Volume 12
Number 10
October 1973

Inorganic Chemistry

Contribution from the Institute of Polymer Science,
The University of Akron, Akron, Ohio 44325

Depolymerization of Germanium Dioxide Glass by Copper(I) and Copper(II) Oxides[1]

E. F. RIEBLING

Received April 4, 1973

Copper germanate glasses containing either Cu_2O up to 12 mol % or Cu(II):Cu(I) ratios up to 0.175 (and as little as 70 mol % GeO_2) were prepared by allowing Cu_2O and GeO_2 to react in alumina crucibles in air above 1100°. Higher Cu_2O content binary germanate glasses were not obtained because of (a) CuO formation on heating, (b) incomplete CuO decomposition above 1026° if larger amounts of Cu_2O were used, and (c) practical glass-melting considerations above 1000°. Small additions of Cu_2O (<8 mol %) cause refraction and volume deviations that are (a) different from those caused by the similar size Na^+ and (b) explainable in terms of a probable linear coordination for the $3d^{10}$ Cu^+. Larger amounts of Cu_2O produce a more open glass structure than anticipated from similar additions of Na_2O or Ag_2O. The presence of copper(II) in ternary glasses with more than 78 mol % GeO_2 creates large negative refraction deviations and nearly ideal volume, both of which can be associated with network retention. The more ideal refractivities and large negative volume deviations encountered with lower GeO_2 content ternary glasses both suggest the onset of extensive network depolymerization. The infrared spectra of these dark greenish black binary and ternary glasses exhibit frequency shifts for the main Ge–O vibration that confirm the analysis of the other physical properties. A recently developed infrared isofrequency contour technique clearly reveals the structural changes that accompany the substitution of copper(I) by copper(II).

Introduction

The depolymerizing influence of a modifying cation on an amorphous SiO_2, GeO_2, or B_2O_3 network can depend quite strongly on cation type. Thus, alkali and pseudoalkali cations tend to act as depolymerizing species while small alkaline earth contents reflect a network bridging role (larger amounts can cause macro phase separation).[2] Recently, the specific influence of a modifier's electronic configuration has been explored by using the polarizing $4d^{10}$ Ag^+ and $4f^{14}5d^{10}6s^2$ Tl^+ ions, both of which are similar in size to K^+ and introduce a degree of covalency not encountered with the latter ion.[3,4]

Copper offers an additional pseudoalkali modifier for study because of (a) the fact that Cu^+ is quite similar in size to Na^+, (b) the unusual linear coordination[5] that Cu^+ can adopt in certain oxide environments,[6] (c) the possibility of obtaining glasses with two coexisting oxidation states for the same modifier,[7-9] and (d) the distorted octahedral (square-planar) coordination[6] of Cu^{2+}. Also, most glass studies involving copper have been generally, but not always,[10,11] restricted to relatively small Cu_2O or CuO contents.[12-14]

This paper reports the preparation and properties of germanate glasses that contain as much as either 12 mol % Cu_2O or 10 mol % CuO and 22 mol % Cu_2O. Synthetic limitations in air are related to the temperature dependence of the Cu(II):Cu(I) ratio. The infrared spectra, volumes, and refractive indices are discussed within the framework of (a) the coordination of the $3d^{10}$ Cu^+ and $3d^9$ Cu^{2+} ions and (b) the depolymerization of the random network of corner-shared GeO_4 tetrahedra.

Experimental Section

Electronic grade GeO_2 powder (Eagle Picher Co.) and reagent grade Cu_2O powder (Fisher Scientific Co.) were used to prepare the glass batches which were all melted in a Blue M muffle furnace (Model No. Rg-2090A-1). Recrystallized alumina crucibles (McDanel Refractory Porcelain Co.) of 20-cm^3 capacity were used to contain the 20–30-g batches. Platinum was not used because of a reported tendency of Cu_2O to react with it at elevated temperatures.[15] While Cu_2O can react with Al_2O_3 at 1030° to form Cu_2AlO_4, the latter melts incongruently in air to Al_2O_3 and a Cu_2O-rich liquid at 1238°.[16] Hence, all final mixtures of Cu_2O and GeO_2 were heated as rapidly as possible and held above 1260° prior to quenching.

---

[1] Presented in part before the Symposium on Solid State Chemistry at the 165th National Meeting of the American Chemical Society, Dallas, Tex., April 1973; see Abstracts, No. INOR 148.

[2] E. F. Riebling in "Phase Diagrams—Materials Science and Technology," Vol. III, A. M. Alper, Ed., Academic Press, New York, N. Y., 1970, Chapter VII.

[3] E. F. Riebling, *J. Chem. Phys.*, 55, 804 (1971).

[4] E. F. Riebling, *J. Chem. Phys.*, 57, 1811 (1972).

[5] G. A. Bowmaker, L. D. Brockliss, and R. Whiting, *Aust. J. Chem.*, 26, 29 (1973).

[6] P. J. Durrant and B. Durrant, "Introduction to Advanced Inorganic Chemistry," 2nd ed, Wiley, New York, N. Y., 1970, pp 1105-1114.

[7] H. J. Tress, *Phys. Chem. Glasses*, 3, 28 (1962).

[8] C. B. Alcock, *Chem. Brit.*, 5, 216 (1969).

[9] L. Nunez, G. Pilcher, and H. A. Skinner, *J. Chem. Thermodyn.*, 1, 31 (1969).

[10] P. L. White, *Phys. Chem. Glasses*, 12, 11 (1971).

[11] P. L. White, *Phys. Chem. Glasses*, 12, 109 (1971).

[12] I. Siegel and J. A. Lorenc, *J. Chem. Phys.*, 45, 2315 (1966).

[13] W. D. Johnston and A. Chelko, *J. Amer. Ceram. Soc.*, 49, 562 (1966).

[14] H. G. Hecht, *Phys. Chem. Glasses*, 9, 179 (1968).

[15] H. S. Roberts and F. H. Smyth, *J. Amer. Chem. Soc.*, 43, 1061 (1921).

[16] A. M. M. Gadalla and J. White, *Trans. Brit. Ceram. Soc.*, 63, 39 (1964).

Since CuO decomposes to Cu_2O and O_2 at 1026° in air,[17] while Cu_2O melts at 1235°, it was initially felt that "quick melting" of the GeO_2 (mp 1115°) around solid particles of Cu_2O above 1115° would (a) eliminate reaction of large pools of Cu_2O with Al_2O_3 above 1235° and (b) inhibit copper(II) formation. However, attempts to obtain copper(I) glasses with relatively large Cu_2O contents (~20–45 mol %) from batches that contained more than 20 wt % Cu_2O always resulted in the formation of some copper(II). Even the use of relatively short heating times (~2–3 min) below 1026° resulted in the formation of some CuO. Apparently, not all of this CuO could rapidly revert to Cu_2O during subsequent heating from 1026 to 1115°. Microscopic observation of Cu_2O and CuO revealed that (a) Cu_2O powder slowly cooled in air from 1100° had turned completely black (CuO) while Dry Ice quenching produced mostly red material and (b) CuO wire (Merck reagent) held at 1100° for 30 min and Dry Ice quenched gave a glassy red material (Cu_2O).

The Cu_2O used to prepare the glasses was found to contain about 2.5% CuO. Attempts to remove the CuO *via* dissolution in warm glacial acetic acid[18] were not successful in significantly reducing the CuO content. That finding, coupled with the fact that CuO forms on the surface of the Cu_2O as it is rapidly heated, led to the use of $^1/_2$-hr hold times at temperatures above 1020° (but below 1235°) to decompose any CuO. These hold times were insufficient to decompose *all* of the CuO formed when *large* amounts of Cu_2O (>20 wt %) were used. However, if held for longer times either (a) at ~1075°, solid Cu_2O itself could have reacted more extensively with the Al_2O_3 crucible to form $CuAlO_2$ or (b) at ~1150°, the GeO_2 would fuse around the CuO-coated Cu_2O grains to entrap the Cu^{2+} ions.

Consequently, most batches were inserted at 1150° and rapidly heated to not less than 1300° or more than 1450°. The highest temperatures were used for the highest GeO_2 content batches. Total reaction times were from 2 to 4 hr. Several attempts to prepare very high Cu_2O content melts (28–45 mol %) at ~1400° resulted in gross attack of the alumina crucibles. Those glasses were discarded. Relatively small amounts of crucible attack were noted for glasses G and K (1450 and 1400°, respectively), both of which were attempts to prepare a 20 mol % Cu_2O glass. The suspected presence of relatively small amounts of Al_2O_3 in these two glasses appears not to have significantly altered their measured properties (see Results).

All of the glass melts were rapidly quenched either by being poured directly into a liquid N_2 pool on a steel plate or by dropping the crucible and contents into a larger reservoir of liquid N_2 (higher GeO_2 content glasses). These procedures avoided (a) extensive body or surface formation of copper(II) on cooling and (b) crystallization (particularly for the lower GeO_2 content glasses). Each glass sample was then immediately placed in a vacuum chamber to remove any adhering frost (formed during subsequent warming to 25°) and thereby prevent hydration during storage in a desiccator.

The composition of each glass was obtained by determining first the total copper content *via* a thiosulfate titration[19] and second the copper(I) content *via* a cerate titration.[20] Copper(II), if present, was calculated by difference. The as-received Cu_2O was used to check (a) the thiosulfate procedure for total copper [label 0.8515 weight fraction from Cu(I) and 0.0203 from Cu(II); total, 0.8718; found, 0.8719 ± 0.0009] and (b) the cerate procedure for copper(I) [label 96.2% by weight Cu_2O; found, 96.0 ± 0.1% Cu_2O].

The possible interference of GeO_2 with the copper(I) determinations was checked by analyzing synthetic mixtures of Cu_2O and GeO_2. Treatment of a 15 wt % Cu_2O mixture with HF (to dissolve the GeO_2) and boric acid (to complex the excess HF) was followed by a cerate titration for copper(I) (label 95.95%; found 94.84%). Similar treatment of a 30 wt % Cu_2O mixture gave only 91.95 ± 0.16% Cu_2O. It was found necessary *first* to add HCl and a 10-fold excess of $Fe_2(SO_4)_3$ in order to dissolve all of the Cu_2O. A 30 wt % Cu_2O mixture so treated gave 95.2% Cu_2O.

For the determination of total copper[10,13,21] each glass was dissolved in excess HNO_3 to produce copper(II), excess HNO_3 was removed by heating with H_2SO_4, the pH was adjusted to 3.7, a large excess of KI was added to produce copper(I) and I_3^-, and finally starch was added. Then, standard 0.1 *N* thiosulfate was titrated until the color disappeared, KSCN was added (to yield a sharper end point *via* formation of CuSCN), and the titration was continued until the blue color disappeared. The amounts of glass used were varied from 0.2 to 1.5 g (depending upon the anticipated total copper content) so that from 5 to 20 ml of thiosulfate solution would be used per titration. Duplicate analysis for total copper permitted the calculation of average per cent copper values that had uncertainties of from ±0.2 to ±2.5%.

For the determination of copper(I),[10,13,21] each glass was dissolved in HCl (that contained $Fe_2(SO_4)_3$) to produce copper(II); the solution was heated to boiling and then cooled to 25° (necessary for good end points because the ferroin indicator is labile at elevated temperatures), with the resultant iron(II) being titrated with standard 0.1 *M* cerate solution in the presence of the ferroin indicator. The amounts of glass used were varied from 0.2 to 1.5 g (depending upon the anticipated copper(I) content) so that from 5 to 15 ml of cerate solution would be used per titration. Duplicate analysis for weight per cent Cu_2O permitted the calculation of average values that had uncertainties of from ±0.1 to ±2.0%.

The total copper determinations for the five binary glasses amounted to 93–98% of the weight per cent copper determined with the copper(I) procedure. Hence, the latter values were used to calculate the final compositions for these glasses.

The glass densities were determined with a Kraus–Jolly balance (Eherbach Corp., Model No. 5000) using benzene as the immersion fluid.[3] Refractive indices were obtained *via* the Beche line technique with a series of certified index-of-refraction liquids (Cargille Laboratories, Inc.) and a microscope.[3]

The infrared spectra were recorded with a Perkin-Elmer Model No. 521 Grating infrared spectrophotometer. Selected glass samples were first ground in a mullite pestle and mortar. Samples of ground glass from 4 to 13 mg (largest amounts for the smaller GeO_2 contents) were then mixed with 400 mg of KBr (Matheson Coleman and Bell) and heated for $^1/_2$ hr at 100°. The KBr pellets were then formed by pressing the evacuated mixtures at 16 tons for 10 min.[22]

Results

Table I gives the analyzed compositions of the binary and ternary glasses together with their measured densities and refractive indices. None of the binary glasses prepared were found to possess the deep red color associated with crystalline Cu_2O. Instead, all were dark greenish black, with the color deepening with increase of the Cu_2O content. All of the ternary glasses possessed the dark greenish black color characteristic of copper(II).[23] The glass compositions are shown for reference on an enlarged portion of the Cu_2O-CuO-GeO_2 ternary system in Figure 1. Essentially three glass series emerge: (a) binary copper(I) germanates that contain as much as 12 mol % Cu_2O, (b) ternary glasses with a Cu(II):Cu(I) ratio of 0.125, and (c) ternary glasses with a Cu(II):Cu(I) ratio of 0.175.

The infrared spectra of these binary and ternary glasses are shown in Figures 2 and 3, respectively, for the 1100–400-cm^{-1} region. This spectral region is of particular interest because it contains the main Ge-O stretching frequency, the position of which is sensitive to structure.[22] The spectra of (a) a 4-mg sample of freshly ground pure GeO_2 glass and (b) a 3-mg sample of crystalline Cu_2O are also shown for comparison in Figure 2. The position obtained for the main Cu-O frequency is quite close to the known value.[24] The position of this vibration is far enough removed, and the Cu_2O contents small enough, so as to cause no significant interference with the analysis of ν_{Ge-O} results.

Discussion

Refractive Indices. The compositional dependence of refractive index for the binary and ternary glasses is shown in

---

[17] A. M. M. Gadalla, W. F. Ford, and J. White, *Trans. Brit. Ceram. Soc.*, 62, 45 (1963).

[18] L. C. Klein, U. S. Patent 2,474,533 (1949); *Chem. Abstr.*, 43, 7202 (1949).

[19] W. Rieman, III, J. D. Neuss, and B. Naiman, "Quantitative Analysis," 3rd ed, McGraw-Hill, New York, N. Y., 1951, pp 221–231.

[20] W. Rieman, III, ref 19, pp 185–186, 323.

[21] W. P. Close and J. F. Tillman, *Glass Technol.*, 10, 134 (1969).

[22] E. F. Riebling, *J. Mater. Sci.*, 7, 40 (1972).

[23] V. Balzai and V. Carassiti, "Photochemistry of Coordination Compounds," Academic Press, London, 1970, Chapter 13.

[24] J. C. W. Taylor and F. L. Weichman, *Can. J. Phys.*, 49, 601 (1971).

Table I. Compositions and Physical Properties of Cu_2O-GeO_2 and $Cu_2O-CuO \cdot GeO_2$ Glasses

Glass	Mol %			Density, g/cm^3	Refractive index
	Cu_2O	CuO	GeO_2		
A	1.69	0.0	98.31	3.663	1.618 (±0.004)[a]
B	4.62	0.0	95.38	3.761	1.626 (±0.000)[a]
C	10.0	0.0	90.0	4.005	1.698
D	10.4	0.0	89.6	3.992	1.698
E	12.1	0.0	87.9	4.047	1.715
F	5.61	3.49	90.9	3.860	1.646
G	14.6	4.50	80.9	4.065	1.725 (±0.000)[a]
H	14.3	5.30	80.4	4.046	1.720 (±0.005)[a]
I	13.1	5.70	81.2	4.083	1.715
J	13.9	6.40	79.7	4.093	1.735 (±0.000)[a]
K	13.6	7.24	79.2		1.725
L	17.5	9.32	73.2	4.392	1.810
M	21.8	7.33	70.9	4.522	1.870

[a] Uncertainty in duplicate determinations on two different crushed samples.

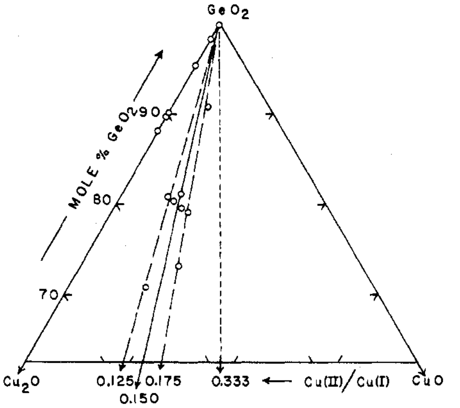

Figure 1. Glass compositions studied in the GeO_2-rich portion of the $Cu_2O-CuO-GeO_2$ system.

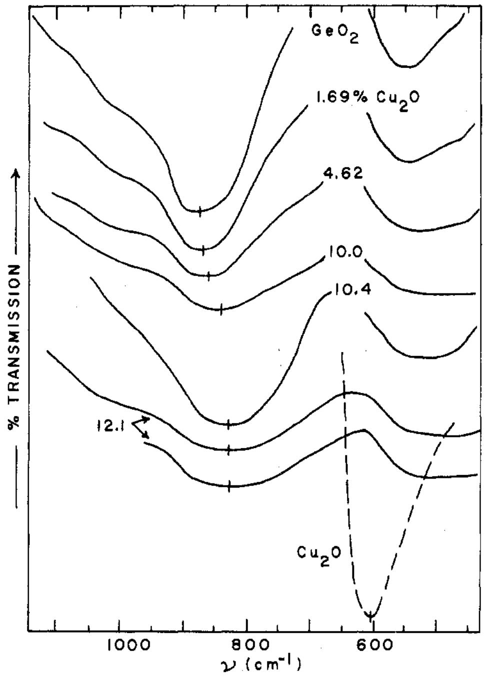

Figure 2. Infrared spectra of GeO_2 glass, binary Cu_2O-GeO_2 glasses, and crystalline Cu_2O.

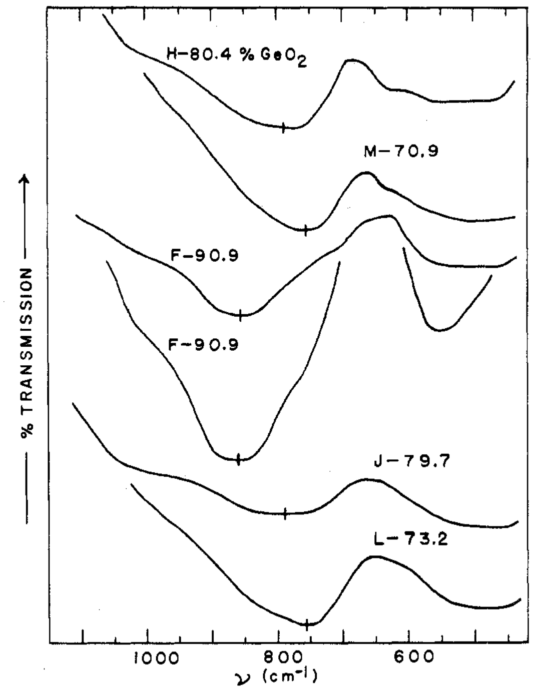

Figure 3. Infrared spectra of ternary $Cu_2O-CuO-GeO_2$ glasses.

Figure 4. The refraction increase that accompanies initial Cu_2O additions to GeO_2 is somewhat similar to those previously reported for Na_2O[25] and Ag_2O[3,4] additions. However, the behavior of Cu^+ would appear to differ from that of Na^+ and Ag^+ at larger modifier concentrations.

Pure Cu_2O has a rather high refractive index (2.705)[26] compared to the calculated values for Na_2O and Ag_2O (~1.47 and ~2.03, respectively) that can be estimated from information for the corresponding sulfates with the Lorentz-Lorenz equation.[3] Thus, neither the refraction maxima noted for Na_2O additions nor the refraction plateau noted for Ag_2O additions appears to exist for larger additions of Cu_2O.

There appear to be small negative deviations from additivity (−2% at 95 mol % GeO_2) for the refraction of the Cu_2O glasses studied. Such deviations do not occur with similar Na_2O or Ag_2O additions and may be indicative of a relatively open structure. Retention by copper(I) of the unusual linear coordination found in crystalline Cu_2O[5] could explain such a situation. In essence, small amounts of copper(I) might act as a network-bridging species that could buttress the open amorphous network of corner-shared GeO_4 tetrahedra instead of causing it to collapse *via* formation of GeO_6 octahedra (as it does with similar Na_2O or Ag_2O additions).

The presence of copper(II) serves to lower the refraction to a level that is below that observed for copper(I) alone (Figure 4). This occurs in spite of the relatively high refractive index of crystalline CuO (2.63).[26] The refraction line drawn for the Cu(II):Cu(I) = 1.50 ± 0.25 glasses actually curves upward (but at lower GeO_2 contents) in a fashion that is similar to that observed for Cu_2O additions alone. However, the negative deviations are more pronounced (−6% at the 14% Cu_2O-6% CuO-80% GeO_2 composition) with copper(II) present. The refraction would appear to approach

---

(25) M. K. Murthy and J. Aguayo, *J. Amer. Ceram. Soc.*, 47, 444 (1964).

(26) R. C. Weast, Ed., "Handbook of Chemistry and Physics," 53rd ed, Chemical Rubber Co., Cleveland, Ohio, 1972-1973, p B-89.

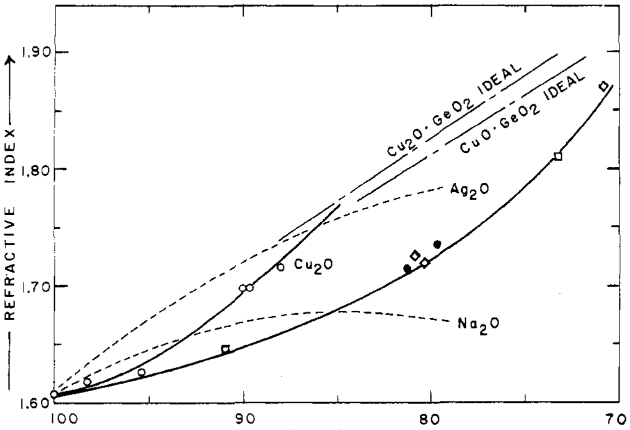

Figure 4. Refractive index *vs.* mole per cent GeO_2 for Cu_2O–GeO_2 glasses (○) and ternary glasses with Cu(II):Cu(I) = 0.125 (◇), 0.150 (●), and 0.175 (□). Data for Ag_2O additions from ref 3 and 4 and data for Na_2O from ref 25.

additivity for ternary glasses that contain less than 70 mol % GeO_2.

The above phenomena could be caused by copper(II) also acting as a network-bridging species that could "prop open" the GeO_4 network, particularly for small CuO contents. Such a behavior is not unexpected for a divalent modifier cation. The alkaline earths appear to act likewise when added to SiO_2 or GeO_2.[2]

Molar Volumes. The molar volumes of the binary and ternary glasses were calculated from the densities and compositions of Table I and are shown as a function of network former concentration in Figure 5. Small amounts of Cu_2O (up to 4%) appear to expand the network of GeO_4 tetrahedra. Larger Cu_2O contents produce (a) a shrinkage and (b) negative deviations from additivity ($v^0_{GeO_2\,glass}$ and $v^0_{Cu_2O\,crystal}$ assumed). Both of the latter effects are similar to those observed for Na_2O and Ag_2O additions.[3] The start of a volume minimum also seems to occur in the 10 mol % Cu_2O region.

The overall shrinkage and deviations from ideal mixing that accompany the addition of 15 mol % Cu_2O are both considerably less pronounced than those changes that accompany similar Na_2O and Ag_2O additions (Figure 5). This difference is not due to any volume difference between the modifier oxides because $v^0_{Ag_2O}$ (32.44 cm^3) $> v^0_{Na_2O}$ (27.31 cm^3) $> v^0_{Cu_2O}$ (23.85 cm^3).[26] Thus, Cu_2O definitely causes a relative "bloating" of the GeO_2 structure. The unusual linear coordination of copper(I) in some oxide environments may create all of these effects by "propping open" both the damaged GeO_4 network at lower Cu_2O contents and the mix of GeO_4 tetrahedra and GeO_6 octahedra at higher Cu_2O contents.

The volume and refraction results for these copper(I) germanate glasses thus tend to complement each other. Both properties exhibit deviations that suggest a more open glass structure, which in turn can be rationalized in terms of the coordination expected for copper(I).

While the volume deviations from ideality observed for the Cu(II):Cu(I) = 0.150 ternary glasses are relatively small for GeO_2 contents greater than 78%, they do become appreciable as the GeO_2 content drops to the 70% region (Figure 5). Thus, at least 15% of the Cu^+ ions can be replaced by Cu^{2+} at higher GeO_2 contents (with a concomitant decrease in the copper atom concentration) without a significant change in the polyhedral packing efficiency. This suggests that copper(II) can also "prop open" the glass network at higher GeO_2 contents (>78%).

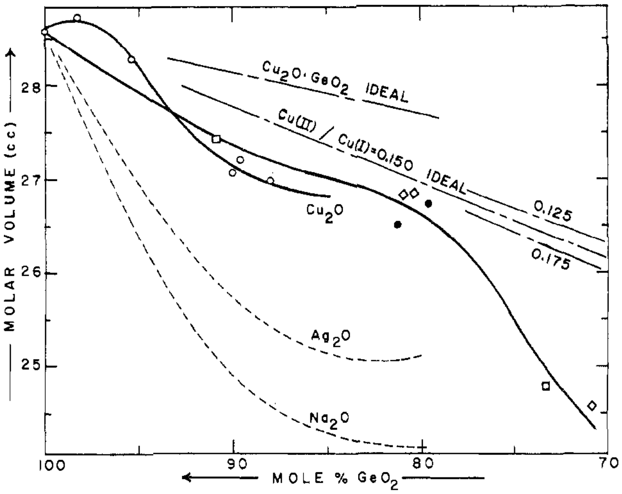

Figure 5. Molar volume *vs.* mole per cent GeO_2 for Cu_2O–GeO_2 glasses (○) and ternary glasses with Cu(II):Cu(I) = 0.125 (◇), 0.150 (●), and 0.175 (□). Data for Ag_2O additions from ref 3 and data for Na_2O from ref 25.

The small negative volume deviations observed for ternary glasses that contain less than 6 mol % CuO ($r_{Cu^{2+}} \approx 0.69$ Å) are similar in magnitude to those reported for a 4.6 mol % MgO ($r_{Mg^{2+}} \approx 0.65$ Å) germanate melt at 1500°.[2] Some sort of network-bridging role would be expected for smaller concentrations of divalent cations in both SiO_2 and GeO_2. Thus, the present finding for smaller CuO contents appears to provide another example of the previously reported inverse relationship between modifier cation field strength and GeO_6 octahedra stability.[2]

The significant volume decrease noted for the ternary glasses in the 70 mol % GeO_2 region of Figure 5 may reflect a change in the bridging role probably played by Cu^{2+} at higher GeO_2 contents. While a 70 mol % GeO_2 glass with Cu(II):Cu(I) = 0.150 contains 7 mol % CuO, it contains 23 mol % Cu_2O. This concentration of Cu^+, at such a low GeO_2 content, could easily create enough network disruption, *via* GeO_6 octahedra formation, to more than compensate for any network bridging or repair caused by Cu^{2+}. In essence, one observes the structural disruption for such a ternary glass that would be expected at about the 15 mol % Cu_2O binary composition. As with the binary glasses, the refraction and volume results for the ternary glasses tend to complement each other. That is, the negative refraction deviations (a) are accompanied by small volume deviations (when amount of $GeO_2 > 78$ mol %) and (b) shrink when the negative volume deviations become significant (when amount of $GeO_2 < 78$ mol %).

The oxygen coordination experienced by modifying or bridging cations in a ternary oxide glass can be uncertain because the atomic level structure of any glass is closely related to that of the melt just above the glass transition temperature.[27,28] Hence, the packing requirements are not those imposed by a given rigid-lattice symmetry. For example, Cu^{2+} exhibits a variety of packing arrangements in the crystalline state such as square planar in CuO,[6] distorted octahedral in turquoise $CuGeO_3$,[29] square planar or greatly

---

(27) E. F. Riebling, *J. Amer. Ceram. Soc.*, 51, 143 (1968).

(28) M. D. Ingram and J. A. Duffy, *J. Amer. Ceram. Soc.*, 53, 317 (1970).

(29) H. Vollenkle, A. Wittmann, and H. Nowotny, *Monatsh. Chem.*, 98, 1352 (1967).

distorted octahedral in deep blue CuB_2O_4,[30] and distorted trigonal bipyramidal in $CuTeO_3$.[31] Usually, four of the Cu-O bond lengths are quite close to those found in CuO. Most of these crystalline solids are blue or green because of overlapping d-d bonds involving the $3d^9$ Cu^{2+} ion.[23] All of the ternary copper(II) glasses under discussion are also deeply colored.

Infrared Spectra. The frequency of the main Ge-O stretching vibration (ν_{Ge-O}) is known to be a sensitive indicator of structural changes in crystalline GeO_2. Thus, ν_{Ge-O} shifts to smaller frequencies in tetragonal GeO_2 (GeO_6 octahedra) compared to hexagonal GeO_2 (GeO_4 tetrahedra).[32] This vibration occurs in GeO_2 glass as a broad band centered at 875 cm^{-1} (Figure 2) that can be associated with a random network of corner-shared GeO_4 tetrahedra. The addition of alkali oxides to GeO_2 glass was found to cause a shift of ν_{Ge-O} to smaller frequencies[33] that could be associated with the formation of GeO_6 octahedra and a concomitant depolymerization of the GeO_4 network. The same was subsequently found to be the case for both (a) additions of either Ag_2O or Tl_2O[22] and (b) various additions of two different modifying oxides[34].

The compositional dependence of ν_{Ge-O} at maximum absorption for the binary and ternary copper germanate glasses is shown in Figure 6. The average curve for alkali germanate glasses[33] is also shown for comparison. Such curves have been shown to be capable of reflecting different modes of network depolymerization in a variety of oxide glass systems.[22,33-36] Although the ν_{Ge-O} shift to smaller frequencies is less pronounced with Cu^+, the trend is consistent and a bit greater than the experimental uncertainty of about 5 cm^{-1} (two spectra were obtained for the same sample of glass E). Thus, the limited infrared data for the binary copper(I) germanate glasses suggest that Cu^+ may only be slightly less effective than Na^+ in depolymerizing the GeO_4 network *via* GeO_6 octahedra formation.

The substitution of about 20% of the Cu^+ ions by Cu^{2+} ions at GeO_2 contents above 88 mol % definitely appears to postpone the ν_{Ge-O} shift. The conclusion is supported by the closeness of the two data points for glass F that were obtained with two different samples of that glass. However, ν_{Ge-O} does decrease significantly for the ternary glass series as the GeO_2 content drops below 88 mol %. For a 70 mol % GeO_2 ternary glass with Cu(II):Cu(I) = 0.150, ν_{Ge-O} is actually smaller than either that reported for the alkali glasses or that expected for the Cu_2O glasses.

An infrared isofrequency contour technique was recently developed to aid in detecting polymerization changes in ternary oxide glasses.[22,35,36] Such contours, while they connect ternary compositions that possess the same frequency for the vibration being studied, do not necessarily connect glasses of similar structure because several depolymerization mechanisms can cause frequency shifts. However, the trends between contours can reflect broad regional differences in the degree of depolymerization.

Figure 7 shows such isofrequency contours for the main Ge-O vibration in the copper(I) and copper(II) germanate glasses involved in this study. The trend of these contours at higher GeO_2 contents suggests that the substitution of about 15% of the Cu^+ ions by Cu^{2+} ions tends to "repair" the damaged GeO_4 network. However, the ν_{Ge-O} contour trends at GeO_2 contents below about 85 mol % suggest a significantly greater degree of depolymerization for such ternary glasses. Thus, the analysis of the isofrequency contour trends for these ternary glasses yields an overall depolymerization sequence that is somewhat similar to that suggested by the refraction and volume analysis.

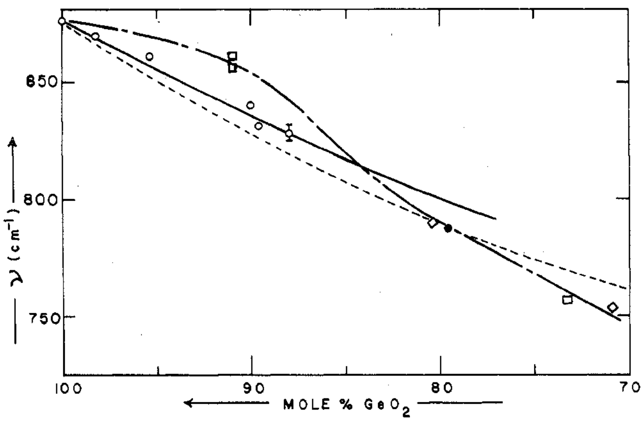

Figure 6. Frequency of ν_{Ge-O} *vs.* mole per cent GeO_2 for Cu_2O-GeO_2 glasses (○) and ternary glasses with Cu(II):Cu(I) = 0.125 (◇), 0.150 (●), and 0.175 (□). Alkali data (- - - -) from ref 33.

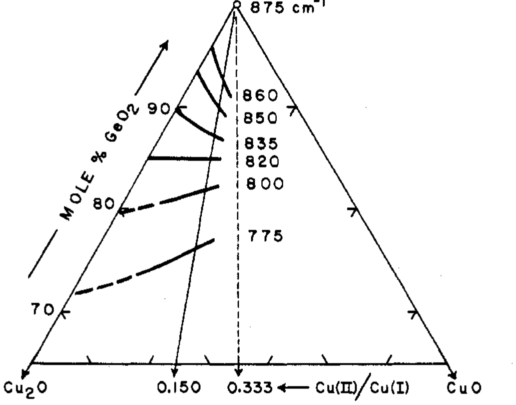

Figure 7. Constant-frequency contours of ν_{Ge-O} for GeO_2-rich glasses in the Cu_2O-CuO-GeO_2 system.

Conclusions

Binary copper(I) germanate glasses that contain more than 12 mol % Cu_2O are difficult to prepare in air. All of the small amount of CuO formed during heating to 1026° cannot rapidly decompose if the original Cu_2O content of the glass batch exceeds 20 wt %. Practical glass melting considerations such as possible container corrosion by Cu_2O, the melting points of Cu_2O and GeO_2, the high viscosity of GeO_2, and volatilization all combine to entrap some copper(II) within the structure of such glasses. The use of an inert atmosphere during heating and melting may provide a route to higher Cu_2O content copper(I) germanate glasses.

Copper(I) does not always behave like other univalent modifiers, be they alkali or pseudoalkali in electronic configuration. The $3d^{10}$ copper(I) tends to alter the GeO_4 network so as to yield a much more open glass structure than would be predicted from the effect of either the similar size Na^+ or the electronically similar $4d^{10}$ silver(I). The refraction and volume results for the binary glasses can best be

---

(30) M. Martinez-Ripoll, S. Martinez-Carrera, and S. Garcia-Blanco, *Acta Crystallogr., Sect. B*, 27, 677 (1971).

(31) O. Lindqvist, *Acta Chem. Scand.*, 26, 1423 (1972).

(32) C. B. Sclar, L. C. Carrison, and C. M. Schwartz, *Science*, 138, 525 (1962).

(33) M. K. Murthy and E. M. Kirby, *Phys. Chem. Glasses*, 5, 144 (1964).

(34) E. F. Riebling, *J. Amer. Ceram. Soc.*, 56, 25 (1973).

(35) E. F. Riebling, *J. Amer. Ceram. Soc.*, 56, 303 (1973).

(36) E. F. Riebling and V. Kotian, *J. Mater. Sci.*, in press.

understood in terms of (a) the probable linear O–Cu–O arrangement that tends to buttress the altered GeO_4 structure and (b) the possibility that extensive GeO_6 octahedra formation may not occur with the first few per cent of Cu_2O added. The infrared results for both binary and ternary glasses suggest that further additions of Cu_2O can create extensive network depolymerization *via* GeO_6 octahedra formation.

Copper(II) appears to play an important network-bridging role in all ternary glasses studied that contain more than 78 mol % GeO_2. Although it may continue to do so in the smaller GeO_2 content Cu(II):Cu(I) = 0.150 glasses, its influence is diminished because the relatively large amounts of Cu_2O (glass M has 21.8 mol % Cu_2O) have greatly depolymerized the GeO_4 network *via* extensive GeO_6 octahedra formation. In essence, as the GeO_2 content decreases for the Cu(II):Cu(I) = 0.150 glasses, (a) both copper(I) and copper(II) appear to buttress the open network at higher GeO_2 levels and (b) the structure-breaking effect of copper(I) outweighs the structure-making effect of copper(II) at lower GeO_2 levels.

It is possible to confirm GeO_4 network polymerization changes that have been suggested from other physical property measurements for such oxide glasses by monitoring the frequency of the main infrared-active Ge–O vibration as a function of composition. The trends between infrared isofrequency contours for ν_{Ge-O} appear to be reasonably sensitive indicators of the contrasting roles played by copper(I) and copper(II) in altering or maintaining such oxide networks. This latest application of the aforementioned spectral technique thus serves to strengthen its validity as a structural survey tool for ternary oxide glass systems that involve network depolymerization.

Acknowledgment. Mr. J. Sprinkle assisted with the preparation and analysis of the glasses and also with the measurement of some of the densities and refractive indices.

Registry No. $[(CH_3)_3C]_2PF_3$, 29120-68-1; $[(CH_3)_3C]_2PCl$, 13716-10-4.

Contribution from the Department of Polymer Science, Faculty
of Science, Osaka University, Toyonaka, Osaka, 560, Japan

Bis(dialkylaluminum) Oxide from Lithium Dialkylaluminates and Dialkylaluminum Chlorides[1,2]

NORIKAZU UEYAMA, TAKEO ARAKI,* and HISAYA TANI

Received February 26, 1973

A synthetic method for the preparation of bis(dialkylaluminum) oxides using the condensation of lithium dialkylaluminates and dialkylaluminum chlorides was investigated. The reaction products were found to show identical properties with the bis(dialkylaluminum) oxides obtained by Storr, Jones, and Laubengayer in the hydrolysis of trialkylaluminum with water in a 2:1 ratio under high dilution. Synthetic studies indicate that the new method is promising for preparing some derivatives of the bis(aluminum) oxides. On the basis of ir and conductivity experiments, the nature of the Al–O–Al bond in the $Et_2AlOAlEt_2$ compound is suggested to be considerably polarizable. 5,6-Benzoquinolinate complexes were isolated in crystalline forms and investigations of the complexes together with their related compounds showed that the monocoordinated complexes are more stable than the dicoordinated ones. The unusual electron-accepting nature of the $R_2AlOAlR_2$ compounds can be due to the bidentate property of two aluminum atoms in a molecule.

Introduction

Bis(dialkylaluminum) oxides have been synthesized by the hydrolysis of the corresponding trialkylaluminums.[3,4] Recently, Storr, Jones, and Laubengayer[4] presented a report on the characterizations of the bis(dialkylaluminum) oxides obtained by this method under highly diluted conditions. Since there is little information on the mechanism of the hydrolysis of trialkylaluminum compounds,[5] however, one might have considered the product to be a mixture of the hydrolysates involving different numbers of the Al–O bonding unit. In one study[6] the Lewis acidity of the system containing the hydrolysates was suggested to increase with extensive hydrolysis of the triethylaluminum, $AlEt_3$. In such a case, attack of a water molecule on the bis(dialkylaluminum) oxide formed would be more probable than attack on trialkylaluminum, resulting in the higher members of condensation product. In order to clarify the problems involved in the bis(dialkylaluminum) oxide compound, it would be desirable to find a new synthetic procedure of preparing such compounds by a different route. Although several reactions giving this compound have been reported,[7-12] few are useful because of the formation of organoaluminum by-products.

---

(1) This study constitutes a part of the Ph.D. thesis of Dr. N. Ueyama, Osaka University, 1970.

(2) Preliminary publications: (a) H. Tani, T. Araki, N. Oguni, and N. Ueyama, *J. Amer. Chem. Soc.*, 89 173 (1967); (b) T. Araki, T. Aoyagi, N. Ueyama, T. Aoyama, and H. Tani, *J. Polym. Sci., Part A-1*, 11, 699 (1973).

(3) A. F. Zhigach, G. B. Sakharovskaya, N. N. Korneev, A. F. Popov, and E. I. Larikov, *Zh. Obshch. Khim.*, 34, 3478 (1964).

(4) A. Storr, K. Jones, and W. Laubengayer, *J. Amer. Chem. Soc.*, **90**, 311 (1968).

(5) S. Amadurski, C. Eden, and H. Feilchenfeld, *J. Inorg. Nucl. Chem.*, **23**, 133 (1961).

(6) H. Imai, T. Saegusa, and J. Furukawa, *Makromol. Chem.*, **81**, 92 (1965).

(7) (a) K. Ziegler, *Angew. Chem.*, 68, 721 (1956); (b) K. Ziegler, F. Krupp, K. Weyer, and W. Larbig, *Justus Liebigs Ann. Chem.*, 629, 251 (1960).

(8) H. Hock, H. Hopf, and F. Ernst, *Angew. Chem.*, 71, 541 (1959).

(9) (a) G. Zweifel, and R. B. Steele, *Tetrahedron Lett.*, 6021 (1966); (b) M. Fukui, T. Araki, H. Yasuda, and H. Tani, paper presented at the Meeting of the Chemical Society of Japan, Chugoku-Shikoku District, Okayama, Oct 1967; M. Fukui, M.Sc. Thesis, Osaka University, 1967; (c) T. Sakakibara, T. Hirabayashi, and Y. Ishii, *J. Organometal. Chem.*, 46, 231 (1972).

(10) (a) H. Reinheckel and D. Jahnke, *Angew. Chem.*, **78**, 947 (1966); (b) H. Reinheckel and D. Jahnke, *Chem. Ber.*, **99**, 1718 (1966).

(11) R. Koster and Y. Morita, *Justus Liebigs Ann. Chem.*, **704**, 70 (1967).