Novel Layered Sulfides of Tin: Synthesis and Structural Characterization of Cs$_4$Sn$_5$S$_{12}$·2H$_2$O and Sn$_5$S$_{12}$(N$_2$C$_4$H$_{11}$)$_2$(N$_4$C$_{10}$H$_{24}$)

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Framework compositions [Sn$_5$S$_{12}$]$^{4-}$ have been synthesized hydrothermally in the presence of triethylenediamine (Dabco) and caesium, respectively; the cations are accommodated between the sheets with orientation relationships suggestive of a templating mechanism and their crystal structures have been determined.

Recently, in a development inspired by the hydrothermal chemistry of the aluminosilicate zeolites,[1,2] sulfides were recrystallized in the presence of organic materials, usually amines.[3–6] Workers at OUP in particular have described a rich chemistry based upon Sn- and Ge-sulfides.[3,4]

We have concentrated on several materials produced from Sb$_2$S$_3$, which form a variety of new two- and three-dimensional frameworks composed of corner and edge-shared SbS-polyhedra.[5–7] Colour changes have been observed as a function of the density; powdered Sb$_2$S$_3$ is black, open frameworks containing K, Rb and Cs are wine red while the lower density materials produced from tetramethylammonium and tetrapropylammonium salts are orange and pale yellow, respectively. Similar colour changes are observed when semiconducting chalcogenides are synthesized in the pores of molecular sieves.[8–13] In this case the confined particles are of a size that give rise to quantum size effects.[13] The production of open sulfide frameworks by recrystallization using a template is conceptually the complement of this effect; instead of confining semiconductors within the regular, restricted pores of molecular sieves, pores of regular size are placed into the prototype semiconductor. Ozin[14] has introduced the concepts of *endo-* and *exo-*semiconductors to highlight the complementary nature of these approaches, especially in the case of materials based upon SnS$_2$.

In this report we describe the syntheses and structural characterization of two layered materials produced according to the philosophy outlined above. Both are materials not previously described and are designated Dab–SnS–SB1 and Cs–SnS–SB1 in keeping with the system of nomenclature adopted by Bedard and coworkers.[3]

The compound designated Dab-SnS-SB1 is produced from the reaction of SnS$_2$, Dabco (1,4-diazabicyclo[2.2.2]octane) and H$_2$O in slurries with a mole ratio of reactants of 1 : 3 : 15. Dabco was treated with H$_2$S prior to mixing with the other components. These were heated under autogenous hydrothermal conditions in glass lined bombs. The yields of these reactions were greater than 90% based on SnS$_2$ and two novel materials with distinct X-ray powder diffraction patterns were produced. At 200 °C crystals of Dab–SnS–SB1 were obtained as slightly yellow rhombs up to 300 μm in size. Below 150 °C colourless hexagonal crystals less than 50 μ on edge were produced. The structure of the latter product is being determined from powder diffraction data. The material Cs–SnS–SB1 can be synthesized in 90% yield from SnS$_2$, Cs$_2$CO$_3$ or CsSH and H$_2$O at 200 °C in the mole ratio 1 : 1 : 20.

(a)

(b)
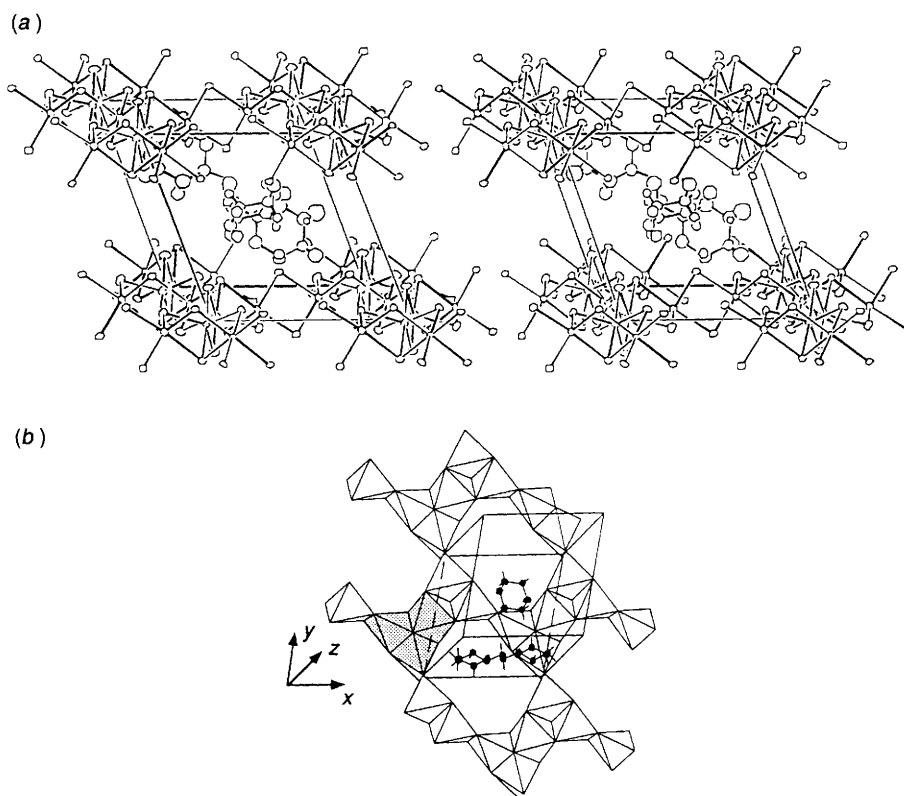
Fig. 1 (a) Stereo ORTEP[17] representation of the structure of Dab–SnS–SB1 with atoms shown as 50% probability ellipsoids. The origin of the unit cell is in the top back left corner with the *x*-axial direction to the right, *z* down and *y* out of the plane of the paper. Note that not all the organic molecules between the SnS-layers are shown. (b) Polyhedral representation of a single layer in Dab–SnS–SB1; the sheet occurring in Cs–SnS–SB1 is similar to this. The origin of the unit cell is in the bottom back left corner with the axial directions as specified.

The structure‡ of the SnS-framework for both Dab–SnS–SB1 and Cs–SnS–SB1 is shown in Fig. 1. It consists of layers with composition $[Sn_5S_{12}]^{4-}$ containing edge linked polyhedra of five- and six-coordinated tin. A formal oxidation state of 4^+ was assigned to tin on the basis of calculations of the bond strength[15] sums from the surrounding sulfur atoms. Between the layers reside piperazinium and 4,4'-ethylenedipiperazinium ions for Dab–SnS–SB1 and Cs^+ and H_2O for Cs–SnS–SB1. The former are products of the decomposition of the Dabco. This molecule is known to be unstable with decomposition beginning at 86 °C and decomposition products recombining to form either piperazine or 4,4'-ethylenedipiperazine.[16]

With each layer there are holes surrounded by ten Sn–S polyhedra (Fig. 1). One of the molecules between the layers, 4,4'-ethylenedipiperazine, is oriented to point between the holes in two adjacent layers suggesting a templating mechanism in the growth of Dab–SnS–SB1. The close contacts between hydrogens attached to the 4,4'-ethylenedipiperazinium ion and the sulfurs of the framework, for example S(1)···H(8) 2.52(7) Å, S(6)···H(3) 2.23(7) Å, are also suggestive of a structure directing role for the organic molecule.

The stacking of the $[Sn_5S_{12}]^{4-}$ layers is similar in the two materials except for the interlayer spacing; this is 10.5 and 7.06 Å, measured as the perpendicular distance from the centre of each layer, for Dab– and Cs–SnS–SB1, respectively. This may be the reason for differences in the diffuse reflectance spectra for the two materials. Preliminary results suggest a more pronounced blue shift for Dab–SnS–SB1 with respect to the Cs compound, consistent with a decrease in the interaction between the layers.

Thanks to W. J. Marshall for the X-ray data collection. The software used for the crystallographic calculations was developed and maintained by J. Calabrese of DuPont. This work is supported by NSF through grant DMR-9024249 and the DuPont Company.

Received, 15th July 1993; Com. 3/04146H

Footnotes

† Center for High Pressure Research: NSF funded Science and Technology Center.

‡ *Crystal data* for Dab–SnS–SB1: $Sn_5S_{12}(N_2C_4H_{11})_2(N_4C_{10}H_{24})$, triclinic, space group $P\bar{1}$ $a = 10.342(1)$, $b = 10.483(1)$, $c = 10.716(2)$ Å, $\alpha = 68.10(1)$, $\beta = 70.82(1)$, $\gamma = 79.71(1)°$, $U = 1016.0$ Å^3, $D_c =$ 2.207 g cm^{-3}, μ(Mo-Kα) = 36.65 cm^{-1}, $Z = 1$, $\lambda = 0.7107$ Å, crystal anhedral, equidimensional *ca.* 0.10 mm on edge, $R = 0.032$, $R_w = 0.032$, $\chi^2 = 1.05$, for 4398 reflections with $I > 3\sigma(I)$. For Cs–SnS–SB1: $Cs_4Sn_5S_{12}\cdot2H_2O$), orthorhombic, space group *Pbca*, $a = 14.121(5)$, $b = 13.117(2)$, $c = 16.272(7)$ Å, $U = 3014.0$ Å^3, $D_c = 2.832$ g c^{-3}, μ(Mo-Kα) = 57.15 cm^{-1}, $Z = 4$, $\lambda = 0.7107$ Å, crystal euhedral tablet $0.14 \times 0.14 \times 0.02$ mm, $R = 0.047$, $R_w = 0.041$, $\chi^2 = 1.16$, for 2337 reflections with $I > 3\sigma(I)$. Data for both materials collected at 20 °C on an Enraf-Nonius CAD-4 diffractometer and processed using a suite of programs written by J. C. Calabrese, E. I. Dupont de Nemours and Company.

References

1 R. M. Barrer, *Hydrothermal Chemistry of Zeolites*, Academic Press, London, 1982.
2 D. W. Breck, *Zeolite Molecular Sieves*, Krieger, Malabar, FL, 1984.
3 R. L. Bedard, L. D. Vail, S. T. Wilson and E. M. Flanigen, US Pat. 4 880 761, 1989.
4 R. L. Bedard, S. T. Wilson, L. D. Vail, J. M. Bennett and E. M. Flanigen, in *Zeolites: Facts, Figures, Future. Proceedings of the 8th International Zeolite Conference*, Elsevier, Amsterdam, 1989.
5 J. B. Parise, *Science*, 1991, **251**, 292.
6 J. B. Parise and Y. Ko, *Chem. Mater.*, 1992, **4**, 1446.
7 J. B. Parise, *J. Chem. Soc., Chem. Commun.*, 1990, 1553.
8 J. B. Paise, J. E. MacDougall, N. Herron, R. Farlee, A. W. Sleight, Y. Wang, T. Bein, K. Moller and L. M. Moroney, *Inorg. Chem.*, 1988, **27**, 221.
9 K. Moller, M. M. Eddy, G. D. Stucky, N. Herron and T. Bein, *J. Am. Chem. Soc.*, 1989, **111**, 2564.
10 N. Herron, Y. Wang, M. M. Eddy, G. D. Stucky, D. E. Cox, K. Moller and T. Bein, *J. Am. Chem. Soc.*, 1989, **11**, 530.
11 G. A. Ozin, A. Kuperman and A. Stein, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 359.
12 G. A. Ozin, S. Kirkby, M. Mezaros, S. Özkar, A. Stein and G. D. Stucky, in *Materials for non-linear optics, chemcial perspectives*, 1990, p. 554.
13 G. D. Stucky and J. E. MacDougall, *Science*, 1990, **247**, 669.
14 G. A. Ozin, in *ACS Symposium Solid State Chemistry, An Emerging Subdiscipline*; ACS, Washington, D.C., 1992, in the press.
15 I. D. Brown, *The bond-valence method: an empirical approach to chemical structure and bonding*, Academic Press, New York, London, 1981, vol. II, p. 1.
16 J. R. Allan, G. H. W. Milburn and F. Richmond, *Thermochimica Acta*, 1990, **170**, 147.
17 C. K. Johnson, ORTEP, Oak Ridge National Laboratory, Oak Ridge, TN, 1965.