

BRIEF COMMUNICATION

Electron Transfer between Eu^{3+} and Tb^{3+} in BaB_4O_7 Matrix

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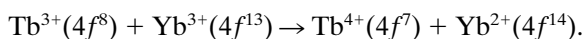
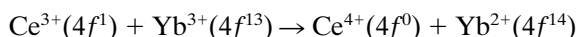
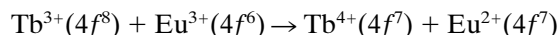
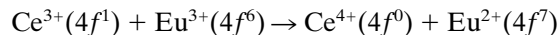
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The $\text{BaB}_4\text{O}_7:\text{Eu}$, Tb phosphors are first synthesized in air atmosphere. We investigate their luminescent properties, and find that europium(II) and europium(III) can coexist in the $\text{BaB}_4\text{O}_7:\text{Eu}$ phosphor. We observed that the relative intensity of europium(II) is increased when terbium(III) is incorporated. The electron spin resonance (ESR) spectra are carried out. The intensity of ESR peaks corresponding to europium(II) is also increased when terbium(III) is increased, so the valency state of europium is influenced by terbium(III). We explain these phenomena by an electron transfer mechanism. © 1996 Academic Press, Inc.

1. INTRODUCTION

It is well known that the most common valence state of rare earth ions is trivalent. Some ions are inclined to exist in an abnormal valency state, such as Sm^{2+} , Eu^{2+} , Yb^{2+} , Ce^{4+} , Pr^{4+} , and Tb^{4+} , because they all have more stable electronic configurations. We find that two rare earth ions, whose number of $4f$ electrons is seven or a multiple of seven, have conjugate electronic configuration, and we advanced that two conjugate electronic configuration ions tend to transfer an electron to get a more stable electronic configuration (1). For example,



There has been growing interest recently in studies on luminescence of rare earth ions in alkaline earth borates (2–5). The divalent rare earth ions can be stabilized in

alkaline earth borates, especially Eu^{2+} activated alkaline borates.

In this paper, we report the luminescence and ESR properties of $\text{BaB}_4\text{O}_7:\text{Eu}$, Tb phosphors which are synthesized in air atmosphere. We conclude that there is an electron transfer between Eu^{3+} and Tb^{3+} ions in the BaB_4O_7 matrix.

2. EXPERIMENTAL

The following starting materials are used for the preparation of $\text{BaB}_4\text{O}_7:\text{Eu}$, Tb phosphors: the purity of BaCO_3 and H_3BO_3 is AR, and that of rare earth oxides (Eu_2O_3 and Tb_4O_7) is 99.99%. The calculated amounts of reagents are thoroughly mixed and ground together; a 10% excess of the boric acid is used to compensate for the evaporation of B_2O_3 that is produced in high-temperature solid state reactions. The mixture is heated at 300°C for 3 h, then reground and reheated at 800°C for 9 h. All the samples are white powder.

The samples are checked by means of a Rigaku Denki “2028 D/max-IIB” diffractometer, using $\text{CuK}\alpha$ ($\lambda = 0.1542$ nm). X-ray powder patterns show that all samples are single structure.

The room temperature luminescence spectra of powder samples are carried out with a SPEX DM3000F spectrofluorometer using a xenon arc lamp as the excitation source.

The ESR spectra are obtained using an X-band spectrometer (JEOL model JES-FE-3AX), and the resonant frequency of its cavity is 9.467 GHz.

3. RESULTS AND DISCUSSION

3.1. Luminescence Spectra

The excitation and emission spectra of $\text{BaB}_4\text{O}_7:0.02\text{Eu}^{3+}$ phosphors at room temperature are illustrated in Fig. 1.

The excitation spectrum has some sharp lines, and the strongest excitation peak is at 394 nm. These line excitation

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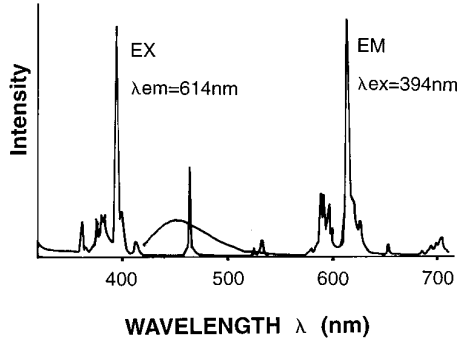


FIG. 1. Photoluminescence excitation (EX) and emission (EM) spectra of the Eu^{3+} ion in the $\text{BaB}_4\text{O}_7:0.02\text{Eu}^{3+}$ phosphor.

peaks are attributed to the $4f-4f$ transitions between the ground state of Eu^{3+} ion and its excitation states. The emission spectra of Eu^{3+} peaks are observed under 394 nm excitation. These emission spectra are attributed to the ${}^5D_0-{}^7F_J$ transitions in the Eu^{3+} ion, and the strongest emission peak is at 614 nm which is attributed to the ${}^5D_0-{}^7F_2$ transition. In addition, we find a broad band emission spectrum whose maximum is at 452 nm in Fig. 1. We think this broad band is corresponding to Eu^{2+} according to its wavelength. The europium is an abnormal valency rare earth element, and the Eu^{2+} ion can exist in the BaB_4O_7 matrix under a certain condition more easily than that of Eu^{3+} , because a charge compensation could take place when the Eu^{3+} ion enters the matrix. BaB_4O_7 is monoclinic. Its structure framework consists of a three-dimensional $(\text{B}_4\text{O}_7)_\infty$ network of BO_4 tetrahedral as the structure of EuB_4O_7 (6). The Eu atoms are located in a so-called cage formed by the BO_4 units of the $(\text{BO}_4)_\infty$ network. The Eu^{2+} ion can be stabilized in this structure, because the Eu^{2+} ions are completely surrounded by the BO_4 units of the $(\text{BO}_4)_\infty$ network, and are therefore hardly expected to be attacked by oxygen. Figure 2 shows the excitation and emission spectra of Eu^{2+} in the $\text{BaB}_4\text{O}_7:0.02\text{Eu}$ phosphor.

The excitation band of emission ($\lambda_{\text{em}} = 376$ nm) shows

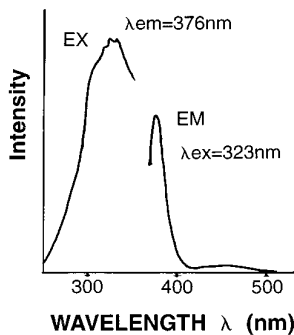


FIG. 2. Photoluminescence excitation (EX) and emission (EM) spectra of the Eu^{2+} ion in the $\text{BaB}_4\text{O}_7:0.02\text{Eu}^{3+}$ phosphor.

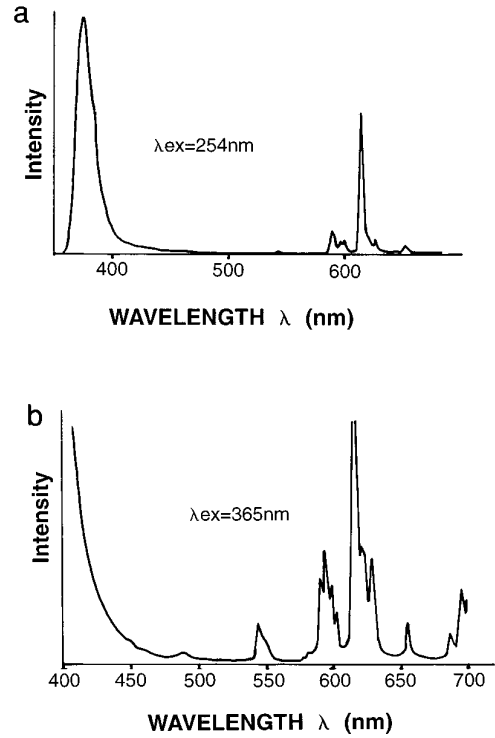


FIG. 3. Photoluminescence emission spectra of the $\text{BaB}_4\text{O}_7:0.06\text{Eu}^{3+}, 0.008\text{Tb}^{3+}$ phosphor under (a) 254 and (b) 365 nm excitation.

a broad band whose maximum is situated at 323 nm. Two emission broad bands of Eu^{2+} ions whose maxima are at 376 and 452 nm, respectively, are observed under 323 nm excitation, which is attributed to allowed electronic transitions from states of the $4f^65d$ configuration to the ground state of $\text{Eu}^{2+} 4f^7 ({}^8S_{7/2})$.

We investigate the luminescence spectra of the $\text{BaB}_4\text{O}_7:0.004\text{Tb}^{3+}$ phosphor. The emission spectrum of Tb^{3+} ion has some strong emission peaks, which are attributed to the transitions of the 5D_4 level. The four group emission peaks are observed. They are at 490, 543, 586, and 622 nm which correspond to ${}^5D_4-{}^7F_6$, ${}^5D_4-{}^7F_5$, ${}^5D_4-{}^7F_4$, and ${}^5D_0-{}^7F_3$ transitions, respectively, and the strongest emission spectra of Tb^{3+} is at 543 nm.

The emission spectra peaks of Eu^{3+} , Eu^{2+} , and Tb^{3+} ions are all observed in $\text{BaB}_4\text{O}_7:6\% \text{Eu}^{3+}, 0.8\% \text{Tb}^{3+}$ phosphor under UV excitation, as seen in Fig. 3.

We find that the incorporation of the Tb^{3+} ion does not influence the wavelength position of Eu^{3+} , Eu^{2+} , and Tb^{3+} ions in the $\text{BaB}_4\text{O}_7: \text{Eu}, \text{Tb}$ phosphor, and the luminescence intensity of the Eu^{2+} ion is influenced by the incorporation of the Tb^{3+} ion. This is shown in Fig. 4.

The intensity of emission spectra of Eu^{2+} becomes stronger with the increasing of Tb^{3+} ion under UV excitation. This can be explained by the electron transfer reaction mechanism: Eu^{3+} and Tb^{3+} ions are a pair of conjugate

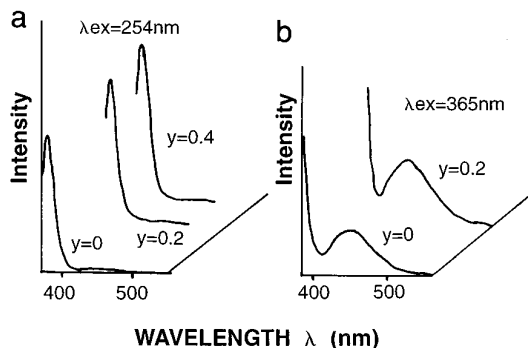


FIG. 4. Relative intensity of emission spectra of the Eu^{2+} ion in the $\text{BaB}_4\text{O}_7:0.02\text{Eu}^{3+}, y\%\text{Tb}^{3+}$ phosphor under (a) 254 and (b) 365 nm excitation.

electronic configuration rare earth ions, and if they are codoped in the BaB_4O_7 matrix, an electron transfer may take place between Eu^{3+} and Tb^{3+} ions to get the more stable electronic configuration of $4f^7$ that is Eu^{2+} and Tb^{4+} ions, respectively. The Tb^{4+} ions have been proven to exist in fluoride systems (7).

3.2. ESR Spectra

In order to prove the electron transfer between Eu^{3+} and Tb^{3+} ions, we investigate the electron spin resonance spectra. Because Eu^{3+} is a non-Kramers ion, its ESR spectra should be silent at room temperature due to short spin-lattice relaxation times. But the electron spin S of the Eu^{2+} ion is $7/2$ and nuclear spin I is $5/2$ for both ^{151}Eu and ^{153}Eu ; the characteristic hyperfine patterns due to the two isotopes can be used to identify Eu^{2+} . We investigate the ESR spectra of Tb_4O_7 at the certain condition and find no signal, so the ESR intensity can be used to detect the concentration of Eu^{2+} in matrices. Figure 5 shows the signals of Eu^{2+} ion in $\text{BaB}_4\text{O}_7:0.02\text{Eu}, y\%\text{Tb}$ phosphors.

The results given by the ESR spectra are in agreement with those from the fluorescence spectra. In $\text{BaB}_4\text{O}_7:0.02\text{Eu}, y\%\text{Tb}$ phosphors, the intensity of ESR spectra peaks corresponding to Eu^{2+} increases with the concentration of Tb^{3+} increasing, so the concentration of the Eu^{2+} ion increases.

In summary, the luminescence and ESR spectra show that there is an electron transfer between Eu^{3+} and Tb^{3+} ions, if they are codoped in BaB_4O_7 , so Eu^{3+} , Eu^{2+} , and Tb^{3+} ions can coexist in one matrix. If we appropriately readjust the concentration of Eu^{3+} and Tb^{3+} ions to enhance the emission intensity of Tb^{3+} ion, we probably get a new kind of valuable lamp phosphor that two rare earth

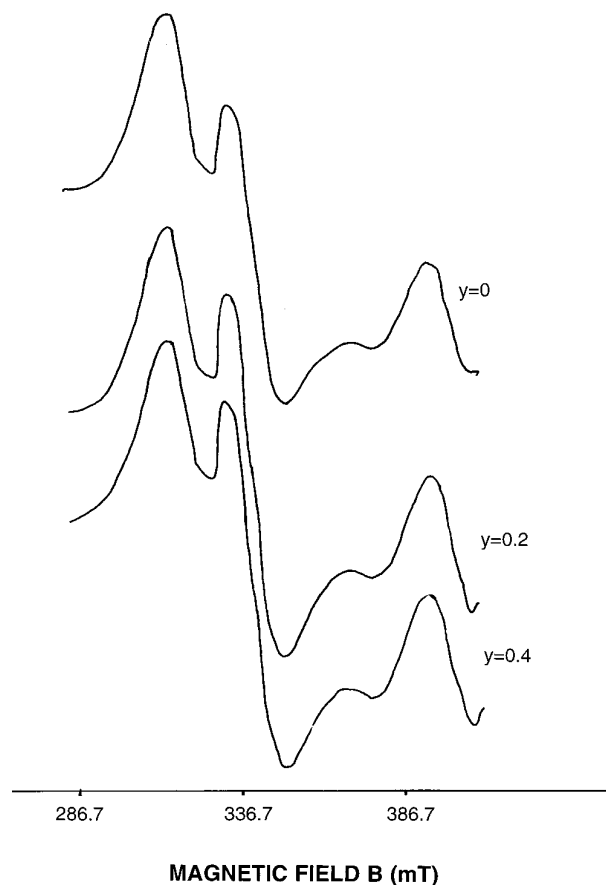


FIG. 5. ESR spectra of Eu^{2+} in $\text{BaB}_4\text{O}_7:0.02\text{Eu}, y\%\text{Tb}$ phosphors.

ions are codoped in one matrix that is synthesized in air atmosphere.

ACKNOWLEDGMENT

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