



Pergamon

Materials Research Bulletin 37 (2002) 1981–1989

Materials
Research
Bulletin

UV–VUV excited luminescence of SrBPO₅:Sm phosphor prepared in air

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(Refereed)

Received 5 July 2001; accepted 10 October 2001

Abstract

The high-resolution luminescent spectrum of divalent samarium excited by 355 nm UV light at 77 K, the VUV excitation spectra, the VUV excited emission spectra and EXAFS at Sm-L₃ edge were reported for samarium doped strontium borophosphate, SrBPO₅:Sm prepared by solid state reaction in air at high temperature. The high-resolution luminescent spectrum showed that the divalent samarium ions occupied the C_{2v} lattice sites. The VUV excitation spectra indicated that the sample exhibited absorption bands with the maxima at 129 and 148 nm, respectively. The performance of EXAFS at Sm-L₃ absorption edge suggested that the samarium ions were nine-coordinated and the mean distances of bond Sm–O were 2.38 Å.

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Keywords: A. Inorganic compounds; D. Luminescence

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PII: S0025-5408(01)00790-5

1. Introduction

In general, the reduction of trivalent rare earth ions can be accomplished in a reducing atmosphere, but in several special composite oxide matrixes, rare earth ions can exhibit abnormal reduction in an oxygenating atmosphere. For example, by solid reaction at high temperature in air, Eu^{3+} can be reduced in host $\text{Ba}_3(\text{PO}_4)_2$ [1], Sm^{3+} , Eu^{3+} , Yb^{3+} and Tm^{3+} could be reduced in matrix SrB_4O_7 [2,3]. The anions of these matrixes share same structural characteristics, viz. they are AO_4 ($A = \text{B}, \text{P}$) rigid three-dimensional tetrahedral network structure.

In the silica-like network anion units BPO_4 of borophosphates, it is suggested by Raman spectra [4,5] that B and P are tetrahedral form. These anions of tetrahedral structure have been confirmed [6] in compound SrBPO_5 by crystal structural studies. In SrBPO_5 , the anions are stillwellite type [7] and contain central three single chains of BO_4 tetrahedron and linked to terminal PO_4 tetrahedron to form loop-branched chains. So it is expected that SrBPO_5 would be suitable matrixes for the reduction of rare earth ions in air by solid state reaction at high temperature also.

In this paper, the luminescent properties of divalent samarium, the vacuum ultraviolet (VUV) spectra and extended X-ray absorption fine structure (EXAFS) at Sm-L_3 edge in $\text{SrBPO}_5:\text{Sm}$ prepared in air are reported.

2. Experimental

The powder samples, samarium activated strontium borophosphate, $\text{SrBPO}_5:\text{Sm}$ were prepared by the method of solid phase reaction in air atmosphere. The reactant mixtures, analytical-grade strontium carbonate, boric acid (excess 3 mol% to compensate the evaporation), ammonium dihydrogen phosphate and samarium oxide (99.99%) were heated at 400°C for 4 h, and then fired at 1000°C for another 4 h in air atmosphere.

The structure of matrix and samarium doped samples were checked by X-ray powder diffraction using $\text{Cu K}\alpha_1$ radiation. The XRD data indicated all of the synthesized samples were single hexagonal phase, and were coincident with JCPDS 18-1270. The constants of matrix crystal cell which calculated from observed d values were $a = 6.869(2) \text{ \AA}$, $c = 6.797(7) \text{ \AA}$, and that of JCPDS 18-1270 values were $a = 6.857 \text{ \AA}$, $c = 13.66 \text{ \AA}$. (The constants we calculated from d values of JCPDS 18-1270 were $a = 6.8447 \text{ \AA}$, $c = 6.8160 \text{ \AA}$.)

The high-resolution emission spectrum was performed with a SPEX-1403 spectrophotometer under the excitation of YAG laser beam (355 nm) with a cryostat of liquid nitrogen at 77 K.

The VUV spectra and EXAFS at Sm-L_3 edge of the sample were measured by Beijing Synchrotron Radiation Facilities (BSRF) on beam 3B1B at VUV spectral experimental station or on beam 4W1B at XAFS experimental station under normal operating conditions (2.2 GeV, 60 mA), respectively. For the determination of VUV spectra, an ARC-502 monochromator was used for excitation spectrum, an ARC-308

monochromator was used for emission spectrum and the signal was detected by a H7421-50 photomultiplier. The relative VUV excitation intensities of the samples were corrected by comparing the measured excitation intensities of the samples with the excitation intensities of sodium salicylate at the same excitation condition. For EXAFS measurement, X-ray photon was defined by a slit of size $1.0(\text{H}) \times 10(\text{V}) \text{ mm}^2$ and monochromatized by a Si(1 1 1) double crystal monochromator whose energy resolution was $1.2 \times 10^{-4} \Delta E/E$. Because of the low contents of europium in the doped sample, the sample measurement was made in fluorescence detector and Sm_2O_3 (which was used as reference sample) was measured by transmission mode. All VUV and XAFS experimental data were collected at 293 K.

3. Results and discussion

3.1. The high-resolution emission spectrum of Sm^{2+}

In previous work, we have reported [8] that the excitation and the low resolution emission spectra of Sm^{2+} and Sm^{3+} in $\text{SrBPO}_5:\text{Sm}$ prepared in air. The high-resolution emission spectrum of Sm^{2+} in $\text{Sr}_{0.99}\text{Sm}_{0.01}\text{BPO}_5$ performed at 77 K was shown in Fig. 1. The assignment and the peak positions of the emission line were exhibited in Table 1. The emergence of ${}^5\text{D}_0-{}^7\text{F}_0$ transition for Sm^{2+} in $\text{SrBPO}_5:\text{Sm}$ indicated the Sm^{2+} ions occupied the sites without centro-symmetry in Sm^{2+} . The transitions of Sm^{2+} in $\text{SrBPO}_5:\text{Sm}$ were from ${}^5\text{D}_0-{}^7\text{F}_J$ ($J = 0, 1, 2$), and the numbers of transition line for ${}^5\text{D}_0-{}^7\text{F}_J$ were 1, 3, 4 for $J = 0, 1, 2$, respectively. The results were in good agreement with the theoretical splitting of the ${}^7\text{F}_J$ levels into a maximum of 1, 3 and 4 sublevels for the site symmetry of C_{2v} in the host [9]. Fig. 2 showed the temperature effected on the integrated emission intensities of the ${}^5\text{D}_0-{}^7\text{F}_J$

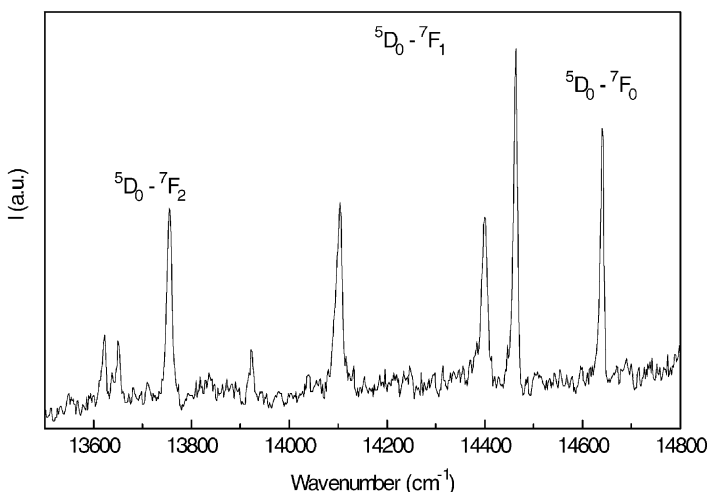


Fig. 1. High-resolution emission spectrum of $\text{Sr}_{0.99}\text{Sm}_{0.01}\text{BPO}_5$ prepared in air at 77 K.

Table 1

The assignment and the peak positions of the emission line of Sm^{2+} in $\text{SrBPO}_5:\text{Sm}$ at 77 K

Transition ${}^5\text{D}_0-{}^7\text{F}_J$	J		
	0	1	2
Wavenumber (cm^{-1})	14640	14464, 14402, 14104	13922, 13756, 13650, 13622
Barycenter (cm^{-1})	14640	14323	13727

($J = 0, 1, 2$) transitions in the range 30–250 K. It can be observed that the intensities of the ${}^5\text{D}_0-{}^7\text{F}_J$ decrease with the temperature.

We think the processes of this abnormal reduction of Sm^{3+} in $\text{Sr}_{1-x}\text{Sm}_x\text{BPO}_5$ in oxygenating atmosphere are connected with two reasons. First, aliovalent substitution brings about reduction, and second, the rigid tetrahedron structure of anions AO_4 ($A = \text{B}, \text{P}$) guarantees the reduced valence state steadiness.

When Sm^{3+} cations were built into the matrix, they would first replace the Sr^{2+} cations. In order to keep the electroneutrality of the compound, two Sm^{3+} ions would substitute for three Sr^{2+} ions. Therefore, two positive defects of $[\text{Sm}_{\text{Sr}}]^\bullet$ and one negative Sr^{2+} vacancy of $[\text{V}_{\text{Sr}}]''$ would be created by each substitution. The free electrons are carried on the negative Sr^{2+} vacancy, which are produced by aliovalent substitution between doped Sm^{3+} and Sr^{2+} in host lattice. By thermally stimulated movement, the electrons on the $[\text{V}_{\text{Sr}}]''$ vacancies would be transferred to doped Sm^{3+} ions and the doped Sm^{3+} ions are reduced by these free electrons. The similar process had been suggested for the reduction of Eu^{3+} in $\text{Sr}_2\text{B}_5\text{O}_9\text{Cl}:\text{Eu}$ [10] by our group.

It is reported [6] that all anions are in the form of the rigid tetrahedron structure of AO_4 ($A = \text{B}, \text{P}$) in the host SrBPO_5 , and Sm^{2+} ion has similar radius with Sr^{2+} ion when they both are nine-coordinated [11]. We think that these factors are suitable to stabilize the Sm^{2+} ions. Because the replacement easily occurred between cations that

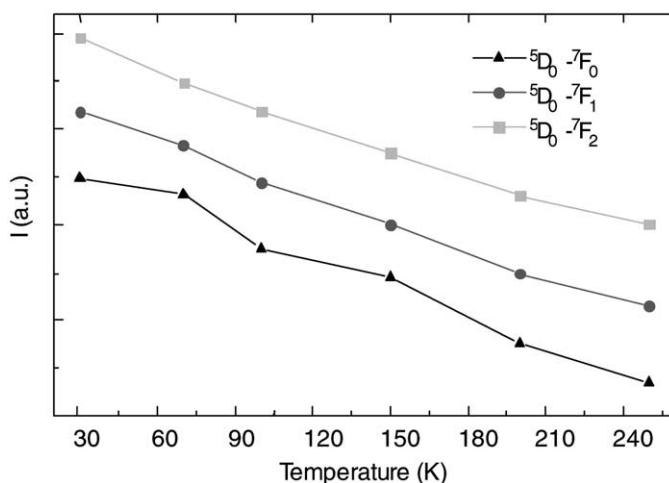


Fig. 2. The temperature effected on the integrated emission intensities of the ${}^5\text{D}_0-{}^7\text{F}_J$ ($J = 0, 1, 2$).

have similar radii, Sm^{2+} ions occupy the substituted lattice sites of Sr^{2+} ions, this replacement cannot lead to obvious defection for tetrahedral anion AO_4 . This rigid tetrahedral structure can efficiently enclose Sm^{2+} ion, protect the inserted Sm^{2+} from the attack of the oxygen in air, so the reduced state is easy to be stabilized. The point had been supported by the facts that the reduction of rare earth ions in the matrixes such as SrB_4O_7 , $\text{SrB}_6\text{O}_{10}$, $\text{Sr}_3\text{B}_2\text{O}_6$, $\text{Sr}_2\text{B}_2\text{O}_5$ and SrB_2O_4 . In host SrB_4O_7 [2] all anions existed in the form of tetrahedron BO_4 , the Eu^{3+} or Sm^{3+} can be reduced in air, and in host $\text{SrB}_6\text{O}_{10}$ [12], the anions are consisted of triangular structure BO_3 and tetrahedron BO_4 , the Eu^{3+} or Sm^{3+} can also be reduced in air. While in $\text{Sr}_3\text{B}_2\text{O}_6$, $\text{Sr}_2\text{B}_2\text{O}_5$ and SrB_2O_4 [2], the anions contain only triangular BO_3 group, RE^{3+} cannot be reduced in air by aliovalent substitution.

3.2. The VUV spectra

Fig. 3 showed the VUV excitation spectra of the sample $\text{Sr}_{0.99}\text{Sm}_{0.01}\text{BPO}_5$ prepared in air when monitored the emission of Sm^{3+} at 610 nm and Sm^{2+} at 693 nm. There were two bands with the maximum at about 129 and 148 nm in the excitation spectra, no matter monitored the emission of Sm^{2+} or Sm^{3+} . It indicated that these bands were impendent on the valences of the doped ions. The results implied that the matrix probably exhibited absorption in the region. The luminescent spectra of Sm^{2+} and Sm^{3+} excited by VUV light of 130 nm were depicted in Fig. 4. Both the emission of Sm^{2+} and Sm^{3+} can be observed. The emission of Sm^{3+} was caused by a group transition ${}^6\text{G}_{5/2} - {}^6\text{H}_J$ ($J = 5/2, 7/2, 9/2$), and the strongest transition was ${}^6\text{G}_{5/2} - {}^6\text{H}_{7/2}$ at 610 nm. The emission of Sm^{2+} was caused by transitions ${}^5\text{D}_0 - {}^7\text{F}_J$ ($J = 0, 1, 2$), and the prominent transition was ${}^5\text{D}_0 - {}^7\text{F}_0$ at 693 nm. This emission spectrum was identical with that excited by ultraviolet (UV)

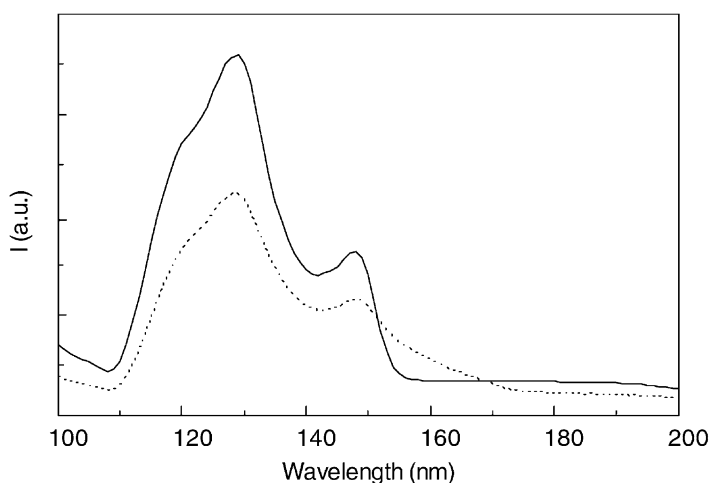


Fig. 3. VUV excitation spectra of Sm^{2+} (solid line) and Sm^{3+} (dotted line) in $\text{Sr}_{0.99}\text{Sm}_{0.01}\text{BPO}_5$ prepared in air.

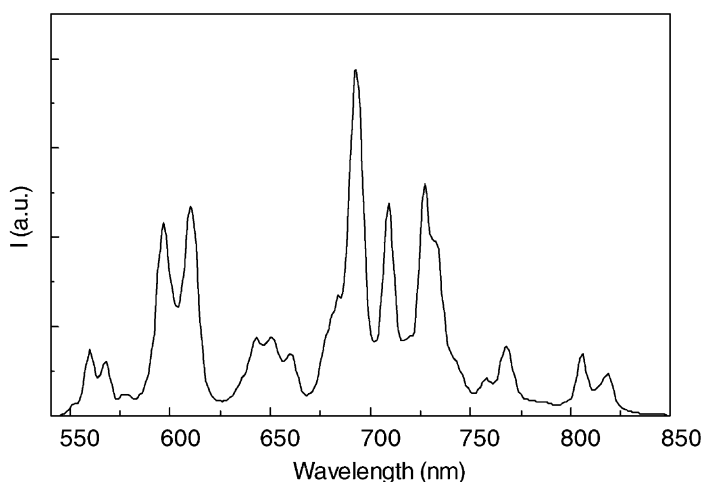


Fig. 4. VUV excited luminescent spectrum of $\text{Sr}_{0.99}\text{Sm}_{0.01}\text{BPO}_5$ prepared in air.

[8]. Sm^{2+} and Sm^{3+} coexisted in $\text{SrBPO}_5:\text{Sm}$, it implied that Sm^{3+} ions could be reduced partly by solid state reaction at high temperature in air atmosphere.

3.3. EXAFS at Sm- L_3 edge

A higher dopant sample, $\text{Sr}_{0.92}\text{Sm}_{0.08}\text{BPO}_5$ was used to perform the EXAFS at Sm- L_3 edge. Data processing of EXAFS at Sm- L_3 edge in the samples followed standard procedures for pre-edge background subtraction and EXAFS background removal, the EXAFS χ is defined as

$$\chi(E) = \frac{\mu(E) - \mu_0(E)}{\mu_0(E)} \quad (1)$$

where $\mu(E)$ and $\mu_0(E)$ are the X-ray absorption coefficients for the sample and the isolated atom, respectively. The normalized EXAFS data were converted to a wave vector (k) space, using

$$k = \left[\frac{2m(E - E_0)}{\hbar^2} \right]^{1/2} \quad (2)$$

where E_0 is the maximum of the first derivative of the spectra, m the mass of an electron, E the photon energy, and \hbar is Planck's constant divided by 2π . The resulting oscillations were weighed with k^3 factor and Fourier transformed, which give the radical structure function of the edge. The main peak was inverse Fourier transformed into k space again, and was curve-fitted by the non-linear least square curve-fitting method with the following EXAFS formula:

$$\chi(k) = \sum \left(\frac{N_j S}{k r_j^2} \right) f_j(k) \exp(-2\sigma_j^2 k^2) \sin[2kr_j + \phi_j(k)] \quad (3)$$

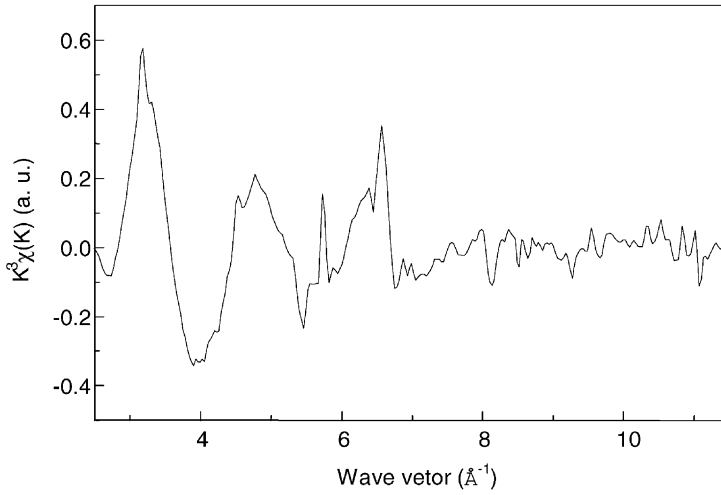


Fig. 5. Isolated k^3 -weighted EXAFS oscillation of Sm-L₃ edge in Sr_{0.92}Sm_{0.08}BPO₅ prepared in air.

where $f_j(k)$ is the backscattering amplitude function and $\phi_j(k)$ the total phase shift function derived from reference sample Sm₂O₃, respectively. N_j is the number of atoms in the j -shell at the average distances r_j , viz. the true coordination number of photon–electron scatters at distance r_j . S is damping factor which was fixed and evaluated also from the coordination number of the reference sample Sm₂O₃, and σ_j^2 , the Debye–Waller factor, represents the variance at the distance r_j and Debye–Waller

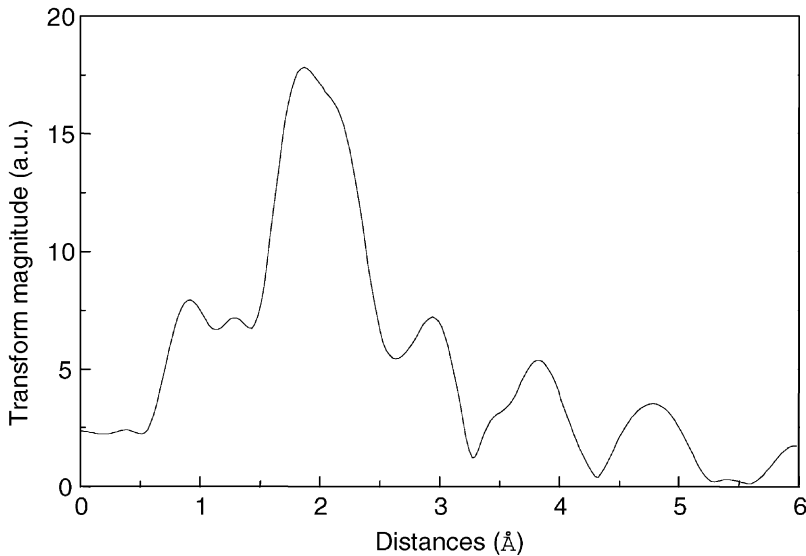


Fig. 6. Fourier transform of the k^3 -weighted EXAFS spectrum of Sm-L₃ edge in Sr_{0.92}Sm_{0.08}BPO₅ (phase shift had not been corrected in the figure) prepared in air.

factor contains the contribution from both static disorder and thermally induced vibration displacements within a shell of neighbors.

The isolated and k^3 -weighed EXAFS oscillations were shown in Figs. 5 and 6, respectively. The EXAFS results indicated the doped samarium atoms were nine-coordinated (calculated value is 8.78) by oxygen and average bond distances of Sm–O were 2.38 Å, $\sigma_1^2 = 0.0027 \text{ \AA}^2$.

4. Conclusions

The following conclusions could be suggested:

1. The high-resolution emission spectrum of divalent samarium in strontium borophosphate, SrBPO₅:Sm prepared in air were determined at 77 K. The results showed that the line numbers of $^5D_0 - ^7F_J$ transitions were 1, 3, 4 for $J = 0, 1, 2$, respectively, which indicated that Sm²⁺ ions occupied the sites without central symmetry in Sm²⁺, and were in the C_{2v} lattice sites in the matrix.
2. From the results of EXAFS at Sm-L₃ edge, it could be calculated that the coordination numbers of samarium atoms were nine and average bond distances of Sm–O were 2.38 Å in the host.
3. VUV excitation spectra at the emission of Sm²⁺ and Sm³⁺ all presented the bands located at 129 and 148 nm, which implied that the matrix exhibited absorption in the region. The emission spectra of 130 nm VUV excited were identical with that excited by 400 nm UV. UV–VUV excited emission spectra implied that Sm³⁺ ions could be reduced in SrBPO₅:Sm in air atmosphere.

Acknowledgments

The work is supported by Project supported by State Key Project of Basic Research of China, the National Natural Science Foundation of China, the Foundation of Laboratory of Excited State Processes, Changchun Institute of Optical Fine Mechanics and Physics, Chinese Academy of Sciences and the Foundation of Laboratory of Beijing Synchrotron Radiation, Institute of High Energy Physics, Chinese Academy of Sciences.

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