A new chalcogenide homologous series $A_2[M_{5+n}Se_{9+n}]$ (A = Rb, Cs; M = Bi, Ag, Cd)

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The ternary and quaternary selenides, β-CsBi₃Se₅, Rb₂-CdBi₆Se₁₁, CsAg₀.₅Bi₃.₅Se₆, CsCdBi₃Se₆, Rb₂Ag₁.₅Bi₇.₅Se₁₃, and Cs₂Ag₁.₅Bi₇.₅Se₁₃, are all members of the new homologous series $A_2[M_{5+n}Se_{9+n}]$ and crystallize in structures related to each other in a systematic way; these compounds are mid gap semiconductors and are of interest as thermoelectric materials.

The excellent thermoelectric properties of Bi_2Te_3 near room temperature have motivated extensive studies in bismuth chalcogenide chemistry over the past decade.[1–3] In recent exploration of new compounds incorporating alkali metals, extraordinarily diverse structures and compositions have emerged. One of the notable features in these compounds is that they are built with relatively few common structural motifs. When compounds can be recognized and grouped in series of homologs defined by their structural modules, we then have a powerful way to correlate and understand large classes of materials, thereby allowing useful generalizations and predictions. Some examples of homologies are the megaseries of $A_m[M_{1+l}Se_{2+l}]_{2m}[M_{2l+n}Se_{2+3l+n}]$ (A = K, Rb, Cs, Sr, Ba; M = Sn, Pb, Eu, Bi, Sb),[4] $CsPb_mBi_3Te_{5+m}$,[5] $(Sb_2Te_3)_m \cdot (Sb_2)_n$[6] and the gustavite–lillianite series[7] and the kobellite series[8] of mineral sulfosalts. The archetypal modules in these series are built from structural units excised from the NaCl- and Sb_2Se_3-type lattices.[9] These modules are uniquely expressed in each homology by a predictable evolution in size. The megaseries $A_m[M_{1+l}Se_{2+l}]_{2m}[M_{2l+n}Se_{2+3l+n}]$, for example, is composed of NaCl-type $[M_{1+l}Se_{2+l}]_{2m}$ and $[M_{2l+n}Se_{2+3l+n}]$ slabs, which are interconnected to create frameworks with tunnels accommodating the alkali metal (A_m) ions.[4] The size of each module can be tuned by varying the integers l, m and n while retaining the sites for alkali metals.

The general insights obtained by understanding the building principles in homologies have implications in the rational design of solid state compounds. This directed us to search for new homologies and identify their members. In this communication, we describe the compounds β-CsBi₃Se₅, Rb₂CdBi₆Se₁₁, CsAg₀.₅Bi₃.₅Se₆, CsCdBi₃Se₆, Rb₂Ag₁.₅Bi₇.₅Se₁₃ and Cs₂Ag₁.₅Bi₇.₅Se₁₃, all of which can be organized under the novel homologous series $A_2[M_{5+n}Se_{9+n}]$ (A = Rb, Cs; M = Bi, Ag, Cd; n = 1, 2, 3, 4). The previously reported γ-RbBi₃Se₅[10] can now be viewed as a member of this series.

The ternary β-CsBi₃Se₅, γ-RbBi₃Se₅ and the quaternary Rb₂CdBi₆Se₁₁, CsAg₀.₅Bi₃.₅Se₆, CsCdBi₃Se₆, Rb₂Ag₁.₅Bi₇.₅Se₁₃ and Cs₂Ag₁.₅Bi₇.₅Se₁₃ present a new "aufbau" motif according to the homologous series $A_2[M_{5+n}Se_{9+n}]$ (n = 1, 2, 3, 4). This is a simple series defined by a single NaCl[111]-type module which evolves with n and gives rise to unique layers. The structural evolution, member organization and hierarchy are shown in Fig. 1. The NaCl[111]-type $[M_{5+n}Se_{9+n}]$ (or $[M_5Se_9 + n$ 'MSe']) units, which are infinite in one direction, repeat side by side to build up infinite slabs with thicknesses defined by the value of n (*i.e.* the number of 'MSe' units). The alkali metal ions reside in capped trigonal prismatic sites in the spaces between the slabs which present stepped surfaces.

The structures of all compounds were confirmed by single crystal and powder X-ray diffraction studies and the refined unit cell parameters and space groups are listed in Table 1. Successive members in this series can be differentiated just by the increased thickness (~2 Å) of NaCl[111]-type modules when n increases. It is interesting to note that the members with an odd n number crystallize in the space group *Pnma* while those with an even n number in *Pnnm*. The alternating symmetry change is caused by the sequential addition of 'MSe' units in the $[M_{5+n}Se_{9+n}]$ layer.

The isostructural γ-RbBi₃Se₅ and β-CsBi₃Se₅ are the first members (n = 1) of this series, shown in Fig. 2. In terms of the homology they can be expressed as $A_2Bi_6Se_{10}$ (A = Rb, Cs) featuring the $[M_6Se_{10}]^{2-}$ (M = Bi) modules. This module is three "BiSe₆" octahedra wide and two octahedra thick, and is propagated by linking with identical neighboring modules through sharing an edge of the Bi(1)–Se octahedron to form a stepwise
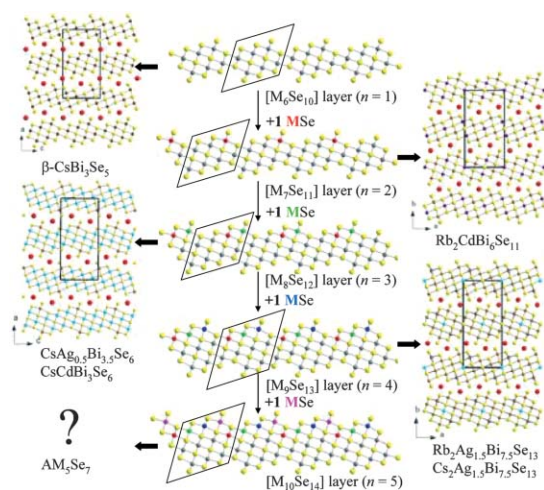

Fig. 1 Structural evolution of the homologous series $A_2[M_{5+n}Se_{9+n}]$ (A = Rb, Cs; M = Bi, Ag, Cd; n = 1, 2, 3, 4). The various sizes of the NaCl[111]-type ($[M_{5+n}Se_{9+n}]$) units as a function of integer n are shown. With every increase of n by 1 a unit of "MSe" is added to produce the next member (shown with a different color). The particular modules in each case are shown within shaded parallelograms.

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Table 1 Summary of crystallographic data for members of $A_2[M_{5+n}Se_{9+n}]$ and their band gaps

Formula	n	Space group	Z	a (Å)	b (Å)	c (Å)	Band gap (eV)
γ-RbBi$_3$Se$_5$	1	Pnma	4	21.956(7)	4.136(1)	12.357(4)	0.80
β-CsBi$_3$Se$_5$		Pnma	4	22.740(13)	4.171(2)	12.472(7)	0.63
Rb$_2$CdBi$_6$Se$_{11}$	2	Pnnm	2	12.385(3)	23.839(6)	4.1124(10)	0.74
CsAg$_{0.5}$Bi$_{3.5}$Se$_6$	3	Pnma	4	26.537(11)	4.1311(18)	12.392(5)	0.54
CsCdBi$_3$Se$_6$		Pnma	4	26.512(8)	4.1192(13)	12.396(4)	0.40
Rb$_2$Ag$_{1.5}$Bi$_{7.5}$Se$_{13}$	4	Pnnm	2	12.386(2)	27.642(5)	4.1107(8)	0.56
Cs$_2$Ag$_{1.5}$Bi$_{7.5}$Se$_{13}$		Pnnm	2	12.432(8)	28.553(18)	4.136(3)	0.60

slab. The structure has three crystallographically different Bi atoms. In γ-RbBi$_3$Se$_5$, for example, Bi(1) is in the least distorted octahedral site with Bi–Se distances at 2.864(4)–2.961(4) Å and Se–Bi–Se angles at 88.58(14)°–91.05(8)°. Bi(2) is in a slightly distorted octahedron (approximately a square pyramid) with one short bond at 2.773(3) Å, four bonds between 2.901(3) and 3.012(4) Å, and one long bond at 3.131(4) Å, which faces *trans* to the short bond. The Bi(3) octahedron is distorted along a *pseudo* three-fold axis forming three short bonds at 2.840(5) Å to Se(1) and 2.784(4) Å to two Se(2) atoms and three long bonds at 3.064(4) Å and 3.227(4) Å to Se(4) and Se(5), respectively. As in all members of this series Rb$^+$ atoms are in a bicapped trigonal prismatic co ordination with Rb–Se distances between 3.413(6) and 3.796(6) Å.

Rb$_2$CdBi$_6$Se$_{11}$ is the second member (n = 2) in the series $A_2[M_{5+n}Se_{9+n}]$. It too has a layered framework but the slabs are assembled from a wider module, namely the $[M_7Se_{11}]^{2-}$ (M = Bi, Cd), see Fig. 1 and 2. This module is three and four "MSe$_6$" octahedra wide and two octahedra thick. All metal atoms except Bi(4) are in distorted octahedral sites with bonding distances to Se atoms from 2.822(3) to 3.0512(16) Å. The Bi(4) octahedron, as the Bi(3) in γ-RbBi$_3$Se$_5$, shows the highest distortion with three short bonds ranging from 2.784(3) Å to 2.828(5) Å and three long ones from 3.114(4) Å to 3.195(4) Å. The Rb$_2$CdBi$_6$Se$_{11}$ has Cd atoms mixed in two bismuth sites, Bi(1) and Bi(3), at the fraction of 27% and 36%, respectively, to preserve charge neutrality. Therefore, the formally Cd^{2+} ions are situated in an octahedral environment of Se atoms, which is a rather unusual coordination for this ion which generally prefers a tetrahedral environment.
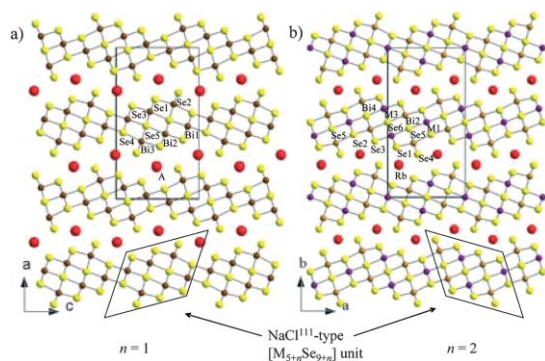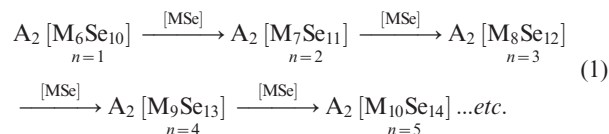
Rb$_2$Ag$_{1.5}$Bi$_{7.5}$Se$_{13}$ is the fourth member (n = 4) of the $A_2[M_{5+n}Se_{9+n}]$ series. It has structural characters in common with the above members but of course features the larger size $[M_9Se_{13}]^{2-}$ (M = Bi, Ag) modules. These are four "MSe$_6$" octahedra wide and three octahedra thick. Four of the Bi sites are mixed with Ag at the rate of 33%, 28%, 7% and 22%, which preserves charge neutrality.

As the result of the defined structural and compositional relationship from the three compounds above, the second member conceptually derives from the first by adding one neutral 'MSe' unit on the surface of the $[M_6Se_{10}]^{2-}$ unit as shown in Fig. 1. The third member derives from the second by a similar process. Successive additions ($n \geqslant 3$) of neutral MSe equivalents to the $[M_6Se_{10}]^{2-}$ unit are easily predicted to produce new member compounds as follows.

$$A_2\underset{n=1}{[M_6Se_{10}]} \xrightarrow{[MSe]} A_2\underset{n=2}{[M_7Se_{11}]} \xrightarrow{[MSe]} A_2\underset{n=3}{[M_8Se_{12}]}$$
$$\xrightarrow{[MSe]} A_2\underset{n=4}{[M_9Se_{13}]} \xrightarrow{[MSe]} A_2\underset{n=5}{[M_{10}Se_{14}]} ...etc. \quad (1)$$

Based on the above analysis, we searched for new members predicted by the series $A_2[M_{5+n}Se_{9+n}]$. CsAg$_{0.5}$Bi$_{3.5}$Se$_6$, CsCdBi$_3$Se$_6$ and Cs$_2$Ag$_{1.5}$Bi$_{7.5}$Se$_{13}$ were discovered by such targeted synthetic reactions. The new isostructural compounds CsAg$_{0.5}$Bi$_{3.5}$Se$_6$ and CsCdBi$_3$Se$_6$ are members with n = 3, and Cs$_2$Ag$_{1.5}$Bi$_{7.5}$Se$_{13}$ is a member with n = 4 according to the scheme of Fig. 1. This structural evolution leads to n = 5, AM$_5$Se$_7$ depicted in Fig. 1, which is predicted to exist.

All homolog compounds presented here are valence precise and are narrow band gap semiconductors. Their energy gaps determined spectroscopically are in the range of 0.4–0.8 eV, see Table 1 and Fig. 3.

We succeeded in preparing highly oriented polycrystalline ingots of β-CsBi$_3$Se$_5$ and CsCdBi$_3$Se$_6$ using a vertical Bridgman growth

Fig. 2 Comparison between two successive homologues to show relationship. Projection of (a) ABi$_3$Se$_5$ (A = Rb, Cs; n = 1) down the *b*-axis with *Pnma* space group and (b) Rb$_2$CdBi$_6$Se$_{11}$ (n = 2) down the *c*-axis with *Pnnm* space group. The NaCl^{111}-type building units with n = 1 and n = 2 are highlighted in both structures. M1 and M3 sites are mixed occupied by Bi^{3+} with Cd^{2+}.
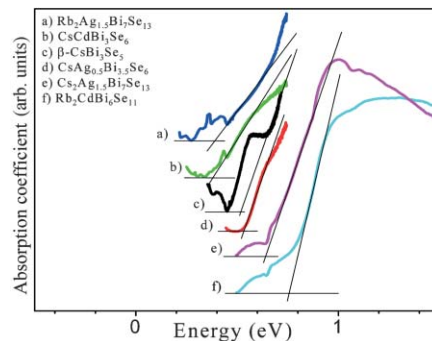

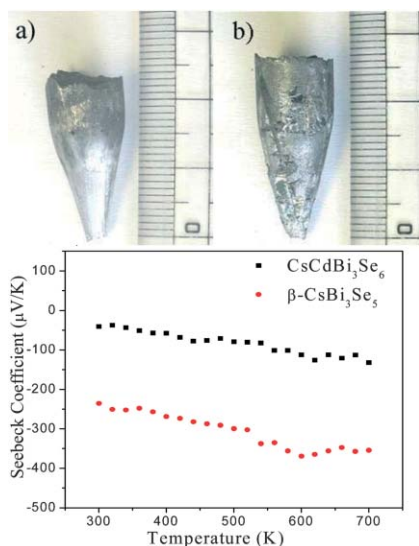**Fig. 3** Solid-state electronic absorption spectra for all homologs.

Fig. 4 Top: Ingots of (a) β-CsBi$_3$Se$_5$ and (b) CsCdBi$_3$Se$_6$ grown in a Bridgman furnace. Bottom: Temperature dependence of the thermopower for single crystal samples of β-CsBi$_3$Se$_5$ and CsCdBi$_3$Se$_6$.

technique,[11] Fig. 4. The crystalline orientation in these ingots was very high with the short ~4 Å axis of the crystal being parallel to their length. Preliminary thermopower and electrical conductivity measurements on rectangular samples were carried out along the crystal growth direction (*i.e.* crystallographic *b*-axis). At room temperature the thermopower was −40 and −235 μV K^{-1} for β-CsBi$_3$Se$_5$ and CsCdBi$_3$Se$_6$ respectively and increased steadily with rising temperature, Fig. 4. Their corresponding electrical conductivities (four-probe) were 1.3 and 1.0 S cm^{-1}, respectively. The negative thermopower and low electrical conductivity suggest n-type semiconductor character with a small number of electrons as the charge carriers. Despite the comparable conductivity, the much larger thermopower of the Cd compound is noteworthy and may point to a potential promise of octahedral Cd-containing chalcogenides for thermoelectric investigations.

In conclusion, a new homologous series A$_2$[M$_{5+n}$Se$_{9+n}$] (A = Rb, Cs; M = Bi, Ag, Cd; *n* = 1–4) was established which can precisely describe, structurally and compositionally, a large number of complex phases including β-CsBi$_3$Se$_5$, Rb$_2$CdBi$_6$Se$_{11}$ and Rb$_2$Ag$_{1.5}$Bi$_{7.5}$Se$_{13}$. This series is based on a single evolving module NaCl^{111}-type block and can describe in a unified fashion a relative large number of seemingly unrelated compounds. The predictive ability of the homology was then exploited to produce CsAg$_{0.5}$Bi$_{3.5}$Se$_6$, CsCdBi$_3$Se$_6$ and Cs$_2$Ag$_{1.5}$Bi$_{7.5}$Se$_{13}$. Low dimensional structures such as these may be suitable for doping investigations aimed at optimizing the thermoelectric properties.[12] Further investigations on the A$_2$[M$_{5+n}$Se$_{9+n}$] series could lead to higher order members in this group.

Notes and references

† β-CsBi$_3$Se$_5$ and CsCdBi$_3$Se$_6$ were prepared by a direct combination of elements. The mixtures, sealed in evacuated fused silica tubes, were heated at 750 °C for 2 h with rocking, followed by cooling to 550 °C at a rate of 20 °C h^{-1} then to room temperature in 10 h. Lustrous polycrystalline ingots made from needle-like crystals randomly oriented were obtained in

quantitative yield. The Bridgman technique[11] was then applied to grow highly oriented ingots of β-CsBi$_3$Se$_5$ and CsCdBi$_3$Se$_6$ at a descending speed 4.17 mm h^{-1} at 750 °C. The Rb$_2$CdBi$_6$Se$_{11}$, Rb$_2$Ag$_{1.5}$Bi$_{7.5}$Se$_{13}$, and Cs$_2$Ag$_{1.5}$Bi$_{7.5}$Se$_{13}$ were synthesized from direct combination reactions of the corresponding elements targeting these compositions. The thoroughly mixed elements were sealed in evacuated fused silica tubes and heated at 750 °C for 72 h, followed by cooling to 550 °C at a rate of −5 °C h^{-1}, and then to 50 °C in 10 h. The products were shiny silvery polycrystalline ingots and each phase was identified by X-ray powder diffraction. A fast cooling (10 h from 750 °C to 50 °C) in the reaction for CsAg$_{0.5}$Bi$_{3.5}$Se$_6$ produced Cs$_2$Ag$_{1.5}$Bi$_{7.5}$Se$_{13}$ as an impurity (~10% yield) and all products were analyzed by XRD. Crystal data for β-CsBi$_3$Se$_5$, Rb$_2$CdBi$_6$Se$_{11}$, CsCdBi$_3$Se$_6$, Rb$_2$Ag$_{1.5}$Bi$_{7.5}$Se$_{13}$, CsAg$_{0.5}$Bi$_{3.5}$Se$_6$ and Cs$_2$Ag$_{1.5}$Bi$_{7.5}$Se$_{13}$: A Bruker SMART Platform CCD diffractometer was used for data collection at room temperature and 173 K with an omega angle rotation of 0.3° and an acquisition time of 30 sec. An analytical absorption correction was performed using face indexing and the program XPREP, followed by a semiempirical absorption correction based on symmetrically equivalent reflections with the program SADABS. Structures were solved and refined using the SHELXTL program. *Crystal data*: for *n* = 1: β-CsBi$_3$Se$_5$: M_w = 1154.65, orthorhombic, space group *Pnma*, *a* = 22.740(13) Å, *b* = 4.171(2) Å, *c* = 12.472(7) Å, *T* = 293 K, *Z* = 4, λ = 0.71073 Å, d_{calc} = 6.483 g cm^{-3}, μ(Mo-Kα) = 62.867 mm^{-1}, F(000) = 1896, 8168 reflections measured, 1542 unique (R_{int} = 0.0688), R_1 = 0.0670, wR_2 = 0.1688 [for $I > 2\sigma(I)$]. For *n* = 2: Rb$_2$CdBi$_6$Se$_{11}$: M_w = 2405.78, orthorhombic, space group *Pnnm*, *a* = 12.385(3) Å, *b* = 23.839(6) Å, *c* = 4.1124(10) Å, *T* = 173 K, *Z* = 2, λ = 0.71073 Å, d_{calc} = 6.581 g cm^{-3}, μ(Mo-Kα) = 64.636 mm^{-1}, F(000) = 1988, 10010 reflections measured, 1681 unique (R_{int} = 0.1763), R_1 = 0.0640, wR_2 = 0.1497 [for $I > 2\sigma(I)$]. For *n* = 3: CsCdBi$_3$Se$_6$: M_w = 1346.01, orthorhombic, space group *Pnma*, *a* = 26.512(8) Å, *b* = 4.1192(13) Å, *c* = 12.396(4) Å, *T* = 293 K, *Z* = 4, λ = 0.71073 Å, d_{calc} = 6.604 g cm^{-3}, μ(Mo-Kα) = 59.161 mm^{-1}, F(000) = 2224, 10826 reflections measured, 1819 unique (R_{int} = 0.0621), R_1 = 0.0503, wR_2 = 0.1269 [for $I > 2\sigma(I)$]. CsAg$_{0.5}$Bi$_{3.5}$Se$_6$ is isostructural to CsCdBi$_3$Se$_6$. For *n* = 4: Rb$_2$Ag$_{1.5}$Bi$_{7.5}$Se$_{13}$: M_w = 2926.57, orthorhombic, space group *Pnnm*, *a* = 12.386(2) Å, *b* = 27.642(5) Å, *c* = 4.1107(8) Å, *T* = 173 K, *Z* = 2, λ = 0.71073 Å, d_{calc} = 6.906 g cm^{-3}, μ(Mo-Kα) = 67.966 mm^{-1}, F(000) = 2418, 11237 reflections measured, 1956 unique (R_{int} = 0.0922), R_1 = 0.0389, wR_2 = 0.0831 [for $I > 2\sigma(I)$]. Cs$_2$Ag$_{1.5}$Bi$_{7.5}$Se$_{13}$ was also refined and is isostructural to Rb$_2$Ag$_{1.5}$Bi$_{7.5}$Se$_{13}$ (data not shown). CCDC [291021–291024]. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b516790f

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