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## DICALCIUM SILICATE SOLID SOLUTIONS

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## ABSTRACT

Studies on the manner of combination of  $\text{Na}_2\text{O}$  in portland cement clinker have revealed crystalline phases of chemical composition near that of  $2\text{CaO} \cdot \text{SiO}_2$ , but possessing properties quite different from those heretofore reported for the  $\beta$  form of this compound. These phases result when certain compositions in the quaternary systems  $\text{Na}_2\text{O}-\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$  and  $\text{Na}_2\text{O}-\text{CaO}-\text{Fe}_2\text{O}_3-\text{SiO}_2$  are quenched from high temperatures. Optical, thermal, and X-ray diffraction data have been obtained which indicate that they are solid solutions of  $\text{Na}_2\text{O}$  and  $\text{Al}_2\text{O}_3$  and of  $\text{Na}_2\text{O}$  and  $\text{Fe}_2\text{O}_3$ , in a high-temperature form of  $2\text{CaO} \cdot \text{SiO}_2$  having a hexagonal structure. There is also evidence that this hexagonal lattice is the fundamental structure of the  $\alpha$  form of  $2\text{CaO} \cdot \text{SiO}_2$ .

In the pure compound the  $\alpha$ - $\beta$  inversion temperature has been reported to be  $1,420^\circ \pm 2^\circ \text{C}$ , whereas in the phases described in this paper the transformation temperature may be lowered by as much as  $245^\circ \text{C}$ , e. g., to  $1,175^\circ \pm 10^\circ \text{C}$ . The inversion from  $\alpha$  to  $\beta$  is accompanied by considerable ex-solution of dissolved material, showing that the extent of solid solution of these oxides in  $\beta$ - $2\text{CaO} \cdot \text{SiO}_2$  is much less than in the  $\alpha$  form. As a result of this precipitation the grains of  $\beta$   $2\text{CaO} \cdot \text{SiO}_2$  are more or less densely clouded, closely resembling the grains of  $2\text{CaO} \cdot \text{SiO}_2$  in some commercial clinkers. The data also indicate that the complex twinning structure often observed in  $2\text{CaO} \cdot \text{SiO}_2$  in portland cement clinker and in experimental preparations is the result of inversion from the  $\alpha$  to the  $\beta$  phase, and is not typical of the  $\alpha$  modification, as some investigators have believed.

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## I. INTRODUCTION

In the course of a series of investigations on the phase relations of soda in portland cement clinker, there have been observed at times crystalline phases, which, although undoubtedly near in composition to that of dicalcium silicate, nevertheless differ rather markedly in optical properties from the  $\beta$  form of this compound as found in clinker. These phases resulted when charges composed of  $2\text{CaO} \cdot \text{SiO}_2$  and small amounts of  $\text{Na}_2\text{O}$  and  $\text{Al}_2\text{O}_3$  or of  $\text{Na}_2\text{O}$  and  $\text{Fe}_2\text{O}_3$  were quenched at temperatures of  $1,450^\circ$  to  $1,500^\circ \text{C}$ . X-ray diffraction patterns of these preparations contain lines which are entirely absent from that of  $\beta$ - $2\text{CaO} \cdot \text{SiO}_2$  and are of a much simpler type. In order to understand these optical and X-ray results, a considerable amount of experimental work has been carried out, but until recently no satisfactory explanation had been found.

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It was at first believed that a ternary compound of  $\text{Na}_2\text{O}$ ,  $\text{CaO}$ , and  $\text{SiO}_2$  might be formed, but this idea was abandoned because the distinctive X-ray patterns could not be produced unless a fourth component,  $\text{Al}_2\text{O}_3$  or  $\text{Fe}_2\text{O}_3$ , was present in the heated charges. The possibility of a solid solution of  $\text{Na}_2\text{O}$  and  $\text{Al}_2\text{O}_3$  or of  $\text{Na}_2\text{O}$  and  $\text{Fe}_2\text{O}_3$  in  $\alpha$   $2\text{CaO} \cdot \text{SiO}_2$  had been considered, but the sharp disagreement with the optical properties of " $\alpha$   $2\text{CaO} \cdot \text{SiO}_2$ ", as reported by Rankin and Wright [1]<sup>1</sup> and with the diffraction pattern as given by Hansen [2], was unexplained. The clue to the answer appeared in a recent paper by Bredig [3] on compounds of the type  $\text{A}_2\text{XO}_4$ , to which  $2\text{CaO} \cdot \text{SiO}_2$  belongs. Using data obtained on solid solutions of  $2\text{CaO} \cdot \text{SiO}_2$  and  $3\text{CaO} \cdot \text{P}_2\text{O}_5$ , and by analogy to other similar structures among compounds such as the alkali sulfates, he presents strong evidence for the existence at high temperatures of a hexagonal crystal structure of  $2\text{CaO} \cdot \text{SiO}_2$ . Bredig assumes that this form is unstable at room temperature, and when in a pure state, always inverts upon cooling to one of the lower-temperature forms of  $2\text{CaO} \cdot \text{SiO}_2$ . He contends that this hexagonal form may be maintained at room temperature by foreign material in solid solution.

In Bredig's paper are reproduced diffraction data for the substance  $7\text{CaO} \cdot \text{P}_2\text{O}_5 \cdot 2\text{SiO}_2$ , which was originally studied by Nagelschmidt [4]. This phase is a solid solution of  $3\text{CaO} \cdot \text{P}_2\text{O}_5$  in  $2\text{CaO} \cdot \text{SiO}_2$ , and Bredig found that the pattern may be satisfactorily explained by assuming a hexagonal crystal lattice of the type possessed by glaserite,  $(\text{K}, \text{Na})_2\text{SO}_4$ . Casual examination by the present author revealed a remarkable similarity between the interplanar spacings of this substance and those of the new crystalline phases obtained in the present work, and it was found that these heretofore unexplained results were in excellent agreement with calculated values based on a hexagonal lattice. It is the purpose of the present paper to offer this additional evidence relative to  $2\text{CaO} \cdot \text{SiO}_2$ , together with other optical and thermal data which have been obtained.

This new development has a direct bearing on the much-debated problem of the  $\alpha$ - $\beta$  relationship of  $2\text{CaO} \cdot \text{SiO}_2$ . The  $\alpha$ - $\beta$  inversion was found by Rankin and Wright [1] to take place at  $1,420^\circ \pm 2^\circ \text{C}$  in the pure compound. The evidence for the existence of the  $\alpha$  form at room temperature, either in portland cement clinker or in laboratory preparations, has been questioned by a number of authors. Hansen [2] and Insley [5] have pointed out the similarity in optical properties and powder diffraction patterns between the forms of  $2\text{CaO} \cdot \text{SiO}_2$  commonly known as  $\alpha$  and  $\beta$ , and conclude that the  $\alpha$  form actually may never have been observed by them, but may have already inverted to the  $\beta$  modification in the samples studied. The contention of Bredig [3] that  $\alpha$ - $2\text{CaO} \cdot \text{SiO}_2$  has a hexagonal crystal structure will be discussed in later paragraphs.

Solid solution of foreign substances in the  $2\text{CaO} \cdot \text{SiO}_2$  of clinker has been mentioned by various investigators. Sundius [6], Tavasci [7], and Insley, Flint, Newman, and Swenson [8] all consider the fine inclusions often observed in the  $2\text{CaO} \cdot \text{SiO}_2$  of commercial clinker to be due to ex-solution. They note that these inclusions are often arranged in definite directions, with the result that the twinning structure is accentuated.

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

Other cases of solid solution in  $2\text{CaO} \cdot \text{SiO}_2$  are found in the literature. Rankin and Wright [1] observed a lowering of the  $\alpha$ - $\beta$  inversion temperature of  $25^\circ \text{C}$  in certain compositions in the system  $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ , although they were not able to detect solid solution in  $2\text{CaO} \cdot \text{SiO}_2$  by optical means. Bowen, Schairer, and Posnjak [9] found limited solid solution of  $2\text{FeO} \cdot \text{SiO}_2$  in  $\beta$ - $2\text{CaO} \cdot \text{SiO}_2$ , and comment on the difficulty of distinguishing the  $\alpha$  and  $\beta$  forms of the latter compound. Flint and Wells [10], in a study of the system  $\text{CaO} \cdot \text{B}_2\text{O}_3 \cdot \text{SiO}_2$ , encountered considerable solid solution of the calcium borates in  $2\text{CaO} \cdot \text{SiO}_2$ , resulting in a maximum lowering of the  $\alpha$ - $\beta$  inversion temperature from  $1,420^\circ \text{C}$  to about  $1,230^\circ \text{C}$ . Burdick [11] found that  $\text{Fe}_2\text{O}_3$  lowers the  $\alpha$ - $\beta$  inversion temperature of  $2\text{CaO} \cdot \text{SiO}_2$  to about  $1,360^\circ \text{C}$  in the system  $\text{CaO} \cdot \text{Fe}_2\text{O}_3 \cdot \text{SiO}_2$ , although it was concluded that the amount of solid solution does not exceed 0.5 percent of  $\text{Fe}_2\text{O}_3$ . Since the lowering of an inversion temperature indicates a greater amount of solid solution in the high-temperature phase, it may be concluded that in these latter two systems the solid solution was relatively greater in the  $\alpha$  than in the  $\beta$  modification.

## II. EXPERIMENTAL RESULTS

### 1. PREPARATIONS CONTAINING $\text{Na}_2\text{O}$ AND $\text{Fe}_2\text{O}_3$

The preparation that gave the sharpest powder diffraction pattern contained 90.2 percent of  $2\text{CaO} \cdot \text{SiO}_2$ , the remaining 9.8 percent being  $\text{Na}_2\text{O}$  and  $\text{Fe}_2\text{O}_3$ . The oxide composition after heating was as follows:

	Percent
$\text{CaO}$ -----	58.7
$\text{SiO}_2$ -----	31.5
$\text{Fe}_2\text{O}_3$ -----	5.6
$\text{Na}_2\text{O}$ -----	4.2

The sample from which the X-ray pattern was made was held at  $1,450^\circ \text{C}$  for 45 minutes and quenched in mercury. The interplanar spacings obtained from the pattern,<sup>2</sup> and the values calculated for a hexagonal lattice, as suggested by Bredig's paper, are presented in Table 1.

TABLE 1.—Powder diffraction pattern of preparation composed of  $2\text{CaO} \cdot \text{SiO}_2$ ,  $\text{Na}_2\text{O}$  and  $\text{Fe}_2\text{O}_3$ , quenched at  $1,450^\circ \text{C}$ .  
(Composition given above.)

[vs=very strong; m=medium; s=strong; w=weak.]

Hexagonal indices, $hkl$	Estimated intensity	$d_{hkl}$ , experimental	$d_{hkl}$ , calculated
10.2	vs	2.81	2.81
11.0	vs	* 2.70	2.70
20.1	m	2.218	2.219
20.2	s	1.945	1.946
00.4	w	* 1.749	1.749
12.2	m	1.579	1.578
30.0	m	1.559	1.559
11.4	m	1.470	1.471
22.0	m	1.350	1.350
13.2	w	1.217	1.216
30.4	w	1.164	1.166

\* Values used in calculation of  $a_0$  and  $c_0$ .

<sup>2</sup> The X-ray diffraction photographs were taken by H. F. McMurdie.

Using the spacings with the indices 11.0 and 00.4, the lattice constants are calculated to be  $d_0=5.40$  Å and  $c_0=7.00$  Å. The axial ratio,  $c/a=1.30$ . The agreement between experimental and calculated values of  $d_{hkl}$  is so excellent that there seems to be no doubt of the correctness of the assumption of a hexagonal unit cell.

A microscopical examination of this sample shows clear, slightly yellow crystalline grains with a small amount of dark-brown interstitial glass containing quench growths of high birefringence. Some of this glass is also included in the individual grains. Between crossed nicols the interference color of the crystalline material is a low-order gray in some fragments and in others an anomalous Berlin blue. The birefringence is probably not greater than 0.005 and the mean index of refraction is  $1.713 \pm 0.003$ . An interference figure suitable for a determination of the optical character could not be obtained. Figure 1, A and B,<sup>3</sup> shows this preparation in ordinary transmitted light and between crossed nicols.

When other samples of this composition were allowed to cool in the quenching furnace to various temperatures below  $1,420^\circ$  C and after quenching in mercury were examined microscopically, a striking change in appearance was noted in those which has been cooled below  $1,175^\circ \pm 10^\circ$  C. Above this temperature the crystalline material is clear and, with the exception of a few relatively large inclusions of glass, homogeneous. Below  $1,175^\circ$  C, however, the material becomes inhomogeneous, being filled with a precipitate of fine-grained brown material. This condition indicates that ex-solution of material from the solid phase has occurred. The charges cooled below the precipitation temperature also show optical properties for the matrix that differ from those of the high-temperature quenches. Samples cooled slowly to  $1,150^\circ$  C show higher indices of refraction and a higher birefringence than the clear phase stable above  $1,175^\circ$  C. These properties suggest  $\beta$ - $2\text{CaO} \cdot \text{SiO}_2$ , and its presence was verified by an X-ray diffraction pattern of a charge which was heated to  $1,450^\circ$  C and cooled to  $1,150^\circ$  C at an average rate of about 23 degrees per minute. No lines of the hexagonal form are evident, and it is apparent that a discontinuous change in crystal structure has taken place. Figure 2, A and B, illustrates this preparation in ordinary light and between crossed nicols. There seems to be little doubt that ex-solution of the  $\text{Na}_2\text{O}$  and  $\text{Fe}_2\text{O}_3$  from the high-temperature form has occurred during transition to the  $\beta$  modification. There may also be some remaining solid solution of these oxides in  $\beta$ - $2\text{CaO} \cdot \text{SiO}_2$ , but it is apparently much less.

## 2. PREPARATIONS CONTAINING $\text{Na}_2\text{O}$ AND $\text{Al}_2\text{O}_3$

The results obtained with certain compositions in the quaternary system  $\text{Na}_2\text{O}-\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$  are analogous in most respects to those in the  $\text{Na}_2\text{O}-\text{CaO}-\text{Fe}_2\text{O}_3-\text{SiO}_2$  system. The best diffraction pattern resulted from quenching at  $1,500^\circ$  C a charge that had the following composition after having been heated:

	Percent
$\text{CaO}$ -----	62.1
$\text{SiO}_2$ -----	31.3
$\text{Al}_2\text{O}_3$ -----	3.8
$\text{Na}_2\text{O}$ -----	2.8

<sup>3</sup> The photomicrographs were taken by G. W. Ward. The immersion medium in each case was an oil of  $n=1.675$ .



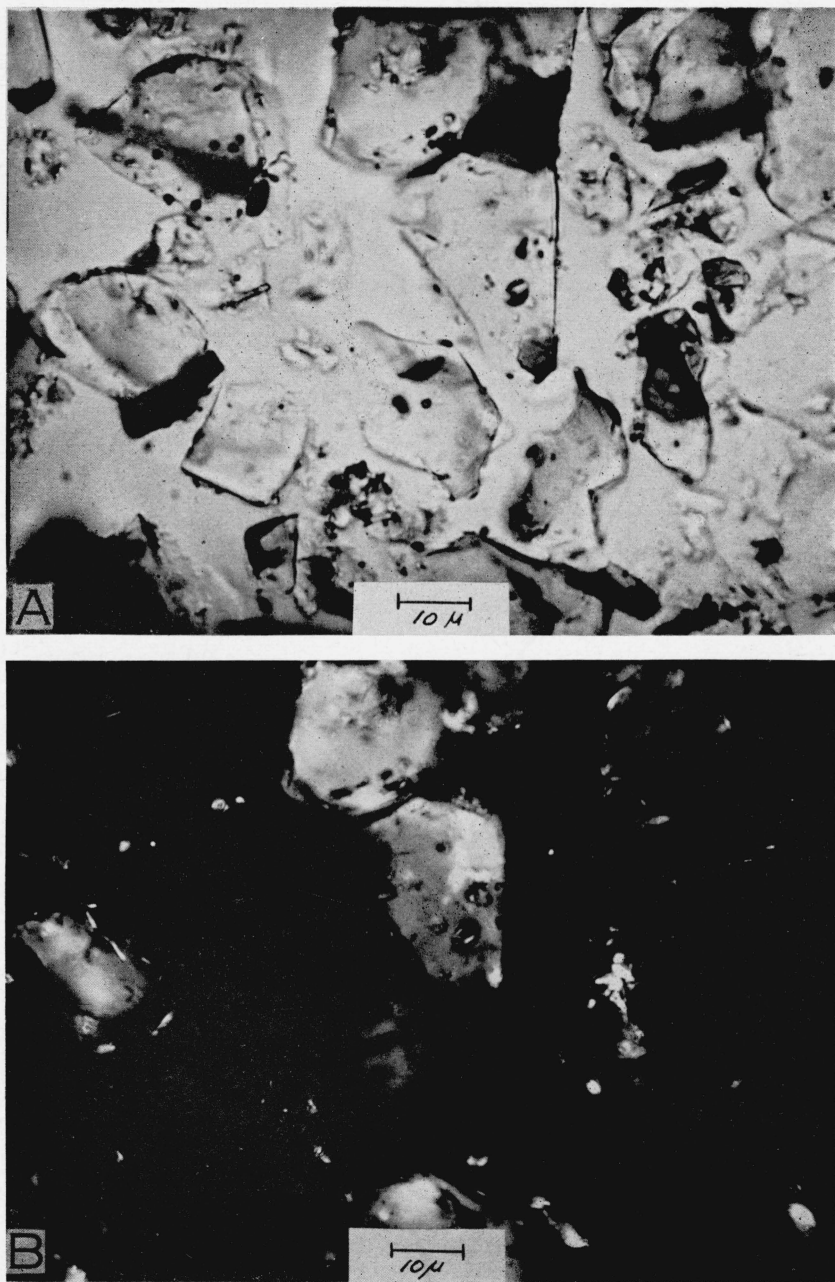


FIGURE 1.—Preparation composed of  $2\text{CaO} \cdot \text{SiO}_2$ ,  $\text{Na}_2\text{O}$ , and  $\text{Fe}_2\text{O}_3$ , quenched at  $1,450^\circ \text{C}$ .

A, Ordinary transmitted light; B, crossed nicols. Magnification  $\times 900$ .

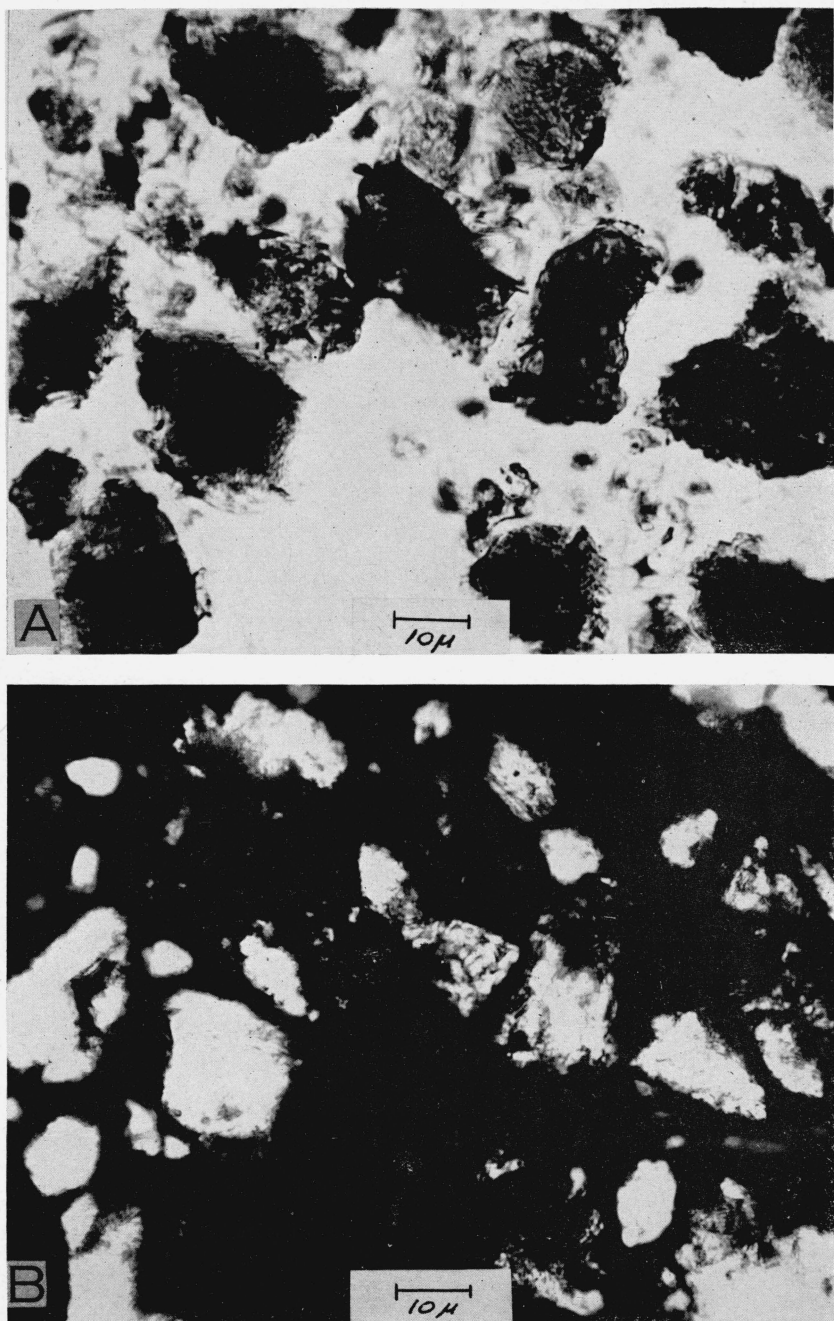


FIGURE 2.—Preparation composed of  $2\text{CaO} \cdot \text{SiO}_2$ ,  $\text{Na}_2\text{O}$ , and  $\text{Fe}_2\text{O}_3$ , cooled slowly from  $1,450^\circ$  to  $1,150^\circ \text{C}$  and quenched.

A, Ordinary transmitted light; B, crossed nicols. Magnification  $\times 900$ .

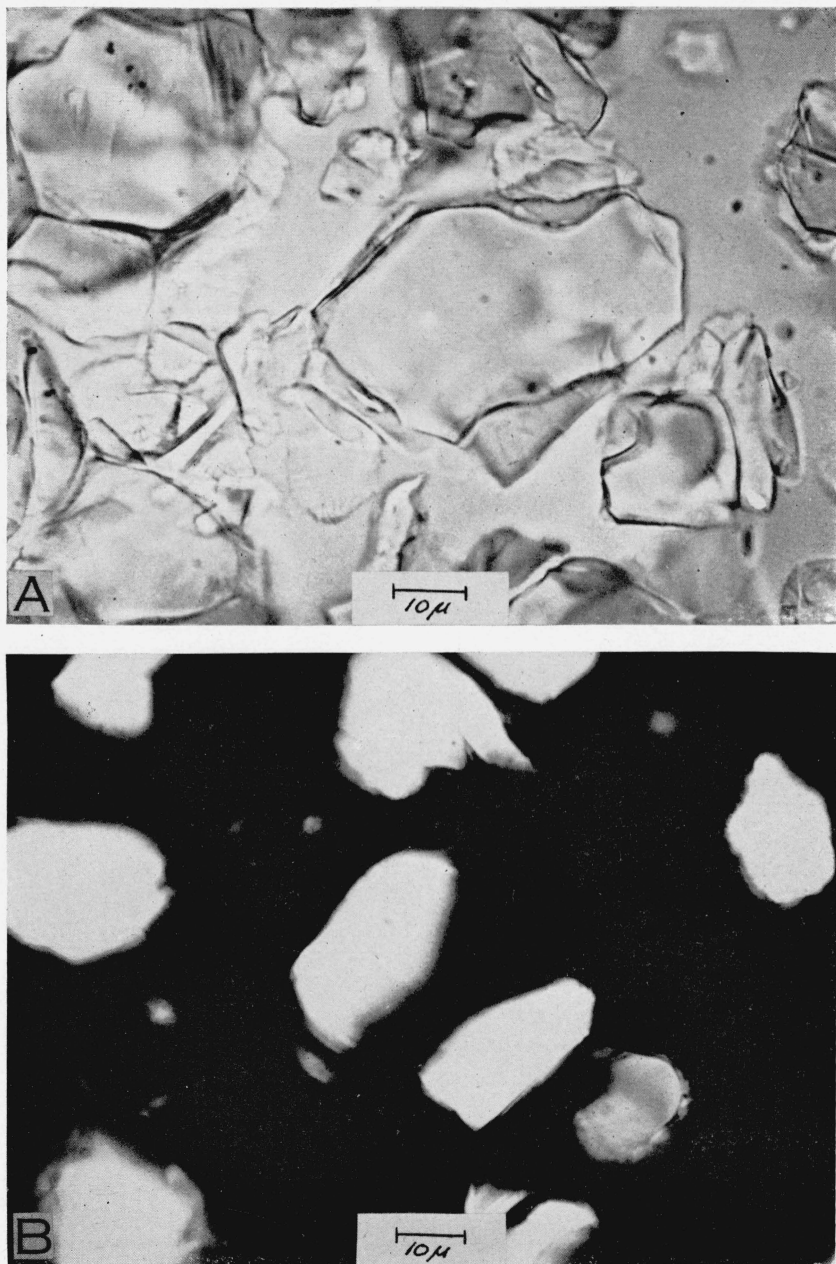


FIGURE 3.—Preparation composed of  $2\text{CaO} \cdot \text{SiO}_2$ ,  $\text{Na}_2\text{O}$ , and  $\text{Al}_2\text{O}_3$ , quenched at  $1,500^\circ \text{C}$ .

A, Ordinary transmitted light; B, crossed nicols. Magnification  $\times 900$ .

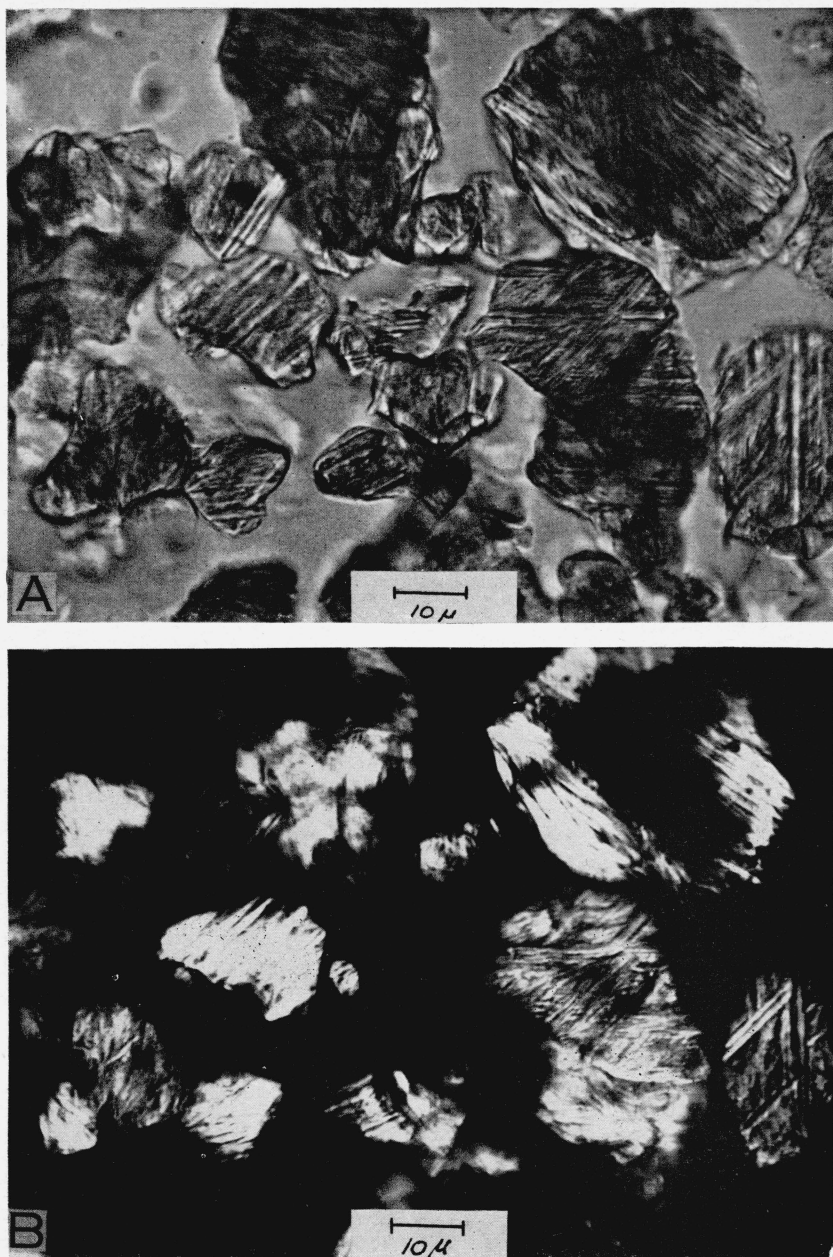


FIGURE 4.—Preparation composed of  $2\text{CaO} \cdot \text{SiO}_2$ ,  $\text{Na}_2\text{O}$ , and  $\text{Al}_2\text{O}_3$ , cooled slowly from  $1,450^\circ$  to  $1,150^\circ \text{C}$  and quenched.

A, Ordinary transmitted light; B, crossed nicols. Magnification  $\times 900$ .



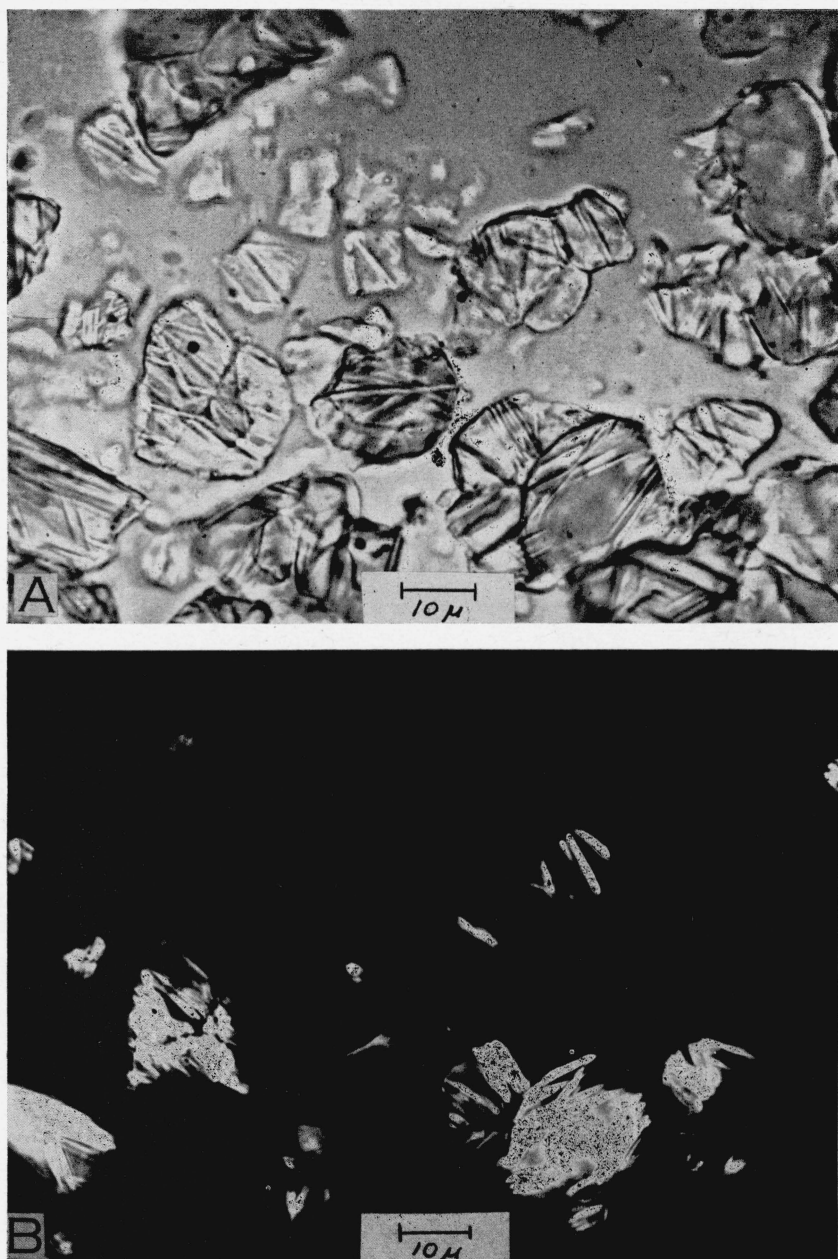


FIGURE 5.—Preparation composed of  $2\text{CaO} \cdot \text{SiO}_2$ ,  $\text{Na}_2\text{O}$ , and  $\text{Al}_2\text{O}_3$ , cooled slowly from  $1,450^\circ$  to  $1,200^\circ \text{C}$  and quenched.

A, Ordinary transmitted light; B, crossed nicols. Magnification  $\times 900$ .

This represents 89.8 percent of  $2\text{CaO} \cdot \text{SiO}_2$ , an excess of 3.6 percent of  $\text{CaO}$ , with the balance being  $\text{Na}_2\text{O}$  and  $\text{Al}_2\text{O}_3$ . When a hexagonal structure is assumed for this material, and the theoretical interplanar spacings calculated as in the preceding section, the agreement with experimental values is quite satisfactory, although not as close as in the case of the material containing  $\text{Fe}_2\text{O}_3$ . This is explained by the fact that the pattern itself is less distinct. Two of the lines given in table 1 have corresponding lines too weak to measure on this film. The data are given in table 2.

This lattice constants in this case are  $a_0=5.44$  Å and  $c_0=7.02$  Å. These are slightly greater than for the iron-bearing phase, although the ratio  $c/a$  is nearly the same, 1.29.

TABLE 2.—Powder diffraction pattern of preparation composed of  $2\text{CaO} \cdot \text{SiO}_2$ ,  $\text{Na}_2\text{O}$  and  $\text{Al}_2\text{O}_3$ , quenched at  $1,500^\circ \text{C}$ .

Composition given on page 4.

[vs=very strong; m=medium; s=strong; w=weak; vw=very weak.]

Hexagonal indices, $hkl$	Estimated intensity	$d_{hkl}$ , experimental	$d_{hkl}$ , calculated
10. 2	vs	2.81	2.81
11. 0	vs	2.71	2.72
20. 1	m	2.238	2.233
20. 2	s	* 1.955	1.955
00. 4			1.755
12. 2	m	1.588	1.588
30. 0	m	1.569	1.570
11. 4	w	1.469	1.474
22. 0	m	* 1.361	1.361
13. 2	vw	1.225	1.224
30. 4			1.170

\* Values used in calculation of  $a_0$  and  $c_0$ .

Under the microscope the grains are for the most part clear and of irregular shape. The birefringence is rather low, and is estimated to be about 0.01. The optical character is positive, and uniaxial or biaxial, with a very small axial angle. It is believed that strain brought about by quenching may be the cause of the apparent biaxiality observed in some fragments. The indices of refraction as measured in immersion oils are  $\omega=1.702 \pm 0.003$ ,  $\epsilon=1.712 \pm 0.003$ . The preparation is shown in ordinary light and between crossed nicols in figure 3, A and B, respectively.

Upon subjection to slow cooling and quenching at different temperatures, this material was found to undergo a transition analogous to that described above for the material containing  $\text{Fe}_2\text{O}_3$ . Below  $1,180^\circ \pm 10^\circ \text{C}$  the transformation from the high-temperature form seems to be complete. The diffraction pattern of a sample heated to  $1,450^\circ \text{C}$  and cooled to  $1,150^\circ \text{C}$  at about 19 degrees per minute corresponds to that of  $\beta\text{-}2\text{CaO} \cdot \text{SiO}_2$ . Here again the microscope reveals inhomogeneity, indicating that precipitation from solid solution has occurred. Also prominent in the grains is a complex twinning structure comprising several sets of parallel laths intersecting at acute angles. The birefringence is somewhat increased and the indices of refraction are greater than in the higher-temperature form. Figure 4, A, is a photomicrograph of these grains as seen in ordinary transmitted light and with the same field between crossed nicols shown in figure 4, B.

In the course of the cooling experiments on this material, it was noticed that charges quenched from certain temperatures somewhat above  $1,180^{\circ}\text{C}$  had an appearance not entirely like that described in either of the two previous cases. This is well shown in figure 5, A and B. This sample was quenched at  $1,200^{\circ}\text{C}$  after being cooled from  $1,450^{\circ}\text{C}$  at approximately 17 degrees per minute. It appears to represent an intermediate state in which narrow blades of  $\beta\text{-}2\text{CaO}\cdot\text{SiO}_2$  have formed within the residual high-temperature solid solution. The minute inclusions resulting from rapid ex-solution, as seen in figure 4, A, are not present in this quenched charge. The blade-like forms have a higher index of refraction than the crystalline material which they penetrate, and also a greater birefringence, as figure 5, B, taken with crossed nicols, shows. The diffraction pattern of this sample contains lines of  $\beta\text{-}2\text{CaO}\cdot\text{SiO}_2$  as well as of the higher-temperature solid solution, and it is apparently a composite pattern. Although it is, of course, possible that the blades of  $\beta\text{-}2\text{CaO}\cdot\text{SiO}_2$  may be strictly quench growths, the appearance suggests rather that they were in equilibrium with the matrix at the quenching temperature. Such a condition is possible in a type of system where the extent of solid solution is unequal in two crystalline phases of the same substance. Certain compositions will exhibit an inversion interval over which both of the forms exists in equilibrium, but in varying proportions. If such is true in this instance, the temperature  $1,180^{\circ}\text{C}$  represents the lower limit of the inversion interval for this particular composition.

Just why a similar inversion temperature-interval was not observed in the charges containing  $\text{Fe}_2\text{O}_3$  is not clear, unless the over-all percentages of  $\text{Na}_2\text{O}$  and  $\text{Fe}_2\text{O}_3$  exceed the limiting amounts that can be taken up by the  $2\text{CaO}\cdot\text{SiO}_2$ . In such a case the transformation from the hexagonal to the  $\beta$  form takes place completely, under equilibrium conditions, at a temperature corresponding to the lower limit of the interval. This conclusion is supported by the fact that considerable glass was observed in the  $\text{Na}_2\text{O}\text{-}\text{Fe}_2\text{O}_3$ , but very little in the  $\text{Na}_2\text{O}\text{-}\text{Al}_2\text{O}_3$  charges, and may also explain why the intricate twinning of the  $2\text{CaO}\cdot\text{SiO}_2$  is much more distinct in one case than in the other, as seen by comparing figures 2, A, and 4, A.

### III. DISCUSSION

The foregoing data seem to demonstrate the existence at high temperatures of solid solutions composed chiefly of  $2\text{CaO}\cdot\text{SiO}_2$ , possessing hexagonal crystal structures. Furthermore, it seems reasonable to conclude that this hexagonal type of structure is fundamentally that of the  $\alpha$  form of  $2\text{CaO}\cdot\text{SiO}_2$ , since it has been shown to invert directly to the  $\beta$  form upon cooling. Bredig [3] reaches this conclusion, based upon data for the system  $\text{CaO}\text{-}\text{P}_2\text{O}_5\text{-}\text{SiO}_2$  and upon the fact that similar hexagonal structures were found to exist at high temperatures for  $\text{Na}_2\text{SO}_4$ ,  $\text{K}_2\text{SO}_4$  and the solid solution  $(\text{K},\text{Na})_2\text{SO}_4$  (glaserite), as well as for the compounds  $\text{CaNaPO}_4$  and  $\text{CaKPO}_4$ . Since  $2\text{CaO}\cdot\text{SiO}_2$  belongs to the same  $\text{A}_2\text{XO}_4$  molecular type, and since solid solutions of phosphates in  $2\text{CaO}\cdot\text{SiO}_2$  take on this hexagonal structure at high temperatures, he argues that the pure compound may be expected to do likewise. Presumably this hexagonal  $\alpha\text{-}2\text{CaO}\cdot\text{SiO}_2$  cannot be preserved at room temperature when pure.

Bredig reports another solid solution of  $3\text{CaO}\cdot\text{P}_2\text{O}_5$  in  $2\text{CaO}\cdot\text{SiO}_2$

in addition to the hexagonal phases. This material is isomorphous at room temperature with  $\beta$ - $\text{K}_2\text{SO}_4$ , which is orthorhombic. He believes that the X-ray diffraction pattern given by Taylor [12] for the substance  $\text{K}_2\text{O} \cdot 23\text{CaO} \cdot 12\text{SiO}_2$  indicates that it also is isomorphous with  $\beta$ - $\text{K}_2\text{SO}_4$ . This question needs further experimental data for confirmation. In the present work no evidence of such an orthorhombic form was obtained. Only the hexagonal diffraction patterns and the familiar pattern of  $\beta$ - $2\text{CaO} \cdot \text{SiO}_2$  were observed. The twinned grains of figure 4, A and B, are seemingly indistinguishable from those illustrated by Taylor [12] and given by him the formula  $\text{K}_2\text{O} \cdot 23\text{CaO} \cdot 12\text{SiO}_2$ . Thus far it has not been found possible to distinguish between them by optical means alone. The X-ray patterns seem to offer the only method of differentiation. There is also need for more information on this important point.

The postulation of an  $\alpha$  form of  $2\text{CaO} \cdot \text{SiO}_2$  unstable at room temperature provides an explanation for the practically identical optical properties and diffraction patterns given for the  $\alpha$  and  $\beta$  forms [1, 2, 6]. The only usable distinguishing feature of  $\alpha$ - $2\text{CaO} \cdot \text{SiO}_2$  has been considered to be an intricate twinning structure. It has been suggested by Insley [5] that the complex twinning so often observed in grains of  $2\text{CaO} \cdot \text{SiO}_2$  indicates that they have at some time been in the  $\alpha$  state, rather than that they are at present in that state. The results reported in this paper tend to substantiate this belief, since the preparations shown in figure 4, A and B, exhibit the twinned structure very strongly and yet give the X-ray pattern of the  $\beta$  form. The complicated twinning probably results, then, from the transition to the  $\beta$  phase, and it appears that the transition is accompanied by precipitation of much of the material which was in solid solution in the  $\alpha$  phase. This precipitation is not to be confused with the formation of prismatic  $\beta$ - $2\text{CaO} \cdot \text{SiO}_2$  (fig. 5, A and B), which takes place continuously over a temperature interval. From all indications, the fine-grained precipitate is produced suddenly at the temperature below which the hexagonal  $\alpha$  structure is unstable, in this case  $1,180^\circ \text{C}$ .

It is of interest to note that Tavasci [7] also considered the twinning of  $2\text{CaO} \cdot \text{SiO}_2$  to be related to the inversion from the  $\alpha$  to the  $\beta$  form, and that he observed in some grains needles which he believed to consist of an unstable intermediate form. The description of these needles fits rather well the prismatic phase of figure 5, A and B.

When  $2\text{CaO} \cdot \text{SiO}_2$  in portland cement clinker is examined microscopically, it often exhibits an optical character that is nearly uniaxial.<sup>4</sup> If the internal crystal structure of this phase is shown by X-ray studies to be basically that of a uniaxial crystal, then the presence in commercial clinker of hexagonal  $\alpha$ - $2\text{CaO} \cdot \text{SiO}_2$  would be definitely indicated. If, however, the structure should be shown to be fundamentally biaxial, it would merely mean that the optic axial angle is nearly zero. Since the X-ray diffraction pattern of  $\beta$ - $2\text{CaO} \cdot \text{SiO}_2$  indicates that its symmetry is that of a biaxial crystal, an investigation of clinkers of recent manufacture would doubtless give a definite answer to the question of whether the phase observed is actually  $\alpha$ - $2\text{CaO} \cdot \text{SiO}_2$  or  $\beta$ - $2\text{CaO} \cdot \text{SiO}_2$  with a small optic axial angle. That  $\beta$ - $2\text{CaO} \cdot \text{SiO}_2$  can exhibit a very small axial angle was shown by Hansen [2]. Since this was in disagreement with Rankin and Wright [1], who reported large angles for

<sup>4</sup> Personal communication from L. S. Brown, Portland Cement Association, Chicago, Ill.



both  $\alpha$ - and  $\beta$ - $2\text{CaO} \cdot \text{SiO}_2$ , Hansen concluded that "the size of the optic axial angle alone is not a safe criterion to use in identifying a crystalline phase in such mixtures as portland cement."

It must be borne in mind that the greater the purity of  $2\text{CaO} \cdot \text{SiO}_2$ , the higher is the  $\alpha$ - $\beta$  inversion temperature, approaching as a limit  $1,420^\circ \text{C}$ . With increased purity there is an increased difficulty in retaining the  $\alpha$  form at room temperature. Thus the rate of cooling must be correspondingly greater in order to prevent inversion. How rapid this cooling must be is indicated by experiments on the compositions given in this paper. Charges of less than a gram were found to require quenching in mercury to insure complete retention of the  $\alpha$  solid solutions. Air-cooling by lifting the charges from the furnace was not sufficient, and resulted in a partial inversion of the phases. Commercial clinker certainly cools more slowly than these small laboratory charges. Furthermore, the alkali content of clinker is considerably lower than that of these experimental preparations. Therefore, it is probable that in portland cement clinker and in most laboratory preparations the conditions of composition and of cooling have not been favorable for the preservation of the  $\alpha$ - $2\text{CaO} \cdot \text{SiO}_2$  solid solutions which exist at high temperatures.

From the present investigation it appears that a considerably greater percentage of  $\text{Na}_2\text{O}$  than is customarily found in commercial clinker is necessary to insure the retention of the  $\alpha$ - $2\text{CaO} \cdot \text{SiO}_2$  structure under prevailing rates of cooling. Although the ratio of  $\text{Na}_2\text{O}$  to calculated  $2\text{CaO} \cdot \text{SiO}_2$  may be appreciable in some clinkers, experimental results indicate that aside from the cooling rate the retention of the  $\alpha$  form does not depend upon this ratio as much as upon the over-all concentration of  $\text{Na}_2\text{O}$  in the mixture. However, these results do not preclude the preservation of  $\alpha$ - $2\text{CaO} \cdot \text{SiO}_2$  in portland cement clinker by components other than  $\text{Na}_2\text{O}$ . It may possibly be found that the combined effect of minor oxides, such as the alkalies,  $\text{P}_2\text{O}_5$ ,  $\text{TiO}_2$ , and  $\text{FeO}$ , is sufficient to bring this about under conditions of quick cooling.

The percentages of  $\text{Na}_2\text{O}$  reported as present, after heating, in the preparations described in this paper were determined by chemical analysis. However, it is not known how much  $\text{Na}_2\text{O}$  actually enters the crystal lattice in either of the two solid solution phases. It is quite certain that both  $\text{Na}_2\text{O}$  and  $\text{Fe}_2\text{O}_3$  in the one case, and  $\text{Na}_2\text{O}$  and  $\text{Al}_2\text{O}_3$  in the other, enter into the high-temperature form of  $2\text{CaO} \cdot \text{SiO}_2$ , but the ratios in which they are taken up are not easily determined. The inclusions resulting from precipitation are very fine-grained and are surrounded by the crystalline matrix, so that analysis by optical means is extremely difficult.

There is evidence that oxides and combinations of oxides other than those for which data are given may pass into solid solution in  $\alpha$ - $2\text{CaO} \cdot \text{SiO}_2$ . Preliminary experiments show that  $\text{K}_2\text{O}$  and  $\text{Fe}_2\text{O}_3$  added in certain proportions will preserve the  $\alpha$  structure and it is probable, though not certain, that  $\text{K}_2\text{O}$  and  $\text{Al}_2\text{O}_3$  can accomplish the same result. Complexly twinned grains of  $2\text{CaO} \cdot \text{SiO}_2$  have been observed in the system  $\text{Na}_2\text{O}$ - $\text{CaO}$ - $\text{SiO}_2$  by the writer and also by Taylor, of this laboratory. These grains give the diffraction pattern of  $\beta$ - $2\text{CaO} \cdot \text{SiO}_2$ , but the writer believes that at high temperatures they were in the  $\alpha$  state and that there existed at least a small amount of solid solution. Apparently the inversion cannot be prevented by quenching with

only these three components present. The degree of solid solution which may occur in  $\beta$ - $2\text{CaO} \cdot \text{SiO}_2$  is also of importance in the study of the oxide systems of cement. The data presented in this paper show that for the compositions investigated, at least, this solid solution is much less than in the higher-temperature, or  $\alpha$  form. The exact amount in any particular case is difficult to determine, but quenching experiments with examination for glass have indicated that in the system  $\text{Na}_2\text{O} \cdot \text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$  it is very small, probably less than 2 percent of  $\text{Na}_2\text{O}$  and  $\text{Al}_2\text{O}_3$  combined. A slight lowering of the indices of refraction of  $\beta$ - $2\text{CaO} \cdot \text{SiO}_2$  has been observed, and seems to be due largely to the influence of the  $\text{Na}_2\text{O}$ . X-ray diffraction patterns have shown small shifts in some of the lines, but scarcely more than the variation to be expected from experimental error.

The industrial significance of the information presented in this paper lies mainly in the value which it may have in better understanding the structure of portland cement clinker. Investigators have recognized that  $2\text{CaO} \cdot \text{SiO}_2$  varies in appearance and properties in different clinkers, and even in different samples of the same clinker. Classifications of the  $2\text{CaO} \cdot \text{SiO}_2$  into types have been made on the basis of its microscopic appearance in polished and etched specimens of clinker [5, 7, 8]. The formation of these types is dependent, among other factors, upon the conditions of heating and cooling, as well as upon the chemical composition, and it is reasonable to expect that future studies on the structure of clinker will result in the correlation of the data concerning the observed types of  $2\text{CaO} \cdot \text{SiO}_2$  with the solid solution and  $\alpha$ - $\beta$  inversion relationships as determined on laboratory preparations.

It is also possible that these results may help to explain the greater difficulty of bringing about the combination of  $\text{CaO}$  with the other components in clinkers high in alkalis. Taylor [12] has discussed this matter in connection with the potash systems of cement. If  $2\text{CaO} \cdot \text{SiO}_2$  solid solutions containing  $\text{Na}_2\text{O}$  or  $\text{K}_2\text{O}$  are formed in clinker, the tendency to react with  $\text{CaO}$  to produce  $3\text{CaO} \cdot \text{SiO}_2$  may be considerably affected. It is possible that the  $\alpha$  form of  $2\text{CaO} \cdot \text{SiO}_2$  may behave quite differently from the  $\beta$  as regards its reactivity with  $\text{CaO}$ , just as  $\beta$ - and  $\gamma$ - $2\text{CaO} \cdot \text{SiO}_2$  have different rates of hydration. Thus far there are no experimental data on this point.

#### IV. SUMMARY

X-ray diffraction, optical, and thermal data are presented as evidence that at high temperatures  $2\text{CaO} \cdot \text{SiO}_2$  forms, with  $\text{Na}_2\text{O}$  and  $\text{Al}_2\text{O}_3$  and with  $\text{Na}_2\text{O}$  and  $\text{Fe}_2\text{O}_3$ , solid solutions which have hexagonal crystal structures. These solid solutions probably possess the fundamental crystal lattice of  $\alpha$ - $2\text{CaO} \cdot \text{SiO}_2$ . The oxides in solid solution preserve the  $\alpha$  form, so that it may be quenched to room temperature.

The  $\alpha$ - $\beta$  inversion temperature of the crystalline phases described in this paper was lowered to a minimum of about  $1,175^\circ$  to  $1,180^\circ \text{C}$ . Accompanying the inversion to  $\beta$ - $2\text{CaO} \cdot \text{SiO}_2$  is the precipitation of much of the material held in solid solution in the  $\alpha$  form. In the case of the preparations containing both  $\text{Na}_2\text{O}$  and  $\text{Al}_2\text{O}_3$ , there appears to be an inversion interval over which both modifications may exist in equilibrium. A possible explanation is given on the basis of the solid-solution relations.

Data are given to support the view that complex twinning in  $2\text{CaO} \cdot \text{SiO}_2$ , as observed in laboratory charges and in portland cement clinker, is evidence that the inversion from the  $\alpha$  to the  $\beta$  modification has already taken place.

It is concluded from optical and X-ray data that in the compositions studied in this investigation the amount of solid solution in  $\beta\text{-}2\text{CaO} \cdot \text{SiO}_2$  is very small in comparison with that which may exist in the  $\alpha$  form.

A brief discussion of the industrial significance of the results is given.

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