Luminescent Properties and Energy Transfer Mechanism of Gd^{3+} and Eu^{2+} Co-doped Phosphate Glasses

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Received: 27 March 2014 / Revised: 22 September 2014 / Published online: 6 February 2015
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Abstract The phosphate glasses doped with Eu^{2+} , Gd^{3+} , respectively, and co-doped with Gd^{3+} and Eu^{2+} were prepared by high-temperature melting method. The transmission spectra, the excitation spectra, the emission spectra and the fluorescent decay time were investigated. The energy transfer process between Gd^{3+} and Eu^{2+} was studied. From the excitation spectra and the emission spectra of the phosphate glasses doped with Eu^{2+} , we observed that the emission intensity of Eu^{2+} shows higher for 0.02 mol% Eu^{2+} -doped phosphate glass. According to the excitation spectra and the emission spectra and the fluorescence decay curves, when the concentration of Eu^{2+} was 0.02 mol%, the optimal concentration of Gd^{3+} was 0.3 mol%. Based on Dexter theory, it is shown that the energy transfer between Gd^{3+} and Eu^{2+} was nonradiation energy transfer by analyzing the energy-level diagram. The fluorescence decay curves of Gd^{3+} were expressed by the Inokuti–Hirayama’s model and were used to analyze energy transfer mechanism between Gd^{3+} and Eu^{2+} . And the energy transfer efficiency was also calculated.

KEY WORDS: Europium oxide; Phosphate glass; Luminescent properties; Energy transfer; Inokuti–Hirayama’s model

1 Introduction

Rare-earth ions-doped glasses are of practical interest for a wide range of applications in high-energy physics experiments and gamma ray medical imaging (PET and SPET) [1]. Glasses doped with rare-earth ions have important advantages over crystals because of their low production cost, high transparency, compositional variety, drawn to flexible geometry and easy mass production, such as optic fibers. Detecting high-energy particles and gamma

rays usually requires scintillators with high light yield and short decay time [2].

As the potential materials for the memory devices and phosphors, Eu^{2+} -doped materials have attracted great attention. The luminescent properties of Eu^{2+} -activated materials have been investigated for a long time, and the divalent europium ions have been widely used as activators in phosphors [3–5]. Generally, a reductive atmosphere is needed to synthesize Eu^{2+} -activated luminescent materials because the raw material of Eu source is usually Eu_2O_3 [6]. The reduction of $\text{Eu}^{3+} \rightarrow \text{Eu}^{2+}$ in Al_2O_3 – SiO_2 glass prepared in air atmosphere had been reported by Nogami and Yamazaki [7]. The choice of host materials is a critical parameter for determining the optical properties of the Eu^{2+} . Eu^{2+} -doped silicate glasses have been reported widely. Qiao et al. [8] studied the blue emission from Eu^{2+} -doped high silica glass by near-infrared femtosecond laser irradiation. Thereafter, scintillation from Eu^{2+} in nanocrystallized glass had been investigated by Fu et al. [9]. Xiong et al. [10] reported the synthesis and

Available online at <http://link.springer.com/journal/40195>

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luminescent properties of $\text{CaO-SiO}_2\text{-B}_2\text{O}_3\text{:Eu}^{2+}$. Ye *et al.* [11] studied about the optical properties of $\text{Eu}^{2+}/\text{Sm}^{3+}$ co-doped silicate glass. However, the optical properties and energy transfer mechanism of $\text{Gd}^{3+}/\text{Eu}^{2+}$ -doped phosphate glasses have not been reported so far.

In this work, we studied the phosphate glasses doped with Eu^{2+} , Gd^{3+} , respectively, and co-doped with Gd^{3+} and Eu^{2+} at high temperature using aluminum powders and graphite powders as strong reducing agents. The excitation and emission spectra, the fluorescent decay time and energy transfer efficiency from Gd^{3+} to Eu^{2+} were investigated. Based on the fluorescence decay curves, Inokuti–Hirayama’s model was used to analyze energy transfer mechanism between Gd^{3+} and Eu^{2+} , proving that the energy transfer process of the electric dipole–dipole interaction is dominant in this system.

2 Experimental

Compositions of as-studied glasses are shown in Table 1. The starting materials were high-purity (99.99%) Eu_2O_3 and Gd_2O_3 powders, while P_2O_5 , BaO and Al_2O_3 were introduced from analytical purity ($\geq 99.7\%$) $\text{NH}_4\text{H}_2\text{PO}_4$, BaCO_3 and $\text{Al}(\text{OH})_3$ powders. Then, aluminum powders prepared with a half of the weight of Eu_2O_3 in all glass samples except sample G were completely mixed with the chemical agents. The powders of these starting materials were thoroughly mixed in appropriate proportions and placed in covered corundum crucibles in 20-g batches. The melting condition was 1,350 °C for 30 min in the reduced atmosphere. The reduced atmosphere was provided by using graphite powders which can avoid the oxidation of Eu^{2+} to Eu^{3+} during melting. The glass melts were poured into a preheated stainless steel plate, then annealed for 2 h at 480 °C in a muffle furnace to release the inner stress and cooled to room temperature slowly, and transparent glasses

were obtained herein. The size of these samples was 30 mm × 30 mm × 10 mm. All obtained glass samples were cut and polished to 5 mm thickness for experiments.

The transmission spectra were measured by Perkin-Elmer Lambda35 spectrometer. The luminescence spectra under UV excitation were obtained by Hitachi F-4500 spectrometer. The fluorescence decay curves were recorded under H_2 lamp pulse excitation. All the above measurements were taken at room temperature.

3 Results and Discussion

3.1 Transmission Spectra

Figure 1 shows the transmission spectra of the glass samples doped with 0.02 mol% Eu^{2+} and y mol% Gd^{3+} ($y = 0, 0.1, 0.2, 0.3, 0.4$ and 0.5) ranging from 200 to 600 nm. The glass samples exhibit high transparency in the visible and near UV region. The UV absorption edge of E2 glass sample starts to increase sharply at wavelengths slightly about 250 nm. The small absorption peak at about 312 and 394 nm is ascribed to the $4f^7 \rightarrow 4f^65d$ transitions of Eu^{2+} and the $^7F_0 \rightarrow ^5L_6$ transitions of Eu^{3+} [12]. By comparison, the transmission of $\text{Eu}^{2+}/\text{Gd}^{3+}$ co-doped glass samples starts to increase sharply at wavelengths slightly about 240 nm. The apparent absorption band peaks were observed at 312 nm in the glass samples can be attributable to the transitions of Eu^{2+} : $4f^7 \rightarrow 4f^65d$ and Gd^{3+} : $^6P \rightarrow ^8S_{7/2}$ [2, 13].

3.2 Excitation and Emission Spectra of Eu^{2+} -Doped Glasses

Figure 2 shows the excitation and emission spectra of Eu^{2+} -doped glasses. From Fig. 2, it can be observed that

Table 1 Compositions of the experimental glass samples (in mol%)

Sample	P_2O_5	BaO	Al_2O_3	Eu_2O_3	Gd_2O_3
E1	49.99	45.00	5.00	0.01	–
E2	49.98	45.00	5.00	0.02	–
E3	49.97	45.00	5.00	0.03	–
E4	49.96	45.00	5.00	0.04	–
E5	49.95	45.00	5.00	0.05	–
EG1	49.88	45.00	5.00	0.02	0.10
EG2	49.78	45.00	5.00	0.02	0.20
EG3	49.68	45.00	5.00	0.02	0.30
EG4	49.58	45.00	5.00	0.02	0.40
EG5	49.48	45.00	5.00	0.02	0.50
G	49.70	45.00	5.00	–	0.30

Fig. 1 Transmission spectra of the glass samples E2 and EG1–EG5 which doped with 0.02 mol% Eu^{2+} and (0–0.5) mol% Gd^{3+}

Fig. 2 Excitation spectra of Eu²⁺ monitored at 445 nm (left) and the emission spectra of Eu²⁺ excited at 312 nm (right) of Eu²⁺ singly doped glass samples E1–E5

the excitation spectra (left) were monitored with 445 nm and the sharp excitation peak located at 312 nm. Two emission peaks are located at 355 and 445 nm, which can be attributable to ${}^6P_{7/2} \rightarrow {}^8S_{7/2}$ transitions and $4f^65d \rightarrow 4f^7$ transitions of Eu²⁺ [8]. As shown in Fig. 2, the emission intensity of the Eu²⁺ is apparently enhanced with the concentration of Eu²⁺ increasing within 0.02 mol%. It can be explained by the fact that the efficient luminescence centres of Eu²⁺ ions increases with the increase in the concentration of Eu²⁺. However, the emission intensity of the Eu²⁺ decreases when the concentration of Eu²⁺ increases more than 0.02 mol%. It may be attributable to the short distance and the high collision probability between Eu²⁺, which results in the concentration quenching of Eu²⁺ luminescence. With the concentration of Eu²⁺ arriving at 0.02 mol%, the emission intensity of Eu²⁺ shows much higher than others for all the glass samples doped with Eu²⁺.

3.3 Energy Transfer from Gd³⁺ to Eu²⁺

Figure 3 shows the excitation spectra of E2 sample and emission spectra of G sample. As illustrated in Fig. 3, the emission spectrum of the 0.3 mol% Gd³⁺-doped phosphate glass sample excited with 275 nm and the excitation spectrum of the 0.02 mol% Eu²⁺-doped phosphate glass sample monitored at 445 nm exist overlap from 308 to 315 nm. It demonstrates efficient resonant energy transfer process from Gd³⁺ to Eu²⁺, increasing the intensity of the luminescent spectra of Eu²⁺, which can be explained by Dexter energy transfer theory [14].

Figure 4 shows the emission spectra for the glass samples doped with 0.02 mol% Eu²⁺ and different concentration of Gd³⁺ which are excited with a 275-nm UV light source. The emission spectrum of the E2 specimen exhibits

Fig. 3 Excitation spectrum of Eu²⁺ at 445-nm emission of sample E2, and the emission spectrum of Gd³⁺ at 275-nm excitation of sample G

Fig. 4 Emission spectra at 275-nm excitation of glass samples E2 and EG1–EG5 which doped with 0.02 mol% Eu²⁺ and 0–0.5 mol% Gd³⁺

two emission peaks located at 355 and 445 nm, which are mainly ascribed to the ${}^6P_{7/2} \rightarrow {}^8S_{7/2}$ and $4f^65d \rightarrow 4f^7$ transitions of Eu²⁺ [8]. Emission peaks for other specimens are located at 312, 355 and 445 nm, which are mainly attributable to the ${}^6P \rightarrow {}^8S_{7/2}$ transition of Gd³⁺ [2] and the ${}^6P_{7/2} \rightarrow {}^8S_{7/2}$ and $4f^65d \rightarrow 4f^7$ transitions of Eu²⁺ [8]. It can be found in Fig. 4 that the emission intensity of the Eu²⁺ in the glass samples co-doped with Eu²⁺ and Gd³⁺ shows stronger than the Eu²⁺ singly doped glass sample. This implies that the Gd³⁺ can sensitize the luminescence of Eu²⁺ and Gd³⁺ transfer energies to Eu²⁺ more efficiently. The emission intensity of the Eu²⁺ increases rapidly when the concentration of the Gd³⁺ increases within 0.3 mol%. It may be speculated that the distances between Eu²⁺ and Gd³⁺ decrease with the concentration of the Gd³⁺ increases, which results in more energy transfer

efficiency from Gd^{3+} to Eu^{2+} . However, when the concentration of Gd^{3+} is over 0.3 mol% at the 0.02 mol% Eu^{2+} -doping level, the emission intensity of the Eu^{2+} decreases. It may result from the efficient energy transfer process between Gd^{3+} increasing when the Gd^{3+} concentration reaching more than 0.3 mol%. The efficient energy transfer process between Gd^{3+} increasing leads to the suppressing of the energy transfer process from Gd^{3+} to Eu^{2+} . It could be known that the efficiency of energy transfer depends on the concentration of Gd^{3+} [15]. When the concentration of Eu^{2+} arrives at 0.02 mol% and Gd^{3+} arrives at 0.3 mol%, the emission intensity of the Eu^{2+} shows much stronger than other glass samples co-doped with Eu^{2+} and Gd^{3+} .

Figure 5 shows the energy-level diagram of Eu^{2+} and Gd^{3+} emissions and the processes of energy transfer from Gd^{3+} to Eu^{2+} , which further illustrate the energy transfer mechanism in the glass samples co-doped with Gd^{3+} and Eu^{2+} . This energy-level diagram indicates that energy transfer process from 6P , 6I and 6D states of Gd^{3+} to $4f^65d$ state of Eu^{2+} is possible. ${}^6P_{7/2}$ level of Gd^{3+} is very closer with $4f^65d$ state of Eu^{2+} , which results in the improvement of the probability of energy transfer efficiency between the two levels. Meanwhile, the ${}^6P_{7/2}$ level of Gd^{3+} is slightly higher than the $4f^65d$ state of Eu^{2+} , so the energy transfer process from Gd^{3+} to Eu^{2+} is irreversible and it is nonradiation resonant process. When Gd^{3+} is excited by 275-nm UV light source, Gd^{3+} can be excited from ${}^8S_{7/2}$ state to 6I state, then, down to the level ${}^6P_{7/2}$ state through resonant energy transfer process rapidly. Meanwhile, parts of the energy in the ${}^6P_{7/2}$ level of Gd^{3+} are transferred to the $4f^65d$ state of Eu^{2+} by resonant energy transfer process and then relax to ${}^6P_{7/2}$ state of Eu^{2+} , which can enhance the luminescence of Eu^{2+} .

Fig. 5 Energy-level diagram of Eu^{2+} and Gd^{3+} emissions and the processes of energy transfer from Gd^{3+} ions to Eu^{2+}

3.4 Decay Time

Figure 6 shows that the fluorescence decay curves of Gd^{3+} at 312 nm are excited by 275 nm for Gd^{3+} singly doped glass sample and Eu^{2+} and Gd^{3+} co-doped glass samples, which can get further insight in the energy transfer mechanism. With the increase in the concentration of Gd^{3+} at the 0.02 mol% Eu^{2+} -doping level, the fluorescent intensity decays of the Gd^{3+} in the Eu^{2+} and Gd^{3+} co-doped glass samples decrease rapidly, which can be ascribed to the energy transfer from Gd^{3+} to Eu^{2+} . However, when the concentration of Gd^{3+} is higher than 0.3 mol% at the 0.02 mol% Eu^{2+} -doping level, the fluorescent decay time increases clearly, which may be ascribed to the fact that the energy transfer efficiency from Gd^{3+} to Eu^{2+} decreases. It may indicate that the efficient energy transfer process between Gd^{3+} increased with the Gd^{3+} concentration reaching more than 0.3 mol%, which leads to the suppressing of the energy transfer process from Gd^{3+} to Eu^{2+} . And the average fluorescent lifetimes can be calculated by the following equation [16]:

$$\bar{\tau} = \frac{\int I(t)dt}{\int I(t)dt}, \quad (1)$$

where $I(t)$ represents the luminescence intensities during the decay time t as shown in Fig. 6.

The experimental measured decay curves (Fig. 6) are expressed by following the Inokuti–Hirayama's (I–H) model [17]:

$$I(t) = I(0) \exp \left[\left(-\frac{t}{\tau_s} \right) - \Gamma \left(1 - \frac{3}{n} \right) \frac{C}{C_0} \left(\frac{t}{\tau_s} \right)^{\frac{3}{n}} \right], \quad (2)$$

where τ_s is intrinsic life of sensitizer; n is the distance dependence of the crossrelaxation, where $n = 6, 8$ and 10

Fig. 6 Decay curves of Gd^{3+} for 0.3 mol% Gd^{3+} -doped sample (G) and 0.02 mol% Eu^{2+} and 0.1–0.5 mol% Gd^{3+} co-doped samples (EG1–EG5)

Table 2 The energy transfer efficiency (η_{ETE}) of the sample with 0.02 mol% Eu^{2+} and 0.1–0.5 mol% Gd^{3+} doping

Sample	η_{ETE} (%)
EG1	59.8
EG2	71.6
EG3	76.6
EG4	50.3
EG5	21.8

denote the electric dipole–dipole (Edd), electric dipole–quadrupole (Edq) and electric quadrupole–quadrupole (Eqq) interactions between luminescent centers; C is the concentration of activator; $C_0 = \frac{3}{4\pi R_0^3}$ is the critical concentration; $\Gamma(1 - \frac{3}{n})$ is a Gamma function.

By fitting the experimental fluorescent decay data to the I–H model, the fluorescent decays of Gd^{3+} singly doped glass sample and 0.02 mol% Eu^{2+} – x mol% Gd^{3+} ($x = 0.1, 0.2, 0.3, 0.4, 0.5$) co-doped glass samples obey the I–H model. From the fitting processes, τ_s from the data fitted with $n = 6$ by Eq. (2).

From the fluorescent decay curves, the energy transfer efficiency (η_{ETE}) can be determined, which is defined as the ratio of Gd^{3+} that depopulated by transferring energy to Eu^{2+} over the total number of Gd^{3+} being excited. The η_{ETE} is obtained as a function of the Gd^{3+} concentration as follows [17]:

$$\eta_{\text{ETE}} = 1 - \frac{\int I_{\text{EGX}} dt}{\int I_{\text{G}} dt}, \quad (3)$$

where I represents the intensity of 312 nm at time t , and EGX ($X = 1$ –5) and G are stand for samples EG1–EG5 and sample G. According to the fluorescent decay curves and Eq. (3), η_{ETE} for samples EG1–EG5 is obtained, as listed in Table 2.

4 Conclusions

Phosphate glasses doped with Eu^{2+} , Gd^{3+} , respectively, and co-doped with Gd^{3+} and Eu^{2+} were studied. The sample doped with 0.02 mol% Eu^{2+} has the highest luminescent intensity in the Eu^{2+} -doped samples group. Gd^{3+} can sensitize the luminescence of Eu^{2+} , and the nonradiation energy transfer process from Gd^{3+} to Eu^{2+} is

irreversible. When the concentration of Gd^{3+} arriving at 0.3 mol% (where Eu^{2+} is 0.02 mol%), the emission intensity of the Eu^{2+} in the Eu^{2+} and Gd^{3+} co-doped sample much stronger than that of other glass samples in the group of samples co-doped with 0.02 mol% Eu^{2+} and (0.1–0.5) mol% Gd^{3+} . The energy transfer process from Gd^{3+} to Eu^{2+} is nonradiation resonant process which was verified by Dexter theory. The energy transfer efficiency (η_{ETE}) of the 0.02 mol% Eu^{2+} – x mol% Gd^{3+} ($x = 0.1, 0.2, 0.3, 0.4, 0.5$) co-doped glass samples is 59.8, 71.6, 76.6, 50.3 and 21.8%, respectively.

Acknowledgments This work was financially supported by the National Natural Science Foundation of China (Nos. 61275180 and 51472125), the Natural Science Foundation of Ningbo City (No. 2013A610126), the Outstanding Dissertation Growth Foundation of Ningbo University (No. PY2013009) and the K. C. Wong Magna Fund in Ningbo University.

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