

## Studies in the system $\text{BaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ III. The binary system sanbornite-celsian

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**SUMMARY.** The system sanbornite-celsian has been investigated by the quenching method, and the results compared with earlier studies. The system is essentially a simple binary eutectic system with little or no solid solution. The eutectic is located at a composition of 69 % sanbornite and 31 % celsian (by weight) and at a temperature of  $1227 \pm 3$  °C. No evidence for substantial solid solution of celsian in sanbornite, as reported in previous work, was found. Paracelsian, a naturally occurring polymorph of celsian, was not encountered in the study.

THE compound  $\text{BaSi}_2\text{O}_5$  occurs in nature as the rare mineral, sanbornite. The compound  $\text{BaAl}_2\text{Si}_2\text{O}_8$  is the principal component of the barium-feldspar, celsian. Both compounds are important constituents of synthetic products, including fluorescent phosphors, barium crown glasses, electrical porcelains, refractories, and so-called glass-ceramics. Their phase relations with each other, as well as with other compounds in the  $\text{BaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$  system, are thus of considerable mineralogical and technological interest. This study is the third of a series included in a comprehensive reinvestigation of the  $\text{BaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$  system. Previous reports in the series dealt with the polymorphism of celsian (Lin and Foster, 1968) and the binary system celsian-silica (Foster and Lin, 1969).

*Previous work.* Bowen (1918) determined the melting point of pure  $\text{BaSi}_2\text{O}_5$  as 1426 °C. Rogers (1932) believed that the polysynthetic twinning of natural sanbornite indicated polymorphism. Klasens, Hoekstra, and Cox (1957) and Roth and Levin (1959) detected an inversion in synthetic sanbornite at about 1350 °C. Lin and Foster (1968) reviewed the latest findings on the melting and polymorphism of pure synthetic celsian. They selected 1760 °C as the melting temperature of hexacelsian, and 1590 °C as the inversion temperature of celsian to hexacelsian.

The system sanbornite-celsian has not previously been systematically studied. It was included however, in several general investigations of the  $\text{BaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$  system (Thomas, 1950; Toropov, Galakhov, and Bondar, 1954, 1955). That by Thomas presented a theoretically possible diagram for the system, based on limited experimental data. Toropov and his co-workers (1955) gave no direct plot for the sanbornite-celsian join. However, their traverses in the ternary system at  $\text{SiO}_2$ -levels of 36, 39, and 42 % permit the deduction of a sanbornite-celsian diagram that closely resembles that of Thomas. The approximate relations deduced from these previous

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investigations are shown as a composite diagram in fig. 1. Both renditions depict eutectic relations between the end-members. Both show substantial solid solution (roughly 30–5 %) of celsian in sanbornite at the eutectic temperature, located at or slightly above 1300 °C. Neither version takes cognizance of polymorphism in the sanbornite and celsian end-members.

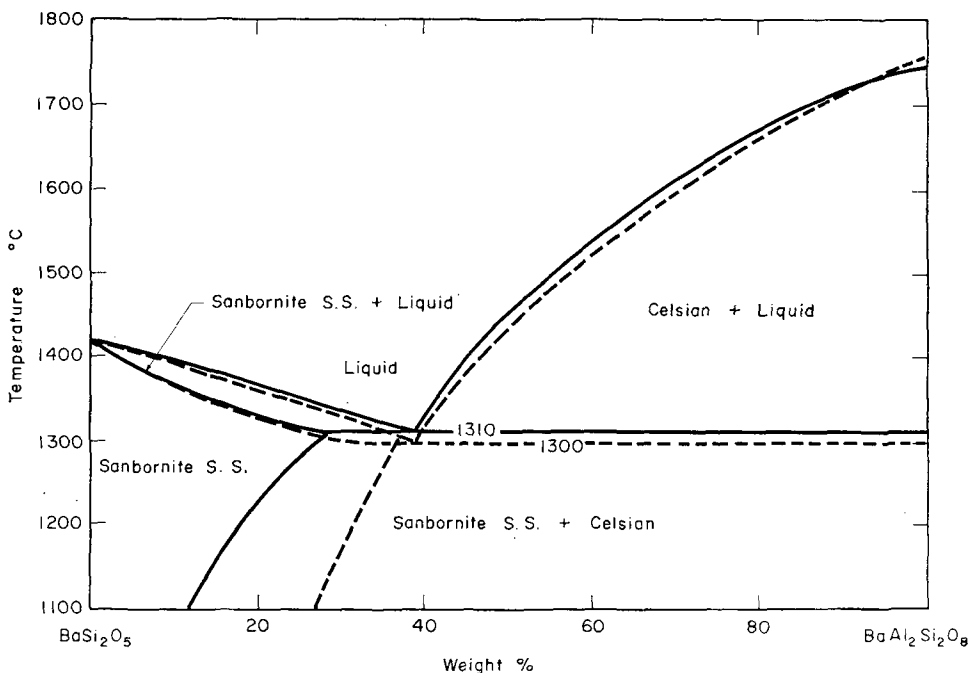


FIG. 1. Phase diagram for the  $\text{BaSi}_2\text{O}_5$ - $\text{BaAl}_2\text{Si}_2\text{O}_8$  system, deduced from Thomas (solid lines) and Toropov, Galakhov, and Bondar (dashed lines).

*Experimental procedure.* Raw materials of chemical reagent grade were used in this study. The source of BaO was C. P. Baker's analysed barium carbonate of 99.5 % purity, sulphates of calcium and strontium making up the bulk of the impurity. Linde Type B-5125  $\gamma$ -alumina of 99.9 % purity served as the source of  $\text{Al}_2\text{O}_3$ . For  $\text{SiO}_2$ , crystalline quartz in the form of 5- $\mu\text{m}$  'Min-U-Sil' of the Pennsylvania Glass Sand Corporation (purity 99.9 %) was used.

From the above raw materials eight selected compositions between sanbornite and celsian were prepared in the form of homogeneous glasses. Each composition was fused three times in a platinum crucible with intermittent crushing and grinding, to achieve homogeneity. The refractive index of each glass was microscopically determined as a check on both homogeneity and bulk composition. The variation of refractive index with composition, thus obtained, is shown in fig. 2. These glasses were then devitrified by heating for about 24 hours at approximately 1050 °C, resulting in an intimate mixture of finely crystallized sanbornite and celsian with very subordinate interstitial glass.

The quenching method developed at the Geophysical Laboratory (Roedder, 1951; Schairer, 1959) was used to establish the phase relations. In each run a 10 mg sample of devitrified glass wrapped in platinum foil was held at a selected temperature in a platinum-rhodium resistance

furnace for a time believed sufficient to establish equilibrium, whereupon it was quenched in mercury to retain the phases present at the elevated temperature. Sample temperatures were measured with a Pt:10% Rh,Pt thermocouple, which was calibrated periodically against the melting points of gold (1063 °C), diopside (1391.5 °C), and gehlenite (1590 °C).

In those runs used to establish the liquidus curves, phase identification was carried out with the polarizing microscope. The optical characteristics that served to distinguish the primary crystalline phases were: Crystals of  $\text{BaSi}_2\text{O}_5$ , whether in the low- or the high-form, almost always showed higher indices than the enclosing glass. They usually appeared in a stout, blocky form with high birefringence, parallel extinction, and occasional polysynthetic twinning. No satisfactory optical criteria for distinguishing the two forms of sanbornite could be established. In contrast, crystals of  $\text{BaAl}_2\text{Si}_2\text{O}_8$ , whether in the celsian or hexacelsian form, usually showed lower indices than the surrounding glass. Birefringence was also distinctly lower than that of sanbornite crystals of equivalent size. Celsian crystals usually appeared as elongated blades or needles with inclined extinction up to  $28^\circ$ , whereas hexacelsian exhibited blocky crystals with parallel extinction and negative elongation.

Confirmation of the identity of the primary phases at the liquidus was made by the X-ray powder diffraction method, on charges treated considerably below the liquidus temperatures. For this purpose a Norelco high-angle X-ray diffractometer with  $\text{Cu-K}\alpha$  radiation was used. The X-ray powder method was used also to establish the eutectic temperature, to confirm the polymorphism of sanbornite and to investigate the alleged solid solution of celsian in sanbornite. The diffraction peaks that proved to be most diagnostic of the several crystalline phases were: low-sanbornite, 3.09 Å; high-sanbornite, 3.55 Å; celsian, 3.35 Å; and hexacelsian, 3.95 Å. However, additional strong peaks served to confirm the identification of each phase.

**Results.** Approximately 110 runs were made on the 8 different sanbornite-celsian compositions. Only about one-third of these runs were of critical significance in establishing the phase relations, the remainder being confirmatory in nature. The more critical runs are presented in table I, and have been used to prepare the revised phase diagram for the system, shown in fig. 3.

The sanbornite-celsian system is a simple binary eutectic system with congruently melting end-members, each of which exhibits polymorphism. The  $\text{BaSi}_2\text{O}_5$  melting-point of 1426 °C is taken from the study by Bowen (1918). The 1359 °C inversion temperature determined in the present study for the low- to high-sanbornite transition agrees well with the 1350 °C value suggested by Klasens, Hoekstra, and Cox (1957) and by Roth and Levin (1959). The  $\text{BaAl}_2\text{Si}_2\text{O}_8$  melting point of 1760 °C, as well as

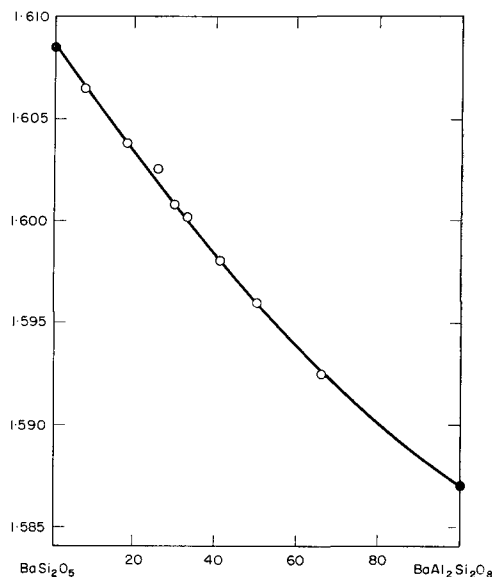


FIG. 2. Refractive index chart for glasses in the  $\text{BaSi}_2\text{O}_5$ - $\text{BaAl}_2\text{Si}_2\text{O}_8$  system.

TABLE I. *Quenching data for the system sanbornite-celsian*

Composition (wt %)		Temp. (°C)	Time (hours)	Phases
Sa*	Ce†			
<i>Primary phase: high-sanbornite</i>				
94.0‡	3.5	1361	12	high-sanbornite + glass
92.5	7.5	1391	5½	glass
		1385	30	high-sanbornite + glass
<i>Primary phase: low-sanbornite</i>				
94.0‡	3.5	1357	20	low-sanbornite + glass
		1353	20	low-sanbornite + glass
82.0	18.0	1324	4	glass
		1320	8	low-sanbornite + glass
74.5	25.5	1268	30	glass
		1262	12	low-sanbornite + glass
70.0	30.0	1236	10.5	glass
		1230	19	low-sanbornite + glass
<i>Primary phase: hexacelsian</i>				
34.0	66.0	1648	7.5	glass
		1642	5	hexacelsian + glass
<i>Primary phase: celsian</i>				
67.0	33.0	1282	12	glass
		1278	6	celsian + glass
59.5	40.5	1398	8	glass
		1394	10	celsian + glass
50.0	50.0	1513	5	glass
		1507	10	celsian + glass
<i>Eutectic horizontal</i>				
92.5	7.5	1224	22	low-sanbornite + celsian
82.0	18.0	1224	60	low-sanbornite + celsian
74.5	25.5	1230	19	low-sanbornite + glass
		1224	22	low-sanbornite + celsian
70.0	30.0	1230	19	low-sanbornite + glass
		1224	22	low-sanbornite + celsian
67.0	33.0	1239	9	low-sanbornite + glass
		1224	60	low-sanbornite + celsian
<i>Possibility of sanbornite solid solution</i>				
92.5	7.5	1200	270	low-sanbornite + celsian
82.0	18.0	1200	270	low-sanbornite + celsian
74.5	25.5	1200	270	low-sanbornite + celsian
70.0	30.0	1200	270	low-sanbornite + celsian

\* BaSi<sub>2</sub>O<sub>3</sub>.† BaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>.

‡ Composition not exactly on sanbornite-celsian join, by virtue of 2.5 % excess silica.

the 1590 °C inversion of celsian to hexacelsian, are taken from the recent study of Lin and Foster (1968).

Liquidus temperatures were established with an accuracy of  $\pm 3$  °C or better. Smooth, continuous liquidus curves could have been drawn through the determined

liquidus points for  $\text{BaSi}_2\text{O}_5$  and  $\text{BaAl}_2\text{Si}_2\text{O}_8$ . Theoretically, however, the occurrence of polymorphism should occasion a change of slope, be it ever so slight, at the temperatures of the inversions. Accordingly, a slight inflection is shown in the liquidus curves of  $\text{BaSi}_2\text{O}_5$  and  $\text{BaAl}_2\text{Si}_2\text{O}_8$ , at 1359 and 1590 °C, respectively.

The eutectic point in the system has been located at a temperature of  $1227 \pm 3$  °C, and at a composition of 69 % sanbornite and 31 % celsian by weight. The point was fixed by the intersection of the determined liquidus curves of  $\text{BaSi}_2\text{O}_5$  and  $\text{BaAl}_2\text{Si}_2\text{O}_8$ ,

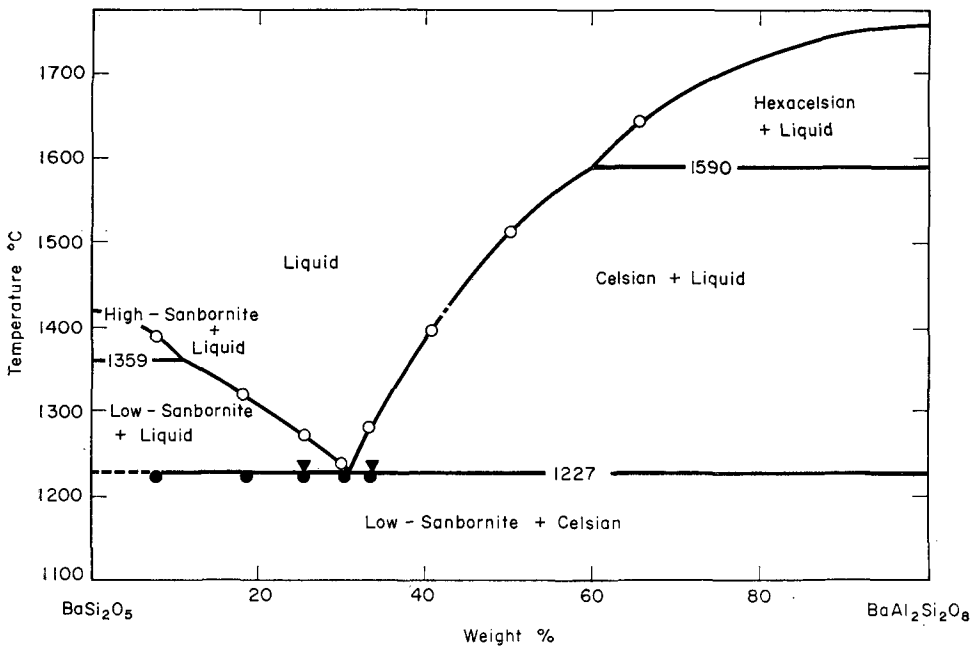


FIG. 3. Revised phase diagram for the  $\text{BaSi}_2\text{O}_5$ - $\text{BaAl}_2\text{Si}_2\text{O}_8$  system. ○ liquidus temperatures; ▼ temperatures above eutectic; ● temperatures below eutectic.

coupled with the determination of the lowest temperature at which one of the two crystalline phases disappeared from selected devitrified glasses.

The data of Table I offer no indication of the existence of solid solutions in the sanbornite-rich portion of the system, as depicted in earlier studies. Runs of 270 hours duration at temperatures only 25 °C below the eutectic yielded two phases (sanbornite and celsian) rather than a single sanbornite solid solution. The range of composition covered extends from 70 to 92.5 % sanbornite, and embraces the range of solid solutions of the earlier studies. A crystalline mixture of 94 % sanbornite and 6 % celsian, prepared as a standard, gave no clear-cut X-ray evidence for the celsian known to be present, presumably due to near-coincidence of several of the strong diffraction lines of low-sanbornite and celsian. It is therefore believed that conclusive proof for the complete absence of solid solution in the 92.5-100 % sanbornite range is not to be

obtained by the method utilized. For that reason, the eutectic horizontal in that composition range is shown as a dashed, rather than a solid, line.

*Discussion.* The sanbornite-celsian diagram obtained in the present study (fig. 3) differs in several important respects from those deduced from earlier investigations (fig. 1). The revised diagram features a eutectic at a temperature about 75–85 °C lower than in the earlier diagrams, and a composition almost 10 % richer, by weight, in sanbornite. Polymorphism has been indicated in each end-member. A major point of difference from the earlier versions is the omission of the region of solid solution at the sanbornite end of the diagram. Thomas (1950) based his belief in the presence of solid solution in sanbornite on the study of optical properties. That such observations can be subject to misinterpretation is evinced by Eskola's (1922) optical determination of solid solution between sanbornite and  $2\text{BaO} \cdot 3\text{SiO}_2$ , and the later refutation of this claim by Roth and Levin (1959) on the basis of X-ray diffraction study. The evidence for solid solution presented by Toropov, Galakhov, and Bondar (1955) cannot be dismissed by a similar argument, since the Russian investigators based their claim on X-ray diffraction data, which indicated progressive changes in the cell-dimensions with change of composition. It is to be noted, however, that their samples were prepared by fusion in an electric arc, presumably involving a very short thermal treatment. In contrast, the present test of possible solid solution effects involved runs of 270 hours. It is here suggested that the former treatment might be conducive to the formation of metastable solid solutions. Such transient phases have been observed in the systems  $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$  (Roy, 1959) and  $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$  (Schreyer and Schairer, 1961), and have been found to be unstable in the face of prolonged thermal treatment. It is here suggested that the 270-hour runs might be expected to effect a closer approach to stable equilibrium than would the electric-arc fusion experiments of the earlier studies. Reasoning from structural consideration, Douglass (1958) has questioned the likelihood of substantial solid solution of celsian in sanbornite. On both theoretical and experimental grounds, therefore, there is reason for doubting the solid solution effects depicted in fig. 1.

Natural sanbornite contains very little alumina, suggesting that under the conditions of formation in nature, solid solution of celsian in sanbornite is negligible. This fact, in itself, does not establish fig. 3 as the preferred diagram, since both versions of fig. 1 indicate a pronounced decrease in solid solution with decreasing temperature. Extrapolation of the solvus curves marking the limit of the alleged solid solution in fig. 1 would suggest that in the Thomas diagram solid solution becomes negligible at about 900 °C, whereas it disappears at about 600 °C in the diagram of Toropov *et al.* Evidence from the natural minerals as to the presence or absence of substantial solid solution in the region of the eutectic horizontal of the phase diagram is thus inconclusive.

The low-sanbornite and celsian phases encountered in this study correspond to the natural minerals, sanbornite and celsian, respectively. High-sanbornite and hexacelsian, on the other hand, have no counterparts among the natural minerals. The celsian-polymorph, paracelsian, was not encountered in this study. This is

understandable, in view of earlier findings (Lin and Foster, 1968), which strongly suggested that paracelsian is a metastable phase, changing readily to celsian at temperatures of 550 °C or higher.

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