Intense green luminescence in Mn-doped gallogermanate nanostructured glass

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Abstract
Mn-activated optical materials have been demonstrated to be promising for various applications such as light-emitting device, tunable lasers and smart sensors. Most of the candidates belong to the single crystals and crystalline powders, and few reports involve about the glass-derived materials. This letter reports the fabrication of active Mn-doped nanostructured glass sample via control of the crystallization of a typical gallogermanate glass. LiGa2O4 and LiGaGeO4 can precipitate after heat-treatment, and Mn centers selectively incorporate into the crystalline phase. Importantly, the luminescence can be switched from red to green colour and the intensity can be enhanced simultaneously. Furthermore, the luminescence properties can be tuned via control of the phase of the nanostructured glass.

1. Introduction
Mn is an engaging type of active dopants. On the one hand, it belongs to the typical transition metal dopant, and its d-d electronic transition is sensitive to the local structure, thus potentially showing tunable optical response [1–5]. On the other hand, it has multiple valence states (e.g., Mn2+, Mn4+ and Mn6+), and these centers show totally different spectral features [6–9]. For examples, Mn2+-doped nanoparticles and nanostructured glasses exhibit green emission and have been demonstrated to be promising as phosphor in light emitting diode (LED) and anti-counterfeiting [10–13]. Mn4+-doped oxide and fluoride show unusual, high-efficiency red luminescence and can find application in ‘warm-white’ LED devices [14–17]. Mn6+-doped sulfate crystals can support electronic transition in the infrared waveband, and the broadband infrared luminescence feature is promising for applications in tunable and ultra-short pulse laser [18–20]. Despite of the substantial progress in the development of various Mn-activated materials, most of them are strictly limited to the single crystals and crystalline powders. Glass-derived composite (e.g., glass-ceramic) is an important type of candidate with several unique advantages such as suitable for large-scale construction and easy shaping into fiber. Thus, it is interesting if the Mn-doped active materials can be extended to the nanostructured glass composite. Indeed, several reports involving Mn-doped nanostructured glass have been reported, and special applications such as smart candidates for sensing have been demonstrated [4, 12, 21–32]. Unfortunately, the suitable host candidates for Mn dopants with the combinations of excellent chemical stability and tunable luminescence are still highly limited.

This letter proposes that the gallogermanate nanostructured glass can be a potential candidate for hosting of Mn dopant with tunable luminescence. The synthesis of Mn-doped nanostructured glass with controllable optical response is reported. Mn can effectively incorporate into the crystalline phase inside nanostructured glass. Through nanocrystallization, luminescence can be switched from weak red to intense green colour, mainly originated from the change of the local environment around the Mn dopant. Luminescence can be further enhanced by tuning the crystallized phase.

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2. Experimental section

2.1. Methods and synthesis
The material system of (mol%) 15Li₂O–4K₂O–64GeO₂–15Ga₂O₃–2Al₂O₃ was designed as the host for Mn dopant. It was doped with 0.1 mol% MnO. Glass samples were fabricated via the classic melting-quenching approach. In a typical procedure, high-purity Li₂CO₃, K₂CO₃, GeO₂, Ga₂O₃ and MnO in batches of 20–50 g were used as the raw materials, mixed and then melted in a covered corundum crucible. After keeping the melts for 30 min at 1600 °C, they were cast into the copper and then quickly pressed with another copper plate. The thickness of the sample was controlled to be 1.5 mm. The obtained as-made glass was annealed for 24 h to release the stress. Guided by the thermal analysis results, the glass samples exhibit great tendency for crystallization at above the glass transition temperature. Therefore, the samples were cut into small pieces and heat-treated above the glass transition temperatures from 600 to 700 °C for 2 h. During heat-treatment, the nanocrystallization may occur and Mn dopant can be potentially incorporated into the crystalline phase. All of the samples were carefully polished before optical measurements.

2.2. Characterizations
The thermal properties of the glass sample were characterized by differential scanning calorimetry (DSC) in the range of 20 °C–1000 °C at a heating rate of 10 K min⁻¹ at air atmosphere by using a NETZSCH STA449C differential thermal analyzer. The measurement error was estimated to be ∼5 K. X-ray diffraction (XRD) measurements were performed on an x-ray diffractometer (Rigaku International Corp. Tokyo, Japan) with Cu Kα₁ radiation at a scanning rate of 4 °/min. Transmission electron microscopy (TEM) analysis was performed on a JEOL 2010F transmission electron microscope. Absorption spectra were characterized with a Lambda 900 UV/VIS/NIR spectrometer. Excitation and luminescence spectra were characterized using an FLS920 fluorescence spectrometer (Edinburgh Instrument Ltd, Edinburgh, UK) equipped with a xenon lamp. Luminescence decay dynamics was measured with a microsecond flash-lamp (µF900).

3. Results and discussion
Figure 1 shows the DSC curve. Glass transition temperature (T_g) and crystallization temperature (T_x) were estimated to be 538 °C and 700 °C, respectively. Based on the DSC result, the glass sample was heat-treated to obtain nanostructured glass. The phases of the glass and the nanostructured glass samples were characterized by XRD and presented in figure 2. Only broad diffraction halos can be observed in the as-made glass and the sample heat-treated at 600 °C, indicating their amorphous nature. By contrast, sharp diffraction peaks appear for the samples heat-treated above 650 °C, confirming the precipitation of the crystalline phase. The diffraction peaks can be ascribed to the fingerprint bands of LiGa₅O₈ (JCPDS 76-0199) and LiGaGeO₄ (JCPDS 97-2009). The crystal sizes of LiGa₅O₈ and LiGaGeO₄ were calculated by using the characteristic bands at 36.7 and 34° based on the Scherrer equation and it is estimated to be ∼7 and 10 nm, respectively [33]. Importantly, the ratio of these two phases can be tuned via changing the heat-treatment temperatures.
The microstructures of the nanostructured glass sample heat-treated at 700 °C for 2 h were characterized by TEM. The left image of figure 3 shows that dense nanoparticles with an average size of ∼8 nm are homogeneously distributed inside the glass matrix. High-resolution TEM picture (right image of figure 3) on the local region clearly indicates the existence of the multiple crystalline phases. The lattice spacing of nanoparticles in figure 3 was measured to be ∼0.413 and ∼0.361 nm, which are consistent with the (12-1) plane of LiGaGeO₄ and the (210) plane of LiGa₅O₈, respectively. The results match the XRD characterizations in figure 2.

The absorption features of the as-made glass and the nanostructured glass samples were analyzed by absorption spectroscopy, and the results are presented in figure 4. The absorption at less than 350 nm can be ascribed to the intrinsic absorption of the hosts of glass and nanostructured glass. In addition, two sharp absorption peaks can be observed at 380 and 395 nm, and can be indexed to the $^6A_1 \rightarrow ^4E(^4D)$ and $^6A_1 \rightarrow ^4T_{2g}(^4D)$ characteristic electronic absorption of Mn²⁺ in octahedral sites, respectively [33]. In the nanostructured glass sample heat-treated at 700 °C, a broad absorption band can be observed in the range of 400–500 nm, which can be ascribed to the $^6A_1 \rightarrow [^4E(^4G), ^4A_1(^4G)]$ electronic transition of Mn²⁺ in tetrahedral sites [33]. The above results indicate that the Mn²⁺ dopant selectively incorporates into the...

Figure 2. XRD patterns of as-made glass and nanostructured glass samples heat-treated at 600 °C, 650 °C and 700 °C for 2 h.

Figure 3. TEM (left) and high-resolution TEM (right) images of nanostructured glass sample heat-treated at 700 °C for 2 h.
tetrahedral position and most probably occupies the tetrahedral Ga position in LiGaGeO₄ or LiGa₅O₈ in nanostructured glass.

The glass and the nanostructured glass samples exhibit great difference in luminescence features. Figure 5 shows the luminescence pictures of the samples under excitation with the 254 and 365 nm. The as-made glass and the sample heat-treated at a relatively low temperature (600 °C) exhibit red luminescence, and luminescence is relatively strong excited at 254 nm. By contrast, the nanostructured glass samples heat-treated at 650 °C and 700 °C show intense blue-green luminescence under excitation with the 254 nm and 365 nm. This finding is associated with the selective incorporation of Mn²⁺ dopant in the tetrahedral position and most probably occupies the tetrahedral Ga position in LiGaGeO₄ or LiGa₅O₈ in nanostructured glass. With the switch of excitation wavelength from 254 nm to 365 nm, the luminescence of the nanostructured glass sample changes from green to blue-green colour. This result might be associated with the change in the excitation efficiency for emission at different wavebands.

To investigate the physical mechanism of luminescence, steady excitation and emission were characterized, and the results are exhibited in figure 6. In the excitation spectrum, the as-made glass and the sample heat-treated at a relatively low temperature (600 °C) exhibit a single broad excitation band with the central wavelength at ~285 nm, which is originated from the O²⁻→Mn²⁺ charge transfer transition [32]. In the emission spectrum, they show a broad emission band with the central wavelength at ~645 nm, which can be ascribed to

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**Figure 4.** Absorption spectra of as-made glass and nanostructured glass samples heat-treated at 600 °C, 650 °C and 700 °C for 2 h.

**Figure 5.** The luminescence photos of the as-made glass and nanostructured glass samples heat-treated at 600 °C, 650 °C and 700 °C for 2 h. The excitation wavelengths are 254 nm (left) and 365 nm (right).
the $4T^6(G) \rightarrow 6A_1(^6S)$ transitions of Mn$^{2+}$ dopant. The nanostructured glass samples heat-treated at 650 °C and 700 °C exhibit different excitation and emission features. In the excitation spectrum, an intense band with the central wavelength of 264 nm can be observed, which is blue-shift compared with the excitation band in the glass sample. In the luminescence spectrum, an intense band with the central wavelength of 521 nm is dominated, in addition to the broad emission band at $\sim 645$ nm.

The luminescence decay dynamics of the glass and the nanostructured glass samples were characterized and exhibited in figure 7. The decay curves of the as-made and the glass samples heat-treated at 600 °C are similar to each other, consistent with a similar emission spectral shape. The decay curves cannot be fitted by using the simple exponential function, indicating the existence of multiple Mn$^{2+}$ emission centers in the glass matrix. The average lifetime was calculated to be $\sim 10.20$ ms. For the nanostructured glass sample heat-treated at 650 °C, the decay lifetime was estimated to be $\sim 4.90$ ms. For the nanostructured glass sample with the heat-treatment temperature up to 700 °C, the decay curve follows the simple exponential function, and the decay lifetime was calculated to be $\sim 4.79$ ms.

Mn$^{2+}$ is a typical transition metal dopant with the 4d$^5$ electronic configuration. Its optical response is extremely sensitive to the local structure around it $[^{34}]$. In our case, the drastic change of the luminescence
properties is most probably associated with the selective doping of Mn$^{2+}$ dopant into the crystalline phase inside the nanostructured glass. It can be understood based on the ligand field theory. The spectral features can be described by crystal field strength $Dq$ and Racah parameter $B$. In the as-made glass, Mn$^{2+}$ is supposed to occupy the distorted sites with a relatively high $Dq$ value. Thus, the energy gap between the $^6A_1(^6S)$ ground state and $^4T_2(^4G)$ excited state is low, and luminescence is mainly located in the low-energy waveband region. For the nanostructured glass sample after heat-treatment, the nanocrystalline phase precipitates and Mn$^{2+}$ can selectively incorporate the crystalline phase. The process leads to the change of the local chemical environment around the Mn$^{2+}$, and it can be expected to be more regular. As a result, the energy gap between the $^6A_1(^6S)$ ground state and $^4T_2(^4G)$ excited state increases, and luminescence shows an apparent blue-shift. In addition to the crystallization, the change of the precipitated phase may affect the optical properties of the nanostructured glass samples. Figure 2 shows that the samples heat-treated at 650 °C and 700 °C are mainly dominated by LiGaGeO$_4$ and LiGa$_2$O$_3$, respectively. Importantly, the formation of LiGa$_2$O$_3$ spinel phase is favourable for luminescence enhancement. The precipitation of LiGa$_2$O$_3$ spinel phase also changes the luminescence dynamics and induces the simple exponential decay (figure 7). The above results indicate that tunable optical properties can be achieved via control of the precipitated phase.

4. Conclusions

This paper reports on the synthesis and the characterization of the Mn-doped optical materials via crystallization of glass. Luminescence colour can be switched from red to green through nanocrystallization of the glass phase, and luminescence intensity can also be greatly enhanced simultaneously. Furthermore, luminescence properties can be tuned via control of the precipitated crystalline phase inside nanostructured glass. The engaging phenomenon is contributed by the selective doping of Mn into the crystalline phase in the nanostructured glass.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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