A study of the luminescence properties of Eu^{3+}-doped borate crystal and glass

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Abstract

Eu^{3+}-doped La$_2$O$_3$–3B$_2$O$_3$ crystal and glass were prepared by solid state reaction under different calcination temperature. The emission spectrum, phonon sideband (PSB), charge transfer band (C.T.B.) and lifetime of the Eu^{3+} ion in the two materials, with the same composition but with different phase, were investigated. With excitation at 394 nm light, the glass presented intense 618 nm red luminescence; however, the crystal gave 696 nm red luminescence. This difference is ascribed to the discrepancy of the local structure around the Eu^{3+} ion in the crystal and glass. To clarify the discrepancy, the coordination of Eu^{3+} in the borate glass and crystal was investigated. The results show that Eu^{3+} ions formed a complex Eu^{3+}–O^{2-}–B^{3+} bond in glass; however, in the crystal, it formed a complex Eu^{3+}–O^{2-}–La^{3+} bond. The lifetime of Eu^{3+} ions in the crystal and the glass is 3.08 ms and 1.98 ms, respectively. This indicates that the discrepancy in the local structure around the Eu^{3+} ions between the crystal and the glass leads to different fluorescence properties.

1. Introduction

Glasses and crystals containing rare earths have attracted great attention because of their extensive applications in fields such as information display, advanced laser materials and fiber optical communication [1,2]. Among these rare-earth-containing materials, Eu^{3+}-doped fluorescent materials have recently been generating much interest for applications as lighting, cathode ray tube (CRT), plasma display panels (PDPs) and field emission devices (FED). For the Eu^{3+} ion, as the energy gap for ^{5}D$_0$–^{7}F$_J$ ($J = 0$–6) is much larger than that for ^{5}D$_{J+1}$–^{5}D$_J$ ($J = 0$–3), the multiphonon relaxation process is predominant between the ^{5}D$_J$ levels, and radiative emission mainly occurs from the ^{5}D$_0$ level to ^{7}F$_J$ ($J = 0$–6) in oxide hosts with higher phonon energy. Also, the phonon sideband (PSB) can be clearly observed on the high energy side of the ^{5}D$_0$–^{7}F$_2$ transition. It is known that the transitions ^{5}D$_0$–^{7}F$_J$ ($J = 0$–6) are sensitive to the local structure around the Eu^{3+} ion. Thus, the Eu^{3+} ion is a good probe [3]. In this paper, we present the prepared method and an investigation of the luminescence properties of Eu^{3+} in La$_2$O$_3$–3B$_2$O$_3$ crystal and glass phases. Eu^{3+}-doped La$_2$O$_3$–3B$_2$O$_3$ crystal and glass were prepared by solid state reaction under different calcination temperatures. It was found that, with excitation by 394 nm light, the glass presented intense 618 nm red luminescence, while the crystal gave 696 nm red luminescence. In order to clarify the causes that make the Eu^{3+} ion present different luminescence, the emission spectroscopy, phonon sideband, charge transfer band and lifetime of the as-prepared samples were measured. Results show that the coordination of Eu^{3+} is different, which leads to the microstructure around the Eu^{3+} ion being different. It was concluded that the difference in spectroscopy of Eu^{3+} is ascribed to the discrepancy of the local structure around the Eu^{3+} ion in the crystal and glass.

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2. Experimental

The glass and crystal samples with composition La_2O_3–$3B_2O_3$–$0.06Eu_2O_3$ were prepared by using reagent grade H_3BO_3 powder and 4N grade La_2O_3 and Eu_2O_3 powders. The powders were well mixed in an agate mortar and melted in a corundum crucible with a cover in a muffle furnace. By controlling the reaction temperature at 960 °C for 2 h, H_3BO_3 breaks down. The samples were cooled, rubbed well, and put back in the muffle furnace again. With the reaction temperature kept at 960 °C for 30 min, one sample was removed, cooled to room temperature, and thus the crystal sample was obtained. For the other sample, the temperature was kept at 1200 °C for 2 h, then the melt was poured into a stainless steel mold quickly, and pressed with another steel plate, then a transparent glass sample was obtained.

The emission and excitation spectra were measured with an MPF-4 and a Hitachi F-4500 Fluorescence Spectrophotometer, respectively. A Xe lamp was used as the excitation source. In the excitation spectra of Eu^{3+}: monitoring $^5D_0 \rightarrow {}^7F_2$ emission at 612 nm, the phonon sideband associated with the pure electronic $^7F_0 \rightarrow {}^5D_2$ transition was measured to study the phonon mode relative to the rare-earth ions. Under the excitation of the fourth frequency pulse of a Nd:YAG laser at 266 nm (pulse width: 9 ns, pulse repeat frequency: 3–30 Hz, single pulse energy in 1.064 μm: 750 mJ), the decay curves of Eu^{3+} ions were recorded by monitoring the output of an R456 photomultiplier tube with a Tektronic TDS 3052 digital oscillosynchroscope. All the measurements were performed at room temperature.

3. Results and discussion

3.1. The emission spectra

The emission spectra of La_2O_3–$3B_2O_3$ crystal and glass containing 0.06 mol% Eu_2O_3 under the excitation wavelength of 394 nm corresponding to the absorption transition of $^7F_0 \rightarrow {}^5L_6$ line are given in Fig. 1. According to our work [4], the Eu^{3+} ion mainly presented 696 nm emission (corresponding to $^5D_0 \rightarrow {}^7F_4$) in the $La(BO_2)_3$:Eu^{3+} system. Both figures give the characteristic emission of the Eu^{3+} ion. All PL (photoluminescence) bands are assigned to the transition from $^5D_0$ to ^7F_j ($j = 0, 1, 2, 3, 4$), 590 nm ($^5D_0 \rightarrow {}^7F_1$), 618 nm ($^5D_0 \rightarrow {}^7F_2$), 650 nm ($^5D_0 \rightarrow {}^7F_3$), 696 nm ($^5D_0 \rightarrow {}^7F_4$). With excitation by 394 nm light, the glass presented intense 618 nm red luminescence; however, the crystal gave 696 nm red luminescence. The $^5D_0 \rightarrow {}^7F_1$ transition is a magnetic dipole transition. And the $^5D_0 \rightarrow {}^7F_2$ transition is an electric dipole transition, which is relative to parameter Ω_2. According to J–O theory [5,6].

$$S_{JJ'} = \sum_{\lambda=2,4,6} \Omega_\lambda |\langle f^n \psi, J \| U^\lambda \| f^n \psi', J' \rangle|^2$$

where Ω_λ is relative to J. For the $^5D_0 \rightarrow {}^7F_2$ transition, $U_{JJ'}^{(4)}$ and $U_{JJ'}^{(6)}$ can be ignored to calculate the parameter Ω_2; consequently, the equation only contains the parameter Ω_2 [7].
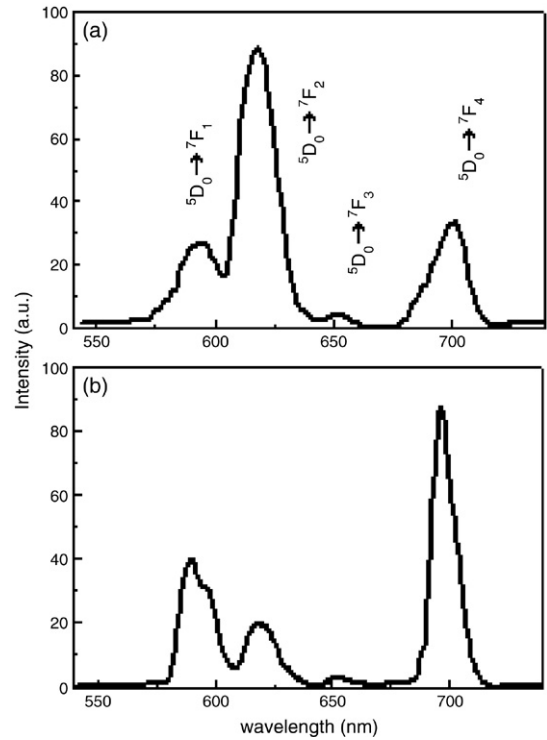

Fig. 1. Emission spectrum of Eu^{3+}-doped La_2O_3–$3B_2O_3$ glass (a) and $La(BO_2)_3$:Eu^{3+} crystal (b) under 394 nm excitation.

Thus, the emission intensity $S_{JJ'}$ is directly proportional to Ω_2. According to J–O theory, parameter Ω_2 can qualitatively analyze the local structure and coordination symmetry around the rare earth ion. The numerical value of Ω_2 is strongly correlated with the symmetry of coordination and the short range ligand structure of fluorescent ions. The larger the numerical value of Ω_2, the stronger the covalency and the lower the symmetry, and vice versa. Comparing the relative intensity of the $^5D_0 \rightarrow {}^7F_2$ transition in curves (a) and (b) in Fig. 1, it was obvious to see that, with the phase change from crystal to glass, the numerical value of Ω_2 increased. Therefore, it was concluded that the coordination symmetry of the crystal is higher than that of the glass. This indicated that the FL difference of Eu^{3+} is attributed to the discrepancy of the microstructure around Eu^{3+} ions.

3.2. Phonon sideband spectra

The phonon sideband spectra of Eu^{3+} associated with the $^7F_0 \rightarrow {}^5D_2$ transition was investigated for the La_2O_3–$3B_2O_3$ crystal and glass. Monitoring the $^5D_0 \rightarrow {}^7F_2$ emission at 612 nm, the phonon sideband associated with the $^7F_2 \rightarrow {}^5D_0$ transition can be clearly observed in the wavelength range 420–480 nm, on the high energy side of the $^7F_0 \rightarrow {}^5D_2$ transition, as shown in Fig. 2. Clearly, two peaks were observed around 438 nm and 426 nm, with phonon energy at 1500 cm^{-1} and 1900 cm^{-1}, respectively. These data are in good agreement with the results described by Tanabe et al. [8]. The former is assigned to the B–O vibrational mode inside the various borate rings and the latter to nonbridging B–O$^-$ bonds. Fig. 2(a)
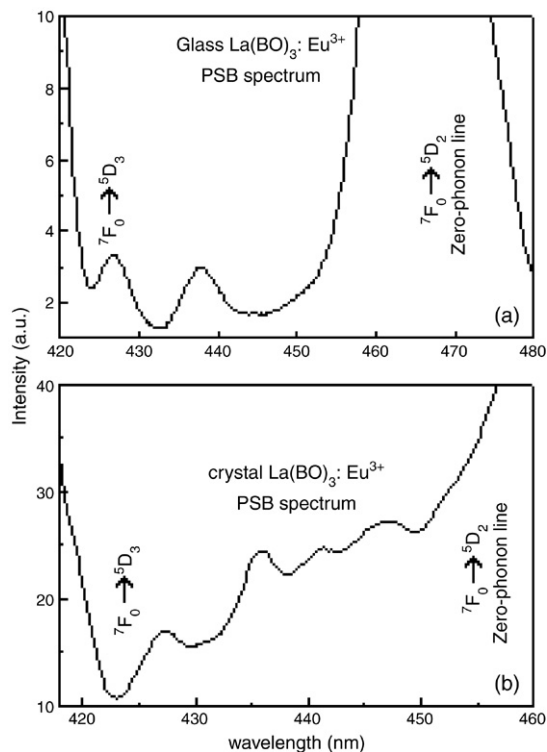
Fig. 2. Phonon sideband spectrum of Eu^{3+}-doped La_2O_3–$3B_2O_3$ glass (a) and $La(BO_2)_3$:Eu^{3+} crystal (b).

Fig. 3. Excitation spectrum of $La(BO_2)_3$:Eu^{3+} crystal (a) and Eu^{3+}-doped La_2O_3–$3B_2O_3$ glass (b).

shows that no other vibration mode in the vicinity of the zero-phonon line can be observed except the two peaks around 438 nm and 426 nm. Thus, it is B–O$^-$ bonds that are present around Eu^{3+} ions in borate glass. This indicated that B–O$^-$ bonds are coupled with Eu^{3+} in the doped borate glass: B–O$^-$ bonds formed by the introduction of Eu_2O_3 itself dominantly coordinate Eu^{3+} instead of a large number of boroxol rings, which have the highest phonon energy and contribute to nonradiative decay. In Fig. 2(b), in addition to the peaks due to B–O$^-$ bonds, in the vicinity of zero-phonon line, there are two weak peaks (their phonon energy is smaller) which probably come from the vibration of La–O bonds [4]. Therefore, it can be concluded that B–O$^-$ bond coordinations are dominant in glass; La–O bonds, however, coordinate with the Eu^{3+} ion in the crystal sample.

3.3. Charge transfer bands of Eu^{3+}

Excitation spectra were recorded for wavelengths corresponding to the maximum intensity of the emission spectra as shown in Fig. 3(a) and (b). They contain a large band in the UV and some lines which correspond to the Eu^{3+} 4f–4f transitions. The large band is a charge transfer band (C.T.B.), which corresponds to an electron transfer from an oxygen 2p orbital to an empty orbital of europium. The position of the band regularly shifted with the change of the local structure of the rare-earth ions. It is known that the position of the C.T.B. tends to lower with increasing coordination number [9] and is strongly dependent on the Eu–O distance [10]. The C.T.B. of borate crystal and glass, whose peak is located around 256 nm and 240 nm,
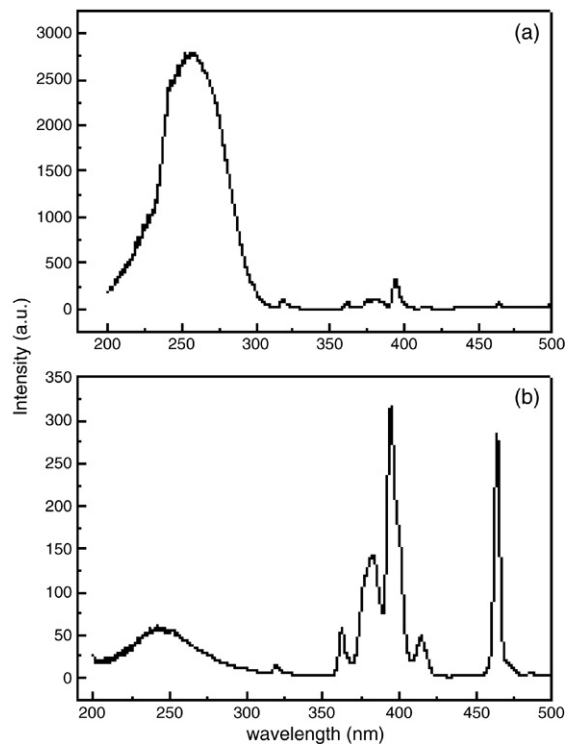
respectively, can be observed in Fig. 3. The C.T.B. appeared to blue shift with the phase change from crystal to glass; namely, the electron transfer bands of Eu^{3+} shifted to the high energy zone. The position of the C.T.B. was determined by the coupling strength caused by the stretching modes between O^{2-} ions and other ions around the O^{2-} ions.

From the analysis of the phonon sideband, it was known that Eu^{3+} ion formed Eu^{3+}–O^{2-}–B^{3+} and Eu^{3+}–O^{2-}–La^{3+} compound bonds in borate glass and crystal, respectively. Compared to the cation La^{3+}, the coupling strength of the B–O$^-$ bonds is more intense. Consequently, it needs more energy when an electron transfers from an oxygen 2p orbital to an empty orbital of europium in the glass, which leads to the charge transfer band of Eu^{3+} in glass shifting to the high energy zone. Comparing the relative intensity of the C.T.B. and the f–f transition of Eu^{3+} ions, it was found that the intensity of the C.T.B. is stronger than that of the f–f transition in the crystal; however, the result is the opposite in the glass.

3.4. Lifetime

The lifetime of phosphor is determined by the combination of probabilities for radiative (A) and nonradiative (w) processes. The lifetime (τ^{-1}) of an excited states is given by $\tau^{-1} = \sum A + \sum W$, where the summation of A is for radiative transitions terminating on all lower final states and that of W includes those by ion–phonon and ion–ion interactions. Among nonradiative processes, the relaxation by multiphonon emission due to the ion–phonon interaction is significant. Fig. 4 reports the $^5D_0$-fluorescence decay curves for Eu^{3+}-doped La_2O_3–$3B_2O_3$ crystal and glass at room temperature, for the
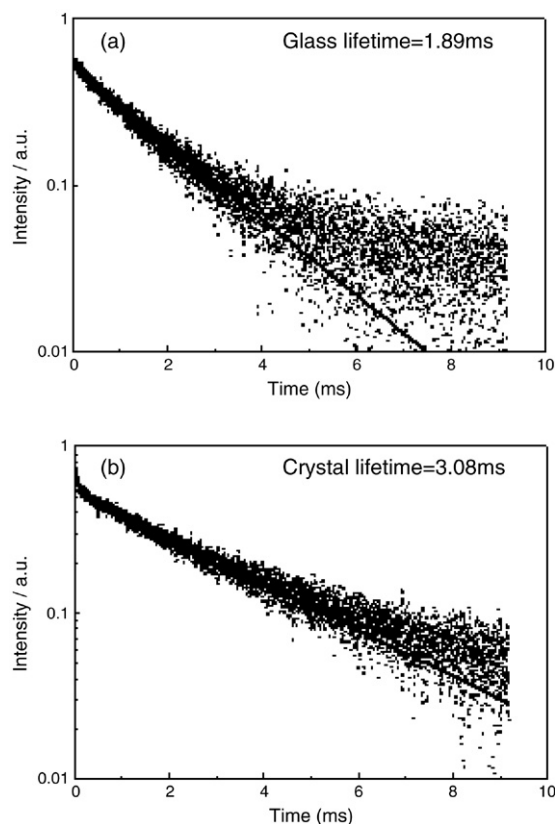
Fig. 4. Decay curves of Eu^{3+} ion in borate glass (a) and crystal (b).

most intense emission lines with excitation at the maximum of the C.T.B. By single-exponential fitting, the lifetime of the Eu^{3+} ion in La_2O_3–$3B_2O_3$ crystal and glass is 3.08 ms, 1.98 ms, respectively. It is noteworthy that the decay curves of the luminescence from $^5D_0$ is exponential in the crystal; however, it exhibits a non-exponential character in the glass. This non-exponential character of the decay curve demonstrates that the highest energy phonons appear in borate glass. The highest energy phonons are usually considered to make the dominant contribution to multiphonon relaxation [11]. Through the analysis of the emission spectra, the phonon sideband and C.T.B. as shown above, it was known that B–O^- bonds are coupled with Eu^{3+} in the doped glass; the bonds have the highest phonon energy, and contribute to the nonradiative decay by multiphonon relaxation of Eu^{3+} ions. Therefore, the rate of multiphonon decay is higher in the glass because of the high oscillation energy of B–O^- bonds, which leads to the lifetime of the glass being shorter. Similarly, the non-exponential character of the decay curve in the glass can be

confirmed from the emission spectra and C.T.B. It was known that the relative intensities of magnetic and electric dipole transitions are strongly correlated with the C.T.B. positions. The lower the energy of the C.T.B., the more important is the electric dipole transition contribution to the emission spectrum, and the shorter is the decay time. From the C.T.B. in Fig. 3, it is obvious that the energy of the C.T.B. of the crystal is larger than that of the glass. With respect to the emission spectra in Fig. 1, intense 618 nm red luminescence corresponding to the electric dipole transitions is predominant in the glass. Therefore, the glass exhibits non-exponential character and the decay time is shorter.

4. Conclusions

The fluorescence properties and local structure of Eu^{3+}-doped La_2O_3–$3B_2O_3$ crystal and glass were investigated by means of the emission spectra, the phonon sidebands, the charge transfer bands and the lifetime. It was found that B–O^- bonds with high phonon energy preferentially coordinate to the Eu^{3+} ion in the glass host.

The results show that the Eu^{3+} ion formed Eu^{3+}–O^{2-}–B^{3+} and Eu^{3+}–O^{2-}–La^{3+} compound bonds in borate glass and crystal, respectively. With excitation by 394 nm light, the glass presented intense 618 nm red luminescence, and the crystal gave 696 nm red luminescence. The lifetime of the Eu^{3+} ion in the crystal and in the glass is 3.08 ms, 1.98 ms, respectively. This difference of the optical properties of Eu^{3+} is ascribed to the discrepancy of the local structure around the Eu^{3+} ion in the crystal and the glass.

References

[1] M. Nogami, Y. Abe, J. Non-Cryst. Solids 197 (1996) 73.
[2] C.F. Wu, W.P. Qin, B.J. Chen, et al., Chin. J. Lumin. 22 (2001) 393.
[3] H. Toratani, T. Izumitani, H. Kuroda, J. Non-Cryst. Solids 52 (1983) 303.
[4] C.F. Wu, D.C. Li, C. Lin, et al., Chin. J. Lumin. 21 (2000) 210.
[5] G.S. Ofelt, J. Chem. Phys. 37 (1962) 511.
[6] B.R. Judd, Phys. Rev. 127 (1962) 750.
[7] B.J. Chen, H.Y. Wang, S.L. E, et al., Chin. J. Lumin. 22 (2001) 139.
[8] S. Tanabe, S. Todoroki, K. Hirao, et al., J. Non-Cryst. Solids 122 (1990) 59.
[9] G. Blasse, J. Solid State Chem. 4 (1972) 52.
[10] H.E. Hoefdraad, J. Solid State Chem. 15 (1975) 175.
[11] L.A. Riseberg, H.W. Moos, Phys. Rev. 174 (1968) 429.