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Mixed-Cation Effect in Copper(I) Germanate Glasses[1]

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Ternary glasses were prepared that contain at least 85 mol % GeO_2 and equimolar amounts of Cu_2O and Na_2O (or K_2O or Ag_2O). Refractive indices, densities, and infrared spectra were measured and colors noted. The refractivity and molar volume trends reflect rather voluminous ternary glass structures that appear to contain linear O–Cu–O arrangements and GeO_4 tetrahedra as well as GeO_6 octahedra. The dependence of glass volume upon cation size for all mixed-cation and binary germanate glasses is such as to suggest the unusual buttressing role of copper(I) in amorphous oxide environments. These findings confirm the different structural role played by the $3d^{10}$ Cu^+ compared to the $4d^{10}$ Ag^+. The enhanced infrared shift to lower frequencies of the Ge–O vibration depends upon composition in a manner similar to that observed for copper(I)-free germanate glasses, but for slightly different reasons.

Introduction

Copper(I) does not always behave as do other univalent network-modifying cations when they are added to amorphous GeO_2. The $3d^{10}$ copper(I) ion yields a more open glass structure than expected when compared with either the electronically similar $4d^{10}$ silver(I) ion or the alkali cations. These differences have been ascribed to the linear O–Cu–O arrangement, known to be present in crystalline oxides, that could buttress the altered GeO_4 tetrahedral network.[2]

The presence of two different alkali cations in an oxide glass can produce nonideal deviations of physical properties such as electrical conductance, ionic mobility, and internal friction.[3–5] The maxima or minima that are usually noted for such properties at equimolar cation compositions have been referred to as the "mixed-alkali" effect. However, the reasons for such behavior are not at all completely understood. Equimolar mixed-alkali germanate glasses, as well as equimolar mixed-cation germanate glasses that contain one or more pseudoalkali cations such as Tl^+ or Ag^+, also exhibit deviations from ideal mixing behavior.[6] The mixed-alkali germanate glasses tend to be less voluminous, while the glasses that contain one or more pseudoalkali cations tend to be more voluminous than expected from ideal mixing considerations.

The mixing of copper(I) with other cations in GeO_2-rich glasses could permit an examination of the effect of electronic and size differences on network depolymerization that had not been previously explored. The physical properties of such mixed-cation glasses could also furnish additional confirmatory information concerning the proposed buttressing role of copper(I) in tetrahedral oxide networks. This paper reports the preparation and properties of ternary GeO_2-based glasses that contain equimolar amounts of Cu_2O and Na_2O, or K_2O, or Ag_2O and at least 84 mol % GeO_2. The refractive indices, densities, and infrared spectra of these glasses are then discussed within the framework of the mode of depolymerization experienced by the random network of corner-shared GeO_4 tetrahedra.

Experimental Section

The equimolar Cu–Na, Cu–K, and Cu–Ag germanate glasses were prepared by weighing and mixing predetermined amounts of selected copper(I) germanate glasses[2] with previously prepared sodium, or potassium, or silver germanate glasses.[6,7] Approximately 10 g of each ternary glass was prepared in recrystallized alumina crucibles (McDanel Refractory Porcelain Co.) of 5-cm^3 capacity. All final mixtures of the ground and mixed glasses were inserted directly into the hot furnace (Blue M, Model No. Rg-2090A-1) and melted in air for periods of from 1 to 2 hr. The longer times were used for the highest GeO_2 content glasses because of their greater viscosities. The temperatures varied from 1300–1385° for the GeO_2-rich melts to the 1230–1300° range for the lower GeO_2 content melts. Each glass batch was removed from the furnace several times and swirled to facilitate homogenization and then finally air blast quenched.

The above procedures aided in lessening any reaction between copper(I) and the alumina (none was noted) and in retaining the copper in the univalent state.[2] Weight changes during melting were small and ranged from −0.30 to +0.15% by weight. There was a tendency for the GeO_2-poor glasses in each series to surface crystallize to a slight extent during the quenching operations.

Reactions between Cu^+ and Ag^+, to produce either Cu^0 and Ag^{2+} or Cu^{2+} and Ag^0, are possible at the elevated temperatures encountered with the described glass-melting conditions. However, the first pair of products is not too likely because of the relatively large free energy of formation of Cu_2O compared to that of AgO.[8] The latter decomposes at about 100° and is therefore less stable than Ag_2O. No dispersed copper metal was microscopically noted in the glasses. The second pair of products is more of a possibility because the reaction involves a $\Delta G°_{25°}$ of about −11.5 kcal/g-atom of silver metal produced. It can be estimated that $\Delta G°$ for this process decreases to about −5.0 kcal at 1200°. This arises mainly because CuO is thermodynamically unstable with respect to Cu_2O above about 950°.[2] No dispersions of silver metal were observed in the glasses. The regularity of the physical property trends to be presented also suggests the presence of only Cu^+ and Ag^+. The nature of the solvent, in this case the damaged germanate network melt, appears to shift emf values so as to favor retention of the two univalent ions at high temperature.

The densities were determined with a Kraus-Jolly balance (Eberbach Corp., Model No. 5000) using benzene as the immersion fluid. Refractive indices were obtained *via* the Becke line technique with a series of certified index-of-refraction liquids (Cargille Laboratories, Inc.) and a microscope. The infrared spectra were recorded for the 4000–400-cm^{-1} region with a Perkin-Elmer Model No. 521 grating infrared spectrophotometer. Samples of ground glass weighing from 4 to 9 mg (largest amounts for the GeO_2-poor glasses) were mixed with 400 mg of KBr (Matheson Coleman and Bell) and heated for 0.5 hr at 75°. The KBr pellets were then formed by pressing the evacuated mixtures at 16 tons for 10 min.

Results

All of the mixed-cation ternary glasses exhibit dark black colors in thick sections. However, microscopic examination of thin sections revealed transparent, colored specimens that possessed the approximate colors noted in Table I which also gives the measured densities and refractive indices. The binary copper(I) germanate glasses[2] behave in a similar fashion. Qualitatively, the color of a mixed-cation copper(I) germanate glass appears to be more intense than that of a binary copper(I) germanate glass, even when the second cation is an alkali. Thus, the presence of an equal Na^+ content appears to intensify the color associated with Cu^+ and apparently shifts the absorption edge to longer wavelengths. Similar observations have been reported for mixed-cation germanate glasses that contain no copper(I).[6]

The infrared spectra for the 1100–400-cm^{-1} region are shown in Figure 1. This spectral region is of significance because it contains the main Ge–O stretching frequency, the position of which is sensitive to both the coordination of germanium(IV) and the degree of polymerization.[9] The

Table I. Compositions and Physical Properties of Mixed-Cation Copper(I) Germanate Glasses

Glass	Compn, mol %					Density,[a] g/cm^3	Refractive index[b]	Approx color[c] in thin section
	GeO_2	Cu_2O	Na_2O	K_2O	Ag_2O			
AA	96.88	1.56	1.56			3.718 ± 0.009	1.617 ± 0.002	LYG
BB	92.82	3.59	3.59			3.802 ± 0.005	1.637 ± 0.002	DYG
CC	87.74	6.13	6.13			3.945 ± 0.012	1.685 ± 0.000	DO
DD	84.18	7.91	7.91			3.995 ± 0.022	1.705 ± 0.000	vDO
EE	96.86	1.57		1.57		3.690 ± 0.005	1.614 ± 0.002	DYG
FF	92.06	3.97		3.97		3.740 ± 0.004	1.636 ± 0.002	DO
GG	85.14	7.43		7.43		3.824 ± 0.004	1.672 ± 0.000	vDO
HH	94.74	2.63			2.63	3.902 ± 0.002	1.640 ± 0.002	YO
II	90.36	4.82			4.82	4.147 ± 0.001	1.704 ± 0.016	O
JJ	85.42	7.29			7.29	4.267 ± 0.012	1.720 ± 0.010	DO

[a] Uncertainty in duplicate determinations. [b] Uncertainty due to bracketing procedure of the technique. [c] L = light, D = dark, G = green, Y = yellow, O = orange, v = very. For comparison on this qualitative scale, thin sections of glass B (~4.6% Cu_2O) were LYO, while glasses C and D (~10% Cu_2O) were DO (see ref 2).

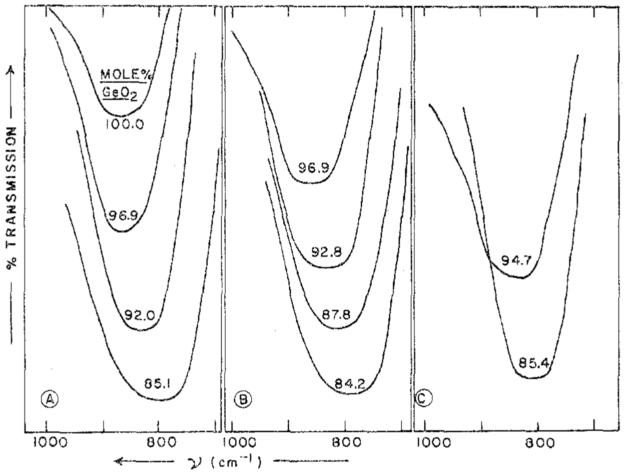

Figure 1. Infrared spectra of (A) K-Cu, (B) Na-Cu, and (C) Ag-Cu germanate glasses.

spectrum of a 4-mg sample of freshly ground pure GeO_2 glass (completely cross-linked GeO_4 tetrahedra) is shown for comparison.

Discussion

Refractive Indices. The velocity of light through a solid is inversely proportional to the efficiency of the atomic packing. The more readily measured index of refraction is in turn inversely dependent upon the velocity of light. For example, oxide glasses exhibit refraction increases for pressure-induced densification as well as for structure changes caused by composition changes.[7] Hence, refractive index can directly reflect changes in the packing arrangements of the relatively large oxygen species which occupy most of the volume in such solids.

The compositional dependencies of refractive index for the Cu–Na, Cu–K, and Cu–Ag glasses of constant GeO_2 content are depicted in Figure 2. Nine of the ten glasses exhibit smaller than expected refractivities. These negative deviations appear to be quite regular and to become more pronounced (up to −2.3%) as the GeO_2 content is decreased. This behavior is quite different from what was previously reported for other mixed-cation germanate glasses[6] and suggests a slight packing efficiency decrease when equimolar amounts of other ions substitute for copper(I).

The refraction behavior of binary copper(I) germanate glasses was such (negative refraction deviations from additivity) as to suggest an unusual structural role for copper(I).[2] Apparently, moderate amounts of copper(I) can serve to buttress the open network of GeO_4 tetrahedra instead of destroying it *via* the formation of GeO_6 octahedra (as do Na^+, K^+, and Ag^+). In the case of these mixed-cation copper(I) germanate glasses, it appears that half of the copper(I) may be replaced at a fixed GeO_2 level without collapsing the relatively open glass structure. More definitive evidence is discussed below.

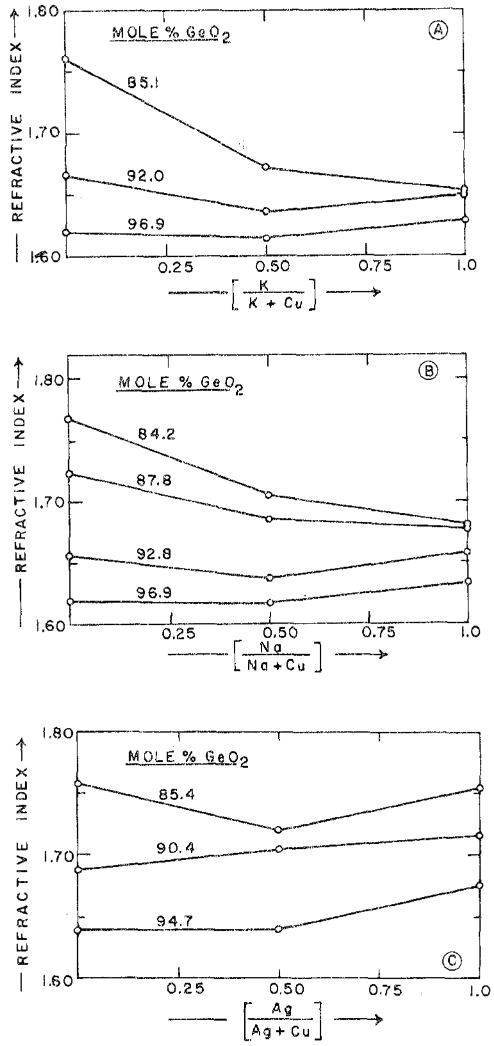

Figure 2. Refractive indices of mixed-cation germanate glasses containing (A) K–Cu, (B) Na–Cu, and (C) Ag–Cu combinations.

Molar Volumes. Figure 3 depicts the compositional dependence of molar volume for the three series of copper(I) mixed-cation glasses studied. All of the glasses exhibit positive deviations from additivity that can amount to as much as +4.8% at the 85 mol % GeO_2 level. These deviations are larger and more consistently positive than those previously reported for the Tl–Ag, Tl–K, and Ag–K combinations.[6] Also, the $3d^{10}$–$4d^{10}$ or Cu–Ag glasses exhibit significantly positive volume deviations in contrast to their alkali–alkali or Na–K

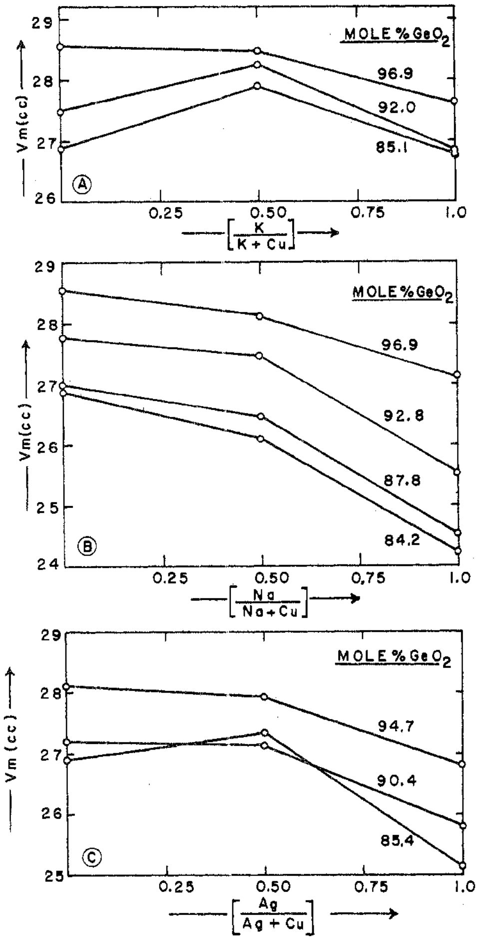

Figure 3. Molar volumes of mixed-cation germanate glasses, per mole of the stoichiometric mixture, containing (A) K–Cu, (B) Na–Cu, and (C) Ag–Cu combinations.

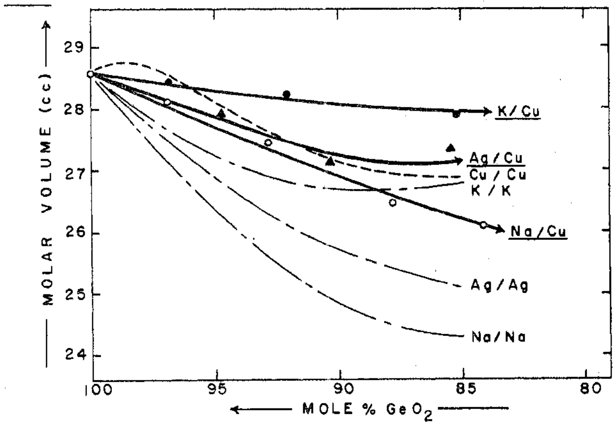

Figure 4. Molar volume *vs.* composition for mixed-cation germanate glasses containing K–Cu (●), Na–Cu (○), and Ag–Cu (▲) combinations. Related binary glass volumes shown for reference.

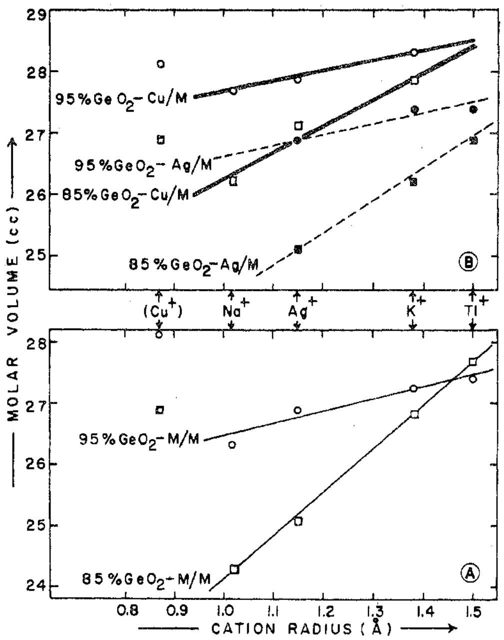

Figure 5. Molar volume *vs.* cation radius for (A) binary germanate glasses and (B) mixed-cation germanate glasses containing the Ag–M and Cu–M combinations.

analogs[6] which exhibit significantly negative volume deviations. It therefore appears that the presence of an equimolar amount of a second cation favors the retention of the relatively open copper(I) germanate structure, at least in GeO_2-rich glasses.

The volume of a given Cu–M glass can be quite close to that of the corresponding Cu–Cu glass (Figure 4). The Cu–K glasses possess structures that are about as open as that of pure GeO_2 glass. Although the proposed linear O–Cu–O arrangement[10] could buttress the open GeO_4 network, the cavities in such a glass may not be large enough to accommodate the rather large K^+ without the introduction of some additional degree of network expansion. In contrast, the slightly smaller Ag^+ produces a mixed-cation copper(I) glass that is more voluminous than the Cu–Cu specimens *only* at the 85 mol % GeO_2 composition (Figure 4). The much smaller Na^+ does not create as open a glass structure as is found for K^+ and Ag^+ additions. Thus, there appears to be a relationship between glass volume and cation size for the mixed-cation copper(I) germanate glasses. The existence of such a relationship implies that mixed-cation copper(I) germanate glasses may possess degrees of polymerization, at fixed GeO_2 content, that are partially independent of the nature of the second cation.

At the 95 mol % GeO_2 level, the Cu–Na and Cu–Ag glasses are 5.5% more voluminous, while the Cu–K glasses are 3.5% more voluminous than their M–M counterparts. At the 85 mol % GeO_2 level, the Cu–Na and Cu–Ag glasses are 8% more voluminous, while the Cu–K glasses are 3.5% more voluminous than their M–M counterparts. Thus, most of the expansion accompanies the substitution of the first half of the cations with Cu^+. This implies the presence of the linear O–Cu–O arrangement in glasses for which $[M^+] > [Cu^+]$.

A quantitative rationalization of some of these points can be developed by considering the dependence of glass volume on the exact size of the second cation. Several different types of cation radii are available for use in such an analysis. However, a fair degree of linearity is achieved only with the use of "effective ionic radii" for octahedral coordination[11] which are based on an O^{2-} radius of 1.40 Å. The latter value has been used to interpret successfully numerous solid-state phenomena.

The linearity and positive slope observed for the M–M germanate glass volumes (Figure 5A) implies that the extent of network disruption in GeO_2-rich environments may be independent of cation type. The volume becomes quite dependent upon cation size as the per cent GeO_2 decreases, with the total change in volume with change of composition being the largest for the small Na^+. A previous analysis of similar data for alkali germanate liquids at elevated temperatures[12] has shown that the increased dependence of volume upon cation size at lower GeO_2 contents is associated with the appearance of GeO_6 octahedra. The volume trends for the M–M germanate glasses (Figure 5A)[2,7,13,14] are most readily rationalized within that framework.

The Cu^+ should be about 76% as large as Ag^+ for a given coordination.[11] However, the Cu–Cu volume results (Figure 5A) do not adhere to the above size relationships. Hence, Cu^+ is obviously not present in these glasses in an octahedral environment with an estimated ionic octahedral radius of 0.87 Å. The Cu^+ would appear to be behaving like a relatively large cation, which it is not. The most likely rationalization of this contradiction is that Cu^+ is present in a linear O–Cu–O arrangement that buttresses the oxide glass structure.

The volumes of the Cu–M and Ag–M glasses exhibit dependencies upon cation size at both the 95 and 85 mol % GeO_2 levels (Figure 5B) that are similar to those exhibited by the M–M glasses in Figure 5A. However, the Cu–M glasses can be from 4 to 8% more voluminous than their Ag–M and M–M counterparts. While the Ag–Ag glass volumes lie on the Ag–M data plots, the Cu–Cu glass volumes clearly do not lie on the Cu–M data plots (Figure 5B). Although the Cu–Ag glass volumes lie on linear plots of the Cu–M data, the Ag–Cu combinations do not lie on the linear plots of the Ag–M data (Figure 5B).

The foregoing suggests that (a) the $3d^{10}$ Cu^+ and $4d^{10}$ Ag^+ species may occur in similar environments in such mixed-cation germanate glasses and (b) the structure of the mixed-cation germanate glasses resembles, to a fair degree, that of the binary or M–M germanate glasses. However, the mixed-cation glasses that contain copper(I) definitely possess *more open* arrangements of germanate polyhedra than do either their Ag–M or M–M counterparts. The copper(I) appears to be buttressing the Cu–M glass structure *via* linear O–Cu–O arrangements, while the second cation appears to be creating network alteration *via* the formation of GeO_6 octahedra. Thus, the GeO_2-rich copper(I) mixed germanate glasses appear to exhibit structures that are intermediate in nature between the two binary extremes.

Several recently prepared crystalline oxides that contain equimolar amounts of an alkali cation and a second univalent cation such as Ag^+, Cu^+, Au^+, and Tl^+ exhibit unusual structural features that may be similar to those proposed for these mixed-cation copper(I) germanate glasses. For example, KAgO, CsAgO, NaCuO, CsAuO, etc. contain nearly planar M_4O_4 groups, such as Ag_4O_4, with the oxygens at the corners of a square.[15] The alkali cations lie between the oxygens of the parallel planar M_4O_4 groups. Infinite 2.5-Å diameter channels that run down the center of the M_4O_4 groups may reflect rather open structures for these crystalline materials.

Infrared Spectra. Mixed-cation germanate glasses were previously found to exhibit an *enhancement*[6] of the *shift*[9,16] of the main Ge–O absorption band to lower frequencies. The latter is related to either an increase of the GeO_6:GeO_4 ratio[9] or GeO_4 decoupling[17-19] that can accompany depolymerization *via* modifier additions to GeO_2. The ν_{Ge-O} shift to lower frequencies that accompanies a decrease in the GeO_2 content has also been found to be slightly less pronounced with copper(I) additions[2] than with alkali additions. One might expect the ν_{Ge-O} shifts for the Cu–M glasses to be intermediate between those of either Cu_2O or alkali oxide additions. However, Figure 6 reveals significant shifts of ν_{Ge-O} to lower frequencies that are similar to those exhibited by other mixed-cation germanate glasses.[6]

The extent of the enhanced ν_{Ge-O} shift exhibited by these Cu–M germanate glasses can also be depicted by connecting the compositions on a ternary diagram that possess the same frequency.[9,20] These isofrequency contours do not necessarily connect glasses of similar structure because several possible depolymerization mechanisms can cause frequency changes. However, in the case of the ternary glasses under consideration, the depolymerization modes encountered with the binary systems are not unknown.

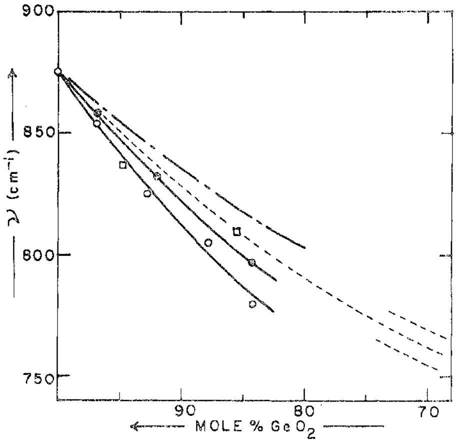

Figure 6. Frequency of ν_{Ge-O} *vs.* mole per cent GeO_2 for mixed-cation germanate glasses containing the K–Cu (⊖), Na–Cu (○), and Ag–Cu (□) combinations. Related binary data for Cu_2O and alkali germanate glasses shown for reference.

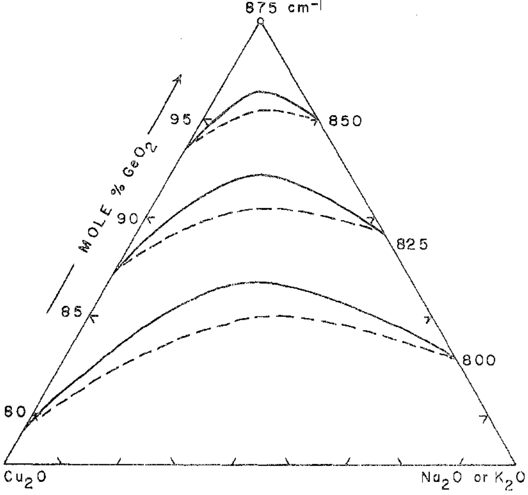

Figure 7. Isofrequency contours of ν_{Ge-O} for GeO_2-rich glasses containing the K–Cu (- - -), Na–Cu (——), and Ag–Cu (——) combinations.

Figure 7 shows several such isofrequency contours for the three series of Cu–M glasses studied. The enhanced ν_{Ge-O} shift to lower frequencies when two types of cations are present is readily apparent.

The other evidence thus far discussed suggests that there should be a slight enhancement of the GeO_6:GeO_4 ratio as Na^+, Ag^+, or K^+ substitutes for the proposed O–Cu–O arrangement in a copper(I) glass at a fixed GeO_2 content. A shift of ν_{Ge-O} to smaller frequencies would accompany such a process. For those glasses in which $[M^+] > [Cu^+]$, the last of the relative expansion caused by the O–Cu–O arrangements is eliminated. The glass structure collapses to the more efficient mode of packing exhibited by alkali and silver germanate glasses. Such a densification process could easily lead to a more energetic Ge–O vibration and hence to the bending of the isofrequency contours shown in Figure 7.

These bent isofrequency contours are quite similar to those that can be developed for other mixed-alkali and mixed-cation germanate glasses.[6] Thus, the enhanced ν_{Ge-O} shift appears to be characteristic of mixed-cation germanate glasses in general, rather than of just Cu–M germanate glasses in particular. The enhanced ν_{Ge-O} shift that accompanies the addition of two different network-modifying cations to GeO_2 may therefore be caused by the asymmetry of the surrounding cation force fields. Thus, the manner in which GeO_6 octahedra and GeO_4 tetrahedra are joined within polyanion clusters could be sensitive to the asymmetry of the surrounding counterion force fields.

Conclusions

Mixed-cation GeO_2-rich glasses that contain equimolar amounts of copper(I) and a second cation exhibit physical property changes that reflect a unique structural situation. These GeO_2-rich ternary glasses appear to retain some of the features of both the copper(I) germanate glasses and the alkali or silver germanate glasses. Thus, they may contain (1) some of the linear O–Cu–O arrangements that characterize GeO_2-rich copper(I) glasses and (2) some of the GeO_6 octahedra that are found in the GeO_2-rich alkali and silver glasses. The rather voluminous nature of these ternary glasses suggests that they may contain a relatively open arrangement of germanate polyhedra.

Although the mixed-cation copper(I) germanate glasses are more voluminous than their copper(I)-free analogs, the volume–composition relationships of the copper(I) ternary glasses depend upon cation size in a manner similar to that of their copper-free ternary and binary analogs. It is thereby possible to gain an idea of the approximate size of the cation cavity in the mixed-cation copper(I) germanate glasses. Such information could be of possible practical value in a number of ion-exchange processes that involve amorphous oxide materials.

Additional confirmatory evidence for the possible linear O–Cu–O arrangement of copper(I) in binary GeO_2-rich glasses was uncovered by this study. It is evident that copper(I) does not experience the structural role encountered by other univalent cations in network-former-rich oxide glasses. The $3d^{10}$ electronic nature of copper(I) creates a bonding situation that can be quite different from that of $4d^{10}$ Ag^+. Caution should be exercised in attempts to substitute or exchange Cu^+ for Ag^+ and *vice versa* in oxide environments. Caution will also have to be exercised in attempts to substitute or exchange Cu^+ for the alkali cations and *vice versa*. This study suggests a new route to possibly unusual amorphous materials *via* the exchange (below the T_g of the glass) of an alkali ion for a Cu^+ in surface layers. The alkali ions would find themselves in unusual coordination sites. This could significantly alter selected physical properties of the resultant material.

The enhanced shift to lower frequencies of the main infrared Ge–O vibration that accompanies a change of composition (such as per cent GeO_2) for mixed-cation copper(I) germanate glasses is quite similar to that previously reported for other mixed-cation germanate glasses. While the reasons for the frequency shift observed for the former ternary glasses are more complex, they are readily interpretable in terms of the depolymerization sequences of the corresponding binary glasses. The copper(I) ternary glasses thus offer another example of the usefulness of infrared isofrequency contours as a unique structural probe.

Registry No. GeO_2, 1310-53-8; Cu_2O, 1317-39-1; Ag_2O, 20667-12-3.

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Interpretation of Electronic and Magnetic Circular Dichroism Spectra Using Complete Operator Matrices (eZ, L$_z$, ∇_x) and Their Application to Evaluate Semiempirical LCAO–MO State Functions of Large Transition Metal Complexes

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Magnetic circular dichroism and electronic absorption parameters of charge-transfer excitations, $^2T_{2g} \rightarrow {}^2T_{1u}{}^{a,b}$ and $^2T_{2u}$, were computed for the prototype "covalent" transition metal complex $[Fe(CN)_6]^{3-}$. All valence electrons (65) and valence orbitals (57) were included, and a semiempirical LCAO–MO model in common use for such large molecules was employed. The construction and use of the complete multicenter orbital angular momentum (**L**), electric dipole (e**R**), and velocity dipole (∇) matrices and their artificially incomplete counterparts lead to the conclusions that (i) the MCD Faraday ratios, C/D, can be computed reliably with unmodified or overlap-optimized iron functions, (ii) these C/D ratios can be computed reliably with the incomplete, block-diagonal matrix, $\mathbf{L}^{(b)}$, composed of only the one-center and two-center integrals, (iii) complete electric dipole transition moment matrices should be employed, (iv) the dipole strength of $^2T_{2g} \rightarrow {}^2T_{2u}$ is predicted to be the most intense of the three transitions, as found experimentally, by using either optimized or unmodified iron functions, and (v) the use of optimized iron functions has the advantage of not making $t_{2g}(\pi)$ and $t_{1u}(\sim\sigma)$ accidentally degenerate.

Introduction

It was the premise of this study that the practice of using molecular orbitals of semiempirical LCAO–MO procedures for assigning electronic excitation bands of transition metal complexes by means of magnetic circular dichroism (MCD)[2] is best tested by evaluating all one-, two-, and three-center AO integrals of appropriate operator matrices. By this means any discrepancy between computed and experimental Faraday parameters can be directly attributed to the molecular orbitals, so that the quality of the latter can become known with certainty. In other words, it was felt necessary to employ this procedure, because using semiempirically derived molecular