EA−07 Influence of fluorine on weatherability in sulfophosphate glass

(Nippon Electric Glass Co., Ltd) ○S. Konoshita

Weatherability of almino-sulfophosphate glass with various content of fluorine substituted for oxygen was investigated. By analyzing short range structure with Raman spectroscopy and X-ray photoelectron spectroscopy, it is suggested that fluorine is preferentially bonded to Al^{3+}, and then bonded to P^{5+} in almino-sulfophosphate glass. The weatherability of almino-sulfophosphate glass is drastically deteriorated by formation of PF bond.

e-mail: skonoshita@neg.co.jp

Introduction

Sulfophosphate glass has ionic structure, consisting of mainly Q^1 and Q^0. By the structure, sulfophosphate glass shows high chemical durability and low glass transition temperature compared to phosphate glass[1-3]. In general, the incorporation of fluorine into phosphate glass conducts depolymerization of the network by breaking phosphate chains[4] and it could cause the increase chemical durability. This work is focused on a relationship between weatherability and short-range structure of almino-sulfophosphate glass with varied fluorine content.

Experimental

Almino-sulfophosphate glasses, $18Na_2O$-xZnF-(45-x)ZnO-$1Al_2O_3$-$9SO_3$-$27P_2O_5$, x=0, 6, 8.4, 11, 17, 23 were prepared by using reagent-grade of $ZnSO_4$, ZnF, Na_2PO_4, and Na_2O. The batches were mixed and melted at 800°C for 1.5 hours in a platinum crucible in the air. The melt was casted on a glassy carbon plate, and annealed at 400℃ for 0.5 hours. 100g of transparent plate-like glass samples were obtained. Compositions of the glass were analyzed by X-ray fluorescence spectroscopy (ZSM Primus Ⅱ, Rigaku Co.Ltd.). Raman spectra and F1s Binding energy of the glass were measured by Raman spectroscopy (NFS-230HKG, JASCO Co. Ltd.) and X-ray photoelectron spectroscopy (PHI5000, ULVAC PHI, Inc.) respectively. The F1s binding energy was fitted into two peak of P-F bond and Al-F bond by using Gaussian distribution. Weathrability were tested by following procedure. The glass samples were also cut in size of 20×20×2mm and surfaces were polished. Surface state of the glass samples exposed to moisture in 90%RH, 60℃ for 720 hours were observed under microscope.

Results and discussion

Microscopic images of the glass surface after weatherability test are shown on Table 1. There are no visible change in x=0~8.4, clouded part is observed in x=11 and crystallization are observed in x=17 and 23.

Table 1. Microscopic images of glass surface after weatherability test.

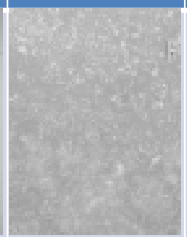
	X=0	X=6	X=8.4	X=11	X=17	X=23
60℃ 90% 720 h						

Figure 1 shows the Raman spectra of glass. The peak near 850cm^{-1} assigned to the P-F bond [4] was appeared at X=11 and the intensity increased with increasing X. Figure 2 shows F1s XPS spectra of the glass. The lower binding energy peak (~685.5eV) are assigned to F bonded to Al, and the higher binding energy peak are assigned to F bonded to P[4]. The higher peak was appeared at x=11 and increased with increasing X.

It has been reported that F is preferentially bonded to Al in almino-phosphate glass [4,5]. It is estimated that P-F bonds fraction is considered to be F-4Al fraction defined as the value subtracted 4Al from F at% when it is assumed that P-F bonds are formed after the four sites around the six-coordinated Al^{3+} with two bridging oxygen are occupied by fluorine. Figure 3 shows P-F bonds or AlF bonds fractions obtained from XPS spectra versus F-4Al. P-F bonds fraction was not observed in -1 > F-4Al (X= ~8.4) and increased with increasing F-4Al (X=11~) value. Coordination number of Al^{3+} seems to be lower than six because P-F bonds are formed from F-4Al is below 0. The weatherability of glass is thought to be deteriorated by forming P-F bonds.

Conclusions

The weatherability, Raman spectra and XPS of almino-sulfophosphate glass series, $18Na_2O$- xZnF-(45-x)ZnO- $1Al_2O_3$- $9SO_3$- $27P_2O_5$, were investigated. It has been found that weatherability of glass is related to F-4Al value. Raman and XPS spectra suggest that F is preferentially bonded to Al until six coordinated Al are fully occupied then P-F bond are formed. The formed P-F bonds deteriorate weatherability of glass.

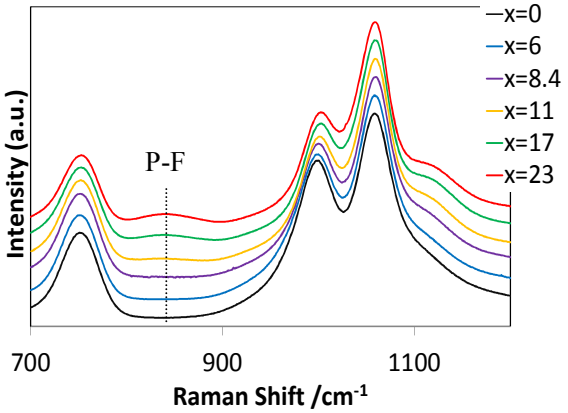


Figure 1. Raman spectra of fluoro-sulfophosphate glass.

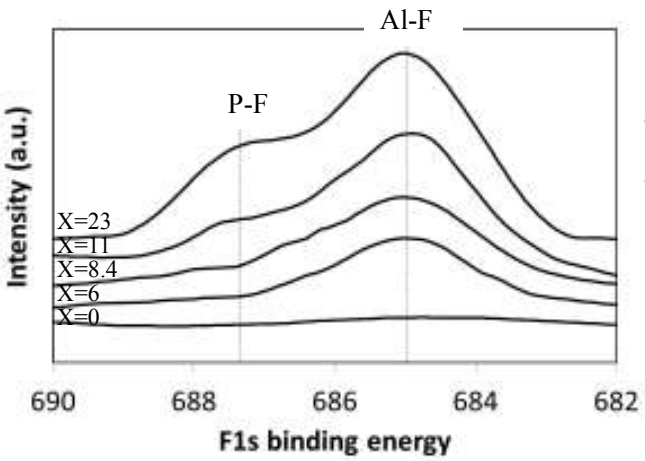


Figure 2. F1s XPS spectra of fluoro-sulfophosphate glass.

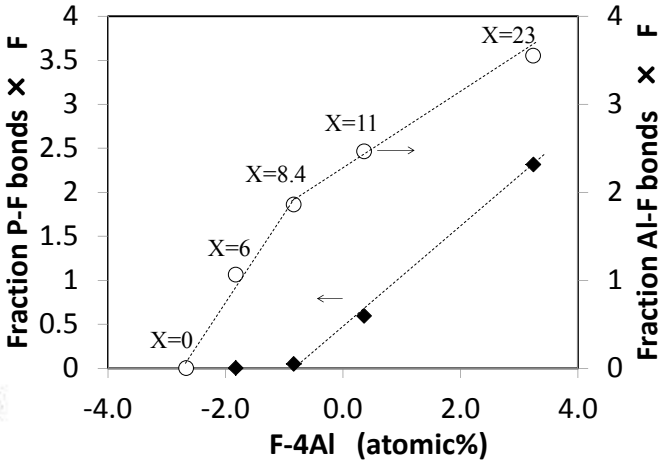


Figure 3. Quantitative fluorine bonding determined from respective F1s spectra.

Reference

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