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Journal of Solid State Chemistry 177 (2004) 3752–3756
JOURNAL OF SOLID STATE CHEMISTRY
www.elsevier.com/locate/jssc

Synthesis and crystal structure of $EuBi_2$

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Received 26 May 2004; received in revised form 3 July 2004; accepted 7 July 2004
Available online 28 August 2004

Abstract

The new hypervalent binary phase $EuBi_2$ was obtained from high temperature solid-state reactions of the pure metal elements in welded Ta tubes under argon atmosphere. Its structure was established by single-crystal X-ray diffraction. The title compound crystallizes in the tetragonal space group $I4_1/amd$ (No. 141) with cell parameters of $a = 4.726(1), c = 34.221(9)$ Å, $V = 764.3(3)$ Å^3, and $Z = 8$. The structure of $EuBi_2$ is isotypic with $HfGa_2$ and features 1D Bi^- zigzag anionic chains along both *a*- and *b*-axes and 2D Bi^- square sheets normal to *c*-axis. It can be formulated as $Eu^{2+}(Bi)^-_{chain}(Bi)^-_{square}$.

Keywords: Polar intermetallics; Solid-state reaction; Crystal structure; Hypervalent compound

1. Introduction

The study of phases formed by alkaline earths and rare earths with elements of group 15 is of particular interest. The electronegative Sb and Bi alloyed with electronpositive metals can form many types of anionic sublattices, the bond often lies at the boundary between the metallic and the iono-covalent state [1]. The majority of these anionic networks obey classical Zintl-Klemm electron counting rules that are the most important and useful tools in solid-state chemistry [2]. On the other hand, many networks built from main group elements show an unusual, nonclassical local coordination such as 2D square sheets, whose bonding schemes can be explained by the concept of "hypervalent bonding" proposed by Hoffmann [3]. Much less is known about the polar intermetallics of binary compounds of Bi compared with corresponding Sb compounds, so far the alkaline earth bismuth binary compounds reported include M_2Bi (M = Ca, Sr, Ba) [4–6], M_5Bi_3 (M = Ca, Sr, Ba) [5,7–9], $M_{11}Bi_{10}$ (M = Ca, Sr, Ba) [1,10,11], Sr_2Bi_3 [1], MBi_3 (M = Sr, Ba) [12]. Eu^{2+} and Yb^{2+} ions have a similar ionic radius to alkaline earth metals and are expected to be able to form a number of binary bismuth phases, so far there are no reports on their crystal structures, and only the cell parameters of $EuBi_2$ were indexed from X-ray powder diffractions (orthorhombic *Cmcm*, $a = b = 4.726(1), c = 17.11(2)$ Å) and its crystal structure was assumed to be isomorphous with $YbSb_2$ in a $ZrSi_2$ structure type [1]. The refinement of $YbSb_2$ itself is however, unsatisfactory with a very high R_1 factor (11.8%) [13]. Hence we deem that an accurate structure determination based on single crystal X-ray diffraction is important. We obtained single crystals of $EuBi_2$ by high temperature solid-state reactions of Eu and Bi metals under an argon atmosphere. Herein we report its synthesis, crystal structure and bonding.

2. Experimental

2.1. Synthesis

The title compound was synthesized through high-temperature reactions of the pure Eu and Bi elements in a molar ratio of 1:2, in welded Ta tubes within an

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doi:10.1016/j.jssc.2004.07.006

evacuated quartz jacket. The reactions were performed at 950 °C for 7 days with prior heating under dynamic vacuum at 300 °C for 1 day, then were allowed to slowly cool (0.1 °C/min) to room temperature. As a general precaution, all sample manipulations were done within a purified argon atmosphere glovebox that had a moisture level <0.1 ppm. All diffraction lines observed in the X-ray powder patterns could be indexed according to patterns calculated on the basis of the single crystal refinement results.

2.2. Crystal structure determination

Single crystals were chosen and isolated from reaction product and sealed within thin-walled glass capillaries under argon atmosphere. A shiny black needle-shaped single crystal with dimensions of $0.50 \times 0.10 \times 0.06\,mm^3$ was mounted on Rigaku Mercury CCD (Mo$K\alpha$ radiation, graphite monochromator) at 293(2) K. A total of 2839 reflections were measured, of which 477 reflections were independent and 380 reflections with $I>2\sigma(I)$ were observed. The data was corrected for Lorentz factor, polarization, air absorption and absorption due to variations in the path length through the detector faceplate. Absorption correction was applied by using SADABS program [14a].

The structure of $EuBi_2$ was initially solved in orthorhombic space group *Fdd*2 (No. 43) with a $R_1 = 0.0551$ for 585 reflections with $I>2\sigma(I)$. However, the atomic positions of two Eu atoms are symmetrically related to each other, so are four Bi positions. Hence a search of space group with a higher symmetry is necessary. For tetragonal system, the space group was determined to be either $I\bar{4}2d$ (No. 122) or $I4_1md$ (No. 109) based on strict systematic absence, and subsequent refinements on $I\bar{4}2d$ (No. 122) gave a satisfactory solution ($R_1 = 0.0508$ and w$R_2 = 0.125$ for 380 observed reflections with $I>2\sigma(I)$). One Bi position is disordered when $I4_1md$ (No. 109) was used. A careful examination of the crystal structure based on $I\bar{4}2d$ (No. 122) indicated that the compound should be centrosymmetric. A centrosymmetric space group $I4_1/amd$ (No. 141) could be selected if 3 (for 4_1 screw axis), 6 (for glide plane *a*) and 9 (for glide plane *d*) systematic absence exceptions were ignored. Subsequent structure refinements in $I4_1/amd$ were satisfactory and gave the lowest *R* values. Therefore $I4_1/amd$ with a highest symmetry is the correct space group and used for the structural refinements. The crystal structure was solved using direct methods (SHELXTL) and refinement by least-square methods with atomic coordinates and anisotropic thermal parameters [14b]. The final stage of least squares refinement showed no abnormal behaviors in the thermal and occupancy parameters. Final difference Fourier maps was essentially featureless with residual peaks of 6.877 and $-4.080\,e\,Å^{-3}$, which are 0.61 and 0.78 Å from Bi(1) and Bi(2), respectively. The relatively higher residual peaks are due to the fact that all elements in the compound are very heavy. Another possible reason is that the data set is of relatively poor quality ($R_{int} = 12.40\%$). Efforts to obtain a better data set were tried but were unsuccessful. The data collection and refinement parameters are summarized in Table 1, and the atomic coordinates and displacement parameters, important bond lengths and angles are listed in Tables 2 and 3, respectively.

Table 1
Summary of crystal data and structure refinement for $EuBi_2$

Empirical formula	$EuBi_2$
Formula weight	569.92
Crystal system	Tetragonal
Space group	$I4_1/amd$ (No.141)
Unit cell dimensions	$a = 4.726(1)$ Å $c = 34.221(9)$ Å
Volume	$764.3(3)\,Å^3$
Z	8
Density (calculated)	$9.906\,g/cm^3$
μ	$107.811\,mm^{-1}$
F(000)	1832
Color and habit	Black, needle
Crystal size	$0.50 \times 0.10 \times 0.06\,mm^3$
2θ range for data collection	4.74–56.5°
HKL ranges	$-6 \leqslant h \leqslant 6$, $-6 \leqslant k \leqslant 6$, $-45 \leqslant l \leqslant 32$
Reflections collected	2821
Independent reflections	296 [R(int) = 0.124]
Reflections observed ($I>2\sigma(I)$)	241
Absorption correction	SADABS
Max. and min. transmission	1.0 and 0.0965
Solution methods	Direct methods
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	296/0/14
S (on F^2)	1.138
Final *R* indices [$I>2\sigma(I)$]	$R_1 = 0.0462$, w$R_2 = 0.1118$
R indices (all data)	$R_1 = 0.0642$, w$R_2 = 0.1196$
Residual extremes/e. $Å^{-3}$	6.877 (0.61 Å from Bi(1) atom) and −4.080 (0.78 Å from Bi(2) atom)

3. Results and discussion

The intermetallic compound $EuBi_2$ crystallizes in the tetragonal system, space group $I4_1/amd$ (No. 141) with $a = 4.726(1)$, and $c = 34.221(9)$ Å. The current *c*-axis is twice of the one reported in the literature, and the current symmetry of tetragonal $I4_1/amd$ (No. 141) for $EuBi_2$ is much higher than the orthorhombic *Cmcm* previously reported [1]. This discrepancy is probably due to the overlook of some weak reflections in old experiments.

Different from $YbSb_2$ (*Cmcm*, $ZrSi_2$ type), $EuBi_2$ actually belongs to the $HfGa_2$ structural type [15], but it can also be seen a distorted form of the $ZrSi_2$ structure

Table 2
Atomic coordinates ($\times 10^4$) and displacement parameters ($Å^2 \times 10^3$) for $EuBi_2$

Atom site	x	y	z	U(eq)[a]		
Eu(1) 8[e]	0	2500	3013(1)	7(1)		
Bi(1) 8e	0	2500	7821(1)	10(1)		
Bi(2) 8e	0	2500	1231(1)	8(1)		
Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Eu(1)	11 (1)	8(1)	3(1)	0	0	0
Bi(1)	10(0)	8(1)	12(1)	0	0	0
Bi(2)	7(1)	13(1)	4(1)	0	0	0

The anisotropic displacement factor exponent U_{ij} takes the form: $-2\pi^2[h^2a^2U_{11} + \cdots + 2hkabU_{12}]$, where *a, b, c* are reciprocal lattice constants.
[a] U(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 3
Selected bond lengths (Å) and angles (°) for $EuBi_2$

Eu(1)–Bi(1)	3.406(6) × 4	Eu(1)–Bi(2)	3.409(6) × 2
Eu(1)–Bi(2)	3.505(6) × 2	Eu(1)–Bi(1)	3.704(6) × 2
Bi(1)–Bi(1)	3.225(5) × 2	Bi(2)–Bi(2)	3.344(6) × 4
Bi(1)–Bi(1)–Bi(1)	94.24(19)	Bi(2)–Bi(2)–Bi(2)	175.51(8) × 2
Bi(2)–Bi(2)–Bi(2)	89.912(3) × 4		

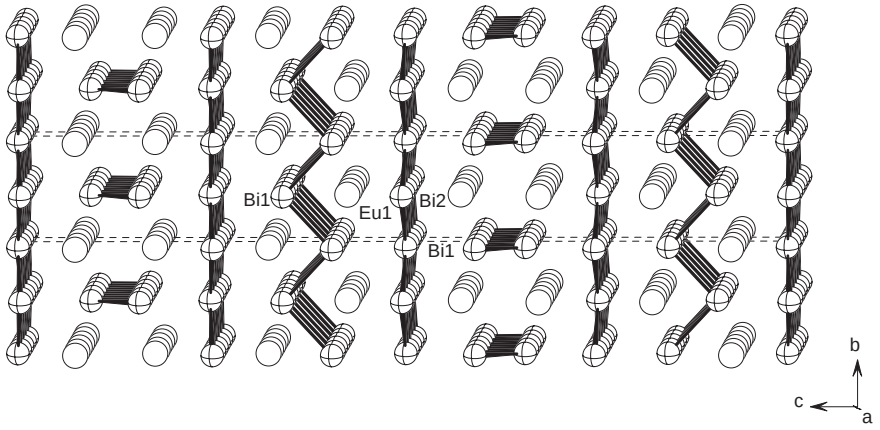

Fig. 1. View of the structure of $EuBi_2$ down the *a*-axis. The Eu and Bi atoms are drawn as open and crossed circles, respectively.

type [13]. Another example of $HfGa_2$ structural type is $ZrIn_2$ [16]. Similar to that of $YbSb_2$ and $ZrIn_2$, the structure of $EuBi_2$ is composed of 1D Bi^- zigzag chains and 2D Bi^- square sheet, and Eu^{2+} ions as spacers (Fig. 1). Within the 1D Bi^- chain, the Bi–Bi distance of 3.2244(16) Å corresponds to a Pauling single bond. The Bi–Bi bond lengths of 3.274(5) and 3.286(4) Å were reported for Bi_4^{4-} square and Bi_2^{4-} dumbbell for $Sr_{11}Bi_{10}$ [11], Bi–Bi double bond lengths of 2.83 Å were reported for molecular compounds [17,18]. A nearly square planar anion Bi_4^{2-} was reported in which the Bi–Bi distance of 2.94 Å was intermediate between a single and double bond [19]. The Bi–Bi distance of 2.976 Å (bond order larger than 1.0) was found for a Bi_2 dumbbell in solid K_3Bi_2 [20]. In Bi metal, the Bi–Bi distances are 3.07 Å [21] and a single bond of 3.11 Å has been reported for the Bi_2^{4-} dimer in KBa_4Bi_3O [22]. The Bi–Bi–Bi bond angle within the 1D zigzag chain is 94.24(19)°, which is much smaller than 109.9° for an ideal tetrahedron, due to the presence of two lone pairs per Bi^- anion (Table 3, Fig. 2a).

The 2D Bi^- square sheet normal to the *c*-axis are formed by Bi(2) atoms (Fig. 2b). The Bi–Bi distance of 3.3442(7) Å is much larger than that of a single bond and can be considered to be a "hypervalent" Bi–Bi bond. The Bi–Bi–Bi angles are 89.912(3)° and 175.51(8)°, respectively, which are slightly derived from those for an ideal 2D square net, thus the sheet is slightly puckered. Similar square Sb sheets have been reported in $EuSb_2$ and $BaZnSb_2$ [23,24]. The Eu^{2+} ion is ten-coordinated by Bi atoms (Fig. 3). Its coordination geometry can be described as a distorted bicapped

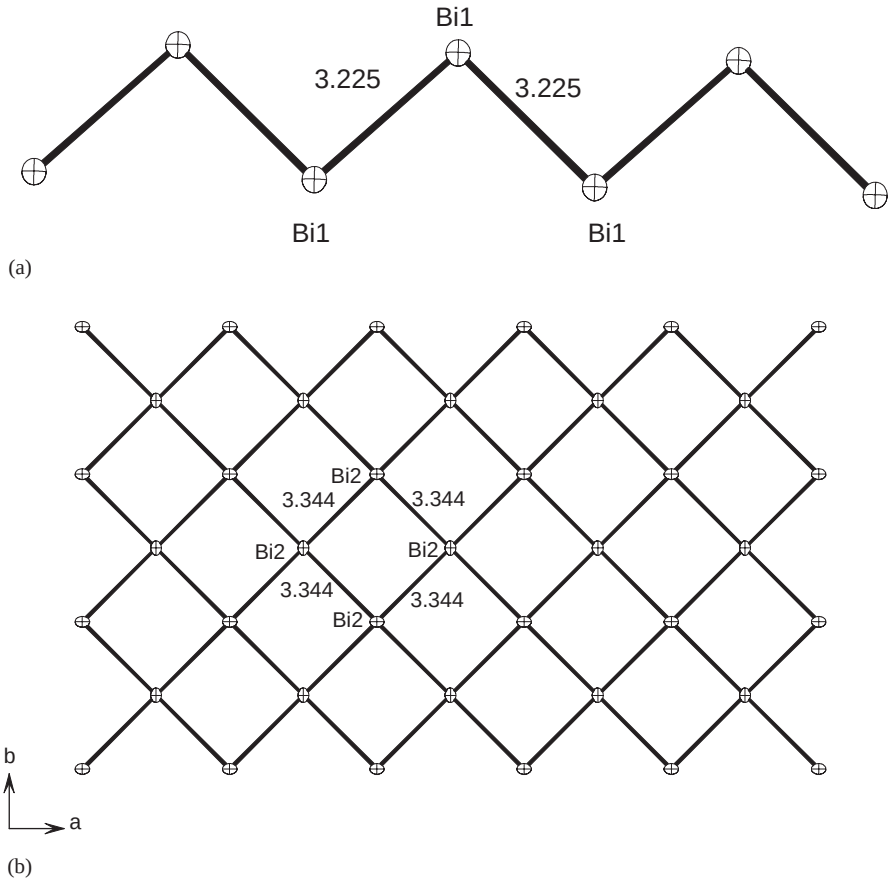

Fig. 2. ORTEP drawing of a 1D zigzag chain of Bi^{-} (a) and a 2D square sheet of Bi^{-} (b) in $EuBi_2$. The thermal ellipsoids are drawn at 75% probability.

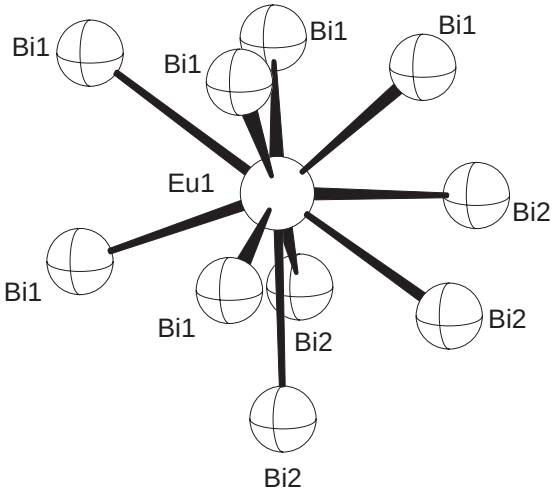

Fig. 3. The coordination geometry around the europium atom.

square prism. One square plane is defined by four Bi(1) atoms, and the other by two Bi(1) and two Bi(2) atoms. One Bi(2) caps on the bottom of the square and another Bi(2) atom is capping on the waist of the square prism. The Eu–Bi distances are in the range 3.4058(8)–3.704 (1) Å (Table 3).

It is interesting to note that the 1D Sb^{-} chains in $YbSb_2$ are orientated to only one axis (*c*-axis) whereas the Bi^{-} chains are along both *a*- and *b*-axes, this is due to the higher symmetry for $EuBi_2$. Such Bi^{-} chains are similar to the In^{3-} chains in $ZrIn_2$ [16]. In $YbSb_2$, the *a*-axis is longer than the *c*-axis by 0.265 Å, the discrepancy between the two axes for $EuBi_2$ is expected to be greater if it maintains a same structure as $YbSb_2$ due to slightly larger sizes of Eu and Bi than those of Yb and Sb, and also due to the longer Bi–Bi and Eu–Bi bond distances than the corresponding Sb–Sb and Yb–Sb bonds. However the *a*- and *b*-axes in $EuBi_2$ are actually equal, hence a severe distortion from $YbSb_2$ structure type is expected. Some intra chain Bi–Bi bonds are broken and some inter chain Bi–Bi bonds are formed, resulting in two types of 1D Bi^{-} chains which are perpendicular to each other. The nearest Bi–Bi separation between neighboring 1D chains are 4.726(1) Å, the nearest Bi–Bi distances between 2D square sheet to the 1D chain along *a*- and *b*-axes are 3.910(1) and 4.015(1) Å. These distances indicate that there is little Bi–Bi interaction between the above two building blocks.

The electron count scheme for $EuBi_2$ can be easily developed by using the classical Zintl concept as well as

the concept of "hypervalent bonding" to 2D system. The Bi atoms in the zigzag chain is two-bonded and each Bi is assigned to be -1 in charge according to the Zintl concept. Similar to that in the Sb^- square net, each Bi atom of the 2D square sheet in $EuBi_2$ is -1 according to the concept of "hypervalent" bonding. Hence $EuBi_2$ can be formulated as $Eu^{2+}(Bi)^-_{chain}(Bi)^-_{square}$. The oxidation state of europium of $2+$ is expected to be the most stable one in such binary system.

Acknowledgments

This work is supported by National Natural Science Foundation of China (No. 20371047). We thank the helpful comments from the referees.

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