

# A Study on the Mechanism of the Abnormal Reduction of $\text{Eu}^{3+} \rightarrow \text{Eu}^{2+}$ in $\text{Sr}_2\text{B}_5\text{O}_9\text{Cl}$ Prepared in Air at High Temperature

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**This paper reports a new observation of the abnormal reduction of  $\text{Eu}^{3+} \rightarrow \text{Eu}^{2+}$  in  $\text{Sr}_2\text{B}_5\text{O}_9\text{Cl}$  when prepared in air at high temperature. A model based on the nature of substitution defects is proposed to explain this abnormal reduction. Electrons, which reduced the  $\text{Eu}^{3+}$  ions, are created by the substitution of cations first and then transferred to the target  $\text{Eu}^{3+}$  ions via tetrahedral borate anion groups. Codoping experiments are designed and performed. The results of these experiments support the model proposed.** © 1999 Academic Press

## INTRODUCTION

As is well known, some kinds of reducing agents, such as  $\text{H}_2$ , are needed to reduce the  $\text{Eu}^{3+}$  ion to  $\text{Eu}^{2+}$  in a solid state compound. But in some special compounds, this reduction process could be thermally achieved in a nonreducing atmosphere at high temperature, such as in air and/or  $\text{N}_2$ . Two of us have systematically studied and reported the valence change from  $\text{RE}^{3+}$  to  $\text{RE}^{2+}$  ( $\text{RE} = \text{Eu}, \text{Sm}, \text{Yb}$ ) in  $\text{SrB}_4\text{O}_7:\text{RE}$  prepared in air (1), after which Peterson *et al.* successfully prepared the compound of  $\text{SrB}_4\text{O}_7:\text{Tm}^{2+}$  in air with  $\text{Tm}^{3+}$  as the starting material (2).

In recent years, our research group has worked on the abnormal reduction of  $\text{RE}^{3+} \rightarrow \text{RE}^{2+}$  ( $\text{RE} = \text{Eu}, \text{Sm}, \text{Yb}, \text{Tm}$ ) in borates of  $\text{BaB}_4\text{O}_7$ ,  $\text{BaB}_8\text{O}_{13}$ , and  $\text{SrB}_6\text{O}_{10}$  (3–5). However, the mechanisms of this reduction has not been fully understood.

In this paper, we report a new compound,  $\text{Sr}_2\text{B}_5\text{O}_9\text{Cl}:\text{Eu}$ , in which the abnormal reduction of  $\text{Eu}^{3+} \rightarrow \text{Eu}^{2+}$  occurs when prepared in air. A model based on the nature of substitution defects is proposed to explain this abnormal reduction and experiments used to prove the above model are also presented.

## EXPERIMENTAL

The host compounds of  $\text{Sr}_2\text{B}_5\text{O}_9\text{Cl}$  were prepared by firing intimate mixtures of high-purity  $\text{SrCO}_3$ ,  $\text{H}_3\text{BO}_3$ , and

$\text{SrCl}_2$  with the mole ratio of 2 : 5.15 : 2. The 3 mol% excess of  $\text{H}_3\text{BO}_3$  was used for the compensation of evaporation. The excess  $\text{SrCl}_2$  was washed out with distilled water after preparation. The concentration of all doping ions of  $\text{Eu}^{3+}$ ,  $\text{Na}^{1+}$ ,  $\text{La}^{3+}$ , and  $\text{Zr}^{4+}$  were 1 mol% of the  $\text{Sr}^{2+}$  ion in  $\text{Sr}_2\text{B}_5\text{O}_9\text{Cl}$ . The mixtures of the corresponding starting materials were thoroughly ground and then heated in air at  $400^\circ\text{C}$  for 4 hr. After being ground, these mixtures were fired in air at  $900^\circ\text{C}$  for another 4 hr. The products were finally washed with distilled water and dried. All samples were checked by X-ray powder diffraction and were found to have a single phase of  $\text{Sr}_2\text{B}_5\text{O}_9\text{Cl}$ .

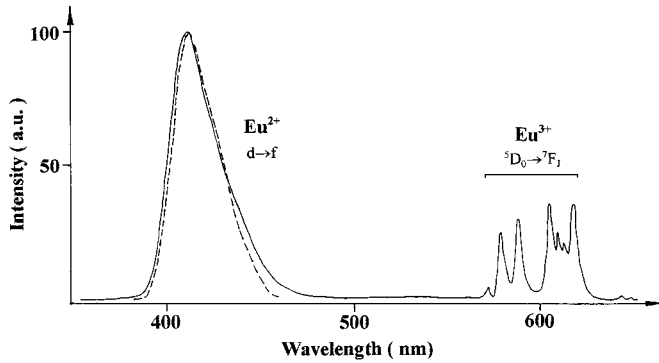
The luminescence measurements of samples were carried out at room temperature with a SPEX FL-2 fluorescence spectrophotometer.

## RESULTS AND DISCUSSION

Under short-wavelength excitation, the emission character of  $\text{Sr}_2\text{B}_5\text{O}_9\text{Cl}:\text{Eu}$  prepared in air was as shown in Fig. 1. In the blue spectral region, there is a broad-emission band; and in the red spectral region, a series of sharp-emission lines exists. For comparison, the emission spectrum of  $\text{Sr}_2\text{B}_5\text{O}_9\text{Cl}:\text{Eu}^{2+}$  from literature (6) was also presented in Fig. 1 (dashed line).

In solid state compounds, the luminescent characteristics of  $\text{Eu}^{2+}$  ( $4f^7$ ) and  $\text{Eu}^{3+}$  ( $4f^6$ ) have been well studied. The  $\text{Eu}^{2+}$  ion shows a broad-band emission of  $d \rightarrow f$  transition generally in the violet–blue spectral region, and in some cases, a sharp-line emission at about 367 nm also exists (7). However, a series of sharp emission lines in the red spectral region is the character of  $\text{Eu}^{3+}$  emission (8). Therefore, the luminescence measurement could be a convenient and precise way to identify the valence states of europium ions in solid state compounds.

Peters and Baglio have reported the luminescence and structural properties of  $\text{Sr}_2\text{B}_5\text{O}_9\text{Cl}:\text{Eu}^{2+}$  prepared in a reducing atmosphere of  $\text{H}_2/\text{N}_2$  (6). Their phosphor showed a broadband emission at about 425 nm. Our sample also



**FIG. 1.** The emission spectra of  $\text{Sr}_2\text{B}_5\text{O}_9\text{Cl}:\text{Eu}$  phosphors: (Solid line) Spectrum in this work,  $\lambda_{\text{ex}} = 290 \text{ nm}$ ; (Dashed line) spectrum from Ref. (7), prepared in  $\text{H}_2/\text{N}_2$ .

showed a broadband emission with the maximum at about 423 nm. Since the matrix of the sample has no emission around 423 nm, the blue emission of our sample must be due to the doped Eu ion. The sharp line emissions in the red spectral region of Fig. 1 are easily assigned to the  ${}^5D_0 \rightarrow {}^7F_1$  transition emissions of the  $\text{Eu}^{3+}$  ion unreduced in host. Comparing the emission spectrum of our sample with that of Ref. (6) as shown in Fig. 1, we could draw the conclusion that the doped  $\text{Eu}^{3+}$  ions were partially reduced to their  $\text{Eu}^{2+}$  form in our sample although it was prepared in air. The abnormal reduction of  $\text{Eu}^{3+} \rightarrow \text{Eu}^{2+}$  reported here makes  $\text{Sr}_2\text{B}_5\text{O}_9\text{Cl}$  a new member of the borate compounds in which the abnormal reduction of rare earth ions happens.

In Ref. (1), we have proposed four conditions for the abnormal reduction of rare earth ions in solid state compounds:

- (1) No oxidizing ions present in hosts.
- (2) The doped trivalent rare earth ions  $RE^{3+}$  replace the cations with lower valences in the hosts, such as alkaline earth ion  $M^{2+}$ .
- (3) The substituted cations have similar radii to the corresponding divalent  $RE^{2+}$  ions.
- (4) The host compounds have appropriate crystal structures.

Checking the sample of  $\text{Sr}_2\text{B}_5\text{O}_9\text{Cl}:\text{Eu}$  against the above four conditions, we could easily see that all  $\text{Sr}^{2+}$ ,  $\text{B}^{3+}$ , and  $\text{Cl}^-$  are nonoxidizing ions, which meets condition 1. The  $\text{Eu}^{3+}$  ion replaces the  $\text{Sr}^{2+}$  ion and the latter has a radius almost the same as the  $\text{Eu}^{2+}$  ion, which satisfies conditions 2 and 3. The crystal structure of  $\text{Sr}_2\text{B}_5\text{O}_9\text{Cl}$  is isomorphous with that of  $\text{Eu}_2\text{B}_5\text{O}_9\text{Cl}$  with orthorhombic symmetry (9). In its anion groups, three  $\text{BO}_4$  tetrahedra and two triangular  $\text{BO}_3$  groups are linked with each other. This structure feature is in accordance with that of all the borates, which contain tetrahedral  $\text{BO}_4$  groups and show the abnormal-reduction properties on  $RE^{3+}$  ions. Therefore,  $\text{Sr}_2\text{B}_5\text{O}_9\text{Cl}$  fit condition 4.

Now let us take some considerations about the mechanisms of this abnormal reduction into account.

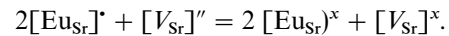
From a chemistry point of view, the occurrence of the  $\text{Eu}^{3+} \rightarrow \text{Eu}^{2+}$  reaction needs an electron anyway. However, in the case of the abnormal reduction of  $\text{Eu}^{3+}$  ions in borates, such as  $\text{SrB}_4\text{O}_7$  and  $\text{Sr}_2\text{B}_5\text{O}_9\text{Cl}$ , it is obvious that no reducing materials exist in the starting materials and in the atmosphere when prepared in air. Therefore, the questions would be the following:

(a) Where does the reducing electron come from in the reaction?

(b) How does it transfer to the doped  $\text{Eu}^{3+}$  ion?

Here, we propose a model based on the nature of defects caused by the substitution of cations, and it works as follows.

When trivalent  $\text{Eu}^{3+}$  ions were built into  $\text{Sr}_2\text{B}_5\text{O}_9\text{Cl}$ , they would replace the  $\text{Sr}^{2+}$  ions of  $\text{Sr}_2\text{B}_5\text{O}_9\text{Cl}$ . To keep the electroneutrality of the compound, two  $\text{Eu}^{3+}$  ions would substitute for three  $\text{Sr}^{2+}$  ions. Therefore, two positive defects of  $[\text{Eu}_{\text{Sr}}]^*$  and one negative  $\text{Sr}^{2+}$  vacancy of  $[\text{V}_{\text{Sr}}]''$  would be created by each substitution for every two  $\text{Eu}^{3+}$  ions in the compound. By thermal stimulation, electrons of the  $[\text{V}_{\text{Sr}}]''$  vacancies would be then transferred to doped  $\text{Eu}^{3+}$  ions and reduce them to their  $\text{Eu}^{2+}$  from as shown in the following equation:



If this model worked, we may imagine that the more electrons carried by negative defects were created, the more  $\text{Eu}^{3+}$  ions would be reduced to  $\text{Eu}^{2+}$  ions. As a result, the ratio of  $\text{Eu}^{2+}$  and  $\text{Eu}^{3+}$  emission intensities,  $I_{\text{Eu}^{2+}}/I_{\text{Eu}^{3+}}$ , would be increasing.

Keeping the above ideas in mind, we designed and conducted in air the following codoping experiments in the compound of  $\text{Sr}_2\text{B}_5\text{O}_9\text{Cl}$ .

Together with the  $\text{Eu}^{3+}$  ion, a second cation of  $M^{n+}$  ( $M^{n+} = \text{Na}^{1+}$ ,  $\text{Sr}^{2+}$ ,  $\text{La}^{3+}$ ,  $\text{Zr}^{4+}$ ) was codoped into the matrix of  $\text{Sr}_2\text{B}_5\text{O}_9\text{Cl}$ . This way, we could make different defects with various negative charges in the compounds concerned. Table 1 summarizes the experimental results and Fig. 2 shows the emission spectra of the codoped Eu samples from which the  $R_b$  ratio was calculated.

With the codoping of  $\text{Eu}^{3+} + \text{Na}^{1+}$ , one positive defect of  $[\text{Eu}_{\text{Sr}}]^*$  and one negative defect of  $[\text{Na}_{\text{Sr}}]'$  would be created since  $\text{Eu}^{3+}$  and  $\text{Na}^{1+}$  occupy two  $\text{Sr}^{2+}$  sites. By the attraction of the positive charge of the  $\text{Na}^{1+}$  ion, the effective negative charge of the electron on the  $[\text{Na}_{\text{Sr}}]'$  defects is less than 1, and hence  $R_a$  (the ratio of the number of effective electrons on negative defects and the number of  $\text{Eu}^{3+}$  ions to be reduced) is also less than 1. In the case of the codoping of  $\text{Eu}^{3+} + \text{Sr}^{2+}$ , two  $[\text{Eu}_{\text{Sr}}]^*$  defects and one  $[\text{V}_{\text{Sr}}]''$  vacancy appear and the two electrons on the  $[\text{V}_{\text{Sr}}]''$  vacancy retain their total effective negative charge as 2

**TABLE 1**  
**Experimental Results of the Codoping Samples of  $\text{Sr}_2\text{B}_5\text{O}_9\text{Cl}$ :**  
 $x\text{Eu}^{3+}$ ,  $yM^{n+}$  ( $M^{n+}=\text{Na}^{1+}$ ,  $\text{Sr}^{2+}$ ,  $\text{La}^{3+}$ ,  $\text{Zr}^{4+}$ )

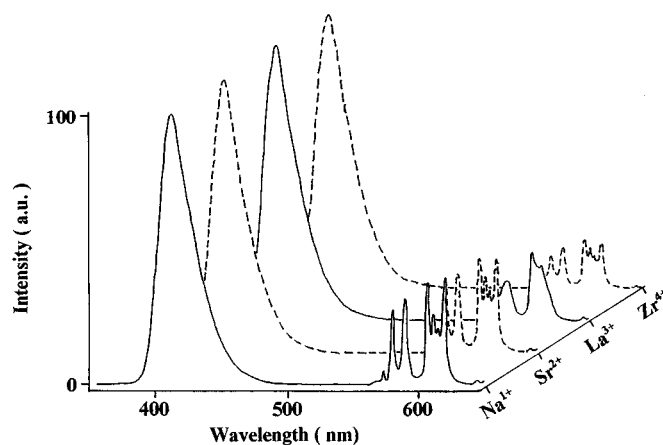
Substitution	Positive defect	Negative defect	$R_a^a$	$R_b^b$
$\text{Eu}^{3+} + \text{Na}^+ \rightarrow 2\text{Sr}^{2+}$	$[\text{Eu}_{\text{Sr}}]^+$	$[\text{Na}_{\text{Sr}}]'$	$< 1/1 \Rightarrow < 1$	4.11
$2\text{Eu}^{3+} \rightarrow 3\text{Sr}^{2+}$	$2[\text{Eu}_{\text{Sr}}]^+$	$[\text{V}_{\text{Sr}}]''$	$2/2 \Rightarrow 1$	4.42
$(2\text{Eu}^{3+} + 2\text{Sr}^{2+} \rightarrow 5\text{Sr}^{2+})$				
$\text{Eu}^{3+} + \text{La}^{3+} \rightarrow 3\text{Sr}^{2+}$	$[\text{Eu}_{\text{Sr}}]^+$	$[\text{V}_{\text{Sr}}]''$	$2/1 \Rightarrow 2$	6.28
	$[\text{La}_{\text{Sr}}]^+$			
$2\text{Eu}^{3+} + 2\text{Zr}^{4+} \rightarrow 7\text{Sr}^{2+}$	$2[\text{Eu}_{\text{Sr}}]^+$	$3[\text{V}_{\text{Sr}}]''$	$6/2 \Rightarrow 3$	7.88
	$2[\text{Zr}_{\text{Sr}}]^{++}$			

<sup>a</sup>Ratio of the number of effective electrons on negative defects and the number of  $\text{Eu}^{3+}$  ions to be reduced.

<sup>b</sup>Ratio of the contents of  $\text{Eu}^{2+}$  ions reduced and  $\text{Eu}^{3+}$  ions unreduced calculated from the emission spectra of Fig. 2.

since there is no positive charge on the vacancy. Subsequently  $R_a$  is 1. With the same consideration, we could calculate the above ratios of  $R_a$  as 2 and 3 in the cases of codoping with  $\text{Eu}^{3+} + \text{La}^{3+}$  and  $\text{Eu}^{3+} + \text{Zr}^{4+}$ , respectively, as shown in column 4, Table 1. According to this model, the increase of  $R_a$  should have a favorable effect on the abnormal reduction of  $\text{Eu}^{3+} \rightarrow \text{Eu}^{2+}$ ; in other words, the number of  $\text{Eu}^{2+}$  ions reduced should be increased with the increase of the charges of the second doping ions from  $\text{Na}^{1+}$  to  $\text{Zr}^{4+}$ .

Below quenching concentrations of  $\text{Eu}^{2+}$  and  $\text{Eu}^{3+}$  luminescence, the emission intensities of  $\text{Eu}^{2+}$   $d \rightarrow f$  transition ( $I_{\text{Eu}^{2+}}$ ) in the blue region of the spectrum and  $\text{Eu}^{3+}$   $f \rightarrow f$  transitions ( $I_{\text{Eu}^{3+}}$ ) in the red spectral region, as shown in Fig. 2, are proportional to the contents of  $\text{Eu}^{2+}$  and  $\text{Eu}^{3+}$  ions in compounds, respectively. In our samples, the sum of the doped europium ions for each sample was



**FIG. 2.** Emission spectra of codoped samples of  $\text{Sr}_2\text{B}_5\text{O}_9\text{Cl}$ :  $x\text{Eu}^{3+}$ ,  $yM^{n+}$  ( $M^{n+} = \text{Na}^{1+}$ ,  $\text{Sr}^{2+}$ ,  $\text{La}^{3+}$ ,  $\text{Zr}^{4+}$ ) from which the  $R_b$  ratio in Table 1 was calculated,  $\lambda_{\text{ex}} = 290$  nm.

fixed to 1 mol.% of the  $\text{Sr}^{2+}$  ion in  $\text{Sr}_2\text{B}_5\text{O}_9\text{Cl}$ , and so the concentration of either  $\text{Eu}^{2+}$  or  $\text{Eu}^{3+}$  ion is  $< 1$  mol.% and below their quenching concentration ( $> 1$  mol.%). Therefore the ratio of  $R_b = I_{\text{Eu}^{2+}}/I_{\text{Eu}^{3+}}$  could be taken as the relative content ratio of the  $\text{Eu}^{2+}$  ion reduced and the  $\text{Eu}^{3+}$  ion unreduced in compounds. The value of  $R_b$  was listed in column 5, Table 1.

With the codoping of  $\text{Eu}^{3+} + \text{Na}^{1+}$  in  $\text{Sr}_2\text{B}_5\text{O}_9\text{Cl}$ , one defect of  $[\text{Eu}_{\text{Sr}}]^+$  with 1 positive charge and one defect of  $[\text{Na}_{\text{Sr}}]'$  with  $< 1$  negative charge were created. This made  $R_a < 1$  and  $R_b = 4.11$ . In the case of the codoping with  $\text{Eu}^{3+}$  and  $\text{Sr}^{2+}$ , two  $[\text{Eu}_{\text{Sr}}]^+$  defects and one  $[\text{V}_{\text{Sr}}]''$  vacancy with two negative charges were created. Since the ratio of the effective electrons and the number of  $[\text{Eu}_{\text{Sr}}]^+$  defects was 1, which is large than that in  $\text{Eu}^{3+} + \text{Na}^{1+}$  codoping,  $R_b$  was increased subsequently from 4.11 to 4.42. Similarly, with the increase of  $R_a$  from 1 to 2 and 3, when codoped with  $\text{La}^{3+}$  and  $\text{Zr}^{4+}$ ,  $R_b$  was correspondingly increased from 4.42 to 6.289 and 7.88, respectively. The above results indicated that when more electrons on negative defects were created, more  $\text{Eu}^{3+}$  ions were reduced to their lower oxidation state of  $\text{Eu}^{2+}$ . This is well in line with our model proposed above.

However, the defects discussed in our model could be created in almost any solid state borates if the cations involved in the substitution had different valence states. But only a few of them owned the abnormal reduction character on  $\text{RE}^{3+}$  ions. In fact, all the borates which showed abnormal reduction character on  $\text{RE}^{3+}$  ions contain the tetrahedral anion groups of  $\text{BO}_4$ . This implies to us that besides the necessary existence of the defect electrons, the anion structures of compounds played a very important role in the transfer process of the defect electrons to the doped  $\text{RE}^{3+}$  ions by thermal stimulation. To understand the nature of this transfer process, more research work is needed.

## CONCLUSIONS

In  $\text{Sr}_2\text{B}_5\text{O}_9\text{Cl}$ , the doped  $\text{Eu}^{3+}$  ion could be reduced to  $\text{Eu}^{2+}$  when prepared in air at high temperature. The abnormal reduction of  $\text{Eu}^{3+} \rightarrow \text{Eu}^{2+}$  in borates could be partially explained by the proposed model based on the electron transferring from negative defects to the doped  $\text{Eu}^{3+}$  ions by thermal stimulation. To understand the mechanism of this abnormal reduction completely, more work has to be done on how the anion groups of  $\text{BO}_4$  and  $\text{BO}_3$  affect the electron transferring process in the solid state compounds.

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