Defect Formation by Radiation in Silver-Doped Phosphate Glasses

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Keywords: Glass, Defects, Radiation, Luminescence

ABSTRACT

Defect formation by irradiation in glass is often observed compared with that in crystal. Although interactions of glass and radiation are complicated, generated defects can work as emission centers in optically active glass. We have reviewed our recent work on Ag-doped phosphate glasses exhibiting radiophotoluminescence behavior.

1 Introduction

Glass possessing the glass transition behavior has various excellent characteristics, such as the transparency, chemical durability, thermal stability, hardness, and a wide range of chemical compositions. The notable advantage of glass materials is their ability to be mass produced, with relatively cheaper fabrication costs compared with other single crystalline substances. On the other hand, because glass lacks the long-range structural order without grain boundary, various shapes of optical materials can be prepared. However, there are many defects whose origins are the chemical composition, preparation process, and post treatment in glasses. It is reported that irradiation by ionizing particles, such as X-rays or thermal neutrons, to glass often induces the formation of defects in the matrix. The formation of defects by ionizing-particle irradiation are affected by various kinds of radiation sources.

Here, we have examined the relationship between radiation-induced defect formation and luminescence of oxide glass. Because it is expected that defects are easily generated in lower-melting glass, we focus on phosphate glasses whose optical changes after X-ray irradiation have been reported in several papers [1]. Among phosphate glasses, we have examined silver-doped phosphate glass exhibiting radiophotoluminescence (RPL) [2]. RPL is luminescence owing to electronic transitions within luminescent centers which are generated in phosphors by ionizing radiation [2-3].

Recently, we measured the valence states of Ag in phosphate glasses using both L-edge X-ray near edge structure (XANES) analyses [3]. During the measurement, we have found that Ag species was generated depending on the irradiation doses. On the other hand, it is also found that RPL behavior is observed in FD-7 glass after positron annihilation spectroscopy (PAS) [4]. Both Ag-related species were erased after heat-treatment. Considering the conventional understanding, it is assumed that the generated Ag species during XANES measurement are correlated with the RPL behavior.

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2 Experiment

The commercial FD-7 glass (Chiyoda Technol Corporation) was used for examination. On the other hand, Ag-doped aluminophosphate glasses, whose chemical composition is the identical to the FD-7glass, were prepared using a conventional melt-quenching method in a platinum crucible. The mixture of $(NH_4)_2HPO_4$, Al_2O_3, Na_2CO_3 was calcined at 800 °C for 3 h in a Pt crucible under an ambient atmosphere. After heat treatment, the calcined matrix was mixed with Ag_2O and melted in an electric furnace at 1150°C for 30 min. The glass melt was quenched on a stainless-steel plate at 200 °C and then annealed at the glass transition temperature, T_g.

The Ag L_{III}-edge (3.35 keV) XANES measurements were carried out on the BL11 beamline at SAGA Light Source (SAGA-LS, Saga, Japan). The spectra of the samples were measured in the fluorescence mode using 1-SSD at room temperature using a Si (111) double-crystal monochromator. The XANES data for Ag-foil (0.001mm), AgO, and Ag_2O were also collected in the transmission mode.

Positron irradiation was performed using a PSA Type L-Ⅱ system (Toyo Seiko Co., Ltd.) with an anti-coincident system.(11) The glass samples were directly placed on ^{22}Na isotope sealed in Kapton (<1 MBq) with a diameter of 15 mm at room temperature without a spacer.

3 Results

3.1 Examination of valence states of silver cations

The prepared Ag-doped glasses were transparent, similar to the commercial FD-7 glass. We measured optical absorption spectra, refractive index, ^{31}P magic angle spinning nuclear magnetic resonance (MAS NMR), ^{27}Al MAS NMR, and high energy X-ray diffraction (XRD) spectra to confirm the similarity between the commercial and prepared FD-7 glasses. We have found that slight differences between the commercial and prepared FD-7 glasses in the T_g, refractive index, unit fractions of PO_x and AlO_y in glass, and longitudinal elastic modulus.

However, we assume that the obtained results are enough to conclude that the prepared FD-7 glass behaves the same as the commercial glass. As shown in inset of Fig. 1, clear RPL by UV irradiation is observed at the irradiation spot. We measured Ag L_{III}-edge XANES spectra with repeat scans to check their time-dependent spectra change. Figure 1 shows the Ag L_{III}-edge XANES spectra of prepared FD-7 glasses after different irradiation doses. Three references are shown for comparison (Ag foil, Ag_2O, and AgO). The absorption band at 3.349 keV was generated in the glasses by increasing irradiation. It is notable that the peak energy of the white line shifts toward lower energy as the oxidation state increases. We have confirmed that RPL intensity increases with increasing irradiation doses. Considering the valence of reference samples, it is expected that generated Ag species correlate with Ag with higher valence state, and correlate with the RPL behavior.

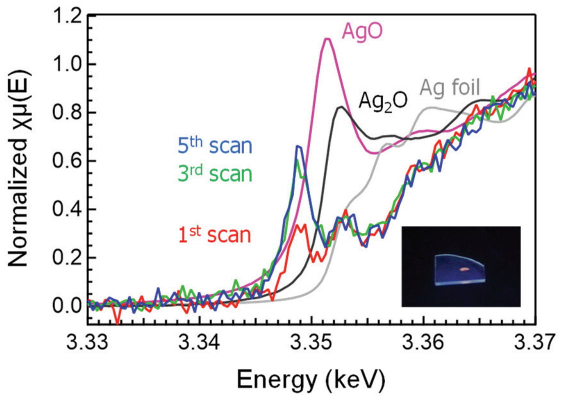

Fig. 1 Ag L_{III}-edge XANES spectra of FD-7 glass depending on the number of measurement scans. Inset shows photograph of FD-7 glass under 365 nm irradiation.

3.2 Positron-induced luminescence in FD-7 glass

PAS has been used for evaluation of cavity size in various materials. From the decay constant of *o*-positronium, the cavity diameter in an insulator can be quantified. Although this technique is considered a nondestructive measurement method, we have found positron-induced RPL in FD-7 glass. [4]. By using RPL dosimeter reader FGD-670 to monitor RPL intensity, it is found that RPL behavior is observed from the glass even after positron irradiation for several seconds.

After positron irradiation for 10 days, the irradiated part was colored, indicating that color centers were generated by the irradiation. Figure 2 shows optical absorption spectra of FD-7 glasses irradiated with positrons for 5 and 10 days and a non-irradiated sample. We have confirmed that there is a linearity between the irradiation dose (duration) and the RPL intensity.

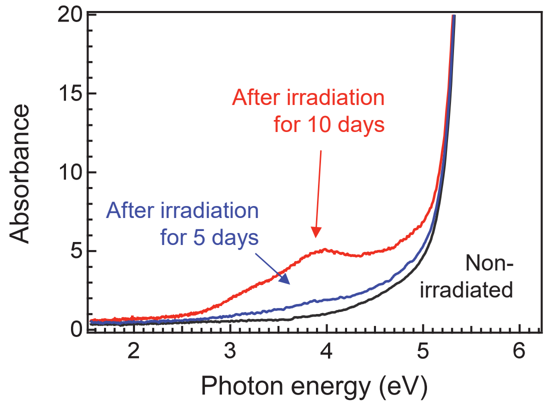

Fig. 2 Optical absorption spectra of FD-7 glasses after positron irradiation from ^{22}Na along with that of non-irradiated FD-7 glass.

4 Effect of annealing on the radiation-induced change

It is reported that radiation induced change in the Ag-doped phosphate glasses can be erased by a thermal annealing. On the other hand, not only the radiation-induced change but also the erasing by thermal annealing depends on the chemical composition, i.e., local coordination state at the vicinity of Ag cations. It is expected that structural understanding of glass will help the RPL behavior of glass.

5 Conclusions

We have found a radiation-induced coordination change of Ag cations by XANES analysis. To understand Ag cations in oxide glasses, it is important to have not only luminescence properties but also combined measurement techniques.

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