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High quantum yield and low concentration quenching of Eu^{3+} emission in oxyfluoride glass with high BaF_2 and Al_2O_3 contents

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ABSTRACT

New oxyfluoride glasses of $1Eu_2O_3$–$50BaF_2$–xAl_2O_3–$(50-x)B_2O_3$ ($x = 0$–25), yEu_2O_3–$50BaF_2$–$25Al_2O_3$–$25B_2O_3$ ($y = 0$–10) (mol), and zEu_2O_3–$1Tb_4O_7$–$50BaF_2$–$25Al_2O_3$–$25B_2O_3$ ($z = 0,\ 0.5$) (mol) with a high fluorine content ($F/(F + O) = 0.4$) were synthesized by using a conventional melt-quenching method, and photoluminescence properties such as quantum yield (η), lifetime (τ), and concentration quenching effect of Eu^{3+} ions were clarified. The glass with $25Al_2O_3$ showed an excellent red luminescence with extremely high quantum yield (η) of 97% in the visible region at the excitation of the wavelength $\lambda = 396$ nm and a long lifetime of $\tau = 3.29$ ms for the emission ($\lambda = 612$ nm) of Eu^{3+} ions at the $^5D_0$ level. The effect of concentration quenching in these glasses was also very small, e.g., $\eta = 72\%$ even for the glass with $10Eu_2O_3$. The values of $\eta = 52\%$ for the green emission of Tb^{3+} ions and of $\eta = 81\%$ for the yellow emission of Eu^{3+}–Tb^{3+} co-doped ions were also achieved in the glasses. The present study indicates that rare-earth ions of Eu^{3+} and Tb^{3+} are dispersed homogeneously in these oxyfluriode glasses and the degree of their its asymmetry (i.e., the electric field gradient) is also widely distributed due to the coordination of both F^- and O^{2-} ions. The new oxyfluoride glasses with high BaO and Al_2O_3 contents have a high potential as hosts for new phosphors with rare-earth ions.

1. Introduction

Phosphors are key materials for contemporary society, especially in photonics applications, such as lasers, amplifiers, illuminations, and displays. Trivalent rare earth ion (RE: Er^{3+}, Nd^{3+} etc.)-doped glasses have been developed for infrared light active devices such as fiber lasers. Recently, RE doped glasses have also much attention as candidates for visible light optical devices due to their excellent optical transparency and shape formability. The light emitting diode (LED) has become an essential device in the realms of illuminations and displays due to its high efficiency in the conversion of electrical energy into light, high reliability, long operating lifetime, and environmentally friendly character. Usually, white LEDs are fabricated by the combination of blue or ultraviolet LEDs and crystalline phosphors showing excellent photoluminescence (PL) such as YAG:Ce [1]. Furthermore, it should be pointed out that organic resins have been used for the packing and dispersion of powdered crystalline phosphors [2], resulting in poor heat-resistance. Therefore, the use of glasses as phosphors and packages is considered to be a key point in the development of new and reliable LED devices.

Fluoride glasses are attractive host materials for RE^{3+}-based phosphors because of their low phonon energy, large RE^{3+} solubility, low melting temperature, and wide transparent wavelength region. Fluoride glasses, however, have poor water resistance and a mechanically brittle nature. On the other hand, oxide glasses, in particular those based on B_2O_3 and SiO_2, generally exhibit excellent mechanical properties and high water resistance, although their high phonon energies generate multi-phonon relaxations for RE^{3+} ions and result in low emissions. Recently, oxyfluoride glasses consisting of both fluorides and oxides such as CaF_2–CaO–Al_2O_3–SiO_2 glasses have received much attention. In particular, transparent oxyfluoride glass–ceramics (crystallized glasses) containing RE^{3+}-doped fluoride nanocrystals such as Er^{3+}-doped CaF_2 have been considered to be promising materials as new PL candidate [3–7].

Very recently, Shinozaki et. al. [7] succeeded in synthesizing new transparent oxyfluoride ($50BaF_2$–$25Al_2O_3$–$25B_2O_3$) glass–ceramics consisting of nonlinear optical $BaAlBO_3F_2$ nanocrystals and in patterning $BaAlBO_3F_2$ single crystal lines by using laser irradiation. It should be noted that the glass of $50BaF_2$–$25Al_2O_3$–$25B_2O_3$ corresponding to the stoichiometric composition of $BaAlBO_3F_2$ is a new oxyfluoride glass with a high fluorine content, i.e., $F/(F + O) = 0.4$. They also found that Eu^{3+} ions (1 mol%) in $50BaF_2$–$25Al_2O_3$–$25B_2O_3$ glass exhibit a high quantum yield (η)

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of ~88% for the emission in the visible light region [7]. It is of interest to study oxyfluoride glasses based on the composition of $50BaF_2$–$25Al_2O_3$–$25B_2O_3$, in particular PL properties of RE^{3+} ions in those glasses more deeply and quantitatively.

In this paper, oxyfluoride $50BaF_2$–xAl_2O_3–$(50-x)B_2O_3$ glasses (x = 0–25) with different contents of Eu^{3+} and Tb^{3+} ions were synthesized by using a melt-quenching method, and the quantum yield, lifetime, and concentration quenching of Eu^{3+} and Tb^{3+} ions were measured. The present study proposes that oxyfluoride glasses with high BaO and Al_2O_3 contents have a high potential as hosts for new phosphors with RE^{3+} ions.

2. Experimental

Glasses with the compositions of $1Eu_2O_3$–$50BaF_2$–xAl_2O_3–$(50-x)B_2O_3$ (x = 0, 10, 20, 25), yEu_2O_3–$50BaF_2$–$25Al_2O_3$–$25B_2O_3$ (y = 0.5, 1, 3, 5, 10), and zEu_2O_3–$1Tb_4O_7$–$50BaF_2$–$25Al_2O_3$–$25B_2O_3$ (z = 0, 0.5) (mol) were prepared using a conventional melt-quenching method. Commercial powders of reagent grade Eu_2O_3, Tb_4O_7, BaF_2, Al_2O_3, and B_2O_3 were mixed, and mixtures (10 g batch) were melted in a platinum crucible at 1000–1250 °C for 20 min in an electric furnace in air. Melts were poured onto an iron plate and pressed into a thickness of ~1 mm using another iron plate. The glass transition, T_g, and crystallization peak, T_p, temperatures were determined using differential thermal analysis (DTA) at a heating rate of 10 K/min. Densities (d) of the glasses at room temperature were determined with the Archimedes method using distilled kerosene as an immersion liquid. Refractive indices (n) at a wavelength of λ = 632.8 nm (He–Ne laser) at room temperature were measured with a prism coupler (Metricon Model 2010).

The glass plates were mechanically polished using colloidal silica. PL and photoluminescence excitation (PLE) spectra were measured at room temperature with a spectrofluorophotometer (Shimadzu, RF-5300PC). Fluorescence lifetime (τ) measurements were performed on a FluoroCube (Horiba Jobin Yvon) with a 395 nm LED excitation source by a time-correlated single photon counting method. The red fluorescence emitted at λ = 612 nm ($^5D_0 \rightarrow {}^7F_2$) was collected using a detector. PL quantum yields in the visible region of Eu^{3+} ions were measured with a PL spectrometer with an integrating sphere (Hamamatsu Photonics: Absolute PL Quantum Yield Measurement System C9920-02) at room temperature.

3. Results and discussion

For all compositions of Eu_2O_3–BaF_2–Al_2O_3–B_2O_3 examined in the present study, optically transparent glasses were obtained. DTA curves for the glasses with the compositions of $1Eu_2O_3$–$50BaF_2$–xAl_2O_3–$(50-x)B_2O_3$ with x = 0–25 are shown in Fig. 1. The endothermic dips corresponding to the glass transition and exothermic peaks corresponding to the crystallization are observed in all samples. The values of T_g and T_p obtained from the DTA curves are summarized in Table 1. These glasses have values of T_g = 486–510 °C and T_p = 575–645 °C. As reported in the previous paper [7], the exothermic peak in the sample with $25Al_2O_3$ addition ($1Eu_2O_3$–$50BaF_2$–$25Al_2O_3$–$25B_2O_3$) is due to the crystallization of nonlinear optical $BaAlBO_3F_2$ crystals. It was confirmed that the glass with no Al_2O_3, $1Eu_2O_3$–$50BaF_2$–$50B_2O_3$, provided the formation of BaF_2 (the data are not shown here). It is then clear that the crystallization behavior in $1Eu_2O_3$–$50BaF_2$–xAl_2O_3–$(50-x)B_2O_3$ glasses changes largely with the addition of Al_2O_3. Bocker et al. [7] reported that fluorine is lost due to an unavoidable evaporation during melting. For instance, for the melting of $(100-x)(2Na_2O$–$16K_2O$–$8Al_2O_3$–$74SiO_2)$–$xBaF_2$ (mol%) with x = 0–5 at 1590 °C for 1.5 h, an average of about 34% of fluorine was lost during melting.

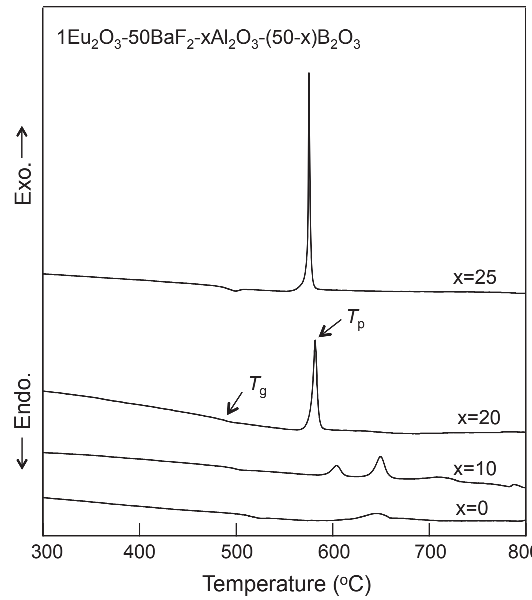

Fig. 1. DTA curves for $1Eu_2O_3$–$50BaF_2$–xAl_2O_3–$(50-x)$ B_2O_3 (x = 0, 10, 20, 25) glasses. T_g and T_p are the glass transition and crystallization peak temperatures, respectively. Heating rate was 10 K/min.

Table 1
Values of density (d), refractive index (n), glass transition temperature (T_g), crystallization peak temperature (T_p), and thermal stability parameter of $\Delta T = T_x - T_g$ for $1Eu_3O_3$–$50BaF_2$–xAl_2O_3–$(50-x)B_2O_3$ (x = 0.5–10) glasses.

	x = 0	x = 10	x = 20	x = 25
d (g/cm^3) ± 0.005	4.270	4.180	4.093	4.064
n	1.616	1.593	1.573	1.573
T_g (°C)	510	494	485	486
T_x (°C)	608	593	570	566
T_p (°C)	645	604	582	575
$\Delta T = T_x - T_g$ (°C)	98	99	85	80

In the present study, the glasses were melted at 1000–1250 °C for 20 min. Thus, the melting temperature is much lower and the melting time is shorter compared with the case reported by Bocker [7]. Parnice et al. [8] reported the glass transition temperature in $(50-x/2)BaO$–$(50-x/2)B_2O_3xAl_2O_3$ glass. For instance, the glass transition temperature in a glass with the composition of $49BaO$–$49B_2O_32Al_2O_3$ has reported as 571 °C. On the other hand, $1Eu_2O_3$–$50BaF_2$–$50B_2O_3$ glass, prepared in this study, has a much lower glass transition temperature (T_g = 510 °C) when compared with $49BaO$–$2Al_2O_3$–$49B_2O_3$ glass (T_g = 571 °C). It indicates that a large amount of fluorine is still present in the oxyfluoride glass prepared in this study.

The values of density and refractive index at room temperature for $1Eu_2O_3$–$50BaF_2$–xAl_2O_3–$(50-x)B_2O_3$ glasses are also summarized in Table 1. It can be seen that both density (d = 4.064–4.270 g/cm^3) and refractive index (n = 1.573–1.616) decrease with increasing Al_2O_3 content. The molecular weights of B_2O_3 and Al_2O_3 are 69.6 and 102.0 g/mol, respectively. Furthermore, the electronic polarizabilities of oxide ions (α_{O2-}) of B_2O_3 and Al_2O_3 are 1.345 and 1.460 Å^3, respectively [9]. It is expected simply from these values that the density and refractive index of $1Eu_2O_3$–$50BaF_2$–xAl_2O_3–$(50-x)B_2O_3$ glasses would increase with the substitution of Al_2O_3 for B_2O_3. The present results show the opposite trend, therefore, and suggest strongly that the structure of $1Eu_2O_3$–$50BaF_2$–xAl_2O_3–$(50-x)B_2O_3$ glasses changes significantly with the addition of Al_2O_3.

The PLE spectrum at room temperature for $1Eu_2O_3$–$50BaF_2$–$25Al_2O_3$–$25B_2O_3$ glass is shown in Fig. 2, in which the emission