

Journal of Physics and Chemistry of Solids 60 (1999) 515-520

JOURNAL OF PHYSICS AND CHEMISTRY OF SOLIDS

# The luminescent properties of $\text{Sm}^{2+}$ in strontium tetraborates $(\text{SrB}_4\text{O}_7: \text{Sm}^{2+})$

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Received 1 July 1998; accepted 16 September 1998

# Abstract

The luminescence of Sm<sup>2+</sup> in SrB<sub>4</sub>O<sub>7</sub> was studied as a function of temperature from 10 K up to 600 K. According to the high-resolution spectra of Sm<sup>2+</sup> in matrix at 10 K, the line numbers of  ${}^{5}D_{0}-{}^{7}F_{J}$  transitions were 1, 3, 5 for J = 0, 1, 2, respectively. The  ${}^{5}D_{1}-{}^{7}F_{J}$  (J = 0, 1, 2) transitions were observed at high temperature. The intensities of  ${}^{5}D_{1}-{}^{7}F_{J}$  transitions increased up to 400 K and then decreased with increase in temperature. 4f<sup>5</sup>d<sup>1</sup>-4f<sup>6</sup> transition of Sm<sup>2+</sup> appeared at high temperature. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: A. Inorganic compounds; D. Luminescence

## 1. Introduction

The structure of  $SrB_4O_7$  had an unusual type in the borates [1,2]. All of the boron atoms were tetrahedrally coordinated in the form of three-dimensional network  $BO_4$  units and all tetrahedra shared all corners. Such framework was thought to be a rigid structure for preventing the divalent metal ions from being oxidized and gave rise to high efficient luminescence [3,4]. The luminescence of these ions were characterized by small Stokes shifts and vibrational structure at low temperature.

Some authors reported the luminescence of  $\text{Sm}^{2+}$  in  $\text{SrB}_4\text{O}_7$  [5,7]. But one of the perplexities in these literatures was that the line number of  ${}^5\text{D}_0-{}^7\text{F}_2$  transition of  $\text{Sm}^{2+}$  ion in  $\text{SrB}_4\text{O}_7$  was four. According to the structure of  $\text{SrB}_4\text{O}_7$ , the site symmetry of  $\text{Sr}^{2+}$  in matrix was,  $C_s$  and therefore, the line number of  ${}^5\text{D}_0-{}^7\text{F}_2$  transition should be five [8,9]. This prompted us to investigate the luminescence of  $\text{Sm}^{2+}$  in this host.

In this article, we reported the luminescent properties of  $Sm^{2+}$  in  $SrB_4O_7$  at different temperatures.

#### 2. Experimental

The samples of SrB<sub>4</sub>O<sub>7</sub> doped with Sm<sub>2</sub>O<sub>3</sub> were prepared by an intimate mixture of analytical-grade strontium carbonates, boric acid and Sm<sub>2</sub>O<sub>3</sub>. The concentration of the dopant Sm<sub>2</sub>O<sub>3</sub> (99.99%) were 2 mol % of Sr<sup>2+</sup> ions. The samples were heated at 800°C in H<sub>2</sub>/N<sub>2</sub>.

The crystal structure was checked by X-ray powder diffraction using  $CuK\alpha_1$  radiation. Samples appeared to be of single phase.

The low-resolution spectra were performed on a SPEX DM3000F spectrofluorometer equipped with 0.22 m SPEX 1680 double monochromators (resolution 0.1 nm) and a 450 W xenon lamp as excitation source.

The high-resolution spectra was checked with a SPEX-1403 spectrophotometer under the excitation of  $N_2$  laser beam (337.1 nm) (National Research Instruments Co.) with a flow cryostat of gaseous helium. The temperature could be varied from 10 to 300 K.

## 3. Results and discussion

The luminescence of  $\text{Sm}^{2+}$  in  $\text{SrB}_4\text{O}_7$  were reported by some authors [5–7]. The low-resolution emission and

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Fig. 1. The low-resolution excitation and emission spectra of  $\text{Sm}^+$  in  $\text{SrB}_4\text{O}_7$  at room temperature. (The inset shows the enlargement of emission spectra in the range of 610–670 nm).

excitation spectra of Sm<sup>2+</sup> in SrB<sub>4</sub>O<sub>7</sub> were shown in Fig. 1. The excitation spectrum consisted of two bands at 365 and 490 nm together with some sharp lines in the band. From the position of two excitation bands, it was suggested that the  $4f^{5}5d$  levels of  $Sm^{2+}$  in  $SrB_{4}O_{7}$  be located in relatively higher energy position than in alkaline earth halides [10-12]. In SrB<sub>4</sub>O<sub>7</sub>, the strontium (and  $\text{Sm}^{2+}$ ) coordination was irregular but could be approximated by  $C_{4v}$  symmetry, as eight of the nine coordinating oxygens were approximately on the corner of cubic, and the ninth was on one of the tetragonal axes [8,13]. To assign the bands we should take into account both the crystal field splitting of the 5d electron and additional splitting of 4f<sup>5</sup> configuration. In cubic coordination, 5d level was split into a lower eg and a higher  $t_{2g}$  levels by crystal field. The crystal field splitting of 5d for Sm<sup>2+</sup> in this host was about 6990 cm<sup>-1</sup> which was very close to the crystal field splitting of  $\text{Sm}^{2+}$  in cubic coordination in LiBaF<sub>3</sub> [14]. The splitting of 4f<sup>5</sup> configuration was well known in the spectroscopy of  $\text{Sm}^{3+}$  free ion [15]. Similarities in the spectra of  $\text{Sm}^{2+}$  in present case were expected. The lines in the spectrum were corresponded to the <sup>6</sup>H<sub>J</sub> (J = 13/2, 11/2, 9/2, 7/2) states of he 4f<sup>5</sup> configuration.

In the emission spectra, several groups of narrow lines were observed. No broad band was found at room temperature. These lines centered at about 686, 700, 730 and 765 nm. The dominant line was at about 686 nm which could be assigned to  ${}^{5}D_{0}-{}^{7}F_{0}$  transitions of Sm<sup>2+</sup> and it showed that the Sm<sup>2+</sup> ions occupied a site without central symmetry in Sr<sup>2+</sup>, viz, C<sub>s</sub>. The other groups were assigned to the transitions of  ${}^{5}D_{0}$  to  ${}^{7}F_{J}$  (J = 1, 2, 3) levels, respectively. Theoretically, the line numbers of  ${}^{5}D_{0}-{}^{7}F_{J}$  (J = 0, 1, 2) transitions of Sm<sup>2+</sup> in C<sub>s</sub> site should be 1, 3, 5 [9]. But



Fig. 2. The high-resolution emission spectra of  $\text{Sm}^{2+}$  in  $\text{SrB}_4\text{O}_7$  at 10 K.

only four lines could be seen for  ${}^{5}D_{0}-{}^{7}F_{2}$  transition in Fig. 1. We therefore detected the emission spectra of Sm<sup>2+</sup> by high-resolution spectra (see below).

In Fig. 1, the inset spectrum showed that some weak sharp lines in the range of 620 to 670 nm appeared at room temperature. Considering the position and the line shape, these lines were corresponded to the  ${}^{5}D_{1}-{}^{7}F_{J}$  (0, 1, 2,) transitions of Sm<sup>2+</sup> in matrix. The vibrational modes of BO<sub>4</sub> and BO<sub>3</sub> were around 1200  $\sim$  1400 cm<sup>-1</sup> in energy which was very close to the energy gap between  ${}^{5}D_{1}$  and  ${}^{5}D_{0}$  level ( $\Delta E \approx 1350$  cm<sup>-1</sup>) [16]. This energy gap could be bridged by only one phonon. Therefore, the non-radiative transition probability from  ${}^{5}D_{1}$  to  ${}^{5}D_{0}$  level must be very high and no transitions between  ${}^{5}D_{1}$  and  ${}^{7}F_{J}$  could be observed.

Table 1

The assignments and peak positions of the transitions of  $\text{Sm}^{2+}$  ${}^{5}\text{D}_{0-}{}^{7}\text{F}_{J}$  (J = 0, 1, 2) in SrB<sub>4</sub>O<sub>7</sub> at 10 K.

Transition $({}^{5}D_{0} - {}^{7}F_{J})$	Wavenumber (cm <sup>-1</sup> )	Barycenter (cm <sup>-1</sup> )
J = 0	14567	14567
J = 1	14360	
	14288	14272
	14169	
J = 2	13823	
	13788	
	13730	13711
	13607	
	13604	

However, in present case,  ${}^{5}D_{1}-{}^{7}F_{J}$  (0, 1, 2) transitions occurred even at room temperature. Such observation was because of the fact that the  ${}^{5}D_{1}$  level was thermally populated by  ${}^{5}D_{0}$  level and resulted in the transition of  ${}^{5}D_{0} \rightarrow {}^{5}D_{1} \rightarrow {}^{7}F_{J}$ . The thermal population was also observed in the transition between 4f<sup>5</sup>5d and  ${}^{7}F_{J}$  level of Sm<sup>2+</sup> in the same host and gave rise to 4f<sup>5</sup>5d  $\rightarrow {}^{7}F_{J}$  transition (see below).

The high-resolution emission spectra of  $\text{Sm}^{2+}$  in  $\text{SrB}_4\text{O}_7$ at 10 K was shown in Fig. 2. The transitions of  $\text{Sm}^{2+}$  in  $\text{SrB}_4\text{O}_7$  were from  ${}^5\text{D}_0-{}^7\text{F}_J$  (J = 0, 1, 2). The assignment and the peak positions of the emission band were shown in Table 1. The numbers of the transition lines for  ${}^5\text{D}_0-{}^7\text{F}_J$ were 1, 3, 5 for J = 0, 1, 2 respectively. This was in good agreement with the theoretical splitting of the  ${}^7\text{F}_J$  levels into a maximum of 1, 3 and 5 sublevels for the site symmetry of  $C_s$  in the host.

Fig. 3 showed the enlargement of high-resolution emission spectra of  ${}^{5}D_{0}-{}^{7}F_{0}$  transition of Sm<sup>2+</sup> in SrB<sub>4</sub>O<sub>7</sub> at 77 and 300 K. Two weak lines which was denoted as  $\nu$  (lowerenergy side) and  $\nu'$  (higher-energy side) beside  ${}^{5}D_{0}-{}^{7}F_{0}$  line were ascribed to the vibronic emission transition. The energy displacement with zero-phonon line  ${}^{5}D_{0}-{}^{7}F_{0}$  (ZPL) was about 95 cm<sup>-1</sup>. The intensities of the vibronic lines increased with temperature. The vibration involved was a vibrational mode in which Sm moved relative to the borate group [6]. The Huang–Rhys factor *S* was calculated to be about 0.02 from the relative intensities of vibronic lines and ZPL [17–20].

It was reported that in the spectra of Sr<sub>0.99</sub>Eu<sub>0.02</sub>B<sub>4</sub>O<sub>7</sub>, a



Fig. 3. The enlargement of vibronic transitions and ZPL of  $\text{Sm}^{2+}$  in  $\text{SrB}_4\text{O}_7$  at (a) 77 K and (b) 300 K.



Fig. 4. The emission spectra of  ${\rm Sm}^{2+}$  in  ${\rm SrB_4O_7}$  at 450 K ( $\lambda_{ex}=365$  nm).



Fig. 5. The temperature-dependence of the integrated intensities of  ${}^{5}D_{0} - {}^{7}F_{0}(I_{0})$ ,  ${}^{5}D_{1} - {}^{7}F_{0}(I_{1})$  and  $4f^{5}5d-4f^{6}(I_{d})$  transitions of  $Sm^{2+}$  in  $SrB_{4}O_{7-}$ 

wide band which stretched from ZPL to  $1200 \text{ cm}^{-1}$  was found [4]. Such band with energy high up to  $1200 \text{ cm}^{-1}$ resulted from the vibrations of BO<sub>4</sub> group as the asymmetrical and symmetrical vibration were at around 1200 and 900 cm<sup>-1</sup>, respectively, together with the borate bending vibrations ranging from 400 to  $800 \text{ cm}^{-1}$ . This continuous band of vibrational structure could be explained by the multiphonon–configuration–coordinate mechanism in which it was assumed that all of the vibrational mode of

the borate groups could be coupled with the transitions and resulted in continuous band. In  $SrB_4O_7$ :  $Sm^{2+}$ , we did not find such continuous band with energy up to 1200 cm<sup>-1</sup> while only sharp lines were found beside ZPL. Therefore, in present case, only the vibrational mode with single frequency was coupled with the transitions.

Under the excitation of 254 nm, the sample  $SrB_4O_7$ :  $Sm^{2+}$  emitted deep red emission at room temperature whereas it emitted yellow emission at high temperature.



Fig. 6. Energy level scheme of  $\text{Sm}^{2+}$  in  $\text{SrB}_4\text{O}_7$ .

The emission spectrum of Sm<sup>2+</sup> in SrB<sub>4</sub>O<sub>7</sub> at 450 K was shown in Fig. 4. A broad band with the maximum at about 585 nm could be seen. This band was assigned to the  $4f^55d \rightarrow 4f^6$  transition of  $Sm^{2+}$ . Fig. 5 shows the temperature dependence of the intensities of  ${}^{5}D_{0}-{}^{7}F_{0}$ ,  ${}^{5}D_{1}-{}^{7}F_{0}$  and  $4f^{5}5d-4f^{6}$  transitions. The rapid decrease of <sup>5</sup>D<sub>0</sub> fluorescence above 300 K was caused by two-step quenching through 5d level, whereas 5d levels was thermally populated by <sup>5</sup>D<sub>0</sub> and then gave rise to a strong radiative transition to the ground state. Thus the yellow  $5d \rightarrow 4f$ broad band emission occurred at the expense of <sup>5</sup>D<sub>0</sub> fluorescence. The  ${}^{5}D_{1}-{}^{7}F_{0}$  and  $4f^{5}5d-4f^{6}$  transitions first increased with temperatures and then decreased. At first glance, it was conflict with the results that the  ${}^{5}D_{1}-{}^{7}F_{J}$  (J = 0, 1, 2) transitions were previously quenched by temperature before  ${}^{5}D_{0}-{}^{7}F_{I}$  (J = 0, 1, 2) transitions. In the present case,  ${}^{5}D_{1}-{}^{7}F_{J}$  transitions increased in intensities and  ${}^{5}D_{0}-{}^{7}F_{I}$  transitions decreased with temperature. This was also as a result of the thermal population of  ${}^{5}D_{1}$  level by  ${}^{5}D_{0}$  via 4f ${}^{5}$ 5d level in the process as  ${}^{5}D_{0} \rightarrow 4f^{5}$ 5d  $\rightarrow {}^{5}D_{1} \rightarrow$  $^{7}F_{J}$ . The mechanism of the appearance of  $^{5}D_{1}$  transition was the same as the appearance of the 4f<sup>5</sup>5d transition. But as the 4f<sup>5</sup>5d transition was an allowed one, its intensity was higher than that of the  ${}^{5}D_{1}-{}^{7}F_{J}$  parity-forbidden transitions. The thermal population of  ${}^{5}D_{0}$  and 5d level would result in the thermal depopulation of  ${}^{5}D_{0}$  level and the intensities of  ${}^{5}D_{0}-{}^{7}F_{J}$  transitions decreased with temperature. The depopulation of  ${}^{5}D_{0}$  via the  ${}^{5}D_{1}$  and 5d band was also observed in Sm<sup>2+</sup>- doped KCl and SrF<sub>2</sub> [20]. The indirect  ${}^{5}D_{1} \rightarrow {}^{5}D_{0}$  radiationless channel through 5d band was considered to be a novel situation and a direct  ${}^{5}D_{1} \rightarrow {}^{5}D_{0}$ coupling should be more likely event owing to the relatively close proximity of these two J levels.

From the high-temperature luminescence and high-resolution spectra of  $\text{Sm}^{2+}$  in  $\text{SrB}_4\text{O}_7$ , the position of 5d energy level could be calculated to be about 18783 cm<sup>-1</sup> higher than the ground state and a possible energy level scheme of  $\text{Sm}^{2+}$  in the host was suggested in Fig. 6.

#### 4. Conclusions

The high-resolution spectra showed that the divalent samarium ion occupied the strontium sites with lower symmetry  $C_s$  and five lines were observed for  ${}^5D_0 - {}^7F_2$  transition. The luminescence of divalent samarium was

temperature-dependence. The phonon lines were observed with energy about 95 cm<sup>-1</sup>. The  ${}^{5}D_{1}-{}^{7}F_{J}$  transitions appeared at room temperature and increased with the increasing of temperature while the intensity of  ${}^{5}D_{0}-{}^{7}F_{J}$ transitions decreased. At high temperature, it emitted yellow light of 4f<sup>5</sup>5d-4f<sup>6</sup> transitions. The  ${}^{5}D_{1}$  and 4f<sup>5</sup>5d levels could be thermally populated by  ${}^{5}D_{0}$  level and gave rise to the radiative transition to the ground state multiplets.

### Acknowledgements

This work was supported by National Key Project for Fundamental Research, National Nature Science Foundation of China and laboratory of Excited State Processes of Chinese Academy of Sciences.

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