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Influence of WO_3 content on the optical properties of Eu^{3+}-doped Bi_2O_3–B_2O_3–WO_3 glasses

Z. WANG[*], R. TONG, H. LIN, D. YANG

School of Chemical Material, Dalian Polytechnic University, Dalian 116034, P.R. China

Eu^{3+}-doped bismuth borate based glasses with various contents of WO_3 were fabricated by melt quenching. Optical properties of Eu^{3+} ions in these ternary systems and their dependence on the WO_3 content were investigated: absorption and emission spectra were studied as the WO_3 molar ratio was adjusted from 1 to 5 mol %. The Judd–Ofelt parameters were calculated from the emission spectra and expressed in terms of reduced matrix U^t (t = 2, 4, 6) characters for optical transitions. The influence of WO_3 content on the Judd–Ofelt intensity parameter Ω_2 was also investigated. Experimental results lead us to conclude that the optimum luminescence of Eu^{3+}-doped bismuth borate based glasses is achieved if the WO_3 content is 3 mol %.

Key words: *Bi_2O_3–B_2O_3–WO_3 system glasses; Eu^{3+} ions; Emission spectrum, Judd-Ofelt parameters*

1. Introduction

Rare-earth doped glasses have attracted considerable attention owing to their applications in optical communications, bulk lasers and sensors, etc. [1–4]. Among conventional glasses, borate glasses are known to be excellent host matrices of rare earth oxides. Bismuth oxide glass has a high refractive index and a low phonon energy system, which enhances the radiative transitions of rare earth ions and is expected to have high fluorescence quantum efficiency. Besides, adding a low quantity of WO_3 improves luminescence, a fact which has been confirmed by optical measurements in TeO_2–WO_3–Tm_2O_3 systems [5, 6]. Therefore, we expect that the introduction of WO_3 into the bismuth borate matrix will influence the spectral properties of rare earth ions. Additionally, doping with suitable rare earth ions is important for studying the structure and bonding characteristics of different material: thus Eu^{3+} ions have been chosen due to their unsplit $^7F_0$ ground state and relatively simple system of electronic levels [7–12].

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[*] Corresponding author, e-mail: wangzhiqiang_dlpu@hotmail.com

The Judd–Ofelt theory is used to estimate the local structure and bonding states of rare-earth ions in host materials. Some important optical parameters such as the oscillator strength, radiative transition probability, fluorescence branching ratio and radiative lifetime can be calculated by the parameter Ω_λ. Up to now, the Judd–Ofelt parameters have been calculated from absorption and emission spectra of Eu^{3+}-doped glasses. However, Gao Tang et al. [9] have shown that the Ω_λ parameters obtained from the emission spectrum is more reliable than that obtained from the absorption spectrum in the case of Eu^{3+}-doped GaF_3–InF_3–CdF_2–ZnF_2–PbF_2–SnF_2 glasses.

In this paper, we report the optical properties of Bi_2O_3–B_2O_3–WO_3 glasses doped with Eu^{3+} ions. The Judd–Ofelt parameters were calculated from the emission spectrum. The influence of WO_3 on the change of Ω_2 was also analyzed.

2. Experimental

A series of glass samples in molar composition: $(99 - x)[Bi_2O_3 \cdot B_2O_3]xWO_3 \cdot Eu_2O_3$ (x =1, 3, 5 mol %) were prepared. The starting materials were Bi_2O_3 (99.0%), H_3BO_3 (99.5%), WO_3 (99.0%), Eu_2O_3 (99.9%). A batch of 15 g in a platinum crucible was melted at 850 °C for 30 min in an electrical furnace. The melt was then quickly poured onto a preheated steel block, and the transparent samples were annealed at approximately the glass transition temperature T_g. Then the glass samples were polished in order to facilitate subsequent test measurements. The samples had a typical thickness of approximately 0.5 cm.

The density of the glasses was measured according to Archimedes' principle. The refractive indices of the glass samples were measured according to Brewster's law [13, 14] with an FGY 201 spectrometer. The absorption spectrum of each sample was recorded with a Perkin-Elmer Lambda 35 UV-VIS double-beam spectrophotometer. The emission spectrum of each sample was obtained with a P-E LS 55 spectrofluorimeter. All the spectra were measured at room temperature.

3. Results and discussion

3.1. Absorption spectrum

Figure 1 shows the absorption spectra of the samples. Three absorption peaks are observed in the Eu^{3+}-doped Bi_2O_3–B_2O_3–WO_3 glasses at 462, 526 and 579 nm. The first excited state, ${}^7F_1$, is very close in energy to the ground state ${}^7F_0$. The absorption transitions from ${}^7F_1$ cannot be ignored at room temperature [15]. In view of this, the absorption peaks corresponding to the following transitions: ${}^7F_0 \to {}^5D_2$, ${}^7F_{0,1} \to {}^5D_1$ and ${}^7F_1 \to {}^5D_0$. As can be seen in Fig. 1, the absorption edge wavelength shifts towards the longer wavelengths as the WO_3 content increases because the content of Bi_2O_3 with intense absorption at UV relatively decreases. However, several absorption bands of Eu^{3+} ions in the ultraviolet range were covered with strong absorption bands of the host glasses, especially Bi_2O_3. Only three weak absorption peaks were observed, ranging from 460 to 600 nm.

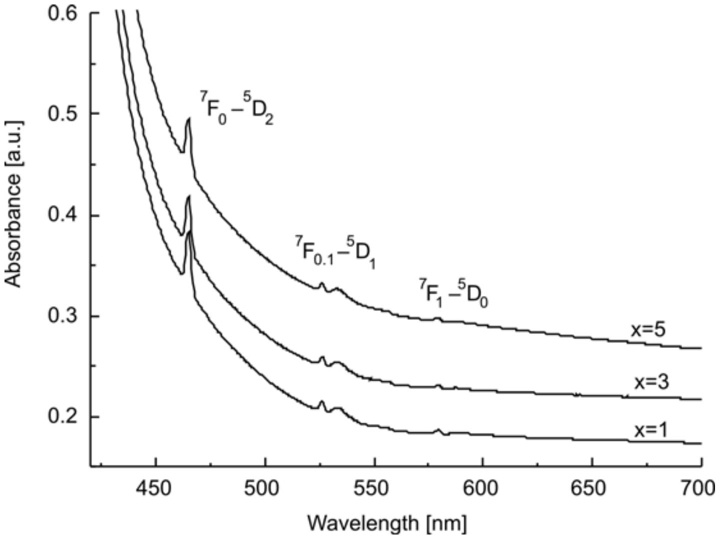

Fig. 1. Absorption spectra of Eu^{3+}-doped Bi_2O_3–B_2O_3–WO_3 glasses

3.2. Emission spectrum and the Judd–Ofelt theory

Figure 2 shows the emission spectra of Eu^{3+}-doped Bi_2O_3–B_2O_3–WO_3 glasses in the 550–750 nm region. From the figure, it is clear that there are four peaks at around 590, 615, 650 and 698 nm in the spectrum corresponding to $^5D_0 \to {}^7F_1$, $^5D_0 \to {}^7F_2$, $^5D_0 \to {}^7F_3$ and $^5D_0 \to {}^7F_4$ transitions, respectively. As seen in Fig. 2, the band around 615 nm is most intense, thus Eu^{3+}-doped Bi_2O_3–B_2O_3–WO_3 glasses emit bright red light under UV light excitations. Furthermore, the intensity of the transitions initially increases and then subsequently decreases as the of WO_3 content increases: the most intense light emitted by the glasses appears when the WO_3 content is 3 mol %.

The Judd–Ofelt theory [16, 17] provides a very useful method for analyzing the local structure around rare-earth ions. As in this glass system some absorption peaks of Eu^{3+} ions at the ultraviolet range could not be observed and other peaks were very weak, we are unable to accurately calculate the Judd–Ofelt parameters from the absorption spectra. More recently, some scholars have extended the Judd–Ofelt theory by calculating the optical parameters from the emission spectrum [14, 18].

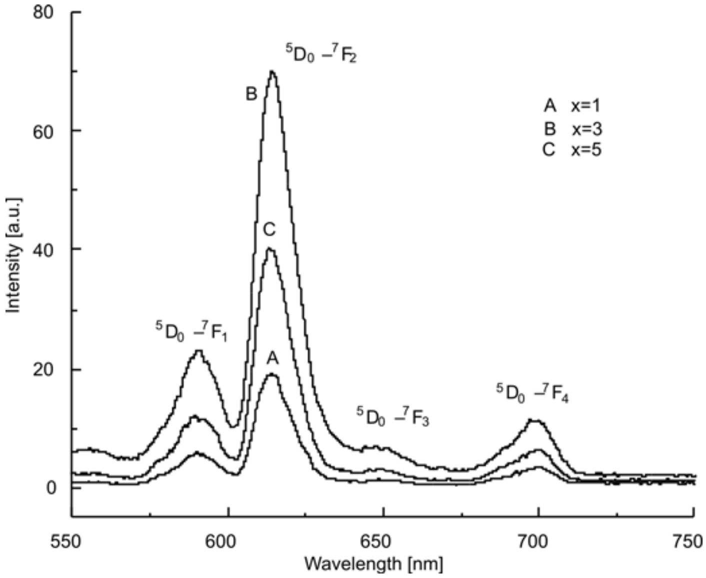

Fig. 2. Emission spectra of Eu^{3+}-doped Bi_2O_3–B_2O_3–WO_3 glasses (λ_{exc} = 465 nm)

Based on the optical transition law of rare-earth ions [19], the $^5D_0 \rightarrow {}^7F_J\left(J = 2,4,6\right)$ transition is allowed by the electric dipole, and electric dipole radiative transition probability A_{ed} can be calculated from the formula:

$$A_{ed} = \frac{64\pi^4 e^2}{3h}\frac{\bar{v}^3}{2J'+1}\frac{n\left(n^2+2\right)^2}{9} \times \sum_{t=2,4,6} \Omega_t \left\langle \psi J \left\| U^t \right\| \psi' J' \right\rangle^2 \tag{1}$$

where e, c and n are the charge of electron, velocity of light and refractive index of the glasses, respectively; h is the Planck constant, $\bar{v}$ is the average wavenumber of the transition, J is the quantum number of angular momentum of the initial state and J' is that of the final state. $\left\langle \psi J \left\| U^t \right\| \psi' J' \right\rangle^2$ represents the square of the matrix elements of the unit tensor operation U^t connecting the initial and final states and the its value for the Eu^{3+} ion is given in Table 1. The $^5D_0 \rightarrow {}^7F_1$ transition is allowed by the magnetic dipole, and the magnetic dipole radiative transition probability A_{md} is given by:

$$A_{md} = \frac{64\pi^4}{3h}\frac{\bar{v}^3}{2J'+1} n^3 S_{md} \tag{2}$$

where S_{md} is the line strength for magnetic dipole transition. The local rare earth environment does not affect S_{md}, thus it is generally accepted as a constant. The value of S_{md} can be obtained from

$$S_{md} = \frac{e^2 h^2}{16\pi^2 m^2 c^2}\left\langle \psi J \left\| U^t \right\| \psi' J' \right\rangle^2 \tag{3}$$

Table 1. Square of the matrix elements for $^5D_0 \to {}^7F_J\ (J = 2, 4, 6)$ of Eu^{3+} ions

Parameter	Transition		
	$^5D_0 \to {}^7F_2$	$^5D_0 \to {}^7F_4$	$^5D_0 \to {}^7F_6$
$U^{(2)2}$	0.0032	0	0
$U^{(4)2}$	0	0.0023	0
$U^{(6)2}$	0	0	0.0002

Neglecting the fact that the different transition wavelengths of $^5D_0 \to {}^7F_1$ and $^5D_0 \to {}^7F_J\ (J = 2, 4, 6)$ should result in a difference in the refractive index, the transition intensity ratio of the electric dipole to the magnetic dipole is as follows:

$$\frac{\int I_J(v)dv}{\int I_{md}(v)dv} = \frac{e^2}{S_{md}} \frac{v_J^3}{v_{md}^3} \frac{\left(n^2+2\right)^2}{9n^2} \Omega_J \times \left\langle \psi J \left\| U^t \right\| \psi' J' \right\rangle^2 \tag{4}$$

Thus the optical transition intensity parameter Ω_J can be calculated from Eqs. (1)–(4). Since the emission band for the $^5D_0 \to {}^7F_6$ transition centres at around 810 nm could not be detected, due to measurement limitations, we can only determine the value of Ω_2 and Ω_4. As a matter of fact, the parameter Ω_6 can be negligibly small compared with Ω_2 and Ω_4, because $U^{(6)2}$ is comparatively small. The value of Ω_J (J = 2, 4) is given in Table 2.

Table 2. Transition intensity parameter Ω_J (J = 2, 4) and refractive index n

x	Ω_2 (10^{-20}cm^2)	Ω_4 (10^{-20}cm^2)	n
1	3.83	1.70	2.3790
3	3.37	1.39	2.3751
5	3.75	1.44	2.3711

According to previous studies, Ω_2 is a useful parameter, because it is sensitive to the local symmetry of the ligand field and bond covalency [19–21]. The value of Ω_2 increases as the local symmetry of the ligand field decreases and as the bond covalency increases. It is necessary to consider these two aspects. The structure units ([WO_4] or [WO_6]) of WO_3 gradually participate in the glass network as the WO_3 content increases, these then lower the symmetry of the glass network, thus leading to an increase in the value of Ω_2. On the other hand, the electric field of W^{6+} has a strong attraction to the O^{2-} ion, the W^{6+} ion decreases the covalency of Eu–O by means of increasing the Eu–O distance, because the attractive function of W^{6+} to the O^{2-} ion is higher than to the Eu^{3+} ion. From Table 2, we can see that Ω_2 shows a minimum when the WO_3 content is 3 mol %, Ω_2 tends to decrease initially and then to increase subsequently. When the content of WO_3 is lower than 3 mol %, the influence of WO_3 on the covalency of Eu–O plays a dominant role in changing Ω_2 compared with the local symmetry of the ligand field, so the value of Ω_2 initially decreases. However, the value of Ω_2 increases as the WO_3 content increases beyond a critical level, thus the influence of the WO_3 content on the symmetry of the ligand field plays a dominant role in changing Ω_2 compared with the covalency of Eu–O.

4. Conclusions

Eu^{3+}-doped Bi_2O_3–B_2O_3–WO_3 glasses having different WO_3 contents were prepared. The Judd–Ofelt parameters Ω_2, Ω_4 for Eu^{3+} were calculated from the emission spectra. The bright red emission is observed in Eu^{3+}-doped glasses under UV light excitations. It is found that the glass with 3 mol % WO_3 content has the best optical properties in this system. The effect of WO_3 on the change of Ω_2 was also analyzed. When the content of WO_3 is lower than 3 mol %, the influence of WO_3 on the covalency of Eu–O plays a dominant role in changing Ω_2, compared with the local symmetry of the ligand field, thus the value of Ω_2 initially decreases. However, the value of Ω_2 increases as the WO_3 content increases beyond a critical level; this is due to the influence of WO_3 on the symmetry of the ligand field, which plays a dominant role in changing Ω_2, compared with the covalency of Eu–O.

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