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Synthesis and crystal structures of La_3MgBi_5 and $LaLiBi_2$

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Abstract

Two new ternary bismuthides, La_3MgBi_5 and $LaLiBi_2$, have been prepared by solid-state reactions of the corresponding pure metals in welded niobium tubes at high temperature. Their structures have been established by single-crystal X-ray diffraction studies. La_3MgBi_5 crystallizes in the hexagonal space group $P6_3/mcm$ (No.193) with cell parameters of $a = b = 9.7882(7)$ Å, $c = 6.5492(9)$ Å, $V = 543.41(9)$ Å^3, and $Z = 2$. $LaLiBi_2$ belongs to tetragonal space group $P4/nmm$ (No.129) with cell parameters of $a = b = 4.5206(4)$ Å, $c = 10.9942(19)$ Å, $V = 224.68(5)$ Å^3, and $Z = 2$. The structure of La_3MgBi_5 is of the "anti" Hf_5Sn_3Cu type, and features 1D linear Bi^- anionic chains and face-sharing $[MgBi_{6/2}]^{7-}$ octahedral chains. The structure of $LaLiBi_2$ is isotypic with $HfCuSi_2$, and is composed of 2D Bi^- square sheets and 2D LiBi layers with La^{3+} ions as spacers. Band calculations indicate that both compounds are metallic.

Keywords: Polar intermetallics; Solid-state reaction; Crystal structure; Bismuth compound; Mixed cation method

1. Introduction

During the past three decades, considerable efforts have been devoted to the studies of the ternary rare-earth transition metal antimonides, $RE_xM_ySb_z$ [1–18]. These antimonides exhibit varied electrical and magnetic properties arising from the interaction of *f* and *d* electrons. 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 [5–13], which is composed of 2D Sb^- square sheet and $[MSb]^{2-}$ layers with lanthanide cations as spacers, and $REMSb_3$ (M = Cr, V) [14–18]. It is interesting to note that $LaCrSb_3$ exhibits ferromagnetic ordering at T_C = 120−140 K and a spin-reorientation transition at T_{sr} = 95 K [18]. The corresponding transition metal bismuth analogs are relatively rare. A few Bi phases reported are $RE_{14}MPn_{11}$ (RE = Eu, Yb; M = Mn, In; Pn = Sb, Bi) with a $Ca_{14}AlSb_{11}$ structure [19,20], RE_5M_2Pn (M = Ni, Pd; Pn = Sb, Bi) with a Mo_5B_2Si structure [21]; $REMPn$ (M = Rh, Ni; Pn = Sb, Bi) with a TiNiSi structure [22], and $Yb_9Zn_4Bi_9$ features $[Zn_4Bi_9]^{19-}$ ribbons running along the *c*-axis [23].

It is possible that Li and Mg metals may replace the transition metals in above phases to form new polar intermetallic phases. Moreover, using two types of cations with different size and charge has been found to be an effective route for the preparation of novel polar intermetallic phases, due to the lessening of cation packing limitation and changing of electronic requirements [24–28]. The aim of our study is to explore the new intermetallic *Ln*–Li(Mg)–Bi ternary phases and to understand their crystal structures and chemical bonding as well as their electronic properties. By using this synthetic strategy, we have successfully synthesized two new rare-earth bismuth ternary phases, namely, La_3MgBi_5 and $LaLiBi_2$. Herein, we report their syntheses, crystal structures, and chemical bonding.

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2. Experimental

2.1. Synthesis

All manipulations were performed inside an argon-filled glove box with moisture level below 1 ppm. Magnesium turnings (99.9%, Acros), lithium ingot (99.9%, Aldrich), lanthanum chip (99.9%, Aldrich) and bismuth block (99.9%, Alfa) were used as received. Single crystals of La_3MgBi_5 were initially obtained by the solid-state reaction of magnesium (0.012 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, arc-welded and then sealed in an evacuated quartz tube ($\sim 10^{-4}$ Torr). The tube was put into an oven and heated at 980 °C for 2 days, and annealed at 800 °C for 7 days. Afterwards, the reaction tube was allowed to cool at a rate of 0.1 °C/min to the room temperature. Brick-shaped gray crystals of La_3MgBi_5 were obtained. Single crystals of $LaLiBi_2$ (brick in shape and gray in color) were obtained in a similar way by using lithium (0.069 g, 1.0 mmol) instead of magnesium. Several single crystals of La_3MgBi_5 and $LaLiBi_2$ were analyzed by using energy-dispersive X-ray spectroscopy (EDAX 9100), and the results indicate that atomic ratios to be 2.8: 1.0: 5.1 for La, Mg, and Bi in La_3MgBi_5 and 1: 2.2 for La and Bi in $LaLiBi_2$, respectively, which are in good agreement with those of the structural refinements. After the determination of single crystal structures, great efforts were subsequently made to synthesize pure phases of La_3MgBi_5 and $LaLiBi_2$. The reactions were carried out in a stoichiometric ratio of the metals, as well as using of an excess of ~20% lithium to compensate possible loss during arc welding. The samples were heated at 980 °C for 1 day, quenched in water, and annealing at different temperatures (600, 700, 800, and 850 °C, respectively, for each individual reaction) for 1 month. However, X-ray powder patterns of the resultant products revealed the presence of impurity phases, such as LaBi (*Fm3-m*), Mg_3Bi_2 (*P3-m1*), as well as other unidentified compounds. Attempts were also made to obtain the $LaMgBi_2$ phase, but only La_3MgBi_5 was formed. The highest yields of ~60% and ~70%, for La_3MgBi_5 and $LaLiBi_2$, were obtained by annealing at 800 and 700 °C, respectively. Physical properties were not measured due to the difficulty to obtain mono-phase products.

2.2. Crystal structure determination

Single crystals of La_3MgBi_5 (size: $0.15 \times 0.07 \times 0.04\,mm^3$) and $LaLiBi_2$ (size: $0.12 \times 0.12 \times 0.10\,mm^3$) were selected from the reaction products and sealed within thin-walled glass capillaries under an argon atmosphere. Data collections for both compounds were performed on a Rigaku Mercury CCD (Mo$K\alpha$ radiation, graphite monochromator) at room temperature. A total of 255 and 191 independent reflections for La_3MgBi_5 and $LaLiBi_2$, respectively, were measured, of which 238 and 176 reflections with $I > 2\sigma(I)$ were considered observed. Both data sets were 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 [29].

Both structures were solved using direct methods (SHELXTL) and refined by least-square methods with atomic coordinates and anisotropic thermal parameters [30]. The final stage of least-squares refinement showed no abnormal behaviors in the occupancy factors. The larger thermal parameters and their standard deviations in $LaLiBi_2$ are due to that the lithium atom is very light. Final difference Fourier maps showed featureless residual peaks of 3.208 (0.87 Å from Bi(1)) and $-2.477\,e Å^{-3}$ (0.65 Å from Bi(2)) for La_3MgBi_5; 4.688 (1.20 Å from La(1)) and $-2.670\,e Å^{-3}$ (1.18 Å from Bi(2)) for $LaLiBi_2$, respectively. The relatively higher residual peaks were due to the fact that bismuth element in the compound has a large atomic number, which may result in absorption correction problem and higher residual peaks. Crystal data and further details of data collection are given in Table 1, and the atomic coordinates, important bond lengths and angles are listed in Tables 2 and 3, respectively. Crystallographic data in CIF format for La_3MgBi_5 and $LaLiBi_2$ have been deposited as CSD number 415727 and 415728. 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. Band structure

3D band structure calculations for La_3MgBi_5 and $LaLiBi_2$ 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 [31]. The following atomic orbital energies and exponents were employed for the calculations (H_{ii} = orbital energy, ζ = Slater exponent): La 6s, $H_{ii} = -6.56$ eV, $\zeta = 2.14$; 6p, $H_{ii} = -4.38$ eV, $\zeta = 2.08$; 5*d*, $H_{ii} = -7.52$ eV, $\zeta = 3.78$ [32]; Bi 6s, $H_{ii} = -15.19$ eV, $\zeta = 2.56$; 6p, $H_{ii} = -7.79$ eV, $\zeta = 2.07$; Mg 3s, $H_{ii} = -9.00$ eV, $\zeta = 1.10$; 3p, $H_{ii} = -4.50$ eV, $\zeta = 1.11$; Li 2s, $H_{ii} = -5.40$ eV, $\zeta = 0.65$; 2p, $H_{ii} = -3.50$ eV, $\zeta = 0.65$.

3. Results and discussion

By using the "mixed cation" method, we obtained two new ternary bismuth phases, La_3MgBi_5 and $LaLiBi_2$. Results also indicate that magnesium and lithium can replace the transition metals in *Ln–TM*–Bi systems.

As shown in Fig. 1, La_3MgBi_5 can be regarded as an "anti"-type structure of Hf_5Sn_3Cu with the bismuth atoms on the hafnium sites, and lanthanum and magnesium atoms occupy the tin and copper sites, respectively. It is also isostructural with RE_3MSb_5 (M = Ti, Zr, Hf, Nb) reported previously [1–4]. Bi(2) atoms form a linear chain along the *c*-axis (Fig. 2a). Within the Bi chains, the Bi–Bi distance of 3.2746(5) Å corresponds to a Pauling