Effects of substitution of BaF₂ for GdF₃ on optical properties of dense oxyfluoride borogermanate scintillating glasses

SUN Xinyuan (孙心瑗)[1,*], YANG Qingmei (杨庆梅)[2], XIE Peng (谢鹏)[1], GAO Pan (高攀)[3], WU Hongshu (吴泓澍)[3]

(1. Department of Physics, Jinggangshan University, Ji'an 343009, China; 2. Library of Jinggangshan University, Ji'an 343009, China; 3. Research and Development Center, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 201800, China)

Abstract: Eu^{3+}-activated B_2O_3-GeO_2-$37Gd_2O_3$-$3Eu_2O_3$-$(15-x)GdF_3$-$xBaF_2$ ($0 \leq x \leq 15$) scintillating glasses with the density of 6.1–6.3 g/cm₃ were synthesized by a melt-quenching method. The substitution of BaF_2 for expensive GdF_3 in oxyfluoride borogermanate glasses slightly decreased the glass density within 3.0%. Their optical properties were characterized by transmittance, photoluminescence (excitation and emission), and X-ray excited luminescence (XEL) spectra in detail. The emission intensity of Eu^{3+} ions increased with the elevated x values. The Eu–O covalancey nature and the local environment of Eu^{3+} ions were evaluated by Judd-Ofelt results. It was found that the covalency property of Eu–O bond increased with increasing x values.

Keywords: Eu^{3+}-activated borogermanate scintillating glasses; energy transfer; Judd-Ofelt theory; X-ray excited luminescence; rare earths

Rare earth (RE) activated scintillating glasses, owing to the advantages of low-cost, large-volume production as well as easy shaping of elements, have been extensively considered to be one of the most promising candidates to scintillating crystals and ceramics[1–3]. From the practical point of view, a scintillator used in high-energy physics, as well as industrial and medical imaging should be featured with high light-yield and density, which may remarkably improve both the signal-to-noise ratio and the resolution of images. Recently, a number of scintillating glasses enriched with RE oxides have been developed to exceed 5.0 (even 6.0 g/cm³) in different silicate, borosilicate, phosphate, germanate, borogermanate and tellurite glass systems[2–12]. Regarding the borogermanate system, we have proposed a novel Eu^{3+}-, Tb^{3+}-activated borogermanate scintillating glass with a density of 5.6–5.8 g/cm³ to detect high energy X-rays[10,11]. Most importantly, the density of borogerrmante glasses were improved up to 6.0 g/cm³ by adding gadolinium fluoride and/or Lu_2O_3 components[12]. This provides us a guidance to enhance the density by adding other heavier RE oxides and fluorides.

Undoubtedly, these dense scintillating glasses are becoming alternatives to scintillating crystals or ceramics. However, the expensive RE oxides and/or fluorides may dramatically increase the raw material cost of glass. Therefore, in the present work, a substitution of the economic BaF_2 for the expensive GdF_3 was proposed, and detailed insights into the substituting effects on the glass density, structure, optical properties (transmittance, photoluminescence and X-ray excited luminescence) were given.

1 Experimental

Oxyfluoride borogermanate glasses with the nominal composition of B_2O_3-GeO_2-$37Gd_2O_3$-$3Eu_2O_3$-$(15-x)$ GdF_3-$xBaF_2$ ($0 \leq x \leq 15$) (x=0.0, 3.0, 6.0, 9.0, 12 and 15) were synthesized by melt-quenching method. The starting materials were H_3BO_3, BaF_2 (A.R. purity, Shanghai Sinopharm Chemical Reagent Co., Ltd.), GeO_2 (99.999%, Nanjing Hope Tech. Development Inc.), Eu_2O_3 (99.99%, Shanghai Sinopharm Chemical Reagent Co., Ltd.), Gd_2O_3 (99.99%, Jiangxi Ketai Advanced Materials Co., Ltd., 99.99%), GdF_3 (99.99%, Jiangxi Ketai Advanced Materials Co., Ltd) and BaF_2 (A.R. purity, Shanghai Sinopharm Chemical Reagent Co., Ltd.). Batches of about 20 g precursor materials were well mixed in an agate mortar and subsequently melted in an alumina crucible at 1375 ºC for about 1 h in air. The melts were quickly poured out on a preheated stainless steel mold and finally annealed at 550–600 ºC for 4–8 h followed by a natural cooling down to room temperature.

Glass density was evaluated by Archimedes' principle

using distilled water as an immersed liquid. Raman spectra were recorded using a Jobin-Yvon T64000 Raman spectrometer with an Ar-laser at 514.5 nm as the excitation source. Transmittance spectra were recorded on a Perkin-Elmer Lambda 750S UV/VIS spectrometer. Excitation and emission spectra were examined on a Hitachi F-7000 fluorescence spectrophotometer equipped with a 150 W xenon lamp as the excitation source. Luminescence decay curves of Eu^{3+} emission at 616 nm were performed in an Edinburgh FLS980 spectrometer using TCSPC technique excited by 394 nm. XEL spectra were examined using an X-ray excited spectrometer, in which an Au anticathode target was used as the X-ray source operating at 40 kV and 50 μA. All the measurements were taken at room temperature.

2 Results and discussion

2.1 Raman spectra

The unpolarized Raman scattering spectra of dense oxyfluoride borogermanate glasses are presented in Fig. 1. The broad bands centered at about 330, 792, 930 and 1350 cm^{-1} are characteristic of amorphous states. The broad band centered at 330 cm^{-1} band may be related to the combination RE–O (RE=Gd and Eu) vibration mode according to our assignments in borogermanate oxide glasses[10,11]. The strong Raman band at 801 cm^{-1} is assigned to the stretching vibrations of [GeO₄] tetrahedra with a small contribution of the vibrations of [BO₄] tetrhedra. The latter one is completely masked by the strong broad band due to [GeO₄] vibration. The 930 cm^{-1} Raman band is associated with the presence of isolated orthobrate units $(BO_3)^{3-}$ with three non-bridging oxygens[10], and the band at 1300 cm^{-1} should be assigned to the B–O⁻ bonds vibration occurring in a large borate network instead of a specific group[10,13]. The mentioned broad bands show the same profile and approximately equal intensity in all the Raman curves, which suggests that glass structure hardly changes with the elevated *x* values.
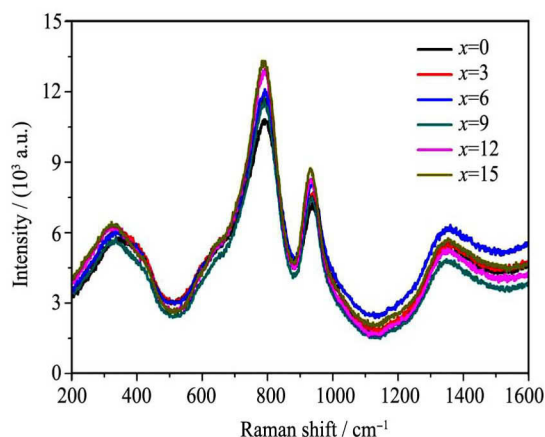
2.2 Glass density

The density of oxyfluoride borogermanate glasses as a function of *x* values is shown in Fig. 2. The glass density decreases gradually from about 6.28 to 6.12 g/cm^3 with the increasing content of BaF₂, i.e. *x* values. Namely, the glass density decreases within the range of 3% with the complete substitution of BaF₂ for GdF₃, which is of significance in lowering the raw material cost of glass, because the price of BaF₂ is always much lower than that of GdF₃. In addition, the complete substitution does not dramatically affect the glass density, which indicates that the borogemanate scintillating glasses still have a strong stopping power for the incident high-energy rays.

2.3 Transmittance spectra

Fig. 3 shows the transmittance spectra of oxyfluoride borogermanate glasses against a function of *x* values in 200–800 nm region. The apparent absorption peaks at 362, 380, 394, 414, 465, 530 and 578 nm are associated with the optical transitions from $^7F_0$ to $^5D_4$, $^5G_4$, $^5L_6$, $^5D_3$, $^5D_2$, $^5D_1$ and $^5D_0$ of Eu^{3+} ions, respectively[10]. The relative intensity of these featured absorption peaks hardly changes owing to the same molar concentration of Eu₂O₃. The oxyfluoride borogermanate glasses show a linear transmittance coefficient of 84%–86% in the 450–800 nm
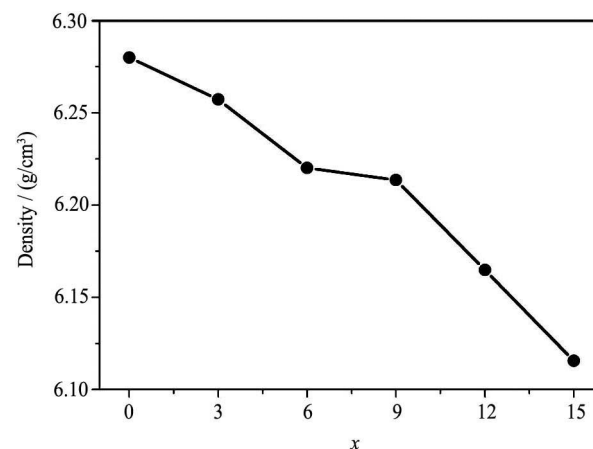
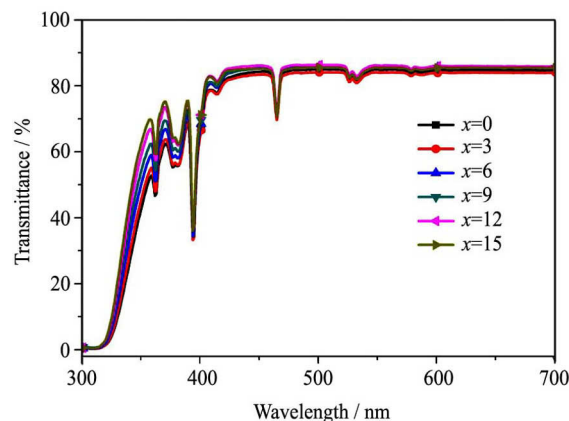Fig. 2 Glass density of oxyfluoride borogermanate glasses as a function of *x* values

Fig. 1 Raman spectra of dense oxyfluoride borogermanate glasses

Fig. 3 Transmittance spectra of oxyfluoride borogermanate glasses against a function of *x* values

region. It is worthy noting that the cut-off edge of the dense oxyfluoridge borogermanate glass slightly shifts towards high energy side with the elevated x values, i.e. the so-called blue-shift phenomena. The blue-shift may be associated with the discrepancy in both the electronegativity of Ba (0.89) and Gd (1.20) elements and the optical basicity of BaF_2 (0.50) and Gd (0.58)[14].

2.4 Photoluminescence spectra

Fig. 4 shows photoluminescence (excitation and emission) spectra of oxyfluoride borogermanate glasses. As shown in Fig. 4(a), the excitation spectra monitored at 616 nm of Eu^{3+} ions consist of two parts. The former broad band ranging from 200 to 340 nm is mainly associated with the charge-transfer state (CTS) moving from the 2p orbital of O^{2-} to the 4f one of Eu^{3+} ions. It is clear that the featured excitation peaks of both Gd^{3+} ions at 313 nm ($^8S_{7/2} \rightarrow ^6P_J$) and Eu^{3+} ions at 320 nm ($^7F_0 \rightarrow ^5H_J$) are overlapped on the broad CTS band[10,12]. The latter sharp lines in 340–550 nm region correspond to the direct excitation of the intra-4f forbidden transitions of Eu^{3+} ions: $^7F_0 \rightarrow ^5D_4$ (364), $^5G_4$ (383), $^5L_6$ (395), $^5D_3$ (415), $^5D_2$ (466) and $^5D_1$ (534 nm), respectively. It is found that the intensity of the mentioned excitation peaks always get stronger with increasing x values. The corresponding emission spectra excited by 394 nm are shown in Fig. 4(b). The intensive red emission peaks at 592, 616, 654 and 705 nm are attributed to the optical transition of Eu^{3+} $^5D_0 \rightarrow ^7F_J$ (J=1, 2, 3 and 4), respectively. These featured emission intensities get stronger with the increasing x values.

The possible energy transfer from Gd^{3+} to Eu^{3+} ions has been reported in our previous works, where the featured excitation and emission spectra of Gd^{3+} ions can be observed[10]. However, these characteristic emissions of Gd^{3+} ions completely varnish in the present work, which is speculated to be related to the highly concentrated Gd_2O_3 in the present oxyfluoride borogermanate glasses. It is well known that the optimal concentration of a sensitizer usually contributes to improving energy transfer efficient, thus enhancing the emission intensity of an ac-
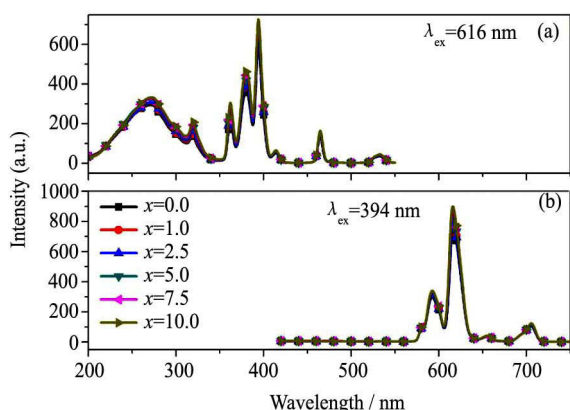
tivator. However, the extremely high concentration of a sensitizer will result in decreasing emission intensity of an activator. To confirm this assumption, we calculate the mean distances for Gd^{3+}-Eu^{3+} ion pairs according to the following equation[10,11],

$$R = (\frac{M}{N_A \rho y})^{\frac{1}{3}} \tag{1}$$

where M is the mean molecular weight of glass, N_A is Avogadro number, ρ is the bulk density, and y is the total incorporated concentration of donor-acceptor ions. The calculated results clearly suggest that the mean distance for Gd^{3+}–Eu^{3+} ion pairs increases with the y values from 3.91 (x=0) to 4.14 (x=15) angstroms. These mean distances are much shorter than those in our previous works[10,11]. On the one hand, the extreme-shorter Gd^{3+}– Eu^{3+} distance attributes to higher energy transfer efficiency, and completely quenches Gd^{3+} emission. On the other hand, the energy transfer mechanism from Gd^{3+} to Eu^{3+} ions may change from the exchange to multipolar interaction type when the critical distance exceeds 0.4 nm[15]. In a word, the mentioned two factors should be responsible for the enhanced red emission of Eu^{3+} ions, as observed in Fig. 4(b).

2.5 Judd-Ofelt analysis

The optical transition intensity parameters, namely Judd-Ofelt parameters, are important for understanding the spectral properties of RE ions in the host materials. In the case of Eu^{3+} ions, the values of Ω_t parameters can be determined from their intensity ratios of the $^5D_0 \rightarrow ^7F_J$ (J=2, 4 and 6) transitions, $\int I_J d\overline{v}$, to the intensity of the $^5D_0 \rightarrow ^7F_1$ transition, $\int I_1 dv$ [16,17],

$$\frac{\int I_J d\overline{v}}{\int I_1 d\overline{v}} = \frac{A_J}{A_1} = \frac{e^2}{S_{md}} \frac{\overline{v}_J^3}{\overline{v}_1^3} \frac{(n^2+2)^2}{9n} \Omega_t < \left\| U^{(t)} \right\| >^2 \tag{2}$$

where n is the refractive index of glass, e=4.80×10^{-10} esu is the charge of an electron, S_{md} is the magnetic dipole transition line strength that is independent on host matrix, and equals to 7.83×10^{-42} (dimensionless), $\overline{v}$ is the wavenumber for $J \rightarrow J'$ transition. It is worthy noting that $<\|U^{(t)}\|>^2$ is the squared values of reduced matrix elements of Eu^{3+} ions. The squared values of reduced matrix elements are $<\|U^{(t)}\|>^2$=0.0032 for $^5D_0 \rightarrow ^7F_2$, $<\|U^{(2)}\|>^2$= 0.0032 for $^5D_0 \rightarrow ^7F_4$, and $<\|U^{(6)}\|>^2$=0.0002 for $^5D_0 \rightarrow ^7F_6$, respectively. However, the values of other matrix elements for these transitions are zero.

To determine the Ω_t values, the integral emission intensity ratios of $I(^5D_0 \rightarrow ^7F_2)/I(^5D_0 \rightarrow ^7F_1)$ and $I(^5D_0 \rightarrow ^7F_4)/I(^5D_0 \rightarrow ^7F_1)$ are calculated from the spectral data in Fig. 4(b), respectively. Given these ratios in formula (2), the Ω_2 and Ω_4 values are determined and plotted against as a function of x values, as shown in Fig. 5. It is found that the Ω_2 values increase from 22.5×10^{-20} cm^2 (x=0.0) to 24.1×10^{-20} cm^2 (x=15) with the elevated x values, the lin-

Fig. 4 Excitation spectra monitored at 616 nm emission (a) and emission spectra excited by 394 nm (b), respectively
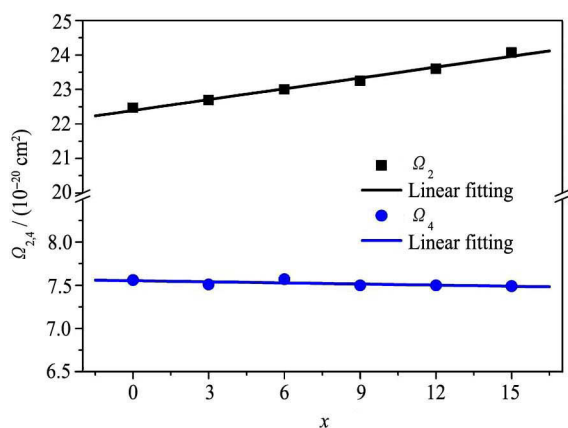
Fig. 5 Values of Ω_2 and Ω_4 parameters are plotted as a function of x values

Fig. 6 Luminescence decay curves of Eu³⁺ emission assigned to the $^5D_0 \rightarrow {}^7F_2$ optical transition

ear fitting lines are drawn as a guide to the eyes. However, the Ω_4 values keep almost at about 7.52×10^{-20} cm². However, the Ω_6 values are unknow due to the absence of $^5D_0 \rightarrow {}^7F_6$ spectral data in Fig. 4(b). In general, the Judd-Ofelt parameters Ω_t of Eu³⁺ ions in glass reveal information regarding the covalence and local environment of RE ion. The value of Ω_2 parameter depends on the magnitude of intensity of hypersensitive transition, which exhibits the relationship between RE and ligand anions on the covalence (short-range effect) and gives the asymmetry information around RE ions local environment. A larger value of Ω_2 is an indication of a high covalence of the metal-ligand bonds and more distortion of the symmetry of Eu³⁺ sites in that matrix compared to a matrix with smaller Ω_2 value[18]. The increasing values of Ω_2 parameter in the investigated borogermanate glasses indicate the stronger Eu–O covalency property with the gradual substitution of BaF₂ for GdF₃. On the other hand, the values of Ω_4 and Ω_6 parameters are related to not only the rigidity of glass network (long-range effect), but also the bulk properties influenced by the vibronic transition of the RE-ligand bond[16,17]. The Ω_4 values hardly change with the gradual substitution of BaF₂ for GdF₃ in the investigated borogermanate, as shown in Fig. 5.

Additionally, we have summarized some Ω_t values of Eu³⁺ ions in different Eu³⁺-doped borosilicate glass, fluoroborate glass, fluorogallate glass and lead tungstate tellurite glass[12]. The main trend of the Judd-Ofelt parameters with $\Omega_2 > \Omega_4$ are clearly determined, which confirms the dominant covalency nature between Eu³⁺ ions and their surrounding ligands in the investigated oxyfluoride borogermanate glasses.

2.6 Luminescence decay curves

The luminescence decay curves of Eu³⁺ emission assigned to the $^5D_0 \rightarrow {}^7F_2$ optical transition ($\lambda_{ex}=394$ nm, $\lambda_{em}=616$ nm) are shown in Fig. 6. All the decay curves show single exponential decay behaviour, which indicate the homogeneous distribution of Eu³⁺ ions in borogermanate scintillating glass. The fitted decay times (τ) re-
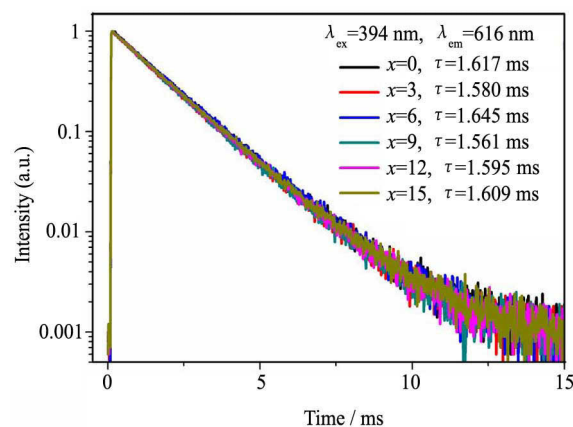
main at about 1.60 ms for the constant content of the incorporated Eu₂O₃, which is in good accordance with the feature of the forbidden intra-4f transitions of Eu³⁺ ions.

2.7 XEL spectra

The XEL spectra of Eu³⁺-activated oxyfluoride borogermanate glasses are displayed in Fig. 7, and the inset shows the integral emission intensity of Eu³⁺ ions in 604–640 nm region. The XEL intensity of the $x=0$ glass equals approximately to that of the $x=9$ one, as shown in the inset of Fig. 7. Both of them are the strongest XEL intensity. The lowest XEL intensity is the $x=6$ glass, whose intensity is about 82% of the strongest one, i.e., the $x=9$ glass. Compared with the emission intensity of the emission spectra (Fig. 4(b)), the XEL intensity seems irregular with the x values (Fig. 7). The different luminescence behaviors under photoluminescence and X-ray excitation could be attributed to the discrepancy of excitation mechanism between ultraviolet light and X-ray initiated processes[10,11]. The ultraviolet light excitation process is regarded as the direct excitation of Eu³⁺ ions in borogermanate scintillating glasses. However, during the X-ray excitation, the X-ray energy has a first interaction with holes and electrons from borogermanate glass. Then, a large number of secondary electrons are produced. Fi-
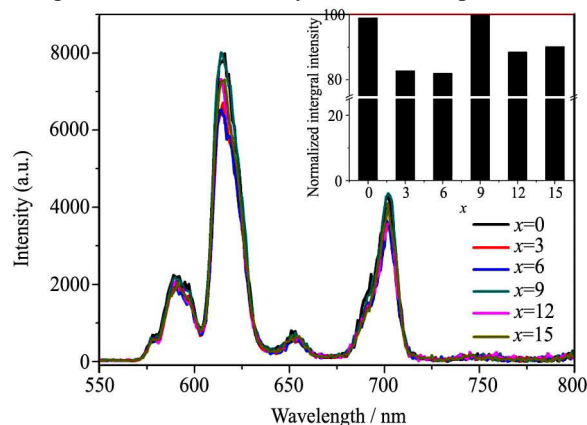

Fig. 7 XEL spectra of Eu³⁺-activated oxyfluoride borogermanate glasses (Inset shows the integral emission intensity of Eu³⁺ ions in 604–640 nm regions)

nally, the produced secondary electrons indirectly or directly excite Eu^{3+} ions and result in the stronger red emission.

3 Conclusions

Eu^{3+}-activated B_2O_3-GeO_2-$37Gd_2O_3$-$3Eu_2O_3$-$(15–x)GdF_3$-$xBaF_2$ $(0{\leq}x{\leq}15)$ scintillating glasses were successfully synthesized by a melt-quenching method. The partial and complete substitution of BaF_2 for GdF_3 hardly influenced the glass structure observed by the Raman spectra, but it slightly decreased glass density within 3% range. The photoluminescence intensity increased gradually with the elevated x values. The Eu–O covalency property increased with the elevated x values by the Judd-Ofelt results. However, the XEL intensity of Eu^{3+} ions seemed irregular with various x values, and the strongest XEL intensity of Eu^{3+} ions was in the $x=9$ glass. The substitution of BaF_2 for the expensive GdF_3 was expected to remarkably decrease the raw material cost of glass, which gave us a guidance to design some heavy scintillating glass.

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