Designing New Inorganic Compounds from 2D Building Blocks

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Early on the design of inorganic compounds was recognized as a challenging task in Material Sciences. Even now, it is quite rare that the synthesis of new inorganic compounds really proceeds from a prior prediction of both their compositions and structures. Serendipity still plays an important role in inorganic chemistry. However, to take control of the structure of new compounds is of prime importance. This is the main prerequisite to design the physical properties of solids. This would propel the search of new inorganic solids in the age of crystal engineering an approach that was shown to be very powerful in the field of manganites or cuprates. For this reason, studies on structure predictions have recently seen a renewed interest, and major breakthroughs in the rational design of inorganic compounds have been reached. Two main ways have been explored. The first approach is based on novel theoretical methods to explore the energy landscapes of chemical systems and to predict the possible structure candidates.[1] On the other hand, Ferey, and Yaghi and O'Keeffe developed a second approach based on the fruitful concept of building blocks.[2] They were able to design the inorganic skeleton of new porous hybrid compounds by understanding that isolated building blocks could be assembled together in a predictive manner. This is this concept that we have tried to explore further.

For a long time mineralogists or solid-state chemists have classified structures depending on the degree of relationship that they present with very simple structure types or closed packing. It is of great importance indeed to realize a posteriori that many structures contain fragments of the rock salt, perovskite, or fluorite types, and that many other structures can be described from ABAB hexagonal or ABCABC cubic closed packing. But it would be more useful for the chemist to use these fragments or packing to design a priori new solid state compounds. The complexity to predict the stacking or assembling of building units increases with the number of degrees of freedom required to predict their connection or relative positions. For example, the prediction of the stacking of 0D building units such as clusters to form 3D networks requires three degrees of freedom per unit. Considering 1D building units, i.e., infinite chains, strongly simplifies the prediction, as it requires only two degrees of freedom per building unit. Finally the stacking of 2D building units is the simplest to predict, as it requires only one degree of freedom. For this reason, we have first decided to concentrate our efforts on the structure prediction using 2D building blocks.

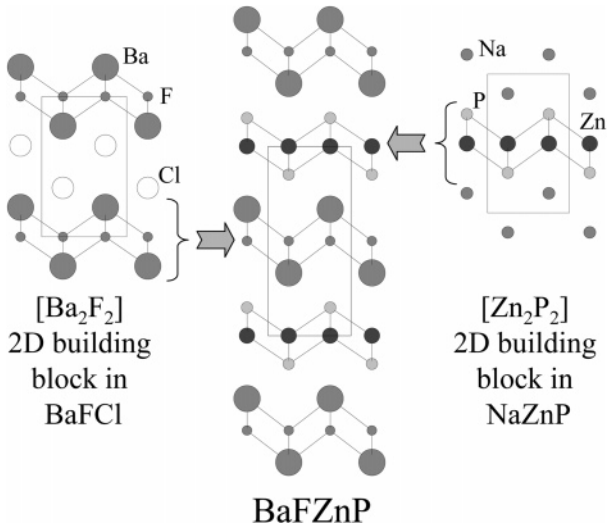

Figure 1. Structure of BaFZnP is predicted from the stacking of 2D building blocks $[Ba_2F_2]$ found in BaFCl and $[Zn_2P_2]$ found in NaZnP.

Table 1. Comparison of the Cell and Atomic Position Parameters Obtained by Optimization or Refinement of the Structure of BaFZnP[a]

	optimization	refinement
a	4.1403	4.15637(3)
c	9.3949	9.4574(1)
Ba on 2c (1/4 1/4 *z*) *z* =	0.3288	0.33179(7)
P on 2c (3/4 3/4 *z*) *z* =	0.1499	0.1488(3)

[a] Space Group *P*4/*nmm*; Zn on 2a ($^1/_4$, $^3/_4$, 0); F on 2b ($^1/_4$, $^3/_4$, $^1/_2$).

A careful analysis of the structure databases demonstrates that some slabs (perovskite, fluorite, or rock salt types, for example) are encountered in many structures and in many different chemical environments. This observation led us to propose the simplest assumption that these slabs could be considered as 2D building blocks. In turn, the stacking of 2D building blocks of distinct chemical natures would offer a unique opportunity to imagine new inorganic compounds. The purpose of this Communication is to give an insight of the concept of design from 2D building blocks. This idea provides a novel approach to the field of structure prediction and has potential for significantly helping solid state chemists to rationally design new inorganic compounds.

Designing new compounds from 2D building blocks requires paying attention to several obvious structural and electronic factors. First, both 2D building blocks have to be chosen to avoid mismatch, meaning that they need to have similar in-plane parameters or be sufficiently flexible. The second requirement is to achieve the charge balance for the target composition that is the sum of the compositions of both building blocks. This simply means that the 2D building blocks have to be chosen with complementary acceptor versus donor character. At this step the structure of the target

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(1) Jansen, M. *Angew. Chem., Int. Ed.* **2002**, *41*, 3746.
(2) (a) Ferey, G. *J. Sol. State Chem.* **2000**, *152*, 37. (b) Yaghi, O. M.; O'Keefe, M.; Ockwig, N. W.; Chae, H. K.; Eddaoudi, M.; Kim, J. *Nature* **2003**, *423*, 705. (c) Mellot-Draznieks, C.; Ferey, G. *Curr. Opin. Solid State Mater. Sci.* **2003**, *7*, 13.

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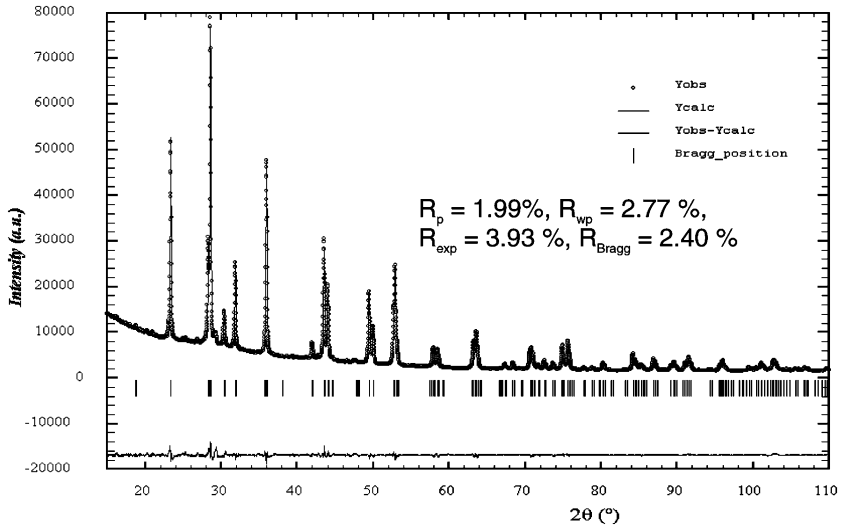

Figure 2. Rietveld refinement of the structure of BaFZnP.

compound (space group and atomic positions) can be built by hand by fixing the in-plane parameters and stacking alternatively the 2D building blocks.

With their flexible accordion-like structure, tetragonal tetrahedral 2D building blocks (named hereafter fluorite or anti-fluorite) seemed to be the most appropriate to succeed in structure prediction. NaZnP and BaFCl present, respectively, anti-fluorite and fluorite-type 2D building blocks of tetragonal symmetry that have similar in-plane parameters.[3,4] Figure 1 presents how we could imagine the structure of BaFZnP from these types of blocks. The alternative stacking of these building blocks leads to a tetragonal structure of the ZrSiCuAs type. To get a better prediction we have optimized the handmade structure using the program VASP that allows relaxing both the cell and atomic parameters.[5] This calculation confirmed our structure and Table 1 gives all the details about the optimized structure.

The electronic transfer between the donor fluorite block $[Ba_2F_2]$ and the acceptor anti-fluorite $[Zn_2P_2]$ block is expected to stabilize the target compound BaFZnP. However, to get an insight of the thermodynamic stability of this compound we have used quantum chemistry methods. Band structure calculation methods give fairly accurate access to the total energy of a compound. For a chemical reaction it is then possible to calculate the difference of total energy between the products and the reactants, which means the free energy of this reaction at 0 K if we neglect the $P\Delta V$ term. As suggested in Figure 1, the smartest way to synthesize BaFZnP is to perform the metathesis reaction

$$\mathrm{NaZnP} + \mathrm{BaFCl} \rightarrow \mathrm{BaFZnP} + \mathrm{NaCl} \qquad (1)$$

By optimizing with VASP the reported structures of NaZnP (CSD 61083), BaFCl (CSD 201514), and NaCl (CSD 41439) we were able to obtain the total energy of these compounds.[5] With the total energy calculated by VASP for the optimized structure of BaFZnP we could predict the enthalpy of the metathesis reaction 1. We found an enthalpy of −26.0 kJ/mole, which means that this reaction is thermodynamically possible at 0 K.

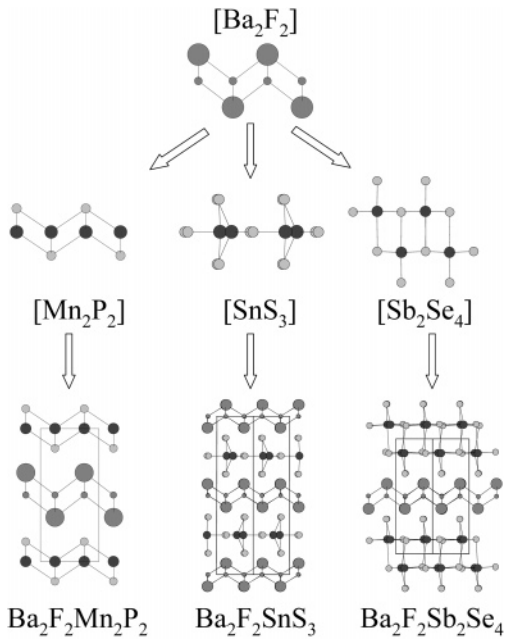

Figure 3. Design of new inorganic compounds containing the 2D-building blocks $[Ba_2F_2]$ associated with the $[Zn_2P_2]$, $[SnSe_3]$, or $[Sb_2Se_4]$ 2D building blocks.

As the predicted compound BaFZnP should be stable we have performed the metathesis reaction. As expected, the reaction of NaZnP with BaFCl at 600 °C led to a mixture of BaFZnP and NaCl.[6] From the X-ray powder pattern we could refine the structure of BaFZnP (see Figure 2 and Table 1).[7] This structural analysis confirmed our hypothetical structure,

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(4) Sauvage, M. *Acta Crystallogr. B* **1974**, *30*, 2786−2787.

(5) The cell and atomic parameters of BaFZnP, BaFCl, NaZnP, and NaCl were optimized using the program VASP written by Georg Kresse and Jürgen Furthmüller (*http://cms.mpi.univie.ac.at/vasp/*). The calculations were performed with the generalized gradient approximations (GGA) using the Perdew−Wang 91 functional (*Phys. Rev. B* **1992**, *45*, 13244.) and PAW pseudopotentials (Kresse, G.; Joubert, D. *Phys. Rev. B* **1999**, *59*, 1758.). The cutoff energy was 400 eV with an 8 × 8 × 4 (or 8 × 8 × 8 for NaCl) Monkhorst−Pack k-point mesh (*Phys. Rev. B* **1976**, *13*, 5188.). The geometry convergence criterion chosen was the forces with |F-max| = 0.03 eV/Å.

(6) The direct synthesis of BaFZnP from a mixture of BaF_2, Ba, Zn, and P heated at 900 °C was also successful.

and showed its good accuracy, as the difference observed between the refined and optimized structures is lower than 2% (see Table 1).

BaFZnP was our first success in designing new inorganic compounds from 2D building blocks. Since then we have been able to design and synthesize a dozen new compounds, and Figure 3 shows a few of them. For example, replacing either the $[Zn_2P_2]$ or the $[Ba_2F_2]$ 2D building blocks in BaFZnP leads to a whole family of compounds, and so far we have synthesized SrFZnP, BaFMnP, and BaFZnSb.[8] We have also tried to design compounds that have more complex structures and compositions. For example, by designing $Ba_2F_2SnS_3$ and $Ba_2F_2Sb_2Se_4$ we succeeded in increasing the thickness of the 2D building blocks alternating with the $[Ba_2F_2]$ block (see Figure 3).[8]

In conclusion, we have demonstrated that it is possible to design new inorganic compounds from 2D building blocks. We believe that this concept enlarges the toolbox of crystal engineering and will help solid-state chemists design a large variety of new compounds.

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(7) The X-ray powder diffraction pattern was collected on a Bruker D5000 equipped with a linear detector, in a Bragg−Brentano geometry, and using the Cu Kα radiation ($\lambda K_{\alpha 1} = 1.540598$ Å and $\lambda K_{\alpha 2} = 1.54439$ Å). The 10−110° 2θ range data collection with an acquisition time of 400 s/deg was performed at room temperature using sieved powder gently deposited in the cylindrical cavity of a Plexiglas plate. Subsequent crystallographic structure refinements were done using the FullProf package. Rodriguez-Carvajal, J. *Physica B* **1993**, *192*, 55−69.

(8) Kabbour, H.; Meerschaut, A.; Cario, L., manuscripts in preparation.