

Ternary Bismuthides Li_3REBi_2 ($\text{RE} = \text{Ce}, \text{Pr}, \text{Sm}, \text{Gd}$) with Li_3LaSb_2 -type Structure

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The ternary lithium bismuthides Li_3REBi_2 ($\text{RE} = \text{Ce}, \text{Pr}, \text{Sm}, \text{Gd}$) were synthesized from the elements in sealed niobium ampoules and characterized by powder X-ray diffraction. They crystallize with the Li_3LaSb_2 -type structure, space group $P\bar{3}m1$.

Key words: Lithium, Bismuthides, Rare Earth Compounds

Introduction

The CaAl_2Si_2 -type structure ($\equiv \text{Ca}^{2+}2\text{Al}^{3+}2\text{Si}^{4-}$) [1] occurs for a variety of alkaline earth tetrelides and pnictides and is also formed with divalent europium and ytterbium [2]. Striking examples are EuMn_2Sb_2 [3] or EuCd_2P_2 [4]. All these phases show Zintl-conform electron partitioning. Structurally related pnictides with a trivalent rare earth element can only be realized as a stuffed version with an additional cation, first observed for Li_3LaSb_2 [5]. Some isotypic phosphides, arsenides, and bismuthides have later been reported [6–11]. Interestingly, isopointal phases of compositions $\text{AE}_2\text{H}_3\text{X}$ ($\text{AE} = \text{Ca}, \text{Sr}, \text{Ba}$; $\text{X} = \text{Cl}, \text{Br}, \text{I}$) [12–16] as well as Fe_xZrSe_2 [17] have been presented.

These ternary lithium rare earth metal pnictides (Pn) are interesting candidates when searching for lithium mobility in the context of battery materials [18, 19]. We have recently studied the series of diamagnetic pnictides Li_3LaPn_2 ($\text{Pn} = \text{P}, \text{As}, \text{Sb}, \text{Bi}$) by temperature-dependent ^7Li solid-state NMR spectroscopy [11]. These investigations revealed almost fully ionized lithium, in agreement with the Zintl formulation $3\text{Li}^+\text{La}^{3+}2\text{Pn}^{3-}$. However, in all four com-

pounds the lithium atoms show no mobility on the NMR timescale. During further phase-analytic studies of the Li-RE-Bi systems we obtained the new bismuthides Li_3REBi_2 ($\text{RE} = \text{Ce}, \text{Pr}, \text{Sm}, \text{Gd}$) which are reported herein.

Experimental

Synthesis

Starting materials for the syntheses of the Li_3REBi_2 samples were small rare earth ingots (Smart Elements, > 99.5%), lithium rods (Merck, > 99%), and bismuth granules (ABCR, > 99.99%). The lithium rods were cut into small pieces under dried paraffin oil and the oxidized surface cusp was scratched off. The silvery pieces were then washed with dried (over sodium wire) cyclohexane and kept in Schlenk tubes under argon. The argon was purified over titanium sponge (900 K), silica gel and molecular sieves.

Lithium, rare earth metal, and bismuth pieces were then weighed in the ideal 3 : 1 : 2 ratios and arc-welded [20] in niobium tubes under reduced argon pressure of *ca.* 700 mbar. The arc-welded ampoules were subsequently sealed in evacuated silica ampoules for oxidation protection and then placed in a muffle furnace. The samples were first heated to 1273 K within 10 h, kept at this temperature for 6 h, followed by cooling to 923 K within 24 h. After a dwell time of 72 h at 923 K, the samples were cooled to r. t. within another 24 h. The samples were separated mechanically from the ampoules. No reactions with the niobium wall were evident. The dark-grey polycrystalline Li_3REBi_2 samples are sensitive to moisture and were kept in Schlenk tubes.

X-Ray diffraction

Basic characterization of the Li_3REBi_2 samples was carried out by powder X-ray diffraction using the Guinier technique: imaging plate detector, Fujifilm BAS-1800, $\text{CuK}\alpha_1$ radiation and α -quartz ($a = 491.30$, $c = 540.46$ pm) as an internal standard. The trigonal lattice parameters (Table 1) were

Table 1. Lattice parameters (Guinier powder data) of the trigonal bismuthides Li_3REBi_2 with Li_3LaSb_2 -type structure.

Compound	a (pm)	c (pm)	V (nm^3)	Reference
Li_3YBi_2	460.65(5)	729.0(1)	0.1340	[5]
Li_3LaBi_2	470.4(2)	752.7(3)	0.1442	[5]
Li_3CeBi_2	469.7(3)	750.6(3)	0.1434	this work
Li_3PrBi_2	468.2(2)	747.0(2)	0.1418	this work
Li_3SmBi_2	464.9(1)	738.0(1)	0.1381	this work
Li_3GdBi_2	462.8(3)	734.9(4)	0.1363	this work

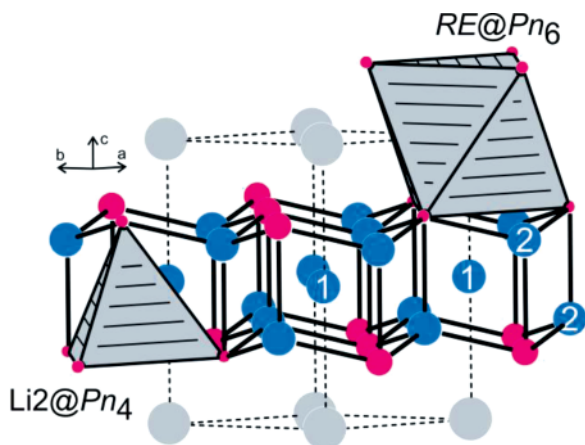


Fig. 1 (color online). View of the Li_3REPN_2 structure approximately along the (110) direction. Lithium, rare earth and pnictogen atoms are drawn as blue, medium gray and red circles, respectively. The two crystallographically independent lithium sites and relevant coordination polyhedra are emphasized.

deduced from least-squares refinements of the Guinier powder data. Correct indexing was ensured by comparison of the experimental patterns with calculated ones [21].

Discussion

The series of lithium-based pnictides Li_3REPN_2 has been extended by four new bismuthides (Table 1). They crystallize with the Li_3LaSb_2 type, space group $P\bar{3}m1$, with four independent Wyckoff sites: Li1 on 1b, Li2 on 2d ($z \sim 0.35$), RE on 1a, and Pn on 2d ($z \sim 0.74$). The Li2 and Pn atoms build up double layers of puckered Li_2Pn_3 hexagons which are filled by

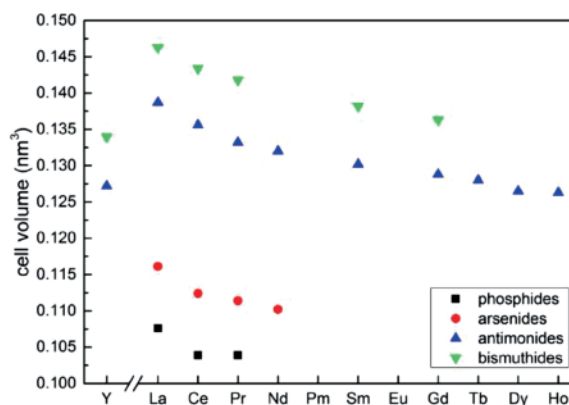


Fig. 2 (color online). Course of the cell volumes of the pnictides Li_3REPN_2 . The older data were taken from refs. [5–11].

the Li1 atoms (Fig. 1). These double layers are charge-compensated and separated by the rare earth cations which have octahedral pnictide coordination.

The changes in the cell volumes of the compounds in the four Li_3REPN_2 series follow the lanthanide contraction, and for a given rare earth element they increase from the phosphide to the bismuthide (Fig. 2). The phase-pure synthesis of these pnictides is difficult. Similar to the recent studies on the antimonide series [10], we also observed formation of small amounts of Li_3Bi and of the equiatomic REBi phases as by-products, which render systematic physical property studies difficult.

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