



The reduction of Eu^{3+} in $\text{SrB}_6\text{O}_{10}$ prepared in air and the luminescence of $\text{SrB}_6\text{O}_{10}:\text{Eu}$

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Abstract

The reduction of Eu^{3+} to Eu^{2+} in $\text{SrB}_6\text{O}_{10}$ prepared in air by a high-temperature solid state reaction was studied. The luminescent properties of Eu^{2+} in this matrix show f–d broad band emission peaking at about 386 and 432 nm at room temperature. A charge compensation mechanism is proposed as a possible explanation. The luminescence of Eu^{3+} with f–f transitions was studied in this sample and reflected that the Eu^{3+} ion occupied a site with non-centro-symmetry. The ESR spectrum was used to detect the existence of Eu^{2+} in the samples. © 1998 Elsevier Science S.A.

Keywords: Borate; Europium; Luminescence; Preparation; Reduction

1. Introduction

The luminescent properties of Eu^{2+} -activated alkaline-earth matrices have been investigated for a long time because Eu^{2+} has emissions consisting of a $4f^7-4f^65d$ band and/or a $4f^7-4f^7$ line spectrum [1–5]. For example, $\text{BaB}_8\text{O}_{13}:\text{Eu}^{2+}$ was reported to be an efficient photoluminescence material and shows a deep-blue band emission [3]. But, in these hosts, the reduction of Eu^{3+} to Eu^{2+} conventionally requires a reducing agent, such as CO, C, H_2 , etc. Su et al. [2] have reported that Eu^{3+} , Sm^{3+} and Yb^{3+} can be reduced to the corresponding divalent rare-earth ions in SrB_4O_7 by a solid state reaction at high temperature in air. They proposed that the rigid three-dimensional network of BO_4 tetrahedra is necessary to stabilize the divalent rare-earth ions at high temperature in an oxidizing atmosphere. Mn^{2+} and Pb^{2+} were reported to retain the divalent state in $\text{SrB}_6\text{O}_{10}$ by firing in air [6,7]. This suggests that $\text{SrB}_6\text{O}_{10}$ should also be a good host for stabilizing divalent rare-earth ions since it also contains a BO_4 tetrahedral network on the basis of its infrared spectrum [1]. The present paper reports on the reduction of Eu^{3+} to Eu^{2+} in $\text{SrB}_6\text{O}_{10}$ and the luminescence of $\text{SrB}_6\text{O}_{10}:\text{Eu}$.

2. Experimental details

The preparation of Eu^{2+} -activated $\text{SrB}_6\text{O}_{10}$ was carried out according to the literature [1], but heating in air instead of H_2/N_2 . The structure of the sample was in good agreement with the JCPDS 20-1190 card.

The dopant Eu ion concentration was 2 mol% of the Sr^{2+} ions in the host compound. The structure of the sample was checked on a Rigaku D/MAX-IIB X-ray powder diffractometer, using $\text{Cu K}\alpha_1$ radiation.

Photoluminescence measurements were performed on a SPEX DM3000f spectrofluorometer equipped with 0.22 m SPEX 1680 double monochromator (resolution 0.1 nm) and a 450 W xenon lamp as excitation source. The excitation spectra were corrected for the lamp output. The emission spectra were corrected for the photomultiplier sensitivity. All luminescence spectra were recorded at room temperature.

3. Results and discussion

3.1. Luminescence of $\text{SrB}_6\text{O}_{10}:\text{Eu}^{2+}$

The excitation and emission spectra of $\text{SrB}_6\text{O}_{10}:\text{Eu}^{2+}$ prepared in air are shown in Fig. 1. There are two broad emission bands peaking at 386 and 432 nm and the

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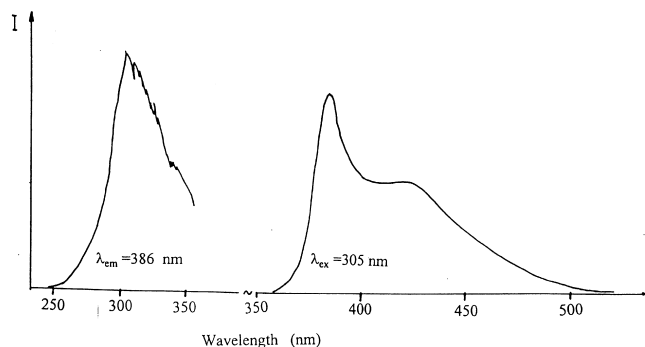


Fig. 1. Excitation and emission spectra at room temperature of $\text{SrB}_6\text{O}_{10}:\text{Eu}^{2+}$ prepared in air.

excitation spectrum exhibits a peak with a maximum near 305 nm. This is the permitted $4f^65d-4f^7$ ($^8S_{7/2}$) transition for Eu^{2+} . Blasse et al. [7,8] and Machida et al. [1] reported the luminescence properties of this sample at 4.2 and 77 K which was prepared in a H_2 stream. The former observed three efficient emission bands with maxima at 386, 432 and 470 nm with almost the same intensity under 305 nm excitation at 4.2 K; the latter observed only 387 and 432 nm emission at 77 K. According to Blasse's data, the emission band at 470 nm was quenched at room temperature, and the 432 nm emission band was quenched to less than 5% of its original intensity at room temperature. So our result for emissions peaking at 386 and 432 nm under 305 nm excitation of $\text{SrB}_6\text{O}_{10}:\text{Eu}^{2+}$ prepared in air is in good agreement with theirs. It is demonstrated that Eu^{3+} in $\text{SrB}_6\text{O}_{10}$ containing the tetrahedral BO_4 group can be reduced to divalent Eu^{2+} even in air at high temperature. The spectra suggest that Eu^{2+} fill more than one lattice site in the $\text{SrB}_6\text{O}_{10}$ matrix. However, the intensity of the 432 nm emission is much lower than that of 380 nm at room temperature due to temperature quenching.

For divalent europium a high emission intensity and a narrow band width require a weak Stokes shift. Due to the high strength of the boron–oxygen bonds, borates with a high B_2O_3 content can form a rigid three-dimensional network which reduces the atomic displacements responsible for the Stokes shift. Among the Eu-doped alkaline earth borates, only the B_2O_3 -richest phases (SrB_4O_7 , $\text{SrB}_6\text{O}_{10}$) show weak thermal quenching at 300 K [9]. The intensity of the Eu^{2+} emission depends strongly on the fraction of tetrahedrally coordinated boron atoms in Sr-borates. In these borates, Eu^{2+} -doped SrB_4O_7 has the highest quantum efficiency and shows the strongest emission intensity while the other Sr-borates show weaker luminescence.

3.2. Luminescence of $\text{SrB}_6\text{O}_{10}:\text{Eu}^{3+}$

The excitation spectrum at room temperature of the $\text{Eu}^{3+} \ ^5\text{D}_0-^7\text{F}_2$ ($\lambda_{\text{em}}=614$ nm) emission in $\text{SrB}_6\text{O}_{10}$ is shown in Fig. 2. It consists of some sharp lines belonging to transitions within the $4f^6$ configuration of Eu^{3+} and a

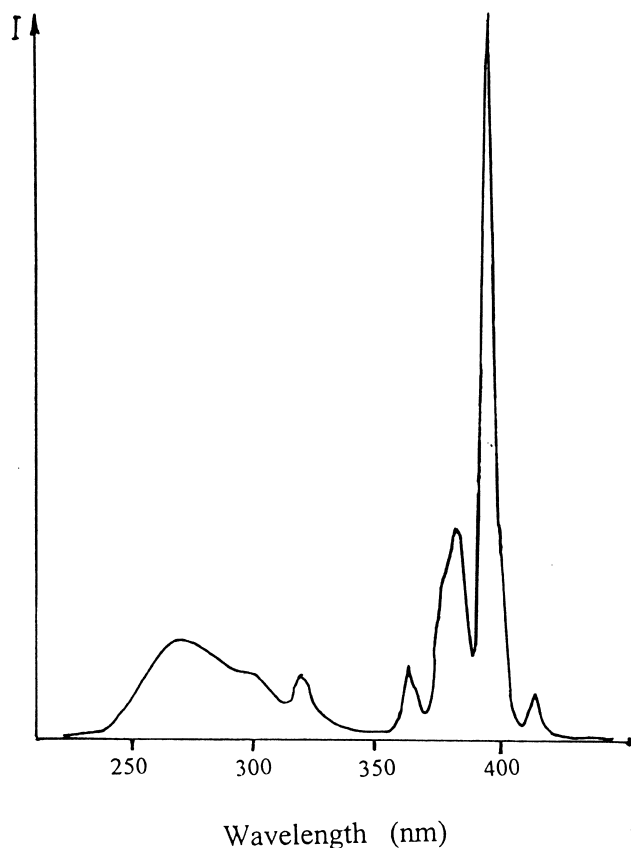


Fig. 2. Excitation spectrum at room temperature of $\text{SrB}_6\text{O}_{10}:\text{Eu}^{3+}$ prepared in air ($\lambda_{\text{em}}=614$ nm).

broad band with a maximum at about 270 nm due to the $\text{O}^{2-}-\text{Eu}^{3+}$ charge-transfer (CT) transition. Compared with SrB_4O_7 , in which the CT band is at about 254 nm [10], it can be seen that $\text{SrB}_6\text{O}_{10}$ is not so rigid as SrB_4O_7 . As in the complex oxide the Eu^{3+} CT band is affected by its nearest neighbor O^{2-} and next nearest neighbor ion like the boron atom in the present case, the transfer of the 2p electron in the fully filled oxygen orbit to the internal partially filled $4f^6$ orbit of Eu^{3+} and the energy needed depend on the potential field produced by the neighboring ions surrounding O^{2-} [11]. Because each O^{2-} ion in SrB_4O_7 is bonded to three boron atoms and forms rigid BO_4 tetrahedral units, the electron clouds of the oxygen ions are drawn toward the boron atoms; the mixing of the wave functions of O^{2-} and Eu^{3+} , namely the coupling between Eu^{3+} and lattice wave functions, decreases, and the degree of covalency of the $\text{Eu}^{3+}-\text{O}^{2-}$ bonding and the nephelauxetic effect will also decrease; more energy is then needed to transfer the electron from O^{2-} to the 4f shell of Eu^{3+} , hence the CT band shifts to the higher energy region. But in the $\text{SrB}_6\text{O}_{10}$ matrix, O^{2-} is only bonded to two boron atoms and forms BO_3 triangular and BO_4 tetrahedral units; the overlap of the electron cloud between O^{2-} and Eu^{3+} will be more intense than in SrB_4O_7 , and it becomes easier to transfer the electron from O^{2-} to the 4f shell of Eu^{3+} and the CT band shifts to the

longer wavelength region. As a conclusion, the formation of BO_3 will shift the CT band to the low energy region.

The emission spectra of the Eu^{3+} -doped sample are shown in Fig. 3 by sharp lines at RT. The dominant line with a maximum at 614 nm corresponds to the electric-dipole transition ${}^5\text{D}_0-{}^7\text{F}_2$. Only emission from the ${}^5\text{D}_0$ level is observed. This is to be expected, since borate vibrations in the lattice with frequencies up to 1300 cm^{-1} are able to bridge nonradiatively the energy gaps between the higher lying levels ${}^5\text{D}_{3,2,1}$ of the Eu^{3+} ion and the ${}^5\text{D}_0$ level. There are also lines at 589, 601, 653 and 700 nm corresponding to ${}^5\text{D}_0-{}^7\text{F}_J$ ($J=1, 3, 4$) transitions. In the present case, the electric-dipole transition is dominant which must be ascribed to the absence of a center of symmetry. It should be noted that, in the $\text{SrB}_6\text{O}_{10}$ lattice, the incorporation of Eu^{3+} on a Sr^{2+} site will distort the surroundings of the cation. In view of the need for charge compensation, it is likely that the distortion is due to the Sr^{2+} vacancy or interstitial O^{2-} defects, which will lower the symmetry of the cation site and the electric-dipole transitions will become allowed. As $\Delta J=2$ is the hypersensitive transition, which depends strongly on the surroundings, the intensity of the ${}^5\text{D}_0-{}^7\text{F}_2$ transition of Eu^{3+} is higher than those of other transitions in this matrix.

3.3. ESR spectrum of $\text{SrB}_6\text{O}_{10}:\text{Eu}^{2+}$

The ESR spectrum is useful for establishing the presence of Eu^{2+} because the electron spin S of Eu^{2+} is $7/2$ and the nuclear spin I is $5/2$ for both the ${}^{151}\text{Eu}$ and ${}^{153}\text{Eu}$ isotopes. Fig. 4 shows the ESR spectrum of $\text{SrB}_6\text{O}_{10}:\text{Eu}^{2+}$ prepared in air at room temperature. The hyperfine structure of the $1/2 \leftrightarrow -1/2$ transition is not completely resolved with broadening and overlap. The inability to observe the ESR hyperfine structure may be attributed to a site of low symmetry for Eu^{2+} or even to its presence in more than one lattice site [12]. This prevents determination of the hyperfine coupling constant A . The value of the parameter g of Eu^{2+} in the ESR spectrum is 1.995.

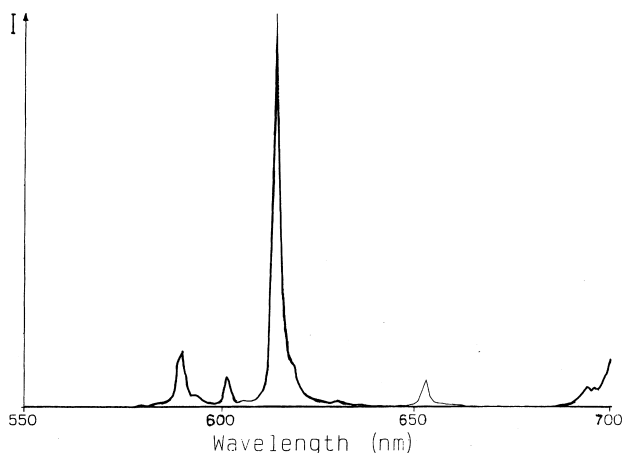


Fig. 3. Emission spectrum at room temperature of $\text{SrB}_6\text{O}_{10}:\text{Eu}^{3+}$ prepared in air ($\lambda_{\text{ex}}=394\text{ nm}$).

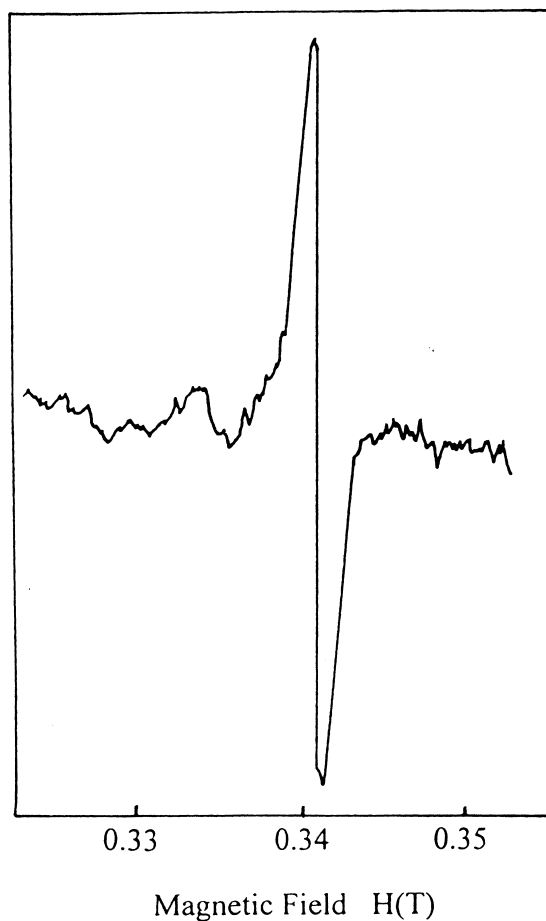


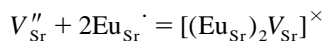
Fig. 4. ESR spectrum at 300 K of $\text{SrB}_6\text{O}_{10}:\text{Eu}^{2+}$ prepared in air. Microwave frequency 9.44 GHz.

3.4. Charge compensation mechanism

Block et al. [13] reported that in the known alkaline and alkaline earth borates, when the borates are expressed in the form $\text{M}_x\text{O}\cdot n\text{B}_2\text{O}_3$ (with the exception of $n=2$ for strontium and lead), the number of triangularly coordinated boron atoms per tetrahedrally coordinated boron is equal to $n-1$ for the region greater than $n=1$ and when one oxygen atom is bonded to only two boron atoms. So in the case of $\text{SrB}_6\text{O}_{10}(\text{SrO}\cdot 3\text{B}_2\text{O}_3)$, $n-1=2$, therefore, it contains four triangularly and two tetrahedrally coordinated boron atoms. It has been reported [1] that it consists of a three-dimensional network of B_3O_5 rings containing two triangular and one tetrahedral boron atom, on the basis of its infrared spectrum pattern. However, the structure of $\text{SrB}_6\text{O}_{10}$ has still not been elucidated.

When trivalent Eu^{3+} occupies the lattice site of divalent Sr^{2+} , two Eu^{3+} should be needed to substitute three Sr^{2+} in order to maintain the charge balance. Hence, a vacancy defect is formed at the Sr^{2+} site. This vacancy defect is represented as V_{Sr}'' with two negative charges due to the absence of Sr^{2+} and it then becomes a donor of electrons, while the two Eu^{3+} become acceptors of electrons. Consequently, the negative charges in the charged vacancy defects will be transferred to the Eu^{3+} site and the trivalent

Eu^{3+} is reduced to divalent Eu^{2+} . Here, if this vacancy defect can be regarded as an associate, the association should be represented by Kroger and Vink's notation [14]:



A valence change for Eu^{3+} to Eu^{2+} has also been observed in SrB_4O_7 prepared in air [2]. The reduction process would be accompanied by the same charge compensation mechanism as in $\text{SrB}_6\text{O}_{10}$ mentioned above. It has been reported [15] that Eu^{3+} can be reduced to the divalent state in the high-pressure phase of SrB_2O_4 (III) and SrB_2O_4 (IV) in H_2 , but no Eu^{2+} exist in Eu^{3+} -doped $\text{Sr}_2\text{B}_2\text{O}_5$ and SrB_2O_4 (I) (atmospheric pressure phase) even when prepared in flowing hydrogen, and only a very small amount of Eu^{2+} is detected in $\text{Sr}_3\text{B}_2\text{O}_6$ with considerable effort [15] which is in contrast to the results of Machida et al. [1], who did not observe Eu^{2+} in $\text{Sr}_3\text{B}_2\text{O}_6$. The following explanation may be reasonable.

For the borates $\text{Sr}_3\text{B}_2\text{O}_6$, $\text{Sr}_2\text{B}_2\text{O}_5$ and SrB_2O_4 (I) [16] containing only planar triangular BO_3 units, the charge compensation would take place by introducing one interstitial oxygen ion per two Eu^{3+} rather than by forming a negatively charged vacancy defect. The interstitial oxygen ion links two planar BO_3 groups and forms two corner sharing BO_4 tetrahedra [8], hence Eu^{3+} still retains its trivalent state in these matrices. But in the high pressure phase of SrB_2O_4 (III) and SrB_2O_4 (IV), the hosts contain BO_4 tetrahedral units which can prevent Eu^{2+} from being attacked by oxygen.

As discussed above, it can be seen that the reduction of Eu^{3+} depends strongly on the structure of the boron units. The three-dimensional network of BO_4 tetrahedra acts as a shield; it can isolate the Eu^{2+} ions from each other and completely or partly surround the Eu^{2+} ions and resist the attack of oxygen, so Eu^{2+} can retain the divalent state in air even at high temperature. This can be verified from the different oxidation temperatures for europium borates: 673 K for $\text{Eu}_3\text{B}_2\text{O}_6$, 683 K for $\text{Eu}_2\text{B}_2\text{O}_5$, 753 K for EuB_2O_4 and 1033 K for EuB_4O_7 . $\text{Eu}_3\text{B}_2\text{O}_6$ and $\text{Eu}_2\text{B}_2\text{O}_5$ contain BO_3^{3-} and $\text{B}_2\text{O}_5^{4-}$, respectively, and EuB_2O_4 consists of $(\text{BO}_2)_\infty$ chains. Eu^{2+} in SrB_4O_7 located in the "cage" of BO_4 units are completely surrounded by these units of the $(\text{B}_4\text{O}_7)_\infty$ network, and therefore it becomes difficult for it to be attacked by oxygen [17]. However, no information has been reported discussing the structure of $\text{EuB}_6\text{O}_{10}$ until now; it was thought that all Eu(II) -borates are isostructural with the corresponding Sr-borates because of their closely similar effective ionic radii ($\gamma_{\text{Eu}^{2+}} = 125$ pm, $\gamma_{\text{Sr}^{2+}} = 126$ pm).

3.5. Charge compensator

In order to verify the charge-compensation mechanism discussed above, a charge compensator such as KF was

added to the sample. The results show that the emission intensity of Eu^{2+} sharply decreases while the Eu^{3+} emission increases with increasing K^+ and F^- . This is reasonable considering that K^+ should occupy the strontium vacancy, viz V_{Sr}'' , to neutralize the overall negative charge.

4. Conclusions

Eu^{3+} can be reduced to Eu^{2+} in $\text{SrB}_6\text{O}_{10}$ in air by a high-temperature solid-state reaction. The luminescence of Eu^{2+} and Eu^{3+} in this matrix at room temperature was studied. The results show that Eu^{3+} occupies a low symmetry site in the host lattice due to the low original symmetry cation site or to distortion near defects by substitution of Eu^{2+} on the Sr^{2+} site. A possible charge-compensation mechanism is proposed. It is concluded that BO_4 tetrahedral units are needed as a rigid framework to stabilize the divalent rare-earth ions in strontium borates.

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