

# Phase Equilibria in the Subsystem Barium Disilicate—Dibarium Trisilicate

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A revised phase equilibrium diagram for the subsystem  $\text{BaO} \cdot 2\text{SiO}_2 - 2\text{BaO} \cdot 3\text{SiO}_2$  is presented. The previously published diagram showing a complete solid solution series was not verified. Instead, two new compounds were identified by X-ray diffraction powder pattern techniques, and two eutectics were located by the quenching method. The compound  $3\text{BaO} \cdot 5\text{SiO}_2$  melts incongruently at  $1,423^\circ \text{C}$  to form  $5\text{BaO} \cdot 8\text{SiO}_2$  and liquid. The latter compound melts congruently at  $1,446^\circ \text{C}$ . Barium disilicate was found to have a quenchable and slowly reversible phase transformation at about  $1,350^\circ \text{C}$ . The X-ray diffraction powder pattern for  $2\text{BaO} \cdot 3\text{SiO}_2$  was indexed for the first time on the basis of a monoclinic unit cell.

## 1. Introduction

In a study of the phase equilibria of the binary system  $\text{BaO} \cdot \text{SiO}_2$ , P. Eskola [1]<sup>1</sup> confirmed the existence of barium disilicate, previously reported by Bowen [2]. The phase diagram published by Eskola showed complete solid solution between  $\text{BaO} \cdot 2\text{SiO}_2$  and  $2\text{BaO} \cdot 3\text{SiO}_2$ . Rogers [3] discovered the existence of barium disilicate in nature and gave it the mineral name of sanbornite. In order to reconcile his findings with those of Bowen and Eskola, Rogers postulated dimorphism in  $\text{BaSi}_2\text{O}_5$ , indicating that sanbornite was probably triclinic, whereas the synthetic material was apparently orthorhombic. In a study of the  $\text{BaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$  system, R. H. Thomas [4] concluded that dibarium trisilicate probably was not a compound, but rather a fortuitous end-member of a solid solution series.

Levin and Ugrinic [5] and Toropov, Galakhov, and Bondar [6] concluded that dibarium trisilicate most likely was a true compound and that complete solid solution existed between it and barium disilicate. Levin and Ugrinic, nevertheless, state, "The X-ray data, however, did not conclusively show a solid solution series. The powder pattern for the composition containing 70.8 percent  $\text{BaO} \cdot 2\text{SiO}_2$  (29.2 percent of  $2\text{BaO} \cdot 3\text{SiO}_2$ ) showed several double peaks which indicated the presence of two phases. Even after an additional melting and grinding of the mixture, these double peaks persisted."

R. M. Douglass [7] recently reported the crystal structure of the mineral sanbornite. The unit cell was found to be orthorhombic with  $a=4.63 \text{ \AA}$ ,  $b=8.69 \text{ \AA}$ , and  $c=13.53 \text{ \AA}$ . Douglass concluded that barium disilicate did not show polymorphism although his X-ray diffraction powder pattern did not match that of Levin and Ugrinic [5].

On the basis of the structure determined for sanbornite, Douglass [7] doubted that extensive solid

solution existed between barium disilicate and dibarium trisilicate.

The opinions expressed by Douglass led to a re-examination of the possibilities of polymorphism in barium disilicate. Unpublished high-temperature X-ray patterns prepared during the original investigation of Levin and Ugrinic [5] had not been interpreted as showing conclusive evidence of polymorphism. However, with the ability to index the low-temperature form, as a result of Douglass' work, polymorphic transformation was clearly indicated in these patterns. In a note preliminary to this publication [8] polymorphism in barium disilicate was announced. The complete data supporting that statement are presented in this paper. In an attempt, also, to resolve the controversial question of solid solution in barium disilicate, a detailed re-examination is reported for the subsystem  $\text{BaO} \cdot 2\text{SiO}_2 - 2\text{BaO} \cdot 3\text{SiO}_2$ .

## 2. Apparatus and Method

Phase equilibrium relationships in the system were studied by the well-established quenching technique. It was found that all liquids could be readily quenched to glasses. Constant temperature control of the quench furnace to within  $\pm 3^\circ \text{C}$  was achieved with a self-adjusting, a-c bridge-type controller [9]. Quenched samples were examined with the polarizing microscope and by X-ray powder diffraction patterns (Ni-filtered  $\text{CuK}$  radiation) using a high-angle Geiger-counter diffractometer.

Temperatures were measured with a platinum versus platinum-rhodium (10%) thermocouple which was taken from lengths of thermocouple wire which had been originally calibrated by the Pyrometry Laboratory. Temperatures are given on the International Temperature Scale of 1948. During the course of the experiments the thermocouple was checked three times against the melting point of barium disilicate ( $1,420^\circ \text{C}$ ).

<sup>1</sup> Figures in brackets indicate the literature references at the end of this paper.

### 3. Preparation of Mixtures

Starting materials for the preparation of mixtures consisted of reagent grade (ACS) barium carbonate and silica gel of 99.99-percent purity on an ignited weight basis. The silica gel was specially prepared by an acid digestion process in the Chemistry Division.

The end-members  $\text{BaO} \cdot 2\text{SiO}_2$  and  $2\text{BaO} \cdot 3\text{SiO}_2$  as well as the composition containing 37.4-mole percent BaO were specimens used in a previous study [5], and their preparation was described therein. Six intervening mixtures with BaO contents ranging from 34- to 39-mole percent, in 1-mole-percent increments, were prepared as follows: Calculated amounts, for 3-g mixtures, of barium carbonate and silica gel were thoroughly blended for  $\frac{1}{2}$  hr with a high-speed mechanical mixer. The mixtures were

then ground for  $\frac{1}{2}$  to  $\frac{3}{4}$  hr in an agate mechanical grinder. Specimens,  $\frac{5}{8}$  in. in diameter, were formed by pressing the material in a mold at approximately 20,000 psi. The pressed disks were fired in a pot furnace at about  $1,300^\circ \text{C}$  for 24 hr. The disks were ground through a No. 200 sieve, pressed as before, and given a second heat treatment at  $1,375^\circ \pm 15^\circ \text{C}$  for 84 hr. Finally, the disks were ground to pass a No. 200 sieve. The two relatively long-time, high-temperature, heat treatments of pressed specimens were sufficient, apparently, to give homogeneous samples, as determined by inspection with the polarizing microscope.

For locating compounds and eutectics, 5 additional 1-g samples were prepared from the appropriate amounts of previously prepared adjacent samples. The method of combination was similar to that for the 3-g samples.

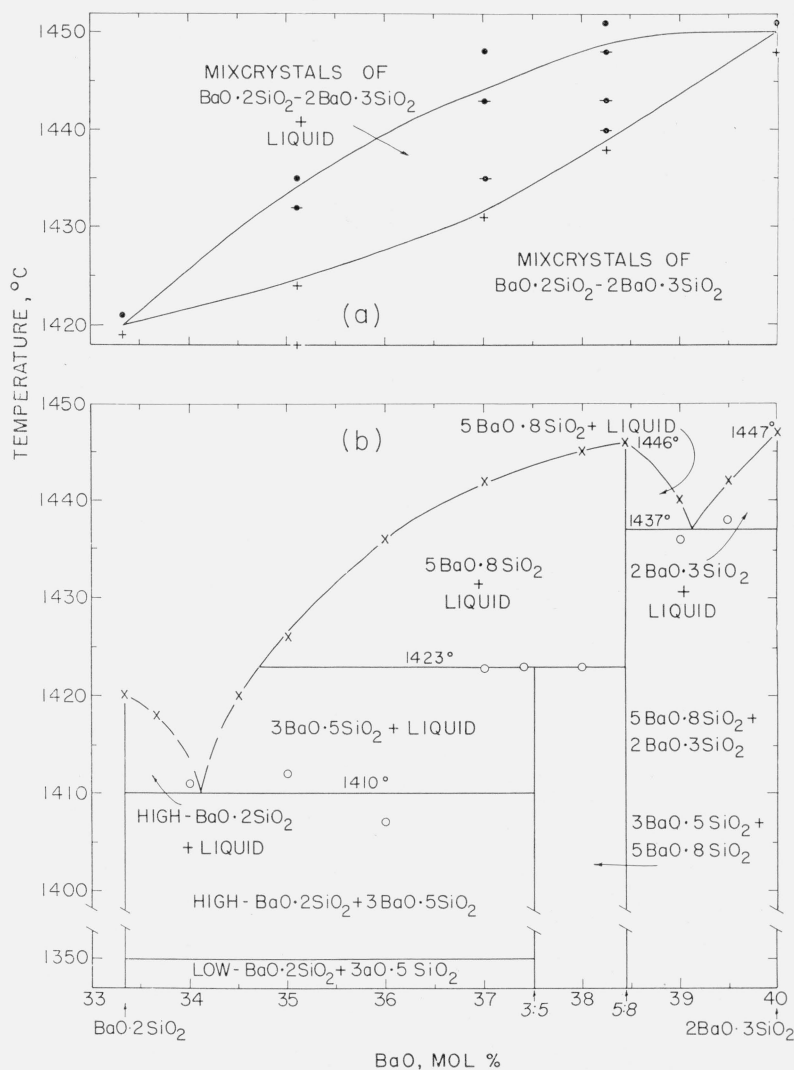


FIGURE 1. Phase equilibrium diagrams proposed for the subsystem  $\text{BaO} \cdot 2\text{SiO}_2$ – $2\text{BaO} \cdot 3\text{SiO}_2$ .

(a) Continuous solid solution diagram according to Eskola [1], with data converted to mole percent. ●, glass; ●•, mixcrystals and glass; +, mixcrystals.  
(b) Diagram without solid solution, according to the present work, showing two compounds and two eutectics. x, liquidus value; o, solidus value.

## 4. Results and Discussion

The results of the experiments in the system  $\text{BaO} \cdot 2\text{SiO}_2$ - $2\text{BaO} \cdot 3\text{SiO}_2$  are listed in table 1 for the 14 different compositions studied. These results have been interpreted to give the phase diagram shown in figure 1. Identification of crystalline phases by the polarizing microscope is given in the table only for those cases in which X-ray identification was not possible, because of a large proportion of glass. Because of overlapping indices of refraction, accurate identification of the crystalline phases present was difficult or impossible for many of the specimens. However, maximum and minimum indices usually were determined, and they were found to be compatible with the X-ray data.

### 4.1. Polymorphism of Barium Disilicate

Results of the experiments listed in table 1 for the 2 specimens containing 33.33-mole-percent  $\text{BaO}$  prove the existence of polymorphism in  $\text{BaSi}_2\text{O}_5$ . The heat treatment used to prepare the first composition listed in table 1 yielded the low-temperature form of  $\text{BaO} \cdot 2\text{SiO}_2$ , or sanbornite. It may be seen that the low-temperature form remains stable at temperatures below  $1,340^\circ\text{C}$ . At temperatures of  $1,352^\circ\text{C}$  and above, however, the high-temperature form appears, in amounts which increase with the time and temperature of heat treatment. For example, the sample heated at  $1,360^\circ\text{C}$  for 1.5 hr failed to produce any detectable amounts of the high-temperature form, whereas the sample heated at  $1,358^\circ\text{C}$  for 16 hr showed appreciable conversion.

High-temperature X-ray diffraction patterns of the original low-temperature form were available from a previous study [5]. Upon re-examination the following features were observed: Except for slight shifts in interplanar spacings due to thermal expansion, no change was observed up to  $1,300^\circ\text{C}$ . After several hours at  $1,375^\circ\text{C}$ , notable differences were apparent in the diffraction pattern. The X-ray

pattern of the sample, furnace-cooled to room temperature, still showed the high form of barium disilicate.

The second composition listed in table 1 was not initially heat treated below  $1,390^\circ\text{C}$ . It showed the pure high-temperature form. When it was heated at  $1,335^\circ\text{C}$  for 18 hr, the low-temperature form appeared in abundance. Interpretation of these data leads to the conclusion that barium disilicate exhibits a slowly reversible polymorphic transformation at  $1,350^\circ\text{C} \pm 10^\circ\text{C}$ .

Figure 2 shows schematically the X-ray diffraction powder patterns of the 2 polymorphs compared with the patterns reported by Austin [10] and Douglass [7] for  $\text{BaO} \cdot 2\text{SiO}_2$ . It is obvious from this figure that sanbornite (Douglass [7]) is identical with the low-temperature form of  $\text{BaO} \cdot 2\text{SiO}_2$ , found in the present work. Austin's data appear to represent, at least in part, a poorly resolved pattern for high  $\text{BaO} \cdot 2\text{SiO}_2$ .

The X-ray diffraction powder pattern for high-temperature  $\text{BaO} \cdot 2\text{SiO}_2$  obtained in the present study is compared in table 2 with the pattern published by Levin and Ugrinic [5]. The present pattern is probably more accurate as it seems likely that the X-ray diffraction equipment used for the earlier work was out of alignment. The final accuracy of the  $d$  values must await indexing of the pattern following a determination of the unit-cell parameters.

The X-ray diffraction powder patterns of the 2 polymorphs are superficially similar in that many of the strong lines of both patterns almost coincide. However, when an attempt is made to index the pattern of the high-temperature form, it is found that many of the interplanar spacings cannot be assigned indices on the basis of a structure resembling sanbornite. The diffraction peak at  $2\theta = 25.1^\circ$  or  $d = 3.54\text{ \AA}$ , is diagnostic of the high-temperature form. A number of other peaks cannot be reconciled with the sanbornite structure, as, for example, those at approximately  $16^\circ$  and  $19^\circ$  and the triplet at  $28.5^\circ$   $2\theta$  (see fig. 2). It may be concluded that Douglass'

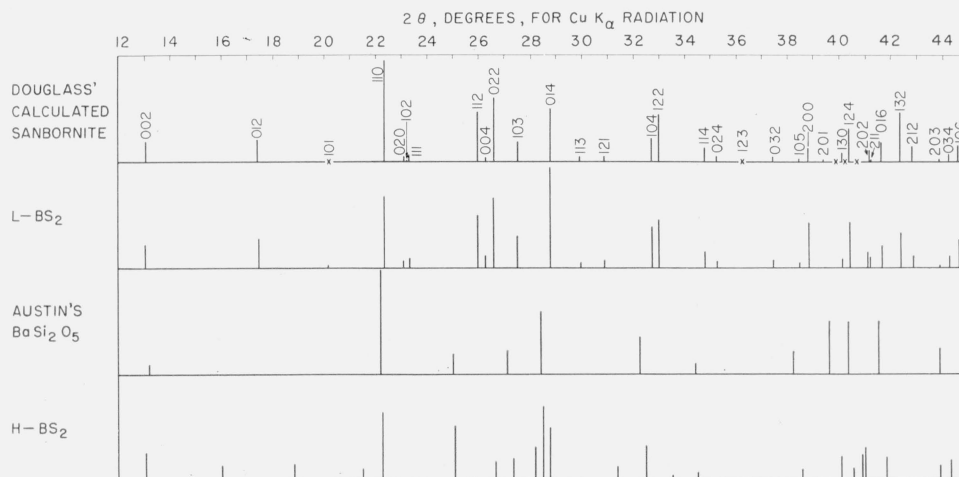


FIGURE 2. Schematic X-ray diffraction powder patterns for the polymorphs of  $\text{BaO} \cdot 2\text{SiO}_2$  compared with two previously published patterns [7, 10].

pattern is different from those reported by any of the authors mentioned in his paper [7]. Although Douglass correlated his pattern with Austin's published data, the present work proves that this correlation is incorrect. Austin's data should actually be correlated with the high-temperature form, as was done originally by Levin and Ugrinic [5].

#### 4.2. Compound $2\text{BaO} \cdot 3\text{SiO}_2$

In order to obtain sufficient data to index the powder pattern, single crystals of  $2\text{BaO} \cdot 3\text{SiO}_2$  were grown by A. Perloff of the Bureau on a hot-wire apparatus [11]. Precession patterns established the symmetry of the crystal as monoclinic, probably space group  $C_2^2-P2_1$  or  $C_{2h}^2-P2_{1/m}$ . Using the approximate cell dimensions provided by Perloff, the X-ray diffraction powder pattern was indexed (table 3). The unit-cell parameters calculated from the powder pattern are:  $a=12.51 \text{ \AA}$ ;  $b=4.69 \text{ \AA}$ ;  $c=6.97 \text{ \AA}$ ; and  $\beta=93^\circ 23'$ .

Specimens of the composition containing 40-mole-percent BaO heated at  $1,400^\circ \text{C}$  for 3 hr or at  $1,442^\circ \text{C}$  for 0.5 hr (table 1) showed the same phase, namely, that present in the original starting material and in the crystals grown from the melt. The  $d$  values for this phase did not change regardless of composition or time and temperature of treatment. Consequently, within the limits of the present experiments, dibarium triclicate shows neither polymorphism nor solid solution. The liquidus temperature of  $2\text{BaO} \cdot 3\text{SiO}_2$  was determined to be  $1,447^\circ \text{C}$ , or about  $3^\circ$  less than that reported by Eskola.

#### 4.3. Phase Diagram for the System $\text{BaO} \cdot 2\text{SiO}_2$ — $2\text{BaO} \cdot 3\text{SiO}_2$

The phase diagram as reported by Eskola [1] (Fig. 1a) shows a continuous solid solution between  $\text{BaO} \cdot 2\text{SiO}_2$  and  $2\text{BaO} \cdot 3\text{SiO}_2$ , without maximum or minimum. It should be noted that this diagram is based on only 3 intermediate compositions.

TABLE 1. Compositions studied and phases identified in the system  $\text{BaO} \cdot 2\text{SiO}_2$ — $2\text{BaO} \cdot 3\text{SiO}_2$

Composition		Heat treatment <sup>a</sup>		Phases		
BaO	SiO <sub>2</sub>	Tempera- ture	Time	X-ray diffraction <sup>b</sup>	Polarizing microscope	
					Crystals <sup>c</sup>	Amt. glass
<i>mole %</i>	<i>mole %</i>	<i>° C</i>	<i>hr</i>			
33.33	66.67	d e 1,200	2.0	Low-BaO-2SiO <sub>2</sub> .....		
(BaO-2SiO <sub>2</sub> )		1,340	52.0	do.....		
		1,352	5.0	Low- +high-BaO-2SiO <sub>2</sub> .....		
		1,358	16.0	do.....		
		1,360	1.5	Low-BaO-2SiO <sub>2</sub> .....		
		1,373	16.0	High- +low-BaO-2SiO <sub>2</sub> .....		
		1,385	2.5	do.....		
33.33	66.67	d f 1,390	1.75	High-BaO-2SiO <sub>2</sub> .....		
33.67	66.33	1,335	18.0	Low- +high-BaO-2SiO <sub>2</sub> .....		
		1,419	0.33	High-BaO-2SiO <sub>2</sub> .....		
		1,388	16.0	High- +low-BaO-2SiO <sub>2</sub> +3BaO-5SiO <sub>2</sub> .....		None.
34.00	66.00	1,415	1.0	High-BaO-2SiO <sub>2</sub> .....		Moderate.
		1,418	1.0		BaO-2SiO <sub>2</sub> .....	Large.
		d h 1,375	84.0	High-BaO-2SiO <sub>2</sub> +3BaO-5SiO <sub>2</sub> .....		
		1,407	1.0	do.....		None.
		1,414	1.0	High-BaO-2SiO <sub>2</sub> <sup>i</sup> +3BaO-5SiO <sub>2</sub> <sup>i</sup> .....		Small.
34.50	65.50	1,417	3.0	do.....		Moderate.
		1,420	0.5		3BaO-5SiO <sub>2</sub> <sup>i</sup> +BaO-2SiO <sub>2</sub> .....	Large.
		1,424	.5			All.
		1,395	16.0	High-BaO-2SiO <sub>2</sub> +3BaO-5SiO <sub>2</sub> .....		None.
		1,415	0.5	3BaO-5SiO <sub>2</sub> .....		Large.
35.00	65.00	1,418	1.0		Trace.....	Do.
		1,421	1.0			All.
		d h 1,375	84.0	High-BaO-2SiO <sub>2</sub> +3BaO-5SiO <sub>2</sub> .....		None.
		1,410	1.0	do.....		Do.
		1,416	1.0	3BaO-5SiO <sub>2</sub> .....		Moderate.
36.00	64.00	1,419	0.5		3BaO-5SiO <sub>2</sub> .....	Large.
		1,423	.5		do.....	Do.
		1,429	.5			All.
		d h 1,375	84.0	3BaO-5SiO <sub>2</sub> +high-BaO-2SiO <sub>2</sub> .....		
		1,340	16.0	3BaO-5SiO <sub>2</sub> +high-+low-BaO-2SiO <sub>2</sub> .....		
37.00	63.00	1,404	1.0	3BaO-5SiO <sub>2</sub> +high-BaO-2SiO <sub>2</sub> .....		None.
		1,410	1.0	3BaO-5SiO <sub>2</sub> .....		Small.
		1,416	1.0	do.....		Moderate.
		1,434	0.75		3BaO-5SiO <sub>2</sub> <sup>i</sup> .....	Large.
		1,438	.5			All.
37.00	63.00	d h 1,375	84.0	3BaO-5SiO <sub>2</sub> +high-BaO-2SiO <sub>2</sub> .....		
		1,411	1.0	3BaO-5SiO <sub>2</sub> .....		None.
		1,419	1.0	do.....		Trace.
		1,423	1.0	3BaO-5SiO <sub>2</sub> +5BaO-8SiO <sub>2</sub> (tr).....		Do.
		1,426	0.75	3BaO-5SiO <sub>2</sub> <sup>i</sup> +5BaO-8SiO <sub>2</sub> .....		Small.
37.00	63.00	1,431	1.25	5BaO-8SiO <sub>2</sub> .....		Moderate.
		1,440	0.5		Trace.....	Large.
		1,445	.75			All.

See footnotes at end of table.



TABLE 1. Compositions studied and phases identified in the system BaO·2SiO<sub>2</sub>-2BaO·3SiO<sub>2</sub>—Continued

Composition		Heat treatment <sup>a</sup>		Phases		
BaO	SiO <sub>2</sub>	Temperature	Time	X-ray diffraction <sup>b</sup>	Polarizing microscope	
					Crystals <sup>c</sup>	Amt. glass
<i>mole %</i> 37.41	<i>mole %</i> 62.59	<i>° C</i> d f 1,390 1,415 1,423 1,426	<i>hr</i> 1.75 0.75 1.0 0.75	3BaO·5SiO <sub>2</sub> ..... 5BaO·8SiO <sub>2</sub> +3BaO·5SiO <sub>2</sub> ..... 5BaO·8SiO <sub>2</sub> +3BaO·5SiO <sub>2</sub> <sup>i</sup> .....		None. Trace. Small.
<sup>k</sup> 37.50	62.50	1,388	16.0	3BaO·5SiO <sub>2</sub> .....		
(3BaO·5SiO <sub>2</sub> )		1,437 1,440	1.0 1.0	5BaO·8SiO <sub>2</sub> ..... do.....		Small. Moderate.
38.00	62.00	d h 1,375 1,405 1,415 1,423 1,432 1,441 1,443 1,447	84.0 2.0 1.25 1.0 1.25 1.25 0.75 1.00	5BaO·8SiO <sub>2</sub> +3BaO·5SiO <sub>2</sub> ..... do..... do..... 5BaO·8SiO <sub>2</sub> ..... do..... do..... 5BaO·8SiO <sub>2</sub> .....		None. Do. Do. Trace. Small. Moderate. Large. All.
<sup>l</sup> 38.46	61.54	1,388	16.0	do.....		
(5BaO·8SiO <sub>2</sub> )		1,440 1,444 1,447	1.0 1.0 1.0	do..... do..... 5BaO·8SiO <sub>2</sub> .....		None. Large. All.
39.00	61.00	d h 1,375 1,405 1,425 1,433 1,438 1,442	84.0 2.0 1.0 1.0 0.8 1.0	5BaO·8SiO <sub>2</sub> +2BaO·3SiO <sub>2</sub> ..... do..... do..... do..... 5BaO·8SiO <sub>2</sub> .....		None. Do. Do. Large. All.
<sup>m</sup> 39.50	60.50	1,388 1,437 1,440 1,444	16.0 1.0 1.0 1.0	2BaO·3SiO <sub>2</sub> +5BaO·8SiO <sub>2</sub> ..... do..... 2BaO·3SiO <sub>2</sub> +5BaO·8SiO <sub>2</sub> (tr) <sup>i</sup> .....		None. Moderate. All.
40.00	60.00	d e 1,200	20.0	2BaO·3SiO <sub>2</sub> .....		
(2BaO·3SiO <sub>2</sub> )		1,400 1,442 1,445 1,450	3.0 0.5 .5 1.5	do..... do..... 2BaO·3SiO <sub>2</sub> ..... do.....		None. Trace. All.

<sup>a</sup> Except where noted, all specimens were quenched in water, from the temperature indicated.

<sup>b</sup> Listed in order of relative amounts present, major phase first.

<sup>c</sup> Listed only when no X-ray identification was available.

<sup>d</sup> Starting material; not quenched.

<sup>e</sup> Sample previously heated at 1,460° C for ¾ hr, 1,100° C for 17 hr, and 1,400° C for 1 hr.

<sup>f</sup> Sample previously heated at 1,460° C for 1.5 hr, 1,390° C for 1 hr, 1,450° C for 1 hr.

<sup>g</sup> Prepared by mixing the appropriate amounts of the compositions low-BaO·2SiO<sub>2</sub> and 34.00 BaO·66.00 SiO<sub>2</sub>.

<sup>h</sup> Sample previously heated at 1,300° C for 24 hr, 1,375° C for 3.5 hr, 1,360° C for 15.5 hr.

<sup>i</sup> Interpreted as non-equilibrium phase at the temperature indicated.

<sup>j</sup> Prepared by mixing the appropriate amounts of the compositions 34.00 BaO:66.00 SiO<sub>2</sub> and 35.00 BaO:65.00 SiO<sub>2</sub>.

<sup>k</sup> Prepared by mixing the appropriate amounts of the compositions 37.00 BaO:63.00 SiO<sub>2</sub> and 38.00 BaO:62.00 SiO<sub>2</sub>.

<sup>l</sup> Prepared by mixing the appropriate amounts of the compositions 38.00 BaO:62.00 SiO<sub>2</sub> and 39.00 BaO:61.00 SiO<sub>2</sub>.

<sup>m</sup> Prepared by mixing the appropriate amounts of the compositions 39.00 BaO:61.00 SiO<sub>2</sub> and 2BaO·3SiO<sub>2</sub>.

The present diagram (fig. 1b) differs from Eskola's in several important respects. It shows no solid solution. Instead, 2 discrete compounds occur: 5BaO·8SiO<sub>2</sub>, melting congruently at 1,446° C; and 3BaO·5SiO<sub>2</sub>, melting incongruently at approximately 1,423° C to form liquid and 5BaO·8SiO<sub>2</sub>. In addition, 2 eutectics are located at approximately 34-mole-percent BaO and 1,410° C and about 39-mole-percent BaO and 1,437° C.

The exact location of the first eutectic relative to the 34-mole-percent BaO composition could not be established because nonequilibrium conditions prevailed for this composition. Specimens quenched from a comparatively large temperature range of about 10° contained 2 crystalline phases and glass. However, the 34- and 35-mole-percent BaO compositions definitely began melting at about 1,410° C, 10° below the melting point of BaO·2SiO<sub>2</sub>, proving the existence of a eutectic in this region.

All compositions between 33.33-mole-percent BaO and 37.5-mole-percent BaO, when heated below the solidus, contained barium disilicate plus a second phase. The *d* values of barium disilicate remained essentially constant, indicating the absence of solid solution. A single phase was found to occur at the composition containing 37.5-mole-percent BaO, corresponding to the compound 3BaO·5SiO<sub>2</sub>. The X-ray diffraction powder pattern for this compound is given in table 4.

That the compound 3BaO·5SiO<sub>2</sub> melts incongruently was ascertained by the observation that this phase does not occur in specimens heated above about 1,423° C. Above this temperature, for the composition range 37- to 38-mole-percent BaO, a new phase was detected in equilibrium with glass.

Below the solidus, for the composition 38-mole-percent BaO, the new phase occurs with 3BaO·5SiO<sub>2</sub>, whereas the specimen containing 39-mole-percent

TABLE 2. X-ray diffraction data for the high temperature form of BaO·2SiO<sub>2</sub> (CuK<sub>α</sub><sub>1</sub> radiation)

Levin and Ugrinic		Roth and Levin	
<i>d</i> <sup>a</sup>	<i>I</i>	<i>d</i>	<i>I</i> / <i>I</i> <sub>0</sub> <sup>b</sup>
<i>A</i>	%	<i>A</i>	%
7.00	14	6.763	39
6.87	13		21
5.63	17		23
4.75	12		17
4.15	8		93
4.02	77	3.981	74
3.57	52	3.539	26
3.39	14	3.331B	31
3.36	23		46
3.27	25	3.250	100
3.15	100	3.129	71
3.11	87	3.095	21
2.86	27	2.843	49
2.76	40	2.749	7
2.69	7	2.667	11
2.61	12	2.593	7
2.36	16	2.349	14
2.35	16	2.329	33
2.26	32	2.245	17
2.23	29	2.220	37
2.21	51	2.204	46
2.16	25	2.198	31
2.06	21	2.155	19
2.05	32	2.059	29
2.00	7	2.040	7
1.923	12	1.992	34
1.877	17	1.916	31
		1.911	9
		1.876	11
		1.870	11
1.827	8	1.862	14
1.783	16	1.824	21
1.732	9	1.778	7
1.706	31	1.727	21
1.601	13	1.703	7
1.584	9	1.669	11
1.571	15	1.640	11
1.481	8	1.582	9
1.458	11	1.570	11
1.408	6	1.560	13
1.392	6	1.502	7
1.378	9	1.477	7
1.292	16	1.456	11
1.288	16	1.405	4
1.285	10	1.387	6
1.281	10	1.375	6
		1.362	10
		1.328	6
		1.306	6
		1.290	9
		1.286	13
		1.278	9

<sup>a</sup> The *d* values for this pattern are consistently larger than those found in the present work. As the two patterns were made from the same specimen, it seems likely that the X-ray diffraction equipment used for the older work was out of alignment.

<sup>b</sup> The intensities listed are given relative to the strongest peak.

BaO contains the new phase and 2BaO·3SiO<sub>2</sub>. Therefore the composition of the new compound occurs between 38- and 39-mole-percent BaO, most probably 5BaO·8SiO<sub>2</sub> (containing 38.46-mole-percent BaO). No change in the X-ray diffraction powder pattern (table 5) was observed up to the liquidus of 5BaO·8SiO<sub>2</sub> (1,446° C). The congruent melting point of the 5 : 8 compound is supported by the unequivocal existence of the eutectic at about 39-

TABLE 3. X-ray diffraction powder pattern for the compound 2BaO·3SiO<sub>2</sub>

Indexed up to *d*~2.1 (CuK<sub>α</sub><sub>1</sub> radiation)

<i>d</i>	<i>I</i> / <i>I</i> <sub>0</sub>	$\frac{1}{d^2 \text{obs.}}$	$\frac{1}{d^2 \text{cal.}}$	<i>hkl</i>
<i>A</i>	%			
12.44	4	0.0065	0.0064	100
6.948	20	.0207	.0207	001
6.204	5	.0257	.0256	200
5.909	10	.0286	.0257	101
4.384	5	.0520	.0285	101
			.0520	110
4.164	3	.0577	.0577	300
3.880	10	.0664	.0662	011
3.746	100	.0713	.0712	210
3.669	60	.0743	.0713	111
3.469	5	.0831	.0743	301
			.0827	002
3.409	7	.0861	.0865	102
3.299	50	.0919	.0919	102
3.249	55	.0947	.0946	211
3.123	30	.1026	.1026	400
3.125	30	.1030	.1029	202
			.1032	310
2.794	15	.1281	.1280	311
2.780	40	.1294	.1287	401
2.756	35	.1317	.1321	112
2.597	10	.1482	.1323	302
2.495	5	.1606	.1481	410
			.1603	500
2.475	5	.1633	.1634	411
2.391	5	.1749	.1744	402
2.343	20	.1821	.1822	020
2.305	5	.1883	.1885	103
2.267	45	.1945	.1886	120
			.1941	312
2.221	20	.2027	.2028	021
2.199	15	.2067	.2058	510
2.177	5	.2110	.2078	220
2.132	90	.2200	.2106	121
2.080	15		.2199	203
			.2200	412
2.076	17	(c)	(c)	(c)
2.033	8			
1.975	12			
1.970	17			
1.911	13			
1.874	11			
1.820	8			
1.806	6			
1.794	8			
1.780	14			
1.776	15			
1.753	7			
1.738	9			
1.703	3			
1.686	3			
1.648	8			
1.632	8			
1.628	8			
1.609	3			
1.598	3			
1.550	12			
1.508	7			

<sup>a</sup> *I*/*I*<sub>0</sub> represents the relative intensity of the diffraction peak relative to the strongest peak.

<sup>b</sup> These values were calculated on the basis of a unit cell size of *a*=12.51 Å, *b*=4.69 Å, *c*=6.97 Å, *β*=93°23'.

<sup>c</sup> No attempt was made to index the rest of the pattern due to the large cell size and low symmetry of the material.

mole-percent BaO (see compositions containing 39- and 39.5-mole-percent BaO in table 1).

Figure 3 shows a schematic comparison of the X-ray diffraction powder patterns of 2BaO·3SiO<sub>2</sub>, 5BaO·8SiO<sub>2</sub>, and 3BaO·5SiO<sub>2</sub>. One notable feature should be mentioned. With decreasing BaO content, from 2BaO·3SiO<sub>2</sub> to 3BaO·5SiO<sub>2</sub>, the doublet in

TABLE 4.—X-ray diffraction powder data for the compound  $3\text{BaO} \cdot 5\text{SiO}_2$ (CuK $\alpha_1$  radiation)

$d$	$I/I_0^a$	$d$	$I/I_0^a$
$\text{\AA}$	%	$\text{\AA}$	%
6.79	23	2.039	6
6.09	15	2.024	9
5.17	6	1.999	23
4.253	13	1.908	20
3.983	6	1.888	5
3.847	100	1.876	6
3.778	81	1.842	21
3.723	19	1.817	35
3.424	10	1.800	14
3.329	13	1.786	13
3.250	81	1.764	11
3.197	53	1.729	10
3.100	23	1.702	5
2.910	6	1.627	10
2.875	15	1.617	9
2.788	56	1.612	9
2.769	28	1.556	9
2.428	5	1.551	10
2.366	9	1.527	6
2.354	28	1.474	5
2.268	34	1.459	5
2.230	19	1.440	9
2.211	38	1.414	6
2.173	9	1.394	6
2.156	10	1.367	5
2.120	6	1.340	11
2.068	15		

<sup>a</sup> The intensity of these peaks is given relative to the height of the strongest peak.

$2\text{BaO} \cdot 3\text{SiO}_2$ , occurring at about  $2\theta = 23.5^\circ$  and  $24^\circ$  is shifted to a lower angle while the doublet at  $2\theta = 27^\circ$  and  $28.5^\circ$  is shifted to a higher value. This shift is discontinuous. Instead of a continuous shift in  $d$  values, as expected for solid solution, 2 phases of unvarying  $d$  values were always found for intermediate compositions. Therefore, it must be concluded that there is no appreciable solid solution in the  $\text{BaO} \cdot 2\text{SiO}_2$ - $2\text{BaO} \cdot 3\text{SiO}_2$  system.

#### 4.4. Criticism of the Solid Solution Diagram

The reason for the differences between the present diagram and the continuous solid solution interpretation may be found in reviewing the method used and data obtained by Eskola [1].

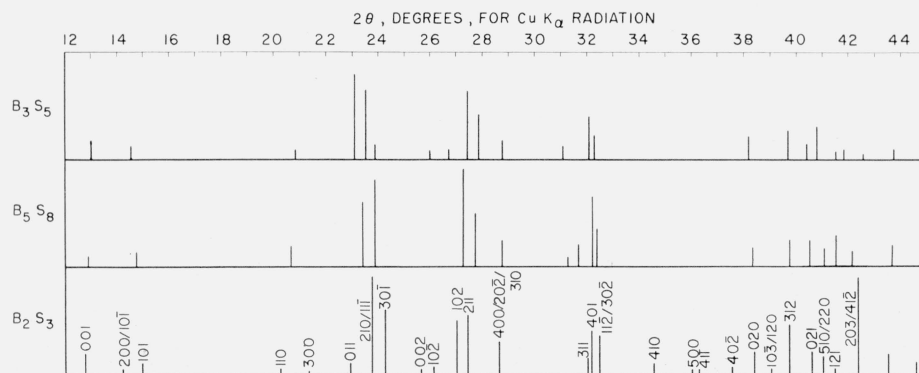
TABLE 5. X-ray diffraction powder data for the compound  $5\text{BaO} \cdot 8\text{SiO}_2$ .(CuK $\alpha_1$  radiation)

$d$	$I/I_0^a$	$d$	$I/I_0^a$
$\text{\AA}$	%	$\text{\AA}$	%
6.85	11	2.195	18
5.99	13	2.173	31
4.287	31	2.141	13
3.795	78	2.071	18
3.735	89	1.984	22
3.264	100	1.906	18
3.209	56	1.870	7
3.099	38	1.823	18
2.852	11	1.796	31
2.820	22	1.755	13
2.778	78	1.732	11
2.761	40	1.635	18
2.345	18	1.623	9
2.265	27	1.614	16
2.224	27	1.551	13

<sup>a</sup>  $I/I_0$  represents the intensity of the diffraction peaks relative to the strongest peak.

Table 6 compares the melting point data reported by Eskola with those found in the present investigation. It may be seen that the liquidus values given by Eskola for the 3 intermediate compositions are  $3.5^\circ$  to  $4.5^\circ$  higher than the interpolated values obtained from figure 1(b), for the corresponding compositions. If only these compositions had been studied in the present investigation, essential agreement would have been obtained for the liquidus curve. However, an investigation of additional compositions revealed the existence of 2 eutectics, thus eliminating the possibility of complete solid solution. As solidus values obtained by the quenching technique in glass-forming systems are less accurate than liquidus values, especially for compositions remote from the eutectic, a difference of as much as  $20^\circ$  (table 6) is quite possible.

In table 7 the indices of refraction of the discrete phases found in the present study are compared with the values given by Eskola for 6 compositions. As in the case of the melting point data, if only these compositions are considered, solid solution would be indicated. However, the indices of refraction obtained by Eskola are compatible with the indices found for the discrete phases, identified in the present

FIGURE 3. Schematic X-ray diffraction powder patterns for the compounds  $3\text{BaO} \cdot 5\text{SiO}_2$ ,  $5\text{BaO} \cdot 8\text{SiO}_2$ , and  $2\text{BaO} \cdot 3\text{SiO}_2$ .

work by X-ray methods. The interpretation of the indices for the specimen containing 35.11-mole-percent BaO, for example, is that the extreme indices reported by Eskola are the  $\alpha$  for BaO·2SiO<sub>2</sub> and the  $\gamma$  for 3BaO·5SiO<sub>2</sub>.

In postulating solid solution, Eskola placed great reliance on the observation that for the mixture containing 37-mole-percent of BaO, crystals formed at temperatures below the solidus possessed lower indices than crystals formed above the solidus. However, the present diagram, in which the compound  $3\text{BaO} \cdot 5\text{SiO}_2$  is shown to melt incongruently to  $5\text{BaO} \cdot 8\text{SiO}_2$  and liquid, is equally consistent with this observation.

Concerning the polymorphism of  $\text{BaO} \cdot 2\text{SiO}_2$ , the corresponding indices of refraction of the high and low forms are the same within the limits of accuracy of the immersion method ( $\pm 0.003$ ). Thus the 2 forms are optically indistinguishable.

The conclusion that little or no solid solution exists in the binary system BaO-SiO<sub>2</sub>, is in agreement with the opinions of Douglass [7], based on the structure of sanbornite. However, considerable solid solution has been postulated in BaO·2SiO<sub>2</sub> with Al<sub>2</sub>O<sub>3</sub> by Thomas [4] and with B<sub>2</sub>O<sub>3</sub> by Levin and Ugrinic [5]. Such systems might be reviewed with the idea of detecting the presence of the 3:5 and 5:8 compounds within the ternary system. It seems likely that a further study of these, or other ternary systems involving BaO and SiO<sub>2</sub>, would reveal that little solid solution occurs between any of the 4 compounds discussed here, involving a change in the ratio of the large cation to the tetrahedrally coordinated cation.

TABLE 6. Comparison of melting point data for compositions in the system  $\text{BaO} \cdot 2\text{SiO}_2$ - $2\text{BaO} \cdot 3\text{SiO}_2$

Composition		Liquidus		Solidus	
BaO	SiO <sub>2</sub>	Eskola [1]	Roth & Levin <sup>a</sup>	Eskola [1]	Roth & Levin <sup>a</sup>
<i>mole %</i>	<i>mole %</i>	<sup>o</sup> <i>C</i>	<sup>o</sup> <i>C</i>	<sup>o</sup> <i>C</i>	<sup>o</sup> <i>C</i>
33.33	66.67	1, 420	1, 420		
35.11	64.89	<sup>b</sup> 1, 433.5	1, 429	<sup>b</sup> 1, 421	1, 410
37.02	62.98	<sup>b</sup> 1, 445.5	1, 442	<sup>b</sup> 1, 433	1, 410
38.25	61.75	<sup>b</sup> 1, 449.5	1, 445	<sup>b</sup> 1, 439	1, 423
40.00	60.00	<sup>b</sup> 1, 449.5	1, 447	-----	-----

<sup>a</sup> Obtained from figure 1(b), to correspond to the listed compositions, which were studied by Eskola.

<sup>b</sup> Interpolated from data in table 2 of reference [1].

## 5. Summary

The phase equilibrium diagram for the subsystem  $\text{BaO} \cdot 2\text{SiO}_2$ - $2\text{BaO} \cdot 3\text{SiO}_2$  within the binary system  $\text{BaO}$ - $\text{SiO}_2$  has been revised. Fourteen compositions were studied by the quenching method. Phases were identified by X-ray diffraction powder patterns and with the aid of the polarizing microscope. The subsystem includes 4 binary compounds: the end-members,  $\text{BaO} \cdot 2\text{SiO}_2$  and  $2\text{BaO} \cdot 3\text{SiO}_2$ , and 2 new compounds,  $3\text{BaO} \cdot 5\text{SiO}_2$  and  $5\text{BaO} \cdot 8\text{SiO}_2$ . No perceptible solid solution was found between any of these compounds, contrary to previously published diagrams, which show complete solid solution between barium disilicate and dibarium trisilicate. Barium disilicate was found to have a quenchable and slowly reversible phase transformation at about  $1,350^\circ \text{C}$ . The mineral sanbornite corresponds to the low temperature form. The compound  $5\text{BaO} \cdot 8\text{SiO}_2$  and the end-member  $2\text{BaO} \cdot 3\text{SiO}_2$  melt congruently at  $1,446^\circ$  and  $1,447^\circ \text{C}$ , respectively. A eutectic exists between the 2 at about  $1,437^\circ \text{C}$ , and 39-mole-percent  $\text{BaO}$ . The compound  $3\text{BaO} \cdot 5\text{SiO}_2$  melts incongruently at about  $1,423^\circ \text{C}$  to form  $5\text{BaO} \cdot 8\text{SiO}_2$  and liquid. A eutectic between  $\text{BaO} \cdot 2\text{SiO}_2$  and  $3\text{BaO} \cdot 5\text{SiO}_2$  occurs at about  $1,410^\circ \text{C}$  and 34-mole-percent  $\text{BaO}$ . Dibarium trisilicate was found to be monoclinic with  $a=12.51 \text{ \AA}$ ,  $b=4.69 \text{ \AA}$ ,  $c=6.97 \text{ \AA}$ , and  $\beta=93^\circ 23'$ .

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TABLE 7. *Comparison of optical data for compositions in the system BaO·2SiO<sub>2</sub>-2BaO·3SiO<sub>2</sub>*  
(Indices of refraction by Eskola for continuous solid solution series; indices by Roth and Levin for discrete compounds)

Composition		Compound	Indices of refraction ( $\lambda_D$ , 30° C)							Index of quenched glass (30°)
BaO	SiO <sub>2</sub>		Eskola [1]			Roth and Levin			Sign and 2V	
<i>Mole %</i> 33.33	<i>Mole %</i> 66.67	L-BaO·2SiO <sub>2</sub>	-----	-----	-----	1.596	1.612	1.621	Negative, large	1.608
		H-BaO·2SiO <sub>2</sub>	1.597	1.612	1.621	1.596	1.611	1.619	Negative, 70°	
35.11	64.89	-----	1.597	1.612	1.636	-----	-----	-----	-----	1.625
37.02	62.98	-----	1.612	1.615	1.638	-----	-----	-----	-----	
37.50	62.50	3BaO·5SiO <sub>2</sub>	-----	-----	-----	1.612	1.616	1.636	Positive, 35°	1.629
38.25	61.75	-----	1.616	1.620	1.639	-----	-----	-----	-----	
38.46	61.54	5BaO·8SiO <sub>2</sub>	-----	-----	-----	1.617	1.622	1.638	Positive, 40°	1.635
39.50	60.50	-----	1.619	1.624	1.644	-----	-----	-----	-----	
40.00	60.00	2BaO·3SiO <sub>2</sub>	1.620	1.625	1.645	1.618	1.623	1.643	Positive, 35°	