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Structure and High-Pressure Polymorphism of Strontium Metasilicate

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Abstract

Single crystals of α-, δ- and δ'-$SrSiO_3$ were prepared at pressures of 3·5, 4·0 and 5·5 GPa using KCl as a flux. The atmospheric-pressure phase, α-$SrSiO_3$, is monoclinic, space group $C2$, with $Z = 12$, $a = 12{\cdot}323\,(5)$, $b = 7{\cdot}139\,(2)$, $c = 10{\cdot}873\,(5)$ Å, $\beta = 111{\cdot}58\,(4)^\circ$, and $V = 889{\cdot}5\,(6)$ Å^3. The two high-pressure phases, δ- and δ'-$SrSiO_3$, are, respectively, triclinic, space group $P\bar{1}$, with $Z = 6$, $a = 6{\cdot}874\,(2)$, $b = 6{\cdot}894\,(2)$, $c = 9{\cdot}717\,(3)$ Å, $\alpha = 85{\cdot}01\,(3)$, $\beta = 110{\cdot}57\,(3)$ and $\gamma = 104{\cdot}01\,(2)^\circ$, and monoclinic, space group $P2_1/c$, with $Z = 8$, $a = 7{\cdot}452\,(4)$, $b = 6{\cdot}066\,(2)$, $c = 13{\cdot}479\,(7)$ Å and $\beta = 117{\cdot}09\,(4)^\circ$. Of these phases, the structure of α-$SrSiO_3$ was determined and refined to $R = 0{\cdot}053$ for 730 observed reflections with isotropic thermal parameters. The Sr atoms occupy three kinds of sites [Sr(1), Sr(2) and Sr(3)], which are surrounded by eight O atoms with Sr—O distances of 2·39 (1) to 2·83 (1) Å. Three of the distorted SiO_4 tetrahedra with Si—O bond lengths of 1·48 (1) to 1·85 (2) Å form a $(Si_3O_9)^{6-}$ ring by sharing O atoms. The structure consists of Sr^{2+} ions and $(Si_3O_9)^{6-}$ rings alternately packed along the direction perpendicular to (001).

Introduction

Alkaline-earth metasilicates have been found to show various high-temperature and high-pressure polymorphs (Toropov, Barzakovskii, Lapin & Kurtseva, 1972). At atmospheric pressure, $CaSiO_3$ crystallizes in α (pseudowollastonite) or β (wollastonite or parawollastonite) forms. The β phase transforms into the α phase above *ca* 1400 K. The structure of β-$CaSiO_3$ consists of $(SiO_3)_\infty$ chains of SiO_4 tetrahedra (Mamedov & Belov, 1956; Trojer, 1968), while α-$CaSiO_3$ has been presumed to contain an $(Si_3O_9)^{6-}$ ring of three SiO_4 tetrahedra (Jeffery & Heller, 1953). This silicate also forms two high-pressure polymorphs, δ- and ε-$CaSiO_3$, by treatments at 3–20 GPa and 1170–1770 K (Ringwood & Major, 1967; Liu & Ringwood, 1975). Trojer (1969) has determined the structure of δ-$CaSiO_3$, the structural framework of which involves the same $(Si_3O_9)^{6-}$ rings as α-$CaSiO_3$. The ε phase crystallizes in the cubic system (perovskite type) and the structure consists of an $(SiO_3)_\infty$ network of SiO_6 octahedra (Liu & Ringwood, 1975). For $SrSiO_3$, three polymorphs have been obtained: one atmospheric-pressure phase (α form) and two high-pressure forms (Shimizu, Syono & Akimoto, 1970). It has been confirmed by the X-ray analyses of Hilmer (1962) that α-$SrSiO_3$ contains $(Si_3O_9)^{6-}$ rings in a similar manner as α-$CaSiO_3$, although the crystals used were not good enough to be able to perform a detailed structure analysis. In this study we have determined the structure of α-$SrSiO_3$, and characterized its high-pressure polymorphism.

Experimental

Single crystals of $SrSiO_3$ polymorphs were grown from a mixture of polycrystalline α-$SrSiO_3$ containing KCl as flux. The $SrSiO_3$:KCl molar ratio was 10 : 1, and the pressures applied were 3·5, 4·0 and 5·5 GPa for the α, δ and δ' phases, respectively. For some runs, for samples containing a larger proportion of KCl than the above-mentioned ratio, an unknown phase was formed as a by-product. The high-pressure treatments were carried out with a cubic anvil-type apparatus according to the method previously reported (Shimada, Ogawa, Koizumi, Dachille & Roy, 1979). The samples were maintained under the appropriate pressures at 1570 or 1670 K for 60 min and then allowed to cool to 1070 K at a rate of 2 K min^{-1}. Transparent single crystals (0·3 mm long) were obtained; the crystal habits were plates for the α and δ' forms, and needles for the δ. Polycrystalline samples of the $SrSiO_3$ polymorphs were obtained as follows: α-$SrSiO_3$ was prepared by twice heating a stoichiometric mixture of $SrCO_3$ and SiO_2 at about 1575 K for 3 h in air, and δ- and δ'-$SrSiO_3$ were obtained by treatments of α-$SrSiO_3$ at 4 and 6 GPa at about 1275 K.

The symmetries, space groups and approximate cell parameters of $SrSiO_3$ polymorphs were determined from oscillation and Weissenberg photographs. From

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Table 1. *Additional crystal data for* α-SrSiO$_3$

$M_r = 163{\cdot}70$
$\lambda = 0{\cdot}71069$ Å
μ(Mo $K\alpha$) = 17·83 mm^{-1}
$D_m = 3{\cdot}64$ Mg m^{-3}
$D_x = 3{\cdot}67$
$F(000) = 912$
Crystal size: 0·20 × 0·20 × 0·07 mm

Table 2. *Final positional and thermal parameters for* α-SrSiO$_3$

Standard deviations are given in parentheses.

	x	y	z	B (Å^2)
Sr(1)	0·0873 (11)	0	0·2494 (9)	0·34 (2)
Sr(2)	0·2455 (16)	0·4780 (19)	0·2458 (18)	0·33 (2)
Sr(3)	0·4128 (11)	−0·0207 (14)	0·2516 (9)	0·42 (2)
Si(1)	0	0·417 (6)	0	0·34 (7)
Si(2)	0·116 (4)	0·790 (5)	−0·001 (4)	0·45 (5)
Si(3)	0	1·075 (7)	$\frac{1}{2}$	0·31 (7)
Si(4)	0·130 (4)	0·702 (5)	0·498 (3)	0·39 (5)
O(1)	0	0·874 (16)	0	0·28 (18)
O(2)	0·042 (12)	0·323 (13)	0·139 (10)	0·74 (16)
O(3)	0·107 (11)	0·532 (14)	−0·009 (9)	0·73 (14)
O(4)	0·130 (11)	0·842 (12)	−0·142 (11)	0·52 (14)
O(5)	0·223 (12)	0·835 (14)	0·139 (11)	0·90 (17)
O(6)	0	0·605 (16)	$\frac{1}{2}$	0·34 (19)
O(7)	0·049 (9)	1·185 (13)	0·635 (9)	0·69 (15)
O(8)	0·110 (11)	0·911 (12)	0·511 (9)	0·41 (14)
O(9)	0·119 (12)	0·659 (14)	0·350 (11)	1·12 (16)
O(10)	0·213 (9)	0·643 (12)	0·630 (9)	0·40 (13)

the observed systematic absences (α-SrSiO$_3$, $h + k = 2n + 1$ for hkl; δ-SrSiO$_3$, no conditions; δ'-SrSiO$_3$, $l = 2n + 1$ for $h0l$ and $k = 2n + 1$ for $0k0$), α- and δ'-SrSiO$_3$ were found to belong to the monoclinic space groups $C2$, Cm or $C2/m$ and $P2_1/c$, and δ-SrSiO$_3$ to the triclinic $P1$ or $P\bar{1}$, respectively. Accurate cell parameters were determined by least-squares treatments for the X-ray powder diffraction patterns (Cu $K\bar{\alpha}$) of polycrystalline samples calibrated with high-purity Si as an internal standard. The crystal data of α-SrSiO$_3$ are shown in the *Abstract* and in Table 1. The cell parameters which have been previously reported by Hilmer (1962) (a monoclinic system with $\gamma = 120°$) were not consistent with our result. The intensity data of α-SrSiO$_3$ were collected on a Rigaku automated four-circle diffractometer with Mo $K\alpha$ radiation monochromated by a graphite plate. The ω–2θ scan method was employed with a scanning rate of 4° min^{-1}. All possible hkl and $\bar{h}kl$ reflections were collected up to $2\theta = 60°$. Three standard reflections were monitored every 100 reflections and no apparent decay in intensity was detected. The 730 unique reflections with $|F_o| > 3\sigma(|F_o|)$ were considered as observed. The usual Lorentz and polarization corrections were applied, but the absorption and anomalous-dispersion effects for heavy atoms were not considered.

Structure determination

The structure of α-SrSiO$_3$ was solved by the direct method (*MULTAN* 78; Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) and refined by the block-diagonal least-squares method (*HBLS*-V; Ashida, 1979), the function minimized being $\sum w(|F_o| - |F_c|)^2$. The space group $C2$ gave a satisfactory result: Sr(1), Sr(2) and Sr(3) atoms occupy the general positions [site 4(c)]. The coordinates of the remaining atoms (Si and O) were determined from the difference Fourier maps. Among them, the coordinates of Si(1), Si(3), O(1) and O(6) could be located at the special sites 2(a) and 2(b) and those of the other atoms at general positions. Isotropic refinements for all atomic parameters gave $R = 0{\cdot}053$ and $R_w = 0{\cdot}082$ for 730 observed reflections, where $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$.* The atomic scattering factors for Sr, Si and O were those in *International Tables for X-ray Crystallography* (1974). The weighting scheme $w = (F_m/F_o)^2$ for $F_o > F_m$ (=30·0) and $w = 1{\cdot}0$ for $F_o \le F_m$ (=30·0) was employed. The final positional and thermal parameters are listed in Table 2.

Results and discussion

The interatomic distances and angles of α-SrSiO$_3$ are summarized in Table 3. Projections of the α-SrSiO$_3$

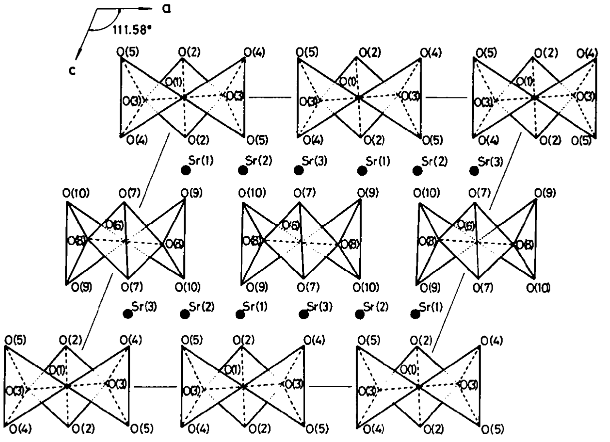

Fig. 1. A projection of the α-SrSiO$_3$ structure viewed along the b axis.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36368 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Interatomic distances* (Å) *and angles* (°) *in* α-$SrSiO_3$

Standard deviations are given in parentheses.

(*a*) The Si_3O_9 rings

Si(1) tetrahedron

Si(1)–O(2)	1·56 (1) (×2)	O(2)–Si(1)–O(2^{i})	129·0 (8)
–O(3)	1·59 (2) (×2)	O(2)–Si(1)–O(3)	107·2 (8) (×2)
Average	1·58	O(2)–Si(1)–O(3^{i})	98·6 (8) (×2)
		O(3)–Si(1)–O(3^{i})	117·7 (8)
		Average	109·7

Si(2) tetrahedron

Si(2)–O(1)	1·55 (2)	O(1)–Si(2)–O(3)	110·2 (8)
–O(3)	1·85 (2)	O(1)–Si(2)–O(4)	109·3 (8)
–O(4)	1·65 (1)	O(1)–Si(2)–O(5)	110·2 (8)
–O(5)	1·64 (2)	O(3)–Si(2)–O(4)	101·9 (7)
Average	1·67	O(3)–Si(2)–O(5)	104·7 (7)
		O(4)–Si(2)–O(5)	119·8 (7)
		Average	109·4

Si(3) tetrahedron

Si(3)–O(7)	1·58 (1) (×2)	O(7)–Si(3)–O(7^{i})	120·2 (8)
–O(8)	1·76 (1) (×2)	O(7)–Si(3)–O(8)	104·3 (7) (×2)
Average	1·67	O(7)–Si(3)–O(8^{i})	114·6 (7) (×2)
		O(8)–Si(3)–O(8^{i})	96·7 (6)
		Average	109·1

Si(4) tetrahedron

Si(4)–O(6)	1·75 (2)	O(6)–Si(4)–O(8)	101·9 (7)
–O(8)	1·53 (1)	O(6)–Si(4)–O(9)	101·4 (8)
–O(9)	1·60 (2)	O(6)–Si(4)–O(10)	100·6 (8)
–O(10)	1·48 (1)	O(8)–Si(4)–O(9)	109·0 (7)
Average	1·59	O(8)–Si(4)–O(10)	105·4 (7)
		O(9)–Si(4)–O(10)	133·9 (8)
		Average	108·7

(*b*) Sr–O distances

Sr(1) dodecahedron

Sr(1)–O(1)	2·68 (2)	Sr(1)–O(7^{i})	2·78 (1)
–O(2)	2·57 (1)	–O(8)	2·83 (1)
–O(4^{i})	2·74 (1)	–O(9)	2·64 (1)
–O(5^{i})	2·67 (1)	–O(10^{iii})	2·54 (1)
		Average	2·68

Sr(2) dodecahedron

Sr(2)–O(2)	2·59 (1)	Sr(2)–O(7^{i})	2·80 (1)
–O(3)	2·69 (1)	–O(8^{iii})	2·63 (1)
–O(4^{iii})	2·42 (1)	–O(9)	2·59 (1)
–O(5)	2·77 (1)	–O(19^{iii})	2·70 (1)
		Average	2·65

Sr(3) dodecahedron

Sr(3)–O(2^{ii})	2·59 (1)	Sr(3)–O(6^{ii})	2·67 (2)
–O(3^{iii})	2·59 (1)	–O(7^{iii})	2·39 (1)
–O(4^{i})	2·82 (1)	–O(9^{ii})	2·69 (1)
–O(5)	2·43 (1)	–O(10^{iii})	2·63 (1)
		Average	2·60

Symmetry code: O(n^{i}) ($\bar{x}, y, \bar{z}$); O(n^{ii}) ($\frac{1}{2} + x, \frac{1}{2} + y, z$); O($n^{iii}$)($\frac{1}{2} - x, \frac{1}{2} + y, \bar{z}$).

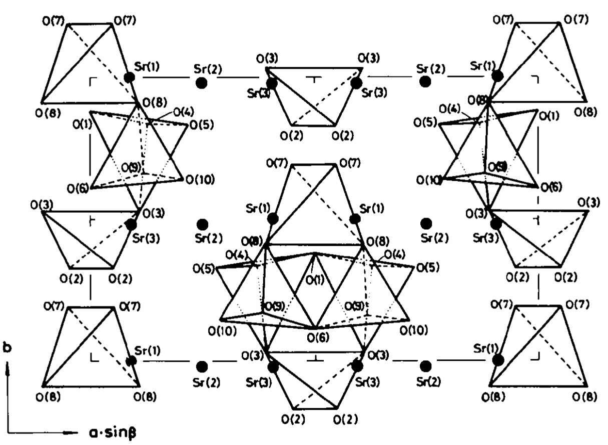

Fig. 2. A projection of the α-$SrSiO_3$ structure viewed along the *c* axis.

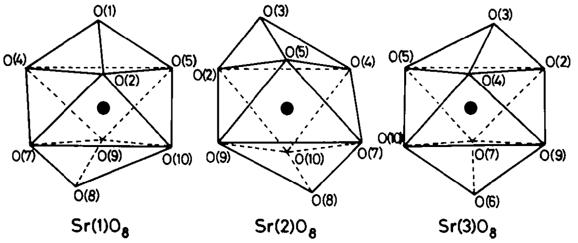

Fig. 3. Schematic illustrations of the SrO_8 polyhedra in α-$SrSiO_3$.

structure viewed along the *b* and *c* axes are shown in Figs. 1 and 2. The structure consists of Sr atoms and $(Si_3O_9)^{6-}$ rings, which are alternately pseudohexagonally packed along the direction perpendicular to (001). Because of this arrangement, the symmetry of α-$SrSiO_3$ has been reported to be pseudohexagonal. There are two kinds of $(Si_3O_9)^{6-}$ rings, one type comprising one Si(1)O_4 and two Si(2)O_4 tetrahedra and the other one Si(3)O_4 and two Si(4)O_4 tetrahedra with shared O atoms. The atoms Si(1), Si(3), O(1) and O(6) are located on twofold axes parallel to the *b* axis, and the centers of gravity for those $(Si_3O_9)^{6-}$ rings also lie on these axes. Consequently, the $(Si_3O_9)^{6-}$ rings should show twofold rotation symmetry. The Si–O bond lengths of the SiO_4 tetrahedra vary from 1·48 (1) to 1·85 (2) Å and the O–Si–O angles [96·7 (6)–133·9 (8)°] deviate considerably from the value for a regular tetrahedron (109·47°).

Atoms of Sr occupy the sites Sr(1), Sr(2) and Sr(3). Each Sr is surrounded by eight O atoms, with Sr–O distances from 2·39 (1) to 2·83 (1) Å, to form an SrO_8 dodecahedron (Fig. 3). The polyhedra Sr(1)O_8, Sr(2)O_8 and Sr(3)O_8 are alternately connected with one another to form layers of SrO_8 on planes (004) and (00$\bar{4}$). The crystal lattice is a three-dimensional arrangement of these layers linked together with the $(Si_3O_9)^{6-}$ rings by the O atoms.

Lattice parameters for the polymorphs of $CaSiO_3$ and $SrSiO_3$ are summarized in Table 4. Both these silicates have two high-pressure phases in addition to the atmospheric-pressure phase (α form). Among them,

Table 4. *High-pressure polymorphs for* $CaSiO_3$ *and* $SrSiO_3$

The values in parentheses represent the calculated densities ($Mg\ m^{-3}$).

	α Form	δ Form	δ′ Form	ε Form
$CaSiO_3$	a = 6·90 Å[a] b = 11·78 c = 19·65 β = 90·8° (2·90)	a = 6·695 (5) Å[b] b = 9·257 (7) c = 6·666 (6) α = 86·63 (5)° β = 76·13 (5) γ = 70·38 (5) (3·06)		a = 3·485 (8) Å[c] (4·56)
$SrSiO_3$[d]	a = 12·323 (5) Å b = 7·139 (2) c = 10·873 (5) β = 111·58 (4)° (3·67)	a = 6·874 (2) Å b = 6·894 (2) c = 9·717 (3) α = 85·01 (3)° β = 110·57 (3) γ = 104·01 (2) (3·90)	a = 7·452 (4) Å b = 6·066 (2) c = 13·479 (7) β = 117·09 (4)° (4·01)	

References: (*a*) Jeffery & Heller (1953). (*b*) Trojer (1969). (*c*) Liu & Ringwood (1975). (*d*) This work.

δ-$SrSiO_3$ is isostructural with the $CaSiO_3$ analog, where the *a*, *b* and *c* axes of δ-$CaSiO_3$ correspond to the −*a*, *c* and *b* axes of δ-$SrSiO_3$. On the basis of the structural analysis for δ-$CaSiO_3$ (Trojer, 1969), the space group of δ-$SrSiO_3$ can be assigned as $P\bar{1}$ and the structure consists of $(Si_3O_9)^{6-}$ rings. Each Sr atom occupies the eight- or six-coordinated site. The crystal lattice of α-$CaSiO_3$ is also presumed to have a similar arrangement of atoms to that of α-$SrSiO_3$, but δ′ is the phase which has not been observed for $CaSiO_3$.

The structural framework of ε-$CaSiO_3$ (perovskite type) is a three-dimensional $(SiO_3)_\infty$ network of SiO_6 octahedra. The density of $CaSiO_3$ considerably increases on changing from SiO_4 to SiO_6 units, *i.e.* on transforming into the ε form. From Table 4, the D_x value for $SrSiO_3$ can be seen not to change appreciably with the phase transformation. This suggests that the structure of δ′-$SrSiO_3$ consists of anions of SiO_4 tetrahedra in a similar manner to the α and δ forms.

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