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Local structure around europium ions doped in borate glasses

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Photostimulated luminescence phenomenon has been observed in Eu^{2+}-doped borate glasses. In this work, europium ions doped in borate glasses are studied by europium L_{III} x-ray absorption spectroscopy to reveal the relationship between optical function and local structure. XANES spectra showed that a part of Eu^{2+} converted to Eu^{3+} upon the irradiation of x-ray. The nearest neighbor Eu-O distance in Eu^{3+}-doped glasses obtained by EXAFS analysis is longer than that of Eu_2O_3 by 0.02-0.09Å. The oxygen coordination number of europium in Eu^{2+}-doped glass is different from that of the Eu^{3+}-doped glass with the same composition while the nearest neighbor Eu-O distances are closely the same. The coordination number of highly Eu^{3+}-doped glasses decreased with an increase of Na_2O content.

Keywords: Photostimulated luminescence; Eu^{2+}-doped borate glasses; Eu L_{III} XAFS.

1. Introduction

The phenomenon of photostimulated luminescence (PSL) in BaFX:Eu^{2+} (X=Br, I) has been widely used for two-dimensional x-ray detector. Although it is widely used, the physical process of the PSL process in BaFX:Eu^{2+} (X=Br, I) is still under discussion. Takahashi et al. proposed the model (Takahashi et al. 1984) in which Eu^{2+} is expected to ionize to Eu^{3+} ion upon x-ray irradiation and remain stable until photostimulation. But their model is considered to be questionable for the lack of the evidence of the existence of Eu in a stable 3+ charge state after x-ray irradiation (Subramanian et al. 1997).

X-ray absorption fine structures (XAFS) analysis is a powerful method to investigate the local structure around particular ions in materials. Especially the peak of x-ray absorption near edge structure (XANES) spectra assigned to 2p→5d transition are separated by the valence of rare earth ions. In the case of BaFX:Eu^{2+} (X=Br, I), Eu L_{III}XAFS spectra cannot be observed because of the high absorption coefficient of barium and halide ions. Recently Qiu et al. have observed PSL phenomenon in reduced rare-earth doped glasses; Eu^{2+}-doped borate glasses (Qiu et al. 1997a), Ce^{3+}-doped borate glasses (Qiu et al. 1997b) and Ce^{3+}-doped silicate glasses (Qiu et al. 1997c). Sodium borate glasses are consisted of relatively light atoms. Therefore XAFS spectra of rare-earth ion are expected to be observable. In this study, we investigate Eu^{2+}-doped and Eu^{3+}-doped borate glasses by Eu L_{III} XAFS in order to reveal the relationship between PSL phenomenon and the local structure around reduced rare earth ions.

2. Experimental

$(100\text{-}X)B_2O_3 \cdot XNa_2O$ (X=15, 20, 25) glasses (BN15, BN20, BN25) doped with 1mol% Eu_2O_3 and $(100\text{-}X)B_2O_3 \cdot XNa_2O$ (X=10, 15, 20, 25, 30) glasses (BEN10, BEN15, BEN20, BEN25, BEN30) doped with 10mol% Eu_2O_3 were prepared by quenching melts. Reduced rare-earth doped borate glasses were prepared by remelting 1mol% Eu_2O_3 doped borate glasses in a reducing atmosphere furnace. Batched compositions of glass samples are listed in Table 1.

The details of XAFS measurement were written in the electronic archive. In order to observe the ionization of Eu^{2+} ion by x-ray irradiation, XANES spectra around Eu L_{III} edge were also measured after x-ray (6.941 keV) irradiation for 30 and 60 minutes.

Table 1
Chemical composition of examined glasses

Sample	Composition(mol%)
BN15	$85B_2O_3 \cdot 15Na_2O$
BN20	$80B_2O_3 \cdot 20Na_2O$
BN25	$75B_2O_3 \cdot 25Na_2O$
BEN10	$90B_2O_3 \cdot 10Na_2O \cdot 10Eu_2O_3$
BEN15	$85B_2O_3 \cdot 15Na_2O \cdot 10Eu_2O_3$
BEN20	$80B_2O_3 \cdot 20Na_2O \cdot 10Eu_2O_3$
BEN25	$75B_2O_3 \cdot 25Na_2O \cdot 10Eu_2O_3$
BEN30	$70B_2O_3 \cdot 30Na_2O \cdot 10Eu_2O_3$

3. Results and discussion

Europium L_{III} XANES spectra of Eu^{2+}-doped BN25 glasses x-ray irradiated for various durations are shown in Fig. 1 with those of reference samples. The peaks located at 6.972 keV and 6.980 keV are assignable to 2p→5d transition in Eu^{2+} and Eu^{3+}, respectively. It is clear that a peak at 6.980 keV of Eu^{2+}-doped BN25 glass becomes apparent upon the x-ray irradiation. It means that some Eu^{2+} ions doped in BN25 glasses were converted into Eu^{3+} ions upon x-ray irradiation. Therefore we propose that Eu^{2+} ions capture holes to form Eu^{3+} ions after the irradiation of x-rays. Although we do not directly observe Eu^{2+} ions in BaFX:Eu^{2+} phosphors, we consider the same mechanism may be

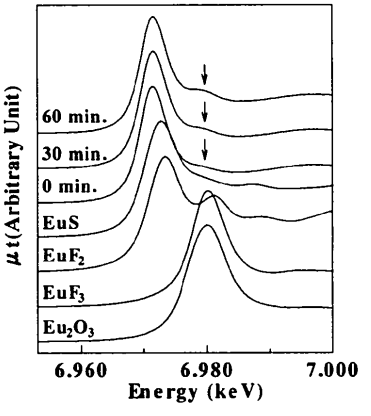

Figure 1
XANES spectra of Eu^{2+}-doped BN25 glasses x-ray irradiated for various durations. The peak at 6.980 keV of Eu^{2+}-doped BN25 glass which is assignable to 2p→5d transition in Eu^{3+} becomes apparent upon the x-ray irradiation.

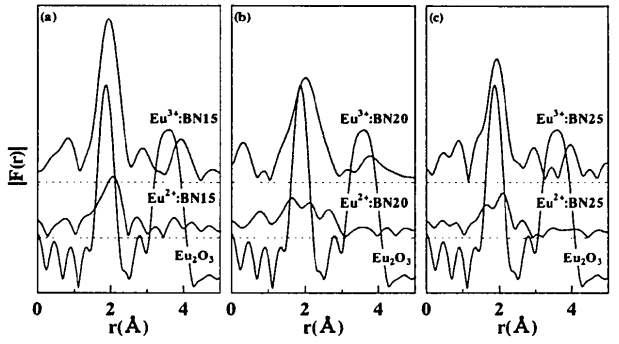

Figure 2
Radial structure functions of Eu^{2+} and Eu^{3+}-doped BN glasses with that of crystalline Eu_2O_3. (a) BN15 glasses, (b) BN20 glasses and (c) BN25 glasses. Notations are listed in Table 1.

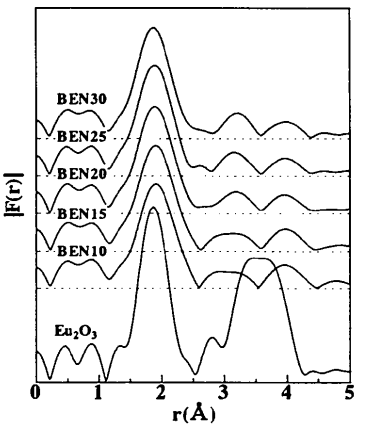

Figure 3
Radial structure functions of BEN glasses with that of crystalline Eu_2O_3. Notations are listed in Table 1.

Table 2
Results of curve fitting analysis of Eu^{3+}-doped $B_2O_3 \cdot Na_2O$ glasses. N:coordination number, r:Eu-O bond length, σ :Debye-Waller factor, R:residual and estimated standard deviation in parentheses. Notations are listed in Table 1.

Sample	N	r(Å)	σ (Å)	R(%)
Eu_2O_3	6.0	2.34	0.050(16)	2.9
Eu^{3+}:BN15	6.5(2)	2.43(1)	0.080(20)	4.3
Eu^{3+}:BN20	6.4(3)	2.41(1)	0.098(24)	8.9
Eu^{3+}:BN25	5.9(2)	2.39(1)	0.099(22)	2.1

occurred. The optical features of Eu^{2+}-doped glasses were described elsewhere (Qiu et al. 1997a).

The details of EXAFS analysis were written in the electronic archive. The radial structure function |F(r)| for Eu^{2+} and Eu^{3+}-doped BN glasses and those of BEN glasses are shown in Fig. 2 and Fig. 3, respectively. The first peak of each |F(r)| curve corresponds to the nearest Eu-O bonds. The peak area corresponds to Eu-O bonds of Eu^{2+}-doped BN glasses in Fig. 2 are much decreased by the reduction. Therefore we applied the curve-fitting method only to Eu^{3+}-doped BN glasses. The results for BN glasses and BEN glasses are shown in Table 2 and Table 3, respectively.

As mentioned of the peak area corresponds to Eu-O bonds are much decreased by the reduction (Fig. 2). In the case of Sm^{2+}-doped BN glasses (Shimizugawa et al. 1997), oxygen coordination number of samarium in Sm^{2+}-doped BN glasses are also decreased from Sm^{3+}-doped BN glass of the same Na_2O content. Oxygen around rare earth ion is also removed in the case of Eu^{2+}-doped glass. The decrease of the peak area corresponds to the first Eu-O bonds of |F(r)| is not concerned with Na_2O content. This tendency corresponds to that the intensity of photostimulated luminescence is not concerned with Na_2O content of BN glasses. And the decrease of the peak area in Eu^{2+}-doped glasses is much larger than the case of Sm^{2+}-doped BN glasses. This difference may be caused by the stability of each rare-earth ion which 1 mol% doped in BN glasses.

As shown in Table 3 and Fig. 3, the average coordination number of Eu^{3+} ions in BEN glasses, which involve 10 mol% of Eu_2O_3, decreased with an increase of Na_2O content. And the nearest neighbor of Eu-O distance is slightly decreased with an increase of Na_2O content. These tendencies are much concerned

Table 3
Results of curve fitting analysis of Eu^{3+}-doped $B_2O_3 \cdot Na_2O$ glasses. N:coordination number, r:Eu-O bond length, σ :Debye-Waller factor, R:residual and estimated standard deviation in parentheses. Notations are listed in Table 1.

Sample	N	r(Å)	σ (Å)	R(%)
Eu_2O_3	6.0	2.34	0.050(16)	2.9
BEN10	8.4(3)	2.40(1)	0.113(20)	4.4
BEN15	7.6(3)	2.39(1)	0.107(20)	4.3
BEN20	7.2(3)	2.38(1)	0.103(21)	5.2
BEN25	7.1(2)	2.38(1)	0.100(23)	7.3
BEN30	6.5(2)	2.36(1)	0.096(24)	9.7

with the property of $B_2O_3 \cdot Na_2O$ glass systems that three coordinated boron atoms are changed to four coordinated with an increase of Na_2O content up to 30 mol% (Shelby, 1983). The change of coordination number of boron atom may consume oxygen atom around doped Eu^{3+} ion, and causes the change of the coordination number of europium in Eu^{3+}-doped BN glasses. In the case of Sm^{3+}-doped $B_2O_3 \cdot Na_2O$ glasses (Shimizugawa et al. 1997), it is also reported that the average coordination number of Sm^{3+} ions is decreased with an increase of Na_2O content. The flexibility of the coordination number of rare-earth ions in $B_2O_3 \cdot Na_2O$ glasses may cause high solubility to glasses while rare-earth oxides are not considered as glass forming oxides.

4. Conclusion

The essential conclusions are as follows:
(1) XANES spectra of Eu^{2+}-doped borate glass, which has PSL phenomena, shows that a part of Eu^{2+} converted to Eu^{3+} upon the irradiation of x-ray.
(2) In Eu^{2+}-doped glasses, oxygen around rare earth ion is removed during a remelting process in reducing atmosphere.
(3) The average coordination number of highly Eu^{3+}-doped glasses decreased with an increase of Na_2O content.

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