Gallium triggered crystallization of spinel glass-ceramic and enhancement in colorization and luminescence

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Abstract
Spinel glass–ceramic is an important class of composites with promising applications in transparent antiriot shields, tunable lasers and broadband optical amplifiers. Although the crystallization process of spinel has been well studied, the approach for tuning it and the optical response of the resultant glass–ceramic still need urgent attention. Here, we posit that the addition of Ga2O3 can significantly improve the crystallization tendency of the spinel phase and greatly change the optical response of the glass–ceramic. On one hand, the colourization of glass–ceramic can be tuned, and an unusual blue colour can be achieved. On the other hand, the luminescence can be notably enhanced, and the resultant spinel glass–ceramic exhibits intense green–yellow luminescence. The present findings about the Ga2O3–mediated structure modification and optical response tuning can provide an effective avenue for the functionalization of spinel glass–ceramic and may be general for various types of material candidates.

1. Introduction
Glass–ceramic materials are the composites with the crystalline phase homogeneously distributed inside the glass phase [1–11]. Attractively, they could combine the easy fabrication advantage of glass and the robust performance of crystal materials. Furthermore, enhanced functionalities can also be achieved via rational control of the glass and crystal combinations [2, 11]. As a typical example, spinel glass–ceramic materials have been widely used in transparent antiriot shield because of their high thermal, mechanical and chemical stability [12]. In addition, they also show great promise as the gain matrix in tunable lasers and broadband optical amplifiers [9]. Studies conducted in the past decades have revealed the crystallization thermodynamics, dynamics and atomic mechanism of the spinel crystalline phase from the glass. In these studies, classic nucleation agents, such as TiO2 and ZrO2, were generally utilized and they have been confirmed to play important roles in changing the crystallization habit of the spinel phase [13, 14]. By contrast, only a few studies examined the effect of glass network intermediates on the crystallization of spinel from the glass phase. Ga2O3, which is a typical glass network intermediate, usually appears in the composition of glass–ceramics. Several researchers have found that Ga2O3 could potentially precipitate from the glass and endow the samples with improved optical performance [7, 9].

In this work, we study the effect of Ga2O3 on the crystallization habit of the spinel phase from the glass. Research has shown that the addition of Ga2O3 can greatly improve the crystallization tendency of the spinel phase and considerably change the optical properties of the resultant glass–ceramic. On one hand, the unusual colorization can be realized, and a blue colour can be achieved. On the other hand, the luminescence can be greatly enhanced, and the glass–ceramic can exhibit intense green–yellow luminescence.

2. Experimental procedures

2.1. Methods and synthesis
A glass system (MgO–Al2O3–SiO2–TiO2) containing Ga2O3 with various mole ratios of 2.5, 5, 7.5 and 10 was fabricated through the classic melting–quenching method. In a typical synthesis process, the raw materials of
MgO, Al₂O₃, SiO₂, TiO₂ and Ga₂O₃ with high purity (99.99%) were homogeneously mixed and melted in a Pt–Rh crucible at 1600 °C for 2 h. The melt was quenched on a preheated copper plate and pressed using another copper plate. The fabricated glass samples were annealed at 700 °C for 12 h to remove the thermal stress. In accordance with the thermal analysis results, the samples were heat-treated at various temperatures around the crystallization temperatures to obtain glass–ceramic samples. The obtained samples were then cut and polished to a thickness of 2 mm for further optical characterizations.

2.2. Characterizations

The thermal properties were analyzed through differential scanning calorimetry (DSC), which was performed under air atmosphere at a heating rate of 10° min⁻¹ on a STA449C Jupiter (Netzsch, Bavaria, Germany). The phase of the samples was identified via x-ray diffraction (XRD) measurement, which was performed using a PANalytical x-ray diffractometer (Almelo, Netherlands) with Cu Kα radiation (40 mA, λ = 1.54 Å). The scanning speed was 1.2° min⁻¹, and the 2θ range was 5° ∼ 90°. The microstructures of the samples were characterized by the transmission electron microscopy (TEM), which was performed on an FEI Tecnai G2F20. The sample was prepared by grinding the glass–ceramic and homogeneously dispersing the powder in acetone. Then, the Cu grid covered with carbon film was carefully dipped into the solution and dried for several minutes for measurement. The absorption spectra were measured with a Lambda 900 UV/VIS/NIR spectrometer. The excitation and luminescence spectra were characterized using the Edinburgh Instruments FLS980 spectrometer.

3. Results and discussion

The thermal properties of the glass samples were characterized through DSC and the results are shown in figure 1. The glass transition temperature appeared at ∼750 °C. Broad and weak exothermic bands were found in the region of 780 °C–850 °C and were associated with the nanocrystallization of the spinel phase. In addition, the intense exothermic bands were observed in the region of 850 °C–950 °C, which may have originated from the bulk crystallization of the glass phase. Notably, the addition of Ga₂O₃ decreased the peak location of the exothermic bands, indicating that it is favorable for the crystallization of the glass phase.

Figure 1. DSC curves of the glass samples with various Ga contents of 2.5, 5, 7.5 and 10 mol%.

The phase of the as-made glass samples was characterized by XRD and the results are presented in figure 2(a). Only two broadband halos at ∼25° and 68° were observed, indicating the amorphous nature of the samples. Figure 2(b) shows the XRD patterns of the glass–ceramic samples heat-treated at 800 °C for 2 h. Several diffraction peaks were observed at 31.2, 36.4, 44.4, 59.1, and 65.3° for the glass–ceramic containing Ga₂O₃ with the mole ratios of 5, 7.5 and 10. These peaks can be indexed to the characteristic diffraction peaks of (220), (311), (400), (511) and (440) planes of spinel MgAl₂O₄. Notably, the diffraction intensity gradually increased with the
enhancement of Ga$_2$O$_3$ content. The average size of the precipitated nanocrystals was estimated based on the Debye–Scherrer relation as follows:

\[ D = \frac{K\lambda}{\beta \cos \theta} \]

where \( D \) is the crystallite size, \( K \) is the Scherrer constant, \( \lambda \) is the wavelength of the x-ray, \( \beta \) is the full half-height width of the characteristic peak and \( \theta \) is the diffraction angle. The crystallite size was calculated to be \( \sim 5 \text{ nm} \). By contrast, no obvious characteristic peaks were observed in the sample without Ga$_2$O$_3$. These results demonstrate that the crystallization of the spinel phase was promoted by the addition of Ga$_2$O$_3$. Notably, the XRD peak exhibited a slight blue-shift compared with the pure spinel MgAl$_2$O$_4$, implying the incorporation of Ga inside the crystalline phase. Thus, we assume that the physical mechanism of Ga$_2$O$_3$-triggered crystallization may be associated with the Ga ion-induced local clustering in glass, which may act as the nucleating center for the spinel phase.

The chemical bonding features of the glass and glass–ceramic samples were characterized by using the Raman scattering spectra. Figure 3(a) presents the Raman scattering spectra of the as-made glass samples. The incorporation of Ga$_2$O$_3$ did not obviously change the Raman characteristic bands of the glass samples. The characteristic bands at 480 and 918 cm$^{-1}$ were assigned to the bending vibration of Si–O–Si bonds and the symmetric stretching vibration of the SiO$_4$ tetrahedra, respectively [15]. Figure 3(b) shows the Raman scattering spectra of the glass–ceramic samples. The characteristic bands of the samples without Ga were similar to those of the as-made glass samples. This result indicates that no obvious crystallization occurred after heat-treatment. By contrast, with the incorporation of Ga and an increase in its content, the strong bands at 430 and 805 cm$^{-1}$ dominated the Raman scattering spectra; these bands were ascribed to the vibration of AlO$_4$ groups in spinel MgAlO$_4$ [16]. The Raman scattering characterization further demonstrated that the addition of Ga$_2$O$_3$ was favorable for the precipitation of spinel MgAlO$_4$, a result that is consistent with the XRD results.

The microstructures of the typical glass–ceramic samples were characterized and are presented in Figure 4. Figure 4(a) shows the low-resolution TEM image of the glass–ceramic sample with a Ga content of 10 mol%. The dense nanocrystals were homogeneously distributed. The average size of the nanocrystals was estimated to be 5 nm, which is close to the value estimated based on the XRD pattern. Figure 4(b) presents a typical high-resolution TEM image and figure 4(c) shows a TEM image of a single particle. The crystalline lattice can be clearly observed in the image despite the relatively small size of the particle, indicating the high crystallinity of the
precipitated nanocrystals. The lattice spacing of the particle in figure 3(c) is ∼0.202 nm, which is consistent with the (400) plane of the spinel MgAl2O4.

The addition of Ga2O3 can greatly change the optical properties of samples. Figure 5 shows photos of the glass and glass–ceramic samples. All of the glass and glass–ceramic samples were highly transparent. Impressively, in the glass–ceramic samples, the addition of Ga2O3 induced blue colorization and the colour deepened with the increase in Ga2O3 content. By contrast, only slight colorization was observed in the as-made glass samples. This finding indicates that the addition of Ga2O3 and nanocrystallization collaboratively contributed to the colorization of the samples. The absorption features of the glass and glass–ceramic samples were measured to investigate the physical mechanism behind the colorization phenomenon, and the results are presented in figure 6. All of the glass samples had a similar ultraviolet absorption feature with the absorption band edge at ∼330 nm (figure 6(a)). Additionally, another broad band with the central wavelength at ∼500 nm was observed, and it was ascribed to the characteristic
absorption of the Ti$^{3+}$ center [17–19]. Notably, the absorption intensity of this broad band gradually increased with the enhancement of Ga content possibly because of the transformation of Ti$^{4+}$ into the Ti$^{3+}$ center induced by the addition of Ga. A completely different absorption feature was observed in the glass–ceramic samples. As shown in figure 6(b), the samples without and with a small content of Ga exhibited a similar absorption feature as that of the as-made glass samples. For the glass–ceramic samples with a Ga content of 5, 7.5 and 10 mol%, the strong absorption with the central wavelength at the near-infrared waveband region ($\sim$750 nm) was observed. With the increase in the Ga content, the absorption intensity sharply increased, but the central wavelength did not exhibit obvious changes. This unusual infrared absorption is believed to contribute to the blue colorization phenomenon in figure 5. The physical origin of this absorption band might be associated with the pairs of Ti$^{3+}$–Ti$^{4+}$ [18]. During the precipitation of the spinel phase, Ti$^{3+}$ and Ti$^{4+}$ centers can be selectively incorporated into the nanocrystals because of the suitable position of these centers. As a result, Ti$^{3+}$ and Ti$^{4+}$ can be enriched in the spinel phase, and their separation distance can decrease, leading to a notable enhancement in their interaction and increased absorption.

Furthermore, the addition of Ga$_2$O$_3$ and nanocrystallization can also change the luminescence properties of samples. Under excitation by ultra-violet light, all of the glass samples exhibited weak green luminescence (figure 7(a)). Notably, the addition of Ga$_2$O$_3$ and nanocrystallization can obviously increase the luminescence brightness (figure 7(b)). The luminescence spectra of the samples were characterized and are presented in figure 8. Figure 8(a) shows the excitation and luminescence spectra of the glass samples. The luminescence spectra had a broad band with the central wavelength at $\sim$550 nm. This band can be ascribed to the $^2B_{1g} \rightarrow ^2B_{2g}$ transition of the Ti$^{3+}$ center [20]. The slight enhancement in the luminescence intensity due to the addition of

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Figure 5. Photos of the glass (a) and glass–ceramic (b) samples showing the colorization phenomenon.

Figure 6. (a) Absorption spectra of the glass samples without and with various Ga contents of 2.5, 5, 7.5 and 10 mol%. (b) Absorption spectra of the glass–ceramic samples without and with various Ga contents of 2.5, 5, 7.5 and 10 mol%.
Ga$_2$O$_3$ might be associated with the transformation of Ti$^{4+}$ to Ti$^{3+}$ active centers. Figure 8(b) shows the excitation and luminescence spectra of the glass–ceramic samples. Compared with the luminescence of glass samples, that of the glass–ceramic samples presented two notable changes. Firstly, the emission bands exhibited a blue shift after nanocrystallization. Secondly, the emission of the glass–ceramics showed a fourfold increase in the intensity. Ti$^{3+}$ ion is a typical transition metal dopant with a 3d$^1$ configuration. The prominent feature of this type of dopant is that its energy level configuration is extremely sensitive to the local structure of the host [21, 22]. According to the Tanabe–Sugano theory for transition metal dopant, an increase in the local crystal field strength may lead to an enhancement of the transition energy between the ground and excited states [23]. Notably, the precipitation of the spinel crystalline phase can induce the local atomic ordering inside the glassy phase and is thus favorable for the increase in crystal field strength around the dopant. As a result, the luminescence of Ti$^{3+}$ ion exhibits a blue shift after nanocrystallization. Furthermore, according to the Mott and Gurney model, the relaxation of the excited state depends on the activation energy [24]. The larger the activation energy is, the higher the radiation transition probability is. Moreover, an increase in the crystal field strength around the dopant may lead to increased activation energy of electron transition, resulting in an enhancement in

Figure 7. (a) Luminescent photos of the glass samples without and with various Ga contents of 2.5, 5, 7.5 and 10 mol%.
(b) Luminescent photos of the glass samples without and with various Ga contents of 2.5, 5, 7.5 and 10 mol%. The excitation source is 254 nm ultra-violet light.

Figure 8. (a) Excitation and luminescence spectra of the glass samples without and with various Ga content of 2.5, 5, 7.5 and 10 mol%.
(b) Excitation and luminescence spectra of the glass–ceramic samples without and with various Ga contents of 2.5, 5, 7.5 and 10 mol%.
luminescence. Additionally, the precipitated spinel crystalline phase can provide an environment with relatively low phonon energy, which is also favorable for the efficient radiation transition.

4. Conclusions

In summary, we have found that the addition of Ga₂O₃ can greatly improve the crystallization tendency of the spinel phase in glass–ceramic. This approach enables to tune the colorization phenomenon and achieve an unusual blue colour. Furthermore, the approach also enhances the luminescence of glass–ceramic. These researches not only serve practical purpose for construction of novel optical glass–ceramic with controllable color and luminescence, but also provide valuable references for the exploration of microstructure–optical response relation in nanostructured glass.

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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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