Role of Sb^{3+} as a network-forming cation in oxide glasses

A. J. G. Ellison and S. Sen

Glass Research Division, Corning Incorporated, Corning, New York 14831

Sb K-edge extended x-ray-absorption fine-structure spectroscopy has been used to determine the coordination environment of Sb^{3+} ions in a wide range of Sb_2O_3-M_xO_y glasses ($M=$Si, Ge, B, and As) with Sb_2O_3 concentrations ranging from ~ 20 to up to 80 mol %. The Sb-O coordination number and bond length are found to be insensitive to glass composition. In all glasses the Sb^{3+} ions are coordinated to three oxygen nearest-neighbors and the Sb-O nearest-neighbor distances vary within a narrow range of 1.945 to 1.970 Å. It is concluded that Sb^{3+} behaves as a classic "network-forming" cation in oxide glasses, creating a continuous random network of Sb-O-M bonds, where $M=$Sb, As, Ge, Si, or B.

Certain simple oxide compounds can be induced to form glasses without the addition of any other components: B_2O_3, SiO_2, P_2O_5, GeO_2, and As_2O_3 comprise a brief but fairly comprehensive list. As noted by Zachariasen, glasses of these compounds share numerous features in common.[1]

(i) The cations (M) are surrounded by either three oxygen ions (B_2O_3, As_2O_3) or four oxygen ions (SiO_2, P_2O_5, GeO_2). With the exception of P_2O_5, the coordination number of the cation is equal to its formal valence.

(ii) The M-O distance and the intra-trigonal or intra-tetrahedral angle $\angle OMO$ vary little with glass composition or with the conditions under which the glass is made. The only exception is when a change in coordination occurs, such as the well-known threefold to fourfold coordination change of boron in alkali borates and borosilicates.

(iii) In all but P_2O_5, oxygen ions form bonds with only two cations, e.g., Si-O-Si, and are generally referred to as "bridging" oxygens. The double-bonded oxygen in a PO_4 tetrahedron is an exception, each of the remaining oxygen ions is bonded to exactly two phosphorus cations.

The corner-sharing of M-O coordination polyhedra through twofold coordinated oxygen forms a three-dimensional network, and thus the cations involved are referred to as network-forming cations. As noted by Zachariasen, simple oxides that do not share most or all of the attributes above tend not to form glasses on their own.[1] An example is TeO_2, which forms glass when other oxides are added, but is a very poor glass-former on its own. The oxide of trivalent antimony, Sb_2O_3, does not readily form a glass by itself, but readily forms glasses when other oxides are added: less than 5 mol % of "classic" network forming oxides ($SiO_2, B_2O_3, GeO_2, As_2O_3$) added to Sb_2O_3 is sufficient to make stable, readily quenched glasses.[2] This observation suggests that Sb^{3+} itself might be a network-forming cation. If it is a network former, then according to the criteria of Zachariasen the Sb^{3+} ions should be threefold coordinated by oxygen, the Sb-O distance and $\angle OSbO$ angle will be nearly invariant with the glass composition, and each Sb^{3+} ion should be linked through twofold-coordinated oxygen ions to adjacent cations.[1] Previous studies of antimony borate glasses have evaluated Sb coordination by x-ray diffraction,[2] Sb coordination and Sb-O-Sb linkages by vibrational spectroscopy[3,4] and Sb-O bond character using oxygen x-ray

photoelectron spectroscopy.[5] However, antimony coordination in binary systems containing other glass formers (e.g., Si, As, Ge) remains unknown.

Besides being of scientific interest, antimony containing glasses are also of significant technological interest. Binary antimony borate glasses with high antimony contents were recently considered as prospective materials for nonlinear optical applications due to their large third-order nonlinear optical susceptibility.[4] Antimony silicate glasses have been identified in the past as potential core glasses for low-loss optical waveguides,[6,7] and more recently as vitreous hosts for rare-earth element dopants for lasers and optical amplifiers.[8] The valuable properties conferred by Sb^{3+} to rare-earth environments have been found to be substantially independent of the oxide glass system, and thus it is of interest to characterize the structural role of Sb^{3+} in diverse oxide glasses. Here we report the results of a detailed Sb K-edge extended x-ray absorption fine structure (EXAFS) study of the local coordination environment of Sb^{3+} in binary glasses containing 20–80-mol % Sb_2O_3 in the systems SiO_2-Sb_2O_3, GeO_2-Sb_2O_3, B_2O_3-Sb_2O_3, and As_2O_3-Sb_2O_3. The results show unambiguously that Sb^{3+} is indeed a network forming cation in the sense of Zachariasen.[1]

All glasses were prepared from reagent-grade oxide starting materials. 50–500-g batches of glasses containing SiO_2, GeO_2, and B_2O_3 were melted in silica crucibles at temperatures ranging from 800 °C to 1600 °C, with lower temperatures applying to glasses rich in Sb_2O_3 or B_2O_3. Glasses containing As_2O_3 were melted in small batches in fused silica ampoules held in a rocking furnace at temperatures between 750 and 950 °C. The compositions of all glasses were determined by standard wet chemical methods and are listed in Table I. Melting conditions were optimized to produce a minimal SiO_2 pickup ($\leqslant 1$ mol % SiO_2) from the crucibles.

Sb K-edge (30491 eV) EXAFS spectra were collected at beam line X18B at the National Synchrotron Light Source at Brookhaven National Laboratory. The stored electron-beam energy was 2.58 GeV, and typical beam currents were between 150 and 300 mA. A channel-cut Si(111) monochromator was used without any detuning as higher harmonics at the Sb K edge are not of concern. The EXAFS data were collected in transmission mode in energy steps of 2 eV. Glass

TABLE I. Analyzed compositions for the binary $(Sb_2O_3)_x$ $-(M_yO_z)_{100-x}$ glasses $(M_yO_z = B_2O_3, SiO_2, GeO_2,$ or $As_2O_3)$ studied here. The compositions for each glass series are expressed as the mol% of M_yO_z.

Sb borates B_2O_3 (mol %)	Sb silicates SiO_2 (mol %)	Sb germanates GeO_2 (mol %)	Sb arsenates (As_2O_3) (mol %)
13.0	12.0	37.4	20.0
53.0	25.0	46.4	40.0
33.8	32.0	57.7	60.0
79.2	46.0	84.7	80.0
	51.0		
	65.0		
	81.0		

samples were ground to a fine powder and spread uniformly across a mylar tape. The tapes were mounted in a liquid-nitrogen-cooled cryostat cooled to 80–90 K, in order to lower the effect of the thermal Debye-Waller factor on the signal. Crystalline polymorphs of Sb_2O_3 (valentinite and senarmontite) were used as model compounds. The Sb K-edge EXAFS data were analyzed using the standard software packages EXBROOK and EXCURV92 developed by the Daresbury Laboratory.[9] The details of the procedure for fitting the EXAFS spectra can be found elsewhere.[10] The uncertainties in the coordination numbers of Sb atoms as obtained from fitting the Sb EXAFS spectra are on the order of ±0.15 or less in all glasses studied here.

The k^3-weighted experimental Sb K-edge EXAFS spectra and the fitted curves for glasses with the lowest and the highest Sb_2O_3 contents in each series are shown in Fig. 1. The corresponding Fourier transforms are shown in Fig. 2. The period of the dominant oscillation in these Sb EXAFS spectra varies little with composition, and coherent oscillation is seen up to large wave numbers (Fig. 1). All EXAFS spectra have been fitted with a shell of three nearest-neighbor oxygen atoms around the central Sb atom at an average distance of $\sim1.945–1.970$ Å, with Debye-Waller factors ranging between 0.008 and 0.010 Å^2. Fourier transforms of the Sb EXAFS spectra of glasses containing $\sim80\%$ As_2O_3 and $\sim85\%$ GeO_2 show a second peak between 3 and 4 Å [Fig. 2(a)]. The corresponding EXAFS spectra were fitted with a next-nearest-neighbor shell of 0.5 As atoms at 3.65 Å or 0.9 Ge atoms at 3.31 Å with Debye-Waller factors in both cases of ~0.01 Å^2. The fitting of the second shell has no detectable effect on the fit parameters of the first coordination shell, and is significant at the 95% probability level according to the criterion of Joyner et al.[11] Figure 3 shows the compositional variation of the intensity of the peak corresponding to the second shell in Sb_2O_3-GeO_2 and Sb_2O_3-As_2O_3 glasses which clearly decreases rather sharply with increasing Sb_2O_3 content. No such peak corresponding to a second shell is resolved in any of the glasses containing B_2O_3 or SiO_2 with comparable Sb concentrations (Fig. 2).

Figure 4 plots the nearest-neighbor Sb-O distances as a function of Sb_2O_3 content for all compositions in each of the glass families evaluated in this study. Sb silicates with ≤70-
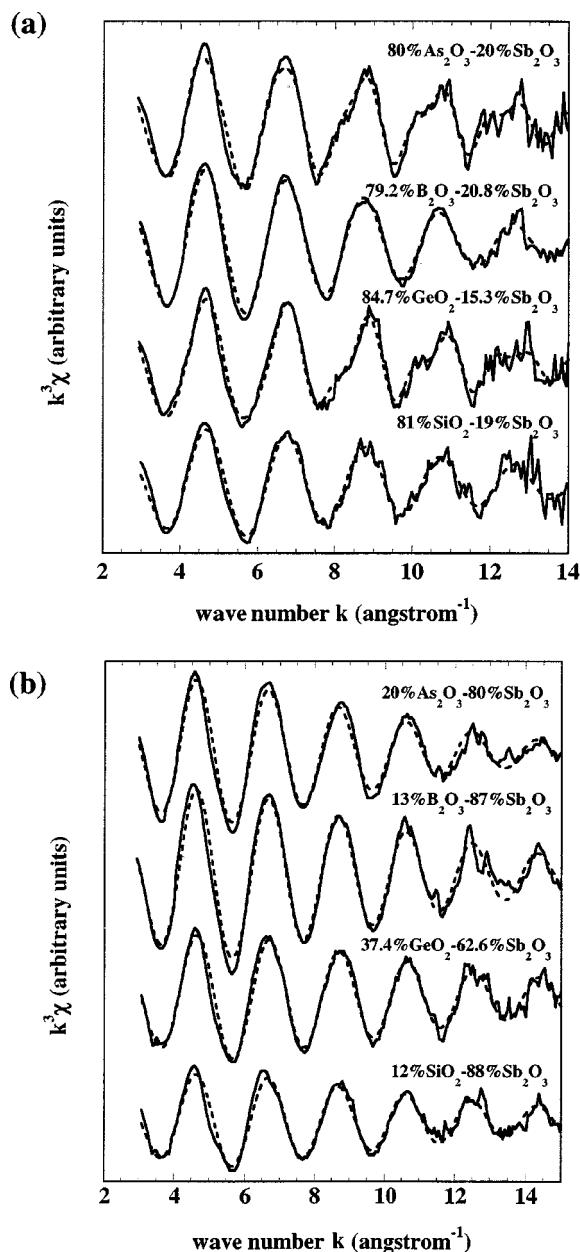

FIG. 1. k^3-weighted Sb K-edge EXAFS spectra of glasses with the lowest (a) and highest (b) Sb_2O_3 contents in each series. The corresponding glass compositions are indicated above each spectrum. Solid lines represent experimental data and dashed lines correspond to least-squares fits obtained using EXCURV92.

mol % Sb_2O_3 tend to have slightly shorter Sb-O bond distances than the other glasses with comparable Sb_2O_3 contents and glasses containing B_2O_3 or GeO_2 with low Sb_2O_3 contents (≤40-mol % Sb_2O_3) tend to have slightly shorter Sb-O distances than glasses with higher Sb_2O_3 contents. However, Sb-O distances in all glasses vary within an extremely tight range of 1.945–1.970 Å. Moreover, the best-fit nearest-neighbor coordination number for Sb in all glasses is 3.00 ± 0.15.

Taken together, the analyses of the Sb K-edge EXAFS spectra of these glasses illustrate the following

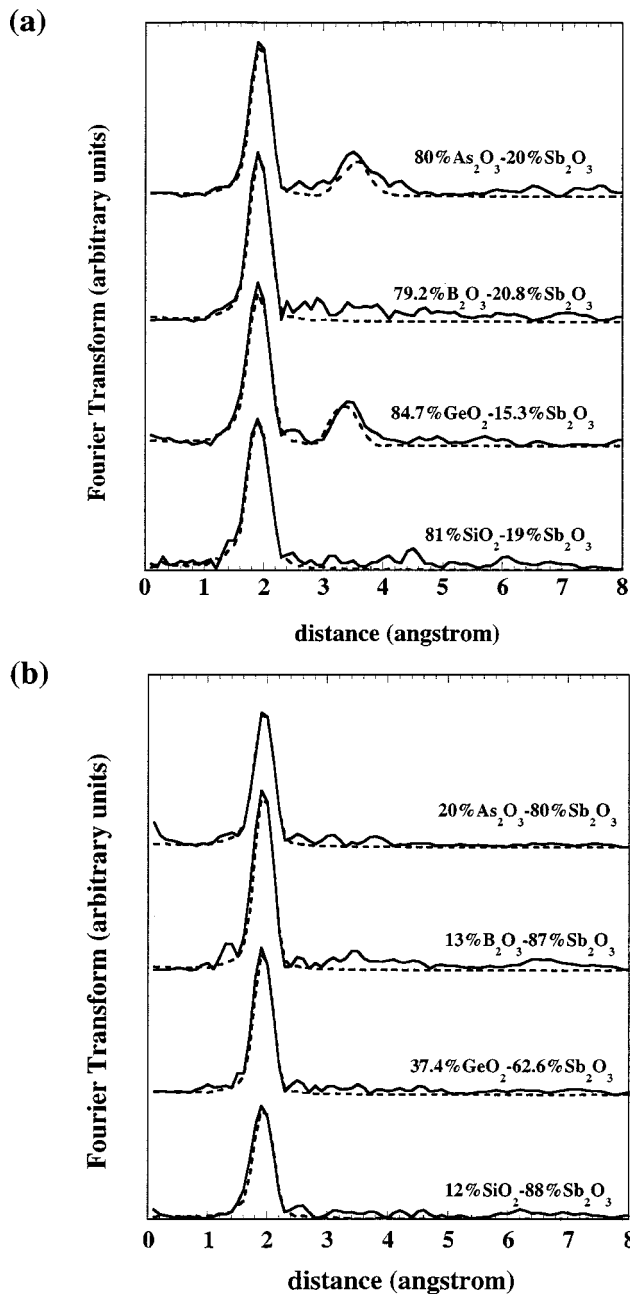(i) Sb^{3+} is surrounded by three oxygen atoms, indepen-

(a)

(b)

FIG. 2. Magnitudes of the Fourier-transform of the k^3-weighted experimental Sb K-edge EXAFS spectra of glasses with the lowest (a) and highest (b) Sb_2O_3 contents in each series. The corresponding glass compositions are indicated above each spectrum. Solid lines represent experimental data and dashed lines correspond to least-squares fits obtained using EXCURV92.

dent of its concentration in a glass, and independent of the identity or the coordination number of the other cation in the glass.

(ii) The coordination number of Sb^{3+} equals its formal valence, indicating that oxygen ions bonded to antimony are generally bonded to only one other cation, whether B^{3+}, Ge^{4+}, or Si^{4+}, or an adjacent Sb^{3+} in Sb_2O_3-rich compositions.

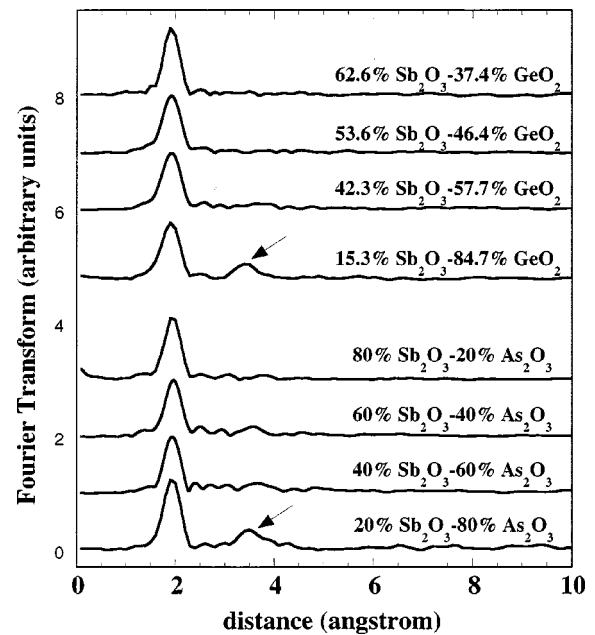(iii) The Sb-O bond length shows little dependence on the conditions under which the glasses were made, the identity

FIG. 3. Magnitudes of the Fourier-transform of the k^3-weighted experimental Sb K-edge EXAFS spectra of Sb germanate and arsenate glasses as a function of Sb_2O_3 content in each series. The glass compositions are indicated above each transform. Arrows indicate signal from next-nearest-neighbor Ge (As) ions around Sb in germanate (arsenate) glasses.

of the other glass forming oxide, or the concentration of Sb_2O_3 in the glass. The total range of Sb-O bond lengths is only 0.025 Å. For comparison, in the case of classic network-forming cations such as Si^{4+} the Si-O bond lengths in SiO_2 and alkali disilicate glasses range from 1.608 to 1.631 Å, or an absolute variation of 0.023 Å.[12]

Therefore, the geometry of the SbO_3 coordination polyhedra is extremely well constrained from one glass family to another, so the $\angle OSbO$ angle is inferred to be approximately
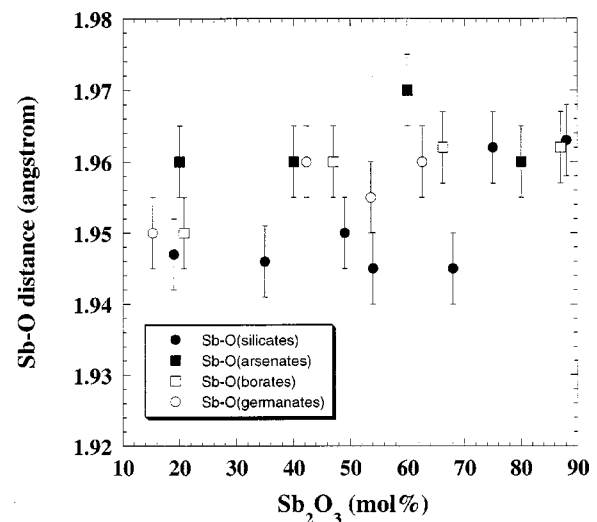

FIG. 4. Compositional variation of average Sb-O distances for Sb borate, silicate, germanate, and arsenate glasses as determined from fits to the Sb K-edge EXAFS spectra.

invariant with composition. As noted in the introduction, these are the hallmarks of classic glass-forming oxides, and hence it is concluded that Sb^{3+} shares in common all the features associated with classic network-forming cations.

The Sb-O distances obtained in all glasses ($\sim$1.95–1.97 Å) are similar to that (1.977 Å) observed in the cubic crystalline polymorph of Sb_2O_3, senarmontite.[13] In senarmontite the three oxygen nearest neighbors and the $5s^2$ lone pair of electrons of the Sb^{3+} ions form a near-regular tetrahedron, with $\angle OSbO$ of 95.9°.[13] In the high-temperature orthorhombic polymorph of Sb_2O_3, valentinite, these tetrahedra are considerably distorted with three different $\angle OSbO$ ranging between 79.8 and 98.1° and the mean Sb-O bond length is 2.013 Å.[14] Such a tetrahedral Sb coordination geometry (3 oxygen ions+the $5s^2$ lone pair) is consistent with the Sb K-edge EXAFS data obtained from the glasses in this study.

The most unexpected result is that a next-nearest neighbor peak is resolved only in glasses containing As_2O_3 or GeO_2, and then only at relatively low Sb_2O_3 contents (Fig. 2). Furthermore, even when observed the amplitude of this peak decreases with increasing Sb_2O_3 content (Fig. 3). This trend and the best fits to the EXAFS spectra indicate that this next-nearest neighbor peak is most likely to be due to Sb-O-As or Sb-O-Ge types of linkages in the glass rather than due to Sb-O-Sb linkages. At minimum, this indicates that antimony mixes very homogeneously with other glass-forming constituents; however, the Sb-Ge/As second shell coordination numbers of $\sim$0.5 to 0.9 are well below the expected values of nearly 3 for Sb_2O_3-poor compositions. The absence of a second shell in corresponding borate or silicate glasses may be indicative of the fact that B and Si are weak backscatterers compared to heavier Ge and As atoms.

It is surprising that negligible coherent back-scatter amplitude is obtained from next-nearest-neighbor Sb atoms, especially in Sb_2O_3-rich glasses in which Sb-O-Sb linkages are required by stoichiometry. A second shell of Sb was clearly observed in the Sb EXAFS spectra of both valentinite and senarmontite, the crystalline polymorphs of Sb_2O_3. Therefore, a possible explanation for the absence of Sb-Sb correlation in the glass spectra would then be a highly disordered spatial distribution of Sb next-nearest neighbors in glasses due to variations in $\angle Sb$-O-Sb which results in a large Debye-Waller factor for the next-nearest neighbor shell.

In light of the results obtained in this study it is interesting to compare the coordination of antimony in the oxide glasses with that of other cations that carry nonbonding lone pairs of electrons, particularly As^{3+}, Te^{4+} and Pb^{2+}. As^{3+} is well known to form coordination polyhedra analogous to those proposed for Sb^{3+} in oxide glasses.[15] However, both Te^{4+} and Pb^{2+} show variable coordination behavior in oxide glasses. For example, Te^{4+} forms tetrahedra consisting of three Te-O bonds and a lone pair, but only in glasses with low TeO_2 concentrations. At higher TeO_2 concentrations, Te^{4+} becomes fourfold coordinated by oxygen with the lone pair forming a fifth apex to an irregular coordination polyhedron.[16] On the other hand Pb^{2+} has been shown to form both PbO_4 and PbO_3 pyramids in binary PbO-SiO_2 glasses over large compositional range.[17] Therefore, the only precedent for the nearly static coordination chemistry of Sb^{3+} in oxide glasses is that of As^{3+}.

Sb^{3+} ions in a wide variety of glasses form a threefold coordination environment with oxygen, it has a nearly fixed Sb-O bond length and its local coordination environment appears to be highly insensitive to the glass composition. These results indicate that Sb^{3+} is a true network-forming cation. Next-nearest-neighbor backscattering from Ge and As proves that at least in these glasses Sb^{3+} forms mixed linkages through oxygen with other cations. The absence of a Sb next-nearest neighbor peak in glasses with high Sb_2O_3 contents indicates that there is considerable disorder in relative rotational conformations of the corner-sharing SbO_3 polyhedra resulting from variations in the $\angle Sb$-O-Sb angle.

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