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Cation coordination in oxychloride glasses

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Abstract

Glasses containing mixtures of cations and anions of nominal compositions $[\text{Sb}_2\text{O}_3]_x-[\text{ZnCl}_2]_{1-x}$ where $x = 0.25, 0.50, 0.75$, and 1.00 , have been studied by means of neutron diffraction and Raman and Mössbauer spectroscopy. There is preferential bonding within the system with the absence of Sb–Cl bonds. Antimony is found to be threefold coordinated to oxygen, and zinc fourfold coordinated. The main contributing species are of the form $[\text{Sb}(\text{OSb})_2(\text{OZn})]$ and $[\text{Zn}(\text{ClZn})_2(\text{OSb})_2]$.

1. Introduction

The majority of glasses which have been studied and exploited have contained combinations of cations ranging from the very simple (one cation) to the highly complex (commercial glasses often contain as many as ten different cations). Very rarely have glasses with a mixture of anions been subject to any structural investigation. Such glasses have become increasingly significant in a variety of technical areas. Oxynitrides are of importance as the residual glass phase in engineering ceramics and mixed chalcogenide glasses and oxyhalide glasses are of relevance to optical applications. The structures of oxychloride glasses have previously been investigated as part of the search for glasses with good IR transmission at selected wavelengths and with potential as low-phonon-energy hosts for lasing ions [1, 2]. They were prepared from combinations of Sb_2O_3 , PbCl_2 and ZnCl_2 and melted in alumina crucibles under normal atmospheric pressure. Retention of chlorine in the glass is very variable under these conditions, being lost by oxidation and probably assisted by hydrolysis.

An understanding of the properties of such glasses requires knowledge of the interconnectivity of the different cations and anions. In particular, it is important to know whether the anions are simply statistically distributed amongst the coordination spheres of the cations or whether there is segregation to produce specific $[\text{MX}_n]$ polyhedra.

The particular glasses studied here are formed from Sb_2O_3 , SbCl_3 , and ZnCl_2 in binary combinations. Of the components, Sb_2O_3 and ZnCl_2 are known to be glass formers though

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Table 1. Densities and nominal ('Nom') and analysed ('An') compositions (at.%) for the glasses studied (estimated accuracy $\pm 5\%$ of value, repeated measurements agreed to within this value).

Sample	Density (g cm ⁻³)	Sb		Zn		O		Cl	
		Nom	An	Nom	An	Nom	An	Nom	An
1.0Sb	5.05	33.3	40.6	—	—	33.3	59.4	33.3	0.0
0.75Sb	4.76	33.3	36.2	5.5	5.6	50.0	53.6	11.0	4.6
0.50Sb	4.60	25.0	27.9	12.5	12.9	37.5	48.8	25.0	10.4
0.25Sb	3.92	14.3	15.7	21.4	22.1	21.4	34.0	42.9	28.1

Sb₂O₃ is usually difficult to make as a single-component glass by conventional melt quenching and requires the addition of a second component, e.g. B₂O₃ [3]. The structure of Sb₂O₃ has been determined by Hasegawa *et al* [3] using conventional x-ray diffraction. Their data gave the Sb–O interatomic distance, $R_{\text{Sb-O}}$, as 1.99 Å, and the Sb–O coordination, $C_{\text{Sb-O}}$, as 3.15. The Sb–Sb distance, $R_{\text{Sb-Sb}}$, was observed to be 3.6 Å and they deduced an O–Sb–O bond angle of $\sim 92^\circ$ by assuming an O–O distance of 2.8 Å. They compared their values with those for the crystalline polymorphs of Sb₂O₃ and concluded that the glass was closest in structure to valentinite [4, 5], where [SbO₃] pyramids are linked to form a double-chain structure in which four polyhedra are linked to form rings. In more recent work, Masuda *et al* [6] failed to produce a single-component Sb₂O₃ glass and their x-ray fluorescence measurements indicated that both Sb³⁺ and Sb⁵⁺ were present in binary antimonate glasses. The structure of ZnCl₂ glass has been investigated using neutron diffraction [7] and interpreted as a 'distorted random close-packed array of Cl⁻ ions with Zn²⁺ ions occupying tetrahedral holes in such a way as to maximize corner sharing of the resulting [ZnCl₄]²⁻ tetrahedra. The interatomic distances observed were 2.288 Å for Zn–Cl with a Zn coordination of 3.8, and 3.72 Å for both Cl–Cl and Zn–Zn. The Zn–Zn coordination was fixed at 4, giving a Cl–Cl coordination of 9.5. Their anhydrous sample devitrified to δ -ZnCl₂ [7].

In a glass, coordination polyhedra may differ from those in the starting components, particularly if there is a redistribution of anions, and other nearest neighbours must be considered. The structural role of SbCl₃ in glass has not been described in any detail, but the crystal structures would suggest the likely formation of [SbCl₃] pyramids. ZnO is regarded as a modifier oxide, forming [ZnO₄] tetrahedra.

2. Experimental results

2.1. Glass preparation

Glasses of the nominal compositions given in table 1 were prepared from the appropriate combinations of Sb₂O₃, SbCl₃, and ZnCl₂. All the starting materials were initially anhydrous but are likely to adsorb some H₂O during weighing and mixing. The mixed powders were heated to 1000–1200 °C in an alumina crucible, with a lid, held at temperature for 2 h and then quenched between two cooled copper plates to form sheets of glass ~ 2 mm thick. X-ray diffraction was used to check the amorphicity of the glasses. Density was determined using an autopycnometer. Since the glasses were known to lose chlorine during melting, their compositions were determined by wet chemical analysis by the Analytical Chemistry group at Argonne National Laboratory. The chlorine content was obtained by difference but in this analysis there was no calculable chlorine in the nominal 0.5Sb₂O₃ and 0.5SbCl₃ to make v-Sb₂O₃, which turned out to be a convenient base glass for these measurements. There was no detectable contamination from the alumina crucible.

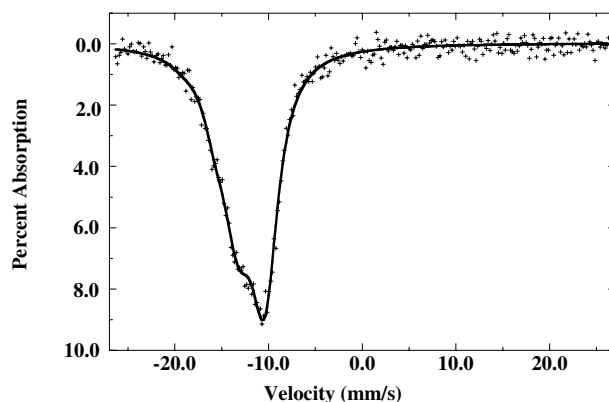


Figure 1. The ^{121}Sb Mössbauer spectrum of the 0.50Sb glass at 77 K. The zero of the velocity scale is relative to the centre of an iron spectrum.

2.2. Mössbauer spectroscopy

Mössbauer spectra were taken using a constant-acceleration velocity drive with a source of $^{121}\text{Sn}^{\text{m}}$ (the parent for ^{121}Sb) in a matrix of CaSnO_3 . The source was at room temperature and the samples were held at 77 K.

Calibrations were made with a ^{57}Co source and an iron foil absorber at room temperature. The velocities displayed in figure 1 can be related to the more conventional InSb standard by adding 8.6 mm s^{-1} to the displayed value. The spectra were fitted with a program incorporating the known nuclear parameters of the $7/2^+ - 5/2^+$ transition in ^{121}Sb , which calculates the relative line positions and also relative line intensities for a powder sample.

2.3. Raman spectroscopy

Raman spectra were excited with $\sim 50 \text{ mW}$ of 476 nm radiation from a Kr-ion laser. The incident beam impinged on the sample at an angle close to 45° from the normal. Scattered light was collected along the surface normal with an $f/1.4$ lens. The scattered light was analysed with a triple Jobin-Yvon grating spectrometer and detected with a CCD detector from Princeton Instruments.

2.4. Neutron diffraction

Neutron diffraction measurements were carried out using the glass, liquids and amorphous materials diffractometer (GLAD) at the intense pulsed neutron source (IPNS) at Argonne National Laboratory. The crushed glasses were loaded into thin-walled vanadium tubes. Time-of-flight diffraction data were collected in groups of detectors at scattering angles ranging from 4° to 117° using momentum transfers (Q) from 0.3 up to 30 \AA^{-1} . The counts were corrected for background as previously described [8] to yield the neutron-weighted average structure factor $S(Q)$.

Total real-space correlation functions, $T(r)$, were evaluated by Fourier transformation:

$$T(r) = 4\pi\rho_0r + \frac{2}{\pi} \int_{Q_{\min}}^{Q_{\max}} [S(Q) - 1] \sin Qr Q dQ$$

where ρ_0 is the total number density. A Lorch modification function was used to reduce termination effects associated with the cut-off at Q_{\max} , which in this case was 30 \AA^{-1} .

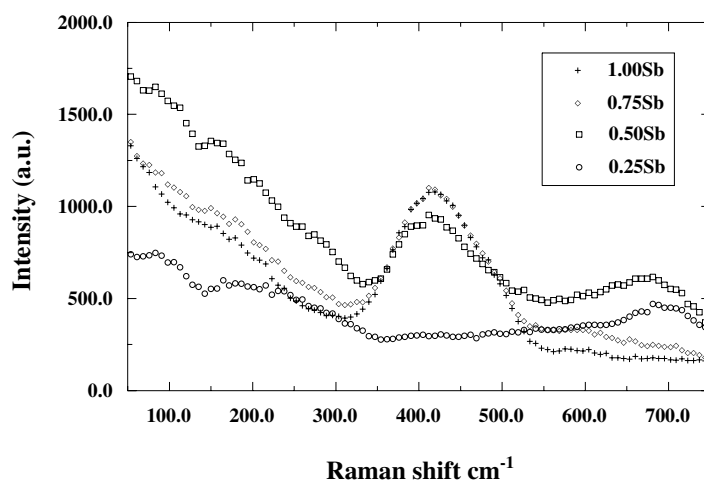


Figure 2. Raman spectra for oxychloride glasses containing nominally 0.25, 0.50, 0.75, and 1.00 mol fraction of Sb_2O_3 .

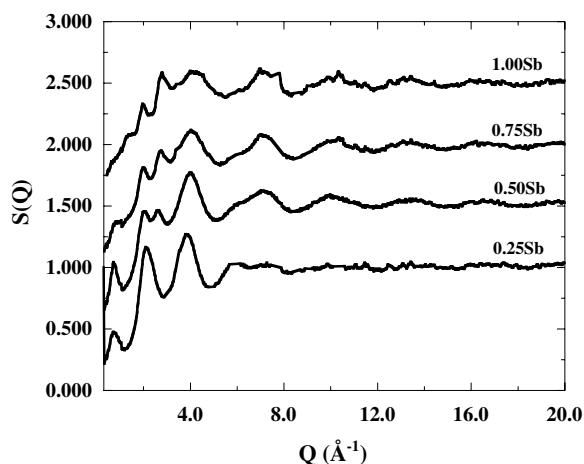


Figure 3. Structure factors $S(Q)$ for oxychloride glasses containing nominally 0.25, 0.50, 0.75, and 1.00 mol fraction of Sb_2O_3 . Successive curves are displaced vertically by 0.5 for clarity.

3. Results

Table 1 gives the densities and the nominal and analysed compositions of the glasses examined. The compositions are given in atomic % in order to allow comparison of the losses occurring during melting. X-ray diffraction confirmed the glassy nature of the samples.

A typical ^{121}Sb Mössbauer spectrum from these glasses is shown in figure 1. The fit shows that the spectrum can be fitted with a single component, though typical linewidths are $\sim 25\%$ greater than the source linewidth of 2.5 mm s^{-1} , as would be expected for an amorphous solid.

Raman spectra are shown in figure 2. There is a significant change in the spectrum containing 0.25Sb; the dominant peak completely disappears.

Figure 3 shows the neutron diffraction structure factor, $S(Q)$, the spectra are displaced by 0.5 for clarity. The 0.25Sb sample, which contained the most chlorine, had to undergo

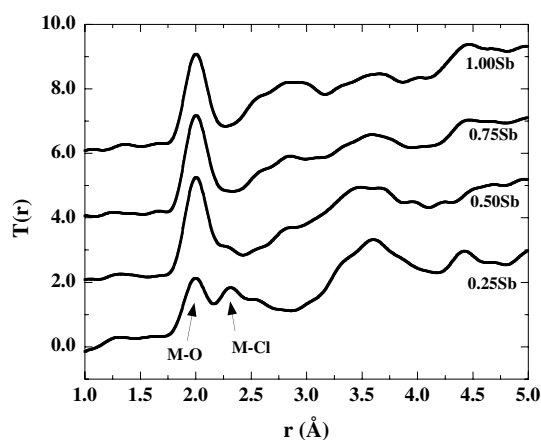


Figure 4. Correlation functions, $T(r)$, for the alkali oxychloride glasses of figure 3. Successive curves are displaced vertically by 2.0 for clarity.

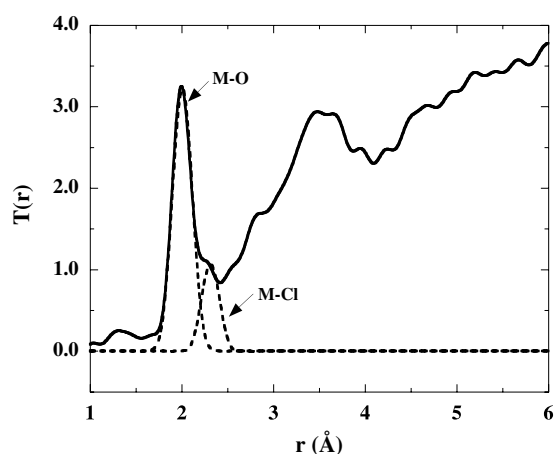


Figure 5. The correlation function, $T(r)$, for the oxychloride glass containing $0.50\text{Sb}_2\text{O}_3$ with Gaussians fitted to the peaks, showing the contributions for each bond.

an extra correction due to the large absorption cross-section of chlorine. There is significant change in $S(Q)$ on the addition of increasing amounts of ZnCl_2 . The increased structure at low Q signifies an increase in the medium-range order on the addition of ZnCl_2 . This implies an increased regularity in the packing of structural units.

Figure 4 shows the real-space $T(r)$ function for the various glasses along with the peak assignments. The distinguishable peaks were fitted with deconvoluted Gaussians and a representative fit is shown in figure 5, from which the peak positions and coordination numbers are derived. These are summarized in table 2.

4. Discussion

4.1. Glass composition

Table 1 shows that there is significant loss of chlorine from the glasses, with the proportion lost decreasing as the total chlorine increases. Relative to Sb, some Zn is lost from the

Table 2. Mössbauer data.

Sample	Shift (δ) (mm s ⁻¹ \pm 0.1)	Shift (δ) relative to InSb (mm s ⁻¹ \pm 0.1)	Quadrupole splitting (Δ) (mm s ⁻¹ \pm 0.2)	Width (mm s ⁻¹ \pm 0.05)	Reference
a-Sb ₂ O ₃		-3.2	17.0		[9]
1.0Sb	-12.2	-3.6	16.9	3.68	
0.75Sb	-12.0	-3.4	16.9	3.37	
0.50Sb	-12.1	-3.5	17.7	3.33	
0.25Sb	-12.0	-3.4	17.9	3.06	
SbCl ₃		-5.7	12.2		[10]

glasses at lower concentrations of Zn; the Sb/Zn ratio deviates from the nominal by 8% for the 0.75Sb₂O₃ glass but by less than 1% for the 0.25Sb₂O₃ glass. The change in the glass density with composition is consistent with replacement of Sb₂O₃ (MW = 291.5) by ZnCl₂ (MW = 136.3) and is enhanced by loss of Cl.

4.2. Mössbauer spectroscopy

The peaks in the Mössbauer spectra were at chemical shifts consistent with Sb³⁺ only and can be fitted with a single-site contribution using a lineshape consistent with the 7/2 \leftrightarrow 5/2 transition. Chemical shifts, quadrupole splittings, and peak widths were refined and are given in table 2. The values obtained showed little change with composition. Relative to InSb, the chemical shift is found to be between -3.4 and -3.6 mm s⁻¹. This can be compared with values of -3.18 mm s⁻¹ for valentinite and -3.2 mm s⁻¹ for amorphous Sb₂O₃ [9] and a value of -5.7 mm s⁻¹ reported for crystalline SbCl₃ [10]. The observed shift range suggests that the antimony atoms are in an entirely oxygen environment. Values of quadrupole splitting between 16.9 and 17.9 mm s⁻¹ were observed but this parameter is difficult to separate from the linewidth contribution. The published values are 17.0 for valentinite [9] and 12.2 for SbCl₃ [10].

4.3. Raman scattering

The Raman spectra reproduce strongly the features of v-Sb₂O₃ as shown by Miller *et al* [11]. These features are the 160, 408, and 465 cm⁻¹ vibrational modes. Miller's study indicates that the structural unit [O₂Sb-O-SbO₂] can account for the gross features of the observed vibrational spectrum of vitreous Sb₂O₃. In the lowest-concentration Sb sample, evidence for the [O₂Sb-O-SbO₂] structural unit has disappeared, implying a dilution of the Sb-O network in this glass.

These results support the Mössbauer data in that Sb appears to be bonded only to oxygen. Miller disagrees with Hasegawa in that he thinks that the structure does not resemble that of valentinite but is a structure unique for the glass. Miller indicates strongly in his paper that the structure of vitreous Sb₂O₃ closely resembles that of well-studied As₂O₃ in its glass form.

The dominant Raman line for pure vitreous ZnCl₂ is seen at approximately 230 cm⁻¹ [12]. While our spectra do not show a sharp line at this wavelength, there is intensity, so other vibrations could mask the line.

The only other feature to note is the broad line between 680 and 700 cm⁻¹ for the higher-concentration Zn samples. As this feature does not appear for the nominally 0.75Sb₂O₃ sample or the vitreous Sb₂O₃ glass, we can attribute the line to a Zn-containing structural unit.

Table 3. Observed interatomic separations and coordination numbers compared with literature values.

Sample	R_{M-O} ($\text{\AA} \pm 0.005$)	R_{M-Cl} ($\text{\AA} \pm 0.005$)	$C_{M-O} \pm 0.2$	$C_{M-Cl} \pm 0.2$
1.0Sb	1.997		2.1	
0.75Sb	2.006		2.5	
0.5Sb	2.001	2.307	3.5	2.6
0.25Sb	1.985	2.320	5.0	2.5
Bond valence calculation [16]	Zn–O, 1.960 Sb–O, 1.973	Zn–Cl, 2.266 Sb–Cl, 2.350	4.0 3.0	4.0 3.0
v-ZnCl ₂ [7]		2.288		3.8
v-Sb ₂ O ₃ [3]	1.990		3.2	
c-ZnCl ₂ [13]		Average 2.273		4.0
c-Sb ₂ O ₃ [5]	2.000		3.0	
c-ZnO [14]	1.974		4.0	
c-SbCl ₃ [15]		Average 2.360		3.0

Galeener *et al* [12] show a broad feature around 650 cm^{-1} in their polarized neutron spectra of ZnCl₂ but it is not discussed in the text.

4.4. Neutron diffraction

The observed peak positions, reported in table 3, are compared with interatomic distances observed for v-Sb₂O₃ [3], v-ZnCl₂ [7], valentinite [5], c-ZnCl₂ [13], c-ZnO [14], c-SbCl₃ [15], and also the distances calculated from bond valence parameters [16]. It is immediately obvious that the peak at $\sim 2.0 \text{ \AA}$ arises from metal–oxygen correlations and the peak at $\sim 2.3 \text{ \AA}$ from metal–chlorine correlations. The bond valence calculations show that the interatomic distances Sb–X and Zn–X are very similar for a given X if coordinations of 3 and 4 are assumed respectively. The scattering lengths of Sb and Zn are also very close (Sb: 5.57; Zn: 5.68). Therefore, to identify the cations that are contributing to the diffraction peaks, we must utilize this difference in preferred coordinations. The samples are discussed individually as follows:

- (i) 0.5Sb₂O₃:0.5SbCl₃. No chlorine could be detected in this sample by chemical analysis. The density of the sample was found to be 5.05 g cm^{-3} , close to the value of 5.07 g cm^{-3} measured by Hasegawa *et al* [3] for Sb₂O₃. The peak at 1.997 \AA is consistent with the anticipated Sb–O separation and compares closely with the value observed by Hasegawa *et al* [3] of 1.99 \AA and the average value for crystalline valentinite of 2.00 \AA . The second peak in the $T(r)$ can be fitted to two contributions at 2.463 and 2.903 \AA . These correlations involve oxygen and were therefore not well resolved by Hasegawa *et al*. By comparison with the valentinite structure, the peak at 2.463 can be assigned to a longer Sb–O distance, not part of the [SbO₃] polyhedron. The peak at 2.903 \AA is then assigned to the O–O distance in the polyhedron. These interatomic distances can be used to calculate an O–Sb–O bond angle of 93.2° which is comparable to the value of $\sim 92^\circ$ deduced by Hasegawa from x-ray diffraction data and also to the values of 79.8° , 91.9° , and 98.1° observed for valentinite [5].
- (ii) 0.5Sb₂O₃:0.5ZnCl₂. Given the Mössbauer and Raman results that both suggest Sb as being in an oxygen environment only, it is reasonable to assume that the peak at $\sim 2.3 \text{ \AA}$ contains only Zn–Cl correlations and that Zn has a coordination of 4. So, the area under this peak would indicate that out of the 12.9% Zn polyhedra, 8.4 are [ZnCl₄] tetrahedra. This leaves 4.5Zn to form [ZnO₄] tetrahedra. Thus this means that the intensity of the peak at $\sim 2.0 \text{ \AA}$ contains contributions from 4.5×4 Zn–O correlations plus $27.9 \times C_{Sb-O}$

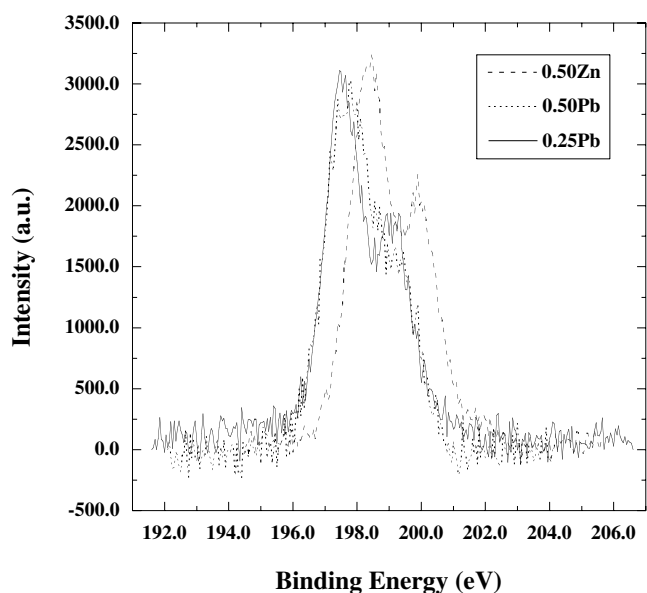


Figure 6. Binding energies of the Cl $2p_{3/2}$ photoelectron for $PbCl_2$ - and $ZnCl_2$ -containing glasses.

Sb–O correlations. This gives a value for C_{Sb-O} of 2.85, close to the expected value of 3. It should be noted that 8.4Zn as $[ZnCl_4]$ tetrahedra would require more chlorine (16.7) than is actually detected in the glass (10.4). A higher coordination of 3 for Cl would be consistent with a value of 10.4 but this is most unusual and would result in glass instability if it involved a significant proportion of the network. There will be greater inaccuracy in both the measured C_{Zn-Cl} and measured Cl content at this low concentration and this may contribute to the discrepancy. The other possibility is that there is hydrogen in the system but this would have shown in the neutron data.

- (iii) 0.25 Sb_2O_3 :0.75 $ZnCl_2$. A similar argument applied to the 25 Sb_2O_3 :75 $ZnCl_2$ sample, indicates that 13.8 of the 22.1% Zn occupy $[ZnCl_4]$ tetrahedra and 8.3 have O nearest neighbours. This leaves Sb bonded to oxygen with a coordination number of 2.88, close to 3.
- (iv) 0.75 Sb_2O_3 :0.25 $ZnCl_2$. There is insufficient chlorine retained in this glass to allow resolution of the M–Cl peak in the $T(R)$.

The above calculations have assumed that the coordination polyhedra of Zn are exclusively oxygen *or* chlorine but have ignored the possibility of mixed coordinations. Distributing the O and Cl equally among the Zn gives average coordinations of $[ZnO_{1.4}Cl_{2.6}]$ for the nominal 0.5:0.5 and $[ZnO_{1.5}Cl_{2.5}]$ for the 0.25:0.75 sample. If the polyhedra are assumed to be combinations of $[ZnO_2Cl_2]$ and $[ZnOCl_3]$, then this would indicate nearly equal amounts of each species irrespective of overall composition.

5. Conclusions

This work clearly shows that there is preferential bonding within the system with no evidence for Sb–Cl bonds whatsoever. The assumptions made are consistent with all the results and lead to the expected value for coordination of O around Sb of 3. Further evidence for this

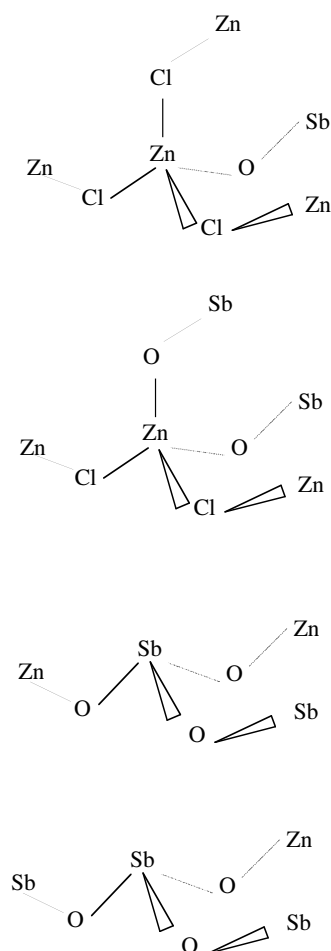


Figure 7. Models for the likely polyhedra of these glasses.

is furnished by x-ray photoelectron spectroscopy of related glasses in which PbCl_2 replaces ZnCl_2 in the binary system [17]. The binding energy of the Cl $2p_{3/2}$ photoelectron (figure 6) is 197.5 ± 0.1 eV for the PbCl_2 -containing glasses but 198.3 ± 0.1 eV for the ZnCl_2 -containing glasses. The difference would not be so great if a significant fraction of the Cl were bonded to Sb. The structure is driven by the replacement of Cl by O; this could be due to the avoidance of the formation of energetically unfavourable Zn–Cl–Sb and Sb–Cl–Sb linkages in the network. The proportions of various correlations, and the linkages which they imply, are summarized in table 4. The likely polyhedra are illustrated in figure 7.

High energy x-ray diffraction experiments on these materials along with $[\text{Sb}_2\text{O}_3]_{0.5}$ – $[\text{PbCl}_3]_{0.5}$ have been completed at the Advanced Photon Source at Argonne National Laboratory. These results will be combined with the neutron structure factors (including $[\text{Sb}_2\text{O}_3]_{0.5}$ – $[\text{PbCl}_3]_{0.5}$) to reveal the partial pair correlation functions, and a detailed analysis will be performed on the medium/extended-range order within the glasses. These results will be published along with the x-ray photoelectron spectroscopy data for these systems.

Table 4. Structural units present based on at.% values presented in table 1.

Structural units	0.50Sb	0.25Sb
Zn–Cl bonds	33.5	55.2
Zn–O bonds	18.1	33.2
Sb–O bonds	83.7	47.1
Zn–Cl–Zn links	16.8	27.6
Zn–O–Sb links	18.1	33.2
Sb–O–Sb links	32.8	7.0
Sb–O–Sb:Zn–O–Sb	2:1	0.2:1

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