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HIGH-TEMPERATURE BORATE LIQUIDS:
PHYSICAL PROPERTIES OF GLASS-FORMING COMPOSITIONS

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HIGH TEMPERATURE BORATE MELTS: PHYSICAL PROPERTIES OF
GLASS FORMING COMPOSITIONS

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ABSTRACT

Several experimental routes can be used to develop a better understanding of the polymeric constitution (poly-anionic and/or polyhedral distribution) of borate, germanate, and silicate glasses. Spectral, chemical, physical-chemical, and mechanical property information can be determined directly for the glass compositions of interest. Generally, only physical-chemical information is readily accessible for the corresponding high temperature liquids. It will be shown that information on each state of matter has its own particular merits.

Most of the evidence thus far published suggests an excellent agreement between polyhedral distributions in an oxide glass and its corresponding high temperature liquid state. There is no well known oxide glass forming system for which such a state of affairs does not exist. In spite of this, occasional efforts are put forth which ignore some of what is known for oxide liquids, glasses, and crystals. Such attempts therefore invariably imply, if only indirectly, that significant changes occur in the polyhedral distributions close to the glass transition temperature region. Specific examples to be discussed will include efforts that avoid well known coordination change equilibria such as $\text{BO}_3 \rightleftharpoons \text{BO}_4$ and $\text{GeO}_4 \rightleftharpoons \text{GeO}_6$.

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INTRODUCTION

A pure network liquid such as molten SiO_2 is essentially a random three-dimensional arrangement of corner shared SiO_4 tetrahedra. In contrast, the orthosilicate composition (33 mole % SiO_2) contains a completely depolymerized mixture of SiO_4^{-4} anions. Any composition between these two extremes must therefore contain a relatively complex mixture of partially polymerized anions. Practice has shown that physical-chemical properties of such mixtures are highly dependent upon structure and composition.

Many of the structurally sensitive techniques that were originally developed to examine crystalline solids have also been successfully extended to amorphous oxides. Thus, X-ray, infrared, and NMR have all been used to develop a more sophisticated picture of the polymeric nature of alkali borate, silicate, germanate, and phosphate glasses [1]. However, only with the case of binary phosphate glasses has it been possible to identify both the type (chain, ring, sheet) and relative concentration of each polyanion in a given distribution [2]. The fragment distributions agreed quite well with predictions based on condensation polymer theory. While binary silicate glasses close to the orthosilicate composition have been partially characterized [3, 4], extensive solvent/glass interactions [5, 6] have inhibited efforts to characterize polyanion distributions in higher silica content glasses and crystals [7-10].

In contrast, the depolymerizations that accompany modifier additions (between 15 and 50 mole %) to B_2O_3 and GeO_2 create a

change of coordination for a fraction of the network forming cations [11-13]. The resultant polyanions can therefore contain mixtures of two different types of polyhedra (BO_3 and BO_4 or GeO_4 and GeO_6). Hence, solvent/glass interactions and polyanion separation/identification procedures can be rather different from those thus far encountered with silicate and phosphate glasses. An initial approach to this problem involves the preparation of binary and ternary borate or germanate glasses that are likely to contain relatively simple polyanion distributions. Such distributions can be obtained by adding large amounts of either a network former or a modifier that does not create a coordination change. Special physical-chemical property techniques can be developed to aid the search for such glasses. Examples of progress in this area include, but are not limited to, glasses in the $\text{Sb}_2\text{O}_3\cdot\text{B}_2\text{O}_3\cdot\text{GeO}_2$ [14], $\text{Bi}_2\text{O}_3\cdot\text{GeO}_2$ [15], and $\text{Tl}_2\text{O}\cdot\text{Bi}_2\text{O}_3\cdot\text{GeO}_2$ [16] systems.

Another approach to the problem of glass characterization is based upon the fact that the available evidence confirms the absence of significant polyanion or polyhedral coordination distribution changes within the glass transformation range [13, 17]. In some cases, the physical-chemical properties of a high-temperature liquid can be either more structure sensitive or more obtainable than the corresponding glass properties. For example, either microphase separation or partial crystallization can occur on cooling and make it difficult to achieve a one phase glass for the exact compositions of interest.

Relatively fluid oxide liquids such as the alkali borates can be hygroscopic, corrosive, and volatile. Also, the properties of viscous network liquids such as pure B_2O_3 can be quite sensitive to impurity concentration levels. Hence, compositional control is essential. However, precise physical-chemical studies of the above types of liquids have been completed and the results used to gain a greater insight into the nature of the glass state. Most of what follows will of necessity be brief and restricted to borate liquids. Information concerning silicates and germanates will be used only for comparative purposes.

NETWORK BORATES

Most ionic liquids expand and become less viscous at higher temperatures. However, temperature can alter the structure of covalently bonded liquids in a number of ways. Thus, although the viscosity of water-free B_2O_3 decreases with increase of temperature, it does so in such a fashion as to suggest the existence of a more complex flow mechanism above 1300°C [18]. Also, the density and expansivity changes suggest a gradual tightening of the arrangement of BO_3 polyhedra at temperatures within the 1100°

to 1400° C range. Several types of B-O regroupings are possible. However, it is still not at all certain if the two phenomena are related to the same type of B-O regrouping.

Small SiO_2 or GeO_2 additions (0 to 20 mole %) to molten B_2O_3 increase both the density and viscosity, but decrease the expansivity [19]. The actual deviations from ideal mixing behavior suggest the presence of a nearly normal O-B-O solvent network that contains widely separated silicon or germanium atoms. Similar additions of Al_2O_3 increase the density and expansivity, but decrease the viscosity [18]. The aluminum atoms thus appear to occur as widely separated network modifiers.

Larger additions of either SiO_2 or GeO_2 (up to 60 mole %) to molten B_2O_3 create significant property deviations from ideal mixing [19]. Gross disruptions of the O-B-O solvent are apparently accompanied by microclustering of SiO_4 or GeO_4 tetrahedra at the 40 mole % SiO_2 and 60 mole % GeO_2 compositions. Thus, the higher field strength Si^{+4} appears to be more effective in altering the O-B-O structure. However, electron microscopic examination of the resultant glasses did not reveal actual phase separation.

ALKALI BORATES

For a simple crystalline oxide, one usually encounters an either/or situation with respect to the stability of a given coordination polyhedron. Thus, either tetrahedra or octahedra are the stable species for a given cation at a fixed temperature and pressure [20]. Examples include the pressure dependent cristobalite to stishovite transformation for SiO_2 and the temperature dependent rutile to quartz-like transformation for GeO_2 .

The presence of a second type of cation represents a change of electronic environment (composition, oxidation state, etc.) for the original cation. In such a situation, different coordination polyhedra of a given cation can readily coexist as part of a thermodynamic equilibrium mixture. Thus, BO_3 trigonal planar polyhedra and BO_4 tetrahedra, as well as GeO_4 tetrahedra and GeO_6 octahedra, coexist in crystalline alkali borates and germanates respectively. The ratio of BO_4/BO_3 and $\text{GeO}_6/\text{GeO}_4$ is quite specific because of (a) the different structural role played by each type of polyhedron, (b) the fixed composition of a given compound, (c) the fixed pressure and temperature, and (d) the fixed geometry of the unit cell.

A gross structure change upon melting, such as from molecular to ionic bonding, is usually characterized by abnormal heats, entropies, and temperatures of fusion. In the absence of any such

evidence for a given compound, there is no reason why polyhedral mixtures characteristic of the crystal may not exist in the liquid. The absence of the constraining electrostatic force field of the crystalline lattice may introduce a slight temperature dependence of the BO_4/BO_3 and $\text{GeO}_6/\text{GeO}_4$ ratios. However, an equilibrium mixture of polyhedra should still prevail in the liquid. Further, there is no thermodynamic reason, other than phase separation, incongruent melting behavior, and the like, why such mixtures of coordination polyhedra should not be retained during rapid cooling to obtain a glass. This should be particularly true of relatively viscous liquids that are rapidly quenched. There is no convincing evidence to suggest that the glass transformation (T_g) region is one of gross atomic level structure change. If anything, the density and expansivity evidence [17], together with the relatively small heats of glass transformation, suggest the existence of only minor structure changes within the T_g region.

Thus, it was not entirely unexpected that the addition of alkali oxide to molten GeO_2 was found to induce a partial change of coordination for germanium from tetrahedral to octahedral [11] and that similar conclusions could be drawn for the corresponding alkali germanate glasses [17]. A most convincing piece of evidence in these studies was the smaller than normal partial molar volume exhibited by GeO_2 in these mixtures. Higher coordination polyhedra can represent a more efficient mode of cation/oxygen packing. Also, octahedra can be packed more efficiently, via edge sharing, than tetrahedra. What was surprising was that these studies had not been attempted earlier.

Subsequent work with molten alkali borates revealed a pronounced melt densification that accompanied the known viscosity decrease [12]. The partial molar volume decrease exhibited by B_2O_3 in such liquids also suggested a more efficient packing of O-B-O polyhedra. The deviation from ideal mixing at the 40 mole % Na_2O composition (Figure 1) is of the magnitude expected for an equimolar mixture of BO_4 tetrahedra and BO_3 polyhedra. This conclusion agreed with that reported for an NMR study of alkali borate glasses [21]. Both studies also reported a complete return to some form of trigonal coordination for boron at higher alkali contents.

In spite of our present knowledge of the glass transformation range and also of coordination changes that can occur for network forming cations, occasional efforts are put forth which ignore some of what is known for oxide liquids, glasses, and crystals. Such attempts therefore imply, if only indirectly, that significant polyhedral distribution changes occur within the glass transformation range. Several of these attempts will be briefly analyzed below.

Fig. 1. Partial molar volume of B_2O_3 isotherms for binary sodium borate melts.

Non-bridging oxygen atoms are going to exist if an ionic modifier is added to a covalent network former, regardless of the exact mode of depolymerization (disturbed network, island, discrete anion model with silicates versus coordination change, discrete anion model with borates and germanates). However, some of the physical property changes that accompany the addition of alkali oxide can be highly dependent upon the specific network former. This suggests that given physical property changes can be rather sensitive indicators of a particular mode of network depolymerization. Thus, molten silica can apparently accommodate 10 mole % M_2O without undergoing significant disruption. The supporting evidence includes the nearly ideal partial molar volume of SiO_2 and the absence of an expansivity increase. Larger amounts of modifier successively create a disturbed network, silica-rich "islands," and discrete anions as non-bridging oxygen atoms are gradually introduced [22]. In contrast, the partial molar volumes of molten and amorphous GeO_2 and B_2O_3 decrease significantly, with simultaneous expansivity increases, as modifier is added. Therefore, it should be readily apparent that non-bridging oxygen atoms are not completely responsible for the property changes observed with borate and germanate melts.

However, the "spector" of non-bridging oxygen atoms continues to be raised for borates and germanates, usually in such a way as to subtly cast doubt on the coordination change model [23]. Equally obfuscating are statements to the effect that structural models cannot be proved by physical property information [23]. Unfortunately, such semantics tend to cast doubt on all that has gone before, theoretical as well as experimental. Modern physical science is based on a vast body of information and ideas, not all

of which are readily accepted by every scientist. While "blindness" are to some extent necessary, they must be used with caution to avoid myopia. Thus, in trying to develop a proper appreciation of borate structures, one should consider all of the information that is available for liquid, glass, and crystalline borates, germanates, and silicates.

More recently, a viscosity study of sodium borate melts concluded that the results could be explained without resorting to a change of coordination for boron [24]. The significant viscosity decrease that accompanies initial modifier additions was instead rationalized in terms of the appearance of progressively smaller, BO_3 -containing, sheet-like discrete polyanions. Unfortunately, such a model implies a gross structure change in the glass transformation range (BO_4 tetrahedra do exist in alkali borate glasses) and therefore casts doubt on the validity of several of the established "milestones" of borate glass science [1].

Thus, if the above model is correct, one or more of the following situations would arise. Borate tetrahedra exist in the glass, but not in the liquid (this would require that a significant polyanion population shift occurs in the glass transformation range). Borate tetrahedra do not exist in either the glass or liquid (this would imply that most of the NMR, density, infrared, etc., measurements and related conclusions are in error). There is no significant evidence to support the first possibility for a binary borate or any other oxide system. There is very little likelihood that the second possibility represents atomic-level reality because many of the same physical property changes (viscosity, density, etc.) are known for alkali germanate liquids and glasses [11, 17, 25, 26]. Mixtures of discrete, sheet-like germanate anions have not been reported or postulated for such liquids, glasses, and crystals. Hence, the sheet-like model for molten borates represents another example of a failure to consider all of the available liquid, glass, and crystalline information, not just for borates, but also for germanates, silicates, etc.

TERNARY BORATES THAT CONTAIN A SECOND NETWORK FORMER

Silica-rich compositions that contain less than 40 mole % M_2O in the $\text{Na}_2\text{O} \cdot \text{B}_2\text{O}_3 \cdot \text{SiO}_2$ system have been extensively studied because of the various practical applications of borosilicate glasses. Also, silica-rich borosilicate-type glasses are of current interest for possible use as the long-term storage media for selected radioactive wastes that remain from nuclear weapons production [27]. The atomic level structure of any glass directly influences the mechanical, chemical, and processing properties such as strength, durability, and annealing characteristics. Hence, an appreciation of the atomic level structure of such

glasses will greatly facilitate the final selections of compositions and processing conditions. A brief examination of some salient features of these high-temperature borosilicate liquids is therefore warranted. Equally important phenomena such as micro- and/or macro-phase separation are not within the scope of this paper.

A density study of the relatively fluid B_2O_3 -rich ternary liquids in the $Na_2O \cdot B_2O_3 \cdot SiO_2$ system concluded that BO_4 tetrahedra exist in most compositions that contain between 15 and 45 mole % Na_2O [12]. For example, the concentration of BO_4 tetrahedra was estimated to be highest (about 50 percent of the boron atoms) for ternary melts close to the 40 mole % Na_2O composition in the sodium borate system. In contrast, only about 25 percent of the boron atoms appeared to be tetrahedrally coordinated in the ternary melts with B/Si ratios close to 2.00.

A recent viscosity and NMR examination of several silica-rich glasses in the above system confirmed the presence of significant concentrations of BO_4 tetrahedra [28]. An appreciation of the equilibrium control of the BO_4/BO_3 ratio was also presented. For example, in a series of silica-rich glasses that contained 15 mole % Na_2O , the fraction of tetrahedrally coordinated boron atoms was proportional to the silica content. This confirmed the earlier prediction, based on a viscosity and density study of $B_2O_3 \cdot SiO_2$ liquids and glasses [19], that the boron atoms could be forced to adopt a tetrahedral configuration in silica-rich compositions.

The nature of similar liquids and glasses that contain less than 40 mole % Na_2O in the $Na_2O \cdot B_2O_3 \cdot GeO_2$ system was also examined [13]. The objectives were to examine the compositional stability of BO_4 tetrahedra and the influence of the $BO_4 \rightleftharpoons BO_3$ equilibrium on the stability of GeO_6 octahedra. Only the former phenomenon will be briefly discussed at this time.

Initial substitutions of GeO_2 for B_2O_3 in sodium borate compositions produced viscosity increases that were attributed to the potential network forming role of GeO_4 tetrahedra under such conditions. Both the molar volume and expansivity results also suggested a significant concentration of BO_4 tetrahedra at most ternary compositions. Therefore, there is a high degree of similarity for the structure of B_2O_3 -rich liquids and glasses in the ternary silicate and germanate systems.

The expansivities of the above ternary borosilicate and borogermanate liquids were also found to be highly sensitive indicators of structural change. In this technique, compositions that contain the same expansion coefficient are joined to form iso-expansivity contours on a ternary composition diagram (Figure 2). Only the liquid phase iso-expansivity contour patterns were readily

Fig. 2. Iso-expansion coefficient contours for melts in the Na₂O · GeO₂ · B₂O₃ system.

associated with the presence of BO_4 tetrahedra. The absence of a similar correlation for the corresponding glasses was not unexpected. There are known structure-sensitive factors that influence the liquid expansivity to a much greater extent [17, 29].

Crystalline Sb_2O_3 has a double-chain polymeric structure that appears to be retained in the liquid and glass states. Visually estimated viscosities of GeO_2 -rich liquids in the $\text{Sb}_2\text{O}_3\cdot\text{B}_2\text{O}_3\cdot\text{GeO}_2$ system suggested that moderate concentrations of Sb_2O_3 depolymerize the GeO_2 network more effectively than does B_2O_3 , but less effectively than does an alkali oxide [14]. However, extensive depolymerization of either a Ge-O-Ge or a B-O-Ge network appeared to require at least 10 to 15 mole % Sb_2O_3 . This was confirmed by the density and infrared changes that were observed for the corresponding glasses [14]. For example, Figure 3 shows the compositional dependence of the transmission minima for the main Ge-O and B-O vibrations. Thus, at least 30 mole % B_2O_3 can be added to GeO_2 without causing a significant frequency shift for $\nu_{\text{Ge-O}}$. Such a situation can reflect the absence of gross depolymerization of GeO_2 (condensed or polymerized polyhedra can possess higher stretching frequencies than their isolated counterparts). The linear increase of $\nu_{\text{B-O}}$ confirms the retention of a network for all $\text{B}_2\text{O}_3\cdot\text{GeO}_2$ compositions.

In contrast, the addition of Sb_2O_3 to GeO_2 causes a substantial shift of $\nu_{\text{Ge-O}}$ to lower frequencies. While 30 mole % Sb_2O_3 causes a frequency shift that is comparable to that caused by 30 mole % alkali oxide additions, the absence of relatively large volume deviations ruled out a coordination change for the Ge atoms. A distribution of smaller Ge-O-Sb species seemed more likely. For B_2O_3 , the substitution of just 50 percent of the B atoms by Sb appeared to create a $\nu_{\text{B-O}}$ shift that is twice that observed for the substitution of 99 percent of the B atoms by Ge atoms. That suggested that Sb_2O_3 causes extensive depolymerization of the B-O-B network.

A technique had been previously developed to more clearly illustrate the relation between infrared frequency and the extent of cross-linking in ternary oxide glasses [30]. Isofrequency contours for a given vibration (B-O, Ge-O, etc.) can be developed by connecting ternary compositions that exhibit the same frequency for that vibration. Such contours can, but not necessarily, connect glasses of similar structure because more than one depolymerization mechanism can cause a frequency shift. Figure 4 depicts these $\nu_{\text{Ge-O}}$ contours for GeO_2 -rich glasses in the $\text{Sb}_2\text{O}_3\cdot\text{B}_2\text{O}_3\cdot\text{GeO}_2$ system. The bent $\nu_{\text{Ge-O}}$ patterns of Figure 4 may partially reflect the more limited network-forming ability of Sb in a B-O-Ge glass compared to that in a Ge-O-Ge glass. On the other hand, GeO_2 -rich B-O-Ge networks may simply be more susceptible to scission by

Fig. 3. (A) Frequency of Ge-O vibration vs mol% GeO_2 for Sb_2O_3 - GeO_2 , B_2O_3 - GeO_2 , and $\text{Sb/B} = 1.00$ germanate glasses. Alkali germanate data (dashed line). (B) Frequency of B-O vibration vs mol% GeO_2 for B_2O_3 - GeO_2 and $\text{Sb/B} = 1.00$ germanate glasses.

Fig. 4. Constant-wave-number contours for Ge-O vibration in GeO_2 -rich Sb_2O_3 - B_2O_3 - GeO_2 glasses.

Sb atoms. In any event, it was possible to readily associate these observations with the differing structural roles of Sb_2O_3 (O-Sb-O chains) and B_2O_3 (O-B-O network).

CONCLUSIONS

It was concluded that several experimental approaches will have to be used if we are to develop a better and more useful understanding of the polymeric constitution of oxide glasses. The state of knowledge for borates was selectively reviewed and used as an example to emphasize the need to consider all of the information that is available for other similar materials such as germanates and silicates. The narrow approach of examining just the properties of the amorphous solids themselves was shown to be insufficient. Instead, a broad approach that also involves a consideration of the corresponding crystals and high-temperature liquids was shown to be superior. It was also concluded that if BO_4 tetrahedra exist in borate crystals, then they may also exist in similar borate high-temperature liquids and their corresponding glasses.

REFERENCES

1. D. L. Griscom, "Borate Glass Structure," pp 1-128, this volume.
2. A.E.R. Westman, in "Modern Aspects of the Vitreous State," Vol. 1, J. D. Mackenzie, ed., Butterworths, London (1960) chapter 4.
3. C. R. Masson, I. B. Smith, and S. G. Whiteway, Canadian J. Chem. 48 (1970) 1456.
4. P. C. Hess, Geochimica et Cosmochimica Acta 35 (1971) 289.
5. D. A. Crerar and G. M. Anderson, Chemical Geology 8 (1971) 107.
6. R.W. Luce, R. W. Bartlett, and G. A. Parks, Geochimica et Cosmochimica Acta 36 (1972) 35.
7. J. Gotz and C. R. Masson, J. Chem. Soc. A1970 (1970) 2683.
8. C. R. Masson, Polymer Preprints 13 (1972) 792.
9. B. R. Currell, H. G. Midgley, and M. A. Seaborne, J. Chem. Soc., Dalton 1972 (1972) 490.
10. B. R. Currell, H. G. Midgley, and M. A. Seaborne, Nature, Physical Science 236 (1972) 108.

11. E. F. Riebling, J. Chem. Phys. 39 (1963) 3022.
12. E. F. Riebling, J. Amer. Ceram. Soc. 50 (1967) 46.
13. E. F. Riebling, P. E. Blaszyk, and D. W. Smith, J. Amer. Ceram. Soc. 50 (1967) 641.
14. E. F. Riebling, J. Amer. Ceram. Soc. 56 (1973) 303.
15. E. F. Riebling, J. Mater. Sci. 9 (1974) 753.
16. E. F. Riebling, J. Mater. Sci. 10 (1975) 1565.
17. E. F. Riebling, J. Amer. Ceram. Soc. 51 (1968) 143.
18. E. F. Riebling, J. Amer. Ceram. Soc. 49 (1966) 19.
19. E. F. Riebling, J. Amer. Ceram. Soc. 47 (1964) 478.
20. E. F. Riebling, in "Phase Diagrams, Materials Science and Technology," Vol. 3, A. M. Alper, ed., Academic Press, New York (1970), chapter 7.
21. P. J. Bray and J. G. O'Keefe, Phys. Chem. Glasses 4 (1963) 37.
22. J. O'M. Brockris, J. W. Tomlinson, and J. L. White, Trans. Faraday Soc. 52 (1956) 299.
23. J. E. Shelby, J. Amer. Ceram. Soc. 57 (1974) 436.
24. G. H. Kaiura and J. M. Toguri, Phys. Chem. Glasses 17 (1976) 62.
25. E. F. Riebling, J. Chem. Phys. 30 (1963) 1889.
26. E. F. Riebling and S. D. Gabelnick, J. Electrochem. Soc. 112 (1965) 822.
27. M. J. Kupfer and W. W. Schulz, Bull. Amer. Ceram. Soc. 56 (1977) 338.
28. M. P. Brungs and E. R. McCartney, Phys. Chem. Glasses 16 (1975) 48.
29. E. F. Riebling, in "Proceedings of the 12th Symposium on the Art of Glassblowing," American Scientific Glassblowers Society (1968), p. 42.
30. E. F. Riebling, J. Mater. Sci. 7 (1972) 40.