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Ammonothermal Crystal Growth of Sulfide Materials

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Single crystals of refractory materials are often difficult to obtain from the melt due to the high temperatures involved. Obtaining crystals at temperatures below the melting point can be accomplished by methods that involve growth from the gas phase (i.e., iodine transport) or growth from solution such as the use of molten salt fluxes and solvothermal methods. To perform solvothermal crystal growth, a feedstock, solvent, and a solubilizing agent known as a mineralizer are heated in an autoclave that is subjected to a temperature gradient. This method has been used to grow crystals of a wide variety of materials in supercritical H_2O, including sulfides.[1] Crystals of numerous sulfur compounds (mostly polysulfides and sulfosalts), selenides, and tellurides have been grown in ammonia and ethylenediamine.[2] Usually, polysulfides (S_n^{2-}) and salts of soft thioanions (AsS_4^{3-}, $Sn_2S_6^{4-}$, etc.) are grown at more modest temperatures than sulfides of hard cations. Since alkaline earth sulfides hydrolyze to some extent in water,[3] nonaqueous solvents such as NH_3 are probably more suitable than H_2O for growing crystals of these materials. As part of a study of ternary sulfide materials, the application of ammonothermal methods of crystal growth to binary and ternary alkaline earth sulfides was examined.

The source sulfide(s), an acidic mineralizer (usually NH_4I), and liquid ammonia were sealed in a thick-walled tube which was then heated in an upright position in a water-filled pressure vessel for 12−60 h at the desired temperature.[4] The top of the tubes was significantly cooler than the bottom, but the precise thermal gradient experienced by the tubes could not be measured with my apparatus.[5] Up to about 300 °C, the experiments produced only highly solvated crystals that rapidly decomposed when removed from the tube (in a glovebag). Those crystals are believed to be hydrosulfide compounds based on a similar experiment with Y_2S_3 and NH_4I at 300 °C in ethylenediamine (en) that produced crystals of the hydrosulfide $Y(en)_4(SH)_{2.72}I_{0.28}$.[6]

At temperatures above 300 °C, NH_4I mineralizer facilitated growth of CaS and SrS crystals in NH_3.[7] Large (several mm) crystals could be obtained at the top of the quartz tubes, but the crystal sizes were not very reproducible. With strontium sulfide, larger crystals were produced more easily. Growth rates increased substantially with higher reactant concentrations. Crystal growth was also attempted with CaO at 450 °C to determine if ammonothermal methods are generally applicable to the chalcogenide group. The exclusive formation of hexagonal plates of $Ca(OH)_2$ at the top of the tube can be explained by the high thermal stability of the hydroxide (dec 580 °C).[8]

The effect of temperature on the growth of CaS crystals was examined in some detail. The effect of temperature on a system with a constant charge, fill (constant within ±5%), and run time is presented in Figure 1. Deposition of CaS starts around 335 °C, and the deposited mass generally increased with increasing temperature. There is some scatter in the data indicating low reproducibility. One possible cause of irreproducibility is variation in the number of seeds present at the top of the tube. In some runs, a solid polycrystalline mass formed at the top of the tube, in others single crystals fell down from the top of the tube onto the charge. The mechanical integrity of any deposited polycrystalline mass of CaS appeared to increase with increasing temperature. Infrared spectra of CaS crystals showed the presence of ammonium ion/ammonia with strong absorption bands at 3110, 2940, and 2805 cm^{-1} (NH stretch) and 1420 cm^{-1} (NH bend). Heating the CaS crystals under vacuum to 500 °C evolved only CO_2 and organic compounds (which were probably absorbed onto the surface), and did not change the IR spectra. No ammonia was evolved from the crystals,

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(4) (a) Material sources: CaS, SrS, CdS, and Y_2S_3 (Cerac); NH_4I (Aldrich); anhydrous NH_3 (air products). The NH_4I was sublimed under vacuum before use. In a typical CaS growth experiment, a 5 mm o.d. 3 mm i.d. quartz tube (QSI) was sealed at one end and charged (in the Dri-Lab) with CaS (250 mg, 3.5 mmol) and NH_4I (168 mg, 1.2 mmol), and 18.5 mmol of anhydrous NH_3 was condensed into the tube on the vacuum line. The tube was flame sealed at a height of about 14 cm, giving a overall fill of 64−71%. (*Caution: Tubes with liquid NH_3 can burst at room temperature. Be sure to wear adequate eye, hand, and face protection!*) After loading the tube into the pressure vessel, the vessel was pressurized to about 10 000 psi with distilled water and heated to the desired temperature for 1000 min. Typically, the temperature measured in the thermowell of the pressure vessel was 50 °C below the furnace temperature. All reported temperatures are those measured in the thermowell. The deposited crystals (at the top of the tube) were removed by freezing the tube at −196 °C, opening the tube, and scraping the crystals out with a stiff wire. The crystals were washed with ethanol and acetone several times and dried (in air). Whenever a crystal had fallen down onto the charge, the use of water was necessary to wash the charge from the crystal. (b) NH_4I (18 mg), CaS (250 mg), 395 °C. (c) SrS (200 mg), NH_4I (85 mg), 400 °C.

(5) Leco HR-1B hydrothermal system using a MRA-114R or MRA-138R vessel, Leco Corporation, Bellefonte, PA.

(6) George, C. F.; Purdy, A. P. *Acta Crystallogr.* **1997**, *C53*, 1381.

(7) (a) Crystals of known materials CaS, SrS, CdS, $Ca(OH)_2$, and $NH_4Cu_7S_4$ were characterized by X-ray diffraction; the unit cells in all were within esd of literature values. (b) *Crystal Data Determinative Tables*, 3rd ed.; Volume II: Inorganic Compounds; Donnay, J. D. H., Ondik, H. M., Eds.; National Bureau of Standards and JCPDS: Washington, D.C., 1973. (c) JCPDS CaS (8-464), SrS (8-489).

(8) Weast, R. C., Ed. *CRC handbook of Chemistry and Physics*, 66th ed.; CRC Press Inc.: Boca Raton, FL; p B-82.

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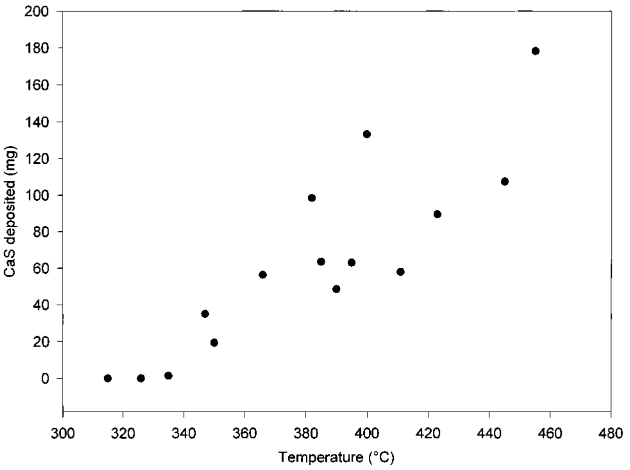

Figure 1. A plot of the mass of CaS deposited vs growth temperature.

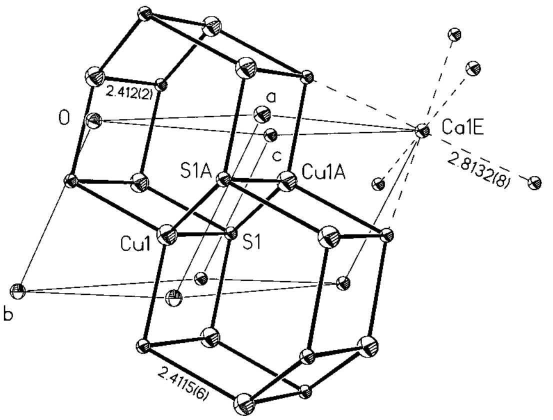

Figure 2. Structure fragment of $CaCu_2S_2$ (**2**). The thermal ellipsoids are at the 50% level, and the Ca atoms at each vertex of the unit cell are also shown. Atom coordinates: Ca1 [0, 1, 1], Cu1 [$^1/_3$, $^2/_3$, 0.3765(2)], S1 [$^1/_3$, $^2/_3$, 0.7463(2)].

which indicated that ammonia-filled inclusions were not present in large enough amounts to break the heated crystal. When the CaS crystals were grown with smaller amounts of mineralizer,[4b] the absorption peaks from ammonium ion were absent and the small IR absorption peaks from ammonia-filled inclusions became visible. Some SrS crystals grown with a high mineralizer concentration[4c] had only weak peaks from ammonium ion, but large numbers of inclusions were visible under the microscope and an IR spectrum showed NH_3 to be present.

Attempts were also made to grow crystals of solid solution and ternary sulfides. A mixture of CaS and SrS in the starting charge resulted in the growth of a mixture of solid solutions of CaS and SrS. Powder patterns showed numerous peaks from solid solutions of different composition, and even individual crystals had broad streaks instead of well-defined spots on a rotation photograph. Attempts to grow CaY_2S_4[9] ammonothermally with acidic mineralizers using either a CaY_2S_4 powder or a mixture of CaS and Y_2S_3 as source material were not successful at temperatures up to 500 °C. Using a CaS−CdS solid solution ($Ca_{0.75}Cd_{0.25}S$)[10] as source material at 370 °C resulted only in crystals of CaS at the top, cooler portion of the tube and small hexagonal plates of CdS at the bottom. Manganese-doped CaS crystals (0.9 mol %) were produced at 400 °C by the addition of a small amount (1 mol % metals basis) of MnI_2 to the initial charge. In a similar manner, brown copper-doped (0.2 mol %) CaS crystals were produced at 365 °C by adding 1 mol % CuI.[11] Black square plates of $NH_4Cu_4S_3$ (**1**) also formed near the bottom of the tube in the latter case.[12] Reactions with higher concentrations (20−40%) of CuI were also run at temperatures from 350 to 360 °C. In these reactions larger quantities of **1** formed, which also formed near the top of the tube. Yellow to orange (by transmitted light) hexagonal plates of a previously unknown ternary sulfide, $CaCu_2S_2$ (**2**), formed near the middle to the top of the tube and were intermixed with crystals of **1**, CaS, and thin black wire-like crystals of the known ammonium copper(I) sulfide, $NH_4Cu_7S_4$ (**3**).[13] An experiment at 425 °C produced **3** and copper-containing CaS, but not **1** or **2**. With both **1** and **2**, there was not sufficient material for bulk elemental analysis, but a qualitative energy-dispersive X-ray spectrum showed the correct elements to be present in **1**−**3**.

The structure of the mixed valence ammonium copper sulfide **1** is isotypic with the other known compounds in the $M^ICu_4S_3$ series (M^I = K, Rb, Cs, Tl).[14] The only real difference between these structures is the spacing between the $(Cu_4S_3)_n$ layers resulting from the size of the cation, which is reflected in the unit cell parameter c (NH_4^+, 9.48 Å; K^+, 9.26 Å; Rb^+, 9.41 Å; Cs^+, 9.69 Å). The synthesis of a selenium analogue ($CsCu_4Se_3$) by hydrothermal methods has been reported.[1c]

The ternary sulfide **2** has a $CaAl_2Si_2$-type structure,[15] which consists of a double layer of fused six-membered nonplanar Cu−S rings ($Cu_2S_2^{2-}$) separated by the Ca^{2+} ions (Figure 2). The only other known alkaline earth−copper sulfide of the $M^{II}Cu_2S_2$ stoichiometry is $BaCu_2S_2$, which is found in both a tetragonal and an orthorhombic structure.[16] However, a barium−silver sulfide ($BaAg_2S_2$) was recently found to have a $CaAl_2Si_2$-type structure.[17] An infrared spectrum was obtained from a crystal of **2**

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(10) Lehmann, W. *J. Luminescence* **1972**, *5*, 87−107.

(11) Cu and Mn concentrations in the doped crystals were measured by ICP.

(12) Single crystals of **1** and **2** were analyzed at 293(2) K on a Siemens P4 diffractometer using Mo Kα radiation. An absorption correction was applied to the data by crystal face integration, the structures were solved by Patterson methods (SHELXTL 94), and the resulting structural parameters were refined to convergence using SHELXTL 96. $NH_4Cu_4S_3$ (**1**): $P4/mmm$, $a = 3.9101(1)$, $c = 9.4758(6)$ Å, $Z = 1$, $V = 144.87(1)$ Å^3, $\mu = 15.419$ mm^{-1}; 680 reflections, 239 independent, $2.15 \le \theta \le 34.98°$, GOF = 1.07, $R1 = 2.7\%$, $R1$ (all data) = 3.3%, wR^2 (all data) = 7.0%. $CaCu_2S_2$ (**2**): $P\text{-}3m$, $a = 3.9400(4)$, $c = 6.523(1)$ Å, $V = 87.69(2)$ Å^3, $Z = 1$, $\mu = 14.498$ mm^{-1}; 752 reflections, 306 independent, $3.12 \le \theta \le 44.85°$, GOF = 1.13, $R1 = 4.6\%$, $R1$ (all data) = 6.0%, wR^2 (all data) = 13.9%. Only 1.8 of the 4 NH_4 hydrogens were located in the difference maps for **1**.

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using an IR microscope and showed no absorptions from 4000 to 700 cm^{-1}.

Ammonothermal synthesis using acidic mineralizers has proven to be a very versatile technique for crystal growth of both binary and ternary sulfide materials. While this method clearly cannot afford crystals of every possible material, crystal growth of many novel, interesting, and potentially useful materials should be possible, and extensive study is warranted.

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Supporting Information Available: Two X-ray crystallographic files in CIF format (12 pages) and structure factors (2 pages). Access and ordering information is given on any current masthead page.

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