DESIGN AND DISCOVERY OF NEW PIEZOELECTRIC MATERIALS USING DENSITY FUNCTIONAL THEORY

by

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ABSTRACT

Piezoelectric materials find applications in microelectromechanical systems (MEMS), such as surface acoustic wave (SAW) resonators, radio frequency (RF) filters, resonators, and energy harvesters. Using density functional theory calculations, the present study illustrates the influence of alloying and co-alloying with different nitrides on piezoelectric and mechanical properties of an existing piezoelectric material such as aluminum nitride (AlN). Besides improving the performance of existing piezoelectric material, a high-throughput screening method is used to discover new piezoelectric materials.

AlN has several beneficial properties such as high temperature stability, low dielectric permittivity, high hardness, large stiffness constant, high sound velocity, and complementary metal-oxide-semiconductor (CMOS) compatibility. This makes it widely accepted material in RF and resonant devices. However, it remains a challenge to enhance the piezoelectric modulus of AlN. The first part of this thesis establishes that the piezoelectric modulus of AlN could be improved by alloying with rocksalt transition metal nitrides such as scandium nitride (ScN), yttrium nitride (YN), and chromium nitride (CrN). As the content of the rocksalt end member in the alloy increases, the accompanying structural frustration enables a greater piezoelectric response. This structural frustration is also accompanied by thermodynamic driving forces for phase separation which, with increased alloy concentration, lead to the destruction of the piezoelectric response upon transition to the (centrosymmetric, cubic) rocksalt structure. Thus, it becomes necessary to identify suitable alloying elements that may yield highest piezoelectric response with minimal alloying additions. The study reveals that the alloying with CrN would lead to the lowest transition composition (occurring at approximately 25% CrN concentration) between the wurtzite and rocksalt structures, thereby allowing piezoelectric enhancements at alloying levels that are easier to stabilize during the synthesis. The present study indicates that, for 25% CrN alloying, the piezoelectric modulus
is about 4 times larger than that of pure AlN. Thus, it is proposed to use $\text{Cr}_x\text{Al}_{1-x}\text{N}$ as a suitable replacement for AlN.

One of the adverse effects of transition metal nitride alloying for improvement of piezoelectric response is accompanied by the softening of AlN lattice. This would make the material less desirable for resonant applications. Our subsequent research establishes that co-alloying with YN and BN would enable the most superior combination of piezoelectric and mechanical properties of AlN.

The rest of the thesis describes our efforts for identifying new piezoelectric materials. This requires high-throughput screening of inorganic materials for their piezoelectric properties. Our quest to search for new piezoelectric compounds is motivated by the notion that soft materials have the opportunity to exhibit large piezoelectric response (piezoelectric modulus $d$), and the knowledge that the van der Waals (vdW) layered materials are typically soft in the layer stacking direction. From a pool of 869 vdW structures, we have discovered 50 new compounds such as $\text{In}_2\text{Te}_5$, $\text{GeTe}$, and $\text{CuVO}_3$ having piezoelectric response larger than AlN. Remarkably, 70% of our discovered piezoelectric candidates do not contain any toxic elements like Pb. Our analysis reveals that the large components of $d$ always couple with the deformations (shearing or axial) of van der Waals “gaps” between the layers. This research establishes a wide scope of synthesizing vdW materials for applications demanding high piezoelectric modulus.
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LIST OF SYMBOLS

Electric field intensity or field strength ........................................................................ E
Polarization or electric moment per unit volume ................................................................. P
Electric displacement ........................................................................................................ D
Strain tensor ..................................................................................................................... ε
Stress tensor ..................................................................................................................... σ
Dielectric susceptibility .................................................................................................... χ
Dielectric permittivity of vacuum. .................................................................................... ϵ₀
Stiffness tensor ................................................................................................................ C
Compliance tensor .......................................................................................................... S
Identity matrix ................................................................................................................ I
Piezoelectric strain modulus or piezoelectric modulus tensor ........................................ d
Piezoelectric stress coefficient or piezoelectric coefficient tensor .................................. e
Piezoelectric voltage constant ......................................................................................... g
Energy transmission coefficient ...................................................................................... λₘₐₓ
Curie temperature .......................................................................................................... Tₐ₉
Mechanical quality factor .............................................................................................. Q or Qₘ₉
Electromechanical coupling constant .............................................................................. k
Acoustic impedance ........................................................................................................ Z
Dielectric constant .......................................................................................................... ϵ

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<th>Abbreviation</th>
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<tr>
<td>AC</td>
<td>Alternating Current</td>
</tr>
<tr>
<td>RF</td>
<td>Radio Frequency</td>
</tr>
<tr>
<td>SAW</td>
<td>Surface Acoustic Wave</td>
</tr>
<tr>
<td>BAW</td>
<td>Bulk Acoustic Wave</td>
</tr>
<tr>
<td>IC</td>
<td>Integrated Circuit</td>
</tr>
<tr>
<td>PT</td>
<td>Piezoelectric Transformer</td>
</tr>
<tr>
<td>GPS</td>
<td>Global Positioning System</td>
</tr>
<tr>
<td>MEMS</td>
<td>Microelectromechanical System</td>
</tr>
<tr>
<td>FOM</td>
<td>Figure of Merit</td>
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<tr>
<td>WLAN</td>
<td>Wireless Local Area Networks</td>
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<tr>
<td>CAGR</td>
<td>Compound Annual Growth Rate</td>
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<tr>
<td>CMOS</td>
<td>Complementary Metal-Oxide-Semiconductor</td>
</tr>
<tr>
<td>PZT</td>
<td>Lead Zirconate Titanate or Pb(Zr,Ti)O$_3$</td>
</tr>
<tr>
<td>PMN</td>
<td>PbMg$<em>{1/3}$Nb$</em>{2/3}$O$_3$</td>
</tr>
<tr>
<td>LN</td>
<td>Lithium niobate or LiNbO$_3$</td>
</tr>
<tr>
<td>LT</td>
<td>Lithium tantalate or LiTaO$_3$</td>
</tr>
<tr>
<td>LGS</td>
<td>La$_3$Ga$<em>5$SiO$</em>{14}$</td>
</tr>
<tr>
<td>VIF</td>
<td>Visual Information Fidelity</td>
</tr>
<tr>
<td>DFT</td>
<td>Density Functional Theory</td>
</tr>
<tr>
<td>KNN</td>
<td>K$<em>{0.5}$Na$</em>{0.5}$NbO$_3$</td>
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Bi$_4$Ti$_3$O$_{12}$  .................................................................................... BIT
Pb(Zn$_{1/3}$Nb$_{2/3}$)O$_3$  .............................................................................. PZN
Morphotropic Phase Boundary  ................................................................ MPB
Transmission Electron Microscopy  .......................................................... TEM
Wurtzite  .................................................................................................... WZ
Rocksalt  ..................................................................................................... RS
Vienna $ab$ initio Software Package  ............................................................. VASP
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To my parents
CHAPTER 1
INTRODUCTION

Piezoelectric devices have played a crucial role in enabling technology for a vast range of industrial and consumer products [1, 2, 3, 4]. As published in the new market research report “Piezoelectric Devices Market-Industry Trends, Opportunities and Forecasts to 2023”, the piezoelectric device market is expected to witness a compound annual growth rate (CAGR) of 4.35% to reach a total market size of US$ 24.9 billion by 2023, from US$ 20.1 billion in 2018. Material, product, and application are considered as three major pillars of the piezoelectric device market [3, 4]. The material division is further subdivided into piezocrystals, piezoceramics, piezopolymers, and piezocomposites [5]. On the basis of product, the piezoelectric device market is subdivided into sensors, actuators, transducers, motors, and generators [3]. The application of piezoelectric devices is extensive in manufacturing aerospace, defense, automotive, healthcare, and consumer electronics segment [3, 6, 7].

In spite of its vast applicability, only a handful of piezoelectric materials are technologically relevant and cover all piezoelectric devices in microelectromechanical (MEMS) applications. The design and discovery of new piezoelectric materials is key to finding solutions to drive the growth of piezoelectric device market. These solutions demand superior properties and performance in the new devices, and have been the focus of research over the past decade [8, 9]. While standard engineering techniques are successful in meeting these challenges, such techniques are mostly experimental. As a result, the laborious identification of individual materials with improved performance is inherently slow. It is possible to accelerate the discovery of these materials by understanding the processes that control material properties at atomistic level. This enables the tailoring of the structural and mechanistic features that lead to the improvement of the piezoelectric properties.
Density functional theory (DFT) is one of the most viable atomistic simulation techniques in this regard. In the expansive utilization of ab initio techniques for the identification and design of new materials, DFT is particularly fast and accurate [10, 11, 12, 13]. Design of materials driven by computational techniques is heading the thrust to direct and guide syntheses of new piezoelectric materials. DFT technique is an ideal method for investigating atomistic phenomena in these materials. Additionally, this technique can also be utilized to investigate the response of these materials to external parameters such as pressure and lattice strain.

The central theme of this thesis is to utilize DFT calculations to develop novel design strategies to enhance the properties of existing piezoelectric materials such as AlN. These strategies aim to enhance the functional properties, such as piezoelectric response using alloying, co-alloying, and external parameters such as strain. Subsequently, a high-throughput DFT screening technique is employed to aid the discovery of new piezoelectric materials. The conclusions from this work harbor the potential for the discovery of new piezoelectric materials with large piezoelectric response. Efficient combination of theoretical predictions supported with experimental confirmation will help the development of these materials with improved functionality, thus accelerating the discovery of novel and functionally advanced piezoelectric materials.

1.1 Piezoelectric Effect and Applications

Piezoelectric materials are a special class of materials that generate a voltage under the application of stress. Since this effect is also observed in a reverse manner, a voltage across the sample will produce strain (or deformation) in the sample. The schematic representation of direct and converse piezoelectric effects are shown in Figure 1.1. This particular property is used in wide range of microelectromechanical devices [6, 14].

Piezoelectricity is observed in crystals having no center of symmetry, i.e., this effect does not occur in centrosymmetric materials. In centrosymmetric materials, there is no way for mechanical stress to generate a dipole moment as any motion of an ion in centrosymmetric
Figure 1.1: Schematics of direct piezoelectric effects: (a) at applied compressive stress, (b) at applied tension. (c) and (d) describe the schematics of converse piezoelectric effect at applied electric field.

materials is reflected by symmetry to an equal and opposite motion that cancels out the dipole moment.

1.2 Classification of Piezoelectric Materials

One subgroup of piezoelectric materials show pyroelectric behavior. Pyroelectricity refers to the change in polarization by the changes in structure due to thermal effects [15]. In some of these pyroelectric materials, the polarization along the polar axis can be reversed by reversing the polarity of the electric field. Such crystals are called ferroelectric, i.e., these are spontaneously polarized materials with reversible polarization. The special characters of ferroelectric materials are [16, 17]: (1) hysteresis behavior ($P \sim E$ curve), (2) spontaneous polarization, (3) reversibility of polarization, (4) ferro-paraelectric transition temperature or Curie temperature ($T_C$). Above $T_C$, the ferroelectric material transforms to a high symmetry paraelectric phase, where all piezoelectric activity disappears. Below $T_C$, it shows a ferroelectric behavior and there is a ferroelectric to paraelectric transition at $T_C$. The classification
Dielectric
Piezoelectric
Pyroelectric
Ferroelectric

Figure 1.2: Classification of piezoelectric materials. They are classified into of piezoelectric, pyroelectric, and ferroelectric materials.

of piezoelectric materials are shown in Figure 1.2 and described in more detail in Appendix A.

1.3 Vector/Tensor Quantities Related to Piezoelectricity

Piezoelectricity is the combination of (a) the materials’ elastic behavior, \textit{i.e.} obey Hooke’s law) and (b) the materials’ electrical behavior. In this section, we will introduce several vector/tensor quantities related to these two behaviors.

\underline{Vectors related to electrical properties:}

From the electrical properties of material perspective, we are concerned with the following three vectors:

(1) $\mathbf{E}$ or the electric field intensity or field strength; equal to the force that would be exerted on a small unit charge placed at a point.

(2) $\mathbf{P}$ or the polarization; the electric dipole moment per unit volume.

(3) $\mathbf{D}$ or the electric displacement; defined by the charge per unit area that would be displaced across a layer of conductor placed across an electric field.

\underline{Tensors related to mechanical properties:}
Strain, $\varepsilon$ is the response of a system to an applied stress $\sigma$. In matrix notation, the symmetric $2^{nd}$-rank strain tensor is given as,

$$
\varepsilon = \begin{bmatrix}
\varepsilon_{11} & \varepsilon_{12} & \varepsilon_{13} \\
\varepsilon_{21} & \varepsilon_{22} & \varepsilon_{23} \\
\varepsilon_{31} & \varepsilon_{32} & \varepsilon_{33}
\end{bmatrix}
$$

(1.1)

The stress tensor $\sigma$, similar in nature to the strain tensor—both are symmetric second-order tensors, is given in matrix form as,

$$
\sigma = \begin{bmatrix}
\sigma_{11} & \sigma_{12} & \sigma_{13} \\
\sigma_{21} & \sigma_{22} & \sigma_{23} \\
\sigma_{31} & \sigma_{32} & \sigma_{33}
\end{bmatrix}
$$

(1.2)

The Voigt notation or Voigt form is used to utilize the symmetry of condensed matter to transform second-order tensors (such as strain tensor and stress tensor) to vectors [18]. In Voigt notation $\varepsilon$ is simplified to a 6-dimensional vector:

$$
\varepsilon \equiv \begin{pmatrix}
\varepsilon_{11} \\
\varepsilon_{22} \\
\varepsilon_{33} \\
\varepsilon_{23} \\
\varepsilon_{13} \\
\varepsilon_{12}
\end{pmatrix} \equiv \begin{pmatrix}
\varepsilon_1 \\
\varepsilon_2 \\
\varepsilon_3 \\
\varepsilon_4 \\
\varepsilon_5 \\
\varepsilon_6
\end{pmatrix}
$$

(1.3)

Similarly, representation in Voigt notation of $\sigma$ is,

$$
\sigma \equiv \begin{pmatrix}
\sigma_{11} \\
\sigma_{22} \\
\sigma_{33} \\
\sigma_{23} \\
\sigma_{13} \\
\sigma_{12}
\end{pmatrix} \equiv \begin{pmatrix}
\sigma_1 \\
\sigma_2 \\
\sigma_3 \\
\sigma_4 \\
\sigma_5 \\
\sigma_6
\end{pmatrix}
$$

(1.4)

### 1.4 Constitutive Equations

The constitutive equations for linear piezoelectric materials are well documented in the IEEE Standard on Piezoelectricity [19]. Here, we briefly describe the constitutive relations among different variables involved in piezoelectric effect and define various coupling coefficients that connect these variables.

**Dielectric permittivity:**
The induced polarization $\mathbf{P}$ in a dielectric material by an applied electric field vector $\mathbf{E}$, except for very high electric field, is expressed as,

$$\mathbf{P} = \varepsilon_0 \chi \mathbf{E} \quad (1.5)$$

where, $\chi$ is the dielectric susceptibility of the material and $\chi$ is a second-rank tensor. $\varepsilon_0 = 8.854 \times 10^{-12} \text{ F/m}$ is the dielectric permittivity of vacuum. The vectors $\mathbf{P}$, $\mathbf{E}$ and $\mathbf{D}$ are connected by the following relation [20],

$$\mathbf{D} = \varepsilon_0 \mathbf{E} + \mathbf{P} \quad (1.6)$$

Combining eqs. (1.5) and (1.6),

$$\mathbf{D} = \varepsilon_0 \mathbf{E} + \varepsilon_0 \chi \mathbf{E} = \varepsilon_0 (1 + \chi) \mathbf{E} = \varepsilon \mathbf{E} \quad (1.7)$$

where, $\varepsilon = \varepsilon_0 (1 + \chi)$ is the dielectric permittivity of the material. In practice, the relative dielectric permittivity, $\varepsilon^r = \varepsilon / \varepsilon_0$, also called the dielectric constant of the material, is more often used than the dielectric permittivity [15].

**Elastic stiffness tensor:**

The relationship between the applied stress $\sigma$ and resulting strain $\epsilon$ in a linear elastic material is given by Hooke’s law,

$$\sigma = \mathbb{C} \epsilon \quad (1.8)$$

And $\mathbb{C}$ defines the elastic stiffness tensor. The inverse relation expressed as,

$$\epsilon = \mathbb{S} \sigma \quad (1.9)$$

where, $\mathbb{S}$ is the elastic compliance tensor and related to $\mathbb{C}$ defined by,

$$\mathbb{S} \mathbb{C} = \mathbb{C} \mathbb{S} = \mathbb{I} \quad (1.10)$$

Where, $\mathbb{I}$ is an identity matrix.

**Piezoelectric strain modulus and piezoelectric stress coefficients:**

The differential form of eqn. (1.6),

$$d\mathbf{D} = \varepsilon_0 d\mathbf{E} + d\mathbf{P} \quad (1.11)$$
Therefore, if the electric field in the crystal is held constant, \( d\mathbf{P} = d\mathbf{D} \).

The linear relationship between stress \( \sigma \) applied to a piezoelectric material and \( \mathbf{P} \) is written as,

\[
\mathbf{P} = d\sigma
\]  
(1.12)

where, \( d \) is known as piezoelectric strain modulus or piezoelectric modulus. Whereas, piezoelectric stress coefficients or piezoelectric coefficient tensor, \( \varepsilon \) which relate \( \mathbf{P} \) and strain \( \varepsilon \) expressed by,

\[
\mathbf{P} = \varepsilon\varepsilon
\]  
(1.13)

Then, the relation between \( \varepsilon \) and \( d \) can be obtained straightforwardly from the strain-stress relation, \( i.e. \), eqn. (1.8). The relation between these two piezoelectric constants is simply,

\[
\varepsilon = d\varepsilon \quad \text{and} \quad d = \varepsilon S
\]  
(1.14, 1.15)

1.5 **Figures of Merit of Piezoelectric Devices**

Piezoelectric materials find wide variety of applications in MEMS devices. Each type of MEMS device has their own figures of merit (FOMs) that characterizes the performance of the corresponding devices. The various type of FOMs associated with different piezoelectric devices have been reviewed in this section.

1.5.1 **Figures of Merit**

There are five FOMs in piezoelectric devices that dictate the effectiveness of the piezoelectric device. They are described below:

* **Piezoelectric strain modulus or \( d \):** The absolute magnitude of the piezoelectric strain modulus which is expressed in eqn. (1.12). This is one of the important FOM in most of the piezoelectric devices particularly in actuators [6].
Piezoelectric voltage constant or $g$: The piezoelectric voltage constant related to piezoelectric sensor devices is expressed by the following equation [6],

$$g = \frac{d}{\varepsilon \varepsilon_0} \quad (1.16)$$

where, $d$ is piezoelectric strain modulus, $\varepsilon$ is dielectric constant, and $\varepsilon_0$ is the permittivity of free space.

Electromechanical coupling factor or $k$: The electromechanical coupling factor dictates the performance of piezoelectric devices in energy conversion. This is written as [6],

$$k^2 = \frac{\text{Stored mechanical energy}}{\text{Input electrical energy}} \quad (1.17)$$

or,

$$k^2 = \frac{\text{Stored electrical energy}}{\text{Input mechanical energy}} \quad (1.18)$$

Energy transmission coefficient or $\lambda_{\text{max}}$: All the stored energy cannot be used. The mechanical load defines the actual work done. This means that the systems with zero mechanical load or a complete clamp (no strain), no output work is done. The energy transmission coefficient is defined by [14],

$$\lambda_{\text{max}} = \frac{\text{Output mechanical energy}}{\text{Input electrical energy}} \quad (1.19)$$

Mechanical quality factor or $Q_M$: The mechanical quality factor ($Q_M$) of a piezoelectric devices characterizes the sharpness of the electromechanical resonance spectrum. $(Q_M)^{-1}$ is also equal to the mechanical loss ($\tan \delta_m$). The $Q_M$ value is very important in evaluating the magnitude of the resonant displacement and strain. The term $\tan \delta_m$ describes the heat in the piezoelectric sample operated at its resonance mode [14].

Acoustic impedance or $Z$: The acoustic impedance ($Z$) is an important FOM of piezoelectric devices which is used for evaluating the acoustic energy transfer between two materials.
[6]. It is defined as,

\[ Z^2 = \frac{\text{pressure}}{\text{volume} \cdot \text{velocity}} \]  

(1.20)

In solid materials,

\[ Z = \sqrt{\rho C} \]  

(1.21)

where \(\rho\) is the density and \(C\) is the elastic stiffness of the material.

Apart from above mentioned FOMs, the value of the dielectric constant also has an important role on the electrical matching in all piezoelectric devices.

1.5.2 Piezoelectric Devices

The wide variety piezoelectric devices can be classified into the following areas: (a) Sensors, (b) Actuators, (c) Ultrasonic transducers, (d) Resonators and Filters, (e) Transformers, and (f) Energy harvesters. Their description, applications, and FOMs are described below:

**Sensors:** A piezoelectric sensor is a versatile tool that finds applications in quality assurance, process control, and for research and development in many industries [21, 22]. The sensitivity of a piezoelectric sensor needs to be adequately high such that the generated signal can be detected above the background noise [23, 24]. The sensitivity of the piezoelectric sensor is maximized when the piezoelectric voltage constant (\(g\)) is maximized [22]. Hence, an important FOM of a piezoelectric sensor is the ‘\(g\)’ constant.

In practice, a large dielectric constant (or capacitance) is also desirable for sensors in order to overcome the losses associated with the electrical circuit. Unfortunately, an increase in \(\epsilon\) results in a lower \(g\) constant, as described in 1.5.1. Another important FOM of the piezoelectric sensor is the electromechanical coupling factor \(k\). The sensitivity of a piezoelectric sensor increases with increasing value of \(k\).

Currently, two main groups of piezoelectric materials are used for piezoelectric sensor applications: (a) polycrystalline piezoceramics (such as PZT-based [25]) and (b) single crystalline piezoceramics (such as gallium phosphate, quartz, and tourmaline). Usually, PZT-based piezoceramics have roughly two orders higher piezoelectric sensitivity compared to
those natural single crystal piezoelectric materials [21]. On the other hand, the less-sensitive single-crystal materials have high and long term temperature stability and high $Q_M$ [21].

**Actuators:** In converse piezoelectric effect, the piezoelectric materials expand or contract (deform) when an electrical field is applied. They generate mechanical motion and force on the application of electric field. Piezoelectric actuators (often called motors) harness this mechanical motion and provide very short strokes with high-frequency and fast response times [26].

The material requirements for these classes of devices are somewhat different from sensors applications. For instance, the piezoelectric materials for ultrasonic motors require a very hard piezoelectric with a high $Q_M$ to suppress heat generation. Likewise, in pulse-drive motors a low permittivity piezoelectric materials is used for its small hysteresis [27].

**Ultrasonic transducers:** In ultrasonic transducers, the AC voltage makes piezoelectric-crystal oscillate at the same frequency and produce ultrasonic sound [28, 6]. In these devices, two of the most important FOMs are the electromechanical coupling factor of the main vibration mode and the acoustic impedance. Another materials parameter dielectric constant also has an important role on the electrical matching [7, 6].

For low and medium ultrasonic frequencies (between 20 Hz and a few hundred kHz), a high values of permittivity are required in obtaining sufficient practical values for the electrical impedance. The high values of elastic compliance are favorable to maintain the dimensionality of the piezoelectric crystal. The linear dimension governs the resonance of the piezoelectric element. However, the higher the frequency devices, the less convenient are these high values. In pulse-echo transducers, the use of short ultrasonic pulses requires a mechanical $Q_M$ as low as possible for broad bandwidth.

The piezoceramics present the widest variety in their elastic, electric and piezoelectric constants and, in general terms they have the most favorable properties for ultrasonic transducers. The choice of a piezoelectric material depends on the specific application to which the transducer will be destined.
**Resonators and Filters:** The piezoelectric resonators are used to either generate waves of specific frequencies whereas the filters are employed to remove unwanted frequency components from the signal, to enhance wanted ones or both [29]. They find applications in cell phones, global positioning system (GPS), wireless local area networks (WLAN), and bluetooth. The high dimensional stability (i.e., piezoelectric materials with high mechanical stability or high stiffness) and the low-temperature coefficient is required to keep resonant frequency constant [30, 31]. To select a piezoelectric material for these applications, several parameters must be taken into account such as electromechanical coupling factor $k$, mechanical quality factor $Q_M$, chemical composition, and film deposition temperature [32]. The last two material parameters are essential for integration of filters above integrated circuit (IC) configuration [33].

The piezoelectric resonators, commonly made from quartz, are used as frequency references. Piezoelectric materials such as PZT, quartz, GaPO$_4$, and AlN are used in commercial filters [6]. Each material exhibits advantages and drawbacks. However, AlN provides the best trade-off in terms of electrical and mechanical properties. This is used in microelectronics technologies and for above IC component [34]. It provides the best balance of performance, CMOS compatibility, manufacturability, and reliability [34, 35].

Table 1.1: Piezoelectric devices and relevant FOMs. Each type of piezoelectric device has its own FOMs which characterize their performances.

<table>
<thead>
<tr>
<th>FOM</th>
<th>Sensors</th>
<th>Actuators</th>
<th>Ultrasonic transducers</th>
<th>Resonators &amp; Filters</th>
<th>Transformer</th>
<th>Energy Harvesters</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varepsilon_{ij}$</td>
<td>✔</td>
<td>✔</td>
<td>✔</td>
<td>✔</td>
<td></td>
<td>✔</td>
</tr>
<tr>
<td>$d$</td>
<td>✔</td>
<td>✔</td>
<td></td>
<td></td>
<td>✔</td>
<td>✔</td>
</tr>
<tr>
<td>$g$</td>
<td>✔</td>
<td>✔</td>
<td></td>
<td></td>
<td></td>
<td>✔</td>
</tr>
<tr>
<td>$k/k^2$</td>
<td>✔</td>
<td>✔</td>
<td>✔</td>
<td></td>
<td></td>
<td>✔</td>
</tr>
<tr>
<td>$\lambda_{\text{max}}$</td>
<td>✔</td>
<td>✔</td>
<td></td>
<td></td>
<td></td>
<td>✔</td>
</tr>
<tr>
<td>$Q_M$</td>
<td>✔</td>
<td>✔</td>
<td>✔</td>
<td></td>
<td></td>
<td>✔</td>
</tr>
<tr>
<td>$Z$</td>
<td>✔</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>✔</td>
</tr>
</tbody>
</table>
**Transformers:** The operation principle of a piezoelectric transformer is a combined function of actuators and sensors so that energy can be transformed from electrical form to electrical form via mechanical vibration [36, 3]. Hence, the combined figure of merits of sensors and actuators are required for the piezoelectric transformer materials.

The materials used for piezoelectric transformers includes PZT-series and LiNbO$_3$ [36, 3]. Most of the high-voltage piezoelectric transformers are made of PZT material [37, 36]. The newly developed thickness extensional mode piezoelectric transformer is made of PbTiO$_3$ and is very efficient at high frequencies [36].

**Energy harvesters:** Vibration-based energy harvesting has received growing attention over the last decade. There are three major steps associated with piezoelectric energy harvesting as stated in the words of Uchino [6]:

- **“Mechanical-mechanical energy transfer:** This includes mechanical stability of the piezoelectric transducer under large stresses, and mechanical impedance matching”.

- **“Mechanical-electrical energy transduction:** This relates to the electromechanical coupling factor in the composite transducer structure”.

- **“Electrical-electrical energy transfer:** This includes electrical impedance matching, a d.c./d.c. converter to accumulate the energy into a capacitor or a rechargeable battery”.

Electromechanical coupling factor and the product of $g$ and $d$ are the most widely used FOMs in piezoelectric energy harvesters for evaluating the energy conversion efficiency of the harvester devices [38]. Cantilever geometric structure also plays an important role in enhancing the performance of the harvester efficiency. The rectangular shaped cantilever structure are most widely used MEMS based piezoelectric harvesters. AlN and PZT based thin films are widely used piezoelectric materials for energy harvesters. However, the output power of AlN-harvester is limited to low power levels due to the low piezoelectric modulus of AlN. On the other hand, the efficiency of PZT based energy harvester is low as they cannot withstand large amount of strain due to the low stiffness modulus of PZT [38].
Figure 1.3: Correlation between different FOMs (a) Mechanical quality factor ($Q$ or $Q_M$) vs. electromechanical coupling factor ($k$), (b) Electromechanical coupling factor vs. dielectric constant ($\varepsilon$), and (c) Thickness mode coupling factor ($k_i$) vs acoustic impedance ($Z$). Reproduced from Ref. [39, 40, 41], with the permissions from Springer and Wiley.

In summary, a wide variety of FOMs and material parameters have been used to compare the performance of piezoelectric materials on diverse types of piezoelectric devices. This is shown in Table 1.1. It is very difficult to define a universal figure of merit for a large range of configurations or applications. For instance, in actuating and sensing, maximizing ‘$d$’ and ‘$g$’-constant is the goal to improve their performance. Likewise, ‘$k$’ for energy harvester devices quantify the ability in energy conversion. In similar fashion, high ‘$Q_M$’ and high ‘$k$’ are desired to meet the demands of the advanced high power resonator devices. However, piezoelectric materials with high ‘$Q_M$’ and high ‘$k$’ are incompatible (shown in Figure 1.3-
a). Similarly, high dielectric constant of a sensor materials is desirable to overcome the losses associated with the electrical circuit. Despite the fact that no material co-exhibit high dielectric constant and high $Q_M$ (as shown in Figure 1.3-b). It can be observed that no material allows to obtain both high coupling factor and low acoustic impedance ($Z$) (as shown in Figure 1.3-c). High $k$-constant is necessary to enhance the sensitivity of the medical imaging transducers whereas, another FOM $Z$ should be as low as possible to match with the acoustic impedance of biological tissues. Thus, a compromise must be made depending on the target devices. In addition, a high $T_C$ is always desired for improved temperature stability for high temperature piezoelectric devices [42] and high $Q_M$ for dimensional stability and low mechanical loss. All these explain the complexity of optimizing piezoelectric properties in existing piezoelectric materials.

In chapter 3, we develop novel alloying strategies, and it reveals that co-alloying with YN and BN enables the most superior combination of piezoelectric and mechanical properties in AlN.

1.6 Piezoelectric Materials: Present Status and Motivation for Computational Investigations

This section describes the state-of-the-art reviews of modern piezoelectric materials, primarily the materials based on ceramics (piezoceramics). The piezoceramics are the most widely used and commercially accepted piezoelectric material. They display large displacements or induce large electric voltages. Furthermore, they are cost-effective and can easily be tailored to meet the requirements of specific applications. Therefore, piezoceramics are the most preferred material for manufacturing piezoelectric devices and occupy the largest size of the overall piezoelectric device market [4].

Piezoceramics are broadly categorized based on their form of use, such as materials used in single crystal, polycrystalline, and thin film form.
1.6.1 Materials based on Single Crystal

Quartz [43, 44, 45] and some other piezoelectric crystals such as LiNbO$_3$ [45] or LiTaO$_3$ [45], GaPO$_4$ [46] and more recently crystals from the Langasite [45] family are used in their single crystal form. These materials find applications as raw materials to build resonators, filters, oscillator, and sensors [47]. This section reviews the application, properties, and limitations of various piezoelectric single crystal materials (Figure 1.4).

![Diagram of piezoelectric single crystals](image)

Figure 1.4: The advancement of piezoelectric single crystals with year. Schematic is sourced from Ref. [48]
Quartz: Quartz is one of the earliest piezoelectric materials used as timers in clocks and is also used for various acoustic devices, voltage controlled oscillators, and micro biosensors [43, 44, 45, 49]. In Figure 1.5 schematics of different internal components of a watch (including quartz oscillator) are shown.

The dielectric constant and piezoelectric modulus of single crystal quartz were found to be 4.5 and 2 pC/N [50], respectively. Piezoelectric α-quartz has a phase transition temperature of 573°C (α-quartz → β-quartz). However, its maximum use temperature is normally limited to 350°C. Beyond 350°C crystal structure in quartz experiences twinning, that causes the piezoelectric properties of quartz to disappear [45, 17].

The main advantage of quartz crystal is its extremely high mechanical quality factor $Q_M (=10^6)$ [49]. This property of quartz crystal befitting for applications demanding very high mechanical stability. Another important feature of quartz is its high abundance in nature. As a result, quartz crystals are available at low cost, and with relatively high purity and perfection. However, their applications in large strain applications are often limited due to its low piezoelectric modulus (compared to AlN, PZT-based, BaTiO$_3$-based), low coupling constant (compared to PZT-based, BaTiO$_3$-based), low voltage constant (compared to PZT-based, BaTiO$_3$-based), and low phase transition temperature (compared to AlN, langasite-based piezoelectrics).

Lithium niobate/tantalate: Lithium niobate (LiNbO$_3$ or LN) and lithium tantalate (LiTaO$_3$ or LT) crystals belong to an isomorphous crystal system and are structurally composed of oxygen octahedrons. Thus, both materials hold very important positions in the SAW device application field. The Curie temperatures of LiNbO$_3$ and LiTaO$_3$ are 1210 and 660°C, respectively [52]. Piezoelectric single crystals such as 128°Y-X (128°-rotated-Y-cut and X-propagation)-LiNbO$_3$ and X-112°Y (X-cut and 112°-rotated-Y-propagation)-LiTaO$_3$ have been extensively used as SAW substrates for applications in VIF filters [53, 54].

The piezoelectric modulus of LiNbO$_3$ and LiTaO$_3$ are 8.3 and -21 pC/N, respectively [52, 54]. These materials have high electromechanical coupling coefficients compared to
quartz for surface acoustic waves. In addition, large single crystals can easily be obtained from their melt using the conventional Czochralski technique [55]. However, they have less mechanical quality factor compared to quartz [42]. The application temperature range for the LN crystals is limited to 650°C due to their low resistivity [53].

**Langasite-based piezoelectrics:** Langasite (R₃Ga₅SiO₁₄, R= rare earth element) crystals have recently become attractive for high-temperature bulk acoustic wave (BAW) and surface acoustic wave (SAW) applications [56, 57]. La₃Ga₅SiO₁₄ or LGS has the highest piezoelectric modulus among this family of crystals [58]. Contrary to quartz, LN, and LT piezoelectric crystal, LGS has no phase transition up to its melting point at 1475°C [42]. Therefore, it becomes a suitable candidate for high-temperature applications in sensors. They can be conventionally grown by the Czochralski technique [59].

The dielectric constants and piezoelectric coefficients of LGS are found to be in the range of 18-25 and 5-8 pC/N, respectively [57]. The piezoelectric modulus d₁₁ of LGS is about 2.7 times larger than quartz. This allows realizing piezoelectric sensors with langasite family of crystals significantly with higher sensitivity. The electromechanical coupling factor is 2.3-3 times larger than quartz. As a result, the resonators with high pullability can be
fabricated with LGS piezoelectrics, having temperature stability with broad temperature and a high $Q$-factor. The $Q$-factors of Langasite piezoelectric crystals are in the same order of magnitude as those of quartz resonators. Langasite family is well suited for operating at high temperatures and mechanical loads as wireless acoustic and piezoelectric sensors.

*GaPO$_4$ piezoelectrics:* Gallium orthophosphate is a quartz-analogue crystal. Currently, GaPO$_4$ with its properties is by far the best suited piezoelectric material to be used in sensor applications for machine monitoring and pressure measurements [60]. SAW micro-devices based on GaPO$_4$ operate at temperatures of up to 800°C [60]. It possess a high $d_{11}$ value of 4.5 pC/N and a low dielectric constant of 6 [46, 61]. In comparison with quartz, GaPO$_4$ exhibits nearly all the advantages of quartz, additionally it also possess higher electromechanical coupling and has thermally stable physical properties up to 950 °C [61, 62]. At 950°C, an irreversible phase transformation occurs and GaPO$_4$ transforms into a cristobalite-like phase [42]. They can be grown using hydrothermal techniques and presently are produced commercially in autoclaves [63].

Single crystal relaxor ferroelectrics with the morphotropic phase boundary (MPB) composition show tremendous promise as ultrasonic transducers and electromechanical actuators [64, 65]. The single crystals of Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ (PMN), Pb(Zn$_{1/3}$Nb$_{2/3}$)O$_3$ (PZN) and their binary systems with PbTiO$_3$ (PMN-PT and PZN-PT) have extremely large electromechanical coupling factors [66, 67, 65]. PZN-8%PT single crystals are found to possess a high $k_{33}$ value of 0.94 for the (001) crystal cuts [65]. This is much higher compared to the $k_{33}$ of conventional PZT ceramics of around 0.70-0.80 [67, 65]. The single crystal of KNbO$_3$ (KN) is known to have high piezoelectric activities [68, 69]. However, it is difficult to obtain a dense ceramic body of KN by the ordinary firing process [70].

### 1.6.2 Materials Based on Polycrystalline Materials

Polycrystalline materials in bulk form (ceramics and thick films) with randomly oriented grains must be ferroelectric for exhibiting piezoelectricity. By the process called ‘poling’, the randomly distributed ferroelectric domains orients on the direction of electric field [17].
Contrary to bulk samples, the thin film samples allow the controlled growth of thin layers (on the order of 0.1 to 1.55 µm) of many materials [71]. In case of non-ferroelectric polycrystalline films, to achieve piezoelectricity, one should orient the grains in a direction which is piezoelectrically active. Many non-ferroelectric materials which cannot be grown as single crystals and which cannot show piezoelectricity in the bulk form can thus be used in piezoelectric applications as thin films. This has significant technological consequences because thin layers may be deposited on different substrates and can be microstructured and integrated with other electronic or mechanical components [72].

The polycrystalline piezoelectric materials are broadly classified into following groups: (a) perovskite-based, (b) non-perovskite based, and (c) thin-film based. The following sections summarize the applications, properties, and limitations of several commercial polycrystalline piezoelectric materials.

(a) Perovskite-based

The well-known piezoelectric perovskite materials are BaTiO$_3$ (BT), PbTiO$_3$, KNbO$_3$, and mixed-cation compounds such as Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ [17, 23, 73]. Perovskites easily form solid solutions with other perovskites, and hundreds of compounds have been synthesized with very interesting dielectric, optical, and piezoelectric properties [7, 6].

The chemically simple perovskite materials may undergo a complex sequence of phase transitions. Some materials, like BaTiO$_3$, KNbO$_3$, and NaNbO$_3$, undergo several phase transitions into successive ferroelectric phases, whereas, others like relaxor-ferroelectric solid solutions, may exhibit a relaxor phase over a narrow temperature range before transforming into a ferroelectric phase [74]. In Na$_{1/2}$Bi$_{1/2}$TiO$_3$ based compositions, a phase transition sequence from a paraelectric to antiferroelectric relaxor to ferroelectric phase has been observed [75].

In general, the piezoelectric coefficients in ferroelectrics are higher than in nonferroelectrics and in perovskites range from tens to hundreds of pC [7, 71, 76]. Besides this high piezoelectric activity, an advantage of ferroelectric materials over nonferroelectric ones is that
they can be prepared in polycrystalline form (as bulk ceramics). They exhibit piezoelectric effect after poling with a strong electric field [77]. As ceramics are usually easier and less expensive to prepare than single crystals, ferroelectric perovskites have been widely used for various piezoelectric applications, almost exclusively in polycrystalline form [71, 78].

**PZT-based:** Among polycrystalline piezoceramic materials, by far the most important piezoelectric materials are solid solutions of PbZrO$_3$ and PbTiO$_3$ (Pb(Zr, Ti)O$_3$ or PZT) which have been used in hundreds of different devices [79]. For a long time, PZT was considered as the best piezoelectric material and main research efforts have been directed toward optimization of PZT based compositions for specific applications. Although this material has a high piezoelectric response, 410 pC/N [76], it is limited by its maximum operating temperature of 250°C. Recently, however, it has been shown that the piezoelectric properties superior to those in PZT ceramics may be obtained in single crystals of some perovskites [80]. However, considering the toxicity of lead oxide, development of lead-free piezoceramics is encouraged in recent years.

**BaTiO$_3$(BT)-based:** Barium titanate was the first piezoelectric ceramic developed and is still widely used [7]. This is because with the exception of Rochelle salt, its coupling factors are substantially higher than that of any previously known material [81, 31]. These ceramics have a relatively high electromechanical coupling factor, $k_{33}$ (0.50), and piezoelectric strain constant, $d_{33}$ (190 pC/N), and have been used in piezoelectric applications such as sonars [82, 81]. In addition, they are chemically more stable than Rochelle salt, have a wider temperature range of operation, and superior manufacturability.

The dielectric and piezoelectric properties of ferroelectric ceramic BaTiO$_3$ can be affected by its own stoichiometry and microstructure. Modified ceramic BaTiO$_3$ with dopants such as Pb or Ca ions have been developed to stabilize the tetragonal phase over a wider temperature range and have been used as commercial piezoelectric materials. After the discovery of PZT, BT’s role in piezoelectric devices faded out and they are primarily used as capacitors at present days[17]. Other major disadvantages of BaTiO$_3$-based piezoelectrics is its low Curie
temperature. Thus, the working temperature range of this ceramic is narrow for actual piezoelectric applications [83].

**KNbO$_3$-based:** Solid solutions of potassium niobate (KNbO$_3$) with sodium niobate (NaNbO$_3$) leads to a system with many MPBs, showing ferroelectricity up to about 90% NaNbO$_3$ [84]. There is a MPB near the 50/50 composition separating two orthorhombic phases. This composition shows a rather high piezoelectric longitudinal response, a transverse coupling coefficient between those in modified lead titanate and hard PZT ($d_{33}$ reported to be as high as 160 pC/N for (K$_{0.5}$Na$_{0.5}$NbO$_3$ (KNN)), and a relatively low dielectric constant (around 400 at room temperature) [84, 85, 86]. KNN is one of the most lead-free candidates for high-frequency transducers, with its low density, high Curie temperature, and relatively high electromechanical coupling factor [85]. They could, therefore, be considered as a viable alternative to PZTs for selected applications. In addition, this material in a form of fully dense ceramics appears to be compatible with animal and human tissues.

KNbO$_3$ and K$_{1-x}$Na$_x$NbO$_3$ ceramics are difficult to process to full densities by natural sintering for several reasons [83, 6]. One is that the phase stability is limited to 1040°C for KNbO$_3$ and 1140°C for K$_{1-x}$Na$_x$NbO$_3$. Therefore, the high sintering temperatures are not possible. In addition, slight changes in stoichiometry (both on the niobium rich and the potassium-rich side) lead to the formation of extra phases [83]. Potassium excess might provide some densification, helping liquid phase but some of the formed extra phases are highly hygroscopic and lead to a quick disintegration of the final sample once exposed to humidity. Some concern has been raised about high dielectric losses in these materials [83].

**(b) Non-perovskite-based:**

**Bismuth Titanate Based Layered Compounds:** The crystal structure of Bi$_4$Ti$_3$O$_{12}$ (BIT) and related compositions, first described by Aurivillus [87, 88], is characterized by pseudoperovskite layers. They have a high ferroelectric Curie temperature (up to 980°C) and show high-temperature piezoelectric behavior. They are potential candidate lead-free materials in piezoelectric device applications, especially under high temperature and high-frequency
conditions [88]. They have relatively low dielectric constant, low aging rate, and strong anisotropic electromechanical coupling factors. Unfortunately, the piezoelectric activity if BITs is relatively low, with values less than 20 pC/N [88].

**(c) Thin film-based:** Both zinc oxide (ZnO) and aluminum nitride (AlN) are simple binary compounds with a Wurtzite-type structure, which can be sputter-deposited as a $c$-axis oriented thin film on a variety of substrates [89, 71]. Since ZnO has a reasonable piezoelectric coupling, thin films of this material are widely used in bulk acoustic and surface acoustic wave devices. The fabrication of highly oriented (along $c$-axis) ZnO films have been studied and developed extensively. However, the performance of ZnO devices is limited, due to their low piezoelectric coupling (20-30%) [89, 71].

PZT thin films are expected to exhibit higher piezoelectric properties. At present, the development of PZT thin films is being carried out for use in micro-transducers and micro-actuators [71]. AlN and ZnO exhibit much higher mechanical quality factors than PZT, and in comparison to LiNbO$_3$, they are much more easily grown in thin film form. Moreover, integration and process compatibility with the rest of the device is less difficult using the relatively simple wurtzite materials. The strong polarity of their crystalline structure allows for a polar growth and a stable piezoelectric response with time, whereas ferroelectrics always risk depoling.

**AlN-based:** It is a hard material with light atoms and exhibits a high mechanical quality up to very large microwave frequencies. Moreover, it is CMOS compatible, in contrast to PZT and ZnO. A rather specific feature of AlN is its high sound velocity. AlN exhibits quite a large bandgap of 6.1 eV at room temperature. Consequently, it is a good dielectric material up to high temperatures. PZT thin film solutions in micro-sensors and actuators are very competitive when current signal and force or power outputs are demanded. When voltage signal, intrinsic signal-to-noise ratio, or power efficiency is an issue, the nonferroelectric AlN is competitive, or even better [71].
1.6.3 Toxicity of Lead-based Piezoelectrics

Lead oxide based piezoelectric, which are commonly represented by lead zirconate titanate (Pb(Zr,Ti)O$_3$) or PZT) are the most widely used materials for piezoelectric actuators, sensors and transducers due to their excellent piezoelectric properties [77, 17]. Nonetheless, there is a raising concern about the recycling and disposal of piezoelectric devices containing PZT due to the toxicity of lead oxide [90, 91]. Lead oxides vaporizes during processing and stays in the environment causing damage to brain and nervous system [92, 93]. This is particularly important in PZT containing consumer products such as cars, various kinds of smart systems, and sound generators [91]. Thus, there is an increasing tendency to look for alternative piezoelectric materials that does not contain Pb.

1.6.4 Motivation for Computational Research on Improving Piezoelectric Materials

The piezoelectric properties and applications of various commercial piezoelectric materials have been extensively discussed in section 1.6. For convenience, the primary merits and demerits of such piezoelectric materials are summarized in Table 1.2. This infers that each commercial piezoelectric has their own drawbacks. Thus, it is necessary to improve the piezoelectric and related properties of existing materials, as well as discover new piezoelectric materials. Enhance the properties of existing piezoelectric materials would help to make them technologically more attractive. On the other hand, discovery of new piezoelectric materials will expand the pool of existing piezoelectric materials, which would broaden the range of their applications and could potentially replace the toxic materials presently in use.

Over the past century, materials scientists have successfully engineered the functionality of materials by chemical substitution (cation and anion) or alloying. This technique leads to enormous possibilities to combine the elements of the periodic table into different alloys if we allow any number of components at any concentrations. Manufacturing each of these materials and measuring the properties of each one of them would take an unbearably long time and require vast resources. Therefore, it is imperative that we realize how materials
Table 1.2: Merits and demerits of several commercially used piezoelectric materials

<table>
<thead>
<tr>
<th>Materials</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>(a) High mechanical quality factor</td>
<td>(a) Low piezoelectric modulus</td>
</tr>
<tr>
<td></td>
<td>(b) Temperature stability</td>
<td>(b) Low coupling constant</td>
</tr>
<tr>
<td></td>
<td>(c) High dimensional stability</td>
<td>(c) Low phase transition temperature</td>
</tr>
<tr>
<td>LiNbO$_3$ &amp; LiTaO$_3$</td>
<td>(a) High Curie temperature</td>
<td>(a) Low mechanical stability</td>
</tr>
<tr>
<td></td>
<td>(b) Non-toxic</td>
<td>(b) CMOS incompatible</td>
</tr>
<tr>
<td>Langasite-based (La$_3$Ga$<em>5$SiO$</em>{14}$)</td>
<td>(a) No phase transition up to its melting point</td>
<td>(a) Twinning and softness of this materials may limit its applications at high pressure</td>
</tr>
<tr>
<td>(La$_3$Ga$<em>5$SiO$</em>{14}$)</td>
<td>(b) High piezoelectric and electromechanical properties</td>
<td></td>
</tr>
<tr>
<td>(La$_3$Ga$<em>5$SiO$</em>{14}$)</td>
<td>(c) Low acoustic wave propagation losses</td>
<td></td>
</tr>
<tr>
<td>BaTiO$_3$-based</td>
<td>(a) High piezoelectric properties</td>
<td>(a) Low mechanical stability</td>
</tr>
<tr>
<td>(a) High Coupling Constants</td>
<td>(b) Low Curie temperature</td>
<td>(b) Low operational temperature</td>
</tr>
<tr>
<td>(b) Non-toxic</td>
<td>(c) Risk of depoling</td>
<td>(c) Risk of depoling</td>
</tr>
<tr>
<td>PbTiO$_3$-based</td>
<td>(a) High piezoelectric properties</td>
<td>(a) Low mechanical stability</td>
</tr>
<tr>
<td>(b) High Coupling Constants</td>
<td>(b) Low operational temperature</td>
<td>(b) High Coupling Constants</td>
</tr>
<tr>
<td>(c) Non-toxic</td>
<td>(c) Risk of depoling</td>
<td>(c) Risk of depoling</td>
</tr>
<tr>
<td>KNbO$_3$-based</td>
<td>(a) Non-toxic</td>
<td>(a) Low piezoelectric properties</td>
</tr>
<tr>
<td>(b) High Curie temperature</td>
<td>(b) High dielectric losses</td>
<td>(b) High Curie temperature</td>
</tr>
<tr>
<td>(c) Bio-compatibility</td>
<td>(c) High temperature synthesizability</td>
<td>(c) Bio-compatibility</td>
</tr>
<tr>
<td>(d) Volatility of alkali components at higher temperature</td>
<td>(d) CMOS incompatible</td>
<td></td>
</tr>
<tr>
<td>(e) Low sintered density; difficult to fabricate the ceramics</td>
<td>(e) Risk of depoling</td>
<td></td>
</tr>
<tr>
<td>ZnO-based</td>
<td>(a) High mechanical quality factor</td>
<td>(a) Low piezoelectric modulus</td>
</tr>
<tr>
<td>(b) Non-toxic</td>
<td>(b) Low coupling constant</td>
<td>(b) Low operational temperature</td>
</tr>
<tr>
<td>(c) CMOS compatible</td>
<td>(c) CMOS incompatible</td>
<td>(c) CMOS compatible</td>
</tr>
<tr>
<td>AlN-based</td>
<td>(a) High mechanical quality factor</td>
<td>(a) Low piezoelectric modulus</td>
</tr>
<tr>
<td>(b) Temperature stability</td>
<td>(b) Low coupling constant</td>
<td>(b) Low operational temperature</td>
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<td>(c) CMOS compatible</td>
<td>(c) CMOS compatible</td>
<td>(c) CMOS compatible</td>
</tr>
</tbody>
</table>
work at an atomic and electronic scale, and use that knowledge to guide our search for better materials with improved properties.

There are plenty of advantages with computer simulations compared to experiments. It is possible to execute simulations with toxic or radioactive materials. It is also feasible to test costly materials without any cost. Although, there is also a constraint in computer simulations. There is often a choice to be made whether a simulation should be accurate or if it should be large (e.g. include many atoms or long time scales). This Ph.D. thesis is an effort to extend the frontiers of disordered multicomponent nitrides for efficient designing of nitride piezoelectrics and to discover novel piezoelectric materials for replacing non-toxic piezoelectrics. The first half of this work, we have explored the effect of alloying and co-alloying on improving the properties of AlN. Another half of this work, we have described our effort in finding new piezoelectrics by means of high-throughput DFT. Note that, materials properties can controlled by the processes that occur at other length scales such as macroscale [94, 95] and mesoscale [96, 97, 98, 99], which are not the focus of the present thesis.

1.6.5 Prior Computational Studies of Piezoelectric Properties

**AlN-Based Piezoelectrics:** Numerous efforts were made over the years to predict piezoelectric properties of AlN by DFT. Kamiya [100] calculated the piezoelectric properties of AlN. The predicted $d_{33}$ of AlN is 6.7 pC/N which is about 20% higher than the experimentally measured values. Later, Bernardini and Fiorentini [101] calculated $d_{33}$ as 5.4 pC/N. The latter value is very close to the experimental value. Tasnadi et al. [102] published an $e_{33}$ value of 1.55 C/m$^2$, identical to the experimental value. With the discovery of improvement of piezoelectric constant by Sc doping, the efforts are being done more systematically in order to predict Al$_{1-x}$Sc$_x$N properties. The most complete work was published by Caro et al. [103]. The values for $e_{33}$, and $d_{33}$ were obtained as 1.46 C/m$^2$, and 5.12 pC/N respectively. All values are thus about 10% smaller than in reality.

Recently, it was discovered that Al substitution by Sc allows for an increase of the piezoelectric response [103, 102] of AlN. The origins of this enhancement in piezoelectric response
have been studied [102]. As the content of the rocksalt end member in the alloy increases, the accompanying structural frustration enables a greater piezoelectric response.

Although the peak of the piezoelectric increase is found at around 50% Sc, it becomes increasingly difficult to maintain good enough crystalline quality in the films to realize the exceptional piezoelectric response. Therefore, it is expected that practical device applications will be using lower concentrations of Sc. However, there are several other challenges involved in AlN based thin piezoelectric thin films.

- The possible route for improving its piezoelectric modulus is addition of transition metal element. Increasing piezoelectric modulus is also accompanied by elastic softening which make this material less appealing for resonator based devices where mechanical stability of the thin film is one of the important figure of merit.

- The increasing alloy content results in severe degradation of thin film texture. The piezoelectric responses of piezoelectric thin film strongly depend on the texture of the thin film. So it is preferable to choose proper alloying with the highest piezoelectric sensitivity to alloy composition.

**Computational Searches for New Piezoelectric Materials:** Identifying new piezoelectric systems required high-throughput screening of inorganic materials for their piezoelectric properties. The need for new piezoelectrics was recognized before and was the main motivation behind recent computational efforts in high-throughput screening of inorganic materials for piezoelectric performance. These include the work on perovskite alloys, and creation of a database of piezoelectric properties of compounds. Materials with reduced dimensionality, such as 2D mono- and multi-layers have also been investigated recently.

1.7 Objectives

My doctoral research work aims to discover novel piezoelectric materials and enhance the properties of existing (AlN) ones to make them technologically attractive.
1.7.1 Improving Performance of Existing Piezoelectric Materials

In section 1.6.5, we have identified that main drawback of AlN piezoceramics is its low piezoelectric modulus. Addition of transition metal elements is a suggested method to improve the piezoelectric modulus of AlN. However, such alloying severely degrades the thin film texture, ultimately deteriorating the piezoelectric properties. Thus, it becomes necessary to identify suitable alloying elements that may yield highest piezoelectric response with minimal additions.

In my doctoral research, we approached the problem by conducting DFT calculations of structure and properties of AlN system alloyed with different transition elements such as Sc$^{3+}$, Y$^{3+}$, Cr$^{3+}$, and La$^{3+}$. The study revealed that alloying with Cr$^{3+}$ would lead to the lowest wurtzite/rocksalt transition point, thereby allowing piezoelectric enhancements at alloying levels that are easier to stabilize during the synthesis. The significant enhancement of piezoelectric modulus, with minimal alloying additions, establish Cr$_x$Al$_{1-x}$N as a suitable replacement for AlN [104].

However, such alloying is also accompanied by a softening of the AlN lattice. Our subsequent research focused to develop novel alloying strategies, and it was revealed that co-alloying with YN and BN enables superior combination of piezoelectric and mechanical properties in AlN [105].

1.7.2 Searching for New Piezoelectric Materials

Besides improving the existing piezoelectrics, we also used high-throughput DFT approach to discover new piezoelectrics. The main goal of this work is not to discover the single piezoelectric material that will replace all others, instead, expand the pool of existing piezoelectric materials with different set of other properties with the focus on large piezoelectric modulus. This would efficiently guide users towards new materials that will best fit their needs.
Our focus is to find new piezoelectric materials with large piezoelectric response \textit{i.e.} materials with large $d$-value. Here, we have used the relationship between $d$ and $C$ as discussed in 1.14, where, we see that piezoelectric modulus $d$ is inversely related to its $C$. This implies that the softer materials tend to have larger piezoelectric modulus compared to a stiffer materials with similar $e$. Even if materials with non-interesting $e$, because of softness one might get large $d$ in the softer direction(s). This knowledge encourages us to inspect in the quasi-2D van der Waals (vdW) bonded layered materials for new piezoelectric materials. The quasi-2D materials exist in layers and the layers are held together by soft vdW bond. Hence, they are very soft in vdW-bonded direction. As a result, one may expect large $d$ in that softer direction because of low stiffness in that direction. 51 vdW layered materials are predicted to have piezoelectric response larger than that of AlN and 3 materials with response even larger than PbTiO$_3$. More importantly, we identified 33 materials with large piezoelectric response that do not contain toxic elements such as Pb. None of these predicted candidates have previously been considered as piezoelectric materials. Furthermore, our analysis shows that large piezoelectric response in layered materials is indeed enabled by the soft vdW bonds, \textit{i.e.}, large $d$ originates from the direct shear or axial deformations of the vdW bonds. This research established a wide scope to synthesize quasi-2D materials for applications demanding high piezoelectric modulus.

1.8 Organization of the Thesis

This thesis is organized in the following chapters:

- \textbf{Chapter 2} presents the work titled “Enhanced piezoelectric response of AlN via CrN alloying” published in Physical Review Applied. Here, we have studied the effect of Cr alloying on piezoelectric and mechanical properties of AlN. The study revealed that alloying with CrN would lead to the lowest wurtzite/rocksalt transition point, thereby allowing piezoelectric enhancements at alloying levels that are easier to stabilize during the synthesis. The significant enhancement of piezoelectric modulus, with minimal
alloying additions, establish (Cr,Al)N as a suitable replacement for AlN.

**Author’s contribution:** In this work, I took part in planning, performed all the theoretical calculations, participated in the evaluation and interpretation of the results, and was responsible for writing the manuscript.

- **Chapter 3** describes the effect of co-alloying on the piezoelectric and mechanical properties of AlN. My initial research established that the piezoelectric response of Aluminum Nitride (AlN), a common piezoelectric for resonators, could be improved by alloying with trivalent transition elements like chromium Cr$^{+3}$, yttrium Y$^{+3}$, scandium Sc$^{+3}$ and lanthanum La$^{+3}$. However, such alloying is also accompanied by a softening of the AlN lattice. Our subsequent research focused to develop novel alloying strategies, and it was revealed that co-alloying with YN and BN enables the most superior combination of piezoelectric and mechanical properties to develop in AlN. This work is published Journal of Applied Physics titled “Tuning the piezoelectric and mechanical properties of the AlN system via alloying with YN and BN”.

**Author’s contribution:** In this work, I took part in planning, performed all the theoretical calculations, participated in the evaluation and interpretation of the results, and was responsible for writing the manuscript.

- **Chapter 4** describes the high throughput discovery of new piezoelectric materials using first principle density functional theory. The discovery of new piezoelectric materials would broaden the range of applications and offer cost-effective, non-toxic alternatives. In this work, we have performed a large-scale computational investigation of the piezoelectric properties of 869 vdW layered materials, including binary and ternary chemistries. The results confirm our expectation. Our search has revealed a number vdW layered materials that exhibit large piezoelectric response; 51 vdW layered materials are predicted to have piezoelectric response larger than that of AlN, a commonly used piezoelectric material in resonators and 3 materials with response even larger than
PbTiO$_3$. More importantly, we identified 33 materials with large piezoelectric response that do not contain toxic elements such as Pb. None of these predicted candidates have previously been considered as piezoelectric materials. Furthermore, our analysis shows that large piezoelectric response in layered materials is indeed enabled by the soft vdw bonds, \textit{i.e.}, large $d$ originates from the direct shear or axial deformations of the vdw bonds.

Author’s contribution: In this work, I took part in planning, performed majority the theoretical calculations, participated in the evaluation and interpretation of the results, and was responsible for writing the manuscript.

- Chapter 5 summarizes the work presented in this thesis, highlights the main conclusions and provides directions for future work.
CHAPTER 2

ENHANCED PIEZOELECTRIC RESPONSE OF AlN via CrN ALLOYING

A paper published in Physical Review Applied

Sukriti Manna², Kevin R Talley³, Prashun Gorai³, John Mangum³, Andriy Zakutayev⁴, Geoff L Brennecka³, Vladan Stevanović³, Cristian V Ciobanu²

Since AlN has emerged as an important piezoelectric material for a wide variety of applications, efforts have been made to increase its piezoelectric response via alloying with transition metals that can substitute for Al in the wurtzite lattice. Herein, we report density functional theory calculations of structure and properties of the Cr-AlN system for Cr concentrations ranging from zero to beyond the wurtzite-rocksalt transition point. By studying the different contributions to the longitudinal piezoelectric coefficient, we propose that the physical origin of the enhanced piezoelectricity in CrₓAl₁₋ₓN alloys is the increase of the internal parameter u of the wurtzite structure upon substitution of Al with the larger Cr ions. Among a set of wurtzite-structured materials, we have found that CrₓAl₁₋ₓN has the most sensitive piezoelectric coefficient with respect to alloying concentration. Based on these results, we propose that (Cr, Al)N is a viable piezoelectric material whose properties can be tuned via Cr composition. We support this proposal by combinatorial synthesis experiments, which show that Cr can be incorporated in the AlN lattice up to 30% before a detectable transition to rocksalt occurs. At this Cr content, the piezoelectric modulus d₃₃ is approximately four times larger than that of pure AlN. This finding, combined with the relative ease of synthesis under non-equilibrium conditions, may propel (Cr, Al)N as a prime piezoelectric material for applications such as resonators and acoustic wave generators.

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2.1 Introduction

Aluminum nitride has emerged as an important material for micro-electromechanical (MEMS) based systems [106, 107] such as surface and bulk acoustic resonators [106, 108], atomic force microscopy (AFM) cantilevers [106], accelerometers [109, 110], oscillators [111], resonators for energy harvesting [112, 113], and band-pass filters [114]. The advantages of using AlN in MEMS devices include metal–oxide–semiconductor (CMOS) compatibility, high thermal conductivity, and high temperature stability. In addition, its low permittivity and high mechanical stiffness are particularly important for resonator applications [106, 115]. However, the piezoelectric constants of AlN thin films are lower than those of other commonly used piezoelectric materials. For example, the out-of-plane piezoelectric strain modulus [116] $d_{33}$ of reactively sputtered AlN films is reported to be 5.5 pC/N, whereas $d_{33}$ for ZnO can be at least twice as large [117], and PZT films can be over 100 pC/N [107].

It is therefore desirable to find ways to increase the piezoelectric response of AlN in order to integrate AlN-based devices into existing and new systems. A common way to engineer piezoelectric properties of AlN is by alloying with transition metal nitrides (Sc, Y, others), which can lead to a several-fold increase in the field-induced strain via increases in the longitudinal piezoelectric coefficient $e_{33}$ and simultaneous decreases in the longitudinal elastic stiffness $C_{33}$ [76, 103, 105, 102]. In the case of ScN alloying, the origins of this response have been studied [102], and it is presumed that other such systems which also involve AlN alloyed with rocksalt-structured end members are similar:as the content of the rocksalt end member in the alloy increases, the accompanying structural frustration enables a greater piezoelectric response. This structural frustration, however, is also accompanied by thermodynamic driving forces for phase separation [118] which, with increased alloy concentration, lead to the destruction of the piezoelectric response upon transition to the (centrosymmetric, cubic) rocksalt structure. The experimental realization of large alloy contents without phase separation or severe degradation of film texture and crystalline quality can be quite difficult [118, 119], even when using non-equilibrium deposition processes such as sputtering.
Thus, it is desirable to find alloy systems for which the structural transition from wurtzite to rocksalt occurs at low alloying concentrations since these may be more easily synthesized and more stable, while also (hypothetically) providing comparable property enhancements as those observed in the more-studied (Sc, Al)N alloy system. Among the AlN-based systems presently accessible experimentally, (Cr, Al)N has the lowest transition composition between the wurtzite and rocksalt structures, occurring at approximately 25% CrN concentration [120, 121]. This motivates the investigation of the piezoelectric properties of the Cr$_x$Al$_{1-x}$N system, which we also refer to, for simplicity, in terms of Cr substitution for Al.

In this article, we study Cr-substituted AlN using density functional theory (DFT) calculations of structural, mechanical, and piezoelectric properties. Given that Cr has unpaired $d$ electrons, a challenge to overcome in these calculations is the simulation of a truly representative random distribution of the spins of Cr ions, whose placement in the AlN lattice involves not only chemical disordering, but spin disordering as well. Among a set of wurtzite-based materials, we have found that Cr-doped AlN is the alloy whose piezoelectric stress coefficient $e_{33}$ is the most sensitive to alloying concentration and also has the lowest wurtzite-to-rocksalt transition composition. The key factor leading to the enhanced piezoelectricity in Cr$_x$Al$_{1-x}$N alloys is the ionic contribution to the coefficient $e_{33}$; this ionic contribution is increased through the internal $u$ parameter of the wurtzite structure when alloyed with the (larger) Cr ions. Therefore, we propose Cr$_x$Al$_{1-x}$N as a viable piezoelectric material with properties that can be tuned via Cr composition. To further support this proposal, we have performed combinatorial synthesis and subsequent characterization of Cr$_x$Al$_{1-x}$N films, and have showed that Cr can be incorporated in the AlN lattice up to 30% before a detectable transition to rocksalt occurs. At this Cr content, the piezoelectric modulus $d_{33}$ is four times larger than that of AlN. Pending future device fabrication and accurate measurements of properties and device performance, this significant increase in $d_{33}$ can propel Cr-AlN to be the choice material for applications such as resonators, GHz telecommunications, or acoustic wave generators.
2.2 Methods

2.2.1 Paramagnetic Representation of Cr-AlN Alloys

Starting with a computational supercell of wurtzite AlN, any desired Cr concentration is realized by substituting a corresponding number of Al ions with Cr ions in the cation sub-lattice. In order to realistically simulate the chemical disorder of actual (Cr, Al)N alloys while maintaining a tractable size for the computational cell, we use special quasirandom structures (SQS) [122, 123, 124]. The Cr$^{3+}$ ions have unpaired $d$ electrons, which require spin-polarized DFT calculations. Another important aspect of the calculations is that the Cr$_x$Al$_{1-x}$N alloys are paramagnetic [120, 125, 126], and this state has to be captured explicitly in the DFT calculations. Therefore, in addition to the configurational disorder simulated via SQS, the paramagnetic state requires truly random configurations for the spins associated with the Cr$^{3+}$ ions [127, 128]. However, as shown by Abrikosov et al. [128], the paramagnetic state can be approximated by using disordered, collinear, static spins because such state yields zero spin-spin correlation functions. To represent the paramagnetic state of Cr$_x$Al$_{1-x}$N, for a given alloy structure with $n$ Cr sites, we performed a minimum of $\binom{n}{2}$ and maximum 20 calculations. In these calculations, the spins on Cr sites are randomly initialized subject to the restriction of zero total spin for each concentration and each SQS structure. An example of such a random distribution of initial spins is illustrated in Figure 2.1 for $x = 25\%$ Cr concentration.

2.2.2 Details of the DFT Calculations

Structural optimizations and calculations of piezoelectric and elastic constants were carried out using the Vienna Ab-initio Simulation Package (VASP) [129], with projector augmented waves (PAW) in the generalized gradient approximation using the Perdew-Burke-Ernzerhof (PBE) exchange-correlation function [130] and an on-site Hubbard term [131] $U$ for the Cr 3$d$ states. The plane wave cutoff energy was set to 540 eV in all calculations. For the wurtzite structures, we have used $4 \times 4 \times 2$ (128 atoms) and $2 \times 2 \times 2$ (32 atoms)
Figure 2.1: Schematics of cation sublattice of Cr$_x$Al$_{1-x}$N alloy. Al (Cr) sites are shown as gray (green) spheres. At a given Cr concentration, the Cr sites of each configuration have a different and random spin initialization with zero total spin in order to capture the paramagnetic state.

SQS supercells; for the rocksalt structures, the computations were carried out on $2 \times 2 \times 2$ (64 atoms) SQS supercells. Brillouin zone sampling was performed by employing $1 \times 1 \times 1$ and $2 \times 2 \times 2$ Monkhorst-Pack [132] $k$-point meshes for the wurzite and rocksalt structures, respectively, with the origin set at the $\Gamma$ point in each case. Piezoelectric coefficients were calculated using density functional perturbation theory, and the elastic constants were computed by finite differences [133, 134]. The on-site Coulomb interaction for Cr atoms was set at 3 eV, through a Dudarev approach [131]. Before performing the calculations for elastic and piezoelectric constants, we performed cell shape, volume, and ionic relaxations in order to obtain the equilibrium lattice parameters and ionic positions at each particular Cr
concentration and SQS alloy.

2.2.3 Experimental Procedures

Combinatorial synthesis of Cr$_x$Al$_{1-x}$N films was performed through reactive physical vapor deposition (PVD). Two inch diameter circular aluminum (99.9999%) and chromium (99.999%) metallic targets were arranged at 45° angles measured from the normal to a plasma-cleaned Si(100) substrate inside a custom vacuum system with a base pressure of 5 × 10$^{-6}$ torr. Magnetron RF sputtering with a power of 60 W for aluminum targets and 40 W for the chromium targets was performed at a deposition pressure of 3 × 10$^{-3}$ torr, with 8 sccm of argon and 4 sccm of nitrogen, and a substrate temperature of 400 °C. Aluminum glow discharges were oriented opposite to each other, with the chromium target perpendicular to both, resulting in a film library with a compositional range in one direction [135, 136]. Each sample library was subdivided into eleven regions across the composition gradient, which were subsequently characterized by x-ray diffraction (XRD) and x-ray fluorescence (XRF), performed on a Bruker D8 Discovery diffractometer with a 2D area detector in a theta-2theta configuration and a Fischer XUV vacuum x-ray spectrometer, respectively.

2.3 Results and Discussion
2.3.1 Enthalpy of Mixing

The enthalpy of mixing as a function of the Cr concentration $x$, at zero pressure, is defined with respect to the pure wurzite-AlN and rocksalt-CrN phases via

$$\Delta H_{\text{mix}}(x) = E_{\text{Cr}_x\text{Al}_{1-x}\text{N}} - xE_{\text{rs-CrN}} - (1 - x)E_{\text{w-AlN}},$$

(2.1)

where $E_{\text{Cr}_x\text{Al}_{1-x}\text{N}}$, $E_{\text{rs-CrN}}$, and $E_{\text{w-AlN}}$ are the total energies per atom of the SQS alloy, pure AlN phase, and pure CrN phase, respectively. The DFT calculated mixing enthalpies for the wurzite and rocksalt phases of Cr$_x$Al$_{1-x}$N are shown in Figure 2.2(a). The wurzite phase is found to be favorable up to $x = 0.25$, beyond which rocksalt alloys are stable; this wurzite to rocksalt phase transition point is consistent with previous experimental observations and other theoretical predictions [120, 121].
We have compared the mixing enthalpy of the $\text{Cr}_x\text{Al}_{1-x}\text{N}$ alloys with that of several other common wurzite-based nitrides [76, 137, 138, 105, 119], $\text{Sc}_x\text{Al}_{1-x}\text{N}$, $\text{Y}_x\text{Al}_{1-x}\text{N}$, and $\text{Y}_x\text{In}_{1-x}\text{N}$, with the results shown in Figure 2.2(b). The mixing enthalpies are positive for all cases, meaning that the alloying of AlN or InN with their respective end members is an endothermic process. In practice, these alloys are formed as disordered solid solutions obtained using physical vapor deposition techniques operating at relatively low substrate temperatures because of the energetic plasmas involved [118, 139]. Figure 2.2(b) shows that the mixing enthalpy in $\text{Cr}_x\text{Al}_{1-x}\text{N}$ lies between values corresponding to other systems synthesized experimentally, hence $\text{Cr}_x\text{Al}_{1-x}\text{N}$ is no more difficult to synthesize than the others. More importantly, the enthalpy calculations show that the transition to rocksalt occurs at the lowest alloy concentration across the wurzite systems considered, which is important for achieving maximum piezoresponse-enhancing structural frustration with a minimum of dopant concentration in order to retain the single-phase wurzite.

### 2.3.2 Piezoelectric Stress Coefficients

The piezoelectric coefficients $e_{ij}$ for different spin configurations in SQS supercells with the same Cr content are shown in Figure 2.3. For clarity, the panels in Figure 2.3 are arranged in the same fashion as the piezoelectric tensor when represented as a matrix in Voigt notation. The vertical scale is the same for all coefficients except $e_{33}$, $e_{31}$, and $e_{32}$. The scatter in the results corresponds to different SQS supercells at each Cr concentration; this is an effect of the finite size of the system, in which local distortions around Cr atoms lead to small variations of the lattice constants and angles. It is for this reason that we average the SQS results at each Cr concentration, thereby obtaining smoother variations of the piezoelectric coefficients. At 25% Cr, the value of $e_{33}$ becomes $\sim 1.7$ times larger than that corresponding to pure AlN.
Figure 2.2: (a) DFT-calculated mixing enthalpies of the wurtzite and rocksalt phases of Cr$_x$Al$_{1-x}$N as functions of Cr concentration. (b) Calculated mixing enthalpies for several wurtzite-based nitride alloys grown experimentally.
Figure 2.3: The 18 components of the piezoelectric tensor calculated for SQS supercells with different spin configurations and compositions of Cr. At each Cr composition, the open circles represent data for each SQS cell used, while the red solid circles represent the average values across the random initial configurations.
Figure 2.4: Variation of (a) $e_{33}^{\text{total}}$, (b) $e_{33}^{\text{clamped}}$ component of $e_{33}$, (c) $e_{33}^{\text{nonclamped}}$, (d) 33 component of the Born effective charge tensor, (e) strain sensitivity of internal parameter, (f) $c/a$ ratio with respect to Cr addition.
Figure 2.5: (a) Variation of internal parameter, \( u \) with Cr addition. (b) Crystal structure of wurzite AlN.

The piezoelectric coefficient \( e_{33} \) of wurzite \( Cr_xAl_{1-x}N \) is shown Figure 2.4(a) as a function of Cr concentration, and can be written as [101]

\[
e_{33}(x) = e_{33}^{\text{clamped}}(x) + e_{33}^{\text{non-clamped}}(x),
\]

in which \( e_{33}^{\text{clamped}}(x) \) describes the electronic response to strain and is evaluated by freezing the internal atomic coordinates at their equilibrium positions. The term \( e_{33}^{\text{non-clamped}}(x) \) is due to changes in internal coordinates, and is given by

\[
e_{33}^{\text{non-clamped}}(x) = \frac{4eZ_{33}^*(x)}{\sqrt{3}a(x)^2} \frac{du(x)}{d\epsilon} \tag{2.3}
\]

where \( e \) is the (positive) electron charge, \( a(x) \) is the equilibrium lattice constant, \( u(x) \) is the internal parameter of the wurzite, \( Z_{33}^*(x) \) is the dynamical Born charge in units of \( e \), and \( \epsilon \) is the macroscopic applied strain. \( e_{33}^{\text{non-clamped}}(x) \) describes the piezoelectric response coming from the displacements of internal atomic coordinates produced by the macroscopic strain. Based on Eqs. (2.2) and (2.3), panels (b) through (f) in Figure 2.4 show the different relevant quantities contributing to \( e_{33} \) in order to identify the main factors responsible for the increase of piezoelectric response with Cr addition. Direct inspection of Figures Figure 2.4(a-c) indicates that the main contribution to the increase of \( e_{33} \) comes from the non-clamped
ionic part, Figure 2.4(c). Since the Born charge $Z_{33}^*$ [Figure 2.4(d)] is practically constant, the key factor that leads to increasing the piezoelectric coefficient is the strain sensitivity $du/d\epsilon$ of the internal parameter $u$ [Figure 2.4(e)].

Although the internal parameter $u$ is an average value across the entire supercell, the individual average $u$ parameters can also be determined separately for AlN and CrN tetrahedra [Figure 2.5(a,b)]. The internal parameter $u$ of AlN tetrahedra [Figure 2.5(b)] does not change significantly, while that of the CrN tetrahedra grows approximately linearly with Cr concentration [Figure 2.5(a)]. In an alloy system where AlN tetrahedra are the majority, this variation can be understood based on (i) the fact that the ionic radius of Cr is about 10\% larger than that of Al, and (b) the increase in Cr concentration will lead to average $u$ parameters mimicking the variation of the $u$ parameter corresponding to CrN tetrahedra.

### 2.3.3 Comparison with Other Wurtzite-Based Alloys

![Graph showing comparison of change in $e_{33}$ with addition of different transition metals for $x \leq 25\%$ regime.]

Figure 2.6: Comparison of change in $e_{33}$ with addition of different transition metals for $x \leq 25\%$ regime.
The results from calculations of the piezoelectric properties of Cr$_x$Al$_{1-x}$N with $x$ from 0 to 25% Cr are plotted in Figure 2.6, together with the calculated values for Sc$_x$Al$_{1-x}$N, Y$_x$Al$_{1-x}$N, and Y$_x$In$_{1-x}$N. In Cr$_x$Al$_{1-x}$N, $e_{33}$ increases rapidly from 1.46 to 2.40 C/m$^2$ for Cr concentrations from 0 to 25%. For all other alloys considered, the increase is smaller in the same interval of solute concentration: for Sc$_x$Al$_{1-x}$N, Y$_x$Al$_{1-x}$N, and Y$_x$In$_{1-x}$N, $e_{33}$ increases, respectively, from 1.55 to 1.9 C/m$^2$, 1.55 to 1.7 C/m$^2$, and 0.9 to 1.2 C/m$^2$. Within the $x \leq 25\%$ range, Cr is more effective than any of the other studied transition elements in improving piezoelectric response of AlN-based alloys.

Figure 2.7: Variation of (a) $C_{33}$ and (b) $d_{33}$ for several nitride-based wurtzite alloys.

The experimentally measurable property is $d_{33}$, which is commonly known as piezoelectric strain modulus and relates the electric polarization vector with stress. The relationship
between the piezoelectric strain and stress moduli is \[15\]

\[d_{ij} = \sum_{k=1}^{6} e_{ik}(C^{-1})_{kj}, \quad (2.4)\]

where \(C_{ij}\) are the elements of the stiffness tensor in Voigt notation. The variation of the elastic constant \(C_{33}\) in \(Cr_xAl_{1-x}N\) with \(x\) is shown in Figure 2.7(a), along with the other systems considered here. For all of these wurtzite-based piezoelectrics, the increase in piezoelectric response with alloying element concentration is accompanied by mechanical softening (decrease in \(C_{33}\)). From Eq. (2.4), it follows that the increase in \(e_{33}\) [Figure 2.6] and the mechanical softening [Figure 2.7(a)] cooperate to lead to the increase of \(d_{33}\) values with alloy concentration \(x\). Our calculated \(d_{33}\) values for \(Cr_xAl_{1-x}N\) are in good agreement with experimental data from Ref. [139] [Figure 2.7(b)] for Cr concentrations up to 6.3%. Beyond this concentration, Luo et al. [139] report a drop in the \(d_{33}\) values of their films, which is attributed to changes in film texture. We have also extended our calculations of piezoelectric coefficients beyond 25% Cr composition in wurtzite structures. Figure 2.8 shows that \(e_{33}\) continues to increase at least up to 37.5% Cr. The calculations done at 50% Cr, which start with wurtzite SQS configurations, evolve into rocksalt configurations during relaxation, which explains the decrease of \(e_{33}\) to zero in Figure 2.8.

It is worthwhile to compare the performance of several AlN wurtzite-based materials for their use in applications. These applications, which are mainly resonators, ultrasound wave generators, GHz telecommunications, FBAR devices, bulk or surface acoustic generators, and biosensors, lead to a multitude of application-specific figures of merit for different utilization modes of the piezoelectric material. However, most figures of merit rely on the piezoelectric properties \(e_{33}\) and \(d_{33}\), both of which in general should be as large as possible for increased piezoelectric device sensitivity. The most used wurtzite material for these applications is AlN, although there are several other options as well (refer to Table I). Alloying with ScN is promising in that it offers an increased \(d_{33}\) for about 10% Sc concentration; larger Sc concentrations are possible, but the growth process becomes more costly and the material
Figure 2.8: Variation of $e_{33}$ as function of Cr concentration for wurtzite phase alloys up to 50%.

is likely to lose texture with increased Sc content. Options such as alloying with YN offer marginal improvement at 6% Y content, and YN-doped InN (14% Y content) fares similarly [Table 2.1]. Our results indicate that CrN alloying of AlN can reach superior values for the piezoelectric properties, nearly quadrupling the value of $d_{33}$ [Table 2.1] with respect to AlN. The fact that the transition point is the lowest [Figure 2.2] of all wurtzite-based materials relevant for the technologies mentioned above, makes the CrN alloying easier compared with the other materials (which require higher alloy content) and hence renders Cr-AlN a prime candidate for synthesis of new, CrN-alloyed piezoelectrics for resonators and acoustic generators. As we shall see in Sec.2.3.4, the non-equilibrium growth techniques can bring Cr content past the transition point without significant formation of the (non-piezoelectric) rocksalt phase. Consequently, the piezoelectric properties are expected to be significantly better than those of AlN, especially $d_{33}$ (refer to Table 2.1). Indeed, this is born out in experiments (data points in Figure 2.7b). Measurements of figures of merit for specific
device configurations will be needed in the future, as those require not only combinations of elastic and piezoelectric properties, but dielectric properties as well [105].

Table 2.1: Piezoelectric properties of AlN and a few wurtzite alloys for piezoelectric device applications.

<table>
<thead>
<tr>
<th>Material</th>
<th>$e_{33}$ (C/m²)</th>
<th>$d_{33}$ (pC/N)</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlN</td>
<td>1.55</td>
<td>4.5-5.3</td>
<td>[106, 107, 115]</td>
</tr>
<tr>
<td>Sc-AlN, 10% Sc</td>
<td>1.61</td>
<td>7.8</td>
<td>[140, 141]</td>
</tr>
<tr>
<td>Y-AlN, 6% Y</td>
<td>1.5</td>
<td>4.0</td>
<td>[119]</td>
</tr>
<tr>
<td>Y-InN, 14% Y</td>
<td>1.1</td>
<td>5.1</td>
<td>[137]</td>
</tr>
<tr>
<td><strong>this work:</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr-AlN, 12.5% Cr</td>
<td>1.84</td>
<td>9.86</td>
<td></td>
</tr>
<tr>
<td>Cr-AlN, 25.0% Cr</td>
<td>2.35</td>
<td>16.45</td>
<td></td>
</tr>
<tr>
<td>Cr-AlN, 30.0% Cr</td>
<td>2.59</td>
<td>19.52</td>
<td></td>
</tr>
</tbody>
</table>

2.3.4 Experimental Results

To bring experimental support to our proposal that the Cr-AlN system can become a key piezoelectric material to replace AlN and perhaps even ZnO for future applications, we have to ensure that the texture obtained during growth is stable for sufficiently high CrN concentrations. After synthesizing Cr-AlN alloys through reactive PVD, we have performed transmission electron microscopy (TEM) analysis of the films grown in order to check for textural integrity (i.e., grains oriented primarily with the $c$ axis close to the surface normal) and for the onset of the rocksalt phase. At CrN content below 25% [the theoretical boundary shown in Figure 2.2(a)], our films display no significant texture variations. For example, Figure 2.9(a) shows a typical TEM micrograph wherein texture is preserved over the film thickness. Additionally, our energy dispersive spectroscopy (EDS) characterization shows nearly constant Cr content through the sample [Figure 2.9(b)]. Further characterization by XRD was performed for all CrN compositions in the combinatorially synthesized films. Figure 2.10 shows the XRD results for the 88 discrete Cr$_x$Al$_{1-x}$N compositions produced in an effort to test the possibilities of synthesizing alloys in a wide range of concentrations, including alloys beyond the wurtzite-to-rocksalt transition point. At low alloying levels,
Figure 2.9: Representative transmission electron microscopy (TEM) image (a) and an energy dispersive spectroscopy (EDS) line scan (b) of an \((\text{Al}_{1-x}\text{Cr}_x)\text{N}\) film cross section containing \(\sim 7\% \) Cr, confirming the incorporation of Cr into wurtzite solid solution. EDS data were collected along the dashed black line shown in panel (a).

the films grow exclusively with the wurtzite structure and a (002) preferred orientation, as indicated by the dominant presence of the wurtzite (002) diffraction peak [Figure 2.10, left side]. Films grown by reaction PVD under the conditions used here accept chromium into the wurtzite lattice and grow primarily with the ideal (002) orientation. With increased CrN content, the wurtzite (012) and (010) peaks appear, indicating some deviations from the original, and still predominant (002) orientation of the film. The metastability of this alloy is overcome at an approximate composition of \(x \simeq 30\%\), where the polycrystalline rocksalt phase appears, as revealed by the rocksalt (002) and (111) peaks (Figure 2.10, right hand side). These experimental results show that wurtzite \(\text{Cr}_x\text{Al}_{1-x}\text{N}\) solid solutions can be synthesized without observable phase separation up to concentrations of 30% Cr. Wurtzite material still exists at global compositions beyond 30%, but in a wurtzite-rocksalt phase mixture, which will diminish the piezoelectric properties because of the presence of a significant amount of centrosymmetric rocksalt phase in the mixture.
Figure 2.10: X-ray diffraction patterns of the thin film combinatorial libraries plotted against the film composition, with comparison to the patterns for wurtzite (WZ) [142] and rocksalt (RS) [143] structures. For alloying content $x < 30\%$, the films grow predominantly with the wurtzite structure. At higher Cr concentrations, $x > 30\%$, both rocksalt and wurtzite phases are detected, and the wurtzite exhibits degraded texture. No films were produced with compositions in regions where no intensity is shown.

There are few studies of Cr alloyed into wurtzite AlN, [139, 144, 126] reporting Cr-doped alloys grown by magnetron sputtering. The Cr concentration previously attained is below 10\%, although the limits of Cr alloying were not actually tested in the previous reports [139, 144, 126]. Our combinatorial synthesis results show that Cr can be doped into the wurtzite lattice up to 11\% before the predominant (002) film texture starts to change, and up to 30\% before the rocksalt phase appears.

2.4 Concluding Remarks

By using a physical representation of the paramagnetic state of substitutional Cr in a wurtzite AlN matrix and performing the necessary averaging over spin configurations at each Cr concentration, we computed the structural, mechanical, and piezoelectric properties of (Cr, Al)N alloys. Our combinatorial synthesis experiments showed that (Cr, Al)N are relatively easy to synthesize, and also showed that the reactive PVD procedure resulted in (Cr, Al)N alloys retaining the wurtzite structure for alloying concentrations up to 30\% Cr. Remarkably, our DFT calculations of piezoelectric properties revealed that for 12.5\% Cr $d_{33}$
is twice that of pure AlN, and for 30% Cr this modulus is about four times larger than that of AlN.

From a technological standpoint, this finding should make (Cr, Al)N the prime candidate to replace the current-wurtzite based materials in resonators and acoustic wave generators. The larger piezoelectric response (than AlN) may lead to smaller power consumption and perhaps even to avenues to further miniaturize various devices. While the substitutional alloying with Cr would improve the piezoelectric response for every type of device in which currently AlN is being used, one may wonder why not alloying with other trivalent metals, such as Y or Sc. In particular, Sc has been shown to significantly increase the piezoelectric modulus as well [102]. Even though (Sc, Al)N has more exciting properties [103, 102] than (Cr, Al)N, the reason why (Sc, Al)N alloys have not taken over the resonator market so far is that the outstanding enhancements in piezoelectric properties occur at very high Sc concentration (Figure 2.2, $x > 55%$), at which the stability of the wurtzite phase is rather poor. (Cr, Al)N has a low wurtzite-to-rocksalt transition concentration, and therefore can offer certain piezoelectric enhancements at alloying levels that are easier to stabilize during the synthesis.

In order to ensure significant impact of (Cr, Al)N alloys as materials to outperform and replace the established piezoelectrics AlN and ZnO, two avenues should be pursued in the near future. First, to benefit from the 300% increase in $d_{33}$ at 30% Cr content, it is not sufficient that the rocksalt phase does not form up to that Cr concentration: we also have to avoid the formation of (012) and (010)-oriented grains during growth, which would downgrade (simply through directional averaging) the piezoelectric enhancements associated with the (002)-oriented grains. To that end, we envision changing substrates so as to enable better lattice matching with Cr-alloys with over 25% Cr. This can effectively prevent the (012) and (010) textures from emerging, therefore creating the conditions to take advantage of the large increase in $d_{33}$ reported here. Second, future experimental efforts should measure device performance especially to understand the additional aspect of how Cr content in
wurtzite affects the bandgap and whether there would be deleterious leakage effects at larger Cr concentrations. Assuming a worst case scenario, these effects can be mitigated by co-alloying with a non-metallic atomic species (e.g. boron).

Pursuing the two directions above can make (Cr, Al)N suitable for simultaneous optical and mechanical resonators, [145, 146] which are relatively new applications that currently exploit multi-physics aspects of AlN. At present, the characterization of (Cr, Al)N for these multifunctional applications that require simultaneous engineering of the photonic and acoustic band structure is rather incipient, and only few relevant properties of the (Cr, Al)N alloys are known: for example, for a Cr concentration of about 2%, the bandgap is virtually unchanged, while the adsorption band decreases from 6 to 3.5 eV [4]. Future theoretical and experimental work to investigate, e.g., photoelastic effect and optical attenuation, is necessary in order to fully uncover the potential of Cr-doped AlN for these applications. For now, we surmise that the technological reason for which one would replace AlN with (Cr, Al)N for use in multifunctional resonators is the trade-off between the increase in vibrational amplitude and decrease in frequency: while low amounts of Cr may lower the frequency somewhat, the oscillation amplitude would increase due to larger piezoelectric response. The decrease in frequency can be mitigated by co-doping with a small trivalent element (boron), as shown for other doped AlN alloys [105]. Last but not least, it is worth noting that doping with Cr could enable magnetic polarization of the Cr ions in the wurtzite lattice and/or of the minority carriers: these effects are non-existent in pure AlN, and could be pursued for spintronic applications or for low-hysteresis magnets [126].

The significant increase of piezoelectric modulus reported here provides significant drive to pursue the two directions identified above, and overcome routine barriers towards establishing (Cr, Al)N as a replacement for AlN with large performance enhancements.

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Energy Computing Organization) and at National Renewable Energy Laboratory (NREL). Synthesis and characterization facilities at NREL were supported by the US Department of Energy, Office of Science, Office of Basic Energy Sciences, as part of the Energy Frontier Research Center “Center for Next Generation of Materials by Design: Incorporating Metastability” under contract No. DE-AC36-08GO28308.
CHAPTER 3
TUNING THE PIEZOELECTRIC AND MECHANICAL PROPERTIES OF THE AlN SYSTEM VIA ALLOYING WITH YN AND BN

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Recent advances in microelectromechanical systems often require multifunctional materials, which are designed so as to optimize more than one property. Using density functional theory calculations for alloyed nitride systems, we illustrate how co-alloying a piezoelectric material (AlN) with different nitrides helps tune both its piezoelectric and mechanical properties simultaneously. Wurtzite AlN-YN alloys display increased piezoelectric response with YN concentration, accompanied by mechanical softening along the crystallographic c direction. Both effects increase the electromechanical coupling coefficients relevant for transducers and actuators. Resonator applications, however, require superior stiffness, thus leading to the need to decouple the increased piezoelectric response from the softened lattice. We show that co-alloying of AlN with YN and BN results in improved elastic properties while retaining some of the piezoelectric enhancements from YN alloying. This finding may lead to new avenues for tuning the design properties of piezoelectrics through composition-property maps.

3.1 Introduction

Recent technological advances in microelectromechanical systems require materials to be more efficiently designed, often leading to optimization of more than one property [147, 148]. An electromechanical (piezoelectric) material requires the best piezoelectric coefficient, while materials for damping high mechanical loads require the high stiffness moduli [149, 14].

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The high stiffness value is also associated with thermal stability, enabling the use of these materials over a large temperature range [71]. Pseudo-binary alloys, i.e., solid solutions between two compounds, have been extensively investigated for use in electromechanical applications [102, 150, 103, 119, 137]. Most of these alloys have large miscibility gaps, which makes them less appealing for applications where mechanical stability is an important figure of merit. The presence of miscibility gaps is not particularly restrictive, since current non-equilibrium processing techniques allow for fabricating pseudo-binary alloys in which one can seek a given functionality by, e.g., changing composition (often through the miscibility gaps) so as to optimize piezoelectric coefficients, stiffness, electromechanical coupling constants, or electronic properties. However, achieving optimal or desired values for more than one such property is challenging since optimizing one property often changes another towards undesirable values. In such cases, more degrees of freedom may help create a framework in which advanced materials can be optimized for multiple functionalities. In this article, we focus on a piezoelectric system to show that alloying with more than one compound enables us to tune two properties, specifically, the piezoelectric coefficient and the mechanical stiffness.

With the discovery of the anomalously large increase in the piezoelectric moduli of wurtzite AlN when alloyed with ScN [76] or YN [119, 151], AlN-based alloys have received a lot of attention as materials for improved telecommunications, sensors, and surface acoustic wave devices [32, 152]. The origin of the enhanced piezoelectricity was revealed to be an intrinsic effect of alloying, as opposed to textural or microstructural effects [102], with the obvious implication that controlling the piezoelectric enhancement can be done mainly by increasing composition of YN or ScN. However, such alloying softens the material significantly [102], which actually makes the material less attractive for resonant applications for which $k^2Q$ is a common figure of merit [153] wherein $k$ is an electromechanical coupling coefficient and $Q$ is a quality factor that is inversely proportional to mechanical dissipation [153]. It is therefore desirable to control the mechanical properties as well, which could in principle be achieved by alloying with other species.
Herein, we focus on AlN-YN alloys and advance the premise that further alloying this system with BN can increase the elastic constants of the material, thus leading to new avenues for piezoelectric design based on precise control YN and BN compositions. The choice for YN is motivated by the scarcity of literature reports on AlN-YN alloys [151, 154], and by the fact that Y may be a less expensive alternative for Sc. While the elastic stiffening of AlN-YN upon alloying with BN would be enabled by the presence of shorter and stiffer B-N bonds, the effect of alloying with BN on the piezoelectric properties is presently unknown. Using density functional theory (DFT), we have found that the presence of BN, by itself, indeed leads to increases in the relevant elastic constant $C_{33}$, but does not significantly change the piezoelectric coefficient $\varepsilon_{33}$. Furthermore, we have uncovered the combined effect of alloying with YN and BN on the properties of the AlN system for total alloying concentrations up to 50 at.%. The addition of BN to AlN-YN alloys counters to some extent the piezoelectric enhancement obtained via YN alloying, but increases the elastic modulus. Overall, the alloying of AlN with BN and YN leads to a high degree of control over the piezoelectric and elastic properties of the resulting alloy, and therefore over the coupling coefficients and various figures of merit commonly used in piezoelectric device design.

Figure 3.1: Atomic structure of a representative SQS Al$_{50}$Y$_{25}$B$_{25}$N alloy structure
3.2 Methods

To assess the changes in elastic and piezoelectric properties driven by different levels of YN and BN in Al$_{1x}$Y$_x$B$_y$N alloys, we first performed DFT relaxations of atomic positions and lattice constants using the VASP package [129], with projector augmented waves [130] in the generalized gradient approximation using the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional [155]. Out of caution more than necessity, we introduced an on-site Coulomb interaction (parameter $U = 3$ eV) for the yttrium d state since this state is explicit in the pseudopotential. When compared with calculations done with plain PBE ($U = 0$ eV), the results for lattice constants are nearly identical, while the piezo and stiffness tensor component vary by less than 2%.

![Figure 3.2: [(a) and (b)] Lattice constants $a$ and $c$ for AlN-YN and AlN-BN alloys as a function of dopant (Y or B) cation concentration $x$. Panel (c) shows the $c/a$ ratio for these alloys.](image)

The parent structure is wurtzite AlN, in which Al is substituted with Y and B in desired amounts. Supercells with 32 atoms are simulated using special quasirandom structures [SQS, more details in Appendix D] [124] (Figure 3.1), whose pair correlation functions are the same as those of random alloys up to second-nearest neighbors. A $5 \times 5 \times 3$ Monkhorst-Pack [132] $k$-point mesh was used to sample the Brillouin zone, resulting in 38 irreducible $k$-points. A plane wave cutoff energy of 500 eV was used; the energy tolerance stopping criteria were $10^{-8}$ and $10^{-7}$ for the electronic and ionic convergence, respectively. These
criteria were obtained by progressive tightening of the convergence until the relaxed SQS supercells stopped changing. This resulted in smoother curves for lattice parameters and properties, in which the only source of noise remained the use of small number of atoms coupled with a limited number of individual SQS supercells at each concentration (refer to Fig. SM-1 FI for an assessment of the dispersion of individual SQS values). Due to the variability of atomic-scale environments in the SQS supercells [103], we performed five calculations at each composition and used them to average the properties, including the lattice constants. For the separate alloying only with YN or with BN, the lattice constants $a$ and $c$ are plotted in Figure 3.2(a) and Figure 3.2(b) as functions of the cation concentration. Alloying with YN increases the lattice constants, while alloying with BN alone decreases them: these trends are simply due to the larger (smaller) cation radius of Y (B) compared to that of Al in AlN. The $c/a$ ratio is more sensitive to doping for the case of Y compared to BN [Figure 3.2(c)].

Our DFT calculations of mixing enthalpies for alloy wurtzite and rocksalt phases of AlN-YN revealed that wurtzite is more stable than rocksalt for up to 72% Y content, above which rocksalt becomes more stable [Figure 3.3(a)]. The mixing enthalpies in Figure 3.3(a) are positive, meaning that mixing is not spontaneous. From the mixing enthalpies and combinatorial expression for mixing entropy in this pseudo-binary alloy, we have obtained the temperature composition phase diagram in a manner similar to that described by, e.g., Burton et. al. [156] for other wurtzite systems. This phase diagram is shown in Figure 3.3(b), in which the temperature axis is rather qualitative since we have not considered lattice vibrations in deriving it; it is similar to the one that would be obtained in the presence of vibrations [156]. As would be expected, the diagram shows a miscibility gap-the white space between the metastable regions in Figure 3.3(b). This means that compositions in that gap cannot be achieved under thermodynamic equilibrium. However, the current growth techniques (e.g., reactive dc magnetron co-sputtering) [157, 104] rely on non-equilibrium processes to overcome the solubility limits [158, 159, 160] and create alloys with better control over properties.
3.3 Results and Discussions

Focusing now on describing the piezoelectric properties of the alloys, we note that the piezoelectric coefficient $e_{33}$ is evaluated at each Y($x$) and B($y$) composition via

$$
e_{33} = e_{33}^{clamped-ion} + \frac{4eZ^*}{\sqrt{3}a_0^2} \frac{du}{d\epsilon} \tag{3.1}
$$

where, $e_{33}^{clamped-ion}$ is the clamped-ion contribution to $e_{33}$, $e$ is the electron charge, $Z^*$ is the axial component of the dynamical Born effective charge tensor, $a_0$ is the equilibrium lattice constant, and $du/d\epsilon$ is the sensitivity of the internal parameter $u$ to strains along the crystallographic $c$-axis [161]. The elastic constants were computed by finite differences.
between the energies of the lattices subjected to small applied strains [162].

Figure 3.4 shows the effects of separate BN and YN alloying on the properties of AlN. As seen in Figure 3.4(a) the piezoelectric coefficient \( e_{33} \) increases with Y concentration up to 50%, while the elastic constant \( C_{33} \) decreases; this is consistent with previous works on the similar AlN-ScN system [102, 103]. The physical origin of this effect arises from the larger radius of the Y ion, which changes the internal parameter \( u \) of the alloyed wurtzite structure and its sensitivity to strain, \( du/d\epsilon \) [refer to Eq. (3.3)]. The value of \( e_{33} \) that can be achieved
by alloying with 50% Y is doubled compared to that of pure AlN (Figure 3.4). Figure 3.4(b) shows that alloying with BN alone increases the elastic modulus, which is consistent to another report [163]. Interestingly, we also note that substituting B for Al does not alter the piezoelectric coefficient significantly up to concentrations of 50% B. When AlN-YN films are deposited, there is usually strain in the lattice stemming from the mismatch with the substrate, changing film texture with alloy concentration, or from insufficient annealing. It is therefore relevant to assess what the effect of this strain is on the piezoelectric coefficient, so we have redone the DFT calculations for the situations were strain is applied in plane (along the a and b directions) or out of plane (along the c direction).

Figure 3.5: Variation of piezoelectric coefficient in Al$_{1-x}$Y$_x$N with strained applied along the a and c axes.
The results of these calculations are displayed in Figure 3.5: $e_{33}$ can increase up to about 3.75 C/m$^2$ (i.e., 2.5 times that of pure AlN) either by alloying with 50% Y and applying 2% tension along the $a$ axis [Figure 3.5(a)], or by alloying with 50% Y and applying 2% compression along the $c$ axis [Figure 3.5(b)]. The opposite trends of $e_{33}$ with strain along different directions (Figure 3.5) suggest that, for homogeneous and isotropic strain in the AlN-YN lattice, the effects of strain along $c$ and $a$ directions may cancel each other at least partially and thus not affect the piezoelectric coefficient significantly. This is important when alloying with a secondary species, such as BN, which would amount to roughly isotropic strain when B is (nearly) homogeneously doped throughout the AlN-YN lattice. Based on these results, we have set out to analyze how co-alloying with both YN and BN changes properties, aiming to find composition regimes where the piezoelectric coefficient increases while the elastic modulus does not decrease to the same extent as in the case of alloying with Y alone.

Figure 3.6 shows the variation of $e_{33}$ and $C_{33}$ with the Y concentration $x$, at a fixed level of B doping, $y$ (such that $x + y \leq 50\%$). The data points in Figure 3.6 represent averages over SQS configurations. Other properties (i.e., $e_{31}$ and $C_{11}$) are shown as functions of $x$ and $y$ in Fig. SM-2. Our starting premise that the presence of boron can mitigate or control the decrease in elastic modulus $C_{33}$ brought about by Y alloying-while still retaining some increase of the piezoelectric coefficient is borne out by the results in Figure 3.6. For example, going from 0% B in Al$_{50}$Y$_{50}$N to 18.75% B concentration in Al$_{50}$Y$_{31.25}$B$_{18.75}$N results in a 50 MPa increase of the elastic constant $C_{33}$ with 33% decrease in the piezoelectric coefficient. For ease of reference, some of the results shown in Figure 3.6 are also tabulated in Table 3.1. BN alloying has a strong effect on mechanical properties (Table 3.1): increasing BN content from 31.25% to 50% at the expense of YN concentration nearly doubles the elastic modulus (from 238 GPa to 470 GPa).

Next, we discuss the electromechanical coupling coefficients resulting from co-alloying of AlN with YN and BN. These coefficients are key parameters in designing transducers for
Figure 3.6: The key piezoelectric ($e_{33}$, red, left vertical axis) and elastic ($C_{33}$, green, right axis) properties of Al-Y-B nitrides as functions of the Y concentration at constant boron levels ranging from (a) 0.00% B to (h) 43.75% B

energy harvesting and sensing applications [167, 71]. Applications such as pressure sensors, accelerometers, and gyroscopes commonly require the piezoelectric medium to operate in the
Table 3.1: Comparison between the properties of some of the Al-Y-B nitrides computed in this work and those of three commercial piezoelectrics.

<table>
<thead>
<tr>
<th>Material</th>
<th>$e_{33}$ (C/m²)</th>
<th>$C_{33}$ (GPa)</th>
<th>$d_{33}$ (pC/N)</th>
<th>$k_{33}^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PZT-7A Ref. [164]</td>
<td>9.5</td>
<td>131</td>
<td>153</td>
<td>0.67</td>
</tr>
<tr>
<td>PZT-4 Ref. [164]</td>
<td>13.84</td>
<td>113</td>
<td>225</td>
<td>0.35</td>
</tr>
<tr>
<td>$K_{0.5}Na_{0.5}NbO_3$ Ref. [165, 166]</td>
<td>4.14</td>
<td>104</td>
<td>80, 130</td>
<td>0.51</td>
</tr>
<tr>
<td>this work:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AlN</td>
<td>1.46</td>
<td>353</td>
<td>5.16</td>
<td>0.12</td>
</tr>
<tr>
<td>Al$<em>{50}$Y$</em>{50}$N</td>
<td>3.02</td>
<td>158.07</td>
<td>37.67</td>
<td>0.57</td>
</tr>
<tr>
<td>Al$<em>{50}$Y$</em>{43.75}$B$_{6.25}$N</td>
<td>2.51</td>
<td>161.36</td>
<td>22.48</td>
<td>0.47</td>
</tr>
<tr>
<td>Al$<em>{50}$Y$</em>{37.50}$B$_{12.50}$N</td>
<td>1.7</td>
<td>180.23</td>
<td>12.92</td>
<td>0.27</td>
</tr>
<tr>
<td>Al$<em>{50}$Y$</em>{31.25}$B$_{18.75}$N</td>
<td>1.85</td>
<td>209.3</td>
<td>13.34</td>
<td>0.27</td>
</tr>
<tr>
<td>Al$<em>{50}$Y$</em>{25}$B$_{25}$N</td>
<td>1.58</td>
<td>223.4</td>
<td>11.5</td>
<td>0.2</td>
</tr>
<tr>
<td>Al$<em>{50}$Y$</em>{18.75}$B$_{31.25}$N</td>
<td>1.93</td>
<td>238</td>
<td>13.03</td>
<td>0.26</td>
</tr>
<tr>
<td>Al$<em>{50}$Y$</em>{12.5}$B$_{37.50}$N</td>
<td>1.54</td>
<td>253.4</td>
<td>8.8</td>
<td>0.17</td>
</tr>
<tr>
<td>Al$<em>{50}$Y$</em>{6.25}$B$_{43.75}$N</td>
<td>1.73</td>
<td>328</td>
<td>7.7</td>
<td>0.17</td>
</tr>
<tr>
<td>Al$<em>{50}$B$</em>{50}$N</td>
<td>1.34</td>
<td>469.7</td>
<td>3.42</td>
<td>0.08</td>
</tr>
</tbody>
</table>

longitudinal length mode [168], for which the relevant coupling coefficient is

$$k_{33}^2 = \frac{e_{33}^2}{\varepsilon_{33}C_{33} + e_{33}^2}$$ (3.2)

where $e_{33}$ is the 33 component of the dielectric tensor. The static dielectric constants vary by about 10%-15% from their value at $x = 12.5\%$ (separate calculation) for the entire range of equimolar Y-B doping (i.e., $x = 25\%$ in Al$_{1-2x}$Y$_x$B$_x$N), so a constant value of $\varepsilon_{33} = 11.0$ was assumed in computing the coupling coefficients. High $k_{33}^2$ coupling factor corresponds to transducers with better axial resolution, broader bandwidth, and higher sensitivity [169]. Actuators based on cantilevers operate in the transverse length mode (bending) [167, 6], for which the relevant coupling coefficient is

$$k_{31}^2 = \frac{e_{31}^2}{\varepsilon_{33}C_{11} + e_{31}^2}$$ (3.3)

where $e_{31}$ and $C_{11}$ are components of the piezoelectric and elastic tensor, respectively. The two coupling coefficients are plotted in Figure 3.7(a) and Figure 3.7(b), for the range of Y and B concentrations considered. High coupling constants require large piezoelectric co-
Figure 3.7: The coupling constants (a) $k_{33}^2$ and (b) $k_{31}^2$ as functions of the Y and B concentrations in Al$_{1-x-y}$Y$_x$B$_y$N with at least 50% Al.

increases the piezoelectric and coupling coefficients but softens the system elastically [102], which is true for both coupling modes addressed here. The two coupling coefficients exhibit similar trends
(Figure 3.7), with larger values achieved for higher Y concentrations. However, variations of $k_{31}^2$ are significantly smaller, and larger values can also be achieved using equiatomic Y:B alloys. With the piezoelectric and elastic tensor components obtained from DFT calculations, it is useful to compare some of the properties of the co-alloyed AlN system with those of known piezoelectrics. Table 3.1, which also includes the longitudinal piezoelectric modulus $d_{33}$, shows the properties of three well-known piezoelectrics in comparison with a few selected alloy compositions computed here (for completeness, piezoelectric moduli are also plotted in Fig. SM-3 for the entire range of compositions used). Direct inspection shows that AlN co-alloyed with Y and B can achieve parameters comparable to those of commercial piezoelectrics. More importantly, the simultaneous enhancement of $e_{33}$ and $C_{33}$ in comparison to the pure AlN values can be seen for boron levels of up 25%, illustrating that co-alloying with different species represents a valuable route for simultaneously engineering the piezoelectric and the elastic properties of a parent wurtzite structure such as that of AlN.

3.4 Conclusion

In conclusion, we have shown that co-alloying of AlN with YN and BN leads to superior control of both piezoelectric and mechanical properties. The idea of introducing BN into the systems arose as a way to stiffen the material, which otherwise would have becomes increasingly softer with increased YN content. In the process of assessing the influence of BN and YN composition on properties, we have separately calculated the effect of straining the lattice in different directions, and found that enhancements of the piezoelectric coefficient can be made by applied strain as well: this strain effect could become important for certain substrates, or for electromechanical applications where strain develops in the structure during operation.

The results presented here could carry over to other parent phases and alloying phases as well, provided that each alloying agent offers a clear advantage in terms of engineering one specific property. In our case, YN leads to increasing the piezoelectric coefficient and BN leads to increasing the stiffness. The use of both YN and BN offers intrinsic and simultaneous
control over the mechanical and piezoelectric properties of the Al-Y-B-N system, even though the maximal value for each individual parameter can be achieved in the presence of only one dopant.
CHAPTER 4
LARGE PIEZOELECTRIC RESPONSE OF VAN DER WAALS LAYERED SOLIDS

A paper submitted to Journal of Materials Chemistry C

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The bulk piezoelectric response, as measured by the piezoelectric modulus tensor ($d$), is determined by a combination of charge redistribution due to strain and the amount of strain produced by the application of stress (stiffness). Motivated by the notion that less stiff materials could exhibit large piezoelectric responses, herein we investigate the piezoelectric modulus of van der Waals-bonded quasi-2D ionic compounds using first-principles calculations. From a pool of 869 known binary and ternary quasi-2D materials, we have identified 135 non-centrosymmetric crystals of which 48 systems are found to have $d$ components larger than the longitudinal piezoelectric modulus of AlN (a common piezoelectric for resonators), and three systems with the response greater than that of PbTiO$_3$, which is among the materials with largest known piezoelectric modulus. None of the identified materials have previously been considered for piezoelectric applications. Furthermore, we find that large $d$ components always couple to the deformations (shearing or axial) of van der Waals “gaps” between the layers and are indeed enabled by the weak intra-layer interactions.

4.1 Introduction

Coupling between the mechanical degrees of freedom and the electric polarization in a solid, a hallmark of piezoelectric materials, has found use in applications that range from sensors, resonators, motors, and actuators, to high-resolution ultrasound devices and miniature filters for cellular communications [81, 170, 171]. Interestingly, only about 10 piezoelectric

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materials, including SiO$_2$ (quartz), LiTaO$_3$, LiNbO$_3$, PZT (lead zirconate titanate)-based, BaTiO$_3$-based, (K,Na)NbO$_3$-based, Bi$_4$Ti$_3$O$_{12}$-based, AlN, and ZnO, are technologically relevant and cover virtually all of these applications [172, 173, 6]. Expanding the pool of known piezoelectric materials would help broaden the range of applications and allow earth-abundant and non-toxic [174] replacements for materials that are presently in use. Furthermore, it would offer more cost- and performance-effective choices beyond a relatively limited set of materials that are at present used for their piezoelectric properties.

The need for new piezoelectrics was recognized before and was the main motivation behind recent computational efforts in high-throughput screening of inorganic materials for piezoelectric performance. These include the work on perovskite alloys, [175, 176] and creation of a database of piezoelectric properties of compounds [177]. Materials with reduced dimensionality, such as 2D mono- and multi-layers have also been investigated recently [178, 179, 180, 181, 182, 183]. In virtually all of these works, the quantity of interest was the piezoelectric coefficient tensor $e_{ij}$, which relates the polarization $P_i$ to strain $\epsilon_j$, [15, 116] (in Voigt notation, [18] $P_i = \sum_j e_{ij} \epsilon_j$) and is typically obtained from first-principles calculations.

In this work, we also apply first-principles calculations to screen for candidate piezoelectrics, but instead of the piezoelectric coefficient tensor we consider the piezoelectric modulus tensor $d_{ij}$, which relates the induced polarization to the applied stress, $P_i = \sum_j d_{ij} \sigma_j$ [15, 116]. The advantage of using $d_{ij}$ is in that it represents an important figure of merit in a wide range of technological applications [81, 170] and is a more commonly measured piezoelectric property, especially for materials in the thin film form. Because the induced polarization depends on the applied stress through a combination of the charge redistribution due to strain and the amount of strain that is produced by the applied stress, the piezoelectric modulus tensor $d_{ij}$ depends on both the piezoelectric coefficient tensor $e_{ij}$ and the elastic tensor $C_{ij}$ as:

$$d_{ij} = \sum_{k=1}^{6} e_{ik}(C^{-1})_{kj}. \quad (4.1)$$
From equation (4.1), we can infer that large piezoelectric modulus $d_{ij}$ can be expected in materials with large large $e_{ij}$, but also in systems with low stiffness $C_{ij}$. Softer (less stiff) materials can exhibit large piezoelectric response, as measured by $d_{ij}$, compared to stiffer materials with similar $e_{ij}$. This is illustrated in Figure 4.2, where we notice less stiff materials overall exhibit larger piezoelectric responses in the corresponding direction.

For this reason, we concentrate our investigation on layered (quasi-2D) van der Waals bonded solids, which can be expected to have relatively low stiffness in the out-of-plane direction due to the presence of weak van der Waals (vdW) interactions between the layers. The questions we are addressing are: (a) whether materials that belong to this class and exhibit strong piezoelectric response ($d_{ij}$) can be found, and (b) if this is true, what is the role of vdW interactions in enabling the strong response. To our knowledge, these questions have not been previously addressed in a systematic way.
Figure 4.2: Correlation between experimentally measured longitudinal piezoelectric modulus ($d_{33}$) and their elastic modulus ($C_{33}$). Green circles denote data from either single crystals or single-crystal, single-domain samples in case of ferroelectric materials. Orange circles denote polycrystalline samples. Data is sourced from Refs. [81, 170, 184, 185, 186, 187, 188, 189].

Our results confirm the expectations. The search has revealed a number of quasi-2D materials with relatively large $d_{ij}$ components. Out of 869 considered binary and ternary layered VdW systems, we have identified 135 non-centrosymmetric crystals. Out of those we find more than one third (48 compounds) exhibit piezoelectric moduli greater than that of AlN ($d_{33}$=5.5 pC/N), a commonly used piezoelectric material in resonator applications. In addition, we found three layered systems with piezoelectric moduli even larger than that of PbTiO$_3$ ($d_{33}$=119 pC/N), another established piezoelectric material known for its very large response. It is important to note that none of these vdW systems have been considered previously for piezoelectric applications.

After performing a thorough analysis of the coupling between various stress and $d_{ij}$ components, we find that in all of these systems, large piezoelectric response is always coupled...
to the stress components that imply deformations (axial or shear) of the van der Waals “gaps”
between the layers. This is consistent with the fact that the softest elastic constants are
related to these deformations. Ultimately, our results point to the layered vdW systems as a
rich chemical space for finding new piezoelectric materials, and introduce elastic properties
as additional design criteria for finding materials with large piezoelectric modulus.

4.2 Computational Methodology

In this section, we discuss the details of the computational methodology used in our
calculations, broadly divided into three main subsections. The first subsection describes the
procedure for identifying quasi-2D structures from the Inorganic Crystal Structure Database
(ICSD) [190, 191]. Next, we describe the drawbacks of GGA exchange correlation functionals for predicting the properties of layered materials and our approach to overcome this
issue. Then, we provide detailed descriptions of our workflow for evaluating the piezoelectric
modulus tensors (\(d\)) of quasi-2D solids.

4.2.1 Automated Identification of Quasi-2D Materials

An essential component of this work is the identification of layered (quasi-2D) vdW
materials from ICSD. To accomplish this, we extend the applications of our previously-
developed procedure [192] for automated identification of the binary quasi-2D materials from
the ICSD to include ternary chemistries. Similar algorithms have been developed and used
for the purpose of broad identification of vdW bonded layered systems by others, including
the work of Ashton et al., [193] Mounet et al., [194] and Cheon et al. [195]

Our procedure relies on a slab cutting routine and bond counting. In the first step,
we cut out stoichiometric slabs of a certain thickness for all symmetry inequivalent sets of
Miller indices (\(hkl\)) within a certain range (\(-3 \leq h, k, l \leq 3\)). Next, for each slab we find
the terminations of its surfaces that minimize the number of broken bonds by translating
surface atoms from one side of the slab to the other using appropriate lattice vectors. We
then count the (minimal) number of broken bonds, i.e., the under-coordination, of the surface
atoms. The condition of quasi low-dimensional crystals then implies the existence of \((hkl)\) directions for which the corresponding slabs do not have any under-coordinated atom relative to their bulk coordination in the first shell. If there is exactly one such \((hkl)\), the material is a layered material with relatively large spatial gaps separating individual layers. If the number of directions is larger than one, then the corresponding systems are of lower dimensionality, quasi-1D for two such directions and molecular crystals for larger than two. If there are no such directions, the structure is then a connected 3D structure without large spatial gaps.

In Ref. [192] we demonstrated the success of our algorithm in searching complex quasi-2D materials, including those with layer stacking in oblique directions, materials with corrugated, accordion-like layers, and those with individual layers composed of multiple atomic layers. Using the described automated algorithm, we have in this work considered 3500 binary and 8000 additional ternary compounds from the ICSD and classified them into layered (quasi-2D) and not layered materials. We restricted our search to stoichiometric and ordered systems that do not contain rare earth elements and have 50 of less atoms in the unit cell. From our calculations, we have identified 426 binary and 443 ternary quasi-2D compounds. A full list of these materials can be found in supplementary information with their ICSD id.

### 4.2.2 Calculating Piezoelectric Properties of Quasi-2D Materials

In quasi-2D structures considered in this work, the individual layers are held together by relatively weak vdW interactions. The standard exchange-correlation functionals typically employed in density functional theory (DFT) calculations, including the calculations of elastic and piezoelectric properties, are known to fail to describe the vdW interactions. This is evident from relatively large errors in the out-of-plane lattice constants and the associated elastic properties [196]. To overcome this issue, we employed a vdW-corrected functional (optB86) as implemented in VASP (Vienna Ab-initio Simulation Package) code [197, 198] to calculate the lattice parameters, elastic, and piezoelectric properties of quasi-2D materials [199, 200]. To evaluate the piezoelectric coefficient tensors, we utilize the VASP implemen-
Figure 4.3: Elastic constants of quasi-2D materials calculated with (a) GGA and (b) vdW-corrected functional. The calculated values are compared with experimental ones. The calculations with the vdW-corrected functional are all within 50% error relative to the measurements. Details of measurement techniques, measurement temperatures, *etc.*, are provided in the supplementary informations.

...tation of the density functional perturbation theory (DFPT) [201, 202, 203] calculations. A relatively large plane wave cutoff energy of 540 eV is used for structural relaxation, calculation of elastic tensors, and piezoelectric coefficient tensors. A dense k-point grid, defined by $n_{\text{atoms}} \times n_{\text{kpoints}} \approx 1000$, where $n_{\text{atoms}}$ is number of atoms in the primitive cell and $n_{\text{kpoints}}$...
Figure 4.4: Workflow for calculations of piezoelectric coefficient tensor $e_{ij}$, the elastic stiffness $C_{ij}$, and the piezoelectric modulus tensor $d_{ij}$ of quasi-2D materials. A vdW-corrected functional (optB86) is used in all calculations. We have calculated piezoelectric modulus of 80 quasi-2D materials.

is the number of k-points, is employed. In all our calculations, a very high tolerance of $10^{-8}$ eV for energy convergence is used, which is an important consideration for conducting DFPT calculations [177]. For calculation of elastic tensors we use a finite difference method. Here, the full elastic tensor is calculated by conducting six finite distortions of the lattice and obtaining elastic constants ($C_{ij}$) from the stress-strain relationship [204, 205].

The importance of incorporating vdW-corrections is illustrated in Figure 4.3, where we notice significant improvement in predicting elastic constants, particularly $C_{33}$ and $C_{44}$, with vdW-corrected functional (optB86) [199, 200] compared to standard GGA-PBE functional [130]. The GGA-PBE predicted elastic constants are sourced from Ref.[11]. A more detailed analysis of the data presented in Figure 4.3 reveals that the GGA-PBE is still better in predicting in-plane elastic coefficients $C_{11}$ and $C_{12}$, but the error in reproducing $C_{33}$ and $C_{44}$ is a factor of 10 or larger. This is due the fact that these particular two elastic constants are directly related to the deformations of the spatial gaps between the layers and the failure of GGA-PBE in reproducing relatively weak vdW interactions. The comparison of predicted properties with GGA-PBE and vdW-corrected functional is limited only to the elastic constants (Figure 4.3); the lack of experimental data on piezoelectric properties of
quasi-2D materials prevented us from making similar comparisons for predicted piezoelectric properties. In Table F.1 of Appendix F, we have provided the experimental details (e.g. measurement techniques, measuring temperatures, etc.) for each compound shown in Figure 4.3. The comparison of calculated and experimental values for the piezoelectric modulus of a few commercially important piezoelectric materials (including AlN and PbTiO$_3$) are shown supplementary information. Predicted piezoelectric moduli are found to be in good agreement with experimental values.

4.2.3 Workflow for identifying quasi-2D piezoelectrics

A complete workflow we developed for identifying promising quasi-2D piezoelectric materials is illustrated in Figure 4.4. The binary and ternary crystal structures from the ICSD database are first screened using the automated algorithm for identifying quasi-2D structures. Then, we filter out all centrosymmetric structures based on the space group assigned in ICSD. Out of $\sim$11500 binary and ternary materials we find 869 layered systems, out of which 135 are identified as having non-centrosymmetric structures. Next, the non-centrosymmetric, structures are relaxed using the previously described first-principles calculations employing a vdW-corrected functional. As the piezoelectric materials need to have sizable band gaps for their properties to not be screened by the existence of free charge carriers we next employ a band-gap filter. As suggested in the previous works, [192, 206] for electronic structure calculation, we perform self-consistent GGA-PBE calculations on the vdW-relaxed structures using dense k-point grids. Because of the known band gap error in DFT calculations we use a relatively generous band gap cutoff of 0.1 eV. Fifty additional materials with their band gap smaller than 0.1 eV are discarded as a result. Finite difference calculations are performed with vdW-corrected functional to obtain the elastic constants ($\mathbf{C}$). Five materials with elastic tensors with negative eigenvalues are also discarded. According to Born stability criteria,[207] the elastically stable materials always have positive eigenvalues of stiffness matrix. This means that an elastically stable materials always have positive elastic energy for arbitrary homogeneous deformation by an infinitesimal strain [208]. With the remaining 80
candidates, we proceed our calculations by performing Density Functional Perturbation Theory (DFPT) [201, 202, 203] calculations to assess their piezoelectric coefficient tensor, $e$. Out of the remaining 80 candidates, 38 materials contain transition metal elements. For these, we perform a limited search of the magnetic ground state by enumerating all magnetic configurations in the unit cell and calculating their total energies. The elastic and piezo calculations are then performed only on the lowest energy spin state. This step is necessary because of the strong dependence of the electronic structure and other properties on spin configuration discussed in more details in Ref. [209]. The automated DFT calculations including initial file generation, calculating properties, data extraction and data handling are performed with the help of PyLada, [210] a Python framework for high-throughput first-principles calculations.

4.3 Results and Discussions

4.3.1 Promising Quasi-2D Piezoelectric Materials

Based on the calculated piezoelectric modulus tensor, a number of candidate materials with relatively large $d_{ij}$ components have emerged. They are shown in Figure 4.5 with the full list together with the corresponding $d_{ij}$, $C_{ij}$ and $e_{ij}$ values provided in the supplementary
information. In addition, the top 20 most promising systems, based on the largest $d_{ij}$ component, are listed in Table 4.1.

The piezoelectric modulus tensor ($d$) is a third rank tensor, and any isotropic averaging scheme will yield zero [211]. To rank these materials based on the merit of their piezoelectric response, we define $d_{\text{max}} = \max(|d_{ij}|)$ as the largest element of the absolute $d_{ij}$ matrix.

Then the $d_{\text{max}}$ is plotted against the space group number in Figure 4.5. The two reference lines have been drawn for categorizing these candidates – one representing calculated $d_{33}$ of PbTiO$_3$ and the other representing calculated $d_{33}$ of AlN (see supplementary information for the benchmark against experiments).

Please note that PbTiO$_3$ is also a ferroelectric and here we are only using the value for its piezoelectric response. More precisely, the PbTiO$_3$ reference line corresponds to the bulk piezoelectric modulus corresponding to the single-crystal single-domain samples.

The materials shown in the left panel of Figure 4.5 can broadly be divided in three categories. The first category is comprised of quasi-2D compounds with $d_{\text{max}}$ larger than the longitudinal piezoelectric modulus of PbTiO$_3$ ($d_{33}$=119 pC/N) [81] – the key end member of most commercial high-strain piezoelectrics. We found three materials (In$_2$Te$_5$, PbS, and GeTe) in this category. Among them PbS is not in its ground state rocksalt phase, but in the hypothetical distorted NiAs structure which has found its way into the ICSD [212]. The other two compounds have previously been experimentally synthesized, [213, 214] but their piezoelectric moduli have not been reported so far.

In the second category we group all compounds which have $d_{\text{max}}$ larger than the longitudinal piezoelectric modulus of AlN ($d_{33}$=5.5 pC/N) [78] and lower than the longitudinal piezoelectric modulus of PbTiO$_3$. The majority (48 compounds) of the piezoelectric candidates from our study fall in this category revealing that overall the vdW bonded quasi-2D systems indeed exhibit a propensity toward large piezo-response. This group is composed from oxides and other chalcogenides such as CuVO$_3$, SnO, BiInO$_3$, MoV$_2$O$_8$, SnS$_2$, InSe, Cs$_2$Te$_3$ and other (total of 30); halides such as KSn$_2$F$_5$, AgI, MgCl$_2$, and PbI$_2$ (total of 4);
Table 4.1: List of top 20 candidate quasi-2D piezoelectric materials are shown with their space group (SG) number, calculated DFT band gap ($E_g$), maximal piezoelectric modulus $d_{\text{max}}$, the $d_{ij}$ component that appears as $d_{\text{max}}$, maximal $e_{ij}$ ($e_{\text{max}}$), the $e_{\text{max}}$ component of $e_{ij}$.

<table>
<thead>
<tr>
<th>Compound</th>
<th>SG</th>
<th>$E_g$(eV)</th>
<th>$d_{\text{max}}$ (pC/N)</th>
<th>max $d_{ij}$</th>
<th>$e_{\text{max}}$ (C/m$^2$)</th>
<th>max $e_{ij}$</th>
<th>$e_{\text{max}}$ (C/m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>In$_2$Te$_5$</td>
<td>9</td>
<td>0.7</td>
<td>351.7</td>
<td>$d_{15}$</td>
<td>2.6</td>
<td>$e_{15}$</td>
<td>2.6</td>
</tr>
<tr>
<td>PbS‡</td>
<td>186</td>
<td>0.2</td>
<td>161.4</td>
<td>$d_{33}$</td>
<td>8.3</td>
<td>$e_{33}$</td>
<td>8.3</td>
</tr>
<tr>
<td>GeTe</td>
<td>160</td>
<td>0.6</td>
<td>148.4</td>
<td>$d_{15}$</td>
<td>3.3</td>
<td>$e_{15}$</td>
<td>3.3</td>
</tr>
<tr>
<td>CuVO$_3$</td>
<td>1</td>
<td>0.9</td>
<td>106.9</td>
<td>$d_{22}$</td>
<td>0.8</td>
<td>$e_{32}$</td>
<td>0.2</td>
</tr>
<tr>
<td>SnO</td>
<td>31</td>
<td>1.6</td>
<td>67.1</td>
<td>$d_{22}$</td>
<td>1.1</td>
<td>$e_{22}$</td>
<td>1.1</td>
</tr>
<tr>
<td>BiInO$_3$</td>
<td>33</td>
<td>2.8</td>
<td>56.1</td>
<td>$d_{33}$</td>
<td>4.7</td>
<td>$e_{33}$</td>
<td>4.7</td>
</tr>
<tr>
<td>Bi$_2$WO$_6$‡</td>
<td>41</td>
<td>1.7</td>
<td>54.1</td>
<td>$d_{24}$</td>
<td>3.9</td>
<td>$e_{33}$</td>
<td>2.9</td>
</tr>
<tr>
<td>NaI$_3$O$_8$</td>
<td>81</td>
<td>2.8</td>
<td>48.4</td>
<td>$d_{14}$</td>
<td>0.7</td>
<td>$e_{31}$</td>
<td>0.6</td>
</tr>
<tr>
<td>NaN$_3$</td>
<td>12</td>
<td>1.4</td>
<td>40.7</td>
<td>$d_{36}$</td>
<td>0.3</td>
<td>$e_{34}$</td>
<td>0.1</td>
</tr>
<tr>
<td>KSn$_2$F$_5$</td>
<td>143</td>
<td>3.0</td>
<td>40.5</td>
<td>$d_{15}$</td>
<td>0.3</td>
<td>$e_{15}$</td>
<td>0.3</td>
</tr>
<tr>
<td>MoV$_2$O$_8$</td>
<td>35</td>
<td>0.8</td>
<td>40.4</td>
<td>$d_{33}$</td>
<td>2.9</td>
<td>$e_{33}$</td>
<td>2.9</td>
</tr>
<tr>
<td>TlBrO$_3$</td>
<td>160</td>
<td>3.0</td>
<td>38.8</td>
<td>$d_{24}$</td>
<td>1.0</td>
<td>$e_{24}$</td>
<td>1.0</td>
</tr>
<tr>
<td>NaSnN</td>
<td>186</td>
<td>1.1</td>
<td>36.6</td>
<td>$d_{15}$</td>
<td>0.6</td>
<td>$e_{15}$</td>
<td>0.6</td>
</tr>
<tr>
<td>Cs$_2$Te$_3$‡</td>
<td>36</td>
<td>0.5</td>
<td>31.3</td>
<td>$d_{36}$</td>
<td>0.6</td>
<td>$e_{11}$</td>
<td>0.4</td>
</tr>
<tr>
<td>Bi$_2$MoO$_6$</td>
<td>61</td>
<td>1.7</td>
<td>28.7</td>
<td>$d_{26}$</td>
<td>1.6</td>
<td>$e_{11}$</td>
<td>1.3</td>
</tr>
<tr>
<td>AgI</td>
<td>186</td>
<td>1.3</td>
<td>27.8</td>
<td>$d_{15}$</td>
<td>0.3</td>
<td>$e_{33}$</td>
<td>0.1</td>
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<tr>
<td>SbF$_2$Cl$_3$</td>
<td>79</td>
<td>1.5</td>
<td>24.4</td>
<td>$d_{15}$</td>
<td>0.2</td>
<td>$e_{33}$</td>
<td>0.1</td>
</tr>
<tr>
<td>MgCl$_2$</td>
<td>115</td>
<td>4.9</td>
<td>23.5</td>
<td>$d_{15}$</td>
<td>0.2</td>
<td>$e_{15}$</td>
<td>0.2</td>
</tr>
<tr>
<td>PbRb$_2$O$_3$</td>
<td>36</td>
<td>1.3</td>
<td>22.2</td>
<td>$d_{34}$</td>
<td>0.7</td>
<td>$e_{34}$</td>
<td>0.7</td>
</tr>
<tr>
<td>BiGeO$_5$</td>
<td>9</td>
<td>2.3</td>
<td>21.1</td>
<td>$d_{33}$</td>
<td>3.0</td>
<td>$e_{33}$</td>
<td>3.0</td>
</tr>
</tbody>
</table>

‡ hypothetical structures ‡ dynamically unstable
pnictides such as NaSnN, NaSnP, KSnAs, and NaN$_3$ (total of 4). Also, a number of materials in this group (10) are the mixed anion systems, *e.g.*, NaI$_3$O$_8$, SbF$_2$Cl$_3$. Not surprisingly, the more ionic systems like oxides, halides and nitrides are more frequently found closer to the top of the range. Finally, two compounds Cs$_2$Te$_3$ and Bi$_2$WO$_6$ are found in calculations to be dynamically unstable, but both have been experimentally synthesized (likely high-temperature phases) [215, 216].

The last group is composed of materials with the piezoelectric response lower than the longitudinal piezoelectric modulus of AlN. Though these candidates exhibit low piezoelectric response, they could still be useful as the calculated moduli are comparable with that of quartz ($d_{11}=2.27$ pC/N) [217]. We found a total of 12 compounds which fall in this category. Examples include: WS$_2$, RhF$_3$, ZrCl$_2$, and GaInS$_3$. The moduli $d$, $e$ and $C$ with other information such as band gap, space group of these compounds are provided in the supplementary information.

We also observe that the piezoelectric compounds in the quasi-2D family of solids are clustered mainly in three specific space groups, *i.e.*, space group no. 36 ($Cmc2_1$), 160 ($R3m$), and 186 ($P6_3mc$). This is mainly a reflection of the population bias, as these are the three most frequently occurring non-centrosymmetric space groups in the quasi-2D family of crystals.

Table ?? shows that in 9 of the high-response quasi-2D piezoelectric compounds, the $d_{15}$ component appears as $d_{\text{max}}$. Note that because of the freedom in choosing the in-plane axes, $d_{15}$ and $d_{24}$ are virtually indistinguishable (see the discussion section). This component corresponds to the thickness shearing deformation where the material shears like a deck of cards in the in-plane direction, with no change in the other dimension. Materials with large $d_{15}$ can be used in a variety of applications including: sensors, actuators, accelerometer, material testing structural health monitoring, non-destructive testing (NDT), and non-destructive evaluation (NDE) [218]. The components of $d_{ij}$ appearing as $d_{\text{max}}$ usually coincide with the components of $e_{ij}$ appearing as $e_{\text{max}}$. The distribution of different components of $d_{ij}$ (and
Figure 4.6: Histogram of the maximum components of (a) the piezoelectric coefficient tensor, $e_{\text{max}}$ and (b) piezoelectric modulus tensor, $d_{\text{max}}$. The most frequent $e_{\text{max}}$ is $e_{33}$, whereas for $d_{\text{max}}$ the most frequent maximum values are $d_{15}$, $d_{24}$ and $d_{33}$. (c) Schematics of several important piezoelectric operating modes with their corresponding deformation types. The schematics of other relevant piezoelectric operating modes, i.e., components of $d_{ij}$ are shown in the supplementary information.

$e_{ij}$ appearing as $d_{\text{max}}$ (and $e_{\text{max}}$) are discussed in more detail in the next section.
Another quantity that could influence the piezoelectric response is the band gap of the material. In this work the band gaps are calculated at the DFT level. Only about 1/3 of the studied materials are found to have DFT band gaps below 1 eV. Given the well known underestimation of band gaps in DFT based methods we do not think that materials with DFT band gaps larger than 1 eV would suffer from problems related to the existence of free charge carriers due to thermal fluctuations. However, for those with smaller gaps thermal fluctuation may cause sufficient number of free charge carriers, which may lower the polarization upon straining these materials despite having large piezoelectric moduli. Of course, provided that the real band gap is sufficiently close to the DFT one. For these materials, a more accurate assessment of the electronic structure might be needed before they are considered for applications.

In relation to the chemical composition and toxicity it is also important to not that currently, the most widely used piezoelectric material is lead zirconate titanate (PbZr$_{1-x}$Ti$_x$O$_3$ or PZT) [91]. However, PZT causes significant environmental problems because of its high lead content [91]. Hence, significant efforts have been made to develop lead-free piezoelectric materials [91, 73, 219]. In our work, we have identified 44 candidates that do not contain any toxic elements including Pb. Out of 44 candidates, 33 of them have their piezoelectric modulus larger than AlN.

### 4.3.2 Role of van der Waals Interactions

In order to understand the role of van der Waals interactions on the piezoelectric response of quasi-2D materials, we analyze the relationships of $e_{max}$ and $d_{max}$ to the corresponding strain and stress components, respectively. A histogram showing the number of compounds with a given $e_{ij}$ component appearing as $e_{max}$ is shown in Figure 4.6 (a). We observe that the most frequent $e_{max}$ is $e_{33}$. This indicates that in the majority of quasi-2D materials the largest piezoelectric response, as measured by the $e_{ij}$, is along the layer stacking direction. The reason for this behavior is that the relatively weak vdW interactions allow large charge redistribution in the layering direction upon straining the system.
On the other hand, the piezoelectric modulus tensor $d$ relates stress to polarization and combines two types of effects: (1) amount of strain due to application of stress, and (2) amount of charge redistribution (polarization) due to resultant strain produced by the applied stress. A similar histogram of the $d_{ij}$ components appearing as $d_{\text{max}}$ is shown in Figure 4.6(b). We divide the $d_{ij}$ components into three groups depending on the deformation types (stress components) and the polarization direction. The schematics of the polarization directions and the associated stress components is shown in Figure 4.6(c) together with the $d_{ij}$ components connecting the two. Every component of $d_{ij}$ represents a separate piezoelectric operating mode. Schematics of all possible piezoelectric modes are provided in supplementary information.

Group I: Applied stress deforms van der Waals bonds and the measured polarization coincides with the direction of the deformations. The longitudinal mode ($d_{33}$) and shear modes ($d_{15}$ and $d_{24}$) fall in this class. As evident from the histogram in Figure 4.6(b) these are the most frequently appearing $d_{\text{max}}$ components. In our considered materials, the modes $d_{24}$ and $d_{15}$ are indistinguishable because of the arbitrariness of the choice of axes ‘1’ and ‘2’, while the axis ‘3’ is fixed by layer stacking directions. In both of these modes, the same stress component ($\sigma_4$) is responsible for the deformation, which implies shearing of the van der Waals gaps. On the other hand, in the $d_{33}$, the applied stress axially deforms (stretches or compresses) van der Waals gaps. Hence, the large piezoelectric responses are achieved by deforming (axial or shear) the relatively soft van der Waals bonds. The bar-heights of $d_{15}$ and $d_{24}$ in the histogram of $d_{\text{max}}$ in Figure 4.6(b) are larger compared to $d_{33}$. This is because the shearing resistance values ($C_{44}$) of quasi-2D materials are lower compared to their axial resistance values ($C_{33}$) (refer to Figure 4.3(b)).

Group II: Applied stress deforms van der Waals bonds, but the measuring polarization directions are different from their deformation directions. The face shear modes ($d_{14}$ and $d_{25}$) and the thickness-extension modes ($d_{31}$ and $d_{32}$) fall in this class. The schematics of $d_{31}$ and $d_{32}$ are provided in the supplementary information. Usually, the direction of polarization is
facilitated by the direction of deformation. In such modes, the deformation directions are different from their measured polarization directions. This is the reason behind their low occurrence in the histogram of $d_{max}$ though the van der Waals bond are deformed by the applied stress.

Group III: The van der Waals bond does not deform by the applied stress in these modes. This is why these modes do not appear frequently in the histogram of $d_{max}$. This includes length or width extension modes ($d_{11}$ or $d_{22}$) and shearing modes of type $d_{16}$ and $d_{36}$.

The above discussion implies that the large piezoelectric response is always accompanied and caused by the stress that deforms the “soft” van der Waals gaps either through stretching, compression, or shearing. In addition, the analysis of the maximal piezoelectric moduli and the associated stress components provided guidance to experimentalists of how thin films should be grown to utilize large $d_{max}$. It also describes what kind of mechanical actuation is necessary to achieve large piezoelectric response. This also helps in the design of new devices to take advantage of large $d_{max}$. Finally, these findings can open up a wide variety of devices based on their operation modes or based on new materials for non-conventional modes. For example, materials with large face-shear ($d_{14}$) mode response will be attractive for torsional applications, like novel gyroscopic sensors or high-precision torsional MEMS actuators [218].

4.3.3 Axial Piezoelectric and Elastic Anisotropy

In addition to revealing new candidate piezoelectric materials and explaining the origin of strong piezoelectric response, we have also investigated the anisotropy in axial piezoelectric response in relation to the axial elastic anisotropy. We analyze how the response in the out-of-plane direction compares to the in-plane responses. The in-plane and out-of-plane directions in quasi-2D materials are trivial to define and are illustrated in Figure 4.1. We define the axial anisotropy in both elastic and piezoelectric responses by the ratio of the out-of-plane component to the in-plane component. Here, the in-plane component is defined by the arithmetic mean of the ‘11’ and ‘22’-components (invariant to the choice of the in-plane
Figure 4.7: Correlation between axial anisotropy, i.e., out-of-plane to in-plane response ratio) of (a) d and e (b) d and C. The results reveal that majority of quasi-2D piezoelectric materials are dominated by out-of-plane piezoelectric responses (both in e and d) but elastically they are dominated in in-plane direction.

axes), whereas the out-of-plane response is solely defined by the ‘33’-component. Hence, the axial anisotropy of d, e, and C can be expressed as $2d_{33}/(d_{11} + d_{22})$, $2e_{33}/(e_{11} + e_{22})$, and $2C_{33}/(C_{11} + C_{22})$ respectively. If the axial anisotropy equals or nearly equals 1 then the
material is considered to be isotropic in the corresponding quantity responses with respect to the in-plane and out-of-plane directions. If the axial anisotropy is greater (or lower) than 1 the response of a material to axial deformation is dominated in out-of-plane (in-plane) direction.

All possible correlations among the axial anisotropy of $d$, $e$, and $C$ have been investigated. The correlation between axial anisotropy of $d$ with respect to the axial anisotropy of $e$ and $C$ are shown in Figure 4.7 (a) and (b) respectively. From the comparative studies between Figure 4.7 (a) and (b), we see that the axial anisotropy of $d$ is mainly dictated by the axial anisotropy of $e$ not by the axial anisotropy of $C$. The plot between axial anisotropy of $C$ and $e$ is provided in the supplementary information.

From Figure 4.7 (a) and (b), we observe that most quasi-2D materials have axial piezoelectric anisotropy parameter (both in $d$ and $e$) $> 1$ and axial elastic anisotropy parameter $< 1$. This implies that the quasi-2D piezoelectric materials are dominant in out-of-plane piezoelectric responses but elastically they are dominant in-plane directions. This result corroborates the correlation between elastic softness and large piezoelectric response, i.e., the large piezoelectric responses are observed in elastically softer directions. We found quasi-2D piezoelectric compounds such as CuVO$_3$ and Li$_7$SbO$_6$ are dominated by in-plane piezoelectric response. Compounds such as Bi$_2$WO$_6$, Al$_2$ZnS$_4$, GeZnO$_3$, and GeTe are nearly isotropic in their axial elastic responses but highly anisotropic in axial piezoelectric responses.

4.4 Conclusions

In conclusion, we performed a large-scale computational (first-principles) assessment of the bulk piezoelectric properties of layered (quasi-2D), vdW bonded materials. In our study we concentrate on the piezoelectric modulus as the measure of the piezoelectric response, which relates mechanical stress and electric polarization and depends on a combination of charge redistribution due to strain and the amount of strain produced by the stress. Overall, out of 135 non-centrosymmetric quasi-2D binary and ternary structures from ICSD we have discovered 51 materials with piezoelectric response larger than that of AlN, a well-
known piezoelectric materials used in applications. Out of these 51 systems, we find three with the piezoelectric modulus even larger than that of PbTiO$_3$ that has the piezoelectric modulus among the largest known. More importantly, 33 out of the 51 layered compounds do not contain any toxic elements including Pb. Our results also reveal that the large piezoelectric modulus in vdW systems is directly enabled by the vdW interactions between layers as in majority of compounds the large components of the piezoelectric modulus tensor couple to the stress components that imply deformations (both shear and axial) of the “soft” vdW bonds between layers. Our results suggest that quasi-2D layered materials are a rich structural space for discovering new piezoelectric materials.
CHAPTER 5
SUMMARY & CONCLUSIONS

In this chapter, we summarize the results of this thesis and highlight its key accomplishments. In addition, we suggest a few future research directions that could provide the next steps towards the ultimate goal of designing novel piezoelectric materials with tailored physical properties.

5.1 Conclusions

This thesis is composed of these three works: (a) Improving piezoelectric response of AlN by alloying, (b) Tuning the piezoelectric and mechanical properties of AlN by co-alloying, and (c) Discovering new piezoelectric materials with large piezoelectric modulus

By density functional theory, we conclude that (Cr, Al)N has a low wurtzite-to-rocksalt transition concentration, and therefore can offer certain piezoelectric enhancements at alloying levels that are easier to stabilize during the synthesis. Among a set of wurtzite-structured materials, we have found that (Cr, Al)N has the most sensitive piezoelectric coefficient with respect to alloying concentration. Our results reveal that, for 12.5% Cr $d_{33}$ is twice that of pure AlN, and for 30% Cr this modulus is about four times larger than that of AlN. This finding, combined with the relative ease of synthesis under non-equilibrium conditions, may establish (Cr,Al) N as a prime piezoelectric material for applications such as resonators and acoustic wave generators.

Improvement of piezoelectric properties by transition metal alloying is also accompanied by elastic softening in AlN. Co-alloying of boron nitride and transition metal metal nitride such as YN with AlN offers superior combination of both the mechanical and piezoelectric properties of AlN.

For discovery of new piezoelectric materials, we perform high-throughput screening in layered binary and ternary materials for their piezoelectric properties. We discovered 50
new compounds such as In$_2$Te$_5$, GeTe, and CuVO$_3$ with piezoelectric response larger than AlN. As a matter of fact, 70% of our discovered piezoelectric candidates do not contain any toxic elements like Pb. Our analysis revealed that the large components of d always couple with the shearing or axial deformations of van der Waals “gaps” between the layers.

5.2 Recommendations for Future Work

This dissertation focuses on designing and discovering new piezoelectric materials using density functional theory. Here, we list following two areas which can be explored in the future:

(1) The effect of alloying at cationic site of AlN on piezoelectric and mechanical properties has been studied chapter 2 and chapter 3. The future work can be extended on the studying the effect of N-site alloying by alloying with P on piezoelectric properties of AlN. AlP has a low bulk modulus compared to AlN. The systematic studies on enthalpy of formation, $T - x$ curve will also reveal the stability of Al(P,N) alloys which have not been explored previously.

(2) In the initial investigations mentioned previously, we found several candidate materials with high piezoelectric response. Ferroelectrics are a subset of piezoelectrics with spontaneous polarization switchable by an applied electric field. In future investigations, one could identify the potential quasi-2D ferroelectric materials from this set of quasi-2D piezoelectric materials. Identification of ferroelectric materials with unique responses such as spontaneous polarization and polarization reversibility would befit their application in capacitors, non-volatile memory, and transpolarizers.
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By convention, we refer to the $e_{ij}$ values, which couple strain and dielectric displacement (or electric field and stress), as piezoelectric coefficients, while the $d_{ij}$ values, which couple strain with electric field (or stress with dielectric displacement), are referred to as piezoelectric moduli. In both cases, we express the individual matrix elements in standard reduced Voigt notation.


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APPENDIX A
CLASSIFICATION OF PIEZOELECTRIC MATERIALS

The crystallographic symmetry of materials play crucial role on piezoelectricity. From crystallographic symmetry perspective, all the components of piezoelectric coefficient tensor are zero for centrosymmetric materials. Here, we provide detail description of crystal classes from symmetry perspective and their piezoelectric behavior.

![Table of Centrosymmetric and Non-centrosymmetric Crystal Classes](image)

Figure A.1: Centrosymmetric and non-centrosymmetric (polar and non-polar) point groups. Only non-centrosymmetric point groups allow piezoelectricity.

The whole family of material systems can be classified into 32 crystallographic points groups. Out of these 32 point groups, 21 are non-centrosymmetric, i.e., crystals not having a center of symmetry. Out of these 21 point groups, except group 432, crystals containing all other point groups exhibit piezoelectric effect. Out of these 20 non-centrosymmetric point
groups, 10 belong to polar crystals \textit{i.e.}, crystals which possess a unique polar axis, an axis showing different properties at the two ends. The classification of point groups based on their crystallographic symmetry is described in detail in Figure A.1.

The polar crystals can be spontaneously polarized. The polarization can be compensated through external or internal conductivity or domain formation. The Spontaneous polarization is effected by the temperature. An electric charge is developed on the faces of the crystal perpendicular to the polar axis, if a change in temperature is imposed. This is known as pyroelectricity. The 10 classes of polar crystals are pyroelectric materials. In some of these pyroelectric crystals, the polarization along the polar axis can be reversed by reversing the polarity of electric field. Such crystals are called ferroelectric \textit{i.e.}, these are spontaneously polarized materials with reversible polarization.
This chapter briefly reviews the major concepts, equations, and common approximations of density functional methods that applied throughout this thesis. The more detailed derivations can be found in the original work by Kohn et al. [220, 221] and the textbook by R Martin [222].

B.1 Many-body Schrödinger equation

The time-independent Schrödinger equation can be written as follows:

\[ H\Psi = E\Psi \quad (B.1) \]

where, \( \Psi(R_I, r_i) \) corresponds to the many-electron wave function with \( R_I \) and \( r_i \) describing the positions of the ions (\( I \)) and electrons (\( i \)) respectively. The total energy \( E \) of a system can then be evaluated by operating on \( \Psi \) with the Hamiltonian \( H \).

The system of interacting electrons (\( e \)) and nuclei (\( N \)) includes kinetic (\( T \)) and Coulomb interaction (\( V \)) terms is expressed by the following Hamiltonian,

\[ H = T_e + T_N + V_{NN} + V_{ee} + V_{eN} \quad (B.2) \]

where, the electronic (\( T_e \)) and nuclear (\( T_N \)) kinetic terms are expressed as follows,

\[ T_e = \frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 \quad (B.3) \]

\[ T_N = \frac{\hbar^2}{2M_I} \sum_I \nabla_I^2 \quad (B.4) \]

where, \( \hbar \) is the reduced Planck constant.

The nuclear-nuclear (\( NN \)), electron-electron (\( ee \)), and the nuclear-electrons (\( eN \)) Coulombic interactions are expressed as,
\[ V_{NN} = \frac{1}{2} \sum_{i \neq J} \frac{Z_i Z_J e^2}{|r_j - R_i|} \]  
\[ V_{ee} = \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|r_j - r_i|} \]  
\[ V_{eN} = -\sum_{i,l} \frac{Z_l e^2}{|r_i - R_l|} \]

where, \( m_e \) and \( M_I \) describes the mass of the electron and ion respectively, \( Z_I \) is the atomic number of \( I \)-th ion, and \( e \) is the electron charge. Since, \( M_I \geq m_e \), one can decouple the dynamics of the electrons from dynamics the nuclei. This decoupling is known as the *Born-Oppenheimer approximation* [223]. As a result, the quantum many body interacting Hamiltonian of condensed systems can be simplified to the so-called electronic Hamiltonian,

\[ H_e = T_e + V_{NN} + V_{ee} + V_{eN} \]  

where, the \( V_{NN} \) is now a classical interaction, which may be approximated using a variety of approaches.

### B.2 Density Functional Theory

The basic theorems of the density functional formalism were proved by Hohenberg and Kohn [220]. The key idea in density functional theory is to use the electron density \( n(r) \) as the basic variable instead of the wave function. This simplifies the problem of working with 3n spatial variables for a n-electron problem to only 3.

#### B.2.1 Hohenberg-Kohn Theorem

In 1964, Hohenberg and Kohn published their paper on inhomogeneous electron gas [220], for density functional theory. The two theorems are stated in the words of Martin [222] as follows:

*Theorem 1: For any system of interacting particles in an external potential \( V_{ext}(r) \), the potential \( V_{ext}(r) \) is determined uniquely, except for a constant, by the ground state particle
density $n_0(r)$.

Theorem 2: A universal functional for the energy $E[n]$ in terms of the density $n(r)$ can be defined, valid for any external potential $V_{\text{ext}}(r)$. For any particular $V_{\text{ext}}(r)$, the exact ground state energy of the system is the global minimum value of this functional, and the density $n(r)$ that minimizes the functional is the exact ground state density $n_0(r)$.

The first theorem states that all properties of a system are evaluated by the ground state density $n_0(r)$, and the second that $E[n]$ alone is enough to evaluate the exact ground state energy and density. The general form of the functional is

$$E[n] = T[n] + E_{\text{int}}[n] + \int d^3r V_{\text{ext}}(r)n(r) + E_{II}$$

where, the terms on the right side of the equation represent the kinetic energy of the electrons ($T[n]$), the electron-electron interaction energy ($E_{\text{int}}[n]$), the interaction energy with an external potential in the form of Coulomb interaction with the nuclei, and the interaction energy between the nuclei ($E_{II}$).

B.2.2 The Kohn-Sham Equations

Kohn and Sham suggested in 1965 [221] that the real system with interacting particles should be replaced with a system of non-interacting particles. This is accomplished by replacing the purely external potential with an effective potential $V_{\text{eff}}$. The single particle interacting with the effective potential is then described by the single particle wave function $\psi_j$, that can be found by solving the single-particle equation [224]

$$\left(-\frac{1}{2}\nabla^2 + V_{\text{eff}}(r) - \epsilon_j\right)\psi_j(r) = 0$$

(B.10)

where $\epsilon_j$ is the eigenvalue of the non-interacting single particle, and the effective potential is given by

$$V_{\text{eff}}(r) = V_{\text{ext}}(r) + \int \frac{n(r')}{|r-r'|}d^3r' + V_{\text{xc}}(r)$$

(B.11)
where
\[ V_{xc} = \frac{\delta E_{xc}[n(r)]}{\delta n(r)} \] (B.12)

The electron density in a system with N electrons is then calculated using the wave functions according to
\[ n(r) = \sum_{j=1}^{N} |\psi_j(r)|^2 \] (B.13)

The total energy is given by the Kohn-Sham total energy functional
\[ E_{KS}[n] = T_s[n] + \int d\mathbf{r} V_{ext}(\mathbf{r}) n(\mathbf{r}) + E_{Hartree}[n] + E_{II} + E_{xc}[n] \] (B.14)

Here, \( V_{ext}(\mathbf{r}) \) is the external potential due to the nuclei and any other external fields (assumed to be independent of spin), \( E_{II} \) is the interaction between the nuclei, and \( E_{Hartree} \) is the classical Coulomb interaction energy of the electron density with itself given by,
\[ E_{Hartree} = \frac{1}{2} \int d^3r d^3r' \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \] (B.15)

Although the Kohn-Sham total energy functional is exact in the form presented in eq. (B.14), the exchange-correlation term \( E_{xc}[n] \), where all many-body effects are included, pose a problem because there is no universal form for it. There also exist approximate functionals which capture many-body effects with good accuracy, \( e.g. \), the local-density approximation and the generalized gradient approximation which are described below.

### B.2.3 Local Density Approximation

The local-density approximation (LDA) was first suggested in the original paper by Kohn and Sham [221]. The basic idea comes from the observation that exchange-correlation effects are to a large extent local in character. Therefore, they proposed to calculate the exchange-correlation energy \( E_{xc}^{LDA}[n] \) with a simple integral over all space, where the exchange-correlation energy density is assumed to be the same as in homogeneous electron
gas with that density $\epsilon_{xc}^{\text{hom}}[n(r)]$,

$$E_{xc}^{\text{LDA}}[n] = \int d^3 n(r) \epsilon_{xc}^{\text{hom}}[n(r)].$$  \hspace{1cm} (B.16)

To summarize the performance of LDA, it works well for covalent-, metallic-, and ionic-type bonds, even though it generally tends to over bind slightly. Although, the over binding causes gives lattice parameters which are lower than those experimentally obtained, trends in lattice parameters are well reproduced. However, for long range interactions such as Van der Waals interactions LDA does not work.

\subsection*{B.2.4 Generalized Gradient Approximation}

The generalized gradient approximation (GGA) improves the LDA by including the absolute value of the gradient of the density with the value of $n$ at each point. There are a number of implementations to introduce the gradient corrections [225, 226, 130] which still force the system to behave correctly in important limiting cases [222]. The work in this thesis has been performed using the implementation by Perdew, Burke, and Ernzerhof (PBE-GGA) [226, 130]. Although it tends to under bind and provide slightly larger lattice constants than experiment, PBE-GGA is better at providing reasonable geometries for the nitride systems investigated in this thesis, as compared to the LDA.

\subsection*{B.3 Technical implementation}

The theoretical results presented in this dissertation are based on the density functional theory formalism we have outlined in this chapter as implemented the Vienna ab initio Soware Package (VASP). The technical details regarding choice of exchange-correlation functional, plane wave energy cutoff, and electronic configuration of valence electrons in PAWs are provided as necessary in the results chapters.
Elastic constants provide important information on the mechanical properties of materials and on their structural stability. Under a linear elastic deformation,

$$\sigma_{ij} = \sum_{kl} C_{ijkl} \epsilon_{kl}$$

(C.1)

where, $i, j, k, l = 1, 2, 3$, $\sigma_{ij}$ is the stress, $\epsilon_{kl}$ is the strain, and $C_{ijkl}$ is the stiffness tensor.

The stiffness tensor is related to the total energy of the crystal by Taylor expansion in terms of the strain components truncated to the second-order,

$$E(V, \epsilon) = E(V_0) + V \sum_\alpha \sigma_\alpha \epsilon_\alpha + \frac{V}{2} \sum_{\alpha\beta} C_{\alpha\beta} \epsilon_\alpha \epsilon_\beta + ...$$

(C.2)

where the Voigt’s notations are used, ($\alpha, \beta = 1, 2, ..., 6$) and $V_0$ is the equilibrium volume. The crystalline structure is assumed to be stress-free. The stiffness moduli are related to the strain second derivatives of the total energy:

$$C_{\alpha\beta} = \left. \frac{1}{V} \frac{\partial^2 E}{\partial \epsilon_\alpha \epsilon_\beta} \right|_0$$

(C.3)

The calculation of elastic constants for an arbitrary crystal then requires the ability to accurately calculate derivatives of the total energy as a function of crystal deformation. For ab-initio methods, this can be done either fully numerically, from total energy curves as a function of the applied strain for different deformations, or from strain first derivatives of the energy. In VASP, IBRION=6 and ISIF\leq3 allows to calculate the elastic constants. The elastic tensor is determined by performing six finite distortions of the lattice and deriving the elastic constants from the strain-stress relationship.
APPENDIX D
MODELING OF RANDOM ALLOYS

D.1 Details for Generating SQS Structures

The disordered alloys in these systems are simulated using special quasirandom structures (SQS), which we have generated with the mcsqs code of the Alloy Theoretic Automated Toolkit (ATAT). To keep calculations efficient, we generate wurtzite SQS unit cell has 32 atoms. The starting lattice constants are those of AlN; the lattice constants and angles will change after the full lattice and ionic relaxation. An example of the variation of the lattice constant with alloy concentration is shown in Figure 3.2 of the Chapter 2. The SQS match the pair correlations of the ideal disordered state up to second nearest neighbor, as well as the triplet correlations at least up to the second nearest neighbor. The key details of the procedure are presented below.

Procedure: Example for 12.5%B and 12.5%Y rest Al Command:

1. corrdump \( l = \text{rndstr.in} \) – \( ro \) – \( noe \) – \( nop \) – \( clus \) – \( 2 = 3.5 \) – \( 3 = 2.5 \)

2. mcsqs \( rc \) – \( n = 32 \)

To execute these commands, two files are necessary: \( \text{rndstr.in} \) (input for random alloys) and \( \text{sqscell.out} \) (instructions for the spatial repetition of the cell). These files have the following content:

\( \text{rndstr.in} \)

3.12858812 3.12858812 5.01695523 90 90 120
1.000000 0.000000 0.000000
0.000000 1.000000 0.000000
0.000000 0.000000 1.000000
0.666667 0.333333 0.499287 Al=0.75, B=0.125, Y=0.125

118
D.2 Dispersion of $e_{33}$ and $C_{33}$ values for different Y concentration

![Graph showing dispersion of $e_{33}$ and $C_{33}$ values](image)

Figure D.1: Calculated $e_{33}$ and $C_{33}$, for each individual SQS and averaged, at each concentration.

At every alloy concentration, all properties (*i.e.* lattice constants, piezoelectric tensor components, elastic tensor component) were calculated for five different SQS structures, and for each property the average between the five SQS calculations was reported. The dispersion of values is a function of the composition. The reason is that there are more possible combinations for, *e.g.*, AlN-YN structures as the YN concentration is increased. As
and example of dispersion, Figure D.1 shows the individual and average values for $e_{33}$ and $C_{33}$ at selected Y concentrations up to 50%.
APPENDIX E
ADDITIONAL SUPPLEMENTARY INFORMATION OF CHAPTER 3

E.1 Variations of $e_{31}$ and $C_{11}$ with Y and B composition

In the main text, we discussed the $e_{33}$ and $C_{33}$ coefficients which are important for thin film bulk acoustic wave resonators (TFBARs) in sensor, transducer, and actuator applications. Piezoelectric materials in the bending mode, *e.g.*, contracting actuators, tube actuators, or bending actuators, the important piezoelectric and stiffness coefficients are $e_{31}$ and $C_{11}$. For completeness, these are plotted in Figure E.1 as a function of the Y concentration, at fixed boron levels.

E.2 Piezoelectric moduli as functions of composition

The piezoelectric moduli are calculated from,

\[ d_{33} = \frac{e_{33}(C_{11} + C_{12}) - 2e_{31}C_{12}}{(C_{11} + C_{12})C_{33} - 2C_{13}^2} \]  
\[ d_{31} = \frac{e_{31}C_{33} - e_{33}C_{13}}{(C_{11} + C_{12})C_{33} - 2C_{13}^2} \]

and are plotted in Figure E.2.
Figure E.1: Piezoelectric coefficient $e_{31}$ and elastic modulus $C_{11}$ as functions of Y and B concentrations.
Figure E.2: Calculated $d_{33}$ and $d_{31}$ surface in yttrium-boron composition space
This chapter contains the supplemental information of Chapter 4.

F.1 Comparison of Experimental and Calculated Piezoelectric Modulus

Using density functional theory, we have calculated longitudinal piezoelectric modulus ($d_{33}$) of well-known piezoelectric compounds. The predicted modulus are found to be in good agreement with experimentally measured values. Since, they are all exist in bulk 3D crystal, standard GGA-PBE exchange correlation functionals have been used for these calculations. Plane wave cutoff energy of 540 eV is used for structural relaxation, calculation of elastic tensors and piezoelectric coefficient tensor. k-point grid, defined by $n_{\text{atoms}} \times n_{\text{kpoints}} \approx 1000$, where $n_{\text{atoms}}$ is number of atoms in the primitive cell and $n_{\text{kpoints}}$ is the number of k-points, is used throughout the calculations. A very high tolerance of $10^{-8}$ eV for energy convergence is used for all three calculations.

![Figure F.1: Calculated $d_{33}$ with GGA functional vs experimentally measured $d_{33}$](image-url)

Figure F.1: Calculated $d_{33}$ with GGA functional vs experimentally measured $d_{33}$
F.2 Axial Anisotropies: \( C \) vs \( e \)

We have investigated all the possible correlations among the axial anisotropies of \( d \), \( e \), and \( C \). In the main text, we have described the axial anisotropy dependence of \( d \) on the axial anisotropies of \( C \) and \( e \). The remaining plot between axial anisotropy of \( C \) and \( e \) is shown in Figure F.2.

\[
\frac{C_{33}}{C_{11}+C_{22}} \quad \text{vs} \quad \frac{e_{33}}{e_{11}+e_{22}}
\]

Figure F.2: Axial anisotropy in \( C \) vs axial anisotropy in \( e \)

F.3 Experimentally Measured Elastic Constants of Quasi-2D Materials

Table F.1: Reference table for Figure 6. The measured values of \( C_{ij} \) are reported in GPa unit

<table>
<thead>
<tr>
<th>Material</th>
<th>SG</th>
<th>( C_{11} )</th>
<th>( C_{12} )</th>
<th>( C_{33} )</th>
<th>( C_{44} )</th>
<th>Technique</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiSe(_2) [227]</td>
<td>164</td>
<td>120</td>
<td>42</td>
<td>39</td>
<td>14.3</td>
<td>Neutron Inelastic Scattering</td>
<td>300K</td>
</tr>
<tr>
<td>Bi(_2)Te(_3) [228]</td>
<td>166</td>
<td>74</td>
<td>-</td>
<td>52</td>
<td>31.35</td>
<td>Wave Resonance Technique</td>
<td>4.2K</td>
</tr>
<tr>
<td>GaSe [229]</td>
<td>187</td>
<td>103</td>
<td>28.9</td>
<td>34.1</td>
<td>9</td>
<td>Brillouin Scattering</td>
<td>300K</td>
</tr>
<tr>
<td>InSe [229]</td>
<td>194</td>
<td>73</td>
<td>27</td>
<td>36</td>
<td>11.7</td>
<td>Brillouin Scattering</td>
<td>300K</td>
</tr>
<tr>
<td>GaS [229]</td>
<td>194</td>
<td>123.3</td>
<td>34.7</td>
<td>38.2</td>
<td>9.96</td>
<td>Brillouin Scattering</td>
<td>300K</td>
</tr>
<tr>
<td>PbI(_2) [230]</td>
<td>166</td>
<td>27.7</td>
<td>9.6</td>
<td>20.2</td>
<td>6.2</td>
<td>Neutron Inelastic Scattering</td>
<td>293K</td>
</tr>
<tr>
<td>BiI(_3) [231]</td>
<td>162</td>
<td>29</td>
<td>5</td>
<td>26</td>
<td>7</td>
<td>Brillouin Scattering</td>
<td>83K</td>
</tr>
<tr>
<td>NiTe(_2) [232]</td>
<td>164</td>
<td>109.5</td>
<td>41.9</td>
<td>52.6</td>
<td>20.4</td>
<td>Neutron Spectrometry</td>
<td>300K</td>
</tr>
<tr>
<td>TaSe(_2) [233]</td>
<td>194</td>
<td>229</td>
<td>36.6</td>
<td>54</td>
<td>18.5</td>
<td>Neutron Spectrometry</td>
<td>300K</td>
</tr>
<tr>
<td>NbSe(_2) [233]</td>
<td>194</td>
<td>194</td>
<td>91</td>
<td>42</td>
<td>17.6</td>
<td>Neutron Spectrometry</td>
<td>300K</td>
</tr>
<tr>
<td>HgI(_2) [234]</td>
<td>137</td>
<td>33</td>
<td>5.6</td>
<td>16.3</td>
<td>7.23</td>
<td>Ultrasound Propagation Technique</td>
<td>293K</td>
</tr>
<tr>
<td>CdI(_2) [235]</td>
<td>164</td>
<td>41.21</td>
<td>16</td>
<td>21.8</td>
<td>18.6</td>
<td>Brillouin Scattering</td>
<td>-</td>
</tr>
<tr>
<td>SnS(_2) [235]</td>
<td>164</td>
<td>124</td>
<td>33</td>
<td>28.9</td>
<td>10.2</td>
<td>Brillouin Scattering</td>
<td>-</td>
</tr>
<tr>
<td>MoS(_2) [236]</td>
<td>194</td>
<td>238</td>
<td>-54</td>
<td>51</td>
<td>21.7</td>
<td>Neutron Inelastic Scattering</td>
<td>308K</td>
</tr>
</tbody>
</table>
Figure F.3: Schematics of the modes of $\mathbf{d}$ with their measuring polarization directions and deformation stresses. Each mode represents each component of $\mathbf{d}$-matrix.
F.5 Rotation of \( d, e, \) and \( C \)-matrices

In our reported 63 quasi-2D piezoelectric materials, we found that in 19 candidates the layer stacking direction is not along \([001]\)-direction. To maintain consistency and capture the effect of van der Waals bond on piezoelectric response, we rotate their \( d, e, \) and \( C \)-matrix into the co-ordinate frame such that the layering direction is always along \([001]\)-direction. The matrix transformation in going from the old to the new coordinate system\([15, 237]\) is,

\[
\begin{pmatrix}
    x_0' \\
    x_1' \\
    x_2' \\
    x_3'
\end{pmatrix} = \begin{pmatrix}
    \cos^{-1} a_{23} \\
    \cos^{-1} a_{21} \\
    \cos^{-1} a_{22}
\end{pmatrix}
\]

Figure F.4: (a) ‘old’ and ‘new’ co-ordinate frames. (b) The angular relations between the axes is specified by drawing up a table of direction cosines which is denoted by \( a \)-matrix

\[
e' = (a)(e)(\alpha^{-1}) \quad (F.1)
\]
\[
d' = (a)(d)(\alpha^{-1}) \quad (F.2)
\]
\[
C' = (\alpha)(C)(\alpha_t) \quad (F.3)
\]

Where, \( a \) is the direction cosine matrix, given by,

\[
\begin{pmatrix}
    a_{11} & a_{12} & a_{13} \\
    a_{21} & a_{22} & a_{23} \\
    a_{31} & a_{32} & a_{33}
\end{pmatrix}
\]

Elements of \( \alpha \) is given by,

\[
\begin{pmatrix}
    (a_{11}^2) & (a_{12}^2) & (a_{13}^2) & (2a_{12}a_{13}) & (2a_{13}a_{11}) & (2a_{11}a_{12}) \\
    (a_{21}^2) & (a_{22}^2) & (a_{23}^2) & (2a_{22}a_{23}) & (2a_{23}a_{21}) & (2a_{21}a_{22}) \\
    (a_{31}^2) & (a_{32}^2) & (a_{33}^2) & (2a_{32}a_{33}) & (2a_{33}a_{31}) & (2a_{31}a_{32}) \\
    (a_{21}a_{31}) & (a_{22}a_{32}) & (a_{23}a_{33}) & (a_{22}a_{33} + (a_{23}a_{32}) & (a_{21}a_{33} + a_{23}a_{31}) & (a_{22}a_{31} + a_{21}a_{32}) \\
    (a_{31}a_{11}) & (a_{32}a_{12}) & (a_{33}a_{13}) & (a_{12}a_{33} + (a_{13}a_{32}) & (a_{13}a_{31} + a_{11}a_{33}) & (a_{12}a_{31} + a_{11}a_{32}) \\
    (a_{11}a_{21}) & (a_{12}a_{22}) & (a_{13}a_{23}) & (a_{12}a_{23} + (a_{13}a_{22}) & (a_{13}a_{21} + a_{11}a_{23}) & (a_{12}a_{21} + a_{11}a_{22})
\end{pmatrix}
\]
For detail derivation of these transformations please see reference [15, 237].
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To: Sukriti Manna <smanna@mymail.mines.edu>, Cristian Ciobanu <cciobanu@mines.edu>, Geoff Brennecka <gbrennec@mines.edu>

I, Vladan Stevanovic, hereby authorize Sukriti Manna to use any part or all of the article entitled "Tuning the piezoelectric and mechanical properties of the AlN system via alloying with YN and BN" published in Journal of Applied Physics (https://doi.org/10.1063/1.4993254) in his published dissertation.

Best,

Vladan

From: Sukriti Manna <smanna@mymail.mines.edu>
Date: Monday, July 23, 2018 at 12:23 PM
To: Cristian Ciobanu <cciobanu@mines.edu>, Vladan Stevanovic <vstevano@mines.edu>, Geoff
I, Cristian Ciobanu, hereby authorize Sukriti Manna to use any part or all of the article entitled “Tuning the piezoelectric and mechanical properties of the AlN system via alloying with YN and BN” published in Journal of Applied Physics (https://doi.org/10.1063/1.4993254) in his published dissertation.
Sukriti Manna <smanna@mymail.mines.edu>

Permission to Reuse Submitted JMCC paper for Dissertation

5 messages

Sukriti Manna <smanna@mymail.mines.edu> Mon, Jul 23, 2018 at 12:25 PM
To: Prashun Gorai <prashun.itm4@gmail.com>, Geoff Brennecka <gbrennec@mines.edu>, cciobanu <cciobanu@mines.edu>, Vladan Stevanovic <vstevano@mines.edu>

Dear All,

I am uploading my Ph.D. thesis, and the graduate school requires the permissions from co-authors on a published paper that used in the thesis. Could you please reply to this email with your permissions on our paper "Large Piezoelectric Response of van der Waals Layered Solids" submitted to Journal of Materials Chemistry C?

Please use this specific wording for the permission:

It will be great if I can get your permissions by today or as soon as possible. Thank you so much for helping.

Sukriti

Geoff Brennecka <gbrennec@mines.edu> Mon, Jul 23, 2018 at 12:51 PM
To: Sukriti Manna <smanna@mymail.mines.edu>


Vladan Stevanovic <vstevano@mines.edu> Mon, Jul 23, 2018 at 12:51 PM
To: Sukriti Manna <smanna@mymail.mines.edu>, Prashun Gorai <prashun.itm4@gmail.com>, Geoff Brennecka <gbrennec@mines.edu>, Cristian Ciobanu <cciobanu@mines.edu>

Hi Sukriti,


Best,

Vladan

From: Sukriti Manna <smanna@mymail.mines.edu>
Date: Monday, July 23, 2018 at 12:26 PM
Prashun Gorai <prashun.iitm4@gmail.com>  
To: Sukriti Manna <smanna@mymail.mines.edu>  

Mon, Jul 23, 2018 at 1:03 PM


[Quoted text hidden]

Cristian Ciobanu <cciobanu@mines.edu>  
To: Vladan Stevanovic <vstevano@mines.edu>, Sukriti Manna <smanna@mymail.mines.edu>  

Mon, Jul 23, 2018 at 10:40 PM


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Cristian V. Ciobanu, PhD  
Fellow of the Institute of Physics (UK)  
Professor, Dept of Mechanical Engineering  
and Materials Science Program  
Colorado School of Mines  
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