 150 hours. For compounds **II** through **V** the furnace was ramped to 725°C where it remained for 150 hours. In both cases the furnace was allowed to cool back to room temperature at 4°C/hr.

$K_2EuSiSe_5$, I, was synthesized by combining 44.3 mg (0.561 mmol) Se, 147.4 mg (0.374 mmol) K_2Se_4, 5.3 mg (0.188 mmol) Si, and 28.4 mg (0.188 mmol) Eu. After cooling, the reaction product was washed with dimethylformamide (DMF) yielding a binary crystalline product composed of EuSe,[87] and orange plates of $K_2EuSiSe_5$.

$K_2EuGeSe_5$, II, was synthesized by combining 38.9 mg (0.493 mmol) Se, 125.4 mg (0.318 mmol) K_2Se_4, 11.9 mg (0.164 mmol) Ge, and 25.0 mg (0.164 mmol) Eu. The

reaction product was washed with DMF yielding a ternary crystalline product composed of K_2GeSe_4,[88] EuSe,[87] and red rods of $K_2EuGeSe_5$.

$KEuSiS_4$, III, was synthesized by combining 63.2 mg (1.97 mmol) S, 80.2 mg (0.563 mmol) K_2S_2, 8.1 mg (0.288 mmol) Si, and 42.8 mg (0.288 mmol) Eu. Washing the product with DMF yielded brown plates of $KEuSiS_4$.

$KEuGeS_4$, IV, was synthesized by combining 43.1 mg (1.34 mmol) S, 54.7 mg (0.384 mmol) K_2S_2, 13.9 mg (0.191 mmol) Ge, and 29.2 mg (0.191 mmol) Eu. The product was washed with DMF yielding deep red plates of $KEuGeS_4$.

$Eu_8Sn_4Se_{20}$ or $Eu_8(Sn_4Se_{14})(Se_3)_2$, V, was prepared by reacting 41.1 mg (0.5205 mmol) Se, 136.7 mg (0.3470 mmol) K_2Se_4, 20.6 mg (0.1735 mmol) Sn, and 26.4 mg (0.1735 mmol) Eu. Crystalline products were separated from excess flux with dimethylformamide yielding a yellow polycrystalline material and large, well-formed black rods of $Eu_8(Sn_4Se_{14})(Se_3)_2$. Qualitative EDS measurements confirm that the yellow polycrystalline material was composed of K, Sn, and Se. The stoichiometrically equivalent sulfur reaction yielded crystals of Eu_2SnS_5.[74]

Physical Measurements

Single Crystal X-ray Diffraction. Intensity data sets for compounds **I-V** were collected using a Bruker Smart CCD diffractometer. The intensity data set for **I** was integrated using SAINT-NT,[59] a SADABS correction was applied,[44] and the structure was solved by direct methods using SHELXTL.[60] Intensity data sets for **II-V** were integrated using SAINT,[43] a SADABS correction was applied,[44] and the structures were solved by direct methods using SHELXTL.[45] Relevant crystallographic data collection

and refinement parameters for $K_2EuSiSe_5$, $K_2EuGeSe_5$, $KEuSiS_4$, $KEuGeS_4$, and $Eu_8Sn_4Se_{20}$ are reported in Table 5.1.

Raman Spectroscopy. The Solid-State Raman spectrum of compounds **I, II and IV** were taken with a Nicolet Magna-IR 760 Spectrometer with a FT-Raman Module attachment using a Nd:YAG excitation laser (1064 nm). A Raman spectrum could not be obtained for compound **III and V** due to sample heating.

UV-Vis Spectroscopy. Diffuse reflectance measurements for all compounds were taken with a Varian Cary 500 Scan UV-VIS-NIR Spectrophotometer equipped with a Praying Mantis accessory. A polyteflon standard was used as a reference. The Kubelka-Munk function was applied to obtain band-gap information.[46,47]

Fluorescence Spectroscopy. The solid-state low temperature emission spectra of compounds **III** and **IV** were taken on a SPEX Fluorlog-3 Spectrofluorometer using bulk powders cooled to liquid nitrogen temperatures.

Table 5.1. Crystallographic data for $K_2EuSiSe_5$, $K_2EuGeSe_5$, $KEuSiS_4$, $KEuGeS_4$, and $Eu_8(Sn_4Se_{14})(Se_3)_2$.

	$K_2EuSiSe_5$	$K_2EuGeSe_5$	$KEuSiS_4$	$KEuGeS_4$	$Eu_8Sn_4Se_{20}$
fw	653.05	697.55	347.39	391.89	3269.64
a, Å	11.669(3)	11.8056(3)	6.426(4)	6.510(2)	11.990(2)
b, Å	9.844(2)	9.9630(1)	6.582(5)	6.649(2)	16.425(4)
c, Å	8.917(2)	8.9456(1)	8.566(7)	8.603(3)	8.543(1)
α, deg	90.0	90.0	90.0	90.0	90.0
β, deg	91.583(5)	91.195(1)	107.83(6)	107.80(2)	90.0
γ, deg	90.0	90.0	90.0	90.0	90.0
V, $Å^3$	1023.9(4)	1051.95(3)	344.9(4)	354.5(2)	1682.5(5)
Z	4	4	2	2	2
λ(Mo Kα), Å	0.71073	0.71073	0.71073	0.71073	0.71073
space group	$P2_1/c$ #14	$P2_1/c$ #14	$P2_1$ #4	$P2_1$ #4	$P2_12_12$
Temp., K	171(2)	167(2)	170(2)	167(2)	169(2)
$\rho_{calc.}$, mg/cm^3	4.236	4.404	3.345	3.671	6.454
μ (mm^{-1})	24.751	26.781	10.952	14.645	39.208
R1 % [a]	5.19	4.36	4.71	3.46	4.13
wR2 % [a]	11.38	8.31	12.50	8.57	8.96

[a] $R1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ $\quad wR2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]\ ]^{1/2}$

Results and Discussion

K_2EuTSe_5 I & II

A single crystal of **$K_2EuSiSe_5$, I,** was selected, 6822 (2477 independent) reflections were collected, and an absorption correction was applied to a monoclinic cell (R_{int} = 0.0880). The structure was solved in $P2_1/c$ by direct methods with final electron density residuals of 2.542 and -2.773 $eÅ^{-3}$, and all atoms were refined anisotropically with SHELXTL using full-matrix least squares refinement on F^2 for 83 variables.[60] Table 5.2 lists fractional atomic coordinates and isotropic displacement parameters for $K_2EuSiSe_5$.

As shown in Figure 5.1, $K_2EuSiSe_5$ is a two dimensional layered structure with layers of $^{2}_{\infty}[Eu(SiSe_5)]^{2-}$ separated by potassium cations. Each layer is constructed of 9-coordinate Eu(II) atoms linked together with $(SiSe_5)^{4-}$ distorted tetrahedra. This building block, shown in Figure 5.2, is composed of a Si(IV) tetrahedron with one of its $(Se)^{2-}$ corners replaced by a $(Se_2)^{2-}$ unit. This di-selenide unit distorts the tetrahedron slightly. Table 5.3 reports selected bond distances and angles in $K_2EuSiSe_5$. Each Eu(II) is bound to five different $(SiSe_5)^{4-}$ tetrahedra as shown in Figure 5.3. Interestingly, each $(SiSe_5)^{4-}$ unit bonds to Eu(II) in a different manner. Si(1) bonds to the europium atom with two of its single selenium atoms, Si(1A) bonds to europium with one of its single selenium atoms and the terminal selenium atom on its di-selenide arm, Si(1B) bonds to europium with one of its single selenium atoms and both selenium atoms on the di-selenide arm, Si(1D) bonds to europium with only one of its single selenium atoms, and finally Si(1E) bonds to europium with only the terminal selenium atom on its di-selenide arm. The average

Table 5.2. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$)[a] for $K_2EuSiSe_5$.

	x	y	z	U(eq)
Eu(1)	-0.0162(1)	0.7337(1)	0.1029(1)	9(1)
Se(1)	-0.0937(1)	0.4363(1)	0.1556(1)	10(1)
Se(2)	-0.1023(1)	1.0405(1)	0.1390(1)	9(1)
Se(3)	-0.2145(1)	0.7404(1)	-0.1505(1)	11(1)
Se(4)	0.5742(1)	1.0159(1)	0.1947(1)	13(1)
Se(5)	0.2573(1)	0.6220(1)	0.0056(1)	11(1)
Si(1)	-0.2474(3)	0.9782(3)	0.2879(3)	8(1)
K(1)	0.3041(2)	0.9419(3)	0.1282(3)	14(1)
K(2)	0.4398(3)	1.1973(3)	0.4557(3)	25(1)

[a] U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

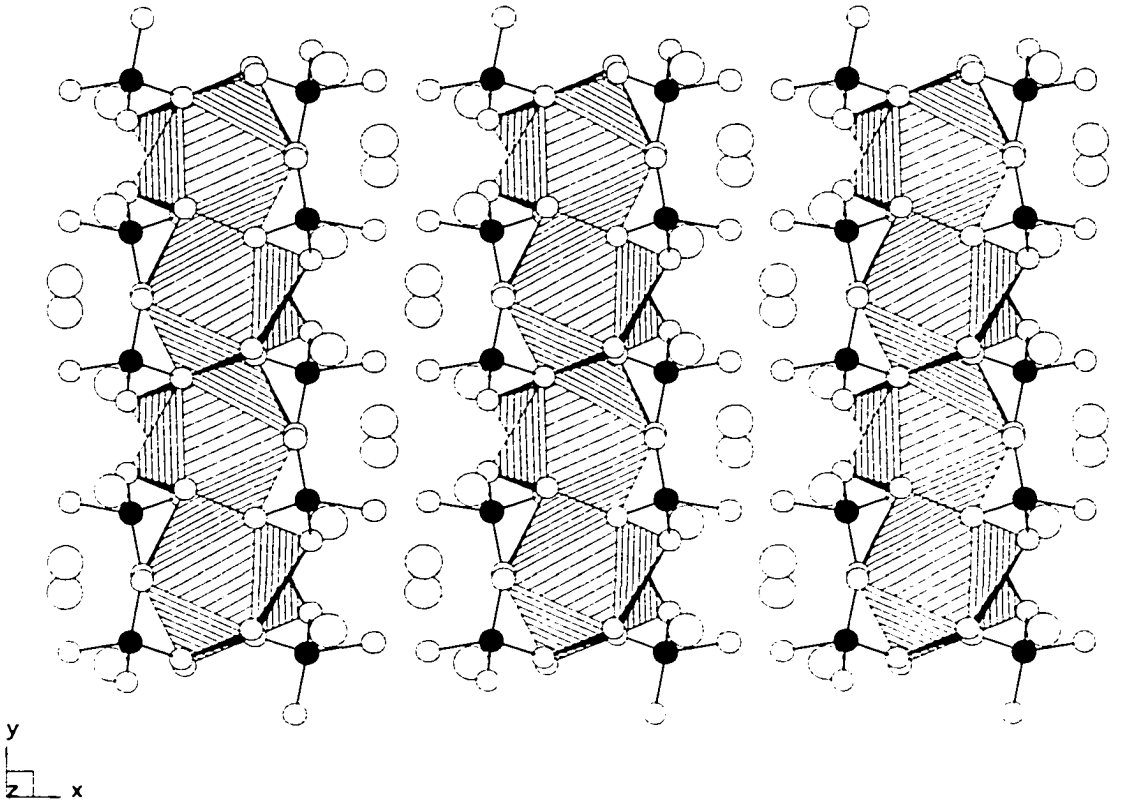


Figure 5.1. Packing plot of $K_2EuSiSe_5$. Striped europium polyhedra, filled silicon atoms, small unfilled selenium atoms, large unfilled potassium atoms.

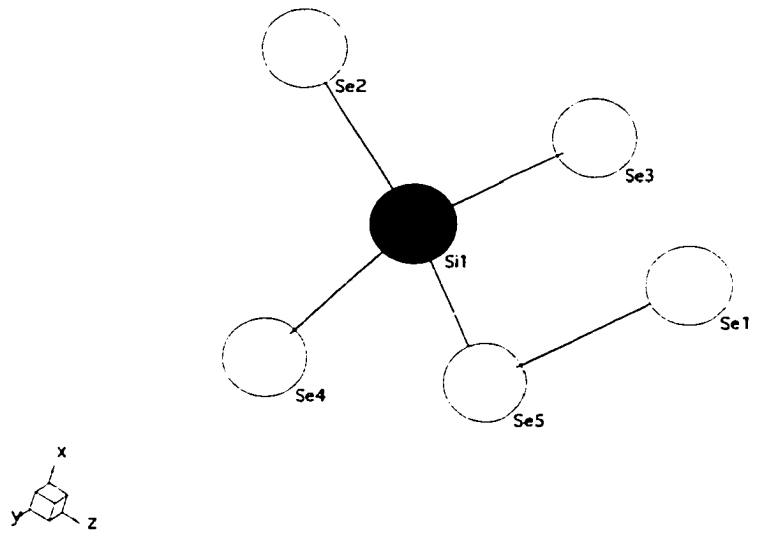


Figure 5.2. $(SiSe_5)^{4-}$ unit.

Table 5.3. Selected bond distances (Å) and angles (Deg.) for $K_2EuSiSe_5$.

Eu(1)-Se(1)	3.104(1)	Eu(1)-Se(1'')	3.150(1)
Eu(1)-Se(1')	3.179(1)	Eu(1)-Se(3)	3.190(2)
Eu(1)-Se(2)	3.202(1)	Eu(1)-Se(3')	3.246(1)
Eu(1)-Se(2')	3.263(1)	Eu(1)-Se(2'')	3.417(1)
Eu(1)-Se(5)	3.508(2)	Si(1)-Se(4)	2.251(5)
Si(1)-Se(2)	2.264(3)	Si(1)-Se(5)	2.328(3)
Si(1)-Se(3)	2.251(5)	Se(5)-Se(1)	2.427(2)
Se(1)-Eu (1)-Se(1')	74.69(4)	Se(1)-Eu (1)-Se(1')	127.07(3)
Se(1')-Eu (1)-Se(1')	131.63(5)	Se(1)-Eu (1)-Se(3)	85.30(3)
Se(1')-Eu (1)-Se(3)	78.14(3)	Se(1')-Eu (1)-Se(3)	137.57(3)
Se(1)-Eu (1)-Se(2')	141.35(4)	Se(1')-Eu (1)-Se(2')	135.23(3)
Se(1')-Eu (1)-Se(2')	57.45(3)	Se(3)-Eu (1)-Se(2')	80.12(3)
Se(1)-Eu (1)-Se(3')	75.85(3)	Se(1')-Eu (1)-Se(3')	148.19(3)
Se(1')-Eu (1)-Se(3')	76.91(3)	Se(3)-Eu (1)-Se(3')	87.79(4)
Se(2')-Eu (1)-Se(3')	68.04(3)	Se(1)-Eu (1)-Se(2')	57.52(3)
Se(1')-Eu (1)-Se(2')	91.92(4)	Se(1')-Eu (1)-Se(2')	74.50(3)
Se(3)-Eu (1)-Se(2')	142.79(3)	Se(2')-Eu (1)-Se(2')	127.36(3)
Se(3')-Eu (1)-Se(2')	82.20(3)	Se(1)-Eu (1)-Se(2')	146.52(3)
Se(1')-Eu (1)-Se(2')	72.75(3)	Se(1')-Eu (1)-Se(2')	81.78(3)
Se(3)-Eu (1)-Se(2')	80.66(3)	Se(2')-Eu (1)-Se(2')	65.38(4)
Se(3')-Eu (1)-Se(2')	133.24(3)	Se(2')-Eu (1)-Se(2')	130.81(4)
Se(1)-Eu (1)-Se(5)	90.72(3)	Se(1')-Eu (1)-Se(5)	42.34(3)
Se(1')-Eu (1)-Se(5)	90.66(3)	Se(3)-Eu (1)-Se(5)	118.59(4)
Se(2')-Eu (1)-Se(5)	127.65(3)	Se(3')-Eu (1)-Se(5)	149.64(3)
Se(2')-Eu(1)-Se(5)	67.73(3)	Se(2')-Eu (1)-Se(5)	70.17(3)
Se(3)-Si(1)-Se(2)	106.07(13)	Se(3)-Si(1)-Se(4)	113.39(14)
Se(3)-Si(1)-Se(5)	113.59(14)	Se(4)-Si(1)-Se(2)	115.96(14)
Se(2)-Si(1)-Se(5)	110.71(13)	Se(4)-Si(1)-Se(5)	97.24(12)
Si(1)-Se(5)-Se(1)	105.61(9)		

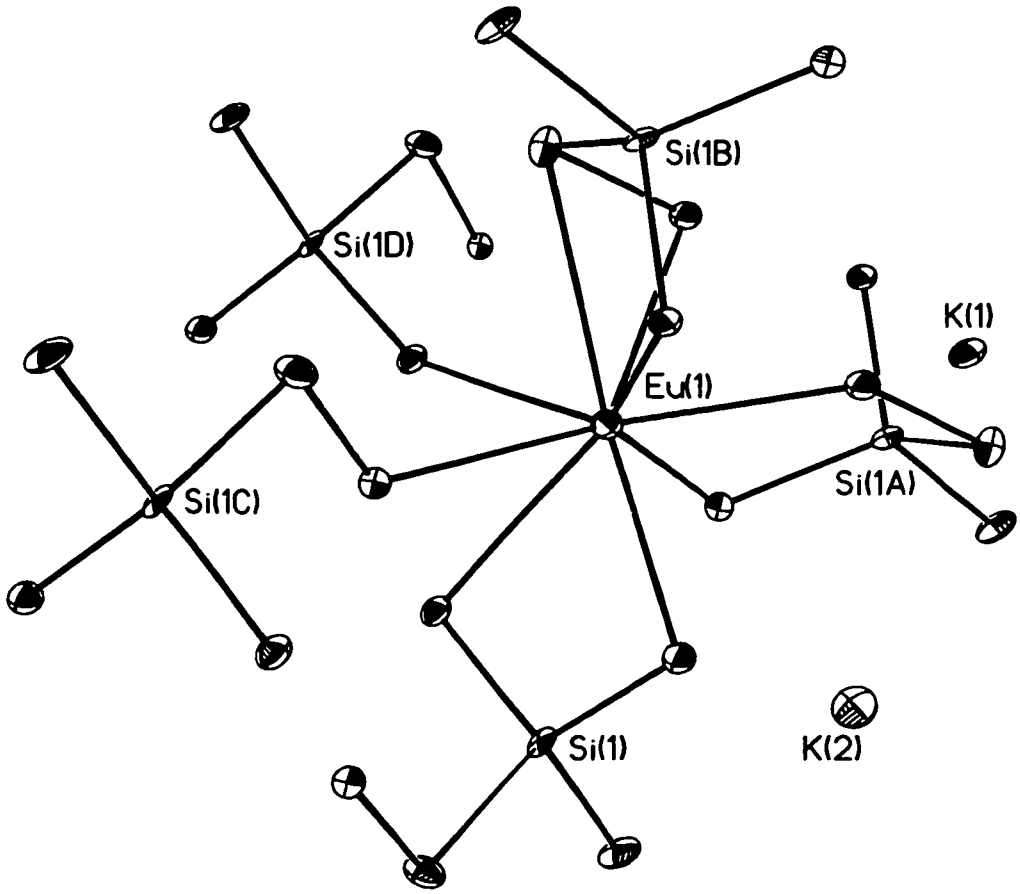


Figure 5.3. ORTEP plot showing the coordination environment around europium in $K_2EuSiSe_5$. Thermal ellipsoids plotted at the 70% probability level.

Eu-Se bond distance is 3.251(4) Å. Two crystallographically distinct potassium atoms are found with K-Se bond distances ranging from 3.164(3) Å to 3.846(3) Å. Within each $(SiSe_5)^{4-}$ unit, the average Si-Se bond distance is 2.274(6) Å, and the Se-Se bond distance is 2.427(2) Å.

A single crystal of **$K_2EuGeSe_5$, II,** was selected, 6796 (2518 independent) reflections were collected, and an absorption correction was applied to a monoclinic cell (R_{int} = 0.0841). The structure was solved in $P2_1/c$ by direct methods with final electron density residuals of 2.169 and -2.436 $eÅ^{-3}$, and all atoms were refined anisotropically with SHELXTL using full-matrix least squares refinement on F^2 for 83 variables.[45] Table 5.4 lists fractional atomic coordinates and isotropic displacement parameters for $K_2EuGeSe_5$.

$K_2EuGeSe_5$ is isostructural to its silicon counterpart. It is a 2-dimensional layered structure in which 9-coordinate Eu(II) atoms are linked into a layer by $(GeSe_5)^{4-}$ units. This unit, shown in Figure 5.4, comprises a Ge(IV) tetrahedron with one of its $(Se)^{2-}$ corners replaced by a $(Se_2)^{2-}$ unit. Table 5.5 reports selected bond distances and angles in $K_2EuGeSe_5$. The longest Ge-Se bond length is 2.408(1) Å, and the average Ge-Se bond length is 2.362(3) Å. The Se(5)-Se(1) bond length is 2.435(2) Å, and the Ge(1)-Se(5)-Se(1) bond angle is 104.59(5)°. A structure with a related building block is Cs_4GeTe_6.[89] It contains $(GeTe_6)^{4-}$ units with two di-selenide arms. Five different $(GeSe_5)^{4-}$ units are coordinated to each europium atom. Two units are bound to europium with one selenium atom, two units are bound with two selenium atoms, and the fifth $(GeSe_5)^{4-}$ unit is bound to europium with three of it's selenium atoms.

Table 5.4. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$)[a] for $K_2EuGeSe_5$

	x	y	z	U(eq)
Eu(1)	0.4837(1)	0.7306(1)	0.1053(1)	9(1)
Se(1)	0.4037(1)	1.0381(1)	0.1352(1)	9(1)
Se(2)	0.2878(1)	0.7446(1)	-0.1428(1)	11(1)
Se(3)	0.0697(1)	1.0143(1)	0.1945(1)	13(1)
Se(4)	0.4079(1)	0.4340(1)	0.1589(1)	10(1)
Se(5)	0.7532(1)	0.6306(1)	-0.0004(1)	13(1)
Ge(1)	0.2530(1)	0.9793(1)	0.2908(1)	9(1)
K(1)	0.8022(2)	0.9441(2)	0.1257(3)	14(1)
K(2)	0.0559(2)	0.6995(3)	0.0395(3)	27(1)

[a] U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

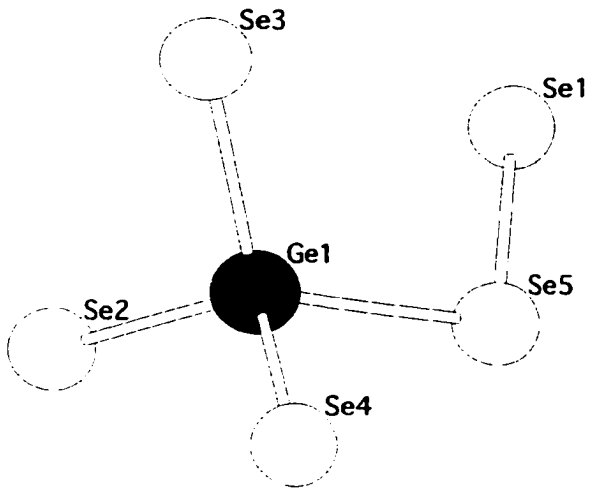


Figure 5.4. $(GeSe_5)^{4-}$ unit.

Table 5.5. Selected bond distances (Å) and angles (Deg.) for $K_2EuGeSe_5$.

Eu(1)-Se(1)	3.127(1)	Eu(1)-Se(1')	3.168(1)
Eu(1)-Se(3)	3.174(1)	Eu(1)-Se(1'')	3.174(1)
Eu(1)-Se(2)	3.219(1)	Eu(1)-Se(2')	3.271(1)
Eu(1)-Se(3')	3.272(1)	Eu(1)-Se(2'')	3.438(1)
Eu(1)-Se(5)	3.483(1)	Ge(1)-Se(4)	2.339(2)
Ge(1)-Se(3)	2.342(1)	Ge(1)-Se(2)	2.356(2)
Ge(1)-Se(5)	2.408(1)	Se(5)-Se(1)	2.435(2)
Se(1)-Eu (1)-Se(1')	75.34(3)	Se(1)-Eu (1)-Se(3)	86.68(3)
Se(1')-Eu (1)-Se(3)	78.52(3)	Se(1)-Eu (1)-Se(1')	127.87(2)
Se(1')-Eu (1)-Se(1')	131.49(4)	Se(3)-Eu (1)-Se(1')	135.55(3)
Se(1)-Eu (1)-Se(2)	143.24(3)	Se(1')-Eu (1)-Se(2)	132.70(3)
Se(3)-Eu (1)-Se(2)	78.78(3)	Se(1')-Eu (1)-Se(2)	56.78(3)
Se(1)-Eu (1)-Se(2')	56.69(3)	Se(1')-Eu (1)-Se(2')	93.54(3)
Se(3)-Eu (1)-Se(2')	143.23(3)	Se(1')-Eu (1)-Se(2')	75.56(3)
Se(2)-Eu (1)-Se(2')	127.91(2)	Se(1)-Eu (1)-Se(3')	75.94(3)
Se(1')-Eu (1)-Se(3')	148.79(3)	Se(3)-Eu (1)-Se(3')	87.88(3)
Se(1')-Eu (1)-Se(3')	77.00(3)	Se(2)-Eu (1)-Se(3')	70.00(3)
Se(2')-Eu (1)-Se(3')	80.69(3)	Se(1)-Eu (1)-Se(2')	147.65(3)
Se(1')-Eu (1)-Se(2')	73.30(3)	Se(3)-Eu (1)-Se(2')	79.55(3)
Se(1')-Eu (1)-Se(2')	80.34(3)	Se(2)-Eu (1)-Se(2')	62.10(3)
Se(2')-Eu (1)-Se(2')	132.85(4)	Se(3')-Eu (1)-Se(2')	131.93(3)
Se(1)-Eu (1)-Se(5)	92.15(3)	Se(1')-Eu (1)-Se(5)	42.63(3)
Se(3)-Eu (1)-Se(5)	118.62(3)	Se(1')-Eu (1)-Se(5)	90.29(3)
Se(2)-Eu (1)-Se(5)	124.47(3)	Se(2')-Eu (1)-Se(5)	70.44(3)
Se(3')-Eu(1)-Se(5)	150.61(3)	Se(2')-Eu (1)-Se(5)	69.79(3)
Se(4)-Ge(1)-Se(3')	113.06(6)	Se(4)-Ge(1)-Se(2)	116.72(6)
Se(3')-Ge(1)-Se(2)	104.83(5)	Se(4)-Ge(1)-Se(5')	98.66(5)
Se(3')-Ge(1)-Se(5')	114.00(5)	Se(2)-Ge(1)-Se(5')	109.87(6)
Ge(1)-Se(5)-Se(1)	104.59(5)		

Figure 5.5 shows that the $^{2}_{\infty}[Eu(GeSe_5)]^{2-}$ layers in $K_2EuGeSe_5$ lie parallel to the (011) plane. Layers are separated from one another by potassium cations resulting in a van der Waals gap of 3.828 Å. A section of one layer, Figure 5.6, shows the intricate bonding between each $(GeSe_5)^{4-}$ unit and europium atoms. The bonding in these layers is quite intricate with selenium atoms bonding to several europium atoms within the layer. The 9-coordinate europium atoms have an average Eu-Se bond length of 3.323(3) Å. The shortest Eu-Se bond is from Se(1), which bonds to three different europium atoms as seen in Figure 5.6. Se(4) is the only terminal selenium that points into the gap between layers. Two crystallographically distinct potassium atoms are found with K-Se bond distances ranging from 3.174(2) Å to 3.818(3) Å.

The $(TSe_5)^{n-}$ anionic unit has been observed before as $(PSe_5)^{3-}$, but to our knowledge the $(GeSe_5)^{4-}$ and $(SiSe_5)^{4-}$ units have not been found in a rare-earth metal structure. Kanatzidis *et. al.* has reported several structures with $(PSe_5)^{3-}$ anionic units including $K_4In_2(PSe_5)_2(P_2Se_6)$ and $Rb_3Sn(PSe_5)(P_2Se_6)$,[90] and $Rb_5Sn(PSe_5)_3$.[21] The $(PSe_5)^{3-}$ unit in these structures is similar to the $(GeSe_5)^{4-}$ unit, however, the interactions of $(PSe_5)^{3-}$ with tin or indium is very different from that found in $K_2EuGeSe_5$. In both $K_4In_2(PSe_5)_2(P_2Se_6)$, and $Rb_3Sn(PSe_5)(P_2Se_6)$ the $(PSe_5)^{3-}$ units only bond to indium or tin respectively with the second selenium atom in the di-selenide arm (see Scheme 5.1). In contrast, both selenium atoms on the di-selenide arm in $(GeSe_5)^{4-}$ are intricately bound to europium atoms in $K_2EuGeSe_5$.

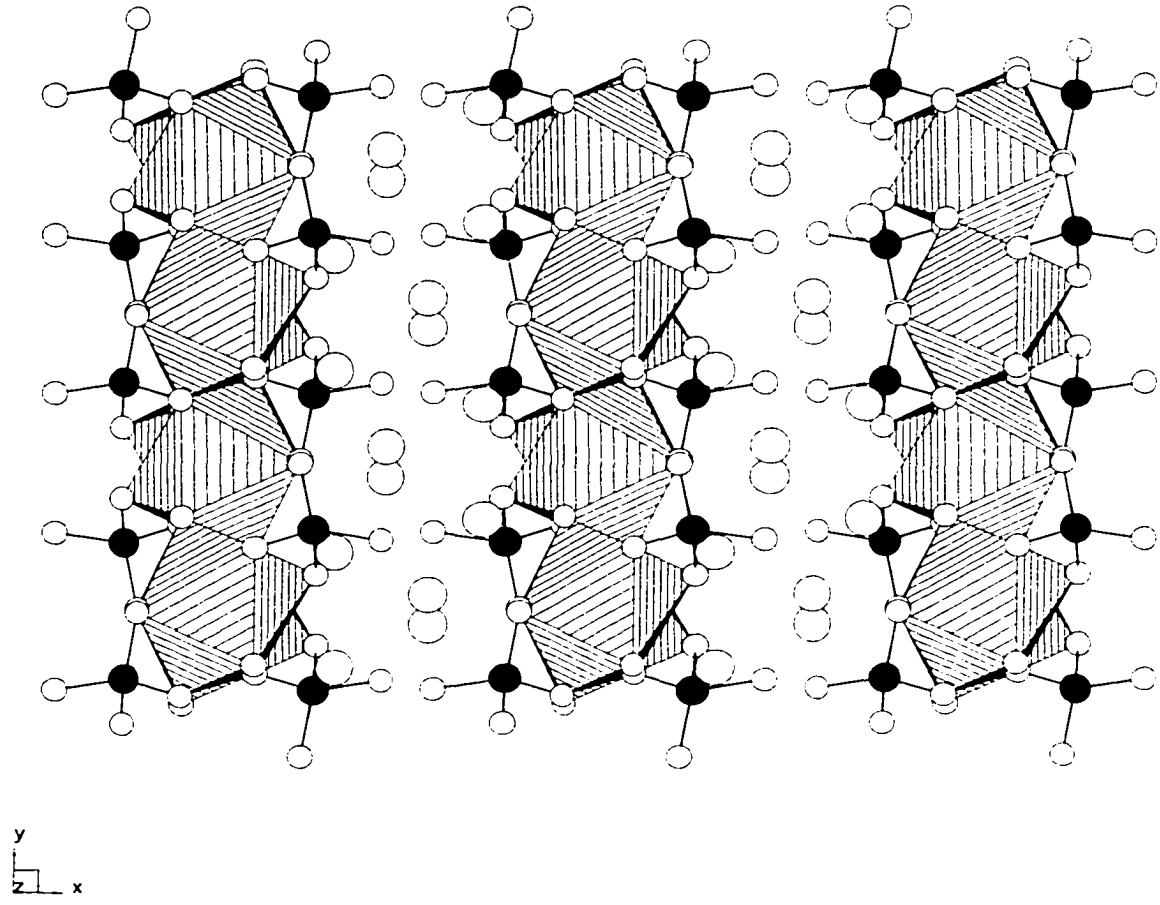


Figure 5.5. Packing plot of $K_2EuGeSe_5$. Striped europium polyhedra, filled germanium atoms, small unfilled selenium atoms, large unfilled potassium atoms.

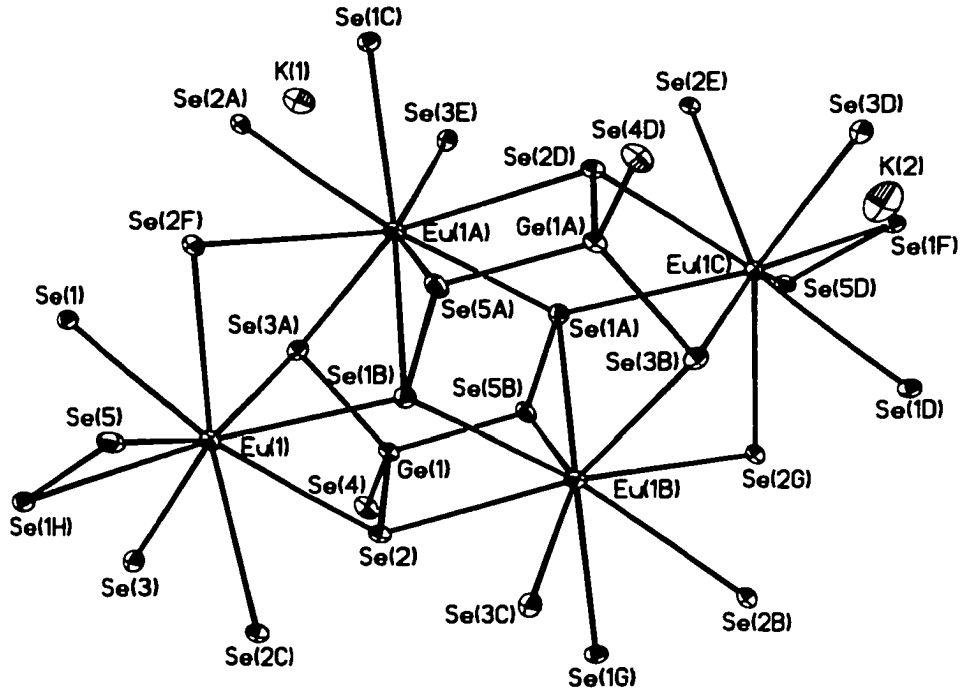
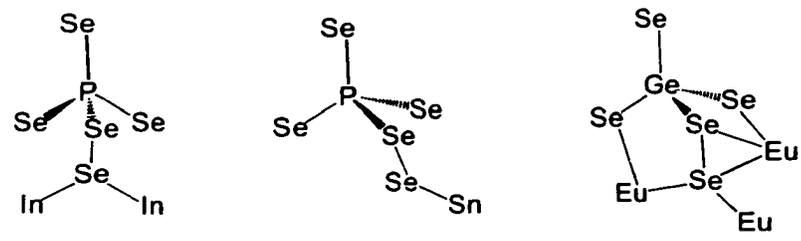


Figure 5.6. ORTEP plot showing the coordination sphere of europium and intricate bonding from $(GeSe_5)^{4-}$ units in $K_2EuGeSe_5$. Thermal ellipsoids are plotted at the 50 % probability level.



Scheme 5.1

$KEuTS_4$ III & IV

$KEuSiS_4$ and $KEuGeS_4$ are isostructural to $KLaGeS_4$.[81] While the structure is not new, it is of interest because of the Eu(III) cation and the comparisons made to compounds **I** and **II** containing Eu(II).

A single crystal of **$KEuSiS_4$, III,** was selected, 2293 (1536 independent) reflections were collected, and an absorption correction was applied to a monoclinic cell (R_{int} = 0.0512). The structure was solved in $P2_1$ by direct methods to electron density residuals of 2.243 and -2.777 $eÅ^{-3}$, and all atoms were refined anisotropically with SHELXTL using full-matrix least squares refinement on F^2 for 64 variables.[45] Table 5.6 lists fractional atomic coordinates and isotropic displacement parameters for $KEuSiS_4$. A related compound discussed in Chapter 3, $KEuPS_4$ crystallized in the $P2_1/c$ space group so a centrosymmetric solution was assumed. Systematic absence analysis suggested either $P2_1/m$ or $P2_1$ as possible space groups and PLATON [61] suggested $P2_1/m$ as the correct space group. However, the structure could not be solved in the centrosymmetric space group. Comparison of Friedel pairs confirmed the non-centrosymmetric space group.

Table 5.6. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$)[a] for $KEuSiS_4$.

	x	y	z	U(eq)
Eu(1)	0.2701(1)	0.0003(1)	0.9493(1)	6(1)
Si(1)	0.7165(6)	0.0332(5)	0.8200(4)	6(1)
S(1)	0.4795(5)	-0.7308(5)	0.7733(5)	8(1)
S(2)	0.4811(5)	-0.7302(5)	0.2095(4)	6(1)
S(3)	-0.0884(5)	-0.9661(5)	0.6645(4)	8(1)
S(4)	0.0858(4)	-0.4207(5)	0.9343(4)	7(1)
K(1)	0.2251(5)	0.0202(7)	0.4340(3)	16(1)

[a] U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

$KEuSiS_4$ is a two-dimensional structure with $^{2}_{\infty}[Eu(SiS_4)]^{-}$ layers separated by potassium cations as shown in Figure 5.7. Within each layer (Figure 5.8), seven-coordinate distorted mono-capped trigonal prisms of $Eu(III)S_7$ are linked together by distorted $(SiS_4)^{4-}$ tetrahedra. Figure 5.9 shows that each europium atom is coordinated by three $(SiS_4)^{4-}$ units in an edge-sharing manner, and bonded to a fourth $(SiS_4)^{4-}$ tetrahedron in a corner-sharing manner. The average Eu-S bond length is 2.867(11) Å and each $(SiS_4)^{4-}$ tetrahedron has an average bond length of 2.114(10) Å. Each potassium atom is coordinated by eight sulfur atoms with an average K-S bond distance of 3.351(15) Å. Selected bond distances and angles for $KEuSiS_4$ are reported in Table 5.7.

A single crystal of **$KEuGeS_4$, IV,** was selected, 2400 (1572 independent) reflections were collected, and an absorption correction was applied to a monoclinic cell (R_{int} = 0.0355). The structure was solved in $P2_1$ by direct methods to electron density residuals of 2.653 and -2.557 $eÅ^{-3}$, and all atoms were refined anisotropically with SHELXTL using full-matrix least squares refinement on F^2 for 64 variables.[45] Table 5.8 lists fractional atomic coordinates and isotropic displacement parameters for $KEuGeS_4$. Selected bond distances and angles for $KEuGeS_4$ are reported in Table 5.9.

$KEuGeS_4$ is isostructural to $KEuSiS_4$. It is a two-dimensional structure with $^{2}_{\infty}[Eu(GeS_4)]^{-}$ layers separated by potassium cations. Within each layer, seven-coordinate distorted mono-capped trigonal prisms of $Eu(III)S_7$ are linked together by distorted $(GeS_4)^{4-}$ tetrahedra. Figure 5.10 shows that each europium atom is coordinated by three $(GeS_4)^{4-}$ units in an edge-sharing manner, and bonded to a fourth

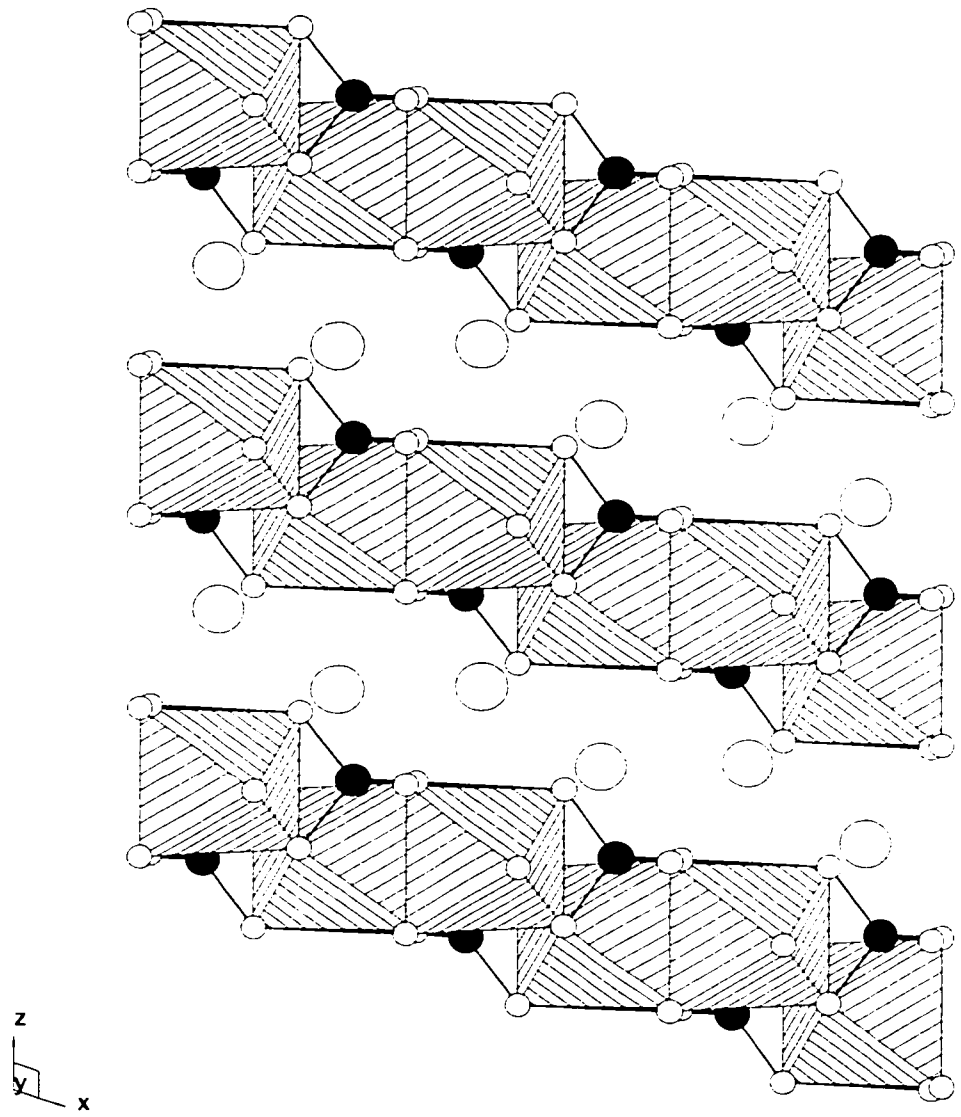


Figure 5.7. Packing plot of $KEuSiS_4$. Striped europium polyhedra, filled silicon atoms, small unfilled sulfur atoms, and large unfilled potassium atoms.

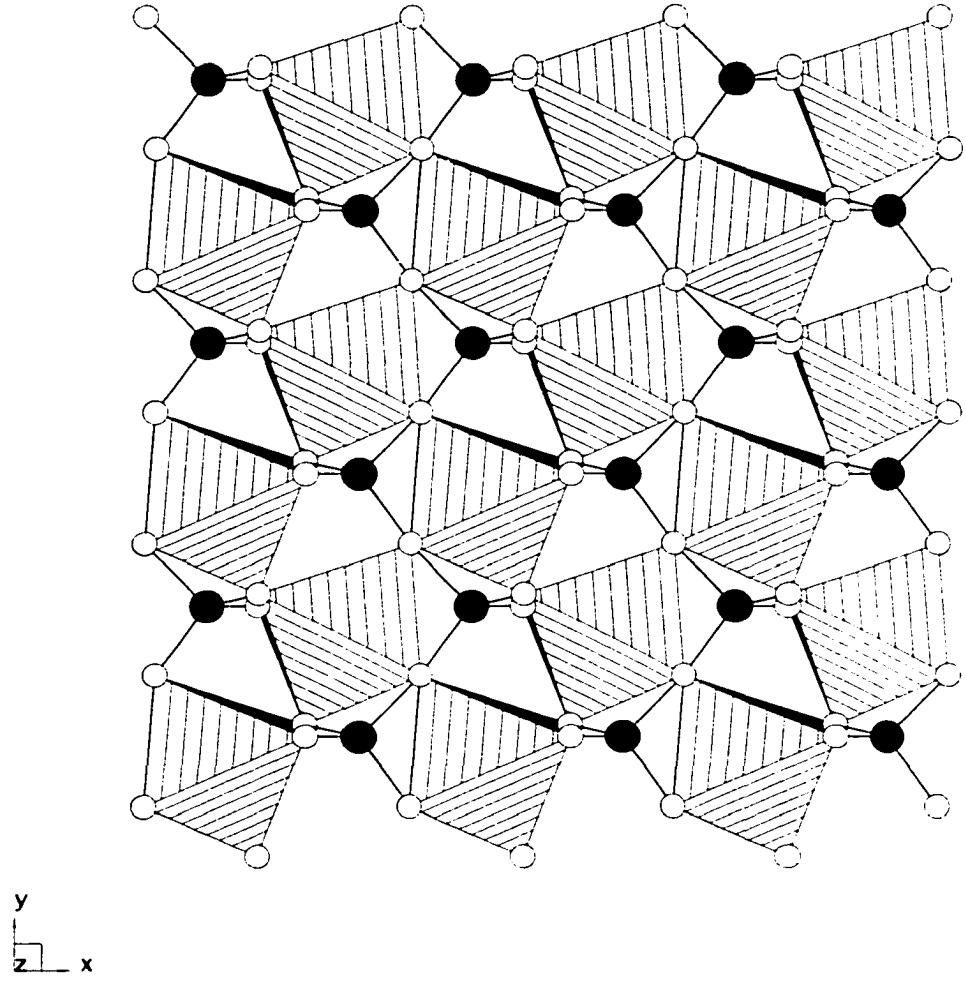


Figure 5.8. $(EuSiS_4)^-$ layer in $KEuSiS_4$. Striped europium mono-capped trigonal prisms, filled silicon atoms, unfilled sulfur atoms. Potassium not shown for clarity.

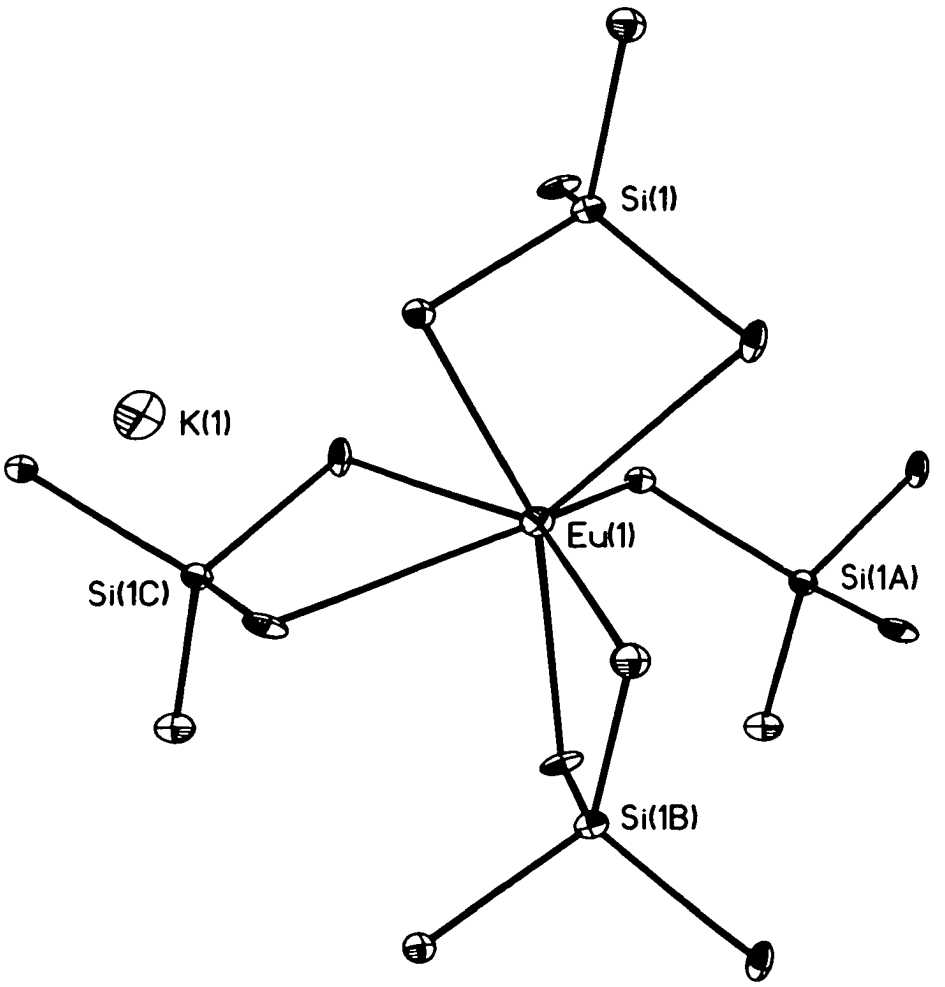


Figure 5.9. ORTEP plot of the coordination environment around europium in $KEuSiS_4$. Thermal ellipsoids plotted at the 70% probability level.

Table 5.7. Selected bond distances (Å) and angles (Deg.) for $KEuSiS_4$.

Eu(1)-S(3)	2.805(4)	Si(1)-S(1)	2.126(5)
Eu(1)-S(2')	2.836(4)	Si(1)-S(2)	2.118(5)
Eu(1)-S(1)	2.865(4)	Si(1)-S(3)	2.091(5)
Eu(1)-S(4)	3.001(4)	Si(1)-S(4)	2.120(5)
Eu(1)-S(4')	2.809(4)		
Eu(1)-S(2)	2.847(4)		
Eu(1)-S(1')	2.908(4)		
S(3')-Eu(1)-S(4')	75.71(11)	S(4')-Eu (1)-S(1')	96.62(11)
S(4')-Eu (1)-S(2')	155.40(10)	S(2')-Eu (1)-S(1')	70.69(10)
S(4')-Eu (1)-S(2')	81.43(11)	S(4')-Eu (1)-S(1')	128.88(7)
S(3')-Eu (1)-S(1')	150.07(10)	S(2')-Eu (1)-S(1')	80.89(11)
S(2')-Eu (1)-S(1')	81.84(11)	S(3')-Eu (1)-S(4)	80.07(12)
S(3')-Eu (1)-S(1')	83.59(10)	S(2')-Eu (1)-S(4)	76.04(10)
S(2')-Eu (1)-S(1')	70.03(10)	S(1')-Eu (1)-S(4)	70.08(10)
S(1')-Eu (1)-S(1')	121.43(8)	S(3)-Si(1)-S(2)	112.3(2)
S(4')-Eu (1)-S(4)	80.35(7)	S(2)-Si(1)-S(4)	113.0(2)
S(2')-Eu (1)-S(4)	134.10(9)	S(2)-Si(1)-S(1)	101.9(2)
S(1')-Eu (1)-S(4)	141.18(9)	S(3)-Si(1)-S(4)	109.8(2)
S(3')-Eu (1)-S(2')	93.35(11)	S(3)-Si(1)-S(1)	114.4(2)
S(3')-Eu (1)-S(2')	134.38(10)	S(4)-Si(1)-S(1)	105.0(2)
S(2')-Eu (1)-S(2)	120.38(7)		

Table 5.8. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($Å^2$ x 10^3)[a] for $KEuGeS_4$.

	x	y	z	U(eq)
Eu(1)	0.2698(1)	0.9642(1)	0.9475(1)	6(1)
Ge(1)	0.7208(1)	0.9986(1)	0.8208(1)	5(1)
S(1)	0.4741(4)	1.2375(4)	0.7753(3)	7(1)
S(2)	0.4843(3)	1.2280(4)	1.2084(3)	6(1)
S(3)	-0.0792(3)	1.0008(4)	0.6589(3)	10(1)
S(4)	0.0729(3)	0.5567(4)	0.9270(3)	7(1)
K(1)	0.2329(3)	0.9821(5)	0.4361(2)	15(1)

[a] U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 5.9. Selected bond distances (Å) and angles (Deg.) for $KEuGeS_4$.

Eu(1)-S(3)	2.817(2)	Ge(1)-S(1)	2.206(2)
Eu(1)-S(2')	2.853(2)	Ge(1)-S(2)	2.208(3)
Eu(1)-S(1')	2.882(2)	Ge(1)-S(3)	2.178(2)
Eu(1)-S(4)	2.979(3)	Ge(1)-S(4)	2.209(2)
Eu(1)-S(4')	2.828(2)		
Eu(1)-S(2)	2.854(2)		
Eu(1)-S(1)	2.910(3)		
S(3)-Eu(1)-S(4')	78.46(7)	S(4')-Eu (1)-S(1')	97.01(7)
S(4')-Eu (1)-S(2')	157.04(7)	S(2')-Eu (1)-S(1')	69.56(7)
S(4')-Eu (1)-S(2)	79.61(7)	S(4')-Eu (1)-S(1)	126.56(7)
S(3)-Eu (1)-S(1')	151.74(7)	S(2)-Eu (1)-S(1)	80.03(7)
S(2')-Eu (1)-S(1')	80.51(7)	S(3)-Eu (1)-S(4)	79.03(7)
S(3)-Eu (1)-S(1)	82.44(7)	S(2')-Eu (1)-S(4)	76.37(7)
S(2')-Eu (1)-S(1)	72.23(7)	S(1')-Eu (1)-S(4)	72.71(7)
S(1')-Eu (1)-S(1)	120.60(4)	S(3')-Ge(1)-S(1)	115.24(9)
S(4')-Eu (1)-S(4)	81.09(5)	S(1)-Ge (1)-S(2')	100.63(9)
S(2)-Eu (1)-S(4)	134.73(7)	S(1)-Ge (1)-S(4')	103.85(10)
S(2)-Eu (1)-S(4)	142.43(7)	S(3')-Ge (1)-S(2')	113.04(10)
S(3)-Eu (1)-S(2')	92.89(7)	S(3')-Ge (1)-S(4')	108.92(9)
S(3)-Eu (1)-S(2)	135.15(7)	S(2')-Ge (1)-S(4')	114.77(10)
S(2')-Eu (1)-S(2)	119.86(4)		

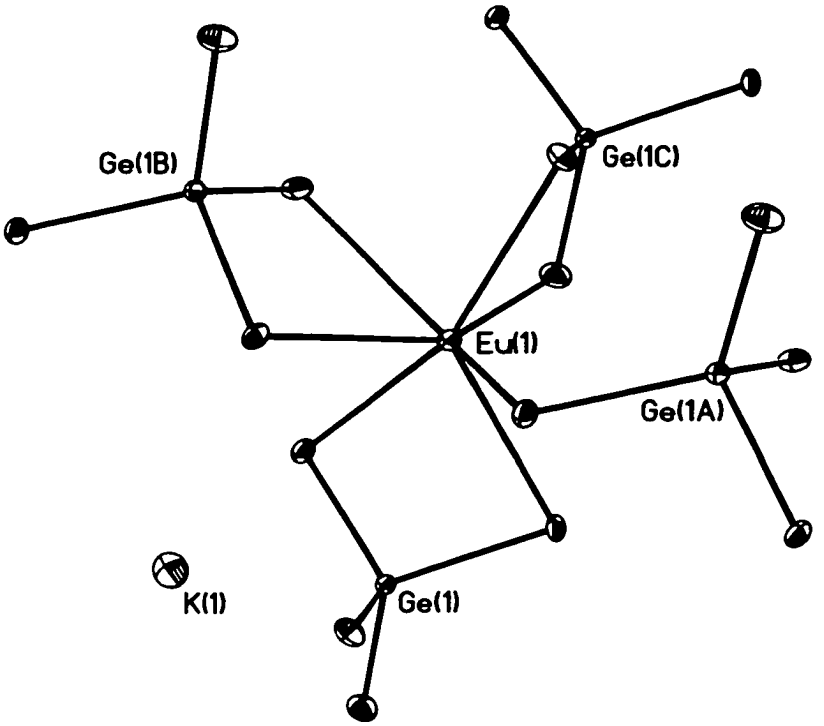


Figure 5.10. ORTEP plot of the coordination environment around europium in $KEuGeS_4$. Thermal ellipsoids plotted at the 50% probability level.

$(GeS_4)^{4-}$ tetrahedron in a corner-sharing manner. The average Eu-S bond length is 2.875(6) Å. Each $(GeS_4)^{4-}$ tetrahedron bonds to three Eu(III) atoms in an edge-sharing manner and to a fourth Eu(III) in a corner-sharing manner. Each potassium atom is coordinated by eight sulfur atoms with an average K-S bond distance of 3.368(9) Å.

The structure of $KEuGeS_4$ is very similar to $KEuPS_4$ with some significant differences. Figure 5.11 shows packing diagrams for $KEuGeS_4$ and $KEuPS_4$. The non-centrosymmetric nature of $KEuGeS_4$ can clearly be seen compared to the centrosymmetric $KEuPS_4$ structure. The europium trigonal prisms in $KEuGeS_4$ are capped on only one side, while the europium trigonal prisms in $KEuPS_4$ are capped on both sides.

$Eu_8(Sn_4Se_{14})(Se_3)_2$

A single crystal of **$Eu_8(Sn_4Se_{14})(Se_3)_2$** was mounted on a Bruker CCD single crystal diffractometer, 11377 (4101 independent) reflections were collected, and an absorption correction (SADABS) was applied to an orthorhombic cell (R_{int} = 0.0731). The structure was solved by direct methods in $P2_12_12$ and all atoms were refined anisotropically with SHELXTL using full-matrix least squares refinement on F^2 for 149 variables.[45] The program PLATON [61] was used to determine if the structure of $Eu_8(Sn_4Se_{14})(Se_3)_2$ could be solved in a centrosymmetric space group. The program suggested Pbam as an alternative space group, however, the structure could not be solved in this space group. Second harmonic generation experiments are needed to

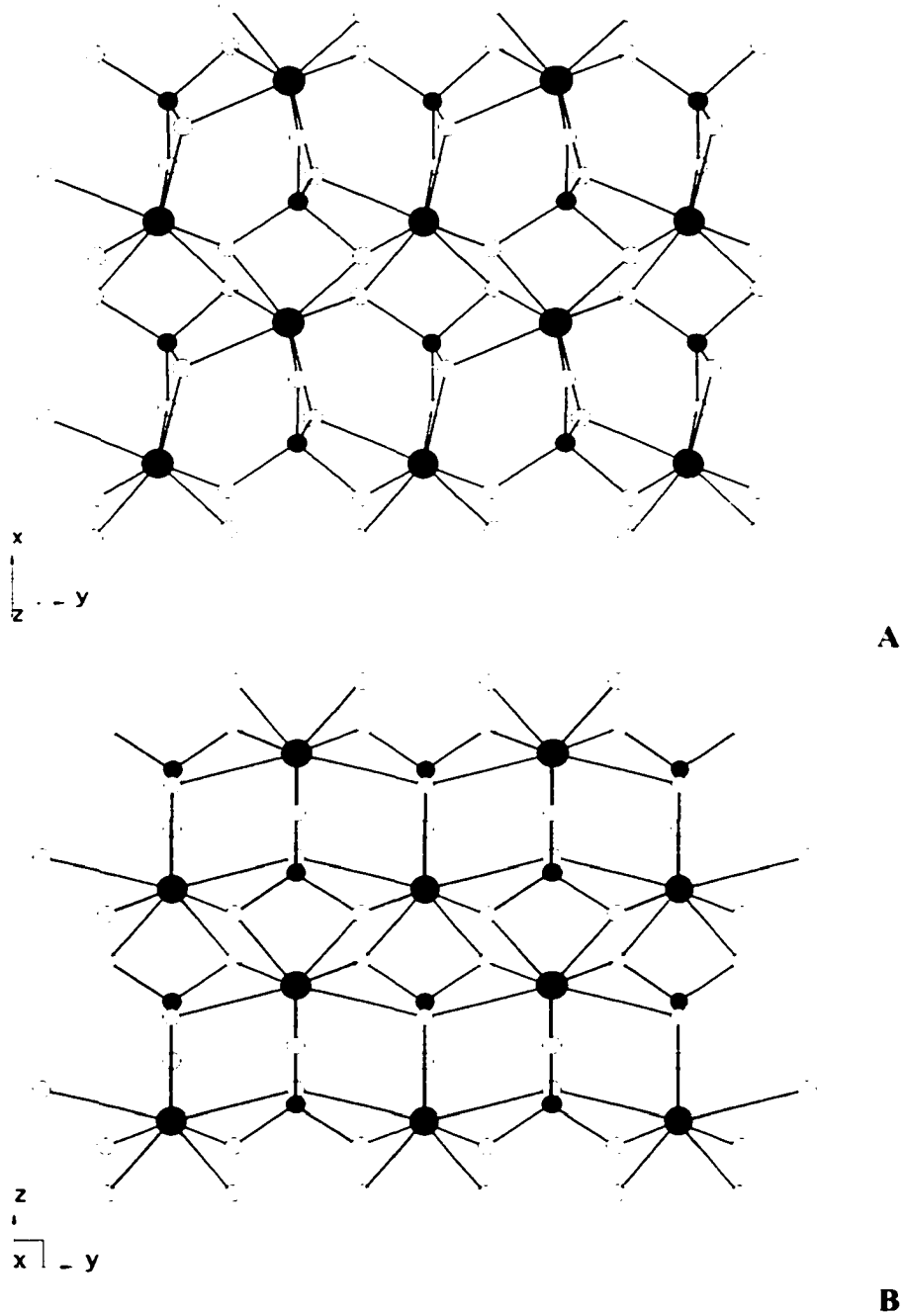


Figure 5.11. Packing diagram of **A:** $KEuGeS_4$ and **B:** $KEuPS_4$. Large filled europium atoms, small filled germanium or phosphorus atoms, and open sulfur atoms. Potassium atoms have been removed.

determine if $P2_12_12$ is indeed the correct space group. Nevertheless, the only space group with an acceptable solution was found to be $P2_12_12$. Atomic positional parameters and relevant bond distances and angles are found in Table 5.10 and Table 5.11 respectively.

Figure 5.12 shows the structure of the $(Sn_4Se_{14})^{12-}$ unit and the coordination environment of one europium atom in the structure. Generally speaking, $Eu_8(Sn_4Se_{14})(Se_3)_2$ is a 3-dimensional structure in which eight Eu(II) atoms are each coordinated by nine selenium atoms with an average Eu-Se bond distance of 3.213(6) Å, a typical bond distance for Eu(II)-Se.[91] These europium atoms are linked together by two different anions: the C-shaped $(Sn_4Se_{14})^{12-}$ unit and the bent $(Se_3)^{2-}$ chain. In the $(Se_3)^{2-}$ chain, the average Se-Se bond distance is 2.407(4) Å and the average Se-Se-Se bond angle is 106.2(1)°. The $(Sn_4Se_{14})^{12-}$ unit, shown in Figure 5.12, results from two $(SnSe_4)^{4-}$ tetrahedra and one $(Sn_2Se_6)^{4-}$ unit linked through a long Sn-Se bond, 3.028(2) Å, formed between Sn(1) and Se(9). This bond is 0.4-0.5 Å longer than a typical Sn-Se bond observed in isolated $(SnSe_4)^{4-}$ and $(Sn_2Se_6)^{4-}$ units.[66,73,92] Figure 5.13 shows the packing diagram for four unit cells.

An isolated $(SnSe_4)^{4-}$ tetrahedron would be expected to have nearly ideal tetrahedral angles. This is what was observed for K_4SnSe_4 where Se-Sn-Se bond angles are reported as 109.09(4)°, 108.76(2)°, 109.84(2)°, and 110.51(3)°.[73] The tin atoms in $K_4Sn_2Se_6$[92] are also tetrahedral, but the angles would be expected to be slightly distorted due to the bridging selenium atoms in the $(Sn_2Se_6)^{4-}$ unit. In $K_4Sn_2Se_6$, the inner Se-Sn-Se angle is 94.5° and the outer Se-Sn-Se angle is 121.2°, both of which are significantly distorted from 109.5°. A significant difference in

Table 5.10. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$)[a] for $Eu_8(Sn_4Se_{14})(Se_3)_2$.

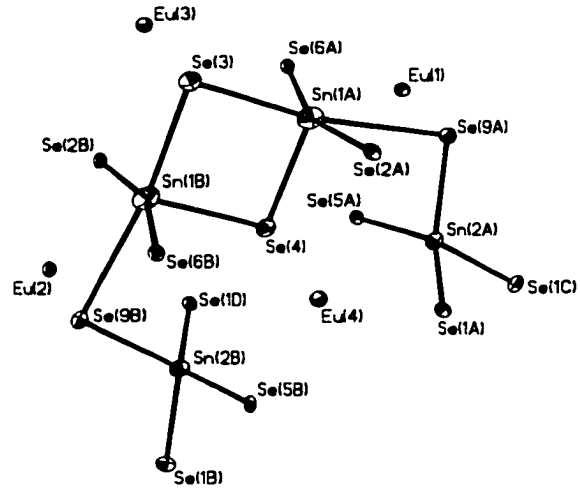
	x	y	z	U(eq)
Eu(1)	0.6153(1)	0.8220(1)	0.7447(1)	6(1)
Eu(2)	0.6171(1)	0.8213(1)	0.2414(1)	7(1)
Eu(3)	0.7473(1)	0.5712(1)	0.7581(1)	6(1)
Eu(4)	0.2483(1)	0.9286(1)	0.7394(1)	6(1)
Sn(1)	0.4464(1)	0.6049(1)	0.4996(1)	13(1)
Sn(2)	0.4088(1)	0.6720(1)	0.0148(1)	8(1)
Se(1)	0.6209(1)	0.6752(1)	0.0054(2)	6(1)
Se(2)	0.6303(1)	0.6822(1)	0.5048(2)	6(1)
Se(3)	0.5000	0.5000	0.7289(2)	9(1)
Se(4)	0.5000	0.5000	0.2766(2)	9(1)
Se(5)	0.7527(1)	0.9314(1)	0.9868(2)	6(1)
Se(6)	0.7410(1)	0.9281(1)	0.4857(2)	6(1)
Se(7)	0.4389(1)	0.8918(1)	0.9887(2)	7(1)
Se(8)	0.4422(1)	0.8905(1)	0.4884(2)	7(1)
Se(9)	0.8697(1)	0.7616(1)	0.7199(2)	8(1)
Se(10)	0.5000	0.0000	0.1600(2)	6(1)
Se(11)	0.3674(2)	0.7468(1)	0.7638(2)	8(1)
Se(12)	0.5000	0.0000	0.6555(2)	6(1)

[a] U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

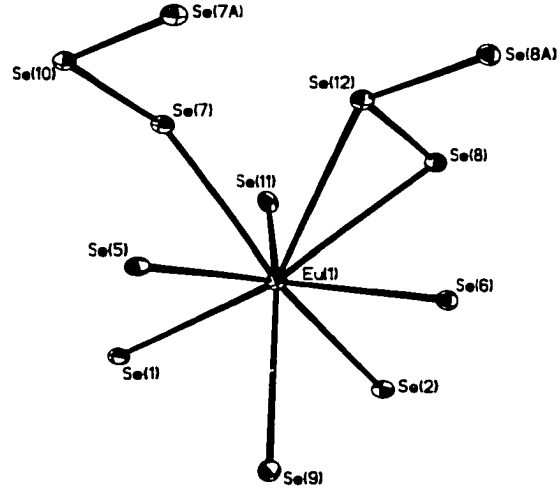
Table 5.11. Relevent Bond Lengths (Å) and Angles (Deg.) Found in $Eu_8(Sn_4Se_{14})(Se_3)_2$.

Sn(1)-Se(3)	2.687(2)	Sn(2)-Se(9)	2.558(2)
Sn(1)-Se(4)	2.649(2)	Sn(2)-Se(5)	2.528(1)
Sn(1)-Se(6)	2.526(1)	Sn(2)-Se(1)	2.545(1)
Sn(1)-Se(2)	2.544(1)	Sn(2)-Se(11)	2.520(2)
Sn(1)-Se(9)	3.028(2)	Eu(1)-Se(2)	3.084(2)
Eu(1)-Se(7)	3.183(2)	Eu(1)-Se(6)	3.194(2)
Eu(1)-Se(5)	3.196(2)	Eu(1)-Se(9)	3.214(2)
Eu(1)-Se(8)	3.220(2)	Eu(1)-Se(11)	3.224(2)
Eu(1)-Se(1)	3.283(2)	Eu(1)-Se(12)	3.323(2)
Se(10)-Se(7)	2.416(2)	Se(10)-Se(7')	2.416(2)
Se(12)-Se(8)	2.398(2)	Se(12)-Se(8')	2.398(2)

Se(3)-Sn(1)-Se(4)	92.82(5)	Sn(1)-Se(9)-Sn(2)	100.65(6)
Se(3)-Sn(1)-Se(6)	93.39(4)	Se(9)-Sn(2)-Se(5)	98.91(6)
Se(3)-Sn(1)-Se(2)	95.75(4)	Se(9)-Sn(2)-Se(1)	101.69(6)
Se(3)-Sn(1)-Se(9)	171.32(5)	Se(9)-Sn(2)-Se(11)	120.67(5)
Se(6)-Sn(1)-Se(9)	83.67(5)	Se(5)-Sn(2)-Se(1)	138.93(5)
Se(6)-Sn(1)-Se(2)	162.11(5)	Se(5)-Sn(2)-Se(11)	100.17(6)
Se(6)-Sn(1)-Se(4)	97.59(5)	Se(11)-Sn(2)-Se(1)	99.21(6)
Sn(1)-Se(3)-Sn(1')	86.41(7)	Se(8)-Se(12)-Se(8')	106.93(10)
Se(7)-Se(10)-Se(7')	105.43(10)		



a



b

Figure 5.12a: ORTEP view of the $(Sn_4Se_{14})^{12-}$ unit with surrounding europium atoms. **12b:** ORTEP view of Eu(1) coordination sphere including $(Se_3)^{2-}$ chains. Thermal ellipsoids are drawn at the 70% probability level.

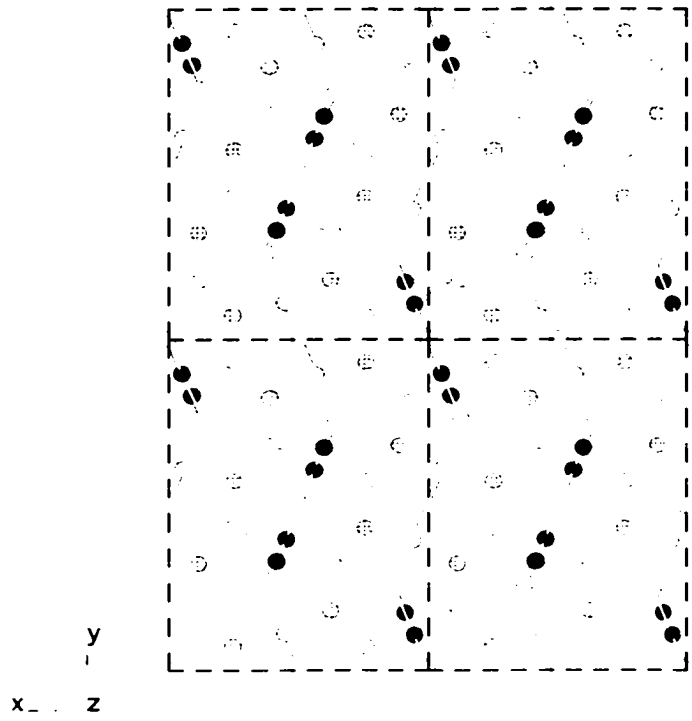


Figure 5.13. Packing arrangement of $(Sn_4Se_{14})^{12-}$ and $(Se_3)^{2-}$ in four unit cells. Unbonded filled circles are europium atoms.

bond angles can be seen by comparing these angles with those found in the $(Sn_4Se_{14})^{12-}$ anion, Table 5.11. Sn(1) is coordinated by 5 selenium atoms. Four of the Sn(1)-Se have bond lengths between 2.526(1) Å and 2.687(2) Å. The fifth Sn(1)-Se bond is the relatively long bond of 3.028(2) Å between Sn(1) and Se(9). This long bond forces the Se(6)-Sn(1)-Se(2) angle to open up significantly to 162.11(5)° compared to the outer Se-Sn-Se angle of 121.2° in $K_4Sn_2Se_6$. The inner Se(3)-Sn(1)-Se(4) bond angle is 92.82(5)°, which is similar to the equivalent inner Se-Sn-Se angle of 94.5° in $K_4Sn_2Se_6$. Additional evidence for this long bond can be found by comparing Sn-Se bond distances for the selenium atoms on Sn(2). The average Sn(2)-Se bond length is 2.538(4) Å, while the Sn(2)-Se(9) bond is the longest at 2.558(2) Å. The long Sn(1)-Se(9) bond makes Sn(1) a distorted octahedron with five Sn-Se bonds and a lone pair. This type of bonding has been observed before in $Cs_2Sn_4S_9$[93] and β-$Rb_2Sn_2S_8$.[94] In these two structures, Kanatzidis *et. al.* reported long Sn-S bond distances of 2.859 Å and 2.875 Å respectively.

The structures of Eu_2SnS_5 [74] and $Eu_8(Sn_4Se_{14})(Se_3)_2$ are similar in many ways. Both contain 9-coordinate Eu(II) atoms, both contain $(Q_3)^{2-}$ anionic chains (Q = S, Se), and both contain two crystallographically distinct tin atoms. The main differences between Eu_2SnS_5 and $Eu_8(Sn_4Se_{14})(Se_3)_2$ are the bonding environments around each tin atom. In Eu_2SnS_5, both tin atoms are described as SnS_6 octahedra where at least two Sn-S bonds in each octahedron are extremely long bonds. The bonding environment around these tin atoms is shown in Figure 5.14B. The two tin atoms are separated by only 1.017(5) Å and Guittard *et. al.* describe each tin atom as being half occupied. A possible arrangement of these SnS_6 octahedra assuming the

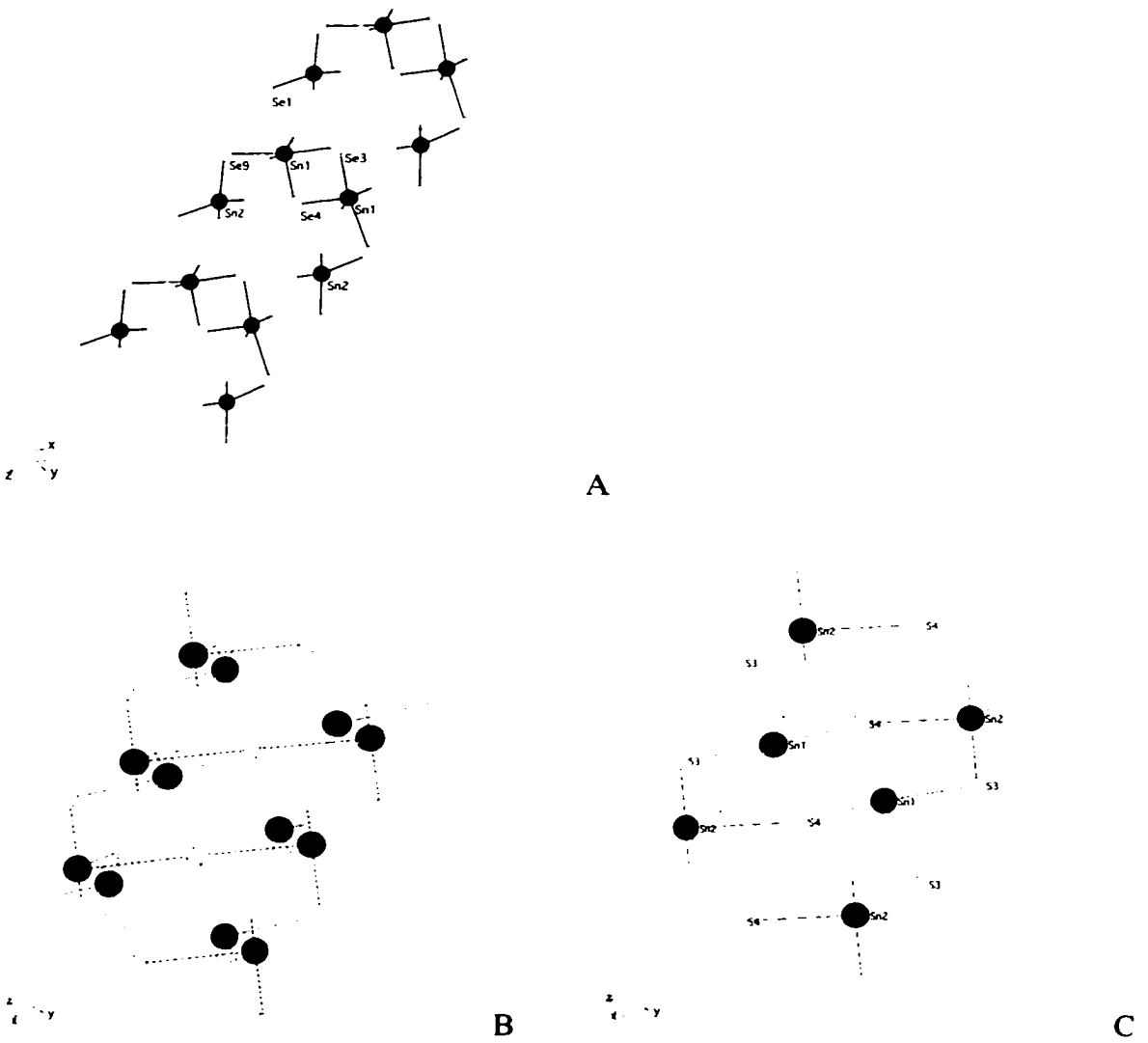


Figure 5.14. Comparison of $Eu_8Sn_4Se_{20}$ and Eu_2SnS_5. Filled tin circles, open selenium or sulfur circles. (A) Packing arrangement of $(Sn_4Se_{14})^{12-}$ units $Eu_8(Sn_4Se_{14})(Se_3)_2$. (B) Arrangement of SnS_6 octahedra in Eu_2SnS_5. (C) Possible SnS_6 arrangement if each tin is half occupied.

half occupancy is shown in Figure 5.14C. The SnS_6 octahedra are continuously linked together through long Sn-S bonds to S(3) and S(4). This is different from the coordination environment around the tin atoms in $Eu_8(Sn_4Se_{14})(Se_3)_2$. Figure 5.14A shows that within each $(Sn_4Se_{14})^{12-}$ unit, Sn(1) is found in a trigonal bi-pyramidal arrangement and Sn(2) is found as a distorted tetrahedron. The Sn-Se bonds required to place each tin in an octahedral geometry would all be greater than 3.3 Å, and are therefore not considered Sn-Se bonds.

The following table compares the unit cell dimensions of these two structures.

	$Eu_8(Sn_4Se_{14})(Se_3)_2$	Eu_2SnS_5
Space Group	$P2_12_12$	Pmcb
a (Å)	11.990(2)	4.100(1)
b (Å)	16.425(4)	15.621(3)
c (Å)	8.543(1)	11.507(2)

It is clear that the two structures may be related by a simple matrix where our $Eu_8(Sn_4Se_{14})(Se_3)_2$ has one axis that is doubled compared to the Eu_2SnS_5 structure. This doubled axis allows $Eu_8(Sn_4Se_{14})(Se_3)_2$ to contain isolated C-shaped $(Sn_4Se_{14})^{12-}$ anionic units while Eu_2SnS_5 contains continuously linked SnS_6 octahedra.

Vibrational and Electronic Spectroscopy

Raman Spectroscopy

The Raman spectra of $K_2EuSiSe_5$, and $K_2EuGeSe_5$ are shown in Figures 5.15 and 5.16 respectively. In both figures the four peaks expected for a normal tetrahedral molecule are not observed due to the distortion of the tetrahedron by the di-selenide arm in the $(TSe_5)^{4-}$ (T = Si, Ge) tetrahedron. In Figure 5.16 the large peak at 216.7 cm^{-1} is attributed to the totally symmetric stretch of the distorted $(GeSe_5)^{4-}$

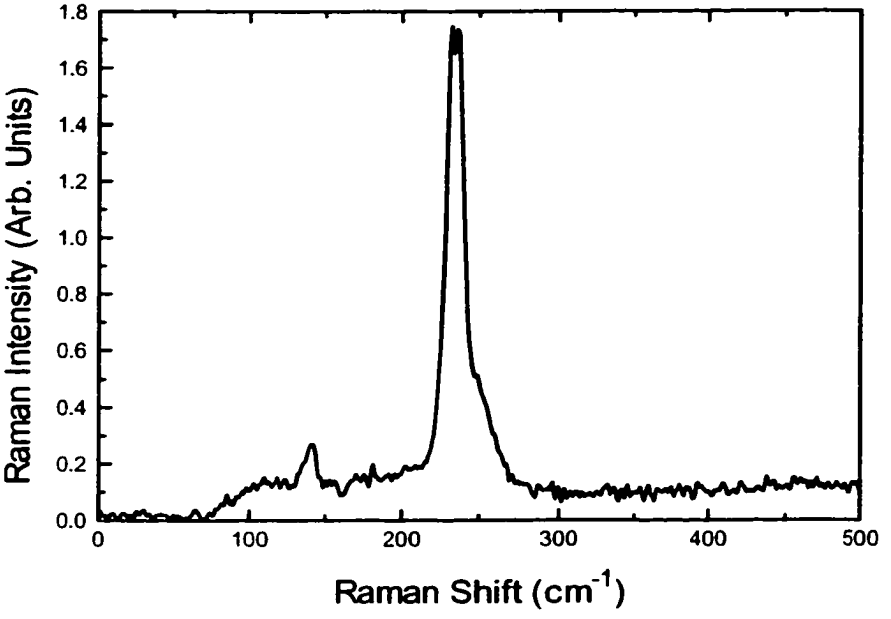


Figure 5.15. Raman spectrum of $K_2EuSiSe_5$.

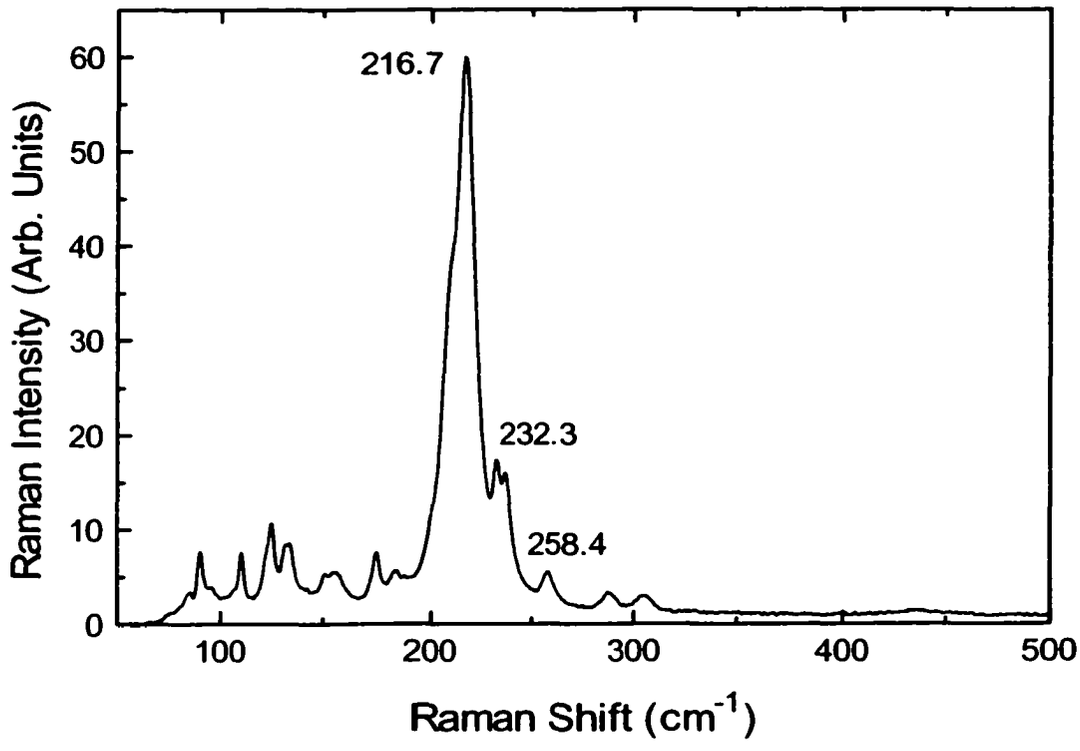


Figure 5.16. Raman spectrum of $K_2EuGeSe_5$.

tetrahedron and the weak peak at 437.0 cm^{-1} is attributed to the anti-symmetric stretch. The peak at 258.4 cm^{-1} is tentatively assigned to the Se-Se stretching vibration in the (Se_2) arm of $(GeSe_5)^{4-}$. Definitive assignments can only be made by normal mode analysis. However, in $K_2EuSiSe_5$ (Figure 5.15), the most intense peak was found at 234 cm^{-1}, indicating a reasonable assignment for the $(SiSe_5)^{4-}$ pseudo-tetrahedral symmetric stretch. This peak is broad enough to obscure the higher energy Se-Se stretch around 250 cm^{-1}. Figure 5.17 shows the Raman spectra for $KEuGeS_4$. The large peak at 380.0 cm^{-1} is assigned to the totally symmetric stretch of the tetrahedral $(GeS_4)^{4-}$ unit. Table 5.12 lists the Raman peaks for K_2EuTSe_5 and $KEuGeS_4$.

UV-Vis Spectroscopy

UV-Visible optical band-gap analysis of compounds **I-V** shows that $K_2EuSiSe_5$, $K_2EuGeSe_5$, $KEuSiS_4$, $KEuGeS_4$, and $Eu_8(Sn_4Se_{14})(Se_3)_2$ are all likely semiconductors with optical band-gaps of 2.00 eV, 1.84 eV, 1.72 eV, 1.71 eV, and 1.07 eV respectively. Figure 5.18 shows the optical band-gap curve for $K_2EuSiSe_5$. Two band-gaps are observed: one at 1.78 eV corresponding to the crystalline impurity EuSe, and the second at 2.00 eV corresponding to $K_2EuSiSe_5$. Figures 5.19, 5.20 and 5.21 show the optical band-gap curves for $K_2EuGeSe_5$, $KEuSiS_4$, and $KEuGeS_4$ respectively. Figure 5.22 shows the optical band-gap for $Eu_8(Sn_4Se_{14})(Se_3)_2$.

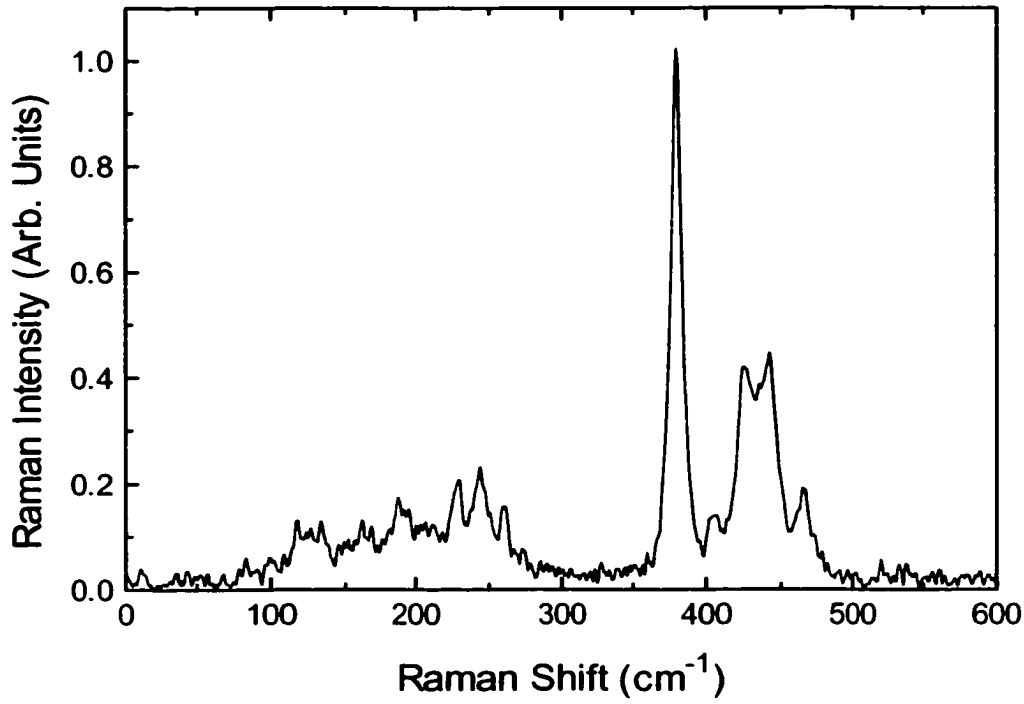


Figure 5.17. Raman spectrum of $KEuGeS_4$.

Table 5.12. Raman peaks (cm^{-1}) Found in $K_2EuGeSe_5$ and $KEuGeS_4$.

$K_2EuGeSe_5$	$KEuGeS_4$
90.1	117.1
110.3	133.2
125.0	162.0
133.4	188.0
155.7	229.8
174.7	243.9
183.9	259.8
216.7	379.9
232.3	425.1
258.4	442.5
287.4	465.1
305.8	
437.0	

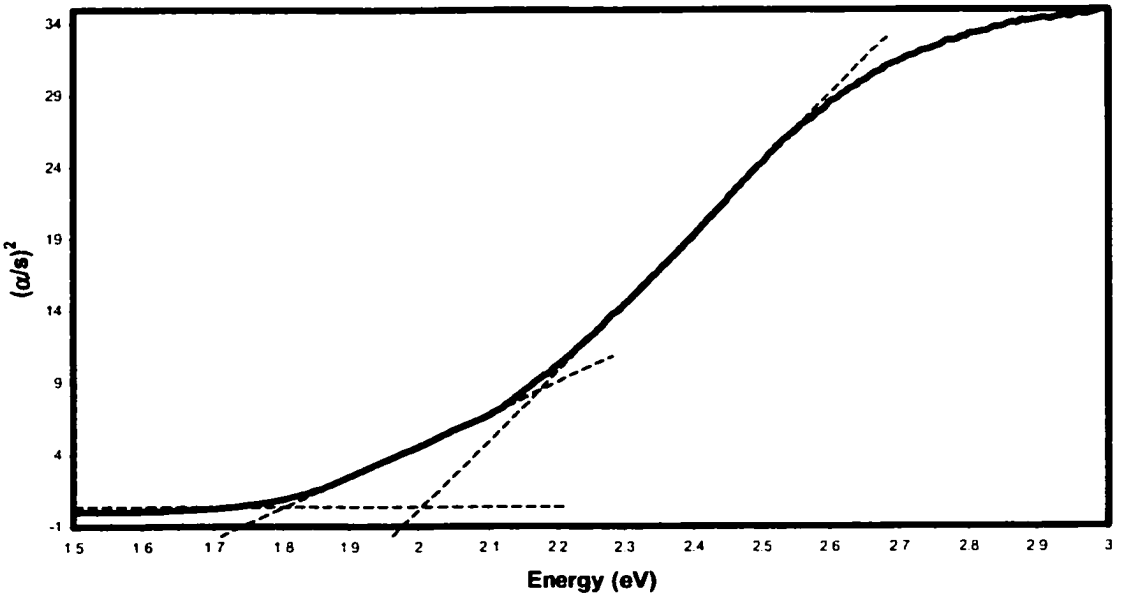


Figure 5.18. Optical band-gap of $K_2EuSiSe_5$.

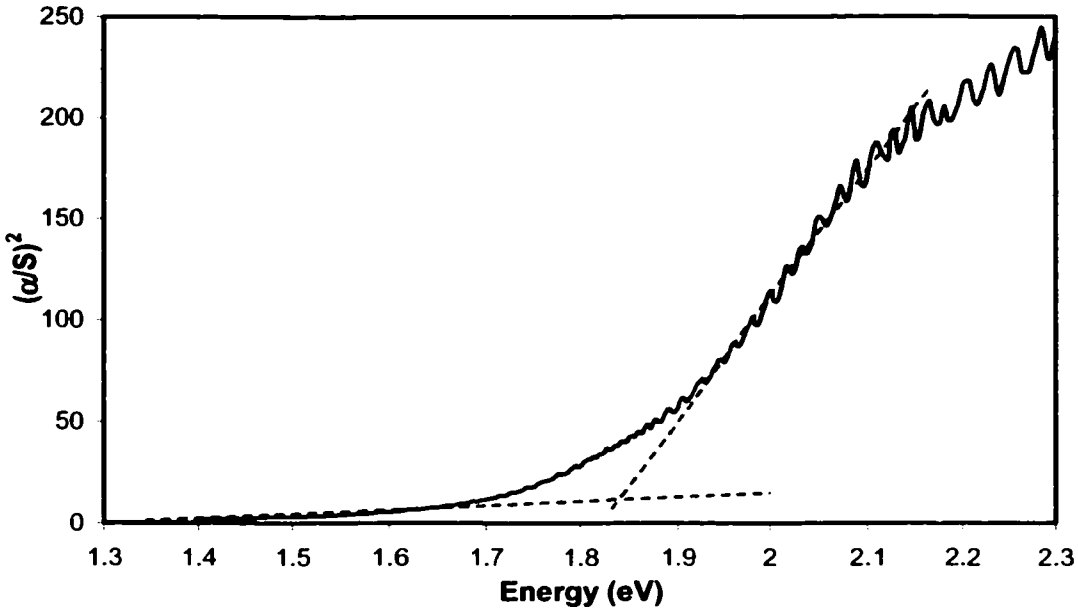


Figure 5.19. Optical band-gap of $K_2EuGeSe_5$.

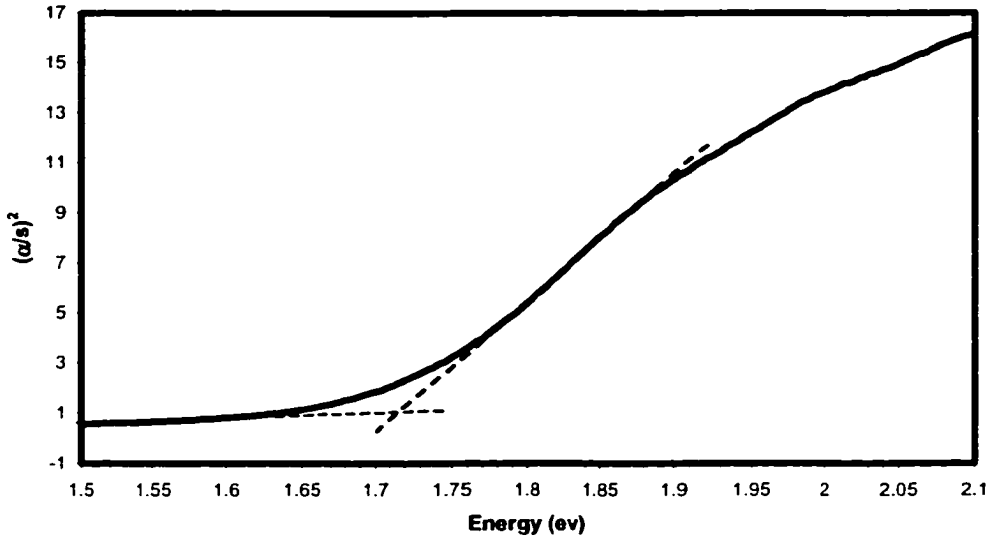


Figure 5.20. Optical band-gap of $KEuSiS_4$.

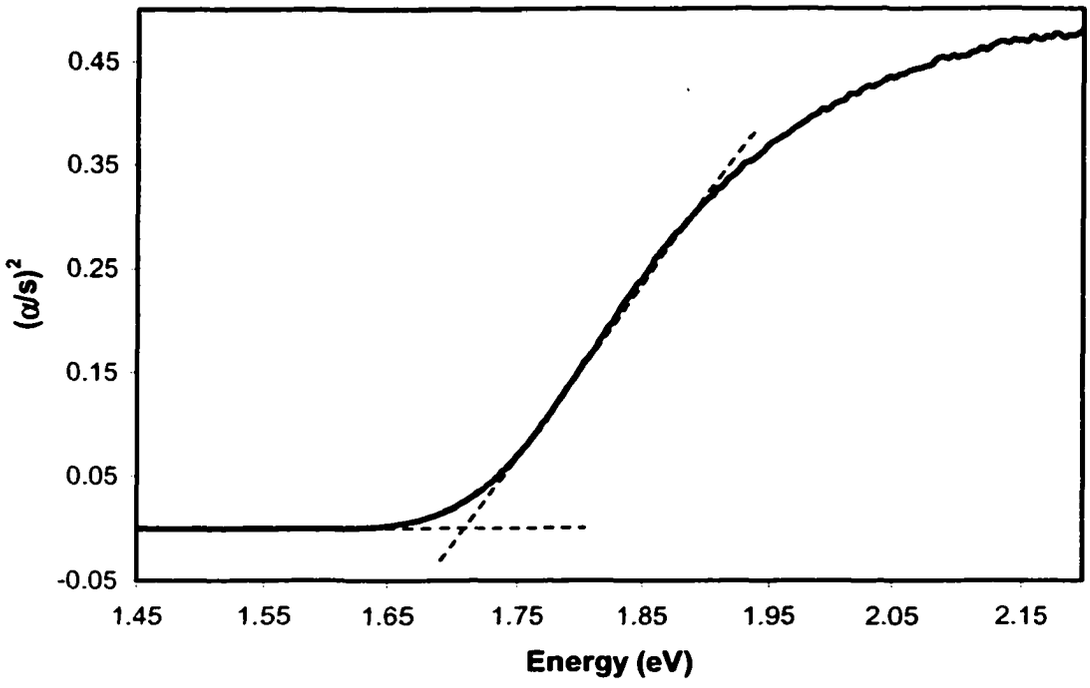


Figure 5.21. Optical band-gap of $KEuGeS_4$.

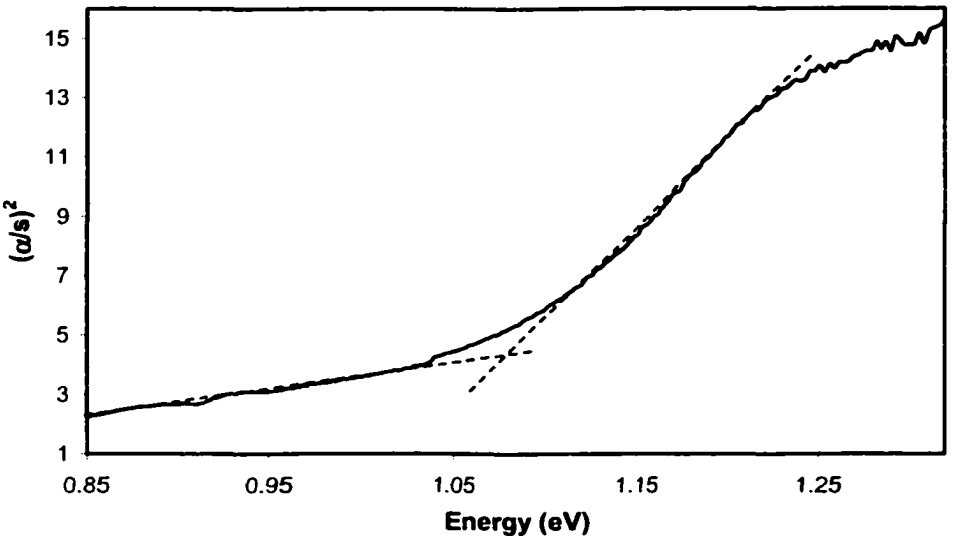


Figure 5.22. Optical band-gap of $Eu_8(Sn_4Se_{14})(Se_3)_2$.

Emission Spectroscopy

Emission spectroscopy was performed on compounds **III** and **IV**. Using a 327 nm excitation wavelength, intense Eu(III) fluorescence was observed at 614 nm in both compounds. The emission spectra for $KEuSiS_4$ and $KEuGeS_4$ are shown in Figures 5.23 and 5.24 respectively. In $KEuGeS_4$ the 614 nm peak is found as a shoulder on the very intense frequency doubled 654 nm peak. These peaks were not observed in either compound **I** or **II**.

Conclusions

The quaternary compounds K_2EuTSe_5 and $KEuTS_4$ (T = Si, Ge) and the ternary compound $Eu_8(Sn_4Se_{14})(Se_3)_2$ were all synthesized under equivalent reactant ratios. The difference in structures clearly shows the effect of different oxidizing agents and group XIV elements on the crystalline product observed. By comparing compounds **I** & **II** to **III** & **IV** one can see the effect of using sulfur as an oxidizing agent in the flux reaction instead of selenium. All four reactions were done with equivalent reactant stoichiometries. In $K_2EuSiSe_5$ and $K_2EuGeSe_5$ europium exists as Eu(II) and Se-Se bonding is observed. The analogous sulfur reactions yields structures with Eu(III) and no S-S bonding in $KEuSiS_4$ and $KEuGeS_4$. This can be rationalized by citing the better oxidizing ability of sulfur versus selenium. It is interesting to note from Chapters 2 and 3 that when using phosphorus as the main group metal neither the di-selenide unit nor Eu(III) were observed in reaction products. $Eu_8(Sn_4Se_{14})(Se_3)$ has the same empirical formula as Eu_2SnS_5 reported by Guittard *et. al.*, but has a unique structure containing the novel C-shaped $(Sn_4Se_{14})^{12-}$

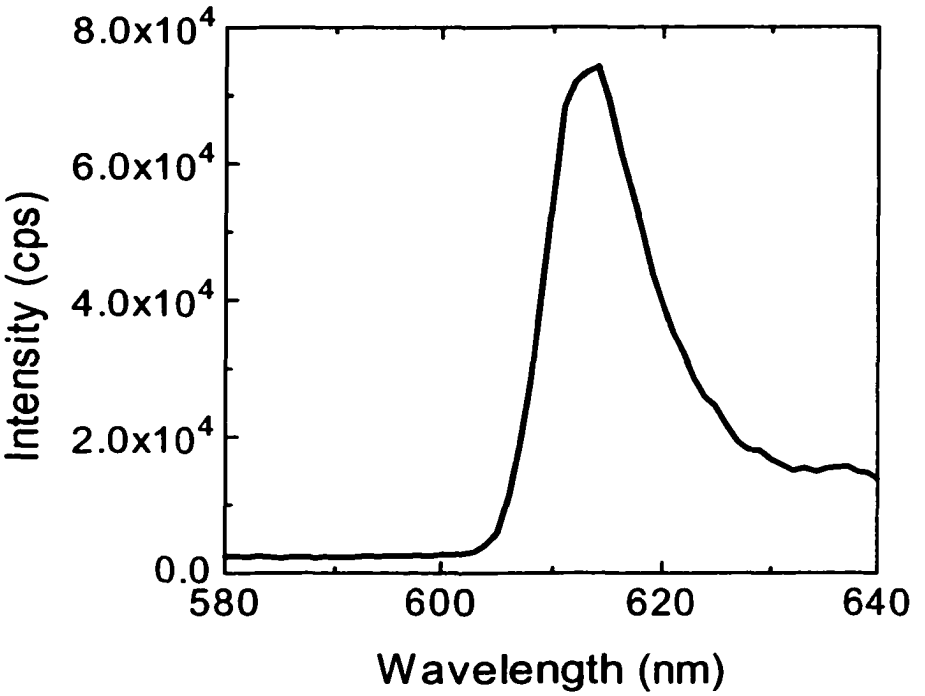


Figure 5.23. Fluorescence emission spectrum for $KEuSiS_4$.

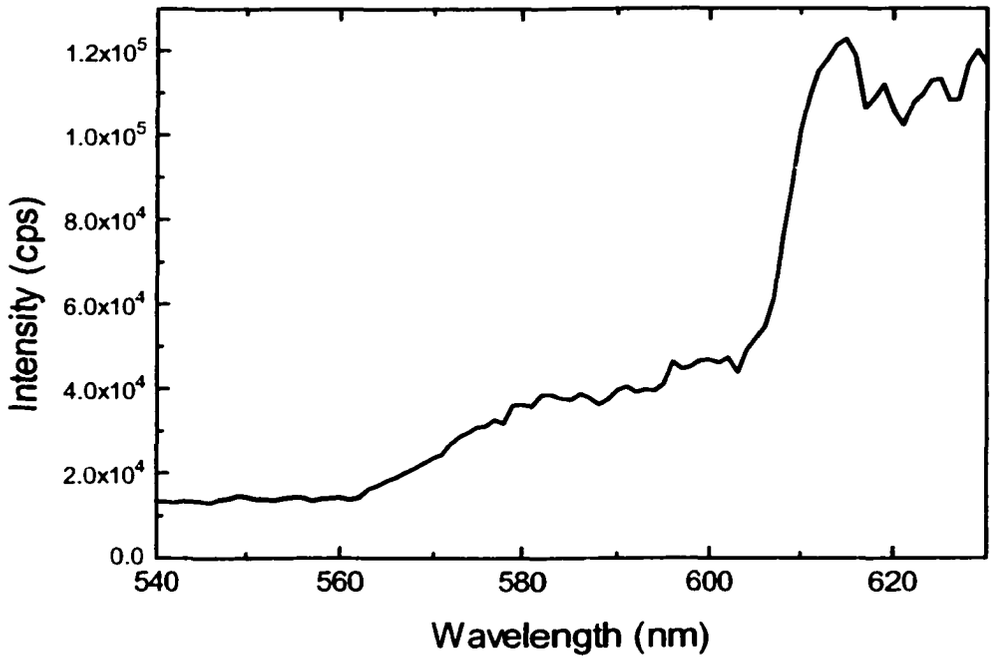


Figure 5.24. Fluorescence emission spectrum for $KEuGeS_4$.

anionic unit. Future work includes synthesizing additional quaternary rare-earth chalcosilicates, germanates, and stannates.

Tables of additional crystallographic details, all bond distances and angles, and anisotropic thermal parameters can be found in Appendix E, Tables E.1-E.20.

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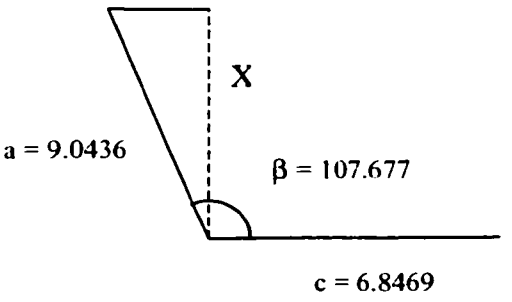
Appendix A: Conversion of monoclinic $KEuPSe_4$ reported by Kanatzidis *et. al.* to an orthorhombic cell to show the relationship to $KEuPSe_4$ reported by Dorhout *et. al.*

Kanatzidis *et. al.*

$P2_1/m$
a = 6.8469(6) Å
b = 6.9521(6) Å
c = 9.0436(8) Å
β = 107.677(2)°

Step 1: Switch the reported a and c axes.
Step 2: Convert from a monoclinic cell to an orthorhombic cell.



sin (180-107.677) = X / 9.0436

X = 8.6166

Step 3: Double the new a-axis

a = 2X = 17.2332 Å

The resulting orthorhombic unit cell is essentially equivalent to the cell reported by Dorhout *et. al.*

Dorhout *et. al.*	New cell for Kanatzidis *et. al.*
a = 17.5156(11) Å	a = 17.2332 Å
b = 7.0126(5) Å	b = 6.9521 Å
c = 6.9015(4) Å	c = 6.8469 Å

Appendix B:

Supplementary Information for Chapter Two

Table B.1. Crystal data and structure refinement for $K_2La(P_2Se_6)_{1/2}(PSe_4)$.

Identification code	cre125	
Empirical formula	$K_2La(P_2Se_6)_{1/2}(PSe_4)$	
Formula weight	831.77	
Temperature	298(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 9.42690(10) Å	α= 90°.
	b = 7.20540(10) Å	β= 97.4840(10)°.
	c = 21.0276(5) Å	γ = 90°.
Volume	1416.12(4) $Å^3$	
Z	4	
Density (calculated)	3.901 Mg/m^3	
Absorption coefficient	21.775 mm^{-1}	
F(000)	1452	
Crystal size	0.15 x 0.12 x 0.06 mm^3	
Theta range for data collection	1.95 to 28.29°.	
Index ranges	-12<=h<=11, -9<=k<=9, -27<=l<=24	
Reflections collected	8862	
Independent reflections	3385 [R(int) = 0.0513]	
Absorption correction	SADABS	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3385 / 0 / 110	
Goodness-of-fit on F^2	1.061	
Final R indices [I>2sigma(I)]	R1 = 0.0429, wR2 = 0.0890	
R indices (all data)	R1 = 0.0666, wR2 = 0.0970	
Extinction coefficient	0.00209(13)	
Largest diff. peak and hole	1.285 and -1.503 $e.Å^{-3}$	

Table B.2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for $K_2La(P_2Se_6)_{1/2}(PSe_4)$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
La(1)	8072(1)	4726(1)	1499(1)	19(1)
Se(1)	7175(1)	4614(1)	-40(1)	26(1)
Se(2)	5838(1)	7758(1)	1045(1)	27(1)
Se(3)	8091(1)	780(1)	2193(1)	23(1)
Se(4)	10527(1)	4794(1)	2592(1)	34(1)
Se(5)	10565(1)	2591(1)	991(1)	26(1)
Se(6)	10224(1)	7512(1)	967(1)	25(1)
Se(7)	5281(1)	2543(1)	1068(1)	27(1)
P(1)	5933(2)	10164(3)	1685(1)	18(1)
P(2)	9184(2)	4903(3)	-432(1)	20(1)
K(1)	12576(2)	75(3)	91(1)	40(1)
K(2)	13425(3)	5411(4)	1865(1)	54(1)

Table B.3. Bond lengths [Å] and angles [°] for $K_2La(P_2Se_6)_{1/2}(PSe_4)$.

La(1)-Se(4)	3.0421(10)	Se(4)-La(1)-K(2)#2	121.50(4)
La(1)-Se(7)	3.0979(10)	Se(7)-La(1)-K(2)#2	46.24(4)
La(1)-Se(2)	3.0980(9)	Se(2)-La(1)-K(2)#2	49.32(4)
La(1)-Se(5)	3.1127(9)	Se(5)-La(1)-K(2)#2	153.40(4)
La(1)-Se(6)	3.1609(9)	Se(6)-La(1)-K(2)#2	131.64(4)
La(1)-Se(3)#1	3.1830(9)	Se(3)#1-La(1)-K(2)#2	51.93(4)
La(1)-Se(3)	3.1937(9)	Se(3)-La(1)-K(2)#2	88.17(4)
La(1)-Se(1)	3.2380(9)	Se(1)-La(1)-K(2)#2	92.28(4)
La(1)-K(2)#2	4.572(2)	P(2)-Se(1)-La(1)	104.46(7)
Se(1)-P(2)	2.171(2)	P(2)-Se(1)-K(1)#3	90.92(7)
Se(1)-K(1)#3	3.390(2)	La(1)-Se(1)-K(1)#3	92.64(5)
Se(1)-K(2)#4	3.806(3)	P(2)-Se(1)-K(2)#4	68.92(7)
Se(1)-K(1)#4	3.836(2)	La(1)-Se(1)-K(2)#4	173.37(4)
Se(2)-P(1)	2.189(2)	K(1)#3-Se(1)-K(2)#4	88.02(6)
Se(2)-K(1)#4	3.362(2)	P(2)-Se(1)-K(1)#4	80.46(6)
Se(2)-K(2)#2	3.469(3)	La(1)-Se(1)-K(1)#4	89.66(4)
Se(2)-K(1)#5	3.829(2)	K(1)#3-Se(1)-K(1)#4	171.38(7)
Se(3)-P(1)#6	2.216(2)	K(2)#4-Se(1)-K(1)#4	88.76(5)
Se(3)-La(1)#7	3.1830(9)	P(1)-Se(2)-La(1)	113.39(6)
Se(3)-K(2)#8	3.617(3)	P(1)-Se(2)-K(1)#4	94.74(7)
Se(4)-P(1)#7	2.195(2)	La(1)-Se(2)-K(1)#4	101.49(5)
Se(4)-K(2)	3.330(2)	P(1)-Se(2)-K(2)#2	93.27(7)
Se(4)-K(2)#8	3.458(3)	La(1)-Se(2)-K(2)#2	88.05(5)
Se(5)-P(2)#4	2.184(2)	K(1)#4-Se(2)-K(2)#2	163.89(7)
Se(5)-K(1)	3.376(2)	P(1)-Se(2)-K(1)#5	86.71(7)
Se(5)-K(2)	3.673(3)	La(1)-Se(2)-K(1)#5	159.46(4)
Se(6)-P(2)#4	2.184(2)	K(1)#4-Se(2)-K(1)#5	80.02(6)
Se(6)-K(1)#9	3.576(2)	K(2)#2-Se(2)-K(1)#5	86.52(6)
Se(6)-K(1)#4	3.662(2)	P(1)#6-Se(3)-La(1)#7	88.30(6)
Se(6)-K(2)	3.671(3)	P(1)#6-Se(3)-La(1)	90.47(6)
Se(7)-P(1)#6	2.189(2)	La(1)#7-Se(3)-La(1)	128.66(3)
Se(7)-K(2)#2	3.302(3)	P(1)#6-Se(3)-K(2)#8	163.77(7)
Se(7)-K(1)#2	3.539(2)	La(1)#7-Se(3)-K(2)#8	84.23(4)
Se(7)-K(1)#3	3.855(2)	La(1)-Se(3)-K(2)#8	105.45(5)
P(1)-Se(7)#9	2.189(2)	P(1)#7-Se(4)-La(1)	92.37(6)
P(1)-Se(4)#1	2.195(2)	P(1)#7-Se(4)-K(2)	158.03(8)
P(1)-Se(3)#9	2.216(2)	La(1)-Se(4)-K(2)	104.15(5)
P(2)-Se(5)#4	2.184(2)	P(1)#7-Se(4)-K(2)#8	93.46(7)
P(2)-Se(6)#4	2.184(2)	La(1)-Se(4)-K(2)#8	113.02(6)
P(2)-P(2)#4	2.226(4)	K(2)-Se(4)-K(2)#8	93.28(6)
P(2)-K(2)#4	3.641(3)	P(2)#4-Se(5)-La(1)	85.19(6)
K(1)-Se(2)#4	3.362(2)	P(2)#4-Se(5)-K(1)	91.95(7)
K(1)-Se(1)#3	3.390(2)	La(1)-Se(5)-K(1)	164.21(5)
K(1)-Se(7)#10	3.539(2)	P(2)#4-Se(5)-K(2)	71.83(8)

La(1)-Se(5)-K(2)	95.31(4)	Se(1)#3-K(1)-Se(6)#6	63.35(4)
K(1)-Se(5)-K(2)	98.54(6)	Se(7)#10-K(1)-Se(6)#6	114.10(7)
P(2)#4-Se(6)-La(1)	84.01(6)	Se(2)#4-K(1)-Se(6)#4	72.56(5)
P(2)#4-Se(6)-K(1)#9	85.90(7)	Se(5)-K(1)-Se(6)#4	70.89(5)
La(1)-Se(6)-K(1)#9	168.57(5)	Se(1)#3-K(1)-Se(6)#4	120.11(7)
P(2)#4-Se(6)-K(1)#4	106.10(7)	Se(7)#10-K(1)-Se(6)#4	121.48(6)
La(1)-Se(6)-K(1)#4	94.09(4)	Se(6)#6-K(1)-Se(6)#4	96.44(6)
K(1)#9-Se(6)-K(1)#4	83.56(6)	Se(2)#4-K(1)-Se(2)#11	99.98(6)
P(2)#4-Se(6)-K(2)	71.87(7)	Se(5)-K(1)-Se(2)#11	114.31(7)
La(1)-Se(6)-K(2)	94.51(5)	Se(1)#3-K(1)-Se(2)#11	61.81(4)
K(1)#9-Se(6)-K(2)	87.42(6)	Se(7)#10-K(1)-Se(2)#11	56.35(4)
K(1)#4-Se(6)-K(2)	170.89(6)	Se(6)#6-K(1)-Se(2)#11	90.80(5)
P(1)#6-Se(7)-La(1)	93.55(6)	Se(6)#4-K(1)-Se(2)#11	172.52(7)
P(1)#6-Se(7)-K(2)#2	108.39(8)	Se(2)#4-K(1)-Se(1)#4	58.84(4)
La(1)-Se(7)-K(2)#2	91.11(5)	Se(5)-K(1)-Se(1)#4	61.37(4)
P(1)#6-Se(7)-K(1)#2	94.37(7)	Se(1)#3-K(1)-Se(1)#4	171.38(7)
La(1)-Se(7)-K(1)#2	160.99(5)	Se(7)#10-K(1)-Se(1)#4	58.19(4)
K(2)#2-Se(7)-K(1)#2	102.70(6)	Se(6)#6-K(1)-Se(1)#4	125.03(6)
P(1)#6-Se(7)-K(1)#3	82.04(7)	Se(6)#4-K(1)-Se(1)#4	63.35(4)
La(1)-Se(7)-K(1)#3	86.47(4)	Se(2)#11-K(1)-Se(1)#4	113.68(6)
K(2)#2-Se(7)-K(1)#3	169.44(7)	Se(2)#4-K(1)-Se(7)#3	57.33(4)
K(1)#2-Se(7)-K(1)#3	77.56(6)	Se(5)-K(1)-Se(7)#3	174.86(8)
Se(7)#9-P(1)-Se(2)	105.65(9)	Se(1)#3-K(1)-Se(7)#3	56.50(4)
Se(7)#9-P(1)-Se(4)#1	110.65(9)	Se(7)#10-K(1)-Se(7)#3	102.44(6)
Se(2)-P(1)-Se(4)#1	110.52(9)	Se(6)#6-K(1)-Se(7)#3	118.95(6)
Se(7)#9-P(1)-Se(3)#9	107.32(9)	Se(6)#4-K(1)-Se(7)#3	104.14(6)
Se(2)-P(1)-Se(3)#9	114.59(9)	Se(2)#11-K(1)-Se(7)#3	70.51(4)
Se(4)#1-P(1)-Se(3)#9	108.04(9)	Se(1)#4-K(1)-Se(7)#3	115.57(6)
Se(1)-P(2)-Se(5)#4	116.38(10)	Se(2)#4-K(1)-K(1)#12	54.42(5)
Se(1)-P(2)-Se(6)#4	114.42(9)	Se(5)-K(1)-K(1)#12	133.64(9)
Se(5)#4-P(2)-Se(6)#4	109.15(9)	Se(1)#3-K(1)-K(1)#12	84.31(6)
Se(1)-P(2)-P(2)#4	103.96(13)	Se(7)#10-K(1)-K(1)#12	54.27(5)
Se(5)#4-P(2)-P(2)#4	105.96(13)	Se(6)#6-K(1)-K(1)#12	135.56(9)
Se(6)#4-P(2)-P(2)#4	105.95(13)	Se(6)#4-K(1)-K(1)#12	126.98(8)
Se(1)-P(2)-K(2)#4	77.27(7)	Se(2)#11-K(1)-K(1)#12	45.56(4)
Se(5)#4-P(2)-K(2)#4	73.42(7)	Se(1)#4-K(1)-K(1)#12	87.51(6)
Se(6)#4-P(2)-K(2)#4	73.38(7)	Se(7)#3-K(1)-K(1)#12	48.18(4)
P(2)#4-P(2)-K(2)#4	178.78(14)	Se(2)#4-K(1)-K(1)#3	119.40(8)
Se(2)#4-K(1)-Se(5)	118.88(6)	Se(5)-K(1)-K(1)#3	54.77(4)
Se(2)#4-K(1)-Se(1)#3	113.67(6)	Se(1)#3-K(1)-K(1)#3	92.77(6)
Se(5)-K(1)-Se(1)#3	126.81(7)	Se(7)#10-K(1)-K(1)#3	134.37(8)
Se(2)#4-K(1)-Se(7)#10	79.95(5)	Se(6)#6-K(1)-K(1)#3	48.98(4)
Se(5)-K(1)-Se(7)#10	79.60(5)	Se(6)#4-K(1)-K(1)#3	47.46(4)
Se(1)#3-K(1)-Se(7)#10	118.12(7)	Se(2)#11-K(1)-K(1)#3	139.75(8)
Se(2)#4-K(1)-Se(6)#6	165.66(8)	Se(1)#4-K(1)-K(1)#3	94.88(6)
Se(5)-K(1)-Se(6)#6	63.73(4)	Se(7)#3-K(1)-K(1)#3	122.99(8)

K(1)#12-K(1)-K(1)#3	170.47(11)
Se(2)#4-K(1)-K(2)#6	142.93(7)
Se(5)-K(1)-K(2)#6	89.40(6)
Se(1)#3-K(1)-K(2)#6	49.42(4)
Se(7)#10-K(1)-K(2)#6	82.60(5)
Se(6)#6-K(1)-K(2)#6	47.07(4)
Se(6)#4-K(1)-K(2)#6	143.50(6)
Se(2)#11-K(1)-K(2)#6	43.73(4)
Se(1)#4-K(1)-K(2)#6	133.29(7)
Se(7)#3-K(1)-K(2)#6	95.53(5)
K(1)#12-K(1)-K(2)#6	88.96(7)
K(1)#3-K(1)-K(2)#6	96.05(6)
Se(7)#10-K(2)-Se(4)	132.07(8)
Se(7)#10-K(2)-Se(4)#13	126.27(7)
Se(4)-K(2)-Se(4)#13	100.77(7)
Se(7)#10-K(2)-Se(2)#10	68.14(5)
Se(4)-K(2)-Se(2)#10	157.50(9)
Se(4)#13-K(2)-Se(2)#10	62.69(5)
Se(7)#10-K(2)-Se(3)#13	79.69(6)
Se(4)-K(2)-Se(3)#13	119.93(8)
Se(4)#13-K(2)-Se(3)#13	63.39(5)
Se(2)#10-K(2)-Se(3)#13	68.24(5)
Se(7)#10-K(2)-P(2)#4	83.46(7)
Se(4)-K(2)-P(2)#4	82.28(6)
Se(4)#13-K(2)-P(2)#4	117.58(9)
Se(2)#10-K(2)-P(2)#4	91.97(8)
Se(3)#13-K(2)-P(2)#4	157.70(9)
Se(7)#10-K(2)-Se(6)	116.81(8)
Se(4)-K(2)-Se(6)	67.83(5)
Se(4)#13-K(2)-Se(6)	88.49(7)
Se(2)#10-K(2)-Se(6)	95.24(7)
Se(3)#13-K(2)-Se(6)	151.41(8)
P(2)#4-K(2)-Se(6)	34.75(4)
Se(7)#10-K(2)-Se(5)	78.61(6)
Se(4)-K(2)-Se(5)	64.10(5)
Se(4)#13-K(2)-Se(5)	146.10(9)
Se(2)#10-K(2)-Se(5)	120.45(8)
Se(3)#13-K(2)-Se(5)	150.44(8)
P(2)#4-K(2)-Se(5)	34.75(4)
Se(6)-K(2)-Se(5)	57.98(4)
Se(7)#10-K(2)-Se(1)#4	60.27(5)
Se(4)-K(2)-Se(1)#4	116.06(7)
Se(4)#13-K(2)-Se(1)#4	109.61(8)
Se(2)#10-K(2)-Se(1)#4	61.42(5)
Se(3)#13-K(2)-Se(1)#4	123.90(7)
P(2)#4-K(2)-Se(1)#4	33.81(4)
Se(6)-K(2)-Se(1)#4	58.60(5)
Se(5)-K(2)-Se(1)#4	59.30(4)
Se(7)#10-K(2)-La(1)#10	42.65(3)
Se(4)-K(2)-La(1)#10	157.56(9)
Se(4)#13-K(2)-La(1)#10	85.14(5)
Se(2)#10-K(2)-La(1)#10	42.63(3)
Se(3)#13-K(2)-La(1)#10	43.84(3)
P(2)#4-K(2)-La(1)#10	114.37(7)
Se(6)-K(2)-La(1)#10	134.37(7)
Se(5)-K(2)-La(1)#10	120.86(6)
Se(1)#4-K(2)-La(1)#10	81.35(5)
Se(7)#10-K(2)-K(2)#13	168.30(9)
Se(4)-K(2)-K(2)#13	58.69(7)
Se(4)#13-K(2)-K(2)#13	42.34(2)
Se(2)#10-K(2)-K(2)#13	102.35(4)
Se(3)#13-K(2)-K(2)#13	90.55(7)
P(2)#4-K(2)-K(2)#13	104.18(8)
Se(6)-K(2)-K(2)#13	69.67(6)
Se(5)-K(2)-K(2)#13	112.74(8)
Se(1)#4-K(2)-K(2)#13	122.16(8)
La(1)#10-K(2)-K(2)#13	125.71(7)
Se(7)#10-K(2)-K(2)#8	93.77(4)
Se(4)-K(2)-K(2)#8	44.38(6)
Se(4)#13-K(2)-K(2)#8	126.45(10)
Se(2)#10-K(2)-K(2)#8	157.77(8)
Se(3)#13-K(2)-K(2)#8	96.72(9)
P(2)#4-K(2)-K(2)#8	98.88(7)
Se(6)-K(2)-K(2)#8	104.74(8)
Se(5)-K(2)-K(2)#8	65.10(4)
Se(1)#4-K(2)-K(2)#8	121.70(7)
La(1)#10-K(2)-K(2)#8	115.21(6)
K(2)#13-K(2)-K(2)#8	93.76(9)

Symmetry transformations used to generate equivalent atoms:

#1 -x+3/2,y+1/2,-z+1/2 #2 x-1,y,z #3 -x+2,-y,-z

#4 -x+2,-y+1,-z #5 x-1,y+1,z #6 x,y-1,z #7 -x+3/2,y-1/2,-z+1/2

#8 -x+5/2,y-1/2,-z+1/2 #9 x,y+1,z #10 x+1,y,z

#11 x+1,y-1,z #12 -x+3,-y,-z #13 -x+5/2,y+1/2,-z+1/2

Table B.4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $K_2La(P_2Se_6)_{1/2}(PSe_4)$. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
La(1)	22(1)	18(1)	16(1)	1(1)	4(1)	-1(1)
Se(1)	22(1)	34(1)	22(1)	-1(1)	3(1)	-2(1)
Se(2)	38(1)	19(1)	23(1)	-4(1)	-3(1)	4(1)
Se(3)	21(1)	25(1)	23(1)	5(1)	0(1)	-3(1)
Se(4)	21(1)	59(1)	22(1)	0(1)	6(1)	1(1)
Se(5)	37(1)	18(1)	26(1)	6(1)	11(1)	6(1)
Se(6)	36(1)	17(1)	24(1)	-4(1)	10(1)	-4(1)
Se(7)	31(1)	19(1)	29(1)	7(1)	-6(1)	-1(1)
P(1)	19(1)	17(1)	16(1)	0(1)	2(1)	1(1)
P(2)	25(1)	16(1)	19(1)	1(1)	6(1)	0(1)
K(1)	50(1)	33(1)	42(1)	1(1)	17(1)	0(1)
K(2)	36(1)	64(2)	66(2)	-15(1)	17(1)	-12(1)

Table B.5. Crystal data and structure refinement for $K_3La(PSe_4)_2$.

Identification code	cre127	
Empirical formula	$K_3La(PSe_4)_2$	
Formula weight	949.83	
Temperature	170(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 9.5782(2) Å	α= 90°.
	b = 17.6623(4) Å	β= 90.1200(10)°.
	c = 9.9869(3) Å	γ = 90°.
Volume	1689.51(7) $Å^3$	
Z	4	
Density (calculated)	3.734 Mg/m^3	
Absorption coefficient	20.657 mm^{-1}	
F(000)	1664	
Crystal size	0.24 x 0.18 x 0.12 mm^3	
Theta range for data collection	2.13 to 28.30°.	
Index ranges	-12<=h<=12, -9<=k<=22, -13<=l<=13	
Reflections collected	10987	
Independent reflections	4059 [R(int) = 0.0478]	
Absorption correction	SADABS	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4059 / 0 / 127	
Goodness-of-fit on F^2	1.054	
Final R indices [I>2sigma(I)]	R1 = 0.0476, wR2 = 0.1036	
R indices (all data)	R1 = 0.0773, wR2 = 0.1161	
Largest diff. peak and hole	2.658 and -1.607 $e.Å^{-3}$	

Table B.6. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for $K_3La(PSe_4)_2$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
La(1)	2266(1)	138(1)	9704(1)	17(1)
Se(1)	-365(1)	1268(1)	9681(1)	22(1)
Se(2)	567(1)	186(1)	12558(1)	24(1)
Se(3)	5378(1)	246(1)	8193(1)	19(1)
Se(4)	3088(1)	-1320(1)	8226(1)	25(1)
Se(5)	2172(1)	1167(1)	7183(1)	25(1)
Se(6)	-1278(1)	1815(1)	6308(1)	28(1)
Se(7)	5709(1)	-1259(1)	5680(1)	25(1)
Se(8)	3325(1)	1611(1)	10911(1)	24(1)
K(3)	1195(3)	2058(2)	13727(3)	43(1)
P(1)	5251(2)	-991(1)	7750(2)	17(1)
K(2)	3826(3)	-2856(2)	6259(3)	47(1)
P(2)	-77(3)	1036(1)	7507(2)	17(1)
K(1)	2699(2)	-323(1)	5138(2)	31(1)

Table B.7. Bond lengths [Å] and angles [°] for $K_3La(PSe_4)_2$.

La(1)-Se(8)	3.0403(11)	K(3)-Se(1)#11	3.448(3)
La(1)-Se(4)	3.0712(11)	K(3)-Se(6)#6	3.531(3)
La(1)-Se(5)	3.1060(11)	K(3)-Se(5)#11	3.618(3)
La(1)-Se(1)#1	3.1406(11)	K(3)-P(2)#11	3.782(4)
La(1)-Se(3)#2	3.1533(11)	K(3)-Se(8)#11	3.798(3)
La(1)-Se(1)	3.2152(11)	K(3)-Se(5)#6	3.906(3)
La(1)-Se(2)	3.2856(10)	K(3)-Se(6)#11	3.922(3)
La(1)-Se(3)	3.3496(10)	K(3)-K(1)#6	4.662(4)
La(1)-K(2)#3	4.570(3)	K(3)-K(1)#1	4.960(4)
Se(1)-P(2)	2.228(3)	P(1)-Se(8)#2	2.200(3)
Se(1)-La(1)#1	3.1406(11)	P(1)-K(1)	3.761(3)
Se(1)-K(3)#4	3.448(3)	P(1)-K(2)	3.863(4)
Se(1)-K(2)#5	3.775(3)	K(2)-Se(4)#12	3.434(3)
Se(2)-P(2)#1	2.209(3)	K(2)-Se(3)#13	3.481(3)
Se(2)-K(1)#6	3.406(3)	K(2)-Se(6)#14	3.496(3)
Se(2)-K(3)	3.557(3)	K(2)-Se(8)#13	3.613(3)
Se(2)-K(1)#1	3.895(3)	K(2)-Se(1)#14	3.775(3)
Se(3)-P(1)	2.232(3)	K(2)-La(1)#12	4.570(3)
Se(3)-La(1)#2	3.1533(11)	K(2)-K(1)	4.735(4)
Se(3)-K(2)#7	3.481(3)	K(2)-K(3)#2	4.972(4)
Se(3)-K(1)#8	3.808(3)	K(2)-K(3)#1	5.011(4)
Se(4)-P(1)	2.204(2)	P(2)-Se(2)#1	2.209(3)
Se(4)-K(2)	3.424(3)	P(2)-K(3)#4	3.782(4)
Se(4)-K(2)#3	3.434(3)	P(2)-K(1)#10	3.852(3)
Se(4)-K(1)	3.570(3)	K(1)-Se(7)#8	3.288(3)
Se(5)-P(2)	2.191(3)	K(1)-Se(6)#10	3.298(3)
Se(5)-K(1)	3.370(3)	K(1)-Se(2)#9	3.406(3)
Se(5)-K(3)#4	3.618(3)	K(1)-Se(3)#8	3.808(3)
Se(5)-K(3)#9	3.906(3)	K(1)-P(2)#10	3.852(3)
Se(6)-P(2)	2.155(3)	K(1)-Se(2)#1	3.895(3)
Se(6)-K(1)#10	3.298(3)	K(1)-K(1)#8	4.562(5)
Se(6)-K(2)#5	3.496(3)	K(1)-K(3)#9	4.662(4)
Se(6)-K(3)#9	3.531(3)		
Se(6)-K(3)#4	3.922(3)	Se(8)-La(1)-Se(4)	145.30(3)
Se(7)-P(1)	2.167(2)	Se(8)-La(1)-Se(5)	80.20(3)
Se(7)-K(1)#8	3.288(3)	Se(4)-La(1)-Se(5)	96.18(3)
Se(7)-K(3)#2	3.336(3)	Se(8)-La(1)-Se(1)#1	142.40(3)
Se(7)-K(1)	3.366(3)	Se(4)-La(1)-Se(1)#1	65.19(3)
Se(7)-K(2)	3.396(3)	Se(5)-La(1)-Se(1)#1	127.23(3)
Se(8)-P(1)#2	2.200(3)	Se(8)-La(1)-Se(3)#2	71.50(3)
Se(8)-K(3)	3.566(3)	Se(4)-La(1)-Se(3)#2	87.48(3)
Se(8)-K(2)#7	3.613(3)	Se(5)-La(1)-Se(3)#2	133.26(3)
Se(8)-K(3)#4	3.798(3)	Se(1)#1-La(1)-Se(3)#2	96.54(3)
K(3)-Se(7)#2	3.336(3)	Se(8)-La(1)-Se(1)	74.48(3)

Se(4)-La(1)-Se(1)	135.95(3)	P(1)-Se(3)-La(1)	89.15(6)
Se(5)-La(1)-Se(1)	67.02(3)	La(1)#2-Se(3)-La(1)	108.89(3)
Se(1)#1-La(1)-Se(1)	92.16(3)	P(1)-Se(3)-K(2)#7	170.24(8)
Se(3)#2-La(1)-Se(1)	134.29(3)	La(1)#2-Se(3)-K(2)#7	86.93(6)
Se(8)-La(1)-Se(2)	78.45(3)	La(1)-Se(3)-K(2)#7	100.30(5)
Se(4)-La(1)-Se(2)	124.51(3)	P(1)-Se(3)-K(1)#8	83.59(7)
Se(5)-La(1)-Se(2)	132.40(3)	La(1)#2-Se(3)-K(1)#8	104.05(4)
Se(1)#1-La(1)-Se(2)	64.06(3)	La(1)-Se(3)-K(1)#8	145.92(5)
Se(3)#2-La(1)-Se(2)	77.47(3)	K(2)#7-Se(3)-K(1)#8	89.83(6)
Se(1)-La(1)-Se(2)	66.45(3)	P(1)-Se(4)-La(1)	97.17(7)
Se(8)-La(1)-Se(3)	80.40(3)	P(1)-Se(4)-K(2)	83.68(8)
Se(4)-La(1)-Se(3)	66.54(2)	La(1)-Se(4)-K(2)	173.41(7)
Se(5)-La(1)-Se(3)	68.01(3)	P(1)-Se(4)-K(2)#3	96.31(9)
Se(1)#1-La(1)-Se(3)	130.54(3)	La(1)-Se(4)-K(2)#3	89.09(5)
Se(3)#2-La(1)-Se(3)	71.11(3)	K(2)-Se(4)-K(2)#3	97.33(4)
Se(1)-La(1)-Se(3)	131.27(3)	P(1)-Se(4)-K(1)	77.32(8)
Se(2)-La(1)-Se(3)	146.34(3)	La(1)-Se(4)-K(1)	88.61(5)
Se(8)-La(1)-K(2)#3	120.77(5)	K(2)-Se(4)-K(1)	85.20(7)
Se(4)-La(1)-K(2)#3	48.70(4)	K(2)#3-Se(4)-K(1)	172.90(7)
Se(5)-La(1)-K(2)#3	143.16(4)	P(2)-Se(5)-La(1)	81.12(7)
Se(1)#1-La(1)-K(2)#3	54.92(4)	P(2)-Se(5)-K(1)	98.96(8)
Se(3)#2-La(1)-K(2)#3	49.52(5)	La(1)-Se(5)-K(1)	91.76(5)
Se(1)-La(1)-K(2)#3	143.69(4)	P(2)-Se(5)-K(3)#4	76.91(8)
Se(2)-La(1)-K(2)#3	83.71(4)	La(1)-Se(5)-K(3)#4	99.71(5)
Se(3)-La(1)-K(2)#3	85.00(4)	K(1)-Se(5)-K(3)#4	166.96(7)
P(2)-Se(1)-La(1)#1	96.76(7)	P(2)-Se(5)-K(3)#9	86.51(8)
P(2)-Se(1)-La(1)	78.10(7)	La(1)-Se(5)-K(3)#9	163.47(5)
La(1)#1-Se(1)-La(1)	87.84(3)	K(1)-Se(5)-K(3)#9	79.33(6)
P(2)-Se(1)-K(3)#4	80.44(8)	K(3)#4-Se(5)-K(3)#9	88.02(4)
La(1)#1-Se(1)-K(3)#4	169.68(6)	P(2)-Se(6)-K(1)#10	87.24(8)
La(1)-Se(1)-K(3)#4	101.19(5)	P(2)-Se(6)-K(2)#5	95.33(8)
P(2)-Se(1)-K(2)#5	86.77(8)	K(1)#10-Se(6)-K(2)#5	98.58(7)
La(1)#1-Se(1)-K(2)#5	82.17(5)	P(2)-Se(6)-K(3)#9	97.17(8)
La(1)-Se(1)-K(2)#5	160.77(6)	K(1)#10-Se(6)-K(3)#9	93.10(7)
K(3)#4-Se(1)-K(2)#5	87.74(6)	K(2)#5-Se(6)-K(3)#9	163.26(7)
P(2)#1-Se(2)-La(1)	93.15(7)	P(2)-Se(6)-K(3)#4	70.20(8)
P(2)#1-Se(2)-K(1)#6	83.74(8)	K(1)#10-Se(6)-K(3)#4	157.43(7)
La(1)-Se(2)-K(1)#6	110.60(5)	K(2)#5-Se(6)-K(3)#4	84.80(7)
P(2)#1-Se(2)-K(3)	162.40(9)	K(3)#9-Se(6)-K(3)#4	89.01(6)
La(1)-Se(2)-K(3)	103.00(5)	P(1)-Se(7)-K(1)#8	98.38(8)
K(1)#6-Se(2)-K(3)	84.05(7)	P(1)-Se(7)-K(3)#2	96.01(9)
P(2)#1-Se(2)-K(1)#1	84.68(7)	K(1)#8-Se(7)-K(3)#2	89.48(7)
La(1)-Se(2)-K(1)#1	156.07(5)	P(1)-Se(7)-K(1)	82.59(8)
K(1)#6-Se(2)-K(1)#1	92.89(6)	K(1)#8-Se(7)-K(1)	86.54(6)
K(3)-Se(2)-K(1)#1	83.33(6)	K(3)#2-Se(7)-K(1)	175.54(7)
P(1)-Se(3)-La(1)#2	87.69(7)	P(1)-Se(7)-K(2)	84.89(8)

K(1)#8-Se(7)-K(2)	173.98(8)	Se(5)#11-K(3)-Se(5)#6	131.62(9)
K(3)#2-Se(7)-K(2)	95.22(7)	P(2)#11-K(3)-Se(5)#6	136.06(9)
K(1)-Se(7)-K(2)	88.88(7)	Se(8)#11-K(3)-Se(5)#6	67.33(6)
P(1)#2-Se(8)-La(1)	91.18(7)	Se(7)#2-K(3)-Se(6)#11	149.26(8)
P(1)#2-Se(8)-K(3)	89.19(8)	Se(1)#11-K(3)-Se(6)#11	58.23(5)
La(1)-Se(8)-K(3)	108.12(5)	Se(6)#6-K(3)-Se(6)#11	96.08(6)
P(1)#2-Se(8)-K(2)#7	91.52(8)	Se(2)-K(3)-Se(6)#11	99.67(8)
La(1)-Se(8)-K(2)#7	103.73(6)	Se(8)-K(3)-Se(6)#11	88.43(7)
K(3)-Se(8)-K(2)#7	148.13(8)	Se(5)#11-K(3)-Se(6)#11	56.92(5)
P(1)#2-Se(8)-K(3)#4	171.38(9)	P(2)#11-K(3)-Se(6)#11	32.43(5)
La(1)-Se(8)-K(3)#4	97.11(5)	Se(8)#11-K(3)-Se(6)#11	111.25(7)
K(3)-Se(8)-K(3)#4	90.48(5)	Se(5)#6-K(3)-Se(6)#11	153.13(7)
K(2)#7-Se(8)-K(3)#4	84.24(6)	Se(7)#2-K(3)-K(1)#6	44.84(5)
Se(7)#2-K(3)-Se(1)#11	134.35(10)	Se(1)#11-K(3)-K(1)#6	145.45(9)
Se(7)#2-K(3)-Se(6)#6	114.62(9)	Se(6)#6-K(3)-K(1)#6	82.95(6)
Se(1)#11-K(3)-Se(6)#6	67.07(5)	Se(2)-K(3)-K(1)#6	46.60(5)
Se(7)#2-K(3)-Se(2)	79.34(6)	Se(8)-K(3)-K(1)#6	82.05(6)
Se(1)#11-K(3)-Se(2)	144.54(9)	Se(5)#11-K(3)-K(1)#6	146.15(7)
Se(6)#6-K(3)-Se(2)	90.78(6)	P(2)#11-K(3)-K(1)#6	178.48(10)
Se(7)#2-K(3)-Se(8)	62.39(5)	Se(8)#11-K(3)-K(1)#6	102.68(7)
Se(1)#11-K(3)-Se(8)	131.06(8)	Se(5)#6-K(3)-K(1)#6	45.25(4)
Se(6)#6-K(3)-Se(8)	159.18(9)	Se(6)#11-K(3)-K(1)#6	146.07(8)
Se(2)-K(3)-Se(8)	68.41(5)	Se(7)#2-K(3)-K(1)#1	111.53(7)
Se(7)#2-K(3)-Se(5)#11	102.21(7)	Se(1)#11-K(3)-K(1)#1	98.04(6)
Se(1)#11-K(3)-Se(5)#11	59.15(5)	Se(6)#6-K(3)-K(1)#1	41.60(4)
Se(6)#6-K(3)-Se(5)#11	126.21(7)	Se(2)-K(3)-K(1)#1	51.25(5)
Se(2)-K(3)-Se(5)#11	135.19(9)	Se(8)-K(3)-K(1)#1	118.37(8)
Se(8)-K(3)-Se(5)#11	72.96(5)	Se(5)#11-K(3)-K(1)#1	145.90(8)
Se(7)#2-K(3)-P(2)#11	136.00(9)	P(2)#11-K(3)-K(1)#1	112.44(7)
Se(1)#11-K(3)-P(2)#11	35.52(5)	Se(8)#11-K(3)-K(1)#1	130.87(8)
Se(6)#6-K(3)-P(2)#11	97.30(7)	Se(5)#6-K(3)-K(1)#1	74.20(5)
Se(2)-K(3)-P(2)#11	131.88(10)	Se(6)#11-K(3)-K(1)#1	90.04(6)
Se(8)-K(3)-P(2)#11	97.33(8)	K(1)#6-K(3)-K(1)#1	66.78(6)
Se(5)#11-K(3)-P(2)#11	34.36(5)	Se(7)-P(1)-Se(8)#2	110.15(11)
Se(7)#2-K(3)-Se(8)#11	71.55(6)	Se(7)-P(1)-Se(4)	109.87(11)
Se(1)#11-K(3)-Se(8)#11	62.82(5)	Se(8)#2-P(1)-Se(4)	108.64(11)
Se(6)#6-K(3)-Se(8)#11	90.93(7)	Se(7)-P(1)-Se(3)	113.09(11)
Se(2)-K(3)-Se(8)#11	148.66(9)	Se(8)#2-P(1)-Se(3)	109.49(11)
Se(8)-K(3)-Se(8)#11	106.40(7)	Se(4)-P(1)-Se(3)	105.43(10)
Se(5)#11-K(3)-Se(8)#11	64.48(5)	Se(7)-P(1)-K(1)	62.57(8)
P(2)#11-K(3)-Se(8)#11	78.83(7)	Se(8)#2-P(1)-K(1)	168.20(11)
Se(7)#2-K(3)-Se(5)#6	57.42(5)	Se(4)-P(1)-K(1)	67.81(8)
Se(1)#11-K(3)-Se(5)#6	101.80(7)	Se(3)-P(1)-K(1)	82.26(8)
Se(6)#6-K(3)-Se(5)#6	57.70(5)	Se(7)-P(1)-K(2)	61.14(7)
Se(2)-K(3)-Se(5)#6	87.45(6)	Se(8)#2-P(1)-K(2)	91.60(9)
Se(8)-K(3)-Se(5)#6	118.12(7)	Se(4)-P(1)-K(2)	61.77(7)

Se(3)-P(1)-K(2)	158.41(11)	La(1)#12-K(2)-K(1)	132.74(8)
K(1)-P(1)-K(2)	76.78(8)	Se(7)-K(2)-K(3)#2	41.92(5)
Se(7)-K(2)-Se(4)	63.28(5)	Se(4)-K(2)-K(3)#2	88.46(7)
Se(7)-K(2)-Se(4)#12	108.09(7)	Se(4)#12-K(2)-K(3)#2	108.57(6)
Se(4)-K(2)-Se(4)#12	143.13(11)	Se(3)#13-K(2)-K(3)#2	93.60(7)
Se(7)-K(2)-Se(3)#13	135.23(10)	Se(6)#14-K(2)-K(3)#2	135.73(9)
Se(4)-K(2)-Se(3)#13	135.91(9)	Se(8)#13-K(2)-K(3)#2	49.47(5)
Se(4)#12-K(2)-Se(3)#13	76.98(6)	Se(1)#14-K(2)-K(3)#2	163.42(7)
Se(7)-K(2)-Se(6)#14	128.90(8)	P(1)-K(2)-K(3)#2	54.50(6)
Se(4)-K(2)-Se(6)#14	65.66(5)	La(1)#12-K(2)-K(3)#2	124.32(7)
Se(4)#12-K(2)-Se(6)#14	113.56(8)	K(1)-K(2)-K(3)#2	87.20(6)
Se(3)#13-K(2)-Se(6)#14	83.30(6)	Se(7)-K(2)-K(3)#1	106.08(8)
Se(7)-K(2)-Se(8)#13	73.29(5)	Se(4)-K(2)-K(3)#1	64.94(6)
Se(4)-K(2)-Se(8)#13	135.06(8)	Se(4)#12-K(2)-K(3)#1	85.75(7)
Se(4)#12-K(2)-Se(8)#13	60.96(5)	Se(3)#13-K(2)-K(3)#1	118.69(7)
Se(3)#13-K(2)-Se(8)#13	71.20(6)	Se(6)#14-K(2)-K(3)#1	51.20(5)
Se(6)#14-K(2)-Se(8)#13	154.50(9)	Se(8)#13-K(2)-K(3)#1	143.23(9)
Se(7)-K(2)-Se(1)#14	139.83(10)	Se(1)#14-K(2)-K(3)#1	43.43(5)
Se(4)-K(2)-Se(1)#14	106.58(7)	P(1)-K(2)-K(3)#1	95.60(7)
Se(4)#12-K(2)-Se(1)#14	55.08(5)	La(1)#12-K(2)-K(3)#1	86.32(6)
Se(3)#13-K(2)-Se(1)#14	80.57(6)	K(1)-K(2)-K(3)#1	61.11(6)
Se(6)#14-K(2)-Se(1)#14	59.39(5)	K(3)#2-K(2)-K(3)#1	147.22(8)
Se(8)#13-K(2)-Se(1)#14	114.06(7)	Se(6)-P(2)-Se(5)	111.99(11)
Se(7)-K(2)-P(1)	33.97(4)	Se(6)-P(2)-Se(2)#1	119.67(12)
Se(4)-K(2)-P(1)	34.56(4)	Se(5)-P(2)-Se(2)#1	107.90(11)
Se(4)#12-K(2)-P(1)	140.71(9)	Se(6)-P(2)-Se(1)	110.88(11)
Se(3)#13-K(2)-P(1)	133.11(11)	Se(5)-P(2)-Se(1)	104.36(11)
Se(6)#14-K(2)-P(1)	96.92(7)	Se(2)#1-P(2)-Se(1)	100.47(10)
Se(8)#13-K(2)-P(1)	100.78(7)	Se(6)-P(2)-K(3)#4	77.37(9)
Se(1)#14-K(2)-P(1)	139.01(9)	Se(5)-P(2)-K(3)#4	68.73(8)
Se(7)-K(2)-La(1)#12	147.95(7)	Se(2)#1-P(2)-K(3)#4	161.32(11)
Se(4)-K(2)-La(1)#12	145.69(7)	Se(1)-P(2)-K(3)#4	64.04(8)
Se(4)#12-K(2)-La(1)#12	42.22(3)	Se(6)-P(2)-K(1)#10	58.78(7)
Se(3)#13-K(2)-La(1)#12	43.55(3)	Se(5)-P(2)-K(1)#10	124.97(10)
Se(6)#14-K(2)-La(1)#12	82.02(5)	Se(2)#1-P(2)-K(1)#10	61.51(7)
Se(8)#13-K(2)-La(1)#12	79.22(5)	Se(1)-P(2)-K(1)#10	130.29(10)
Se(1)#14-K(2)-La(1)#12	42.90(3)	K(3)#4-P(2)-K(1)#10	136.14(9)
P(1)-K(2)-La(1)#12	176.53(10)	Se(7)#8-K(1)-Se(6)#10	139.62(8)
Se(7)-K(2)-K(1)	45.30(5)	Se(7)#8-K(1)-Se(7)	93.46(6)
Se(4)-K(2)-K(1)	48.70(5)	Se(6)#10-K(1)-Se(7)	91.74(7)
Se(4)#12-K(2)-K(1)	98.38(8)	Se(7)#8-K(1)-Se(5)	63.71(5)
Se(3)#13-K(2)-K(1)	175.31(9)	Se(6)#10-K(1)-Se(5)	145.81(8)
Se(6)#14-K(2)-K(1)	99.35(7)	Se(7)-K(1)-Se(5)	114.55(7)
Se(8)#13-K(2)-K(1)	106.06(7)	Se(7)#8-K(1)-Se(2)#9	82.25(6)
Se(1)#14-K(2)-K(1)	97.40(8)	Se(6)#10-K(1)-Se(2)#9	68.49(5)
P(1)-K(2)-K(1)	50.65(6)	Se(7)-K(1)-Se(2)#9	139.78(8)

Se(5)-K(1)-Se(2)#9	99.33(7)
Se(7)#8-K(1)-Se(4)	125.89(8)
Se(6)#10-K(1)-Se(4)	91.52(6)
Se(7)-K(1)-Se(4)	62.03(5)
Se(5)-K(1)-Se(4)	82.92(6)
Se(2)#9-K(1)-Se(4)	147.69(8)
Se(7)#8-K(1)-P(1)	97.93(7)
Se(6)#10-K(1)-P(1)	108.68(8)
Se(7)-K(1)-P(1)	34.84(4)
Se(5)-K(1)-P(1)	85.54(7)
Se(2)#9-K(1)-P(1)	174.59(9)
Se(4)-K(1)-P(1)	34.87(4)
Se(7)#8-K(1)-Se(3)#8	61.79(4)
Se(6)#10-K(1)-Se(3)#8	81.13(5)
Se(7)-K(1)-Se(3)#8	75.08(5)
Se(5)-K(1)-Se(3)#8	125.11(7)
Se(2)#9-K(1)-Se(3)#8	67.67(5)
Se(4)-K(1)-Se(3)#8	136.26(7)
P(1)-K(1)-Se(3)#8	107.60(7)
Se(7)#8-K(1)-P(2)#10	114.17(8)
Se(6)#10-K(1)-P(2)#10	33.98(5)
Se(7)-K(1)-P(2)#10	120.44(8)
Se(5)-K(1)-P(2)#10	124.92(8)
Se(2)#9-K(1)-P(2)#10	34.76(5)
Se(4)-K(1)-P(2)#10	119.87(7)
P(1)-K(1)-P(2)#10	142.66(9)
Se(3)#8-K(1)-P(2)#10	74.25(6)
Se(7)#8-K(1)-Se(2)#1	117.87(7)
Se(6)#10-K(1)-Se(2)#1	88.69(6)
Se(7)-K(1)-Se(2)#1	128.60(7)
Se(5)-K(1)-Se(2)#1	58.11(4)
Se(2)#9-K(1)-Se(2)#1	87.11(6)
Se(4)-K(1)-Se(2)#1	66.58(5)
P(1)-K(1)-Se(2)#1	97.53(7)
Se(3)#8-K(1)-Se(2)#1	154.75(7)
P(2)#10-K(1)-Se(2)#1	84.39(6)
Se(7)#8-K(1)-K(1)#8	47.45(5)
Se(6)#10-K(1)-K(1)#8	124.85(9)
Se(7)-K(1)-K(1)#8	46.01(5)
Se(5)-K(1)-K(1)#8	89.28(7)
Se(2)#9-K(1)-K(1)#8	117.80(9)
Se(4)-K(1)-K(1)#8	94.38(8)
P(1)-K(1)-K(1)#8	59.58(6)
Se(3)#8-K(1)-K(1)#8	57.94(5)
P(2)#10-K(1)-K(1)#8	131.99(9)
Se(2)#1-K(1)-K(1)#8	142.88(9)
Se(7)#8-K(1)-K(3)#9	45.68(5)
Se(6)#10-K(1)-K(3)#9	117.48(7)
Se(7)-K(1)-K(3)#9	139.09(7)
Se(5)-K(1)-K(3)#9	55.41(5)
Se(2)#9-K(1)-K(3)#9	49.36(5)
Se(4)-K(1)-K(3)#9	137.51(7)
P(1)-K(1)-K(3)#9	133.82(8)
Se(3)#8-K(1)-K(3)#9	81.58(5)
P(2)#10-K(1)-K(3)#9	83.50(7)
Se(2)#1-K(1)-K(3)#9	82.79(5)
K(1)#8-K(1)-K(3)#9	93.10(8)

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y,-z+2 #2 -x+1,-y,-z+2 #3 x,-y-1/2,z+1/2

#4 x,-y+1/2,z-1/2 #5 -x,y+1/2,-z+3/2 #6 x,y,z+1

#7 -x+1,y+1/2,-z+3/2 #8 -x+1,-y,-z+1 #9 x,y,z-1

#10 -x,-y,-z+1 #11 x,-y+1/2,z+1/2 #12 x,-y-1/2,z-1/2

#13 -x+1,y-1/2,-z+3/2 #14 -x,y-1/2,-z+3/2

Table B.8. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $K_3La(PSe_4)_2$. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
La(1)	20(1)	13(1)	16(1)	-1(1)	10(1)	0(1)
Se(1)	25(1)	22(1)	18(1)	-4(1)	11(1)	-5(1)
Se(2)	36(1)	14(1)	21(1)	0(1)	10(1)	1(1)
Se(3)	22(1)	13(1)	21(1)	1(1)	7(1)	-1(1)
Se(4)	22(1)	19(1)	33(1)	-7(1)	16(1)	-5(1)
Se(5)	21(1)	34(1)	19(1)	3(1)	11(1)	-3(1)
Se(6)	35(1)	21(1)	28(1)	8(1)	4(1)	6(1)
Se(7)	32(1)	27(1)	16(1)	-5(1)	12(1)	-1(1)
Se(8)	36(1)	13(1)	25(1)	0(1)	1(1)	3(1)
K(3)	40(1)	24(1)	63(2)	-2(1)	21(1)	6(1)
P(1)	19(1)	16(1)	15(1)	-2(1)	7(1)	-2(1)
K(2)	71(2)	24(1)	45(2)	-12(1)	32(1)	-12(1)
P(2)	21(1)	16(1)	14(1)	1(1)	7(1)	1(1)
K(1)	36(1)	29(1)	29(1)	0(1)	-2(1)	-2(1)

Table B.9. Crystal data and structure refinement for $K_4La_{0.67}(PSe_4)_2$.

Identification code	ibam	
Empirical formula	$K_4La_{0.67}(PSe_4)_2$	
Formula weight	943.09	
Temperature	159(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Ibam	
Unit cell dimensions	a = 19.0962(2) Å	α= 90°.
	b = 9.14080(10) Å	β= 90°.
	c = 10.2588(2) Å	γ = 90°.
Volume	1790.72(4) $Å^3$	
Z	4	
Density (calculated)	3.498 Mg/m^3	
Absorption coefficient	18.957 mm^{-1}	
F(000)	1665	
Crystal size	0.06 x 0.09 x 0.15 mm^3	
Theta range for data collection	2.13 to 28.26°.	
Index ranges	-25<=h<=24, -8<=k<=12, -13<=l<=13	
Reflections collected	5519	
Independent reflections	1150 [R(int) = 0.0413]	
Absorption correction	SADABS	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1150 / 0 / 42	
Goodness-of-fit on F^2	1.106	
Final R indices [I>2sigma(I)]	R1 = 0.0353, wR2 = 0.0755	
R indices (all data)	R1 = 0.0473, wR2 = 0.0812	
Largest diff. peak and hole	1.367 and -1.477 $e.Å^{-3}$	

Table B.10. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for $K_4La_{0.67}(PSe_4)_2$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
P(1)	3710(1)	2054(2)	5000	15(1)
La(1)	5000	0	2500	14(1)
Se(1)	4218(1)	3012(1)	3271(1)	23(1)
Se(2)	3939(1)	324(1)	0	27(1)
Se(3)	2586(1)	2530(1)	5000	24(1)
K(2)	2572(1)	0	2500	39(1)
K(1)	4168(1)	3812(2)	0	32(1)

Table B.11. Bond lengths [Å] and angles [°] for $K_4La_{0.67}(PSe_4)_2$.

P(1)-Se(3)	2.190(2)	K(1)-Se(1)#4	3.631(2)
P(1)-Se(1)	2.2029(13)	K(1)-Se(1)#17	3.631(2)
P(1)-Se(1)#1	2.2029(13)	K(1)-K(1)#18	3.851(4)
P(1)-Se(2)#2	2.218(2)	K(1)-K(2)#19	4.335(3)
P(1)-K(2)	3.850(2)	K(1)-K(2)#11	4.335(3)
P(1)-K(2)#1	3.850(2)		
La(1)-Se(1)#3	3.2305(6)	Se(3)-P(1)-Se(1)	110.66(6)
La(1)-Se(1)	3.2305(6)	Se(3)-P(1)-Se(1)#1	110.66(6)
La(1)-Se(1)#4	3.2306(6)	Se(1)-P(1)-Se(1)#1	107.22(9)
La(1)-Se(1)#5	3.2306(6)	Se(3)-P(1)-Se(2)#2	112.86(9)
La(1)-Se(2)#2	3.2812(5)	Se(1)-P(1)-Se(2)#2	107.60(6)
La(1)-Se(2)	3.2812(5)	Se(1)#1-P(1)-Se(2)#2	107.60(6)
La(1)-Se(2)#4	3.2812(5)	Se(3)-P(1)-K(2)	62.85(5)
La(1)-Se(2)#6	3.2812(5)	Se(1)-P(1)-K(2)	84.62(3)
La(1)-K(1)#2	4.609(2)	Se(1)#1-P(1)-K(2)	168.13(7)
La(1)-K(1)#4	4.609(2)	Se(2)#2-P(1)-K(2)	68.51(5)
La(1)-K(1)#6	4.609(2)	Se(3)-P(1)-K(2)#1	62.85(5)
La(1)-K(1)	4.609(2)	Se(1)-P(1)-K(2)#1	168.13(7)
Se(1)-K(1)#7	3.404(2)	Se(1)#1-P(1)-K(2)#1	84.62(3)
Se(1)-K(1)	3.4361(7)	Se(2)#2-P(1)-K(2)#1	68.51(5)
Se(1)-K(1)#4	3.631(2)	K(2)-P(1)-K(2)#1	83.53(6)
Se(2)-P(1)#8	2.218(2)	Se(1)#3-La(1)-Se(1)	124.93(2)
Se(2)-K(1)	3.217(2)	Se(1)#3-La(1)-Se(1)#4	151.64(2)
Se(2)-La(1)#6	3.2813(5)	Se(1)-La(1)-Se(1)#4	63.09(2)
Se(2)-K(2)#9	3.672(2)	Se(1)#3-La(1)-Se(1)#5	63.09(2)
Se(2)-K(2)	3.672(2)	Se(1)-La(1)-Se(1)#5	151.64(2)
Se(3)-K(2)#10	3.4304(6)	Se(1)#4-La(1)-Se(1)#5	124.93(2)
Se(3)-K(2)#11	3.4304(6)	Se(1)#3-La(1)-Se(2)#2	80.17(2)
Se(3)-K(2)	3.4532(6)	Se(1)-La(1)-Se(2)#2	66.43(2)
Se(3)-K(2)#1	3.4532(6)	Se(1)#4-La(1)-Se(2)#2	123.62(2)
Se(3)-K(1)#11	3.566(2)	Se(1)#5-La(1)-Se(2)#2	90.97(2)
K(2)-Se(3)#12	3.4304(6)	Se(1)#3-La(1)-Se(2)	66.43(2)
K(2)-Se(3)#11	3.4304(6)	Se(1)-La(1)-Se(2)	80.17(2)
K(2)-Se(3)#8	3.4532(6)	Se(1)#4-La(1)-Se(2)	90.97(2)
K(2)-Se(2)#2	3.672(2)	Se(1)#5-La(1)-Se(2)	123.62(2)
K(2)-P(1)#8	3.850(2)	Se(2)#2-La(1)-Se(2)	103.78(2)
K(2)-K(1)#13	4.335(3)	Se(1)#3-La(1)-Se(2)#4	123.62(2)
K(2)-K(1)#11	4.335(3)	Se(1)-La(1)-Se(2)#4	90.97(2)
K(2)-K(2)#14	4.5786(3)	Se(1)#4-La(1)-Se(2)#4	80.17(2)
K(2)-K(2)#11	4.5786(3)	Se(1)#5-La(1)-Se(2)#4	66.43(2)
K(1)-Se(1)#15	3.404(2)	Se(2)#2-La(1)-Se(2)#4	77.18(2)
K(1)-Se(1)#16	3.404(2)	Se(2)-La(1)-Se(2)#4	169.64(3)
K(1)-Se(1)#9	3.4361(7)	Se(1)#3-La(1)-Se(2)#6	90.97(2)
K(1)-Se(3)#11	3.566(2)	Se(1)-La(1)-Se(2)#6	123.62(2)

Se(1)#4-La(1)-Se(2)#6	66.43(2)	P(1)-Se(1)-K(1)	149.15(6)
Se(1)#5-La(1)-Se(2)#6	80.17(2)	La(1)-Se(1)-K(1)	87.42(4)
Se(2)#2-La(1)-Se(2)#6	169.64(3)	K(1)#7-Se(1)-K(1)	109.06(2)
Se(2)-La(1)-Se(2)#6	77.18(2)	P(1)-Se(1)-K(1)#4	93.49(5)
Se(2)#4-La(1)-Se(2)#6	103.78(2)	La(1)-Se(1)-K(1)#4	84.18(3)
Se(1)#3-La(1)-K(1)#2	48.14(2)	K(1)#7-Se(1)-K(1)#4	66.28(6)
Se(1)-La(1)-K(1)#2	110.39(3)	K(1)-Se(1)-K(1)#4	117.25(3)
Se(1)#4-La(1)-K(1)#2	160.04(2)	P(1)#8-Se(2)-K(1)	176.37(7)
Se(1)#5-La(1)-K(1)#2	51.60(3)	P(1)#8-Se(2)-La(1)	91.92(4)
Se(2)#2-La(1)-K(1)#2	44.27(3)	K(1)-Se(2)-La(1)	90.34(3)
Se(2)-La(1)-K(1)#2	106.88(3)	P(1)#8-Se(2)-La(1)#6	91.92(4)
Se(2)#4-La(1)-K(1)#2	81.15(2)	K(1)-Se(2)-La(1)#6	90.34(3)
Se(2)#6-La(1)-K(1)#2	125.42(3)	La(1)-Se(2)-La(1)#6	102.82(2)
Se(1)#3-La(1)-K(1)#4	160.05(2)	P(1)#8-Se(2)-K(2)#9	77.31(4)
Se(1)-La(1)-K(1)#4	51.60(3)	K(1)-Se(2)-K(2)#9	100.15(3)
Se(1)#4-La(1)-K(1)#4	48.14(2)	La(1)-Se(2)-K(2)#9	167.82(3)
Se(1)#5-La(1)-K(1)#4	110.39(3)	La(1)#6-Se(2)-K(2)#9	83.44(3)
Se(2)#2-La(1)-K(1)#4	81.15(2)	P(1)#8-Se(2)-K(2)	77.31(4)
Se(2)-La(1)-K(1)#4	125.42(3)	K(1)-Se(2)-K(2)	100.15(3)
Se(2)#4-La(1)-K(1)#4	44.27(3)	La(1)-Se(2)-K(2)	83.44(3)
Se(2)#6-La(1)-K(1)#4	106.88(3)	La(1)#6-Se(2)-K(2)	167.82(3)
K(1)#2-La(1)-K(1)#4	112.38(3)	K(2)#9-Se(2)-K(2)	88.59(6)
Se(1)#3-La(1)-K(1)#6	51.60(3)	P(1)-Se(3)-K(2)#10	102.51(6)
Se(1)-La(1)-K(1)#6	160.05(2)	P(1)-Se(3)-K(2)#11	102.51(6)
Se(1)#4-La(1)-K(1)#6	110.39(3)	K(2)#10-Se(3)-K(2)#11	96.77(2)
Se(1)#5-La(1)-K(1)#6	48.14(2)	P(1)-Se(3)-K(2)	82.80(6)
Se(2)#2-La(1)-K(1)#6	125.42(3)	K(2)#10-Se(3)-K(2)	174.48(3)
Se(2)-La(1)-K(1)#6	81.15(2)	K(2)#11-Se(3)-K(2)	83.386(4)
Se(2)#4-La(1)-K(1)#6	106.88(3)	P(1)-Se(3)-K(2)#1	82.80(6)
Se(2)#6-La(1)-K(1)#6	44.27(3)	K(2)#10-Se(3)-K(2)#1	83.386(4)
K(1)#2-La(1)-K(1)#6	81.79(4)	K(2)#11-Se(3)-K(2)#1	174.48(3)
K(1)#4-La(1)-K(1)#6	139.65(5)	K(2)-Se(3)-K(2)#1	95.92(2)
Se(1)#3-La(1)-K(1)	110.39(3)	P(1)-Se(3)-K(1)#11	148.44(7)
Se(1)-La(1)-K(1)	48.14(2)	K(2)#10-Se(3)-K(1)#11	98.28(5)
Se(1)#4-La(1)-K(1)	51.60(3)	K(2)#11-Se(3)-K(1)#11	98.28(5)
Se(1)#5-La(1)-K(1)	160.05(2)	K(2)-Se(3)-K(1)#11	76.26(5)
Se(2)#2-La(1)-K(1)	106.88(3)	K(2)#1-Se(3)-K(1)#11	76.26(5)
Se(2)-La(1)-K(1)	44.27(3)	Se(3)#12-K(2)-Se(3)#11	169.93(9)
Se(2)#4-La(1)-K(1)	125.42(3)	Se(3)#12-K(2)-Se(3)	83.465(4)
Se(2)#6-La(1)-K(1)	81.15(2)	Se(3)#11-K(2)-Se(3)	96.614(4)
K(1)#2-La(1)-K(1)	139.65(5)	Se(3)#12-K(2)-Se(3)#8	96.614(4)
K(1)#4-La(1)-K(1)	81.79(4)	Se(3)#11-K(2)-Se(3)#8	83.465(4)
K(1)#6-La(1)-K(1)	112.38(3)	Se(3)-K(2)-Se(3)#8	179.11(9)
P(1)-Se(1)-La(1)	93.56(5)	Se(3)#12-K(2)-Se(2)	129.62(6)
P(1)-Se(1)-K(1)#7	84.68(5)	Se(3)#11-K(2)-Se(2)	59.15(2)
La(1)-Se(1)-K(1)#7	150.19(4)	Se(3)-K(2)-Se(2)	117.33(5)

Se(3)#8-K(2)-Se(2)	61.95(3)	Se(3)#12-K(2)-K(2)#11	130.68(2)
Se(3)#12-K(2)-Se(2)#2	59.15(2)	Se(3)#11-K(2)-K(2)#11	48.520(12)
Se(3)#11-K(2)-Se(2)#2	129.62(6)	Se(3)-K(2)-K(2)#11	48.093(11)
Se(3)-K(2)-Se(2)#2	61.96(3)	Se(3)#8-K(2)-K(2)#11	131.978(13)
Se(3)#8-K(2)-Se(2)#2	117.33(5)	Se(2)-K(2)-K(2)#11	87.83(4)
Se(2)-K(2)-Se(2)#2	89.34(6)	Se(2)#2-K(2)-K(2)#11	97.07(5)
Se(3)#12-K(2)-P(1)	82.68(3)	P(1)-K(2)-K(2)#11	63.07(4)
Se(3)#11-K(2)-P(1)	103.09(4)	P(1)#8-K(2)-K(2)#11	121.37(6)
Se(3)-K(2)-P(1)	34.35(3)	K(1)#13-K(2)-K(2)#11	101.78(6)
Se(3)#8-K(2)-P(1)	144.77(8)	K(1)#11-K(2)-K(2)#11	72.78(5)
Se(2)-K(2)-P(1)	91.40(6)	K(2)#14-K(2)-K(2)#11	173.13(13)
Se(2)#2-K(2)-P(1)	34.19(3)	Se(2)-K(1)-Se(1)#15	148.11(2)
Se(3)#12-K(2)-P(1)#8	103.09(4)	Se(2)-K(1)-Se(1)#16	148.11(2)
Se(3)#11-K(2)-P(1)#8	82.68(3)	Se(1)#15-K(1)-Se(1)#16	62.80(4)
Se(3)-K(2)-P(1)#8	144.77(8)	Se(2)-K(1)-Se(1)	78.05(3)
Se(3)#8-K(2)-P(1)#8	34.35(3)	Se(1)#15-K(1)-Se(1)	70.84(2)
Se(2)-K(2)-P(1)#8	34.19(3)	Se(1)#16-K(1)-Se(1)	133.60(5)
Se(2)#2-K(2)-P(1)#8	91.40(6)	Se(2)-K(1)-Se(1)#9	78.05(3)
P(1)-K(2)-P(1)#8	111.28(8)	Se(1)#15-K(1)-Se(1)#9	133.60(5)
Se(3)#12-K(2)-K(1)#13	102.13(5)	Se(1)#16-K(1)-Se(1)#9	70.84(2)
Se(3)#11-K(2)-K(1)#13	69.84(4)	Se(1)-K(1)-Se(1)#9	155.22(7)
Se(3)-K(2)-K(1)#13	127.82(7)	Se(2)-K(1)-Se(3)#11	62.11(4)
Se(3)#8-K(2)-K(1)#13	53.04(4)	Se(1)#15-K(1)-Se(3)#11	108.65(6)
Se(2)-K(2)-K(1)#13	98.74(2)	Se(1)#16-K(1)-Se(3)#11	108.65(6)
Se(2)#2-K(2)-K(1)#13	159.71(3)	Se(1)-K(1)-Se(3)#11	87.31(4)
P(1)-K(2)-K(1)#13	161.58(6)	Se(1)#9-K(1)-Se(3)#11	87.31(4)
P(1)#8-K(2)-K(1)#13	85.19(3)	Se(2)-K(1)-Se(1)#4	85.15(5)
Se(3)#12-K(2)-K(1)#11	69.84(4)	Se(1)#15-K(1)-Se(1)#4	83.87(4)
Se(3)#11-K(2)-K(1)#11	102.13(5)	Se(1)#16-K(1)-Se(1)#4	113.72(6)
Se(3)-K(2)-K(1)#11	53.04(4)	Se(1)-K(1)-Se(1)#4	57.07(3)
Se(3)#8-K(2)-K(1)#11	127.82(7)	Se(1)#9-K(1)-Se(1)#4	114.23(6)
Se(2)-K(2)-K(1)#11	159.70(3)	Se(3)#11-K(1)-Se(1)#4	136.73(5)
Se(2)#2-K(2)-K(1)#11	98.74(2)	Se(2)-K(1)-Se(1)#17	85.15(5)
P(1)-K(2)-K(1)#11	85.19(3)	Se(1)#15-K(1)-Se(1)#17	113.72(6)
P(1)#8-K(2)-K(1)#11	161.58(6)	Se(1)#16-K(1)-Se(1)#17	83.87(4)
K(1)#13-K(2)-K(1)#11	79.96(6)	Se(1)-K(1)-Se(1)#17	114.23(6)
Se(3)#12-K(2)-K(2)#14	48.520(12)	Se(1)#9-K(1)-Se(1)#17	57.07(3)
Se(3)#11-K(2)-K(2)#14	130.68(2)	Se(3)#11-K(1)-Se(1)#17	136.73(5)
Se(3)-K(2)-K(2)#14	131.978(13)	Se(1)#4-K(1)-Se(1)#17	58.47(4)
Se(3)#8-K(2)-K(2)#14	48.094(11)	Se(2)-K(1)-K(1)#18	132.13(10)
Se(2)-K(2)-K(2)#14	97.07(5)	Se(1)#15-K(1)-K(1)#18	59.69(5)
Se(2)#2-K(2)-K(2)#14	87.83(4)	Se(1)#16-K(1)-K(1)#18	59.69(5)
P(1)-K(2)-K(2)#14	121.37(6)	Se(1)-K(1)-K(1)#18	95.56(4)
P(1)#8-K(2)-K(2)#14	63.07(4)	Se(1)#9-K(1)-K(1)#18	95.56(4)
K(1)#13-K(2)-K(2)#14	72.78(5)	Se(3)#11-K(1)-K(1)#18	165.76(10)
K(1)#11-K(2)-K(2)#14	101.78(6)	Se(1)#4-K(1)-K(1)#18	54.02(5)

Se(1)#17-K(1)-K(1)#18	54.02(5)
Se(2)-K(1)-K(2)#19	98.31(5)
Se(1)#15-K(1)-K(2)#19	96.67(5)
Se(1)#16-K(1)-K(2)#19	59.98(3)
Se(1)-K(1)-K(2)#19	130.74(6)
Se(1)#9-K(1)-K(2)#19	59.79(3)
Se(3)#11-K(1)-K(2)#19	50.70(3)
Se(1)#4-K(1)-K(2)#19	171.90(5)
Se(1)#17-K(1)-K(2)#19	114.34(2)
K(1)#18-K(1)-K(2)#19	119.42(6)
Se(2)-K(1)-K(2)#11	98.31(5)
Se(1)#15-K(1)-K(2)#11	59.98(3)
Se(1)#16-K(1)-K(2)#11	96.67(5)
Se(1)-K(1)-K(2)#11	59.79(3)
Se(1)#9-K(1)-K(2)#11	130.74(6)
Se(3)#11-K(1)-K(2)#11	50.70(3)
Se(1)#4-K(1)-K(2)#11	114.34(2)
Se(1)#17-K(1)-K(2)#11	171.90(5)
K(1)#18-K(1)-K(2)#11	119.42(6)
K(2)#19-K(1)-K(2)#11	72.55(5)
Se(2)-K(1)-La(1)	45.39(2)
Se(1)#15-K(1)-La(1)	110.19(2)
Se(1)#16-K(1)-La(1)	157.67(6)
Se(1)-K(1)-La(1)	44.44(2)
Se(1)#9-K(1)-La(1)	111.90(5)
Se(3)#11-K(1)-La(1)	93.67(4)
Se(1)#4-K(1)-La(1)	44.21(2)
Se(1)#17-K(1)-La(1)	80.02(4)
K(1)#18-K(1)-La(1)	98.15(6)
K(2)#19-K(1)-La(1)	141.53(5)
K(2)#11-K(1)-La(1)	97.15(2)

Symmetry transformations used to generate equivalent atoms:

#1 x,y,-z+1 #2 x,-y,z+1/2 #3 x+0,-y+0,-z+1/2

#4 -x+1,y+0,-z+1/2 #5 -x+1,-y,z #6 -x+1,-y,-z

#7 x,-y+1,z+1/2 #8 x,-y,z-1/2 #9 x,y,-z #10 -x+1/2,-y+1/2,z+1/2

#11 -x+1/2,-y+1/2,-z+1/2 #12 -x+1/2,y-1/2,-z+1

#13 -x+1/2,y-1/2,-z #14 -x+1/2,-y-1/2,-z+1/2

#15 x+0,-y+1,-z+1/2 #16 x,-y+1,z-1/2 #17 -x+1,y,z-1/2

#18 -x+1,-y+1,-z #19 -x+1/2,-y+1/2,z-1/2

Table B.12. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $K_4La_{0.67}(PSe_4)_2$. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
P(1)	13(1)	14(1)	16(1)	0	0	2(1)
La(1)	14(1)	14(1)	15(1)	0	0	0
Se(1)	34(1)	19(1)	16(1)	3(1)	2(1)	-1(1)
Se(2)	15(1)	14(1)	53(1)	0	0	1(1)
Se(3)	15(1)	27(1)	30(1)	0	0	7(1)
K(2)	60(2)	32(1)	24(1)	-6(1)	0	0
K(1)	42(1)	22(1)	32(1)	0	0	-3(1)

Table B.13. Crystal data and structure refinement for $K_{8.5}La_{1.17}(PSe_4)_4$.

Identification code	ortho	
Empirical formula	$K_{8.5}La_{1.17}(PSe_4)_4$	
Formula weight	1881.42	
Temperature	158(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Ccca	
Unit cell dimensions	a = 18.21330(10) Å	α= 90°.
	b = 38.0914(4) Å	β= 90°.
	c = 10.26650(10) Å	γ = 90°.
Volume	7122.59(11) $Å^3$	
Z	8	
Density (calculated)	3.509 Mg/m^3	
Absorption coefficient	18.919 mm^{-1}	
F(000)	6655	
Crystal size	0.09 x 0.09 x 0.3 mm^3	
Theta range for data collection	1.07 to 28.30°.	
Index ranges	-24<=h<=24, -50<=k<=24, -13<=l<=13	
Reflections collected	21677	
Independent reflections	4392 [R(int) = 0.0855]	
Absorption correction	SADABS	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4392 / 0 / 140	
Goodness-of-fit on F^2	1.092	
Final R indices [I>2sigma(I)]	R1 = 0.0542, wR2 = 0.1143	
R indices (all data)	R1 = 0.1052, wR2 = 0.1324	
Extinction coefficient	0.000111(9)	
Largest diff. peak and hole	1.774 and -1.935 $e.Å^{-3}$	

Table B.14. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for $K_{8.5}La_{1.17}(PSe_4)_4$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
La(1)	0	2500	7500	7(1)
La(2)	-2500	0	7535(1)	8(1)
Se(1)	155(1)	1966(1)	5230(1)	12(1)
Se(2)	1492(1)	2867(1)	6789(1)	14(1)
Se(3)	-1270(1)	1291(1)	5148(1)	17(1)
Se(4)	-1545(1)	2079(1)	3354(1)	17(1)
Se(5)	-4006(1)	394(1)	3306(1)	20(1)
Se(6)	-4011(1)	388(1)	6750(1)	24(1)
Se(7)	-3770(1)	1208(1)	5040(1)	23(1)
Se(8)	-2340(1)	535(1)	5040(1)	32(1)
K(1)	1891(2)	2917(1)	10138(2)	22(1)
K(3)	0	1259(1)	7500	28(1)
K(2)	0	2500	2500	31(2)
K(5)	-2533(1)	1216(1)	7610(2)	29(1)
K(4)	-596(2)	404(1)	5001(2)	31(1)
K(6)	0	1324(2)	2500	42(1)
P(1)	-1037(2)	1845(1)	5085(2)	8(1)
P(2)	-3530(2)	637(1)	5039(2)	15(1)

Table B.15. Bond lengths [Å] and angles [°] for $K_{8.5}La_{1.17}(PSe_4)_4$.

La(1)-Se(1)	3.1079(11)	Se(5)-K(4)#8	3.470(3)
La(1)-Se(1)#1	3.1079(11)	Se(5)-K(4)#6	3.577(4)
La(1)-Se(1)#2	3.1079(11)	Se(5)-K(3)#12	3.851(4)
La(1)-Se(1)#3	3.1079(11)	Se(6)-P(2)	2.179(3)
La(1)-Se(2)#2	3.1413(12)	Se(6)-K(4)#12	3.402(4)
La(1)-Se(2)#1	3.1413(12)	Se(6)-K(4)#5	3.414(3)
La(1)-Se(2)	3.1413(12)	Se(6)-K(4)#6	3.585(4)
La(1)-Se(2)#3	3.1414(12)	Se(7)-P(2)	2.219(5)
La(2)-Se(5)#4	3.2249(14)	Se(7)-K(6)#12	3.405(2)
La(2)-Se(5)#5	3.2250(14)	Se(7)-K(5)#8	3.443(3)
La(2)-Se(6)	3.2261(14)	Se(7)-K(3)#12	3.4439(14)
La(2)-Se(6)#6	3.2262(14)	Se(7)-K(5)	3.469(2)
La(2)-Se(8)#6	3.285(2)	Se(7)-K(1)#10	3.548(4)
La(2)-Se(8)	3.285(2)	Se(8)-P(2)	2.202(5)
La(2)-Se(8)#5	3.293(2)	Se(8)-K(4)	3.215(5)
La(2)-Se(8)#4	3.293(2)	Se(8)-La(2)#11	3.293(2)
La(2)-K(4)#5	4.561(4)	Se(8)-K(5)#8	3.608(4)
La(2)-K(4)#4	4.561(4)	Se(8)-K(5)	3.718(4)
La(2)-K(4)#6	4.600(4)	K(1)-Se(1)#3	3.215(4)
La(2)-K(4)	4.600(4)	K(1)-Se(4)#13	3.361(3)
Se(1)-P(1)	2.223(4)	K(1)-Se(4)#14	3.387(4)
Se(1)-K(1)#3	3.215(4)	K(1)-Se(2)#15	3.404(4)
Se(1)-K(2)	3.4755(12)	K(1)-Se(7)#14	3.547(4)
Se(1)-K(3)	3.570(4)	K(1)-Se(4)#1	3.600(4)
Se(1)-K(6)	3.729(4)	K(1)-Se(2)#3	3.652(4)
Se(2)-P(1)#2	2.226(3)	K(1)-K(1)#16	3.883(7)
Se(2)-K(1)#7	3.404(4)	K(1)-K(5)#14	4.297(5)
Se(2)-K(1)	3.518(3)	K(1)-K(5)#2	4.362(5)
Se(2)-K(1)#3	3.652(4)	K(1)-K(2)#17	4.501(4)
Se(3)-P(1)	2.154(4)	K(3)-Se(3)#1	3.3454(13)
Se(3)-K(3)	3.3453(13)	K(3)-Se(7)#5	3.4438(14)
Se(3)-K(5)#8	3.411(3)	K(3)-Se(7)#18	3.4439(14)
Se(3)-K(5)	3.429(3)	K(3)-Se(1)#1	3.570(4)
Se(3)-K(6)	3.5714(13)	K(3)-P(1)#1	3.833(4)
Se(3)-K(4)	3.597(5)	K(3)-P(1)	3.833(4)
Se(4)-P(1)	2.193(3)	K(3)-Se(5)#5	3.851(4)
Se(4)-K(2)	3.3551(13)	K(3)-Se(5)#18	3.851(4)
Se(4)-K(1)#9	3.361(3)	K(3)-K(4)	4.287(5)
Se(4)-K(1)#10	3.387(4)	K(3)-K(4)#1	4.287(5)
Se(4)-K(1)#1	3.600(4)	K(2)-Se(4)#19	3.3550(13)
Se(4)-K(5)#8	3.772(4)	K(2)-Se(4)#2	3.3551(13)
Se(5)-P(2)	2.183(3)	K(2)-Se(4)#20	3.3551(13)
Se(5)-La(2)#11	3.2249(14)	K(2)-Se(1)#20	3.4755(12)
Se(5)-K(4)#12	3.379(4)	K(2)-Se(1)#2	3.4755(12)

K(2)-Se(1)#19	3.4755(12)
K(2)-K(6)#2	4.480(6)
K(2)-K(6)	4.480(6)
K(2)-K(1)#9	4.501(4)
K(2)-K(1)#1	4.501(4)
K(5)-Se(3)#5	3.411(3)
K(5)-Se(7)#5	3.443(3)
K(5)-Se(8)#5	3.608(4)
K(5)-Se(4)#5	3.772(4)
K(5)-P(2)#5	3.852(5)
K(5)-K(1)#10	4.298(5)
K(5)-K(1)#2	4.362(5)
K(5)-K(6)#12	4.514(2)
K(4)-Se(5)#18	3.379(4)
K(4)-Se(6)#18	3.402(4)
K(4)-Se(6)#8	3.414(3)
K(4)-Se(5)#5	3.470(3)
K(4)-Se(5)#6	3.578(4)
K(4)-Se(6)#6	3.585(4)
K(4)-K(4)#21	3.769(9)
K(4)-P(2)#18	3.866(6)
K(4)-K(6)	4.477(6)
K(6)-Se(7)#8	3.405(2)
K(6)-Se(7)#18	3.405(2)
K(6)-Se(3)#20	3.5714(13)
K(6)-Se(1)#20	3.729(4)
K(6)-P(1)#20	3.815(4)
K(6)-P(1)	3.815(4)
K(6)-K(4)#20	4.477(6)
K(6)-K(5)#8	4.514(2)
P(1)-Se(2)#2	2.226(3)
P(2)-K(5)#8	3.852(5)
P(2)-K(4)#12	3.866(6)

Se(1)-La(1)-Se(1)#1	98.13(5)
Se(1)-La(1)-Se(1)#2	82.82(5)
Se(1)#1-La(1)-Se(1)#2	169.57(5)
Se(1)-La(1)-Se(1)#3	169.57(5)
Se(1)#1-La(1)-Se(1)#3	82.82(5)
Se(1)#2-La(1)-Se(1)#3	98.13(5)
Se(1)-La(1)-Se(2)#2	67.25(3)
Se(1)#1-La(1)-Se(2)#2	78.72(3)
Se(1)#2-La(1)-Se(2)#2	92.20(3)
Se(1)#3-La(1)-Se(2)#2	122.95(3)
Se(1)-La(1)-Se(2)#1	122.95(3)
Se(1)#1-La(1)-Se(2)#1	92.20(3)
Se(1)#2-La(1)-Se(2)#1	78.72(3)
Se(1)#3-La(1)-Se(2)#1	67.25(3)
Se(2)#2-La(1)-Se(2)#1	60.18(4)
Se(1)-La(1)-Se(2)	92.20(3)
Se(1)#1-La(1)-Se(2)	122.95(3)
Se(1)#2-La(1)-Se(2)	67.25(3)
Se(1)#3-La(1)-Se(2)	78.72(3)
Se(2)#2-La(1)-Se(2)	153.14(4)
Se(2)#1-La(1)-Se(2)	127.24(4)
Se(1)-La(1)-Se(2)#3	78.72(3)
Se(1)#1-La(1)-Se(2)#3	67.25(3)
Se(1)#2-La(1)-Se(2)#3	122.95(3)
Se(1)#3-La(1)-Se(2)#3	92.19(3)
Se(2)#2-La(1)-Se(2)#3	127.24(4)
Se(2)#1-La(1)-Se(2)#3	153.14(4)
Se(2)-La(1)-Se(2)#3	60.18(4)
Se(5)#4-La(2)-Se(5)#5	151.58(5)
Se(5)#4-La(2)-Se(6)	63.22(4)
Se(5)#5-La(2)-Se(6)	124.98(4)
Se(5)#4-La(2)-Se(6)#6	124.98(4)
Se(5)#5-La(2)-Se(6)#6	63.22(4)
Se(6)-La(2)-Se(6)#6	151.07(5)
Se(5)#4-La(2)-Se(8)#6	80.08(4)
Se(5)#5-La(2)-Se(8)#6	123.72(4)
Se(6)-La(2)-Se(8)#6	90.78(4)
Se(6)#6-La(2)-Se(8)#6	66.21(4)
Se(5)#4-La(2)-Se(8)	123.73(4)
Se(5)#5-La(2)-Se(8)	80.08(4)
Se(6)-La(2)-Se(8)	66.22(4)
Se(6)#6-La(2)-Se(8)	90.78(4)
Se(8)#6-La(2)-Se(8)	77.51(6)
Se(5)#4-La(2)-Se(8)#5	91.20(4)
Se(5)#5-La(2)-Se(8)#5	66.15(4)
Se(6)-La(2)-Se(8)#5	80.58(4)
Se(6)#6-La(2)-Se(8)#5	123.63(4)
Se(8)#6-La(2)-Se(8)#5	169.85(6)
Se(8)-La(2)-Se(8)#5	103.51(5)
Se(5)#4-La(2)-Se(8)#4	66.15(4)
Se(5)#5-La(2)-Se(8)#4	91.19(4)
Se(6)-La(2)-Se(8)#4	123.64(4)
Se(6)#6-La(2)-Se(8)#4	80.58(4)
Se(8)#6-La(2)-Se(8)#4	103.51(5)
Se(8)-La(2)-Se(8)#4	169.84(6)
Se(8)#5-La(2)-Se(8)#4	77.30(6)
Se(5)#4-La(2)-K(4)#5	51.28(6)
Se(5)#5-La(2)-K(4)#5	110.67(6)

Se(6)-La(2)-K(4)#5	48.35(5)	P(1)-Se(1)-K(6)	74.98(8)
Se(6)#6-La(2)-K(4)#5	160.36(5)	La(1)-Se(1)-K(6)	170.44(4)
Se(8)#6-La(2)-K(4)#5	125.08(6)	K(1)#3-Se(1)-K(6)	94.48(6)
Se(8)-La(2)-K(4)#5	106.91(6)	K(2)-Se(1)-K(6)	76.81(7)
Se(8)#5-La(2)-K(4)#5	44.81(6)	K(3)-Se(1)-K(6)	89.48(9)
Se(8)#4-La(2)-K(4)#5	80.94(5)	P(1)#2-Se(2)-La(1)	94.54(11)
Se(5)#4-La(2)-K(4)#4	110.67(6)	P(1)#2-Se(2)-K(1)#7	84.45(11)
Se(5)#5-La(2)-K(4)#4	51.28(6)	La(1)-Se(2)-K(1)#7	152.78(7)
Se(6)-La(2)-K(4)#4	160.36(5)	P(1)#2-Se(2)-K(1)	144.90(11)
Se(6)#6-La(2)-K(4)#4	48.35(5)	La(1)-Se(2)-K(1)	88.60(7)
Se(8)#6-La(2)-K(4)#4	106.91(6)	K(1)#7-Se(2)-K(1)	107.78(5)
Se(8)-La(2)-K(4)#4	125.08(6)	P(1)#2-Se(2)-K(1)#3	92.91(10)
Se(8)#5-La(2)-K(4)#4	80.94(5)	La(1)-Se(2)-K(1)#3	86.26(6)
Se(8)#4-La(2)-K(4)#4	44.81(6)	K(1)#7-Se(2)-K(1)#3	66.67(10)
K(4)#5-La(2)-K(4)#4	112.58(8)	K(1)-Se(2)-K(1)#3	122.18(7)
Se(5)#4-La(2)-K(4)#6	48.87(5)	P(1)-Se(3)-K(3)	85.48(12)
Se(5)#5-La(2)-K(4)#6	159.32(5)	P(1)-Se(3)-K(5)#8	100.68(10)
Se(6)-La(2)-K(4)#6	50.90(6)	K(3)-Se(3)-K(5)#8	172.10(12)
Se(6)#6-La(2)-K(4)#6	110.37(6)	P(1)-Se(3)-K(5)	103.69(11)
Se(8)#6-La(2)-K(4)#6	44.33(6)	K(3)-Se(3)-K(5)	85.92(4)
Se(8)-La(2)-K(4)#6	80.40(5)	K(5)#8-Se(3)-K(5)	97.29(4)
Se(8)#5-La(2)-K(4)#6	125.60(6)	P(1)-Se(3)-K(6)	79.36(13)
Se(8)#4-La(2)-K(4)#6	107.54(6)	K(3)-Se(3)-K(6)	95.92(4)
K(4)#5-La(2)-K(4)#6	81.61(9)	K(5)#8-Se(3)-K(6)	80.52(4)
K(4)#4-La(2)-K(4)#6	140.70(11)	K(5)-Se(3)-K(6)	176.59(12)
Se(5)#4-La(2)-K(4)	159.32(5)	P(1)-Se(3)-K(4)	148.42(14)
Se(5)#5-La(2)-K(4)	48.87(5)	K(3)-Se(3)-K(4)	76.16(9)
Se(6)-La(2)-K(4)	110.37(6)	K(5)#8-Se(3)-K(4)	96.12(9)
Se(6)#6-La(2)-K(4)	50.90(6)	K(5)-Se(3)-K(4)	100.43(9)
Se(8)#6-La(2)-K(4)	80.39(5)	K(6)-Se(3)-K(4)	77.28(10)
Se(8)-La(2)-K(4)	44.33(6)	P(1)-Se(4)-K(2)	92.95(11)
Se(8)#5-La(2)-K(4)	107.54(6)	P(1)-Se(4)-K(1)#9	151.25(11)
Se(8)#4-La(2)-K(4)	125.60(6)	K(2)-Se(4)-K(1)#9	84.15(7)
K(4)#5-La(2)-K(4)	140.70(11)	P(1)-Se(4)-K(1)#10	85.36(11)
K(4)#4-La(2)-K(4)	81.61(9)	K(2)-Se(4)-K(1)#10	147.65(8)
K(4)#6-La(2)-K(4)	111.11(8)	K(1)#9-Se(4)-K(1)#10	111.95(5)
P(1)-Se(1)-La(1)	95.52(8)	P(1)-Se(4)-K(1)#1	94.89(11)
P(1)-Se(1)-K(1)#3	168.77(9)	K(2)-Se(4)-K(1)#1	80.56(6)
La(1)-Se(1)-K(1)#3	94.92(6)	K(1)#9-Se(4)-K(1)#1	112.70(7)
P(1)-Se(1)-K(2)	89.26(8)	K(1)#10-Se(4)-K(1)#1	67.44(10)
La(1)-Se(1)-K(2)	102.33(3)	P(1)-Se(4)-K(5)#8	89.87(11)
K(1)#3-Se(1)-K(2)	84.46(6)	K(2)-Se(4)-K(5)#8	137.48(5)
P(1)-Se(1)-K(3)	79.14(8)	K(1)#9-Se(4)-K(5)#8	73.84(8)
La(1)-Se(1)-K(3)	89.81(5)	K(1)#10-Se(4)-K(5)#8	74.87(8)
K(1)#3-Se(1)-K(3)	105.05(7)	K(1)#1-Se(4)-K(5)#8	141.43(7)
K(2)-Se(1)-K(3)	164.02(5)	P(2)-Se(5)-La(2)#11	93.42(12)

P(2)-Se(5)-K(4)#12	85.19(13)	K(4)-Se(8)-K(5)#8	99.54(8)
La(2)#11-Se(5)-K(4)#12	149.41(9)	La(2)-Se(8)-K(5)#8	168.37(7)
P(2)-Se(5)-K(4)#8	151.02(13)	La(2)#11-Se(8)-K(5)#8	84.21(6)
La(2)#11-Se(5)-K(4)#8	86.72(8)	P(2)-Se(8)-K(5)	77.54(10)
K(4)#12-Se(5)-K(4)#8	108.90(6)	K(4)-Se(8)-K(5)	102.11(8)
P(2)-Se(5)-K(4)#6	92.51(12)	La(2)-Se(8)-K(5)	82.58(6)
La(2)#11-Se(5)-K(4)#6	84.03(7)	La(2)#11-Se(8)-K(5)	167.84(7)
K(4)#12-Se(5)-K(4)#6	65.54(13)	K(5)#8-Se(8)-K(5)	89.00(10)
K(4)#8-Se(5)-K(4)#6	116.28(8)	Se(1)#3-K(1)-Se(4)#13	86.02(8)
P(2)-Se(5)-K(3)#12	89.98(12)	Se(1)#3-K(1)-Se(4)#14	139.73(9)
La(2)#11-Se(5)-K(3)#12	138.20(4)	Se(4)#13-K(1)-Se(4)#14	133.51(11)
K(4)#12-Se(5)-K(3)#12	72.39(8)	Se(1)#3-K(1)-Se(2)#15	156.49(9)
K(4)#8-Se(5)-K(3)#12	71.46(8)	Se(4)#13-K(1)-Se(2)#15	70.90(6)
K(4)#6-Se(5)-K(3)#12	137.46(7)	Se(4)#14-K(1)-Se(2)#15	62.73(8)
P(2)-Se(6)-La(2)	93.31(12)	Se(1)#3-K(1)-Se(2)	71.96(6)
P(2)-Se(6)-K(4)#12	84.68(13)	Se(4)#13-K(1)-Se(2)	157.14(12)
La(2)-Se(6)-K(4)#12	149.80(9)	Se(4)#14-K(1)-Se(2)	69.23(5)
P(2)-Se(6)-K(4)#5	149.85(13)	Se(2)#15-K(1)-Se(2)	131.46(10)
La(2)-Se(6)-K(4)#5	86.72(8)	Se(1)#3-K(1)-Se(7)#14	62.09(7)
K(4)#12-Se(6)-K(4)#5	109.77(6)	Se(4)#13-K(1)-Se(7)#14	87.71(8)
P(2)-Se(6)-K(4)#6	92.39(12)	Se(4)#14-K(1)-Se(7)#14	105.40(11)
La(2)-Se(6)-K(4)#6	84.80(7)	Se(2)#15-K(1)-Se(7)#14	111.10(11)
K(4)#12-Se(6)-K(4)#6	65.23(13)	Se(2)-K(1)-Se(7)#14	87.34(8)
K(4)#5-Se(6)-K(4)#6	117.59(8)	Se(1)#3-K(1)-Se(4)#1	90.15(10)
P(2)-Se(7)-K(6)#12	104.90(13)	Se(4)#13-K(1)-Se(4)#1	63.18(7)
P(2)-Se(7)-K(5)#8	82.71(12)	Se(4)#14-K(1)-Se(4)#1	112.55(10)
K(6)#12-Se(7)-K(5)#8	171.77(14)	Se(2)#15-K(1)-Se(4)#1	83.52(8)
P(2)-Se(7)-K(3)#12	100.59(12)	Se(2)-K(1)-Se(4)#1	109.65(10)
K(6)#12-Se(7)-K(3)#12	97.24(5)	Se(7)#14-K(1)-Se(4)#1	141.80(10)
K(5)#8-Se(7)-K(3)#12	84.21(4)	Se(1)#3-K(1)-Se(2)#3	81.69(8)
P(2)-Se(7)-K(5)	83.19(12)	Se(4)#13-K(1)-Se(2)#3	119.92(11)
K(6)#12-Se(7)-K(5)	82.08(4)	Se(4)#14-K(1)-Se(2)#3	82.98(7)
K(5)#8-Se(7)-K(5)	95.95(4)	Se(2)#15-K(1)-Se(2)#3	113.33(10)
K(3)#12-Se(7)-K(5)	176.20(13)	Se(2)-K(1)-Se(2)#3	52.08(5)
P(2)-Se(7)-K(1)#10	148.8(2)	Se(7)#14-K(1)-Se(2)#3	133.27(9)
K(6)#12-Se(7)-K(1)#10	94.58(11)	Se(4)#1-K(1)-Se(2)#3	58.33(6)
K(5)#8-Se(7)-K(1)#10	77.20(9)	Se(1)#3-K(1)-K(1)#16	131.9(2)
K(3)#12-Se(7)-K(1)#10	100.84(9)	Se(4)#13-K(1)-K(1)#16	100.49(11)
K(5)-Se(7)-K(1)#10	75.52(9)	Se(4)#14-K(1)-K(1)#16	58.90(9)
P(2)-Se(8)-K(4)	178.51(13)	Se(2)#15-K(1)-K(1)#16	59.72(9)
P(2)-Se(8)-La(2)	91.29(9)	Se(2)-K(1)-K(1)#16	90.14(9)
K(4)-Se(8)-La(2)	90.10(7)	Se(7)#14-K(1)-K(1)#16	163.8(2)
P(2)-Se(8)-La(2)#11	91.25(9)	Se(4)#1-K(1)-K(1)#16	53.66(9)
K(4)-Se(8)-La(2)#11	88.98(7)	Se(2)#3-K(1)-K(1)#16	53.61(8)
La(2)-Se(8)-La(2)#11	102.59(5)	Se(1)#3-K(1)-K(5)#14	101.66(9)
P(2)-Se(8)-K(5)#8	79.02(10)	Se(4)#13-K(1)-K(5)#14	57.46(6)

Se(4)#14-K(1)-K(5)#14	96.33(10)	Se(7)#18-K(3)-P(1)#1	101.69(7)
Se(2)#15-K(1)-K(5)#14	62.44(7)	Se(1)#1-K(3)-P(1)#1	34.72(6)
Se(2)-K(1)-K(5)#14	132.00(11)	Se(1)-K(3)-P(1)#1	86.84(10)
Se(7)#14-K(1)-K(5)#14	51.42(6)	Se(3)-K(3)-P(1)	34.06(6)
Se(4)#1-K(1)-K(5)#14	118.02(7)	Se(3)#1-K(3)-P(1)	141.83(14)
Se(2)#3-K(1)-K(5)#14	175.29(10)	Se(7)#5-K(3)-P(1)	101.69(7)
K(1)#16-K(1)-K(5)#14	122.12(14)	Se(7)#18-K(3)-P(1)	82.19(6)
Se(1)#3-K(1)-K(5)#2	95.04(9)	Se(1)#1-K(3)-P(1)	86.84(10)
Se(4)#13-K(1)-K(5)#2	129.14(11)	Se(1)-K(3)-P(1)	34.72(6)
Se(4)#14-K(1)-K(5)#2	56.58(7)	P(1)#1-K(3)-P(1)	108.8(2)
Se(2)#15-K(1)-K(5)#2	96.13(10)	Se(3)-K(3)-Se(5)#5	82.02(6)
Se(2)-K(1)-K(5)#2	60.99(6)	Se(3)#1-K(3)-Se(5)#5	101.59(8)
Se(7)#14-K(1)-K(5)#2	50.32(6)	Se(7)#5-K(3)-Se(5)#5	58.82(5)
Se(4)#1-K(1)-K(5)#2	166.87(9)	Se(7)#18-K(3)-Se(5)#5	114.81(11)
Se(2)#3-K(1)-K(5)#2	110.47(7)	Se(1)#1-K(3)-Se(5)#5	117.86(3)
K(1)#16-K(1)-K(5)#2	115.00(13)	Se(1)-K(3)-Se(5)#5	145.32(4)
K(5)#14-K(1)-K(5)#2	72.73(8)	P(1)#1-K(3)-Se(5)#5	126.22(6)
Se(1)#3-K(1)-K(2)#17	50.23(5)	P(1)-K(3)-Se(5)#5	113.94(7)
Se(4)#13-K(1)-K(2)#17	47.87(5)	Se(3)-K(3)-Se(5)#18	101.59(8)
Se(4)#14-K(1)-K(2)#17	159.48(11)	Se(3)#1-K(3)-Se(5)#18	82.02(6)
Se(2)#15-K(1)-K(2)#17	111.95(7)	Se(7)#5-K(3)-Se(5)#18	114.81(11)
Se(2)-K(1)-K(2)#17	110.47(9)	Se(7)#18-K(3)-Se(5)#18	58.82(5)
Se(7)#14-K(1)-K(2)#17	95.02(8)	Se(1)#1-K(3)-Se(5)#18	145.32(4)
Se(4)#1-K(1)-K(2)#17	47.34(5)	Se(1)-K(3)-Se(5)#18	117.85(3)
Se(2)#3-K(1)-K(2)#17	81.49(7)	P(1)#1-K(3)-Se(5)#18	113.94(7)
K(1)#16-K(1)-K(2)#17	100.87(13)	P(1)-K(3)-Se(5)#18	126.22(6)
K(5)#14-K(1)-K(2)#17	98.04(6)	Se(5)#5-K(3)-Se(5)#18	62.27(8)
K(5)#2-K(1)-K(2)#17	142.46(9)	Se(3)-K(3)-K(4)	54.57(7)
Se(3)-K(3)-Se(3)#1	175.8(2)	Se(3)#1-K(3)-K(4)	129.40(12)
Se(3)-K(3)-Se(7)#5	95.67(4)	Se(7)#5-K(3)-K(4)	104.17(9)
Se(3)#1-K(3)-Se(7)#5	84.57(4)	Se(7)#18-K(3)-K(4)	70.62(7)
Se(3)-K(3)-Se(7)#18	84.57(4)	Se(1)#1-K(3)-K(4)	160.60(6)
Se(3)#1-K(3)-Se(7)#18	95.67(4)	Se(1)-K(3)-K(4)	101.63(5)
Se(7)#5-K(3)-Se(7)#18	173.4(2)	P(1)#1-K(3)-K(4)	162.64(11)
Se(3)-K(3)-Se(1)#1	112.91(9)	P(1)-K(3)-K(4)	86.01(8)
Se(3)#1-K(3)-Se(1)#1	63.65(5)	Se(5)#5-K(3)-K(4)	50.14(6)
Se(7)#5-K(3)-Se(1)#1	59.82(4)	Se(5)#18-K(3)-K(4)	48.70(8)
Se(7)#18-K(3)-Se(1)#1	126.09(10)	Se(3)-K(3)-K(4)#1	129.40(12)
Se(3)-K(3)-Se(1)	63.65(5)	Se(3)#1-K(3)-K(4)#1	54.58(7)
Se(3)#1-K(3)-Se(1)	112.91(9)	Se(7)#5-K(3)-K(4)#1	70.62(7)
Se(7)#5-K(3)-Se(1)	126.09(10)	Se(7)#18-K(3)-K(4)#1	104.17(9)
Se(7)#18-K(3)-Se(1)	59.82(4)	Se(1)#1-K(3)-K(4)#1	101.63(5)
Se(1)#1-K(3)-Se(1)	82.25(10)	Se(1)-K(3)-K(4)#1	160.60(6)
Se(3)-K(3)-P(1)#1	141.84(14)	P(1)#1-K(3)-K(4)#1	86.01(8)
Se(3)#1-K(3)-P(1)#1	34.06(6)	P(1)-K(3)-K(4)#1	162.64(11)
Se(7)#5-K(3)-P(1)#1	82.18(6)	Se(5)#5-K(3)-K(4)#1	48.70(8)

Se(5)#18-K(3)-K(4)#1	50.14(6)	K(6)#2-K(2)-K(6)	180.0
K(4)-K(3)-K(4)#1	81.09(12)	Se(4)#19-K(2)-K(1)#9	52.10(5)
Se(4)#19-K(2)-Se(4)	65.95(4)	Se(4)-K(2)-K(1)#9	47.98(4)
Se(4)#19-K(2)-Se(4)#2	122.96(4)	Se(4)#2-K(2)-K(1)#9	161.98(4)
Se(4)-K(2)-Se(4)#2	149.71(4)	Se(4)#20-K(2)-K(1)#9	109.43(5)
Se(4)#19-K(2)-Se(4)#20	149.71(4)	Se(1)-K(2)-K(1)#9	106.87(5)
Se(4)-K(2)-Se(4)#20	122.96(4)	Se(1)#20-K(2)-K(1)#9	45.31(5)
Se(4)#2-K(2)-Se(4)#20	65.95(4)	Se(1)#2-K(2)-K(1)#9	125.37(5)
Se(4)#19-K(2)-Se(1)	123.96(3)	Se(1)#19-K(2)-K(1)#9	80.46(4)
Se(4)-K(2)-Se(1)	65.02(3)	K(6)#2-K(2)-K(1)#9	110.64(5)
Se(4)#2-K(2)-Se(1)	90.05(3)	K(6)-K(2)-K(1)#9	69.36(5)
Se(4)#20-K(2)-Se(1)	82.11(3)	Se(4)#19-K(2)-K(1)#1	47.98(4)
Se(4)#19-K(2)-Se(1)#20	90.05(3)	Se(4)-K(2)-K(1)#1	52.10(5)
Se(4)-K(2)-Se(1)#20	82.11(3)	Se(4)#2-K(2)-K(1)#1	109.43(5)
Se(4)#2-K(2)-Se(1)#20	123.96(3)	Se(4)#20-K(2)-K(1)#1	161.98(4)
Se(4)#20-K(2)-Se(1)#20	65.03(3)	Se(1)-K(2)-K(1)#1	80.46(4)
Se(1)-K(2)-Se(1)#20	108.27(4)	Se(1)#20-K(2)-K(1)#1	125.37(5)
Se(4)#19-K(2)-Se(1)#2	82.11(3)	Se(1)#2-K(2)-K(1)#1	45.31(5)
Se(4)-K(2)-Se(1)#2	90.05(3)	Se(1)#19-K(2)-K(1)#1	106.87(5)
Se(4)#2-K(2)-Se(1)#2	65.02(3)	K(6)#2-K(2)-K(1)#1	69.36(5)
Se(4)#20-K(2)-Se(1)#2	123.96(3)	K(6)-K(2)-K(1)#1	110.64(5)
Se(1)-K(2)-Se(1)#2	72.52(4)	K(1)#9-K(2)-K(1)#1	80.17(8)
Se(1)#20-K(2)-Se(1)#2	170.68(4)	Se(3)#5-K(5)-Se(3)	170.07(14)
Se(4)#19-K(2)-Se(1)#19	65.03(3)	Se(3)#5-K(5)-Se(7)#5	83.55(6)
Se(4)-K(2)-Se(1)#19	123.96(3)	Se(3)-K(5)-Se(7)#5	94.16(7)
Se(4)#2-K(2)-Se(1)#19	82.11(3)	Se(3)#5-K(5)-Se(7)	99.59(7)
Se(4)#20-K(2)-Se(1)#19	90.05(3)	Se(3)-K(5)-Se(7)	82.88(6)
Se(1)-K(2)-Se(1)#19	170.67(4)	Se(7)#5-K(5)-Se(7)	176.77(9)
Se(1)#20-K(2)-Se(1)#19	72.52(4)	Se(3)#5-K(5)-Se(8)#5	59.42(6)
Se(1)#2-K(2)-Se(1)#19	108.27(4)	Se(3)-K(5)-Se(8)#5	127.80(10)
Se(4)#19-K(2)-K(6)#2	61.48(2)	Se(7)#5-K(5)-Se(8)#5	62.39(6)
Se(4)-K(2)-K(6)#2	118.52(2)	Se(7)-K(5)-Se(8)#5	118.54(10)
Se(4)#2-K(2)-K(6)#2	61.48(2)	Se(3)#5-K(5)-Se(8)	131.41(11)
Se(4)#20-K(2)-K(6)#2	118.52(2)	Se(3)-K(5)-Se(8)	58.15(5)
Se(1)-K(2)-K(6)#2	125.86(2)	Se(7)#5-K(5)-Se(8)	116.30(9)
Se(1)#20-K(2)-K(6)#2	125.86(2)	Se(7)-K(5)-Se(8)	61.01(5)
Se(1)#2-K(2)-K(6)#2	54.14(2)	Se(8)#5-K(5)-Se(8)	89.69(10)
Se(1)#19-K(2)-K(6)#2	54.14(2)	Se(3)#5-K(5)-Se(4)#5	59.13(6)
Se(4)#19-K(2)-K(6)	118.52(2)	Se(3)-K(5)-Se(4)#5	112.01(10)
Se(4)-K(2)-K(6)	61.48(2)	Se(7)#5-K(5)-Se(4)#5	99.66(8)
Se(4)#2-K(2)-K(6)	118.52(2)	Se(7)-K(5)-Se(4)#5	82.69(7)
Se(4)#20-K(2)-K(6)	61.48(2)	Se(8)#5-K(5)-Se(4)#5	117.32(7)
Se(1)-K(2)-K(6)	54.14(2)	Se(8)-K(5)-Se(4)#5	142.63(7)
Se(1)#20-K(2)-K(6)	54.14(2)	Se(3)#5-K(5)-P(2)#5	82.82(8)
Se(1)#2-K(2)-K(6)	125.86(2)	Se(3)-K(5)-P(2)#5	100.83(9)
Se(1)#19-K(2)-K(6)	125.86(2)	Se(7)#5-K(5)-P(2)#5	34.85(7)

Se(7)-K(5)-P(2)#5	144.45(14)	Se(5)#18-K(4)-Se(6)#8	133.03(12)
Se(8)#5-K(5)-P(2)#5	34.14(7)	Se(6)#18-K(4)-Se(6)#8	70.19(6)
Se(8)-K(5)-P(2)#5	90.70(10)	Se(8)-K(4)-Se(5)#5	77.48(8)
Se(4)#5-K(5)-P(2)#5	126.32(8)	Se(5)#18-K(4)-Se(5)#5	71.09(6)
Se(3)#5-K(5)-K(1)#10	103.30(9)	Se(6)#18-K(4)-Se(5)#5	133.92(12)
Se(3)-K(5)-K(1)#10	70.39(8)	Se(6)#8-K(4)-Se(5)#5	155.79(14)
Se(7)#5-K(5)-K(1)#10	127.11(11)	Se(8)-K(4)-Se(5)#6	86.39(10)
Se(7)-K(5)-K(1)#10	53.07(7)	Se(5)#18-K(4)-Se(5)#6	114.46(13)
Se(8)#5-K(5)-K(1)#10	161.10(9)	Se(6)#18-K(4)-Se(5)#6	84.25(9)
Se(8)-K(5)-K(1)#10	98.10(7)	Se(6)#8-K(4)-Se(5)#6	57.79(6)
Se(4)#5-K(5)-K(1)#10	48.70(6)	Se(5)#5-K(4)-Se(5)#6	115.06(12)
P(2)#5-K(5)-K(1)#10	161.05(11)	Se(8)-K(4)-Se(6)#6	85.78(10)
Se(3)#5-K(5)-K(1)#2	69.70(7)	Se(5)#18-K(4)-Se(6)#6	84.47(9)
Se(3)-K(5)-K(1)#2	101.25(9)	Se(6)#18-K(4)-Se(6)#6	114.77(13)
Se(7)#5-K(5)-K(1)#2	52.48(7)	Se(6)#8-K(4)-Se(6)#6	115.65(12)
Se(7)-K(5)-K(1)#2	129.30(11)	Se(5)#5-K(4)-Se(6)#6	57.24(6)
Se(8)#5-K(5)-K(1)#2	98.68(6)	Se(5)#6-K(4)-Se(6)#6	59.16(8)
Se(8)-K(5)-K(1)#2	157.81(9)	Se(8)-K(4)-Se(3)	61.18(9)
Se(4)#5-K(5)-K(1)#2	48.55(7)	Se(5)#18-K(4)-Se(3)	106.35(12)
P(2)#5-K(5)-K(1)#2	85.07(8)	Se(6)#18-K(4)-Se(3)	109.17(12)
K(1)#10-K(5)-K(1)#2	80.46(9)	Se(6)#8-K(4)-Se(3)	89.23(9)
Se(3)#5-K(5)-K(6)#12	51.30(4)	Se(5)#5-K(4)-Se(3)	84.16(9)
Se(3)-K(5)-K(6)#12	129.92(6)	Se(5)#6-K(4)-Se(3)	138.57(11)
Se(7)#5-K(5)-K(6)#12	134.82(7)	Se(6)#6-K(4)-Se(3)	134.57(10)
Se(7)-K(5)-K(6)#12	48.35(4)	Se(8)-K(4)-K(4)#21	134.1(2)
Se(8)#5-K(5)-K(6)#12	91.09(7)	Se(5)#18-K(4)-K(4)#21	59.77(11)
Se(8)-K(5)-K(6)#12	98.04(7)	Se(6)#18-K(4)-K(4)#21	59.72(11)
Se(4)#5-K(5)-K(6)#12	58.82(7)	Se(6)#8-K(4)-K(4)#21	96.07(11)
P(2)#5-K(5)-K(6)#12	124.66(9)	Se(5)#5-K(4)-K(4)#21	96.40(11)
K(1)#10-K(5)-K(6)#12	70.84(8)	Se(5)#6-K(4)-K(4)#21	54.69(10)
K(1)#2-K(5)-K(6)#12	102.28(8)	Se(6)#6-K(4)-K(4)#21	55.05(10)
Se(3)#5-K(5)-K(3)	130.88(6)	Se(3)-K(4)-K(4)#21	164.6(2)
Se(3)-K(5)-K(3)	46.28(4)	Se(8)-K(4)-P(2)#18	157.9(2)
Se(7)#5-K(5)-K(3)	47.91(4)	Se(5)#18-K(4)-P(2)#18	34.25(6)
Se(7)-K(5)-K(3)	129.09(6)	Se(6)#18-K(4)-P(2)#18	34.13(6)
Se(8)#5-K(5)-K(3)	96.13(6)	Se(6)#8-K(4)-P(2)#18	101.41(9)
Se(8)-K(5)-K(3)	85.04(6)	Se(5)#5-K(4)-P(2)#18	102.48(9)
Se(4)#5-K(5)-K(3)	114.73(8)	Se(5)#6-K(4)-P(2)#18	112.74(13)
P(2)#5-K(5)-K(3)	62.25(7)	Se(6)#6-K(4)-P(2)#18	113.09(13)
K(1)#10-K(5)-K(3)	101.66(8)	Se(3)-K(4)-P(2)#18	96.74(13)
K(1)#2-K(5)-K(3)	73.70(7)	K(4)#21-K(4)-P(2)#18	68.03(14)
K(6)#12-K(5)-K(3)	172.17(9)	Se(8)-K(4)-K(3)	97.22(10)
Se(8)-K(4)-Se(5)#18	147.40(9)	Se(5)#18-K(4)-K(3)	58.91(7)
Se(8)-K(4)-Se(6)#18	148.00(9)	Se(6)#18-K(4)-K(3)	96.59(11)
Se(5)#18-K(4)-Se(6)#18	62.85(9)	Se(6)#8-K(4)-K(3)	130.69(13)
Se(8)-K(4)-Se(6)#8	78.93(8)	Se(5)#5-K(4)-K(3)	58.41(6)

Se(5)#6-K(4)-K(3)	171.24(11)	Se(3)-K(6)-K(4)	51.62(7)
Se(6)#6-K(4)-K(3)	112.99(6)	Se(3)#20-K(6)-K(4)	124.51(14)
Se(3)-K(4)-K(3)	49.27(6)	Se(1)#20-K(6)-K(4)	157.73(7)
K(4)#21-K(4)-K(3)	118.37(14)	Se(1)-K(6)-K(4)	95.75(5)
P(2)#18-K(4)-K(3)	65.53(9)	P(1)#20-K(6)-K(4)	157.89(13)
Se(8)-K(4)-K(6)	97.25(10)	P(1)-K(6)-K(4)	83.60(8)
Se(5)#18-K(4)-K(6)	95.51(10)	Se(7)#8-K(6)-K(4)#20	68.45(8)
Se(6)#18-K(4)-K(6)	60.34(7)	Se(7)#18-K(6)-K(4)#20	99.44(11)
Se(6)#8-K(4)-K(6)	60.28(7)	Se(3)-K(6)-K(4)#20	124.51(14)
Se(5)#5-K(4)-K(6)	128.34(12)	Se(3)#20-K(6)-K(4)#20	51.62(7)
Se(5)#6-K(4)-K(6)	115.81(7)	Se(1)#20-K(6)-K(4)#20	95.75(5)
Se(6)#6-K(4)-K(6)	174.08(11)	Se(1)-K(6)-K(4)#20	157.73(7)
Se(3)-K(4)-K(6)	51.10(7)	P(1)#20-K(6)-K(4)#20	83.60(8)
K(4)#21-K(4)-K(6)	119.95(15)	P(1)-K(6)-K(4)#20	157.89(13)
P(2)#18-K(4)-K(6)	65.09(9)	K(4)-K(6)-K(4)#20	77.03(12)
K(3)-K(4)-K(6)	71.77(9)	Se(7)#8-K(6)-K(2)	97.47(10)
Se(7)#8-K(6)-Se(7)#18	165.1(2)	Se(7)#18-K(6)-K(2)	97.47(10)
Se(7)#8-K(6)-Se(3)	97.70(4)	Se(3)-K(6)-K(2)	91.99(9)
Se(7)#18-K(6)-Se(3)	81.78(4)	Se(3)#20-K(6)-K(2)	91.99(9)
Se(7)#8-K(6)-Se(3)#20	81.78(4)	Se(1)#20-K(6)-K(2)	49.05(7)
Se(7)#18-K(6)-Se(3)#20	97.70(4)	Se(1)-K(6)-K(2)	49.05(7)
Se(3)-K(6)-Se(3)#20	176.0(2)	P(1)#20-K(6)-K(2)	58.62(9)
Se(7)#8-K(6)-Se(1)#20	58.53(5)	P(1)-K(6)-K(2)	58.62(9)
Se(7)#18-K(6)-Se(1)#20	133.82(12)	K(4)-K(6)-K(2)	141.49(6)
Se(3)-K(6)-Se(1)#20	123.08(10)	K(4)#20-K(6)-K(2)	141.49(6)
Se(3)#20-K(6)-Se(1)#20	59.98(4)	Se(7)#8-K(6)-K(5)#8	49.58(4)
Se(7)#8-K(6)-Se(1)	133.82(12)	Se(7)#18-K(6)-K(5)#8	128.67(5)
Se(7)#18-K(6)-Se(1)	58.53(5)	Se(3)-K(6)-K(5)#8	48.18(4)
Se(3)-K(6)-Se(1)	59.98(4)	Se(3)#20-K(6)-K(5)#8	131.33(4)
Se(3)#20-K(6)-Se(1)	123.08(10)	Se(1)#20-K(6)-K(5)#8	90.18(5)
Se(1)#20-K(6)-Se(1)	98.10(13)	Se(1)-K(6)-K(5)#8	96.68(5)
Se(7)#8-K(6)-P(1)#20	82.96(6)	P(1)#20-K(6)-K(5)#8	123.89(8)
Se(7)#18-K(6)-P(1)#20	104.94(7)	P(1)-K(6)-K(5)#8	62.44(7)
Se(3)-K(6)-P(1)#20	150.2(2)	K(4)-K(6)-K(5)#8	70.90(7)
Se(3)#20-K(6)-P(1)#20	33.70(6)	K(4)#20-K(6)-K(5)#8	100.64(9)
Se(1)#20-K(6)-P(1)#20	34.26(6)	K(2)-K(6)-K(5)#8	95.23(7)
Se(1)-K(6)-P(1)#20	98.28(13)	Se(3)-P(1)-Se(4)	109.86(14)
Se(7)#8-K(6)-P(1)	104.94(7)	Se(3)-P(1)-Se(1)	113.1(2)
Se(7)#18-K(6)-P(1)	82.96(6)	Se(4)-P(1)-Se(1)	112.52(14)
Se(3)-K(6)-P(1)	33.70(6)	Se(3)-P(1)-Se(2)#2	112.70(14)
Se(3)#20-K(6)-P(1)	150.2(2)	Se(4)-P(1)-Se(2)#2	106.2(2)
Se(1)#20-K(6)-P(1)	98.28(13)	Se(1)-P(1)-Se(2)#2	102.11(13)
Se(1)-K(6)-P(1)	34.26(6)	Se(3)-P(1)-K(6)	66.94(12)
P(1)#20-K(6)-P(1)	117.2(2)	Se(4)-P(1)-K(6)	81.79(8)
Se(7)#8-K(6)-K(4)	99.44(11)	Se(1)-P(1)-K(6)	70.76(9)
Se(7)#18-K(6)-K(4)	68.45(8)	Se(2)#2-P(1)-K(6)	171.13(14)

Se(3)-P(1)-K(3)	60.45(10)
Se(4)-P(1)-K(3)	165.64(15)
Se(1)-P(1)-K(3)	66.14(9)
Se(2)#2-P(1)-K(3)	87.83(8)
K(6)-P(1)-K(3)	84.43(10)
Se(6)-P(2)-Se(5)	108.3(2)
Se(6)-P(2)-Se(8)	108.6(2)
Se(5)-P(2)-Se(8)	108.4(2)
Se(6)-P(2)-Se(7)	110.3(2)
Se(5)-P(2)-Se(7)	109.70(15)
Se(8)-P(2)-Se(7)	111.5(2)
Se(6)-P(2)-K(5)#8	166.6(2)
Se(5)-P(2)-K(5)#8	85.08(9)
Se(8)-P(2)-K(5)#8	66.84(11)
Se(7)-P(2)-K(5)#8	62.44(11)
Se(6)-P(2)-K(4)#12	61.19(12)
Se(5)-P(2)-K(4)#12	60.56(12)
Se(8)-P(2)-K(4)#12	156.6(2)
Se(7)-P(2)-K(4)#12	91.9(2)
K(5)#8-P(2)-K(4)#12	127.84(11)

Symmetry transformations used to generate equivalent atoms:

#1 -x,y,-z+3/2 #2 -x+0,-y+1/2,z #3 x+0,-y+1/2,-z+3/2

#4 x,-y,z+1/2 #5 -x-1/2,y,z+1/2 #6 -x-1/2,-y,z

#7 -x+1/2,y,z-1/2 #8 -x-1/2,y,z-1/2 #9 -x+0,-y+1/2,z-1

#10 x-1/2,-y+1/2,z-1/2 #11 x,-y,z-1/2 #12 x-1/2,y,-z+1

#13 -x+0,-y+1/2,z+1 #14 x+1/2,-y+1/2,z+1/2 #15 -x+1/2,y,z+1/2

#16 -x+1/2,-y+1/2,-z+2 #17 x,y,z+1 #18 x+1/2,y,-z+1

#19 x+0,-y+1/2,-z+1/2 #20 -x,y,-z+1/2 #21 -x,-y,-z+1

Table B.16. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $K_{8.5}La_{1.17}(PSe_4)_4$. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
La(1)	7(1)	7(1)	7(1)	0	0	0
La(2)	6(1)	10(1)	9(1)	0	0	1(1)
Se(1)	8(1)	14(1)	14(1)	-8(1)	-1(1)	1(1)
Se(2)	9(1)	21(1)	10(1)	6(1)	0(1)	-2(1)
Se(3)	22(1)	12(1)	18(1)	0(1)	-4(1)	-6(1)
Se(4)	18(1)	24(1)	10(1)	6(1)	-3(1)	1(1)
Se(5)	17(1)	31(1)	14(1)	1(1)	-5(1)	-1(1)
Se(6)	18(1)	39(1)	14(1)	-2(1)	4(1)	-3(1)
Se(7)	21(1)	14(1)	33(1)	-1(1)	0(1)	5(1)
Se(8)	8(1)	14(1)	74(1)	1(1)	-1(1)	0(1)
K(1)	16(2)	29(2)	21(1)	-5(1)	-1(1)	6(2)
K(3)	33(3)	28(2)	24(2)	0	-9(2)	0
K(2)	38(4)	26(4)	28(3)	0	0	0
K(5)	18(2)	52(2)	17(1)	-2(1)	0(1)	4(1)
K(4)	16(2)	42(3)	35(2)	1(1)	-1(1)	-1(2)
K(6)	38(3)	60(3)	29(2)	0	8(2)	0
P(1)	5(2)	7(2)	10(1)	3(1)	-1(1)	1(1)
P(2)	16(2)	15(2)	13(2)	1(1)	0(1)	4(2)

Table B.17. Crystal data and structure refinement for $KEuPSe_4$.

Identification code	pnma	
Empirical formula	$KEuPSe_4$	
Formula weight	537.87	
Temperature	170(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pnma	
Unit cell dimensions	a = 17.5156(11) Å	α= 90°.
	b = 7.0126(5) Å	β= 90°.
	c = 6.9015(4) Å	γ = 90°.
Volume	847.71(9) $Å^3$	
Z	4	
Density (calculated)	4.214 Mg/m^3	
Absorption coefficient	25.150 mm^{-1}	
F(000)	932	
Crystal size	0.09 x 0.12 x 0.15 mm^3	
Theta range for data collection	2.33 to 28.03°.	
Index ranges	-22<=h<=19, -9<=k<=6, -9<=l<=8	
Reflections collected	5130	
Independent reflections	1080 [R(int) = 0.0368]	
Absorption correction	SADABS	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1079 / 0 / 41	
Goodness-of-fit on F^2	1.094	
Final R indices [I>2sigma(I)]	R1 = 0.0237, wR2 = 0.0523	
R indices (all data)	R1 = 0.0278, wR2 = 0.0565	
Extinction coefficient	0.0058(3)	
Largest diff. peak and hole	0.829 and -1.193 $e.Å^{-3}$	

Table B.18. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for $KEuPSe_4$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Eu(1)	4754(1)	2500	2893(1)	15(1)
Se(1)	3275(1)	2500	341(1)	17(1)
Se(2)	4727(1)	-2500	1492(1)	18(1)
Se(3)	3795(1)	-28(1)	5948(1)	15(1)
P(1)	4035(1)	2500	-2212(2)	10(1)
K(1)	2135(1)	2500	4768(3)	25(1)

Table B.19. Bond lengths [Å] and angles [°] for $KEuPSe_4$.

Eu(1)-Se(1)	3.1324(8)	Se(2)#1-Eu(1)-Se(3)#4	140.873(11)
Eu(1)-Se(2)#1	3.1598(8)	Se(3)#2-Eu(1)-Se(3)#4	87.246(14)
Eu(1)-Se(3)#2	3.1793(5)	Se(3)#3-Eu(1)-Se(3)#4	123.452(12)
Eu(1)-Se(3)#3	3.1793(5)	Se(3)-Eu(1)-Se(3)#4	66.67(2)
Eu(1)-Se(3)	3.2259(5)	Se(1)-Eu(1)-Se(2)	80.791(11)
Eu(1)-Se(3)#4	3.2259(5)	Se(2)#1-Eu(1)-Se(2)	75.474(11)
Eu(1)-Se(2)	3.6374(3)	Se(3)#2-Eu(1)-Se(2)	127.07(2)
Eu(1)-Se(2)#5	3.6374(3)	Se(3)#3-Eu(1)-Se(2)	63.359(13)
Eu(1)-K(1)#6	4.558(2)	Se(3)-Eu(1)-Se(2)	68.732(13)
Eu(1)-K(1)	4.766(2)	Se(3)#4-Eu(1)-Se(2)	134.167(15)
Se(1)-P(1)	2.209(2)	Se(1)-Eu(1)-Se(2)#5	80.790(11)
Se(1)-K(1)#7	3.6008(5)	Se(2)#1-Eu(1)-Se(2)#5	75.474(11)
Se(1)-K(1)#8	3.6008(5)	Se(3)#2-Eu(1)-Se(2)#5	63.361(13)
Se(1)-K(1)	3.649(2)	Se(3)#3-Eu(1)-Se(2)#5	127.071(15)
Se(2)-P(1)#1	2.225(2)	Se(3)-Eu(1)-Se(2)#5	134.167(15)
Se(2)-Eu(1)#1	3.1599(8)	Se(3)#4-Eu(1)-Se(2)#5	68.732(13)
Se(2)-K(1)#7	3.472(2)	Se(2)-Eu(1)-Se(2)#5	149.14(2)
Se(2)-Eu(1)#9	3.6374(3)	Se(1)-Eu(1)-K(1)#6	122.04(3)
Se(3)-P(1)#10	2.2207(10)	Se(2)#1-Eu(1)-K(1)#6	49.50(3)
Se(3)-Eu(1)#3	3.1793(5)	Se(3)#2-Eu(1)-K(1)#6	50.92(2)
Se(3)-K(1)	3.5014(14)	Se(3)#3-Eu(1)-K(1)#6	50.92(2)
Se(3)-K(1)#11	3.5513(15)	Se(3)-Eu(1)-K(1)#6	137.70(2)
P(1)-Se(3)#12	2.2208(10)	Se(3)#4-Eu(1)-K(1)#6	137.70(2)
P(1)-Se(3)#13	2.2208(10)	Se(2)-Eu(1)-K(1)#6	84.531(12)
P(1)-Se(2)#1	2.225(2)	Se(2)#5-Eu(1)-K(1)#6	84.531(12)
K(1)-Se(2)#11	3.472(2)	Se(1)-Eu(1)-K(1)	49.96(2)
K(1)-Se(3)#4	3.5014(14)	Se(2)#1-Eu(1)-K(1)	122.50(3)
K(1)-Se(3)#7	3.5513(15)	Se(3)#2-Eu(1)-K(1)	134.52(2)
K(1)-Se(3)#14	3.5513(15)	Se(3)#3-Eu(1)-K(1)	134.52(2)
K(1)-Se(1)#11	3.6008(5)	Se(3)-Eu(1)-K(1)	47.28(2)
K(1)-Se(1)#15	3.6008(5)	Se(3)#4-Eu(1)-K(1)	47.28(2)
K(1)-Eu(1)#16	4.558(2)	Se(2)-Eu(1)-K(1)	93.429(12)
		Se(2)#5-Eu(1)-K(1)	93.428(12)
Se(1)-Eu(1)-Se(2)#1	72.54(2)	K(1)#6-Eu(1)-K(1)	172.00(2)
Se(1)-Eu(1)-Se(3)#2	143.400(11)	P(1)-Se(1)-Eu(1)	87.13(5)
Se(2)#1-Eu(1)-Se(3)#2	90.621(15)	P(1)-Se(1)-K(1)#7	91.86(3)
Se(1)-Eu(1)-Se(3)#3	143.400(11)	Eu(1)-Se(1)-K(1)#7	103.10(3)
Se(2)#1-Eu(1)-Se(3)#3	90.621(15)	P(1)-Se(1)-K(1)#8	91.86(3)
Se(3)#2-Eu(1)-Se(3)#3	66.08(2)	Eu(1)-Se(1)-K(1)#8	103.10(3)
Se(1)-Eu(1)-Se(3)	86.39(2)	K(1)#7-Se(1)-K(1)#8	153.69(6)
Se(2)#1-Eu(1)-Se(3)	140.873(12)	P(1)-Se(1)-K(1)	176.09(5)
Se(3)#2-Eu(1)-Se(3)	123.451(12)	Eu(1)-Se(1)-K(1)	88.95(3)
Se(3)#3-Eu(1)-Se(3)	87.245(14)	K(1)#7-Se(1)-K(1)	89.03(2)
Se(1)-Eu(1)-Se(3)#4	86.384(15)	K(1)#8-Se(1)-K(1)	89.03(2)

P(1)#1-Se(2)-Eu(1)#1	86.17(4)
P(1)#1-Se(2)-K(1)#7	172.87(6)
Eu(1)#1-Se(2)-K(1)#7	86.70(3)
P(1)#1-Se(2)-Eu(1)#9	85.88(2)
Eu(1)#1-Se(2)-Eu(1)#9	104.526(11)
K(1)#7-Se(2)-Eu(1)#9	95.920(13)
P(1)#1-Se(2)-Eu(1)	85.88(2)
Eu(1)#1-Se(2)-Eu(1)	104.526(11)
K(1)#7-Se(2)-Eu(1)	95.921(13)
Eu(1)#9-Se(2)-Eu(1)	149.14(2)
P(1)#10-Se(3)-Eu(1)#3	98.06(4)
P(1)#10-Se(3)-Eu(1)	80.60(4)
Eu(1)#3-Se(3)-Eu(1)	92.755(14)
P(1)#10-Se(3)-K(1)	83.43(4)
Eu(1)#3-Se(3)-K(1)	176.95(2)
Eu(1)-Se(3)-K(1)	90.11(3)
P(1)#10-Se(3)-K(1)#11	92.97(4)
Eu(1)#3-Se(3)-K(1)#11	85.05(3)
Eu(1)-Se(3)-K(1)#11	172.87(3)
K(1)-Se(3)-K(1)#11	92.22(2)
Se(1)-P(1)-Se(3)#12	110.02(5)
Se(1)-P(1)-Se(3)#13	110.02(5)
Se(3)#12-P(1)-Se(3)#13	105.93(7)
Se(1)-P(1)-Se(2)#1	114.16(7)
Se(3)#12-P(1)-Se(2)#1	108.18(5)
Se(3)#13-P(1)-Se(2)#1	108.18(5)
Se(2)#11-K(1)-Se(3)#4	134.46(4)
Se(2)#11-K(1)-Se(3)	134.46(4)
Se(3)#4-K(1)-Se(3)	60.84(3)
Se(2)#11-K(1)-Se(3)#7	79.83(3)
Se(3)#4-K(1)-Se(3)#7	143.20(5)
Se(3)-K(1)-Se(3)#7	107.84(3)
Se(2)#11-K(1)-Se(3)#14	79.83(3)
Se(3)#4-K(1)-Se(3)#14	107.84(3)
Se(3)-K(1)-Se(3)#14	143.20(5)
Se(3)#7-K(1)-Se(3)#14	58.44(3)
Se(2)#11-K(1)-Se(1)#11	77.01(3)
Se(3)#4-K(1)-Se(1)#11	129.27(4)
Se(3)-K(1)-Se(1)#11	69.32(2)
Se(3)#7-K(1)-Se(1)#11	60.98(2)
Se(3)#14-K(1)-Se(1)#11	117.74(4)
Se(2)#11-K(1)-Se(1)#15	77.01(3)
Se(3)#4-K(1)-Se(1)#15	69.32(2)
Se(3)-K(1)-Se(1)#15	129.27(4)
Se(3)#7-K(1)-Se(1)#15	117.74(4)
Se(3)#14-K(1)-Se(1)#15	60.98(2)
Se(1)#11-K(1)-Se(1)#15	153.69(6)
Se(2)#11-K(1)-Se(1)	143.20(5)
Se(3)#4-K(1)-Se(1)	74.96(3)
Se(3)-K(1)-Se(1)	74.96(3)
Se(3)#7-K(1)-Se(1)	68.24(3)
Se(3)#14-K(1)-Se(1)	68.24(3)
Se(1)#11-K(1)-Se(1)	101.59(3)
Se(1)#15-K(1)-Se(1)	101.59(3)
Se(2)#11-K(1)-Eu(1)#16	43.80(2)
Se(3)#4-K(1)-Eu(1)#16	148.62(2)
Se(3)-K(1)-Eu(1)#16	148.62(2)
Se(3)#7-K(1)-Eu(1)#16	44.03(2)
Se(3)#14-K(1)-Eu(1)#16	44.03(2)
Se(1)#11-K(1)-Eu(1)#16	82.06(3)
Se(1)#15-K(1)-Eu(1)#16	82.06(3)
Se(1)-K(1)-Eu(1)#16	99.40(4)
Se(2)#11-K(1)-Eu(1)	175.72(5)
Se(3)#4-K(1)-Eu(1)	42.60(2)
Se(3)-K(1)-Eu(1)	42.60(2)
Se(3)#7-K(1)-Eu(1)	103.88(4)
Se(3)#14-K(1)-Eu(1)	103.88(4)
Se(1)#11-K(1)-Eu(1)	102.80(3)
Se(1)#15-K(1)-Eu(1)	102.80(3)
Se(1)-K(1)-Eu(1)	41.08(2)
Eu(1)#16-K(1)-Eu(1)	140.48(4)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y,-z #2 -x+1,y+1/2,-z+1 #3 -x+1,-y,-z+1
#4 x,-y+1/2,z #5 x,y+1,z #6 x+1/2,y,-z+1/2
#7 -x+1/2,-y,z-1/2 #8 -x+1/2,-y+1,z-1/2 #9 x,y-1,z
#10 x,y,z+1 #11 -x+1/2,-y,z+1/2 #12 x,y,z-1
#13 x,-y+1/2,z-1 #14 -x+1/2,y+1/2,z-1/2 #15 -x+1/2,-y+1,z+1/2
#16 x-1/2,y,-z+1/2

Table B.20. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $KEuPSe_4$. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Eu(1)	12(1)	21(1)	13(1)	0	1(1)	0
Se(1)	11(1)	23(1)	16(1)	0	5(1)	0
Se(2)	9(1)	31(1)	16(1)	0	1(1)	0
Se(3)	16(1)	8(1)	20(1)	-3(1)	-2(1)	-1(1)
P(1)	9(1)	8(1)	12(1)	0	0(1)	0
K(1)	17(1)	21(1)	37(1)	0	-4(1)	0

Appendix C:

Supplementary Information for Chapter Three

Table C.1. Crystal data and structure refinement for $KLaP_2S_6$.

Identification code	p21c	
Empirical formula	$KLaP_2S_6$	
Formula weight	432.31	
Temperature	169(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 11.963(12) Å	α= 90°.
	b = 7.525(10) Å	β= 109.88(4)°.
	c = 11.389(14) Å	γ = 90°.
Volume	964.1(20) $Å^3$	
Z	4	
Density (calculated)	2.978 Mg/m^3	
Absorption coefficient	6.415 mm^{-1}	
F(000)	808	
Crystal size	0.04 x 0.06 x 0.09 mm^3	
Theta range for data collection	1.81 to 28.44°.	
Index ranges	-16<=h<=15, -9<=k<=9, -15<=l<=12	
Reflections collected	6077	
Independent reflections	2307 [R(int) = 0.0929]	
Absorption correction	SADABS	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2307 / 0 / 92	
Goodness-of-fit on F^2	1.071	
Final R indices [I>2sigma(I)]	R1 = 0.0583, wR2 = 0.1120	
R indices (all data)	R1 = 0.1140, wR2 = 0.1564	
Extinction coefficient	0.0100(9)	
Largest diff. peak and hole	1.563 and -1.677 $e.Å^{-3}$	

Table C.2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for $KLaP_2S_6$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
La(1)	6505(1)	1060(1)	9037(1)	9(1)
P(1)	7921(3)	1184(4)	12341(3)	8(1)
P(2)	3258(3)	1015(4)	7530(3)	9(1)
K(1)	11291(2)	921(4)	13744(3)	15(1)
S(1)	6765(3)	1927(4)	6396(3)	11(1)
S(2)	4439(3)	-152(4)	6828(3)	12(1)
S(3)	8875(3)	233(4)	11341(3)	12(1)
S(4)	4090(3)	1867(4)	9311(3)	11(1)
S(5)	8738(3)	2968(4)	9104(3)	12(1)
S(6)	7801(3)	-2131(4)	8570(3)	12(1)

Table C.3. Bond lengths [Å] and angles [°] for $KLaP_2S_6$.

La(1)-S(6)	3.002(4)	S(1)#1-La(1)-S(5)	85.16(10)
La(1)-S(1)#1	3.006(4)	S(2)-La(1)-S(5)	129.45(11)
La(1)-S(2)	3.007(4)	S(6)-La(1)-S(4)	137.46(9)
La(1)-S(5)	3.011(4)	S(1)#1-La(1)-S(4)	67.97(9)
La(1)-S(4)	3.070(4)	S(2)-La(1)-S(4)	67.12(11)
La(1)-S(2)#2	3.101(5)	S(5)-La(1)-S(4)	139.52(11)
La(1)-S(4)#3	3.131(4)	S(6)-La(1)-S(2)#2	146.41(10)
La(1)-S(1)	3.196(5)	S(1)#1-La(1)-S(2)#2	74.73(11)
La(1)-S(3)	3.201(5)	S(2)-La(1)-S(2)#2	84.61(8)
P(1)-S(3)	1.998(5)	S(5)-La(1)-S(2)#2	78.11(11)
P(1)-S(5)#1	2.016(5)	S(4)-La(1)-S(2)#2	66.22(9)
P(1)-S(1)#1	2.019(5)	S(6)-La(1)-S(4)#3	77.33(12)
P(1)-P(2)#3	2.212(5)	S(1)#1-La(1)-S(4)#3	78.08(13)
P(1)-K(1)	3.803(6)	S(2)-La(1)-S(4)#3	89.97(12)
P(2)-S(6)#2	2.010(5)	S(5)-La(1)-S(4)#3	134.51(9)
P(2)-S(4)	2.035(5)	S(4)-La(1)-S(4)#3	70.38(11)
P(2)-S(2)	2.044(5)	S(2)#2-La(1)-S(4)#3	134.82(10)
P(2)-P(1)#3	2.212(5)	S(6)-La(1)-S(1)	76.98(10)
K(1)-S(1)#4	3.206(5)	S(1)#1-La(1)-S(1)	136.43(8)
K(1)-S(6)#5	3.229(5)	S(2)-La(1)-S(1)	65.76(11)
K(1)-S(3)#5	3.250(6)	S(5)-La(1)-S(1)	63.68(9)
K(1)-S(3)	3.277(5)	S(4)-La(1)-S(1)	116.85(9)
K(1)-S(6)#4	3.302(5)	S(2)#2-La(1)-S(1)	69.80(9)
K(1)-S(5)#6	3.316(5)	S(4)#3-La(1)-S(1)	145.49(9)
K(1)-S(5)#1	3.324(5)	S(6)-La(1)-S(3)	67.85(10)
K(1)-S(4)#7	3.596(5)	S(1)#1-La(1)-S(3)	64.66(11)
S(1)-P(1)#8	2.019(5)	S(2)-La(1)-S(3)	150.87(10)
S(1)-La(1)#8	3.006(4)	S(5)-La(1)-S(3)	62.68(11)
S(1)-K(1)#4	3.206(5)	S(4)-La(1)-S(3)	123.85(11)
S(2)-La(1)#9	3.101(5)	S(2)#2-La(1)-S(3)	124.37(9)
S(3)-K(1)#6	3.250(6)	S(4)#3-La(1)-S(3)	71.93(10)
S(4)-La(1)#3	3.131(4)	S(1)-La(1)-S(3)	117.93(11)
S(4)-K(1)#10	3.596(5)	S(3)-P(1)-S(5)#1	120.3(2)
S(5)-P(1)#8	2.016(5)	S(3)-P(1)-S(1)#1	111.6(2)
S(5)-K(1)#5	3.316(5)	S(5)#1-P(1)-S(1)#1	108.7(2)
S(5)-K(1)#8	3.323(5)	S(3)-P(1)-P(2)#3	105.7(2)
S(6)-P(2)#9	2.011(5)	S(5)#1-P(1)-P(2)#3	105.9(2)
S(6)-K(1)#6	3.229(5)	S(1)#1-P(1)-P(2)#3	103.0(2)
S(6)-K(1)#4	3.302(5)	S(3)-P(1)-K(1)	59.48(15)
		S(5)#1-P(1)-K(1)	60.81(13)
S(6)-La(1)-S(1)#1	131.19(10)	S(1)#1-P(1)-K(1)	134.2(2)
S(6)-La(1)-S(2)	86.33(11)	P(2)#3-P(1)-K(1)	122.8(2)
S(1)#1-La(1)-S(2)	134.97(10)	S(6)#2-P(2)-S(4)	113.2(2)
S(6)-La(1)-S(5)	83.02(12)	S(6)#2-P(2)-S(2)	115.3(2)

S(4)-P(2)-S(2)	110.9(2)
S(6)#2-P(2)-P(1)#3	106.2(2)
S(4)-P(2)-P(1)#3	106.0(2)
S(2)-P(2)-P(1)#3	104.2(2)
S(1)#4-K(1)-S(6)#5	109.55(13)
S(1)#4-K(1)-S(3)#5	134.73(13)
S(6)#5-K(1)-S(3)#5	64.68(11)
S(1)#4-K(1)-S(3)	107.54(13)
S(6)#5-K(1)-S(3)	141.29(12)
S(3)#5-K(1)-S(3)	96.05(11)
S(1)#4-K(1)-S(6)#4	72.75(11)
S(6)#5-K(1)-S(6)#4	122.33(13)
S(3)#5-K(1)-S(6)#4	74.58(10)
S(3)-K(1)-S(6)#4	79.21(13)
S(1)#4-K(1)-S(5)#6	77.21(12)
S(6)#5-K(1)-S(5)#6	71.89(13)
S(3)#5-K(1)-S(5)#6	132.47(13)
S(3)-K(1)-S(5)#6	106.47(13)
S(6)#4-K(1)-S(5)#6	149.68(12)
S(1)#4-K(1)-S(5)#1	152.48(13)
S(6)#5-K(1)-S(5)#1	78.24(11)
S(3)#5-K(1)-S(5)#1	72.74(10)
S(3)-K(1)-S(5)#1	63.66(12)
S(6)#4-K(1)-S(5)#1	126.48(12)
S(5)#6-K(1)-S(5)#1	80.61(11)
S(1)#4-K(1)-S(4)#7	70.82(13)
S(6)#5-K(1)-S(4)#7	68.10(10)
S(3)#5-K(1)-S(4)#7	65.59(10)
S(3)-K(1)-S(4)#7	136.56(12)
S(6)#4-K(1)-S(4)#7	58.43(10)
S(5)#6-K(1)-S(4)#7	114.87(12)
S(5)#1-K(1)-S(4)#7	134.43(13)
S(1)#4-K(1)-P(1)	134.18(13)
S(6)#5-K(1)-P(1)	109.98(11)
S(3)#5-K(1)-P(1)	83.70(10)
S(3)-K(1)-P(1)	31.70(8)
S(6)#4-K(1)-P(1)	103.85(12)
S(5)#6-K(1)-P(1)	94.01(11)
S(5)#1-K(1)-P(1)	31.97(9)
S(4)#7-K(1)-P(1)	147.20(12)
P(1)#8-S(1)-La(1)#8	88.0(2)
P(1)#8-S(1)-La(1)	84.86(15)
La(1)#8-S(1)-La(1)	158.50(12)
P(1)#8-S(1)-K(1)#4	96.9(2)
La(1)#8-S(1)-K(1)#4	98.57(12)
La(1)-S(1)-K(1)#4	102.41(11)
P(2)-S(2)-La(1)	91.3(2)
P(2)-S(2)-La(1)#9	107.1(2)
La(1)-S(2)-La(1)#9	130.67(12)
P(1)-S(3)-La(1)	83.1(2)
P(1)-S(3)-K(1)#6	109.5(2)
La(1)-S(3)-K(1)#6	98.15(11)
P(1)-S(3)-K(1)	88.8(2)
La(1)-S(3)-K(1)	159.67(13)
K(1)#6-S(3)-K(1)	102.13(11)
P(2)-S(4)-La(1)	89.69(15)
P(2)-S(4)-La(1)#3	104.1(2)
La(1)-S(4)-La(1)#3	109.62(11)
P(2)-S(4)-K(1)#10	81.78(15)
La(1)-S(4)-K(1)#10	157.58(12)
La(1)#3-S(4)-K(1)#10	92.60(11)
P(1)#8-S(5)-La(1)	90.0(2)
P(1)#8-S(5)-K(1)#5	113.6(2)
La(1)-S(5)-K(1)#5	96.10(11)
P(1)#8-S(5)-K(1)#8	87.2(2)
La(1)-S(5)-K(1)#8	164.05(13)
K(1)#5-S(5)-K(1)#8	99.39(11)
P(2)#9-S(6)-La(1)	114.3(2)
P(2)#9-S(6)-K(1)#6	102.3(2)
La(1)-S(6)-K(1)#6	102.87(12)
P(2)#9-S(6)-K(1)#4	90.2(2)
La(1)-S(6)-K(1)#4	104.54(12)
K(1)#6-S(6)-K(1)#4	141.74(15)

Symmetry transformations used to generate equivalent atoms:

#1 x,-y+1/2,z+1/2 #2 -x+1,y+1/2,-z+3/2 #3 -x+1,-y,-z+2

#4 -x+2,-y,-z+2 #5 -x+2,y+1/2,-z+5/2 #6 -x+2,y-1/2,-z+5/2

#7 x+1,-y+1/2,z+1/2 #8 x,-y+1/2,z-1/2 #9 -x+1,y-1/2,-z+3/2

#10 x-1,-y+1/2,z-1/2

Table C.4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $KLaP_2S_6$. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
La(1)	9(1)	9(1)	8(1)	0(1)	3(1)	0(1)
P(1)	8(2)	9(2)	7(2)	0(1)	2(1)	-1(1)
P(2)	8(2)	8(2)	9(2)	0(1)	3(1)	1(1)
K(1)	14(2)	16(1)	14(2)	1(1)	4(1)	2(1)
S(1)	13(2)	10(2)	8(2)	-1(1)	2(1)	-1(1)
S(2)	12(2)	13(2)	10(2)	-4(1)	5(1)	-2(1)
S(3)	13(2)	13(2)	9(2)	1(1)	6(1)	1(1)
S(4)	11(2)	13(2)	8(2)	-3(1)	3(1)	-3(1)
S(5)	10(2)	15(2)	10(2)	2(1)	3(1)	-1(1)
S(6)	13(2)	9(2)	13(2)	-5(1)	4(1)	0(1)

Table C.5. Crystal data and structure refinement for $K_2La(P_2S_6)_{1/2}(PS_4)$.

Identification code	p21n	
Empirical formula	$K_2La(P_2S_6)_{1/2}(PS_4)$	
Formula weight	503.47	
Temperature	169(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 9.066(6) Å	α= 90°.
	b = 6.793(3) Å	β= 97.54(3)°.
	c = 20.112(7) Å	γ = 90°.
Volume	1227.9(10) $Å^3$	
Z	4	
Density (calculated)	2.724 Mg/m^3	
Absorption coefficient	5.552 mm^{-1}	
F(000)	948	
Crystal size	0.01 x 0.03 x 0.18 mm^3	
Theta range for data collection	2.04 to 28.37°.	
Index ranges	-11<=h<=10, -9<=k<=8, -25<=l<=26	
Reflections collected	7846	
Independent reflections	2978 [R(int) = 0.0796]	
Absorption correction	SADABS	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2976 / 0 / 109	
Goodness-of-fit on F^2	1.016	
Final R indices [I>2sigma(I)]	R1 = 0.0493, wR2 = 0.0765	
R indices (all data)	R1 = 0.1036, wR2 = 0.0956	
Largest diff. peak and hole	1.353 and -1.214 $e.Å^{-3}$	

Table C.6. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for $K_2La(P_2S_6)_{1/2}(PS_4)$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
La(1)	3109(1)	9770(1)	1505(1)	12(1)
P(1)	943(2)	5158(3)	1678(1)	13(1)
P(2)	5847(2)	10101(3)	442(1)	12(1)
S(1)	2224(2)	9695(3)	-60(1)	16(1)
S(2)	3046(2)	5650(3)	2172(1)	14(1)
S(3)	5499(2)	9932(3)	2630(1)	19(1)
S(4)	802(3)	12754(3)	1082(1)	20(1)
S(5)	5591(3)	7637(3)	990(1)	17(1)
S(6)	5305(2)	12489(3)	963(1)	15(1)
S(7)	386(3)	7485(3)	1067(1)	18(1)
K(2)	-1508(2)	10262(3)	1918(1)	29(1)
K(1)	7606(2)	5110(3)	94(1)	20(1)

Table C.7. Bond lengths [Å] and angles [°] for $K_2La(P_2S_6)_{1/2}(PS_4)$.

La(1)-S(3)	2.922(2)	K(2)-S(2)#1	3.430(3)
La(1)-S(7)	2.951(3)	K(2)-S(5)#10	3.506(3)
La(1)-S(4)	2.956(2)	K(2)-P(2)#10	3.564(3)
La(1)-S(5)	2.974(2)	K(2)-S(6)#10	3.587(3)
La(1)-S(6)	3.022(2)	K(2)-S(1)#8	3.707(3)
La(1)-S(2)#1	3.045(2)	K(2)-K(2)#11	4.621(3)
La(1)-S(2)	3.107(2)	K(2)-K(2)#12	4.621(3)
La(1)-S(1)	3.145(2)	K(1)-S(4)#5	3.268(3)
La(1)-K(2)	4.386(3)	K(1)-S(1)#2	3.268(3)
La(1)-K(1)#2	4.605(2)	K(1)-S(7)#6	3.390(3)
P(1)-S(4)#3	2.021(3)	K(1)-S(6)#3	3.396(3)
P(1)-S(7)	2.025(3)	K(1)-S(1)#5	3.534(3)
P(1)-S(3)#4	2.036(3)	K(1)-S(6)#5	3.560(3)
P(1)-S(2)	2.058(3)	K(1)-S(7)#2	3.604(3)
P(2)-S(1)#5	2.005(3)	K(1)-S(4)#13	3.659(3)
P(2)-S(6)	2.026(3)	K(1)-P(2)#3	3.861(3)
P(2)-S(5)	2.034(3)	K(1)-K(1)#14	4.408(4)
P(2)-P(2)#5	2.195(4)		
P(2)-K(2)#6	3.564(3)	S(3)-La(1)-S(7)	139.19(6)
P(2)-K(1)	3.850(3)	S(3)-La(1)-S(4)	128.46(7)
P(2)-K(1)#7	3.861(3)	S(7)-La(1)-S(4)	75.06(7)
S(1)-P(2)#5	2.005(3)	S(3)-La(1)-S(5)	76.70(7)
S(1)-K(1)#2	3.268(3)	S(7)-La(1)-S(5)	106.34(7)
S(1)-K(1)#5	3.534(3)	S(4)-La(1)-S(5)	140.60(6)
S(1)-K(2)#8	3.707(3)	S(3)-La(1)-S(6)	78.45(7)
S(2)-La(1)#4	3.045(2)	S(7)-La(1)-S(6)	141.16(6)
S(2)-K(2)#4	3.430(3)	S(4)-La(1)-S(6)	87.25(7)
S(3)-P(1)#1	2.036(3)	S(5)-La(1)-S(6)	66.91(6)
S(3)-K(2)#6	3.238(3)	S(3)-La(1)-S(2)#1	67.72(7)
S(3)-K(2)#4	3.393(3)	S(7)-La(1)-S(2)#1	89.64(7)
S(4)-P(1)#7	2.021(3)	S(4)-La(1)-S(2)#1	78.79(6)
S(4)-K(1)#5	3.268(3)	S(5)-La(1)-S(2)#1	139.70(6)
S(4)-K(2)	3.317(3)	S(6)-La(1)-S(2)#1	120.92(6)
S(4)-K(1)#9	3.659(3)	S(3)-La(1)-S(2)	75.72(6)
S(5)-K(1)	3.224(3)	S(7)-La(1)-S(2)	65.97(6)
S(5)-K(2)#6	3.505(3)	S(4)-La(1)-S(2)	133.58(6)
S(6)-K(1)#7	3.396(3)	S(5)-La(1)-S(2)	76.64(6)
S(6)-K(1)#5	3.560(3)	S(6)-La(1)-S(2)	139.15(6)
S(6)-K(2)#6	3.587(3)	S(2)#1-La(1)-S(2)	76.80(4)
S(7)-K(2)	3.195(3)	S(3)-La(1)-S(1)	147.28(6)
S(7)-K(1)#10	3.390(3)	S(7)-La(1)-S(1)	66.39(6)
S(7)-K(1)#2	3.604(3)	S(4)-La(1)-S(1)	69.22(6)
K(2)-S(3)#10	3.238(3)	S(5)-La(1)-S(1)	75.45(6)
K(2)-S(3)#1	3.393(3)	S(6)-La(1)-S(1)	75.08(6)

S(2)#1-La(1)-S(1)	143.74(6)	P(2)#5-S(1)-La(1)	105.16(10)
S(2)-La(1)-S(1)	113.61(6)	P(2)#5-S(1)-K(1)#2	90.89(9)
S(3)-La(1)-K(2)	118.66(6)	La(1)-S(1)-K(1)#2	91.76(6)
S(7)-La(1)-K(2)	46.74(6)	P(2)#5-S(1)-K(1)#5	83.18(9)
S(4)-La(1)-K(2)	49.12(6)	La(1)-S(1)-K(1)#5	89.83(6)
S(5)-La(1)-K(2)	152.55(5)	K(1)#2-S(1)-K(1)#5	174.06(9)
S(6)-La(1)-K(2)	135.41(5)	P(2)#5-S(1)-K(2)#8	70.10(8)
S(2)#1-La(1)-K(2)	51.18(5)	La(1)-S(1)-K(2)#8	175.15(7)
S(2)-La(1)-K(2)	85.11(5)	K(1)#2-S(1)-K(2)#8	89.39(6)
S(1)-La(1)-K(2)	93.81(5)	K(1)#5-S(1)-K(2)#8	88.56(6)
S(3)-La(1)-K(1)#2	126.15(5)	P(1)-S(2)-La(1)#4	89.21(9)
S(7)-La(1)-K(1)#2	51.49(5)	P(1)-S(2)-La(1)	90.38(9)
S(4)-La(1)-K(1)#2	105.24(6)	La(1)#4-S(2)-La(1)	125.59(7)
S(5)-La(1)-K(1)#2	56.62(5)	P(1)-S(2)-K(2)#4	165.90(11)
S(6)-La(1)-K(1)#2	103.13(5)	La(1)#4-S(2)-K(2)#4	85.05(7)
S(2)#1-La(1)-K(1)#2	135.95(5)	La(1)-S(2)-K(2)#4	103.44(7)
S(2)-La(1)-K(1)#2	69.15(5)	P(1)#1-S(3)-La(1)	93.14(10)
S(1)-La(1)-K(1)#2	45.19(5)	P(1)#1-S(3)-K(2)#6	161.33(11)
K(2)-La(1)-K(1)#2	97.85(4)	La(1)-S(3)-K(2)#6	103.85(7)
S(4)#3-P(1)-S(7)	106.21(12)	P(1)#1-S(3)-K(2)#4	93.57(10)
S(4)#3-P(1)-S(3)#4	110.40(13)	La(1)-S(3)-K(2)#4	108.61(8)
S(7)-P(1)-S(3)#4	110.04(13)	K(2)#6-S(3)-K(2)#4	88.34(7)
S(4)#3-P(1)-S(2)	113.57(13)	P(1)#7-S(4)-La(1)	113.31(11)
S(7)-P(1)-S(2)	107.89(12)	P(1)#7-S(4)-K(1)#5	94.08(10)
S(3)#4-P(1)-S(2)	108.67(12)	La(1)-S(4)-K(1)#5	98.62(8)
S(1)#5-P(2)-S(6)	115.18(13)	P(1)#7-S(4)-K(2)	96.10(10)
S(1)#5-P(2)-S(5)	115.57(13)	La(1)-S(4)-K(2)	88.52(8)
S(6)-P(2)-S(5)	109.03(12)	K(1)#5-S(4)-K(2)	164.10(9)
S(1)#5-P(2)-P(2)#5	104.27(14)	P(1)#7-S(4)-K(1)#9	87.29(10)
S(6)-P(2)-P(2)#5	106.12(15)	La(1)-S(4)-K(1)#9	159.40(8)
S(5)-P(2)-P(2)#5	105.67(15)	K(1)#5-S(4)-K(1)#9	78.83(7)
S(1)#5-P(2)-K(2)#6	77.96(9)	K(2)-S(4)-K(1)#9	89.48(8)
S(6)-P(2)-K(2)#6	74.16(9)	P(2)-S(5)-La(1)	86.16(9)
S(5)-P(2)-K(2)#6	71.70(9)	P(2)-S(5)-K(1)	91.27(10)
P(2)#5-P(2)-K(2)#6	177.19(14)	La(1)-S(5)-K(1)	164.59(9)
S(1)#5-P(2)-K(1)	65.69(8)	P(2)-S(5)-K(2)#6	74.87(9)
S(6)-P(2)-K(1)	158.96(10)	La(1)-S(5)-K(2)#6	96.65(8)
S(5)-P(2)-K(1)	56.85(8)	K(1)-S(5)-K(2)#6	97.34(8)
P(2)#5-P(2)-K(1)	93.45(11)	P(2)-S(6)-La(1)	85.01(9)
K(2)#6-P(2)-K(1)	85.91(6)	P(2)-S(6)-K(1)#7	86.94(10)
S(1)#5-P(2)-K(1)#7	57.83(8)	La(1)-S(6)-K(1)#7	169.83(8)
S(6)-P(2)-K(1)#7	61.45(9)	P(2)-S(6)-K(1)#5	105.61(10)
S(5)-P(2)-K(1)#7	154.51(11)	La(1)-S(6)-K(1)#5	91.35(7)
P(2)#5-P(2)-K(1)#7	99.79(11)	K(1)#7-S(6)-K(1)#5	84.83(7)
K(2)#6-P(2)-K(1)#7	82.82(6)	P(2)-S(6)-K(2)#6	72.92(9)
K(1)-P(2)-K(1)#7	123.52(8)	La(1)-S(6)-K(2)#6	94.10(7)

K(1)#7-S(6)-K(2)#6	89.45(8)	P(2)#10-K(2)-S(1)#8	31.93(5)
K(1)#5-S(6)-K(2)#6	174.18(8)	S(6)#10-K(2)-S(1)#8	55.59(6)
P(1)-S(7)-La(1)	95.60(10)	S(7)-K(2)-La(1)	42.28(5)
P(1)-S(7)-K(2)	104.15(11)	S(3)#10-K(2)-La(1)	162.66(7)
La(1)-S(7)-K(2)	90.98(8)	S(4)-K(2)-La(1)	42.36(5)
P(1)-S(7)-K(1)#10	94.94(10)	S(3)#1-K(2)-La(1)	83.76(5)
La(1)-S(7)-K(1)#10	162.18(8)	S(2)#1-K(2)-La(1)	43.76(5)
K(2)-S(7)-K(1)#10	100.32(9)	S(5)#10-K(2)-La(1)	121.90(7)
P(1)-S(7)-K(1)#2	84.54(9)	P(2)#10-K(2)-La(1)	113.23(6)
La(1)-S(7)-K(1)#2	88.67(7)	S(6)#10-K(2)-La(1)	130.72(7)
K(2)-S(7)-K(1)#2	171.29(8)	S(1)#8-K(2)-La(1)	81.66(5)
K(1)#10-S(7)-K(1)#2	78.08(7)	S(7)-K(2)-K(2)#11	96.30(6)
S(7)-K(2)-S(3)#10	137.44(9)	S(3)#10-K(2)-K(2)#11	47.21(6)
S(7)-K(2)-S(4)	67.06(7)	S(4)-K(2)-K(2)#11	160.98(8)
S(3)#10-K(2)-S(4)	151.77(9)	S(3)#1-K(2)-K(2)#11	131.34(8)
S(7)-K(2)-S(3)#1	123.41(8)	S(2)#1-K(2)-K(2)#11	100.12(8)
S(3)#10-K(2)-S(3)#1	99.11(7)	S(5)#10-K(2)-K(2)#11	65.25(6)
S(4)-K(2)-S(3)#1	59.52(6)	P(2)#10-K(2)-K(2)#11	97.79(7)
S(7)-K(2)-S(2)#1	79.21(8)	S(6)#10-K(2)-K(2)#11	103.99(8)
S(3)#10-K(2)-S(2)#1	122.04(8)	S(1)#8-K(2)-K(2)#11	119.22(7)
S(4)-K(2)-S(2)#1	68.72(7)	La(1)-K(2)-K(2)#11	118.98(6)
S(3)#1-K(2)-S(2)#1	65.74(6)	S(7)-K(2)-K(2)#12	167.84(7)
S(7)-K(2)-S(5)#10	80.39(8)	S(3)#10-K(2)-K(2)#12	54.72(7)
S(3)#10-K(2)-S(5)#10	65.58(7)	S(4)-K(2)-K(2)#12	101.27(6)
S(4)-K(2)-S(5)#10	117.97(8)	S(3)#1-K(2)-K(2)#12	44.45(4)
S(3)#1-K(2)-S(5)#10	140.84(8)	S(2)#1-K(2)-K(2)#12	93.59(7)
S(2)#1-K(2)-S(5)#10	153.29(8)	S(5)#10-K(2)-K(2)#12	109.20(8)
S(7)-K(2)-P(2)#10	83.46(7)	P(2)#10-K(2)-K(2)#12	100.40(7)
S(3)#10-K(2)-P(2)#10	81.66(7)	S(6)#10-K(2)-K(2)#12	67.77(6)
S(4)-K(2)-P(2)#10	89.65(8)	S(1)#8-K(2)-K(2)#12	118.45(7)
S(3)#1-K(2)-P(2)#10	112.35(7)	La(1)-K(2)-K(2)#12	126.61(6)
S(2)#1-K(2)-P(2)#10	156.26(7)	K(2)#11-K(2)-K(2)#12	94.61(7)
S(5)#10-K(2)-P(2)#10	33.43(5)	S(5)-K(1)-S(4)#5	120.29(8)
S(7)-K(2)-S(6)#10	114.47(8)	S(5)-K(1)-S(1)#2	125.10(7)
S(3)#10-K(2)-S(6)#10	66.62(7)	S(4)#5-K(1)-S(1)#2	113.71(7)
S(4)-K(2)-S(6)#10	91.78(8)	S(5)-K(1)-S(7)#6	81.77(8)
S(3)#1-K(2)-S(6)#10	85.36(7)	S(4)#5-K(1)-S(7)#6	80.84(7)
S(2)#1-K(2)-S(6)#10	150.41(8)	S(1)#2-K(1)-S(7)#6	117.00(7)
S(5)#10-K(2)-S(6)#10	55.55(6)	S(5)-K(1)-S(6)#3	63.90(6)
P(2)#10-K(2)-S(6)#10	32.91(5)	S(4)#5-K(1)-S(6)#3	164.74(8)
S(7)-K(2)-S(1)#8	60.03(6)	S(1)#2-K(1)-S(6)#3	61.38(6)
S(3)#10-K(2)-S(1)#8	113.59(8)	S(7)#6-K(1)-S(6)#3	114.39(8)
S(4)-K(2)-S(1)#8	61.55(6)	S(5)-K(1)-S(1)#5	60.54(6)
S(3)#1-K(2)-S(1)#8	105.55(7)	S(4)#5-K(1)-S(1)#5	61.18(6)
S(2)#1-K(2)-S(1)#8	124.36(7)	S(1)#2-K(1)-S(1)#5	174.06(9)
S(5)#10-K(2)-S(1)#8	56.47(6)	S(7)#6-K(1)-S(1)#5	60.32(6)

S(6)#3-K(1)-S(1)#5	124.38(7)
S(5)-K(1)-S(6)#5	70.10(7)
S(4)#5-K(1)-S(6)#5	74.19(7)
S(1)#2-K(1)-S(6)#5	118.57(7)
S(7)#6-K(1)-S(6)#5	124.29(7)
S(6)#3-K(1)-S(6)#5	95.17(7)
S(1)#5-K(1)-S(6)#5	63.99(6)
S(5)-K(1)-S(7)#2	173.66(8)
S(4)#5-K(1)-S(7)#2	55.92(6)
S(1)#2-K(1)-S(7)#2	57.93(5)
S(7)#6-K(1)-S(7)#2	101.92(7)
S(6)#3-K(1)-S(7)#2	118.27(7)
S(1)#5-K(1)-S(7)#2	116.68(6)
S(6)#5-K(1)-S(7)#2	103.58(7)
S(5)-K(1)-S(4)#13	113.33(7)
S(4)#5-K(1)-S(4)#13	101.17(7)
S(1)#2-K(1)-S(4)#13	62.52(6)
S(7)#6-K(1)-S(4)#13	54.49(6)
S(6)#3-K(1)-S(4)#13	89.29(7)
S(1)#5-K(1)-S(4)#13	114.46(7)
S(6)#5-K(1)-S(4)#13	175.32(7)
S(7)#2-K(1)-S(4)#13	72.94(6)
S(5)-K(1)-P(2)	31.88(5)
S(4)#5-K(1)-P(2)	88.47(7)
S(1)#2-K(1)-P(2)	154.80(7)
S(7)#6-K(1)-P(2)	76.72(7)
S(6)#3-K(1)-P(2)	94.07(7)
S(1)#5-K(1)-P(2)	31.13(5)
S(6)#5-K(1)-P(2)	54.03(5)
S(7)#2-K(1)-P(2)	143.60(6)
S(4)#13-K(1)-P(2)	127.16(6)
S(5)-K(1)-P(2)#3	95.17(7)
S(4)#5-K(1)-P(2)#3	139.02(7)
S(1)#2-K(1)-P(2)#3	31.28(5)
S(7)#6-K(1)-P(2)#3	127.48(7)
S(6)#3-K(1)-P(2)#3	31.61(5)
S(1)#5-K(1)-P(2)#3	154.66(7)
S(6)#5-K(1)-P(2)#3	102.73(7)
S(7)#2-K(1)-P(2)#3	86.69(6)
S(4)#13-K(1)-P(2)#3	80.37(6)
P(2)-K(1)-P(2)#3	123.52(8)
S(5)-K(1)-K(1)#14	134.63(8)
S(4)#5-K(1)-K(1)#14	54.51(6)
S(1)#2-K(1)-K(1)#14	85.12(6)
S(7)#6-K(1)-K(1)#14	53.13(6)
S(6)#3-K(1)-K(1)#14	134.81(8)
S(1)#5-K(1)-K(1)#14	89.22(6)
S(6)#5-K(1)-K(1)#14	128.70(8)
S(7)#2-K(1)-K(1)#14	48.79(5)
S(4)#13-K(1)-K(1)#14	46.65(5)
P(2)-K(1)-K(1)#14	118.79(7)
P(2)#3-K(1)-K(1)#14	114.88(7)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1/2,y+1/2,-z+1/2 #2 -x+1,-y+1,-z #3 x,y-1,z

#4 -x+1/2,y-1/2,-z+1/2 #5 -x+1,-y+2,-z #6 x+1,y,z

#7 x,y+1,z #8 -x,-y+2,-z #9 x-1,y+1,z #10 x-1,y,z

#11 -x-1/2,y-1/2,-z+1/2 #12 -x-1/2,y+1/2,-z+1/2

#13 x+1,y-1,z #14 -x+2,-y+1,-z

Table C.8. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $K_2La(P_2S_6)_{1/2}(PS_4)$. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
La(1)	13(1)	14(1)	9(1)	1(1)	2(1)	-1(1)
P(1)	14(1)	14(1)	11(1)	-1(1)	3(1)	-2(1)
P(2)	15(1)	10(1)	11(1)	0(1)	2(1)	-1(1)
S(1)	12(1)	21(1)	15(1)	-1(1)	3(1)	-2(1)
S(2)	14(1)	15(1)	14(1)	2(1)	2(1)	-1(1)
S(3)	14(1)	32(1)	12(1)	0(1)	3(1)	1(1)
S(4)	26(1)	14(1)	19(1)	-4(1)	2(1)	1(1)
S(5)	23(1)	14(1)	14(1)	4(1)	6(1)	4(1)
S(6)	20(1)	11(1)	14(1)	-2(1)	4(1)	-3(1)
S(7)	20(1)	15(1)	18(1)	2(1)	-1(1)	-1(1)
K(2)	19(1)	35(1)	34(1)	-6(1)	7(1)	-5(1)
K(1)	25(1)	15(1)	23(1)	0(1)	8(1)	-1(1)

Table C.9. Crystal data and structure refinement for $K_3La(PS_4)_2$.

Identification code	p21c	
Empirical formula	$K_3La(PS_4)_2$	
Formula weight	574.63	
Temperature	168(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 9.141(2) Å	α= 90°.
	b = 17.056(4) Å	β= 90.290(15)°.
	c = 9.470(2) Å	γ = 90°.
Volume	1476.5(6) $Å^3$	
Z	4	
Density (calculated)	2.585 Mg/m^3	
Absorption coefficient	5.046 mm^{-1}	
F(000)	1088	
Crystal size	0.06 x 0.12 x 0.12 mm^3	
Theta range for data collection	2.23 to 28.38°.	
Index ranges	-11<=h<=11, -15<=k<=22, -12<=l<=12	
Reflections collected	9659	
Independent reflections	3559 [R(int) = 0.0499]	
Absorption correction	SADABS	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3559 / 0 / 127	
Goodness-of-fit on F^2	1.014	
Final R indices [I>2sigma(I)]	R1 = 0.0386, wR2 = 0.0766	
R indices (all data)	R1 = 0.0600, wR2 = 0.0843	
Largest diff. peak and hole	1.197 and -1.974 $e.Å^{-3}$	

Table C.10. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for $K_3La(PS_4)_2$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
La(1)	2269(1)	137(1)	9697(1)	10(1)
K(1)	1194(2)	2039(1)	13761(2)	31(1)
K(2)	3843(2)	-2881(1)	6299(2)	37(1)
K(3)	2702(1)	-272(1)	5147(1)	21(1)
S(1)	-399(2)	1276(1)	9631(1)	14(1)
S(2)	479(2)	150(1)	12546(1)	15(1)
S(3)	5371(1)	195(1)	8151(1)	13(1)
S(4)	3129(2)	-1312(1)	8226(1)	17(1)
S(5)	2091(2)	1201(1)	7189(1)	16(1)
S(6)	-1304(2)	1742(1)	6302(1)	20(1)
S(7)	5651(2)	-1270(1)	5745(1)	17(1)
S(8)	3379(2)	1587(1)	10919(1)	17(1)
P(1)	5231(1)	-1001(1)	7761(1)	11(1)
P(2)	-84(2)	1040(1)	7528(1)	12(1)

Table C.11. Bond lengths [Å] and angles [°] for $K_3La(PS_4)_2$.

La(1)-S(8)	2.9112(14)	K(3)-S(2)#2	3.652(2)
La(1)-S(4)	2.9452(14)	K(3)-P(2)#9	3.714(2)
La(1)-S(5)	2.9929(14)	K(3)-K(3)#10	4.314(3)
La(1)-S(3)#1	3.0142(14)	K(3)-K(1)#11	4.375(2)
La(1)-S(1)#2	3.0246(14)	S(1)-P(2)	2.054(2)
La(1)-S(1)	3.1187(15)	S(1)-La(1)#2	3.0246(14)
La(1)-S(2)	3.1629(14)	S(1)-K(1)#12	3.327(2)
La(1)-S(3)	3.2000(15)	S(1)-K(2)#13	3.567(2)
La(1)-S(2)#2	3.317(2)	S(2)-P(2)#2	2.062(2)
La(1)-P(2)	3.3421(15)	S(2)-K(3)#5	3.265(2)
La(1)-La(1)#2	4.2164(12)	S(2)-La(1)#2	3.3173(15)
La(1)-K(2)#3	4.376(2)	S(2)-K(3)#2	3.652(2)
K(1)-S(7)#1	3.201(2)	S(3)-P(1)	2.077(2)
K(1)-S(1)#4	3.327(2)	S(3)-La(1)#1	3.0141(14)
K(1)-S(6)#5	3.363(2)	S(3)-K(2)#14	3.399(2)
K(1)-S(8)	3.447(2)	S(3)-K(3)#10	3.595(2)
K(1)-S(5)#4	3.452(2)	S(4)-P(1)	2.043(2)
K(1)-S(2)	3.482(2)	S(4)-K(2)#3	3.283(2)
K(1)-S(5)#5	3.636(2)	S(5)-P(2)	2.034(2)
K(1)-P(2)#4	3.668(2)	S(5)-K(1)#12	3.452(2)
K(1)-S(8)#4	3.691(2)	S(5)-K(1)#11	3.636(2)
K(1)-K(3)#5	4.375(2)	S(6)-P(2)	2.004(2)
K(1)-K(2)#1	4.760(2)	S(6)-K(3)#9	3.127(2)
K(1)-K(3)#2	4.782(2)	S(6)-K(2)#13	3.319(2)
K(2)-S(7)	3.251(2)	S(6)-K(1)#11	3.363(2)
K(2)-S(4)#6	3.283(2)	S(7)-P(1)	2.003(2)
K(2)-S(4)	3.307(2)	S(7)-K(3)#10	3.149(2)
K(2)-S(6)#7	3.319(2)	S(7)-K(1)#1	3.201(2)
K(2)-S(3)#8	3.398(2)	S(8)-P(1)#1	2.039(2)
K(2)-S(8)#8	3.426(2)	S(8)-K(2)#14	3.426(2)
K(2)-S(1)#7	3.567(2)	S(8)-K(1)#12	3.691(2)
K(2)-P(1)	3.713(2)	P(1)-S(8)#1	2.039(2)
K(2)-La(1)#6	4.376(2)	P(2)-S(2)#2	2.063(2)
K(2)-K(3)	4.698(2)	P(2)-K(1)#12	3.668(2)
K(2)-K(1)#1	4.760(2)	P(2)-K(3)#9	3.714(2)
K(2)-K(1)#2	4.823(2)		
K(3)-S(6)#9	3.127(2)	S(8)-La(1)-S(4)	143.84(4)
K(3)-S(7)#10	3.149(2)	S(8)-La(1)-S(5)	79.51(4)
K(3)-S(5)	3.222(2)	S(4)-La(1)-S(5)	98.45(4)
K(3)-S(7)	3.235(2)	S(8)-La(1)-S(3)#1	69.13(4)
K(3)-S(2)#11	3.265(2)	S(4)-La(1)-S(3)#1	88.31(4)
K(3)-S(4)	3.433(2)	S(5)-La(1)-S(3)#1	133.35(4)
K(3)-S(3)#10	3.595(2)	S(8)-La(1)-S(1)#2	142.15(4)
K(3)-P(1)	3.601(2)	S(4)-La(1)-S(1)#2	65.38(4)

S(5)-La(1)-S(1)#2	128.44(4)	P(2)-La(1)-La(1)#2	60.29(3)
S(3)#1-La(1)-S(1)#2	96.39(4)	S(8)-La(1)-K(2)#3	119.70(4)
S(8)-La(1)-S(1)	75.50(4)	S(4)-La(1)-K(2)#3	48.59(4)
S(4)-La(1)-S(1)	136.38(4)	S(5)-La(1)-K(2)#3	145.56(3)
S(5)-La(1)-S(1)	64.34(4)	S(3)#1-La(1)-K(2)#3	50.76(3)
S(3)#1-La(1)-S(1)	133.42(4)	S(1)#2-La(1)-K(2)#3	53.96(4)
S(1)#2-La(1)-S(1)	93.33(4)	S(1)-La(1)-K(2)#3	144.13(3)
S(8)-La(1)-S(2)	80.54(4)	S(2)-La(1)-K(2)#3	83.17(3)
S(4)-La(1)-S(2)	123.37(4)	S(3)-La(1)-K(2)#3	83.98(3)
S(5)-La(1)-S(2)	130.27(4)	S(2)#2-La(1)-K(2)#3	109.80(3)
S(3)#1-La(1)-S(2)	78.23(4)	P(2)-La(1)-K(2)#3	145.85(3)
S(1)#2-La(1)-S(2)	62.02(4)	La(1)#2-La(1)-K(2)#3	100.21(2)
S(1)-La(1)-S(2)	66.71(4)	S(7)#1-K(1)-S(1)#4	135.46(6)
S(8)-La(1)-S(3)	81.24(4)	S(7)#1-K(1)-S(6)#5	116.64(6)
S(4)-La(1)-S(3)	64.53(4)	S(1)#4-K(1)-S(6)#5	69.71(4)
S(5)-La(1)-S(3)	70.31(4)	S(7)#1-K(1)-S(8)	59.81(4)
S(3)#1-La(1)-S(3)	71.48(4)	S(1)#4-K(1)-S(8)	129.98(5)
S(1)#2-La(1)-S(3)	128.60(4)	S(6)#5-K(1)-S(8)	157.37(6)
S(1)-La(1)-S(3)	131.80(4)	S(7)#1-K(1)-S(5)#4	101.74(5)
S(2)-La(1)-S(3)	148.63(4)	S(1)#4-K(1)-S(5)#4	57.37(4)
S(8)-La(1)-S(2)#2	129.89(4)	S(6)#5-K(1)-S(5)#4	127.09(5)
S(4)-La(1)-S(2)#2	77.07(4)	S(8)-K(1)-S(5)#4	73.61(4)
S(5)-La(1)-S(2)#2	62.83(4)	S(7)#1-K(1)-S(2)	80.61(5)
S(3)#1-La(1)-S(2)#2	160.43(4)	S(1)#4-K(1)-S(2)	143.07(6)
S(1)#2-La(1)-S(2)#2	65.81(4)	S(6)#5-K(1)-S(2)	88.29(5)
S(1)-La(1)-S(2)#2	59.33(4)	S(8)-K(1)-S(2)	69.13(4)
S(2)-La(1)-S(2)#2	98.86(3)	S(5)#4-K(1)-S(2)	134.97(5)
S(3)-La(1)-S(2)#2	112.42(4)	S(7)#1-K(1)-S(5)#5	60.63(4)
S(8)-La(1)-P(2)	94.30(4)	S(1)#4-K(1)-S(5)#5	102.43(5)
S(4)-La(1)-P(2)	105.56(4)	S(6)#5-K(1)-S(5)#5	56.86(4)
S(5)-La(1)-P(2)	36.93(4)	S(8)-K(1)-S(5)#5	118.69(5)
S(3)#1-La(1)-P(2)	163.39(4)	S(5)#4-K(1)-S(5)#5	132.37(6)
S(1)#2-La(1)-P(2)	97.70(4)	S(2)-K(1)-S(5)#5	88.43(4)
S(1)-La(1)-P(2)	36.87(3)	S(7)#1-K(1)-P(2)#4	134.25(5)
S(2)-La(1)-P(2)	100.77(4)	S(1)#4-K(1)-P(2)#4	33.71(3)
S(3)-La(1)-P(2)	105.88(4)	S(6)#5-K(1)-P(2)#4	98.39(4)
S(2)#2-La(1)-P(2)	36.08(3)	S(8)-K(1)-P(2)#4	97.82(5)
S(8)-La(1)-La(1)#2	112.41(3)	S(5)#4-K(1)-P(2)#4	33.02(3)
S(4)-La(1)-La(1)#2	103.69(3)	S(2)-K(1)-P(2)#4	131.49(6)
S(5)-La(1)-La(1)#2	97.22(3)	S(5)#5-K(1)-P(2)#4	134.85(5)
S(3)#1-La(1)-La(1)#2	126.03(3)	S(7)#1-K(1)-S(8)#4	72.20(5)
S(1)#2-La(1)-La(1)#2	47.60(3)	S(1)#4-K(1)-S(8)#4	63.30(4)
S(1)-La(1)-La(1)#2	45.74(3)	S(6)#5-K(1)-S(8)#4	93.84(5)
S(2)-La(1)-La(1)#2	51.02(3)	S(8)-K(1)-S(8)#4	105.08(5)
S(3)-La(1)-La(1)#2	160.14(3)	S(5)#4-K(1)-S(8)#4	63.73(4)
S(2)#2-La(1)-La(1)#2	47.83(3)	S(2)-K(1)-S(8)#4	150.56(5)

S(5)#5-K(1)-S(8)#4	68.67(4)	S(3)#8-K(2)-S(8)#8	71.45(4)
P(2)#4-K(1)-S(8)#4	77.26(4)	S(7)-K(2)-S(1)#7	138.53(6)
S(7)#1-K(1)-K(3)#5	45.95(3)	S(4)#6-K(2)-S(1)#7	55.99(4)
S(1)#4-K(1)-K(3)#5	147.31(5)	S(4)-K(2)-S(1)#7	106.61(5)
S(6)#5-K(1)-K(3)#5	82.18(4)	S(6)#7-K(2)-S(1)#7	58.12(4)
S(8)-K(1)-K(3)#5	81.35(4)	S(3)#8-K(2)-S(1)#7	80.48(4)
S(5)#4-K(1)-K(3)#5	146.91(5)	S(8)#8-K(2)-S(1)#7	113.44(5)
S(2)-K(1)-K(3)#5	47.45(3)	S(7)-K(2)-P(1)	32.58(3)
S(5)#5-K(1)-K(3)#5	46.30(3)	S(4)#6-K(2)-P(1)	139.36(5)
P(2)#4-K(1)-K(3)#5	178.84(5)	S(4)-K(2)-P(1)	33.19(3)
S(8)#4-K(1)-K(3)#5	103.73(5)	S(6)#7-K(2)-P(1)	98.66(4)
S(7)#1-K(1)-K(2)#1	42.87(4)	S(3)#8-K(2)-P(1)	134.83(6)
S(1)#4-K(1)-K(2)#1	99.24(5)	S(8)#8-K(2)-P(1)	101.79(5)
S(6)#5-K(1)-K(2)#1	134.80(5)	S(1)#7-K(2)-P(1)	137.67(5)
S(8)-K(1)-K(2)#1	60.12(4)	S(7)-K(2)-La(1)#6	148.61(5)
S(5)#4-K(1)-K(2)#1	60.25(4)	S(4)#6-K(2)-La(1)#6	42.29(3)
S(2)-K(1)-K(2)#1	116.92(4)	S(4)-K(2)-La(1)#6	146.89(5)
S(5)#5-K(1)-K(2)#1	85.34(4)	S(6)#7-K(2)-La(1)#6	80.65(4)
P(2)#4-K(1)-K(2)#1	91.63(4)	S(3)#8-K(2)-La(1)#6	43.39(3)
S(8)#4-K(1)-K(2)#1	45.70(3)	S(8)#8-K(2)-La(1)#6	78.35(3)
K(3)#5-K(1)-K(2)#1	88.67(4)	S(1)#7-K(2)-La(1)#6	43.28(3)
S(7)#1-K(1)-K(3)#2	112.45(5)	P(1)-K(2)-La(1)#6	178.11(5)
S(1)#4-K(1)-K(3)#2	99.40(4)	S(7)-K(2)-K(3)	43.46(4)
S(6)#5-K(1)-K(3)#2	40.67(3)	S(4)#6-K(2)-K(3)	98.53(5)
S(8)-K(1)-K(3)#2	117.59(5)	S(4)-K(2)-K(3)	46.92(4)
S(5)#4-K(1)-K(3)#2	145.10(5)	S(6)#7-K(2)-K(3)	100.78(5)
S(2)-K(1)-K(3)#2	49.44(3)	S(3)#8-K(2)-K(3)	175.31(5)
S(5)#5-K(1)-K(3)#2	73.98(4)	S(8)#8-K(2)-K(3)	105.82(4)
P(2)#4-K(1)-K(3)#2	113.30(4)	S(1)#7-K(2)-K(3)	97.43(5)
S(8)#4-K(1)-K(3)#2	133.00(4)	P(1)-K(2)-K(3)	48.99(3)
K(3)#5-K(1)-K(3)#2	66.50(4)	La(1)#6-K(2)-K(3)	132.83(4)
K(2)#1-K(1)-K(3)#2	154.66(4)	S(7)-K(2)-K(1)#1	42.05(4)
S(7)-K(2)-S(4)#6	108.08(5)	S(4)#6-K(2)-K(1)#1	107.53(4)
S(7)-K(2)-S(4)	60.43(4)	S(4)-K(2)-K(1)#1	87.31(4)
S(4)#6-K(2)-S(4)	142.17(7)	S(6)#7-K(2)-K(1)#1	137.44(5)
S(7)-K(2)-S(6)#7	129.20(5)	S(3)#8-K(2)-K(1)#1	95.32(5)
S(4)#6-K(2)-S(6)#7	112.91(5)	S(8)#8-K(2)-K(1)#1	50.44(4)
S(4)-K(2)-S(6)#7	68.80(4)	S(1)#7-K(2)-K(1)#1	163.49(4)
S(7)-K(2)-S(3)#8	137.21(6)	P(1)-K(2)-K(1)#1	54.55(3)
S(4)#6-K(2)-S(3)#8	76.82(4)	La(1)#6-K(2)-K(1)#1	124.96(4)
S(4)-K(2)-S(3)#8	137.68(6)	K(3)-K(2)-K(1)#1	85.52(3)
S(6)#7-K(2)-S(3)#8	81.73(4)	S(7)-K(2)-K(1)#2	103.43(5)
S(7)-K(2)-S(8)#8	75.27(4)	S(4)#6-K(2)-K(1)#2	85.92(5)
S(4)#6-K(2)-S(8)#8	59.33(4)	S(4)-K(2)-K(1)#2	64.80(4)
S(4)-K(2)-S(8)#8	134.55(5)	S(6)#7-K(2)-K(1)#2	52.77(4)
S(6)#7-K(2)-S(8)#8	153.08(6)	S(3)#8-K(2)-K(1)#2	119.37(4)

S(8)#8-K(2)-K(1)#2	141.44(5)	S(2)#11-K(3)-P(2)#9	33.60(3)
S(1)#7-K(2)-K(1)#2	43.60(3)	S(4)-K(3)-P(2)#9	117.87(5)
P(1)-K(2)-K(1)#2	94.10(4)	S(3)#10-K(3)-P(2)#9	74.78(4)
La(1)#6-K(2)-K(1)#2	86.88(3)	P(1)-K(3)-P(2)#9	139.16(5)
K(3)-K(2)-K(1)#2	60.28(3)	S(2)#2-K(3)-P(2)#9	85.18(4)
K(1)#1-K(2)-K(1)#2	145.07(5)	S(6)#9-K(3)-K(3)#10	122.71(6)
S(6)#9-K(3)-S(7)#10	138.34(5)	S(7)#10-K(3)-K(3)#10	48.35(4)
S(6)#9-K(3)-S(5)	144.78(6)	S(5)-K(3)-K(3)#10	92.43(5)
S(7)#10-K(3)-S(5)	66.03(4)	S(7)-K(3)-K(3)#10	46.65(4)
S(6)#9-K(3)-S(7)	89.62(5)	S(2)#11-K(3)-K(3)#10	120.44(5)
S(7)#10-K(3)-S(7)	95.00(5)	S(4)-K(3)-K(3)#10	93.39(5)
S(5)-K(3)-S(7)	116.87(5)	S(3)#10-K(3)-K(3)#10	56.94(4)
S(6)#9-K(3)-S(2)#11	66.11(4)	P(1)-K(3)-K(3)#10	59.76(4)
S(7)#10-K(3)-S(2)#11	84.84(5)	S(2)#2-K(3)-K(3)#10	143.60(5)
S(5)-K(3)-S(2)#11	99.87(5)	P(2)#9-K(3)-K(3)#10	131.04(5)
S(7)-K(3)-S(2)#11	139.72(5)	S(6)#9-K(3)-K(1)#11	117.61(5)
S(6)#9-K(3)-S(4)	90.18(5)	S(7)#10-K(3)-K(1)#11	46.94(4)
S(7)#10-K(3)-S(4)	127.34(5)	S(5)-K(3)-K(1)#11	54.68(4)
S(5)-K(3)-S(4)	84.96(4)	S(7)-K(3)-K(1)#11	141.94(5)
S(7)-K(3)-S(4)	59.24(4)	S(2)#11-K(3)-K(1)#11	51.76(4)
S(2)#11-K(3)-S(4)	145.31(5)	S(4)-K(3)-K(1)#11	138.95(4)
S(6)#9-K(3)-S(3)#10	81.35(4)	S(3)#10-K(3)-K(1)#11	82.04(4)
S(7)#10-K(3)-S(3)#10	59.96(4)	P(1)-K(3)-K(1)#11	135.85(4)
S(5)-K(3)-S(3)#10	125.44(5)	S(2)#2-K(3)-K(1)#11	82.96(4)
S(7)-K(3)-S(3)#10	76.11(4)	P(2)#9-K(3)-K(1)#11	84.96(4)
S(2)#11-K(3)-S(3)#10	69.07(4)	K(3)#10-K(3)-K(1)#11	95.29(4)
S(4)-K(3)-S(3)#10	134.63(5)	P(2)-S(1)-La(1)#2	97.45(6)
S(6)#9-K(3)-P(1)	106.51(5)	P(2)-S(1)-La(1)	77.49(6)
S(7)#10-K(3)-P(1)	99.59(5)	La(1)#2-S(1)-La(1)	86.67(4)
S(5)-K(3)-P(1)	88.24(4)	P(2)-S(1)-K(1)#12	82.29(6)
S(7)-K(3)-P(1)	33.54(3)	La(1)#2-S(1)-K(1)#12	171.49(6)
S(2)#11-K(3)-P(1)	171.82(5)	La(1)-S(1)-K(1)#12	101.53(5)
S(4)-K(3)-P(1)	33.66(3)	P(2)-S(1)-K(2)#13	88.14(6)
S(3)#10-K(3)-P(1)	107.12(5)	La(1)#2-S(1)-K(2)#13	82.76(4)
S(6)#9-K(3)-S(2)#2	89.06(5)	La(1)-S(1)-K(2)#13	160.90(5)
S(7)#10-K(3)-S(2)#2	119.74(5)	K(1)#12-S(1)-K(2)#13	88.73(5)
S(5)-K(3)-S(2)#2	56.99(4)	P(2)#2-S(2)-La(1)	93.17(6)
S(7)-K(3)-S(2)#2	126.18(5)	P(2)#2-S(2)-K(3)#5	85.21(6)
S(2)#11-K(3)-S(2)#2	86.81(5)	La(1)-S(2)-K(3)#5	108.60(5)
S(4)-K(3)-S(2)#2	66.96(4)	P(2)#2-S(2)-La(1)#2	72.62(5)
S(3)#10-K(3)-S(2)#2	155.88(5)	La(1)-S(2)-La(1)#2	81.14(3)
P(1)-K(3)-S(2)#2	96.80(4)	K(3)#5-S(2)-La(1)#2	156.42(5)
S(6)#9-K(3)-P(2)#9	32.66(3)	P(2)#2-S(2)-K(1)	162.60(7)
S(7)#10-K(3)-P(2)#9	114.78(5)	La(1)-S(2)-K(1)	101.04(4)
S(5)-K(3)-P(2)#9	124.83(5)	K(3)#5-S(2)-K(1)	80.78(4)
S(7)-K(3)-P(2)#9	117.87(5)	La(1)#2-S(2)-K(1)	119.24(5)

P(2)#2-S(2)-K(3)#2	86.38(6)	K(1)#1-S(7)-K(3)	172.09(6)
La(1)-S(2)-K(3)#2	158.10(5)	P(1)-S(7)-K(2)	86.52(6)
K(3)#5-S(2)-K(3)#2	93.19(4)	K(3)#10-S(7)-K(2)	173.64(6)
La(1)#2-S(2)-K(3)#2	77.83(4)	K(1)#1-S(7)-K(2)	95.08(5)
K(1)-S(2)-K(3)#2	84.15(4)	K(3)-S(7)-K(2)	92.82(5)
P(1)-S(3)-La(1)#1	88.79(6)	P(1)#1-S(8)-La(1)	92.44(6)
P(1)-S(3)-La(1)	89.81(5)	P(1)#1-S(8)-K(2)#14	92.51(7)
La(1)#1-S(3)-La(1)	108.52(4)	La(1)-S(8)-K(2)#14	103.82(5)
P(1)-S(3)-K(2)#14	171.26(7)	P(1)#1-S(8)-K(1)	89.60(6)
La(1)#1-S(3)-K(2)#14	85.85(4)	La(1)-S(8)-K(1)	107.35(5)
La(1)-S(3)-K(2)#14	98.43(4)	K(2)#14-S(8)-K(1)	148.63(6)
P(1)-S(3)-K(3)#10	84.97(5)	P(1)#1-S(8)-K(1)#12	169.86(7)
La(1)#1-S(3)-K(3)#10	104.02(4)	La(1)-S(8)-K(1)#12	97.62(4)
La(1)-S(3)-K(3)#10	146.91(5)	K(2)#14-S(8)-K(1)#12	83.86(5)
K(2)#14-S(3)-K(3)#10	89.63(4)	K(1)-S(8)-K(1)#12	88.63(4)
P(1)-S(4)-La(1)	97.95(6)	S(7)-P(1)-S(8)#1	110.51(8)
P(1)-S(4)-K(2)#3	96.68(7)	S(7)-P(1)-S(4)	109.33(8)
La(1)-S(4)-K(2)#3	89.12(4)	S(8)#1-P(1)-S(4)	108.99(8)
P(1)-S(4)-K(2)	84.40(6)	S(7)-P(1)-S(3)	112.45(8)
La(1)-S(4)-K(2)	173.77(6)	S(8)#1-P(1)-S(3)	109.55(8)
K(2)#3-S(4)-K(2)	96.35(4)	S(4)-P(1)-S(3)	105.87(8)
P(1)-S(4)-K(3)	77.68(6)	S(7)-P(1)-K(3)	63.18(6)
La(1)-S(4)-K(3)	86.52(4)	S(8)#1-P(1)-K(3)	170.61(7)
K(2)#3-S(4)-K(3)	172.31(6)	S(4)-P(1)-K(3)	68.66(6)
K(2)-S(4)-K(3)	88.36(5)	S(3)-P(1)-K(3)	79.73(6)
P(2)-S(5)-La(1)	80.91(5)	S(7)-P(1)-K(2)	60.90(6)
P(2)-S(5)-K(3)	99.31(6)	S(8)#1-P(1)-K(2)	90.93(6)
La(1)-S(5)-K(3)	89.68(4)	S(4)-P(1)-K(2)	62.41(5)
P(2)-S(5)-K(1)#12	79.35(6)	S(3)-P(1)-K(2)	159.23(7)
La(1)-S(5)-K(1)#12	101.37(5)	K(3)-P(1)-K(2)	79.91(4)
K(3)-S(5)-K(1)#12	168.44(6)	S(6)-P(2)-S(5)	111.67(8)
P(2)-S(5)-K(1)#11	88.74(6)	S(6)-P(2)-S(1)	111.35(8)
La(1)-S(5)-K(1)#11	163.29(5)	S(5)-P(2)-S(1)	105.58(8)
K(3)-S(5)-K(1)#11	79.03(4)	S(6)-P(2)-S(2)#2	118.15(9)
K(1)#12-S(5)-K(1)#11	89.45(4)	S(5)-P(2)-S(2)#2	107.38(8)
P(2)-S(6)-K(3)#9	89.99(7)	S(1)-P(2)-S(2)#2	101.59(7)
P(2)-S(6)-K(2)#13	96.20(7)	S(6)-P(2)-La(1)	170.48(7)
K(3)#9-S(6)-K(2)#13	99.77(6)	S(5)-P(2)-La(1)	62.16(5)
P(2)-S(6)-K(1)#11	97.27(7)	S(1)-P(2)-La(1)	65.64(5)
K(3)#9-S(6)-K(1)#11	94.84(5)	S(2)#2-P(2)-La(1)	71.30(5)
K(2)#13-S(6)-K(1)#11	160.08(6)	S(6)-P(2)-K(1)#12	79.97(6)
P(1)-S(7)-K(3)#10	99.13(7)	S(5)-P(2)-K(1)#12	67.64(6)
P(1)-S(7)-K(1)#1	97.55(7)	S(1)-P(2)-K(1)#12	64.01(5)
K(3)#10-S(7)-K(1)#1	87.10(5)	S(2)#2-P(2)-K(1)#12	160.97(7)
P(1)-S(7)-K(3)	83.29(6)	La(1)-P(2)-K(1)#12	90.75(4)
K(3)#10-S(7)-K(3)	85.00(5)	S(6)-P(2)-K(3)#9	57.35(6)

S(5)-P(2)-K(3)#9	124.54(6)
S(1)-P(2)-K(3)#9	129.60(7)
S(2)#2-P(2)-K(3)#9	61.19(5)
La(1)-P(2)-K(3)#9	131.85(5)
K(1)#12-P(2)-K(3)#9	137.31(5)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y,-z+2 #2 -x,-y,-z+2 #3 x,-y-1/2,z+1/2

#4 x,-y+1/2,z+1/2 #5 x,y,z+1 #6 x,-y-1/2,z-1/2

#7 -x,y-1/2,-z+3/2 #8 -x+1,y-1/2,-z+3/2 #9 -x,-y,-z+1

#10 -x+1,-y,-z+1 #11 x,y,z-1 #12 x,-y+1/2,z-1/2

#13 -x,y+1/2,-z+3/2 #14 -x+1,y+1/2,-z+3/2

Table C.12. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $K_3La(PS_4)_2$. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
La(1)	11(1)	8(1)	12(1)	0(1)	2(1)	0(1)
K(1)	31(1)	19(1)	45(1)	4(1)	16(1)	7(1)
K(2)	49(1)	21(1)	41(1)	-14(1)	24(1)	-14(1)
K(3)	23(1)	19(1)	20(1)	1(1)	-3(1)	-1(1)
S(1)	17(1)	13(1)	13(1)	-2(1)	5(1)	-2(1)
S(2)	19(1)	9(1)	16(1)	0(1)	1(1)	1(1)
S(3)	15(1)	10(1)	15(1)	0(1)	2(1)	0(1)
S(4)	15(1)	14(1)	24(1)	-5(1)	8(1)	-4(1)
S(5)	14(1)	17(1)	17(1)	2(1)	5(1)	-1(1)
S(6)	24(1)	15(1)	21(1)	7(1)	1(1)	5(1)
S(7)	22(1)	18(1)	13(1)	-4(1)	5(1)	-1(1)
S(8)	21(1)	11(1)	19(1)	1(1)	-2(1)	2(1)
P(1)	12(1)	9(1)	13(1)	-1(1)	4(1)	-1(1)
P(2)	13(1)	10(1)	12(1)	0(1)	3(1)	-1(1)

Table C.13. Crystal data and structure refinement for $K_4La_{0.67}(PS_4)_2$.

Identification code	ibam	
Empirical formula	$K_4La_{0.67}(PS_4)_2$	
Formula weight	567.89	
Temperature	170(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Ibam	
Unit cell dimensions	a = 18.2020(15) Å	α= 90°.
	b = 8.7596(7) Å	β= 90°.
	c = 9.7699(8) Å	γ = 90°.
Volume	1557.7(2) $Å^3$	
Z	4	
Density (calculated)	2.421 Mg/m^3	
Absorption coefficient	4.171 mm^{-1}	
F(000)	1089	
Crystal size	0.09 x 0.12 x 0.15 mm^3	
Theta range for data collection	2.24 to 28.46°.	
Index ranges	-24<=h<=21, -11<=k<=8, -12<=l<=10	
Reflections collected	4880	
Independent reflections	1031 [R(int) = 0.0737]	
Absorption correction	SADABS	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1031 / 0 / 42	
Goodness-of-fit on F^2	1.055	
Final R indices [I>2sigma(I)]	R1 = 0.0469, wR2 = 0.1043	
R indices (all data)	R1 = 0.0661, wR2 = 0.1115	
Largest diff. peak and hole	1.154 and -1.064 $e.Å^{-3}$	

Table C.14. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for $K_4La_{0.67}(PS_4)_2$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
La(1)	0	0	2500	10(1)
P(1)	1290(1)	2064(2)	5000	15(1)
S(1)	807(1)	2986(2)	3312(1)	24(1)
S(2)	1069(1)	245(2)	0	28(1)
S(3)	2383(1)	2468(2)	5000	27(1)
K(1)	-820(1)	-3741(2)	0	32(1)
K(2)	2446(1)	0	2500	37(1)

Table C.15. Bond lengths [Å] and angles [°] for $K_4La_{0.67}(PS_4)_2$.

La(1)-S(1)	3.1024(14)	K(1)-K(2)#17	4.140(2)
La(1)-S(1)#1	3.1025(14)	K(2)-S(3)#9	3.2637(13)
La(1)-S(1)#2	3.1025(14)	K(2)-S(3)#8	3.3140(14)
La(1)-S(1)#3	3.1025(14)	K(2)-S(3)#18	3.3140(14)
La(1)-S(2)#4	3.1302(12)	K(2)-S(2)#4	3.506(2)
La(1)-S(2)	3.1302(12)	K(2)-P(1)#9	3.696(2)
La(1)-S(2)#5	3.1302(12)	K(2)-S(1)#8	3.722(2)
La(1)-S(2)#2	3.1302(12)	K(2)-S(1)#19	3.722(2)
La(1)-K(1)#5	4.351(2)	K(2)-K(1)#12	4.140(2)
La(1)-K(1)#2	4.351(2)	K(2)-K(1)#20	4.140(2)
La(1)-K(1)#4	4.351(2)		
La(1)-K(1)	4.351(2)	S(1)-La(1)-S(1)#1	123.50(5)
P(1)-S(3)	2.020(2)	S(1)-La(1)-S(1)#2	65.09(5)
P(1)-S(1)#6	2.036(2)	S(1)#1-La(1)-S(1)#2	150.37(5)
P(1)-S(1)	2.036(2)	S(1)-La(1)-S(1)#3	150.37(5)
P(1)-S(2)#4	2.062(3)	S(1)#1-La(1)-S(1)#3	65.09(5)
P(1)-K(2)	3.696(2)	S(1)#2-La(1)-S(1)#3	123.50(5)
P(1)-K(2)#6	3.696(2)	S(1)-La(1)-S(2)#4	64.15(4)
P(1)-K(1)#7	3.773(3)	S(1)#1-La(1)-S(2)#4	81.23(4)
S(1)-K(1)#5	3.3028(14)	S(1)#2-La(1)-S(2)#4	123.47(4)
S(1)-K(1)#7	3.308(2)	S(1)#3-La(1)-S(2)#4	92.12(4)
S(1)-K(1)#4	3.454(2)	S(1)-La(1)-S(2)	81.23(4)
S(1)-K(2)#8	3.722(2)	S(1)#1-La(1)-S(2)	64.15(4)
S(2)-P(1)#9	2.062(3)	S(1)#2-La(1)-S(2)	92.12(4)
S(2)-K(1)#5	3.096(3)	S(1)#3-La(1)-S(2)	123.47(4)
S(2)-La(1)#5	3.1302(12)	S(2)#4-La(1)-S(2)	103.13(5)
S(2)-K(2)	3.506(2)	S(1)-La(1)-S(2)#5	123.47(4)
S(2)-K(2)#10	3.506(2)	S(1)#1-La(1)-S(2)#5	92.12(4)
S(3)-K(2)	3.2637(13)	S(1)#2-La(1)-S(2)#5	64.15(4)
S(3)-K(2)#6	3.2637(13)	S(1)#3-La(1)-S(2)#5	81.23(4)
S(3)-K(2)#11	3.3140(14)	S(2)#4-La(1)-S(2)#5	172.14(6)
S(3)-K(2)#8	3.3140(14)	S(2)-La(1)-S(2)#5	77.42(5)
S(3)-K(1)#12	3.437(3)	S(1)-La(1)-S(2)#2	92.12(4)
K(1)-S(2)#5	3.096(3)	S(1)#1-La(1)-S(2)#2	123.47(4)
K(1)-S(1)#3	3.3028(14)	S(1)#2-La(1)-S(2)#2	81.23(4)
K(1)-S(1)#5	3.3028(14)	S(1)#3-La(1)-S(2)#2	64.15(4)
K(1)-S(1)#13	3.308(2)	S(2)#4-La(1)-S(2)#2	77.42(5)
K(1)-S(1)#14	3.308(2)	S(2)-La(1)-S(2)#2	172.14(6)
K(1)-S(3)#15	3.437(3)	S(2)#5-La(1)-S(2)#2	103.13(5)
K(1)-S(1)#1	3.454(2)	S(1)-La(1)-K(1)#5	49.18(3)
K(1)-S(1)#9	3.454(2)	S(1)#1-La(1)-K(1)#5	109.20(3)
K(1)-K(1)#16	3.713(4)	S(1)#2-La(1)-K(1)#5	51.98(4)
K(1)-P(1)#14	3.773(3)	S(1)#3-La(1)-K(1)#5	160.18(3)
K(1)-K(2)#15	4.140(2)	S(2)#4-La(1)-K(1)#5	106.04(4)

S(2)-La(1)-K(1)#5	45.34(4)	S(2)#4-P(1)-K(2)#6	68.38(6)
S(2)#5-La(1)-K(1)#5	80.04(3)	K(2)-P(1)-K(2)#6	82.73(5)
S(2)#2-La(1)-K(1)#5	126.85(4)	S(3)-P(1)-K(1)#7	93.01(9)
S(1)-La(1)-K(1)#2	109.20(3)	S(1)#6-P(1)-K(1)#7	61.04(6)
S(1)#1-La(1)-K(1)#2	49.18(3)	S(1)-P(1)-K(1)#7	61.04(6)
S(1)#2-La(1)-K(1)#2	160.18(3)	S(2)#4-P(1)-K(1)#7	155.63(9)
S(1)#3-La(1)-K(1)#2	51.98(4)	K(2)-P(1)-K(1)#7	127.26(4)
S(2)#4-La(1)-K(1)#2	45.34(4)	K(2)#6-P(1)-K(1)#7	127.26(4)
S(2)-La(1)-K(1)#2	106.04(4)	P(1)-S(1)-La(1)	94.44(7)
S(2)#5-La(1)-K(1)#2	126.85(4)	P(1)-S(1)-K(1)#5	150.42(8)
S(2)#2-La(1)-K(1)#2	80.04(3)	La(1)-S(1)-K(1)#5	85.52(5)
K(1)#5-La(1)-K(1)#2	139.86(5)	P(1)-S(1)-K(1)#7	86.37(7)
S(1)-La(1)-K(1)#4	51.98(4)	La(1)-S(1)-K(1)#7	149.51(6)
S(1)#1-La(1)-K(1)#4	160.19(3)	K(1)#5-S(1)-K(1)#7	108.34(4)
S(1)#2-La(1)-K(1)#4	49.18(3)	P(1)-S(1)-K(1)#4	93.44(7)
S(1)#3-La(1)-K(1)#4	109.20(3)	La(1)-S(1)-K(1)#4	82.98(4)
S(2)#4-La(1)-K(1)#4	80.04(3)	K(1)#5-S(1)-K(1)#4	115.84(5)
S(2)-La(1)-K(1)#4	126.85(4)	K(1)#7-S(1)-K(1)#4	66.57(6)
S(2)#5-La(1)-K(1)#4	106.04(4)	P(1)-S(1)-K(2)#8	89.50(7)
S(2)#2-La(1)-K(1)#4	45.34(4)	La(1)-S(1)-K(2)#8	138.54(5)
K(1)#5-La(1)-K(1)#4	82.28(4)	K(1)#5-S(1)-K(2)#8	71.93(4)
K(1)#2-La(1)-K(1)#4	111.71(3)	K(1)#7-S(1)-K(2)#8	71.88(4)
S(1)-La(1)-K(1)	160.19(3)	K(1)#4-S(1)-K(2)#8	138.03(5)
S(1)#1-La(1)-K(1)	51.98(4)	P(1)#9-S(2)-K(1)#5	177.14(11)
S(1)#2-La(1)-K(1)	109.20(3)	P(1)#9-S(2)-La(1)	93.11(6)
S(1)#3-La(1)-K(1)	49.18(3)	K(1)#5-S(2)-La(1)	88.68(4)
S(2)#4-La(1)-K(1)	126.85(4)	P(1)#9-S(2)-La(1)#5	93.11(6)
S(2)-La(1)-K(1)	80.04(3)	K(1)#5-S(2)-La(1)#5	88.68(4)
S(2)#5-La(1)-K(1)	45.34(4)	La(1)-S(2)-La(1)#5	102.58(5)
S(2)#2-La(1)-K(1)	106.04(4)	P(1)#9-S(2)-K(2)	78.48(6)
K(1)#5-La(1)-K(1)	111.71(3)	K(1)#5-S(2)-K(2)	99.50(5)
K(1)#2-La(1)-K(1)	82.28(4)	La(1)-S(2)-K(2)	84.07(3)
K(1)#4-La(1)-K(1)	139.86(5)	La(1)#5-S(2)-K(2)	169.65(6)
S(3)-P(1)-S(1)#6	110.86(8)	P(1)#9-S(2)-K(2)#10	78.48(6)
S(3)-P(1)-S(1)	110.86(8)	K(1)#5-S(2)-K(2)#10	99.50(5)
S(1)#6-P(1)-S(1)	108.17(12)	La(1)-S(2)-K(2)#10	169.65(6)
S(3)-P(1)-S(2)#4	111.36(11)	La(1)#5-S(2)-K(2)#10	84.07(3)
S(1)#6-P(1)-S(2)#4	107.73(7)	K(2)-S(2)-K(2)#10	88.31(7)
S(1)-P(1)-S(2)#4	107.73(7)	P(1)-S(3)-K(2)	85.33(7)
S(3)-P(1)-K(2)	61.66(6)	P(1)-S(3)-K(2)#6	85.33(7)
S(1)#6-P(1)-K(2)	167.22(7)	K(2)-S(3)-K(2)#6	96.90(5)
S(1)-P(1)-K(2)	84.54(5)	P(1)-S(3)-K(2)#11	102.10(7)
S(2)#4-P(1)-K(2)	68.38(6)	K(2)-S(3)-K(2)#11	172.57(6)
S(3)-P(1)-K(2)#6	61.66(6)	K(2)#6-S(3)-K(2)#11	83.595(8)
S(1)#6-P(1)-K(2)#6	84.54(5)	P(1)-S(3)-K(2)#8	102.10(7)
S(1)-P(1)-K(2)#6	167.22(7)	K(2)-S(3)-K(2)#8	83.595(8)

K(2)#6-S(3)-K(2)#8	172.57(6)	S(1)#13-K(1)-P(1)#14	32.59(3)
K(2)#11-S(3)-K(2)#8	94.96(5)	S(1)#14-K(1)-P(1)#14	32.59(3)
P(1)-S(3)-K(1)#12	151.97(10)	S(3)#15-K(1)-P(1)#14	94.84(6)
K(2)-S(3)-K(1)#12	76.26(6)	S(1)#1-K(1)-P(1)#14	112.39(5)
K(2)#6-S(3)-K(1)#12	76.26(6)	S(1)#9-K(1)-P(1)#14	112.39(5)
K(2)#11-S(3)-K(1)#12	96.72(6)	K(1)#16-K(1)-P(1)#14	66.66(6)
K(2)#8-S(3)-K(1)#12	96.72(6)	S(2)#5-K(1)-K(2)#15	98.75(5)
S(2)#5-K(1)-S(1)#3	78.63(4)	S(1)#3-K(1)-K(2)#15	129.58(6)
S(2)#5-K(1)-S(1)#5	78.63(4)	S(1)#5-K(1)-K(2)#15	58.74(3)
S(1)#3-K(1)-S(1)#5	156.87(8)	S(1)#13-K(1)-K(2)#15	58.71(4)
S(2)#5-K(1)-S(1)#13	149.16(3)	S(1)#14-K(1)-K(2)#15	93.95(5)
S(1)#3-K(1)-S(1)#13	131.46(5)	S(3)#15-K(1)-K(2)#15	49.98(4)
S(1)#5-K(1)-S(1)#13	71.65(4)	S(1)#1-K(1)-K(2)#15	170.52(5)
S(2)#5-K(1)-S(1)#14	149.16(3)	S(1)#9-K(1)-K(2)#15	115.02(3)
S(1)#3-K(1)-S(1)#14	71.65(4)	K(1)#16-K(1)-K(2)#15	117.06(6)
S(1)#5-K(1)-S(1)#14	131.46(5)	P(1)#14-K(1)-K(2)#15	64.39(3)
S(1)#13-K(1)-S(1)#14	59.81(6)	S(2)#5-K(1)-K(2)#17	98.75(5)
S(2)#5-K(1)-S(3)#15	63.65(6)	S(1)#3-K(1)-K(2)#17	58.74(3)
S(1)#3-K(1)-S(3)#15	86.87(4)	S(1)#5-K(1)-K(2)#17	129.58(6)
S(1)#5-K(1)-S(3)#15	86.87(4)	S(1)#13-K(1)-K(2)#17	93.95(5)
S(1)#13-K(1)-S(3)#15	105.91(6)	S(1)#14-K(1)-K(2)#17	58.71(4)
S(1)#14-K(1)-S(3)#15	105.91(6)	S(3)#15-K(1)-K(2)#17	49.98(4)
S(2)#5-K(1)-S(1)#1	86.32(6)	S(1)#1-K(1)-K(2)#17	115.02(3)
S(1)#3-K(1)-S(1)#1	59.16(5)	S(1)#9-K(1)-K(2)#17	170.52(5)
S(1)#5-K(1)-S(1)#1	115.02(5)	K(1)#16-K(1)-K(2)#17	117.06(6)
S(1)#13-K(1)-S(1)#1	113.43(6)	P(1)#14-K(1)-K(2)#17	64.39(3)
S(1)#14-K(1)-S(1)#1	85.50(5)	K(2)#15-K(1)-K(2)#17	72.31(5)
S(3)#15-K(1)-S(1)#1	139.18(5)	S(3)-K(2)-S(3)#9	175.97(10)
S(2)#5-K(1)-S(1)#9	86.32(6)	S(3)-K(2)-S(3)#8	96.405(8)
S(1)#3-K(1)-S(1)#9	115.02(5)	S(3)#9-K(2)-S(3)#8	83.975(9)
S(1)#5-K(1)-S(1)#9	59.16(5)	S(3)-K(2)-S(3)#18	83.975(8)
S(1)#13-K(1)-S(1)#9	85.50(5)	S(3)#9-K(2)-S(3)#18	96.404(8)
S(1)#14-K(1)-S(1)#9	113.43(6)	S(3)#8-K(2)-S(3)#18	169.23(10)
S(3)#15-K(1)-S(1)#9	139.18(5)	S(3)-K(2)-S(2)	117.11(6)
S(1)#1-K(1)-S(1)#9	57.04(6)	S(3)#9-K(2)-S(2)	59.61(4)
S(2)#5-K(1)-K(1)#16	134.85(9)	S(3)#8-K(2)-S(2)	60.84(4)
S(1)#3-K(1)-K(1)#16	96.49(4)	S(3)#18-K(2)-S(2)	128.42(6)
S(1)#5-K(1)-K(1)#16	96.49(4)	S(3)-K(2)-S(2)#4	59.61(4)
S(1)#13-K(1)-K(1)#16	58.60(5)	S(3)#9-K(2)-S(2)#4	117.11(6)
S(1)#14-K(1)-K(1)#16	58.60(5)	S(3)#8-K(2)-S(2)#4	128.42(6)
S(3)#15-K(1)-K(1)#16	161.50(9)	S(3)#18-K(2)-S(2)#4	60.84(4)
S(1)#1-K(1)-K(1)#16	54.83(5)	S(2)-K(2)-S(2)#4	88.74(7)
S(1)#9-K(1)-K(1)#16	54.83(5)	S(3)-K(2)-P(1)	33.01(4)
S(2)#5-K(1)-P(1)#14	158.49(8)	S(3)#9-K(2)-P(1)	142.99(8)
S(1)#3-K(1)-P(1)#14	101.35(4)	S(3)#8-K(2)-P(1)	102.30(4)
S(1)#5-K(1)-P(1)#14	101.35(4)	S(3)#18-K(2)-P(1)	83.90(4)

S(2)-K(2)-P(1)	91.35(6)	K(1)#12-K(2)-K(1)#20	80.68(6)
S(2)#4-K(2)-P(1)	33.14(4)		
S(3)-K(2)-P(1)#9	142.99(8)		
S(3)#9-K(2)-P(1)#9	33.01(4)		
S(3)#8-K(2)-P(1)#9	83.90(4)		
S(3)#18-K(2)-P(1)#9	102.30(4)		
S(2)-K(2)-P(1)#9	33.14(4)		
S(2)#4-K(2)-P(1)#9	91.35(6)		
P(1)-K(2)-P(1)#9	110.61(8)		
S(3)-K(2)-S(1)#8	82.85(5)		
S(3)#9-K(2)-S(1)#8	100.63(5)		
S(3)#8-K(2)-S(1)#8	56.32(4)		
S(3)#18-K(2)-S(1)#8	113.22(7)		
S(2)-K(2)-S(1)#8	115.67(3)		
S(2)#4-K(2)-S(1)#8	142.02(4)		
P(1)-K(2)-S(1)#8	113.28(4)		
P(1)#9-K(2)-S(1)#8	125.26(3)		
S(3)-K(2)-S(1)#19	100.63(5)		
S(3)#9-K(2)-S(1)#19	82.85(5)		
S(3)#8-K(2)-S(1)#19	113.22(7)		
S(3)#18-K(2)-S(1)#19	56.32(4)		
S(2)-K(2)-S(1)#19	142.02(4)		
S(2)#4-K(2)-S(1)#19	115.67(3)		
P(1)-K(2)-S(1)#19	125.26(3)		
P(1)#9-K(2)-S(1)#19	113.29(4)		
S(1)#8-K(2)-S(1)#19	62.63(6)		
S(3)-K(2)-K(1)#12	53.76(4)		
S(3)#9-K(2)-K(1)#12	130.15(7)		
S(3)#8-K(2)-K(1)#12	100.66(5)		
S(3)#18-K(2)-K(1)#12	70.85(4)		
S(2)-K(2)-K(1)#12	159.98(4)		
S(2)#4-K(2)-K(1)#12	98.64(3)		
P(1)-K(2)-K(1)#12	85.05(3)		
P(1)#9-K(2)-K(1)#12	162.57(6)		
S(1)#8-K(2)-K(1)#12	49.33(4)		
S(1)#19-K(2)-K(1)#12	49.41(4)		
S(3)-K(2)-K(1)#20	130.15(7)		
S(3)#9-K(2)-K(1)#20	53.76(4)		
S(3)#8-K(2)-K(1)#20	70.85(4)		
S(3)#18-K(2)-K(1)#20	100.66(5)		
S(2)-K(2)-K(1)#20	98.64(3)		
S(2)#4-K(2)-K(1)#20	159.98(4)		
P(1)-K(2)-K(1)#20	162.57(6)		
P(1)#9-K(2)-K(1)#20	85.05(3)		
S(1)#8-K(2)-K(1)#20	49.41(4)		
S(1)#19-K(2)-K(1)#20	49.33(4)		

Symmetry transformations used to generate equivalent atoms:

#1 x+0,-y+0,-z+1/2 #2 -x+0,y+0,-z+1/2 #3 -x,-y,z

#4 x,-y,z+1/2 #5 -x,-y,-z #6 x,y,-z+1 #7 -x+0,y+1,-z+1/2

#8 -x+1/2,-y+1/2,-z+1/2 #9 x,-y,z-1/2 #10 x,y,-z

#11 -x+1/2,-y+1/2,z+1/2 #12 x+1/2,y+1/2,z+1/2

#13 -x,y-1,z-1/2 #14 -x+0,y-1,-z+1/2 #15 x-1/2,y-1/2,z-1/2

#16 -x,-y-1,-z #17 x-1/2,y-1/2,-z+1/2 #18 -x+1/2,y-1/2,-z+1

#19 -x+1/2,y-1/2,z #20 x+1/2,-y-1/2,z

Table C.16. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $K_3La_{0.67}(PS_4)_2$. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
La(1)	11(1)	9(1)	9(1)	0	0	0
P(1)	15(1)	11(1)	18(1)	0	0	-2(1)
S(1)	38(1)	16(1)	17(1)	5(1)	2(1)	1(1)
S(2)	16(1)	11(1)	56(2)	0	0	0(1)
S(3)	13(1)	23(1)	44(1)	0	0	-6(1)
K(1)	37(1)	20(1)	40(1)	0	0	0(1)
K(2)	55(1)	27(1)	28(1)	-9(1)	0	0

Table C.17. Crystal data and structure refinement for $K_{8.5}La_{1.17}(PS_4)_4$.

Identification code	ccca	
Empirical formula	$K_{8.5}La_{1.17}(PS_4)_4$	
Formula weight	1131.02	
Temperature	167(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Ccca	
Unit cell dimensions	a = 17.529(9) Å	α = 90°.
	b = 36.430(28) Å	β = 90°.
	c = 9.782(4) Å	γ = 90°.
Volume	6246.1(63) $Å^3$	
Z	8	
Density (calculated)	2.405 Mg/m^3	
Absorption coefficient	3.995 mm^{-1}	
F(000)	4351	
Crystal size	0.02 x 0.18 x 0.21 mm^3	
Theta range for data collection	1.12 to 28.39°.	
Index ranges	-23<=h<=20, -39<=k<=48, -12<=l<=13	
Reflections collected	19212	
Independent reflections	3880 [R(int) = 0.1352]	
Absorption correction	SADABS	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3879 / 0 / 140	
Goodness-of-fit on F^2	1.049	
Final R indices [I>2sigma(I)]	R1 = 0.0676, wR2 = 0.1160	
R indices (all data)	R1 = 0.1705, wR2 = 0.1550	
Extinction coefficient	0.00014(2)	
Largest diff. peak and hole	2.153 and -1.917 $e.Å^{-3}$	

Table C.18. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for $K_{8.5}La_{1.17}(PS_4)_4$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
La(1)	0	2500	7500	8(1)
La(2)	2500	0	7461(1)	7(1)
S(1)	119(2)	1961(1)	5215(3)	9(1)
S(2)	1474(2)	2124(1)	8226(3)	15(1)
S(3)	-1531(2)	2064(1)	3405(4)	16(1)
S(4)	-1240(2)	1307(1)	5179(4)	17(1)
S(5)	999(2)	407(1)	6644(4)	21(1)
S(6)	2392(3)	535(1)	9959(4)	28(1)
S(7)	4005(2)	400(1)	8284(4)	26(1)
S(8)	1260(3)	1193(1)	4944(3)	24(1)
K(1)	1869(2)	2913(1)	10166(3)	22(1)
K(2)	0	2500	2500	93(4)
K(3)	0	1251(1)	7500	24(1)
K(4)	4364(2)	-410(1)	9995(3)	27(1)
K(5)	-2463(2)	1218(1)	2632(3)	27(1)
K(6)	0	1321(1)	2500	31(1)
P(1)	-1042(2)	1856(1)	5107(3)	11(1)
P(2)	1466(3)	647(1)	4954(3)	13(1)

Table C.19. Bond lengths [Å] and angles [°] for $K_{8.5}La_{1.17}(PS_4)_4$.

La(1)-S(1)#1	2.983(3)	S(4)-K(4)#11	3.440(7)
La(1)-S(1)#2	2.983(3)	S(5)-P(2)	2.043(5)
La(1)-S(1)	2.983(3)	S(5)-K(4)#11	3.284(6)
La(1)-S(1)#3	2.983(3)	S(5)-K(4)#4	3.339(5)
La(1)-S(2)#1	3.009(4)	S(5)-K(4)#5	3.443(6)
La(1)-S(2)	3.009(4)	S(5)-K(3)	3.637(6)
La(1)-S(2)#3	3.010(4)	S(6)-P(2)#12	2.044(7)
La(1)-S(2)#2	3.010(4)	S(6)-K(4)#4	3.112(7)
La(1)-K(1)#3	4.449(4)	S(6)-La(2)#13	3.134(4)
La(1)-K(1)	4.449(4)	S(6)-K(5)#3	3.429(5)
La(1)-K(1)#1	4.449(4)	S(6)-K(5)#14	3.561(5)
La(1)-K(1)#2	4.449(4)	S(7)-P(2)#12	2.040(5)
La(2)-S(7)	3.119(4)	S(7)-K(4)#6	3.278(5)
La(2)-S(7)#4	3.119(4)	S(7)-K(4)#15	3.318(6)
La(2)-S(5)	3.123(4)	S(7)-K(4)	3.449(6)
La(2)-S(5)#4	3.123(4)	S(8)-P(2)	2.018(7)
La(2)-S(6)	3.131(4)	S(8)-K(5)#14	3.262(5)
La(2)-S(6)#4	3.131(4)	S(8)-K(5)#16	3.288(5)
La(2)-S(6)#5	3.134(4)	S(8)-K(6)	3.288(4)
La(2)-S(6)#6	3.134(4)	S(8)-K(3)	3.342(4)
La(2)-K(4)#5	4.327(4)	S(8)-K(1)#2	3.433(7)
La(2)-K(4)#6	4.327(4)	K(1)-S(1)#2	3.124(6)
La(2)-K(4)#4	4.365(4)	K(1)-S(3)#17	3.225(5)
La(2)-K(4)	4.365(4)	K(1)-S(3)#18	3.293(5)
S(1)-P(1)	2.073(5)	K(1)-S(2)#7	3.305(5)
S(1)-K(1)#2	3.125(6)	K(1)-S(2)#2	3.392(5)
S(1)-K(2)	3.311(3)	K(1)-S(8)#2	3.433(7)
S(1)-K(3)	3.424(5)	K(1)-S(3)#3	3.444(6)
S(1)-K(6)	3.540(4)	K(1)-K(1)#7	3.746(8)
S(2)-P(1)#3	2.047(5)	K(1)-P(1)#18	3.759(6)
S(2)-K(1)#7	3.305(5)	K(1)-K(5)#17	4.116(5)
S(2)-K(1)#2	3.392(5)	K(1)-K(5)#18	4.189(5)
S(2)-K(1)	3.511(6)	K(2)-S(3)#19	3.242(4)
S(3)-P(1)	2.021(5)	K(2)-S(3)#1	3.242(4)
S(3)-K(1)#8	3.225(5)	K(2)-S(3)#16	3.242(4)
S(3)-K(2)	3.242(4)	K(2)-S(1)#1	3.311(3)
S(3)-K(1)#9	3.292(5)	K(2)-S(1)#19	3.311(3)
S(3)-K(1)#3	3.444(6)	K(2)-S(1)#16	3.311(3)
S(3)-K(5)	3.569(5)	K(2)-K(1)#3	4.266(4)
S(4)-P(1)	2.030(6)	K(2)-K(1)#8	4.266(4)
S(4)-K(3)	3.149(4)	K(2)-K(1)#20	4.266(4)
S(4)-K(5)	3.303(5)	K(2)-K(1)#2	4.267(4)
S(4)-K(5)#10	3.322(5)	K(3)-S(4)#3	3.149(4)
S(4)-K(6)	3.404(4)	K(3)-S(8)#3	3.342(4)

K(3)-S(1)#3	3.424(5)	S(1)#2-La(1)-S(1)#3	82.97(13)
K(3)-S(5)#3	3.637(6)	S(1)-La(1)-S(1)#3	97.59(14)
K(3)-P(1)	3.697(5)	S(1)#1-La(1)-S(2)#1	79.46(10)
K(3)-P(1)#3	3.697(5)	S(1)#2-La(1)-S(2)#1	65.40(10)
K(3)-K(4)#11	4.073(5)	S(1)-La(1)-S(2)#1	122.44(10)
K(3)-K(4)#4	4.073(5)	S(1)#3-La(1)-S(2)#1	93.61(10)
K(4)-S(6)#4	3.112(7)	S(1)#1-La(1)-S(2)	122.44(9)
K(4)-S(7)#13	3.278(5)	S(1)#2-La(1)-S(2)	93.60(10)
K(4)-S(5)#21	3.284(6)	S(1)-La(1)-S(2)	79.46(10)
K(4)-S(7)#15	3.318(6)	S(1)#3-La(1)-S(2)	65.39(10)
K(4)-S(5)#4	3.339(5)	S(2)#1-La(1)-S(2)	152.70(13)
K(4)-S(4)#21	3.440(7)	S(1)#1-La(1)-S(2)#3	93.61(10)
K(4)-S(5)#12	3.443(6)	S(1)#2-La(1)-S(2)#3	122.45(9)
K(4)-K(4)#15	3.726(9)	S(1)-La(1)-S(2)#3	65.39(10)
K(4)-P(2)#21	3.785(6)	S(1)#3-La(1)-S(2)#3	79.46(10)
K(4)-K(3)#4	4.073(5)	S(2)#1-La(1)-S(2)#3	61.66(14)
K(4)-K(6)#22	4.273(6)	S(2)-La(1)-S(2)#3	125.88(15)
K(5)-S(8)#23	3.262(5)	S(1)#1-La(1)-S(2)#2	65.39(10)
K(5)-S(8)#16	3.288(5)	S(1)#2-La(1)-S(2)#2	79.46(10)
K(5)-S(4)#24	3.322(5)	S(1)-La(1)-S(2)#2	93.61(10)
K(5)-S(6)#3	3.429(5)	S(1)#3-La(1)-S(2)#2	122.44(9)
K(5)-S(6)#23	3.561(5)	S(2)#1-La(1)-S(2)#2	125.88(15)
K(5)-P(2)#23	3.663(5)	S(2)-La(1)-S(2)#2	61.65(14)
K(5)-P(2)#16	3.712(5)	S(2)#3-La(1)-S(2)#2	152.71(13)
K(5)-K(1)#8	4.116(5)	S(1)#1-La(1)-K(1)#3	44.51(8)
K(5)-K(1)#9	4.189(5)	S(1)#2-La(1)-K(1)#3	105.55(9)
K(5)-K(6)	4.336(3)	S(1)-La(1)-K(1)#3	80.50(8)
K(6)-S(8)#16	3.288(4)	S(1)#3-La(1)-K(1)#3	127.60(8)
K(6)-S(4)#16	3.404(4)	S(2)#1-La(1)-K(1)#3	49.63(8)
K(6)-S(1)#16	3.540(4)	S(2)-La(1)-K(1)#3	157.57(8)
K(6)-P(1)#16	3.692(5)	S(2)#3-La(1)-K(1)#3	51.90(9)
K(6)-P(1)	3.692(5)	S(2)#2-La(1)-K(1)#3	109.90(9)
K(6)-K(4)#11	4.273(6)	S(1)#1-La(1)-K(1)	105.55(9)
K(6)-K(4)#25	4.273(6)	S(1)#2-La(1)-K(1)	44.51(8)
P(1)-S(2)#3	2.047(5)	S(1)-La(1)-K(1)	127.60(8)
P(1)-K(1)#9	3.759(6)	S(1)#3-La(1)-K(1)	80.50(8)
P(2)-S(7)#5	2.040(5)	S(2)#1-La(1)-K(1)	109.90(9)
P(2)-S(6)#5	2.044(7)	S(2)-La(1)-K(1)	51.90(9)
P(2)-K(5)#14	3.663(5)	S(2)#3-La(1)-K(1)	157.57(8)
P(2)-K(5)#16	3.711(5)	S(2)#2-La(1)-K(1)	49.63(8)
P(2)-K(4)#11	3.785(6)	K(1)#3-La(1)-K(1)	140.52(10)
		S(1)#1-La(1)-K(1)#1	127.60(8)
S(1)#1-La(1)-S(1)#2	97.59(13)	S(1)#2-La(1)-K(1)#1	80.50(8)
S(1)#1-La(1)-S(1)	82.97(13)	S(1)-La(1)-K(1)#1	105.55(9)
S(1)#2-La(1)-S(1)	171.98(14)	S(1)#3-La(1)-K(1)#1	44.51(8)
S(1)#1-La(1)-S(1)#3	171.98(14)	S(2)#1-La(1)-K(1)#1	51.90(9)

S(2)-La(1)-K(1)#1	109.90(9)	S(5)-La(2)-K(4)#5	52.05(10)
S(2)#3-La(1)-K(1)#1	49.63(8)	S(5)#4-La(2)-K(4)#5	109.27(10)
S(2)#2-La(1)-K(1)#1	157.57(8)	S(6)-La(2)-K(4)#5	127.15(11)
K(1)#3-La(1)-K(1)#1	85.15(10)	S(6)#4-La(2)-K(4)#5	105.42(11)
K(1)-La(1)-K(1)#1	108.23(9)	S(6)#5-La(2)-K(4)#5	79.92(10)
S(1)#1-La(1)-K(1)#2	80.50(8)	S(6)#6-La(2)-K(4)#5	45.94(11)
S(1)#2-La(1)-K(1)#2	127.60(8)	S(7)-La(2)-K(4)#6	49.01(9)
S(1)-La(1)-K(1)#2	44.51(8)	S(7)#4-La(2)-K(4)#6	160.69(9)
S(1)#3-La(1)-K(1)#2	105.55(9)	S(5)-La(2)-K(4)#6	109.27(10)
S(2)#1-La(1)-K(1)#2	157.57(8)	S(5)#4-La(2)-K(4)#6	52.05(10)
S(2)-La(1)-K(1)#2	49.63(8)	S(6)-La(2)-K(4)#6	105.43(11)
S(2)#3-La(1)-K(1)#2	109.90(9)	S(6)#4-La(2)-K(4)#6	127.15(11)
S(2)#2-La(1)-K(1)#2	51.90(9)	S(6)#5-La(2)-K(4)#6	45.94(11)
K(1)#3-La(1)-K(1)#2	108.23(9)	S(6)#6-La(2)-K(4)#6	79.92(10)
K(1)-La(1)-K(1)#2	85.15(10)	K(4)#5-La(2)-K(4)#6	112.26(9)
K(1)#1-La(1)-K(1)#2	140.52(10)	S(7)-La(2)-K(4)#4	109.07(10)
S(7)-La(2)-S(7)#4	150.1(2)	S(7)#4-La(2)-K(4)#4	51.67(10)
S(7)-La(2)-S(5)	123.85(14)	S(5)-La(2)-K(4)#4	49.64(9)
S(7)#4-La(2)-S(5)	64.85(13)	S(5)#4-La(2)-K(4)#4	159.72(9)
S(7)-La(2)-S(5)#4	64.85(13)	S(6)-La(2)-K(4)#4	45.46(11)
S(7)#4-La(2)-S(5)#4	123.85(14)	S(6)#4-La(2)-K(4)#4	79.33(10)
S(5)-La(2)-S(5)#4	150.37(15)	S(6)#5-La(2)-K(4)#4	106.04(10)
S(7)-La(2)-S(6)	63.84(12)	S(6)#6-La(2)-K(4)#4	127.66(11)
S(7)#4-La(2)-S(6)	92.17(13)	K(4)#5-La(2)-K(4)#4	82.49(9)
S(5)-La(2)-S(6)	81.57(12)	K(4)#6-La(2)-K(4)#4	139.82(12)
S(5)#4-La(2)-S(6)	123.07(12)	S(7)-La(2)-K(4)	51.67(10)
S(7)-La(2)-S(6)#4	92.17(13)	S(7)#4-La(2)-K(4)	109.07(10)
S(7)#4-La(2)-S(6)#4	63.84(12)	S(5)-La(2)-K(4)	159.73(9)
S(5)-La(2)-S(6)#4	123.07(12)	S(5)#4-La(2)-K(4)	49.64(9)
S(5)#4-La(2)-S(6)#4	81.57(12)	S(6)-La(2)-K(4)	79.33(10)
S(6)-La(2)-S(6)#4	77.4(2)	S(6)#4-La(2)-K(4)	45.46(11)
S(7)-La(2)-S(6)#5	81.96(12)	S(6)#5-La(2)-K(4)	127.66(11)
S(7)#4-La(2)-S(6)#5	122.90(12)	S(6)#6-La(2)-K(4)	106.03(10)
S(5)-La(2)-S(6)#5	63.67(12)	K(4)#5-La(2)-K(4)	139.81(12)
S(5)#4-La(2)-S(6)#5	92.54(12)	K(4)#6-La(2)-K(4)	82.48(9)
S(6)-La(2)-S(6)#5	103.08(12)	K(4)#4-La(2)-K(4)	110.77(9)
S(6)#4-La(2)-S(6)#5	173.1(2)	P(1)-S(1)-La(1)	95.2(2)
S(7)-La(2)-S(6)#6	122.90(12)	P(1)-S(1)-K(1)#2	170.0(2)
S(7)#4-La(2)-S(6)#6	81.96(12)	La(1)-S(1)-K(1)#2	93.47(11)
S(5)-La(2)-S(6)#6	92.54(12)	P(1)-S(1)-K(2)	90.38(15)
S(5)#4-La(2)-S(6)#6	63.66(12)	La(1)-S(1)-K(2)	101.86(10)
S(6)-La(2)-S(6)#6	173.1(2)	K(1)#2-S(1)-K(2)	83.00(10)
S(6)#4-La(2)-S(6)#6	103.07(13)	P(1)-S(1)-K(3)	80.46(15)
S(6)#5-La(2)-S(6)#6	77.3(2)	La(1)-S(1)-K(3)	90.24(11)
S(7)-La(2)-K(4)#5	160.69(9)	K(1)#2-S(1)-K(3)	104.45(11)
S(7)#4-La(2)-K(4)#5	49.01(9)	K(2)-S(1)-K(3)	165.49(11)

P(1)-S(1)-K(6)	77.44(14)	P(2)-S(5)-K(4)#11	87.3(2)
La(1)-S(1)-K(6)	172.61(12)	La(2)-S(5)-K(4)#11	149.5(2)
K(1)#2-S(1)-K(6)	93.77(11)	P(2)-S(5)-K(4)#4	150.4(2)
K(2)-S(1)-K(6)	77.59(10)	La(2)-S(5)-K(4)#4	84.90(12)
K(3)-S(1)-K(6)	89.37(11)	K(4)#11-S(5)-K(4)#4	108.25(12)
P(1)#3-S(2)-La(1)	95.0(2)	P(2)-S(5)-K(4)#5	93.8(2)
P(1)#3-S(2)-K(1)#7	85.8(2)	La(2)-S(5)-K(4)#5	82.28(12)
La(1)-S(2)-K(1)#7	152.27(15)	K(4)#11-S(5)-K(4)#5	67.22(15)
P(1)#3-S(2)-K(1)#2	146.7(2)	K(4)#4-S(5)-K(4)#5	115.31(13)
La(1)-S(2)-K(1)#2	87.84(11)	P(2)-S(5)-K(3)	90.9(2)
K(1)#7-S(2)-K(1)#2	106.54(11)	La(2)-S(5)-K(3)	138.41(13)
P(1)#3-S(2)-K(1)	91.9(2)	K(4)#11-S(5)-K(3)	71.90(11)
La(1)-S(2)-K(1)	85.68(11)	K(4)#4-S(5)-K(3)	71.30(11)
K(1)#7-S(2)-K(1)	66.59(13)	K(4)#5-S(5)-K(3)	138.54(14)
K(1)#2-S(2)-K(1)	121.38(12)	P(2)#12-S(6)-K(4)#4	176.8(2)
P(1)-S(3)-K(1)#8	153.8(2)	P(2)#12-S(6)-La(2)	93.6(2)
P(1)-S(3)-K(2)	93.3(2)	K(4)#4-S(6)-La(2)	88.72(13)
K(1)#8-S(3)-K(2)	82.57(11)	P(2)#12-S(6)-La(2)#13	93.9(2)
P(1)-S(3)-K(1)#9	86.6(2)	K(4)#4-S(6)-La(2)#13	87.69(13)
K(1)#8-S(3)-K(1)#9	110.90(11)	La(2)-S(6)-La(2)#13	102.64(12)
K(2)-S(3)-K(1)#9	146.64(14)	P(2)#12-S(6)-K(5)#3	79.7(2)
P(1)-S(3)-K(1)#3	94.3(2)	K(4)#4-S(6)-K(5)#3	97.73(14)
K(1)#8-S(3)-K(1)#3	110.07(12)	La(2)-S(6)-K(5)#3	170.3(2)
K(2)-S(3)-K(1)#3	79.24(10)	La(2)#13-S(6)-K(5)#3	84.98(11)
K(1)#9-S(3)-K(1)#3	67.52(13)	P(2)#12-S(6)-K(5)#14	77.8(2)
P(1)-S(3)-K(5)	92.6(2)	K(4)#4-S(6)-K(5)#14	100.43(14)
K(1)#8-S(3)-K(5)	74.38(11)	La(2)-S(6)-K(5)#14	82.82(11)
K(2)-S(3)-K(5)	138.10(13)	La(2)#13-S(6)-K(5)#14	170.4(2)
K(1)#9-S(3)-K(5)	75.12(11)	K(5)#3-S(6)-K(5)#14	88.82(13)
K(1)#3-S(3)-K(5)	141.46(14)	P(2)#12-S(7)-La(2)	94.1(2)
P(1)-S(4)-K(3)	88.3(2)	P(2)#12-S(7)-K(4)#6	149.1(2)
P(1)-S(4)-K(5)	100.5(2)	La(2)-S(7)-K(4)#6	85.08(12)
K(3)-S(4)-K(5)	170.2(2)	P(2)#12-S(7)-K(4)#15	86.4(2)
P(1)-S(4)-K(5)#10	103.8(2)	La(2)-S(7)-K(4)#15	149.9(2)
K(3)-S(4)-K(5)#10	86.85(11)	K(4)#6-S(7)-K(4)#15	109.39(13)
K(5)-S(4)-K(5)#10	95.21(11)	P(2)#12-S(7)-K(4)	93.6(2)
P(1)-S(4)-K(6)	81.4(2)	La(2)-S(7)-K(4)	83.14(13)
K(3)-S(4)-K(6)	96.63(11)	K(4)#6-S(7)-K(4)	116.79(14)
K(5)-S(4)-K(6)	80.53(10)	K(4)#15-S(7)-K(4)	66.78(15)
K(5)#10-S(4)-K(6)	173.9(2)	P(2)-S(8)-K(5)#14	84.4(2)
P(1)-S(4)-K(4)#11	151.8(2)	P(2)-S(8)-K(5)#16	85.2(2)
K(3)-S(4)-K(4)#11	76.21(12)	K(5)#14-S(8)-K(5)#16	96.66(12)
K(5)-S(4)-K(4)#11	93.96(14)	P(2)-S(8)-K(6)	105.3(2)
K(5)#10-S(4)-K(4)#11	98.83(13)	K(5)#14-S(8)-K(6)	170.2(2)
K(6)-S(4)-K(4)#11	77.26(13)	K(5)#16-S(8)-K(6)	82.50(10)
P(2)-S(5)-La(2)	94.2(2)	P(2)-S(8)-K(3)	100.2(2)

K(5)#14-S(8)-K(3)	84.72(10)	S(3)#18-K(1)-P(1)#18	32.45(9)
K(5)#16-S(8)-K(3)	174.5(2)	S(2)#7-K(1)-P(1)#18	32.89(9)
K(6)-S(8)-K(3)	95.23(12)	S(2)#2-K(1)-P(1)#18	101.11(11)
P(2)-S(8)-K(1)#2	151.5(2)	S(8)#2-K(1)-P(1)#18	95.12(14)
K(5)#14-S(8)-K(1)#2	77.43(13)	S(3)#3-K(1)-P(1)#18	112.06(13)
K(5)#16-S(8)-K(1)#2	75.50(13)	S(2)-K(1)-P(1)#18	111.56(13)
K(6)-S(8)-K(1)#2	92.92(15)	K(1)#7-K(1)-P(1)#18	66.64(13)
K(3)-S(8)-K(1)#2	99.7(2)	S(1)#2-K(1)-K(5)#17	101.80(12)
S(1)#2-K(1)-S(3)#17	86.15(12)	S(3)#17-K(1)-K(5)#17	56.63(9)
S(1)#2-K(1)-S(3)#18	140.36(14)	S(3)#18-K(1)-K(5)#17	94.07(12)
S(3)#17-K(1)-S(3)#18	132.05(13)	S(2)#7-K(1)-K(5)#17	61.95(10)
S(1)#2-K(1)-S(2)#7	157.72(14)	S(2)#2-K(1)-K(5)#17	130.94(13)
S(3)#17-K(1)-S(2)#7	72.24(12)	S(8)#2-K(1)-K(5)#17	50.66(10)
S(3)#18-K(1)-S(2)#7	60.10(12)	S(3)#3-K(1)-K(5)#17	119.77(12)
S(1)#2-K(1)-S(2)#2	71.87(11)	S(2)-K(1)-K(5)#17	175.02(13)
S(3)#17-K(1)-S(2)#2	157.6(2)	K(1)#7-K(1)-K(5)#17	121.3(2)
S(3)#18-K(1)-S(2)#2	70.31(11)	P(1)#18-K(1)-K(5)#17	65.76(9)
S(2)#7-K(1)-S(2)#2	130.02(13)	S(1)#2-K(1)-K(5)#18	95.27(11)
S(1)#2-K(1)-S(8)#2	63.27(12)	S(3)#17-K(1)-K(5)#18	127.77(13)
S(3)#17-K(1)-S(8)#2	87.04(12)	S(3)#18-K(1)-K(5)#18	55.44(9)
S(3)#18-K(1)-S(8)#2	102.93(14)	S(2)#7-K(1)-K(5)#18	93.82(12)
S(2)#7-K(1)-S(8)#2	109.06(14)	S(2)#2-K(1)-K(5)#18	60.53(9)
S(2)#2-K(1)-S(8)#2	86.75(12)	S(8)#2-K(1)-K(5)#18	49.46(9)
S(1)#2-K(1)-S(3)#3	90.71(13)	S(3)#3-K(1)-K(5)#18	165.24(13)
S(3)#17-K(1)-S(3)#3	66.02(12)	S(2)-K(1)-K(5)#18	110.72(11)
S(3)#18-K(1)-S(3)#3	112.48(13)	K(1)#7-K(1)-K(5)#18	112.98(15)
S(2)#7-K(1)-S(3)#3	85.52(12)	P(1)#18-K(1)-K(5)#18	63.18(9)
S(2)#2-K(1)-S(3)#3	109.06(13)	K(5)#17-K(1)-K(5)#18	72.18(9)
S(8)#2-K(1)-S(3)#3	144.27(14)	S(3)#19-K(2)-S(3)#1	121.31(14)
S(1)#2-K(1)-S(2)	82.13(12)	S(3)#19-K(2)-S(3)	68.26(13)
S(3)#17-K(1)-S(2)	121.11(14)	S(3)#1-K(2)-S(3)	148.29(13)
S(3)#18-K(1)-S(2)	84.64(12)	S(3)#19-K(2)-S(3)#16	148.29(13)
S(2)#7-K(1)-S(2)	113.41(13)	S(3)#1-K(2)-S(3)#16	68.26(13)
S(2)#2-K(1)-S(2)	53.05(11)	S(3)-K(2)-S(3)#16	121.31(14)
S(8)#2-K(1)-S(2)	134.32(14)	S(3)#19-K(2)-S(1)#1	82.88(9)
S(3)#3-K(1)-S(2)	56.72(11)	S(3)#1-K(2)-S(1)#1	62.75(9)
S(1)#2-K(1)-K(1)#7	133.5(2)	S(3)-K(2)-S(1)#1	91.12(9)
S(3)#17-K(1)-K(1)#7	102.42(15)	S(3)#16-K(2)-S(1)#1	124.21(9)
S(3)#18-K(1)-K(1)#7	58.16(12)	S(3)#19-K(2)-S(1)#19	62.75(9)
S(2)#7-K(1)-K(1)#7	59.33(12)	S(3)#1-K(2)-S(1)#19	82.88(9)
S(2)#2-K(1)-K(1)#7	90.23(13)	S(3)-K(2)-S(1)#19	124.21(9)
S(8)#2-K(1)-K(1)#7	160.6(2)	S(3)#16-K(2)-S(1)#19	91.12(9)
S(3)#3-K(1)-K(1)#7	54.31(12)	S(1)#1-K(2)-S(1)#19	107.18(12)
S(2)-K(1)-K(1)#7	54.08(11)	S(3)#19-K(2)-S(1)#16	91.12(9)
S(1)#2-K(1)-P(1)#18	157.1(2)	S(3)#1-K(2)-S(1)#16	124.21(9)
S(3)#17-K(1)-P(1)#18	100.84(12)	S(3)-K(2)-S(1)#16	82.88(9)

S(3)#16-K(2)-S(1)#16	62.75(9)	K(1)#8-K(2)-K(1)#2	138.75(11)
S(1)#1-K(2)-S(1)#16	172.78(12)	K(1)#20-K(2)-K(1)#2	79.68(10)
S(1)#19-K(2)-S(1)#16	73.30(12)	S(4)-K(3)-S(4)#3	172.5(2)
S(3)#19-K(2)-S(1)	124.21(9)	S(4)-K(3)-S(8)#3	95.02(13)
S(3)#1-K(2)-S(1)	91.12(9)	S(4)#3-K(3)-S(8)#3	85.45(13)
S(3)-K(2)-S(1)	62.75(9)	S(4)-K(3)-S(8)	85.45(13)
S(3)#16-K(2)-S(1)	82.88(9)	S(4)#3-K(3)-S(8)	95.02(13)
S(1)#1-K(2)-S(1)	73.30(12)	S(8)#3-K(3)-S(8)	172.7(2)
S(1)#19-K(2)-S(1)	172.77(12)	S(4)-K(3)-S(1)	61.47(10)
S(1)#16-K(2)-S(1)	107.17(12)	S(4)#3-K(3)-S(1)	112.30(13)
S(3)#19-K(2)-K(1)#3	48.55(8)	S(8)#3-K(3)-S(1)	125.21(14)
S(3)#1-K(2)-K(1)#3	108.47(9)	S(8)-K(3)-S(1)	61.29(11)
S(3)-K(2)-K(1)#3	52.47(9)	S(4)-K(3)-S(1)#3	112.30(13)
S(3)#16-K(2)-K(1)#3	162.63(8)	S(4)#3-K(3)-S(1)#3	61.47(10)
S(1)#1-K(2)-K(1)#3	46.63(8)	S(8)#3-K(3)-S(1)#3	61.29(11)
S(1)#19-K(2)-K(1)#3	105.59(8)	S(8)-K(3)-S(1)#3	125.21(14)
S(1)#16-K(2)-K(1)#3	126.16(8)	S(1)-K(3)-S(1)#3	81.93(14)
S(1)-K(2)-K(1)#3	80.10(8)	S(4)-K(3)-S(5)#3	83.61(11)
S(3)#19-K(2)-K(1)#8	52.47(9)	S(4)#3-K(3)-S(5)#3	102.78(12)
S(3)#1-K(2)-K(1)#8	162.63(8)	S(8)#3-K(3)-S(5)#3	57.04(11)
S(3)-K(2)-K(1)#8	48.55(8)	S(8)-K(3)-S(5)#3	115.88(14)
S(3)#16-K(2)-K(1)#8	108.47(9)	S(1)-K(3)-S(5)#3	144.90(9)
S(1)#1-K(2)-K(1)#8	126.16(8)	S(1)#3-K(3)-S(5)#3	117.32(9)
S(1)#19-K(2)-K(1)#8	80.10(8)	S(4)-K(3)-S(5)	102.78(12)
S(1)#16-K(2)-K(1)#8	46.62(8)	S(4)#3-K(3)-S(5)	83.61(11)
S(1)-K(2)-K(1)#8	105.58(8)	S(8)#3-K(3)-S(5)	115.88(14)
K(1)#3-K(2)-K(1)#8	79.68(10)	S(8)-K(3)-S(5)	57.04(11)
S(3)#19-K(2)-K(1)#20	108.47(9)	S(1)-K(3)-S(5)	117.32(9)
S(3)#1-K(2)-K(1)#20	48.55(8)	S(1)#3-K(3)-S(5)	144.90(9)
S(3)-K(2)-K(1)#20	162.63(8)	S(5)#3-K(3)-S(5)	64.51(14)
S(3)#16-K(2)-K(1)#20	52.47(9)	S(4)-K(3)-P(1)	33.29(10)
S(1)#1-K(2)-K(1)#20	105.58(8)	S(4)#3-K(3)-P(1)	139.3(2)
S(1)#19-K(2)-K(1)#20	46.62(8)	S(8)#3-K(3)-P(1)	100.67(11)
S(1)#16-K(2)-K(1)#20	80.10(8)	S(8)-K(3)-P(1)	83.72(10)
S(1)-K(2)-K(1)#20	126.16(8)	S(1)-K(3)-P(1)	33.57(9)
K(1)#3-K(2)-K(1)#20	138.76(11)	S(1)#3-K(3)-P(1)	86.16(12)
K(1)#8-K(2)-K(1)#20	115.30(9)	S(5)#3-K(3)-P(1)	114.33(10)
S(3)#19-K(2)-K(1)#2	162.63(8)	S(5)-K(3)-P(1)	126.59(9)
S(3)#1-K(2)-K(1)#2	52.47(9)	S(4)-K(3)-P(1)#3	139.3(2)
S(3)-K(2)-K(1)#2	108.47(9)	S(4)#3-K(3)-P(1)#3	33.29(10)
S(3)#16-K(2)-K(1)#2	48.54(8)	S(8)#3-K(3)-P(1)#3	83.72(10)
S(1)#1-K(2)-K(1)#2	80.10(8)	S(8)-K(3)-P(1)#3	100.67(11)
S(1)#19-K(2)-K(1)#2	126.16(8)	S(1)-K(3)-P(1)#3	86.16(12)
S(1)#16-K(2)-K(1)#2	105.58(8)	S(1)#3-K(3)-P(1)#3	33.57(9)
S(1)-K(2)-K(1)#2	46.63(8)	S(5)#3-K(3)-P(1)#3	126.59(9)
K(1)#3-K(2)-K(1)#2	115.30(9)	S(5)-K(3)-P(1)#3	114.33(10)

P(1)-K(3)-P(1)#3	106.8(2)	S(7)#15-K(4)-S(7)	113.21(15)
S(4)-K(3)-K(4)#11	55.11(11)	S(5)#4-K(4)-S(7)	59.06(12)
S(4)#3-K(3)-K(4)#11	132.05(14)	S(4)#21-K(4)-S(7)	137.07(15)
S(8)#3-K(3)-K(4)#11	102.69(11)	S(5)#12-K(4)-S(7)	56.97(14)
S(8)-K(3)-K(4)#11	71.62(11)	S(6)#4-K(4)-K(4)#15	135.2(2)
S(1)-K(3)-K(4)#11	101.16(9)	S(7)#13-K(4)-K(4)#15	95.95(14)
S(1)#3-K(3)-K(4)#11	160.49(8)	S(5)#21-K(4)-K(4)#15	58.42(13)
S(5)#3-K(3)-K(4)#11	50.95(9)	S(7)#15-K(4)-K(4)#15	58.29(13)
S(5)-K(3)-K(4)#11	50.03(10)	S(5)#4-K(4)-K(4)#15	96.53(14)
P(1)-K(3)-K(4)#11	86.21(10)	S(4)#21-K(4)-K(4)#15	161.0(2)
P(1)#3-K(3)-K(4)#11	164.36(11)	S(5)#12-K(4)-K(4)#15	54.36(12)
S(4)-K(3)-K(4)#4	132.05(14)	S(7)-K(4)-K(4)#15	54.92(12)
S(4)#3-K(3)-K(4)#4	55.11(11)	S(6)#4-K(4)-P(2)#21	158.4(2)
S(8)#3-K(3)-K(4)#4	71.62(11)	S(7)#13-K(4)-P(2)#21	100.17(12)
S(8)-K(3)-K(4)#4	102.69(11)	S(5)#21-K(4)-P(2)#21	32.63(9)
S(1)-K(3)-K(4)#4	160.49(8)	S(7)#15-K(4)-P(2)#21	32.55(9)
S(1)#3-K(3)-K(4)#4	101.16(8)	S(5)#4-K(4)-P(2)#21	101.49(12)
S(5)#3-K(3)-K(4)#4	50.03(10)	S(4)#21-K(4)-P(2)#21	94.75(14)
S(5)-K(3)-K(4)#4	50.95(9)	S(5)#12-K(4)-P(2)#21	111.80(14)
P(1)-K(3)-K(4)#4	164.36(11)	S(7)-K(4)-P(2)#21	112.31(14)
P(1)#3-K(3)-K(4)#4	86.20(10)	K(4)#15-K(4)-P(2)#21	66.47(14)
K(4)#11-K(3)-K(4)#4	82.42(13)	S(6)#4-K(4)-K(3)#4	98.84(13)
S(6)#4-K(4)-S(7)#13	79.80(13)	S(7)#13-K(4)-K(3)#4	130.47(15)
S(6)#4-K(4)-S(5)#21	149.10(14)	S(5)#21-K(4)-K(3)#4	58.07(10)
S(7)#13-K(4)-S(5)#21	130.31(15)	S(7)#15-K(4)-K(3)#4	94.39(12)
S(6)#4-K(4)-S(7)#15	149.30(14)	S(5)#4-K(4)-K(3)#4	57.75(9)
S(7)#13-K(4)-S(7)#15	70.59(13)	S(4)#21-K(4)-K(3)#4	48.67(9)
S(5)#21-K(4)-S(7)#15	59.72(14)	S(5)#12-K(4)-K(3)#4	168.89(13)
S(6)#4-K(4)-S(5)#4	78.50(12)	S(7)-K(4)-K(3)#4	113.72(11)
S(7)#13-K(4)-S(5)#4	157.9(2)	K(4)#15-K(4)-K(3)#4	116.13(15)
S(5)#21-K(4)-S(5)#4	71.75(12)	P(2)#21-K(4)-K(3)#4	64.50(8)
S(7)#15-K(4)-S(5)#4	131.47(14)	S(6)#4-K(4)-K(6)#22	98.68(13)
S(6)#4-K(4)-S(4)#21	63.64(13)	S(7)#13-K(4)-K(6)#22	59.75(10)
S(7)#13-K(4)-S(4)#21	90.01(14)	S(5)#21-K(4)-K(6)#22	93.15(11)
S(5)#21-K(4)-S(4)#21	104.33(15)	S(7)#15-K(4)-K(6)#22	59.53(10)
S(7)#15-K(4)-S(4)#21	107.50(15)	S(5)#4-K(4)-K(6)#22	127.96(14)
S(5)#4-K(4)-S(4)#21	84.02(13)	S(4)#21-K(4)-K(6)#22	50.99(10)
S(6)#4-K(4)-S(5)#12	87.08(14)	S(5)#12-K(4)-K(6)#22	116.79(11)
S(7)#13-K(4)-S(5)#12	59.68(13)	S(7)-K(4)-K(6)#22	171.90(14)
S(5)#21-K(4)-S(5)#12	112.78(15)	K(4)#15-K(4)-K(6)#22	117.71(15)
S(7)#15-K(4)-S(5)#12	84.96(14)	P(2)#21-K(4)-K(6)#22	63.96(8)
S(5)#4-K(4)-S(5)#12	114.94(14)	K(3)#4-K(4)-K(6)#22	71.81(9)
S(4)#21-K(4)-S(5)#12	141.93(15)	S(8)#23-K(5)-S(8)#16	175.3(2)
S(6)#4-K(4)-S(7)	86.50(14)	S(8)#23-K(5)-S(4)	84.28(14)
S(7)#13-K(4)-S(7)	115.57(14)	S(8)#16-K(5)-S(4)	99.45(14)
S(5)#21-K(4)-S(7)	85.38(13)	S(8)#23-K(5)-S(4)#24	93.33(14)

S(8)#16-K(5)-S(4)#24	83.57(14)	S(6)#23-K(5)-K(1)#9	158.37(13)
S(4)-K(5)-S(4)#24	168.4(2)	S(3)-K(5)-K(1)#9	49.44(9)
S(8)#23-K(5)-S(6)#3	60.33(13)	P(2)#23-K(5)-K(1)#9	84.53(11)
S(8)#16-K(5)-S(6)#3	118.9(2)	P(2)#16-K(5)-K(1)#9	163.41(12)
S(4)-K(5)-S(6)#3	61.94(12)	K(1)#8-K(5)-K(1)#9	80.53(11)
S(4)#24-K(5)-S(6)#3	126.32(14)	S(8)#23-K(5)-K(6)	135.04(11)
S(8)#23-K(5)-S(6)#23	116.64(15)	S(8)#16-K(5)-K(6)	48.75(8)
S(8)#16-K(5)-S(6)#23	58.70(12)	S(4)-K(5)-K(6)	50.76(8)
S(4)-K(5)-S(6)#23	130.67(14)	S(4)#24-K(5)-K(6)	130.66(10)
S(4)#24-K(5)-S(6)#23	60.35(12)	S(6)#3-K(5)-K(6)	92.69(11)
S(6)#3-K(5)-S(6)#23	89.11(13)	S(6)#23-K(5)-K(6)	96.33(11)
S(8)#23-K(5)-S(3)	100.65(13)	S(3)-K(5)-K(6)	58.38(9)
S(8)#16-K(5)-S(3)	83.86(12)	P(2)#23-K(5)-K(6)	125.35(10)
S(4)-K(5)-S(3)	57.19(10)	P(2)#16-K(5)-K(6)	63.84(9)
S(4)#24-K(5)-S(3)	112.46(14)	K(1)#8-K(5)-K(6)	70.36(8)
S(6)#3-K(5)-S(3)	117.67(13)	K(1)#9-K(5)-K(6)	103.33(9)
S(6)#23-K(5)-S(3)	141.88(13)	S(8)#16-K(6)-S(8)	163.6(2)
S(8)#23-K(5)-P(2)#23	33.26(12)	S(8)#16-K(6)-S(4)	97.41(13)
S(8)#16-K(5)-P(2)#23	143.8(2)	S(8)-K(6)-S(4)	82.35(12)
S(4)-K(5)-P(2)#23	84.40(12)	S(8)#16-K(6)-S(4)#16	82.35(12)
S(4)#24-K(5)-P(2)#23	99.81(12)	S(8)-K(6)-S(4)#16	97.41(13)
S(6)#3-K(5)-P(2)#23	33.28(11)	S(4)-K(6)-S(4)#16	178.3(2)
S(6)#23-K(5)-P(2)#23	91.47(12)	S(8)#16-K(6)-S(1)#16	60.56(11)
S(3)-K(5)-P(2)#23	126.02(12)	S(8)-K(6)-S(1)#16	132.75(13)
S(8)#23-K(5)-P(2)#16	143.4(2)	S(4)-K(6)-S(1)#16	123.34(13)
S(8)#16-K(5)-P(2)#16	32.82(12)	S(4)#16-K(6)-S(1)#16	57.98(10)
S(4)-K(5)-P(2)#16	105.26(12)	S(8)#16-K(6)-S(1)	132.76(13)
S(4)#24-K(5)-P(2)#16	83.38(12)	S(8)-K(6)-S(1)	60.56(11)
S(6)#3-K(5)-P(2)#16	92.56(13)	S(4)-K(6)-S(1)	57.98(10)
S(6)#23-K(5)-P(2)#16	32.56(11)	S(4)#16-K(6)-S(1)	123.34(13)
S(3)-K(5)-P(2)#16	114.35(12)	S(1)#16-K(6)-S(1)	97.6(2)
P(2)#23-K(5)-P(2)#16	111.3(2)	S(8)#16-K(6)-P(1)#16	84.54(11)
S(8)#23-K(5)-K(1)#8	128.43(14)	S(8)-K(6)-P(1)#16	104.19(11)
S(8)#16-K(5)-K(1)#8	53.84(12)	S(4)-K(6)-P(1)#16	148.8(2)
S(4)-K(5)-K(1)#8	101.66(11)	S(4)#16-K(6)-P(1)#16	32.92(10)
S(4)#24-K(5)-K(1)#8	71.00(10)	S(1)#16-K(6)-P(1)#16	33.22(9)
S(6)#3-K(5)-K(1)#8	162.18(13)	S(1)-K(6)-P(1)#16	98.15(13)
S(6)#23-K(5)-K(1)#8	97.97(11)	S(8)#16-K(6)-P(1)	104.20(11)
S(3)-K(5)-K(1)#8	48.99(9)	S(8)-K(6)-P(1)	84.54(11)
P(2)#23-K(5)-K(1)#8	160.78(12)	S(4)-K(6)-P(1)	32.92(10)
P(2)#16-K(5)-K(1)#8	84.97(11)	S(4)#16-K(6)-P(1)	148.8(2)
S(8)#23-K(5)-K(1)#9	53.11(11)	S(1)#16-K(6)-P(1)	98.15(13)
S(8)#16-K(5)-K(1)#9	130.85(14)	S(1)-K(6)-P(1)	33.22(9)
S(4)-K(5)-K(1)#9	70.18(11)	P(1)#16-K(6)-P(1)	116.3(2)
S(4)#24-K(5)-K(1)#9	99.34(12)	S(8)#16-K(6)-K(4)#11	97.54(13)
S(6)#3-K(5)-K(1)#9	98.77(12)	S(8)-K(6)-K(4)#11	69.38(11)

S(4)-K(6)-K(4)#11	51.74(10)
S(4)#16-K(6)-K(4)#11	126.60(14)
S(1)#16-K(6)-K(4)#11	157.85(8)
S(1)-K(6)-K(4)#11	95.54(9)
P(1)#16-K(6)-K(4)#11	159.19(12)
P(1)-K(6)-K(4)#11	83.39(10)
S(8)#16-K(6)-K(4)#25	69.38(11)
S(8)-K(6)-K(4)#25	97.54(13)
S(4)-K(6)-K(4)#25	126.60(14)
S(4)#16-K(6)-K(4)#25	51.74(10)
S(1)#16-K(6)-K(4)#25	95.54(9)
S(1)-K(6)-K(4)#25	157.85(8)
P(1)#16-K(6)-K(4)#25	83.39(9)
P(1)-K(6)-K(4)#25	159.20(12)
K(4)#11-K(6)-K(4)#25	78.08(13)
S(8)#16-K(6)-K(2)	98.18(12)
S(8)-K(6)-K(2)	98.18(12)
S(4)-K(6)-K(2)	90.85(10)
S(4)#16-K(6)-K(2)	90.85(10)
S(1)#16-K(6)-K(2)	48.82(8)
S(1)-K(6)-K(2)	48.82(8)
P(1)#16-K(6)-K(2)	58.15(9)
P(1)-K(6)-K(2)	58.15(9)
K(4)#11-K(6)-K(2)	140.96(7)
K(4)#25-K(6)-K(2)	140.96(7)
S(8)#16-K(6)-K(5)	48.75(8)
S(8)-K(6)-K(5)	129.40(9)
S(4)-K(6)-K(5)	48.71(8)
S(4)#16-K(6)-K(5)	131.10(8)
S(1)#16-K(6)-K(5)	91.18(7)
S(1)-K(6)-K(5)	95.35(8)
P(1)#16-K(6)-K(5)	123.96(8)
P(1)-K(6)-K(5)	62.13(8)
K(4)#11-K(6)-K(5)	69.88(7)
K(4)#25-K(6)-K(5)	102.11(9)
K(2)-K(6)-K(5)	94.96(6)
S(3)-P(1)-S(4)	109.0(2)
S(3)-P(1)-S(2)#3	108.6(3)
S(4)-P(1)-S(2)#3	112.3(2)
S(3)-P(1)-S(1)	112.9(2)
S(4)-P(1)-S(1)	110.3(2)
S(2)#3-P(1)-S(1)	103.6(2)
S(3)-P(1)-K(6)	80.7(2)
S(4)-P(1)-K(6)	65.7(2)
S(2)#3-P(1)-K(6)	170.2(2)
S(1)-P(1)-K(6)	69.34(14)
S(3)-P(1)-K(3)	162.8(2)
S(4)-P(1)-K(3)	58.38(15)
S(2)#3-P(1)-K(3)	87.9(2)
S(1)-P(1)-K(3)	65.97(14)
K(6)-P(1)-K(3)	83.03(11)
S(3)-P(1)-K(1)#9	61.0(2)
S(4)-P(1)-K(1)#9	93.1(2)
S(2)#3-P(1)-K(1)#9	61.3(2)
S(1)-P(1)-K(1)#9	156.1(2)
K(6)-P(1)-K(1)#9	127.65(11)
K(3)-P(1)-K(1)#9	127.26(11)
S(8)-P(2)-S(7)#5	111.0(2)
S(8)-P(2)-S(5)	110.7(2)
S(7)#5-P(2)-S(5)	107.2(3)
S(8)-P(2)-S(6)#5	111.9(3)
S(7)#5-P(2)-S(6)#5	108.0(2)
S(5)-P(2)-S(6)#5	107.7(2)
S(8)-P(2)-K(5)#14	62.4(2)
S(7)#5-P(2)-K(5)#14	167.0(2)
S(5)-P(2)-K(5)#14	85.8(2)
S(6)#5-P(2)-K(5)#14	67.1(2)
S(8)-P(2)-K(5)#16	62.0(2)
S(7)#5-P(2)-K(5)#16	83.8(2)
S(5)-P(2)-K(5)#16	168.7(2)
S(6)#5-P(2)-K(5)#16	69.7(2)
K(5)#14-P(2)-K(5)#16	83.12(11)
S(8)-P(2)-K(4)#11	92.9(2)
S(7)#5-P(2)-K(4)#11	61.0(2)
S(5)-P(2)-K(4)#11	60.1(2)
S(6)#5-P(2)-K(4)#11	155.2(2)
K(5)#14-P(2)-K(4)#11	128.32(12)
K(5)#16-P(2)-K(4)#11	126.55(12)

Symmetry transformations used to generate equivalent atoms:

#1 -x+0,-y+1/2,z #2 x+0,-y+1/2,-z+3/2 #3 -x,y,-z+3/2

#4 -x+1/2,-y,z #5 -x+1/2,y,z-1/2 #6 x,-y,z-1/2

#7 -x+1/2,-y+1/2,-z+2 #8 -x+0,-y+1/2,z-1 #9 x-1/2,-y+1/2,z-1/2

#10 -x-1/2,y,z+1/2 #11 x-1/2,-y,-z+3/2 #12 -x+1/2,y,z+1/2

#13 x,-y,z+1/2 #14 x+1/2,y,-z+1 #15 -x+1,-y,-z+2

#16 -x,y,-z+1/2 #17 -x+0,-y+1/2,z+1 #18 x+1/2,-y+1/2,z+1/2

#19 x+0,-y+1/2,-z+1/2 #20 x,y,z-1 #21 x+1/2,-y,-z+3/2

#22 -x+1/2,-y,z+1 #23 x-1/2,y,-z+1 #24 -x-1/2,y,z-1/2

#25 -x+1/2,-y,z-1

Table C.20. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $K_{8.5}La_{1.17}(PS_4)_4$. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
La(1)	9(1)	9(1)	5(1)	0	0	0
La(2)	8(1)	9(1)	6(1)	0	0	-1(1)
S(1)	5(2)	14(2)	7(1)	-3(1)	0(1)	-2(1)
S(2)	12(2)	23(2)	9(2)	7(1)	-2(1)	3(1)
S(3)	17(2)	20(2)	10(2)	5(1)	-3(1)	-2(1)
S(4)	25(2)	9(2)	15(2)	0(1)	-5(1)	-4(2)
S(5)	19(2)	30(2)	14(2)	1(2)	5(1)	-1(2)
S(6)	20(2)	17(2)	46(3)	-2(2)	0(1)	4(2)
S(7)	19(2)	43(2)	16(2)	0(2)	5(2)	5(2)
S(8)	21(2)	20(2)	32(3)	2(1)	0(1)	6(2)
K(1)	20(2)	29(2)	16(2)	-1(1)	-1(1)	5(2)
K(2)	100(8)	110(9)	70(8)	0	0	0
K(3)	26(2)	23(2)	24(2)	0	-6(2)	0
K(4)	18(2)	31(2)	30(2)	0(1)	-1(1)	5(2)
K(5)	23(2)	46(2)	11(2)	-1(1)	4(2)	-4(1)
K(6)	29(2)	36(2)	29(2)	0	1(2)	0
P(1)	13(2)	16(2)	6(2)	0(1)	0(1)	-1(2)
P(2)	13(2)	13(2)	12(2)	2(1)	1(1)	0(2)

Table C.21. Crystal data and structure refinement for $K_4Eu(PS_4)_2$.

Identification code	ibam	
Empirical formula	$K_4Eu(PS_4)_2$	
Formula weight	626.78	
Temperature	168(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Ibam	
Unit cell dimensions	a = 18.293(51) Å	α= 90°.
	b = 8.813(15) Å	β= 90°.
	c = 9.741(10) Å	γ = 90°.
Volume	1570.4(54) $Å^3$	
Z	4	
Density (calculated)	2.651 Mg/m^3	
Absorption coefficient	6.285 mm^{-1}	
F(000)	1188	
Crystal size	0.03 x 0.09 x 0.09 mm^3	
Theta range for data collection	2.23 to 28.24°.	
Index ranges	-24<=h<=22, -11<=k<=10, -12<=l<=11	
Reflections collected	4965	
Independent reflections	1020 [R(int) = 0.0893]	
Absorption correction	SADABS	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1019 / 0 / 42	
Goodness-of-fit on F^2	1.131	
Final R indices [I>2sigma(I)]	R1 = 0.0495, wR2 = 0.1055	
R indices (all data)	R1 = 0.0825, wR2 = 0.1218	
Largest diff. peak and hole	1.340 and -1.442 $e.Å^{-3}$	

Table C.22. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for $K_4Eu(PS_4)_2$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Eu(1)	5000	0	2500	12(1)
P(1)	3714(2)	2053(3)	0	6(1)
S(1)	3941(2)	238(3)	5000	13(1)
S(2)	4194(1)	2982(3)	1695(2)	13(1)
S(3)	2615(2)	2463(4)	0	13(1)
K(1)	2575(2)	0	2500	20(1)
K(2)	5833(2)	-3763(3)	5000	15(1)

Table C.23. Bond lengths [Å] and angles [°] for $K_4Eu(PS_4)_2$.

Eu(1)-S(2)#1	3.113(5)	K(2)-S(2)#2	3.293(4)
Eu(1)-S(2)#2	3.114(5)	K(2)-S(2)#16	3.310(5)
Eu(1)-S(2)	3.114(5)	K(2)-S(2)#17	3.310(5)
Eu(1)-S(2)#3	3.114(5)	K(2)-S(3)#18	3.435(10)
Eu(1)-S(1)#1	3.119(4)	K(2)-S(2)#3	3.491(8)
Eu(1)-S(1)#4	3.119(4)	K(2)-S(2)#8	3.491(8)
Eu(1)-S(1)	3.119(4)	K(2)-K(2)#19	3.746(9)
Eu(1)-S(1)#5	3.119(4)	K(2)-P(1)#16	3.779(7)
Eu(1)-K(2)#5	4.387(5)	K(2)-K(1)#18	4.157(8)
Eu(1)-K(2)#4	4.387(5)	K(2)-K(1)#20	4.157(8)
Eu(1)-K(2)	4.387(5)		
Eu(1)-K(2)#1	4.387(5)	S(2)#1-Eu(1)-S(2)#2	123.5(2)
P(1)-S(2)	2.041(3)	S(2)#1-Eu(1)-S(2)	64.9(2)
P(1)-S(2)#6	2.041(3)	S(2)#2-Eu(1)-S(2)	150.82(9)
P(1)-S(3)	2.042(7)	S(2)#1-Eu(1)-S(2)#3	150.82(9)
P(1)-S(1)#5	2.062(5)	S(2)#2-Eu(1)-S(2)#3	64.9(2)
P(1)-K(1)	3.680(5)	S(2)-Eu(1)-S(2)#3	123.5(2)
P(1)-K(1)#6	3.680(5)	S(2)#1-Eu(1)-S(1)#1	81.12(11)
P(1)-K(2)#7	3.779(7)	S(2)#2-Eu(1)-S(1)#1	64.28(10)
S(1)-P(1)#8	2.062(5)	S(2)-Eu(1)-S(1)#1	92.33(12)
S(1)-Eu(1)#4	3.119(4)	S(2)#3-Eu(1)-S(1)#1	123.21(9)
S(1)-K(2)#4	3.134(7)	S(2)#1-Eu(1)-S(1)#4	64.28(10)
S(1)-K(1)	3.495(6)	S(2)#2-Eu(1)-S(1)#4	81.12(11)
S(1)-K(1)#9	3.495(6)	S(2)-Eu(1)-S(1)#4	123.21(9)
S(2)-K(2)#4	3.293(4)	S(2)#3-Eu(1)-S(1)#4	92.33(12)
S(2)-K(2)#7	3.310(5)	S(1)#1-Eu(1)-S(1)#4	103.2(2)
S(2)-K(2)#5	3.491(8)	S(2)#1-Eu(1)-S(1)	92.33(12)
S(2)-K(1)#10	3.775(9)	S(2)#2-Eu(1)-S(1)	123.21(9)
S(3)-K(1)	3.263(4)	S(2)-Eu(1)-S(1)	81.12(11)
S(3)-K(1)#6	3.263(4)	S(2)#3-Eu(1)-S(1)	64.28(10)
S(3)-K(1)#10	3.324(4)	S(1)#1-Eu(1)-S(1)	172.28(11)
S(3)-K(1)#11	3.324(4)	S(1)#4-Eu(1)-S(1)	77.3(2)
S(3)-K(2)#12	3.435(10)	S(2)#1-Eu(1)-S(1)#5	123.21(9)
K(1)-S(3)#8	3.263(4)	S(2)#2-Eu(1)-S(1)#5	92.33(12)
K(1)-S(3)#10	3.324(4)	S(2)-Eu(1)-S(1)#5	64.27(10)
K(1)-S(3)#13	3.324(4)	S(2)#3-Eu(1)-S(1)#5	81.12(11)
K(1)-S(1)#5	3.495(6)	S(1)#1-Eu(1)-S(1)#5	77.3(2)
K(1)-P(1)#8	3.680(5)	S(1)#4-Eu(1)-S(1)#5	172.28(11)
K(1)-S(2)#10	3.775(9)	S(1)-Eu(1)-S(1)#5	103.2(2)
K(1)-S(2)#14	3.775(9)	S(2)#1-Eu(1)-K(2)#5	48.51(8)
K(1)-K(2)#12	4.157(8)	S(2)#2-Eu(1)-K(2)#5	109.49(13)
K(1)-K(2)#15	4.157(8)	S(2)-Eu(1)-K(2)#5	52.17(14)
K(2)-S(1)#4	3.134(7)	S(2)#3-Eu(1)-K(2)#5	160.42(5)
K(2)-S(2)#4	3.293(4)	S(1)#1-Eu(1)-K(2)#5	45.58(8)

S(1)#4-Eu(1)-K(2)#5	105.58(12)	S(1)#5-P(1)-K(1)#6	68.44(12)
S(1)-Eu(1)-K(2)#5	126.74(9)	K(1)-P(1)-K(1)#6	82.86(14)
S(1)#5-Eu(1)-K(2)#5	80.40(11)	S(2)-P(1)-K(2)#7	60.95(10)
S(2)#1-Eu(1)-K(2)#4	52.17(14)	S(2)#6-P(1)-K(2)#7	60.95(10)
S(2)#2-Eu(1)-K(2)#4	160.42(5)	S(3)-P(1)-K(2)#7	92.5(2)
S(2)-Eu(1)-K(2)#4	48.51(8)	S(1)#5-P(1)-K(2)#7	155.7(2)
S(2)#3-Eu(1)-K(2)#4	109.49(13)	K(1)-P(1)-K(2)#7	127.15(7)
S(1)#1-Eu(1)-K(2)#4	126.74(9)	K(1)#6-P(1)-K(2)#7	127.15(7)
S(1)#4-Eu(1)-K(2)#4	80.40(11)	P(1)#8-S(1)-Eu(1)#4	93.39(10)
S(1)-Eu(1)-K(2)#4	45.58(8)	P(1)#8-S(1)-Eu(1)	93.39(10)
S(1)#5-Eu(1)-K(2)#4	105.58(12)	Eu(1)#4-S(1)-Eu(1)	102.7(2)
K(2)#5-Eu(1)-K(2)#4	81.80(13)	P(1)#8-S(1)-K(2)#4	176.0(2)
S(2)#1-Eu(1)-K(2)	109.49(13)	Eu(1)#4-S(1)-K(2)#4	89.12(8)
S(2)#2-Eu(1)-K(2)	48.51(8)	Eu(1)-S(1)-K(2)#4	89.12(8)
S(2)-Eu(1)-K(2)	160.42(5)	P(1)#8-S(1)-K(1)	78.30(9)
S(2)#3-Eu(1)-K(2)	52.17(14)	Eu(1)#4-S(1)-K(1)	169.72(9)
S(1)#1-Eu(1)-K(2)	105.58(12)	Eu(1)-S(1)-K(1)	84.0(2)
S(1)#4-Eu(1)-K(2)	45.58(8)	K(2)#4-S(1)-K(1)	98.87(8)
S(1)-Eu(1)-K(2)	80.40(11)	P(1)#8-S(1)-K(1)#9	78.30(9)
S(1)#5-Eu(1)-K(2)	126.74(9)	Eu(1)#4-S(1)-K(1)#9	84.0(2)
K(2)#5-Eu(1)-K(2)	139.37(13)	Eu(1)-S(1)-K(1)#9	169.72(9)
K(2)#4-Eu(1)-K(2)	112.57(10)	K(2)#4-S(1)-K(1)#9	98.87(8)
S(2)#1-Eu(1)-K(2)#1	160.42(5)	K(1)-S(1)-K(1)#9	88.3(2)
S(2)#2-Eu(1)-K(2)#1	52.17(14)	P(1)-S(2)-Eu(1)	93.96(15)
S(2)-Eu(1)-K(2)#1	109.49(13)	P(1)-S(2)-K(2)#4	150.26(15)
S(2)#3-Eu(1)-K(2)#1	48.51(8)	Eu(1)-S(2)-K(2)#4	86.39(9)
S(1)#1-Eu(1)-K(2)#1	80.40(11)	P(1)-S(2)-K(2)#7	86.44(14)
S(1)#4-Eu(1)-K(2)#1	126.74(9)	Eu(1)-S(2)-K(2)#7	149.77(12)
S(1)-Eu(1)-K(2)#1	105.58(12)	K(2)#4-S(2)-K(2)#7	107.83(10)
S(1)#5-Eu(1)-K(2)#1	45.58(8)	P(1)-S(2)-K(2)#5	93.8(2)
K(2)#5-Eu(1)-K(2)#1	112.57(10)	Eu(1)-S(2)-K(2)#5	83.05(14)
K(2)#4-Eu(1)-K(2)#1	139.37(13)	K(2)#4-S(2)-K(2)#5	115.71(10)
K(2)-Eu(1)-K(2)#1	81.79(13)	K(2)#7-S(2)-K(2)#5	66.78(11)
S(2)-P(1)-S(2)#6	108.0(2)	P(1)-S(2)-K(1)#10	89.3(2)
S(2)-P(1)-S(3)	110.64(15)	Eu(1)-S(2)-K(1)#10	138.70(8)
S(2)#6-P(1)-S(3)	110.64(15)	K(2)#4-S(2)-K(1)#10	71.68(8)
S(2)-P(1)-S(1)#5	107.83(14)	K(2)#7-S(2)-K(1)#10	71.50(9)
S(2)#6-P(1)-S(1)#5	107.83(14)	K(2)#5-S(2)-K(1)#10	137.86(13)
S(3)-P(1)-S(1)#5	111.8(2)	P(1)-S(3)-K(1)	84.53(11)
S(2)-P(1)-K(1)	84.58(13)	P(1)-S(3)-K(1)#6	84.53(11)
S(2)#6-P(1)-K(1)	167.38(12)	K(1)-S(3)-K(1)#6	96.55(14)
S(3)-P(1)-K(1)	61.95(13)	P(1)-S(3)-K(1)#10	102.83(12)
S(1)#5-P(1)-K(1)	68.44(12)	K(1)-S(3)-K(1)#10	84.16(11)
S(2)-P(1)-K(1)#6	167.38(12)	K(1)#6-S(3)-K(1)#10	172.64(10)
S(2)#6-P(1)-K(1)#6	84.58(14)	P(1)-S(3)-K(1)#11	102.83(12)
S(3)-P(1)-K(1)#6	61.95(13)	K(1)-S(3)-K(1)#11	172.64(10)

K(1)#6-S(3)-K(1)#11	84.16(11)	S(3)#13-K(1)-S(2)#14	56.02(9)
K(1)#10-S(3)-K(1)#11	94.20(14)	S(1)#5-K(1)-S(2)#14	116.08(14)
P(1)-S(3)-K(2)#12	151.5(2)	S(1)-K(1)-S(2)#14	141.80(9)
K(1)-S(3)-K(2)#12	76.67(9)	P(1)#8-K(1)-S(2)#14	113.03(13)
K(1)#6-S(3)-K(2)#12	76.67(9)	P(1)-K(1)-S(2)#14	125.41(10)
K(1)#10-S(3)-K(2)#12	96.43(10)	S(2)#10-K(1)-S(2)#14	62.0(2)
K(1)#11-S(3)-K(2)#12	96.43(10)	S(3)-K(1)-K(2)#12	53.53(10)
S(3)-K(1)-S(3)#8	177.41(15)	S(3)#8-K(1)-K(2)#12	128.98(12)
S(3)-K(1)-S(3)#10	95.84(11)	S(3)#10-K(1)-K(2)#12	99.93(10)
S(3)#8-K(1)-S(3)#10	84.44(11)	S(3)#13-K(1)-K(2)#12	70.55(9)
S(3)-K(1)-S(3)#13	84.44(11)	S(1)#5-K(1)-K(2)#12	99.0(2)
S(3)#8-K(1)-S(3)#13	95.84(11)	S(1)-K(1)-K(2)#12	160.14(7)
S(3)#10-K(1)-S(3)#13	167.98(15)	P(1)#8-K(1)-K(2)#12	161.93(8)
S(3)-K(1)-S(1)#5	60.25(9)	P(1)-K(1)-K(2)#12	85.3(2)
S(3)#8-K(1)-S(1)#5	117.64(11)	S(2)#10-K(1)-K(2)#12	48.77(11)
S(3)#10-K(1)-S(1)#5	128.73(11)	S(2)#14-K(1)-K(2)#12	49.04(13)
S(3)#13-K(1)-S(1)#5	61.58(11)	S(3)-K(1)-K(2)#15	128.98(12)
S(3)-K(1)-S(1)	117.63(11)	S(3)#8-K(1)-K(2)#15	53.53(10)
S(3)#8-K(1)-S(1)	60.25(9)	S(3)#10-K(1)-K(2)#15	70.55(9)
S(3)#10-K(1)-S(1)	61.58(11)	S(3)#13-K(1)-K(2)#15	99.93(10)
S(3)#13-K(1)-S(1)	128.73(11)	S(1)#5-K(1)-K(2)#15	160.14(7)
S(1)#5-K(1)-S(1)	88.7(2)	S(1)-K(1)-K(2)#15	99.0(2)
S(3)-K(1)-P(1)#8	143.90(14)	P(1)#8-K(1)-K(2)#15	85.3(2)
S(3)#8-K(1)-P(1)#8	33.52(10)	P(1)-K(1)-K(2)#15	161.93(8)
S(3)#10-K(1)-P(1)#8	84.56(11)	S(2)#10-K(1)-K(2)#15	49.04(13)
S(3)#13-K(1)-P(1)#8	102.32(11)	S(2)#14-K(1)-K(2)#15	48.76(11)
S(1)#5-K(1)-P(1)#8	91.5(2)	K(2)#12-K(1)-K(2)#15	79.9(2)
S(1)-K(1)-P(1)#8	33.26(9)	S(1)#4-K(2)-S(2)#4	78.15(6)
S(3)-K(1)-P(1)	33.52(10)	S(1)#4-K(2)-S(2)#2	78.15(6)
S(3)#8-K(1)-P(1)	143.90(14)	S(2)#4-K(2)-S(2)#2	155.80(13)
S(3)#10-K(1)-P(1)	102.32(11)	S(1)#4-K(2)-S(2)#16	149.43(7)
S(3)#13-K(1)-P(1)	84.56(11)	S(2)#4-K(2)-S(2)#16	131.96(9)
S(1)#5-K(1)-P(1)	33.26(9)	S(2)#2-K(2)-S(2)#16	72.14(10)
S(1)-K(1)-P(1)	91.5(2)	S(1)#4-K(2)-S(2)#17	149.43(7)
P(1)#8-K(1)-P(1)	111.0(2)	S(2)#4-K(2)-S(2)#17	72.14(10)
S(3)-K(1)-S(2)#10	82.02(9)	S(2)#2-K(2)-S(2)#17	131.96(9)
S(3)#8-K(1)-S(2)#10	100.24(10)	S(2)#16-K(2)-S(2)#17	59.83(13)
S(3)#10-K(1)-S(2)#10	56.02(9)	S(1)#4-K(2)-S(3)#18	64.08(10)
S(3)#13-K(1)-S(2)#10	112.30(13)	S(2)#4-K(2)-S(3)#18	87.04(7)
S(1)#5-K(1)-S(2)#10	141.80(9)	S(2)#2-K(2)-S(3)#18	87.04(7)
S(1)-K(1)-S(2)#10	116.08(14)	S(2)#16-K(2)-S(3)#18	106.65(11)
P(1)#8-K(1)-S(2)#10	125.41(10)	S(2)#17-K(2)-S(3)#18	106.65(11)
P(1)-K(1)-S(2)#10	113.03(13)	S(1)#4-K(2)-S(2)#3	85.30(10)
S(3)-K(1)-S(2)#14	100.24(10)	S(2)#4-K(2)-S(2)#3	114.11(11)
S(3)#8-K(1)-S(2)#14	82.01(9)	S(2)#2-K(2)-S(2)#3	58.91(10)
S(3)#10-K(1)-S(2)#14	112.30(13)	S(2)#16-K(2)-S(2)#3	85.55(9)

S(2)#17-K(2)-S(2)#3	113.21(11)	K(1)#18-K(2)-K(1)#20	71.7(2)
S(3)#18-K(2)-S(2)#3	138.87(13)		
S(1)#4-K(2)-S(2)#8	85.30(10)		
S(2)#4-K(2)-S(2)#8	58.91(10)		
S(2)#2-K(2)-S(2)#8	114.11(11)		
S(2)#16-K(2)-S(2)#8	113.21(11)		
S(2)#17-K(2)-S(2)#8	85.55(9)		
S(3)#18-K(2)-S(2)#8	138.87(13)		
S(2)#3-K(2)-S(2)#8	56.4(2)		
S(1)#4-K(2)-K(2)#19	133.2(2)		
S(2)#4-K(2)-K(2)#19	96.30(7)		
S(2)#2-K(2)-K(2)#19	96.30(7)		
S(2)#16-K(2)-K(2)#19	58.91(11)		
S(2)#17-K(2)-K(2)#19	58.91(11)		
S(3)#18-K(2)-K(2)#19	162.73(15)		
S(2)#3-K(2)-K(2)#19	54.30(15)		
S(2)#8-K(2)-K(2)#19	54.30(15)		
S(1)#4-K(2)-P(1)#16	159.72(13)		
S(2)#4-K(2)-P(1)#16	101.96(7)		
S(2)#2-K(2)-P(1)#16	101.96(7)		
S(2)#16-K(2)-P(1)#16	32.62(7)		
S(2)#17-K(2)-P(1)#16	32.62(7)		
S(3)#18-K(2)-P(1)#16	95.65(14)		
S(2)#3-K(2)-P(1)#16	112.39(8)		
S(2)#8-K(2)-P(1)#16	112.39(8)		
K(2)#19-K(2)-P(1)#16	67.1(2)		
S(1)#4-K(2)-K(1)#18	99.12(9)		
S(2)#4-K(2)-K(1)#18	59.56(9)		
S(2)#2-K(2)-K(1)#18	129.72(12)		
S(2)#16-K(2)-K(1)#18	94.37(10)		
S(2)#17-K(2)-K(1)#18	59.46(8)		
S(3)#18-K(2)-K(1)#18	49.80(12)		
S(2)#3-K(2)-K(1)#18	170.85(7)		
S(2)#8-K(2)-K(1)#18	115.67(15)		
K(2)#19-K(2)-K(1)#18	118.1(2)		
P(1)#16-K(2)-K(1)#18	64.90(6)		
S(1)#4-K(2)-K(1)#20	99.12(9)		
S(2)#4-K(2)-K(1)#20	129.72(12)		
S(2)#2-K(2)-K(1)#20	59.56(9)		
S(2)#16-K(2)-K(1)#20	59.46(8)		
S(2)#17-K(2)-K(1)#20	94.37(10)		
S(3)#18-K(2)-K(1)#20	49.80(12)		
S(2)#3-K(2)-K(1)#20	115.67(15)		
S(2)#8-K(2)-K(1)#20	170.85(7)		
K(2)#19-K(2)-K(1)#20	118.1(2)		
P(1)#16-K(2)-K(1)#20	64.90(6)		

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y+0,-z+1/2 #2 -x+1,-y,z #3 x+0,-y+0,-z+1/2

#4 -x+1,-y,-z+1 #5 x,-y,z-1/2 #6 x,y,-z #7 -x+1,y+1,-z+1/2

#8 x,-y,z+1/2 #9 x,y,-z+1 #10 -x+1/2,-y+1/2,-z+1/2

#11 -x+1/2,-y+1/2,z-1/2 #12 x-1/2,y+1/2,z-1/2

#13 -x+1/2,y-1/2,-z #14 -x+1/2,y-1/2,z #15 x-1/2,-y-1/2,z

#16 -x+1,y-1,-z+1/2 #17 -x+1,y-1,z+1/2 #18 x+1/2,y-1/2,z+1/2

#19 -x+1,-y-1,-z+1 #20 x+1/2,y-1/2,-z+1/2

Table C.24. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $K_4Eu(PS_4)_2$. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Eu(1)	13(1)	12(1)	11(1)	0	0	0
P(1)	6(1)	5(1)	8(1)	0	0	-2(1)
S(1)	8(1)	7(2)	24(2)	0	0	-1(1)
S(2)	22(1)	10(1)	8(1)	-2(1)	-2(1)	-1(1)
S(3)	9(2)	11(2)	20(2)	0	0	2(1)
K(1)	29(2)	17(1)	13(1)	5(1)	0	0
K(2)	23(2)	9(1)	13(1)	0	0	-4(1)

Table C.25. Crystal data and structure refinement for $KEuPS_4$.

Identification code	pnma	
Empirical formula	$KEuPS_4$	
Formula weight	350.27	
Temperature	168(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pnma	
Unit cell dimensions	a = 16.7816(15) Å	α= 90°.
	b = 6.6141(6) Å	β= 90°.
	c = 6.5142(6) Å	γ = 90°.
Volume	723.04(11) $Å^3$	
Z	4	
Density (calculated)	3.218 Mg/m^3	
Absorption coefficient	10.504 mm^{-1}	
F(000)	644	
Crystal size	0.03 x 0.08 x 0.09 mm^3	
Theta range for data collection	2.43 to 28.30°.	
Index ranges	-12<=h<=22, -8<=k<=8, -8<=l<=8	
Reflections collected	4521	
Independent reflections	977 [R(int) = 0.0581]	
Absorption correction	SADABS	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	977 / 0 / 40	
Goodness-of-fit on F^2	1.069	
Final R indices [I>2sigma(I)]	R1 = 0.0368, wR2 = 0.0687	
R indices (all data)	R1 = 0.0552, wR2 = 0.0749	
Largest diff. peak and hole	1.047 and -1.209 $e.Å^{-3}$	

Table C.26. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for $KEuPS_4$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Eu(1)	4780(1)	2500	2919(1)	14(1)
P(1)	4020(1)	2500	7786(4)	10(1)
K(1)	2117(1)	2500	4815(4)	24(1)
S(1)	3324(1)	2500	338(4)	17(1)
S(2)	4785(1)	-2500	1562(4)	16(1)
S(3)	3786(1)	27(2)	6013(3)	14(1)

Table C.27. Bond lengths [Å] and angles [°] for $KEuPS_4$.

Eu(1)-S(1)	2.966(2)	S(1)-Eu(1)-S(3)#4	85.68(5)
Eu(1)-S(2)#1	3.009(2)	S(2)#1-Eu(1)-S(3)#4	139.89(4)
Eu(1)-S(3)#2	3.012(2)	S(3)#2-Eu(1)-S(3)#4	89.26(4)
Eu(1)-S(3)#3	3.012(2)	S(3)#3-Eu(1)-S(3)#4	125.13(3)
Eu(1)-S(3)#4	3.086(2)	S(1)-Eu(1)-S(3)	85.68(5)
Eu(1)-S(3)	3.086(2)	S(2)#1-Eu(1)-S(3)	139.89(4)
Eu(1)-P(1)	3.417(2)	S(3)#2-Eu(1)-S(3)	125.13(3)
Eu(1)-S(2)#5	3.4232(7)	S(3)#3-Eu(1)-S(3)	89.26(4)
Eu(1)-S(2)	3.4232(7)	S(3)#4-Eu(1)-S(3)	64.03(6)
Eu(1)-P(1)#6	3.579(2)	S(1)-Eu(1)-P(1)	102.62(6)
Eu(1)-K(1)#7	4.308(2)	S(2)#1-Eu(1)-P(1)	172.13(6)
Eu(1)-Eu(1)#8	4.3395(7)	S(3)#2-Eu(1)-P(1)	94.81(5)
P(1)-S(1)#9	2.032(3)	S(3)#3-Eu(1)-P(1)	94.81(5)
P(1)-S(3)#4	2.041(2)	S(3)#4-Eu(1)-P(1)	36.12(3)
P(1)-S(3)	2.041(2)	S(3)-Eu(1)-P(1)	36.12(3)
P(1)-S(2)#3	2.050(3)	S(1)-Eu(1)-S(2)#5	81.70(4)
P(1)-Eu(1)#9	3.579(2)	S(2)#1-Eu(1)-S(2)#5	75.45(4)
P(1)-K(1)	3.734(3)	S(3)#2-Eu(1)-S(2)#5	61.42(5)
K(1)-S(3)	3.335(2)	S(3)#3-Eu(1)-S(2)#5	126.43(5)
K(1)-S(3)#4	3.335(2)	S(3)#4-Eu(1)-S(2)#5	69.99(5)
K(1)-S(3)#10	3.350(3)	S(3)-Eu(1)-S(2)#5	133.01(5)
K(1)-S(3)#11	3.350(3)	P(1)-Eu(1)-S(2)#5	103.92(4)
K(1)-S(2)#12	3.389(3)	S(1)-Eu(1)-S(2)	81.70(4)
K(1)-S(1)#12	3.4060(8)	S(2)#1-Eu(1)-S(2)	75.45(4)
K(1)-S(1)#13	3.4060(8)	S(3)#2-Eu(1)-S(2)	126.43(5)
K(1)-S(1)	3.550(3)	S(3)#3-Eu(1)-S(2)	61.42(5)
K(1)-Eu(1)#14	4.308(2)	S(3)#4-Eu(1)-S(2)	133.01(5)
K(1)-K(1)#13	4.8161(12)	S(3)-Eu(1)-S(2)	69.99(5)
S(1)-P(1)#6	2.032(3)	P(1)-Eu(1)-S(2)	103.92(4)
S(1)-K(1)#10	3.4060(8)	S(2)#5-Eu(1)-S(2)	150.06(8)
S(1)-K(1)#15	3.4060(8)	S(1)-Eu(1)-P(1)#6	34.60(6)
S(2)-P(1)#3	2.050(3)	S(2)#1-Eu(1)-P(1)#6	34.91(6)
S(2)-Eu(1)#1	3.009(2)	S(3)#2-Eu(1)-P(1)#6	120.04(4)
S(2)-K(1)#10	3.389(3)	S(3)#3-Eu(1)-P(1)#6	120.04(4)
S(2)-Eu(1)#16	3.4232(7)	S(3)#4-Eu(1)-P(1)#6	114.69(4)
S(3)-Eu(1)#3	3.012(2)	S(3)-Eu(1)-P(1)#6	114.69(4)
S(3)-K(1)#12	3.350(3)	P(1)-Eu(1)-P(1)#6	137.21(7)
		S(2)#5-Eu(1)-P(1)#6	76.09(4)
S(1)-Eu(1)-S(2)#1	69.51(6)	S(2)-Eu(1)-P(1)#6	76.09(4)
S(1)-Eu(1)-S(3)#2	142.12(4)	S(1)-Eu(1)-K(1)#7	121.05(5)
S(2)#1-Eu(1)-S(3)#2	91.73(5)	S(2)#1-Eu(1)-K(1)#7	51.54(5)
S(1)-Eu(1)-S(3)#3	142.12(4)	S(3)#2-Eu(1)-K(1)#7	50.79(4)
S(2)#1-Eu(1)-S(3)#3	91.73(5)	S(3)#3-Eu(1)-K(1)#7	50.79(4)
S(3)#2-Eu(1)-S(3)#3	67.42(6)	S(3)#4-Eu(1)-K(1)#7	139.67(3)

S(3)-Eu(1)-K(1)#7	139.67(3)	S(3)#11-K(1)-S(2)#12	79.75(6)
P(1)-Eu(1)-K(1)#7	136.33(5)	S(3)-K(1)-S(1)#12	71.51(5)
S(2)#5-Eu(1)-K(1)#7	83.74(4)	S(3)#4-K(1)-S(1)#12	129.44(7)
S(2)-Eu(1)-K(1)#7	83.74(4)	S(3)#10-K(1)-S(1)#12	59.42(5)
P(1)#6-Eu(1)-K(1)#7	86.45(5)	S(3)#11-K(1)-S(1)#12	117.39(7)
S(1)-Eu(1)-Eu(1)#8	119.62(2)	S(2)#12-K(1)-S(1)#12	76.21(5)
S(2)#1-Eu(1)-Eu(1)#8	124.39(2)	S(3)-K(1)-S(1)#13	129.44(7)
S(3)#2-Eu(1)-Eu(1)#8	45.31(3)	S(3)#4-K(1)-S(1)#13	71.51(5)
S(3)#3-Eu(1)-Eu(1)#8	98.20(3)	S(3)#10-K(1)-S(1)#13	117.39(7)
S(3)#4-Eu(1)-Eu(1)#8	43.94(3)	S(3)#11-K(1)-S(1)#13	59.42(5)
S(3)-Eu(1)-Eu(1)#8	95.05(3)	S(2)#12-K(1)-S(1)#13	76.21(5)
P(1)-Eu(1)-Eu(1)#8	58.93(2)	S(1)#12-K(1)-S(1)#13	152.31(11)
S(2)#5-Eu(1)-Eu(1)#8	54.88(4)	S(3)-K(1)-S(1)	73.35(6)
S(2)-Eu(1)-Eu(1)#8	153.79(4)	S(3)#4-K(1)-S(1)	73.35(6)
P(1)#6-Eu(1)-Eu(1)#8	130.118(11)	S(3)#10-K(1)-S(1)	69.56(6)
K(1)#7-Eu(1)-Eu(1)#8	95.93(2)	S(3)#11-K(1)-S(1)	69.56(6)
S(1)#9-P(1)-S(3)#4	110.63(9)	S(2)#12-K(1)-S(1)	144.39(9)
S(1)#9-P(1)-S(3)	110.63(9)	S(1)#12-K(1)-S(1)	101.90(6)
S(3)#4-P(1)-S(3)	106.56(14)	S(1)#13-K(1)-S(1)	101.90(6)
S(1)#9-P(1)-S(2)#3	113.13(14)	S(3)-K(1)-P(1)	32.95(4)
S(3)#4-P(1)-S(2)#3	107.81(9)	S(3)#4-K(1)-P(1)	32.95(4)
S(3)-P(1)-S(2)#3	107.81(9)	S(3)#10-K(1)-P(1)	140.36(6)
S(1)#9-P(1)-Eu(1)	166.81(12)	S(3)#11-K(1)-P(1)	140.36(6)
S(3)#4-P(1)-Eu(1)	63.05(7)	S(2)#12-K(1)-P(1)	129.16(9)
S(3)-P(1)-Eu(1)	63.05(7)	S(1)#12-K(1)-P(1)	97.70(5)
S(2)#3-P(1)-Eu(1)	80.05(9)	S(1)#13-K(1)-P(1)	97.70(5)
S(1)#9-P(1)-Eu(1)#9	55.97(9)	S(1)-K(1)-P(1)	86.45(7)
S(3)#4-P(1)-Eu(1)#9	126.69(7)	S(3)-K(1)-Eu(1)#14	149.44(4)
S(3)-P(1)-Eu(1)#9	126.69(7)	S(3)#4-K(1)-Eu(1)#14	149.44(4)
S(2)#3-P(1)-Eu(1)#9	57.16(8)	S(3)#10-K(1)-Eu(1)#14	44.15(4)
Eu(1)-P(1)-Eu(1)#9	137.22(7)	S(3)#11-K(1)-Eu(1)#14	44.15(4)
S(1)#9-P(1)-K(1)	86.12(10)	S(2)#12-K(1)-Eu(1)#14	44.04(5)
S(3)#4-P(1)-K(1)	62.73(7)	S(1)#12-K(1)-Eu(1)#14	80.99(5)
S(3)-P(1)-K(1)	62.73(7)	S(1)#13-K(1)-Eu(1)#14	80.99(5)
S(2)#3-P(1)-K(1)	160.75(12)	S(1)-K(1)-Eu(1)#14	100.35(7)
Eu(1)-P(1)-K(1)	80.69(6)	P(1)-K(1)-Eu(1)#14	173.21(8)
Eu(1)#9-P(1)-K(1)	142.09(8)	S(3)-K(1)-Eu(1)	41.68(4)
S(3)-K(1)-S(3)#4	58.74(6)	S(3)#4-K(1)-Eu(1)	41.68(4)
S(3)-K(1)-S(3)#10	107.94(5)	S(3)#10-K(1)-Eu(1)	103.83(6)
S(3)#4-K(1)-S(3)#10	142.88(9)	S(3)#11-K(1)-Eu(1)	103.83(6)
S(3)-K(1)-S(3)#11	142.88(9)	S(2)#12-K(1)-Eu(1)	175.83(8)
S(3)#4-K(1)-S(3)#11	107.94(5)	S(1)#12-K(1)-Eu(1)	103.66(5)
S(3)#10-K(1)-S(3)#11	59.85(6)	S(1)#13-K(1)-Eu(1)	103.66(5)
S(3)-K(1)-S(2)#12	135.42(7)	S(1)-K(1)-Eu(1)	39.78(4)
S(3)#4-K(1)-S(2)#12	135.42(7)	P(1)-K(1)-Eu(1)	46.67(4)
S(3)#10-K(1)-S(2)#12	79.75(6)	Eu(1)#14-K(1)-Eu(1)	140.13(6)

S(3)-K(1)-K(1)#13	87.40(6)
S(3)#4-K(1)-K(1)#13	44.04(5)
S(3)#10-K(1)-K(1)#13	164.40(6)
S(3)#11-K(1)-K(1)#13	106.14(4)
S(2)#12-K(1)-K(1)#13	91.38(6)
S(1)#12-K(1)-K(1)#13	131.07(6)
S(1)#13-K(1)-K(1)#13	47.44(5)
S(1)-K(1)-K(1)#13	113.79(6)
P(1)-K(1)-K(1)#13	54.65(4)
Eu(1)#14-K(1)-K(1)#13	121.50(6)
Eu(1)-K(1)-K(1)#13	85.59(6)
P(1)#6-S(1)-Eu(1)	89.43(10)
P(1)#6-S(1)-K(1)#10	92.47(6)
Eu(1)-S(1)-K(1)#10	103.64(5)
P(1)#6-S(1)-K(1)#15	92.47(6)
Eu(1)-S(1)-K(1)#15	103.64(5)
K(1)#10-S(1)-K(1)#15	152.31(11)
P(1)#6-S(1)-K(1)	179.67(12)
Eu(1)-S(1)-K(1)	90.24(7)
K(1)#10-S(1)-K(1)	87.61(5)
K(1)#15-S(1)-K(1)	87.61(5)
P(1)#3-S(2)-Eu(1)#1	87.92(10)
P(1)#3-S(2)-K(1)#10	172.34(13)
Eu(1)#1-S(2)-K(1)#10	84.42(7)
P(1)#3-S(2)-Eu(1)	87.07(5)
Eu(1)#1-S(2)-Eu(1)	104.55(4)
K(1)#10-S(2)-Eu(1)	94.84(4)
P(1)#3-S(2)-Eu(1)#16	87.07(5)
Eu(1)#1-S(2)-Eu(1)#16	104.55(4)
K(1)#10-S(2)-Eu(1)#16	94.84(4)
Eu(1)-S(2)-Eu(1)#16	150.06(8)
P(1)-S(3)-Eu(1)#3	99.21(8)
P(1)-S(3)-Eu(1)	80.82(8)
Eu(1)#3-S(3)-Eu(1)	90.74(4)
P(1)-S(3)-K(1)	84.32(8)
Eu(1)#3-S(3)-K(1)	175.64(6)
Eu(1)-S(3)-K(1)	92.36(5)
P(1)-S(3)-K(1)#12	93.94(8)
Eu(1)#3-S(3)-K(1)#12	85.06(5)
Eu(1)-S(3)-K(1)#12	172.70(7)
K(1)-S(3)-K(1)#12	92.17(5)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y,-z #2 -x+1,y+1/2,-z+1 #3 -x+1,-y,-z+1

#4 x,-y+1/2,z #5 x,y+1,z #6 x,y,z-1 #7 x+1/2,y,-z+1/2

#8 -x+1,-y+1,-z+1 #9 x,y,z+1 #10 -x+1/2,-y,z-1/2

#11 -x+1/2,y+1/2,z-1/2 #12 -x+1/2,-y,z+1/2 #13 -x+1/2,-y+1,z+1/2

#14 x-1/2,y,-z+1/2 #15 -x+1/2,-y+1,z-1/2 #16 x,y-1,z

Table C.28. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $KEuPS_4$. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Eu(1)	13(1)	17(1)	12(1)	0	1(1)	0
P(1)	10(1)	7(1)	12(1)	0	0(1)	0
K(1)	19(1)	17(1)	35(1)	0	-6(1)	0
S(1)	13(1)	20(1)	17(1)	0	6(1)	0
S(2)	9(1)	24(1)	17(1)	0	2(1)	0
S(3)	15(1)	10(1)	18(1)	-2(1)	-3(1)	0(1)

Appendix D:

Supplementary Information for Chapter Four

Table D.1. Crystal data and structure refinement for $K_2Y(P_2S_6)_{1/2}(PS_4)$.

Identification code	c2c	
Empirical formula	$K_2Y(P_2S_6)_{1/2}(PS_4)$	
Formula weight	453.47	
Temperature	170(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 22.739(3) Å	α= 90°.
	b = 6.7385(8) Å	β= 119.816(2)°.
	c = 18.013(2) Å	γ = 90°.
Volume	2394.8(5) $Å^3$	
Z	8	
Density (calculated)	2.516 Mg/m^3	
Absorption coefficient	6.997 mm^{-1}	
F(000)	1752	
Crystal size	0.1 x 0.1 x 0.2 mm^3	
Theta range for data collection	2.06 to 28.35°.	
Index ranges	-29<=h<=27, -8<=k<=8, -14<=l<=23	
Reflections collected	7424	
Independent reflections	2849 [R(int) = 0.1620]	
Absorption correction	SADABS	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2849 / 0 / 109	
Goodness-of-fit on F^2	1.027	
Final R indices [I>2sigma(I)]	R1 = 0.0890, wR2 = 0.1452	
R indices (all data)	R1 = 0.1990, wR2 = 0.1875	
Largest diff. peak and hole	1.261 and -1.281 e.$Å^{-3}$	

Table D.2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for $K_2Y(P_2S_6)_{1/2}(PS_4)$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Y(1)	1540(1)	5472(2)	2344(1)	13(1)
S(1)	2243(2)	9432(5)	2671(2)	13(1)
S(2)	2620(2)	5242(5)	4025(2)	16(1)
S(3)	-138(2)	5316(5)	1032(2)	17(1)
S(4)	986(2)	7785(5)	3136(2)	15(1)
S(5)	1100(2)	2500(5)	1072(2)	17(1)
S(6)	1006(2)	2914(5)	3130(2)	14(1)
S(7)	1060(2)	7723(5)	835(2)	15(1)
K(1)	-111(2)	271(4)	1173(2)	21(1)
K(2)	3105(2)	9987(5)	4790(2)	26(1)
P(1)	1695(2)	10061(5)	1393(2)	12(1)
P(2)	466(2)	5324(5)	3130(2)	12(1)

Table D.3. Bond lengths [Å] and angles [°] for $K_2Y(P_2S_6)_{1/2}(PS_4)$.

Y(1)-S(2)	2.799(4)	K(2)-S(7)#2	3.224(4)
Y(1)-S(4)	2.800(4)	K(2)-S(2)#3	3.287(4)
Y(1)-S(7)	2.815(4)	K(2)-S(5)#2	3.357(4)
Y(1)-S(5)	2.825(4)	K(2)-S(3)#12	3.481(5)
Y(1)-S(6)	2.856(4)	K(2)-P(2)#3	3.540(5)
Y(1)-S(1)#1	2.869(3)	K(2)-S(6)#3	3.549(5)
Y(1)-S(1)	3.015(4)	K(2)-S(4)#3	3.747(5)
Y(1)-P(2)	3.377(3)	K(2)-S(2)#6	3.761(5)
Y(1)-K(2)#1	4.315(3)	K(2)-Y(1)#2	4.315(3)
S(1)-P(1)	2.044(5)	K(2)-K(2)#3	4.632(6)
S(1)-Y(1)#2	2.869(3)	P(1)-S(5)#6	2.022(5)
S(1)-K(2)	3.333(5)	P(1)-S(2)#2	2.043(4)
S(2)-P(1)#1	2.043(4)	P(2)-S(3)#5	1.991(4)
S(2)-K(2)#3	3.287(4)	P(2)-P(2)#5	2.204(7)
S(2)-K(2)	3.439(5)	P(2)-K(2)#3	3.540(5)
S(2)-K(2)#4	3.761(5)	P(2)-K(1)#8	3.789(4)
S(3)-P(2)#5	1.990(4)	P(2)-K(1)#5	3.852(5)
S(3)-K(1)#6	3.347(5)		
S(3)-K(1)	3.407(5)	S(2)-Y(1)-S(4)	81.64(11)
S(3)-K(2)#7	3.481(5)	S(2)-Y(1)-S(7)	141.66(11)
S(4)-P(2)	2.032(5)	S(4)-Y(1)-S(7)	97.78(11)
S(4)-K(1)#8	3.283(4)	S(2)-Y(1)-S(5)	127.21(11)
S(4)-K(1)#6	3.572(5)	S(4)-Y(1)-S(5)	137.78(11)
S(4)-K(2)#3	3.747(5)	S(7)-Y(1)-S(5)	77.77(11)
S(5)-P(1)#4	2.022(5)	S(2)-Y(1)-S(6)	77.95(10)
S(5)-K(1)	3.221(4)	S(4)-Y(1)-S(6)	70.94(10)
S(5)-K(2)#1	3.357(4)	S(7)-Y(1)-S(6)	138.37(11)
S(6)-P(2)	2.035(5)	S(5)-Y(1)-S(6)	84.74(11)
S(6)-K(1)#5	3.382(4)	S(2)-Y(1)-S(1)#1	70.39(9)
S(6)-K(2)#3	3.549(5)	S(4)-Y(1)-S(1)#1	145.23(11)
S(6)-K(1)	3.626(5)	S(7)-Y(1)-S(1)#1	92.01(10)
S(7)-P(1)	2.033(5)	S(5)-Y(1)-S(1)#1	76.89(10)
S(7)-K(2)#1	3.224(4)	S(6)-Y(1)-S(1)#1	120.48(10)
S(7)-K(1)#9	3.436(5)	S(2)-Y(1)-S(1)	75.06(10)
S(7)-K(1)#6	3.466(4)	S(4)-Y(1)-S(1)	74.74(9)
K(1)-S(4)#10	3.283(4)	S(7)-Y(1)-S(1)	67.97(10)
K(1)-S(3)#4	3.347(5)	S(5)-Y(1)-S(1)	136.50(10)
K(1)-S(6)#5	3.382(4)	S(6)-Y(1)-S(1)	138.76(11)
K(1)-S(7)#9	3.436(5)	S(1)#1-Y(1)-S(1)	78.32(6)
K(1)-S(7)#4	3.466(4)	S(2)-Y(1)-P(2)	88.48(9)
K(1)-S(4)#4	3.572(5)	S(4)-Y(1)-P(2)	36.94(9)
K(1)-P(2)#10	3.789(4)	S(7)-Y(1)-P(2)	113.98(10)
K(1)-P(2)#5	3.852(5)	S(5)-Y(1)-P(2)	106.33(10)
K(1)-K(1)#11	4.512(6)	S(6)-Y(1)-P(2)	36.93(9)

S(1)#1-Y(1)-P(2)	153.97(10)	Y(1)-S(5)-K(2)#1	88.09(11)
S(1)-Y(1)-P(2)	111.56(9)	K(1)-S(5)-K(2)#1	158.56(15)
S(2)-Y(1)-K(2)#1	120.48(8)	P(2)-S(6)-Y(1)	85.60(14)
S(4)-Y(1)-K(2)#1	145.79(9)	P(2)-S(6)-K(1)#5	86.92(15)
S(7)-Y(1)-K(2)#1	48.35(8)	Y(1)-S(6)-K(1)#5	169.95(14)
S(5)-Y(1)-K(2)#1	51.04(8)	P(2)-S(6)-K(2)#3	73.08(15)
S(6)-Y(1)-K(2)#1	135.22(9)	Y(1)-S(6)-K(2)#3	97.11(11)
S(1)#1-Y(1)-K(2)#1	50.53(8)	K(1)#5-S(6)-K(2)#3	87.10(11)
S(1)-Y(1)-K(2)#1	85.71(8)	P(2)-S(6)-K(1)	105.1(2)
P(2)-Y(1)-K(2)#1	149.93(8)	Y(1)-S(6)-K(1)	94.55(11)
P(1)-S(1)-Y(1)#2	89.42(14)	K(1)#5-S(6)-K(1)	80.94(11)
P(1)-S(1)-Y(1)	89.77(15)	K(2)#3-S(6)-K(1)	168.00(12)
Y(1)#2-S(1)-Y(1)	129.40(12)	P(1)-S(7)-Y(1)	95.8(2)
P(1)-S(1)-K(2)	161.5(2)	P(1)-S(7)-K(2)#1	102.7(2)
Y(1)#2-S(1)-K(2)	87.83(10)	Y(1)-S(7)-K(2)#1	90.93(11)
Y(1)-S(1)-K(2)	106.03(11)	P(1)-S(7)-K(1)#9	97.8(2)
P(1)#1-S(2)-Y(1)	91.4(2)	Y(1)-S(7)-K(1)#9	165.26(13)
P(1)#1-S(2)-K(2)#3	163.2(2)	K(2)#1-S(7)-K(1)#9	91.60(12)
Y(1)-S(2)-K(2)#3	104.54(11)	P(1)-S(7)-K(1)#6	87.02(15)
P(1)#1-S(2)-K(2)	93.00(15)	Y(1)-S(7)-K(1)#6	93.47(11)
Y(1)-S(2)-K(2)	108.44(12)	K(2)#1-S(7)-K(1)#6	168.91(14)
K(2)#3-S(2)-K(2)	87.02(11)	K(1)#9-S(7)-K(1)#6	81.63(11)
P(1)#1-S(2)-K(2)#4	86.58(14)	S(5)-K(1)-S(4)#10	162.91(15)
Y(1)-S(2)-K(2)#4	112.83(12)	S(5)-K(1)-S(3)#4	116.43(12)
K(2)#3-S(2)-K(2)#4	82.42(10)	S(4)#10-K(1)-S(3)#4	61.83(10)
K(2)-S(2)-K(2)#4	138.72(14)	S(5)-K(1)-S(6)#5	117.70(12)
P(2)#5-S(3)-K(1)#6	86.5(2)	S(4)#10-K(1)-S(6)#5	62.47(9)
P(2)#5-S(3)-K(1)	86.9(2)	S(3)#4-K(1)-S(6)#5	124.18(11)
K(1)#6-S(3)-K(1)	172.2(2)	S(5)-K(1)-S(3)	60.97(10)
P(2)#5-S(3)-K(2)#7	75.18(14)	S(4)#10-K(1)-S(3)	123.06(12)
K(1)#6-S(3)-K(2)#7	94.54(11)	S(3)#4-K(1)-S(3)	172.2(2)
K(1)-S(3)-K(2)#7	87.82(11)	S(6)#5-K(1)-S(3)	60.67(9)
P(2)-S(4)-Y(1)	87.15(15)	S(5)-K(1)-S(7)#9	82.20(11)
P(2)-S(4)-K(1)#8	87.63(15)	S(4)#10-K(1)-S(7)#9	114.72(12)
Y(1)-S(4)-K(1)#8	171.25(15)	S(3)#4-K(1)-S(7)#9	109.53(12)
P(2)-S(4)-K(1)#6	105.0(2)	S(6)#5-K(1)-S(7)#9	90.28(11)
Y(1)-S(4)-K(1)#6	91.49(11)	S(3)-K(1)-S(7)#9	63.28(10)
K(1)#8-S(4)-K(1)#6	83.10(12)	S(5)-K(1)-S(7)#4	57.87(9)
P(2)-S(4)-K(2)#3	68.28(14)	S(4)#10-K(1)-S(7)#4	118.48(12)
Y(1)-S(4)-K(2)#3	93.77(10)	S(3)#4-K(1)-S(7)#4	58.63(9)
K(1)#8-S(4)-K(2)#3	90.81(11)	S(6)#5-K(1)-S(7)#4	169.30(13)
K(1)#6-S(4)-K(2)#3	171.23(12)	S(3)-K(1)-S(7)#4	117.92(11)
P(1)#4-S(5)-Y(1)	115.3(2)	S(7)#9-K(1)-S(7)#4	98.37(11)
P(1)#4-S(5)-K(1)	94.2(2)	S(5)-K(1)-S(4)#4	94.54(11)
Y(1)-S(5)-K(1)	104.62(12)	S(4)#10-K(1)-S(4)#4	68.99(11)
P(1)#4-S(5)-K(2)#1	95.8(2)	S(3)#4-K(1)-S(4)#4	65.47(10)

S(6)#5-K(1)-S(4)#4	97.58(11)	S(2)#3-K(2)-S(5)#2	146.73(13)
S(3)-K(1)-S(4)#4	121.30(12)	S(1)-K(2)-S(5)#2	63.90(10)
S(7)#9-K(1)-S(4)#4	172.12(12)	S(7)#2-K(2)-S(2)	121.25(12)
S(7)#4-K(1)-S(4)#4	73.88(10)	S(2)#3-K(2)-S(2)	92.98(11)
S(5)-K(1)-S(6)	67.70(10)	S(1)-K(2)-S(2)	63.13(10)
S(4)#10-K(1)-S(6)	98.37(11)	S(5)#2-K(2)-S(2)	59.31(9)
S(3)#4-K(1)-S(6)	122.79(12)	S(7)#2-K(2)-S(3)#12	64.61(10)
S(6)#5-K(1)-S(6)	68.90(11)	S(2)#3-K(2)-S(3)#12	111.48(13)
S(3)-K(1)-S(6)	63.91(10)	S(1)-K(2)-S(3)#12	124.27(12)
S(7)#9-K(1)-S(6)	126.86(12)	S(5)#2-K(2)-S(3)#12	63.80(10)
S(7)#4-K(1)-S(6)	100.72(11)	S(2)-K(2)-S(3)#12	103.88(11)
S(4)#4-K(1)-S(6)	57.40(9)	S(7)#2-K(2)-P(2)#3	90.81(11)
S(5)-K(1)-P(2)#10	139.34(12)	S(2)#3-K(2)-P(2)#3	78.60(11)
S(4)#10-K(1)-P(2)#10	32.41(8)	S(1)-K(2)-P(2)#3	155.96(12)
S(3)#4-K(1)-P(2)#10	31.63(8)	S(5)#2-K(2)-P(2)#3	92.21(11)
S(6)#5-K(1)-P(2)#10	94.19(10)	S(2)-K(2)-P(2)#3	108.16(12)
S(3)-K(1)-P(2)#10	154.63(12)	S(3)#12-K(2)-P(2)#3	32.93(8)
S(7)#9-K(1)-P(2)#10	124.71(12)	S(7)#2-K(2)-S(6)#3	90.92(11)
S(7)#4-K(1)-P(2)#10	86.08(10)	S(2)#3-K(2)-S(6)#3	62.56(10)
S(4)#4-K(1)-P(2)#10	54.41(9)	S(1)-K(2)-S(6)#3	162.88(13)
S(6)-K(1)-P(2)#10	105.76(11)	S(5)#2-K(2)-S(6)#3	122.16(12)
S(5)-K(1)-P(2)#5	86.00(10)	S(2)-K(2)-S(6)#3	133.97(13)
S(4)#10-K(1)-P(2)#5	93.57(10)	S(3)#12-K(2)-S(6)#3	58.39(9)
S(3)#4-K(1)-P(2)#5	155.19(12)	P(2)#3-K(2)-S(6)#3	33.36(8)
S(6)#5-K(1)-P(2)#5	31.84(8)	S(7)#2-K(2)-S(4)#3	120.31(12)
S(3)-K(1)-P(2)#5	31.06(8)	S(2)#3-K(2)-S(4)#3	62.31(9)
S(7)#9-K(1)-P(2)#5	82.64(10)	S(1)-K(2)-S(4)#3	143.58(12)
S(7)#4-K(1)-P(2)#5	143.05(11)	S(5)#2-K(2)-S(4)#3	93.17(11)
S(4)#4-K(1)-P(2)#5	104.35(11)	S(2)-K(2)-S(4)#3	81.03(10)
S(6)-K(1)-P(2)#5	53.67(8)	S(3)#12-K(2)-S(4)#3	56.09(9)
P(2)#10-K(1)-P(2)#5	123.74(11)	P(2)#3-K(2)-S(4)#3	32.23(8)
S(5)-K(1)-K(1)#11	59.20(9)	S(6)#3-K(2)-S(4)#3	53.39(9)
S(4)#10-K(1)-K(1)#11	133.23(14)	S(7)#2-K(2)-S(2)#6	56.62(9)
S(3)#4-K(1)-K(1)#11	81.64(10)	S(2)#3-K(2)-S(2)#6	97.57(10)
S(6)#5-K(1)-K(1)#11	139.35(14)	S(1)-K(2)-S(2)#6	77.74(10)
S(3)-K(1)-K(1)#11	90.99(11)	S(5)#2-K(2)-S(2)#6	115.33(11)
S(7)#9-K(1)-K(1)#11	49.48(8)	S(2)-K(2)-S(2)#6	138.72(14)
S(7)#4-K(1)-K(1)#11	48.89(8)	S(3)#12-K(2)-S(2)#6	108.92(11)
S(4)#4-K(1)-K(1)#11	122.76(12)	P(2)#3-K(2)-S(2)#6	113.02(11)
S(6)-K(1)-K(1)#11	126.85(12)	S(6)#3-K(2)-S(2)#6	85.47(10)
P(2)#10-K(1)-K(1)#11	112.40(11)	S(4)#3-K(2)-S(2)#6	138.64(12)
P(2)#5-K(1)-K(1)#11	121.09(12)	S(7)#2-K(2)-Y(1)#2	40.72(7)
S(7)#2-K(2)-S(2)#3	145.74(14)	S(2)#3-K(2)-Y(1)#2	163.47(12)
S(7)#2-K(2)-S(1)	77.14(11)	S(1)-K(2)-Y(1)#2	41.64(7)
S(2)#3-K(2)-S(1)	122.60(12)	S(5)#2-K(2)-Y(1)#2	40.87(7)
S(7)#2-K(2)-S(5)#2	65.06(10)	S(2)-K(2)-Y(1)#2	83.00(9)

S(3)#12-K(2)-Y(1)#2	85.04(8)
P(2)#3-K(2)-Y(1)#2	117.90(9)
S(6)#3-K(2)-Y(1)#2	130.54(10)
S(4)#3-K(2)-Y(1)#2	132.15(9)
S(2)#6-K(2)-Y(1)#2	75.70(8)
S(7)#2-K(2)-K(2)#3	166.33(15)
S(2)#3-K(2)-K(2)#3	47.85(8)
S(1)-K(2)-K(2)#3	92.68(11)
S(5)#2-K(2)-K(2)#3	102.38(12)
S(2)-K(2)-K(2)#3	45.13(8)
S(3)#12-K(2)-K(2)#3	115.98(13)
P(2)#3-K(2)-K(2)#3	95.23(11)
S(6)#3-K(2)-K(2)#3	100.86(12)
S(4)#3-K(2)-K(2)#3	63.54(9)
S(2)#6-K(2)-K(2)#3	130.65(12)
Y(1)#2-K(2)-K(2)#3	126.15(11)
S(5)#6-P(1)-S(7)	106.2(2)
S(5)#6-P(1)-S(2)#2	111.7(2)
S(7)-P(1)-S(2)#2	110.4(2)
S(5)#6-P(1)-S(1)	116.0(2)
S(7)-P(1)-S(1)	106.4(2)
S(2)#2-P(1)-S(1)	106.1(2)
S(3)#5-P(2)-S(4)	115.7(2)
S(3)#5-P(2)-S(6)	116.8(2)
S(4)-P(2)-S(6)	107.6(2)
S(3)#5-P(2)-P(2)#5	104.4(2)
S(4)-P(2)-P(2)#5	105.4(2)
S(6)-P(2)-P(2)#5	105.8(2)
S(3)#5-P(2)-Y(1)	160.1(2)
S(4)-P(2)-Y(1)	55.91(12)
S(6)-P(2)-Y(1)	57.47(12)
P(2)#5-P(2)-Y(1)	95.4(2)
S(3)#5-P(2)-K(2)#3	71.89(15)
S(4)-P(2)-K(2)#3	79.5(2)
S(6)-P(2)-K(2)#3	73.56(15)
P(2)#5-P(2)-K(2)#3	175.0(2)
Y(1)-P(2)-K(2)#3	88.38(9)
S(3)#5-P(2)-K(1)#8	61.86(14)
S(4)-P(2)-K(1)#8	59.97(13)
S(6)-P(2)-K(1)#8	158.4(2)
P(2)#5-P(2)-K(1)#8	94.96(10)
Y(1)-P(2)-K(1)#8	115.53(10)
K(2)#3-P(2)-K(1)#8	86.31(10)
S(3)#5-P(2)-K(1)#5	62.03(14)
S(4)-P(2)-K(1)#5	159.2(2)
S(6)-P(2)-K(1)#5	61.25(13)
P(2)#5-P(2)-K(1)#5	94.88(10)
Y(1)-P(2)-K(1)#5	118.38(10)
K(2)#3-P(2)-K(1)#5	80.39(10)
K(1)#8-P(2)-K(1)#5	123.74(11)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1/2,y-1/2,-z+1/2 #2 -x+1/2,y+1/2,-z+1/2

#3 -x+1/2,-y+3/2,-z+1 #4 x,y-1,z #5 -x,y,-z+1/2

#6 x,y+1,z #7 x-1/2,-y+3/2,z-1/2 #8 -x,y+1,-z+1/2

#9 -x,-y+1,-z #10 -x,y-1,-z+1/2 #11 -x,-y,-z

#12 x+1/2,-y+3/2,z+1/2

Table D.4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $K_2Y(P_2S_6)_{1/2}(PS_4)$. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Y(1)	12(1)	12(1)	14(1)	0(1)	7(1)	0(1)
S(1)	16(2)	12(2)	9(2)	3(2)	6(2)	0(1)
S(2)	14(2)	21(2)	16(2)	0(2)	11(2)	-1(2)
S(3)	23(2)	18(2)	15(2)	-1(2)	13(2)	3(2)
S(4)	13(2)	9(2)	25(2)	-3(2)	11(2)	-3(1)
S(5)	13(2)	14(2)	21(2)	-1(2)	7(2)	1(2)
S(6)	16(2)	9(2)	19(2)	1(2)	8(2)	2(1)
S(7)	20(2)	8(2)	17(2)	2(2)	9(2)	-2(1)
K(1)	24(2)	15(2)	31(2)	3(2)	19(2)	2(1)
K(2)	27(2)	34(2)	21(2)	-3(2)	14(2)	-5(2)
P(1)	13(2)	7(2)	15(2)	-1(1)	8(2)	0(1)
P(2)	11(2)	10(2)	14(2)	-2(2)	6(2)	-4(2)

Table D.5. Crystal data and structure refinement for $K_2Y(P_2Se_6)_{1/2}(PSe_4)$.

Identification code	p1bar	
Empirical formula	$K_2Y(P_2Se_6)_{1/2}(PSe_4)$	
Formula weight	781.77	
Temperature	169(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 7.2394(4) Å	α= 73.337(2)°.
	b = 9.0101(6) Å	β= 74.208(2)°.
	c = 11.3480(7) Å	γ = 87.207(2)°.
Volume	682.01(7) $Å^3$	
Z	2	
Density (calculated)	3.807 Mg/m^3	
Absorption coefficient	23.750 mm^{-1}	
F(000)	690	
Crystal size	0.03 x 0.06 x 0.06 mm^3	
Theta range for data collection	1.95 to 28.27°.	
Index ranges	-7<=h<=9, -11<=k<=10, -14<=l<=14	
Reflections collected	4554	
Independent reflections	3141 [R(int) = 0.0562]	
Absorption correction	SADABS	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3141 / 0 / 109	
Goodness-of-fit on F^2	1.019	
Final R indices [I>2sigma(I)]	R1 = 0.0859, wR2 = 0.1921	
R indices (all data)	R1 = 0.1482, wR2 = 0.2349	
Largest diff. peak and hole	4.205 and -2.759 $e.Å^{-3}$	

Table D.6. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for $K_2Y(P_2Se_6)_{1/2}(PSe_4)$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Y(1)	4089(3)	6589(2)	7967(2)	13(1)
Se(1)	2869(3)	3819(2)	10564(2)	15(1)
Se(2)	5292(3)	7049(2)	4966(2)	16(1)
Se(3)	1335(3)	4925(2)	7235(2)	16(1)
Se(4)	6642(3)	4172(2)	7246(2)	15(1)
Se(5)	6578(3)	9419(2)	6995(2)	14(1)
Se(6)	1694(3)	7754(2)	9939(2)	16(1)
Se(7)	1758(3)	9381(2)	6918(2)	14(1)
K(1)	2995(7)	1523(5)	8735(5)	23(1)
K(2)	128(7)	7512(6)	4847(4)	23(1)
P(1)	1600(7)	5611(6)	11498(5)	12(1)
P(2)	5414(8)	9553(6)	4161(5)	14(1)

Table D.7. Bond lengths [Å] and angles [°] for $K_2Y(P_2Se_6)_{1/2}(PSe_4)$.

Y(1)-Se(6)	2.859(3)	K(2)-Se(2)#11	3.508(5)
Y(1)-Se(4)	2.938(3)	K(2)-Se(5)#5	3.510(5)
Y(1)-Se(5)	2.952(3)	K(2)-Se(5)#11	3.750(5)
Y(1)-Se(3)	2.970(3)	K(2)-Se(4)#11	3.891(5)
Y(1)-Se(1)#1	3.055(3)	K(2)-K(2)#12	4.448(10)
Y(1)-Se(7)	3.091(3)	K(2)-K(2)#7	4.587(10)
Y(1)-Se(2)	3.184(3)	K(2)-K(1)#12	5.017(7)
Y(1)-Se(1)	3.206(3)	P(1)-Se(3)#4	2.203(5)
Y(1)-K(1)	4.463(5)	P(1)-Se(4)#1	2.205(6)
Se(1)-P(1)	2.210(6)	P(2)-Se(7)#5	2.183(5)
Se(1)-Y(1)#1	3.055(3)	P(2)-P(2)#5	2.201(11)
Se(1)-K(1)	3.306(5)	P(2)-Se(5)#5	2.205(6)
Se(2)-P(2)	2.174(6)	P(2)-K(1)#3	3.567(7)
Se(2)-K(2)#2	3.508(5)		
Se(2)-K(2)	3.776(5)	Se(6)-Y(1)-Se(4)	148.66(9)
Se(2)-K(1)#3	3.880(5)	Se(6)-Y(1)-Se(5)	90.80(8)
Se(3)-P(1)#4	2.203(5)	Se(4)-Y(1)-Se(5)	104.34(8)
Se(3)-K(2)	3.318(5)	Se(6)-Y(1)-Se(3)	103.50(8)
Se(3)-K(1)	3.391(5)	Se(4)-Y(1)-Se(3)	81.87(7)
Se(4)-P(1)#1	2.205(6)	Se(5)-Y(1)-Se(3)	141.07(9)
Se(4)-K(1)	3.376(5)	Se(6)-Y(1)-Se(1)#1	86.79(8)
Se(4)-K(2)#3	3.479(5)	Se(4)-Y(1)-Se(1)#1	72.95(7)
Se(4)-K(2)#2	3.891(5)	Se(5)-Y(1)-Se(1)#1	71.08(7)
Se(5)-P(2)#5	2.205(6)	Se(3)-Y(1)-Se(1)#1	144.44(9)
Se(5)-K(2)#5	3.510(5)	Se(6)-Y(1)-Se(7)	67.41(7)
Se(5)-K(1)#6	3.620(5)	Se(4)-Y(1)-Se(7)	143.35(9)
Se(5)-K(2)#2	3.750(5)	Se(5)-Y(1)-Se(7)	71.12(7)
Se(6)-P(1)	2.203(5)	Se(3)-Y(1)-Se(7)	81.22(8)
Se(6)-K(1)#6	3.352(5)	Se(1)#1-Y(1)-Se(7)	133.30(8)
Se(6)-K(1)#4	3.432(6)	Se(6)-Y(1)-Se(2)	143.39(9)
Se(7)-P(2)#5	2.183(5)	Se(4)-Y(1)-Se(2)	67.63(7)
Se(7)-K(2)#7	3.408(5)	Se(5)-Y(1)-Se(2)	77.89(7)
Se(7)-K(1)#6	3.498(5)	Se(3)-Y(1)-Se(2)	69.03(7)
Se(7)-K(2)	3.705(5)	Se(1)#1-Y(1)-Se(2)	120.75(8)
K(1)-Se(6)#8	3.352(5)	Se(7)-Y(1)-Se(2)	75.99(7)
K(1)-Se(6)#4	3.432(6)	Se(6)-Y(1)-Se(1)	70.71(7)
K(1)-Se(7)#8	3.498(5)	Se(4)-Y(1)-Se(1)	79.68(7)
K(1)-P(2)#3	3.567(7)	Se(5)-Y(1)-Se(1)	136.65(8)
K(1)-Se(5)#8	3.620(5)	Se(3)-Y(1)-Se(1)	82.19(7)
K(1)-Se(2)#3	3.880(5)	Se(1)#1-Y(1)-Se(1)	69.10(7)
K(1)-K(1)#9	4.842(10)	Se(7)-Y(1)-Se(1)	129.39(8)
K(1)-K(1)#10	4.944(9)	Se(2)-Y(1)-Se(1)	138.60(8)
K(2)-Se(7)#7	3.408(5)	Se(6)-Y(1)-K(1)	111.52(9)
K(2)-Se(4)#3	3.479(5)	Se(4)-Y(1)-K(1)	49.14(8)

Se(5)-Y(1)-K(1)	153.38(10)	K(2)#5-Se(5)-K(2)#2	78.29(13)
Se(3)-Y(1)-K(1)	49.43(8)	K(1)#6-Se(5)-K(2)#2	173.25(12)
Se(1)#1-Y(1)-K(1)	95.05(9)	P(1)-Se(6)-Y(1)	95.7(2)
Se(7)-Y(1)-K(1)	129.96(9)	P(1)-Se(6)-K(1)#6	146.8(2)
Se(2)-Y(1)-K(1)	91.03(8)	Y(1)-Se(6)-K(1)#6	99.74(11)
Se(1)-Y(1)-K(1)	47.68(8)	P(1)-Se(6)-K(1)#4	91.6(2)
P(1)-Se(1)-Y(1)#1	88.1(2)	Y(1)-Se(6)-K(1)#4	142.69(12)
P(1)-Se(1)-Y(1)	86.44(15)	K(1)#6-Se(6)-K(1)#4	93.57(12)
Y(1)#1-Se(1)-Y(1)	110.90(7)	P(2)#5-Se(7)-Y(1)	83.9(2)
P(1)-Se(1)-K(1)	154.0(2)	P(2)#5-Se(7)-K(2)#7	87.2(2)
Y(1)#1-Se(1)-K(1)	117.69(12)	Y(1)-Se(7)-K(2)#7	167.77(11)
Y(1)-Se(1)-K(1)	86.52(10)	P(2)#5-Se(7)-K(1)#6	73.8(2)
P(2)-Se(2)-Y(1)	103.4(2)	Y(1)-Se(7)-K(1)#6	92.29(11)
P(2)-Se(2)-K(2)#2	84.8(2)	K(2)#7-Se(7)-K(1)#6	93.18(13)
Y(1)-Se(2)-K(2)#2	90.36(10)	P(2)#5-Se(7)-K(2)	106.9(2)
P(2)-Se(2)-K(2)	82.6(2)	Y(1)-Se(7)-K(2)	94.45(10)
Y(1)-Se(2)-K(2)	91.58(9)	K(2)#7-Se(7)-K(2)	80.19(13)
K(2)#2-Se(2)-K(2)	167.4(2)	K(1)#6-Se(7)-K(2)	173.26(13)
P(2)-Se(2)-K(1)#3	65.3(2)	Se(1)-K(1)-Se(6)#8	122.5(2)
Y(1)-Se(2)-K(1)#3	168.23(10)	Se(1)-K(1)-Se(4)	72.29(10)
K(2)#2-Se(2)-K(1)#3	85.39(11)	Se(6)#8-K(1)-Se(4)	146.6(2)
K(2)-Se(2)-K(1)#3	90.25(11)	Se(1)-K(1)-Se(3)	74.69(11)
P(1)#4-Se(3)-Y(1)	118.9(2)	Se(6)#8-K(1)-Se(3)	139.9(2)
P(1)#4-Se(3)-K(2)	96.5(2)	Se(4)-K(1)-Se(3)	69.80(10)
Y(1)-Se(3)-K(2)	105.38(11)	Se(1)-K(1)-Se(6)#4	70.64(11)
P(1)#4-Se(3)-K(1)	92.7(2)	Se(6)#8-K(1)-Se(6)#4	86.43(12)
Y(1)-Se(3)-K(1)	88.86(10)	Se(4)-K(1)-Se(6)#4	126.6(2)
K(2)-Se(3)-K(1)	156.41(14)	Se(3)-K(1)-Se(6)#4	64.26(10)
P(1)#1-Se(4)-Y(1)	91.2(2)	Se(1)-K(1)-Se(7)#8	163.6(2)
P(1)#1-Se(4)-K(1)	113.0(2)	Se(6)#8-K(1)-Se(7)#8	57.69(9)
Y(1)-Se(4)-K(1)	89.68(11)	Se(4)-K(1)-Se(7)#8	117.13(15)
P(1)#1-Se(4)-K(2)#3	100.9(2)	Se(3)-K(1)-Se(7)#8	95.48(14)
Y(1)-Se(4)-K(2)#3	155.55(11)	Se(6)#4-K(1)-Se(7)#8	93.39(13)
K(1)-Se(4)-K(2)#3	104.65(13)	Se(1)-K(1)-P(2)#3	154.0(2)
P(1)#1-Se(4)-K(2)#2	81.7(2)	Se(6)#8-K(1)-P(2)#3	82.00(13)
Y(1)-Se(4)-K(2)#2	87.01(10)	Se(4)-K(1)-P(2)#3	82.27(14)
K(1)-Se(4)-K(2)#2	165.03(13)	Se(3)-K(1)-P(2)#3	91.9(2)
K(2)#3-Se(4)-K(2)#2	74.01(13)	Se(6)#4-K(1)-P(2)#3	123.8(2)
P(2)#5-Se(5)-Y(1)	86.92(15)	Se(7)#8-K(1)-P(2)#3	35.98(10)
P(2)#5-Se(5)-K(2)#5	88.9(2)	Se(1)-K(1)-Se(5)#8	137.1(2)
Y(1)-Se(5)-K(2)#5	165.88(11)	Se(6)#8-K(1)-Se(5)#8	72.71(10)
P(2)#5-Se(5)-K(1)#6	70.8(2)	Se(4)-K(1)-Se(5)#8	77.37(11)
Y(1)-Se(5)-K(1)#6	92.24(10)	Se(3)-K(1)-Se(5)#8	121.62(15)
K(2)#5-Se(5)-K(1)#6	99.11(12)	Se(6)#4-K(1)-Se(5)#8	151.49(15)
P(2)#5-Se(5)-K(2)#2	102.8(2)	Se(7)#8-K(1)-Se(5)#8	59.18(9)
Y(1)-Se(5)-K(2)#2	89.50(10)	P(2)#3-K(1)-Se(5)#8	35.72(11)

Se(1)-K(1)-Se(2)#3	122.90(14)	Se(4)#3-K(2)-Se(5)#5	77.53(11)
Se(6)#8-K(1)-Se(2)#3	114.57(13)	Se(2)#11-K(2)-Se(5)#5	129.74(15)
Se(4)-K(1)-Se(2)#3	59.40(9)	Se(3)-K(2)-Se(7)	68.11(10)
Se(3)-K(1)-Se(2)#3	61.93(9)	Se(7)#7-K(2)-Se(7)	99.81(13)
Se(6)#4-K(1)-Se(2)#3	115.38(15)	Se(4)#3-K(2)-Se(7)	121.36(14)
Se(7)#8-K(1)-Se(2)#3	60.01(9)	Se(2)#11-K(2)-Se(7)	123.85(15)
P(2)#3-K(1)-Se(2)#3	33.62(10)	Se(5)#5-K(2)-Se(7)	69.18(10)
Se(5)#8-K(1)-Se(2)#3	59.90(9)	Se(3)-K(2)-Se(5)#11	94.08(12)
Se(1)-K(1)-Y(1)	45.80(7)	Se(7)#7-K(2)-Se(5)#11	69.68(10)
Se(6)#8-K(1)-Y(1)	167.83(15)	Se(4)#3-K(2)-Se(5)#11	177.8(2)
Se(4)-K(1)-Y(1)	41.18(7)	Se(2)#11-K(2)-Se(5)#11	64.18(9)
Se(3)-K(1)-Y(1)	41.71(7)	Se(5)#5-K(2)-Se(5)#11	101.71(13)
Se(6)#4-K(1)-Y(1)	85.59(11)	Se(7)-K(2)-Se(5)#11	59.97(9)
Se(7)#8-K(1)-Y(1)	131.99(14)	Se(3)-K(2)-Se(2)	58.55(9)
P(2)#3-K(1)-Y(1)	110.10(14)	Se(7)#7-K(2)-Se(2)	127.01(14)
Se(5)#8-K(1)-Y(1)	117.77(12)	Se(4)#3-K(2)-Se(2)	59.72(9)
Se(2)#3-K(1)-Y(1)	77.24(9)	Se(2)#11-K(2)-Se(2)	167.4(2)
Se(1)-K(1)-K(1)#9	82.98(14)	Se(5)#5-K(2)-Se(2)	61.85(9)
Se(6)#8-K(1)-K(1)#9	65.91(11)	Se(7)-K(2)-Se(2)	62.18(9)
Se(4)-K(1)-K(1)#9	89.05(15)	Se(5)#11-K(2)-Se(2)	121.83(14)
Se(3)-K(1)-K(1)#9	152.9(2)	Se(3)-K(2)-Se(4)#11	57.30(8)
Se(6)#4-K(1)-K(1)#9	122.3(2)	Se(7)#7-K(2)-Se(4)#11	118.36(14)
Se(7)#8-K(1)-K(1)#9	109.6(2)	Se(4)#3-K(2)-Se(4)#11	105.99(13)
P(2)#3-K(1)-K(1)#9	102.1(2)	Se(2)#11-K(2)-Se(4)#11	54.65(8)
Se(5)#8-K(1)-K(1)#9	66.78(12)	Se(5)#5-K(2)-Se(4)#11	173.0(2)
Se(2)#3-K(1)-K(1)#9	122.0(2)	Se(7)-K(2)-Se(4)#11	103.96(12)
Y(1)-K(1)-K(1)#9	111.21(15)	Se(5)#11-K(2)-Se(4)#11	74.99(10)
Se(1)-K(1)-K(1)#10	97.7(2)	Se(2)-K(2)-Se(4)#11	114.41(13)
Se(6)#8-K(1)-K(1)#10	43.85(8)	Se(3)-K(2)-K(2)#12	60.11(11)
Se(4)-K(1)-K(1)#10	168.5(2)	Se(7)#7-K(2)-K(2)#12	131.2(2)
Se(3)-K(1)-K(1)#10	102.5(2)	Se(4)#3-K(2)-K(2)#12	57.23(11)
Se(6)#4-K(1)-K(1)#10	42.58(9)	Se(2)#11-K(2)-K(2)#12	79.64(14)
Se(7)#8-K(1)-K(1)#10	71.26(11)	Se(5)#5-K(2)-K(2)#12	134.4(2)
P(2)#3-K(1)-K(1)#10	107.0(2)	Se(7)-K(2)-K(2)#12	128.2(2)
Se(5)#8-K(1)-K(1)#10	114.1(2)	Se(5)#11-K(2)-K(2)#12	123.7(2)
Se(2)#3-K(1)-K(1)#10	125.4(2)	Se(2)-K(2)-K(2)#12	88.12(15)
Y(1)-K(1)-K(1)#10	127.5(2)	Se(4)#11-K(2)-K(2)#12	48.76(10)
K(1)#9-K(1)-K(1)#10	95.4(2)	Se(3)-K(2)-K(2)#7	114.3(2)
Se(3)-K(2)-Se(7)#7	163.5(2)	Se(7)#7-K(2)-K(2)#7	52.75(10)
Se(3)-K(2)-Se(4)#3	88.11(13)	Se(4)#3-K(2)-K(2)#7	130.7(2)
Se(7)#7-K(2)-Se(4)#3	108.14(13)	Se(2)#11-K(2)-K(2)#7	97.6(2)
Se(3)-K(2)-Se(2)#11	111.70(14)	Se(5)#5-K(2)-K(2)#7	53.18(10)
Se(7)#7-K(2)-Se(2)#11	64.76(10)	Se(7)-K(2)-K(2)#7	47.07(10)
Se(4)#3-K(2)-Se(2)#11	114.65(14)	Se(5)#11-K(2)-K(2)#7	48.53(10)
Se(3)-K(2)-Se(5)#5	117.47(15)	Se(2)-K(2)-K(2)#7	94.0(2)
Se(7)#7-K(2)-Se(5)#5	65.16(10)	Se(4)#11-K(2)-K(2)#7	123.2(2)

K(2)#12-K(2)-K(2)#7	171.5(2)
Se(3)-K(2)-K(1)#12	147.03(15)
Se(7)#7-K(2)-K(1)#12	44.11(8)
Se(4)#3-K(2)-K(1)#12	78.89(11)
Se(2)#11-K(2)-K(1)#12	50.44(9)
Se(5)#5-K(2)-K(1)#12	89.32(11)
Se(7)-K(2)-K(1)#12	143.91(14)
Se(5)#11-K(2)-K(1)#12	99.03(12)
Se(2)-K(2)-K(1)#12	132.75(13)
Se(4)#11-K(2)-K(1)#12	97.21(12)
K(2)#12-K(2)-K(1)#12	87.66(15)
K(2)#7-K(2)-K(1)#12	96.85(15)
Se(6)-P(1)-Se(3)#4	110.9(2)
Se(6)-P(1)-Se(4)#1	112.2(2)
Se(3)#4-P(1)-Se(4)#1	104.8(2)
Se(6)-P(1)-Se(1)	105.8(2)
Se(3)#4-P(1)-Se(1)	115.5(2)
Se(4)#1-P(1)-Se(1)	107.7(2)
Se(2)-P(2)-Se(7)#5	116.5(3)
Se(2)-P(2)-P(2)#5	104.2(3)
Se(7)#5-P(2)-P(2)#5	104.9(3)
Se(2)-P(2)-Se(5)#5	117.9(2)
Se(7)#5-P(2)-Se(5)#5	106.5(2)
P(2)#5-P(2)-Se(5)#5	105.6(4)
Se(2)-P(2)-K(1)#3	81.1(2)
Se(7)#5-P(2)-K(1)#3	70.3(2)
P(2)#5-P(2)-K(1)#3	174.2(4)
Se(5)#5-P(2)-K(1)#3	73.4(2)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+2 #2 x+1,y,z #3 -x+1,-y+1,-z+1

#4 -x,-y+1,-z+2 #5 -x+1,-y+2,-z+1 #6 x,y+1,z

#7 -x,-y+2,-z+1 #8 x,y-1,z #9 -x+1,-y,-z+2

#10 -x,-y,-z+2 #11 x-1,y,z #12 -x,-y+1,-z+1

Table D.8. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $K_2Y(P_2Se_6)_{1/2}(PSe_4)$. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Y(1)	14(1)	11(1)	14(1)	-7(1)	-2(1)	0(1)
Se(1)	19(1)	14(1)	17(1)	-11(1)	-5(1)	1(1)
Se(2)	23(1)	10(1)	12(1)	-6(1)	1(1)	-1(1)
Se(3)	13(1)	20(1)	13(1)	-7(1)	0(1)	-1(1)
Se(4)	15(1)	19(1)	16(1)	-11(1)	-5(1)	2(1)
Se(5)	15(1)	13(1)	17(1)	-5(1)	-5(1)	-1(1)
Se(6)	20(1)	12(1)	12(1)	-4(1)	1(1)	1(1)
Se(7)	13(1)	14(1)	13(1)	-4(1)	0(1)	1(1)
K(1)	30(3)	16(2)	27(3)	-13(2)	-5(2)	-1(2)
K(2)	25(3)	23(3)	17(2)	-3(2)	-4(2)	5(2)
P(1)	12(2)	13(3)	11(2)	-4(2)	-1(2)	0(2)
P(2)	17(3)	11(2)	12(3)	-1(2)	-3(2)	-3(2)

Table D.9. Crystal data and structure refinement for $Cs_2Y(P_2S_6)_{1/2}(PS_4)$.

Identification code	p21n	
Empirical formula	$Cs_2Y(P_2S_6)_{1/2}(PS_4)$	
Formula weight	641.09	
Temperature	171(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 9.7033(10) Å	α= 90°.
	b = 6.8543(7) Å	β= 97.492(2)°.
	c = 19.5043(19) Å	γ = 90°.
Volume	1286.1(2) $Å^3$	
Z	4	
Density (calculated)	3.311 Mg/m^3	
Absorption coefficient	11.446 mm^{-1}	
F(000)	1164	
Crystal size	0.06 x 0.06 x 0.10 mm^3	
Theta range for data collection	2.11 to 28.31°.	
Index ranges	-12<=h<=12, -9<=k<=3, -25<=l<=25	
Reflections collected	8380	
Independent reflections	3151 [R(int) = 0.0628]	
Completeness to theta = 28.31°	98.7 %	
Absorption correction	SADABS	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3151 / 0 / 109	
Goodness-of-fit on F^2	0.627	
Final R indices [I>2sigma(I)]	R1 = 0.0327, wR2 = 0.0520	
R indices (all data)	R1 = 0.1112, wR2 = 0.0601	
Largest diff. peak and hole	1.469 and -1.651 $e.Å^{-3}$	

Table D.10. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for $Cs_2Y(P_2S_6)_{1/2}(PS_4)$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cs(1)	7645(1)	4982(1)	287(1)	17(1)
Cs(2)	-1416(1)	50(1)	2064(1)	22(1)
Y(1)	3119(1)	9816(2)	1545(1)	12(1)
S(1)	2402(2)	9981(5)	-260(1)	19(1)
S(2)	3056(2)	5776(3)	2234(1)	15(1)
S(3)	5231(2)	10066(5)	2667(1)	15(1)
S(4)	1109(3)	2711(4)	1077(2)	16(1)
S(5)	5101(3)	7566(4)	1005(2)	17(1)
S(6)	5052(3)	2336(4)	1026(2)	16(1)
S(7)	818(3)	7540(4)	1010(2)	14(1)
P(1)	1198(2)	5196(5)	1649(1)	12(1)
P(2)	5672(2)	-8(5)	505(1)	14(1)

Table D.11. Bond lengths [Å] and angles [°] for $Cs_2Y(P_2S_6)_{1/2}(PS_4)$.

Cs(1)-S(1)#1	3.403(3)	S(4)-P(1)	2.031(4)
Cs(1)-S(4)#1	3.447(3)	S(4)-Y(1)#8	2.848(3)
Cs(1)-S(1)#2	3.453(3)	S(4)-Cs(1)#1	3.447(3)
Cs(1)-S(5)	3.477(3)	S(4)-Cs(1)#10	3.839(3)
Cs(1)-S(7)#1	3.550(3)	S(5)-P(2)#4	2.040(4)
Cs(1)-S(6)	3.556(3)	S(5)-Cs(1)#1	3.840(3)
Cs(1)-S(7)#3	3.662(3)	S(5)-Cs(2)#14	4.096(3)
Cs(1)-S(5)#1	3.840(3)	S(6)-P(2)	2.033(4)
Cs(1)-S(4)#3	3.839(3)	S(6)-Y(1)#8	2.832(3)
Cs(1)-S(6)#1	3.878(3)	S(6)-Cs(1)#1	3.878(3)
Cs(1)-P(2)	3.969(3)	S(6)-Cs(2)#3	4.062(3)
Cs(1)-P(2)#4	3.982(3)	S(7)-P(1)	2.037(4)
Cs(2)-S(2)#5	3.404(2)	S(7)-Cs(1)#1	3.550(3)
Cs(2)-S(1)#6	3.524(2)	S(7)-Cs(2)#4	3.612(3)
Cs(2)-S(3)#7	3.6011(18)	S(7)-Cs(1)#10	3.662(3)
Cs(2)-S(7)#8	3.612(3)	P(1)-S(3)#5	2.048(3)
Cs(2)-S(3)#9	3.621(3)	P(1)-Cs(1)#10	4.071(2)
Cs(2)-S(3)#5	3.641(3)	P(1)-Cs(1)#1	4.078(2)
Cs(2)-S(4)	3.777(3)	P(2)-S(1)#1	1.989(3)
Cs(2)-P(2)#10	3.872(2)	P(2)-S(5)#8	2.040(4)
Cs(2)-S(6)#10	4.062(3)	P(2)-P(2)#16	2.217(4)
Cs(2)-S(5)#7	4.096(3)	P(2)-Cs(2)#3	3.872(2)
Cs(2)-Cs(2)#11	4.4716(7)	P(2)-Cs(1)#8	3.982(3)
Cs(2)-Cs(2)#12	4.4716(7)		
Y(1)-S(5)	2.777(3)	S(1)#1-Cs(1)-S(4)#1	116.88(6)
Y(1)-S(3)	2.8016(19)	S(1)#1-Cs(1)-S(1)#2	177.83(7)
Y(1)-S(7)	2.810(3)	S(4)#1-Cs(1)-S(1)#2	62.29(6)
Y(1)-S(6)#4	2.832(3)	S(1)#1-Cs(1)-S(5)	120.44(6)
Y(1)-S(4)#4	2.848(3)	S(4)#1-Cs(1)-S(5)	114.58(7)
Y(1)-S(2)#13	2.850(2)	S(1)#2-Cs(1)-S(5)	59.21(6)
Y(1)-S(2)	3.082(2)	S(1)#1-Cs(1)-S(7)#1	60.54(6)
Y(1)-Cs(2)#4	4.6451(10)	S(4)#1-Cs(1)-S(7)#1	56.69(5)
Y(1)-Cs(1)#1	4.8411(12)	S(1)#2-Cs(1)-S(7)#1	118.83(6)
S(1)-P(2)#1	1.989(3)	S(5)-Cs(1)-S(7)#1	157.11(7)
S(1)-Cs(1)#1	3.403(3)	S(1)#1-Cs(1)-S(6)	59.16(6)
S(1)-Cs(1)#2	3.453(3)	S(4)#1-Cs(1)-S(6)	152.21(7)
S(1)-Cs(2)#6	3.524(2)	S(1)#2-Cs(1)-S(6)	120.49(6)
S(2)-P(1)	2.042(3)	S(5)-Cs(1)-S(6)	61.29(4)
S(2)-Y(1)#5	2.850(2)	S(7)#1-Cs(1)-S(6)	115.20(6)
S(2)-Cs(2)#13	3.404(2)	S(1)#1-Cs(1)-S(7)#3	119.59(6)
S(3)-P(1)#13	2.048(3)	S(4)#1-Cs(1)-S(7)#3	73.50(6)
S(3)-Cs(2)#14	3.6011(18)	S(1)#2-Cs(1)-S(7)#3	62.34(5)
S(3)-Cs(2)#15	3.621(3)	S(5)-Cs(1)-S(7)#3	101.91(7)
S(3)-Cs(2)#13	3.641(3)	S(7)#1-Cs(1)-S(7)#3	95.60(6)

S(6)-Cs(1)-S(7)#3	133.79(7)	S(2)#5-Cs(2)-S(1)#6	121.58(5)
S(1)#1-Cs(1)-S(5)#1	61.87(5)	S(2)#5-Cs(2)-S(3)#7	136.65(5)
S(4)#1-Cs(1)-S(5)#1	89.16(7)	S(1)#6-Cs(2)-S(3)#7	100.75(4)
S(1)#2-Cs(1)-S(5)#1	115.98(5)	S(2)#5-Cs(2)-S(7)#8	71.60(6)
S(5)-Cs(1)-S(5)#1	91.56(7)	S(1)#6-Cs(2)-S(7)#8	62.20(6)
S(7)#1-Cs(1)-S(5)#1	68.34(6)	S(3)#7-Cs(2)-S(7)#8	145.28(7)
S(6)-Cs(1)-S(5)#1	64.31(5)	S(2)#5-Cs(2)-S(3)#9	79.07(5)
S(7)#3-Cs(1)-S(5)#1	161.28(6)	S(1)#6-Cs(2)-S(3)#9	100.29(6)
S(1)#1-Cs(1)-S(4)#3	67.06(5)	S(3)#7-Cs(2)-S(3)#9	103.82(7)
S(4)#1-Cs(1)-S(4)#3	96.85(6)	S(7)#8-Cs(2)-S(3)#9	55.27(5)
S(1)#2-Cs(1)-S(4)#3	114.87(5)	S(2)#5-Cs(2)-S(3)#5	62.36(5)
S(5)-Cs(1)-S(4)#3	132.46(7)	S(1)#6-Cs(2)-S(3)#5	100.90(6)
S(7)#1-Cs(1)-S(4)#3	70.22(6)	S(3)#7-Cs(2)-S(3)#5	103.42(7)
S(6)-Cs(1)-S(4)#3	105.03(7)	S(7)#8-Cs(2)-S(3)#5	109.28(5)
S(7)#3-Cs(1)-S(4)#3	52.53(5)	S(3)#9-Cs(2)-S(3)#5	141.41(5)
S(5)#1-Cs(1)-S(4)#3	125.12(6)	S(2)#5-Cs(2)-S(4)	58.91(6)
S(1)#1-Cs(1)-S(6)#1	117.21(5)	S(1)#6-Cs(2)-S(4)	66.66(6)
S(4)#1-Cs(1)-S(6)#1	63.08(6)	S(3)#7-Cs(2)-S(4)	147.00(7)
S(1)#2-Cs(1)-S(6)#1	60.63(5)	S(7)#8-Cs(2)-S(4)	57.50(5)
S(5)-Cs(1)-S(6)#1	64.58(5)	S(3)#9-Cs(2)-S(4)	108.34(5)
S(7)#1-Cs(1)-S(6)#1	94.03(6)	S(3)#5-Cs(2)-S(4)	53.40(5)
S(6)-Cs(1)-S(6)#1	93.26(6)	S(2)#5-Cs(2)-P(2)#10	151.65(5)
S(7)#3-Cs(1)-S(6)#1	119.23(6)	S(1)#6-Cs(2)-P(2)#10	30.74(4)
S(5)#1-Cs(1)-S(6)#1	55.36(4)	S(3)#7-Cs(2)-P(2)#10	70.01(4)
S(4)#3-Cs(1)-S(6)#1	159.60(6)	S(7)#8-Cs(2)-P(2)#10	88.78(6)
S(1)#1-Cs(1)-P(2)	30.06(5)	S(3)#9-Cs(2)-P(2)#10	106.83(6)
S(4)#1-Cs(1)-P(2)	134.47(6)	S(3)#5-Cs(2)-P(2)#10	107.89(6)
S(1)#2-Cs(1)-P(2)	149.02(5)	S(4)-Cs(2)-P(2)#10	93.45(6)
S(5)-Cs(1)-P(2)	91.03(6)	S(2)#5-Cs(2)-S(6)#10	147.78(6)
S(7)#1-Cs(1)-P(2)	84.85(5)	S(1)#6-Cs(2)-S(6)#10	53.32(6)
S(6)-Cs(1)-P(2)	30.72(5)	S(3)#7-Cs(2)-S(6)#10	54.68(6)
S(7)#3-Cs(1)-P(2)	139.85(5)	S(7)#8-Cs(2)-S(6)#10	115.45(6)
S(5)#1-Cs(1)-P(2)	51.34(5)	S(3)#9-Cs(2)-S(6)#10	131.88(5)
S(4)#3-Cs(1)-P(2)	90.97(5)	S(3)#5-Cs(2)-S(6)#10	86.43(5)
S(6)#1-Cs(1)-P(2)	100.70(5)	S(4)-Cs(2)-S(6)#10	96.94(6)
S(1)#1-Cs(1)-P(2)#4	149.12(5)	P(2)#10-Cs(2)-S(6)#10	29.57(6)
S(4)#1-Cs(1)-P(2)#4	84.77(6)	S(2)#5-Cs(2)-S(5)#7	161.42(6)
S(1)#2-Cs(1)-P(2)#4	29.96(5)	S(1)#6-Cs(2)-S(5)#7	52.75(6)
S(5)-Cs(1)-P(2)#4	30.81(6)	S(3)#7-Cs(2)-S(5)#7	56.25(6)
S(7)#1-Cs(1)-P(2)#4	138.49(5)	S(7)#8-Cs(2)-S(5)#7	91.81(6)
S(6)-Cs(1)-P(2)#4	91.20(6)	S(3)#9-Cs(2)-S(5)#7	84.63(5)
S(7)#3-Cs(1)-P(2)#4	86.42(6)	S(3)#5-Cs(2)-S(5)#7	133.59(5)
S(5)#1-Cs(1)-P(2)#4	99.21(5)	S(4)-Cs(2)-S(5)#7	119.41(6)
S(4)#3-Cs(1)-P(2)#4	135.62(5)	P(2)#10-Cs(2)-S(5)#7	29.50(6)
S(6)#1-Cs(1)-P(2)#4	50.88(5)	S(6)#10-Cs(2)-S(5)#7	47.27(4)
P(2)-Cs(1)-P(2)#4	119.09(5)	S(2)#5-Cs(2)-Cs(2)#11	115.64(4)

S(1)#6-Cs(2)-Cs(2)#11	107.14(5)
S(3)#7-Cs(2)-Cs(2)#11	52.28(5)
S(7)#8-Cs(2)-Cs(2)#11	101.44(4)
S(3)#9-Cs(2)-Cs(2)#11	51.55(3)
S(3)#5-Cs(2)-Cs(2)#11	145.52(3)
S(4)-Cs(2)-Cs(2)#11	158.84(4)
P(2)#10-Cs(2)-Cs(2)#11	87.66(5)
S(6)#10-Cs(2)-Cs(2)#11	94.40(4)
S(5)#7-Cs(2)-Cs(2)#11	58.32(4)
S(2)#5-Cs(2)-Cs(2)#12	102.04(4)
S(1)#6-Cs(2)-Cs(2)#12	107.71(5)
S(3)#7-Cs(2)-Cs(2)#12	51.95(5)
S(7)#8-Cs(2)-Cs(2)#12	158.20(5)
S(3)#9-Cs(2)-Cs(2)#12	145.52(3)
S(3)#5-Cs(2)-Cs(2)#12	51.47(3)
S(4)-Cs(2)-Cs(2)#12	101.08(4)
P(2)#10-Cs(2)-Cs(2)#12	88.56(4)
S(6)#10-Cs(2)-Cs(2)#12	59.04(4)
S(5)#7-Cs(2)-Cs(2)#12	96.44(4)
Cs(2)#11-Cs(2)-Cs(2)#12	100.07(2)
S(5)-Y(1)-S(3)	81.85(9)
S(5)-Y(1)-S(7)	96.16(9)
S(3)-Y(1)-S(7)	142.05(9)
S(5)-Y(1)-S(6)#4	71.31(6)
S(3)-Y(1)-S(6)#4	77.93(8)
S(7)-Y(1)-S(6)#4	137.49(9)
S(5)-Y(1)-S(4)#4	138.14(9)
S(3)-Y(1)-S(4)#4	127.44(9)
S(7)-Y(1)-S(4)#4	77.89(7)
S(6)#4-Y(1)-S(4)#4	85.32(8)
S(5)-Y(1)-S(2)#13	144.85(9)
S(3)-Y(1)-S(2)#13	70.37(6)
S(7)-Y(1)-S(2)#13	93.05(8)
S(6)#4-Y(1)-S(2)#13	120.90(8)
S(4)#4-Y(1)-S(2)#13	76.97(8)
S(5)-Y(1)-S(2)	73.78(8)
S(3)-Y(1)-S(2)	76.61(8)
S(7)-Y(1)-S(2)	66.61(7)
S(6)#4-Y(1)-S(2)	139.08(8)
S(4)#4-Y(1)-S(2)	135.55(8)
S(2)#13-Y(1)-S(2)	79.05(4)
S(5)-Y(1)-Cs(2)#4	145.53(7)
S(3)-Y(1)-Cs(2)#4	116.39(4)
S(7)-Y(1)-Cs(2)#4	51.00(6)
S(6)#4-Y(1)-Cs(2)#4	138.34(7)
S(4)#4-Y(1)-Cs(2)#4	54.34(6)
S(2)#13-Y(1)-Cs(2)#4	46.84(5)
S(2)-Y(1)-Cs(2)#4	82.10(4)
S(5)-Y(1)-Cs(1)#1	52.42(7)
S(3)-Y(1)-Cs(1)#1	130.11(7)
S(7)-Y(1)-Cs(1)#1	46.49(6)
S(6)#4-Y(1)-Cs(1)#1	101.27(6)
S(4)#4-Y(1)-Cs(1)#1	101.81(6)
S(2)#13-Y(1)-Cs(1)#1	137.28(5)
S(2)-Y(1)-Cs(1)#1	72.64(5)
Cs(2)#4-Y(1)-Cs(1)#1	97.251(19)
P(2)#1-S(1)-Cs(1)#1	90.95(13)
P(2)#1-S(1)-Cs(1)#2	89.91(13)
Cs(1)#1-S(1)-Cs(1)#2	177.83(7)
P(2)#1-S(1)-Cs(2)#6	84.35(8)
Cs(1)#1-S(1)-Cs(2)#6	88.69(6)
Cs(1)#2-S(1)-Cs(2)#6	89.41(6)
P(1)-S(2)-Y(1)#5	90.12(9)
P(1)-S(2)-Y(1)	89.88(11)
Y(1)#5-S(2)-Y(1)	127.24(8)
P(1)-S(2)-Cs(2)#13	157.71(13)
Y(1)#5-S(2)-Cs(2)#13	95.53(6)
Y(1)-S(2)-Cs(2)#13	103.54(6)
P(1)#13-S(3)-Y(1)	91.36(8)
P(1)#13-S(3)-Cs(2)#14	158.45(10)
Y(1)-S(3)-Cs(2)#14	110.17(5)
P(1)#13-S(3)-Cs(2)#15	95.38(13)
Y(1)-S(3)-Cs(2)#15	110.91(9)
Cs(2)#14-S(3)-Cs(2)#15	76.51(5)
P(1)#13-S(3)-Cs(2)#13	100.08(13)
Y(1)-S(3)-Cs(2)#13	103.87(9)
Cs(2)#14-S(3)-Cs(2)#13	76.26(5)
Cs(2)#15-S(3)-Cs(2)#13	141.41(5)
P(1)-S(4)-Y(1)#8	115.50(13)
P(1)-S(4)-Cs(1)#1	92.56(12)
Y(1)#8-S(4)-Cs(1)#1	105.80(9)
P(1)-S(4)-Cs(2)	96.29(12)
Y(1)#8-S(4)-Cs(2)	87.88(7)
Cs(1)#1-S(4)-Cs(2)	158.60(9)
P(1)-S(4)-Cs(1)#10	81.54(10)
Y(1)#8-S(4)-Cs(1)#10	159.73(9)
Cs(1)#1-S(4)-Cs(1)#10	83.15(6)
Cs(2)-S(4)-Cs(1)#10	78.96(6)
P(2)#4-S(5)-Y(1)	88.45(11)
P(2)#4-S(5)-Cs(1)	88.39(12)
Y(1)-S(5)-Cs(1)	176.83(11)
P(2)#4-S(5)-Cs(1)#1	105.42(13)

Y(1)-S(5)-Cs(1)#1	92.62(8)
Cs(1)-S(5)-Cs(1)#1	88.44(7)
P(2)#4-S(5)-Cs(2)#14	69.17(10)
Y(1)-S(5)-Cs(2)#14	98.31(8)
Cs(1)-S(5)-Cs(2)#14	80.35(6)
Cs(1)#1-S(5)-Cs(2)#14	167.57(9)
P(2)-S(6)-Y(1)#8	87.10(11)
P(2)-S(6)-Cs(1)	85.96(12)
Y(1)#8-S(6)-Cs(1)	173.00(10)
P(2)-S(6)-Cs(1)#1	105.25(13)
Y(1)#8-S(6)-Cs(1)#1	95.95(8)
Cs(1)-S(6)-Cs(1)#1	86.74(6)
P(2)-S(6)-Cs(2)#3	70.05(10)
Y(1)#8-S(6)-Cs(2)#3	98.14(8)
Cs(1)-S(6)-Cs(2)#3	78.64(6)
Cs(1)#1-S(6)-Cs(2)#3	164.84(9)
P(1)-S(7)-Y(1)	98.00(12)
P(1)-S(7)-Cs(1)#1	89.54(11)
Y(1)-S(7)-Cs(1)#1	98.47(8)
P(1)-S(7)-Cs(2)#4	95.87(12)
Y(1)-S(7)-Cs(2)#4	91.79(7)
Cs(1)#1-S(7)-Cs(2)#4	167.64(9)
P(1)-S(7)-Cs(1)#10	86.21(10)
Y(1)-S(7)-Cs(1)#10	174.89(9)
Cs(1)#1-S(7)-Cs(1)#10	84.40(6)
Cs(2)#4-S(7)-Cs(1)#10	84.88(6)
S(4)-P(1)-S(7)	109.56(12)
S(4)-P(1)-S(2)	116.19(16)
S(7)-P(1)-S(2)	105.32(16)
S(4)-P(1)-S(3)#5	109.70(17)
S(7)-P(1)-S(3)#5	110.40(17)
S(2)-P(1)-S(3)#5	105.51(12)
S(4)-P(1)-Cs(1)#10	68.90(9)
S(7)-P(1)-Cs(1)#10	63.83(9)
S(2)-P(1)-Cs(1)#10	169.09(13)
S(3)#5-P(1)-Cs(1)#10	80.56(8)
S(4)-P(1)-Cs(1)#1	57.61(10)
S(7)-P(1)-Cs(1)#1	60.50(9)
S(2)-P(1)-Cs(1)#1	101.17(9)
S(3)#5-P(1)-Cs(1)#1	153.31(10)
Cs(1)#10-P(1)-Cs(1)#1	72.95(3)
S(1)#1-P(2)-S(6)	117.48(18)
S(1)#1-P(2)-S(5)#8	116.37(18)
S(6)-P(2)-S(5)#8	106.82(11)
S(1)#1-P(2)-P(2)#16	104.40(13)
S(6)-P(2)-P(2)#16	105.2(2)
S(5)#8-P(2)-P(2)#16	105.3(2)
S(1)#1-P(2)-Cs(2)#3	64.91(8)
S(6)-P(2)-Cs(2)#3	80.38(11)
S(5)#8-P(2)-Cs(2)#3	81.33(11)
P(2)#16-P(2)-Cs(2)#3	169.28(12)
S(1)#1-P(2)-Cs(1)	58.99(12)
S(6)-P(2)-Cs(1)	63.32(12)
S(5)#8-P(2)-Cs(1)	156.69(12)
P(2)#16-P(2)-Cs(1)	97.86(17)
Cs(2)#3-P(2)-Cs(1)	76.26(5)
S(1)#1-P(2)-Cs(1)#8	60.13(12)
S(6)-P(2)-Cs(1)#8	155.88(12)
S(5)#8-P(2)-Cs(1)#8	60.80(11)
P(2)#16-P(2)-Cs(1)#8	98.30(17)
Cs(2)#3-P(2)-Cs(1)#8	77.34(5)
Cs(1)-P(2)-Cs(1)#8	119.09(5)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z #2 -x+1,-y+2,-z #3 x+1,y,z

#4 x,y+1,z #5 -x+1/2,y-1/2,-z+1/2 #6 -x,-y+1,-z

#7 x-1,y-1,z #8 x,y-1,z #9 -x+1/2,y-3/2,-z+1/2

#10 x-1,y,z #11 -x-1/2,y-1/2,-z+1/2 #12 -x-1/2,y+1/2,-z+1/2

#13 -x+1/2,y+1/2,-z+1/2 #14 x+1,y+1,z #15 -x+1/2,y+3/2,-z+1/2

#16 -x+1,-y,-z

Table D.12. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $Cs_2Y(P_2S_6)_{1/2}(PS_4)$. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cs(1)	20(1)	13(1)	21(1)	-1(1)	9(1)	-1(1)
Cs(2)	17(1)	21(1)	29(1)	-2(1)	6(1)	0(1)
Y(1)	11(1)	12(1)	13(1)	0(1)	4(1)	-1(1)
S(1)	16(1)	15(1)	28(1)	1(2)	9(1)	-1(2)
S(2)	13(1)	19(1)	15(1)	2(1)	3(1)	-3(1)
S(3)	13(1)	17(1)	17(1)	1(2)	7(1)	-2(2)
S(4)	19(2)	13(1)	16(2)	-1(1)	2(1)	2(1)
S(5)	22(2)	12(1)	19(2)	2(1)	11(2)	1(1)
S(6)	21(2)	13(1)	17(2)	-2(1)	6(2)	-1(1)
S(7)	19(2)	13(1)	12(2)	1(1)	5(1)	0(1)
P(1)	13(1)	13(1)	11(1)	0(1)	4(1)	-2(1)
P(2)	16(1)	12(1)	15(1)	0(2)	7(1)	3(2)

Table D.13. Crystal data and structure refinement for $Cs_2Y(P_2Se_6)_{1/2}(PSe_4)$.

Identification code	pvc5	
Empirical formula	$Cs_2Y(P_2Se_6)_{1/2}(PSe_4)$	
Formula weight	969.39	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 10.1012(5) Å	α= 90°.
	b = 7.1845(4) Å	β= 97.8970(10)°.
	c = 20.3145(11) Å	γ = 90°.
Volume	1460.28(13) $Å^3$	
Z	4	
Density (calculated)	4.409 Mg/m^3	
Absorption coefficient	26.529 mm^{-1}	
F(000)	1668	
Crystal size	.03 x .06 x .47 mm^3	
Theta range for data collection	2.02 to 28.35°.	
Index ranges	-13<=h<=10, -9<=k<=9, -26<=l<=25	
Reflections collected	9356	
Independent reflections	3538 [R(int) = 0.0565]	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3538 / 0 / 110	
Goodness-of-fit on F^2	1.004	
Final R indices [I>2sigma(I)]	R1 = 0.0483, wR2 = 0.1148	
R indices (all data)	R1 = 0.0884, wR2 = 0.1330	
Extinction coefficient	0.00080(9)	
Largest diff. peak and hole	3.183 and -1.592 $e.Å^{-3}$	

Table D.14. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for $Cs_2Y(P_2Se_6)_{1/2}(PSe_4)$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cs(1)	-2622(1)	21(1)	4716(1)	30(1)
Cs(2)	-3560(1)	-4985(1)	2972(1)	37(1)
Y(1)	-6894(1)	223(1)	1532(1)	10(1)
Se(1)	-6907(1)	4175(2)	2253(1)	23(1)
Se(2)	-6074(1)	2390(1)	3962(1)	23(1)
Se(3)	-5778(1)	-2565(1)	4023(1)	22(1)
Se(4)	-30(1)	2609(1)	3966(1)	23(1)
Se(5)	-89(1)	-2489(1)	3993(1)	22(1)
Se(6)	-4719(1)	-7(2)	2647(1)	24(1)
Se(7)	-2650(1)	4969(2)	4778(1)	27(1)
P(1)	-654(3)	-4989(4)	4514(1)	17(1)
P(2)	-6174(3)	-153(4)	3359(1)	17(1)

Table D.15. Bond lengths [Å] and angles [°] for $Cs_2Y(P_2Se_6)_{1/2}(PSe_4)$.

Cs(1)-Se(7)	3.5569(13)	Se(4)-Cs(1)#3	3.9935(14)
Cs(1)-Se(2)#1	3.5935(13)	Se(4)-Cs(2)#4	4.2188(15)
Cs(1)-Se(5)	3.6034(13)	Se(5)-P(1)	2.199(3)
Cs(1)-Se(7)#2	3.6325(13)	Se(5)-Y(1)#5	2.9054(14)
Cs(1)-Se(3)#1	3.6940(13)	Se(5)-Cs(1)#3	3.9426(14)
Cs(1)-Se(4)	3.7054(13)	Se(6)-P(2)	2.201(3)
Cs(1)-Se(3)	3.7900(14)	Se(6)-Cs(2)#6	3.7007(14)
Cs(1)-Se(5)#3	3.9426(14)	Se(6)-Cs(2)#4	3.8226(14)
Cs(1)-Se(2)	3.9919(14)	Se(7)-P(1)#4	2.157(3)
Cs(1)-Se(4)#3	3.9935(14)	Se(7)-Cs(1)#4	3.6325(13)
Cs(1)-P(1)#4	4.147(3)	Se(7)-Cs(2)#4	3.658(2)
Cs(1)-P(1)	4.159(3)	P(1)-Se(7)#2	2.157(3)
Cs(2)-Se(1)#2	3.5456(15)	P(1)-Se(4)#2	2.194(3)
Cs(2)-Se(7)#2	3.658(2)	P(1)-P(1)#9	2.218(6)
Cs(2)-Se(6)#5	3.7007(14)	P(1)-Cs(1)#2	4.147(3)
Cs(2)-Se(3)	3.7316(14)	P(2)-Se(1)#8	2.208(3)
Cs(2)-Se(6)	3.7928(14)		
Cs(2)-Se(6)#2	3.8226(14)	Se(7)-Cs(1)-Se(2)#1	116.73(3)
Cs(2)-Se(2)#2	3.9325(14)	Se(7)-Cs(1)-Se(5)	121.61(3)
Cs(2)-P(1)	3.989(3)	Se(2)#1-Cs(1)-Se(5)	114.62(3)
Cs(2)-Se(4)#2	4.2188(15)	Se(7)-Cs(1)-Se(7)#2	175.78(5)
Cs(2)-Se(5)	4.2205(15)	Se(2)#1-Cs(1)-Se(7)#2	59.14(3)
Cs(2)-Cs(2)#5	4.7211(11)	Se(5)-Cs(1)-Se(7)#2	61.53(3)
Cs(2)-Cs(2)#6	4.7211(11)	Se(7)-Cs(1)-Se(3)#1	58.32(3)
Y(1)-Se(5)#6	2.9054(14)	Se(2)#1-Cs(1)-Se(3)#1	58.70(3)
Y(1)-Se(3)#7	2.9320(15)	Se(5)-Cs(1)-Se(3)#1	158.86(4)
Y(1)-Se(6)	2.936(2)	Se(7)#2-Cs(1)-Se(3)#1	117.66(3)
Y(1)-Se(2)#8	2.9659(14)	Se(7)-Cs(1)-Se(4)	61.49(3)
Y(1)-Se(4)#5	2.9780(14)	Se(2)#1-Cs(1)-Se(4)	154.34(4)
Y(1)-Se(1)#8	2.9909(14)	Se(5)-Cs(1)-Se(4)	60.15(3)
Y(1)-Se(1)	3.1959(14)	Se(7)#2-Cs(1)-Se(4)	121.66(3)
Y(1)-Cs(2)#7	4.8372(13)	Se(3)#1-Cs(1)-Se(4)	115.99(3)
Se(1)-P(2)#7	2.208(3)	Se(7)-Cs(1)-Se(3)	119.50(3)
Se(1)-Y(1)#7	2.9909(14)	Se(2)#1-Cs(1)-Se(3)	70.44(3)
Se(1)-Cs(2)#4	3.5456(15)	Se(5)-Cs(1)-Se(3)	102.21(3)
Se(2)-P(2)	2.195(3)	Se(7)#2-Cs(1)-Se(3)	60.84(3)
Se(2)-Y(1)#7	2.9659(14)	Se(3)#1-Cs(1)-Se(3)	94.24(3)
Se(2)-Cs(1)#1	3.5935(13)	Se(4)-Cs(1)-Se(3)	134.34(3)
Se(2)-Cs(2)#4	3.9325(14)	Se(7)-Cs(1)-Se(5)#3	62.32(3)
Se(3)-P(2)	2.199(3)	Se(2)#1-Cs(1)-Se(5)#3	90.71(3)
Se(3)-Y(1)#8	2.9320(15)	Se(5)-Cs(1)-Se(5)#3	91.66(3)
Se(3)-Cs(1)#1	3.6940(13)	Se(7)#2-Cs(1)-Se(5)#3	115.76(3)
Se(4)-P(1)#4	2.194(3)	Se(3)#1-Cs(1)-Se(5)#3	69.31(3)
Se(4)-Y(1)#6	2.9780(14)	Se(4)-Cs(1)-Se(5)#3	65.33(3)

Se(3)-Cs(1)-Se(5)#3	159.95(3)	Se(7)#2-Cs(2)-Se(6)	102.24(3)
Se(7)-Cs(1)-Se(2)	64.95(3)	Se(6)#5-Cs(2)-Se(6)	102.38(3)
Se(2)#1-Cs(1)-Se(2)	95.82(3)	Se(3)-Cs(2)-Se(6)	57.64(3)
Se(5)-Cs(1)-Se(2)	133.54(3)	Se(1)#2-Cs(2)-Se(6)#2	61.06(3)
Se(7)#2-Cs(1)-Se(2)	115.38(3)	Se(7)#2-Cs(2)-Se(6)#2	101.14(3)
Se(3)#1-Cs(1)-Se(2)	67.21(3)	Se(6)#5-Cs(2)-Se(6)#2	101.81(3)
Se(4)-Cs(1)-Se(2)	104.93(3)	Se(3)-Cs(2)-Se(6)#2	110.16(3)
Se(3)-Cs(1)-Se(2)	54.58(3)	Se(6)-Cs(2)-Se(6)#2	141.27(4)
Se(5)#3-Cs(1)-Se(2)	123.62(3)	Se(1)#2-Cs(2)-Se(2)#2	58.84(3)
Se(7)-Cs(1)-Se(4)#3	117.20(3)	Se(7)#2-Cs(2)-Se(2)#2	64.73(3)
Se(2)#1-Cs(1)-Se(4)#3	63.37(3)	Se(6)#5-Cs(2)-Se(2)#2	147.46(3)
Se(5)-Cs(1)-Se(4)#3	65.67(3)	Se(3)-Cs(2)-Se(2)#2	56.60(3)
Se(7)#2-Cs(1)-Se(4)#3	60.78(3)	Se(6)-Cs(2)-Se(2)#2	109.60(3)
Se(3)#1-Cs(1)-Se(4)#3	94.94(3)	Se(6)#2-Cs(2)-Se(2)#2	55.35(2)
Se(4)-Cs(1)-Se(4)#3	93.82(3)	Se(1)#2-Cs(2)-P(1)	151.71(5)
Se(3)-Cs(1)-Se(4)#3	118.02(3)	Se(7)#2-Cs(2)-P(1)	32.40(5)
Se(5)#3-Cs(1)-Se(4)#3	54.98(2)	Se(6)#5-Cs(2)-P(1)	70.76(5)
Se(2)-Cs(1)-Se(4)#3	158.29(3)	Se(3)-Cs(2)-P(1)	89.17(5)
Se(7)-Cs(1)-P(1)#4	31.33(4)	Se(6)-Cs(2)-P(1)	108.27(5)
Se(2)#1-Cs(1)-P(1)#4	136.09(5)	Se(6)#2-Cs(2)-P(1)	108.05(5)
Se(5)-Cs(1)-P(1)#4	90.90(4)	Se(2)#2-Cs(2)-P(1)	93.15(5)
Se(7)#2-Cs(1)-P(1)#4	150.87(5)	Se(1)#2-Cs(2)-Se(4)#2	145.35(3)
Se(3)#1-Cs(1)-P(1)#4	84.39(4)	Se(7)#2-Cs(2)-Se(4)#2	55.74(3)
Se(4)-Cs(1)-P(1)#4	31.82(4)	Se(6)#5-Cs(2)-Se(4)#2	54.82(3)
Se(3)-Cs(1)-P(1)#4	141.02(5)	Se(3)-Cs(2)-Se(4)#2	116.84(3)
Se(5)#3-Cs(1)-P(1)#4	51.55(4)	Se(6)-Cs(2)-Se(4)#2	133.64(3)
Se(2)-Cs(1)-P(1)#4	89.94(5)	Se(6)#2-Cs(2)-Se(4)#2	85.09(3)
Se(4)#3-Cs(1)-P(1)#4	100.88(5)	Se(2)#2-Cs(2)-Se(4)#2	96.97(3)
Se(7)-Cs(1)-P(1)	150.99(5)	P(1)-Cs(2)-Se(4)#2	30.84(4)
Se(2)#1-Cs(1)-P(1)	83.43(4)	Se(1)#2-Cs(2)-Se(5)	162.83(3)
Se(5)-Cs(1)-P(1)	31.90(4)	Se(7)#2-Cs(2)-Se(5)	55.49(3)
Se(7)#2-Cs(1)-P(1)	31.21(4)	Se(6)#5-Cs(2)-Se(5)	56.44(3)
Se(3)#1-Cs(1)-P(1)	139.19(4)	Se(3)-Cs(2)-Se(5)	92.53(3)
Se(4)-Cs(1)-P(1)	91.11(4)	Se(6)-Cs(2)-Se(5)	84.30(3)
Se(3)-Cs(1)-P(1)	85.89(5)	Se(6)#2-Cs(2)-Se(5)	134.42(3)
Se(5)#3-Cs(1)-P(1)	99.03(5)	Se(2)#2-Cs(2)-Se(5)	120.22(3)
Se(2)-Cs(1)-P(1)	137.34(5)	P(1)-Cs(2)-Se(5)	30.91(4)
Se(4)#3-Cs(1)-P(1)	51.02(4)	Se(4)#2-Cs(2)-Se(5)	49.35(2)
P(1)#4-Cs(1)-P(1)	119.76(7)	Se(1)#2-Cs(2)-Cs(2)#5	99.40(3)
Se(1)#2-Cs(2)-Se(7)#2	120.35(4)	Se(7)#2-Cs(2)-Cs(2)#5	109.56(3)
Se(1)#2-Cs(2)-Se(6)#5	134.98(4)	Se(6)#5-Cs(2)-Cs(2)#5	51.82(3)
Se(7)#2-Cs(2)-Se(6)#5	103.15(3)	Se(3)-Cs(2)-Cs(2)#5	158.20(3)
Se(1)#2-Cs(2)-Se(3)	72.62(3)	Se(6)-Cs(2)-Cs(2)#5	142.50(3)
Se(7)#2-Cs(2)-Se(3)	61.17(3)	Se(6)#2-Cs(2)-Cs(2)#5	49.99(2)
Se(6)#5-Cs(2)-Se(3)	146.34(3)	Se(2)#2-Cs(2)-Cs(2)#5	101.75(2)
Se(1)#2-Cs(2)-Se(6)	80.49(3)	P(1)-Cs(2)-Cs(2)#5	89.57(4)

Se(4)#2-Cs(2)-Cs(2)#5	58.79(2)	Y(1)-Se(1)-Cs(2)#4	106.03(4)
Se(5)-Cs(2)-Cs(2)#5	97.50(3)	P(2)-Se(2)-Y(1)#7	113.93(9)
Se(1)#2-Cs(2)-Cs(2)#6	114.99(3)	P(2)-Se(2)-Cs(1)#1	91.31(8)
Se(7)#2-Cs(2)-Cs(2)#6	110.41(3)	Y(1)#7-Se(2)-Cs(1)#1	106.04(4)
Se(6)#5-Cs(2)-Cs(2)#6	52.29(3)	P(2)-Se(2)-Cs(2)#4	95.54(8)
Se(3)-Cs(2)-Cs(2)#6	102.67(2)	Y(1)#7-Se(2)-Cs(2)#4	87.88(3)
Se(6)-Cs(2)-Cs(2)#6	50.09(2)	Cs(1)#1-Se(2)-Cs(2)#4	160.45(4)
Se(6)#2-Cs(2)-Cs(2)#6	142.51(3)	P(2)-Se(2)-Cs(1)	80.21(8)
Se(2)#2-Cs(2)-Cs(2)#6	158.99(3)	Y(1)#7-Se(2)-Cs(1)	161.76(4)
P(1)-Cs(2)-Cs(2)#6	89.64(5)	Cs(1)#1-Se(2)-Cs(1)	84.18(3)
Se(4)#2-Cs(2)-Cs(2)#6	96.06(3)	Cs(2)#4-Se(2)-Cs(1)	78.99(3)
Se(5)-Cs(2)-Cs(2)#6	58.94(2)	P(2)-Se(3)-Y(1)#8	97.03(9)
Cs(2)#5-Cs(2)-Cs(2)#6	99.09(3)	P(2)-Se(3)-Cs(1)#1	88.63(8)
Se(5)#6-Y(1)-Se(3)#7	96.26(4)	Y(1)#8-Se(3)-Cs(1)#1	97.51(4)
Se(5)#6-Y(1)-Se(6)	80.48(4)	P(2)-Se(3)-Cs(2)	95.07(8)
Se(3)#7-Y(1)-Se(6)	143.40(4)	Y(1)#8-Se(3)-Cs(2)	92.29(3)
Se(5)#6-Y(1)-Se(2)#8	138.06(4)	Cs(1)#1-Se(3)-Cs(2)	169.03(4)
Se(3)#7-Y(1)-Se(2)#8	76.17(4)	P(2)-Se(3)-Cs(1)	85.09(8)
Se(6)-Y(1)-Se(2)#8	129.21(4)	Y(1)#8-Se(3)-Cs(1)	176.13(4)
Se(5)#6-Y(1)-Se(4)#5	73.56(4)	Cs(1)#1-Se(3)-Cs(1)	85.76(3)
Se(3)#7-Y(1)-Se(4)#5	137.54(4)	Cs(2)-Se(3)-Cs(1)	84.27(3)
Se(6)-Y(1)-Se(4)#5	76.83(4)	P(1)#4-Se(4)-Y(1)#6	85.55(8)
Se(2)#8-Y(1)-Se(4)#5	84.59(4)	P(1)#4-Se(4)-Cs(1)	85.25(8)
Se(5)#6-Y(1)-Se(1)#8	145.41(5)	Y(1)#6-Se(4)-Cs(1)	170.78(4)
Se(3)#7-Y(1)-Se(1)#8	93.43(4)	P(1)#4-Se(4)-Cs(1)#3	104.14(9)
Se(6)-Y(1)-Se(1)#8	72.17(4)	Y(1)#6-Se(4)-Cs(1)#3	96.72(4)
Se(2)#8-Y(1)-Se(1)#8	76.52(4)	Cs(1)-Se(4)-Cs(1)#3	86.18(3)
Se(4)#5-Y(1)-Se(1)#8	118.57(4)	P(1)#4-Se(4)-Cs(2)#4	68.78(9)
Se(5)#6-Y(1)-Se(1)	73.28(3)	Y(1)#6-Se(4)-Cs(2)#4	97.31(3)
Se(3)#7-Y(1)-Se(1)	68.98(3)	Cs(1)-Se(4)-Cs(2)#4	78.71(3)
Se(6)-Y(1)-Se(1)	75.28(4)	Cs(1)#3-Se(4)-Cs(2)#4	163.69(3)
Se(2)#8-Y(1)-Se(1)	135.95(4)	P(1)-Se(5)-Y(1)#5	87.27(8)
Se(4)#5-Y(1)-Se(1)	139.46(5)	P(1)-Se(5)-Cs(1)	88.12(8)
Se(1)#8-Y(1)-Se(1)	79.50(3)	Y(1)#5-Se(5)-Cs(1)	175.39(4)
Se(5)#6-Y(1)-Cs(2)#7	144.72(4)	P(1)-Se(5)-Cs(1)#3	104.45(9)
Se(3)#7-Y(1)-Cs(2)#7	50.43(3)	Y(1)#5-Se(5)-Cs(1)#3	92.73(4)
Se(6)-Y(1)-Cs(2)#7	117.94(3)	Cs(1)-Se(5)-Cs(1)#3	88.34(3)
Se(2)#8-Y(1)-Cs(2)#7	54.33(3)	P(1)-Se(5)-Cs(2)	68.72(9)
Se(4)#5-Y(1)-Cs(2)#7	137.21(4)	Y(1)#5-Se(5)-Cs(2)	98.47(4)
Se(1)#8-Y(1)-Cs(2)#7	46.90(3)	Cs(1)-Se(5)-Cs(2)	79.91(3)
Se(1)-Y(1)-Cs(2)#7	82.42(3)	Cs(1)#3-Se(5)-Cs(2)	166.46(3)
P(2)#7-Se(1)-Y(1)#7	89.19(8)	P(2)-Se(6)-Y(1)	90.75(9)
P(2)#7-Se(1)-Y(1)	89.69(8)	P(2)-Se(6)-Cs(2)#6	158.88(9)
Y(1)#7-Se(1)-Y(1)	129.02(5)	Y(1)-Se(6)-Cs(2)#6	110.33(4)
P(2)#7-Se(1)-Cs(2)#4	155.30(8)	P(2)-Se(6)-Cs(2)	93.37(8)
Y(1)#7-Se(1)-Cs(2)#4	95.09(4)	Y(1)-Se(6)-Cs(2)	111.57(4)

Cs(2)#6-Se(6)-Cs(2)	78.09(3)
P(2)-Se(6)-Cs(2)#4	98.52(8)
Y(1)-Se(6)-Cs(2)#4	105.01(4)
Cs(2)#6-Se(6)-Cs(2)#4	77.72(3)
Cs(2)-Se(6)-Cs(2)#4	141.27(4)
P(1)#4-Se(7)-Cs(1)	89.61(8)
P(1)#4-Se(7)-Cs(1)#4	88.00(8)
Cs(1)-Se(7)-Cs(1)#4	175.78(5)
P(1)#4-Se(7)-Cs(2)#4	82.28(9)
Cs(1)-Se(7)-Cs(2)#4	88.62(3)
Cs(1)#4-Se(7)-Cs(2)#4	87.61(3)
Se(7)#2-P(1)-Se(4)#2	117.28(13)
Se(7)#2-P(1)-Se(5)	116.37(13)
Se(4)#2-P(1)-Se(5)	106.64(12)
Se(7)#2-P(1)-P(1)#9	104.0(2)
Se(4)#2-P(1)-P(1)#9	105.6(2)
Se(5)-P(1)-P(1)#9	105.8(2)
Se(7)#2-P(1)-Cs(2)	65.32(8)
Se(4)#2-P(1)-Cs(2)	80.38(9)
Se(5)-P(1)-Cs(2)	80.37(9)
P(1)#9-P(1)-Cs(2)	169.3(2)
Se(7)#2-P(1)-Cs(1)#2	59.06(7)
Se(4)#2-P(1)-Cs(1)#2	62.93(7)
Se(5)-P(1)-Cs(1)#2	155.93(12)
P(1)#9-P(1)-Cs(1)#2	98.09(14)
Cs(2)-P(1)-Cs(1)#2	76.54(5)
Se(7)#2-P(1)-Cs(1)	60.79(7)
Se(4)#2-P(1)-Cs(1)	154.89(12)
Se(5)-P(1)-Cs(1)	59.98(7)
P(1)#9-P(1)-Cs(1)	98.80(14)
Cs(2)-P(1)-Cs(1)	76.51(5)
Cs(1)#2-P(1)-Cs(1)	119.76(7)
Se(2)-P(2)-Se(3)	108.79(12)
Se(2)-P(2)-Se(6)	110.11(12)
Se(3)-P(2)-Se(6)	111.07(13)
Se(2)-P(2)-Se(1)#8	117.76(13)
Se(3)-P(2)-Se(1)#8	104.18(12)
Se(6)-P(2)-Se(1)#8	104.74(12)
Se(2)-P(2)-Cs(1)	68.92(8)
Se(3)-P(2)-Cs(1)	63.60(8)
Se(6)-P(2)-Cs(1)	80.97(9)
Se(1)#8-P(2)-Cs(1)	167.78(11)

Symmetry transformations used to generate equivalent atoms:

#1 -x-1,-y,-z+1 #2 x,y-1,z #3 -x,-y,-z+1

#4 x,y+1,z #5 -x-1/2,y-1/2,-z+1/2 #6 -x-1/2,y+1/2,-z+1/2

#7 -x-3/2,y+1/2,-z+1/2 #8 -x-3/2,y-1/2,-z+1/2

#9 -x,-y-1,-z+1

Table D.16. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $Cs_2Y(P_2Se_6)_{1/2}(PSe_4)$. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cs(1)	30(1)	21(1)	41(1)	-2(1)	14(1)	-1(1)
Cs(2)	24(1)	40(1)	48(1)	-4(1)	7(1)	-1(1)
Y(1)	7(1)	9(1)	14(1)	0(1)	3(1)	-1(1)
Se(1)	16(1)	25(1)	26(1)	-3(1)	0(1)	4(1)
Se(2)	28(1)	17(1)	24(1)	-3(1)	-1(1)	4(1)
Se(3)	23(1)	17(1)	24(1)	3(1)	1(1)	-2(1)
Se(4)	27(1)	16(1)	27(1)	-2(1)	11(1)	-2(1)
Se(5)	25(1)	15(1)	28(1)	4(1)	11(1)	3(1)
Se(6)	17(1)	33(1)	24(1)	2(1)	7(1)	2(1)
Se(7)	17(1)	22(1)	44(1)	0(1)	11(1)	0(1)
P(1)	17(1)	15(1)	21(1)	0(1)	5(1)	1(1)
P(2)	16(1)	14(1)	20(1)	-1(1)	5(1)	1(1)

Table D.17. Crystal data and structure refinement for $Cs_2La(P_2S_6)_{1/2}(PS_4)$.

Identification code	p21n	
Empirical formula	$Cs_2La(P_2S_6)_{1/2}(PS_4)$	
Formula weight	691.09	
Temperature	172(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 9.8813(15) Å	α= 90°.
	b = 6.9366(10) Å	β= 98.722(3)°.
	c = 19.547(3) Å	γ = 90°.
Volume	1324.3(3) $Å^3$	
Z	4	
Density (calculated)	3.466 Mg/m^3	
Absorption coefficient	9.939 mm^{-1}	
F(000)	1236	
Crystal size	0.05 x 0.09 x 0.12 mm^3	
Theta range for data collection	2.11 to 28.29°.	
Index ranges	-13<=h<=8, -9<=k<=8, -25<=l<=25	
Reflections collected	8799	
Independent reflections	3231 [R(int) = 0.1205]	
Completeness to theta = 28.29°	98.4 %	
Absorption correction	SADABS	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3231 / 0 / 109	
Goodness-of-fit on F^2	0.490	
Final R indices [I>2sigma(I)]	R1 = 0.0350, wR2 = 0.0489	
R indices (all data)	R1 = 0.1767, wR2 = 0.0660	
Largest diff. peak and hole	1.299 and -1.278 $e.Å^{-3}$	

Table D.18. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for $Cs_2La(P_2S_6)_{1/2}(PS_4)$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
La(1)	3084(1)	9847(2)	1498(1)	11(1)
P(1)	1086(4)	5224(8)	1626(2)	13(1)
P(2)	5726(3)	10024(8)	485(2)	11(1)
S(1)	2433(3)	9935(8)	-184(2)	15(1)
S(2)	2993(4)	5718(5)	2168(2)	13(1)
S(3)	5272(3)	10115(8)	2683(2)	16(1)
S(4)	919(6)	12754(6)	1064(3)	20(2)
S(5)	5295(6)	7634(6)	1006(3)	13(1)
S(6)	5208(7)	12363(6)	1017(3)	16(2)
S(7)	654(6)	7521(6)	988(3)	15(1)
Cs(1)	7607(1)	5008(2)	225(1)	16(1)
Cs(2)	-1399(1)	10117(2)	2056(1)	19(1)

Table D.19. Bond lengths [Å] and angles [°] for $Cs_2La(P_2S_6)_{1/2}(PS_4)$.

La(1)-S(3)	2.924(3)	S(6)-Cs(2)#7	3.966(7)
La(1)-S(7)	2.940(6)	S(7)-Cs(1)#2	3.589(6)
La(1)-S(5)	2.949(6)	S(7)-Cs(1)#6	3.600(6)
La(1)-S(4)	2.969(6)	S(7)-Cs(2)	3.607(6)
La(1)-S(6)	2.989(6)	Cs(1)-S(1)#2	3.430(6)
La(1)-S(2)#1	3.022(3)	Cs(1)-S(4)#3	3.463(6)
La(1)-S(2)	3.156(4)	Cs(1)-S(1)#3	3.508(6)
La(1)-S(1)	3.253(3)	Cs(1)-S(6)#4	3.536(6)
La(1)-Cs(2)	4.7242(14)	Cs(1)-S(7)#2	3.589(6)
La(1)-Cs(1)#2	4.7385(15)	Cs(1)-S(7)#7	3.600(6)
La(1)-Cs(1)#3	4.8831(16)	Cs(1)-S(4)#11	3.770(6)
P(1)-S(7)	2.028(7)	Cs(1)-S(6)#3	3.861(6)
P(1)-S(4)#4	2.029(7)	Cs(1)-S(5)#2	3.909(6)
P(1)-S(3)#5	2.046(4)	Cs(1)-P(2)#4	3.995(5)
P(1)-S(2)	2.046(5)	Cs(2)-S(2)#1	3.501(4)
P(1)-Cs(1)#2	4.024(3)	Cs(2)-S(1)#9	3.648(3)
P(1)-Cs(1)#6	4.060(4)	Cs(2)-S(3)#1	3.653(6)
P(2)-S(1)#3	1.995(4)	Cs(2)-S(3)#5	3.656(6)
P(2)-S(5)	2.024(7)	Cs(2)-S(3)#6	3.679(3)
P(2)-S(6)	2.035(7)	Cs(2)-P(2)#6	3.855(3)
P(2)-P(2)#3	2.197(6)	Cs(2)-S(6)#6	3.966(7)
P(2)-Cs(2)#7	3.855(3)	Cs(2)-S(5)#6	3.977(6)
P(2)-Cs(1)#8	3.995(5)	Cs(2)-S(5)#1	4.164(6)
P(2)-Cs(1)	4.013(5)	Cs(2)-Cs(2)#12	4.5732(11)
S(1)-P(2)#3	1.995(4)		
S(1)-Cs(1)#2	3.430(6)	S(3)-La(1)-S(7)	140.50(14)
S(1)-Cs(1)#3	3.508(6)	S(3)-La(1)-S(5)	78.23(15)
S(1)-Cs(2)#9	3.648(3)	S(7)-La(1)-S(5)	102.18(15)
S(2)-La(1)#5	3.022(3)	S(3)-La(1)-S(4)	126.70(14)
S(2)-Cs(2)#5	3.501(4)	S(7)-La(1)-S(4)	76.08(11)
S(3)-P(1)#1	2.046(4)	S(5)-La(1)-S(4)	142.92(16)
S(3)-Cs(2)#5	3.653(6)	S(3)-La(1)-S(6)	75.04(15)
S(3)-Cs(2)#1	3.656(6)	S(7)-La(1)-S(6)	142.21(17)
S(3)-Cs(2)#7	3.679(3)	S(5)-La(1)-S(6)	67.11(9)
S(4)-P(1)#8	2.029(7)	S(4)-La(1)-S(6)	91.34(15)
S(4)-Cs(1)#3	3.463(6)	S(3)-La(1)-S(2)#1	67.62(10)
S(4)-Cs(2)	3.701(6)	S(7)-La(1)-S(2)#1	91.50(14)
S(4)-Cs(1)#10	3.770(6)	S(5)-La(1)-S(2)#1	139.55(14)
S(5)-Cs(1)	3.453(6)	S(4)-La(1)-S(2)#1	77.17(14)
S(5)-Cs(1)#2	3.909(6)	S(6)-La(1)-S(2)#1	120.69(13)
S(5)-Cs(2)#7	3.977(6)	S(3)-La(1)-S(2)	78.07(13)
S(5)-Cs(2)#5	4.164(6)	S(7)-La(1)-S(2)	64.49(12)
S(6)-Cs(1)#8	3.536(6)	S(5)-La(1)-S(2)	74.49(12)
S(6)-Cs(1)#3	3.861(6)	S(4)-La(1)-S(2)	132.07(14)

S(6)-La(1)-S(2)	136.57(14)	S(7)-P(1)-Cs(1)#6	62.38(18)
S(2)#1-La(1)-S(2)	77.73(6)	S(4)#4-P(1)-Cs(1)#6	67.2(2)
S(3)-La(1)-S(1)	143.89(9)	S(3)#5-P(1)-Cs(1)#6	82.61(15)
S(7)-La(1)-S(1)	68.97(14)	S(2)-P(1)-Cs(1)#6	167.10(19)
S(5)-La(1)-S(1)	73.89(14)	Cs(1)#2-P(1)-Cs(1)#6	75.31(6)
S(4)-La(1)-S(1)	71.03(14)	S(1)#3-P(2)-S(5)	115.5(3)
S(6)-La(1)-S(1)	73.25(14)	S(1)#3-P(2)-S(6)	116.8(3)
S(2)#1-La(1)-S(1)	145.72(11)	S(5)-P(2)-S(6)	107.91(18)
S(2)-La(1)-S(1)	115.01(12)	S(1)#3-P(2)-P(2)#3	104.5(2)
S(3)-La(1)-Cs(2)	114.92(6)	S(5)-P(2)-P(2)#3	105.2(4)
S(7)-La(1)-Cs(2)	49.74(12)	S(6)-P(2)-P(2)#3	105.7(4)
S(5)-La(1)-Cs(2)	149.68(10)	S(1)#3-P(2)-Cs(2)#7	68.92(12)
S(4)-La(1)-Cs(2)	51.58(12)	S(5)-P(2)-Cs(2)#7	78.4(2)
S(6)-La(1)-Cs(2)	141.01(11)	S(6)-P(2)-Cs(2)#7	78.0(2)
S(2)#1-La(1)-Cs(2)	47.75(8)	P(2)#3-P(2)-Cs(2)#7	173.5(2)
S(2)-La(1)-Cs(2)	81.55(7)	S(1)#3-P(2)-Cs(1)#8	59.16(19)
S(1)-La(1)-Cs(2)	100.61(6)	S(5)-P(2)-Cs(1)#8	155.6(2)
S(3)-La(1)-Cs(1)#2	128.13(10)	S(6)-P(2)-Cs(1)#8	62.1(2)
S(7)-La(1)-Cs(1)#2	49.17(12)	P(2)#3-P(2)-Cs(1)#8	99.1(3)
S(5)-La(1)-Cs(1)#2	55.39(12)	Cs(2)#7-P(2)-Cs(1)#8	77.64(8)
S(4)-La(1)-Cs(1)#2	105.04(10)	S(1)#3-P(2)-Cs(1)	60.9(2)
S(6)-La(1)-Cs(1)#2	102.95(11)	S(5)-P(2)-Cs(1)	59.4(2)
S(2)#1-La(1)-Cs(1)#2	136.34(8)	S(6)-P(2)-Cs(1)	156.0(2)
S(2)-La(1)-Cs(1)#2	68.90(7)	P(2)#3-P(2)-Cs(1)	97.6(3)
S(1)-La(1)-Cs(1)#2	46.38(10)	Cs(2)#7-P(2)-Cs(1)	79.40(8)
Cs(2)-La(1)-Cs(1)#2	98.81(2)	Cs(1)#8-P(2)-Cs(1)	120.05(9)
S(3)-La(1)-Cs(1)#3	120.59(10)	P(2)#3-S(1)-La(1)	104.43(14)
S(7)-La(1)-Cs(1)#3	98.36(10)	P(2)#3-S(1)-Cs(1)#2	90.9(2)
S(5)-La(1)-Cs(1)#3	100.86(10)	La(1)-S(1)-Cs(1)#2	90.27(11)
S(4)-La(1)-Cs(1)#3	44.53(12)	P(2)#3-S(1)-Cs(1)#3	89.2(2)
S(6)-La(1)-Cs(1)#3	52.25(12)	La(1)-S(1)-Cs(1)#3	92.39(12)
S(2)#1-La(1)-Cs(1)#3	114.70(7)	Cs(1)#2-S(1)-Cs(1)#3	177.22(11)
S(2)-La(1)-Cs(1)#3	159.97(7)	P(2)#3-S(1)-Cs(2)#9	80.40(12)
S(1)-La(1)-Cs(1)#3	45.88(10)	La(1)-S(1)-Cs(2)#9	174.92(12)
Cs(2)-La(1)-Cs(1)#3	95.29(2)	Cs(1)#2-S(1)-Cs(2)#9	88.06(10)
Cs(1)#2-La(1)-Cs(1)#3	92.25(2)	Cs(1)#3-S(1)-Cs(2)#9	89.22(10)
S(7)-P(1)-S(4)#4	109.8(2)	P(1)-S(2)-La(1)#5	89.81(16)
S(7)-P(1)-S(3)#5	109.7(3)	P(1)-S(2)-La(1)	91.08(19)
S(4)#4-P(1)-S(3)#5	108.6(3)	La(1)#5-S(2)-La(1)	125.14(12)
S(7)-P(1)-S(2)	106.2(3)	P(1)-S(2)-Cs(2)#5	162.5(2)
S(4)#4-P(1)-S(2)	114.5(3)	La(1)#5-S(2)-Cs(2)#5	92.53(9)
S(3)#5-P(1)-S(2)	108.0(2)	La(1)-S(2)-Cs(2)#5	101.63(10)
S(7)-P(1)-Cs(1)#2	62.93(19)	P(1)#1-S(3)-La(1)	92.59(16)
S(4)#4-P(1)-Cs(1)#2	59.36(18)	P(1)#1-S(3)-Cs(2)#5	99.2(2)
S(3)#5-P(1)-Cs(1)#2	157.62(19)	La(1)-S(3)-Cs(2)#5	102.91(14)
S(2)-P(1)-Cs(1)#2	94.41(15)	P(1)#1-S(3)-Cs(2)#1	95.1(2)

La(1)-S(3)-Cs(2)#1	110.11(14)	Cs(1)#2-S(7)-Cs(1)#6	86.78(11)
Cs(2)#5-S(3)-Cs(2)#1	143.24(10)	P(1)-S(7)-Cs(2)	96.9(2)
P(1)#1-S(3)-Cs(2)#7	158.27(17)	La(1)-S(7)-Cs(2)	91.81(13)
La(1)-S(3)-Cs(2)#7	109.13(8)	Cs(1)#2-S(7)-Cs(2)	173.82(18)
Cs(2)#5-S(3)-Cs(2)#7	77.17(8)	Cs(1)#6-S(7)-Cs(2)	88.47(14)
Cs(2)#1-S(3)-Cs(2)#7	77.14(8)	S(1)#2-Cs(1)-S(5)	122.10(10)
P(1)#8-S(4)-La(1)	115.0(3)	S(1)#2-Cs(1)-S(4)#3	115.84(10)
P(1)#8-S(4)-Cs(1)#3	90.4(2)	S(5)-Cs(1)-S(4)#3	117.68(12)
La(1)-S(4)-Cs(1)#3	98.51(18)	S(1)#2-Cs(1)-S(1)#3	177.22(11)
P(1)#8-S(4)-Cs(2)	98.0(2)	S(5)-Cs(1)-S(1)#3	58.45(10)
La(1)-S(4)-Cs(2)	89.49(13)	S(4)#3-Cs(1)-S(1)#3	62.60(9)
Cs(1)#3-S(4)-Cs(2)	164.74(18)	S(1)#2-Cs(1)-S(6)#4	59.02(10)
P(1)#8-S(4)-Cs(1)#10	83.1(2)	S(5)-Cs(1)-S(6)#4	63.09(7)
La(1)-S(4)-Cs(1)#10	161.17(16)	S(4)#3-Cs(1)-S(6)#4	159.29(14)
Cs(1)#3-S(4)-Cs(1)#10	86.02(12)	S(1)#3-Cs(1)-S(6)#4	121.51(10)
Cs(2)-S(4)-Cs(1)#10	82.41(13)	S(1)#2-Cs(1)-S(7)#2	60.07(9)
P(2)-S(5)-La(1)	87.75(19)	S(5)-Cs(1)-S(7)#2	164.74(14)
P(2)-S(5)-Cs(1)	90.3(2)	S(4)#3-Cs(1)-S(7)#2	56.11(8)
La(1)-S(5)-Cs(1)	172.6(2)	S(1)#3-Cs(1)-S(7)#2	118.59(9)
P(2)-S(5)-Cs(1)#2	105.4(2)	S(6)#4-Cs(1)-S(7)#2	117.11(12)
La(1)-S(5)-Cs(1)#2	86.23(15)	S(1)#2-Cs(1)-S(7)#7	119.98(10)
Cs(1)-S(5)-Cs(1)#2	87.34(12)	S(5)-Cs(1)-S(7)#7	97.43(13)
P(2)-S(5)-Cs(2)#7	71.71(19)	S(4)#3-Cs(1)-S(7)#7	70.53(12)
La(1)-S(5)-Cs(2)#7	101.37(14)	S(1)#3-Cs(1)-S(7)#7	62.07(9)
Cs(1)-S(5)-Cs(2)#7	84.84(13)	S(6)#4-Cs(1)-S(7)#7	130.08(14)
Cs(1)#2-S(5)-Cs(2)#7	171.62(18)	S(7)#2-Cs(1)-S(7)#7	93.22(12)
P(2)-S(5)-Cs(2)#5	139.0(3)	S(1)#2-Cs(1)-S(4)#11	66.54(9)
La(1)-S(5)-Cs(2)#5	91.49(15)	S(5)-Cs(1)-S(4)#11	127.97(14)
Cs(1)-S(5)-Cs(2)#5	94.66(12)	S(4)#3-Cs(1)-S(4)#11	93.98(12)
Cs(1)#2-S(5)-Cs(2)#5	115.44(12)	S(1)#3-Cs(1)-S(4)#11	115.52(9)
Cs(2)#7-S(5)-Cs(2)#5	68.31(10)	S(6)#4-Cs(1)-S(4)#11	100.93(13)
P(2)-S(6)-La(1)	86.46(19)	S(7)#2-Cs(1)-S(4)#11	67.28(11)
P(2)-S(6)-Cs(1)#8	87.3(2)	S(7)#7-Cs(1)-S(4)#11	53.46(9)
La(1)-S(6)-Cs(1)#8	172.0(2)	S(1)#2-Cs(1)-S(6)#3	116.91(9)
P(2)-S(6)-Cs(1)#3	105.6(2)	S(5)-Cs(1)-S(6)#3	64.34(10)
La(1)-S(6)-Cs(1)#3	90.02(17)	S(4)#3-Cs(1)-S(6)#3	70.93(13)
Cs(1)#8-S(6)-Cs(1)#3	86.94(11)	S(1)#3-Cs(1)-S(6)#3	60.59(9)
P(2)-S(6)-Cs(2)#7	71.9(2)	S(6)#4-Cs(1)-S(6)#3	93.06(11)
La(1)-S(6)-Cs(2)#7	100.88(14)	S(7)#2-Cs(1)-S(6)#3	100.78(13)
Cs(1)#8-S(6)-Cs(2)#7	81.79(14)	S(7)#7-Cs(1)-S(6)#3	120.62(11)
Cs(1)#3-S(6)-Cs(2)#7	168.54(17)	S(4)#11-Cs(1)-S(6)#3	164.67(13)
P(1)-S(7)-La(1)	97.9(2)	S(1)#2-Cs(1)-S(5)#2	60.78(9)
P(1)-S(7)-Cs(1)#2	86.9(2)	S(5)-Cs(1)-S(5)#2	92.66(12)
La(1)-S(7)-Cs(1)#2	92.53(16)	S(4)#3-Cs(1)-S(5)#2	96.49(13)
P(1)-S(7)-Cs(1)#6	87.7(2)	S(1)#3-Cs(1)-S(5)#2	116.74(9)
La(1)-S(7)-Cs(1)#6	174.34(18)	S(6)#4-Cs(1)-S(5)#2	63.12(10)

S(7)#2-Cs(1)-S(5)#2	75.21(12)	S(2)#1-Cs(2)-P(2)#6	152.98(8)
S(7)#7-Cs(1)-S(5)#2	166.24(13)	S(7)-Cs(2)-P(2)#6	86.63(11)
S(4)#11-Cs(1)-S(5)#2	125.49(11)	S(1)#9-Cs(2)-P(2)#6	30.68(7)
S(6)#3-Cs(1)-S(5)#2	56.16(7)	S(3)#1-Cs(2)-P(2)#6	107.42(10)
S(1)#2-Cs(1)-P(2)#4	29.96(8)	S(3)#5-Cs(2)-P(2)#6	105.50(10)
S(5)-Cs(1)-P(2)#4	92.78(10)	S(3)#6-Cs(2)-P(2)#6	71.17(7)
S(4)#3-Cs(1)-P(2)#4	137.38(9)	S(4)-Cs(2)-P(2)#6	91.74(11)
S(1)#3-Cs(1)-P(2)#4	149.80(9)	S(2)#1-Cs(2)-S(6)#6	149.05(10)
S(6)#4-Cs(1)-P(2)#4	30.59(9)	S(7)-Cs(2)-S(6)#6	113.93(13)
S(7)#2-Cs(1)-P(2)#4	86.54(10)	S(1)#9-Cs(2)-S(6)#6	53.39(11)
S(7)#7-Cs(1)-P(2)#4	137.93(10)	S(3)#1-Cs(2)-S(6)#6	85.11(9)
S(4)#11-Cs(1)-P(2)#4	88.59(10)	S(3)#5-Cs(2)-S(6)#6	131.32(9)
S(6)#3-Cs(1)-P(2)#4	100.60(10)	S(3)#6-Cs(2)-S(6)#6	56.05(11)
S(5)#2-Cs(1)-P(2)#4	50.22(9)	S(4)-Cs(2)-S(6)#6	94.57(12)
S(1)#2-Cs(1)-P(2)	149.95(9)	P(2)#6-Cs(2)-S(6)#6	30.12(10)
S(5)-Cs(1)-P(2)	30.28(10)	S(2)#1-Cs(2)-S(5)#6	159.33(10)
S(4)#3-Cs(1)-P(2)	87.57(10)	S(7)-Cs(2)-S(5)#6	88.55(12)
S(1)#3-Cs(1)-P(2)	29.81(7)	S(1)#9-Cs(2)-S(5)#6	52.73(11)
S(6)#4-Cs(1)-P(2)	92.29(10)	S(3)#1-Cs(2)-S(5)#6	133.79(9)
S(7)#2-Cs(1)-P(2)	141.70(9)	S(3)#5-Cs(2)-S(5)#6	82.53(9)
S(7)#7-Cs(1)-P(2)	84.39(10)	S(3)#6-Cs(2)-S(5)#6	57.72(11)
S(4)#11-Cs(1)-P(2)	133.84(9)	S(4)-Cs(2)-S(5)#6	117.92(13)
S(6)#3-Cs(1)-P(2)	50.72(9)	P(2)#6-Cs(2)-S(5)#6	29.89(10)
S(5)#2-Cs(1)-P(2)	100.01(9)	S(6)#6-Cs(2)-S(5)#6	48.80(6)
P(2)#4-Cs(1)-P(2)	120.05(9)	S(2)#1-Cs(2)-S(5)#1	56.92(10)
S(2)#1-Cs(2)-S(7)	73.85(11)	S(7)-Cs(2)-S(5)#1	130.07(12)
S(2)#1-Cs(2)-S(1)#9	122.69(8)	S(1)#9-Cs(2)-S(5)#1	155.77(11)
S(7)-Cs(2)-S(1)#9	60.69(11)	S(3)#1-Cs(2)-S(5)#1	56.13(8)
S(2)#1-Cs(2)-S(3)#1	64.77(8)	S(3)#5-Cs(2)-S(5)#1	103.81(9)
S(7)-Cs(2)-S(3)#1	111.63(9)	S(3)#6-Cs(2)-S(5)#1	79.73(10)
S(1)#9-Cs(2)-S(3)#1	100.52(10)	S(4)-Cs(2)-S(5)#1	99.90(12)
S(2)#1-Cs(2)-S(3)#5	78.48(8)	P(2)#6-Cs(2)-S(5)#1	142.34(11)
S(7)-Cs(2)-S(3)#5	54.61(9)	S(6)#6-Cs(2)-S(5)#1	112.69(12)
S(1)#9-Cs(2)-S(3)#5	99.42(10)	S(5)#6-Cs(2)-S(5)#1	137.12(6)
S(3)#1-Cs(2)-S(3)#5	143.24(10)	S(2)#1-Cs(2)-Cs(2)#12	114.07(6)
S(2)#1-Cs(2)-S(3)#6	134.87(8)	S(7)-Cs(2)-Cs(2)#12	100.52(8)
S(7)-Cs(2)-S(3)#6	143.34(12)	S(1)#9-Cs(2)-Cs(2)#12	107.21(8)
S(1)#9-Cs(2)-S(3)#6	101.84(7)	S(3)#1-Cs(2)-Cs(2)#12	145.00(5)
S(3)#1-Cs(2)-S(3)#6	102.87(12)	S(3)#5-Cs(2)-Cs(2)#12	51.66(5)
S(3)#5-Cs(2)-S(3)#6	102.82(12)	S(3)#6-Cs(2)-Cs(2)#12	51.16(9)
S(2)#1-Cs(2)-S(4)	62.43(11)	S(4)-Cs(2)-Cs(2)#12	160.26(8)
S(7)-Cs(2)-S(4)	59.74(8)	P(2)#6-Cs(2)-Cs(2)#12	87.36(7)
S(1)#9-Cs(2)-S(4)	65.20(11)	S(6)#6-Cs(2)-Cs(2)#12	94.49(8)
S(3)#1-Cs(2)-S(4)	53.46(9)	S(5)#6-Cs(2)-Cs(2)#12	57.78(8)
S(3)#5-Cs(2)-S(4)	110.03(10)	S(5)#1-Cs(2)-Cs(2)#12	92.70(8)
S(3)#6-Cs(2)-S(4)	146.09(12)		

Symmetry transformations used to generate equivalent atoms:

#1 -x+1/2,y+1/2,-z+1/2 #2 -x+1,-y+1,-z #3 -x+1,-y+2,-z

#4 x,y-1,z #5 -x+1/2,y-1/2,-z+1/2 #6 x-1,y,z

#7 x+1,y,z #8 x,y+1,z #9 -x,-y+2,-z #10 x-1,y+1,z

#11 x+1,y-1,z #12 -x-1/2,y-1/2,-z+1/2

Table D.20. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $Cs_2La(P_2S_6)_{1/2}(PS_4)$. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
La(1)	13(1)	12(1)	10(1)	1(1)	4(1)	-1(1)
P(1)	15(2)	18(3)	5(2)	3(2)	3(2)	4(3)
P(2)	13(2)	12(2)	9(2)	1(3)	5(1)	-3(3)
S(1)	11(2)	19(2)	17(2)	5(3)	7(2)	2(3)
S(2)	17(2)	13(2)	10(2)	0(2)	5(2)	-4(2)
S(3)	13(2)	25(2)	11(2)	-3(3)	4(2)	0(3)
S(4)	34(4)	10(2)	16(3)	-3(2)	6(3)	1(2)
S(5)	11(3)	14(2)	14(3)	6(2)	6(3)	2(2)
S(6)	30(4)	7(2)	13(4)	-2(2)	9(3)	-3(2)
S(7)	17(3)	14(2)	13(3)	3(2)	0(2)	-3(2)
Cs(1)	20(1)	11(1)	20(1)	-1(1)	10(1)	-1(1)
Cs(2)	18(1)	20(1)	21(1)	-2(1)	6(1)	0(1)

Table D.21. Crystal data and structure refinement for $Cs_2La(P_2Se_6)_{1/2}(PSe_4)$.

Identification code	p21n	
Empirical formula	$Cs_2La(P_2Se_6)_{1/2}(PSe_4)$	
Formula weight	1019.39	
Temperature	170(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 10.1923(18) Å	α= 90°.
	b = 7.2284(13) Å	β= 98.796(4)°.
	c = 20.446(3) Å	γ = 90°.
Volume	1488.6(4) $Å^3$	
Z	4	
Density (calculated)	4.548 Mg/m^3	
Absorption coefficient	24.976 mm^{-1}	
F(000)	1740	
Crystal size	0.06 x 0.06 x 0.12 mm^3	
Theta range for data collection	2.02 to 28.31°.	
Index ranges	-13<=h<=10, -8<=k<=9, -27<=l<=26	
Reflections collected	9815	
Independent reflections	3642 [R(int) = 0.0966]	
Completeness to theta = 28.31°	98.0 %	
Absorption correction	SADABS	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3642 / 0 / 110	
Goodness-of-fit on F^2	0.647	
Final R indices [I>2sigma(I)]	R1 = 0.0419, wR2 = 0.0682	
R indices (all data)	R1 = 0.1244, wR2 = 0.0811	
Extinction coefficient	0.00069(2)	
Largest diff. peak and hole	1.717 and -1.466 $e.Å^{-3}$	

Table D.22. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for $Cs_2La(P_2Se_6)_{1/2}(PSe_4)$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
La(1)	8082(1)	4802(1)	1499(1)	11(1)
Cs(1)	2584(1)	12(1)	198(1)	17(1)
Cs(2)	3551(1)	5084(2)	2002(1)	20(1)
Se(1)	7366(1)	4906(2)	-151(1)	13(1)
Se(2)	5886(2)	7664(2)	1036(1)	15(1)
Se(3)	8060(2)	748(2)	2188(1)	13(1)
Se(4)	335(1)	5079(2)	2658(1)	14(1)
Se(5)	282(2)	2526(2)	1006(1)	14(1)
Se(6)	180(2)	7433(2)	1015(1)	14(1)
Se(7)	5592(2)	2552(2)	965(1)	13(1)
P(1)	6061(3)	197(6)	1630(2)	10(1)
P(2)	9292(3)	4985(6)	-467(2)	11(1)

Table D.23. Bond lengths [Å] and angles [°] for $Cs_2La(P_2Se_6)_{1/2}(PSe_4)$.

La(1)-Se(4)#1	3.0434(16)	Se(4)-P(1)#8	2.189(3)
La(1)-Se(7)	3.0709(17)	Se(4)-La(1)#12	3.0434(16)
La(1)-Se(5)#1	3.0720(18)	Se(4)-Cs(2)#9	3.817(2)
La(1)-Se(2)	3.0888(18)	Se(4)-Cs(2)#8	3.823(2)
La(1)-Se(6)#1	3.1328(18)	Se(5)-P(2)#4	2.189(4)
La(1)-Se(3)#2	3.1600(17)	Se(5)-La(1)#12	3.0720(18)
La(1)-Se(3)	3.2526(18)	Se(5)-Cs(1)#7	3.9697(19)
La(1)-Se(1)	3.3414(16)	Se(6)-P(2)#4	2.188(4)
La(1)-Cs(2)	4.8862(14)	Se(6)-La(1)#12	3.1328(18)
La(1)-Cs(1)#3	4.8871(14)	Se(6)-Cs(1)#10	3.6776(18)
Cs(1)-Se(1)#3	3.557(2)	Se(6)-Cs(1)#6	3.9186(19)
Cs(1)-Se(5)	3.5676(18)	Se(7)-P(1)	2.186(4)
Cs(1)-Se(2)#4	3.5800(19)	Se(7)-Cs(1)#3	3.7271(19)
Cs(1)-Se(1)#4	3.675(2)	P(1)-Se(4)#9	2.189(3)
Cs(1)-Se(6)#5	3.6776(18)	P(1)-Se(2)#5	2.189(4)
Cs(1)-Se(7)	3.7094(18)	P(1)-Cs(1)#3	4.179(3)
Cs(1)-Se(7)#3	3.7271(19)	P(2)-Se(5)#4	2.189(4)
Cs(1)-Se(6)#6	3.9186(19)	P(2)-Se(6)#4	2.188(4)
Cs(1)-Se(2)#5	3.9217(18)	P(2)-P(2)#13	2.210(7)
Cs(1)-Se(5)#7	3.9697(19)	P(2)-Cs(2)#4	3.934(4)
Cs(1)-P(2)#3	4.163(4)	P(2)-Cs(1)#3	4.163(4)
Cs(1)-P(2)#4	4.166(4)	P(2)-Cs(1)#4	4.166(4)
Cs(2)-Se(3)#2	3.6266(18)		
Cs(2)-Se(7)	3.6774(19)	Se(4)#1-La(1)-Se(7)	142.76(5)
Cs(2)-Se(4)	3.7265(16)	Se(4)#1-La(1)-Se(5)#1	77.81(5)
Cs(2)-Se(1)#4	3.7573(17)	Se(7)-La(1)-Se(5)#1	101.81(5)
Cs(2)-Se(2)	3.806(2)	Se(4)#1-La(1)-Se(2)	128.29(5)
Cs(2)-Se(4)#8	3.817(2)	Se(7)-La(1)-Se(2)	74.04(5)
Cs(2)-Se(4)#9	3.823(2)	Se(5)#1-La(1)-Se(2)	142.10(5)
Cs(2)-P(2)#4	3.934(4)	Se(4)#1-La(1)-Se(6)#1	74.68(5)
Cs(2)-Se(5)	4.0735(19)	Se(7)-La(1)-Se(6)#1	140.87(5)
Cs(2)-Se(6)	4.0800(19)	Se(5)#1-La(1)-Se(6)#1	69.75(4)
Cs(2)-Cs(2)#8	4.8101(12)	Se(2)-La(1)-Se(6)#1	89.65(5)
Cs(2)-Cs(2)#9	4.8101(12)	Se(4)#1-La(1)-Se(3)#2	69.91(4)
Se(1)-P(2)	2.159(4)	Se(7)-La(1)-Se(3)#2	91.45(5)
Se(1)-Cs(1)#3	3.557(2)	Se(5)#1-La(1)-Se(3)#2	140.94(5)
Se(1)-Cs(1)#4	3.675(2)	Se(2)-La(1)-Se(3)#2	76.81(5)
Se(1)-Cs(2)#4	3.7573(17)	Se(6)#1-La(1)-Se(3)#2	119.66(5)
Se(2)-P(1)#10	2.189(4)	Se(4)#1-La(1)-Se(3)	77.10(5)
Se(2)-Cs(1)#4	3.5800(19)	Se(7)-La(1)-Se(3)	67.49(4)
Se(2)-Cs(1)#10	3.9217(18)	Se(5)#1-La(1)-Se(3)	73.34(5)
Se(3)-P(1)	2.214(4)	Se(2)-La(1)-Se(3)	133.13(5)
Se(3)-La(1)#11	3.1600(17)	Se(6)#1-La(1)-Se(3)	137.21(5)
Se(3)-Cs(2)#11	3.6266(18)	Se(3)#2-La(1)-Se(3)	78.42(3)

Se(4)#1-La(1)-Se(1)	143.77(4)	Se(5)-Cs(1)-Se(6)#6	65.99(3)
Se(7)-La(1)-Se(1)	67.15(4)	Se(2)#4-Cs(1)-Se(6)#6	71.43(4)
Se(5)#1-La(1)-Se(1)	74.86(4)	Se(1)#4-Cs(1)-Se(6)#6	61.57(3)
Se(2)-La(1)-Se(1)	68.84(4)	Se(6)#5-Cs(1)-Se(6)#6	93.56(4)
Se(6)#1-La(1)-Se(1)	73.83(4)	Se(7)-Cs(1)-Se(6)#6	120.12(4)
Se(3)#2-La(1)-Se(1)	143.21(5)	Se(7)#3-Cs(1)-Se(6)#6	102.20(4)
Se(3)-La(1)-Se(1)	116.28(5)	Se(1)#3-Cs(1)-Se(2)#5	64.17(4)
Se(4)#1-La(1)-Cs(2)	117.28(3)	Se(5)-Cs(1)-Se(2)#5	126.82(4)
Se(7)-La(1)-Cs(2)	48.76(4)	Se(2)#4-Cs(1)-Se(2)#5	94.22(4)
Se(5)#1-La(1)-Cs(2)	148.42(4)	Se(1)#4-Cs(1)-Se(2)#5	115.43(4)
Se(2)-La(1)-Cs(2)	51.16(4)	Se(6)#5-Cs(1)-Se(2)#5	99.74(4)
Se(6)#1-La(1)-Cs(2)	138.92(4)	Se(7)-Cs(1)-Se(2)#5	55.31(4)
Se(3)#2-La(1)-Cs(2)	47.89(3)	Se(7)#3-Cs(1)-Se(2)#5	65.47(4)
Se(3)-La(1)-Cs(2)	82.94(3)	Se(6)#6-Cs(1)-Se(2)#5	165.05(4)
Se(1)-La(1)-Cs(2)	98.28(3)	Se(1)#3-Cs(1)-Se(5)#7	62.20(4)
Se(4)#1-La(1)-Cs(1)#3	127.29(4)	Se(5)-Cs(1)-Se(5)#7	92.82(4)
Se(7)-La(1)-Cs(1)#3	49.68(3)	Se(2)#4-Cs(1)-Se(5)#7	97.95(4)
Se(5)#1-La(1)-Cs(1)#3	54.20(4)	Se(1)#4-Cs(1)-Se(5)#7	117.23(4)
Se(2)-La(1)-Cs(1)#3	104.11(4)	Se(6)#5-Cs(1)-Se(5)#7	64.49(3)
Se(6)#1-La(1)-Cs(1)#3	103.61(4)	Se(7)-Cs(1)-Se(5)#7	166.67(4)
Se(3)#2-La(1)-Cs(1)#3	136.72(4)	Se(7)#3-Cs(1)-Se(5)#7	76.47(4)
Se(3)-La(1)-Cs(1)#3	69.92(4)	Se(6)#6-Cs(1)-Se(5)#7	55.67(3)
Se(1)-La(1)-Cs(1)#3	46.71(3)	Se(2)#5-Cs(1)-Se(5)#7	124.88(4)
Cs(2)-La(1)-Cs(1)#3	98.40(2)	Se(1)#3-Cs(1)-P(2)#3	31.24(5)
Se(1)#3-Cs(1)-Se(5)	122.33(4)	Se(5)-Cs(1)-P(2)#3	91.88(6)
Se(1)#3-Cs(1)-Se(2)#4	116.12(4)	Se(2)#4-Cs(1)-P(2)#3	139.33(6)
Se(5)-Cs(1)-Se(2)#4	118.41(5)	Se(1)#4-Cs(1)-P(2)#3	151.56(6)
Se(1)#3-Cs(1)-Se(1)#4	176.34(5)	Se(6)#5-Cs(1)-P(2)#3	31.64(5)
Se(5)-Cs(1)-Se(1)#4	61.04(4)	Se(7)-Cs(1)-P(2)#3	137.76(6)
Se(2)#4-Cs(1)-Se(1)#4	60.22(4)	Se(7)#3-Cs(1)-P(2)#3	86.37(6)
Se(1)#3-Cs(1)-Se(6)#5	61.24(4)	Se(6)#6-Cs(1)-P(2)#3	101.09(6)
Se(5)-Cs(1)-Se(6)#5	61.09(3)	Se(2)#5-Cs(1)-P(2)#3	87.00(6)
Se(2)#4-Cs(1)-Se(6)#5	161.84(4)	Se(5)#7-Cs(1)-P(2)#3	51.07(5)
Se(1)#4-Cs(1)-Se(6)#5	122.11(4)	Se(1)#3-Cs(1)-P(2)#4	151.63(6)
Se(1)#3-Cs(1)-Se(7)	119.45(4)	Se(5)-Cs(1)-P(2)#4	31.69(5)
Se(5)-Cs(1)-Se(7)	96.42(4)	Se(2)#4-Cs(1)-P(2)#4	86.79(6)
Se(2)#4-Cs(1)-Se(7)	69.18(4)	Se(1)#4-Cs(1)-P(2)#4	31.17(5)
Se(1)#4-Cs(1)-Se(7)	60.16(4)	Se(6)#5-Cs(1)-P(2)#4	91.66(6)
Se(6)#5-Cs(1)-Se(7)	128.62(4)	Se(7)-Cs(1)-P(2)#4	83.16(6)
Se(1)#3-Cs(1)-Se(7)#3	58.34(4)	Se(7)#3-Cs(1)-P(2)#4	143.09(6)
Se(5)-Cs(1)-Se(7)#3	167.52(4)	Se(6)#6-Cs(1)-P(2)#4	51.27(5)
Se(2)#4-Cs(1)-Se(7)#3	58.04(3)	Se(2)#5-Cs(1)-P(2)#4	134.31(6)
Se(1)#4-Cs(1)-Se(7)#3	118.04(4)	Se(5)#7-Cs(1)-P(2)#4	100.02(6)
Se(6)#5-Cs(1)-Se(7)#3	118.00(4)	P(2)#3-Cs(1)-P(2)#4	120.43(8)
Se(7)-Cs(1)-Se(7)#3	93.15(4)	Se(3)#2-Cs(2)-Se(7)	75.30(4)
Se(1)#3-Cs(1)-Se(6)#6	117.77(4)	Se(3)#2-Cs(2)-Se(4)	131.65(4)

Se(7)-Cs(2)-Se(4)	144.42(5)	Se(1)#4-Cs(2)-Cs(2)#8	111.51(4)
Se(3)#2-Cs(2)-Se(1)#4	122.19(4)	Se(2)-Cs(2)-Cs(2)#8	101.88(3)
Se(7)-Cs(2)-Se(1)#4	59.70(4)	Se(4)#8-Cs(2)-Cs(2)#8	49.56(2)
Se(4)-Cs(2)-Se(1)#4	105.38(4)	Se(4)#9-Cs(2)-Cs(2)#8	140.62(4)
Se(3)#2-Cs(2)-Se(2)	62.92(4)	P(2)#4-Cs(2)-Cs(2)#8	91.48(6)
Se(7)-Cs(2)-Se(2)	59.39(3)	Se(5)-Cs(2)-Cs(2)#8	99.74(4)
Se(4)-Cs(2)-Se(2)	147.29(5)	Se(6)-Cs(2)-Cs(2)#8	60.04(3)
Se(1)#4-Cs(2)-Se(2)	63.59(4)	Se(3)#2-Cs(2)-Cs(2)#9	111.16(4)
Se(3)#2-Cs(2)-Se(4)#8	63.62(3)	Se(7)-Cs(2)-Cs(2)#9	101.43(3)
Se(7)-Cs(2)-Se(4)#8	113.41(4)	Se(4)-Cs(2)-Cs(2)#9	51.22(4)
Se(4)-Cs(2)-Se(4)#8	100.87(5)	Se(1)#4-Cs(2)-Cs(2)#9	111.69(4)
Se(1)#4-Cs(2)-Se(4)#8	101.72(4)	Se(2)-Cs(2)-Cs(2)#9	160.48(3)
Se(2)-Cs(2)-Se(4)#8	55.87(3)	Se(4)#8-Cs(2)-Cs(2)#9	140.62(4)
Se(3)#2-Cs(2)-Se(4)#9	78.86(4)	Se(4)#9-Cs(2)-Cs(2)#9	49.54(2)
Se(7)-Cs(2)-Se(4)#9	57.03(4)	P(2)#4-Cs(2)-Cs(2)#9	90.39(6)
Se(4)-Cs(2)-Se(4)#9	100.76(5)	Se(5)-Cs(2)-Cs(2)#9	59.14(3)
Se(1)#4-Cs(2)-Se(4)#9	101.91(4)	Se(6)-Cs(2)-Cs(2)#9	97.24(4)
Se(2)-Cs(2)-Se(4)#9	111.50(4)	Cs(2)#8-Cs(2)-Cs(2)#9	97.42(3)
Se(4)#8-Cs(2)-Se(4)#9	142.21(5)	P(2)-Se(1)-La(1)	103.55(10)
Se(3)#2-Cs(2)-P(2)#4	154.17(6)	P(2)-Se(1)-Cs(1)#3	90.05(12)
Se(7)-Cs(2)-P(2)#4	86.91(6)	La(1)-Se(1)-Cs(1)#3	90.16(4)
Se(4)-Cs(2)-P(2)#4	72.89(6)	P(2)-Se(1)-Cs(1)#4	87.07(12)
Se(1)#4-Cs(2)-P(2)#4	32.51(5)	La(1)-Se(1)-Cs(1)#4	92.71(4)
Se(2)-Cs(2)-P(2)#4	91.99(6)	Cs(1)#3-Se(1)-Cs(1)#4	176.34(5)
Se(4)#8-Cs(2)-P(2)#4	108.64(7)	P(2)-Se(1)-Cs(2)#4	78.25(10)
Se(4)#9-Cs(2)-P(2)#4	107.17(7)	La(1)-Se(1)-Cs(2)#4	177.87(5)
Se(3)#2-Cs(2)-Se(5)	159.64(5)	Cs(1)#3-Se(1)-Cs(2)#4	88.69(4)
Se(7)-Cs(2)-Se(5)	88.72(4)	Cs(1)#4-Se(1)-Cs(2)#4	88.52(4)
Se(4)-Cs(2)-Se(5)	58.80(4)	P(1)#10-Se(2)-La(1)	113.35(11)
Se(1)#4-Cs(2)-Se(5)	55.87(3)	P(1)#10-Se(2)-Cs(1)#4	89.49(10)
Se(2)-Cs(2)-Se(5)	119.46(4)	La(1)-Se(2)-Cs(1)#4	99.03(5)
Se(4)#8-Cs(2)-Se(5)	135.90(4)	P(1)#10-Se(2)-Cs(2)	97.26(11)
Se(4)#9-Cs(2)-Se(5)	81.89(4)	La(1)-Se(2)-Cs(2)	89.64(4)
P(2)#4-Cs(2)-Se(5)	31.66(6)	Cs(1)#4-Se(2)-Cs(2)	165.93(5)
Se(3)#2-Cs(2)-Se(6)	147.36(5)	P(1)#10-Se(2)-Cs(1)#10	82.66(10)
Se(7)-Cs(2)-Se(6)	115.44(4)	La(1)-Se(2)-Cs(1)#10	163.16(6)
Se(4)-Cs(2)-Se(6)	57.15(4)	Cs(1)#4-Se(2)-Cs(1)#10	85.78(4)
Se(1)#4-Cs(2)-Se(6)	55.93(3)	Cs(2)-Se(2)-Cs(1)#10	82.87(4)
Se(2)-Cs(2)-Se(6)	94.90(4)	P(1)-Se(3)-La(1)#11	88.26(10)
Se(4)#8-Cs(2)-Se(6)	84.32(4)	P(1)-Se(3)-La(1)	90.32(11)
Se(4)#9-Cs(2)-Se(6)	133.47(4)	La(1)#11-Se(3)-La(1)	126.21(5)
P(2)#4-Cs(2)-Se(6)	31.62(6)	P(1)-Se(3)-Cs(2)#11	161.56(12)
Se(5)-Cs(2)-Se(6)	51.59(3)	La(1)#11-Se(3)-Cs(2)#11	91.84(4)
Se(3)#2-Cs(2)-Cs(2)#8	99.32(4)	La(1)-Se(3)-Cs(2)#11	104.36(4)
Se(7)-Cs(2)-Cs(2)#8	161.09(4)	P(1)#8-Se(4)-La(1)#12	91.76(10)
Se(4)-Cs(2)-Cs(2)#8	51.31(4)	P(1)#8-Se(4)-Cs(2)	159.52(10)

La(1)#12-Se(4)-Cs(2)	108.70(4)
P(1)#8-Se(4)-Cs(2)#9	96.93(12)
La(1)#12-Se(4)-Cs(2)#9	104.32(5)
Cs(2)-Se(4)-Cs(2)#9	79.22(4)
P(1)#8-Se(4)-Cs(2)#8	92.71(12)
La(1)#12-Se(4)-Cs(2)#8	111.83(5)
Cs(2)-Se(4)-Cs(2)#8	79.15(4)
Cs(2)#9-Se(4)-Cs(2)#8	142.21(5)
P(2)#4-Se(5)-La(1)#12	86.35(10)
P(2)#4-Se(5)-Cs(1)	89.40(11)
La(1)#12-Se(5)-Cs(1)	171.63(6)
P(2)#4-Se(5)-Cs(1)#7	104.54(11)
La(1)#12-Se(5)-Cs(1)#7	86.92(4)
Cs(1)-Se(5)-Cs(1)#7	87.18(4)
P(2)#4-Se(5)-Cs(2)	70.65(10)
La(1)#12-Se(5)-Cs(2)	100.11(5)
Cs(1)-Se(5)-Cs(2)	85.24(4)
Cs(1)#7-Se(5)-Cs(2)	171.04(5)
P(2)#4-Se(6)-La(1)#12	84.85(11)
P(2)#4-Se(6)-Cs(1)#10	86.50(11)
La(1)#12-Se(6)-Cs(1)#10	170.28(6)
P(2)#4-Se(6)-Cs(1)#6	105.18(11)
La(1)#12-Se(6)-Cs(1)#6	91.54(4)
Cs(1)#10-Se(6)-Cs(1)#6	86.44(4)
P(2)#4-Se(6)-Cs(2)	70.50(10)
La(1)#12-Se(6)-Cs(2)	98.92(5)
Cs(1)#10-Se(6)-Cs(2)	82.32(4)
Cs(1)#6-Se(6)-Cs(2)	168.16(5)
P(1)-Se(7)-La(1)	95.78(10)
P(1)-Se(7)-Cs(2)	96.78(11)
La(1)-Se(7)-Cs(2)	92.34(5)
P(1)-Se(7)-Cs(1)	88.02(10)
La(1)-Se(7)-Cs(1)	175.69(6)
Cs(2)-Se(7)-Cs(1)	89.21(4)
P(1)-Se(7)-Cs(1)#3	85.77(11)
La(1)-Se(7)-Cs(1)#3	91.41(4)
Cs(2)-Se(7)-Cs(1)#3	175.24(5)
Cs(1)-Se(7)-Cs(1)#3	86.85(4)
Se(4)#9-P(1)-Se(7)	109.98(17)
Se(4)#9-P(1)-Se(2)#5	109.32(18)
Se(7)-P(1)-Se(2)#5	108.34(15)
Se(4)#9-P(1)-Se(3)	107.73(15)
Se(7)-P(1)-Se(3)	106.09(17)
Se(2)#5-P(1)-Se(3)	115.29(17)
Se(4)#9-P(1)-Cs(1)#3	158.62(14)
Se(7)-P(1)-Cs(1)#3	62.79(9)
Se(2)#5-P(1)-Cs(1)#3	58.93(9)
Se(3)-P(1)-Cs(1)#3	93.65(10)
Se(4)#9-P(1)-Cs(1)	84.17(10)
Se(7)-P(1)-Cs(1)	60.97(9)
Se(2)#5-P(1)-Cs(1)	66.54(9)
Se(3)-P(1)-Cs(1)	165.44(14)
Cs(1)#3-P(1)-Cs(1)	74.76(6)
Se(1)-P(2)-Se(5)#4	115.61(18)
Se(1)-P(2)-Se(6)#4	116.01(18)
Se(5)#4-P(2)-Se(6)#4	108.36(15)
Se(1)-P(2)-P(2)#13	104.2(2)
Se(5)#4-P(2)-P(2)#13	105.9(3)
Se(6)#4-P(2)-P(2)#13	105.7(3)
Se(1)-P(2)-Cs(2)#4	69.25(9)
Se(5)#4-P(2)-Cs(2)#4	77.69(10)
Se(6)#4-P(2)-Cs(2)#4	77.88(10)
P(2)#13-P(2)-Cs(2)#4	173.5(2)
Se(1)-P(2)-Cs(1)#3	58.71(10)
Se(5)#4-P(2)-Cs(1)#3	155.58(14)
Se(6)#4-P(2)-Cs(1)#3	61.86(10)
P(2)#13-P(2)-Cs(1)#3	98.4(2)
Cs(2)#4-P(2)-Cs(1)#3	78.30(7)
Se(1)-P(2)-Cs(1)#4	61.76(10)
Se(5)#4-P(2)-Cs(1)#4	58.91(10)
Se(6)#4-P(2)-Cs(1)#4	156.21(14)
P(2)#13-P(2)-Cs(1)#4	97.5(2)
Cs(2)#4-P(2)-Cs(1)#4	79.59(7)
Cs(1)#3-P(2)-Cs(1)#4	120.43(8)

Symmetry transformations used to generate equivalent atoms:
#1 x+1,y,z #2 -x+3/2,y+1/2,-z+1/2 #3 -x+1,-y,-z
#4 -x+1,-y+1,-z #5 x,y-1,z #6 -x,-y+1,-z
#7 -x,-y,-z #8 -x+1/2,y+1/2,-z+1/2 #9 -x+1/2,y-1/2,-z+1/2
#10 x,y+1,z #11 -x+3/2,y-1/2,-z+1/2 #12 x-1,y,z
#13 -x+2,-y+1,-z

Table D.24. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $Cs_2La(P_2Se_6)_{1/2}(PSe_4)$. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
La(1)	11(1)	9(1)	14(1)	0(1)	5(1)	0(1)
Cs(1)	19(1)	9(1)	24(1)	-1(1)	9(1)	-1(1)
Cs(2)	16(1)	20(1)	25(1)	-2(1)	5(1)	-1(1)
Se(1)	12(1)	11(1)	17(1)	-2(1)	6(1)	0(1)
Se(2)	21(1)	7(1)	16(1)	-3(1)	3(1)	2(1)
Se(3)	11(1)	13(1)	15(1)	2(1)	1(1)	-2(1)
Se(4)	13(1)	16(1)	15(1)	-1(1)	5(1)	-1(1)
Se(5)	19(1)	8(1)	16(i)	3(1)	7(1)	2(1)
Se(6)	18(1)	7(1)	17(1)	-3(1)	8(1)	-1(1)
Se(7)	15(1)	7(1)	17(1)	3(1)	1(1)	0(1)
P(1)	8(2)	9(2)	13(2)	4(2)	2(2)	1(2)
P(2)	16(2)	3(2)	18(2)	-2(2)	7(2)	-1(2)

Appendix E:

Supplementary Information for Chapter Five

Table E.1. Crystal data and structure refinement for $K_2EuSiSe_5$.

Identification code	p21c	
Empirical formula	$K_2EuSiSe_5$	
Formula weight	653.05	
Temperature	171(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 11.669(3) Å	α= 90°.
	b = 9.844(2) Å	β= 91.583(5)°.
	c = 8.917(2) Å	γ = 90°.
Volume	1023.9(4) $Å^3$	
Z	4	
Density (calculated)	4.236 Mg/m^3	
Absorption coefficient	24.751 mm^{-1}	
F(000)	1140	
Crystal size	0.18 x 0.09 x 0.02 mm^3	
Theta range for data collection	1.75 to 28.32°.	
Index ranges	-15<=h<=13, -12<=k<=12, -11<=l<=11	
Reflections collected	6822	
Independent reflections	2477 [R(int) = 0.0880]	
Completeness to theta = 28.32°	97.1 %	
Absorption correction	SADABS	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2477 / 0 / 83	
Goodness-of-fit on F^2	1.010	
Final R indices [I>2sigma(I)]	R1 = 0.0519, wR2 = 0.1138	
R indices (all data)	R1 = 0.0733, wR2 = 0.1206	
Extinction coefficient	0.0133(5)	
Largest diff. peak and hole	2.542 and -2.773 $e.Å^{-3}$	

Table E.2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for $K_2EuSiSe_5$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Eu(1)	4838(1)	7337(1)	1029(1)	9(1)
Se(1)	4063(1)	4363(1)	1556(1)	10(1)
Se(2)	3977(1)	405(1)	1390(1)	9(1)
Se(3)	2855(1)	7404(1)	-1505(1)	11(1)
Se(4)	742(1)	159(1)	1947(1)	13(1)
Se(5)	7573(1)	6220(1)	56(1)	11(1)
K(1)	8041(2)	9419(3)	1282(3)	14(1)
K(2)	602(3)	6973(3)	443(3)	25(1)
Si(1)	2526(3)	9782(3)	2879(3)	8(1)

Table E.3. Bond lengths [Å] and angles [°] for $K_2EuSiSe_5$.

Eu(1)-Se(1)	3.1040(14)	K(1)-Se(5)#4	3.482(3)
Eu(1)-Se(1)#1	3.1495(13)	K(1)-Si(1)#8	3.833(4)
Eu(1)-Se(1)#2	3.1788(13)	K(1)-K(2)#13	3.925(4)
Eu(1)-Se(3)	3.1904(15)	K(1)-K(2)#2	4.136(4)
Eu(1)-Se(2)#3	3.2017(14)	K(1)-K(2)#8	4.198(4)
Eu(1)-Se(3)#4	3.2462(14)	K(2)-Se(4)#15	3.357(3)
Eu(1)-Se(2)#2	3.2634(13)	K(2)-Se(4)#3	3.413(3)
Eu(1)-Se(2)#1	3.4166(13)	K(2)-Se(5)#16	3.618(3)
Eu(1)-Se(5)	3.5075(15)	K(2)-Si(1)#5	3.679(4)
Eu(1)-K(1)	4.263(3)	K(2)-Se(4)#17	3.765(3)
Eu(1)-Eu(1)#4	4.4703(10)	K(2)-Se(3)#4	3.782(3)
Eu(1)-Eu(1)#5	4.4703(10)	K(2)-Se(5)#1	3.829(3)
Se(1)-Se(5)#1	2.4271(17)	K(2)-Se(4)#12	3.846(3)
Se(1)-Eu(1)#1	3.1495(13)	K(2)-K(1)#16	3.925(4)
Se(1)-K(1)#6	3.164(3)	K(2)-K(1)#6	4.136(4)
Se(1)-Eu(1)#6	3.1788(13)	K(2)-K(2)#12	4.197(6)
Se(2)-Si(1)#7	2.264(3)	Si(1)-Se(3)#4	2.251(3)
Se(2)-Eu(1)#7	3.2017(14)	Si(1)-Se(4)#3	2.251(3)
Se(2)-Eu(1)#6	3.2634(13)	Si(1)-Se(2)#3	2.264(3)
Se(2)-K(1)#1	3.308(3)	Si(1)-Se(5)#2	2.328(3)
Se(2)-Eu(1)#1	3.4167(13)	Si(1)-K(2)#4	3.679(4)
Se(3)-Si(1)#5	2.251(3)	Si(1)-K(1)#8	3.833(4)
Se(3)-K(2)	3.219(3)		
Se(3)-Eu(1)#5	3.2462(14)	Se(1)-Eu(1)-Se(1)#1	74.69(4)
Se(3)-K(1)#8	3.306(3)	Se(1)-Eu(1)-Se(1)#2	127.07(3)
Se(3)-K(2)#5	3.782(4)	Se(1)#1-Eu(1)-Se(1)#2	131.63(5)
Se(4)-Si(1)#7	2.251(3)	Se(1)-Eu(1)-Se(3)	85.30(3)
Se(4)-K(1)#1	3.272(3)	Se(1)#1-Eu(1)-Se(3)	78.14(3)
Se(4)-K(1)#9	3.273(3)	Se(1)#2-Eu(1)-Se(3)	137.57(3)
Se(4)-K(2)#10	3.357(3)	Se(1)-Eu(1)-Se(2)#3	141.35(4)
Se(4)-K(2)#7	3.413(3)	Se(1)#1-Eu(1)-Se(2)#3	135.23(3)
Se(4)-K(2)#11	3.765(3)	Se(1)#2-Eu(1)-Se(2)#3	57.45(3)
Se(4)-K(2)#12	3.846(3)	Se(3)-Eu(1)-Se(2)#3	80.12(3)
Se(5)-Si(1)#6	2.328(3)	Se(1)-Eu(1)-Se(3)#4	75.85(3)
Se(5)-Se(1)#1	2.4271(17)	Se(1)#1-Eu(1)-Se(3)#4	148.19(3)
Se(5)-K(1)	3.372(3)	Se(1)#2-Eu(1)-Se(3)#4	76.91(3)
Se(5)-K(1)#5	3.482(3)	Se(3)-Eu(1)-Se(3)#4	87.79(4)
Se(5)-K(2)#13	3.618(3)	Se(2)#3-Eu(1)-Se(3)#4	68.04(3)
Se(5)-K(2)#1	3.829(3)	Se(1)-Eu(1)-Se(2)#2	57.52(3)
K(1)-Se(1)#2	3.164(3)	Se(1)#1-Eu(1)-Se(2)#2	91.92(4)
K(1)-Se(4)#1	3.272(3)	Se(1)#2-Eu(1)-Se(2)#2	74.50(3)
K(1)-Se(4)#14	3.273(3)	Se(3)-Eu(1)-Se(2)#2	142.79(3)
K(1)-Se(3)#8	3.306(3)	Se(2)#3-Eu(1)-Se(2)#2	127.36(3)
K(1)-Se(2)#1	3.308(3)	Se(3)#4-Eu(1)-Se(2)#2	82.20(3)

Se(1)-Eu(1)-Se(2)#1	146.52(3)	Se(5)#1-Se(1)-Eu(1)#1	76.74(4)
Se(1)#1-Eu(1)-Se(2)#1	72.75(3)	Eu(1)-Se(1)-Eu(1)#1	105.31(4)
Se(1)#2-Eu(1)-Se(2)#1	81.78(3)	Se(5)#1-Se(1)-K(1)#6	75.76(6)
Se(3)-Eu(1)-Se(2)#1	80.66(3)	Eu(1)-Se(1)-K(1)#6	108.06(6)
Se(2)#3-Eu(1)-Se(2)#1	65.38(4)	Eu(1)#1-Se(1)-K(1)#6	142.54(6)
Se(3)#4-Eu(1)-Se(2)#1	133.24(3)	Se(5)#1-Se(1)-Eu(1)#6	123.30(5)
Se(2)#2-Eu(1)-Se(2)#1	130.81(4)	Eu(1)-Se(1)-Eu(1)#6	125.49(4)
Se(1)-Eu(1)-Se(5)	90.72(3)	Eu(1)#1-Se(1)-Eu(1)#6	89.88(3)
Se(1)#1-Eu(1)-Se(5)	42.34(3)	K(1)#6-Se(1)-Eu(1)#6	84.45(6)
Se(1)#2-Eu(1)-Se(5)	90.66(3)	Si(1)#7-Se(2)-Eu(1)#7	92.61(9)
Se(3)-Eu(1)-Se(5)	118.59(4)	Si(1)#7-Se(2)-Eu(1)#6	93.06(9)
Se(2)#3-Eu(1)-Se(5)	127.65(3)	Eu(1)#7-Se(2)-Eu(1)#6	119.52(4)
Se(3)#4-Eu(1)-Se(5)	149.64(3)	Si(1)#7-Se(2)-K(1)#1	84.71(10)
Se(2)#2-Eu(1)-Se(5)	67.73(3)	Eu(1)#7-Se(2)-K(1)#1	101.31(5)
Se(2)#1-Eu(1)-Se(5)	70.17(3)	Eu(1)#6-Se(2)-K(1)#1	139.17(6)
Se(1)-Eu(1)-K(1)	134.75(4)	Si(1)#7-Se(2)-Eu(1)#1	150.28(9)
Se(1)#1-Eu(1)-K(1)	85.41(4)	Eu(1)#7-Se(2)-Eu(1)#1	114.62(4)
Se(1)#2-Eu(1)-K(1)	47.63(4)	Eu(1)#6-Se(2)-Eu(1)#1	83.98(3)
Se(3)-Eu(1)-K(1)	130.19(4)	K(1)#1-Se(2)-Eu(1)#1	78.66(5)
Se(2)#3-Eu(1)-K(1)	79.54(4)	Si(1)#5-Se(3)-Eu(1)	105.57(9)
Se(3)#4-Eu(1)-K(1)	124.53(4)	Si(1)#5-Se(3)-K(2)	82.51(10)
Se(2)#2-Eu(1)-K(1)	83.63(4)	Eu(1)-Se(3)-K(2)	101.67(7)
Se(2)#1-Eu(1)-K(1)	49.54(4)	Si(1)#5-Se(3)-Eu(1)#5	91.70(9)
Se(5)-Eu(1)-K(1)	50.30(4)	Eu(1)-Se(3)-Eu(1)#5	87.97(4)
Se(1)-Eu(1)-Eu(1)#4	84.76(3)	K(2)-Se(3)-Eu(1)#5	169.77(7)
Se(1)#1-Eu(1)-Eu(1)#4	141.20(3)	Si(1)#5-Se(3)-K(1)#8	150.15(10)
Se(1)#2-Eu(1)-Eu(1)#4	44.79(2)	Eu(1)-Se(3)-K(1)#8	101.60(5)
Se(3)-Eu(1)-Eu(1)#4	133.24(3)	K(2)-Se(3)-K(1)#8	80.09(7)
Se(2)#3-Eu(1)-Eu(1)#4	79.82(3)	Eu(1)#5-Se(3)-K(1)#8	101.47(5)
Se(3)#4-Eu(1)-Eu(1)#4	45.50(3)	Si(1)#5-Se(3)-K(2)#5	82.49(10)
Se(2)#2-Eu(1)-Eu(1)#4	49.47(2)	Eu(1)-Se(3)-K(2)#5	171.66(6)
Se(2)#1-Eu(1)-Eu(1)#4	126.46(3)	K(2)-Se(3)-K(2)#5	81.25(8)
Se(5)-Eu(1)-Eu(1)#4	107.12(2)	Eu(1)#5-Se(3)-K(2)#5	89.67(6)
K(1)-Eu(1)-Eu(1)#4	86.38(4)	K(1)#8-Se(3)-K(2)#5	71.04(7)
Se(1)-Eu(1)-Eu(1)#5	103.11(3)	Si(1)#7-Se(4)-K(1)#1	85.78(10)
Se(1)#1-Eu(1)-Eu(1)#5	45.32(2)	Si(1)#7-Se(4)-K(1)#9	155.02(10)
Se(1)#2-Eu(1)-Eu(1)#5	128.28(3)	K(1)#1-Se(4)-K(1)#9	107.94(6)
Se(3)-Eu(1)-Eu(1)#5	46.53(3)	Si(1)#7-Se(4)-K(2)#10	106.06(10)
Se(2)#3-Eu(1)-Eu(1)#5	92.37(3)	K(1)#1-Se(4)-K(2)#10	139.91(8)
Se(3)#4-Eu(1)-Eu(1)#5	133.60(3)	K(1)#9-Se(4)-K(2)#10	77.18(8)
Se(2)#2-Eu(1)-Eu(1)#5	137.18(3)	Si(1)#7-Se(4)-K(2)#7	91.59(10)
Se(2)#1-Eu(1)-Eu(1)#5	46.55(2)	K(1)#1-Se(4)-K(2)#7	77.78(7)
Se(5)-Eu(1)-Eu(1)#5	75.57(2)	K(1)#9-Se(4)-K(2)#7	71.86(7)
K(1)-Eu(1)-Eu(1)#5	89.66(4)	K(2)#10-Se(4)-K(2)#7	137.99(7)
Eu(1)#4-Eu(1)-Eu(1)#5	171.76(3)	Si(1)#7-Se(4)-K(2)#11	70.34(10)
Se(5)#1-Se(1)-Eu(1)	111.15(5)	K(1)#1-Se(4)-K(2)#11	146.03(7)

K(1)#9-Se(4)-K(2)#11	87.84(7)	Se(4)#1-K(1)-Se(5)#4	163.14(9)
K(2)#10-Se(4)-K(2)#11	71.97(8)	Se(4)#14-K(1)-Se(5)#4	92.34(7)
K(2)#7-Se(4)-K(2)#11	79.08(4)	Se(3)#8-K(1)-Se(5)#4	93.11(7)
Si(1)#7-Se(4)-K(2)#12	133.18(10)	Se(2)#1-K(1)-Se(5)#4	125.33(8)
K(1)#1-Se(4)-K(2)#12	66.37(7)	Se(5)-K(1)-Se(5)#4	96.68(7)
K(1)#9-Se(4)-K(2)#12	71.77(7)	Se(1)#2-K(1)-Si(1)#8	118.51(9)
K(2)#10-Se(4)-K(2)#12	78.61(5)	Se(4)#1-K(1)-Si(1)#8	35.86(6)
K(2)#7-Se(4)-K(2)#12	116.26(6)	Se(4)#14-K(1)-Si(1)#8	105.64(8)
K(2)#11-Se(4)-K(2)#12	147.31(5)	Se(3)#8-K(1)-Si(1)#8	79.50(7)
Si(1)#6-Se(5)-Se(1)#1	105.61(9)	Se(2)#1-K(1)-Si(1)#8	36.04(6)
Si(1)#6-Se(5)-K(1)	108.82(10)	Se(5)-K(1)-Si(1)#8	81.71(7)
Se(1)#1-Se(5)-K(1)	122.02(7)	Se(5)#4-K(1)-Si(1)#8	160.98(10)
Si(1)#6-Se(5)-K(1)#5	131.87(10)	Se(1)#2-K(1)-K(2)#13	135.48(9)
Se(1)#1-Se(5)-K(1)#5	61.74(6)	Se(4)#1-K(1)-K(2)#13	63.84(6)
K(1)-Se(5)-K(1)#5	116.97(7)	Se(4)#14-K(1)-K(2)#13	55.72(6)
Si(1)#6-Se(5)-Eu(1)	85.94(9)	Se(3)#8-K(1)-K(2)#13	146.67(9)
Se(1)#1-Se(5)-Eu(1)	60.92(4)	Se(2)#1-K(1)-K(2)#13	115.18(9)
K(1)-Se(5)-Eu(1)	76.55(5)	Se(5)-K(1)-K(2)#13	58.85(6)
K(1)#5-Se(5)-Eu(1)	117.63(5)	Se(5)#4-K(1)-K(2)#13	102.35(8)
Si(1)#6-Se(5)-K(2)#13	96.84(10)	Si(1)#8-K(1)-K(2)#13	93.07(9)
Se(1)#1-Se(5)-K(2)#13	148.80(7)	Se(1)#2-K(1)-K(2)#2	82.46(7)
K(1)-Se(5)-K(2)#13	68.22(7)	Se(4)#1-K(1)-K(2)#2	112.15(8)
K(1)#5-Se(5)-K(2)#13	87.16(7)	Se(4)#14-K(1)-K(2)#2	52.31(6)
Eu(1)-Se(5)-K(2)#13	143.65(6)	Se(3)#8-K(1)-K(2)#2	59.85(6)
Si(1)#6-Se(5)-K(2)#1	68.47(9)	Se(2)#1-K(1)-K(2)#2	136.71(9)
Se(1)#1-Se(5)-K(2)#1	99.69(6)	Se(5)-K(1)-K(2)#2	148.41(9)
K(1)-Se(5)-K(2)#1	135.92(7)	Se(5)#4-K(1)-K(2)#2	59.62(6)
K(1)#5-Se(5)-K(2)#1	68.71(6)	Si(1)#8-K(1)-K(2)#2	127.70(9)
Eu(1)-Se(5)-K(2)#1	143.02(6)	K(2)#13-K(1)-K(2)#2	103.22(7)
K(2)#13-Se(5)-K(2)#1	68.55(8)	Se(1)#2-K(1)-K(2)#8	123.02(8)
Se(1)#2-K(1)-Se(4)#1	154.35(10)	Se(4)#1-K(1)-K(2)#8	52.61(6)
Se(1)#2-K(1)-Se(4)#14	130.77(9)	Se(4)#14-K(1)-K(2)#8	60.46(6)
Se(4)#1-K(1)-Se(4)#14	72.06(6)	Se(3)#8-K(1)-K(2)#8	49.05(6)
Se(1)#2-K(1)-Se(3)#8	74.21(6)	Se(2)#1-K(1)-K(2)#8	87.71(7)
Se(4)#1-K(1)-Se(3)#8	94.50(7)	Se(5)-K(1)-K(2)#8	136.93(9)
Se(4)#14-K(1)-Se(3)#8	94.76(7)	Se(5)#4-K(1)-K(2)#8	125.28(8)
Se(1)#2-K(1)-Se(2)#1	83.74(7)	Si(1)#8-K(1)-K(2)#8	61.87(7)
Se(4)#1-K(1)-Se(2)#1	71.16(6)	K(2)#13-K(1)-K(2)#8	98.76(8)
Se(4)#14-K(1)-Se(2)#1	141.41(9)	K(2)#2-K(1)-K(2)#8	66.63(5)
Se(3)#8-K(1)-Se(2)#1	76.92(6)	Se(1)#2-K(1)-Eu(1)	47.92(4)
Se(1)#2-K(1)-Se(5)	93.43(7)	Se(4)#1-K(1)-Eu(1)	114.57(7)
Se(4)#1-K(1)-Se(5)	84.48(7)	Se(4)#14-K(1)-Eu(1)	162.75(8)
Se(4)#14-K(1)-Se(5)	114.39(8)	Se(3)#8-K(1)-Eu(1)	100.36(7)
Se(3)#8-K(1)-Se(5)	148.69(9)	Se(2)#1-K(1)-Eu(1)	51.80(4)
Se(2)#1-K(1)-Se(5)	73.15(6)	Se(5)-K(1)-Eu(1)	53.15(4)
Se(1)#2-K(1)-Se(5)#4	42.50(4)	Se(5)#4-K(1)-Eu(1)	78.68(5)

Si(1)#8-K(1)-Eu(1)	85.40(7)
K(2)#13-K(1)-Eu(1)	111.47(8)
K(2)#2-K(1)-Eu(1)	130.36(8)
K(2)#8-K(1)-Eu(1)	136.59(8)
Se(3)-K(2)-Se(4)#15	148.05(11)
Se(3)-K(2)-Se(4)#3	93.44(8)
Se(4)#15-K(2)-Se(4)#3	103.57(8)
Se(3)-K(2)-Se(5)#16	141.79(10)
Se(4)#15-K(2)-Se(5)#16	58.89(5)
Se(4)#3-K(2)-Se(5)#16	105.18(8)
Se(3)-K(2)-Si(1)#5	37.34(6)
Se(4)#15-K(2)-Si(1)#5	119.08(10)
Se(4)#3-K(2)-Si(1)#5	130.70(10)
Se(5)#16-K(2)-Si(1)#5	117.13(10)
Se(3)-K(2)-Se(4)#17	64.64(6)
Se(4)#15-K(2)-Se(4)#17	108.03(8)
Se(4)#3-K(2)-Se(4)#17	146.59(10)
Se(5)#16-K(2)-Se(4)#17	82.63(7)
Si(1)#5-K(2)-Se(4)#17	35.18(6)
Se(3)-K(2)-Se(3)#4	78.76(7)
Se(4)#15-K(2)-Se(3)#4	85.19(7)
Se(4)#3-K(2)-Se(3)#4	62.81(6)
Se(5)#16-K(2)-Se(3)#4	139.44(9)
Si(1)#5-K(2)-Se(3)#4	95.69(9)
Se(4)#17-K(2)-Se(3)#4	129.87(9)
Se(3)-K(2)-Se(5)#1	65.19(6)
Se(4)#15-K(2)-Se(5)#1	85.18(7)
Se(4)#3-K(2)-Se(5)#1	141.17(10)
Se(5)#16-K(2)-Se(5)#1	111.45(8)
Si(1)#5-K(2)-Se(5)#1	36.05(6)
Se(4)#17-K(2)-Se(5)#1	53.80(5)
Se(3)#4-K(2)-Se(5)#1	80.74(7)
Se(3)-K(2)-Se(4)#12	86.03(7)
Se(4)#15-K(2)-Se(4)#12	125.72(9)
Se(4)#3-K(2)-Se(4)#12	63.74(6)
Se(5)#16-K(2)-Se(4)#12	73.46(6)
Si(1)#5-K(2)-Se(4)#12	104.30(9)
Se(4)#17-K(2)-Se(4)#12	88.67(7)
Se(3)#4-K(2)-Se(4)#12	122.98(8)
Se(5)#1-K(2)-Se(4)#12	139.27(9)
Se(3)-K(2)-K(1)#16	131.25(10)
Se(4)#15-K(2)-K(1)#16	79.72(7)
Se(4)#3-K(2)-K(1)#16	52.41(6)
Se(5)#16-K(2)-K(1)#16	52.92(6)
Si(1)#5-K(2)-K(1)#16	152.53(11)
Se(4)#17-K(2)-K(1)#16	123.39(10)
Se(3)#4-K(2)-K(1)#16	106.32(8)
Se(5)#1-K(2)-K(1)#16	162.61(9)
Se(4)#12-K(2)-K(1)#16	49.79(6)
Se(3)-K(2)-K(1)#6	99.13(9)
Se(4)#15-K(2)-K(1)#6	50.51(6)
Se(4)#3-K(2)-K(1)#6	105.53(9)
Se(5)#16-K(2)-K(1)#6	107.27(8)
Si(1)#5-K(2)-K(1)#6	85.70(9)
Se(4)#17-K(2)-K(1)#6	102.79(8)
Se(3)#4-K(2)-K(1)#6	49.11(6)
Se(5)#1-K(2)-K(1)#6	51.67(6)
Se(4)#12-K(2)-K(1)#6	168.53(9)
K(1)#16-K(2)-K(1)#6	121.13(8)
Se(3)-K(2)-K(2)#12	107.12(11)
Se(4)#15-K(2)-K(2)#12	58.53(7)
Se(4)#3-K(2)-K(2)#12	159.45(13)
Se(5)#16-K(2)-K(2)#12	58.11(8)
Si(1)#5-K(2)-K(2)#12	69.85(9)
Se(4)#17-K(2)-K(2)#12	49.50(6)
Se(3)#4-K(2)-K(2)#12	120.53(12)
Se(5)#1-K(2)-K(2)#12	53.34(7)
Se(4)#12-K(2)-K(2)#12	116.49(12)
K(1)#16-K(2)-K(2)#12	110.55(12)
K(1)#6-K(2)-K(2)#12	71.94(9)
Se(3)#4-Si(1)-Se(4)#3	113.39(14)
Se(3)#4-Si(1)-Se(2)#3	106.07(13)
Se(4)#3-Si(1)-Se(2)#3	115.96(14)
Se(3)#4-Si(1)-Se(5)#2	113.59(14)
Se(4)#3-Si(1)-Se(5)#2	97.24(12)
Se(2)#3-Si(1)-Se(5)#2	110.71(13)
Se(3)#4-Si(1)-K(2)#4	60.16(9)
Se(4)#3-Si(1)-K(2)#4	74.49(10)
Se(2)#3-Si(1)-K(2)#4	166.01(14)
Se(5)#2-Si(1)-K(2)#4	75.48(10)
Se(3)#4-Si(1)-K(1)#8	117.13(12)
Se(4)#3-Si(1)-K(1)#8	58.36(8)
Se(2)#3-Si(1)-K(1)#8	59.26(8)
Se(5)#2-Si(1)-K(1)#8	129.04(12)
K(2)#4-Si(1)-K(1)#8	127.29(11)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z #2 -x+1,y+1/2,-z+1/2 #3 x,y+1,z

#4 x,-y+3/2,z+1/2 #5 x,-y+3/2,z-1/2 #6 -x+1,y-1/2,-z+1/2

#7 x,y-1,z #8 -x+1,-y+2,-z #9 x-1,y-1,z #10 -x,y-1/2,-z+1/2

#11 x,-y+1/2,z+1/2 #12 -x,-y+1,-z #13 x+1,y,z

#14 x+1,y+1,z #15 -x,y+1/2,-z+1/2 #16 x-1,y,z

#17 x,-y+1/2,z-1/2

Table E.4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $K_2EuSiSe_5$. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Eu(1)	8(1)	9(1)	11(1)	-1(1)	-1(1)	0(1)
Se(1)	9(1)	9(1)	12(1)	1(1)	1(1)	1(1)
Se(2)	6(1)	9(1)	12(1)	2(1)	-1(1)	0(1)
Se(3)	9(1)	9(1)	15(1)	-1(1)	1(1)	-1(1)
Se(4)	4(1)	21(1)	14(1)	-1(1)	-2(1)	1(1)
Se(5)	11(1)	11(1)	12(1)	2(1)	-2(1)	-4(1)
K(1)	8(1)	18(1)	16(1)	-2(1)	0(1)	-1(1)
K(2)	25(2)	21(2)	30(2)	-3(1)	12(1)	-4(1)
Si(1)	2(2)	11(2)	11(2)	-1(1)	-3(1)	-2(1)

Table E.5. Crystal data and structure refinement for $K_2EuGeSe_5$.

Identification code	p21c	
Empirical formula	$K_2EuGeSe_5$	
Formula weight	697.55	
Temperature	167(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 11.8056(3) Å	α= 90°.
	b = 9.96300(10) Å	β= 91.1950(10)°.
	c = 8.94560(10) Å	γ = 90°.
Volume	1051.95(3) $Å^3$	
Z	4	
Density (calculated)	4.404 Mg/m^3	
Absorption coefficient	26.781 mm^{-1}	
F(000)	1212	
Crystal size	0.09 x 0.09 x 0.09 mm^3	
Theta range for data collection	1.73 to 28.19°.	
Index ranges	-13<=h<=15, -13<=k<=10, -11<=l<=11	
Reflections collected	6796	
Independent reflections	2518 [R(int) = 0.0841]	
Absorption correction	SADABS	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2518 / 0 / 83	
Goodness-of-fit on F^2	0.934	
Final R indices [I>2sigma(I)]	R1 = 0.0436, wR2 = 0.0831	
R indices (all data)	R1 = 0.0689, wR2 = 0.0913	
Extinction coefficient	0.0039(2)	
Largest diff. peak and hole	2.169 and -2.436 $e.Å^{-3}$	

Table E.6. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for $K_2EuGeSe_5$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Eu(1)	4837(1)	7306(1)	1053(1)	9(1)
Se(2)	4037(1)	10381(1)	1352(1)	9(1)
Se(3)	2878(1)	7446(1)	-1428(1)	11(1)
Se(4)	697(1)	10143(1)	1945(1)	13(1)
Se(1)	4079(1)	4340(1)	1589(1)	10(1)
Se(5)	7532(1)	6306(1)	-4(1)	13(1)
Ge(1)	2530(1)	9793(1)	2908(1)	9(1)
K(1)	8022(2)	9441(2)	1257(3)	14(1)
K(2)	559(2)	6995(3)	395(3)	27(1)

Table E.7. Bond lengths [Å] and angles [°] for $K_2EuGeSe_5$.

Eu(1)-Se(1)	3.1275(11)	K(1)-Se(2)#5	3.339(3)
Eu(1)-Se(1)#1	3.1684(11)	K(1)-Se(5)#4	3.487(3)
Eu(1)-Se(3)	3.1748(12)	K(1)-Ge(1)#5	3.846(3)
Eu(1)-Se(1)#2	3.1747(11)	K(1)-K(2)#10	3.950(4)
Eu(1)-Se(2)	3.2194(11)	K(1)-K(2)#5	4.207(3)
Eu(1)-Se(2)#3	3.2715(11)	K(1)-K(2)#2	4.247(4)
Eu(1)-Se(3)#4	3.2722(12)	K(2)-Se(4)#11	3.378(3)
Eu(1)-Se(2)#5	3.4387(11)	K(2)-Se(5)#7	3.648(3)
Eu(1)-Se(5)	3.4833(12)	K(2)-Ge(1)#6	3.708(3)
Eu(1)-K(1)	4.321(2)	K(2)-Se(4)#6	3.756(3)
Eu(1)-Eu(1)#6	4.4895(1)	K(2)-Se(4)#9	3.818(3)
Eu(1)-Eu(1)#4	4.4895(1)	K(2)-K(1)#7	3.950(4)
Se(2)-Ge(1)	2.3561(15)	K(2)-K(1)#5	4.207(3)
Se(2)-Eu(1)#2	3.2715(11)	K(2)-K(2)#12	4.243(5)
Se(2)-K(1)#5	3.339(3)	K(2)-K(1)#3	4.247(4)
Se(2)-Eu(1)#5	3.4387(11)	K(2)-K(2)#6	4.5847(11)
Se(3)-Ge(1)#6	2.3426(14)		
Se(3)-K(2)	3.247(3)	Se(1)-Eu(1)-Se(1)#1	75.34(3)
Se(3)-Eu(1)#6	3.2722(12)	Se(1)-Eu(1)-Se(3)	86.68(3)
Se(3)-K(1)#5	3.283(2)	Se(1)#1-Eu(1)-Se(3)	78.52(3)
Se(4)-Ge(1)	2.339(2)	Se(1)-Eu(1)-Se(1)#2	127.87(2)
Se(4)-K(1)#7	3.280(3)	Se(1)#1-Eu(1)-Se(1)#2	131.49(4)
Se(4)-K(1)#5	3.293(3)	Se(3)-Eu(1)-Se(1)#2	135.55(3)
Se(4)-K(2)#8	3.378(3)	Se(1)-Eu(1)-Se(2)	143.24(3)
Se(4)-K(2)	3.432(3)	Se(1)#1-Eu(1)-Se(2)	132.70(3)
Se(4)-K(2)#4	3.756(3)	Se(3)-Eu(1)-Se(2)	78.78(3)
Se(4)-K(2)#9	3.818(3)	Se(1)#2-Eu(1)-Se(2)	56.78(3)
Se(1)-Se(5)#1	2.4354(15)	Se(1)-Eu(1)-Se(2)#3	56.69(3)
Se(1)-Eu(1)#1	3.1684(11)	Se(1)#1-Eu(1)-Se(2)#3	93.54(3)
Se(1)-K(1)#3	3.174(2)	Se(3)-Eu(1)-Se(2)#3	143.23(3)
Se(1)-Eu(1)#3	3.1747(11)	Se(1)#2-Eu(1)-Se(2)#3	75.56(3)
Se(5)-Ge(1)#3	2.4080(14)	Se(2)-Eu(1)-Se(2)#3	127.91(2)
Se(5)-Se(1)#1	2.4355(15)	Se(1)-Eu(1)-Se(3)#4	75.94(3)
Se(5)-K(1)	3.367(2)	Se(1)#1-Eu(1)-Se(3)#4	148.79(3)
Se(5)-K(1)#6	3.487(3)	Se(3)-Eu(1)-Se(3)#4	87.88(3)
Se(5)-K(2)#10	3.648(3)	Se(1)#2-Eu(1)-Se(3)#4	77.00(3)
Ge(1)-Se(3)#4	2.3426(14)	Se(2)-Eu(1)-Se(3)#4	70.00(3)
Ge(1)-Se(5)#2	2.4080(14)	Se(2)#3-Eu(1)-Se(3)#4	80.69(3)
Ge(1)-K(2)#4	3.708(3)	Se(1)-Eu(1)-Se(2)#5	147.65(3)
Ge(1)-K(1)#5	3.846(3)	Se(1)#1-Eu(1)-Se(2)#5	73.30(3)
K(1)-Se(1)#2	3.174(2)	Se(3)-Eu(1)-Se(2)#5	79.55(3)
K(1)-Se(4)#10	3.280(3)	Se(1)#2-Eu(1)-Se(2)#5	80.34(3)
K(1)-Se(3)#5	3.283(2)	Se(2)-Eu(1)-Se(2)#5	62.10(3)
K(1)-Se(4)#5	3.293(3)	Se(2)#3-Eu(1)-Se(2)#5	132.85(4)

Se(3)#4-Eu(1)-Se(2)#5	131.93(3)	Eu(1)-Se(2)-Eu(1)#5	117.90(3)
Se(1)-Eu(1)-Se(5)	92.15(3)	Eu(1)#2-Se(2)-Eu(1)#5	83.95(2)
Se(1)#1-Eu(1)-Se(5)	42.63(3)	K(1)#5-Se(2)-Eu(1)#5	79.19(4)
Se(3)-Eu(1)-Se(5)	118.62(3)	Ge(1)#6-Se(3)-Eu(1)	104.88(4)
Se(1)#2-Eu(1)-Se(5)	90.29(3)	Ge(1)#6-Se(3)-K(2)	81.38(6)
Se(2)-Eu(1)-Se(5)	124.47(3)	Eu(1)-Se(3)-K(2)	104.63(6)
Se(2)#3-Eu(1)-Se(5)	70.44(3)	Ge(1)#6-Se(3)-Eu(1)#6	91.16(4)
Se(3)#4-Eu(1)-Se(5)	150.61(3)	Eu(1)-Se(3)-Eu(1)#6	88.26(3)
Se(2)#5-Eu(1)-Se(5)	69.79(3)	K(2)-Se(3)-Eu(1)#6	166.37(7)
Se(1)-Eu(1)-K(1)	135.27(4)	Ge(1)#6-Se(3)-K(1)#5	148.87(6)
Se(1)#1-Eu(1)-K(1)	85.51(4)	Eu(1)-Se(3)-K(1)#5	103.94(5)
Se(3)-Eu(1)-K(1)	128.94(4)	K(2)-Se(3)-K(1)#5	80.23(6)
Se(1)#2-Eu(1)-K(1)	47.10(4)	Eu(1)#6-Se(3)-K(1)#5	101.23(5)
Se(2)-Eu(1)-K(1)	77.55(4)	Ge(1)-Se(4)-K(1)#7	156.51(6)
Se(2)#3-Eu(1)-K(1)	85.31(4)	Ge(1)-Se(4)-K(1)#5	84.31(6)
Se(3)#4-Eu(1)-K(1)	124.10(4)	K(1)#7-Se(4)-K(1)#5	108.75(6)
Se(2)#5-Eu(1)-K(1)	49.39(4)	Ge(1)-Se(4)-K(2)#8	103.78(7)
Se(5)-Eu(1)-K(1)	49.71(4)	K(1)#7-Se(4)-K(2)#8	79.27(7)
Se(1)-Eu(1)-Eu(1)#6	103.90(2)	K(1)#5-Se(4)-K(2)#8	139.50(7)
Se(1)#1-Eu(1)-Eu(1)#6	45.00(2)	Ge(1)-Se(4)-K(2)	92.77(6)
Se(3)-Eu(1)-Eu(1)#6	46.76(2)	K(1)#7-Se(4)-K(2)	72.06(7)
Se(1)#2-Eu(1)-Eu(1)#6	126.75(2)	K(1)#5-Se(4)-K(2)	77.42(6)
Se(2)-Eu(1)-Eu(1)#6	90.38(2)	K(2)#8-Se(4)-K(2)	139.99(6)
Se(2)#3-Eu(1)-Eu(1)#6	138.51(2)	Ge(1)-Se(4)-K(2)#4	70.63(6)
Se(3)#4-Eu(1)-Eu(1)#6	133.97(2)	K(1)#7-Se(4)-K(2)#4	88.58(7)
Se(2)#5-Eu(1)-Eu(1)#6	46.44(2)	K(1)#5-Se(4)-K(2)#4	144.53(7)
Se(5)-Eu(1)-Eu(1)#6	74.65(2)	K(2)#8-Se(4)-K(2)#4	72.77(7)
K(1)-Eu(1)-Eu(1)#6	88.94(3)	K(2)-Se(4)-K(2)#4	79.11(3)
Se(1)-Eu(1)-Eu(1)#4	85.57(2)	Ge(1)-Se(4)-K(2)#9	131.22(6)
Se(1)#1-Eu(1)-Eu(1)#4	142.78(2)	K(1)#7-Se(4)-K(2)#9	72.25(6)
Se(3)-Eu(1)-Eu(1)#4	132.64(2)	K(1)#5-Se(4)-K(2)#9	67.01(6)
Se(1)#2-Eu(1)-Eu(1)#4	44.89(2)	K(2)#8-Se(4)-K(2)#9	78.89(4)
Se(2)-Eu(1)-Eu(1)#4	80.16(2)	K(2)-Se(4)-K(2)#9	116.51(5)
Se(2)#3-Eu(1)-Eu(1)#4	49.61(2)	K(2)#4-Se(4)-K(2)#9	148.31(4)
Se(3)#4-Eu(1)-Eu(1)#4	44.98(2)	Se(5)#1-Se(1)-Eu(1)	112.51(4)
Se(2)#5-Eu(1)-Eu(1)#4	125.00(2)	Se(5)#1-Se(1)-Eu(1)#1	75.61(4)
Se(5)-Eu(1)-Eu(1)#4	108.30(2)	Eu(1)-Se(1)-Eu(1)#1	104.66(3)
K(1)-Eu(1)-Eu(1)#4	86.19(3)	Se(5)#1-Se(1)-K(1)#3	75.59(6)
Eu(1)#6-Eu(1)-Eu(1)#4	170.10(3)	Eu(1)-Se(1)-K(1)#3	107.02(5)
Ge(1)-Se(2)-Eu(1)	92.23(4)	Eu(1)#1-Se(1)-K(1)#3	143.35(6)
Ge(1)-Se(2)-Eu(1)#2	91.55(4)	Se(5)#1-Se(1)-Eu(1)#3	121.15(4)
Eu(1)-Se(2)-Eu(1)#2	120.07(3)	Eu(1)-Se(1)-Eu(1)#3	126.32(3)
Ge(1)-Se(2)-K(1)#5	83.02(5)	Eu(1)#1-Se(1)-Eu(1)#3	90.11(3)
Eu(1)-Se(2)-K(1)#5	101.71(5)	K(1)#3-Se(1)-Eu(1)#3	85.78(5)
Eu(1)#2-Se(2)-K(1)#5	138.08(5)	Ge(1)#3-Se(5)-Se(1)#1	104.59(5)
Ge(1)-Se(2)-Eu(1)#5	147.45(5)	Ge(1)#3-Se(5)-K(1)	109.13(6)

Se(1)#1-Se(5)-K(1)	124.53(6)	Se(4)#5-K(1)-Se(5)#4	161.74(8)
Ge(1)#3-Se(5)-Eu(1)	85.69(4)	Se(2)#5-K(1)-Se(5)#4	123.29(7)
Se(1)#1-Se(5)-Eu(1)	61.77(3)	Se(5)-K(1)-Se(5)#4	95.31(6)
K(1)-Se(5)-Eu(1)	78.19(5)	Se(1)#2-K(1)-Ge(1)#5	118.40(7)
Ge(1)#3-Se(5)-K(1)#6	128.42(6)	Se(4)#10-K(1)-Ge(1)#5	106.41(6)
Se(1)#1-Se(5)-K(1)#6	61.84(5)	Se(3)#5-K(1)-Ge(1)#5	79.00(5)
K(1)-Se(5)-K(1)#6	119.27(6)	Se(4)#5-K(1)-Ge(1)#5	37.24(3)
Eu(1)-Se(5)-K(1)#6	119.48(5)	Se(2)#5-K(1)-Ge(1)#5	37.45(3)
Ge(1)#3-Se(5)-K(2)#10	95.00(6)	Se(5)-K(1)-Ge(1)#5	80.50(5)
Se(1)#1-Se(5)-K(2)#10	149.10(6)	Se(5)#4-K(1)-Ge(1)#5	160.68(8)
K(1)-Se(5)-K(2)#10	68.39(6)	Se(1)#2-K(1)-K(2)#10	134.76(8)
Eu(1)-Se(5)-K(2)#10	144.87(5)	Se(4)#10-K(1)-K(2)#10	55.76(6)
K(1)#6-Se(5)-K(2)#10	87.27(6)	Se(3)#5-K(1)-K(2)#10	147.09(8)
Se(4)-Ge(1)-Se(3)#4	113.06(6)	Se(4)#5-K(1)-K(2)#10	62.86(6)
Se(4)-Ge(1)-Se(2)	116.72(6)	Se(2)#5-K(1)-K(2)#10	116.10(8)
Se(3)#4-Ge(1)-Se(2)	104.83(5)	Se(5)-K(1)-K(2)#10	59.18(6)
Se(4)-Ge(1)-Se(5)#2	98.66(5)	Se(5)#4-K(1)-K(2)#10	101.37(7)
Se(3)#4-Ge(1)-Se(5)#2	114.00(5)	Ge(1)#5-K(1)-K(2)#10	92.69(7)
Se(2)-Ge(1)-Se(5)#2	109.87(6)	Se(1)#2-K(1)-K(2)#5	124.21(7)
Se(4)-Ge(1)-K(2)#4	72.86(6)	Se(4)#10-K(1)-K(2)#5	59.81(6)
Se(3)#4-Ge(1)-K(2)#4	59.97(5)	Se(3)#5-K(1)-K(2)#5	49.52(5)
Se(2)-Ge(1)-K(2)#4	164.80(6)	Se(4)#5-K(1)-K(2)#5	52.76(5)
Se(5)#2-Ge(1)-K(2)#4	78.70(6)	Se(2)#5-K(1)-K(2)#5	89.96(7)
Se(4)-Ge(1)-K(1)#5	58.45(5)	Se(5)-K(1)-K(2)#5	137.06(8)
Se(3)#4-Ge(1)-K(1)#5	117.38(6)	Se(5)#4-K(1)-K(2)#5	126.34(7)
Se(2)-Ge(1)-K(1)#5	59.53(5)	Ge(1)#5-K(1)-K(2)#5	63.44(5)
Se(5)#2-Ge(1)-K(1)#5	128.53(6)	K(2)#10-K(1)-K(2)#5	98.23(7)
K(2)#4-Ge(1)-K(1)#5	125.51(6)	Se(1)#2-K(1)-K(2)#2	83.86(6)
Se(1)#2-K(1)-Se(4)#10	130.88(8)	Se(4)#10-K(1)-K(2)#2	51.39(5)
Se(1)#2-K(1)-Se(3)#5	75.18(6)	Se(3)#5-K(1)-K(2)#2	61.62(6)
Se(4)#10-K(1)-Se(3)#5	95.81(6)	Se(4)#5-K(1)-K(2)#2	110.89(7)
Se(1)#2-K(1)-Se(4)#5	155.63(9)	Se(2)#5-K(1)-K(2)#2	137.05(8)
Se(4)#10-K(1)-Se(4)#5	71.25(6)	Se(5)-K(1)-K(2)#2	148.69(8)
Se(3)#5-K(1)-Se(4)#5	94.40(6)	Se(5)#4-K(1)-K(2)#2	61.47(5)
Se(1)#2-K(1)-Se(2)#5	81.91(6)	Ge(1)#5-K(1)-K(2)#2	128.37(7)
Se(4)#10-K(1)-Se(2)#5	143.50(8)	K(2)#10-K(1)-K(2)#2	102.58(6)
Se(3)#5-K(1)-Se(2)#5	75.58(5)	K(2)#5-K(1)-K(2)#2	65.68(4)
Se(4)#5-K(1)-Se(2)#5	74.11(5)	Se(1)#2-K(1)-Eu(1)	47.12(4)
Se(1)#2-K(1)-Se(5)	92.45(6)	Se(4)#10-K(1)-Eu(1)	161.16(7)
Se(4)#10-K(1)-Se(5)	114.74(7)	Se(3)#5-K(1)-Eu(1)	100.66(6)
Se(3)#5-K(1)-Se(5)	146.98(8)	Se(4)#5-K(1)-Eu(1)	116.11(6)
Se(4)#5-K(1)-Se(5)	84.49(6)	Se(2)#5-K(1)-Eu(1)	51.42(4)
Se(2)#5-K(1)-Se(5)	72.39(5)	Se(5)-K(1)-Eu(1)	52.10(4)
Se(1)#2-K(1)-Se(5)#4	42.57(4)	Se(5)#4-K(1)-Eu(1)	76.92(5)
Se(4)#10-K(1)-Se(5)#4	92.51(6)	Ge(1)#5-K(1)-Eu(1)	85.82(5)
Se(3)#5-K(1)-Se(5)#4	95.56(6)	K(2)#10-K(1)-Eu(1)	110.51(6)

K(2)#5-K(1)-Eu(1)	138.88(7)
K(2)#2-K(1)-Eu(1)	130.91(7)
Se(3)-K(2)-Se(4)#11	144.72(10)
Se(3)-K(2)-Se(4)	92.46(7)
Se(4)#11-K(2)-Se(4)	103.44(7)
Se(3)-K(2)-Se(5)#7	144.22(9)
Se(4)#11-K(2)-Se(5)#7	61.51(5)
Se(4)-K(2)-Se(5)#7	104.45(7)
Se(3)-K(2)-Ge(1)#6	38.65(4)
Se(4)#11-K(2)-Ge(1)#6	116.76(7)
Se(4)-K(2)-Ge(1)#6	131.02(8)
Se(5)#7-K(2)-Ge(1)#6	118.46(8)
Se(3)-K(2)-Se(4)#6	67.33(5)
Se(4)#11-K(2)-Se(4)#6	107.23(7)
Se(4)-K(2)-Se(4)#6	147.97(9)
Se(5)#7-K(2)-Se(4)#6	82.66(6)
Ge(1)#6-K(2)-Se(4)#6	36.51(3)
Se(3)-K(2)-Se(4)#9	86.74(6)
Se(4)#11-K(2)-Se(4)#9	128.54(8)
Se(4)-K(2)-Se(4)#9	63.49(5)
Se(5)#7-K(2)-Se(4)#9	73.66(6)
Ge(1)#6-K(2)-Se(4)#9	105.73(7)
Se(4)#6-K(2)-Se(4)#9	89.77(6)
Se(3)-K(2)-K(1)#7	131.56(8)
Se(4)#11-K(2)-K(1)#7	81.60(6)
Se(4)-K(2)-K(1)#7	52.18(5)
Se(5)#7-K(2)-K(1)#7	52.43(5)
Ge(1)#6-K(2)-K(1)#7	154.34(9)
Se(4)#6-K(2)-K(1)#7	123.81(9)
Se(4)#9-K(2)-K(1)#7	50.13(5)
Se(3)-K(2)-K(1)#5	50.26(5)
Se(4)#11-K(2)-K(1)#5	153.15(8)
Se(4)-K(2)-K(1)#5	49.82(5)
Se(5)#7-K(2)-K(1)#5	121.38(8)
Ge(1)#6-K(2)-K(1)#5	86.28(6)
Se(4)#6-K(2)-K(1)#5	99.53(7)
Se(4)#9-K(2)-K(1)#5	47.94(5)
K(1)#7-K(2)-K(1)#5	81.77(7)
Se(3)-K(2)-K(2)#12	107.97(9)
Se(4)#11-K(2)-K(2)#12	57.74(6)
Se(4)-K(2)-K(2)#12	159.31(11)
Se(5)#7-K(2)-K(2)#12	60.47(7)
Ge(1)#6-K(2)-K(2)#12	69.32(7)
Se(4)#6-K(2)-K(2)#12	49.50(6)
Se(4)#9-K(2)-K(2)#12	119.51(11)
K(1)#7-K(2)-K(2)#12	112.11(10)
K(1)#5-K(2)-K(2)#12	148.96(11)
Se(3)-K(2)-K(1)#3	96.46(8)
Se(4)#11-K(2)-K(1)#3	49.35(5)
Se(4)-K(2)-K(1)#3	104.35(8)
Se(5)#7-K(2)-K(1)#3	109.11(7)
Ge(1)#6-K(2)-K(1)#3	83.80(6)
Se(4)#6-K(2)-K(1)#3	102.50(7)
Se(4)#9-K(2)-K(1)#3	167.63(8)
K(1)#7-K(2)-K(1)#3	121.43(7)
K(1)#5-K(2)-K(1)#3	126.80(9)
K(2)#12-K(2)-K(1)#3	70.91(8)
Se(3)-K(2)-K(2)#6	57.49(6)
Se(4)#11-K(2)-K(2)#6	144.70(7)
Se(4)-K(2)-K(2)#6	101.10(9)
Se(5)#7-K(2)-K(2)#6	88.04(4)
Ge(1)#6-K(2)-K(2)#6	60.49(5)
Se(4)#6-K(2)-K(2)#6	47.32(4)
Se(4)#9-K(2)-K(2)#6	46.30(5)
K(1)#7-K(2)-K(2)#6	94.04(7)
K(1)#5-K(2)-K(2)#6	57.58(7)
K(2)#12-K(2)-K(2)#6	92.84(9)
K(1)#3-K(2)-K(2)#6	144.23(8)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z #2 -x+1,y+1/2,-z+1/2 #3 -x+1,y-1/2,-z+1/2

#4 x,-y+3/2,z+1/2 #5 -x+1,-y+2,-z #6 x,-y+3/2,z-1/2

#7 x-1,y,z #8 -x,y+1/2,-z+1/2 #9 -x,-y+2,-z

#10 x+1,y,z #11 -x,y-1/2,-z+1/2 #12 -x,-y+1,-z

Table E.8. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $K_2EuGeSe_5$. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Eu(1)	10(1)	11(1)	8(1)	-1(1)	0(1)	0(1)
Se(2)	7(1)	11(1)	8(1)	1(1)	1(1)	0(1)
Se(3)	9(1)	11(1)	13(1)	-1(1)	2(1)	1(1)
Se(4)	5(1)	22(1)	12(1)	-2(1)	-1(1)	1(1)
Se(1)	10(1)	11(1)	9(1)	1(1)	3(1)	1(1)
Se(5)	14(1)	15(1)	9(1)	3(1)	-1(1)	-5(1)
Ge(1)	6(1)	12(1)	7(1)	0(1)	1(1)	0(1)
K(1)	9(1)	22(1)	12(1)	-1(1)	2(1)	-2(1)
K(2)	28(2)	21(1)	31(2)	-2(1)	18(1)	-3(1)

Table E.9. Crystal data and structure refinement for $KEuSiS_4$.

Identification code	p21	
Empirical formula	$KEuSiS_4$	
Formula weight	347.39	
Temperature	170(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 6.426(4) Å	α= 90°.
	b = 6.582(5) Å	β= 107.83(6)°.
	c = 8.566(7) Å	γ = 90°.
Volume	344.9(4) $Å^3$	
Z	2	
Density (calculated)	3.345 Mg/m^3	
Absorption coefficient	10.952 mm^{-1}	
F(000)	320	
Crystal size	0.09 x 0.12 x 0.18 mm^3	
Theta range for data collection	2.50 to 28.47°.	
Index ranges	-7<=h<=8, -8<=k<=8, -10<=l<=11	
Reflections collected	2293	
Independent reflections	1536 [R(int) = 0.0512]	
Absorption correction	SADABS	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1536 / 1 / 64	
Goodness-of-fit on F^2	1.152	
Final R indices [I>2sigma(I)]	R1 = 0.0471, wR2 = 0.1250	
R indices (all data)	R1 = 0.0483, wR2 = 0.1335	
Absolute structure parameter	0.00	
Largest diff. peak and hole	2.243 and -2.777 $e.Å^{-3}$	

Table E.10. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for $KEuSiS_4$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Eu(1)	2701(1)	2114(1)	4493(1)	6(1)
Si(1)	7165(6)	1785(5)	3200(4)	6(1)
K(1)	2251(5)	1914(7)	9340(3)	17(1)
S(1)	4811(5)	-582(5)	7095(4)	6(1)
S(2)	5205(5)	4424(5)	7267(5)	8(1)
S(3)	-884(5)	1777(5)	1645(4)	8(1)
S(4)	858(5)	6324(5)	4343(4)	7(1)

Table E.11. Bond lengths [Å] and angles [°] for $KEuSiS_4$.

Eu(1)-S(3)	2.804(4)	S(3)-Eu(1)-S(4)#1	75.71(11)
Eu(1)-S(4)#1	2.809(4)	S(3)-Eu(1)-S(1)#2	93.35(11)
Eu(1)-S(1)#2	2.836(4)	S(4)#1-Eu(1)-S(1)#2	155.40(10)
Eu(1)-S(1)	2.847(4)	S(3)-Eu(1)-S(1)	134.38(10)
Eu(1)-S(2)	2.865(4)	S(4)#1-Eu(1)-S(1)	81.43(11)
Eu(1)-S(2)#3	2.908(4)	S(1)#2-Eu(1)-S(1)	120.38(7)
Eu(1)-S(4)	3.001(4)	S(3)-Eu(1)-S(2)	150.06(10)
Eu(1)-Si(1)	3.384(4)	S(4)#1-Eu(1)-S(2)	96.62(11)
Eu(1)-Si(1)#4	3.393(4)	S(1)#2-Eu(1)-S(2)	81.84(11)
Eu(1)-Si(1)#2	3.641(4)	S(1)-Eu(1)-S(2)	70.69(12)
Eu(1)-K(1)	4.252(4)	S(3)-Eu(1)-S(2)#3	83.59(10)
Eu(1)-Eu(1)#2	4.329(2)	S(4)#1-Eu(1)-S(2)#3	128.88(10)
Si(1)-S(3)#5	2.091(5)	S(1)#2-Eu(1)-S(2)#3	70.03(10)
Si(1)-S(1)#2	2.118(5)	S(1)-Eu(1)-S(2)#3	80.89(10)
Si(1)-S(4)#3	2.120(5)	S(2)-Eu(1)-S(2)#3	121.43(8)
Si(1)-S(2)#3	2.126(5)	S(3)-Eu(1)-S(4)	80.07(9)
Si(1)-Eu(1)#5	3.393(4)	S(4)#1-Eu(1)-S(4)	80.35(7)
Si(1)-Eu(1)#3	3.641(4)	S(1)#2-Eu(1)-S(4)	76.04(10)
Si(1)-K(1)#6	3.811(6)	S(1)-Eu(1)-S(4)	134.10(9)
K(1)-S(4)#1	3.200(5)	S(2)-Eu(1)-S(4)	70.08(10)
K(1)-S(3)#7	3.224(5)	S(2)#3-Eu(1)-S(4)	141.18(9)
K(1)-S(2)#8	3.301(5)	S(3)-Eu(1)-Si(1)	105.26(10)
K(1)-S(1)	3.323(5)	S(4)#1-Eu(1)-Si(1)	165.54(9)
K(1)-S(3)#9	3.358(6)	S(1)#2-Eu(1)-Si(1)	38.56(9)
K(1)-S(2)	3.399(5)	S(1)-Eu(1)-Si(1)	88.17(10)
K(1)-S(1)#10	3.475(5)	S(2)-Eu(1)-Si(1)	89.32(11)
K(1)-S(3)#1	3.530(6)	S(2)#3-Eu(1)-Si(1)	38.57(9)
K(1)-Si(1)#7	3.811(6)	S(4)-Eu(1)-Si(1)	114.09(9)
K(1)-Eu(1)#7	4.336(4)	S(3)-Eu(1)-Si(1)#4	37.95(9)
K(1)-K(1)#10	4.706(5)	S(4)#1-Eu(1)-Si(1)#4	38.55(9)
S(1)-Si(1)#3	2.118(5)	S(1)#2-Eu(1)-Si(1)#4	124.51(10)
S(1)-Eu(1)#3	2.835(4)	S(1)-Eu(1)-Si(1)#4	114.58(10)
S(1)-K(1)#8	3.475(5)	S(2)-Eu(1)-Si(1)#4	124.81(10)
S(2)-Si(1)#2	2.126(5)	S(2)#3-Eu(1)-Si(1)#4	113.41(10)
S(2)-Eu(1)#2	2.908(4)	S(4)-Eu(1)-Si(1)#4	71.61(9)
S(2)-K(1)#10	3.301(5)	Si(1)-Eu(1)-Si(1)#4	142.98(11)
S(3)-Si(1)#4	2.091(5)	S(3)-Eu(1)-Si(1)#2	114.55(9)
S(3)-K(1)#6	3.224(5)	S(4)#1-Eu(1)-Si(1)#2	81.37(9)
S(3)-K(1)#1	3.358(6)	S(1)#2-Eu(1)-Si(1)#2	83.44(10)
S(3)-K(1)#9	3.530(6)	S(1)-Eu(1)-Si(1)#2	100.05(10)
S(4)-Si(1)#2	2.120(5)	S(2)-Eu(1)-Si(1)#2	35.68(8)
S(4)-Eu(1)#9	2.809(4)	S(2)#3-Eu(1)-Si(1)#2	149.01(9)
S(4)-K(1)#9	3.200(5)	S(4)-Eu(1)-Si(1)#2	35.61(9)
		Si(1)-Eu(1)-Si(1)#2	110.49(9)

Si(1)#4-Eu(1)-Si(1)#2	94.54(8)	S(2)#3-Si(1)-K(1)#6	59.83(14)
S(3)-Eu(1)-K(1)	124.32(9)	Eu(1)-Si(1)-K(1)#6	73.86(10)
S(4)#1-Eu(1)-K(1)	48.80(9)	Eu(1)#5-Si(1)-K(1)#6	142.10(12)
S(1)#2-Eu(1)-K(1)	134.59(9)	Eu(1)#3-Si(1)-K(1)#6	111.44(12)
S(1)-Eu(1)-K(1)	51.28(10)	S(4)#1-K(1)-S(3)#7	106.38(14)
S(2)-Eu(1)-K(1)	52.78(10)	S(4)#1-K(1)-S(2)#8	143.1(2)
S(2)#3-Eu(1)-K(1)	131.91(10)	S(3)#7-K(1)-S(2)#8	71.39(11)
S(4)-Eu(1)-K(1)	85.77(9)	S(4)#1-K(1)-S(1)	68.87(11)
Si(1)-Eu(1)-K(1)	129.46(9)	S(3)#7-K(1)-S(1)	148.6(2)
Si(1)#4-Eu(1)-K(1)	86.48(10)	S(2)#8-K(1)-S(1)	93.70(15)
Si(1)#2-Eu(1)-K(1)	59.56(9)	S(4)#1-K(1)-S(3)#9	80.31(12)
S(3)-Eu(1)-Eu(1)#2	124.26(8)	S(3)#7-K(1)-S(3)#9	90.92(14)
S(4)#1-Eu(1)-Eu(1)#2	130.47(7)	S(2)#8-K(1)-S(3)#9	135.68(14)
S(1)#2-Eu(1)-Eu(1)#2	40.47(8)	S(1)-K(1)-S(3)#9	117.62(12)
S(1)-Eu(1)-Eu(1)#2	100.62(9)	S(4)#1-K(1)-S(2)	79.84(11)
S(2)-Eu(1)-Eu(1)#2	41.80(8)	S(3)#7-K(1)-S(2)	152.5(2)
S(2)#3-Eu(1)-Eu(1)#2	99.84(8)	S(2)#8-K(1)-S(2)	119.74(12)
S(4)-Eu(1)-Eu(1)#2	62.79(8)	S(1)-K(1)-S(2)	58.88(10)
Si(1)-Eu(1)-Eu(1)#2	61.27(7)	S(3)#9-K(1)-S(2)	63.28(11)
Si(1)#4-Eu(1)-Eu(1)#2	134.18(7)	S(4)#1-K(1)-S(1)#10	158.6(2)
Si(1)#2-Eu(1)-Eu(1)#2	49.31(7)	S(3)#7-K(1)-S(1)#10	75.43(11)
K(1)-Eu(1)-Eu(1)#2	94.23(7)	S(2)#8-K(1)-S(1)#10	58.15(11)
S(3)#5-Si(1)-S(1)#2	112.3(2)	S(1)-K(1)-S(1)#10	120.72(12)
S(3)#5-Si(1)-S(4)#3	109.8(2)	S(3)#9-K(1)-S(1)#10	78.38(13)
S(1)#2-Si(1)-S(4)#3	113.0(2)	S(2)-K(1)-S(1)#10	89.34(13)
S(3)#5-Si(1)-S(2)#3	114.4(2)	S(4)#1-K(1)-S(3)#1	67.26(10)
S(1)#2-Si(1)-S(2)#3	101.9(2)	S(3)#7-K(1)-S(3)#1	87.89(12)
S(4)#3-Si(1)-S(2)#3	105.0(2)	S(2)#8-K(1)-S(3)#1	75.81(13)
S(3)#5-Si(1)-Eu(1)	160.5(2)	S(1)-K(1)-S(3)#1	61.26(11)
S(1)#2-Si(1)-Eu(1)	56.58(12)	S(3)#9-K(1)-S(3)#1	145.71(14)
S(4)#3-Si(1)-Eu(1)	89.70(14)	S(2)-K(1)-S(3)#1	118.59(12)
S(2)#3-Si(1)-Eu(1)	58.54(13)	S(1)#10-K(1)-S(3)#1	133.85(13)
S(3)#5-Si(1)-Eu(1)#5	55.58(12)	S(4)#1-K(1)-Si(1)#7	162.62(15)
S(1)#2-Si(1)-Eu(1)#5	121.1(2)	S(3)#7-K(1)-Si(1)#7	88.58(11)
S(4)#3-Si(1)-Eu(1)#5	55.65(12)	S(2)#8-K(1)-Si(1)#7	33.83(9)
S(2)#3-Si(1)-Eu(1)#5	136.6(2)	S(1)-K(1)-Si(1)#7	93.75(13)
Eu(1)-Si(1)-Eu(1)#5	142.98(11)	S(3)#9-K(1)-Si(1)#7	108.84(13)
S(3)#5-Si(1)-Eu(1)#3	115.1(2)	S(2)-K(1)-Si(1)#7	90.99(12)
S(1)#2-Si(1)-Eu(1)#3	132.0(2)	S(1)#10-K(1)-Si(1)#7	33.39(9)
S(4)#3-Si(1)-Eu(1)#3	55.48(12)	S(3)#1-K(1)-Si(1)#7	105.39(14)
S(2)#3-Si(1)-Eu(1)#3	51.82(13)	S(4)#1-K(1)-Eu(1)	41.35(7)
Eu(1)-Si(1)-Eu(1)#3	75.99(8)	S(3)#7-K(1)-Eu(1)	147.22(12)
Eu(1)#5-Si(1)-Eu(1)#3	91.64(9)	S(2)#8-K(1)-Eu(1)	135.38(14)
S(3)#5-Si(1)-K(1)#6	86.92(15)	S(1)-K(1)-Eu(1)	41.95(7)
S(1)#2-Si(1)-K(1)#6	64.57(14)	S(3)#9-K(1)-Eu(1)	79.40(8)
S(4)#3-Si(1)-K(1)#6	161.8(2)	S(2)-K(1)-Eu(1)	42.16(7)

S(1)#10-K(1)-Eu(1)	131.48(12)
S(3)#1-K(1)-Eu(1)	83.25(8)
Si(1)#7-K(1)-Eu(1)	124.20(11)
S(4)#1-K(1)-Eu(1)#7	146.56(12)
S(3)#7-K(1)-Eu(1)#7	40.28(7)
S(2)#8-K(1)-Eu(1)#7	42.10(8)
S(1)-K(1)-Eu(1)#7	135.53(13)
S(3)#9-K(1)-Eu(1)#7	99.07(10)
S(2)-K(1)-Eu(1)#7	130.05(12)
S(1)#10-K(1)-Eu(1)#7	40.73(7)
S(3)#1-K(1)-Eu(1)#7	101.91(10)
Si(1)#7-K(1)-Eu(1)#7	48.55(8)
Eu(1)-K(1)-Eu(1)#7	171.85(9)
S(4)#1-K(1)-K(1)#10	121.19(12)
S(3)#7-K(1)-K(1)#10	115.87(12)
S(2)#8-K(1)-K(1)#10	90.15(13)
S(1)-K(1)-K(1)#10	90.94(13)
S(3)#9-K(1)-K(1)#10	60.87(7)
S(2)-K(1)-K(1)#10	44.54(9)
S(1)#10-K(1)-K(1)#10	44.87(9)
S(3)#1-K(1)-K(1)#10	147.22(13)
Si(1)#7-K(1)-K(1)#10	56.32(11)
Eu(1)-K(1)-K(1)#10	86.70(9)
Eu(1)#7-K(1)-K(1)#10	85.59(9)
Si(1)#3-S(1)-Eu(1)#3	84.9(2)
Si(1)#3-S(1)-Eu(1)	107.0(2)
Eu(1)#3-S(1)-Eu(1)	99.26(12)
Si(1)#3-S(1)-K(1)	95.1(2)
Eu(1)#3-S(1)-K(1)	173.72(14)
Eu(1)-S(1)-K(1)	86.77(12)
Si(1)#3-S(1)-K(1)#8	82.0(2)
Eu(1)#3-S(1)-K(1)#8	86.18(11)
Eu(1)-S(1)-K(1)#8	169.76(14)
K(1)-S(1)-K(1)#8	87.60(11)
Si(1)#2-S(2)-Eu(1)	92.5(2)
Si(1)#2-S(2)-Eu(1)#2	82.9(2)
Eu(1)-S(2)-Eu(1)#2	97.16(13)
Si(1)#2-S(2)-K(1)#10	86.3(2)
Eu(1)-S(2)-K(1)#10	174.20(15)
Eu(1)#2-S(2)-K(1)#10	88.34(12)
Si(1)#2-S(2)-K(1)	88.3(2)
Eu(1)-S(2)-K(1)	85.05(11)
Eu(1)#2-S(2)-K(1)	171.03(14)
K(1)#10-S(2)-K(1)	89.23(12)
Si(1)#4-S(3)-Eu(1)	86.46(15)
Si(1)#4-S(3)-K(1)#6	177.6(2)
Eu(1)-S(3)-K(1)#6	91.71(12)
Si(1)#4-S(3)-K(1)#1	90.0(2)
Eu(1)-S(3)-K(1)#1	112.07(11)
K(1)#6-S(3)-K(1)#1	92.13(12)
Si(1)#4-S(3)-K(1)#9	89.79(15)
Eu(1)-S(3)-K(1)#9	102.14(11)
K(1)#6-S(3)-K(1)#9	89.04(14)
K(1)#1-S(3)-K(1)#9	145.71(14)
Si(1)#2-S(4)-Eu(1)#9	85.80(15)
Si(1)#2-S(4)-Eu(1)	88.91(14)
Eu(1)#9-S(4)-Eu(1)	120.61(12)
Si(1)#2-S(4)-K(1)#9	164.7(2)
Eu(1)#9-S(4)-K(1)#9	89.85(12)
Eu(1)-S(4)-K(1)#9	105.85(13)

Symmetry transformations used to generate equivalent atoms:

#1 -x,y-1/2,-z+1 #2 -x+1,y+1/2,-z+1 #3 -x+1,y-1/2,-z+1

#4 x-1,y,z #5 x+1,y,z #6 x,y,z-1 #7 x,y,z+1

#8 -x+1,y-1/2,-z+2 #9 -x,y+1/2,-z+1 #10 -x+1,y+1/2,-z+2

Table E.12. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $KEuSiS_4$. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Eu(1)	5(1)	7(1)	4(1)	0(1)	0(1)	0(1)
Si(1)	5(1)	7(2)	5(1)	1(1)	1(1)	0(1)
K(1)	21(1)	19(2)	7(1)	1(1)	2(1)	3(2)
S(1)	6(1)	7(2)	4(2)	1(1)	2(1)	0(1)
S(2)	8(1)	3(1)	9(2)	0(1)	-2(1)	1(1)
S(3)	7(1)	10(2)	7(1)	-2(1)	2(1)	-1(1)
S(4)	4(1)	13(1)	5(1)	0(1)	1(1)	3(1)

Table E.13. Crystal data and structure refinement for $KEuGeS_4$.

Identification code	p21	
Empirical formula	$KEuGeS_4$	
Formula weight	391.89	
Temperature	167(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 6.510(2) Å	α= 90°.
	b = 6.649(2) Å	β= 107.80(2)°.
	c = 8.603(3) Å	γ = 90°.
Volume	354.5(2) $Å^3$	
Z	2	
Density (calculated)	3.671 Mg/m^3	
Absorption coefficient	14.645 mm^{-1}	
F(000)	356	
Crystal size	0.09 x 0.12 x 0.18 mm^3	
Theta range for data collection	2.49 to 28.36°.	
Index ranges	-6<=h<=8, -7<=k<=8, -11<=l<=8	
Reflections collected	2400	
Independent reflections	1572 [R(int) = 0.0355]	
Absorption correction	SADABS	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1572 / 1 / 64	
Goodness-of-fit on F^2	1.051	
Final R indices [I>2sigma(I)]	R1 = 0.0346, wR2 = 0.0857	
R indices (all data)	R1 = 0.0356, wR2 = 0.0862	
Absolute structure parameter	0.00	
Largest diff. peak and hole	2.653 and -2.557 $e.Å^{-3}$	

Table E.14. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for $KEuGeS_4$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Eu(1)	2698(1)	9643(1)	9475(1)	6(1)
Ge(1)	7208(1)	9986(1)	8208(1)	5(1)
K(1)	2329(3)	9821(5)	4361(2)	15(1)
S(1)	4741(4)	12375(4)	7753(3)	7(1)
S(2)	4843(3)	12280(4)	12084(3)	6(1)
S(3)	-792(3)	10008(4)	6589(3)	10(1)
S(4)	729(3)	5567(4)	9270(3)	7(1)

Table E.15. Bond lengths [Å] and angles [°] for $KEuGeS_4$.

Eu(1)-S(3)	2.817(2)	S(3)-Eu(1)-S(2)#2	92.89(7)
Eu(1)-S(4)#1	2.828(2)	S(4)#1-Eu(1)-S(2)#2	157.04(7)
Eu(1)-S(2)#2	2.853(2)	S(3)-Eu(1)-S(2)	135.15(7)
Eu(1)-S(2)	2.854(2)	S(4)#1-Eu(1)-S(2)	79.61(7)
Eu(1)-S(1)#2	2.882(2)	S(2)#2-Eu(1)-S(2)	119.86(4)
Eu(1)-S(1)	2.910(3)	S(3)-Eu(1)-S(1)#2	151.74(7)
Eu(1)-S(4)	2.979(3)	S(4)#1-Eu(1)-S(1)#2	97.01(7)
Eu(1)-Ge(1)#3	3.4105(14)	S(2)#2-Eu(1)-S(1)#2	80.51(7)
Eu(1)-Ge(1)	3.4372(13)	S(2)-Eu(1)-S(1)#2	69.56(7)
Eu(1)-Ge(1)#2	3.6720(14)	S(3)-Eu(1)-S(1)	82.44(7)
Eu(1)-K(1)#4	4.284(2)	S(4)#1-Eu(1)-S(1)	126.56(7)
Eu(1)-K(1)	4.334(2)	S(2)#2-Eu(1)-S(1)	72.23(7)
Ge(1)-S(3)#5	2.178(2)	S(2)-Eu(1)-S(1)	80.03(7)
Ge(1)-S(1)	2.206(2)	S(1)#2-Eu(1)-S(1)	120.60(4)
Ge(1)-S(2)#2	2.208(3)	S(3)-Eu(1)-S(4)	79.03(7)
Ge(1)-S(4)#6	2.209(2)	S(4)#1-Eu(1)-S(4)	81.09(5)
Ge(1)-Eu(1)#5	3.4105(14)	S(2)#2-Eu(1)-S(4)	76.37(7)
Ge(1)-Eu(1)#6	3.6720(14)	S(2)-Eu(1)-S(4)	134.73(7)
Ge(1)-K(1)	3.824(3)	S(1)#2-Eu(1)-S(4)	72.71(7)
Ge(1)-K(1)#7	3.964(3)	S(1)-Eu(1)-S(4)	142.43(7)
K(1)-S(4)#8	3.188(3)	S(3)-Eu(1)-Ge(1)#3	39.52(5)
K(1)-S(3)	3.193(3)	S(4)#1-Eu(1)-Ge(1)#3	40.12(5)
K(1)-S(1)	3.326(3)	S(2)#2-Eu(1)-Ge(1)#3	124.78(5)
K(1)-S(2)#9	3.339(3)	S(2)-Eu(1)-Ge(1)#3	115.03(5)
K(1)-S(3)#10	3.378(4)	S(1)#2-Eu(1)-Ge(1)#3	125.73(5)
K(1)-S(1)#11	3.422(3)	S(1)-Eu(1)-Ge(1)#3	113.14(5)
K(1)-S(2)#2	3.486(3)	S(4)-Eu(1)-Ge(1)#3	69.65(5)
K(1)-S(3)#8	3.614(4)	S(3)-Eu(1)-Ge(1)	104.58(5)
K(1)-Ge(1)#11	3.964(3)	S(4)#1-Eu(1)-Ge(1)	163.09(5)
K(1)-Eu(1)#9	4.284(2)	S(2)#2-Eu(1)-Ge(1)	39.76(5)
S(1)-Eu(1)#6	2.882(2)	S(2)-Eu(1)-Ge(1)	87.04(5)
S(1)-K(1)#7	3.422(3)	S(1)#2-Eu(1)-Ge(1)	87.89(6)
S(2)-Ge(1)#6	2.209(3)	S(1)-Eu(1)-Ge(1)	39.60(5)
S(2)-Eu(1)#6	2.853(2)	S(4)-Eu(1)-Ge(1)	115.79(5)
S(2)-K(1)#4	3.339(3)	Ge(1)#3-Eu(1)-Ge(1)	143.84(3)
S(2)-K(1)#6	3.486(3)	S(3)-Eu(1)-Ge(1)#2	115.22(5)
S(3)-Ge(1)#3	2.178(2)	S(4)#1-Eu(1)-Ge(1)#2	81.97(5)
S(3)-K(1)#8	3.378(4)	S(2)#2-Eu(1)-Ge(1)#2	82.66(6)
S(3)-K(1)#10	3.614(4)	S(2)-Eu(1)-Ge(1)#2	99.69(6)
S(4)-Ge(1)#2	2.209(2)	S(1)#2-Eu(1)-Ge(1)#2	36.92(5)
S(4)-Eu(1)#12	2.827(2)	S(1)-Eu(1)-Ge(1)#2	150.24(5)
S(4)-K(1)#10	3.188(3)	S(4)-Eu(1)-Ge(1)#2	36.97(5)
		Ge(1)#3-Eu(1)-Ge(1)#2	94.13(3)
S(3)-Eu(1)-S(4)#1	78.46(7)	Ge(1)-Eu(1)-Ge(1)#2	110.73(3)

S(3)-Eu(1)-K(1)#4	126.17(5)	Eu(1)#5-Ge(1)-K(1)	141.86(4)
S(4)#1-Eu(1)-K(1)#4	48.07(5)	Eu(1)-Ge(1)-K(1)	73.06(4)
S(2)#2-Eu(1)-K(1)#4	133.17(6)	Eu(1)#6-Ge(1)-K(1)	111.44(5)
S(2)-Eu(1)-K(1)#4	51.12(6)	S(3)#5-Ge(1)-K(1)#7	58.39(8)
S(1)#2-Eu(1)-K(1)#4	52.74(6)	S(1)-Ge(1)-K(1)#7	59.52(8)
S(1)-Eu(1)-K(1)#4	130.82(7)	S(2)#2-Ge(1)-K(1)#7	138.04(7)
S(4)-Eu(1)-K(1)#4	86.06(6)	S(4)#6-Ge(1)-K(1)#7	106.19(8)
Ge(1)#3-Eu(1)-K(1)#4	86.79(4)	Eu(1)#5-Ge(1)-K(1)#7	88.94(4)
Ge(1)-Eu(1)-K(1)#4	128.23(4)	Eu(1)-Ge(1)-K(1)#7	116.66(4)
Ge(1)#2-Eu(1)-K(1)#4	59.18(5)	Eu(1)#6-Ge(1)-K(1)#7	68.13(5)
S(3)-Eu(1)-K(1)	47.42(5)	K(1)-Ge(1)-K(1)#7	74.06(5)
S(4)#1-Eu(1)-K(1)	125.20(5)	S(4)#8-K(1)-S(3)	105.11(8)
S(2)#2-Eu(1)-K(1)	53.34(6)	S(4)#8-K(1)-S(1)	140.00(12)
S(2)-Eu(1)-K(1)	130.04(7)	S(3)-K(1)-S(1)	70.73(7)
S(1)#2-Eu(1)-K(1)	133.85(6)	S(4)#8-K(1)-S(2)#9	67.68(7)
S(1)-Eu(1)-K(1)	50.07(6)	S(3)-K(1)-S(2)#9	148.10(12)
S(4)-Eu(1)-K(1)	94.31(6)	S(1)-K(1)-S(2)#9	94.59(9)
Ge(1)#3-Eu(1)-K(1)	86.92(4)	S(4)#8-K(1)-S(3)#10	81.97(8)
Ge(1)-Eu(1)-K(1)	57.58(4)	S(3)-K(1)-S(3)#10	89.22(9)
Ge(1)#2-Eu(1)-K(1)	124.09(5)	S(1)-K(1)-S(3)#10	136.17(9)
K(1)#4-Eu(1)-K(1)	173.14(6)	S(2)#9-K(1)-S(3)#10	118.94(8)
S(3)#5-Ge(1)-S(1)	115.24(9)	S(4)#8-K(1)-S(1)#11	80.55(7)
S(3)#5-Ge(1)-S(2)#2	113.04(10)	S(3)-K(1)-S(1)#11	153.85(13)
S(1)-Ge(1)-S(2)#2	100.63(9)	S(1)-K(1)-S(1)#11	121.23(7)
S(3)#5-Ge(1)-S(4)#6	108.92(9)	S(2)#9-K(1)-S(1)#11	57.87(6)
S(1)-Ge(1)-S(4)#6	103.85(10)	S(3)#10-K(1)-S(1)#11	65.99(7)
S(2)#2-Ge(1)-S(4)#6	114.77(10)	S(4)#8-K(1)-S(2)#2	159.89(12)
S(3)#5-Ge(1)-Eu(1)#5	55.38(6)	S(3)-K(1)-S(2)#2	75.79(7)
S(1)-Ge(1)-Eu(1)#5	137.69(7)	S(1)-K(1)-S(2)#2	59.78(7)
S(2)#2-Ge(1)-Eu(1)#5	121.31(7)	S(2)#9-K(1)-S(2)#2	122.00(7)
S(4)#6-Ge(1)-Eu(1)#5	55.58(6)	S(3)#10-K(1)-S(2)#2	77.95(9)
S(3)#5-Ge(1)-Eu(1)	159.83(7)	S(1)#11-K(1)-S(2)#2	90.30(8)
S(1)-Ge(1)-Eu(1)	57.22(7)	S(4)#8-K(1)-S(3)#8	65.36(7)
S(2)#2-Ge(1)-Eu(1)	55.72(7)	S(3)-K(1)-S(3)#8	85.17(8)
S(4)#6-Ge(1)-Eu(1)	91.25(7)	S(1)-K(1)-S(3)#8	74.64(8)
Eu(1)#5-Ge(1)-Eu(1)	143.84(3)	S(2)#9-K(1)-S(3)#8	63.35(7)
S(3)#5-Ge(1)-Eu(1)#6	115.30(7)	S(3)#10-K(1)-S(3)#8	143.92(9)
S(1)-Ge(1)-Eu(1)#6	51.69(7)	S(1)#11-K(1)-S(3)#8	119.60(8)
S(2)#2-Ge(1)-Eu(1)#6	131.13(7)	S(2)#2-K(1)-S(3)#8	134.12(9)
S(4)#6-Ge(1)-Eu(1)#6	54.21(6)	S(4)#8-K(1)-Ge(1)	161.45(9)
Eu(1)#5-Ge(1)-Eu(1)#6	92.35(3)	S(3)-K(1)-Ge(1)	89.53(6)
Eu(1)-Ge(1)-Eu(1)#6	76.01(2)	S(1)-K(1)-Ge(1)	35.07(5)
S(3)#5-Ge(1)-K(1)	86.99(7)	S(2)#9-K(1)-Ge(1)	93.86(7)
S(1)-Ge(1)-K(1)	60.02(8)	S(3)#10-K(1)-Ge(1)	110.05(8)
S(2)#2-Ge(1)-K(1)	64.22(8)	S(1)#11-K(1)-Ge(1)	91.33(7)
S(4)#6-Ge(1)-K(1)	161.77(7)	S(2)#2-K(1)-Ge(1)	34.78(5)

S(3)#8-K(1)-Ge(1)	105.52(8)
S(4)#8-K(1)-Ge(1)#11	73.21(7)
S(3)-K(1)-Ge(1)#11	122.48(10)
S(1)-K(1)-Ge(1)#11	143.81(8)
S(2)#9-K(1)-Ge(1)#11	86.29(6)
S(3)#10-K(1)-Ge(1)#11	33.31(5)
S(1)#11-K(1)-Ge(1)#11	33.75(5)
S(2)#2-K(1)-Ge(1)#11	89.22(8)
S(3)#8-K(1)-Ge(1)#11	135.28(7)
Ge(1)-K(1)-Ge(1)#11	108.73(7)
S(4)#8-K(1)-Eu(1)#9	41.29(5)
S(3)-K(1)-Eu(1)#9	145.77(7)
S(1)-K(1)-Eu(1)#9	136.20(9)
S(2)#9-K(1)-Eu(1)#9	41.70(5)
S(3)#10-K(1)-Eu(1)#9	80.65(6)
S(1)#11-K(1)-Eu(1)#9	42.09(4)
S(2)#2-K(1)-Eu(1)#9	132.40(8)
S(3)#8-K(1)-Eu(1)#9	84.21(6)
Ge(1)-K(1)-Eu(1)#9	124.68(5)
Ge(1)#11-K(1)-Eu(1)#9	52.69(3)
S(4)#8-K(1)-Eu(1)	145.40(7)
S(3)-K(1)-Eu(1)	40.51(4)
S(1)-K(1)-Eu(1)	42.15(5)
S(2)#9-K(1)-Eu(1)	136.39(8)
S(3)#10-K(1)-Eu(1)	98.06(7)
S(1)#11-K(1)-Eu(1)	131.26(8)
S(2)#2-K(1)-Eu(1)	41.03(5)
S(3)#8-K(1)-Eu(1)	100.45(7)
Ge(1)-K(1)-Eu(1)	49.35(3)
Ge(1)#11-K(1)-Eu(1)	123.62(8)
Eu(1)#9-K(1)-Eu(1)	173.14(6)
Ge(1)-S(1)-Eu(1)#6	91.39(8)
Ge(1)-S(1)-Eu(1)	83.19(8)
Eu(1)#6-S(1)-Eu(1)	98.28(8)
Ge(1)-S(1)-K(1)	84.91(9)
Eu(1)#6-S(1)-K(1)	172.49(10)
Eu(1)-S(1)-K(1)	87.78(8)
Ge(1)-S(1)-K(1)#7	86.73(9)
Eu(1)#6-S(1)-K(1)#7	85.16(7)
Eu(1)-S(1)-K(1)#7	169.41(10)
K(1)-S(1)-K(1)#7	88.10(7)
Ge(1)#6-S(2)-Eu(1)#6	84.52(8)
Ge(1)#6-S(2)-Eu(1)	106.13(9)
Eu(1)#6-S(2)-Eu(1)	100.29(8)
Ge(1)#6-S(2)-K(1)#4	94.47(9)
Eu(1)#6-S(2)-K(1)#4	172.46(9)
Eu(1)-S(2)-K(1)#4	87.17(8)
Ge(1)#6-S(2)-K(1)#6	81.01(9)
Eu(1)#6-S(2)-K(1)#6	85.64(7)
Eu(1)-S(2)-K(1)#6	171.02(10)
K(1)#4-S(2)-K(1)#6	86.82(7)
Ge(1)#3-S(3)-Eu(1)	85.10(8)
Ge(1)#3-S(3)-K(1)	176.31(11)
Eu(1)-S(3)-K(1)	92.07(7)
Ge(1)#3-S(3)-K(1)#8	88.30(8)
Eu(1)-S(3)-K(1)#8	113.23(8)
K(1)-S(3)-K(1)#8	95.01(9)
Ge(1)#3-S(3)-K(1)#10	87.71(8)
Eu(1)-S(3)-K(1)#10	102.12(8)
K(1)-S(3)-K(1)#10	90.57(9)
K(1)#8-S(3)-K(1)#10	143.92(9)
Ge(1)#2-S(4)-Eu(1)#12	84.30(7)
Ge(1)#2-S(4)-Eu(1)	88.82(7)
Eu(1)#12-S(4)-Eu(1)	123.39(8)
Ge(1)#2-S(4)-K(1)#10	160.95(12)
Eu(1)#12-S(4)-K(1)#10	90.63(7)
Eu(1)-S(4)-K(1)#10	109.16(9)

Symmetry transformations used to generate equivalent atoms:

#1 -x,y+1/2,-z+2 #2 -x+1,y-1/2,-z+2 #3 x-1,y,z

#4 x,y,z+1 #5 x+1,y,z #6 -x+1,y+1/2,-z+2

#7 -x+1,y+1/2,-z+1 #8 -x,y+1/2,-z+1 #9 x,y,z-1

#10 -x,y-1/2,-z+1 #11 -x+1,y-1/2,-z+1 #12 -x,y-1/2,-z+2

Table E.16. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $KEuGeS_4$. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Eu(1)	6(1)	5(1)	7(1)	0(1)	3(1)	0(1)
Ge(1)	5(1)	4(1)	7(1)	0(1)	3(1)	0(1)
K(1)	17(1)	19(1)	10(1)	-2(1)	5(1)	-2(1)
S(1)	7(1)	4(1)	10(1)	0(1)	2(1)	1(1)
S(2)	8(1)	4(1)	8(1)	0(1)	3(1)	1(1)
S(3)	9(1)	13(1)	9(1)	3(1)	5(1)	2(1)
S(4)	6(1)	9(1)	6(1)	1(1)	2(1)	-1(1)

Table E.17. Crystal data and structure refinement for $Eu_8Sn_4Se_{20}$.

Identification code	p21212	
Empirical formula	$Eu_8Sn_4Se_{20}$	
Formula weight	6539.28	
Temperature	169(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2	
Unit cell dimensions	a = 11.990(2) Å	α= 90°.
	b = 16.425(4) Å	β= 90°.
	c = 8.5433(11) Å	γ = 90°.
Volume	1682.5(5) $Å^3$	
Z	2	
Density (calculated)	6.454 Mg/m^3	
Absorption coefficient	39.208 mm^{-1}	
F(000)	2768	
Crystal size	0.03 x 0.03 x 0.15 mm^3	
Theta range for data collection	2.10 to 28.33°.	
Index ranges	-15<=h<=12, -21<=k<=21, -11<=l<=11	
Reflections collected	11377	
Independent reflections	4101 [R(int) = 0.0731]	
Absorption correction	SADABS	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4101 / 0 / 149	
Goodness-of-fit on F^2	1.031	
Final R indices [I>2sigma(I)]	R1 = 0.0413, wR2 = 0.0896	
R indices (all data)	R1 = 0.0547, wR2 = 0.0963	
Absolute structure parameter	0.24(3)	
Extinction coefficient	0.00210(6)	
Largest diff. peak and hole	2.232 and -2.582 $e.Å^{-3}$	

Table E.18. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for $Eu_8Sn_4Se_{20}$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Eu(1)	6153(1)	8220(1)	7447(1)	6(1)
Eu(2)	6172(1)	8213(1)	12414(1)	7(1)
Eu(3)	7473(1)	5712(1)	7581(1)	7(1)
Eu(4)	2484(1)	9286(1)	7394(1)	6(1)
Sn(1)	4464(1)	6049(1)	4997(1)	13(1)
Sn(2)	4088(1)	6720(1)	10148(1)	8(1)
Se(1)	6210(1)	6752(1)	10054(2)	6(1)
Se(2)	6303(1)	6822(1)	5048(2)	6(1)
Se(3)	5000	5000	7289(2)	9(1)
Se(4)	5000	5000	2766(2)	9(1)
Se(5)	7527(1)	9314(1)	9868(2)	6(1)
Se(6)	7410(1)	9281(1)	4857(2)	6(1)
Se(7)	4389(1)	8918(1)	9887(2)	7(1)
Se(8)	4422(1)	8905(1)	4884(2)	7(1)
Se(9)	8697(1)	7617(1)	7199(2)	8(1)
Se(10)	5000	10000	11600(2)	6(1)
Se(11)	3674(2)	7468(1)	7638(2)	8(1)
Se(12)	5000	10000	6555(2)	6(1)

Table E.19. Bond lengths [Å] and angles [°] for $Eu_8Sn_4Se_{20}$.

Eu(1)-Se(2)	3.084(2)	Eu(4)-Eu(3)#5	4.2930(10)
Eu(1)-Se(7)	3.183(2)	Eu(4)-Eu(2)#5	4.398(2)
Eu(1)-Se(6)	3.194(2)	Sn(1)-Se(6)#9	2.5260(14)
Eu(1)-Se(5)	3.196(2)	Sn(1)-Se(2)	2.5438(13)
Eu(1)-Se(9)	3.214(2)	Sn(1)-Se(4)	2.649(2)
Eu(1)-Se(8)	3.220(2)	Sn(1)-Se(3)	2.687(2)
Eu(1)-Se(11)	3.224(2)	Sn(1)-Se(9)#9	3.028(2)
Eu(1)-Se(1)	3.283(2)	Sn(2)-Se(11)	2.520(2)
Eu(1)-Se(12)	3.3226(11)	Sn(2)-Se(5)#5	2.5276(14)
Eu(1)-Eu(2)	4.2431(9)	Sn(2)-Se(1)	2.5450(14)
Eu(1)-Eu(2)#1	4.3004(9)	Sn(2)-Se(9)#5	2.558(2)
Eu(1)-Eu(4)#2	4.4111(15)	Se(1)-Eu(4)#4	3.1613(15)
Eu(2)-Se(6)#3	3.105(2)	Se(2)-Eu(4)#8	3.1086(15)
Eu(2)-Se(1)	3.134(2)	Se(2)-Eu(2)#1	3.211(2)
Eu(2)-Se(8)#3	3.186(2)	Se(3)-Sn(1)#11	2.687(2)
Eu(2)-Se(11)#4	3.202(2)	Se(3)-Eu(3)#11	3.1966(9)
Eu(2)-Se(2)#3	3.211(2)	Se(4)-Sn(1)#11	2.649(2)
Eu(2)-Se(7)	3.251(2)	Se(4)-Eu(4)#8	3.2035(9)
Eu(2)-Se(5)	3.262(2)	Se(4)-Eu(4)#12	3.2036(9)
Eu(2)-Se(9)#5	3.282(2)	Se(5)-Sn(2)#4	2.5276(14)
Eu(2)-Se(10)	3.3276(11)	Se(5)-Eu(4)#2	3.124(2)
Eu(2)-Eu(1)#3	4.3004(9)	Se(5)-Eu(3)#13	3.166(2)
Eu(2)-Eu(4)#4	4.398(2)	Se(6)-Sn(1)#8	2.5260(14)
Eu(3)-Se(1)	3.1108(15)	Se(6)-Eu(2)#1	3.105(2)
Eu(3)-Se(6)#6	3.143(2)	Se(6)-Eu(3)#14	3.143(2)
Eu(3)-Se(2)	3.1579(15)	Se(6)-Eu(4)#2	3.202(2)
Eu(3)-Se(5)#7	3.166(2)	Se(7)-Se(10)	2.416(2)
Eu(3)-Se(3)	3.1965(9)	Se(7)-Eu(3)#5	3.214(2)
Eu(3)-Se(8)#8	3.208(2)	Se(8)-Se(12)	2.398(2)
Eu(3)-Se(7)#4	3.214(2)	Se(8)-Eu(2)#1	3.186(2)
Eu(3)-Se(10)#7	3.3227(10)	Se(8)-Eu(3)#9	3.208(2)
Eu(3)-Se(9)	3.471(2)	Se(9)-Sn(2)#4	2.558(2)
Eu(3)-Eu(4)#8	4.2504(10)	Se(9)-Sn(1)#8	3.028(2)
Eu(3)-Eu(4)#4	4.2930(10)	Se(9)-Eu(2)#4	3.282(2)
Eu(4)-Se(2)#9	3.1086(15)	Se(10)-Se(7)#2	2.416(2)
Eu(4)-Se(5)#2	3.124(2)	Se(10)-Eu(3)#13	3.3227(10)
Eu(4)-Se(1)#5	3.1613(15)	Se(10)-Eu(3)#5	3.3227(10)
Eu(4)-Se(7)	3.181(2)	Se(10)-Eu(2)#2	3.3276(11)
Eu(4)-Se(6)#2	3.202(2)	Se(11)-Eu(2)#5	3.202(2)
Eu(4)-Se(4)#10	3.2036(9)	Se(12)-Se(8)#2	2.398(2)
Eu(4)-Se(8)	3.223(2)	Se(12)-Eu(4)#2	3.3157(10)
Eu(4)-Se(12)	3.3158(10)	Se(12)-Eu(1)#2	3.3226(11)
Eu(4)-Se(11)	3.316(2)		
Eu(4)-Eu(3)#9	4.2504(10)	Se(2)-Eu(1)-Se(7)	137.91(4)

Se(2)-Eu(1)-Se(6)	85.33(4)
Se(7)-Eu(1)-Se(6)	124.79(4)
Se(2)-Eu(1)-Se(5)	144.95(4)
Se(7)-Eu(1)-Se(5)	73.52(4)
Se(6)-Eu(1)-Se(5)	84.18(4)
Se(2)-Eu(1)-Se(9)	70.80(4)
Se(7)-Eu(1)-Se(9)	141.70(4)
Se(6)-Eu(1)-Se(9)	71.05(4)
Se(5)-Eu(1)-Se(9)	74.16(4)
Se(2)-Eu(1)-Se(8)	81.14(4)
Se(7)-Eu(1)-Se(8)	83.74(4)
Se(6)-Eu(1)-Se(8)	69.04(3)
Se(5)-Eu(1)-Se(8)	125.15(4)
Se(9)-Eu(1)-Se(8)	132.44(4)
Se(2)-Eu(1)-Se(11)	78.57(4)
Se(7)-Eu(1)-Se(11)	59.47(4)
Se(6)-Eu(1)-Se(11)	132.79(4)
Se(5)-Eu(1)-Se(11)	131.13(4)
Se(9)-Eu(1)-Se(11)	139.48(5)
Se(8)-Eu(1)-Se(11)	64.79(4)
Se(2)-Eu(1)-Se(1)	84.42(4)
Se(7)-Eu(1)-Se(1)	80.43(4)
Se(6)-Eu(1)-Se(1)	149.43(4)
Se(5)-Eu(1)-Se(1)	87.89(4)
Se(9)-Eu(1)-Se(1)	78.38(4)
Se(8)-Eu(1)-Se(1)	136.98(4)
Se(11)-Eu(1)-Se(1)	72.72(4)
Se(2)-Eu(1)-Se(12)	121.82(4)
Se(7)-Eu(1)-Se(12)	63.69(4)
Se(6)-Eu(1)-Se(12)	63.72(3)
Se(5)-Eu(1)-Se(12)	82.44(4)
Se(9)-Eu(1)-Se(12)	130.64(4)
Se(8)-Eu(1)-Se(12)	42.97(3)
Se(11)-Eu(1)-Se(12)	88.00(4)
Se(1)-Eu(1)-Se(12)	144.13(4)
Se(2)-Eu(1)-Eu(2)	131.47(4)
Se(7)-Eu(1)-Eu(2)	49.43(3)
Se(6)-Eu(1)-Eu(2)	133.77(4)
Se(5)-Eu(1)-Eu(2)	49.60(3)
Se(9)-Eu(1)-Eu(2)	93.44(3)
Se(8)-Eu(1)-Eu(2)	133.17(4)
Se(11)-Eu(1)-Eu(2)	87.30(3)
Se(1)-Eu(1)-Eu(2)	47.11(3)
Se(12)-Eu(1)-Eu(2)	103.53(4)
Se(2)-Eu(1)-Eu(2)#1	48.16(3)
Se(7)-Eu(1)-Eu(2)#1	131.24(4)
Se(6)-Eu(1)-Eu(2)#1	46.09(3)
Se(5)-Eu(1)-Eu(2)#1	130.24(4)
Se(9)-Eu(1)-Eu(2)#1	85.90(3)
Se(8)-Eu(1)-Eu(2)#1	47.50(3)
Se(11)-Eu(1)-Eu(2)#1	93.11(3)
Se(1)-Eu(1)-Eu(2)#1	132.55(4)
Se(12)-Eu(1)-Eu(2)#1	77.01(4)
Eu(2)-Eu(1)-Eu(2)#1	179.33(4)
Se(2)-Eu(1)-Eu(4)#2	131.56(3)
Se(7)-Eu(1)-Eu(4)#2	85.33(3)
Se(6)-Eu(1)-Eu(4)#2	46.48(3)
Se(5)-Eu(1)-Eu(4)#2	45.07(3)
Se(9)-Eu(1)-Eu(4)#2	86.23(4)
Se(8)-Eu(1)-Eu(4)#2	84.68(3)
Se(11)-Eu(1)-Eu(4)#2	134.29(4)
Se(1)-Eu(1)-Eu(4)#2	132.96(3)
Se(12)-Eu(1)-Eu(4)#2	48.29(2)
Eu(2)-Eu(1)-Eu(4)#2	90.63(2)
Eu(2)#1-Eu(1)-Eu(4)#2	89.45(2)
Se(6)#3-Eu(2)-Se(1)	149.12(4)
Se(6)#3-Eu(2)-Se(8)#3	70.58(4)
Se(1)-Eu(2)-Se(8)#3	135.16(4)
Se(6)#3-Eu(2)-Se(11)#4	76.03(4)
Se(1)-Eu(2)-Se(11)#4	73.16(4)
Se(8)#3-Eu(2)-Se(11)#4	138.66(4)
Se(6)#3-Eu(2)-Se(2)#3	84.69(4)
Se(1)-Eu(2)-Se(2)#3	84.57(4)
Se(8)#3-Eu(2)-Se(2)#3	79.75(4)
Se(11)#4-Eu(2)-Se(2)#3	73.46(4)
Se(6)#3-Eu(2)-Se(7)	124.02(4)
Se(1)-Eu(2)-Se(7)	81.66(4)
Se(8)#3-Eu(2)-Se(7)	83.10(4)
Se(11)#4-Eu(2)-Se(7)	136.98(4)
Se(2)#3-Eu(2)-Se(7)	138.69(4)
Se(6)#3-Eu(2)-Se(5)	84.08(4)
Se(1)-Eu(2)-Se(5)	89.32(4)
Se(8)#3-Eu(2)-Se(5)	124.88(4)
Se(11)#4-Eu(2)-Se(5)	73.58(4)
Se(2)#3-Eu(2)-Se(5)	146.85(4)
Se(7)-Eu(2)-Se(5)	71.78(3)
Se(6)#3-Eu(2)-Se(9)#5	126.80(4)
Se(1)-Eu(2)-Se(9)#5	76.13(4)
Se(8)#3-Eu(2)-Se(9)#5	59.07(4)
Se(11)#4-Eu(2)-Se(9)#5	134.73(5)
Se(2)#3-Eu(2)-Se(9)#5	71.24(4)
Se(7)-Eu(2)-Se(9)#5	67.69(4)

Se(5)-Eu(2)-Se(9)#5	138.40(4)	Se(6)#6-Eu(3)-Se(3)	73.54(4)
Se(6)#3-Eu(2)-Se(10)	81.00(4)	Se(2)-Eu(3)-Se(3)	75.28(4)
Se(1)-Eu(2)-Se(10)	123.17(4)	Se(5)#7-Eu(3)-Se(3)	77.80(4)
Se(8)#3-Eu(2)-Se(10)	62.96(4)	Se(1)-Eu(3)-Se(8)#8	133.85(4)
Se(11)#4-Eu(2)-Se(10)	134.47(4)	Se(6)#6-Eu(3)-Se(8)#8	71.26(3)
Se(2)#3-Eu(2)-Se(10)	142.64(4)	Se(2)-Eu(3)-Se(8)#8	76.14(4)
Se(7)-Eu(2)-Se(10)	43.08(3)	Se(5)#7-Eu(3)-Se(8)#8	126.43(4)
Se(5)-Eu(2)-Se(10)	65.30(3)	Se(3)-Eu(3)-Se(8)#8	134.12(5)
Se(9)#5-Eu(2)-Se(10)	90.32(4)	Se(1)-Eu(3)-Se(7)#4	77.70(4)
Se(6)#3-Eu(2)-Eu(1)	132.31(4)	Se(6)#6-Eu(3)-Se(7)#4	123.74(4)
Se(1)-Eu(2)-Eu(1)	50.13(3)	Se(2)-Eu(3)-Se(7)#4	132.02(4)
Se(8)#3-Eu(2)-Eu(1)	131.15(4)	Se(5)#7-Eu(3)-Se(7)#4	70.96(3)
Se(11)#4-Eu(2)-Eu(1)	89.54(3)	Se(3)-Eu(3)-Se(7)#4	141.70(5)
Se(2)#3-Eu(2)-Eu(1)	134.68(4)	Se(8)#8-Eu(3)-Se(7)#4	83.33(4)
Se(7)-Eu(2)-Eu(1)	48.05(3)	Se(1)-Eu(3)-Se(10)#7	119.62(4)
Se(5)-Eu(2)-Eu(1)	48.26(3)	Se(6)#6-Eu(3)-Se(10)#7	80.53(4)
Se(9)#5-Eu(2)-Eu(1)	95.58(3)	Se(2)-Eu(3)-Se(10)#7	138.80(4)
Se(10)-Eu(2)-Eu(1)	77.67(4)	Se(5)#7-Eu(3)-Se(10)#7	66.40(3)
Se(6)#3-Eu(2)-Eu(1)#3	47.82(3)	Se(3)-Eu(3)-Se(10)#7	137.19(3)
Se(1)-Eu(2)-Eu(1)#3	130.20(4)	Se(8)#8-Eu(3)-Se(10)#7	62.79(4)
Se(8)#3-Eu(2)-Eu(1)#3	48.18(3)	Se(7)#4-Eu(3)-Se(10)#7	43.35(3)
Se(11)#4-Eu(2)-Eu(1)#3	91.12(3)	Se(1)-Eu(3)-Se(9)	76.97(4)
Se(2)#3-Eu(2)-Eu(1)#3	45.68(3)	Se(6)#6-Eu(3)-Se(9)	126.33(4)
Se(7)-Eu(2)-Eu(1)#3	131.28(4)	Se(2)-Eu(3)-Se(9)	66.62(4)
Se(5)-Eu(2)-Eu(1)#3	131.89(4)	Se(5)#7-Eu(3)-Se(9)	135.91(4)
Se(9)#5-Eu(2)-Eu(1)#3	84.02(3)	Se(3)-Eu(3)-Se(9)	135.61(4)
Se(10)-Eu(2)-Eu(1)#3	101.78(4)	Se(8)#8-Eu(3)-Se(9)	56.88(3)
Eu(1)-Eu(2)-Eu(1)#3	179.33(4)	Se(7)#4-Eu(3)-Se(9)	65.81(4)
Se(6)#3-Eu(2)-Eu(4)#4	109.34(3)	Se(10)#7-Eu(3)-Se(9)	87.20(4)
Se(1)-Eu(2)-Eu(4)#4	45.94(3)	Se(1)-Eu(3)-Eu(4)#8	132.85(4)
Se(8)#3-Eu(2)-Eu(4)#4	122.95(3)	Se(6)#6-Eu(3)-Eu(4)#8	48.54(3)
Se(11)#4-Eu(2)-Eu(4)#4	48.68(3)	Se(2)-Eu(3)-Eu(4)#8	46.80(3)
Se(2)#3-Eu(2)-Eu(4)#4	44.95(3)	Se(5)#7-Eu(3)-Eu(4)#8	133.56(4)
Se(7)-Eu(2)-Eu(4)#4	126.32(3)	Se(3)-Eu(3)-Eu(4)#8	85.71(4)
Se(5)-Eu(2)-Eu(4)#4	111.34(3)	Se(8)#8-Eu(3)-Eu(4)#8	48.79(3)
Se(9)#5-Eu(2)-Eu(4)#4	86.12(4)	Se(7)#4-Eu(3)-Eu(4)#8	132.12(4)
Se(10)-Eu(2)-Eu(4)#4	169.09(4)	Se(10)#7-Eu(3)-Eu(4)#8	102.01(4)
Eu(1)-Eu(2)-Eu(4)#4	92.40(2)	Se(9)-Eu(3)-Eu(4)#8	84.48(3)
Eu(1)#3-Eu(2)-Eu(4)#4	88.11(2)	Se(1)-Eu(3)-Eu(4)#4	47.30(3)
Se(1)-Eu(3)-Se(6)#6	151.96(4)	Se(6)#6-Eu(3)-Eu(4)#4	131.55(4)
Se(1)-Eu(3)-Se(2)	86.11(4)	Se(2)-Eu(3)-Eu(4)#4	133.32(4)
Se(6)#6-Eu(3)-Se(2)	89.85(4)	Se(5)#7-Eu(3)-Eu(4)#4	46.55(3)
Se(1)-Eu(3)-Se(5)#7	86.05(4)	Se(3)-Eu(3)-Eu(4)#4	94.66(4)
Se(6)#6-Eu(3)-Se(5)#7	85.07(5)	Se(8)#8-Eu(3)-Eu(4)#4	130.84(4)
Se(2)-Eu(3)-Se(5)#7	152.94(4)	Se(7)#4-Eu(3)-Eu(4)#4	47.51(3)
Se(1)-Eu(3)-Se(3)	78.61(4)	Se(10)#7-Eu(3)-Eu(4)#4	77.70(4)

Se(9)-Eu(3)-Eu(4)#4	95.26(3)	Se(4)#10-Eu(4)-Se(11)	137.10(4)
Eu(4)#8-Eu(3)-Eu(4)#4	179.63(4)	Se(8)-Eu(4)-Se(11)	63.71(4)
Se(1)-Eu(3)-Eu(1)	47.97(3)	Se(12)-Eu(4)-Se(11)	86.60(4)
Se(6)#6-Eu(3)-Eu(1)	134.15(3)	Se(2)#9-Eu(4)-Eu(3)#9	47.78(3)
Se(2)-Eu(3)-Eu(1)	44.31(3)	Se(5)#2-Eu(4)-Eu(3)#9	132.51(4)
Se(5)#7-Eu(3)-Eu(1)	134.01(3)	Se(1)#5-Eu(4)-Eu(3)#9	133.53(4)
Se(3)-Eu(3)-Eu(1)	90.40(2)	Se(7)-Eu(4)-Eu(3)#9	132.21(4)
Se(8)#8-Eu(3)-Eu(1)	93.50(3)	Se(6)#2-Eu(4)-Eu(3)#9	47.36(3)
Se(7)#4-Eu(3)-Eu(1)	95.56(3)	Se(4)#10-Eu(4)-Eu(3)#9	87.37(4)
Se(10)#7-Eu(3)-Eu(1)	131.35(3)	Se(8)-Eu(4)-Eu(3)#9	48.48(3)
Se(9)-Eu(3)-Eu(1)	46.21(3)	Se(12)-Eu(4)-Eu(3)#9	77.66(4)
Eu(4)#8-Eu(3)-Eu(1)	88.53(2)	Se(11)-Eu(4)-Eu(3)#9	93.73(3)
Eu(4)#4-Eu(3)-Eu(1)	91.49(2)	Se(2)#9-Eu(4)-Eu(3)#5	132.09(4)
Se(2)#9-Eu(4)-Se(5)#2	152.01(4)	Se(5)#2-Eu(4)-Eu(3)#5	47.37(3)
Se(2)#9-Eu(4)-Se(1)#5	85.83(4)	Se(1)#5-Eu(4)-Eu(3)#5	46.32(3)
Se(5)#2-Eu(4)-Se(1)#5	85.91(4)	Se(7)-Eu(4)-Eu(3)#5	48.17(3)
Se(2)#9-Eu(4)-Se(7)	131.69(4)	Se(6)#2-Eu(4)-Eu(3)#5	132.55(4)
Se(5)#2-Eu(4)-Se(7)	71.94(4)	Se(4)#10-Eu(4)-Eu(3)#5	92.26(4)
Se(1)#5-Eu(4)-Se(7)	77.47(4)	Se(8)-Eu(4)-Eu(3)#5	131.89(4)
Se(2)#9-Eu(4)-Se(6)#2	89.66(4)	Se(12)-Eu(4)-Eu(3)#5	102.63(4)
Se(5)#2-Eu(4)-Se(6)#2	85.22(5)	Se(11)-Eu(4)-Eu(3)#5	86.52(3)
Se(1)#5-Eu(4)-Se(6)#2	151.95(4)	Eu(3)#9-Eu(4)-Eu(3)#5	179.63(4)
Se(7)-Eu(4)-Se(6)#2	124.33(4)	Se(2)#9-Eu(4)-Eu(2)#5	46.87(3)
Se(2)#9-Eu(4)-Se(4)#10	76.26(4)	Se(5)#2-Eu(4)-Eu(2)#5	131.33(3)
Se(5)#2-Eu(4)-Se(4)#10	75.84(4)	Se(1)#5-Eu(4)-Eu(2)#5	45.43(3)
Se(1)#5-Eu(4)-Se(4)#10	77.16(4)	Se(7)-Eu(4)-Eu(2)#5	93.13(3)
Se(7)-Eu(4)-Se(4)#10	139.97(5)	Se(6)#2-Eu(4)-Eu(2)#5	136.51(3)
Se(6)#2-Eu(4)-Se(4)#10	74.88(4)	Se(4)#10-Eu(4)-Eu(2)#5	90.62(2)
Se(2)#9-Eu(4)-Se(8)	76.61(4)	Se(8)-Eu(4)-Eu(2)#5	95.85(3)
Se(5)#2-Eu(4)-Se(8)	126.56(4)	Se(12)-Eu(4)-Eu(2)#5	131.59(2)
Se(1)#5-Eu(4)-Se(8)	134.65(4)	Se(11)-Eu(4)-Eu(2)#5	46.48(4)
Se(7)-Eu(4)-Se(8)	83.72(4)	Eu(3)#9-Eu(4)-Eu(2)#5	92.13(2)
Se(6)#2-Eu(4)-Se(8)	70.32(3)	Eu(3)#5-Eu(4)-Eu(2)#5	87.85(2)
Se(4)#10-Eu(4)-Se(8)	135.46(5)	Se(6)#9-Sn(1)-Se(2)	162.11(5)
Se(2)#9-Eu(4)-Se(12)	118.44(4)	Se(6)#9-Sn(1)-Se(4)	97.59(5)
Se(5)#2-Eu(4)-Se(12)	83.65(4)	Se(2)-Sn(1)-Se(4)	97.28(4)
Se(1)#5-Eu(4)-Se(12)	141.23(4)	Se(6)#9-Sn(1)-Se(3)	93.39(5)
Se(7)-Eu(4)-Se(12)	63.79(4)	Se(2)-Sn(1)-Se(3)	95.75(4)
Se(6)#2-Eu(4)-Se(12)	63.72(3)	Se(4)-Sn(1)-Se(3)	92.82(5)
Se(4)#10-Eu(4)-Se(12)	134.99(3)	Se(6)#9-Sn(1)-Se(9)#9	83.67(5)
Se(8)-Eu(4)-Se(12)	43.00(3)	Se(2)-Sn(1)-Se(9)#9	85.02(5)
Se(2)#9-Eu(4)-Se(11)	73.22(4)	Se(4)-Sn(1)-Se(9)#9	95.67(5)
Se(5)#2-Eu(4)-Se(11)	128.49(4)	Se(3)-Sn(1)-Se(9)#9	171.32(5)
Se(1)#5-Eu(4)-Se(11)	71.28(4)	Se(11)-Sn(2)-Se(5)#5	100.17(6)
Se(7)-Eu(4)-Se(11)	58.52(4)	Se(11)-Sn(2)-Se(1)	99.21(6)
Se(6)#2-Eu(4)-Se(11)	133.41(4)	Se(5)#5-Sn(2)-Se(1)	138.93(5)

Se(11)-Sn(2)-Se(9)#5	120.67(5)
Se(5)#5-Sn(2)-Se(9)#5	98.91(6)
Se(1)-Sn(2)-Se(9)#5	101.69(6)
Sn(2)-Se(1)-Eu(3)	119.78(5)
Sn(2)-Se(1)-Eu(2)	88.91(4)
Eu(3)-Se(1)-Eu(2)	149.82(4)
Sn(2)-Se(1)-Eu(4)#4	116.74(5)
Eu(3)-Se(1)-Eu(4)#4	86.38(3)
Eu(2)-Se(1)-Eu(4)#4	88.63(4)
Sn(2)-Se(1)-Eu(1)	90.93(4)
Eu(3)-Se(1)-Eu(1)	87.29(4)
Eu(2)-Se(1)-Eu(1)	82.76(3)
Eu(4)#4-Se(1)-Eu(1)	150.91(4)
Sn(1)-Se(2)-Eu(1)	109.41(5)
Sn(1)-Se(2)-Eu(4)#8	95.24(4)
Eu(1)-Se(2)-Eu(4)#8	155.28(4)
Sn(1)-Se(2)-Eu(3)	96.24(4)
Eu(1)-Se(2)-Eu(3)	90.02(4)
Eu(4)#8-Se(2)-Eu(3)	85.41(3)
Sn(1)-Se(2)-Eu(2)#1	107.47(5)
Eu(1)-Se(2)-Eu(2)#1	86.16(3)
Eu(4)#8-Se(2)-Eu(2)#1	88.18(4)
Eu(3)-Se(2)-Eu(2)#1	155.91(4)
Sn(1)-Se(3)-Sn(1)#11	86.41(7)
Sn(1)-Se(3)-Eu(3)	92.52(3)
Sn(1)#11-Se(3)-Eu(3)	94.01(3)
Sn(1)-Se(3)-Eu(3)#11	94.00(3)
Sn(1)#11-Se(3)-Eu(3)#11	92.52(3)
Eu(3)-Se(3)-Eu(3)#11	171.05(8)
Sn(1)-Se(4)-Sn(1)#11	87.96(7)
Sn(1)-Se(4)-Eu(4)#8	91.01(3)
Sn(1)#11-Se(4)-Eu(4)#8	92.50(3)
Sn(1)-Se(4)-Eu(4)#12	92.50(3)
Sn(1)#11-Se(4)-Eu(4)#12	91.01(3)
Eu(4)#8-Se(4)-Eu(4)#12	175.12(7)
Sn(2)#4-Se(5)-Eu(4)#2	119.61(6)
Sn(2)#4-Se(5)-Eu(3)#13	119.40(6)
Eu(4)#2-Se(5)-Eu(3)#13	86.07(4)
Sn(2)#4-Se(5)-Eu(1)	90.04(5)
Eu(4)#2-Se(5)-Eu(1)	88.51(5)
Eu(3)#13-Se(5)-Eu(1)	148.55(4)
Sn(2)#4-Se(5)-Eu(2)	90.01(5)
Eu(4)#2-Se(5)-Eu(2)	149.01(4)
Eu(3)#13-Se(5)-Eu(2)	86.74(5)
Eu(1)-Se(5)-Eu(2)	82.14(3)
Sn(1)#8-Se(6)-Eu(2)#1	112.21(6)
Sn(1)#8-Se(6)-Eu(3)#14	98.61(5)
Eu(2)#1-Se(6)-Eu(3)#14	89.91(5)
Sn(1)#8-Se(6)-Eu(1)	107.96(5)
Eu(2)#1-Se(6)-Eu(1)	86.09(3)
Eu(3)#14-Se(6)-Eu(1)	152.65(4)
Sn(1)#8-Se(6)-Eu(4)#2	94.91(5)
Eu(2)#1-Se(6)-Eu(4)#2	152.82(4)
Eu(3)#14-Se(6)-Eu(4)#2	84.10(3)
Eu(1)-Se(6)-Eu(4)#2	87.20(5)
Se(10)-Se(7)-Eu(4)	118.91(5)
Se(10)-Se(7)-Eu(1)	117.40(5)
Eu(4)-Se(7)-Eu(1)	96.16(5)
Se(10)-Se(7)-Eu(3)#5	70.71(4)
Eu(4)-Se(7)-Eu(3)#5	84.32(3)
Eu(1)-Se(7)-Eu(3)#5	169.73(5)
Se(10)-Se(7)-Eu(2)	70.16(4)
Eu(4)-Se(7)-Eu(2)	169.84(4)
Eu(1)-Se(7)-Eu(2)	82.52(3)
Eu(3)#5-Se(7)-Eu(2)	95.19(5)
Se(12)-Se(8)-Eu(2)#1	118.15(5)
Se(12)-Se(8)-Eu(3)#9	117.03(5)
Eu(2)#1-Se(8)-Eu(3)#9	96.59(5)
Se(12)-Se(8)-Eu(1)	70.79(5)
Eu(2)#1-Se(8)-Eu(1)	84.33(3)
Eu(3)#9-Se(8)-Eu(1)	169.87(4)
Se(12)-Se(8)-Eu(4)	70.56(4)
Eu(2)#1-Se(8)-Eu(4)	169.97(4)
Eu(3)#9-Se(8)-Eu(4)	82.73(3)
Eu(1)-Se(8)-Eu(4)	94.60(5)
Sn(2)#4-Se(9)-Sn(1)#8	100.65(6)
Sn(2)#4-Se(9)-Eu(1)	89.11(5)
Sn(1)#8-Se(9)-Eu(1)	96.08(5)
Sn(2)#4-Se(9)-Eu(2)#4	85.50(5)
Sn(1)#8-Se(9)-Eu(2)#4	95.05(5)
Eu(1)-Se(9)-Eu(2)#4	168.36(5)
Sn(2)#4-Se(9)-Eu(3)	112.23(5)
Sn(1)#8-Se(9)-Eu(3)	147.03(5)
Eu(1)-Se(9)-Eu(3)	82.56(4)
Eu(2)#4-Se(9)-Eu(3)	89.93(4)
Se(7)-Se(10)-Se(7)#2	105.43(10)
Se(7)-Se(10)-Eu(3)#13	131.52(4)
Se(7)#2-Se(10)-Eu(3)#13	65.94(3)
Se(7)-Se(10)-Eu(3)#5	65.94(3)
Se(7)#2-Se(10)-Eu(3)#5	131.52(4)
Eu(3)#13-Se(10)-Eu(3)#5	155.69(7)
Se(7)-Se(10)-Eu(2)#2	130.35(4)

Se(7)#2-Se(10)-Eu(2)#2	66.76(3)
Eu(3)#13-Se(10)-Eu(2)#2	91.75(3)
Eu(3)#5-Se(10)-Eu(2)#2	83.19(3)
Se(7)-Se(10)-Eu(2)	66.76(3)
Se(7)#2-Se(10)-Eu(2)	130.36(4)
Eu(3)#13-Se(10)-Eu(2)	83.19(3)
Eu(3)#5-Se(10)-Eu(2)	91.75(3)
Eu(2)#2-Se(10)-Eu(2)	155.90(7)
Sn(2)-Se(11)-Eu(2)#5	91.52(5)
Sn(2)-Se(11)-Eu(1)	92.75(5)
Eu(2)#5-Se(11)-Eu(1)	175.72(5)
Sn(2)-Se(11)-Eu(4)	125.24(6)
Eu(2)#5-Se(11)-Eu(4)	84.85(5)
Eu(1)-Se(11)-Eu(4)	92.78(4)
Se(8)#2-Se(12)-Se(8)	106.93(10)
Se(8)#2-Se(12)-Eu(4)#2	66.44(3)
Se(8)-Se(12)-Eu(4)#2	131.07(4)
Se(8)#2-Se(12)-Eu(4)	131.07(4)
Se(8)-Se(12)-Eu(4)	66.44(3)
Eu(4)#2-Se(12)-Eu(4)	155.03(7)
Se(8)#2-Se(12)-Eu(1)	132.52(4)
Se(8)-Se(12)-Eu(1)	66.25(3)
Eu(4)#2-Se(12)-Eu(1)	83.29(3)
Eu(4)-Se(12)-Eu(1)	91.02(3)
Se(8)#2-Se(12)-Eu(1)#2	66.24(3)
Se(8)-Se(12)-Eu(1)#2	132.52(4)
Eu(4)#2-Se(12)-Eu(1)#2	91.02(3)
Eu(4)-Se(12)-Eu(1)#2	83.29(3)
Eu(1)-Se(12)-Eu(1)#2	153.49(7)

Symmetry transformations used to generate equivalent atoms:

#1 x,y,z-1 #2 -x+1,-y+2,z #3 x,y,z+1 #4 x+1/2,-y+3/2,-z+2

#5 x-1/2,-y+3/2,-z+2 #6 -x+3/2,y-1/2,-z+1 #7 -x+3/2,y-1/2,-z+2

#8 x+1/2,-y+3/2,-z+1 #9 x-1/2,-y+3/2,-z+1 #10 -x+1/2,y+1/2,-z+1

#11 -x+1,-y+1,z #12 -x+1/2,y-1/2,-z+1 #13 -x+3/2,y+1/2,-z+2

#14 -x+3/2,y+1/2,-z+1

Table E.20. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $Eu_8Sn_4Se_{20}$. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Eu(1)	6(1)	6(1)	6(1)	-1(1)	0(1)	0(1)
Eu(2)	8(1)	5(1)	7(1)	-1(1)	0(1)	0(1)
Eu(3)	7(1)	6(1)	6(1)	-1(1)	0(1)	1(1)
Eu(4)	7(1)	6(1)	6(1)	-1(1)	0(1)	1(1)
Sn(1)	7(1)	17(1)	14(1)	-1(1)	0(1)	-5(1)
Sn(2)	7(1)	9(1)	8(1)	1(1)	-1(1)	-2(1)
Se(1)	6(1)	6(1)	7(1)	0(1)	0(1)	1(1)
Se(2)	6(1)	5(1)	8(1)	-2(1)	-1(1)	0(1)
Se(3)	7(1)	11(1)	10(1)	0	0	-1(1)
Se(4)	9(1)	10(1)	9(1)	0	0	-3(1)
Se(5)	8(1)	4(1)	7(1)	-1(1)	0(1)	1(1)
Se(6)	6(1)	5(1)	7(1)	0(1)	0(1)	0(1)
Se(7)	7(1)	6(1)	8(1)	0(1)	-1(1)	0(1)
Se(8)	7(1)	5(1)	8(1)	0(1)	0(1)	0(1)
Se(9)	9(1)	7(1)	7(1)	-1(1)	0(1)	1(1)
Se(10)	7(1)	5(1)	7(1)	0	0	0(1)
Se(11)	7(1)	9(1)	9(1)	3(1)	0(1)	-1(1)
Se(12)	6(1)	6(1)	7(1)	0	0	0(1)