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[F I F T H S E R I E S .]

ART. XXXI.—*The Silicates of Strontium and Barium*;
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Introduction.

Among the compounds of the alkaline earth metals (calcium, strontium, and barium), the sulphates and carbonates are common as minerals. In the case of the silicates, however, we find those of calcium common, but natural silicates of strontium and barium are few in number, complicated in composition, and of rare occurrence. Considering the existence of isomorphous carbonates, sulphates, and other compounds of these three elements, the non-occurrence of analogous silicates seems striking and suggests experimental investigation to answer the questions: Do strontium and barium under experimental conditions form such compounds as are known in the case of calcium? And, if they do, what are their properties and relations to the calcium silicates?

The calcium silicates which form from dry melts have been studied, but very little is known about the strontium and barium silicates. G. Stein¹ prepared some silicates and determined their melting points as follows: SrSiO_3 , 1287° ; BaSiO_3 , 1368.5° ; Sr_2SiO_4 , 1593° . R. Wallace²

¹ G. Stein, Z. anorg. Chem., 55, 159, 1907.² R. Wallace, Z. anorg. Chem., 63, 1, 1909.

carried out thermal investigations by the cooling curve method on the binary systems of the metasilicates of sodium and lithium with those of strontium and barium. He gives the melting point of SrSiO_3 , 1529° and of BaSiO_3 , 1490° . All his melting diagrams resulted in the type of complete solid solutions with a minimum. P. Lebedew,³ for the system BaSiO_3 - CaSiO_3 , also found a melting curve of the complete solid solution type with the melting point of BaSiO_3 at 1438° and a minimum at about 1000° . Smolensky,⁴ who studied the system BaSiO_3 - BaTiO_3 , found the melting point of BaSiO_3 at 1470° .

All these results were obtained by the cooling-curve method, using carbon crucibles and porcelain tubes to protect the thermo-elements. No quantitative optical or other physical diagnostics for the crystalline phases were given. In the absence of such characteristics, and in view of the poor agreement of the results, the melting diagrams merely based upon cooling curves are subject to large corrections and often entirely erroneous. The melting point determinations are, in fact, all considerably too low.

Very accurate determinations were carried out by Jaeger and Van Klooster,⁵ who found the melting point of SrSiO_3 , $1578 \pm 1^\circ$, and of BaSiO_3 , $1604 \pm 0.5^\circ$. They, also, emphasize the unreliability of the cooling-curve method and illustrate this by experimental evidence. They determined further some physical constants of the compounds named. Their results will be mentioned later.

The entire field of the physical chemistry of the strontium and barium silicates being open, the first task was to investigate the two binary systems SrO-SiO_2 and BaO-SiO_2 . Among the further problems, those regarding the relations of the metasilicates to the well-known wollastonite minerals seemed to me most interesting and were chosen for study. For still further comparison with corresponding calcium compounds I tried to synthesize the strontium and barium compounds analogous to two important lime silicate minerals, diopside and anorthite.

³ P. Lebedew, *Z. anorg. Chem.*, 70, 301, 1911.

⁴ S. Smolensky, *Z. anorg. Chem.*, 73, 293, 1912.

⁵ F. M. Jaeger and H. S. Van Klooster, *Proc. Kon. Akad. Amsterdam*, 6, XVIII, 896, 1915.

Methods of Working.

The mixtures were made up of pure quartz, specially prepared calcium carbonate, barium carbonate "Squibb's reagent" and strontium carbonate from "Baker's analyzed chemicals." These substances were dried at 150°C before weighing, and mixed together, melted if possible, chilled and crushed, then reheated and ground twice more.

The equilibrium relations were ascertained almost exclusively by the quenching method. Heating curves were run in some cases for the purpose of checking the temperature measurements.

The temperatures were determined by potentiometer and a Pt-PtRh thermoelement calibrated against the melting points of diopside and anorthite. The temperatures, for the most part, are not far from the diopside-point, so that the calibration against diopside, together with the temperature limits taken in the quenchings, show the actual degree of accuracy of the work. Therefore those calibrations are stated below.

Diopside, melting point 1391.5° , in the standard scale corresponds to 14230 microvolts.

Date (1921)	Crystals μv	Melt μv	Correction	The systems under investigation
6 April	14100	14150	+ 105	SrO-SiO ₂
28 April	14110	14130	+ 105	
11 May	14120	14130	+ 105	
17 June	14090	14110	+ 130	BaO-SiO ₂ and SrSiO ₃ -CaSiO ₃
26 June ^a	14310	14330	— 90	
30 June	14310	14330	— 90	BaSiO ₃ -CaSiO ₃
5 August	14290	14310	— 70	
22 August	14270	14290	— 50	

^a New thermoelement.

In the determination of the refractive indices I had the advantage of using the improved immersion method as worked out by Merwin.⁶ This method involves an improvement in accuracy as well as in completeness, making it possible to determine at the same time dispersion as well as refractive indices. One determines directly, using a monochromatic illuminator, the wavelengths for which the refractive indices to be measured

⁶ E. Posnjak and H. E. Merwin, The ternary system $\text{Fe}_2\text{O}_3\text{-SO}_2\text{-H}_2\text{O}$, J. Am. Chem. Soc., 44, 1965, 1922.

match those of two or more members in the set of refractive liquids. The dispersions of the whole series of liquids used having been determined and expressed graphically, it now remains simply to locate, on the diagram, the points determined and to read the refractive index for any wave-length desired. The values obtained in favorable substances are dependable in the third decimal place, provided due care is taken for variations in the temperature.

In the present work the indices of refraction are given for four wave-lengths corresponding with the spectral line F($\lambda = 486\mu\mu$), Tl($\lambda = 535\mu\mu$), D($\lambda = 589\mu\mu$) and C($\lambda = 656\mu\mu$). In the actual determinations wave-lengths between 500 and 625 were commonly used, therefore the values for F and C may sometimes have an uncertainty of ± 0.001 or a little more, due to enlargement of the errors in extrapolation.

The System SrO-SiO₂.

The results of a thermal study of this system are given in table I.

TABLE I.

Composition		Temperature °C.	Time minutes	Resulting phases
wt. per cent SrO	SiO ₂			
Liquidus of cristobalite				
40	60	1636	15	Glass
40	60	1600	60	Glass and cristobalite
Eutectic tridymite-SrSiO ₃				
53.82	46.18	1368	30	Glass
53.82	46.18	1361	60	Glass and a little tridymite
53.82	46.18	1356	60	Tridymite, SrO.SiO ₂ , trace of glass
50	50	1363	25	SrO.SiO ₂ and glass
Liquidus of SrO.SiO ₂				
50	50	1430	30	Glass
50	50	1420	60	Glass and SrO.SiO ₂
60	40	1571	60	Glass
60	40	1552	45	Glass and SrO.SiO ₂
Melting point of SrO.SiO ₂				
63.22	36.78 ^a	1584	15	Glass
63.22	36.78	1580	15	SrO.SiO ₂ and glass
63.22	36.78	1575	15	SrO.SiO ₂ only

Eutectic $\text{SrO} \cdot \text{SiO}_2$ - $2\text{SrO} \cdot \text{SiO}_2$				
65	35	1554	15	Glass
65	35	1546	30	Glass and $\text{SrO} \cdot \text{SiO}_2$
65	35	1538	15	$\text{SrO} \cdot \text{SiO}_2$ and $2\text{SrO} \cdot \text{SiO}_2$
67	33	1544	15	$\text{SrO} \cdot \text{SiO}_2$ and $2\text{SrO} \cdot \text{SiO}_2$

Liquidus of $2\text{SrO} \cdot \text{SiO}_2$				
67	33	1617	15	Glass
67	33	1600	15	Glass and $2\text{SrO} \cdot \text{SiO}_2$
72	28	1628	15	Glass and $2\text{SrO} \cdot \text{SiO}_2$
77.46	22.54 ^b	1634	5	Sr_2SiO_4 only

^a = $\text{SrO} \cdot \text{SiO}_2$

^b = $2\text{SrO} \cdot \text{SiO}_2$

The equilibrium diagram (fig. 1) is based on the above results; the melting point of cristobalite has been placed at 1710° , according to the determinations of Ferguson and Merwin,⁷ and the inversion point cristobalite-tridymite at 1470° according to Fenner.⁸

The liquidus curve of the silica minerals has the same general shape as formerly found in all the other binary systems with silica as one component: starting from the eutectic point first a very steep rise a little above 1600° .

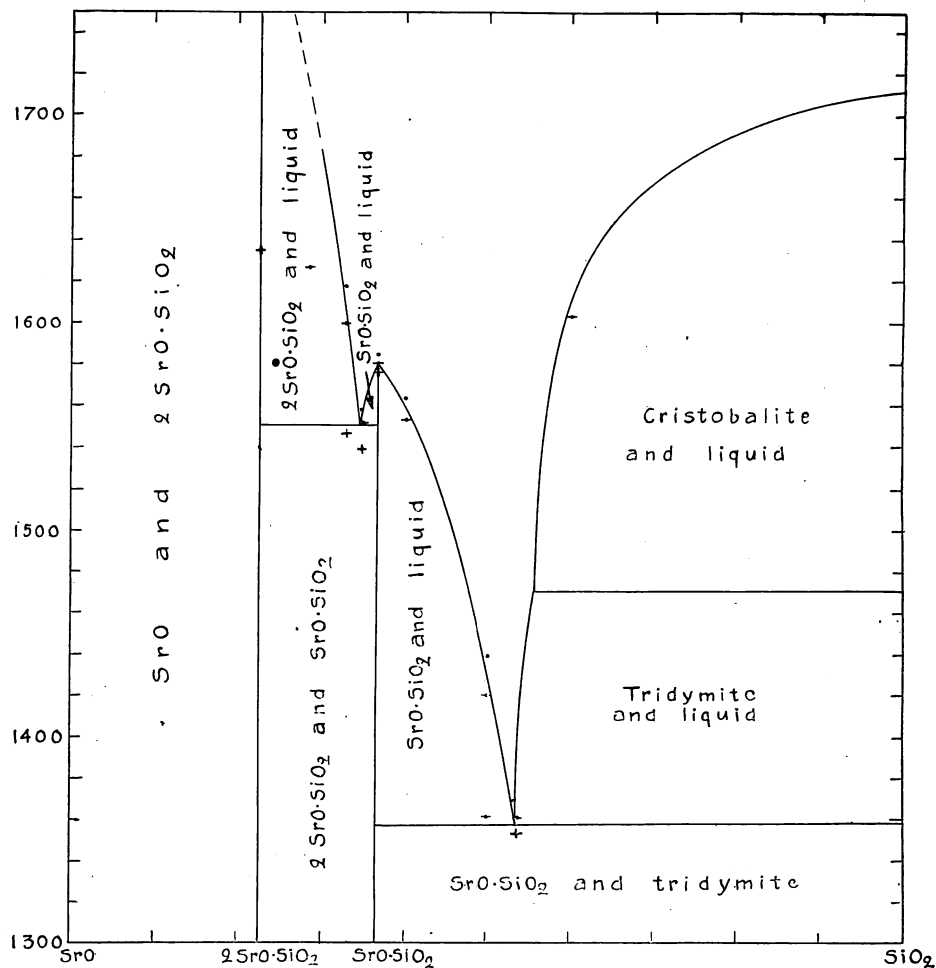
The eutectic tridymite- $\text{SrO} \cdot \text{SiO}_2$.—I prepared incidentally a mixture of 46.18 per cent SrO and 53.82 per cent SiO_2 , corresponding to the proportion $\text{SrO} \cdot 2\text{SiO}_2$, to find out whether there was any disilicate of strontium, analogous to the barium disilicate known formerly. The result was negative, and this happened to be almost exactly the eutectic composition. The tridymite liquidus lying only about five degrees above the solidus, the eutectic composition can be located with a fair degree of accuracy at 46.5 per cent SrO and 53.5 per cent SiO_2 . The temperature is $1358 \pm 4^\circ$.

Strontium metasilicate, $\text{SrO} \cdot \text{SiO}_2$.—Strontium metasilicate was found in only one form which shows a very close resemblance to α - CaSiO_3 , or pseudowollastonite. Its melting point was determined as $1580 \pm 4^\circ$, in agreement with Jaeger and Van Klooster's result, $1578 \pm 1^\circ$. It is apparently of dihexagonal pyramidal symmetry, uniaxial and positive, and its characteristic habit is thick-tabular parallel to (0001). There is a fairly good basal cleavage.

⁷ J. B. Ferguson and H. E. Merwin, this Journal, 46, 417, 1918.

⁸ C. N. Fenner, this Journal, 36, 337, 1913.

FIG. 1.



—Fig. 1.—Temperature-concentration diagram of the binary system SrO-SiO_2 .

The density, at 30° , determined with a pycnometer, is 3.650. This is calculated as real density, compared with water at 4° and making correction for the buoyancy of air. Jaeger and Van Klooster⁹ found $d_4=3.652$ at 25.1° , in good agreement with that found by me which gives $d_4=3.653$.

⁹ Loc. cit.

The refractive indices were determined in granular crystals obtained by cooling a pure melt. They were found to be:

	α	γ
F	1.606	1.646
Tl	1.602	1.641
D	1.599	1.637
C	1.596	1.634

These values were repeatedly checked and are correct in the third decimal place. Jaeger and Van Klooster give less exact values: $n_1 = 1.590 \pm 0.003$, and $n_2 = 1.620 \pm 0.003$.

α -CaO.SiO₂ has¹⁰ $\alpha(D) = 1.610$; $\beta(D) = 1.611$; $\gamma(D) = 1.654$.

In the apparent uniaxial positive character and hexagonal tabular habit the strontium metasilicate is similar to α -CaO.SiO₂ and, as stated later, they form a continuous series of solid solutions. It would seem necessary, therefore, that they should be closely isomorphous. Now Wright¹¹ has proved α -CaO.SiO₂ to be really monoclinic, showing, in plates perpendicular to the optic normal, a polysynthetic twinning along the basal plane. The optic axial angle, though small, is not quite 0°.

Much care was taken to find out whether the strontium metasilicate shows a similar deviation from hexagonal symmetry, but no such phenomena were noticed, although apparent twinning was observed in the mix crystals of SrO.SiO₂ and CaO.SiO₂ (cf. below).

Euhedral crystals of SrO.SiO₂ were obtained from a strontium chloride melt with an excess of silica (cf. below). They are all thick tabular and apparently dihexagonal pyramidal (hemimorphic), one end being terminated only by the basal plane (fig. 2), sometimes with additional narrow pyramid faces, while the other end regularly shows well developed pyramids, usually combinations of two, three, or four simple forms. The pyramid faces are striated parallel to the edge with the basal plane. The greater part of the crystals are twinned on the base (fig. 3).

As the crystals are perfectly hexagonal in aspect and

¹⁰ G. A. Rankin and F. E. Wright: The ternary system CaO-Al₂O₃-SiO₂, this Journal, 39, 1, 1915.

¹¹ E. T. Allen, W. P. White, and F. E. Wright: On wollastonite and pseudowollastonite,—polymorphic forms of calcium metasilicate, this Journal, 21, 89, 1906.

the measurements failed to reveal any deviation from hexagonal symmetry, I shall provisionally describe them as hexagonal, although the isomorphism with the calcium metasilicate makes it probable that the strontium metasilicate is pseudohexagonal and really monoclinic, in that case belonging to the domatic, or monoclinic hemihedral class.

FIG. 2.

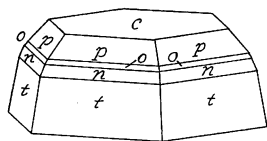


FIG. 3.

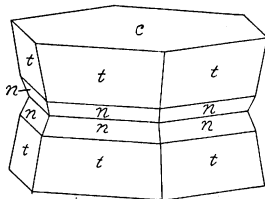
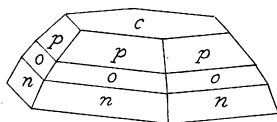


FIG. 4.

FIGS. 2, 3, 4.—Crystals of SrO.SiO_2 .

In examining these crystals with a binocular microscope one was found that was larger (about 0.5 mm in diameter) and better than the rest, but it was incomplete, having only faces in two pyramidal zones developed. These zones were identical, each combined of three different pyramids, $p(10\bar{1}1)$, $o(4045)$ and $n(20\bar{2}1)$ (fig. 4). While searching for evidence of monoclinic symmetry I measured a number of crystals, but unfortunately they were too imperfect to prove anything positively. Often the pyramidal faces were quite curved in their zones so that the signals appeared as lines instead of points. All the forms observed in the best crystals were, however, also identified in other crystals, and some of them at the same time in three pyramidal zones. A further form $t(50\bar{5}1)$ was found to be very common.

The following data are based on the best crystal, except for the last named form t .

The crystals separating from silicate melts and embedded in glass usually were bipyramidal in habit, with large basal planes, and thinner than those obtained from the chloride melt.

In summarizing the evidence regarding the crystal form of SrO.SiO_2 , we may state that, from its solid solubility and apparent isomorphism with $\alpha\text{-CaO.SiO}_2$, it might be expected to be monoclinic, but actually the crystals agree so closely with the dihexagonal pyramidal

	ρ			ϕ	
	Observed		Calculated	Observed	Calculated
	Limits	Average			
<i>c</i> (0001)	— —	— —	0° 0'	— —	— —
<i>p</i> (1011)	49° 10' — 49° 55'	49° 32'	49° 32'	30° 10'	30° —
<i>o</i> (4915)	55° 50' — 56° 2'	55° 56'	55° 41'	— —	— —
<i>n</i> (2021)	66° 32' — 66° 55'	66° 44'	66° 55'	— —	— —
<i>t</i> (5051)	78° 20' — 80° 50'	79° 17'	80° 20'	— —	— —

Axial ratio $a : c = 0.98$

symmetry that, judging only from the characters of the rather poor crystals available, it should belong to this class.

Another question that arose from the similarity to $\alpha\text{-CaO.SiO}_2$ was whether SrO.SiO_2 would also appear in more than one form. Several experiments were made to settle this question.

SrO.SiO_2 -glass was held one hour at 1020° . The result was a crystallized mass showing radiating scaly crystals, uniaxial, positive, $\omega = 1.600 \pm 0.003$, $\epsilon = 1.640 \pm 0.003$. It is consequently identical with the crystals separating from the melt.

The same result was achieved when the glass was held 4 hours at 950° .

SrO.SiO_2 was melted together with SrCl_2 in a Fletcher furnace and allowed to cool very slowly. After dissolving the chloride in water to which finally was added a little HCl to decompose the chloro-silicate that had formed, the result was the same form of SrO.SiO_2 as before.

The last-named experiment was modified so that the $\text{SrO.SiO}_2\text{-SrCl}_2$ -melt was left in the platinum resistance furnace over night at about 1000° . The product was not metasilicate at all, but strontium orthosilicate, which was identified by its refringence and characteristic twinning.

Now, imitating the method that Allen and White¹² found most effective in changing pseudowollastonite into wollastonite, I prepared strontium vanadate, $\text{Sr(VO}_3)_2$, and melted one gram of this with two grams of SrO.SiO_2 . The mixture was held over night at about 900° . After washing away the vanadate, the mass consisted of the

¹² E. T. Allen and W. P. White, this Journal, 21, 89, 1906.

same form of $\text{SrO} \cdot \text{SiO}_2$, as rounded crystal grains and with no euhedral forms.

To prevent the formation of orthosilicate in the strontium chloride melt I finally heated $\text{SrO} \cdot \text{SiO}_2$ with SrCl_2 and a considerable excess of silica, added in the form of coarse quartz grains, which dissolved rapidly in the melt above a gas burner. This mixture, held over night at about 1000° , gave well-developed crystals of the same form of $\text{SrO} \cdot \text{SiO}_2$. The identity, as in all the other cases, was ascertained by determination of the refractive indices.

Thus all the experiments failed to show any other form of $\text{SrO} \cdot \text{SiO}_2$ than the one similar to the pseudowollastonite.¹³

The eutectic $\text{SrO} \cdot \text{SiO}_2$ - $2\text{SrO} \cdot \text{SiO}_2$ was located at 65.5 per cent SrO, as is apparent from the diagram (fig. 1). The steep slope of the liquidus curves at both sides is remarkable. While in the 65 per cent SrO mixture the primary phase is $\text{SrO} \cdot \text{SiO}_2$, it is $2\text{SrO} \cdot \text{SiO}_2$ in the 67 per cent SrO mixture, and the liquidus has risen 60° above the eutectic temperature, 1545° .

The existence of $3\text{SrO} \cdot 2\text{SiO}_2$ not proved.—The primary phase in all the mixtures between the eutectic at 65.5 per cent SrO and $2\text{SrO} \cdot \text{SiO}_2$ is strontium orthosilicate. The following experiments were carried out in order to establish whether there might be formed the compound $3\text{SrO} \cdot 2\text{SiO}_2$, analogous to $3\text{CaO} \cdot 2\text{SiO}_2$, known from the studies on the calcium silicates.

Strontium carbonate and quartz powder in the proportion required to form $3\text{SrO} \cdot 2\text{SiO}_2$ (72 per cent SrO), well mixed together, were held 2 hours at 1475° and quenched. The product consisted of $\text{SrO} \cdot \text{SiO}_2$ and $2\text{SrO} \cdot \text{SiO}_2$. Another time the charge was allowed to cool slowly. The result was the same.

The same mixture was heated 16 hours at 1150° . It was now so fine-grained and poorly individualized, that it could not be decided whether there were one or two phases present. Neither $\text{SrO} \cdot \text{SiO}_2$ nor $2\text{SrO} \cdot \text{SiO}_2$ could be identified.

¹³ Jaeger and Van Klooster (op. cit., p. 903) heated 0.5 g. of pure $\text{SrO} \cdot \text{SiO}_2$ with 1 or 2 g. of sodium tungstate at 860° during 72 hours and always obtained the same form as by direct crystallization from a melt, whether they had started with crystals or with glass.

Strontium orthosilicate, $2\text{SrO}.\text{SiO}_2$.—The melting point of $2\text{SrO}.\text{SiO}_2$ is far above the range of the platinum resistance furnace.

In a search for several polymorphic forms of this compound I heated a preparation of crystalline $2\text{SrO}.\text{SiO}_2$ at different temperatures: 5 minutes at 1634° , 2 hours at 1415° , 1300° , and 990° respectively. The result was always the same form, well characterized by its refringence and twinning. It was also obtained from a SrCl_2 melt at about 1000° (cf. above, p. 339). Nor did the substance change when allowed to cool very slowly. The phenomenon of "dusting" in the case of $2\text{CaO}.\text{SiO}_2$ apparently has no analog here.

For the determination of the optical properties the preparation quenched from 1634° was used, with the following results.

	α	β	γ
F	1.740	1.744	1.766
Tl	1.7325	1.737	1.760
D	1.7275	1.732	1.756
C	1.722	1.727	1.752

The crystals are optically positive with $2E = 58^\circ$ approximately, or $2V = 32^\circ 30'$.

In many of the crystals a twinning was observed, often repeated (fig. 5). In sections normal to γ , the acute bisectrix, the trace of the axial plane forms, with the composition planes of the twinning lamellæ, angles of 17° . Thus, if the crystal system is monoclinic, the plane of the optic axes is normal to the plane of symmetry.

The repeatedly twinned crystals, in their outlines, often display the habit of orthorhombic crystals, and when the lamellæ are very narrow they have apparent straight extinction.

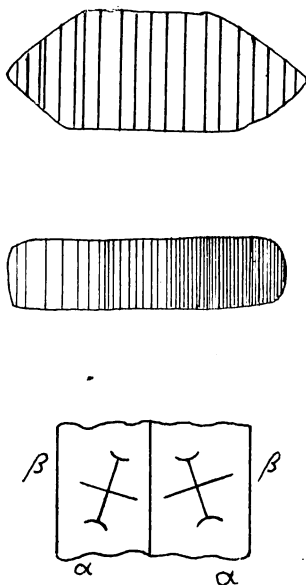
¹⁴ Free strontium oxide attacks platinum on heating. Every mixture does so as soon as it contains an excess, however small, of SrO over $2\text{SrO}.\text{SiO}_2$, while the more acid mixtures may be heated in platinum crucibles without any danger. The phenomenon appears as a blackening of the surface of the platinum and of the charge. This black substance is soluble in HCl , forming chloroplatinic acid.

A probable explanation is that the strontium oxide dissociates at high temperatures, either into metallic strontium or into a strontium suboxide which forms an alloy with platinum. This may be connected with the fact that the strontium oxide is somewhat volatile.

Both the dissociation and the volatilization are, however, very slight at the temperatures of the platinum resistance furnace. 0.300 g. SrO , wrapped in platinum foil and held 4 hours at 1580° , lost only 0.0017 g. in weight.

Strontium oxide, SrO^{14} .—All the mixtures which contained more SrO than $2\text{SrO} \cdot \text{SiO}_2$, resulted in two phases, $2\text{SrO} \cdot \text{SiO}_2$ and SrO , when heated at high temperatures. In these mixtures the strontium oxide could always be identified from its isotropic character and high index of refraction.

FIG. 5.

Fig. 5.—Crystals of $2\text{SrO} \cdot \text{SiO}_2$.

Pure SrO was prepared in two ways, from strontium carbonate and from strontium nitrate. In the first case it forms minute rounded, though clear grains. When these were held 4 hours at 1580° they reacted slowly with water and even with HCl . From nitrate the oxide may be obtained as large clear crystals showing a perfect cubic cleavage.¹⁵

The determination of the index of refraction was very difficult, because the oxide instantly reacts with the high refractive liquids containing iodine. It was found to be somewhat higher than 1.86 for all the colors and may be very roughly estimated at 1.87.

¹⁵ See also G. Brügemann, *Z. anorg. Chem.*, **10**, 415, 1895.

The specific gravity has been determined by Brügelmann (loc. cit.) as 4.750.

According to H. Moissan,¹⁶ strontium oxide melts more easily than calcium oxide, but nothing more is known about its melting temperature.

Wyckoff¹⁷ has determined, by Debye and Scherrer's method, the crystal structures of CaO, SrO, BaO and mixtures of CaO with SrO and BaO, respectively, in samples prepared by me. His results have interest for us in so far as they prove SrO to be perfectly isomorphous with and to form a series of solid solutions with CaO.

The System BaO-SiO₂.

The quenching experiments pertaining to the system BaO.SiO₂ are described in table II.

TABLE II.

Composition wt. per cent		Compounds		Temper- ature °C	Time minutes	Resulting phases
Oxides BaO	SiO ₂	BaO. 2SiO ₂	2BaO. 3SiO ₂			
Liquidus of tridymite						
40	60			1551	90	Glass and tridymite
45	55			1472	120	Glass
45	55			1447	90	Glass and tridymite
Eutectic tridymite-BaO.2SiO ₂						
45	55			1372	135	Tridymite and BaO.2SiO ₂
47.5	52.5			1390	120	Glass
47.5	52.5			1377	60	Glass and tridymite
47.5	52.5			1373	120	BaO.2SiO ₂ and tridymite
50	50			1398	120	Glass
50	50			1385	60	Crystals and glass
50	50			1369	120	Tridymite and BaO.2SiO ₂
Melting point of BaO.2SiO ₂						
55.98	44.02 ^a			1425	90	Glass
55.98	44.02			1421	30	Glass
55.98	44.02			1419	60	BaO.2SiO ₂ (with some glass)
Liquidus of the solid solutions BaO.2SiO ₂ -2BaO.3SiO ₂						
58	42	71	29	1441	60	Glass
58	42	71	29	1435	60	Glass
58	42	71	29	1432	60	Glass and mix crystals
60	40	42	58	1448	60	Glass
60	40	42	58	1443	60	Glass and mix crystals
61.25	38.75	23.9	76.1	1451	60	Glass
61.25	38.75	23.9	76.1	1448	60	Glass and mix crystals

¹⁶ H. Moissan, Ann. Chem. Phys., (7) 4, 136, 1895.

¹⁷ Ralph W. G. Wyckoff, unpublished data.

Solidus of the solid solutions $\text{BaO} \cdot 2\text{SiO}_2$ – $2\text{BaO} \cdot 3\text{SiO}_2$						
58	42	71	29	1418	60	Crystals
58	42	71	29	1424	60	Mix crystals with little glass
60	40	42	58	1435	60	Mix crystals and glass
60	40	42	58	1431	60	Mix crystals
61.25	38.75	23.9	76.1	1443	60	Mix crystals and glass
61.25	38.75	23.9	76.1	1440	60	Mix crystals and glass
61.25	38.75	23.9	76.1	1438	60	Mix crystals
Melting point of $2\text{BaO} \cdot 3\text{SiO}_2$.						
62.90	37.10 ^b			1451	60	Glass
62.90	37.10			1451	30	Glass
62.90	37.10			1448	30	Glass and $2\text{BaO} \cdot 3\text{SiO}_2$
Eutectic $2\text{BaO} \cdot 3\text{SiO}_2$ – $\text{BaO} \cdot \text{SiO}_2$						
65	35			1439	15	Glass
						$\text{BaO} \cdot \text{SiO}_2$ and $2\text{BaO} \cdot 3\text{SiO}_2$
65	35			1435	30	with a little glass.
65	35			1431	30	$\text{BaO} \cdot \text{SiO}_2$ and $2\text{BaO} \cdot 3\text{SiO}_2$.
Eutectic $\text{BaO} \cdot \text{SiO}_2$ – $2\text{BaO} \cdot \text{SiO}_2$						
75	25			1556	15	$2\text{BaO} \cdot \text{SiO}_2$ and glass.
75	25			1546	15	$2\text{BaO} \cdot \text{SiO}_2$ and $\text{BaO} \cdot \text{SiO}_2$
$a = \text{BaO} \cdot 2\text{SiO}_2$ $b = 2\text{BaO} \cdot 3\text{SiO}_2$						

From these determinations results the equilibrium diagram fig. 6. A part of it is given on a larger scale in fig. 7.

The liquidus curves of cristobalite and tridymite in this binary system were, by means of a few quenchings, shown to have the same general character as in the system $\text{SrO} \cdot \text{SiO}_2$, and were not investigated any more closely.

The eutectic tridymite– $\text{BaO} \cdot 2\text{SiO}_2$.—The mixture containing 47.5 per cent BaO was found to be very close to the eutectic composition, and on the tridymite side of it. The eutectic composition was placed at 47 per cent BaO , 53 per cent SiO_2 and the temperature at 1374° .

Barium disilicate, $\text{BaO} \cdot 2\text{SiO}_2$, has previously been studied by N. L. Bowen.¹⁸ Crystals of this composition were found in optical glass of the variety known as “barium crown.” They had the shape of platy elongated hexagons (fig. 8a), about 3 mm long, 2 mm wide,

¹⁸ N. L. Bowen: Crystals of barium disilicate in optical glass. *J. Wash. Acad. Sci.*, 8, 265, 1918. Cf. also N. L. Bowen: Devitrification of glass, *J. Am. Ceram. Soc.*, 2, 261, 1919.

FIG. 6.

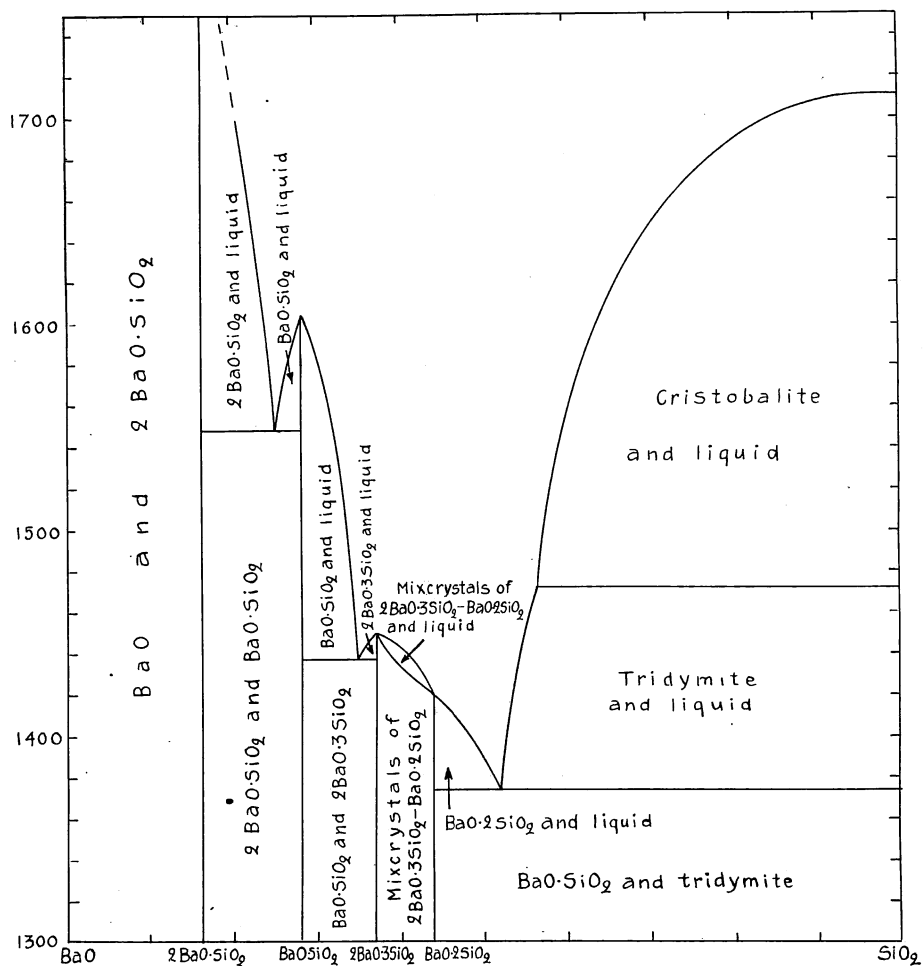


FIG. 6.—Temperature-concentration diagram of the binary system BaO-SiO₂.

and only 0.03 mm thick. The terminal angles were approximately 100° and the lateral angles 130°. The crystals are orthorhombic, the negative acute bisectrix being parallel to the elongation, and the plane of the optic axes parallel to the platy development, which is a good cleavage. $2V_a = 70^\circ$ approximately $\gamma = 1.613$; $a = 1.595$.

In pure crystals obtained by cooling a melt of the composition $\text{BaO} \cdot 2\text{SiO}_2$ were found: $\gamma = 1.617$ and $\alpha = 1.598$. The melting point was determined by the heating curve method at 1426°C . Bowen suggests that the slightly lower values of the indices of refraction of the crystals in the optical glass may represent a real difference and that when formed in the glass they take a small amount of alkaline disilicates into solid solution.

FIG. 7.

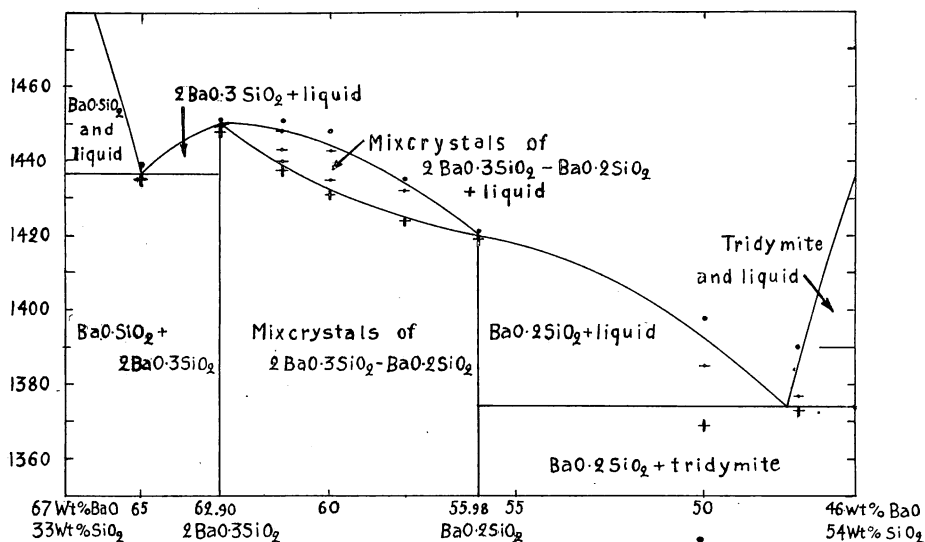


FIG. 7.—Part of the binary system $\text{BaO}-\text{SiO}_2$ showing the melting of the mix crystals of barium disilicate and dibarium trisilicate.

I prepared crystals of $\text{BaO} \cdot 2\text{SiO}_2$ from a BaCl_2 -melt, and also obtained well-formed crystals embedded in Ba-silicate glass from a mixture containing 50 per cent BaO , held at 1385° . In both cases the crystals were bounded only by the three orthorhombic pinacoids, were very much elongated in the direction of a and had almost square cross sections (fig. 8*b* and 8*c*). There are notable cleavages in all the pinacoidal directions, but by far the most perfect is the one parallel to $a\beta$, so that when crystalline masses of this substance, as for example, that obtained by cooling of the pure melt, are ground, there are formed almost exclusively scaly cleavage splinters normal to γ .

FIG. 8.
a. b. c.

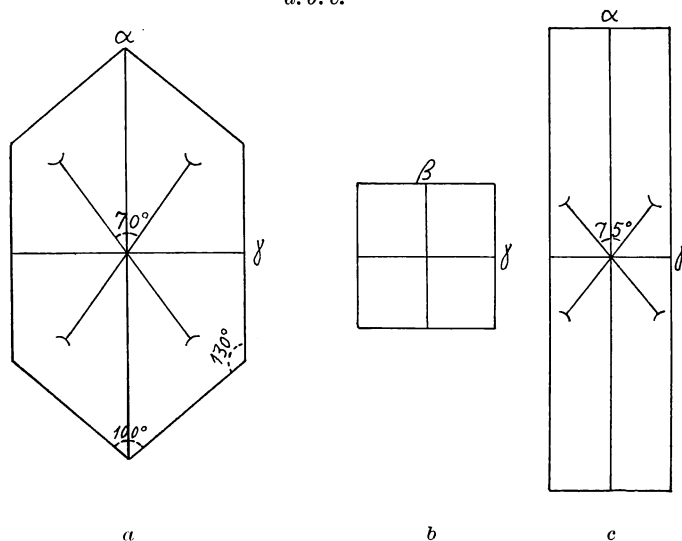


FIG. 8.—Optical orientation in crystals of barium disilicate: α = crystals in optical glass after N. L. Bowen; b and c = crystals from BaCl_2 -flux, and as formed in barium silicate melt.

Thus these crystals are, in their habit, considerably different from those in the barium crown glass, as described by Bowen. In other ways my crystals agree well with the characteristics given by Bowen.

The indices of refraction are as follows:

$$\alpha(D) = 1.597; \beta(D) = 1.612; \gamma(D) = 1.621$$

As appears from these values, also confirmed by direct observation, the optical character is negative and the axial angle approximately 75° . A calculation from the indices of refraction gives $2V = 74^\circ 45'$.

The density, determined with the pycnometer, was found to be 3.73.

The melting point of pure $\text{BaO} \cdot 2\text{SiO}_2$, according to my measurements, is $1420 \pm 4^\circ$.

There was no indication that the barium disilicate takes silica in solid solution; the crystals obtained from the mixture containing 50 per cent SiO_2 showed exactly the same optical properties as those from the pure melt. On the other hand it forms a remarkable solid solution series with another less acid silicate.

Solid solutions of barium disilicate, $\text{BaO} \cdot 2\text{SiO}_2$ and dibarium trisilicate, $2\text{BaO} \cdot 3\text{SiO}_2$.—My first observations pointing to the existence of solid solutions in the system $\text{BaO}-\text{SiO}_2$ were made with the mixture containing 60 per cent BaO . It was found to give only one kind of crystals very similar but not identical with those of $\text{BaO} \cdot 2\text{SiO}_2$. Furthermore I found that the crystals, when formed in a solid state (below the solidus) had lower refractive indices than they had when formed in the presence of a liquid phase (above the solidus). These observations made it probable that there exists a solid solution series without a maximum or minimum. In the course of the work this proved to be the case, the other end member of the series being the compound $2\text{BaO} \cdot 3\text{SiO}_2$.

The gradual change in the physical properties will appear from the following description.

Mixture 29 per cent $2\text{BaO} \cdot 3\text{SiO}_2$ -71 per cent $\text{BaO} \cdot 2\text{SiO}_2$ gives crystals which agree fairly well with the pure disilicate. Among the three pinacoidal cleavages the one parallel to $\alpha\beta$ is most perfect. The optical character, however, is distinctly positive, with $2V = 70^\circ$ approximately.

Density = 3.80.

The crystals of the composition 58 per cent $2\text{BaO} \cdot 3\text{SiO}_2$ -42 per cent $\text{BaO} \cdot 2\text{SiO}_2$ show a different habit, being usually somewhat elongated along β . The cleavage parallel to $\beta\gamma$ is most perfect. Cleavage along $\alpha\beta$ also is good and that parallel to $\alpha\gamma$ distinct. Many crystals are composition twins along a prismatic face in the zone of α . The angle between β and the twinning plane is about 30° , or between β in both individuals about 60° . The optical character is positive and the axial angle quite small. I determined $2E = 44^\circ$, or $2V = 27^\circ$.

Crystals of the composition 76.1 $2\text{BaO} \cdot 3\text{SiO}_2$ -33.9 $\text{BaO} \cdot 2\text{SiO}_2$ are equant grains, not elongated. Cleavage along $\beta\gamma$ is best, next to it that along $\alpha\beta$, while that parallel to $\alpha\gamma$ was hardly observed at all. The same prismatic twinning with the twinning plane parallel to α and inclined 30° to β was observed frequently, and is sometimes polysynthetic. The axial character is positive and the axial angle larger than in the former. I measured $2E = 56^\circ$ or $2V = 33^\circ 30'$.

The mix crystals containing 94.2 per cent $2\text{BaO} \cdot 3\text{SiO}_2$ are in all their characters closely similar to the former ones.

The variation of the refractive indices in this solid solution series appears from table III and from fig. 9.

As may be seen from fig. 9, the indices of refraction, in the series of crystals between $\text{BaO} \cdot 2\text{SiO}_2$ and 2BaO .

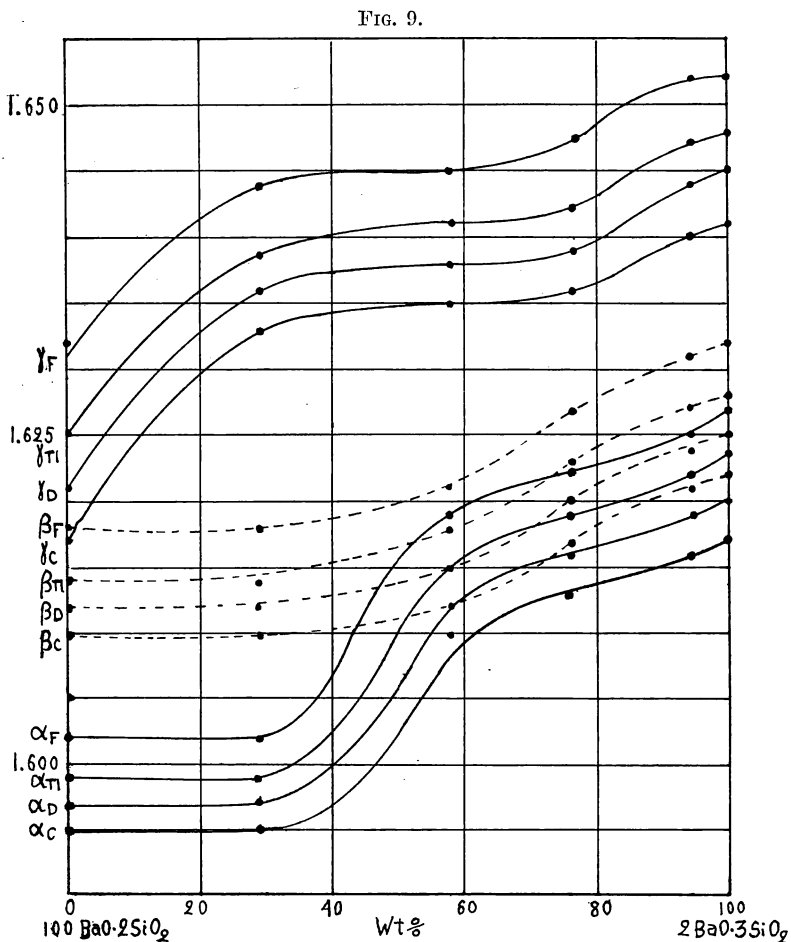


FIG. 9.—Variation of the indices of refraction in the series of mix crystals of barium disilicate and dibarium trisilicate.

3SiO_2 , change gradually along with the composition, and all of them increase towards the latter end member, but their intermediate relations and hence the optic axial angles have rather complicated variations.

TABLE III.

Wt. % $2\text{BaO} \cdot 3\text{SiO}_2$	0	29	58	76.1	94.2	100
Wt. % $\text{BaO} \cdot 2\text{SiO}_2$	100	71	42	23.9	5.8	0
α (F)	1.602	1.602	1.619	1.622	1.625	1.627
α (Tl)	1.599	1.599	1.615	1.619	1.622	1.623
α (D)	1.597	1.597	1.612	1.616	1.619	1.620
α (C)	1.595	1.595	1.610	1.613	1.616	1.617
β (F)	1.617	1.618	1.621	1.627	1.631	1.632
β (Tl)	1.614	1.614	1.618	1.623	1.627	1.628
β (D)	1.612	1.612	1.615	1.620	1.624	1.625
β (C)	1.610	1.610	1.612	1.617	1.621	1.622
γ (F)	1.632	1.644	1.645	1.647	1.652	1.652
γ (Tl)	1.625	1.639	1.641	1.642	1.647	1.648
γ (D)	1.621	1.636	1.638	1.639	1.644	1.645
γ (C)	1.618	1.633	1.635	1.636	1.640	1.641
Density ^a	3.73	3.80				3.93

^a The determinations of density in this series were made on only 0.5 g. of substance and are therefore less accurate than in the other cases.

It might seem probable, from the diagram, that α and β should exchange rôles at about 65 per cent $2\text{BaO} \cdot 3\text{SiO}_2$. Drawn thus, the curves for β would be nearly straight lines. I have not, however, drawn the curves across each other because it was found that the twinning along a prismatic face occurs in the same relation to the three main optical directions, in the two mixtures containing 58 and 76 per cent $2\text{BaO} \cdot 3\text{SiO}_2$. This indicates that the indices α and β have not exchanged rôles.

Dibarium trisilicate, $2\text{BaO} \cdot 3\text{SiO}_2$.—This pure compound was observed only in the form of a granular mass and I did not see any crystalline forms. It does not seem to have any disposition for prismatic or scaly development, the grains being rounded and equant. The only cleavage that appears perfect is that along $\beta\gamma$ while the two other pinacoidal cleavages are poorly developed.

The twinning and composition plane in the zone of α and inclined 30° from β forms polysynthetic lamellæ. In many cases just a few such lamellæ occur and they are so narrow that they appear as what is often called parting planes.

The indices of refraction (cf. table 3) are as follows:

$$\alpha(D) = 1.620; \beta(D) = 1.625; \gamma(D) = 1.645.$$

The optical character is positive and the axial angle is of about the same size as in diopside, or $2V = 58^\circ$. A

calculation from the indices of refraction gives $2V = 53^{\circ}30'$. The density was found to be 3.93.

In summary, it appears that the two silicates $\text{BaO} \cdot 2\text{SiO}_2$ and $2\text{BaO} \cdot 3\text{SiO}_2$ are very perfectly isomorphous, have orthorhombic symmetry and pinacoidal cleavages. Their relations bear some resemblance to the plagioclase feldspar series. The melting diagrams of the solid solution series are quite similar, cleavage variations are similar. The variation of the refractive indices and optic axial angles is irregular in the plagioclases, though in a smaller degree than we have found here.

Very rarely do two compounds of the same element so different in chemical constitution form so perfect an isomorphous series.

Eutectic $2\text{BaO} \cdot 3\text{SiO}_2$ - $\text{BaO} \cdot \text{SiO}_2$.—The mixture of 60 per cent BaO and 40 per cent silica was found to have very exactly the eutectic composition between the barium metasilicate and the dibarium trisilicate, as appears from the fact that a melt of this composition gives the two crystalline phases simultaneously.

Barium metasilicate, $\text{BaO} \cdot \text{SiO}_2$.—In the BaO - SiO_2 mixtures in which $\text{BaO} \cdot \text{SiO}_2$ is a primary phase, this compound was found in the form of rounded globules or short rods with rounded ends. The latter show a negative elongation and parallel extinction. In glasses composed of mixtures of barium and calcium silicates (in the system $\text{CaO} \cdot \text{SiO}_2$ - $\text{BaO} \cdot \text{SiO}_2$) it was frequently observed as small crystallites looking like short needles sharpened on both ends. These always show a parallel extinction and negative elongation. There is a well developed cleavage parallel to $a\beta$. Grains placed parallel to this plane show the axial figures, with $2E = 50^{\circ}$ approximately, or $2V = 29^{\circ}$. Dispersion of the optic axes is strong: $\rho > \nu$. Birefringence is very weak. Grains parallel to $\beta\gamma$, showing the trace of the good cleavage along $a\beta$, display abnormal blue interference colors. The indices of refraction were determined as follows:

	α	β	γ
F	1.682	1.684	1.688
Tl	1.677	1.678	1.682
D	1.673	1.674	1.678
C	1.669	1.670	1.673

The density at 4° was determined to be 4.399.

The melting point of $\text{BaO} \cdot \text{SiO}_2$ is, according to Jaeger and Van Klooster, $1604 \pm 0.5^\circ$.

To find out whether the barium metasilicate could be inverted into some other form I heated a sample of the crystallized compound, first alone and a second time with one-fifth of its weight $\text{Ba}(\text{VO}_3)_2$, over night at about 1100° . No change took place.¹⁹

Eutectic $\text{BaO} \cdot \text{SiO}_2$ - $2\text{BaO} \cdot \text{SiO}_2$.—A mixture of these compounds, containing 75 per cent BaO , gave at 1546° crystals of both kinds, but at 1556° only crystals of $2\text{BaO} \cdot \text{SiO}_2$ and glass. From this it may be concluded that there is a eutectic at about 74.5 per cent BaO with a melting point of $1551 \pm 6^\circ$.

No other compounds except the two named above occur in this part of the system.

Barium orthosilicate, $2\text{BaO} \cdot \text{SiO}_2$.—Barium orthosilicate appears as a granular mass of rounded grains and does not show any cleavages or twinning. The melting point is higher than that of platinum.

$$\alpha(\text{D}) = 1.810 \pm 0.005; \gamma(\text{D}) = 1.830 \pm 0.005.$$

Barium oxide, BaO .—Mixtures of barium orthosilicate and barium oxide were not studied more closely. The fact that all the mixtures containing an excess of BaO over the orthosilicate ratio attack platinum, seems to prove that they contain free BaO .²⁰

Coarsely crystalline barium oxide was prepared from barium nitrate by heating slowly in a graphite crucible. It was obtained in clear translucent crystals showing cubic cleavage.

The refractive index is very high, but difficult to determine; the substance absorbs moisture from the air almost immediately when exposed and also attacks the high-refractive media (in this case mixtures of sulphur and selenium). I found (in red light):

$$n = 2.16 \pm 0.05.$$

Brügelmann has determined the specific gravity of barium oxide as 5.722.

¹⁹ Jaeger and Van Klooster (loc. cit.) were not more successful in their attempt to effect a change by heating 0.5 g. barium metasilicate with 1 g. sodium tungstate at 860° for 72 hours.

²⁰ Barium oxide attacks the platinum in the same way as strontium oxide, but still more strongly.

The System $\text{CaO}.\text{SiO}_2\text{--SrO}.\text{SiO}_2$

The quenches made to establish the melting diagram of mixtures of the metasilicates of calcium and strontium are recorded in table IV.

TABLE IV.

Composition wt. per cent			Silicates		Temperature °C	Time minutes	Resulting phases
Oxides			CaO. SiO ₂	SrO. SiO ₂			
CaO	SrO	SiO ₂					
36.13	15.81	48.06	75	25	1495	15	Glass
36.13	15.81	48.06	75	25	1485	15	Mix crystals
30.11	23.71	46.18	62.5	37.5	1482	15	Mix crystals and glass
30.11	23.71	46.18	62.5	37.5	1474	15	Mix crystals
24.09	31.61	44.30	50	50	1482	15	Glass
24.09	31.61	44.30	50	50	1478	15	Glass and mix crystals
24.09	31.61	44.30	50	50	1474	15	Mix crystals
21.08	35.56	43.36	43.75	56.25	1477	15	Glass
21.08	35.56	43.36	43.75	56.25	1472	15	Mix crystals
12.05	47.41	40.54	25	75	1511	15	Glass
12.05	47.41	40.54	25	75	1507	15	Glass and mix crystals
12.05	47.41	40.54	25	75	1500	15	Mix crystals and glass
12.05	47.41	40.54	25	75	1496	15	Mix crystals

As these data, together with the optical study of the mix crystals obtained, seemed fully to establish the general character of the melting diagram (fig. 10), it was considered unnecessary to determine the curve in more

FIG. 10.

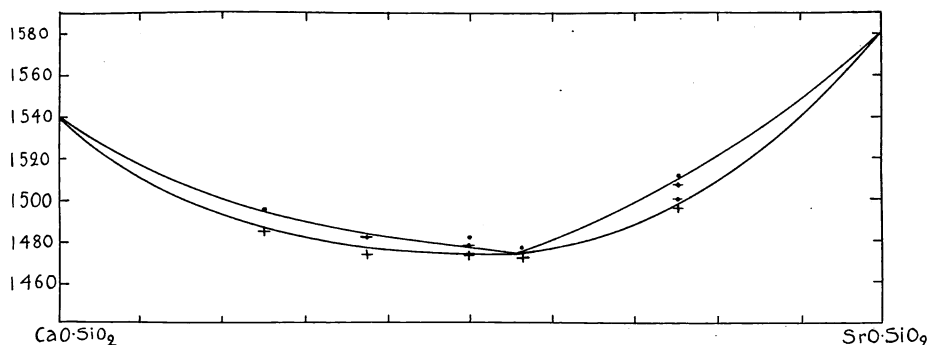


FIG. 10.—Temperature-concentration diagram of the binary system $\text{CaO}.\text{SiO}_2\text{--SrO}.\text{SiO}_2$ showing a complete series of mix crystals with a minimum.

detail. Assuming as the melting point²¹ of $\alpha\text{-CaO}.\text{SiO}_2$, 1540° , and of $\text{SrO}.\text{SiO}_2$, 1578° (cf. above, p. 335), we get the diagram reproduced in fig. 10.

²¹ G. A. Rankin and F. E. Wright, this Journal (4) 39, 1, 1915.

The minimum melting temperature in this series was found to be $1474 \pm 3^\circ$ at the composition 44 per cent CaO.SiO_2 -56 per cent SrO.SiO_2 .

The mix crystals were found to be crystallographically very like α - CaO.SiO_2 . Considerable care was taken to find out whether they show that twinning on the base which, in the case of pseudowollastonite, indicates monoclinic symmetry.

In α - CaO.SiO_2 I found frequently polysynthetic twinning along the basal plane, as described by Wright (loc. cit.). In mix crystals with 12.5 per cent SrO.SiO_2 the twinning was no less clear; in one case I measured an extinction angle of 3° . In the mixture with 25 per cent SrO.SiO_2 twinning was clearly observed, while, in mixtures with 37.5 per cent, 56.25 per cent and 62.5 per cent SrO the extinction angles were apparently so small that the twinning lamellæ, though occasionally positively identified, always appeared extremely faint. In a preparation with 75 per cent SrO.SiO_2 the occurrence of faint twinning along the base was still clearly observed. In the pure SrO.SiO_2 I did not succeed in finding definite twinning appearing as oblique extinction, in spite of much search.

In summary, therefore, it may be stated that all the crystals containing calcium and strontium metasilicates in solid solutions are pseudohexagonal and really monoclinic. In the pure strontium metasilicate, although it may belong to the same class of symmetry as the mix crystals, no deviation from hexagonal symmetry was observed (cf. p. 337).

The indices of refraction for the solid solution series were determined with the following results.

TABLE V.

Wt. % CaO.SiO_2	100	75	50	43.75	25	0
Wt. % SrO.SiO_2	0	25	50	56.25	75	100
α (F)	1.618	1.617	1.614	1.612	1.609	1.606
α (Tl)	1.614	1.612	1.609	1.608	1.605	1.602
α (D)	1.610	1.608	1.606	1.6045	1.602	1.599
α (C)	1.607	1.604	1.602	1.6015	1.599	1.596
γ (F)	1.663					1.646
γ (Tl)	1.667					1.641
γ (D)	1.654	1.651	1.646		1.642	1.637
γ (C)	1.649					1.634

The same is expressed in the diagrams (fig. 11) in which is also shown the variation in the index of refraction in the strontium and calcium metasilicate glass.

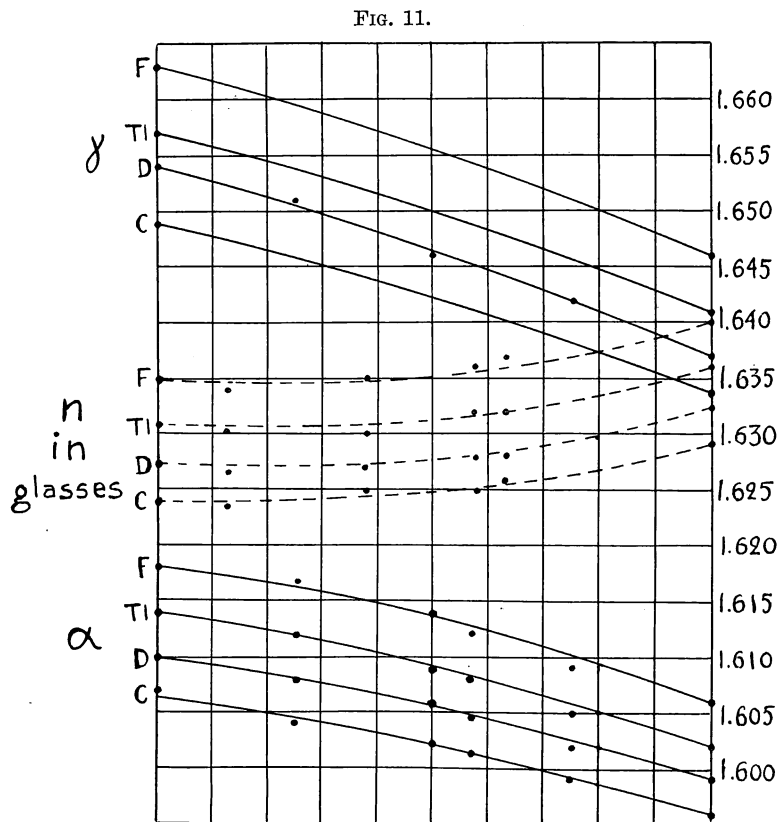


FIG. 11.—Variation of the indices of refraction in the mix crystal series $\text{CaO.SiO}_2\text{-SrO.SiO}_2$.

The System $\text{CaO.SiO}_2\text{-BaO.SiO}_2$.

While strontium and calcium metasilicates give a complete series of solid solutions and apparently are perfectly isomorphous, barium metasilicate does not mix at all with calcium metasilicate. Instead of this there occurs a double compound, 2CaO.BaO.3SiO_2 , which, however, has no true melting point, but breaks up into $\alpha\text{-CaO.SiO}_2$ and liquid. Those quenches which yielded important results are quoted below in table VI.

TABLE VI.

Composition wt. per cent Oxides			Silicates		Temper-	Time	Resulting Phases
CaO	BaO	SiO ₂	CaO. SiO ₂	BaO ₂ SiO ₂	ature °C	min- utes	
Liquidus of α-CaO.SiO ₂							
36.13	17.95	45.92	75	25	1466	15	Glass
36.13	17.95	45.92	75	25	1457	15	Glass and α-CaO.SiO ₂
36.13	17.95	45.92	75	25	1441	15	Glass and α-CaO.SiO ₂
36.13	17.95	45.92	75	25	1344	15	α-CaSiO ₃ and glass
28.90	28.71	42.38	60	40	1394	15	Glass
28.90	28.71	42.38	60	40	1380	15	Glass and α-CaO.SiO ₂
24.09	35.89	40.02	50	50	1342	15	Glass
24.09	35.89	40.02	50	50	1330	15	Glass and α-CaO.SiO ₂
24.09	35.89	40.02	50	50	1326	15	Glass and α-CaO.SiO ₂
24.09	35.89	40.02	50	50	1325	25	Glass and α-CaO.SiO ₂
Invariant point α-CaO.SiO ₂ -2CaO.BaO.3SiO ₂ -liquid.							
24.09	35.89	40.02	50	50	1321	15	Glass and α-CaO.SiO ₂
24.09	35.89	40.02	50	50	1319	15	Glass and 2CaO.BaO.3SiO ₂
24.09	35.89	40.02	50	50	1317	15	Glass and 2CaO.BaO.3SiO ₂
24.09	35.89	40.02	50	50	1300	15	Glass and 2CaO.BaO.3SiO ₂
22.88	37.69	39.43	47.5	52.5	1323	15	Glass
22.88	37.69	39.43	47.5	52.5	1321	15	Glass and 2CaO.BaO.3SiO ₂
22.88	37.69	39.43	47.5	52.5	1314	15	Glass and 2CaO.BaO.3SiO ₂
Decomposition of 2CaO.BaO.3SiO ₂							
25.13	34.32	40.54	52.18	47.82	1320	30	α-CaO.SiO ₂ and glass
			= 2CaO.BaO.3SiO ₂				
25.13	34.32	40.54	52.18	47.82	1315	20	2CaO.BaO.3SiO ₂ only
Liquidus of 2CaO.BaO.3SiO ₂ .							
21.68	39.48	38.84	45	55	1321	30	Glass
21.68	39.48	38.84	45	55	1316	30	Glass and 2CaO.BaO.3SiO ₂
21.68	39.48	38.84	45	55	1301	30	Glass and 2CaO.BaO.3SiO ₂
16.99	46.47	36.54	35.26	64.74	1306	20	Glass
			(BaO.CaO.2SiO ₂)				
16.99	46.47	36.54	35.26	64.74	1300	20	Glass and 2CaO.BaO.3SiO ₂
16.99	46.47	36.54	35.26	64.74	1294	20	Glass and 2CaO.BaO.3SiO ₂
16.38	47.37	36.25	34	66	1293	20	Glass and 2CaO.BaO.3SiO ₂
16.38	47.37	36.25	34	66	1290	20	Glass and 2CaO.BaO.3SiO ₂
15.66	48.45	35.89	32.5	67.5	1289	15	Glass and 2CaO.BaO.3SiO ₂
15.42	48.81	35.77	32	68	1290	15	Glass
15.42	48.81	35.77	32	68	1284	25	Glass and 2CaO.BaO.3SiO ₂
14.45	50.25	35.30	30	70	1280	20	Glass
14.45	50.25	35.30	30	70	1276	20	Glass and 2CaO.BaO.3SiO ₂
14.45	50.25	35.30	30	70	1274	20	Glass and 2CaO.BaO.3SiO ₂
Eutectic 2CaO.BaO.3SiO ₂ -BaO.SiO ₂							
16.99	46.47	36.54	35.26	64.74	1273		2CaO.BaO.3SiO ₂ and glass
16.99	46.47	36.54	35.26	64.74	1271		2CaO.BaO.3SiO ₂ and glass
16.99	46.47	36.54	35.26	64.74	1265		2CaO.BaO.3SiO ₂ and BaO. SiO ₂

14.45	50.25	35.30	30	70	1270	2CaO.BaO.3SiO ₂ and glass
14.45	50.25	35.30	30	70	1268	2CaO.BaO.3SiO ₂ and BaO. SiO ₂
13.25	52.04	34.71	27.5	72.5	1274	Glass
13.25	52.04	34.71	27.5	72.5	1271	Glass
13.25	52.04	34.71	27.5	72.5	1268	2CaO.BaO.3SiO ₂ and BaO. SiO ₂
12.05	53.83	34.12	25	75	1275	BaO.SiO ₂ and glass
12.05	53.83	34.12	25	75	1267	BaO.SiO ₂ and 2CaO.BaO. 3SiO ₂
9.63	57.42	32.95	20	80	1267	BaO.SiO ₂ and 2CaO.BaO. 3SiO ₂

Liquidus of BaO.SiO₂

12.05	53.83	34.12	25	75	1300	Glass
12.05	53.83	34.12	25	75	1292	Glass and BaO.SiO ₂
9.63	57.42	32.95	20	80	1367	Glass and BaO.SiO ₂

The melting diagram resulting from these facts is given in fig. 12.

The liquidus curve of α -CaO.SiO₂ was followed to 50 per cent BaO.SiO₂. The α -CaO.SiO₂ which always separated in the form of thin crystals tabular parallel to the basal plane did not seem to take any BaO.SiO₂ in solid solution, as the crystals in all cases showed the indices of refraction characteristic of pure pseudowollastonite: $\alpha(D) = 1.609 \pm 0.002$; $\gamma(D) = 1.652 \pm 0.002$.

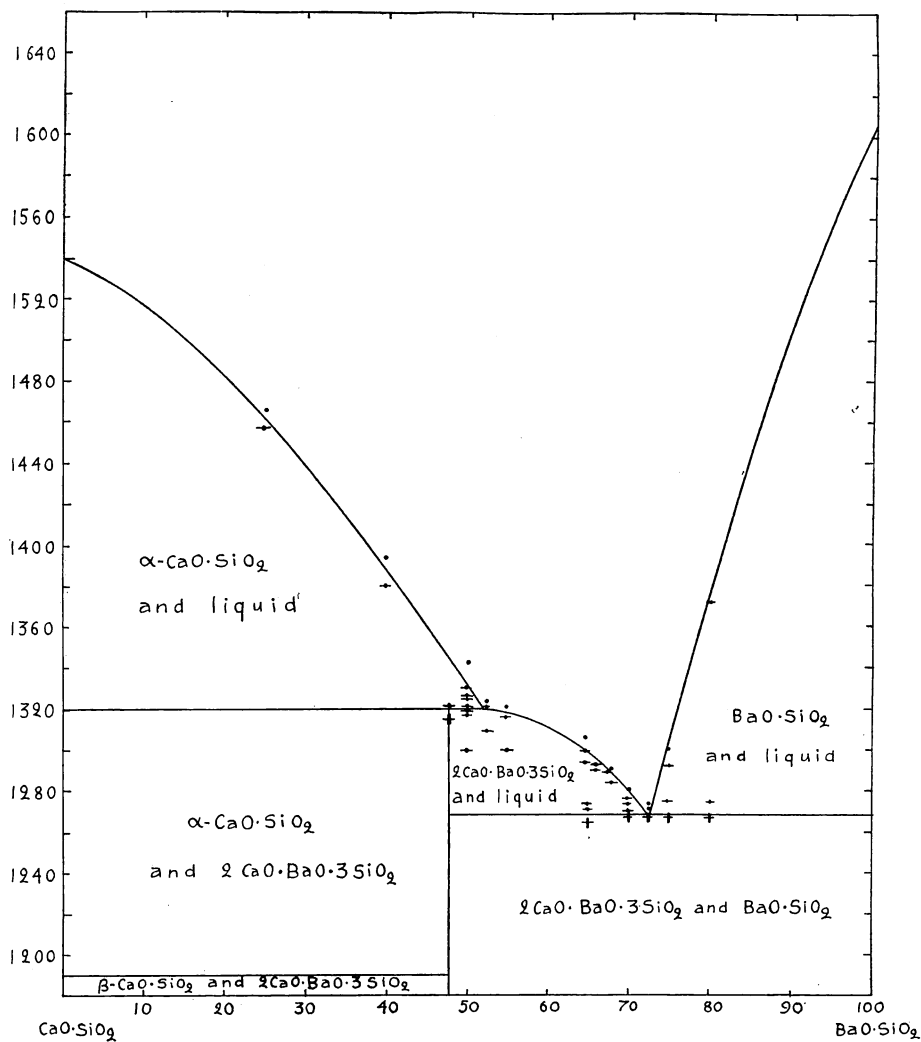
Dicalcium barium silicate, 2CaO.BaO.3SiO₂.—When the mixture composed of 50 per cent BaO.SiO₂ and 50 per cent CaO.SiO₂ was allowed to crystallize on cooling, it formed a coarsely crystalline, fibrous mass, almost like natural wollastonite. The fibers were speckled with minute crystals of another substance (BaO.SiO₂). Supposing the fibrous crystals to have the composition 2CaO.BaO.3SiO₂ I prepared such a mixture, which was now found to crystallize as homogeneous crystals and on heating to break up at $1320 \pm 4^\circ$ into α -CaSiO₂ and liquid.

The crystals are uniaxial and negative, probably hexagonal, and have good cleavages in their prismatic zone. A crystallizing mass develops negatively elongated fibers.

The indices of refraction were determined as follows:

	ω	ϵ
F	1.690	1.678
Tl	1.685	1.672
D	1.681	1.668
C	1.677	1.664

FIG. 12.

FIG. 12.—Temperature-concentration diagram of the binary system $\text{CaO} \cdot \text{SiO}_2$ - $\text{BaO} \cdot \text{SiO}_2$.

As it was thought possible that there could exist solid solutions between the double compound and $\text{BaO} \cdot \text{SiO}_2$, I determined the refractive indices of the exceedingly small crystals in preparations with 55 and 60 per cent

BaO.SiO_2 . I found in both cases $\omega(\text{D}) = 1.683 \pm 0.003$; $\epsilon(\text{D}) = 1.669 \pm 0.003$. The results are not significantly different from those of the pure compound.

The invariant point $\text{CaO.SiO}_2\text{-}2\text{CaO.BaO.}3\text{SiO}_2\text{-melt}$.—In a mixture containing 50 per cent of CaO.SiO_2 and as much BaO.SiO_2 the crystals of $2\text{CaO.BaO.}3\text{SiO}_2$ break up into $\alpha\text{-CaO.SiO}_2$ and liquid before melting entirely. In another mixture with 47.5 per cent CaO.SiO_2 the last crystals before complete melting consist of the double compound. The invariant point therefore is between these limits, and the course of both liquidus curves meeting there indicates it to be at 52 per cent BaO.SiO_2 and 48 per cent CaO.SiO_2 , with the temperature of complete melting $1320 \pm 4^\circ$.

The liquidus of $2\text{CaO.BaO.}3\text{SiO}_2$ has, from the invariant point, a regular course towards a eutectic. I followed its course very closely, because it was suspected that another double compound, $\text{CaO.BaO.}2\text{SiO}_2$, might possibly form here, its composition corresponding to 35.26 weight per cent CaO.SiO_2 and 64.74 weight per cent BaO.SiO_2 . But no such compound could be isolated, and the corresponding mixture crystallized within an interval of 32° into a very fine mixture of BaO.SiO_2 and $2\text{CaO.BaO.}3\text{SiO}_2$.

The liquidus of BaO.SiO_2 was determined, with only a few quenches, to have a steep course towards the high melting point of the barium metasilicate.

The crystals of this compound in melts containing 75 to 80 per cent BaO.SiO_2 were not equant grains as in the system BaO.SiO_2 , but needle-like, sharp at both ends. As they have formed at much lower temperatures than the crystals in BaO-SiO_2 melts, it may be possible that they represent another form of BaO.SiO_2 . The refractive indices, however, so far as they could be determined, were identical, and experiments carried out to establish the transformation expected failed, even when mineralizers were applied (cf. p. 352).

The Properties of the Glasses.

The physical properties of representative glasses studied in the present work are tabulated below.

TABLE VII.

Glasses in the system SrO-SiO_2 .

Wt. % SrO	46.2	50	60	63.2	67
Wt. % SiO_2	53.8	50	40	36.8	33
Formula	$\text{SrO} \cdot 2\text{SiO}_2$	—	—	$\text{SrO} \cdot \text{SiO}_2$	—
$n(\text{F})$	1.591	1.598	1.632	1.640	1.652
$n(\text{Ti})$	1.587	1.595	1.627	1.636	1.648
$n(\text{D})$	1.584	1.5915	1.624	1.632	1.644
$n(\text{C})$	1.581	1.589	1.621	1.629	1.641
Density	3.201	—	—	3.537 ^a	—

^a Calculated from the value of specific gravity, $d(4^\circ) = 3.540$, given by Jaeger and Van Klooster, op. cit. 902.

TABLE VIII.

Glasses in the system BaO-SiO_2 .

Wt. % BaO	45	50	56	65
Wt. % SiO_2	55	50	44	35
Formula	—	—	$\text{BaO} \cdot 2\text{SiO}_2$	—
$n(\text{F})$	1.576	1.593	1.617	1.653
$n(\text{Ti})$	1.571	1.589	1.612	1.648
$n(\text{D})$	1.5665	1.585	1.6085	1.645
$n(\text{C})$	1.5635	1.582	1.605	1.641
Density	—	3.441	—	—

FIGS. 13, 14.

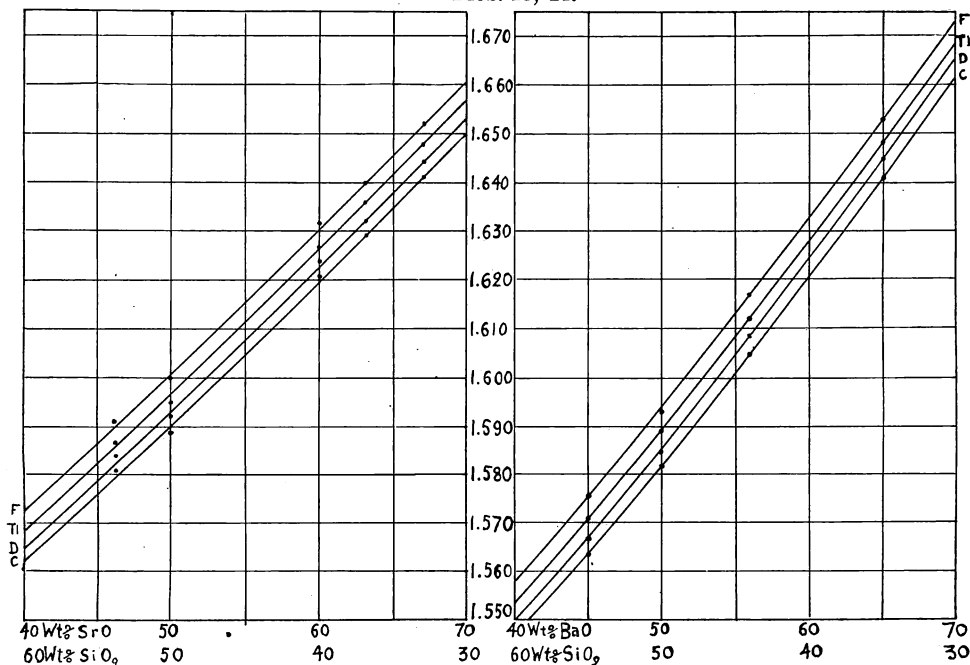


Fig. 13.—Variation of the indices of refraction in strontium silicate glasses.

Fig. 14.—Variation of the indices of refraction in barium silicate glasses.

Figs. 13 and 14 are diagrams of the variations in the refractive indices of glasses of the systems SrO-SiO_2 and BaO-SiO_2 showing also the dispersions.

FIG. 15.

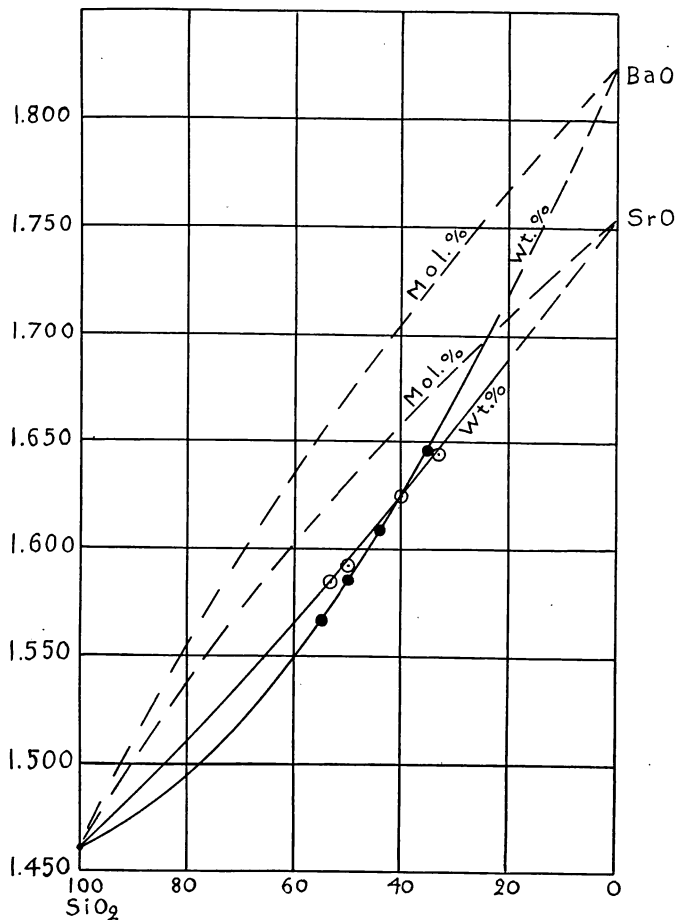


FIG. 15.—Variation of the index of refraction in strontium and barium silicate glasses.

Fig. 15 represents the same for the sodium light. The curves are drawn as far as the point corresponding to the index of refraction of silica glass and extrapolated up to the points of the hypothetical refractive indices of barium and strontium oxide glasses. In this part the curves, of course, can not give the values of the indices

very exactly, while those of the acid end should be fairly accurate, and the data given here may be, in the case of the barium silicate, of some practical interest to the manufacturer of optical glasses.

In tables IX and X are given the determinations of refractive indices of glasses in the systems $\text{CaO} \cdot \text{SiO}_2$ - $\text{SrO} \cdot \text{SiO}_2$ and $\text{CaO} \cdot \text{SiO}_2$ - $\text{BaO} \cdot \text{SiO}_2$. The same is expressed in fig. 16.

FIG. 16.

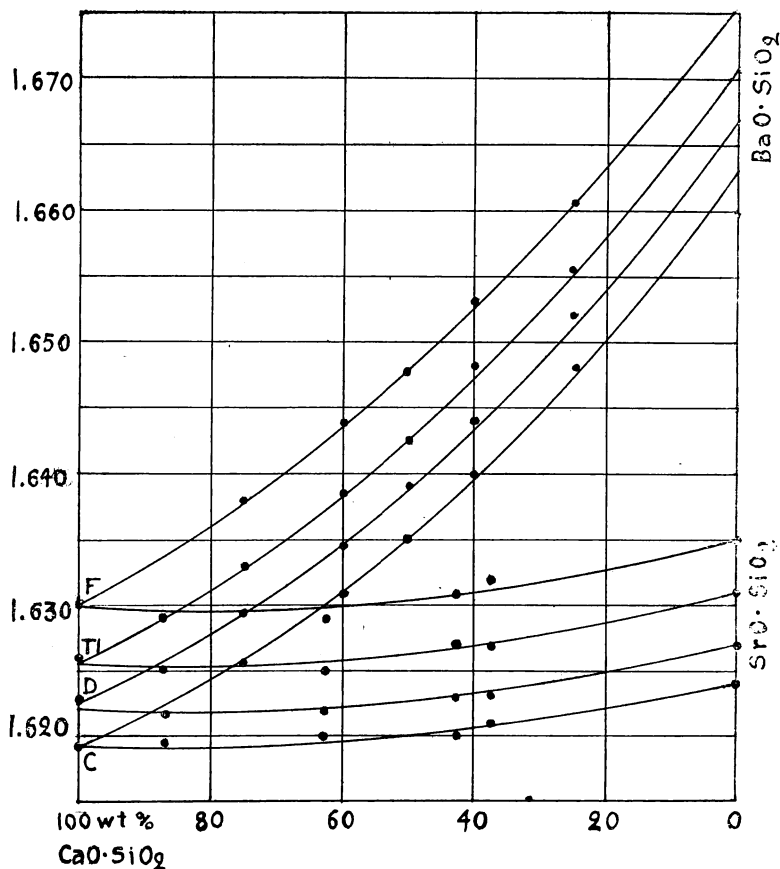


FIG. 16.—Variation of the indices of refraction in glasses of $\text{CaO} \cdot \text{SiO}_2$, $\text{SrO} \cdot \text{SiO}_2$ and $\text{CaO} \cdot \text{SiO}_2$ - $\text{BaO} \cdot \text{SiO}_2$.

TABLE IX.

Glasses in the system $\text{CaO.SiO}_2\text{--SrO.SiO}_2$.

Wt. % CaO.SiO_2	100	87.5	62.5	43.75	37.5	0
Wt. % SrO.SiO_2	0	12.5	37.5	56.25	62.5	100
$n(F)$	1.635	1.634	1.634	1.636	1.637	1.640
$n(Tl)$	1.631	1.630	1.630	1.633	1.632	1.636
$n(D)$	1.628	1.6265	1.627	1.628	1.628	1.632
$n(C)$	1.625	1.6245	1.625	1.625	1.626	1.629

TABLE X.

Glasses in the system $\text{CaO.SiO}_2\text{--BaO.SiO}_2$.

Wt. % CaO.SiO_2	100	75	60	50	40	25	0
Wt. % BaO.SiO_2	0	25	40	50	60	75	100 ^a
$n(F)$	1.635	1.643	1.649	1.6525	1.658	1.6655	(1.681)
$n(Tl)$	1.631	1.638	1.6435	1.647	1.653	1.6605	(1.675)
$n(D)$	1.628	1.6345	1.6395	1.644	1.649	1.657	(1.672)
$n(C)$	1.625	1.6305	1.636	1.640	1.645	1.653	(1.668)
Density					3.633		

^a Extrapolated.

Absence of Diopside Analogs.

A. few experiments were made to ascertain whether strontium and barium metasilicates form double compounds with magnesium metasilicate, analogous to diopside, the calcium compound, CaO.MgO.2SiO_2 . Mixtures corresponding to these proportions were prepared and quenched from different temperatures.

A mixture corresponding to SrO.MgO.2SiO_2 gave only glass at temperatures above 1320 and, at temperatures down to about 1200°, glass and crystals that from their optical properties may have consisted of clinoenstatite. Another mixture of the composition 2SrO.MgO.3SiO_2 gave SrO.SiO_2 as a primary phase. It therefore seems that the metasilicates of strontium and magnesium do not form any double compound at all. At any rate, there is no compound SrO.MgO.2SiO_2 , analogous to diopside.

Furthermore, I made a mixture of 25 weight per cent SrO.MgO.2SiO_2 and 75 weight per cent CaO.MgO.2SiO_2 , heated it above 1400° and let it cool slowly. The product contained diopside, showing $\alpha(D) = 1.665 \pm 0.002$; $\beta(D) = 1.675 \pm 0.003$; $\gamma(D) = 1.695 \pm 0.002$ and $2V = 60^\circ$. These properties agree perfectly with those of pure diopside and consequently the crystals do not contain any strontium compound as isomorphous mix-

ture. This conclusion, however, is not very dependable, as our experience is that strontium replacing calcium changes the optical properties of crystals very little. More weighty evidence proving positively that the amount of the strontium compound entering into solid solution in the diopside must be very small, is that the product consisted of more than one phase, the other phases besides the diopside being present as a fine crystalline mass.

The preparation of the composition BaO.MgO.2SiO_2 , on cooling from a melt heated not above 1370° , also gave several phases, and no double compound analogous to diopside was formed.

This negative result is very remarkable, especially in the case of strontium, which in other ways showed such close similarity with calcium.

The Strontium and Barium Feldspars.

Former investigations.—From melts of the corresponding oxides Fouqué and Michel-Lévy²² believed they had prepared strontium, barium, and lead analogs of anorthite, oligoclase and labradorite.

Their different "feldspars" had the following specific gravities:

	Sr	Ba	Pb
Oligoclase	1.619	2.906	3.196
Labradorite	2.862	3.333	3.609
Anorthite	3.043	3.573	4.093

The products were not well crystallized and their crystal system could not be determined with certainty. The barium feldspar, $\text{BaAl}_2\text{Si}_2\text{O}_8$, always formed microlites showing parallel extinction with negative elongation, and the crystals, being usually rectangular in cross section, seemed to be orthorhombic. Later investigation by E. Dittler,²³ on artificial barium feldspar, confirmed this result and also established it to be biaxial. Ginsberg,²⁴

²² F. Fouqué et A. Michel Lévy: Sur la production artificielle de feldspaths à base de baryte, de strontia et de plomb, correspondant à l'oligoclase, à labradore et à l'anorthite; études des propriétés optiques des ces minéraux, Bull. soc. min. France 3, 124. 1880.

²³ E. Dittler, Tscherm. Min. Petr. Mitt., 30, 122, 1911.

²⁴ A. S. Ginsberg, Ann. de l'Inst. Polytech. Pierre le Grand à Pétrougrade, 1915, XXIII.

however, states that crystals of $\text{BaAl}_2\text{Si}_2\text{O}_8$ obtained by cooling of the pure melt were uniaxial, positive, and he regards this form as presenting a nephelite analog.

There is some evidence to the effect that some amount of lime, in plagioclase feldspars, may be replaced by baryta without changing the triclinic symmetry. Descloizeaux²⁵ found this to be the case in a natural feldspar from unknown locality, whose optical and crystallographic properties were similar to those of labradorite, while its composition resembled that of oligoclase more closely, with 7.30 BaO, 1.83 CaO, 7.45 Na₂O, and 0.83 K₂O. Ginsberg²⁶ investigated the binary system $\text{CaAl}_2\text{Si}_2\text{O}_8$ – $\text{BaAl}_2\text{Si}_2\text{O}_8$ in artificial products and found that the triclinic anorthite may take up limited amounts of barium feldspar in solid solution, whereby the optic axial angle diminishes. The hexagonal $\text{BaAl}_2\text{Si}_2\text{O}_8$, on the other hand, may take up some lime feldspar.²⁷

The relation of barium feldspar and orthoclase is far better known. Penfield²⁸ described barium-bearing orthoclase from Blue Hill, Delaware County, Pennsylvania. Later Sjögren²⁹ and Strandmark³⁰ studied the barium feldspar, or celsian, from Jakobsberg, Sweden, and proved it to have the composition $\text{BaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$. The latter establishes its monoclinic symmetry and crystallographic similarity to adularia. The crystals are usually elongated parallel to $\hat{c}$. The angle $\alpha \wedge \hat{c} = 3^\circ 1'$ in the acute angle β . $\alpha = 1.5835$; $\beta = 1.5886$; $\gamma = 1.5941$. Sp. g. 3.37. Strandmark also proved that the hyalophanes are isomorphous mixtures of celsian and orthoclase.

Rock analyses including determinations of BaO and SrO commonly show small amounts of both of these oxides. As Washington³¹ has pointed out, the highest amount of both of these oxides have been found in certain highly potassic rocks of Wyoming, showing up to 1.10 per cent BaO and 0.30 per cent SrO. A study of the analyses published in Washington's Tables³² shows that

²⁵ A. Descloizeaux, *Tscherm. Min. Petr. Mitt.*, 7, 99, 1877.

²⁶ A. S. Ginsberg, loc. cit.

²⁷ The thermal work of Ginsberg was done by the cooling curve method and is subject to criticism (cf. p. 332).

²⁸ S. L. Penfield, *this Journal*, 36, 326, 1888.

²⁹ Hj. Sjögren, *Geol. Fören., Förh.*, 17, 578, 1895.

³⁰ J. F. Strandmark, *Geol. Fören. Förh.* 25, 289, 1903; 26, 97, 1903.

³¹ H. S. Washington, *J. Franklin Inst.*, 190, 767, 1920.

³² H. S. Washington, *U. S. Geol. Surv., Prof. Paper* 99, 1917.

the ratio of the percentages of BaO and SrO corresponds, to a considerable degree, with the ratio of the percentages of K₂O and CaO, so that it may be presumed that strontia is present in the plagioclase and baryta in the potash feldspar. A chemical investigation of the feldspars from the rocks in question might prove this to be true.

In the present study it was not intended to make any exhaustive experimental investigation of the strontium and barium feldspars, but a few experiments were made to elucidate their behavior.

As both the compounds, SrO.Al₂O₃.2SiO₂ and BaO.Al₂O₃.2SiO₂, were found to have very high melting points (far above 1700°) and to crystallize but poorly when the pure mixtures of the respective oxides were heated up, I applied the vanadate flux method to produce better crystals. In both cases the feldspar mixtures were powdered with about 1/3 of their masses of Sr(VO₃)₂ and Ba(VO₃)₂, respectively, and kept over night at about 1400°. The vanadates were then washed out with very dilute cold HCl.

Artificial barium feldspar, BaO.Al₂O₃.2SiO₂.—The barium feldspar thus obtained formed minute crystals, not more than 0.05 mm in length. They were elongated parallel to *a* and tabular parallel to *a*_γ, so that most crystals placed themselves on that plane and, in convergent light, showed the trace of the optical normal. The terminal faces show an apparent bilateral symmetry, like orthorhombic domes and, as the extinction is almost always parallel so far as can be determined, the crystals give entirely the appearance of orthorhombic symmetry, in agreement with the earlier results of Fouqué and Michel-Lévy, and of Dittler. I found, however, that this is only apparent and due to the fact that most of the crystals are Carlsbad contact twins, so that light has to pass through the two individuals with opposite extinction angles, the individuals being tabular parallel to 010, which is also the composition plane. The other forms are (110), which is the zone of elongation, and (001) and (101). In simple crystals, or in outstanding simple parts of the twins, there may be observed extinction angles of two or three degrees, and the optical orientation is thus: $\beta \parallel b$; $a \wedge c = 3^\circ$. Basal cleavage is not very well developed, though its trace may be seen occasionally. All these characters agree with those found in natural

celsian. No evidence was found of the existence of a nephelite analog, a hexagonal form of $\text{BaAl}_2\text{Si}_2\text{O}_8$ described by Ginsberg.

The indices of refraction indicate a negative character. They were determined as follows and are compared with Strandmark's result on the natural celsian:

	$\alpha(\text{D})$	$\beta(\text{D})$	$\gamma(\text{D})$
Artificial barium feldspar ³³	1.587 ± 0.002	1.593 ± 0.002	1.600 ± 0.002
Natural celsian	1.5835	1.5886	1.5941

The differences in the indices of refraction are somewhat greater than the probable errors, but not more than may be accounted for by the fact that the natural celsian carries a few tenths of a per cent of alkalis and lime.

Artificial strontium feldspar, $\text{SrO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$.—The strontium feldspar obtained from the vanadate flux formed a crystalline mass showing radiating fibrous development but no well-formed crystals. No twinning could be discerned. Therefore nothing can be said about its crystallographic characters. The indices of refraction, however, were readily determined and are stated below, compared with those of anorthite.

	$\alpha(\text{D})$	$\beta(\text{D})$	$\gamma(\text{D})$
$\text{SrO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$	1.574 ± 0.002	1.582 ± 0.002	1.586 ± 0.002
$\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$	1.576	1.584	1.588

It was thus found that the strontium feldspar is, in its optical properties, exactly like the calcium feldspar within the limits of the possible errors. This is not very surprising in itself, as we have found in some cases the indices of refraction of the strontium compounds somewhat lower and in other cases somewhat higher than those of the calcium compounds.

A mixture of 50 weight per cent $\text{SrO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ and 50 weight per cent $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ was prepared and heated at about 1500° . It formed clear homogeneous-looking grains whose indices of refraction agreed with those of anorthite. It did not melt at this temperature and it is therefore probable that the strontium feldspar forms a complete series of solid solutions with anorthite.

³³ $\alpha(\text{F}) = 1.593$; $\alpha(\text{TI}) = 1.590$; $\alpha(\text{D}) = 1.587$; $\alpha(\text{G}) = 1.585$

Some General Considerations Regarding the Relations of the Alkaline Earth Compounds.

With the exception of some rare titanosilicates, the only natural anhydrous silicates of barium known are barium feldspar, or celsian, $\text{BaAl}_2\text{Si}_2\text{O}_8$, notable for its isomorphism with potash feldspar, barylite, $\text{Ba}_4\text{Al}_4\text{Si}_7\text{O}_{24}$, and taramellite, $\text{Ba}_4\text{Fe}''\text{Fe}'''_4\text{Si}_{10}\text{O}_{31}$. Hydrated silicates are more numerous, mostly belonging to the zeolite group, namely: brewsterite, $\text{H}_4(\text{Sr},\text{Ba},\text{Ca})\text{Al}_2\text{Si}_6\text{O}_{18} + 3\text{H}_2\text{O}$, harmotome, $\text{H}_2(\text{K}_2,\text{Ba})\text{Al}_2\text{Si}_5\text{O}_{15} + 4\text{H}_2\text{O}$, edingtonite, $\text{BaAl}_2\text{Si}_3\text{O}_{10} + 3\text{H}_2\text{O}$ and wellsite $(\text{Ba},\text{Sr},\text{Ca},\text{K}_2)\text{Al}_2\text{Si}_3\text{O}_{10} + 3\text{H}_2\text{O}$. Micas sometimes contain appreciable amounts of barium.

No strontium silicates are known as minerals, though this element, in smaller quantities, is contained in some rock-forming feldspars, probably plagioclases (cf. p. 365), and in hancockite, a lead-epidote, and in zeolite minerals heulandite, $\text{H}_4(\text{Ca},\text{Sr})\text{Al}_2\text{Si}_6\text{O}_{18} + 3\text{H}_2\text{O}$, and wellsite and brewsterite, named above.

The present study adds some information concerning the isomorphous relations of a number of other silicates of strontium and barium. Thus the compound $\text{BaO} \cdot 2\text{SiO}_2$ which was suggested by Bowen (loc. cit.) to be isomorphous with the potassium disilicate studied by Morey and Fenner,³⁴ has now been found to be also isomorphous with $2\text{BaO} \cdot 3\text{SiO}_2$. A strontium metasilicate was found to be isomorphous with a form of calcium metasilicate, and a strontium orthosilicate is probably isomorphous with either the α or the β form of calcium orthosilicate. A strontium feldspar was found to be probably isomorphous with the lime feldspar, anorthite, which is also isomorphous with a soda feldspar.

Now taking into account all the compounds of the alkaline earths, silicates as well as others, we may discriminate, according to their isomorphous relations to compounds of other elements, at least four different classes:

(1) Calcium, strontium, and barium compounds isomorphous with each other (all or two of them) and also isomorphous with lead compounds. Examples: The tetrahedral-pentagondodecahedral nitrates of $\text{Ca}(\text{?})$, Sr , Ba , and Pb . The orthorhombic carbonates, aragonite, strontianite, witherite, and cerussite. The sulphates,

³⁴ G. W. Morey and C. N. Fenner, *J. Am. Chem. Soc.*, **36**, 215, 1914.

celestite, barite, and anglesite, form an isomorphous series which excludes calcium sulphate. Among silicates we note the group of hancockite and epidote, and we have now found that the metasilicates form an isomorphous series to which belong only the calcium and strontium, but not the barium metasilicate.³⁵

(2) Calcium and strontium (also barium?) compounds isomorphous with each other and also isomorphous with sodium compounds. Example: Anorthite and strontium anorthite.

(3) Barium compounds isomorphous with potassium compounds. Example: Barium disilicate. Among the natural silicates named above, celsian and harmotome are representatives of this class.

(4) Calcium compounds isomorphous with corresponding compounds of magnesium, ferrous iron and a number of other elements, but not with those of barium or strontium. Example: The rhombohedral carbonates, calcite, magnesite, siderite, etc.

It seems to be a rule that in the compounds in which the lime may possibly be replaced by magnesia and ferrous oxide, it can not be replaced by strontia or baryta. Thus it was found in the present work that there are no strontium or barium compounds analogous to diopside, CaO.MgO.2SiO_2 .

Accordingly we find, in nature, strontium and barium compounds forming mix crystals with lime and alkali minerals, but not with ferromagnesian, although the latter may contain calcium. In other words, these elements are likely to be found in salic rather than in femic rocks, a circumstance that is really very striking in their distribution in the igneous rocks.

The authors of the so-called quantitative classification of igneous rocks make a distinction between salic and femic lime. Now these terms gain added significance, as we find that only the salic but not the femic lime may be replaced by strontia.

It may be of interest, for the sake of comparison, to present together some important properties of the members of some well known simple compounds of the three alkaline earth metals.

³⁵ Bourgeois (Ann. chim. phys., 29, 445, 1883) records a lead metasilicate of a similar appearance to those of calcium and strontium.

		Mol. vol.	$(\alpha+\beta+\gamma)/3$
Carbonates:	Aragonite	34.01	1.632
	Strontianite	39.87	1.615
	Witherite	45.82	1.627
Sulphates:	Anhydrite	45.99	1.586
	Celestite	46.18	1.626
	Barite	51.96	1.641
Metasilicates:	β -CaO.SiO ₂	40.09 ³⁶	1.625
	α -CaO.SiO ₂	40.11 ³⁶	1.625
	SrO.SiO ₂	44.91	1.612
	BaO.SiO ₂	48.57	1.675

The carbonate series exemplifies the rule found to hold good in many other instances that the molecular volumes, in an isomorphous series, increase regularly with the atomic weights of the substituted elements. Compounds which are not isomorphous often show a discrepancy in their molecular volumes, as for example anhydrite in its relation to celestite and barite.

The metasilicate series, in the regular increase of the molecular volumes with the atomic weight, behaves more like an isomorphous series, although we know that barium metasilicate is not isomorphous with the others. Our knowledge of the solid solubility relations of the carbonate and sulphate series is too incomplete to allow any closer comparison.

In the refringence one can hardly see any regular relation. The barium compounds have mostly the highest indices of refraction, but the carbonates make an exception, aragonite having higher indices than witherite. Among the strontium compounds some have higher and others lower indices than the corresponding calcium compounds, without any apparent regularity.

Schaefer³⁷ carried out a thermal study of the binary systems CaCl₂-SrCl₂ and CaCl₂-BaCl₂. He found, in the former case, a complete solid solubility with a minimum in the melting curve, while the latter do not mix at all, but

³⁶ These values have been obtained by computing the specific gravities at 25°, compared with water at 25°, as found by Allen and White (this Journal, 21, 103, 1906), for α -CaO.SiO₂ 2.912 and β -CaO.SiO₂ 2.214, in terms of density, i. e. comparing with water at 4° and making the correction for the buoyancy of air. Thus, for α -CaO.SiO₂, $d = 2.901$ and, for β -CaO.SiO₂, $d = 2.903$.

³⁷ Walter Schaefer, Neues Jahrb. Min. Geol., 1, 15, 1914.

form a double compound $\text{CaCl}_2 \cdot \text{BaCl}_2$ which shows an incongruent melting, breaking up into crystals of BaCl_2 and liquid. These relations are in all particulars, except in the molecular proportion of the double compound, strictly analogous to those of $\alpha\text{-CaO} \cdot \text{SiO}_2$ to the metasilicates of strontium and barium.

In the lime-silica system there occur the basic silicates $3\text{CaO} \cdot \text{SiO}_2$ and $3\text{CaO} \cdot 2\text{SiO}_2$ the analogs of which were not found in the systems strontia-silica or baryta-silica. The last-named system, on the other hand, is the only one in which occur silicates more acid than the metasilicate, namely, $2\text{BaO} \cdot 3\text{SiO}_2$ and $\text{BaO} \cdot 2\text{SiO}_2$. Among the alkali metals, in a similar way, the one having the lowest atomic weight (lithium) forms the most basic silicates and those with higher atomic weights (potassium, etc.) more acid silicates.

Summary.

Fig. 17 gives a synoptical view of the melting diagrams for the three binary systems CaO-SiO_2 , SrO-SiO_2 , and BaO-SiO_2 . To make the diagrams really comparable they are all expressed in terms of molecular percentages.

The compositions and melting or decomposition points of the compounds and eutectics, etc. in the three systems are listed in table XI. Table XII gives all the important properties determined for the strontium and barium silicates.

In the system SrO-SiO_2 the following compounds were found: SrO , $2\text{SrO} \cdot \text{SiO}_2$, $\text{SrO} \cdot \text{SiO}_2$ and SiO_2 . With the exception of silica each of them was found in one form only, although the temperature of formation of the strontium silicates was varied from the melting points down to about 900° .

Especial interest was taken in the strontium metasilicate, $\text{SrO} \cdot \text{SiO}_2$, which was found to be closely isomorphous and optically very similar to $\alpha\text{-CaO} \cdot \text{SiO}_2$. It therefore probably belongs to the monoclinic crystal system, but its crystals agree so closely with the hexagonal system that, judging only from its own properties, it would seem to belong to this system. The crystals are apparently hemimorphic and might belong to the dihexagonal pyramidal or, if they are monoclinic, to the monoclinic domatic class.

FIG. 17.

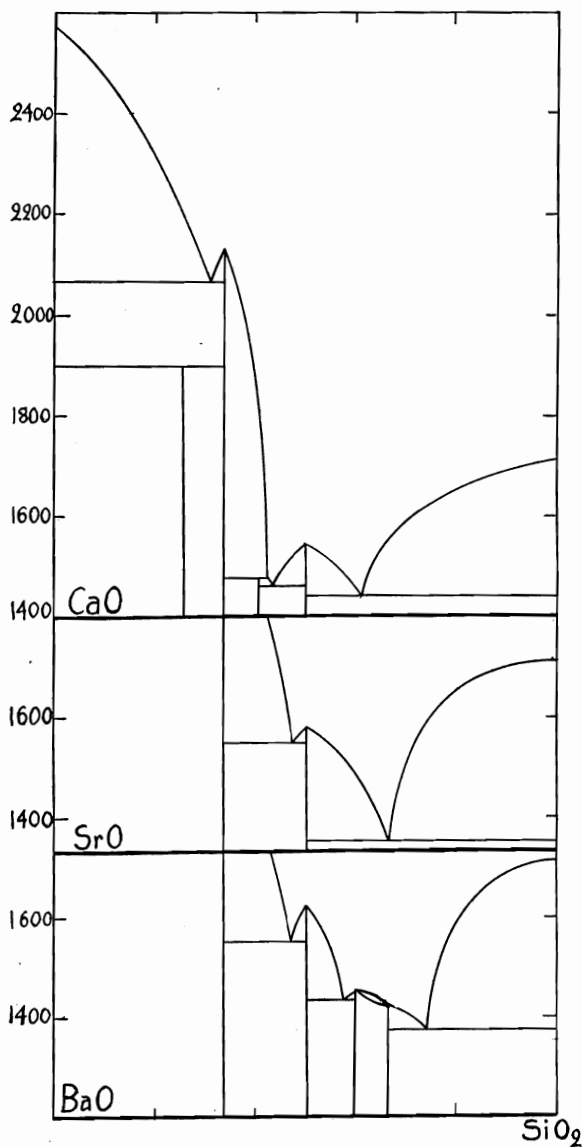


FIG. 17.—Synopsis of the binary systems BaO-SiO_2 , SrO-SiO_2 , and CaO-SiO_2 in mol. %.

TABLE XI.
Compositions and temperatures in the systems
CaO—Si₂, SrO₂, and BaO—SiO₂.

	Wt. %		Mol. %		Tempera- ture °C	Character of change
	CaO	SiO ₂	CaO	SiO ₂		
Eutectic cristobalite (?)— α—CaO.SiO ₂	37.0	63.0	38.7	61.3	1436	Melting
α—CaO.SiO ₂	48.2	51.8	50	50	1540	Melting
Eutectic α—CaO.SiO ₂ —3CaO. 2SiO ₂	54.5	45.5	56.3	43.7	1455	Melting
3CaO.2SiO ₂	58.2	41.8	60	40	1475	Decomposition
Invar. pt. 3CaO.2SiO ₂ — 2CaO.SiO ₂	55.5	44.5	57.3	42.7	1475	Melting
2CaO.SiO ₂	65.0	35.0	66.7	33.3	2130	Melting
3CaO.SiO ₂	73.6	26.4	75	25	1900	Decomposition
Eutectic 2CaO.SiO ₂ —CaO.. CaO	67.5	32.5	69.1	30.9	2065	Melting
	100	—	100	—	2570	Melting
	SrO	SiO ₂	SrO	SiO ₂		
Eutectic tridymite—SrO.SiO ₂	46.5	53.5	33.6	66.4	1358	Melting
SrO.SiO ₂	63.2	36.8	50	50	1578	Melting
Eutectic SrO.SiO ₂ —2SrO. SiO ₂	65.5	34.5	52.5	47.5	1545	Melting
2SrO.SiO ₂	77.5	22.5	66.7	33.3		
Eutectic 2SrO.SiO ₂ —SrO.. SrO	—	—	—	—		
	100	—	100	—		
	BaO	SiO ₂	BaO	SiO ₂		
Eutectic tridymite—BaO. 2SiO ₂	47	53	25.9	74.1	1374	Melting
BaO.2SiO ₂	56	44	33.3	66.7	1420	Melting
2BaO.3SiO ₂	62.9	37.1	40	60	1450	Melting
Eutectic 2BaO.3SiO ₂ —BaO. SiO ₂	65	35	57.8	42.2	1437	Melting
BaO.SiO ₂	71.8	28.2	50	50	1604	Melting
Eutectic BaO.SiO ₂ —2BaO. SiO ₂	74.5	25.5	53.5	46.5	1551	Melting
2BaO.SiO ₂	83.6	16.4	66.7	33.3		
Eutectic 2BaO.SiO ₂ —BaO.. BaO	—	—	—	—		
	100	—	100	—		

In the system BaO—SiO₂ the compounds BaO, 2BaO.SiO₂, BaO.SiO₂, 2BaO.3SiO₂, BaO.2SiO₂, and SiO₂ have been found.

Of these compounds the dibarium trisilicate, 2BaO.3SiO₂, and the barium disilicate, BaO.2SiO₂, showed very remarkable behavior, being isomorphous, of orthorhombic symmetry, and forming a complete series of solid solutions. The melting diagram of this series belongs to Bakhuis Roozeboom's type 1, without maximum or

TABLE XII. Physical properties of the strontium and barium silicates and oxides.

Composition	System and habit	α	β	γ	2 V Dispersion	Cleavage	Density	Remarks
SrO	Isometric		1.87			[100] perfect	4.750 ^a	
2SrO.SiO ₂	Monocl. ?	1.727	1.732	1.756	32°30'			Twinned on [100]
SrO.SiO ₂	Pseudo (?) dihexagonal pyramidal tabular (0001)	1.599 = ω		1.637 = ϵ	0°	good $\perp c$	3.650	Complete series of solid solutions with α -CaO.SiO ₂
BaO	Isometric		2.16			[100] perfect	5.722 ^a	
2BaO.SiO ₂	Granular	1.810		1.830	?	no		
BaO.SiO ₂	Orthorhombic granular or needles	1.673	1.674	1.678	29° strong $\rho > \nu$	good $\alpha\beta$	4.399	
2BaO.3SiO ₂	Orthorhombic granular	1.620	1.625	1.645	53°30'	perfect $\beta\gamma$ poor $\alpha\beta$ and $\alpha\gamma$	3.93	Complete series of solid solutions.
BaO.2SiO ₂	Orthorhombic tabular $\parallel \alpha\beta$	1.597	1.612	1.621	74°45'	perfect $\alpha\beta$ good $\beta\gamma$ and $\alpha\gamma$	3.73	
BaO.2CaO.3SiO ₂	Hexagonal (?) fibrous	1.668 = ϵ		1.641 = ω		prismatic		
SrO.Al ₂ O ₃ .2SiO ₂	Triclinic (?)	0.574	1.582	1.586	large	?	3.043 ^b	Solid solutions with anorthite.
BaO.Al ₂ O ₃ .2SiO ₂	Monoclinic	1.587	1.593	1.600	large	perfect [010] good [001]	3.573 ^b	Solid solutions with orthoclase.

^a Sp. gr. determined by Brüggenmann.^b Sp. gr. determined by Fouqué and Michel-Levy.

minimum. The indices of refraction show a continuous though not linear variation with the composition.

The strontium and calcium metasilicates form a continuous series of solid solutions with a minimum in the melting curve. The indices of refraction and the densities of the mix crystals show continuous variation with the composition.

The barium metasilicate is not isomorphous with the calcium and strontium metasilicates, being optically biaxial, with low birefringence and probably of orthorhombic symmetry. It forms no solid solutions with α -CaO.SiO₂. Instead, there occurs a double compound, 2CaO.BaO.3SiO₂ which melts incongruently, breaking up into α -CaO.SiO and liquid. This compound is optically uniaxial and negative, unlike all the other metasilicates. In its refringence it is similar to BaO.SiO₂.

Neither strontium nor barium metasilicate forms, with magnesium metasilicate, a double compound analogous to diopside, CaO.MgO.2SiO₂. This is considered as a special case of the more common rule which seems to obtain generally in the compounds of the alkaline earth elements, namely, that calcium, in those compounds in which it can be replaced by magnesia and ferrous oxide, cannot be replaced by strontia or baryta, while the isomorphous series including strontium or barium compounds may have isomorphous and miscible analogs among sodium, potassium, or lead compounds.

Both strontium and barium form feldspars, analogous to anorthite. The strontium feldspar has indices of refraction exactly like those of anorthite, and the two seem to be completely miscible. The barium feldspar is monoclinic, like the natural celsian. It forms commonly Carlsbad twins of the contact type and the minute twin crystals therefore appear as if orthorhombic.

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