718 *Chem. Mater.* **1994,** *6,* 718–720

# Material Consisting of Two Interwoven 4-Connected Networks: Hydrothermal Synthesis and Structure of $[Sn_5S_9O_2][HN(CH_3)_3]_2$

John B. Parise* and Younghee Ko

*Department of Earth and Space Sciences and*
*Department of Chemistry*
*State University of New York*
*Stony Brook, New York 11794-2100*

*Received February 24, 1994*
*Revised Manuscript Received March 29, 1994*

Low-temperature hydrothermal synthesis has been used routinely for the production of microporous inorganic frameworks.[1–4] These crystalline networks may consist of interconnected and regularly spaced pores and channels with dimensions which can be negotiated by small organic molecules. These structural features impart desirable selective sorbtive, catalytic, ion-exchange,[3,5] and mechanical properties.[6] The most common primary building unit for these frameworks is $TO_4$ (T = Si, Al, and other group III, IV, and VA elements); these tetrahedra polymerize to form a variety of 4-connected networks.[7] Aluminosilicate molecular sieves have been synthesized for some time using simple oxide starting materials and added organic molecules, which are believed to act as structure-directing agents or templates, during the assembly of these complex arrays. Considerable effort has been devoted to enumerating theoretical frameworks[8,9] understanding the role of template molecules[4,10–13] and attempting to design syntheses which will produce a specific framework type.

The variety of oxide framework compositions has increased as other main-group and transition elements have been used instead of tetrahedrally coordinated aluminum and silicon. Another departure was instigated by the replacement of oxide with sulfide.[14–18] New classes of materials have been synthesized which have structural building principles distinct from the oxide frameworks.[16–20] This is a consequence of the contrasting behavior of the T–S–T and T–O–T linkages; while the latter is flexible, displaying a range over 35° in silicates, for example, the angle of the T–S–T linkage varies by some 5°.[21,22] This is believed to lead to the low-density frameworks observed in the sulfide materials.

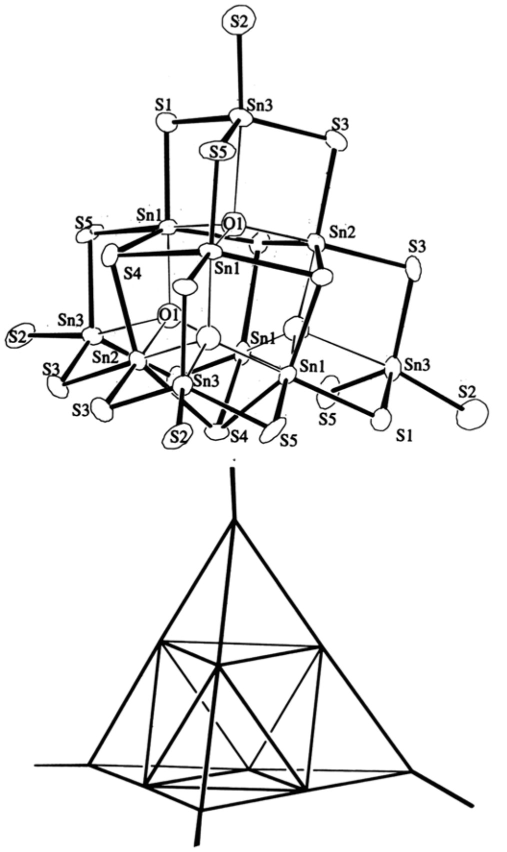

**Figure 1.** ORTEP[32] representation (top) of the $[Sn_{10}S_{20}O_4]^{8-}$ building unit which links to form the full structure shown in Figure 2. For simplicity of depiction in Figure 2, this unit is reduced to the representation shown at bottom, where each node represents a Sn atom and S and O are omitted for clarity.

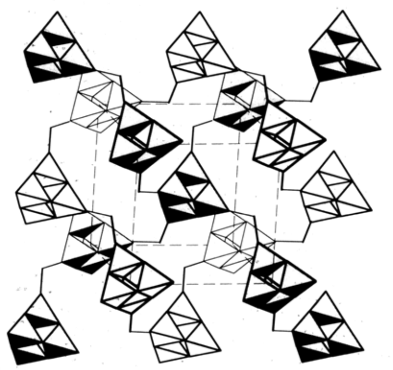

**Figure 2.** Connection of the $[Sn_{10}S_{20}O_4]^{8-}$ building units shown at bottom of Figure 1 to form tetrahedral arrangements and two interwoven networks. For the sake of clarity the molecules of $[HN(CH_3)_3]^+$, which occupy channels between the two frameworks, are not shown. The S(2) atoms bridging the super tetrahedra are located at the elbow of the connections shown. The two nonintersecting networks are emphasized by shading one and leaving the other blank; these networks are related to each other by the symmetry of the unit cell.

---

(1) Barrer, R. M. *Zeolites* **1981**, *1*, 130–140.
(2) Barrer, R. M. *Hydrothermal Chemistry of Zeolites*; Academic Press: London, 1982.
(3) Breck, D. W. *Zeolite Molecular Sieves*; Krieger: Malabar, FL, 1984.
(4) Davis, M. E.; Lobo, P. F. *Chem. Mater.* **1992**, *4*, 756–768.
(5) Barrer, R. M. *Zeolites and Clay Minerals as Sorbents and Molecular Sieves*; Academic Press: London, 1978.
(6) Yeganeh-Haeri, A.; Weidner, D. J.; Parise, J. B. *Science* **1992**, *257*, 650–652.
(7) Meier, W. M.; Olson, D. H. *Atlas of Zeolite Structure Types*; Butterworth: London, 1987, pp 100–101.
(8) Richardson, J. W., Jr.; Smith, J. V.; Pluth, J. J. *J. Phys. Chem.* **1989**, *93*, 8212–8219.
(9) Wells, A. F. *Further Studies of Three Dimensional Nets*; American Crystallography Association Monograph: 1979; Vol. 8.
(10) Drummond, C. J.; Ninham, B. W. *Chem. Aust.* **1992**, *59*, 529–31.
(11) Iton, L. E.; Trouw, F.; Brun, T. O.; Epperson, J. E.; White, J. W.; Henderson, S. J. *Langmuir* **1992**, *8*, 1045–8.
(12) Lok, B. M.; Cannan, T. R.; Messina, C. A. *Zeolites* **1983**, *3*, 282–291.
(13) Zones, S. I.; Olmstead, M. M.; Santilli, D. S. *J. Am. Chem. Soc.* **1992**, *114*, 4195–201.
(14) Sheldrick, W. S.; Braunbeck, H. G. *Z. Naturforsch.* **1989**, *45B*, 1643–1646.
(15) Sheldrick, W. S. *Z. Anorg. Allg. Chem.* **1988**, *562*, 23–30.
(16) Bedard, R. L.; Wilson, S. T.; Vail, L. D.; Bennett, J. M.; Flanigen, E. M. In *Zeolites: Facts, Figures, Future. Proceedings of the 8th International Zeolite Conference*; Elsevier: Amsterdam, 1989, 375–387.
(17) Bedard, R. L.; Vail, L. D.; Wilson, S. T.; Flanigen, E. M. **1989**, U.S. Patent 4,880,761.
(18) Parise, J. B. *Science* **1991**, *251*, 292–294.
(19) Parise, J. B. *J. Chem. Soc., Chem. Commun.* **1990**, 1553–1554.

0897-4756/94/2806-0718$04.50/0

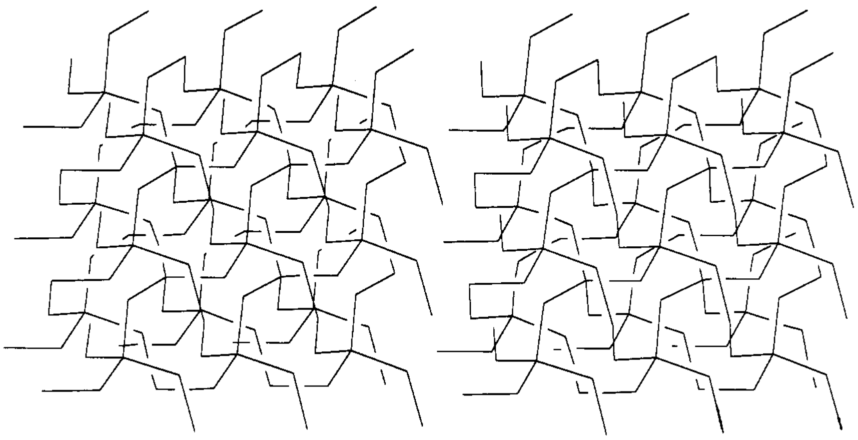

**Figure 3.** Stereo representation of the 4-connected net formed by linking clusters shown in Figure 1 by sulfur bridges which alternate about the six-rings shown. The two interwoven nets have the topology of the cristobalite structure-type, which is itself related to the diamond structure.[27] The nodes in each net represent alternating clusters (Figure 1) and S bridges (Figure 2).

Our goal is to develop thio oxides having building principles which are hybrids of those found in the oxide and sulfide frameworks. Isolated thio oxoanions of tin are known to be stable under hydrothermal conditions and indeed have been cited as candidates for building "silicate-like" structures.[23,24] We report here the synthesis of an oxy-sulfide related to the silica polymorph cristobalite ($SiO_2$). The crystal structure of the new material consists of clusters (Figure 1) of composition $[Sn_{10}S_{20}O_4]^{8-}$, recognized in the previously reported sulfur chemistry of main group elements.[23,24] However they are not isolated but instead are 4-connected to each other via sulfur bridges (Figure 2). The linkages are such that two independent nonintersecting frameworks are formed (Figure 3) with the $(HNMe_3)^+$ molecules contained within the channels between the two frameworks. The clusters can be thought of as supertetrahedra which are linked at all four corners (Figure 1) in a fashion reminiscent of the 4-connected nets common in the zeolites and polymorphs of silica.[9]

The synthesis was effected by heating slurries of $SnS_2$ in thick-walled Pyrex tubes. Freshly prepared $SnS_2$ and TETN, in the molar ratio 3:2, were stirred to form a slurry and heated at 150 °C for 3 weeks. The material produced was colorless, containing single crystals up to 0.07 mm on edge. Qualitative microprobe analysis detected the presence of Sn, S, N, and O only. A comparison of the X-ray powder diffraction pattern with that of known phases suggested the material was novel. This was confirmed by subsequent studies of the single crystals, which also showed that the TETN molecule had decomposed[25] during synthesis to form $[HNMe_3]^+$ cations. Although not located in the structure analysis,[26] the hydrogen required for charge balance are presumed to be attached to the organic molecule rather than the framework on the basis of previous structure determinations of this type.[18-20] However, the possibility of hydrogen attached to the framework cannot be ruled out. The phase was designated TETN-SnS-SB2 following the nomenclature established for the sulfide frameworks by workers at Union Carbide.[16]

All Sn atoms in the main building unit of the structure are four coordinated to S in approximately tetrahedral arrangements. Neglecting oxygen, this structural unit represents a single ABC stacking sequence of the ZnS (zinc blende) structure type.[27] The coordination geometry of the individual units of $SnS_4$ shows the effect of oxygen inserted into the cluster (Figure 1). Oxygen occupies four of the tetrahedral coordination sites formed by close-packed Sn in the cluster (Figure 1). To accommodate this, the $SnS_4$ moieties are distorted away from ideal tetrahedral geometry with the greatest deviation in the S(4)–Sn(2)–S(4) and S(4)–Sn(1)–S(4) angles (Figure 1). The value of 148° reflects attempts to minimize repulsion between oxygen included in the cluster and the sulfur closest to them. Tin is coordinated to S by four bonds, between 2.40 and 2.66 Å.

To simplify depiction of the full structure, the $[Sn_{10}S_{20}O_4]^{8-}$ cluster can be represented as the cubic close-packed array of metal atoms shown in Figure 1. Each cluster is connected at the corner by Sn(3)–S(2)–Sn(3) bridges, all with angles of 113.1(6)°, to four other symmetry related clusters (Figures 1 and 2) in a tetrahedral arrangement. These are at the nodes of two diamond-like structures, identical in topology but displaced by ($^1/_2$,$^1/_2$,$^1/_2$) with respect to one another and connected to form the chair-shaped 6-rings characteristic of this structure type (Figures 2 and 3). Inclusion of the sulfur bridges relates each net to the structure of cristobalite (Figure 3). The structure then consists of two interpenetrating, nonintersecting 4-connected nets related to the topology of cristobalite.[6,27] This is the first example of two interwoven 4-connected nets in the oxy sulfides; examples of interpenetrating diamond nets in $Zn(CN)_2$ have recently been described[28] and been known for

---

(20) Parise, J. B.; Ko, Y. *Chem. Mater.* **1992**, *4*, 1446–1450.

(21) Geisinger, K. L.; Gibbs, G. V. *Phys. Chem. Mineral.* **1981**, *7*, 204–210.

(22) Gibbs, G. V. *Am. Mineral.* **1982**, *67*, 421–450.

(23) Krebs, B.; Voelker, D.; Stiller, K. *Inorg. Chim. Acta* **1982**, L101–L102.

(24) Krebs, B. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 113–134.

(25) Hutchinson, W. M.; Collett, A. R.; Lazzell, C. L. *J. Am. Chem. Soc.* **1945**, *67*, 1966–1968.

(26) $Sn_5S_9O_2[HN(CH_3)_3]_2$: fw 1034.3, space group $P\bar{4}n2$ (No. 118), $a$ = 13.573 (6), $c$ = 14.508(7) Å, $V$ = 2672.8 Å3 at 20 °C, $Z$ = 4, $D_{calc}$ (g/cm$^3$) 2.57. Crystal size (mm) 0.07 × 0.05 × 0.04. Radiation (graphite monochromator) Mo K$\alpha$, $\mu$(Mo) = 53.1 cm$^{-1}$. Diffractometer Enraf-Nonius CAD4, data collected 2810, $2\theta_{max}$ 60.0°, $(h,k,l)_{max}$ 19,19,18; Data octant +++, scan method $\omega$. Absorption correction DIFABS, transmission factors range 0.009–0.138, number of unique data ($I > 3.0\sigma(I)$) 1169, $R_{merge}$ = 0.021. Refinement method full-matrix least-squares on $F$, anomalous dispersion: Sn, S; weighting scheme $[\sigma^2(I)]^{-1/2}$, atoms refined: aniso: Sn, S; iso: all others. Parameters varied 85, data/parameter ratio 13.75, $R$ = 0.058, $R_w$ = 0.055, error of fit = 1.22.

(27) Hyde, B. G.; Andersson, S. *Inorganic crystal structures*; Wiley: New York, 1989.

(28) Hoskins, B. F.; Robson, R. *J. Am. Chem. Soc.* **1990**, *112*, 1546–1554.

sometime in systems such as $Cu_2O$, $Ag_2O$, and $H_2O$.[29] Given the unusual nonlinear optical and mechanical characteristics of the cristobalite family,[6,30] it will be interesting to measure these properties in TETN–SnS–SB2 and its ion-exchanged variants. A preliminary measurement of the second harmonic signal to confirm the absence of a center of symmetry gave a value of 21 times that of quartz. The method of Kurtz and Perry[31] was used for this measurement.

It should be possible to connect the unit shown in Figure 1 in a variety of ways. Because of the rigidity of the T–S–T connection the topologies available may be less various than those of oxide frameworks based upon 4-connected tetrahedra.[8,9] However, the structure of TETN–SnS–SB2 suggests a broader search for new materials based upon the philosophy outlined in this report is warranted and that new families of structures can be anticipated.

**Acknowledgment.** This work was supported through NSF Grant DMR-90-24249.

**Supplementary Material Available:** Tables summarizing the crystal structure analysis, the refined atomic parameters (3 pages); observed and calculated structure factors (3 pages). Ordering information is given on any current masthead page.

---

(29) Wells, A. F. *Structural Inorganic Chemistry*, 4th. ed.; Clarendon Press: Oxford, 1975, pp 106–110.

(30) Parise, J. B.; Gier, T. E. *Chem. Mater.* **1992**, *4*, 1065–1067.

(31) Kurtz, S. K.; Perry, T. T. *J. Appl. Phys.* **1968**, *39*, 943–944.

(32) Johnson, C. K. ORTEP; Oak Ridge National Laboratory: Oak Ridge, TN, 1965.