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Supertetrahedral Sulfide Crystals with Giant Cavities and Channels

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Although aluminosilicates and metal phosphates can form porous open-framework materials such as zeolites, sulfide analogs usually form high-density phases because of the relatively small tetrahedral angle at sulfur atoms. One strategy to overcome this limitation is to use tetrahedral clusters as the building blocks to achieve porous sulfide-based networks. The preparation and crystal structures of two indium sulfide open frameworks (ASU-31 and ASU-32) built of supertetrahedral clusters around organic template and water guests are described. ASU-31, based on the sodalite-tetrahedrite network, contains cavities 25.6 angstroms in diameter, and ASU-32, based on the tetragonal CrB₄ network, contains channels with a minimum diameter of 14.7 angstroms. The organic cations can be completely exchanged with sodium ions in aqueous solution at room temperature without degradation of the crystals.

to replace TS₄ units with tetrahedral clusters or supertetrahedra such as the T2 and T3 units containing 4 and 10 tetrahedra, respectively (9–11) (Fig. 1). Cristobalite topology structures with all T2 units have long been known as the ZnI₂ structure (9). However, in these structures, two contracted frameworks interpenetrate and the anion arrangement is again close-packed—indeed, GeS₂ with this structure (12) is actually the densest of all four known ambient-pressure polymorphs. Nevertheless, a number of more open structures based on T2 units have been described (13, 14). A structure, that of Ag₆B₁₀S₁₈, with T3 units has also been known for some time (15) but the framework of corner-connected supertetrahedra, although unusual, is very dense. More recently, a cristobalite-framework compound with T3 InS clusters and including dimethylamine has been reported (16); in this material, there are again two interpenetrating diamond nets and the structure does not contain large cavities (17). The same is true for the “double diamond” sulfide compound built up from approximately tetrahedral clusters containing 17 Cd atoms (18) and for a T3 Sn-O-S compound (19).

To make very open tetrahedral sulfide materials, three conditions should be met: (i) the

The intense pursuit of open crystalline assemblies extends across the gamut of organic and inorganic compositions (1) and is motivated by the interest in creating structures with cavities and channels that may be exploited in nanotechnology, including shape- and size-selective catalysis, separations, sensors, and optoelectronic and molecular recognition applications. Until recently the largest cavities known in crystalline solids were those in oxide zeolites (2), discussed further below, although a cubic organic crystal with a very large cavity volume has been described (3). Here we use a design strategy for production of materials with even larger cavities and show its implementation in the synthesis of indium sulfide framework structures.

Chalcogenide-based systems should be a fruitful source of porous materials (4–7), but when TO₄ tetrahedra in oxide frameworks (where T is an atom supporting tetrahedral coordination) are replaced by TS₄ tetrahedra, the frameworks tend to contract to higher density because of the smaller T-S-T angles compared with T-O-T angles. Thus the well-known low-

density cristobalite framework of SiO₂ (with Si atoms on a diamond net) contracts to denser structures with close-packed anions (8, 9) in sulfide materials such as chalcopyrite (CuFeS₂) (8). One strategy for making more open structures, and it is the one that we consider here, is

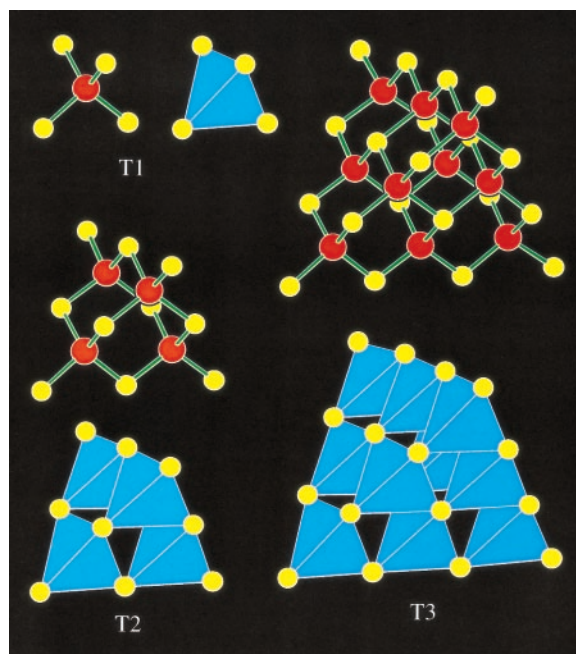


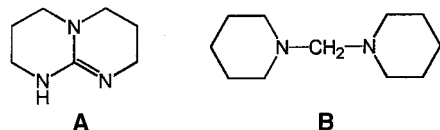
Fig. 1. The first three of the supertetrahedron family T_n. The T3 tetrahedron shown is the real one from the crystal structure of ASU-31 described here (stick-and-ball: In, red; S, yellow; polyhedra: In, blue; S, yellow).

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building units should be supertetrahedra, (ii) the nets should have large cavities even in their contracted forms, and (iii) the nets should not interpenetrate. The structures of the indium sulfide materials to be reported here fulfill all these criteria and contain possibly the largest cavities yet reported for a monocrystalline inorganic or organic material.

These materials can be reproducibly prepared under hydrothermal conditions by combining stoichiometric amounts of indium and sulfur (1:2.5) in the presence of 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine (HPP), **A**, or dipiperidinomethane (DPM), **B**, at 135°C;



crystalline products of ASU-31 (colorless) and ASU-32 (pale yellow) were obtained in unoptimized 10% and 50% yield, respectively, and single crystals selected from the reaction products were analyzed by x-ray diffraction (20). In each case, the crystal contains almost-regular InS_4 tetrahedra in T3 $\text{In}_{10}\text{S}_{20}^{10-}$ building units, which are then condensed to produce frameworks with composition $\text{In}_{10}\text{S}_{18}^{6-}$ (10). Although the In and S positions of the framework were determined accurately, it was not possible to precisely locate the guest cations and water molecules, which are disordered in the giant cavities. Nevertheless, elemental analyses suggest the presence per T3 unit of 6 HPP cations and 15 water molecules in ASU-31 and 3 DPM dications and 7 water molecules in ASU-32, which give overall formulations of $\text{In}_{10}\text{S}_{18} \cdot (\text{HPP})_6 (\text{H}_2\text{O})_{15}$ and $\text{In}_{10}\text{S}_{18} \cdot (\text{DPM})_3 (\text{H}_2\text{O})_7$, respectively (21).

The structure of ASU-31 is based on the sodalite net (9) (Fig. 2, top left). In the sodalite structure with regular TX_4 tetrahedra, the maximum T-X-T angle is 161° (Fig. 2, top middle), but this value can be decreased by concerted rotations of the tetrahedra (9, 22) (Fig. 2, top right). In a typical aluminosilicate sodalite, the angle is about 145°. When T-X-T = 109°, the X array is that of three of four of the positions of cubic closest packing, and this conformation is characteristic of the framework of sulfide minerals of the tetrahedrite group (22). When the tetrahedrite framework is constructed from T3 supertetrahedra as in ASU-31, a very open structure results with large cavities centered at the corners and body center of the body-centered cubic cell (Fig. 2, bottom).

The structure of ASU-32 is based on the tetragonal net often named CrB_4 (9), which is the basis for the aluminosilicate framework in the monoclinic form of $\text{CaAl}_2\text{Si}_2\text{O}_8$ (23), and also found (rather distorted) in a T2 Cd-S structure (12). In this structure again the T-X-T angle can be decreased from a maximum of

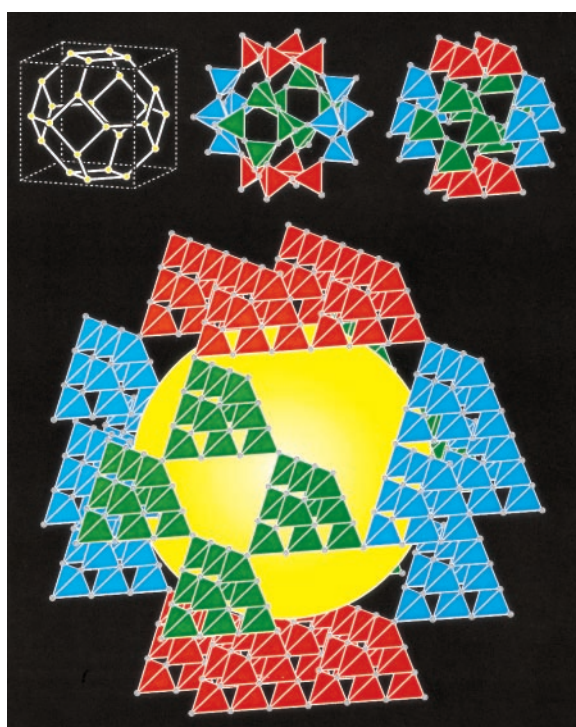


Fig. 2. (Top left) Unit cell of the cubic sodalite TX_2 framework showing only the positions of the T atoms. (Top middle) TX_4 tetrahedra of the sodalite framework in the position of maximum T-X-T angle. (Top right) Same framework contracted so that the T-X-T angles are 109° as in tetrahedrite. (Bottom) Contracted (tetrahedrite) framework constructed from T3 supertetrahedra as in ASU-31. On the scale of the drawing, the difference between the idealized structure with regular InS_4 tetrahedra and the real structure is not readily discernible (compare with Fig. 1). The large sphere fits inside the cavity at the cell body center. For clarity in tetrahedral structures, the same color has been used for every ring of four tetrahedral units.

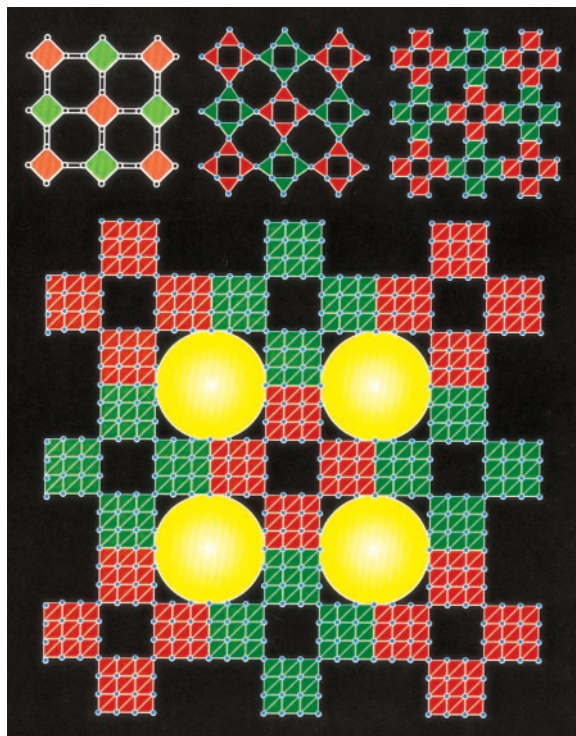


Fig. 3. (Top left) Tetragonal four-connected B net of CrB_4 projected on (001). Red and green squares have elevations differing by $c/2$. Double lines represent bonds up and down out of the plane of the paper. (Top middle) Tetrahedral framework of TX_4 tetrahedra with the same topology in the position of maximum T-X-T angle. (Top right) Same framework contracted to have T-X-T angles of 109°. (Bottom) Contracted framework constructed from T3 supertetrahedra as in ASU-32. Large spheres are in the tunnels that run parallel to the crystallographic c axis. Note that in this projection only 9 of 10 indium tetrahedra in each T3 supertetrahedron are visible and that green and red T3 units have elevations differing by $c/2$.

161° to 109° at which point the X atoms occupy eight of nine of the positions of cubic closest packing (24). The missing atoms now leave one-dimensional channels parallel to the crystallographic c axis as shown in Fig. 3. In ASU-32, the tetrahedral units are again T3 supertetrahedra (Fig. 3).

Preliminary studies aimed at evaluating the mobility of the guest species in the cavities of

ASU-31 and ASU-32 show that the cations can be exchanged with great facility: the addition of aqueous NaCl to a sample of either material at room temperature resulted in nearly complete exchange of the organic cations after 17 hours, as shown by elemental microanalysis, which indicates drastic reductions in the amounts of C and N in the exchanged product (21). Examination by optical microscopy showed that crys-

Table 1. Sizes of fixed and free spheres in some structures. Three-letter symbols for frameworks are zeolite codes (2).

Structure name	Framework type	Pore dimensionality	Free diameter (Å)	Free volume (Å ³)	Fixed diameter (Å)	Fixed volume (Å ³)	Percent crystal occupied by framework atoms
ASU-31	SOD	3	11.2	736	25.6	8785	18
Faujasite	FAU	3	7.1	187	11.1	720	43
Cloverite	CLO	3	6.0	113	15.5	1950	36
ASU-32	CrB ₄	1	14.4	1563	17.2	2664	21
VPI-5	VFI	1	11.7	839	12.2	951	44

tals of both materials maintain their morphology and transparency after base exchange.

Microporous materials are often compared by measuring the number of framework atoms per unit volume, but this procedure is inappropriate for structures of the type discussed here (25). We propose that two useful measures of cavity size are (i) the maximum size of a sphere that can fit inside the largest cavities (we call this the fixed sphere) and (ii) the maximum size of a sphere that can be freely moved along channels through the structure (we call this the free sphere) (26). The sizes of such spheres for ASU-31 and ASU-32 are compared with those of faujasite, which has a three-dimensional channel structure and has the most open of cubic zeolites; VPI-5, a zeolite with the largest one-dimensional channels; and the synthetic gallophosphate cloverite, which has an incomplete tetrahedral framework and even larger pores than faujasite (27) (Table 1). It can be appreciated that the InS materials reported here have substantially larger pores than those known for the most open zeolites. Furthermore, the fixed sphere size (8575 Å³) for ASU-31 is six times larger than that (1375 Å³) claimed to be the size of the largest cavity found in an organic crystal (3).

Each cavity in ASU-31 contains 36 units of HPP (C₇H₆N₃). Assuming a density of about 1 g cm⁻³ for the liquid (typical for liquid N,C heterocycles of this type), we estimate a volume per 36 bases of 7900 Å³. This is sufficiently close to the volume of the fixed sphere calculated above where we believe that the base is functioning as a structure-directing agent. Likewise in ASU-32, 12 units of DPM (C₁₁H₂₂N₂) with an estimated volume of 3600 Å³ have to fit in a channel of length *c* = 17.3 Å and of average diameter 15.7 Å (Table 1)—that is, with volume 3350 Å³. Again these two (rough) estimates are in close agreement. Note that approximating the free volume by spheres and cylinders is a significant underestimate, and sufficient room is left in the actual structure for a substantial amount of water. In fact, about 80% of space in ASU-31 and ASU-32 crystals is “free volume” not occupied by In and S (Table 1) (26).

Open-framework materials of semiconductors such as indium sulfide should have some

interesting physical properties. Nanocrystals of these materials have attracted much interest as “quantum dots”; the materials used in this study are complementary in that they have nanopores in a semiconductor framework. Such structures have been referred to as “antidots” (28) and are expected to have equally interesting physical properties.

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- At -116° ± 2°C ASU-31 is cubic space group *I4* 3m, a = 34.0802(7) Å, V = 39583(1) Å³, Z = 12. Atomic

coordinates for the InS framework [atom type (10⁴x, 10⁴y, 10⁴z)]: In1 (843, 5082, 2495); In2 (0, 5000, 1658); In3 (878, 4269, 1695); S1 (386, 5468, 2072); S2 (1307, 3859, 1307); S3 (1202, 5532, 2892); S4 (1284, 4731, 2078); S5 (-447, 5364, 1258). At -116° ± 1°C, ASU-32 is tetragonal space group *I4* m2, a = 35.4252(7) Å, c = 17.3304(1) Å, V = 21749(1) Å³, Z = 16. Atomic coordinates for the InS framework [atom type (10⁴x, 10⁴y, 10⁴z)]: In1 (3274, 4448, 1454); In2 (3268, 3357, 1657); In3 (3274, 2260, 1687); In4 (3885, 3885, 0); In5 (3890, 2743, 133); In6 (2746, 2746, 0); S1 (3239, 5000, 2287); S2 (3243, 3938, 2399); S3 (3217, 2815, 2492); S4 (3298, 1702, 2500); S5 (3868, 4471, 708); S6 (3867, 3330, 903); S7 (3876, 2215, 1012); S8 (2734, 4465, 592); S9 (2724, 3340, 775); S10 (2717, 2212, 851). The x-ray data were corrected for absorption, and the structures were solved by direct methods. Sulfur and indium were refined with anisotropic displacement parameters, and the remaining atoms were refined with isotropic parameters. Diffuse electron density (solvent and cations) in the large open volumes was modeled by using Babinet’s principle; the atoms thus found in those regions are not necessarily real but serve to account for the residual electron density.

- Elemental microanalysis for as-synthesized ASU-31: calculated, C, 17.82; H, 3.85; N, 8.91; S, 20.39%; found, C, 17.21; H, 3.26; N, 8.72; S, 20.89%. Elemental microanalysis for as-synthesis ASU-32: calculated, C, 16.48; H, 3.61; N, 3.50; S, 24.01%; found, C, 15.70; H, 3.46; N, 4.19; S, 24.09%. Elemental microanalysis for exchanged ASU-31: found, C, 0.41; H, 1.73; N, 0.55; S, 24.05%. Elemental microanalysis for exchanged ASU-32: found, C, 2.18; H, 1.85; N, 0.70; S, 24.16%. We have some evidence that HPP can act as a dication and give a framework identical to that of ASU-32; thus we allow that some ambiguity in precise determination of the number of HPP guests arises, especially if an ASU-32 framework is also produced in the ASU-31 preparation.
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- This can be most easily appreciated by comparing the relative densities of members of a family with a given framework formed by Tn supertetrahedra. As n increases from 1, the volume of the unit cell and thus of the cavities increases as n³, but the number of T atoms also increases cubically (10), and the limiting density as n → ∞ (with infinite cavities) is reduced to only 1/6th the density of T atoms and 1/12th the density of X atoms for n = 1. Note that a unit cell of the cubic Tn structure contains 2(n + 1)(n + 2)(n + 3) = 24 anions (10); the corresponding unit cell of cubic close packing (ccp) contains 32n³ anions. So for n = 1, 3/4 of the ccp sites are occupied. In the limit of n → ∞, 1/16th of the ccp sites are occupied, a 12-fold decrease in density.
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