Angewandte Communications

Layered Compounds Hot Paper

DOI: 10.1002/anie.201409714

Synthesis of Inorganic Structural Isomers By Diffusion-Constrained Self-Assembly of Designed Precursors: A Novel Type of Isomerism**

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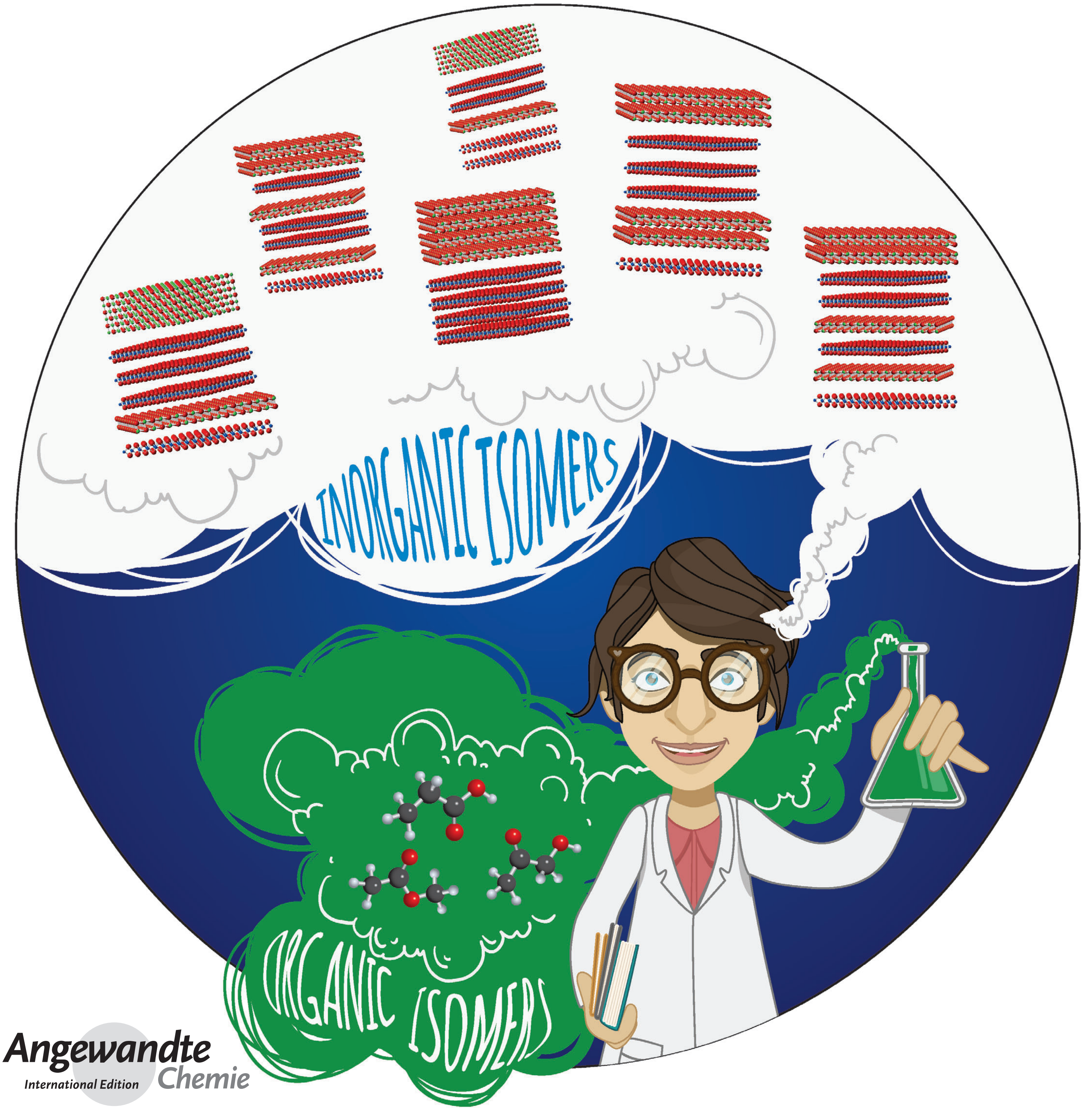

Abstract: *The structure of precursors is used to control the formation of six possible structural isomers that contain four structural units of PbSe and four structural units of* $NbSe_2$*:*
$[(PbSe)_{1.14}]_4[NbSe_2]_4$,
$[(PbSe)_{1.14}]_3[NbSe_2]_3[(PbSe)_{1.14}]_1[NbSe_2]_1$,
$[(PbSe)_{1.14}]_3[NbSe_2]_2[(PbSe)_{1.14}]_1[NbSe_2]_2$,
$[(PbSe)_{1.14}]_2[NbSe_2]_3[(PbSe)_{1.14}]_2[NbSe_2]_1$,
$[(PbSe)_{1.14}]_2[NbSe_2]_2[(PbSe)_{1.14}]_1[NbSe_2]_1[(PbSe)_{1.14}]_1[NbSe_2]_1$,
$[(PbSe)_{1.14}]_2[NbSe_2]_1[(PbSe)_{1.14}]_1[NbSe_2]_2[(PbSe)_{1.14}]_1[NbSe_2]_1$.
The electrical properties of these compounds vary with the nanoarchitecture. For each pair of constituents, over 20 000 new compounds, each with a specific nanoarchitecture, are possible with the number of structural units equal to 10 or less. This provides opportunities to systematically correlate structure with properties and hence optimize performance.

In molecular chemistry, chemists utilize local bonding concepts to predict kinetically stable compounds. Molecules that contain all of their atoms in common coordination numbers and electron counts, for example carbon atoms that form four covalent bonds, are considered reasonable synthetic targets. These predictions allow the development of targeted synthetic strategies and the isolation of increasingly complex molecules by controlling kinetics.[1] Conceptually, there are an infinite number of kinetically stable molecules that satisfy these local bonding rules, including isomers, that is, compounds with the same molecular formula but a different connectivity of atoms. While the synthetic challenge increases with the number of atoms and the complexity of their interconnectivity, chemists have developed synthetic tools that enable the designed synthesis of increasingly complex targets. This ability to kinetically control the synthesis of specific compounds, however, does not extend to engineering the resulting crystal structure, which consists of an ordered array of approximately 10^{23} molecules or atoms with a specific arrangement between them.[2,3]

Here, we ask if similar bonding concepts can be used to predict the structure of kinetically stable extended inorganic solids. We imagined new extended solids that contain interwoven layers of known structures (A and B) with precise control of the number of structural units (m and n) in these new compounds $(A)_m(B)_n$. The known misfit-layered compounds would be examples of this type of compound, where typically only the $m = n = 1$ compound is thermodynamically stable.[4] It is chemically reasonable to expect the presence of a local free-energy minimum for any value of m or n in these $(A)_m(B)_n$ compounds, as only atoms at the interfaces would potentially not have their local bonding needs optimally satisfied. If this hypothesis is correct, then one could also imagine compounds with the same stoichiometry and the same total number of structural units, but with a different connectivity. For example, there are six potential combinations that contain four structural units of A and four structural units of B in the repeating unit: $(A)_4(B)_4$, $(A)_3(B)_3(A)_1(B)_1$, $(A)_3(B)_2(A)_1(B)_2$, $(A)_2(B)_3(A)_2(B)_1$, $(A)_2(B)_1(A)_1(B)_2$-$(A)_1(B)_1$ and $(A)_2(B)_2(A)_1(B)_1(A)_1(B)_1$. (In the rest of this manuscript, the short hand notation 4:**4**, 3:**3**:1:**1**, 3:**2**:1:**2**, 2:**3**:2:**1**, 2:**2**:1:**1**:1:**1**, and 2:**1**:1:**2**:1:**1** will be used where the normal and bold fonts represent the different structural units, the number is the number of consecutive structural units of each type, and the order is the order of the structural units in the unit cell.) While the different connectivity in molecules such as C_4H_8 would lead to different molecular shapes (linear, branched, and cyclic), the different connectivity in these compounds would lead to different numbers of interfaces (two in 4:**4**, four in 3:**3**:1:**1**, 2:**3**:2:**1**, and 3:**2**:1:**2**, and six in 2:**2**:1:**1**:1:**1** and 2:**1**:1:**2**:1:**1**), which would represent a novel type of structural isomerism. The experimental challenge is finding a synthetic technique to control the self-assembly of around 10^{23} atoms to obtain the targeted structure of a particular isomer.[3]

In order to obtain the specific isomers, our idea was to prepare elemental precursors with enough structural similarities to the targeted product that, on low-temperature annealing, the self-assembly of the desired compound would be trapped in the local free-energy minima defined by the precursor structure (Figure 1). This method exploits the enthalpy released during the formation of the constituents of the targeted compounds to direct the self-assembly, but uses small solid-state interdiffusion rates at low temperatures to prevent the system from evolving into the global free-energy minima.[5,6]

We used the $[(PbSe)_{1.14}]_m(NbSe_2)_n$ system to test this concept. In this family of compounds, those with $n = 1, 2$, or 3 and $m = 1$ can be prepared using a traditional high-temperature reaction of the elements by varying the composition of the initial mixture.[7–9] These compounds and several others in this family of compounds have been made as disordered polytypes or ferecrystals by using designed precursors.[10,11] These compounds consist of interleaved layers of PbSe and $NbSe_2$. Each $NbSe_2$ layer consists of a hexagonal layer of niobium between hexagonal layers of selenium with the niobium atoms in trigonal prisms or octahedra of selenium.

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[**] The authors thank the staff in CAMCOR for assistance preparing TEM samples and collecting STEM images, Daniel Moore for helpful discussions and creating Figure 1, and Sharon Betterton for creating the cover image. The authors acknowledge support from the National Science Foundation under grant DMR-1266217. Coauthors MA and DCJ acknowledge support from the National Science Foundation through CCI grant number CHE-1102637. Grant MRI 0923577 provided funding for the dual beam FIB used to make TEM cross-sections. CG and SFF gratefully acknowledge scientific and technical support by Dr. Rüdiger Mitdank.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201409714.

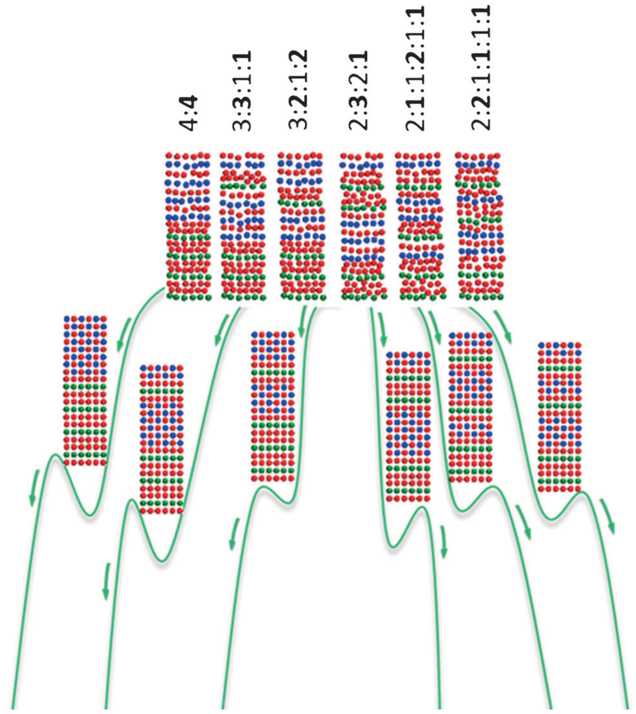


Figure 1. Schematic representation of the free-energy landscape for the formation of the six isomers of $[(PbSe)_{1.14}]_4(NbSe_2)_4$. The images at the top depict the structures of the initial reactants. The images in the middle depict idealized atomic structures of the six $[(PbSe)_{1.14}]_4$-$(NbSe_2)_4$ isomers formed on annealing. The green lines show the energy pathways for the six different reactants transforming into the six different targeted compounds.

Each PbSe layer contains two distorted (001) planes of the rocksalt structure. The rocksalt-structured layers contain equal amounts of Pb and Se atoms and are incommensurate with the close packed Se planes of the selenium layers of $NbSe_2$. The noninteger (1.14) PbSe stoichiometry reflects the difference between the area per cation in the respective layers.

We prepared the designed precursors by physical evaporation from elemental sources. We determined the deposition conditions required to deposit a pair of elemental layers for each constituent, where the ratio of the elements corresponds to the stoichiometric ratio found in each of the constituents.[12] The thickness of the pair of elemental layers was made to correspond to the absolute amount of material required to prepare a single layer of each constituent. We then deposited six different sequences of layer pairs corresponding to the nanoarchitectures of the six potential structural isomers of $[(PbSe)_{1.14}]_4(NbSe_2)_4$.

We followed the evolution of the diffraction patterns of these precursors as a function of annealing time and temperature. The as-deposited diffraction scans of each sample contain Bragg diffraction maxima at low angle from the layering of the precursor. Additional diffraction peaks, all of which can be indexed as (00*l*) reflections from the initial precursor period, grow in intensity with increased annealing time and temperature. By 450 °C, the diffraction patterns are well developed and rocking scans indicate a very strongly preferred (00*l*) orientation. At 500 °C, the isomers decompose.

Figure 2 contains the diffraction patterns of the six isomers of $[(PbSe)_{1.14}]_4(NbSe_2)_4$ annealed at 450 °C. All of the diffraction peaks are located in the same position, indicating identical unit-cell sizes of all six compounds. As expected, the relative intensities of the different Bragg diffraction maxima vary considerably, reflecting the different positions of atomic planes in each of the isomers.

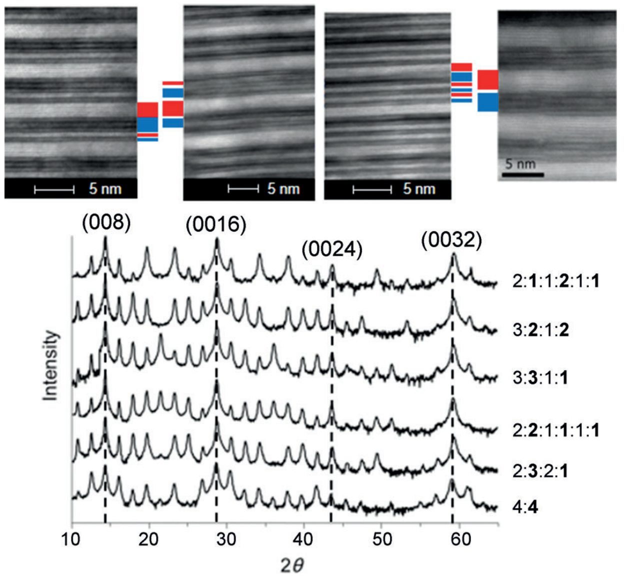


Figure 2. Top: HAADF-STEM images of the 3:**3**:1:**1** (left), 2:**3**:2:**1** (center left), and 2:**2**:1:**1**:1:**1** (center right) and 4:**4** (right) $[(PbSe)_{1.14}]_4$-$(NbSe_2)_4$ isomers. Bottom: High-angle X-ray diffraction pattern of the six $[(PbSe)_{1.14}]_4(NbSe_2)_4$ isomers annealed at 450 °C. Dashed vertical lines were added to select reflections to emphasize the identical positions of Bragg reflections, showing that all isomers have the same *c*-axis lattice parameter.

Above the diffraction patterns in Figure 2, cross-sectional high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images of four of the six isomers are shown. The different layer sequences are clearly distinguishable in the images and are consistent with that expected from the precursor. The *c*-axis lattice parameters from the images agree with the values obtained from our X-ray diffraction study. The atomic planes are highly ordered along the *c*-axis of the compounds, but the rotational orientation of the layers varies. To the best of our knowledge, this is the first report of the targeted synthesis of structural isomers of an extended inorganic solid through a nonepitaxial growth technique.

The temperature dependence of the electrical resistivity of the six $[(PbSe)_{1.14}]_4(NbSe_2)_4$ isomers is shown in Figure 3 A. The magnitude of the resistivity is similar to that reported for $[(PbSe)_{1.14}]_1(NbSe_2)_n$ compounds, where $n = 1$–3.[7–9] The temperature dependencies of all of the isomers are similar, suggesting similar electron–phonon scattering mechanisms. The resistivity and the residual resistivity ratio do not show a systematic trend as the number of interfaces is decreased,

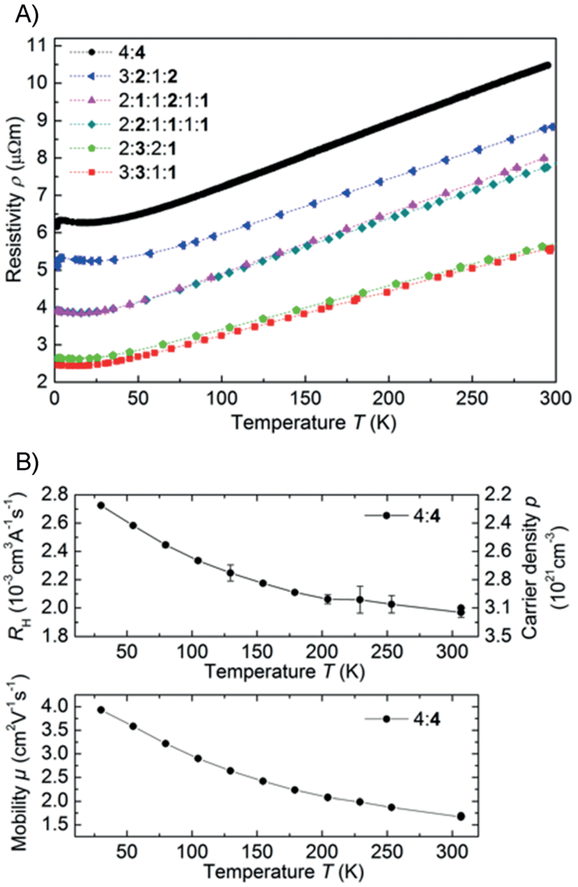
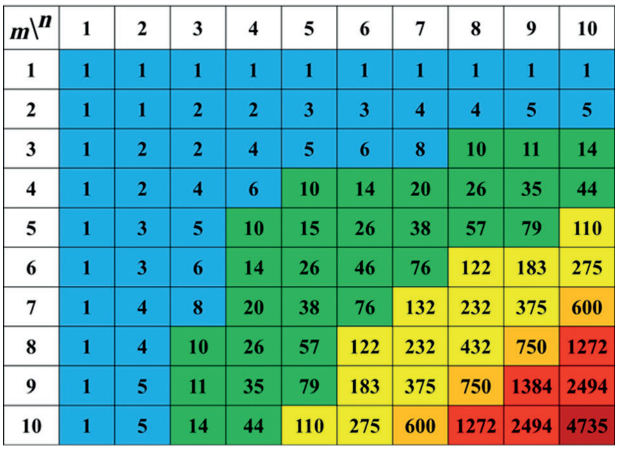


Figure 3. A) In-plane electrical resistivity data obtained for the six isomers of $[(PbSe)_{1.14}]_4(NbSe_2)_4$ for temperatures between 1.4 K and 300 K. B) Hall coefficient R_H and mobility μ for the 4:**4** isomer of $[(PbSe)_{1.14}]_4(NbSe_2)_4$.

perhaps reflecting changes in the structure of the PbSe layers with thickness that change scattering at the interfaces between PbSe and $NbSe_2$ layers.[13,14] Hall measurements using the van der Pauw[15] method of the 4:**4** isomer showed a positive Hall coefficient R_H and a hole density p at room temperature of $p = (3.16 \pm 0.06) \times 10^{21}\,cm^{-3}$, calculated assuming a single-band model. The carrier density ρ increases with increasing temperature (Figure 3B), reflecting the limitations of using the single-band model or suggesting that thermally activated charge carriers also contribute to the transport. The mobility μ of the charge carriers decreases with increasing temperature, which can be attributed to increasing electron–phonon scattering with increasing temperatures. Finally, we note that while there is a slight increase in resistivity with decreasing temperatures below about 50 K for all samples, there is a reduction in resistivity at the lowest temperatures measured for the 4:**4** and 3:**2**:1:**2** isomers, suggesting that these samples become superconducting, which has also been reported previously for the misfit-layered compounds $[(PbSe)_{1.14}]_1(NbSe_2)_1$, $[(PbSe)_{1.14}]_1(NbSe_2)_2$, and $[(PbSe)_{1.14}]_1(NbSe_2)_3$.[7–9]

While electrical data on additional samples with different nanoarchitectures needs to be obtained to understand the observed dependence of electrical properties on structure, this data shows that compounds with different nanoarchitectures have different properties. By using bonding motifs found in thermodynamically stable compounds, it is possible to predict a large number of families of new materials containing interleaved layers in which physical properties would be dependent on the nanoarchitecture of the compound.[16] As shown herein, the use of designed precursors with a nanoarchitecture similar to that of the desired product enables the templated self-assembly of targeted products with predicted structures. Figure 4 contains the calculated number of potential isomers for a given n and m value. The number of different possible arrangements increases rapidly as n and m increase, leading to over 20000 distinct compounds for n and m less than or equal to 10. The large number of potential new compounds, each of which can be altered through traditional alloying or doping approaches, fundamentally changes the approach taken to optimize materials properties. Ideally, theoretical approaches will be developed that use measurements on only a couple of family members to successfully predict the properties of the rest of the family of compounds, accelerating the discovery process of materials with optimized properties.



$m\backslash n$	1	2	3	4	5	6	7	8	9	10
1	1	1	1	1	1	1	1	1	1	1
2	1	1	2	2	3	3	4	4	5	5
3	1	2	2	4	5	6	8	10	11	14
4	1	2	4	6	10	14	20	26	35	44
5	1	3	5	10	15	26	38	57	79	110
6	1	3	6	14	26	46	76	122	183	275
7	1	4	8	20	38	76	132	232	375	600
8	1	4	10	26	57	122	232	432	750	1272
9	1	5	11	35	79	183	375	750	1384	2494
10	1	5	14	44	110	275	600	1272	2494	4735

Figure 4. The number of possible structural isomers for a given A_mB_n stoichiometry are given in each of the boxes. The colors of the boxes reflect the rapid increase in the number of isomers as m and n increase.

Received: October 6, 2014

Keywords: isomers · layered compounds · metastable compounds · nanostructures · solid-state reactions

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