

State of the Art

# Aluminum Oxynitride Spinel: A Review

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## Abstract

*Aluminum oxynitride spinel (ALON) is a relatively new ceramic which can be processed into fully dense transparent material. This material could replace alumina in a variety of applications, especially where optical transparency is important. This report reviews the current status of ALON, including phase equilibria, processing and properties.*

*Aluminiumoxinitridspinnell (ALON) ist eine relativ neue Keramik, die zu einem völlig dichten und transparenten Material gesintert werden kann. Dieser Werkstoff könnte Aluminiumoxid in einer Vielfalt von Anwendungen ersetzen, speziell wenn es auf die optische Durchsichtigkeit ankommt. Dieser Artikel gibt einen Überblick über den derzeitigen Wissensstand der ALON-Keramik, einschließlich der Phasengleichgewichte, des Processing und der Eigenschaften.*

*L'oxynitride d'aluminium spinelle (ALON) est une céramique relativement nouvelle pouvant conduire à un matériau transparent entièrement dense. Il pourrait remplacer l'alumine dans diverses applications, surtout celles où la transparence optique est recherchée. Cet article analyse l'état actuel des connaissances sur l'ALON en ce qui concerne les équilibres de phases, l'élaboration et les propriétés.*

## 1 Introduction

Dense polycrystalline  $\alpha$ -alumina can be processed into a fine grained, translucent material by doping with a small amount of magnesia.<sup>1</sup> In sintered polycrystalline alumina full transparency cannot be obtained because of (a) grain boundary scattering resulting from the anisotropic refractive index of alumina crystals and (b) scattering due to fine

porosity.<sup>2,3</sup> Full transparency in polycrystalline materials can be obtained only in isotropic materials which do not contain secondary phases and are pore free. For applications where transparency is required, nitrogen can be used to stabilize an isotropic alumina-based material.<sup>4</sup> This material, aluminum oxynitride spinel (ALON), has been processed into fully dense transparent material<sup>5,6</sup> and shows promising mechanical and optical properties suitable for use in infrared and visible window applications.<sup>7,8</sup>

This review will focus on the current status of monolithic single phase polycrystalline ALON. The deposition of aluminum, oxygen and nitrogen containing coatings by CVD for electronic<sup>9,10</sup> and cutting tool<sup>11</sup> applications will not be addressed, nor will materials containing ALON with additional phases, although they also show promising tribological properties.<sup>12,13</sup>

## 2 History

In 1946 it was observed that a spinel form of  $\text{Al}_2\text{O}_3$  could be stabilized above  $1000^\circ\text{C}$ .<sup>14</sup> Initially, it was believed this phase was stabilized by reducing the aluminum species from  $\text{Al}^{3+}$  to  $\text{Al}^{2+}$ .<sup>13–17</sup> In 1959 Yamaguchi and Yanagida<sup>4</sup> reported that the spinel phase was stabilized not by  $\text{Al}^{3+}$  but by nitrogen. During the 1960s, French investigators studied different aspects of oxynitride materials including phase relations<sup>18</sup> and processing.<sup>19–23</sup> Adams *et al.*<sup>23</sup> and Long and Foster<sup>24</sup> also reported various aspects of oxynitrides in the early 1960s. Not until interest was sparked in the United Kingdom on materials in the Silicon-Aluminum-Oxygen-Nitrogen ('SIALON') chemical system<sup>25</sup> did aluminum oxynitride materials become of major interest.

The surge of interest which followed focused on obtaining a better understanding of the AlN–Al<sub>2</sub>O<sub>3</sub> phase diagram because this information would provide for a better understanding of the Si–Al–O–N phase relationships. The first reported work involving the production of ALON spinel as a dense transparent material was published by McCauley and Corbin in 1979.<sup>5</sup> Since then the emphasis has been on determining properties of this new and promising material.<sup>7,8,26</sup>

### 3 Phase Relations

The production of single phase ALON requires an understanding of the phase relationships in the AlN–Al<sub>2</sub>O<sub>3</sub> system. Table 1 lists thirteen different aluminum oxynitride phases which have been observed along with their nomenclature and composition. The phases which form can be separated into two groups depending on their basic crystallographic structure. One group is based on polytypes of the wurtzite structure and the other is based on the spinel structure. The Al–O–N phases will be discussed according to their basic crystallographic structure.

The phases commonly termed ‘aluminum nitride polytypes’ are based on the AlN wurtzite structure.<sup>25</sup> Since these phases are compositionally controlled<sup>27,28</sup> they are not ‘true’ polytypes, as are SiC polytypes.<sup>29</sup> The composition of the polytypes given in Table 1 consider that they may only be stable at specific metal/nonmetal ratios,<sup>27–30</sup> allow for charge neutrality, and assume no silicon is in the polytype structure. Most of the studies on these

**Table 1.** Aluminum oxynitride phases observed in the AlN–Al<sub>2</sub>O<sub>3</sub> pseudo binary

Notation	Mol% AlN	Formula	M: X <sup>a</sup>	Structure
2H	100	AlN	1:1	Polytype <sup>b</sup>
32H	93.3	Al <sub>16</sub> O <sub>3</sub> N <sub>14</sub>	16:17	Polytype
20H	88.9	Al <sub>10</sub> O <sub>3</sub> N <sub>8</sub>	10:11	Polytype
2H <sup>o</sup>	—	—	>9:10	Polytype
27R	87.5	Al <sub>9</sub> O <sub>3</sub> N <sub>7</sub>	9:10	Polytype
16H	85.7	Al <sub>8</sub> O <sub>3</sub> N <sub>6</sub>	8:9	Polytype
21R	83.3	Al <sub>7</sub> O <sub>3</sub> N <sub>5</sub>	7:8	Polytype
12H	80.0	Al <sub>6</sub> O <sub>3</sub> N <sub>4</sub>	6:7	Polytype
γ-ALON	35.7	Al <sub>23</sub> O <sub>27</sub> N <sub>5</sub>	23:32	Spinel
γ'-ALON	~21.0	Al <sub>19.7</sub> O <sub>29.5</sub> N <sub>2.5</sub>	19.7:32	Spinel
φ'-ALON	16.7	Al <sub>22</sub> O <sub>30</sub> N <sub>2</sub>	22:32	Spinel
δ-ALON	10	Al <sub>19</sub> O <sub>27</sub> N	19:28	Spinel
φ-ALON	7.1	Al <sub>27</sub> O <sub>39</sub> N	27:40	Monoclinic
Corundum	0	Al <sub>2</sub> O <sub>3</sub>	2:3	Corundum

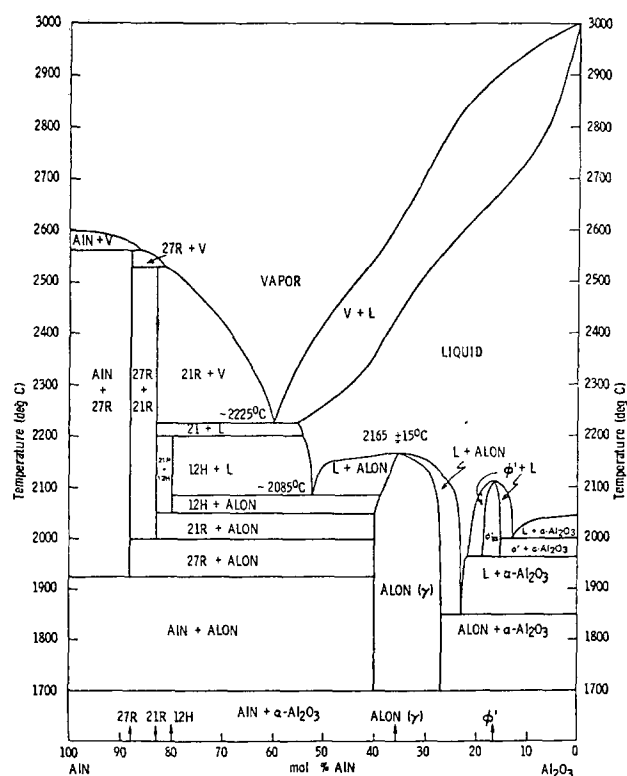
<sup>a</sup> Cation (M): anion (X) ratio.

<sup>b</sup> Composition assumes only Al, O, N present.

‘polytype’ phases had been conducted in the Si–Al–O–N chemical system. As a result, most reported information on these phases show silicon to be present in their structure. Analyses by Zangvil and Doser<sup>31</sup> have reported that some phases can be stabilized without silicon. Polytypes were also synthesized without silicon by Bartram and Slack.<sup>32</sup>

The compositions of the spinel phases γ-ALON and φ'-ALON in Table 1 were taken from the spinel model evaluation of McCauley.<sup>33</sup> Phase γ'-ALON spinel was found upon the oxidation of ALON by Goursat *et al.*<sup>34,35</sup> Phase φ-ALON was observed by Michel and determined to be monoclinic.<sup>36</sup> The δ-ALON phase was observed by many investigators; its reported composition ranges from 12 to 4 mol percent AlN depending on the researcher.<sup>18,23,24,35–8</sup> The composition shown for δ-ALON in Table 1 was taken from Lefebvre.<sup>39</sup>

The first phase diagram for this system was reported by Lejus.<sup>18</sup> Six phases were identified including a phase designated ‘X’ which encompassed all compositions for the polytype phases. In this work the ALON solid solubility field was centered around 25 mol percent AlN. Since this early work the diagram has been modified by Sakai,<sup>27</sup> Gauckler and Petzow,<sup>38</sup> and McCauley and Corbin.<sup>5,40</sup> Figure 1 is the most recent diagram as reported by McCauley and Corbin<sup>40</sup> for an atmosphere of 0.101 MPa (1 atm) N<sub>2</sub>. Extensive micro-structural



**Fig. 1.** Phase diagram for the AlN–Al<sub>2</sub>O<sub>3</sub> pseudo-binary.<sup>40</sup>

characterizations have been conducted to determine the high temperature equilibria in this system.<sup>31,40,41</sup>

The vapor phase was incorporated in Fig. 1 to emphasize its importance on the stability of AlN. No studies were conducted to determine either the composition nor pressure of the 'vapor' phase in this system. The nitrogen-rich portion of the diagram agrees well with the temperature stability relationships observed by Sakai.<sup>27</sup> The ALON solid solubility field in Fig. 1 is centered at a more nitrogen-rich composition than reported by Lejus (35.7 versus 25.0 mol% AlN). ALON was reported to melt congruently at 2165°C in one atmosphere of nitrogen. The line drawn at 1700°C in Fig. 1 is to show that ALON did not form below 1700°C from the reaction of Al<sub>2</sub>O<sub>3</sub> and AlN. As will be discussed later in this review ALON has been observed to form at lower temperatures when gaseous precursors are used. Since the work of McCauley and Corbin was not in the region of δ-ALON, this phase was not entered on their diagram.

The phase relationships were also calculated by Dorner *et al.*<sup>42,43</sup> and Kaufman<sup>44</sup> using thermodynamic data. Both investigators used a 25 mol% AlN composition for the composition for ALON. The resulting calculated phase diagrams had ALON Spinel as the only stable intermediate phase in this system. Dorner determined ALON to melt incongruently at 2000°C and be stable only above 1600°C. Kaufman determined ALON to melt congruently at 1940°C and be stable at room temperature. The differing results are due to the different assumptions used for their calculations. In general, Kaufman's results on the stability of ALON agree with the experimental data.

#### 4 Composition and Structure

Accurate limits of the ALON solid solubility field have yet to be determined. A major finding upon which all recent investigators agree is that the solid solubility limit does not include the 'stoichiometric' spinel composition Al<sub>3</sub>O<sub>3</sub>N (1Al<sub>2</sub>O<sub>3</sub>:1AlN) which is typical for spinel materials for example MgAl<sub>2</sub>O<sub>4</sub> (1MgO:1Al<sub>2</sub>O<sub>3</sub>) and Fe<sub>3</sub>O<sub>4</sub> (1FeO:1Fe<sub>2</sub>O<sub>3</sub>). As shown in Table 2 all models for the composition of the oxynitride spinel use a constant anion lattice of nitrogen and oxygen where the spinel cation vacancies decrease as the nitrogen content increases.<sup>18,23,33</sup>

From the very early results of Yamaguchi<sup>4</sup> it was known that nitrogen would stabilize a spinel form of Al<sub>2</sub>O<sub>3</sub>. Goursat *et al.*<sup>34,35</sup> determined the crystal

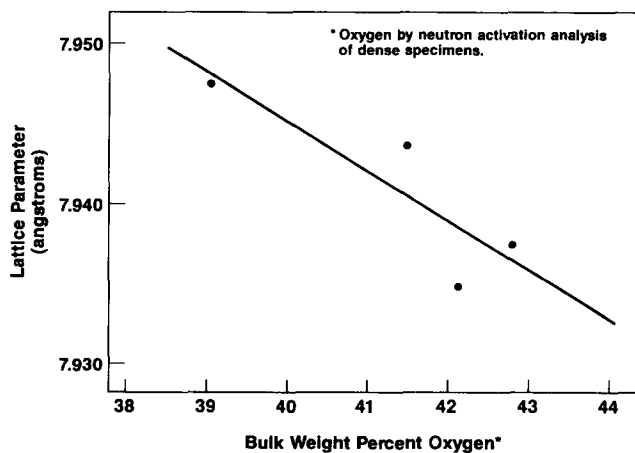
**Table 2.** Comparison of aluminum oxynitride spinel constant anion lattice models

Oxynitride spinel models	Experimental range (mol% AlN)	Reference
$\text{Al} \frac{(64+x)}{3} [\text{S}] \frac{(8-x)}{3} \text{O}_{(32-x)}\text{N}_x$ ( $0 \leq x \leq 8$ )	40-27	McCauley <sup>33</sup>
$\text{Al} \frac{(8+x)}{3} [\text{S}] \frac{(1-x)}{3} \text{O}_{(4-x)}\text{N}_x$ ( $0 \leq x \leq 1$ )	40-27	Lejus <sup>18</sup>
$\text{Al} \frac{(2+x)}{3} [\text{S}] \frac{(3-4x)}{12} \text{O}_{(3-x)}\text{N}_x$ ( $0 \leq x \leq 3/4$ )	50-33	Adams <i>et al.</i> <sup>23</sup>

[S] = Spinel cation vacancies.  
x = Limits from Al<sub>3</sub>O<sub>3</sub>N to Al<sub>2</sub>O<sub>3</sub>.

structure of ALON by neutron diffraction to be (Fd3m) spinel. They confirmed that oxygen and nitrogen occupy the anion sites of a spinel lattice. The aluminum cations were found to occupy both octahedral and tetrahedral sites of the spinel structure. This spinel phase was found to be stable only when a disordered vacancy is in the spinel octahedral position. Since a trivalent ion (Al<sup>3+</sup>) is in the tetrahedral positions of the spinel structure, ALON can be considered as an inverse spinel. Table 3 compares stoichiometric spinels to non-stoichiometric oxynitride spinels.<sup>18,33,34,45</sup>

The lattice parameter of ALON spinel varies with composition from 7.951 Å (nitrogen-rich) to 7.938 Å (oxygen-rich).<sup>5,18</sup> Figure 2 relates the lattice parameter of ALON to the bulk oxygen content of fully dense single phase ALON material.<sup>46</sup> Guillo<sup>47</sup> has



**Fig. 2.** ALON spinel lattice parameter as a function of oxygen content.<sup>46</sup>

**Table 3.** Comparison of anion and cation sites in various spinel materials

Type	Stoichiometric			Nonstoichiometric		
	Normal	Inverse	Oxynitride <sup>a</sup>	$\gamma$ -Oxynitride	$\gamma$ -Oxynitride	$\gamma$ -Alumina
Formula <sup>b</sup>	AB <sub>2</sub> O <sub>4</sub>	B(AB)O <sub>4</sub>	BB <sub>2</sub> O <sub>3</sub> N			
Example	MgAl <sub>2</sub> O <sub>4</sub>	MgFe <sub>2</sub> O <sub>4</sub>	Al <sub>3</sub> O <sub>3</sub> N	Al <sub>5</sub> O <sub>6</sub> N	Al <sub>23</sub> O <sub>27</sub> N <sub>5</sub>	Al <sub>2</sub> O <sub>3</sub>
Anion sites	(32) O <sup>2-</sup>	(32) O <sup>2-</sup>	(24) O <sup>2-</sup>	(27.44) O <sup>2-</sup>	(27) O <sup>2-</sup>	(32) O <sup>2-</sup>
32 Total			(8) N <sup>3-</sup>	(4.56) N <sup>3-</sup>	(5) N <sup>3-</sup>	
Cation sites	(16) Al <sup>3+</sup>	(8) Fe <sup>3+</sup>	(16) Al <sup>3+</sup>	(14.88) Al <sup>3+</sup>	(15) Al <sup>3+</sup>	(13.3) Al <sup>3+</sup>
16 (oct.)		(8) Mg <sup>2+</sup>		(1.12) $\boxed{S}$ <sup>c</sup>	(1) $\boxed{S}$	(2.7) $\boxed{S}$
8 (tet.)	(8) Mg <sup>2+</sup>	(8) Fe <sup>3+</sup>	(8) Al <sup>3+</sup>	(8) Al <sup>3+</sup>	(8) Al <sup>3+</sup>	(8) Al <sup>3+</sup>
Reference	Kingery <i>et al.</i> <sup>45</sup>	Kingery <i>et al.</i> <sup>45</sup>		Goursat <i>et al.</i> <sup>34</sup>	McCauley <sup>33</sup>	Lejus <sup>18</sup>

<sup>a</sup> Not stable<sup>b</sup> A = A<sup>2+</sup>; B = B<sup>3+</sup>; O = O<sup>2-</sup>; N = N<sup>3-</sup><sup>c</sup>  $\boxed{S}$  = Spinel cation vacancies.

determined the relationship between nitrogen content and lattice parameter and found it to follow the equation:

$$\text{\AA} = 7.914 + 0.117(X) \quad (1)$$

where  $\text{\AA}$  = lattice parameter in angstroms and  $X$  = 18 to 32 mol% AlN.

## 5 Synthesis

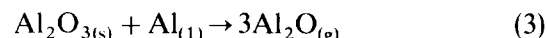
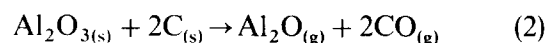
Three methods have been used to synthesize aluminum oxynitride phases. The most common of these involves the simultaneous reduction and nitridation of Al<sub>2</sub>O<sub>3</sub>. A second method starts with aluminum and 'oxynitrides' it by a combustion type reaction. Finally, these phases have also been produced by gas phase reactions. The basic reactions are listed in Table 4. The reactions are unbalanced because of cumbersome formulae.

### 5.1 Alumina based

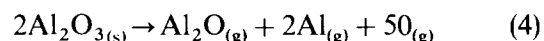
It has been reported by Collongues<sup>21</sup> that alumina is stable in nitrogen unless a reducing agent is present. In the presence of a reducing agent and nitrogen,

aluminum oxynitrides and aluminum nitride will form. Reducing agents which have been used successfully include aluminum, carbon, ammonia and AlN (see Table 4, eqns 1-6).

Vaporization may be an important part of this reduction/nitridation process since it has been reported that the volatility of alumina is several orders of magnitude greater in reducing conditions.<sup>46,47</sup> In strongly reducing conditions the vapor pressures of Al<sub>2</sub>O<sub>(g)</sub> and CO<sub>(g)</sub> are on the order of  $1.01 \times 10^{-3}$  MPa ( $10^{-2}$  atm) at 1800°C for the reactions:<sup>50</sup>



In neutral conditions the partial pressure of Al<sub>2</sub>O<sub>(g)</sub>, Al<sub>(g)</sub> and O<sub>(g)</sub> are approximately  $1.01 \times 10^{-9}$  MPa ( $10^{-8}$  atm) at 1800°C for the reaction:<sup>50</sup>



Pasco and Doremus<sup>51</sup> have reported that vapor transport is important during the formation of aluminum oxycarbides when reacting alumina and carbon. As reported by this author, vapor transport

**Table 4.** Unbalanced chemical reactions known to produce aluminum oxynitride phases

General equations	T(°C) required	Reference
1 Al <sub>2</sub> O <sub>3(s)</sub> + AlN <sub>(s)</sub> → ALON <sub>(s)</sub>	≥ 1650°C	5, 6, 27, 35-7, 52-4
2 Al <sub>2</sub> O <sub>3(s)</sub> + C <sub>(s)</sub> + N <sub>(g)</sub> → ALON <sub>(s)</sub> + CO <sub>(g)</sub>	≥ 1700°C	57-9
3 Al <sub>2</sub> O <sub>3(s)</sub> + C <sub>(s)</sub> + Air → ALON <sub>(s)</sub> + CO <sub>(g)</sub>	≥ 1700°C	4, 16, 17
4 Al <sub>2</sub> O <sub>3(s)</sub> + Al <sub>(l)</sub> + N <sub>2(g)</sub> → ALON <sub>(s)</sub>	> 1500°C	19
5 Al <sub>2</sub> O <sub>3(s)</sub> + Al <sub>(l)</sub> + Air → ALON <sub>(s)</sub>	> 2045°C	19, 20, 36
6 Al <sub>2</sub> O <sub>3(s)</sub> + NH <sub>3(g)</sub> + H <sub>2(g)</sub> → ALON <sub>(s)</sub> + H <sub>2</sub> O?	≥ 1650°C	21, 22
7 Al <sub>(l)</sub> + Air → ALON <sub>(s)</sub>	~ 1500°C	62-4
8 AlCl <sub>3(g)</sub> + CO <sub>2(g)</sub> + NH <sub>3(g)</sub> + N <sub>2(g)</sub> → ALON <sub>(s)</sub> + CO <sub>(g)</sub> + N <sub>2(g)</sub> + HCl <sub>(g)</sub>	900°C	66, 67

is an important mechanism during the reaction–sintering of ALON.<sup>50</sup>

Reacting AlN and Al<sub>2</sub>O<sub>3</sub> mixtures above 1650°C has been used to produce ALON powders,<sup>6,35,36</sup> reaction sintered samples<sup>5</sup> and reaction hot pressed specimens.<sup>26,37,52–4</sup> The major difficulty in this technique is in obtaining AlN powder having high purity and a fine particle size. It has been shown that the characteristics of the AlN powder (especially unreacted Al, metal impurities, and particle size) are important in sintering ALON.<sup>55</sup> Kurihara *et al.*<sup>56</sup> have demonstrated that aluminum dross which occurs as residue from aluminum refining can also be utilized for ALON synthesis since it inherently contains an intimate mixture of Al<sub>2</sub>O<sub>3</sub> and AlN.

Much work has been conducted to synthesize ALON by reacting Al<sub>2</sub>O<sub>3</sub> with carbon in nitrogen above 1700°C.<sup>57–9</sup> This process has also been used for producing AlN by adding enough carbon to remove all the oxygen in alumina.<sup>59,60</sup> Early studies which heated these mixtures in air also produced the spinel phase.<sup>4,16,17</sup> This author has observed the formation of the spinel phase on the surface of an  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> powder pellet when heated above 1800 C at one atmosphere of nitrogen in a carbon furnace. Thus, carbon need not be in direct contact with the alumina in order to produce ALON.<sup>47</sup>

Aluminum oxynitride phases have also been produced by reacting alumina and aluminum mixtures in air.<sup>19,20</sup> Collongues *et al.*<sup>21,22</sup> produced ALON and  $\delta$ -ALON by reacting alumina with an ammonia plus hydrogen gas mixture above 1650°C.

Vardelle and Besson<sup>61</sup> have produced a spinel phase by arc-plasma spraying  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> in both hydrogen/nitrogen and hydrogen/argon plasma-gas mixtures. It is likely that the material produced in the H<sub>2</sub>/N<sub>2</sub> plasma is ALON.

The production of ALON from an alumina precursor is desirable because of the low-cost, high-purity, fine-particle, alumina powder readily available. The major problem with using alumina as a starting component is the high temperatures (>1650°C) required for synthesis. Two possible explanations for the high temperature requirement are: (1) the low vapor pressure of aluminum suboxide vapors species below this temperature, if the reaction is via a gas phase mechanism or (2) a very slow diffusion rate of nitrogen into Al<sub>2</sub>O<sub>3</sub> below 1650°C, if the reaction is by a solid state diffusion mechanism.

## 5.2 Aluminum based

Aluminum oxynitrides have been produced from aluminum metal by Michel and Huber<sup>62</sup> and

Bouriannes *et al.*<sup>63,64</sup> Michel and Huber noted that at high temperatures aluminum liquid can react with air to form various aluminum oxynitrides. Bouriannes *et al.* formed ALON by rapid induction heating of aluminum spheres in air until combustion occurred (initiated ~1500°C). The formation of ALON depended on the air pressure used. This method of synthesis is similar to a technique termed 'Self-Propagating High-Temperature Synthesis' (SHS) used to produce a variety of refractory materials including borides, carbides and nitrides.<sup>65</sup>

## 5.3 Gaseous precursors

Various aluminum oxynitride compositions have been successfully deposited by chemical deposition techniques.<sup>9–11</sup> Irene, Silvestri and coworkers<sup>66,67</sup> were able to use a vapor phase reaction involving AlCl<sub>3(g)</sub> (Reaction 8 in Table 4) to produce thin polycrystalline spinel layers on silicon substrates. At 900°C the ALON spinel phase was observed while at 770°C a  $\zeta$ -Al<sub>2</sub>O<sub>3</sub> type structure was observed (possibly  $\zeta$ -ALON). This work produced ALON spinel at the lowest temperatures yet reported.

## 6 Densification

### 6.1 Processing

In order to use ALON in optical applications it must be sintered to full density, have high purity, and not contain any secondary phases. Optically transparent ALON has been prepared by pressureless sintering and hot pressing. The earliest transparent material was prepared by McCauley and Corbin<sup>5</sup> who used a pressureless reaction–sintering method where a powder mixture of AlN and Al<sub>2</sub>O<sub>3</sub> having the appropriate ratio is fired at 2025°C for 1 h in 0.101 MPa (1 atm) pressure of flowing nitrogen. Since this work, materials with improved optical properties have been prepared by Hartnett and Gentilman.<sup>8</sup> They use a two-step process; first synthesizing ALON powder followed by blending in sintering aids and firing to full density. ALON powder was synthesized by either the reaction of Al<sub>2</sub>O<sub>3</sub> with carbon in nitrogen<sup>58</sup> or reacting AlN and Al<sub>2</sub>O<sub>3</sub>.<sup>68</sup> The ALON powder is blended with ~0.5 wt% of boron, yttrium and/or lanthanum sintering aids and fired at 1930°C for 24–48 h.<sup>58,68,69</sup> An important note is that the sintering aid need not be added directly to the ALON powder. The doping can be accomplished by vapor phase transport of the sintering aid into the powder bed during firing. Figure 3 demonstrates the capabilities of their process for preparing large transparent material.

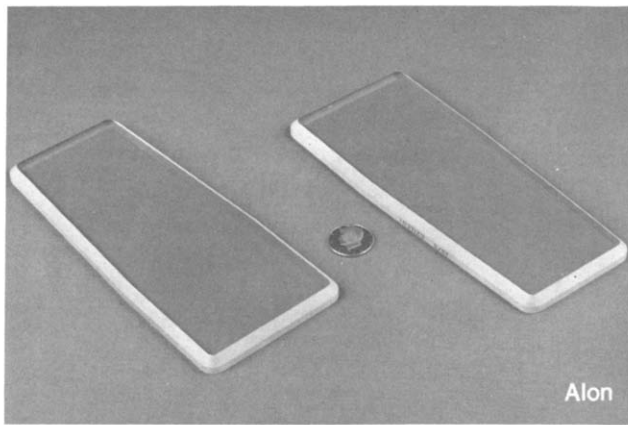


Fig. 3. Transparent ALON spinel. (Courtesy of Raytheon Company, Lexington, Massachusetts.)

Transparent materials have also been obtained by Sakai<sup>52</sup> and Ado *et al.*<sup>70</sup> by hot pressing. Sakai reaction hot pressed powder mixtures of  $\text{Al}_2\text{O}_3$  and  $\text{AlN}$  at  $1900^\circ\text{C}$  at 20 MPa for 1 h to produce transparent ALON.

## 6.2 Mechanisms

Very few studies have been conducted to determine the sintering behavior of ALON. Corbin<sup>50</sup> evaluated the effect of atmosphere on the microstructural development of ALON during the initial stages of reaction sintering. The results reveal that an evaporation–condensation mechanism occurs. To minimize matter transport by this mechanism, which reduces surface area without densification, the atmosphere must be controlled to suppress the volatilization of  $\text{AlN}$  and  $\text{Al}_2\text{O}_3$ . The best means to achieve this are to increase the nitrogen gas pressure, thereby suppressing  $\text{AlN}$  decomposition and using carbon free furnaces to minimize  $\text{Al}_2\text{O}_3$  decomposition. Vapor transport is also important for the uniform distribution of sintering aids within ALON powders.<sup>58,68,69</sup>

The sintering behavior above  $1600^\circ\text{C}$  was studied by Ado *et al.*<sup>71</sup> who reported that ALON densifies by a volume diffusion mechanism. Kim and Richards<sup>72</sup> suggest that ionic conductivity occurs in this material between  $1300$  and  $1500^\circ\text{C}$ . Ionic conductivity is evidence that bulk ionic diffusion is occurring. Maguire *et al.*<sup>69</sup> describes a mechanism where sintering aids form a transient liquid phase which promotes liquid phase sintering during the early stages of densification. Since the components of the liquid phase are soluble in ALON no secondary phases are evident in the dense material after processing. This results in clean grain boundaries and a transparent material.

## 7 Properties

All property data currently available on ALON is on polycrystalline material or powders. As a result, very little is known about its intrinsic behavior. In many instances the properties are dependent on extrinsic variables such as porosity, grain size, impurities and secondary phases.

### 7.1 Optical and dielectric properties

Since ALON is being considered as a potential electromagnetic window material, its optical and dielectric properties are of special interest. As a result there has been a significant amount of effort to evaluate these properties. Harnett *et al.*<sup>6,8</sup> have measured the in-line transmission of a 2.4 mm thick specimen and reported an infrared cutoff at  $5.12\ \mu\text{m}$  and an ultraviolet cutoff near  $0.27\ \mu\text{m}$ . They have also reported the development of a material with 80% in-line transmission at  $4.0\ \mu\text{m}$  with a thickness of 1.45 mm and an optical resolution of  $<1.0\ \text{mrad}$ .<sup>58</sup> Absorption occurs at  $11.2\ \mu\text{m}$ ,  $15.0\ \mu\text{m}$  and  $19.0\ \mu\text{m}$ .<sup>54</sup> The optical scatter and transmittance of ALON at  $0.4762$ ,  $0.6471$  and  $3.39\ \mu\text{m}$  has been evaluated by Archibald and Burge.<sup>73</sup> ALON may have a slight advantage over  $\text{MgAl}_2\text{O}_4$  spinel at  $0.4762\ \mu\text{m}$ . The refractive index for ALON varies with composition from 1.770 (30%

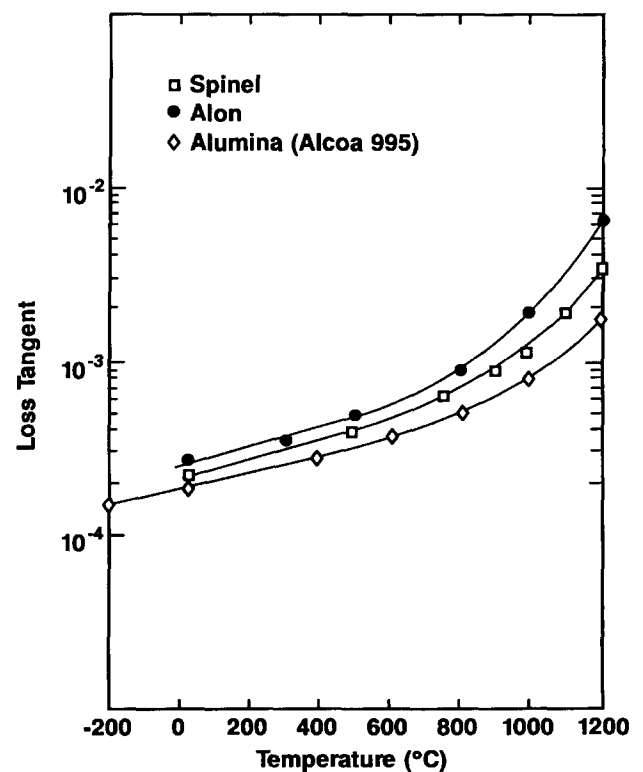


Fig. 4. Comparison of loss tangents for ALON,  $\text{MgAl}_2\text{O}_4$ , and  $\text{Al}_2\text{O}_3$  at 35 GHz as a function of temperature.<sup>74</sup>

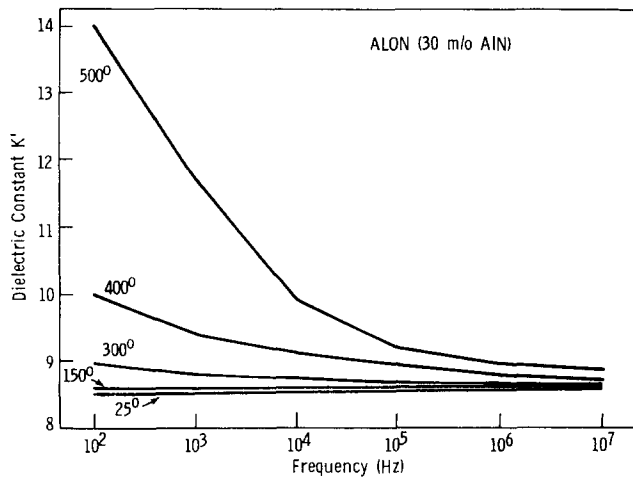


Fig. 5. Dielectric constant as a function of frequency and temperature. (Reproduced from Ref. 7 by permission of the SPIE.)

AlN) to 1.875 (37.5% AlN) at a wavelength of 0.55  $\mu\text{m}$ .<sup>5</sup>

The millimeter-wave dielectric properties were evaluated from 23 to 1000°C at 35 GHz and are shown in Fig. 4.<sup>74</sup> At room temperature the dielectric constant is 9.28 with a loss tangent of 0.00027. Above 900°C a rapid increase in loss tangent occurs. This is to be expected as a result of softening of the intergranular phases leading to increased conductivity via impurities. The variation in the dielectric constant and loss tangent as functions of frequency and temperature have

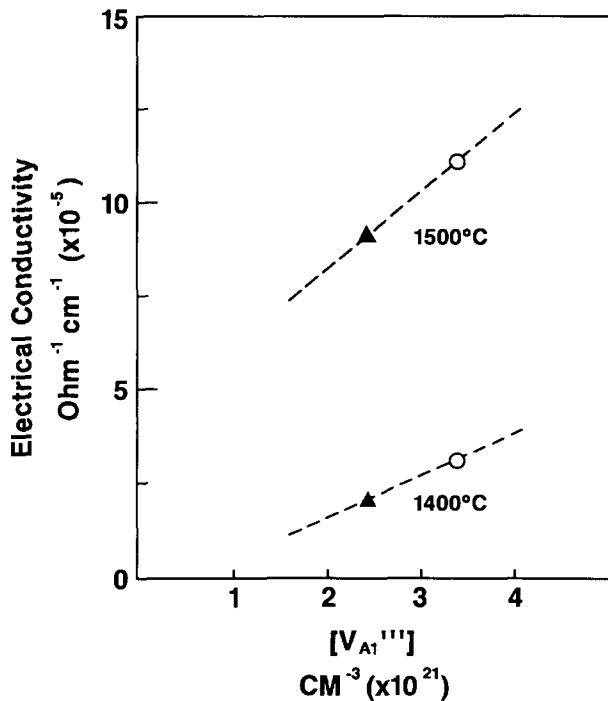


Fig. 6. Electrical conductivity of ALON spinel as a function of temperature and aluminum vacancy concentration.  $\circ$  = 23.7,  $\blacktriangle$  = 30.0 mol % AlN.<sup>72</sup>

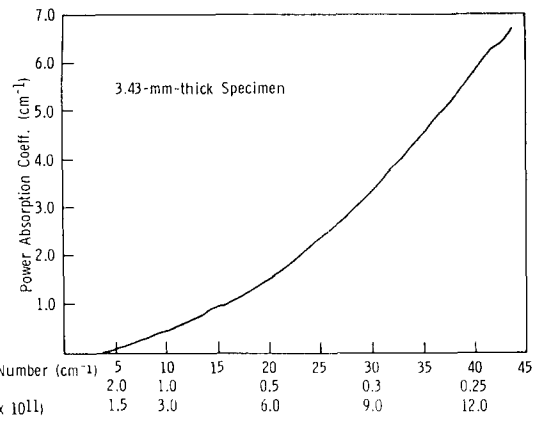


Fig. 7. ALON power absorption coefficient as a function of wave length.<sup>75</sup>

previously been reported.<sup>7</sup> Figure 5 is reproduced from this work.

The high temperature electrical conductivity was evaluated by Kim and Richards.<sup>72</sup> Electrical conductivity increases with the aluminum vacancy concentration (Fig. 6). They noted that the data suggest ALON is an ionic conductor at elevated temperature.

Figure 7 shows the power absorption coefficient of a 3.43 mm thick specimen as a function of wavelength.<sup>75</sup> At less than 1.0 mm wavelength ALON has very low absorption. The magnetic susceptibility was determined by the Gouy method and found to be  $0.34 \times 10^{-5} \text{ g}^{-1}$  with an applied field of 1300 gauss.<sup>4</sup>

Table 5 summarizes the optical and dielectric property data available on ALON spinel.

**7.2 Mechanical and elastic properties**

The mechanical properties have been extensively evaluated by Quinn *et al.*,<sup>26</sup> Hartnett,<sup>8</sup> Graham *et al.*<sup>76</sup> and Lefort.<sup>77</sup> Microhardness values of

Table 5. Representative optical and dielectric properties of single phase ALON spinel

Refractive index at 0.55 $\mu\text{m}$ wavelength	1.77-1.88	5 <sup>a</sup>
IR cut off	5.12 $\mu\text{m}$	8
UV cut off	0.27 $\mu\text{m}$	8
Absorption bands	11.2 $\mu\text{m}$ , 15.0 $\mu\text{m}$ , 19.0 $\mu\text{m}$	54
Dielectric Constant		
Room temperature (20 C), 10 <sup>2</sup> Hz	8.5	7
500 C, 10 <sup>2</sup> Hz	14.0	7
Room temperature (20 C), 35 GHz	9.28	74
1 200 C, 35 GHz	11.37	74
Loss tangent		
Room temperature (20 C), 10 <sup>2</sup> Hz	0.002	7
500 C, 10 <sup>2</sup> Hz	1.0	7
Room temperature (20 C), 35 GHz	0.000 27	74
1 200 C, 35 GHz	0.006	74

<sup>a</sup> Reference number.

**Table 6.** Representative mechanical and elastic properties of ALON spinel with a 35.7 mol% AlN composition

Bulk moduli <sup>a</sup> (Room temperature, 20 °C)	229.8 GPa	76 <sup>d</sup>
Shear moduli <sup>a</sup> (Room temperature, 20 °C)	135.5 GPa	76
Poisson ratio <sup>a</sup>	0.254	76
Strength <sup>b</sup> (Room temperature, 20 °C)	306 MPa	8, 26
Strength <sup>b</sup> (1 000 °C)	267 MPa	26
Fracture toughness <sup>c</sup>	2.0–2.9 MPa√m	8, 26
Hardness (Knoop)	16.5–19.5 GPa	5, 56, 77

<sup>a</sup> Properties determined by pulse superposition interferometry.

<sup>b</sup> Four-point flexure testing.

<sup>c</sup> Toughness by indentation, fractography and short rod.

<sup>d</sup> Reference number.

16.5–19.5 GPa were obtained when using a 0.98 N load with a Knoop indenter.<sup>5,56,77</sup> The elastic modulus for pore free ALON was determined as a function of composition, pressure and temperature by Graham *et al.*<sup>76</sup> The bulk modulus increases from 226.3 GPa to 229.8 GPa as the AlN content is increased from 30 to 35.7 mol%. The shear modulus increases from 132.0 to 135.5 GPa over the same composition range. These results fall midway between those for Al<sub>2</sub>O<sub>3</sub> (corundum) and MgAl<sub>2</sub>O<sub>4</sub> (spinel).

Four-point fracture strengths range from 44.4 × 10<sup>3</sup> psi (306 MPa) at room temperature<sup>8,26</sup> to 38.7 × 10<sup>3</sup> psi (267 MPa) at 1000 °C.<sup>26</sup> In most cases the critical flaw was either a large grain or pore. Strength data was obtained on relatively coarse grained material (25–100 μm). Fracture toughness ranges from 2.0–2.5 MPa√m.<sup>8,26</sup> Table 6 summarizes the mechanical and elastic properties of this material.

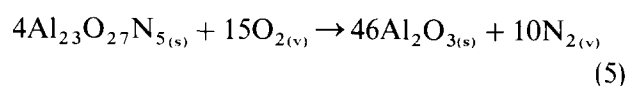
### 7.3 Thermal properties

The thermal expansion coefficient of ALON varies from 5.23 × 10<sup>-6</sup> per degree (25–200 °C) to 7.0 × 10<sup>-6</sup> per degree (20–980 °C) for reaction sintered material<sup>26</sup> while for hot pressed specimens it is 7.59 × 10<sup>-6</sup> per degree (25–1000 °C).<sup>78</sup> Room temperature thermal conductivity, thermal diffusivity and specific heat values are listed in Table 7.<sup>8,26,80</sup> Results from water quench experiments have

determined the critical thermal shock temperature to be 175 ± 5 °C.<sup>7,26</sup> This is somewhat lower than the value determined for α-Al<sub>2</sub>O<sub>3</sub> in the same study. Quinn<sup>26</sup> has proposed that the different thermal conductivities between these two materials (ALON/Al<sub>2</sub>O<sub>3</sub> = 1/3) is the reason for the different thermal shock results.

### 7.4 Oxidation and chemical resistance

There is some disagreement on the stability of ALON in an oxidizing environment. Corbin and McCauley<sup>7</sup> testing bulk samples in air, found the oxidation to produce a protective oxide layer up to ~1200 °C. However, Billy<sup>81</sup> found the oxidation of ALON to start as low as ~650 °C in oxygen and not produce a protective layer. As shown in eqn (5) below, the oxidation of ALON involves the loss of nitrogen.



It is, therefore, reasonable to expect that the partial pressure of nitrogen will influence the stability of ALON at elevated temperatures. In air  $P_{\text{N}_2} = \sim 0.7$ , while in the oxygen environment  $P_{\text{N}_2}$  would be orders of magnitude less.

Goursat *et al.*<sup>34,35</sup> and Lefort *et al.*<sup>80</sup> investigated the oxidation kinetics of ALON. Figure 8 is a thermogravimetric analysis (TGA) trace taken from Goursat, showing the oxidation behavior of a 20–50 μm powder. Oxidation starts near 650 °C and reaches a maximum weight gain at 1150 °C. Heating beyond this temperature produces a weight loss. They attribute this to the oxidation of ALON below 1150 °C without any nitrogen loss resulting in the formation of the oxygen-rich phase γ'-ALON. Above 1150 °C, oxidation occurs with a loss of all nitrogen with the ultimate product being alpha Al<sub>2</sub>O<sub>3</sub> (see eqn (4)). They also found that when a nitrogen-rich ALON composition is used as starting material γ'-ALON phase is not observed.

Resistance of this material to other forms of chemical attack has also been investigated.<sup>4,16,17,82</sup>

**Table 7.** Selected thermal properties of ALON spinel

Thermal shock (ΔT <sub>c</sub> )	448 ± 5 K (175 ± 5 °C)	7, 26 <sup>a</sup>
Thermal conductivity (room temperature, 20 °C)	10.89 W m <sup>-1</sup> K <sup>-1</sup> (0.026 cal cm <sup>-1</sup> s <sup>-1</sup> K <sup>-1</sup> )	8, 26, 79, 80
Thermal expansion coefficient	7.59 × 10 <sup>-6</sup> degree <sup>-1</sup> (at 298–1 273 K (25–1 000 °C)) 5.23 × 10 <sup>-6</sup> degree <sup>-1</sup> (at 293–473 K (20–200 °C))	26, 78
Thermal diffusivity	4.3 × 10 <sup>-6</sup> m <sup>2</sup> s <sup>-1</sup> (0.043 cm <sup>2</sup> s <sup>-1</sup> ) (at 300 K) 2.7 × 10 <sup>-6</sup> m <sup>2</sup> s <sup>-1</sup> (0.027 cm <sup>2</sup> s <sup>-1</sup> ) (at 400 K)	8, 26, 80
Specific heat	708 J kg <sup>-1</sup> K <sup>-1</sup> (0.169 cal g <sup>-1</sup> degree <sup>-1</sup> ) (at 300 K) 1 056 J kg <sup>-1</sup> K <sup>-1</sup> (0.252 cal g <sup>-1</sup> degree <sup>-1</sup> ) (at 450 K)	8, 26, 80

<sup>a</sup> Reference number.



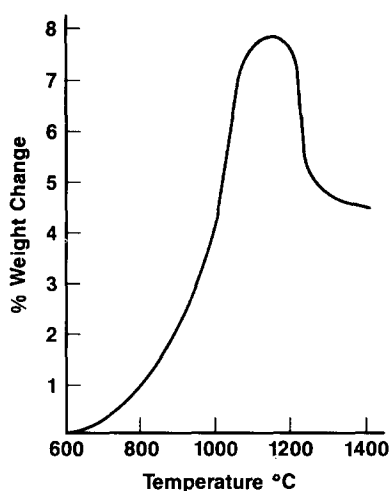


Fig. 8. Thermogravimetric analysis of ALON spinel in  $4.26 \times 10^{-3}$  MPa (32 Torr) of oxygen.<sup>35</sup>

The results show ALON is resistant to various acids, bases and  $H_2O$ .

### 7.5 Irradiation behavior

Some work has been done to determine the stability of ALON when irradiated with fast neutrons<sup>83</sup> and electrons.<sup>84</sup> Irradiation with 0.8 and 1 MeV electrons over the temperature range of 300–1100 K produces no defect aggregation. The lack of any bulk irradiation instability was considered significant by the authors.<sup>84</sup> Neutron irradiation with a dose of  $3 \times 10^{20}$  neutrons  $cm^{-2}$  produced very little change in the lattice parameter (0.071%). In comparison with other oxide, nitride and oxynitride materials ALON appears to be irradiation resistant.

### 7.6 Thermochemical properties

The free energy of formation for ALON can be determined from the data of Dorner *et al.*<sup>42,43</sup> and Kaufman.<sup>44</sup> The free energy of formations using Dorner and Kaufman data are compared in Table 8. The results differ by less than 0.2% between 1427°C

Table 8. Comparison of the ALON spinel free energy of formation ( $\Delta G_f^0$ ) as calculated from the data of Dorner *et al.*<sup>42,43</sup> and Kaufman<sup>44</sup>

T(K)	T(C)	$kcal\ mol^{-1}$			%
		Dorner (D)	Kaufman (K)	$\Delta$	
1700	1427	-841.905	-843.242	-1.337	-0.159
1900	1627	-791.497	-791.667	-0.170	-0.021
2100	1827	-741.090	-740.455	+0.635	+0.086
2300	2027	-690.683	-689.568	+1.115	+0.162
2500	2227	-640.276	-638.998	+1.278	+0.200

$7Al_{(l)} + 9/2 O_2 + 1/2 N_2 = Al_7O_9N$  (25 mol% AlN)

% =  $(D - K)/K \times 100$

$\Delta = D - K$

and 2227°C. These authors used the composition  $Al_7O_9N$  (25 mol% AlN) for ALON which occurs inside the solid-solubility limits reported by Lejus.<sup>18</sup> The reasons for the differences observed in Table 8 are due to the assumptions used in their determinations.

Dorner used the eutectoid decomposition of ALON into  $\alpha-Al_2O_3$  and AlN at 1600°C from the results of Lejus<sup>18</sup> and assumed a positive value of  $1\ JK^{-1}\ mol^{-1}$  for the entropy of formation from  $\alpha-Al_2O_3$  and AlN. He determined  $\Delta H_f^0$  and  $-\Delta S_f^0$  values for ALON as a function of temperature. These values were used to determine the  $\Delta G_f^0$  listed in Table 8 by the equation:

$$\Delta G_{f(ALON)}^0 = \Delta H_{f(ALON)}^0 - T\Delta S_{f(ALON)}^0 \quad (6)$$

Kaufman calculated the free energy of reaction ( $\Delta G^0$ ) for forming ALON from  $Al_2O_3$  and AlN by using lattice stability, solution and compound phase parameters. Using his information and the  $\Delta G_f^0$  for  $Al_2O_{3(s)}$  and  $AlN_{(s)}$  as listed in the JANAF tables,<sup>85</sup> the  $\Delta G_f^0$  for ALON reported in Table 8 was determined by the equation:

$$\Delta G_{f(ALON)}^0 = \Delta G^0 + 3G_{f(\alpha Al_2O_3)}^0 + G_{f(AlN)}^0 \quad (7)$$

As previously mentioned the data of Kaufman are in better agreement with experimental results.

## 8 Future ALON Research

There currently is a significant amount of interest in using ALON as a high temperature window material because of its optical, dielectric and mechanical properties. In order for this material to become commercially viable there are two key technical areas which need further development. The first is to determine and understand the intrinsic properties of ALON, and the second is to investigate alternative synthesis/processing methods. Several specific areas for future research are:

- (1) An experimental evaluation of the thermodynamic properties of ALON. This data could subsequently be used to determine environmental stability and lower temperature synthesis methods.
- (2) Determination of the oxygen, nitrogen and aluminum diffusion coefficients in ALON. This information will aid in determining ALON's intrinsic electrical properties and developing an understanding of its sintering behavior.
- (3) Additional studies are warranted to find sintering aids which will reduce sintering

times and temperatures. This may lead to a more economical process and the development of a finer grained material which should have increased strength.

- (4) Research is needed to determine alternative methods for preparing fine, high-purity ALON powders. The current high temperature method requires comminution of reacted materials to prepare fine powders. This process leads to contamination problems and difficulty in obtaining a uniform particle size distribution.

## 9 Conclusions

Aluminum oxynitride spinel (ALON) is a new material which has the potential to replace  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> in a variety of applications where optical transparency, high strength, high temperature stability, and isotropic properties are important. Current property evaluations of this material show that it is optically transparent from 5.12  $\mu$ m to 0.27  $\mu$ m, has high strength (4 point = 306.1 MPa (44.4  $\times$  10<sup>3</sup> psi)), and is oxidation resistant in air to 1200°C. Future studies should evaluate the stability of this material in a variety of environments to open up new areas where ALON can be utilized.

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