

## Glass Formation in the Systems (Na<sub>2</sub>O, K<sub>2</sub>O or BaO)-TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>

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Glass-forming abilities of melts in the systems (R<sub>2</sub>O or R'O)-TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, where R is Li, Na or K and R' is Ca, Sr, Ba, or Pb, were examined with an ordinary crucible-melting technique, which consist of melting 15 g of raw materials in a Pt10%Rh crucible, pouring the melts onto a steel plate and pressing them into plates 1 mm thick. Clear glasses were obtained from some of the melts in the systems (Na<sub>2</sub>O, K<sub>2</sub>O, or BaO)-TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>. On the basis of X-ray emission spectroscopic and infrared spectroscopic analyses, the structures of the glasses obtained were inferred to be random networks consisting both of the AlO<sub>4</sub> tetrahedra and TiO<sub>6</sub> octahedra in some holes of which are occupied by Na<sup>+</sup>, K<sup>+</sup>, or Ba<sup>2+</sup> ions. The glass-forming abilities of the examined systems were interpreted in terms of the field strengths of R and R' ions situated in some holes of the network.

### I. INTRODUCTION

Among aluminate melts containing no simple glass-forming oxides such as SiO<sub>2</sub>, B<sub>2</sub>O<sub>3</sub>, P<sub>2</sub>O<sub>5</sub>, GeO<sub>2</sub>, As<sub>2</sub>O<sub>3</sub>, and Sb<sub>2</sub>O<sub>3</sub> the CaO-Al<sub>2</sub>O<sub>3</sub> family is the only one heretofore known to form glass on a practically useful scale.<sup>1)</sup> Recently, however, the present authors have found that some aluminate melts in the systems (K or Cs)<sub>2</sub>O-(Nb or Ta)<sub>2</sub>O<sub>5</sub>-Al<sub>2</sub>O<sub>3</sub> also form fairly stable glasses.<sup>2)</sup>

In the present study glass-forming tendencies of the systems (R<sub>2</sub>O or R'O)-TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, where R is Li, Na, or K and R' is Ca, Sr, Ba, or Pb, were examined with an ordinary crucible-melting technique. Structures of the glasses obtained from these systems were also discussed on the basis of their X-ray emission spectra and infrared spectra.

Some melts in the binary systems containing TiO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub>, such as K<sub>2</sub>O-TiO<sub>2</sub>,<sup>3,4)</sup> CaO-TiO<sub>2</sub>,<sup>5)</sup> SrO-TiO<sub>2</sub>,<sup>5)</sup> BaO-TiO<sub>2</sub>,<sup>5)</sup> PbO-TiO<sub>2</sub>,<sup>6)</sup> SrO-Al<sub>2</sub>O<sub>3</sub>,<sup>7)</sup> BaO-Al<sub>2</sub>O<sub>3</sub>,<sup>7)</sup> and PbO-Al<sub>2</sub>O<sub>3</sub><sup>7)</sup> are already known to form glasses, if their melts are quenched in very small amounts and also extraordinarily rapidly by specially designed techniques such as a splat-quenching.<sup>8)</sup> The ternary systems investigated in the present study are combinations of these titanate and aluminate binary systems. Glass-forming tendencies of these ternary systems on a practically useful scale have not yet been investigated.

### II. EXPERIMENTAL

#### 1. Glass-Forming Tendency

For investigating glass-forming tendencies of the systems (R<sub>2</sub>O or R'O)-TiO<sub>2</sub>-

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$\text{Al}_2\text{O}_3$ , where R is Li, Na, or K and R' is Ca, Sr, Ba, or Pb, batch mixtures yielding various oxide compositions (mol %) shown in Fig. 1 were prepared from reagent grade chemicals of  $\text{Li}_2\text{CO}_3$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{K}_2\text{CO}_3$ ,  $\text{CaCO}_3$ ,  $\text{SrCO}_3$ ,  $\text{BaCO}_3$ ,  $\text{Pb}_3\text{O}_4$ ,  $\text{TiO}_2$ ,

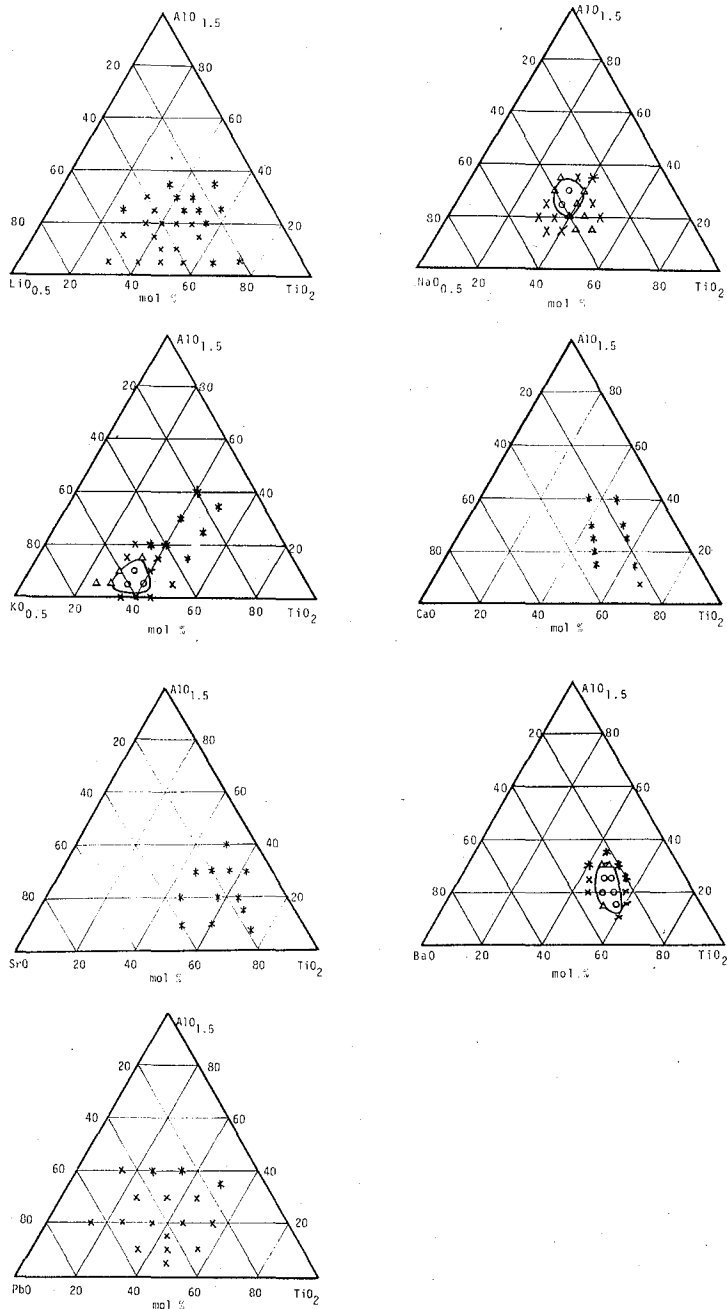


Fig. 1. Glass-forming tendency.

○; Clear glass △; Partially devitrified glass  
 ×; Fully devitrified glass \*; Imperfect melt

and Al<sub>2</sub>O<sub>3</sub>. About 15 g of the batch mixtures were melted in a 50 ml Pt10%Rh crucible covered with a lid in a SiC furnace at 1550°C for 1 hr. The melts were poured onto a steel plate and pressed into plates approximately 1 mm thick. They were then quickly put into a preheated electric furnace, annealed at 400°–500°C for 30 min, and furnace-cooled.

All the resultant substances could be classified into the following four groups by observation with the naked eye and powder X-ray diffraction; clear glass, partially devitrified glass, fully devitrified glass and imperfect melt. The glass-forming tendencies of the compositions and the glass-forming regions are shown in Fig. 1, which indicates that fairly stable glasses can be obtained in the ternary systems Na<sub>2</sub>O-TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, K<sub>2</sub>O-TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, and BaO-TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>.

The glasses in the systems Na<sub>2</sub>O-TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> and BaO-TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> had slight tinges of yellow and brown, respectively, whereas those in the system K<sub>2</sub>O-TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> had a strong tinge of brown. The Na<sub>2</sub>O- and BaO-containing glasses were chemically fairly durable in a laboratory atmosphere, whereas the K<sub>2</sub>O-containing glasses were extremely hygroscopic.

## 2. X-Ray Emission Spectroscopic Analysis

In order to determine the coordination number of Al<sup>3+</sup> ions in the glasses, the glasses of the compositions given in Table I were subjected to X-ray emission spectroscopic analyses. The X-ray emission spectra of α-Al<sub>2</sub>O<sub>3</sub> and K-feldspar crystals, which contain six-fold and four-fold coordinated Al<sup>3+</sup> ions, respectively, were measured as references.

Table I. Glass Compositions (mol %)

No.	NaO <sub>0.5</sub>	KO <sub>0.5</sub>	BaO	TiO <sub>2</sub>	AlO <sub>1.5</sub>	Al/(Na, K or Ba)
1	40.00			35.00	25.00	0.33
2	35.00			35.00	30.00	0.86
3		55.00		35.00	10.00	0.18
4		60.00		35.00	5.00	0.08
5			24.85	50.15	25.00	1.00
6			30.00	50.00	20.00	0.25

The AlKα emission spectra of these specimens were recorded on a Rigaku Denki Geigerflex KG-4 X-ray fluorescence spectrometer with a chromium target at 50 KV and 40 mA. The EDDT analyzing crystal, a soller slit with dispersion angle of 0.15 and a gas-flow proportional counter with a pulse height analyzer were used. A vacuum of 0.1–0.2 torr was maintained to reduce the absorption of the emitted AlKα radiation. The scanning speed was 0.25° (2θ)/min. The chart speed was chosen so that 1° (2θ) was equivalent to 16 cm on a chart paper. Recording of the glass specimens and of the reference materials were alternated so that any drift in the recording process could be taken into account. The positions of their AlKα peaks were determined at 90%-maximum intensity of the recorded peaks with respect to that for Al metal.

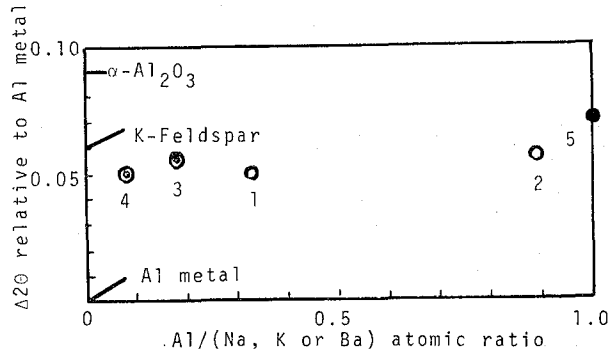


Fig. 2. Chemical shifts of AlK $\alpha$  peaks for (Na<sub>2</sub>O, K<sub>2</sub>O, or BaO)-TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> glasses.

The results are shown in Fig. 2 as a function of Al/(Na, K, or Ba) atomic ratio in the glasses. The position of the AlK $\alpha$  peak for glass 6 containing a large amount of BaO could not be determined since its weak AlK $\alpha$  peak lay upon a tail of a strong BaL $\alpha$  peak. It can be seen from Fig. 2 that the AlK $\alpha$  peaks of the glasses almost coincide in position with that of K-feldspar containing the tetrahedrally coordinated Al<sup>3+</sup> ions, irrespective of the compositions of the glasses.

### 3. Infrared Spectroscopic Analysis

In order to investigate the coordination number of the Ti<sup>4+</sup> ions in the glasses, infrared absorption spectra of all the glasses given in Table I were measured with a double-beam automatic infrared spectrometer (Perkin-Elmer 521) by a KBr disc method. The infrared absorptions of BaTiO<sub>3</sub> crystals prepared by a solid state reaction and the K<sub>2</sub>O·2TiO<sub>2</sub> glass prepared by the splat-quenching technique were also measured as references. Both of them were already confirmed to contain six-fold coordinated Ti<sup>4+</sup> ions by X-ray diffraction technique.<sup>9,10</sup> The results are presented in Fig. 3. All of the (K<sub>2</sub>O, Na<sub>2</sub>O, or BaO)-TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> glasses show a wide absorption bands extending from 900 to 500 cm<sup>-1</sup>.

### 4. Comparison of Glass-Forming Regions Determined by Splat-Quenching and Crucible-Melting Techniques

For comparing the glass-forming region in the system BaO-TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> determined by the crucible-melting technique with that determined by the splat-quenching technique, glass-forming tendency of the binary systems TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> was examined by the splat-quenching technique. Glass-forming tendencies of the binary systems BaO-TiO<sub>2</sub> and BaO-Al<sub>2</sub>O<sub>3</sub> were already determined by the splat-quenching technique by Sarjeant *et al.*<sup>5,7</sup> Batch mixtures yielding various mol ratio of Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> were prepared from reagent grade Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> and heated at 1500°C for 6 hr. About 0.1 g of the resultant materials were melted on an iridium strip heater at 1800°–2000°C and blown off by a compressed oxygen gas against a microscope slide held at room temperature by using a splat-quenching apparatus similar to that described by Sarjeant *et al.*<sup>8</sup> The quenched materials were subjected to X-ray diffraction analysis and observed under a polarizing microscope. The results indicated that none

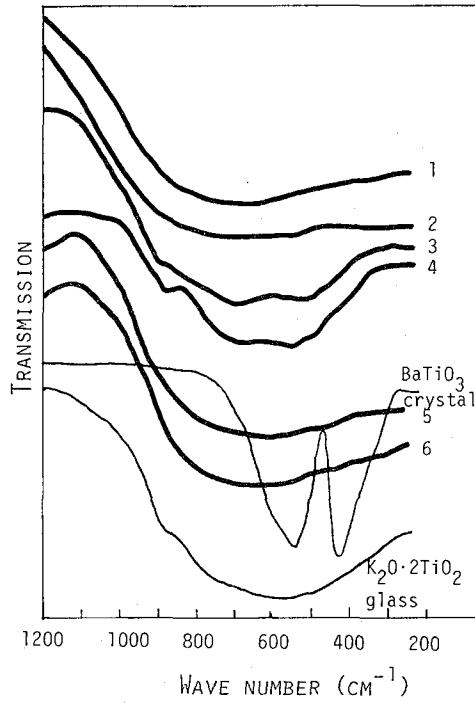


Fig. 3. Infrared spectra of  $(\text{Na}_2\text{O}, \text{K}_2\text{O}, \text{or BaO})\text{-TiO}_2\text{-Al}_2\text{O}_3$  glasses,  $\text{BaTiO}_3$  crystal and  $\text{K}_2\text{O}\cdot 2\text{TiO}_2$  glass.

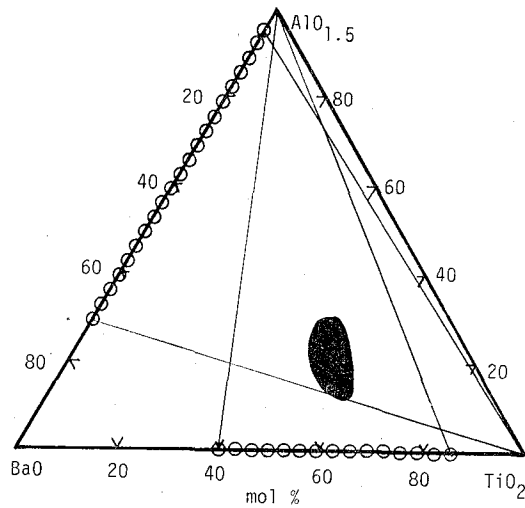


Fig. 4. Glass-forming regions determined by ordinary crucible-melting and splat-quenching techniques.

- ; Glass-forming region determined by crucible-melting.
- ; Glass-forming region determined by splat-quenching.

of the compositions in the system  $\text{TiO}_2\text{-Al}_2\text{O}_3$  could be fully vitrified by the splat-quenching technique. This result is represented in Fig. 4 together with the results for the systems  $\text{BaO-TiO}_2$  and  $\text{BaO-Al}_2\text{O}_3$  obtained by Sarjeant *et al.*<sup>5,7)</sup> The glass-forming region determined by the crucible-melting technique is reproduced in the same figure. The glass-forming region determined by the crucible-melting technique is located in both of the composition triangles formed by joining the both extremes of each binary glass-forming region on the sides  $\text{AlO}_{1.5}\text{-BaO}$  and  $\text{BaO-TiO}_2$  to another end member as shown in Fig. 4.

### III. DISCUSSION

A certain relation exists between the coordination number of  $\text{Al}^{3+}$  ions in oxides and the positions of  $\text{AlK}\alpha$  radiation peak.<sup>11)</sup> The positions of the  $\text{AlK}\alpha$  radiation of the aluminate glasses determined by the X-ray emission spectroscopic analyses in the present study were found to coincide with that of the K-feldspar containing tetrahedrally coordinated  $\text{Al}^{3+}$  ions, which indicates that the  $\text{Al}^{3+}$  ions in the glasses are also tetrahedrally coordinated with oxygen ions.

The  $\text{AlO}_4$  tetrahedra were reported to give an infrared absorption band at wave number of  $900\text{-}650\text{ cm}^{-1}$ .<sup>12)</sup> The corresponding absorption band is observed on all the infrared spectra of the aluminate glasses obtained in the present study. However, the absorption band of the glasses is not limited in this region, but extend to the region of wave number from  $650\text{ to }500\text{ cm}^{-1}$  as shown in Fig. 3. The latter region corresponds to the absorption band produced by the presence of  $\text{TiO}_6$  octahedra as reported by Tarte.<sup>12)</sup> Therefore, a fairly large amount of the  $\text{Ti}^{4+}$  ions are concluded to be octahedrally coordinated in the aluminate glasses.

The amounts of the  $\text{Al}_2\text{O}_3$  in the aluminate glasses obtained in the present study might not be sufficient to form the three-dimensional network of the glasses with only the  $\text{AlO}_4$  tetrahedra. Accordingly, the  $\text{AlO}_4$  tetrahedra and the  $\text{TiO}_6$  octahedra would cooperate in forming the network of the glasses, as shown in Fig. 5. The other ions such as  $\text{Na}^+$ ,  $\text{K}^+$ , or  $\text{Ba}^{2+}$  ions will sit in some holes of the network.

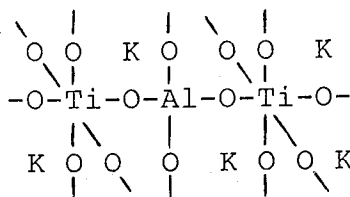


Fig. 5. Structure of  $\text{K}_2\text{O-TiO}_2\text{-Al}_2\text{O}_3$  glass.

It can be seen from Fig. 1 that the glass-forming ability of the system  $(\text{R}_2\text{O}$  or  $\text{R}'\text{O})\text{-TiO}_2\text{-Al}_2\text{O}_3$  is greatly affected by the type of  $\text{R}$  or  $\text{R}'$  ion, where  $\text{R}$  and  $\text{R}'$  are mono- and divalent cation, respectively. Its cause is interpreted as follows.

Each of the  $\text{Al}^{3+}$  and  $\text{Ti}^{4+}$  ions in these glasses forms an  $\text{AlO}_4$  tetrahedron and  $\text{TiO}_6$  octahedron, respectively, using one and two extra oxygen ions accompanied

by an R or R' ion, together with three and four oxygen ions originally accompanied by itself. In such tetrahedral or octahedral structures, electron clouds in the binding region between the bridging oxygen core and Al or Ti core would be more strongly attracted toward the R or R' ions, as the field strength of the R or R' ion increases.<sup>13)</sup> This would weaken the binding forces in the glass network, thus facilitating crystallization in the glasses. The ionic field strengths<sup>14)</sup> given by  $Z_i/(r_i+r_o)^2$  are listed in Table II for all the R and R' ions introduced into the present systems, where  $Z_i$ ,

Table II. Ionic Field Strength<sup>14)</sup>

	Li <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Sr <sup>2+</sup>	Ba <sup>2+</sup>	Pb <sup>2+</sup>
$Z_i/(r_i+r_o)^2$	0.23	0.18	0.13	0.35	0.32	0.27	0.30

$Z_i$ ; Charge of cation  $r_i$ ; Radius of cation  $r_o$ ; Radius of oxygen ion

$r_i$ , and  $r_o$  are the charge and radius of the R or R' ion and the radius of the oxygen ion, respectively. The ionic field strength increases in the order  $K^+ < Na^+ < Li^+ < Ba^{2+} < Pb^{2+} < Sr^{2+} < Ca^{2+}$ . The high glass-forming ability of the systems (K<sub>2</sub>O, Na<sub>2</sub>O, or BaO)-TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> as well as the low glass-forming ability of the systems (PbO, SrO, or CaO)-TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> systems, both confirmed by the present experiments, can thus be explained. The system Li<sub>2</sub>O-TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, is, however, an exception: Although the Li<sup>+</sup> ion has the field strength lower than that of the Ba<sup>2+</sup> ion, the glass-forming ability of the system Li<sub>2</sub>O-TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> was found to be rather low. This would be attributed to the special electron configuration of the Li<sup>+</sup> ion compared to that of the other ions: The former is of the helium-type whereas the latter is of the neon-type. The ions having the helium-type electron configuration are known to be able to penetrate easily into the electron cloud of the polarizable oxygen ions in glasses, thus giving unusual effects on many properties of the glasses.<sup>15)</sup>

#### IV. SUMMARY

Clear glasses could be obtained from some melts in the systems (Na<sub>2</sub>O, K<sub>2</sub>O, or BaO)-TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> by an ordinary crucible-melting technique.

From the results of X-ray emission spectroscopic and infrared spectroscopic analyses, the structures of the glasses were inferred to be random networks consisting of the AlO<sub>4</sub> tetrahedra and TiO<sub>6</sub> octahedra in some holes of which Na<sup>+</sup>, K<sup>+</sup>, or Ba<sup>2+</sup> ions are situated.

The high glass-forming abilities of the Na<sub>2</sub>O-, K<sub>2</sub>O-, and BaO-containing systems were ascribed to the low ionic field strength of the Na<sup>+</sup>, K<sup>+</sup> or Ba<sup>2+</sup> ion.

#### REFERENCES

- (1) H. Rawson, *Inorganic Glass-Forming Systems*, Academic Press, London, 1967, p. 199.
- (2) T. Kokubo, M. Nishimura, and M. Tashiro, *J. Non-Crystalline Solids*, **15**, 329 (1974).
- (3) P. L. Bayton, H. Rawson, and J.E. Stanworth, *Proceedings IV International Congress on Glass, Paris, 1956*, p. 52.

- (4) Bh V. J. Rao, *J. Amer. Ceram. Soc.*, **47**, 455 (1964).
- (5) P. T. Sarjeant and R. Roy, *J. Amer. Ceram. Soc.*, **52**, 57 (1969).
- (6) T. Kokubo, S. Ito, and M. Tashiro, *Bull. Inst. Chem. Res., Kyoto Univ.*, **51**, 315 (1973).
- (7) P. T. Sarjeant, *Reactivity of Solids*, Ed. J. W. Mitchel *et al.*, Wiley-Interscience, New York, 1969, p. 725.
- (8) P. T. Sarjeant and R. Roy, *J. Amer. Ceram. Soc.*, **50**, 500 (1967).
- (9) F. S. Gallasso, *Structure, and Properties of Inorganic Solids*, Pergamon Press, Oxford, 1970, p. 168.
- (10) J. Zarzycki, *J. Materials Sci.*, **6**, 130 (1971).
- (11) R. Wardle and G. W. Brindley, *Amer. Mineral.*, **56**, 2123 (1971).
- (12) P. Tarte, *Physics of Non-Crystalline Solids*, Ed. J. A. Prins, North-Holland Pub., Amsterdam, 1965, p. 549.
- (13) W. A. Weyl and E. C. Marboe, *The Constitution of Glasses*, Vol. II, Part 1, Interscience, New York, 1964, p. 512.
- (14) E. M. Levin, *J. Amer. Ceram. Soc.*, **50**, 29 (1967).
- (15) W. A. Weyl and E. C. Marboe, *The Constitution of Glasses*, Vol. II, Part 1, Interscience, New York, 1964, p. 507, 674.