The Structures of the Polymorphs of Dicalcium Silicate, Ca_2SiO_4

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Abstract

The geometries of the cation arrays in the structures of dicalcium silicate polymorphs (some of which are isostructural with the strontium analogues) are examined. They are found to be $C23$ ($PbCl_2$) type for α' and β, and $B8_b$ (Ni_2In) type for γ. The structures are therefore described as anion-stuffed cation arrays of these known, simple geometries. The $C23/B8_b$ relationship suggests a likely transformation mechanism for $\beta \rightarrow \gamma$: a displacive mechanism which is consistent with the orientation relation observed by Groves [*J. Mater. Sci.* (1983), **18**, 1615–1624]. The α'/β relation is a small topological distortion.

1. Introduction

The difficulty in describing and comparing the structures of the various polymorphs of Ca_2SiO_4 and deciphering the relations between them seems almost to be exacerbated by the wealth of available information. Numerous results (and conjectures) from numerous workers over a long period of time attest to the importance of this compound to the cement industry. Nevertheless, structural descriptions are confused by lack of agreement over details, particularly anion coordinates. This is due to the considerable similarities between the structures of the various polymorphs, confounded by lack of thermodynamic equilibrium and, at last at lower temperatures, irreversibility. But it is our impression that the fundamental difficulty is lack of a simple, adequate description of the structures. Our purpose is to remedy this.

2. Structures and phase relations

It appears to be agreed that, in order of decreasing temperature, the observed Ca_2SiO_4 polymorphs are α, α'_H, α'_L, β and γ. The approximate transformation temperatures are shown in Fig. 1 (after Eysel & Hahn,
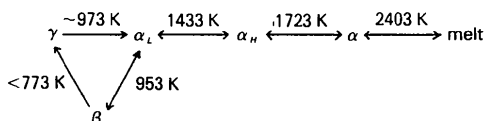
Fig. 1. Transformations between Ca_2SiO_4 polymorphs according to Eysel & Hahn (1970).

1970). Hysteresis attends the reversible transformations while those involving γ-Ca_2SiO_4 are monotropic.

The reported structures are commonly represented as shown in Fig. 2, after Smith, Majumdar & Ordway (1965) but updated as far as possible; *cf.* also Figs. 8 to 11 of Eysel & Hahn (1970). Some comments appear to be necessary at this point.

The α structure is still rather uncertain. It is similar to (if not indeed isostructural with) that of glaserite [$NaK_3(SO_4)_2$] which, however, is itself uncertain (Moore, 1973). Fortunately the main issue here is the relation between the α', β and γ structures and we will largely ignore the α polymorph.

The α'_H and α'_L structures are generally believed to be fairly complex superstructures of the α' structure. The exact nature of these superstructures has, however, not yet been elucidated: Regourd, Bigare, Forest & Guinier (1969) and Barnes, Fentiman & Jeffery (1980) reported a $(2a, b, 2c)$ superstructure from X-ray powder data, whereas Saalfeld (1975) observed an $(a, 3b, c)$ superstructure by means of
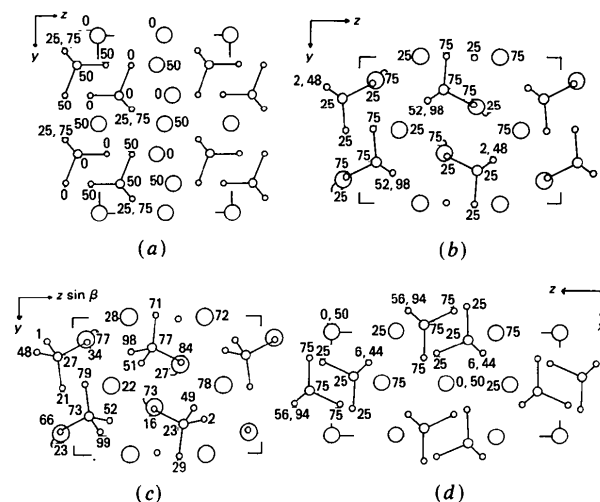
Fig. 2. 'Related projections of Ca_2SiO_4 [and Sr_2SiO_4] polymorphs' after Smith, Majumdar & Ordway (1965). In order of decreasing size the circles represent Ca [or Sr], Si and O atoms: heights are given in units of one hundredth of the projection axis which is, in our settings of the unit cells, the a axis for (*a*) α, (*b*) α' and (*c*) β, and the b axis for (*d*) γ. In (*b*) we show the structure of (ordered) α'-Sr_2SiO_4 (rather than that of α'-Ca_2SiO_4) because, although apparently isostructural with the latter, it is better determined (see text).

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high-temperature single-crystal X-ray diffraction. Eysel & Hahn (1970) have concluded that α'_H and α'_L are extremely similar in structure and that the transformation between them is 'very weak and of the displacive type'. While a precise and reliable structure refinement, by single-crystal X-ray diffraction, is not available for 'α'-Ca_2SiO_4', it has recently been reported for the corresponding phases α'-$Sr_{1.9}Ba_{0.1}SiO_4$ (Catti, Gazzoni & Ivaldi, 1983) and, most usefully, α'-Sr_2SiO_4 (Catti, Gazzoni, Ivaldi & Zanini, 1983). The last is of particular interest because it was carried out at equilibrium, at $T = 383$ K (the transformation β- $\rightleftarrows$ α'-Sr_2SiO_4 occurs at ~358 K). These latest results, showing no indication of a super-structure for α'-Sr_2SiO_4, confirm that in our present state of knowledge we cannot do better than discuss the α' structure in terms of the smaller orthorhombic unit cell.

Catti, Gazzoni, Ivaldi & Zanini (1983) investigated an 'ordered', and a 'disordered' model for the structure of α'-Sr_2SiO_4. The 'ordered' model corresponds to the structure previously proposed for α'-Ca_2SiO_4 (Fig. 2b). However, it leads to rather short Si–O bond lengths and we follow Catti et al. in preferring their 'disordered' model (shown in Fig. 3a; note the small differences with Fig. 2b) which probably also provides a better description of the α'-Ca_2SiO_4 structure.

The structures of β- and γ-Ca_2SiO_4 seem to be well established: the former is monoclinic (Midgley, 1952; Jost, Ziemer & Seydel, 1977) and isostructural with β-Sr_2SiO_4 (Catti, Gazzoni & Ivaldi, 1983; Catti & Gazzoni, 1983). γ-Ca_2SiO_4 has the olivine structure (Smith et al., 1965; Czaya, 1971; Udagawa, Urabe, Natsume & Yano, 1980) while no γ-Sr_2SiO_4 polymorph has been reported.

In attempting to describe a crystal structure the first approach is, conventionally, in terms of the anion packing and/or the articulation of its cation-centred coordination polyhedra. In the present instances, however, with the possible exception of the γ-Ca_2SiO_4 structure, there is no regular, clearly recognizable arrangement of the anions and the SiO_4 tetrahedra are the only obvious coordination polyhedra (cf. Fig. 2). Coordination numbers of the Ca (Sr) atoms by O cannot be unequivocally determined: the Ca–O (Sr–O) bond lengths vary widely in both the α' and β structures with no marked gap separating those Ca–O (Sr–O) distances corresponding to obvious bonds from those which are obviously not bonds. So it is not possible to delineate with confidence any CaO_n (SrO_n) coordination polyhedron, let alone a regular one.* Even in γ-Ca_2SiO_4 the situation is not as straightforward as the label 'olivine

type' might imply: the O array is much further from regular hexagonal eutaxy ('hexagonal close-packing') than in the case of smaller cations, e.g. in Mg_2SiO_4. The CaO_6 octahedra are far from regular, as can be seen from Fig. 2(d) (and also Fig. 3d): edge lengths $d(O\cdots O)$ vary from 2·61 to 4·17 Å for $Ca(1)O_6$ and from 2·60 to 3·93 Å for $Ca(2)O_6$.

The lack of a regular O packing and regular CaO_n (SrO_n) coordination polyhedra in the structures of the Ca_2SiO_4 (Sr_2SiO_4) polymorphs perhaps explains why most previous discussions exclusively considered the arrangement of the SiO_4 tetrahedra. We show in the following that an alternative approach based on a consideration of the geometry and topology of their cation arrays leads to a more complete description of these structures and of the relations between them.

2.1. The cation arrays and the orientation relations between the α', β and γ polymorphs

Following a broader treatment of the description of crystal structures as anion-stuffed cation packings (O'Keeffe & Hyde, 1985), we focus attention on the Ca_2Si (Sr_2Si) arrays of the Ca_2SiO_4 (Sr_2SiO_4) polymorphs. These are emphasized in Figs. 3 and 4 for four structures involved in the present problem: (disordered) α'-Sr_2SiO_4, β-Sr_2SiO_4, β-Ca_2SiO_4 and γ-Ca_2SiO_4.

To avoid the confusion resulting from the variety of possible settings of the unit cells, we have used those set out in Table 1. In this way equivalent axes in each structure bear the same labels. (Note that although α' and γ have the same space group, $Pnma$, it is necessary to give them different settings.)*

In every case the cation arrays are built of Si-centred (or SiO_4-centred) trigonal prisms of Ca (Sr) atoms which are rather regular. These $SiCa_6$ ($SiSr_6$) prisms share triangular faces to form 'columns' parallel to a and these share edges to form 'walls' parallel to b. These walls are stacked in the c direction – adjacent walls differing in height by ~a/2 – so that each prism is capped by Ca (Sr) atoms in the prisms of adjacent walls. This capping results in the trigonal prisms being elongated (Fig. 4). Elsewhere it has been shown that the ideal ratios $h/\bar{l} \approx 1·56$ and 1·18 for 5- and 3-capped prisms respectively, where h is the height of the prism and $\bar{l}$ is the average edge length of its triangular base (O'Keeffe & Hyde, 1977). These values compare quite well with those for the observed structures: approximately 1·55, 1·57 and 1·45 respectively for α'-, β- and γ-Ca_2SiO_4 in which the prisms are 5-, 5- and 3-capped. [The number of caps is based

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* For β-Ca_2SiO_4 Jost et al. (1977) describe a distorted pentagonal bipyramid, $Ca(1)O_7$, and a distorted square antiprism, $Ca(2)O_8$; but these are not of great help in visualizing the structure, or in deducing its relationships to the other structures.

* One of the minor difficulties in comparing the literature on these structures is the many different settings used for the unit cells, particularly as sometimes they are not clearly specified. This is a particular problem for α' and γ for which one finds many variants of the standard $Pnma$ space group.

Table 1. *Unit-cell data for the various* Ca_2SiO_4 *and* Sr_2SiO_4 *polymorphs*

Polymorph	Space group*	a (Å)	b (Å)	c (Å)	β (°)	V (Å³)	Reference
γ-Ca_2SiO_4	$Pcmn$	5·081	6·778	11·224	—	386·5	Udagawa et al. (1980)
β-Ca_2SiO_4	$P2_1/n$	5·502	6·745	9·297	94·59	343·9	Jost et al. (1977)
β-Sr_2SiO_4	$P2_1/n$	5·663	7·084	9·767	92·67	391·4	Catti, Gazzoni & Ivaldi (1983)
α'-Ca_2SiO_4 (subcell)	$Pmnb$	5·59	6·85	9·49	—	363	Saalfeld (1975)
α'-Sr_2SiO_4	$Pmnb$	5·682	7·090	9·773	—	393·7	Catti, Gazzoni, Ivaldi & Zanini (1983)
α-Ca_2SiO_4 (orthohexagonal cell)	$P\bar{3}m1$	5·46	6·76	9·46	—	349	Douglas (1952)

* The space-group settings for γ- and α'-Ca_2SiO_4 differ from those given in the original articles ($Pbnm$ and $Pcmn$ respectively).

on distances $d(Si\cdots Ca) = 3·0$ to 4·3 Å; but there are two more caps at 4·85 Å in γ-Ca_2SiO_4.]

In the α' and β structures (Figs. 3*a*, 3*b* and 3*c*) the Ca_2Si (Sr_2Si) arrays are very similar and correspond to the $C23 = PbCl_2$ (or $C37 = Co_2Si$) structure

type (described, for example, by Schubert, 1964). The differences between the cation arrays are small and most obvious in the (010) projections shown in Figs. 4(*a*), 4(*b*) and 4(*c*): a slight shearing of the trigonal prism walls (and of the prisms themselves) distorts
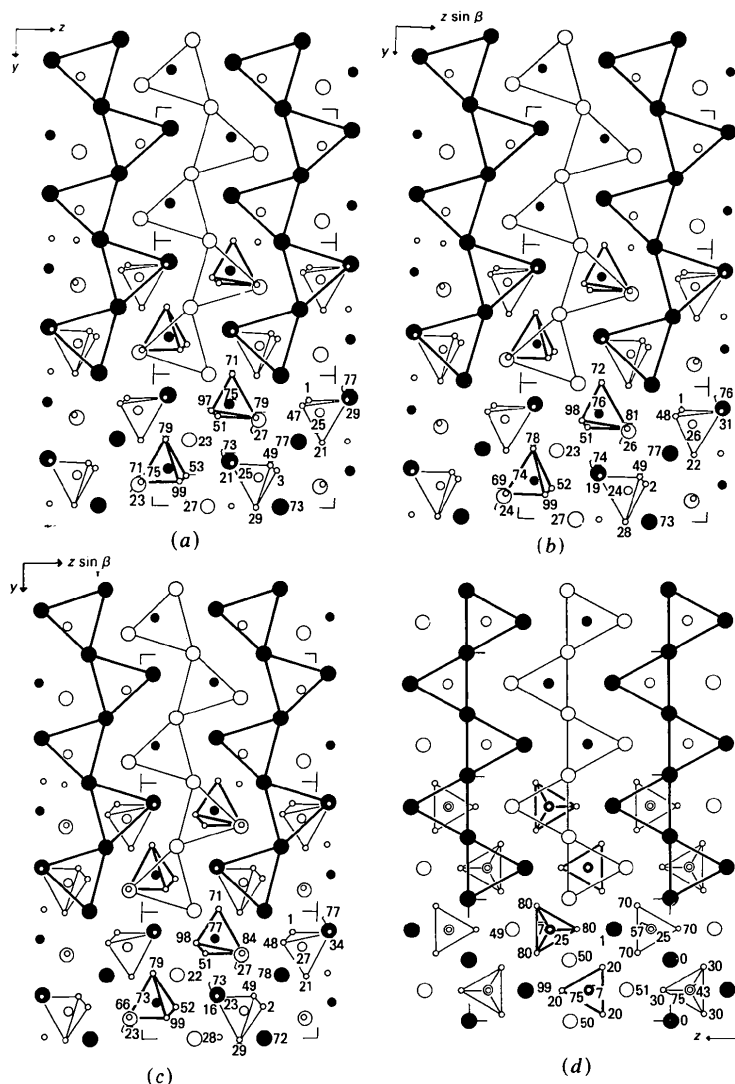

Fig. 3. Related projections of Ca_2SiO_4 (and Sr_2SiO_4) polymorphs - the new descriptions, and our settings of the unit cells: all projections are down **a**. (*a*) is equivalent to Fig. 2(*b*), except that it is (only) one (100) twin component of the 'disordered' α'-Sr_2SiO_4, whereas the latter is the 'ordered' model. (Note how small are the differences between the two structures.) (*b*) is the structure of β-Sr_2SiO_4. (*c*) is β-Ca_2SiO_4 (and identical to Fig. 2*c*): note the close similarity to (*b*). (*d*) is γ-Ca_2SiO_4 (=olivine type). In each case the bottom part of the figure is analogous to Fig. 2, but with SiO_4 tetrahedra drawn instead of Si–O bonds. The top part of each figure shows only the Ca_2Si (or Sr_2Si) array as Si-centred trigonal prisms of Ca_6 (or Sr_6). The arrays are $PbCl_2$ type ($C23$) in (*a*), (*b*) and (*c*), and Ni_2In type ($B8_b$) in (*d*).

the unit-cell angle β from 90° in α' to 94·59° in β-Ca$_2$SiO$_4$ (92·67° in β-Sr$_2$SiO$_4$). This points to the integrity of these walls of prisms as building units in both structures.

Indeed the walls persist in the structure of γ-Ca$_2$SiO$_4$ also. But now in the **b** direction they are straight (Fig. 3d) whereas they are puckered or zigzag in the α' and β structures. The C23 array of Ca$_2$Si (Sr$_2$Si) in the last two has become the $B8_b$ = Ni$_2$In type in the first. Exactly this transformation, $C23 \rightleftarrows B8_b$, is known amongst metal alloys, e.g. in MnCoGe (Johnson, 1975); and there is no doubt that it is displacive (Jeitschko, 1975), not reconstructive, even though the volume change is large enough to cause single crystals to shatter. A similar breaking of single crystals (termed 'dusting') occurs in Ca$_2$SiO$_4$ during the analogous transformation $\beta \rightarrow \gamma$ which also involves a large volume increase, $\Delta V = +11\%$. We

therefore suggest that the $\beta \rightleftarrows \gamma$ transformation may be properly termed 'displacive' also.*

As already stated, the α-Ca$_2$SiO$_4$ structure is the least well substantiated. The reported structure, shown in Fig. 2(a), suggests an array of SiCa$_6$ trigonal prisms similar to that in α', β and γ – particularly the last – but distorted. However, further consideration seems unwarranted.

The orientation relations between the α', β and γ structures, implicit in Figs. 3 and 4, are based only on the geometries of the perceived Ca$_2$Si (Sr$_2$Si) arrays and their topological integrity. The only departure from the previously proposed orientation relationships [e.g. Fig. 2 in Smith *et al.* (1965), and

* The analogy is not complete: $C23 \rightarrow B8_b$ occurs with increasing temperature and $\Delta V < 0$ for MnCoGe, but with decreasing temperature and $\Delta V > 0$ for Ca$_2$SiO$_4$.
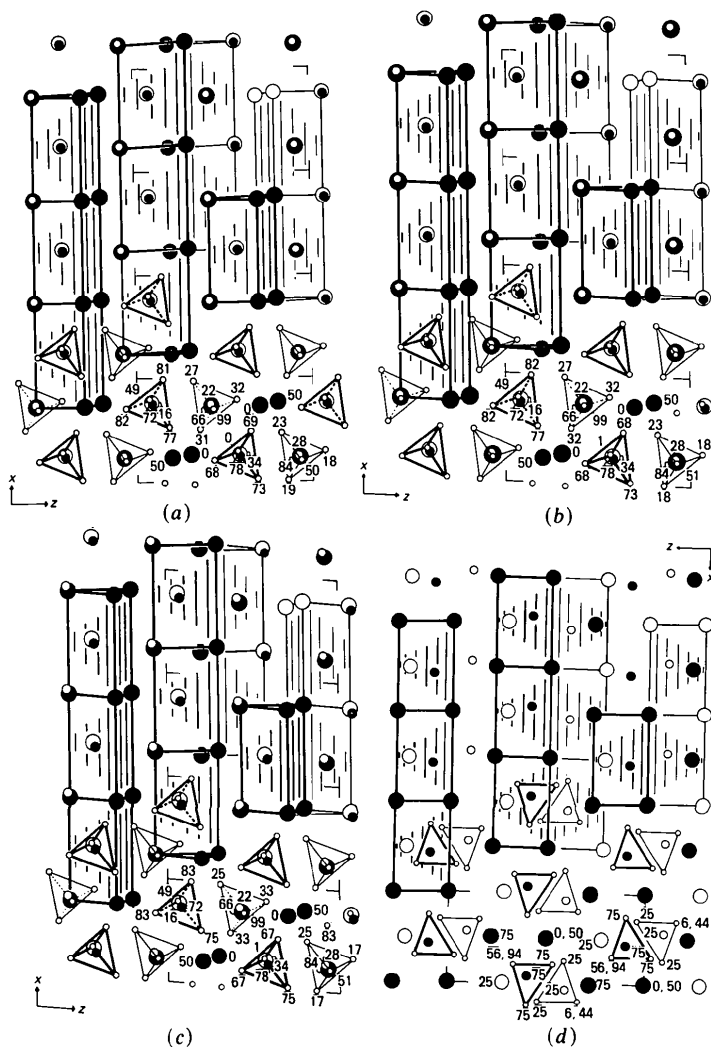

Fig. 4. As Fig. 3, but the structures are now all projected down **b**: (a) 'disordered' α'-Sr$_2$SiO$_4$, (b) β-Sr$_2$SiO$_4$, (c) β-Ca$_2$SiO$_4$, (d) γ-Ca$_2$SiO$_4$. Again the bottom part of each figure shows only the SiO$_4$ tetrahedra and the sites of the larger cations, while the top part emphasizes some of the Si/SiO$_4$-centred Ca$_6$ (Sr$_6$) trigonal prisms.

Figs. 8 to 11 in Eysel & Hahn (1970)] is for the γ structure. The basis of the earlier proposals is not clear to us: it appears to have been surmised pseudo-hexagonal unit cells resembling that of α-Ca_2SiO_4. A recent piece of circumstantial evidence is consistent with our proposed β-γ relation but inconsistent with earlier proposals: Groves (1983) reports observations on exsolved γ-Ca_2SiO_4 in a matrix of β-Ca_2SiO_4, the precipitates being needle- or lath-like particles with their long axis $[010]_\gamma$ parallel to $[010]_\beta$, for our settings of the unit cells. (The previous proposals, see Fig. 2, had $[010]_\gamma$ parallel to $[100]_\beta$.) Groves (1983) also deduced that 'tensile stress normal to the long axis of the [γ] particles has been effective in inducing the transformation'. This we associate with the very large increase in the c axis when β transforms to γ, cf. Table 1: $\Delta c \sim +21\%$ whereas $\Delta a \approx -7 \cdot 7\%$ and $\Delta b \approx +0 \cdot 5\%$ only. Although these observations do not prove the correctness of our proposal for the β-γ orientation relationship, they are consistent with it and with the integrity of the 'walls' of trigonal prisms during their topological distortion from zigzag to straight. Note also that the axial lengths of the unit cells are more consistent in the present description, cf. Table 1.

A last point concerning the α' and β structures merits mentioning. It is the empirical observation that both the silicides Ca_2Si and Sr_2Si have the $C23/C37$ structure type; i.e. their structures are closely similar to the cation arrays in the α' and β forms of the corresponding silicates. Furthermore, it may be noted that their unit-cell volumes are also similar: at room temperature these are (in Å^3) 331 for Ca_2Si, 340 to 356 for 'stabilized' (i.e. impure) α'-Ca_2SiO_4 and 344 for β-Ca_2SiO_4; 398·5 for Sr_2Si, 393·7 (at 373 K) for α'-Sr_2SiO_4 and 391·4 for β-Sr_2SiO_4. There is a small volume increase for $Ca_2Si \rightarrow Ca_2SiO_4$ but a small volume decrease for $Sr_2Si \rightarrow Sr_2SiO_4$.

2.2. The anion arrays

SiO_4 tetrahedra are obvious in all of Figs. 2, 3 and 4 and, since the Si–O bonds are so much stronger than any Ca–O bond, it is reasonable to assume that they retain their integrity during transformations. [The bond strengths are $s(\text{Si–O}) \approx 1 \cdot 0$ compared with $s(\text{Ca–O}) < 1/2$, usually much less, see Table 2.]

During the transformation α'-$Sr_2SiO_4 \rightleftarrows \beta$-$Sr_2SiO_4$ (and, we presume, also during α'-$Ca_2SiO_4 \rightleftarrows \beta$-$Ca_2SiO_4$) there is very little if any tilting of these tetrahedra. Change is largely limited to a slight shearing of the walls of trigonal prisms, as discussed earlier. On the other hand, the transformation $\beta \rightleftarrows \gamma$ involves a very radical change in their orientation; and it seems clear that it is this which is responsible for the attendant, considerable changes in the unit-cell parameters a, c and V. In β (and α') there is only one O atom outside each $SiCa_6$ trigonal prism whereas in γ there

Table 2. *Bond lengths, l, and strengths, s, and bond-strength sums, $\sum s$, at the anions, in Ca_2SiO_4 and Sr_2SiO_4 polymorphs (those in parentheses are not counted as being bonds)*

The bond strengths, s, have been calculated from the following $s = f(l)$ relations given by Brown (1981): $s = (1 \cdot 909/l)^{5 \cdot 4}$ for Ca–O bonds, $s = (2 \cdot 143/l)^{7 \cdot 0}$ for Sr–O bonds and $s = \exp[(1 \cdot 63 - l)/0 \cdot 36]$ for Si–O bonds. [The alternative $s = f(l)$ relation given by Brown for Ca–O bonds leads to identical bond strengths within 0·01.]

	α'-Sr_2SiO_4 $l(\text{Å})$	s	β-Sr_2SiO_4 $l(\text{Å})$	s	β-Ca_2SiO_4 $l(\text{Å})$	s	γ-Ca_2SiO_4 $l(\text{Å})$	s
O(1)–Si	1.62_7	1·01	1.64_6	0·96	1.60_9	1·06	1.61_7	1·04
–M(1)	2.38_4	0·47	2.37_3	0·49	2.22_4	0·44	2.44_1	0·27
–M(2)	2.61_3	0·25	2.62_3	0·24	2.43_4	0·27	2.37_6	0·31 (2×)
–M(2)	2.80_8	0·15	2.78_2	0·16	2.63_5	0·18		
–M(2)	$(3.41_3$	0·04)	$(3.40_4$	0·04)	$(3.48_0$	0·04)		
$\sum s$		1·88		1·85		1·95		1·93
O(2)–Si	1.65_5	0·93	1.64_1	0·97	1.62_8	1·01	1.65_3	0·94
M(1)	2.68_8	0·21	2.56_6	0·28	2.49_1	0·24	2.29_8	0·37
M(1)	2.79_6	0·16	2.80_1	0·15	2.87_7	0·11		
M(1)	3.00_4	0·10	$(3.10_8$	0·07)	$(3.31_8$	0·05)		
M(2)	2.65_2	0·24	2.62_4	0·24	2.38_2	0·30	2.31_1	0·36 (2×)
M(2)	2.64_3	0·23	2.65_0	0·23	2.38_8	0·30		
$\sum s$		1·87		1·87		1·96		2·03
O(3)–Si	1.62_1	1·03	1.64_2	0·97	1.63_9	0·98	1.63_6	0·98
–M(1)	2.61_9	0·25	2.63_1	0·24	2.42_6	0·27	2.38_7	0·30
–M(1)	2.84_1	0·14	2.76_4	0·17	2.54_3	0·21	2.43_5	0·27
–M(1)	$(3.23_3$	0·06)	$(3.34_6$	0·04)	$(3.38_3$	0·05)		
–M(2)	2.56_1	0·29	2.52_7	0·32	2.38_6	0·30	2.40_3	0·29
–M(2)	2.67_9	0·21	2.69_4	0·20	2.64_1	0·17		
$\sum s$		1·92		1·90		1·93		1·84
O(4)–Si	1.62_6	1·01	1.62_1	1·03	1.64_9	0·95		
–M(1)	2.74_3	0·18	2.77_9	0·16	2.36_9	0·31		
–M(1)	$(3.07_7$	0·08)	2.92_6	0·11	2.63_7	0·18		
–M(1)	$(3.20_6$	0·06)	$(3.19_8$	0·06)	$(3.13_7$	0·07)		
–M(2)	2.47_9	0·36	2.51_0	0·32	2.44_3	0·26		
–M(2)	2.57_6	0·28	2.56_5	0·28	2.62_1	0·18		
$\sum s$		1·83		1·90		1·88		

are three. As a consequence the prism walls are pushed further apart ($c_\gamma > c_\beta$).

2.3. Coordination

We have attempted to clarify differences between the coordination numbers in the various polymorphs by considering anion-centred coordination polyhedra, via calculations of bond strengths from the observed bond lengths (Brown, 1981). Bond lengths are shown in Fig. 5, and listed with the corresponding strengths in Table 2. All Si–O bond strengths are close to $s = 1$ but, except in the case of γ-Ca_2SiO_4, Ca–O (and Sr–O) bond strengths vary widely, and more or less continuously, from $\sim0 \cdot 44$ to $\sim0 \cdot 04$ ($\sim0 \cdot 49$ to $\sim0 \cdot 04$). The lowest values ($s < 0 \cdot 1$) we take to be approximately zero so that, as far as can be judged, the 'best' coordination numbers are those given in Table 3. [The O coordination numbers such as I + II + II are for Si + $M(1)$ + $M(2)$, where $M(1)$ is at the least-shared vertex of the trigonal prisms.] Bond-strength sums are given in Table 2 for anions, and Table 4 for cations.

For $\alpha' \rightleftarrows \beta$ the changes are mainly minor variations in the bond lengths. But, for $\beta \rightarrow \gamma$ there is a distinct reduction in the coordination numbers of all the atoms except Si and O(1).

Table 3. *Coordination numbers (excluding weak bonds, $s < 0.1$)*

α'-Sr$_2$SiO$_4$ ^{IV}Si^{VII}Sr(1)^{VIII}Sr(2)$^{I+I+II}$O(1)$^{I+III+II}$O(2)$^{I+II+II}$O(3)$^{I+I+II}$O(4)
β-Sr$_2$SiO$_4$ ^{IV}Si^{VII}Sr(1)^{VIII}Sr(2)$^{I+I+II}$O(1)$^{I+II+II}$O(2)$^{I+II+II}$O(3)$^{I+II+II}$O(4)
β-Ca$_2$SiO$_4$ ^{IV}Si^{VII}Ca(1)^{VIII}Ca(2)$^{I+I+II}$O(1)$^{I+II+II}$O(2)$^{I+II+II}$O(3)$^{I+II+II}$O(4)
γ-Ca$_2$SiO$_4$* ^{IV}Si^{VI}Ca(1)^{VI}Ca(2)$^{I+I+II}$O(1)$^{I+I+II}$O(2)$^{I+II+I}$O(3)$_2$

* Ca(1) and Ca(2) atoms have been interchanged as compared with the original data (Udagawa et al., 1980) in order to be consistent with the atom positions in the other polymorphs.

Table 4. *Bond-strength sums at the cations*

	α'-Sr$_2$SiO$_4$	β-Sr$_2$SiO$_4$	β-Ca$_2$SiO$_4$	γ-Ca$_2$SiO$_4$	Ideal values
Si	3·98	3·92	3·99	3·94	4
M(1)	1·51	1·61	1·76	1·77	2
M(2)	2·01	2·00	1·96	1·90	2

The lower coordination numbers in γ are associated with its considerably larger unit-cell volume and, therefore, lower density. The α' and/or β phases could therefore be regarded as likely high-pressure polymorphs of γ. Experimental studies of the effect of pressure on the structure of γ-Ca$_2$SiO$_4$ (Ringwood & Reid, 1968; Liu, 1978) are therefore of some inter-

est. At very high pressure (24 GPa, $\sim$1273 K) the product is a K$_2$NiF$_4$-type structure (Liu, 1978) with SiO$_6$ octahedra and a density 24% higher than that of the γ form. At intermediate pressures (17 GPa, $\sim$1273 K) both report a complex X-ray powder diffraction pattern which was not indexed. Ringwood & Reid (1968) state that this pattern 'did not correspond to any of the presently known polymorphs of Ca$_2$SiO$_4$'. Nevertheless, the density increase of $\sim$11% associated with the $\gamma \to \beta$ (or α') transition (cf. Table 1) would appear to be compatible with the following hypothetical sequence of high-pressure transformations: $\gamma \to \beta(\alpha') \to$ K$_2$NiF$_4$-type. This in turn would suggest that the complex diffraction pattern observed at intermediate pressures could correspond to a phase or phases with β- and/or α'-related structure(s).

Except in γ (with its obvious O-centred SiCa$_3$ tetrahedra, Fig. 5d) the anion-centred polyhedra are not sufficiently regular to be characterized unequivocally. Figs. 5(a), 5(b), 5(c) and Table 2 reveal that while one can perhaps delineate O-centred tetrahedra, trigonal bipyramids, square pyramids and/or octahedra they are usually deformed as a
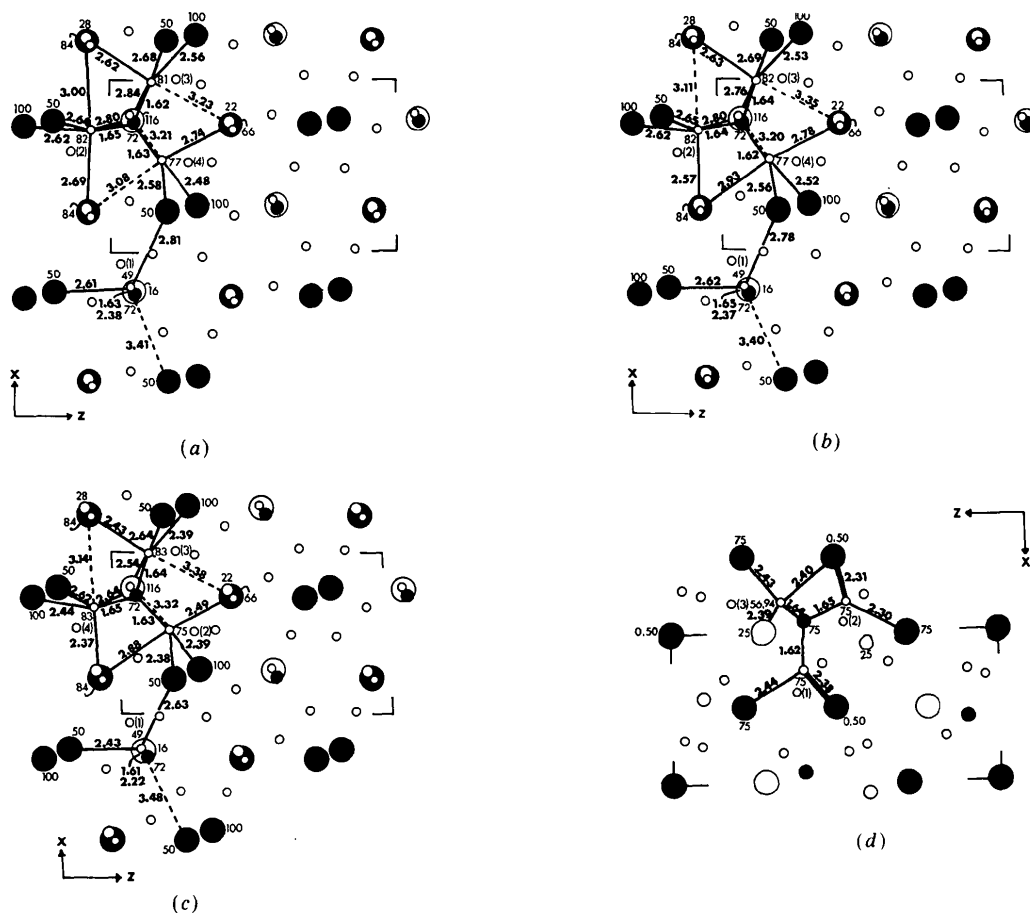

Fig. 5. Bonds from O atoms to their closest cations in (a) α'-Sr$_2$SiO$_4$, (b) β-Sr$_2$SiO$_4$, (c) β-Ca$_2$SiO$_4$, (d) γ-Ca$_2$SiO$_4$. The lighter digits are atom heights in units of $b/100$, and the heavier ones are bond lengths in Å. The broken lines are the weaker 'bonds', $s < 0.1$.

result of variations in Ca–O (Sr–O) bond lengths/strengths, particularly because of the existence of some very weak ($s < 0.1$) bonds (the dashed lines in Fig. 5). It is possible that these reflect 'cation crowding' (O'Keeffe & Hyde, 1984) in the denser structures. This may in turn be responsible for (a) the low-temperature transformation to γ (with its lower coordination numbers) and (b) the relative ease of hydration ('hydraulic activity') of β-Ca_2SiO_4 as compared with γ-Ca_2SiO_4 (Jost et al., 1977). In this connection it is interesting that, in all cases, only $M(1)$ appears to be distinctly underbonded (Table 4), and all the O atoms less so (Table 2).

3. Discussion

An examination of the cation arrangements in the reported structures of the various polymorphs of Ca_2SiO_4 (α?, α', β, γ) and Sr_2SiO_4 (α', β) reveals ubiquitous Si-(or SiO_4-)centred Ca_6 (Sr_6) trigonal prisms connected into walls so that the Ca_2Si or Sr_2Si array is $C23$/$PbCl_2$- ($\approx C37$/Co_2Si-)like in α' and β – as indeed it is in the compounds Ca_2Si and Sr_2Si – and $B8_b$/Ni_2In-like in γ. These arrays are therefore topologically identical, and geometrically similar, in all the polymorphs. At the least they provide a reference frame within which the full structures can be visualized and compared, so as to deduce reasonable structural and orientational relationships between them. In the cases involving γ-Ca_2SiO_4 the relationships are different from those previously proposed.

The deduced relationships suggest that all the transformations between the polymorphs are displacive ('martensitic') in character. The 'dusting' associated with β- → γ-Ca_2SiO_4 is to be ascribed to the accompanying large increase in volume, and not to a reconstructive character. (A similar phenomenon is known for the analogous transformation, $C23 \rightarrow B8_b$, in metal alloys, and there it has been established that the mechanism is displacive.)

The fine-scale twinning always observed in β is understandable in terms of the accompanying small (shear) distortion of the Ca_2Si (Sr_2Si) array when $\alpha' \rightarrow \beta$. Indeed the structure/texture of α'_L may itself involve a similar twinning. As Catti, Gazzoni, Ivaldi & Zanini (1983) point out, it is not possible to distinguish whether the 'disordered' (Fig. 3a) or 'ordered' (Fig. 2b) model of α'-Sr_2SiO_4 is the more appropriate. (In the latter the O atoms have large anisotropic thermal parameters normal to the mirror plane, i.e. towards the disordered sites.) It seems likely that there is some sort of disorder, dynamic and/or static, and that the 'disordered' model represents the extreme configurations. On this basis the *Pmnb* symmetry is a pseudosymmetry for the average structure, the components of which can be represented as two twin-related structures [with a (100) mirror plane at

$x/a = \pm\frac{1}{4}$].* The real symmetry of each twin is $P2_1/n$ exactly as for β [which is also invariably twinned on (100)]. The main difference between α' and β is therefore the difference between microscopic (at about the unit-cell level) and macroscopic twinning – or perhaps simply in the monoclinic angle, which is slightly greater than 90° for β but exactly 90° for α'.

Clearly the elucidation of structural relations and transformation mechanisms in the Ca_2SiO_4 and Sr_2SiO_4 systems has been and is dogged by uncertainties in the determined structures. It seems likely that this arises, at least in part, from the existence of alternative anion sites of equal or approximately equal energy, e.g. in twin-related pairs. The discussions of the structure of α'-Sr_2SiO_4 by Catti, Gazzoni, Ivaldi & Zanini (1983) and Catti & Gazzoni (1983) are consistent with this; and their observation that β- → α'-Sr_2SiO_4 has more than a passing resemblance to α- → β-quartz is well taken. Consequently (cf., for example, Bachheimer, Berge, Dolino, Saint-Gregoire & Zeyen, 1984), one might expect to observe a long-period, incommensurate modulation of (mainly) the anion positions close to the $\beta \rightleftarrows \alpha'$ transition temperature.†

Clearly, electron microscopy/diffraction studies of these phases and of the transformations between them are highly desirable. This is not only because of their technical importance but also as representatives of the important class of (ferroelastic) β-K_2SO_4-related structures, to which our structural approach seems to be equally as relevant and useful (O'Keeffe & Hyde, 1985).

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* Only one twin is shown in Fig. 3(a). The other is generated by the (100) mirror.

† It is probably not germane, although it is interesting, that satellite reflections *have* been observed in diffraction patterns from $6Ca_2SiO_4.Ca_3(PO_4)_2$, the structure of which is described as 'a derivative of that of α'-Ca_2SiO_4' (Saalfeld & Klaska, 1981). More relevant is the 3b superstructure (our setting) of K_2ZnCl_4 (Mikhail & Peters, 1979).

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24-Layer Structure of Tricalcium Germanate, Ca3GeO5

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Abstract

The crystal structure of a 24-layer polytype of tricalcium germanate (C_3G), which was found in a flux melt, has been determined. The crystal data are: $M_r = 272 \cdot 8$, rhombohedral, $R3m$, $a = 7 \cdot 228(2)$, $c = 67 \cdot 42(2)$ Å, $V = 3050(2)$ Å^3, $Z = 24$, $D_x = 3 \cdot 56$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0 \cdot 71069$ Å, $\mu = 92 \cdot 7$ cm^{-1}, $F(000) = 3168$, $T = 298$ K. The structure consists of two kinds of subunits, one is related to the structure of the 2-layer polytype and the other to that of the 9-layer polytype; these occur alternately in the structure. Half of the eight independent germanate tetrahedra show nearly perfect orientational disorder along the c axis. The positions of the Ge atoms of these tetrahedra are split, the separations being in the range $0 \cdot 34(10)$ to $0 \cdot 69(5)$ Å. The coordination numbers of Ca, each calculated as the sum of the occupancies of the Ca-O bonds, are in the range $6 \cdot 0$ to $6 \cdot 56$, giving mean Ca-O bond lengths of $2 \cdot 34$ to $2 \cdot 51$ Å. General principles of deriving polytypes for C_3G are provided and, based on these, the stacking sequences of simple polytypes such as 4-layer, 5-layer and 6-layer structures have been predicted. The derivation of polytypes can be applicable to the case of tricalcium silicate (C_3S).

Introduction

Our study on tricalcium germanate (C_3G) has revealed the existence of various polytypic forms as mentioned in our paper on the crystal structure of the 2-layer variant (Nishi & Takéuchi, 1984a). It appears that polytypism likewise exists in tricalcium silicate (C_3S); in addition to the rhombohedral structure, which may be interpreted as a 9-layer structure (Takéuchi, Nishi & Maki, 1984; Nishi & Takéuchi, 1984b), the existence of a two-layer structure has been reported by Pérez-Méndez, Howie & Glasser (1984).

In view of the common occurrence of polytypic forms in these chemical phases, we propose to denote N-layer variants by the following expressions: tricalcium germanate-N (or C_3G N) or tricalcium silicate-N (or C_3S N) (it is suggested that Roman numerals be used for N).

Although in general C_3G N is isotypic with C_3S N, the space group reported for C_3S II (Pérez-Méndez et al., 1984) is different from the one we found for C_3G II (Nishi & Takéuchi, 1984a), the former being $P6_3/mmc$ and the latter $P6_3mc$. Note that in the structures of these chemical phases the germanate (or silicate) tetrahedron shows a trend towards orientational disorder; a fraction of the tetrahedron points up the c axis (a U orientation) while the remaining fraction points down the c axis (a D orientation). Slight differences in the occupancy between the pairs of differently oriented tetrahedra may cause such a difference in the space group although the structures are based on the same principle. Since, however, the structure determination of C_3S II (Pérez-Méndez et al., 1984) is based on a small number of diffraction intensities, further refinement of the structure is desirable; it is anticipated that the structure would possibly be strictly isotypic with our C_3G II. In any case, the theory of polytypism developed for C_3G will be applicable to C_3S.