

# Design in Solid State Synthesis Based on Phase Homologies: $A_{1-x}Sn_{9-x}Bi_{11+x}Se_{26}$ ( $A=K, Rb, Cs$ )—A New Member of the Grand Homologous Series $A_m[M_6Se_8]_m[M_{5+n}Se_{9+n}]$ with $M=Sn$ and $Bi$

Antje Mrotzek and Mercuri G. Kanatzidis<sup>1</sup>

Department of Chemistry and Center for Fundamental Materials Research, Michigan State University, East Lansing, Michigan 48824

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IN HONOR OF PROFESSOR GALEN STUCKY ON THE OCCASION OF HIS 65TH BIRTHDAY

Both the composition and structure of  $A_{1-x}Sn_{9-x}Bi_{11+x}Se_{26}$  ( $A=K, Rb, Cs$ ) were predicted on the basis of the homologous series  $A_m[M_6Se_8]_m[M_{5+n}Se_{9+n}]$  ( $M=Sn, Bi$ ) and targeted for synthesis.  $A_{1-x}Sn_{9-x}Bi_{11+x}Se_{26}$  adopts a new structure type that fits the structural evolution of the homologous series.

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There is a strong interest in developing new chemical concepts in designing new materials with superior thermoelectric properties (1, 2). Our approach, which has been outlined in detail elsewhere (3), is focused on complex quaternary and ternary bismuth chalcogenides incorporating alkali metals. The examples of  $CsBi_4Te_6$  (4),  $K_2Bi_8Se_{13}$  (5, 6), and  $K_{1.25}Pb_{3.5}Bi_{7.25}Se_{15}$  (7) show that these exploratory investigations can lead to novel thermoelectric materials with promising properties. Our investigations of the quaternary system  $K/Sn/Bi/Se$  led to various compounds, e.g.,  $K_{1+x}Sn_{3-2x}Bi_{7+x}Se_{14}$  (8),  $K_{1+x}Sn_{4-2x}Bi_{7+x}Se_{15}$  (7),  $K_{1-x}Sn_{3-x}Bi_{11+x}Se_{20}$  (8),  $K_{1-x}Sn_{4-x}Bi_{11+x}Se_{21}$  (9), and  $K_{1-x}Sn_{5-x}Bi_{11+x}Se_{22}$  (10), which exhibit a close structural and compositional relationship. This work helped us to identify a grand homologous series of phases with the general formula  $A_m[M_6Se_8]_m[M_{5+n}Se_{9+n}]$  ( $A$  = alkali metal,  $M$  = heavy group IV and V element). The quaternary selenides belong to this series which was recognized after the structural characterization of these compounds. Their structures are composed of  $[M_{5+n}Se_{9+n}]$  ( $NaCl^{111}$ -type) and  $[M_6Se_8]_m$  ( $NaCl^{100}$ -type) units (11) of variable dimensions defined by  $n$  and  $m$ , which link to produce anionic frameworks with alkali metal ( $A_m$ ) filled

tunnels. The terminology “homologous series” was given by Magnéli (12) to characterize chemical series that are expressed by general formulae and built on common structural principles that are found in transition metal oxides (13), as for example the Aurivillius phases  $Bi_2A_{n-1}B_nO_{3n+3}$  ( $A=Na, K, Ca, Sr, Ba, Pb, Ln, Bi, U, Th, etc.$  and  $B=Fe, Cr, Ga, Ti, Zr, Nb, Ta, Mo, W, etc.$ ) (14) and the Jacobson–Dion phases  $A[A'_{n-1}B_nO_{3n+1}]$  ( $A=Li, Na, K, Rb, Cs, Tl, NH_4, A'=Ca, Nd, and B=Nb$ ) (15). The structures of the lamellar oxides are related to the rutile and perovskite type, where the integer  $n$  determines the thickness of the slabs. In contrast to these homologies, the  $A_m[M_6Se_8]_m[M_{5+n}Se_{9+n}]$  series is characterized by two integers  $n$  and  $m$  that can be changed independently and therefore cause evolution of the structure in two different dimensions. While the thickness of the  $NaCl^{100}$ -type units is controlled by  $m$ , the shape of the  $NaCl^{111}$ -type units is given by  $n$ . Our results in the  $A/Sn/Bi/Se$  system suggest that it is “infinitely adaptive” (16). Changes of the ratio of the reactants lead to new compounds with new structure types instead of coexisting phases or solid solutions. The homologous series  $A_m[M_6Se_8]_m[M_{5+n}Se_{9+n}]$  found in the  $A/M/Bi/Se$  system ( $A=K, Rb, Cs$  and  $M=Sn, Pb$ ) has predictive character and generates easily charge-balanced compositions for hypothetical compounds as members of the series. Every member of this series represents a new structure type. Here we report a new member of the grand homologous series that in fact was targeted for synthesis based on the general formula  $A_m[M_6Se_8]_m[M_{5+n}Se_{9+n}]$  with  $m=1, n=9$  predicting a compound with the formula  $K_1Sn_9Bi_{11}Se_{26}$ . The novelty in this particular member lies in its very thick layer nature of its  $[M_{5+n}Se_{9+n}]$  module.

$A_{1-x}Sn_{9-x}Bi_{11+x}Se_{26}$  ( $A=K, Rb, Cs$ ) was prepared according to the predicted composition by combining  $A_2Se, Bi_2Se_3, Sn,$  and  $Se$  (ratio 1:11:18:18) in a sealed

<sup>1</sup>To whom correspondence should be addressed. Fax: 1-517-355-9317.  
E-mail: kanatzid@cem.msu.edu.

evacuated carbon-coated quartz ampoule. The tube was placed under the flame of a natural gas–oxygen torch until the mixture melted and then removed from the flame to solidify. A silver-gray ingot of plates was obtained after annealing the reaction mixture at 800°C for 12 h. EDS analyses of selected plates resulted in the average compositions  $K_{1.1}Sn_{9.5}Bi_{11.6}Se_{26}$ ,  $Rb_{0.9}Sn_{9.4}Bi_{10.9}Se_{26}$ , and  $Cs_{1.3}Sn_{8.9}Bi_{11.3}Se_{26}$ .

$K_{1-x}Sn_{9-x}Bi_{11+x}Se_{26}$  (17) crystallizes in the monoclinic space group  $P2_1/m$  in a new structure type as expected from  $A_m[M_6Se_8]_m[M_{5+n}Se_{9+n}]$ . The crystal structure, shown in Fig. 1, is assembled by two distinct building units of the  $NaCl^{111}$ -type and  $NaCl^{100}$ -type, respectively, to form a three-dimensional anionic framework that features tunnels running along the  $b$  axis. These tunnels accommodate the alkali ions. The structure of  $K_{1-x}Sn_{9-x}Bi_{11+x}Se_{26}$  lies four steps higher in the evolutionary ladder (see Fig. 2) from its closest relative  $K_{1-x}Sn_{5-x}Bi_{11+x}Se_{22}$  ( $m=1$ ,  $n=5$ ) (10) that shows similarly arranged but differently sized fundamental building blocks. It will be interesting to investigate if the missing members of the homologous series with  $n=6$ , 7, and 8 can be prepared and if the thickness of the  $[M_{5+n}Se_{9+n}]$  layers can be further manipulated. In  $K_{1-x}Sn_{9-x}Bi_{11+x}Se_{26}$  five (Bi,Sn)Se<sub>6</sub> octahedra wide and three octahedra thick fragments of the  $NaCl^{111}$ -type are fused to stepped-shaped layers deployed over the  $bc$  plane. The particular  $[M_{5+n}Se_{9+n}]$  building unit for  $n=9$  represents a section of a layer of the  $Bi_3Se_4$  type. In

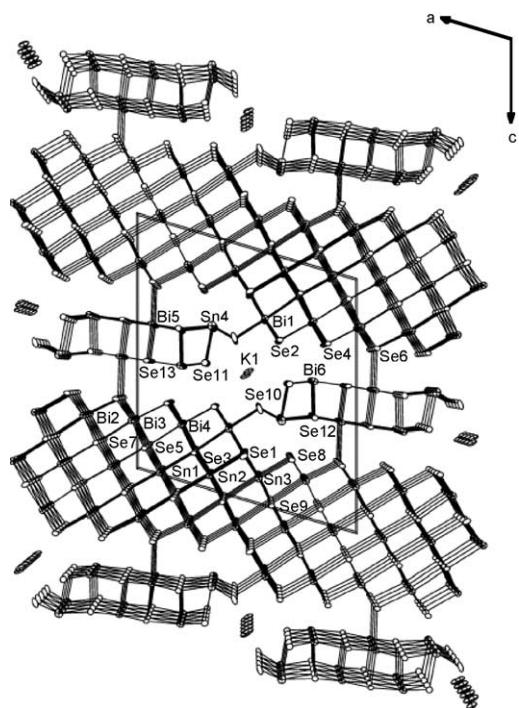


FIG. 1. ORTEP representation of the structure of  $K_{0.76}Sn_{8.76}Bi_{11.24}Se_{26}$  with atom labeling. View down the  $b$  axis.

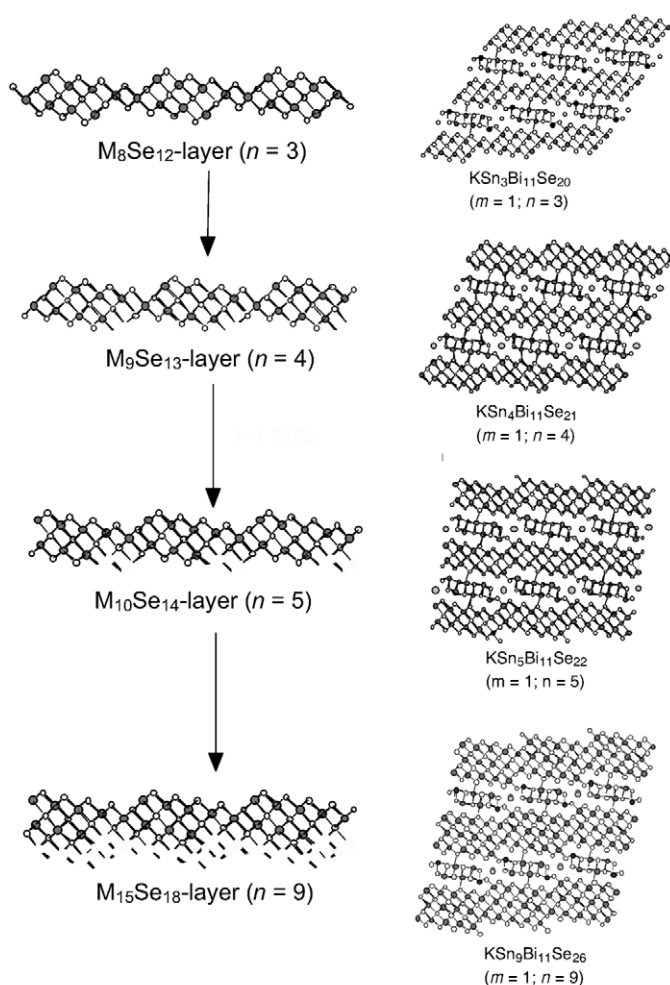


FIG. 2. The homologous series  $A_m[M_6Se_8]_m[M_{5+n}Se_{9+n}]$  for  $m=1$ . A member-generating scheme illustrating successive additions of  $MSe$  units to a  $M_5Se_9$  layer. Small white spheres; Se; large light-gray spheres, K; medium-gray spheres,  $M$ .

contrast, the  $NaCl^{111}$ -type units for  $n=3, 4, 5$  are cuts representing  $Bi_2Te_3$ -type layers. In  $K_{1-x}Sn_{9-x}Bi_{11+x}Se_{26}$  the lone pairs of the  $Bi^{3+}$  and  $Sn^{2+}$  atoms are expressed in a distorted environment (3+3 coordination) in the edge-sharing (Bi,Sn)Se<sub>6</sub> octahedra of the  $NaCl^{111}$ -type unit with interatomic (Bi,Sn)–Se distances ranging from 2.726(8) Å to 3.198(4) Å. The  $NaCl^{100}$ -type  $[M_6Se_8]$  blocks in  $K_{1-x}Sn_{9-x}Bi_{11+x}Se_{26}$  are identical to those found in  $K_{1-x}Sn_{3-x}Bi_{11+x}Se_{20}$  (8),  $K_{1-x}Sn_{4-x}Bi_{11+x}Se_{21}$  (9), and  $K_{1-x}Sn_{5-x}Bi_{11+x}Se_{22}$  (10), all of which are members of the homologous series with  $m=1$  and  $n=3, 4$ , and 5, respectively. The  $NaCl^{100}$ -type units are three (Bi,Sn)Se<sub>6</sub> octahedra wide parallel to the direction of the  $NaCl^{111}$ -type layers and one octahedron high perpendicular to this direction. The distorted tricapped trigonal prismatic sites within the tunnels are partly occupied by K. A high thermal displacement parameter indicates possible “rattling” of K ions besides positional disorder.

Preliminary charge transport measurements on polycrystalline ingots of  $K_{1-x}Sn_{9-x}Bi_{11+x}Se_{26}$  reveal moderately high electrical conductivity (570 S/cm) and Seebeck coefficient ( $-110 \mu\text{V/K}$ ) at room temperature, indicating electrons to be the main charge carriers. These values are promising and further investigations into its electrical properties are under way. The compound is a narrow gap semiconductor with a band gap of  $\sim 0.50 \text{ eV}$  (18).

In summary, the predictive character of the homologous series  $A_m[M_6Se_8]_m[M_{5+n}Se_{9+n}]$  has been demonstrated by the targeted synthesis of  $K_{1-x}Sn_{9-x}Bi_{11+x}Se_{26}$  with  $m=1$  and  $n=9$ , a new member of this series with fundamental building units derived by different cuts of the NaCl lattice perpendicular to the [111] and [100] direction, respectively. In contrast to previously reported members,  $K_{1-x}Sn_{9-x}Bi_{11+x}Se_{26}$  crystallizes in a novel structure type featuring a much thicker  $\text{NaCl}^{111}$ -type layer that resembles a section of a  $\text{Bi}_3\text{Se}_4$ -type layer instead of a  $\text{Bi}_2\text{Te}_3$ -type layer as for the early members of the homologous series. According to our results the system K/Sn/Bi/Se seems to be infinitely adaptive (16) and worth further investigations to prepare new predicted compounds.

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- $\text{NaCl}^{111}$  is meant to indicate that this fragment derives from a section of the NaCl lattice perpendicular to the [111] direction.  $\text{NaCl}^{100}$  refers to a section of the NaCl lattice perpendicular to the [100] direction. In previous publications (6, 7, 9) we addressed the ( $\text{NaCl}^{111}$ ) and ( $\text{NaCl}^{100}$ ) fragments as  $\text{Bi}_2\text{Te}_3$ -type and NaCl-type, respectively. We now realize this is inadequate for large values of  $n$  as for  $K_{1-x}Sn_{9-x}Bi_{11+x}Se_{26}$ .
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- Crystal Data* (Bruker, CCD,  $T=297 \text{ K}$ ) for  $K_{1-x}Sn_{9-x}Bi_{11+x}Se_{26}$ :  $M_w=5471.34$ , monoclinic, space group  $P2_1/m$ ;  $a=17.281(4)$ ,  $b=4.161(1)$ ,  $c=19.249(5) \text{ \AA}$ ,  $\beta=106.582(4)^\circ$ ,  $Z=1$ ,  $\lambda=0.71073 \text{ \AA}$ ,  $D_c=6.849 \text{ g cm}^{-3}$ ,  $\mu(\text{MoK}\alpha)=59.06 \text{ mm}^{-1}$ , 3580 independent reflections, unique data with  $I > 2\sigma(I)$ , 2818,  $RI=0.0406$ ,  $wR2=0.0679$ , number of variables, 166. Structure solved and refined using the SHELXTL-Plus program suite. Crystal plate-like, dimensions  $0.02 \times 0.05 \times 0.16 \text{ mm}$ . An empirical absorption correction was applied to the data (min., max. transmission, 0.2641, 1.0000). The structure refinement revealed unusual thermal displacement parameters for all metal sites requiring a disorder model with mixed Bi/Sn occupancies in the same crystallographic site ( $\text{Bi}1-6$ ,  $\text{Sn}1-4$ ) and statistical disorder in the K1 site. Their occupancies have been constrained to achieve charge balance assuming  $\text{K}^+$ ,  $\text{Sn}^{2+}$ ,  $\text{Bi}^{3+}$ , and  $\text{Se}^{2-}$  which results in the formula  $K_{1-x}Sn_{9-x}Bi_{11+x}Se_{26}$  with  $x=0.24$ .
- Band gaps were obtained as described elsewhere (10).