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24-Layer Structure of Tricalcium Germanate, Ca_3GeO_5

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Abstract

The crystal structure of a 24-layer polytype of tricalcium germanate (C_3G), which was found in a flux melt, has been determined. The crystal data are: $M_r = 272.8$, rhombohedral, $R3m$, $a = 7.228(2)$, $c = 67.42(2)$ Å, $V = 3050(2)$ Å³, $Z = 24$, $D_x = 3.56$ g cm⁻³, $\text{Mo K}\alpha$, $\lambda = 0.71069$ Å, $\mu = 92.7$ cm⁻¹, $F(000) = 3168$, $T = 298$ K. The structure consists of two kinds of subunits, one is related to the structure of the 2-layer polytype and the other to that of the 9-layer polytype; these occur alternately in the structure. Half of the eight independent germanate tetrahedra show nearly perfect orientational disorder along the c axis. The positions of the Ge atoms of these tetrahedra are split, the separations being in the range 0.34(10) to 0.69(5) Å. The coordination numbers of Ca, each calculated as the sum of the occupancies of the Ca-O bonds, are in the range 6.0 to 6.56, giving mean Ca-O bond lengths of 2.34 to 2.51 Å. General principles of deriving polytypes for C_3G are provided and, based on these, the stacking sequences of simple polytypes such as 4-layer, 5-layer and 6-layer structures have been predicted. The derivation of polytypes can be applicable to the case of tricalcium silicate (C_3S).

Introduction

Our study on tricalcium germanate (C_3G) has revealed the existence of various polytypic forms as mentioned in our paper on the crystal structure of the 2-layer variant (Nishi & Takéuchi, 1984a). It

appears that polytypism likewise exists in tricalcium silicate (C_3S); in addition to the rhombohedral structure, which may be interpreted as a 9-layer structure (Takéuchi, Nishi & Maki, 1984; Nishi & Takéuchi, 1984b), the existence of a two-layer structure has been reported by Pérez-Méndez, Howie & Glasser (1984).

In view of the common occurrence of polytypic forms in these chemical phases, we propose to denote N -layer variants by the following expressions: tricalcium germanate- N (or $\text{C}_3\text{G } N$) or tricalcium silicate- N (or $\text{C}_3\text{S } N$) (it is suggested that Roman numerals be used for N).

Although in general $\text{C}_3\text{G } N$ is isotypic with $\text{C}_3\text{S } N$, the space group reported for $\text{C}_3\text{S } \text{II}$ (Pérez-Méndez *et al.*, 1984) is different from the one we found for $\text{C}_3\text{G } \text{II}$ (Nishi & Takéuchi, 1984a), the former being $P6_3/mmc$ and the latter $P6_3mc$. Note that in the structures of these chemical phases the germanate (or silicate) tetrahedron shows a trend towards orientational disorder; a fraction of the tetrahedron points up the c axis (a U orientation) while the remaining fraction points down the c axis (a D orientation). Slight differences in the occupancy between the pairs of differently oriented tetrahedra may cause such a difference in the space group although the structures are based on the same principle. Since, however, the structure determination of $\text{C}_3\text{S } \text{II}$ (Pérez-Méndez *et al.*, 1984) is based on a small number of diffraction intensities, further refinement of the structure is desirable; it is anticipated that the structure would possibly be strictly isotypic with our $\text{C}_3\text{G } \text{II}$. In any case, the theory of polytypism developed for C_3G will be applicable to C_3S .

The present paper describes the result of our structure analysis of a 24-layer variant of C_3G (C_3G XXIV) and discusses the general derivation of polytypes in C_3G .

Experimental

Single crystals of tricalcium germanate were synthesized from a stoichiometric mixture of Ca_2GeO_4 and CaF_2 plus small amounts of Al_2O_3 (about 2 wt%). The mixture was melted at 1720 K and cooled to room temperature. X-ray examination of the product revealed the existence of C_3G XXIV and C_3G II in addition to C_3G IX which was the major product. Electron microprobe analyses of the C_3G XXIV crystals yielded: CaO 62.19, GeO_2 37.07 and Al_2O_3 0.78 wt%; the total was 100.04 wt%. A crystal of C_3G XXIV was ground to the shape of a sphere with diameter 0.18 mm. We determined the cell dimensions (see *Abstract*) from the 2θ values of 10 reflections ($10.2^\circ \leq 2\theta \leq 34.0^\circ$) measured with a Syntex P2₁ four-circle single-crystal diffractometer using graphite-monochromated $Mo K\alpha$ radiation ($\lambda = 0.71069 \text{ \AA}$). In a precession photograph (Fig. 1) very weak extra reflections were observed, as in the case of C_3G II (Nishi & Takéuchi, 1984a), suggesting that the crystal is not ideally of single phase but contaminated with very minor amounts of some other polytypic forms.

The diffraction intensities were measured with the ω - 2θ scan technique up to $2\theta = 70^\circ$. One-twelfth $Mo K\alpha$ diffraction intensities $I(hkl)$ and another one-twelfth $I(\bar{h}\bar{k}\bar{l})$ were collected, the former giving a set of intensities of 524 reflections, while the latter that of 600 reflections. By averaging symmetrically equivalent reflection intensities, we obtained a set of 440 diffraction intensities, reflections whose intensities were smaller than $3\sigma(I)$ being omitted.

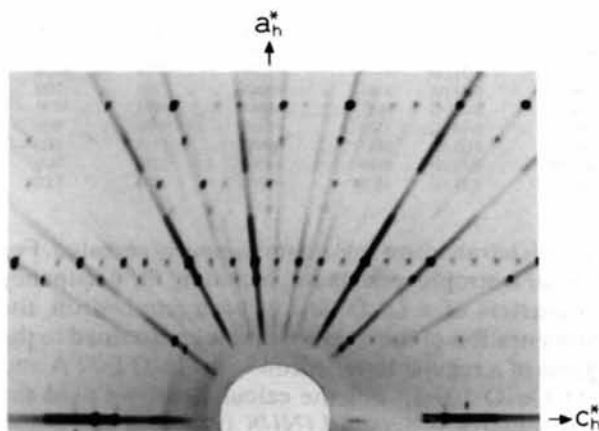


Fig. 1. Precession photograph showing $h0l$ reflections of C_3G XXIV ($Mo K\alpha$). Some of the extra reflections are indicated; a_h^* and c_h^* indicate the reciprocal axes of the hexagonal cell of the rhombohedral substructure.

The ranges of the indices were $0 \leq h \leq 10$, $0 \leq k \leq 9$ and $0 \leq l \leq 96$. The intensity fluctuations of three reference reflections were within 4.4% (of I value). The intensities were corrected for Lorentz, polarization and absorption effects (transmission factors: max. 0.38, min. 0.32) and reduced to structure factors.

Structure determination

Conditions of layer stacking

The unit layer for the polytypic series now considered is illustrated in Fig. 2. The unit cell of the layer, which has plane symmetry $P3m1$, contains one germanate tetrahedron, three Ca atoms and one separate O atom, not associated with Ge, in its asymmetric unit. The possible stacking operations may be classified into two categories: (1) displacement vectors, S_0, S_1 and S_2 , with their horizontal components, s_0, s_1 and s_2 , as illustrated in Fig. 2, and (2) combined operations in which any one of S_0, S_1 and S_2 is followed by a rotation $\varphi = (2t+1) \times 60^\circ$ about an axis which may be represented by a line passing through the unit-cell origin and perpendicular to the layer, where t is an integer. The operation in the latter category may hence be expressed by $S_0\varphi$. Because of the high symmetry of the unit layer, however, we may consider only S_0 in category (1) and $S_0\varphi_{t=1}$ in (2). The displacements ($\pm S_0$), moreover, between any two successive layers can be decided in obedience to the orientation [0° or $180^\circ (= \varphi_{t=1})$] of the layer having lower position. Accordingly, one kind of character representing the orientational sequences is sufficient for the description. For simplicity, these orientational vectors will be represented by $\bar{1}$ [0°] and $\bar{1}$ [$180^\circ (= \varphi_{t=1})$]. This situation implies that possible polytypes

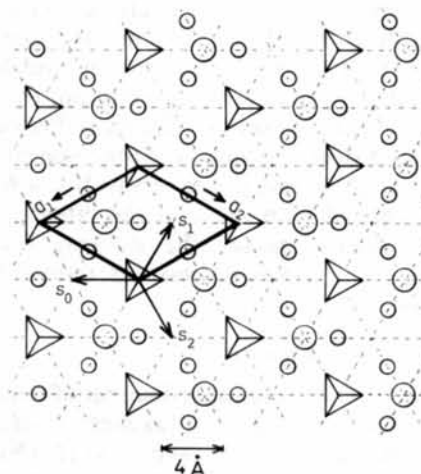


Fig. 2. Structure of the unit layer, showing that the unit cell contains three Ca atoms (small open circles), one separate O atom (large open circles) and one GeO_4 tetrahedron. All tetrahedra are shown in the U orientation. s_0, s_1 and s_2 represent horizontal components of the displacement vectors. In general, the tetrahedra may have U - D orientational disorder.

of C₃G (or C₃S) may well be studied in terms of the sequence of **1** and $\bar{1}$. The symbols **1** and $\bar{1}$ will further be represented by + and -, respectively (see Guinier *et al.*, 1984). Then the stacking sequence

$$++++ \dots = | + |_3$$

gives a 3-layer rhombohedral polytype. And

$$+ - + - + \dots = | + - |$$

gives the 2-layer hexagonal structure.

Between the two symbols there is no restriction in the succession of + and -. Therefore, a layer + (or -) may be followed by either + or -.

In the polytypes thus derived, the threefold axes and mirror planes of the unit layer are preserved. Accordingly, the structure of any polytype will be described by a hexagonal cell and have space group *P3m1* or one which has an order higher than that of *P3m1*. Now consider the case in which *m* layers define a periodicity perpendicular to the layers:

$$\overbrace{+ \dots + - + \dots - - + + \dots + - \dots +}^m. \quad (1)$$

Suppose that layers, -, occur in this sequence at the Q₁th, Q₂th, ..., Q_nth layers, where Q₁ < Q₂ < Q₃ < ... < Q_n (n ≤ m). Then the horizontal shift **X** of all the atoms in the (m + 1)th layer relative to that of the first layer is given by

$$\mathbf{X} = (m - 2n) * \mathbf{s}_0. \quad (2)$$

Then, once the layer number *m* is given, the possible stacking sequence can be derived from the result of (2).

In the case of a 24-layer structure having rhombohedral symmetry, we may consider the mode of stacking of only eight layers, namely *m* = 8 (= 24/3). We then solved equation (2) under the condition [*m* - 2*n* ≡ 1 (mod 3), 0 ≤ *n* ≤ 8, *n*: integer] and derived many sets of sequences from its solution, the result giving ten independent sets of sequences. Preliminary calculations of structure factors of these ten structure models revealed that one gave a relatively low *R* value of 46% compared with those of the others, 54% ~ 70%. This model, having the stacking sequence | + - - + - - + - |₃, was successfully refined as will be shown below.

Refinement of the structure

Since the *U-D* orientational disorder of tetrahedra commonly occurs in C₃S IX (Takéuchi *et al.*, 1984; Nishi & Takéuchi, 1984*b*) and C₃G II (Nishi & Takéuchi, 1984*a*), the refinement of the above model was initiated by carrying out a Fourier synthesis based on structure factors calculated from the positional parameters of Ca, Ge and separate O atoms, the O atoms about Ge being omitted. In the resulting Fourier map, the mode of *U-D* orientational disorder

Table 1. Atomic parameters for 24-layer tricalcium germanate (values of the positional parameters are multiplied by 10⁴)

	Occupancy	x	y	z	B (Å ²)
Ca(1)	1-0	5105 (20)	-5105 (20)	36 (6)	2.8 (5)
Ca(2)	1-0	8112 (17)	-8112 (17)	467 (5)	2.3 (4)
Ca(3)	1-0	5142 (20)	-5142 (20)	856 (6)	4.0 (6)
Ca(4)	1-0	1769 (18)	-1769 (18)	1243 (5)	2.4 (4)
Ca(5)	1-0	4850 (15)	-4850 (15)	1678 (5)	2.0 (4)
Ca(6)	1-0	1716 (15)	-1716 (15)	2080 (5)	1.8 (3)
Ca(7)	1-0	8411 (21)	-8411 (21)	2520 (6)	3.8 (5)
Ca(8)	1-0	1532 (25)	-1532 (25)	2938 (6)	3.8 (6)
Ge(11)	0.56 (4)	0	0	0	1.7 (5)
Ge(21)	0.79 (4)	0	0	7087 (5)	1.2 (4)
Ge(31)	0.56 (4)	0	0	861 (9)	1.0 (3)
Ge(41)	0.79 (4)	0	0	4638 (5)	1.3 (4)
Ge(51)	0.56 (4)	0	0	1643 (5)	0.4 (3)
Ge(61)	0.79 (4)	0	0	5476 (6)	1.7 (4)
Ge(71)	0.56 (4)	0	0	9265 (7)	2.1 (6)
Ge(81)	0.79 (4)	0	0	6273 (6)	2.0 (6)
Ge(12)	0.44 (4)	0	0	102 (8)	1.7 (5)
Ge(22)	0.21 (4)	0	0	7121 (15)	1.2 (4)
Ge(32)	0.44 (4)	0	0	852 (8)	1.0 (3)
Ge(42)	0.21 (4)	0	0	4588 (14)	1.3 (4)
Ge(52)	0.44 (4)	0	0	1703 (5)	0.4 (3)
Ge(62)	0.21 (4)	0	0	5465 (15)	1.7 (4)
Ge(72)	0.44 (4)	0	0	9200 (8)	2.1 (6)
Ge(82)	0.21 (4)	0	0	6244 (18)	2.0 (6)
O(1)	1-0	0	0	3605 (33)	8 (5)
O(2)	1-0	0	0	4028 (33)	4 (4)
O(3)	1-0	0	0	7591 (32)	6 (6)
O(4)	1-0	0	0	8120 (27)	3 (3)
O(5)	1-0	0	0	8563 (32)	6 (4)
O(6)	1-0	0	0	2333 (30)	6 (3)
O(7)	1-0	0	0	2744 (27)	4 (4)
O(8)	1-0	0	0	3188 (13)	1 (2)
OA(11)	0.56 (4)	0	0	262	2 (2)
OA(21)	0.79 (4)	0	0	7349	11 (6)
OA(31)	0.56 (4)	0	0	1123	7 (3)
OA(41)	0.79 (4)	0	0	4900	-1 (1)
OA(51)	0.56 (4)	0	0	1905	5 (3)
OA(61)	0.79 (4)	0	0	5738	1 (1)
OA(71)	0.56 (4)	0	0	9527	2 (2)
OA(81)	0.79 (4)	0	0	6535	5 (2)
OA(12)	0.44 (4)	0	0	-160	2 (2)
OA(22)	0.21 (4)	0	0	6859	11 (6)
OA(32)	0.44 (4)	0	0	590	7 (3)
OA(42)	0.21 (4)	0	0	4326	-1 (1)
OA(52)	0.44 (4)	0	0	1441	5 (3)
OA(62)	0.21 (4)	0	0	5203	1 (1)
OA(72)	0.44 (4)	0	0	8938	2 (2)
OA(82)	0.21 (4)	0	0	5982	5 (2)
OB(11)	0.56 (4)	8667	-8667	-88	2 (2)
OB(21)	0.79 (4)	1333	-1333	6999	11 (6)
OB(31)	0.56 (4)	8667	-8667	773	7 (3)
OB(41)	0.79 (4)	8667	-8667	4551	-1 (1)
OB(51)	0.56 (4)	1333	-1333	1556	5 (3)
OB(61)	0.79 (4)	8667	-8667	5389	1 (1)
OB(71)	0.56 (4)	8667	-8667	9177	2 (2)
OB(81)	0.79 (4)	1333	-1333	6185	5 (2)
OB(12)	0.44 (4)	8667	-8667	189	2 (2)
OB(22)	0.21 (4)	1333	-1333	7209	11 (6)
OB(32)	0.44 (4)	8667	-8667	940	7 (3)
OB(42)	0.21 (4)	8667	-8667	4676	-1 (1)
OB(52)	0.44 (4)	1333	-1333	1790	5 (3)
OB(62)	0.21 (4)	8667	-8667	5553	1 (1)
OB(72)	0.44 (4)	8667	-8667	9288	2 (2)
OB(82)	0.21 (4)	1333	-1333	6332	5 (2)

of each tetrahedron was unambiguously revealed. For further isotropic refinement, including the occupancy parameters of a *U-D* pair of each tetrahedron, the configuration of the tetrahedra was constrained to the shape of a regular tetrahedron with Ge-O 1.77 Å and ∠O-Ge-O 109.5°. For the calculations, we used the least-squares program *LINUS* (Coppens & Hamilton, 1970) and neutral-atom scattering factors with correction for anomalous dispersion taken from *International Tables for X-ray Crystallography* (1974). Unit weights were used.

Table 2. Ca-O bond lengths (\AA)

Ca-O bond				Ca-O bond					
	Symmetry code	Occupancy	Length		Symmetry code	Occupancy	Length		
Ca(1)	OB(21)	i	0.79	2.07 (3)	Ca(5)	OB(42)	viii	0.21	2.34 (3)
	O(8)	ii	1.0	2.31 (5)		OB(52)	xiii	0.44	2.39 (3)
	OB(11)	iii	0.56	2.43 (3)		OB(52)	xiv	0.44	2.39 (3)
	OB(11)	iv	0.56	2.43 (3)		OA(41)	ii	0.79	2.40 (3)
	OA(22)	i	0.21	2.46(3)		O(5)	i	1.0	2.40 (13)
	OA(81)	i	0.79	2.49 (3)		OB(51)	xiii	0.56	2.41 (3)
	OB(12)	iii	0.44	2.50 (3)		OB(51)	xiv	0.56	2.41 (3)
	OB(12)	iv	0.44	2.50 (3)		O(4)	i	1.0	2.43 (12)
	O(1)	ii	1.0	2.52 (14)		OB(61)	viii	0.79	2.62 (3)
	OB(82)	i	0.21	2.56 (3)		OA(62)	ii	0.21	2.62 (3)
	Total		6.0			Total		6.0	
	Average			2.40		Average			2.44
	Ca(2)	OB(12)		0.44		2.00 (3)	Ca(6)	OB(52)	
OB(31)			0.56	2.18 (3)	OB(61)	ix		0.79	2.31 (3)
O(1)		ii	1.0	2.24 (13)	OB(61)	x		0.79	2.31 (3)
OB(22)		v	0.21	2.30 (3)	O(5)	i		1.0	2.38 (11)
OB(22)		vi	0.21	2.30 (3)	OA(72)	i		0.44	2.40 (3)
O(2)		ii	1.0	2.37 (15)	OA(51)			0.56	2.45 (3)
OB(21)		v	0.79	2.42 (3)	OB(62)	ix		0.21	2.49 (3)
OB(21)		vi	0.79	2.42 (3)	OB(62)	x		0.21	2.49 (3)
OA(32)		vii	0.44	2.51 (3)	O(6)			1.0	2.74 (12)
OA(11)		vii	0.56	2.74 (3)	OB(71)	xv		0.56	2.92 (3)
Total			6.0		Total			6.0	
Average				2.36	Average				2.46
Ca(3)		OA(42)	ii	0.21	2.12 (3)	Ca(7)		OB(71)	xvi
	O(2)	ii	1.0	2.20 (11)	OB(71)		xvii	0.56	2.29 (3)
	OB(22)	i	0.21	2.20 (3)	OB(81)		ii	0.79	2.30 (3)
	O(3)	i	1.0	2.31 (5)	OA(61)		ii	0.79	2.32 (3)
	OB(31)	iii	0.56	2.33 (3)	OA(82)		ii	0.21	2.35 (3)
	OB(31)	iv	0.56	2.33 (3)	O(6)		vii	1.0	2.36 (11)
	OB(32)	iii	0.44	2.34 (3)	OB(72)		xvi	0.44	2.39 (3)
	OB(32)	iv	0.44	2.34 (3)	OB(72)		xvii	0.44	2.39 (3)
	OB(41)	viii	0.79	2.45 (3)	O(7)		vii	1.0	2.50 (11)
	OA(21)	i	0.79	2.55 (3)	OB(62)		xviii	0.21	2.83 (3)
	Total		6.0		OB(62)		xix	0.21	2.83 (3)
	Average			2.34	Total			6.21	
					Average				2.39
Ca(4)	OB(51)		0.56	2.18 (3)	Ca(8)	OB(11)	xx	0.56	2.16 (3)
	OB(41)	ix	0.79	2.29 (3)		OB(72)	xv	0.44	2.21 (3)
	OB(41)	x	0.79	2.29 (3)		OB(82)	xxi	0.21	2.31 (3)
	OA(31)		0.56	2.36(3)		OB(82)	xxii	0.21	2.31 (3)
	OB(42)	ix	0.21	2.38 (3)		OA(71)		0.56	2.31 (3)
	OB(42)	x	0.21	2.38 (3)		O(7)		1.0	2.32 (11)
	O(4)	i	1.0	2.42 (11)		OB(81)	vi	0.79	2.34 (3)
	OA(52)		0.44	2.58 (3)		OB(81)	xxii	0.79	2.34 (3)
	OB(32)	xi	0.44	2.86 (3)		O(8)		1.0	2.56 (7)
	OB(32)	xii	0.44	2.86 (3)		OA(12)	xxiii	0.44	2.76 (3)
	O(3)	i	1.0	2.91 (16)		OB(71)	xv	0.56	2.94 (3)
	Total		6.44			Total		6.56	
	Average			2.51		Average			2.42

Symmetry code

None	x, y, z	(i)	$x + \frac{1}{3}, y - \frac{1}{3}, z - \frac{2}{3}$	(ii)	$x + \frac{2}{3}, y - \frac{2}{3}, z - \frac{1}{3}$
(iii)	$-y, x - y - 2, z$	(iv)	$-x + y + 2, -x, z$	(v)	$-y + \frac{1}{3}, x - y - \frac{4}{3}, z - \frac{2}{3}$
(vi)	$-x + y + \frac{4}{3}, -x - \frac{1}{3}, z - \frac{2}{3}$	(vii)	$x + 1, y - 1, z$	(viii)	$x - \frac{1}{3}, y + \frac{1}{3}, z - \frac{1}{3}$
(ix)	$-y - \frac{1}{3}, x - y - \frac{5}{3}, z - \frac{1}{3}$	(x)	$-x + y + \frac{5}{3}, -x + \frac{1}{3}, z - \frac{1}{3}$	(xi)	$-y - 1, x - y - 2, z$
(xii)	$-x + y + 2, -x + 1, z$	(xiii)	$-y, x - y - 1, z$	(xiv)	$-x + y + 1, -x, z$
(xv)	$x - \frac{2}{3}, y + \frac{2}{3}, z - \frac{2}{3}$	(xvi)	$-y + \frac{1}{3}, x - y - \frac{7}{3}, z - \frac{2}{3}$	(xvii)	$-x + y + \frac{7}{3}, -x - \frac{1}{3}, z - \frac{2}{3}$
(xviii)	$-y - \frac{1}{3}, x - y - \frac{4}{3}, z - \frac{1}{3}$	(xix)	$-x + y + \frac{8}{3}, -x + \frac{1}{3}, z - \frac{1}{3}$	(xx)	$x - \frac{2}{3}, y + \frac{2}{3}, z + \frac{1}{3}$
(xxi)	$-y - \frac{1}{3}, x - y - \frac{4}{3}, z - \frac{1}{3}$	(xxii)	$-x + y + \frac{2}{3}, -x + \frac{1}{3}, z - \frac{1}{3}$	(xxiii)	$x + \frac{1}{3}, y - \frac{1}{3}, z + \frac{1}{3}$

Table 3. Splitting distances (\AA) of Ge atoms

Ge(11)-Ge(12)	0.69(5)	Ge(51)-Ge(52)	0.40(5)
Ge(21)-Ge(22)	0.23(11)	Ge(61)-Ge(62)	0.07(11)
Ge(31)-Ge(32)	0.34(10)	Ge(71)-Ge(72)	0.44(7)
Ge(41)-Ge(42)	0.06(8)	Ge(81)-Ge(82)	0.20(13)

occupancies of the pair positions are nearly the same. For the remaining Ge atoms, the separations are in the range 0.06(8) to 0.23(11) \AA and the occupancies of the pair positions of these Ge atoms are significantly different (Table 1).

The above features of the positional splittings of the Ge atoms are well in line with the mode of *U-D* orientational disorder of the Ge tetrahedra. The tetrahedra about the four above-mentioned Ge atoms show nearly perfect *U-D* disorder, while the remaining ones only partial.

such a situation, the pair of positions of the *j*th Ge, namely Ge(*j*), is expressed by Ge(*j*1) and Ge(*j*2) (Table 3). In particular, the separations of Ge(1), Ge(3), Ge(5), Ge(7) are conspicuous, the values being in the range 0.34(10) to 0.69(5) \AA ; in each case the

Table 4. Possible simple polytypes of C_3G and C_3S (only one example is given in each case of the 9- and 24-layer polytypes)

Symbol	Layer sequence	Space group	In each compound the known polytypes are indicated by asterisks.		
			C_3G	C_3S	Compounds having related structures
2H	+-	$P6_3mc$	*[1]	*[2]	(Cd _{0.5} Pb _{0.5}) ₃ SiO ₃ [3] Cd ₃ SiO ₅ [4], Pb ₃ SiO ₅ [5], Ba ₃ SiO ₅ [6], Sr ₃ SiO ₅ [7], Pb ₃ GeO ₅ [8]
3R	+ ₃	$R3m$			
4H	+---+	$P6_3mc$			
5T	+----+	$P3m1$			
6H	+-----+	$P6_3mc$			
6T	+----+	$P3m1$			
9R	+--+ ₃	$R3m$	*[9]	*[10]	
24R	+-----+ ₃	$R3m$	*[15]		

References: [1] Nishi & Takéuchi (1984a), [2] Pérez-Méndez *et al.* (1984), [3] Eysel & Breuer (1983), [4] Eysel (1970), [5] Ott & MacLaren (1970), [6] Tillmanns & Grosse (1978), [7] Dent Glasser & Glasser (1965), [8] Otto (1979), [9] Nishi & Takéuchi (1985), [10] Nishi & Takéuchi (1984b), [11] Takéuchi *et al.* (1984), [12] Golovastikov *et al.* (1975), [13] Bigaré *et al.* (1967), [14] Eysel & Hahn (1970), [15] this work.

Other polytypes

The polytypes of C_3G , C_3S and M_3S ($M = \text{Cd, Pb, Ba, Sr}$) which are known to date are 2-layer, 3-layer, 9-layer and 24-layer structures. In addition to these known polytypes, we may now theoretically derive, using relation (2), the possible series of polytypes of these chemical phases. Some simple cases are summarized in Table 4. Among them, the structures of 4-, 5-, and 6-layer polytypes are illustrated in Fig. 5.

Finally, it is notable that a layer similar to our unit layer has been found in a new mineral, arctite (Egorov-Tismenko, Sokolova & Smirnova, 1984). Although the layer consists of Ca, P and O, it shares

geometrical features with the present unit layer. It hence appears that such a layer configuration is common among silicates, germanates and phosphates having large cations such as Ca^{2+} .

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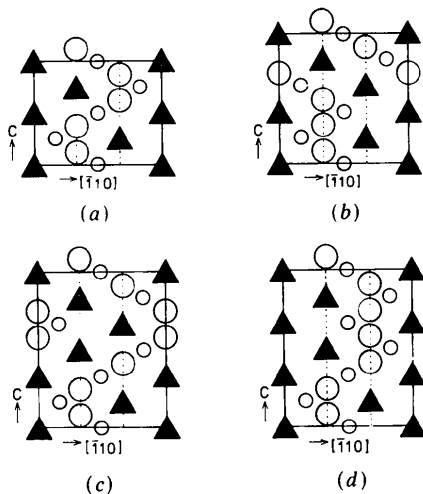


Fig. 5. Predicted structures of some simple polytypes. (a) 4H, (b) 5T, (c) 6H [the origin is shifted by $\frac{1}{3}(a_2 - a_1)$ from the true origin] and (d) 6T. The structures are represented as those in Fig. 3.