

# “Design” in Solid-State Chemistry Based on Phase Homologies. The Concept of Structural Evolution and the New Megaseries



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## ABSTRACT

An attractive way to advance the design and prediction of new compositions and structures of solid-state compounds is to identify large homologies that are amenable to chemical control. Homologies allow the systematization of phases under a common conceptual umbrella and have the potential to capture the vast majority of existing and possible compounds. We have demonstrated this in the broad system  $A/M'/M''/Se$  ( $A = K, Rb, Cs, Sr, Ba$ ;  $M' = Pb, Sn$ ;  $M'' = Sb, Bi$ ) by identifying the homologous “superseries”  $A_m[M_{1+l}Se_{2+l}]_{2m}[M_{2+l+n}Se_{2+3+l+n}]$ . This series generates a large variety of compounds with *predictable* composition and structure. All the compounds contain fundamental building units representing different fragments of the NaCl-type lattice. The three independent integers  $l$ ,  $m$ , and  $n$  determine width, height, and shape of the building units and therefore cause structural evolution of the homologous series in three different dimensions. On the basis of this general formula one can design, in a modular fashion, new compounds that fit the structural evolution of the superseries, predicting simultaneously their structure and composition. Several new phases have been discovered with this approach. Here we give an overview of the character and predictive properties of the superseries and propose the classification of phases into homologies (when possible) which could serve as devices to predict new members.

## 1. Introduction

An undisputed “Holy Grail” in synthetic solid-state chemistry is the ability to design crystalline solids with definitive stoichiometries, compositions, and structures. A large part

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of past and present research has been motivated by a yearning to accelerate progress in the design and prediction of new materials. This great challenge is of primary importance in chemistry, and in fact to a limited extent it has already been met. For example, cases in which “materials design” has been achieved involve simple isomorphous substitutions of one element for another, the synthesis of solid solutions, the insertion of guest species into solids, the synthesis of coordination polymers based on aristotype solid-state structures, and the assembly of templated materials. However, in the majority of cases the ability to broadly design and predict new phases is limited and will remain so for the foreseeable future.

The majority of molecular synthetic chemists (especially organic) have some ability to design, since the small molecular units they work with remain relatively intact throughout reactions, and so their goal is mainly to link one molecule to the next or to perform specific changes on functional groups. The solid-state synthetic chemist is much less able to design, except for the simplest cases mentioned above. Unlike a molecular synthetic target, which can be built one step at a time and through several stable intermediates, the structures of solid-state materials are quasi-infinite, and they have to be constructed almost always in a “single step” (one-pot synthesis). Nevertheless, the comparison between a molecular synthetic chemist and one dealing with compounds with extended structures is neither proper nor correct in the manner it is often made. A more fitting comparison is between the ability of molecular synthetic chemists to predict *how molecules will orient and crystallize* in the solid state vis-à-vis the ability of solid-state chemists to construct extended structures. In this case the difference is none.

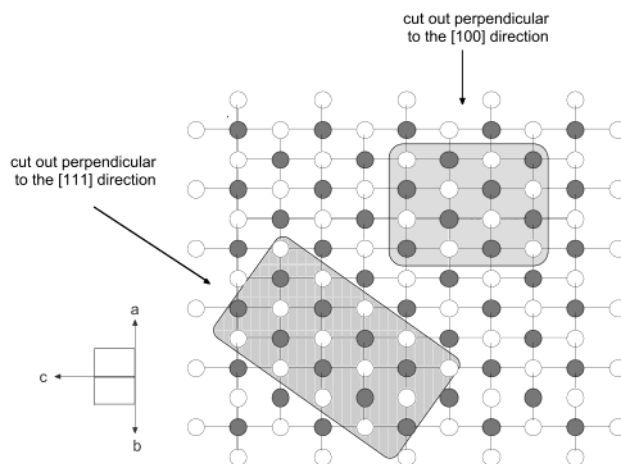
The predictability challenge in solid-state chemistry has two different facets. The first is how to synthesize a certain target phase and avoid unwanted phases, and the second is how to predict new compositions and structures that would be worth making. The first challenge arises in part from the high reaction temperatures (>700 °C) used in typical solid-state syntheses. Because the starting materials used in such reactions are usually solids themselves, very high temperatures are necessary to cause sufficient diffusion for a reaction to take place. In response to these difficulties, lower temperature methods have been developed involving molten salt, hydrothermal techniques, metallic flux, templated self-assembly, and use of “pre-fabricated” molecular tectons. These techniques bring us closer to achieving the goal of successful design, not by giving us predicted phases but by helping us avoid undesirable ones (e.g., thermodynamic traps), thus increasing the odds of discovering desired compounds. The second challenge has to do with predicting what structures would be stable and finding ways to increase the odds and produce specific compounds. One elegant way is through the use of phase homologies. Here we will describe how we can predict not only the composition but also the structure of materials in the very broad system

A/M'/M''/Se while also achieving control in a solid-state reaction. We will then point to some sweeping general implications that arise.

This work has been an outgrowth of our research efforts to design new materials with superior thermoelectric properties.<sup>1,2</sup> Our approach, which has been outlined in detail elsewhere,<sup>3</sup> is focused on complex bismuth chalcogenides. These materials are strongly anisotropic, both structurally and electronically, and this can have a positive impact on the thermoelectric figure of merit. The examples of CsBi<sub>4</sub>Te<sub>6</sub><sup>4</sup> and β-K<sub>2</sub>Bi<sub>8</sub>Se<sub>13</sub>,<sup>5</sup> which possess strongly one-dimensional (1D) characteristics and have promising properties, show that this strategy has considerable potential. By nature, this type of activity is exploratory, and one needs to generate quickly target compounds with high probability of success. Exploratory investigations of the quaternary systems A/M'/M''/Se (A = K, Rb, Cs, Sr, Ba; M' = Sn, Pb, Eu; M'' = Sb, Bi) led to numerous compounds such as AM<sub>4</sub>M'<sub>7</sub>Se<sub>15</sub>,<sup>6</sup> CsPbBi<sub>3</sub>Se<sub>6</sub>,<sup>7</sup> Ba<sub>3</sub>Pb<sub>3</sub>Bi<sub>6</sub>Se<sub>15</sub>,<sup>8</sup> and Eu<sub>2</sub>Pb<sub>2</sub>Bi<sub>6</sub>Se<sub>13</sub>.<sup>8,12</sup> All these phases exhibit impressive structural diversity, with closely inter-related motifs characterized by modular construction that is achieved by combining fragments cut out along different directions of the NaCl lattice. Investigations in the A/M'/Bi/Se (A = K, Rb, Cs; M' = Sn, Pb) system uncovered compounds such as K<sub>1-x</sub>Sn<sub>3-2x</sub>Bi<sub>11+x</sub>Se<sub>22</sub>,<sup>9</sup> A<sub>1-x</sub>M'<sub>4-x</sub>Bi<sub>11+x</sub>Se<sub>21</sub>,<sup>10</sup> and Cs<sub>1-x</sub>Sn<sub>1-x</sub>Bi<sub>9+x</sub>Se<sub>15</sub><sup>11</sup> and helped to identify a homologous megaserie of phases with the general formula A<sub>m</sub>[M<sub>1+l</sub>Se<sub>2+l</sub>]<sub>2m</sub>[M<sub>2+l+n</sub>Se<sub>2+3+l+n</sub>] (A = alkali metal; M = main group IV and V element (or even A)).<sup>12</sup> We chose to call this homology a megaserie or “superserie” because unlike other known homologies, which exhibit one or two variables, the one presented here has three variables, allowing structural evolution in three different dimensions. This superserie describes also ternary compounds such as β-K<sub>2</sub>Bi<sub>8</sub>Se<sub>13</sub>,<sup>8</sup> K<sub>2.5</sub>Bi<sub>8.5</sub>Se<sub>14</sub>,<sup>5</sup> and Cs<sub>1.5-3x</sub>Bi<sub>9.5+x</sub>Se<sub>13</sub>.<sup>11</sup> The members A<sub>1+x</sub>M'<sub>3-2x</sub>Bi<sub>7+x</sub>Se<sub>14</sub>,<sup>13</sup> A<sub>1-x</sub>M'<sub>3-x</sub>Bi<sub>11+x</sub>Se<sub>20</sub>,<sup>13</sup> and A<sub>1-x</sub>Sn<sub>9-x</sub>Bi<sub>11+x</sub>Se<sub>26</sub><sup>14</sup> were designed and targeted for synthesis *after* their structure and composition had been predicted according to the general formula. Here we present the salient characteristics and properties of this massive homology and argue the implications for synthetic design in solid-state chemistry.

## 2. Homologous Series in Solid-State Chemistry

The name “homologous series” was given by Magnèli<sup>15</sup> to characterize chemical series that are expressed by general formulas and built on common structural principles that are found in transition metal oxides.<sup>16</sup> A homologous series is expressed in terms of a mathematical formula that is capable of producing each member. The terminology is now widely used in solid-state chemistry, e.g., as for the Aurivillius phases Bi<sub>2</sub>A<sub>n-1</sub>B<sub>n</sub>O<sub>3n+3</sub> (A = Na, K, Ca, Sr, Ba, Pb, Ln, Bi, U, Th, etc.; B = Fe, Cr, Ga, Ti, Zr, Nb, Ta, Mo, W, etc.)<sup>17</sup> and the Jacobson–Dion phases A[A'<sub>n-1</sub>B<sub>n</sub>O<sub>3n+1</sub>] (A = Li, Na, K, Rb, Cs, Tl, NH<sub>4</sub>; A' = Ca, Nd; B = Nb).<sup>18</sup> The structures of the lamellar oxides are related to the rutile and perovskite types, where the integer



**FIGURE 1.** View of the NaCl structure down the [110] direction. The boxed areas represent some fundamental building blocks found in the members of the superseries A<sub>m</sub>[M<sub>1+l</sub>Se<sub>2+l</sub>]<sub>2m</sub>[M<sub>2+l+n</sub>Se<sub>2+3+l+n</sub>] (●, metal atoms; ○, chalcogen atoms). These blocks (NaCl<sup>100</sup> and NaCl<sup>111</sup> type) are essentially cuts of the NaCl-type lattice along different directions. The lattice can be sectioned in a multitude of ways, generating various blocks.

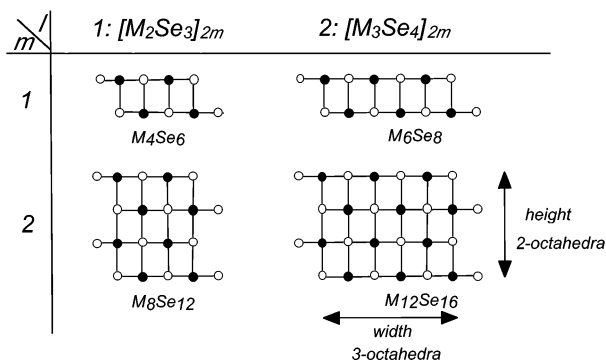
*n* determines the thickness of the slabs. Besides oxides, homologous series are also well known for sulfosalts, e.g., the gustavite–lillianite series,<sup>19,20</sup> the kobellite series,<sup>21</sup> and the pavonite series<sup>22</sup> to name a few. The nonmineral system BaQ/Fe<sub>2</sub>Q<sub>3</sub> (Q = S, Se) was also found to define the fascinating 2D homologous series (BaQ)<sub>n</sub>(Fe<sub>2</sub>Q<sub>3</sub>)<sub>m</sub>.<sup>23</sup> Within a homologous series, the type of fundamental building units and the principles that define how they combine remain preserved, and only the size of these blocks varies incrementally by changing the number of coordination polyhedra in these blocks.

## 3. The Megaserie A<sub>m</sub>[M<sub>1+l</sub>Se<sub>2+l</sub>]<sub>2m</sub>[M<sub>2+l+n</sub>Se<sub>2+3+l+n</sub>]

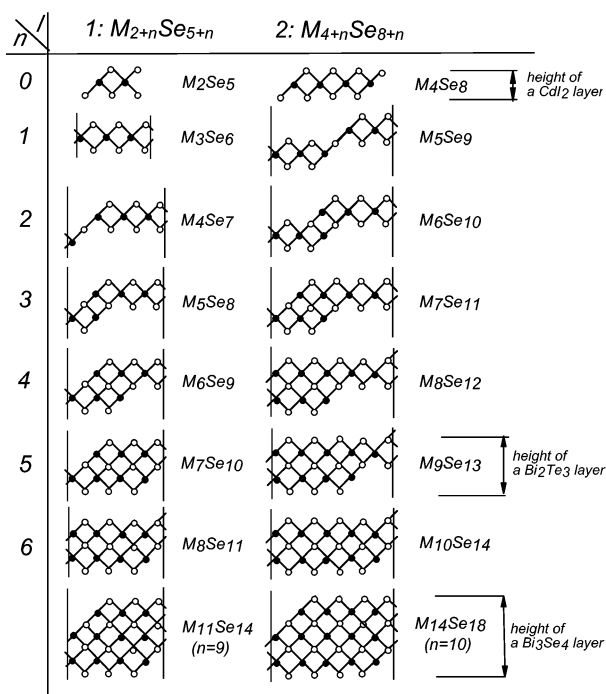
In contrast to the above-mentioned homologies, the series A<sub>m</sub>[M<sub>1+l</sub>Se<sub>2+l</sub>]<sub>2m</sub>[M<sub>2+l+n</sub>Se<sub>2+3+l+n</sub>] discussed here is of considerably larger scope because it presents three variable integers, *l*, *m*, and *n*. The construction of each member is modular, and phase assembly is achieved by two different modules, [M<sub>2+l+n</sub>Se<sub>2+3+l+n</sub>] and [M<sub>1+l</sub>Se<sub>2+l</sub>]<sub>2m</sub>, of adjustable dimensions. The modules are linked to a 3D framework with tunnels that accommodate the alkali ions (A<sub>m</sub>).

### 3.1. Building Blocks: Carving-up the NaCl Lattice.

The [M<sub>1+l</sub>Se<sub>2+l</sub>]<sub>2m</sub> and [M<sub>2+l+n</sub>Se<sub>2+3+l+n</sub>] modules represent various fragments sliced out of the NaCl lattice along different orientations and dimensions. Usually they vary in dimension along two directions of the NaCl lattice, while the third dimension is infinite. This “carving” of the lattice can result in either infinite slabs of various types, or infinite rods of various cross sections. Figure 1 depicts several of many ways the NaCl lattice can be sectioned to produce the building fragments observed in the compounds discussed here. If the cut is made perpendicular to a certain direction, e.g., [100] or [111], the fragment may be called NaCl<sup>100</sup> type or NaCl<sup>111</sup> type, respectively.



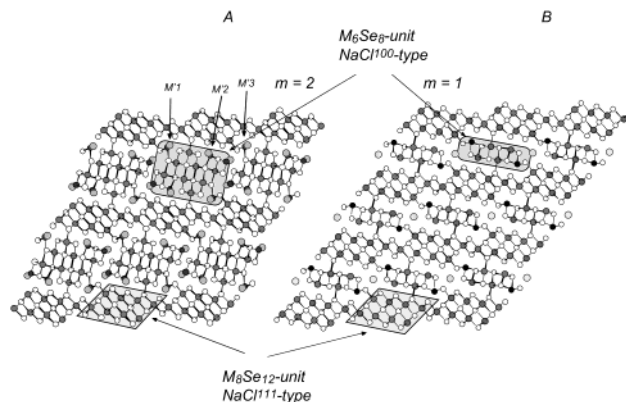
**FIGURE 2.** Structure of NaCl<sup>100</sup>-type modules for various  $l$  and  $m$  values. The height and width, two terms frequently used in the paper, are indicated.



**FIGURE 3.** Structure of NaCl<sup>111</sup>-type modules for various  $l$  and  $n$  values. For  $l = 1$  and  $n = 1$ , we obtain the infinite CdI<sub>2</sub>-type layer found in RbBiSe<sub>2</sub>.

In the general formula  $A_m[M_{1+l}Se_{2+l}]_{2m}[M_{2+l-n}Se_{2+3l+n}]$ ,  $[M_{1+l}Se_{2+l}]_{2m}$  represents the NaCl<sup>100</sup>-type module and  $[M_{2+l-n}Se_{2+3l+n}]$  represents the NaCl<sup>111</sup>-type module. The size and shape of these building blocks are adjustable. While the thickness of the NaCl<sup>100</sup>-type units is given by  $m$ , the shape of the NaCl<sup>111</sup>-type units is controlled by  $n$ . The integer  $l$  sets the width (the number of MSe<sub>6</sub> octahedra) of *both* modules. Figures 2 and 3 illustrate the structures of the two types of modules and how they evolve systematically with the variables  $l$ ,  $m$ , and  $n$ .

**3.2. Classification of Known Members.** Characteristic for all members of this superseries is the modular construction of their structures. It will be convenient to classify the different phases by dividing them into sub-series according to their mutual integers. After general comments applicable to all members of the superseries, we will discuss nine observed structure types defined by the general formula  $A_m[M_{1+l}Se_{2+l}]_{2m}[M_{2+l-n}Se_{2+3l+n}]$ . Of course,

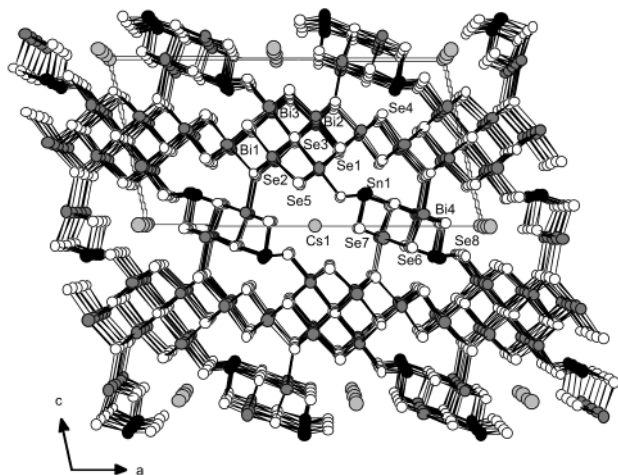


**FIGURE 4.** Comparison between two homologues to show close relationship. (A) The structure of  $KM_3Bi_7Se_{14}$  ( $l = 2$ ,  $m = 2$ ,  $n = 4$ ) viewed down the  $b$ -axis. (B) The structure of  $KM_3Bi_{11}Se_{20}$  ( $l = 2$ ,  $m = 1$ ,  $n = 4$ ) viewed down the  $b$ -axis. Small white spheres, Se; large light gray spheres, K; medium gray spheres, Bi; dark gray spheres, Sn. The archetypal NaCl<sup>100</sup>- and NaCl<sup>111</sup>-type building units are highlighted in both structures. The mixed  $M^{2+}/M^{3+}$  sites can be recognized by the nearly overlapping medium gray/dark gray spheres.

the value of this homology lies in its property to generate countless new structure types.

The organization of the modules into a 3D structure follows the same motif for every member. The infinite rodlike NaCl<sup>111</sup>-type units are linked side by side in a trans fashion to form step-shaped slabs. Strong M–Se interactions between these layers and the NaCl<sup>100</sup>-type rods form an anionic framework, creating tunnels running along the shortest crystallographic axis. Each formula corresponds to a unique structure type that can contain many ternary and quaternary members. In general, the metal atoms can be extensively disordered over all metal sites in the different structures. However, the degree of mixed  $M'/M''$  occupancy varies for each metal site. According to single-crystal structure refinements of the quaternary selenides, the divalent metals in general prefer the periphery of the NaCl<sup>100</sup>-type units (see Figure 4). These positions ( $M'1$ ,  $M'2$ , etc.) can show mixed occupancies of tri-, di-, and even monovalent atoms. Therefore, triple disorder can sometimes occur in these sites.

**3.2.1. Members with  $l = 1$ . The 2D Subseries  $A_m[M_4Se_6]_m[M_{2+n}Se_{5+n}]$ .** When  $l = 1$ , the superseries reduces to the 2D subseries  $A_m[M_4Se_6]_m[M_{2+n}Se_{5+n}]$ . The isostructural phases  $Cs_{1.5-3x}Bi_{9.5+x}Se_{15}^{11}$  and  $A_{1-x}M'_{1-x}Bi_{9+x}Se_{15}^{11,24}$  ( $A = Rb, Cs$ ;  $M' = Sn, Pb$ ) are the currently known members of this series with  $m = 1$  and  $n = 4$ . Figure 5 depicts a projection of this structure type along the  $b$ -axis. Although 1 is the smallest  $l$  value for which we have known members, we cannot rule out—in fact, we expect (i.e., predict)—members with  $l = 0$ . Such members, for example, could be  $KBi_7Se_{11}$  ( $l = 0$ ,  $n = 5$ ,  $m = 1$ ) and  $KPbBi_7Se_{12}$  ( $l = 0$ ,  $n = 6$ ,  $m = 1$ ). In  $A_{1-x}M'_{1-x}Bi_{9+x}Se_{15}$ , the NaCl<sup>111</sup> fragments define the  $[M_6Se_9]$  modules, which are three BiSe<sub>6</sub> octahedra wide and two octahedra thick, (Figure 3). These modules are linked together via an octahedron face to form a step-shaped slab. This kind of linkage is typical for  $n = 4$ . An identical arrangement of



**FIGURE 5.** Projection of the structure of  $AM'Bi_9Se_{15}$  ( $l = 1$ ,  $m = 1$ ,  $n = 4$ ;  $A = Cs, Rb$ ;  $M' = Sn, Pb$ ) with atom labeling. The tunnels in the anionic framework accommodate the alkali ions in distorted tricapped trigonal prismatic sites. In  $Cs_{1.5-3x}Bi_{9.5+x}Se_{15}$ , the Sn1 site is occupied by Cs and Bi.

these modules is also found in  $A_{1-x}M'_3Bi_{11+x}Se_{20}$ ,<sup>13</sup>  $A_{1-x}M'_{3-2x}Bi_{7+x}Se_{14}$ ,<sup>13</sup> and  $K_{2.5}Bi_{8.5}Se_{14}$ <sup>5</sup> (see Figures 4 and 10). In these members (where  $l = 2$ ), the NaCl<sup>111</sup>-type units are wider by one  $BiSe_6$  octahedron compared to those in  $Cs_{1.5-3x}Bi_{9.5+x}Se_{15}$  and  $A_{1-x}M'_{1-x}Bi_{9+x}Se_{15}$  (where  $l = 1$ ) (compare blocks in Figure 3). To match the narrower NaCl<sup>111</sup>-type  $[M_6Se_9]$  blocks in  $A_{1-x}M'_{1-x}Bi_{9+x}Se_{15}$ , the NaCl<sup>100</sup>-type  $[M_4Se_6]$  units are two  $MSe_6$  octahedra wide parallel to the direction of the NaCl<sup>111</sup>-type layers and one octahedron high perpendicular to this direction, while these units are three octahedra wide in  $A_{1-x}Sn_{3-x}Bi_{11+x}Se_{20}$ .

**3.2.2.2. Members with  $l = 2$ . The 2D Subseries  $A_m[M_6Se_8]_m[M_{4+n}Se_{8+n}]$ .** For most currently known members of the  $A_m[M_{1+l}Se_{2+l}]_{2m}[M_{2l+n}Se_{2+3l+n}]$  series,  $l = 2$ . In this case, the general formula is reduced to the subseries  $A_m[M_6Se_8]_m[M_{4+n}Se_{8+n}]$ . To observe the next step in the evolutionary ladder (i.e., going from  $l = 1$  to  $l = 2$ ), the width of the modules has to be changed by adding two  $MSe$  and one  $M_2Se_3$  equivalents to the NaCl<sup>111</sup>- and NaCl<sup>100</sup>-type modules, respectively (see Figure 3).

The known structure types for  $l = 2$  with  $m = 1$  and 2 are depicted in Figure 6, which illustrates how higher members evolve from lower ones by adding  $MSe$  equivalents to the initial NaCl<sup>111</sup>-type layers. For example, in  $RbSnBi_7Se_{12}$  ( $n = 0$ ), the  $[M_4Se_8]$  layer consists of fragments that are one octahedron high and four octahedra wide. Here, the NaCl<sup>111</sup>-type module is so thin that it resembles a "cutout" of a CdI<sub>2</sub>-type layer for  $n = 0$ , 2. Successive addition of  $MSe$  equivalents to these structural modules generates thick NaCl<sup>111</sup>-type units that begin to resemble the  $Bi_2Te_3$ -type ( $n = 4, 5, 6$ ) and the  $Bi_3Se_4$ -type ( $n = 10$ ) structures. The absence of members with  $n = 1, 3$ , etc. means that these members are predicted to exist and are legitimate synthetic targets.

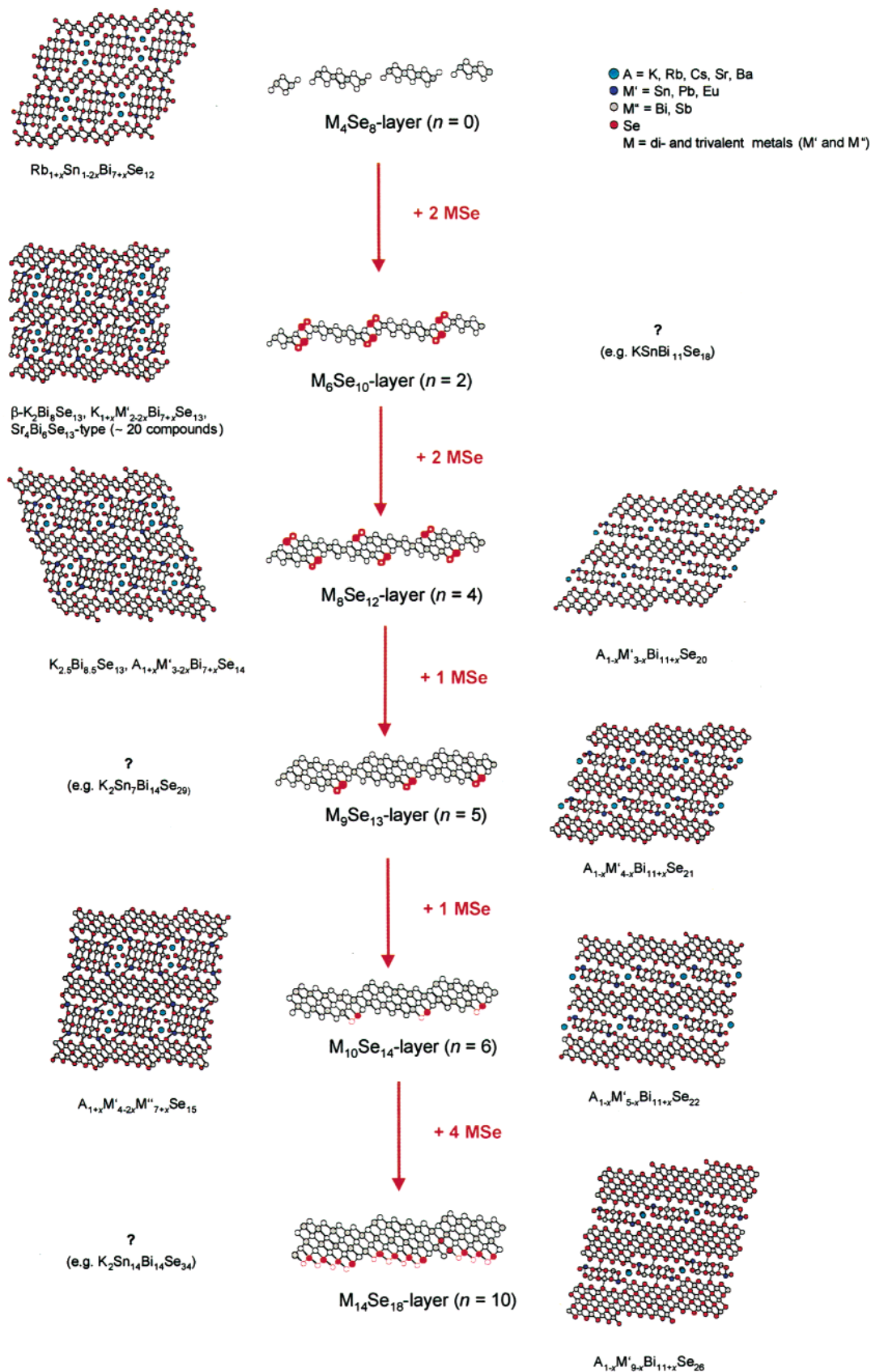
**3.2.2.1. Members with  $m = 1$ . The 1D Subseries  $AM_{10+n}Se_{16+n}$ .** Four different structure types with  $m = 1$  are now known,  $A_{1-x}M'_3Bi_{11+x}Se_{20}$ ,<sup>13</sup>  $A_{1-x}M'_{4-x}Bi_{11+x}Se_{21}$ ,<sup>10</sup>  $A_{1-x}M'_{5-x}Bi_{11+x}Se_{22}$ ,<sup>9</sup> and  $A_{1-x}Sn_{9-x}Bi_{11+x}Se_{26}$ <sup>14</sup> ( $A =$

K, Rb, Cs;  $M' = Sn, Pb$ ), adopted by every possible combination of A and  $M'$ . The value of  $x$  in the general formulas, e.g.,  $A_{1-x}M'_3Bi_{11+x}Se_{20}$ , reflects the different degrees of disorder and deviation from the ideal stoichiometry.

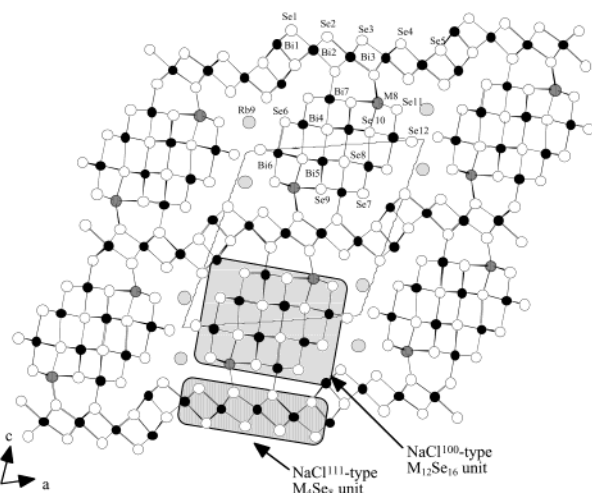
These phases exhibit the same NaCl<sup>100</sup>-type unit,  $[M_6Se_8]$ , which is one octahedron thick in the direction perpendicular to the step-shaped NaCl<sup>111</sup>-type layers and three octahedra wide in the direction parallel to the layers. In  $AM_{10+n}Se_{16+n}$ , structural evolution takes place by varying the size and shape of the NaCl<sup>111</sup>-type module  $[M_{4+n}Se_{8+n}]$  by selecting specific values of the integer  $n$ . Thus, in  $A_{1-x}M'_{3-x}Bi_{11+x}Se_{20}$  ( $n = 4$ ), the NaCl<sup>111</sup>-type module is four octahedra wide and two octahedra thick (compare Figures 3, 4, and 8). Condensation of these units via a single octahedron edge results in a step-shaped layer of the formula  $[M_8Se_{12}]$  ( $n = 4$ ). In contrast, the NaCl<sup>111</sup>-type blocks for  $n = 5$  are two octahedra thick but five octahedra wide. Their connection point is defined by a central octahedral  $M$  atom. However, the same building units, which are also offset, are joined via an octahedron edge in  $A_{1-x}M'_{5-x}Bi_{11+x}Se_{22}$  ( $n = 6$ ) (see Figure 6). The same kind of linkage is found in  $A_{1-x}Sn_{9-x}Bi_{11+x}Se_{26}$  ( $n = 10$ ) as well, but the modules are now three octahedra thick. By adding four  $MSe$  equivalents to  $A_{1-x}M'_{5-x}Bi_{11+x}Se_{22}$  ( $n = 6$ ), the thickness of the slabs, defined by the NaCl<sup>111</sup> units, increases to the point that it now resembles the layers of  $Bi_3Se_4$  instead of  $Bi_2Te_3$ , found for  $n = 4-6$ . For  $n = 0$  the formula becomes  $AM_{10}Se_{16}$ , a hypothetical example of which would be  $BaBi_{10}Se_{16}$ .

**3.2.2.2. Members with  $m = 2$ . The Subseries  $A_2M_{16+n}Se_{24+n}$ .** When the integer  $m$  increases to 2, the height of the NaCl<sup>100</sup>-type modules doubles, resulting in a  $[M_{12}Se_{16}]$  block which is two octahedra thick perpendicular to this direction and three octahedra wide in the direction parallel to the NaCl<sup>111</sup>-type layers. This gives the subseries  $A_2M_{16+n}Se_{24+n}$ . The thicker modules ( $m = 2$ ) now create double tunnels, with two tricapped trigonal prismatic sites per unit cell hosting the A atoms. By comparison, for the above-mentioned structures with  $m = 1$ , the corresponding tunnels have only one tricapped trigonal crystallographic site. When  $m = 2$ , these sites are usually fully occupied by alkali ions, in contrast to the structures with  $m = 1$ , where vacancies are always found. Alkali atoms also are found on the metals sites in the edges of the NaCl<sup>100</sup>-type module in mixed occupancy with the di- and trivalent metals (mixed A/M occupancy) of the anionic framework. To express the composition width of these phases, the formulas are written as, e.g.,  $A_{1+x}M'_{4-2x}Bi_{7+x}Se_{15}$  or  $A_2[A_xM'_{4-2x}Bi_{7+x}]_2Se_{30}$  ( $n = 6$ ). For simplicity, however, hereafter the  $x$  value will be set to 0.

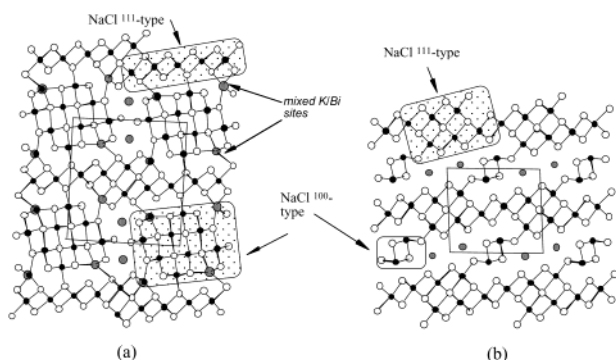
*RbSnBi<sub>7</sub>Se<sub>12</sub>* ( $l = 2$ ,  $m = 2$ ,  $n = 0$ ) (Alternatively *Rb<sub>2</sub>[Sn<sub>2</sub>Bi<sub>14</sub>]Se<sub>24</sub>*). *RbSnBi<sub>7</sub>Se<sub>12</sub>* is the first member of the subseries  $A_2M_{16+n}Se_{24+n}$  for  $l = 2$ ,  $m = 2$ , and  $n = 0$ ; the structure is projected in Figure 7. The proper formula that is consistent with the subseries  $A_2M_{16+n}Se_{24+n}$  is  $Rb_{2-2x}[Rb_{2x}Sn_{2-4x}Bi_{14+2x}]Se_{24}$ , which is simplified to  $Rb_{1+x}Sn_{1-2x}Bi_{7+x}Se_{12}$ . From this formulation, it is already apparent that there are mixed occupancy sites of the type Rb/Sn/Bi in



**FIGURE 6.** Homologous subseries  $A_m[M_6Se_8]_m[M_{4+n}Se_{8+n}]$  for  $l = 2$ . A member-generating scheme illustrating successive additions of MSe units to a  $M_4Se_8$  layer. In the left column, all members have  $m = 2$ . In the right column, members have  $m = 1$ . In the middle column is shown the evolution of the step-shaped slabs with  $n$ . Entries with question marks indicate predicted but so far unobserved phases. Members with  $n = 1, 3$ , etc., such as  $KBi_{11}Se_{17}$  ( $m = 1, n = 1$ ) and  $K_2Pb_3Bi_{17}Se_{25}$  ( $m = 2, n = 1$ ), are also anticipated. Small white spheres, Se; large light gray spheres, A; medium gray spheres, M. Question marks are meant to indicate predicted but as yet undiscovered compositions.



**FIGURE 7.** Projection of the structure of  $\text{RbSnBi}_7\text{Se}_{12}$  down the  $b$ -axis. The shaded areas indicate the  $\text{NaCl}^{100}$ - and  $\text{NaCl}^{111}$ -type building blocks. This particular  $\text{NaCl}^{111}$  module has no correspondence in the subseries  $\text{AM}_{10+n}\text{Se}_{16+n}$  where  $m = 1$ .



**FIGURE 8.** Projection of the structures of (a)  $\beta\text{-K}_2\text{Bi}_8\text{Se}_{13}$  down the  $b$ -axis and (b)  $\alpha\text{-K}_2\text{Bi}_8\text{Se}_{13}$  down the  $c$ -axis.

the structure. Standing first in the evolutionary ladder,  $\text{RbSnBi}_7\text{Se}_{12}$  features "isolated"  $\text{NaCl}^{111}$ -type modules, which are essentially  $\text{CdI}_2$ -type<sup>25</sup> ribbons. Linkage of these fundamental building units via strong  $\text{M}-\text{Se}$  interactions creates a 3D framework (see Figure 7). Successively adding two MSe equivalents leads to the compounds  $\text{KM}'_2\text{Bi}_7\text{Se}_{13}$ ,  $\text{KM}'_3\text{Bi}_7\text{Se}_{14}$ , and  $\text{KM}'_4\text{Bi}_7\text{Se}_{15}$  that vary in the size and shape of the  $\text{NaCl}^{111}$ -type module, while the  $\text{NaCl}^{100}$  module (i.e., the  $[\text{M}_{12}\text{Se}_{16}]$  block) remains unchanged.

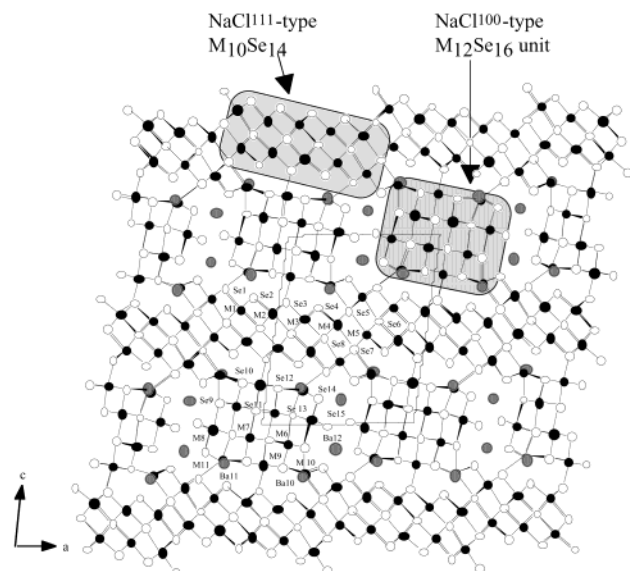
$\text{AM}'_2\text{M}'_7\text{Se}_{13}$  ( $l = 2$ ,  $m = 2$ ,  $n = 2$ ) (Alternatively  $\text{A}_2[\text{M}'_2\text{M}'_7]_2\text{Se}_{26}$ ). When  $l = 2$ ,  $m = 2$ , and  $n = 2$ , we obtain the  $\text{Sr}_4\text{Bi}_6\text{Se}_{13}$  structure type,<sup>26</sup> which is very stable and is adopted by numerous ternary and quaternary systems. Examples include  $\beta\text{-K}_2\text{Bi}_8\text{Se}_{13}$ ,  $\text{Ba}_4\text{Bi}_6\text{Se}_{13}$ ,<sup>27</sup>  $\text{Sr}_2\text{Pb}_2\text{Bi}_6\text{Se}_{13}$ ,  $\text{Ba}_3\text{M}'\text{Bi}_6\text{Se}_{13}$  ( $\text{M}' = \text{Sn, Pb}$ ), and  $\text{Eu}_2\text{Pb}_2\text{Bi}_6\text{Se}_{13}$ . In this case, the formula consistent with the series would be  $\text{A}_2[\text{A}_x\text{M}'_{2-2x}\text{M}'_{7+x}]_2\text{Se}_{26}$ . One example of this family, the structure of  $\beta\text{-K}_2\text{Bi}_8\text{Se}_{13}$ , is depicted in Figure 8a. To obtain  $\text{K}_2\text{Bi}_8\text{Se}_{13}$  from  $\text{A}_2[\text{A}_x\text{M}'_{2-2x}\text{M}'_{7+x}]_2\text{Se}_{26}$ ,  $x$  should be 1, resulting in " $\text{K}_4\text{Bi}_{16}\text{Se}_{26}$ ". The main characteristic is that the  $[\text{Bi}_6\text{Se}_{13}]^{8-}$  part of the  $\text{Sr}_4\text{Bi}_6\text{Se}_{13}$  structure remains intact, while the  $\text{Sr}^{2+}$  positions can be substituted with a variety of similarly sized ions such as  $\text{Ba}^{2+}$ ,  $\text{K}^+$ ,  $\text{Bi}^{3+}$ ,  $\text{Pb}^{2+}$ , etc., so long as they maintain electroneutrality. Often these substitutions result in mixed occupancy between the alkali

or alkaline earth metal and the bismuth atoms. The  $\text{Sr}_4\text{Bi}_6\text{Se}_{13}$  structure type exhibits  $\text{M}_6\text{Se}_{10}$  layers that have no correspondence in the subseries with  $m = 1$ . In the context of the homologous series, the  $\text{KM}'_2\text{Bi}_7\text{Se}_{13}$  ( $\text{M}' = \text{Sn, Pb}$ ) compounds were in fact successfully targeted.

Since these compounds have integers of  $l = 2$  and  $n = 2$ , they all exhibit the same  $\text{NaCl}^{111}$ -type units, which are five octahedra wide and linked via a common edge to form step-shaped slabs. These relatively thin layers (see Figure 3) interact strongly with the  $\text{NaCl}^{100}$ -type modules, resulting in a rigid 3D framework in which the distribution and assignment of various metal atoms in the different building units, especially at the interconnection points, can get ambiguous. Due to the nearly square cross section of the  $\text{NaCl}^{100}$ -type rods ( $m = 2$ ), the tunnels forming along the short  $b$ -axis acquire an elongated cross section, providing two tricapped trigonal prismatic sites. These sites are occupied by alkali, alkaline earth, Sn, or Eu atoms in the different members of the family. Their ionic radii for a coordination number of 9 vary between 1.44 ( $\text{Eu}^{2+}$ ) and 1.69 Å ( $\text{K}^+$ ). It would appear that these metal sites favor only relatively small cations. In contrast to the structures of the superseries with  $m = 1$  and  $l = 2$ , analogues with the larger alkali cations Rb or Cs have not been observed here. Instead, a different structure type is adopted for the same ratio. For example, the isostructural phases  $\text{A}_2\text{Bi}_8\text{Se}_{13}$  ( $\text{A} = \text{Rb, Cs}$ )<sup>28</sup> and also  $\alpha\text{-K}_2\text{Bi}_8\text{Se}_{13}$ <sup>29</sup> (see Figure 8b) exhibit similar building units but are not bona fide members of the homologous series. In this case we can see that the homology predicts only the correct composition but fails to accurately forecast the crystal structure. Instead, they seem to be members of another homologous series.<sup>30</sup>

$\text{A}_{1+x}\text{M}'_{3-2x}\text{M}'_{7+x}\text{Se}_{14}$  ( $l = 2$ ,  $m = 2$ ,  $n = 4$ ) (Alternatively  $\text{A}_2[\text{A}_x\text{M}'_{3-2x}\text{M}'_{7+x}]_2\text{Se}_{28}$ ). Formally, by adding another two MSe equivalents to the  $\text{NaCl}^{111}$ -type fragments of the  $\text{AM}'_2\text{M}'_7\text{Se}_{13}$  (or more descriptively  $\text{A}_2[\text{A}_x\text{M}'_{2-2x}\text{M}'_{7+x}]_2\text{Se}_{26}$ ) structure, we increase  $n$  from 2 to 4, which results in the  $[\text{M}_8\text{Se}_{12}]$  module and in the next member,  $\text{AM}'_3\text{M}'_7\text{Se}_{14}$ . This new building unit is also present in the same step-shaped layers of  $\text{AM}'_3\text{Bi}_{11}\text{Se}_{20}$  ( $l = 2$ ,  $m = 1$ ,  $n = 4$ ) (see Figure 4). Combining these with the  $\text{NaCl}^{100}$ -type blocks found in the  $\text{Sr}_4\text{Bi}_6\text{Se}_{13}$ - and  $\text{RbSnBi}_7\text{Se}_{12}$ -type motifs defines a new structure type, which is adopted by  $\alpha\text{-K}_{2.5}\text{Bi}_{8.5}\text{Se}_{14}$ ,<sup>5,29</sup>  $\gamma\text{-K}_2\text{Bi}_8\text{Se}_{13}$ ,<sup>31</sup> and  $\text{A}_{1+x}\text{M}'_{3-2x}\text{Bi}_{7+x}\text{Se}_{14}$  ( $\text{A} = \text{K, Cs}$ ;  $\text{M}' = \text{Sn, Pb}$ ).<sup>13</sup>

$\text{AM}'_4\text{M}'_7\text{Se}_{15}$  ( $l = 2$ ,  $m = 2$ ,  $n = 6$ ) (or  $\text{A}_2[\text{A}_x\text{M}'_{4-2x}\text{M}'_{7+x}]_2\text{Se}_{30}$ ). Climbing the evolutionary ladder higher, we obtain the  $\text{AM}'_4\text{M}'_7\text{Se}_{15}$  structure type by adding two MSe equivalents to the  $\alpha\text{-K}_{2.5}\text{Bi}_{8.5}\text{Se}_{14}$  type, four MSe equivalents to the  $\text{Sr}_4\text{Bi}_6\text{Se}_{13}$  type, or six MSe equivalents to the  $\text{RbSnBi}_7\text{Se}_{12}$  type, respectively. This structural evolution causes the growth of the  $\text{NaCl}^{111}$ -type modules, while the  $\text{NaCl}^{100}$ -type block remains invariant. The  $\text{AM}'_4\text{M}'_7\text{Se}_{15}$  type is realized for  $\text{A}_{1+x}\text{M}'_{4-2x}\text{Bi}_{7+x}\text{Se}_{15}$  ( $\text{A} = \text{K, Rb}$ ;  $\text{M}' = \text{Sn, Pb}$ ),  $\text{A}_{1+x}\text{Pb}_{4-2x}\text{Sb}_{7+x}\text{Se}_{15}$ , and  $\text{Ba}_{2+x}\text{Pb}_{4-x}\text{Bi}_6\text{Se}_{15}$ . Figure 9 illustrates the structure of  $\text{Ba}_{2+x}\text{Pb}_{4-x}\text{Bi}_6\text{Se}_{15}$ . The tricapped trigonal prismatic sites are exclusively occupied by Ba or alkali metals, while the two bicapped trigonal



**FIGURE 9.** Projection of the structure of  $\text{Ba}_{2+x}\text{Pb}_{4-x}\text{Bi}_6\text{Se}_{15}$  down the  $b$ -axis. The shaded areas indicate the  $\text{NaCl}^{100}$ - and  $\text{NaCl}^{111}$ -type building blocks.

prismatic sites reveal disorder of alkali (or alkaline earth) metal and di-/trivalent metal atoms. Since  $n = 6$ , these compounds reveal the same  $\text{NaCl}^{111}$ -type layers as in  $\text{A}_{1-x}\text{M}'_{5-x}\text{Bi}_{11+x}\text{Se}_{22}$  ( $l = 2, m = 1, n = 6$ ).

#### 4. Corresponding Phases in Minerals

Although the superseries  $\text{A}_m[\text{M}_{1+l}\text{Se}_{2+l}]_{2m}[\text{M}_{2+l+n}\text{Se}_{2+3l+n}]$  features fundamental building blocks similar to those of many naturally occurring mineral sulfosalts, we are aware of no minerals that fit the structural evolution of this newly discovered homologous series. A degenerate case is cannizzarite<sup>32</sup> (and its synthetic Se analogue  $\text{Pb}_5\text{Bi}_6\text{Se}_{14}$ <sup>33</sup>), which formally is an end member with  $l = \infty$  (Figure 11). Infinite layers of the  $\text{Bi}_2\text{Te}_3$  type ( $\text{NaCl}^{111}$  type ( $n = 6$ )) and one-octahedron-thick slabs of the  $\text{NaCl}^{100}$  type ( $m = 1$ ) alternate in the cannizzarite structure. The minerals Junoite,<sup>34</sup> Proudite,<sup>34</sup> and Nordströmte<sup>34</sup> also show close relationships to members of the homology. Interestingly, Proudite,  $\text{Cu}_{0.75}\text{Pb}_{7.5}\text{Bi}_{9.33}\text{Se}_{15}\text{S}_7$ , fits the general formula for  $l = 2, m = 1$ , and  $n = 6$ , exhibiting  $\text{NaCl}^{111}$ - and  $\text{NaCl}^{100}$ -type units, but it is not isostructural to  $\text{A}_{1-x}\text{M}'_{5-x}\text{Bi}_{11+x}\text{Se}_{22}$  and therefore not a member of the series. On the other hand, Junoite,  $\text{Cu}_2\text{Pb}_3\text{Bi}_8(\text{S},\text{Se})_{16}$ , can be regarded as a variation of the hypothetical  $\text{AM}'_2\text{Bi}_9\text{Se}_{16}$  ( $l = 1, m = 1, n = 5$ ). The mineral has the same  $\text{NaCl}^{100}$  type as  $\text{AM}'\text{Bi}_9\text{Se}_{15}$ , but the  $\text{NaCl}^{111}$ -type modules show the expected linkage for  $n = 5$ , as found in  $\text{AM}_4\text{Bi}_{11}\text{Se}_{21}$ . While we expect to find an alkali metal in the nine-fold-coordinated site in the tunnels running along the  $b$ -axis for a real member, Junoite features two copper atoms on tetrahedral sites. In any case, the example of Junoite shows that the anionic framework of a thus far only hypothetical member ( $l = 1, m = 1, n = 5$ ) exists, and it might be stabilized by an alkali metal as well, to give for example  $\text{K}_2\text{Pb}_2\text{Bi}_9\text{Se}_{16}$ . Similarly, Nordströmte,  $\text{CuPb}_3\text{Bi}_7(\text{S},\text{Se})_{14}$ , which also is not a member of the superseries, features  $\text{NaCl}^{100}$ -type ( $l = 3, m = 1$ ) and  $\text{NaCl}^{111}$ -type ( $l = 4, n = 4$ ) units that can be found

in the two hypothetical phases  $\text{AM}'_5\text{Bi}_{13}\text{Se}_{25}$  ( $l = 3, m = 1, n = 4$ ) and  $\text{AM}'_7\text{Bi}_{15}\text{Se}_{30}$  ( $l = 4, m = 1, n = 4$ ), respectively. The modules found in Nordströmte confirm the notion that it should be possible to engineer the *width* of the fundamental building units and design new structures based on phase homologies.

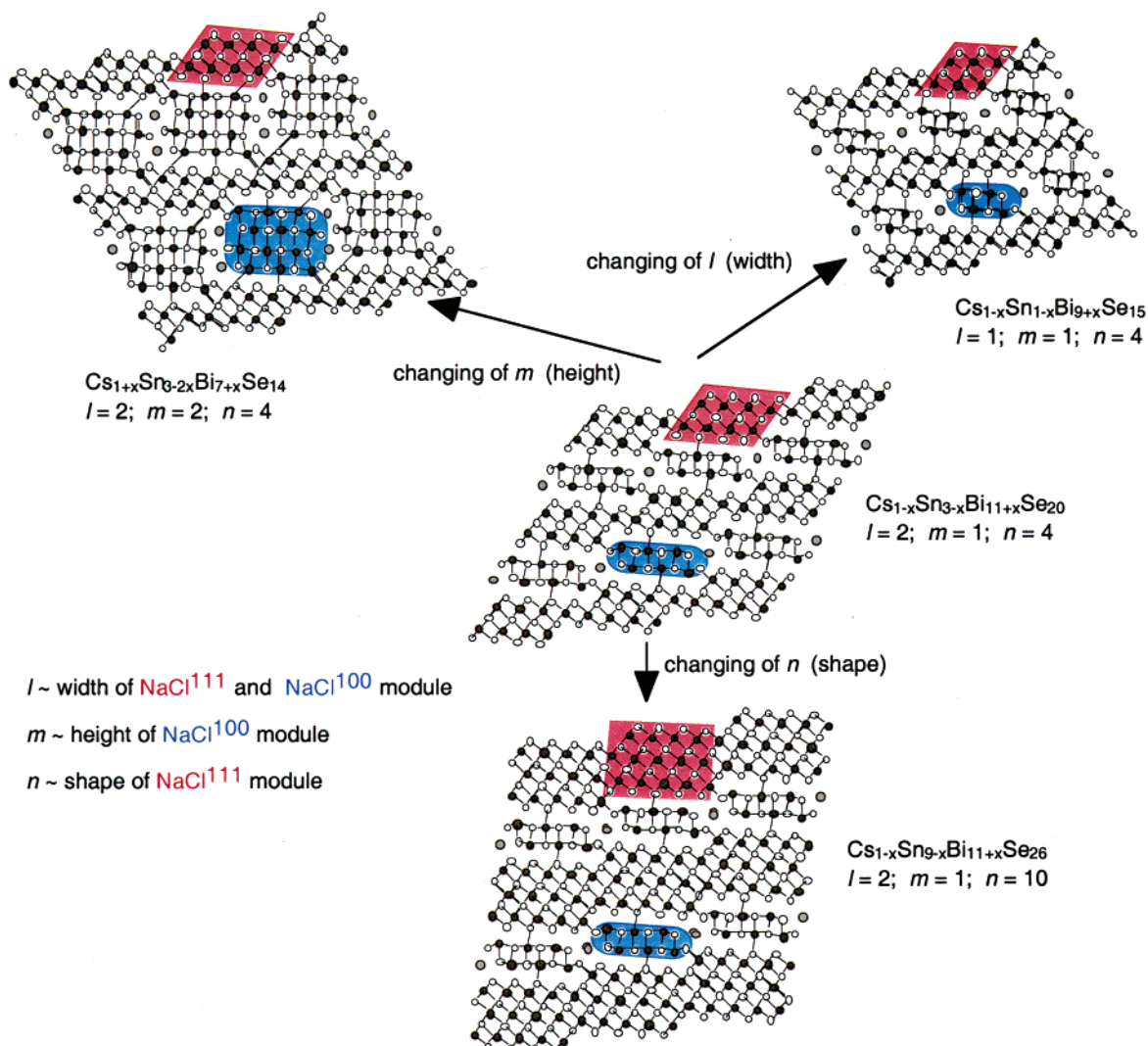
#### 5. Impurity Stabilized Phases?

It is fascinating to point out here that in most members of this megaserie the alkali metal content is  $< 1$  wt %. For example, in  $\text{K}_1\text{Sn}_9\text{Bi}_{11}\text{Se}_{26}$  ( $x = 0$ , FW 5553), the K content is  $\sim 0.7$  wt %, undoubtedly at impurity levels. Yet it is sufficient to stabilize such a complex structure as  $\text{KSn}_9\text{Bi}_{11}\text{Se}_{26}$  and, more remarkably, in quantitative yield, and as a single phase. In the absence of a crystal structure, a synthetic chemist may not be sure whether he or she has a quaternary phase or a slightly impure ternary Sn–Bi–Se phase. The alternative outcome here could have been a mixture, mainly ternary between Sn/Bi/Se phases (of which some are known), and perhaps only very little quaternary phase. In fact, such an outcome is intuitively expected and appears, on the surface, to be more probable on the basis of thermodynamics and entropy. Even though several of these phases are kinetically stabilized and have to be quenched from the liquid, for many this is not necessary. It is therefore astonishing and extraordinary that only a small amount of  $\text{A}_2\text{Se}$  (almost at the impurity level) is enough to stabilize a *single* quaternary phase, namely that dictated by the homology.

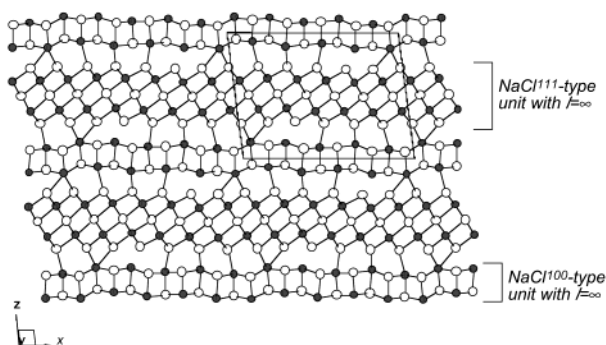
#### 6. Design of Compounds Based on Phase Homologies

The general formula  $\text{A}_m[\text{M}_{1+l}\text{Se}_{2+l}]_{2m}[\text{M}_{2+l+n}\text{Se}_{2+3l+n}]$  (or that of any series) has predictive character. Varying  $l, m$ , and  $n$  independently causes structural evolution in three independent dimensions. Therefore, we are able to predict both the structure *and* the composition of a vast number of new compounds that fit the general formula. According to the series, we can generate, for example, the charge-balanced formula  $\text{CsSn}_7\text{Bi}_9\text{Se}_{21}$  for  $l = 1, m = 1, n = 10$ . We expect this compound to reveal the same kind of  $\text{NaCl}^{100}$ -type module as in  $\text{Cs}_{1-x}\text{Sn}_{1-x}\text{Bi}_{9+x}\text{Se}_{15}$ , but being higher in the evolutionary ladder, the  $\text{NaCl}^{111}$ -type modules should represent “excisions” of a layer of the  $\text{Bi}_3\text{Se}_4$  type, as in  $\text{A}_{1-x}\text{Sn}_{9-x}\text{Bi}_{11+x}\text{Se}_{26}$ .<sup>14</sup> Already we successfully targeted several compounds for synthesis *after* their composition and structure had been predicted by the general formula, namely  $\text{AM}'\text{Bi}_{11}\text{Se}_{20}$ ,<sup>13</sup>  $\text{AM}'_3\text{Bi}_7\text{Se}_{14}$ ,<sup>13</sup>  $\text{KM}_2\text{Bi}_7\text{Se}_{13}$ , and  $\text{ASn}_9\text{Bi}_{11}\text{Se}_{26}$ .<sup>14</sup> ( $\text{A} = \text{K}, \text{Rb}, \text{Cs}$ ;  $\text{M}' = \text{Sn}, \text{Pb}$ ). In general, modifying the three integers  $l, m$ , and  $n$  provides three different ways to change *predictably* the structure of known compounds. Figure 10 depicts some of these ways for  $\text{A}_{1-x}\text{M}'_{3-x}\text{Bi}_{11+x}\text{Se}_{20}$ . Adding or subtracting  $\text{MSe}$  equivalents causes growth or shrinkage of the  $\text{NaCl}^{111}$  modules, to create different step-shaped layers.

Increasing the alkali metal content will result in members with  $l = 1$  or in members with  $m > 2$ . For  $m = \infty$ , we expect compounds that we already found in the Te system, e.g.,  $\text{CsPb}_3\text{Bi}_3\text{Te}_6$  ( $l = 1, m = \infty$ )<sup>35</sup> and  $\text{CsPb}_3\text{Bi}_3\text{Te}_8$



**FIGURE 10.** Structural evolution in the homology  $A_m[M_{1+l}Se_{2+l}]_{2m}[M_{2+l+n}Se_{2+3l+n}]$  ( $A$  = alkali metal;  $M$  = main group IV and V element) in three different dimensions by varying the independent integers  $l$ ,  $m$ , and  $n$ . The  $\text{NaCl}^{100}$ - and  $\text{NaCl}^{111}$ -type units are highlighted. White spheres, Se; large light gray spheres, A; medium gray spheres, M.



**FIGURE 11.** Structure of  $\text{Pb}_5\text{Bi}_6\text{Se}_{14}$ . This is a selenium analogue of the sulfide mineral cannizzarite. It can be regarded as a limiting case where  $l = \infty$ .

( $l = 2$ ,  $m = \infty$ ), with only the  $\text{NaCl}^{100}$ -type module. Because of the modular construction of all members of the homology, the design of new structures, prediction of their composition, and even simulation of their diffraction pattern become possible. It will be interesting to probe the limits of engineering of new materials based on this homology and to study the effect of structure, size, shape,

and arrangement of the  $\text{NaCl}^{100}$  and  $\text{NaCl}^{111}$  blocks on the physical properties.

## 7. Summary

Our investigations of the  $A/M'/\text{Bi}/\text{Se}$  ( $A = \text{K}, \text{Rb}, \text{Cs}$ ;  $M' = \text{Sn}, \text{Pb}$ ) system helped to identify a large homologous series,  $A_m[M_{1+l}Se_{2+l}]_{2m}[M_{2+l+n}Se_{2+3l+n}]$ , that defines a substantial fraction of compounds possible in various ternary  $A/M''/Q$  and quaternary systems  $A/M'/M''/Q$  (with  $A = \text{K}, \text{Rb}, \text{Cs}, \text{Sr}, \text{Ba}, \text{Eu}, \text{Sn}$ ;  $M' = \text{Sn}, \text{Pb}$ ;  $M'' = \text{Bi}, \text{Sb}$ ;  $Q = \text{S}, \text{Se}$ ). Presenting three independent compositional variables, the homology provides a definitive structural evolution in all spatial dimensions. The construction of each member of the homologous series is modular and achieved by two types of variable building units. Each unit represents an excised fragment from the  $\text{NaCl}$  lattice. While the integer  $l$  controls the width of both building units, the size and shape of the  $\text{NaCl}^{111}$ -type block are given by  $n$  and the thickness of the  $\text{NaCl}^{100}$ -type fragment is given by  $m$ , whereas the length of all units is always infinite in one of



the three directions. The special value of this homologous series is that it has predictive character and amounts to a "compound generating machine". Many compounds have been successfully targeted for preparation *after* their structure and composition were predicted by the general formula. The identification of this broad series will enable considerable control in the design of new compounds based on phase homologies and might even help understand the relationship between crystal structure, electronic structure, composition, and properties. The pursuit of new members of the series is currently under way. Of course, the series only designates possible members. What fraction of these can be accessed experimentally remains to be seen. There is also the issue of thermodynamic stability, which has not been addressed. However, all known members that have been described above have been synthesized as pure products (100% yield and >95% purity) by using quenching techniques. More importantly, however, the implications of phase homologies for designing new solid-state compounds go far beyond those discussed here. For example, many reported individual compounds and phases scattered throughout the literature might be classified and placed in the context of phase homologies. Not only will this promote better understanding of their interrelationships, but more critically it will enhance our predictive ability and will bring us closer to the goal of "rational design" for many classes of compounds. Phase homologies could prove to be an important design tool for bulk solid-state materials.

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