Intense luminescence in nanostructured germanate glass

Xiaoyun Xu and Xifeng Liu
Guangzhou City University of Technology, Guangzhou 510800, People’s Republic of China
E-mail: xuxiaoyun@gcu.edu.cn

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Abstract
The phosphors free of active dopants have been attracted much attention due to their interesting optical properties and potentials for construction of rare-earth free functional materials. In this letter, we report the construction of phosphor free of active dopants via nanocrystallization of glass. In a typical example, a single-phase Zn$_2$GeO$_4$ phosphor is fabricated via controllable crystallization of the germinate glass. Intense green luminescence with the central wavelength at 523 nm can be realized in nanostructured glass and it is estimated to be $\sim 150$ times higher than that of the as-made glass. The physical mechanism is associated with the formation of Zn related interstitial defects during the disorder-order phase transformation in glass. The progress in this work indicates that the avenue of glass crystallization provides an effective strategy for the development of novel active photonic materials free of active dopants.

1. Introduction
The wide applications of luminescent materials in telecommunication, laser, photovoltaics and biological imaging have posed an increasing demand for extending the category of the phosphors [1–5]. There are two popular phosphor candidates, which are activated with dopants or free of dopants. For doped phosphors, active dopants such as rare-earth, transition-metal and main-group ions are typically introduced into the inert matrix for realization of the desired luminescence [6–10]. Generally, their performance is limited by the type of dopant and dopant–host interaction. The other type is the phosphors free of active dopants in which the host can support the radiative transition and the optical properties are mainly governed by the microstructure of the host [11, 12]. The phosphors free of active dopants exhibit attractive advantage because the active dopants such as rare-earth are not necessary, thus enabling for alleviating the resource shortage issue. Encouragingly, some important phosphors free of active dopants which present luminescence in the visible and infrared wavebands have been reported [13–15]. Despite great research efforts, it is still necessary and urgent for exploration of new strategy for synthesis of single phase phosphor free of active dopants.

In this letter, we report the success in fabrication of germanate phosphor with intense luminescence via glass crystallization. The strategy involves the controllable relaxation and crystallization of the glass phase. As a typical example, the nanostructured glass embedded with germinate nanoparticles, which have also reported in some references, has been explored [16]. Importantly, the composition of the glass can be tuned and the pure luminescent phase can be obtained. The results indicate that the approach of glass crystallization provides an effective avenue for the development of active photonic materials free of active dopants.

2. Experimental section
2.1. Material synthesis
Two typical glass system with the composition of (mol%) 48GeO$_2$–4Al$_2$O$_3$–10B$_2$O$_3$–30ZnO–8K$_2$O and (mol%) 24GeO$_2$–24SiO$_2$–4Al$_2$O$_3$–10B$_2$O$_3$–30ZnO–8K$_2$O were designed based on the standard phase diagram. The major difference of the samples is the content of Si and Ge, and it has been demonstrated that the hybridization of Si with Ge can greatly change the optical properties of glass sample [17]. The glass materials were synthesized
via the conventional melting-quenching approach. The samples were melted from the raw materials with especially high purity (99.99%) GeO$_2$, SiO$_2$, Al$_2$O$_3$, B$_2$O$_3$, ZnO and K$_2$CO$_3$. The raw materials in powder form with batches of 50 g were thoroughly mixed. The mixtures were transferred to a covered crucible and melted at 1550 °C for 2 h. The melt was cast into a preheated copper mold. The glass samples were quickly transferred to the furnace and annealed at the glass-transition temperature (≈590 °C) for relaxing the stress for 24 h. To obtain the nanostructured glass, the glass samples were heat-treated at glass crystallization temperature for 2 h. The obtained as-made glass and nanostructured glass samples were cut into pieces with the size of 1 cm × 1 cm × 0.5 mm and carefully polished for further optical characterizations.

2.2. Material characterizations

The as-made glass sample was grinded into powder with the average size of ≈100 μm for characterization of thermal properties in the temperature range of 20 °C–1000 °C. The heating rate was controlled to be ≈10 K min$^{-1}$ and the measurement was performed at air atmosphere. The phase of the samples was characterized by X-ray diffraction (XRD) which was carried out on the x-ray diffractometer (Rigaku International Corp. Tokyo, Japan). The radiation is Cu Kα1 and the scanning rate was controlled to be ≈4 °/min. The chemical bonding characteristic of the samples was characterized by using the Raman scattering on a Renishaw inVia Raman spectrometer. The laser source in the Raman spectrometer is 532 nm continuous laser. The microstructure of the sample was analyzed on the high resolution transmission electron microscopy (TEM) which was performed on a JEOL 2010F transmission electron microscope. Optical transmittance properties were studied on a Lambda 900 UV/VIS/NIR spectrometer in the wavelength range of 200–800 nm. The excitation and luminescence spectra were studied on an FLS920 fluorescence spectrometer (Edinburgh Instrument Ltd, Edinburgh, UK). The excitation source is a continuous xenon lamp with the power of 450 W.

3. Results and discussion

The thermal properties of the glass samples in the temperature range of 20 °C–1000 °C were characterized. Figure 1 exhibits the differential scanning calorimetry curves of germanium-silicate and germinate glass samples. The glass transition temperature ($T_g$) of germanium-silicate and germinate glass was estimated to be ≈590 °C. The crystallization temperature ($T_c$) of germanium-silicate and germinate glass is different and it was estimated to be ≈742 and 709 °C, respectively. The results indicate that the element hybridization of Ge with Si decreases increase the crystallization tendency.

Based on the thermal characterization results, the glass samples were heat-treated at 600 and 700 °C for fabrication of nanostructured glass. The phase of the nanostructured glass samples was characterized by XRD. Figure 2 presents the XRD patterns of nanostructured germanium-silicate and germinate glass samples. The diffraction peaks of the nanostructured germinate glass are well consistent with the characteristic peaks of the standard Zn$_2$GeO$_4$ (PDF #00–11–0687) [18, 19]. The diffraction peaks of the nanostructured germanium-silicate sample are similar to that of the nanostructured germinate glass. The difference involves that the
diffraction peaks of the nanostructured germanium-silicate sample shift to the high-angle region, as shown in the inset of figure 2. This is mainly induced by the incorporation of Si into Zn$_2$GeO$_4$, resulting in the formation of alloyed Zn$_2(Ge_{x}Si_{1-x})$O$_4$.

The chemical bonding features of the as-made glass and nanostructured glass were studied via Raman scattering and the results are presented in figure 3. Figure 3(a) exhibits the Raman spectra of as-made germinate glass and nanostructured germinate glass heat-treated at 600 °C and 700 °C for 2 h. For as-made glass sample, two broadband Raman bands can be observed in the range of 400–650 cm$^{-1}$ and 700–960 cm$^{-1}$, which might be associated with the bending and symmetric vibrations of Ge–O–Ge linages [12]. For nanostructured glass heat-treated at 600 °C and 700 °C, several intense Raman bands can be observed at 747, 781 and 802 cm$^{-1}$, which can be indexed to the O–Ge–O bending, Zn–O–Ge bending and O–Ge–O stretching modes of crystalline Zn$_2$GeO$_4$, respectively [12]. These characteristic Raman bands become sharp with the increase of the heat-treatment temperature, confirming the improvement of the crystallinity of the nanostructured samples. Notably, compared with the pure nanostructured germinate sample, the sharp Raman bands in nanostructured
Germanium-silicate sample shift to 753, 783 and 808 cm\(^{-1}\). This is probably associated with the hybridization of Si with Ge.

The microstructures of the nanostructured germinate and germanium-silicate glass were studied by TEM. Figure 4(a) shows the TEM image of the nanostructured germinate glass. It can be observed that the crystalline domains with the average size of \(\sim 100\) nm are homogeneously distributed inside the glass phase. The high-resolution TEM image of a single particle is presented in figure 4(b) and the regular lattice fringe can be clearly observed. The d-spacing is estimated to be \(\sim 4.174\) Å, which is well consistent with the (211) plane of Zn\(_2\)GeO\(_4\). Figure 4(c) shows the TEM image of the nanostructured germanium-silicate glass. The crystalline domains are relatively larger and the average size was calculated to be \(\sim 150\) nm. The high-resolution TEM image of a representative particle is presented in figure 4(b) and it exhibits lattice fringes with a d-spacing of \(\sim 1.926\) Å. This is close to the (333) plane of the alloyed Zn\(_2\)(Ge\(_x\)Si\(_{1-x}\))O\(_4\).

The nanocrystallization leads to the great changes in the luminescence features of the glass samples, especially in the germinate glass system. Figure 5 compares the luminescence properties of as-made and nanostructured samples for germinate and germanium-silicate glass system. As presented in the inset of the left part of figure 5, the nanostructured germinate glass shows intense green luminescence under excitation with the ultra-violet light. In contrast, the as-made glass sample only presents very weak luminescence. The excitation and luminescence spectra were measured and their central wavelength is located at 255 and 523 nm, respectively. Notably, the luminescence intensity of the nanostructured glass is estimated to be \(\sim 150\) times higher compared with the as-made glass. The germanium-silicate glass system exhibits totally different luminescence feature. As shown in the right part of figure 5, both of the as-made and nanostructured samples present very weak green luminescence and the nanocrystallization does not lead to the obvious change of the optical properties. The excitation spectra are featured by an excitation band with the central wavelength at 260 nm, which is similar to the germinate glass system in the left part of the figure 5. The luminescence spectra are characterized by two broad overlapped bands with the central wavelength at 418 and 518 nm. Above results
indicate that the hybridization of Ge with Si has adverse effects for the luminescence and imply that the interesting luminescence should be associated with the Ge induced centers.

The physical mechanism of the interesting luminescence phenomenon can be discussed from the viewpoint of the structure evolution during nanocrystallization and illustrated in figure 6. In as-made glass sample, GeO₄ units are randomly distributed and Zn ions are supposed to occupy the distorted interstitial sites. During nanocrystallization, the ordering of GeO₄ units and their connection with Zn ions occurs, leading to the formation of willemite-type Zn₂GeO₄ nanocrystals. This crystalline phase is unique and is featured by the open structure with six-membered rings [13]. It was supposed that Zn may incorporate into the interstices of the six-membered rings during formation of the crystalline phase, resulting in the formation of interstitial defects. Furthermore, being different from the conventional crystallization, the disorder-order phase transformation in glass can only locally occur because of the extreme viscous feature of the super-cooled liquid [20]. Thus, it is supposed that, a large quantity of defects could potentially form. It is well known that the defects in willemite-type Zn₂GeO₄ may act as emission centers and contribute to the intense and broadband luminescence phenomenon. In contrast, the alloying of Ge with Si may prevent from the formation of active center because Si commonly acts as the quenching center for radiative transition. From this point of view, the glass crystallization

Figure 5. The excitation and luminescence spectra of as-made and the nanostructured samples. The left figure is germinate and the right figure is germanium-silicate glass system. The insets exhibit the luminescence pictures of the samples under excitation with the ultra-violet light.

Figure 6. The illustration drawing summarizes the structural evolution during nanocrystallization of the glass. In as-made glass sample (left image), GeO₄ units are randomly distributed and Zn ions are supposed to occupy the distorted interstitial sites. In nanostructured glass sample (right image), the nanocrystallization leads to the formation of willemite-type Zn₂GeO₄ nanocrystals which is featured by the open structure with six-membered rings.
in the glass system with suitable composition is believed to be an effective avenue for achievement of effective radiative transition.

4. Conclusions

In summary, we have fabricated a single-phase germinate phosphor through nanocrystallization of glass. The nanostructured germinate exhibits intense green luminescence with the central wavelength at 523 nm. Notably, the luminescence intensity of the nanostructured glass is estimated to be ∼150 times higher than that of the as-made glass. The alloying treatment by replacing Ge with Si decreases the luminescence performance. The luminescence is supposed to be originated from the interstitial defects formed during the disorder-order phase transition in glass. The constructed sample can be potentially applied as the phosphor in light emitting device. The avenue is believed to be applicable for other type of multicomponent glass system for exploration of new phosphor free of active dopant.

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Data availability statement

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

ORCID iDs

Xiaoyun Xu https://orcid.org/0000-0002-5467-2019

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