

Exploring the Relationship between Crystalline Structure and Intrinsic Properties for MgGa_2O_4 Transparent Ceramic with the Bond Valence Method

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Abstract

In this work, a novel spinel MgGa_2O_4 transparent ceramic was firstly prepared by means of air-presintering combined with hot isostatic pressing sintering. In contrast to the nearly normal spinel MgAl_2O_4 , the MgGa_2O_4 was confirmed as the approximately inverse spinel with X-ray Rietveld refinement. Meanwhile, the polyhedral bond properties such as bond valence, bond length and bond force constant, which were obtained from the crystal structure parameters by means of the bond valence method, can aid understanding of the relationship between the crystal structure and properties. It was found that the MgGa_2O_4 with smaller anion position parameter (u) and larger lattice parameter (a) has the shorter tetrahedral bond and longer octahedral bond, compared with MgAl_2O_4 , since there is a larger cation inversion parameter (i) in MgGa_2O_4 . Furthermore, the tetrahedral bond in MgGa_2O_4 is much stronger than that in MgAl_2O_4 while the octahedral bond in MgGa_2O_4 is weaker than that in MgAl_2O_4 . From the bulk modulus, Vickers hardness to the thermal expansion coefficient, the influence of tetrahedral bonds on these properties is gradually decreased while the influence of octahedral bonds on them is progressively increased. Thus, MgGa_2O_4 has a slightly larger bulk modulus than MgAl_2O_4 . The hardness and thermal expansion coefficient of MgGa_2O_4 are lower and higher than that of MgAl_2O_4 , respectively.

Keywords: MgGa_2O_4 transparent ceramic, crystal structure, properties, bond valence method

I. Introduction

MgGa_2O_4 spinel has been intensively studied on account of its wide-ranging applications, such as a photoluminescence (PL) host for flat panel display^{1–4}, laser host for optical communication in the eye-safe wavelength region⁵, microwave circuits (MIC), substrate, passive component^{6,7}, barrier waveguide for integrated photonics⁸, light-emitting diodes, Schottky diodes, and high-temperature gas sensors, etc.⁹. With the increasing requirements for solid-state laser hosts⁵, scintillators such as radiation sensors, transparent displays in field emission mode³ and lamp envelopes especially for a strong radiation environment¹⁰, endowing MgGa_2O_4 spinel ceramic with optical transparency is also necessary.

In contrast to the mostly studied nearly normal spinel MgAl_2O_4 transparent ceramic, MgGa_2O_4 is believed to have a nearly inverse spinel crystal structure¹¹. Irrespective of the fourfold or sixfold coordination environment in MgGa_2O_4 , the cations are all arranged disorderly, with most of the trivalent cations being in a fourfold coordination environment while the sixfold coordination environment is shared by trivalent and covalent cations¹¹. As a result, the intrinsic difference in local crystal structure between MgAl_2O_4 and MgGa_2O_4 spinel raises the question

whether the relationship between the crystal structure and properties is the same or different in these two types of spinel. Fortunately, it has been demonstrated that transparent ceramic is a good sample for investigating the correlation between crystal structure and properties¹².

The bond valence method has been developed as an empirical research tool in recent years; it can be used for analyzing inorganic crystal structure and simulating the properties of both crystal and structural units such as the chemical bond, polyhedral properties and so on^{13–16}. Based on the contribution of elementary bonds to the properties of complex bonds at two polyhedra and evaluating the contribution of two polyhedra to the properties of crystal respectively, it is possible to obtain a deep insight into the relationship between the composition, crystal structure, and properties of spinel-type compounds^{16,17}. Compared with other empirical methods, the bond valence method has been proven to have the advantage of great authenticity, simplicity and broad applicability. And this method has been validated in spinel-type crystals with both complex chemical composition and two different coordination sites, like $\text{MgO} \cdot n\text{Al}_2\text{O}_3$, MgAlON and AlON spinel transparent ceramic^{13,14}. Consequently, it can be inferred that the bond valence method is also an efficient

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way to explore the relationship between the composition, crystal structure and properties of MgGa_2O_4 spinel.

Although there is no report on MgGa_2O_4 transparent ceramic, as far as we know, MgGa_2O_4 has the potential to be transparent owing to its spinel crystal structure and wide bandgap of 6.0 eV¹⁸. In this work, the novel spinel MgGa_2O_4 transparent ceramic was firstly prepared by means of air-presintering combined with hot isostatic pressing sintering. The crystal structure of MgGa_2O_4 was refined with the Rietveld method. Then, the bond valence method was employed to fundamentally understand the relationship between the crystal structure and properties such as bulk modulus, hardness, thermal expansion and so on. Based on comparison of the crystal structure-dependent properties between MgAl_2O_4 and MgGa_2O_4 spinel, a deep understanding of the distinctive features of MgGa_2O_4 spinel is possible.

II. Experimental Procedure

(1) Synthesis and characterization of the MgGa_2O_4 powder

The MgGa_2O_4 powder was synthesized based on the solid-state reaction of high-purity MgO (99.99 %, 200 nm) and $\beta\text{-Ga}_2\text{O}_3$ (99.99 %, 600 nm) powder with a molar ratio 1 : 1. Phase identification of the starting powders and bulk sample were conducted by means of X-ray diffractometry (XRD; Model X'pert PRO of Panalytical, Almelo, the Netherlands). The powder X-ray diffraction (PXRD) pattern for refinement was captured at room temperature with monochromatized $\text{CuK}\alpha$ radiation (1.540598 Å, 40 kV, 40 mA). The full measurement range of a 128-channel linear multistrip X'Celerator detector was applied to scan the range from 15° to 145° with a step size of 0.013° and counting time of 11.22 s for each step. The content of Mg and Ga in synthesized MgGa_2O_4 powder was determined by means of inductively coupled plasma-atomic emission spectroscopy (ICP-AES, Model Optima 4300DV; Perkin Elmer Instruments, Boston, MA). After verification of the phase and chemical composition, the structure refinement was performed with the Rietveld profile refinement method using the FULLPROF program based on the random cation arrangement spinel model¹¹. Specifically, Rietveld analysis was performed in the $Fd\bar{3}m$ (space group No. 227) in which Mg^{2+} and Ga^{3+} cations were both located on the sites 8a and 16d randomly, and O^{2-} anions were arranged on the sites 32e. The site occupancies were constrained to the chemical composition of MgGa_2O_4 determined by ICP-AES. Besides, the morphology of MgGa_2O_4 powder was characterized with SEM (Model S-3400; Hitachi, Tokyo, Japan). The particle size of the powder was measured with laser diffractometry (Model 2000; Mastersizer, Malvern, UK).

(2) Fabrication of MgGa_2O_4 spinel transparent ceramic

MgGa_2O_4 powder were compacted into 20-mm-diameter and 3-mm-thick disks with uniaxial pressure of 20 MPa and then cold-isostatic-pressed at 200 MPa for 5 min. The sample was pressureless-sintered at 1450 °C for 4 h under air atmosphere with a heating rate of 5 K/min. Then, the pre-sintered sample was hot-isostatic-pressed (HIP) at 1

575 °C under 180 MPa argon for 5 h with a heating rate of 10 K/min. The sample was annealed in air at 1100 °C for 6 h with a heating rate of 5 K/min. Finally, the HIPed sample was ground and mirror-polished with diamond polishing paste on both surfaces for characterization of the microstructure and properties.

(3) Microstructure and properties of MgGa_2O_4 spinel transparent ceramic

Density measurement of the sample was carried out in deionized water at 25 °C by means of the Archimedes method (GB/T 25995–2010, China). The relative density of sintered sample was calculated based on theoretical density of 5.326 g/cm³. After chemical etching, the microstructure of the mirror-polished surface of ceramic was characterized by means of SEM (Model S-3400; Hitachi, Tokyo, Japan). The grain size of ceramic was measured on representative SEM micrographs using the linear intercept method by counting more than 250 grains. And a coefficient of 1.56 was used as the multiplying factor to obtain the average grain size¹⁹.

In-line transmittance of the polished MgGa_2O_4 spinel transparent ceramic with 2.4 mm thickness was determined in the range of wavelength between 0.2 and 8 μm with spectrometers (Model UV-2550, Shimadzu, Kyoto, Japan for 0.2–1 μm; Model Nexus; Thermo Nicolet Corporation, Madison, WI for 1–8 μm). The Vickers hardness of the sample was measured with a hardness tester (Model 430SVD; Wolpert, Shanghai, China) at a load of 9.8 N for 15 s. The Young's modulus of the sample at 25 °C was measured with a vibration pulse excitation method using a Young's modulus tester (MK7, GrindoSonic, Belgium). The average for Vickers hardness and Young's modulus were both determined from eight valid data readings, respectively. Thermal diffusivity at 25 °C was measured with laser flash apparatus (Model TC-7000H/MELT; Ulvac-Riko, Yokohama, Japan). The thermal expansion coefficient of the sample was examined over the range of 20–800 °C with a dilatometer (DIL402C, Netzsch, Germany). The heat capacity of the MgGa_2O_4 spinel transparent ceramic was measured with an adiabatic vacuum calorimeter BKT-3 (Termis, Russia) at 25 °C.

III. Results and Discussions

(1) Morphology and crystal structure of MgGa_2O_4 powder

Synthesized powder with a narrow particle size distribution and low agglomeration was obtained, as shown in Fig. 1. The average size of 300 nm was observed, which is also confirmed from the particle size distribution curve measured by means of laser diffractometry.

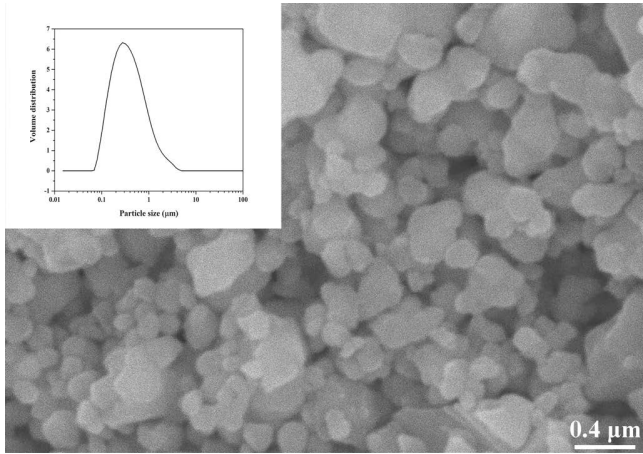


Fig. 1: SEM of the synthesized powders; the inset shows the particle size distribution curve of the powders.

As shown in the XRD patterns in Fig. 2, it is clear that the powder and sintered ceramic were all detected as a pure phase with spinel-type structure. The similar patterns of the ceramic and powder indicated that there was no visible preferred orientation in the sintered ceramic. As determined in the chemical composition analysis, the mole ratio of elements Mg: Ga is equal to 0.998: 1.999. It indicates that the chemical formula MgGa_2O_4 of the starting powder was obtained, which is close to the designed chemical composition in this work.

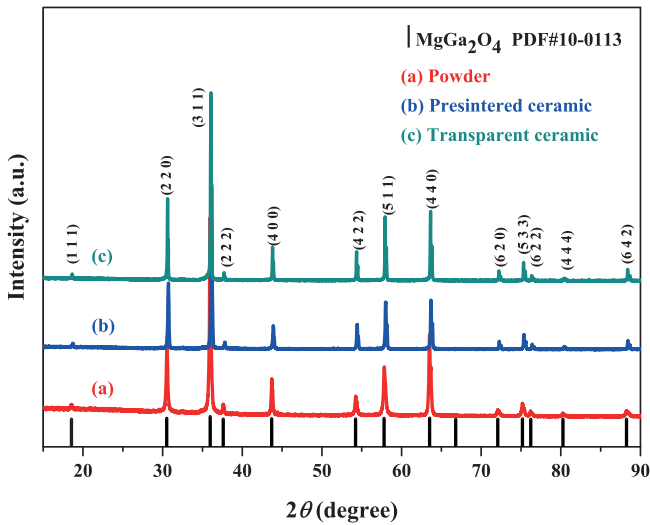


Fig. 2: XRD patterns of MgGa_2O_4 powder and transparent ceramic.

The crystal structure of MgGa_2O_4 was refined by means of the Rietveld method combined with the random cation arrangement structure model of the spinel-type solid solution. From the Rietveld analysis, as shown in Table 1 and Appendix Table A, the crystallographic parameters containing the cell parameter (a), anion position parameter (u) and inversion parameter (i) were obtained. In the last refined cycle, the calculated pattern fitted well to the experimental pattern, as shown in Fig. 3. The final R values are listed as follows: $R_p = 6.3\%$; $R_{wp} = 8.05\%$; $\chi^2 = 1.51$; $Gof = 1.2$. The calculated lattice parameter is $8.2813(3) \text{ \AA}$ and the theoretical density is 5.326 g/cm^3 , which are in good agreement with $8.280 \text{ \AA}$ and 5.328 g/cm^3 in MgGa_2O_4 (PDF#10-0113). It is further suggested that the synthe-

sized powders had high phase purity. Moreover, the inversion parameter (i) was 0.8382, which is consistent with previous investigations for MgGa_2O_4 ^{7, 20}. Furthermore, the crystal structure parameters of MgAl_2O_4 spinel are also shown in Table 1 for comparison. The crystal structure information for the MgAl_2O_4 spinel is from ICSD#97180. The differences between the nearly normal MgAl_2O_4 and the approximately inverse MgGa_2O_4 spinel can be understood on the basis of the polyhedral composition and crystal structure. On one hand, the cation inverse parameter (i) reflects the variance in polyhedral composition. As in the octahedron, the occupancy in MgGa_2O_4 for Mg^{2+} and Ga^{3+} ions is 41.9 % and 58.1 %, respectively, while the occupancy in MgAl_2O_4 for Mg^{2+} and Al^{3+} is 11.6 % and 88.4 % correspondingly. With regard to tetrahedron, similarly, the occupancy in MgGa_2O_4 for Mg^{2+} and Ga^{3+} ions is 16.2 % and 83.8 %, respectively, while the occupancy in MgAl_2O_4 for Mg^{2+} and Al^{3+} is 76.8 % and 23.2 % correspondingly. On the other hand, (a) mainly varies from cation radius to cation radius. Compared with the variance in (a), the difference in (u) is more crucial. The larger (u) in MgAl_2O_4 indicates that the tetrahedral bond length is relatively close to the octahedral one. On the contrary, the smaller (u) in MgGa_2O_4 suggests that the tetrahedral bond length deviates from the octahedral one. As a result, the tetrahedral bond length in MgGa_2O_4 is shorter than that in MgAl_2O_4 while the octahedral bond length in MgGa_2O_4 is longer than that in MgAl_2O_4 .

Table 1: Crystal structure and bond properties of MgGa_2O_4 and MgAl_2O_4 spinels.

Composition	MgGa_2O_4	$\text{MgAl}_2\text{O}_4^a$
a ($\text{\AA}$)	8.28131	8.08400
u	0.25394	0.26214
i	0.838	0.232
ρ (g/cm^3)	5.326	3.580
d_T ($\text{\AA}$)	1.8494	1.9202
d_M ($\text{\AA}$)	2.0382	1.9278
$S_{T(\text{M}^{2+}-\text{O})}$ (vu)	0.6551	0.5411
$S_{T(\text{M}^{3+}-\text{O})}$ (vu)	0.7240	0.4830
$S_{M(\text{M}^{2+}-\text{O})}$ (vu)	0.3933	0.5300
$S_{M(\text{M}^{3+}-\text{O})}$ (vu)	0.4347	0.4731
S_T (vu)	0.7129	0.5276
S_M (vu)	0.4173	0.4797
F_c^T (N m^{-1})	285.7	172.9
F_c^M (N m^{-1})	111.9	149.1

^aThe crystal structure information of MgAl_2O_4 spinel for calculation from ICSD#97180. M = Mg, Al or Ga.

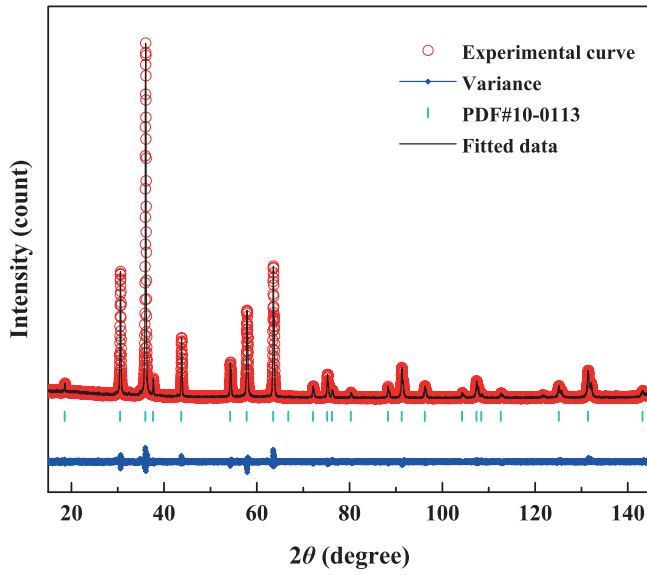


Fig. 3: Measured (circle), calculated (line), and differential (bottom line) XRD patterns of MgGa_2O_4 powders.

After the crystal structure parameters have been obtained, the bond valence method can be used for calculation of the properties. In the bond valence method, the bond valence between atom i and atom j is described by Eq. (1) ¹⁵.

$$S_{ij} = \exp\left(\frac{d_0 - d_{ij}}{b}\right) \quad (1)$$

where S_{ij} is the bond valence, d_{ij} is the bond length between atom i and atom j , d_0 and b are fitted bond valence parameters. d_0 represents the nominal length of a bond of unit valence and depends on the size of atoms forming the chemical bond. The value of d_0 is 1.693 Å, 1.730 Å and 1.651 Å for Mg–O, Ga–O and Al–O bond in spinel correspondingly ²¹. b is a constant equal to 0.37 Å. The composition-weighted average of bond valences could be calculated as follows ¹³:

$$S_{AVE} = \sum_i [X_i \sum_j (Y_j S_{ij})] \quad (2)$$

where S_{AVE} is the composition-weighted average of bond valence, X_i and Y_j are the fraction of one type of cation and anion in coordinated polyhedra, respectively. The elemental bond valences for MgGa_2O_4 and MgAl_2O_4 are shown in Table 1. According to Eq. (1), the differences in the elemental bond valence in two spinels are attributed to various bond length and bond species. As indicated in Eq. (2), the polyhedral bond valence is the composition-weighted average of elemental bond valences. Considering the dissimilarity of polyhedral composition in the two spinels, the tetrahedral bond valence in MgGa_2O_4 is much higher than that in MgAl_2O_4 while the octahedral bond valence in MgGa_2O_4 is lower than that in MgAl_2O_4 . The tetrahedral bond valence is slightly higher than the octahedral bond valence in MgAl_2O_4 .

The bond force constant is given by Eq. (3) ¹³, which has a positive correlation with the bond valence and a negative correlation with the bond lengths,

$$F_c = \frac{\beta \left(\frac{8S_{ij}}{3}\right)^{\frac{3}{2}} \left(\frac{1}{b} - \frac{2}{d_{ij}}\right)}{d_{ij}^2} \quad (3)$$

where $\beta = 23 \text{ nN } \text{\AA}^2 \text{ electrons}^{-2}$ and the d_{ij} and b are as mentioned above. Analogously, the tetrahedral bond force constant in MgGa_2O_4 is much higher than that in MgAl_2O_4 while the octahedral bond force constant in MgGa_2O_4 is lower than that in MgAl_2O_4 , which can be seen in Table 1. The consequence results from the variations in bond valence and bond length for the two spinels, as stated above.

The results also confirm that the difference in polyhedral composition and crystal structure between the two spinels has a fundamental influence on the bond properties. The tetrahedral bond in MgGa_2O_4 is much stronger than that in MgAl_2O_4 while the octahedral bond in MgGa_2O_4 is weaker than that in MgAl_2O_4 . And the tetrahedral bond for MgAl_2O_4 is slightly stronger than the octahedral bond.

(2) Microstructure of MgGa_2O_4 ceramic

Fig. 4(a) shows the microstructure of the sample sintered in air at 1450 °C. Obviously, the pores are closed. Meanwhile, with the Archimedes approach, 0 % open porosity and 99.24 ± 0.13 % relative density were determined, which was appropriate for the subsequent hot isostatic pressing sintering. As seen in Fig. 4(b), the average grain size was $4.72 \pm 0.9 \mu\text{m}$.

Fig. 5(a) shows the microstructure of MgGa_2O_4 spinel transparent ceramic. Clearly, tiny residual pores can be observed in the red circle, which indicate the high densification of specimen. Besides, the measured value of density (5.320 g/cm^3) within the experimental error of the Archimedes method agreed well with the theoretical density (5.326 g/cm^3). As shown in Fig. 5(b), the average grain size was $28.42 \pm 1.8 \mu\text{m}$.

The transmittance spectra of MgGa_2O_4 ceramic with 2.4 mm thickness is shown in Fig. 6. The in-line transmittance of the sample was ~ 50 % in the visible region and higher than 75 % in the infrared region. The ultraviolet cut-on wavelength was about 272 nm, which is nearly equal to 265 nm for single crystal ⁸. The infrared cut-off wavelength was about $7.4 \mu\text{m}$. The low transmittance was mainly attributed to the residual nano-pores, as shown in Fig. 5(a). The red circle represents them. These pores within the grains and grain boundaries acted as light scattering centers in transparent ceramics, resulting in the decrease in transmittance ²². In addition, a weak absorption peak around $3.0 \mu\text{m}$ may be attributed to the OH absorption produced by the water physically adsorbed by the ceramic in air during the test process ²³. The relatively strong absorption peak around $4.4 \mu\text{m}$ can be attributed to the CO_2 asymmetry stretching vibration ²⁴. In a comparison with the infrared cut-off wavelength between MgGa_2O_4 and MgAl_2O_4 spinel transparent ceramics, it is clear that the $7.4 \mu\text{m}$ of MgGa_2O_4 is longer than the $6.7 \mu\text{m}$ of MgAl_2O_4 ²⁵.

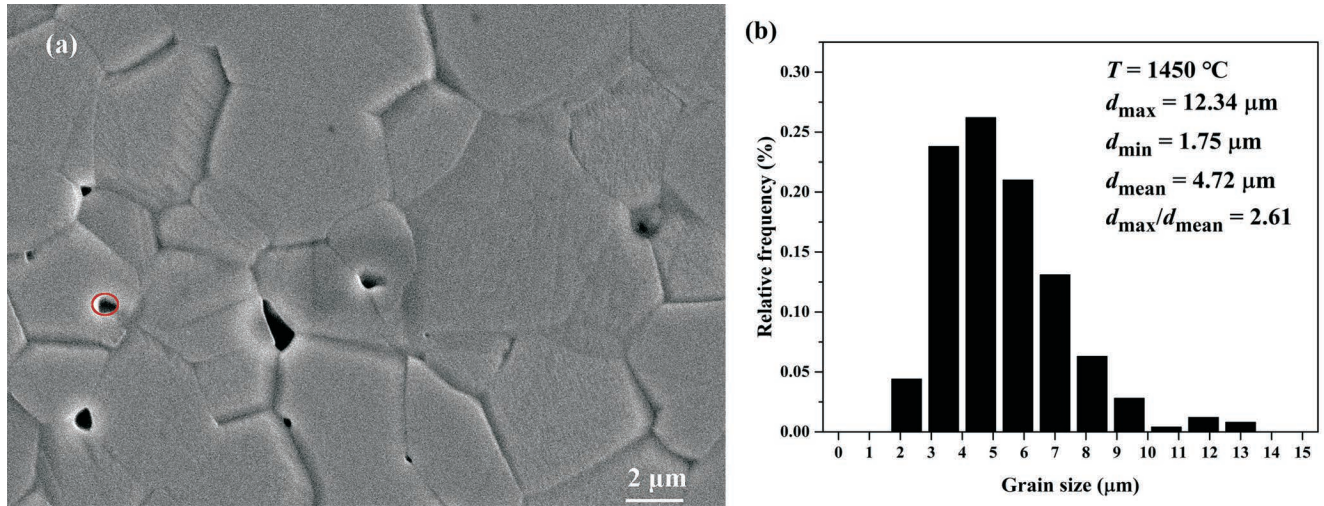


Fig. 4: (a) The microstructure of presintered MgGa_2O_4 spinel ceramic. (b) The grain size distribution of presintered MgGa_2O_4 spinel ceramic. (The red circle represents an intragrain pore).

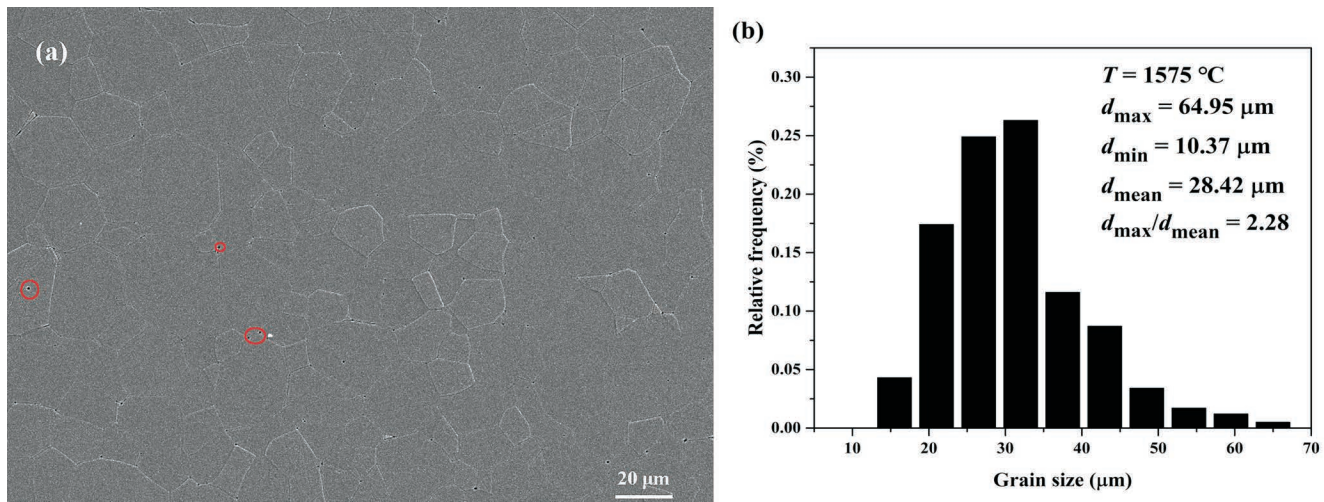


Fig. 5: (a) The microstructure of HIPed MgGa_2O_4 spinel ceramic. (b) The grain size distribution of HIPed MgGa_2O_4 spinel ceramic. (The red circle represents an intragrain pore).

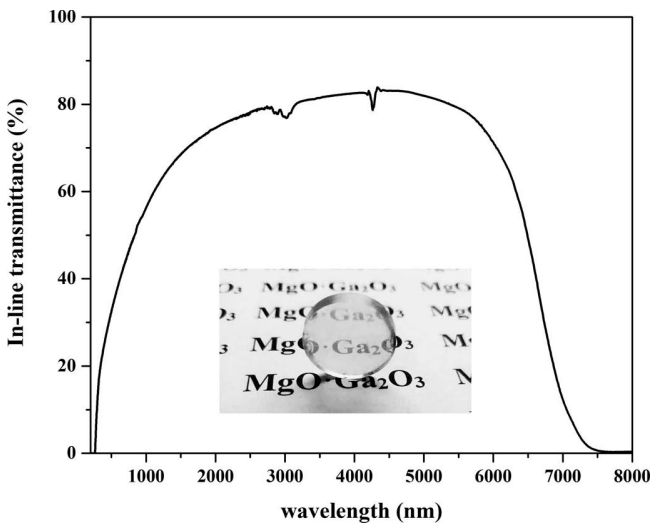


Fig. 6: The in-line transmittance of MgGa_2O_4 spinel transparent ceramic.

(3) Properties of MgGa_2O_4 spinel transparent ceramic

The properties of MgGa_2O_4 and MgAl_2O_4 spinel transparent ceramics are also shown in Table 2, which includes the mechanical and thermal properties. Clearly, there is a difference in properties between MgGa_2O_4 and MgAl_2O_4 spinel transparent ceramics. For example, the Vickers hardness of MgGa_2O_4 is lower than that of MgAl_2O_4 ; the bulk modulus of MgGa_2O_4 is slightly higher than that of MgAl_2O_4 ; the thermal expansion coefficient of MgGa_2O_4 is higher than that of MgAl_2O_4 and so on. Consequently, the bond valence method was employed to understand the relationship between the properties and crystal structure in MgGa_2O_4 and MgAl_2O_4 spinels. At the same time, the mechanical and thermal properties calculated with the bond valence method are also presented in Table 2, which are in accordance with experimental values^{13, 26–35}.

The bulk modulus of polyhedra in spinel could be calculated with Eq. (4) and (5)¹³:

$$B_T = p \frac{F_c^T}{3g_l d_T} \quad (4)$$

$$B_M = p \frac{F_c^M}{3g_2 d_M} \quad (5)$$

where B_T , B_M are the bulk modulus of tetrahedra and octahedra, respectively. F_c^T and F_c^M are the bond force constants in tetrahedrally and octahedrally coordinated polyhedra, respectively. d_T and d_M are the bond lengths in tetrahedra and octahedra. g_1 and g_2 are geometric factors with the values 2.31 and 1, respectively. p and q are the total cation fractions in the tetrahedral and octahedral sites, respectively.

Clearly, the ratio of the F_c to d at polyhedra mainly determines the B_T and B_M . It has been clarified that the differences in F_c and d between MgGa_2O_4 and MgAl_2O_4 originate from their different crystal structure and polyhedral composition. Thus, considering the variance in g between the two coordination environments, the B_T is higher than B_M in MgGa_2O_4 while the B_T is lower than B_M in MgAl_2O_4 . The discrepancy for MgGa_2O_4 between B_T and B_M is less than that for MgAl_2O_4 .

The bulk modulus of spinel-type crystals could be calculated with the average of B_T and B_M :¹³

$$B = \frac{B_T + B_M}{2} \quad (6)$$

To quantify the contribution of the polyhedral bulk modulus to the bulk modulus of the crystal, the contribution ratio of bulk modulus was deduced:

$$C_B^\mu = \frac{1}{2} \frac{B_\mu}{B} \quad (7)$$

where μ is T or M , C_B^μ is the contribution ratio of bulk modulus of μ -type polyhedra, B_μ is the bulk modulus for the μ -type polyhedra. The calculated results based on Eq. (6) and (7) are shown in Table 2, which verifies that B_T is the major contributor to B in MgGa_2O_4 with 54.9 % while the main contributor to B is the B_M in MgAl_2O_4 with 66.5 %.

As far as the hardness is concerned, the hardness H^μ of μ -type chemical bond is determined with the chemical bond density N_v^μ , bond length $d_{ij,\mu}$ and bond valence $S_{ij,\mu}$:¹⁴

$$H^\mu = 680.3 \left(\frac{LS_{ij,\mu}^V}{d_{ij,\mu}^3} \right)^{\frac{2}{3}} N_v^\mu \quad (8)$$

where L and V for the Mg-O and Al-O bond are the fitted constants equal to 0.54 and 1.64, respectively. And, L and V for Ga-O bond are the fitted constants equal to 0.49 and 1.57, respectively, which depend on the number of electrons in the core of the cation³⁶. The divergences in bond composition, bond valence and bond length for MgGa_2O_4 and MgAl_2O_4 between the tetrahedron and octahedron have been stated in Section III. (1). Furthermore, the N_v^T for MgGa_2O_4 is higher than that for MgAl_2O_4 while N_v^M for MgGa_2O_4 is lower than that for MgAl_2O_4 . Consequently, the H_T in MgGa_2O_4 is much higher than that in MgAl_2O_4 , albeit the (a) for MgGa_2O_4 is larger than that for MgAl_2O_4 .

For a complex crystal, the hardness could be simulated by weighing the geometric average hardness of all bonds contained in the crystal. For a multicomponent compound system with n types of binary systems, its hardness can be calculated as¹⁴

$$H = \left(\prod_{\mu=1}^n H_\mu \right)^{1/n} \quad (9)$$

To quantify the contribution of the chemical bonds to the hardness of the crystal, the contribution ratio to the hardness of crystal was deduced³⁷:

$$C_H^\mu = \frac{n^\mu}{\sum n^\mu} \log_H(H_\mu) \quad (10)$$

where C_H^μ is the contribution ratio of the hardness of μ -type bonds, n^μ is the number of μ -type bonds, and H and H_μ are the hardness of crystal and μ -type bonds, respectively. From Eq. (9) and (10), we can learn that H_M , in contrast with H_T , is the major contributor to H , since the number of bonds in the octahedron is three times as many as that in the tetrahedron. As shown in Table 2, the H_M in MgGa_2O_4 is lower than that in MgAl_2O_4 and the C_H^M for MgAl_2O_4 and MgGa_2O_4 are 74.1 % and 66.9 %, respectively. Therefore, H of MgAl_2O_4 is higher than that of MgGa_2O_4 , despite the fact that H_T in MgGa_2O_4 is much higher than that in MgAl_2O_4 .

When it comes to the thermal expansion coefficient, the thermal expansion coefficient of spinel-type compounds could be calculated as follows with Eq. (11) and (12)¹³:

$$\alpha_v = \frac{1.35k_B}{F_c d_{ij}} \quad (11)$$

$$\alpha_{cal} = q \alpha_v^M \quad (12)$$

where k_B is the Boltzmann constant. α_v is the thermal expansion coefficient of the chemical bond. α_v^M is the thermal expansion coefficient of the chemical bonds at octahedral sites. According to Eq. (11) and (12), the α_v^M , which has a negative correlation with the product of d and F_c , determines the α_v of a spinel-type crystal. The discrepancy in d_M between MgGa_2O_4 and MgAl_2O_4 is too small to compensate for the difference in F_c^M . Thus, the difference in F_c^M between the two spinels mainly controls the α_v of spinel. As a result, MgGa_2O_4 has a higher α_v than MgAl_2O_4 .

In addition, Table 2 also shows some mechanical and thermal properties of MgGa_2O_4 and MgAl_2O_4 spinel transparent ceramics, which varied with composition-related structure. For instance, the Debye temperature and thermal conductivity of MgGa_2O_4 spinel are lower than that of MgAl_2O_4 spinel. This is because these properties are basically determined by polyhedral complex bond properties, which are affected by the polyhedral composition and crystal structure. Further investigations of the relationship between the crystal structure and the properties in MgGa_2O_4 nearly inverse spinel and MgAl_2O_4 nearly normal spinel are currently in progress.

Table 2: Mechanical and thermal properties calculated with the bond valence method and experimental values for MgGa_2O_4 and MgAl_2O_4 transparent ceramic.

Composition	$\text{MgGa}_2\text{O}_4(\text{cal})$	$\text{MgGa}_2\text{O}_4(\text{exp})$	$\text{MgAl}_2\text{O}_4(\text{cal})$	$\text{MgAl}_2\text{O}_4(\text{exp})$
$B_T(\text{GPa})$	222.9		129.9	
$B_M(\text{GPa})$	183.0		257.8	
$B(\text{GPa})$	202.9	200.3	193.9	195.8 ^a
C_B^T	0.549		0.335	
C_B^M	0.451		0.665	
$H_T(\text{GPa})$	24.7		14.8	
$H_M(\text{GPa})$	8.7		13.1	
$H(\text{GPa})$	11.3	11.6	13.5	12–15 ^b
C_H^T	0.331		0.259	
C_H^M	0.669		0.741	
$\alpha_v(10^{-6} \text{ K}^{-1})$	8.16	8.15	6.48	6.97 ^c
$G(\text{GPa})$	100.6 ^h	97.7	110.1 ^h	109 ^d
ν	0.28 ⁱ	0.29	0.26 ⁱ	0.26 ^a
$\theta_D(\text{K})$	721.1 ^j	750.0	917.9 ^j	850.0 ^d
$C_v(\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})$	132.3	128.7	113.4	115.1 ^e
γ	1.65 ⁱ		1.55 ⁱ	1.41 ^f
$\kappa(\text{W}\cdot(\text{m}\cdot\text{K})^{-1})$	11.38 ^k	11.68	15.71 ^k	14.60 ^g

^aBulk modulus and Poisson ratio from ref 26. ^bVicker hardness from ref 27. ^cThermal expansion coefficient from ref 13. ^dShear modulus and Deby temperature from ref 28. ^eThermal capacity from ref 29. ^fGruneisen parameter from ref 30. ^gThermal conductivity from ref 31. ^hShear modulus calculation formula from ref 32. ⁱPoisson ratio and Gruneisen parameter calculation formulas from ref 33 and 34. ^jDeby temperature calculation formulas from ref 33. ^kThermal conductivity calculation formula from ref 35. The cal and exp are the calculated values and experimental values, respectively.

IV. Conclusions

In this work, a novel MgGa_2O_4 transparent ceramic was firstly fabricated by means of pressureless sintering combined with hot isostatic pressing sintering. X-ray Rietveld refinement for MgGa_2O_4 powders confirmed the approximately inverse disorder spinel structure. Then, bond valence models based on crystal structure refinement were employed to understand the relationship between the crystal structure and properties. In a comparison of the crystal structure and properties of MgAl_2O_4 and spinels, it was found that the MgGa_2O_4 with smaller anion position parameter (u) and larger lattice parameter (a) has the shorter tetrahedral bond length and longer octahedral bond length. Besides, the much larger cation inversion parameter (i) in MgGa_2O_4 represents a much higher weight of the tetrahedral Ga–O bond valence on the tetrahedral

bond valence and lower weight of the octahedral Ga–O bond valence on the octahedral bond valence. Naturally, the tetrahedral bond in MgGa_2O_4 is much stronger than that in MgAl_2O_4 while the octahedral bond in MgGa_2O_4 is weaker than that in MgAl_2O_4 . As for MgAl_2O_4 , the tetrahedral bond is slightly stronger than the octahedral bond. Furthermore, the influence of tetrahedral bonds on the properties of bulk modulus, Vickers hardness and thermal expansion coefficient is gradually decreased while the influence of the octahedral bonds on them is progressively increased. And, the tetrahedral bond makes a greater contribution to the bulk modulus and hardness in MgGa_2O_4 than that in MgAl_2O_4 spinel. The new understanding does not only pave a way to an insight into the relationship between the crystal structure and properties of AB_2O_4 2–3 spinel, it also provides guidance for the design of new spinel-type compounds with desirable properties.

Appendix:

Table A: Crystallographic data and atomic position of MgGa_2O_4

Formula	MgGa ₂ O ₄					
Space group	<i>Fd</i> $\bar{3}m$					
Radiation	CuK α , λ = 1.5406 Å					
Lattice parameter, a (Å)	8.2813(3)					
Z	8					
Density, ρ_{cal} (g/cm ³)	5.3260					
Profile range (deg)	15.072 $\leq 2\theta \leq$ 139.994					
Step size (deg)	0.0131					
Profile function	Pseudo-Voigt					
Number of varied parameters	17					
Reliability factors	R_{wp} = 8.05 %, R_{p} = 6.3 %, χ^2 = 1.51, Gof = 1.2					
Atomic positions						
Atom	Wyckoff position	x	y	z	B _{iso} ^a (Å ²)	Occupancy
Mg	8a	0.1250(0)	0.1250(0)	0.1250(0)	0.538(0)	0.1618
Ga	8a	0.1250(0)	0.1250(0)	0.1250(0)	0.538(0)	0.8382
Mg	16d	0.5000(0)	0.5000(0)	0.5000(0)	0.576(7)	0.4191
Ga	16d	0.5000(0)	0.5000(0)	0.5000(0)	0.576(7)	0.5809
O	32e	0.2539(4)	0.2539(4)	0.2539(4)	0.213(5)	1.0000

a is the isotropic temperature factor.

Inversion parameter *i* = 0.8382

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