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FULL PAPER

On the formation of framework indium sulfides

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Novel layered and open framework indium sulfide organic/inorganic hybrid materials have been synthesized *via* hydro- and solvo-thermal techniques. Considerable structural diversity within this family of compounds is realized through a variety of structural building units. DEA-InS-SB1 and -SB2 (both $[(CH_3CH_2)_2NH_2]_6In_{10}S_{18}$) consist of corner linked $In_{10}S_{20}$ supertetrahedra; DPA-InS-ML ($[C_6H_{16}N]_4In_4S_{10}H_4$) contains isolated In_4S_{10} thioanions, while TMDP-InS-SB4 ($[C_{13}H_{14}N_2]_4In_9S_{17}$) has a layered structure containing linked In_9S_{20} double adamantane clusters. Factors governing the formation of the structural building units (in the presence of amines) and their subsequent template mediated assembly are discussed with respect to previously reported and novel structure types.

Introduction

Materials possessing open framework structures are of interest to a variety of scientific communities due their utility in areas such as catalysis, sorption, gas storage and separation, ion exchange, microelectronics, sensors and waste remediation. Zeolites and aluminophosphates are exemplary compounds, as their structures consist of channels and pores defined by corner linked TO_4 tetrahedra (T = Si, Al, P). It is these void spaces that are largely responsible for the range in applicability of framework compounds since they allow, on a molecular scale, the selective incorporation and exchange of guest species.[1–4]

The pursuit of novel porous materials has explored diversions from oxide based chemistry in efforts to extend the range of their applicability. Microporous framework sulfides, for example, were first reported by Bedard *et al.* in 1989.[5,6] Reasons for exploration in this system were many, but stemmed largely from the ability of main group metals to coordinate tetrahedrally with sulfur as silicon and aluminium do with oxygen in the framework oxides. Additional coordination geometries, unique to the sulfides, presented the possibility of an even richer family of framework materials. Further, an expansion of the well known applications of framework oxides (sieving, gas storage, ion-exchange *etc.*) to include an electronic (semiconducting) component was envisioned.

Crystal structure determination of these materials revealed that rather than discrete MS_4 tetrahedra, the anticipated structural building unit in structures analogous to the zeolites, these compounds consisted of $[M_xS_y]^{z-}$ clusters as their building units. While such clustering is uncommon in the oxides,[7] examples in the chalcogenides are many.[8,9] Subsequent studies by several researchers have reported a number of materials based on a variety of building units (Fig. 1): (a) $[Sb_3S_6]^{3-}$ semi-cube,[10,11] (b) $[Sn_3S_4]^{3-}$ semi-cube,[5,6,12–15] (c) $[Ge_4S_{10}]^{4-}$ adamantane unit,[5,6,16–24] (d) $[Sn_{10}S_{20}O_4]^{8-}$ supertetrahedron,[25–27] (e) $[In_{10}S_{20}]^{10-}$ supertetrahedron.[28,29]

Several of these materials crystallize with structures resembling the aluminosilicate oxides. The supertetrahedral clusters in the Sn–O–S and In–S systems condense as interwoven cristobalite type nets,[26,28] while analogs of zeolite,[23] neso-,[9,30] iono-[31] and tecto-silicate[17,21,22] type structures are formed in the Ge–S system upon assembly of $[Ge_4S_{10}]^{4-}$ clusters.

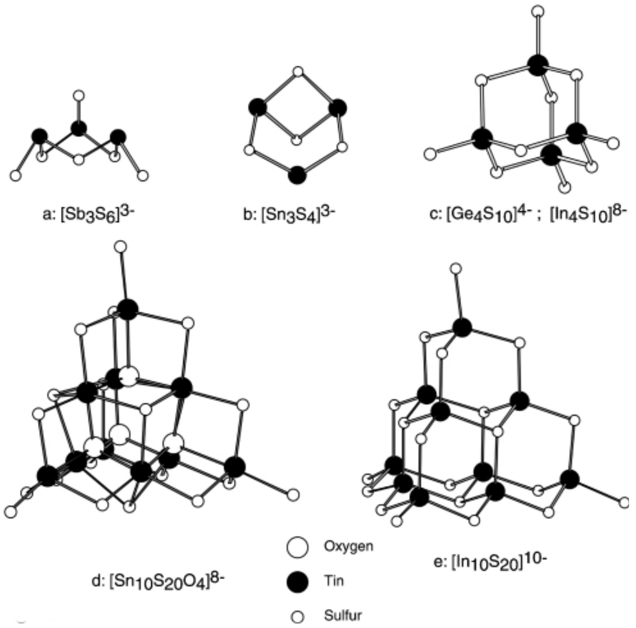
a: $[Sb_3S_6]^{3-}$ b: $[Sn_3S_4]^{3-}$ c: $[Ge_4S_{10}]^{4-}$; $[In_4S_{10}]^{8-}$ d: $[Sn_{10}S_{20}O_4]^{8-}$ e: $[In_{10}S_{20}]^{10-}$

Fig. 1 Representative building units of framework and layered sulfide materials. Black circles are the metal atoms (Ge, Sb, Sn or In) unless otherwise noted. (a) $[Sb_3S_6]^{3-}$ semi-cube, (b) $[Sn_3S_4]^{3-}$ semi-cube, (c) $[Ge_4S_{10}]^{4-}$ (or $[In_4S_{10}]^{8-}$) adamantane cluster, (d) $[Sn_{10}S_{20}O_4]^{8-}$ supertetrahedron, (e) $[In_{10}S_{20}]^{10-}$ supertetrahedron.

Corner linked assemblies of $[M_xS_y]^{z-}$ clusters have a distinct disadvantage when compared to tectosilicate (zeolite) analogs. The range of bond angles exhibited by (for example) Ge–S–Ge linkages is considerably more narrow than the corresponding Si–O–Si linkages: ≈5° *vs.* ≈35° or more respectively.[32] Without this flexibility, it was originally thought that the variety of 3-dimensional structures would be restricted to only a few framework types.[5] To offset this, flexible transition metal centers (MS_4) have been incorporated into the structures of framework Ge–S materials. Such has allowed formation of a considerable range of structure types, even though the building units have been limited to Ge_4S_{10} anions and MS_4 tetrahedra.

An immediate result of employing $[M_xS_y]^{z-}$ clusters as the building units of these materials (as opposed to discrete TO_4 tetrahedra) is an increase in pore size. Fig. 2 is a theoretical schematic of two of the building units to be discussed herein: In_4S_{10} and $In_{10}S_{20}$. In this light, the effect of building unit size is

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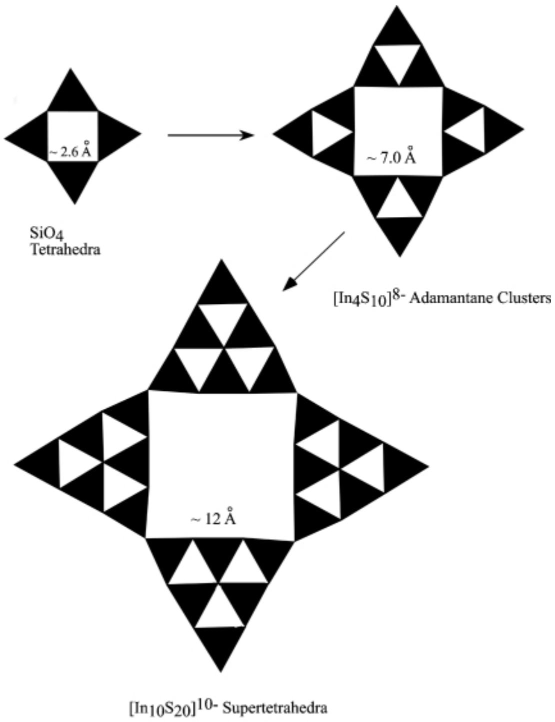

Fig. 2 Pore sizes as a function of framework building unit. Shown is a theoretical four-ring assembly of SiO_4 tetrahedra, Ge_4S_{10} adamantane clusters and $In_{10}S_{20}$ supertetrahedra. Cluster edge length increases from 2.6 to 7 to 12 Å respectively.

readily discernible. Indeed, the increase in pore size has been a goal in the study of porous materials as a new range of applications can be envisioned when the ability to occlude larger guest species is realized.[33]

In the pursuit of new materials, a subset of building unit size expansion has been to extend the catalog of cluster species from which to construct framework materials. While oxide molecular sieves are restricted to TO_4 components and all reported framework Ge–S materials contain Ge_4S_{10} adamantane units, the In–S family exhibits a considerably more diverse chemistry; building units have included $In_{10}S_{20}$ supertetrahedra[28] and In_6S_{15} distorted adamantane clusters.[34]

Recently, our attention has turned to the investigation of materials in the In–S system; there has been considerable interest in In–chalcogenide materials for application as storage devices for optical media, as precursors for chemical vapor deposition (CVD) experiments[35] and as thin film solar cells.[36] We theorized that a family of structures based on the $[In_4S_{10}]^{8-}$ anion would exist (analogous to the Ge–S system) considering that this cluster was known to crystallize in both layered[37] and molecular structures.[38] Interestingly, framework compounds containing the anticipated $[In_4S_{10}]^{8-}$ thioanion remain unobserved from hydro- or solvo-thermal syntheses. Rather, earlier investigations produced compounds based on the $In_{10}S_{20}$ supertetrahedron[28] and the In_6S_{15} distorted adamantane cluster,[34] while experiments described herein have resulted in $[In_4S_{10}]^{8-}$ molecular species as well as a novel layered material based upon In_9S_{20} clusters.

This publication reports the formation of three new In–S materials based on one novel and two known building units: In_9S_{20} edge shared adamantane clusters, $In_{10}S_{20}$ supertetrahedra and In_4S_{10} adamantane units. Their structures are discussed with respect to previously reported In–S materials and possible formation mechanisms during template mediated syntheses are proposed.

Nomenclature

In order to classify and refer to materials discussed in our research, we have retained the system of nomenclature described by Bedard *et al.*[5,6] The designation is as follows: organic component-framework composition-structure type. For example, an indium sulfide synthesized in the presence of dimethylamine, DMA-InS-SB1 has a different topology than DEA-InS-SB2 synthesized utilizing diethylamine, but the same as PYR-InS-SB1 synthesized using pyrollidine. The structure type code is assigned by the research group responsible for the synthesis, thus materials synthesized at SUNY, Stony Brook all contain a suffix -SB. Non-framework or molecular solids have a more arbitrary code as their structures can be quite varied.

Experimental

Syntheses

DEA-InS-SB1 and -SB2. Syntheses of DEA-InS-SB1 were achieved by sealing 0.1 g In (powder, Aldrich), 0.07 g S (Fisher) and 0.5 g diethylamine (DEA, 99%; Aldrich) in a Pyrex® tube and placing in a water filled steel bomb at 180 °C for 7 days. This treatment resulted in colorless octahedral and trigonal antiprism crystals (two habits, same material) of no more than 40 microns on edge. For the -SB2 material, 0.5 g of a 50% (wt/wt) aqueous solution of DEA was used in place of the neat liquid. Identical treatment resulted in plate shaped crystals up to 200 microns on edge and averaging about 10 microns thick. Powder X-ray diffraction (XRD) on a Scintag PAD-X diffractometer (step scan, 0.2° $step^{-1}$; 1.0 s $step^{-1}$, Cu-Kα radiation) indicated that these materials were unique and pure phases, with the exception of any unreacted starting material.

DPA-InS-ML. The synthesis of the layered material DPA-InS-SB3 (DPA = dipropylamine) has been reported previously.[34] Aging (in air) of the supernatant or 'mother-liquor' remaining from these preparations resulted in the formation of fragile hygroscopic crystals. Qualitative electron probe microanalysis of these crystals indicated the presence of In and S. Although moisture sensitive, the crystals could be ground in absolute EtOH and analyzed *via* powder XRD. The resulting pattern did not match that of DPA-InS-SB3 or any known In–S material. As this is an unoptimized synthetic route to this material, it is not practical to comment on experimental yield.

TMDP-InS-SB4. A mass of 7.1 g of a 40% (wt/wt) aqueous solution of 4,4′-trimethylenedipiperidine (TMDP; Aldrich) was combined with 0.5 g In and 0.34 g S in a sample vial to form a slurry of pH = 11.0. The reaction mixture was transferred to Pyrex® tubes through a stainless steel syringe. After sealing under vacuum, the tubes were held static at 180 °C for 5 days in water filled stainless steel bombs. The resultant product, a white powder, was collected, washed with EtOH and H_2O and dried in air. Plate shaped crystals of less than 100 microns on edge were observed, but were not plentiful.

X-Ray crystallography

All diffraction data were collected using a Bruker 1K CCD detector on either a SMART platform or Huber 4-circle goniometer employing Mo-Kα or synchrotron ($\lambda = 0.643$ Å) radiation respectively. Data were processed with the Bruker program SAINT.[39] Solution and refinement were carried out with SHELXTL,[40] while WINGX[41] was used for graphical representation.

DEA-InS-SB1 and -SB2. The structures of both of these compounds were determined from ambient temperature single crystal X-ray studies, details of which may be found in Table 1. The organic component of DEA-InS-SB1 was severely disordered and contained only one ordered cation. The SQUEEZE[42] utility within the program PLATON[43] was used to examine this extra-framework region. It was determined that 43.9% of the volume of the unit cell, or 5394.4 Å^3, was void space. A volume of this size could potentially host seven DEA

Table 1 Crystallographic data and structure refinement for -SB1, -SB2, -ML, and -SB4 materials

Compound	DEA-InS-SB1	DEA-InS-SB2	DPA-InS-ML	TMDP-InS-SB4
Empirical formula	$[(CH_3CH_2)_2NH_2]_6In_{10}S_{18}$ [a]	$[(CH_3CH_2)_2NH_2]_6In_{10}S_{18}$ [a]	$[C_6H_{16}N]_4In_4S_{10}H_4$ [a]	$[C_{13}H_{14}N_2]_4In_9S_{17}$
Formula weight	2234.42	2234.42	1192.84	2371.5
Crystal system	Tetragonal	Tetragonal	Monoclinic	Monoclinic
Space group	$P4_32_12$	$I4_1/amd$	$C2/c$	$P2_1/c$
Wavelength/Å	0.71073	0.71073	0.643	0.643
a/Å	19.6398(1)	11.7958(1)	10.322(2)	11.505(1)
b/Å	19.6398(1)	11.7958(1)	30.803(6)	28.708(1)
c/Å	31.8342(4)	47.0929(2)	15.861(3)	26.240(1)
β/°			105.75(3)	101.95(1)
V/Å^3	12279.1(2)	6552.55(8)	4853.6(17)	8481.18(3)
Z	8	4	4	4
μ/cm^{-1}	40.60	38.04	16.17	17.54
θ range for data collection/°	1.22 to 24.95	1.73 to 24.95	3.17 to 22.05	0.96 to 22.24
Index ranges (collected)	$-15 \le h \le 16, 0 \le k \le 23, 0 \le l \le 37$	$0 \le h \le 9, 0 \le k \le 13, 0 \le l \le 55$	$-11 \le h \le 8, -29 \le k \le 25, -8 \le l \le 16$	$-9 \le h \le 13, -25 \le k \le 29, -23 \le l \le 28$
Reflections collected	58366	14773	19630	33002
Independent reflections	10569 [R(int) = 0.0656]	1589 [R(int) = 0.0746]	2500 [R(int) = 0.0765]	9274 [R(int) = 0.0616]
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0454$	$R1 = 0.0453$	$R1 = 0.0776$	$R1 = 0.0611$
R indices (all data)	$R1 = 0.0655$	$R1 = 0.0653$	$R1 = 0.1048$	$R1 = 0.0983$

[a] Estimated.

cations. The data were treated with SQUEEZE[42] and the effects of the disordered organic were removed. Thus the chemical formula reported herein contains only one ordered organic species; five other DEA cations are assumed to be hosted within the voids for charge balance. No ordered organic molecules were located within the extra-framework region of DEA-InS-SB2. The data were corrected for the effects of disordered species with SQUEEZE[42] after noting a potential void volume of 3640.3 Å^3 per unit cell volume of 6552.5 Å^3, or 55.6%. It is therefore assumed that six DEA cations occupy this region.

DPA-InS-ML. Due to the delicate nature of the crystals, it was decided to analyze this material at beamline X3A1 of the National Synchrotron Light Source (NSLS) given the speed at which a data set could be collected with synchrotron radiation and a CCD area detector. Crystals were kept in the mother-liquor until immediately prior to mounting on a quartz fiber with epoxy. Details of the collection, solution and refinement can be found in Table 1. Only one unique DPA cation was found in the refinement as the others were severely disordered. There is presumably one other cation (with a second symmetry equivalent) in the vicinity of the remaining terminal S atoms (S8 in Fig. 6). Treatment of the one cation containing model with the SQUEEZE[42] utility in PLATON[43] improved the R factor by approximately 1.2%, but did not help find any ordered solvent molecules. No attempts to impart restraints on the model were performed as the remaining Fourier difference peaks were too small to be of any meaningful interpretation (*i.e.* < 2 e Å^{-3}).

TMDP-InS-SB4. Single crystal X-ray analysis of several resultant crystals was attempted on a sealed tube SMART platform CCD diffractometer. The resulting diffraction was too weak to be of any interpretation, thus a crystal was retained for analysis with synchrotron radiation at the NSLS beamline X3A1. Details of the collection, solution and refinement parameters are given in Table 1. Ordered TMDP cations were located, the hydrogen atoms of which were included in the model but not refined.

CCDC reference number 186/1894.

See http://www.rsc.org/suppdata/dt/a9/a909005c/ for crystallographic files in .cif format.

Results and discussion

DEA-InS-SB1

The structure of DEA-InS-SB1 is shown in Fig. 3. Corner linked $[In_{10}S_{20}]^{10-}$ supertetrahedra (Fig. 1e) form six-rings that define two independent, non-intersecting diamond lattices. This framework topology creates voids that contain disordered DEA molecules. This structure type has been described in detail previously[28] as the dimethylamine (DMA) analog of this material is known.

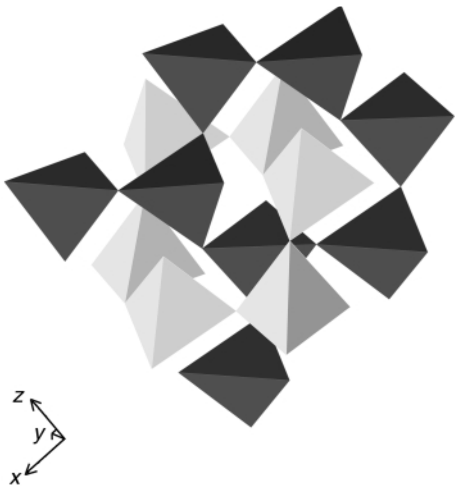

Fig. 3 Polyhedral representation of a portion of the DEA-InS-SB1 framework shown approximately down [010]. Each tetrahedron represents one $[In_{10}S_{20}]^{10-}$ cluster that is corner linked through sulfur atoms to form six-rings. The lighter and darker tetrahedra respectively form two interpenetrating, non-intersecting diamond lattices.

DEA-InS-SB2

A layered arrangement of corner linked $[In_{10}S_{20}]^{10-}$ supertetrahedra (Fig. 1e) found within the structure of DEA-InS-SB2 is shown in Fig. 4 and 5. Each layer (Fig. 4) stacks along [001] and consists of pores measuring approximately 11.8 × 8.5 Å (shortest S–S distance from atom centers). The stacking sequence (Fig. 5) of the layers is staggered such that the pores do not line up exactly, thus decreasing the effective dimensions of a resulting channel. Such an arrangement contrasts the alignment of pores observed in other layered In–S materials (DPA-InS-SB3)[34] and in some zeolites[44,45] and aluminophosphates.[46,47] The stacking topology is similar to that found in the silicate mineral muscovite, $KAl_2(AlSi_3O_{10})(OH)_2$ (Fig. 5).[48] In the silicate, alternate ‘up-down’ layers of SiO_4 tetrahedra stack along (001) and are separated either by K^+ cations or AlO_6 octahedra. DEA-InS-SB2 exhibits the same alternating stack

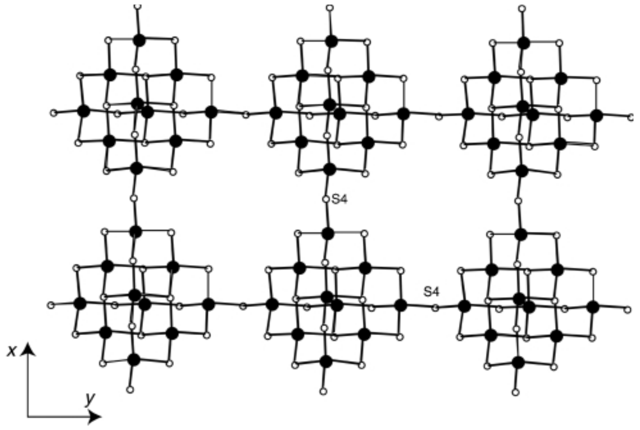

Fig. 4 A single layer of DEA-InS-SB2. Black circles are In, while open circles are S. Clusters corner link through S4. View is down [001].

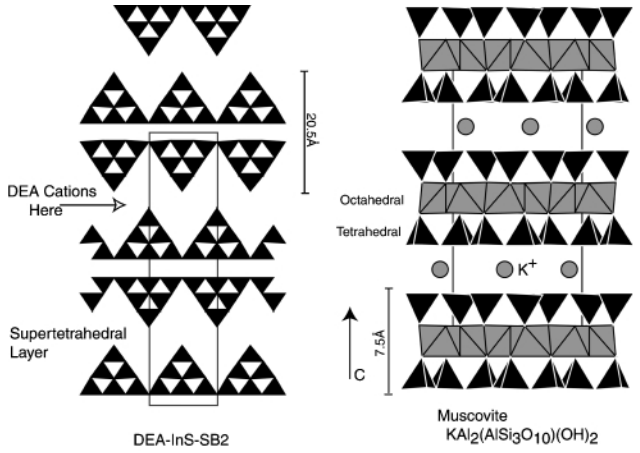

Fig. 5 Stacking sequence of both the DEA-InS-SB2 material and the silicate muscovite ($KAl_2(AlSi_3O_{10})(OH)_2$). Black tetrahedra are InS_4 and SiO_4 in the sulfide and silicate respectively. Gray octahedra in muscovite are AlO_6. The disordered DEA cations are not shown in the sulfide.

sequence, but the layers are instead comprised of $In_{10}S_{20}$ supertetrahedra. Rather than Al or K, layers are separated by DEA cations (not shown). The size of the In–S building units can be appreciated when compared to this similar Si–O structure. It should be noted that the connectivity of the tetrahedra within the layers of each structure is different: supertetrahedra corner link in -SB2 to form four-rings, while SiO_4 tetrahedra form six-rings in muscovite.

DEA-InS-SB2 is related to a layered $KInS_2$ phase[37] that contains In_4S_{10} adamantane units (Fig. 1c). These materials have similar connectivity of building units: four-rings formed from corner linked In–S clusters. The larger $In_{10}S_{20}$ building units however, give rise to larger pore sizes: 11.8 × 8.5 Å here *vs.* 7.7 × 5.2 Å in $KInS_2$.

On the assembly/templating mechanism for DEA-InS-SB2

The amount of water in a synthetic preparation of M–S framework materials has typically not been critical. For example, syntheses of Ge–S compounds has been achieved under a range of H_2O : organic ratios.[6,49] The DEA-InS system however, is an example in which varying the concentration of an organic structure directing agent changes the resulting framework topology. Pure (99%) DEA directs formation of a 3-dimensional structure (InS-SB1, Fig. 3) while at the 50% level, a layered structure is formed (InS-SB2, Figures 4,5). It is possible that a hydrogen bonded water/organic network is formed in solution such that the organic component has a larger effective size. In other words, it is actually a much larger aqueous species that is responsible for structure direction than simply isolated DEA molecules. This species could conceivably be planar in shape and thus direct the resulting topology of the In–S structure. Such speculation suggests that study of the solution phases of these systems is necessary. Organic/water hydrogen bonded networks have been observed previously in the channels of DABCO-MnGeS–SB1 and DABCO-AgGeS–SB2.[16,23]

DPA-InS-ML

The structure of DPA-InS-ML (Fig. 6) consists of isolated In_4S_{10} thioanions (Fig. 1c) arranged in a c-centered stacking sequence. The DPA cations are located between the clusters, with the central N atom approximately 3.5 to 3.7 Å from the terminal (S7) sulfur atoms. There is presumably a second DPA cation in the vicinity of S8 (see above).

Other molecular structures such as this one have been formed from mild hydrothermal treatment of In_2S_3 in aqueous solutions of alkali metal sulfides.[38] Contrasting bond length observations are noted however. Krebs reports an average terminal In–S length of 2.422 Å and an average bridging In–S length of 2.464 Å for $K_8In_4S_{10}{\cdot}16H_2O$. DPA-InS-ML has an average terminal In–S length *longer* than those bridging: 2.505 Å *vs.* 2.459 Å. Many Ge–S materials that contain the Ge_4S_{10} thioanion however, have shorter terminal bond lengths,[50] including those synthesized in the presence of amines.[17,22,23,51] This longer terminal In–S length suggests the possibility that these S atoms are actually -SH groups. Indeed, when considering both bond lengths and charge balance requirements, this scheme is plausible. The structure of DPA-InS-ML contains only 4 DPA cations for each $[In_4S_{10}]^{8-}$ thioanion. The presence of terminal -SH groups would satisfy this charge imbalance; thus rewriting the thioanion as $[In_4S_{10}H_4]^{4-}$. Bond valence sums[52] on S7 and S8 (Fig. 6; 0.74 and 0.68 respectively, without H contribution) further support the assumption of a 1− charge on these groups. Since the H atoms were not located in the X-ray analysis, an IR investigation would confirm this assumption; such is planned for future experiments in this system.

On the formation of DPA-InS-ML

DPA-InS-ML crystallized from a solution from which a separate, distinct structure, (DPA-InS-SB3)[34] formed. The building unit of the -SB3 material is the In_6S_{11} cluster, while the -ML material consists of adamantane In_4S_{10} thioanions. It is possible that during the synthesis of DPA-InS-SB3, both cluster species were present in the hydrothermal fluid and that the In_6S_{11} cluster crystallized first and thus depleted the solution of that component. Following this precipitation, the In_4S_{10} adamantane cluster would be free to crystallize as the mother-liquor is now effectively ‘ripened’ for the formation of the In_4S_{10} solid state material. The In_6S_{11} unit may have been less soluble or more abundant than In_4S_{10} in the reactant fluid and thus was the first to crystallize in a step-wise crystallization sequence. Also possible is that the In_4S_{10} unit is soluble at high (180 °C) temperatures and only begins to crystallize at room temperature. Materials containing isolated In_4S_{10} units have not been reported to form above 100 °C.[38,50]

TMDP-InS-SB4

The structure of TMDP-InS-SB4 (Fig. 7) represents a new topology in the In–S family. Like DEA-InS-SB2 (above) and DPA-InS-SB3,[34] -SB4 is a layered material consisting of large pores (12.1 × 6.6 Å) within the sheets. The building unit is the In_9S_{20} cluster, which condenses to give an overall layer stoichiometry of In_9S_{17}.

The In_9S_{20} cluster is best described as two edge shared adamantane units with four (of six total; S16,18,24,25 Fig. 7) of their “terminal” sulfur atoms bridged by two InS_4 tetrahedra. The layers are realized when the remaining terminal

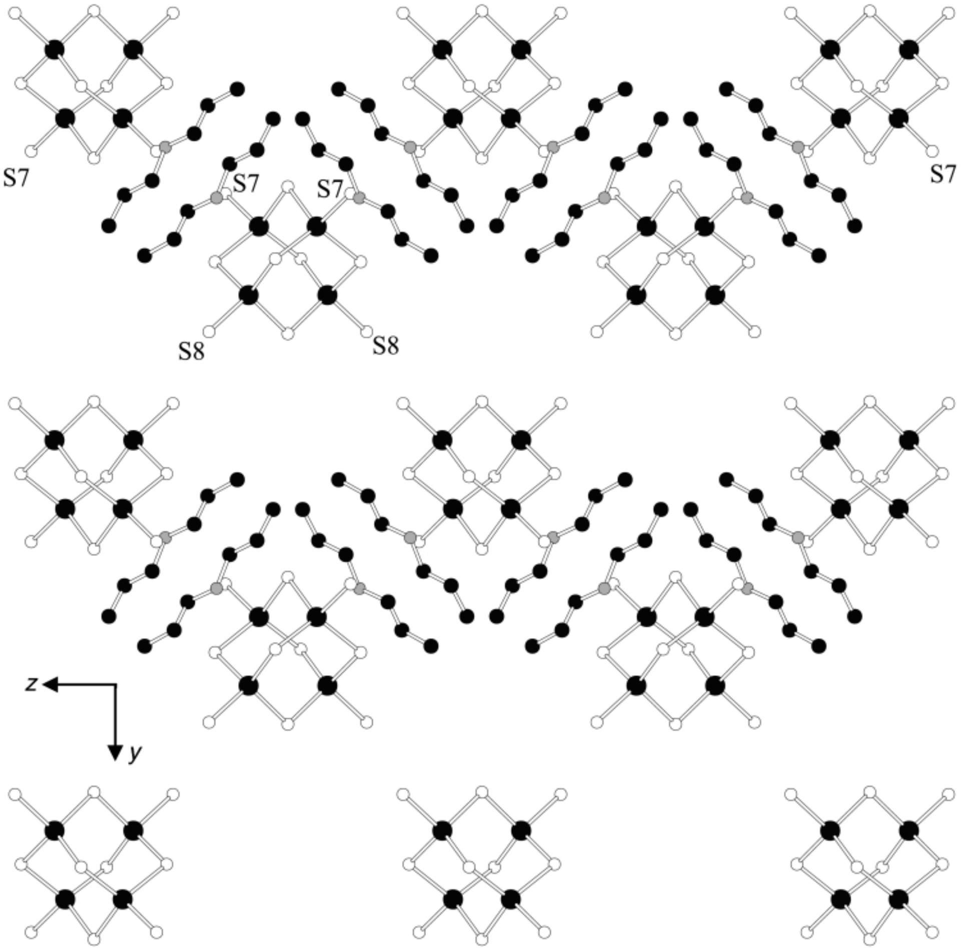

Fig. 6 DPA-InS-ML shown down (100). Only one (of two) symmetrically independent DPA cation was located in the structural analysis. The second is presumably situated near S8. On the organic, black circles are carbon, while gray are nitrogen. The H atoms assumed to be on S7 and S8 are not shown.

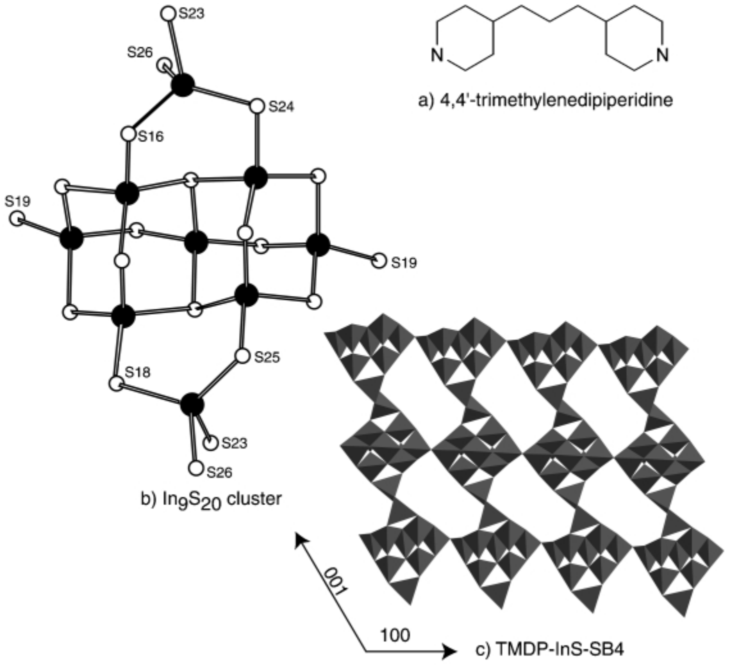

Fig. 7 (a) 4,4′-Trimethylenedipiperidine; (b) the In$_9$S$_{17}$ cluster shown as In$_9$S$_{20}$ for clarity. Black circles are In while open are S; (c) the TMDP-InS-SB4 shown down (010). Clusters corner link along (100) and edge link along (001).

sulfurs (S19) corner link along (100) to form chains which in turn are 'zipped' together *via* edge shared tetrahedra along (001). The resulting layers then stack along (010). This chain/zip topology is similar to the -SB3 material in which In$_6$S$_{15}$ clusters condense to form chains.

The In–S bond lengths of TMDP-InS-SB4 range from 2.405 to 2.563 Å and average 2.465 Å. The mean value is consistent with other reported materials containing In in tetrahedral coordination with S,[34,37,38] while the range is extended slightly to higher values. Terminal sulfurs (S19) have shorter than average

Table 2 Synthetic conditions and structure types for In–S materials

	Reactant stoichiometry/mol					Framework stoichiometry		
Material	In	S	Organic	H_2O	Building Unit	(In : S)	Structure type	Comments
DMA-InS-SB1	1	2.3	4.4	16.6	$In_{10}S_{20}$ Supertetrahedron	1 : 2	3-D Double-Diamond *Pbca*	180 °C; pure[a]
PYR-InS-SB1[b]	1	2.3	1.8	7.0	$In_{10}S_{20}$ Supertetrahedron	1 : 2	3-D Double-Diamond $P4_32_12$	180 °C; pure[a]
DEA-InS-SB1	1	2.3	6.8	trace	$In_{10}S_{20}$ Supertetrahedron	1 : 2	3-D Double-Diamond $P4_32_12$	180 °C; pure[a]
DEA-InS-SB2	1	2.3	3.4	14.0	$In_{10}S_{20}$ Supertetrahedron	1 : 2	Layered $I4_1/amd$	180 °C; co-crystallizes with -SB1 on occasion
DPA-InS-SB3	1	2.3	3.5	trace	In_6S_{15} Distorted adamantane	1 : 2	Layered $P2_1/c$	180 °C; pure, no evidence of -ML
DPA-InS-ML	?	?	?	trace	In_4S_{10} Adamantane	1 : 2	Molecular *C*2/*c*	Room temp.; pure from -SB3 supernatant[c]
TMDP-InS-SB4	1	2.5	3.4	60	In_9S_{20} Edge-shared adamantane	1 : 2	Layered $P2_1/c$	180 °C; structure not representative of bulk
HPP-InS-ASU31[d]	1	2.5	n/a	n/a	$In_{10}S_{20}$ Supertetrahedron	1 : 2	3-D *I*-43*m*	135 °C; low yield
DPM-InS-ASU32[d]	1	2.5	n/a	n/a	$In_{10}S_{20}$ Supertetrahedron	1 : 2	3-D *I*-4*m*2	135 °C

[a] Pure in this case is defined as 'no evidence of any other building unit both in the solid state or aged mother-liquors.' [b] Cahill *et al.*, unpublished results. [c] See Experimental section. [d] Ref. 29.

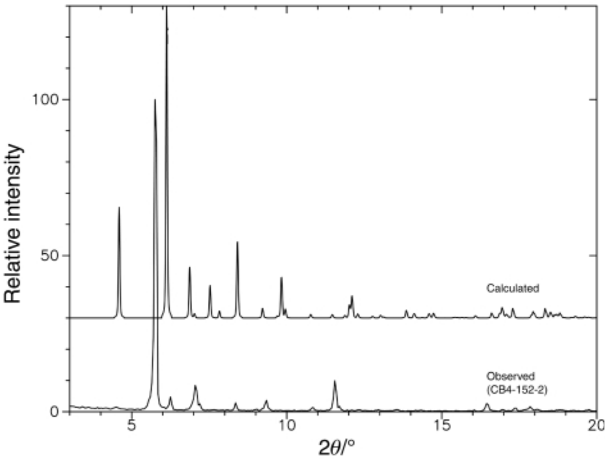

Fig. 8 Observed and calculated powder XRD of TMDP-InS-SB4. The observed data are from a step scan on a Scintag diffractometer, while the calculated pattern was produced with the program GSAS.

In–S lengths (2.441 Å); a phenomena observed previously in In–S materials.[9,28,37,38] The edge sharing of two InS_4 tetrahedra gives one short In–In (In7–In8) contact of 3.324 Å, as opposed to an average of 3.24 Å in In metal.[53] Distortion from ideal tetrahedral In–S–In linkages can be seen in the angular range of 83.35 to 110.52°. The most significant of these (83.35°) is in the In(8)–S(23)–In(7) edge sharing (Fig. 7).

Unlike the -SB3 material, but similar to the -SB2 structure (Fig. 3), the pores in subsequent layers of -SB4 do not align. The TMDP molecules are intact and are (in some locations) less than 3.5 Å from the In–S framework, suggesting a hydrogen bonded relationship. Their disposition suggests a templating role, yet the possibility of the formation of more than one structure type (see below) in the same synthetic preparation indicates a space filling role.[54] An analogous situation was observed in the DABCO-GeS-SB1 system.[23] The TMDP molecules are assumed to be protonated (at least partially) in order to charge balance the anionic layers. No IR investigation was undertaken to confirm this, given the level of impurity of the reaction product (see below).

On the formation of TMDP-InS-SB4

The formation of the -SB4 material from the synthesis described above brings to light a significant experimental problem facing studies of these compounds. The powder pattern of a typical preparation of TMDP-InS-SB4 is shown in Fig. 8 along with the calculated[55] diffraction pattern of the crystal structure. The observed pattern is clearly representative of an open structured material (low angle peaks), yet the calculated pattern of crystals isolated from these preparations (also an open structure) does not correspond well. The structure refinement is of sufficient quality to discard any notion that the structure is wrong. What is more likely is that the crystals formed in these preparations are not truly representative of the bulk powder phase. These crystals are in turn quite weakly diffracting (recall that a synchrotron was required for their analysis) and few so as not to contribute substantially to the observed diffraction pattern obtained from a sealed tube source. Such is an occupational hazard when dealing with kinetically controlled, solvent mediated reactions. The dominant phase is a powder and conceivably resists formation of single crystals while the minor phase, the -SB4 structure, is more amenable to crystallization. This may be another example of what is seen in the DPA-InS-SB3/-ML system (above): a later forming phase makes use of remaining building units and crystallizes after the hydrothermal fluid has been depleted of other components. In this system, such a statement is even more speculative than in DPA-In-S since the structure of the bulk phase remains unknown.

Comments

Table 2 is a summary of reaction conditions and structure types in the organic-In-S system, both from this and other studies. From this arrangement, a number of points can be made.

The $In_{10}S_{20}$ building unit is formed over a range of templates and template concentrations.

The $In_{10}S_{20}$ unit is not observed with longer chained templates.

More than one type of building unit is formed in the DPA-In-S system, and possibly in the TMDP-In-S system.

Building unit geometry resembles that of the adamantane cluster in all cases.

Each solid state material contains a *single* type of building unit.

The amount of H_2O in a preparation appears to direct framework topology, but not building unit speciation.

These observations suggest two possible scenarios for the template mediated formation of open-structured In–sulfides.

(1) Several building units are formed in solution in each preparation. The organic then suppresses crystallization of most, while promoting condensation of a single species.

(2) A single building unit is formed in each preparation, the geometry of which is related to that of the amine, and

(2a) multiple building units are formed when the organic is above a critical chain length.

Scenario 1 can be envisioned as follows: several building units form upon reaction of In and S with the amine. Certain species are then coordinated to the organic (or organic/water network) and prohibited from condensing with like building units. Thus the organic component has effectively selected a single type of building unit for crystallization. The remaining In–S species stay tightly coordinated to the organic and never crystallize.

Scenario 2 is a simpler case than 1: a single building unit is formed for a single type of organic geometry. Support for this is the fact that in solution, the effective shapes of DMA, DEA and PYR are assumed to be similar. All of these organics promote formation of the $In_{10}S_{20}$ building unit and no others. It is not until the geometry of the organic is changed to longer chained (linear) compounds that we begin to see variation in building units. A parallel suggestion to this may be that multiple building units are not observed until linear organics of a specific chain length are used. The DPA-In-S system is the first observation of multiple building units in a single reaction mixture, although TMDP-InS remains a possibility as well.

The results from Li *et al.*[29] contribute to both of these scenarios. They report formation of two distinct structure types ASU-31 and ASU-32 from two different organic structure directing agents: HPP (1,3,4,6,7,8-hexahydro-2*H*-pyrimido-[1,2-*a*]pyrimidine) and DPM (dipiperidinomethane). Both materials contain the $In_{10}S_{20}$ supertetrahedron and crystallize in low yields (10% and 50%). This may suggest the formation of other building units that remain part of the bulk and are not observed as crystalline species (Scenarios 1 and 2a). Alternatively, the range of template geometry responsible for formation of the supertetrahedra may have been extended from the smaller amines to include these larger species (Scenario 2 and Table 2).

ASU-31 and -32 do not exhibit the framework interpenetration observed in the -SB1 structure types. Interpenetration is thought to be a result of pore sizes becoming too large to support a framework; a direct result of larger building units (Fig. 2). It is possible that in the ASU materials HPP and DPM form a sufficiently large organic or organic/water network, which in turn is capable of 'propping open' the giant cavities observed in these structures. Considering this mechanism, several open structures should be possible given the proper choice of organic component.

In order to understand the conditions which promote the formation of specific building units and topologies, a study of the solutions from which these materials crystallize is desirable. Experiments can be performed in which mother-liquors are examined *via* mass spectrometry, ion chromatography or EXAFS in order to determine the speciation in solution. Many previous studies have utilized Raman spectroscopy and have assumed the stretching frequencies of the solid state species are equivalent to those in solution.[9,38] Although attractive for the simplicity of that type of experiment, a more complex speciation in the presence of amines is expected, thus prompting a different mode of investigation. Further, the local geometry of each building unit is quite similar to one another.

A more rudimentary approach may be an effective route to understanding the conditions under which specific building units form. For instance, a classical crystallization study using alkali metal salts may prove most fruitful.[9] Mother-liquors can be prepared at sufficiently low concentrations of building units so as to thwart condensation to framework species. Recall that Table 2 suggests that the concentration of template does not affect speciation, but rather framework topology. The building units (as molecular species) can then be crystallized from solution as (for example) alkali metal salts. A survey of template geometry, concentration and pH *vs.* building unit speciation would be readily attainable after single crystal structure analysis of the salts.

Conclusions

A family of framework sulfide materials exhibiting considerable structural diversity has been discovered in the In–S system. Contributions from several research groups have demonstrated the ability to assemble a variety of building units in different topologies. Both the formation of building units and subsequent structure direction are proposed to be related to the geometry of the organic components (amines) of these structures. Further synthetic efforts will allow a refinement of the reaction conditions governing the formation of each specific building unit and ultimately the design of novel structure types.

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