X-Ray Investigation of Single Crystals of β-Ca$_2$SiO$_4$ (Larnite) at High Temperatures

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Abstract

New data on the polymorphism of Ca$_2$SiO$_4$ have been obtained by single crystal heating experiments. Verneuil-grown crystals of β-Ca$_2$SiO$_4$ (= larnite) were heated up to 1450°C to examine the transformation mechanism. The transformation series $\beta \leftrightarrow \alpha'_L \leftrightarrow \alpha'_H \leftrightarrow \alpha$ is displacive and related to a twin geometry. In the α'_L-range a superstructure along the c axis could be observed. A tilt mechanism of the SiO$_4$-tetrahedra may account for the formation of this superstructure similar to that found in the Ca$_2$SiO$_4$–Ca$_3$(PO$_4$)$_2$ solid solution series.

Introduction

The polymorphism of Ca$_2$SiO$_4$ has been studied extensively in recent years. Lehmann, Niesel, and Thormann (1969) have given a comprehensive summary of previous work. An orthorhombic phase, γ-Ca$_2$SiO$_4$, (*Pmnb*) is stable at room temperature but on heating changes to another orthorhombic phase (*Pmnn*) denoted as α'-Ca$_2$SiO$_4$. Niesel and Thormann (1967) and Regourd *et al* (1968) demonstrated the existence of two α forms: α'_L (low *Pcmn*) $\leftrightarrow$ α'_H (high *Pcmn*) with transition at 1160°C. Further heating to 1450°C produces hexagonal α-Ca$_2$SiO$_4$ (*P6$_3$mc*). On cooling, monoclinic β-Ca$_2$SiO$_4$ (larnite, *P2$_1$/n*) appears at 670°C and is considered a metastable phase. Cooling to room temperature may result in conversion to the stable γ-Ca$_2$SiO$_4$. This conversion can be prevented by small amounts of so-called "stabilizers."

Extensive investigations on the effect of impurities were carried out by Newman and Wells (1946). Moreover Saalfeld (1967) was able to show that the presence of water vapor during heating also stabilizes the β-Ca$_2$SiO$_4$ structure. X-ray investigations of single crystals revealed a twin geometry suggesting the displacive character of the transformation series $\beta \leftrightarrow \alpha' \leftrightarrow \alpha$.

In order to investigate the transformation mechanism, it is necessary to hold single crystals at different temperatures during the X-ray diffraction experiments.

Experimental

Crystals large enough for the investigation were grown by the Verneuil method, and experimental details have been published previously (Saalfeld, 1971). To prevent the $\beta \rightarrow \gamma$ transition, 1-2 mole percent of Ca$_3$(PO$_4$)$_2$ was added. Thin sections of the polycrystalline Verneuil bowl were prepared for electron probe studies. Fragments 0.5 mm long were selected from these thin sections and mounted on top of a thermocouple. This thermocouple simultaneously heated the crystal and measured the temperature. The crystals were investigated by oscillation and Weissenberg techniques at temperatures up to 1450°C.

Results

Chemical Results

Wet-chemical analysis of the bowl material revealed an average content of 0.81 wt percent P$_2$O$_5$, corresponding to 1.77 wt percent Ca$_3$(PO$_4$)$_2$. The P$_2$O$_5$ content is not uniformly distributed in the Verneuil bowl, varying between ± 0.5 wt percent. From the results (Table 1) of two electron probe analyses carried out in the region investigated by X-rays, it can be concluded that 3-4 percent of all tetrahedra are occupied by P.

X-ray Results

In Table 2 crystallographic data for the series $\beta \leftrightarrow \alpha'_L \leftrightarrow \alpha'_H$ are presented. The lattice parameters measured from oscillation and Weissenberg photographs are not of very high accuracy but in general conform with X-ray powder data published by other authors (Regourd *et al*, 1968). At room temperature single crystals of β-Ca$_2$SiO$_4$ exhibit hexagonal and monoclinic twin-geometry due to cooling history. The twin geometry can be described by two

TABLE 1. Electron Probe Analyses of Two Crystals of β-Ca$_2$SiO$_4$

wt percent	1	2
CaO	64.60	64.68
SiO$_2$	34.16	34.27
P$_2$O$_5$	1.29	1.86
Total	100.05	100.81

Atomic Proportions on Basis of 16 Oxygens

Ca	7.90	7.82
Si	3.90	3.87
P	0.12	0.18

twin operations: (a) reflection of the monoclinic cell of β-Ca$_2$SiO$_4$ in (010), (b) 60°-rotations around [001]$_\beta$. The complete twin symmetry is then 6/mmm.

Figure 1a shows an $hk0$ oscillation photograph taken at 650°C. Most reflections belong to β-Ca$_2$SiO$_4$. But weak α'-reflections can be detected between β-twin reflections in the layer lines as indicated between the twin reflections 222_β.

With increasing temperature the monoclinic twin reflections approach a limiting value. This can be explained by reduction of the monoclinic angle γ from 94° to 93°. On further heating the monoclinic reflections abruptly disappear and only the reflections of the α'_L phase are present (Fig. 1b). This suggests a sudden structure change caused by geometrical distortions so that orthorhombic symmetry of α'_L is attained. In the X-ray photographs of the α'_L phase, superstructure reflections are distinctly visible (Fig. 2) between the 121-122 and the 221-222 reflections of α'_L. The superstructure reflections are distributed along the c^*axis so that the unit cell of α'_L (space group: $Pcmn$) has a c axis three times as long as that of the basic cell.

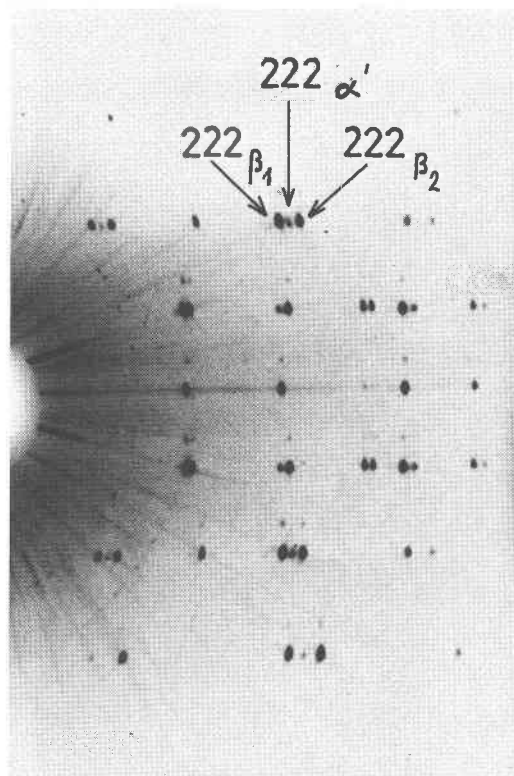Above 1160°C the superstructure reflections disappear, and the α'_H phase exhibits the basic orthorhombic cell with the same space group $Pcmn$. Further transition to the α-modification takes place above 1400°C. At these temperatures there is considerable Pt evaporation from the thermocouple so that the photographs are of inferior quality and for that reason reliable lattice parameters could not be measured. Upon cooling, α-Ca$_2$SiO$_4$ transforms back to the α' and β modifications having the previously mentioned twin geometry.

Fig. 1a. Oscillation photograph ($hk0$) of β-Ca$_2$SiO$_4$ at 650°C. Between twin reflections of the β phase reflections from the α'_L phase appear.

Discussion

These experiments show that the transformations under consideration are displacive and are related to a twin geometry. Ca$_2$SiO$_4$ is a compound containing isolated SiO$_4$-tetrahedra. In the high-temperature α-form the tetrahedra have a hexagonal arrangement with all apices oriented in the same direction (Eysel, 1971). In the α'-modification the tetrahedra have their apices oriented alternately up and down. In the β-modification the tetrahedra are similarly arranged but are tilted with respect to c. The transformations $\beta \leftrightarrow \alpha' \leftrightarrow \alpha$ require appreciable rotation of the tetrahedra, and Eysel and Hahn (1970) consider them

TABLE 2. X-Ray Data of Ca$_2$SiO$_4$ Measured at Different Temperatures*

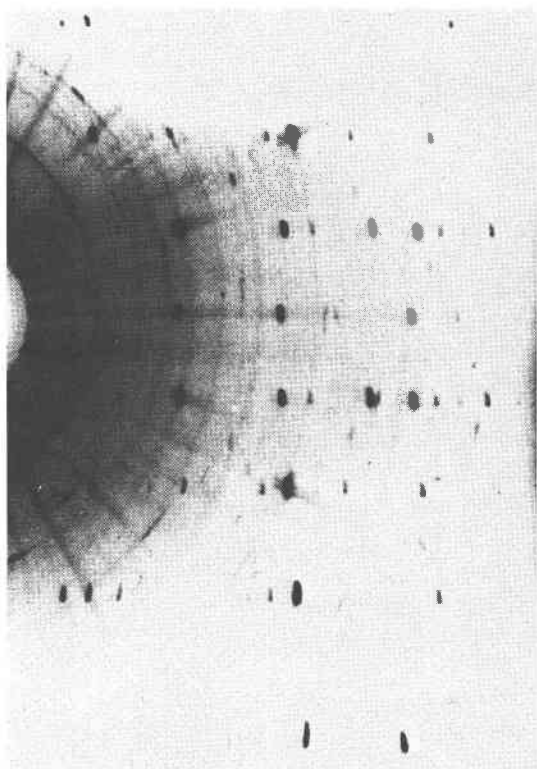| Phase	$\underline{T}^\circ$C	$\underline{a}$(Å)	$\underline{b}$(Å)	$\underline{c}$(Å)	Space Group
β	20	9.34	5.51	6.76	$\underline{P112_1/n}$
		$\gamma = 94.3^\circ$			
α'_L	800	9.41	5.53	6.81x3	$\underline{Pcmn}$
α'_L	1000	9.48	5.59	6.83x3	$\underline{Pcmn}$
α'_L	1200	9.49	5.59	6.85	$\underline{Pcmn}$

*Setting of the axes as given by Eysel (1971).

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FIG. 1b. Oscillation photograph of the same crystal heated at 900°C. Only reflections of the α'_L phase are present.

FIG. 2. Enlarged section of an oscillation photograph $(0kl)\alpha'_L$ taken at 1000°C. Arrows show the superstructure reflections.

to be "semi-reconstructive." Eysel (1971) has pointed out that such transformations can involve tetrahedral rotations up to 70°, and that the transformation $\alpha \leftrightarrow \alpha'$ must involve such rotations. The single crystal investigation described in this paper confirms the more displacive character of this transformation.

X-ray photographs taken at high temperatures reveal superstructure reflections in the α'_L-phase that disappear in the α'_H-phase. The transformation effects of $\alpha'_L \leftrightarrow \alpha'_H$ are very weak and can be detected by sensitive methods only, as Niesel and Thormann (1967) have shown by DTA measurements. Regourd et al (1968) indexed a powder diagram of a specimen of α'_L that had been heated to 1000°C and proposed a doubling of both a and b axes because otherwise five weak lines could not be indexed. The photographs of heated single crystals, however, show clearly that there is a superstructure in the c direction only. It seems unlikely that this superstructure develops in response to the presence of a small amount of P_2O_5, because the P_2O_5 content does not correspond to a stoichiometry consistent with the observed superstructure. One can assume that pure β-Ca_2SiO_4 on heating will also show a reversible transformation

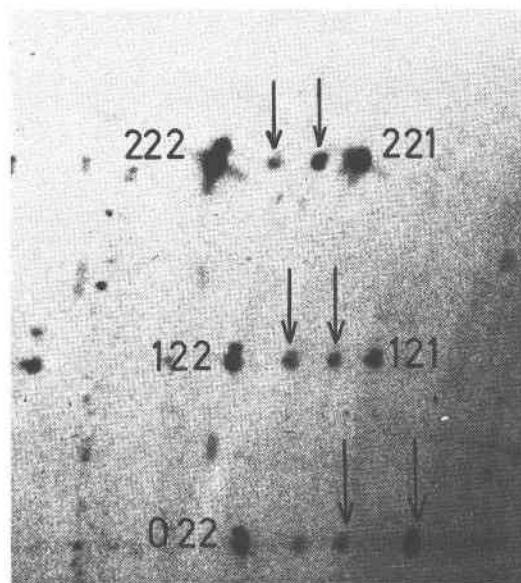involving a similar superstructure. It is not difficult to index at least four of the five powder lines on the basis of the observed superstructure as is demonstrated in Table 3. The very weak reflection 122 respresents an unexplained exception.

The phase diagram of the system Ca_2SiO_4–$Ca_3(PO_4)_2$, revised by Fix, Heymann, and Heinke (1969), shows that with increasing amounts of $Ca_3(PO_4)_2$ the high-temperature forms α' and α of Ca_2SiO_4 can be stabilized at room temperature. X-ray investigations on single crystals of different compositions reveal that the superstructures change with composition (Saalfeld, 1971). Crystal structure determination of the 2:1 compound has been carried out recently in our laboratory and has shown that the superstructure in the c direction is due to tilting of all tetrahedra. It seems likely that the superstructures in Ca_2SiO_4 are also caused by a tilting mechanism.

TABLE 3. α'_L-Ca_2SiO_4 Indexing for Two Different Unit Cells

Regourd (1968) (2a, 2b, c)		This work (a, b, 3c)	
hkl	$d(Å)$	hkl	$d(Å)$
231	3.565	211	3.561
122	3.088	--	--
341	2.699	022	2.697
350	2.658	{121	2.658
		312	2.656
652	1.502	038	1.508

Further structure determinations of Ca_2SiO_4-type compounds with superstructures are presently being initiated.

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