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Structures of Twinned β-Sr_2SiO_4 and of α'-$Sr_{1\cdot9}Ba_{0\cdot1}SiO_4$

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Abstract. β-Sr_2SiO_4, $M_r = 267\cdot32$, space group $P2_1/n$, $a = 5\cdot663$ (1), $b = 7\cdot084$ (2), $c = 9\cdot767$ (2) Å, $\beta = 92\cdot67$ (2)°, $V = 391\cdot39$ Å^3, $Z = 4$, $D_x = 4\cdot536$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 26\cdot6$ mm^{-1}. α'-$Sr_{1\cdot9}Ba_{0\cdot1}SiO_4$, $M_r = 272\cdot29$, space group $Pmnb$, $a = 5\cdot674$ (1), $b = 7\cdot086$ (2), $c = 9\cdot745$ (2) Å, $V = 391\cdot81$ Å^3, $Z = 4$, $D_x = 4\cdot616$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 26\cdot3$ mm^{-1}. Polysynthetic (100) twinning is always present in the β monoclinic form. Final $R = 0\cdot093$ and 0·052, using 1359 and 752 observed counter reflexions, respectively. In the α' modification the SiO_4 tetrahedron is unusually small (average Si—O bond length = 1·61 Å), and the Sr(1) atom is loosely bonded to its coordination environment (average Sr—O distance = 2·85 Å) owing to the constraints of mirror symmetry; bond-valence calculations prove these two features to be consistent. The loss of the (100) symmetry plane in the β structure allows Sr(1) to shift so as to improve its bond-valence balance, and the SiO_4 tetrahedron can attain a normal size. A large component of anisotropic thermal motion is observed normal to the (100) plane in the α' form, and is discussed in relation to possible disorder.

Introduction. The room-pressure phase diagram of solid alkaline-earth orthosilicates is characterized by an increasingly complex polymorphism as the cation size decreases from Ba to Ca. An orthorhombic form, isostructural with low-K_2SO_4, is the only stable modification of Ba_2SiO_4 (O'Daniel & Tscheischwili, 1942; Pieper, Eysel & Hahn, 1972), and its structure was refined by Grosse & Tillmanns (1974). Five crystalline phases were identified from room temperature to the melting point for Ca_2SiO_4: γ, β, α'_L, α'_H and α (Eysel & Hahn, 1970; Kazak, Domanskii, Boikova, Ilyukhin & Belov, 1974). The crystal structures of the olivine-type orthorhombic γ form (Czaya, 1971) and of the monoclinic β form (Jost, Ziemer & Seydel, 1977), which also corresponds to the mineral larnite, are known. Two modifications are observed for the orthosilicate of the intermediate-sized cation, β-Sr_2SiO_4 and α'-Sr_2SiO_4; the former should be presumably isostructural with β-Ca_2SiO_4, and the latter with α'_H-Ca_2SiO_4 and Ba_2SiO_4, on the basis of their powder diagrams (O'Daniel & Tscheischwili, 1942; Pieper *et al.*, 1972).

A very interesting feature of the Sr_2SiO_4 polymorphism is the transition temperature (~358 K) between the low β and the high α' phases, which is unusually low for a silicate; the corresponding $\beta \rightleftharpoons \alpha'_L$ and $\alpha'_L \rightleftharpoons \alpha'_H$ transitions of Ca_2SiO_4 occur at about 973 and 1433 K, respectively. On the other hand, the α' form of Sr_2SiO_4 was shown to be stabilized at room temperature by just a very small amount (2·5%) of Ba substitution (Pieper *et al.*, 1972). As the first step of an investigation on the crystal chemistry of alkaline-earth orthosilicates, and on the detailed mechanism of the β-$Sr_2SiO_4 \rightleftharpoons \alpha'$-$Sr_2SiO_4$ displacive phase transition, the synthesis and room-temperature structural study of β-Sr_2SiO_4 and α'-$Sr_{1\cdot9}Ba_{0\cdot1}SiO_4$ was undertaken. The second part of this research will concern the structure transformation of Sr_2SiO_4 at variable temperature, and is now in progress.

Experimental. Synthesized by crystallization of molten salt solution, cooled very slowly from 1773 K to room temperature; pellets prepared by adding 30% by weight of SrF_2 to stoichiometric mixtures of analytically pure $SrCO_3$ and SiO_2 (with $BaCO_3$ as well in the case of $Sr_{1\cdot9}Ba_{0\cdot1}SiO_4$), and introduced into a platinum crucible; silicon carbide resistivity furnace; transparent and colourless well developed crystals of β-Sr_2SiO_4 and of α'-$Sr_{1\cdot9}Ba_{0\cdot1}SiO_4$ (surrounded by a polycrystalline matrix) obtained in two separate runs by spontaneous

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nucleation and flux growth; synthesis products preliminarily identified by powder photograms (Guinier camera), later by single-crystal Weissenberg photography; in each preparation a single phase of strontium orthosilicate, either β or α', proved to be present. Cell constants redetermined by angular refinement of 25 reflexions, single-crystal automatic diffractometer, Mo $K\alpha$, space groups confirmed on the basis of systematic absences; crystallographic axes chosen according to Jost *et al.* (1977) for β-Ca_2SiO_4, with **b** as unique monoclinic direction; unit cells reported by Pieper *et al.* (1972) may be obtained by the transformation 001/100/010.

All crystals of β-Sr_2SiO_4 examined by Weissenberg photography were found to be twinned on (100). According to the classification of Donnay & Donnay (1974), this is a case of twin-lattice-quasi-symmetry twinning, where the lattices of the two orientations are slightly rotated; the obliquity is $\omega = 2{\cdot}6°$, and the twin symbol $2^{*\prime}/m'$ $2/m$ $2'/m^{*\prime}$. A similar twinning is observed for β-Ca_2SiO_4, but the obliquity is larger ($\omega = 4{\cdot}6°$) and the two lattices are then better resolved. Crystals twin during the cooling as they transform from α' to the β modification; so this is a case of solid-state 'transformation twinning' (Žák, 1973), which differs from the usual growth twinning in the melt or in solution.

The morphology of β-Sr_2SiO_4 is orthorhombic and does not reveal any twinning, so that the crystal habit of the α' form is conserved after the transition to β. Most crystals are elongated along [010], with a pseudo-hexagonal prismatic or tabular habit; the dominant form is {001}, and {101} and {011} are also always observed. Other crystals exhibit the same forms, but with a more equidimensional habit. By observing the crystals normal to (011) or along [010] under a polarizing microscope, in some favourable cases a very fine domain texture was detected, proving that the twinning is polysynthetic; the contact plane was also confirmed to be (100).

Diffraction intensities measured on two crystals 0·31 × 0·13 × 0·12 and 0·33 × 0·15 × 0·10 mm, respectively, for β-Sr_2SiO_4 and α'-$Sr_{1\cdot9}Ba_{0\cdot1}SiO_4$, four-circle automatic Syntex Nicolet $R3$ diffractometer, Mo $K\alpha$ radiation, graphite monochromator. Some difficulties had to be overcome in order to separate the diffraction peaks of the two lattices in the twinned crystal of the β phase, because of the small obliquity of 2·6°. Angular separations $\Delta\varphi$ and $\Delta\chi$ were calculated for pairs of hkl (I) and $h\bar{k}\bar{l}$ (II) reflexions of the two orientations, within the sphere of reciprocal space limited by $2\theta < 70°$. Data were then collected in the four octants hkl, $hk\bar{l}$, $\bar{h}\bar{k}\bar{l}$, $\bar{h}\bar{k}l$ (orientation I), since these showed systematically larger $\Delta\varphi$ values than their four equivalent ones. The ω scan was used with scan width $\Delta\omega = 1{\cdot}2°$, and the horizontal slit of the detector collimator was set to as small a width as possible, to achieve the best $\Delta\varphi$ and $\Delta\chi$ separations. However, the following reflexions of type $hk1$ and $hk\bar{1}$ could not be separated completely from their twin-related ones, and had to be rejected: $24\bar{1}$, $3\bar{1}1$, 321, 331, 351, and those related centrosymmetrically. Scan speed variable between 0·03 and 0·49° s^{-1}, with interpolation for intensities between 300 and 3000 counts s^{-1}; background time = scan time; 3718 data collected and corrected empirically for absorption on the basis of ψ scans of five high-χ reflexions with variable 2θ (North, Phillips & Mathews, 1968); transmission coefficient 0·38 to 1·00. By comparing the intensities of a number of corresponding reflexions of the two twin orientations, the volume ratio of the two kinds of domains proved to be 1 to a good approximation, and therefore the intensities of the $hk0$ and $\bar{h}\bar{k}0$ reflexions were halved. After averaging the intensities of centrosymmetrically related reflexions and removing those systematically absent, a set of 1726 independent data was obtained; 1380 with $I > 2\sigma(I)$ were considered as observed and retained.

As for the α' phase, 1061 data were collected from the hkl octant with $\omega/2\theta$ scan and $\Delta\theta = 3°$, and with the other experimental conditions as above; 937 independent reflexions, 764 considered to be observed $[I > 2\sigma(I)]$.

The atomic coordinates of β-Ca_2SiO_4 (Jost *et al.*, 1977) were taken as starting parameters for the least-squares refinement of the β-Sr_2SiO_4 structure. Using isotropic temperature factors, convergence was attained with $R = 0{\cdot}116$. The anisotropic refinement on F (unit weights) led to $R = 0{\cdot}102$, but the thermal tensors of Si, O(2) and O(3)* became non-positive-definite. At this stage reflexion 200, which proved to be strongly affected by secondary extinction, and 20 reflexions of type $hk1$ or $hk\bar{1}$ partially overlapping their twin-related ones were removed; in addition the following weighting scheme was introduced: $w = 1/[\sigma^2(F_o) + 0{\cdot}001|F_o|^2]$. After a subsequent cycle, only the thermal tensor of O(3) remained non-positive-definite; its U_{11} component was then kept fixed at 0·003 Å², and the final full-matrix cycle converged to $R = 0{\cdot}093$, $wR = 0{\cdot}089$ for 64 parameters. The poor agreement between observed and calculated structure factors should be mainly ascribed to partial overlap of some classes of twin-related reflexions, owing to the small twin obliquity; indeed, better results were obtained by Jost *et al.* (1977) on a twinned crystal of synthetic larnite ($R = 0{\cdot}048$), whose obliquity is 4·6°.

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* A single (or no) figure in parentheses denotes an atom of the asymmetric unit. A second figure, ranging from 2 to 4 for β-Sr_2SiO_4 and from 2 to 8 for α'-$Sr_{1\cdot9}Ba_{0\cdot1}SiO_4$, is included for atoms in the positions $\bar{x},\bar{y},\bar{z}$; $\frac{1}{2}+x,\frac{1}{2}-y,\frac{1}{2}+z$; $\frac{1}{2}-x,\frac{1}{2}+y,\frac{1}{2}-z$; $\frac{1}{2}-x,y,z$; $\frac{1}{2}+x,\bar{y},\bar{z}$; $x,\frac{1}{2}+y,\frac{1}{2}-z$ and $\bar{x},\frac{1}{2}-y,\frac{1}{2}+z$. 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) $-\mathbf{c}$.

The refinement of the α'-$Sr_{1\cdot9}Ba_{0\cdot1}SiO_4$ structure was started with the atomic coordinates of Ba_2SiO_4 (Grosse & Tillmanns, 1974). Convergence was attained at $R = 0{\cdot}124$ and at $R = 0{\cdot}074$ with isotropic and anisotropic temperature factors, respectively; in the latter case, however, the thermal tensors of Si, O(1) and O(2) became non-positive-definite. The weighting scheme $w = 1/[\sigma^2(F_o) + 0{\cdot}001|F_o|^2]$ was introduced, and the reflexion 200 (affected by secondary extinction) and 11 weak observations with large experimental errors were removed. Since O(2) still showed a non-positive-definite thermal tensor, its U_{23} component was fixed at 0·00 Å² and the full-matrix refinement was concluded ($R = 0{\cdot}052$, $wR = 0{\cdot}048$ for 40 parameters). The scattering factor of pure Sr was corrected for the small fraction of Ba present.

All calculations performed by *SHELX* (Sheldrick, 1976), $F(000) = 488$ (β) and 495·2 (α'), scattering factors for neutral atoms and f' and f'' corrections for anomalous scattering from *International Tables for X-ray Crystallography* (1974).*

Discussion. The atomic fractional coordinates and equivalent isotropic thermal parameters of both structures are reported in Table 1.

In order to emphasize structural similarities, the same symbols are used for atoms with corresponding coordinates in the asymmetric units of the two forms (Table 1). Thus O(2) and O(4) in β-Sr_2SiO_4 are interchanged with respect to β-Ca_2SiO_4 (Jost *et al.*, 1977). In addition the **b** and **c** vectors in α'-$Sr_{1\cdot9}Ba_{0\cdot1}SiO_4$ have been interchanged with respect to the unit cell reported by Grosse & Tillmans (1974) for Ba_2SiO_4, so as to make the cells of both structures consistent. The translation vector of intermediate length in the orthorhombic cell corresponds to the unique twofold axis in the low-temperature monoclinic β form, but to the unique sixfold axis in the high-temperature hexagonal α form (for Ca_2SiO_4 and other compounds), so that it is named either **b** or **c** in the literature according to the type of comparison which is wanted.

Both structures show a hexagonal pseudo-symmetry along [010], as is confirmed by the c/a ratio which is close to $\sqrt{3}$ (Figs. 1 and 2). The SiO_4 tetrahedra have their Si—O(1) bonds approximately parallel to [010]; half of them are 'pointing upwards' and half are 'pointing downwards'. The structural type is characterized by [010] chains of Sr coordination polyhedra sharing faces, which are linked with one another forming a three-dimensional framework of polyhedra. In the orthorhombic α' form, the SiO_4 tetrahedra and Sr polyhedra have m symmetry parallel to the (100) plane; in the monoclinic form that mirror symmetry disappears, all polyhedra are distorted, and (100) becomes a twinning plane (Figs. 3 and 4).

Bond lengths and angles in the SiO_4 tetrahedra of both structures are reported in Table 2. According to Baur's (1978) survey of 50 SiO_4 tetrahedra in nesosilicates, the mean, minimum and maximum values observed for the average Si—O bond length are 1·636 (8),

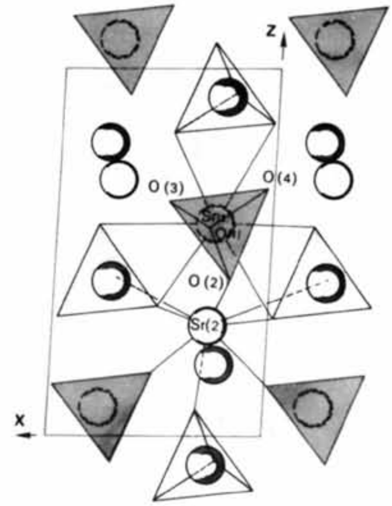

Fig. 1. Projection of the crystal structure of β-Sr_2SiO_4 onto the (010) plane, emphasizing SiO_4 tetrahedra and Sr—O coordination bonds within the two independent Sr polyhedra.

Table 1. *Atomic fractional coordinates and equivalent isotropic temperature factors* (Å² × 10²), *with e.s.d.'s in parentheses*

$$U_{eq} = \tfrac{1}{3}\textstyle\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j .$$

	β-Sr_2SiO_4				α'-$Sr_{1\cdot9}Ba_{0\cdot1}SiO_4$			
	x	*y*	*z*	U_{eq}	*x*	*y*	*z*	U_{eq}
Sr(1)	0·2618 (2)	0·3425 (2)	0·5778 (1)	1·10 (5)	0·25	0·3403 (1)	0·57983 (8)	1·13 (2)
Sr(2)	0·2698 (2)	0·0007 (2)	0·3023 (1)	0·91 (4)	0·25	−0·0014 (1)	0·30222 (8)	1·03 (2)
Si	0·2427 (6)	0·7781 (5)	0·5813 (4)	0·3 (1)	0·25	0·7788 (3)	0·5835 (2)	0·64 (5)
O(1)	0·280 (2)	1·008 (2)	0·571 (1)	1·0 (4)	0·25	1·004 (1)	0·5683 (8)	3·8 (3)
O(2)	0·191 (2)	0·679 (1)	0·431 (1)	0·7 (4)	0·25	0·676 (1)	0·4339 (7)	4·1 (4)
O(3)	0·488 (2)	0·679 (1)	0·642 (1)	0·8 (4)	0·480 (1)	0·7070 (9)	0·6639 (7)	3·3 (2)
O(4)	0·023 (2)	0·726 (1)	0·675 (1)	0·8 (4)				

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* Lists of F_o and F_c and anisotropic temperature factors for both structures have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38173 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

1·622 and 1·654 Å, respectively. Thus the size of the silicate oxyanion appears to be quite regular in the β form, but unusually small in the α' form. Also the tetrahedron contracts inhomogeneously in the passage from β to α', since all the Si–O distances except Si–O(2) shorten substantially; on the other hand, the angular configuration is approximately the same in both cases.

Bond distances in the two independent Sr polyhedra are shown in Table 3. The coordination numbers of Sr(1) and Sr(2) in the α' form can be assumed to be 10 and 9, respectively, taking into account that the distances to the next neighbours are greater than 3·6 and 4·0 Å. The Sr(1) polyhedron has hexagonal pseudo-symmetry along the y axis (Fig. 2); it shares the face O(2)–O(3)–O(3,5) and the vertex O(1$^{\text{I}}$) with the two SiO_4 tetrahedra which are vertically above and below it, respectively, and the three edges

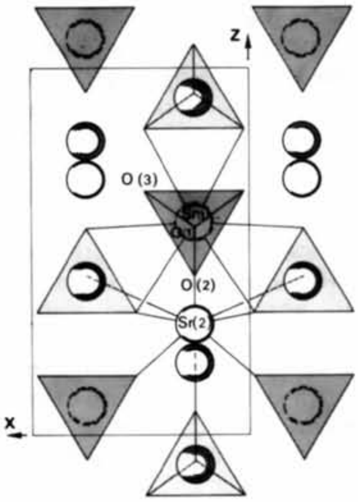

Fig. 2. Projection of the crystal structure of α'-$Sr_{1\cdot9}Ba_{0\cdot1}SiO_4$ onto the (010) plane.

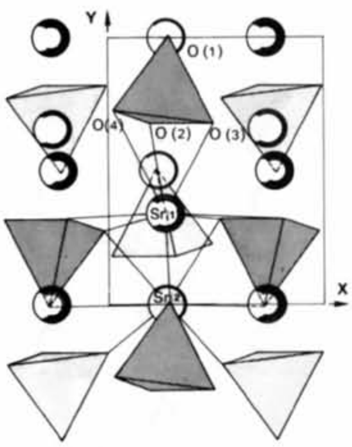

Fig. 3. Crystal structure of β-Sr_2SiO_4, projected along [001].

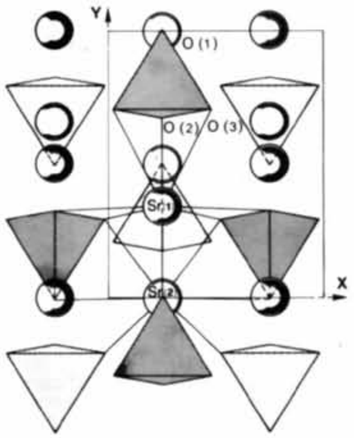

Fig. 4. Crystal structure of α'-$Sr_{1\cdot9}Ba_{0\cdot1}SiO_4$, projected along [001].

Table 2. *Interatomic distances* (Å) *and* O–Si–O *angles* (°) *in the* SiO_4 *tetrahedra of* β-Sr_2SiO_4 *and* α'-$Sr_{1\cdot9}Ba_{0\cdot1}SiO_4$, *with e.s.d.'s in parentheses*

	β	α'
Si–O(1)	1·65 (1)	1·603 (7)
Si–O(2)	1·64 (1)	1·630 (7)
Si–O(3)	1·64 (1)	1·605 (6) (×2)
Si–O(4)	1·62 (1)	—
Average	1·64	1·611

	β	α'	β	α'
O(1)–O(2)	2·74 (1)	2·67 (1)	112·8 (5)	111·3 (4)
O(1)–O(3)	2·69 (1)	2·646 (6) (×2)	109·7 (5)	111·2 (2) (×2)
O(1)–O(4)	2·70 (1)	—	111·3 (5)	—
O(2)–O(3)	2·60 (1)	2·603 (7) (×2)	104·6 (5)	107·2 (2) (×2)
O(2)–O(4)	2·63 (1)	—	107·3 (5)	—
O(3)–O(4)	2·69 (1)	—	110·9 (5)	—
O(3)–O(3,5)	—	2·610 (8)	—	108·8 (3)
Average	2·68	2·630	109·4	109·5

Table 3. *Bond distances* (Å) *in the* Sr *coordination polyhedra of* β-Sr_2SiO_4 *and* α'-$Sr_{1\cdot9}Ba_{0\cdot1}SiO_4$, *with e.s.d.'s in parentheses*

	β	α'
Sr(1)–O(1$^{\text{I}}$)	2·37 (1)	2·386 (7)
Sr(1)–O(2)	2·801 (8)	2·771 (7)
Sr(1)–O(2,2$^{\text{III}}$)	2·57 (1)	2·842 (6) (×2)
Sr(1)–O(2,2$^{\text{II}}$)	3·11 (1)	
Sr(1)–O(3)	2·764 (8)	3·021 (6) (×2)
Sr(1)–O(4)	3·199 (8)	
Sr(1)–O(3,2$^{\text{II}}$)	2·63 (1)	2·846 (6) (×2)
Sr(1)–O(4,2$^{\text{III}}$)	2·93 (1)	
Sr(1)–O(3,4$^{\text{V}}$)	3·35 (1)	2·972 (7) (×2)
Sr(1)–O(4,4$^{\text{V}}$)	2·78 (1)	
Average	2·850	2·852
Sr(2)–O(1$^{\text{I}}$)	2·62 (1)	2·593 (8)
Sr(2)–O(2$^{\text{I}}$)	2·651 (8)	2·622 (7)
Sr(2)–O(2,4$^{\text{I}}$)	2·624 (9)	2·622 (7)
Sr(2)–O(1,2$^{\text{III}}$)	3·40 (1)	3·105 (3) (×2)
Sr(2)–O(1,2$^{\text{II}}$)	2·78 (1)	
Sr(2)–O(3,2$^{\text{II}}$)	2·694 (8)	2·609 (6) (×2)
Sr(2)–O(4,2$^{\text{III}}$)	2·565 (8)	
Sr(2)–O(3,3$^{\text{VI}}$)	2·527 (9)	2·507 (6) (×2)
Sr(2)–O(4,3$^{\text{VIII}}$)	2·519 (9)	
Average	2·709	2·698

$O(2,2^{ii})\cdots O(3,2^{ii})$, $O(2,2^{iii})\cdots O(3,6^{iv})$ and $O(3,4^{v})\cdots O(3,7^{v})$ [approximately lying on the (010) plane] with three SiO_4 tetrahedra. The Sr(2) polyhedron is much less symmetrical and shares neither edges nor faces with any SiO_4 tetrahedra, but it is tightly condensed with the Sr polyhedra related to it by the 2_1 operation along [010] columns. Average Sr—O distances are significantly different in the two polyhedra; Sr(2) shows a regular value (2·70 Å), whereas the situation in Sr(1) is peculiar, as one very short bond length with $O(1^{i})$ (2·386 Å) is observed but all other bonds are very long (2·90 Å on average), with a rather large overall mean value (2·85 Å). The lengthening of Sr—O distances caused by 5% Ba substitution is reckoned to be very small (within 2σ), on the basis of a linear interpolation towards the Ba—O distances in Ba_2SiO_4.

In the $\alpha' \to \beta$ phase transition a rotation of SiO_4 tetrahedra occurs, so that the Sr polyhedra lose their mirror symmetry, and every pair of symmetrical Sr—O bonds splits into a shorter and a longer bond, keeping their average length approximately constant. It may be questioned whether some of the O atoms still belong to the Sr coordination environment in the β form, *i.e.* $O(3,4^{v})$ and perhaps O(4) for Sr(1) and $O(1,2^{iii})$ for Sr(2). By keeping them, the average values of Sr—O distances in both polyhedra do not change appreciably in the passage from α' to β structure; by removing them, those values are lowered to 2·795 (or 2·744) and 2·623 Å, respectively. However, such O atoms have been maintained formally in the coordination spheres of Sr(1) and Sr(2), since they give them a significant, even though very small, contribution of bond valence (*cf.* below).

The main structural differences between the α' and β phases can be summarized as follows: (i) the SiO_4 tetrahedron is unusually small in the orthorhombic modification; (ii) bond lengths in Sr polyhedra are scattered over a wider range of values in the monoclinic than in the orthorhombic form, although their averages are about the same (Fig. 5). Both these features can be accounted for quantitatively by a bond-valence s calculation according to the formula $s = (R_1/R)^N$, where R is the bond distance and the two empirical parameters R_1 and N take different values for Si—O and Sr—O bonds (Brown & Wu, 1976). The results for the two structures of β-Sr_2SiO_4 and α'-$Sr_{1\cdot9}Ba_{0\cdot1}SiO_4$ are reported in Table 4. The bond-valence balance shows that Sr(1) is clearly underbonded in the α' with respect to the β phase; also, in the α' phase the smaller bond-valence contributions to O atoms from Sr(1) are compensated by larger ones from Si.

The evidence that Sr(1) is loosely bonded in the α' relative to the β structure, according to bond-valence calculations, does not conflict with the fact that the average Sr(1)—O distances are equal in both cases. In fact, because of the decreasing slope of the $s(R)$ curve as R increases, a shortening of the Sr—O bond length causes an increase of bond valence which is larger than the decrease caused by a corresponding lengthening of the same amount. Thus in the $\alpha' \to \beta$ transition an overall increase of the Sr—O bond valence is produced by splitting of each pair of symmetry-related Sr—O bonds into a shorter and a longer one. For instance, each of the equivalent bonds $Sr(1)—O(2,2^{iii})$ and $Sr(1)—O(2,2^{ii})$ in α' has $s = 0\cdot14$ v.u., whereas the corresponding bonds in β take $s = 0\cdot28$ and 0·07 v.u., respectively, with an overall gain of 0·07 v.u., although the average of the two Sr—O distances is 2·84 Å in both structures. This 'splitting gain' of bond valence following the $\alpha' \to \beta$ transition is observed in the Sr(2) polyhedron as well, but it is compensated by a lengthening of the three Sr—O bonds lying on the mirror plane in α', so that $\sum_l s_l$ for Sr(2) is about the same in both phases.

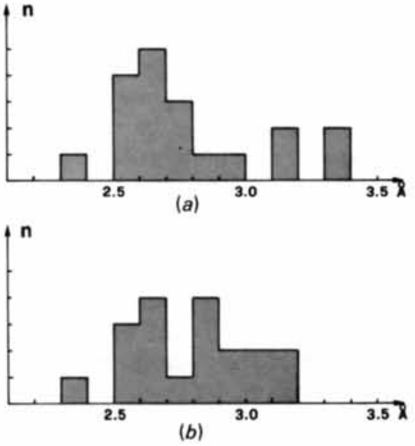

Fig. 5. Histograms of bond length for the 19 Sr—O coordination bonds of (*a*) β-Sr_2SiO_4 and (*b*) α'-$Sr_{1\cdot9}Ba_{0\cdot1}SiO_4$.

Table 4. *Bond-valence balance for* β-Sr_2SiO_4 (*upper lines*) *and* α'-$Sr_{1\cdot9}Ba_{0\cdot1}SiO_4$

	O(1)	O(2)	O(3)	O(4)	$\sum_l s_l$
Si	0·93 1·05	0·95 0·98	0·93 1·05 (×2)	1·01	3·82 4·13
Sr(1)	0·49 0·47	0·51 0·44	0·45 0·33 (×2)	0·33	1·78 1·57
Sr(2)	0·45 0·41	0·47 0·49	0·52 0·58 (×2)	0·61	2·05 2·06
$\sum_l s_l$	1·87 1·93	1·93 1·91	1·90 1·96 (×2)	1·95	

Thus the SiO_4 tetrahedron is forced to shrink in the orthorhombic structure, so that shorter Si—O bonds provide the supplementary bond valence necessary to counterbalance the deficient contribution given by Sr to O atoms.

An examination of equivalent atomic temperature factors (Table 1) shows that all atoms, and in particular O atoms, are affected by a much larger overall thermal motion in the α' than in the β phase. To investigate the effects of thermal anisotropy, the r.m.s. displacements along the principal directions of vibration have been reported in Table 5. All O atoms in α' have a very anisotropic vibration, and the principal direction with largest displacement is normal to the (100) mirror plane for all atoms lying on it. Two different interpretations are possible for this vibrational behaviour in the orthorhombic structure: (i) the SiO_4 tetrahedra are dynamically disordered and 'jump' between two different orientation states of the monoclinic phase, related by the twinning plane (100); (ii) some microdomains of the β phase, in its two possible orientations, are contained in the α' modification. A refinement of the α' structure according to a split-atom model for O(1) and O(2) was tried, but gave no satisfactory results: this probably means that either the dynamic disorder is only partial, or the amount of monoclinic microdomains present in the α' phase is small. Such phenomena of dynamic disorder or permanency of low-symmetry domains in the high-symmetry phase very often seem to be associated with displacive phase transitions between structures related by point group/subgroup symmetry relations; a typical example is the case of the $\alpha \rightleftharpoons \beta$ quartz transformation (Liebau & Böhm, 1982).

Table 5. *R.m.s. displacements along the principal directions of vibration*

	β Form	α' Form		β Form	α' Form
Sr(1)	0·12 Å	0·14 Å	O(1)	0·13 Å	0·32 Å
	0·11	0·09		0·11	0·09
	0·08	0·08		0·05	0·08
Sr(2)	0·11	0·14	O(2)	0·11	0·34
	0·09	0·09		0·09	0·09
	0·08	0·05		0·01	0·05
Si	0·08	0·10	O(3)	0·11	0·29
	0·04	0·08		0·10	0·11
	0·01	0·05		0·02	0·07
			O(4)	0·12	
				0·09	
				0·05	

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Structure of Pyroelectric Lithium Potassium Sulphate, $LiKSO_4$

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Abstract. $M_r = 142\cdot10$, hexagonal, $P6_3$, $a = 5\cdot1452$ (2), $c = 8\cdot6343$ (6) Å, $V = 197\cdot952$ (1) Å^3, $Z = 2$, $D_x = 2\cdot384$ Mg m^{-3}, $T = 298$ K, λ(Mo $K\alpha$) = 0·71069 Å, refinement with all 1575 independent measured X-ray intensities with $\sin\theta/\lambda \leq 1\cdot12$ Å^{-1} gave $R_w(F^2) = 0\cdot035$. The structure was derived from a lamellar twin crystal formed by alternating layers of laevo- and dextrorotatory-type crystals with opposite polarity along the optic axis. The inclusion of third-order cumulants in the refinements demonstrates highly anharmonic thermal motion of the O atoms.

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