

trois faces à une distance supérieure. Ces polyèdres, associés par deux, conduisent à une vaste cage de 14 Se, dans laquelle sont piégé deux In<sup>+</sup>. Dans les deux structures, les distances moyennes ⟨In<sup>+</sup>–Se⟩ sont comparables (3,3 Å pour In<sub>3</sub>Mo<sub>15</sub>Se<sub>19</sub> et 3,4 Å pour In<sub>2</sub>Mo<sub>15</sub>Se<sub>19</sub>). De même, nous retrouvons une grande agitation thermique ( $B_{\text{eq}} \sim 3 \text{ \AA}^2$ ) fortement anisotrope ( $\bar{\sigma}_{\perp} = 0,22 \text{ \AA}$ ;  $\bar{\sigma}_{\parallel} = 0,10 \text{ \AA}$ ).

In<sub>2</sub>Mo<sub>15</sub>Se<sub>19</sub> est la structure type d'une grande famille de composés M<sub>2</sub>Mo<sub>15</sub>X<sub>19</sub> (M = K, Ba, In, Tl, X = Se; M = K, Rb, Cs, X = S) qui sont conducteurs métalliques et présentent une transition supraconductrice ( $T_c = 3,3 \text{ K}$  pour K<sub>2</sub>Mo<sub>15</sub>S<sub>19</sub>).

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## The Structure and Polytypes of $\alpha$ -CaSiO<sub>3</sub> (Pseudowollastonite)

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### Abstract

A single crystal of  $\alpha$ -CaSiO<sub>3</sub> (pseudowollastonite) was grown by using a flux of CaCl<sub>2</sub>. In the grown samples, four-layer, six-layer and disordered stacking polytypes were found from X-ray photographs. The four-layer polytype was dominant. The structure of the four-layer type was analyzed and the crystal data were found to be: space group  $C\bar{1}$ ,  $Z = 24$ ,  $a = 6.853(3)$ ,  $b = 11.895(5)$ ,  $c = 19.674(13) \text{ \AA}$ ,  $\alpha = 90.12(3)$ ,  $\beta = 90.55(3)$ ,  $\gamma = 90.00(3)^\circ$ ;  $R = 0.040$  for 1935 reflections. The structure is characterized by four layers, one of which is composed of ternary rings of three tetrahedra of Si<sub>3</sub>O<sub>9</sub> and a seemingly octahedral layer. Thus the structure is similar to that of SrGeO<sub>3</sub>, except that the latter is a six-layer type. The ternary rings are elongated in the stacking direction, while the octahedral layers are contracted in the same direction. Accordingly, Ca atoms are coordinated with eight O atoms instead of six. Space groups of possible polytypes of  $\alpha$ -CaSiO<sub>3</sub> composed of ideal ternary rings and octahedral layers have been derived by stacking operators and the enumeration of the distinct polytypes has also been conducted by the multiplication of these operators. Four-layer polytypes occur in two distinct space groups and have only four structure

types including enantiomorphs. Six-layer polytypes have nine space groups and ten structure types excluding enantiomorphic and congruent structures belonging to the space groups.

### Introduction

$\alpha$ -CaSiO<sub>3</sub>, pseudowollastonite, one of the CaSiO<sub>3</sub> polymorphs, is commonly found in slags or cement materials. However, the structure of  $\alpha$ -CaSiO<sub>3</sub> has never been analyzed because it was difficult to prepare single crystals large enough for X-ray studies, while structures of the other polymorphs of CaSiO<sub>3</sub>, triclinic  $\beta$ -CaSiO<sub>3</sub> (wollastonite), monoclinic  $\beta$ -CaSiO<sub>3</sub> (parawollastonite) and high-pressure CaSiO<sub>3</sub>, have been studied by Ito (1950), Buerger & Prewitt (1961), and Trojer (1968, 1969).

Jeffery & Heller (1953) carried out an X-ray study of the diffraction symmetry of  $\alpha$ -CaSiO<sub>3</sub>. Hilmer (1963) and Dornberger-Schiff (1962) discussed the symmetry and the structure of  $\alpha$ -CaSiO<sub>3</sub> by using the structurally analogous material SrGeO<sub>3</sub> in order to overcome difficulties encountered in the sample preparation.

In the present study, the successful growth of a single crystal of  $\alpha$ -CaSiO<sub>3</sub> enables us to discuss the structure

and polytypism together with the structure of SrGeO<sub>3</sub> related thereto.

### Preparation of $\alpha$ -CaSiO<sub>3</sub>

The stoichiometric composition of CaSiO<sub>3</sub> was prepared by mixing CaCO<sub>3</sub> and anhydrous SiO<sub>2</sub>. These starting materials were heated at 1373 K for 48 h. The heated product was found, using an X-ray powder diffractometer, to be well crystallized  $\beta$ -CaSiO<sub>3</sub>. When again powdered, pelleted and heated at 1673 K for 3 d, the product was sintered and found to be transformed to  $\alpha$ -CaSiO<sub>3</sub>. The sintered product was placed in an evacuated silica tube together with 10 mg of TiCl<sub>4</sub>, a sintering accelerator, and heated at 1523 K for 4 d. The crystals of  $\alpha$ -CaSiO<sub>3</sub> grown were an aggregate of hexagonal platy crystals. The largest grain among the aggregate was 2 mm long and 0.3 mm thick. Single crystals of  $\alpha$ -CaSiO<sub>3</sub> were also prepared by using a flux of CaCl<sub>2</sub>. Reagents CaCO<sub>3</sub> and anhydrous SiO<sub>2</sub> were weighed together with the flux to synthesize a stoichiometric compound of CaSiO<sub>3</sub>. These mixed reagents were heated and gradually cooled from 1723 to 1423 K at the rate of 25 K h<sup>-1</sup>. The largest hexagonal prismatic crystal grown was 5 mm in diameter and 1 mm thick.

Chemical analyses by an electron microprobe analyzer of the grown crystals proved the stoichiometric composition of CaSiO<sub>3</sub> and the absence of any impurities.

X-ray precession photographs of several grown crystals elucidated the presence of polytype structures of  $\alpha$ -CaSiO<sub>3</sub>. A four-layer polytype was predominant in these polytypes, though, in a few cases only, we also found a six-layer type, a mixed structure of four- and six-layer polytypes and disordered structures. The six-layer polytype with pseudosymmetry  $C2/c$  is probably isostructural with SrGeO<sub>3</sub>, described by Hilmer (1963) and Dornberger-Schiff (1962). The disordered structure was confirmed by diffuse streaks along the  $c^*$  axis, and suggests the presence of many polytypes with different stacking periods along the  $c$  axis.

### Structure of the four-layer polytype of $\alpha$ -CaSiO<sub>3</sub>

With reference to the X-ray precession photographs of the four-layer structure of the dominant polytype, the diffraction patterns of even layers corresponding to  $l = 2n$  were characterized by pseudo-hexagonal symmetry, while those of layers with  $l = 2n + 1$  revealed simple pseudomirror symmetry. The systematic absence of  $hkl$  reflections, when  $h + k = 2n + 1$ , indicates that the structure of  $\alpha$ -CaSiO<sub>3</sub> may be represented by a  $C$ -centered lattice. According to the diffraction symmetry and to aid the discussion of the polytype structures, the  $C$ -centered triclinic structure, which has

a pseudomonoclinic symmetry  $C2/c$ , is more applicable than the primitive cell.

The lattice parameters of the four-layer structure of  $\alpha$ -CaSiO<sub>3</sub> are  $a = 6.853$  (3),  $b = 11.895$  (5),  $c = 19.674$  (13) Å,  $\alpha = 90.12$  (3),  $\beta = 90.55$  (3),  $\gamma = 90.00$  (3)°. These were determined by the least-squares method using data obtained on a four-circle diffractometer. These parameters are similar to those reported by Jeffery & Heller (1953):  $a = 6.90$ ,  $b = 11.78$ ,  $c = 19.65$  Å,  $\alpha = \gamma = 90$ ,  $\beta = 90.82$ °. It is apparent that the space group of this sample is  $C\bar{1}$  or  $C1$  and that the unit cell is composed of 24 molecules ( $Z = 24$ ) of CaSiO<sub>3</sub>.

Further systematic absences of  $h0l$  reflections, when  $h = 2n + 1$  and  $l = 2n + 1$ , indicate that the structure has pseudo  $c$  glide planes perpendicular to the  $b$  axis. Reflection intensities of indices having  $k = 3n$  in the even layers  $l = 2n$  are much higher than the rest, indicating the presence of the pseudo-orthorhombic subcell whose  $b$  axis has a length one third of the  $b$  axis of the true cell.

Intensity data were collected up to a  $2\theta$  limit of 55° on an automatic four-circle X-ray diffractometer (Syntex P2<sub>1</sub>) with Mo  $K\alpha$  radiation monochromatized by pyrolytic graphite. The  $\omega$ - $2\theta$  scanning was carried out at 1° ( $2\theta$ ) min<sup>-1</sup>. Data for 1935 reflections having  $I > 2\sigma(I)$  were used in the structure analysis. After correction for Lorentz and polarization factors, the intensities were reduced to structure factors. No correction was made for absorption or secondary extinction. Structure determination was carried out by the direct method with the XRAY system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). Initially, a comparison of calculated and observed statistical averages of normalized structure factors was made. Since the observed average values were very close to the theoretical values of the centrosymmetric structure, the space group was taken to be  $C\bar{1}$ . Secondly, determination of the phase signs was made using  $\sum_2$  relations. From the  $E$  map drawn with the phase signs determined, several models for the arrangement of the Ca and Si atoms were derived. One, which satisfied the pseudosymmetry of  $C2/c$ , was adopted for the most reasonable model in consideration of the diffraction symmetry of the X-ray photographs. The least-squares refinement based on the above model reduced the residual parameter to  $R = 0.080$ . In three additional cycles, isotropic thermal parameters were varied and, thereafter, the  $R$  value decreased to 0.044. After anisotropic thermal parameters were varied in two more cycles, the  $R$  value converged to 0.040. The final atomic coordinates and isotropic thermal parameters are presented in Table 1.\*

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35859 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Interatomic distances are presented in Table 2. The program used in the least-squares refinement is the sub-program *CRYLSQ* in the *XRAY* system.

The structure of the four-layer polytype of  $\alpha$ -CaSiO<sub>3</sub> consists of four Ca-octahedra layers and ternary rings of three tetrahedra of Si<sub>3</sub>O<sub>9</sub>, interposed between the layers. Ca atoms in the unit cell occupy seven independent positions: two on inversion centers and five at general positions. These Ca octahedra in a layer are compressed in the *c* direction, while tetrahedra of the rings are elongated in the same direction. Thus distances between Ca and two bridging O atoms in the tetrahedra are short enough for Ca atoms to coordinate these O atoms. All Ca atoms have an eightfold coordination in the structure, though they seemingly occupy octahedral sites. The eight Ca—O bond distances in all Ca polyhedra are  $\sim 2.54$  Å and they are much longer than those in the  $\beta$ -CaSiO<sub>3</sub> (wollastonite) structure, whose mean value is 2.39 Å. This is a reasonable feature because  $\alpha$ -CaSiO<sub>3</sub> is a higher-temperature polymorph of CaSiO<sub>3</sub>.

The octahedral layers are periodically bridged by the Si<sub>3</sub>O<sub>9</sub> rings as shown in Fig. 1. The ternary rings are located above a void space of the trigonal pyramid defined by three octahedra, and these rings appear in every third void space in an octahedral layer. The void

space connected to a Si<sub>3</sub>O<sub>9</sub> ring is expanded more than the remaining void spaces, and thereby the octahedra in a layer are deformed, as can easily be seen in Fig. 1.

For each tetrahedron, two O atoms, other than the bridging O atoms, link the upper and lower octahedral layers. The Si—O distances involving the former O atoms are longer than those involving the latter (Table 2), and the O—O distance between the former O atoms, whose average value in three tetrahedra is 2.84 Å, is much longer than the other edge distances of the

Table 1. Atomic positional parameters and isotropic temperature factors

	<i>x</i>	<i>y</i>	<i>z</i>	<i>G</i>	<i>B</i> (Å <sup>2</sup> )
Ca(1)	0.5000 (0)	0.5000 (0)	0.0000 (0)	0.5	0.86
Ca(2)	0.5115 (2)	0.8357 (1)	0.0004 (5)	1.0	0.97
Ca(3)	0.5002 (3)	0.4964 (1)	0.2501 (4)	1.0	0.96
Ca(4)	0.5004 (3)	0.8436 (1)	0.2500 (4)	1.0	0.89
Ca(5)	0.0006 (3)	0.6722 (2)	0.2500 (4)	1.0	1.02
Ca(6)	0.5000 (0)	0.5000 (0)	0.5000 (0)	0.5	1.06
Ca(7)	0.4886 (2)	0.8357 (3)	0.4995 (4)	1.0	0.82
Si(1)	0.2066 (3)	0.5387 (1)	0.1249 (5)	1.0	0.63
Si(2)	0.2021 (3)	0.7975 (2)	0.1222 (5)	1.0	0.77
Si(3)	0.5926 (2)	0.6702 (1)	0.1278 (5)	1.0	0.66
Si(4)	0.4068 (3)	0.6701 (2)	0.3720 (5)	1.0	0.74
Si(5)	0.7933 (3)	0.5387 (1)	0.3749 (5)	1.0	0.66
Si(6)	0.7983 (3)	0.7972 (2)	0.3778 (5)	1.0	0.72
O(1)	0.1584 (7)	0.4853 (5)	0.0523 (15)	1.0	1.16
O(2)	0.1533 (8)	0.8448 (5)	0.0479 (14)	1.0	1.10
O(3)	0.7001 (7)	0.6704 (4)	0.0562 (16)	1.0	1.29
O(4)	0.1554 (8)	0.4869 (5)	0.1968 (15)	1.0	1.11
O(5)	0.1451 (8)	0.8505 (4)	0.1927 (17)	1.0	1.46
O(6)	0.6907 (9)	0.6712 (5)	0.2016 (17)	1.0	1.40
O(7)	0.3094 (8)	0.6712 (5)	0.2981 (16)	1.0	1.14
O(8)	0.8435 (8)	0.4873 (4)	0.3030 (15)	1.0	1.06
O(9)	0.8544 (8)	0.8494 (4)	0.3067 (16)	1.0	1.27
O(10)	0.3002 (7)	0.6708 (5)	0.4420 (16)	1.0	1.41
O(11)	0.8426 (7)	0.4855 (4)	0.4460 (17)	1.0	1.42
O(12)	0.8478 (8)	0.8458 (4)	0.4512 (16)	1.0	1.46
O(13)	0.1117 (7)	0.6669 (4)	0.1235 (14)	1.0	0.80
O(14)	0.4480 (7)	0.5584 (4)	0.1261 (14)	1.0	1.04
O(15)	0.4428 (7)	0.7797 (4)	0.1254 (14)	1.0	0.95
O(16)	0.5538 (7)	0.5580 (4)	0.3741 (14)	1.0	0.91
O(17)	0.5566 (6)	0.7803 (4)	0.3748 (14)	1.0	1.09
O(18)	0.8898 (7)	0.6676 (4)	0.3757 (14)	1.0	0.99

Table 2. Interatomic distances (Å)

Ca(1)—O(1)	2.571 (7)	Ca(5)—O(4)	2.666 (7)
O(1')		O(5)	2.609 (7)
O(2)	2.320 (6)	O(6)	2.312 (7)
O(2')		O(7)	2.312 (7)
O(3)	2.679 (7)	O(8)	2.667 (7)
O(3')		O(9)	2.588 (7)
O(14)	2.603 (6)	O(13)	2.612 (7)
O(14')		O(18)	2.595 (7)
Average	2.543	Average	2.545
Ca(2)—O(1)	2.278 (7)	Ca(6)—O(10)	2.701 (7)
O(1')	2.636 (7)	O(10')	
O(2)	2.638 (7)	O(11)	2.594 (7)
O(2')	2.601 (6)	O(11')	
O(3)	2.590 (7)	O(12)	2.311 (7)
O(3')	2.281 (7)	O(12')	
O(13)	2.573 (6)	O(16)	2.600 (6)
O(15)	2.600 (6)	O(16')	
Average	2.525	Average	2.551
Ca(3)—O(4)	2.573 (7)	Ca(7)—O(10)	2.599 (7)
O(5)	2.302 (7)	O(10')	2.302 (7)
O(6)	2.637 (7)	O(11)	2.295 (6)
O(7)	2.628 (7)	O(11')	2.639 (7)
O(8)	2.567 (7)	O(12)	2.654 (6)
O(9)	2.308 (7)	O(12')	2.614 (7)
O(14)	2.570 (7)	O(17)	2.584 (7)
O(16)	2.570 (7)	O(18)	2.582 (7)
Average	2.519	Average	2.535
Ca(4)—O(4)	2.271 (7)		
O(5)	2.674 (7)		
O(6)	2.619 (7)		
O(7)	2.618 (7)		
O(8)	2.272 (7)		
O(9)	2.659 (7)		
O(15)	2.591 (7)		
O(17)	2.595 (7)		
Average	2.537		
Si(1)—O(1)	1.596 (7)	Si(4)—O(7)	1.593 (7)
O(4)	1.590 (7)	O(10)	1.565 (7)
O(13)	1.658 (6)	O(16)	1.669 (6)
O(14)	1.670 (6)	O(17)	1.666 (6)
Average	1.629	Average	1.623
Si(2)—O(2)	1.600 (7)	Si(5)—O(8)	1.585 (7)
O(5)	1.574 (7)	O(11)	1.571 (7)
O(13)	1.671 (6)	O(16)	1.659 (6)
O(15)	1.662 (6)	O(18)	1.669 (6)
Average	1.627	Average	1.621
Si(3)—O(3)	1.598 (7)	Si(6)—O(9)	1.586 (7)
O(6)	1.598 (7)	O(12)	1.588 (7)
O(14)	1.659 (6)	O(17)	1.668 (6)
O(15)	1.659 (6)	O(18)	1.662 (6)
Average	1.629	Average	1.626

tetrahedra, whose mean values are about 2.60 Å. This feature indicates that the tetrahedron seems to undergo a tensile force in the direction of the *c* axis. The ternary rings of  $\text{Si}_3\text{O}_6$  are deformed from an ideal ternary ring having symmetry  $\bar{6}2m$ .

The following structures reported to date have ternary rings of  $\text{Si}_3\text{O}_6$  or  $\text{Ge}_3\text{O}_6$ :  $\text{K}_2\text{ZrSi}_3\text{O}_9$  (wadeite) (Henshaw, 1955),  $\text{Ca}_3\text{Si}_3\text{O}_9$  (high-pressure wollastonite) (Trojer, 1969),  $\text{Ca}_2\text{BaSi}_3\text{O}_9$  (Glasser & Dent Glasser, 1961),  $\text{Sr}_3\text{Ge}_3\text{O}_9$  (Hilmer, 1963) and the benitoite-type structures,  $\text{BaTiSi}_3\text{O}_9$  (Fisher, 1969),

$\text{BaSnGe}_3\text{O}_9$  (Choisnet, Deschanvres & Raveau, 1972) and  $\text{Bi}_2\text{Ge}_3\text{O}_9$  (Grabmaier, Haussühl & Klüfers, 1979). The ternary rings in the structure of  $\alpha\text{-CaSiO}_3$  have similar features to those in the above structures, except for the benitoite-type structures and high-pressure wollastonite.

As inferred by Hilmer (1963) and Dornberger-Schiff (1962),  $\text{SrGeO}_3$  is isostructural with  $\alpha\text{-CaSiO}_3$  in the sense that both are layer structures having ternary rings. The former is, however, a six-layer structure, while the latter is predominantly a four-layer type that was newly analyzed. Further, the relative positions of the rings in these structures are quite different, as shown in Fig. 2.

Several possible arrangements of the ternary rings relative to the octahedral layers may give rise to other structure types of  $\alpha\text{-CaSiO}_3$ . In fact, besides the four-layer polytype, the presence of such other polytypes as six-layer and stacking-disordered polytypes was proved by the X-ray precession photographs, though they were rarely found.

### Polytypes of $\alpha\text{-CaSiO}_3$

In the present study four-layer, six-layer and disordered-layer polytypes have been found in  $\alpha\text{-CaSiO}_3$ . The structure of the four-layer polytype is now found to have space group  $C\bar{1}$  and it is also confirmed that this structure was formed by the deformation of an ideal structure having space group  $C2/c$ . The structure of  $\alpha\text{-CaSiO}_3$ , similarly to  $\text{SrGeO}_3$ , consists of alternate identical layers. A unit of them is composed of an octahedral layer and ternary rings of  $\text{Si}_3\text{O}_6$ . In the unit structure, octahedra are markedly contracted in the *c* direction, parallel to the stacking direction, while tetrahedra in the rings are elongated in the same direction. If the octahedra and ternary rings could preserve symmetries of  $\bar{3}$  and  $3/m$ , respectively, all layers would be geometrically equivalent to each other. The periodic stacking sequence of these layers brings about the polytypic structures. The ideal unit structure (Fig. 3) has a symmetry of  $P\bar{6}m2$  or  $mP3m2$  in the diperic groups proposed by Niggli (1959).

Certain restrictions are imposed on the relative positions of the neighboring layers, because the ternary rings bridge the octahedral layers which are related by mirror symmetry. These positional relations between layers can be expressed by the rotation of the base

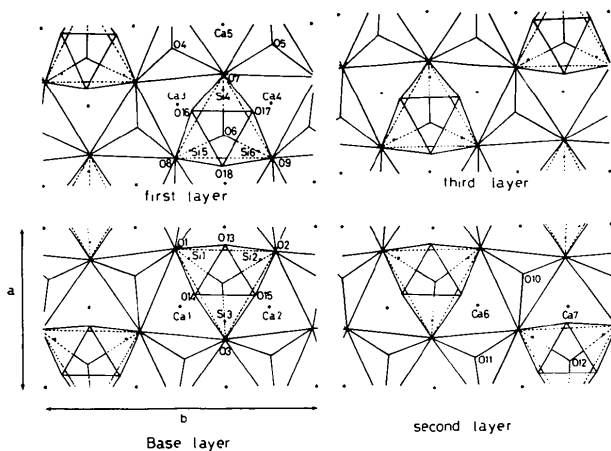


Fig. 1. Projection of the four-layer type of  $\alpha\text{-CaSiO}_3$  (pseudowollastonite). The atoms Ca(1) and Ca(6) are at the inversion center.

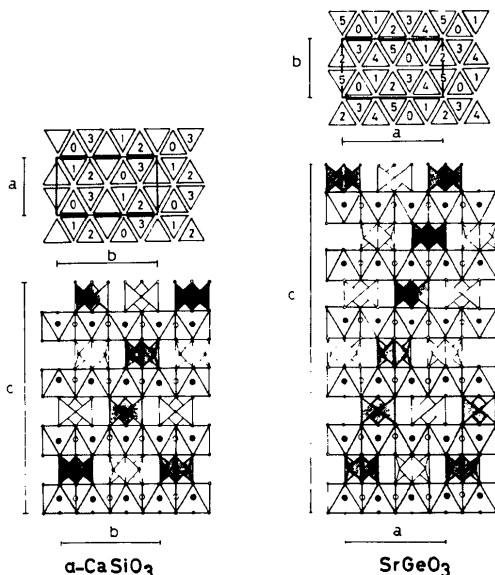


Fig. 2. Structure differences between  $\alpha\text{-CaSiO}_3$  and  $\text{SrGeO}_3$ . The schematic projections along the *a* and *c* axes reveal the difference in their stacking sequences. The numerals indicate the ordering number of the layers from the base layer and the triangles represent the bridging O atoms of the ternary rings in the projection along the *c* axis.

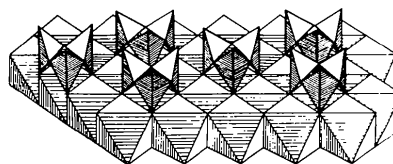


Fig. 3. Arrangement of the ternary tetrahedral rings on the octahedral layer. The ternary rings are located at the void spaces defined by three octahedra. The unit-layer structure has a symmetry of the diperic group  $mP3m2$ .

layer. The rotation axis is located at the octahedral cations. The odd-numbered layers take positions rotated by the angle  $(2n + 1)\pi/3$  relative to the base layer, and the even-numbered layers take the positions rotated by  $2n\pi/3$ . The positions of the upper layers relative to the base layer are given by:

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix}_j = \begin{pmatrix} \cos \theta & -\sin \theta & 0 \\ \sin \theta & \cos \theta & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}_{\text{base}} + \begin{pmatrix} 0 \\ 0 \\ j/N \end{pmatrix},$$

where  $\theta = a_j\pi/3$ ,  $a_j$  is an integer defining the  $j$ th layer, and  $N$  is the number of stacking layers. The periodic repetition of the stacking layers requires  $N$  to be an even number. Since  $a_j$  indicates the rotated positions of the  $j$ th layer,  $|a_j|$  can be a number smaller than 6. A polytype, which is represented by the polytype symbol  $A$ , can be expressed by a numerical row such as

$$A = (a_0 a_1 a_2 \dots a_j \dots a_{N-1}) \quad |a_j| < 6.$$

If the stacking mode is referred to in terms of  $a_j$ , several restrictions are imposed by the symmetry of the unit-layer structure and the linkage of the layers; for example,  $a_{2n}$  is restricted to  $a_{2n} = 0, 2, 4$  and  $a_{2n-1}$  to  $a_{2n-1} = 1, 3, 5$ . Since the unit layer has a threefold rotation symmetry, when polytypes of  $A$  and  $A'$  have a relation such as  $a'_{2n-1} = a_{2n-1} \pm 2$  with  $a'_{2n} = a_{2n}$ , these polytype structures are congruent to each other. Then a polytype  $A$  represents the following three congruent polytypes:

$$\begin{aligned} & (a_0 a_1 a_2 \dots a_j a_{j+1} \dots a_{N-1}) \\ & = (a_0 a_1 \pm 2a_2 \dots a_j \pm 2a_{j+1} \dots a_{N-1} \pm 2) \\ & = (a_0 \pm 2a_1 a_2 \pm 2 \dots a_j a_{j+1} \pm 2 \dots a_{N-1}). \end{aligned} \quad (1)$$

Since polytype structures have cyclic stacking sequences, polytype  $A'$ , derived from the shifting of the position of the base layer by  $q$  layers in polytype  $A$ , has the relation  $a'_j = a_{j+q}$  and is congruent to  $A$ . The following equation is then derived:

$$\begin{aligned} & (a_0 a_1 a_2 \dots a_j \dots a_{N-1}) \\ & = (a_q a_{q+1} a_{q+2} \dots a_{q+j} \dots a_0 a_1 \dots a_{q-1}), \end{aligned} \quad (2)$$

and all the stacking modes  $\{a_j\}$  derived from the permutation of  $N$  layers include  $N$  equivalent modes.

In addition to the above relations (1) and (2), the relative positions of the stacking layers have several other systematic relations derived from stacking operations. The following stacking operations can be given in the stacking sequences: mirror operation represented by operator  $\sigma$  perpendicular to the stacking direction, twofold rotation at the intralayer position by  $\varphi$  and at the interlayer position by  $\lambda$ , and inversion by operator  $\tau$ . These operators are expressed by the following relations according to (1) and (2):

$$\sigma A = (a_{N-1} a_{N-2} \dots a_j \dots a_2 a_1 a_0)$$

$$\varphi A = (-a_{N-1} - a_{N-2} \dots -a_j \dots -a_2 - a_1 - a_0)$$

$$\lambda A = (-a_{N-1} \pm 3 - a_{N-2} \pm 3 \dots -a_j \pm 3 \dots -a_2 \pm 3 - a_1 \pm 3 - a_0 \pm 3)$$

$$\tau A = (a_{N-1} \pm 3a_{N-2} \pm 3 \dots a_j \pm 3 \dots a_2 \pm 3a_1 \pm 3a_0 \pm 3).$$

When the stacking operations introduced by these operators are located on or in the  $N/2$  layer, polytype  $A'$  is represented by

$$A'_\sigma = \{A, \sigma A\} = \{a'_j\} \quad (j = 0, N-1) \\ \text{with } a'_j - a'_{N-j} \equiv 0 \pmod{6}$$

$$A'_\varphi = \{A, \varphi A\} = \{a'_j\} \quad (j = 0, N-1) \\ \text{with } a'_j + a'_{N-j} \equiv 0 \pmod{6}$$

$$A'_\lambda = \{A, \lambda A\} = \{a'_j\} \quad (j = 0, N-1) \\ \text{with } a'_j + a'_{N-j} \equiv 3 \pmod{6}$$

$$A'_\tau = \{A, \tau A\} = \{a'_j\} \quad (j = 0, N-1) \\ \text{with } a'_j - a'_{N-j} \equiv 3 \pmod{6}.$$

When these operations are on or in the  $N/4$  and  $3N/4$  layers, where  $N = 4n$ , and on or in the  $(N-2)/4$  and  $3(N-2)/4$  layers, where  $N = 4n + 2$ , polytype  $A''$  is represented by:

$$A''_\sigma = \xi\{A, \sigma A\} = \{a''_j\} \quad (j = 0, N-1) \\ \text{with } a''_j - a''_{N/2-j} \equiv 0 \pmod{6}$$

$$A''_\varphi = \xi\{A, \varphi A\} = \{a''_j\} \quad (j = 0, N-1) \\ \text{with } a''_j + a''_{N/2-j} \equiv 0 \pmod{6}$$

$$A''_\lambda = \xi\{A, \lambda A\} = \{a''_j\} \quad (j = 0, N-1) \\ \text{with } a''_j + a''_{N/2-j} \equiv 3 \pmod{6}$$

$$A''_\tau = \xi\{A, \tau A\} = \{a''_j\} \quad (j = 0, N-1) \\ \text{with } a''_j - a''_{N/2-j} \equiv 3 \pmod{6}$$

where operator  $\xi$  indicates a shift of the base layer to the  $N/4$  layer.

Many stacking modes of the polytypes can be derived from more than two stacking operations, because multiplications of the above four operators are possibly generated. If these operators are simultaneously imposed on or in the same position, all  $a_j$  in the  $\{a_j\}$  are either  $a_j = 0$  or  $a_j = 3$  with any  $j$ . If the conditions  $a_{2n} = 0, 2, 4$ , and  $a_{2n-1} = 1, 3, 5$  are considered, these operations generate only two-layer polytypes. Stacking modes, except in the two-layer models, may be given by the multiplications of operators which are imposed on or in the different layer positions; for example,  $N/4$  and  $N/2$ .

Multiplications of two operators, such as  $\sigma\varphi$ ,  $\sigma\lambda$ ,  $\sigma\tau$ ,  $\varphi\lambda$ ,  $\varphi\tau$  and  $\lambda\tau$  can be derived. Those of any three operators naturally produce the fourth operator and, therefore, multiplications of all four operators, such as  $\sigma\varphi\lambda\tau$ , are present, but those of any three are not present.

$A^*_{\sigma\varphi}$  and  $A^*_{\lambda\tau}$ , derived from the multiplications of  $\sigma\varphi$  and  $\lambda\tau$ , respectively, give the stacking modes of polytypes with  $N = 4n$ , because

$$\begin{aligned} A^*_{\sigma\varphi} & = \{A, \sigma A\} \cap \xi\{A, \varphi A\} \\ & = \{A, \varphi A\} \cap \xi\{A, \sigma A\} = \{a^*\}, \end{aligned}$$

and, in addition to each constraint in  $\{a_j^*\}$  introduced by the independent operator of  $\sigma$  and  $\varphi$ ,  $\{a_j^*\}$  has the further constraint

$$a_{N-j}^* + a_{N/2-j}^* = 0 \pmod{6},$$

and

$$\begin{aligned} A_{\lambda\tau}^* &= \{A, \lambda A\} \cap \xi\{A, \tau A\} \\ &= \{A, \tau A\} \cap \xi\{A, \lambda A\} = \{a_j^*\}, \end{aligned}$$

with the further constraint

$$a_{N-j}^* - a_{N/2-j}^* = 0 \pmod{6}.$$

The other multiplications of the operators, such as  $\sigma\lambda$ ,  $\sigma\tau$ ,  $\varphi\lambda$  and  $\varphi\tau$ , give the modes of polytypes with  $N = 4n - 2$  and  $\{a_j^*\}$  has an additional constraint, as follows:

$$\begin{aligned} A_{\sigma\lambda}^* &= \{A, \sigma A\} \cap \xi\{A, \lambda A\} = \{A, \lambda A\} \cap \xi\{A, \sigma A\} = \{a_j^*\} \\ &\quad \text{with } a_{N-j}^* + a_{N/2-j}^* \equiv 3 \pmod{6} \end{aligned}$$

$$\begin{aligned} A_{\sigma\tau}^* &= \{A, \sigma A\} \cap \xi\{A, \tau A\} = \{A, \tau A\} \cap \xi\{A, \sigma A\} = \{a_j^*\} \\ &\quad \text{with } a_{N-j}^* - a_{N/2-j}^* \equiv 3 \pmod{6} \end{aligned}$$

$$\begin{aligned} A_{\varphi\lambda}^* &= \{A, \varphi A\} \cap \xi\{A, \lambda A\} = \{A, \lambda A\} \cap \xi\{A, \varphi A\} = \{a_j^*\} \\ &\quad \text{with } a_{N-j}^* - a_{N/2-j}^* \equiv 3 \pmod{6} \end{aligned}$$

$$\begin{aligned} A_{\varphi\tau}^* &= \{A, \varphi A\} \cap \xi\{A, \tau A\} = \{A, \tau A\} \cap \xi\{A, \varphi A\} = \{a_j^*\} \\ &\quad \text{with } a_{N-j}^* + a_{N/2-j}^* \equiv 3 \pmod{6}. \end{aligned}$$

Symmetries of the polytype structures are defined by the combination of these stacking operations and the symmetry of the unit-layer structure which has symmetry  $P6m2$ .

The enumeration of each distinct polytype is also derived from the combination. Numbers of possible stacking modes symbolized by  $Q$  of the  $N$ -layer polytypes are represented by the permutation of layers given by  $Q = {}_3\Pi_N$ . However, the relations introduced by equations (1) and (2) reduce  $Q$  to  $Q = {}_3\Pi_{N-2}$ . Since  $N$ -layer polytypes include polytypes of subfamilies composed of  $K, L, M, \dots$ -layer polytypes, where  $K, L, M, \dots$  are divisors of  $N$ , the number of distinct polytypes of  $Q_N$  is given by

$$\begin{aligned} Q_N &= Q - (Q_K + Q_L + Q_M + \dots) \\ &= {}_3\Pi_{N-2} - ({}_3\Pi_{K-2} + {}_3\Pi_{L-2} + {}_3\Pi_{M-2} + \dots). \end{aligned} \quad (3)$$

$Q_N$ , thus obtained, is composed of the summation of the number of distinct polytypes, including their enantiomorphs. A detailed discussion of the derivations of the symmetries and enumerations of the distinct polytypes from the stacking operations in arbitrary-number layer polytypes will be reported later. The results obtained from the derivations in the only two-, four- and six-layer polytypes are presented below.

#### (a) Two-layer polytypes

Though neighboring layers in the two-layer structures can take three possible different positions,  $A = (0\ 1)$ ,  $(0\ 3)$  or  $(0\ 5)$ , they are all congruent to each other

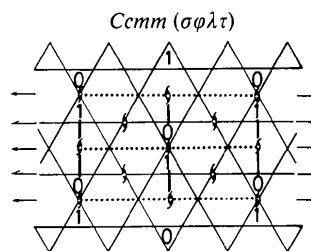


Fig. 4. Projection of the two-layer polytype along the stacking direction. The symbols in parentheses indicate the stacking operators, driving this polytype structure.

due to equation (1). Therefore, two-layer structures are essentially one type and this is also proved by equation (3) as  $Q_2 = {}_3\Pi_0 = 1$ . As previously described, two-layer polytypes are generated by multiplications of all four operators,  $\sigma\varphi\lambda\tau$ . The space group of the polytypes is then  $Ccmm$ , as shown in Fig. 4.

#### (b) Four-layer polytypes

In the four-layer polytypes eight types are given by equation (3) as  $Q_4 = Q - Q_2 = {}_3\Pi_2 - {}_3\Pi_0$ . Some of them are, however, regarded as enantiomorphic or congruent structures. Only two distinct polytypes having space group  $C2cm$  or  $C2/c$  are given by the stacking operations therein.

Structures derived from the operation of  $\lambda\tau$  have space group  $C2/c$ . They are expressed by the following four stacking modes:  $A^1 = (0\ 1\ 2\ 3)$ ,  $A^2 = (0\ 1\ 2\ 5)$ ,  $A^3 = (0\ 1\ 4\ 3)$  and  $A^4 = (0\ 1\ 4\ 5)$ . Each pair of  $A^1$  and  $A^4$  and  $A^2$  and  $A^3$  is in an enantiomorphic relation and the first pair is congruent with the last, according to equations (1) and (2). Then  $A^1$  is an enantiomorph of  $A^4$  and congruent with  $A^2$  which is an enantiomorph of  $A^3$ .

Four-layer polytypes given by the multiplication of the operators, such as  $\sigma\varphi$ , introduce structures having space group  $C2cm$ . Four polytypes,  $A^5 = (0\ 1\ 0\ 3)$ ,  $A^6 = (0\ 1\ 0\ 5)$ ,  $A^7 = (0\ 1\ 2\ 1)$  and  $A^8 = (0\ 1\ 4\ 1)$ , belong

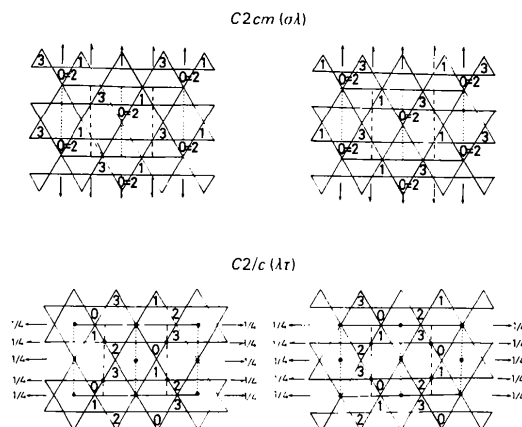


Fig. 5. Four-layer polytypes and their enantiomorphs.

Table 3. Numbers of polytypes and their space groups

Family	$\sigma\phi\lambda\tau$	$\sigma\phi$	$\lambda\tau$	$\sigma\lambda$	$\sigma\tau$	$\phi\lambda$	$\phi\tau$	$\sigma$	$\phi$	$\lambda$	$\tau$	$\chi$
Number of layer ( <i>N</i> )	2	4	4	6	6	6	6	6	6	6	6	6
Space group	<i>Cm</i>	<i>C2cm</i>	<i>C2/c</i>	<i>C2cm</i>	<i>C2<sub>1/m</sub></i>	<i>P6<sub>1</sub>22</i> <i>P6<sub>5</sub>22</i>	<i>C2/c</i>	<i>Cm</i>	<i>C2</i>	<i>C2</i>	<i>P1</i>	<i>P1</i>
Distinct type ( <i>Pd</i> )	1	1	1	1	1	1	1	1	1	1	1	2
Enantiomorphs ( <i>Pe</i> )	1	2	2	2	2	2	1	2	2	2	2	4
Congruent type ( <i>Pc</i> )	1	2	2	3	3	1	2	6	2	6	6	6
<i>Pc</i> × <i>Pe</i>	1	4	4	6	6	2	2	12	4	12	12	24
Total number ( <i>Q</i> )	1	8						80				

to the above structures. The first two are in an enantiomorphic relation and they are congruent with the last two. Then only two are distinct polytypes, one is *C2/c* and the other *C2cm*. They are presented in Fig. 5.

### (c) Six-layer polytypes

In the six-layer polytypes, according to equation (3),  $Q_6 = Q - Q_2 = {}_3\Pi_4 - {}_3\Pi_0$ , 80 types can be produced. 10 distinct polytypes are found which belong to the structures having the nine space groups *P6<sub>1</sub>22*, *P6<sub>5</sub>22*, *C2cm*, *C2<sub>1/m</sub>*, *C2/c*, *Cm*, *C2*, *P1* and *P1*.

When six layers have the stacking operations defined by the operator of  $\phi\lambda$ , these layers take continuously rotated positions of  $\pi/3$  or  $-\pi/3$  relative to the base layer. Their polytypes are expressed by  $A = (0\ 1\ 2\ 3\ 4\ 5)$  or  $A = (0\ 5\ 4\ 3\ 2\ 1)$ , which is congruent to  $A = (0\ 1\ 4\ 5\ 2\ 3)$ . They are *P6<sub>1</sub>22* and *P6<sub>5</sub>22*, respectively, and are enantiomorphic structures.

When the six-layer polytypes are derived from the stacking operations of the multiplication of  $\phi\tau$ , the six layers are alternately rotated by  $2\pi/3$  and  $-2\pi/3$  in the even and odd layers, such as  $A = (0\ 1\ 2\ 5\ 4\ 3)$  or  $A = (0\ 1\ 4\ 3\ 2\ 5)$ . These structures inherently have the symmetry of a *c* glide plane and, therefore, their space group is *C2/c*. In the six-layer polytypes, only two types belong to the structure. Since they are, however,

enantiomorphs of each other, the distinct polytype having the symmetry is only one type.

When the six-layer polytypes are constructed by the stacking operations of  $\sigma\lambda$  or  $\sigma\tau$ , their structures have space group *C2cm* or *C2<sub>1/m</sub>*. Each gives only one distinct polytype which has two enantiomorphic polytypes.

When only one of the operators,  $\sigma$ ,  $\phi$ ,  $\lambda$  and  $\tau$ , independently constitutes the stacking sequences of the six layers, the structures have the space groups *Cm*, *C2*, *C2* and *P1*, respectively. Only one distinct polytype belongs to each structure and forms two enantiomorphs.

Finally six layers having no special stacking operations are of space group *P1*. Two distinct polytypes, each of which gives four enantiomorphs, belong to the structure. Several distinct polytypes having different space-group symmetries in the six-layer polytypes are presented in Fig. 6.

### (d) Enumeration of the distinct polytypes

Enumeration of distinct polytypes of the two-, four- and six-layer polytypes is subjected to the combinations of the stacking operations. These polytypes are classified into several families in terms of the stacking operations. The numbers of distinct polytypes in the families are presented in Table 3. Numbers of distinct (*Pd*), enantiomorphic (*Pe*) and congruent polytypes (*Pc*) have also been confirmed by the computer analysis concerning all permutations of layers.

In the four-layer polytype structure presently analyzed, deformations due to the contraction of the octahedral layers and the elongation of the ternary rings may have been caused by the cooling process in the sample preparation of  $\alpha$ -CaSiO<sub>3</sub>. The sample may essentially have an ideal polytype structure of *C2/c* in the structurally stable region at temperatures higher than 1373 K. We shall soon test the assumption by using a high-temperature apparatus for single-crystal X-ray diffraction studies (Yamanaka, Takéuchi & Sadanaga, 1980).

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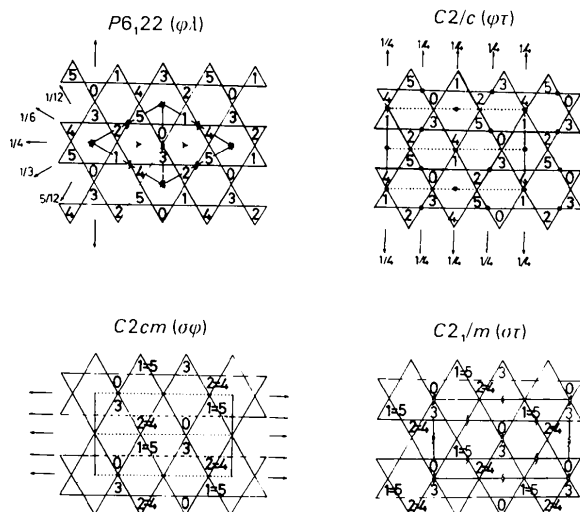


Fig. 6. Several examples of the six-layer polytypes.

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## Structures and Phase Transition of $\beta$ - and $\gamma$ -Ag<sub>3</sub>IS

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### Abstract

Single-crystal X-ray data for the fast ionic conductor Ag<sub>3</sub>IS were measured in the temperature range 135–295 K. Structure refinement was carried out for the cubic room-temperature ( $\beta$ ) phase in space group *Pm3m* with three Ag<sup>+</sup> ions distributed among twelve (I,S) tetrahedra. The final refinement [ $R(w) = 0.041$  for 49 reflections] resulted in very anisotropic temperature factors for Ag (r.m.s. displacement 0.19–0.39 Å). An alternative structure model with Ag on octahedral sites and anharmonic temperature factors up to the sixth order resulted in  $R(w) = 0.042$ . At the transition to the  $\gamma$  phase (155 K) the reflection symmetry did not change; the intensities of only a few reflections increased considerably (a maximum of more than 100 times). The single-crystal features were not destroyed by cycling between the  $\beta$  and  $\gamma$  phases. It could be shown definitely by Patterson synthesis that in the  $\gamma$  phase the crystal was composed of 16 differently oriented domains with completely occupied Ag sites. The domains scattered incoherently. The space group of each domain is *R3*. A special program was written to calculate a least-squares refinement for the superimposed intensities of this 16-domain crystal. The weighted  $R$  value for the intensities was  $R_w(I) = 0.16$

for 55 independent reflections. Additional weak reflections were found in the  $\beta$  and the  $\gamma$  phases, indicating that small domains of monoclinic  $\alpha$ -Ag<sub>2</sub>S were included in the crystal.

### 1. Introduction

Silver iodide sulfide is a fast ionic conductor with a close structural relationship to the archetype superionic conductor  $\alpha$ -AgI. The major difference is the much higher density of mobile ions: the cubic unit cell with  $a = 4.987$  Å contains 3Ag<sup>+</sup> in Ag<sub>3</sub>IS compared to  $a = 5.05$  Å and 2Ag<sup>+</sup> in  $\alpha$ -AgI. As a consequence, both the structural and the dynamic properties of Ag<sub>3</sub>IS are expected to be much more affected by the repulsive interaction between the Ag<sup>+</sup> ions than is the case for  $\alpha$ -AgI.

All presently known structural data on Ag<sub>3</sub>IS have been derived from powder investigations, but they already evidence the considerable structural richness of this compound.

Reuter & Hardel (1961) reported the existence of a room-temperature ( $\beta$ ) phase and a high-temperature ( $\alpha$ ) phase with the  $\beta \rightarrow \alpha$  transition at 508 K. They measured an ionic conductivity of  $0.001 \Omega^{-1} \text{mm}^{-1}$  at