coordinated cations, can account for practically any stoichiometry in the composition range between $CaUO_4$ and $CaUO_{3.50}$.

The given explanation is not only in agreement with all known experimental data, but also with the results of Thornber & Bevan (1970), who studied mixed oxides of the type MO_2 (fluorite)-M_2O_3, which can accommodate large departures in stoichiometry in fluorite-related structures. The defect complex in these compounds, which enables the variation in composition, is equivalent to type A ordering, one of the possible ways of reducing $CaUO_4$.

There is a perfect intrinsic order in the arrangement of O vacancies in both types of microdomains and the observed disorder is only a result of more than one energetically equivalent possibility of stacking the reduced layers along the original inversion triad. If the nearest-neighbour interaction between reduced layers could be extended to the next-nearest neighbours at sufficiently low temperatures, a complete three-dimensional ordering would be achieved. As the favoured alternation of both types of ordering can only be explained on the basis of the most convenient charge balancing during reduction, it is obvious that this kind of ordering is conditioned by the possibility of U taking on a whole series of

different ionization states with close ionization energies.

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Crystallographic Relations between the β and γ Forms of (Ca₂,Ca₁.₈Sr₀.₂)SiO₄*

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Abstract

Crystal associations of β and γ forms of synthetic $(Ca_2,Ca_{1.8}Sr_{0.2})SiO_4$ showing a paramorphosis relationship are studied by optical microscopy and X-ray diffraction. The mutual crystallographic orientation is unequivocally established. The cell parameters are: $(a \sin \beta)_\beta = 5.48$, $a_\gamma = 5.08$; $b_\beta = 6.74$, $b_\gamma = 6.76$; $c_\beta = 9.30$, $c_\gamma = 11.23$ Å. On the basis of experimental evidence the structural relationships between the β and γ forms are analyzed both qualitatively and quantitatively. An atom-by-atom correspondence is established between the two structures and the transformation mechanism from the β into the γ form is discussed. The reconstructive and displacive components of the semi-reconstructive atomic rearrangement are singled out.

Introduction

The structural relationships among the five phases: α, α'_H, α'_L, β, and γ of calcium orthosilicate, the atomic mechanisms of transformation and their connections with equilibrium solid-phase relations are

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extensively studied topics (see, among others, Eysel & Hahn, 1970; Saalfeld, 1975; Barnes, Fentiman & Jeffery, 1980; Catti, Gazzoni & Ivaldi, 1984). In particular, the structural aspects involved in the transformation into the γ form, stable at room temperature, are of relevant interest. Their comprehension may help in understanding some important crystallo-chemical problems such as the metastability of the β form at room temperature, the role played by this phase in the transition from the high-temperature α' to the low-temperature γ phase and, from a more technological point of view, the rate of hydration and the hydraulic activity of Ca_2SiO_4 polymorphs.

A serious obstacle to establishing experimentally the crystallographic relationships between the β and γ forms is the dusting phenomenon accompanying this transition, due to the large volume expansion.

Smith, Majumdar & Ordway (1965) first pointed out some similarities in the general arrangement of atoms of the β and γ forms, suggesting that the transformation is semi-reconstructive. The comparison was made on the basis of the common hexagonal pseudosymmetry alone, since the authors did not have experimental evidence of the mutual crystallographic orientation. The mechanism of atomic rearrangement deriving from these similarities has been studied by other authors (Kazak, Domanskii, Boikova, Ilyukhin & Belov, 1974; Eysel & Hahn, 1970). Recently Prodan, Marinkovic, Vene, Kurbus & Boswell (1983), taking into account the minimal necessary rearrangement of atoms, suggested another relationship that allows an accord among the lattice constants

$$(a_\beta = \tfrac{1}{2}a_\gamma + \tfrac{1}{2}b_\gamma;\ b_\beta = c_\gamma;\ c_\beta = \tfrac{3}{2}a_\gamma - \tfrac{1}{2}b_\gamma).$$

At the same time Groves (1983), by transmission electron microscopy (TEM) on specimens of the β form partially transformed into the γ form, found the orientation relationship: $[001]_\gamma \| [010]_\beta$ [parallelism of the axis with 6·7 Å parameter, already suggested by Prodan et al. (1983)].

During a series of investigations on the polymorphism and solid-state transitions in the $(Ca, Sr)_2SiO_4$ system, Catti et al. (1984) found a range of compositions with high Ca content, $Ca_2SiO_4-Ca_{1.8}Sr_{0.2}SiO_4$, favorable to a detailed study of these problems. The progressive substitution of Ca with Sr leads to the following sequence of products: γ form, $\gamma + \beta$ association, α' form (for Sr content of 10%) at room temperature. The experimental conditions of synthesis that produced single crystals suitable for structural analysis proved to be useful in obtaining an intimate association of the β and γ forms, characterized by a paramorphosis relation.

In this paper the crystallographic relationships between these forms are studied, using both optical microscopy and X-ray single-crystal diffraction, with the aim of interpreting, on an experimental basis, the atomic mechanism of transformation.

Experimental

The samples were synthesized by crystallization of molten salt solutions starting from stoichiometric mixtures of analytically pure SiO, CaO, $CaCO_3$, $SrCO_3$ and CaF_2, SrF_2 as flux, with a 30% ratio silicate/fluoride. The composition was varied in steps by substituting 2% of the Ca with Sr; the pelletized mixtures were heated in platinum crucibles at 1773 K for 30 min; the melt was then cooled to room temperature with a T gradient of 5 K min^{-1}, thus avoiding the possible formation of $(Ca_2SiO_4)_2 \cdot CaF_2$.

The product of the synthesis was a microcrystalline bulk including well developed 'crystals', locally iso-oriented, which showed an elongated prismatic pseudo-hexagonal habit. These crystals could be easily isolated by breaking the rather incoherent bulk, and presented a cleavage along the plane orthogonal to their elongation axis, allowing laminae of variable thickness to be readily separated. These laminae were composed of zones of iso-oriented fibres, lined along the cleavage plane, which are typical of the γ modification. Alternating with these fibrous aggregates there were zones of transparent crystalline material, which, when observed under the microscope in polarized transmitted light, revealed a texture of lamellar domains parallel to the cleavage plane, i.e. the polysynthetic twinning characteristic of the β modification (see Fig. 1).

For the same composition, the relative amounts of the two forms present in different laminae was variable, as one could deduce from the number and extension of the zones, whose pattern in laminae cut from the same crystal was also irregular. As a consequence the ratio between the two forms, as measured from a single lamina, is not indicative of the composition. An evaluation of the relative amounts of the β and γ modifications carried out over a large number of laminae, however, gives good general information about the starting composition
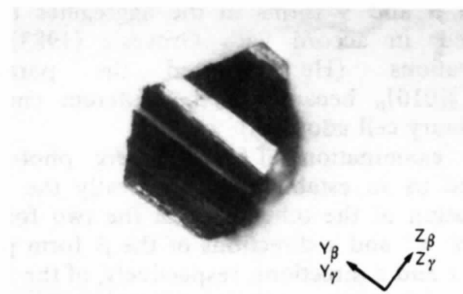

Fig. 1. Photograph showing the transparent β and the fibrous γ forms in association in a lamina of composition $(Ca_{1.92}Sr_{0.08})SiO_4$.

of the sample. In particular, in samples of composition $Ca_{1.96}$ there are a few, very thin bands of transparent β form; on the other hand, the fibrous aggregates of the γ form are present only in small quantity for composition $Ca_{1.84}$.

Tabular sections of various compositions, chosen in such a way as to present different amounts of β and γ forms, were examined by the X-ray Weissenberg technique. The β and γ components showed a marked tendency to come apart; furthermore, the γ fibres tended to misorient themselves under mechanical stress (in some cases the tension caused by the glue upon drying was enough to produce this effect). For all these reasons the sample preparation was by no means a trivial operation.

Mutual crystallographic orientation of the β and γ forms

To avoid possible confusion, the choice of the elementary cells that were adopted for both forms, on the basis of the experimental evidence presented below, are anticipated here.

β form (monoclinic, $P2_1/n$): $a = 5.502$ (1), $b = 6.745$ (1), $c = 9.297$ (1) Å, $\beta = 94.59$ (2)° (Jost, Ziemer & Seydel, 1977).

γ form (orthorhombic, $Pcmn$): $a = 5.078$ (2), $b = 6.760$ (2), $c = 11.225$ (3) Å (Czaya, 1971).

The y and z axes of the γ form are interchanged with respect to Czaya (1971), and consequently the space group $Pbnm$ becomes $Pcmn$. Table 1 lists the atomic coordinates of the two structures, modified according to this choice of elementary cells, to which we shall refer from now on.

For the Weissenberg photographs several choices of the rotation axis are possible on the basis of the morphological characteristics of the aggregates. Among these, given the simultaneous presence of three lattices (the two β twins and the γ form), the most convenient is to rotate around the elongation axis of the γ fibres; in fact, in this way, a complete coincidence of the reflection layers of both modifications is obtained, corresponding to an interplanar spacing of 6·7 Å. This means that the y axes of the β and γ forms in the aggregates are iso-oriented, in accord with Groves's (1983) TEM observations. (He reported the parallelism $[001]_\gamma\|[010]_\beta$ because of the different choice of elementary cell adopted.)

The examination of Weissenberg photographs allowed us to establish unequivocally the mutual orientation of the other axes of the two forms, as follows: x^* and z directions of the β form parallel to the x and z directions, respectively, of the γ form.

The orientation relationships in the crystal aggregates can therefore be summarized in the following manner: $\perp(100)_\beta\|[100]_\gamma$; $[010]_\beta\|[010]_\gamma$; $[001]_\beta\|[001]_\gamma$.

Table 1. *Fractional atomic coordinates for β and γ forms*

	x	y	z
β-Ca_2SiO_4 (Jost *et al.*, 1977)			
Ca(1)	0·2738	1·3428	0·5694
Ca(2)	0·2798	0·9976	0·2981
Si(1)	0·2324	0·7814	0·5817
O(1)	0·2864	1·0135	0·5599
O(2)	0·0202	0·7492	0·6919
O(3)	0·4859	0·6682	0·6381
O(4)	0·1558	0·6710	0·4264
γ-Ca_2SiO_4 (Czaya, 1971)			
Ca(1)	1·0000	1·0000	0·0000
Ca(2)	0·9904	0·7500	0·2809
Si(1)	0·4283	0·7500	0·0959
O(1)	0·7498	0·7500	0·0926
O(2)	0·2981	0·7500	-0·0393
O(3a)	0·2954	0·9433	0·1620
O(3b)	0·2954	0·5567	0·1620

The twin domains of the β form are in the usual mutual orientation: $[010]_{\beta'}\|[010]_{\beta''}$; $[001]_{\beta'}\|[001]_{\beta''}$ with (100) twinning contact plane.

For those samples containing almost only the γ form (typically $Ca_{1.96}$) the fibres were practically iso-oriented, and the reflections on Weissenberg photographs were almost sharp. For those samples that included both β and γ modifications the reflections corresponding to the β form were sharp, while those of the γ form were diffuse and, in some instances, they appeared as double diffuse spots.

The misorientation of the γ fibres was of the order of a few degrees. At the present stage of investigation it is not possible to decide whether the diffuseness of the γ reflections is due to a misorientation induced by the handling of the samples or whether it is a characteristic of the aggregates.

Structural relationships between the β and γ forms

Qualitative analysis

The correspondence found above, between the axial orientations of the two forms, was used as a basis for the search for structural relations at the atomic level. The similarity between the two structures compared at this level is not so evident; however, one should expect to find only an approximate correspondence, atom by atom, given the semi-reconstructive character of the transformation and the large difference between the cell parameters ($a_\gamma < a_\beta \approx 8\%$; $c_\gamma > c_\beta \approx 21\%$; about 5° difference in the β angle). To ascertain to what extent the correspondence of structural units exists may, however, give useful information in establishing the transformation mechanism.

The comparison between the two structures is facilitated by looking at the projections along the y axes which are almost equal in length. An inspection of these projections (Fig. 2a, b) shows that in the general arrangement of the atoms one can find similar

trends. The most evident of these is the chain of Ca polyhedra [Ca(1) in γ and Ca(2) in β] in the proximity of the twofold screw axes along y, at $x = z = 0$, $x = z = \frac{1}{2}$ for the γ and $x = z = \frac{1}{4}$, $x = z = \frac{3}{4}$ for the β form. In the γ form the Ca(1) cations are located in a special position (inversion centre on the screw axis); in the β form, the Ca(2) cations are located in a general position very close to the screw axis.

A second feature common to the two structures is the pairs of chains, each composed of alternating Ca–Si polyhedra, [Ca(2)–Si for γ and Ca(1)–Si for β] related by the screw axes along y, at $x = 0$, $z = \frac{1}{2}$; $x = \frac{1}{2}$, $z = 0$ for γ and $x = \frac{1}{4}$, $z = \frac{3}{4}$; $x = \frac{3}{4}$, $z = \frac{1}{4}$ for β.

The Ca–Ca chains are obviously linear in the γ modification, and are zigzag-shaped in the β. The opposite is true for the Ca–Si chains. The screw axes, which are the only symmetry elements common to the two structures, provide, therefore, a good reference point for the comparison. A general correspondence of the position of these chains in the xz plane can be found by translating the cell origin of the β form by $\frac{1}{4}x$, $\frac{1}{4}z$, so that it lies on the screw axis. This cell is represented by dotted lines in Fig. 2(a), and it is this cell that we will refer to from now on.

A further shift of $\frac{1}{2}$ along the y axis is also needed to obtain correspondence among all the Ca and Si cations. In the above characterization of the structures, the cation positions, rather than those of the O atoms, were considered. For a more detailed comparison it is useful to consider the relative orientation of the Si tetrahedra (see Fig. 2). As representative components of this, the orientation of the edge O(2)–O(3)$_\beta$ with respect to O(1)–O(2)$_\gamma$ in the projection plane, and of the edge O(1)–O(4)$_\beta$ with respect to O(3a)–O(3b)$_\gamma$ normal to the plane can be chosen. Two different situations of local agreement are present: for the tetrahedra located in the proximity of the screw axis at $x = 0$, $z = \frac{1}{2}$ [Si(1)$_\beta$ and Si(1, 4)$_\gamma$]* there is a more pronounced orientational accord, and the correspondence among the O atoms O(3), O(2)$_\beta$ with

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* A single digit in parentheses indicates an atom of the asymmetric unit. A second digit, ranging from 1 to 3 for β and from 4 to 6 for γ, indicates equivalent atoms in the positions: (1) $1-x$, $2-y$, $1-z$; (2) $\frac{1}{2}-x$, $\frac{1}{2}+y$, $\frac{3}{2}-z$; (3) $\frac{1}{2}+x$, $\frac{3}{2}-y$, $\frac{1}{2}+z$; (4) $x-\frac{1}{2}$, $1-y$, $\frac{1}{2}-z$; (5) $1-x$, $y-\frac{1}{2}$, $1-z$; (6) $\frac{1}{2}-x$, $\frac{3}{2}-y$, $\frac{1}{2}+z$. Roman-numeral superscripts represent the following translations: (i) $x+1$; (ii) $x-1$; (iii) $y-1$; (iv) $z-1$; (v) $x+1$, $z-1$; (vi) $y+1$, $z-1$.
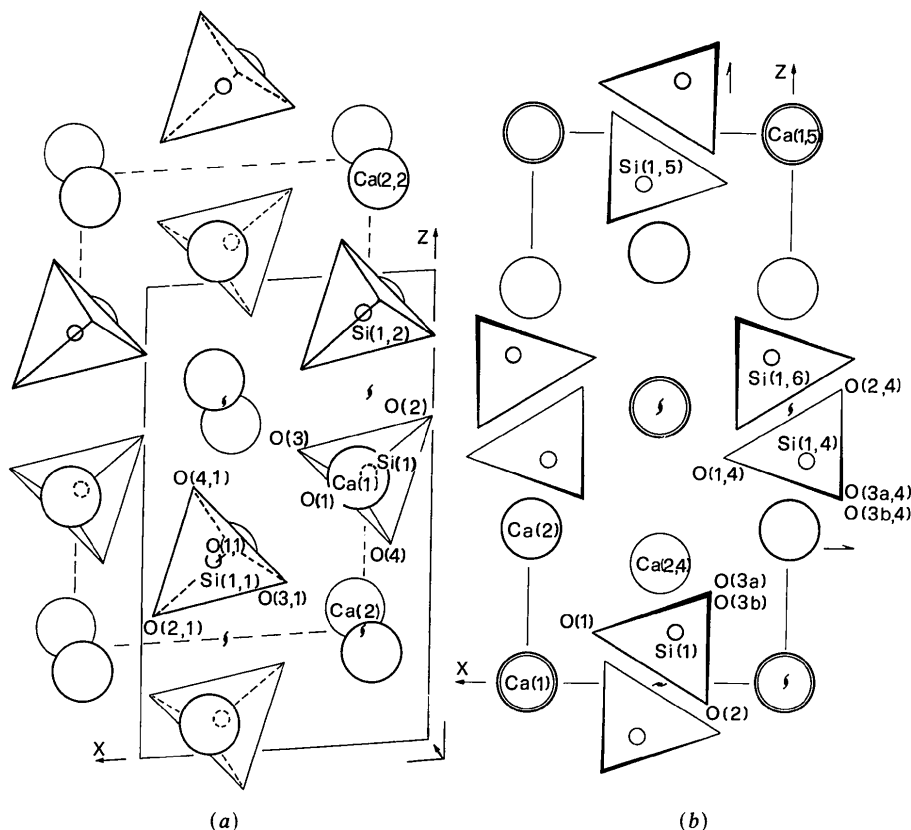

Fig. 2. Structures of Ca$_2$SiO$_4$ projected on (010): (a) β form; (b) γ form. For the β form atoms with y coordinates in the range 0·5–1·5 are shown.

Table 2. *Distances (Å) for corresponding atoms calculated by best-fitting the β on the γ structure for different centroids (first two columns) and by attributing the β cell parameters to the γ coordinates (third column)*

Centroid coordinates		$0,\frac{1}{2},\frac{1}{2}$	$\frac{1}{2},\frac{1}{2},0$	$\frac{1}{2},\frac{1}{2},\frac{1}{2}$
Ca(1)	Ca(2^{ii})	0·80	0·88	0·53
Ca(1,1)	Ca(2,4)	0·77	0·82	0·87
Ca(2)	Ca(1,5^{iv})	1·44	0·51	0·62
Ca(2,2^{iv})	Ca(1^{ii})	0·56	0·79	0·83
Ca(2,1)	Ca(1,6^{i})	0·69	1·52	0·46
Ca(2,3)	Ca(1,4)	0·67	0·49	0·72
Si(1)	Si(1,4)	0·49	1·35	0·70
O(1)	O(3b,4)	1·28	1·37	1·40
O(2)	O(2,4)	0·76	1·90	0·80
O(3)	O(1,4)	0·55	0·92	0·63
O(4)	O(3a,4)	1·25	2·09	1·63
r.m.s.d. (tetrahedron)		0·93	1·58	1·11
Si(1,1)	Si(1)	1·28	0·52	0·81
O(1,1)	O(3b)	1·37	0·83	1·13
O(2,1)	O(1)	0·23	0·66	0·59
O(3,1)	O(2)	2·17	1·47	1·34
O(4,1)	O(3a)	2·51	1·77	2·11
r.m.s.d. (tetrahedron)		1·71	1·16	1·33
r.m.s.d. (48 atoms)		1·40	1·33	1·11

$O(1)$, $O(2)_\gamma$ is evident; the disagreement concerns mainly the pairs of atoms $O(1)$, $O(4)_\beta$ and $O(3b)$, $O(3a)_\gamma$; for the tetrahedra located near the screw axis at $x=\frac{1}{2}$, $z=0$ [$Si(1,1)_\beta$ and $Si(1)_\gamma$] the accord is poorer since there is also a different reciprocal orientation between the $O(2)$–$O(3)_\beta$ and $O(1)$–$O(2)_\gamma$ edges. This is because the units, related in the two structures by different symmetry elements, are being compared. The $Si(1)$ and $Si(1,1)$ tetrahedra in β are related by a centre of symmetry, while $Si(1,4)$ and $Si(1)$ in γ are related by the screw axis along x; obviously the correspondence between symbols is inverted [$O(3)$ and $O(2)_\beta$ that in the first case were related to $O(1)$ and $O(2)_\gamma$ are instead related to $O(2)$ and $O(1)$, respectively, in the second case].

Passing from a local level of comparison to a more general one, together with the effect of symmetry elements, there is also the effect of the cell parameters. In the y direction, in addition to the screw axes common to the two structures, there is also an almost equal length of the b parameter. Therefore, the positional relationship among atoms is almost indefinitely preserved for translation in the y direction, which assumes a special character, confirmed by the fact of being the fibre axis of the γ form. In the x and z directions the situation is completely different. A large difference in the cell parameters (particularly c) is associated with the effect of symmetry. Positional relationships are not preserved with respect to translations in the x and z directions, and situations of good or bad local agreement can be found, depending upon the origin selected for the comparison and whether the two effects described above compensate, or do not compensate for each other. This can be seen qualitatively by superposing the projections of Fig. 2

Table 3. *Distances (Å) for corresponding atoms and transformation matrices calculated by local best-fitting for Ca–Si chains along y and for single tetrahedra*

Centroid coordinates		$\frac{1}{2},\frac{1}{2},0$			$0,\frac{1}{2},\frac{1}{2}$
β	γ		β	γ	
Ca(1,1)	Ca(2,4)	0·98	Ca(1,2^{iii})	Ca(2,5)	0·93
Si(1,1)	Si(1)	0·34	Si(1,2)	Si(1,6)	0·27
O(1,1)	O(3b)	0·33	O(1,2)	O(3b,6)	0·96
O(2,1)	O(1)	0·69	O(2,2)	O(2,6)	0·53
O(3,1)	O(2)	1·21	O(3,2)	O(1,6)	0·75
O(4,1)	O(3a)	0·74	O(4,2)	O(3a,6)	1·18
Ca(1,3^{vi})	Ca(2,6^{v})	1·22	Ca(1)	Ca(2^{ii})	0·61
Si(1,3^{iv})	Si(1,5^{iv})	0·30	Si(1)	Si(1,4)	0·32
O(1,3^{iv})	O(3b,5^{iv})	0·86	O(1)	O(3b,4)	0·73
O(2,3^{iv})	O(1,5^{iv})	0·50	O(2)	O(2,4)	0·47
O(3,3^{iv})	O(2,5^{iv})	1·31	O(3)	O(1,4)	1·07
O(4,3^{iv})	O(3a,5^{iv})	1·34	O(4)	O(3a,4)	0·63
r.m.s.d.		0·90			0·76

Transformation matrix

0·911	−0·031	−0·410	0·959	0·012	0·281
0·090	0·988	0·126	−0·051	0·990	0·132
0·401	−0·151	0·903	−0·277	−0·141	0·950

Centroid coordinates		0·41, 0·75, 0·09			−0·09, 0·25, 0·40
β	γ		β	γ	
Si(1,1)	Si(1)	0·059	Si(1)	Si(1,4)	0·110
O(1,1)	O(3b)	0·079	O(1)	O(3b,4)	0·077
O(2,1)	O(1)	0·066	O(2)	O(2,4)	0·049
O(3,1)	O(2)	0·040	O(3)	O(1,4)	0·123
O(4,1)	O(3a)	0·071	O(4)	O(3a,4)	0·128
r.m.s.d.		0·064			0·102

Transformation matrix

0·712	0·120	−0·691	0·845	−0·440	0·302
0·285	0·851	0·442	0·285	0·850	0·443
0·641	−0·512	0·572	−0·452	−0·288	0·844

and alternatively matching the screw axes at x, $z = 0, \frac{1}{2}$; $\frac{1}{2}, 0$ and $\frac{1}{2}, \frac{1}{2}$ respectively.

Quantitative analysis

To verify in a different way the correlations described above and to obtain a quantitative evaluation of them, a series of calculations was carried out using the program *XFIT* (model fitting) of the package *SHELXTL* (Nicolet, 1983), which allows superposition of fragments of different structures, by optimizing three rotational and three translational parameters to obtain the best fit among the atoms given as the basic set for the comparison. The program calculates the transformation matrix, the coordinates of the centroid of the group of atoms selected, the distance between each pair of specified atoms and the shortest distance between each of the remaining atoms in the two structures.

The β form was fitted on the γ form.* In the initial stages the basic set of atoms was limited to certain

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* The structures under comparison are the β and γ forms of the pure calcium silicate. The modifications induced in the atomic positions by the substitution of small quantities of Ca with Sr are not known. It is possible, therefore, that the real situation in the β and γ association under study would be slightly different from that of the prototypes here analyzed.

Table 4. Ca–O distances (Å) showing the modifications of Ca coordination in the two structures

β		γ		β		γ	
Ca(2,1)		Ca(1,6^i)		Ca(1,1)		Ca(2,4)	
2·64	O(1)			2·43	O(3)	2·44	O(1,4)
2·64	O(3)	2·36	O(1,4)				
				2·88	O(2^i)		
2·38	O(2^i)	2·31	O(2,4^i)	2·37	O(4^i)	2·43	O(3a,4^i)
		2·39	O(3b,4^i)			2·43	O(3b,4^i)
2·39	O(2,2)	2·31	O(2,6)	2·22	O(1,1)	2·38	O(3b)
		2·39	O(3a,6)				
				2·54	O(3,1^iii)		
2·39	O(3,2^i)	2·36	O(1,6^i)	2·64	O(4,1^iii)	2·38	O(3a^iii)
2·43	O(1,1)			2·49	O(2,3^iv)		
2·62	O(4,1)						
2·44	O(4,3)					2·29	O(2,5^iv)

Ca and Si cations, selected in such a number and spatial distribution as to impose, as much as possible, to the rotational and translational parameters optimized by XFIT, the orientational constraints observed experimentally. It was possible to enlarge progressively the initial fragment to obtain a whole unit cell, by fitting the surroundings of two different centroids. However, given the difference in the cell parameters, for atoms far away from the origin of the fitting, the correspondence could not be unequivocally assigned on the basis of a single fitting (one atom of the model corresponded to two atoms of the other structure or to one atom of a different species).

Table 2 shows part of the results of these calculations of fitting sets of Ca atoms and tetrahedra, having centroids at $0, \frac{1}{2}, \frac{1}{2}$ and $\frac{1}{2}, \frac{1}{2}, 0$. The values omitted are those of atoms related by the centroid or by a translation along x, because these are very similar to the ones reported. From Table 2 it can be seen that the distances between corresponding atoms change substantially depending upon the position of the centroid. The same is true for average tetrahedral distances.

A way of minimizing the discrepancies due to the cell parameters is to assign to one form the cell of the other. By this method all the atoms except O(4) and O(4, 1) were automatically paired by a single fitting (column 3 in Table 2). By combining all this information, an atom-by-atom correspondence was obtained which agrees with the qualitative description reported above.

In Table 3 the most relevant data of some local best-fit results are reported; in particular the transformation matrix concerning a single tetrahedron gives information on the rotation that takes place passing from one structure to the other.

Transformation mechanism

The main features of the transformation mechanism from the β into the γ form are implicit in the structural relationships described above. Different rotations, as defined in Table 3, involve the Si(1) and Si(1, 1) type of tetrahedra. These rotations can be visualized in Fig. 2 as the result of three components: a small rotation of about 12° around the normal to the O(2)–O(3) edge and parallel to (010) moves O(2) and O(3) onto the projection plane; a subsequent rotation around the same edge of about 30° causes O(1) and O(4) to be symmetrically related with respect to the projection plane (these two rotations are common to both tetrahedra); a further rotation, smaller for Si(1) (~20°) than for Si(1, 1) (~45°), around the normal to the projection plane gives rise to the final situation. Reduction of the coordination number to six for both Ca cations takes place, maintaining four Ca–O bonds of the β form. In Table 4 the O atoms which are maintained or lost or gained from the Ca coordination sphere are shown. The most important change in coordination is the loss by Ca(1)$_\gamma$ with respect to Ca(2)$_\beta$ of all three bonds linking tetrahedra of the Ca–Si chains in the z direction. In the x direction, however, there is a strengthening of the links between tetrahedra belonging to the Ca–Si chains. This explains the general relaxation of the structure, the large increase of the c parameter and the moderate reduction of the a parameter.

The linking action of Ca(2)$_\gamma$ with respect to Ca(1)$_\beta$ does not change substantially; beside the four bonds which are preserved, there is an exchange of Ca–O bonds involving O atoms belonging to the same tetrahedra. The only lost bond is inside the Ca–Si chain.

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