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Preparation and optical spectroscopy of $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ glasses containing divalent and trivalent europium ions

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Abstract

Eu_2O_3 was incorporated into $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ glasses by a melting technique in air atmosphere. Optical absorption, fluorescence, excitation and time-resolution spectra and fluorescence dynamics were studied in the glasses. The results indicate that Eu^{2+} and Eu^{3+} ions co-exist in the glass and the energy transfers from Eu^{2+} ions to Eu^{3+} ions, in which the energy corresponding to the $4f^65d$ to $8S_{7/2}$ transition of Eu^{2+} ions causes to excite the Eu^{3+} ion to the $5D_J$ level. © 2002 Elsevier Science B.V. All rights reserved.

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Glasses containing rare earths such as Nd^{3+} and Er^{3+} have attracted great attentions as materials for optical devices [1]. Among other rare earth-containing glasses, divalent rare earth ions doped glasses are generating much interest for their important potential applications such as hole burning memory materials [2]. Recently, borate and fluoro-aluminate glasses doped with Eu^{2+} ions were fabricated and their fluorescence characteristics were investigated, and those glasses were expected to be used as detectors of two-dimensional image of radio rays and tunable laser in the wavelength region from violet to blue [3,4]. The glasses were prepared by melting the starting

materials under H_2 gas atmosphere. Although Eu^{3+} ions are reduced to the Eu^{2+} ions state during melting, some problems still exist: they are not very durable due to the borate and fluoride composition. In order to obtain Eu^{2+} ions in glass matrices, glasses should be treated under a strong reducing atmosphere because of the stability of Eu^{3+} in these glass matrices. This prevents the use of the glasses in practical applications.

It has been demonstrated that the basicity of the oxygens in the aluminosilicate glasses is lowered by the addition of Al^{3+} ions, which is expected to obtain Eu^{2+} in glass [6,7]. In this paper, we prepared the $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ doped europium ion glasses and demonstrated the Eu^{2+} ions existing in the glasses without a reducing atmosphere, and studied the fluorescence characteristics of the glasses. The understanding of the host of the fluorescence behavior is

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significant to search for new host glasses for divalent rare earth.

The composition of glass in weight percent containing normally 0, 0.5, 1, 2 wt.% is $65.1\text{SiO}_2\text{-}22.6\text{Al}_2\text{O}_3\text{-}4.2\text{Li}_2\text{O}\text{-}0.6\text{MgO}\text{-}0.9\text{Na}_2\text{O}\text{-}0.6\text{K}_2\text{O}\text{-}2.0\text{TiO}_2\text{-}2.3\text{ZrO}_2\text{-}1.2\text{P}_2\text{O}_5\text{-}0.5\text{Sb}_2\text{O}_3$. Al_2O_3 is introduced in the form of reagents $\text{Al}(\text{OH})_3$, other raw materials are 99.9% purity oxides or carbonates. The batches of 100 g were mixed in an Al_2O_3 corundum crucible under air atmosphere. After keeping at 1550–1600 °C for 2 h, the glass melt was poured onto a stainless-steel plate. Each glass was annealed for 2 h at 600 °C temperature and cooled it to room temperature slowly. The glass samples were cut into small pieces with thickness of 1 mm and well polished. The absorption, excitation and fluorescence spectra were all recorded with a Hitachi F-4500 fluorescence spectrometer with resolution of 1 nm. The absorption spectra were detected with a UV/visible spectrophotometer (cary 100). The time-resolution spectra and the fluorescence dynamics were investigated using a 266-nm pulsed light as pumping. The 266-nm light was generated by the $\text{Nd}^{3+}:\text{YAG}$ laser with line width of 0.2 cm^{-1} , pulse duration of 10 ns and repetition frequency of 10 Hz passing a multi-frequency crystal. A Boxcar and a Spex 1403 spectrometer were used as detection.

Fig. 1 is the optical absorption spectra of the Eu-doped glass in comparison with the undoped one. It can be seen from Fig. 1 that the absorption coefficient,

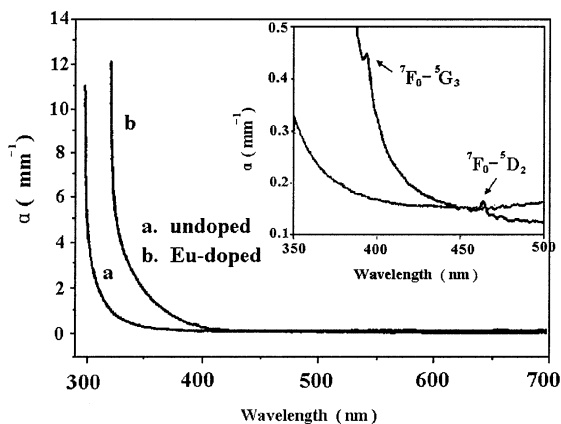


Fig. 1. Optical absorption spectra in one host and one Eu-doped (2 wt.%) glass. Inset: The sample spectra in a small scale.

cient, α , in the visible range of 400–700 nm, almost does not vary with wavelength, for both the two glasses. While α increases significantly with the decreasing wavelength, compared to the host glass in the UV range, the absorption limit of the Eu-doped glass is red-shifted, indicating the absorption band caused by Eu ions occurs below 400 nm. This broad band may be related to the transition from the $4f^7$ to $4f^65d$ level of Eu^{2+} ions. From the inset, two sharp absorption peaks at 393 and 464 nm were observed in the Eu-doped glass, which is attributed to the ${}^7\text{F}_0\text{-}{}^5\text{G}_3$ and the ${}^7\text{F}_0\text{-}{}^5\text{D}_2$ transition of Eu^{3+} by the analogy with the electric energy diagram of free ions. It can be noticed from Fig. 1 that the absorption caused by the f–f transition of Eu^{3+} ions was not changed.

Fig. 2 is the fluorescence spectra of the Eu^{2+} and Eu^{3+} ions in the glass. A broad emission band is observed, and the band can be deconvoluted into components for convenience using Gaussian functions. The peaks and the full widths of the half maximum of the two Gaussian functions are 475, 93 and 550, 132 nm, respectively [5]. The 5d orbital of Eu^{2+} is split into two components of E_g and T_{2g} of the coordinates surrounding the Eu^{2+} ions. Therefore, the two bands can be assigned to E_g and T_{2g} , respectively [5]. The sharp lines of ${}^5\text{D}_0\text{-}{}^7\text{F}_J$ of the Eu^{3+} ions are also observed in the glass. Among them, the emission of ${}^5\text{D}_0\text{-}{}^7\text{F}_2$ is strongest. Here, the transitions of ${}^5\text{D}_J$ ($J=1,2,4$), ${}^5\text{G}_3$ and ${}^5\text{L}_6$ to the ground states ${}^7\text{F}_J$ are not clearly observed because they are weak and are covered by the 4f5d fluorescence of Eu^{2+} ions.

Fig. 3 shows the excitation spectrum of the Eu-doped glass while the transition of ${}^5\text{D}_0\text{-}{}^7\text{F}_2$ is monitored at 614-nm wavelength. A broad band having a peak at 240 nm is observed, which is attributed to the transition from the ${}^8\text{S}_{7/2}$ to $4f^65d$ level. The result suggests that the energy transfer may occur from Eu^{2+} to Eu^{3+} ions. Under coexistence of the Eu^{2+} and Eu^{3+} ions, the excited Eu^{2+} in the $4f^65d$ level of E_g nonradiatively relax to the ground state ${}^8\text{S}_{7/2}$, and the energy corresponding to the $4f^65d \rightarrow {}^8\text{S}_{7/2}$ transition causes to excite the Eu^{3+} ion to the ${}^5\text{D}_J$ state. The sharp lines are observed at 340, 362, 387, 393, 414, 464 and 531 nm, respectively. These lines are caused by the f–f transition of Eu^{3+} . Their detailed origins are labeled in Fig. 3. The absorption, excita-

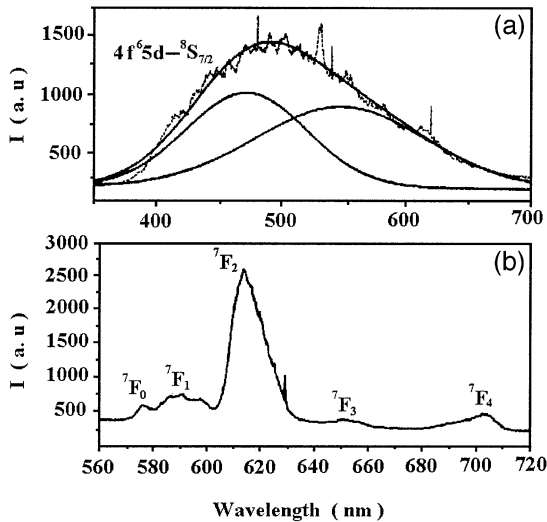


Fig. 2. Fluorescence spectra of Eu^{2+} (a) and Eu^{3+} ions (b) in the Eu-doped (2 wt.%, this glass is used as a typical one) glass.

tion and fluorescence spectra strongly indicate that the Eu^{2+} and Eu^{3+} ions co-exist in the glass.

In general, europium ions in the highly reduced glass become the divalent state, while some of the europium ions still exist as trivalent state for the slightly reduced glass, and the state of europium ions should be also strongly affected by composition and structure of the glass. Nogami and Abe [6] had already found that the europium ions were preferentially coordinated with Al–O polyhedra and the covalency of the Eu–O bond was decreased by the

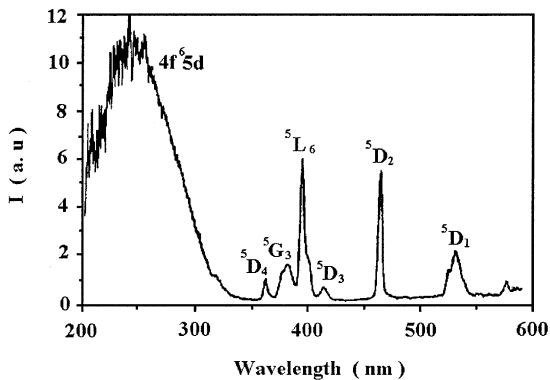


Fig. 3. Excitation spectrum of the Eu-doped glass (the monitor position is at 614 nm, within the ${}^5\text{D}_0$ – ${}^7\text{F}_2$ transition of Eu^{3+} ions).

coordinated Al^{3+} ions in the Al_2O_3 – SiO_2 glasses. In the glass system, the Eu ions are coordinated with nonbridging and bridging oxygens. The composition of Al_2O_3 or alkaline oxide in the glass generates nonbridging oxygens, causing a more open network structure. The inducing Li_2O into glass is mainly to lower the melting temperature of the glass. The electron donation ability of the oxygen surrounding the Eu ions is mainly affected by the alkaline ions or Al^{3+} ions. A phenomenon classified by the microscopic optical basicity had been proposed and found by Duffy and Ingram [7]. The introduction of alkaline ions caused the basicity to increase thus stabilizing the upper oxide state of the Eu ions. On the other hand, the basicity was lowered by the addition of Al^{3+} ions, which favored the reduction of Eu^{3+} ions [7]. Fig. 4 is the Raman spectrum of the host glass, which was measured by the excitation of a 488-nm light at room temperature. Two phonon bands at 1153 and 623 cm^{-1} are observed. Their origins are attributed to the vibration bands of Si–O and Al–O bonds, respectively. The width of the two bands is both about 100 cm^{-1} , indicating that the high content of Al–O occupy in the network of glass. In the present cause, the molar ratios of $\text{Al}^{3+}/\text{Si}^{4+}$ and $\text{Al}^{3+}/(\text{Li}^+ + \text{Mg}^{2+} + \text{Na}^+ + \text{K}^+)$ are 0.41 and 1.4, respectively. Such high Al_2O_3 content and the molar ratio between Al^{3+} and alkaline ions generated very lower basicity of the glass and are well in favor of reduction of Eu^{3+} to Eu^{2+} ions. Therefore, the Eu^{2+} ions exist in the glass without treatment under reduction atmosphere.

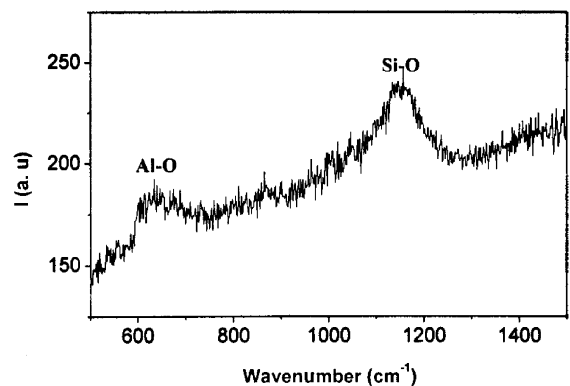


Fig. 4. Raman spectrum of the host glass.

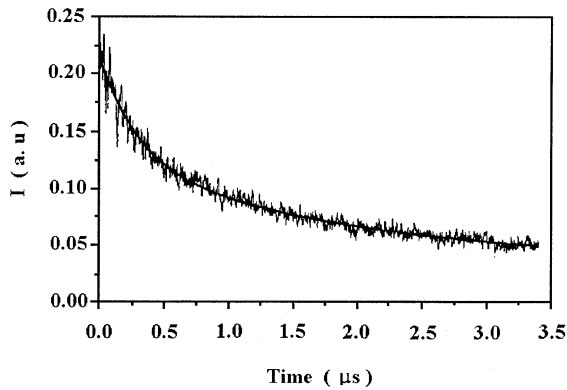


Fig. 5. Fluorescence dynamics of Eu^{2+} . The excitation wavelength is 266 nm, the monitor position is 500 nm. The smooth lines are bi-exponential fitting functions.

Fig. 5 shows the fluorescence dynamics of Eu^{2+} in the time scale of several microseconds. The dynamics is well fitted by bi-exponential functions. The two exponential decay constants are determined to be 0.30 ± 0.03 and $2.8 \pm 0.2 \mu\text{s}$ by fitting. Roughly to estimate, the increasing time constant should be shorter than several 10 ns. Fig. 6(a) and (b) shows

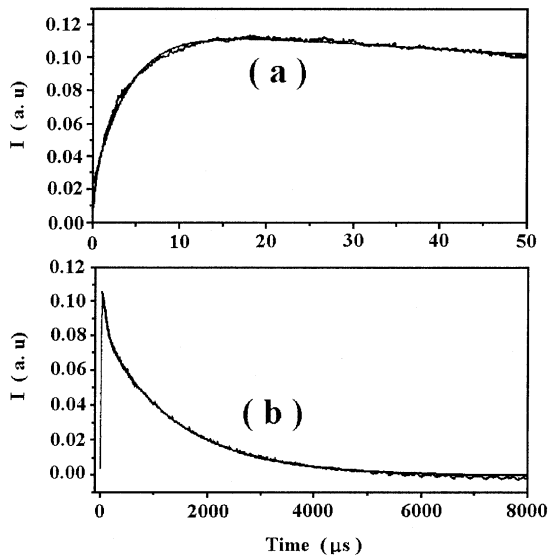


Fig. 6. Fluorescence dynamics of Eu^{3+} (a) in a short time scale and (b) in a long time scale. The excitation wavelength is 266 nm, the monitor position is 614 nm. The smooth lines are exponential fitting functions.

Table 1

Variation of relative emission intensity and fluorescence lifetime of the ${}^5\text{D}_0-{}^7\text{F}_2$ transition of Eu^{3+} ions on Eu concentration

Eu concentration (wt.%)	0.5	1	2
Relative intensity	0.75	0.84	1.00
Lifetime (μs)	1800	1650	1500

the fluorescence dynamics of the Eu^{3+} ions in different time scales. It is obvious that the fluorescence of Eu^{3+} increases firstly. Then, it decays with a long exponential tail. There exist two increasing time constants: one constant is $3.2 \pm 0.2 \mu\text{s}$ and the other one is smaller than $0.5 \mu\text{s}$. The two increasing constants of Eu^{3+} ions are properly united with the two decay constants of Eu^{2+} ions. The decay time constant of Eu^{3+} ions in the 2 wt.% Eu-doped glass is $1500 \pm 50 \mu\text{s}$. The fluorescence intensity and the decay time constants of the glasses with different Eu concentration were measured and compared, as listed in Table 1. The fluorescence intensity increases with the increase of Eu concentration. On the other hand, the decay time constant becomes slightly small. This result indicates that the concentration quenching is not serious when the Eu_2O_3 concentration is smaller than 2% in the glasses.

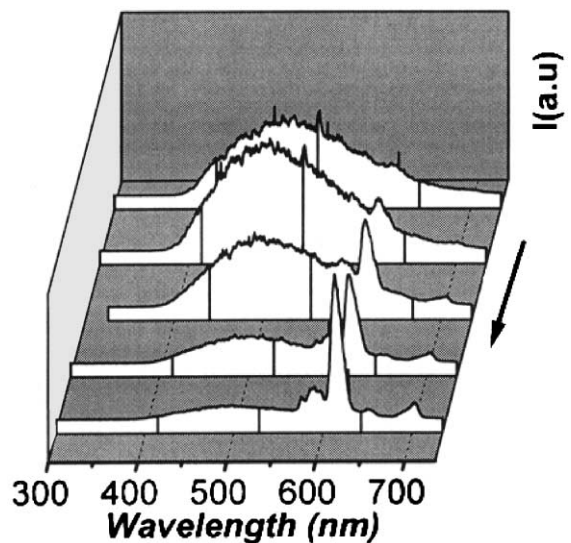


Fig. 7. Time-resolution spectra of the Eu-doped glass. In the measurement, the excitation wavelength is 266 nm. The arrow in the figure indicates the increasing delay time.

Fig. 7 shows the time resolution spectra of the glass. It is more obvious that the emission increase of Eu^{3+} ions is accompanied by the fluorescence decrease of Eu^{2+} ions. The above results strongly support that the energy transfer happened between Eu^{2+} and Eu^{3+} ions. When excited with a laser light within the $8\text{S}^{7/2}-4\text{f}^65\text{d}$ transition of the Eu^{2+} ions, the energy corresponding to the $4\text{f}^65\text{d}$ to $8\text{S}_{7/2}$ transition of Eu^{2+} ions caused to excite the Eu^{3+} ion to the 5D_J level.

In conclusion, aluminosilicate glass containing high Al_2O_3 was prepared by high-temperature melting technique at air atmosphere. The Eu^{2+} and Eu^{3+} ions co-exist in the glass confirming from the absorption, excitation and fluorescence spectra. The Al^{3+} ions in particular affected the state of Eu ions. The basicity of the oxygens in the aluminosilicate glasses was lowered by the addition of Al^{3+} ions, thus resulting in the existence of Eu^{2+} in the glass. At the meantime, the energy transition from Eu^{2+} ions to Eu^{3+} was confirmed from the time resolution spectra.

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References

- [1] V.P. Gapontsev, S.M. Mtisin, A.A. Isineev, et al., *Opt. Laser Technol.* 14 (4) (1982) 189.
- [2] K. Hirao, S. Todoroki, D.H. Cho, N. Soga, *Opt. Lett.* 18 (1993) 1586.
- [3] J. Qiu, N. Sugimoto, K. Hirao, *J. Appl. Phys. Lett.* 71 (6) (1997) 759.
- [4] J. Qiu, K. Miura, N. Sugimoto, K. Hirao, *Phys. Chem. Glasses* 38 (2) (1997) 66.
- [5] M. Nogami, T. Yamazaki, Y. Abe, *J. Lumin.* 78 (1998) 63.
- [6] M. Nogami, Y. Abe, *J. Non-Cryst. Solids* 197 (1996) 73.
- [7] J.A. Duffy, M.D. Ingram, *J. Non-Cryst. Solids* 21 (1976) 373.