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Depolymerization of GeO_2 and $GeO_2 \cdot Sb_2O_3$ glasses by Bi_2O_3

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Glasses that contain at least 60 mol% GeO_2 were prepared in the $Bi_2O_3 \cdot GeO_2$ and $Bi_2O_3 \cdot Sb_2O_3 \cdot GeO_2$ systems. Their densities, refractive indices, and infra-red spectra were recorded. Negative molar volume deviations and positive refraction deviations occur for all of the binary glasses. These create deviations for the 60 to 80 mol % GeO_2 ternary glasses that indicate non-ideal mixing when Sb^{3+} substitutes for Bi^{3+}. Also, the main Ge-O stretching vibration shifts to as low as 695 cm^{-1} for the Bi_2O_3-rich binary and ternary glasses. All of these findings show that Bi_2O_3 more effectively depolymerizes GeO_2 than does Sb_2O_3. The probable structural reasons for this behaviour are discussed.

1. Introduction

Recently, small amounts of Sb_2O_3 (< 10 mol %) were found to favour network retention in Ge—O—Ge and Ge—O—B glasses, while larger amounts caused extensive depolymerization [1]. This behaviour of Sb_2O_3 is in contrast to that of B_2O_3 which favours network retention at all concentrations in GeO_2. The difference of behaviour can be related to the Sb—O—Sb double chain-like nature of the high temperature form of Sb_2O_3 when compared to the network structure of B_2O_3.

In contrast to Sb_2O_3, Bi_2O_3 possesses several crystalline polymorphs, the structures of which do not resemble those of either As_2O_3 or Sb_2O_3. Thus, the low temperature or α form of Bi_2O_3 contains layers of Bi and O atoms with the bismuth-oxygen polyhedra sharing corners and edges to form a three-dimensional network with tunnels [2]. The high temperature or δ form of Bi_2O_3 obtained from the melt forms a face centred cubic CaF_2 structure with an oxygen deficient lattice [3], while the orthorhombic β form (obtained from the supercooled melt) possesses a two-dimensional superstructure of the δ form [4].

Although the $Bi_2O_3 \cdot GeO_2$ phase diagram indicates convenient liquid temperatures [5] from a glass formation standpoint, most attention has been focused on the unusual structure and properties of the crystalline phases such as $Bi_{12}GeO_{20}$ [6] and $Bi_4Ge_3O_{12}$ [7-10]. The former contains geometrically regular GeO_4 tetrahedra and is piezoelectric, while the latter possesses the readily substituted garnet-like structure of eulytine ($Bi_4Si_3O_{12}$) and exhibits the electro-optic effect.

Pure Bi_2O_3 does not form a glass as readily as either As_2O_3 or Sb_2O_3. However, glasses can be obtained when it is present in moderate concentrations in other glass forming oxide mixtures such as the alkali borates [11]. Apparently, Bi_2O_3 can play several structural roles in such glasses. As part of a continuing study of oxide glasses that contain two or more glass forming species [1, 12, 13], it was decided to examine the influence of Bi_2O_3 on Ge—O—Ge networks and also on the Ge—O—Sb polymers present in $Sb_2O_3 \cdot GeO_2$ glasses. This paper describes the preparative techniques used and selected physical property information obtained for binary $Bi_2O_3 \cdot GeO_2$ and ternary $Bi_2O_3 \cdot Sb_2O_3 \cdot GeO_2$ glasses that contain as much as 40 mol% Bi_2O_3. These results are then discussed in terms of network depolymerization in the absence of the typical ionic modifiers such as the alkali oxides.

2. Experimental

The glasses were prepared from electronic-grade GeO_2 (Eagle-Picher Industries, Inc), yellow reagent grade Bi_2O_3 (Matheson Coleman and Bell), and reagent grade Sb_2O_3 (Matheson Coleman and Bell). A muffle furnace (Blue-M Electric Co, Model RG-2090A-1) with an air atmosphere was used for the melting reactions.

Preliminary heating experiments with Bi_2O_3 (m.p. = 820°C) in recystallized Al_2O_3 containers (McDanel Refractory Porcelain Co) showed that molten Bi_2O_3 at 960°C is a dark, non-volatile, extremely fluid liquid that cools to a yellow solid (the dark coloured Bi_2O_5 is thermodynamically unstable above 357°C [14]). A $\frac{1}{2}$ h hold at 960°C showed just a slight penetration, but no gross attack, of the recrystallized Al_2O_3. Hence, 32 g of each $Bi_2O_3 \cdot GeO_2$ glass were prepared in 20 cc recrystallized Al_2O_3 crucibles in such a fashion as to minimize contamination via container corrosion.

The carefully weighed and mixed batches were inserted directly into the furnace at the highest temperature to be used (1320°C for the highest GeO_2 content and 1160°C for the lowest GeO_2 content). This facilitated the reaction between the relatively viscous GeO_2 ($\eta \sim 10^6$P at its m.p. of 1115°C) and the denser, but more fluid Bi_2O_3. Although the initial melting reactions occurred within 10 min, the mixtures were reacted and repeatedly swirled over a total of 45 to 60 min to ensure complete homogenization. No penetration or attack of the Al_2O_3 crucibles was observed and volatilization losses were about 0.3 wt %.

10 g of each ternary glass were subsequently prepared by weighing specific amounts of selected $Bi_2O_3 \cdot GeO_2$ and $Sb_2O_3 \cdot GeO_2$ [1] glasses. All samples were ground, weighed, and thoroughly mixed prior to melting in recrystallized Al_2O_3 crucibles. Homogenization temperatures ranged from 1140 to 1280°C (for the highest GeO_2 content), while the times were about 30 min. Volatilization losses ranged from 0.2 to 1.0% of the initial glass batch and were highest for the higher Sb_2O_3 content glasses. No crucible attack was noted.

Refractive indices were determined by using several series of certified index-of-refraction liquids (Cargille Laboratories, Inc) and a microscope. Specific gravities were determined with a Kraus-Jolly balance (Model 5000, Eherbach Corp.) using benzene as the immersion fluid. The details of both types of measurement are described elsewhere [15].

The infra-red spectra were recorded with a Perkin-Elmer Model 521 Grating Infra-red Spectrophotometer equipped with a reference-beam attenuator. From 6 to 17 mg of selected glass compositions were taken from the larger finely ground samples and mixed with 400mg, of KBr. The larger samples were taken from the glasses with the lower GeO_2 contents and higher Bi_2O_3 contents. Details of the pellet preparation are given elsewhere [12]. A rather shallow OH-absorption at $\approx$ 3400 cm^{-1} confirmed the relatively low H_2O content of the binary and ternary glasses.

3. Results

The compositions, densities, refractive indices, and colours of the binary and ternary glasses prepared in the $Bi_2O_3 \cdot Sb_2O_3 \cdot GeO_2$ system are given in Table I. For the binary glasses, all of the weight losses during melting were assumed to be Bi_2O_3. For the ternary glass melting conditions used, Sb_2O_3 has a much greater volatility than Bi_2O_3. Hence, from 67 to 90% of each ternary

TABLE I Physical properties of glasses in the system $Bi_2O_3 \cdot Sb_2O_3 \cdot GeO_2$

Composition (mol %)			Density (g cm^{-3})	Refractive index	Colour
Bi_2O_3	Sb_2O_3	GeO_2			
9.16	—	90.84	4.643 ± 0.004	1.715 ± 0.005	Orange red
18.14	—	81.86	5.557 ± 0.017	1.873 ± 0.033*	Dark orange red
24.59	—	75.41	6.065 ± 0.013	1.910 ± 0.010	Dark orange red
32.95	—	67.05	6.525 ± 0.016	2.05 ± 0.01	Darker red
39.24	—	60.76	6.846 ± 0.036	2.07 (at least)	Darker red‡
6.50	6.50	87.00	4.561 ± 0.000	1.758 ± 0.018†	Lighter yellow
11.62	11.16	77.22	5.155 ± 0.013	1.840 ± 0.010	Lighter yellow
16.96	16.38	66.66	5.597 ± 0.048	1.930 ± 0.010	Light yellow
19.49	8.45	72.06	5.867 ± 0.003	1.905 ± 0.010	Lighter yellow
7.42	20.20	72.38	4.909 ± 0.033	1.830 ± 0.010	Light yellow

*Average of three samples.

†Average of two samples.

‡Crystalline $Bi_4Ge_3O_{12}$ is light yellow [7, 16].

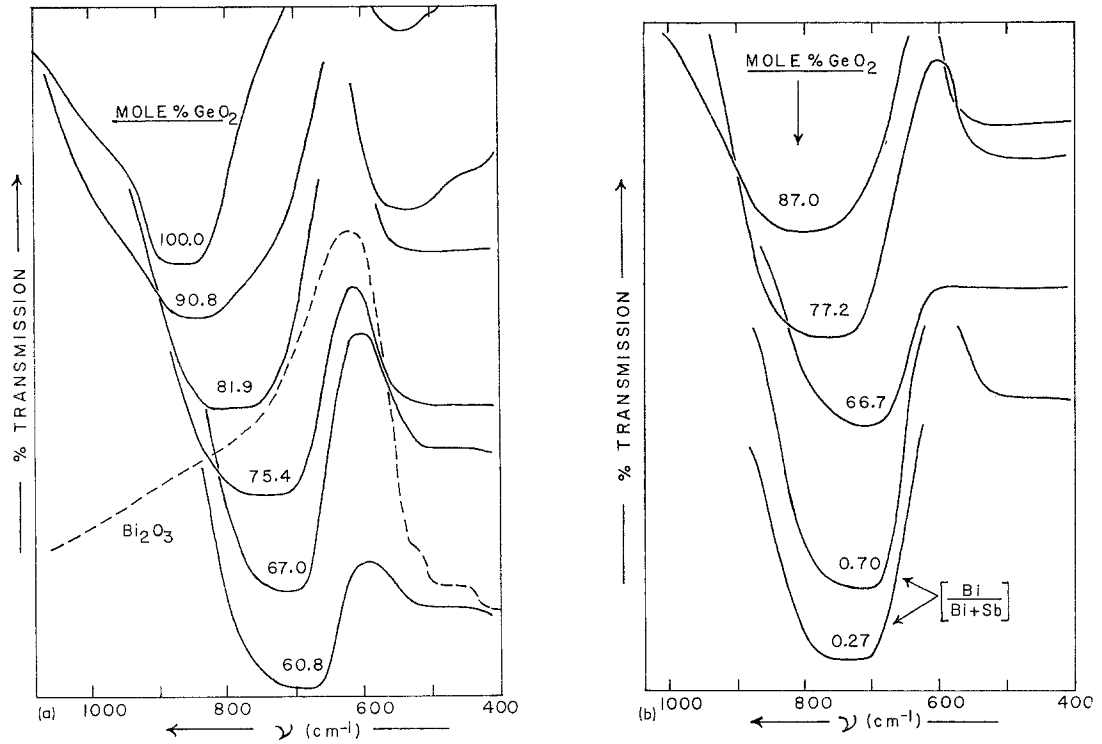

Figure 1 Infra-red spectra for (a) $Bi_2O_3 \cdot GeO_2$ glasses and (b) $Bi_2O_3 \cdot Sb_2O_3 \cdot GeO_2$ glasses.

melt weight loss (depending upon the original Sb_2O_3 content) was assumed to be Sb_2O_3. The final compositions given in Table I reflect these relatively minor adjustments. It was also qualitatively observed that the high temperature melt viscosity decrease caused by the two smallest Bi_2O_3 additions appeared to be more pronounced than that caused by comparable Sb_2O_3 additions [1].

Fig. 1a shows the infra-red spectra, in the frequency region that contains the main Ge—O stretching vibration for the binary $Bi_2O_3 \cdot GeO_2$ glasses. Also shown are the spectra of pure GeO_2 glass and of a crystalline sample of Bi_2O_3 that had been quenched from 960° C. Of interest is the progressive shift of ν_{Ge-O} to lower frequencies as the Bi_2O_3 content increases. Fig. 1b shows the infra-red spectra of the five ternary glasses prepared in the $Bi_2O_3 \cdot Sb_2O_3 \cdot GeO_2$ system.

4. Discussion

4.1. Molar volumes

The molar volumes of the binary $Bi_2O_3 \cdot GeO_2$ glasses tend to increase as the Bi_2O_3 content increases (Fig. 2). This trend is similar to that observed for the addition of Sb_2O_3 to GeO_2 glass where negative deviations from additivity were noted [1]. Although the molar volume of pure Bi_2O_3 glass is unknown, it is possible to estimate a value by using the known values for the various polymorphs of Bi_2O_3, Sb_2O_3 and As_2O_3.

The high temperature or δ form of Bi_2O_3 crystallizes from the supercooled melt and possesses a volume of 53.7 cc at 750°C [3], but transforms to the β form at $\sim$650°C. The β form of Bi_2O_3, obtained by fast quenching of the melt (because the $\beta \rightarrow \alpha$ transformation is rapid below 640°C [17]), possesses a room temperature volume of 50.37 cc [4]. This is quite close to the well documented 50.0 cc volume of $\alpha \cdot Bi_2O_3$ [2, 3, 17] and the extrapolated value (from the high temperature expansion coefficients of the α and δ forms [3]) for the δ form. Now, the volume of As_2O_3 glass is about 5% greater than that of the high temperature monoclinic form (As—O—As chain) [18], while the volume of Sb_2O_3 glass is about 10% greater than that of the high temperature rhombohedral form (Sb—O—Sb chains) [18]. Thus, one can estimate a molar volume of about 55.0 cc for Bi_2O_3 glass and use

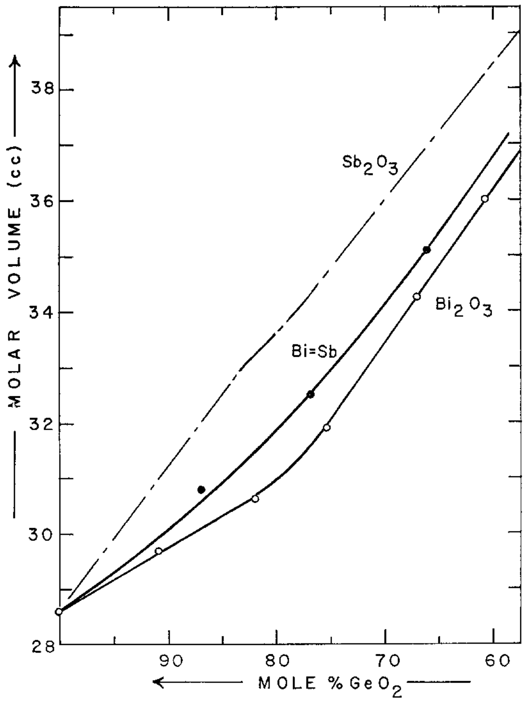

Figure 2 Molar volume as a function of composition for $Bi_2O_3 \cdot GeO_2$ glasses and for ternary glasses with $[Bi^{3+}] = [Sb^{3+}]$.

it to calculate ideal mixing volumes for $Bi_2O_3 \cdot GeO_2$ glasses.

Use of the above procedure leads one to conclude that the $Bi_2O_3 \cdot GeO_2$ glasses do exhibit considerable negative deviations from ideality (Fig. 2). For example, the deviation is -9.0% at 20 mol % Bi_2O_3 and -7.5% at 40 mol % Bi_2O_3. These deviations are six and three times, respectively, the contractions observed for similar additions of Sb_2O_3 [1]. They suggest a considerable degree of interaction between Bi_2O_3 and GeO_2, so considerable that the GeO_4 tetrahedral network may have experienced considerable alteration with the addition of 20 mol % Bi_2O_3.

Normally, a glass is about 5 to 10% more voluminous than its stable high temperature polymorph. Thus, GeO_2 glass is 17.7% more voluminous than its quartz-like form, while SiO_2 glass is only about 5% more voluminous than cristobalite, but 19% more voluminous than quartz. However, the observed volume of a 40 mol % Bi_2O_3 glass (Fig. 2) is only 2.4% larger than that reported for crystalline $Bi_4Ge_3O_{12}$ [9, 10]. Thus, either the 40 mol % Bi_2O_3 glass is not as voluminous as expected and/or crystalline $Bi_4Ge_3O_{12}$ is more voluminous than expected.

Crystalline $Bi_4Ge_3O_{12}$ is isomorphous with eulytine ($Bi_4Si_3O_{12}$) which is known to contain irregularly co-ordinated Bi ions (BiO_6 octahedra) that link *discrete* SiO_4 tetrahedra [19]. In addition, the Ge—O distance in Bi_2GeO_5 [20] is within the range normally found for GeO_4 tetrahedra is a variety of crystals [6]. Finally, GeO_4 tetrahedra are known to exist in crystalline $Bi_{12}GeO_{20}$ [6]. Thus, there is little doubt that GeO_4 tetrahedra exist at practically all crystalline compositions in the $Bi_2O_3 \cdot GeO_2$ system. Thus, it is rather unlikely that the relative densification exhibited by a 40 mol % Bi_2O_3 germanate glass is associated with a change of co-ordination for germanium. It is also doubtful that there is any significant change of co-ordination experienced by the bismuth because (a) BiO_5 and BiO_6 exist in $\alpha \cdot Bi_2O_3$ [2], (b) BiO_6 quite probably exist in the β [4] and δ [3] forms, (c) BiO_7 (really BiO_5) exist in $Bi_{12}GeO_{20}$ [6], (d) BiO_6 exist in Bi_2GeO_5 and Bi_2SiO_5 [20], and (e) irregular BiO_6 exist in $Bi_4Si_3O_{12}$ (and, therefore, in $Bi_4Ge_3O_{12}$) [19].

A molar volume plot for the crystalline phases in the $Bi_2O_3 \cdot GeO_2$ system reveals that the volume of $Bi_{12}GeO_{20}$ is about 1.5 cc (or $\sim -3.3\%$) less than the ideal mixing line between Bi_2O_3 (as noted above, all three forms possess volumes close to 50.0 cc) and quartz-like GeO_2. In contrast, the volume of $Bi_4Ge_3O_{12}$ is about 1.0 cc (or $\sim +3\%$) greater than the ideal mixing line. The relatively efficient packing in $Bi_{12}GeO_{20}$ may be related to the regular tetrahedral angle of the GeO_4 tetrahedra (it usually varies by about $\pm 4°$ [6]). The garnet-like structure exhibited by $Bi_4Ge_3O_{12}$ is characteristic of a variety of silicates of the formula $X_3Y_2Si_3O_{12}$ and is known to involve $2YO_6$ octahedra and $3XO_8$ dodecohedra that effectively *separate* the SiO_4 tetrahedra [21]. However, in $Bi_4Si_3O_{12}$ and $Bi_4Ge_3O_{12}$ there are only four, not five, cations to fill the octahecral and dodecahedral "holes". In addition *all* of the four cations are Bi^{3+}. Thus, the eulytine structure of $Bi_4Ge_3O_{12}$ contains completely isolated, from each other, GeO_4 tetrahedra as well as empty cation sites. These two factors could thereby account for a relative "bloating" of the crystal and, hence, create the relatively small volume difference between the crystal and its glass.

The molar volumes for various GeO_2 levels are shown in Fig. 3 for the ternary $Bi_2O_3 \cdot Sb_2O_3 \cdot GeO_2$ glasses. Particularly striking are the nega-

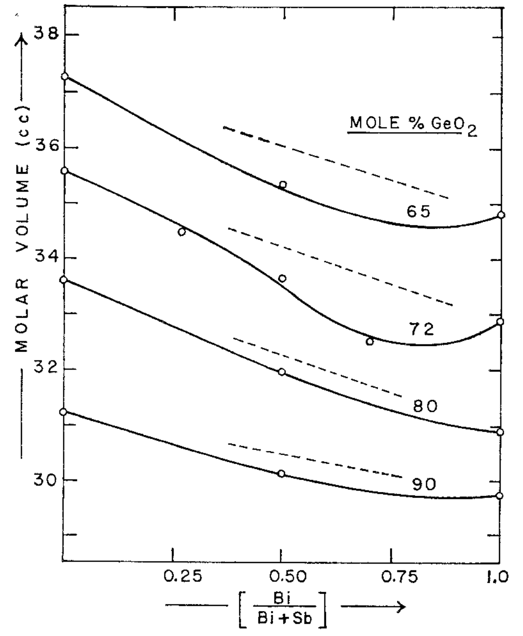

Figure 3 Molar volume as a function of [Bi/Bi + Sb] for $Bi_2O_3 \cdot Sb_2O_3 \cdot GeO_2$ glasses of constant GeO content.

tive deviations exhibited by all of the Bi = Sb glasses and by the lower GeO_2 content glasses with higher [Bi/Bi + Sb] ratios. These volume trends show that ideal mixing is not commonplace in these ternary glasses. The substitution of Sb^{3+} for Bi^{3+}, particularly at the lower GeO_2 levels, appears to cause no significant bloating of the proposed amorphous, garnet-like structure of the 30 to 40 mol % Bi_2O_3 glasses until about a third of the bismuth atoms have been replaced. Then, the volume starts to increase significantly. This phenomenon suggests that Sb^{3+} and Bi^{3+} depolymerize the GeO_4 network differently. They may do this because of the aforementioned structural dissimilarities between their various high temperature polymorphs.

4.2. Refractive indices

Fig. 4a shows the linear dependence of refraction on composition for the binary $Bi_2O_3 \cdot GeO_2$ glasses and also for those ternary glasses with $[Bi^{3+}] = [Sb^{3+}]$. Normally, the refraction of a crystal is greater than that of its glass form because of the more efficient packing in the former. For example, the refractive indices of the quartz forms of GeO_2 and SiO_2 are about 6 to 6.5 % larger than those of their respective glasses [22]. However, the refractive index of the 40 mol % Bi_2O_3 binary glass shown in Fig. 4a is about 2 % larger than the value of its crystalline counterpart $Bi_4Ge_3O_{12}$ [7]. The latter value ($N = 2.07$) is about 2 % less than the crystalline value expected for ideal mixing between quartz-like GeO_2 and cubic $Bi_{12}GeO_{20}$ ($N = 2.55$ [23]). This finding also suggests that the packing in

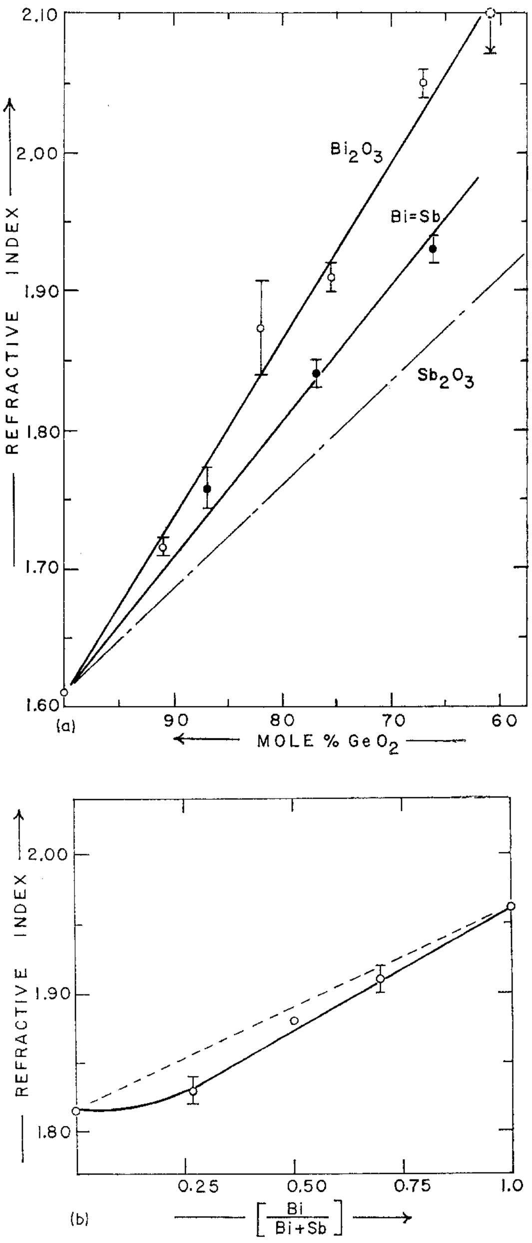

Figure 4 Refractive index versus composition for (a) $Bi_2O_3 \cdot GeO_2$ glasses and for ternary glasses with $[Bi^{3+}] = [Sb^{3+}]$ and (b) ternary glasses containing 72 mol % GeO_2.

crystalline $Bi_4Ge_3O_{12}$ is not as efficient as expected and, hence, agrees with the volume analysis.

Both As_2O_3 and Sb_2O_3 glasses possess refractive indices that are about 8% less than those of their respective high temperature crystalline polymorphs [18]. Simple extrapolation of the known refractive indices of $Bi_4Ge_3O_{12}$ and $Bi_{12}GeO_{20}$ allows a refraction estimate of about 2.70 for the face centred $\delta\cdot Bi_2O_3$. These two pieces of information allow a predicted refraction of ~ 2.50 for Bi_2O_3 glass. A similar value of about 2.60 is obtained from an extrapolation of a refraction versus molecular weight for the group V trioxide glasses.

The above analysis allows one to conclude that the binary $Bi_2O_3\cdot GeO_2$ glasses do in fact exhibit positive deviations of refraction from additivity. The deviation amounts to + 7.5% for the 40 mol % Bi_2O_3 glass (Fig. 4a) and is indicative of a more efficient mode of packing than expected for these glasses. This conclusion agrees with that derived separately from the volume results.

It can be inferred from the $[Sb^{3+}] = [Bi^{3+}]$ glass results (Fig. 4a) and seen directly for the 72 mol % GeO_2 glasses in Fig. 4b that there are respectively, small or slightly negative, refraction deviations for these ternary glasses. However, since both the $Bi_2O_3\cdot GeO_2$ and $Sb_2O_3\cdot GeO_2$ glasses exhibit fairly significant refraction deviations from ideality (+5 to +7% at lower GeO_2 levels) these ternary glasses also exhibit the same deviations. The latter deviations are just a little less positive.

4.3. Infra-red spectra

The frequency of each transmission minimum has been plotted as a function of composition in Fig. 5. There is no significant difference between the effects of Sb_2O_3 and Bi_2O_3 for GeO_2 contents above ~ 87 mol %. However, the shift of ν_{Ge-O} to longer wavelengths is significantly more pronounced with Bi_2O_3 additions than with Sb_2O_3 additions for the lower GeO_2 levels. Such frequency shifts for a given vibration have been associated with a change from condensed or polymerized polyhedra to discrete or less polymerized polyhedra in a variety of crystals [24] and glasses [1, 12, 13]. The present results (Fig. 5) therefore, suggest that Bi_2O_3 tends to depolymerize GeO_2 to a considerable degree.

The shift of ν_{Ge-O} to 695 cm^{-1} for the 40 mol % Bi_2O_3 glass is similar to the ν_{Ge-O} reported for ortho germanates [25] and for germanate garnets [26], all of which contain discrete GeO_4 tetrahedra. Since the garnet-like $Bi_4Ge_3O_{12}$ (also contains 40 mol % Bi_2O_3) is known to contain discrete GeO_4 tetrahedra, their presence in the 40 mol % Bi_2O_3 germanate glass can be directly inferred. Thus, the addition of 40 mol % Bi_2O_3 can completely depolymerize the random three-dimensional network found in GeO_2 glass.

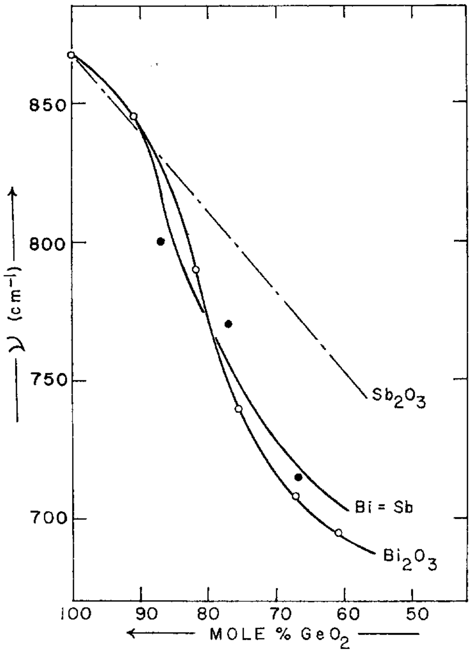

Figure 5 Dependence of ν_{Ge-O} on composition for $Bi_2O_3\cdot GeO_2$ glasses and for ternary glasses with $[Bi^{3+}] = [Sb^{3+}]$.

Fig. 5 also shows that the substitution of Sb^{3+} for Bi^{3+} in the lower GeO_2 content ternary glasses appears to have little effect on the value of ν_{Ge-O}. This is readily apparent in Fig. 6 which depicts the value of ν_{Ge-O} as a function of [Bi/Bi + Sb] for several series of constant GeO_2 content glasses. Most of the ν_{Ge-O} increase observed for the lower GeO_2 content glasses occurs only after two-thirds of the Bi^{3+} have been replaced by Sb^{3+}. These results suggest that in contrast to the 90 mol % GeO_2 glasses, there is a change in the degree of cross-linking that occurs for glasses close to the $Sb_2O_3\cdot GeO_2$ binary in the 60 to 70 mol % GeO_2 region. The GeO_4 tetrahedra in such glasses may actually be partially clustered, compared to their Bi_2O_3-rich

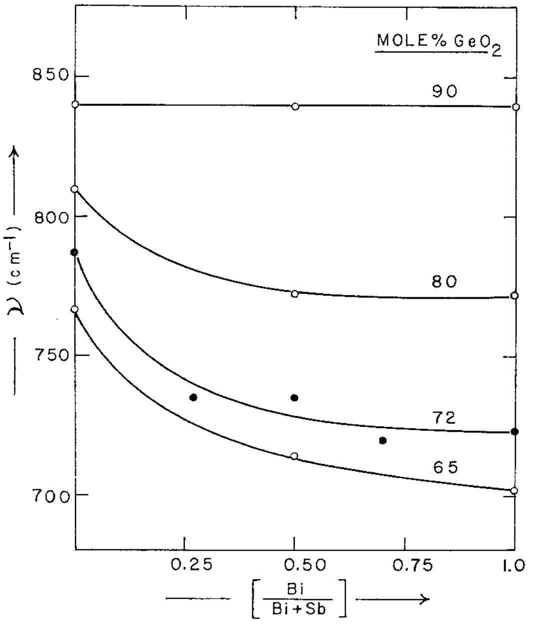

Figure 6 Dependence of ν_{Ge-O} on [Bi/Bi + Sb] for $Bi_2O_3 \cdot Sb_2O_3 \cdot GeO_2$ glasses of constant GeO_2 content.

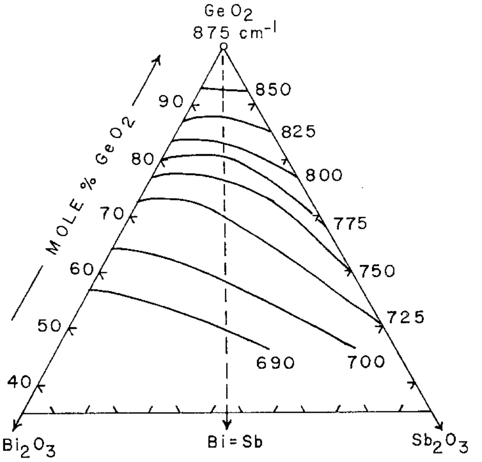

Figure 7 Isofrequency contours for ν_{Ge-O} in $Bi_2O_3 \cdot Sb_2O_3 \cdot GeO_2$ glasses.

counterparts. The cause of this clustering may be the tendency for the antimony-oxygen polyhedra to adapt a chain-like arrangement, with concurrent clustering, at elevated temperatures.

Thus, essentially two types of behaviour can be deduced from the infra-red results. First, almost ideal substitution of Sb^{3+} for Bi^{3+} at the higher GeO_2 contents. Second, for the lower GeO_2 contents, (a) almost complete separation of the bismuth polyhedra and GeO_4 tetrahedra for compositions close to the $Bi_2O_3 \cdot GeO_2$ binary, (b) considerable, but not nearly complete, separation of antimony polyhedra and GeO_4 tetrahedra for compositions close to the $Sb_2O_3 \cdot GeO_2$ binary, and (c) a non-ideal change from (a) to (b) as the [Bi/Bi + Sb] ratio decreases.

Isofrequency contours for ν_{Ge-O} can be developed from the information presented in Figs. 5 and 6 and plotted on a ternary composition diagram as in Fig. 7. Such contours do not necessarily join glass compositions with the same degree of cross-linking because there are several ways in which a tetrahedral network can be depolymerized. However, trends between such isofrequency contours can be sensitive indicators of broad regional differences in the degree of cross-linking [1, 12, 13].

The contour trends for the GeO_2-rich ternary glasses are symmetrically parallel to the ν_{Ge-O} maximum at GeO_2 (Fig. 7). This suggests that there are no significant differences in the degree of cross-linking between the two binary systems at GeO_2 contents above 88 mol %. However, the trends are no longer symmetrical with respect to GeO_2 for smaller GeO_2 contents. Instead, the contours start to bend around the Bi = Sb line and thereby become parallel to some $Sb_2O{\cdot}_3$ GeO_2 composition. Thus, the Sb_2O_3-rich ternary glasses that contain less than 80 mol % GeO_2 would appear to be more highly cross-linked than their Bi_2O_3-rich counterparts.

5. Conclusions

All of the physical property evidence strongly suggests that Bi_2O_3 does not necessarily depolymerize the GeO_4 network in GeO_2 glass in quite the same manner as Sb_2O_3. Thus, there appears to be little difference of effect between Bi_2O_3 and Sb_2O_3 for GeO_2 contents above 90 mol %. The result is to produce nearly ideal mixing behaviour for such GeO_2-rich ternary glasses in the $Bi_2O_3 \cdot Sb_2O_3 \cdot GeO_2$ systems. However, significant deviations from ideal mixing occur at lower GeO_2 contents in both binary $Bi_2O_3 \cdot GeO_2$ and ternary $Bi_2O_3 \cdot Sb_2O_3 \cdot GeO_2$ glasses. It would appear, therefore, that 40 mol % Bi_2O_3 more effectively depolymerizes GeO_2 than the same amount of Sb_2O_3.

It has been possible to relate the depolymerizing behavioural differences of Bi_2O_3 and Sb_2O_3 to the crystalline structures adopted at elevated temperatures by these oxides and their related compounds. Thus, the high temperature form of Bi_2O_3 is decidedly less cross-linked than that of Sb_2O_3. In addition, the structure of $Bi_4Ge_3O_{12}$ is known to contain discrete or completely depolymerized GeO_4 tetrahedra. Both of these structural factors were found to contribute to the greater effectiveness of Bi^{3+} in eliminating the GeO_4 tetrahedral network present in GeO_2 glass.

Finally, it was possible to develop isofrequency contours of ν_{Ge-O} that were readily interpretable in terms of the degree of cross-linking present for GeO_2-rich glasses in the $Bi_2O_3 \cdot Sb_2O_3 \cdot GeO_2$ system. This should serve to expand the role of this diagnostic technique in future glass characterization studies.

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