Catalyzed Growth of a Metastable InS Crystal Structure as Colloidal Crystals

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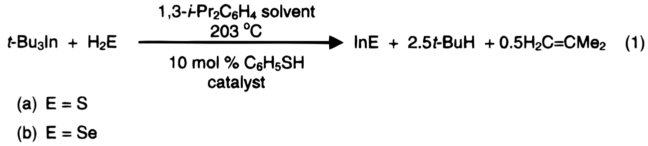
Biosynthesis and organic synthesis, adept at controlling molecular structure, produce selectively a rich variety of lowest-energy and higher-energy (metastable) structures. However, materials synthesis, which affords nonmolecular substances such as ceramics and semiconductors, generally produces *only* the lowest-energy *crystal* structure.[1,2] Molecular synthesis achieves the structural diversity lacking in nonmolecular synthesis through kinetic control, wherein the structure obtained is the one that forms the fastest under conditions that prevent its equilibration to the lowest-energy, most-stable structure. Kinetic control is often achieved by chemical catalysis, but the absence of catalytic strategies in materials synthesis has historically precluded application of kinetic control to the formation of metastable nonmolecular solids.[1] Recently, Johnson and co-workers have achieved kinetic control in noncatalyzed syntheses of metastable solids by using thin-film multilayer reactants.[3−5] Metastable solids have also been recently grown by chemical vapor deposition[6,7] and electrodeposition.[8] We now report the *catalyzed* synthesis of a metastable InS crystal structure under kinetic control.

Catalyzed syntheses of InS and InSe were conducted under solution-phase reaction conditions analogous to those used in molecular synthesis (eq 1). When benzenethiol (C_6H_5SH) was



$$t\text{-Bu}_3\text{In} + \text{H}_2\text{E} \xrightarrow[\text{10 mol \% } \text{C}_6\text{H}_5\text{SH catalyst}]{\text{1,3-}i\text{-Pr}_2\text{C}_6\text{H}_4\text{ solvent, 203 °C}} \text{InE} + 2.5t\text{-BuH} + 0.5\text{H}_2\text{C=CMe}_2 \quad (1)$$

(a) E = S
(b) E = Se

employed as a catalyst (in 10 mol %), the InS and InSe products precipitated in 85−95% yields as polycrystalline powders having sharp X-ray powder diffraction (XRD) lines. Elemental analyses of the bulk InS powder established a 1:1 In:S ratio, and low levels of residual carbon (<2%) and hydrogen (<0.5%). When the reactions were conducted without the benzenethiol catalyst, the product powders were crystallographically amorphous, as evidenced by broad, featureless XRD patterns. Amorphous products are expected from low synthesis temperatures such as the 203 °C employed here. Crystal-growth barriers for covalent nonmolecular solids are typically high and require synthesis temperatures of ≥400 °C to be surmounted.[9,10] The results established that the benzenethiol catalyst activated low-barrier crystallization pathways in the InS and InSe syntheses.

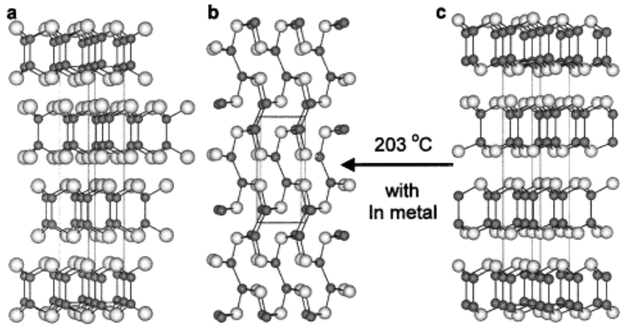


Figure 1. Crystal structures of III−VI compounds. In atoms are dark gray; Se and S atoms are light gray:[25] (a) InSe;[11−13] (b) InS, lowest-energy network form;[14] (c) InS, metastable layered form from eq 1a.[16]

The XRD pattern of the InSe product from reaction 1b (eq 1) corresponded to that of the known, standard-pressure (1 atm) structure (Figure 1a).[11,12] The structure contains planar, covalently bonded sheets that are 4 atomic layers thick and are separated by van der Waals gaps. This layered, pseudographitic structural form is also exhibited by GaS and several other III−VI members of the GaS family.[13]

However, the known structure of InS (Figure 1b) at standard pressure differs from that of the GaS family.[14] The greater ionic character of InS relative to InSe, GaS, and the other family members destabilizes the layered structure relative to the 3D network structure shown in Figure 1b.[15] Until the present work, a layered form of InS was unknown.

The XRD pattern of the InS product from reaction 1a (eq 1) did not match any known InS phase. Consequently, the crystal structure was solved from XRD data collected on an as-precipitated, unannealed powder sample, and refined by the Rietveld method.[16] As shown in Figure 1c, the new InS structure is a close variant of the layered, pseudographitic GaS (InSe) structure (Figure 1a). Thus, InS exists in both layered and network structural forms; we show below that the layered structure is a higher-energy, metastable form.

The InS and InSe materials from eq 1 precipitated with colloidal-crystal nanostructures. Both materials were found primarily in platelet morphologies. The InSe platelets approximated hexagonal shapes (Figure 2a,b), whereas the InS platelets exhibited triangular features (Figure 2d). Electron-diffraction patterns collected perpendicular to the large-area platelet surfaces and over large areas (collection radii ≈ 150 nm) established that the crystallographic *c* axes were perpendicular to these platelet surfaces and that the platelets diffracted coherently, as single crystals would. However, examination of TEM

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(16) Crystallographic and refinement data: space group $R3m$ (no. 160); hexagonal axes, $a = b = 3.86714(75)$ Å, $c = 24.2580(48)$ Å; $R_F = 0.053$ for 60 reflections, $R_{wp} = 0.067$, $R_p = 0.052$. Atomic fractional coordinates: In(1), [0, 0, 0]; In(2), [0, 0, 0.11487(11)]; S(1), [0, 0, 0.8297(4)]; S(2), [0, 0, 0.2964(6)].

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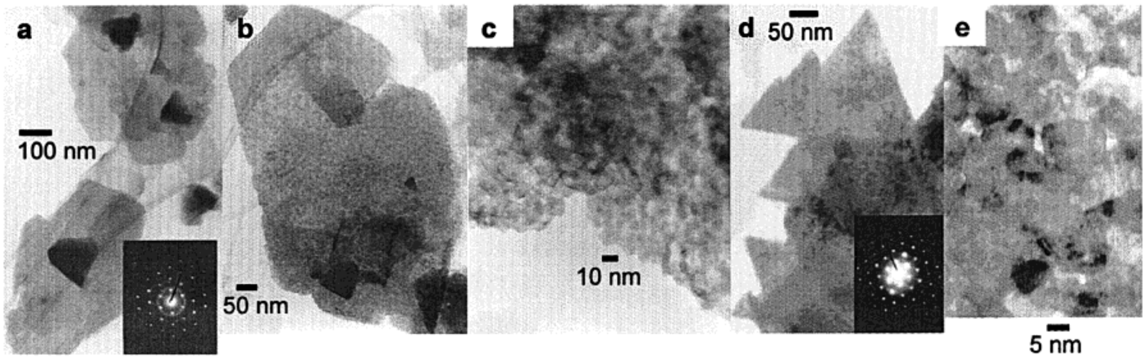

Figure 2. Transmission electron micrographs of InSe and InS platelets: (a) InSe platelets approximating hexagonal shapes; inset, electron-diffraction pattern collected along the [0001] zone axis of a platelet; (b) InSe platelet revealing texture; (c) InSe platelet edge revealing constituent hexagonal nanocrystallites; (d) InS platelets with triangular features; inset, electron-diffraction pattern collected along the [0001] zone axis of a platelet; and (e) InS platelet center revealing internal structure.

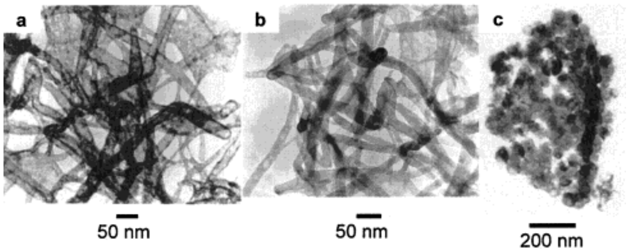

Figure 3. Transmission electron micrographs of fullerene-like morphologies of InS from eq 1a: (a) nanotubes with TEM aperture in; note the grainy texture, thickened walls, and closed ends; (b) nanotubes with TEM aperture out; and (c) nanospheres; note some hollow, incomplete shells.

images revealed texture and ragged edges in the platelets consistent with internal structure (Figure 2c,e). Close inspection of the hexagonal InSe platelet edges showed that the platelets were constructed of hexagonal nanocrystallites having ca. 10-nm lateral dimensions (Figure 2c). Similarly, the InS platelets were constructed of irregularly shaped nanocrystallites having 10−20-nm lateral dimensions (Figure 2e). In both cases the nanocrystallites were assembled in a crystallographically coherent manner to build papier-mâché-like colloidal crystals. We surmise that the nanocrystallites consist of one or a few tetra-atomic-layer sheets, the basic structural units of the InSe and InS crystal structures (Figure 1a,c), which grew in solution to the 10−20-nm lateral dimension, and concurrently or subsequently stacked into colloidal-crystal assemblies.

The morphological distribution found in the InS precipitates was ca. 80−85% platelets (Figure 2d), 13−19% nanotubes and nanorods (Figure 3a,b), and 1−2% nanospheres (Figure 3c).[17] The nanotube and nanosphere morphologies appeared to be hollow structures reminiscent of those found in carbon and pseudographitic (e.g. MoS_2) fullerene samples,[18−21] and in clays.[22] At higher magnifications, some of the nanotubes and nanospheres appeared to be incompletely closed trough, ribbon, and bowl morphologies. All of the InS morphologies possessed the papier-mâché-like texture observed in the platelets, establishing similar colloidal-sheet nanostructures. Because of the nanosheet texturing, the InS nanotube and nanosphere walls lacked the parallel-fringe patterns characteristic of carbon and pseudographitic fullerene nanotubes and nano-onions grown at conventionally high temperatures of $\geq$1000 °C.[18−21]

The conversion of layered to network InS (Figure 1) under equilibration conditions strongly suggested a greater relative stability for the network structure. Layered InS from reaction 1a (eq 1) was suspended in the reaction solvent (1,3-diisopropylbenzene) in the presence of indium-metal powder (30 mol %), and the mixtures were heated to reflux at 203 °C. The resulting molten-indium recrystallization catalyst[23] effected equilibration of the layered and network crystalline forms, yielding complete conversion to the network crystal structure, in support of a greater stability for the network structure. When conducted in the solid state, the same layered-to-network structural transformation required temperatures of $\geq$400 °C. The results indicated the layered InS crystal structure to be metastable under the low-temperature conditions of its formation, and to have therefore been produced by a kinetically controlled synthetic pathway.

The mechanism of the benzenethiol-catalyzed crystal growth in 1 is presently unknown. The catalyst apparently promotes condensation of an isolable $[InS(t\text{-}Bu)]_x$ polymer intermediate;[24] a proposed pathway will be described subsequently in a full report. This work demonstrates that the syntheses of nonmolecular solids having metastable crystal structures, which are generally inaccessible by conventional crystal-growth methods, may be catalyzed.

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[24] The intermediate $[InS(t\text{-}Bu)]_x$ was isolated as a white, insoluble solid having a chemical analysis corresponding to the formula $C_{3.78}H_{8.77}InS$. Calculated weight percentages for C_4H_9InS: C, 23.55; H, 4.45; S, 15.72. Found: C, 22.34; H, 4.32; S, 15.79.

[25] The ball-and-stick structures were generated with PowderCell freeware (www.bam.de/a_v/v_1/powder/e_cell.html) and rendered with Pov-Ray freeware (www.povray.org).