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Luminescent properties of rare Earth ions in $M_2B_5O_9Cl$: RE (M=Ca, Sr, Ba; RE= (Eu, Tb))

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ABSTRACT

The luminescent properties as well as the influences of the matrix composition and other doping ions on the luminescence of the rare earth ions of the co-doped phosphors $M_2B_5O_9Cl$: RE (M=Ca, Sr, Ba; RE=(Eu, Tb)) were investigated. The coexistence of Eu^{3+} , Eu^{2+} and Tb^{3+} were observed in these matrices. The phenomenon may be explained by the electron transfer theory. The intensity of Eu^{2+} emission increases under 365nm excitation and decreases under 254nm excitation with increasing the Tb^{3+} concentration. The competition between electron transfer and energy migration might be the reason for the observation. © 2008 Trade Science Inc. - INDIA

KEYWORDS

Luminescence;
Electronic transport;
Chemical synthesis.

INTRODUCTION

Recently, white-light-emitting luminescence is attracting much attention due to potential application such as backlighting liquid crystal displays and producing full-color displays using micropatterned color filters, or other illumination purposes^[1]. In order to achieve maximum efficiency and high color purity, white light should have three discrete peaks in the blue, green, and red regions. The control of light primary colors is essential for image devices. To improve high spatial resolution with wide color gamut, new solid-state materials have been developed. For this purpose, the most suitable materials are rare-earth (RE) ions, because the emission of f-f

transition of RE ions is very sharp due to the shielding of the 4f orbital by the outer $5s^2$ and $5p^6$ orbital^[2]. For example, J.E.C. Silva et al. have developed a glassy material doped with rare earth ions (Eu^{3+} , Tb^{3+} and Tm^{3+}), named full-color glass, which generated by carefully selected 4f-4f transitions^[3].

According to the concept of conjugate electronic configuration ions which was proposed by Shi et al.^[4], Eu^{3+} and Tb^{3+} are important conjugated ions for luminescence activator. When they are co-doped in same host, an electron will transfer from Tb^{3+} to Eu^{3+} as^[5,6].

$Eu^{3+}(4f^6) + Tb^{3+}(4f^8) \rightarrow Eu^{2+}(4f^7) + Tb^{4+}(4f^7)$

Eu^{3+} , Eu^{2+} and Tb^{3+} will co-exist in the host. If one can find a suitable matrix and dope Eu^{3+} and Tb^{3+} in it, a

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simultaneous emission of Eu^{3+} , Eu^{2+} and Tb^{3+} will be achieved. If one adjusts the matrix composition and the rare earth ion concentration and make their emission comfortable, the synthesis of a novel trichromatic phosphor codoped with two rare earth ions in a single matrix in air atmosphere should be possible. Such co-existence phenomena have been observed in some borates^[7], phosphates^[8], borate-phosphate^[9], zeolite-Y^[10] and so on.

Alkaline earth haloborates have been paid much attention as luminescent matrices, while investigations have been mainly concentrated on their structures^[11,12] and luminescent properties after X-ray excitation^[13]. We find that their emission efficiency is high under UV excitation. It is necessary to investigate their luminescent properties with co-doped Eu and Tb.

EXPERIMENTAL

All the luminescent property measurements were performed on powder samples, which were synthesized in air atmosphere. The stoichiometric amounts of H_3BO_3 (excess of 10%) with alkaline earth carbonate and chloride, BaCO_3 and $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$, CaCO_3 and CaCl_2 , SrCO_3 and SrCl_2 , and Eu_2O_3 , Tb_4O_7 (99.99%) together are mixed and well ground. The mixture is then pre-fired at 300°C for 2h and fired at $850\sim 950^\circ\text{C}$ for 3~5h. All materials obtained are white powders.

All products were characterized by X-ray powder diffraction (XRD) on Rigaku D/max-II B diffractometer with a rotating target with Ni-filtered $\text{Cu-K}\alpha$ radiation at room temperature. The XRD data for indexing and cell-parameter calculation were collected by a scanning mode with a step length of 0.02° in the 2θ range from 10 to 60° and a scanning rate of $0.2^\circ \cdot \text{min}^{-1}$. Silicon was used as an internal standard. Luminescent properties at room temperature are performed on SPEX F1 2 spectrofluorometer with a Xenon arc lamp as excitation source.

RESULTS AND DISCUSSION

The XRD of $\text{M}_2\text{B}_5\text{O}_9\text{Cl}:\text{Eu}^{3+}, \text{Tb}^{3+}$ (M=Ca, Sr, Ba)

The XRD patterns of all products were characterized. No other peaks or impurities are detected. There-

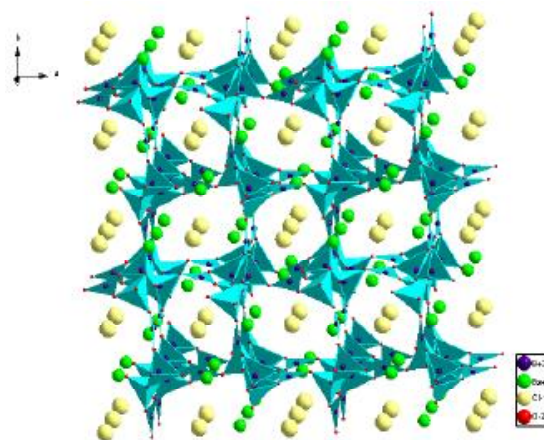


Figure 1 : The structure diagram of $\text{Ba}_2\text{B}_5\text{O}_9\text{Cl}:0.02\text{Eu}, 0.02\text{Tb}$

TABLE 1 : The emission of $\text{Eu}^{3+}, \text{Eu}^{2+}$ and Tb^{3+} in $\text{M}_2\text{B}_5\text{O}_9\text{Cl}$

	Eu^{3+} ($\lambda_{\text{ex}}=391\text{nm}$)	Eu^{2+} ($\lambda_{\text{ex}}=330\text{nm}$)	Tb^{3+} ($\lambda_{\text{ex}}=378\text{nm}$)
Ca-system	613nm	405nm	544nm
Sr-system	613nm	420nm, 378nm	544nm
Ba-system	613nm	430nm, 378nm	544nm

fore, XRD confirmed the phase purity of the resulting $\text{M}_2\text{B}_5\text{O}_9\text{Cl}$. The compound crystallizes in the orthorhombic; Space group $Pn\bar{2}$ (no. 34). Figure 1 shows the structure diagram of $\text{Ba}_2\text{B}_5\text{O}_9\text{Cl}:0.02\text{Eu}, 0.02\text{Tb}$. The unit cell dimensions for the product are $a = 11.63585\text{Å}$, $b = 11.581\text{Å}$, $c = 6.6828\text{Å}$.

Luminescent properties of $\text{M}_2\text{B}_5\text{O}_9\text{Cl}:\text{Eu}^{3+}$ and $\text{M}_2\text{B}_5\text{O}_9\text{Cl}:\text{Tb}^{3+}$ (M=Ca, Sr, Ba)

The luminescent properties of single-doped $\text{M}_2\text{B}_5\text{O}_9\text{Cl}:\text{Eu}^{3+}$ and $\text{M}_2\text{B}_5\text{O}_9\text{Cl}:\text{Tb}^{3+}$ (M=Ca, Sr, Ba) have been studied at room temperature. The main results are shown in TABLE 1.

From the data listed in TABLE 1, one can conclude that both Eu^{2+} and Eu^{3+} exist in Eu doped products. The emission spectra of the compounds show that the shape of the Eu^{3+} spectrum consists of a series of sharp lines and the shape of Eu^{2+} spectrum is a broad band.

The emission lines of Eu^{3+} in the products observed under 391nm excitation are attributed to $^5\text{D}_0 - ^7\text{F}_j$ ($j=0,1,2,3,4$) transition in Eu^{3+} ion, and the strongest emission peak is at 613nm, which is ascribed to $^5\text{D}_0 - ^7\text{F}_2$ transitions.

In these products, broadband emission spectra with

maxima at around 405, 420 and 430nm were observed for M=Ca, Sr and Ba, respectively, under 330nm excitation. These broad bands correspond to the $4f^65d-4f^7$ transition in Eu^{2+} ion. The occurrence of Eu^{2+} can be explained by the model, which the Eu^{3+} CTS dissociate into Eu^{2+} and a free hole^[14]. It should be remembered that already the reduction of Eu^{3+} to Eu^{2+} in oxide materials via a charge transfer process requires an energy equal to approx. $30,000\text{cm}^{-1}$ which can be provided by radiation in the near UV region^[2]. So ${}^7\text{F} \rightarrow \text{CTS}$ excitation takes place under 330nm, and then the CTS of Eu^{3+} dissociates thermally into Eu^{2+} and a free hole. And Eu^{2+} ion enters more easily into the M^{2+} site than Eu^{3+} ion because charge compensation is necessary if Eu^{3+} ion enters the $\text{M}_2\text{B}_5\text{O}_9\text{Cl}$ matrix. So we can observe the broadband emission of Eu^{2+} .

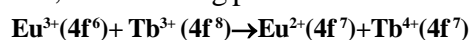
In addition, the maximum emission wavelength of Eu^{2+} shifts towards longer wavelength with increasing radius of the M^{2+} ions. This can be explained with crystal field effect. The emission intensity of Eu^{2+} is strongest in Sr-containing matrices. The reason is that the radius of Eu^{2+} is closer to Sr^{2+} than Ca^{2+} and Ba^{2+} and made more of the Eu^{2+} enter into the Sr^{2+} sites.

The luminescent properties of Tb^{3+} in $\text{Ca}_2\text{B}_5\text{O}_9\text{Cl}:\text{Tb}^{3+}$ are similar to those of other alkaline earth systems but its intensity is strongest. The shape of the spectrum is a series of sharp lines due to ${}^5\text{D}_4-{}^7\text{F}_j$ transitions. The strongest emission line of Tb^{3+} is at 544nm, which is due to ${}^5\text{D}_4-{}^7\text{F}_5$ transition.

Influence of Tb^{3+} on Eu^{2+} emission in $\text{Sr}_2\text{B}_5\text{O}_9\text{Cl}:\text{Eu}^{3+}$ (0.2mol%), yTb^{3+}

The emission spectra of $\text{Sr}_2\text{B}_5\text{O}_9\text{Cl}:\text{Eu}^{3+}$ (0.2mol%), yTb^{3+} under 365nm excitation are given in figure 2.

The results show that the emission of Eu^{3+} , Eu^{2+} and Tb^{3+} can co-exist in this matrix, which can be a good matrix for this kind of phosphor. The intensity of Eu^{2+} is increased under 365nm excitation when Tb^{3+} concentration is increased. It can be explained by electron transfer process. When Eu^{3+} and Tb^{3+} are co-doped in matrix, the following process could occur. That is:



When the concentration of Tb^{3+} is increased, the balance shift to the right side, the concentration of Eu^{2+} increases and the emission intensity is increased, too. Gao et al.^[7] studied it in details in $\text{BaB}_8\text{O}_{13}:\text{Eu}, \text{Tb}$ with

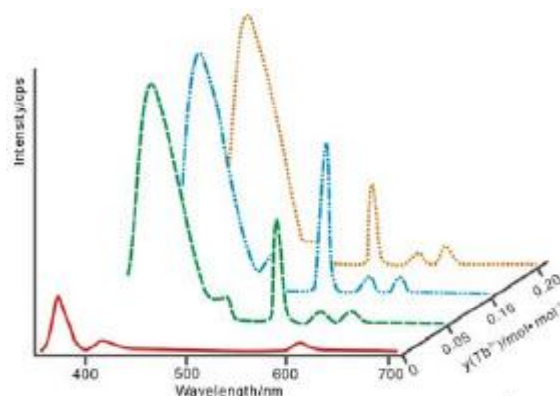


Figure 2 : The emission spectra of $\text{Sr}_2\text{B}_5\text{O}_9\text{Cl}:\text{Eu}^{3+}$, yTb^{3+}

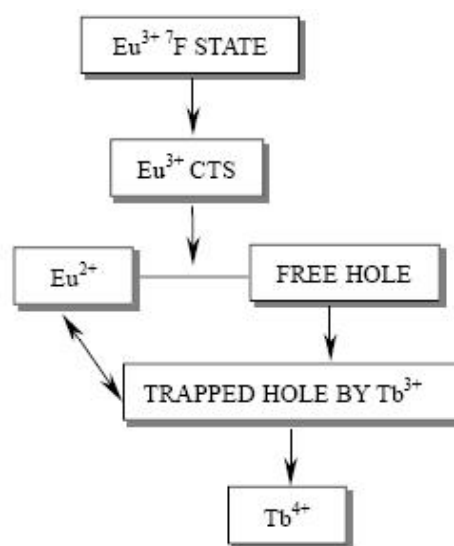


Figure 3 : The diagram of the model of the electron transfer mechanism

ESR spectroscopy. We know that the oxidation of Tb^{3+} to Tb^{4+} is impossible near UV excitation available under mild ambient condition, because this process requires much higher energy than UV energy. So the mechanism of this phenomenon may be described as follow: the free hole which was produced via the dissociation of CTS of Eu^{3+} may be trapped by Tb^{3+} , then create Tb^{4+} , and Tb^{3+} may have a large cross section for the hole, Eu^{2+} and trapped-hole subsequently recombine non-radioactively^[15]. The diagram of the model is summarized in figure 3.

Another interesting phenomenon is observed when it is excited under 254nm. The results are shown in figure 4.

From figure 4, one can see that the Eu^{2+} emission intensity is decreased with increasing the Tb^{3+} concen-

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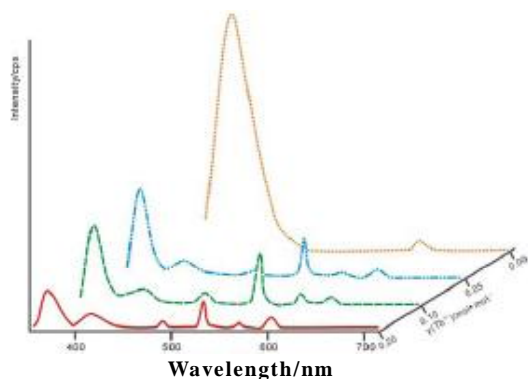


Figure 4 : The emission spectra of $\text{Sr}_2\text{B}_5\text{O}_9\text{Cl}:0.02\text{Eu}^{3+}, y\text{Tb}^{3+}$

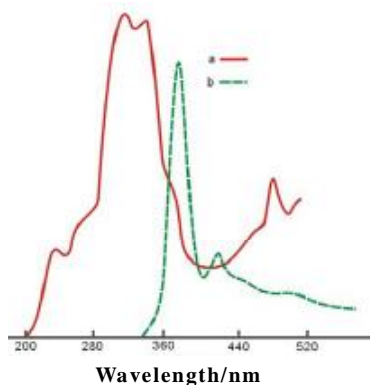


Figure 5 : Tb^{3+} excitation spectrum (a) and Eu^{3+} emission spectrum (b) in Sr-system

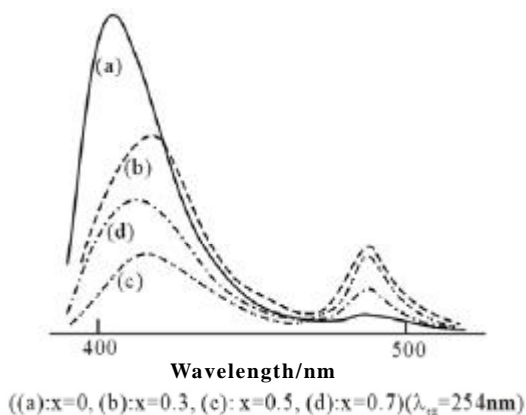


Figure 6 : The emission spectra of $\text{Ca}_{2-x}\text{Ba}_x\text{B}_5\text{O}_9\text{Cl}:0.02\text{Eu}^{3+}, 0.02\text{Tb}^{3+}$

tration under 254nm excitation, which is in contrary to that of 365nm excitation. A possible explanation is that there is a competition between electron transfer and energy migration. Under 365nm excitation it is due to the emission of Tb^{3+} while it contributes little to that the electron transfer between Eu^{3+} and Tb^{3+} therefore increasing over the energy migration between Eu^{3+} - Tb^{3+} .

Because of this, the emission intensity of Eu^{2+} becomes stronger. Under 254nm excitation, the matrix is suitable for both the Eu^{2+} and Tb^{3+} . But Tb^{3+} absorbs the emission energy of Eu^{2+} since there is a cross section between Eu^{2+} emission spectrum and Tb^{3+} excitation spectrum. In this case energy migration becomes the main factor and the Eu^{2+} emission intensity is decreased with increasing the Tb^{3+} concentration. Some evidences can be seen from figure 5.

Effect of matrix composition

Figure 2 shows the emission position of Eu^{2+} and the emission intensity ratio of Eu^{2+} , Tb^{3+} and Eu^{3+} are poor as trichromatic phosphor. The matrix compositions have been adjusted according to the luminescent properties in order to get a better trichromatic phosphor. The results obtained for these new samples are shown in figure 6.

The Eu^{2+} emission shifts from 405nm to longer wavelength when Ba^{2+} ions partially substitute for Ca^{2+} , whereas the positions of Tb^{3+} and Eu^{3+} emission do not change.

CONCLUSION

$\text{M}_2\text{B}_5\text{O}_9\text{Cl}:\text{Eu}^{3+}, \text{Tb}^{3+}$ ($\text{M}=\text{Ca}, \text{Sr}, \text{Ba}$) phosphors were synthesized in ambient atmosphere and co-existence of Eu^{3+} , Eu^{2+} and Tb^{3+} emission in these matrices have been observed. The mechanism of the phenomenon may be elucidated that electron transfer occurs due to Eu^{3+} CTS dissociating into Eu^{2+} and a free hole, which is trapped by Tb^{3+} . The emission of Eu^{2+} shifts towards longer wavelengths in the order of Ca-Sr-Ba. The intensity of Eu^{2+} emission is increased under 365nm excitation but decreased under 254nm excitation with increasing the concentration of Tb^{3+} in the $\text{Sr}_2\text{B}_5\text{O}_9\text{Cl}$ matrix, which the reason might be the competition between electron transfer and energy migration. By adjusting the matrix composition, a shift of the Eu^{2+} emission towards longer wavelengths in (Ca, Ba) system is observed and a novel white-light luminescent material is expected.

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