

XANES at Eu-L₃ edge and valence of europium in SrB₄O₇:Eu and BaB₈O₁₃:Eu

LIANG, Hong-Bin^a(梁宏斌) HU, Tian-Dou^b(胡天斗) WANG, Shu-Bin^a(王淑彬)

ZENG, Qing-Hua^a(曾庆华) PEI, Zhi-Wu^a(裴治武) SU, Qiang^{*a}(苏锵)

^a Laboratory of Rare Earth Chemistry and Physics, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, Jilin 130022, China

^b Laboratory of Synchrotron Radiation, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing, 100039, China

The luminescent materials SrB₄O₇:Eu and BaB₈O₁₃:Eu were synthesized, and the valence states of europium in the materials were measured by means of XANES at Eu-L₃ edge. It is found that the Eu³⁺ and Eu²⁺ ions are all present in the materials, and more Eu³⁺ ions can be reduced in SrB₄O₇:Eu than in BaB₈O₁₃:Eu. The excitation and emission spectra of Eu³⁺ in SrB₄O₇:Eu and BaB₈O₁₃:Eu were determined.

Keywords Strontium tetraborate, barium octaborate, europium, valence state, XANES, luminescence

Introduction

By XANES (X-ray absorption near edge structure) investigation of some rare earth compounds, it has been reported¹ that L₂ and L₃ edges of RE²⁺ and RE³⁺ ions locate at different peak positions, and the discrepancy is about 7.5 eV. Furthermore, the relative intensity of the absorption edge can reflect the relative quantity of RE²⁺ and RE³⁺ in the compounds.²

On the other hand, when some trivalent RE³⁺ ions such as Eu³⁺, Sm³⁺ are used to substitute for the divalent ions (M²⁺) such as the alkaline earth ions Sr²⁺, Ba²⁺ in the host, we found the electrons carried on the produced vacant V^{''}_{M²⁺} can be used as reductant to reduce the doped trivalent rare earth ions into divalent state at high temperature even in air. The reduction of

Eu³⁺ to Eu²⁺ in air in some matrixes, such as SrB₄O₇,³ SrB₆O₁₀,⁴ BaB₈O₁₃,^{5,6} and MBPO₅ (M = Ca, Sr, Ba)⁷ has been achieved, and by comparing the structure characteristic of different matrixes and dopant ions, we have ever proposed four necessary conditions³ for reduction of RE³⁺ to RE²⁺ in air in solid compounds. (1) There is no oxidizing ions in matrix. (2) The dopant trivalent ions must replace the cations with different valence in host. (3) The RE²⁺ ions must have similar radii to the substituted cations and have a suitable lattice site in matrix. (4) The host compound must have an appropriate structure, for example, the rigid tetrahedral structure of anion group such as BO₄, PO₄ or SO₄ in composite oxides matrixes. The luminescent properties of Eu²⁺ in matrixes SrB₄O₇³ and BaB₈O₁₃^{5,6} have been reported, in order to probe the reduction situation of Eu³⁺ in the matrixes, the valence states of europium in the matrixes were measured by XANES at Eu-L₃ edge.

Experimental

Samples SrB₄O₇:Eu and BaB₈O₁₃:Eu were synthesized by means of solid state reaction, stoichiometric analytical grade strontium carbonate or barium carbonate, boric acid (excess 3% to compensate evaporation) and europium oxide (99.9%, the dopant concentration

Received August 23, 1999; accepted December 14, 1999.

Project supported by the State Key Project of Basic Research (Project 973) (No. G1998061312), the National Natural Science Foundation of China (No. 29771029) and the Foundation of Laboratory of Beijing Synchrotron Radiation, Institute of High Energy Physics, Chinese Academy of Sciences (No. 980010).

of europium is a molar ratio of 6%) were mixed, ground and heated at 500°C for 2 h. The samples were reground and heated at 650°C ($\text{BaB}_8\text{O}_{13}:\text{Eu}$) or 850°C ($\text{SrB}_4\text{O}_7:\text{Eu}$) for another 2 h. The results of XRD analyses for the synthesized samples are coincident with JCPDS 23-42 and 15-801, respectively.

XANES at Eu-L₃ edge of the samples was measured on beam 4W1B by means of XAFS station in Beijing Synchrotron Radiation Facilities. The spot of X-ray photons from storage ring at 2 GeV position was defined by a slit of size 1.0(H) × 10(W) mm² and monochromatized by a Si (111) double crystal monochromator, which yielded a resolution of approximately 2 eV at 10 keV. The ring current was about 60 mA. Calibration of the energy was made by using Fe-metal foil. The X-ray data were collected at 293 K under Ar atmosphere in the ion chamber. The excitation spectra and emission spectra for the samples were determined at room temperature on a SPEX FLUOROLOG-2 fluorescence spectrophotometer.

Results and discussion

XANES at Eu-L₃ edge of the samples

Fig. 1a and 1b show the results of XANES at Eu-L₃ edge in $\text{SrB}_4\text{O}_7:\text{Eu}$ and $\text{BaB}_8\text{O}_{13}:\text{Eu}$. Fitted curves and deconvolution lines are also depicted. It is obvious that:

(1) In $\text{SrB}_4\text{O}_7:\text{Eu}$ and $\text{BaB}_8\text{O}_{13}:\text{Eu}$, double peaks appear in XANES at Eu-L₃ edge. The lower energy edge is corresponding to Eu^{2+} ions, while the higher one is corresponding to Eu^{3+} ions. The positions of L₃ edge of Eu^{3+} and Eu^{2+} in $\text{SrB}_4\text{O}_7:\text{Eu}$ are at 6982.7 eV and 6974.4 eV, respectively, and the energy of L₃ edge of Eu^{2+} is 8.3 eV lower than that of Eu^{3+} . The positions of L₃ edge of Eu^{3+} and Eu^{2+} in $\text{BaB}_8\text{O}_{13}:\text{Eu}$ are at 6982.5 eV and 6973.8 eV, respectively, and the energy of L₃ edge of Eu^{2+} is 8.7 eV lower than that of Eu^{3+} .

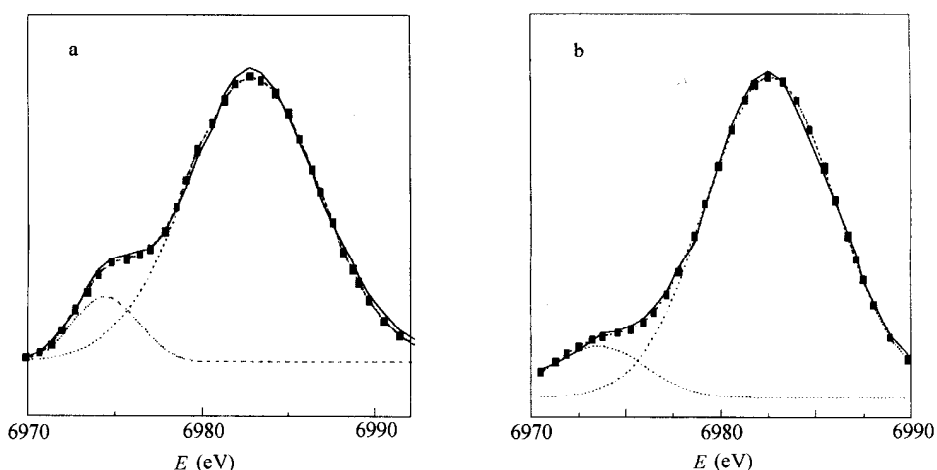


Fig. 1 XANES at Eu-L₃ edge in $\text{SrB}_4\text{O}_7:\text{Eu}$ (a) and $\text{BaB}_8\text{O}_{13}:\text{Eu}$ (b) (— experimental, -■- fitted line, ··· deconvolution line).

(2) According to the corresponding peak area, the molar percentages for Eu^{3+} and Eu^{2+} ions account for about 88.0% and 12.0% in $\text{SrB}_4\text{O}_7:\text{Eu}$, and about 91.6% and 8.4% in $\text{BaB}_8\text{O}_{13}:\text{Eu}$, respectively. It indicates that more Eu^{3+} ions can be reduced in $\text{SrB}_4\text{O}_7:\text{Eu}$ than in $\text{BaB}_8\text{O}_{13}:\text{Eu}$ in air.

The results above are probably related to the following factors.

(1) The rigid tetrahedron structures of BO_4 exist in host SrB_4O_7 ⁸ and $\text{BaB}_8\text{O}_{13}$,⁹ and the divalent Eu^{2+} ion has similar radii with the substituted alkaline earth ions in matrixes. These meet the necessary conditions that we

have proposed, therefore the Eu^{3+} ions can be reduced in air at high temperature in these matrixes.

(2) The rigid structures of AO_4 (A = B, P, S) of the anion in alkaline earth borates, phosphates and sulphates are suitable to stabilize the divalent rare earth ions.³ In host SrB_4O_7 , all anions are in the form of tetrahedron BO_4 ,⁸ and this rigid tetrahedral structure can efficiently enclose the divalent rare earth ions. So the divalent rare earth ions are easy to be stabilized. While in host $\text{BaB}_8\text{O}_{13}$, it consists of two separated interlocking three-dimensional infinite network, each of which was built up from alternating triborate and pentaborate groups

and triborate groups are linked only to pentaborate groups.⁹ Each triborate group contains one tetrahedron BO_4 and two triangular BO_3 , and each pentaborate group contains one tetrahedron BO_4 and four triangular BO_3 . The plane triangle structure BO_3 can not enclose the divalent rare earth ions, so the divalent rare earth ions are hard to be stabilized. For example, Eu^{3+} ion can not be reduced in air by above aliovalent substitution method if Eu^{3+} is doped and fired in those alkaline earth borates such as $\text{Sr}_3\text{B}_2\text{O}_6$, $\text{Sr}_2\text{B}_2\text{O}_5$ and SrB_2O_4 which contain only triangular BO_3 group, although these borates meet also the condition-3 mentioned above. This is due to the fact that the plane triangular group can not protect the Eu^{2+} ion from the attack of the oxygen in air. Therefore, the rigid tetrahedron structure of BO_4 anion is probably one of the reasons that more Eu^{3+} ions are reduced in $\text{SrB}_4\text{O}_7:\text{Eu}$ than in $\text{BaB}_8\text{O}_{13}:\text{Eu}$.

(3) Comparing the radii of the cations, Sr^{2+} (131

pm) and Ba^{2+} (147 pm) with the radius of Eu^{2+} (130 pm) ion, it is obvious that Eu^{2+} ion matches with Sr^{2+} cation preferably, and this probably is one reason that more reduced Eu^{3+} existed in $\text{SrB}_4\text{O}_7:\text{Eu}$ than in $\text{BaB}_8\text{O}_{13}:\text{Eu}$ either.

Luminescence of Eu^{3+}

The luminescence of Eu^{2+} in $\text{SrB}_4\text{O}_7:\text{Eu}^3$ and $\text{BaB}_8\text{O}_{13}:\text{Eu}^{10}$ has been reported. The excitation spectra and the emission spectra of Eu^{3+} in the materials at the same experimental conditions are shown in Fig. 2. It can be found that the intensities of excitation spectra and the emission spectra of Eu^{3+} in $\text{BaB}_8\text{O}_{13}:\text{Eu}$ are stronger than those in $\text{SrB}_4\text{O}_7:\text{Eu}$, which implies the contents of Eu^{2+} in $\text{BaB}_8\text{O}_{13}:\text{Eu}$ are lower than those in $\text{SrB}_4\text{O}_7:\text{Eu}$, and the results are coincident with the results of XANES.

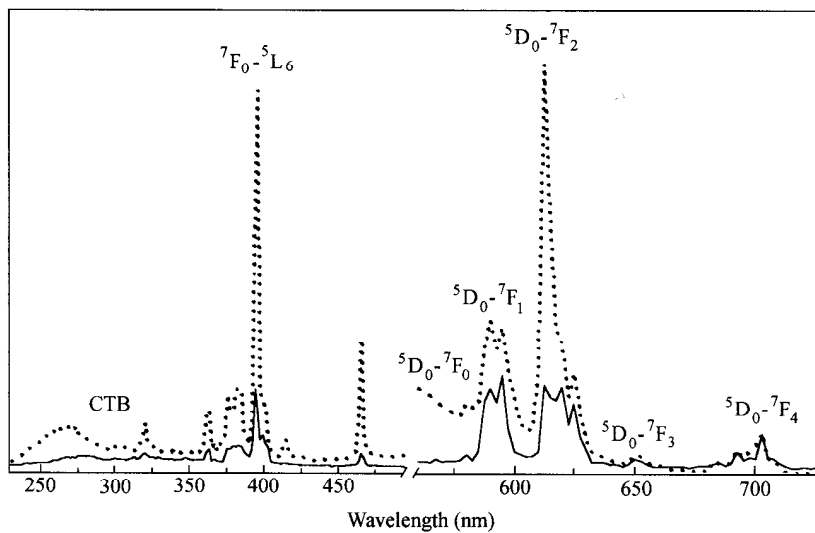


Fig. 2 Excitation (em = 612 nm) and emission (ex = 393 nm) spectra of Eu^{3+} in $\text{SrB}_4\text{O}_7:\text{Eu}$ (—) and $\text{BaB}_8\text{O}_{13}:\text{Eu}$ (···).

References

- Hu, Z.; Kaindl, G.; Meyer, G., *J. Alloys Compds.*, **246**, 186(1997).
- Singhal, R.K.; Garg, K.B., *Proceedings of the 2nd International Conference on Rare Earths Development application*, Vol. 1, Internation Academic Publishers, Beijing, 1991, p.112.
- Pei, Z.; Su, Q.; Zhang, J., *J. Alloys Compds.*, **198**, 51(1993).
- Zeng, Q.; Pei, Z.; Wang, S.; Su, Q., *J. Alloys Compds.*, **275—277**, 238(1998).
- Zeng, Q.; Pei, Z.; Su, Q., *J. Rare Earths*, Special Issue (*Proceedings of the 3rd International Conference on Rare Earths Development Application*), 274(1995).
- Zeng, Q.; Pei, Z.; Wang, S.; Su, Q., *Chin. J. Lumin.* (in Chinese), **17**, 111(1996).
- Jing, H.; Wu, G.; Du, B., *Chem. J. Chin. Univ.* (in Chinese), **18**, 1425(1997).
- Perloff, A.; Block, S., *Acta Cryst.*, **20**, 274(1966).
- Krogh-Moe, J., *Acta Cryst.*, **B25**, 2153(1969).
- Blasse, G.; Bril, A., *J. Electrochem. Soc.*, **115**, 977(1968).

(E9908109 SONG, J.P.; DONG, L.J.)