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Crystal structure, electronic structure and electrical conductivity of the antimony selenide $BaLaSb_2Se_6$

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ABSTRACT

$BaLaSb_2S_6$ and $BaLaSb_2Se_6$ were prepared by heating the elements in the stoichiometric ratio under exclusion of air at 850 °C. Both chalcogenides adopt the $KThSb_6Se_6$ structure type, crystallizing in the space group $P2_1/c$ ($Z = 4$) with $a = 4.324(3)$ Å, $b = 14.7057(16)$ Å, $c = 15.910(2)$ Å, $\beta = 92.741(3)°$, $Z = 4$ for the sulfide and $a = 4.4173(3)$ Å, $b = 15.333(1)$ Å, $c = 16.816(1)$ Å, $\beta = 92.545(2)°$, $Z = 4$ for the selenide. The structure of $BaLaSb_2Se_6$ is composed of ribbons of distorted $SbSe_6$ octahedra and Se_2^{2-} pairs. Electronic structure calculations show that the selenide is a semiconductor, in accord with the electrical conductivity measurement.

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1. Introduction

Binary lanthanum and antimony chalcogenides may be potential thermoelectric materials [1,2]. This is true for sulfides, selenides, and tellurides alike, e.g. Sb_2S_3 [3] and Sb_2Te_3 [4,5], a major component of the Bi_2Te_3/Sb_2Te_3 thin film device with $ZT > 2$ [6]. Similarly, several reports about lanthanum sulfides [7–10], selenides [11] and tellurides [12–14] are testimony to the interest in lanthanum chalcogenides. For example, γ-$La_{3-\delta}S_4$ ($\delta = 0.33$, Th_3P_4 type) attained a ZT value of 0.5 at 1000 K [7], and isostructural $La_{3-\delta}Te_4$ achieved $ZT = 1.1$ at 1275 K [15].

During our investigation of the system La-Sb-Q, (Q = S, Se, Te) we discovered $La_{7+\delta}Sb_{9-\delta}S_{24}$, which exists on the quasi-binary section La_2S_3–Sb_2S_3. Therein, one site is mixed occupied by La and Sb atoms in a new structure type, giving rise to a small phase width [16]. As we were unable to identify new selenides and tellurides in that system, we added a third heavy cation, namely Ba, and subsequently synthesized two new chalcogenides, namely $BaLaSb_2S_6$ and $BaLaSb_2Se_6$, which are being introduced with this contribution.

2. Experimental section

2.1. Synthesis and analysis

The quaternary antimony chalcogenides were synthesized from the elements in the stoichiometric 1:1:2:6 ratio. The elements were stored in an argon-filled glovebox (Ba, pieces, 99.999%, Aldrich; La, powder, −40 mesh, 99.9%, Alfa Aesar; Sb, powder, −100 mesh, 99.5%, Aldrich; S, pieces, 99.999%, Alfa Aesar; Se, powder, −100 mesh, 99.99%, Sigma Aldrich). Because of the air and moisture sensitivity of barium and lanthanum, they were purchased in small amounts and – prior to use – checked for any oxide traces on the surface. The elements were weighed accordingly and placed into silica tubes, which were then sealed under dynamic vacuum.

The sealed tubes were heated in a resistance furnace to 850 °C and kept at that temperature for four days, followed by slow cooling to 300 °C. Then, the furnace was switched off to cool to room temperature. Black needle-like crystals were formed. Phase pure $BaLaSb_2Se_6$ was obtained by annealing the sample at 800 °C for two weeks. Attempts of replacing lanthanum with samarium or with yttrium resulted in mixtures of binary and ternary compounds, namely Ln_2Se_3, Sb_2Se_3 and $BaLn_2Se_4$.

Powder diagrams of the ground samples were collected for 20 min in the 2θ-range between 5° and 110° utilizing the INEL powder diffractometer with position-sensitive detector and Cu-Kα radiation. Only reflections of the title compounds were found in the powder diagrams.

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Table 1
Crystallographic data of $BaLaSb_2Q_6$.

Empirical formula	$BaLaSb_2Se_6$	$BaLaSb_2S_6$
Formula weight/(gmol^{-1})	933.51	712.11
Temperature/K	298(2)	298(2)
Wavelength/Å	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a/Å	4.4173(3)	4.324(3)
b/Å	15.333(1)	14.73(2)
c/Å	16.816(1)	15.93(2)
β/°	92.545(2)	92.70(3)
Volume/Å^3	1137.8(1)	1014(2)
Z, Density/(gcm^{-3})	4, 5.80	4, 4.67
Absorption coeff./mm^{-1}	30.919	14.397
F(000)	1676	1244
Crystal size/mm^3	0.140 × 0.080 × 0.060	0.090 × 0.020 × 0.006
Independent reflections, R_{int}	3310, 0.0324	
Refinement method	Full-matrix least-squares on F^2	
Data\restraints\parameters	3310\0\92	
Goodness-of-fit on F^2	1.050	
R indices (all data)	$R1 = 0.0290$ $wR2 = 0.0578$	
Largest diff. peak and hole/(e Å^{-3})	3.35 and −1.36	

EDS analysis using LEO 1530, with integrated EDAX Pegasus 1200, with an acceleration voltage of 21 kV, showed the presence of all four elements in all selected crystals in the approximate 1:1:2:6 ratio, consistent with the formula $BaLaSb_2Se_6$ obtained from the single crystal structure refinement.

2.2. Crystal structure determination

Data collections were carried out on a Smart Apex CCD (Bruker) at room temperature utilizing Mo-Kα radiation on needle-like single crystals. The data were collected overnight by ω scans of 0.3° in two blocks of 606 frames at $\varphi = 0°$ and 120°, with exposure times of 60 s per frame. The data were corrected for Lorentz and polarization effects using the program SAINT, and absorption corrections were based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements using SADABS, because the crystal faces could not be determined reliably for numerical absorption corrections [17].

The structure of $BaLaSb_2Se_6$ was solved via the direct method and refined using the least-squares method within the SHELXTL package [18]. After realizing that $BaLaSb_2Se_6$ adopts the $KThSb_6Se_6$ structure [19], its published coordinates were used for the final refinement to ease comparison. A refinement of the structure of $BaLaSb_2S_6$ failed because of the small size of the crystal, and all needles of this sulfide were consistently too thin for single crystal structure studies. The lattice parameters and the matching powder diagram experimentally obtained are indicative of $BaLaSb_2S_6$ adopting the same structure type. Crystallographic details are summarized in Table 1, atomic coordinates of the selenide in Table 2, and selected interatomic distances of the selenide in Table 3. Further details of the crystal structure investigation can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, (fax: (49) 7247 808 666; e-mail: crysdata@fiz-karlsruhe.de) on quoting the depository number CSD- 421269.

Table 2
Fractional atomic coordinates and equivalent isotropic displacement parameters of $BaLaSb_2Se_6$.

Atom	Wykoff	x	y	z	U_{eq}/Å^2
Ba1	4e	0.2613(1)	0.7913(1)	0.1728(1)	0.015(1)
La1	4e	0.2941(1)	0.6278(1)	0.4066(1)	0.012(1)
Sb1	4e	0.6995(1)	0.8688(1)	0.4735(1)	0.017(1)
Sb2	4e	0.7264(1)	0.5281(1)	0.1962(1)	0.016(1)
Se1	4e	0.2540(2)	0.8288(1)	0.3724(1)	0.018(1)
Se2	4e	0.7680(1)	0.7089(1)	0.5228(1)	0.014(1)
Se3	4e	0.6978(2)	0.0885(1)	0.4101(1)	0.020(1)
Se4	4e	0.7779(1)	0.6742(1)	0.2784(1)	0.014(1)
Se5	4e	0.3298(2)	0.4668(1)	0.2938(1)	0.018(1)
Se6	4e	0.8278(1)	0.4865(1)	0.4422(1)	0.015(1)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3
Selected bond distances in $BaLaSb_2Se_6$.

Bond	Distance/Å	Bond	Distance/Å
Ba–Se2	3.2604(7)	La–Se2	3.0620(7) × 2
Ba–Se5	3.2751(8)	La–Se5	3.1225(8)
Ba–Se4	3.3496(7)	La–Se1	3.1386(8)
Ba–Se4	3.3568(7)	La–Se4	3.1498(7)
Ba–Se1	3.4056(7)	La–Se6	3.1537(7)
Ba–Se3	3.4165(8)	La–Se4	3.1835(7)
Ba–Se2	3.4470(7)	La–Se6	3.2386(7)
Ba–Se6	3.5752(8)	La–Se2	3.3406(7)
Ba–Se5	3.8079(8)		
Sb1–Se2	2.6021(8)	Sb2–Se5	2.6266(8)
Sb1–Se1	2.6154(8)	Sb2–Se4	2.6368(8)
Sb1–Se3	2.7654(8)	Sb2–Se3	2.6963(8)
Sb1–Se1	3.104(3)	Sb2–Se5	3.208(3)
Sb1–Se3	3.300(3)	Sb2–Se1	3.269(1)
Sb1–Se3	3.532(1)	Sb2–Se3	3.306(3)
Se6–Se6	2.451(1)		

2.3. Electronic structure calculation

The electronic structure of $BaLaSb_2Se_6$ was computed employing the LMTO method (linear muffin tin orbitals), which utilizes the atomic spheres approximation (ASA) [20,21]. In the LMTO approach, the density functional theory is used with the local density approximation (LDA) to approximate the exchange-correlation energy functional [22]. The integration in k space was performed by

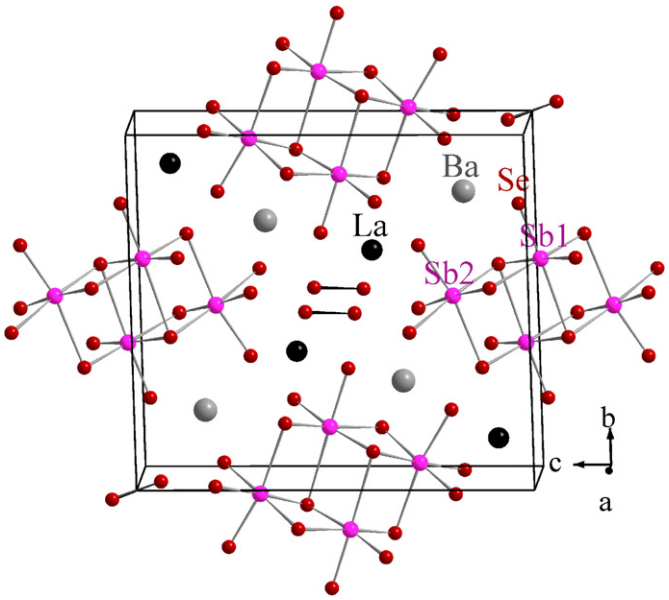

Fig. 1. Crystal structure of $BaLaSb_2Se_6$. Ba–Se and La–Se bonds were omitted for clarity.

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