A novel spinel-type $\text{Mg}_{0.55}\text{Al}_{2.36}\text{O}_{3.81}\text{N}_{0.19}$ transparent ceramic with infrared transmittance range comparable to c-plane sapphire

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**Abstract**

A novel $\text{Mg}_{0.55}\text{Al}_{2.36}\text{O}_{3.81}\text{N}_{0.19}$ transparent ceramic with an infrared transmission range comparable to c-plane sapphire was prepared based on the intentional design of the composition. This material possesses outstanding optical properties, such as a high in-line transmittance up to 86.5% at 3.7 μm, a refractive index of 1.7240 at 589.3 nm and an absorption coefficient of 0.8 cm$^{-1}$ at 5 μm. The effects of chemical composition on the crystal structure and optical properties of spinel material were discussed. In particular, the chemical bond strength of disordered tetrahedron varying with the composition largely determines the infrared transparent range of transparent ceramic.

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Sapphire, $\text{MgAl}_2\text{O}_4$ and AlON have been well-developed as mid-IR transparent materials for infrared window application during the past decade. It has been demonstrated that the infrared cut-off edge ($\lambda_{\text{cut-off}}$) increases in the order $\lambda_{\text{AlON}} < \lambda_{\text{c-plane sapphire}} < \lambda_{\text{MgAl}_2\text{O}_4}$, while AlON has higher hardness and fracture strength than $\text{MgAl}_2\text{O}_4$ [1,2]. Yet, the optical properties between $\text{MgAl}_2\text{O}_4$, c-plane sapphire and AlON, especially the infrared transmission range, have a large gap to fill.

Since the microstructure of transparent ceramics has the characteristics of high density, few pores, no second phase and large crystalline grains, some physical properties of transparent ceramics are less affected by microstructure, while mainly depend on the intrinsic properties of crystalline grains which are determined by their composition, crystal structure and bonding properties [3,4]. Krell et al. have indicated that the infrared cut-off wavelength of $\text{MgO}_n\text{Al}_2\text{O}_3$ transparent ceramics is significantly shortened as the value of $n$ increases [5]. Willems et al. have noted that as the content ratio of O/N increases, the hardness and elastic modulus of AlON transparent ceramics tend to decrease, while the infrared cut-off wavelength is extended [6,7]. Compared with $\text{MgAl}_2\text{O}_4$ and AlON, a quaternary disordered solid solution MgAlION has an extremely extensive solubility range of the spinel-type phase [8,9]. Moreover, the crystal structure of MgAlION may be easily adjusted by its composition, which supposed to endue MgAlION with ample combination of mechanical and optical properties.

Currently, MgAlON spinel-type transparent ceramic with excellent optical properties and good mechanical properties has been prepared [10–12]. Compared with AlON transparent ceramic, the infrared cut-off of MgAlION transparent ceramic is red-shifted. Besides, it is demonstrated to prepare high-quality transparent ceramics with large and complex shapes by aqueous gelcasting due to no obvious hydration [13]. However, for MgAlION transparent ceramics, the influences of composition, crystal structure and bonding properties of crystalline grains on the optical properties and mechanical properties of transparent ceramics have not been reported.

In this work, a novel highly transparent $\text{Mg}_{0.55}\text{Al}_{2.36}\text{O}_{3.81}\text{N}_{0.19}$ ceramic with an infrared transmission range comparable to that of c-plane sapphire was prepared and characterized. The crystal structure of $\text{Mg}_{0.55}\text{Al}_{2.36}\text{O}_{3.81}\text{N}_{0.19}$ was refined by the Rietveld method combined with the structure model of spinel-type solid solutions. Besides, the microstructure, optical, mechanical, and thermal properties were investigated. Furthermore, we focused on the effect of compositional change on crystal structure, infrared cut-off edge and refractive index of the spinel-type transparent ceramic.

The raw powders $\text{Mg}_{0.55}\text{Al}_{2.36}\text{O}_{3.81}\text{N}_{0.19}$ were synthesized by solid-state reaction with high-purity MgO (99.99%), AlN (99.9%), and $\alpha$-Al$_2$O$_3$ (99.99%) powders. After gelcasting, the green bodies were presintered to the pore-closed state by pressureless sintering at 1825 °C for 2 h under N$_2$ atmosphere. Then HIP sintering was carried out at 1880 °C for 5 h in Ar (180 MPa). The sintered sam-

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samples (φ20 × 2 mm) were ground and then mirror-polished with diamond polishing paste on both surfaces.

The chemical composition of initial powders was conducted by the oxygen-nitrogen determinator (TC6000, Leco, USA) and inductively coupled plasma-atomic emission spectroscopy (ICP-AES, Optima4300DV, PerkinElmer, USA). The phase was identified by X-ray diffractometry (XRD, X’Pert PRO of Panalytical, Netherlands) recording the XRD pattern of the powder with monochromatized Cu Kα radiation at room temperature. The crystal structure was determined with Rietveld method using the FULLPROF program combined with the structure model of spinel-type solid solutions proposed by Lavina et al [14,15]. Particle size of the synthesized $\text{Mg}_{0.55}\text{Al}_{2.36}\text{O}_{3.81}\text{N}_{0.19}$ powders was measured by the laser diffractometry (Mastersizer2000, Malvern, UK). The morphology of the raw powders and microstructure of the chemically etched ceramic were observed by scanning electron microscopy (SEM, S-3400, Hitachi, Japan). The average grain size of the ceramic was estimated from micrographs using the linear intercept method by counting over 250 grains. The density of sample was tested by the Archimedes method. The Vickers hardness of the sintered sample was measured by a hardness tester (430SVD, Wolpert, China) with a testing load of 1 kg and a holding time of 15 s. The elastic modulus of the sample at room temperature was measured by a vibration pulse excitation method using an elastic modulus tester (MK7, GrindoSonic, Belgium). The thermal expansion coefficient of the sample was examined over the range of 30–600 °C by a dilatometer (DIL402C, Netzsch, Germany). The thermal conductivity of the sample was measured using the laser flash method by a laser flash apparatus (TC-700HT/MELT, Ulvac-Riko, Japan). In-line transmittance of the polished sample was determined in the range of wavelength between 0.2 μm and 7 μm using spectrometers (UV-2550, Shimadzu, Japan for 0.2–1 μm; Nicolet6700, ThermoNicolet, USA for 1–7 μm). Refractive index and dispersion of the sample were measured by a spectroscopic ellipsometer (ME-L, Wuhan Eoptics Technology Co., China) at a reflection measurement mode [16,17]. The infrared reflectance spectrum of the sample was recorded by a Fourier transform infrared spectrometer (FTIR-Vertex80v, Bruker, Germany) under vacuum at room temperature using the SIC Globar lamp as an infrared source. The incident angle of light was 10° and the reference spectrum was obtained by the gold mirror sample.

The XRD patterns of $\text{Mg}_{0.55}\text{Al}_{2.36}\text{O}_{3.81}\text{N}_{0.19}$ powders and transparent ceramic were compared as shown in Fig. 1a. Both the synthesized powders and the sintered ceramic were detected to be spinel-type structure, and there was no apparent preferred orientation in the ceramic. In addition, as illustrated in Fig. 1b, the synthesized powders exhibited a narrow particle size distribution ($d_{0.5} = 1.2$ μm) and low agglomeration, which was advantageous for the preparation of high quality transparent ceramics.

Fig. 2a displays the microstructure of $\text{Mg}_{0.55}\text{Al}_{2.36}\text{O}_{3.81}\text{N}_{0.19}$ transparent ceramic. The average grain size of the sample was 42.21 ± 1.8 μm and the grain boundary was clean without any secondary phase. In addition, almost no residual pores were observed in the sample, and the density measured by the Archimedes method was 3.585 g/cm³, which is very close to the theoretical density of 3.598 g/cm³ calculated from the composition and lattice parameters. This uniform, pure and dense microstructure of the specimen is not only an important guarantee for the good optical properties of the ceramic, but also makes the physical properties of the transparent ceramic mainly depend on the intrinsic properties of its crystalline grain. As revealed by the in-line transmission spectra of the transparent $\text{MgAl}_2\text{O}_4$ [18], $\text{Mg}_{0.55}\text{Al}_{2.36}\text{O}_{3.81}\text{N}_{0.19}$, $\text{Mg}_{0.27}\text{Al}_{2.52}\text{O}_{3.71}\text{N}_{0.27}$ [13], AlON [19] and c-plane sapphire [20] samples (Fig. 2b, all samples are 2 mm thickness), $\text{Mg}_{0.55}\text{Al}_{2.36}\text{O}_{3.81}\text{N}_{0.19}$ transparent ceramic exhibited very high optical transmittance (86.5% at 3.7 μm). Moreover, the infrared cut-off of $\text{Mg}_{0.55}\text{Al}_{2.36}\text{O}_{3.81}\text{N}_{0.19}$ transparent ceramic is comparable to that of c-plane sapphire. Meanwhile, we calculated the absorption coefficient of $\text{Mg}_{0.55}\text{Al}_{2.36}\text{O}_{3.81}\text{N}_{0.19}$ at 5 μm by measuring the transmittance of $\text{Mg}_{0.55}\text{Al}_{2.36}\text{O}_{3.81}\text{N}_{0.19}$ transparent ceramics with different thicknesses (0.54 and 2 mm), which is the same as the absorption coefficient ~0.8 cm⁻¹ of c-plane sapphire at 5 μm (Fig. 3b) [21].

It is well known that the infrared cut-off of a dielectric material depends on multi-phonon absorption, which is primarily affected by composition and crystal structure [22]. In order to study the influence of the composition on the crystal structure, the chemical formulation of the initial powders was determined to be $\text{Mg}_{0.55}\text{Al}_{2.36}\text{O}_{3.81}\text{N}_{0.19}$ according to the analysis of elements content, which is the starting point for the refinement of crystal structure. Then the structural parameters and the occupancy of the cations in the tetrahedral and octahedral sites were obtained by the Rietveld method (Fig. 1a) combined with the structure model of spinel-type solid solutions as shown in Table 1. The final R values of Rietveld analysis were listed as follows: $R_p = 4.43\%$, $R_{wp} = 5.75\%$, $\chi^2 = 1.44$, $Gof = 1.2$. It is observed from the final structural formula that a part of the Al and Mg cations changed the site by inversion. This result is consistent with previous reports on spinel structure [23]. In addition, the calculated bond valence and bond force constant of $\text{Mg}_{0.55}\text{Al}_{2.36}\text{O}_{3.81}\text{N}_{0.19}$, $\text{Mg}_{0.27}\text{Al}_{2.52}\text{O}_{3.71}\text{N}_{0.27}$ [4], as well as MgAl₂O₄ (ICSD no. 97180) [24] and AlON (ICSD no. 70033) [25], which are important parameters for describing character of the chemical bond, were listed in Table 1 (Supporting Information). 1. With the ratio of Al/Mg increasing, the unit cell parameter (a) and the anion position parameter (u) became smaller. Besides, the bond length of chemical bond in tetrahedra (R₁) is decreased, which leads to the bond valence (S₁) and bond force con-
Table 1

<table>
<thead>
<tr>
<th>Measured composition</th>
<th>Cation distribution</th>
<th>a (Å)</th>
<th>u</th>
<th>R_f (Å)</th>
<th>R_m (Å)</th>
<th>S_1 [μm]</th>
<th>S_0 [μm]</th>
<th>F_21 (N m−1)</th>
<th>F_22 (N m−1)</th>
</tr>
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<tr>
<td>MgAl_2O_4 [24]</td>
<td>Mg_0.16Al_0.84</td>
<td>8.084</td>
<td>0.3871</td>
<td>1.920</td>
<td>1.928</td>
<td>0.528</td>
<td>0.480</td>
<td>172.95</td>
<td>149.13</td>
</tr>
<tr>
<td>Mg_0.5Al_2O_3O_13N_0.19</td>
<td>Mg_0.65Al_2O_3</td>
<td>7.9435</td>
<td>0.3813</td>
<td>1.806</td>
<td>1.937</td>
<td>0.683</td>
<td>0.442</td>
<td>276.37</td>
<td>130.99</td>
</tr>
<tr>
<td>Mg_0.5Al_2O_3O_13N_0.27 [4]</td>
<td>Al_0.82C_0.18</td>
<td>7.9435</td>
<td>0.3813</td>
<td>1.806</td>
<td>1.937</td>
<td>0.683</td>
<td>0.442</td>
<td>276.37</td>
<td>130.99</td>
</tr>
<tr>
<td>AlON [25]</td>
<td>AlO_2C_0.01</td>
<td>7.9435</td>
<td>0.3813</td>
<td>1.806</td>
<td>1.937</td>
<td>0.683</td>
<td>0.442</td>
<td>276.37</td>
<td>130.99</td>
</tr>
</tbody>
</table>

Note: □ represents the cation vacancy.

Fig. 2. (a) Microstructure of the chemically etched surface of Mg_0.55Al_2O_3O_13N_0.27 transparent ceramic. (b) In-line transmittance of the transparent MgAl_2O_4 [18], Mg_0.55Al_2O_3O_13N_0.19, Mg_0.27Al_2O_3O_13N_0.27 [13], AlON [19] and c-plane sapphire [20] samples with the same thickness of 2 mm and inset is the photograph of Mg_0.55Al_2O_3O_13N_0.19 transparent ceramic.

Fig. 3. (a) Infrared reflectivity spectra of Mg_0.55Al_2O_3O_13N_0.19 and Mg_0.27Al_2O_3O_13N_0.27 transparent ceramics at room temperature. The black circles and red line represent experimental data and the fitted spectra from the four-parameter semiquantum model. (b) Absorption coefficient and maximum longitudinal optical mode frequency of MgAl_2O_4 [21,26], Mg_0.55Al_2O_3O_13N_0.19, Mg_0.27Al_2O_3O_13N_0.27 [13], AlON [21,26] and sapphire [21,26]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

As with a thickness of a few millimeters [26], the absorption coefficients at 5 μm and ν_m of MgAl_2O_4 [21,26], Mg_0.55Al_2O_3O_13N_0.19, Mg_0.27Al_2O_3O_13N_0.27 [13], AlON [21,26] and sapphire are shown in Fig. 3b. As the ν_m of the transparent material increases, the absorption coefficient at 5 μm becomes larger which means that the infrared absorption is enhanced. Fabian et al. have reported that the highest frequency of vibration mode occurring in the infrared reflectance spectrum is related to Al^3+ ions occupying tetrahedral coordination [27]. From the above analysis of the composition-structure relationship of spinels (Table 1), it is known that as the Al/Mg ratio in tetrahedron increases, the R_f is decreased which enhances the F_21. According to the diatomic molecular vibration model, the expression of the frequency of vibration mode ν is as follows [28]:

\[
ν = \frac{1}{2πc} \sqrt{\frac{E}{\mu}}
\]

(1)
Table 2
Refractive index, Abbé number, electronic polarizability and mechanical and thermal properties of MgAl2O4 [29,33,34], Mg0.55Al2.36O3.18N0.19, Mg0.27Al2.58O3.73N0.27 [4,10,13] and AlON [6,19,29].

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Refractive index (589.3 nm)</th>
<th>Abbé number</th>
<th>$\alpha_e (\AA^3)$</th>
<th>Vickers hardness (9.8 N) (GPa)</th>
<th>Young's moduli (GPa)</th>
<th>Shear Moduli (GPa)</th>
<th>Thermal expansion coefficient ($10^{-6}$ K$^{-1}$)</th>
<th>Specific heat (J$^\circ$K$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgAl2O4 [29,33,34]</td>
<td>1.7161</td>
<td>60.67</td>
<td>6.086</td>
<td>12.157</td>
<td>273</td>
<td>110</td>
<td>6.97</td>
<td>0.82</td>
</tr>
<tr>
<td>Mg0.55Al2.36O3.18N0.19</td>
<td>1.7240</td>
<td>80.48</td>
<td>6.255</td>
<td>13.48 ± 0.29</td>
<td>284</td>
<td>111</td>
<td>6.36</td>
<td>0.86</td>
</tr>
<tr>
<td>Mg0.27Al2.58O3.73N0.27</td>
<td>1.7499</td>
<td>73.66</td>
<td>6.288</td>
<td>15.1 ± 0.5</td>
<td>297</td>
<td>117</td>
<td>6.12</td>
<td>0.84</td>
</tr>
<tr>
<td>AlON [6,19,29]</td>
<td>1.7888</td>
<td>58.20</td>
<td>6.492</td>
<td>17.67 ± 1.13</td>
<td>321</td>
<td>127</td>
<td>6.66</td>
<td>0.83</td>
</tr>
</tbody>
</table>

\[ \mu = \frac{m_e m_f}{m_e + m_f} \]  

where $c$ is the velocity of light, $m_e$ and $m_f$ are the masses of the atoms corresponding to the vibration mode, and $F$ is the force constant. In present spinel crystals, the atomic masses of Mg and Al are similar, and the atomic masses of O and N are also similar. Hence, the force constant has a greater influence on the vibration frequency. The larger the $F^2$, the higher the corresponding lattice vibration frequency is, which results in enhanced phonon absorption.

In addition, the refractive index of samples was changed due to the difference in chemical composition. Table 2 lists the refractive indices at 589.3 nm ($n_D$) and Abbé numbers of MgAl2O4 [29], Mg0.55Al2.36O3.18N0.19, Mg0.27Al2.58O3.73N0.27 [13] and AlON [29] transparent ceramics (Supporting Information 3). The larger the Abbé number, the less changeable the refractive index becomes with increasing wavelength. Shannon et al. have pointed out that $n_D$ is related to the volume of unit cell ($V_m$) and the total molar electronic polarizability ($\alpha_e$) of a compound [30]:

\[ n_D = \sqrt[4]{\frac{4\pi \alpha_e}{2.26 - \alpha_e}} + 1 \]  

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. In general, the electronic polarizability of an anion is much larger than that of a cation, and the $\alpha_e (N^3-)$ is almost twice as large as $\alpha_e (O^{2-})$ [31,32]. Thus the increase of $N^3-$ ion leads to the $\alpha_e$ obviously improved as demonstrated in Table 2. Meanwhile, as the ratio of Al/Mg increases, the volume of unit cell decreases which means a tighter crystal structure. Then the refractive index of transparent ceramic eventually increases in the order $n_D$ of MgAl2O4 < $n_D$ of Mg0.55Al2.36O3.18N0.19 < $n_D$ of Mg0.27Al2.58O3.73N0.27 < $n_D$ of AlON.

Table 2 displays the mechanical and thermal properties of MgAl2O4 [33,34], Mg0.55Al2.36O3.18N0.19, Mg0.27Al2.58O3.73N0.27 [4,10] and AlON [6,19] transparent ceramics which also varied regularly with the chemical composition. This is because the properties of these compounds are largely determined by the nature of the chemical bonding, which are affected by composition and crystal structure. Further investigations of the relationship between composition, crystal structure and these properties are currently in progress.

In summary, based on the rational composition design, we have prepared a new Mg0.55Al2.36O3.18N0.19 transparent ceramic with high transmittance ($\sim 85.5%$ at 3.7 mm), and its absorption coefficient ($0.8\, \text{cm}^{-1}$ at 5 mm) is comparable to that of c-plane sapphire. The crystal structure of Mg0.55Al2.36O3.18N0.19 was obtained by the Rietveld method combined with the structure model of spinel-type solid solutions, and the influence of composition on crystal structure and chemical bond parameters was obtained. Besides, the effects of chemical composition and crystal structure on the optical properties of transparent ceramics such as the infrared cut-off and refractive index were investigated. The $F^2$ varying with the Al/Mg ratio in the tetrahedron largely determines the infrared transparent range of the transparent ceramic through the influence on the maximum longitudinal optical mode frequency. In addition, the change in the content of N$^3-$ ion has a great influence on the total molar electronic polarizability and refractive index of the compound. Therefore, the structure, optical behavior, mechanical and thermal properties of MgAlON can be conveniently adjusted by changing the composition. These results provide a promising strategy for designing new optical functional materials with good performance.

Declaration of Competing Interest
None.

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Supplementary materials

References


