Refinement of the crystal structure of Bi-II, *at 2.54 GPa*

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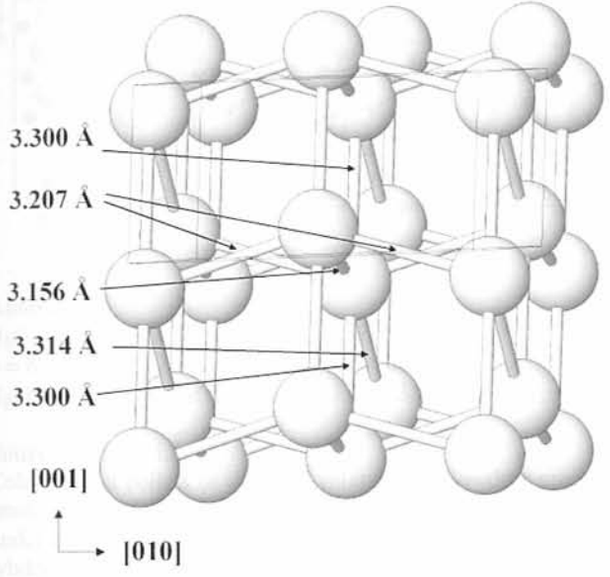

Abstract

Bi, monoclinic, *C*12/*m*1 (No. 12), $a = 6.67256(1)$ Å, $b = 6.1108(2)$ Å, $c = 3.30013(9)$ Å, $\beta = 110.412(2)°$, $V = 126.1$ Å^3, $Z = 4$, $R(P) = 0.118$, $R(I) = 0.087$, $T = 295$ K, $P = 2.54$ GPa.

Source of material

Bismuth of 99.999% purity (ABCR GmbH, Germany) was used for the experiments. Polycrystalline samples were obtained by grinding of bismuth granules at ambient conditions.

Experimental details

Angle-dispersive X-ray powder diffraction experiments were performed on ID-9 at ESRF using an image plate detector. The powdered particles were placed in a gasketed diamond anvil high-pressure cell using a small sphere of ruby for pressure calibration and a 4:1 mixture of ethanol and methanol as a pressure transmitting medium.

Discussion

The crystal structure of the high-pressure modification Bi-II was proposed using time-of-flight neutron diffraction data [1]. Hereby, the atomic coordinates were determined only approximately: Bi in the 4*i* site with $x = 1/4$ and $z = 1/8$. The need for more detailed values for the atomic parameters in the Bi-II structure was recognized in the course of our investigations on crystal structures and chemical bonding at elevated pressures [2,3]. The re-established coordinates for the unique bismuth position in the Bi-II crystal structure (cf. Table 2) differ remarkably from the previously found values [1]. This does not change the general interpretation of the structure as a strongly distorted cubic primitive packing [4]. The level of deformation with respect to the rhombohedral phase is definitely higher as supposed previously, which can be illustrated by comparison of the shortest interatomic distances: 1 × 3.156(3) Å, 2 × 3.2073(8) Å, 2 × 3.300(3) Å and 1 × 3.314(3) Å in the present work and 1 × 3.145 Å, 2 × 3.165 Å, 2 × 3.300 Å and 1 × 3.391 Å by applying the atomic coordinates from [1]. This could explain the difficulties to simulate the Bi-I to Bi-II transformation by means of the density functional calculations [5]. With the re-determined atomic parameters, the structure of Bi-II at 2.54 GPa is more distinct from the Bi-I modification, as it could be assumed before. The Bi-II structure can be derived by distortion of the Bi-I arrangement. The according interatomic distances in the Bi-I structure at 2.2 GPa are 3 × 3.070(3) Å and 3 × 3.385(3) Å (own data).

Table 1. Data collection and handling.

Powder:	black, size 5 – 10 μm
Wavelength:	synchrotron radiation (0.41844 Å)
μ:	365.4 cm^{-1}
Diffractometer:	MAR 3450
$2\theta_{max}$, stepwidth:	24.8°, 0.01°
$N(points)_{measured}$:	2178
$N(hkl)_{measured}$:	80
$N(param)_{refined}$:	8
Programs:	WinCSD [6], ImageIntegrator [7]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Bi	4*i*	0.2518(3)	0	0.1490(6)	0.049(1)	0.049(1)	0.069(2)	0	0.028(1)	0

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