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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 $mmmF2/m$) 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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sponding $\beta \rightleftarrows \alpha'$ transition. The orthorhombic α′ structure is the same as that of the low-temperature phase of K_2SO_4, and corresponds to a slight distortion of hexagonal high-temperature K_2SO_4; it is shown by K, Rb, NH_4 sulphates, selenates, chromates and tetrafluoroberyllates, by Ca, Sr, Ba orthosilicates and by other compounds such as Rb_2ZnCl_4 and $[N(CH_3)_4]_2CuCl_4$ (O'Daniel & Tscheischwili, 1942; Unruh, 1981). The β structure is observed for Ba_2TiO_4 (Bland, 1961). Further, Ca_2SiO_4, Na_2BeF_4 and Eu_2SiO_4 are reported to crystallize in both forms (Pieper *et al.*, 1972). The phase transition for Ca_2SiO_4, which occurs at about 973 K, was investigated by Saalfeld (1975) using X-ray oscillation photographs.

A single-crystal study of the β-$Sr_2SiO_4 \rightleftarrows \alpha'$-$Sr_2SiO_4$ transformation by X-ray diffractometry and polarizing microscopy at variable temperatures is presented here, in close relation with the structure analysis of the α′ form reported in part I (Catti, Gazzoni, Ivaldi & Zanini, 1983). The thermal properties of the phase change and the β–α′ lattice relationships should be related to the positional order–disorder observed in high-temperature Sr_2SiO_4. Moreover, since the low-temperature β phase shows twin domains (Catti, Gazzoni & Ivaldi, 1983) and can be formally classified as Aizu's (1969) ferroelastic species *mmmF*2/*m*, the possible presence of true ferroelastic behaviour is also investigated in this work.

Thermal investigation

Single-crystal diffractometry

For this experiment, we used the same crystal of Sr_2SiO_4 from which X-ray intensities had been collected at 298 (β form) and 383 K (α′ form). The sample was mounted along [2$\bar{3}$0] on a Syntex Nicolet *R*3 diffractometer (Mo *K*α radiation) equipped with the same heating device described in part I. In the monoclinic β phase the crystal shows (100) twinning with separated lattices for the two twin orientations. The *hkl* reciprocal-lattice points of orientation (I) are close to the $\bar{h}\bar{k}l$ points of orientation (II) (Fig. 1), so that an ω scan of reflection *hkl*(I) shows a second peak from reflection $\bar{h}\bar{k}l$(II); the Δω separation between the two peaks depends on the *h*, *k*, *l* indices and also on how the crystal is mounted on the goniometer head. After a search for very intense reflections with convenient Δω values, the pair $1\bar{2}1$(I)/$\bar{1}21$(II) was selected (Δω = 1·16° at 298 K), and the ω-scan profile over a range of 3° centred on the $1\bar{2}1$ reflection was recorded repeatedly at different temperatures as a probe for the $\beta \rightleftarrows \alpha'$ phase transition. Indeed, when the crystal transformed to the α′ form the $\bar{1}21$(II) peak disappeared from the profile and the $1\bar{2}1$(I) peak shifted off-centre because of the sharp change of the β lattice angle.

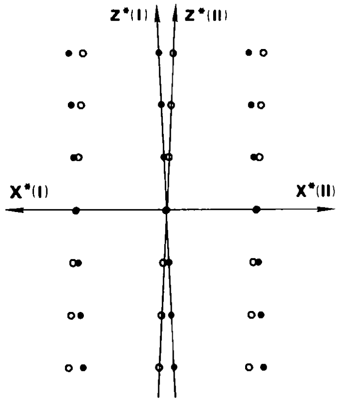

Fig. 1. Reciprocal lattices of orientation states (I) (black circles) and (II) (open circles) in a (100) twinned crystal of β-Sr_2SiO_4. The y^*(I) and y^*(II) axes point upwards and downwards, respectively.

Table 1. *Lattice constants of the β and α′ phases of* Sr_2SiO_4 *at different temperatures* (*single-crystal diffractometry*)

T (K)	298	353	367	383
Phase	β	β	α′	α′
a (Å)	5·663 (1)	5·668 (2)	5·681 (1)	5·682 (1)
b (Å)	7·084 (2)	7·090 (2)	7·085 (2)	7·090 (1)
c (Å)	9·767 (2)	9·784 (3)	9·764 (2)	9·773 (2)
β (°)	92·67 (2)	92·55 (3)	90	90
V (Å³)	391·4	392·8	393·0	393·7

Starting from room temperature, a very low heating rate (about 5 K h^{-1}) was applied; for $T > 353$ K the scan profiles were recorded at 1 K intervals, and the β → α′ transition occurred sharply at 364 K. The crystal was then cooled at the same rate and showed a sharp α′ → β reversion at 355 K. Several thermal cycles were performed confirming the above two temperature values and the presence of a 9 K hysteresis. The lattice constants of the two phases were determined by angular refinement of 22 reflections in the neighbourhood of the transition, at 367 (α′ phase) and 353 K (β phase), and are reported in Table 1 together with data for $T = 298$ and 383 K already published (*cf.* part I). The β angle hardly appears to decrease over the whole heating cycle, till the transition temperature when it jumps sharply to 90°. This is confirmed by the Δω peak separation in the scan profile, which changes from 1·15 to 1·12° at 353 K, and then remains constant up to 363 K just before the transition. A similar sharp change is observed in the cooling cycle. This discontinuous character of the phase transformation agrees with DSC data (Pieper *et al.*, 1972), which would support a first-order thermodynamic classification. A peculiar behaviour is also shown by the *c* cell edge, which increases regularly with temperature both for the β and for the α′ phases, but decreases sharply and significantly in the β → α′ passage. On the other hand, the volume change at the transition temperature is hardly significant.

The orientation matrices of the crystal were determined together with the lattice constants of Table 1 at 353 and 367 K, obtaining the components of the reciprocal-cell vectors with respect to the laboratory reference frame for the monoclinic and orthorhombic forms, respectively. By comparing these data, the relative movement of crystallographic axes during the phase change can be determined. It turns out that **b*** and **a*** do not tilt significantly, whereas the **c*** vector rotates by 2·55° in the $\beta \rightleftarrows \alpha'$ passage. Thus the (100) plane (which is the twinning plane in the β form) keeps the same orientation in both phases, as do the y and z direct axes; the lattice mechanism of the phase transition is simply provided by a rotation of the x axis between two orientations, so that the β angle switches from 92·55 to 90° and *vice versa*.

Optical microscopy

A Leitz polarizing microscope with heating stage was used. The temperature read by the working thermometer was checked by a thermocouple located at the sample position. The crystals of Sr_2SiO_4 previously synthetized (Catti, Gazzoni & Ivaldi, 1983) showed {001}, {101} and {011} as dominant forms. Polysynthetic twinning with (100) contact plane and very thin lamellar domains was present in all crystals observed along the [010] direction; those with smallest [010] elongation and largest {011} development were selected, together with a few showing {010} tabular habit, so as to attain the best conditions of observation of twin domains in the β phase. Observing the {010} tabular crystals at room temperature, the plane of the optical axes showed an angle of 25° with the (100) contact plane; the optical sign was positive. The relative orientations of optical indicatrices and of crystallographic axes in the twin domains of the monoclinic form are reported in Fig. 2.* An examination of the orthorhombic α' phase at high temperature showed that the plane of the optical axes is parallel to (001), and the optical sign is positive.

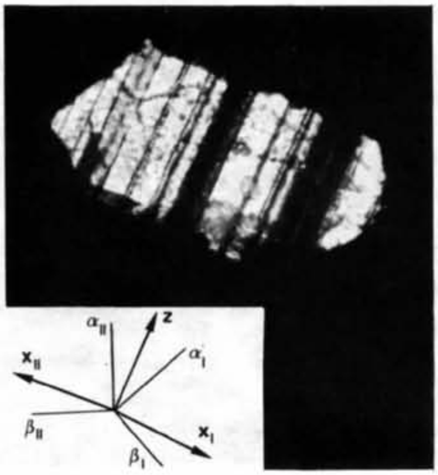

Fig. 2. Twinned domains in a {010} tabular crystal of β-Sr_2SiO_4 under crossed polarizers. The relative orientations of crystallographic axes and principal optical directions are shown.

Table 2. *Temperature values* (K) *of the* $\beta \rightarrow \alpha'$ *or* $\alpha' \rightarrow \beta$ *phase transition, observed by optical microscopy on three single crystals* (1,2,3) *in consecutive thermal cycles*

Starting temperature (K), ageing times (h) and heating (↑) or cooling (↓) rates (K h^{-1}) are reported in the first three columns.

			(1)	(2)	(3)
298		5↑	375·5	371·5	370·5
383		5↓	364·0	361·5	362·0
353		5↑	373·5	369·0	369·0
383		5↓	363·5	361·0	361·5
353		60↑	371·5	368·5	367·5
383		60↓	359·0	359·5	361·0
353	20	5↑	372·0	369·0	368·5
383	20	5↓	357·5	359·0	360·5
298		10↑	375·0	371·5	369·5
383	60	10↓	353·0	358·5	360·5
353		5↑	369·0	370·0	369·0
423	4	5↓	354·0	357·5	359·5
353		2↑	371·5	368·0	368·5
473	4	2↓	352·5	356·5	358·0
353	4	5↑	370·0	368·0	367·0
383	4	5↓	355·0	357·5	360·0

The crystals were observed in conditions of extinction for one of the two twin orientations in the heating cycles of the β form, and in overall extinction in the cooling cycles of the α' form; the phase transition was detected by disappearance ($\beta \rightarrow \alpha'$) or appearance ($\alpha' \rightarrow \beta$) of twin domains, just as in the X-ray study. Heating and cooling rates from 2 to 60 K h^{-1} in the temperature range 298–473 K were applied, using a number of crystals of different sizes. The phase transition always occurred sharply at a well defined temperature which, however, varied within some K according to the shape and size of the crystal and to its thermal history; a thermal hysteresis of about 10 K between the $\beta \rightarrow \alpha'$ and the $\alpha' \rightarrow \beta$ phase-change directions was always observed. The most significant results of several subsequent thermal cycles are reported in Table 2 for three crystals: {010} tabular and 0·08 mm thick (1), prismatic with 0·3 mm between the (011) and $(0\bar{1}\bar{1})$ faces (2), prismatic and 0·5 mm thick (3). The largest hysteresis and scatter of transition-temperature values are shown by sample (1), whereas results for samples (2) and (3) are closer to X-ray data (obtained also from a prismatic crystal). By a long ageing of the crystal near the transition point, the hysteresis range is generally reduced. Therefore, the transition temperatures observed for crystals (2) and (3) after a 20 h ageing at 353 K and a 20 or 60 h ageing

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* A check was performed by precession photographs.

at 383 K can be considered as the most reliable; their values are approximately 369 K for the $\beta \to \alpha'$ and 359 K for the $\alpha' \to \beta$ transitions, respectively, with a 10 K thermal hysteresis. These temperatures are slightly higher than those determined by single-crystal diffractometry, and this could be due either to the use of different crystals in the two experiments, or to a possible inadequacy of the experimental set-ups.

The influence of thermal treatment on the twin-domain structure of the β form was also investigated. By performing several thermal cycles just between the $\beta \to \alpha'$ and $\alpha' \to \beta$ transformation temperatures, the number of domains decreased with an increase of their size, until only two or three large ones remained. On the other hand, by cooling the α' form from higher temperatures many thin domains reappeared at the $\alpha' \to \beta$ transition.

Ferroelasticity of β-Sr_2SiO_4

According to twinning theory (Donnay & Donnay, 1974), the crystals of β-Sr_2SiO_4 are TLQS† twins with obliquity $\omega = 2{\cdot}67°$ of type $2^{*\prime}/m'\,2/m2'/m^{*\prime}$. This kind of twinning corresponds formally to the pure ferroelastic species $mmmF2/m$, for which coupling with ferroelectricity is excluded on symmetry grounds (Aizu, 1969). A test to detect actual ferroelastic properties of β-Sr_2SiO_4 was performed at room temperature, by observing twin domains normal to the (011) face on crystals held between two slides under a polarizing microscope. A mechanical stress was applied laterally onto the [010] edges, and also normal to the (101) faces of the crystals, with the aid of thin plates between the slides; in both cases the walls of the domains were observed to shift with a change of thickness (Fig. 3), proving that the two orientation states are transformed into each other by action of the stress, as required by ferroelastic behaviour. Thus the high-temperature α' modification is the prototypic or paraelastic phase associated with the ferroelastic β phase, and the $\beta \rightleftharpoons \alpha'$ transformation belongs to the class of ferroelastic phase transitions. Pure ferroelastic substances are not known in great number: $Pb_3(PO_4)_2$, $\bar{3}mF2/m$ (Brixner, Bierstedt, Jaep & Barkley, 1973), $BiVO_4$, $4/mF2/m$ (David, Glazer & Hewat, 1979), $RbAlF_4$, $4/mmmFmmm$ (Bulou & Nouet, 1982), VO_2, $4/mmmF2/m$ (Fillingham, 1967), Sb_5O_7I, $6/mF2/m$ (Büchele & Buck, 1980), $Rb_2Hg(CN)_4$, $m3mF\bar{3}m$ (Haussühl, 1978) are examples.

According to Aizu (1970), ferroelasticity can be measured by the 'spontaneous strain' ε_s which is involved in the lattice change from the prototype to any of the orientation states of the ferroelastic phase. This scalar quantity is independent of the lattice reference frame, and is defined as $\varepsilon_s \equiv (\Sigma_{ij}\,\varepsilon_{ij}^2)^{1/2}$; ε_{ij} is a general element of the spontaneous strain tensor $\boldsymbol{\varepsilon} \equiv \boldsymbol{\varepsilon}(\mathrm{I}) - \frac{1}{2}[\boldsymbol{\varepsilon}(\mathrm{I}) + \boldsymbol{\varepsilon}(\mathrm{II})]$, where $\boldsymbol{\varepsilon}(\mathrm{I})$ and $\boldsymbol{\varepsilon}(\mathrm{II})$ are the linear Lagrangian strain tensors relative to the orientation states (I) and (II). For the monoclinic lattice of β-Sr_2SiO_4, we have (Morimoto & Tokonami, 1969; Schlenker, Gibbs & Boisen, 1978):

$$\boldsymbol{\varepsilon}(\mathrm{I}) = \begin{bmatrix} \sin\beta - 1 & 0 & \frac{1}{2}\cos\beta \\ 0 & 0 & 0 \\ \frac{1}{2}\cos\beta & 0 & 0 \end{bmatrix};$$

also, $\boldsymbol{\varepsilon}(\mathrm{II}) = \mathbf{F}^{-1}\,\boldsymbol{\varepsilon}(\mathrm{I})\,\mathbf{F}$, where $\mathbf{F}$ is the matrix of the symmetry operation F (equivalent to the twinning operation), which is the (100) m plane in this case; thus, $\varepsilon_{ii}(\mathrm{II}) = \varepsilon_{ii}(\mathrm{I})$, and $\varepsilon_{ij}(\mathrm{II}) = -\varepsilon_{ij}(\mathrm{I})$ $(i \neq j)$. The spontaneous strain is $\varepsilon_s = \sqrt{2}|\varepsilon_{13}| = |\cos\beta|/\sqrt{2} = 0{\cdot}033$; this value would show that ferroelasticity of β-Sr_2SiO_4 is numerically important (*cf.* Toledano, 1974), in accord with the rather large distortion of its lattice from orthorhombic geometry.

A quantitative evaluation of the ferroelastic phenomenon is also feasible on atomic scale, by calculating the shifts of atoms in the transformation between the

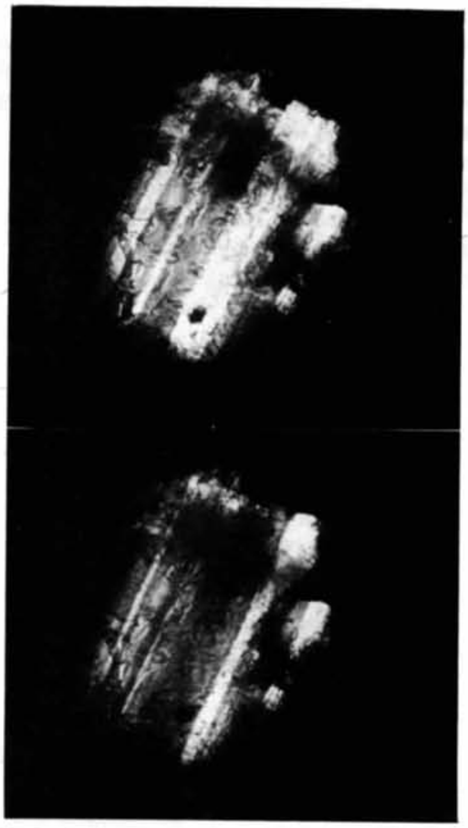

Fig. 3. Shift of domain walls caused by a lateral stress, showing ferroelastic behaviour of a prismatic crystal of β-Sr_2SiO_4 seen on the (011) face.

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† Twin-lattice quasi-symmetry.

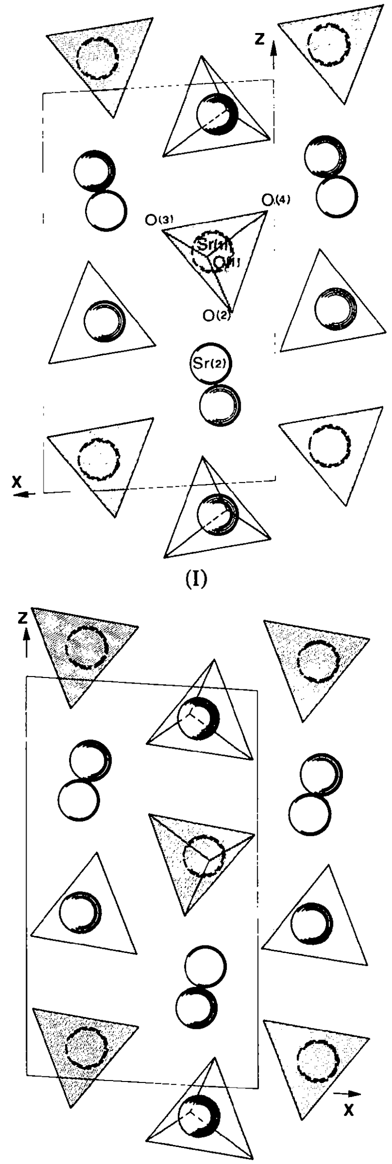

Fig. 4. Projection onto (010) of the crystal structure of the two orientation states of β-Sr_2SiO_4.

two orientation states (Abrahams & Keve, 1971; Svensson, Abrahams & Bernstein, 1979), which can be thought as due to the action of the F operation (Fig. 4). Within the asymmetric unit, the position of any atom i can be related to that of another one j of the same atomic species according to $\mathbf{x}_i = \mathbf{F}\mathbf{x}_j + \mathbf{\Delta}_{ij}$ ($i = j$ is possible); $\mathbf{\Delta}_{ij}$ is the displacement vector of atoms i and j in the ferroelastic reaction, whose length is generally less than 1 Å (Guimaraes, 1979). Clearly F is a pseudosymmetry operation of the crystal structure itself. Using the orthogonal absolute atomic coordinates $X_i = a(x_i - \frac{1}{4}) \sin \beta$, $Y_i = by_i$, $Z_i = cz_i + a(x_i - \frac{1}{4}) \cos \beta$, the F operation simply transforms X_i into $-X_i$, and the atomic displacements, Δ, can be calculated on the basis of the β-Sr_2SiO_4 structural data (Catti, Gazzoni & Ivaldi, 1983). The results are reported in Table 3.

Table 3. *Atomic displacements caused by ferroelastic switching of* β-Sr_2SiO_4 *between orientation states* (I) *and* (II) *at room temperature*

(I)	(II)	Δ
Sr(1) →	Sr(1)	0·13 Å
Sr(2) →	Sr(2)	0·22
Si →	Si	0·08
O(1) →	O(1)	0·34
O(2) →	O(2)	0·67
O(3) →	O(4)	0·56
O(4) →	O(3)	0·56
Average		0·37

Discussion

According to optical and X-ray diffraction results, the $\beta \rightleftharpoons \alpha'$ phase transition of Sr_2SiO_4 occurs sharply in both directions with a thermal hysteresis of 9–10 K. These properties, together with the enthalpy change of 210 J mol^{-1} observed by Pieper *et al.* (1972), would be evidence for the transformation being of first order. On the basis of structural data, the high-temperature form appears to be positionally (Sr atoms) and orientationally (SiO_4 groups) disordered (however, *cf.* the discussion of possible anharmonic motion simulating disorder in part I), so that the phase change should belong to the order/disorder type; a second-order thermodynamic behaviour would then be more probable, according to simple theory of phase transitions. A similar case is that of the transition high $\rightleftharpoons$ low quartz, where a small latent heat of 360 J mol^{-1} is observed (Rao & Rao, 1966), and yet the high-temperature phase proves to be affected by orientational disorder (*cf.* part I). On the other hand, in both instances the structure analysis of the high-temperature form has shown that the symmetrical model, though less reliable, cannot be rejected completely, so that a minor degree of order may be present; further, the enthalpy changes measured are small in comparison with most values observed in first-order transformations (Rao & Rao, 1966), and the volume changes are even smaller. Therefore, such processes can be classified as 'mixed transformations' (Buerger, 1961), characterized by a number of order–disorder microscopic and first-order macroscopic features, and not completely elucidated yet.

The atomic mechanism of the $\beta \rightarrow \alpha'$ process shows a central aspect: the two orientation states (I) and (II) of the monoclinic form persist within the orthorhombic lattice of the α' phase as local or instant states of its disordered structure ('obverse' and 'reverse' configurations, in Buerger's terminology). Thus no significant variation of the structural pattern occurs at the transition, but just a decrease of domain size below the coherence range of X-rays (static disorder) or a continuous fluctuation of domain walls (dynamic disorder). In this respect the onset of dynamic switching between the two states at the transformation temperature seems to be more probable, in order to account for the sharp character of the process; moreover, a small fraction of time would also be spent in a third state corresponding to the mirror-symmetrical configuration. The second important aspect is the abrupt lattice change observed, which is required by a ferroelastic → paraelastic transition. A similar mechanism can be surmised for the low → high quartz process, except that no lattice change occurs in this case.

We can also analyse the microscopic path of the isothermal transformation (I) ⇄ (II) between the two orientation states of the Sr_2SiO_4 structure, passing through the intermediate symmetrical configuration, which can take place in both the β and α' phases. In the former case, mechanical energy must be supplied to the crystal so as to attain reversion of ferroelastic domains; in the latter, the process is spontaneous and is driven by thermal energy, and corresponds to dynamic disorder. A common atomic mechanism, however, can be proposed for both processes. The simplest would involve rotation of a rigid SiO_4 group between configurations (I) and (II), which are related by a symmetry plane; but this cannot be accepted because the distorted tetrahedron is not mirror-symmetrical; thus two different mechanisms are considered. (i) The four O atoms jump between their (I) and (II) positions in a quite uncorrelated way. (ii) The swinging of O atoms between the two orientation states is correlated, through a combined rotation and deformation of the SiO_4 polyhedron. Midway between the (I) and (II) positions the silicate group lies on the mirror plane and is deformed so as to attain the corresponding symmetry. The overall movement is symmetrical with respect to such an intermediate configuration. The mechanism (i) would be more feasible for dynamic disorder in the α' form than for ferroelastic switching in β; however, even in the first case it should be rejected because of the large distortion of the SiO_4 group involved, with O—Si—O angles ranging from 92 to 123°. On the other hand, the mechanism (ii) seems to fit the (I) ⇄ (II) transformation quite reasonably in both phases, taking into account that in the ferroelastic reversion of the monoclinic form the β lattice angle must change in a correlated way with the movement of the SiO_4 group.

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

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