Chemical States of Fluorine in Fluoride and Oxyfluoride Glasses

Akiyoshi Osaka*, Yusuke Himei**,
Tokurou Nanba** and Yoshinari Miura**

X-ray photoelectron spectra (XPS) of F 1s core electrons were measured for lead fluorotellurite and ZrF₄-based ZBLA and ZBLAN fluoride glasses. The 685 eV component of a doublet F 1s peak for the fluorotellurite glasses was attributed to fluorine atoms in F-Te bonds and 683 eV one to those surrounded by lead ions. The binding energy of F 1s core level for the fluorine atoms bonded to network forming (NWF) cations could be well correlated to single bond strength of F-NWF cation bonds. The fluoride glasses, however, gave only a single peak near 685 eV though terminal (F-Zr) and bridging (Zr-F-Zr) fluorines were present. This fact was explained in terms of a charge density model as : electron clouds of fluoride ions were so hard that terminal and bridging ones would have practically the same electron density.

1. INTRODUCTION

Since the discovery of vitrification of the system ZrF₄-BaF₂-NaF by Poulain *et al.*[1] structure and properties of fluoride glasses have been studied extensively. Motivation of such investigation includes an interest to provide optical devices like fibers and laser amplifiers[2] and to account for relatively high fluoride-ion conductivity.[3] Little effort has been paid to compare them with oxide counterparts in glass formation.[4] Full understanding the properties and constitution of the fluoride glasses may be achieved by investigating the chemical state of fluoride ions and their role of glass formation and by comparing those with oxyfluoride glasses where oxygen and fluorine atoms coexist.

Several X-ray photoelectron spectroscopic studies reported different chemical states of fluorine in oxyfluoride glasses. Miura *et al.*[5] measured X-ray photoelectron spectra (XPS) of F 1s core electrons for the glasses in the system Al-Cd-O-F, and observed a singlet peak, while Wang *et al.*[6] observed a doublet peak of F 1s for lead oxyfluoroborate glasses. Similar doublet F 1s XPS peaks were reported for lead fluorosilicate[7] and fluorophosphate[8,9] glasses as well as the glasses in the system MnF₂-SiO₂.[10] A component peak with a higher binding energy (BE) of the F 1s XPS doublets has been assigned to[4] fluoride ions bonded to network forming (NWF) cations and the other with a lower BE to those surrounded by network modifying (NWM)

* 尾坂明義 : Department of Bioengineering Science, Faculty of Engineering, Okayama University,
Tsushima, Okayama-shi 700 Japan.
** 姫井祐助, 難波徳郎, 三浦嘉也 : Department of Environmental Chemistry and Materials, Faculty of
Environmental Science and Technology, Okayama University, Tsushima, Okayama-shi 700 Japan.

cations.   It seems strange, however, that Iwamoto and Makino[11] observed a singlet peak of F 1s for oxyfluorosilicate glasses containing Ca as the NWM cation instead of Pb.   It is proposed in the ZrF_4 based fluoride systems[12] that glass consists of ZrF_6 chains and two kinds of fluorine atoms are present: namely, the terminal ones bonded to a single Zr atom (F-Zr) and bridging ones bonded to adjacent two Zr atoms (Zr-F-Zr).   Nevertheless Almeida et al.[12] could observe only a singlet Auger peak in a pure fluoride glass of composition $BaF_2 \cdot 2ZrF_4$.   Thus, despite the previous studies, what controls the chemical state of fluorine in glass has not been well understood, and less is known about their role in glass formation.

In the present study, we measured XPS of the F 1s core electrons for lead fluorotellurite glasses and for some ZrF_4-based fluoride glasses.   The results will be discussed in terms of electron density on fluorine atoms and single bond strength of fluorine-metal bonds.

2. EXPERIMENTAL

Fluorotellurite glasses of compositions $xPbF_2 \cdot (20-x)PbO \cdot 80TeO_2$ (in mol% ; batch ; $x=4$, 10, 13, 20) were prepared in air through a conventional melt-quench method with a platinum crucible and an electric furnace.   Raw materials employed were reagent grade PbF_2, PbO and TeO_2.   Two ZrF_4-based pure fluoride glasses were also prepared in a glove box filled with nitrogen.   The glass compositions (in mol%) were $57ZrF_4 \cdot 34BaF_2 \cdot 5LaF_3 \cdot 4AlF_3$ (ZBLA) and $56ZrF_4 \cdot 14BaF_2 \cdot 16LaF_3 \cdot 4AlF_3 \cdot 20NaF$ (ZBLAN).   The raw materials were the component fluorides of reagent grade.   The XPS of F 1s core electrons were recorded for polished samples with a Shimadzu ESCA 750 by the use of Mg $K\alpha$ radiation as the X-ray source.   The binding energy (BE) was represented in eV unit as convention, and was standarized to C 1s (=285.0 eV).

3. RESULTS

F 1s XPS profiles were indicated in Figs. 1(a) and (b) for $10PbF_2 \cdot 10PbO \cdot 80TeO_2$ and ZBLA glasses.   An Asymmetric peak profile and relatively larger width at half height maximum (2.6 eV) were observed for the fluorotellurite glasses.   The results suggested that the measured spectrum was an envelope of two component peaks.   Thus, as illustrated in Fig. 1(a), the peak was deconvoluted into two components of Gaussian profile locating at 685.6 and 683.4 eV. Similar deconvolution was applied to the F 1s spectra of the rest of the fluorotellurite glasses. However, the spectrum profiles of ZBLA and ZBLAN glasses were sharp and symmetric, and hence no deconvolution was applicable.   Table 1 summarizes the BE for the present glasses and relevant oxyfluoride ones.[6-8]

4. DISCUSSION

O 1s XPS for condensed silicate crystals[13] and silicate glasses[14] consisted of two-component peaks : the higher BE component was attributed to bridging oxygen (BO) atoms and the lower one to non-bridging oxygen (NBO) atoms.   The difference in BE between BO and NBO was accounted for in terms of electron density on those atoms : larger electron density corresponds to smaller BE.   This electron density model has been applied to interpret doublet peaks of F 1s XPS observed for lead fluoroborate,[7] lead fluorosilicate[6] and stannous fluorophosphate[8] glasses : that is, the higher BE components were attributed to fluorine atoms bonded to an
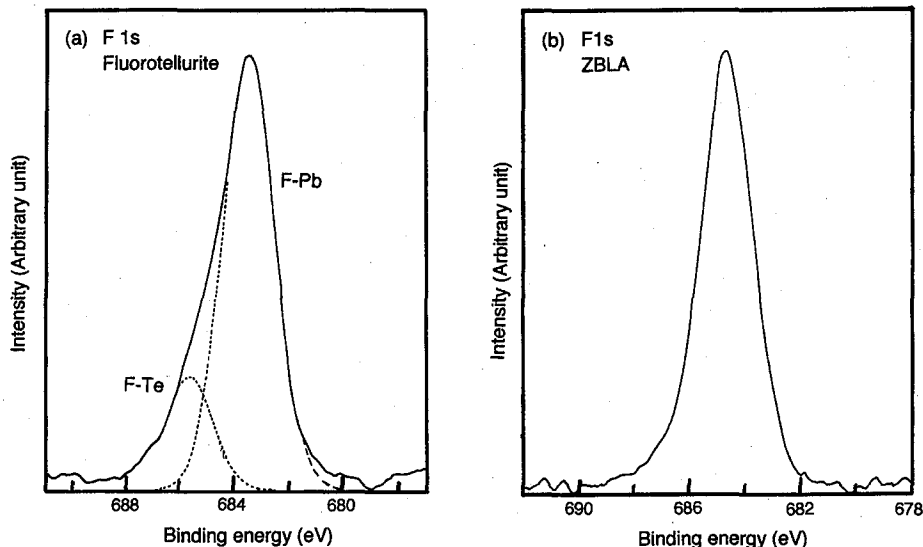
Fig. 1. X-ray photoelectron spectra of (a) a fluorotellurite glass of composition (batch, mol%) $10PbF_2 \cdot 10PbO \cdot 80TeO_2$ and (b) a ZBLA glass $57ZrF_4 \cdot 34BaF_2 \cdot 5LaF_3 \cdot 4AlF_3$.

Table 1. Binding energy of F 1s core electrons for fluoride and lead fluorotellurite glasses due to X-ray photoelectron spectroscopy. (C 1s = 285.0 eV).

Composition	Binding energy (eV)		Area fraction (%)[a]
$xPbF2 \cdot (20-x)PbO \cdot 80TeO_2$			
$x = 4$	685.4 (1.7)[b]	683.3 (2.0)	13.8
10	685.6 (2.0)	683.4 (2.2)	19.2
13	685.2 (2.0)	683.1 (1.9)	16.0
20	685.8 (2.2)	683.7 (2.4)	23.2
$57ZrF_4 \cdot 34BaF_2 \cdot 5LaF \cdot 4AlF_3$			
(ZBLA)	685.5 (2.1)		
$56ZrF_4 \cdot 14BaF_2 \cdot 16LaF_3 \cdot 4AlF_3 \cdot 20NaF$			
(ZBLAN)	685.4 (2.2)		

a) Area fraction for the 685 eV components.
b) Width at half height maxima.

NWF cation, while the lower BE ones to those surrounded by lead or stannous ions. This model can be applied to interpret the F 1s XPS for lead fluorotellurite glasses. Then the 685.5 eV and 683.4 eV components have been attributed to the fluorine atoms in F-Te and F-Pb bonds, respectively.

Bridging and non-bridging fluorine (BF and NBF) atoms are present in ZrF_4-based fluoride glasses since the glasses are considered to consist of chains of ZrF_6 octahedra[12]. Thus a doublet peak might appear in F 1s spectra if the electron density model were valid in such fluoride glasses. However, previous efforts turned out to be vain since the F 1s core level gave only a sharp and symmetric peak[12] as did in the present ZBLA and ZBLAN glasses (Fig. 1(b)).

The electron density model has been applied to several inorganic and organic molecular

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species, such as ligand compounds of Ni,[15] Sn,[16] Ge and Si,[17] and P[18] as well as simpler organic compounds.[19]   All of the series of compounds cited here gave good linear correlation between BE and atomic charge of the relevant elements though the basis of evaluating the atomic charges ranged from quantum-chemical calculation[19] to some electronegativity scales.

   Take an idea of Pauling's electronegativity[20] and estimate the order of increasing BE of the F 1s level for fluorines bonded to B, P, Si, and Te atoms.   A larger BE will be given for NWF cations with a larger value of electronegativity (c).   With Allred-Rochow electronegativity scale (χ_{Si}=1.74, χ_B=2.01, χ_{Te}=2.01, χ_P=2.06)[20] as an alternative of the Pauling's original one we can predict the increasing order of F 1s BE as: F-Si<F-B, F-Te<F-P.   This prediction contradicts the experimental results shown in Table 1: F-Te<F-P<F-B<F-Si.   Therefore, the electronegativity concept does not seem capable to explain the increasing or decreasing order of BE, though it is applicable to inorganic and organic compounds[15-19] as mentioned above.   The electronegativity was proposed first by Pauling to explain an excess bond energy of a hetero-bond A-B over a sum of relevant homo-bonds, A-A and B-B, in terms of covalent-ionic resonance.[20] It is considered the partial atomic charges that are localized on a specific pair of atoms may determine the bond energy between them.   On this basis, we consider that bond energy is a good scale for BE values.   Sun[21] introduced "single bond strength" for metal-oxygen bonds in oxide glasses.   Baldwin and Mackenzie[22] followed Sun to apply his idea for fluoride systems.   Table 2 lists the values of single bond strength of the relevant bonds together with assumed coordination numbers.   Some of the single bond strength values were updated by the use of thermochemical

Table 2.   Binding energy of F 1s and single bond strength for related F-metal bonds.

Bond	Binding energy (eV)		Single bond strength	CN[a]
Si-F	688.5	[7][b]	142.3	4
P-F	687.4	[8]	136.8	4
B-F	688.2	[6]	154.0	3
Pb-F	684.1	[7]	30.8	8
Te-F	685.5	[this work]	85.1	4
Zr-F	685.5	[this work]	84.5	6

a) Asummed coordination numbers.
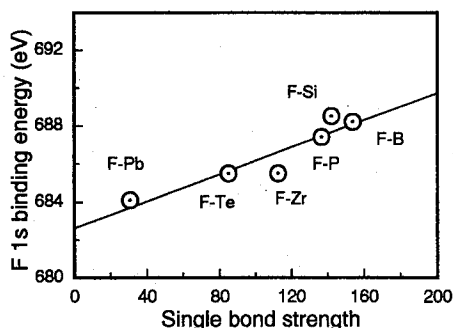b) References.

Fig. 2.   F 1s binding energy of fluorine-metal bonds plotted as a function of single bond strength.

data given by Kubachewski *et al.*.[23]   Fig. 2 represents the plot of BE of F 1s versus single bond strength.   Good linear correlation has been confirmed, and the increasing order of BE agrees well with that of the single bond strength despite one exception (F-Si and F-B, again). Incidentally, linear extrapolation to 0 in bond strength according to least-squares approximation gives 683 eV.   This value corresponds to BE of fluoride ions under no chemical interactions.   It is thus indicated that the single bond strength is a good parameter to interpret the BE of core levels.

A question may arise why a singlet XPS peak of the F 1s level, but not a doublet, is observed for fluoride glass, though bridging and non-bridging fluorine atoms may exist.   Let us evaluate ionic character of metal-fluorine bonds according to Pauling's empirical equation, eq. (1)[24]

$$\text{Amount of ionic character} = 1 - \exp\left(-\Delta\chi^2/4\right) \tag{1}$$

Employing Allred-Rochow scale for the electronegativity difference, $\Delta\chi$, we have plotted in Fig. 3 the ionic character for metal-fluorine (M-F) and metal-oxygen (M-O) bonds as a function of their single bond strength.   The filled and open symbols represent M-F and M-O bonds, respectively.   The circles are for the oxides and fluorides assigned to as a network former[21,22] while the triangles and squares are for those assigned to as an intermediate and a network modifier,[21,22] respectively.   M-O bonds can be grouped into three categories in the plot of ionic character versus single bond strength : the network formers are located in the lower-right portion of the plot and the network modifiers are near the upper-left corner.   However, M-F bonds practically have no difference in ionic character, and the plots are scattered above 75% to 90% ionic character and spread from 25 to 100 in single bond strength.   Pb-F and Pb-O are two distinctive exceptions : their plots are apart from their group because of high covalent character due to high polarizability of lead.   We have observed that BF and NBF cannot be distinguished in XPS giving only a singlet peak despite that BE of the F 1s level is well correlated to the single bond strength in Fig. 2.   On the basis of Fig. 3 this issue can be interpreted as : O-Si and O-Na bonds, involving representative NWF and NWM cations, differ greatly in both ionic character
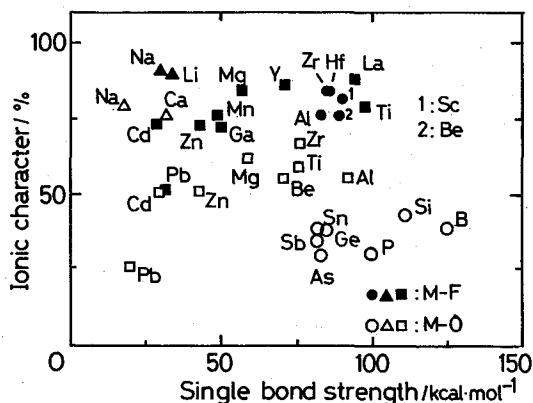

Fig. 3.   The ionic character (eq. 1) for metal-fluorine bonds (M-F, filled symbols) and metal-oxygen ones (M-O, open symbols) as a function of their single bond strength.   Circles : network formers ; triangles : intermediates ; squares : network modifiers after Sun[21] and Baldwin and Mackenzie.[22]

and single bond strength. It has been experimentally established[13,14] that BO and NBO are distinguished in XPS peaks whose profiles are deconvoluted into the components attributed to each of them. Therefore, the fact that BF and NBF cannot be distinguished in XPS of the F 1s level should be attributed to similarity in electron density of the fluorine atoms that are involved in Zr-F-Zr and Zr-F-Na bonds. Then, what causes the larger single bond strength of Zr-F. We can assign the large positive charge (4+) on zirconium ions to the origin of the large bond energy. In other words, because of a very hard electron cloud the fluoride ions may experience very little degree of polarization or their electron density are practically invariable whether they are in bridging or non-bridging positions.

5. SUMMARY

X-ray photoelectron spectra (XPS) of F 1s core electrons were measured for lead fluorotellurite glasses of compositions $xPbF_2 \cdot (20-x)PbO \cdot 80TeO_2$ (in mol% ; batch ; $x=4, 10, 13, 20$) and ZrF_4-based fluoride glasses of compositions $57ZrF_4 \cdot 34BaF_2 \cdot 5LaF_3 \cdot 4AlF_3$ (ZBLA) and $56ZrF_4 \cdot 14BaF_2 \cdot 16LaF_3 \cdot 4AlF_3 \cdot 20NaF$ (ZBLAN) (mol%) The fluorotellurite glasses showed doublet F 1s XPS peaks : the 685 eV component peak was attributed to fluorine atoms in F-Te bonds and 683 eV one to those surrounded by lead ions. The binding energy of F 1s core level for the fluorine atoms bonded to network forming (NWF) cations depended linearly on single bond strength of F-NWF cation bonds. The fluoride glasses, however, gave only a single peak near 685 eV though terminal (F-Zr) and bridging (Zr-F-Zr) fluorines were present. Amount of ionic character of the metal-oxygen and metal-fluorine bonds was plotted as a funciton of single bond strength. The metal-oxygen bonds were grouped into three categories, namely, the network formers, intermediates, and network modifiers. However, all the metal-fluorine bonds had large ionic character more than 75%, and no such grouping as in the oxide systems was possible. The fluorines in Zr-F and Zr-F-Zr bonds could not be distinguished in the F 1s XPS. This was attributed to the fact that the electron density on the fluorine on any metal-fluorine bonds was almost invariable.

REFERENCES

(1) M. Poulain et al., Mat. Res. Bull., **10**, 243–46 (1975).
(2) Y. Ohishi, Proc. 5th Meeting on Glasses for Optoelectronics (Glass and Photonics Materials Division, the Ceram. Soc. Japan), p. 37 (1994).
(3) D. Leroy et al., Mat. Res. Bull., **13**, 1125–33 (1978).
(4) C.M. Baldwin and J.D. Mackenzie, J. Am. Ceram. Soc., **62**, 537–38 (1979).
(5) Y. Miura et al., "Science and Technology of New Glasses" (Proc. Internatl. Conf. Sci. Techn. New Glasses), ed. S. Sakka and N. Soga, Tokyo, p. 370–75 (1991).
(6) Y-H. Wang et al., J. Mat. Sci. Let., **8**, 421–23 (1989).
(7) A. Osaka et al., J. Mat. Sci., **26**, 2778–82 (1991).
(8) A. Osaka et al., J. Non-Crystal. Solids, **125**, 87–92 (1990).
(9) M. Anma et al., J. Non-Crystal. Solids, **135**, 79–84 (1991).
(10) K. Hirao et al., Mat. Sci. Forum, **32–33**, 415–20 (1988).
(11) N. Iwamoto and Y. Makino, J. Non-Crystal. Solids, **46**, 81–94 (1981).
(12) R.M. Almeida et al., J. Non-Crystal. Solids, **69**, 161–65 (1984).
(13) L-I. Yin et al., Science, **173**, 633–35 (1971).
(14) B.M.J. Smets and D.M. Krol, Phys. Chem. Glasses, **25**, 113–18 (1984).
(15) L.J. Matienzo et al., Inorg. Chem., **12**, 2762–69 (1973).
(16) W.E. Swartz et al., Inorg. Chem., **11**, 2632–34 (1972).

(17) J.E. Drake *et al.*, *Inorg. Chem.*, **17**, 2333–36 (1978).

(18) S.C. Avanzino *et al.*, *Inorg. Chem.*, **14**, 1595–97 (1975).

(19) J.C. Carver *et al.*, *J. Am. Chem. Soc.*, **96**, 6851–56 (1974).

(20) J.E. Huheey, E.A. Keiter, and R.L. Keiter, "Inorganic Chemistry," 4th ed., HarperCollins College Publishers, p. 182–199 (1993).

(21) K-H. Sun, *J. Am. Ceram. Soc.*, **30**, 277–81 (1947).

(22) C.M. Baldwin and J.D. Mackenzie, *J. Am. Ceram. Soc.*, **62**, 537–38 (1979).

(23) D. Kubachewski, C.B. Alcock, and P.J. Spencer, "Materials Thermochemistry," 6th ed., Pergamon Press, Oxford, chap. 5 (1993).

(24) B.E. Douglas, D.H. McDaniel, and J.J. Alexander, "Concepts and Models of Inorganic Chemistry," 2nd ed., Wiley, New York, chap. 2.4.5 (1983).