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

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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” Am[M1+1Se2+l]2m[M2l+nSe2+3l+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 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 “prefabricated” 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.\(^1,2\) Our approach, which has been outlined in detail elsewhere,\(^3\) is focused on complex bismuth chalco-
genides. 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\(_4\)Te\(_6\)\(^4\) and \(\beta\)-K\(_2\)Bi\(_3\)Se\(_5\)\(^5\) 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 A\(_M\)M'/\(\phi\)Se\(_m\), CsPbBi\(_3\)Se\(_6\), Ba\(_3\)Pb\(_2\)Bi\(_3\)Se\(_5\), \(^8\) and Eu\(_3\)Pb\(_2\)Bi\(_3\)Se\(_5\)\(^8,12\). All these phases exhibit impressive structural diversity, with closely interrelated 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\(_{1+x}\)Sn\(_x\)Bi\(_{11+y}\)Se\(_{20}\), A\(_1\)M\(_x\)\(_4\)Bi\(_{11+y}\)Se\(_{20}\), and Cs\(_1\)Sn\(_1\)Bi\(_{9+y}\)Se\(_{11}\)\(^11\) and helped to identify a homologous megaseries of phases with the general formula \(A_m[\text{M}_2+n\text{Se}_{2+3}+n]\) (\(A = \text{alkali metal; } M = \text{main group IV and V element (or even A)}\)).\(^12\) We chose to call this homology a megaseries or “superseries” 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 superseries describes also ternary compounds such as \(\beta\)-K\(_2\)Bi\(_3\)Se\(_5\), Ba\(_3\)Pb\(_2\)Bi\(_3\)Se\(_5\),\(^5\) and Cs\(_1\)Sn\(_1\)Bi\(_{9+y}\)Se\(_{11}\)\(^11\) The members A\(_1\)M\(_x\)\(_4\)Bi\(_{11+y}\)Se\(_{20}\), A\(_1\)Sn\(_1\)Bi\(_{11+y}\)Se\(_{20}\), and A\(_1\)Sn\(_3\)Bi\(_{11+y}\)Se\(_{20}\)\(^14\) 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 Magnéli\(^15\) to characterize chemical series that are expressed by general formulas and built on common structural principles that are found in transition metal oxides.\(^16\) 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 the field of structural chemistry, e.g., as for the Aurivillius phases Bi\(_2\)A\(_{n-1}\)\(_3\)\(_Bi\(_{3}\)O\(_{3n+3}\) (A = Na, K, Ca, Sr, Ba, Pb, Ln, Bi, U, Th, etc.; B = Fe, Cr, Ga, Ti, Zr, Nb, Ta, Mo, W, etc.)\(^17\) and the Jacobson–Dion phases \(\text{A}[A'_{n-3}Bi_{3}O_{3n+1}]\) (A = Li, Na, K, Rb, Cs, Ti, Nh; A' = Ca, Nd; B = Nb)\(^18\). The structures of the lamellar oxides are related to the rutile and perovskite types, where the integer n determines the thickness of the slabs. Besides oxides, homologous series are also well known for sulfosalts, e.g., the gustavite–lillianite series,\(^19,20\) the kobellite series,\(^21\) and the paveonite series\(^22\) to name a few. The nonmineral system BaQ/Fe\(_2\)O\(_3\) (Q = S, Se) was also found to define the fascinating 2D homologous series (BaQ)\(_m\)(Fe\(_2\)O\(_3\))\(_n\). 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 Megaseries \(A_m[\text{M}_2+n\text{Se}_{2+3}+n]\) [\(\text{M}_{2l+n\text{Se}_{2}+3l+n}\)]

In contrast to the above-mentioned homologies, the series \(A_m[\text{M}_2+n\text{Se}_{2+3}+n]\) [\(\text{M}_{2l+n\text{Se}_{2}+3l+n}\)] 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, [\(\text{M}_{2l+n\text{Se}_{2}+3l+n}\)] and \([\text{M}_1\text{Se}_{2+3}+2m^n]\), of adjustable dimensions. The modules are linked to a 3D framework with tunnels that accommodate the alkali ions (A\(_m\)).

3.1. Building Blocks: Carving-up the NaCl Lattice

The \([\text{M}_1\text{Se}_{2+3}]\)\(_m^n\) and \([\text{M}_{2l+n\text{Se}_{2}+3l+n}\]) 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\(_{100}\) type or NaCl\(_{111}\) type, respectively.
In the general formula $A_{m}[(M_{1}Se_{2})_{2m}]+[M_{2}nSe_{3n+1}],\ [M_{2}nSe_{2}+3n]+$ represents the NaCl$^{[100]}$-type module and $[M_{2}nSe_{2}+3n]$ represents the NaCl$^{[111]}$-type module. The size and shape of these building blocks are adjustable. While the thickness of the NaCl$^{[100]}$-type units is given by $m$, the shape of the NaCl$^{[111]}$-type units is controlled by $n$. The integer $l$ sets the width (the number of MSe$_{6}$ 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 subseries 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 $A_{m}[(M_{1}Se_{2})_{2m}]+[M_{2}nSe_{3n+1}].$ Of course, 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$^{[111]}$-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$^{[100]}$-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. 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$^{[100]}$-type units (see Figure 4). These positions ($M^1', M^2', M^3'')$ 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 $A_{m}[(M_{1}Se_{2})_{2m}]+[M_{2}nSe_{3n+1}].$ When $l = 1$, the superseries reduces to the 2D subseries $A_{m}[(M_{1}Se_{2})_{2m}]+[M_{2}nSe_{3n+1}].$ The isostructural phases $Cs_{l_{15}}Bi_{l_{10}}Se_{l_{15}}$ and $A_{l_{1}}M_{1-l_{1}}Bi_{l_{1}}Se_{l_{15}}$ ($A = Rb, Cs, M' = Sn, Pb$) 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 $l$ is the smallest integer 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 $KBi_{l_{10}}Se_{l_{15}}$ ($l = 0, n = 5, m = 1$) and $KPBi_{l_{10}}Se_{l_{15}}$ ($l = 0, n = 6, m = 1$). In $A_{l_{1}}M_{1-l_{1}}Bi_{l_{1}}Se_{l_{15}}$, the NaCl$^{[111]}$ fragments define the [M$_{l_{1}}$Se$_{l_{15}}$] modules, which are three BiSe$_{6}$ 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...
these modules are also found in $A_2\cdot M^+_{3-x} \cdot Bi_{11-x} \cdot Se_{20}$, $A_1 \cdot x \cdot M^{+}_{3-x} \cdot Bi_{7+x} \cdot Se_{14,13}$ and $K_2 \cdot Bi_{8} \cdot Se_8$ (see Figures 4 and 10).

In these members (where $l = 2$), the NaCl111-type units are wider by one Bi$_2$Te$_2$ octahedron compared to those in Cs$_{1.5}$Sn$_{2}$Bi$_{11}$Se$_{24}$ and $A_1 \cdot M^+_{3-x} \cdot Bi_{9+x} \cdot Se_{15}$ (where $l = 1$) (compare blocks in Figure 3). To match the narrower NaCl111-type $[M_8 Se_8]$ blocks in $A_1 \cdot x \cdot M^+_{3-x} \cdot Bi_{9+x} \cdot Se_{15}$, the NaCl100-type $[M_6 Se_9]$ blocks in $A_1 \cdot x \cdot Sn_{3} \cdot Bi_{11} \cdot Se_{15}$, the NaCl100-type units are two $M Se_6$ octahedra wide parallel to the direction of the NaCl111-type layers and one octahedron high perpendicular to this direction, while these units are three octahedra wide in $A_1 \cdot x \cdot Sn_{3} \cdot Bi_{11} \cdot Se_{20}$.

### 3.2.2. Members with $l = 2$. The 2D Subseries $A^m \cdot M^+_{16-n} \cdot Se_{24-n}$

For most currently known members of the $A_n[M_{17} Se_{24}] \cdot [M_{16-n} Se_{24-n}]$ series, $l = 2$. In this case, the general formula is reduced to the subseries $A^m_n[M_{17} Se_{24}] \cdot [M_{16-n} Se_{24-n}]$. 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 $M Se$ and one $M_2 Se_2$ equivalents to the NaCl111 and NaCl111-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 $M Se$ equivalents to the initial NaCl111-type layers. For example, in $RbSnBi_{2}Se_{20}$ ($n = 0$), the $[M_{17} Se_{24}]$ layer consists of fragments that are an octahedron high and four octahedra wide. Here, the NaCl111-type module is so thin that it resembles a “cutout” of a CdI$_2$-type layer for $n = 0, 2$. Successive addition of $M Se$ equivalents to these structural modules generates thick NaCl111-type units that begin to resemble the Bi$_2$Te$_2$-type (n = 4, 5, 6) and the Bi$_2$Te$_2$-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 $A^m_n \cdot Se_{6-n}$

Four different structure types with $m = 1$ are now known, $A_1 \cdot x \cdot M^+_{3-x} \cdot Bi_{11-x} \cdot Se_{20}$, $A_1 \cdot x \cdot M^+_{3-x} \cdot Bi_{11-x} \cdot Se_{20}$, $A_1 \cdot x \cdot M^+_{3-x} \cdot Bi_{9-x} \cdot Se_{15}$ and $A_1 \cdot x \cdot Sn_{3} \cdot Bi_{11-x} \cdot Se_{20}$ ($A = K, Rb, Cs; M' = Sn, Pb$), adopted by every possible combination of $A$ and $M'$. The value of $x$ in the general formulas, e.g., $A_1 \cdot x \cdot M^+_{3-x} \cdot Bi_{11-x} \cdot Se_{20}$, reflects the different degrees of disorder and deviation from the ideal stoichiometry.

These phases exhibit the same NaCl110-type unit, $[M_6 Se_9]$, which is one octahedron thick in the direction perpendicular to the step-shaped NaCl111-type layers and three octahedra wide in the direction parallel to the layers. In $A_m \cdot x \cdot M^+_{6-n} \cdot n \cdot Se_{16-n}$ structural evolution takes place by varying the size and shape of the NaCl111-type module $[M_{4-n} \cdot n \cdot Se_{16-n}]$ by selecting specific values of the integer $n$. Thus, in $A_1-x \cdot M^{+}_{3-x} \cdot Bi_{11-x} \cdot Se_{20}$ ($n = 4$), the NaCl111-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 $[M_8 Se_{12}]$ ($n = 4$). In contrast, the NaCl111-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 $A_1-x \cdot M^+_{5-x} \cdot Bi_{11-x} \cdot Se_{22}$ ($n = 6$) (see Figure 6). The same kind of linkage is found in $A_1-x \cdot Sn_{9-x} \cdot Bi_{11-x} \cdot Se_{26}$ ($n = 10$) as well, but the modules are now three octahedra thick. By adding four $M Se$ equivalents to $A_1-x \cdot M^+_{5-x} \cdot Bi_{11-x} \cdot Se_{22}$ ($n = 6$), the thickness of the slabs, defined by the NaCl111 units, increases to the point that it now resembles the layers of Bi$_2$Se$_6$, instead of Bi$_2$Te$_2$, found for $n = 4-6$. For $n = 0$ the formula becomes $A_1 \cdot x \cdot Bi_{11} \cdot Se_{16}$, a hypothetical example of which would be BaBi$_{10}Bi_{16}$.
FIGURE 6. Homologous subseries \( A_n[M_6Se_8]_m[M_4Se_8]_n \) 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 \( K\text{Bi}_1\text{Se}_{17} \) (\( m = 1, n = 1 \)) and \( K\text{Pb}\text{Bi}_1\text{Se}_{25} \) (\( m = 2, n = 1 \)), 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.
or alkaline earth metal and the bismuth atoms. The Sr$_x$Bi$_8$Se$_{13}$ structure type exhibits M$_x$Se$_{10}$ layers that have no correspondence in the subseries with $m = 1$. In the context of the homologous series, the KM$_x$Bi$_8$Se$_{13}$ ($M = $ Sn, Pb) compounds were in fact successfully targeted.

Since these compounds have integers of $l = 2$ and $n = 2$, they all exhibit the same 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 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 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 (Eu$^{2+}$) and 1.69 Å ($K^+$. 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 $A_1$Bi$_8$Se$_{13}$ ($A = $ Rb, Cs)$^{28}$ and also $\alpha$-K$_2$Bi$_6$Se$_{13}$ ($A = $ Rb, Cs)$^{29}$ (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.$^{30}$

$A_{l=2}M_{n=2}^{\prime\prime}$Se$_{13}$ (l = 2, m = 2, n = 2) (Alternatively $A_2^{a}$[A$_2$M$_{n=2}^{\prime\prime}$Se$_{12}$]). Formally, by adding another two MSe equivalents to the NaCl$_{111}$-type fragments of the AM$_x$M$_y$Se$_{13}$ (or more descriptively $A_2^{a}$[A$_2$M$_{n=2}^{\prime\prime}$Se$_{12}$]) structure, we increase n from 2 to 4, which results in the [M$_2$Se$_{12}$] module and in the next member, AM$_x$M$_y$Se$_{14}$. This new building unit is also present in the same step-shaped layers of AM$_x$Bi$_{12}$Se$_{20}$ (l = 2, m = 1, n = 4) (see Figure 4). Combining these with the NaCl$_{100}$-type blocks found in the Sr$_4$Bi$_{13}$ and RbSnBi$_2$Se$_{12}$-type motifs defines a new structure type, which is adopted by $K_2$Bi$_3$Se$_{15}$,$^{5,29}$ $\gamma$-K$_2$Bi$_6$Se$_{13}$,$^{31}$ and $A_{l=2}M_{n=2}^{\prime\prime}$Bi$_{12}$Se$_{14}$ ($A = $ K, Cs; M$^+ = $ Sn, Pb).$^{13}$

$A_{l=2}M_{n=2}^{\prime\prime}$Se$_{15}$ (l = 2, m = 2, n = 6) (or $A_2^{a}$[A$_2$M$_{n=2}^{\prime\prime}$Se$_{14}$]). Climing the evolutionary ladder higher, we obtain the AM$_x$M$_y$Se$_{15}$ structure type by adding two MSe equivalents to the $K_2$Bi$_3$Se$_{15}$ type, four MSe equivalents to the Sr$_4$Bi$_{13}$Se$_{15}$ type, or six MSe equivalents to the RbSnBi$_2$Se$_{12}$ type, respectively. This structural evolution causes the growth of the NaCl$_{111}$-type modules, while the NaCl$_{100}$-type block remains invariant. The AM$_x$M$_y$Se$_{15}$ type is realized for $A_1$M$_{n=2}^{\prime\prime}$Bi$_{17}$Se$_{15}$ ($A = $ K, Rb; M$^+ = $ Sn, Pb), $A_1$M$_{n=2}^{\prime\prime}$Bi$_{17}$Se$_{15}$, and Ba$^{2+}$Pb$_4$Bi$_{15}$Se$_{15}$. Figure 9 illustrates the structure of Ba$_{1+x}$Pb$_x$Bi$_{15}$Se$_{15}$. The tricapped trigonal prismatic sites are exclusively occupied by Ba or alkali metals, while the two bicapped trigonal...
Infinite layers of the Bi$_2$Te$_3$ type (NaCl$_{111}$ type (nizzarite) and its synthetic Se analogue Pb$_5$Bi$_6$Se$_{14}$33), of no minerals that fit the structural evolution of this newly many naturally occurring mineral sulfosalts, we are aware

In any case, the example of Junoite shows that the anionic

4. Corresponding Phases in Minerals

Although the superseries $A_n[M_{1-1}(\text{Se})_{1-1}]_{2m}[M_{2-n}(\text{Se})_{2-n}]_{1-1}$ 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 can-
nizzarite$^{32}$ (and its synthetic Se analogue Pb$_5$Bi$_6$Se$_{14}$33), which formally is an end member with $l = \infty$ (Figure 11). Infinite layers of the Bi$_2$Te$_3$ type (NaCl$_{111}$ type ($n = 6$)) and one-octahedron-thick slabs of the NaCl$_{100}$ type ($m = 1$) alternate in the canizzarite structure. The minerals Junoite,$^{34}$ Proudite,$^{34}$ and Nordströmite$^{34}$ also show close relationships to members of the homology. Interestingly, Proudite, Cu$_{0.75}$Pb$_{7.5}$Bi$_{9.33}$Se$_{15}$S$_7$, fits the general formula for $l = 2$, $m = 1$, $n = 6$.

5. Impurity Stabilized Phases?

It is fascinating to point out here that in most members of this megaseries the alkali metal content is <1 wt %. For example, in K$_x$Sn$_9$Bi$_{11}$Se$_{26}$ ($x = 0$, FW 5553), the K content is ~0.7 wt %, undoubtedly at impurity levels. Yet it is sufficient to stabilize such a complex structure as KSn$_2$Bi$_{11}$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 $A_2$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 $A_n[M_{1-1}(\text{Se})_{1-1}]_{2m}[M_{2-n}(\text{Se})_{2-n}]_{1-1}$ (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 CsSn$_2$Bi$_9$Se$_{21}$ for $l = 1$, $m = 1$, $n = 10$. We expect this compound to reveal the same kind of balanced formula CsSn$_7$Bi$_9$Se$_{21}$ for $l = 1$, $m = 1$, $n = 6$. The modules found in Nordströmite 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.

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

In the two hypothetical phases AM$_2$Bi$_3$Se$_{25}$ ($l = 3$, $m = 1$, $n = 4$) and AM$_2$Bi$_5$Se$_{23}$ ($l = 4$, $m = 1$, $n = 4$), respectively. The modules found in Nordströmite 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.
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 NaCl\textsuperscript{100} and NaCl\textsuperscript{111} blocks on the physical properties.

7. Summary

Our investigations of the A/M'/Bi/Se (A = K, Rb, Cs; M' = Sn, Pb) system helped to identify a large homologous series, A\textsubscript{m}[M_1\textsubscript{l}Se_2\textsubscript{l}][M_2\textsubscript{l}Se_2\textsubscript{3\textsubscript{l}+\textsubscript{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 NaCl\textsuperscript{100} and NaCl\textsuperscript{111}-type units are highlighted. White spheres, Se; large light gray spheres, A; medium gray spheres, M.

**FIGURE 10.** Structural evolution in the homology A\textsubscript{m}[M_1\textsubscript{l}Se_2\textsubscript{l}][M_2\textsubscript{l}Se_2\textsubscript{3\textsubscript{l}+\textsubscript{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 NaCl\textsuperscript{100} and NaCl\textsuperscript{111}-type units are highlighted. White spheres, Se; large light gray spheres, A; medium gray spheres, M.

**FIGURE 11.** Structure of Pb\textsubscript{5}Bi\textsubscript{6}Se\textsubscript{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 NaCl\textsuperscript{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,
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 the pursuit of new compounds and phases scattered throughout the literature. For example, many reported individual compounds and phases could prove to be an important design tool for bulk solid-state materials.

Some of the key points discussed in the article include:

- 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.
- The pursuit of new compounds and phases scattered throughout the literature could be facilitated by the identification of this broad series.
- The special value of this homologous series is that it has predictive character and amounts to a “compound generating machine.”

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References


Although the series formula appears to represent ternary systems made of only A, M, and Se, M can be a combination of monovalent, divalent, and trivalent elements, and so in principle it also represents quaternary or even higher order systems.

The next generation of thermoelectric materials could prove to be an important design tool for bulk solid-state materials.