

Function, S_n , that gives both the stoichiometry and aspects of the bond topology of the structures. We may thus write the structure-generating function, S_n , for the biopyrribole structures as follows: $S_n = X_i[M_{(3n-1)}\Psi_{2(n-1)}\{T_{2n}\Theta_{(3n-1)}^{\text{br}}\Theta_{2n}^{\text{ap}}\Theta_{2n}^{\text{br}}\}_2]$. This function generates: $n = 1$, the pyroxenes; for $n = 2$, the amphiboles; for $n = 3$, the triple-chain pyrriboles; for $n = 4$, $S_4 = X_i[M_{11}\Psi_6\{T_8\Theta_{21}\}_2]$; for $n = \infty$, the micas. Where $N = 2$, the general form of the T component is $\{T_{2n}\Theta_{5n+2}\}$ which corresponds to the T component of H-layers in the polysomatic H-O-H series in which the ribbons are linked laterally by [5]- or [6]-coordinated cations, D, which have the coordination $(D\Theta_4^{\text{ap}}\Phi_{0-1}^{\text{t}})$. The general formula for an H layer is $[D\Phi^{\text{ap}}\{T_{2n}\Theta_{3n-2}^{\text{br}}\Theta_{2n}^{\text{ap}}\Theta_{4n}^{\text{br}}\}\Phi_{0-1}^{\text{t}}]$, where Φ^{t} after the T component occurs on the outside of the H-layer and is involved in linkage between adjacent H-O-H sheets. The H-layer links via its apical anions to the O-layer, giving the general formula of an H-O-H sheet as $[M_{3n+1}D\Phi^{\text{ap}}\Psi_n\{T_{2n}\Theta_{5n+2}\}\Phi_{0-1}^{\text{t}}]$. These H-O-H sheets can link directly through the Φ^{t} anions of the $(D\Theta_4^{\text{ap}}\Phi_{0-1}^{\text{t}})$ octahedra, giving $S_n = X_i[M_{(3n+1)}\Psi_{2n}(D_2\Phi_2\{T_{2n}\Theta_{5n+2}\}_2)\Phi_{0-2}^{\text{t}}]$. This function generates: for $n = 1$, the group-1 TS-block structures; for $n = 2$, the astrophyllite-group structures; for $n = 3$, nafertisite: ideally $\text{Na}_2[\text{Fe}^{2+}_{10}\text{O}_2(\text{OH})_6(\text{Ti}_2\{\text{Si}_{12}\text{O}_{34}\})](\text{H}_2\text{O})_{0-2}$; for $n = \infty$, the micas.

We may combine the two generating functions (above) into a single function: $S_{(N+n)} = X_i[M_{(3n+2N-3)}\Psi_{2(n+N-2)}(D_{2(N-1)}\Phi_{2(N-1)}^{\text{ap}}\{T_{2n}\Theta_{(3n-N)}^{\text{br}}\Theta_{2n}^{\text{ap}}\Theta_{2N}^{\text{br}}\}_2)\Phi_{0-2(N-1)}^{\text{t}}]$ that gives all the above structures. This expression also generates mixed-ribbon polysomatic structures. $S_{(1,2+3)} = X_i[M_{13}\Psi_6\{T_{10}\Theta_{13}^{\text{br}}\Theta_{10}^{\text{ap}}\Theta_{4}^{\text{br}}\}_2]$ gives the chemical composition and structure of the mixed-chain pyrribole, chesterite: $\text{Mg}_4[\text{Mg}_{13}(\text{OH})_6\{\text{Si}_{10}\text{O}^{\text{br}}_{13}\text{O}^{\text{ap}}_{10}\text{O}^{\text{t}}_{4}\}_2]$, and $S_{(2,1+4)} = X_i[M_{17}\Psi_{10}(D_4\Phi_4\{T_2\text{O}^{\text{br}}\text{O}^{\text{ap}}\text{O}^{\text{t}}_{4}\}_2\{T_8\text{O}^{\text{br}}_{10}\text{O}^{\text{ap}}_{8}\text{O}^{\text{t}}_{4}\}_2)\Phi_{0-4}^{\text{t}}]$ gives the chemical composition and structure of the mixed-chain H-O-H mineral, veblenite: $\text{KNa}(\text{H}_2\text{O})_3[(\text{Fe}^{2+}_5\text{Fe}^{3+}_4\text{Mn}_6\text{Ca}\square)(\text{OH})_{10}(\text{Nb}_4\text{O}_4\{\text{Si}_2\text{O}_7\}_2\{\text{Si}_8\text{O}_{22}\}_2)\text{O}_2]$.

Keywords: topology, prediction, mineral

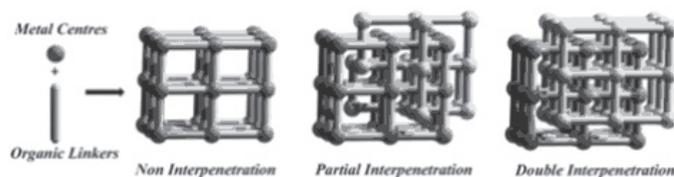
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Modulation of structures and gas storage properties in MOF materials

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A range of anionic metal-organic framework (MOF) materials has been prepared by combination of In(III) with tetracarboxylate isophthalate ligands. These materials incorporate organic cations, either $\text{H}_2\text{ppz}^{2+}$ (ppz = piperazine) or Me_2NH_2^+ , that are hydrogen bonded to the pore wall [1], [2]. These cations act as a gate controlling entry of N_2 and H_2 gas into and out of the porous host. Thus, hysteretic adsorption/desorption for N_2 and H_2 is observed in these systems reflecting the role of the bulky hydrogen bonded organic cations in controlling the kinetic trapping of substrates. Post-synthetic cation exchange with Li^+ leads to removal of the organic cation and the formation of the corresponding Li^+ salts. Replacement of the organic cation with smaller Li^+ leads to an increase in internal surface area and pore volume of the framework material, and in some cases to a change in the overall network topology and structure [3]. An increase in the isosteric heat of adsorption of H_2 at zero coverage has also been observed on incorporation of Li^+ ions, as predicted by theoretical modeling [4], [5], [6]. Furthermore, a new doubly-interpenetrated network system has been identified in which the second net is only partially formed (0.75 occupancy; see Figure). This material undergoes a structural re-arrangement on desolvation, and shows high selective storage uptake for CO_2 . The structures, characterisation and analyses of these charged porous materials as storage portals for gases are discussed.



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New findings in topological crystal chemistry with TOPOS

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The multipurpose crystallographic program TOPOS [1] has been used extensively in the analysis of entanglement of coordination polymers/MOFs and H-bonded supramolecular architectures [2], [3]. Three recent applications will be briefly illustrated.

We formalized the analysis of extended architectures by successive simplifications in an automated mode that allowed us to classify all 3-periodic structures from the Cambridge Structural Database (CSD). Different levels of representations (standard and cluster) are considered and some application illustrated. [4], [5].

Another new application of TOPOS is in the structural chemistry of intermetallic compounds, where the crystal structure is perceived as an ensemble of clusters based on convex polyhedra. We developed a computer procedure for fast automated searching for cluster fragments of any complexity in crystal structures of any nature [6]. The occurrences of two-shell clusters with the first shell as a Frank-Kasper polyhedron Z12 (dodecahedron), Z14, Z15, or Z16 (Frank-Kasper nanoclusters) will be briefly illustrated.

This latter approach has been extended in the study of zeolites, and from our result of description of all zeolites as natural tiling [7], we were able to develop a model of assembling zeolite-type frameworks as a packing of natural building units (minimal cages) or essential rings (minimal windows).

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The role of metal cations as template species in zeolite framework formation

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Zeolites are crystalline aluminosilicates used for many applications. Numerous zeolitic materials and topologies are known, but their formation, especially on molecular level and the stage of nucleation remains in the dark. Experience taught the formation of a specific framework critically depends on conditions like gel composition, temperature and time. Small changes in pH or variation of the metal cation can entirely change the obtained topology from one type to another or prevent crystallization at all. The cation effect most probably is due to their direct interaction with and stabilization of elemental aluminosilicate oligomers (AOs) and should depend on hardness, size and charge of the participating species. Strategies to study the stabilization of specific structural elements by metal ions are *in-situ* and *ex-situ* analysis of framework formation and transformation from one topology into another. Here we report the results of studies of the crystallization of two topologically related low silica zeolites from amorphous gels (FAU and LTA), [1], [2], and of the framework transformation of zeolite Y (FAU) into chabazite (CHA) [3].

Simultaneous *in-situ* XRD-Raman study of the crystallization of low silica zeolite X (FAU) and zeolite A (FAU) from amorphous gels have been performed. Both frameworks contain sodalite cages as a building unit linked via double 6-rings (D6R) in FAU and double 4-rings (D4R) in LTA. The oligomeric species in solution were monitored by UV-Raman, while the transition from amorphous to crystalline state was simultaneously recorded by XRD. A very important role has been assigned to the presence of K^+ in solution, directing the synthesis to the FAU topology. Probably, interaction with silica 4-rings (4Rs) blocks the pathway leading to the LTA structure [5]. Furthermore, the absence of 6Rs during FAU formation excluded the sodalite cage as a possible common building unit for both topologies.

As initial compound for the framework transformation of FAU into CHA served commercial zeolite Y with different ion contents (Na^+ , NH_4^+ , H^+ , K^+ , Ca^{2+}). NMR, powder XRD, and AAS were used for the characterization of the initial, intermediate and final materials. CHA and FAU topologies both contain edgewise connected double six rings (D6R) resulting in the sodalite cavity in FAU and chabazite cages in CHA. Surprisingly, the Na/Al ratio of the starting material was not as crucial as reported in literature [3]. Formation of CHA by decomposition of the Na-form of FAU was as successful as the transformation of NH_4^+ , H^+ , or K^+ forms of FAU in KOH. But the presence of Ca ions in the FAU structure fully prevented transformation. It has been observed that this cation has remarkable stabilizing effect on the FAU structure [4]. Presence of K^+ cations appeared as critical factor for CHA formation. With other alkali hydroxides synthesis of CHA failed.

Our investigation reveals the crucial role of nature and concentration of the cations play as template species in final zeolite framework formation.

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A new approach to crystal-structure prediction

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The general failure to make reliable crystal structure predictions from chemical composition has long been identified as a continuing scandal in Crystallography [1]. Recent techniques have exploited the principle of minimum energy in conjunction with a combinatorial analysis, in a computational simulation, to obtain and classify a large number of arrangements on energy grounds. Despite limited success, the fact is that no scientific insight into the process of crystallization is gained. We therefore suggest a different approach which should provide intuitive insight into the factors affecting structure stability.

Brown and Shannon [2] showed a correlation between 'cation-anion' bond length and bond strength in crystals for a variety of chemical compositions and coordination numbers. This approach was developed further by Brown [3] [4] into Bond-Valence Theory, with two key rules: (1) the Valence-Sum Rule which states that the sum of the bond valences around an ion is equal to its formal valence, and (2) the Valence-Matching Principle which states that a chemical bond may form when the Lewis-acid strength of the cation matches the Lewis-base strength of the anion. The latter rule is of particular importance as it allows a *a priori* examination of structure stability whereas, for example, Pauling's rules [5] only allow a *posteriore* examination. Brown [4] has shown how the valence-sum rule can be combined with what he calls Loop Equations to solve a bond network for the bond-valence values that exactly satisfy these equations. The question then becomes whether there is a specific combination of cations and anions that can adopt this arrangement.

The International Crystal Structure Database (ICSD) enables comprehensive evaluation of bond-valence ranges by surveying the database for dispersion of bondlengths for all combinations of atoms, oxidation states and coordination numbers. Sites of candidate structures can then be assigned suitable ion species. A logical path to crystal-structure prediction thus arises: (1) solve the valence-sum rule and loop equations to get ideal bond-valences for a particular bond topology and combination of formal charges at the various sites; (2) convert the resultant bond-valences to bond lengths for possible combinations of candidate ions; (3) if the resultant values lie within the observed dispersion of bondlengths for the candidate ions, the structure is possible with regard to bond-valence criteria. Competing structures of the same formula may then be evaluated in the usual way (distance-least-squares calculations followed by a Molecular Orbital Theory energy evaluation [6]). This procedure thus relies upon well-developed techniques that are applied in a novel way, avoiding the stochastic component of a computer simulation, and allowing careful analysis at any step of the process.

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