

Table I. Comparison of Linear Thermal Expansion Coefficients of V_2O_5 with Some Other Layer-Structure Compounds

Compound	Temp. range ($^{\circ}C$)		$\times 10^{-7}/^{\circ}C$			Randomly oriented polycrystalline specimen ($\times 10^{-7}/^{\circ}C$)	
	Dilatometer	X ray	<i>a</i>	<i>b</i>	<i>c</i> *	Dilatometer	X ray
V_2O_5	30–450	30–629	95 ± 9	69 ± 13	352 ± 18	6.3	172 ± 14
Graphite [†]		0–800	0		283		
BN [‡]			–23		410		
USi ₂ S [§]		20–215	–260		570		

* Perpendicular to layers.

[†] See Ref. 4.

[‡] See Ref. 5.

[§] See Ref. 6.

^{||} See Ref. 1.

was temperature calibrated with platinum powder intimately mixed with the V_2O_5 and the two diffraction patterns were recorded simultaneously. The diffraction patterns of the V_2O_5 (Fisher reagent grade) were indexed with ASTM Card 9–387. The lattice parameters were obtained at different temperatures by a least-squares computational method² using all the diffraction data.

The structure of V_2O_5 ³ is orthorhombic and consists of atomic layers perpendicular to the *c* axis. In the [001] direction there is an exceptionally long O—V distance of 2.8 Å between the layers; whereas the other O—V bond distances in this compound range from 1.54 to 2.02 Å. The interlayer forces in the [001] direction can therefore be considered essentially van der Waals in nature and a larger thermal expansion would be expected than in the other directions. V_2O_5 is compared with other layer structure materials in Table I. These compounds, as well as the V_2O_5 , show marked thermal expansions along the *c* axis, the direction perpendicular to the layers, where the binding forces are also generally considered to be van der Waals in nature. Linear thermal expansion coefficients ranging from 300 to $500 \times 10^{-7}/^{\circ}C$ are recorded for the interlayer directions.

The thermal expansion coefficients of Ta_2O_5 were also determined by the dilatometer method by King and Suber.¹ To compare the two methods further the linear thermal expansion co-

efficients of low-temperature Ta_2O_5 were also determined by the X-ray method and good agreement was obtained with the dilatometer value of $20 \times 10^{-7}/^{\circ}C$. With the X-ray method the anisotropic linear thermal expansion coefficients of Ta_2O_5 were determined as (*a*) $88 \pm 10 \times 10^{-7}/^{\circ}C$, (*b*) $0 \pm 10 \times 10^{-7}/^{\circ}C$, and (*c*) $0 \pm 10 \times 10^{-7}/^{\circ}C$, giving a value for the linear thermal expansion coefficient for a randomly oriented polycrystalline specimen of $29 \pm 10 \times 10^{-7}/^{\circ}C$. The good agreement between the X-ray and dilatometer measurements on Ta_2O_5 and the discrepancy between the V_2O_5 values suggests an error in the dilatometer measurements of V_2O_5 .

² R. P. Elliott; in *Advances in X-Ray Analysis*, Vol. 8. Edited by W. M. Mueller and Marie Fay. Plenum Press, New York, 1964.

³ Anders Byström, K. A. Wilhelmi, and Otto Brotzen, "Vanadium Pentoxide, a Compound with Five Coordinated Vanadium Atoms," *Acta Chem. Scand.*, **4**, 1119–30 (1950) (in English).

⁴ J. B. Nelson and D. P. Riley, "Thermal Expansion of Graphite from 15° to 800°C: I–III," *Proc. Phys. Soc. (London)*, **B57** [Pt. 6] 477–95 (1945).

⁵ S. N. Ruddlesden; pp. 3–23 in *Special Ceramics—Proceedings of a Symposium Held at the British Ceramic Research Association, July 1959*. Edited by P. Popper. Academic Press, Inc., New York, 1960.

⁶ Gunvor Beckman and Roland Kiessling, "Thermal Expansion Coefficients for Uranium Boride and β -Uranium Silicide," *Nature*, **178**, 1341 (1956).

Metastable Liquid Immiscibility in the System Silica–Sodium Tetraborate

by T. J. ROCKETT, W. R. FOSTER, and ROBERT G. FERGUSON, JR.

SINCE Hood and Nordberg¹ obtained a patent involving two immiscible liquid phases in the system $Na_2O-B_2O_3-SiO_2$ many workers have reported on the nature of the separation and on the ternary compositions in which separation takes place. The patentees of the effect showed that from an opalescent glass a phase rich in B_2O_3 and Na_2O could be chemically leached leaving a porous silica-rich phase. They further showed that this phenomenon took place below the liquidus temperature for the compositions. More recently Ohlberg and Hammel, using the electron microscope to observe the immiscible glass phases which cause the opalescence, confirmed that the phenomenon takes place at temperatures below the liquidus and stated that the effect is the result of a metastable subliquidus liquid miscibility gap.²

During an investigation of the system $SiO_2-Na_2B_8O_{13}$ this area of metastable immiscibility was defined in relation to the phase

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The writers are, respectively, research ceramist, Aerospace Research Laboratories, United States Air Force, Wright-Patterson Air Force Base, Ohio; chairman, Department of Mineralogy, The Ohio State University, Columbus, Ohio; and assistant engineer, Systems Research Laboratories, Inc., Dayton, Ohio.

¹ H. P. Hood and M. E. Nordberg, "Treated Borosilicate Glass," U. S. Pat. 2,106,744, February 1938.

² S. M. Ohlberg and J. J. Hammel, "Multiphase Glass Structure"; presented at the Sixty-Fifth Annual Meeting, The American Ceramic Society, Inc., Pittsburgh, Pa., May 1, 1963 (Glass Division, No. 23-G-63); for abstract see *Am. Ceram. Soc. Bull.*, **42** [4] 229 (1963).

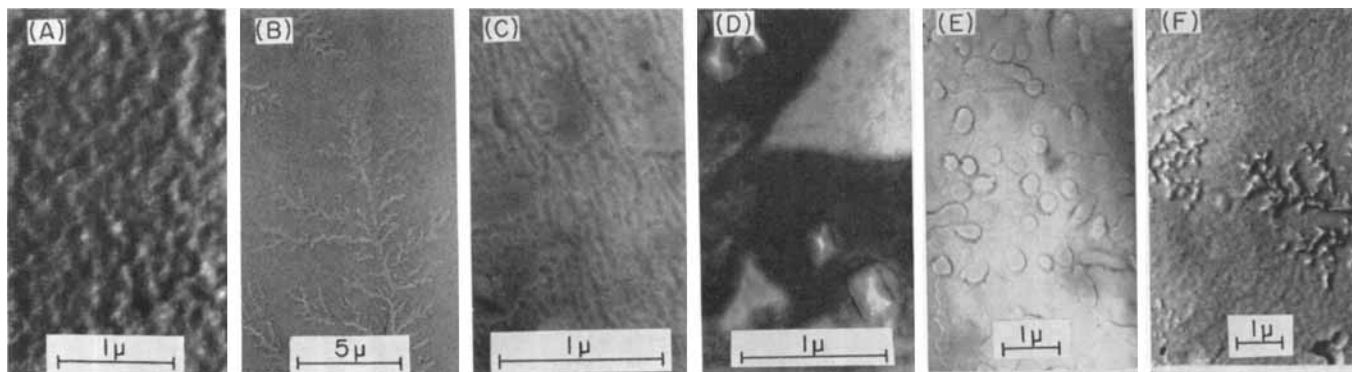


Fig. 1. Electron micrographs of fractured glass showing two phases in the system silica-sodium tetraborate. (A) 50 Si : 50 NaB₄ quenched from 1000°C showing spinodal separation; (B) 50 Si : 50 NB₄ heat-treated for 15 hr at 690°C showing silica-rich dendrite in soda borate matrix; (C) second-phase growth in the system 60 Si : 40 NB₄ heat-treated for 16 hr at 700°C; (D) octahedra of cristobalite in dendrite leaf of 50 Si : 50 NaB₄ heat-treated 50 hr at 603°C; (E) spheres of silica-rich phase in the 50 Si : 50 NaB₄ composition heat-treated 20 hr at 700°C; (F) depletion of spinodal phase in the area of the dendrites 50 Si : 50 NaB₄ heat-treated 50 hr at 603°C. All samples were etched in warm water.

equilibria of the system.³ Glasses were prepared at 10 wt% intervals across the system using α -quartz (99.97%) and synthesized Na₂O·4 B₂O₃ (99.983%) as starting materials.* The glasses were quenched from temperatures above the liquidus after firing for 2 to 50 hr. Figure 1(A) is a fracture-graph of the surface of the 50 Si:50 NaB₄ glass quenched from 1000°C.† In this study, the fractured surfaces were replicated for electron microscopy using a 20% solution of collodion in amyl acetate. These films were shadowed at 45° with chromium and then a carbon film was deposited normal to the surface. Figure 1(A) shows phase separation of the type recently described by Charles.⁴ This type of interconnecting separation which forms on quenching was described by Vogel⁵ and, more recently, Cahn proposed a theory of spinodal decomposition as a mechanism for its formation.⁶ These quenched glasses were transparent. Pieces of these glasses were then fired to produce bluish-white opalescence or dense white translucence. Table I‡ gives the temperatures and times of firing and Fig. 2 shows the area in which opalescence was produced.

All opalescent glasses examined under the electron microscope showed a distinct separation of two phases (Figs. 1(B) and (C)). Assuming then that all observed opalescence indicated pronounced liquid-liquid separation, the limits of the liquid immiscibility area in the system were defined by the limits of observed opalescence. The growth of the second phase was strikingly reversible. Dense white glasses fired above the critical temperature of immiscibility regained the clear appearance in less than 2 hr in all cases. Electron microscopy of fractured surfaces showed that the opalescent glasses contained two distinct phases and that only the spinodal-type phases, which are believed to form on quenching, were observed in the clear glasses after firing above the immiscibility area and quenching to that area. The 40 Si:60 NaB₄ glass was cycled from opalescent to transparent condition six times. One hour at 670°C produced white opalescence

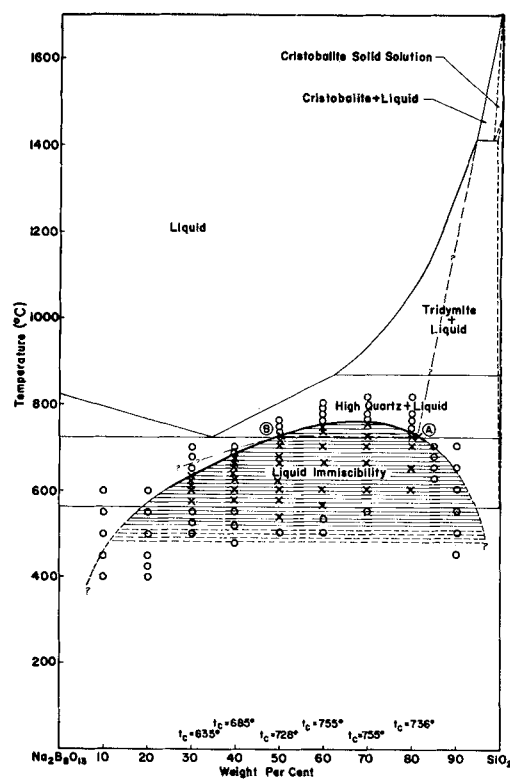


Fig. 2. Phase diagram for the system silica-sodium tetraborate showing the metastable liquid immiscibility area. × = firings of glasses which yielded opalescence; ○ = firings in which the glasses remained clear.

³ T. J. Rockett and W. R. Foster, "The System Silica-Sodium Tetraborate"; presented at the Sixty-Seventh Annual Meeting, The American Ceramic Society, Inc., Philadelphia, Pa., May 5, 1965 (Basic Science Division, No. 78-B-65); for abstract see *Am. Ceram. Soc. Bull.*, **44** [4] 319 (1965).

* Analysis by Battelle Memorial Institute, Columbus, Ohio.

† In this note the following abbreviations are used: Si = SiO₂, Na = Na₂O, and B = B₂O₃.

⁴ R. J. Charles, "Phase Separation in Borosilicate Glasses," *J. Am. Ceram. Soc.*, **47** [11] 559-63 (1964).

⁵ W. Vogel; pp. 17-25 in *Structure of Glass: Vol. 2, Proceedings of the Third All-Union Conference on the Glassy State*, Leningrad, 1959. Edited by E. A. Poraĭ-Koshits. Translated from Russian, 1960. Consultants Bureau Enterprises, Inc., New York, 1960.

⁶ J. W. Cahn, "Phase Separation by Spinodal Decomposition in Isotropic Systems," *J. Chem. Phys.*, **42** [1] 93-99 (1965).

‡ Tabulated data are available from T. J. Rockett.

and the glass was cleared by firing for 1 hr at 690°C. No opalescence was observed in the 90% and 80% NaB₄ or the 85% and 90% Si compositions. It is impossible to state that the immiscibility area does not extend into these composition ranges. The miscibility temperatures of these compositions may be so low that firings of longer than 300 hr may be necessary to produce the effect. Indeed only slight opalescence was observed in the 80% SiO₂ glass at 600°C after 130 hr and opalescence was never observed in any of the glasses below 500°C.

Since no chemical analyses were made on the two phases, it is not certain that the immiscibility area is a binary feature. The two phase tie lines may not lie in the plane of the system silica-sodium tetraborate, but may connect two compositions in the ternary Na₂O-B₂O₃-SiO₂ so that the tie lines cross the join. The tie lines connecting the compositions of the soluble and insoluble

phases given by Hood and Nordberg¹ parallel the binary and, therefore, suggest that this is a binary feature.

The 60 Si:40 NaB₄, 50 Si:50 NaB₄, and 40 Si:60 NaB₄ compositions were examined under the electron microscope. As shown in Fig. 1 the separation of the two phases takes place either by an entrenching of the spinodal structure with growth of one of the phases or by the growth of dendrites of the silica-rich phase as shown in the 40% and 50% silica compositions. Near the miscibility temperature, the dendrites spheroidize after many hours as shown in Fig. 1 (E). That the dendrites are silica-rich was shown by the fact that crystallization of cristobalite takes place within

the dendritic phase as it becomes spherical (Fig. 1 (D)). An electron diffraction pattern of a pullout of a crystal has been indexed as cristobalite. It can be noted in Fig. 1 (F) that as the dendrites grow the matrix glass in the immediate area of the dendrite is free of the spinodal structure. This is predictable from Cahn's theory.⁶

The top portion of the miscibility gap should offset a portion of the metastable extension of the cristobalite liquidus as is suggested from points A to B in Fig. 2. Continuing work on devitrification may permit experimental location of the metastable cristobalite liquidus.

Noncrystalline Microphase Separation in Soda-Lime-Silica Glass

by S. M. OHLBERG, H. R. GOLOB, J. J. HAMMEL, and R. R. LEWCHUK

DURING the preparation of a soda-lime-silica glass for use in an X-ray study,¹ glass which had been given a long annealing was observed to be slightly turbid. Such turbidity could be caused by fine seed, devitrification, or a noncrystalline phase separation. The latter seemed highly unlikely because the composition, 13% Na₂O, 11% CaO, and 76% SiO₂, was so similar to the widely studied commercial glasses.

The question was readily resolved by heating the same glass for a period of time at 685°C (well above the strain point). The turbidity was substantially increased (surface devitrification was removed before examination). An X-ray diffraction pattern of the turbid sample failed to reveal any crystalline peaks. Electron microscopic examination of a fresh fracture surface did, however, reveal an abundance of droplets typical of the liquidlike immiscibility observed in many borosilicate glass compositions.²

Annealed samples of soda-lime-silica glass were held for 17 hr in a furnace in which the thermal gradient ranged from 686° to 800°C. Light scattering, indicative of phase separation, could be detected in all samples heat-treated below 750°C, establishing the latter as the miscibility temperature. In a second experiment, a fresh set of annealed samples was placed in a thermal gradient furnace so that all samples were held above the miscibility temperature for 1 hr. The samples were then transferred to lower temperatures and held for 3 hr in a thermal gradient ranging from 634° to 739°C. Phase separation could be detected in all samples heat-treated below 701°C, indicating that phase separation will not occur unless the thermal history of the glass includes a period of time below 701°C. (It should be pointed out that these temperatures will vary considerably with slight variation in composition.)

Representative electron micrographs of platinum-preshadowed carbon replicas of fractured surfaces which were etched in dilute

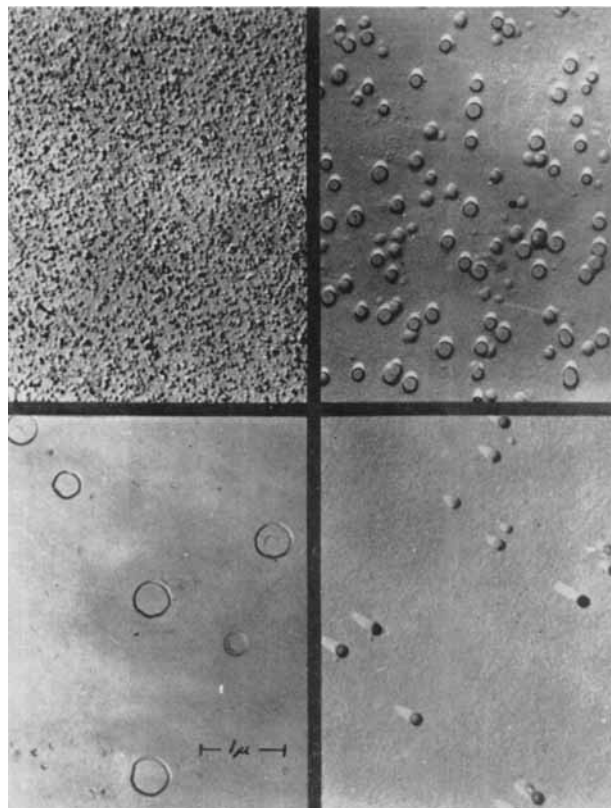


Fig. 1. Fracture surfaces of phase-separated soda-lime-silica glass after mild HF etch.

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The writers are, respectively, scientist, research chemist, research associate, and chemist, Pittsburgh Plate Glass Company, Glass Research Center, Pittsburgh, Pennsylvania.

¹ S. M. Ohlberg and J. M. Parsons; to be published in Proceedings International Conference on Physics of Non-Crystalline Solids, July 6-10, 1964. North Holland Publishing Company, Amsterdam.

² S. M. Ohlberg, J. J. Hammel, and H. R. Golob, "Phenomenology of Noncrystalline Microphase Separation in Glass," *J. Am. Ceram. Soc.*, **48** [4] 178-80 (1965).

HF are shown in Fig. 1. The droplet phase is elevated, i.e. the matrix is preferentially etched by HF. It is concluded, therefore, that the disperse phase is silica rich. The variation in size and number of droplets illustrated in the four micrographs shown in Fig. 1 is the result of variation in time and temperature for nucleation and growth. From the micrograph in the lower left, it can be seen that fracture propagates through the disperse phase and also that there is a loss of sphericity when the droplets are large.

Low-angle X-ray scattering measurements were made on a thin section of glass which had been held at 680°C for 4³/₄ hr.