

## X-ray induced reduction of rare earth ion doped in $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3$ glasses

Yutaka Shimizugawa,<sup>a\*</sup> Norimasa Umesaki,<sup>a</sup> Katsumi Hanada,<sup>b</sup> Ichiro Sakai<sup>b</sup> and Jianrong Qiu<sup>c</sup>

<sup>a</sup>Osaka National Research Institute, AIST, Midorigaoka, Ikeda, Osaka 563-8577, Japan, <sup>b</sup>Department of Photonics, Faculty of Science and Engineering, Ritsumeikan University, Kusatsu, Shiga 525-8577, Japan, <sup>c</sup>Photon Craft Project, ICORP, JST, Keihanna Plaza, Seika-cho, Kyoto 619-0237, Japan. Email:shimizug@onri.go.jp

$5\text{Na}_2\text{O}-10\text{Al}_2\text{O}_3-85\text{B}_2\text{O}_3$  glasses doped with 0.05 mol%  $\text{Sm}_2\text{O}_3$  or 0.05 mol%  $\text{Eu}_2\text{O}_3$  turn to orange after irradiation by focussed femtosecond pulsed laser or x-ray irradiation. To know the mechanism of photo-induced coloring, the glasses were studied by Sm or Eu  $L_{\text{III}}$  XANES before and after x-ray or UV irradiation. XANES in both edges showed that a part of trivalent ion converted to divalent ion upon the irradiation of x-ray. These facts reveal that photoreduction of rare earth ion is the mechanism of photo-induced coloring. However no photoreduction upon UV irradiation occurred in both glasses.

**Keywords:** Photo-induced coloring,  $\text{Eu}^{3+}$  or  $\text{Sm}^{3+}$ -doped aluminoborate glasses,  $L_{\text{III}}$  XANES

### 1. Introduction

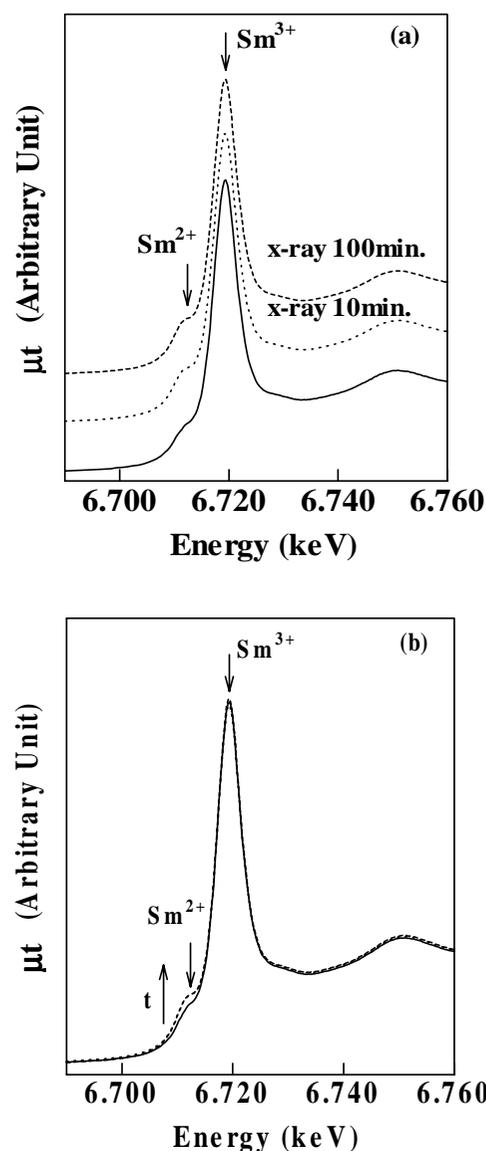
A femtosecond laser is used not only a light source for investigating non-linear optical processes in times of the order of  $10^{-12}$  s but also an instrument for changing the structure of materials because of its ability to make large electric fields. Multiphoton ionization (Stuart et al., 1995), permanent refractive-index change (Davis et al., 1996), formation of high-density plasma (Nakano et al., 1997), Joule heating (Cho et al., 1998) and color center generation (Efimov et al., 1998) have been reported as results from interactions between femtosecond pulses and glasses. In the case of  $\text{Sm}^{3+}$ -doped (Qiu et al., 1999a) and  $\text{Eu}^{3+}$ -doped (Qiu et al., 1999b) glasses the focused part of the laser in the glass became orange after irradiation by an 800 nm focussed femtosecond pulsed laser. These phenomena are considered to be laser induced photoreduction. When x-ray irradiated  $\text{Sm}^{3+}$ -doped and  $\text{Eu}^{3+}$ -doped aluminoborate glasses, they turned orange in the same way.

The peak of x-ray absorption near edge structure (XANES) spectra of rare earth assigned to  $2p \rightarrow 5d$  transition are separated by the valence. Based on this fact, Shimizugawa et al. (1999) showed that a part of  $\text{Eu}^{2+}$  ion doped in borate glass converted to  $\text{Eu}^{3+}$  ion due to x-ray irradiation by Eu  $L_{\text{III}}$  XANES. If x-ray irradiation effects on  $\text{Sm}^{3+}$ -doped and  $\text{Eu}^{3+}$ -doped aluminoborate glasses are photo-induced reduction,  $L_{\text{III}}$  XANES study can reveal the mechanism of photo-induced coloring. Therefore we studied these glasses by rare earth  $L_{\text{III}}$  XANES before and after x-ray or UV irradiation.

### 2. Experimental

$5\text{Na}_2\text{O}-10\text{Al}_2\text{O}_3-85\text{B}_2\text{O}_3$  (NAB) glasses doped with 0.05 mol%  $\text{Sm}_2\text{O}_3$  or 0.05 mol%  $\text{Eu}_2\text{O}_3$  were prepared by quenching melts in air. Plate samples were used for measurements.

Sm  $L_{\text{III}}$  and Eu  $L_{\text{III}}$  XANES spectra were measured in a fluorescence mode using a Si(111) double crystal monochromator at BL-9A at the Photon Factory, National Laboratory for High Energy Physics(KEK-PF), with an electron beam energy of 2.5 GeV and a maximum stored current of 400 mA. Harmonics were rejected by detuning the monochromator. Nitrogen gas filled the  $I_0$  ionization chamber, and a mixture of nitrogen (85 %) and argon (15 %) filled Lytle chamber. X-ray absorption data in the neighborhood of the Sm  $L_{\text{III}}$  edge (6.718 keV) and Eu  $L_{\text{III}}$  edge (6.981 keV) were collected at 263 energy points ranging from 6.607 keV to 6.787 keV and 263 energy points ranging from 6.861 keV to 7.041 keV, respectively. The scan time for one data-point was 1 second. In order to observe the ionization of Sm or Eu ion, XANES spectra around  $L_{\text{III}}$  edge were also measured after



**Figure 1**

(a) Sm  $L_{\text{III}}$  XANES spectra of  $\text{Sm}^{3+}$ -doped NAB glass x-ray irradiated for various duration. The peak correspond to  $\text{Sm}^{2+}$  becomes large by x-ray irradiation. (b) The change is clearly shown by overwriting.

x-ray (6.718 keV for Sm and 6.982 keV for Eu) irradiation for 10 and 100 minutes. To reveal mechanism of 800 nm femtosecond laser induced photo-coloring,  $L_{III}$  XANES after UV (254 nm) irradiation for 30 minutes were measured in both edge.

3. Results and Discussion

After XANES measurement, x-ray irradiated parts of both  $Sm^{3+}$ -doped and  $Eu^{3+}$ -doped NAB glasses turned to orange in the same way as 800 nm femtosecond laser irradiation. As far as in appearance, x-ray irradiation effect on these glasses should be the same phenomenon as 800 nm femtosecond laser induced photo-coloring.

Samarium  $L_{III}$  XANES spectra of  $Sm^{3+}$ -doped NAB glass x-ray irradiated for various duration are shown in Fig. 1. The peaks located at 6.712 keV and 6.720 keV are assignable to  $2p \rightarrow 5d$  transition in  $Sm^{2+}$  and  $Sm^{3+}$ , respectively. (Herbst J. F. &

Wilkins J. W., 1982) The peak at 6.712 keV becomes large by x-ray irradiation. It means that some  $Sm^{3+}$  ions doped in NAB glass were converted into  $Sm^{2+}$  ions upon x-ray irradiation. Therefore photo-reduction of rare-earth ion should be the mechanism of photo-induced coloring. In Fig.1, non-irradiated sample reveals a small fraction of  $Sm^{2+}$  ion. The sample was irradiated by x-ray at least 1 minute before the peak of divalent ion (6.172 keV) had been measured. Therefore we consider that  $Sm^{2+}$  ion in non-irradiated sample was produced by x-ray irradiation during measuring pre-edge region. There is a possibility of small fraction of  $Sm^{2+}$  existing in the sample before x-ray irradiation. However we cannot decide the origin of divalent ion in the sample. Farther study, for example time-resolved XANES measurement by using position sensitive detector, will be necessary for this purpose.

Figure 2 shows Eu  $L_{III}$  XANES spectra of  $Eu^{3+}$ -doped NAB glass x-ray irradiated for various duration. The peaks located at 6.972 keV and 6.980 keV are assignable to  $2p \rightarrow 5d$

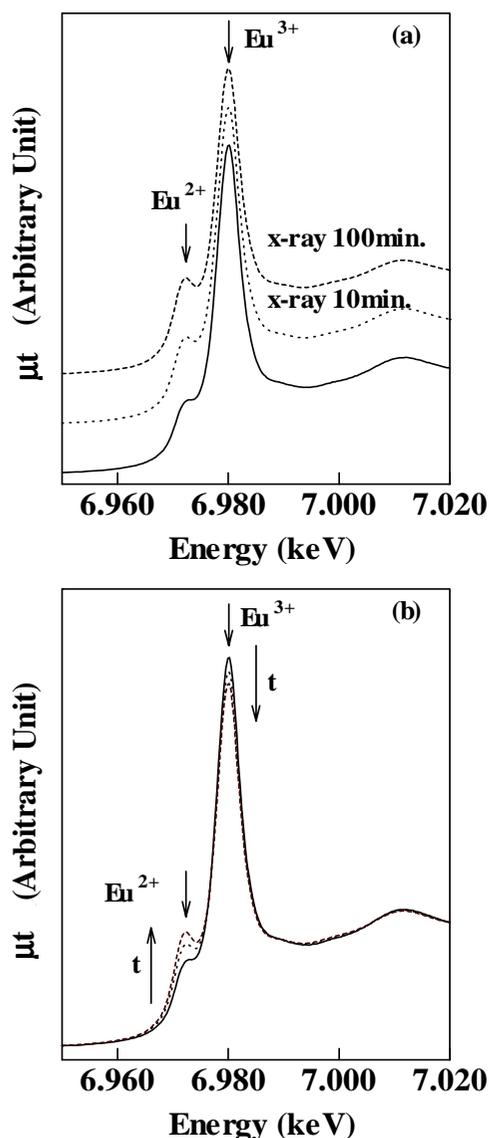


Figure 2 (a) Eu  $L_{III}$  XANES spectra of  $Eu^{3+}$ -doped NAB glass x-ray irradiated for various duration. (b) The change from  $Eu^{2+}$  to  $Eu^{3+}$  by x-ray irradiation is clearly shown by overwriting.

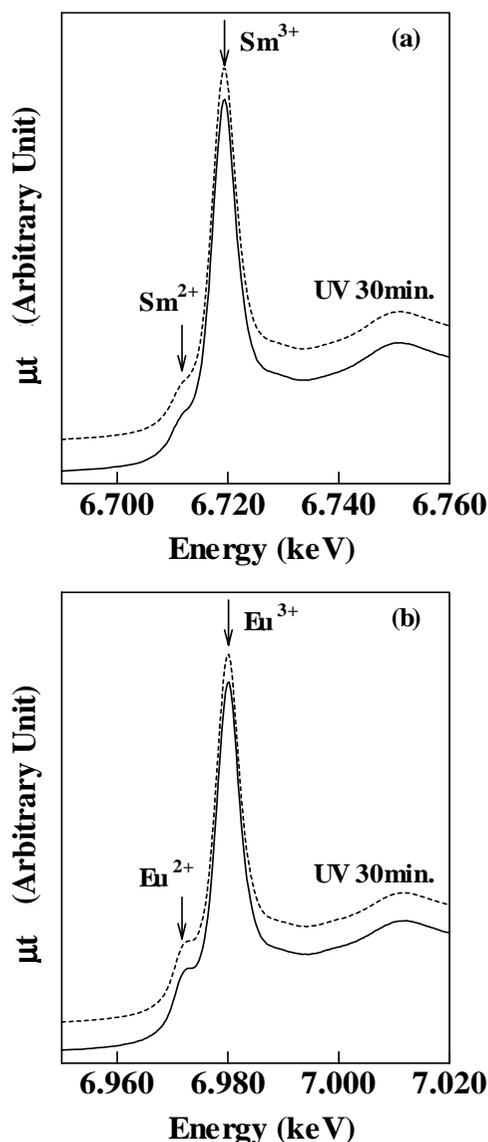


Figure 3 (a)  $Sm L_{III}$  XANES spectra of  $Sm^{3+}$ -doped NAB glass and (b)  $Eu L_{III}$  XANES spectra of  $Eu^{3+}$ -doped NAB glass before and after UV (254 nm) irradiation. No change is occurred in both edge.

transition in  $\text{Eu}^{2+}$  and  $\text{Eu}^{3+}$ , respectively. (Herbst J. F. & Wilkins J. W., 1982) Non-irradiated  $\text{Eu}^{3+}$ -doped NAB glass also reveals a small fraction of  $\text{Eu}^{2+}$  ion, and it also should be produced by x-ray irradiation during measuring pre-edge region. The change from  $\text{Eu}^{3+}$  to  $\text{Eu}^{2+}$  is also shown by x-ray irradiation in Fig.2. In the case of  $\text{Eu}^{3+}$ -doped NAB glass, x-ray induced photoreduction occurred more easily than  $\text{Sm}^{3+}$ -doped NAB glass. The change from  $\text{Sm}^{3+}$  to  $\text{Sm}^{2+}$  is stopped after 10 minutes x-ray irradiation. (Fig. 1) However the change from  $\text{Eu}^{3+}$  to  $\text{Eu}^{2+}$  is continued after 100 minutes irradiation. (Fig. 2) Moreover the fraction of trivalent ions in  $\text{Eu}^{3+}$ -doped NAB glass which turned to divalent ions by x-ray irradiation are longer than that in  $\text{Sm}^{3+}$ -doped NAB glass. These facts correspond that  $\text{Eu}^{3+}$  ion can be easily reduced than  $\text{Sm}^{3+}$  ion.

XANES spectra before and after UV irradiation in both edges are shown in Fig.3. As far as Fig.3, a fraction of divalent ions did not change during 30 minutes of UV irradiation. And samples color was not changed during UV irradiation. Therefore we suggest that no photo reduction occur in both glasses by UV (254 nm) irradiation. The energy of photon that causes photo reduction of trivalent ion may be up to UV light (254 nm). Hence 800 nm femtosecond laser induced coloring is considered to be occur in multiphoton process.

#### 4. Conclusion

Photo-induced coloring of samarium or europium ion doped in  $5\text{Na}_2\text{O}-10\text{Al}_2\text{O}_3-85\text{B}_2\text{O}_3$  glasses are studied by Sm or Eu L<sub>III</sub> XANES before and after x-ray or UV irradiation. The essential conclusions are as follows,

- (1) The origin of x-ray induced photo-coloring of these glasses is photo reduction of rare earth ion.
- (2) 800 nm femtosecond laser pulse induced coloring may be occurred in multiphoton process.

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#### References

- Cho S., Kumagai H., Yokota I., Midorikawa K. and Obara M. (1998). *Jpn J. Appl. Phys.* **37**, L737-740
- Efimov O. M., Gabel K., Garnov S. V., Glebov L. B., Grantman S., Richardson M. and Soileau M. J. (1998). *J. Opt. Soc. Am.* **B15**, 193-199.
- Herbst J. F., and Wilkins J. W.(1882). *Phys. Rev.* **B26**, 1689-1701.
- Nakano H., Nishikawa T., and Uesugi N. (1997). *Appl. Phys. Lett.* **71**, 16-18.
- Qiu J. R., Miura K., Suzuki T., Mitsuyu T. and Hirao K. (1999a). *Appl. Phys. Lett.* **74**, 10-12.
- Qiu J. R., Kojima K. Miura K., Mitsuyu T. and Hirao K. (1999b). *Opt. Lett.* **24**, 786-788.
- Shimizugawa Y., Umesaki N., Qiu J. R. and Hirao K. (1999). *J. Synchrotron Rad.* **6**, 624-626.
- Stuart B. C., Feit M. D., Rubenchik A. M., Shore B. W. and Perry M. D.(1995) *Phys. Rev. Lett.* **74**, 2248-2251.