THE ROLE OF IMPURITIES, LIF, AND PROCESSING ON THE SINTERING, MICROSTRUCTURE, AND OPTICAL PROPERTIES OF TRANSPARENT POLYCRYSTALLINE MAGNESIUM ALUMINATE (MgAl₂O₄) SPINEL

by

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Transparent polycrystalline magnesium aluminate (MgAl$_2$O$_4$) spinel has an exceptional combination of properties that is well-suited to fulfill demanding optical applications that few other materials can satisfy. However, spinel is inherently difficult to densify due to high defect formation energies, variable stoichiometry, and extreme sensitivity to powder and processing parameters. In addition, the LiF sintering additive typically required to impart transparency degrades optical and mechanical properties, precluding wider application. Furthermore, there remains a fundamental lack of understanding of the processing-structure-property relationships required to obtain high transparency and good mechanical properties.

In this work, hot-press experiments were designed to determine the role of impurities and LiF and the key variables required to obtain transparent spinel. Hot-pressed compacts were characterized with electron microscopy, chemical spectroscopy, and spectrophotometry, and impurities present in parts-per-million in starting powders were found to cause restricted grain size and opacity. LiF addition was found to reduce the content of some impurities by one order of magnitude, counteract absorption, and impart transparency, but also to cause grain coarsening, grain-boundary embrittlement, and scatter. Thermal analysis and residual gas analysis of prepared powders in combination with thermodynamic modeling demonstrated for the first time the specific mechanism by which LiF acts as a cleanser. LiF reacts with impurities to form volatile fluorides, and the temperature at which pressure is applied during hot-pressing determines the extent to which compact-scale differential sintering either traps LiF and volatile fluorides or allows their removal, the latter enabling transparency. The main cause of absorption in hot-pressed spinel compacts was found to be carbon contamination from graphitic hot-press components and it could be completely eliminated with proper shielding. Hot-press experiments with Al$_2$O$_3$, lithium, and fluorine additives, along with thermodynamic simulations and spectrophotometry indicated that aluminum oxy-carbides were likely partly responsible for absorption and that lithium was likely responsible for counteracting absorption.

Dilatometry was conducted to study the effect of processing variables, and for the first time of neutron irradiation of starting powders, on the sintering behavior of cold-pressed powder
comacts. Green-body density, stoichiometry, and impurities had the greatest effect on densification, whereas powder neutron irradiation and reducing atmosphere had small, but non-negligible effects. Dilatometry in combination with sintering experiments demonstrated that LiF coarsens crystallites by vapor and likely surface transport. Although these mechanisms do not contribute to densification, when combined with high grain-boundary transport and pressure, enhanced densification takes place. Dilatometry also demonstrated that transparent compacts could be fabricated by pressureless sintering. Pressureless field-assisted sintering of spinel was also demonstrated for the first time, producing translucent compacts with fine grain size.

Electrochemical impedance spectroscopy, secondary-ion mass spectroscopy, and Raman spectroscopy, in combination with characterization by electron microscopy, were used to relate the dielectric properties of hot-pressed spinel compacts to microstructure. This was the first study to characterize the conductivity of fully-dense, transparent polycrystalline spinel compacts. The higher conductivity of polycrystalline spinel compacts compared to single crystals was attributed to increased conductance from impurities at grain boundaries parallel to the applied field. The lower conductivity of compacts with LiF addition compared to those without LiF addition was attributed to larger grain size and lower impurity content. Compacts with LiF addition exhibited distinct bulk and grain boundary impedances and the uniform distribution of lithium in the bulk was postulated to lower bulk conductivity compared to compacts without LiF addition.
# TABLE OF CONTENTS

ABSTRACT ........................................................................................................................................... iii

LIST OF FIGURES ............................................................................................................................. ix

LIST OF TABLES .................................................................................................................................. xvii

ACKNOWLEDGEMENTS .................................................................................................................... xviii

CHAPTER 1 INTRODUCTION .............................................................................................................. 1

1.1. Material Background .................................................................................................................. 1

1.2. Motivation ................................................................................................................................... 2

1.3. Objectives ................................................................................................................................... 2

1.4. Structure of Thesis ..................................................................................................................... 3

REFERENCES CITED .......................................................................................................................... 4

CHAPTER 2 EXPERIMENTAL METHODS .......................................................................................... 6

2.1. Powder Characterization ......................................................................................................... 6

2.2. Powder Treatment .................................................................................................................... 8

2.3. STA-MS Experiments .............................................................................................................. 9

2.4. Thermodynamic Simulations ................................................................................................... 9

2.5. Dilatometry Experiments ....................................................................................................... 10

2.6. Hot Press Experiments .......................................................................................................... 14

2.7. Pressureless Sintering, Hot Isostatic Press, Quenching, and Single-Crystal Experiments .......... 18

2.8. Field-Assisted Sintering .......................................................................................................... 19

2.9. Grain boundary grooving experiments ............................................................................... 20

3.0. EIS Experiments .................................................................................................................... 20

3.1. Compact Characterization ....................................................................................................... 24

REFERENCES CITED ........................................................................................................................ 29
CHAPTER 3 ..... 50 Years of Research and Development Coming to Fruition; Unraveling the Complex Interactions during Processing of Transparent Magnesium Aluminate (MgAl\textsubscript{2}O\textsubscript{4}) Spinel .......................................................... 31

3.1. Introduction .................................................................................. 32

3.2. Background .................................................................................. 35

3.2.1 Thermodynamics ........................................................................ 35

3.2.2. Crystal Structure and Defects ....................................................... 37

3.2.3. Diffusion ...................................................................................... 41

3.2.4. Optical Properties ....................................................................... 42

3.2.5. Mechanical Properties ................................................................. 45

3.2.6. Physical Requirements ................................................................. 46

3.3. Key Variables ................................................................................ 47

3.4. Particle-Size Characteristics ............................................................ 49

3.4.1. Synthesis ...................................................................................... 49

3.4.2. Green Body Formation ................................................................ 50

3.4.3. Particle-Size, Size Distribution, and Agglomeration ...................... 51

3.4.4. Microstructure Evolution ............................................................... 52

3.5. Stoichiometry .................................................................................. 54

3.5.1. Stoichiometry Gradients ............................................................... 55

Sidebar 1: Defect Chemistry and Grain-Boundary Mobility: ....................... 56

3.5.2. Grain Growth ............................................................................... 59

3.5.3. Densification ............................................................................... 59

3.6. Impurities & Additives .................................................................... 60

3.6.1. Impurities .................................................................................... 60

3.6.2. Sintering Additives ...................................................................... 62

Sidebar 2: Electronic Impedance Spectroscopy – Assessing Defect Chemistry: 67
<table>
<thead>
<tr>
<th>Fig.</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1.</td>
<td>STA-MS apparatus</td>
<td>10</td>
</tr>
<tr>
<td>2.2.</td>
<td>Netzsch 402C Dilatometer</td>
<td>11</td>
</tr>
<tr>
<td>2.3.</td>
<td>Schematic of anisotropic shrinkage of thickness ($L$) and diameter ($\Phi$) as a function of temperature ($T$).</td>
<td>14</td>
</tr>
<tr>
<td>2.4.</td>
<td>Graphite (a) and Al$_2$O$_3$ (b) hot-press die setups.</td>
<td>15</td>
</tr>
<tr>
<td>2.5.</td>
<td>Hot press, shown with residual gas analyzer (RGA) hooked up. RGA analysis in the hot press was not successful due to outgassing from the graphite insulation.</td>
<td>15</td>
</tr>
<tr>
<td>2.6.</td>
<td>Standard hot press regime including ramp at 6°C/min. to 1550°C with 1 h hold at 400°C, 0.25 h hold at 1200°C, 1 h hold at 1550°C, application of 35 MPa at 1200°C and removal at 900°C. Modified regime with pressure applied at 900°C shown by dashed line.</td>
<td>16</td>
</tr>
<tr>
<td>2.7.</td>
<td>Field-assisted sintering using; (a) cylindrical specimen and (b) dog-bone specimen.</td>
<td>20</td>
</tr>
<tr>
<td>2.8.</td>
<td>EIS apparatus.</td>
<td>22</td>
</tr>
<tr>
<td>3.1.</td>
<td>Select applications and transparent spinel components, reproduced with permission.</td>
<td>34</td>
</tr>
<tr>
<td>3.2.</td>
<td>Spinel phase diagram, adapted with permission.</td>
<td>36</td>
</tr>
<tr>
<td>3.3.</td>
<td>Spinel volatility diagram, $p_x$ refers to the partial pressures of species formed during reduction, adapted with permission.</td>
<td>37</td>
</tr>
<tr>
<td>3.4.</td>
<td>(a) Unit cell of spinel depicting symmetry (shaded) and octahedral and tetrahedral interstices and (b) perspective of the close-packed structure.</td>
<td>38</td>
</tr>
<tr>
<td>3.5.</td>
<td>Kroger-Vink notation and schematic of point defects in spinel.</td>
<td>38</td>
</tr>
<tr>
<td>3.6.</td>
<td>Diffusion coefficients for spinel species, adapted with permission.</td>
<td>41</td>
</tr>
<tr>
<td>3.7.</td>
<td>Typical transmission spectrum for transparent polycrystalline spinel.</td>
<td>42</td>
</tr>
<tr>
<td>3.8.</td>
<td>Light transmission through a polycrystalline spinel compact.</td>
<td>43</td>
</tr>
<tr>
<td>3.9.</td>
<td>(a) Nano-pores at triple junctions in HIP spinel compact (arrows, TEM-brightfield) and (b) intra-crystalline pores in HIP spinel compact (arrows, TEM-darkfield).</td>
<td>44</td>
</tr>
</tbody>
</table>
Fig. 3.10 Calculated transmittance versus pore diameter for spinel (t = 1 mm, 0.01% porosity), adapted with permission.

Fig. 3.11 Scattering centers in transparent spinel compacts; (a) impurity-rich (Fe,Ni, S) phases in compact HP with high-purity powder (arrows), (b) micro-cracked grain boundaries in reactive-sintered HP/HP compact (bright areas, arrows), reproduced with permission.

Fig. 3.12 Fracture surfaces of spinel showing mixed-mode inter- and trans-granular fracture for (a) HP lower-purity powder and (b) HP higher-purity powder, without additives. With LiF addition, fracture becomes predominantly inter-granular.

Fig. 3.13 Fabrication and Key Variables.

Fig. 3.14 Green bodies made from two different powders/processing, diamonds (pink) represent impurities or additives: (GB1) fine, narrow particle-size distribution leading to narrow pore-size distribution, and (GB2) agglomerated, wide particle-size distribution leading to wide pore-size distribution, large inter-agglomerate pores, and inhomogeneous additive dispersal.

Fig. 3.15 Agglomerates in (a) synthesized sulfate-derived powder, (b) commercial sulfate-derived powder.

Fig. 3.16 (a) Optical microscopy image of microstructure of 2 mm thick HP stoichiometric spinel compact, and (b) similarly processed compact, but 4 mm thick and with pressure applied at a lower temperature.

Fig. 3.17 (a) MgO precipitates (arrows) in \( x \approx 0.995 \) HP compact and (b) \( Al_2O_3 \) precipitates (arrows) and \( Al_2O_3 \)-rich grain boundaries in HP/HP compact, reproduced with permission.

Fig. 3.18 Composite SEM cross-section of pressureless-sintered stoichiometric spinel compacts, reproduced with permission.

Fig. 3.19 (a) Atomic concentration versus distance from grain boundary in \( x = 1.05 \) PS/HP spinel compact (adapted with permission), (b) schematic of MgO-depleted grain boundaries.

Fig. 3.20 (a) Brouwer diagram and (b) log grain-boundary mobility versus stoichiometry; adapted from Ting & Lu, Chiang & Kingery, and Uematsu et al. with permission.

Fig. 3.21 Compact density as a function of time for pressureless-sintered compacts with various stoichiometries (0.8 > \( x \) > 1.5), adapted with permission.
Fig. 3.22 Impurity phases causing opacity in 2 mm thick compact (inset) HP with high-purity spinel powder; (a) amorphous impurity (C,S,K) phase at grain boundary and (b) decorated grain boundary. (c) Amorphous phase at triple junction in HIP compact ................................................................. 61

Fig. 3.23 Hot-pressed spinel/LiF/spinel sandwich structure and highly-defected grains revealed by etching ................................................................. 63

Fig. 3.24 HIP spinel compact with LiF; (a) Fluorine-rich xenomorphic grain (TEM-brightfield) and (b) coffee-bean contrast (arrow, STEM-ABF), possibly indicating oxygen vacancies ................................................................. 63

Fig. 3.25 Log-log plot of grain-size change versus time for air-sintered spinel powders with 1 wt. % LiF at 1000°C, 1100°C, and 1200°C, SEM images of air-sintered spinel powders (a) without LiF and (b) with LiF (I.E. Reimanis, Unpublished Work) ................................................................. 65

Fig. 3.26 Optical defects due to LiF (a) decorated grain boundaries, (b) remnant liquid phase at grain boundaries, (c) amorphous phase at triple-junctions (TEM), (d) typical mottled-contrast magnesium- and fluorine-rich phase at triple-junction (TEM) ................................................................. 66

Fig. 3.27 Fracture behavior in PS high-purity spinel compacts with (a) no LiF 1650°C 10 hrs. (SEM), 1 wt. % LiF 1650°C 10 hrs (SEM) (I.E. Reimanis, Unpublished Work) ................................................................. 66

Fig. 3.28 Typical microstructures observed in translucent or transparent spinel; (a) HP/HP, (b) HP/HP with LiF, (c) SPS, (d) SPS with LiF, (e) HP, (f) HP with LiF, optical and SEM micrographs, reproduced with permission ................................................................. 67

Fig. 3.29 (a) Electronic impedance spectroscopy Nyquist plot for spinel compacts at 850°C with and without LiF, and (b) activation energies for conductivity .............. 68

Fig. 3.30 Dislocations in a HP stoichiometric spinel compact, adapted with permission .... 70

Fig. 3.31 SEM fracture surface of pressureless field-assisted sintered (a) opaque lower-purity compact with 1 wt.% LiF and 5 wt.% PVA, (b) translucent high-purity compact with 5 wt.% PEG, pores shown by arrows ................................................................. 72

Fig. 3.32 (a) Absorption as a function of processing in high-purity HP spinel compacts .... 74

Fig. 3.33 Increased absorption in SPS compacts with; (a) increasing heating rate, (b) sintering temperature, (c) temperature of pressure application, and (d) applied pressure ................................................................. 74

Fig. 3.34 (a) Carbon-rich phase at triple junction in spinel compact, (b) HRTEM image of Graphitic carbon at triple junction in spinel compact ................................................................. 75
Fig. 4.1 Hot press regimes and compacts (*LP compacts 1 wt% LiF, HP compact 0.25 wt% LiF). .............................................................. 103

Fig. 4.2 OM images and average grain size for compacts hot pressed with pressure applied at 1200°C; (a) LP without LiF, (b) HP without LiF, (c) LP with 1 wt% LiF, (d) HP with 0.25 wt% LiF. ........................................ 106

Fig. 4.3 OM images and average grain size for LP powder with 1 wt% LiF hot pressed with 1.5 g of powder and pressure applied at (a) 1200°C and (b) 900°C, and with 3.5 g of powder and pressure applied at (c) 1200°C and (d) 900°C. ........................................................................................................... 107

Fig. 4.4 % transmission vs. wavelength from 200 nm to 750 nm for compacts hot pressed with pressure applied at 1200°C and 1.5 g of (a) LP powder without LiF, (b) LP powder with 1 wt% LiF, (c) HP powder without LiF........................................ 108

Fig. 4.5 SEM images of fracture surface of compact hot pressed with 1.5 g of LP powder without LiF with pressure applied at 1200°C; (a) transgranular matrix grain fracture, (b) submicrometer grains. .................................................. 109

Fig. 4.6 TEM images of compact hot pressed with 1.5 g of LP powder without LiF and pressure applied at 1200°C; (a) submicrometer grains, (b) amorphous phase at interface between submicrometer and matrix grains, (c) amorphous phase at triple junction, (d) dark-contrast grain boundary phase in submicrometer grains, (e) dark-contrast grain boundary phase, (f) matrix grain boundary. ................................................................................................. 109

Fig. 4.7 SEM images of fracture surface of compact hot pressed with 1.5 g of LP powder with 1 wt% LiF and pressure applied at 1200°C; (a) matrix grains, (b) aggregates of smaller grains, (c), (d) second phases in aggregates of smaller grains, (e) TEM of matrix grain boundary.......................................................... 110

Fig. 4.8 TEM images of compact hot pressed with LP powder with 1 wt% LiF and pressure applied at 900°C; (a) F-rich phase at matrix grain triple junction, (b) matrix grain boundary, (c) strain at matrix grain boundary........................................ 111

Fig. 4.9 SEM fracture surface images for compacts hot pressed with pressure applied at 1200°C and (a) HP powder without LiF, Fe-rich phase (inset), (b) HP powder with 0.25 wt% LiF, TEM image of MgO nodule (inset). ..................... 111

Fig. 4.10 STA-MS results for masses 32, 48, and 64 for (a) LP powder with 1 wt% LiF in argon, and (b) LP powder without LiF in argon. .......................................................... 111

Fig. 5.1 Nyquist plot for an equivalent circuit (inset) representing an electrode and polycrystalline solid. Z is the complex impedance, $\omega$ is angular frequency, $R$ is resistance, $C$ is capacitance, subscript ‘e’ refers to electrode, ‘b’ to bulk, and ‘gb’ to grain boundaries. .................................................................................. 126
Fig. 5.2 Microstructure of compacts HP with sulfate-derived powder without LiF. (a) SEM fracture surface (average matrix grain size 12 µm), arrows show areas of sub-micron grains, note trans-granular fracture (inset: compact images). (b) Areas of sub-micron grains constituting ~5 vol.%. (c) TEM image of sub-micron grains, arrows show location of amorphous impurity phase shown in (d). (e) TEM image of impurity phase decorating a sub-micron grain. Reprinted with permission from Ref. [7] .................................................. 130

Fig. 5.3 Microstructure of HP sulfate-derived powder compacts with 1 wt% LiF. (a) SEM fracture surface (GS ≈ 25 µm), arrows show areas of smaller grains, note inter-granular fracture (inset: compact image). (b) SEM image of micron-sized grain areas constituting < 1 vol%. (c) SEM image of impurity-rich phases. (d) TEM image of typical grain boundary devoid of amorphous phases but with higher impurity content. Reprinted with permission from Ref. [7] .................................................. 131

Fig. 5.4 SIMS results for compacts HP with sulfate-derived powder. (a) Lithium map (50 µm x 50 µm) on a compact without LiF. (b) Lithium map (25 µm x 25 µm) on a compact HP with 1 wt% LiF and pressure applied at 900°C (similar results with lower lithium content were obtained when pressure was applied at 1100°C). (c) Li depth profile for sample without LiF and two samples with 1 wt% LiF showing relatively constant lithium concentration with depth. 131

Fig. 5.5 Microstructure of HP flame-spray pyrolysis derived powder compact. (a) SEM image of fracture surface (average grain size 4 µm) arrows show location of MgO nodules at grain surface (inset: image of compact). (b) TEM image of MgO nodule.................................................. 132

Fig. 5.6 EIS spectra for the dark-colored HP sulfate-derived powder compact without additives. Insets: high-frequency region and image of compact and sample with electrode (note smaller electrode).................................................. 133

Fig. 5.7 EIS spectra for the cream-colored HP sulfate-derived powder compact without additives. Inset: high-frequency region, image of compact and of sample with electrode. .................................................. 133

Fig. 5.8 EIS spectra for the transparent HP sulfate-derived powder compact with 1 wt. % LiF addition. Inset: high-frequency region, image of compact and of sample with electrode. .................................................. 133

Fig. 5.9 Comparison of EIS spectra for sulfate-derived powder compacts at 850°C. Resistance differences in the high-frequency bulk arcs are due in part to electrode geometry differences. Solid lines are equivalent circuit (inset) simulations using ZView®. .................................................. 134

Fig. 5.10 Arrhenius plots and activation energies for conductivity for sulfate-derived powder samples.................................................. 134
Fig. 5.11  EIS spectrum for the transparent HP flame-spray pyrolysis-derived powder compact without LiF addition at 850°C. EIS spectra for sulfate-derived powder compacts at 850°C shown for comparison. ........................................ 134

Fig. 6.1   SEM image of Baikowski powder (a) agglomerates and (b) individual crystallites. .............................................................................. 145

Fig. 6.2   (a) Brightfield TEM image of (a) Baikowski powder crystallites, (b) High-resolution TEM (HR-TEM) image of Baikowski powder crystallite, (c) Nanocerox powder crystallites, (d) HR-TEM image of Nanocerox powder crystallites. .............................................................................. 146

Fig. 6.3   HR-TEM image of sinter-necks in as-received Nanocerox powder. ....................... 146

Fig. 6.4   Indexed electron-diffraction ring-patterns for (a) Baikowski powder and (b) Nanocerox powder. .......................................................... 147

Fig. 6.5   SEM image of Baikowski powder mixed with 1 wt% LiF. ................................ 147

Fig. 6.6   STA-MS results for empty crucible calibration in argon at 10K/min. TGA mass loss scaled to primary vertical axis, MS pressures not corrected, and only m/z with significant signals shown. Note convex endothermic rise >550°C, relatively constant water vapor signals, and m/z = 20 increase >1300°C. .............................................................................. 148

Fig. 6.7   STA-MS results for pure LiF. Mass loss has been scaled to fit on the graph. Note melting endotherm at 850°C, vaporization endotherm between 1000°C and 1400°C concomitant with complete mass loss. ................................................ 149

Fig. 6.8   STA-MS results for Nanocerox powder in argon at 10K/min. TGA mass loss scaled to primary vertical axis, MS pressures not corrected, and only m/z with significant signals shown. Note concave endothermic rise >1300°C, higher water vapor signals, organics outgassing <800°C, and m/z = 32 increase >1300°C. ............................................................................... 151

Fig. 6.9   STA-MS results for Baikowski powder in argon at 5K/min. shown to 1300°C. TGA mass loss below detection sensitivity limit, MS pressures not corrected, and only m/z with significant signals shown. Note concave endothermic rise >1100°C, water evaporation especially at lower temperatures and CO$_2$ from organics. ......................................................... 151

Fig. 6.10  STA-MS results for Baikowski powder with 1 wt% LiF in argon at 5K/min. MS pressures not corrected, and only m/z with significant signals shown. The choppy TGA curve was due to instrument sensitivity when disturbed by a person walking in the room. Note the small endotherms between 1000°C and 1200°C, sulfur species outgassing not visible with this scale. ....................... 153
STA-MS results for Baikowski powder with 10 wt% LiF. Mass loss has been scaled to fit on the graph. Note the smaller LiF melting endotherm at 850°C and prominent vaporization endotherm between 1000°C and 1400°C.

HSC equilibrium composition simulation diagram for MgAl\(_2\)O\(_4\) (not shown) and LiF in air.

HSC equilibrium composition simulation diagram for equal amounts of MgAl\(_2\)O\(_4\) and LiF in vacuum.

HSC equilibrium composition simulation diagram for MgSO\(_4\), Al\(_2\)(SO\(_4\))\(_3\), and LiF in vacuum (O\(_2\) not shown).

HSC equilibrium composition simulation diagram for MgAl\(_2\)O\(_4\) and carbon in vacuum.

Fractional sintered density relative to theoretical as a function of temperature for cold-pressed Baikowski and Nanocerox samples.

HP Baikowski powder compacts, samples 10 mm above template, transparent compacts in bold font. Standard processing conditions (Std.) consisted of ramping temperature at 6°C/min. to 1550°C, a 15 min. hold at 1200°C followed by application of 35 MPa, and incorporation of additives by ultrasonic mixing (U.S. Mix) and rotary evaporation (Ac. Mix = acoustic mixing). Compacts HP in 12.7 mm dies with 1.5 g of powder were ~2 mm thick and with 3.5 g ~5 mm thick, and compacts HP in 25.4 mm dies with 6 g of powder were ~2 mm thick. Compacts HP in 38.4 mm dies were opaque and are not shown.

Nanocerox powder compacts. Compacts are 12.7 mm in diameter, 2 mm thick, and 10 mm above template. Standard processing conditions (Std.) consisted of hot pressing 1.5 g of powder at 6°C/min. to 1550°C, holding at 1200°C for 0.25 h followed by application of 35 MPa. Add scale, size same as Baikowski compacts. Optimal conditions consisted of using molybdenum foil, insulated spacers, 0.05 wt% LiF, applying pressure at 900°C, and a maximum sintering temperature of 1400°C.

Displacement versus temperature corrected for thermal expansion and pressure strain (subtraction of calibration run) during hot pressing for 1.5 g Baikowski powder with 1 wt% LiF using the standard run (note displacement is negative as it indicates shrinkage).

Pressure and thermal expansion corrected fractional theoretical sintered density versus temperature for the same conditions as Fig. 6.19, 1.5 g Baikowski powder with 1 wt% LiF using the standard run.

Displacement versus temperature corrected for thermal expansion and pressure strain during hot pressing of 3.5 g Baikowski powder with 1 wt% LiF using the standard run.
LiF with pressure applied at 900°C instead of 1200°C (note displacement is negative as it indicates shrinkage) .......................................................... 163

Fig. 6.22 Pressure and thermal expansion corrected fractional theoretical sintered density for the same conditions as Fig. 6.21, 3.5 g Baikowski powder with 1 wt% LiF with pressure applied at 1200°C ........................................... 163

Fig. 6.23 Raman spectra for (a) a spinel single crystal and compacts hot pressed with Baikowski powder with 1 wt% LiF and with Nanocerox powder, and (b) compacts hot-pressed with Baikowski powder with and without 1 wt% LiF .......................................................... 164

Fig. 6.24 SEM images of fracture surfaces for; (a) HP compact with Baikowski powder with 1 wt% LiF, (b) after quenching, (c) HP Nanocerox compact with 0.25 wt% LiF, (d) after quenching .......................................................... 166

Fig. 6.25 (a) FIB sample from compact HP with Baikowski powder without additives viewed along the [011] zone axis (insets), (b) CBED in grain showing FOLZ, (c) CBED at grain boundary, (d) FIB sample from compact HP with Baikowski powder with 1 wt% LiF viewed along the [001] zone axis, (e) CBED pattern in grain, (f) CBED pattern at grain boundary .......................................................... 166

Fig. 6.26 AFM surface maps for compacts HP with (a) Baikowski powder and (b) Baikowski powder with 1 wt% LiF (20 µm x 20 µm, vertical scale 180 nm per division) .......................................................... 167

Fig. 6.27 SEM fracture surface images of FAST (a) and (b) dog-bone specimen with Baikowski powder with 5 wt% PVA (grain size ~5 µm, pores indicated by arrows), (c) and (d) dog-bone specimen with Nanocerox powder with 5 wt% PEG (grain size ~1 µm, pores indicated by arrows) .......................................................... 168
## LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Table 2.1</td>
<td>Dilatometry Conditions</td>
<td>11</td>
</tr>
<tr>
<td>Table 2.2</td>
<td>Variation of Processing Parameters</td>
<td>17</td>
</tr>
<tr>
<td>Table 3.1</td>
<td>Structure of Paper</td>
<td>32</td>
</tr>
<tr>
<td>Table 3.2</td>
<td>Calculated Point Defect Formation Energies and Diffusion Barriers</td>
<td>40</td>
</tr>
<tr>
<td>Table 3.3</td>
<td>Physical Properties of Transparent Polycrystalline Spinel Compacts</td>
<td>47</td>
</tr>
<tr>
<td>Table 3.4</td>
<td>Transparent Spinel Processing and Properties</td>
<td>77</td>
</tr>
<tr>
<td>Table 4.1</td>
<td>Typical Properties for LP and HP Spinel Powders</td>
<td>101</td>
</tr>
<tr>
<td>Table 4.2</td>
<td>LA ICP-OES/MS Results from Geometric Center and Exterior Surface of LP Compacts Hot Pressed with 3.5 g of Powder with and without LiF and with Pressure Applied at 1200°C</td>
<td>114</td>
</tr>
<tr>
<td>Table 5.1</td>
<td>Selected dielectric properties of polycrystalline samples HP under different conditions</td>
<td>135</td>
</tr>
<tr>
<td>Table 6.1</td>
<td>Effect of Cleaning Treatments on Baikowski Powders</td>
<td>144</td>
</tr>
<tr>
<td>Table 6.2</td>
<td>Powder Size Characteristics</td>
<td>147</td>
</tr>
<tr>
<td>Table 6.3</td>
<td>Dilatometry Results</td>
<td>158</td>
</tr>
<tr>
<td>Table 6.4</td>
<td>Grain boundary grooving results</td>
<td>167</td>
</tr>
</tbody>
</table>
ACKNOWLEDGMENTS

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CHAPTER 1
INTRODUCTION

There has been a renewed interest in ceramics as advances in understanding, powder synthesis, and processing have overcome some of their limitations, most notably their brittle nature. Transparent polycrystalline ceramics are a new development that has engendered considerable interest for optical applications that only few materials can satisfy. Polycrystalline magnesium aluminate spinel (spinel) is one exceptionally well-suited ceramic for applications requiring transparency from the visible to the infra-red in combination with low density, high-hardness and strength, chemical resistance, and excellent thermal properties. However, spinel is inherently difficult to sinter due to high defect formation energies, variable stoichiometry, and sensitivity to processing parameters. Despite over 50 years of research and development, there remains a fundamental lack of understanding of the processing-structure-property relationships. Although technological advances have recently enabled the production of large transparent components, reliability has been problematic and mechanical and optical properties have been below requirements for many potential applications. Small amounts of impurities are thought to degrade optical properties, and the LiF sintering additive typically required to impart transparency embrittles grain boundaries and causes scatter at short wavelengths. In addition, the effects of variable stoichiometry are still not well-understood. A greater understanding of the material and processing variables and their interactions during the entirety of processing, especially during green-body formation and sintering, at scales ranging from the compact to the atomic, is required for spinel to find wider application.

1.1. Material Background

Magnesium aluminate spinel (MgAl$_2$O$_4$) is a naturally-occurring, cubic, often twinned gemstone with octahedral habit.\(^1\) It is transparent to opaque and exhibits various colors, most notably red due to chromium impurity.\(^1\) Spinel with the general chemical formula (Mg,Fe)(Al,Cr)$_2$O$_4$ is a common constituent of peridotite, the main mineral constituting the Earth’s upper mantle.\(^2\) The spinel structure is the prototype of the larger spinel group, with formula unit $AB_2X_4$, where $A$ and $B$ are cations with net charges of +2 and +3, respectively, and $X$
is an anion with a net charge of -2. A wide range of cations, including aliovalent substitutions, can occupy the A and B positions, with iron (Fe$^{2+}$ and Fe$^{3+}$) occupying both in magnetite (Fe$_3$O$_4$). The X anion is typically oxygen, but can also be sulfur or other aliovalent substitutions. This wide variety of elemental substitutions leads to a wide range of minerals and compounds with the spinel structure.

S
Spinel was first accidentally synthesized in the mid-18th century, but polycrystalline spinel only found commercial use starting in the 1960’s, mainly as refractory brick material for the steel-making industry, with limited use in applications such as anode materials and catalyst supports. Transparent polycrystalline spinel was first fabricated by The General Electric Corp. in the 1960’s. It was used sporadically on a small scale in specialty military applications in the following decades and only recently became commercially available. It has since garnered interest for a wide range of applications due to its excellent optical properties and good mechanical, chemical, and thermal properties. A comprehensive background on transparent spinel is provided in Chapter 3.

1.2. Motivation

The research was motivated by the desire to produce larger, thicker, less expensive spinel components with better mechanical and optical properties. The goal was to identify and understand the key processing-structure-property relationships in the fabrication of transparent spinel. In particular, it was sought to better understand the role and effect of impurities and LiF sintering additive on microstructure and optical properties.

1.3. Objectives

Research objectives included:

- Understanding why certain processing parameters resulted in transparency.
- Determining the role of impurities, stoichiometry, pressure, and sintering atmosphere, and the effect of neutron irradiation of starting powders on densification, microstructure, and optical properties.
- Determining the specific mechanisms by which LiF enhances sintering, counteracts absorption, and enables transparency.
- Determining the causes of absorption.
- Determining if pressureless sintering without additives was possible.

Attention was paid to identifying relationships between variables during the entirety of processing and identifying effects spanning from the compact to the atomic scale. Key experiments were designed, a variety of characterization techniques were used, and results correlated to explain the fundamental mechanisms occurring during the fabrication of transparent spinel.

1.4. Structure of Thesis

This thesis is a subset of work conducted and defended at both the Colorado School of Mines and the Technische Universität Darmstadt and has not previously been published, except for chapters 3 and 4, which were published in peer reviewed journals. A different dissertation is concurrently submitted at the Technische Universität Darmstadt and the work in chapters 3, 4, 5, and parts of chapters 2 and 6 are contributions unique to the Colorado School of Mines thesis.

The thesis is structured in eight chapters and an appendix:

1. Chapter 1 is an introduction consisting of a brief background, the motivation for the research, and the goals and objectives.
2. Chapter 2 discusses the experimental program.
3. Chapter 3 consists of the work titled “50 Years of Research and Development Coming to Fruition; Understanding the Complex Interactions during Processing of Transparent Magnesium Aluminate (MgAl$_2$O$_4$) Spinel”, published as an invited feature article in the Journal of the American Ceramic Society. It serves as a detailed introduction to transparent spinel and also ties together complexities of the fabrication of transparent spinel not previously realized.
4. Chapter 4 consists of the work titled “The Role of LiF and Impurities in the Sintering and Optical Properties of Transparent Polycrystalline MgAl$_2$O$_4$ Spinel”, published in the International Journal of Applied Ceramic Technology. This chapter discusses the research related to chemical interactions between LiF, impurities, and spinel.
5. Chapter 5 consists of the work titled “Electrochemical Impedance Spectroscopy of Transparent Polycrystalline MgAl$_2$O$_4$ Spinel”, to be submitted for publication in the Journal of the American Ceramic Society. This chapter discusses the use of electrochemical impedance spectroscopy to relate the dielectric properties of the bulk and grain boundaries of spinel compacts to processing and microstructure.

6. Chapter 6 presents results not covered in Chapters 3-5, including powder characterization, thermal analysis and mass spectroscopy, thermodynamic simulations, dilatometry, powder neutron irradiation; hot-press, pressureless sinter, and field-assisted sinter experiments; lattice-parameter measurements, and grain boundary grooving experiments.

7. Chapter 7 is a general discussion of results.

8. Chapter 8 is a summary of the main findings.

9. The appendix contains additional documentation.

References are provided at the end of each chapter.

REFERENCES CITED


CHAPTER 2
EXPERIMENTAL METHODS

Commercial powders, with and without additives and pre-treatments, were pressureless sintered (PS), hot pressed (HP), or field-assisted sintered (FAST) to obtain transparent or translucent compacts. Some PS and HP compacts were subsequently hot-isostatic pressed (HIP). Powders and compacts were characterized using laser-scattering particle-size analysis, zeta-potential analysis, simultaneous thermal analysis (STA), STA in combination with mass spectroscopy (STA-MS), inductively-coupled plasma MS/optical emission spectroscopy (ICP-MS/OES), laser ablation ICP-OES/MS (LA-ICP OES/MS), variable-atmosphere dilatometry, X-ray diffraction (XRD), Archimedes density measurements, optical microscopy (OM), polarized light microscopy (PLM), field-emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), scanning TEM (STEM), energy dispersive X-ray spectroscopy (EDS), wavelength dispersive X-ray spectroscopy (WDS), electron energy loss spectroscopy (EELS), electron diffraction (ED), convergent-beam electron diffraction (CBED), electron backscatter diffraction (EBSD), secondary ion mass spectroscopy (SIMS), neutron activation analysis (NAA), Raman spectroscopy, ultraviolet-visible-infrared (UV-Vis-IR) spectrophotometry, atomic force microscopy (AFM), electrostatic force microscopy (EFM), electrochemical impedance spectroscopy (EIS), and thermodynamic simulations. Characterization techniques that did not yield useable results are not discussed.

2.1. Powder Characterization

Two commercial, near-stoichiometric spinel powders were used; Baikowski S30CR (Baikowski powder, lot #061113, Baikowski, Charlotte, NC) and Nanocerox spinel powder (Nanocerox powder, lot #4CZ143B1, Nanocerox, Ann Arbor, MI). Baikowski powder was selected due to its extensive use in industry. It is synthesized via an aqueous sulfate process and may contain unreacted sulfate and hydrate species. Nanocerox powder was selected due to its high purity, allowing the elimination of impurities as a variable and quantification of their effect on densification by comparing with Baikowski powder compacts. Nanocerox powder is synthesized by flame-spray pyrolysis of single or mixed-metal metal-organic alcohol solutions.
and has similar particle-size characteristics to Baikowski powder. Powder characteristics are summarized in Chapters 4 and 6.

Powder phase analysis was conducted using XRD (X’Pert, Philips, Eindhoven, Netherlands), indicating stoichiometry and the absence of second phases within instrument detection limits. Powder chemistry was analyzed with ICP-OES (Spectro Arcos ICP-OES; Kleve, Germany; 3000 ICP-OES; Perkin Elmer, Waltham, MA, USA). Powder samples ~0.1 g were diluted in 4-40 ml of spectroscopic grade H$_3$PO$_4$ in Teflon beakers and dissolved by microwave digestion. Sulfur and carbon content were determined using a carbon/sulfur analyzer (CS-400; LECO, St. Joseph, MI, USA), which determines weight percent carbon and sulfur by combustion and measurement of IR absorption of CO$_2$ and SO$_2$. The analyzer was calibrated with a standard prior to each run with spinel powder. Spinel powder was poured into a nickel basket with tungsten-tin and/or iron accelerants and placed inside the analyzer. The analyzer chamber was evacuated, heated, and carbon and sulfur content determined. Nitrogen content was measured using a nitrogen/oxygen determinator (LECO TC-456), which determines nitrogen content by thermal conductivity after removal of other gases.

Powder particle size characteristics were examined using OM, SEM (Quanta 600i; FEI, Hillsboro, OR, USA), FE-SEM (JSF-7000; JEOL, Tokyo, Japan), and TEM (CM12, CM200; FEI Philips, Eindhoven, Netherlands). For TEM, powders were dispersed in ethanol in a glass beaker, placed in an ultrasonic bath and scooped onto lacy polymer/carbon grids. The TEM camera length was calibrated prior to ED using silicon and MoO$_3$ standards. Selected-area diffraction (SAD) ring patterns of spinel powders were indexed, intensities and lattice spacings calculated, and results matched to ICDD (International Center for Diffraction Data) PDF Files. Powder particle-size was also assessed by laser scattering (S3500; Microtrac, York, PA). Prior to analysis, the particle-size analyzer was calibrated with a silica standard. Small powder samples were dispersed in water using Darvan$^\text{©}$C-N (ammonium polymethacrylate) dispersant for analysis. Particle colloid-stability was assessed by dispersing powders in water and measuring the zeta potential with an analyzer (Zetasizer Nano ZS; Malvern Instruments, Worcestershire, UK).
2.2. Powder Treatment

To study the effect of LiF, 0.05 - 1.0 w % LiF (99.99% metal basis, lot #20307, Puratronic, Alfa Aesar, MA) was added to spinel powder prior to hot pressing. LiF addition was scaled to impurity content, with less added to Nanocerox powder. To study whether lithium or fluorine was responsible for obtaining transparency and eliminating dark color, 0.5 wt% Li₂O (corresponding to ~1 wt% LiF), and separately 0.5 wt% Al₂F₃ (corresponding to ~0.25 wt% LiF) were added to Nanocerox powder prior to hot pressing. To study the effect of stoichiometry on grain growth and absorption, 0.05 wt% and 0.1 wt% Al₂O₃ (99.99%, 20 nm average particle size (APS), obtained through CoorsTek, Golden, CO) were added to Nanocerox powder prior to hot pressing.

Additives were added using ball milling, acoustic mixing, or ultrasonic mixing. For ball milling, spinel powder and additives were weighed to ±0.1 mg, poured into a Nalgene bottle filled with methanol or water (30% solids loading) and milled with high purity Al₂O₃ media (CoorsTek) on a roller mill for 24 hours, and dried at 60°C for 3 days. For acoustic mixing, dry powders were mixed with an acoustic mixer (Resodyne, Butte, MT). For ultrasonic mixing, spinel and additive powders were poured into a Nalgene bottle filled with methanol (40% solids loading) and mixed using an ultrasonic processor (CPX 130; Cole Parmer, Vernon Hills, IL) with a tungsten horn for 1 min. with a power setting of 40 W, solvent was removed by rotary evaporation (R-210; Buchi, Switzerland), and powders were allowed to dry in ambient conditions for 3 days. Due to better results, the ultrasonic mixing/rotary evaporation method was used for all experiments requiring additives. Subsequent to mixing, powders were ground with an agate mortar and pestle and sieved through 100 or 425 steel mesh sieves using a vibratory mixer. To examine the effect of the mixing method, powders without additives were processed in the same manner as mixed powder and hot-pressed compacts compared.

To study the effect of radiation-induced point defects on sintering, Baikowski and Nanocerox powders were irradiated with neutrons at the USGS TRIGA reactor (peak flux of \(3 \times 10^{13} \text{n/cm}^2\)-s at 1 MW) with a calculated fluence of \(6 \times 10^6 \text{n/cm}^2\). The fluence is above that at which oxygen vacancies are formed, with primarily antisite defects formed at lower fluences.\(^9,10,11,12\) Subsequent to irradiation, NAA was used to determine activity, although this
was not used to quantify impurity concentration. The powders were allowed to cool for one year for short-lived isotopes to decay sufficiently for powders to be safely handled. Irradiated powders were then cold-pressed and sintered in a dilatometer.

2.3. STA-MS Experiments

STA (409 STA; Netzsch, Selb, Germany), combining differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), was conducted on powder samples to determine thermal behavior. To analyze evolved gases, an atmospheric residual gas analyzer (Cirrus; MKS, Andover, MA) equipped with a 100-channel quadrupole mass spectrometer (MS) operated at 40 eV, was connected to the STA chamber via a 3.175 mm stainless steel capillary heated to ~250°C with resistive tape (Fig. 2.1.). Powder was poured into an alumina crucible and weighed to ±0.1 mg. The crucible was placed in the STA chamber, which was filled with air or evacuated and back-filled three times with ultra-high purity argon. The chamber was heated at 5°C/ min., 10°C/min., or 20°C/min. to 1450°C. The analyzer software output pressures based on calibrated counts for each mass-to-charge (m/z) ratio, which were divided by total pressure to obtain partial pressures and expressed as ideal gas vol% or ppm volume percent (ppmv). Species of equal mass were differentiated based on species known to be present, known chemical interactions, and Gibb’s energy minimization simulations with thermodynamic software. Calibration runs were conducted with empty crucibles and served as correction files for STA and as a baseline for residual gas analysis. Duplicate runs were performed in air and in argon for each of six conditions; pure LiF, Nanocerox powder with 0 wt%, 1 wt%, and 10 wt% LiF, and Baikowski powder with 0 wt% and 1 wt% LiF. A run was also performed with MgF$_2$ and LiAlO$_2$, which are products of a reversible reaction with LiF and spinel.

2.4. Thermodynamic Simulations

Thermodynamic simulations were conducted using HSC Chemistry (Outototec, Espoo, Finland) to determine chemical interactions between processing constituents and species evolution. HSC simulations are based on thermodynamic equilibrium calculations using an internal thermochemical database. Solid and gaseous species arising from chemical interactions between starting constituents (MgO, Al$_2$O$_3$, MgAl$_2$O$_4$, LiF, Li$_2$O, AlF$_3$, LiAlO$_2$, MgF$_2$), impurities (C, S, Ca, Fe, MgSO$_4$, Al$_2$(SO$_4$)$_3$), and atmospheres (air, O$_2$, N$_2$, argon), were selected
from the software database. Initial species concentrations, atmosphere, pressure, and temperature (typically 25°C to 1500°C) were input, Gibb’s energy minimization simulations were conducted, and the software output plots of species concentration as a function of temperature. Limitations of HSC include that it does not take into account kinetic effects, stoichiometry, solubility for species in spinel, and it does not model mixed-metal oxides or point defects.

![STA Furnace, Argon/H₂, Mass Spec., Capillary](image)

Fig. 2.1. STA-MS apparatus.

### 2.5. Dilatometry Experiments

Dilatometry was conducted on cold-pressed samples to assess the sintering behavior of spinel powder as a function of powder synthesis and properties, neutron irradiation, LiF addition, and atmosphere (Table 2.1.). To make cylindrical compacts with a sintered width to height ratio close to (1:1), 0.350 g of powder was used. Powder samples were weighed with an analytical balance with an accuracy of ±0.0001 g, poured into a 6.35 mm diameter cylindrical steel die lubricated with a solution of 5 wt% stearic acid and polyvinyl alcohol, and hydraulically cold-pressed to 530 MPa. Cold-pressed compacts were re-weighed and dimensions were measured using a micrometer. Compacts were loaded in a Netzsch 402C (Netzsch, Selb, Germany) horizontal dilatometer with alumina spacers placed on either side to prevent reaction with the alumina pushrod and backrest (Fig. 2.2). A force of 30 mN was applied to the alumina push-rod and temperature was ramped at 2°C/min. to 1500°C. Atmosphere was either uncirculated ambient air or argon with 2% H₂ using flow rate of 20 l/min., in which case the dilatometer
chamber was evacuated with a roughing pump and backfilled three times prior to starting. Compacts were subsequently re-weighed and dimensions re-measured.

![Image of Netzsch 402C Dilatometer](image)

**Fig. 2.2. Netzsch 402C Dilatometer**

**Table 2.1. Dilatometry Conditions.**

<table>
<thead>
<tr>
<th>Powder</th>
<th>Treatment</th>
<th>Atmosphere</th>
</tr>
</thead>
<tbody>
<tr>
<td>Baikowski S30CR</td>
<td>As-Received</td>
<td>Air, Argon + 2% H₂</td>
</tr>
<tr>
<td>Baikowski S30CR</td>
<td>Addition 1 wt% LiF</td>
<td>Air</td>
</tr>
<tr>
<td>Baikowski S30CR</td>
<td>Irradiated</td>
<td>Air, Argon + 2% H₂</td>
</tr>
<tr>
<td>Nanocerox Spinel</td>
<td>As-Received</td>
<td>Air, Argon + 2% H₂</td>
</tr>
</tbody>
</table>

The dilatometer recorded linear displacement ($ΔL$) as a function of time and temperature. Displacement was corrected for system thermal expansion by applying a calibration correction made with an alumina standard. The error due to the slight length and linear coefficient of thermal expansion (linear CTE, $α_L$) difference between the standard ($L_{std} = 10$ mm, $α_L_{Al₂O₃} = 8.1x10^{-6}$ K⁻¹)¹³,¹⁴ and compacts ($L_{compact} = 6$ mm, $α_L_{Spinel} = 8.0x10^{-6}$ K⁻¹)¹⁴ was corrected for. Displacement was normalized by length by dividing by the initial compact length. Sample thermal expansion was subtracted from displacement based on the sintered compact thickness. It was desired to display sintering behavior as a function of temperature ($T$) in terms of fractional sintered density ($P_S$) rather than linear shrinkage ($ΔL/L₀$);¹⁵

$$P_S = \frac{ρ_i}{ρ_{th}},$$  \hspace{1cm} (2.5.1)

where $ρ_i$ is instantaneous density and $ρ_{th}$ is theoretical density. If no mass loss occurs, then instantaneous density is initial weight ($W_0$) divided by instantaneous volume ($V_i$);
\[ \rho_i = \frac{W_0}{V_i} \] (2.5.2)

If shrinkage is isotropic, the ratio of initial volume to instantaneous volume \((V_0/V_i)\) is equal to the ratio of the volume of a cube with initial side length \((L_0)\), to that of a cube with instantaneous side length \((L_i)\):

\[
\frac{V_0}{V_i} = \left(\frac{L_0}{L_i}\right)^3
\] (2.5.3)

Thus,

\[
P_S = \frac{\left(\frac{W_0}{V_i}\right)}{\rho_{th}} = \frac{\left(\frac{W_0}{V_0}\right) \times \left(\frac{V_0}{V_i}\right)}{\rho_{th}} = \frac{\left(\frac{W_0}{V_0}\right) \times \left(\frac{L_0}{L_i}\right)^3}{\rho_{th}}
\] (2.5.4)

Since \((W_0/V_0)\) is the green density \((\rho_g)\):

\[
P_S = \frac{\rho_g}{\rho_{th}} \left(\frac{L_0}{L_i}\right)^3
\] (2.5.5)

Noting that \(L_i = L_0 + \Delta L\) and that \(\Delta L\) is negative for sintering;

\[
\frac{L_0}{L_i} = \frac{1}{\left(\frac{L_i}{L_0}\right)} = \frac{1}{\left(\frac{L_0 + \Delta L}{L_0}\right)} = \frac{1}{\left(1 + \frac{\Delta L}{L_0}\right)}
\] (2.5.6)

Thus,

\[
P_S = \frac{\rho_g}{\rho_{th}} \frac{1}{\left(1 + \frac{\Delta L}{L_0}\right)^3}
\] (2.5.7)

For cylindrical compacts in these experiments, shrinkage is anisotropic and the thickness \((L)\) shrinks more than the diameter \((\Phi)\) due to geometry and cold-pressing density gradients. Thus, \(L_0/L_i > \Phi_0/\Phi_i\), \(V_0/V_i \neq L_0^3/L_i^3\), but rather;

\[
V_i = L_i \times L_i' \times L_i',
\] (2.5.8)

where \(L_i'\) is a radial direction with anisotropic shrinkage. If \(\Phi_0\) is the initial diameter and \(\Phi_i\) is the instantaneous diameter;
\[
\frac{V_0}{V_i} = \left( \frac{L_0}{L_i} \right) \times \left( \frac{\Phi_0}{\Phi_i} \right) \times \left( \frac{\Phi_0}{\Phi_i} \right)^3 \times \left( \frac{L_i \times \Phi_0}{L_0 \times \Phi_i} \right)^2 = \frac{1}{\left( \frac{L_i}{L_0} \right)^3 \left( \frac{L_0 \times \Phi_i}{L_i \times \Phi_0} \right)^2} = \frac{1}{\left( 1 + \frac{\Delta L}{L_0} \right)^3 \xi^2},
\]

(2.5.9)

where \( \xi \) is the anisotropy parameter. Some authors\textsuperscript{15} assume

\[
\xi = \frac{L_0}{L_i} \times \frac{\Phi_i}{\Phi_0} = \frac{L_0 \times F_i}{L_F \times \Phi_0}
\]

(2.5.10)

However:

\[
\frac{\Phi_i}{L_i} \neq \frac{\Phi_F}{L_F},
\]

(2.5.11)

since \( \Phi \) changes less per unit increase in temperature (or time) than \( L \) (Fig. 2.3). Rather, assuming a similar temporal shrinkage behavior for \( L \) and \( \Phi \);

\[
\Phi_i \approx \Phi_0 - \left( \frac{L_i - L_0}{L_F - L_0} \right) \left( \Phi_0 - \Phi_F \right) = \Phi_0 - \left( \frac{\Delta L}{L_F - L_0} \right) \left( \Phi_0 - \Phi_F \right)
\]

(2.5.12)

Thus:

\[
\xi = \frac{L_0 \times \Phi_i}{L_i \times \Phi_0} \approx \frac{\Phi_0 - \left( \frac{\Delta L}{L_F - L_0} \right) \left( \Phi_0 - \Phi_F \right)}{\Phi_0}
\]

(2.5.13)

and

\[
P_s = \frac{\rho_G}{\rho_{th}} \frac{1}{\xi^2 \left( 1 + \frac{\Delta L}{L_0} \right)^3}
\]

(2.5.14)

Eq. (2.5.14) was applied to calculate fractional sintered density as a function of time and temperature. The onset of sintering was determined from the temperature associated with the intersection of tangents to the linear portions of the displacement curves before and after the onset. The temperature of maximum sintering rate was determined by differentiating the normalized displacement versus temperature curves. Where applicable, the onset of closed porosity was estimated from the attainment of 92% theoretical density for the fractional density versus temperature curve.\textsuperscript{15}
2.6. Hot Press Experiments

Hot pressing was used to densify compacts as it achieves transparency with the least steps. Powders were poured into a graphite die lined with graphite foil (99.5%, GrafTech, Lakewood, OH) with two graphite foil spacers placed above and two below the powder (Fig. 2.4). The graphite foil was cleaned and edges were smoothed to avoid contamination from graphite foil particles. To study the effect of sample size, three die sizes were used; 12.7 mm, 25.4 mm, and 38.1 mm. To study the effect of sample thickness, powder amount was varied; 1.5 g or 3.5 g (25.4 mm die), 9 g or 12 g (25.4 mm die), and 12 g (38.1 mm die). To study the effect of carbon contamination from the graphite dies and foil, a high-purity alumina die was constructed, in which Nanocerox powder was processed with and without molybdenum foil (Fig. 2.4). The graphite or alumina die were placed in an instrumented hot press (Thermal Technology Inc., Santa Rosa, CA) with a water-cooled, stainless steel chamber and graphitic elements (Fig. 2.5). The hot press chamber was evacuated using rotary and diffusion pumps and vacuum levels were monitored with an ion gauge (Model 563; Varian, Palo Alto, CA). Vacuum levels deteriorated to \( \sim 13 \text{ MPa} \times 10^{-4} \text{ Torr} \) between 50°C and 300°C, but were better than \( \sim 1.3 \text{ MPa} \times 10^{-5} \text{ Torr} \) for the remainder of the runs. Temperature was recorded with a type C (tungsten/rhenium) hafnia-insulated thermocouple located within the hot zone. Ram displacement was measured using a linear variable differential transformer (LVDT). Pressure was measured using a strain-gauge pressure-cell calibrated to a maximum load of 222 kN (50,000 lbs).
The starting hot press regime was based on prior research\textsuperscript{16,17} and consisted of ramping temperature from ambient to 1550°C. A heating rate of 10°C/min. was used to avoid grain growth. The minimum controllable instrument pressure of 3 MPa was applied at the outset to prevent plunger damage during subsequent pressure application. A 60 min. temperature hold was used at 400°C to ensure volatile species outgassing. A 5 min. hold was used at 900°C, presumably to allow LiF to melt and spread by capillarity. A 15 min. hold was used at 1200°C, presumably to allow interaction between LiF and spinel. A 60 min. hold was used at the maximum sintering temperature of 1550°C to ensure complete densification. A slower cooling
rate of 6°C/min. was used to avoid thermal shock. A pressure of 35 MPa was applied at 1200°C upon heating and maintained during sintering. Application of pressure at lower temperature (1100°C) resulted in opacity, presumably because of trapped volatile impurities and LiF. Application of pressure at higher temperature (1300°C) also resulted in opacity, presumably due to evaporation of LiF without interaction. Pressure was maintained until 900°C upon cooling, presumably to avoid pore coarsening.

Hot press parameters from the initial regime were varied and optimized. Heating rates of 2°C/min., 3°C/min., 6°C/min., and 10°C/min. were used to determine the optimal rate for volatile species outgassing and grain growth minimization. High-temperature intermediate holds at 900°C, 1050°C, 1150°C, and 1200°C were used to determine the optimal conditions for LiF interaction and outgassing. Maximum sintering temperatures of 1200°C, 1300°C, 1400°C, and 1550°C were used to determine the minimum temperature at which densification could be achieved. The temperature of pressure application was found to be an important parameter and temperatures of 800°C, 900°C, 1100°C, 1200°C, 1300°C, and 1400°C were used. A pressure of 60 MPa was also used to gauge the effect on microstructure and optical properties. Although optimal parameters were found to depend on the starting powder and sample size, the regime shown in Fig. 2.6 was generally used. The variation of processing and hot press parameters is summarized in Table 2.2.

![Graph](image)

**Fig. 2.6.** Standard hot press regime including ramp at 6°C/min. to 1550°C with 1 h hold at 400°C, 0.25 h hold at 1200°C, 1 h hold at 1550°C, application of 35 MPa at 1200°C and removal at 900°C. Modified regime with pressure applied at 900°C shown by dashed line.
Table 2.2. Variation of Processing Parameters.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Powder type (manufacturer)</td>
<td>Baikowski, Nanocerox</td>
</tr>
<tr>
<td>LiF Addition (wt%)</td>
<td>0, 0.05, 0.25, 1.0</td>
</tr>
<tr>
<td>Al₂O₃ addition (wt%)</td>
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<td>Other additives</td>
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<tr>
<td>Mixing method</td>
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<tr>
<td>Die size (mm)</td>
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<tr>
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<tr>
<td>Powder amount (25.4 mm die, g)</td>
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<tr>
<td>Powder amount (38.1 mm die, g)</td>
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<tr>
<td>Die material</td>
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<td>Shielding type</td>
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<tr>
<td>Sintering method</td>
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<tr>
<td>Atmosphere</td>
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<tr>
<td>Temp. ramp rate (°C/min.)</td>
<td>2, 3, 6, 10</td>
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<tr>
<td>Max. sintering temp. (°C)</td>
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<tr>
<td>Hold at sintering temp. (min.)</td>
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<td>Intermediate hold temp. (°C)</td>
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<td>Intermediate hold time (min.)</td>
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<td>Temp. pressure applied (°C)</td>
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<tr>
<td>Max. Pressure (MPa)</td>
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Vacuum, temperature, ram displacement, and pressure voltages were acquired and recorded by a data acquisition system every second, averaged to one value per 10 seconds, and imported into Excel software. Thermocouple voltage was converted to temperature using a linear best-fit to a calibration based on Type-C thermocouple voltages. Load-cell strain-gauge voltage was converted to load using a linear best-fit to a calibration based on manufacturer’s conversions, and converted to pressure by dividing by the plunger cross-sectional area. LVDT voltage was converted to displacement using a linear best-fit to an empirical calibration, and where necessary corrected for pressure and thermal expansion. Strain due to pressure was assumed to occur mainly in the graphite components due to the lower modulus ($E$) than the steel rams ($E_{ISO 63 Graphite} \approx 12-20 \text{ GPa} < E_{\text{Stainless Steel}} \approx 195 \text{ GPa}$), and subtracted from displacement. Although the modulus of graphite varies with temperature, a modulus of 19 GPa correlated well with observations. The system linear thermal expansion was estimated from the displacement for a
standard hot press run without a compact, and subtracted from displacement. The calculated system linear CTE \( (\alpha_{\text{System}} = 5.6 \times 10^{-6} \text{ K}^{-1}) \) closely matched experimental values. For higher accuracy, displacement values for the standard run without a compact were subtracted from identical standard runs with compacts. Compact linear thermal expansion was estimated based on the fully-densified thickness and \( \alpha_{\text{Spinell}} \), and subtracted from displacement. Compact density was calculated from corrected displacement, measured compact final thickness and density, and was plotted as percent theoretical. Vacuum thermocouple and ion gauge voltages were converted to pressure based on manufacturer’s conversions. For each hot press run, calibrated temperature, pressure, displacement, density, and vacuum levels were plotted as a function of time. The onset of sintering and temperature at which closed porosity occurred were determined in the same manner as for dilatometry experiments.

Subsequent to hot pressing, compacts were ground using SiC grinding discs down to 600-grit and polished on a glass platen using napless Nylon cloths and Al\(_2\)O\(_3\) polishing media diluted in water down to 0.05 \( \mu \)m. Diamond media was avoided due to greater grain pull-out. When higher grain contrast was required, a final polish with colloidal silica using a vibratory polisher was used. Compacts had a diameter of 12.7 mm or 25.4 mm, and were ~2 mm thick (1.5 g of powder) or ~5 mm thick (3.5 g of powder) after polishing.

2.7. Pressureless Sintering, Hot Isostatic Press, Quenching, and Single-Crystal Experiments

Pressureless sintering experiments were conducted to assess scaling-up transparency achieved with dilatometry to larger specimens and to gauge the effect of powder synthesis and properties on subsequent HIPing. 1.5 g of Baikowski or Nanocerox powder was poured into a 12.7 mm (1/2 in.) diameter steel die and cold-pressed at 175 MPa using a hydraulic press. Cold-pressed compacts were sintered in air in a vertical furnace with MoSi\(_2\) elements (Deltech, Denver, CO) at 2°C/min. to 1550°C, with a 1 hour hold at 1550°C, and a ramp to ambient at 10°C/min. Compacts were cut in half and HIPed in a graphite furnace in argon at 5°C/min. to sintering temperature with a 2 hr. hold at 300°C. One half of each sample was HIPed at 1550°C for 10 hrs., and the other at 1650°C for 15 hrs.
Quenching experiments were conducted to determine whether impurities and additives segregated at grain boundaries could be re-dissolved into the matrix to alter fracture behavior. Samples from compacts hot pressed with Baikowski powder with 1 wt% LiF were heated in an air furnace to 1200°C and quenched in water at ambient temperature. The samples were sectioned with a diamond saw and the slices obtained were fractured and the fracture surfaces examined with SEM and compared to those of un-quenched samples.

Spinel single crystals (Los Alamos National Laboratory, Los Alamos, NM) were oxidized by heating to 1200°C in air, or reduced by heating to 1200°C in vacuum in a graphitic furnace and visually examined to determine whether reduction was responsible for dark color. Unfortunately, heating in a graphitic furnace did not allow distinguishing between reduction and carbon contamination.

2.8. Field-Assisted Sintering

Field-assisted sintering (FAST) was performed with Baikowski and Nanocerox powder, with and without LiF addition, and with and 5 wt% polyvinyl alcohol or poly-ethylene glycol binder using cylindrical and dog-bone geometries (Fig. 2.7). Cylindrical specimens were cold-pressed into 4 mm thick by 6 mm diameter green compacts using a separable three-piece steel die and a hydraulic press. Specimens were placed between alumina platens in an air furnace equipped with MoSi₂ heating elements. A nominal force of 3 MPa was applied to the top alumina platen by means of weights and the furnace was heated at 10°C/min. A power source applied a constant voltage of 300 V (~600 V/cm) and a maximum current of 0.5 A to compacts using two sacrificial stainless steel electrodes placed above and below compacts and connected to the power source by platinum wires. A horizontally-mounted CCD camera recorded specimen shrinkage through a viewport during sintering. Dog-bone specimens were cold pressed into 20 x 3 x 1.5 mm (reduced section) green compacts using a specially-constructed die and a hydraulic press. Compacts were heated in an air furnace at 10°C/min to 1500°C and shrinkage was recorded by a CCD camera. A voltage of 2000 V (~1000 V/cm) and a maximum current of 0.5 A were applied by means of platinum wires attached to small holes in the specimen dog-bone extremities. Processing data was collected with a LabView®-based data acquisition system.
2.9. Grain boundary grooving experiments

Grain-boundary grooving experiments were conducted to detect changes in the grain-boundary surface energy related to embrittlement caused by LiF. Polished Baikowski powder compacts hot pressed without and with 1 wt% LiF and the standard run were examined. Polished compacts were thermally etched for 15 min. at 800°C in a vertical drop-down furnace and quenched in air. Three-dimensional (3D) surface roughness maps were generated by scanning an AFM (Nanoscope 310D; Digital Instruments, Tonawanda, NY) tip over selected areas of the samples. Dihedral angles were measured from line scans cut across the 3D surface maps with the AFM software for five grain boundaries. Grain boundary to surface energy was calculated from

\[ \gamma_{gb} = \gamma_s \cos\left(\frac{\theta}{2}\right), \]

where \( \gamma_{gb} \) is the grain boundary energy, \( \gamma_s \) is the surface energy and \( \theta \) is the dihedral angle.

3.0. EIS Experiments

Electrochemical impedance spectroscopy (EIS) was conducted to determine the bulk and grain boundary dielectric properties of hot-pressed compacts as a function of processing. The
aim was to relate the dielectric properties to microstructure and obtain information regarding removal of absorption and grain-boundary embrittlement caused by LiF addition.

EIS samples were prepared from four polished compacts hot-pressed with the standard run; one processed with Baikowski powder that appeared white (oxidized), one identically processed that appeared dark (reduced), one transparent compact processed with Baikowski powder and 1 wt% LiF, and one transparent compact processed with Nanocerox powder. The difference in appearance of the Baikowski compacts was attributed to varying vacuum levels present in the hot press chamber. To ensure plane-parallel surfaces, polished compacts were glued with Crystalbond™ to a steel plate placed on a magnetic bed surface grinder and ground with a 600-grit diamond grinding wheel to a thickness of ~1 mm, subsequent to which the ground side was fine-ground and polished to a thickness of ~0.75 mm. Compact thickness was measured at five locations with a micrometer. Gold electrodes ~7 mm or ~10 mm in diameter were magnetron sputtered on each sample side through a mask using a setting of 20 mA for 8 min. Silver wire leads were attached to the electrodes by tying the wire to silver mesh and gluing the mesh onto the electrodes using silver paste that was cured at 200°C for 30 min.

EIS sample electrode leads were threaded through a 2-bore alumina tube placed inside a larger closed-end alumina tube in a tube furnace, leaving the sample hanging freely. The alumina tube was inserted through an UltraTorr™ fitting mounted on a ported steel flange attached to a closed-end large-diameter alumina tube. A type K thermocouple was inserted through an UltraTorr™ fitting and positioned adjacent to the sample. Alumina gas inlet and outlet tubes were also fitted through UltraTorr™ fittings. The assembled EIS rig was placed in a tube furnace and thermocouple leads were connected to a thermocouple reader. The gas inlet tube was connected to a synthetic air cylinder or argon with 2% H₂, set to a flow rate of 70 cm³/m controlled by a mass-flow controller. The furnace was ramped to 900°C and sequentially cooled at 50°C intervals to 500°C with temperature allowed to stabilize at each interval. A potentiostat (Reference 3000; Gamry, Warminster, PA) applied an alternating voltage (AC) of 100 mV rms from 0.1 Hz to 1 MHz at ten points per decade and measured impedance response (Fig. 2.8).
Impedance is given by:

\[ Z = Z_0 e^{i \omega t} = Re\{ Z \} - Im\{ Z \} = \frac{V_0 \cos(\omega t)}{i_0 \cos(\omega t - \phi)}, \tag{3.0.1} \]

where \( Z \) is the impedance, \( j = \sqrt{-1} \), \( V_0 \) is the voltage amplitude, \( i_0 \) is the current amplitude, \( \omega \) is the angular frequency, \( t \) is time, and \( \phi \) is the phase shift. The real (resistive) and imaginary (phase difference) components of the EIS impedance results were plotted on Nyquist plots. Compacts were modeled as equivalent parallel resistor-capacitor (RC) circuits matching the impedance response. Resistances were estimated from the real-axis Nyquist plot semi-circle intercepts. Resistivity:

\[ \rho = RL/A, \tag{3.0.2} \]

where \( R \) is resistance, \( L \) is the electrode separation distance, and \( A \) is electrode cross-sectional area, corresponding to the semi-circles was calculated based on measured sample-electrode geometry. Conductivity:

\[ \sigma = 1/\rho, \tag{3.0.3} \]

was calculated from resistivity. The imaginary component of the impedance is maximized when:

\[ \omega_0 \tau = 2\pi f_0 \tau = 1, \tag{3.0.4} \]
where \( \omega_0 \) is the resonant angular frequency, \( f_0 \) is the resonant AC frequency, and \( \tau \) is the relaxation time, which for a parallel RC-circuit is equal to \( RC \). At the resonant frequency, \( \omega_0 \tau = 1 \) and thus;

\[
2\pi f_0 = 1/RC,
\]

\((3.0.5)\)

The capacitance for each Nyquist plot semi-circle was calculated using resonant frequency and resistance values and Eq. 2.9.4. The capacitance is related to the permittivity

\[
\varepsilon = C \left( L/A \right),
\]

\((3.0.6)\)

where \( C \) is the capacitance, \( L \) is the electrode separation distance, and \( A \) is the electrode cross-sectional area. The complex modulus is given by;

\[
M = j\omega C_0 Z,
\]

\((3.0.7)\)

where \( M \) is the modulus, \( C_0 = \varepsilon_0 A/L \), is the capacitance of the empty cell and \( \varepsilon_0 = 8.854E^{-12} \) F/m is the permittivity of free space. Modulus plots of \( \text{Im}(M) \) versus \( f \) were constructed to emphasize components with the smallest capacitance when arcs are not resolvable in Nyquist plots.

Nyquist plot semi-circles were attributed to bulk and grain boundary polarizing mechanisms based on their frequencies, time-constants, and capacitances, and resistances and capacitances corresponding to the bulk and grain boundaries were calculated. Specific bulk and grain boundary conductivities were estimated using the brick-layer model\(^{21,22}\) and also from the calculated grain boundary volume fraction (Section 3.1). In the brick-layer model;

\[
x_{gb} \approx 3d/D,
\]

\((3.0.8)\)

where \( x_{gb} \) is the grain boundary volume fraction, \( d \) is the grain boundary width and \( D \) is the grain size. In the brick-layer model, it is assumed bulk volume fraction \( x_{bulk} = 1 \). From geometrical considerations;

\[
d/D \approx C_{bulk}\varepsilon_{bulk}/C_{gb}\varepsilon_{gb}
\]

\((3.0.9)\)

Since resistivities weighted by volume add for series circuits;

\[
\rho_{total} = x_{bulk}\rho_{bulk} + x_{gb}\rho_{gb},
\]

\((3.0.10)\)
Specific bulk and grain boundary capacitances were calculated from Eqs. (3.0.8)-(3.0.10) assuming \( x_{\text{bulk}} = 1 \) and \( \varepsilon_{\text{bulk}} = \varepsilon_{\text{gb}} \). As conductivity in ionic compounds is temperature-activated,

\[
\sigma = \sigma_0 e^{-\frac{E_a}{kT}},
\]

(3.0.11)

where \( \sigma \) is the conductivity, \( E_a \) is the activation energy for conductivity, \( k \) is Boltzmann’s constant, and \( T \) is temperature. Activation energies for total conductivity, bulk conductivity, and grain boundary conductivity were calculated using Eq. (3.0.11). Performing EIS in oxidizing/reducing atmospheres was conducted to give further insights into the defect chemistry.

To determine the presence of overlapping impedance responses, responses were simulated using ZView® software. Compacts were modeled as series combinations of resistors, parallel RC-circuits, and Warburg element or constant-phase elements (CPE). CPE’s model the behavior of an electrical double layer or imperfect capacitor:

\[
Z(\omega) = Q^{-1}(j\omega)^{-n},
\]

(3.0.12)

where the parameter \( Q \) becomes equal to capacitance when \( n = 1 \).\(^{24}\) To simulate non-linearity in capacitance for individual polarizing mechanisms, capacitors in RC-circuits were replaced with CPE’s.

### 3.1. Compact Characterization

The density of polished compacts was calculated using the Archimedes method and ASTM standards B962 and C373. Compacts were boiled in de-ionized water for 5 hours, weighed to \( \pm 0.1 \) mg with an analytical balance (BA 210S; Sartorius, Elk Grove, IL), and adjustments were made for ambient temperature and pressure.

The microstructure of polished compacts was examined using optical microscopy (OM; 10X objective, 10X-50X magnification, PMG 3; Olympus, Tokyo, Japan) with an attached digital camera (PX-CM; Paxcam, Villa Park, IL). Decorated grain boundaries, second phases, inclusions, and other optical defects were observed by focusing the image plane to the interior of transparent compacts. Digital images with annotated calibrated scale bars were imported into Image J image analysis software (National Institute of Health, Bethesda, MD). Average grain
size was calculated using a circle-intercept method as per ASTM standard E112. Grain boundary surface area per unit volume was calculated by modeling grains as tetrakaidecahedrons with diameters equal to the measured average grain size. Total grain boundary area for each grain size type was found by multiplying the calculated grain boundary surface area per unit volume for each grain size type (i.e. matrix grains, sub-micron grains, abnormal grains) by the area fraction of that type determined from Image J analysis of SEM images. Compacts were examined with polarized light microscopy (PLM; AxioScope A1; Zeiss, Oberkochen, Germany) using a full-wavelength filter for green light to examine birefringent features and residual stress.

Microstructure and chemistry of polished compacts and fracture surfaces (to ensure retention of brittle second phases), and of precipitate collected from the periphery of compacts subsequent to hot pressing were examined with field-emission scanning electron microscopy (FE-SEM; JSF-7000; JEOL, Tokyo, Japan) with attached energy dispersive spectroscopy (EDS) and wavelength dispersive spectroscopy (WDS) detectors. Surface crystallography and texture of polished samples was examined using an electron backscatter diffraction (EBSD) detector, although no texture was observed. Volume percent of phases and fracture features were determined using Image J.

Transmission electron microscopy (TEM) and scanning TEM (STEM; CM200, CM12; FEI Phillips, Eindhoven, Netherlands; JEM 2100F, JEOL) and STEM-EDS (S/TEM-EDS, Tecnai G2 F20 S-Twin 200 keV FE S/TEM, FEI; ARM, JEOL) were performed on specimens that were dimple ground and ion milled (Duo Mill 600, Gatan, Warrendale, PA, USA) with argon or alternatively prepared with a dual-beam focused ion beam (Helios 600i; FEI). Compacts were examined in brightfield (BF) mode, with electron diffraction (ED), convergent beam electron diffraction (CBED), and chemistry examined with EDS and electron energy loss spectroscopy (EELS). Lithium was not identified by EELS, likely due to the low K-edge edge/background ratio intensity combined with low concentration and overlap with other edges.

Changes in lattice parameter at grain boundaries were studied by performing CBED on FIB samples. The cameral length for the TEM was calibrated using standard methodology with silicon and polycrystalline aluminum samples using:

$$R = \frac{\lambda L}{g}$$  \hspace{1cm} (3.1.1)
where \( R \) is the distance between selected-area diffraction pattern reflections, \( d \) is the lattice spacing of the crystal, \( \lambda \) is the electron wavelength, and \( L \) is the camera length. The voltage of the TEM was determined by collecting CBED patterns for a silicon single crystal and matching central-disc Kikuchi line patterns of low-index zone axes to simulated patterns with JEMS (EPFL, Lausanne, Switzerland) electron diffraction simulation software\(^{25}\) using:

\[
\lambda = \left( \frac{h}{(2m_0eV)^{1/2}} \right),
\]

(3.1.2)

where \( \lambda \) is the electron wavelength, \( h \) is Planck’s constant, \( m_0 \) is the electron mass, \( e \) is the charge of one electron, and \( V \) is the TEM voltage. CBED patterns were collected at grain interiors and grain boundaries of FIB samples. The relationship between electron wavelength, TEM camera length and voltage, and lattice parameter are given by:

\[
\frac{1}{H} = \left( \frac{2}{\lambda} \right) \left( \frac{\lambda L}{r} \right)^2,
\]

(3.1.3)

where \( H \) is the spacing of reciprocal lattice planes parallel to the electron beam, \( \lambda \) is the electron wavelength, \( L \) is the camera length, and \( r \) is the measured radius of the first-order Laue zone (FOLZ) ring. The lattice parameter was calculated from:

\[
\frac{1}{H} = \left( \frac{a_0(U^2 + V^2 + W^2)^{1/2}}{P} \right),
\]

(3.1.4)

where \( a_0 \) is the lattice parameter, \( U, V, \) and \( W \) are the zone axis plane indices, \( P = 1 \) when \((U + V + W)\) is odd and \( P = 2 \) when \((U + V + W)\) is even.

Electronic-force microscopy (EFM) was performed on polished compacts hot pressed with and without LiF to try and detect changes in dielectric constant across grain boundaries. However, EFM did not detect any changes, either because the sensitivity of the instrument was too low or because the gradients are too shallow or simply not present.

Confocal Raman spectroscopy (Alpha 3000; WiTec, Ulm, Germany), using a Nd:YAG laser emitting light at 532 nm, was used to probe the point-defect structure of compacts, to determine the chemistry of second phases and inclusions, and to examine fluorescent behavior, both on the surface and within the interior of polished compacts. Raman shift as a function of wavelength
was recorded for various compacts, graphite, and spinel single crystals and compared to known spectra from the literature.

Laser ablation inductively coupled plasma by optical emission and mass spectroscopy (LA-ICP OES/MS; Spectro-Arcos ICP/OES; Varian 820 MS ICP/MS; Cetac LSX-500 LA, Omaha, NB) was used to quantify impurity content within and among compacts. Two compacts hot pressed with 3.5 g of LP powder and pressure applied at 1200°C were analyzed; one without LiF and one with 1 wt% LiF. For each compact, two areas were analyzed; the center of a face and the geometric center (by cutting compacts in half with a diamond saw). Prior to LA-ICP a compact hot pressed so as to maximize retained impurity content was analyzed with LA-ICP and also dissolved for analysis by solution ICP-OES to establish a reference for LA-ICP. The spectral counts of the ICP analyses were integrated and the element counts normalized by dividing them by the aluminum, magnesium, or gallium counts. The normalized counts from LA-ICP were compared to those from solution-ICP to establish absolute concentrations. Alumina levels were obtained by difference, lithium content was measured directly and LiF content estimated from it, and boron was detected but not in enough quantity to establish a calibration curve.

SIMS (IMS 5f, Cameca, Gennevilliers, France) was conducted on hot pressed compacts in order to quantify lithium content as a function of processing. A dynamic SIMS spectrometer using either cesium or oxygen ion beams, equipped with a normal-incidence electron gun for charge neutralization, and parts-per-billion sensitivity and depth profiling with 3-15 nm resolution was used. Three compacts were examined; one hot pressed with Baikowski powder without LiF using the standard run, one with 1 wt% LiF with pressure applied at 900°C, and one with 1 wt% LiF and pressure applied at 1100°C. Hot pressed compacts were coated with 200 nm of copper to reduce charging. For the compact without LiF, SIMS was conducted over an area of 50 µm², using 32 s. analyze time, 10 s. sputter time, and no charge compensation. For the compacts with LiF, SIMS was conducted over an area of 25 µm², using 16 s. analyze time, 10 s. sputter time, and with charge compensation. Lithium counts were normalized by the sum of magnesium and aluminum counts and plotted as a function of analysis time. Surface scans at the bottom of ion craters were conducted for 30 min. for the compact without LiF and for 8 min. for compacts with LiF.
Spectrophotometry (Lambda 950 UV-Vis-NIR; Perkin Elmer, Cary 5G UV-Vis-NIR; Varian) was used to measure the transmittance, reflectance, and fluorescence of surface ground and polished compacts. In-line transmittance ($I_{ILT}$) was measured from 175 nm to 3000 nm by placing samples between the radiation source and detector. Total transmittance ($I_{TT}$), total reflectance ($R_T$), and diffuse reflectance ($R_D$) were measured from 175 nm to 3000 nm using an integrating sphere. For total transmittance, samples were placed at the integrating sphere entrance aperture and a reflective plug placed at the sample reflection measurement location. For total and diffuse reflectance, samples were placed at the rear sample reflection measurement location, which was set to include specular reflectance within the sphere for total reflectance measurement, or to reflect it out the entrance aperture for diffuse reflectance measurement. For all measurements, 0% and 100% transmittance baselines were set by measuring transmittance with the source blocked and without a sample, respectively. For the 100% reflectance measurement a highly reflective polytetrafluoroethylene standard was used. Sample fluorescence was measured using a 6 W continuous wave UV source with and without a UV filter (9683).

Incident, transmitted, reflected, and absorbed intensity are related by;

$$I_0 = I_{TT} + R_T + A = 1,$$

(3.1.1)

where $I_0$ is incident intensity, $I_{TT}$ is the total transmittance, $R_T$ is the total reflectance, and $A$ is absorptance. Total transmittance the sum of in-line and diffuse transmittance; $I_{TT} = I_{ILT} + I_{DT}$, and total reflectance is the sum of specular and diffuse reflectance; $R_T = R_S + R_D$. Diffuse transmittance ($I_{DT}$, or forward scatter) was calculated as the difference between total ($I_{TT}$) and in-line transmittance ($I_{ILT}$), from ($I_{TT} = I_{ILT} + I_{DT}$). Specular reflectance ($R_S$) was calculated as the difference between total ($R_T$) and diffuse reflectance ($R_D$), from ($R_T = R_S + R_D$). Absorptance ($A$) was calculated as the incident intensity minus total transmittance and total reflectance ($A = 1 - I_{TT} - R_T$). Where different thickness compacts were compared, values were normalized per unit thickness.

Characterization techniques that did not yield useable results included mercury pycnometry, TEM-CBED, TEM-EELS, and EFM. Mercury pycnometry did not yield accurate porosity
values, likely due to the large chamber size in comparison to samples. Lattice parameter variation across grain boundaries using TEM-CBED could not be determined with certainty either because the variation gradient was too shallow or too narrow. In addition, limited probe size and beam asphericity noted in first-order Laue line (FOLZ) circles limited analysis. TEM-EELS was unable to identify lithium. Electrostatic force microscopy (EFM) did not detect changes in dielectric constant across grain boundaries, possibly because of insufficient sensitivity or because property gradients were too shallow.

REFERENCES CITED


CHAPTER 3

50 YEARS OF RESEARCH AND DEVELOPMENT COMING TO FRUITION;
UNRAVELING THE COMPLEX INTERACTIONS DURING PROCESSING OF
TRANSPARENT MAGNESIUM ALUMINATE (MgAl$_2$O$_4$) SPINEL

A paper published as an invited feature article in the Journal of the American Ceramic Society

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ABSTRACT

The need for materials for demanding optical applications has engendered a resurgent interest in transparent ceramics. Transparent polycrystalline magnesium aluminate spinel is one especially promising and rapidly-maturing technology that can fill this niche. Although it has been studied for over 50 years, it is only recently that highly-transparent components with acceptable mechanical properties have been reliably fabricated at reasonable cost. Development has been hindered by the inherent difficulty in sintering spinel to the near-theoretical density required for transparency, a high sensitivity to powder and processing parameters, variable stoichiometry, and a lack of understanding of the synthesis-processing-property relationships. The driver of recent success is an emerging understanding of complex, multi-scale, multi-variable interactions that occur during green-body formation and sintering. In particular, certain key variables play a decisive role in determining compact properties and their evolution must be controlled from synthesis to the finished product. This paper features the interactions between these key variables during processing and gives an exposé of the state-of-the-art in transparent polycrystalline spinel fabrication.
3.1. Introduction

This paper is organized into eight sections (Table 3.1). Section 3.1 is a general introduction, Section 3.2 is a background on properties, Section 3.3 introduces the key variables, Section 3.4 discusses particle-size effects, Section 3.5 discusses stoichiometry, Section 3.6 discusses impurities and additives, Section 3.7 discusses processing parameters, and Section 3.8 is a summary. Three sidebars are included; (1) defect chemistry and grain boundary mobility, (2) electrochemical impedance spectroscopy; assessing defect chemistry, and (3) shedding light on absorption.

<table>
<thead>
<tr>
<th>Section</th>
<th>Topic</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td>Introduction</td>
</tr>
<tr>
<td>3.2</td>
<td>Background</td>
</tr>
<tr>
<td>3.3</td>
<td>Key Variables</td>
</tr>
<tr>
<td>3.4</td>
<td>Particle-Size Characteristics</td>
</tr>
<tr>
<td>3.5</td>
<td>Stoichiometry (Sidebar 1)</td>
</tr>
<tr>
<td>3.6</td>
<td>Impurities and Additives (Sidebar 2)</td>
</tr>
<tr>
<td>3.7</td>
<td>Processing Parameters (Sidebar 3)</td>
</tr>
<tr>
<td>3.8</td>
<td>Summary</td>
</tr>
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The need for materials for ever-more demanding optical applications combined with research and technological advances have spurred a resurgent interest in transparent polycrystalline ceramics.\(^1\)\(^-\)\(^8\) Transparent ceramics have a unique combination of properties not obtainable with other materials\(^9\) and, unlike single crystals, polycrystalline ceramics can be formed into complex near-net shapes from commercially available powders at lower cost.\(^10\) Transparent polycrystalline magnesium aluminate spinel (spinel) is one especially promising and rapidly-maturing technology that can fill this niche. Although it has been studied for over 50 years, only recently have highly-transparent components with acceptable mechanical properties been reliably fabricated at reasonable cost.\(^1\)\(^,\)\(^7\)\(^,\)\(^10\)\(^-\)\(^14\) Spinel is difficult to sinter to the near-theoretical density required for transparency and fabrication is complicated by variable stoichiometry and extreme sensitivity to starting powder and processing parameters.\(^1\)\(^,\)\(^5\)\(^,\)\(^15\) These difficulties combined with a lack of understanding of the synthesis-processing-structure-property relationships have hindered development.\(^1\) Key to recent success is an emerging understanding of complex, multi-scale, multi-variable interactions that occur during green-body formation and
sintering.\textsuperscript{5,16,17} In particular, particle-size characteristics, stoichiometry, and impurities play a decisive role in determining compact properties and successful fabrication entails tracking these variables from synthesis to the finished product. This article features the complex interactions that occur between these key variables, especially during sintering, and gives an exposé of the state-of-the-art in transparent spinel fabrication.

Spinel has a combination of isotropic cubic structure, low density, high hardness, erosion resistance, high strength, transparency from the near-UV (ultra-violet) to the mid-IR (infra-red), and high-temperature stability possessed by few materials.\textsuperscript{1,18} Transparent non-oxides such as ZnS, ZnSe, Si\textsubscript{3}N\textsubscript{4}, and SiC possess good IR transmittance, but have to date exhibited lower visible transmittance than spinel.\textsuperscript{18} Alkaline and alkali-metal halides like MgF\textsubscript{2}, and also glasses and glass-ceramics, have lower mechanical and thermal properties.\textsuperscript{18} Transparent ceramics with competing properties to spinel include sapphire and polycrystalline ceramics such as Al\textsubscript{23}O\textsubscript{25}N\textsubscript{5} (AlON), Al\textsubscript{2}O\textsubscript{3}, MgO, cubic ZrO\textsubscript{2}, Y\textsubscript{2}O\textsubscript{3}, Y\textsubscript{2}Al\textsubscript{5}O\textsubscript{12} (YAG), and diamond.\textsuperscript{3,8,17-25} Sapphire and AlON have excellent mechanical and optical properties, but birefringence in sapphire requires single crystal use, and has a lower density, is easier to polish, has lower production cost.\textsuperscript{1,10,26} Spinel also has a higher IR absorption edge and transmission at the 4.8 \(\mu\)m exhaust signature wavelength used for-IR targeting than AlON and sapphire, especially at higher temperature.\textsuperscript{9} ZrO\textsubscript{2} has a higher IR absorption edge than spinel, but also higher density, erosion resistance and visible transmittance.\textsuperscript{18-20} YAG and Y\textsubscript{2}O\textsubscript{3} are used in laser applications, both have high transmittance and wider transmission windows than spinel, and Y\textsubscript{2}O\textsubscript{3} lower emittance.\textsuperscript{3,8,18-21,25} However, they are significantly denser, have lower hardness and erosion resistance, and are more expensive.\textsuperscript{3,8,18-21,25} Polycrystalline MgO and Al\textsubscript{2}O\textsubscript{3} have excellent mechanical properties, but MgO has poor visible transmittance\textsuperscript{18} and polycrystalline Al\textsubscript{2}O\textsubscript{3}, although showing promise for IR windows and domes, is translucent in thick sections due to birefringence, even with nanometer-sized grains.\textsuperscript{18-20,22} Single crystal and polycrystalline diamond produced by chemical vapor deposition have excellent optical and mechanical properties, but are difficult to and expensive to fabricate and not yet commercially available.\textsuperscript{18,23,24}

Spinel has been used sporadically in challenging military applications such as transparent armor, IR-transparent windows for missile launchers and reconnaissance pods, and transparent
domes for IR-seeking missiles. However, spinel is now being used or considered for a host of applications including: windows for UV lithography, spacecraft, barcode scanners, watches, night-vision systems, high-temperature sight-glasses, and laser ignitors. Moreover; multi-spectral windows for imaging, ranging, and targeting in ground, sea, and air vehicles. In addition; UV, miniaturized, and graded refractive index lenses; laser and scintillator hosts, and laser Q-switches (Fig. 3.1).

![Fig. 3.1 Select applications and transparent spinel components, reproduced with permission.](image)

Transparent spinel development began in the 1960’s in the U.S. and The General Electric Co. (Fairfield, CT) was the first to successfully fabricate visibly transparent material, which also had an IR transmittance >60% at ~3 mm thickness. Compacts were cold-pressed (CP) from calcined Al₂O₃ and MgO powders with Li₂O and SiO₂ additives, embedded in powder of similar stoichiometry in a molybdenum enclosure and sequentially pressureless sintered (PS) up to 1900°C in H₂. Development continued in the 1970’s–1990’s with hot press (HP), HP/hot isostatic press (HIP), and fusion-cast spinel (which suffered from residual stress), however production was fraught with difficulties. Initially, obtaining high transparency was an issue, but reproducibility and optical defects became prime concerns. These were attributed to small differences in stoichiometry and impurity content that often precluded transparency, a condition
which only improved once higher-quality powders became available. Sintering additives were initially necessary for transparency, but they interfered with transmittance, and LiF emerged as the most useful additive. Since the 1990’s, many of the inherent issues with achieving transparency were solved and interest shifted towards optimizing processing, lowering cost, and improving mechanical properties, mainly through grain-size reduction.

Translucent or transparent spinel has since been produced by PS, HP, HP/HIP, PS/HIP, spark plasma sintering (SPS), field-assisted sintering (FAST), fusion casting, and melt-casting, sometimes in combination with reactive sintering (RS). However, nearly all commercial manufacture is currently with HP/HIP or PS/HIP, producing components up to 10 cm thick and 50 cm in diameter, and larger windows up to 0.52 m² by diffusion edge-bonding of smaller panes. LiF sintering additive (0.25–4 wt%) is typically required for transparency with pressure-assisted sintering (HP, HP/HIP, and SPS), but with the advent of high-purity nano-powders and improved pre-treatment, the trend is towards not using additives. The ultimate goal is pressureless sintering without HIP, but only translucency has been achieved and all commercial fabrication uses pressure to increase sintering kinetics (HP, SPS) or close residual pores (HP, HP/HIP, PS/HIP, SPS). Electric fields (SPS, FAST) increase kinetics and reduce grain size, but geometry is limited and sintering rates comparable to HP appear necessary for high transparency. Increasing kinetics by irradiating powders and microwave sintering have also been attempted without significant success. Despite progress achieved, considerable headway remains, including increasing reproducibility, scaling-up fine grain-size technologies, grain-boundary engineering with new additives, lowering absorption near transmission absorption edges, and lowering cost. In addition, many questions remain only partially answered, such as the causes of grain growth, absorption, and optical defects, as well as the specific role of stoichiometry, defect chemistry, and sintering additives.

3.2. Background

This section provides a background on the properties of transparent spinel properties and processing.
3.2.1 Thermodynamics

Spinel is the only intermediate compound of the MgO-Al₂O₃ phase system (Fig. 3.2). Formation from its constituents is exothermic and occurs by cation counter-diffusion through a stationary oxygen lattice with an accompanying ~5-8 vol% expansion. Although spinel forms a line compound of equal mol% MgO and Al₂O₃ at equilibrium below ~1200ºC, it has increasing solubility with temperature, especially for Al₂O₃, as described by $x$ in MgO:$x$Al₂O₃, with a maximum range of $0.6 \leq x \leq 9.1$. The solid-solubility end-member on the Al₂O₃-rich side is the highly-defected cubic $\gamma$-Al₂O₃ polymorph. In practice, single-phase variable stoichiometry $1 \leq x \leq 3$ is quenched in with moderate cooling rates (<5ºC/min).

![Fig. 3.2 Spinel phase diagram, adapted with permission.](image)

The vapor pressure of Mg or MgO over spinel is up to $10^3$ higher than that of Al₂O₃, resulting in Mg/MgO loss and variable stoichiometry during sintering. Mg/MgO loss is greater at high temperature and low oxygen partial pressure ($pO_2$) (Fig. 3.3) and reducing conditions favor the decomposition of MgO($g$) into Mg($g$) and O₂($g$). Stoichiometry may also be affected by formation of AlO₂ gas, which is exacerbated by carbon present in graphitic
furnaces.\textsuperscript{77,78} Variable stoichiometry affects virtually every property and is both a source of complexity and a key to understanding spinel (Section 3.5).

![Schematic diagram of spinel volatility](image)

Fig. 3.3 Spinel volatility diagram, \( p_x \) refers to the partial pressures of species formed during reduction, adapted with permission.\textsuperscript{73}

### 3.2.2. Crystal Structure and Defects

In spinel, the larger \( \text{O}^{2-} \) anions form a cubic close-packed sub-lattice, rendering isotropic properties, and the cations occupy only \( \frac{1}{4} \) of the interstices (Fig. 3.4). The cubic symmetry is visualized by considering a larger unit cell composed of 8 formula units (\( \text{MgAl}_2\text{O}_4 \)), with the lattice parameter \( (a) \) determined by the cations. In normal spinel, larger \( \text{Mg}^{2+} \) cations occupy \( \frac{1}{8} \) of the smaller tetrahedral interstices and smaller \( \text{Al}^{3+} \) cations occupy \( \frac{1}{2} \) of the larger octahedral interstices, dilating anions from their ideal cubic arrangement, characterized by the anion parameter \( (u) \). The structure can accommodate significant cation site-exchange, characterized by the inversion parameter \( (i, \ i = 0 \ \text{normal}, \ i = 1 \ \text{inverse}) \), with \( i \sim 0.1-0.6 \) for synthetic spinels.\textsuperscript{79,80}

A wide variety of point defects exist in spinel (Fig. 3.5) and defect chemistry is a key parameter that influences many properties (Sections 3.5-3.7, Sidebars 1-3).\textsuperscript{70,79,81-85} In turn it is affected by stoichiometry, impurities, additives\textsuperscript{31}, mechanical treatment\textsuperscript{86}, irradiation\textsuperscript{87}, sintering atmosphere\textsuperscript{69,73-77}, temperature\textsuperscript{88}, and applied pressure.\textsuperscript{70,79,81-85}
Intrinsic point defects expressed in Kroger-Vink notation include:

\[
M_{8\text{Mg}}^x \rightarrow M_{8\text{Mg}}^{**} + V_{\text{Mg}}''
\]  
(3.1)

\[
Al_{\text{Al}}^x \rightarrow Al_{\text{Al}}^{**} + V_{\text{Al}}''
\]  
(3.2)

\[
O_{\text{O}}^x \rightarrow O_{\text{O}}^{*} + V_{\text{O}}^{**}
\]  
(3.3)

Null = \[V_{\text{Mg}}'' + 2V_{\text{Al}}'' + 4V_{\text{O}}^{**}\]  
(3.4)

Point defects in high-bandgap ionic compounds like spinel are typically charge-compensated by ionic rather than electronic defects, with interstitial (Frenkel) and anionic defects \((O_i^*, V_o^{**})\) less favorable than Schottky defects due to strain in the close-packed anion lattice. Cation inversion (antisite defect) is the predominant intrinsic point defect in spinel and is self-compensating:

\[
M_{8\text{Mg}}^x + Al_{\text{Al}}^x \rightarrow Mg_{\text{Al}}' + Al_{\text{Mg}}^*
\]  
(3.5)
Inversion causes variation in $u$, affecting the path of diffusing species and altering the equilibria of other defects.\textsuperscript{79} For example, Eq. (3.5) combines with Eqs. (3.1-3.4) to replace $V''_{Al}$ with $V''_{Mg} + Mg'_{Al}$ or $V''_{Mg}$ with $V''_{Al} + Al'^*_{Mg}$. Inversion is induced simply by heating to higher temperature and has been quantified by X-ray diffraction (XRD),\textsuperscript{90} nuclear magnetic resonance (NMR),\textsuperscript{88,91} electron spin/paramagnetic resonance,\textsuperscript{92} neutron diffraction,\textsuperscript{93} optical absorption,\textsuperscript{94} Raman spectroscopy,\textsuperscript{95,96} and simulations.\textsuperscript{87,97}

Extrinsic point defects are created by stoichiometry [Eqs. (3.6) and (3.7)], introduced during synthesis, or caused by Mg/MgO volatilization [Eq. (3.8)]. Sintering in graphitic furnaces adds an additional reaction affecting defect equilibrium by generating oxygen vacancies [Eq. (3.9)].

\begin{align*}
\text{Al}_2\text{O}_3-\text{rich} & \rightarrow \text{Al}^*_{Mg}, \text{compensated by } V''_{Mg}, V''_{Al}, \text{or } O''_i \quad (3.6) \\
\text{MgO-} & \text{rich} \rightarrow \text{Mg}^*_{Al}, \text{compensated by } Mg'^*_{i}, Al'^*_{i}, \text{or } V'^*_{O} \quad (3.7) \\
\text{Null} & = V''_{Mg} + 2Al^*_{Al} + 3O^*_{O} + V'^*_{O} + MgO_{(g)} \quad (3.8) \\
C + O^*_{O} & \rightarrow V'^*_{O} + CO_{(g)} \quad (3.9)
\end{align*}

The consensus is that excess aluminum occupies magnesium sites and excess magnesium occupies aluminum sites, but experimental studies are contradictory as to compensating defects. XRD and magic-angle NMR indicate $V''_{Al}$ are preferred in $\text{Al}_2\text{O}_3$-rich spinel,\textsuperscript{93,98} although $V''_{Mg}$ may exist simultaneously and the viability of $O''_i$ is not addressed. In MgO-rich compositions, enhanced sintering is explained by charge-compensation with $V'^*_{O}$,\textsuperscript{43,85,89,99} with possible confirmation by optical methods.\textsuperscript{94,100} Simulations also conflict as to compensating defects (see Table 3.2), indicating aluminum defects may be even less favorable than oxygen defects. Oxygen interstitials have the highest mobility even though their formation energy is higher and Schottky defects have the lowest formation energy apart from inversion. Simulations also indicate that charged defects attract oppositely-charged defects, leading to defect associates, with lower formation energies noted for defect pairs, trimmers, and cluster.\textsuperscript{101,102} Simulations indicate impurities lower defect formation energies, and aliervalent substitutions require charge-
compensating defects that likely affect properties similarly to stoichiometry. UV irradiation affects lower-energy defects such as electron-hole recombination, gamma-ray irradiation induces point defects such as inversion, and neutron irradiation induces higher-energy defects such as cation and oxygen vacancies.

Table 3.2 Calculated Point Defect Formation Energies and Diffusion Barriers.

<table>
<thead>
<tr>
<th>Defect</th>
<th>Formation Energy E_F (eV)</th>
<th>E_F Per Defect (eV)</th>
<th>Diffusion Barrier (eV)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgAl_2O_4</td>
<td>-21.8^{67,104}</td>
<td>-</td>
<td>-</td>
<td>Exothermic, 5-8% vol. increase</td>
</tr>
<tr>
<td>MgO</td>
<td>-5.68^{104}</td>
<td>-</td>
<td>-</td>
<td>Lowest stability</td>
</tr>
<tr>
<td>Al_2O_3</td>
<td>-15.63^{104}</td>
<td>-</td>
<td>-</td>
<td>γ-Al_2O_3 also stable</td>
</tr>
<tr>
<td>Anti-site</td>
<td>0.48-0.6^{101}</td>
<td>0.32^{101}</td>
<td>-</td>
<td>Defect pair, E_F decreases with separation</td>
</tr>
<tr>
<td></td>
<td>2.3, 4.6^{115}</td>
<td>-</td>
<td>-</td>
<td>Defect pair, replacement (Al_{Mg}^{+}, Mg_{Al}^{-})</td>
</tr>
<tr>
<td>M_{Si}^{**}</td>
<td>7.58^{101}</td>
<td>2.2^{101}</td>
<td>0.56^{116}</td>
<td>Two Split M_{G}'' + V_{Mg}''</td>
</tr>
<tr>
<td></td>
<td>6.6-6.7^{101}</td>
<td>-</td>
<td>-</td>
<td>Frenkel (interstitial + vacancy)</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>3.34^{101}, 5.46^{102}</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Al_{i}^{***}</td>
<td>9.7^{101}</td>
<td>9.7^{101}</td>
<td>0.56^{101,116}</td>
<td>Decays → Al_{Mg}^{+} +2Mg_{Al}'' +V_{Mg}''</td>
</tr>
<tr>
<td></td>
<td>8.4-8.8^{101}</td>
<td>4.4^{101}</td>
<td>-</td>
<td>Split (Al_{i}'''' + M_{G}'''' + V_{Mg}''')</td>
</tr>
<tr>
<td></td>
<td>7.3-7.7^{101}</td>
<td>-</td>
<td>-</td>
<td>Ring defect (3Al_{i}'''' + 3V_{Al}''')</td>
</tr>
<tr>
<td></td>
<td>4.39^{101}, 6.93^{102}</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>O_{i}^{-}</td>
<td>8.9-9.2^{101}</td>
<td>4.5^{101}</td>
<td>0.29^{116}</td>
<td>Two split O_i including V_{O}''</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>4.43^{101}, 5.50^{102}</td>
<td>-</td>
<td>Frenkel (interstitial + vacancy)</td>
</tr>
<tr>
<td>V_{Mg}^{*}</td>
<td>6.65^{101}</td>
<td>3.34^{101}</td>
<td>0.68^{116}</td>
<td>Frenkel (interstitial + vacancy)</td>
</tr>
<tr>
<td>V_{Al}^{*}</td>
<td>8.78^{101,102}</td>
<td>4.39^{101}</td>
<td>2.00^{116}</td>
<td>Frenkel (interstitial + vacancy)</td>
</tr>
<tr>
<td>V_{O}^{**}</td>
<td>8.86^{101}</td>
<td>4.43^{101}</td>
<td>1.67^{116}</td>
<td>Frenkel, E_F reduced by inversion</td>
</tr>
<tr>
<td>V_{O}^{-}</td>
<td>1.29-6.73^{104}</td>
<td>6.73^{104}</td>
<td>1.8-4.3^{104}</td>
<td>V_{O}^{x}, reduced by P_{O2}, Ca, Zn, Cu</td>
</tr>
<tr>
<td>Schottky</td>
<td>24.7^{101,117}</td>
<td>3.5-4.3^{81,101}</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>3.5-5.3^{102,117}</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Bandgap</td>
<td>7.75-7.8^{118,119}</td>
<td>-</td>
<td>-</td>
<td>[e^+ h^+], reduced by Ca, Zn, Cu</td>
</tr>
</tbody>
</table>

Density Functional Theory (DFT),^{101,104} Temperature Accelerated Dynamics & Kinetic Monte Carlo,^{116} Pair Potential Simulations.^{102}

Deformation, microstructure evolution, and properties are also significantly affected by planar defects and dislocations [Sections 3.2.4, 3.4.4, 3.5, 3.6.1, 3.7.2]. Surface energy is anisotropic, yielding a faceted octahedral habit, with crystallites^{108} and polycrystal grains^{109} typically terminating on (111) planes, although (100) planes may actually have lower surface energy.{^{110,111} Interface energies are in turn affected by stoichiometry, impurities, additives, and
Grain-boundary grooving studies indicate a variable ratio of grain boundary to surface energy, and grain-boundary mobility is generally low. Dislocations move primarily on (110), (111), and sometimes (100) planes, depending on stoichiometry, and slip occurs along <110> directions, while cleavage is typically along (111) planes.

### 3.2.3. Diffusion

Mg$^{2+}$ has the highest diffusivity of the constituent ions and Al$^{3+}$ is slightly lower (Fig. 3.6). Ionic conductivities mirror diffusivities and transport occurs by a defect-assisted interstitial mechanism that is accentuated by stoichiometry. O$^{2-}$ diffusivity is orders of magnitude lower than cation diffusivities, as expected for the largest ion and the close-packed lattice. Sintering experiments indicate similar activation energies to O$^{2-}$ self-diffusion, indicating this is rate-limiting. However, the O$^{2-}$ grain-boundary diffusivity is expected to be rate-limiting as it may be lower. Understanding is complicated because of the dependence of diffusion on stoichiometry and planar defects, which both vary during sintering. O$^{2-}$ diffusion is expected to be higher in MgO-rich compositions due to the higher oxygen vacancy concentration indicated by sintering experiments. However, studies indicate either a slight increase or much higher O$^{2-}$ diffusion for Al$_2$O$_3$-rich compositions.

Fig. 3.6 Diffusion coefficients for spinel species, adapted with permission.
3.2.4. Optical Properties

Spinel has a wide transmission window (~190 nm < \( \lambda \) < 6000 nm) that is limited by the UV and IR absorption edges (Fig. 3.7). IR transmission decreases starting at ~4-5 \( \mu \)m and reaches zero by ~7 \( \mu \)m, with the IR absorption edge lowered by up to ~1 \( \mu \)m for \( \text{Al}_2\text{O}_3 \)-rich compositions.\(^1\) Some transparency is exhibited in the microwave range (70 GHz–105 GHz, 2-4 mm).\(^9\)

![Typical transmission spectrum for transparent polycrystalline spinel.](image)

The total intensity transmitted through a window is the total forward transmittance (TFT, \( I_T \)), while that within a narrow cone (3°–5°) along the incident direction is the in-line transmittance (ILT, \( I_{ILT} \)), the difference between the two is the diffuse transmittance (\( I_{DT} \)), or forward scatter. The ILT best characterizes the intensity and accuracy with which the spatial relationship and resolution of image details are transmitted. However, most optical imaging applications require high ILT along a narrower cone and the real in-line transmittance (RIT) is defined for an aperture of ~0.5°.\(^{19}\) In highly transparent compacts with an RIT of >95% theoretical (or >82.2% measured), transmittance becomes nearly thickness-independent as in window glass, and the term translucent is used for RIT <95%.\(^{19,54,130}\) Three main factors reduce transmittance within the transmission window: (i) reflectance (\( R \)), (ii) scatter (\( S \)), and (iii) absorptance (\( A \)) (Fig. 3.8). The relationship between incident radiation of intensity \( I_0 \) and transmitted radiation \( I_T \) is given by:

\[
I_0 = I_T + R + S + A = 1
\]

(3.10)
For stoichiometric spinel at $\lambda = 532$ nm, the specular reflectance from a single surface ($R_{S1}$) is $\sim 7\%$, implying a minimum theoretical reflectance ($R_{S2}$, two surfaces including multiple reflections) of $\sim 13\%$ for a window, limiting the maximum theoretical ILT without anti-reflective coatings to $\sim 87\%$. The diffuse reflectance ($R_D$) can be minimized by ensuring planarity and smoothness. The refractive index ($n$) and reflectivity increase with decreasing wavelength, significantly reducing the theoretical ILT below $\lambda \approx 200$ nm.

![Light transmission through a polycrystalline spinel compact.](image)

Fig. 3.8 Light transmission through a polycrystalline spinel compact.

Scatter is thickness-dependent and caused by phases with different $n$ (pores, precipitates, and impurity and additive phases), regions with variable $n$ (variation in stoichiometry and stress), and variation of $n$ along different crystallographic directions. Light-scattering models are mostly based on Mie theory, with approximations dependent on the size of the scattering center ($d$) relative to the wavelength ($\lambda$): (i) Rayleigh-Gans-Debye scatter ($d > \lambda$), (ii) Mie scatter ($d \approx \lambda$) and (iii) Rayleigh scatter ($d < \lambda/10$). Scatter scales to $d^2$ for Mie scatter and to $d^4 / \lambda^4$ for Rayleigh scatter. Porosity (Fig. 3.9) is a main source of scatter in spinel, the most detrimental being pores the size of the transmitted wavelength. Using a numerical Mie model at $\lambda = 600$ nm, 0.1% porosity (1000 parts per million, ppm) of 400 nm diameter pores reduces theoretical ILT to nearly zero for an 0.8 mm thick polycrystalline compact with $n = 1.76$. Even 0.01% (100 ppm) of 400 nm diameter pores at $\lambda = 600$ nm or of 40 nm pores at $\lambda = 200$ nm reduces theoretical ILT to $\sim 50\%$ for a 1 mm thick spinel compact (Fig. 3.10). Even at longer IR
wavelengths, in the case of imaging applications, only very thin windows tolerate smaller pores (<100 nm). Reducing the pore size by half reduces Rayleigh scatter by one order of magnitude\(^3\) and thus pore concentration and size reduction are one of the main goals of fabrication. Scatter also occurs due to inclusions, impurity phases, and cracks (Fig. 3.11).\(^1,15,44\) Grain boundaries and point defects contribute minimally to scatter at visible and IR wavelengths due to the small thickness (<5 nm) and size, respectively.\(^{131}\)

Fig. 3.9 (a) Nano-pores at triple junctions in HIP spinel compact (arrows, TEM-brightfield) and (b) intra-crystalline pores in HIP spinel compact (arrows, TEM-darkfield).

Fig. 3.10 Calculated transmittance versus pore diameter for spinel (t = 1 mm, 0.01% porosity),\(^{133}\) adapted with permission.
Fig. 3.11 Scattering centers in transparent spinel compacts; (a) impurity-rich (Fe, Ni, S) phases in compact HP with high-purity powder (arrows), (b) micro-cracked grain boundaries in reactive-sintered HP/HIP compact (bright areas, arrows), reproduced with permission.

Another source of scatter in spinel is intrinsic birefringence (IBR, ~50 nm/cm) at UV wavelengths due to refractive index difference along the more densely-packed <111> unit cell cube diagonals versus the <001> cube edges. However, IBR is ~0 in polycrystalline compacts. Stress birefringence (SBR) also occurs due to local strain variation and is in the order of ~5 nm/cm. The refractive index of spinel does not change significantly with wavelength, as indicated by the low Abbé number (~60), resulting in reduced chromatic aberration. Its variation with temperature is also low (dndT ~3 × 10^{-6} K^{-1} from 3 to 5 μm).

Absorption in spinel arises from several sources and even ppm volume fractions of absorbing centers can lead to opacity in thicker compacts (Sidebar 3). As for scatter, absorption is thickness-dependent and obeys a Beer-Lambert relationship [Eq. (3.11)]. In the case of scatter, the absorption coefficient (α) is dependent upon a volume fraction and a scattering cross-section. The sensitivity of transmittance to ppm volume fractions of scattering or absorbing centers is arguably the main challenge of transparent spinel fabrication.

\[ I_T = I_0 e^{-\alpha t} \]  

(3.11)

3.2.5. Mechanical Properties

The fracture toughness of spinel varies between ~1.4-2.0 MPa m^{1/2}, with an apparent Hall-Petch dependency for coarse grains (greater than ~50 μm). Lower toughness has been correlated with inter-granular fracture (Fig. 3.12), predominantly in coarse-grained microstructures, probably due to grain-boundary embrittlement by residual LiF, impurities, or
residual stress. Somewhat in contrast, coarse-grained microstructures exhibit limited $R$-curve behavior due to frictional grain-bridging and grain-wedging. Thus, strengthening grain boundaries should improve toughness. Strength decreases for inter-granular fracture that persists in coarse-grained microstructures. In fact, weak boundaries of large grains have been proposed to serve as critical surface flaws. Porosity and second phases do not necessarily serve as limiting flaws in highly-transparent compacts as they demand <0.01% porosity and second phases, of sizes typically <50 nm. Coarse-grained microstructures have long been recognized as a source of lower strength, but fine-grained, highly-transparent spinel compacts have only recently been produced. Microstructure refinement exhibits significant hardness increases for grain sizes less than ~1 µm and a Hall-Petch relation is observed. Despite the relevance to projectile erosion during penetration, the mechanism for hardness changes in spinel is not known. Nevertheless, reducing grain size is one of the main goals of transparent spinel processing. However, for transparent armor, cost outweighs small additional hardness gains associated with fine grain sizes and sizes in the hundreds of microns are often acceptable. Relatively little is known about the effect of grain size on ballistic performance due to the complexity of failure. Spinel is susceptible to moisture-assisted crack growth, but the effect is significant mainly for coarse-grained microstructures. It appears that no slow crack growth studies for single crystals exist; nonetheless, the results demonstrate the importance of grain boundaries in dictating strength.

![Fracture surfaces of spinel showing mixed-mode inter- and trans-granular fracture](image)

**Fig. 3.12** Fracture surfaces of spinel showing mixed-mode inter- and trans-granular fracture for (a) HP lower-purity powder and (b) HP higher-purity powder, without additives. With LiF addition, fracture becomes predominantly inter-granular.

### 3.2.6. Physical Requirements

Spinel physical requirements depend on application. Requirements for transparent armor are high ILT in the visible range, compatibility with near-IR (0.4-0.92 µm) night-vision and
thermal imaging systems,\textsuperscript{7} low areal density, high hardness, multi-hit capability, and low cost due to the volumes required.\textsuperscript{11,18} In the case of spacecraft windows, fracture strength and toughness are more important.\textsuperscript{4} Requirements for IR windows and domes are high RIT in the atmospheric windows from the UV to the mid-IR, possibly transmittance in the microwave region,\textsuperscript{10} low absorption near the IR absorption edge and especially at 4.8 $\mu$m, low emissivity, flexural strength, impact and erosion resistance, thermo-mechanical stability, low $dn/dT$, and thermal shock resistance.\textsuperscript{7,18} Military requirements are increasingly calling for multi-spectral capability\textsuperscript{11} and tri-mode multi-spectral seeker domes satisfying additional RF shielding requirements\textsuperscript{145} have been successfully fabricated.\textsuperscript{146} Transmittance requirements are most stringent for imaging applications, with sensor windows requiring error of $<$1/10 of $\lambda$ over the aperture size.\textsuperscript{7} UV lithography components require high RIT, especially near the UV absorption edge but less stringent mechanical properties. UV and IR absorption edges need to be pushed towards theoretical energies and absorption near the edges lowered to enable UV-lithography and increased demands for IR-targeting applications.\textsuperscript{30} A combination of low Abbé number combined with high refractive index (compared to glasses) enables miniaturized lenses\textsuperscript{7} and refractive index variation with stoichiometry may enable flat graded refractive-index lenses. Properties of polycrystalline spinel compacts are summarized in Table 3.3.

3.3. Key Variables

Spinel is inherently difficult to sinter due to: (i) low oxygen lattice-diffusion that requires high sintering temperature, (ii) Mg/MgO volatilization that causes stoichiometry variation and gradients, (iii) a propensity for coarsening exacerbated by high grain-boundary versus surface energy, surface-energy anisotropy, and LiF additive, and (iv) extreme sensitivity to impurities, additives, processing parameters, and compact size. These issues accentuate the difficulty in attaining the near-theoretical density required for transparency. In addition, the multitude of fabrication variables combined with property variation with stoichiometry further complicates processing, and in turn understanding. The crux of transparent spinel fabrication lies in understanding the complexities of fabrication, and in particular of green-body formation and of interactions during sintering between material, microstructure, compact, and process variables, from the nanometer to the compact scale (Fig. 3.13). In particular, three variables are key to successful processing: (i) particle-size characteristics, (ii) stoichiometry, and (iii) impurities.
Gross deficiencies in these variables cannot be compensated for by adjusting processing parameters and achieving transparency entails controlling them throughout processing. Post-treatment and finishing are not described here, but grinding and polishing can be the most time-consuming and expensive step for components like missile domes and new methods are being explored to reduce costs. 

Table 3.3 Physical Properties of Transparent Polycrystalline Spinel Compacts.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting point (°C)</td>
<td>2105°C–2135°C</td>
</tr>
<tr>
<td>Lattice parameter (a, 3.0 &gt; x &gt; 1.0, Å)</td>
<td>8.797–8.808</td>
</tr>
<tr>
<td>Stoichiometry range max. (mol.% Al₂O₃, MgO:xAl₂O₃)</td>
<td>38.2(1996°C)–90.1(1994°C), 0.6–9.1</td>
</tr>
<tr>
<td>Stoichiometry range in practice (MgO:xAl₂O₃)</td>
<td>1.0–3.0</td>
</tr>
<tr>
<td>Max. solubility Al₂O₃ in MgO (mol.% , 2269K)</td>
<td>9.4</td>
</tr>
<tr>
<td>Max. solubility MgO in Al₂O₃ (mol.% , 2073K)</td>
<td>0.012</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>3.58 g/cm³</td>
</tr>
<tr>
<td>Young’s modulus (GPa)</td>
<td>19318; 260–31066,147</td>
</tr>
<tr>
<td>Shear modulus (GPa)</td>
<td>192147</td>
</tr>
<tr>
<td>Poisson’s ratio</td>
<td>0.26</td>
</tr>
<tr>
<td>Hardness Knoop (GPa, 200 g). (GPa, unspecified 500°C)</td>
<td>1.03810, 1.450–1.6505,18,147</td>
</tr>
<tr>
<td>Hardness Vickers (GPa, 2.5 Kg, 5 Kg, 10 Kg)</td>
<td>12.0–16.8138</td>
</tr>
<tr>
<td>Flexure strength (MPa)</td>
<td>70–2505,7,18,147,148, 470138, (~500)5,37a</td>
</tr>
<tr>
<td>Fracture toughness (MPa/µm)</td>
<td>1.4–2.018,147</td>
</tr>
<tr>
<td>Dielectric constant (ε, 1 KHz – 1 MHz)</td>
<td>9.1918, 8.217</td>
</tr>
<tr>
<td>Loss tangent (δ, 1 KHz, 1 MHz, 35 GHz)</td>
<td>0.0002517, 0.000217, 0.0002218</td>
</tr>
<tr>
<td>Refractive Index (n, 532 nm)</td>
<td>1.7108</td>
</tr>
<tr>
<td>Abbé number</td>
<td>~60720</td>
</tr>
<tr>
<td>Refractive index homogeneity (dn/dλ, &gt;3” diameter)</td>
<td>&lt;5x10^-6.10</td>
</tr>
<tr>
<td>dn/dT (3-5 µm, 3 GHz) 10⁶/K</td>
<td>~3, 207,18,34</td>
</tr>
<tr>
<td>Band gap (eV)</td>
<td>7.7SC30</td>
</tr>
<tr>
<td>Absorption coefficient (3.39 µm, 532 nm, 193 nm, cm⁻¹)</td>
<td>0.0187, 0.4147, 2.730</td>
</tr>
<tr>
<td>Absorption coefficient (5 µm, 25°C, 250°C, 500°C, cm⁻¹)</td>
<td>0.4, 0.7, 1.3147</td>
</tr>
<tr>
<td>Intrinsic birefringence (IBR, 193 nm, 365 nm, nm/cm)</td>
<td>541SC20,30, 3.620, &lt;2PC(193 nm) 20,30</td>
</tr>
<tr>
<td>Stress birefringence (SBR, 193 nm, nm/cm)</td>
<td>~3SC30, ~5PC30</td>
</tr>
<tr>
<td>Transmission Window (µm)</td>
<td>~0.19–7.0147</td>
</tr>
<tr>
<td>Theoretical in-line transmittance (window, 532 nm)</td>
<td>87%147 , typical 70–84%5,</td>
</tr>
<tr>
<td>Emittance (2000K, 1 mm thick)</td>
<td>~0.9 (6-10 µm), ~0 (&lt;3.5 µm)18</td>
</tr>
<tr>
<td>Thermal expansion (30-200°C, 25°C–1000°C, 30°C–1400°C, range not given, K⁻¹)</td>
<td>6.97-10, 7.90-10, ~8-106,18,147, 5.6-5.9-106,18,34</td>
</tr>
<tr>
<td>Thermal conductivity (T_Amb, W/m-K, 25°C)</td>
<td>13.434, 14.618, 14.7147, ~1618,257,10</td>
</tr>
<tr>
<td>Thermal shock resistance (R’ = σ(1- υ)/καE, kW/m)</td>
<td>1.11, 1.410, 1.9-2.1138, 1.918</td>
</tr>
<tr>
<td>Chemical resistance</td>
<td>HF, H₂SO₄, HNO₃, NaOH45,147</td>
</tr>
<tr>
<td>Erosion (rain, 756 km/hr., 20 min., 2 mm drop size)</td>
<td>No damage 147, High resistance138</td>
</tr>
<tr>
<td>Erosion (sand, 75 m/s, 3 mg/cm² loading, 38-44 µm)</td>
<td>No damage 147, High resistance138</td>
</tr>
</tbody>
</table>

SC (single crystal), PC (polycrystal), all quantities stoichiometric unless indicated, *Unusually high value
3.4. Particle-Size Characteristics

This section details the effects of particle-size characteristics during processing of transparent spinel compacts.

3.4.1. Synthesis

Spinel has been synthesized from a wide variety of precursors (metals, oxides, hydroxides, chlorides, nitrates, carbonates, sulfates, and alkoxides) and methods (mechanical alloying, freeze drying, spray drying, solid-state sintering, sol-gel, hydrothermal, co-precipitation, gelcasting, flame-spray pyrolysis, self-propagating high-temperature synthesis, chemical vapor deposition, atomic layer deposition, and plasma spray). Acceptable powders for transparent spinel fabrication typically require nanometer-sized particles with high surface area (>10 m²/g) to provide a higher driving force for sintering. In addition, it is desired to have narrow particle-size distribution, minimal agglomeration, adequate flow properties, stoichiometry control, minimal impurities, and cost matching the intended application. However, powder properties are difficult to characterize in practice. Particle-size analysis by laser scattering can be flawed due to inadequate dispersion and shielding of smaller particles by larger ones, and microscopy samples only small volume fractions, possibly missing large inclusions. Stoichiometry is difficult to quantify by chemical analysis and XRD with an accuracy that reflects processing sensitivity to it. Volatile impurities such as carbon, nitrogen, and sulfur are difficult to quantify.
and are often not quoted by suppliers. These issues make it difficult to pinpoint problems caused by the starting powders that occur later during processing.

3.4.2. Green Body Formation

The green-body state determines the sintering activity and it is profoundly influenced by particle size characteristics. The goal of synthesis, pre-treatment, and shaping is obtaining green bodies composed of fine, uniformly-sized particles with high coordination and homogeneity. Achieving this may require involved particle sizing, such as centrifugation, filtration, and sedimentation. Perfect packing of spheres yields theoretical pore-size distributions of \( \sim \frac{1}{5} \) of particle size. Yet even with optimal processing pore sizes are at least twice that, likely reflecting particle packing resembling GB1 in Fig. 3.14. Nevertheless, defect-free, homogeneous, highly-coordinated green bodies with narrow pore-size distributions like GB1, when obtained with high-purity nano-powders, allow sintering forces alone to achieve high densification (>95%) at temperatures up to 200°C lower than less optimal bodies. With additional pressure, full density has been reached without additives while exhibiting high transparency and nanometer-sized grains. The best results have been obtained using flame-spray pyrolysis powders, whose better flow properties likely contribute to higher coordination and smaller pore-size distributions. Consolidation methods yielding the best results are shaping from aqueous or organic slurries or colloidal suspensions using organic dispersants combined with slip- or gel-casting. However, these methods require drying, solvent debinding, or lengthy thermal cycles to ensure complete, defect-free organics outgassing. Optimal dispersion of binders, dispersants, and sintering additives, typically added during milling or wet processing, is also essential. Alternatively to wet processing, high solids-loading slurries have been spray- or freeze-dried into better-flowing powders consisting of soft-agglomerate granules, which have been dried and cold-pressed into acceptable green bodies. However, cold-pressing or CIP require high loads (\( \sim 100-500 \) MPa) to achieve high green densities, and cold-pressing introduces density gradients due to friction from die walls. Acceptable green bodies have also been obtained by additionally milling or freeze-drying more agglomerated powders followed by dry or wet consolidation.
3.4.3. Particle-Size, Size Distribution, and Agglomeration

Smaller particles result in smaller green-body inter-particle porosity and sizes <50-60 nm decrease PS/HIP temperature <1400°C, improving compact visible and near-IR transmittance and mechanical properties.\(^3\)\(^8\) However, small size and high surface-area increase susceptibility to agglomeration from weak attractive forces, such as friction-induced charging during dry-milling or hydrogen-bonding during aqueous processing.\(^5\)\(^,\)\(^3\)\(^8\)\(^,\)\(^4\)\(^2\) High surface-area powders also provide more residence sites for adsorbed gases, water, and impurities and may be more susceptible to chemical reactions.\(^4\)\(^8\)\(^,\)\(^1\)\(^5\)\(^0\) Nanometer-sized powders are also more expensive, are cumbersome to handle, require large volume reduction, and are difficult to disperse and to sieve to uniform particle-size.\(^2\)\(^9\) In addition, compacts HP/HIPed with nanometer-sized powders (<50 nm) exhibit reduced UV-transmittance and higher refractive-index variation due to a concentration of nanometer-sized small pores (<400 nm) that is one order of magnitude higher than for similarly-made compacts using coarser powders (~70-120 nm).\(^3\)\(^8\)\(^,\)\(^3\)\(^4\)\(^2\) A balance between small particle-size, avoiding agglomeration, and attaining high green-body particle-coordination and homogeneity leads to an optimal particle-size.\(^3\)\(^8\) The lower size-limit with HP/HIP using high-purity powders without additives for maximum transmission at low HIP temperatures (<1300°C) and fine grain-size (<500 nm) with current technology is near ~55 nm.\(^3\)\(^8\) However, even with careful processing, 50-200 ppm nanopores have been observed to survive HIP up to 1700°C.\(^3\)\(^8\) For lower-cost, high-volume applications, lower purity powders, or high additive contents, the optimal size for HP or HP/HIP is perhaps >70-120 nm.\(^1\)\(^5\)\(^,\)\(^3\)\(^8\)\(^,\)\(^4\)\(^2\) Even larger particle or aggregate size (>1-10 μm) may be desirable as coarser powders attain closed porosity at higher temperatures and enable increased outgassing of volatile impurities and additives.\(^1\)\(^5\)\(^1\)
Agglomeration is the most detrimental powder-size characteristic as inter- and intra-agglomerate pores are frequently orders of magnitude larger than intrinsic crystallites (Fig. 3.15).\textsuperscript{38,151} Dense agglomerates differentially sinter; enlarging inter-agglomerate porosity, inducing stresses that can cause cracking, and forming solid skeletons (even during calcining) that limit particle re-arrangement during consolidation and sintering.\textsuperscript{150} These can be difficult to remove without resorting to higher pressures or temperatures, where excessive grain growth occurs, and at worst impossible to remove.\textsuperscript{150} In addition, lower-temperature sintering and tortuous diffusion paths in dense agglomerates trap volatile species.\textsuperscript{149} Some of these features result in optical defects such as pore clusters,\textsuperscript{29} large impurity/additive phases,\textsuperscript{15} and microstructural inhomogeneity.\textsuperscript{151} Agglomerates are best dealt with before green-body formation, and are typically broken down by mechanical milling, ultrasonic or acoustic methods, or removed by sieving.\textsuperscript{38} The best case, although difficult to achieve in practice, is forming soft agglomerates that can be broken by sintering stresses alone.\textsuperscript{29}

![Fig. 3.15 Agglomerates in (a) synthesized sulfate-derived powder,\textsuperscript{38} (b) commercial sulfate-derived powder.\textsuperscript{61}](image)

Wide particle-size distributions are also detrimental and result in wide pore-size distributions in green bodies, making it impossible to tailor sintering regimes that close all pores simultaneously.\textsuperscript{151} They also exacerbate Ostwald ripening and microstructural coarsening. Conversely, narrow particle-size distributions allow higher green-body coordination and homogeneity, lower sintering temperature, and similar-sized particles have similar driving forces for grain growth, resulting in finer-grain size.\textsuperscript{38,151}

3.4.4. Microstructure Evolution

Microstructure evolution during sintering is strongly affected by the green-body state, and also by stoichiometry, impurities and additives, and processing parameters (Sections 3.5-3.7).
Particle re-arrangement in the initial sintering stages is inhibited by green bodies like GB2 in Fig. 3.14 and aided by liquid phases [Section 3.6.2] and pressure [Section 3.7.2]. Higher surface and vapor transport (compared to bulk mechanisms) in initial stages result in coarsening, which is exacerbated by green bodies like GB2 and LiF addition, and inhibited by high heating rates [Sections 3.6.2, 3.7.1, 3.7.4]. Coarsening is also strongly affected by interface energies. The driving force for sintering is reduction of excess interfacial energy\textsuperscript{151} which is accomplished by transforming surfaces into grain boundaries (resulting in densification), or by reducing surface area through coarsening (without shrinkage); \(\Delta(\gamma A) = \Delta\gamma A + \gamma \Delta A\), where \(\gamma\) is the interfacial energy and \(A\) is the interfacial surface area.\textsuperscript{152} High surface energy drives both processes, but high grain boundary versus surface energy favors coarsening and also makes it less favorable for grain boundaries to advance into pores.\textsuperscript{152} Interface energies are in turn affected by stoichiometry, impurities, additives, and processing parameters (Sections 3.5-3.7).

Volatile species outgassing during initial and intermediate sintering stages is essential to obtaining transparency (Section 3.6) and is inhibited by differential sintering. Differential sintering also occurs on a compact-scale as surfaces sinter more rapidly than the interior due to exposure to higher temperatures and shorter diffusion paths for densification-impeding volatile species to escape.\textsuperscript{151} Compact-scale differential sintering traps volatile species in compact interiors, restricting grain size (Fig. 3.16), and if impurity concentration is high enough, scattering second phases form that display as a hazy central region in compacts.\textsuperscript{15} Differential sintering is exacerbated by green bodies like GB2 in Fig. 3.14, high heating rates (higher temperature gradients), large sample size (longer diffusion distances), sintering atmosphere (Mg/MgO loss), and any variable that accelerates sintering or lowers sintering temperatures (Sections 3.5-3.7).\textsuperscript{151} Green bodies like GB1 in Fig. 3.14, although they attain closed porosity homogeneously, do so at lower temperature and trap higher boiling-point volatiles.

Once closed porosity is attained in the final stage of sintering, densification slows as the sintering stress decreases and mass transport is forced along slower grain boundary and lattice paths. As pore content and size diminish, the pinning effect of remaining porosity on grain boundaries decreases, leading to grain growth. Increasing kinetics with higher temperature [Section 3.7.1] or applied fields [Section 3.7.1] exacerbates grain-boundary mobility and grain
growth and can cause pore occlusion, which is virtually impossible to remove. Thus, long sintering times or pressure [Section 3.7.1] are used to close remaining porosity.

Fig. 3.16 (a) Optical microscopy image of microstructure of 2 mm thick HP stoichiometric spinel compact, and (b) similarly processed compact, but 4 mm thick and with pressure applied at a lower temperature.\textsuperscript{15}

3.5. Stoichiometry

Stoichiometry affects virtually every property of spinel and its variability and spatial and temporal variation during sintering greatly increases processing complexity.\textsuperscript{1,5,45,48,54,70,71,84,94,134,153,154-156} However, as the cubic structure and transparency are retained,\textsuperscript{71} stoichiometry offers opportunities to vary properties\textsuperscript{71} and may even enable graded-property compacts.\textsuperscript{7} Transparent components have successfully been made with $0.98 < x < 3.0$,\textsuperscript{1,70,71} with MgO and Al$_2$O$_3$ precipitates (Fig. 3.17) typically observed beyond this range.\textsuperscript{4,15,67,70} These scatter wavelengths on the length scale of the precipitates and surrounding strain fields, and also affect mechanical properties.\textsuperscript{15} Mechanical properties comparable to stoichiometric compositions have been observed for $x = 1.2$.\textsuperscript{71} However, other studies report increased hardness (up to $x = 2.0$),\textsuperscript{157} fracture strength (up to $x = 2.0$),\textsuperscript{157} and fracture toughness (up to $x = 1.3$\textsuperscript{157} and $x = 2.0$\textsuperscript{45,153}) for Al$_2$O$_3$-rich stoichiometry. Increased fracture toughness in one case was attributed to transgranular fracture and greater plasticity at grain boundaries,\textsuperscript{153} whereas in another increased properties were attributed to hard Al$_2$O$_3$ precipitates and associated crack deflection and bridging.\textsuperscript{157} However, other studies indicate Al$_2$O$_3$ precipitates and Al$_2$O$_3$-rich grain boundaries decrease mechanical properties due to residual stress and intergranular fracture,\textsuperscript{4} and Al$_2$O$_3$-rich compositions exhibit substantial hardness decrease above $x > 2$.\textsuperscript{141} Nevertheless, Al$_2$O$_3$-rich compositions ($x = 2$) appear less sensitive to microcracking and display higher transmission and fracture toughness compared to stoichiometric compositions when using reactive sintering and HP/HIP.\textsuperscript{44,45} High transmittance for Al$_2$O$_3$-rich stoichiometry has also
been obtained using reactive-sintering with PS/HIP (2 < x < 2.5), with opacity observed for x < 1.8.\textsuperscript{51} However, with HP/HIP of precalcined powders, the best transmittance was noted for x = 1.2.\textsuperscript{71} Although advantageous in yielding high transparency and fracture toughness in some instances, stoichiometry has major drawbacks of precipitation and scattering for MgO-rich compositions, and lower IR absorption edge, densification rate, and hardness for Al$_2$O$_3$-rich compositions. Stoichiometric compositions likely still yield the best combination of densification and properties.\textsuperscript{134}

![Fig. 3.17](image)

Fig. 3.17 (a) MgO precipitates (arrows) in x ~0.995 HP compact\textsuperscript{15} and (b) Al$_2$O$_3$ precipitates (arrows) and Al$_2$O$_3$-rich grain boundaries in HP/HIP compact\textsuperscript{4}, reproduced with permission.

### 3.5.1. Stoichiometry Gradients

Mg/MgO evaporation occurs preferentially at surfaces, causing stoichiometry gradients within grains,\textsuperscript{70,81,84} and it is exacerbated by: (i) high temperature, (ii) low pO$_2$, (iii) reducing conditions, and (iv) LiF addition.\textsuperscript{31,88} Stoichiometry gradients between grain boundaries and cores\textsuperscript{70,81,84,129} may cause scatter at UV wavelengths as the lattice parameter decreases with Al$_2$O$_3$-rich stoichiometry according to Vegard’s law,\textsuperscript{70} implying a concomitant change in refractive index.\textsuperscript{158} Differences in thermal expansion coefficient between Al$_2$O$_3$-rich boundaries and grain cores may also cause residual stress and grain-boundary embrittlement.\textsuperscript{15} Preferential Mg/MgO loss at compact surfaces causes compact-scale stoichiometry gradients.\textsuperscript{74,75} As Mg/MgO volatilization is compensated by oxygen vacancies [Eq. (3.8)], densification of the compact exterior is enhanced, exerting a backstress that opposes densification of the interior.\textsuperscript{75} Interior densification is further inhibited by species diffusing along the slower paths of the densified exterior.\textsuperscript{75} With pressureless sintering, by the time Mg/MgO loss leads to Al$_2$O$_3$-rich stoichiometry and exterior densification slows, there is already increased porosity in the interior,
entrapped pores in the coarsened Al₂O₃-rich zone, and a gradient towards smaller grain size in the compact interior (Fig. 3.18). In addition to porosity, transmittance may be further reduced by refractive index inhomogeneity due to the stoichiometry gradient. The microstructural features that distinguish this effect are obscured in later stages and for thinner compacts. MgO volatilization can be reduced via pressureless sintering in air, embedding compacts in powder of similar stoichiometry, shielding with refractory foils, or introducing inert atmosphere once closed porosity is reached during vacuum sintering.

![Fig. 3.18 Composite SEM cross-section of pressureless-sintered stoichiometric spinel compacts, reproduced with permission.](image)

**Sidebar 1: Defect Chemistry and Grain-Boundary Mobility:**

Astoichiometry is especially relevant for interfaces, which are a key determinant of microstructure evolution. Al₂O₃-rich grain boundaries and triple junctions have been observed in polycrystalline compacts [Fig. 3.19(a)], even for MgO-rich compositions. Stoichiometry gradients imply defect-chemistry gradients and suggest a space-charge layer surrounding a charged grain-boundary core [Fig. 3.19(b)]. However, disagreement exists as to the charge-compensating defects. Chiang and Kingery argued that in stoichiometric and Al₂O₃-rich compositions, anion defects were unlikely due to the close-packed anion lattice and cation interstitials were also unlikely as charge-compensation is expected by cation vacancies. As anti-sites are the predominant intrinsic defects, only Al_{Mg} remain to account for Al₂O₃-rich boundaries. They suggested a positive space-charge layer enriched in Al_{Mg} adjacent to a negative grain-boundary core, assumed to consist of cation vacancies or oxygen interstitials, as these are more likely to reside there. Based on thermodynamic considerations, Nuns et al. also suggested a positive space-charge with segregated Al_{Mg} and assigned a negative
grain-boundary core, but based on simulations\textsuperscript{115} assumed it to be composed of $V_{Mg}^*$.\textsuperscript{159} For MgO-rich compositions, Chiang and Kingery again assumed a positive space-charge, this time occupied by $Al^{***}$, to account for $Al_2O_3$-rich stoichiometry at the boundaries. However, Ting and Lu argued that charge-compensation by cation interstitials in MgO-rich compositions contradicted increased densification\textsuperscript{154,160,161} attributed to $V_{O}^{**}$.\textsuperscript{43,75,99,128} Based on the Brouwer equilibrium diagram [Fig. 3.20(a)] they argued MgO-rich stoichiometry was charge-compensated by $V_{O}^{**}$. Based on proton diffusion experiments, optical absorption, and density measurements, Okuyama suggested that both cation interstitials and $V_{O}^{**}$ charge-compensate MgO-rich stoichiometry.\textsuperscript{85}

![Fig. 3.19](image)

Fig. 3.19 (a) Atomic concentration versus distance from grain boundary in $x = 1.05$ PS/HIP spinel compact\textsuperscript{\textsuperscript{84,159}} (adapted with permission), (b) schematic of MgO-depleted grain boundaries.
Uncertainty also exists as to grain-boundary mobility variation with stoichiometry. Chiang and Kingery noted $10^2$ to $10^3$ higher grain-boundary mobility in MgO-rich compositions and decreasing mobility, after a slight initial increase, with increasingly Al$_2$O$_3$-rich compositions [Fig. 3.20(b)]. Reduced mobility was attributed to solute drag caused by segregated native cation defects. Uematsu et al. noted a large initial increase, followed by a decrease in grain-boundary mobility for increasingly MgO-rich compositions and a steadily increasing mobility for Al$_2$O$_3$-rich compositions. Chiang and Kingery noted the discrepancy may be due to different experimental conditions; they used reducing H$_2$ atmosphere and packed compacts in powder of similar stoichiometry enclosed in molybdenum foil, restricting MgO loss and solute segregation, whereas Uematsu et al. used open H$_2$ atmosphere, where Mg/MgO volatilization occurs.
3.5.2. Grain Growth

Grain-boundary mobility (Sidebar 1) and grain growth are related phenomena, and abnormal grain growth has been observed in MgO-rich and more prevalently in Al₂O₃-rich compositions. However, it occurs primarily at surfaces, where Mg/MgO volatilization is greater. MgO-rich compositions generally display smaller grain size, even though mobility is greater, possibly influenced MgO precipitate drag. On the other hand, smaller grain size is also observed in stoichiometric compositions, where MgO precipitates are not expected. These discrepancies, including those discussed in Sidebar 1, highlight the sensitivity of spinel to small variations in stoichiometry, processing, and experimental conditions, and indicate a complex defect chemistry. In order for accurate comparisons, stoichiometry, defect chemistry, sintering atmosphere, Mg/MgO outgassing, and impurity content all need accurate spatial and temporal quantification. In the case of grain-boundary mobility and grain growth in ceramics, there is growing evidence that triple junctions and quadruple points play a determining role, yet in the case of spinel they are often entirely overlooked. The variation in interface energy with stoichiometry, with relevance to coarsening and densification, has also not been quantified. The remaining uncertainty as to the mechanisms occurring at interfaces requires further research as it precludes enabling greater control over densification and properties.

3.5.3. Densification

Stoichiometry strongly affects densification and deformation, and pressureless-sintered MgO-rich compositions densify one order of magnitude faster and attain higher densities than Al₂O₃-rich compositions (Fig. 3.21), attributed to higher oxygen vacancy concentration. The effect of stoichiometry in pressure-assisted sintering is discussed in Section 3.7.2.
3.6. Impurities & Additives

This section describes the effects of impurities and additives in the processing of transparent spinel.

3.6.1. Impurities

Impurities affect interface energy and grain-boundary mobility, and are a key determinant of microstructure and properties. Even a few ppm impart color\textsuperscript{19} and tens to hundreds of ppm can cause absorption over a broad range (Sidebar 3).\textsuperscript{42,94,103,118,167} The tolerable impurity content depends on the specific impurity, processing, and compact size. Generally, starting powders require \( \sim 99.99\% \) purity, <500 ppm cation impurities,\textsuperscript{5,39} and removal of higher vapor pressure volatiles.\textsuperscript{15} Even in thin compacts (<2 mm), as little as 0.1 wt. % of remnant impurity or additive can cause opacity (Fig. 3.22).\textsuperscript{5,15,39} Impurities are present in MgO and Al\textsubscript{2}O\textsubscript{3} constituents, due to incomplete removal of precursors, binders, and processing fluids, and are inadvertently introduced during processing.\textsuperscript{15} As temperature increases during sintering, adsorbed gases, water vapor, organic binders and dispersants, hydroxides, sulfates, sintering additives, and others outgas at different temperatures.\textsuperscript{15} Their removal requires knowledge of outgassing behavior, as assessed by vacuum gauge,\textsuperscript{9} thermal analysis,\textsuperscript{15} or residual gas analysis.\textsuperscript{15} Volatiles are more
easily trapped when inhomogeneously distributed, present in dense agglomerates (GB1 in Fig. 14) or in green bodies that attain closed porosity at lower temperatures (GB2 in Fig. 14), in which case powders may need to be pre-coarsened to reduce sintering activity.\textsuperscript{15} Incomplete volatile impurity removal is exacerbated by high heating rates, insufficient holds, differential sintering, and larger compacts.\textsuperscript{15} Volatile impurities are also trapped by pressure application, use of sintering aids, and applied electric fields, all of which lower densification temperature.\textsuperscript{15,151} Vacuum sintering is beneficial in removing most volatiles, whereas air sintering allows formation of volatiles from organics, carbon, and sulfur, although it may result in swelling as in Al\textsubscript{2}O\textsubscript{3}.\textsuperscript{168} High volatilization temperature species like sulfates 1050°C-1250°C\textsuperscript{9} require careful attention to remove during pressure-assisted sintering.\textsuperscript{15}

![Fig. 3.22 Impurity phases causing opacity in 2 mm thick compact (inset) HP with high-purity spinel powder; (a) amorphous impurity (C,S,K) phase at grain boundary\textsuperscript{15} and (b) decorated grain boundary.\textsuperscript{15} (c) Amorphous phase at triple junction in HIP compact.](image)

Impurities (C, S, Si, Ca, Fe, K, Ti, Na, F, Li, lanthanide cations, and likely others) segregate at surfaces and later reside at grain boundaries.\textsuperscript{15,16,50,70,81,84,112,129,169} Some studies suggest impurities have little effect on grain-boundary mobility and grain growth.\textsuperscript{70,81} However, more recent studies indicate the opposite,\textsuperscript{5,15} with some impurities restricting grain growth by solute drag\textsuperscript{15} and others forming liquid phases or increasing surface diffusion and enhancing grain growth (LiF, CaO).\textsuperscript{15,39} Impurities also modify interface energy. For example, TiO\textsubscript{2} increases the grain boundary relative to surface energy and exacerbates coarsening.\textsuperscript{112} As the microstructure coarsens during sintering and grain-boundary area decreases, segregated impurities concentrate\textsuperscript{140} and further affect grain-boundary mobility, microstructure evolution, strength, and can cause fracture behavior to change from transgranular to intergranular.\textsuperscript{15} In high concentration, impurities and additives form second phases, especially at triple junctions, pining grain boundaries, opposing densification if they have high vapor pressures, causing scatter and
absorption, and reducing mechanical properties. In addition, preferential surface volatilization causes impurity and additive gradients that result in compact-scale microstructure gradients (Fig. 3.16). Impurities like LiF and some transition-metal cations appear to have limited solubility in spinel and incorporate into the lattice, creating defects that affect diffusion and optical properties. The effect of impurities on grain-boundary strength has not been systematically studied, but additives like Y$_2$O$_3$ refine grain size, and increase hardness, flexure strength, and erosion resistance. Composite compacts made with Si$_3$N$_4$ nanodispersoids have recently demonstrated enhanced mechanical properties while still retaining >70% IR transmittance.

### 3.6.2. Sintering Additives

Sintering additives and impurities are inextricably linked, demonstrated by the need for additives with impure powders and the ability to sinter high-purity powders to transparency without them. Many sintering additives have been used to produce translucent or transparent spinel, including Li$_2$O + SiO$_2$, CaO, LiF + NaF, LiF, LiF + CaCO$_3$, AlCl$_3$, AlF$_3$, Na$_3$AlF$_6$, and B$_2$O$_3$. However, LiF (~0.25-4 wt%) is the only sintering aid that consistently enables obtaining highly transparent spinel and likely most commercially manufactured transparent spinel is made with LiF. LiF melts at ~850°C, wets spinel, and likely aids densification by particle rearrangement and liquid-phase sintering. Near its melting point and in sufficient quantity, LiF reacts with spinel and forms a eutectic with MgF$_2$. The products may enhance densification by solution re-precipitation [Eqs. (3.12) and (3.13)].

\[
3\text{LiF} + \text{MgAl}_2\text{O}_4 \rightarrow \text{LiF} : \text{MgF}_2(\text{l}) + 2\text{LiAlO}_2(\text{s}) \tag{3.12}
\]

\[
\text{MgF}_2 + 2\text{LiAlO}_2 \rightarrow \text{MgAl}_2\text{O}_4 + 2\text{LiF} \tag{3.13}
\]
LiF is unique in that lithium and fluorine are highly reactive and can substitute for magnesium and oxygen, respectively, with a valence difference of one. It has even been suggested that a requirement for sintering additives is the ability to create both cation and anion vacancies.\textsuperscript{149} Auger electron spectroscopy,\textsuperscript{169} optical absorption,\textsuperscript{180} secondary ion mass spectroscopy,\textsuperscript{61} transmission electron microscopy,\textsuperscript{182} and sintering experiments\textsuperscript{43} indicate lithium and fluorine are both incorporated in the lattice [Eq. (3.14)].\textsuperscript{180} If fluorine reacts with impurity cations (see below), then only lithium remains to create defects [Eq. (3.15)].\textsuperscript{58} The resulting oxygen vacancies may explain the \(~200\) kJ/mol\textsuperscript{43,173} and \(~200^\circ\)C\textsuperscript{58,173} lower densification activation energy and temperature, respectively. Enhanced formation of spinel during RS\textsuperscript{50,58} has been partially attributed to vacancies caused by lithium incorporation in Al\textsubscript{2}O\textsubscript{3} that allow higher cation diffusion.\textsuperscript{184}
\[ LiF \xrightarrow{MgAl,O_4} Li'_Mg + 2Al^{x}_A l + 3O^{x}_O + F^{*}_O + MgO_{(g)} \] (3.14)

\[ 2Li \xrightarrow{MgAl,O_4} 2Li'_Mg + 4Al^{x}_A l + 7O^{x}_O + V^{**}_O + \frac{1}{2}O_{2(g)} \] (3.15)

Fluorine forms volatile compounds with many impurity cations, which along with LiF have volatilization temperatures below that at which spinel compacts typically reach closed porosity, enabling their removal. LiF removes carbon,\textsuperscript{58,185} sulfur, iron, calcium, and likely other impurities\textsuperscript{15} in the vapor phase [Eqs. (3.16)-(3.18)] and hence LiF addition must be tailored to impurity content. Less LiF is also required with alumina-rich powders.\textsuperscript{54} LiF also lowers magnesium content\textsuperscript{15,173} due to MgF\textsubscript{2} evaporation and perhaps Eq. (3.14).

\[ LiF + C \rightarrow Li + (CF)_{(g)} \] (3.16)

\[ 2LiF + 3(Mg,Al)SO_4 \rightarrow MgAl_2O_4 + 3SO_{2(g)} + O_{2(g)} + LiF_{(g)} \] (3.17)

\[ (2yz)LiF + zMe_xO_y \rightarrow yzLi_2O + xzMeF_{(g)} \] (3.18)

LiF vaporizes between 1000°C and 1400°C and above 1200°C it coarsens spinel crystallites (I.E. Reimanis, Unpublished Work). The slopes of the grain-growth curves in Fig. 3.25 indicate vapor-phase transport (I.E. Reimanis, Unpublished Work), which requires the formation of magnesium- and aluminum-containing volatile species, likely similar to that observed for LiCl.\textsuperscript{184} Although coarsening is detrimental to densification, it is mitigated in pressure-assisted sintering, especially if surface diffusion or grain-boundary diffusional creep is enhanced\textsuperscript{178} and as long as pores migrate as fast as grain boundaries.\textsuperscript{149,151,186} Large or exaggerated grain size and lack of intragranular porosity with LiF indeed suggest enhanced surface or vapor-phase diffusion.\textsuperscript{42,184} In addition, wetting, reaction with spinel, and defect creation suggest interface-energy modification. High surface energy favors pore-boundary attachment and may decrease the ratio of grain boundary to surface energy, favoring densification.\textsuperscript{187} Atomic force microscopy and grain-boundary grooving experiments indicate surface mobility is increased and the interface energy ratio is altered by LiF.\textsuperscript{61}
LiF also counteracts dark color observed in spinel compacts processed in graphitic furnaces by removing carbon and possibly color centers, as suggested by EIS (Sidebar 2).\textsuperscript{16} To work effectively, LiF must be evenly distributed\textsuperscript{178,181} and must leave the compact as it has a different refractive index. LiF can be trapped if too much is used (accelerating sintering\textsuperscript{54}) and hold times are insufficient (especially in larger compacts), with high-sintering activity powders, or with pressure application forcing densification to lower temperatures.\textsuperscript{15} Excess or trapped LiF accumulates at grain boundaries and triple junctions and results in scatter (Fig. 3.26)\textsuperscript{15,46,50,172,179,181} and possibly restricted grain size.\textsuperscript{42} Formation of lithium aluminate and/or Mg/MgO evaporation may also result in MgO-rich regions with poor transmission.\textsuperscript{172,181}

In addition to coarsening and scatter, a major drawback of LiF is grain-boundary embrittlement and intergranular fracture (Fig. 3.27). Although LiF will likely continue to be used in bulk applications; where lower-cost powders are not required or for more stringent applications the trend is to minimize or eliminate LiF entirely. Figure 28 shows typical microstructures with and without LiF for various processing methods.
Fig. 3.26 Optical defects due to LiF (a) decorated grain boundaries,\textsuperscript{46} (b) remnant liquid phase at grain boundaries,\textsuperscript{179} (c) amorphous phase at triple-junctions (TEM), (d) typical mottled contrast magnesium- and fluorine-rich phase at triple-junction (TEM).

Fig. 3.27 Fracture behavior in PS high-purity spinel compacts with (a) no LiF 1650°C 10 hrs. (SEM), 1 wt. % LiF 1650°C 10 hrs (SEM) (I.E. Reimanis, Unpublished Work).
Fig. 3.28 Typical microstructures observed in translucent or transparent spinel; (a) HP/HIP, (b) HP/HIP with LiF, (c) SPS, (d) SPS with LiF, (e) HP, (f) HP with LiF, optical and SEM micrographs, reproduced with permission.

Sidebar 2: Electronic Impedance Spectroscopy – Assessing Defect Chemistry:

Electronic impedance spectroscopy (EIS) is a powerful technique to assess the defect state. It consists of calculating the impedance of a compact by measuring the time-varying current response to an applied alternating current across a compact as a function of frequency. The Nyquist plot is constructed by modeling the compact as an equivalent circuit, where each data point represents the impedance for one particular frequency. The resistance can be extracted from the Nyquist plot where the imaginary impedance component equals zero at lower frequency. Resistivity and conductivity can be calculated from the geometry of the compact and of the electrodes attached to it. The Nyquist plot for three different spinel compacts at 850°C is shown in Fig. 3.29 (a). As conductivity is temperature dependent, performing EIS at different temperatures allows construction of an Arrhenius plot and extraction of activation energies for conductivity [Fig. 3.29 (b)]. EIS indicates lower conductivity and higher activation energy for conductivity in compacts processed with LiF, suggesting removal or counteraction of charge
Similarly, lower conductivity is noted for oxidized versus reduced compacts. In addition, one component of conductivity (grain-boundary or bulk) dwarfs the other in compacts without LiF.

![Image](image.png)

Fig. 3.29 (a) Electronic impedance spectroscopy Nyquist plot for spinel compacts at 850°C with and without LiF, and (b) activation energies for conductivity.\(^{16}\)

### 3.7. Processing Parameters

This section describes the effect of processing parameters on the properties of transparent spinel compacts.

#### 3.7.1. Temperature and Heating Rate

Temperature and heating rate are used to control microstructure evolution in spinel.\(^{15}\) High heating rates are beneficial in attaining temperatures where lattice and grain-boundary diffusion and diffusion-assisted dislocation motion and grain-boundary creep are active, avoiding the formation of densification-resistant sintering necks and grain coarsening by surface or vapor transport mechanisms. However, excessive heating rates provide insufficient time for volatiles
removal and enhance compact-scale differential sintering. High cooling rates can also be
detrimental by causing residual stress and cracking. High sintering temperatures enable greater
diffusion, allowing deformation mechanisms to become active, but are limited by degradation of
spinel at \( \sim 1650 \degree C \) in vacuum. To avoid grain growth, carbon contamination, and Mg/MgO
volatilization, the lowest possible sintering temperatures are used that still allow densification
within reasonable times.

### 3.7.2. Pressure

Although transparent spinel was first made by PS, to date only small, thin compacts made
with high-purity nanometer-sized powders CP at high pressures have been PS to translucency
using high temperatures or long sintering times with various atmospheres. Attempts with
larger compacts lead to cracking and opacity, possibly due to density gradients, differential
sintering, pore coarsening, and swelling. Consequently, spinel is invariably densified using
pressure. Pressure provides an additional driving force for densification, driving mass transport
from regions of higher compressive stress at interparticle contacts and adjacent to pores, to
regions of lower stress. Densification also occurs by plastic flow assisted by dislocation
motion and diffusional creep along dislocations (Fig. 3.30) and grain boundaries. Applied
pressure lowers sintering temperature, allowing finer grain size. In PS/HIP, high pressure
(>150 MPa) is applied to remove the last few percent porosity at high temperatures (>1600\degree C),
where grain boundary and lattice diffusion and deformation mechanisms are all active, although
exaggerated grain growth also results. Very high pressures (2-5 GPa) and low temperatures
(<800\degree C) have been used to obtain transparency while maintaining small grain size (<100
nm). However, transparency is degraded by porosity and strain, the latter having low recovery
at such temperatures. Application of pressure at too low a temperature during sintering traps
volatile species.

Based on the wide range of stress exponents reported in creep experiments, opinions vary as
to the dominant deformation mechanism and the underlying reason for strain softening and
hardening. However, there is agreement that dislocations and grain boundaries are critical and
oxygen diffusion is in some form rate-limiting. Dominant mechanisms have been attributed to
slip, dislocation glide, dislocation creep, grain-boundary sliding, diffusional
reaction diffusion,
rich stoichiometry, consistent with decreased oxygen vacancy
Herring diffusional creep controlled by oxygen lattice diffusion,
- 
Herring diffusional creep dominates at lower 
3 
rich stoichiometries display lower densification rates (early stage) to Nabarro-Herring diffusional creep controlled by oxygen lattice diffusion. Lack of consensus as to the dominant deformation mechanism is likely due to its variability, which depends on the densification method and also on the density and distribution of planar defects, grain size, stoichiometry, impurities, additives, temperature, pressure, and strain rate, which all vary during processing. In hot pressing, Nabarro-Herring diffusional creep dominates at lower temperatures (<1350°C) with a transition to dislocation glide at higher temperatures (> 1450°C). During deformation, the effective pressure changes from an initially high value due to stress concentration at inter-particle contacts (early stage) to a lower value as densification proceeds (late stage). In the case of hot pressing, the predominant densification mechanism changes at a critical stress ($\sigma_T$), from climb-controlled dislocation creep at high effective stress (early stage) to Nabarro-Herring diffusional creep controlled by oxygen lattice diffusion, possibly in combination with grain-boundary sliding at low effective stress (late stage).

In $\text{Al}_2\text{O}_3$-rich stoichiometry, the critical resolved shear stress (CRSS) for dislocation motion is up to several orders of magnitude lower than for stoichiometric compositions. For example, the CRSS drops from ~1 GPa for $x = 1$ to ~100 MPa for $x = 1.7$ and ~20 MPa for $x = 3-3.5$. $\text{Al}_2\text{O}_3$-rich compositions thus give enhanced densification with lower applied stress early during pressure-assisted sintering, so long as the CRSS is within the range of contact stresses. However, as sintering progresses, the effective stress decreases and transition to diffusion control occurs, in which $\text{Al}_2\text{O}_3$-rich stoichiometries display lower densification rates (attributed to lower $\text{O}^2-$ diffusion). During hot pressing, the transition stress from dislocation to diffusion control decreases with increasing $\text{Al}_2\text{O}_3$-rich stoichiometry, consistent with decreased oxygen vacancy
concentration ($\sigma_T = 25$ MPa for $x = 1.15$ vs. $\sigma_T = 40$ MPa for $x = 0.92$ at 1450°C).\textsuperscript{82} Hence, although Al\textsubscript{2}O\textsubscript{3}-rich stoichiometries initially densify more rapidly, they require longer time, higher temperature, or greater pressure to reach full density (>300 min at 1450°C and 12 MPa, >1500°C and 300 min for 25 MPa, >12 MPa and 300 min for 1550°C).\textsuperscript{82} In contrast, for MgO-rich stoichiometry the transition to diffusion control occurs at higher stress (earlier during densification) and as they densify at higher rates in this regime, they achieve full density at even low effective stress within reasonable times (2 h at 12 MPa). For stoichiometric compositions using HP, ~33 MPa is just enough to attain full density at 1550°C.\textsuperscript{43} Impurities, additives, and atmosphere likely affect the deformation mechanism, although their effect has not been systematically studied.

### 3.7.3. Atmosphere

Sintering atmospheres including vacuum, air, oxygen, hydrogen, helium, argon, and combinations have been used to obtain transparent spinel. Vacuum provides a greater driving force for removal of volatile species and is typically used with HP, SPS, and with graphitic furnaces. However, vacuum exacerbates Mg/MgO volatilization at higher temperatures. Reducing atmospheres are beneficial in removing sulfur,\textsuperscript{15} but exacerbate color center formation, and CO atmosphere causes carbon contamination (see Sidebar 3). Air or oxygen assists in binder burnout and formation of volatile oxide impurities.\textsuperscript{19} For PS, higher densification rates initially occur with vacuum sintering (as compared with air sintering)\textsuperscript{75} due to Mg/MgO loss and differential sintering, but densification rates are eventually surpassed by air sintering.\textsuperscript{38} Sintering atmospheres other than air have found limited benefit in the case of PS.\textsuperscript{37,38}

### 3.7.4. Electric Fields

Applied electric fields enable high heating and densification rates,\textsuperscript{197} lower sintering temperature, and attaining fine grain size.\textsuperscript{16,60} Many mechanisms have been proposed,\textsuperscript{197-200} including enhanced diffusion at grain boundaries early during sintering,\textsuperscript{60,197,199,20} although the exact cause is not known with certainty. Applied electric fields lower the flow stress, possibly by reducing the electrochemical potential of rate-controlling vacancies in the space-charge adjacent to grain boundaries,\textsuperscript{201} perhaps with relevance to the discussion in Sidebar 1. SPS is one FAST technique that has enabled the rapid fabrication of transparent spinel compacts with
fine grain size. Densification starts as low as \( \sim 850^\circ\text{C}-950^\circ\text{C} \)\textsuperscript{60,140} and can be complete by \( \sim 1200^\circ\text{C} \).\textsuperscript{60,140} The densification mechanism is attributed to grain-boundary sliding accommodated by interface-reaction (controlling) and oxygen-lattice diffusion.\textsuperscript{202} However, despite benefits, high heating rates with SPS exacerbate differential sintering and allow insufficient time for pore elimination.\textsuperscript{140} In addition, grain-boundary mobility appears to increase, resulting in occluded porosity, a feature not usually observed in HP. The pulsed field also appears to enhance diffusion of carbon and/or CO gas from graphite fixtures, leading to absorption (Sidebar 3), which in the case of SPS zirconia has been attributed to oxygen vacancies\textsuperscript{203} and carbon.\textsuperscript{204} LiF addition has been used to counteract dark color, but it requires lower heating rates to ensure its removal. As with hot pressing, addition of pressure lowers the densification temperature, exacerbating compact-scale differential sintering. In addition, due to increased CO gas concentration, high pressure or application of pressure at too low a temperature traps CO in pores, further increasing absorption.\textsuperscript{59,140} Due to enhanced sintering, pressure also forms stronger bonds for a given temperature, making it more difficult to remove intervening porosity.\textsuperscript{57} Consequently, applying pressure at higher temperature where increased diffusion and deformation takes places leads to smaller residual pores.\textsuperscript{205} Increased trapping of pores, occluded porosity, and absorption with SPS relegates heating rates to those used in hot pressing.\textsuperscript{57,167} In addition, as with HP, shapes and sizes are limited. Thus, although demonstrating promise, SPS has significant hurdles to overcome before becoming competitive. Pressureless FAST suffers from similar problems to SPS in that high densification rates trap everything from pores to binders, additives, and impurities (Fig. 3.31).\textsuperscript{16}

![SEM fracture surface of pressureless field-assisted sintered](image)

Fig. 3.31 SEM fracture surface of pressureless field-assisted sintered (a) opaque lower-purity compact with 1 wt.% LiF and 5 wt.% PVA, (b) translucent high-purity compact with 5 wt.% PEG, pores shown by arrows.\textsuperscript{16}
Side-Bar 3: Shedding Light on Absorption:

Dark color is observed in spinel compacts sintered in graphitic furnaces (HP, HIP, and SPS, Fig.3.32 and 3.33), and several sources have been identified:

2. Organic additives and binders.
3. Transition metal impurities.
4. $\text{Al}_2\text{O}_3\text{C}$ formation at spinel-graphite interfaces.
5. Carbon precipitation from trapped CO/CO$_2$ gas in pores.
6. Diffusion and precipitation of carbon from graphitic components.
7. Color center formation by reduction of spinel in reducing atmospheres.

Gross inclusions in starting powders, graphite foil flakes, atmospheric dust, and remnant organic precursors and binders, can result in significant absorption and/or can decompose into pore clusters. As little as 0.01 wt% transition-metal impurities such as Mn, Cr, and Fe cause significant absorption, and even 10-50 ppm can result in color and detrimental absorption at shorter wavelengths. Absorption occurs due to electronic transitions, charge-transfer transitions, and intervalence charge transfer ($\text{Fe}^{2+} \leftrightarrow \text{Fe}^{3+}$, absorbs at 194 and 258 nm). Absorption over the entire visible spectrum requires overlapping absorption bands from multiple impurities present in sufficient quantity; not likely the case for high-purity powders. Charged defects, such as antisites (absorb at 300, 328 nm) and vacancies, can trap electrons or holes, forming F-centers (two trapped electrons, absorbs at 200-233 nm), F+ centers (single trapped electron, absorbs at 260-270 nm) and V-centers (trapped hole, absorbs at 391 nm). These defects can interact with impurities and modify absorption characteristics. Vacancies and color centers can form under reducing conditions present in graphitic furnaces, and their presence is supported by experiments with single- and poly-crystals that exhibit dark color when reduced with H$_2$ under carbon-free conditions (M. Müller, Unpublished Work).
Fig. 3.32 (a) Absorption as a function of processing in high-purity HP spinel compacts.\textsuperscript{16}

Fig. 3.33 Increased absorption in SPS compacts with; (a) increasing heating rate,\textsuperscript{57} (b) sintering temperature,\textsuperscript{140} (c) temperature of pressure application,\textsuperscript{206} and (d) applied pressure.\textsuperscript{69}

CO\textsubscript{2} or CO (above \textasciitilde 500°C, depending on \(pO\textsubscript{2}\)) gas is present in graphitic furnaces\textsuperscript{19,73,213,221} and in open porosity early during sintering. It becomes trapped in pores in later stages, and with
increased pressure and/or decreasing temperature precipitates as carbon or graphite, possibly by stress graphitization \([\text{Eq. (3.19)}\text{ and Fig. 3.34}]\). Individual carbon atoms may also migrate along grain boundaries, perhaps exacerbated by applied fields during SPS (Fig. 3.33), and accumulate into particles at grain boundaries and triple junctions.\(^5,167\) Spinel also reacts with carbon at interfaces to form Al\(_2\)OC, which contributes to absorption.\(^77\) Use of polished vitreous graphite dies alleviates absorption in HP and allows components with modest optical properties to be used without subsequent polishing.\(^220\) Although often only present in detectable quantities at triple junctions, the presence of carbon has been unequivocally demonstrated in alumina and spinel compacts and models confirm absorption between 0.2–2.0 \(\mu\)m.\(^58,167,215\)

\[
2\text{CO}_{(g)} \rightarrow \text{CO}_{2(g)} + \text{C}_{(s)} \quad (3.19)
\]

![Image](image.png)

**Fig. 3.34** (a) Carbon-rich phase at triple junction in spinel compact, (b) HRTEM image of Graphitic carbon at triple junction in spinel compact.

Increasing absorption with temperature in HP and SPS compacts and with Al\(_2\)O\(_3\)-rich stoichiometry in HP compacts is consistent with increased carbon diffusion and Al\(_2\)OC formation, respectively (Fig. 3.32). Absorption is also observed in MgO-rich compositions, possibly at Al\(_2\)O\(_3\)-rich grain boundaries or due to greater oxygen vacancy and color center concentration. The possibility of absorption due to magnesium and its compounds has not been addressed. Absorption at the periphery of HP compacts and decreased absorption with increased shielding is consistent with carbon contamination from contact with graphite foil or graphitic components (Fig. 3.32). In SPS compacts, increasing absorption with heating rate, with applied pressure, and with decreasing temperature of pressure application is consistent with differential sintering of compact exteriors, trapping CO containing pores, in which CO subsequently transforms to carbon (Figs. 3.33 and 3.34). LiF effectively removes dark color in HP and SPS
compacts [Section 3.6.2], with lithium possibly playing a larger role (Fig. 3.32). Pre-heating\textsuperscript{51,55} and postannealing in air have been shown to remove dark color in SPS and PS/HIP compacts,\textsuperscript{216} indicating either reaction of oxygen with carbon or neutralization of oxygen vacancies with no distinguishing between them.

### 3.8. Summary

Consensus is emerging that successful fabrication of transparent spinel, and likely transparent ceramics in general, entails a holistic approach. All material and processing variables need consideration, quantification, and tracking, through every step of fabrication. For spinel, increased attention must be paid to three variables that play a critical role during processing: (i) particle-size characteristics, (ii) stoichiometry, and (iii) impurities. In addition, effects that occur from the nanometer-scale to the compact scale must be considered. In this respect, scaling technologies for larger or thicker components is arguably one of the most challenging aspects of fabrication and size is also a major limitation for techniques such as HP and SPS. Although large-scale variables such as agglomeration and gross inclusions are tackled first since they have an immediately visible impact on optical properties, atomic-scale variables such as point defects and color centers, may in some cases be controlling and cannot be overlooked. In between these scales are effects of gradients in stoichiometry, impurities, microstructure, and residual stress. Despite the complexity of the spinel processing system, the identification of key variables, attention to multiscale effects, and understanding of the complexities of green-body formation and interactions that occur during sintering has enabled production of large, transparent components using a variety of methods (Table 3.4). However, significant progress remains, particularly in scaling-up fine grain-size technologies, strengthening grain boundaries, pushing absorption edges towards the theoretical limits, and lowering cost. In addition, understanding still lacks regarding the causes of grain growth and absorption, and the specific role of impurities, additives, and point defects. Variable stoichiometry, although a source of complexity, is a potentially powerful tool to control processing and properties. However, understanding of stoichiometry gradients on microstructural and compact scales also lacks. Perhaps with a deeper knowledge of these issues and with optimal powders and green bodies and careful use of atmosphere, additives, electric
fields, and other methods, it may be possible to achieve the ultimate goal of pressureless sintering.

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<table>
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<tr>
<th>Reference</th>
<th>Process Details</th>
<th>Transmittance</th>
<th>$GS$ (µm)</th>
<th>Young’s Modulus (GPa)</th>
<th>Hardness (GPa)</th>
<th>Flexure Strength (MPa)</th>
<th>Fracture Toughness (MPa√m)</th>
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<tr>
<td>(36)</td>
<td>CP/PS 1900°C ($H_2$) 2-4 wt.% Li$_2$O SiO$_2$</td>
<td>50-62% TFT 2-5 µm (3 mm)</td>
<td>-</td>
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<td>(39)</td>
<td>CIP350MPa/PS 1900°C 0.5-1.0 wt.% CaO</td>
<td>67-78% TFT Vis. (&lt;1 mm) 79% ILT 5 µm (0.4 mm)</td>
<td>-</td>
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<td>(40)</td>
<td>CP70MPa/PS 1680°C ($H_2$)</td>
<td>&lt;50% ILT 2-7 µm (1.9 mm)</td>
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<td>(41)</td>
<td>CIP200MPa/PS 1530°C (Vac.)</td>
<td>Translucent Vis. (1 mm)</td>
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<td>-</td>
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<td>PS/HIP</td>
<td>CIP/(RS)PS/HIP150MPa/1750°C (1&gt;x&gt;3) Ann. 24 hrs. &gt;1000°C</td>
<td>87-90% ILT 1-5 µm (2.3 mm)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>250</td>
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<tr>
<td>(29)</td>
<td>CIP/PS/HIP</td>
<td>79% ILT 650 nm (12 mm)</td>
<td>-</td>
<td>-</td>
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<tr>
<td>(52)</td>
<td>CIP/HIP150MPa 1300°C (150 nm APS) 0.15 wt.% B$_2$O$_3$</td>
<td>81% TFT(?) 550 nm (1 mm) 1-2</td>
<td>-</td>
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<td>(207)</td>
<td>PS/HIP 1780°C (100 nm APS)/0.3 wt.% MgF$_2$, AlF$_3$ HP/(RS)H/1800°C 4% LiF</td>
<td>76% ILT 193 nm (10 mm)</td>
<td>-</td>
<td>-</td>
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<tr>
<td>(53)</td>
<td>PS/HIP 1360°C-1440°C &lt;0.5% Add.</td>
<td>81-85% RIT 640 nm (0.8-1.6 mm) 0.4-0.6</td>
<td>-</td>
<td>14.5-15.0</td>
<td>200-250</td>
<td>1.8-2.2$^{KIC}$</td>
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<tr>
<td>(53)</td>
<td>PS/(RS)/HIP 1540°C &lt;0.5% Add.</td>
<td>80% RIT 640 nm (0.8 mm) 3.0-5.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<td>(80)(133)(5)</td>
<td>CP/CIP350MPa/PS/HIP200MPa 4% Binders (53 nm APS) 1260°C (57 nm APS) 1440°C-1500°C (120 nm APS) 1400°C-1580°C (9 m$^2$/g) 1730°C</td>
<td>84% RIT 640 nm (4 mm) 0.3-0.6</td>
<td>84% RIT 640 nm (4 mm) 81-82% RIT 640 nm (4 mm) 0.8-2.0</td>
<td>275</td>
<td>12.1$^{HV,10}$ 200-250</td>
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<td>(133)</td>
<td>GC/PS/HIP200MPa (120 nm) 1700°C-1750°C</td>
<td>83% RIT 640 nm (4 mm)</td>
<td>-</td>
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<td>(134)</td>
<td>CP/CIP/(RS)PS/HIP 1750°C-1850°C x = 1.0</td>
<td>&gt;80% Vis. 87% IR ILT (4 mm) 3.0-5.0</td>
<td>-</td>
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<td>(138)</td>
<td>PS/HIP Y$_2$O$_3$ Add.</td>
<td>87% ILT 4 um (1 mm) 2.1</td>
<td>88% ILT 4 um (1 mm) 0.3</td>
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<td>16.8$^{HV}$ 470$^{BR}$</td>
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<td>(209)</td>
<td>CIP200MPa/PS/HIP200MPa (20-50 nm APS) 1700°C</td>
<td>77% RIT 550 nm (2 mm) 17</td>
<td>300</td>
<td>12.8$^{HV5}$</td>
<td>-</td>
<td>-</td>
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<td>(139)(5)</td>
<td>CIP200MPa/PS/HIP150-220MPa (20-50 nm APS) 1700°C</td>
<td>RIT 75% 550 nm (2 mm) 0.45</td>
<td>290</td>
<td>14-14.5$^{HV5}$ 180-220</td>
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<tr>
<td>(210)</td>
<td>PS/HIP200MPa (60 nm APS) 1520°C</td>
<td>72% 550 nm 1.7 mm 2.5</td>
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<td>13.8</td>
<td>200</td>
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<tr>
<td>(210)</td>
<td>PS/HIP200MPa (60 nm APS) 1580°C</td>
<td>80% 550 nm 1.7 mm 3.5</td>
<td>-</td>
<td>13.8</td>
<td>200</td>
<td>-</td>
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<tr>
<td>(211)(137)</td>
<td>PS/HIP200MPa 1650°C</td>
<td>75% RIT, 83% ILT 5</td>
<td>210$^{IE}$-270$^{I}$</td>
<td>15-17$^{HV1-98N}$</td>
<td>155,169$^{BR}$</td>
<td>1.6-1.8$^{BR,4P}$</td>
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<td>Reference</td>
<td>Process Details</td>
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<td>(212) HP (RS)75 MPa/1400°C</td>
<td>ILT 50% 550 nm (1.2 mm)</td>
<td>-</td>
<td>1-2</td>
<td>-</td>
<td>-</td>
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<tr>
<td>(188)(33) HP3-5GPa 540°C-700°C</td>
<td>~15% TFT 550nm (4 mm)</td>
<td>&lt;0.10</td>
<td>-</td>
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<td></td>
<td>50% TFT 1.5µm (4 mm)</td>
<td>-</td>
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<td>HP4GPa 600C (35 nm APS)</td>
<td>~60%,70% TFT 550 nm, 1 µm</td>
<td>0.04</td>
<td>-</td>
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<td>(46) HP20MPa/1650C/0.75 wt.% LiF</td>
<td>40% RIT 500 nm (6 mm)</td>
<td>100</td>
<td>-</td>
<td>-</td>
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<td>(15) HP35MPa/1550°C</td>
<td>ILT 75% 550 nm (2 mm)</td>
<td>25</td>
<td>-</td>
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<tr>
<td></td>
<td>0.25-1 wt.% LiF</td>
<td>ILT 82% 1-3 um (2 mm)</td>
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<td>(50) HP(RS)40MPa 1 wt.% LiF</td>
<td>77-79% RIT (2 mm)</td>
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<td>-</td>
<td>14HV1.0</td>
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<td>HP/HP</td>
<td>HP/HP (CoorsTek)</td>
<td>82 TFT</td>
<td>&gt;50</td>
<td>265</td>
<td>13HK0.2</td>
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<td></td>
<td>HP/HP (NRL/MER)</td>
<td>82 TFT</td>
<td>25</td>
<td>280</td>
<td>16</td>
<td>300</td>
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<tr>
<td>(10)(5) CIP/PS or HP/HP205MPa</td>
<td>I LT 80% 550 nm (3.5 mm)</td>
<td>&gt;50</td>
<td>280</td>
<td>16.4HK0.2</td>
<td>210</td>
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<td>(213) HP+41MPa/ HP207MPa</td>
<td>I LT 88% 4 um (3.5 mm)</td>
<td>-</td>
<td>2</td>
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<td>(60 nm APS) 1500°C</td>
<td>I LT 72% 700 nm (2 mm)</td>
<td>-</td>
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<td>(45) HP(RS)50MPa/IP189MPa/1900°C n = 1</td>
<td>36% ILT 550 (2 mm)</td>
<td>52% ILT 550 (2 mm)</td>
<td>55% ILT 550 (2 mm)</td>
<td>-</td>
<td>15-16HV0.65-5</td>
<td>1.5-1.8Kic</td>
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<tr>
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<td>n = 1.5</td>
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<td>-</td>
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<td>n = 2</td>
<td>-</td>
<td>-</td>
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<tr>
<td>(46) HP20MPa/ HP200MPa</td>
<td>RIT 82.5% 632 nm (6 mm)</td>
<td>200-300</td>
<td>-</td>
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<tr>
<td></td>
<td>(60 nm APS) 1900°C 0.75 LiF</td>
<td>RIT 87% 3.4 um (6 mm)</td>
<td>-</td>
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<tr>
<td>(71)(48) HP(RS)20MPa/HP200MPa/1850°C/0.75wt%</td>
<td>84.2% ILT 550 nm (4 mm)</td>
<td>488</td>
<td>287US</td>
<td>12HK2</td>
<td>157BR</td>
<td>-</td>
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<td>n = 1.0</td>
<td>84.8% ILT 550 nm (4 mm)</td>
<td>1018</td>
<td>293US</td>
<td>12HK2</td>
<td>177BR</td>
<td>-</td>
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<tr>
<td></td>
<td>n = 1.2</td>
<td>84.8% ILT 550 nm (4 mm)</td>
<td>25-100</td>
<td>282</td>
<td>16</td>
<td>350</td>
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<tr>
<td>(34) HP/HIP206MPa/1600°C LiF(100-200 nm)</td>
<td>&gt;80 IR</td>
<td>84.2% ILT 550 nm (4 mm)</td>
<td>48</td>
<td>270HV1.1</td>
<td>13-17DR1(1.98N)</td>
<td>169BR</td>
<td>1.8 LBR,4P</td>
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<td>(137) PS or HP/HIP200MPa/1600°C</td>
<td>Transparent (6.2 mm)</td>
<td>5</td>
<td>270HV1.1</td>
<td>13-17DR1(1.98N)</td>
<td>77BR</td>
<td>1.1 LBR,4P</td>
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<tr>
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<td>(70 nm APS)</td>
<td>Transparent (6.2 mm)</td>
<td>-</td>
<td>60</td>
<td>169</td>
<td>74</td>
<td>77BR</td>
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<tr>
<td>PS SPS 1600°C 64 Mpa &lt;20°C/min. 1 wt. % LiF</td>
<td>65% ILT 550 nm (2.7 mm)</td>
<td>&gt;20</td>
<td>289US</td>
<td>13HV</td>
<td>-</td>
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<td>(57)(140) SPS 1300°C 80 MPa</td>
<td>47% ILT 550 nm (1.8 mm)</td>
<td>0.45</td>
<td>-</td>
<td>15</td>
<td>~500*</td>
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<tr>
<td></td>
<td>&lt;10°C/min.</td>
<td>75% ILT &gt;1.4 µm (1.8 mm)</td>
<td>-</td>
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<tr>
<td></td>
<td>(58) SPS(RS)1600°C/64MPa/100°C/min/1wt%LiF</td>
<td>70% ILT 550 nm (2.1 mm)</td>
<td>~10</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<td>(59) SPS 1300°C 5/100 MPa</td>
<td>51% ILT 550 nm (1.8 mm)</td>
<td>0.65</td>
<td>-</td>
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<tr>
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<td>100°C/min.</td>
<td>&gt;85% ILT &gt;2 m (1.8 mm)</td>
<td>-</td>
<td>-</td>
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<td>(206) SPS 1300°C 90 MPa</td>
<td>35% ILT 550 nm (1.8 mm)</td>
<td>0.4</td>
<td>-</td>
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<tr>
<td></td>
<td>100°C/min.</td>
<td>74% ILT &gt;1.4 µm (1.8 mm)</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td></td>
<td>(167) SPS (SC) 1400°C 60 MPa 100°C/min.</td>
<td>46% ILT 550 nm (1.2 mm)</td>
<td>0.53</td>
<td>-</td>
<td>-</td>
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<td>(60) SPS 1300°C 72 MPa</td>
<td>74% RIT 550 nm (2.3 mm)</td>
<td>0.25-0.30</td>
<td>15-16HV3</td>
<td>-</td>
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<td>&lt;10°C/min.</td>
<td>84% RIT 2 µm (2.3 mm)</td>
<td>-</td>
<td>-</td>
<td>-</td>
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**Notes:**
REFERENCES CITED


Sintering of Oxide and Non-Oxide Ceramics, Tokyo Institute of Technology, Tokyo, Japan, 1979.


CHAPTER 4
EFFECT OF IMPURITIES AND LIF ADDITIVE IN HOT-PRESSED TRANSPARENT MAGNESIUM ALUMINATE SPINEL

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ABSTRACT

The effect of impurities and LiF sintering additive on the microstructure and optical properties of hot-pressed transparent MgAl\textsubscript{2}O\textsubscript{4} spinel was investigated. A lower and a higher purity powder were hot pressed with and without LiF and process parameters were varied. Microstructure was examined using optical and electron microscopy optical properties using spectrophotometry, and chemistry using various spectroscopic techniques. Impurities present in parts-per million were found to segregate at grain boundaries and form an amorphous phase, restricting grain growth and causing scatter and opacity. It was found that LiF reacts with impurities to form volatile species that can be removed with proper processing, resulting in larger grain size and increased transmittance. LiF also counteracts absorption caused by reduction of spinel, but results in MgO loss, grain boundary embrittlement, and if trapped in higher concentration, restricts grain growth and causes scatter and opacity.
4.1. Introduction

Magnesium aluminate spinel (MgAl$_2$O$_4$) has a combination of properties well suited for use as transparent armor, infrared (IR) and possibly ultraviolet (UV) transparent windows, and IR-seeking missile domes. However, it is difficult to sinter to the near-theoretical density required for transparency. Current processing methods are complex, expensive, and not easily scalable to mass production.$^{1-6}$ In addition, compacts are susceptible to powder and process variability and often contain optical defects.$^7$ Furthermore, mechanical properties are degraded by exaggerated grain growth during hot isostatic pressing and grain boundary embrittlement caused by the LiF additive typically required for transparency.$^3$ A better understanding of the role of LiF, impurities, point defects, mass transport, stoichiometry, interface energy, and how these affect sintering is required if transparent spinel is to find wider application.

Spinel is inherently difficult to sinter. Defects required for mass transport, such as oxygen vacancies, which are rate limiting in late-stage sintering, have high formation and diffusion barrier energies.$^{8-10}$ Spinel may have a high grain boundary energy, favoring coarsening over densification.$^{1,11}$ Grain boundary mobility is significantly influenced by stoichiometry, which is variable during sintering.$^{12,13}$ The vapor pressure of MgO is higher than that of Al$_2$O$_3$ over spinel, resulting in MgO loss and Al$_2$O$_3$-rich grain boundaries in sintered compacts, even for MgO-rich compositions.$^{12-14}$ Grain boundary mobility in hot pressed MgO-rich compacts is reported as $10^2$ to $10^3$ times higher than Al$_2$O$_3$-rich compacts$^{12,13}$ and densification rates of pressureless sintered MgO-rich powders are up to five times greater than stoichiometric compositions.$^{15}$ Proposed sintering mechanisms include different rate-limiting intrinsic defects depending on stoichiometry$^{12,13}$ and an increase in oxygen vacancies based on the Brouwer diagram.$^{15}$ However, reports using different processing conditions suggest increasing grain boundary mobility in compacts with Al$_2$O$_3$-rich stoichiometry,$^{16}$ with a possible explanation for the discrepancy being differences in sintering atmosphere.$^{17}$ In graphitic furnaces, carbon reacts with spinel and forms CO gas at temperatures as low as 500°C.$^{2,4}$ and aluminum oxy-carbides at temperatures as low as 1250°C,$^{18}$ likely influencing chemical evolution, stoichiometry, and oxygen vacancy concentration, complicating processing. Spinel is also sensitive to impurities and does not typically sinter to transparency in air, likely due to swelling.$^{3,9,12,13}$ Impurities also restrict grain boundary mobility and form scattering second phases, reducing transmittance.$^{1,19}$
Transparent polycrystalline spinel was first made by General Electric Co. in the 1960’s. Calcined Al₂O₃ and MgO powders with Li₂O and SiO₂ additives were cold pressed and sequentially sintered in H₂ to 1900°C while embedded in spinel powder to maintain stoichiometry.⁷,¹⁹,²⁰ Transparent components have since been produced using combinations of pressureless sintering, cold, and hot pressing, cold isostatic pressing (CIP), and hot isostatic pressing (HIP), and also by spark-plasma sintering and fusion casting.⁷ Current commercial processing typically involves high-purity starting powders, powder pre-treatment, LiF additive, hot pressing or CIP and sintering, followed by HIP. Powder pre-treatment, involving cleaning, calcining, deagglomeration, sieving for uniform particle size, forming aqueous slurries with dispersants and binders, blending, de-gassing, and cold-pressing to high green densities all improve densification.⁷,¹⁹-²⁶ High-purity, high-surface energy, deagglomerated nanometer-sized powders have also been synthesized.²⁴ However, they are too expensive for use in bulk applications such as transparent armor. Other process parameters, such as temperature and pressure profiles, sintering atmosphere, and impurity content, have been examined and have a significant effect on properties.⁴ However, systematic studies have not been undertaken and the underlying mechanisms are not fully understood.

Although fully dense spinel compacts can be obtained by vacuum hot pressing, sintering additives are typically required to obtain transparency. Various additives have been examined, mainly metal halides, with LiF giving the best results and being the most widely used.³ LiF forms a low-temperature eutectic and wets spinel,²⁸ likely aiding in particle rearrangement and liquid-phase sintering.³,²⁷ LiF reacts with spinel at higher temperature to form LiAlO₂ and MgF₂, possibly assisting sintering by solution-reprecipitation.²⁸ LiF coarsens spinel by vapor-phase transport, implying the formation of volatile magnesium and aluminum-containing species, results in grain growth during the initial stages of sintering, and increases transparency in hot pressed compacts.³,⁴ Lithium and fluorine incorporate into the lattice in the grain boundary region,²⁹ likely replacing magnesium and oxygen, respectively, and resulting in the formation of MgO⁴. Addition of LiF possibly creates diffusion-enhancing defects, although the defect chemistry is not known with certainty.³,¹⁵,²⁹ Both MgF₂ and MgO outgas during hot pressing, resulting in reduced magnesium content in compacts hot pressed with LiF.¹²,¹³,³⁰ Altered
stoichiometry, diffusion-enhancing defects, and lower grain boundary energy may all contribute to increased grain growth. Another suggested role of LiF is impurity removal, although this has not been verified experimentally.\textsuperscript{3,27} LiF must be properly mixed and can result in scatter and opacity if trapped in excessive amount.\textsuperscript{31}

In this work, the effect of impurities, LiF additive, and processing conditions on microstructure and optical properties of hot-pressed spinel compacts was examined. Hot-press experiments were performed using a higher and a lower purity powder, with and without LiF addition, and the amount of powder and the temperature at which pressure is applied were varied. Compacts were examined with various analytical techniques to understand the fundamental mechanisms and interactions that occur during sintering with the goal of formulating strategies for sintering dense, transparent spinel.

4.2. Experimental Procedure

Two commercial spinel powders were used; Baikowski S30CR (lot #061113, Baikowski, Charlotte, NC, USA) hereafter termed the LP (low purity) powder, and Nanocerox spinel powder (lot #4CZ143B1, Nanocerox, Ann Arbor, MI, USA), hereafter termed the HP (high-purity) powder. LP powder is synthesized via an aqueous sulfate process and may contain unreacted sulfate and hydrate species. Baikowski reports an average particle diameter ($d_{50}$) of 0.2 $\mu$m, surface area of 30 m$^2$/g, and impurity species present in the 10 ppm range (Table 4.1). Sulfur content was quoted in private communication to be ~800 ppm. For verification, as-received powder was analyzed with inductively coupled plasma optical emission spectroscopy (ICP-OES, Spectro Arcos ICP-OES, Kleva, Germany; 3000 ICP-OES, Perkin Elmer, Waltham, MA), yielding similar results to reported values. Sulfur, carbon, and nitrogen content were determined using a carbon/sulfur analyzer (CS-400, LECO, St. Joseph, MI) and a nitrogen/oxygen determinator (LECO TC-456). The results show higher readings compared to ICP, likely due to contamination by adsorbed gases. The HP powder is synthesized by flame-spray pyrolysis of single or mixed-metal metallorganic alcohol solutions. Powder characteristics are similar to LP powder, except for lower agglomeration and higher purity. Nanocerox reports an average crystallite size of 58 nm, surface area of 29 m$^2$/g, and total impurity content of 109 ppm (Table 4.1). The powders are stoichiometric within the uncertainty of X-ray diffraction (XRD),
typically ~1%. However, the LP powder is estimated to be Al$_2$O$_3$-rich (~MgO:1.01Al$_2$O$_3$) based on ICP while the HP powder is enriched in MgO (~MgO:0.995Al$_2$O$_3$) based on image analysis of MgO nodules in hot-pressed compacts.

Table 4.1 Typical Properties for LP and HP Spinel Powders*

<table>
<thead>
<tr>
<th>Property</th>
<th>LP Powder</th>
<th>HP Powder</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystallite Size (TEM, XRD, nm)</td>
<td>50</td>
<td>58</td>
</tr>
<tr>
<td>Agglomerate Size Distribution ($d_{50}, \mu m$)</td>
<td>0.2</td>
<td>-</td>
</tr>
<tr>
<td>Surface Area (BET, m$^2$/g)</td>
<td>30</td>
<td>29</td>
</tr>
<tr>
<td>Element</td>
<td>ICP (ppm)</td>
<td>GDMS (ppm)</td>
</tr>
<tr>
<td>B</td>
<td>88</td>
<td>0.4</td>
</tr>
<tr>
<td>C</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>N</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>F</td>
<td>-</td>
<td>&lt; 10</td>
</tr>
<tr>
<td>Na</td>
<td>39</td>
<td>2.3</td>
</tr>
<tr>
<td>Si</td>
<td>40</td>
<td>17</td>
</tr>
<tr>
<td>P</td>
<td>-</td>
<td>2.0</td>
</tr>
<tr>
<td>S</td>
<td>~800†‡</td>
<td>7</td>
</tr>
<tr>
<td>Cl</td>
<td>-</td>
<td>13</td>
</tr>
<tr>
<td>K</td>
<td>39</td>
<td>1.4</td>
</tr>
<tr>
<td>Ca</td>
<td>10</td>
<td>3</td>
</tr>
<tr>
<td>Ti</td>
<td>2</td>
<td>1.6</td>
</tr>
<tr>
<td>Cr</td>
<td>1</td>
<td>0.8</td>
</tr>
<tr>
<td>Mn</td>
<td>-</td>
<td>5.7</td>
</tr>
<tr>
<td>Fe</td>
<td>5</td>
<td>8-16</td>
</tr>
<tr>
<td>Cu</td>
<td>2</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>Zn</td>
<td>1</td>
<td>&lt; 10</td>
</tr>
<tr>
<td>Ga</td>
<td>-</td>
<td>0.9</td>
</tr>
<tr>
<td>Y</td>
<td>-</td>
<td>1.1</td>
</tr>
<tr>
<td>Total Volatiles</td>
<td>-</td>
<td>32</td>
</tr>
</tbody>
</table>

*Manufacturer’s data.  
†Private communication.  
‡Independent ICP analysis.  
- Not reported.

LiF (99.99% metal basis, lot #20307, Puratronic, Alfa Aesar, MA) was mixed with spinel powder in methanol using an ultrasonic processor (CPX 130, Cole Parmer, Vernon Hills, IL) with a tungsten horn for 1 min. with a power setting of 40 W. Solvent was removed by rotovap (Buchi Labortechnik AG, R-210, Flavil, Switzerland). Powder without additive was processed as for mixed powder and the ultrasonic mixing method was found to have no effect on compact microstructure and transmittance. To study the effect of stoichiometry on grain growth and absorption, HP powder was also mixed with 0.05 wt. % and 0.1 wt% Al$_2$O$_3$ (High purity, 20 nm average grain size, obtained through CoorsTek, Golden, CO).
Spinel powder with and without additives was poured into a 25.4 mm diameter graphite die lined with graphite foil (99.5%, GrafTech, Lakewood, OH) and with graphite foil spacers above and below the powder. The graphite die was placed in an instrumented hot press (Thermal Technology Inc., Santa Rosa, CA) with graphitic elements. The hot press chamber was evacuated and pre-programmed hot-press regimes were initiated. Vacuum levels were monitored using an ion gauge (Model 563, Varian, Palo Alto, CA) and deteriorated to ~13 mPa ($10^{-4}$ Torr) between 50°C and 300°C, but were better than ~1.3 mPa ($10^{-5}$ Torr) during the remainder of the regimes. To study the effect of carbon contamination, some HP powder compacts were hot pressed in an alumina die lined with molybdenum foil.

Two hot press regimes were used (Fig. 4.1). Regime 1 consisted of ramping temperature from ambient to 1550°C at 6°C/min., with a 60 min. hold at 400°C, a 15 min. hold at 1200°C, a 60 min. hold at 1550°C, followed by a ramp to ambient at 6°C/min. A pressure of 35 MPa was applied at 1200°C on heating and maintained until 900°C on cooling. Regime 2 was identical to regime 1, except a 60 min. hold at 900°C was used instead of the hold at 1200°C and pressure was applied at 900°C on heating. Compacts were hot pressed with regimes 1 and 2, with 1.5 g and 3.5 g of both LP and HP powders, and with and without LiF (Fig. 4.1). To study the onset of reduction, compacts were also hot pressed with HP powder to maximum sintering temperatures of 1300°C, 1400°C, and 1550°C with regime 1. Compacts were ground and polished to 0.05 µm using alumina polishing media. Compacts had a diameter of 25.4 mm and compacts with 1.5 g of powder were ~2 mm thick, and those with 3.5 g of powder ~5 mm thick after polishing.

The density of polished compacts was calculated using the Archimedes method as per ASTM standards B962 and C373. Weighing was performed using an analytical balance (BA 210S, Sartorius, Elk Grove, IL) with an accuracy of ±0.1 mg and adjustments made for ambient temperature and pressure.

Transmittance of the polished compacts was measured using a spectrophotometer (Perkin Elmer Lambda 950 UV-Vis-NIR, Varian, Palo Alto, CA) with and without a UV filter (9863) and using an integrating sphere. Total and in-line transmittance and total and diffuse reflectance
were measured from 175 nm to 3000 nm as a fraction of incident intensity. The relationship between transmittance, reflectance, scatter, and absorptance is given by:

\[ i = r + s + a + t = 1 \]  

(4.1)

where \( i \) is incident intensity, \( r \) is specular reflectance, \( s \) is scatter (diffuse reflectance plus diffuse transmittance), \( a \) is absorptance, and \( t \) is in-line transmittance. Diffuse transmittance (or forward scatter) was calculated as the difference between total and in-line transmittance. Specular reflectance was calculated as the difference between total and diffuse reflectance. Absorptance was calculated as incident intensity minus specular reflection, scatter, and in-line transmittance. Where different sized compacts were compared, transmittance and absorptance were normalized per unit thickness.

<table>
<thead>
<tr>
<th>No LiF</th>
<th>With LiF*</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5 g</td>
<td>1.5 g</td>
</tr>
<tr>
<td>~2 mm thick</td>
<td>~2 mm thick</td>
</tr>
</tbody>
</table>

**Fig. 4.1** Hot press regimes and compacts (*LP compacts 1 wt% LiF, HP compact 0.25 wt% LiF).

Compact microstructure was examined using optical microscopy (OM), field emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), and chemistry with scanning TEM (STEM), energy dispersive spectroscopy (EDS), wavelength dispersive spectroscopy (WDS), and Raman spectroscopy. An image of the microstructure at the center of polished compact faces was obtained using OM (10× objective; PMG 3, Olympus,
Tokyo, Japan) with an attached digital camera (PX-CM; Paxcam, Villa Park, IL). Grain size was calculated using a circle-intercept method as per ASTM standard E112. Grain boundary surface area per unit volume for each grain size type was calculated by modeling grains as tetrakaidecahedrons with diameters equal to the measured average grain size for that grain size type. Total grain boundary area for each grain size type was found by multiplying the modeled grain boundary area per type by the area fraction obtained using Image J (Image J; National Institutes of Health, Bethesda, MD) image analysis software for each grain size type. FE-SEM (JSF-7000; JEOL, Tokyo, Japan) was performed on fracture surfaces transverse to the hot pressing direction. EDS was conducted using an accelerating voltage of 15-20 kV were performed on fracture surfaces and on precipitate collected from the periphery of compacts subsequent to hot pressing. TEM-EDS (CM200, CM12; FEI Phillips, Eindhoven, Netherlands; JEM 2100F; JEOL) and S/TEM-EDS (Tecnai G2 F20 S-Twin 200 keV FE S/TEM; FEI) were performed on specimens that were dimple ground and ion milled (Duo Mill 600; Gatan, Warrendale, PA) with argon. Volume percent of phases and fracture features were determined using Image J. Raman spectroscopy was conducted on polished compacts using a confocal Raman microscope (Alpha 3000; WiTec, Ulm, Germany) with an Nd-YAG laser emitting light at 532 nm.

Simultaneous thermal analysis (STA, 409 STA; Netzsch, Selb, Germany), combining differential scanning calorimetry and thermogravimetric analysis, was conducted on powder samples. Powder was poured into an alumina crucible, weighed to ± 0.1 mg, and placed in the STA chamber. The chamber was filled with air or evacuated and back-filled three times with ultra-high purity argon and heated at 10°C/min. or 20°C/min. to a maximum temperature of 1500°C. Runs were performed twice for each condition; pure LiF, LP powder without and with 1 wt. % and 10 wt. % LiF, and HP powder without LiF and with 1 wt. % LiF. A 100-channel environmental residual gas analyzer (Cirrus, MKS, Andover, MA) was attached to the STA chamber via 3.175 mm stainless steel tubing to analyze evolved gases. The tubing was wrapped with resistive tape heated to ~200°C for the duration of the runs. The Cirrus software output pressures based on calibrated calculations from counts for each mass, which were divided by total pressure to obtain partial pressures. Since only the charge to mass ratio is measured, differentiating between species with the same mass was based on species known to be present,
known chemical interactions, and simulation with HSC Chemistry (Outotec, Espoo, Finland) thermodynamic software.

Laser ablation ICP OES/mass spectroscopy (LA-ICP OES/MS; Spectro-Arcos ICP/OES; Varian 820 MS ICP/MS; Cetac LSX-500 LA, Omaha, NB) was used to quantify impurity content within and among compacts. Two compacts hot pressed with 3.5 g of LP powder and pressure applied at 1200°C were analyzed; one without LiF and one with 1 wt% LiF. For each compact, two areas were analyzed; the center of a face and the geometric center (by cutting compacts in half with a diamond saw). Prior to LA-ICP a compact hot pressed to maximize retained impurity content was analyzed with LA-ICP and also dissolved for analysis by solution ICP-OES to establish a reference for LA-ICP. The spectral counts of the ICP analyses were integrated and the element counts normalized by dividing them by the aluminum, magnesium, or gallium counts. The normalized counts from the compacts analyzed by LA were compared to those from the compacts analyzed by solution to establish absolute concentrations. Alumina levels were obtained by difference, lithium content was measured directly and LiF content estimated from it, and boron was detected but not in enough quantity to establish a calibration curve.

4.3. Results

LP and HP compacts hot pressed without LiF and with pressure applied at 1200°C are shown in Figs. 4.2a and b. The LP compact was dark and opaque and the HP compact dark and transparent. Both compacts displayed bimodal grain size distributions and abnormal grains that occurred predominantly at compact surfaces. The HP matrix grains were smaller, with occasional clusters of abnormal grains. Addition of 1 wt% LiF to LP powder and 0.25 wt% LiF to HP powder resulted in clear, transparent compacts with uniform grain size distributions and roughly twice the average grain size (Figs. 4.2c and d). Less LiF was used for HP compacts due to lower impurity content. Numerous optical defects were observed by focusing into transparent compacts; clusters of carbon-rich submicrometer-sized inclusions, micrometer-sized scattering features decorating grain boundaries (LP compacts), submicrometer-sized triple junction phases (LP compacts), and ~1 mm diameter cloudy areas degrading transparency in HP compacts with LiF. In HP compacts, dark color increased with increasing sintering temperature and with
Al₂O₃-rich stoichiometry and was eliminated by shielding with molybdenum foil and use of alumina dies (not shown).

Fig. 4.2 OM images and average grain size for compacts hot pressed with pressure applied at 1200°C; (a) LP without LiF, (b) HP without LiF, (c) LP with 1 wt% LiF, (d) HP with 0.25 wt% LiF.

The temperature at which pressure is applied and amount of powder were found to be important parameters and varying them was assessed in LP powder with 1 wt% LiF. The compact hot pressed with 1.5 g of powder and pressure applied at 900°C was hazy with a bimodal grain size distribution (Fig. 4.3b) and half the average grain size compared to application of pressure at 1200°C (Fig. 4.3a). The compact with pressure applied at 1200°C and 3.5 g of powder was cloudy (Fig. 4.3c), as opposed to transparent when 1.5 g of powder was used with the same regime (Fig. 4.3a). The compact hot pressed with pressure applied at 900°C and 3.5 g of powder was opaque, except for a transparent region at the outer rims, with approximately half the average grain size as when 1.5 g of powder was used (Figure 4.3d). Grain morphology varied from smaller and bi-modal to larger and uniform from geometric center to outer rim of the compacts, concomitant with increased transparency.
Fig. 4.3 OM images and average grain size for LP powder with 1 wt% LiF hot pressed with 1.5 g of powder and pressure applied at (a) 1200°C and (b) 900°C, and with 3.5 g of powder and pressure applied at (c) 1200°C and (d) 900°C.

Transmittance, reflectance, scatter, and absorptance for wavelengths from 200 nm to 2500 nm were quantified for LP and HP compacts hot pressed with 1.5 g of powder with and without LiF and with pressure applied at 1200°C (shown up to 750 nm in Fig. 4.4). In LP compacts without LiF, in-line transmittance was negligible, forward scatter increased in the visible up to ~40% in the IR, and absorptance peaked to 95% at 250 nm and remained above ~45% into the IR. In LP compacts with 1 wt% LiF, in-line transmittance was greater than 80% (theoretical ~87%\(^{33}\)) between 500 nm and 2500 nm, forward scatter was significant at shorter wavelengths, up to ~40% at 200 nm, and absorptance was negligible. In HP compacts without LiF, forward scatter peaked to 20% at 270 nm and was negligible at longer wavelengths, whereas absorptance was significant over the visible, peaking near 90% at 210 nm and remaining above 35% in the IR. Transmittance from 200 to 2500 nm, normalized for thickness, was quantified for LP compacts hot pressed with 1 wt% LiF with more powder and/or with pressure applied at 900°C (not shown). The compact hot pressed with 1.5 g of powder with pressure applied at 900°C displayed much lower in-line transmittance than the compact with pressure applied at 1200°C, being greater than 80% only between 1200 and 2500 nm. Compacts hot pressed with 3.5 g of powder displayed significantly lower in-line transmittance. All compacts hot pressed with LiF displayed fluorescence at shorter wavelengths upon irradiation with laser light at 532 nm.
Fig. 4.4 % transmission vs. wavelength from 200 nm to 750 nm for compacts hot pressed with pressure applied at 1200°C and 1.5 g of (a) LP powder without LiF, (b) LP powder with 1 wt% LiF, (c) HP powder without LiF.

SEM was conducted to assess transmittance variability and opacity. Fracture surfaces were used to ensure retention of second phases and to examine fracture mode. The dark, opaque compact hot pressed with 1.5 g of LP powder without LiF and pressure applied at 1200°C displayed a bi-modal grain size distribution consisting of ~20 µm matrix grains and aggregates of submicrometer grains occupying ~5 vol% with an average diameter of ~5 µm and containing submicrometer grains with an average grain size of 0.4 µm (Fig. 4.5a). Using the method outlined in the Experimental Procedure, the total grain boundary area of the submicrometer grains was estimated to be more than twice that of the matrix grains. The matrix grain fracture mode was predominantly transgranular, while that of the submicrometer grains was predominantly intergranular (Fig. 4.5b). TEM-EDS revealed an impurity-rich (carbon, sulfur, silicon, and potassium), partially wetting amorphous phase (determined by electron diffraction) decorating the submicrometer grain boundaries and occupying all or part (likely removed by dimpling) of triple junctions in aggregates of submicrometer grains (Figs. 4.6a-e). The 120-degree triple junction dihedral angles indicate stable junctions and equal grain boundary and
grain-amorphous phase interface energies (Fig. 4.6a and c). Matrix grain boundaries were generally clean (Fig. 4.6f), with occasional gallium-rich precipitates (Fig. 4.5b). Impurity content at grain boundaries was below the detection limit of SEM-EDS, typically < 1,000 ppm per species, likely due to the large grain boundary area.

Fig. 4.5 SEM images of fracture surface of compact hot pressed with 1.5 g of LP powder without LiF with pressure applied at 1200°C; (a) transgranular matrix grain fracture, (b) submicrometer grains.

Fig. 4.6 TEM images of compact hot pressed with 1.5 g of LP powder without LiF and pressure applied at 1200°C; (a) submicrometer grains, (b) amorphous phase at interface between submicrometer and matrix grains, (c) amorphous phase at triple junction, (d) dark-contrast grain boundary phase in submicrometer grains, (e) dark-contrast grain boundary phase, (f) matrix grain boundary.

The clear, transparent compact hot pressed with 1.5 g of LP powder with 1 wt% LiF, and pressure applied at 1200°C displayed predominantly intergranular fracture (Fig. 4.7a). The grain size distribution was uniform, but aggregates of small grains remained (Fig. 4.7b). The grains within the aggregates grew to micrometer-size, as opposed to submicrometer-size for compacts.
without LiF. Due to reduced grain boundary area associated with grain growth, impurities in the aggregates concentrated into submicrometer-sized polyhedral iron, nickel, carbon, and gallium-rich triple junction and grain boundary phases that were detectable by SEM-EDS (Figs. 4.7 c and d). The matrix grain boundaries were generally clean (Fig. 4.7e) with occasional strain contours (not shown).

Fig. 4.7 SEM images of fracture surface of compact hot pressed with 1.5 g of LP powder with 1 wt% LiF and pressure applied at 1200°C; (a) matrix grains, (b) aggregates of smaller grains, (c), (d) second phases in aggregates of smaller grains, (e) TEM of matrix grain boundary.

The compact hot pressed with 1.5 g of LP powder, 1 wt% LiF, and pressure applied at 900°C showed occasional mottled fluorine-rich phases, indicative of trapped LiF (Figure 4.8a). TEM analysis of matrix grain boundaries occasionally showed strain contrast, more so than in compacts hot pressed without LiF (Fig. 4.8c). S/TEM-EDS profile scans of a matrix grain boundary indicated segregation of sulfur, calcium, and carbon and depletion of MgO at the grain boundary core (not shown). EDS analysis of precipitate collected from the periphery of LP compacts with LiF subsequent to hot pressing indicated the presence of sulfur, iron, and calcium.
Fracture surfaces of HP compacts hot pressed with pressure applied at 1200°C without LiF were predominantly transgranular (Fig. 4.9a), whereas those of HP compacts with LiF were predominantly intergranular (Fig. 4.9b), similar to LP compacts. In compacts without LiF, a disseminated, white-contrast phase occurring as clusters of particles ~100 nm in diameter and occupying less than 0.5 vol% were determined by SEM-WDS to be iron-rich (Fig. 4.9a inset). This phase was nearly absent in HP compacts with LiF. Nodules ~125 nm in diameter and determined by TEM-EDS to be pure MgO, were observed in HP compacts (Fig. 4.9b inset), suggesting MgO-rich stoichiometry. The nodules occurred predominantly at grain boundaries and were more prevalent in compacts with LiF, occupying ~0.9% of the grain boundaries (0.27 vol% or 0.08 wt%). It should be noted that all the compacts were found to be 99.5% dense or greater based on a theoretical density of 3.58 g/cm³ and porosity was not observed.³⁴
STA-MS results for all test conditions in air indicated signals for atmospheric gases and water vapor and in argon additionally indicated signals for atmospheric gases and water vapor and in argon additionally indicated argon and its isotopes throughout the runs. Some of these species may have obscured outgassing of species of the same mass, for example Ar-40 and MgO (40). Masses 7 (Li), 19 (F), and 26 (LiF) were not detected for any of the runs, despite vaporization of LiF with mass loss equal to the amount added, suggesting LiF is condensed on the vapor-transfer tube, reacted to form species with molecular weight greater than the detection limit of the MS (MW = 100), or was not detected. Fluorine is difficult to ionize and may have passed through undetected and fluorine gas (F₂) may have been obscured by Ar-38. Lithium may have outgassed in masses 16 (O, Li₂H₂), 30 (NO, Li₂O), and 44 (N₂O, CO₂, Li₄O²⁺), which were detected within the vaporization range of LiF for pure LiF and LP powder with 10 wt% LiF (not shown).

Pure LiF displays a melting endotherm at ~850°C and a vaporization endotherm between 1000°C and 1400°C, committant with complete mass loss and consistent with results in the literature. Outgassing of masses 17 (OH) and 18 (H₂O) increased with increasing temperature up to 900°C, consistent with the hygroscopic nature of LiF. Masses 16 (O, Li₂H₂) and 44 (CO₂, N₂O, Li₄O²⁺) increased from 700°C and peaked at 850°C, coincident with the melting endotherm of LiF, and increased again between 1150°C and 1500°C, coincident with the vaporization endotherm of LiF. Mass 28 (N₂, CO) increased between 1150°C and 1500°C, peaking at 1350°C and mass 30 (NO, Li₂O) increased from 1350°C to 1500°C.

For LP powder with 1 wt% LiF, masses 18 (H₂O), 32 (O₂, CH₃OH), and 44 (CO₂) rise and peak below 300°C. A secondary mass 18 (H₂O) peak associated with a slight endothermic rise appears near 400°C and a more distinct peak with an endothermic rise centered at 700°C occurs, likely the decomposition of a hydrate of magnesium or aluminum. Distinct peaks corresponding to masses 32 (O₂, S), 48 (SO), and 64 (SO₂) with an endothermic rise occur at 1050°C (Fig. 10) in air or argon and only with LiF addition. Mass 16 (O) and 32 (O₂) peaks increase starting from 1300°C and rise more steeply from 1400°C. For LP powder with 10 wt% LiF, masses 2 (H₂), 28 (N₂, CO), 30 (NO, Li₂O), and 44 (N₂O, CO₂, Li₄O²⁺) peak more prominently within the vaporization range of LiF. Thermal features for LP powder with 1 wt% LiF and 10 wt% LiF are
intermediate between those for pure spinel and pure LiF. Similar thermal behavior to LP powder was noted for HP powder with or without LiF at lower temperature, but without significant outgassing at higher temperature.

![Fig. 4.10 STA-MS results for masses 32, 48, and 64 for (a) LP powder with 1 wt% LiF in argon, and (b) LP powder without LiF in argon.](image)

LA ICP-OES/MS results for LP compacts hot pressed with 3.5 g of powder, with and without 1 wt% LiF, and with pressure applied at 1200°C, show a concentration gradient for iron, sulfur, and calcium from geometric center to exterior surface (Table 4.2). This gradient may be present for species below the detection limit of ICP. In compacts with LiF, magnesium and impurity content is lower, for some species by an order of magnitude, and significant LiF remains. The high silica concentration in LP compacts suggests contamination from glassware during processing, although no detectable correlation was found with microstructure and optical properties.
Table 4.2  LA ICP-OES/MS Results from Geometric Center and Exterior Surface of LP Compacts Hot Pressed with 3.5 g of Powder with and without LiF and with Pressure Applied at 1200°C.

<table>
<thead>
<tr>
<th>Species</th>
<th>Units</th>
<th>No LiF Center</th>
<th>No LiF Surface</th>
<th>LiF Center</th>
<th>LiF Surface</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>wt%</td>
<td>73.6</td>
<td>72</td>
<td>74</td>
<td>74.2</td>
</tr>
<tr>
<td>MgO</td>
<td>wt%</td>
<td>26.2</td>
<td>27.8</td>
<td>25.4</td>
<td>25.3</td>
</tr>
<tr>
<td>CaO</td>
<td>ppm</td>
<td>93</td>
<td>32</td>
<td>19</td>
<td>4</td>
</tr>
<tr>
<td>SiO₂</td>
<td>ppm</td>
<td>1,211</td>
<td>1,428</td>
<td>1,208</td>
<td>764</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>ppm</td>
<td>323</td>
<td>81</td>
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<td>25</td>
</tr>
<tr>
<td>S</td>
<td>ppm</td>
<td>272</td>
<td>468</td>
<td>339</td>
<td>34</td>
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<tr>
<td>LiF</td>
<td>ppm</td>
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<td>-</td>
<td>14,545</td>
<td>11,794</td>
</tr>
<tr>
<td>xMgO:Al₂O₃ Ratio</td>
<td></td>
<td>0.90</td>
<td>0.98</td>
<td>0.87</td>
<td>0.86</td>
</tr>
</tbody>
</table>

4.4. Discussion

Impurities and stoichiometry differences (Al₂O₃:MgO ~1.01 for LP powder and ~0.995 for HP powder) in the starting powders are the main source of microstructural variation in spinel compacts hot-pressed without LiF in this study. The LP powder contains ~800 ppm sulfur and other impurities in the 10 ppm range that segregate at grain boundaries. In regions of higher impurity concentration, impurities form an amorphous phase that occupies triple junctions and partially de-wets grain boundaries. Impurity-rich grain boundaries and amorphous phase filled triple junctions restrict grain growth by solute drag and grain boundary pinning, respectively. Nonuniform impurity distribution, possibly exacerbated by agglomeration, results in aggregates of submicrometer grains within a matrix of micrometer-sized grains. The lack of curvature where the submicrometer grains impinge on matrix grains and the intergranular fracture of the submicrometer grains are indicative of impurities at the boundaries.³⁵

Smaller grain size in HP compacts may be due to grain boundary pinning by MgO nodules or to MgO-rich stoichiometry, as opposed to larger grain size in HP compacts with Al₂O₃-rich stoichiometry (Al₂O₃ additions). These results contrast with Chiang and Kingery, who show insensitivity to impurity content and increased grain boundary mobility and larger grain size in MgO-rich compacts due to native cation defects.¹²,¹³ Chiang and Kingery performed grain growth studies on hot-pressed nitrate-derived powder compacts packed in powder of similar
stoichiometry within molybdenum foil in H₂ atmosphere, restricting MgO loss and grain boundary impurity segregation, and eliminating carbon contamination, all of which affect defect chemistry. The results seem to agree with those of Uematsu,¹⁶ who performed grain growth studies on unshielded compacts in H₂ atmosphere, where MgO volatilization is greater, as in this study. These apparent discrepancies highlight the sensitivity of spinel to differences in processing conditions.

Addition of LiF to starting powders has a dramatic effect on compact microstructure, with as little as 0.25 wt% doubling grain size. Larger grain size is caused by crystallite coarsening,⁴ reduction in densification temperature and earlier grain growth,³ and is also found to result from reaction of LiF with, and removal of, impurities. Outgassing of SOₓ species at 1050°C in the LP powder, observed only with LiF addition, is consistent with a vapor-phase reduction reaction between LiF and a sulfate species involving reduction to volatile SO₂ [proposed Eqs. (4.2) and (4.3) below] and is also consistent with controlled-atmosphere furnace experiments with LP powder in which sulfur content decreased only upon reduction in hydrogen and not oxidation, even up to 1500°C in oxygen.⁴ Eq. (4.2) is shown to highlight the formation of intermediate products Li₂O and F₂, which may occur simultaneously. LiF and by-product MgF₂ may react similarly with other impurities, such as iron and calcium [proposed Eqs. (4.4) and (4.5)]. Gibb’s energy minimization using HSC Chemistry software determines Eqs. (4.4) and (4.5) to be energetically favorable. Unfortunately, HSC Chemistry does not allow modeling of mixed-metal oxides as in (4.2) and (4.3). Outgassing of volatile impurities during hot pressing results in reduced sulfur, iron, and calcium concentration in LP compacts and reduced iron concentration in HP compacts, which in turn results in larger grain size.

\[
(Mg,Al)SO₄ + 2LiF \rightarrow (Mg,Al)O + SO₂ + Li₂O + F₂
\]  
\[\text{(4.2)}\]

\[
(Mg,Al)O + SO₂ + Li₂O + F₂ \rightarrow (Mg,Al)O + SO₂ + 2LiF + \frac{1}{2}O₂
\]  
\[\text{(4.3)}\]

\[
MgF₂ + CaO \rightarrow CaF₂ + MgO
\]  
\[\text{(4.4)}\]

\[
Fe₂O₃ + 4LiF \rightarrow 2FeF₂ + 2Li₂O + \frac{1}{2}O₂
\]  
\[\text{(4.5)}\]

Understanding how compacts sinter during hot pressing is essential to explain the effect of LiF and impurities. Compact surfaces, especially rims, which are adjacent to the escape route between the annular die and plunger, sinter and attain closed porosity more rapidly than the
interior due to higher thermal gradients and shorter diffusion distances for volatile species to escape.\textsuperscript{1,2,35} Closed porosity at surfaces can trap volatile species that evolve within compact interiors, resulting in solute grain boundary drag, vapor-filled pores that pin grain boundaries and oppose densification, and formation of second phases upon cooling. Application of pressure increases the stress at inter-particle contacts and provides an additional driving force for mass transport, resulting in densification at lower temperatures and a greater likelihood of trapping volatile species. Using more powder results in greater total impurity and/or LiF content, yet the outlet for volatile species to escape is fixed for a given die size. In addition, the larger compact size associated with more powder results in longer diffusion distances for volatile species to escape. Pressure and amount of powder do not affect the grain growth mechanism and varying them in the absence of impurities would not be expected to affect grain size.\textsuperscript{35}

The effect of impurities and LiF was found to be particularly sensitive to the temperature at which pressure is applied during hot pressing. SO\textsubscript{x} species and LiF are trapped during hot pressing by application of pressure below their volatilization ranges (1050°C-1150°C for SO\textsubscript{x} and 1000°C-1300°C for LiF), restricting grain growth. Although LiF typically increases grain growth, trapped LiF in excess of its solubility in spinel accumulates at triple junctions and pins grain boundaries. Grain growth restriction by impurities and LiF is demonstrated by the gradient in impurity and LiF concentration from geometric center to exterior surface concomitant with increased grain size in many of the LP compacts. The effect is less prominent in HP compacts due to lower impurity content. However, HP compacts densify at lower temperatures and are more prone to trapping LiF. Use of less LiF or pre-coarsening powders may be required to ensure complete removal of LiF in both LP and HP compacts.

LiF addition was found to result in grain boundary embrittlement and intergranular fracture. LiF results in grain growth, reduction of grain boundary area, and higher impurity concentration at grain boundaries despite reduced total impurity content. The lack of second phases in many compacts hot pressed with LiF is consistent with impurities and LiF residing at the boundaries. Increased MgO-depletion at grain boundaries due to LiF should result in a decreased lattice parameter\textsuperscript{6} and possibly formation of the defected \(\gamma\)-alumina polymorph.\textsuperscript{36} In either case the coefficient of thermal expansion is likely different, possibly explaining strain contours at grain boundaries observed by TEM. Grain boundary embrittlement is thus thought to be caused by
impurities (LP compacts), lithium and fluorine solutes, increased lattice defects, and residual tensile stress and MgO nodules (HP compacts).

In LP compacts hot pressed without LiF, second phases within aggregates of submicrometer grains combined with the large grain boundary area of the aggregates are thought to be the main source of scatter and opacity. Scatter arises from differences in refractive index between second phases and spinel grains. Scatter scales to a power of the size of scattering features (sixth power for Rayleigh, second power for Mie) and scales to the fourth power of frequency for Tyndall and Rayleigh scatter. Impurities and amorphous phases at larger micron-sized features, such as planar interfaces between aggregates of submicrometer grains and matrix grains, scatter longer wavelengths (Mie scatter), whereas when present at smaller features, such as grain surfaces (~500 nm, Tyndall scatter), triple junctions (~50 nm, Rayleigh scatter), and grain boundaries (< 5 nm, Rayleigh scatter), scatter shorter wavelengths. Scatter in HP compacts is much lower than in LP compacts and is may be caused by MgO nodules (n = 1.735 vs n = 1.710 for spinel)\textsuperscript{34,37} and strain fields that surround them.

In compacts hot pressed with LiF, trapped LiF is present in greater concentration than other impurities (Table II) and is thought to be the main cause of scatter. In LP compacts hot pressed with LiF and pressure applied at 900°C or with pressure applied at 1200°C but with more powder, impurities and LiF trapped at triple junctions in combination with increased grain boundary area result in scatter and opacity. However, in hazy or opaque compacts hot pressed with LiF and pressure applied at 1200°C and with less powder, second phases are not observed, suggesting another source of scatter. MgO-depletion due to LiF addition may result in scatter due to a grain boundary region with a different refractive index, tending towards that of γ-Al\textsubscript{2}O\textsubscript{3} (n ~ 1.73).\textsuperscript{31,38} In transparent LP compacts with LiF and with pressure applied at 1200°C, impurity phases in areas of smaller grains likely cause scatter at shorter wavelengths. In HP compacts hot pressed with LiF, trapped LiF results in cloudy areas and the increased incidence of MgO nodules likely contribute to scatter at shorter wavelengths. Fluorescence in compacts with LiF addition may be due to the presence of fluorine.

Absorption in compacts hot pressed without LiF is thought to be caused by reduction of spinel by carbon and formation of aluminum oxy-carbides\textsuperscript{18} and possibly color centers. Spinel is reduced
by carbon from the graphite foil liners and the CO atmosphere, is consistent with lower absorption observed with increased shielding. STA-MS experiments indicate reduction is more significant above 1300°C, consistent with the onset of darkening in HP compacts hot pressed above 1300°C. Absorption is exacerbated by off-stoichiometry, especially Al$_2$O$_3$-rich compositions, possibly due to greater aluminum oxy-carbide formation. The iron-rich phase observed in HP compacts may contribute to absorption through intervalence charge transfer between Fe$^{2+}$ and Fe$^{3+}$, however, the concentration is likely too small to be the sole source of absorption. Other possible causes of absorption, such as reduction of MgO to metal, have not been quantified. The mechanism by which LiF counteracts absorption is not known with certainty and is the subject of future work.

4.5. Conclusion

Impurities in the ppm range and stoichiometry differences in starting powders significantly affect microstructure in hot pressed spinel compacts. Impurities form an amorphous phase at grain boundaries and triple junctions that partially de-wets upon cooling. Impurities and amorphous phases restrict grain growth, likely by solute drag and grain boundary pinning, and along with increased grain boundary area cause scatter and opacity. LiF reacts with impurity species in the vapor-phase to form volatile species that are removable by proper selection of the temperature at which pressure is applied, resulting in larger grain size and increased transmittance. However, larger grain size results in impurity concentration at grain boundaries and formation of second phases at triple junctions that scatter visible wavelengths. Application of pressure below the volatilization range of impurities and LiF forces densification of compact surfaces to lower temperatures and traps these species. Trapped LiF in excess of its solubility in spinel accumulates at triple junctions, pins grain boundaries, and causes scatter. For high-purity, high sintering activity nanometer-sized powders, less LiF must be used or powders must be pre-coarsened to ensure LiF removal. LiF addition also results in increased MgO loss at grain boundaries due to formation of volatile MgF$_2$ and replacement of magnesium by lithium and oxygen and fluorine in the lattice, possibly causing scatter due to increased refractive index. Absorption is caused by reduction of spinel by carbon from graphitic components and can be reduced by proper shielding. LiF counteracts absorption, possibly by preventing aluminum oxy-carbide formation or by forming defects that counteract color centers. Although MgO loss
(Al₂O₃-rich stoichiometry) has been reported to lower grain boundary mobility, larger grain size is observed when hot pressing Al₂O₃-rich powders in a graphitic furnace. In MgO-rich powders, excess MgO forms nodules that pin grain boundaries and scatter shorter wavelengths. Altered grain boundary stoichiometry and chemistry due to LiF results in grain boundary embrittlement and intergranular fracture.

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CHAPTER 5
ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY OF TRANSPARENT POLYCRYSTALLINE MAGNESIUM ALUMINATE (MgAl$_2$O$_4$) SPINEL

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ABSTRACT

Transparent polycrystalline magnesium aluminate spinel (MgAl$_2$O$_4$, spinel) is one of few promising materials that can satisfy certain demanding optical applications. However, LiF additive used to enhance sintering and impart transparency during fabrication causes grain-boundary embrittlement, MgO loss and scatter, precluding wider application. To determine the mechanisms responsible for altered properties, electrochemical impedance spectroscopy was performed between 500°C and 900°C, in oxidizing and reducing atmosphere, on fully-dense, polycrystalline spinel compacts hot-pressed with and without LiF. In combination with electron microscopy, chemical analysis, and secondary-ion mass spectroscopy, the dielectric behavior of the bulk and grain boundaries was related to microstructure and chemistry. Higher conductivity in polycrystalline compacts compared to single crystals correlates with impurities at the boundaries. Addition of LiF reduces conductivity by one order of magnitude and increases the activation energy for conductivity, attributed to larger grain size, reduced impurity content, and altered grain-boundary and bulk point-defect chemistry, the latter caused by uniform incorporation of lithium. Conductivity for higher purity, fine grain-size, MgO-rich compacts, was one order of magnitude higher than for lower-purity, larger grain size, Al$_2$O$_3$-rich compacts, indicating the strong influence of stoichiometry and impurities.

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5.1 Background

Transparent polycrystalline magnesium aluminate spinel (MgAl$_2$O$_4$, spinel) has an excellent combination of properties possessed by few materials, promising use in demanding optical applications.$^{1,2,3,4}$ However, 1-4 wt% LiF required to impart transparency during hot press (HP) or HP/hot isostatic press (HIP) fabrication degrades properties, precluding wider application.$^{1,3,5}$ LiF removes impurities by forming volatile fluorides$^{6,7}$ and it is thought to incorporate into the lattice, creating point defects that may enhance densification.$^{5,8,9,10,11,12}$ Moreover, LiF likely alters surface mobility and energy, increasing kinetics and the driving force for sintering.$^{13}$ Furthermore, LiF counteracts absorption observed in compacts processed in graphitic furnaces.$^3$ However, LiF addition results in large grain size$^5$, grain-boundary embrittlement,$^7$ and MgO loss.$^7$ The latter occurs preferentially at surfaces and grain boundaries, even without LiF addition.$^{14,15,16,17}$ MgO deficient stoichiometry, expressed by $x$ in MgO:$x$Al$_2$O$_3$, exhibits a lower IR absorption edge$^1$ and also has a smaller lattice parameter.$^{14}$ Grain-boundary stoichiometry gradients are expected to cause tensile strain and refractive index variation, resulting in scatter at ultra-violet (UV) wavelengths. Although LiF removes impurities, remnant LiF and impurities are concentrated as grain-boundary area diminishes with increasing grain size,$^7$ possibly contributing to embrittlement. To better understand the role and effect of LiF, and of interfaces during sintering, the bulk and grain boundaries of transparent spinel compacts need characterization, especially in terms of point defects. However, determining the cause of altered grain-boundary behavior has proven elusive, even with advanced transmission electron microscopy (TEM).

Electrochemical impedance spectroscopy (EIS) is a powerful technique used to characterize the dielectric properties of solids and their interfaces.$^{18}$ As different polarization mechanisms respond to different frequencies, EIS permits their identification and quantification. Samples are modeled as equivalent circuits matching the impedance response and the properties of the impeding polarizing mechanisms are determined from the values of the corresponding circuit elements. An alternating (AC) voltage spanning a range of frequencies is applied across a sample with electrodes and the current is measured, from which the impedance is calculated:

\[
Z = Z_0e^{j\omega t} = Re[Z] - Im[Z] = \frac{V_0\cos(\omega t)}{i_0\cos(\omega t - \theta)},
\]

(5.1)
where $Z$ is the impedance, $j = \sqrt{-1}$, $V_0$ is the voltage amplitude, $i_0$ is the current amplitude, $\omega$ is the angular frequency, $t$ is time, and $\phi$ is the phase shift. The real (resistive) and imaginary (phase difference) components of the impedance are plotted as a function of frequency on a Nyquist plot. Dielectric solids are modeled as equivalent parallel resistor-capacitor (RC) circuits, where capacitors act as open circuits at low frequencies (current flowing through resistors) and as closed circuits at high frequencies as capacitance is reduced due to dielectric lag at these frequencies. At intermediate frequencies the current magnitude and phase shift results in a semi-circle for ideal RC-circuit Nyquist plots. The difference between the high- and low-frequency real-axis semi-circle intercepts is equal to the RC-circuit resistance. Resistivity ($\rho = RL/A$, where $R$ is resistance, $L$ is the electrode separation distance, and $A$ is electrode cross-sectional area) and conductivity ($\sigma = 1/\rho$) are calculated from the resistance and the solid-electrode geometry. The imaginary component of the impedance is maximized when $\omega_0\tau = 2\pi f_0\tau = 1$, where $\omega_0$ is the resonant angular frequency, $f_0$ is the resonant frequency, and $\tau$ is the relaxation time, which for a parallel RC-circuit is equal to $RC$, allowing RC-circuit capacitance to be determined from $\omega_0$ and $R$ from EIS plots. The capacitance is related to the complex permittivity $\varepsilon = C(L/A)$, where $C$ is the capacitance. Although permittivity is related to the complex refractive index, it is frequency-dependent and the frequencies used in EIS are too low to permit direct calculation of the optical refractive index. Modulus plots of $\text{Im}(M)$ versus $f$, where $M = j\omega C_c Z_c$, $C_c = \varepsilon_0 A/L$ is the capacitance of the empty cell and $\varepsilon_0 = 8.854E^{-12}$ F/m is the permittivity of free space, emphasize components with the smallest capacitance and are useful when arcs are not resolvable in Nyquist plots.\textsuperscript{18,19}

A widely-used model for polycrystalline solids consists of a resistance and two parallel RC-circuits in series, representing the resistance and capacitance of the electrode, bulk and grain boundaries (Fig. 5.1).\textsuperscript{18} If the RC-circuits time-constants differ by an order of magnitude or more, two separate semi-circles appear on impedance plots. As grain boundaries have smaller thickness and greater capacitance, the larger time constant positions their impedance semi-circle at lower frequencies, permitting bulk and grain boundary properties to be separated. If the grain size and grain-boundary width are known, bulk and grain-boundary conductivity can be estimated by considering cubic grains with intervening boundaries.\textsuperscript{18,19} In the brick-layer model, the grain boundary volume fraction $v_{gb}$, is approximately $3d/D$, where $d$ is the grain boundary...
width and $D$ is the grain size and $d/D \approx C_{\text{bulk}} \varepsilon_{\text{bulk}}/C_{\text{gb}} \varepsilon_{\text{gb}}$. Assuming $\varepsilon_{\text{bulk}} = \varepsilon_{\text{gb}}$ and as resistivities weighted by volume add for series circuits, grain boundary and bulk resistivities can be calculated from EIS plot capacitance values. Moreover, conductivity in ionic compounds is temperature-activated, $\sigma = \sigma_0 e^{-E_a/kT}$, where $\sigma$ is the conductivity, $E_a$ is the activation energy for conductivity, $k$ is Boltzmann’s constant, and $T$ is temperature. Thus, performing EIS at different temperatures permits calculation of the activation energy for conductivity. Furthermore, ionic conductivity is related to diffusivity and is therefore relevant to sintering. Performing EIS in oxidizing/reducing atmospheres can also give further insights into the defect chemistry.

EIS interpretation can be ambiguous as different equivalent circuits can yield similar impedance responses. Typically, the simplest circuit reflecting the microstructural and conductive properties of a sample is used. Impedance spectra non-linearity is attributed to various factors, including surface roughness and heterogeneities, electrode porosity, variation of coating composition, slow adsorption reactions, and non-uniform potential and current distribution, and is modeled using constant phase circuit elements (CPE’s), which model the behavior of an electrical double layer or imperfect capacitor: $Z(\omega) = Q^1(j\omega)^n$, where the parameter $Q$ becomes equal to capacitance when $n = 1$. Diffusional processes are modeled using a particular type of CPE called a Warburg element.

Spinel is a wide, direct band gap insulator exhibiting mainly ionic or mixed ionic-electronic conduction. Ionic transference numbers ranging from 0.5 to 1.0 have been reported in the temperature range used in this study. Conductivity varies with an Arrhenius
relation from $\sim10^{-12}$ S-cm$^{-1}$ at 500°C to $\sim10^{-4}$ S-cm$^{-1}$ at 1600°C and activation energies vary from 0.4-2.6 eV. 26,29,31 Magnesium ions have the highest self-diffusivity, but it is unclear whether they or magnesium vacancies are the main charge carriers.28,29,30,32,33,34,35,36 Cation transport is by interstitial diffusion accentuated by magnesium vacancies in alumina-rich stoichiometry.27,33,35 Aluminum ion diffusivity is up to several orders of magnitude lower35,36,37 and oxygen ion diffusivity lower still,36,38,39,40 with conductivities expected to mirror diffusivities. Conductivity for polycrystalline samples is generally 1-2 orders of magnitude higher than for single crystals and is attributed to grain-boundary dominated conduction.26,33,34,41,42,43 Oxygen ion grain-boundary conductivity is higher than bulk conductivity44 but cation grain-boundary conductivities have not been reported.36 However, cations are likely the main grain-boundary charge carriers as conductivity in single crystals and polycrystalline compacts is not greatly influenced by oxygen partial pressure.28,33,34 Conductivity is likely highly dependent on porosity, grain size, stoichiometry, and impurity concentration.31 Indeed, hopping of protons along surface-adsorbed hydroxyl ions in high relative humidity is the main charge carrier in porous compacts used for oxygen sensors (at lower temperatures).45,46

There are few EIS studies of polycrystalline spinel compacts28,43,45,47 and none for fully-dense or transparent compacts. Based on conductivity literature, ionic conduction along grain boundaries is expected to dominate, especially for fine-grained or Al$_2$O$_3$-rich spinel, increasing total conductance. However, conduction across grain boundaries is expected to be low, among other factors, due to charged defects in a space-charge layer.14,15,17 Grain-boundary conduction in the direction of the applied field is parallel to bulk conduction, resulting in a single equivalent RC-circuit and Nyquist plot arc, from which components cannot be unambiguously extracted. Impedance across grain boundaries, if significant and if the time constant difference versus bulk impedance is large enough, should result in a low-frequency semi-circle. As grain-boundary width is not expected to change appreciably, the contribution from grain-boundary conduction is expected to decrease with increasing grain size due to the longer path, resulting in a greater contribution from conduction through the bulk and across grain boundaries. Larger grain size and intergranular fracture associated with LiF, the latter suggestive of a defected grain-boundary structure, are expected to decrease conductance. Whereas, MgO loss resulting in Al$_2$O$_3$-rich stoichiometry should increase conductance. The MgO-rich stoichiometry of compacts HP with
flame-spray pyrolysis powders is expected to decrease conductance while the fine grain size should increase it.

5.2 Experimental

Spinels compacts were prepared from sulfate-derived (Baikowski S30CR, Charlotte, NC, USA) powders with ~1000 ppm impurities and flame-spray pyrolysis-derived (Nanocerox Spinel Powder, Nanocerox, Ann Arbor, MI, USA) powders with <100 ppm impurities. 1 wt% LiF (Alfa Aesar, MA, USA) was added by ultrasonic mixing (CPX 130, Cole Palmer, Vernon Hills, IL, USA) in ethanol followed by rotary evaporation (R-210, Buchi Labortechnik AG, Flavil, Switzerland). Prepared spinel powders were poured inside a graphite die lined with graphite foil (GrafTech, Lakewood, OH, USA) and placed inside a graphitic furnace (Thermal Technology Inc., Santa Rosa, CA, USA). Temperature was ramped at 6°C/min. with an intermediate 60 min. hold at 400°C, maintained at 1550°C for 60 min., and ramped to ambient at 6°C/min. A pressure of 35 MPa was applied at 1200°C upon heating and removed at 900°C upon cooling. A vacuum of less than 13 MPa (10⁻⁴ Torr) was maintained throughout the runs. Compact density was assessed using the Archimedes method and ASTM B962 and C373. Compact microstructure was examined with optical microscopy (PMG3; Olympus, Tokyo, Japan), scanning electron microscopy (SEM; JSF-7000; JEOL, Tokyo, Japan), and transmission electron microscopy (TEM; CM200; FIE Phillips, Eindhoven, The Netherlands). Chemistry of grain-boundary and second phases was assessed with SEM, TEM, and scanning TEM (STEM; Tecnai G2 F20 S-Twin 200 keV FE S/TEM; FEI) in combination with energy-dispersive spectroscopy (EDS). Impurity content was assessed with laser ablation inductively-coupled plasma in combination with optical emission spectroscopy and mass spectroscopy (LA-ICP OES/MS; Spectro-Arcos ICP/OES; Varian 820 MS ICP/MS; Cetac LSX-500 LA; Varian, Palo Alto, CA) and secondary-ion mass spectroscopy (SIMS; IMS 5f, Cameca, Gennevilliers, France). Grain size was determined using a circle-intercept method and ASTM E112. Total grain boundary area was estimated by modelling grains as tetrakeidecahedrons with diameters equal to the average grain size and grain-boundary width was estimated from high-resolution TEM images and Fresnel-fringe defocussing.
Cylindrical (~12.7 mm x 2 mm), hot-pressed polycrystalline spinel compacts were surface-ground to ~0.7 mm thick and polished down to 0.05 µm alumina grinding media. Gold electrodes ~7 mm or ~10 mm in diameter were sputtered on each side and silver wire leads attached using silver mesh and silver adhesive paint cured at 200°C for 30 min. Electrode leads were threaded through a 2-bore alumina tube placed inside a larger closed-end alumina tube in a tube furnace. A type-K thermocouple was positioned adjacent to the sample. Atmosphere was synthetic air or argon with 2% H₂, set to a flow rate of 70 cm³/min. The furnace was ramped to 900°C and sequentially cooled at 50°C intervals to 500°C with temperature allowed to stabilize at each interval. A potentiostat (Gamry Reference 3000, Gamry, Warminster, PA, USA) applied an alternating voltage (AC) of 100 mV rms from 0.1 Hz to 1 MHz at ten points per decade.

EIS samples were modeled as equivalent RC-circuits based on observed microstructure and reported conductivity characteristics and the circuit elements related to Nyquist plots and plots of the complex modulus versus frequency. Resistances and capacitances were calculated from the real-component intercepts and imaginary-component maxima, respectively. Where two semi-circles appeared on the Nyquist plot, the bulk and grain-boundary components were assumed to be associated with the lower and higher-frequency semi-circles, respectively. Impedance response was modeled using ZView® (Scribner Associates, Southern Pines, NC, USA) electrochemistry modelling software. Grain-boundary contribution to impedance was calculated using the estimated grain boundary volume fraction or using the brick-layer model with cubic elements with a grain size equal to the measured average grain size. Although, the assumption of equal permittivities in the brick layer model is in general applicable only in the presence of a second phase at grain boundaries. Bulk and grain boundary conductivities were calculated based on the calculated grain and grain-boundary volume fractions. Sample, bulk, and grain boundary permittivities were calculated from corresponding capacitance values.

5.3 Results

All compacts were greater than 99.5% of theoretical density, and although occasional second phases were noted, porosity was not. Compacts HP with sulfate-derived powder without LiF were opaque and microstructure consisted of matrix grains (GS =12 µm) and regions (~5 vol.%) of submicrometer grains (GS < 0.5 µm), in which grain boundaries were decorated with
an amorphous impurity phase (Fig. 5.2). One of the compacts was cream-colored and the other dark, attributed to increased reduction caused by vacuum fluctuations during HP. The compact HP with sulfate-derived powder and 1 wt% LiF was transparent with uniform grain size (GS = 25 µm), occasional second phases at triple junctions, and clean grain boundaries (Fig. 5.3). However, STEM-EDS indicated higher impurity (C, Ca, S) content at the boundaries and Fresnel ridges were sometimes observed with TEM. LA-ICP OES/MS indicated lower total impurity content than compacts HP without LiF and 0.5 wt% remnant lithium. TEM-EDS indicated the presence of fluorine, especially at triple junctions. SIMS indicated uniform lithium distribution in the bulk (Fig. 5.4). All sulfate-derived compacts were slightly Al₂O₃-rich, estimated at $x = 1.01$ based on LA-ICP OES/MS. Compacts HP with flame-spray pyrolysis powders were dark but transparent, with a much smaller uniform grain size (GS = 4 µm) and occasional MgO nodules ~100-200 nm in diameter (Fig. 5.5). Based on image analysis of the volume fraction of MgO nodules, the compacts were MgO-rich, estimated at $x = 0.995$. Grain boundary width for all compacts was estimated at less than 0.5 nm, and less than 1 nm in compacts with LiF.

![Microstructure of compacts HP with sulfate-derived powder without LiF.](image)

Fig. 5.2 Microstructure of compacts HP with sulfate-derived powder without LiF. (a) SEM fracture surface (average matrix grain size 12 µm), arrows show areas of sub-micron grains, note trans-granular fracture (inset: compact images). (b) Areas of sub-micron grains constituting ~5 vol.%. (c) TEM image of sub-micron grains, arrows show location of amorphous impurity phase shown in (d). (e) TEM image of impurity phase decorating a sub-micron grain. Reprinted with permission from Ref. [7].
Fig. 5.3 Microstructure of HP sulfate-derived powder compacts with 1 wt% LiF. (a) SEM fracture surface (GS ≈ 25 µm), arrows show areas of smaller grains, note inter-granular fracture (inset: compact image). (b) SEM image of micron-sized grain areas constituting < 1 vol%. (c) SEM image of impurity-rich phases. (d) TEM image of typical grain boundary devoid of amorphous phases but with higher impurity content. Reprinted with permission from Ref. [7].

Fig. 5.4 SIMS results for compacts HP with sulfate-derived powder. (a) Lithium map (50 µm x 50 µm) on a compact without LiF. (b) Lithium map (25 µm x 25 µm) on a compact HP with 1 wt% LiF and pressure applied at 900°C (similar results with lower lithium content were obtained when pressure was applied at 1100°C). (c) Li depth profile for sample without LiF and two samples with 1 wt% LiF showing relatively constant lithium concentration with depth.
EIS results for samples HP with sulfate-derived powder are shown in Figures 5.6-5.8, with insets showing the high-frequency region for higher temperatures, and a comparison of samples at 850°C, including simulation fits, is shown in Figure 5.9. All EIS spectra were depressed semi-circles with centers below the real axis, indicating distributed capacitance, and were simulated by replacing capacitances in RC-circuits with CPE’s. The spectra also displayed Warburg-like low-frequency tails, possibly due to sample-electrode effects, with phase angles varying from $\pi/5$ to $\pi/8$, which were simulated with CPE’s or Warburg elements. High frequency semi-circle intercepts were consistently near zero Ohms, whereas the low-frequency intercepts and imaginary maxima decreased with increasing temperature, indicating increasing conductivity. Deviations near the low-frequency intercepts indicated the possible presence of a small semi-circle. Impedance spectra for the sample hot-pressed with 1 wt% LiF displayed two clearly defined semi-circles, with low-frequency intercepts and imaginary maxima decreasing with increasing temperature. Conductivity increased with temperature with an Arrhenius relation and activation energies shown in Figure 5.10. Impedance plots for compacts HP with flame-spray derived powders displayed a single arc with much higher resistance and imaginary maximum. All compacts appeared to display higher resistance and imaginary maxima in reducing conditions, contrary to some reports. Sample parameters and calculated dielectric properties are tabulated in Table 5.1.
Fig. 5.6 EIS spectra for the dark-colored HP sulfate-derived powder compact without additives. Insets: high-frequency region and image of compact and sample with electrode (note smaller electrode).

Fig. 5.7 EIS spectra for the cream-colored HP sulfate-derived powder compact without additives. Inset: high-frequency region, image of compact and of sample with electrode.

Fig. 5.8 EIS spectra for the transparent HP sulfate-derived powder compact with 1 wt. % LiF addition. Inset: high-frequency region, image of compact and of sample with electrode.
Fig. 5.9 Comparison of EIS spectra for sulfate-derived powder compacts at 850°C. Resistance differences in the high-frequency bulk arcs are due in part to electrode geometry differences. Solid lines are equivalent circuit (inset) simulations using ZView®.

Fig. 5.10 Arrhenius plots and activation energies for conductivity for sulfate-derived powder samples.

Fig. 5.11 EIS spectrum for the transparent HP flame-spray pyrolysis-derived powder compact without LiF addition at 850°C. EIS spectra for sulfate-derived powder compacts at 850°C shown for comparison.
Table 5.1 Selected dielectric properties of polycrystalline samples HP under different conditions at 850°C (activation energies calculated for ranges between 450°C and 900°C).

<table>
<thead>
<tr>
<th>Powder</th>
<th>Sulfate</th>
<th>Sulfate</th>
<th>Sulfate</th>
<th>Flame-spray</th>
</tr>
</thead>
<tbody>
<tr>
<td>Comments</td>
<td>No additives</td>
<td>No additives</td>
<td>1 wt% LiF</td>
<td>No additives</td>
</tr>
<tr>
<td>Grain size (µm)</td>
<td>Opaque, dark</td>
<td>Opaque, cream</td>
<td>Transparent</td>
<td>Transparent</td>
</tr>
<tr>
<td>ρ&lt;sub&gt;bulk&lt;/sub&gt; (Ω)</td>
<td>1.6E+05</td>
<td>7.0E+05</td>
<td>1.4E+06</td>
<td>5.6E+06</td>
</tr>
<tr>
<td>ρ&lt;sub&gt;gb&lt;/sub&gt; (Ω)</td>
<td>1.1E+09</td>
<td>4.5E+09</td>
<td>8.2E+10</td>
<td>1.5E+09</td>
</tr>
<tr>
<td>σ&lt;sub&gt;bulk&lt;/sub&gt; (S/cm)</td>
<td>6.2E-06</td>
<td>1.4E-06</td>
<td>7.3E-07</td>
<td>1.8E-07</td>
</tr>
<tr>
<td>σ&lt;sub&gt;gb&lt;/sub&gt; (S/cm)</td>
<td>9.1E-10</td>
<td>2.2E-10</td>
<td>1.2E-11</td>
<td>6.6E-10</td>
</tr>
<tr>
<td>σ&lt;sub&gt;total&lt;/sub&gt; (S/cm)</td>
<td>5.2E-06</td>
<td>1.3E-06</td>
<td>4.1E-07</td>
<td>8.4E-08</td>
</tr>
<tr>
<td>E&lt;sub&gt;σ&lt;/sub&gt; (eV)</td>
<td>0.63</td>
<td>0.71</td>
<td>1.06</td>
<td>-</td>
</tr>
<tr>
<td>E&lt;sub&gt;σ&lt;/sub&gt; bulk (eV)</td>
<td>-</td>
<td>-</td>
<td>1.1</td>
<td>-</td>
</tr>
<tr>
<td>ω&lt;sub&gt;gb&lt;/sub&gt; (rad/s)</td>
<td>7.1E+04</td>
<td>2.5E+05</td>
<td>1.3E+05</td>
<td>3.5E+03</td>
</tr>
<tr>
<td>C&lt;sub&gt;bulk&lt;/sub&gt; (F)</td>
<td>7.1E-11</td>
<td>1.0E-11</td>
<td>1.0E-11</td>
<td>4.1E-11</td>
</tr>
<tr>
<td>C&lt;sub&gt;gb&lt;/sub&gt; (F)</td>
<td>5.0E-10</td>
<td>3.7E-09</td>
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<tr>
<td>ε&lt;sub&gt;gb&lt;/sub&gt;</td>
<td>2.6E-03</td>
<td>8.4E-01</td>
<td>1.2E-01</td>
<td>-</td>
</tr>
</tbody>
</table>

Note: ρ<sub>bulk</sub> and σ<sub>bulk</sub> values based on R<sub>bulk</sub> (< R<sub>total</sub>) from EIS plots. ρ<sub>gb</sub>, σ<sub>gb</sub> and ε<sub>gb</sub> values based on brick-layer geometry with series resistances, D = grain size, d = 1 nm.

5.4 Discussion

In compacts HP with sulfate-derived powders without LiF, the near-zero high-frequency Nyquist plot intercepts imply the single arcs were at least in part due to bulk impedance. Given expected time-constant differences, that other high-frequency arcs were not indicated in modulus plots, and that arc capacitances were consistent with expected values for bulk oxides, it is unlikely that an overlapping grain-boundary component contributed to the single arcs at higher frequencies. Additionally, resistances associated with the arcs were one order of magnitude lower than that calculated using single-crystal conductivities, even when the Al₂O₃-rich stoichiometry of the sulfate-derived powders was taken into account; a series grain-boundary component should result in increased resistance. Electrode misalignment and leakage were not expected to cause such significant differences. The low resistivities indicated by the arcs
suggested either higher bulk conductivity or high grain-boundary conductivity in parallel. The latter was suggested by small grain size and high reported grain-boundary ionic conductivity in spinel. A lower-resistance RC-circuit in parallel to the bulk results in a single equivalent RC-circuit producing a single, lower-resistance arc in which components are not resolvable. Based on the calculated grain-boundary area and a width of one nanometer, a specific grain-boundary conductivity several orders of magnitude higher than the bulk would be required to produce the increased conductivity. Alternatively, the higher impurity content of sulfate-derived powder compacts could have resulted in charged, conductive species that increased bulk conductivity. However, impurities were preferentially segregated at grain boundaries, if anything contributing to grain-boundary conductivity. Another possibility was that carbon contamination from the graphite foil, dies, and CO atmosphere present in graphitic furnaces formed mobile charge carriers in the bulk. Such defects would also explain the higher absorption in these samples, especially increased conductivity and absorption in the darker one. However, the higher-purity flame-spray powder derived compacts displayed very low conductivity, despite being subjected to the same carbon contamination. Arc non-linearity in the samples was attributed to microstructural variation and a good fit was obtained by simulation using a CPE with $n \sim 0.9$. The amorphous impurity phase in regions of sub-micron grains likely contributed to non-linearity as current lines make detours around hindrances and either favor or avoid these regions.\textsuperscript{50}

Single arcs in EIS spectra due to bulk impedance imply that intervening grain boundaries perpendicular to the applied field should contribute to impedance, even if a parallel component exists. Thus, the bulges in impedance spectra at lower frequencies in compacts HP with sulfate-derived powder without LiF were attributed to grain boundary-impedance across boundaries. It is also possible that the bulges were due to sample-electrode effects, such as partial blocking, or to microstructural variation. However, the time constants where the bulges occurred were similar to those for the grain-boundary arcs in samples with LiF and capacitances for arcs causing the bulge were similar to expected values for grain boundaries in oxides.\textsuperscript{18,49} Simulating the spectra as two parallel RC-circuits in series, representing bulk and grain-boundary components, and with capacitances replaced with CPE’s yielded good fits. However, as the arcs were not fully-resolved and potentially overlapping, the grain-boundary properties for these
samples involve uncertainty. The Warburg-like low frequency tail was attributed to sample-electrode effects\textsuperscript{47} and a good fit was obtained by modelling with a CPE with \( n = 0.9 \).

Different dielectric properties in the sample with LiF addition was somewhat expected given the microstructural, fracture, and optical property differences. The two well-resolved arcs at higher temperatures were attributed to bulk (higher frequency) and grain boundary (lower frequency) impedances. Lower total conductivity was attributed to increased grain size and decreased impurity content, resulting in lower impurity content at grain boundaries in the direction of the applied field per unit volume. Although bulk resistivity was slightly higher, the time constant was similar to that for samples HP without LiF and the high-frequency intercept was still near zero. Higher bulk resistivity was attributed to scatter and trapping caused by the uniform incorporation of lithium (indicated by SIMS) and associated charge-compensating defects. The counteraction of absorption by lithium and associated defects may also indicate lower bulk charge-carrier concentration. Higher grain-boundary resistance and resistivity compared to samples without LiF, and despite larger grain size, was partially attributed to charge-flow effects due to increasing grain-boundary path length, while grain-boundary width remained relatively constant. This was expected to resulting in increased charge transport through (and corresponding impedance from) the bulk and intervening grain boundaries. An additional contributing factor may have been the presence of lithium and fluorine and associated charge-compensating defects. Based on EIS at 800°C and 850°C, where separate arcs were well resolved, the activation energies for bulk and grain boundary conductivities were estimated at 1.1 eV and 0.8 eV, respectively. These values involve considerable uncertainty due to the limited temperature range over which they are calculated.

If conductivity is predominantly ionic in spinel, decreased bulk conductivity with LiF addition is not necessarily contradictory to sintering studies suggesting enhanced densification from increased bulk diffusion. This is because conductivity is limited by the fastest species (cations) and sintering by the slowest (anions). In addition, most sintering studies were conducted using pressure, which drives mass flow from surfaces and grain boundaries to voids without the need for bulk transport (grain-boundary transport suffices). It is also possible that the transference numbers for bulk and grain boundary conductivity are different in spinel and that decreased bulk conductivity does not correlate with decreased diffusion.
The conductivity of the sample HP with flame-spray pyrolysis powder was an order of magnitude lower than reported polycrystalline values and similar to reported single-crystal values, but still an order of magnitude higher than reported MgO-rich single crystal values. The lower conductivity was attributed to higher grain-boundary area consisting of cleaner grain boundaries and to the presence of MgO nodules. However, the small amount of impurities at boundaries likely contributes to higher conductivity than for single crystals of similar stoichiometry. The lower conductivity (compared to sulfate-derived powder compacts) demonstrates that greater grain-boundary area does not necessarily lead to increased conductivity and that carbon and associated defects likely play a lesser role than stoichiometry and impurity content, as this sample was also exposed to reduction and displayed absorption. Arc non-linearity in these samples was attributed to microstructural variation and a good fit was obtained by simulation using a CPE with $n \approx 0.9$.

Although the results indicate impurities at grain boundaries increase conductivity, the specific impurities and associated defects responsible were not identified. Additionally, the respective contributions from grain boundaries, impurities, and stoichiometry could not be determined with certainty. Analysis is complicated as conduction mechanisms and transference numbers as a function of stoichiometry in spinel are not known with certainty. For example, grain-boundary conduction may be predominantly ionic, whereas bulk conduction could be primarily electronic. EIS studies varying grain size, stoichiometry, or grain-boundary impurity concentration while keeping the other variables fixed, using blocking and non-blocking electrodes, combined with measurement of grain-boundary conductivities with microelectrodes, would help determine the contributions of each to conductivity. Decoration with cathodoluminescence and SEM or TEM to better identify and quantify resistive features such as second phases at triple junctions and grain boundaries would also be valuable.

5.5 Conclusion

EIS was conducted on fully-characterized, dense, opaque and transparent, MgO-rich and Al$_2$O$_3$-rich, polycrystalline spinel compacts HP with and without LiF, in reducing and oxidizing atmosphere between 500°C and 900°C. Conductivity was up to several orders of magnitude higher than, and activation energies lower than, reported values for single-crystals, consistent
with reports in the literature. Higher conductivity correlated with higher impurity content and smaller grain size, suggesting the cause was increased conductance along impurity-rich grain boundaries in parallel to conductance across grains and intervening boundaries. It is possible that higher bulk conductivity, possibly caused by increased charge-carrier concentration due to contamination and reduction by carbon, contributed to the increased total conductivity. However, the parallel high-conductivity component makes determining specific bulk and grain boundary conductivities difficult. Additionally, high-conductivity pathways are expected to increase current line detouring around hindrances such as grain boundaries running across the field, further complicating analysis. Regardless, conductivity across grain boundaries was lower than conductivity in the bulk and conductivity along boundaries, and all conductivity components exhibited an Arrhenius relation with temperature.

LiF addition decreased bulk and grain boundary conductivity and increased activation energy for conductivity. Lower total conductivity was attributed to lower grain boundary area in the direction of the applied field and lower total impurity content, even though specific grain boundary impurity content was higher. Thus conductance across the bulk and intervening grain boundaries was greater, resulting in larger impedance semi-circles from these components. It is possible that conductivity along and across grain boundaries may have been reduced due to the presence of lithium, fluorine, and associated defects and/or an enhanced grain-boundary space-charge layer exacerbated by MgO-loss. Lower bulk conductivity was attributed to trapping and scatter due to the uniform incorporation of lithium and the associated formation of charge-compensating defects, and also possibly due to decreased bulk charge-carrier concentration, as indicated by decreased absorption. Low-impurity, MgO-rich samples with fine grain size HP from flame-spray powders displayed conductivity up to one order of magnitude lower than higher-impurity, Al₂O₃-rich, samples with larger grain size made from sulfate-derived powders. The lower conductivity was attributed to MgO-rich stoichiometry, the presence of MgO nodules, and lower impurity content. Results indicate that Impurity content may play a larger role than grain size, stoichiometry, and defects caused by reduction due to carbon. As with other properties, this study demonstrates that spinel is extremely sensitive to small changes in microstructure, stoichiometry, and impurity content and further study is required to elaborate on the exact mechanisms contributing to conductivity behavior.
REFERENCES CITED


CHAPTER 6
RESULTS

This chapter contains additional information and experimental results not covered in Chapters 3-5. Section 6.1 provides additional details on powder characterization, Section 6.2 provides STA-MS results not discussed in Chapter 4 (calibration runs, LiF, LiAl$_2$O$_4$ and MgF$_2$, Nanocerox powder, and Baikowski powder with and without LiF in argon and air), Section 6.3 provides thermodynamic simulation plots, Section 6.4 presents dilatometry results including those on irradiated powders, Section 6.5 presents additional hot press results not covered in Chapter 4, Section 6.6 presents Raman spectroscopy results, Chapter 6.7 presents details of miscellaneous thermal experiments, Chapter 6.8 discusses grain-boundary grooving experiments, and Section 6.9 provides field-assisted sintering results.

6.1. Powder Characterization

ICP-MS impurity concentrations for Baikowski and Nanocerox powders were generally similar to reported values. Sulfur content by carbon/sulfur analysis for Baikowski powder was similar to reported values. Nanocerox powder contained significantly higher carbon content than reported, possibly due to organic synthesis remnants. Nitrogen content was high at >40,000 parts-per-million weight (ppmw), likely due to atmospheric adsorption on the high surface-area powders. Reduction in H$_2$ appeared to be the most effective treatment for sulfur removal for Baikowski powder, whereas oxygen treatment had little effect (Table 6.1).

<table>
<thead>
<tr>
<th>Powder</th>
<th>Condition</th>
<th>C (ppmw)</th>
<th>S (ppmw)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nanocerox</td>
<td>As-Received</td>
<td>1,267</td>
<td>154</td>
</tr>
<tr>
<td>Baikowski</td>
<td>As-Received</td>
<td>592</td>
<td>1,034</td>
</tr>
<tr>
<td>Baikowski</td>
<td>H$_2$O Treat$^{25}$</td>
<td>1,003</td>
<td>840</td>
</tr>
<tr>
<td>Baikowski</td>
<td>O$_2$ Treat @ 800°C$^1$</td>
<td>341</td>
<td>994</td>
</tr>
<tr>
<td>Baikowski</td>
<td>H$_2$ Treat @ 800°C$^1$</td>
<td>303</td>
<td>618</td>
</tr>
</tbody>
</table>

XRD results of Baikowski and Nanocerox powders showed only indexed peaks corresponding to spinel, indicating stoichiometry within the uncertainty of XRD. However, Baikowski powder was estimated Al$_2$O$_3$-rich (~MgO:1.01Al$_2$O$_3$) based on LA-ICP OES/MS and Nanocerox powder...
MgO-rich (~MgO:0.995Al$_2$O$_3$) based on image analysis of MgO nodules in hot pressed compacts.

Agglomerates were observed by OM in Baikowski and Nanocerox powders. Crystallites of ~50 nm and agglomerates up to 300 nm in diameter were observed by SEM for Baikowski (Fig. 6.1) and Nanocerox powders. TEM examination determined Baikowski crystallites had an average size of 35 nm and Nanocerox crystallites 30 nm, with few crystallites up to 100 nm in diameter (especially for Nanocerox powder) and agglomerates joined by sinter-necks up to 300 nm in diameter (Figs. 6.2, 6.3, Table 6.2). Nanocerox crystallites were generally spherical with some faceting, whereas Baikowski crystallites were more facetted. Intensities, positions, and calculated lattice spacings of indexed selected-area diffraction (SAD) ring patterns for Baikowski and Spinel powders matched spinel ICDD PDF Files 00-021-1152 and 00-005-0672$^2$ (Fig. 6.4, calculations in Appendix A).

![SEM image of Baikowski powder](image)

Fig. 6.1 SEM image of Baikowski powder (a) agglomerates and (b) individual crystallites.

Laser-scattering particle-size analysis results varied depending on dispersion, but were generally similar to reported values. Baikowski powder had a zeta potential of +13.5 mV and Nanocerox powder -0.6 mV, the low values indicating both powders form an unstable colloidal suspension and have a tendency to flocculate. SEM examination indicated LiF was well dispersed by the various mixing methods, although LiF crystallites were much larger than those of spinel powders (Fig. 6.5).
Fig. 6.2 (a) Brightfield TEM image of (a) Baikowski powder crystallites, (b) High-resolution TEM (HR-TEM) image of Baikowski powder crystallite, (c) Nanocerox powder crystallites, (d) HR-TEM image of Nanocerox powder crystallites.

Fig. 6.3 HR-TEM image of sinter-necks in as-received Nanocerox powder.
Table 6.2 Powder Size Characteristics

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Baikowski</th>
<th>Nanocerox</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle Size* (nm)</td>
<td>35</td>
<td>30</td>
</tr>
<tr>
<td>Agglomerate Size (nm)</td>
<td>100-300</td>
<td>100-300</td>
</tr>
<tr>
<td>Particle Morphology</td>
<td>Facetted</td>
<td>Spherical and Facetted</td>
</tr>
</tbody>
</table>

*Average 50 particles

Fig. 6.4 Indexed electron-diffraction ring-patterns for (a) Baikowski powder and (b) Nanocerox powder.

Fig. 6.5 SEM image of Baikowski powder mixed with 1 wt% LiF.

6.2. STA-MS Experiments

STA calibration runs with empty crucibles in argon indicated weak endotherms at 185°C (associated with vaporization of adsorbed water) and at 425°C (associated with organics), and an
instrument-related endothermic rise above 500°C (Fig. 6.6). These features were removed from subsequent runs by applying a correction within the instrument software. STA-MS indicated 99.96 vol. % argon species initially, with the remainder atmospheric gases and water vapor, indicating effective sealing. Argon species ($^{36}$Ar, $^{38}$Ar, $^{39}$Ar, $^{40}$Ar) concentrations matched isotopic distributions with weak signals (<0.01 vol. %, 100 ppmv total) for charge to mass ratios (m/z) 20 (Ar++), 41 (ArH+), and 80 (Ar$_2$+). Weak signals (<100 ppmv total) for m/z 14 (N+), 16 (O+), 28 (N$_2$+), and 32 (O$_2$+) matched atmospheric gas concentrations and fragmentation patterns. Weak signals (<200 ppmv total) for m/z 17 (OH+) and 18 (H$_2$O+) were consistent with water vapor and increased slightly >1300°C. A weak signals (10 ppmv) for m/z 44 (CO$_2$+, N$_2$O+) between 400°C and 1000°C were likely evaporation or combustion of organic contaminants, and for m/z 30 (NO+) and 44 (CO$_2$+, N$_2$O+) >1000°C were consistent with thermal N$_2$O formation and fragmentation patterns. Small (20-30 ppmv), sharp increases in m/z 20 and 32 >1350°C were of unknown origin. STA-MS of empty crucibles in air indicated atmospheric gases and water vapor in expected concentrations.

Fig. 6.6 STA-MS results for empty crucible calibration in argon at 10K/min. TGA mass loss scaled to primary vertical axis, MS pressures not corrected, and only m/z with significant signals shown. Note convex endothermic rise >550°C, relatively constant water vapor signals, and m/z = 20 increase >1300°C.
STA of pure LiF in argon displayed melting (850°C) and vaporization (1000°C – 1400°C) endotherms, the latter concommittant with complete mass loss, consistent with results in the literature (Fig. 6.7). STA-MS indicated 99.78 vol. % argon species initially, the rest atmospheric gases and water vapor. Signals for water vapor increased to 0.4 vol% with temperature, consistent with hygroscopic LiF. Signals for m/z 16 (O+) and 44 (CO2+, N2O+) increased >700°C to 10 ppmv at 850°C, coincident with the melting of LiF, and peaked again between 1150°C and 1500°C, coincident with the vaporization of LiF. Signals for m/z 28 (N2+, CO+) increased by 500 ppmv with temperature and peaked at 1350°C, and for m/z 30 (NO+, Li2O+) increased by 50 ppmv >1350°C. Signals for m/z 7 (Li+), 19 (F+), and 26 (LiF+) were not detected, despite mass loss equal to the amount added, most likely due to condensation of LiF in the vapor-transfer capillary. This suggests m/z 16, 28, 30, and 44 were adsorbed atmospheric gases or reaction products of LiF with these gases or with the crucible, rather than lithium or fluorine species. Although, it is possible that LiF formed species that were neutral, negatively-charged, with greater molecular weight than the MS detection limit (m/z = 100), or that were obscured by other signals (F2 by 38Ar).

Fig. 6.7 STA-MS results for pure LiF. Mass loss has been scaled to fit on the graph. Note melting endotherm at 850°C, vaporization endotherm between 1000°C and 1400°C concomitant with complete mass loss.
STA of MgF$_2$ and LiAlO$_2$ in argon indicated 15% mass loss between 1000°C and 1350°C, corresponding to the 16 wt% LiF calculated to form along with spinel (not shown). An endotherm at 740°C was likely the formation the eutectic liquid MgF$_2$:LiF, an exotherm at 760°C may have been the formation of spinel, and a small endotherm at 1270°C was consistent with the melting of unreacted MgF$_2$ ($T_M$ 1263°C). STA-MS indicated >97% argon species initially (likely higher but the signal saturated due to a higher sensitivity setting), with the rest atmospheric gases and water vapor. Water vapor signals peaked (0.1 vol. %) at 140°C and 220°C and a weak (50 ppmv) m/z 44 (CO$_2$) peak was observed at 450°C, similar to the calibration run. Weak (30 ppmv) m/z 2 (H$_2$) peaks at 675°C and 975°C were of unknown origin. No signals were observed for m/z 7 (Li$^+$), 19 (F$^+$), 26 (LiF$^+$), 38 (F$_2$$^+$), or 62 (MgF$_2$$^+$), likely due to condensation in the capillary.

STA of undoped Nanocerox powder in argon indicated <0.5 wt% mass loss, attributed to vaporization of adsorbed water (Fig. 6.8). The thermal profile was featureless, apart from a small endotherm at 1050°C and a steep, concave endothermic rise >1300°C. A shallow dip expected between 900°C and 1200°C from sintering was not apparent and the steep rise was possibly MgO evaporation or a calibration artifact. STA-MS indicated 99.91 vol. % argon species initially, trace atmospheric gases, and high (750 ppmv, calibration <200 ppmv) but decreasing water vapor signals, likely from adsorption on the powders. A weak (~15 ppmv, calibration <5 ppmv) m/z 44 (CO$_2$+) signal <400°C indicated residual organics or carbon, possibly from the flame-spray pyrolysis synthesis. A small (30 ppmv) increase in m/z 32 (O$_2$+) signal >1350°C was similar to calibration runs. A slight rise in m/z 39 and 80 signals (20 ppmv) with temperature was of unknown origin. Expected MgO outgassing as $^{24}$Mg+, $^{25}$Mg+, $^{26}$Mg+, O$_2$+, or as an increase in the m/z 40 ($^{40}$Ar+, MgO+) signal was not detected, likely due to condensation in the capillary. Similar results were obtained in air, but with mainly atmospheric gases detected.

STA of undoped Baikowski powder in argon was similar to undoped Nanocerox, with less than 0.5 wt% mass loss attributed to vaporization of adsorbed water, and a much shallower concave endothermic rise above 1100°C (Fig. 6.9). STA-MS indicated 99.77 vol. % argon species initially, the rest atmospheric gases and water vapor. Vaporization of adsorbed water resulted in distinct peaks up to 0.4 vol. % at 100°C and 150°C. Weak (<100 ppmv), distinct m/z
44 (CO$_2$+) peaks at 150°C and 675°C were likely evaporation or combustion of organic contamination. Similar results were obtained in air, with mainly atmospheric gases detected.

Fig. 6.8 STA-MS results for Nanocerox powder in argon at 10K/min. TGA mass loss scaled to primary vertical axis, MS pressures not corrected, and only m/z with significant signals shown. Note concave endothermic rise >1300°C, higher water vapor signals, organics outgassing <800°C, and m/z = 32 increase >1300°C.

Fig. 6.9 STA-MS results for Baikowski powder in argon at 5K/min. shown to 1300°C. TGA mass loss below detection sensitivity limit, MS pressures not corrected, and only m/z with significant signals shown. Note concave endothermic rise >1100°C, water evaporation especially at lower temperatures and CO$_2$ from organics.
STA of Baikowski powder with 1 wt% LiF indicated 1.5 wt% mass loss, corresponding to the amount of LiF and adsorbed water (Fig. 6.10). Thermal features were different from undoped powder, with an endothermic rise from 600°C–800°C, and the melting endotherm at 850°C barely visible. The vaporization endotherm was smaller and split into peaks at 1100°C and 1175°C, possibly indicating an exotherm in between. STA-MS indicated 99.90% argon species initially, with the remainder atmospheric gases and water vapor. Water vapor signals occurred throughout, with peaks up to 0.2 vol. % between 100°C and 350°C consistent with vaporization of adsorbed water. A secondary peak (0.1 vol. %) with an associated endothermic rise between 650°C and 750°C was likely water adsorbed on LiF or the decomposition of a magnesium or aluminum hydrate. A weak m/z 44 (CO$_2$) signal <800°C, peaking at 300°C (50 ppmv) and associated with weak m/z 16 (O+, CH$_4$+) and 32 (O$_2$, CH$_3$OH+) signals, was likely the evaporation or combustion of methanol used in mixing. More importantly, distinct m/z 32 (O$_2$, S+), 48 (SO+), and 64 (SO$_2$+) peaks (20 ppmv, 20 ppmv, and 150 ppmv, respectively) coincident with the vaporization endotherm of LiF occurred at 1075°C. These peaks were consistent the decomposition of the intermediate synthesis product (Mg,Al)SO$_4$ and the release of SO$_x$ species. HSC simulations indicate reaction of cation sulfates with LiF forms SO$_2$, rather than SO$_4$ (m/z above the detection limit), consistent with the observed fragmentation pattern. Magnesium and aluminum are expected to be oxidized and to contribute to spinel formation and thus would not be detected. A sharp increase (200 ppmv) in m/z 32 (O$_2$+) >1300°C was similar to other runs.

STA of Baikowski powder with 10 wt% LiF indicated 10 wt% mass loss (equal to the amount of LiF, Fig. 6.11). Thermal features were intermediate between Baikowski powder with 1 wt% LiF and pure LiF. STA-MS indicated 99.58 vol. % argon species initially, with the rest atmospheric gases and water vapor. Significant water vapor signals (up to 0.6 vol. %) throughout were consistent with hygroscopic LiF. Broad peaks (<200 ppmv each) between 150°C and 550°C for m/z 15 (CH$_3$+), 29 (COH+), 30 (CHOH+), 31 (CH$_2$OH+), and 32 (CH$_3$OH+) were consistent with the evaporation and fragmentation of methanol used in mixing. An increase in m/z 2 (H$_2$+) of 500 ppmv and 28 (N$_2$+) of 100 ppmv at 500°C indicate the formation or decomposition of amine or ammonium compounds. Signals for m/z 2 (H$_2$+), 16
(O+), 28 (N₂+, CO+), 30 (NO+, Li₂O+), and 44 (N₂O+, CO₂+) increased within the vaporization range of LiF, up to 0.15 vol. % for m/z 28 and 44. The lack of corresponding Li+, F+, or LiF+

Fig. 6.10 STA-MS results for Baikowski powder with 1 wt% LiF in argon at 5K/min. MS pressures not corrected, and only m/z with significant signals shown. The choppy TGA curve was due to instrument sensitivity when disturbed by a person walking in the room. Note the small endotherms between 1000°C and 1200°C, sulfur species outgassing not visible with this scale.

signals indicated these signals were likely adsorbed atmospheric gases or reaction products of LiF with these gases or with crucible constituents. Small peaks (<20 ppmv) for m/z 48 (SO+) occurred at 1050°C and 1225°C, similar to Baikowski powder with 1 wt% LiF, but without m/z 64 peaks.

STA-MS analysis was complicated by condensation in the capillary, ionization chamber reactions, fragmentation, cluster formation, formation of neutral or negative species, multiple ionizations, and the presence of isotopes. The main difficulty was condensation in the capillary of species such as LiF and MgO, which are not gaseous at the heating tape temperature (250°C). Using an integrated STA-MS system with the MS immediately above the STA chamber would
alleviate this effect. An extended bake-out of the STA, capillary, and MS chamber could reduce adsorbed water vapor. Use of helium instead of argon would permit identification of species with m/z 36, 38, 40, and 41. Lowering the ionization potential could permit clearer identification of species with lower potentials by lowering the argon signals. Calibration with standards for which no ionization spectra exist would facilitate fragmentation analysis. Selection of a smaller, higher precision, detection range would enable better detection of species such as SO$_2$. Using a detector with a higher maximum (m/z) detection limit would enable determination of heavier species. The amount of outgassing of detected species could be quantified by integrating a flow rate based on the argon flow rate and the calculated partial pressures. XRD and ICP of remaining material could identify reaction products and quantity remaining. For STA analysis, examination of cooling endotherms may have yielded additional information.

Although STA-MS analysis was problematic, it helped identify chemical reactions with LiF and determine the outgassing behavior of volatile species. A main finding was the repeatable obtainment of distinct m/z signals consistent with the fragmentation of SO$_3$ species, within a narrow temperature range centered at 1075°C, only for Baikowski powder with LiF addition. This confirmed a vapor-phase reaction between LiF and unreacted magnesium and/or aluminum.
sulfates, which was corroborated by HSC simulations and ICP chemical analysis. This identified the cleansing mechanism of LiF, whereby it reacts with impurities to form volatile species that can be removed, and partially answers why LiF is required to obtain transparency in Baikowski powder compacts. Another significant finding was determining the outgassing behavior of LiF and its reaction products, and of other volatile species such as water vapor. Outgassing of unwanted volatile species dictates the pressure-temperature regime required for their removal, and is essential for attaining high transparency. For example, removal of LiF requires a longer hold at lower outgassing at 1050°C or a shorter hold at higher outgassing at 1250°C. However, LiF must be allowed to interact with impurities prior to its removal, thus a hold between 1075°C and 1250°C is recommended. This knowledge is applicable to other ceramic systems where LiF or other reactive sintering aids are used, for example MgO. STA-MS also indicated different thermal and outgassing behavior depending on the amount of LiF and indicated the reformation behavior of spinel from MgF₂ and LiAlO₂. Thermodynamic modelling with HSC was able to yield nearly the same results, without the need for experiments.

6.3. Thermodynamic Simulations

Despite limitations, thermodynamic simulations with HSC helped identify reacting species and confirm postulated reactions. Selected examples of HSC equilibrium composition diagrams are shown in Figs. 6.12-6.14. Simulations in vacuum and air predicted the reaction of MgAl₂O₄ and LiF to form MgF₂ and LiAlO₂, consistent with reports in the literature. In air, the products were predicted to form >1000°C along with a small amount of LiF gas (Fig. 6.12). Simulations with equal amounts of LiF and spinel in vacuum indicated a lower reaction temperature (Fig. 6.13). Simulations with MgF₂ and LiAlO₂ in vacuum indicated the reformation of spinel, consistent with reports in the literature [Eq. (6.3.1.)]. Simulations in vacuum predicted Mg(SO₄), Al₂(SO₄)₃, and LiF reacted to form MgF₂, LiAlO₂, MgAl₂O₄, and SO₂ [Eq. (6.3.2.), Fig. 6.14]. Simulations with spinel and carbon confirmed the formation of aluminum oxycarbides, thought to be in part responsible for absorption in hot-pressed compacts (Fig. 6.15).

\[ \text{LiF} + \text{MgAl}_2\text{O}_4 \rightarrow \text{MgF}_2 + \text{LiAlO}_2 \]  \hspace{1cm} (6.3.1.)

\[ 2\text{MgSO}_4 + 2\text{Al}_2(\text{SO}_4)_3 + 2\text{LiF} \rightarrow \text{MgF}_2 + 2\text{LiAlO}_2 + \text{MgAl}_2\text{O}_4 + 8\text{SO}_2 + 4\text{O}_2 \]  \hspace{1cm} (6.3.2.)
Fig. 6.12 HSC equilibrium composition simulation diagram for MgAl$_2$O$_4$ (not shown) and LiF in air.

Fig. 6.13 HSC equilibrium composition simulation diagram for equal amounts of MgAl$_2$O$_4$ and LiF in vacuum.
6.4. Dilatometry Experiments

Sintered fractional theoretical density as a function of temperature for dilatometry experiments with cold-pressed Baikowski, Nanocerox, and irradiated Nanocerox powder samples in air and in argon with 2% H\textsubscript{2}, are shown in Figure 6.16. The onset of sintering,
average shrinkage slope during densification, and the temperature of maximum sintering rate for all conditions are tabulated in Table 6.3. Nanocerox powder samples achieved near-theoretical density, whereas Baikowski powder samples achieved <92% theoretical density. Increased densification and densification rate and lower sintering onset temperature for Nanocerox compacts were attributed to MgO-rich stoichiometry and more optimal green-body particle coordination. Although the same cold-pressing conditions were used for both powders, the green density of Nanocerox compacts reached 55% theoretical, whereas that of Baikowski compacts only reached 51% theoretical. Delayed densification for Baikowski samples was attributed to Al₂O₃-rich stoichiometry, swelling due to impurities, and lower green density. Densification curves for oxidizing and reducing conditions showed little difference, but Nanocerox compacts sintered in H₂ exhibited higher transparency than those sintered in air. Neutron irradiation had little effect on the densification behavior.

![Fractional sintered density relative to theoretical as a function of temperature for cold-pressed Baikowski and Nanocerox samples.](image)

**Fig. 6.16** Fractional sintered density relative to theoretical as a function of temperature for cold-pressed Baikowski and Nanocerox samples.

<table>
<thead>
<tr>
<th>Powder</th>
<th>Treatment</th>
<th>Cold-press pressure (MPa)</th>
<th>Atmosphere</th>
<th>Onset (°C)</th>
<th>Slope (m/m-°C)</th>
<th>Max. Sintering Rate (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Baikowski</td>
<td>-</td>
<td>521</td>
<td>Air</td>
<td>1100</td>
<td>1.3</td>
<td>1350</td>
</tr>
<tr>
<td>Baikowski</td>
<td>-</td>
<td>521</td>
<td>Argon + H₂</td>
<td>1090</td>
<td>1.1</td>
<td>1375</td>
</tr>
<tr>
<td>Nanocerox</td>
<td>-</td>
<td>521</td>
<td>Air</td>
<td>1082</td>
<td>2.6</td>
<td>1200</td>
</tr>
<tr>
<td>Nanocerox</td>
<td>-</td>
<td>521</td>
<td>Argon + H₂</td>
<td>1076</td>
<td>2.5</td>
<td>1190</td>
</tr>
<tr>
<td>Nanocerox</td>
<td>-</td>
<td>-</td>
<td>Air</td>
<td>1030</td>
<td>2.3</td>
<td>1130</td>
</tr>
<tr>
<td>Nanocerox</td>
<td>-</td>
<td>-</td>
<td>Air</td>
<td>1050</td>
<td>2.6</td>
<td>1160</td>
</tr>
</tbody>
</table>

**Table 6.3 Dilatometry Results.**
6.5. Hot Press Experiments

Hot-pressed Baikowski powder compacts are shown in Figure 6.17. Characterization with spectrophotometry, optical and electron microscopy, and chemical analysis for compacts analyzed is discussed in Chapter 4. Baikowski compacts without LiF addition were grey and opaque, indicating absorption and scatter. Compacts with LiF were transparent to opaque, indicating scatter, but without dark color. Compacts hot pressed in 12.7 mm dies, LiF, and 1.5 g of powder had the highest transmittance with ultrasonic mixing, ramping at 6°C/min., and pressure applied at 1200°C. Ultrasonic mixing yielded the highest transmittance, followed by ball milling, with acoustic milling yielding opaque compacts. Applying pressure at 1200°C yielded the highest transmittance, followed closely by application at 1300°C and 1400°C, with haze observed when applied at 900°C and opacity when applied at 800°C.

Compacts with LiF and 3.5 g of powder using standard conditions were opaque with a transparent rim. A longer hold before applying pressure increased transmittance more than varying other parameters. Holding at 1150°C yielded higher transmittance than doing so at lower temperature, with marginal improvement for holding at 1050°C or 1100°C, even for 2 hrs. Using a lower ramp rate of 3°C/min. resulted in greater optical anisotropy between the center of compacts (opaque) and the exterior surfaces (transparent). Increasing time at sintering temperature from 1 hr. to 2 hr. increased transmittance, but less so than using a longer hold at 1150°C. Increasing temperature of pressure application from 1200°C to 1300°C increased transmittance only slightly. Applying 60 MPa versus 35 MPa significantly increased transmittance. Optimal conditions consist of using smaller samples, less powder, 1 wt% LiF, ultrasonic mixing followed by rotary evaporation, ramp at 6°C/min., pressure of 60 MPa, 60 min. hold at 1150°C, application of pressure at 1200°C, and sintering at 1550°C.

Compacts hot pressed in 24.5 mm dies displayed lower transmittance when pressure was applied at 900°C versus 1200°C. These compacts had higher transmittance than compacts hot pressed in 12.7 mm dies with 3.5 g of powder, demonstrating the effect of thickness on scatter, but also possibly indicating that the diffusion distance to surfaces (face, side, or rim) may be a greater determinant of transmittance than the diffusion distance to the rims, where an escape route for volatile impurities is available.
Fig. 6.17 HP Baikowski powder compacts, samples 10 mm above template, transparent compacts in bold font. Standard processing conditions (Std.) consisted of ramping temperature at 6°C/min. to 1550°C, a 15 min. hold at 1200°C followed by application of 35 MPa, and incorporation of additives by ultrasonic mixing (U.S. Mix) and rotary evaporation (Ac. Mix = acoustic mixing). Compacts HP in 12.7 mm dies with 1.5 g of powder were ~2 mm thick and with 3.5 g ~5 mm thick, and compacts HP in 25.4 mm dies with 6 g of powder were ~2 mm thick. Compacts HP in 38.4 mm dies were opaque and are not shown.

Hot-pressed Nanocerox powder compacts are shown in Fig. 6.18. The highest transmittance with the least absorbance for Nanocerox compacts was obtained using a maximum sintering temperature of 1400°C. Decreasing the sintering temperature increased scatter, although full density (and transparency) was attained even with 1300°C, while increasing it increased absorption. Applying pressure at 900°C versus 1200°C resulted in higher transmittance (unlike Baikowski compacts) and lower absorption. Using Al₂O₃ spacers to insulate the die set and
prevent conduction (and formation) of charged point defects resulted in higher transmittance. The absorption pattern was different in this compact, with a clear periphery and a dark band 2 mm from the periphery, as opposed to increased absorption at the periphery without the spacers. Using molybdenum foil to shield compacts resulted in higher transmittance and lower scatter and absorption, indicating absorption is likely caused by proximity to carbon (contamination or reduction). Hot pressing using Al₂O₃ dies and molybdenum foil eliminated absorption, but scatter increased considerably. Increasing Al₂O₃ addition resulted in increasing absorption in the form of dark micron-sized features. LiF addition eliminated absorption, but increased scatter and significantly reduced transmittance, especially when acoustically mixed. Addition of Li₂O appeared to eliminate absorption but increased scatter, whereas addition of AlF₃ did not increase scatter as much but also did not reduce absorption.

Fig. 6.18 Nanocerox powder compacts. Compacts are 12.7 mm in diameter, 2 mm thick, and 10 mm above template. Standard processing conditions (Std.) consisted of hot pressing 1.5 g of powder at 6°C/min. to 1550°C, holding at 1200°C for 0.25 h followed by application of 35 MPa. Add scale, size same as Baikowski compacts. Optimal conditions consisted of using molybdenum foil, insulated spacers, 0.05 wt% LiF, applying pressure at 900°C, and a maximum sintering temperature of 1400°C.

Corrected hot press displacement and fractional theoretical sintered density as a function of temperature for two conditions are shown in Figs. 6.19 – 6.22. Although partially corrected for,
discontinuities from hot press instrumentation proportional-integral-derivative (PID) settings are apparent in all the figures. The onset of sintering from displacement curves was consistent with dilatometry results. However, as dilatometry was more precise and did not contain as many correction errors, displacement analyses from hot pressing are only shown for these two conditions. As noted in Figs. 6.19 and 6.21 significant displacement occurred upon pressure application. The temperature at which closed porosity occurred was estimated from attainment of 92% theoretical density in Figs. 6.20 and 6.22. For the compact with more powder and pressure applied at 900°C, linear shrinkage became flat at a lower temperature (1200°C), indicating incomplete densification.

Fig. 6.19 Displacement versus temperature corrected for thermal expansion and pressure strain (subtraction of calibration run) during hot pressing for 1.5 g Baikowski powder with 1 wt% LiF using the standard run (note displacement is negative as it indicates shrinkage).

Fig. 6.20 Pressure and thermal expansion corrected fractional theoretical sintered density versus temperature for the same conditions as Fig. 6.19, 1.5 g Baikowski powder with 1 wt% LiF using the standard run.
Fig. 6.21 Displacement versus temperature corrected for thermal expansion and pressure strain during hot pressing of 3.5 g Baikowski powder with 1 wt% LiF with pressure applied at 900°C instead of 1200°C (note displacement is negative as it indicates shrinkage).

Fig. 6.22 Pressure and thermal expansion corrected fractional theoretical sintered density for the same conditions as Fig. 6.21, 3.5 g Baikowski powder with 1 wt% LiF with pressure applied at 1200°C.

The effect of LiF in removing absorption and imparting transparency some compacts is evident. Hot pressed ball-milled powders yielded transparent compacts, but higher transparency was achieved with ultrasonically mixed powders. Rotary evaporation resulted in better flow properties, likely resulting in better particle coordination, smaller inter-particle porosity, and higher transmittance. Compacts made with acoustically mixed powders were opaque, likely due to agglomerates generated by frictional charging. For compacts hot-pressed with 1.5 g of powder, the optimal temperature of pressure application with a 15 min. hold was 1200°C, although pressures as low as 900°C and as high as 1300°C yielded transparent compacts. For compacts hot-pressed with 3.5 g of powder, a longer high-temperature hold was required, for
which a temperature of 1150°C appeared optimal for pressure application. Longer holds at lower temperatures yielded opaque compacts. Increasing time at sintering temperature had a smaller effect than proper selection of the temperature and hold time for pressure application. Increasing pressure resulted in increased transparency.

6.6. Raman Spectroscopy

The Raman spectra of dark spots on surfaces and within compacts HP with Baikowski and Nanocerox powder, with and without LiF, matched spectra acquired for graphite foil and pyrolytic graphite, indicating these features were due to carbon impurities. Raman spectra for several transparent HP compacts and a transparent stoichiometric single crystal are shown in Fig. 6.23. The broad shoulder at 350 cm\(^{-1}\) and the peak at 680 cm\(^{-1}\) in Figure 6.23a have been associated with low inversion parameter\(^{14}\) and these features are more significant in the Raman spectrum for the single crystal. The Raman spectra for hot pressed Nanocerox compacts and Baikowski compacts without LiF closely matched the single-crystal spectrum, whereas compacts hot pressed with Baikowski powder with LiF displayed features attributed to higher inversion parameter. The compact hot pressed with Baikowski powder without LiF exhibited an unknown peak at 525 cm\(^{-1}\), whereas the compact hot pressed with Baikowski powder with LiF did not exhibit this peak and exhibited fluorescence at higher wave numbers (Fig. 6.23b).

![Raman Spectroscopy](image)

Fig. 6.23 Raman spectra for (a) a spinel single crystal and compacts hot pressed with Baikowski powder with 1 wt% LiF and with Nanocerox powder, and (b) compacts hot-pressed with Baikowski powder with and without 1 wt% LiF.
6.7. Pressureless sintering, Hot Isostatic Pressing, Quenching, and Single-Crystal Experiments

Pressureless sintered compacts did not exhibit absorption, but enough scatter was present to cause opacity. Examination with OM revealed that scatter was caused by cracks, likely due to areas with inadequate green-body particle coordination and to compact-scale differential sintering. The half of the compact pressureless sintered with Baikowski powder and subsequently HIPed at 1550°C was opaque with micron-sized grains, whereas the half HIPed at 1650°C was translucent with regions of millimeter-sized grains. The half of the compact pressureless sintered with Nanocerox powder and subsequently HIPed at 1550°C was dark and translucent, whereas the half HIPed at 1650°C was clear and translucent, and both displayed micron-sized grains. The HIPed compacts contained a significant amount of dark, spherical millimeter-sized optical defects.

Fracture surfaces of quenched Baikowski and Nanocerox compacts HP with LiF exhibited a larger fraction of transgranular fracture than compacts that were un-quenched (Fig. 6.24), possibly indicating that additives and impurities diffused from grain boundaries into the lattice.

Single crystals subjected to hot pressing conditions (without pressure) appeared dark, whereas those subjected to the same thermal profile in an air furnace did not. However, whether the effect was caused by carbon contamination or reduction of the oxide could not be determined. In comparison, transparent compacts sintered in the dilatometer under reducing conditions (Argon + 2% H$_2$) did not display dark color.

6.8. Lattice parameter measurements

FIB samples, CBED patterns collected at grain interiors and boundaries, and calculated lattice parameters are shown in Fig. 6.25. The lattice parameters did not match the known lattice parameter for spinel (8.0898 Å), likely due to calibration errors. In addition, even with optimal convergence, the beam probe size was wider than the grain boundary core, giving contributions from adjacent grains and beam anisotropy manifested by aspherical FOLZ patterns did not permit accurate measurements. Nevertheless, lattice parameters appeared to remain constant for
compacts hot-pressed without LiF and possibly slightly decrease at grain boundaries of compacts hot pressed with LiF.

Fig. 6.24 SEM images of fracture surfaces for; (a) HP compact with Baikowski powder with 1 wt% LiF, (b) after quenching, (c) HP Nanocerox compact with 0.25 wt% LiF, (d) after quenching.

Fig. 6.25 (a) FIB sample from compact HP with Baikowski powder without additives viewed along the [011] zone axis (insets), (b) CBED in grain showing FOLZ, (c) CBED at grain
boundary, (d) FIB sample from compact HP with Baikowski powder with 1 wt% LiF viewed along the [001] zone axis, (e) CBED pattern in grain, (f) CBED pattern at grain boundary.

6.9. Grain Boundary Grooving Experiments

Typical AFM surface maps for samples hot pressed with Baikowski powder with and without 1 wt% LiF are shown in Fig. 6.26. The surface of the sample without LiF exhibited roughness typical of a polished surface and differential grain etching, and grain-boundary grooves were not well-formed. The sample with 1 wt% LiF addition exhibited a smooth surface, indicative of high surface energy and/or high surface mobility. Grain boundary dihedral angles were too large to make accurate determinations. As grain-boundary grooves were not deemed reflective of the actual surface energies, only five grain boundaries were examined for each condition.

![AFM surface maps](image)

Fig. 6.26 AFM surface maps for compacts HP with (a) Baikowski powder and (b) Baikowski powder with 1 wt% LiF (20 µm x 20 µm, vertical scale 180 nm per division).

<table>
<thead>
<tr>
<th>Baikowski</th>
<th>θ (degrees)</th>
<th>$\gamma_{gb}/\gamma_S$</th>
</tr>
</thead>
<tbody>
<tr>
<td>No LiF</td>
<td>20</td>
<td>1.97</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>1.97</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>2.00</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>1.99</td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td></td>
<td><strong>1.98</strong></td>
</tr>
<tr>
<td>1 wt. %</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LiF</td>
<td>130</td>
<td>0.85</td>
</tr>
<tr>
<td></td>
<td>125</td>
<td>0.92</td>
</tr>
<tr>
<td></td>
<td>130</td>
<td>0.85</td>
</tr>
<tr>
<td></td>
<td>160</td>
<td>0.35</td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td></td>
<td><strong>0.74</strong></td>
</tr>
</tbody>
</table>

Table 6.4 Grain boundary grooving results.
6.10. Field-Assisted Sintering Experiments

The cylindrical field-assisted sintered (FAST) sample with Baikowski powder with 1 wt% LiF exploded at approximately 780°C. The FAST cylindrical sample with Nanocerox powder exhibited enhanced sintering, with densification occurring in approximately 3 min. During sintering, numerous cracks appeared along which volume displacement occurred. The dog-bone FAST sample with Baikowski powder without LiF exhibited dielectric-like breakdown at approximately 1280°C. Microstructure consisted of fine (5 µm) grains, lack of sintering, and extensive porosity attributed to swelling caused by trapped binder (Fig. 6.27). The dog-bone FAST sample with Nanocerox powder was translucent to transparent. The microstructure consisted of fine grains (1 µm) and smaller (< 1 µm) pores attributed to trapped binder.

![SEM fracture surface images](image)

Fig. 6.27 SEM fracture surface images of FAST (a) and (b) dog-bone specimen with Baikowski powder with 5 wt% PVA (grain size ~5 µm, pores indicated by arrows), (c) and (d) dog-bone specimen with Nanocerox powder with 5 wt% PEG (grain size ~1 µm, pores indicated by arrows).
REFERENCES CITED


CHAPTER 7
GENERAL DISCUSSION

Characterization with electron microscopy, chemical analysis, and spectrophotometry unequivocally demonstrated that as little as ~1000 ppm impurities were responsible for regions of submicrometer grains in compacts hot-pressed with Baikowski powder without additives. The amorphous impurity-rich phase decorating the boundaries of submicrometer grains suggested impurities formed a eutectic melt with spinel, and the morphology of the phase suggested that it de-wet grain boundaries upon cooling. A liquid phase likely has an associated vapor, the presence of which at triple junctions would pin grain boundaries and inhibit densification, explaining the small grain size. A vapor phase was indeed indicated by triple junctions that were only partially filled with the amorphous phase. The areal size range (covering grain surfaces of differing size) and extent of the amorphous impurity phase resulted in enough scatter over a range of wavelengths to cause opacity in the visible and low transmittance in the IR. However, the amorphous phase was not responsible for all of the absorption; high-purity Nanocerox compacts displayed only slightly lower absorptance than Baikowski compacts, suggesting the main cause was carbon contamination. It was found that absorption could be completely eliminated by shielding with molybdenum foil and using alumina dies. Moreover, absorption correlated with Al2O3-rich stoichiometry, possibly substantiating the formation of aluminum oxy-carbides as a source. The specific mechanism whereby LiF counteracts absorption was not determined, but doping experiments suggested lithium rather than fluorine was responsible. Scatter at short wavelengths (<200-400 nm) in Nanocerox compacts was consistent with MgO nodules (~100-150 nm) and surrounding strain fields.

The repeatable outgassing of sulfur species at 1075°C only with Baikowski powder with LiF, whether in argon, air, or vacuum during STA-MS experiments unambiguously demonstrated that LiF reacts with sulfur impurities to form volatile fluorides. Chemical analysis with LA-ICP OES/MS and EDS in combination with thermodynamic simulations confirmed that LiF also removes iron and calcium, and likely other impurities by a similar mechanism. Hot press experiments, electron microscopy, and chemical analysis indicated that compact exterior surfaces densified before compact interiors, trapping volatile impurities and LiF. Application of pressure
was found to force densification to lower temperatures and exacerbate compact-scale differential sintering. Rapid densification upon pressure application was indicated by hot press displacement data. Compact-scale differential sintering exacerbated by pressure application in combination with the formation of volatile species explained the importance of the temperature of pressure application. The cause of smaller grain size and opacity in larger compacts was also explained as larger compacts were associated with greater total impurity and additive content and longer distances for volatile species to escape. For 12 x 2 mm HP Nanocerox powder compacts without additives, application of pressure at 900°C permitted adsorbed gases, water vapor, and organics to be removed, while forcing densification to lower temperatures, resulting in smaller grain size for a given transmittance. For 12 mm x 2 mm HP Baikowski powder compacts with 1 wt% LiF, 1100°C was the optimal temperature of pressure application, with higher temperatures or longer holds at temperature required for larger compacts. As Nanocerox powders have less impurities and sinter at lower temperatures than Baikowski powder compacts, less LiF was required to impart transparency (~0.05 wt%). Since Nanocerox powders sinter more readily, a longer hold within the lower end of the vaporization range of LiF is required.

LiF was determined to be a multi-role additive; imparting transparency by reacting with impurities to form removable volatile fluorides, enhancing densification by increasing surface energy, contributing to surface and vapor-phase transport, likely increasing grain-boundary diffusion, and counteracting absorption caused by carbon contamination. The detrimental aspects of LiF were also demonstrated; it reacts with spinel to form volatile species that result in vapor-phase coarsening and large grain size; it forms volatile MgF₂, exacerbating MgO loss and altering stoichiometry, and it embrittles grain boundaries and causes scatter at UV wavelengths. Although LiF was found to result in near-theoretical transmittance at longer wavelengths by removing impurities in HP Baikowski powder compacts, chemical analysis showed that approximately half of the initial LiF remained. The presence of LiF at triple junctions was consistent with increased scatter at UV wavelengths. Chemical analysis and thermodynamic simulations determined that LiF forms volatile MgF₂, shifting stoichiometry to the Al₂O₃-rich side. As chemical interactions are expected to occur preferentially at interfaces, it was presumed that stoichiometry and associated refractive index gradients were present at grain boundaries, contributing to scatter at UV wavelengths. Although strain gradients were observed in TEM specimens prepared from compacts hot pressed with Baikowski with 1 wt% LiF, attempts at
quantifying the gradients were not successful. CBED at grain boundaries in Baikowski compacts HP with LiF possibly indicated a reduced lattice parameter, but the results were inconclusive.

Dilatometry experiments determined that green-body density, stoichiometry, and impurity content had the greatest effect on densification. The beneficial effect of higher green density is well-known and better flow properties, whether obtained using flame-spray pyrolysis powders or ultrasonic mixing followed by rotary evaporation, contributed significantly to obtaining higher green density. The enhanced densification behavior of MgO-rich powders and inhibited densification caused by impurities (likely due to swelling) were demonstrated. Reducing atmosphere had only a small effect on densification, perhaps indicating that oxygen vacancies are less important than originally thought. Nevertheless, cold-pressed Nanocerox compacts sintered in reducing atmosphere exhibited higher transmittance and demonstrated that pressureless sintering, at least for very small compacts, is possible. Neutron irradiation of powders had little influence on densification, likely because radiation-induced defects were essentially annealed during sintering.

Field-assisted sintering of spinel was demonstrated for the first time and translucent compacts with grain sizes approximately one fifth of those obtained by hot pressing similar powders were obtained. However, rapid densification with applied fields traps everything from binders to impurities and additives. It is possible that with high-purity, slightly MgO-rich powders formed into dense green bodies with optimal particle coordination, with careful use of electric fields, and ensuring species outgassing while avoiding differential sintering, that highly-transparent components can be fabricated. Although such a methodology may be amenable for fabricating small windows for UV lithography, for bulk applications like armor impurities and LiF must be dealt with, their effects and interactions understood, and processing methodologies designed to optimize their removal.

Although the ratio of grain-boundary to surface energy could not be conclusively determined from grain-boundary grooving experiments on thermally-etched samples, the smooth surface caused by LiF addition indicated increased surface energy and/or mobility. As polished compact surfaces examined with AFM were cut through the bulk and smoothing was observed even at the center of grains up to 50 um in diameter, this indicated either that LiF was present in
the bulk or had high enough mobility to affect surfaces tens of micrometers away from boundaries during the 15 min. thermal etch. Examination with SIMS confirmed that lithium was uniformly present in the bulk and Raman spectroscopy indicated that LiF addition resulted in fluorescence and possibly increased the inversion parameter. Although the specific point defects associated with lithium incorporation were not identified, they were assumed to be responsible for decreased bulk conductivity and likely (at least partially) responsible for counteracting absorption caused by aluminum oxy-carbides and color centers.

Shallow grain-boundary dihedral angles on thermally-etched polished surfaces of compacts HP with Baikowski powder with 1 wt% LiF indicated a low grain-boundary to surface-energy ratio. This can be caused either by increased surface energy, suggested by smooth surfaces, or by lower grain-boundary energy. However, intergranular fracture in these compacts suggested higher grain-boundary energy. The simplest explanation is that LiF increases both grain-boundary and surface energy, but more so surface energy. Increased surface energy drives sintering, but higher grain-boundary energy makes it unfavorable for boundaries to advance into pores, apparently inconsistent with enhanced densification due to LiF addition. However, these effects are entirely consistent with the coarsening and grain growth behavior of LiF. Moreover, during pressure-assisted sintering, increased mass transport from surface processes is directed from regions of higher stress at inter-particle (or grain) contacts to regions of lower stress (at pores), mitigating coarsening and enhancing densification as long as grain-boundary diffusion is high. Thus, contrary to previous studies, this work indicates enhanced densification due to LiF is not necessarily due only to increased bulk diffusion. Densification is controlled by the slowest species along the fastest path, which reports suggest is grain-boundary oxygen-ion diffusion. If conductivity in spinel is predominantly ionic, conductivity results indicate higher transport along grain boundaries compared to the bulk (although not specifically oxygen ion transport). Thus, LiF likely enhances densification in pressure-assisted sintering by increasing grain-boundary, surface, and vapor-phase transport mechanisms. It is likely that for spinel containing impurities and LiF, several densification mechanisms operate, possibly simultaneously at times, and in a complex manner that changes during sintering and is dependent upon continually evolving microstructure and impurity and additive content. Thus, the use of activation energies alone to determine the rate-limiting sintering mechanism may not be entirely justified.
CHAPTER 8
SUMMARY

The processing-structure-property relations in the fabrication of polycrystalline transparent spinel were studied using a variety of experiments. Starting powders with differing impurity contents and stoichiometry, with varying amounts of LiF added using different mixing methods, and subjected to neutron irradiation were used. The morphology, chemistry, and outgassing behavior of prepared powders were characterized using electron microscopy, laser-scattering particle-size analysis, Zeta potential, X-ray diffraction, electron diffraction, inductively coupled plasma in combination with mass and optical emission spectroscopy, carbon/sulfur analysis, and simultaneous thermal analysis in combination with mass spectroscopy. Thermodynamic simulations were used to confirm chemical interactions between spinel, LiF, and impurities. The sintering behavior of prepared powders was studied using variable-atmosphere dilatometry. Transparent spinel compacts were fabricated using hot pressing, pressureless sintering, hot-isostatic pressing, and field-assisted sintering. Compacts were characterized with optical and electron microscopy, energy and wavelength dispersive spectroscopy, electron-energy loss spectroscopy, convergent-beam electron diffraction, laser-ablation inductively-coupled plasma in combination with mass and optical-emission spectroscopy, spectrophotometry, Raman spectroscopy, and electrochemical impedance spectroscopy. Grain-boundary grooving studies were conducted to determine changes in the surface- to grain-boundary energy.

The use of different powders, additives, sintering methods, and a wide-range of characterization techniques, allowed the identification of the key variables involved in the densification and transparency of polycrystalline spinel compacts: (i) particle-size characteristics, (ii) stoichiometry, and (iii) impurities and additives. The importance of recognizing effects occurring from the compact-scale (differential sintering, impurity and microstructure gradients) to the atomic-scale (point defects caused by the incorporation of lithium) and spanning different periods during processing was demonstrated. Many of the questions asked at the outset of the research, such as the role of impurities, LiF, stoichiometry, pressure, and sintering atmosphere, and the causes of scatter and absorption, were answered (even if only partly in some cases). Despite successes, the specific cause of grain boundary
embrittlement and the specific defect responsible for absorption and its counteraction by LiF were not determined. The work indicated that for successful fabrication of transparent spinel, and likely transparent ceramics in general, a holistic approach that considers all variables and their interactions, over different length scales, and throughout the entire sintering process is required.

Impurities present in the parts-per-million range were found to strongly influence microstructure and cause enough scatter to result in opacity. Absorption was found to be caused by carbon contamination from the graphitic furnace components and it could be completely eliminated with proper shielding. The effect of compact-scale differential sintering during pressure-assisted sintering was shown and guidance was given for selection of the temperature of pressure application.

Small, highly-transparent, pressureless sintered spinel compacts were fabricated, possibly for the first time. Enhanced sintering of spinel under an applied field was demonstrated for the first time and translucent samples with fine grain size were produced. Although little benefit was noted, this was the first work to study the effect of neutron irradiation on the sintering behavior of starting powders.

LiF was found to be a multi-role additive; acting as a cleanser, altering interface energies, and increasing grain-boundary, surface, and vapor transport, which together with pressure-assisted sintering resulted in enhanced densification and transparency. Although lithium was found to be uniformly incorporated in the bulk, and may possibly increase bulk diffusion, this was not deemed a necessary condition for enhanced sintering. The specific mechanism by which LiF removes impurities was determined and quantified for the first time. Although the specific mechanism by which LiF counteracts absorption was not determined, lithium was determined to be responsible. LiF was also found to embrittle grain boundaries, result in MgO loss, and cause scatter at UV wavelengths.

The dielectric properties of the bulk and grain boundaries of fully-dense, transparent spinel compacts were quantified for the first time and increased conductivity in polycrystalline compacts was attributed to impurity conductance along grain boundaries. LiF was found to
decrease bulk conductivity by creating lattice defects and total conductivity by reducing impurities and grain boundary area.

8.0 Future Work

Despite advancements made in the understanding and development of transparent polycrystalline spinel in recent years, significant work remains.

Stoichiometry is a potentially powerful tool that can be used to modify densification behavior and compact properties. However, the role and properties of stoichiometry, and of stoichiometry gradients ranging from the compact-scale to that of grain boundaries, are not well-understood. In particular, the interface energies and ion diffusivities of stoichiometric compositions, and the effect of grain-boundary stoichiometry gradients on stress and refractive index need to be quantified.

The role of point defects and a grain-boundary space charge layer are not well-understood. Simulations in combination with experimental verification of the actual defects that are caused by stoichiometry, reduction, and incorporation of lithium would be helpful. In this respect, determining whether oxygen vacancies are actually present and contributing to absorption and the specific mechanisms whereby LiF counteracts absorption and increases bulk conductivity would be valuable. With respect to conductivity, consensus on the transference numbers for spinel would be helpful.

There is indication that grain-boundary diffusion could be rate-limiting for the densification of spinel. Yet, the diffusivity of the constituent ions along grain boundaries is not known. Tracer studies in polycrystalline compacts would be invaluable in helping to understand and control sintering and densification.

Significant progress also remains for manufacturing, particularly in scaling-up fine grain-size technologies, strengthening grain boundaries, pushing absorption edges towards the theoretical limits, and lowering cost.
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