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Infra-red detection of depolymerization in Tl_2O-GeO_2-SiO_2 glasses

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Three series of glasses containing 15, 26, and 35 mol % Tl_2O were prepared in the Tl_2O-GeO_2-SiO_2 system and their infra-red spectra, densities, and refractive indices determined. Refraction decreases as SiO_2 substitutes for GeO_2 and is additive with respect to the two binary series, except for slight positive deviations with the low SiO_2 content 35 mol % Tl_2O glasses. All glass series exhibit small negative molar volume deviations from additivity at low SiO_2 contents and small positive deviations from additivity at higher SiO_2 contents. The strong compositional dependence of the main infra-red stretching frequency values (1100 cm^{-1} for SiO_2 and 875 cm^{-1} for GeO_2) are shown to be relatively sensitive indicators of changes in the polymeric makeup of these ternary oxide glasses. Loosening and/or depolymerization of either pure or damaged MO_4 networks is accompanied by ν_{Si-O} and/or ν_{Ge-O} shifts to smaller frequencies. The frequency changes that accompany the progressive replacement of GeO_2 by SiO_2 suggest that (a) SiO_4 tetrahedra initially replace GeO_4 tetrahedra, (b) GeO_6 octahedra subsequently transform to GeO_4 tetrahedra, and (c) GeO_4 tetrahedra finally take part in repair of damaged SiO_4 networks. Use of a previously developed infra-red isofrequency contour technique revealed similar ternary trends for the two vibrational modes of interest. This emphasizes the ability of such contour trends to reflect the overall degree of network crosslinking present in ternary oxide glasses.

1. Introduction

The infra-red frequency for absorption by a particular metal-oxygen linkage in a crystal is known to occur at a smaller value when that linkage occurs in an isolated polyhedron instead of in a polyhedron that is part of a larger polymeric species [1]. Recently, a technique was developed for illustrating the relationship between such infra-red frequency shifts and the extent of crosslinking in ternary oxide glasses [2]. In that study, isofrequency contours were developed for the main antisymmetric Ge-O and Si-O stretching vibrations in germania and silica glasses that also contained AlO_4 tetrahedra. Different modes of network depolymerization were shown to directly influence the compositional dependence of the respective isofrequency contours.

Since numerous oxide glasses of interest can contain more than one network former, it was decided to extend the infra-red isofrequency contour technique to ternary glasses that contained two network formers that were known to depolymerize differently. The mutual influence of each network former on the other could then be simultaneously examined by noting the frequency shift of each linkage in the same glass composition.

This paper describes the extension of the aforementioned technique to silicogermanate glasses of varying Si/Ge ratios that contain from 15 to 35 mol % Tl_2O. Densities and refractive indices were also determined. This system was chosen because GeO_2 and SiO_2, are known to depolymerize differently [3] and because some pertinent structural information was available for the three binary systems [2, 4-8].

2. Experimental

The glasses were prepared from Electronic Grade GeO_2 powder (Eagle Picher Co), 200 mesh ceramic grade SiO_2 (Pennsylvania Glass Sand Co), and $TlNO_3$ (K and K Laboratories, Inc). The dried batches were mixed in 25 cc platinum crucibles and air melted in a Blue M Muffle Furnace (Model No. RG-2090 A-1). The carefully weighed batches were usually held for 0.5 h at 275°C, 0.5 h at 400°C, inserted at 650°C and heated to about 1100°C during 2 h, and then held at that temperature for 0.5 h. Slightly longer times and higher temperatures were used for the SiO_2-rich glasses. Final glass compositions were determined by the mass balance technique [4].

Densities were measured with a Kraus Jolly Balance (Eberbach Corporation, Model No. 5000) using benzene as the immersion fluid [4]. Refractive indices were determined by using several series of certified liquids (Cargille Laboratories) and a microscope to follow the movement of the Becke line [4, 5].

The infra-red spectra were recorded with a Perkin-Elmer Model 521 Grating Infra-red Spectrophotometer. From 3 to 6 mg of each ground glass were mixed with 400 mg of KBr and heated for 0.5 h at 125°C. The KBr pellets were then formed by pressing the evacuated samples at 16 tons for 10 min. Smaller amounts of glass could produce ill-defined absorption minima, while larger amounts of glass could produce overlap of the Ge-O and Si-O absorption bands. Several pellets usually had to be prepared in order to obtain a satisfactory spectrum in the region of specific interest (1100 to 400 cm^{-1}).

3. Results

The compositions, refractive indices, densities, and colours of the three constant Tl_2O content glass series are given in Table I. The compositional dependence of refractive index was close to additive for all three series. The only exceptions are (a) a + 1% deviation for Si/Ge < unity glasses (N, O, and P) at the 35 mol % Tl_2O level, (b) a + 1% deviation for glass G, and (c) a − 0.5% deviation for glasses L and R. In this regard, the measured refractive indices of the two thallium silicate glasses (M and S) form a straight line when plotted versus composition together with the value for SiO_2 glass from [9].

The densities were converted into the more meaningful molar volumes which are shown in Fig. 1. Slight negative deviations from additivity occur for small SiO_2 contents, while slight

TABLE I Compositions and properties of Tl_2O-GeO_2-SiO_2 glasses

Glass	Tl_2O	Mol % GeO_2	SiO_2	Density ($g\ cc^{-1}$)	Refractive index	Colour
A	15.0	80.0	5.0	5.411	1.810	VFY/G†
B	15.0	72.0	13.0	5.294	1.785*	VFY/G†
C	15.0	63.0	22.0	5.091	1.765*	VFY/G
D	15.0	54.0	31.0	4.966	1.755*	VFY/G
E	15.0	42.5	42.5	4.726	1.735*	VFY/G
F	14.4	24.9	60.7	4.385	1.698*	VFY/G
G	26.0	69.0	5.0	6.355	1.950	YG†
H	26.0	61.0	13.0	6.101	1.930	YG†
I	26.0	52.0	22.0	5.963	1.910	YG
J	25.9	44.1	30.0	5.840	1.890	YG
K	25.8	37.1	37.1	5.674	1.870	YG
L	26.0	22.0	52.0	5.474	1.830	YG
M	24.3	0.0	75.7	5.048	1.755*	YG
N	34.9	60.1	5.0	6.941	2.07	Y†
O	35.0	53.0	12.0	6.794	2.05	Y†
P	34.9	42.0	23.0	6.572	2.03	Y
Q	34.9	32.6	32.5	6.428	1.99	Y
R	34.9	19.0	46.1	6.154	1.95	Y
S	34.7	0.0	65.3	5.999	1.93	Y

*± 0.005 or less, all of rest ± 0.010.

†Slightly darker colour than the corresponding Tl_2O-GeO_2 binary glass. Others comparable to the Tl_2O-GeO_2 binary glass colour (see [4]). VFY/G = very faint yellow green, YG = yellow green, Y = yellow.

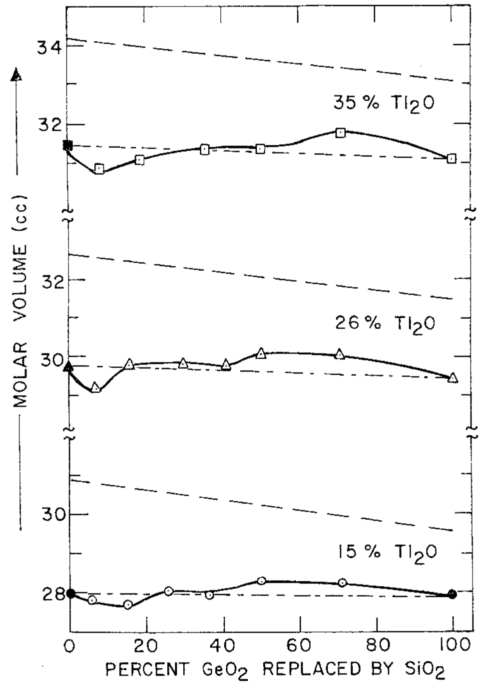


Figure 1 Molar volume as a function of % GeO_2 replaced by SiO_2 for Tl_2O-GeO_2-SiO_2 glasses. Ideal mixing (- - -) and additivity (– • –) also shown).

positive deviations from additivity occur for the SiO_2-rich glasses. These volume trends occur at all Tl_2O levels studied. In this regard, the measured densities of the two thallium silicate glasses (M and S) are located directly on a plot of the density results from [8].

The individual infra-red spectra in the frequency region of interest are shown for the three different Tl_2O content glass series in Figs. 2a, b and c. The spectra of the two thallium silicate glasses (marked 100% GeO_2 replaced by SiO_2 in Figs. 2b and c) were also previously unreported. In general, both ν_{Si-O} and ν_{Ge-O} appear to shift to lower frequencies and then back slightly as the shift to lower frequencies and then back slightly as the SiO_2 continues to replace GeO_2.

4. Discussion

4.1. Molar volume and refraction

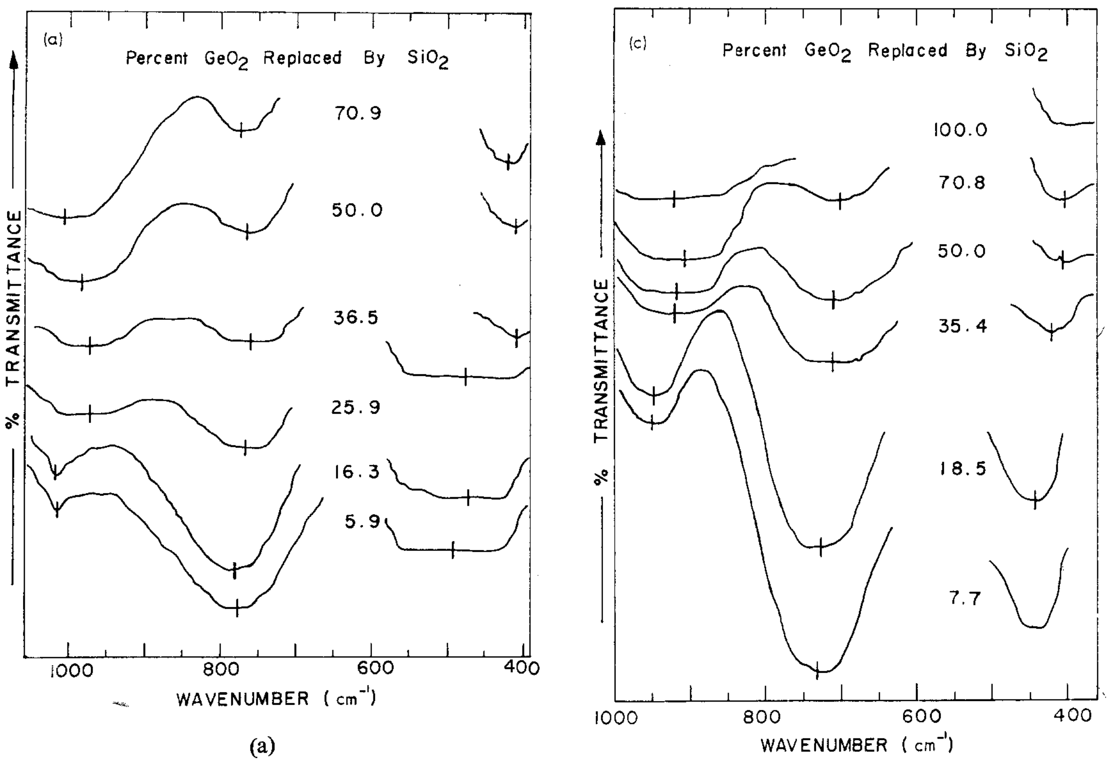
The depolymerization of a GeO_4 tetrahedral network that accompanies the addition of modifiers such as alkali oxides involves the formation of GeO_6 octahedra. In contrast, the depolymerization of an SiO_4 tetrahedral network by similar species involves the retention of SiO_4 tetrahedra [3]. This structural difference can manifest itself in a number of ways. For example, the increased packing efficiency of an octahedron compared to a tetrahedron can create partial molar volume changes for GeO_2 that lead to measurable molar volume changes for glasses that contain a significant concentration of such species. Fig. 1 depicts such a situation for the binary thallium germanate glasses whose deviations from ideality (----) are much larger than those of their silicate analogues.

An earlier study of 25 mol % Na_2O melts in the Na_2O-SiO_2-GeO_2 system at 1300°C revealed positive volume deviations from additivity as SiO_2 was substituted for GeO_2 [10]. This trend was rationalized with partial molar volume models that incorporated (a) the elimination of some GeO_6 octahedra at SiO_2 substitutions of less than 10% and (b) the elimination of the remaining GeO_6 octahedra when the SiO_2 substitutions rose to the 35 to 50% range. The small positive volume deviations observed for the higher Si/Ge ratio glasses in Fig. 1 are also reconcilable with a partial molar volume model that involves GeO_4 tetrahedra [11].

However, the negative volume deviations from additivity (minima) that are observed at *all* Tl_2O levels for small SiO_2 concentrations in Fig. 1 are difficult to rationalize completely within the scope of a partial molar volume approach. Thus, all of the 15 and 26 mol % Tl_2O glasses with 50% or less of the GeO_2 replaced, except for glass G, can be rationalized in terms of partial molar volume models that involve the retention of the approximate binary concentration of GeO_6 octahedra up to about 35 to 40% GeO_2 replaced [11].

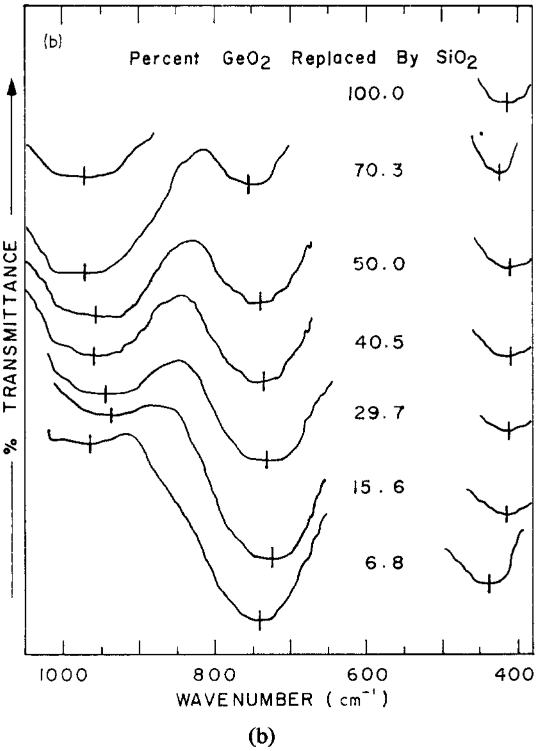
Only in the case of glass G is there the suggestion that the addition of a small amount of SiO_2 creates an increase in the GeO_6 octahedron concentration. The lack of appropriate information for binary thallium germanate glasses that contain more than 35 mol % Tl_2O precludes an effective partial molar volume analysis of the 35 mol % Tl_2O ternary glass series. However, the fact that the volume minima and maxima occur for all three glass series studied (Fig. 1) suggests that the compositional dependence of the structural changes is not different at the 35 mol % Tl_2O level.

A slightly more efficient mode of atom packing would be expected to produce a small refraction increase, and vice versa. The previously mentioned refraction deviations for these glasses,



(a)

(c)



(b)

Figure 2 Infra-red spectra of Tl_2O-GeO_2-SiO_2 glasses containing (a) 15 mol% Tl_2O, (b) 26 mol% Tl_2O, and (c) 35 mol % Tl_2O.

although small, are nevertheless in the same direction as the volume trends. Thus, the two experimental parameters complement each other, particularly at the higher Tl_2O levels where the deviations are slightly larger.

4.2. Infra-red spectra

The KBr pellet preparation procedures were such that the products were of almost identical thickness and contained similar concentrations of the main absorbing species. It was possible to avoid quantitative restrictions associated with the use of just A_{M-O} (where $A = \log 1/T =$ absorbence at ν) by calculating the A_{Si-O}/A_{Ge-O} ratio for each glass. The Si-O and Ge-O vibrations are close enough in wavenumber (ν) to assume a common T_0. The linear dependence of this ratio upon concentration (Fig. 3) suggests not only a reasonable adherence to the Lambert-Beer Law as Si replaces Ge, but also that the Si-O and Ge-O vibrations may behave in an independent fashion. As would be expected, the inverse ratios (A_{Ge-O}/A_{Si-O}) are not linearly related to the % GeO_2 replaced by SiO_2. They

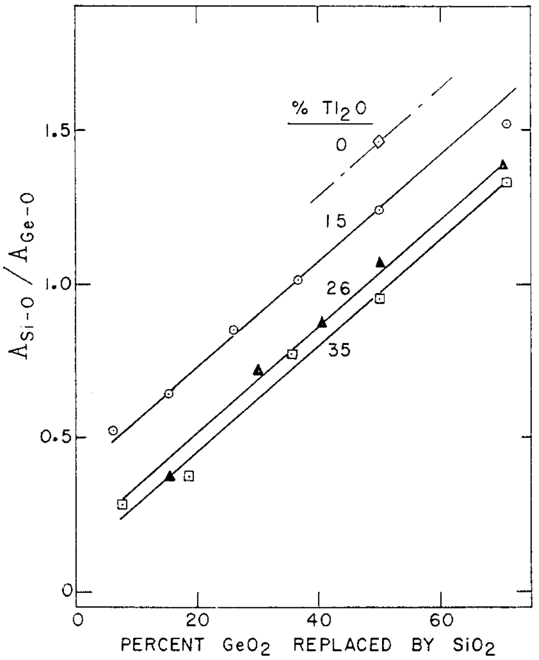


Figure 3 Ratio of A_{Si-O}/A_{Ge-O} versus % GeO_2 replaced by SiO_2. Value on 0% Tl_2O line obtained for a glass prepared in [6].

decrease rather sharply, particularly at the higher Tl_2O levels, for GeO_2 replacements below 30% and then gradually level off for higher Si/Ge ratios.

The Lambert-Beer Law states that $A = \alpha bc$ (where α = molar extinction coefficient, b = path length, and c = concentration). The path length, b, was held constant in these experiments. Since the Si to Ge concentration ratio is effectively fixed for any constant Si/Ge ratio glass series, the ratio of A_{Si-O}/A_{Ge-O} for that series should vary directly with the $\alpha_{ei-O}/\alpha_{Ge-O}$ ratio. In this regard, the molar extinction (α) is characteristic of both the frequency at which absorption occurs and parameters such as coordination ($\alpha_{MO_4} > \alpha_{MO_6}$ [12]) or structure.

The A_{Si-O}/A_{Ge-O} ratio also appears to decrease linearly as the Tl_2O content increases at a given Si/Ge ratio for these glasses (Fig. 4). Only SiO_4 and GeO_4 tetrahedra, not GeO_6 octahedra, should be present in the Si/Ge = 1.0 glasses, regardless of the Tl_2O level. However, gross structure change could be responsible for the observed A_{Si-O}/A_{Ge-O} decrease. Thus, the *binary* Si/Ge = 1.0 germanium silicate glass is known to possess a highly crosslinked structure [6, 7] in which the Si-O vibration appears to be the better of the two absorbers (Fig. 3). A more fluid, ionic liquid (from which the glass is obtained) is created when the Tl_2O content is increased to 35 mol % at the expense of SiO_2 and GeO_2. In such a glass, both the SiO_4 and GeO_4 tetrahedra probably belong to relatively small polyanions. Apparently, there is a tendency for either the Si-O vibration to absorb less or the Ge-O vibration to absorb more in just such an environment.

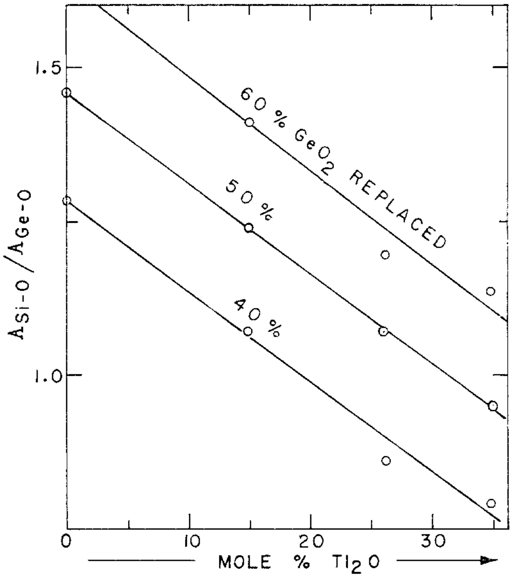


Figure 4 Ratio of A_{Si-O}/A_{Ge-O} versus mol % Tl_2O for fixed Si/Ge ratio glasses.

The Si/Ge ratio at which the Si-O and Ge-O vibrations are comparable absorbers ($A_{Si-O}/A_{Ge-O} = 1.0$) shifts from 0.25 to 1.00 as the Tl_2O content increase from zero to 35 mol % respectively (Fig. 3). More SiO_2 is "required" at the higher Tl_2O levels to make the Si-O vibration the better absorber of the two. All of these results strongly suggest that the Si-O vibration is the better absorber only when it is present (a) in a highly crosslinked environment and/or (b) in relatively large concentrations.

The values of ν_{Si-O} and ν_{Ge-O} at maximum absorption are shown as functions of composition for the constant Tl_2O glass series in Figs. 5 and 6 respectively. The 108 cm^{-1} ν_{Si-O} shift that accompanies the addition of 20 mol % Tl_2O to SiO_2 (Fig. 5) is more than twice the 46 cm^{-1} shift observed for a similar addition of Na_2O [2]. This *difference* is also much larger than that

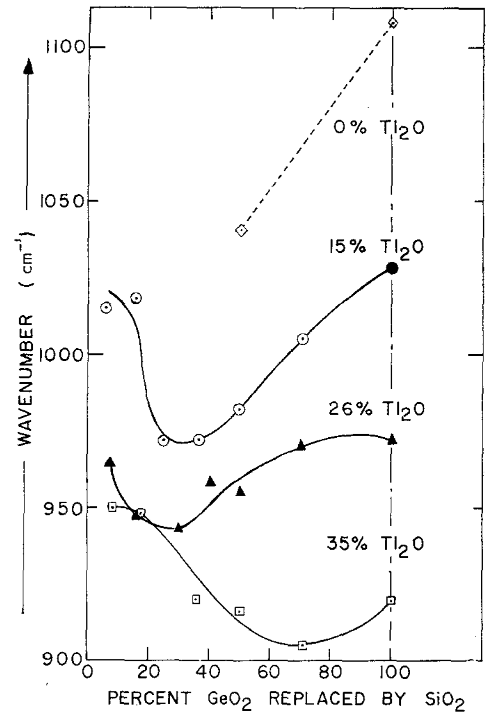


Figure 5 Dependence of ν_{Si-O} on % GeO_2 replaced by SiO_2 for constant Tl_2O content glass series.

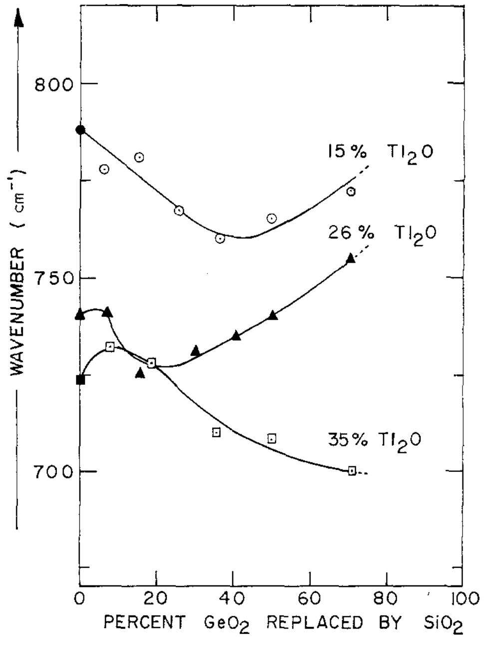


Figure 6 Dependence of ν_{Ge-O} on % GeO_2 replaced by SiO_2 for constant Tl_2O content glass series.

found for similar additions of Tl_2O and Na_2O to GeO_2 [2]. Both of these effects may be related to the larger mass of Tl and Ge, compared to Na and Si, that can produce less energetic vibrations. In this regard, although SiO_2 and GeO_2 depolymerize differently, the addition of 20 mol% Tl_2O to each shifts *both* ν_{Si-O} and ν_{Ge-O} by about 100 cm^{-1}.

The limited ν_{Si-O} data for binary GeO_2-SiO_2 glasses (dashed zero % Tl_2O line in Fig. 5) reveals a low frequency shift even in the absence of extensive depolymerization.* Substitution of 50% of the SiO_4 tetrahedra in SiO_2 by GeO_4 tetrahedra appears to produce a ν_{Si-O} shift of 50 cm^{-1}. The corresponding ν_{Ge-O} band was not as resolveable. This ν_{Si-O} shift could be associated with any of the following: (a) the larger mass of Ge compared to Si, (b) the irregular nature of the GeO_4 tetrahedron, and (c) the slightly loosened network [6]. Thus, the initial ν_{Si-O} decrease observed for GeO_2 substitutions of SiO_2 at all Tl_2O levels in Fig. 5 is not entirely unexpected. The SiO_4 tetrahedra simply exist within looser, less crosslinked, and smaller polymeric fragments compared to pure SiO_2.

More unusual are the ν_{Si-O} increases that occur at the lowest SiO_2 contents for all Tl_2O levels studied (Fig. 5). They closely parallel the ν_{Ge-O} trends in the same regions (Fig. 6) and may reflect the unique role suggested for SiO_4 tetrahedra in such situations [10]. That is, the SiO_4 tetrahedra may act as bridging MO_4 species for GeO_6 clusters and thus be selectively bound to moderately large, but finite polymeric anions.

The substitution of SiO_2 for GeO_2 at the 15 and 26 mol% Tl_2O levels creates a ν_{Ge-O} decrease (Fig. 6) that may be related to the role played by SiO_4 tetrahedra in these glasses. If the SiO_4 tetrahedra merely replace GeO_4 tetrahedra, the GeO_6/GeO_4 ratio would rise with a concomitant increase of the lower frequency GeO_6 contribution to ν_{Ge-O} (with GeO_6 octahedra and GeO_4 tetrahedra present, ν_{Ge-O} is an average). The subsequent increase of ν_{Ge-O} at higher Si/Ge ratios (beyond 40 and 20% GeO_2 replaced at the 15 and 26% Tl_2O levels respectively) can readily be associated with the conversion of GeO_6 octahedra to GeO_4 tetrahedra. The latter engage in repair of the now damaged, predominantly SiO_4 network. The most likely reason for the gradual ν_{Ge-O} decrease and levelling noted at

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*The infra-red spectrum presently obtained for this equimolar GeO_2-SiO_2 glass, prepared for [6], was quite similar to that reported for the same sample by Borelli [7].

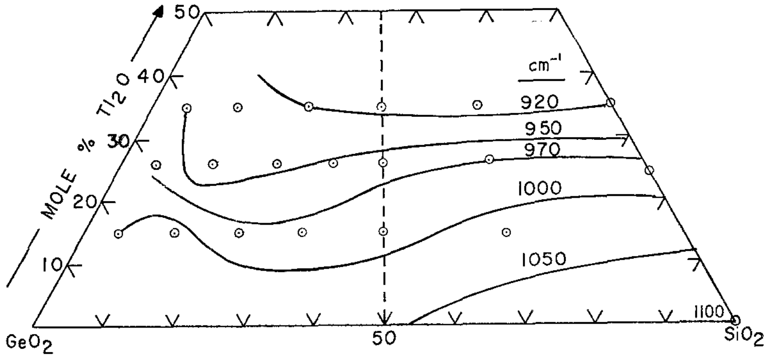

Figure 7 Isofrequency contours for ν_{Si-O} in Tl_2O-GeO_2-SiO_2 glasses.

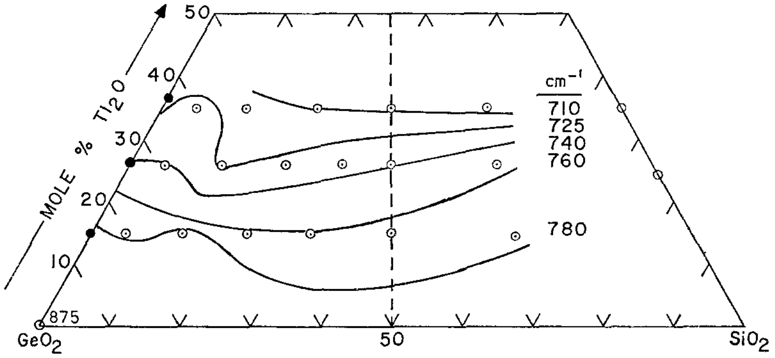

Figure 8 Isofrequency contours for ν_{Ge-O} in Tl_2O-GeO_2-SiO_2 glasses.

higher Si/Ge ratios for the 35 mol % Tl_2O level is that even the damaged SiO_4-rich network no longer exists. Instead, the GeO_4 tetrahedra exist as constituents of a mixture of relatively small polyanions.

Isofrequency contours can be developed for a given linkage or vibration (Si-O, Ge-O, etc.) and sketched on a ternary composition diagram [2]. Such a contour, while it connects ternary compositions that possess the same frequency for a given linkage, does not necessarily connect glasses of similar structure. This arises because several different depolymerization mechanisms can cause frequency shifts. However, trends between given contours may readily illustrate the compositional dependence of the degree of crosslinking in a ternary glass system.

Figs. 7 and 8 depict such isofrequency ν_{Si-O} and ν_{Ge-O} contours for the ternary glasses studied. Significant features of Fig. 7 include (a) the ν_{Si-O} peak at pure SiO_2, (b) the nearly parallel nature of the ν_{Si-O} contours for the higher Si/Ge ratio glasses, and (c) the irregularity of the ν_{Si-O} contours for Si/Ge ratios $<$ unity. These features suggest (a) a highly polymerized structure at and close to pure SiO_2, (b) degrees of depolymerization for ternary glasses with Si/Ge $>$ unity that resemble those of binary thallium silicate glasses of similar network former content, and (c) a somewhat more varied polymeric environment for SiO_4 tetrahedra in the ternary glasses with Si/Ge $<$ unity. The latter occurs within a region in which GeO_6 octahedra appear to transform to GeO_4 tetrahedra.

The most interesting aspect of Fig. 8 is that the overall ν_{Ge-O} contour trends are quite similar to those reported for ν_{Si-O} in Fig. 7. This suggests that *such* frequency *contour trends* may be general indicators of the *overall* degree of network crosslinking that is present at a given composition rather than *highly specific* indicators of localized Ge-O and/or Si-O bonding. Thus, while the isofrequency contour trends in Figs. 7 and 8 reflect *broad regional* depolymerization differences, the compositional dependence of frequency curves in Figs. 5 and 6 reflect the *specific* nature of localized polymerization changes.

5. Conclusions

Some depolymerization changes that accompany composition changes in multicomponent oxide glasses can be complex enough to render incomplete the analysis of volume, refraction, etc. information. It has now been demonstrated that infra-red spectra can be used to study the mutual influence of two different network forming species in ternary oxide glasses.

Specifically, infra-red spectra have been used to examine, in the presence of a relatively heavy, polarizing network modifier (Tl^+), (a) the mutual influence of one tetrahedral network former (GeO_2) on larger amounts of another network former (SiO_2), and (b) the mutual influence of a tetrahedral network former (SiO_2) on larger amounts of another network former (GeO_2) that is present as a mixture of octahedra and tetrahedra.

The infra-red approach has now been extended to include (a) a semi-quantitative analysis, for certain composition series (fixed ratio of network former concentrations), of molar extinction coefficients for two structurally significant vibrations ($\nu_{Si-O} = 1100$ cm^{-1} and $\nu_{Ge-O} = 875$ cm^{-1}) and (b) an analysis of the dependence of ν_{Si-O} (or ν_{Ge-O}) on the variable concentration ratio of the two network formers. The ternary *trends* of the infra-red isofrequency contours for the SiO and Ge-O vibrations were found to be somewhat similar. That finding emphasizes the close relationship of such contour trends to the various depolymerizing processes that can occur in complex oxide glasses.

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