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$Cs_{1-x}Sn_{1-x}Bi_{9+x}Se_{15}$ and $Cs_{1.5-3x}Bi_{9.5+x}Se_{15}$: members of the homologous superseries $A_m[M_{1+l}Se_{2+l}]_{2m}[M_{1+2l+n}Se_{3+3l+n}]$ (A = alkali metal, M = Sn and Bi) allowing structural evolution in three different dimensions

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$Cs_{1-x}Sn_{1-x}Bi_{9+x}Se_{15}$ and $Cs_{1.5-3x}Bi_{9.5+x}Se_{15}$ crystallize in a new structure type which does not belong to but is closely related to the members of the homologous series $A_m[M_6Se_8]_m[M_{5+n}Se_{9+n}]$; the new phases reveal a third dimension of structural evolution for this series according to the formula $A_m[M_{1+l}Se_{2+l}]_{2m}[M_{1+2l+n}Se_{3+3l+n}]$.

Recent efforts[1] in our laboratory aimed at defining new chemical concepts[2] identified the grand homologous series of phases $A_m[M_6Se_8]_m[M_{5+n}Se_{9+n}]$ (A = alkali metal, M = heavy group IV or V element). Members of this series include β-$K_2Bi_8Se_{13}$,[3] $K_{2.5}Bi_{8.5}Se_{14}$,[4] $K_{1+x}Sn_{4-2x}Bi_{7+x}Se_{15}$,[5] $K_{1-x}Sn_{4-x}Bi_{11+x}Se_{21}$[6] and $K_{1-x}Sn_{5-x}Bi_{11+x}Se_{22}$,[7] which exhibit a close structural and compositional relationship. This homology has predictive properties leading to charge-balanced hypothetical members that can be easily generated by the general formula. In fact, the following members of this series, $K_{1+x}Sn_{3-2x}Bi_{7+x}Se_{14}$,[8] $K_{1-x}Sn_{3-x}Bi_{11+x}Se_{20}$,[8] and $K_{1-x}Sn_{9-x}Bi_{11+x}Se_{26}$,[9] have been successfully targeted for synthesis *after* their compositions and structures had been predicted. The construction of each member of the homologous series is modular and assembled by two different modules, $[M_{5+n}Se_{9+n}]$ ($NaCl^{111}$-type) and $[M_6Se_8]_m$ ($NaCl^{100}$-type)[10] of variable dimensions defined by *n* and *m*, which are linked to an anionic framework with tunnels that accommodate the alkali ions (A_m). The terminology of 'homologous series' was given by Magnèli[11] to characterize chemical series that are expressed by general formulae and built on common structural principles, that are found in transition metal oxides.[12] 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.*)[13] 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, B = Nb)[14] are examples of known homologous series in solid state chemistry. 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 which evolve in only one dimension, the above mentioned series presents 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 induced by *n*. Interestingly, the width of the $NaCl^{100}$-type modules in $A_m[M_6Se_8]_m[M_{5+n}Se_{9+n}]$ is constant for all members. Here we report $Cs_{1-x}Bi_{9+x}Se_{15}$ and its isostructural ternary analog, $Cs_{1.5-3x}Bi_{9.5+x}Se_{15}$, both revealing a novel structure type that is closely related to the known members of the grand homologous series but are not members themselves because they differ in the *width* of the $NaCl^{100}$-type modules. In fact, $Cs_{1-x}Sn_{1-x}Bi_{9+x}Se_{15}$ represents structural evolution of the series in a *third* dimension. Therefore the general formula has to be expanded to the superseries $A_m[M_{1+l}Se_{2+l}]_{2m}[M_{1+2l+n}Se_{3+3/+n}]$ where now the additional integer *l* determines the width of the building modules. The mineral cannizzarite, $Pb_{46}Bi_{54}S_{127}$, represents one end member of this new homologous series with $l = \infty$, $m = 1$ and $n = 5$. $Cs_{1-x}Sn_{1-x}Bi_{9+x}Se_{15}$ shows the same motif of assembling the fundamental building units that is found for the members of the homologous series (now a sub-series) we described earlier. Therefore we had to introduce a third integer to account for the structural evolution by changing the width of the $NaCl^{100}$- and $NaCl^{111}$-type units. In order to achieve the next step of the evolutionary ladder in this new direction two MSe equivalents and one M_2Se_3 have to be added. For $l = 2$ this formula is reduced to $A_m[M_6Se_8]_m[M_{5+n}Se_{9+n}]$. This homologous superseries predicts the structure and composition of countless compounds by modifying the three independent integers *l, m* and *n*. Fig. 1 depicts the different ways the structure can develop. $Cs_{1-x}Sn_{3-x}Bi_{11+x}Se_{20}$ ($l = 2$, $m = 1$, $n = 3$) evolves by changing only one integer at a time leading to $Cs_{1-x}Sn_{1-x}Bi_{9+x}Se_{15}$ ($l = 1$, $m = 1$, $n = 3$), $Cs_{1+x}Sn_{3-2x}Bi_{7+x}Se_{14}$ ($l = 2$, $m = 2$, $n = 3$) and $Cs_{1-x}Sn_{9-x}Bi_{11+x}Se_{26}$ ($l = 2$, $m = 1$, $n = 9$). It will be interesting to attempt to prepare further compounds that can be predicted, for example $CsSn_7Bi_9Se_{21}$ ($l = 1$, $m = 1$, $n = 9$),

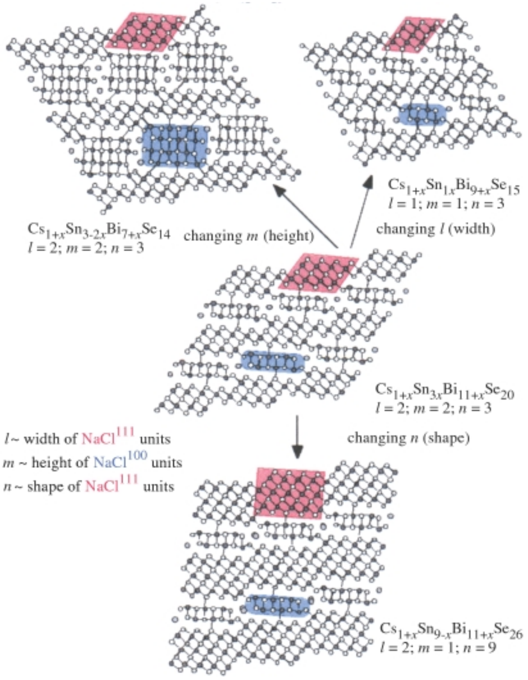

Fig. 1 Structural evolution of the homologous superseries $A_m[M_{1+l}Se_{2+l}]_{2m}[M_{1+2l+n}Se_{3+3l+n}]$ (A = alkali metal, M = heavy group IV or V element) in three different dimensions by varying the independent integers *l, m* and *n*. The $NaCl^{111}$-type units are highlighted in red and the $NaCl^{100}$-type units in blue. Small white spheres: Se, large light-gray spheres: A medium-gray spheres: M.

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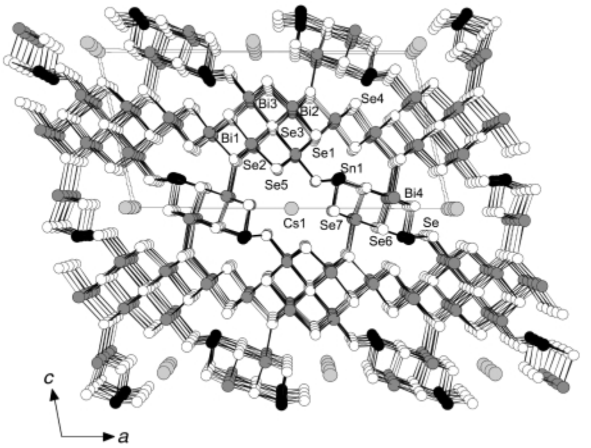

Fig. 2 Projection of the structure of $Cs_{0.65}Sn_{0.65}Bi_{8.35}Se_{15}$ with atom labeling. The tunnels in the anionic framework accommodate the Cs ions in distorted tri-capped trigonal prismatic sites. In $Cs_{1.5-3x}Bi_{9+x}Se_{15}$ the Sn1 site is occupied by Cs and Bi.

$Cs_2Sn_2Bi_{12}Se_{21}$ ($l = 1, m = 2, n = 3$) and $CsSn_6Bi_{12}Se_{25}$ ($l = 3, m = 1, n = 3$).

$Cs_{1-x}Sn_{1-x}Bi_{9+x}Se_{15}$ was prepared involving Cs_2Se, Bi_2Se_3, Sn and Se (ratio 1 : 2 : 11 : 2) in a sealed evacuated carbon coated quartz ampoule. The tube was heated within 24 h to 800 °C and kept at this temperature for 24 h, followed by slow cooling to 400 °C at a rate of 0.1 °C min^{-1} and then to 50 °C in 10 h resulting in a silver, shiny, polycrystalline ingot of $Cs_{1-x}Sn_{1-x}Bi_{9+x}Se_{15}$ as the major phase with $Cs_{1-x}Sn_{3-x}Bi_{11+x}Se_{20}$ as impurity (about 10%). EDS analyses of selected needles gave the average composition $Cs_{1.1}Sn_{0.9}Bi_{9.3}Se_{15}$. The ternary phase $Cs_{1.5-3x}Bi_{9.5+x}Se_{15}$ was obtained as follows. A mixture of 0.040 g (0.116 mmol) Cs_2Se and 0.380 g (0.580 mmol) was transferred to a silica tube which was flame-sealed under vacuum. The tube was placed under the flame of a natural gas-oxygen torch until the mixture melted and then was removed from the flame and let to solidify. The product consisted of a silvery chunk with needles growing across its surface. $Cs_{1.5-3x}Bi_{9.5+x}Se_{15}$ is the main phase with $CsBi_{3.67}Se_6$[15] as a minor phase as evidenced by X-ray powder diffraction.

The isostructural $Cs_{1.5-3x}Bi_{9.5+x}Se_{15}$ and $Cs_{1-x}Sn_{1-x}Bi_{9+x}Se_{15}$ crystallize in a new structure type as expected from $A_m[M_{1+l}Se_{2+l}]_{2m}[M_{1+2l+n}Se_{3+3l+n}$.[16] The crystal structure is shown in Fig. 2. Similar to the known members of the homologous series ($l = 2$) the structure is assembled by two distinct building units of the $NaCl^{111}$-type and $NaCl^{100}$-type, respectively, forming a three-dimensional anionic framework with tunnels running along the *b* axis which are filled by Cs ions. In $Cs_{1-x}Sn_{1-x}Bi_{9+x}Se_{15}$ three $BiSe_6$ octahedra wide and two octahedra thick fragments of the $NaCl^{111}$-type form a step-shaped layer by two adjacent units sharing an octahedra face. The distorted 3 + 3 coordination of Bi with interatomic distances in the range 2.74–3.07 Å is caused by the lone pair of Bi. In contrast to $A_{1-x}M_{3-x}Bi_{11+x}Se_{20}$ which shows the same linkage of the $NaCl^{111}$-type units to a step-shaped layer, the units in $Cs_{1-x}Bi_{9+x}Se_{15}$ represent a narrower cut out of a Bi_2Se_3-layer. In order to adjust to the narrower $NaCl^{111}$-type $[M_6Se_9]$ blocks in $Cs_{1-x}Sn_{1-x}Bi_{9+x}Se_{15}$ the $NaCl^{100}$-type $[M_4Se_6]$ units are shorter as well. They are two $(Bi,Sn)Se_6$ octahedra wide parallel to the direction of the $NaCl^{111}$-type layers and one octahedron high perpendicular to this direction while these units are three octahedra wide in $A_{1-x}Sn_{3-x}Bi_{11+x}Se_{20}$. M–Se interactions between the $NaCl^{100}$-type blocks and the stepped-shaped $NaCl^{111}$-type layers cause the formation of a three-dimensional anionic framework with tunnels along the *b*-direction that accommodate the Cs ions. Besides positional disorder a high thermal displacement parameter indicates possible ‘rattling’ of Cs ions in their partly occupied sites.

Preliminary charge transport measurements on polycrystalline ingots of $Cs_{1-x}Sn_{1-x}Bi_{9+x}Se_{15}$ reveal moderate electrical conductivity (370 S cm^{-1}) and Seebeck coefficient (-70 μV K^{-1}) at room temperature. The negative sign indicates electrons as the main charge carriers. The compound is a narrow gap n-type semiconductor with a band gap of *ca.* 0.53 eV.

In summary, $Cs_{1-x}Sn_{1-x}Bi_{9+x}Se_{15}$ and $Cs_{1.5-3x}Bi_{9.5+x}Se_{15}$ help reveal a new superseries $A_m[M_{1+l}Se_{2+l}]_{2m}[M_{1+2l+n}Se_{3+3l+n}]$ that presents three different and independent compositional variables. The new integer l controls the width of both building units, while the shape of the $NaCl^{111}$-type block is given by n and the thickness of the $NaCl^{100}$-type fragment by m. According to our results the systems A/M/Bi/Se, M = Sn, Pb, seems to be *infinitely adaptive*[17] and the identification of this broad series will permit considerable control in the design of new compounds based on phase homologies.

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16 *Crystal data* (Bruker, CCD, T = 273, *173* K) for $Cs_{1-x}Sn_{1-x}Bi_{9+x}Se_{15}$ and $Cs_{1.5-3x}Bi_{9.5+x}Se_{15}$ [in italics]: M_w = 3303.18; *3344.41*, monoclinic, space group C2/*m*; a = 27.287(8); *27.547(9)*, b = 4.116(1); *4.162(1)*, c = 14.004(4); *14.132(5)* Å, β = 103.346(5); *103.350(6)*, Z = 2, λ = 0.71073 $Å^3$, D_c = 7.168, *7.046* g cm^{-3}, μ(Mo-Kα) = 72.544; *72.112* mm^{-1}, 2020; *2087* independent reflections, unique data with $I > 2\sigma(I)$, 1531; *1735*, $R1$ = 0.0403; *0.0524*, $wR2$ = 0.0911; *0.1423*, number of variables 84; *88*. Structure solved and refined using the SHELXTL-Plus program suite. Crystal dimensions 0.06 × 0.08 × 0.32; *0.10 × 0.12 × 0.25* mm. Absorption corrections were applied to the data. Both structure refinements of $Cs_{1.5-3x}Se_{15}$ and $Cs_{1-x}Sn_{1-x}Bi_{9+x}Se_{15}$ revealed unusual thermal displacement parameters for the Bi5 and Cs1 sites which introduced a disorder model with mixed Bi/Cs occupancies and mixed Bi/Sn occupancies, respectively, in the same crystallographic site for Bi5 and statistical disorder in the Cs1 site. Their occupancies were constrained to give charge balance and resulted in the formulae $Cs_{1.11}Bi_{9.63}Se_{15}$ and $Cs_{0.65}Sn_{0.65}Bi_{9.35}Se_{15}$. CCDC reference numbers 165415 and 165416. See http://www.rsc.org/suppdata/cc/b1/b103870m/ for crystallographic data in CIF or other electronic format.
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