

Preparation and optical spectroscopy of phosphate glasses containing divalent europium ions

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P₂O₅.BaO.Na₂O.K₂O glasses doped with various content of Eu₂O₃ were prepared using high temperature melting method, and the Eu²⁺ ions in the phosphate glasses were obtained with the aid of the reductive action of silicon powder. The fabricating conditions, fluorescence, excitation spectra of the glasses were then studied. The glasses containing europium show a broad emission band at 450 nm and sharp bands from 580 to 650 nm, and the co-existence of Eu²⁺ and Eu³⁺ is identified. Also, a good glass with a dominant proportion and large quantity of Eu²⁺ ions can be obtained by the reductive action of silicon powder and proper processing.

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Glasses containing rare earth ions have been extensively studied and widely used in optical devices^[1,2]. Rare-earth ions are energetically preferred to remain in the trivalent state. Some rare-earth ions such as Eu, Sm, and Yb can be presented as divalent ions in some hosts. Recently, Eu²⁺ ion doped borate and fluoro-aluminate glasses were fabricated and their optical properties were also investigated^[3,4]. They have large potential applications in optical fields such as Faraday rotator, phosphor, electro-luminescent device, detectors of radio rays' two-dimensional image, tunable laser with wave band from blue to violet and high-density optical storage device^[3-7]. When the glass is melted, the rare earth ions are incorporated as trivalent state ions. Some technical methods were applied to obtain divalent europium. For example, the glasses containing europium ions are melted under strong reducing atmosphere of H₂. For the practical application of the Eu²⁺ doped glass, we must find a convenient and effective technique to make the glass with high concentration of the Eu²⁺ ions. In this work, we prepared Eu²⁺ ions doped glasses using silicon powder as a strong reducing agent. In this paper, the fabrication conditions and the spectra of Eu²⁺ ions-doped phosphate glass have been described. The phosphate glass was chosen to be the host for europium ions because of high solubility for rare earth elements which allows the high Eu²⁺ ion concentration in the glass.

The components of the Eu₂O₃ in mole percent in glasses and the silicon powder used in weight percent are listed in Table 1. Na₂O, and K₂O were introduced in the

form of reagents Na₂CO₃ and K₂CO₃. All the chemical agents were of 99.9% purity. The Eu₂O₃ and Si powder were completely mixed with the chemical agents. The batches of 50 g were melted in an Al₂O₃ corundum crucible under air atmosphere.

After keeping at 1200 °C for 1 hour, the glass melt was poured on a stainless steel plate. The cooling rate was estimated at about 10 °C/s. Each glass was annealed for 2 hours at 450 °C and cooled to room temperature slowly. Transparent light-yellow glasses were obtained herein. The samples were cut into small pieces with thickness of 2 mm and well polished. The excitation and emission spectra were afterwards recorded with a Hitachi F-4500 fluorescence spectrophotometer at room temperature.

The Eu³⁺ ions, of which the lowest excited level (⁵D₀) of the 4f⁶ configuration is situated below the 4f⁵5d configuration, show very sharp emission lines ranging from 650 nm to near infrared due to f - f transitions. However, the Eu²⁺ ions have complex energy levels. The energy level of Eu²⁺ ion is expressed in Fig. 1. The first excited 4f⁶5d configuration lies close to the 4f⁷ ground level. The transitions between the first excited 4f⁶5d configuration and 4f⁷ ground state are dipole allowed and give a very intense emission intensity. Meanwhile, the emission spectra due to the f - d transition of Eu²⁺ ions are usually wide because of the large spatial extension of the 5d wave function. The emissions due to 5d-4f transition and ⁶P_{7/2} - ⁸S_{7/2} transition of Eu²⁺ ions are strongly influenced by the glass matrixes. The 4f levels of Eu²⁺ ion are little influenced by the ligand field of the first coordinating sphere, while 5d levels are highly affected by the state of chemical bonds between Eu²⁺ ions and the anions of the first coordinating sphere. It has been demonstrated that only a broad emission band due to the transition of 5d levels and ground state of Eu²⁺ ions are observed when Eu²⁺ ions are incorporated in oxide glasses excited by UV light^[3,4]. However, when Eu²⁺ ions are coordinated by relative weak fluorine anion ions, the emission at 360 nm due to the transition ⁶P_{7/2} - ⁸S_{7/2}

Table 1. Chemical Compositions of Base Glasses in mol%

	P ₂ O ₅	BaO	Na ₂ O	K ₂ O	Eu ₂ O ₃ *	Si**
0.5 EuP	45	35	10	10	0.5	0.2
1.0 EuP	45	35	10	10	1.0	1.0
3.0 EuP	45	35	10	10	3.0	3.0

*In wt.%. **Si powder, also in wt.%.

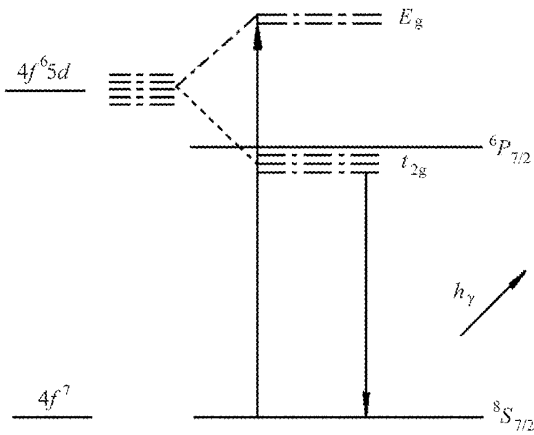


Fig. 1. Energy levels of Eu^{2+} ions.

of Eu^{2+} ions appears.

Figure 2 shows the emission spectra of the glasses with different content of Eu_2O_3 and silicon powder by 394 nm excitation. It can be seen from the curve of 0.5 EuP sample that some small sharp emission peaks between 580 – 650 nm, which are assigned to the transition of ${}^5D_0 - {}^7F_j$ ($j = 1, 2$) of Eu^{3+} ion, are observed. However, as the ratio in weight between Si powder and Eu_2O_3 increases from 0.4 to 1, it appears a new broad emission band at 470 nm of 1.0 EuP sample and 500 nm of 3.0 EuP, which is ascribed to the $5d - 4f$ transition of Eu^{2+} ion. The intensity of bands between 580 – 650 nm reduces gradually from the curve of 0.5 EuP sample to that of 3.0 EuP sample. And the peaks almost disappeared in 3.0 EuP sample. However, the emission intensity of 450 nm band increases greatly, indicating that overall Eu^{3+} ions are reduced to Eu^{2+} ions in 1.0 EuP and 3.0 EuP samples.

It can be noted from Fig. 2 that the remaining Eu^{3+} ions in 1.0 EuP glass is higher than that in 3.0 EuP although the same ratio in weight ratio of silicon powder and Eu_2O_3 in 1.0 EuP and 3.0 EuP glasses. The relatively high quantity of Eu_2O_3 and silicon powder in 3.0

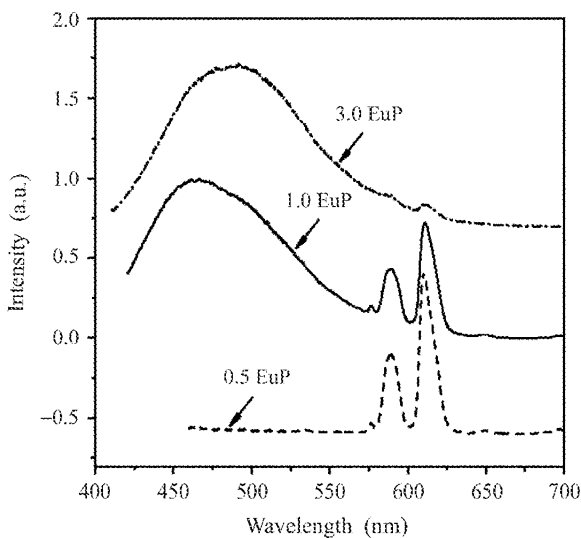


Fig. 2. Emission spectra of glasses containing various contents of Eu_2O_3 and silicon powder at 394 nm excitation.

EuP glass provides more reacting opportunities between Eu^{3+} ion and silicon powder, resulting in fewer remaining Eu^{3+} ions in 3.0 EuP glass; it is probably the main reason of the above case although the detailed ones are not clear at present time.

It should be noted that the peak position of Eu^{2+} ions emission is red-shifted as europium ion concentration increases. This phenomenon is very similar to that reported for Eu^{2+} ions in fluoroaluminate glass. Qiu *et al.*^[3] supposed that the probability of Eu^{2+} ions at higher level of $5d$ relax or energy transfer to the lower $5d$ levels of Eu^{2+} ions in the same or different sites increases with the increase of Eu^{2+} ion concentration. The reason of the occurrence of the red shift of the emission may go to the increase of the ratio of the emission between lower $5d$ level and ground state of Eu^{2+} ions compared to those between higher $5d$ levels and ground state transition.

Figure 3 shows the emission spectra of 3.0 EuP sample by 290- and 430-nm excitation, respectively. Broad emission bands at 470 and 500 nm of Eu^{2+} are observed under the excitation of the above samples by 290- and 430-nm light. The band of Eu^{2+} is red-shifted as the wavelength of excited light increases. Because the Eu^{2+} ions are excited to a higher level of $5d$ by 290-nm light, the emission band wavelength excited by 290 nm should be shorter than that excited by 430 nm, although some processes such as relaxation and energy transfer occur. This corresponds to that shown in Fig. 3.

Figure 4 shows the excitation spectra of 1.0 EuP glass for emission at 465 nm is monitored, and 3.0 EuP glass when the emission at 487 nm is monitored. Broad bands at 400 and 260 nm in 1.0 EuP glass and at 450 and 260 nm in 3.0 EuP glass are observed. The occurrence of the bands at 400 and 450 nm are ascribed to the $5d - 4f$ transition of Eu^{2+} ion, while the band at 260 nm probably originates from the transition of the charge transfer state of the Eu^{3+} ion. By comparing the relative intensity of 260-nm bands in 1.0 EuP and 3.0 EuP, it can be further demonstrated that the remaining Eu^{3+} ions in 3.0 EuP glass are fewer. Meanwhile, it should be considered that ${}^6P_{7/2}$ level lies above the lower $5d$ levels of Eu^{2+} ion

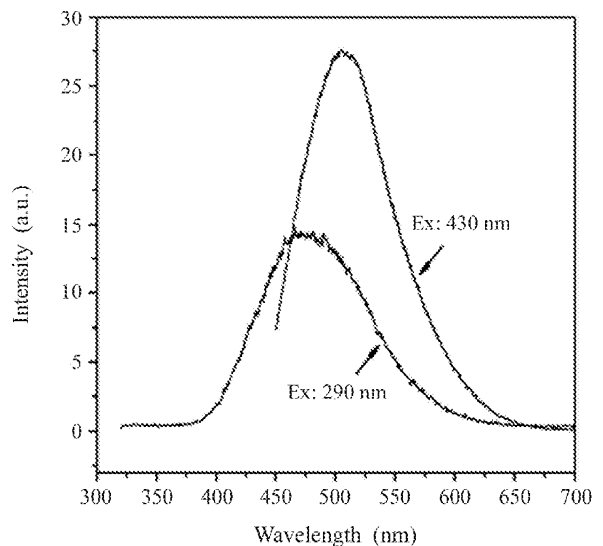


Fig. 3. Emission spectra of 3.0 EuP glass by 290 and 430 nm excitations.

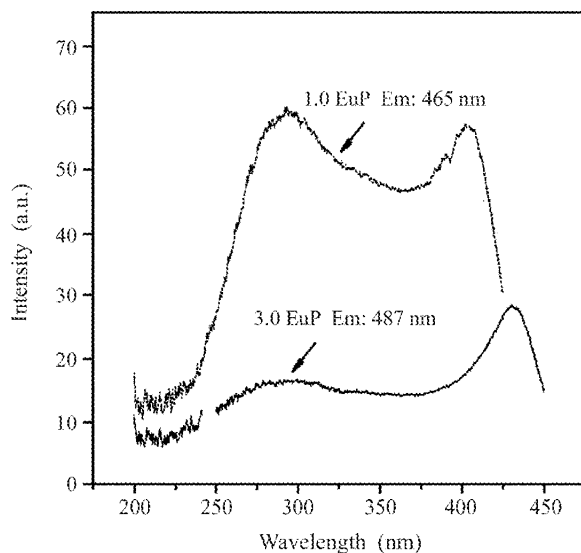


Fig. 4. Excitation spectrum of 1.0 EuP glass at 465 nm monitored and excitation spectrum of 3.0 EuP glass at 487 nm monitored.

via a comparison of the maximum emission wavelength of 450 nm in Fig. 4 with the emission wavelength of 360 nm for ${}^6P_{7/2}$ to ${}^8S_{7/2}$ level^[6].

Figure 5 shows the excitation spectra of the Eu-doped glass monitored with 610 nm. A broadband having a peak at 240 nm is observed, which probably originated from the transition of the charge transfer state of the Eu^{3+} ion. Sharp peaks are also observed at 362, 387, 393, 414, 464 and 531 nm, respectively. These peaks are associated with the $f-f$ transitions of Eu^{3+} ions and can be attributed to 5D_4 , 5G_3 , 5L_6 , 5D_3 , 5D_2 and 5D_1 energy levels, respectively.

As shown in the above figures, the presence and change of the emission and excitation spectra bands confirm that Eu^{2+} ions exist in the glasses under the effect of silicon powder. The content of silicon and composition of raw materials strongly affect the state of europium ions.

In conclusion, the fabrication conditions and fluorescence characteristics of a phosphate glass containing Eu^{2+} ions have been described. Eu^{3+} ions in the reducible effect of silicon powder become divalent, while some of europium ions still exist as trivalent state. The glasses with 3% in weight of Eu_2O_3 containing a dominant proportion of Eu^{2+} ions can be obtained by the processing and under reaction of silicon powder. The emission peak of Eu^{2+} ion is red-shifted as the content of Eu^{3+} ion and the wavelength of excited light increase. Our experiments demonstrate that the present processing is an appropriate and feasible way for incorporating the reduced ions in glass.

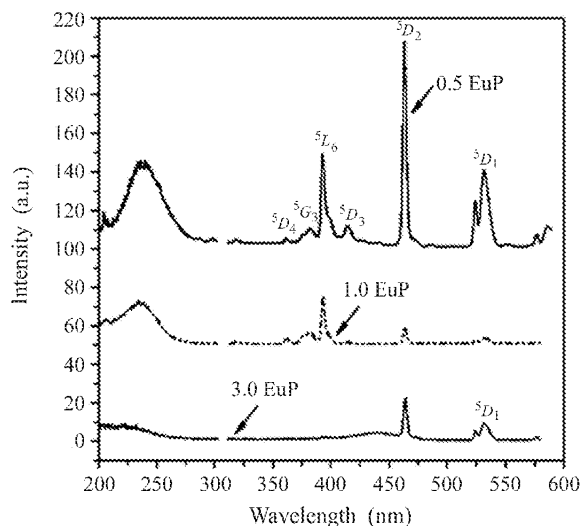


Fig. 5. Excitation spectra of glasses with different content of Eu_2O_3 and silicon powder at 610 nm monitored.

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