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Journal of Alloys and Compounds 421 (2006) 190–194

Journal of ALLOYS AND COMPOUNDS

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Synthesis and crystal structure of a new Zintl phase $Sr_5In_2Bi_6$

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Received 16 July 2005; accepted 22 September 2005
Available online 20 December 2005

Abstract

A new Zintl phase, $Sr_5In_2Bi_6$, has been synthesized by solid-state reactions of the corresponding elements in a stoichiometric ratio in welded niobium tube at 750 °C. Its structure was established by single-crystal X-ray diffraction. $Sr_5In_2Bi_6$ crystallizes in the orthorhombic space group *Pbam* (No. 55) with cell parameters of $a = 24.4500(3)$, $b = 7.8800(8)$, $c = 4.7400(5)$ Å and $V = 913.2(2)$ Å^3. It belongs to the $Ca_5Al_2Bi_6$ structure type and its structure features one-dimensional anionic double chains of $[In_2Bi_6]^{10-}$ with the Sr^{2+} ions as spacers. Within the double anionic chain, the In atom is four-bonded by four Bi atoms in a tetrahedral geometry, and these $InBi_4$ tetrahedra are interconnected into a 1D chain via corner-sharing, each pair of such chains are further condensed into a double chain via Bi–Bi bonds. Results of extended Hückel band structure calculations indicate that $Sr_5In_2Bi_6$ is a semiconductor with a band gap of ~1.5 eV. $Sr_5In_2Bi_6$ is diamagnetic based on magnetic property measurements.

Keywords: Zintl phase; Crystal structure; Solid state reaction; Band structure calculation; Polar intermetallics; Magnetic property

1. Introduction

Most of Zintl phases formed by alkali or alkali earth elements and p-block elements are semiconductors [1,2]. The Zintl phases containing heavier p-block elements usually exhibit a narrowed band gap. For example, $Ba_8In_4Sb_{16}$ [3] and $BaGa_2Sb_2$ [4] are found to be narrow band gap p-type semiconductors. The $Ae_5Tr_2Pn_6$ (Ae = Ca, Sr, Ba; Tr = Al, Ga, In; Pn = As, Sb, Bi) phases are also known as Zintl phases with narrow band gaps [5–11]. They have been extensively investigated due to their interesting thermoelectronic properties, including electrical conductivity, thermopowder and thermal conductivity [5–11]. One disadvantage of the above intermetallics is that they are very air-sensitive which greatly limits their actual applications. The lanthanide analogues of the above phases, however, are usually much more air stable and hence are more suitable to be used as new thermoelectric materials [10,11]. For instance, $Yb_5In_2Sb_6$, the first lanthanide analogue of $Ca_5Al_2Bi_6$, exhibits rather low electrical conductivity [10]. The isostructural $Eu_5In_2Sb_6$ is also a narrow band gap semiconductor. More interestingly, when the 25% indium atoms were replaced by Zn, the band gap almost disappeared and the resultant compound became metallic [11].

Studies on alkaline earth–indium–bismuth ternary phases are still scarce. A few such ternary phases reported include $Ca_{11}In_xBi_{10-x}$ [12], $Ba_{14}InBi_{11}$ [13], $Sr_{11}InBi_6$ [14] and $Ba_5In_4Bi_5$ [15]. Our exploration on new intermetallic phases in the alkaline earth–indium–bismuth ternary system afforded a new Zintl phase, $Sr_5In_2Bi_6$, which belongs to the $Ca_5Al_2Bi_6$ structure type. Herein, we report its synthesis, crystal structure, band structure and magnetic property.

2. Experimental

2.1. Synthesis

All manipulations were performed inside an argon-filled glove box with moisture level below 1 ppm. 0.175 g (2.0 mmol) of strontium pieces (99.9%, Acros), 0.092 g (0.8 mmol) of indium powder (99.99%, Aldrich) and 0.502 g (2.4 mmol) of bismuth powder (99.999%, Shanghai fourth factory) was loaded in a niobium tube, and the tube was then sealed in an evacuated quartz jacket. The mixture was allowed to heat at 750 °C for 1 week and then slowly cooled down (10 °C/h) to room temperature. $Sr_5In_2Bi_6$ was obtained in high yield as a single phase. Its purity was confirmed by XRD powder patterns (X'Pert diffractometer using Cu Kα radiation, λ = 1.5406 Å).

2.2. Crystal structure determination

A dark gray prismatic crystal of $Sr_5In_2Bi_6$ was selected from reaction product and sealed within a thin-walled glass capillary under an argon atmosphere. Data collections were performed on a Rigaku Mercury CCD (Mo Kα radiation,

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doi:10.1016/j.jallcom.2005.09.074

Table 1
Summary of cell parameters, data collection and structure refinements for $Sr_5In_2Bi_6$

Formula	$Sr_5In_2Bi_6$
fw	1921.62
Space group	*Pbam* (No. 55)
a (Å)	24.450(3)
b (Å)	7.8800(8)
c (Å)	4.7400(5)
V (Å^3)	913.2(2)
Z	2
D_{calcd} (g cm^{-3})	6.988
μ (mm^{-1})	74.474
F(0 0 0)	1572
Size (mm)	0.24 × 0.12 × 0.06
Color and habit	Gray, brick
Reflections collected	6717
Unique reflections	1168 (R_{int} = 9.51%)
Reflections ($I > 2\sigma(I)$)	1031
GOF on F^2	1.102
R1, wR2 ($I > 2\sigma(I)$)[a]	0.0470/0.1061
R1, wR2 (all data)	0.0550/0.1108
Largest diff. peak and hole (eÅ^{-3})	5.988 (0.93 Å from Bi(1) atom) and −5.583 (0.77 Å from Bi(1) atom)

[a] $R1 = \sum ||Fo| - |Fc|| / \sum |Fo|$, $wR2 = \left\{ \sum w[(Fo)^2 - (Fc)^2]^2 / \sum w[(Fo)^2]^2 \right\}^{1/2}$.

graphite monochromator) at 293(2) K. The data set was corrected for Lorentz factor, polarization, air absorption and absorption due to variations in the path length through the detector faceplate. Absorption correction based on multi-scan method was also applied [16].

The space group was determined to be *Pbam* (No. 55). The structure was solved using direct methods (SHELXTL) and refined by least-squares method with atomic coordinates and anisotropic thermal parameters [17]. None of atoms is disordered and each atomic site is fully occupied according to site occupancy refinements. Final Fourier maps showed featureless residual peaks of 5.988 and −5.583 eÅ^{-3}, which are 0.93 and 0.77 Å from Bi(2) atom, respectively. The relatively higher residual peaks are probably due to the relatively poor quality (R_{int} = 9.6%) of the data set as well as due to the fact that all atoms present are very heavy. Efforts to obtain a better data set were tried but were unsuccessful. Some of the data collection and refinement parameters are summarized in Table 1. The atomic coordinates, important bond lengths and angles are listed in Tables 2 and 3, respectively.

Crystallographic data in CIF format for $Sr_5In_2Bi_6$ have been deposited as CSD 415576. These data may be obtained free of charge by contacting FIZ Karlsruhe at +49 7247 808 666 (fax) or crysdata@fizkarlsruhe.de (e-mail).

2.3. Extended Hückel band structure calculations

Band structure calculations for $Sr_5In_2Bi_6$ along with the density of states (DOS) and crystal orbital overlap population (COOP) curves were performed using the Crystal and Electronic Structure Analyzer (CAESAR) software package [18–20]. The atomic parameters used in the calculations along with the H_{ii} and Slater exponents are presented in Table 4.

2.4. Magnetic property measurements

Magnetic susceptibility measurements on polycrystalline samples of $Sr_5In_2Bi_6$ were performed with a PPMS-9T magnetometer at a field of 10,000 Oe in the temperature range of 6–300 K.

Table 2
Atomic coordinates and thermal displacement parameters (×10^3 Å^2) for $Sr_5In_2Bi_6$

Atom	Site symm	X	Y	Z	U(eq)[a]
Sr(1)	2c	0	1/2	0	11(1)
Sr(2)	4g	0.7451(1)	0.7752(2)	0	11(1)
Sr(3)	4g	0.0881(1)	0.0316(3)	0	12(1)
In(1)	4h	0.8796(1)	0.3261(2)	1/2	13(1)
Bi(1)	4h	0.4981(1)	0.2996(1)	1/2	11(1)
Bi(2)	4h	0.3116(1)	0.4848(1)	1/2	10(1)
Bi(3)	4g	0.8639(1)	0.5452(1)	0	11(1)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Sr(1)	6(1)	8(1)	18(2)	0	0	0(1)
Sr(2)	7(1)	7(1)	18(1)	0	0	0(1)
Sr(3)	5(1)	16(1)	16(1)	0	0	1(1)
In(1)	12(1)	12(1)	14(1)	0	0	−1(1)
Bi(1)	10(1)	11(1)	12(1)	0	0	−2(1)
Bi(2)	8(1)	12(1)	10(1)	0	0	3(1)
Bi(3)	5(1)	10(1)	19(1)	0	0	−1(1)

[a] U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor. 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.

Table 3
Important bond lengths (Å) and angles (°) for $Sr_5In_2Bi_6$

Sr(1)–Bi(1)	3.3456(6) ×4	Sr(1)–Bi(3)	3.3474(8) ×2
Sr(2)–Bi(3)	3.410(2)	Sr(2)–Bi(3)	3.423(2)
Sr(2)–Bi(2)	3.426(1) ×2	Sr(2)–Bi(2)	3.441(1) ×2
Sr(3)–Bi(2)	3.429(2) ×2	Sr(3)–Bi(1)	3.498(2) ×2
Sr(3)–Bi(3)	3.535(2)	Sr(3)–Bi(1)	3.661(2) ×2
Sr(3)–In(1)	3.766(2) ×2	In(1)–Bi(3)	2.957(1) ×2
In(1)–Bi(2)	2.960(2)	In(1)–Bi(1)	3.062(2)
Bi(1)–Bi(1)	3.159(2)		
In(1)–Bi(1)–Bi(1)	110.56(4)	Bi(3)–In(1)–Bi(3)	106.53(5)
Bi(3)–In(1)–Bi(2)	114.22(4) ×2	Bi(3)–In(1)–Bi(1)	108.17(4) ×2
Bi(2)–In(1)–Bi(1)	105.27(5)	In(1)–Bi(3)–In(1)	106.53(5)

Table 4
Atomic parameters used for extended Hückel calculations for $Sr_5In_2Bi_6$[a]

Atom type	Orbital	H_{ii} (eV)	ξ_1	c_1
Sr	s	−6.620	1.214	1.00
	p	−3.920	1.214	1.00
In	s	−12.60	1.903	1.00
	p	−6.190	1.677	1.00
Bi	s	−15.19	2.560	1.00
	p	−7.790	2.072	1.00

[a] H_{ii} values are the diagonal matrix elements $\langle\chi_i|H^{eff}|\chi_i\rangle$ where H^{eff} is the effective Hamiltonian. In our calculations of the off-diagonal matrix elements $H_{ij} = \langle\chi_i|H^{eff}|\chi_j\rangle$, the weighted formula was used.

3. Results and discussion

The new Zintl phase, $Sr_5In_2Bi_6$, belongs to the $Ca_5Al_2Bi_6$ structure type [8]. Its structure features 1D $In_2Bi_6^{10-}$ double chains along c-axis with the Sr^{2+} ions as spacers (Fig. 1). In(1) is four-bonded by 1 Bi(1), 1 Bi(2) and 2 Bi(3) in a tetrahedral geometry. These $InBi_4$ tetrahedra are interconnected through corner sharing (Bi(3)) to form a 1D chain along the c-axis. Two neigh-