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## VUV and Eu-L<sub>3</sub> edge XANES spectra of europium-doped strontium tetraborate prepared in air

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### Abstract

VUV-UV and Eu-L<sub>3</sub> edge XANES spectra were measured for europium-doped strontium tetraborate prepared by solid state reaction at high temperature in air. The VUV-UV spectra show that the host absorption band of SrB<sub>4</sub>O<sub>7</sub> appears below 170 nm. The charge transfer band of Eu<sup>3+</sup> doped in SrB<sub>4</sub>O<sub>7</sub> is peaked at 272 nm. The 4f–5d transitions of Eu<sup>2+</sup> consist of a band peaked at 310 nm with a shoulder at 280 nm and also include the bands peaked at 238 (weak) and 203 (strong) nm. The result of XANES spectrum at Eu-L<sub>3</sub> edge of the synthesized sample indicates that Eu<sup>3+</sup> and Eu<sup>2+</sup> coexist in SrB<sub>4</sub>O<sub>7</sub>:Eu prepared in air, which is consistent with the results of the VUV-UV spectra. © 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** Strontium tetraborate; Luminescence; Vacuum ultraviolet (VUV); X-ray absorption near edge structure (XANES)

### 1. Introduction

The study of vacuum ultraviolet (VUV,  $\lambda < 200$  nm) excitation spectra of rare earth (RE) ion-doped luminescent materials is a challenging and rapidly developing area, because it is important both for theoretical research and industrial applications. There are two reasons that prompt the development of

research on RE ions in the VUV region. Firstly, experimental data for RE ions in the VUV range are scarce, although the energy levels below 50 000 cm<sup>-1</sup> have been observed and calculated. Secondly, these spectra are fundamental data for exploring efficient VUV excited luminescent materials that could be used in mercury-free fluorescent lamps or plasma display panels.

It is well known that the RE-L<sub>3</sub> edge XANES spectra from mixed-valence compounds appear as a double-peaked ‘white line’ (WL) structure [1,2]. These two peaks are assigned to the divalent and trivalent species, whose energies are separated by

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about 7–9 eV. This property makes us possible to use the XANES spectroscopy at RE-L<sub>3</sub> as a standard method to determine the valence of rare earth compounds.

Generally speaking, the reduction of rare earth ions can be achieved with chemical reagents, such as H<sub>2</sub>, H<sub>2</sub>/N<sub>2</sub>, NH<sub>3</sub>, activated carbon or CO. However, reduction can be performed in air (an oxidizing atmosphere) in some complex oxides [3]. We proposed some necessary conditions for the reduction of trivalent rare earth in air [4]. One of these conditions is that tetrahedral anions such as BO<sub>4</sub> or PO<sub>4</sub> must exist in the alkali earth complex oxides.

According to the crystal structure of SrB<sub>4</sub>O<sub>7</sub> [5,6], all boron atoms are in a tetrahedral BO<sub>4</sub> form. So it is expected that Eu<sup>3+</sup> could be reduced in this host in air, and the UV excited luminescence of Eu<sup>2+</sup> in SrB<sub>4</sub>O<sub>7</sub>:Eu prepared in air was performed in our previous work [4]. As a systematized investigation, in this paper, the VUV excitation spectra of SrB<sub>4</sub>O<sub>7</sub>:Eu prepared in air are reported and the reduction of Eu<sup>3+</sup> is demonstrated by using of spectroscopy method and XANES at Eu-L<sub>3</sub> edge.

## 2. Experimental

Europium-activated tetraborate samples were prepared by solid state reactions at high temperature in air. The starting materials were SrCO<sub>3</sub> (A.R., analytical pure reagent), H<sub>3</sub>BO<sub>3</sub> (A.R., excess 3 mol% to compensate the evaporation in the fired processes) and Eu<sub>2</sub>O<sub>3</sub> (99.99%, doped concentration was 3 mol%). The starting materials were first thoroughly mixed and fired at 500°C for 2 h, and subsequently fired in an air atmosphere at 850°C for another 2 h. Then the temperature was slowly decreased to room temperature. The synthesized samples were confirmed to be single phases by X-ray powder diffraction using Cu Kα<sub>1</sub> radiation and were consistent with JCPDS 15-801 (SrB<sub>4</sub>O<sub>7</sub>).

VUV excitation spectra and Eu-L<sub>3</sub> edge XANES spectra of the samples were measured at the beamline 3B1B and at the beamline 4W1B in Beijing Synchrotron Radiation Facilities (BSRF) under normal operating conditions (2.2 GeV, 100 mA), respectively. For the VUV spectral measurements, an ARC-VM-502-S monochromator (1200 g/mm) and an

ARC SP-308 monochromator (1200 g/mm) were used for excitation spectrum and for emission spectrum, respectively, and the signal was detected with a Hamamatsu H7421-50 photomultiplier. The pressure of the sample chamber was 2×10<sup>-5</sup> mbar. VUV excitation intensities of the samples were normalized by those of sodium salicylate at the same excitation condition [7,8]. XANES measurement was performed with a fluorescence detector. All VUV and XANES experiments were done at 293 K.

UV excitation spectra and luminescent spectra were recorded on a SPEX 2T2 spectrofluorometer equipped with 0.22-m SPEX 1680 double monochromators (resolution 0.1 nm) and a 450-W xenon lamp as excitation source. The excitation power output was corrected.

## 3. Results and discussion

VUV-UV excitation spectra from Eu<sup>2+</sup> and Eu<sup>3+</sup> can be sorted out by monitoring the characteristic emission bands or lines of these ions. Fig. 1 shows the VUV-UV spectra for Eu<sup>2+</sup> and Fig. 2 shows those for Eu<sup>3+</sup> in SrB<sub>4</sub>O<sub>7</sub>:Eu prepared in air. As shown in Fig. 1, an intense emission appears at 367 nm when excited by UV irradiation (315 nm). This peak is associated with the f–d transition of Eu<sup>2+</sup>, as reported by Pei et al. [4] and Machida et al. [9]. The excitation spectra of the sample measured at 367 nm of Eu<sup>2+</sup> emission show several peaks in the wavelength range of 130–350 nm. The peak at about 310 nm is clearly observed both in VUV and UV excitation spectra, whose position is nearly the same as that reported by Machida et al. (302 nm) [9] and that by Pei et al. (320 nm) [4]. In addition to the peak, another faint f–d transition band is observed at about 280 nm. Excitation spectra of Eu<sup>3+</sup> are clearly different from those of Eu<sup>2+</sup>. The main UV excitation line of Eu<sup>3+</sup> is <sup>7</sup>F<sub>0</sub>–<sup>5</sup>L<sub>6</sub> transition at 395 nm, and the dominant emission of Eu<sup>3+</sup> is <sup>5</sup>D<sub>0</sub>–<sup>7</sup>F<sub>2</sub> transition at 613 nm.

We can expect five kinds of absorption bands in the VUV spectra of rare earth activated luminescent materials: (1) the absorption of the host lattice [10–17]; (2) the charge transfer band from the ligand atoms to the rare earth ions [18]; (3) the 4f–5d transition of rare earth ions [10,12,15,16]; (4) the

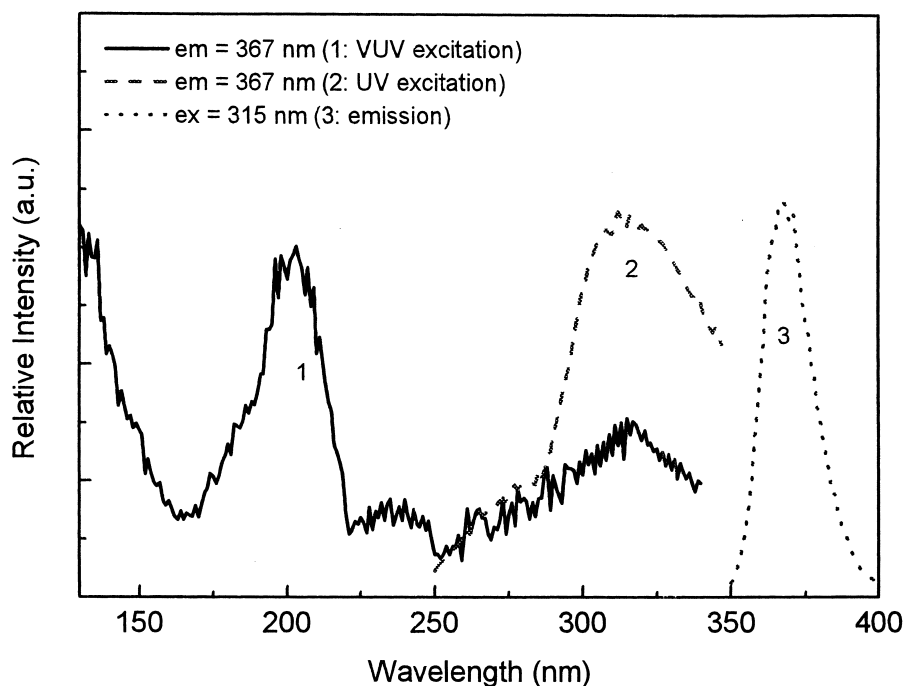


Fig. 1. VUV-UV spectra of  $\text{Eu}^{2+}$  in  $\text{SrB}_4\text{O}_7:\text{Eu}$  prepared in air (solid line, VUV excitation spectrum at 367 nm of  $\text{Eu}^{2+}$  emission; dashed line, UV excitation spectrum at 367 nm of  $\text{Eu}^{2+}$  emission; dotted line, emission spectrum under excitation at 315 nm).

4f–6s transition of rare earth ions [19,20]; and (5) the 4f intra-configuration transition of rare earth ions [21,22].

The host absorptions of some borates have been reported. For example, the host absorption bands of  $\text{REBO}_3:\text{Ln}^{3+}$  (RE=Y, Gd, Sc, Lu; Ln=Eu, Tb) [10,11],  $\text{LnAl}_3\text{B}_4\text{O}_{12}:\text{RE}^{3+}$  (Ln=Y, Gd; RE=Eu, Tb) [14],  $\text{Tb}^{3+}$ -doped  $\text{YBO}_3\text{--GdBO}_3$  solid solution [15],  $\text{LnB}_3\text{O}_6:\text{RE}^{3+}$  [Ln=La, Gd, (Gd, Tb); RE=Tb, Eu] [13],  $\text{Ln}_x\text{La}_{1-x}\text{MgB}_5\text{O}_{10}$  (Ln=Eu, Tb) [12] and  $\text{BaLa}_{0.09}\text{Tb}_{0.1}\text{B}_9\text{O}_{16}$  [16] are in the wavelength range between 130 and 170 nm. Anions of the above-described hosts contain  $\text{B}_3\text{O}_9^{9-}$ ,  $\text{BO}_3^{3-}$  and  $\text{BO}_4^{5-}$ . Since the anions of  $\text{SrB}_4\text{O}_7$  consist of  $\text{BO}_4^{5-}$ , we deduce that the band below 170 nm should include the absorption band of  $\text{SrB}_4\text{O}_7$ .

As shown in Fig. 2, when monitoring the emission of  $\text{Eu}^{3+}$  at 613 nm, the band at 272 nm in VUV excitation spectrum of  $\text{Eu}^{3+}$  can be observed. Obviously, this band is the charge transfer band of  $\text{Eu}^{3+}$ , and the position of this band is the same as that in UV excitation spectrum.

As shown in Fig. 1, when monitoring the emission

of  $\text{Eu}^{2+}$  at 367 nm, we can find a strong and broad band at 203 nm, weak bands at around 238 and 280 nm, and a band at 310 nm. These bands can be assigned to the group of 4f–5d transitions. According to the structure of  $\text{SrB}_4\text{O}_7$ , the site symmetry of  $\text{Sr}^{2+}$  is  $C_s$ . The crystal and luminescence of  $\text{EuB}_4\text{O}_7$  and  $\text{Sr}_{1-x}\text{Eu}_x\text{B}_4\text{O}_7$  prepared in reducing condition showed that doped  $\text{Eu}^{2+}$  ions also occupied the  $C_s$  sites [9], which implied that  $\text{Eu}^{2+}$  ions entered the substituted  $\text{Sr}^{2+}$  sites. The 5d state splits into five sublevels in  $C_s$  symmetry. Provided that the band at 310 nm ( $32\,258\text{ cm}^{-1}$ ) is the lowest  $^8\text{S}_{7/2}\text{--}5\text{d}$  transition of  $\text{Eu}^{2+}$  in  $\text{SrB}_4\text{O}_7$ , and the band at 203 nm ( $49\,261\text{ cm}^{-1}$ ) is the highest one, the crystal field splitting energy of 5d orbits of  $\text{Eu}^{2+}$  in  $\text{SrB}_4\text{O}_7$  would be about  $17\,000\text{ cm}^{-1}$ .

VUV-UV spectra indicate the reduction of  $\text{Eu}^{3+}$  in  $\text{SrB}_4\text{O}_7:\text{Eu}$  prepared in air. This reduction can also be confirmed by XANES at Eu- $L_3$  edge. The measured XANES spectrum at Eu- $L_3$  edge of the sample  $\text{Sr}_{0.97}\text{Eu}_{0.03}\text{B}_4\text{O}_7$  is exhibited in a solid symbolized square curve in Fig. 3. The spectrum is characterized by the superposition of two well-known WLs with

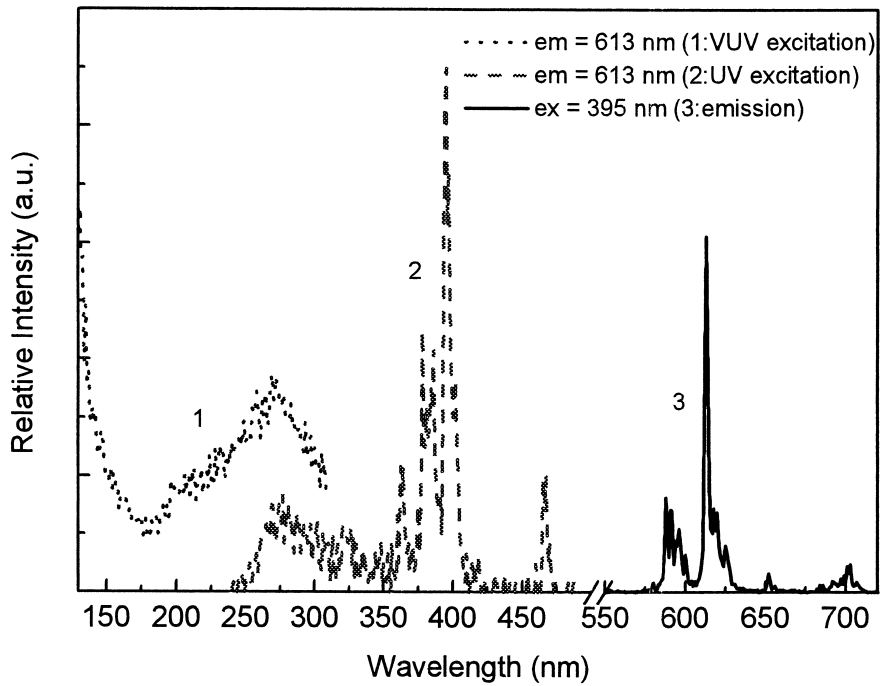


Fig. 2. VUV-UV spectra of  $\text{Eu}^{3+}$  in  $\text{SrB}_4\text{O}_7:\text{Eu}$  prepared in air (solid line, emission spectrum under the excitation at 395 nm; dash line, UV excitation spectrum under the emission at 613 nm; dotted line, VUV excitation spectrum under emission at 613 nm).

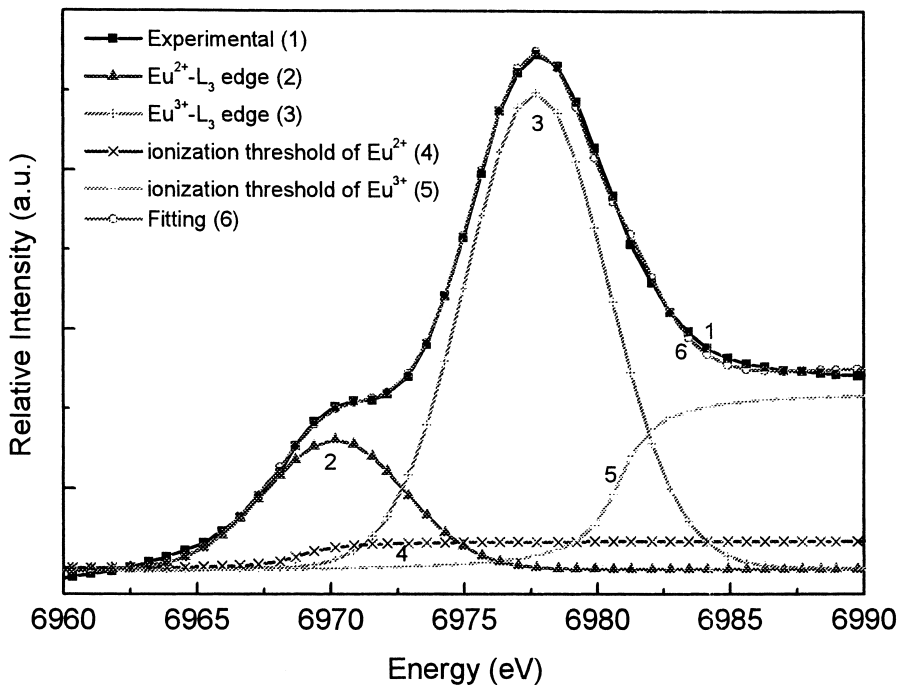


Fig. 3. XANES at  $\text{Eu-L}_3$  edge of  $\text{SrB}_4\text{O}_7:\text{Eu}$  prepared in air.

two corresponding step-like ionization thresholds. The spectrum in Fig. 3 was fitted and deconvoluted using the expression (1), i.e., the superposition of two Gaussian functions, representing the WLs of  $\text{Eu}^{3+}$  and  $\text{Eu}^{2+}$ , plus two arctan functions, representing the step-like absorptions.

$$Y = P_1 + P_2 \exp[-2(x - P_3)^2/P_4^2] + P_5 \exp[-2(x - P_6)^2/P_7^2] + P_8 \arctan(x - P_9) + P_{10} \arctan(x - P_{11}) \quad (1)$$

The fitted and deconvoluted results are also shown in Fig. 3. The XANES at  $\text{Eu-L}_3$  edge of  $\text{Sr}_{0.97}\text{Eu}_{0.03}\text{B}_4\text{O}_7$  prepared in air consists of a dominant  $\text{Eu}^{3+}\text{-L}_3$  edge component, which is located at 6977.7(1) eV. In addition, it contains a weak WL component of  $\text{Eu}^{2+}\text{-L}_3$  edge, which is located at 6970.1(6) eV. The energy of  $\text{Eu}^{2+}\text{-L}_3$  edge is 7.5(5) eV lower than that of  $\text{Eu}^{3+}\text{-L}_3$  edge. The XANES spectrum clearly indicates that the divalent and trivalent europium coexist in  $\text{SrB}_4\text{O}_7\text{:Eu}$  prepared in air. The results imply that  $\text{Eu}^{3+}$  ions can be reduced in  $\text{SrB}_4\text{O}_7\text{:Eu}$  prepared in air by solid state reaction at high temperature. Such an abnormal reduction of  $\text{Eu}^{3+}$  in  $\text{SrB}_4\text{O}_7\text{:Eu}$  can be realized by the following reasons.

- Doped  $\text{Eu}^{3+}$  would substitute  $\text{Sr}^{2+}$  in  $\text{SrB}_4\text{O}_7$  host lattice [9]. Because of this aliovalent substitution, the defects with negative charge must be created to keep electro-neutrality of the compound. By thermally stimulated movement, the electrons on the defects would be transferred to the doped  $\text{Eu}^{3+}$  ions and the doped  $\text{Eu}^{3+}$  ions are reduced by these free electrons.
- Both  $\text{Eu}^{2+}$  and  $\text{Sr}^{2+}$  ions are nine coordinated in  $\text{SrB}_4\text{O}_7\text{:Eu}$  [6,9].  $\text{Eu}^{2+}$  (130 pm) ions have similar ionic radii with  $\text{Sr}^{2+}$  (131 pm) ions, which might be suitable to stabilize the  $\text{Eu}^{2+}$  ions. When  $\text{Eu}^{2+}$  ions occupy the substituted lattice sites of  $\text{Sr}^{2+}$  ions, the replacement would not cause further distortion.
- The rigid tetrahedral  $\text{BO}_4$  anions are favorable to the stabilization of  $\text{Eu}^{2+}$  ions, because this rigid tetrahedral  $\text{BO}_4^{5-}$  efficiently encloses the  $\text{Eu}^{2+}$  ion and protects them from the attack of the oxygen in air. Thus, the reduced state is easy to

be stabilized. This point is supported by the facts that rare earth ions can be reduced in the matrixes such as  $\text{SrB}_6\text{O}_{10}$ ,  $\text{BaB}_8\text{O}_{13}$ ,  $\text{Sr}_3\text{B}_2\text{O}_6$ ,  $\text{Sr}_2\text{B}_2\text{O}_5$  and  $\text{SrB}_2\text{O}_4$ . In hosts  $\text{SrB}_6\text{O}_{10}$  and  $\text{BaB}_8\text{O}_{13}$ , the anions are composed both of triangular structure  $\text{BO}_3$  and tetrahedron  $\text{BO}_4$ , and the  $\text{Eu}^{3+}$  can be reduced even in air [23,24], while in  $\text{Sr}_3\text{B}_2\text{O}_6$ ,  $\text{Sr}_2\text{B}_2\text{O}_5$  and  $\text{SrB}_2\text{O}_4$ , the anions contain only triangular  $\text{BO}_3$  group, and the  $\text{Eu}^{3+}$  ion cannot be reduced in air by aliovalent substitution [4].

#### 4. Conclusions

The VUV-UV spectra and XANES at  $\text{Eu-L}_3$  edge of  $\text{SrBO}_4\text{:Eu}$  prepared in air were determined. Part of  $\text{Eu}^{3+}$  can be reduced to  $\text{Eu}^{2+}$  in this compound prepared in air. This is confirmed by XANES and VUV-UV spectral observations. The VUV excitation spectra indicate that the host absorptions are below 170 nm, and the bands at 203, 238, 280 and 310 nm are probably a group of f–d transitions of  $\text{Eu}^{2+}$ , the charge transfer band of  $\text{Eu}^{3+}$  is peaked at 272 nm.

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