Effects of CaF_2 Addition on the Structure of $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ Glasses

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XPS and NMR analyses were done on the $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ and $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-CaF}_2$ glasses to investigate the effect of fluoride on the glass structure. The XPS spectra showed that most of the fluoride combined with Ca and Al or existed as a free ion in the glasses. The number of F per Ca atom and the fraction of free F^- ion decreased with increasing $\text{Al}/(\text{Al}+\text{Si})$ ratio in the glasses with $\text{Ca}/\text{Al}=0.5$. The fraction of free F^- ion increased at high CaO content in the glasses containing about 45 mol% SiO_2 . The chemical shift of the fluoride-containing glasses in ^{29}Si NMR spectra was smaller than that of the non-fluoride glasses. The chemical shift of the glasses in ^{27}Al NMR spectra also showed the same tendency as in ^{29}Si NMR spectra. The addition of fluoride caused an increase in the average number of bridging oxygen atoms in the aluminosilicate glass network. However, the average number of Al around a SiO_4 tetrahedron (n) decreased in the species, $\text{Si}(\text{O-Si})_{4-n}(\text{O-Al})_n$.

Key words: XPS, NMR, Calcium aluminosilicate glass

INTRODUCTION

The powder in commercial glass-ionomer cements is aluminosilicate glasses containing fluorides and phosphates¹⁾. The liquid component of the cement is a concentrated solution of polymeric acid, for instance, polyacrylic acid or a copolymer of acrylic and itaconic acids^{1,2)}. The liquid also contains tartaric acid to improve the workability of the cement³⁾. When the powder and the liquid are mixed, the cement hardens within a few minutes in the oral environment. Fluoride addition to the glass prolongs the working time of the cement⁴⁾ and results in an anticariogenic property of the cement by fluoride release⁵⁾. Thus the fluoride plays an important role in the clinical use of the cement.

The effect of fluoride addition on the structure of silicate or aluminosilicate glasses has been investigated by many researchers^{6–9)}. Among those, fluoride behavior in the silicate glasses is classified into three ways; 1) acts as a network modifier, 2) exists as a free fluoride ion, 3) combines with modifying cation such as Ca^{2+} or Al^{3+} ions. Kumar *et al.*⁶⁾ reported that the fluoride behavior varied with the content of modifying oxide in the glass. When the content was less than 55–60 mol%, fluoride combined with a silicon atom according to the following equation,

However, with increased oxide content, fluoride existed as a free F^- ion. Yamane⁷⁾ also revealed the existence of the free F^- ion in SiO_2 -CaO- CaF_2 glasses based on X-ray photoelectron spectroscopy (XPS), concluding that the Si-F bond did not exist in the glasses. Iwamoto⁸⁾ reported that fluoride combined with an Si atom in SiO_2 -CaO- CaF_2 glasses containing less than 7 mol% of CaF_2 and combined with Ca in glasses containing more than 7 mol% of CaF_2 . On the other hand, there are only a few studies on the effects of fluoride addition on the structure of aluminosilicate glasses. Kohn⁹⁾ described in their ^{27}Al magic angle spinning nuclear magnetic resonance (MAS NMR) study that four, five and six-coordinated Al coexisted in SiO_2 - Al_2O_3 -Na₂O-NaF glasses and that five-coordinated Al existed as the AlF_5^{2-} species. It was also reported^{10,11)} that fluoride probably combined with both Ca and Si in the glass with a composition of $2\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot 2(1-x)\text{CaO} \cdot x\text{CaF}_2$. Thus, there is still controversy on the fluoride behavior in silicate or aluminosilicate glasses.

In the present study, we investigated the structure of the calcium aluminosilicate glasses and those in which a part of the CaO was substituted with CaF_2 . For this purpose, ^{29}Si and ^{27}Al MAS NMR spectroscopy and XPS for F1s were carried out with the glasses. The aim of this study was to elucidate the fluoride behavior in the glasses.

MATERIALS AND METHODS

Materials

Four series of the glass samples were prepared by melting the component oxides or fluoride in a Pt crucible. The analyzed composition of the glasses prepared are plotted on the triangle diagram in Fig. 1. Series I a glasses (L, F, S) had a composition range of 36.0–56.6 mol% SiO_2 with an equimolar ratio of Al_2O_3 and CaO. In series I b glasses, the composition was the same as series I a glasses except that a part of the CaO was replaced by CaF_2 (L': 12 mol%, F': 11.1 mol%, S': 9.8 mol%). Series II a glasses (F, X, Y) contained about 44 mol% SiO_2 with Al_2O_3 content varying between 13.7 and 28.8 mol%. In series II b glasses, a part of the CaO was replaced by CaF_2 (X': 11.4 mol%, Y: 11.0 mol%) in a similar way to series I b. The CaF_2 content of about 11 mol% was equivalent to that of 5–6.4 wt% F and was adopted according to the content of 4–9 wt% F in the commercial glass ionomer cements. With the glass containing CaF_2 , the nominal composition differed greatly from the analyzed one, because of the volatilization of fluorine as SiF_4 . Therefore the composition of the glasses containing fluoride was determined by chemical analysis. Fluoride was analyzed with a fluoride ion electrode attached to an ion meter (Ionalyzer 901, Orion Research, Cambridge, MA, USA). An equal volume of TISABII solution (Total ionic strength adjustor, Orion Research, Cambridge, MA, USA) was added to adjust the pH and to break the aluminum fluoride complexes before analysis. Al- and Ca-contents

Fig. 1 Composition of the glass samples used in this study.
 CaO-Al₂O₃-SiO₂ glasses: series I a(L, F, S); series II b(F, X, Y)
 CaO-Al₂O₃-SiO₂-CaF₂ glasses: series I b(L', F', S');
 series II b(F', X', Y')

were determined with an atomic absorption spectrometer (AA630, Shimadzu, Kyoto, Japan).

The glass prepared was ground and passed through a 75 μ m sieve. The powder sample was used for NMR measurement. For XPS analysis, a surface of the bulk glass with a size of ca. 4 $\times$ 4 $\times$ 3 mm³ was polished with fine alumina powder.

XPS of F1s

F1s XPS spectra of the glasses were obtained by an X ray photoelectron spectrometer (ESCA750, Shimadzu, Kyoto, Japan) equipped with MgK α X-ray source operating at 10 kV and 30 mA. The binding energy was corrected with a binding energy of Au4f7/2 coated on the surface of the glass sample. The surface of the glass sample was etched by an Argon ion beam for 30 min to eliminate surface contamination before XPS measurement. The XPS spectra was obtained after confirmation that the spectra were unaffected by the Ar ion beam etching.

²⁹Si and ²⁷Al MAS NMR

²⁷Al and ²⁹Si MAS NMR spectra were taken by an FT-NMR spectrometer (AM400, Bruker, Germany) equipped with a CP/MAS unit. The resonance frequencies were 104.3 MHz for ²⁷Al and 79.5 MHz for ²⁹Si. The spinning rate of the sample was 4 kHz unless otherwise noted. References for the chemical shift were AlCl₃6H₂O and tetramethylsilane, and their chemical shifts were set at 0ppm. The repetition time was 0.5s for ²⁷Al and 5s for ²⁹Si, respectively.

RESULTS AND DISCUSSION

F1s XPS spectra of the glasses containing fluoride

Figs. 2 (a) and (b) show F1s XPS spectra of the glasses in series I b (L', F' and S') and those of the glasses in series II b (F', X' and Y'), respectively. Each of the glasses showed a single broad peak around 686 eV, which changed its position depending on the glass composition. In series I b glasses, the chemical shift of the peak maxima shifted to a slightly higher energy with decreasing the SiO₂ content. In series II b glasses, the glass Y' showed a peak maximum at the lowest binding energy. The binding energy of each atom combining with an F atom is reported to be 687.8 eV (2 eV) for Si-F, 686.5 eV for Al-F and 685.3 eV (2 eV) for Ca-F⁷⁾. The figures in parentheses show the half width of the peak. The observed peaks appeared in the region of those binding energies (Fig. 2). Yamane *et al.*⁷⁾ reported that F1s spectra for CaO-SiO₂-CaF₂ glasses showed a single peak at 684.5 eV with a half width of 2eV.

Fig. 2 F1s XPS spectra of the glasses in series I b (a) and the glasses in series II b (b).

Fig. 3 A typical example of the peak separation for F1s XPS spectra of glass L'.

Fig. 4 Change in the number of F atom per Si, Al or Ca atom and fraction of free F⁻ ion with Al/(Al+Si) ratio in series Ib glasses (a) and with CaO content in series IIb glasses (b).

The chemical shift was lower by 0.8 eV than that of the F1s peak for Ca-F in a crystalline CaF₂. They concluded that the F⁻ ion existed as a free ion bonded with no other cations in the CaO-SiO₂-CaF₂ glasses. In the present study, however, the observed F1s peak had a higher binding energy (686 eV) than that for the free F⁻ ion in the CaO-SiO₂-CaF₂ glasses. Moreover, the peak widths of 2.5-3 eV were slightly too large to regard those peaks as a single peak. Thus it is suggested that fluorine atoms would bond with Si, Al or Ca atoms or exist as free ions in these glasses. To determine the fraction of each binding state, we attempted peak separation assuming that a peak for the binding state was expressed in a Gaussian form. The peak separation was carried out using a least-square method, changing the peak height and half-width of each separated peak¹²⁾. Fig. 3 shows a typical example of the peak separation for glass L'. The fraction of each bond was determined based on the peak area. To make comparison easy, the number of F atoms per each atom was calculated from the fraction obtained. Figs. 4 (a) and (b) show the change in the number of F atom per Si, Al and Ca atoms in the glasses containing fluoride with Al/(Al+Si) ratio (series Ib) and with CaO content (series IIb). The fraction of the free F⁻ ion is also plotted in Fig. 4. In series Ib glasses, it was noted that the number of F per Ca atom and the fraction of free F⁻ ion decreased with an increase in Al/(Al+Si) ratio. On the other hand, in series IIb glasses, the fraction of free F⁻ ion increased at high CaO content. The number of F per Si atom was less than 0.1 and most of the fluoride ions preferentially bond to Al or Ca ions in both series of glasses. It was reported⁷⁾ that F⁻ ion existed as a free ion in the CaO-SiO₂-CaF₂ glasses. Our result does not agree with this description, probably because the Al³⁺ ion tended to form fluoride or oxyfluoride complexes in the aluminosilicate glasses, as described later.

²⁹Si MAS NMR spectra for the glasses

Fig. 5 shows ²⁹Si MAS NMR spectra for the CaO-Al₂O₃-SiO₂ glasses (L, F, S, X, Y) and the CaO-Al₂O₃-SiO₂-CaF₂ glasses (L', F', S', X', Y'). A broad peak was observed between -70 and -120 ppm in both of the glasses. Fig. 6 shows the ²⁹Si NMR chemical

Fig. 5 ^{29}Si MAS NMR spectra for the $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ glasses (a) and the $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-CaF}_2$ glasses (b).

Fig. 6 ^{29}Si MAS NMR chemical shift of a peak maximum plotted against the $\text{Al}/(\text{Al}+\text{Si})$ ratio in series Ia and Ib glasses (a) and against CaO or $\text{CaO} + \text{CaF}_2$ content in series IIa and IIb glasses (b).

shift of a peak maximum plotted against the $\text{Al}/(\text{Al}+\text{Si})$ ratio in series Ia and Ib glasses (a) and against CaO or $\text{CaO} + \text{CaF}_2$ content in series IIa and IIb glasses (b). The glasses containing fluoride showed more negative chemical shift compared with those of glasses without fluorides. It was reported¹³⁾ that the chemical shift of a tetrahedrally-coordinated Si atom was between -60 and -130 ppm and that of six-coordinated Si atom between -190 and -215 ppm. The glasses synthesized in the present study contained only tetrahedrally-coordinated Si atoms. The structure of calcium aluminosilicate glasses is represented by a network consisting of SiO_4 tetrahedra and AlO_4 tetrahedra. Connection of both tetrahedra are defined by $\text{Q}^m(\text{nAl})$ species, $\text{Si}(\text{O-Si})_{m-n}(\text{O-Al})_n(\text{O}^-)_{4-n}$, where m is the number of bridging oxygen atoms per Si atom and n the number of Al as nearest neighbors¹²⁾. It is not known whether ^{29}Si MAS NMR spectra are altered by the coordination of F around the Si atom. However, the Si-F bond was not formed much in the glasses used in this study, as shown in the results of XPS (Figs. 4(a) and (b)). Moreover, the environment of Al next to a SiO_4 tetrahedron seemed not to greatly affect the ^{29}Si peak in its NMR spectrum. From

Table 1 $Q^m(nAl)$ distribution in the glasses calculated from ^{29}Si NMR spectra

glass	$Q^4(0Al)$	$Q^4(1Al)$	$Q^4(2Al)$	$Q^4(3Al)$	$Q^4(4Al)$	$Q^3(1Al)$	$Q^3(2Al)$	$Q^3(3Al)$	Ave.m	Ave.4n	Ave.3n
L	5.2	4.7	24.4	41.3	13.3	8.1	3.2	0.0	3.89	2.60	1.28
L'	9.1	12.0	38.1	27.8	4.7	8.3	0.0	0.0	3.92	2.08	1.00
F	0.0	0.0	4.7	26.6	31.2	31.1	6.3	0.0	3.63	3.43	1.17
F'	0.0	0.0	7.2	43.6	36.6	9.4	3.1	0.0	3.87	3.34	1.25
S	0.0	0.0	0.0	2.5	33.6	37.2	23.2	3.6	3.36	3.93	1.47
S'	0.0	0.0	0.0	29.8	30.9	39.3	0.0	0.0	3.61	3.51	1.00
X	0.0	0.0	2.6	13.2	36.7	37.8	9.7	0.0	3.53	3.65	1.20
X'	0.0	0.0	8.3	29.7	30.8	19.5	11.7	0.0	3.69	3.33	1.37
Y	0.0	0.0	0.0	0.0	38.6	48.2	13.3	0.0	3.39	4.00	1.22
Y'	0.0	0.0	0.0	12.0	29.8	42.0	16.3	0.0	3.42	3.71	1.28

Fig. 7 ^{27}Al MAS NMR spectra for the $CaO-Al_2O_3-SiO_2$ glasses (a) and the $CaO-Al_2O_3-SiO_2-CaF_2$ glasses (b). ("●" denotes spinning side bands.)

the above consideration, each $Q^m(nAl)$ species in the glasses containing fluoride can be obtained in the same way as in the oxide glasses. Thus the ^{29}Si MAS NMR peaks of the glasses containing fluoride were separated in the manner reported by our previous study¹²⁾ and the fraction of each $Q^m(nAl)$ species was determined based on the peak area of each separated peak. Table 1 shows the the distribution of $Q^m(nAl)$ species in all glasses used in the present study. Fluoride addition caused much difference in the distribution of $Q^m(nAl)$ species in the glasses. However, it seemed to be difficult to describe the change in distribution of each species by the fluoride addition. Therefore we calculated the average number of bridging oxygen (Ave.m) and the average number of Al around a SiO_4 tetrahedron in $Q^4(nAl)$ and $Q^3(nAl)$ species (Ave.4n and Ave.3n). Table 1 also shows the values of Ave.m, Ave.4n and Ave.3n and discussion of those values will be given later. .

^{27}Al MAS NMR spectra for the glasses

Fig. 7 shows ^{27}Al MAS NMR spectra for the glasses. A mark (●), denotes spinning side bands, which appears every 38 ppm away from a main peak around 60 ppm. The

chemical shift of Al depends on the coordination number around the Al atom. Six-coordinated Al shows a chemical shift between 20 and -10 ppm, five-coordinated Al between 30 and 40 ppm and tetrahedrally coordinated Al shows between 50 and 80 ppm¹³⁾. The existence of six- or five-coordinated Al in the glasses was not clear because of overlapping of those peak with the spinning side bands. Detection of five-coordinated Al was almost impossible at the low rotating speed (4 kHz) used in this study. A high rotating speed over 10kHz is needed for full detection of five-coordinated Al¹⁴⁾, that is, as the rotating speed at a magic angle increases, broadening of the NMR signal due to quadrupole interaction is depressed¹⁵⁾ and the spinning side band is kept away from the central peak. However, even at such a high speed rotation, five- or six-coordinated Al have been proven not to exist in calcium aluminosilicate glasses containing about 50 mol% SiO₂ with an equimolar ratio of CaO/Al₂O₃¹⁴⁾. Therefore most of the Al ions seemed to exist as tetrahedrally coordinated ones in the glasses (except for glass S') used in the present study. Fig. 8 shows the ²⁷Al MAS NMR spectra of glasses S and S' taken at a rotating speed of 5.8 kHz, which was the maximum limit in the apparatus used in this study. The spectrum of the glass containing CaF₂ (glass S') showed a shoulder around 30 ppm (as indicated by an arrow), suggesting that a part of Al ion is five-coordinated by the addition of fluoride.

It is yet unknown how the fluoride ion is coordinated to an Al³⁺ ion in the glasses. However, Kohn *et al.*⁹⁾ described in their ²⁷Al NMR study that five- and six-coordinated aluminum fluoride complexes existed in F-containing sodium aluminosilicate glasses. NMR signals appeared around 22 ppm with five-coordinated species AlF₅²⁻, and around -4 ppm with six-coordinated species AlF₆³⁻. Later, Tossel¹⁶⁾ reported that the five-coordinated species was expressed in the form of AlO₂F₃²⁻ rather than AlF₅²⁻.

Fig. 8 ²⁷Al MAS NMR spectra of glasses S and S' taken at a rotating speed of 5.8 kHz. ("●" denotes spinning side bands.)

Fig. 9 ^{27}Al MAS NMR chemical shift of the four-coordinated Al plotted against the $\text{Al}/(\text{Al}+\text{Si})$ ratio in series Ia and Ib glasses (a) and against CaO or $\text{CaO} + \text{CaF}_2$ content in series IIa and IIb glasses (b).

Fig. 10 The number of bridging oxygen (BO) obtained from ^{29}Si MAS NMR experiments plotted against the $\text{Al}/(\text{Al}+\text{Si})$ ratio in series Ia and Ib glasses (a) and against CaO or $\text{CaO} + \text{CaF}_2$ content in series IIa and IIb glasses (b).

Fig. 9 shows the chemical shift of the four-coordinated Al plotted against the $\text{Al}/(\text{Al}+\text{Si})$ ratio in series Ia and Ib glasses (a) and against $\text{CaO} + \text{CaF}_2$ content in series IIa and IIb glasses (b). The ^{27}Al chemical shift increased with the $\text{Al}/(\text{Al}+\text{Si})$ ratio in series Ia and Ib glasses. On the other hand, the ^{27}Al chemical shift was almost independent of the CaO content in series IIa glasses and slightly increased with $\text{CaO} + \text{CaF}_2$ content in series IIb glasses. The chemical shift was decreased by the addition of fluoride in both series of glasses and this tendency was similar to that in the ^{29}Si chemical shift.

Effect of fluoride addition on $Q^n(n\text{Al})$ distribution

Fig. 10 shows the changes in the average number of bridging oxygen with $\text{Al}/(\text{Al}+\text{Si})$ ratio in series I glasses (a) and with CaO content in series II glasses (b). The addition of fluoride to the aluminosilicate glasses tended to increase in the average number of bridging oxygen. This fact suggests that the role of Ca^{2+} as a network

Fig. 11 The number of Al around a SiO₄ tetrahedron in Q⁴(nAl) species obtained from ²⁹Si MAS NMR experiments plotted against the Al/(Al+Si) ratio in series Ia and Ib glasses (a) and against CaO or CaO + CaF₂ content in series IIa and IIb glasses (b).

modifier weakened because of bonding with fluoride. Fig. 11 shows changes in the average number of Al around a SiO₄ tetrahedron of Q⁴(nAl) species (Ave 4n) with Al/(Al+Si) ratio in series I glasses (a) and with CaO content in series II glasses (b). The value of Ave 4n tended to decrease with the addition of fluoride. A part of the aluminum was no longer a network former and would act as a network modifier or be involved in a fluoride-rich phase. This caused a decrease in the ratio of Al/Si in the glass network and resulted in the decrease of n in Q⁴(nAl) species. On the other hand, with Q³(nAl) species, the average number of Al around a SiO₄ tetrahedron (Ave 3n) did not show a systematic change with fluoride addition in series I glasses and was not affected in series II glasses (Table 1).

The composition of the fluoride-rich phase was not known and its existence has not yet been confirmed experimentally. However, the phase seemed to be a solid solution of CaO, CaF₂, Al₂O₃ and AlF₃ with any composition. It was reported that CaF₂ was crystallized from calcium aluminosilicate glasses containing fluoride¹⁰. This finding would offer an indirect evidence of the fluoride-rich phase in the glasses.

CONCLUSION

The effect of CaF₂ addition on the structure of CaO-Al₂O₃-SiO₂ glasses was investigated with XPS and NMR analyses. The XPS spectra showed that most of the fluoride combined with Ca and Al or existed as a free ion in the glasses. The number of F per Ca atom and the fraction of free F⁻ ion decreased with increasing Al/(Al+Si) ratio in the glasses with Ca/Al=0.5. The fraction of free F⁻ ion increased at high CaO content in the glasses containing about 45 mol% SiO₂. Chemical shift of the fluoride-containing glasses in ²⁹Si NMR and ²⁷Al NMR spectra was smaller than that of the non-fluoride glasses. The addition of CaF₂ caused an increase in the average number of bridging oxygen in the aluminosilicate glass network. However, the average number of Al around a SiO₄ tetrahedron (n) decreased in Q⁴(nAl) species.

REFERENCES

- 1) Kent, B. E., Lewis, B. G. and Wilson, A. D.: The properties of a glass ionomer cement, *Br Dent J* **135**(7) : 322-326, 1973.
- 2) Crisp, S., Lewis, B. G. and Wilson, A. D.: Gelation of polyacrylic acid aqueous solutions and the measurement of viscosity, *J Dent Res* **54** : 1173-1175, 1975.
- 3) Barry, T. I., Clinton, D. J. and Wilson, A. D.: The structure of a glass-ionomer cement and its relationship to the setting process, *J Dent Res* **58**(3) : 1072-1079, 1979.
- 4) Crisp, S. and Wilson, A. D.: Reaction in glass ionomer cements: I. Decomposition of the powder, *J Dent Res* **53**(6) : 1408-1413, 1974.
- 5) Wilson, A. D., Groffman, D. M. and Kuhn, A. T.: The release of fluoride and other chemical species from a glass-ionomer cement, *Biomaterials* **6** : 431-434, 1985.
- 6) Kumar, D., Ward, R. G. and Williams, D. J.: Effect of fluorides on silicate and phosphates, *Discuss Farad Soc* **32** : 147-154, 1961.
- 7) Yamane, M., Mizoguchi, K., Suginochara, Y. and Kaneko, Y.: Structural analysis for fluorosilicate glasses by X-ray photoelectron spectroscopy, *Research Report of Kyushu Institute of Technology (Engineering)* **51** : 41-48, 1985. (in Japanese)
- 8) Iwamoto, N. and Makino, Y.: A structural investigation of calcium fluorosilicate glasses, *J Non-Cryst Solids* **46** : 81-94, 1981.
- 9) Kohn, S. C., Dupree, R., Mortuza, M. G. and Henderson, C. M. B.: NMR evidence for five- and six-coordinated aluminum fluoride complexes in F-bearing aluminosilicate glasses, *Am Mineral* **76** : 309-312, 1991.
- 10) Hill, R. G., Goat, C. and Wood, D.: Thermal analysis of a $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO-CaF}_2$ glass, *J Am Ceram Soc* **75**(4) : 778-785, 1992.
- 11) Wood, D. and Hill, R.: Structure-property relationships in ionomer glasses, *Clinical Materials* **7** : 301-312, 1991.
- 12) Maeda, T., Matsuya, S. and Ohta, M.: ^{29}Si and ^{27}Al NMR and ESCA studies on $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO}$ glasses, *J Jpn Soc Dent Mater Dev* **12**(6) : 765-772, 1993. (in Japanese)
- 13) Chemical Society of Japan ed., Jikken Kagaku Kouza 4th ed. No.5 NMR, Maruzen, Tokyo, 1990 p.231 (in Japanese)
- 14) Sato, R. K., McMillan, P. F., Dennison, P. and Dupree, R.: A structural investigation of high alumina glasses in the $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ system via Raman and magic angle spinning nuclear magnetic resonance spectroscopy, *Phys Chem Glasses* **32**(4) : 149-156, 1991.
- 15) Akitt, J. W. NMR and Chemistry: An introduction to modern NMR spectroscopy, 3rd ed. Chapman & Hall, London, 1992 pp.250-255.
- 16) Tossel, J. A.: Theoretical studies of the speciation of Al in F-bearing aluminosilicate glasses, *Am Mineral* **78** : 16-22, 1993.