Effect of nitrogen content on optical properties of transparent γ-AlON polycrystalline ceramics

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ABSTRACT

A series of transparent ceramics with the composition of Al(8–x)/3O4–N x (x = 0.299–0.575) were prepared without any sintering additives by presintering combined with high isostatic pressing (HIP). The composition of the samples was accurately determined to investigate the effect of nitrogen content on optical properties in γ-AlON. The samples with x = 0.299–0.510 possessed excellent in-line transmittance (>80 %) from the visible light to middle-infrared wavelengths, which was attributed to rare pores and high density in these ceramics. As the increasing nitrogen content, the refractive index increased, the UV absorption edge presented a red-shift, and the transmittance at about 5.5 μm decreased. The Sellmeier optical coefficients E o, λ o, S o, and E ν were obtained on the basis of the single-term oscillator equation, which associates directly with the electronic energy band structure. The origin of the high refractive index is ascribed to the large electronic polarizability of nitrogen ions.

1. Introduction

Over the past several decades, spinel-type solid solution aluminum oxynitride (γ-AlON) has gained increasing attention due to its excellent optical transparency (>80 % transmittance in the wavelength range from ultraviolet (UV) to mid-infrared light (MIR)) and outstanding thermomechanical properties, which are essential for various technological applications such as transparent armor, missile domes, lenses and point of sale (POS) scanning windows [1]. In this regard, the γ-AlON transparent ceramics have a distinct advantage compared with polycrystalline alumina and could be used as promising candidate instead of sapphire. The spinel-type structure consists of almost cubic close-packed anion arrangement in which cations are distributed in tetrahedral and octahedral coordination [2]. It is obvious that the structure of spinel-type compounds can vary by tuning the element species and proportion of cations or anions, which plays a crucial role in optical properties of compounds. For instance, Krell et al. [3] have suggested that the infrared (IR) cut-off wavelength of MgO-Al2O3 transparent ceramics shifts significantly to shorter wavelength with the increasing n value. Zong et al. [4] reported a new γ-AlON transparent ceramic with infrared transmittance range equivalent to c-plane sapphire by tuning the content of nitrogen. Meanwhile, it is also found the refractive index of MgAlON transparent ceramics significantly increases as the content of nitrogen increases [4,5]. Tu et al. [6] carried out the first-principle investigation on the composition-dependent structure and optical properties of MgO-nAl2O3 solid solution and found the UV absorption peak presents a slight blue-shift as the value of n increases. Shannon [7] pointed out the refractive index of MgO-nAl2O3 compounds ascends with increasing n over the entire wavelength range, which is also supported by our theoretical calculation [6]. On the basis of these premises, optical properties of spinel-type transparent ceramics could be significantly tuned by varying element species and content of cations and anions. It is well known that the spinel-type γ-AlON is present in the AlN-Al2O3 system and its homogeneous region is experimentally identified to be ~16–35 mol% AlN [8,9]. According to the previous investigation, the formula of γ-AlON solid solution could be described as Al(8–x)/3O4–N x. In principle, the γ-AlON transparent ceramics could be fabricated in the full solubility range due to their cubic spinel-type structure characteristics [10]. As a solid solution, it is expected that the optical properties of γ-AlON could be effectively tuned by varying the ratio of O/N.

Although optical properties of γ-AlON with specific composition have been considered extensively in the previous investigation, relatively little work directed toward the evaluation of composition-dependent structure and optical properties...
dependent optical properties including both theoretical and experimental investigation. Hartnett et al. [11] have investigated the optical properties of γ-AlON with three different compositions (x = 0.40, 0.45, and 0.49). A slightly increasing refractive index with the nitrogen content over the entire wavelength range was observed, which was also confirmed by our theoretical research [12]. Furthermore, by measuring the in-line transmittance of two samples with different thicknesses, the extinction coefficients both at 5.4 μm and 5.6 μm were determined, which increased with increasing nitrogen content. Tu et al. [12] examined the optical properties of γ-AlON and their dependence on composition in a wide solid solution range by the first-principle approaches. The results indicated the absorption edge in the UV region presents a slightly red-shift as the content of nitrogen increases. Recently, Gao et al. [13] developed a number of examinations on mechanical and optical properties of γ-AlON with different compositions prepared by the carbothermal reduction nitridation method. Although the final compositions of the samples may unavoidably deviate from the initially designed values, a slight increase in refractive index from 1.688 to 1.702 at 400 nm with increasing nitrogen content was observed. Even though, there are still lacks of systematic experimental investigation on the band gap, optical dispersion, and infrared transmittance of γ-AlON with different compositions. In addition, the mechanism of the variation of refractive index is also not clarified.

In the present work, based on our experience of fabricating highly transparent MgAlON [10] and MgAlO₃ [14] by pressureless sintering and HIP post-treatment, the different compositions of highly transparent Al₂[8-x/3]O₃+xNₓ (x = 0.299–0.575) ceramics were fabricated without any sintering additives in order to investigate the intrinsic optical properties of γ-AlON, and the simultaneous effects of the N³⁺ substitute for O²⁻ on the refractive index, dispersion characteristic, and optical performances of the materials were studied. These experimental results provide insight deeply for understanding the optical properties of γ-AlON.

2. Experimental procedure

The γ-AlON powders were prepared by a conventional solid-state method, which has been employed to synthesize spinel-type MgO-nAl₂O₃ [14,15] and MgAlON [5,10] in our previous studies. The commercial AlN (~98%) and α-Al₂O₃ (~99.99%) powders as starting reagents were used to synthesize Al₂[8-x/3]O₃+xNₓ powders with designed compositions of x = 0.239, 0.308, 0.381, 0.459, 0.542, respectively. The actual chemical composition of the synthesized γ-AlON powders was identified by the well-established hot gas extraction method (model TC-600; Leco, St. Joseph, MI), where SiO₂ and TaN were used as calibration standards for O and N, respectively. The concentration of N was directly determined from this method to be 3.03 wt%, 3.64 wt%, 4.24 wt%, 5.12 wt%, and 5.75 wt%, respectively. According to the formula of γ-AlON, Al₂[8-x/3]O₃+xNₓ, the chemical formula of the obtained powders could be expressed as Al₂.766O₃.701N₂.299, Al₂.786O₃.640N₀.360, Al₂.807O₃.570N₀.420, Al₂.827O₃.406N₀.510, and Al₂.828O₃.423N₀.575, respectively, which are close to the designed nominal proportions. The Al content was determined by inductively coupled plasma atomic emission spectroscopy (model Optima 4300DV; PerkinElmer Instruments, Boston, MA), which matches well with the calculated content of Al in γ-AlON.

The received powders were compacted into 20-mm-diameter and 3-mm-thickness pellets with uniaxial pressure of 15 MPa. Then these compact pellets were cold isostatically pressed at 200 MPa. The specimens were firstly pressureless sintered at 1900 °C for 2 h under N₂ atmosphere and then fully densified by HIP at 1880 °C for 5 h under argon pressure of 180 MPa. Finally, as-sintered samples were ground and then mirror polished with diamond polishing paste on both sides to a thickness of 2 mm for optical transmittance measurement.

Density of the sintered bulk samples was measured by Archimedes method. The crystalline structure of γ-AlON transparent ceramics was characterized by X-ray diffraction with CuKα radiation (XRD, Bruker D8 focus, PANalytical Co, Netherlands). Microstructure of the chemically etched samples was characterized by SEM (Model S-3400; Hitachi, Tokyo, Japan). Refractive index and dispersion of the transparent samples were measured by a spectroscope ellipsometer (SE, ME-L, Wuhan Eoptics Technology Co., Ltd, China) [14]. The Raman spectra of the samples were recorded at room temperature with a Raman spectrometer (inVia, Renishaw, Britain) using a 532 nm laser of an Ar⁺ laser source (20 mW). In the ellipsometric analysis, the dispersive properties of the optical constants were described by Cauthy model, and a Bruggeman EMA layer (that contains 50 % sample and 50 % void) with a thickness of about 3.76 nm was introduced to account for the surface roughness of the sample [14]. The optical transmission spectra of transparent samples were recorded using spectrometers (Model UV-2550; Shimadzu, Kyoto, Japan for 0.2 – 1 μm; Model Nexus; Thermo Nicolet Corporation, Madison, WI; for 1 – 7 μm).

3. Results and discussion

Fig. 1 depicts the refractive index (n) and extinction coefficient (k) of the γ-AlON transparent ceramics as a function of wavelength measured by SE. The enlarged picture of extinction coefficient in the UV region is displayed in the inset of Fig. 1 (b). In general, the refractive index exhibits a normal dispersion behavior in the non-absorbing region of spectra [16]. The refractive index of all γ-AlON samples exhibits strong dispersion relation and decreases dramatically with an increase of wavelength in the entire wavelength range owing to the light frequency away from the resonant frequency of the oscillator [17]. Similarly, the extinction coefficient is relatively large at ~0.193 μm and decreases sharply to zero when the wavelength increases to ~0.4 μm, which indicates that γ-AlON is transparent over the visible light region when neglecting the effect of microstructure. The sharp decrease of extinction coefficient with increasing wavelength indicates a shift from absorption to dominant transmission as the value of the bandgap energy is approached [18]. In the visible light and infrared region, increased N-content leads to the raise of refractive index at the same wavelength, which corresponds with the suggestion made by Hartnett [11]. It has been pointed out that the electronic polarizability of materials is closely related to their refractive index [19]. Owing to the higher electronic polarizability of nitrogen than that of oxygen, the total electronic polarizability of γ-AlON was enhanced when the oxygen atoms are substituted by nitrogen atoms, which ultimately leads to the raise of refractive index.

According to the simple dispersion theory, the refractive index (n) can be given with high accuracy by the modified Sellmeier equation in the region of low absorption: [20]

\[ n^2 = A + \frac{B}{\lambda^2 - C} + D\lambda^2 \]  

(1)

where \( \lambda \) is the incident wavelength in micrometer, while A, B, C, and D are all constants and can be obtained in terms of least square fitting, which is summarized in Table 1. As indicated in Table 1, the parameters A, C, and D slightly increase with increasing \( \lambda \), while B ascends first and then descends, and reaches the maximum at \( \lambda = 0.510 \). Since the spinel structure can be regarded as cubic close-packed anion arrangement, the octahedron building block plays a decisive role in band structure [2]. Therefore, all the γ-AlON transparent ceramics display normal dispersion characteristics in the visible range. The refractive index of the γ-AlON transparent ceramics in the wavelength region of 0.2–1.8 μm can be precisely calculated according to Eq. (1), which fits the dispersion of the refractive index quite well. However, the parameters A, B, C, and D in the equation possess no special physical significance. According to the single oscillator model from the Wemple-DiDomenico (WD) relationship, which has the physical significance of the oscillator parameters, the refractive index (n) can be expressed as a function of the wavelength and energy of light using
The Sellmeier optical parameters of \( \gamma \)-AlON transparent ceramics and several Mg-Al spinel materials at room temperature.

## Table 2

<table>
<thead>
<tr>
<th>Materials</th>
<th>( S_o \times 10^{14} ) ( m^2 )</th>
<th>( \lambda_o (\mu m) )</th>
<th>( E_o ) (eV)</th>
<th>( E_d ) (eV)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>( x = 0.299 )</td>
<td>2.0080</td>
<td>0.1013</td>
<td>11.89</td>
<td>24.51</td>
<td>This work</td>
</tr>
<tr>
<td>( x = 0.360 )</td>
<td>2.0449</td>
<td>0.1010</td>
<td>11.91</td>
<td>24.83</td>
<td>This work</td>
</tr>
<tr>
<td>( x = 0.421 )</td>
<td>2.0202</td>
<td>0.1020</td>
<td>11.71</td>
<td>24.60</td>
<td>This work</td>
</tr>
<tr>
<td>( x = 0.510 )</td>
<td>2.0163</td>
<td>0.1028</td>
<td>11.65</td>
<td>24.81</td>
<td>This work</td>
</tr>
<tr>
<td>( x = 0.575 )</td>
<td>2.0877</td>
<td>0.1015</td>
<td>11.72</td>
<td>25.18</td>
<td>This work</td>
</tr>
<tr>
<td>( MgAl_2O_4 )</td>
<td>1.8182</td>
<td>0.1020</td>
<td>12.42</td>
<td>23.51</td>
<td>[27]</td>
</tr>
<tr>
<td>( Mg_{0.41}Al_{2.59}O_4 )</td>
<td>1.9231</td>
<td>0.0999</td>
<td>12.65</td>
<td>24.33</td>
<td>[27]</td>
</tr>
<tr>
<td>( Mg_{0.34}Ti_{2.66}O_4 )</td>
<td>1.8182</td>
<td>0.1028</td>
<td>12.26</td>
<td>23.58</td>
<td>[27]</td>
</tr>
</tbody>
</table>

The \( E_o \) values of \( \gamma \)-AlON are obviously smaller than those of Mg-Al spinel as shown in Table 2. According to the previous report [24], the \( E_o \) is associated with the optical band gap energy by an extraordinarily simple empirical formula: \( E_o = 2E_d \). It was noticed that the optical band gap energy of \( \gamma \)-AlON is significantly lower than those of Mg-Al spinel [25], which results in the variation of \( E_o \) in these systems based on the above simple formula. Moreover, the \( E_o \) of \( \gamma \)-AlON presents a descending trend with increasing \( x \), which also can be explained by the variation of the band gap energy determined by the first-principles calculations [12]. Besides, it is well known that the parameter \( E_d \) is used to estimate the strength of the interband optical transitions [22,26], which obeys the simple empirical relationship \( E_d = \beta N_c Z_a N_e \), where \( N_c \) is the coordination number of the cation nearest to the anion, \( Z_a \) is the formal chemical valency of the anion, \( N_e \) is the effective number of valence electrons per anion, and \( \beta \) is a constant \( \beta_l = 0.26 \pm 0.04 \) eV and \( \beta_c = 0.37 \pm 0.05 \) eV for ionic and covalent compounds, respectively. According to the previous literature [22], as for simple spinel compounds, the parameters \( N_e \) and \( N_c \) have the same values due to the same spinel type crystalline structure, whereas the value \( Z_a \) of \( \gamma \)-AlON may be higher than those of

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**Fig. 1.** Wavelength dependence of the refractive index \( n \) (a) and extinction coefficient \( k \) (b) of \( \gamma \)-AlON transparent ceramics with different compositions.

**Fig. 2.** The dependence of (a) \( (n^2-1)^{-1} \) on \( \lambda^{-2} \), and (b) \( (n^2-1)^{-1} \) on \( E^2 \) for \( \gamma \)-AlON transparent ceramics. The lines are fitted linearly with experimental data (symbols).
Mg-Al spinel due to the higher valency of nitrogen. In addition, consistent with the previous results [12], the covalence of bond of γ-AlON is obviously stronger than those of Mg-Al spinel, which leads to the larger β value in γ-AlON. Therefore, the γ-AlON ceramics possess higher $E_d$ values than Mg-Al spinel under the influence of these factors, as illustrated in Table 2. Similarly, as the nitrogen content increasing, more Al—O bonds were substituted by Al—N bonds, which leads to a slight enhancement in covalence in γ-AlON. As a consequence, the $E_d$ of γ-AlON ultimately showed an increasing trend with the increasing composition of $x$.

Fig. 3 presents a photograph of γ-AlON transparent ceramics of different compositions with $x$ from 0.299 to 0.575 standing on a piece of paper. It can be seen that all the obtained samples were colorless and transparent, the word “AlON” behind them could be clearly seen. In addition, by comparing the visual appearance of these samples, it also can be seen that the left four samples are more transparent.

In general, the theoretical transmittance of a sample can be calculated from the following two equations: [28–30]

$$T = (1 - R)^2 \exp(-\alpha t)$$  \hspace{1cm} (3)

and

$$R = \frac{(n - 1)^2}{(n + 1)^2} \frac{1}{T}$$  \hspace{1cm} (4)

where $R$ is reflection loss, $n$ is the refractive index and $\alpha$ is the absorption coefficient. Therefore, assuming the absorption coefficient is close to zero, the surface reflection and theoretical transmittance of γ-AlON transparent ceramics with the different compositions in the wavelength range of 0.2–1.7 μm can be calculated using the above equations and the refractive index data from Fig. 1(a), which were plotted in Fig. 4. As can be seen from these curves, the theoretical transmittance, which increases over the entire wavelength range due to the decrease of the reflection losses, as observed for all the samples. Nevertheless, a decrease in the theoretical transmittance at the same wavelength with increasing nitrogen content is found. At the incident wavelength of 0.63 μm, the transmittance of the γ-AlON predicted from refractive index varies from 85.76 % at $x = 0.299$ to 85.12 % at $x = 0.575$. The variation in theoretical transmission suggests that the intrinsic optical properties can be tuned to some extent by the control of composition.

Fig. 5 presents typical transmittance spectra of the obtained γ-AlON transparent ceramics with $x$ from 0.299 to 0.575 in the UV–Vis–NIR region. In the visible range, the transmittance exhibits a decreasing trend with the increasing content of nitrogen. The in-line transmittance of the samples with $x$ from 0.299 to 0.510 for which the transmittance curves were relatively flat can exceed 80 % in the visible regions. The values were 84.1 %, 83.2 %, 81.5 %, and 80.2 %, respectively at 0.63 μm, which are close to the theoretical limit, implying excellent quality of the fabricated ceramics, and they are available as optical materials. Considering that the samples were prepared without any sintering aids, the result was quite satisfying. The result was superior to that of previous reports on the γ-AlON transparent ceramic with Y$_2$O$_3$ and La$_2$O$_3$ as sintering aids [31]. However, the specimen with $x = 0.575$ showed the lowest transmittance among these samples. In order to further explain the difference in transparency of all samples, the phase composition and microstructure of γ-AlON transparent ceramics were studied, which are illustrated in Figs. 6 and 7. The XRD patterns showed all samples belong to the cubic phase with the space group $Fd\overline{3}m$ since there were no detected secondary phases, which suggests the phase composition should not be the cause of the variation in transparency. However, the SEM images showed some differences in these samples. It is pointed out that the most seriously optical scattering loss will occur when the size of the scattering center is equal to the wavelength of incident light [32]. For the samples with $x$ from 0.299 to 0.510, a dense and homogeneous microstructure without obvious pores was observed, which leads to the high transmittance of the sintered samples in agreement with the visual appearance of these specimens (Fig. 3). Nevertheless, residual pores were observed in the grain and grain boundaries of $x = 0.575$ sample (Fig. 7e), which would definitely deteriorate the optical quality of the ceramic. It suggests that the microstructure with residual pores as light.
scattering centers should be the main reason for the change of transparency of all samples. According to the previous investigation of Tu et al. [12], the bond strength of Al—N is stronger than that of Al—O in γ-AlON system. As all samples are sintered at the same temperature, the sample with a higher nitrogen content is more difficult to be densified, which leads to the existence of residual pores in the sintered body [13]. Further investigation of the effect of sintering temperature on the optical properties of the γ-AlON ceramics is currently in progress. In addition, the UV absorption edge of the γ-AlON ceramics shifted to longer wavelength with increasing nitrogen content, which can be seen in the enlarged transmittance curves shown in the inset of Fig. 5. In general, absorption edge in the UV region is caused by electronic transitions from the valence band to the conduction band, and the cut-off wavelength is determined by the energy gap between these two bands.

The absorption coefficients (α) versus photon energy (hv) of incident light are displayed in Fig. 8, which is determined by the following equation: [33]

$$\alpha = \frac{1}{L} \ln \left( \frac{1}{R} \right) + \frac{\sqrt{\left(1 - R\right)^2 + 4R^2T^2}}{2RT}$$  (5)

where $R$ is the surface reflectivity, $L$ is the thickness of the samples and $T$ is the transmittance. It is obvious that a significant increase in the absorption coefficient is observed at about 5.2 eV for γ-AlON ceramics, which coincides with the abrupt decrease of transmittance as shown in Fig. 5.

**Fig. 6.** XRD patterns of γ-AlON transparent ceramics with different compositions.

**Fig. 7.** Surface morphologies of the chemically etched transparent Al$_{(8+x)/3}$O$_x$N$_x$ ceramics: (a) $x = 0.299$, (b) $x = 0.360$, (c) $x = 0.421$, (d) $x = 0.510$, (e) $x = 0.575$. 
In order to further interpret the red-shift of UV absorption edge shown in the inset of Fig. 5, the band gap energies \( E_g \) of \( \gamma\)-AlON ceramics can be deduced from the absorption coefficients through Tauc equation: [33,34]

\[
\alpha h\nu = C(h\nu - E_g)^n
\]  

(6)

where \( C \) is a constant, \( E_g \) is the optical band gap energy, \( h\nu \) is the energy of incident light, and \( n \) is an index determined by the nature of the electron transition during the absorption process [35]. For direct and indirect transitions, \( n \) can be taken as 1/2 and 2, respectively. So far, there are still lacks of experimental investigation on band gap of \( \gamma\)-AlON with different compositions. The \((\alpha h\nu)^2\) as a function of \( h\nu \) curves for all samples are plotted in Fig. 9. It can be seen that the straight lines near the absorption edge manifest the direct optical band gap characteristic of all ceramics (\( n = 1/2 \)). The result indicates that the electron can be excited by photons directly from the upper valence band to the bottom of conduction band without the participation of phonons, which is in agreement with the previous theoretical study [12]. By extrapolating the plot to \((\alpha h\nu)^2 = 0\), the optical band gap energies for all samples can be obtained, which were displayed in the inset of Fig. 9. As can be seen, a decrease in the optical band gap energy with increasing nitrogen content is found, which could explain the shift of UV absorption edge shown in the inset of Fig. 5.

Fig. 8 illustrates typical MIR transmittance spectra of the obtained \( \gamma\)-AlON transparent ceramics with different compositions. The maximum transmittance for the ceramics can be obtained at approximately 3.7 \( \mu \)m, which are 85.88 %, 85.85 %, 84.29 %, 82.52 %, and 78.02 %, respectively, implying excellent optical properties for Mid-IR targeting. It is obvious that the transmittance of the sample with \( x = 0.575 \) is the lowest in these ceramics, which is mainly ascribed to the optical scattering caused by structural inhomogeneities such as the residual pores (Fig. 7c). Since multiphonon processes in the ceramics give rise to absorption, the transmittance decreased with the further increasing wavelength. The cut-off wavelength for 5% transmission in the IR region is \(~5.8 \mu \)m, which is consistent with the previous results reported by other researchers [36]. The absorption edges in the IR region did not show any clear compositional dependence, indicating the absorption coefficient is unchanged. Nevertheless, it is also noteworthy that the transmittance at about 5.5 \( \mu \)m decreased with increasing \( x \), meaning the absorption coefficients are enhanced in this region when substituting \( \text{Al}_2\text{O}_3 \) with \( \text{AlN} \). The results agreed well with the report confirmed by Hartnett that an increase in the extinction coefficient in the infrared region with increasing nitrogen content [11], which is probably ascribed to the enhancement of force constant with increasing \( x \) [4]. In addition, a weak absorption band around 3 \( \mu \)m is attributed to the presence of free hydroxyl (OH) or NH group [10], those are generally observed in spinel transparent ceramics [14].

In order to further understand how the intrinsic optical properties of the \( \gamma\)-AlON ceramics were affected by the concentration of nitrogen, normalized Raman scattering spectra were utilized, which are presented in Fig. 11. Broad peaks around 307, 389, 616, 762, and 913 cm\(^{-1}\) are observed for the \( \gamma\)-AlON ceramics, which agreed well with the previous reports [37,38]. Owing to the complex crystalline structure of \( \gamma\)-AlON, the detailed assignments of the vibrational modes could not be accomplished so far. According to the previous investigation on spinel [39], we carried out simple assignments on \( \gamma\)-AlON. The modes observed at about 307 cm\(^{-1}\) can be assigned to lattice stretching (\( T_{2g} \)), while the modes located at about 389 cm\(^{-1}\) can be assigned to bend stretching (\( E \)). Furthermore, the modes at about 762 cm\(^{-1}\) could correspond to symmetric stretching of \( \text{AlO}_4 \) tetrahedra. However, the other modes cannot be assigned due to the disordered crystal structure of \( \gamma\)-AlON. [2] It has been pointed out that the maximum phonon frequency of ceramics is of great importance to the infrared cut-off edge [4]. As can been seen, the phonon frequency (\(~913 \)cm\(^{-1}\)) presented hardly any change with increasing \( x \), which supports that the infrared cut-off wavelength is
Fig. 11. Raman spectra of γ-AlON transparent ceramics with different compositions.

almost unchanged. In addition, the relatively high phonon frequency of γ-AlON is probably due to the fact that these ceramics contain Al–N with strong covalent characteristics.

Although there are many reports on the optical properties of γ-AlON, there is still a lack of documented values for the refractive index and the Abbe number along with their dependence on x. The Abbe number νd, which represents the degree of the refractive index dispersion, was determined using the formula:

\[ \nu_d = \frac{n_d - 1}{n_v - n_C} \]  

where \( n_d \), \( n_v \), and \( n_C \) are the refractive index at the wavelengths of 587.6, 486.1, and 656.27 nm, respectively. We calculated \( n_d \), \( n_v \), and \( n_C \) from Eq. (3) and obtained \( \nu_d \) from Eq. (7). The refractive index \( n_d \) at 587.6 nm and the Abbe number \( \nu_d \) of all the samples as a function of x are shown in Fig. 12. It is well known that the spectroscopic ellipsometer is not accurate enough to estimate \( v_d \) when the refractive index of a material is below 2. However, one can determine the general trend of \( v_d \) dependent on the nitrogen content [40]. It is pointed out that the greater wave length dispersion in optical materials corresponds to a smaller value of \( v_d \). From the viewpoint of optical material applications, such as lenses for microscopes and endoscopes, a high refractive index and low wavelength dispersion are desirable [41]. As can be seen from Fig. 12, \( n_d \) increases monotonically from 1.76 to 1.79 with the increasing composition proportion of nitrogen in the Al\(_{18-x}O_3\)O\(_x\)N\(_y\). The values are obviously higher than those of MgAlON and MgAl\(_2\)O\(_4\) [4]. Nevertheless, \( n_d \) shows an irregular change from 60.44 to 62.63 with increasing x, which is slightly higher than the reported value of 58.2 [42]. As reported in previous researches [43], it is demonstrated that the \( v_d \) is closely related to the inherent absorption wavelength, \( \lambda_o \) (as shown in Table 2). The shorter inherent absorption wavelength, \( \lambda_o \), the larger \( v_d \) is. This relationship also fits very well in γ-AlON. The irregular variation in \( \lambda_o \) with composition is probably ascribed to the complicated band structure as nitrogen replaces oxygen [43,44]. The unique characteristics indicated that γ-AlON transparent ceramics should be attractive materials for achromatic lenses.

The variation in \( n_\alpha \) is associated with the volume of unit cell (\( V_m \)) and the total molar electronic polarizability (\( \alpha_N \)) of a compound proposed by Shannon [45]

\[ n_\alpha = \frac{4\pi\alpha_N}{\sqrt{\left(2.26 - \frac{\pi^2}{3}\right)\alpha_i + V_m}} + 1 \]  

where \( N \) is the total number of types of ions in the formula unit. \( n_i \) and \( \alpha_i(\text{ion}) \) are the number and electronic polarizability of the i-type ion in the formula unit, respectively. Considering the electronic polarizability of anions is much larger than that of cations, the investigation of total electronic polarizability is mainly focused on the change in the composition of anion. Meanwhile, it is obvious that the variation in \( V_m \) is relatively small due to a slight change in lattice parameters gained by other researchers [9]. The refractive index and density of AlN are known relatively small due to a slight change in lattice parameters. As reported by other researchers [9], the refractive index and density of AlN are known as 2.1 and 2.36 g/cm\(^3\), respectively [46]. Therefore, the electronic polarizability of N is obtained as 2.6 Å, which is close to the calculated value determined by Schmidt et al [47]. This value is more than double that of O (~1.15 Å) [48]. As the amounts of anions in γ-AlON are fixed due to the constant anion structural model, the concentration of aluminum slightly arises and aluminum vacancy decreases when O atoms were substituted by N atoms. Therefore, the total electronic polarizability is expected to be remarkably enhanced with increasing x. As a result, the refractive index of the present ceramics is enhanced with increasing content of nitrogen under the combined effect of \( \alpha_N \) and \( V_m \).

This work addresses the important contributions of N atoms to the high refractive index of γ-AlON ceramics and suggests an alternative approach for the design of high index materials by varying the composition content of nitrogen in the compound.

4. Conclusion

In this work, the composition-dependent refractive index, extinction coefficients, and optical transmittance of Al\(_{18-x}O_3\)O\(_x\)N\(_y\) transparent ceramics were systematically investigated. The refractive index of all samples exhibits a normal dispersion behavior. The modified Sellmeier dispersion equation was obtained through the least-square fitting and the Sellmeier optical coefficients (\( E_o \), \( \lambda_o \), \( \sigma_o \), \( E_d \)) were derived from single-oscillator dispersion relation for all γ-AlON transparent ceramics. Contrary to the sample with \( x = 0.575 \), the specimens with \( x = 0.299-0.510 \) exhibited high in-line transmittance in the visible light region, which could be ascribed to rare pores and high density in these ceramics. It is also found that a slight red-shift occurred in the ultraviolet range with increasing x, which corresponds to the variation in optical bandgap energy determined by Tauc equation in γ-AlON. It is also noteworthy that the transmittance at about 5.5 μm significantly decreased with the increasing composition of x. Owing to the relatively large electronic polarizability of nitrogen, the refractive index of the γ-AlON transparent ceramics ultimately increased with increasing nitrogen content. Our work is helpful to provide deep insight for the
investigation of optical properties of the γ-AlON transparent ceramics.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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