X-ray and UV irradiation effects on Ce^{3+} ion doped in UV sensitive glass

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Introduction

Cerium, Ag-doped Li_2O-Na_2O-K_2O-SiO_2-Al_2O_3 glass is used as UV-sensitive glass for chemical etching. When UV radiation irradiated on this glass, Ag^+ ion is reduced to Ag atom. The role of Ce^{3+} ion in this glass is considered to be a sensitizer which sensitize the reduction of Ag^+ ion. The mechanism of the sensitization is considered to be oxidation of Ce^{3+} ion. However the evidence of oxidation of Ce^{3+} ion has not been known yet.

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. showed that Eu^{2+} ion doped in borate glass converted to Eu^{3+} ion due to x-ray irradiation by Eu L_{III} XANES[1] and that Eu^{3+} ion and Sm^{3+} ion doped in aluminoborate glasses are reduced to Eu^{3+} ion and Sm^{3+} ion, respectedly.[2] If UV irradiation effect on Ce^{3+} ion in the glass is photo-induced oxidation, L_{III} XANES study can reveal the mechanism of the sensitization. Therefore we studied this glass by Ce L_{III} XANES before and after x-ray or UV irradiation.

Experimental

UV sensitive glass ($17.84Li_2O$-$1.49Na_2O$-$2.52K_2O$-$75.86SiO_2$-$2.29Al_2O_3$, SA) doped with 0.1 mol% CeO_2 and 0.05 mol% Ag_2O was prepared by quenching melts in air. Plate samples were used for measurements.

Cerium L_{III} XANES spectra were measured in a fluorescence mod×e using a Si(111) double crystal monochromator at BL-9A. X-ray absorption data around the Ce L_{III} edge (5.723 keV) were collected at 301 energy points ranging from 5.643 keV to 5.793 keV before and after x-ray (5.730 keV) or UV (254 nm) irradiation for 30 minutes. Higher harmonics were removed by mirror. A mixture of nitrogen (75 %) and helium (25 %) was used in the I_0 ionization chamber and argon in the Lytle chamber. The scan time for one data-point was 1 second.

Results and Discussion

Cerium L_{III} XANES spectra of Ce, Ag-doped SA glass before and after x-ray irradiation are shown in Fig. 1. The peaks located at 5.726 keV and 5.736 keV are assignable to $2p \rightarrow 5d$ transition of Ce^{3+} ion and Ce^{4+} ion, respectively. [3] The peak at 5.736 keV becomes large by x-ray irradiation. It means that some Ce^{3+} ions doped in SA glass were converted into Ce^{4+} ions upon x-ray irradiation.

XANES spectra before and after UV irradiation in both edges are shown in Fig.2. Photo-oxidation of Ce^{3+} ion was also occurred by UV irradiation. Therefore photo-oxidation of Ce^{3+} ion should be the mechanism of mechanism of the sensitisation. In the case of UV irradiation, the change of Ce^{3+} ion to Ce^{4+} ion is much increased than that of x-ray irradiation. This fact shows that the energy of photon causing photo oxidation of trivalent ion may be close to that of UV light (254 nm = 4.88 eV).

References

[1] Y. Shimizugawa et al. J. Synchrotron Rad. 6, 624 (1999)
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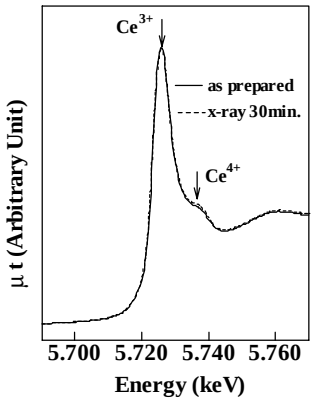

Fig.1 Ce L_{III} XANES spectra of Ce, Ag-doped SA glass before and after x-ray irradiation

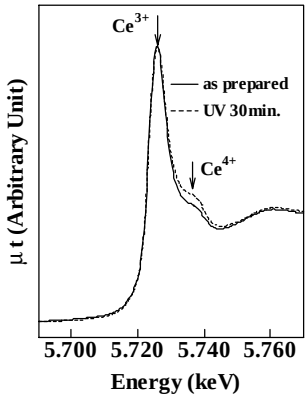

Fig.2 Ce L_{III} XANES spectra of Ce, Ag-doped SA glass before and after UV irradiation