$KThSb_2Se_6$ and $BaLaBi_2Q_6$ ($Q = S, Se$) Adopt a New Structure Type Stabilized with Dichalcogenide Groups

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Recently, there is renewed interest in the solid-state chemistry of Bi and Sb chalcogenide compounds because of their relevance in thermoelectric applications. This class of compounds is responsible for the astoundingly rich structural and compositional diversity of mineral sulfosalts. The plethora of structural and compositional types in the mineral sulfosalts derives from the ability of the Bi and Sb lone ns^2 pair to stereochemically express itself. Most of the known synthetic chalcoantimonate and bismuthate compounds are ternary phases with alkali or alkaline-earth metal (e.g. K_3SbSe_4,[1] $RbSb_3Se_5$,[2] $Cs_3Sb_5Se_9$,[3] $RbBiQ_2$ ($Q = S, Se$),[4] $RbBi_3S_5$,[5] $CsBi_3S_5$,[6] $Sr_4Bi_6Se_{13}$,[7] and α- and β-$BaBi_2S_4$[8]). Many ternary compounds with transition metal (e.g., Cu_3SbSe_4[9]) or main group metal (e.g. $PbSb_2Se_4$,[10] $Tl_4Bi_2S_5$[11]) are also known, most of them minerals. Recently, we reported on the synthesis and thermoelectric properties of several new ternary Bi chalcogenide compounds such as $K_2Bi_8S_{13}$,[12] $KBi_{6.33}S_{10}$,[12] α-[13] and β-$K_2Bi_8Se_{13}$,[14] $K_{2.5}Bi_{8.5}Se_{14}$,[14] and $BaBiTe_3$.[15] Much less is known about the solid-state chemistry of quaternary compounds, and so this communication deals with some of the first members of this class.

The compound $KThSb_2Se_6$ was first prepared by the flux method,[16] but later we found that it could also be prepared with a direct stoichiometric combination reaction.[17] Similar reactions with La/Ba/Bi/Q ($Q = S, Se$) at 830 °C led to two isostructural chalcobithmuthates, $BaLaBi_2Q_6$[18] ($Q = S, Se$). The similar sizes between K^+ and Ba^{2+} and Th^{4+} and La^{3+} and the retention of the isoelectronic relationship between the K^+/Th^{4+} and Ba^{2+}/La^{3+} pairs explain the isostructural nature of these compounds. Since all three compounds have the same structure shown in Figure 1A, only $KThSb_2Se_6$ will be discussed in detail.

$KThSb_2Se_6$ has a three-dimensional tunnel framework with Th^{4+} centers. The K^+ filled tunnels run parallel to the *a*-axis. The compound contains diselenide ions, Se_2^{2-}, and so it could be described as $K^+Th^{4+}Sb_2^{3+}(Se^{2-})_5(Se_2)^{2-}_{0.5}$. The coordination geometry around the Th is a 9-coordinate tricapped trigonal prism. A notable feature in this structure is that Th atoms form one-dimensional infinite double chains parallel to the [100] direction. Three of the Se atoms bound to Th belong to diselenide groups. The latter play an important role in the construction of the double chains, see Figure 1B, by bridging single chains composed of $ThSe_6$ prisms sharing opposite

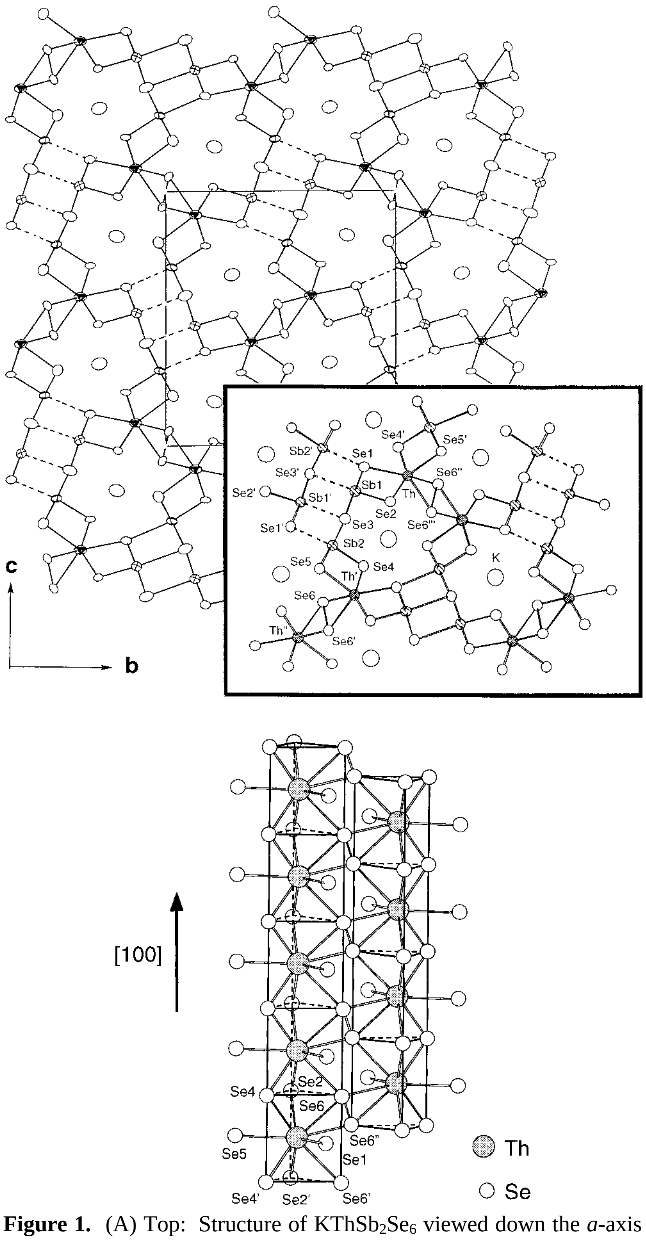

Figure 1. (A) Top: Structure of $KThSb_2Se_6$ viewed down the *a*-axis with thermal vibrational (98%) ellipsoids. The atom-labeling scheme is shown in the inset. The labeling scheme for the $BaLaB_2Se_6$ is analogous. The K ions are surrounded by nine Se atoms with an average K−Se distance of 3.45 Å. (B) Bottom: Double chains of Th atoms run in the [100] direction. Each single chain is composed of $ThSe_6$ prisms sharing opposite triangular faces.

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Table 1. Selected Bond Distances and Angles for $KThSb_2Se_6$ and $BaLaBi_2S_6$ (M = Th, La, B = Sb, Bi, Q = Se, S)

	$KThSb_2Se_6$	$BaLaBi_2S_6$		$KThSb_2Se_6$	$BaLaBi_2S_6$
		Bond Distances (Å)			
M−Q(1)	3.086(2)	3.052(6)	B(1)−Q(2)	2.629(2)	2.554(6)
M−Q(2)	2.968(2)	2.937(6)	B(1)−Q(3)	3.413(2)	3.350(6)
M−Q(2)	3.135(2)	3.212(6)	B(1)−Q(3)	3.223(2)	3.102(7)
M−Q(4)	3.059(2)	3.030(6)	B(1)−Q(3)	2.791(2)	2.829(7)
M−Q(4)	3.024(2)	3.026(6)	B(2)−Q(1)	3.262(2)	3.093(6)
M−Q(5)	3.049(2)	3.008(6)	B(2)−Q(3)	3.239(2)	3.116(7)
M−Q(6)	3.154(2)	3.148(7)	B(2)−Q(3)	2.731(2)	2.739(7)
M−Q(6)	3.142(2)	2.984(7)	B(2)−Q(4)	2.644(2)	2.592(6)
M−Q(6)	3.052(2)	2.911(5)	B(2)−Q(5)	3.070(2)	2.970(7)
B(1)−Q(1)	3.035(2)	2.878(7)	B(2)−Q(5)	2.636(2)	2.633(6)
B(1)−Q(1)	2.632(2)	2.627(7)	Q(6)−Q(6)	2.494(4)	2.14(1)
		Bond Angles (deg)			
Q(1)−M−Q(2)	74.32(5)	73.4(2)	Q(1)−B(1)−Q(2)	89.85(7)	90.3(2)
Q(1)−M−Q(6)	134.46(5)	134.1(2)	Q(1)−B(1)−Q(3)	175.42(7)	177.8(2)
Q(2)−M−Q(4)	144.05(5)	142.3(2)	Q(1)−B(1)−Q(3)	89.19(6)	89.1(2)
Q(2)−M−Q(6)	71.85(5)	69.5(2)	Q(2)−B(1)−Q(3)	94.75(7)	90.6(2)
Q(4)−M−Q(5)	73.72(5)	75.4(2)	Q(1)−B(2)−Q(3)	92.23(6)	95.2(2)
Q(4)−M−Q(6)	78.91(5)	82.0(2)	Q(1)−B(2)−Q(4)	170.66(7)	170.3(2)
Q(5)−M−Q(6)	92.81(5)	91.8(2)	Q(1)−B(2)−Q(5)	86.06(6)	84.5(2)
M−Q(6)−M	132.64(6)	137.5(2)	Q(3)−B(2)−Q(4)	93.06(6)	90.8(2)
M−Q(6)−M	87.09(5)	88.5(2)			

triangular faces. The Th double chains are separated by bridging $[Sb_4Se_{10}]_n$ blocks. Each Se_2^{2-} is simultaneously connected to four Th atoms in an arrangement unusual for a dichalcogenide. This extensive bonding gives rise to a longer Se−Se distance of 2.494(4) Å than normal of 2.34 Å. The corresponding S−S distance in $BaLaBi_2S_6$ is 2.14(1) Å also longer than the normal of 2.05 Å.

The Sb^{3+} ion occupies two different sites in this structure. Both Sb^{3+} centers have three short Sb−Se bonds (see solid lines in Figure 1A) ranging from 2.629(2) to 2.791(2) Å and three longer bonds (see dotted lines) ranging from 3.035(2) to 3.413(2) Å indicating that the coordination geometry of Sb^{3+} is intermediate between trigonal pyramidal and octahedral. However, because the longest distance is still shorter than the sum of the Sb−Se van der Waals radii (3.510 Å) the local symmetry of Sb^{3+} is regarded as distorted octahedral. The gross distortion of $SbSe_6$ octahedra is due to the stereochemically active lone pair of Sb^{3+} ions. The $SbSe_6$ octahedra share edges with neighboring octahedra. In $BaLaBi_2S_6$ the geometry around the Bi atoms is much less distorted and closer to octahedral; see Table 1.

The compounds reported here are valence-precise and should be semiconductors. The absorption spectra confirm this by showing the presence of abrupt optical gaps. For $KThSb_2Se_6$ we observe two absorption edges at 0.95 and 0.80 eV suggesting the presence of closely lying gaps. The band gap of $BaLaBi_2S_6$ is 0.85 eV. $KThSb_2Se_6$ melts incongruently at 659 °C decomposing to $ThSe_2$ and unidentified K/Sb/Se compounds. $BaLaBi_2S_6$ and $BaLaBi_2Se_6$ melt congruently at 908 and 866 °C, respectively.

$KThSb_2Se_6$ and $BaLaBi_2Q_6$ (Q = S, Se) represent new structural types in which the multiply bonded Q_2^{2-} groups are key for stabilization. In the $BaLnBi_2Q_6$ family we have already prepared many more members. Once the Q_2^{2-} group is ensured, the structure type seems to be exceptionally stable so long as cations with large ionic radii and isoelectronic relationship with the K^+/Th^+ pair are used.

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Note Added in Proof. While this paper was in the galley proof stage, we became aware that the recently reported compounds $K_2(RE)_{2-x}Sb_{4+x}Se_{12}$ (RE = La, Ce, Pr, Gd) are related to those reported here and contain Se_3^{2-} groups. This implies a much larger stability range for this structure type than even what is credited here. See: Chen, J. H.; Dorhout, P. K. *J. Alloys Compd.* **1997**, *249*, 199.

Supporting Information Available: Tables listing detailed crystallographic data, atomic positional and thermal parameters, bond length and angles, and calculated and observed X-ray powder patterns of $KThSb_2Se_6$ and $BaLaBi_2S_6$ (29 pages). Ordering information is given on any current masthead page.

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(17) (a) Single crystals of $KThSb_2Se_6$ were obtained from a mixture of Th (2 mmol), Sb_2Se_3 (4 mmol), K_2Se (2 mmol), and Se (20 mmol) that was sealed under vacuum in a pyrex tube and heated to 540 °C for 5 days followed by cooling to 150 °C at 3°/h. The excess $K_xSb_ySe_z$ flux was removed with DMF to reveal black needle crystals (yield 20%). The crystals are air- and water-stable. Pure material was obtained by heating Th/K_2Se/Sb_2Se_3/Se in a stoichiometric ratio in a quartz tube at 650 °C for 4 days. (b) A Siemens SMART platform CCD diffractometer was used to collect data from a crystal of 0.5 × 0.04 × 0.04 mm dimensions and Mo Kα ($\lambda = 0.710\,73$ Å) radiation. An empirical absorption correction was applied to the data. Crystal data at 23 °C: $a = 4.2676(1)$ Å, $b = 15.1746(4)$ Å, $c = 16.9909(4)$ Å, $\beta = 92.217(1)°$, $Z = 4$, $D_{calc} = 6.230$ g/cm^3, space group $P2_1/c$ (No. 14), μ(Mo Kα) = 376.39 cm^{-1}; index range $-5 < h < 5$, $0 < k < 18$, $0 < l < 20$; total data, 5557; unique data, 2011 ($R_{int} = 0.0514$); data with $F_o^2 > 3\sigma(F_o)^2$, 1530; no. of variables, 91; final $R/R_w = 0.045/0.050$, GOF = 1.67. (c) Reagents: The purity in every case was better than 99.9%.

(18) (a) $BaLaBi_2S_6$ was synthesized by mixing Ba/La/Bi/S in a stoichiometric ratio. The mixture was sealed under vacuum in a carbon coated tube and heated to 830 °C for 5 days followed by cooling to 530 °C at 10 °C/h and then to 100 °C in 12 h. The product was washed with degassed water, methanol, and ether (yield > 95%). (b) A Rigaku AFC6S four-circle automated diffractometer was used to collect data (ω scan) from a crystal of 0.4 × 0.035 × 0.035 mm dimensions and Mo Kα ($\lambda = 0.710\,69$ Å) radiation. An empirical absorption correction based on ψ scans was applied to the data. Crystal data at −100 °C: $a = 4.232(4)$ Å, $b = 14.787(5)$ Å, $c = 16.360(9)$ Å, $\beta = 92.22(6)°$, $Z = 4$, $D_{calc} = 5.755$ g/cm^3, space group $P2_1/c$ (No. 14), μ(Mo Ka) = 432.3 cm^{-1}; angle range 5.0−60.0° in 2θ; total data, 3536; unique data, 3036; data with $F_o^2 > 3\sigma(F_o^2)$, 1551; no. of variables, 91; final $R/R_w = 0.046/0.045$, GOF = 1.58. (c) Under the same heating profile a stoichiometric ratio of Ba/Bi_2Se_3/La/Se gave the isostructural phase $BaLaBi_2Se_6$ as evidenced by X-ray powder-diffraction (yield > 95%).