La_3ScBi_5 的合成与晶体结构

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摘要: 在氩气保护下,将金属单质置于钽管中进行高温固相反应得到了一个新的三元极性金属间化合物,La_3ScBi_5。通过 X-射线单晶衍射确定了它的晶体结构。La_3ScBi_5 晶体属六方晶系,空间群为 $P6_3/mcm$(No.193),晶胞参数为:$a=b=0.975\,73(5)$ nm,$c=0.655\,92(6)$ nm,$V=0.543\,41(9)$ nm^3,$Z=2$。La_3ScBi_5 属反式 Hf_5Sn_3Cu 结构类型,其结构特征为 Bi 的一维直线链和由 $ScBi_6$ 八面体之间通过共面形成的{$ScBi_3$}链。能带计算表明 La_3ScBi_5 呈金属导电性。

关键词: 极性金属间化合物; 高温固相反应; 晶体结构; 铋化物; 混合阳离子法
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Synthesis and Crystal Structure of La_3ScBi_5

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Abstract: The new ternary phase, La_3ScBi_5 was obtained by the 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 hexagonal space group $P6_3/mcm$ (No.193) with cell parameters of $a=b=0.975\,73(5)$ nm, $c=0.655\,92(6)$ nm, $V=0.543\,41(9)$ nm^3, and $Z=2$. The structure of La_3ScBi_5 belongs to the "anti" Hf_5Sn_3Cu type, and features 1D linear Bi chains and {$ScBi_3$} chains composed of face-sharing $ScBi_6$ octahedra. Band calculations indicate that La_3ScBi_5 is metallic. CSD: 416609.

Key words: polar intermetallics; high temperature solid-state reaction; crystal structure; bismuth compound; mixed cation method

0 Introduction

Ternary rare-earth transition metal antimonides and bismuthides are of research interest during the last three decades due to their possible use as new magnetic materials and their interesting structure chemistry[1~16]. Most of compounds have been structurally determined by single crystal X-ray diffraction. Several examples include RE_3MSb_5 (M=Ti, Zr, Hf, Nb) with the hexagonal Hf_5Sn_3Cu structure[1~4], whose structure features chains of face-sharing MSb_6 octahedra and linear Sb chains; $REMSb_2$ (M=Mn-Zn, Pd, Ag, Au) with the $HfCuSi_2$ structure[5~7], which is composed of 2D Sb^- square sheet and $[MSb]^{2-}$ layers with rare earth ions as spacers, and $REMSb_3$ (M=Cr, V)[8~11]. However, the corresponding bismuth compounds have been rarely documented. Several such phases reported are $RE_{14}MPn_{11}$ (RE=Eu, Yb; M=Mn, In; Pn=Sb, Bi) with a $Ca_{14}AlSb_{11}$ structure[12,13], RE_5M_2Pn (M=Ni, Pd; Pn=Sb, Bi) with a Mo_5B_2Si structure[14]; REMPn (M=Rh, Ni; Pn=Sb, Bi) with a TiNiSi structure[15], and $Yb_9Zn_4Bi_9$ features $[Zn_4Bi_9]^{19-}$ ribbons running along the c-axis[16].

Mixing two types of cations with different size

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and charge has been found to be an effective route to prepare novel polar intermetallic phases, due to the lessening of cation packing limitation and changing of electronic requirements[17~21]. By using such technique, we have successfully isolated two new polar intermetallic phases, namely La_3MgBi_5 and $LaLiBi_2$[22]. As an extension of the work, we used two different lanthanide metals (La and Sc) as cations. Our research efforts resulted in a new ternary phase, La_3ScBi_5. Herein, we report its synthesis, crystal structure and chemical bonding.

1 Experimental

1.1 Synthesis

All manipulations were performed inside an argon-filled glove box with moisture level below 1 ppm. Scandium turnings (99.9%, Acros), lanthanum chip (99.9%, Aldrich) and bismuth block (99.9%, Alfa) were used as received. Single crystals of La_3ScBi_5 were initially obtained by the solid state reaction of scandium (0.023 g, 0.5 mmol), lanthanum (0.138 g, 1.0 mmol) and bismuth (0.313 g, 1.5 mmol). The mixture was loaded into a niobium tube. The tube was then arc-welded and sealed in a quartz tube under vacuum (~10^{-4} Torr). It was put into an oven and heated at 1 080 ℃ for 2 days, and annealed at 980 ℃ for 7 days. Afterwards, it was allowed to cool at a rate of 0.1 ℃·min^{-1} to the room temperature. Brick-shaped gray single crystals of La_3ScBi_5 were obtained. Several single crystals of La_3ScBi_5 were analyzed by using energy-dispersive X-ray spectroscopy (EDAX 9100). The measured La∶Sc∶Bi molar ratio of 3.14∶1.0∶5.50 is in good agreement with the one from structural refinement. After its structural analysis, a lot of efforts were subsequently made to synthesize a pure phase of La_3ScBi_5, however, X-ray powder patterns of the resultant products revealed the presence of impurity phases, such as LaBi ($Fm\bar{3}m$), as well as other unidentified compounds. The highest yield is about 70% based on XRD powder studies. Physical properties of La_3ScBi_5 were not studied because of no pure sample available.

1.2 Crystal structure determination

Single crystals of La_3ScBi_5 were selected from the reaction products and sealed within thin-walled glass capillaries under an argon atmosphere. Data collection was performed on a Rigaku Mercury CCD (Mo $K\alpha$ radiation, graphite monochromator) at room temperature. A total of 252 independent reflections were measured, of which 247 reflections with $I>2\sigma(I)$ were considered as observed. 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 corrections based on Multi-scan method were also applied[23].

The structure was solved using direct methods (SHELXTL) and refined by least-square methods with atomic coordinates and anisotropic thermal parameters[24]. The final stage of least squares refinement showed no abnormal behaviors in the occupancy factors. Final difference Fourier maps showed featureless residual peaks of 352 7 (0.0 nm from Bi(2)) and −5 821 e·nm^{-3} (0.055 nm from Bi (2)). The relatively higher residual peaks were due to the fact that bismuth element in the compound is very heavy. Crystal data and further details of data collection are given in Table 1, important bond lengths and angles are listed in Table 2.

CSD: 416609.

Table 1 Summary of crystal data and structure refinement for La_3ScBi_5

Formula	La_3ScBi_5
Formula weight	1 506.57
Crystal system	Hexagonal
Space group	$P6_3/mcm$ (No.193)
$a=b$ / nm	0.975 73(5)
c / nm	0.655 92(6)
V / nm^3	0.540 80(6)
Z	2
D_{calcd} / (g·cm^{-3})	9.252
μ / mm^{-1}	93.106
F(000)	1 254
Size / mm	0.15 × 0.10 × 0.10
Color and habit	Gray, brick
Range in hkl	$-12<h<12$, $-12<k<11$, $-4<l<8$
Reflections collected	3894
Unique reflections	252 (R_{int}=6.23%)
Reflections ($I>2\sigma(I)$)	247
GOF on F^2	1.225
R_1, wR_2 ($I>2\sigma(I)$)[a]	0.035 4 / 0.070 9
R_1, wR_2 (all data)	0.036 1 / 0.071 3
Residual extremes / (e·nm^{-3})	3 527 (0.0 nm from Bi(2)) and −5 821 (0.055 nm from Bi(2))

[a] $R_1=\sum||F_o|-|F_c||/\sum|F_o|$, $wR_2=[\sum w(F_o^2-F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$

Table 2　Important bond lengths (nm) and angles (°) for La_3ScBi_5

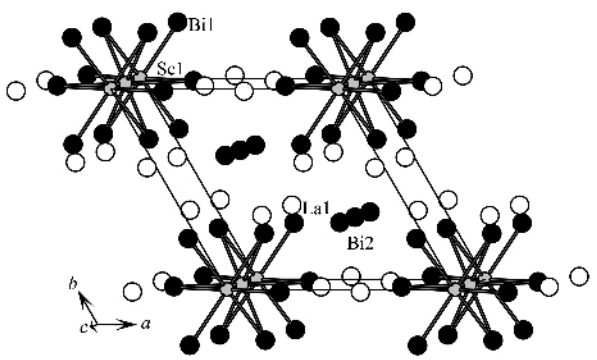
Sc(1)-Bi(1)	0.302 30(7)	Bi(2)-Bi(2)	0.327 96(3)	La(1)-Bi(1)	0.329 81(9)
La(1)-Bi(1)	0.348 81(6)	La(1)-Bi(1)	0.349 0(1)	La(1)-Bi(2)	0.345 66(4)
Bi(2)-Bi(2)-Bi(2)	180.0	Bi(1)-Sc(1)-Bi(1)	86.64(1)	Bi(1)-Sc(1)-Bi(1)	93.36(1)
Bi(1)-Sc(1)-Bi(1)	180.00(2)				

1.3　Band structure calculations

3D band structure calculation for La_3ScBi_5 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[25]. The following atomic orbital energies and exponents were employed for the calculations (H_{ii}=orbital energy, ξ=Slater exponent): La 6*s*, H_{ii}=−6.56 eV, ξ=2.14; 6*p*, H_{ii}=−4.38 eV, ξ=2.08; 5*d*, H_{ii}=−7.52 eV, ξ=3.78; Bi 6*s*, H_{ii}=−15.19 eV, ξ=2.56; 6*p*, H_{ii}=−7.79 eV, ξ=2.07; Sc 4*s*, H_{ii}=−8.87 eV, ξ=1.30; 4*p*, H_{ii}=−2.75 eV, ξ=1.30; 3*d*, H_{ii}=−8.51 eV, ξ=4.35.

2　Results and discussion

As shown in Fig.1, La_3ScBi_5 can be considered as an "*anti*"-type of Hf_5Sn_3Cu with the bismuth atoms on the hafnium sites, and lanthanum and scandium atoms occupy the tin and copper sites, respectively. It is also isostructural with La_3MgBi_5 previously reported[22]. Its structure features linear chains of Bi and $\{ScBi_3\}$ chains composed of face-sharing $ScBi_6$ octahedra. The linear Bi chain along the *c*-axis is formed by Bi(2) atoms (Fig.2a). Within the Bi chains, the Bi-Bi distance of 0.327 96(3) nm corresponds to a Pauling single bond, and it is very close to that of the linear Bi chain (0.327 46(5) nm) in La_3MgBi_5[22], as well as the Bi-Bi bond distance found in the dumbbell (0.327 nm) of $Sr_{11}Bi_{10}$[26]. The Sc atoms are octahedrally-coordinated by six Bi(1) atoms with Sc-Bi distances of 0.302 30(7) nm, which is slightly shorter than that of $\{MgBi_3\}$ octahedral chains (0.307 2 nm) in La_3MgBi_5 (Fig.2b). These $ScBi_6$ octahedra are further interconnected into an infinite $\{ScBi_3\}$ chain along the *c*-axis via face sharing (Fig.2b). The La atom is surrounded by five Bi(1) and four Bi(2) atoms with La-Bi distances in the range of 0.329 81(9)~0.349 0(1) nm, which are comparable to the sum of covalent radii of La and Bi atoms (0.347 nm). Its coordination geometry can be described as a distorted tricapped trigonal prism (Fig.3).



The La, Sc and Bi atoms are drawn as open, gray and black circles, respectively. The cell edges are drawn as thin solid lines

Fig.1　View of the structure of La_3ScBi_5 down the *c*-axis

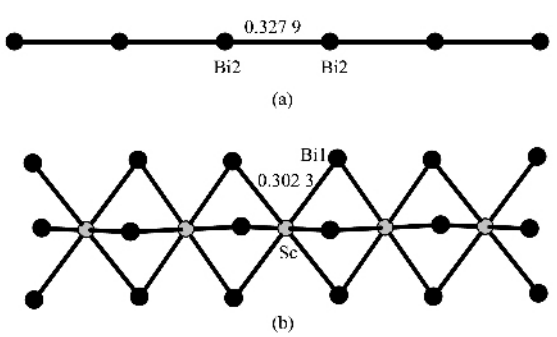


Fig.2　Drawing of a 1D liner Bi chain (a) and a face-sharing $ScBi_6$ octahedral chain (b) in La_3ScBi_5

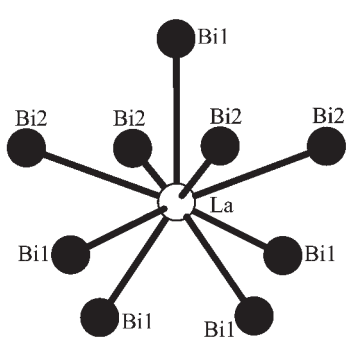
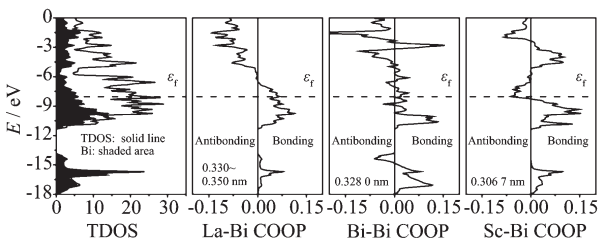


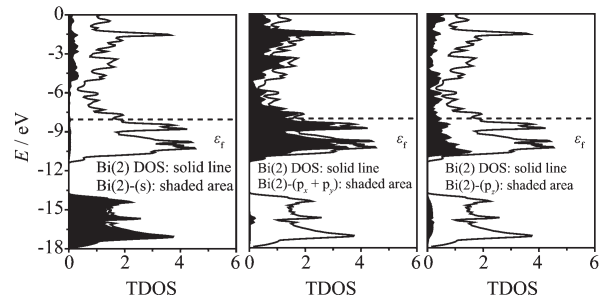
Fig.3　Coordination geometry around the lanthanum atom in La_3ScBi_5

To further understand the chemical bonding of La_3ScBi_5, 3D band structure calculations were performed by using the CAESAR program[25]. Results are shown in Fig.4 and 5. There is no observable band gap around the Fermi level, indicating that La_3ScBi_5 is expected to be metallic. The states just below and above Fermi level are predominately from *p*-orbitals of the bismuth and *d*-orbitals of the scandium and lanthanum atoms. The states below −14 eV are predominately from *s*-orbitals of the bismuth atoms. The COOP curves are more informative. The Sc-Bi (0.306 7 nm) has a large average overlap population (OP) value of 0.302, and those for the Bi-Bi (0.328 0 nm) and La-Bi (0.33~0.35 nm) are 0.278 and 0.295, respectively. These results indicate significant Bi-Bi, La-Bi bonding interactions. The Bi-Bi interaction is weakly bonding around the Fermi level. Such interaction is composed of significant $\sigma_{Bi\text{-}Bi}$ interaction as well as weak $\pi_{Bi\text{-}Bi}$ interaction, since states around the Fermi level show significant contributions from the Bi(2) p_x and p_y orbitals in addition to p_z characters. Weak $\pi \cdots \pi$ bonding interaction may be responsible to the short Bi-Bi distance in La_3ScBi_5.



The Fermi level is set at −8.05 eV

Fig.4 Density-of State (DOS) (contributions of the Bi atoms shown in the blackened area) and COOP curves for La_3ScBi_5



The Fermi level is set at −8.05 eV

Fig.5 Relevant densities-of-states (DOS) curves showing the contribution of Bi linear chain in La_3ScBi_5

References:

[1] Bolloré G, Ferguson M J, Hushagen R W, et al. *Chem. Mater.*, **1995**,**7**:2229~2231

[2] Ferguson M J, Hushagen R W, Mar A. *J. Alloys Compd.*, **1997**,**249**:191~198

[3] Moore S H D, Deakin L, Ferguson M J, et al. *Chem. Mater.*, **2002**,**14**:4867~4873

[4] Brylak M, Jeitschko W. *Z. Naturforsch. B*, **1994**,**49**:747~752

[5] Brylak M, Möller M H, Jeitschko W. *J. Solid State Chem.*, **1995**,**115**:305~308

[6] Wollesen P, Jeitschko W, Brylak M, et al. *J. Alloys Compd.*, **1996**,**245**:L5~L8

[7] Thomas E L, Moldovan M, Young D P, et al. *Chem. Mater.*, **2005**,**17**:5810~5816

[8] Raju N P, Greedan J E, Ferguson M J, et al. *Chem. Mater.*, **1998**,**10**:3630~3635

[9] Deakin L, ferguson M J, Mar A. *Chem. Mater.*, **2001**,**13**:1407~1412

[10]Deakin L, Mar A. *Chem. Mater.*, **2003**,**15**:3343~3346

[11]Crerar S J, Deakin L, Mar A. *Chem. Mater.*, **2005**,**17**:2780~2784

[12]Chan J Y, Wang M E, Rehr A, et al. *Chem. Mater.*, **1997**,**9**:2131~2138

[13]Chan J Y, Wang M E, Kauzlarich S M. *Chem. Mater.*, **1998**, **10**:3583~3588

[14]Mozharivskyj Y, Franzen H F. *J. Solid State Chem.*, **200**0, **152**:478~485

[15]Haase M G, Schmidt T, Richter C G, et al. *J. Solid State Chem.*, **2002**,**168**:18~27

[16]Kim S J, Salvador J, Bilc D, et al. *J. Am. Chem. Soc.*, **2001**, **123**:12704~12705

[17]Papoian G A, Hoffmann R. *Angew. Chem. Int. Ed.*, **2000**,**39**:2428~2448

[18]Sun Z M, Mao J G, Pan D C. *Inorg. Chem.*, **2005**,**44**:6545~6549

[19]Mao J G, Goodey J, Guloy A M. *Inorg. Chem.*, **2004**,**43**:282~289

[20]Todorov I, evov S C. *Inorg. Chem.*, **2005**,**44**:5361~5369

[21]Todorov I, Sevov S C. *Inorg. Chem.*, **2004**,**43**:6490~6494

[22]Pan D C, Sun Z M, Mao J G. *J. Solid State Chem.*, **2006**,**179**:1032~1037

[23]CrystalClear Cersion 1. 3. 5. Rigaku Corporation, Woodlands, TX, **1999**.

[24]Sheldrick G M. *SHELXTL*-97, *Program for the Refinement of Crystal Structure*, University of Göttingen, Germany, **1997**.

[25]Ren J, Liang W, Whangbo M H. *CAESAR for Windows; Prime-Color Software*, *Inc*., North Carolina State University: Raleigh, NC, **1998**.

[26]Derrien G, Tillard-Charbonnel M, Manteghetti A, et al. *J. Solid State Chem.*, **2002**,**164**:169~175