Synthesis and Characterization of Ba_2SnTe_5: A New Zintl Phase Containing Unique One-Dimensional Chains of $(SnTe_3)^{2-}$ and Dimeric Units of $(Te_2)^{2-}$

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Syntheses of solid-state chalcogenides at intermediate (200−500 °C) and low (<200 °C) temperatures have led to the discovery of many novel compounds having unique structures and interesting properties. Synthetic routes that have been developed and employed in the crystal growth of these materials include crystallization from alkali-metal polychalcogenide salts (fluxes),[1] reactions involving nonaqueous solvents,[2] solvent extraction of intermetallic phases,[3] electrochemical dissolution of alloy electrodes,[4] and hydro(solvo)thermal synthesis.[5] One of the areas we have been pursuing is investigation of mixed-metal tellurides. By applying flux growth techniques, we have prepared and characterized structures of a number of new compounds in this category.[6−8] In most of the reactions, the alkali-metal polytelluride salt serves both as a flux and as a reactant, so that the alkali metals are usually found in the final products. We have found, however, several cases in which the products do not contain these metals. Such exceptions seem more pronounced when alkaline-earth metals are involved in the reactions.[8−10] In this communication we report the synthesis, structure determination and electronic properties of Ba_2SnTe_5, the first ternary barium metal telluride crystallized from a potassium polytelluride flux.

Bronze-colored, platelike crystals of Ba_2SnTe_5 (**1**) can be obtained from molten-salt reactions using either a Na_2Te/BaTe/Te or a K_2Te/BaTe/Te flux. The precursors Na_2Te, K_2Te, and BaTe were prepared by stoichiometric reactions of metals with tellurium in liquid ammonia.[11] The crystal used for the data collection was grown from a sample containing 0.1029 g (0.5 mmol) of K_2Te (K 98%, Te 99.8%, Strem Chemicals, Inc.), 0.3974 g (1.5 mmol) of BaTe (Ba 99.9%, Strem Chemicals, Inc.), 0.0594 g (0.5 mmol) of Sn (99.8%, Aldrich Chemical Co.) and 0.3190 g (2.5 mmol) of Te. The starting materials were weighed and mixed in a glovebox and subsequently sealed in a Pyrex tube under vacuum. The temperature was raised slowly to 450 °C (over 10 h) and the sample was kept at this temperature for 4 days. The tube was then cooled to 150 °C at a rate of 4 °C/h. The final product was isolated from the excess flux by washing first with dimethylformamide (DMF) followed by absolute ethanol (100%) and anhydrous diethyl ether. Microprobe analysis gave approximately an atomic ratio of Ba:Sn:Te = 2:1:5. Crystals of **1** were also found in other reactions where a different temperature (525 °C), different flux, and different ratio of the starting materials (Na_2Te/BaTe/Sn/6Te or Na_2Te/2BaTe/2Sn/6Te) were used.

The crystal structure of **1** was analyzed by X-ray diffraction methods.[12] Ba_2SnTe_5 is a Zintl phase containing two types of Zintl anions, the $(SnTe_3)^{2-}$ one-dimensional (1-D) chain and the $(Te_2)^{2-}$ dimer. The alkaline-earth-metal ions, Ba^{2+}, are located between the anionic layers filled by these chains and dimers (see Figure 1) and are in a 9-coordinated arrangement (9 × 3.62(3)Å (ave) Ba···Te long contacts) of a distorted capped square antiprism (point symmetry C_4). The distorted $SnTe_4$ tetrahedra form "Zweireinfach"-chains[13] by sharing common corners (see Figure 2, top). The chain, having a periodicity of two $SnTe_4$ tetrahedra, runs parallel to [1 0 0] with band symmetry $P2_1am$ (No. 26),[14] with each tetrahedron alternatively twisted by ±180° respect to each other. The corrugation of tetrahedra along the chain is measured by a small stretching

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(12) Crystal data for Ba_2SnTe_5: orthorhombic, *Pnma* (No. 62), a = 6.825(1), b = 24.476(5), c = 6.889(1) Å, V = 1150.8(3) Å^3, Z = 4. Dc = 5.953 Mg m^{-3}, Mo Kα radiation (λ = 0.710 73 Å), μ = 212.76 cm^{-1}. The data collection was performed at 293 K on an Enraf-Nonius CAD-4 diffractometer, by the ω-scan method, within the limits $3 < \theta < 27°$. The structure was solved by direct methods (SIR92) and refined by full-matrix least-squares against F_o^2 (SHELX93). The final agreement indexes R = 0.054 and $wR2$ = 0.156 for 1196 independent significant ($I > 3\sigma(I)$) absorption corrected data. The high value of $wR2$ reflect the high variance in the transmission coefficient for the Ψ-scan absorption correction, partially balanced with the data collection of two equivalents for each reflection [R(int) = 0.0254]. Anisotropic thermal factors were assigned to all atoms. EDX analysis gave a averaged Ba/Sn/Te ratio of in agreement with the molecular formula.
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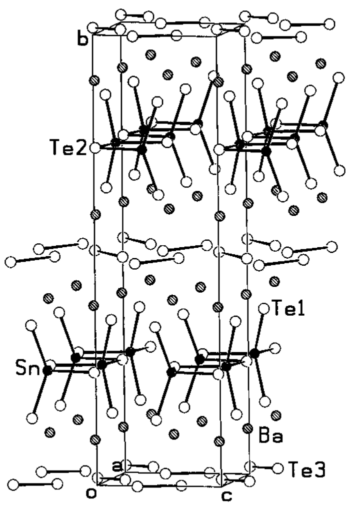

Figure 1. View of the unit-cell content of Ba_2SnTe_5. Important bond distances (Å) and angles (deg): Sn–Te(1) 2.7299(14), 2.7300(14); Sn–Te(2) 2.806(2), 2.825(2); Te(3)–Te(3) 2.808(3); Ba···Te 8× 3.62(3); Te(1)–Sn–Te(1) 135.07(8), Te(2)–Sn–Te(2) 112.87(7), Sn–Te(2)–Sn 93.07(6).

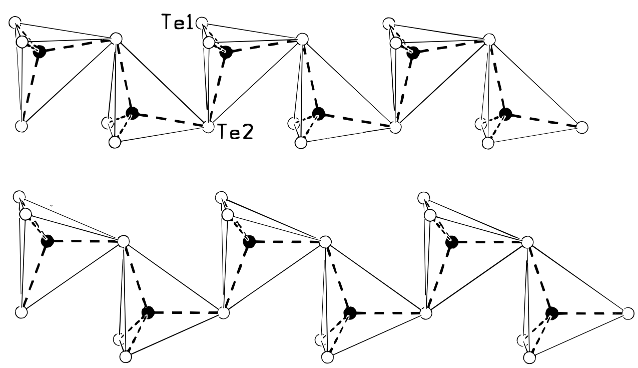

Figure 2. View of the 1-D chain of $(SnTe_3)^{2-}$ with the outline of the distorted tetrahedra (top) to be compared with an idealized 1-D chain of regular tetrahedra (Sn–Te 4× 2.77 Å Te–Sn– and Sn–Te–Sn 109.47; bottom). The real chain has a shorter period hence a smaller f_s (0.727 vs 0.816).

factor[13] $f_s = 0.727$ (smaller than an ideal chain formed from regular tetrahedra with $f_s = 0.816$ (see Figure 2, bottom)). To our knowledge this is the first example of 1-D chain formed by corner-sharing tetrahedra with $P2_1am$ band symmetry among all known compounds containing MX_4 tetrahedra (M = group 14, X = group 16 elements). Chains that have lower symmetry and are more stretched have been observed in Na_2SnSe_3-I,[15] Na_2GeSe_3[16] ("Zweireinfach"-chains with $P11b$ symmetry, $f_s = 0.818$, $f_s = 0.859$, respectively); Na_2SnSe_3-II ("Sechsereinfach"-chains with $P1m1$ symmetry, $f_s = 0.995$).[17] The interatomic distances between tin and the two terminal tellurium Te(1) are 2.729(1) and 2.730(1) Å, respectively. For the bridging tellurium, Te(2), the Sn–Te(2) bonds are somewhat longer, 2.806(2) and 2.825(2) Å. These are within the range 2.68–2.75 Å observed for terminal Sn–Te bonds, and 2.79–2.82 Å for bridging Sn–Te bonds. There are no significant Te···Te contacts (<4.0 Å) within nor between the chains. The Te(3)–Te(3) distance in the $(Te_2)^{2-}$ dimer is 2.808(3) Å, slightly longer than that found in $BaTe_2$, 2.772(1) Å,[9] but still close to a fully bonded tellurium–tellurium distance. The dimers pack in a herring-bone pattern in the plane (0 1 0) with each Te having four in-plane contacts (ave 3.72(1) Å) with three nearest dimers and two asymmetric contacts with Te(1) above and below the plane (2.758(2) and 3.964(2) Å).

The stability of $(SnQ_4)^{4-}$ (Q = S, Se) and $(Sn_2Q_6)^{4-}$ ions and their coordination ability toward themselves and other metal elements to form extended structures have been discussed elsewhere.[18] We have shown that the tellurium analogue, $(SnTe_4)^{4-}$, may also have the potential as basic building blocks.[8] To date, several such structures have been found. Among these are Na_4SnTe_4[19] and $K_2BaSnTe_4$[8] with isolated $SnTe_4$ tetrahedra; $K_6Sn_2Te_6$[20] with dimers of fused tetrahedra (i.e., with direct Sn–Sn bond); $Cs_4Sn_2Te_7$[21] with dimers of corner-sharing tetrahedra; Tl_2SnTe_3,[22] $(Et_4N)_4Sn_2Te_6$,[23] and $(Me_4N)_4Sn_2Te_6$[24] with dimers of edge-sharing tetrahedra; Rb_2SnTe_5,[21] K_2SnTe_5,[25] and Tl_2SnTe_5[26] with 1-D chains of $SnTe_4$ tetrahedra interconnected by planar Te_5; $K_2HgSnTe_4$[27] and $(Et_4N)_4HgSnTe_4$[27] with 1-D chains of $Sn_{0.5}Hg_{0.5}Te_4$ edge-sharing tetrahedra; Cs_2SnTe_4[28] with 1-D chains of individual $SnTe_4$ tetrahedra linked via Te–Te bonds; and $K_2Ag_2SnTe_4$,[8] the first 3-D network formed by corner- and edge-sharing $SnTe_4$ and $AgTe_4$ tetrahedra. The title compound, Ba_2SnTe_5, is another example of 1-D material built from $SnTe_4$ tetrahedra, uniquely characterized by the presence of isolated dimers of tellurium.

Electronic band calculations employing the extended Hückel method[29,30] have indicated strong covalent bonding interactions between Sn and Te within the chain. A substantial electron density is found on tin ($2.44e^-$). The terminal Te carries a considerably higher charge than that on the bridging Te (a difference of $0.45e^-$).

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The calculations have generated a −1 charge on each Te(3), consistent with its bond order in the $[Te(3)]_2^{2-}$ dimer. The weak interactions between the chain and the dimer is repulsive, with a calculated overlap population[31] value of −0.03 for the shorest Te(1)···Te(3) interatomic distance (3.758(2) Å). All interdimer interactions are also slightly repulsive. The band structure of Ba_2SnTe_5 shows a large bandgap between the valence bands, mainly on the $5p_z$ of Te(3), and the conducting bands, Te(3)−Te(3) σ^*-antibonding combinations, therefore suggesting that the compound is most likely insulating (or semiconducting).

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Supporting Information Available: Summary of crystal data (Table 1), atomic positional parameters (Table 2), bond distances and bond angles (Table 3), and thermal displacement parameters (Table 4) (4 pages); structure factors (5 pages). Ordering information is given on any current masthead page.

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