

Shape of the Liquidus Surface as a Criterion of Stable Glass Formation

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The slope of the liquidus curve or surface at a point in a phase diagram representing a specific chemical composition has been found to be a reliable indication of the glass-forming tendency of that composition. The observed effect is interpreted in terms of the structure of the glass.

1. Introduction

The structure of glass has been the subject of much discussion, but no theory has been propounded that will explain all the known facts about glass. Much of the present theory is based on the assumption of a continuous and completely random network as developed by Zachariassen [1]¹ and considered to be confirmed by Warren and his associates [2]. Supporters of the network theory associate discontinuities and anomalies in properties with the "silicon to oxygen ratio", number of "single-bonded" oxygen ions, polarizability of ions, deformability of the large O^{2-} ions and changes in coordination number, particularly of the boron ion. While discontinuities in physical properties may be explained in terms of these concepts, some evidence has been presented indicating a structural arrangement in glass other than a random three-dimensional network.

A number of investigators, including Faick and Finn [3], Glaze, Young, and Finn [4], and Preston and Turner [5] have found evidence suggesting the existence of compounds in Na_2OSiO_2 glasses. Huggins [6] has presented his "structon" theory and Tilton [7] his "vitron" theory, both based on data on silicate glasses.

In the present paper some observations on the stability of glasses as indicated by the shape of the liquidus surface or curve will be discussed. Throughout the paper, glass stability means resistance to crystallization.

Grauer and Hamilton [8] have pointed out that in any study of glass stability one must take into account (1) the liquidus temperature or maximum temperature at which equilibrium exists between the glass and the primary crystalline phase and (2) the rates of crystal growth at various temperatures. The rate of crystal growth at the liquidus temperature is zero, it reaches a maximum at some lower temperature, and then approaches zero as the temperature is further reduced. Because the melt must be cooled through these temperatures during fabrication and annealing, the rate of crystal growth is of practical as well as theoretical importance.

2. Experimental Procedure

In the course of the development of new optical glasses for various purposes, data have been collected on a large number of systematically arranged series

of glasses. Most of the series are in the following systems: $BaO-B_2O_3-SiO_2$ [9], $BaO-BeO-B_2O_3-SiO_2$ [10], $Na_2O-TiO_2-SiO_2$ [11], $BaO-TiO_2-SiO_2$ [12], $ZnO-B_2O_3-SiO_2$ [11], $BaO-La_2O_3-SiO_2$ [11], $BaO-Ta_2O_5-SiO_2$ [11], and multicomponent glasses, including rare-earth oxide glasses based on the above systems. Data were also collected on a number of series of multicomponent glasses that had base compositions in the $CaO-MgO-Al_2O_3-SiO_2$ system. The latter series of glasses contained from 0 to 12 mole percent of SiO_2 . The glasses were developed by the partial substitution of one oxide for another in a base composition on a mole for mole basis, i. e. one La_2O_3 for one BaO .

The change in liquidus temperature as a function of SiO_2 content when SiO_2 is substituted for B_2O_3 in the $BaO-B_2O_3-SiO_2$ glasses is plotted in figure 1. The letters under each curve indicate the primary phase, which crystallizes at the liquidus. Similar curves for the change in liquidus temperature as a function of BaO content when BaO is substituted for TiO_2 in the $BaO-TiO_2-SiO_2$ glasses are given in figure 2. The primary phases have not been identified in this system, and consequently the curves as drawn may be subject to revision when the primary phases are known.

The details of the procedure of melting and annealing the glasses have been published elsewhere [12]. Briefly, the procedure is as follows: The glasses were made in 500- to 600-g melts in platinum crucibles. The melts were stirred with platinum-10-percent-rhodium propeller-type stirrers to obtain homogeneity. Compositions that could not be cooled as homogeneous glasses in blocks 3 by 3 by $\frac{1}{2}$ to $\frac{3}{4}$ in. in size are not here considered to be glass forming. The size of the block will affect the cooling rate of the glass in the interior, which in turn will affect the range of glass formation. Many compositions that can be melted in small melts and then cooled in thin pieces as homogeneous glasses would consist of a mass of crystals and glass under the conditions for glass formation discussed above.

3. Discussion

Hamilton, Cleek, and Grauer [9] observed that for a given system, the composition ranges of most stable glass formation are found in the primary fields that have relatively flat liquidus surfaces. These authors suggest that the glasses may contain

¹ Figures in brackets indicate the literature references at the end of this paper.

units of the same compositions as the compounds indicated by the vertices of the composition triangles of the phase diagram of the system. The relation between relatively flat liquidus fields and stable glasses has been observed for the $3\text{BaO}\cdot 3\text{B}_2\text{O}_3\cdot 2\text{SiO}_2$ primary field in the $\text{BaO}\text{-}\text{B}_2\text{O}_3\text{-}\text{SiO}_2$ system [9], $\text{BaO}\cdot \text{TiO}_2\cdot 2\text{SiO}_2$ in the $\text{BaO}\text{-}\text{TiO}_2\text{-}\text{SiO}_2$ system [12], and $\text{ZnO}\cdot \text{B}_2\text{O}_3$ in the $\text{ZnO}\text{-}\text{B}_2\text{O}_3\text{-}\text{SiO}_2$ system [11]. Similar observations have been made on the rare-earth-barium-crown [10] and $\text{Na}_2\text{O}\text{-}\text{TiO}_2\text{-}\text{SiO}_2$ glasses [11] for which phase diagrams are not available. In the development at the Bureau of new optical glasses, such as the rare-earth-barium-crown glasses and barium-titanium silicate infrared-transmitting glasses, the liquidus curves have been very valuable guides.

Compounds which have flat liquidus fields possess a high degree of dissociation at the liquidus [13]. The flatter the liquidus field, the more highly dissociated will be the primary phase. Then, if the other factors that affect the rate of crystallization are equal, the less will be the tendency for crystal formation during the cooling of the melt to glass, because it is necessary for the primary compound to reassociate before crystals can form. Of course other factors, such as viscosity, polarizability, etc., would affect the rate at which the molecules reassociate and then orient themselves and continue to associate to form crystals.

Another factor that affects the stability of the glasses is the presence of, and also the amount of, phases other than the primary phase in the melt. In composition ranges where part of the liquidus surface is steep and two curves intersect to form a minimum, the most stable glasses are found near the minimum and on the side of the minimum with the lesser slope (see figs. 1 and 2). In the vicinity of the minimum, the percentage of the primary phase is approaching a minimum and the percentage of the other compounds present, a maximum. This does not mean that the percentage of the primary compound is approaching zero, for after the minimum is passed the amount of this compound will continue to decrease, but it will no longer be the primary phase because on passing the minimum, a new primary field is entered.

As the compositions change along a steep slope, the difficulties encountered in cooling the melts as glasses increase until homogeneous glasses can be obtained, if at all, only by drastic quenching of the melt. The liquidus curves are also solubility curves and indicate the change in solubility of the primary phase in the melt with change in temperature. As the melt is cooled below the liquidus, it will become supersaturated with respect to the primary phase, and crystallization can take place. The steeper the curve and the higher the composition is located on the curve, the greater the amount of supersaturation and the greater the probability of crystallization. The ease and greatly increased rates of crystallization of melts of compositions on steep curves over melts with compositions on flat curves or flat liquidus fields suggest the presence in the former of molten species of the same chemical compositions as the crystals that form so rapidly.

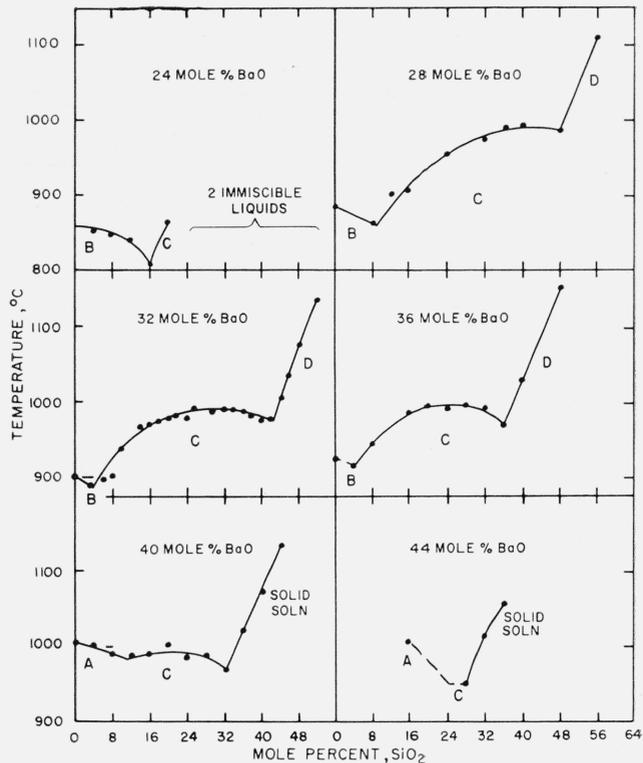


FIGURE 1. Changes in liquidus temperature as a function of SiO_2 content of glasses in the $\text{BaO}\text{-}\text{B}_2\text{O}_3\text{-}\text{SiO}_2$ system; change in composition obtained by the substitution of SiO_2 for B_2O_3 on a mole for mole basis.

Primary phases are indicated by the following symbols: A, $\text{BaO}\cdot \text{B}_2\text{O}_3$; B, $\text{BaO}\cdot 2\text{B}_2\text{O}_3$; C, $3\text{BaO}\cdot 3\text{B}_2\text{O}_3\cdot 2\text{SiO}_2$; D, $\text{BaO}\cdot 2\text{SiO}_2$. Solid solution is between $2\text{BaO}\cdot 3\text{SiO}_2$ and $\text{BaO}\cdot 2\text{SiO}_2$.

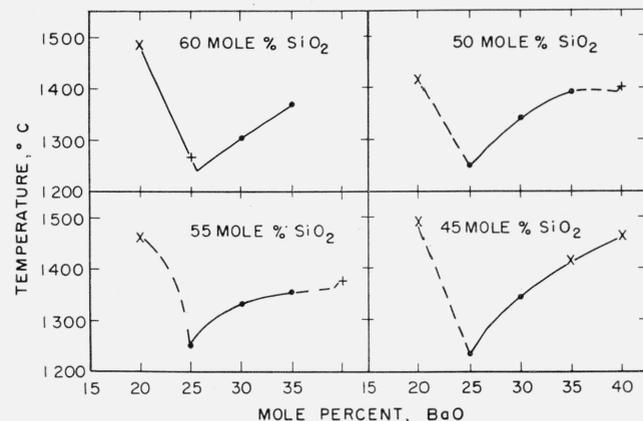


FIGURE 2. Change in liquidus temperature as a function of BaO -content for some glasses in the $\text{BaO}\text{-}\text{TiO}_2\text{-}\text{SiO}_2$ -system; change in composition obtained by the substitution of BaO for TiO_2 on a mole for mole basis.

●, All glass; +, small amount of crystals present; X, devitrified, opaque.

The foregoing observations apply equally well to all the glass systems that have been studied by the authors. Because of the unusual shape of part of the glass-forming area in the BaO-TiO₂-SiO₂ system, it has been chosen to illustrate the relation between glass formation and the chemical compositions of structural entities or units. The properties of the glasses in this system were reported by Cleek and Hamilton [12], and the glass-forming compositions are indicated in figure 3. SiO₂ is the only oxide in the system that can form a glass and therefore can be rightfully called a glass-former. If SiO₂ alone is responsible for glass formation in this system, it is to be expected that the glass-forming area would be continuous along the BaO-TiO₂-SiO₂ join to the SiO₂ vertex. However, such is not the case. Hence it is necessary to explain why, along the BaO-TiO₂-SiO₂ join, glasses are formed only in the narrow composition range of 40 to 50 mole percent of SiO₂, and in particular, why, as SiO₂ is increased slightly to 52.5 mole percent or more, a mixture of glass and crystals is obtained. The phase diagram of the BaO-TiO₂-SiO₂ system [14] suggests a simple explanation. The portion of the liquidus curve for the SiO₂-rich region of the system is extremely steep; therefore, it is difficult to keep the primary phase, SiO₂, in solution as the melt is cooled. This phenomenon is not confined to the system under discussion. Na₂O-SiO₂ melts with high SiO₂ contents become opaque when cooled to glasses in blocks of the dimensions specified under experimental procedure, and the crystallization continues during the annealing of the glasses. Although there is no doubt that SiO₂ can form glass in a limited-composition region, it appears to lose this ability in the region between the glass-forming area of the BaO-TiO₂-SiO₂ system and the SiO₂ vertex. Hence it is necessary to look for a structural unit other than SiO₂ that is responsible for glass formation in that system. For a limited high-silica range, Dietzel and Wickert [15] attribute similar lowered glass-forming ability of SiO₂ to the severe loosening of the silica

network produced by small amounts of Na₂O. In other composition ranges, richer in Na₂O, they find a definite correlation between the degree of glass-forming ability of compositions in the Na₂O-SiO₂ system and the primary phases present at the liquidus.

Of course, the BaO-TiO₂-SiO₂ system is not the only system with SiO₂ as a component in which SiO₂ itself does not seem to be responsible for glass formation. The most stable glasses on the high-Al₂O₃ side of the CaO-MgO-Al₂O₃-SiO₂ system contained 8 mole percent of SiO₂. Glasses have been made in the BaO-Ta₂O₅-SiO₂ system containing 42 mole percent of SiO₂. In these glasses the Si/O ratio is less than 0.25, which is the conventional ratio for isolated silicon-oxygen tetrahedra, and a silicon-oxygen network would require an even higher ratio.

Glass formation in the BaO-TiO₂-SiO₂ system appears to be associated with the compound, BaO·TiO₂·2SiO₂, which has a narrow primary field with a very flat liquidus surface. BaO·TiO₂·2SiO₂ is the only compound that occurs in the glass-forming area, and this area extends from it in all directions except toward the SiO₂-TiO₂ side of the system.

In the half of the system to the left of the BaO·TiO₂-SiO₂ join, glass formation extends practically to the compound compositions, 2BaO·3SiO₂ and BaO·2SiO₂, which can be cooled as glasses when cast as thin plates. The compound composition, BaO·SiO₂, cannot be cooled as a glass and glass formation ceases midway between this composition and BaO·TiO₂·2SiO₂.

On the BaO·TiO₂-SiO₂ join, the compound composition, BaO·TiO₂·SiO₂, is not glass forming. Glass formation extends slightly over halfway from BaO·TiO₂·2SiO₂ toward this compound.

To the right of the BaO·TiO₂-SiO₂ join there is only one series of glasses. This glass-forming area extends from the BaO·TiO₂·2SiO₂ composition halfway toward the compound, BaO·3TiO₂, which melts incongruently at 1,357° C. For the glasses in this series a change in composition of plus or minus 2½ mole percent of BaO produces a mixture of glass and crystals. Hence the glass-forming area in this region is extremely narrow, less than 5 mole percent wide, and approaches a straight line. Such an extremely narrow field may indicate that the glasses are composed of two chemical entities whose compositions lie on the line or the extension of the line. If there were a third entity, the area should have appreciable width. The relative amounts of each entity in a glass would be a function of the composition.

The shape of the liquidus curve for the glasses containing 25 mole percent of BaO, figure 4, indicates that the composition of the second chemical entity is beyond the glass-forming region. It could be BaO·3TiO₂ or a three-component entity with a composition intermediate between BaO·3TiO₂ and BaO·TiO₂·2SiO₂ and containing less than 20 mole percent of SiO₂. Because glass formation extends over half the composition range between BaO·TiO₂·2SiO₂ and BaO·3TiO₂, as it did between BaO·TiO₂·2SiO₂ and the other two contiguous nonglass-

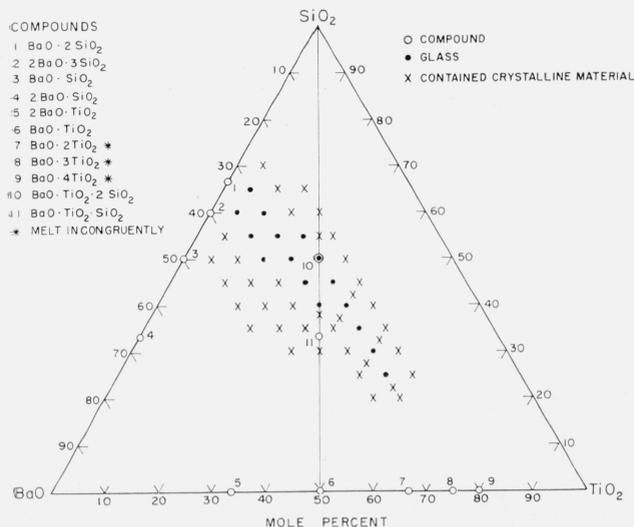


FIGURE 3. Glass-forming area of the BaO-TiO₂-SiO₂ system.

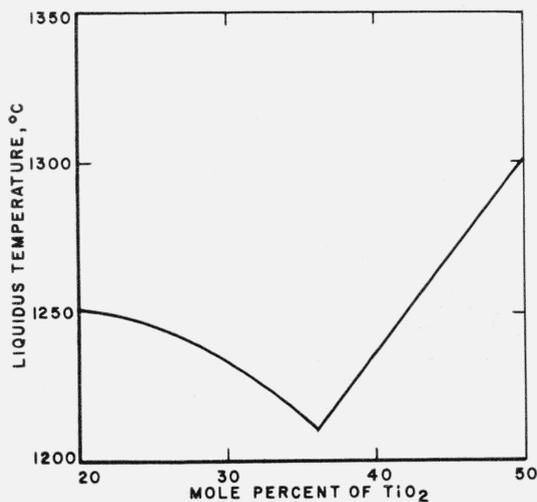


FIGURE 4. Liquidus curve for BaO-TiO₂-SiO₂ glasses containing 25 mole percent of BaO.

forming compounds, and, as the liquidus temperatures of all the glasses in the series are 50 to 140 deg C below the temperature at which BaO·3TiO₂ melts incongruently, the second chemical entity could have the same composition as the compound, BaO·3TiO₂. Then the shape and size of the glass-forming area of the BaO-TiO₂-SiO₂ system would be a function of the solubilities at glass-forming temperatures of the contiguous compounds in BaO·TiO₂·2SiO₂.

4. Summary

Some of the criteria that have been adopted as guides in the development of new glasses are discussed in the light of the phase diagrams. After comparing the shapes of the liquidus curves and surfaces with rates of crystallization, it is postulated (1) that certain chemical entities or structures are in the glasses and, with the possible exception of single-component glasses, (2) that the presence of a compound with a high degree of dissociation in the glass-forming temperature range is essential to permit glass formation.

Thus, it seems probable that multicomponent glasses are essentially solutions of one or more chemical entities or structures in highly dissociated

chemical entities that have developed such high viscosities as a result of cooling that they possess many of the properties normally associated with solids. In the case of three-component glasses these chemical entities probably have the same compositions as the compounds indicated by the vertices of the composition triangles and are present in the proportions indicated by the position of the glass composition in the composition triangle.

5. References

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