Crystal structure of SrGeO₃ in the high-pressure perovskite-type phase

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Single crystals of the SrGeO₃ (strontium germanium trioxide) high-pressure phase have been synthesized successfully at 6 GPa and 1223 K. The compound crystallizes with the ideal cubic perovskite-type structure (space group $Pm\overline{3}m$), which consists of a network of corner-linked regular GeO₆ octahedra (point-group symmetry $m\overline{3}m$), with the larger Sr atoms located at the centers of cavities in the form of SrO₁₂ cuboctahedra (point-group symmetry $m\overline{3}m$) in the network. The degrees of covalencies included in the Sr—O and the Ge—O bonds calculated from bond valences are 20.4 and 48.9%, respectively. Thus, the Ge—O bond of the GeO₆ octahedron in the SrGeO₃ perovskite has a strong covalency, comparable to those of the Si—O bonds of the SiO₄ tetrahedra in silicates with about 50% covalency. The thermal vibrations of the O atoms in the title compound are remarkably suppressed in the directions of the Ge—O bonds. This anisotropy ranks among the largest observed in stoichiometric cubic perovskites.

1. Chemical context

The phase transitions of the perovskite-type compounds ABO_3 have long attracted much attention for various industrial applications, as represented in ferroelectric substances such as BaTiO₃. The strontium germanate SrGeO₃ undergoes a sequence of phase transitions at high pressures and high temperatures of pyroxenoid (pseudowollastonite) type → walstromite type → perovskite type (Shimizu *et al.*, 1970; Akaogi *et al.*, 2005). In a recent study (Mizoguchi *et al.*, 2011), it was reported that the high-pressure perovskite-type phase of SrGeO₃ is a promising transparent electronic conductor. A detailed structural study of this perovskite-type phase is important to elucidate the origin of the conduction mechanism. Despite such importance, the high-pressure perovskite-type phase has been studied so far only on the basis of polycrystalline samples and its powder X-ray diffraction pattern has only suggested that it adopts the ideal cubic perovskite structure. Perovskite-type compounds are well-known to have various symmetries owing to a slight tilting of the BO_6 octahedra (Glazer, 1972, 1975). However, it is often difficult to determine their actual symmetries from powder X-ray diffraction techniques. Thus, more precise data based on single crystal X-ray diffraction are indispensable for the determination of the crystal structure of the SrGeO₃ high-pressure perovskite-type phase. We recently succeeded in the growth of SrGeO₃ perovskite-type single crystals at high pressure and high temperature. The crystal structure refined from single-crystal X-ray diffraction data is reported here.

ZrO₂ End Plug — Boron Epoxy Resin
BN Capsule — Sample
Mo Electrode — LaCrO₃ Heater
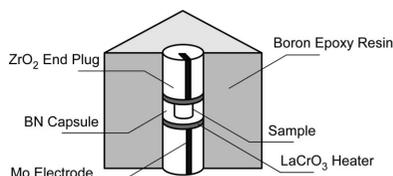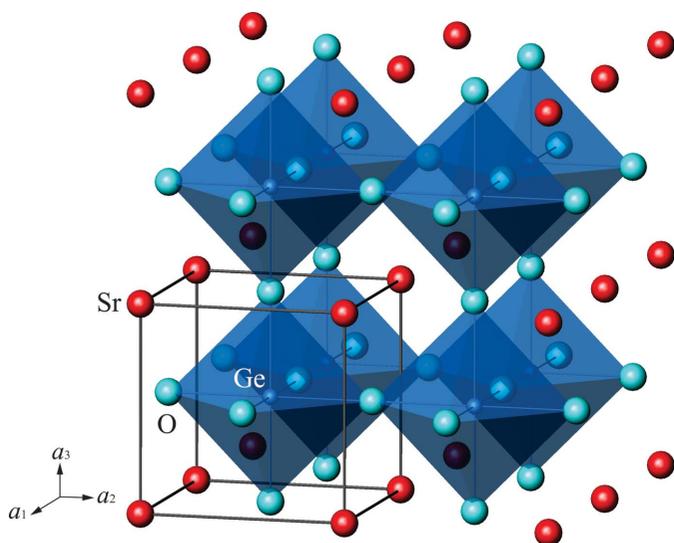
Figure 1
Representation of the SrGeO$_3$ perovskite-type structure showing corner-linked GeO$_6$ octahedra.

Figure 2
The unit cell of the cubic SrGeO$_3$ perovskite with displacement ellipsoids drawn at the 80% probability level.

2. Structural commentary

The high-pressure phase of SrGeO$_3$ crystallizes with the cubic perovskite-type structure (space group $Pm\bar{3}m$). The crystal structure consists of a network of corner-linked regular GeO$_6$ octahedra with the larger Sr atoms located at the centers of cavities in the network, forming SrO$_{12}$ cuboctahedra (Fig. 1). As a result of the ideal symmetry, tilts and distortions of the GeO$_6$ octahedra are not present. The Sr, Ge and O atoms occupy Wyckoff positions 1a (0, 0, 0), 1b (0.5, 0.5, 0.5) and 3c (0, 0.5, 0.5), respectively, without any freedom of atomic positions. The corresponding site symmetries are $m\bar{3}m$, $m\bar{3}m$ and 4/$mm.m$, respectively. The observed Sr—O distance in the SrO$_{12}$ cuboctahedron and the Ge—O distance in the GeO$_6$ octahedron are 2.6855 (1) Å and 1.8989 (1) Å, respectively, which are much shorter than the distances expected from the effective ionic radii (Sr—O = 2.84 Å, Ge—O = 1.93 Å; Shannon, 1976). The ratios of covalency included in the bonds calculated from f'_c/s (= as^{M-1}) are 20.4% for the Sr—O bond and 48.9% for the Ge—O bond, where f'_c, given by as^M (Brown & Shannon, 1973), is the covalence in bonds; s is the bond valence; a and M are parameters relating covalence to bond valence. This value of the present Ge—O bond ranks among the largest in B—O bonds of BO_6 octahedra in $A^{2+}B^{4+}O_3$-type cubic perovskites (A = twelvefold-coordinated cations, B = sixfold-coordinated cations) [cf. 39.8% for the Ti—O bond in SrTiO$_3$ (Abramov et al., 1995) and 37.8% for the Zr—O bond in BaZrO$_3$ (Levin et al., 2003)]. It is noteworthy, thus, that the Ge—O bond of the GeO$_6$ octahedron in the present crystal has a strong covalency comparable to those of the Si—O bonds of the SiO$_4$ tetrahedra in silicates with about 50% covalency.

The site-symmetry constraints require that the displacement ellipsoids of the Sr and Ge atoms are always spherical and that of the O atom is an uniaxial ellipsoid with one determinable ellipsoid-axis in the direction of the Ge—O bond and two undeterminable ones in the directions perpendicular to it. The mean-square displacement (MSD) of the O atom is the smallest [$\langle u_S^2 \rangle$ = 0.0011 (8) Å^2] in the former direction and the largest [$\langle u_L^2 \rangle$ = 0.0077 (7) Å^2] in the latter directions. The $\langle u_S^2 \rangle / \langle u_L^2 \rangle$ ratio of 0.14 calculated for the present crystal indicates that the displacement ellipsoid of the O atom is remarkably compressed in the former directions, as shown in Fig. 2. Such remarkable anisotropy is commonly observed in cubic perovskites with stoichiometric compositions, and the present $\langle u_S^2 \rangle / \langle u_L^2 \rangle$ ratio ranks among the smallest observed [cf. $\langle u_S^2 \rangle / \langle u_L^2 \rangle$ = 0.14 for LaAlO$_3$ (Nakatsuka et al., 2005), 0.43 for SrTiO$_3$ (Abramov et al., 1995), 0.38 for KTaO$_3$ (Zhurova et al., 2000), 0.50 for SrFeO$_3$ (Hodges et al., 2000) and 0.29 for BaZrO$_3$ (Levin et al., 2003)]. The remarkable anisotropy of the MSD of the O atom in the SrGeO$_3$ perovskite-type structure might be related to the strong covalency of the Ge—O bond.
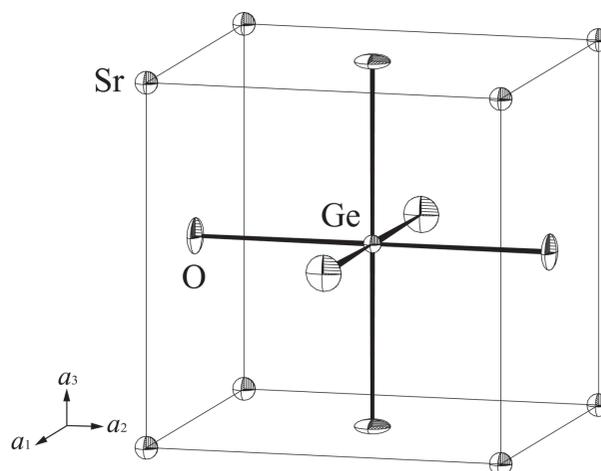
3. Synthesis and crystallization

A polycrystalline sample of SrGeO$_3$ pseudowollastonite as the starting material was prepared by solid-state reaction of
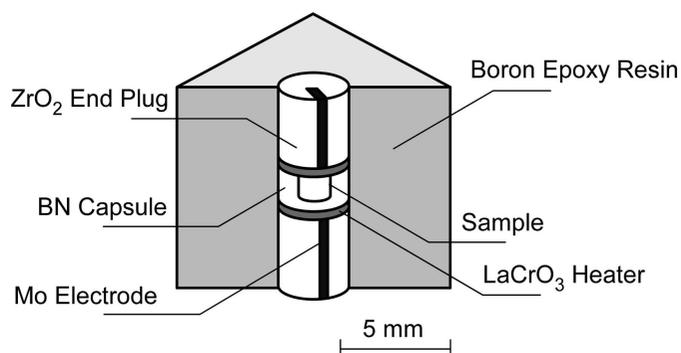
Figure 3
Cell assembly used in the synthetic experiment at high pressure.

Table 1
Experimental details.

Crystal data	
Chemical formula	$SrGeO_3$
M_r	208.23
Crystal system, space group	Cubic, $Pm\bar{3}m$
Temperature (K)	296
a (Å)	3.7978 (2)
V (Å^3)	54.78 (1)
Z	1
Radiation type	Mo $K\alpha$
μ (mm^{-1})	37.73
Crystal size (mm)	$0.10 \times 0.08 \times 0.08$
Data collection	
Diffractometer	Rigaku AFC-7R
Absorption correction	ψ scan (North *et al.*, 1968)
T_{min}, T_{max}	0.037, 0.049
No. of measured, independent and observed [$F > 3\sigma(F)$] reflections	521, 116, 66
R_{int}	0.023
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	1.219
Refinement	
$R[F > 3\sigma(F)]$, $wR(F)$, S	0.011, 0.010, 1.95
No. of reflections	64
No. of parameters	6
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.04, -1.38

Computer programs: *WinAFC* (Rigaku, 1999), *RADY* (Sasaki, 1987), *ATOMS for Windows* (Dowty, 2000) and *publCIF* (Westrip, 2010).

special grade reagents $SrCO_3$ and GeO_2. The resulting $SrGeO_3$ pseudowollastonite material was charged in a gold capsule and then put into a BN sample chamber. As shown in Fig. 3, the sample chamber was put between a pair of $LaCrO_3$ disc heaters and encased in a cubic-shaped pressure-transmitting medium made of boron-epoxy resin. This cell assembly was compressed with a 700 ton cubic anvil-type press. After being kept at 6 GPa and 1223 K for 1 h, the product was quenched by shutting off the electric power supply. The pressure was then released slowly and the product was recovered at ambient conditions. Single crystals of $SrGeO_3$ perovskite were found in the recovered sample, together with an unknown single-crystal phase.

4. Refinement

The unit-cell parameters of the crystal under investigation assuming a triclinic cell only exhibit a minute deviation from a cubic unit cell [$a = 3.7979$ (2), $b = 3.7978$ (3), $c = 3.7972$ (3) Å, $\alpha = 89.984$ (6), $\beta = 89.997$ (6), $\gamma = 89.988$ (5)°]. Systematic absences of reflections also agreed with space group $Pm\bar{3}m$. Indeed, the present crystal was satisfactorily refined in the ideal cubic perovskite structure as judged from the excellent reliability indices (Table 1).

Intensity data were averaged in Laue symmetry $m\bar{3}m$ to give 116 independent reflections. Of these, independent

reflections with $F_o \leq 3\sigma(F_o)$ were omitted for refinement. Even if independent reflections had intensities of $F_o > 3\sigma(F_o)$ after averaging, those averaged from a data set of equivalent reflections including reflection(s) with $F_o \leq 3\sigma(F_o)$ were also discarded since these reflections were potentially affected by multiple diffraction. Moreover, independent reflections with $(\sin\theta)/\lambda < 0.220$ Å^{-1} were eliminated to reduce secondary extinction effects and to avoid dependence on atomic charge as far as possible in the choice of atomic scattering factors. Finally, 64 independent reflections were used in the present refinement. Several correction models for the secondary extinction effects were attempted during the refinement, and the isotropic correction of Type I (Becker & Coppens, 1974*a*,*b*) with a Gaussian mosaic spread distribution model yielded the best fits. Crystal data, data collection and structure refinement details are summarized in Table 1.

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Computing details

Data collection: *WinAFC* (Rigaku, 1999); cell refinement: *WinAFC* (Rigaku, 1999); data reduction: *RADY* (Sasaki, 1987); program(s) used to refine structure: *RADY* (Sasaki, 1987); molecular graphics: *ATOMS for Windows* (Dowty, 2000); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Strontium germanium trioxide

Crystal data

$SrGeO_3$	$D_x = 6.315$ Mg m^{-3}
$M_r = 208.23$	Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å
Cubic, $Pm\bar{3}m$	Cell parameters from 25 reflections
Hall symbol: -P 4 2 3	$\theta = 21.5–25.0°$
$a = 3.7978$ (2) Å	$\mu = 37.73$ mm^{-1}
$V = 54.78$ (1) Å^3	$T = 296$ K
$Z = 1$	Fragment, colorless
$F(000) = 94$	$0.10 \times 0.08 \times 0.08$ mm

Data collection

Rigaku AFC-7R diffractometer	66 reflections with $F > 3.0\sigma(F)$
$\omega–2\theta$ scans	$R_{int} = 0.023$
Absorption correction: ψ scan (North *et al.*, 1968)	$\theta_{max} = 60.0°$
	$h = 0 \rightarrow 9$
$T_{min} = 0.037$, $T_{max} = 0.049$	$k = 0 \rightarrow 9$
521 measured reflections	$l = 0 \rightarrow 9$
116 independent reflections	3 standard reflections every 150 reflections
	intensity decay: none

Refinement

Refinement on F	Weighting scheme based on measured s.u.'s $w = 1/\sigma^2(F)$
$R[F^2 > 2\sigma(F^2)] = 0.019$	
$wR(F^2) = 0.020$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.95$	$\Delta\rho_{max} = 1.04$ e Å^{-3}
64 reflections	$\Delta\rho_{min} = -1.38$ e Å^{-3}
6 parameters	Extinction correction: isotropic Type I (Becker & Coppens, 1974*a*,*b*)
	Extinction coefficient: 0.40 (1)E3

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	y	z	U_{iso}*/U_{eq}
Sr	0.0000	0.0000	0.0000	0.00300 (9)

Ge	0.5000	0.5000	0.5000	0.00182 (9)
O	0.0000	0.5000	0.5000	0.0055 (7)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Sr	0.0030 (2)	0.0030	0.0030	0.0000	0.0000	0.0000
Ge	0.0018 (2)	0.0018	0.0018	0.0000	0.0000	0.0000
O	0.0011 (8)	0.0077 (7)	0.0077	0.0000	0.0000	0.0000

Geometric parameters (Å, º)

Sr—O	2.6855 (1)	Ge—O^{i}	1.8989 (1)
Sr—O^{i}	2.6855 (1)	Ge—O^{ii}	1.8989 (1)
Sr—O^{ii}	2.6855 (1)	Ge—O^{xii}	1.8989 (1)
Sr—O^{iii}	2.6855 (1)	Ge—O^{xiii}	1.8989 (1)
Sr—O^{iv}	2.6855 (1)	Ge—O^{xiv}	1.8989 (1)
Sr—O^{v}	2.6855 (1)	O—O^{i}	2.6855 (1)
Sr—O^{vi}	2.6855 (1)	O—O^{ii}	2.6855 (1)
Sr—O^{vii}	2.6855 (1)	O—O^{v}	2.6855 (1)
Sr—O^{viii}	2.6855 (1)	O—O^{vi}	2.6855 (1)
Sr—O^{ix}	2.6855 (1)	O—O^{xv}	2.6855 (1)
Sr—O^{x}	2.6855 (1)	O—O^{xvi}	2.6855 (1)
Sr—O^{xi}	2.6855 (1)	O—O^{xii}	2.6855 (1)
Ge—O	1.8989 (1)	O—O^{xiii}	2.6855 (1)
O—Sr—O^{i}	60.00	Sr—O—O^{vi}	60.00
O—Sr—O^{ii}	60.00	Sr—O—O^{xv}	120.00
O—Sr—O^{iii}	120.00	Sr—O—O^{xvi}	120.00
O—Sr—O^{iv}	120.00	Sr—O—O^{xii}	120.00
O—Sr—O^{v}	60.00	Sr—O—O^{xiii}	120.00
O—Sr—O^{vi}	60.00	Ge—O—Ge^{xx}	180.00
O—Sr—O^{vii}	180.00	Ge—O—O^{i}	45.00
O—Sr—O^{viii}	90.00	Ge—O—O^{ii}	45.00
O—Sr—O^{ix}	120.00	Ge—O—O^{v}	135.00
O—Sr—O^{x}	90.00	Ge—O—O^{vi}	135.00
O—Sr—O^{xi}	120.00	Ge—O—O^{xv}	135.00
O—Sr^{i}—O^{ii}	60.00	Ge—O—O^{xvi}	135.00
O—Sr^{i}—O^{iii}	120.00	Ge—O—O^{xii}	45.00
O—Sr^{ii}—O^{iv}	120.00	Ge—O—O^{xiii}	45.00
O—Ge—O^{i}	90.00	Ge—O^{xx}—O^{v}	45.00
O—Ge—O^{ii}	90.00	Ge—O^{xx}—O^{vi}	45.00
O—Ge—O^{xii}	90.00	Ge—O^{xx}—O^{xv}	45.00
O—Ge—O^{xiii}	90.00	Ge—O^{xx}—O^{xvi}	45.00
O—Ge—O^{xiv}	180.00	O—O^{i}—O^{ii}	60.00
O—Ge^{i}—O^{ii}	90.00	O—O^{i}—O^{xvi}	180.00
O—Ge^{i}—O^{xii}	90.00	O—O^{i}—O^{xii}	60.00
O—Ge^{ii}—O^{xiii}	90.00	O—O^{ii}—O^{xv}	180.00

Sr—O—Sr^{xvii}	90.00	O—O^{ii}—O^{xiii}	60.00
Sr—O—Sr^{xviii}	90.00	O—O^{v}—O^{vi}	60.00
Sr—O—Sr^{xix}	180.00	O—O^{v}—O^{xv}	60.00
Sr—O—Ge	90.00	O—O^{v}—O^{xiii}	180.00
Sr—O—Ge^{xx}	90.00	O—O^{vi}—O^{xvi}	60.00
Sr—O—O^{i}	60.00	O—O^{vi}—O^{xii}	180.00
Sr—O—O^{ii}	60.00	O—O^{xv}—O^{xvi}	60.00
Sr—O—O^{v}	60.00	O—O^{xii}—O^{xiii}	60.00

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