Study on the X-ray Characteristics of Ca_2SiO_4 with the Single Crystals synthesized and isolated from Portland Cement Clinker

By

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1. Introduction

About the transformation of Ca_2SiO_4 , many investigators have reported on their crystal structures, hydraulic properties and the stabilizing mechanics. But the analyses of the crystal structure were mostly attempted basing on the powder X-ray diffraction in reference to the other crystals that were supposed to be isomorphic to each transformation of Ca_2SiO_4 such as α - and β - K_2SO_4 ^{1,2,3,4)}, and their atomic parameters were proposed as a reliable data⁵⁾. But only on the β -form, Midgley⁶⁾ has decided the atomic parameters by the structural analysis of a single crystal that was synthesized. Douglas⁷⁾ isolated the single crystal of α - and α' -form from the slags and calculated the lattice lengths as a 5.46 Å, c 6.76 Å for the α -form and a 10.91 Å, b 18.41 Å and c 6.76 Å for the α' -form. Bredig, Nurse⁸⁾ and others tried the synthesis of each transformation by substituting several ions for Si or Ca respectively and found that many ions were useful for the stabilization. P, Al, Fe and alkalis act for the α -form, Ba, Mn, Mg, K, Na and P act for the α' -form and almost all of them act for the β -form. But many of these researches on the crystal structure excepting those of Douglas' or Midgley's are based on the structure of K_2SO_4 as mentioned above, and are not based on the really calculated unit cell dimensions.

The authors took notice of these stabilizing actions of each ion and tried to make a unified view about whether those transformations had respectively the same lattice spacings or the same characters irrespective of the sorts of stabilizing ions. And adding to these investigations the phases of Ca_2SiO_4 that had grown in the commercial portland cement clinker were investigated by isolating their single crystals, and their lattice constants and their X-ray characters were investigated in comparison with the synthesized each transformation.

2. Experimental Method

The compositions were prepared from CaCO_3 , silica gel and the stabilizers supposing the substi-

Table 1. The α -, α' - and β -form of Ca_2SiO_4 stabilized by the substituting ions.

Substituting ion	Mixing ratio	Produced phase
α -form		
Ca $\leftarrow$ Ba	$(\text{Ca}_{0.75}\text{Ba}_{0.25})_2\text{SiO}_4$	α , α'
	$(\text{Ca}_{0.70}\text{Ba}_{0.30})_2\text{SiO}_4$	α^*
Si $\leftarrow$ P	$\text{Ca}_2\text{P}_{0.2}\text{Si}_{0.8}\text{O}_4$	α , α' (dil.)
	$\text{Ca}_2\text{P}_{0.2}\text{Si}_{0.7}\text{O}_4$	α^*
Si $\leftarrow$ V	$\text{Ca}_2\text{V}_{0.2}\text{Si}_{0.8}\text{O}_4$	α , α' (dil.)
	$\text{Ca}_2\text{V}_{0.3}\text{Si}_{0.7}\text{O}_4$	α^*
α' -form		
Ca $\leftarrow$ Ba	$(\text{Ca}_{0.95}\text{Ba}_{0.05})_2\text{SiO}_4$	β , α' (dil.)
	$(\text{Ca}_{0.90}\text{Ba}_{0.10})_2\text{SiO}_4$	α'^*
Ca $\leftarrow$ Sr	$(\text{Ca}_{0.95}\text{Sr}_{0.05})_2\text{SiO}_4$	α' , β (bil.)
	$(\text{Ca}_{0.90}\text{Sr}_{0.10})_2\text{SiO}_4$	α'^*
Si $\leftarrow$ B	$\text{Ca}_2\text{B}_{0.15}\text{Si}_{0.85}\text{O}_4$	α'^*
Si $\leftarrow$ P	$\text{Ca}_2\text{P}_{0.15}\text{Si}_{0.85}\text{O}_4$	α'^*
Si $\leftarrow$ V	$\text{Ca}_2\text{V}_{0.15}\text{Si}_{0.85}\text{O}_4$	α'^*
β -form		
Ca $\leftarrow$ Ba	$(\text{Ca}_{0.95}\text{Ba}_{0.05})_2\text{SiO}_4$	β
	$(\text{Ca}_{0.97}\text{Ba}_{0.03})_2\text{SiO}_4$	β^*
	$(\text{Ca}_{0.95}\text{Ba}_{0.05})_2\text{SiO}_4$	β
Ca $\leftarrow$ Sr	$(\text{Ca}_{0.95}\text{Sr}_{0.05})_2\text{SiO}_4$	β , γ (dil.)
	$(\text{Ca}_{0.97}\text{Sr}_{0.03})_2\text{SiO}_4$	β^*
	$(\text{Ca}_{0.95}\text{Sr}_{0.05})_2\text{SiO}_4$	β
Si $\leftarrow$ B	$\text{Ca}_2\text{B}_{0.01}\text{Si}_{0.99}\text{O}_4$	β^*
	$\text{Ca}_2\text{B}_{0.02}\text{Si}_{0.98}\text{O}_4$	β
	$\text{Ca}_2\text{B}_{0.05}\text{Si}_{0.95}\text{O}_4$	β , α' (dil.)
Si $\leftarrow$ Al	$\text{Ca}_2\text{Al}_{0.04}\text{Si}_{0.96}\text{O}_4$	β , γ
	$\text{Ca}_2\text{Al}_{0.06}\text{Si}_{0.94}\text{O}_4$	β^*
	$\text{Ca}_2\text{Al}_{0.08}\text{Si}_{0.92}\text{O}_4$	β
	$\text{Ca}_2\text{Al}_{0.10}\text{Si}_{0.90}\text{O}_4$	β
	$\text{Ca}_2\text{Fe}_{0.02}\text{Si}_{0.98}\text{O}_4$	β , γ
Si $\leftarrow$ Fe	$\text{Ca}_2\text{Fe}_{0.04}\text{Si}_{0.96}\text{O}_4$	β^*
	$\text{Ca}_2\text{Fe}_{0.06}\text{Si}_{0.94}\text{O}_4$	β
	$\text{Ca}_2\text{Fe}_{0.10}\text{Si}_{0.90}\text{O}_4$	β
	$\text{Ca}_2\text{P}_{0.01}\text{Si}_{0.99}\text{O}_4$	β^*
Si $\leftarrow$ P	$\text{Ca}_2\text{P}_{0.02}\text{Si}_{0.98}\text{O}_4$	β , α'
	$\text{Ca}_2\text{V}_{0.02}\text{Si}_{0.98}\text{O}_4$	β^*
Si $\leftarrow$ V	$\text{Ca}_2\text{V}_{0.02}\text{Si}_{0.98}\text{O}_4$	β , α'
	$\text{Ca}_2\text{Cr}_{0.01}\text{Si}_{0.99}\text{O}_4$	β , γ
	$\text{Ca}_2\text{Cr}_{0.02}\text{Si}_{0.98}\text{O}_4$	β , γ

Note: All were quenched from 1500°C.

* Single crystal was isolated.

tution of each stabilizing ion to Ca or Si with the formula $(\text{Ca}_{1-x}\text{M}_x)_2\text{SiO}_4$ or $\text{Ca}_2\text{N}_x\text{Si}_{1-x}\text{O}_4$, and burned at 1500°C for about 1~5 hours in platinum boats in a platinum/rhodium resistance furnace and quenched. Table 1 shows the sorts of the stabilizers, their mixing ratios and the crystal phases after burning. The single crystals were picked up from the samples that were synthesized adding the minimum quantity of stabilizer in each transformation.

The single crystals of Ca_2SiO_4 in the commercial portland cement clinker were also isolated from the coarse crushed clinker as the unique crystal. In most case, this clinker was etched with dilute HCl solution to remove the matrix materials that stuck on the Ca_2SiO_4 crystals.

The X-ray powder diffraction patterns were taken with a Nihon Denshi diffractometer with Ni-filtered $\text{Cu K}\alpha$ radiation. The single crystal analyses were accomplished by Laue method, rotating crystal method and Weissenberg goniometry. The differential thermal analysis and

infrared absorption were carried out to investigate the crystal characteristics of each transformation. Their data were obtained using the Shimadzu model DT-2B (for DTA) and Nihon Bunko model IRG (for infrared absorption).

3. Experiments and Discussions

3.1 Powder X-ray diffraction of α -, α' - and β - Ca_2SiO_4

The quantity of the stabilizers to grow each transformation separately is limited to a narrow substituting range as shown in Table 1. The X-ray diffraction patterns of each transformation are similar one another irrespective of the sort of stabilizer. Fig. 1 shows their patterns and these have been well recognized by many investigators qualitatively.

3.2 Thermal analysis of each transformation

The DTA analyses of the α' - and the β -form were employed to confirm each transformation. Fig. 2 shows the results.

Condition of X-ray diffraction
 X-ray : $\text{Cu K}\alpha$, Filter : Ni, Voltage : 40 kV, Current : 20 mA
 Divergence slit : 1° , Scatter slit : 1° , Receiving slit : 0.2, Time constant : 2 sec, Scanning speed : $1/2^\circ/\text{min}$,
 Chart speed 10 mm/min, Detector : Scintillation counter

Fig. 1. Powder X-ray diffraction patterns of each transformation.

Fig. 2. The inversion temperature of $\beta \rightarrow \alpha'$ and $\alpha' \rightarrow \alpha$ Condition of the DTA analysis.

The inversion temperature of each form into the upper stable form changes by the sorts and the amounts of the substituting ions. If the differences of their ion radii from Ca^{2+} or Si^{4+} are great, the inversion temperature $\alpha' \rightarrow \alpha$ and $\beta \rightarrow \alpha'$ go down greatly. On the stabilizing action of the ions, Dietzel⁹⁾ has reported by fairly reliable explanation that "the stabilization of high temperature stable form is affected by the ratio of the ion radius of cation (Ca^{2+}) to anion ($[\text{SiO}_4]^{4-}$), and when the ion that makes the former bigger or the ion that makes the latter smaller is substituted respectively, the high temperature stable phases are easily formed". In our experiments, the actions of Ba and Sr or V, P and B on the α - or the α' -form conforms to this theory, thus the inversion temperature goes down in proportion to the difference between the ion radius of Ca and that of Ba or Sr and the difference between the ion radius of Si and that of V, P or B.

On the β -form all of these ions and others serve for the stabilization and the changes of the inversion temperature of $\beta \rightarrow \alpha'$ nearly correspond to Dietzel's theory but not correctly exact. This may be explained by the physical stabilizing action of liquid that surround the β -crystal, adding to the action of the substitution of the stabilizing ion.

The phases arose by the inversion were investigated by the high temperature X-ray diffraction expecting the exact confirmation of their transformations before or after the inversion.

The energy changes involved in the $\beta \rightarrow \alpha'$ and $\alpha' \rightarrow \alpha$ inversions were measured by the quantitative differential thermal analysis. The heat of transformation is proportional to peak areas and the

Table 2. Heats of the inversion $\beta \rightarrow \alpha'$ and $\alpha' \rightarrow \alpha$.

Sample	Stabilizing ion and its substituting mole for 1 mole of Ca_2SiO_4	Phase components	Temperature of transformation (beginning of the signal during heating, $^\circ\text{C}$)	Heat of transformation*	
				cal/g	cal/mole
Ca←Ba	(0.01 mole) β		612	1.8	313
	(0.03 mole) β		590	1.6	284
	(0.05 mole) β		566	1.5	272
Ca←Sr	(0.01 mole) β, γ (dil.)		637	1.8	311
	(0.03 mole) β		622	1.7	297
	(0.05 mole) β		613	1.4	247
Si←B	(0.01 mole) β		547	1.4	240
	(0.02 mole) β		534	1.5	257
Si←Al	(0.06 mole) β		679	1.7	292
	(0.10 mole) β		674	1.7	292
Si←Fe	(0.04 mole) β		670	1.1	190
	(0.01 mole) β		655	1.0	174
Si←V	(0.01 mole) β		657	2.1	362
Si←P	(0.01 mole) β		624	1.9	327
Ca←Ba	(0.07 mole) β, α' (dil.)		1256	0.4	74
	(0.10 mole) α'		1245	3.2	613
Ca←Sr	(0.07 mole) α', β (dil.)		1284	3.0	536
	(0.10 mole) α'		1276	3.4	617
Si←B	(0.15 mole) α'		1213	2.6	441
Si←V	(0.15 mole) α'		1314	3.3	579
Si←P	(0.15 mole) α'		1326	3.5	604

* These were calculated from the area of the peaks in comparison with the area of the peak obtained in $\alpha \rightarrow \beta$ quartz transition (2.4 cal/g) and CaCO_3 dissociation (410 cal/g)¹⁵⁾. CaCO_3 dissociation was used for the confirmation of the invariable sensitivity according to the change of the inversion temperature.

quartz and CaCO_3 were used as standards for the determination of the energy. In all samples the heat of transformation of $\alpha' \rightarrow \alpha$ is greater than that of $\beta \rightarrow \alpha'$, the latter is weak and smaller than the $\alpha \rightarrow \beta$ transformation of quartz (2.4 cal/g), but the quantitative change of heat according to the Dietzel's theory was not systematically observed. The results are shown in Table 2. These results make us suppose that the crystal structure of the α -form is very different from the structures of the α' and β -form. This agrees with many studies suggesting the same results. The most recent work on this point is proposed by Yamaguchi, Ono, Kawamura and Soda¹⁰⁾. They investigated that the peak $\alpha \rightarrow \alpha'$ is sharp and the area is greater but the peak area of $\beta \rightarrow \alpha'$ is smaller. Thus they explained that the difference between the crystal structures of β and α' is smaller while that of α' and α is considerably greater. The same observation was reported by Nurse explaining that "a large and sharply-defined thermal effect denotes the inversion from α' to α On cooling, the formation of β at 670°C is marked by a small but fairly well-defined thermal arrest".

3.3 Infra-red absorption

The use of infra-red absorption spectrometry is also useful to confirm the difference of each transformation. Fig. 3 shows the results.

Fig. 3. Infra-red absorption spectra for the α -, α' - and β -form (KBr pellet technique).

The great difference of the infra-red absorption between α - and α' -form is characterized by the absorption of α -form at $1400\sim 1500\text{ cm}^{-1}$. The characteristic difference between α' - and β -form is not clearly recognized. In both forms the bands at $800\sim 1000\text{ cm}^{-1}$ and at 500 cm^{-1} are divided respectively into three close absorptions. These characteristics in each form are quite similar to one another without regard to the differences of the substituting ion and the substituting type to Ca or to Si. Thus the difference of the absorption is perhaps only affected by the differences of the crystal structure of α -, α' - and β -form.

3.4 X-ray diffraction of each transformation

3.4.1 The α - Ca_2SiO_4 phase synthesized

This phase is synthesized by substituting fairly great quantity of Ba to Ca or P and V to Si respectively and quenching from 1500°C . They had the continuous solubilities with the pure α -form, and this was confirmed by the high temperature X-ray diffraction and DTA analysis. The diffraction patterns of them at high temperature about 1450°C were similar to the pure α -form and the remarkable change of diffraction angles such as to show the discontinuous solubility with the pure α -form was not observed. In the DTA analysis the temperature of endothermic reaction falls continuously in proportion to the quantity of stabilizer. Fig. 1 shows the X-ray diffraction

pattern of α - Ca_2SiO_4 phase stabilized by P and the high temperature diffraction pattern of pure α - Ca_2SiO_4 at 1470°C .

3.4.2 The α' - Ca_2SiO_4 phase synthesized

This phase is synthesized by substituting far small quantity of stabilizer. Ba, Sr, V, P and B are useful to stabilize this phase and the diffraction patterns of them are quite similar to that of pure α' -form of the high temperature X-ray diffraction.

3.4.3 X-ray investigation of the single crystal

The α - and α' -form crystallize as the fairly large crystal by heating at 1500°C for about 4 hours. These products were pulverized softly and the single crystals with about $120\sim 180\text{ }\mu$ size were picked up in the irregular shape. The α' -form is optically biaxial and the Laue's symmetries along two axes as orthorhombic are with crossed mirror planes and along the other axis is 6-fold. The α -form is optically uniaxial and the Laue's symmetries along c -axis as hexagonal is 6-fold. The lattice lengths of α' -form were decided by rotating and Weissenberg methods, thus a - and b -axes are two times as long as those in Trömel¹¹⁾ or Bredig's data and closely similar to Douglas' data as shown in Table 5. Douglas investigated that his α' -form (bredigite) considerably coincides with the α' -form synthesized by Rait and Goldschmidt¹²⁾ but shows some difference in the powder photographs of Trömel or Bredig. This structural difference, he presumed, is not due to the presence of metallic elements other than Ca in bredigite. And with the fact that the a and b dimensions are approximately twice those given by Bredig, he explained that the dimensions for bredigite were obtained from the single crystal photographs, while those for α' - Ca_2SiO_4 were obtained from powder photographs, and perhaps this comes from the fact that the single crystal photographs show that the intensities of reflections with h and k odd are weaker than those with h and k even, and thus the powder lines corresponding to the former reflections might not have been detected. He concluded that this difference of bredigite from Trömel's data or the pure α' - Ca_2SiO_4 must be clarified hereafter. On this point the authors investigated by the powder X-ray diffraction and with the Weissenberg photographs. On the Weissenberg photographs the diffraction patterns with h and k odd are observed, and on the powder diffraction the pattern (152) gives the clear proof of the author's lattice dimensions. The other patterns with h and k odd is not observed because of their weak reflections and their overlaps above the patterns with h and k even. This was also recognized in the high temperature diffraction pattern of pure Ca_2SiO_4 at the temperature range up to 1370°C . This is the

one form of Ca_2SiO_4 that Regourd¹³⁾ discovered. She recognized two forms of α' - Ca_2SiO_4 : the low temperature stable form α'_l and the high temperature stable form α'_h . The former corresponds to our α' -form, and perhaps coincides with Douglas' α' - Ca_2SiO_4 from the slag.

The space group of the α' -form was already decided as $Cmc2_1$ by Yamaguchi and Suzuki in the 5th international symposium on the chemistry of cement which was held in Tokyo¹⁴⁾. The proof for this decision came from two points, one was from the extinction of the reciprocal lattice projections and the other came from the assumption of piling two α' -structures of Trömel or Bredig's toward a - and b -axes. In this piling the slight distortion or shift of any Ca ion or SiO_4 tetrahedra such as makes two times of lattice intervals may need but the exact analysis of this crystal structure needs far more precise investigations.

While the crystal system of α -form is supposed as hexagonal because of fully exact 6-fold symmetry of c -axis in Laue photograph and of the uniaxial extinction under the crossed nicols. The extinction of the reflection is only seen in $hh2\bar{h}l$ when l is odd and the space group belongs perhaps to $P6mm$. The single crystals used for Laue's diffraction were picked up from the uniform crystal phases that were stabilized by V, P and Ba respectively, and these phases showed the similar powder X-ray diffraction patterns as the α -form and have their continuous solubilities with the pure α - Ca_2SiO_4 under the high temperature X-ray diffraction and DTA analysis. These are the proofs to make us suppose that the α -form is hexagonal. But in many past reports its space group was suggested as trigonal ($P\bar{3}m1$). The first investigation that offered this suggestion was carried out by Bredig²⁾. He stated on a comparison of X-ray powder patterns, that the crystal structure of α - Ca_2SiO_4 is similar to that of glaserite, $\text{K}_3\text{Na}(\text{SO}_4)_2$, and thus this phase has a trigonal unit cell identical with that of glaserite.

Then to satisfy our space group the atomic parameters must be reinvestigated. When we try to draw the unit cell of α -form from the structure of α' -form, the crystal system of the α -form necessarily becomes trigonal with the symmetry $\bar{3}$. This is easily understood from Midgley's diagrammatic projection that shows the relation among the α -, α' - and β -form. But to make the hexagonal crystal the packing of Ca and SiO_4 tetrahedra must be fairly changed. This change is guessed by the great difference of the infrared absorption spectra of the α -form from those of the α' - or β -form and by the difference of the Laue photographs between the α - and α' -crystals.

This is also understood by Nurse's investigation that the inversion $\alpha' \rightarrow \alpha$ at 1447°C or $\alpha \rightarrow \alpha'$ at 1425°C is denoted by a large and sharply defined thermal effect. This coincides also to our results of DTA analysis as above mentioned.

On the substitution of the stabilizing ions for the α - or α' -form, it is very difficult to investi-

Table 3. Powder X-ray diffraction data of α - Ca_2SiO_4 phase stabilized by P.
 $a=5.401 \text{ \AA}$ $c=7.144 \text{ \AA}$ Hexagonal

h	k	l	Observed		Calculated $d \text{ (\AA)}$
			$d \text{ (\AA)}$	I	
0	1	1	3.92	23	3.913
0	1	2	2.839	85	2.839
1	1	0	2.700	100	2.700
0	2	0			2.339*
0	2	1	2.219	19	2.223
1	1	2			2.154*
0	2	2	1.955	29	1.957

* Observed in the Weissenberg photograph as the weak pattern.

Table 4. Powder X-ray diffraction data of α' - Ca_2SiO_4 stabilized by Sr.
 $a=11.091 \text{ \AA}$ $b=18.683 \text{ \AA}$ $c=6.829 \text{ \AA}$ Orthorhombic

h	k	l	Observed		Calculated $d \text{ (\AA)}$
			$d \text{ (\AA)}$	I	
2	2	0			4.769*
0	4	0	4.66	4	4.671
1	5	1			4.250*
2	2	1			3.910*
0	4	1			3.855*
0	0	2	3.42	2	3.415
1	1	2	3.21	2	3.215
0	2	2			3.207
2	4	1	3.17	15	3.166
2	0	2	2.907	10	2.908
1	3	2	2.893	5	2.891
0	6	1	2.837	7	2.833
2	2	2	2.776	75	2.776
4	0	0	2.773	95	2.773
0	4	2			2.757
2	6	0	2.715	100	2.715
1	5	2	2.460	4	2.458
4	4	0	2.384	8	2.384
3	6	0			2.382
0	6	2	2.301	15	2.301
4	4	1	2.249	17	2.251
3	6	1			2.249
1	1	3	2.213	19	2.214
0	2	3			2.212
0	8	1	2.212	24	2.210
2	6	2			2.125*
4	2	2	2.098	7	2.098
2	2	3	2.054	5	2.054
2	8	1			2.053
0	4	3	2.049	9	2.046
3	8	0	1.977	7	1.974
4	4	2	1.955	15	1.955
3	6	2			1.953
0	8	2	1.931	3	1.928

* Observed in the Weissenberg photograph as the weak pattern.

α -form
stabilized by V.

α' -form
picked up from the clinker
(Synthesized α' -form shows the same photograph).

X-ray condition : Target W, 35 kV, 15mA, $D=5$ cm Radiation time : 2 hours

Fig. 4. Laue photographs of the α - and α' -form along c -axis.

gate whether this substitution is caused to the particular position or to the random position of Ca or Si. To make this problem clear, it is need to investigate the difference between the structural factors calculated and observed. But for this purpose the atomic parameters must be decided with a fairly good reliability. While the great change of the axial ratios may be also caused by the substitution for the special position, but in our experiment the change to acknowledge this substitution was not clearly observed. And also the change of the intensities of high order diffraction patterns arose by the scattering power of each substituting ion is not observed clearly even by the measurement with a microphotometer. We are now trying to investigate these problem and to decide the new atomic parameters of α - and α' -form by the single crystal analysis. But these will be left behind for another report. The diffraction data of α - and α' -form stabilized by P and Sr respectively are listed on Table 3 and 4 and Laue photograph of α -form that shows the 6-fold symmetry is listed in Fig. 4 in comparison with that of α' -form.

3.4.4 The α' - Ca_2SiO_4 phase in the portland cement clinker The Ca_2SiO_4 phase in the clinker grows chiefly into the β -form in process of burning, but the higher temperature stable form α or α' may grow by the elongation of the burning hours. The authors isolated the single crystals different from the β -form or Alite phase out of the clinker that was experimentally reheated in the electric furnace at 1450°C about 6 hours and

quenched. The number of these crystals is very few and we picked up only five or six pieces of it from about 100 pieces of β -crystal having the irregular shape with about $100\sim 150\ \mu$ diameter. The extinction under the crossed nicols is uniform and biaxial, and the refracting index is nearly same to α' -form synthesized. The diffraction patterns of Laue or Weissenberg photographs and the periodicities of a -, b - and c -axes calculated from them are also same each other to the synthesized α' -form. Thus it is not so difficult to suppose that this crystal from the clinker is structurally all the same crystal with α' -form we have synthesized. The lattice lengths of these α' -form calculated from the rotation photographs and the optical data are shown in Table 5.

Table 5. Lattice lengths of the α' -form and the optical data.

Sample	Lattice length ($\text{\AA}$)			Crystal system	Index of refraction		
	a	b	c		α	β	γ
Single crystal from the portland cement clinker	10.98	18.61	6.82	biaxial (positive)	1.702	1.706	1.726
α' -form synthesized							
substituting Ba for Ca	11.07	18.80	6.85	biaxial (positive)	1.722	1.725	1.736
substituting Sr for Ca	11.02	18.69	6.83	biaxial (positive)	1.718	1.722	1.738
substituting B for Si	10.93	18.41	6.85	biaxial (positive)	1.608	1.683	1.704
α' -form							
by Tromel	5.30	9.55	6.78				
by Bredig	5.20	9.20	6.78				
by Douglas	10.91	18.41	6.76

β -form
stabilized by Al.

β -form
picked up from the clinker.

X-ray condition : Target W, 35 kV, 15 mA, $D=5$ cm Radiation time : 2 hours

Fig. 5. Laue photographs of the axis of 2-fold symmetry.

β -form
stabilized by Al.

β -form
picked up from the clinker.

X-ray condition : Cu K_{α} , Ni filter, 40 kV, 20 mA Radiation time : 100 hours

Fig. 6. Weissenberg zero-layer photographs about the monoclinic b -axis.

3.4.5 The β - Ca_2SiO_4 synthesized by the stabilizers

This form is stabilized by many sorts of stabilizers as shown in Table 1. The Laue photographs along a - and c -axes are fairly similar respectively to a - and b -axes of α' -form, but the axis that corresponds to c -axis of α - or α' -form (6-fold symmetry axis) becomes to show the 2-fold symmetry by the slight change of the diffraction intensity. But the difference of Laue photograph between the α' - and β -form is comparatively smaller than the difference between the α - and α' -form.

While the energy change involved in the $\beta \rightarrow \alpha'$ inversion is also smaller than that in the $\alpha' \rightarrow \alpha$ inversion as shown in Table 2 and described before. These give us the reasonable suggestion that the crystal structure of the β -form is quite similar to the α' -form, thus the β -structure involves only a slight distortion of the α' -structure and a slight re-arrangements will produce the plausible β - and α' -structure. However, a larger distortion is required to produce the hexagonal α -structure from the orthorhombic α' -crystal as mentioned before. The characteristic as the twin seems on each divided pattern of the Weissenberg photographs, and the relative intensities of all patterns don't greatly change by the sort of the stabilizer that acts on the β -crystal. Fig. 5 shows the axis of 2-fold symmetry of the β -form stabilized by Al, and Fig. 6 shows its Weissenberg zero-layer photograph about this axis. Optically all of the crystal are biaxial. The lattice lengths of a - and c -axes measured by rotating crystal method are two times as long as those of Midgley's data and the diffraction patterns of each layer are fairly sharp and don't show the characteristics as the super lattice. The crystal structure of this form must be henceforth reinvestigated basing on the new conditions that these new periodicities of a - and c -axes are intrinsically inherent dimensions non affected by the impurities and that the space group may change to suit the new extinction. Table 6 shows the diffraction data of this form stabilized by Al.

3.4.6 The β -form in the portland cement clinker

The β -form grows into fairly great uniform crystal as the most commonly produced transformation in the portland cement clinker. The authors picked up this crystal easily from the clinker that was coarse crushed and was etched by dilute acid for a short time. These

Table 6. Powder X-ray diffraction data of β - Ca_2SiO_4 stabilized by Al.

$a=11.067 \text{ \AA}$ $b=6.746 \text{ \AA}$ $c=18.575 \text{ \AA}$ $\beta=94.40^\circ$ Monoclinic									
h	k	l	Observed		Calculated	h	k	l	Calculated
			$d(\text{\AA})$	I				$d(\text{\AA})$	I
2	0	2	4.90	10	4.908	1	1	7	2.368*
0	0	4	4.36	15	4.630	3	1	5	2.375
2	0	2			4.588	0	0	8	2.315
2	1	2	4.00	7	3.969	4	1	4	2.306
0	1	4	3.82	15	3.817	4	0	4	2.294
2	1	2	3.81	12	3.794	0	2	6	2.277
0	2	0	3.38	12	3.373	1	3	1	2.192
2	1	4	3.24	12	3.237	0	1	8	2.190
3	1	1	3.21	5	3.218	0	3	2	2.185
1	2	1	3.19	5	3.190	1	3	1	2.184
1	1	5	3.17	5	3.173	4	1	4	2.172
0	2	2			3.169	2	2	6	2.148*
1	2	1	3.04	12	3.166	4	2	0	2.135
2	1	4			3.050	3	2	5	2.116
3	1	3	2.973	4	2.944	4	2	2	2.108
1	2	3	2.896	7	2.886	5	1	0	2.098
2	2	0	2.878	20	2.878	2	1	8	2.087
0	1	6	2.813	15	2.807	1	3	3	2.085
2	0	6	2.791	70	2.786	2	3	0	2.082*
3	1	3	2.787	70	2.786	1	3	3	2.065
2	2	2	2.782	70	2.780	2	2	6	2.064
4	0	0	2.748	100	2.759	4	2	2	2.053
0	2	4	2.729	35	2.726	2	3	2	2.050
2	2	2	2.720	30	2.717	4	1	6	2.045
2	0	6	2.610	40	2.610	1	2	7	2.028
2	1	6	2.544	15	2.575*	0	3	4	2.023
4	1	0			2.553	2	3	2	2.021
4	1	2	2.518	10	2.508	3	2	5	2.018
2	2	4	2.471	5	2.489*	2	1	8	1.986
1	2	5			2.460	4	2	4	1.984
4	0	4	2.452	20	2.454	0	2	8	1.913
1	1	7			2.441	1	3	5	1.911
2	1	6	2.416	10	2.434*	4	1	6	1.904
4	1	2			2.418	4	2	4	1.895
2	2	4	2.409	15	2.401	1	3	5	1.885

* Observed in the Weissenberg photograph as the weak pattern.

single crystals have the big sized irregular shapes of about 150~200 μ and optically biaxial. The extinction is uniform and noncrystalline (liquidus) phase does not adhere on it. The Laue photographs and the lattice periodicities from the rotation photographs are same each other to those of synthesized. The diffraction characteristic of the Weissenberg photographs and the intensity of each corresponding diffraction spots are all quite

Table 7. Lattice constants of the β -form calculated from the rotation and Weissenberg photographs.

Sample	Lattice constant			
	a ($\text{\AA}$)	b ($\text{\AA}$)	c ($\text{\AA}$)	β ($^\circ$)
Single crystal from the portland cement clinker	10.98	6.69	18.52	94 $^\circ$
β -form stabilized by Al	11.00	6.71	18.58	94 $^\circ$
stabilized by Fe	11.09	6.75	18.59	94 $^\circ$
Midgley's β -form	5.48	6.76	9.28	94.5 $^\circ$

similar respectively to those synthesized. These show that their crystals have the same crystal structure to those β -crystals synthesized, without regard to the stabilizing matters that are contained in the clinker such as Al, Fe, Mg, alkalis and etc.. The ion Ca^{2+} or Si^{4+} may be perhaps substituted at random positions by the stabilizing ions and not at the special position. But the highly developed investigation must be done by comparing the intensities of the patterns of high order diffraction to analyze the crystal structure and to ascertain this random substitution. This must be also ascertained for the α - and α' -form. Table 7 shows the lattice constants of the β -form synthesized or isolated from the portland cement clinker. Laue and Weissenberg photographs of the β -form from the clinker are shown in Fig. 5 and Fig. 6 comparing with the β -form synthesized.

4. Conclusion

We investigated the X-ray characteristic of the Ca_2SiO_4 transformations α , α' and β with their single crystals synthesized by the stabilizers.

1) The α -form is stabilized at room temperature by substituting Ba (for Ca), V or P (for Si) in fairly quantities. These are biaxial crystals and their c -axes have 6-fold symmetry as hexagonal, and these forms have continuous solubilities with pure α - Ca_2SiO_4 at high temperature. The substituting ions act for Ca^{2+} to make this position big and for Si^{4+} to make small, thus their action agrees with the Dietzel's theory.

2) The α' -form has the lattice constants with the similar periodicity to those of Douglas' α' -forms isolated from slag, and the stabilization by Ba, Sr, B, V and P takes place with the same substituting manner to those for α -form. This α' -form corresponds to the low temperature stable α' -form by Regourd.

3) The β -form synthesized by many sorts of

stabilizers has the lattice lengths of two times as long as Midgley's α - and c -axes. The twin characteristic is observed in the Weissenberg photographs, and the axis of 2-fold symmetry is confirmed by the Laue photographs with a slight change of the diffraction intensities from the axis of 6-fold symmetry in the α - or α' -form.

4) The α' - and β -form isolated from the portland cement clinker perhaps have the same crystal structure with those synthesized respectively. This was ascertained by the Laue and Weissenberg photographs and optical observations. In all of their investigations they proposed the results exactly similar to the synthesized α' - and β -form respectively.

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[Received August 27, 1970]

合成 Ca_2SiO_4 およびクリンカー中の Ca_2SiO_4 の

単結晶による X 線回折

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Ca_2SiO_4 の変態である α , α' および β 型について適当な安定剤を用いて単結晶を合成し、ラウエ工法、ワイセンベルグ法等によりその回折上の特徴から、これらの結晶の特質を検討した。

α 型は 6 回対称ラウエ写真から六方格子と考えられ、Bredig による glaserite と同形の三方格子とは大きくことなっている。著者らが合成したものは V, P, Ba などの安定剤をかなり多く置換しなければならないが、こ

れらは高温 X 線回折によると純粋な α - Ca_2SiO_4 と連続的な固溶関係をもつ。P を置換した α 型結晶相の格子の大きさは $a=5.401 \text{ \AA}$, $c=7.144 \text{ \AA}$ であった。

Ba, Sr, B, V その他により合成した α' 型は, Douglas がスラグから採取したものと同周期の軸長をもつ。著者らはこれが単位格子として最小の大きさであることを確認し, その空間群は $\text{Cmc}2_1$ であった。クリンカー中の α' 型結晶も合成物と全く同様な X 線回折を示し, 同様な構造であることを認めた。Sr により合成した α' 型の格子の大きさは $a=11.091 \text{ \AA}$, $b=18.683 \text{ \AA}$, $c=6.829 \text{ \AA}$ であった。

β 型は多くの安定剤により簡単に合成できる。これらも Midgley が合成単結晶を用いて結晶解析を行なった

ものとはことなり, a , c 軸が 2 倍の周期をもち, またこれはクリンカー中の β 型についても全く同様であった。Al により安定化した β 型の格子恒数は $a=11.067 \text{ \AA}$, $b=6.746 \text{ \AA}$, $c=18.575 \text{ \AA}$; $\beta=94.40^\circ$ であった。

α , α' 間の構造上の相違は β , α' 間の相違よりも大きいことが推察された。これは示差熱分析による前者のより大きな熱変化と, ラウエ写真, 赤外吸収スペクトルの前者の大きな相違により考えられた。

β , α' 間のウラエ写真は β の 2 回軸生成のためのわずかな回折点強度の相違が見られるのみで, 相互のごくわずかな格子の変移により小さな熱変化をともなって移行できると考えられた。

[8/27/1970 受付]