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Alteration of amorphous $Bi_4Ge_3O_{12}$ by Tl_2O and Na_2O

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Ternary thallium and sodium bismuth germanate glasses were prepared and their densities refractive indices, and infra-red spectra obtained. The effect of univalent cations on the stability of the arrangement of decoupled GeO_4 tetrahedra in amorphous $Bi_4Ge_3O_{12}$ was compared with the effect of divalent cations. The molar volumes of glasses with the nominal mol % composition 20 $M_2O(MO)$.20 Bi_2O_3.60 GeO_2 are directly related to the size and charge type of M^{z+}. However, the molar volumes of such glasses are inversely related to the ionic potential (z/r) of M^{z+}. The infra-red spectra of these ternary glasses exhibit ν_{Ge-O} shifts that reflect the presence of both isolated and small clusters of GeO_4 tetrahedra compared to amorphous $Bi_4Ge_3O_{12}$. This slight increase in the degree of polymerization appears to be directly related to the ionic potential of M^{z+}.

1. Introduction

Bismuth germanate glasses are of interest because of the unusual electronic properties of some of their crystalline counterparts. Thus, $Bi_4Ge_3O_{12}$ contains isolated GeO_4 tetrahedra arranged in a eulytine structure that exhibits the electro-optic effect [1-3]. Bismuth germanate glasses close to the $Bi_4Ge_3O_{12}$ composition also appear to contain completely decoupled or isolated GeO_4 tetrahedra [4]. The garnet-like arrangements of polyhedra in such amorphous solids are only slightly more voluminous than their crystalline counterparts. The substitution of Sb^{3+} for Bi^{3+} in such a glass occurs in a non-ideal manner, but causes no significant structural expansion until about a third of the Bi^{3+} are replaced. This can be explained by the fact that Sb_2O_3 depolymerizes GeO_2 in a slightly different manner than does Bi_2O_3 [4].

In contrast, the influence of divalent cations such as Ca^{2+} and Pb^{2+} is such that the amorphous eulytine arrangement of a $Bi_4Ge_3O_{12}$ glass does not exist at the $MO.Bi_2O_3.2GeO_2$ composition [5]. Those glasses appear to contain discrete GeO_4 tetrahedra as well as the $Ge_2O_7^{-6}$ dimers and short chains of GeO_4 tetrahedra that are found in $Pb_5Ge_3O_{11}$ [6] and $PbGeO_3$, respectively. The decoupled condition of these liquids and glasses has been shown to be responsible for the growth of crystals that can possess important electronic properties [7].

Univalent cations can also create non-bridging oxygen sites at the expense of oxygen atoms that bridge polyhedra in polymeric oxide fragments. Thus, alkali oxide additions to antimony germanate glasses create more decoupling of GeO_4 tetrahedra than do either Na_2O or Sb_2O_3 alone [8]. However, the coupling or polymerizing influence of univalent cations on the amorphous $Bi_4Ge_3O_{12}$ arrangement has not been explored. Accordingly, several series of $Tl_2O.Bi_2O_3.GeO_2$ glasses were prepared and examined. Similar Na_2O-containing glasses were prepared in order to compare the influence of cation size and electronic structure.

2. Experimental

10 g of each ternary glass were prepared in 20 cm³ recrystallized Al_2O_3 crucibles after grinding, weighing, and mixing selected sodium or thallium germanate glasses with selected bismuth germanate glasses. The preparation of the various binary glasses from electronic grade GeO_2 (Eagle-Picher Industries, Inc) and reagent grade materials is described elsewhere [4, 9]. A muffle furnace with an air atmosphere was used for all melting.

The GeO_2-poor ternary mixtures were melted

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for 45 to 60 min at 1175°C (Na_2O) or 1125°C (Tl_2O), while the GeO_2-rich ternary mixtures were melted for 45 to 60 min at 1300°C (Na_2O) or 1200°C (Tl_2O). Each melt was removed several times during the heating and swirled in the crucible to facilitate complete mixing. Each glass was air-quenched *in situ*. No penetration or attack of the dense Al_2O_3 crucibles was expected or found because of (a) the moderate Na_2O and Tl_2O contents of the ternary melts, (b) the use of relatively short mixing times and moderate temperatures, and (c) the moderate viscosities of these ternary melts. The smooth property trends to be discussed also support the absence of any significant Al_2O_3 contamination.

Post-run weight determinations revealed volatilization losses of about 0.05 wt% for the ternary sodium glasses and from 0.2 to 1.0 wt% for the ternary thallium glasses. The latter losses were most likely to be Tl_2O because they were proportional to the Tl_2O contents. The final compositions were adjusted accordingly.

Refractive indices were determined by using several series of certified index-of-refraction liquids (Cargille Laboratories, Inc) and a microscope (the Becke line technique). Specific gravities were determined with a Kraus-Jolly balance (Model 5000, Eberbach Corp) and benzene as the immersion fluid.

The infra-red spectra were recorded with a grating instrument (Model 521, Perkin-Elmer Corp). A reference-beam attenuator was used in conjunction with KBr/sample pellets. From 7 to 16 mg of each ternary glass were taken from larger, finely ground samples, mixed with 400 mg of KBr, and heated at 115°C for 30 min. The larger samples were taken from the GeO_2-poor glasses. The pellets were obtained by pressing the evacuated samples at 16 ton for 10 min. The shallow OH-absorption at $\approx$ 3400 cm^{-1} confirmed the relatively low H_2O content of the ternary glasses.

3. Results

The ternary glass compositions studied are related to the $Bi_4Ge_3O_{12}$ composition in Fig. 1. The glass series correspond to (M/M + Bi) ratios of 0.25 and 0.50. Selected physical properties of these glasses are given in Table I. The orange to red colour of most of the ternary glasses was not unexpected because the binary bismuth germanate glasses are similarly coloured [4]. Only the Tl_2O-rich glasses are not some shade of red.

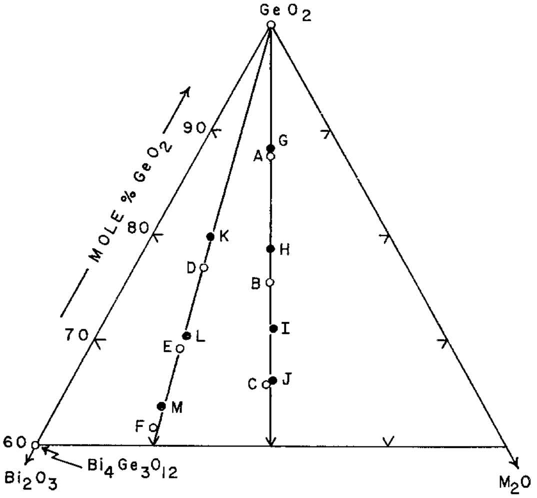

Figure 1 GeO_2-rich portion of the $M_2O.Bi_2O_3.GeO_2$ systems showing the glasses prepared (—○— Tl_2O, —●— Na_2O) and the $Bi_4Ge_3O_{12}$ composition.

The infra-red spectra covered the 4000 to 400 cm^{-1} region. The only absorption minima noted were those associated with the main Ge–O stretching vibration at 875 cm^{-1} in pure GeO_2 glass. Fig. 2 shows the spectral region of interest for some of the glasses prepared for this study.

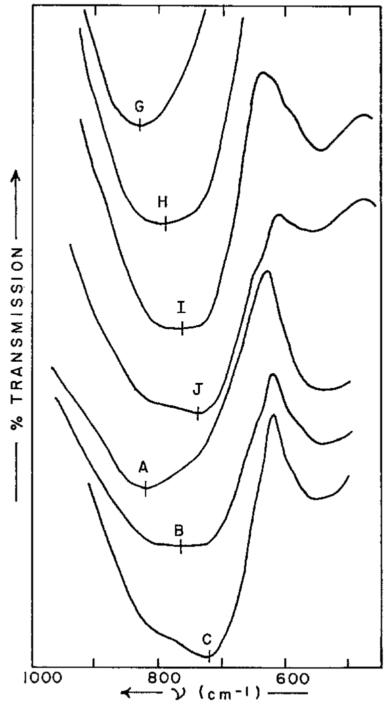

Figure 2 Infra-red spectra of thallium glasses (A, B, C) and sodium glasses (G, H, I, J) with (M/M + Bi) = 0.50.

TABLE I Physical properties of sodium and thallium bismuth germanate glasses

	Composition (mol %)				Density (g cm^{-3})*	Refractive index†	Colour‡
Glass	Na_2O	Tl_2O	Bi_2O_3	GeO_2			
A	—	6.18	6.27	87.56	5.118 ± 0.020	1.770 ± 0.010	LO
B	—	12.02	12.11	75.88	5.770 ± 0.030	1.860 ± 0.010	LO
C	—	16.89	17.38	65.73	6.295 ± 0.020	1.950 ± 0.010	Y
D	—	5.87	17.33	76.80	5.821 ± 0.012	1.860 ± 0.010	OR
E	—	7.60	23.34	69.05	6.080 ± 0.000	1.910 ± 0.010	DR
F	—	9.35	29.00	61.95	6.541 ± 0.000	1.990 ± 0.010	LY
G	5.82	—	5.80	88.37	4.436 ± 0.033	1.699 ± 0.013	O
H	10.67	—	10.78	78.55	4.802 ± 0.024	1.775 ± 0.005	OR
I	14.64	—	14.16	71.20	4.923 ± 0.020	1.795 ± 0.005	B
J	16.87	—	16.99	66.14	4.984 ± 0.030	1.810 ± 0.010	DB
K	5.04	—	15.07	79.89	(5.137) ± 0.004	—§	R
L	7.63	—	21.97	70.40	(5.494) ± 0.010	—§	DR
M	8.89	—	27.52	63.59	(5.827) ± 0.006	—§	DR

*Uncertainty results from duplicate determinations.

†Uncertainty results from bracketing procedure used with the refraction technique.

§Opal glass.

‡Colours judged in comparison with binary bismuth germanate glasses from [4].

Colours: L = light, D = dark, O = orange, B = brown, R = red, Y = yellow.

Macroscopic phase separation yielded opal glasses for the three glasses with (Na/Na + Bi) = 0.25 (glasses K, L, and M). This effect was not noted for the corresponding thallium glasses (D, E, and F). Hence, the atomic level structural arrangements of bismuth germanate glasses may be sensitive to the size and electronic nature of any added univalent cations.

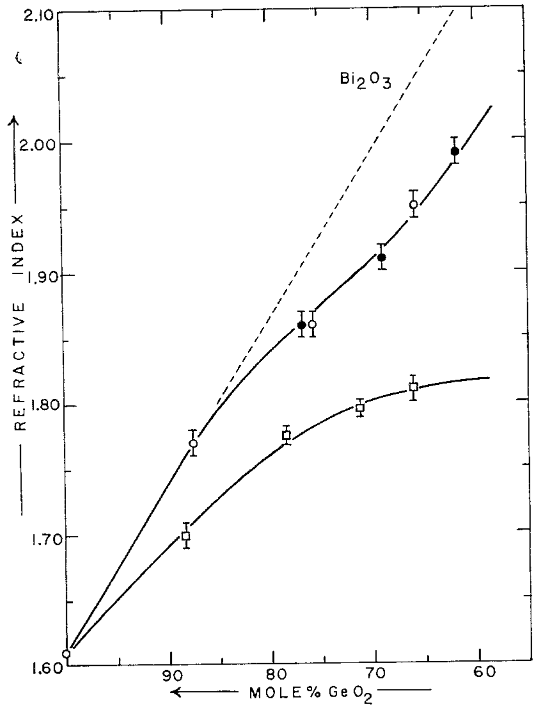

Figure 3 Refractive index versus composition for glasses with (Tl/Tl + Bi) = 0.50 (—○—), (Tl/Tl + Bi) = 0.25 (—●—), (Na/Na + Bi) = 0.50 (—□—), and $Bi_2O_3.GeO_2$ glasses (- - -) (see [4]).

4. Discussion

4.1. Refractive indices

The compositional dependence of refractive index for the various ternary glass series is shown in Fig. 3. The addition of small amounts of Tl_2O to GeO_2-rich bismuth germanate glasses appears to have little effect on refractive index compared to the effect of larger amounts of Tl_2O added to GeO_2-poor glasses. In the latter case, the refraction decrease appears to be independent of the (Tl/Tl + Bi) ratio. However, Fig. 4 shows that the refraction decrease is actually a minimum for GeO_2-poor ternary glasses.

The presence of such a pronounced refraction minimum indicates a decrease in the atomic packing efficiency for such thallium-containing ternary glasses [4, 6]. The molar volume results to be discussed below confirm such a situation. In contrast to the thallium glasses, the sodium-containing ternary glasses exhibit nearly additive refractivities at all GeO_2 levels studied (Fig. 4).

4.2. Molar volumes

The addition of both Bi_2O_3 and Tl_2O (or Na_2O) to amorphous GeO_2 produces the molar volume trends depicted in Fig. 5. The volume trend for

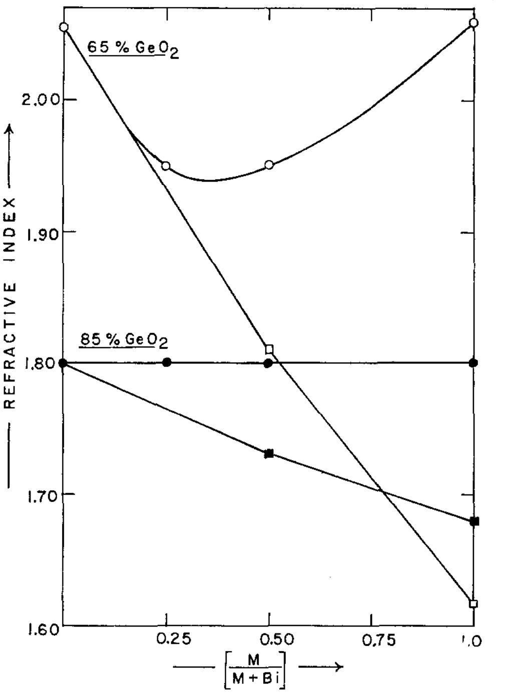

Figure 4 Refractive index versus (M/M + Bi) ratio for constant GeO_2-content glasses: Tl_2O (—○—, —●—) and Na_2O (—□—, —■—). Binary thallium germanate data from [9] and [10]. Binary sodium germanate data from [11].

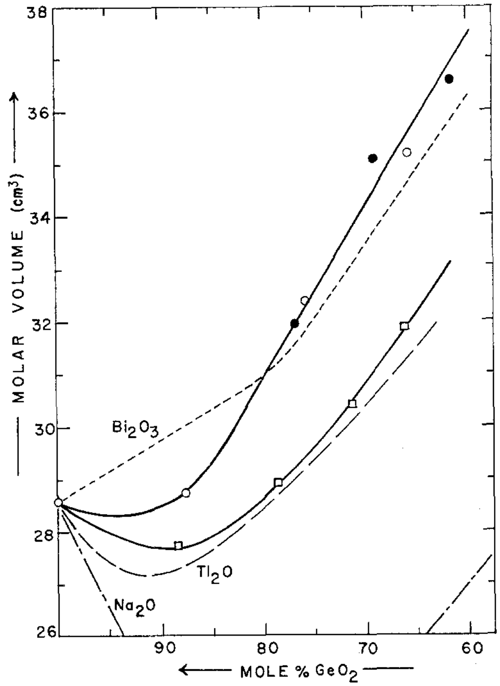

Figure 5 Molar volume versus composition for glasses with (Tl/Tl + Bi) = 0.50 (—○—), (Tl/Tl + Bi) = 0.25 (—●—), (Na/Na + Bi) = 0.50 (—□—), and $Bi_2O_3 . GeO_2$ glasses (- - -).

the (Na/Na + Bi) = 0.50 glasses is intermediate between the data plots for sodium germanate and bismuth germanate glasses. However, the corresponding (Tl/Tl + Bi) = 0.25 and 0.50 volume trends are not intermediate between the data plots for thallium germanate and bismuth germanate glasses. Fig. 6 shows that while nearly ideal mixing occurs in the GeO_2-rich thallium glasses, such is not the case at lower GeO_2 levels. The addition of Tl_2O to an amorphous $Bi_4Ge_3O_{12}$ composition clearly preserves the rather open structure. The positive deviations from volume additivity amount to 7.5% at the (Tl/Tl + Bi) = 0.25 composition and actually represent a slight expansion of the amorphous $Bi_4Ge_3O_{12}$ structure. This finding confirms the looser packing anticipated from the refractive index minimum (Fig. 4).

A similar, but slightly less pronounced effect occurs with the addition of 15 to 20 mol% Na_2O to amorphous $Bi_4Ge_3O_{12}$ (Fig. 6). However, a two-phase system that probably involves a GeO_2-rich phase appears to be more stable than an expanded $Bi_4Ge_3O_{12}$ arrangement at *lower* (Na/Na + Bi) ratios (glasses K, L, and M in Table I).

The addition of significant quantities of either CaO or PbO collapses the amorphous $Bi_4Ge_3O_{12}$ arrangement to a considerable extent [5]. All these results suggest a possible relationship between glass volume (essentially oxygen packing) and cation size or ionic potential. Effective ionic radii have been developed for octahedral and other co-ordination situations involving cations in crystalline oxide environments [12]. The use of these ionic radii can produce linear relationships between glass molar volume and cation size [13]. Fig. 7a shows such relationships for different charge types in a 60 mol% GeO_2 glass with M_2O (or MO)/Bi_2O_3 = 1.00. Such a glass composition is midway between $Bi_4Ge_3O_{12}$ and an approximate metagermanate composition in which short chains of GeO_4 tetrahedra exist. Hence, the ternary glass would be expected to contain relatively small polyanionic fragments that contain GeO_4 tetrahedra.

Fig. 7b shows that the molar volume of such a ternary bismuth germanate glass is also inversely related to the ionic potential (z/r) of the added cation. This relationship suggests that the sub-

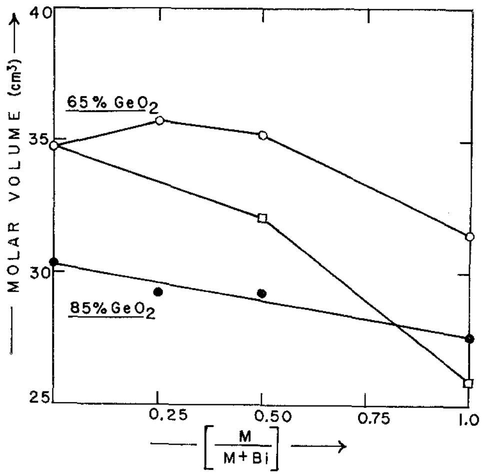

Figure 6 Molar volume versus (M/M + Bi) ratio for constant GeO_2-content glasses: Tl_2O (—○—, —●—), Na_2O (—□—).

stitution of 15 to 20 mol% of either M_2O or MO for some of the Bi_2O_3 in amorphous $Bi_4Ge_3O_{12}$ occurs in a manner that (a) is independent of the electronic nature of the added cation and (b) involves the introduction of a considerable degree of ionic bonding. The latter must replace the covalent Bi–O–Ge-linkages in amorphous $Bi_4Ge_3O_{12}$.

Fig. 7b also suggests that such a 60 mol% GeO_2 glass contains octahedrally and/or eight-fold co-ordinated cation sites that are about the size of K^+ (~ 1.38 Å). The Tl^+ is apparently too large to occupy such a site without expanding the amorphous arrangement of polyhedra. Smaller ions with higher ionic potentials contract the arrangement of polyhedra to a degree that suggests smaller octahedral sites, as well as incomplete separation of the GeO_4 tetrahedra from each other (compared to the complete isolation in $Bi_4Ge_3O_{12}$). The evidence for the latter effect in Ca^{2+} and Pb^{2+} containing bismuth germanate glasses has been presented elsewhere [5].

4.3. Infra-red spectra

The binary alkali and thallium germanate glasses at the 65 mol% GeO_2 level do contain some GeO_6 octahedra which have caused ν_{Ge-O} to shift to a frequency well below 875 cm^{-1} [14]. The latter frequency is observed for the random arrangement of corner shared GeO_4 tetrahedra in pure GeO_2 glass. However, a *ternary* 60 mol % GeO_2 glass *with* (M/M + Bi) = 0.50 would not be expected to contain a significant concentration of GeO_6 octahedra. The magnitudes of the molar volumes and the positive volume deviations from ideality observed for such ternary glasses (Figs. 5 and 6) confirm that conclusion.

The moderate increase of ν_{Ge-O} that accompanies the substitution of Ca^{2+} or Pb^{2+} for Bi^{3+} in amorphous $Bi_4Ge_3O_{12}$ has been related to the presence of some coupled GeO_4 tetrahedra [5]. Now, the ν_{Ge-O} shift from 875 cm^{-1} in pure GeO_2 glass to the 725 to 675 cm^{-1} range in a 60 mol% GeO_2 glass with (M/M + Bi) = 0.50 is indicative of almost complete decoupling of GeO_4 tetrahedra (Fig. 8). The shift of ν_{Ge-O} is not quite as pronounced with Na^+ as it is with Tl^+ (Fig. 9). However, this small difference is not necessarily related to the ν_{Ge-O} difference between comparable *binary* sodium and thallium germanate glasses that

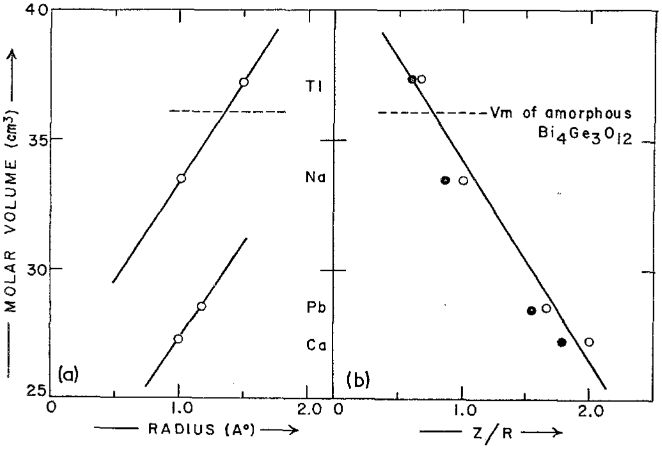

Figure 7 Molar volumes of 60 mol % GeO_2 glasses with M_2O (or MO)/Bi_2O_3 = 1.00 versus (a) cation radius and (b) cation ionic potential (*z*/*r*). Octahedral (—○—) and eight-fold (—●—) co-ordination.

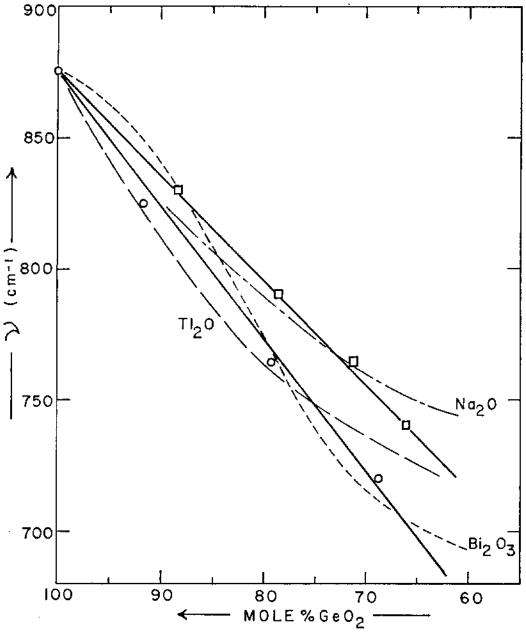

Figure 8 Dependence of $\nu_{\text{Ge-O}}$ on composition for ternary bismuth germanate glasses with (Tl/Tl + Bi) = 0.50 (—○—) and (Na/Na + Bi) = 0.50 (—□—). Binary bismuth (- - -), thallium (— —), and sodium (— — —) germanate glass data also shown.

contain a considerable concentration of GeO_6 octahedra (Fig. 9). The small difference may be caused by a slightly larger degree of coupling for the GeO_4 tetrahedra in the *ternary* sodium bismuth germanate glass.

The above results and conclusions suggest a moderate dependence of the degree of decoupling on modifier ionic potential for a 60 mol % GeO_2 *ternary* bismuth germanate glass. However, such a statement must remain speculative until additional evidence concerning the actual polyanionic fragment distributions is accumulated.

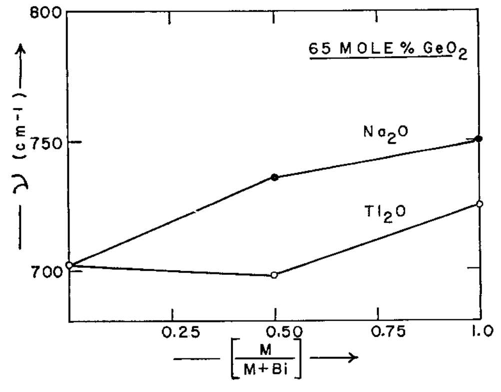

Figure 9 Dependence of $\nu_{\text{Ge-O}}$ on (M/M + Bi) for sodium and thallium germanate glasses containing 65 mol % GeO_2.

5. Conclusions

Tl_2O or Na_2O can be added to amorphous $Bi_4Ge_3O_{12}$ to produce stable ternary glasses that are both dense and highly refractive. The molar volumes of glasses with the nominal composition ($2M^+$, M^{2+}) $Bi_2Ge_3O_{10}$ have been found to be directly dependent upon the size and charge type, and inversely dependent upon the ionic potential (z/r), of the cation M.

The cation size dependence for molar volume suggests the presence of octahedral or eight-fold univalent cation sites that are about 1.3 Å radius. The inverse dependence upon ionic potential confirms the dominant influence of ionic bonding in such ternary bismuth germanate glasses. The arrangement of decoupled GeO_4 tetrahedra in amorphous $Bi_4Ge_3O_{12}$ appears to collapse with the substitution of very high ionic potential cations for bismuth.

While the glasses with the nominal composition (Tl, Na)$_2$$Bi_2Ge_3O_{10}$ are about as voluminous as amorphous $Bi_4Ge_3O_{12}$, the infra-red results for the sodium glasses suggest that they may not necessarily contain just decoupled GeO_4 tetrahedra. They resemble their (Ca, Pb)$Bi_2Ge_3O_{10}$ counterparts in that they may contain small anionic clusters of GeO_4 tetrahedra in addition to some anionic decoupled GeO_4 tetrahedra. Hence, the substitution of either M_2O or MO for Bi_2O_3 in amorphous $Bi_4Ge_3O_{12}$ may increase, if only slightly, the degree of polymerization experienced by GeO_4 tetrahedra.

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