

## Bi<sub>4</sub>Ge<sub>3</sub>O<sub>12</sub> at the onset of pressure-induced amorphization

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Received 3 July 2009

Accepted 31 July 2009

Online 26 September 2009

The crystal structure of tetrabismuth tris(germanate), Bi<sub>4</sub>Ge<sub>3</sub>O<sub>12</sub> ( $I\bar{4}3d$ ,  $Z = 4$ ), is stable to at least 7.30 GPa, as demonstrated by hydrostatic single-crystal X-ray diffraction measurements in a diamond anvil cell at room temperature. The highest pressure reached in this study is close to the onset of amorphization at about 8 GPa. The Bi and Ge atoms are located at the 16c (3) and 12a ( $\bar{4}$ ) Wyckoff positions, respectively. The compression mainly affects the distorted BiO<sub>6</sub> octahedra, while the GeO<sub>4</sub> tetrahedra are relatively rigid. When compared with the values obtained under ambient conditions, the long Bi—O distances decrease with increasing pressure, while the short Bi—O distances do not change.

### Comment

Tetrabismuth tris(germanate), Bi<sub>4</sub>Ge<sub>3</sub>O<sub>12</sub> (BGO), is an important material for scintillation detectors (Milenov *et al.*, 2007) and holographic applications (Marinova *et al.*, 2009). At atmospheric pressure, its crystal structure ( $I\bar{4}3d$ ,  $Z = 4$ ) is built up of isolated GeO<sub>4</sub> tetrahedra and strongly deformed BiO<sub>6</sub> octahedra (Durif & Averbuch-Pouchot, 1982; Fischer & Waldner, 1982; Milenov *et al.*, 2007). The asymmetric coordination sphere around the Bi<sup>3+</sup> cations, with three Bi—O distances of 2.16 Å and three others of 2.60 Å (Milenov *et al.*, 2007), is due to the stereoactivity of its nonbonded lone electron pair (Pushkin *et al.*, 2000).

The onset of irreversible pressure-induced amorphization of Bi<sub>4</sub>Ge<sub>3</sub>O<sub>12</sub> occurs at about 8.0 GPa at room temperature, as evidenced by the decrease of the intensities of the powder X-ray diffraction peaks (Arora *et al.*, 2004), with the process being complete above 12 GPa (Meng *et al.*, 1998; Arora *et al.*, 2004). The compound has a bulk modulus of 48 (2) GPa with a first pressure derivative of 9 (1).

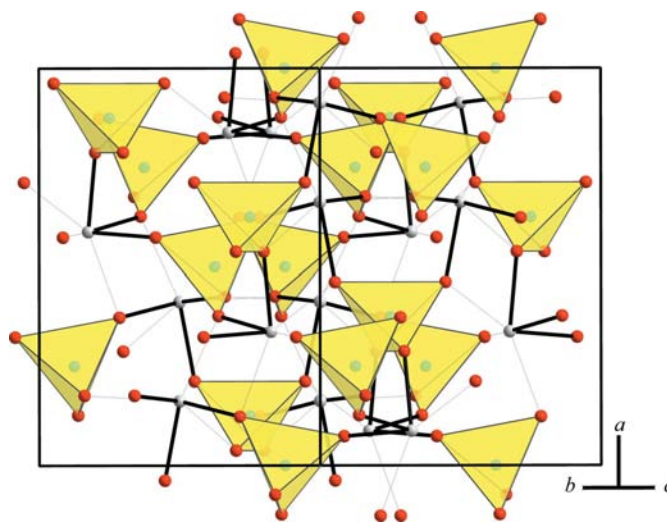
At atmospheric pressure, the coordination numbers (CN) of the Bi<sup>3+</sup> cations in BiO<sub>*n*</sub> polyhedra of crystalline solids vary from 3 to 10 (Pushkin *et al.*, 2000). The volume and activity of the lone pair of electrons (*E*) diminish when the number of O atoms bonded to the cation increases. The effect of pressure, which is associated with the increase in CN and with the

coordination polyhedra becoming more regular, is similar, and the stereochemical activity of the lone pair is suppressed on compression (Grzechnik, 2007). For instance,  $\alpha$ -Bi<sub>2</sub>O<sub>3</sub> ( $P2_1/c$ ,  $Z = 4$ ) has a structure with two non-equivalent Bi atoms in distorted BiO<sub>5</sub>*E* and BiO<sub>6</sub> octahedral coordinations under ambient conditions (Ivanov *et al.*, 2001). A new polymorph of Bi<sub>2</sub>O<sub>3</sub> synthesized at 6 GPa and 1153 K (Atou *et al.*, 1998) has the structure of the *A*-type rare earth sesquioxides ( $P\bar{3}m1$ ,  $Z = 1$ ), with the Bi atom coordinated by seven O atoms in a capped octahedron. In this new phase, the stereoactivity of the *E* pair on the Bi<sup>3+</sup> cation is completely suppressed.

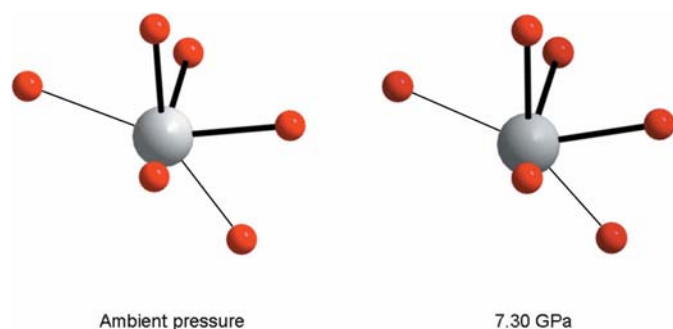
The purpose of this study was to determine the crystal structure of Bi<sub>4</sub>Ge<sub>3</sub>O<sub>12</sub> close to the onset of its pressure-induced amorphization at room temperature. Of special interest was the pressure dependence of the coordination environment around the Bi<sup>3+</sup> cation. Intuitively, one could argue that BGO reaches a limit of its stability at about 8.0 GPa because either the CN of the Bi<sup>3+</sup> cation has increased or the octahedron around the Bi<sup>3+</sup> cation has become regular. To clarify this issue, hydrostatic single-crystal X-ray diffraction measurements were performed in a diamond anvil cell at room temperature.

The indexing of the single-crystal X-ray diffraction data and analysis of the reconstructed reciprocal space at 7.30 GPa indicate that BGO did not undergo any phase transition. This observation supports the previous report that the material is structurally stable up to the onset of pressure-induced amorphization at about 8.0 GPa (Arora *et al.*, 2004).

Refinement of the data based on the structural model obtained using the program *SIR97* (Altomare *et al.*, 1999) produced a structure with GeO<sub>4</sub> tetrahedra and distorted BiO<sub>6</sub> octahedra (Fig. 1) isotypical with that reported for Bi<sub>4</sub>Ge<sub>3</sub>O<sub>12</sub> ( $I\bar{4}3d$ ,  $Z = 4$ ) under ambient conditions (Durif & Averbuch-Pouchot, 1982; Fischer & Waldner, 1982; Milenov *et al.*, 2007). A comparison of the Ge—O bond distances and O—Ge—O



**Figure 1**  
The crystal structure of Bi<sub>4</sub>Ge<sub>3</sub>O<sub>12</sub> at 7.30 GPa. The tetrahedra around the Ge atoms are shaded. Thin and thick lines indicate long and short Bi—O bonds, respectively.


**Figure 2**

The coordination environment around the  $\text{Bi}^{3+}$  cation at two different pressures. Thin and thick lines indicate long and short Bi–O bonds, respectively.

angles in Table 1 with those at atmospheric pressure (1.74 Å, and 105.6 and 117.5°, respectively; Durif & Averbuch-Pouchot, 1982; Fischer & Waldner, 1982; Milenov *et al.*, 2007) shows that the  $\text{GeO}_4$  tetrahedra are rigid and insensitive to increased pressure. The small bulk modulus of the material can be explained by significant shortening of the three long Bi–O bond distances (2.60 Å at room temperature and ambient pressure) in the octahedral coordination environment around the  $\text{Bi}^{3+}$  cation, while the other three shorter Bi–O distances (2.16 Å at room temperature and ambient pressure) do not change on compression (Milenov *et al.*, 2007). On the other hand, increased pressure hardly influences the angular distortion of the  $\text{BiO}_6$  octahedron (Fig. 2).

The results of this study demonstrate that the structural instability of  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$  at high pressure is due neither to an increased CN of the  $\text{Bi}^{3+}$  cation nor to the octahedron around the  $\text{Bi}^{3+}$  cation becoming more regular. However, they do not contradict the argument by Arora *et al.* (2004) that the pressure-induced amorphization of BGO arises from kinetically hindered decomposition of the material, favourable at all pressures.

## Experimental

The crystal used for analysis was cut from a larger crystal synthesized using the Czochralski method in the same batch as that previously investigated by Milenov *et al.* (2007). High-pressure data at 7.30 GPa were collected in a diamond anvil cell of the Boehler–Almax type (Boehler & de Hantsetters, 2004; Boehler, 2006) at room temperature using a Stoe IPDS 2T diffractometer with Mo  $K\alpha$  radiation. A 0.25 mm hole was drilled into a stainless steel gasket preindented to a thickness of about 0.08 mm. The intensities were indexed and integrated using *X-AREA* (Stoe & Cie, 1998). Areas of the images shaded by the diamond anvil cell were masked prior to integration. Corrections for the effects of absorption by the diamond anvil and the crystal were made using the programs *ABSORB* (Angel, 2006) and *X-RED* (Stoe & Cie, 1998), respectively. The shape of the crystal was approximated by 20 faces using the program *X-SHAPE* (Stoe & Cie, 1998). The ruby luminescence method (Mao *et al.*, 1986) was used for pressure calibration, and a mixture of methanol and ethanol (4:1 v/v) was used as the pressure medium. The error in the pressure determination was estimated to be 0.02 GPa.

## Crystal data

$\text{Bi}_4\text{Ge}_3\text{O}_{12}$	$Z = 4$
$M_r = 1245.7$	Mo $K\alpha$ radiation
Cubic, $I\bar{4}3d$	$\mu = 75.24 \text{ mm}^{-1}$
$a = 10.1680 (10) \text{ \AA}$	$T = 293 \text{ K}$
$V = 1051.25 (18) \text{ \AA}^3$	$0.10 \times 0.09 \times 0.06 \text{ mm}$

## Data collection

Stoe IPDS 2T diffractometer	2935 measured reflections
Absorption correction: numerical ( <i>X-RED</i> ; Stoe & Cie, 1998)	212 independent reflections
$T_{\min} = 0.009$ , $T_{\max} = 0.018$	174 reflections with $I > 3\sigma(I)$
	$R_{\text{int}} = 0.085$

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.056$	$\Delta\rho_{\text{max}} = 8.04 \text{ e \AA}^{-3}$ (1.58 Å from atom O1)
$wR(F^2) = 0.056$	$\Delta\rho_{\text{min}} = -5.36 \text{ e \AA}^{-3}$
$S = 2.72$	Absolute structure: Flack (1983)
212 reflections	Flack parameter: 0.00 (9)
8 parameters	

**Table 1**

Selected geometric parameters (Å, °).

Bi1–O1	2.167 (19)	Ge1–O1	1.72 (2)
Bi1–O1 <sup>i</sup>	2.499 (19)		
O1–Ge1–O1 <sup>ii</sup>	118.3 (9)	O1–Ge1–O1 <sup>iii</sup>	105.2 (10)

Symmetry codes: (i)  $-x + 2, -y + \frac{1}{2}, z$ ; (ii)  $-x + \frac{3}{2}, y, -z + 1$ ; (iii)  $z + \frac{1}{4}, -y + \frac{3}{4}, -x + \frac{5}{4}$ .

Isotropic displacement parameters were used for all atoms. To confirm the absolute structure, the model was refined as an inversion twin. The refined twin fraction corresponds with a Flack parameter of 0.00 (9) (Flack & Bernardinelli, 1999).

Data collection: *X-AREA* (Stoe & Cie, 1998); cell refinement: *X-AREA*; data reduction: *JANA2006* (Petříček *et al.*, 2006); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *JANA2006*; molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *JANA2006*.

The author thanks K. Friese for advice. Also acknowledged are the University of the Basque Country, the Gobierno Vasco, and the Ministerio de Ciencia e Innovación for supporting the high-pressure laboratory in Bilbao. The crystal was provided by V. Marinova and M. M. Gospodinov.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3206). Services for accessing these data are described at the back of the journal.

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