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Synthesis and Structure of $[CH_3NH_3]_2Sb_8S_{13}$: A Nanoporous Thioantimonate(III) with a Two-Dimensional Channel System

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$[CH_3NH_3]_2Sb_8S_{13}$ has been synthesized as dark-red plate-like crystals by heating Sb and S with an aqueous solution of CH_3NH_2 between 130 and 190°C. It is triclinic, space group $P\bar{1}$, with $a = 15.866(3)$ Å, $b = 11.581(2)$ Å, $c = 8.295(2)$ Å, $\alpha = 71.46(2)°$, $\beta = 75.71(2)°$, $\gamma = 82.25(2)°$, and $Z = 2$. The structure was determined and refined with 3342 independent single crystal X-ray reflections (235 parameters, $R = 0.061$, $R_w = 0.052$). Each Sb atom forms three short bonds to S reflecting the influence of a lone electron pair. Of the eight nonequivalent Sb atoms, three have one longer bond and four other Sb atoms have two longer bonds to S. The $[SbS_n]$ polyhedra share corners and edges to form a three-dimensional framework. This framework is traversed by a system of two types of intersecting channels parallel to [010] and [001]. $[CH_3NH_3]^+$ cations located in the channel intersections are orientationally disordered; those in pockets of the [010] channels are ordered.

INTRODUCTION

Porous arrays on a nanometer scale are found in many crystalline substances with tetrahedral oxide framework structures such as zeolites and AlPOs (1). Recently, nanoporous framework structures based on nonoxide and/or nontetrahedral units have attracted increasing attention because of their potential usages as new families of selective sorbents, catalysts, and ion exchangers (2–7). Chalcogenoantimonates(III) seem to be particularly suitable to form porous structures. They form phases with wide tubular one-dimensional $[Sb_mX_n]$ arrays—$A_3Sb_7O_9X_3 \cdot 3H_2O$, A = Na, K; X = S, Se (8–11)—as well as phases with three-dimensional porous frameworks. Most of these latter framework phases, e.g. $TlSb_3S_5$ (12), $K_2Sb_4S_7 \cdot H_2O$ (13), $TlSb_5S_8$ (14), and $Cs_2Sb_8S_{13}$ (15), contain *inorganic* monovalent cations. Recently, Parise has reported a new framework thioantimonate $[N(CH_3)_4]Sb_3S_5$ containing *organic* cations (16). During our systematic studies of nontetrahedral nanoporous structures, we have synthesized a new thioantimonate(III), $[CH_3NH_3]_2Sb_8S_{13}$, which also contains organic cations in a two-dimensional channel system.

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EXPERIMENTAL

A. Synthesis and Chemical Analysis

$[CH_3NH_3]_2Sb_8S_{13}$ has been synthesized hydrothermally from a mixture of elemental antimony, sulfur, and CH_3NH_2 between 130 and 190°C. In a typical experiment dark-red plate-like crystals, which were subsequently used for structure determination, were obtained from a mixture of 0.24 g Sb and 0.10 g S powders and 2.0 g of an aqueous solution (40 wt%) of CH_3NH_2. The mixture was sealed in a teflon-coated steel autoclave (50 ml inner volume) in air and heated at 130°C for 4 days. The crystals of $[CH_3NH_3]_2Sb_8S_{13}$ formed together with two other needle-like novel phases which will be reported separately.

The chemical composition was derived from electron microprobe analysis (Table 1) and confirmed by subsequent structure refinement.

B. Data Collection

A (100) plate of size 0.07 × 0.07 × 0.03 mm³ was selected for single crystal study. Intensity data were collected on a Philips PW1100 automatic four circle diffractometer at room temperature. Lattice constants were determined with the program LAT (17) and are listed in Table 2 together with experimental details. The cell constants and chemical composition suggest that this phase is isotypic with $Cs_2Sb_8S_{13}$ reported by Volk and Schäfer (15). This was confirmed by single crystal structure determination.

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TABLE 1
Electron Microprobe Analysis of $[CH_3NH_3]_2Sb_8S_{13}$

	Weight percents			Atomic ratio
	Sb	S	Sum	Sb : S
Microprobe[a]	65.40	27.94	93.34	8 : 12.98
Title formula	66.95	28.65	95.60	8 : 13

[a] CAMEBAX-MICROBEAM; acceleration voltage-15 kV; electron beam current-15 nA; standard, Sb_2S_3.

C. Structure Determination

Complex scattering factors for neutral atoms (International Tables, 1974) were used. The coordinates of electron density maxima obtained with SHELXS86 (18) were interpreted with the aid of the structure reported for $Cs_2Sb_8S_{13}$ (15). Refinement with SHELX76 (19) of the resulting structure model, not including the organic cations, converged to $R = 0.086$ after appointing anisotropic atomic displacement parameters to all Sb and S atoms. At this stage, electron density peaks corresponding to C or N atoms were found in the difference maps when giving higher weights to reflections with larger θ angles. Half of the $[CH_3NH_3]^+$ groups (C(2) and N(2) in Table 3) were found to randomly occupy two different orientations. The site occupation factors (sof) of the C(2A, 2B) and N(2A, 2B) sites varied between 0.48(4) and 0.66(6) when set free in a late stage of the refinement. The hydrogen atoms of the $[CH_3NH_3]^+$ cations were introduced as rigid (C, N)H_3 groups with fixed bond lengths (C, N)–H = 1.08 Å and bond angles H–(C, N)–H = 109.5°, and they were given a variable common isotropic displacement factor. In the final refinement, the sum of the sof of $H_3C(2A)$–$N(2A)H_3$ and $H_3C(2B)$–$N(2B)H_3$ groups was fixed to 1 and the sof ratio of the two groups was refined to 0.51(2)/0.49(2). Final full-matrix refinement converged at $R = 0.061$, $R_w = 0.052$, with the largest residual peak of 2.5 e/Å^3 at 0.92 Å from the Sb(4) atom (for comparison, the corresponding peak height of C(2B) was 3.3 e/Å^3). Final atomic coordinates and displacement parameters are given in Table 3. Since the calculated H–N–C angles within the $[CH_3NH_3]$ groups are unrealistic (78–145°), hydrogen atoms are not listed in Table 3. Selected bond lengths are listed in Table 4. Projections of the structure were plotted with the program ATOMS (20).

TABLE 2
Crystal and Experimental Data for $[CH_3NH_3]_2Sb_8S_{13}$

Cell parameters	a (Å)	15.866(3)
	b (Å)	11.581(2)
	c (Å)	8.295(2)
	α (°)	71.46(2)
	β (°)	75.71(2)
	γ (°)	82.25(2)
	V (Å^3)	1397.7(5)
Space group	$P\bar{1}$	
Unit cell content	$Z = 2$ $[CH_3NH_3]_2Sb_8S_{13}$	
Radiation; wavelength	Mo$K\alpha$; 0.7107 Å	
2θ-interval	4–60°	
θ-2θ scan width	1.3°	
Scan speed	0.06°/sec	
Total background time	Equal to scan time	
Measured independent reflections	6514	
Independent reflections with $I > 3\sigma(I)$ used in final refinement	3342	
Number of parameters refined	235	
Absorption correction	Not made ($\mu = 8.60$ mm^{-1})	
Extinction parameter g $F_c' = F_c[1 - gF_c^2(\sin\theta)^{-1}]$	4(2) × 10^{-9}	
$R(F)$	0.061	
$R_w(F)$ [$w \approx 1/\sigma^2(F)$]	0.052	

TABLE 3
Fractional Atom Coordinates and Equivalent Isotropic Displacement Parameters (Å^2) of $[CH_3NH_3]_2Sb_8S_{13}$

Atom	x	y	z	B_{eq}
Sb(1)	0.2799(1)	0.0353(1)	0.8899(2)	1.32(4)
Sb(2)	0.4188(1)	0.2299(2)	0.4917(2)	1.40(4)
Sb(3)	0.4091(1)	0.0002(2)	0.2596(2)	1.38(4)
Sb(4)	0.4146(1)	0.4738(2)	0.7153(2)	1.30(4)
Sb(5)	0.5408(1)	0.2730(2)	0.0274(2)	1.32(4)
Sb(6)	0.2813(1)	0.7996(2)	0.6475(2)	1.22(4)
Sb(7)	0.0673(1)	0.6462(2)	0.8474(2)	1.48(4)
Sb(8)	0.1838(1)	0.3283(2)	0.0152(2)	1.67(4)
S(1)	0.4381(5)	0.3893(6)	0.2080(9)	1.5(2)
S(2)	0.4331(5)	0.1580(6)	0.9749(9)	1.6(2)
S(3)	0.3097(4)	0.3694(6)	0.6252(9)	1.6(2)
S(4)	0.5647(5)	0.3566(6)	0.5473(9)	1.5(1)
S(5)	0.3043(5)	0.1326(6)	0.4138(9)	1.8(2)
S(6)	0.5688(4)	0.1107(6)	0.2752(9)	1.3(2)
S(7)	0.0934(4)	0.4420(6)	0.8083(9)	1.9(1)
S(8)	0.0631(4)	0.3337(6)	0.2699(9)	1.9(2)
S(9)	0.2891(4)	0.6043(6)	0.8699(8)	1.5(2)
S(10)	0.3009(4)	0.9044(6)	0.1764(8)	1.5(2)
S(11)	0.1482(5)	0.7599(6)	0.5615(9)	1.9(2)
S(12)	0.1856(4)	0.8929(6)	0.8676(9)	1.6(2)
S(13)	0.1387(5)	0.1360(6)	0.0155(10)	2.5(2)
N(1)	0.260(1)	0.601(2)	0.291(3)	3.2(5)
C(1)	0.177(2)	0.541(3)	0.319(5)	6(1)
N(2A)[a]	0.992(3)	0.140(5)	0.747(6)	3(1)
N(2B)[b]	0.082(3)	0.029(4)	0.443(6)	3(1)
C(2A)[a]	0.081(3)	0.168(5)	0.651(7)	4(1)
C(2B)[b]	0.067(5)	0.074(6)	0.596(7)	5(2)

Note. $B_{eq} = (8\pi^2/3)\ \Sigma_i\ \Sigma_j\ U_{ij}a_i^*a_j^*\mathbf{a}_i\cdot\mathbf{a}_j$. A table of anisotropic displacement parameters can be obtained from the second author upon request.

[a] sof = 0.49(2).

[b] sof = 0.51(2).

TABLE 4
Selected Interatomic Distances (Å) of $[CH_3NH_3]_2Sb_8S_{13}$

Sb(1)–S(12)	2.446(8)	Sb(2)–S(1)		2.465(6)
–S(10)	2.454(7)	–S(3)		2.504(7)
–S(13)	2.526(7)	–S(5)		2.564(9)
–S(6)	3.042(7)	–S(6)		3.062(7)
–S(2)	3.293(9)	–S(4)		3.100(8)
–other S	≥3.68	–other S		≥3.80
Sb(3)–S(2)	2.463(6)	Sb(4)–S(4)		2.410(6)
–S(10)	2.497(8)	–S(3)		2.554(9)
–S(5)	2.502(8)	–S(9)		2.656(7)
–S(6)	3.037(8)	–S(4)		2.854(7)
		–S(1)		3.278(9)
–S(2)	3.470(7)			
–other S	≥3.75	–other S		≥3.62
Sb(5)–S(6)	2.392(6)	Sb(6)–S(9)		2.433(6)
–S(1)	2.490(7)	–S(12)		2.499(7)
–S(2)	2.497(9)	–S(11)		2.530(9)
		–S(6)		2.997(8)
–S(10)	3.480(7)	–S(4)		3.252(7)
–S(9)	3.602(8)			
–other S	≥3.72	–other S		≥3.65
Sb(7)–S(11)	2.444(6)	Sb(8)–S(13)		2.429(8)
–S(8)	2.450(8)	–S(7)		2.450(7)
–S(7)	2.456(8)	–S(8)		2.488(7)
–S(7)	3.309(6)	–S(3)		3.282(7)
–S(9)	3.529(7)	–S(9)		3.529(7)
–other S	≥3.69	–other S		>4.00
N(1)–C(1)	1.48(4)	N(1)–S	×6	3.36(2)–3.57(2)
		C(1)–S	×5	3.38(4)–3.79(4)
N(2A)–C(2A)	1.46(6)	N(2A)–S	×5	3.58(6)–3.85(4)
		C(2A)–S	×5	3.19(5)–3.83(7)
N(2B)–C(2B)	1.48(9)	N(2B)–S	×5	3.08(4)–3.99(4)
		C(2B)–S	×5	3.32(7)–3.99(7)

STRUCTURE DESCRIPTION

Figure 1 shows two projections of the structure along [001] and [010]. At first sight, each of the eight nonequivalent Sb atoms is coordinated to the three nearest S atoms to form a ψ-$[SbS_3]$ tetrahedron,[2] with Sb–S distances ranging from 2.39 to 2.66 Å and the S–Sb–S angles averaged over each such tetrahedron ranging from 90.1 to 95.2°. The coordination environments of four of these eight Sb atoms (Sb(1, 2, 4, 6)) are each complemented by two additional S atoms at distances between 2.85 and 3.29 Å, while those of another three Sb atoms (Sb(3, 7, 8)) are each complemented by one additional S atom at 3.04–3.31 Å, to form ψ-$[SbS_5]$ or ψ_2-$[SbS_4]$ octahedra,[2] respectively. If, instead, all S atoms with Sb · · · S distances up to 3.6 Å are considered, then all Sb atoms have ψ-$[SbS_5]$ octahedral coordination (Table 4). Using the bond-valence parameter r_0 = 2.474 Å of Brown and Altermatt (21), a Sb(III)–S bond length of 3.33 Å corresponds to a bond valence of 0.10 v.u. Sb(III)–S bonds shorter than 3.33 Å should, therefore, not be neglected in discussions of $[Sb(III)S_n]$ coordination.

The $[Sb(1–6)S_n]$ polyhedral groups share edges and corners to form infinite ribbons parallel to [011] (Fig. 2). The infinite ribbons are packed parallel, thus forming slabs parallel to (100). Within each slab the lone electron pairs of Sb occupy the spaces between the ribbons and there is no direct bonding between the adjacent ribbons. The slabs are interconnected by the $[Sb(7)S_4]$ and $[Sb(8)S_4]$ groups, forming a three-dimensional framework. Each two $[Sb(7)S_4]$ and two $[Sb(8)S_4]$ groups share S–S edges to form a chair-shaped structural unit which is connected with four ribbons of two neighboring slabs (Fig. 2).

The interconnectedness of the infinite ribbons and the chair-shaped units outlines two intersecting channel systems, one parallel to [010] and the other parallel to [001] (Fig. 1). The $[CH_3NH_3]^+$ cations are located within these channels: those in pockets of the channels parallel to [010] are ordered (C(1), N(1)), those located at the intersections of the two channel systems are orientationally disordered (C(2), N(2)). The free apertures of the two channel systems are 6.5 × 1.5 Å and 3.1 × 2.2 Å, respectively; the latter should be just wide enough to let cations diffuse parallel to [001]. Also in the isotypic phase $Cs_2Sb_8S_{13}$[3] (15) and in the nonisotypic phase $Cs_4Sb_{14}S_{20}(S, O)_3$ (22) the 50% of the Cs^+ ions located in wider channels are disordered, while the other 50% located in narrower channels are ordered.

DISCUSSION

The framework of the first known porous thioantimonate(III) with organic cations, $[N(CH_3)_4]Sb_3S_5$, has been described as being constructed entirely from edge-sharing $[SbS_4]$ bipyramids (16). In contrast, the framework of $[CH_3NH_3]_2Sb_8S_{13}$ is formed from $[SbS_3]$-, $[SbS_4]$-, and $[SbS_5]$-polyhedra which share corners as well as edges, similar to chalcogenoantimonates(III) of inorganic cations.

Taking into consideration the fact that the use of organic templates in zeolite and clathrasil chemistry leads to a wealth of new $[TO_4]$-framework topologies, an even greater diversity of $[SbX_n]$-frameworks (X = O, S, Se) might be expected. In fact, systematic syntheses with larger organic templates aimed at expanding the channel width have led to a number of novel crystalline compounds which show systematic structural relationships with $[CH_3NH_3]_2Sb_8S_{13}$ (23).

[2] A ψ_m-$[SbS_n]$ polyhedron is a distorted $[SbS_{n+m}]$ polyhedron with m of its $n + m$ ligands missing due to the presence of a lone electron pair of antimony.

[3] According to Volk and Schäfer (15) in $Cs_2Sb_8S_{13}$ coordination polyhedra $[SbS_3]$ and $[SbS_4]$ are linked to sheets because only Sb–S bonds shorter than 2.80 Å, i.e., stronger than 0.41 v.u., were considered.

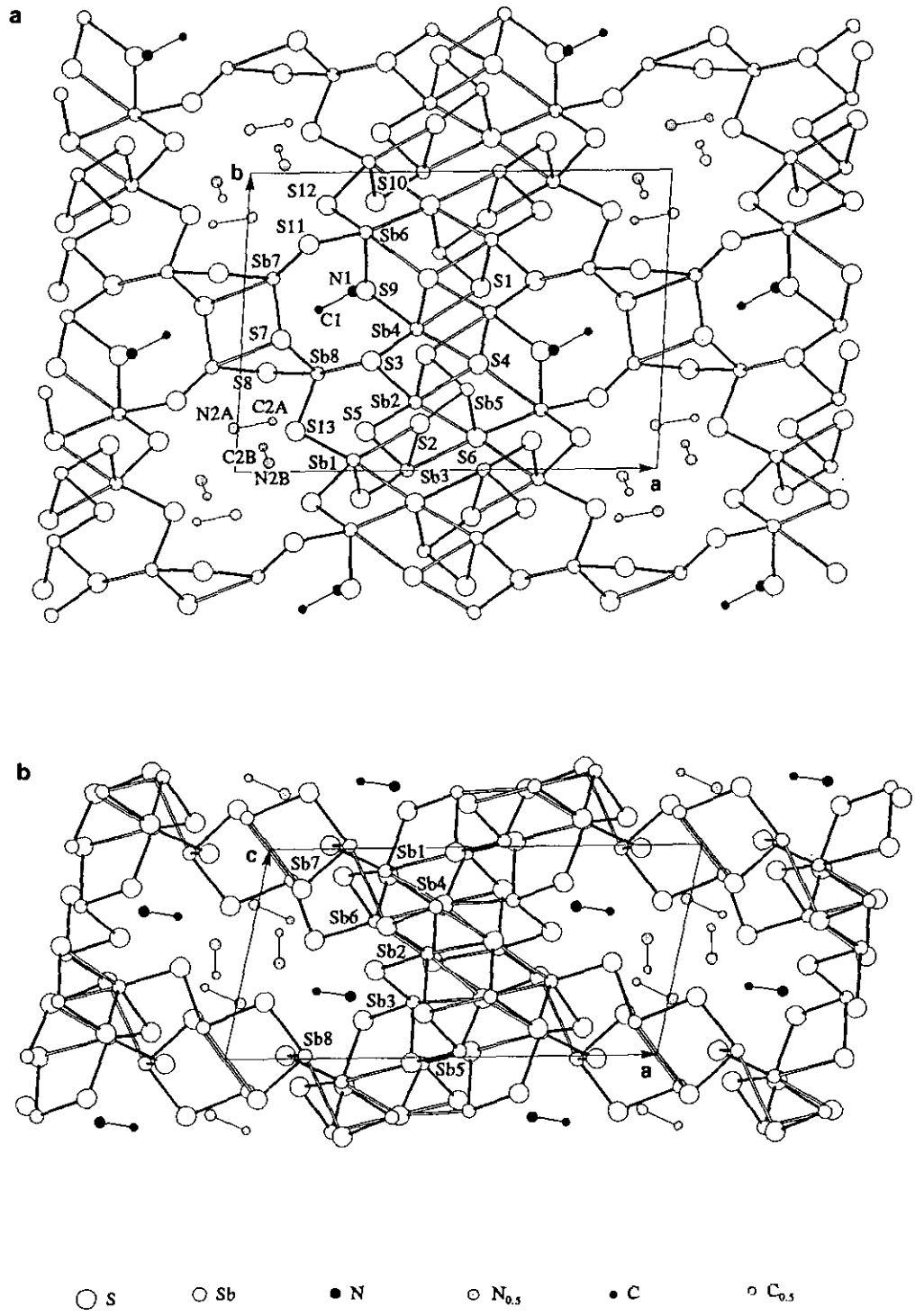

FIG. 1. Projections of the structure of $[CH_3NH_3]_2Sb_8S_{13}$ (a) along [001] and (b) along [010]. Solid bonds ≤2.66 Å; open bonds 2.85–3.31 Å. The subscripts of $N_{0.5}$ and $C_{0.5}$ indicate that site occupancy factors are about 0.5.

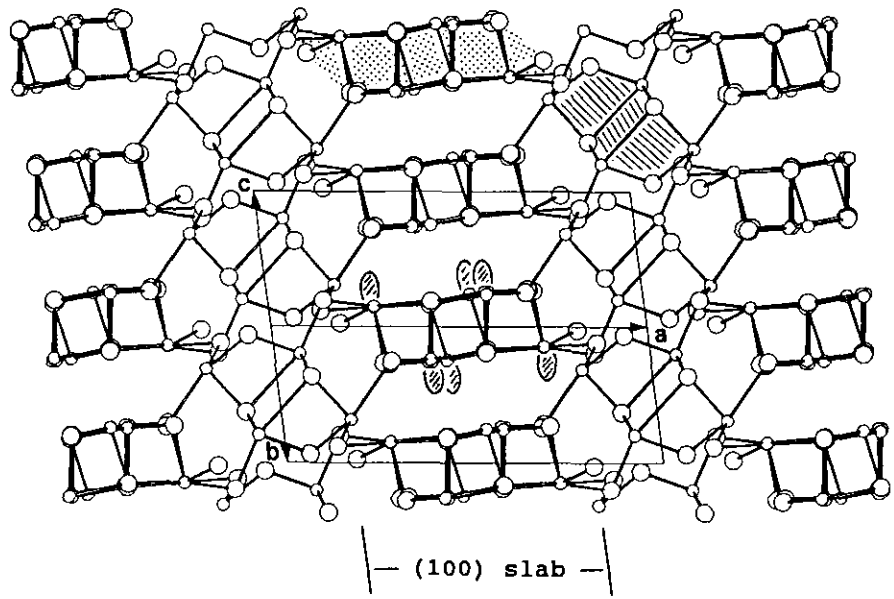

FIG. 2. The $[Sb_8S_{13}]$ framework viewed along [011], $[CH_3NH_3]^+$ cations omitted. A [011] ribbon is marked by stippling and a chair-shaped unit by hatching. Lone electron pairs of the Sb atoms of one [011] ribbon are indicated as lobes. Other symbols are the same as in Fig. 1.

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REFERENCES

1. J. V. Smith, *Chem. Rev.* **88,** 149 (1988).
2. P. B. Moore and J. Shen, *Nature* **306,** 356 (1983).
3. R. L. Bedard, S. T. Wilson, L. D. Vail, J. M. Bennett, and E. M. Flanigen, *in* "Zeolites: Facts, Figures and Future" (P. A. Jacobs and R. A. van Santen, Eds.), p. 375. Elsevier, Amsterdam, 1989.
4. R. C. Haushalter, K. G. Strohmaier, and F. W. Lai, *Science* **246,** 1289 (1989).
5. J. Zemann, *Mitt. Oesterr. Mineral. Ges.* **136,** 21 (1991).
6. S. Dhingra and M. G. Kanatzidis, *Science* **258,** 1769 (1992).
7. Y. F. Shen, R. P. Zerger, R. N. DeGuzman, S. L. Suib, L. McCurdy, D. I. Potter, and C. L. O'Young, *Science* **260,** 511 (1993).
8. C. Sabelli, I. Nakai, and S. Katsura, *Am. Mineral.* **73,** 398 (1988).
9. F. Kluger and F. Pertlik, *Monatsh. Chem.* **116,** 149 (1985).
10. H. A. Graf and H. Schäfer, *Z. Anorg. Allg. Chem.* **414,** 220 (1975).
11. X. Wang and F. Liebau, *Eur. J. Mineral.* **3,** Beih. 1, 288 (1991).
12. M. Gostojić, W. Nowacki, and P. Engel, *Z. Kristallogr.* **159,** 217 (1982).
13. B. Eisenmann and H. Schäfer, *Z. Naturforsch.* **34b,** 383 (1979).
14. P. Engel, *Z. Kristallogr.* **151,** 203 (1980).
15. K. Volk and H. Schäfer, *Z. Naturforsch.* **34b,** 1637 (1979).
16. J. B. Parise, *Science* **251,** 293 (1991).
17. J. Hornstra and H. Vossers, *Philips Tech. Rundsch.* **33,** 3, 65 (1973/74).
18. G. M. Sheldrick, "SHELXS86 Program for the Solution of Crystal Structures." Univ. of Göttingen, Germany, 1986.
19. G. M. Sheldrick, "SHELX76 Program for Crystal Structure Determination." Univ. of Cambridge, England, 1976.
20. E. Dowty, "ATOMS: A Computer Program for Displaying Atomic Structures." 1992.
21. I. D. Brown and D. Altermatt, *Acta Crystallogr., Sect. B* **41,** 244 (1985).
22. F. Liebau and X. Wang, *Acta Crystallogr., Sect. A* **49** *Suppl.*, 259 (1993).
23. X. Wang, Dissertation, University of Kiel, Germany, 1993.