Refinement of the crystal structure of zirconium monobismuthide, ZrBi

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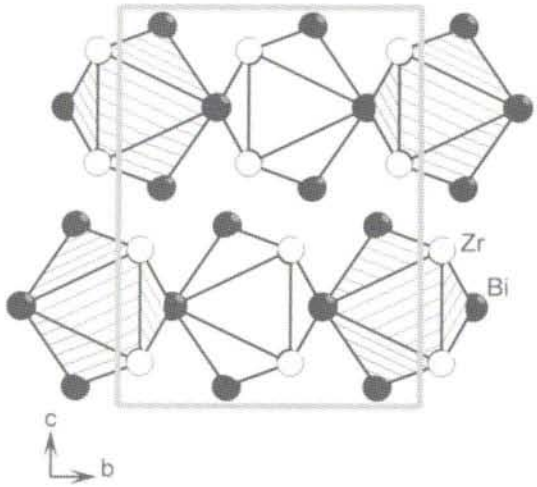

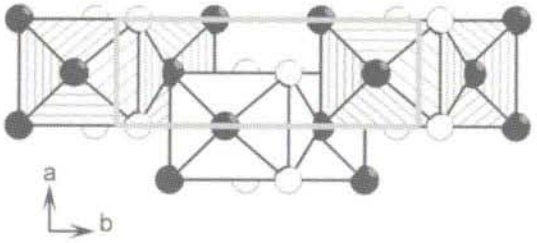

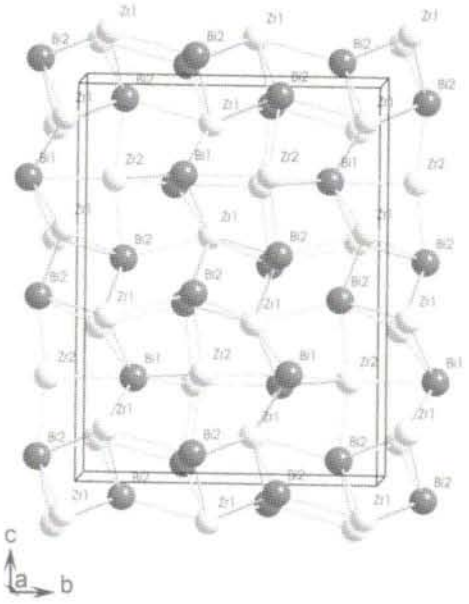

Abstract

BiZr, orthorhombic, *Cmcm* (no. 63),
$a = 3.858(2)$ Å, $b = 10.770(2)$ Å, $c = 14.325(3)$ Å,
$V = 595.2$ Å^3, $Z = 12$,
$R_{gt}(F) = 0.026$, $wR_{ref}(F) = 0.044$, $T = 293$ K.

Source of material

A mixture of 0.152 g zirconium foil (99.8 %, Chempur) and 0.862 g bismuth (99.999 %, Strem Chemicals) were sealed by welding inside a tantalum container. The tantalum container was placed in a quartz ampoule, which was evacuated and sealed. The sample was annealed at 1113 K for 4 days and then quenched in water. ZrBi decomposes in air and therefore all handling was performed in a glove box with argon atmosphere. Rod shaped single crystals were separated from the regulus for the diffraction experiment. The single crystal was mounted in a glass capillary that was sealed in argon atmosphere.

Discussion

Five intermetallic compounds are known in the Zr-Bi system; $ZrBi_2$, ZrBi, Zr_5Bi_3, Zr_2Bi and Zr_3Bi [1-3]. $ZrBi_2$ is isotypic to $TiAs_2$ (Pearson symbol *oP*24) and Zr_3Bi is isotypic to Ni_3P (*tI*32) [4]. Zr_5Bi_3 is possibly impurity stabilised and isotypic to Mn_5Si_3 (*hP*16) [3]. Zirconium monobismuthide was recently found to have a certain homogeneity range and to be isotypic to ZrSb (*oC*24) [3], but no structure refinement has been reported.

The crystal structure of ZrBi can be pictorially described in terms of the capped triangular prisms around the Zr2 atoms. The prism vertices are four zirconium and two bismuth atoms, while the capping atoms all are bismuth. These polyhedra build up columns parallel to [100] by sharing triangular faces (figure, top). The neighbouring columns share a part of the vertices and are shifted by a half of the *c* axis (figure, middle). The Zr—Bi distances in this polyhedron are 2.89 Å - 3.08 Å and the Zr—Zr distances are 3.40 Å. The formed columns are merged to form isolated layers perpendicular to [001]. In each unit cell there are two such layers. In the whole structure, the Zr—Bi distances range from 2.88 Å to 3.21 Å. The Zr—Zr and the Bi—Bi distances are all longer than 3.35 Å, which is more than the sum of their atomic radii for CN = 12 (1.60 Å for Zr and 1.55 Å for Bi [5]), indicating that mainly Zr—Bi interaction governs the structure of ZrBi (figure, bottom).

The systematic appearance of $U_{33} < U_{11} \approx U_{22}$ for all positions can have been caused by slightly insufficient absorption correction. The unit cell parameters of ZrBi determined in the present study fall within the limits of the homogeneity range reported in [3]. No indications for mixed occupancy of the atomic sites were found.

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Table 1. Data collection and handling.

Crystal:	metallic prism, size 0.025 × 0.035 × 0.090 mm
Wavelength:	Mo K_α radiation (0.7107 Å)
μ:	993.32 cm^{-1}
Diffractometer, scan mode:	Rigaku AFC7/Mercury CCD, oscillation
$2\theta_{max}$:	67.45°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	2862, 649
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 3\,\sigma(I_{obs})$, 572
$N(param)_{refined}$:	22
Programs:	SHELXS-97 [6], Jana2000 [7], DIAMOND [8]

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}
Zr(1)	8*f*	0	0.0719(2)	0.1096(1)	0.0100(7)	0.0092(7)	0.0055(7)	0	0	0.0002(5)
Zr(2)	4*c*	0	0.3912(2)	1/4	0.016(1)	0.010(1)	0.0036(9)	0	0	0
Bi(1)	4c	0	0.67745(9)	1/4	0.0099(4)	0.0113(4)	0.0060(4)	0	0	0
Bi(2)	8*f*	0	0.64055(6)	0.54941(5)	0.0108(3)	0.0089(3)	0.0050(3)	0	0	0.0000(2)

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