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Strontium Tetragermanate, $SrGe_4O_9$

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Abstract

The structure of tetragermanium strontium nonaoxide, $SrGe_4O_9$, comprises two different types of sheet structure stacked alternately along the *c* axis. One sheet comprises GeO_6 octahedra and SrO_8 polyhedra while the other sheet contains three-membered rings of GeO_4 tetrahedra. In addition, this crystal structure shows a basic unit of the superstructures which are found for $PbGe_4O_9$.

Comment

Three tetragermanates of formula $MeGe_4O_9$ (*Me* = Sr, Pb, Ba) were studied by Robbins & Levin (1961). They showed that these compounds were isostructural on the basis of indexed powder X-ray diffraction patterns. In addition, they discussed a structural relationship with the mineral benitoite, $BaTiSi_3O_9$, the structure of which had been determined by Zachariasen (1930) and was later refined by Fischer (1969). Eulenberger, Wittmann & Nowotny (1962) synthesized two forms of $CaGe_4O_9$ (α and β types) and suggested that the α form was isostructural with the compounds studied by Robbins & Levin (1961).

Robbins, Perloff & Block (1966) determined the crystal structure of $BaGe_4O_9$ by single-crystal X-ray diffraction: $a = 11.61$, $c = 4.74$ Å, *P*3, *Z* = 3, final *R* value 6.8% for 327 reflections. Smolin (1969) also studied the structure of the same compound. He reported unit-cell parameters that were consistent with those given by Robbins *et al.* (1966) but gave the space group as *P*321 with a final *R* value of 5.8% for 848 reflections.

Venevtsev *et al.* (1982) studied the structure and physical properties of the four polymorphs (α, β_1, β_2, γ) of $PbGe_4O_9$ and the solid solutions $(Pb_{1-x}M_x)Ge_4O_9$ (*M* = Sr, Ba). Both α- and γ-$PbGe_4O_9$ showed ferroelectric properties, while γ-$PbGe_4O_9$ also displayed ferroelastic properties. We have attempted to solve the crystal structure of $SrGe_4O_9$, which seems to be analogous to $BaGe_4O_9$, and to confirm which space group, *P*3 or *P*321, is correct.

As a result of the structure analysis, the space group of $SrGe_4O_9$ is *P*321, as reported by Smolin (1969) for $BaGe_4O_9$. The crystal structure of $SrGe_4O_9$ has two different types of sheet structure within it. One is formed by a combination of GeO_6 octahedra and SrO_8 polyhedra (Fig. 1) and the other by three-membered rings of GeO_4 tetrahedra (Fig. 2). The sheets are stacked alternately along the *c* axis (Fig. 3).

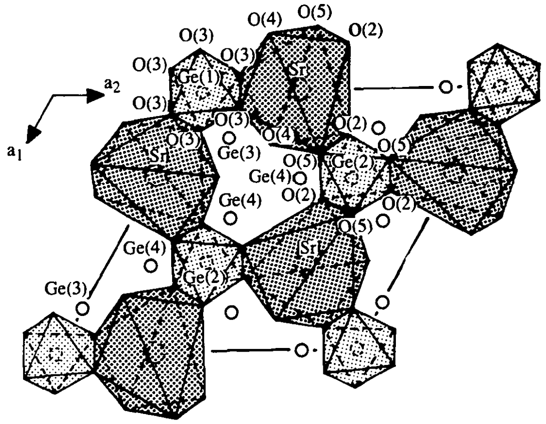

Fig. 1. The arrangement of the GeO_6 octahedra and the SrO_8 polyhedra viewed down the *c* axis.

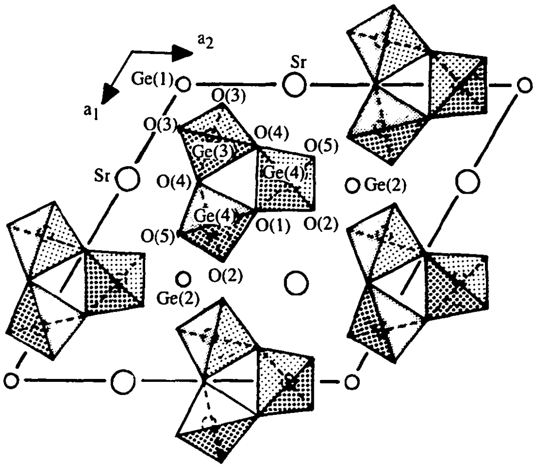

Fig. 2. The arrangement of the three-membered rings of GeO_4 tetrahedra viewed down the *c* axis.

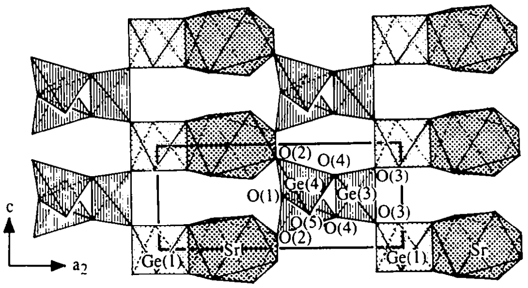

Fig. 3. The arrangement of the polyhedra about the cation sites with $|x| \leq 0.15$ projected on (100). Heavy lines indicate the unit cell.

The polymorphs of $PbGe_4O_9$ found by Venevtsev *et al.* (1982) are superstructures with different *c* periods. The lengths of their *c* axes are 4.75 (α phase), 9.49 (β_1 phase) and 19.09 Å (β_2 phase), suggesting that the α, β_1 and β_2 phases comprise a single unit, double units and four units of the basic structure, respectively. In conclusion, the structures of $SrGe_4O_9$ (c = 4.75 Å) and $BaGe_4O_9$ (c = 4.74 Å) are formed from the basic unit, and the structure of the mineral benitoite ($BaTiSi_3O_9$: c = 9.76 Å) is a superstructure with double units.

Experimental

Single crystals of strontium tetragermanate were synthesized from a stoichiometric mixture of $SrCl_2$ and GeO_2 at 1570 K. Electron microprobe analyses of the crystals showed that they had the chemical formula $SrGe_4O_9$.

Crystal data

$SrGe_4O_9$	Mo $K\alpha$ radiation
M_r = 521.98	λ = 0.71073 Å
Trigonal	Cell parameters from 24 reflections
$P321$	θ = 19.8–35.8°
a = 11.344 (2) Å	μ = 25.9 mm^{-1}
c = 4.750 (2) Å	T = 293 K
V = 529.4 (3) $Å^3$	Sphere
Z = 3	0.14 mm (radius)
D_x = 4.91 Mg m^{-3}	Colourless
D_m not measured	

Data collection

Rigaku AFC-5 diffractometer	R_{int} = 0.025
$\omega/2\theta$ scans	θ_{max} = 40.0°
Absorption correction: spherical	$h = 0 \rightarrow 17$
T_{min} = 0.0113, T_{max} = 0.0147	$k = 0 \rightarrow 17$
1452 measured reflections	$l = 0 \rightarrow 8$
1343 independent reflections	3 standard reflections monitored every 150 reflections
929 observed reflections [$I > 3\sigma(I)$]	intensity decay: 0.5%

Refinement

Refinement on F	Extinction correction: secondary isotropic
R = 0.049	Extinction coefficient: 4.40×10^{-5}
wR = 0.052	Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)
S = 1.35	
929 reflections	
73 parameters	
Unit weights applied	
$(\Delta/\sigma)_{max}$ = 0.05	
$\Delta\rho_{max}$ = 0.45 e $Å^{-3}$	
$\Delta\rho_{min}$ = −0.38 e $Å^{-3}$	

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters ($Å^2$)*

$$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Sr	0.3280 (1)	0	0	1.40 (2)
Ge(1)	0	0	0	0.63 (3)
Ge(2)	1/3	2/3	0.1076 (4)	0.62 (3)
Ge(3)	0.8209 (1)	0	1/2	0.68 (4)
Ge(4)	0.4908 (1)	0.3410 (1)	0.3990 (2)	0.64 (3)
O(1)	0.5112 (9)	0	1/2	1.29 (8)
O(2)	0.6022 (8)	0.4222 (8)	0.1245 (14)	0.95 (7)
O(3)	0.1546 (7)	0.0616 (8)	0.7636 (13)	0.76 (7)
O(4)	0.3255 (8)	0.2145 (8)	0.2949 (16)	0.94 (8)
O(5)	0.5102 (7)	0.2496 (8)	0.6722 (13)	0.79 (7)

Table 2. *Selected geometric parameters (Å, °)*

Sr—O(2^{i})	2.601 (7)	Ge(2)—O(5^{viii})	1.860 (7)
Sr—O(2^{ii})	2.601 (7)	Ge(2)—O(5^{x})	1.860 (7)
Sr—O(3^{iii})	2.644 (9)	Ge(2)—O(5^{xi})	1.860 (7)
Sr—O(3^{iv})	2.644 (9)	Ge(2)—O(2^{xii})	1.872 (9)
Sr—O(4)	2.820 (9)	Ge(2)—O(2^{xiii})	1.872 (9)
Sr—O(4^{v})	2.820 (9)	Ge(2)—O(2^{xiv})	1.872 (9)
Sr—O(5^{iii})	2.977 (8)	Ge(3)—O(3^{i})	1.747 (6)
Sr—O(5^{iv})	2.977 (8)	Ge(3)—O(3^{xv})	1.747 (6)
Ge(1)—O(3^{iii})	1.897 (7)	Ge(3)—O(4^{i})	1.789 (7)
Ge(1)—O(3^{iv})	1.897 (7)	Ge(3)—O(4^{xv})	1.789 (7)
Ge(1)—O(3^{vi})	1.897 (7)	Ge(4)—O(2)	1.726 (7)
Ge(1)—O(3^{vii})	1.897 (7)	Ge(4)—O(5)	1.743 (8)
Ge(1)—O(3^{viii})	1.897 (7)	Ge(4)—O(1^{xvi})	1.755 (12)
Ge(1)—O(3^{ix})	1.897 (7)	Ge(4)—O(4)	1.769 (7)
Ge(4^{i})—O(1)—Ge(4^{xv})	123.8 (5)	Ge(3^{xvi})—O(4)—Ge(4)	121.2 (4)

Symmetry codes: (i) $1-y, x-y, z$; (ii) $1-x, y-x, -z$; (iii) $x, y, z-1$; (iv) $x-y, -y, 1-z$; (v) $x-y, -y, -z$; (vi) $-y, x-y, z-1$; (vii) $y-x, -x, z-1$; (viii) $y, x, 1-z$; (ix) $-x, y-x, 1-z$; (x) $1-x, 1+y-x, 1-z$; (xi) $x-y, 1-y, 1-z$; (xii) $y, x, -z$; (xiii) $1-x, 1+y-x, -z$; (xiv) $x-y, 1-y, -z$; (xv) $1-x, y-x, 1-z$; (xvi) $1+y-x, 1-x, z$.

The intensities of the reflections were measured at the X-ray laboratory of Nihon University, Japan.

Data collection, cell refinement and data reduction: *AFC/MSC Diffractometer Control Program* (Rigaku Corporation, 1991). Program used to solve and refine structure: *LINUS* (Coppens & Hamilton, 1970).

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: OH1096). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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