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X-ray photoelectron spectroscopy of lead fluorosilicate glasses

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X-ray photoelectron spectra were measured of F 1s, O 1s, Pb 4f, and Si 2p core levels for lead fluorosilicate glasses of analysed compositions $x\text{PbF}_2 \cdot (69 - x)\text{PbO} \cdot (27\text{–}29)\text{SiO}_2$ ($x < 18$ mol %). The observed binding energies were discussed in terms of atomic charges and repulsion with taking the binding energy data of relevant compounds in the literature as the reference. The 688 eV component of an F 1s doublet was attributed to fluorines of $[\text{O}_{4-\alpha}\,\text{SiF}_\alpha]$ units and the 684 eV component to free fluoride ions under ionic interaction with lead ions. The fraction of the fluoride ions increased with x up to 51 %. The Si–F bonds were confirmed in the glasses with $3 < x < 18$ mol %.

1. Introduction

Fluorines can be introduced in oxide glasses as being bonded to network-forming cations or as "free" fluoride ions ("free" meaning not being bonded to network-forming cations). The free fluoride ions are more mobile and contribute to ionic conduction [1–4]. Several studies have been reported on fluorines in oxide glasses [5]. A Raman band at 940 cm^{-1} for the series of lead fluorosilicate glasses was deconvoluted into four component peaks [6]. But the presence of Si–F bonds could not be derived from the deconvolution of the Raman spectra, because an Si–F Raman band appears in the same frequency region (930–950 cm^{-1}) as the Si–O Raman bands [6–9]. X-ray photoelectron spectroscopy (XPS) could distinguish bridging oxygens from non-bridging oxygens in silicate [10–12], phosphate [13, 14] and germanate [15] glasses. XPS technique was also applied to a few series of oxyfluoride glasses. Iwamoto and Makino [16] conducted an XPS study of the glasses of compositions $x\text{CaF}_2 \cdot (1 - x)\text{CaO} \cdot \text{SiO}_2$. They proposed from a chemical shift of the F 1s peak that the Si–F bonds were formed in the glasses with < 7 mol % CaF_2. Hirao *et al.* [17] reported for the glasses in the system $\text{MnF}_2\text{–SiO}_2$ that a satellite F 1s peak with higher binding energy disappeared with increase in the atomic ratio F/O. The results can be interpreted as showing that the fluorines linked with silicons are changed to be free fluoride ions with increasing fluorine content. Kumar *et al.* [18] took the infrared (IR) spectrum of Na_2SiF_6 as a reference and assigned a 764 cm^{-1} IR peak found for fluorine-containing silicate glasses to an Si–F band (the same assignment was adopted later by Takusagawa [19]). From IR spectra of the glasses in the system $x\text{NaF} \cdot y\text{Na}_2\text{O} \cdot \text{SiO}_2$, Kumar *et al.* postulated [18] that the fluorines linked with silicons were present in a glass ($x/y = 0.54/0.85$; $\text{Na}_2\text{O} = 36$ mol %), whereas fluorines were present largely as free fluoride ions in more basic glasses ($x/y = 0.65/1.25$ and $0.73/1.5$; $\text{Na}_2\text{O} = 43$ and 46 mol %). Wang *et al.* [20] indicated for the glasses of batch composition $x\text{PbF}_2 \cdot (70 - x)\text{PbO} \cdot 30\text{B}_2\text{O}_3$ ($x < 25$ mol %) that a larger fraction of fluorines became free fluoride ions with increase in x.

Previous investigations therefore have indicated a tendency of fluorines in glass to be bonded to the network-forming cations in lower fluorine contents, whilst they are predominantly present as free fluoride ions in higher fluorine contents. However, the fraction of the fluorines which is bonded to the network-forming cations may depend on the component oxides in glass. For example, a considerable fraction of fluorines was still bonded to boron atoms in the lead borate glass of $\text{PbO} = 50$ mol % [20] whilst the Si–F IR band disappeared at $\text{Na}_2\text{O} = 43$ mol % in the sodium fluorosilicate system [19]. It is therefore worth studying the behaviour of fluorine in lead silicate glasses by the use of XPS technique.

2. Experimental details

The same glasses for conductivity and Raman spectra measurements [4] were employed in this work. Starting materials were reagent grade PbF_2, PbO, and silica. Batches for 30 g glasses of compositions $x\text{PbF}_2 \cdot (70 - x)\text{PbO} \cdot 30\text{SiO}_2$ (mol %, $x < 25$) were charged in a Pt crucible with a cover and were heated in an electric furnace at about 800 °C in air for 10–30 min. The quenched glasses were annealed for 30 min at appropriate temperatures below T_g determined by DTA traces. Analysed compositions are

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shown in Table I. Each glass is denoted hereafter by batch parameter x for simplicity.

Disc samples were polished on one side to optical flatness by the use of kerosene and fine-grain emery papers, and were rinsed in an ethanol bath for several minutes prior to XPS measurements. XPS spectra of F 1s, O 1s, Si 2p, and Pb 4f core levels were recorded with a Shimadzu ESCA-750 spectrometer with Mg K_α radiation. Drift of the electron binding energy due to a surface charging effect was calibrated by assuming C 1s = 285.0 eV. The binding energy is expressed in eV (1 eV = 96.48 kJ mol^{-1}). Experimental uncertainty of XPS binding energy was about ± 0.1–2 eV.

3. Results

3.1. XPS spectra of each element in the glasses

Fig. 1a–c show XPS spectra of O 1s, Si 2p, and Pb 4f core levels, respectively, for a glass with $x = 15$ mol %. Similar spectra have been observed for the other glasses. The spectrum of the Pb 4f consists of a $4f_{5/2}$–$4f_{7/2}$ doublet. The peaks in Fig. 1 are very sharp without any apparent shoulders on either side. Fig. 2 shows XPS spectra of F 1s core level for the present glasses. It is evident that such spectrum, except for that of $x = 5$ mol %, has a doublet with component peaks at about 688 and 684 eV and that the 684 eV component grows greatly with increase in x with respect to the 688 eV peak. Because the spectral intensity is normalized to the strongest peak, Fig. 2 indicates that the fraction of the fluorines corresponding to the 684 eV peak increases with increasing fluorine content. The 684 eV peak, however, is affected by the background noise as is indicated by the peak profiles for $x = 5$ and 10 with a background vibration and a vague maximum. For elimination of the background effect and precise determination of the binding energy, the spectra in Fig. 2 have been deconvoluted by the use of three Gaussian peaks. Deconvolution of the F 1s spectrum of a glass of $x = 15$, for example, is shown in Fig. 3. Difference between the measured profile and the Gaussian approximation is seen on both sides of the peak at 688 eV. This is also a background effect. The assignment of the peaks will be discussed in Section 4.2.

3.2. Binding energy data

The observed binding energies of the core levels of O 1s, Pb 4f, and Si 2p as well as those of the component peaks of the F 1s level have been tabulated in Table II together with their full width at half maximum (FWHM). Table III shows the binding energies of reference compounds cited from the literatures [12, 15, 16, 20–22]. In Table II the variation of the binding

TABLE I Analysed compositions of the lead fluorosilicate glasses of batch compositions $x\text{PbF}_2 \cdot (70 - x)\text{PbO} \cdot 30\text{SiO}_2$

x	Analysed composition (mol %)		
	PbF_2	PbO	SiO_2
5	3.2	68.7	28.1
10	9.0	63.7	27.3
15	12.7	58.2	29.1
20	15.6	56.0	28.4
25	17.2	54.3	28.5

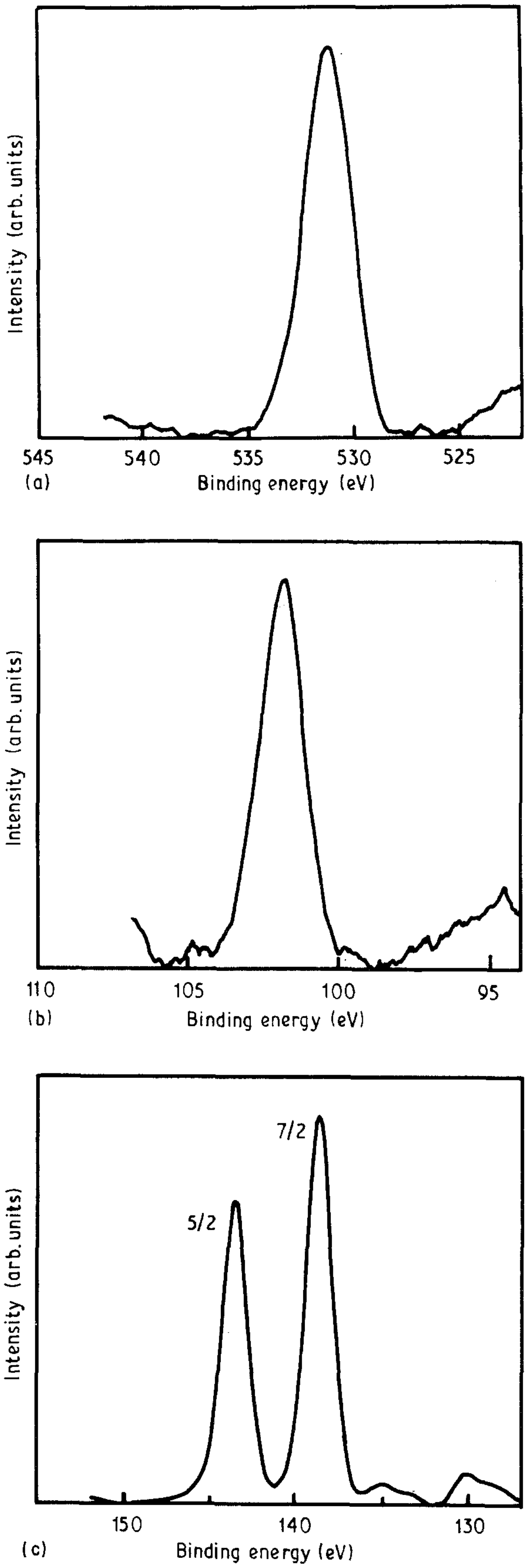

Figure 1 XPS spectra of (a) O 1s, (b) Si 2p, and (c) Pb 4f core levels for a glass of batch composition $30SiO_2 \cdot 55PbO \cdot 15PbF_2$. The binding energies were calibrated by the use of C 1s as the reference (= 285.0 eV).

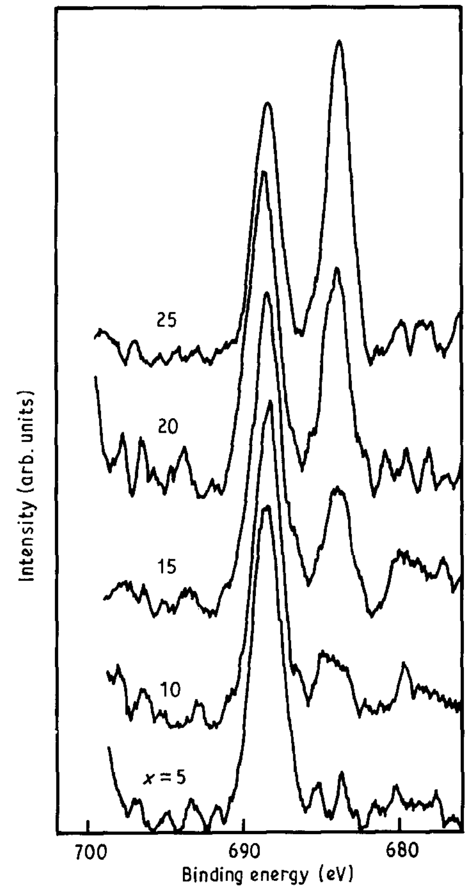

Figure 2 XPS spectra of the F 1s level for glasses of batch composition $x\mathrm{PbF_2} \cdot (70 - x)\mathrm{PbO} \cdot 30\mathrm{SiO_2}$. The binding energy was calibrated with that of the C 1s level (= 285.0 eV) as the reference.

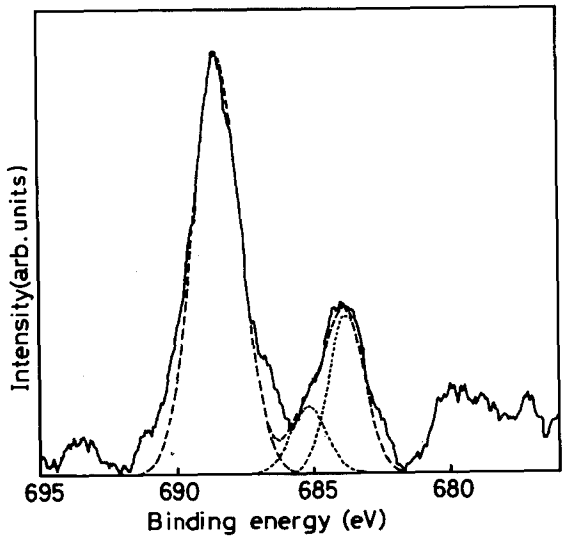

Figure 3 Deconvolution of (——) the observed F 1s profiles for a glass of batch composition $30\mathrm{SiO_2} \cdot 55\mathrm{PbO} \cdot 15\mathrm{PbF_2}$ into (– – –, - - -) three Gaussian peaks.

energy for each element is within an experimental uncertainty of ± 0.2 eV. The area ratio of Pb $4f_{7/2}$: Pb $4f_{5/2}$ is predicted to be 4:3 or 1:0.75 from a simple free-atom model. The present ratio of 1:0.78 in Table II agrees fairly well with the prediction. The Pb 4f doublet has a constant energy separation of 4.8 ± 0.1 eV for all the glasses which is much the same as that for $\mathrm{PbF_2}$ and PbO reported by Morgan and van Wazer [21]. The O 1s spectra indicate a larger FWHM than the F 1s, Pb 4f, and Si 2p spectra. The O 1s spectra were employed to evaluate the fractions of the bridging and non-bridging oxygens [10–15] where an apparent shoulder was seen on the lower binding energy side. In this study, however, deconvolution of the O 1s spectra has not been conducted, but the binding energy of the O 1s level will be employed in the discussion below.

TABLE II The binding energy (BE) data of (a) F 1s and O 1s, (b) Si 2p, and Pb $4f_{5/2}$ and $4f_{7/2}$ core levels for the glasses of batch compositions $x\mathrm{PbF_2} \cdot (70 - x)\mathrm{PbO} \cdot 30\mathrm{SiO_2}$. BE and FWHM in eV.

(a) F 1s and O 1s

x	F 1s BE (FWHM, area[a])			O 1s BE (FWHM)
5	688.4 (2.3, 100)			531.4 (2.85)
10	688.3 (1.9, 78.1)	684.9 (1.4, 11.2)	683.75 (1.5, 10.7)	531.4 (2.75)
15	688.5 (2.0, 71.3)	685.2 (1.5, 8.5)	683.8 (1.5, 20.3)	531.2 (2.70)
20	688.7 (2.1, 60.8)	685.0 (1.4, 11.7)	683.8 (1.5, 27.4)	531.4 (2.95)
25	688.5 (1.9, 46.0)	685.2 (1.6, 9.5)	683.8 (1.5, 44.5)	531.3 (2.95)

[a] Area in %

(b) Si 2p and Pb 4f

x	Pb $4f_{5/2}$ BE (FWHM, area[a])	Pb $4f_{7/2}$ BE (FWHM)	Δ[b]	Si 2p BE (FWHM)
5	143.4 (1.7, 0.77)	138.6 (1.7)	4.8	101.8 (1.95)
10	143.4 (1.7, 0.78)	138.6 (1.7)	4.8	101.7 (2.0)
15	143.5 (1.7, 0.76)	138.7 (1.7)	4.8	101.8 (1.70)
20	143.7 (1.8, 0.79)	138.9 (1.8)	4.9	102.0 (2.0)
25	143.6 (1.5, 0.79)	138.7 (1.55)	4.9	101.7 (1.90)

[a] Normalized to the $4f_{7/2}$ peak area.

[b] BE($4f_{5/2}$)–BE($4f_{7/2}$) separation.

4. Discussion

4.1. Bonding states of Si

Bond distance, coordination number, adjacent atoms or bond energy [20] are predominant factors in controlling charges of atoms in an atomic unit, on which the XPS binding energy of the atoms is dependent. This is the reason for the past attempts to quantitatively evaluate the charges of the relevant elements [16, 22]. For qualitative discussion, however, a simple scheme may be useful as a first-order approximation in which we assume an inductive effect of cations and anions, and take residual charges on atomic units into consideration. Because fluorine has the greatest electron withdrawing ability, the positive charge on Si of silicon tetrahalides supposedly increases in the order $\mathrm{SiBr_4} < \mathrm{SiCl_4} < \mathrm{SiF_4}$. This is the exact order of increase in the Si 2p binding energy [22]. Thus the fact that, as shown in Table III, the $[\mathrm{SiF_6}]^{2-}$ units have

TABLE III Reference XPS binding energy (BE) data of the elements in relevant compounds. BE (FWHM) in eV

	F 1s	O 1s	Pb $4f_{5/2}$	Pb $4f_{7/2}$	Si 2p
Mg_2SiO_4 [12]		530.9			
SiO_2		532.4 [12][a] (2.0)			103.9 [21][b] 103.5 [15][b]
PbO_2 [21]			142.6	137.8	
Pb_3O_4 [21]			142.9	138.2	
PbO		529.4 [12]	143.5 [21]	138.6 [21]	
PbF_2	684.1 [20] (2.2)		144.0 [21]	139.1 [21]	
CaF_2 [16]	684.2				
AlF_3 [20]	686.9 (3.1)				
$CaSiF_6$ [16]	684.4 (3.1[c])				104.9 (3.2[c])
K_2SiF_6 [21]					104.8
SiF_4 [22]	694.56				111.79

[a] No difference was observed between silica glass, quartz and cristobalite.

[b] Being vitreous or crystalline was not specified.

[c] Read by the present authors from the reported spectra [15].

larger Si 2p binding energies than SiO_2, is attributed to the larger positive charge on Si of the hexafluoride units. A greater difference (about 7 eV) in the Si 2p binding energy between SiF_4 and the $[SiF_6]^{2-}$ units is explained by the effect of the formal negative charge of -2 which reduces the positive charge on the Si of the hexafluorosilicate units.

On the basis of above discussion, the fact that the present glasses have very low Si 2p binding energies of about 102 eV can be interpreted as indicating the presence of a smaller positive charge on the Si. It is hence suggested that the Si atoms are surrounded by the most basic oxygens. This is supported by the fact that the O 1s binding energy for the present glasses, about 531 eV, is as small as that for Mg_2SiO_4 (Table III) or other orthosilicates (531–532 eV [12]). When the inverted compositions for the present glasses are taken into consideration, too, it is concluded that the Si atoms are in the form of orthosilicate anions. Moreover, the presence of Si–F bonds, as discussed below, indicates the formation of $[SiO_{4-\alpha} F_\alpha]$ tetrahedra in the glasses of such low silica contents (< 30 mol %) and high PbO contents (up to about 64 mol %) although the Si–F bonds have been postulated in high-silica glasses [5]. It should be noted here that not all of the Si atoms in those glasses are in discrete orthosilicate anions, but a few of them are in polymerized silicate anions such as a pyrosilicate anion [6, 23].

4.2. Bonding states of F

Fluorines are incorporated in oxide glasses by being bonded to network-forming cations and as free fluoride ions under ionic interaction with modifying cations. The observation of a doublet for the F 1s core level in Figs 2 and 3 strongly supports such a model. It is evident in Table III that simple oxides or fluorides of the cations of higher valence give higher core level binding energies. The high binding energy component of the F 1s doublet for the present glasses can thus be ascribed to the fluorines of Si–F bonds, and the low binding energy component to the free fluoride ions. A similar assignment of an F 1s doublet in fluoroborate glasses has already been proposed [20]. In Fig. 3, however, we have observed the third component around 685 eV in the F 1s spectrum which is considered to be a background effect in the previous section.

One can propose three probable bonding states of fluorines, each of which might correspond to each component peak. They are (a) Si–F–Pb, (b) Pb–F–Pb, and (c) Si–F–Si. Among the three fluorines above, fluorine (c) has the least negative charge and the greatest rests on fluorine (b). Thus it is confirmed the 683.8 eV component of the F 1s doublet is assigned to fluorine (b). And the 685 and 688 eV components might correspond to either of fluorines (a) and (c).

The presence of bridging fluorines, Zr–F–Zr, is assumed to explain the vitrification of heavy metal fluoride systems. It is favoured by a long Zr–F distance (about 0.21 nm [24, 25]) and larger coordination number of Zr (CN = 7–8 [24, 25]). These factors reduce the charge density in a Zr–F coordination sphere, as shown below. It can be assumed that the formal charge -2 of a ZrF_6 unit is distributed in a sphere of radius 0.32 nm which is evaluated by taking a sum of the radius of Zr^{4+} ions ($r(Zr^{4+}) = 0.086$ nm for CN = 6) and the diameter of a fluoride ion (0.229 nm derived from $r(F^-) = 0.1145$ nm for CN = 2). The ionic radius data are adopted from Shannon [25]. In the present silicate glasses most of the silicons are in $[SiO_4]^{4-}$ units, as discussed above. The formal charges of -4 are then considered to be distributed in the spherical space of radius 0.28 nm where $r(Si^{4+}) = 0.04$ nm (CN = 4) and $r(O^{2-}) = 0.121$ nm (CN = 2) [26] are employed for evaluation. The assumed charge density values are -15.3 and $-42.6\ nm^{-3}$ for the ZrF_6 and SiO_4 units, respectively. Suppose that two $[(^-O\text{-})_3Si]$ units are combined by an Si–F–Si bond after introduction of fluorines yielding assumed silicate groups $[O_3Si\text{–}F\text{–}SiO_3]^{6-}$. A much stronger repulsion will be expected than the repulsion for the combination of two $[F_5Zr]$ units by a Zr–F–Zr bond. The reason is that larger negative charges of higher density are faced together via the shorter distance of the Si–F–Si bond. The repulsion in the assumed silicate group is even higher than in a pyrosilicate anion, $[Si_2O_7]^{6-}$, hence the group involving an Si–F–Si bond will be unstable. The possibility that six-coordinated silicons are bonded together through an Si–F–Si bond is very scarce because such bonding induces far greater repulsion due to large formal charges on $[O_{6-\alpha}\ SiF_\alpha]$ units. Formation of the $[SiF_6]^{2-}$ units can be denied in the present glasses from the absence of a Raman peak at about 750 cm^{-1} found for hexafluorosilicates [27]. Thus the Si–F–Si bond bridging two six-coordinated silicate units is ruled out of the discussion.

On this basis we have assigned the F 1s peaks at about 688 and 684 eV to fluorines (a) and (b), respectively. From the peak area data in Table II the fractions of fluorines (a) ranges from 100%–51%.

5. Conclusions

X-ray photoelectron spectra were measured of F 1s, O 1s, Pb 4f, and Si 2p core levels for lead fluorosilicate glasses of analysed compositions $x\text{PbF}_2\cdot(69-x)\text{PbO}\cdot(27\text{–}29)\text{SiO}_2$ ($x < 18$ mol %). The component peaks of an F 1s doublet were observed for the glasses at about 688 and 684 eV. Contribution of background noise to the 684 eV peak was eliminated by deconvolution. The observed binding energies were varied within experimental error: O 1s at 531.3 ± 0.1 eV, F 1s at 688.5 ± 0.2 and 683.8 eV, Pb $4f_{5/2}$ at 143.5 ± 02 eV and $4f_{7/2}$ at 138.7 ± 0.2 eV, and Si 2p at 101.8 ± 0.2 eV. They were compared with the values reported for the reference compounds and discussed in terms of atomic charges and repulsion between the structure units. The Si atoms were tetrahedrally coordinated by oxygens and fluorine. The 688 eV component of the F 1s doublet was attributed to the fluorines of $[O_{4-\alpha}\ SiF_\alpha]$ units and the 684 eV component to the free fluoride ions under ionic interaction with lead ions. The fraction of the fluoride ions increased with x up to 49% (at $x = 17.2$ mol %). The Si–F bonds were confirmed in all the glasses with $3 < x < 18$ mol %.

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References

1. P. C. SCHULTZ and I. MOZZONI, *J. Amer. Ceram. Soc.* **56** (1973) 65.
2. J. E. SHELBY, *ibid.* **68** (1985) 551.
3. H. G. K. SUNDER, S. W. MARTIN and C. A. ANGELL, *Solid State Ionics* **18–19** (1986) 437.
4. Y.-H. WANG, M. KOBAYASHI, A. OSAKA, Y. MIURA and K. TAKAHASHI, *J. Amer. Ceram. Soc.* **71** (1988) 864.
5. E. M. RABINOVICH, *Phys. Chem. Glasses* **24** (1983) 54.
6. A. OSAKA, Y.-H. WANG, M. KOBAYASHI, Y. MIURA and K. TAKAHASHI, *J. Non-Cryst. Solids* **105** (1988) 63.
7. P. DUMAS, J. CORSET, W. CARALHO, Y. LEVY and Y. NEUMAN, *ibid.* **47** (1982) 239.
8. K. NOGUCHI, Y. MURAKAMI, N. UESUGE and K. ISHIHARA, *Appl. Phys. Lett.* **44** (1984) 491.
9. H. IMAI, K. ARAI, Y. FUJINO, Y. ISHII and H. NAMIKAWA, *Phys. Chem. Glasses* **29** (1988) 54.
10. L-I. YIN, S. GHOSE and I. ADLER, *Science* **173** (1971) 633.
11. R. BRUECKNER, H-U. CHUN and H. GORETZKI, *Glastechn. Ber.* **51** (1978) 1.
12. Y. KANEKO and Y. SUGINOHARA, *J. Jpn Inst. Metals* **41** (1977) 375.
13. R. GRESCH, W. MULLER-WARMUTH and H. DUTZ, *J. Non-Cryst. Solids* **34** (1979) 127.
14. Y. KANEKO and Y. SUGINOHARA, *Yogyo-Kyokai-Shi* (*J. Ceram. Soc. Jpn*) **89** (1981) 440.
15. Y. KANEKO, *ibid.* **87** (1979) 248.
16. N. IWAMOTO and Y. MAKINO, *J. Non-Cryst. Solids* **46** (1981) 81.
17. K. HIRAO, A. TSUJIMURA, S. TANABE and N. SOGA, *Mater. Sci. Forum* **32–33** (1988) 415.
18. D. KUMAR, R. F. WARD and D. J. WILLIAMS, *Trans. Faraday Soc.* **61** (1965) 1850.
19. N. TAKUSAGAWA, *J. Non-Cryst. Solids* **42** (1980) 35.
20. Y-H. WANG, A. OSAKA, Y. MIURA and T. TSUGARU, *J. Mater. Sci. Lett.* **8** (1988) 421.
21. W. E. MORGAN and J. R. VAN WAZER, *J. Phys. Chem.* **77** (1973) 964.
22. W. L. JOLLY and W. B. PERRY, *Inorg. Chem.* **13** (1974) 2688.
23. R. J. KIRKPATRICK, T. DUNN, S. SCHRAMM, K. A. SMITH, R. OESTRIKE and G. TURNER, in "Structure and Bonding in Non-Crystalline Solids", edited by G. E. Walrafen and A. G. Roves (Plenum, New York, 1983) pp. 303–27.
24. R. M. ALMEIDA, *Mater. Sci. Forum* **6** (1985) 427.
25. J. LUCAS, D. LOUER and C. A. ANGELL, *ibid.* **6** (1985) 449.
26. R. D. SHANNON, *Acta Crystallogr.* **A32** (1976) 751.
27. R. A. NYQUIST and R. O. KAGEL, in "Infrared Spectra of Inorganic Compounds" (Academic, New York, 1971) Chart no. 653-664.

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