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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 Eu³⁺, Eu²⁺and Tb³⁺ were observed in these matrices. The phenomenon may be explained by the electron transfer theory. The intensity of Eu²⁺ emission increases under 365nm excitation and decreases under 254nm excitation with increasing the Tb³⁺ concentration. The competition between electron transfer and energy migration might be the reason for the observation.

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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 5s² and 5p⁶ orbital^[2]. For example, J.E.C. Silva et al. have developed a glassy material doped with rare earth ions (Eu³⁺, Tb³⁺ and Tm³⁺), 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], Eu³⁺and Tb³⁺ are important conjugated ions for luminescence activator. When they are co-doped in same host, an electron will transfer from Tb³⁺ to Eu³⁺ as^[5,6].
 $Eu^{3+}(4f^6)+Tb^{3+}(4f^8)?Eu^{2+}(4f^7)+Tb^{4+}(4f^7)$

Eu³⁺, Eu²⁺and Tb³⁺ will co-exist in the host. If one can find a suitable matrix and dope Eu³⁺ and Tb³⁺ in it, a

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simultaneous emission of Eu³⁺, Eu²⁺ and Tb³⁺ 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 H₃BO₃ (excess of 10%) with alkaline earth carbonate and chloride, BaCO₃ and BaCl₂·2H₂O, CaCO₃ and CaCl₂, SrCO₃ and SrCl₂, and Eu₂O₃, Tb₄O₇ (99.99%) together are mixed and well ground. The mixture is then prefired at 300°C for 2 h and fired at 850~950°C for 3~5 h. 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 Cu-K α 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°C in the 2θ range from 10 to 60°C and a scanning rate of 0.2°C·min⁻¹. Silicon was used as an internal standard. Luminescent properties at room temperature are performed on SPEX Fl 2 spectrofluorometer with a Xenon arc lamp as excitation source.

RESULTS AND DISCUSSION

The XRD of M₂B₅O₉Cl: Eu³⁺, Tb³⁺ (M=Ca, Sr, Ba)

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

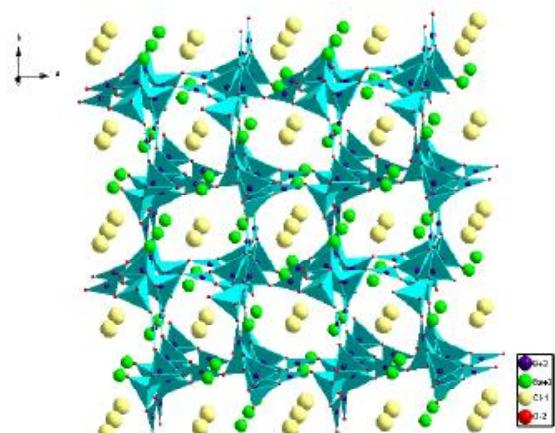


Figure 1 : The structure diagram of Ba₂B₅O₉Cl:0.02Eu, 0.02Tb

TABLE 1 : The emission of Eu³⁺, Eu²⁺ and Tb³⁺ in M₂B₅O₉Cl

	Eu ³⁺ (λ _{ex} =391nm)	Eu ²⁺ (λ _{ex} =330nm)	Tb ³⁺ (λ _{ex} =378nm)
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 M₂B₅O₉Cl. The compound crystallizes in the orthorhombic; Space group Pn n 2 (no. 34). Figure 1 shows the structure diagram of Ba₂B₅O₉Cl:0.02Eu, 0.02Tb. The unit cell dimensions for the product are a = 11.63585 Å, b = 11.581 Å, c = 6.6828 Å.

Luminescent properties of M₂B₅O₉Cl: Eu³⁺ and M₂B₅O₉Cl: Tb³⁺ (M=Ca, Sr, Ba)

The luminescent properties of single-doped M₂B₅O₉Cl: Eu³⁺ and M₂B₅O₉Cl: Tb³⁺ (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 Eu²⁺ and Eu³⁺ exist in Eu doped products. The emission spectra of the compounds show that the shape of the Eu³⁺ spectrum consists of a series of sharp lines and the shape of Eu²⁺ spectrum is a broad band.

The emission lines of Eu³⁺ in the products observed under 391 nm excitation are attributed to ⁵D₀-⁷F_J (J=0,1,2,3,4) transition in Eu³⁺ ion, and the strongest emission peak is at 613 nm, which is ascribed to ⁵D₀-⁷F₂ transitions.

In these products, broadband emission spectra with

maxima at around 405, 420 and 430 nm were observed for M=Ca, Sr and Ba, respectively, under 330 nm excitation. These broad bands correspond to the 4f⁶5d-4f⁷ transition in Eu²⁺ ion. The occurrence of Eu²⁺ can be explained by the model, which the Eu³⁺ CTS dissociate into Eu²⁺ and a free hole^[14]. It should be remembered that already the reduction of Eu³⁺ to Eu²⁺ in oxide materials via a charge transfer process requires an energy equal to approx. 30,000 cm⁻¹ which can be provided by radiation in the near UV region^[2]. So 7F[→]CTS excitation takes place under 330 nm, and then the CTS of Eu³⁺ dissociates thermally into Eu²⁺ and a free hole. And Eu²⁺ ion enters more easily into the M²⁺ site than Eu³⁺ ion because charge compensation is necessary if Eu³⁺ ion enters the M₂B₅O₉Cl matrix. So we can observe the broadband emission of Eu²⁺.

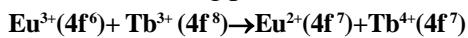
In addition, the maximum emission wavelength of Eu²⁺ shifts towards longer wavelength with increasing radius of the M²⁺ ions. This can be explained with crystal field effect. The emission intensity of Eu²⁺ is strongest in Sr-containing matrices. The reason is that the radius of Eu²⁺ is closer to Sr²⁺ than Ca²⁺ and Ba²⁺ and made more of the Eu²⁺ enter into the Sr²⁺ sites.

The luminescent properties of Tb³⁺ in Ca₂B₅O₉Cl: Tb³⁺ 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 ⁵D₄-⁷F_J transitions. The strongest emission line of Tb³⁺ is at 544 nm, which is due to ⁵D₄-⁷F₅ transition.

Influence of Tb³⁺ on Eu²⁺ emission in Sr₂B₅O₉Cl: Eu³⁺(0.2 mol%), yTb³⁺

The emission spectra of Sr₂B₅O₉Cl: Eu³⁺(0.2 mol%), yTb³⁺ under 365 nm excitation are given in figure 2.

The results show that the emission of Eu³⁺, Eu²⁺ and Tb³⁺ can co-exist in this matrix, which can be a good matrix for this kind of phosphor. The intensity of Eu²⁺ is increased under 365 nm excitation when Tb³⁺ concentration is increased. It can be explained by electron transfer process. When Eu³⁺ and Tb³⁺ are co-doped in matrix, the following process could occur. That is:



When the concentration of Tb³⁺ is increased, the balance shift to the right side, the concentration of Eu²⁺ increases and the emission intensity is increased, too. Gao et al.^[7] studied it in details in BaB₈O₁₃: Eu, Tb with

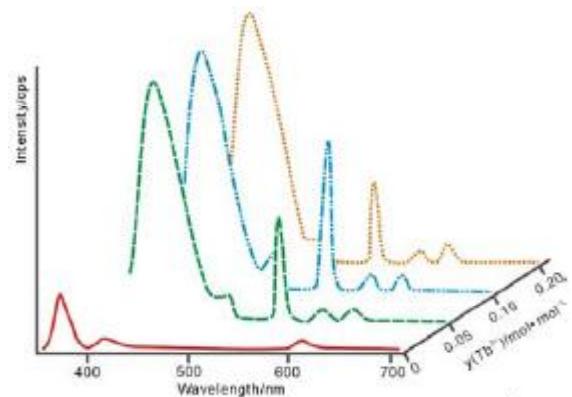


Figure 2 : The emission spectra of Sr₂B₅O₉Cl: 0.02Eu³⁺, yTb³⁺

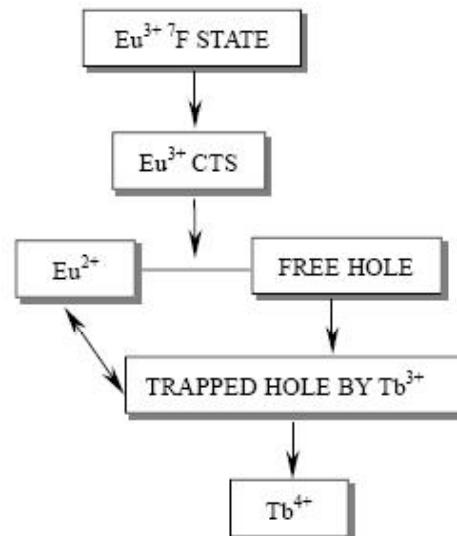


Figure 3 : The diagram of the model of the electron transfer mechanism

ESR spectroscopy. We know that the oxidation of Tb³⁺ to Tb⁴⁺ 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 Eu³⁺ may be trapped by Tb³⁺, then create Tb⁴⁺, and Tb³⁺ may have a large cross section for the hole, Eu²⁺ 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 254 nm. The results are shown in figure 4.

From figure 4, one can see that the Eu²⁺ emission intensity is decreased with increasing the Tb³⁺ concen-

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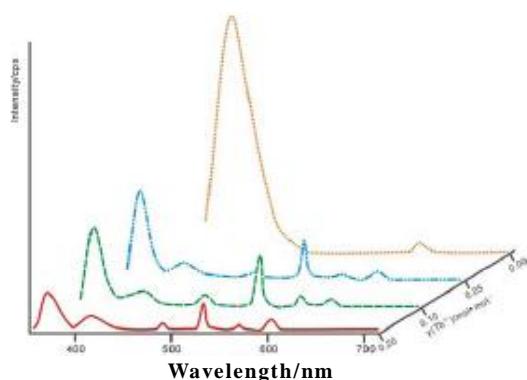


Figure 4 : The emission spectra of $\text{Sr}_2\text{B}_5\text{O}_9\text{Cl}:0.02\text{Eu}^{3+}$, $y\text{Tb}^{3+}$

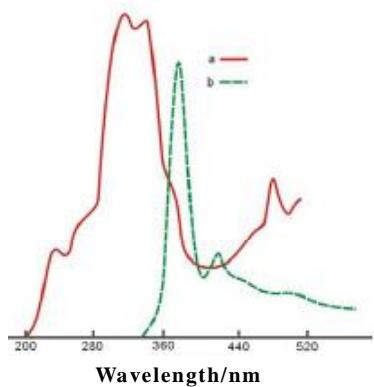


Figure 5 : Tb^{3+} excitation spectrum (a) and Eu^{3+} emission spectrum (b) in Sr-system

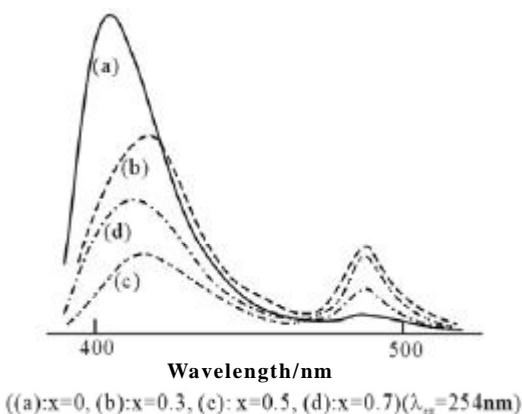


Figure 6 : The emission spectra of $\text{Ca}_{2-x}\text{Ba}_x\text{B}_5\text{O}_9\text{Cl}:0.02\text{Eu}^{3+}, 0.02\text{Tb}^{3+}$

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 $\text{Ca}-\text{Sr}-\text{Ba}$. 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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