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The crystal structure of 6 $Ca_2SiO_4 \cdot 1\ Ca_3(PO_4)_2$

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Abstract. Single crystals of the composition 6 $Ca_2SiO_4 \cdot 1\ Ca_3(PO_4)_2$ have been grown by the Verneuil-method. The crystals represent a structure derivative of α'-Ca_2SiO_4. Due to twinning of the crystals a structure determination was possible only on the basis of the weak superlattice reflections [$Pnm2_1$; $a = 9.40(8)$, $b = 21.71(2)$, $c = 6.83(3)$ Å, $Z = 2$]. Important features are: (1) All tetrahedra are tilted away from the ideal positions, (2) there is no strong ordering nor statistic distribution of Si, P, Ca, (3) there exists a relation between the tetrahedra positions enriched in P and the occupancies of the neighbouring Ca positions. (4) In reality the superlattice reflections proved to be satellites suggesting a modulated structure.

Introduction

Ca_2SiO_4 can incorporate certain amounts of phosphate that stabilize the high temperature modifications β, α', α whereas the γ-modification does not occur. The phase diagram $Ca_2SiO_4 - Ca_3(PO_4)_2$ (Fix, Heymann, and Heinke, 1969) shows that with increasing amounts of phosphate first the β-phase and then the α'-phase of Ca_2SiO_4 is stabilized. With about 50 wt% $Ca_3(PO_4)_2$ finally the high temperature form α (phase "*A*") is stable at room temperature. This feature allows the high temperature modifications of Ca_2SiO_4 to be studied that are not stable at room temperature. The phosphate content, however, alters the chemical composition and probably the crystallographic properties too. Nevertheless such crystals might give important insights into the crystal chemistry of the Ca_2SiO_4-modifications. This paper deals with the compound 6 $Ca_2SiO_4 \cdot 1\ Ca_3(PO_4)_2$ displaying a structure derivative of α'-Ca_2SiO_4.

Experimental

The Verneuil technique was used to grow single crystals of the α'-modification. Starting material was a mixture of Ca_2SiO_4 and $Ca_3(PO_4)_2$. The bowls reached a length of 2 cm but on cooling transformations took place and the bowls got turbid due to many microcracks. Thin sections showed a coarse microstructure of grains that proved to be single crystals suitable for chemical and X-ray investigations.

Chemical composition

By microprobe analyses of some grains the content of Ca, Si and P was determined (Table 1). The analyses show a slight variation in composition. The resulting numbers of atoms in relation to the basic-cell of α'-Ca_2SiO_4 are also given in Table 1. The wet-chemical analysis of the inner part of the bowl yielded a content of 22.5 wt% $Ca_3(PO_4)_2$. This means an average content of 7.5 Ca, 3.0 Si and 1.0 P in the basic cell. This agrees well with the results of the microprobe analyses. With little variations the ratio Si : P proves to be 3 : 1. The average number of Ca ions necessary for electrostatic balance is 7.5 in the basic cell. The resulting chemical formula is $6\,Ca_2SiO_4 \cdot 1\,Ca_3(PO_4)_2$. The orthorhombic unit-cell of α'-Ca_2SiO_4 contains $4\,SiO_4$ tetrahedra. The formula unit $6\,Ca_2SiO_4 \cdot 1\,Ca_3(PO_4)_2$ therefore needs two basic-cells to locate 15 Ca, 6 Si, 2 P. There must occur vacancies on the Ca-sublattice due to the relation

$$2\,SiO_4 \rightarrow 2\,PO_4 + \Box_{Ca}\,.$$

X-ray investigation

Photographs of several single crystals taken by Weissenberg and precession technique showed the reflections of an orthorhombic subcell with additional

Table 1. Electron probe analyses of 4 crystal grains

wt%	1	2	3	4
CaO	62.7	62.9	63.0	61.9
SiO_2	28.5	28.0	28.4	26.3
P_2O_5	7.1	9.6	8.4	11.8
	98.3	100.5	99.8	100.0
Atomic proportions of the basic-cell:				
Ca	7.7	7.5	7.6	7.4
Si	3.3	3.1	3.2	2.9
P	0.7	0.9	0.8	1.1

superlattice reflections. The intensities were measured with a Siemens AED-diffractometer equipped with a graphite monochromator (radiation: Cu$K\alpha$, $\lambda = 1.5418$ Å).

a) The orthorhombic sublattice (basic-cell)

The cell parameters of the sublattice were obtained after a least-squares refinement using diffractometer data as follows: $a = 9.40(8)$, $b = 5.42(8)$, $c = 6.83(3)$ Å. The cell has nearly orthohexagonal geometry because

$$\frac{b\sqrt{3}}{a} \sim 1.$$

All crystals show three twin positions leading to systematic coincidences of all reflections. Twin-axis is [001] with an orientation relation that is given by the following transformation scheme:

$$\underset{\text{I}}{\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}} \underset{\text{II}}{\begin{pmatrix} \frac{1}{2} & \frac{3}{2} & 0 \\ -\frac{1}{2} & \frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}} \underset{\text{III}}{\begin{pmatrix} -\frac{1}{2} & \frac{3}{2} & 0 \\ -\frac{1}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}}.$$

The observed reflections indicate the space group *Pcmn* in accordance with the space group for α'_H-Ca_2SiO_4 (Eysel, 1971). The twinning is probably due to transformation from the hexagonal high temperature phase.

b) The superlattice-cell

The X-ray photographs show superlattice reflections running parallel to the b-axis with a period $4 \times b$ ($b_s = 4 \times 5.428 = 21.712$ Å). The exact measurement of these reflections, however, revealed shifts away from the definite superlattice positions and proved them to be sattelite reflections. They can be described by the following lattice vector:

$$H_{(hkl)} = ha^* + kb^* + lc^* + s \cdot n \cdot b^*$$

with $n = \pm (1, 2)$ and $s = 0.267$.

There exists periodic disorder with a modulation wavelength $\lambda = (b^* \cdot s)^{-1}$. Setting $b^* = 1$ this wavelength turns out to be $\lambda = s^{-1} = 3.75$. Thus, 16 modulation wavelengths coincide with 15 periods in b-direction. The following reflections can be observed:

$0kl$: $k + l = 2n$,
$h0l$: no satellites,
$hk0$: no condition.

This points to the space groups $Pnm2_1$ and $Pnmm$ for the superlattice. The latter space group conflicts with the basic structure so that $Pnm2_1$ may be the correct space group for the supercell.

There are two ways to get information about the crystal structure: the satellites are treated as true superlattice reflections and represent the basis of a normal structure determination or they are seen as satellites that can be interpreted by the corresponding theories. In this paper the first way was chosen. The shift of the satellites relative to the main reflections is small and their influence on the intensities therefore negligeable.

Table 2. Positional parameters of the average structure. Standard deviations are given in parantheses

Atom	Occupation factor	x	y	z
T(1)	0.5	0.872(2)	0	0.778(3)
T(2)	1.0	0.170(2)	0.253(1)	0.246(4)
T(3)	0.5	0.203(3)	0	0.208(5)
T(4)	1.0	0.342(3)	0.123(1)	0.781(4)
T(5)	1.0	0.697(2)	0.128(1)	0.303(3)
Ca(1)	0.5	0.208(3)	0	0.656(4)
Ca(2)	0.45	−0.136(2)	0	0.210(4)
Ca(3)	0.63	0.348(3)	0.129(1)	0.353(5)
Ca(4)	0.88	0.704(2)	0.117(1)	0.852(4)
Ca(5)	1.0	0.174(2)	0.242(1)	0.692(3)
Ca(6)	0.5	0.492(2)	0	0
Ca(7)	0.5	0.574(2)	0	0.482(3)
Ca(8)	1.0	0.460(1)	0.241(1)	0.016(3)
Ca(9)	0.98	0.067(2)	0.133(1)	0.012(3)
Ca(10)	0.98	−0.014(2)	0.116(1)	0.508(3)
O(1)	0.5	0.706(3)	0	0.791(9)
O(2)	0.5	0.951(7)	0	0.574(6)
O(3)	1.0	0.918(5)	0.059(2)	0.897(7)
O(4)	1.0	0.195(6)	0.229(3)	0.029(6)
O(5)	1.0	0.134(4)	0.193(1)	0.370(5)
O(6)	1.0	0.058(4)	0.307(2)	0.206(7)
O(7)	1.0	0.312(4)	0.280(3)	0.337(8)
O(8)	0.5	0.351(6)	0	0.329(11)
O(9)	1.0	0.134(6)	−0.063(2)	0.288(9)
O(10)	0.5	0.246(5)	0	−0.020(5)
O(11)	1.0	0.398(3)	0.186(1)	0.692(5)
O(12)	1.0	0.329(6)	0.129(2)	0.008(5)
O(13)	1.0	0.433(5)	0.067(2)	0.712(8)
O(14)	1.0	0.182(3)	0.114(2)	0.732(7)
O(15)	1.0	0.723(5)	0.105(2)	0.518(5)
O(16)	1.0	0.586(3)	0.181(1)	0.274(6)
O(17)	1.0	0.612(4)	0.071(2)	0.219(6)
O(18)	1.0	0.841(3)	0.148(2)	0.204(6)

Structure determination of 6 $Ca_2SiO_4 \cdot 1\ Ca_3(PO_4)_2$

The structure determination can only be based on the superlattice reflections because the reflections of the subcell proved to be unsuitable due to twinning. The intensities of 650 reflections of one twin position were collected on a diffractometer and corrected for Lorentz and polarization factors and absorption. The superstructure cell contains 2 formula units. An initial model for the orthorhombic structure was derived from the positions of Ca and Si given by Eysel and Hahn (1970) for α-Ca_2SiO_4. A subsequent Fourier synthesis phased by Ca and Si revealed the position of nearly all oxygen atoms. Successive difference syntheses resolved uncertain atomic positions. A structure refinement with full-matrix least squares procedure followed including the occupation factors of all atomic positions. Refinement was terminated at $R = 0.16$. Compared with usual structure determinations this result does not seem satisfactory. However, one has to consider that only the weak superlattice reflections could be used. The atomic positions are listed in Table 2.

The result can be summarized as follows:

a) The structure is a derivative of the atomic arrangement of α'-Ca_2SiO_4.

b) The structure refinement confirmed the space group $Pnm2_1$.

c) The tetrahedra are not arranged in ideal positions (vertices up and down) as assumed for α'-Ca_2SiO_4, but they are tilted.

d) The tilt-directions of the tetrahedra are comparable with those found in β-Ca_2SiO_4.

e) In an ordered structure only 30 of the possible 32 Ca-positions should be occupied. The refinement revealed that all positions are occupied differing only in site occupancy. The sum of the electrons reaches 29.68 (theoretical value: 30.0).

f) The T—O distances and T—O—T angles are in conformance with those usually found in silicates and phosphates (Table 3).

g) The Ca positions with low occupation factors are located near the tetrahedra with short T—O distances (PO_4 tetrahedra).

Description of the structure

The superstructure cell contains 16 tetrahedra (Fig. 1). As in β-Ca_2SiO_4 (Jost, Ziemer, and Seydel, 1977) and in bredigite (Moore and Araki, 1976) the tetrahedra are tilted away from the ideal positions. The similarity of the tetrahedra positions with those in β-Ca_2SiO_4 around the 2_1-axis is apparent. Four tetrahedra are located on mirror planes, their degree of freedom being thus reduced. A full independance of these tetrahedra would be only achieved in a space group of lower symmetry. This is in contrast to the X-ray photographs.

Table 3. Interatomic distances (Å) and angles (°). Standard deviations in parentheses. $T = Si,P$

T(1)–O(1)	1.57(2)	O(2)–T(1)–O(1)	121(6)
O(2)	1.58(2)	O(3)–T(1)–O(1)	2 × 104(2)
O(3)	2 × 1.58(2)	O(3)–T(1)–O(2)	109(2)
mean:	1.577	mean:	109.4
T(2)–O(4)	1.59(2)	O(5)–T(2)–O(4)	105(3)
O(5)	1.59(2)	O(6)–T(2)–O(4)	113(3)
O(6)	1.58(2)	O(6)–T(2)–O(5)	116(3)
O(7)	1.58(2)	O(7)–T(2)–O(4)	111(3)
		O(7)–T(2)–O(5)	106(3)
		O(7)–T(2)–O(6)	106(3)
mean:	1.585	mean:	109.5
T(3)–O(8)	1.61(2)	O(9)–T(3)–O(8)	2 × 100(3)
O(9)	2 × 1.61(2)	O(10)–T(3)–O(8)	106(4)
O(10)	1.61(2)	O(10)–T(3)–O(9)	2 × 116(3)
mean:	1.610	mean:	107.6
T(4)–O(11)	1.58(2)	O(12)–T(4)–O(11)	110(3)
O(12)	1.56(2)	O(13)–T(4)–O(11)	112(3)
O(13)	1.56(2)	O(13)–T(4)–O(12)	114(5)
O(14)	1.55(2)	O(14)–T(4)–O(11)	110(3)
		O(14)–T(4)–O(12)	98(3)
		O(14)–T(4)–O(13)	112(3)
mean:	1.563	mean:	109.3
T(5)–O(15)	1.57(2)	O(16)–T(5)–O(15)	117(3)
O(16)	1.58(2)	O(17)–T(5)–O(15)	100(3)
O(17)	1.58(2)	O(17)–T(5)–O(16)	101(3)
O(18)	1.57(2)	O(18)–T(5)–O(15)	111(3)
		O(18)–T(5)–O(16)	108(2)
		O(18)–T(5)–O(17)	120(2)
mean:	1.575	mean:	109.5

There is neither perfect Si/P order nor random distribution but a preferential site occupancy of P in the tetrahedra T(1), T(4), and T(5). The structure determination therefore revealed only an "average" structure. From many structure determinations it is known that the average P–0 distance is 1.54 Å, the average Si–O distance in silicates being 1.61 Å. Assuming a linearity between P content and T–O distance an estimation of the P or Si content should be possible. Table 4 gives these contents in comparison with the occupations of the nearest Ca position. There is a clear correlation of P content of a tetrahedral position with the degree of deficiency of the nearest Ca position. This can be explained by the electrostatic charge balance.

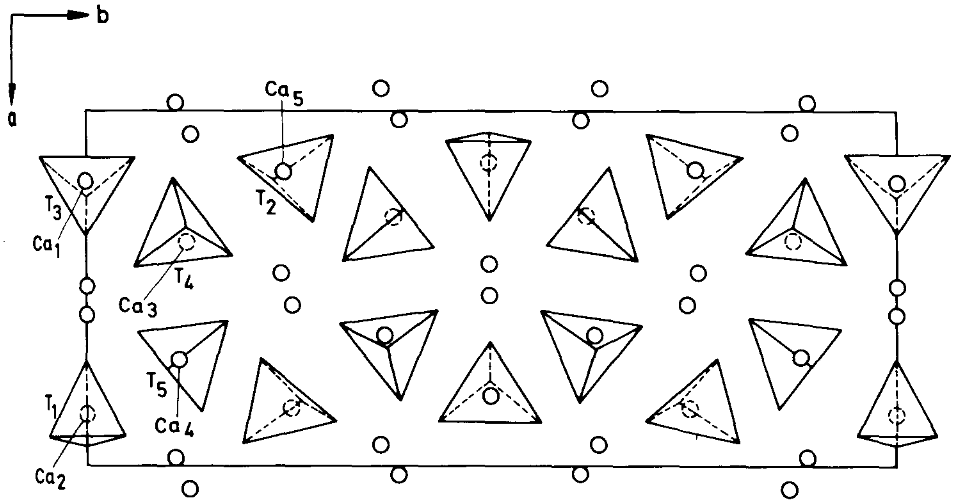

Fig. 1. Dispositions of the tetrahedra in the structure of $6 Ca_2SiO_4 \cdot 1 Ca_3(PO_4)_2$

The structure determination revealed 10 irregular Ca – O_x polyhedra. In Table 5 the coordination numbers, x, are summarized together with the average Ca – O_x distances. For comparison, the Ca – O-distances calculated for different coordination numbers according to Shannon and Prewitt (1969) are given in brackets. The coordination numbers vary between 7 and 10. They are in good agreement with those found in β-Ca_2SiO_4. Only Ca(2) – O and Ca(4) – O show larger deviations that may be due to distortions of the neighbouring tetrahedra T(1) and T(5).

Conclusion

The atomic arrangement proposed here can only be regarded as average structure. Conclusions about the structure of pure α'-Ca_2SiO_4 cannot be drawn even if the basic cells display a comparable geometry. Tilting of the tetrahedra in bredigite (Moore and Araki, 1976) and in the structure described here suggests a correlation of the tilt mechanism with the formation of superstructures. In the case of β-Ca_2SiO_4, however, there is no superlattice formation but a lowering of the symmetry can be observed. Further investigations must clarify the relation between crystal structure, formation of superlattice and symmetry.

The shift of the superstructure reflections away from their 'ideal' positions suggests a periodic disordered structure. There is no doubt that the

Table 4. Relation between the occupancies of $(Si,P)O_4$ tetrahedra and the nearest Ca-positions

T (*n*)	Estimated occupancy		Ca (*n*)	Occupancy of the nearest Ca-position (%)
	Si	P		
4	$\frac{1}{3}$	$\frac{2}{3}$	3	63
5	$\frac{1}{2}$	$\frac{1}{2}$	4	88
1	$\frac{1}{2}$	$\frac{1}{2}$	2	90
2	$\frac{2}{3}$	$\frac{1}{3}$	5	100
3	1	0	1	100

Table 5. Mean Ca(*n*) – O_x distances. In parantheses are listed the distances given by Shannon and Prewitt (1969) for the coordination number *x*

Ca(*n*)	*x*	Ca – O_x (Å)
1	7	2.52 (2.46)
2	7	2.78 (2.46)
3	10	2.68 (2.68)
4	7	2.65 (2.47)
5	8	2.58 (2.52)
6	7	2.47 (2.47)
7	8	2.50 (2.52)
8	8	2.54 (2.52)
9	8	2.46 (2.52)
10	7	2.46 (2.46)

P/Si distribution and the vacancies on the Ca sublattice are involved in the modulation structure. Perhaps this modulation is related to the microstructure of antiphase domains comparable with those found in the plagioclases (Korekawa et al., 1979) or in mullite (Saalfeld, 1979). The satellite theories presented by Korekawa (1968) and Boehm (1977) may give further information.

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