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Infra-red Study of Polymerisation in Silver, Thallium, and Thallium Aluminogermanate Glasses

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The infra-red spectra of silver germanate, thallium germanate, and thallium aluminogermanate glasses are presented for the 1100 cm^{-1} to 400 cm^{-1} region. The pseudo rare gas type Tl^+ and Ag^+ ions produce spectral shifts in binary germanate glasses that are similar to those reported for alkali ions. Differences for Tl^+ may be due to its high atomic weight and polarising power. The infra-red spectral shifts observed for thallium aluminogermanate glasses are those expected if GeO_6 octahedra disappear while AlO_4 tetrahedra engage in network repair. A structurally sensitive technique for displaying ternary oxide glass infra-red spectra is outlined. This technique is capable of discerning different modes of network depolymerisation and polymerisation in ternary germanate and silicate glasses.

1. Introduction

Tarte [1] examined Al-O stretching frequencies in a variety of crystalline materials and was able to differentiate between isolated and condensed (polymeric) AlO_6 octahedra. Infra-red can also distinguish LiO_4 tetrahedra from LiO_6 octahedra in crystalline oxides [2] and show that compounds such as Cd_2GeO_4 possess an olivine structure with isolated GeO_4 tetrahedra [3]. It is also possible to calculate infra-red spectra for specific silicate structures such as framework, sheets, and chains that agree reasonably well with experiment [4].

Zarzycki recently used X-ray diffraction [5] to confirm infra-red studies that had suggested the presence of TiO_6 octahedra, known to exist in crystals such as rutile, in alkali-titanate glasses. Infra-red spectral differences have also been used to differentiate the various amorphous and crystalline polymorphs of SiO_2 and GeO_2 [6-9]. For example, Sclar *et al* [7] showed that stishovite, the high pressure form of SiO_2, contains SiO_6 octahedra, while Borrelli [10] used infra-red to support the interconnecting SiO_4/GeO_4 network that was suggested by other physical property measurements [11] of binary SiO_2-GeO_2 glasses. Also, Chen and Su recently determined the far infra-red spectrum of vitreous GeO_2 and found good agreement with calculated values [12].

Infra-red has also been used to show the possible presence of AlO_4 tetrahedra and AlO_6 octahedra in ternary silicate glasses. Thus, Day and Rindone found that both Al_2O_3 and Na_2O additions tend to shift the main Si-O-Si vibration to longer wavelengths [13]. This shift has been associated with the presence of AlO_4 tetrahedra in crystals as well as these glasses. Similarly, the early work of Lippencott *et al* [6] as well as that of Sclar *et al* [7] showed that the main Ge-O-Ge vibration shifts to longer wavelengths when GeO_4 tetrahedra transform to GeO_6 octahedra in the crystalline state. Murthy and Kirby subsequently found similar absorption band shifts for several series of alkali germanate glasses [14] and ascribed them to the presence of mixtures of GeO_4 tetrahedra and GeO_6 octahedra.

Recently, silver and thallium germanate glasses [15] as well as thallium aluminogermanate glasses [16] were prepared and their structures partially characterised. Those results also suggested the presence of GeO_6 octahedra and AlO_4 tetrahedra in the binary and ternary glasses respectively. This paper compares the infra-red spectra of these pseudo rare gas type ion containing glasses with those of related alkali germanate and alkali aluminosilicate glasses. A different, structurally significant, technique for depicting the infra-red results of such ternary oxide glasses is also described.

2. Experimental

The preparation of the silver germanate, thallium germanate, and thallium aluminogermanate glasses from reagent grade materials in recrystallised alumina crucibles has been described in detail elsewhere [15, 16].

The infra-red spectra between 4000 cm^{-1} and 400 cm^{-1} were recorded on a Perkin-Elmer Model 521 Grating Infra-red Spectrophotometer. Each glass was first ground in a mullite pestle and mortar. From 5 to 15 mg of each ground glass, depending on its composition (the largest amounts were related to the Tl_2O content), were then mixed with about 400 mg of KBr (Matheson Coleman and Bell powder for infra-red spectra) and heated for $\frac{1}{2}$ h at 125°C. The KBr pellets were formed by pressing the evacuated mixtures at 16 tons for about 10 min.

3. Results

Only the spectral region between 1100 cm^{-1} and 400 cm^{-1} is of interest for this study. That region contains the main Ge-O-Ge asymmetric stretching mode, present as a broad absorption band in the glass state, at 875 cm^{-1}, as well as the Ge stretching modes (540 cm^{-1} and 515 cm^{-1} in hexagonal GeO_2) that are centred about 550 cm^{-1} in the glass state. These are shown in fig. 1 for a pure GeO_2 glass that had been melted in air for 5 h at 1470°C in a Pt crucible and then quenched to room temperature. The spectrum of this sample is quite similar to that obtained by previous workers [6, 12, 14].

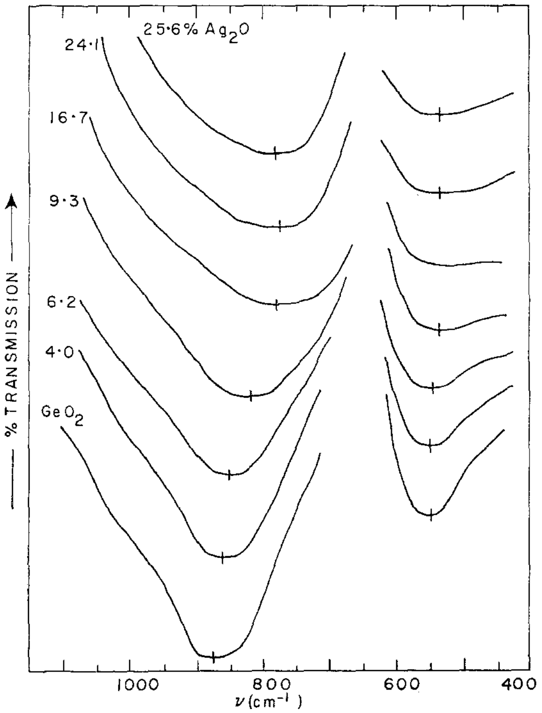

Figure 1 Infra-red spectra of pure GeO_2 glass and of a series of silver germanate glasses.

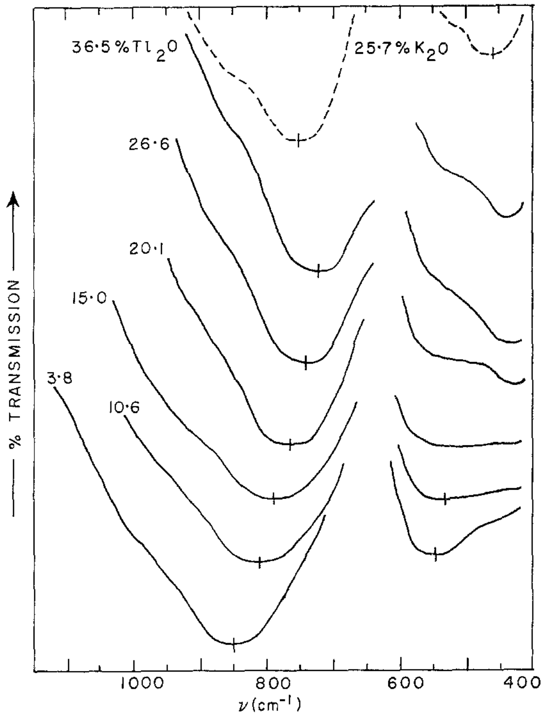

Figure 2 Infra-red spectra of a series of thallium germanate glasses.

The compositional dependence of the above absorption minima, in the presence of Ag$^+$, are also depicted in fig. 1. The shift of the main band at 875 cm^{-1} to longer wavelengths is more pronounced than any change in the position of the 550 cm^{-1} band. Fig. 2 shows similar band shifts in the presence of Tl$^+$. The position of the main band in the presence of 25.7 mole % K_2O (751 cm^{-1}) compares favourably with the value of 758 cm^{-1} calculated from the Murthy and Kirby results [14].

Spectra for the two series of ternary thallium aluminogermanate glasses (Al/Tl = 0.44 and 1.00) are shown in fig. 3. As before, the 875 cm^{-1}

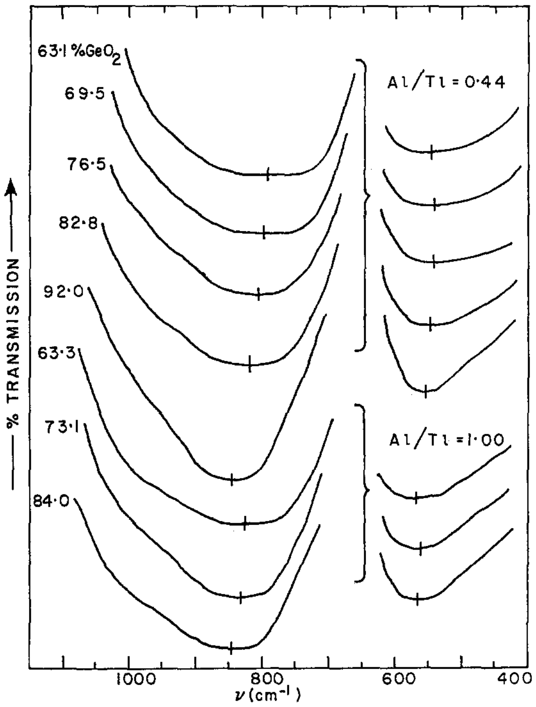

Figure 3 Infra-red spectra of thallium aluminogermanate glasses with Al/Tl = 0.44 and 1.00.

band is more sensitive to change of composition than is the 550 cm^{-1} band. It shifts to longer wavelengths with decreasing GeO_2 content.

All of the glass/KBr pellets exhibited a rather shallow (just a few per cent change of transmittance) minimum at about 3400 cm^{-1} that can be attributed to small amounts of OH^- [17]. However, a pure KBr pellet exhibited the same band. Thus, the glasses appear to be relatively free of H_2O.

4. Discussion

4.1. Binary Glasses

The infra-red stretching frequencies of polymerised polyhedra are usually higher than those of isolated ionic polyhedra. Qualitatively, the observed frequencies for the former are not those of a polyhedron, but rather those of the chain, ring, sheet, or network [1]. Hence, the result of gradually modifying a network of polyhedra via the substitution of non-bridging oxygens for bridging oxygens, should be to cause the M-O-M vibration to occur at lower frequencies.

The above phenomenon appears to be responsible for the frequency shifts observed for alkali oxide additions to fused silica (fig. 4). Those frequency results shown were compiled from the available literature [6, 7 18] and are shown as functions of mole % Na_2O. Note that the addition of 20 mole % Na_2O to pure fused SiO_2 decreases frequency of the main Si-O-Si band by 46 cm^{-1}.

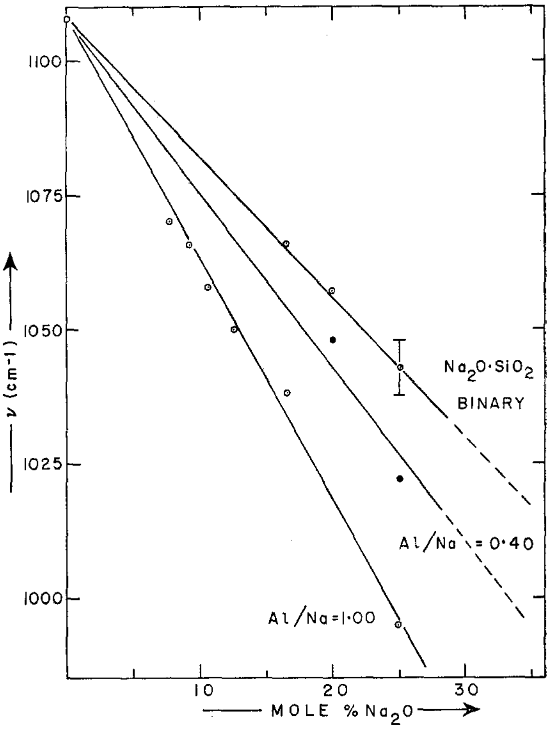

Figure 4 Frequency versus composition for sodium silicate and also sodium aluminosilicate glasses with Al/Na = 0.40 and 1.00.

Fig. 5, in addition to the present results, also shows the composition dependence of the 875 cm^{-1} Ge-O-Ge mode in the presence of alkali as a dashed line [14]. Note that the addition of 20 mole % Na_2O to pure fused GeO_2 creates a frequency shift (87 cm^{-1}) that is about twice that observed for the corresponding silicate glasses.

If the alkali silicate glass results (fig. 4) are representative of the gradual depolymerisation of a random network, then the additional shift observed for alkali germanate glasses (fig. 5) is suggestive of a slightly different process. The most likely phenomenon is the formation of GeO_6 octahedra. The overall shift of the Ge-O-Ge stretching mode to longer wavelengths,

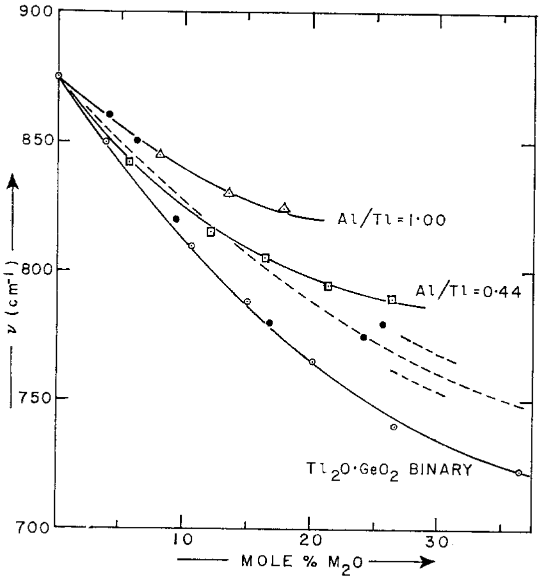

Figure 5 Frequency versus composition for silver (—●—) and thallium germanate (—○—) and also thallium alumino germanate glasses with Al/Tl = 0.44 and 1.00. Dashed line in the alkali germanate glass curve from [14].

in the presence of alkali, has been previously associated with the formation of GeO_6 octahedra [14] and discussed [19]. Zarzycki, on the basis of X-ray [5] and infra-red [20] results for alkali titanate glasses, has suggested still another possible mode of depolymerisation. It appears that the addition of alkali oxide may induce strands of TiO_6 octahedra to depolymerise via the opening of shared TiO_6 edges.

The dashed limits for the Murthy and Kirby results (dashed line in fig. 5) represent the approximate spread that appears to depend on the weight of the alkali cation. This approximate relationship seems to be most direct for glasses that contain less than about 22 mole % of alkali oxide. The thallium induced wavelength shifts, particularly for Tl_2O contents greater than 10 mole %, appear to be consistently larger than those caused by the alkali cations. Thus, the shift amounts to 110 cm^{-1} at 20% Tl_2O and 87 cm^{-1} at 20% Na_2O. In contrast, most of the silver induced wavelength shifts fall within the alkali "band".

Thallium weighs considerably more than most of the alkali ions, while the weight of silver falls between that of rubidium and caesium. Also, the highly polarising, pseudo rare gas type thallium ion may engage in covalent bonding to a considerable extent at higher Tl_2O contents in B_2O_3 [21] and GeO_2 glasses [15]. Both factors, the heavier weight and Ge-O-Tl coupling, may play a role in creating the larger than normal shifts to longer wavelengths at higher Tl_2O contents (fig. 5).

In this connection, Rao's infra-red study of alkali titanate glasses [20] had apparently revealed several strong alkali-oxygen vibrations in the 1450 cm^{-1} to 700 cm^{-1} region. As a result, 3, 10, and 23 mg of $TlNO_3$ (2.5, 8, and 18 mg Tl_2O respectively) were each mixed with 400 mg KBr and pressed into discs, as with the glasses. In contrast, the Tl_2O contents of the glass/KBr discs were between 1 and 5 mg for the binary series, between 2 and 9 mg for the Al/Tl = 0.44 series, and between 4 and 7 mg for the Al/Tl = 1.00 series. The high Tl_2O contents in each case were associated with the higher Tl_2O content glasses. Thus, the Tl_2O content of the 23 mg $TlNO_3$/KBr disc was far higher than that of any of the glass/KBr discs prepared.

The $TlNO_3$/KBr disc spectra revealed weak absorption bands at 2300 cm^{-1} and 1340 cm^{-1} that (a) were barely detectable at the 2.5 mg Tl_2O level and (b) increased with increase of $TlNO_3$ content. As with Rao's results for Cs_2O, Rb_2O, KNO_3, etc., these bands are probably associated with Tl-O stretching frequencies. No significant bands appeared at longer wavelengths as with the alkali oxides. Thus, it can be concluded that extensive Tl-O-Tl absorption does not interfere to any measurable extent with the Ge-O-Ge mode at 875 cm^{-1}.

Another possible explanation of the larger than expected frequency shift that is observed for the thallium germanate glasses could be that Tl^+ is simply more effective than the alkali ions with respect to GeO_6 octahedra formation. However, this does not seem too likely in view of the previous analysis of molar volumes and refractivities for the thallium glasses [15].

A minor difference between the silver and thallium germanate glass spectra (figs. 1 and 2) and those reported for (a) the alkali germanate glasses by Murthy and Kirby [14] and (b) the alkali silicate glasses [18] is the absence of a splitting of the main M-O-M mode for modifier oxide contents greater than about 25 mole %. Indeed, this splitting was not observed for the "control" potassium germanate glass (fig. 2). It is possible that differences of glass concentration in the KBr discs could be responsible. The previous studies did not report the approximate glass concentrations used in either mulls or KBr discs. However, attempts to explain this splitting in silicate and germanate glasses are not in complete agreement.

4.2. Ternary Glasses

The 875 cm^{-1} mode frequency decrease that is observed for binary thallium germanate glasses is also observed in the presence of AlO_4 tetrahedra (fig. 5). However, the decrease is less pronounced than in the binary system. Comparison of the three series in fig. 5 at a Tl_2O content of 20 mole % shows that as Al_2O_3 is substituted for GeO_2, the wavenumber *increases* from 760 cm^{-1} at the binary to 825 cm^{-1} for the Al/Tl = 1.00 glass. This is the exact opposite of what occurs for glasses in the corresponding alkali aluminosilicate system (fig. 4). There, the substitution of Al_2O_3 for SiO_2 at 20 mole % Na_2O causes the wavenumber to *decrease* from 1060 cm^{-1} at the binary to 1020 cm^{-1} for the Al/Na = 1.00 glass.

This difference of behaviour can be rationalised within the context of (a) the rather different structures of the 20 mole % M_2O binary glasses, (b) the different roles played by AlO_4 tetrahedra, and (c) the similarity of polyhedral arrangements for Al/M = 1.00 glasses.

First, the mode of network depolymerisation differs for GeO_2 and SiO_2. The co-ordination change that occurs for germanium with the addition of network modifiers, creates most of this difference [14, 15, 22]. Second, initial Al_2O_3 substitutions for GeO_2 in a 20 mole % M_2O binary glass lead to substitution of AlO_4 tetrahedra for GeO_4 tetrahedra. Further additions of AlO_4 tetrahedra create an unstable environment for GeO_6 octahedra and lead to their elimination [23]. In contrast, AlO_4 tetrahedra appear to simply replace SiO_4 tetrahedra. Third, ternary germanate and silicate glasses with (a) Al/M ratios of 1.00 and (b) 20 or more mole % of M_2O appear to possess relatively open, cristobalite-like random networks of corner shared AlO_4 and GeO_4 or SiO_4 tetrahedra [22].

Once again, adoption of (a) silicate glass infra-red behaviour as typical of the gradual alteration of a network, (b) Tarte's suggestion [1] that condensed or polymerised polyhedra usually exhibit higher stretchng frequencies than do isolated polyhedra, and (c) the known fact that an increase of co-ordination number leads to a decrease of stretching frequency, will all prove of value, this time in understanding these ternary oxide glass spectra.

Day and Rindone examined several series of sodium aluminosilicate glasses starting with the 25 mole % Na_2O binary composition [13]. They considered (a) the longer wavelength shift of the Si-O-Si mode that accompanies an increase of the Al_2O_3 content and (b) the opposite effect associated with a decrease of the Na_2O content. It was concluded that the infra-red spectra supported the presence of AlO_4 tetrahedra. Burdick and Day subsequently used infra-red to examine the co-ordination of aluminium in crystalline tricalcium aluminate [24]. They used harmonic oscillator approximations to calculate the frequency shift expected when an aluminium substitutes for a silicon (ν = 1003 cm^{-1}) in a tetrahedral site. The calculated shift to 125 cm^{-1} less was in fair agreement with that observed in tricalcium aluminate (186 cm^{-1} less).

All of the above therefore strongly suggests that the infra-red behaviour observed for sodium aluminosilicate glasses in fig. 4 is that expected if AlO_4 tetrahedra "repair" the damaged random SiO_4 network found in binary alkali silicate glasses. That is, at constant Na_2O content, the main Si-O-Si mode should shift somewhat to longer wavelengths as AlO_4 tetrahedra enter the network.

A different way of demonstrating the above point is shown in fig. 6. There, constant wavenumber contours are superimposed on the SiO_2-rich portion of the Na_2O-Al_2O_3-SiO_2 system. These contours were compiled from careful interpolation along selected composition series for the available data. The contours do not join compositions with similar structures. Instead they actually connect Na_2O and Al_2O_3/Na_2O combinations that produce the same *overall* long wavelength shift of the Si-O-Si vibration mode. This method of infra-red data depiction emphasises the rather gradual nature of the network depolymerisation that occurs with SiO_2, regardless of which oxides are added.

In direct contrast to the above is fig. 7 which depicts constant wavenumber contours for glasses in the thallium aluminogermanate system. These contours bend at a completely different angle with respect to the peak at GeO_2 than do the fig. 6 contours with respect to the peak at SiO_2. The possible reasons for this difference are discussed below.

First, the depolymerisation of the GeO_4 network is more complete, at a given binary

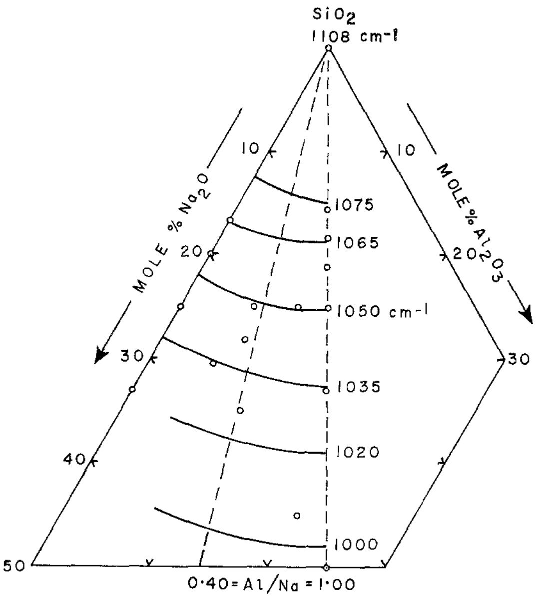

Figure 6 Constant wavenumber contours for SiO_2-rich glasses in the sodium aluminosilicate system

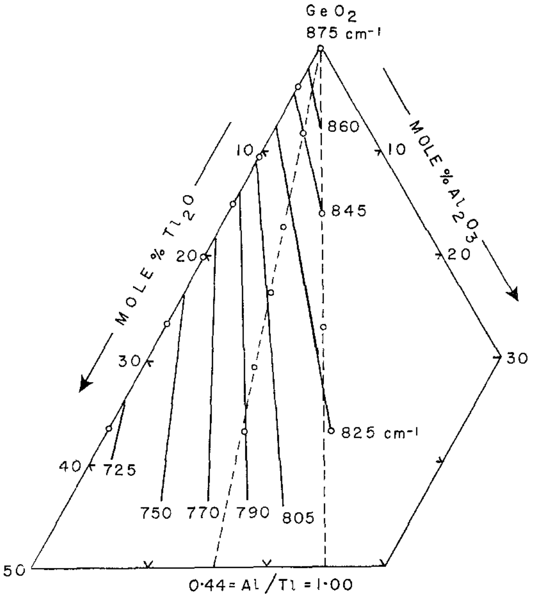

Figure 7 Constant wavenumber contours for GeO_2-rich glasses in the thallium aluminogermanate system.

composition, than is the depolymerisation of the SiO_4 network [25]. This results in the previously discussed, more pronounced frequency shift observed for the binary germanate glasses.

Second, the expected frequency shift caused by the replacement of a germanium by an aluminium in a tetrahedral site is less than the replacement of a silicon. The reason for this is that the condensed or polymerised AlO_4 tetrahedral frequency should lie in the 900 cm^{-1} to 700 cm^{-1} region [1, 24]. While this is less than the 1108 cm^{-1} mode for the pure SiO_2 network, it brackets the 875 cm^{-1} mode for the pure GeO_2 network.

The above phenomenon is confirmed by examination of the Al/M = 1.00 series in figs. 4 and 5. It is apparent that AlO_4 substitution for GeO_4, starting at pure GeO_2, produces only a 52 cm^{-1} decrease of the main Ge-O-Ge mode at the 60 mole % GeO_2 composition (fig. 5). In contrast, comparable AlO_4 substitution for SiO_4 decreases the frequency of main Si-O-Si mode by 91 cm^{-1} (fig. 4), or almost twice as much. Any difference of effect between Tl^+ and Na^+ on the frequency shift of such loose tetrahedral networks (Al/M = 1.00) should be small and hence can be ruled out as a significant factor in this case.

The more significant factor of the two thus discussed is obviously the relatively sharp frequency shift, due to the change of co-ordination number for germanium, in the binary germanate glasses. Without this effect, the frequency contours of fig. 7 would most likely be aligned with respect to the network-former peak, just as they are in fig. 6 for the silicate system. The peak at pure GeO_2 would then simply be less pronounced than its SiO_2 analogue.

Thus, this particular technique of infra-red data presentation appears to be a valid indicator of both (a) different modes of network depolymerisation in binary systems and (b) different modes of network "repair" that occur as Al_2O_3 is substituted for either GeO_2 or SiO_2. Behavioural differences such as those just discussed may thus be of value for ternary glass systems where other supporting evidence is lacking or incomplete.

5. Conclusions

Infra-red spectral shifts can be a sensitive index of various depolymerisation/polymerisation phenomena that are known to occur in different binary and ternary oxide glasses.

Pseudo rare gas type ions such as Tl^+ and Ag^+ create infra-red spectral shifts in germanate glasses that are similar to those observed for the alkali ions. Slight differences for Tl^+ may be related to (a) its much larger atomic weight and or (b) covalent bonding caused by its high polarising power.

The infra-red spectral shifts observed for Al_2O_3 additions to thallium germanate glasses can be interpreted in terms of the presence of AlO_4 tetrahedra that initially replace GeO_4 tetrahedra and then eliminate GeO_6 octahedra. Glasses with Al/Tl = 1.00 appear to consist of a loose corner-shared network of AlO_4 and GeO_4 tetrahedra.

A structurally sensitive technique of displaying infra-red spectra was developed for ternary oxide glass systems. This technique is capable of discerning the different modes of network "repair" or polymerisation that occur in thallium aluminogermanate and sodium aluminosilicate glasses.

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