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Luminescence properties of Ce^{3+} and Tb^{3+} doped rare earth borate glasses

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Abstract

Ce^{3+}- and Tb^{3+}-doped rare earth borate glasses were synthesized and their luminescence properties have been studied. The sample containing Ce^{3+} ions has a strong purplish-blue emission and that doped with Tb^{3+} emits a green light under UV excitation. The Ce^{3+} ions in the host form two kinds of emission centers, owing to different lattice sites occupied by Ce^{3+} in the host glass. In the Ce^{3+} and Tb^{3+} co-activated samples the Ce^{3+} ions strongly sensitize the luminescence of the Tb^{3+} ions.

Keywords: Luminescence; Ce^{3+} ion; Tb^{3+} ion; Borate glass; Sensitization

1. Introduction

Recently, with the development of fiber optic communication, up-conversion and laser, there has been much research into new optical glasses. Since the particular 4f electronic configuration of trivalent rare earth ions in numerous hosts leads to emissions from ultraviolet to infrared, studies on rare earth doped glasses have gained much interest [1–6]. Moreover, rare earth borate glasses have attracted much attention due to their high transparency, low melting point, easily-shaped and cost-effective properties.

Both Ce^{3+} and Tb^{3+} ions are important activators and they are widely used in phosphors for fluorescent lamps and displays [7–11]. The Ce^{3+} ion has one 4f electron and its lowest excited configuration is $5d^1$. It usually gives a band emission in the visible and near UV regions [12–16]. The configuration of the Tb^{3+} ion is $4f^8$. Its emissions mainly originate from $^5D_4$ and $^5D_3$ to ^7F_J ($J=6,5,4,3$) transitions within the $4f^8$ configuration in which Tb^{3+} emission intensities depend on the dopant concentration. In this work the luminescence properties of these two kinds of ions in a new sort of rare earth borate glasses and the sensitization from Ce^{3+} to Tb^{3+} have been investigated.

2. Experimental

The glasses used in this work are of the general composition $70B_2O_3\cdot(15-x-y)La_2O_3\cdot 7BaO\cdot 8Li_2O\cdot xCe_2O_3\cdot yTb_2O_3$ (hereafter called BLBL). For the samples reported here $x=0.1$ and $y=0$, $x=0$ and $y=1$, and $x=0.1$ and $y=1$, respectively. The well-mixed stoichiometric mixture was put into an alumina crucible. In a muffle furnace the mixture was heated at 800°C for 30 min and then at 1150°C for 2 h under a reduction atmosphere (CO gas) avoiding produce of Ce^{4+} ions. The samples were then obtained by pouring the melt into a preheated brass mould. The samples were annealed from 600°C to room temperature over 24 h and well polished.

The excitation and emission spectra were measured using a Hitachi MPF-4 model spectrophotometer. The absorption spectrum of BLBL:Ce^{3+} glass sample was measured at room temperature using a Perkin-Elmer Lambda 9 spectrophotometer. The fluorescence decay curves of Ce^{3+} ions in BLBL glass were obtained by using a Spex-1404 double grating monochromator equipped with a RCAC31034 photomultiplier and a 4400 Boxcar integrator. The 337.1 nm N_2 pulse laser was used as exciting light in the measurements for the fluorescence decay. All

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spectral measurements were carried out at room temperature.

3. Results and discussion

Under UV irradiation the BLBL:Ce sample gives rise to a bright purplish-blue emission. From the emission spectrum under 250 nm excitation it is obvious that the emission band consists of two sub-bands. In order to study the emission spectrum in detail the selective excitation was used. First, the emission spectrum of Ce^{3+} in BLBL glass under 310 nm excitation was obtained as shown as curve 1 in Fig. 1. It is evidently not symmetric. Its emission peak is at 368 nm and the full width at half maximum (FWHM) is about 48 nm, while there is a clear emission peak around 420 nm in the range 400–480 nm. However, the luminescence intensity of the latter is much weaker than that of the former. Therefore, the emission spectrum of Ce^{3+} in BLBL glass under 370 nm excitation was also obtained as shown as curve 2 in Fig. 1. The emission band shifts to a longer wavelength and widens. Its peak is at about 424 nm and the FWHM is ~70 nm. The energy difference between the two peaks is ~2900 cm^{-1} and larger than that between the $^2F_{5/2}$ and $^2F_{7/2}$ doublets in the $4f^1$ configuration of the Ce^{3+} ion. These results indicate that two kinds of Ce^{3+} emission centers exist due to different lattice sites occupied by Ce^{3+} ions in the host glass.

In order to verify the two kinds of Ce^{3+} emission centers in the glass, the excitation and absorption spectra of Ce^{3+} have also been studied, as shown in Fig. 2. Curve 1 in Fig. 2 shows the excitation spectrum of Ce^{3+} 340 nm emission, while curve 2 shows the excitation spectrum of Ce^{3+} 440 nm emission. It is clear that there are some differences: their peaks of the two excitation bands are at 304 and 334 nm, respectively. Their energy difference is also about 2900 cm^{-1}. This result verifies that there are

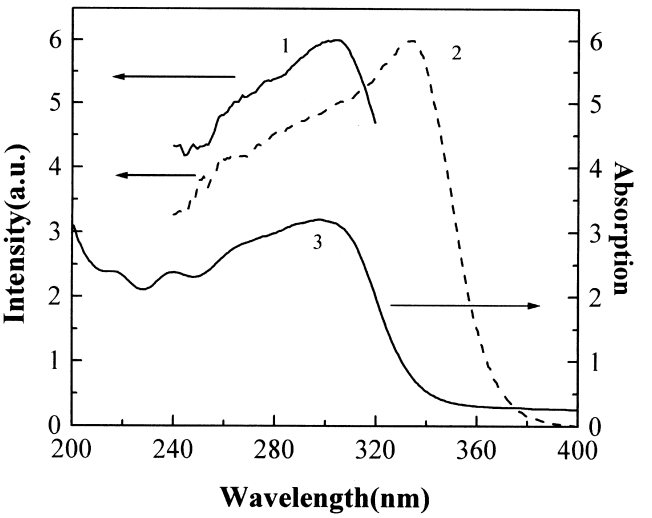

Fig. 2. Excitation and absorption spectra of BLBL:Ce^{3+} glass. (1) λ_{em} = 340 nm (solid line); (2) λ_{ex} = 440 nm (dashed line); (3) absorption spectrum in the range of 200–400 nm (solid line).

two kinds of Ce^{3+} emission centers in the glass, expressed as Ce^{3+}(1) and Ce^{3+}(2) centers. Curve 3 in Fig. 2 shows the absorption spectrum of Ce^{3+} ions in the range of 200–400 nm in the glass. It is very well in accord with the two excitation spectra. Therefore, it also indicates that the Ce^{3+} ions occupied two different crystallographic sites in the glass.

Each center has its own particular configuration environment in the host, so it has its own particular decay mechanism. The fluorescence decay curves of Ce^{3+}(1) and Ce^{3+}(2) centers in BLBL glass at room temperature are shown in Fig. 3. In the fluorescence decay experiment the 337.1 nm N_2 pulse laser was used as exciting light, which can simultaneously excite the two kinds of centers. The

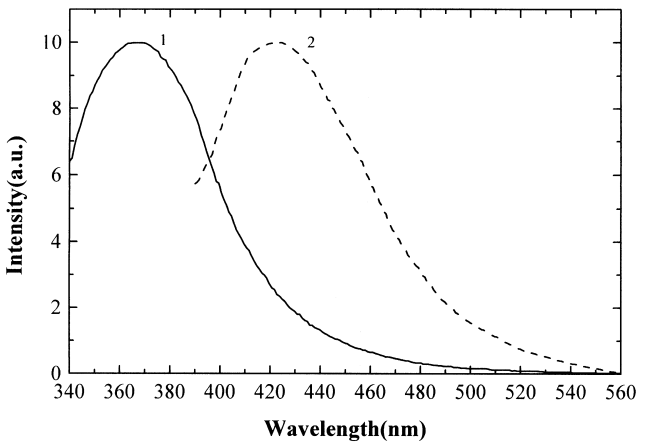

Fig. 1. Emission spectra of BLBL:Ce^{3+} glass. (1) λ_{ex} = 310 nm (solid line); (2) λ_{ex} = 370 nm (dashed line).

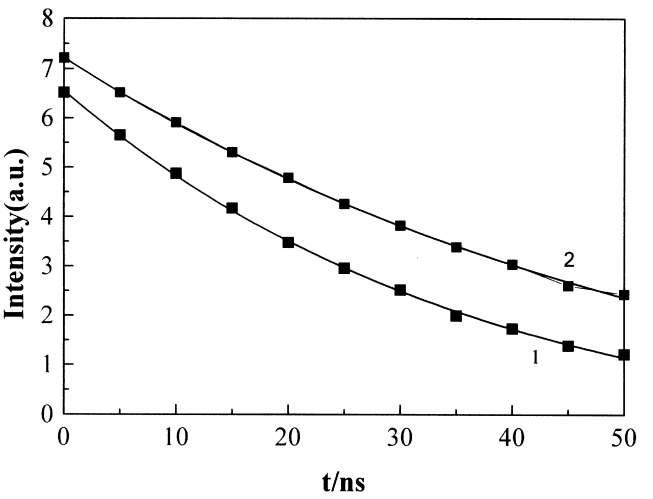

Fig. 3. Fluorescence decay fitting curves for BLBL:Ce^{3+} glass (337.1 nm laser beam, RT). (1) λ_{em} = 360 nm; (2) λ_{em} = 435 nm.

monitored wavelengths 360 and 435 nm corresponding to centers of Ce^{3+}(1) and Ce^{3+}(2), respectively, were selected in order to minimize the interaction between the two kinds of centers. The experimental data display exponential behavior. By fitting the experimental data to the formula $I = I_0 \exp(-t/\tau)$, the decay curves were obtained and were plotted in Fig. 3. The curves obtained are very well in accord with the data. The fluorescence lifetimes are $\tau_1 = 31$ ns for Ce^{3+}(1) center and $\tau_2 = 46$ ns for Ce^{3+}(2) center. The order of ns magnitude of the lifetime is one of the characteristics of the electric dipole allowed 5d→4f allowed transition of Ce^{3+} ions.

The BLBL:Tb glass sample emits weak green light under UV excitation. Fig. 4 curve 1 (multiplied by two) is the emission spectrum of BLBL:Tb obtained under 320 nm excitation. The spectrum mainly consists of four groups of lines in the regions near 492, 547, 590 and 626 nm, respectively. They originate from $^5D_4 \rightarrow {}^7F_J$ ($J = 6,5,4,3$) transitions. The most intensive one is due to the $^5D_4 \rightarrow {}^7F_5$ transition.

Fig. 4 curve 2 gives the emission spectra of BLBL:Ce, Tb glass under the excitation of 320 nm light. It consists of a band centered at 380 nm due to the 5d→4f transitions of the Ce^{3+} ions and four groups of lines peaked at 492, 547, 590 and 626 nm, respectively, owing to the $^5D_4 \rightarrow {}^7F_J$ ($J = 6,5,4,3$) transitions within the $4f^8$ configuration of the Tb^{3+} ions. It is obvious that the emission intensity of the Tb^{3+} ions was strongly enhanced since the Ce^{3+} ions sensitized the Tb^{3+} ions.

Fig. 5 shows the excitation spectra of Tb^{3+} single doped (curve 1) and Ce^{3+} and Tb^{3+} co-doped (curve 2) BLBL glasses. In the spectral region from 260 to 500 nm there are six excitation subbands situating at 270, 300, 318, 353, 374 and 490 nm; they belong to the transitions from the ground state $^7F_6$ to $^5D_4$, $^5D_3$, $^5D_2$ and other higher excited states, respectively. Between the emission spectrum of the Ce^{3+} ions (Fig. 1) and the excitation spectrum of the Tb^{3+} ions (Fig. 5 curve 1), there is an obvious overlap, which indicates the possibility of energy transfers from the Ce^{3+} ions to the Tb^{3+} ions. Compared the two curves in Fig. 5 with the emission spectra given in Fig. 4 shows that energy transfer processes from the Ce^{3+} ions to the Tb^{3+} ions occur. The emission band of the Ce^{3+} ions has a shoulder on the left side and is concave in the middle. This distortion is due to the absorption of the Tb^{3+} ions.

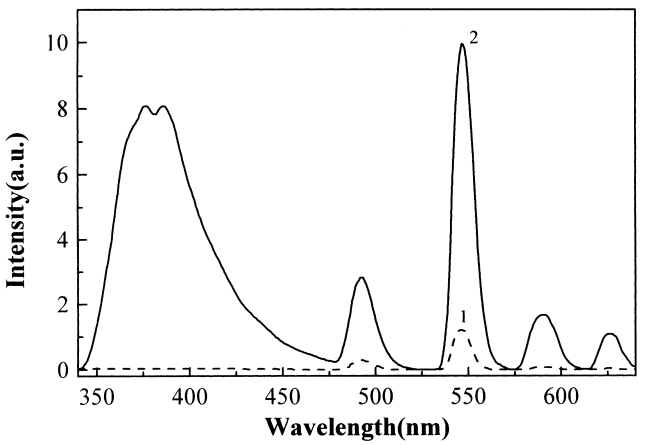

Fig. 4. Emission spectra of BLBL:Tb^{3+} glass (curve 1, dashed line, multiplied by 2) and BLBL:Ce^{3+},Tb^{3+} glass (curve 2, solid line), λ_{ex} = 320 nm.

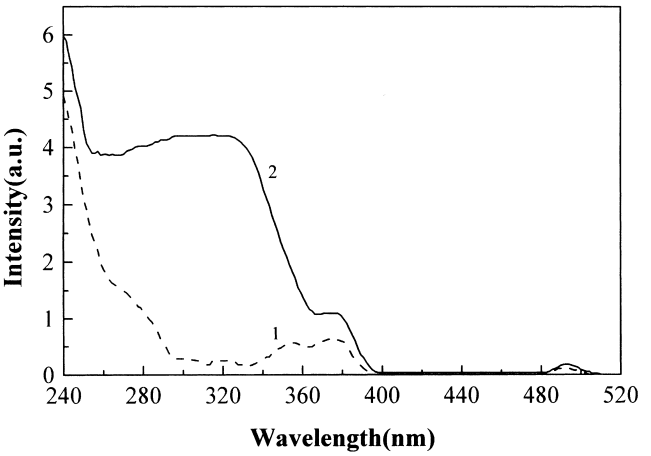

Fig. 5. Excitation spectra of BLBL:Tb^{3+} glass (curve 1, dashed line) and BLBL:Ce^{3+},Tb^{3+} glass (curve 2, solid line), λ_{em} = 547 nm.

4. Conclusion

A new sort of rare earth borate (BLBL) glass was synthesized. Ce^{3+} doped BLBL glass gives rise to strong purplish-blue light while Tb^{3+} activated BLBL glass produces green light under UV radiation. There are two kinds of Ce^{3+} emission centers due to different lattice sites occupied by the Ce^{3+} ions in the Ce^{3+} doped BLBL glass. In the Ce^{3+} and Tb^{3+} co-activated BLBL glass the Ce^{3+} ions sensitize the Tb^{3+} ions and strongly strengthen the luminescence coming from the Tb^{3+} ions.

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