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Crystal growth, structure, and physical properties of $Bi_2Ge_3O_9$

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Abstract. Single crystals of $Bi_2Ge_3O_9$ of optical quality with dimensions of approximately $15 \times 15 \times 50$ mm^3 have been grown by the Czochralski technique from a stoichiometric melt. The space group is $P\ 6_3/m$, $Z = 2$, $a_1 = 0.7006$ nm, $a_3 = 0.9786$ nm. The structure ($R = 0.052$) is closely related to that of benitoite. Trigermanate rings are located in planes perpendicular to the six-fold axis. The elastic and thermoelastic constants, the indices of refraction, and the coefficients of thermal expansion have been measured. The elastic properties reveal strong covalent bonds which are assigned to the trigermanate rings. Thermal expansion parallel to the six-fold axis is extremely small. The crystals are potentially feasible for X-ray spectrometer applications and photoacoustic deflector devices.

Crystal Growth

The phase diagram of the system $Bi_2O_3 - GeO_2$ as published by Speranskaya and Arshakuni (1964) shows two compounds with a $Bi_2O_3 : GeO_2$ mole ratio of 2 : 3 and 7 : 1, respectively. Levin and Roth (1964) studied the effect of small oxide additions on the polymorphism of Bi_2O_3. On the Bi_2O_3 side they found a stable compound containing 6 moles Bi_2O_3 and 1 mole GeO_2. Ballman (1967) has grown large single crystals of the composition $Bi_{12}GeO_{20}$. These crystals possess a body-centered cubic lattice with point group 23. They are pale yellow, strongly piezoelectric, and exhibit photoconductivity. Single crystals of another compound, $Bi_4Ge_3O_{12}$, have been grown by Nitsche (1965). These crystals, belonging to point group $\bar{4}3m$, are colorless. They scintillate at room temperature under X-ray and alpha-particle excitation.

Our own investigations concerning compounds of the GeO_2-rich side of the phase diagram have revealed the existence of a new compound with a mole ratio of $Bi_2O_3 : GeO_2 = 1 : 3$ (Grabmaier, 1977). Single crystals of this new compound were grown from the melt by the conventional Czochralski method. The experiments were carried out in a platinum crucible ($\varnothing = 40$ mm, wall thickness = 2 mm) provided with a ceramic heat insulation. The crucible temperature was kept constant within 0.2 K. Starting materials were high purity bismuth-trioxide (99.995 %) and high purity germanium-dioxide (99.999 %). The melts were prepared by melting the oxides directly within the crucible, the mole ratio being $Bi_2O_3 : GeO_2 = 1 : 3$.

Single crystals obtained by spontaneous nucleation on a platinum wire served as seeds from which crystals of smaller diameter were subsequently pulled. The growth of the desired single crystal required several necking-in procedures. The crystals were grown in an atmosphere of either oxygen or air to prevent reduction of the molten oxides. Pyrometer readings of the melt indicated a temperature of about 1263 K – 1273 K during growth. Chemical analysis confirmed that the crystals are of the same composition as the melt. Single crystals of $Bi_2Ge_3O_9$ were grown as large as 50 mm in length and 15 mm in diameter. A rotational speed of 100 rpm and a pulling rate of about 5 mm per hour resulted in crystals free of inclusions. All crystals grown under these conditions were colorless and of optical quality. At higher pulling rates typical microscopic inclusions of platinum (crucible) in the form of small triangular or hexagonal sheets scattered throughout the crystal as well as gas bubbles were observed. A photograph of two crystals as grown is shown in Figure 1.

Structure

Transmission Laue photographs revealed the point group to be 6 or 6/m. Since even with highly sensitive methods no optical rotatory power and no piezoelectric, pyroelectric or nonlinear optical (second harmonic generation) effects could be observed, we assumed the existence of a center of inversion and therefore 6/m to be the correct point symmetry. In oscillation, Weissenberg, and precession photographs only one type of extinction was detected: reflexions ($00h_3$) for h_3 odd. The only space group compatible with 6/m and these extinctions is $P\,6_3/m$. The lattice constants $a_1 = 0.7006$ nm and $a_3 = 0.9786$ nm at 293 K were derived from Bragg reflexions employing large single crystals. The measured density $\varrho = 6.262\,g \cdot cm^{-3}$ yields two formula units per unit cell.

The intensities of 1065 reflexions ($4° \leq \vartheta \leq 45°$) were measured on a CAD 4 4-circle diffractometer (Enraf-Nonius) using a crystal of dimensions

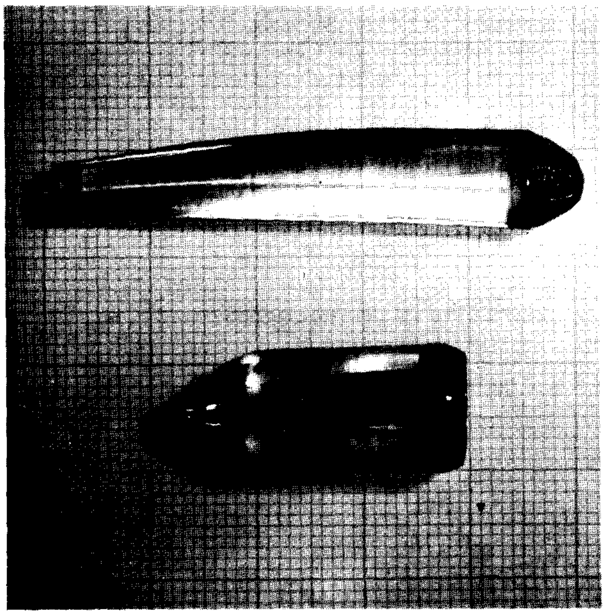

Fig. 1. Crystals of $Bi_2Ge_3O_9$ as grown

0.06 mm × 0.10 mm × 0.11 mm in a position of minimum absorption and employing Mo*Kα* radiation. Of these reflections 437 were considered as unobserved ($I \leq 2\sigma\,[I]$). No further correction for absorption was made. The crystal structure was determined by Patterson and Fourier methods employing the X-ray 72 system of programs (Stewart et al., 1972). After a least squares refinement of the atomic positions, introducing anisotropic thermal parameters for Ge and Bi and isotropic ones for O as well as a parameter for secondary extinction (Larson, 1967), we obtained a final value for $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ of 0.052. The atomic scattering factors of the neutral atoms were used in these calculations (Cromer and Mann, 1968). The results are given in Table 1.

The structure of $Bi_2Ge_3O_9$ (Fig. 2) is closely related to that of benitoite (space group $P\bar{6}c2$). The benitoite type structure of $BaSnGe_3O_9$ (Choisnet et al., 1972) is given in Figure 3 for comparison. The unit cell as chosen by Choisnet et al. has been rotated by 60° and shifted by a translation of $[00\frac{1}{2}]$. The trigermanate rings with Ge at $z = \frac{1}{4}$ occupy almost the same positions in both structures. The other rings with Ge at $z = \frac{3}{4}$, however, are rotated by approximately 34° about the six-fold axis in benitoite, and by 60° in $Bi_2Ge_3O_9$ as a result of the different space group symmetry. This is the most significant difference between the two structures. In $BaSnGe_3O_9$ the Ba and Sn atoms are octahedrally surrounded by six O atoms of almost equal

Table 1. Positional and thermal parameters[a] ($\times 10^2$) for $Bi_2Ge_3O_9$

Site		x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
Bi	4f	$\frac{1}{3}$	$\frac{2}{3}$	0.02645(9)	0.97(2)	0.97(2)	1.16(3)	0.48(2)	0	0
Ge	6h	0.2917(3)	0.0778(3)	$\frac{1}{4}$	0.38(6)	0.51(6)	1.04(6)	0.25(5)	0	0
O(1)	6h	0.197(2)	0.267(2)	$\frac{1}{4}$	0.9(2)	0.9(2)	0.9(2)	0.45(1)	0	0
O(2)	12i	0.431(2)	0.082(2)	0.105(1)	1.7(2)	1.7(2)	1.7(2)	0.85(1)	0	0

Bond lengths [nm]

Bi–O(2) 3 × 0.2141(11), 3 × 0.2743(13); Ge–O(1) 1 × 0.1753(18), 1 × 0.1770(10); Ge–O(2) 2 × 0.1714(13)

[a] The temperature factor T is of the form $T = \exp\left\{-2\pi^2\left(\sum_{i,j} U_{ij} h_i h_j a_i^* a_j^*\right)\right\}$

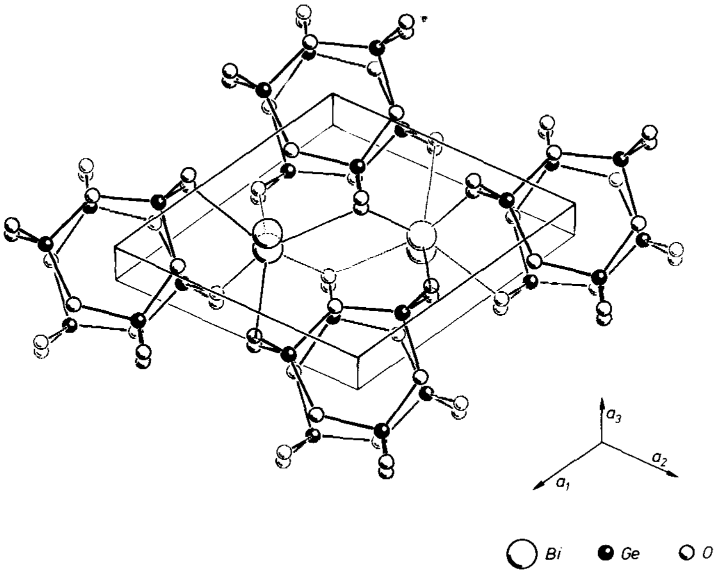

Fig. 2. Structure of $Bi_2Ge_3O_9$. Shaded: atoms with $0 \leq z < \frac{1}{2}$, filled: atoms with $\frac{1}{2} \leq z \leq 1$

distances of 0.2858 nm and 0.1972 nm respectively. The bismuth atoms in $Bi_2Ge_3O_9$, however, possess two groups of three oxygen neighbors with different distances of 0.2743 nm and 0.2141 nm respectively. In addition the bismuth atoms are shifted slightly towards the three more distant oxygen atoms compared with the positions of barium and tin atoms in $BaSnGe_3O_9$ (Fig. 4).

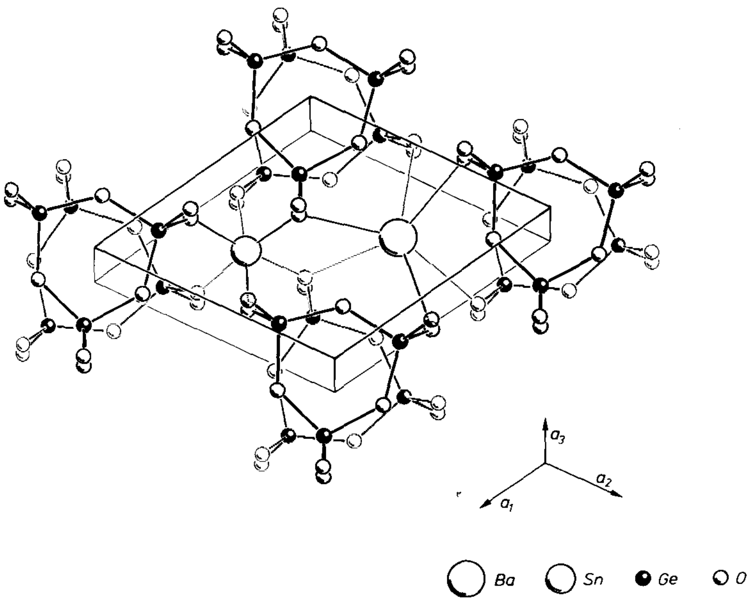

Fig. 3. Structure of $BaSnGe_3O_9$ (Choisnet et al., 1972). Ba and Sn at $z = 0$ and $z = 1$ omitted. Shaded: atoms with $0 \leq z < \frac{1}{2}$, filled: atoms with $\frac{1}{2} \leq z \leq 1$

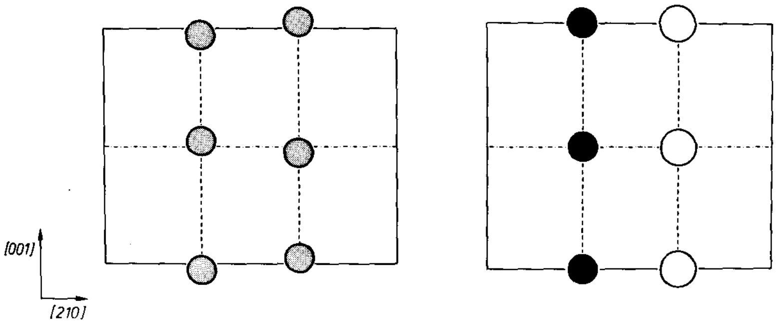

Fig. 4. $(1\bar{2}0)$-plane of $Bi_2Ge_3O_9$ (left) and $BaSnGe_3O_9$ (right); shaded: Bi, empty: Ba, filled: Sn

Physical Properties

Crystals of $Bi_2Ge_3O_9$ exhibit excellent cleavage parallel to the six-fold axis. They can be readily cleaved into extremely thin plane plates similar to those obtainable with mica, but are much more brittle than mica. They are optically transparent within the range of 0.290 µm to several µm. The crystals can be easily polished, and the polished surfaces remain stable when kept in normal atmosphere.

Table 2. Elastic constants c_{ij} (293 K), thermoelastic constants $T_{ij}(273\ \mathrm{K}) = \frac{\partial \log c_{ij}}{\partial T}$ (T temperature), indices of refraction n_i (293 K), α_i coefficients of thermal expansion (273 K).
Units: c_{ij} 10^{11} dyn cm^{-2}, T_{ij} 10^{-3}/K, α_i 10^{-6}/K

c_{11}	c_{33}	c_{44}	c_{66}[a]	c_{12}	c_{13}
10.994	7.290	3.218	4.537	1.920	2.916
T_{11}	T_{33}	T_{44}	T_{66}	T_{12}	T_{13}
−0.245	−0.216	−0.028	−0.300	0.002	−0.435

Wave length	625 nm	578	546	436
$n_1(\lambda)$	2.084	2.096	2.106	2.164
$n_3(\lambda)$	2.015	2.024	2.034	2.079

$\alpha_1 = 6.4$, $\alpha_2 = -0.8$.

Limits of error: c_{11}, c_{33}, c_{44}, c_{66}: 2‰; c_{12}, c_{13}: 1%. T_{11}, T_{33}, T_{66}: 4%; T_{13}, T_{44}: 10%

[a] $c_{66} = (c_{11} - c_{12})/2$

The physical properties listed in Table 2 are referred to a Cartesian reference system with axes e_i which are connected to the crystallographic axes a_i according to:

$e_1 // a_1$, $e_3 // a_3$ and $e_2 = e_3 \times e_1$.

The indices of refraction were measured with the aid of a large prism, the direction of incidence being perpendicular to the six-fold axis. The elastic and thermoelastic constants were determined employing the Schaefer-Bergmann method (diffraction of monochromatic light by ultrasonic waves at approximately 20 MHz, propagating in [100] and [001] as well as intermediate directions) and by using the temperature dependence of resonance frequencies of thick plates (Haussühl, 1956, 1959) in the temperature range between 253 K and 293 K. The coefficients of thermal expansion were measured with the aid of a Fizeau interferometer.

The results show that the elastic and thermoelastic constants of $Bi_2Ge_3O_9$ are comparable with those of α-quartz. The relations $c_{11} > c_{33}$ and $c_{66} > c_{44}$ express predominating bonds within the planes perpendicular to the six-fold axis. The excellent cleavage observed is in accordance with the elastic anisotropy and also with the structural details of the crystal (trigermanate ring). The remarkably strong deviation from Cauchy's relation, $c_{66} > c_{12}$, reveals the existence of covalent bonds in these planes (Haussühl, 1967). These covalent bonds can be assigned to the trigermanate rings.

When measuring light diffraction by ultrasonic waves, unusually strong photoelastic effects were observed. These properties and the high optical quality render the new material suitable for applications in photoacoustic deflector devices. The extremely small coefficient of thermal expansion parallel to the six-fold axis, the excellent cleavage perpendicular to that axis, the small lattice constant a_3, and the high values for the structure factors of $(00h_3)$ reflexions represent desirable properties for use as X-ray spectrometer crystals.

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