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A new ternary antimonide phase, LiBaSb

Laure Monconduit* and Claude Belin

Laboratoire des Agrégats Moléculaires et Matériaux Inorganiques, UMR 5072 CC15, Université de Montpellier II, Sciences et Techniques du Languedoc, 2 Place Eugène Bataillon, 34095 Montpellier CEDEX 5, France

Correspondence e-mail:
moncondu@univ-montp2.fr

Lithium barium antimony, LiBaSb, crystallizes in the centrosymmetric hexagonal space group $P6_3/mmc$. Ba atoms sit on positions with $\bar{3}m$ symmetry, while the Sb and Li atoms occupy sites of $\bar{6}2m$ symmetry. The structure of LiBaSb contains alternate hexagonal layers of (LiSb) and Ba. In this compound, antimony is present as isolated Sb^{3-} species. The Ba atom lies inside a hexagonal prism (6 × Li and 6 × Sb).

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(Li–Sb) = 0.0006 Å
R factor = 0.022
wR factor = 0.055
Data-to-parameter ratio = 16.0

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

The structure of LiBaSb has been determined in the centrosymmetric space group $P6_3/mmc$ (No. 194). Ba and Sb atoms were refined anisotropically, and an attempt to refine the Li atom anisotropically resulted in an uncertainties/U_{ij} ratio that was too large. This compound is isostructural with KZnSb (Savelsberg & Schaefer, 1986) and NaBeSb (Tiburtius & Schuster, 1977), but the atomic positions of the monovalent and divalent cations are exchanged. In the LiBaSb structure, Li occupies the $\bar{6}m2$ site and Ba the $\bar{3}m$ site, while in KZnSb (or NaBeSb), K (or Na) sits at $\bar{3}m$ and Zn (or Be) at $\bar{6}m2$. The ionic radius of Li^+ (0.90 Å) is closer to that of Zn^{2+} (0.88 Å) (or Be^{2+} 0.60 Å) than to that of K^+ (1.52 Å) [or Na^+ (1.20 Å)]. This favors exchange of monovalent/divalent atom positions. This structure can be considered as a filled NiAs-type structure or is better described as a substituted Li_3Sb structure; one Ba^{2+} substitutes two Li^+ cations. The LiBaSb structure adopts the same space group as Li_3Sb. Owing to the very large size of the barium cations (Ba^{2+} 1.49 Å) compared with Li^+ (0.9 Å), the cell parameters of the ternary phase are expanded (a = 4.701 Å and c = 8.309 Å in Li_3Sb). Atomic positions are different from those in the binary phase. The structure of LiBaSb may be described with hexagonal prisms $Ba(Li_3Sb_3)_2$ fused along the c axis. The barium cations are surrounded by 6 Li and 6 Sb atoms at 3.616 (1) Å. The Sb atoms are coordinated to three Li cations at 2.828 Å, close to the Li—Sb distance in Li_3Sb (2.71 and 2.77 Å), and to six Ba cations at 3.616 (1) Å.

Unlike the parent $Li_4Ba_3As_4$ compound (Monconduit & Belin, 1999), which contains two anionic moieties, namely As_2^{4-} dumbbells and isolated As^{3-} anions, and was characterized as a large band semi-conductor, the LiBaSb ($Li^+Ba^{2+}Sb^{3-}$) compound contains only isolated Sb^{3-} anions in association with Li^+ and Ba^{2+} cations and is an insulator.

Experimental

With the aim of obtaining the ternary compound $Li_4Ba_3Sb_4$, amounts of Li, Ba and Sb (in proportion 4/3/4) were inserted in a niobium

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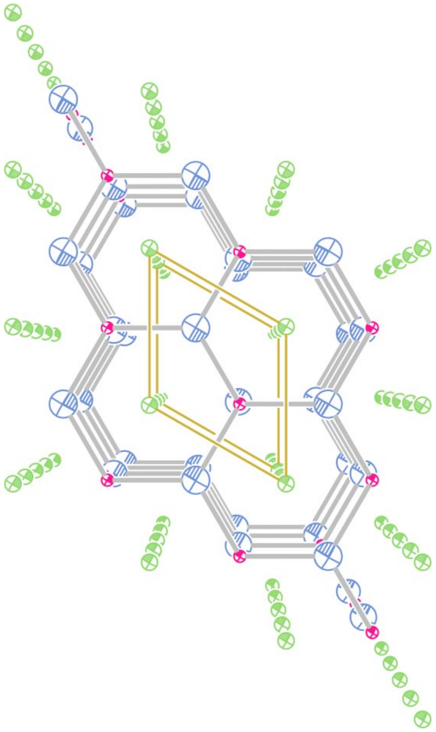

Figure 1
Representation of the hexagonal unit cell of LiBaSb. Barium cations are shown inside the hexagonal Li_6Sb_6 prism. Li atoms are represented by blue circles, Ba atoms by green circles and Sb atoms by red circles. Displacement ellipsoids are drawn at the 90% probability level.

reactor, then weld-sealed under argon. The niobium reactor was protected against oxidation inside an evacuated silica tube. Single crystals of LiBaSb were obtained as side products by heating the initial mixture at 780 K for 10 h, maintaining at 580 K for 3 d and quenching in air. Elemental analyses (SEM) of crystals confirmed the presence of barium and antimony approximately in the ratio 1:1. The air-sensitive crystals were inserted into Lindemann glass capillaries for X-ray data investigations.

Crystal data

LiBaSb
$M_r = 266.03$
Hexagonal, $P6_3/mmc$
$a = 4.8982\ (10)$ Å
$c = 9.014\ (3)$ Å
$V = 187.29\ (9)$ Å^3
$Z = 2$
$D_x = 4.717$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 9.6–19.5°$
$\mu = 17.38$ mm^{-1}
$T = 293\ (2)$ K
Roughly spherical, metallic light grey
0.07 × 0.06 × 0.05 mm

Data collection

Nonius CAD- 4 diffractometer
$\omega–\theta$ scans
Absorption correction: numerical
$T_{min} = 0.439$, $T_{max} = 0.541$
552 measured reflections
128 independent reflections
123 reflections with $I > 2\sigma(I)$
$R_{int} = 0.041$
$\theta_{max} = 29.8°$
$h = -6 \rightarrow 6$
$k = -6 \rightarrow 6$
$l = 0 \rightarrow 12$
3 standard reflections
every 100 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.022$
$wR(F^2) = 0.055$
$S = 1.08$
128 reflections
8 parameters
$(\Delta/\sigma)_{max} = 0.009$
$\Delta\rho_{max} = 0.44$ e Å^{-3}
$\Delta\rho_{min} = -0.74$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.083 (8)

Table 1
Selected geometric parameters (Å).

Ba—Sb	3.6160 (7)	Sb—Li	2.8280 (6)
Ba—Li	3.6160 (7)		

Parameters and crystallographic space group were initially determined by oscillation and Weissenberg techniques. The best diffracting crystal was used for accurate intensity measurements on a CAD-4 Nonius diffractometer. Space group was found to be $P6_3/mmc$ (No. 194) (observation conditions: $00(0)l$ for $l = 2n$ and $hh(-2h)l$ for $l = 2n$). All computations were carried out on a Pentium II 266 computer. The structure representation has been drawn with the program *ORTEP*-3 *for Windows* (Farrugia, 1997) which is a MS–Windows version of the current release of *ORTEP*III (Burnett & Johnson, 1996).

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software* (Enraf–Nonius, 1989); data reduction: local program; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997).

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