

Synthesis and characterization of $\text{Na}_2\text{Ba}_4\text{Ga}_2\text{Sb}_6$ and $\text{Li}_{13}\text{Ba}_8\text{GaSb}_{12}$

Iliya Todorov and Slavi C. Sevov*

Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, IN 46556, U.S.A.

In commemoration of the 100th anniversary of Fritz Laves' birthday

Received September 9, 2005; accepted November 11, 2005

Intermetallics / Zintl phases / Thermoelectric materials / Single crystal structure analysis / X-ray diffraction

Abstract. The title compounds were synthesized from the elements by heating the corresponding stoichiometric mixtures at high temperature. Their structures were determined from single-crystal X-ray diffraction. $\text{Na}_2\text{Ba}_4\text{Ga}_2\text{Sb}_6$ ($Pnma$, $Z = 8$, $a = 12.3468(10)$ Å, $b = 10.6621(10)$ Å, $c = 13.8344(10)$ Å) contains chains of $_{\infty}[\text{Ga}_2\text{Sb}_6]^{10-}$. The repeating unit is made of an edge-sharing Ga-centered tetrahedron $\text{GaSb}_2(\mu\text{-Sb})_2$ and another Ga-centered tetrahedron but with additional antimony that is exo-bonded to one of the corners forming Sb–Sb dumbbells, *i.e.* $\text{GaSb}(\text{Sb}–\text{Sb})(\mu\text{-Sb})_2$. The unit connects to neighboring units via sharing two corners of the tetrahedra, *i.e.* $[\text{Ga}_2\text{Sb}_5\text{Sb}_{2/2}]$. $\text{Li}_{13}\text{Ba}_8\text{GaSb}_{12}$ ($C2/m$, $Z = 2$, $a = 18.0650(10)$ Å, $b = 4.9407(10)$ Å, $c = 13.0123(10)$ Å, $\beta = 126.728(10)^\circ$) contains three different types of anions: single-atom anions of Sb^{3-} , dumbbells of Sb^{4-} , and isolated Ga-centered tetrahedra of GaSb_4^{9-} . The two compounds are electronically balanced, and this is confirmed by four-probe conductivity and magnetic measurements. Their very narrow band gaps, 0.014 and 0.049 eV for $\text{Na}_2\text{Ba}_4\text{Ga}_2\text{Sb}_6$ and $\text{Li}_{13}\text{Ba}_8\text{GaSb}_{12}$, respectively, make them potential thermoelectric materials.

Introduction

The polar intermetallics made of the very electropositive alkali (A), alkaline-earth (AE) and/or rare-earth (RE) metals and the relatively more electronegative *p*-block metals represent a very diverse and interesting class of compounds. Undoubtedly, the most intriguing among them are compounds that contain anions with delocalized bonding such as the observed clusters of groups 13 and 14 [1, 2] and the aromatic and conjugated species of group 14 [3]. One very useful approach to further expand the structural diversity of these compounds is to use two or more different types of counteranions, *i.e.* mix small and large cations or cations with different charges, etc. These different cations have different packing requirements and coordinating capability, and often stabilize species that can not be

achieved otherwise. Thus, cluster species such as Tl_5^{7-} , Tl_9^{9-} , Tl_{10}^{13-} , Tl_6^{8-} , Sn_8^{6-} , Sn_{12}^{12-} , Sn_{56}^{44-} are known only with mixed cations [1c, 4]. The same is true for the recently characterized aromatic pentagonal rings of Sn_5^{6-} and Pb_5^{6-} that are analogous to the cyclopentadienyl anion C_5H_5^- and some π -conjugated species of Sn [3]. The corresponding compounds utilized combinations of light alkali-metal cations such as Li or Na and heavy alkaline-earth or rare-earth cations of Ba, Sr, and Eu. Following on this approach we also investigated the possibility to form heteroatomic species made of groups 13 and 15 that would be eventually isoelectronic and structurally analogous to the aromatic rings of Sn_5^{6-} and Pb_5^{6-} . This, of course, complicates the system even further by employing four instead of three different elements but, at the same time, it provides additional flexibility as well as potential for valuable properties, thermoelectric efficiency, for example. It is well known that narrow-band semiconducting compounds with complex and anisotropic structures, large cells, and relatively heavy elements are good candidates for thermoelectric materials [5]. Often this structural complexity is achieved in compounds with complex stoichiometries, *i.e.* multinary compounds made of three and more elements and/or with partially occupied positions and disorder in the crystal lattices. Some examples of such compounds with relatively good thermoelectric properties are BaBiTe_3 [6], CsBi_4Te_6 [7], $\text{KBi}_{6.33}\text{S}_{10}$ [8], $\text{AgSb}_{0.3}\text{Bi}_{2.7}\text{S}_5$ [9], $\text{A}_2\text{BaCu}_8\text{Te}_{10}$ [10], $\text{Ba}_4\text{In}_8\text{Sb}_{16}$ [11], and the series $\text{A}_{1+x}\text{Tt}_{4-2x}\text{Pn}_{7+x}\text{Se}_{15}$ where $\text{A} = \text{K}$ or Rb , $\text{Tt} = \text{Sn}$ or Pb , and $\text{Pn} = \text{Sb}$ or Bi [5]. Here we present results of our studies of quaternary systems of gallium and antimony as representatives of groups 13 and 15, respectively, in combination with alkali and alkaline-earth counteranions.

Experimental section

Synthesis

All manipulations were carried out in an argon-filled glovebox with a moisture level below 1 ppm (vol.). The starting materials Li (granular, Acros, 99+%), Ba (rod, Alfa, 99.2%), Ga (splatter, Alfa, 99.999%) and Sb (ingot, Alfa,

* Correspondence author (e-mail: ssevov@nd.edu)

99.999%) were used as received while the surface of Na (ingot, Alfa, 99.9%) was cleaned with scalpel before use. In a typical synthesis, a mixture of the elements is placed in a niobium tube that is then sealed by arc welding. The tube is in turn jacketed in a silica ampule that is then flame-sealed under vacuum. These assemblies are placed in tubular furnaces and are heated at various temperature regimes. The two title compounds were initially discovered as minor products from exploratory reactions loaded with various ratios between the elements. After their stoichiometries were determined from single-crystal X-ray diffraction, both compounds were synthesized as single-phase products from the corresponding stoichiometric mixtures of the elements. The mixtures were heated at 860 °C for 1 week and were then cooled down to room temperature with a rate of 6°C/h. The purity of the compounds was confirmed by powder X-ray diffraction on an Enraf-Nonius Guinier camera under vacuum ($\text{CuK}\alpha_1$ radiation, $\lambda = 1.540562 \text{ \AA}$).

X-ray diffraction studies

Black block-shaped crystals were selected from each compound and were mounted inside thin-walled glass capillaries that were subsequently flame-sealed at both ends. The crystals were checked for singularity on an Enraf-Nonius CAD4 diffractometer with graphite monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). X-ray diffraction data sets were collected at room temperature for the best ones ($\text{Na}_2\text{Ba}_4\text{Ga}_2\text{Sb}_6$: $0.18 \times 0.09 \times 0.05 \text{ mm}$, $\text{Li}_{13}\text{Ba}_8\text{GaSb}_{12}$: $0.12 \times 0.12 \times 0.10 \text{ mm}$). The raw data (an octant of a sphere for $\text{NaBa}_2\text{GaSb}_3$ and a quarter of a sphere for $\text{Li}_{13}\text{Ba}_8\text{GaSb}_{12}$, $\omega - 2\theta$ scans, $\theta_{\max} = 25^\circ$) were corrected for absorption with the aid of the average of 3 ψ -scans. The observed extinction conditions and intensity statistics suggested the centrosymmetric space groups $Pnma$ and $C2/m$ for $\text{Na}_2\text{Ba}_4\text{Ga}_2\text{Sb}_6$ and $\text{Li}_{13}\text{Ba}_8\text{GaSb}_{12}$, respectively. Accordingly, the structures were solved and refined in these space groups with the aid of the SHELXTL-V5.1 software package [12]. Due to the large scattering factors of the heavy atoms surrounding the very light lithium in $\text{Li}_{13}\text{Ba}_8\text{GaSb}_{12}$ the latter was refined isotropically. Further details for the data collections and structure refinements are given in Table 1. The atomic coordinates and their equivalent isotropic displacement parameters are listed in Table 2 while important distances are provided in Table 3¹.

Direct methods provided the positions of Ba, Ga, and Sb in the two compounds. The refinement of $\text{Na}_2\text{Ba}_4\text{Ga}_2\text{Sb}_6$ indicated that one of the three barium positions was partially occupied. This position was refined as fully occupied but as mixed with sodium to add to the full occupancy. The fractional occupancies of the two elements refined very closely to 50% and they were fixed at this for

Table 1. Selected data collection and refinement parameters for $\text{NaBa}_2\text{GaSb}_3$ and $\text{Li}_{13}\text{Ba}_8\text{GaSb}_{12}$.

| Chemical formula | $\text{Na}_2\text{Ba}_4\text{Ga}_2\text{Sb}_6$ | $\text{Li}_{13}\text{Ba}_8\text{GaSb}_{12}$ |
|--|--|---|
| Formula weight | 1465.28 | 1350.81 |
| Space group, Z | $Pnma$, 8 | $C2/m$, 2 |
| a (Å) | 12.3468(10) | 18.0650(10) |
| b (Å) | 10.6621(10) | 4.9407(10) |
| c (Å) | 13.8344(10) | 13.0123(10) |
| β (Å) | | 126.728(10) |
| V (Å ³) | 1821.2(3) | 930.8(2) |
| Radiation, λ (Å) | $\text{MoK}\alpha$, 0.710 73 | $\text{MoK}\alpha$, 0.710 73 |
| ρ_{calc} ($\text{g} \cdot \text{cm}^{-3}$) | 5.344 | 4.852 |
| μ (cm^{-1}) | 20.150 | 17.540 |
| $R1/wR2$, ^a $I \geq 2\sigma_1$ (%) | 4.53/11.20 | 2.72/7.33 |
| $R1/wR2$, ^a all data (%) | 6.21/12.05 | 2.92/7.43 |

a: $R1 = \frac{|\sum |F_o| - |F_c||}{\sum |F_o|}$; $wR2 = \frac{\{[\sum w[(F_o)^2 - (F_c)^2]^2] / [\sum w(F_o^2)]\}^{1/2}}$; $w = [\sigma^2(F_o)^2 + (AP)^2 + BP]^{-1}$, where $P = [(F_o)^2 + 2(F_c)^2]/3$.

the final refinement. The possibility of having this site partially occupied by barium only was also considered. However, this was found unlikely because of the successful synthesis of the pure phase only when using mixture of composition $\text{Na}_2\text{Ba}_4\text{Ga}_2\text{Sb}_6$ but not with $\text{NaBa}_{4.25}\text{Ga}_2\text{Sb}_6$ which would correspond to the Ba-only occupancy of that site. Furthermore, the refined formula with equal amounts of Na and Ba at that position, *i.e.* $\text{Na}_2\text{Ba}_4\text{Ga}_2\text{Sb}_6$, is consistent with an electronically balanced compound which

Table 2. Atomic coordinates and equivalent isotropic displacement parameters for $\text{Na}_2\text{Ba}_4\text{Ga}_2\text{Sb}_6$ and $\text{Li}_{13}\text{Ba}_8\text{GaSb}_{12}$.

| Atom | site | x | y | z | $U_{\text{eq}}/U_{\text{iso}}$ |
|--|------|---------------|----------------|-----------------|--------------------------------|
| $\text{Na}_2\text{Ba}_4\text{Ga}_2\text{Sb}_6$ | | | | | |
| Sb1 | 4c | 0.45548(12) | $1/4$ | 0.38478(10) | 0.0119(4) |
| Sb2 | 4c | 0.37211(12) | $1/4$ | 0.11159(10) | 0.0117(4) |
| Sb3 | 8d | 0.17465(9) | $-0.06121(9)$ | 0.31750(8) | 0.0151(3) |
| Sb4 | 4c | 0.13950(12) | $1/4$ | 0.56362(10) | 0.0103(4) |
| Sb5 | 4c | 0.49699(12) | $1/4$ | 0.58633(10) | 0.0108(4) |
| Ga1 | 4c | 0.6937(2) | $-1/4$ | 0.30911(17) | 0.0102(5) |
| Ga2 | 4c | 0.4086(2) | $1/4$ | $-0.07961(18)$ | 0.0131(6) |
| Ba1 | 8d | 0.67004(8) | 0.01968(9) | 0.46545(7) | 0.0145(3) |
| Ba2 | 4c | 0.16545(12) | $1/4$ | 0.30903(10) | 0.0139(4) |
| Ba3/Na3 | 8d | 0.42256(13) | $-0.02995(16)$ | 0.24628(12) | 0.0166(4) |
| Na1 | 4b | $1/2$ | 0 | 0 | 0.039(3) |
| $\text{Li}_{13}\text{Ba}_8\text{GaSb}_{12}$ | | | | | |
| Sb1 | 4i | 0.103161(13) | 0 | 0.454779(18) | 0.01526(6) |
| Sb2 | 4i | 0.085535(12) | $1/2$ | 0.124494(17) | 0.01201(6) |
| Sb3 | 4i | 0.341181(13) | 0 | 0.183513(18) | 0.01634(6) |
| Ga1/Li1A | 4i | $-0.08561(9)$ | 0 | 0.34637(13) | 0.0313(5) |
| Ba1 | 4i | 0.238543(11) | 0 | 0.340395(15) | 0.01335(6) |
| Ba2 | 4i | 0.071563(11) | 0 | $-0.085575(16)$ | 0.01369(5) |
| Li1 | 4i | 0.0430(3) | $1/2$ | 0.3179(4) | 0.0000(9) |
| Li2 | 4i | 0.2348(4) | $1/2$ | 0.0900(5) | 0.0220(14) |
| Li3 | 2d | 0 | $1/2$ | $1/2$ | 0.061(4) |

¹ Additional material to this paper can be ordered referring to the no. CSD 415733 (for $\text{Li}_{13}\text{Ba}_8\text{GaSb}_{12}$) and 415734 (for $\text{Na}_2\text{Ba}_4\text{Ga}_2\text{Sb}_6$), names of the authors and citation of the paper at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany.

Table 3. Important distances (Å) and angles (°) in Na₂Ba₄Ga₂Sb₆ and Li₁₃Ba₈GaSb₁₂.

| Na ₂ Ba ₄ Ga ₂ Sb ₆ | | Li ₁₃ Ba ₈ GaSb ₁₂ | |
|---|----------|---|----------|
| Sb1–Sb5 | 2.834(2) | Sb1–Ga1/Li1A | 2.788(2) |
| –Na3/Ba3 × 2 | 3.570(2) | –Ga1/Li1A | 2.805(2) |
| –Ba2 | 3.729(2) | –Li1 × 2 | 2.852(2) |
| –Ba2 | 3.731(2) | –Li3 × 2 | 3.351(1) |
| Sb2–Ga2 | 2.683(2) | –Ba1 × 2 | 3.502(1) |
| –Na1 × 2 | 3.461(1) | –Ba1 | 3.542(2) |
| –Na3/Ba3 × 2 | 3.573(2) | Sb2–Sb2 | 2.841(1) |
| –Ba1 × 2 | 3.659(2) | –Li2 | 2.988(7) |
| –Ba2 | 3.738(2) | –Li1 | 3.040(5) |
| –Ba2 | 3.784(2) | –Ba1 × 2 | 3.514(1) |
| Sb3–Ga2 | 2.670(2) | –Ba2 × 2 | 3.562(1) |
| –Ga1 | 2.678(2) | –Ba2 × 2 | 3.579(1) |
| –Na3/Ba3 | 3.233(2) | Sb3–Li2 × 2 | 2.912(3) |
| –Na3/Ba3 | 3.252(2) | –Li2 | 2.948(6) |
| –Ba2 | 3.323(2) | –Li1 | 2.953(4) |
| –Ba1 | 3.590(2) | –Ga1/Li1A × 2 | 2.998(1) |
| Sb4–Ga1 | 2.709(2) | –Li3 | 3.325(1) |
| –Ga2 | 2.860(2) | –Ba1 | 3.483(1) |
| –Na1 × 2 | 3.293(2) | –Ba2 × 2 | 3.551(1) |
| –Na3/Ba3 | 3.532(2) | Ga1/Li1A – Li2 | 2.951(4) |
| –Ba2 | 3.536(2) | –Li3 × 2 | 2.965(1) |
| –Ba1 × 2 | 3.736(1) | –Ba2 | 3.551(2) |
| Sb5–Ga1 | 2.763(2) | | |
| –Na3/Ba3 × 2 | 3.443(2) | | |
| –Ba1 × 2 | 3.610(2) | | |
| –Ba1 | 3.659(2) | | |
| Ga1–Ba1 × 2 | 3.610(2) | | |
| –Ba3 | 3.751(2) | | |
| Ga2–Na1 × 2 | 3.097(1) | | |
| –Ba3 | 3.894(2) | | |

was proven to be the case (below). The refinement of the second compound indicated also a partially occupied position, this time of gallium. Again, the position was refined as fully occupied but mixed with lithium. The refined ratio of Ga:Li was close to 1:3 and it was fixed as such for the final refinement. We point out that although Li/Ga mixing is unusual it is not unprecedented. Similar Li/In mixing in interconnected clusters was reported recently [13].

Magnetic measurements

The magnetizations of NaBa₂GaSb₃ and Li₁₃Ba₈GaSb₁₂, were measured on a Quantum Design MPMS SQUID magnetometer at a field of 3T over a temperature range of 10 to 250 K. Each sample was flame-sealed in a quartz tube between two quartz rods that fit tightly in the tube. The data were corrected for the holder and for ion-core diamagnetism. The resulting molar magnetic susceptibilities for both compounds were temperature-independent and negative, $-(2.590 \text{ to } 2.621) \times 10^{-3}$ emu/mol for NaBa₂GaSb₃ and $-(1.665 \text{ to } 1.629) \times 10^{-3}$ emu/mol for Li₁₃Ba₈GaSb₁₂, and indicated diamagnetism.

Resistivity measurements

The electrical resistivities of the compounds were measured by the four-probe method (an in-line probe from Jandel) on pressed pellets (3000 psi, 1 mm and 1.4 mm thick) over the temperature range 224–294 K inside a cold well of a dry box. Measured was the drop of voltage across the samples at constant currents. The resistivities of both compounds decreased with increasing the temperature and indicated semiconducting properties. The measured resistivities at room temperature were *ca.* 3496 and 14380 Ω · cm for NaBa₂GaSb₃ and Li₁₃Ba₈GaSb₁₂, respectively.

Results and discussion

Na₂Ba₄Ga₂Sb₆

The anionic part of the structure of this compound consists of polymeric chains along the *a*-axis of the orthorhombic cell (Fig. 1). The chains can be viewed as made of monomers of [Ga₂Sb₇] (Fig. 2, outlined) where each monomer shares two antimony corners with its two neighboring identical units, *i.e.* [Ga₂Sb₅Sb_{2/2}]. This results in overall stoichiometry of [Ga₂Sb₆] for the repeating unit of the chain. The chains are well separated by the sodium and barium counteranions.

The monomer [Ga₂Sb₇] is made of two edge-sharing gallium-centered tetrahedra of antimony where one additional antimony atom is exo-bonded to a corner of one of the tetrahedra and forms a dimer of Sb–Sb. Such dimerization and higher oligomerization or even polymerization are very common for the pnictides, especially for the less electronegative ones [2]. Also, the tetrahedral coordination of gallium by antimony is quite common in compounds with the alkali metals [14]. The edge-shared tetrahedra form a four-membered ring of two Sb and two Ga atoms. This ring is bent at 18.4° along its Sb–Sb diagonal, most likely due to packing requirements. Exactly the same units but made of indium and arsenic, [In₂As₇], were characterized in K₂Ba₄In₂As₆ before [15].

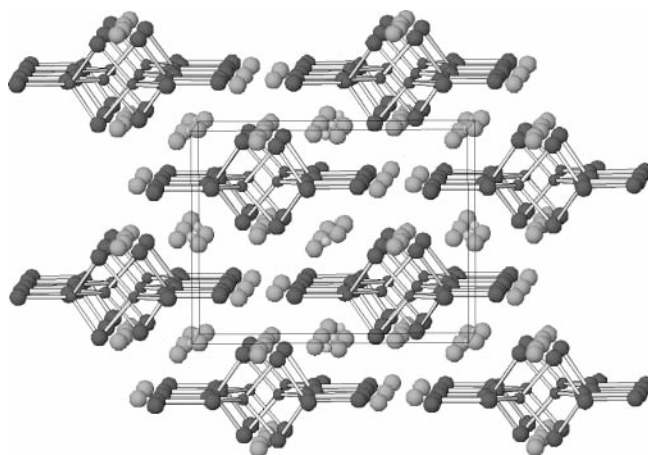


Fig. 1. The structure of Na₂Ba₄Ga₂Sb₆ viewed along *a* (*c* is horizontal). Ga and Sb: small and large dark spheres, Na and Ba: small and large lighter spheres. The chains of [Ga₂Sb₆]⁶⁻ that run along *a* are well separated with the Na- and Ba-counteranions.

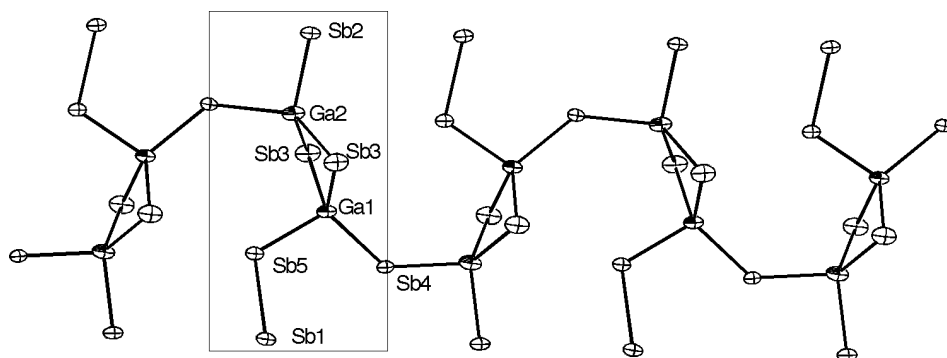


Fig. 2. Shown is the chain of $\infty[\text{Ga}_2\text{Sb}_6]^{10-}$ in $\text{Na}_2\text{Ba}_4\text{Ga}_2\text{Sb}_6$. It can be viewed as made of fused monomers of $[\text{Ga}_2\text{Sb}_7]$ as shown outlined. The same type monomers, but isolated, as well as differently-bonded chains of the same monomers are found in $\text{K}_2\text{Ba}_4\text{In}_2\text{As}_6$.

Despite their identical stoichiometry, though, the two compounds are not isostructural, in fact they are quite different. $\text{K}_2\text{Ba}_4\text{In}_2\text{As}_6$ contains two different types of anions, both based on the fragment $[\text{In}_2\text{As}_7]$. One type are simply isolated units of $[\text{In}_2\text{As}_7]$ while the second type are chains of the same units but where all four terminal arsenic atoms of each unit are shared with the two neighboring monomers. This results in repeating stoichiometry of $[\text{In}_2\text{As}_3\text{As}_{4/2}]$, *i.e.* $[\text{In}_2\text{As}_5]$. The four-membered rings in the In–As units are also bent but quite more than in the Ga–Sb counterpart, their dihedral angles are 39.99 and 37.71°.

The Ga–Sb distances are in the range 2.670(2) – 2.860(2) Å and are quite typical for single-bond distances. They compare well with the corresponding distances in similarly bonded gallium in Sr_3GaSb_3 [16]. The Sb–Sb distance of 2.834(2) Å is also typical for single-bond distances such as those observed in the helical chains of β -CsSb [17], 2.845(3) and 2.871(3) Å, and in the helical hexamers in Sr_2Sb_3 [18], 2.887(4) Å.

The stoichiometry and structure of the new compound $\text{Na}_2\text{Ba}_4\text{Ga}_2\text{Sb}_6$ suggest an electronically balanced compound, *i.e.* the number of provided electrons from the cations equals the number of electrons needed for the anions. Thus, each repeating unit of $[\text{Ga}_2\text{Sb}_6]$ has two 4-bonded Ga[−], four 2-bonded Sb[−], and two 1-bonded Sb^{2−} species and, therefore, the unit carries a charge of 10[−] and needs 10 extra electrons. Exactly the same number of electrons are provided by two Na⁺ and four Ba²⁺ cations, and the formula can be written as $(\text{Na}^+)_2(\text{Ba}^{2+})_4[\text{Ga}_2\text{Sb}_6]^{10-}$.

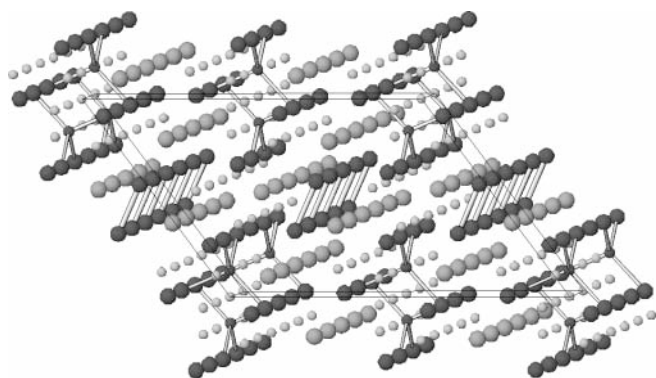


Fig. 3. The structure of $\text{Li}_{13}\text{Ba}_8\text{GaSb}_{12}$ viewed along b (a is horizontal). Ga and Sb: small and large dark spheres, Li and Ba: small and large lighter spheres. The anionic part of the structure consists of isolated $[\text{Sb}_2]^{4-}$ dimers, isolated Sb^{3-} atoms, and isolated Ga-centered tetrahedra of $[\text{GaSb}_4]^{9-}$.

$\text{Li}_{13}\text{Ba}_8\text{GaSb}_{12}$

The structure contains three types of isolated anions: single atom-anions of Sb^{3-} , dimers of Sb_2^{4-} , and tetrahedra of GaSb_4^{9-} (Fig. 3). The Ga – Sb distances 2.788(2) – 2.805(2) Å are in an excellent agreement with those in the previously reported Sr_3GaSb_3 [16]. The Sb – Sb distance in the dimers of 2.841(1) Å compares well with the distances of the dimers of $\text{Na}_2\text{Ba}_3\text{Sb}_4$ [19], 2.867(2) and 2.907(2) Å, respectively. The structure can be easily rationalized as a Zintl phase. Assuming complete electron transfer from Li and Ba to Ga and Sb, the formula can be rewritten as $(\text{Li}^+)_{13}(\text{Ba}^{2+})_8\{[\text{Sb}^{3-}]_4[\text{Sb}_2^{4-}]_2[\text{GaSb}_4^{9-}]\}$.

Properties

Often compounds are classified as Zintl phases based only on their stoichiometry, crystal structure, and formal electron count, *i.e.* without further investigation on their physical properties. Many such phases have been found later to be metallic and have been named metallic Zintl phases. In order to determine which class the title compounds belong to we measured their electrical resistivity and magnetization at different temperatures. Both compounds showed negative and temperature independent molar magnetic susceptibilities, $-(2.612\text{--}2.590) \times 10^{-3}$ and $-(1.665\text{--}1.629) \times 10^{-3}$ emu/mol for $\text{Na}_2\text{Ba}_4\text{Ga}_2\text{Sb}_6$ and $\text{Li}_{13}\text{Ba}_8\text{GaSb}_{12}$, respectively, over the range of 10–250 K. This indicates diamagnetic properties and is a good indication for semiconducting and electronically balanced compound. However, since the absolute values of the magnetic susceptibility of both diamagnetic and Pauli-like paramagnetic (metallic) compounds are usually very small, defining the character of the compound is often ambiguous. This is why an additional test such as electrical resistivity is very helpful. The resistivities of the title compounds at room temperature measured by the four-probe method were *ca.* 3496 and 14380 $\Omega \cdot \text{cm}$ for $\text{Na}_2\text{Ba}_4\text{Ga}_2\text{Sb}_6$ and $\text{Li}_{13}\text{Ba}_8\text{GaSb}_{12}$, respectively. These numbers alone also suggest semiconducting properties. The more important observation was that these numbers increase with decreasing temperature, and this unequivocally indicates a semiconducting compound. The plots of $\ln(\rho)$ versus the reciprocal temperature (Fig. 4) were fitted with straight lines and band gaps were calculated from their slopes. These gaps for $\text{Na}_2\text{Ba}_4\text{Ga}_2\text{Sb}_6$ and $\text{Li}_{13}\text{Ba}_8\text{GaSb}_{12}$ are 0.0137(7) and 0.0489(1) eV, respectively. Therefore, based on the two types of measurements, it can be concluded that the

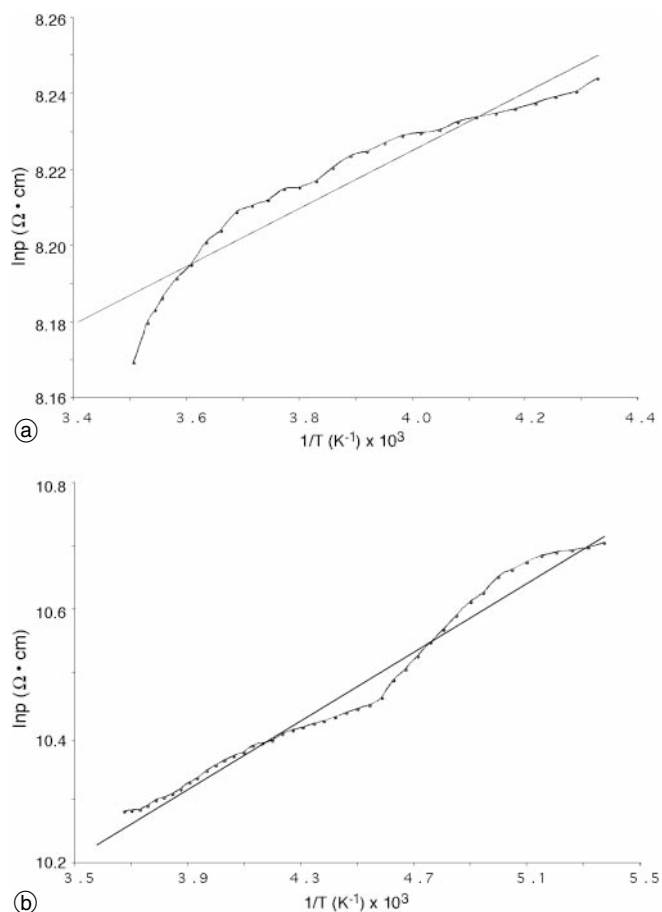


Fig. 4. Plots of the temperature dependence of the resistivity of (a) Na₂Ba₄Ga₂Sb₆ and (b) Li₁₃Ba₈GaSb₁₂. The slopes indicate that both compounds are semiconductors.

two compounds are indeed closed shell narrow band gap semiconductors and qualify as true Zintl phases.

Discussion

The two title compounds present an excellent example of how Nature uses everything possible in order to achieve, if possible at all, an electronically balanced compound. In one case barium and sodium are mixed at the same site exactly in the right ratio, 1:1, to produce the necessary number of electrons for the anionic part of the structure. The second case is even more surprising because mixed in one site are two elements, lithium and gallium, that are very different in electronegativity and in size. Again, their ratio of 3:1 is exactly what is needed for balancing the negative charges of the anions.

The two title compounds exemplify very clearly the great potential for structural diversity that mixed cations can provide. As mentioned above, although Na₂Ba₄Ga₂Sb₆ and K₂Ba₄In₂As₆ have the same stoichiometry, their structures are very different, mainly due to the different sizes of the cations and the corresponding anionic units. The latter are the same in both structures, *i.e.* [Ga₂Sb₇] and [In₂As₇], but in Na₂Ba₄Ga₂Sb₆ they are interconnected in chains by sharing two atoms, *i.e.* [Ga₂Sb₅Sb_{2/2}]¹⁰⁻, while in K₂Ba₄In₂As₆ they exist both as isolated species of [In₂As₇]¹³⁻ and as interconnected in chains by sharing four atoms, *i.e.* [In₂As₃As_{4/2}]⁷⁻. Despite the structural dif-

ferences, both compounds are electronically balanced and semiconducting.

According to the measured band gaps, *ca.* 0.014 and 0.049 eV, the two title compounds may have the potential to be good thermoelectric materials. These gaps compare very well with those of materials with high thermoelectric efficiency such as AgBi₃S₅ (0.17 eV) [9], Ba₄In₈Sb₁₆ (0.10 eV) [11], CsBi₄Te₆ (0.04 to 0.08 eV) [7], and A₂Ba₂Cu₈Te₁₀ (0.28 eV) [10]. The measured room-temperature resistivities, *ca.* 3496 and 14380 Ω · cm, are also similar to those of the mentioned compounds, for example Rb₂Ba₂Cu₈Te₁₀ with 3200 Ω · cm. Further measurements of thermopower and thermal conductivity are needed in order to fully characterize the thermoelectric efficiency of the compounds.

References

- [1] (a) Corbett, J. D.: Polyatomic Zintl anions of the post-transition elements. *Chem. Rev.* **85** (1985) 383–397. (b) Corbett, J. D.: Polyanionic Clusters and Networks of the Early p-Element Metals in the Solid State: Beyond the Zintl Boundary. *Angew. Chem. Int. Ed.* **39** (2000) 670–690. (c) Corbett, J. D.: Exploratory Synthesis in the Solid State. *Endless Wonders. Inorg. Chem.* **39** (2000) 5178–5191.
- [2] Kauzlarich, S. (Ed.): *Structure and Bonding of Zintl Phases and Ions*. VCH Publishers Inc., New York, 1996.
- [3] (a) Todorov, I.; Sevov, S. C.: Heavy-Metal Aromatic Rings: Cyclopentadienyl Anion Analogues Sn₅⁶⁻ and Pb₅⁶⁻ in the Zintl Phases Na₈BaPb₆, Na₈BaSn₆, and Na₈EuSn₆. *Inorg. Chem.* **43** (2004) 6490–6494. (b) Todorov, I.; Sevov, S. C.: Heavy-Metal Aromatic and Conjugated Species: Rings, Oligomers, and Chains of Tin in Li_{9-x}EuSn_{6+x}, Li_{9-x}CaSn_{6+x}, Li₅Ca₇Sn₁₁, Li₆Eu₅Sn₉, LiMgEu₂Sn₃, and LiMgSr₂Sn₃. *Inorg. Chem.* **44** (2005) 5361–5369 and references therein.
- [4] (a) Bobev, S.; Sevov, S. C.: Naked Clusters of 56 Tin Atoms in Solid State. *J. Am. Chem. Soc.* **124** (2001) 3359–3365. (b) Bobev, S.; Sevov, S. C.: Synthesis and Characterization of the Largest Isolated Clusters of Tin, [Sn₁₂]¹²⁻ in Na₁₀AeSn₁₂ (Ae = Ca or Sr). *Inorg. Chem.* **40** (2001) 5361–5364.
- [5] Choi, K. S.; Chung, D. Y.; Mrotzek, A.; Brazis, P.; Kannewurf, C. R.; Uher, C.; Chen, W.; Hogan, T.; Kanatzidis, M. G.: Modular Construction of A_{1+x}M_{4-2x}M'_{7+x}Se₁₅ (A = K, Rb; M = Pb, Sn; M' = Bi, Sb): A New Class of Solid State Quaternary Thermoelectric Compounds. *Chem. Mater.* **13** (2001) 756–764.
- [6] Chung, D.-Y.; Jobic, S.; Hogan, T.; Kannewurf, C. R.; Brec, R.; Rouxel, J.; Kanatzidis, M. G.: Oligomerization Versus Polymerization of Te_xⁿ⁻ in the Polytelluride Compound BaBiTe₃. *Structural Characterization, Electronic Structure, and Thermoelectric Properties.* *J. Am. Chem. Soc.* **119** (1997) 2505–2515.
- [7] Chung, D.-Y.; Hogan, T. P.; Lane, M. R.; Brazis, P.; Ireland, J. R.; Kannewurf, C. R.; Bastea, M.; Uher, C.; Kanatzidis, M. G.: A New Thermoelectric Material: CsBi₄Te₆. *J. Am. Chem. Soc.* **126** (2004) 6414–6428.
- [8] Kanatzidis, M. G.; McCarthy, T. J.; Tanzer, T. A.; Chen, L.-H.; Iordanidis, L.; Hogan, T.; Kannewurf, C. R.; Uher, C.; Chen, B.: Synthesis and Thermoelectric Properties of the New Ternary Bismuth Sulfides KBi_{6.33}S₁₀ and K₂Bi₈S₁₃. *Chem. Mater.* **8** (1996) 1465–1474.
- [9] Kim, J. H.; Chung, D. U.; Bile, D.; Loo, S.; Short, J.; Subhendra, D.; Hogan, T.; Kanatzidis, M. G.: Crystal Growth, Thermoelectric Properties, and Electronic Structure of AgBi₃S₅ and AgSb_xBi_{3-x}S₅ (x = 0.3). *Chem. Mater.* **17** (2005) 3606–3614.
- [10] Patschke, R.; Zhang, X.; Singh, D.; Schindler, J.; Kannewurf, C. R.; Lowhorn, N.; Tritt, T.; Nolas, G. S.; Kanatzidis, M. G.: Thermoelectric Properties and Electronic Structure of the Cage Compounds A₂BaCu₈Te₁₀ (A = K, Rb, Cs): Systems with Low Thermal Conductivity. *Chem. Mater.* **13** (2001) 613–621.
- [11] Kim, S. J.; Hu, S.; Uher, C.; Kanatzidis, M. G.: Ba₄In₈Sb₁₆: Thermoelectric Properties of a New Layered Zintl Phase with Infinite Zigzag Sb Chains and Pentagonal Tubes. *Chem. Mater.* **11** (1999) 3154–3159.

- [12] Bruker Analytical Systems. Madison, WI 1997.
- [13] Li, B.; Corbett, J.D.: Phase Stabilization through electronic tuning: Electron-poorer alkali-metal-indium compounds with unprecedented In/Li clusters. *J. Am. Chem. Soc.* **127** (2005) 926–932.
- [14] (a) Cordier, G.; Ochmann, H.: Crystal-structure of Dipotassium Phyllo-triantimonidogallate, $K_2Ga_2Sb_3$. *Z. Kristallogr.* **197** (1991) 289–290. (b) Cordier, G.; Ochmann, H.: Crystal-structure of Potassium Phyllo-diantimonidogallate, $KGaSb_2$. *Z. Kristallogr.* **197** (1991) 297–298. (c) Cordier, G.; Ochmann, H.: Crystal-structure of Potassium Tecto-tetraantimonidogallate, $KGaSb_4$. *Z. Kristallogr.* **195** (1991) 306–307. (d) Cordier, G.; Ochmann, H.; Shafer, H.: $Na_2Ga_3Sb_3$, A New Zintl Phase with Layer Structure. *Mater. Res. Bull.* **21** (1986) 331–336.
- [15] Gascoin, F.; Sevov, S. C.: KBa_2InAs_3 with Coexisting Monomers of $[In_2As_7]^{13-}$ and Their One-Dimensional Polymers. *Inorg. Chem.* **41** (2002) 2292–2295.
- [16] Cordier, G.; Schäfer, H.; Stelter, M.: Sr_3GaSb_3 und Sr_3InP_3 , zwei neue Zintlphasen mit komplexen anionen. *Z. Naturforsch. B* **42** (1987) 1268–1272.
- [17] Emmerling, F.; Hirschele, C.; Röhr, C.: Cs_5Sb_8 and β - $CsSb$: Two New Binary Zintl Phases. *Z. Anorg. Allg. Chem.* **628** (2002) 559–563.
- [18] Eisenmann, B.: Sr_2Sb_3 , a Zintl-Phase with a Sb_6 -chain Anion. *Z. Naturforsch. B* **34** (1979) 1162–1164.
- [19] Chi, L.; Corbett, J. D.: Two Ternary Phases Containing Sb_2^{4-} Ions: $Na_2M_3Sb_4$, $M = Sr, Ba$. Synthesis, Structure, and Properties. *J. Solid State Chem.* **162** (2001) 327–332.

Incommensurate Crystallography of Modulated and Composite Crystals

Edited by Sander van Smaalen

Z. Kristallogr. Issue 11 Volume **219** (2004)



Within the last thirty years incommensurate crystal structures were discovered in many compounds. Consideration of the possibility of aperiodic order instead of 3D translational symmetry has become a necessity for solid state chemists and solid state physicists, when studying new compounds or new states of matter. This issue provides a complete introduction to aperiodic crystallography and presents overviews of the superspace theory and its use in structural analysis.

The **Special Topic Issue** contains Original Papers by: S. van Smaalen/V. Petříček *et al.* / R. L. Withers *et al.* / J.-P. Pouget / S. van Smaalen *et al.* / G. Chapuis *et al.* / N. L. Speziali *et al.* / M. McMahon *et al.* / K. Takemura *et al.* / E. Gaudin *et al.* and M. L. Carter *et al.*

Now at € 49.– (regular price € 208.–)!
For orders please see the ad at the back of this issue!
For Abstracts see: www.zkristallogr.de



Oldenbourg