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The $\beta \leftrightharpoons \alpha'$ Phase Transition of Sr_2SiO_4. I. Order–Disorder in the Structure of the α' Form at 383 K

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(*Received* 28 *January* 1983; *accepted* 27 *July* 1983)

Abstract

The high-temperature α' orthorhombic phase of strontium orthosilicate was studied structurally by single-crystal diffractometry at 383 K $\{a = 5{\cdot}682\,(1)$, $b = 7{\cdot}090\,(1)$, $c = 9{\cdot}773\,(2)$ Å, $V = 393{\cdot}7$ Å^3, $Z = 4$, space group *Pmnb* [non-standard setting of *Pnma* (No. 62); equivalent positions $\pm(x,y,z;\ \tfrac{1}{2}+x,\ \tfrac{1}{2}-y,\ \tfrac{1}{2}+z;\ \tfrac{1}{2}-x,\ y,\ z;\ x,\ \tfrac{1}{2}+y,\ \tfrac{1}{2}-z)$], $M_r = 267{\cdot}32$, $D_x = 4{\cdot}510$ Mg m^{-3}, λ(Mo $K\alpha$) $= 0{\cdot}7107$ Å, $\mu = 26{\cdot}6$ mm$^{-1}\}$, using 741 observed reflexions. Least-squares refinements were performed on: (i) an ordered model, with Sr atoms and SiO_4 tetrahedra lying on (100) mirror planes ($R = 0{\cdot}060$, anisotropic); (ii) a disordered model, with atoms statistically distributed between mirror-related positions ($R = 0{\cdot}069$, isotropic); (iii) a mixed model,

0108-7681/83/060674-06$01.50

which yielded 84% disorder ($R = 0{\cdot}068$, isotropic). A very large anisotropic thermal motion normal to the mirror plane appeared in (i), whereas the anisotropic refinement failed in (ii). The disordered configuration is favoured on crystal-chemical grounds, and probably coexists with a minor amount of ordered structure as a result of the ferroelastic transition from the monoclinic β phase. Similarities with order–disorder in the structure of high quartz are discussed, also in relation to the static or dynamic nature of the disorder.

Introduction

This study forms part of a research programme on polymorphism and crystal-chemical properties of alkaline-earth orthosilicates, which play an important role both in earth sciences (olivine family) and in technological applications (cements). In previous work, crystals of Sr_2SiO_4 were synthetized by flux growth and the crystal structure of the room-temperature monoclinic β phase was determined (Catti, Gazzoni & Ivaldi, 1983), proving it to be isostructural with larnite, β-Ca_2SiO_4 (Jost, Ziemer & Seydel, 1977), and to show the same kind of (100) twinning. Both silicates have high-temperature orthorhombic α' modifications which cannot be quenched; however, the $\beta \leftrightarrows \alpha'$ phase reversion occurs at 973 K for Ca_2SiO_4 (Kazak, Domanskii, Boikova, Ilyukhin & Belov, 1974), but at about 358 K for Sr_2SiO_4 (Pieper, Eysel & Hahn, 1972), so that a high-temperature structural study of the α' form is more feasible experimentally in the latter case. The results of such a structural analysis are shown here and compared with those of α'-$Sr_{1\cdot9}Ba_{0\cdot1}SiO_4$ (Catti *et al.*, 1983), in order to check the congruency of cation substitution and thermal treatment in the α' phase stabilization, and to investigate some problems left open by the refinement of the latter structure, in particular the high thermal motion normal to the (100) mirror plane. In part II (Catti & Gazzoni, 1983) an account is given of a detailed crystallographic and optical study at variable temperature of the phase reversion β-$Sr_2SiO_4 \leftrightarrows \alpha'$-$Sr_2SiO_4$, and the ferroelastic behaviour of the β modification is analysed. The discussion of the displacive mechanism of the transition and of the ferroelastic switching of domains in the β phase is based substantially on structural results shown in this work.

Experimental

The same crystal of Sr_2SiO_4 was used as for the room-temperature structure determination of the β phase. A Syntex Nicolet *R*3 diffractometer (graphite-monochromatized Mo $K\alpha$ radiation) was equipped with an LT-1 low-temperature attachment suitably modified so as to have the crystal heated rather than cooled. A stream of hot N_2 gas was directed onto the sample along the φ axis by a Dewar transport line provided with an electric heater and with swivel joints; pressure and flow were set at $0{\cdot}7 \times 10^5$ Pa and $0{\cdot}57$ m^3 h^{-1}. The temperature was checked by a chromel–alumel thermocouple: its position in the nozzle just above the crystal was optimized so as to achieve the best agreement with the reading of another thermocouple located at the site of the crystal. The latter temperature turned out to be constantly lower than the former by 1 K over the whole thermal range of the experiment, and the working thermocouple output was corrected for that value. The crystal was heated to 383 K and all measurements were performed at that temperature, checking that the $\beta \rightarrow \alpha'$ phase transition had occurred by disappearance of reflection splitting due to twinning and by change of monoclinic to orthorhombic unit cell.

The lattice constants of α'-Sr_2SiO_4 were determined by angular refinement of 25 reflections, and are reported in the *Abstract*. The intensities of 942 reflexions were measured for one octant ($2\theta \le 70°$) with the following conditions: $\omega/2\theta$ scan, $\Delta\theta = 2{\cdot}4°$, scan speed variable between $0{\cdot}03$ and $0{\cdot}49°$ s^{-1} with interpolation for intensities between 300 and 2500 counts s^{-1}, background time $= \frac{1}{2}$ scan time. Two reference reflexions were checked periodically. Absorption was corrected empirically by ψ scans of three high-χ reflexions with different 2θ (North, Phillips & Mathews, 1968): the transmission coefficient ranged from $0{\cdot}61$ to $1{\cdot}00$. All data with $I \le 2\sigma(I)$ were removed, and a final set of 751 independent observations was obtained (index range h 0–9, k 0–11, l 0–15).

Refinements

The least-squares refinement was started from the positional parameters obtained for the structure of α'-$Sr_{1\cdot9}Ba_{0\cdot1}SiO_4$ (Catti *et al.*, 1983), which correspond to an ordered model with five out of six atoms in the asymmetric unit lying on the (100) mirror plane of space group *Pmnb*. Using isotropic thermal factors convergence was reached at $R = 0{\cdot}101$, but the O atoms showed very large temperature factors; introducing anisotropic thermal parameters, R dropped to $0{\cdot}072$, but the thermal tensors of O(2) and O(3) became non-positive-definite. The very strong 200 and 103 reflexions, presumably affected by secondary extinction, were then removed together with eight weak observations with large experimental errors: in addition, the weighting scheme $w = 1/[\sigma^2(|F_o|) + 0{\cdot}001|F_o|^2]$ was introduced, and further full-matrix cycles led to $R = 0{\cdot}060$; however, the thermal tensor of O(3) remained non-positive-definite. Moreover, the two O atoms lying on the mirror plane, O(1) and O(2), had very large components of anisotropic thermal motion normal to the symmetry plane (U_{11} = 0·09 and 0·12 Å^2, respectively), which correspond to thermal ellipsoids with dimensions of 0·60 and 0·70 Å along [100]. Also the equivalent isotropic temperature factors of the O atoms are unusually large (Table 1); similar anomalies of atomic thermal motion were observed also in α'-$Sr_{1.9}Ba_{0.1}SiO_4$.

A second model was tried, which involves positional disorder across the (100) mirror plane at x = 0·25. Each atom lying on it was split into two, in very close positions equivalent by m symmetry, with 0·5 occupation factors (o.f.'s), and refined isotropically. A difference map showed two close residual peaks of equal height in general positions, one of which corresponded to O(3); the other was named O(4), and both were included in the refinement with 0·5 occupation factors. Since Si had not shifted significantly from the mirror plane, it was constrained at x = 0·25 as in the ordered model. The isotropic refinement of this model converged at R = 0·077, and the thermal factors lowered to less than one third, on the average, of the values obtained in the ordered case. An attempt to refine anisotropic temperature parameters failed, as the R value increased, the e.s.d.'s attained very large values and nearly all thermal factors became non-positive-definite. The isotropic refinement was concluded by introducing the same weighting scheme and omitting the same reflexions as in the case of the ordered model, and R = 0·069 was obtained. The final positional and thermal parameters are reported in Table 1* for refinements of both the disordered (isotropic) and ordered (anisotropic) model. Bond distances and angles are shown in Table 2.

A mixed-model isotropic refinement was also attempted, splitting atoms O(1) and O(2) into O(1'), O(2') out of the mirror plane ($x \neq 0{\cdot}25$, occupation factor = p) and O(1''), O(2'') in the mirror plane ($x = 0{\cdot}25$, o.f. = $0{\cdot}5 - p$). The o.f.'s of O(3) and O(4) were constrained to be $1 - p$ and p, respectively; Sr atoms were kept in general positions ($x \neq 0{\cdot}25$) as in the pure disordered model. The p parameter, ranging from 0 (pure order) to 0·5 (pure disorder), was refined to 0·42 (4) resulting in R = 0·068; no atom shifted significantly from the positions reported in Table 1. This test confirms that, within an isotropic thermal-motion scheme, the disordered model allows a better F_o/F_c agreement; however, a small but significant fraction of the crystal should correspond to the ordered structure.

Table 1. *Fractional atomic coordinates and temperature factors* (Å^2 × 10^2) *for the disordered isotropic* (*upper lines*) *and the ordered anisotropic* (*lower lines*) *models*

E.s.d.'s are shown in parentheses. $U_{eq} = \frac{1}{3}\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j$.

	x	y	z	U or U_{eq}	o.f.
Sr(1)	0·2651 (5)	0·3403 (1)	0·5794 (1)	0·70 (3)	0·5
	0·25	0·3403 (1)	0·57938 (9)	0·97 (2)	0·5
Sr(2)	0·2663 (4)	−0·0014 (1)	0·30208 (9)	0·37 (3)	0·5
	0·25	−0·0013 (1)	0·30213 (8)	0·68 (2)	0·5
Si	0·25	0·7788 (4)	0·5832 (3)	0·32 (5)	0·5
	0·25	0·7786 (3)	0·5831 (3)	0·32 (6)	0·5
O(1)	0·292 (2)	1·005 (1)	0·569 (1)	0·8 (2)	0·5
	0·25	1·005 (1)	0·5683 (9)	3·6 (4)	0·5
O(2)	0·207 (2)	0·676 (1)	0·4332 (9)	1·0 (2)	0·5
	0·25	0·676 (1)	0·4333 (8)	4·5 (5)	0·5
O(3)	0·488 (2)	0·687 (2)	0·646 (1)	0·8 (2)	0·5
	0·480 (1)	0·706 (1)	0·6639 (7)	3·2 (2)	1·0
O(4)	0·028 (2)	0·726 (2)	0·681 (1)	0·8 (2)	0·5
	—	—	—	—	—

Table 2. *Interatomic distances* (Å) *and* O—Si—O *angles* (°) *for the disordered* (*D*) *and ordered* (*O*) *models, with e.s.d.'s in parentheses*

	D	*O*
Si—O(1)	1·627 (7)	1·612 (9)
Si—O(2)	1·655 (8)	1·635 (8)
Si—O(3)	1·62 (1)	1·611 (6) (×2)
Si—O(4)	1·63 (1)	
Average	1·633	1·617

	D	*O*	*D*	*O*
O(1)—O(2)	2·73 (1)	2·68 (1)	112·3 (4)	111·3 (4)
O(1)—O(3)	2·62 (2)	2·660 (7) (×2)	107·8 (6)	111·2 (3) (×2)
O(1)—O(4)	2·71 (1)		113·0 (6)	
O(2)—O(3)	2·62 (1)	2·614 (7) (×2)	106·4 (5)	107·3 (2) (×2)
O(2)—O(4)	2·65 (1)		107·7 (5)	
O(3)—O(4)	2·65 (2)		109·4 (5)	
O(3)—O(3,5)		2·614 (8)		108·4 (3)
Average	2·663	2·640	109·4	109·5

	D	*O*
Sr(1)—O(1^{i})	2·384 (7)	2·380 (9)
Sr(1)—O(2)	2·796 (8)	2·775 (7)
Sr(1)—O(2,2^{iii})	2·69 (1)	2·846 (6) (×2)
Sr(1)—O(2,2^{ii})	3·00 (1)	
Sr(1)—O(3)	2·84 (1)	3·019 (7) (×2)
Sr(1)—O(4)	3·21 (1)	
Sr(1)—O(3,2^{ii})	2·62 (1)	2·849 (6) (×2)
Sr(1)—O(4,2^{iii})	3·08 (1)	
Sr(1)—O(3,4^{v})	3·23 (1)	2·985 (7) ×2)
Sr(1)—O(4,4^{v})	2·74 (1)	
Average	2·859	2·855
Sr(2)—O(1^{i})	2·61 (1)	2·602 (9)
Sr(2)—O(2^{i})	2·643 (8)	2·623 (7)
Sr(2)—O(2,4^{i})	2·625 (8)	2·622 (8)
Sr(2)—O(1,2^{iii})	3·41 (1)	3·111 (3) (×2)
Sr(2)—O(1,2^{ii})	2·81 (1)	
Sr(2)—O(3,2^{ii})	2·68 (1)	2·617 (7) (×2)
Sr(2)—O(4,2^{iii})	2·58 (1)	
Sr(2)—O(3,3^{vi})	2·56 (1)	2·507 (6) (×2)
Sr(2)—O(4,3^{viii})	2·48 (1)	
Average	2·711	2·702

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* Lists of structure factors (disordered model) and anisotropic thermal parameters (ordered model) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38748 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

In the structure determination of α'-$Sr_{1.9}Ba_{0.1}SiO_4$ the ordered model only had been refined, whereas an anisotropic refinement of the disordered model failed (Catti *et al.*, 1983). Now that model has been refined successfully with isotropic thermal factors (R = 0·058), obtaining structural parameters which are very close to those of α'-Sr_2SiO_4 for the disordered case. The scattering factors (including corrections for anomalous scattering) for neutral atoms reported in *International Tables for X-ray Crystallography* (1974), and the *SHELX* package of crystallographic programs (Sheldrick, 1976) were used in the calculations.

Discussion

Analysis of positional disorder

The crystal structures of α'-Sr_2SiO_4 at 383 K and of α'-$Sr_{1.9}Ba_{0.1}SiO_4$ at room-temperature are nearly identical, and show the same apparent ambiguity between an ordered (1) and a positionally disordered (2) model. Indeed, the R values are slightly smaller for case (1) (0·060 and 0·052) than for case (2) (0·069 and 0·058) in both structures, but that difference can be ascribed entirely to the larger number of parameters included in the anisotropic refinement (1) with respect to the isotropic refinement (2). On the other hand, model (2) may not be refinable anisotropically because the split-atom positions are too close. Some recent structural studies just above a phase-transition temperature [*cf.* the cubic perovskite $CsPbCl_3$ (Hutton & Nelmes, 1981)] have shown that an anharmonic single-site model for atomic thermal motion can often provide a comparable or even better fit to diffraction data than do harmonic multi-site (disordered) refinements. Further, by investigating the relations between anharmonic two-site, anharmonic single-site and harmonic two-site one-particle potentials and the corresponding Debye–Waller factors, Mair (1982) has proved that these cases can be discriminated only by very careful measurements of high-order diffraction data against temperature. As our data are not suitable for this kind of study, the problem of possible anharmonicity in orthorhombic Sr_2SiO_4 is left open, and all results (here and in part II) are discussed in terms of traditional ordered or disordered harmonic models.

In order to check that the disordered model is better than the ordered one, as is suggested by the mixed-model refinement, a careful comparison on crystal–chemical grounds will be performed below. The only significant differences between the structural results for α'-Sr_2SiO_4 and α'-$Sr_{1.9}Ba_{0.1}SiO_4$ are in the x coordinates of Sr(1) and Sr(2) in the disordered model, which are 0·2694 (3) and 0·2703 (3) for the latter compound against 0·2651 (5) and 0·2663 (4) for the former. A larger separation between the mirror-related split-atom positions is apparently caused in the two Sr sites by 5% Ba substitution.

The ordered model implies an unusually small SiO_4 tetrahedron, with an average Si—O bond length of 1·617 Å in α'-Sr_2SiO_4, whereas the minimum value observed in nesosilicates is 1·622 Å (Baur, 1978). This is undoubtedly the weak point of the model. Another feature already discussed in the previous paper (Catti *et al.*, 1983) is shown by the two independent Sr coordination polyhedra: the Sr—O bonds can be grouped in pairs equivalent by mirror symmetry, which approximate in length to the average of the two corresponding non-equivalent bonds in the monoclinic structure of β-Sr_2SiO_4; this causes some imbalance of bond valence on Sr(1).

The disordered model is a statistical average of two structural configurations with $P2_1/n$ symmetry (but characterized by a geometrically orthorhombic lattice), which are related by the (100) mirror plane (Fig. 1). Therefore the apparent overall structure is orthorhombic *Pmnb*, while the local or instant structure is monoclinic $P2_1/n$ in two distinct orientations related by m symmetry. In Table 2, only Sr—O bonds belonging to one of the two structural orientations (*i.e.* that corresponding to the published β-Sr_2SiO_4 structure) are reported, excluding possible bonds between Sr and O atoms of different orientations.

Obviously no information about the static or dynamic nature of the disorder can be drawn from the diffraction experiment. In the static case the crystal of the α' phase would be formed by very small monoclinic domains in their two orientations; in the dynamic case all atoms would be continuously swinging in double-well potentials in each single unit cell. By comparing atomic coordinates and bond distances of

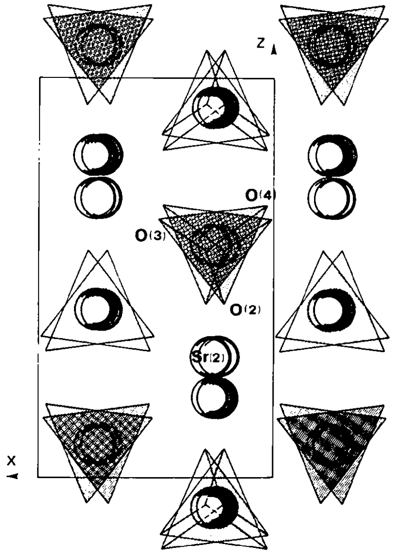

Fig. 1. Crystal structure of α'-Sr_2SiO_4 projected on (010), showing disorder of Sr atoms and SiO_4 tetrahedra.

the disordered model of α'-Sr_2SiO_4 with those of the low-temperature β phase (Catti *et al.*, 1983), it turns out that the local (or instant) monoclinic structure of the α' phase is very close to the monoclinic structure of the β phase, except for the lattice β angle which is a right-angle in the former and oblique in the latter case. In particular, the average Si—O bond length in the disordered α' model is quite normal (1·633 Å), which is similar to that observed in the β structure: this point decisively favours model (2) with respect to model (1). Indeed, it cannot be explained easily why a low-energy displacive phase transition (β-Sr_2SiO_4 → α'-Sr_2SiO_4) should cause the high-energy Si—O bonds to shorten below normal values, as is required by the ordered α' model. Comparing the Sr coordination polyhedra in the α' (model 2) and β phases, all corresponding Sr—O bond lengths are very similar, particularly for Sr(2); the largest variation is observed for Sr(1)—O(3,4^{v}),[*] which changes from 3·35 Å in β to 3·23 Å in α'. On the whole, the longest Sr—O bonds tend to shorten in the transition $\beta \rightarrow \alpha'$, but the average Sr(1)—O and Sr(2)—O distances do not change appreciably. A bond-valence calculation (Brown & Wu, 1976) for models (1) and (2) of α'-Sr_2SiO_4 has shown similar results to those obtained for α'-$Sr_{1.9}Ba_{0.1}SiO_4$ and β-Sr_2SiO_4 by Catti *et al.* (1983), respectively. Thus Sr(1) appears to be underbonded in the ordered ($\sum_i s_i =$ 1·58 v.u.) with respect to the disordered model ($\sum_i s_i =$ 1·68 v.u.), so that the latter would provide a more satisfactory bond-valence balance.

Comparison with the high-temperature β phase of quartz

Taking into account the very high atomic thermal motion and the unusually small size of the SiO_4 tetrahedron which are involved in model (1), and the results of the mixed-model refinement, the disordered model (2) appears to be more reliable for the crystal structure of α'-Sr_2SiO_4. However, since the ordered configuration cannot be completely rejected on the basis of diffraction data, the following assumption seems to be reasonable: within a common orthorhombic lattice, three different atomic configurations are present together in a crystal of the α' phase, *i.e.* the two orientations of the asymmetrical, monoclinic structure and (in minor amount) the symmetrical, orthorhombic structure as well. Whether the effect is time- or space-controlled could be ascertained only by vibrational spectroscopy and electron microscopy techniques. In the former (dynamic) case the atoms would jump 'tunnelling' between three alternative positions; in the latter (static) case the three structural configurations would be confined to different microdomains in the crystal.

This situation can be compared to that found in crystals of the high-temperature β phase of quartz (Wright & Lehmann, 1981; Liebau & Böhm, 1982). By cooling β-quartz (space group $P6_222$) to 843 K, a transition occurs to the α phase ($P3_221$), which shows two orientation states related by a twofold axis along [001] (Dauphiné law twinning, with black-and-white point symmetry 6′22′). Unlike the phase reversion of Sr_2SiO_4, in this case the lattice geometry does not change, so that α-quartz forms twins by merohedry or TLS instead of TLQS (Donnay & Donnay, 1974), and is ferrobielastic instead of ferroelastic (Laughner, Newnham & Cross, 1982). However, similarly to α'-Sr_2SiO_4 the crystal structure of β-quartz can be refined according to both an ordered $P6_222$ model and a disordered model where atoms are split between two positions related by the [001] twofold axis, so that a statistical average is obtained over two trigonal configurations corresponding to the two orientations of the $P3_221$ structure of α-quartz in a Dauphiné twin; the disordered model is reported to give a lower R factor (Wright & Lehmann, 1981). Following the analysis of disorder in β-quartz proposed by Liebau & Böhm (1982), the real structure of α'-Sr_2SiO_4 can be considered to contain ordered microdomains (with dimensions within the coherence range of X-rays) of the two states of the $P2_1/n$ structure, separated by domain boundaries of finite thickness; these would show either a dynamic fluctuation of SiO_4 tetrahedra between the above orientation states, or a static orthorhombic configuration with the tetrahedra in a single-well potential on the mirror plane.

In the case of both Sr_2SiO_4 and quartz, order–disorder in the high-temperature form and high-temperature ⇆ low-temperature phase reversion are indissolubly connected phenomena.

This research was supported financially by the Consiglio Nazionale delle Ricerche and by the Ministero Pubblica Istruzione, Roma.

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[*] A second figure in parentheses, ranging from 2 to 8, denotes atoms in the positions $\bar{x},\bar{y},\bar{z}$; $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$; $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; $\frac{1}{2}-x, y, z$; $\frac{1}{2}+x, \bar{y}, \bar{z}$; $x, \frac{1}{2}+y, \frac{1}{2}-z$; $\bar{x}, \frac{1}{2}-y, \frac{1}{2}+z$. Roman numerals represent the following translations: (i) $-\mathbf{b}$; (ii) $\mathbf{a}+\mathbf{b}+\mathbf{c}$; (iii) $\mathbf{b}+\mathbf{c}$; (iv) $-\mathbf{a}+\mathbf{b}+\mathbf{c}$; (v) $-\mathbf{b}+\mathbf{c}$; (vi) $-\mathbf{a}-\mathbf{c}$; (vii) $\mathbf{a}-\mathbf{c}$; (viii) $-\mathbf{c}$.

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The $\beta \rightleftarrows \alpha'$ Phase Transition of Sr_2SiO_4.
II.* X-ray and Optical Study, and Ferroelasticity of the β Form

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(*Received* 28 *January* 1983; *accepted* 27 *July* 1983)

Abstract

The transition between the monoclinic β and orthorhombic α' phases of strontium orthosilicate was investigated by single-crystal diffractometry and polarizing microscopy at variable temperatures, on the basis of the disappearance or appearance of twin domains of the β form. The phase change occurred sharply with thermal hysteresis in both experiments, at 364 and 355 K (X-rays) and at 369 and 359 K (light, best values out of a number of samples) for $\beta \rightarrow \alpha'$ and $\alpha' \rightarrow \beta$, respectively; the optical study showed that transition temperatures are influenced by the size and habit of crystals. The orientations of β and α' lattices are related by a simple rotation of the x axis. A first-order character is suggested by thermal results for the phase change, though it relates ordered and disordered structures. Crystals of β-Sr_2SiO_4 prove to be ferroelastic (Aizu's species *mmmF*2/*m*) with a spontaneous strain of 0·033. The mechanisms of the phase transition and of the transformation between mirror-related orientation states are discussed in relation to structural disorder of the paraelastic α' form.

Introduction

Displacive phase transformations are characterized by small structural rearrangements, without breaking any primary coordination bonds (Buerger, 1961), and are fast, reversible and nonquenchable. In most cases, the space group of the low-temperature (or high-pressure) distorted phase is a subgroup of that of the high-temperature (or low-pressure) undistorted form, so that crystals of the low-symmetry modification often show twin domains and ferroelastic or ferrobielastic behaviour. Preserving the single-crystal integrity, such phase transitions are ideally suited to optical and crystallographic studies at variable temperatures or pressures, in order to follow lattice and structural changes over a convenient thermodynamic range and to investigate the atomic mechanism of the transformation. In particular, data on crystallographic paths of displacive transitions are useful in understanding why some show first-order and others show second-order thermodynamic behaviour, and to account for hysteresis phenomena often observed in the phase change.

In the frame of an investigation of the crystal chemistry and the polymorphism of alkaline-earth orthosilicates, the structures of β-Sr_2SiO_4, monoclinic $P2_1/n$ (Catti, Gazzoni & Ivaldi, 1983), and of α'-Sr_2SiO_4, orthorhombic *Pmnb* (Catti, Gazzoni, Ivaldi & Zanini, 1983), were previously determined from the same crystal at 298 and 383 K, respectively. The transition between the low-β and the high-α' forms is reported by Pieper, Eysel & Hahn (1972) to occur at about 358 K by DTA measurements, with a small but significant enthalpy change of 210 J mol^{-1} (DSC results). A large number of compounds in the A_2BX_4 family are isostructural with either α'- or β-Sr_2SiO_4, and some show both modifications and the corre-

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* Part I: Catti, Gazzoni, Ivaldi & Zanini (1983).

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