The Novel Thiogermanate $[(CH_3)_4N]_4Ge_4S_{10}$ with a High Cubic Cell Volume. Ab Initio Structure Determination from Conventional X-ray Powder Diffraction

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A novel thiogermanate, $[(CH_3)_4N]_4Ge_4S_{10}$, has been synthesized through soft hydrothermal treatments. Despite a cubic symmetry and a high unit-cell volume ($V = 7470.9$ Å^3) the crystal structure has been solved *ab initio* from high-resolution conventional powder diffraction data. The unit-cell dimension is $a = 19.5490(4)$ Å and the space group is $P\bar{4}3n$. The structure solution has been obtained from the direct methods, except for the tetramethylammonium groups found from one subsequent difference Fourier map. The structure refinement with the Rietveld method converged to $R_F = 0.06$ and $R_{wp} = 0.12$. The new structure type consists of isolated condensed thioanions $Ge_4S_{10}^{4-}$ with tetrahedral $(CH_3)_4N^+$ cations as positive counterparts. A simple representation of the structure is based on a subcell formed by the quasi perfect fcc arrangement of the four terminal S atoms of Ge_4S_{10} groups. All octahedral voids are filled by the $(CH_3)_4N$ groups, while only one-eighth of the tetrahedral voids are occupied by the adamantine-like Ge_4S_6 moieties. The complete structure is generated from eight similar subcells with different locations of the adamantine group. The new structure type sheds new light on the hydrothermal chemistry of thiogermanates.

Introduction

Over the past two decades, preparative works have led to a wide family of germanium–sulfur compounds based upon the monomeric tetrahedral GeS_4^{4-} anion.[1,2] When considering the ability of this thioanion to condense some features of these materials are reminiscent of the chemistry of silicon–oxygen compounds. So, it is not surprising that solids displaying microporous properties have been recently obtained, by using hydrothermal conditions, when framework transition-metal elements are incorporated.[3,4] However, in light of the literature data, very few precise crystal structure features are available in this new class of materials. In the course of the study of similar systems, a novel thiogermanate containing tetramethylammonium groups has been prepared in a powder form and its structure has been investigated by X-ray powder diffraction. Although powder diffraction suffers from the inevitable loss of information resulting from the collapse of 3D crystallographic data on to a 1D diffraction pattern, the advances in instrumentation and methodology have contributed to the recent development of structure determination of powder materials.[5,6] Most of these studies were carried out by means of conventional X-ray sources.[7-9] The major problem for solving a structure from powder diffraction data is the overlap of independent reflections, which is related to the size and symmetry of the unit cell. Nevertheless, the structure of a tetragonal clathrasil phase with a cell volume of 3604 Å^3 has been solved.[10] For indexing methods a large unit cell is not a difficulty, provided that the data are complete and accurate.[11] Here we describe the structure of $[(CH_3)_4N]_4Ge_4S_{10}$ with an exceptionally high cubic unit-cell volume of 7470.9 Å^3, solved *ab initio* from laboratory X-ray powder diffraction data and using equipartitioned intensities for overlapping reflections in the starting dataset. Its structure exhibits a novel network based on isolated $Ge_4S_{10}^{4-}$ groups.

Experimental Section

The new thiogermanate $TMA_4Ge_4S_{10}$ [TMA = $(CH_3)_4N$] was obtained hydrothermally from a mixture of amorphous GeS_2, TMACl, and H_2O (molar ratios 1:1:10), heated at 393 K in a glass ampule for 2 days. To obtain a high starting pH value (~12), sodium carbonate has been added to the mixture as a mineralizer (0.5 mol of Na_2CO_3 for 1 mol of GeS_2). The white polycrystalline product was filtered off and then washed with alcohol and ether. Thermogravimetric data and analysis by ionic chromatography indicated a TMA content close to 33 wt %.

Two diffraction data sets were collected with a conventional monochromatic X-ray source (λ = 1.540 59 Å). One was obtained

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Table 1. X-ray Powder Diffraction Data for $[(CH_3)_4N]_4Ge_4S_{10}$

hkl	$2\theta_{obs}$ (deg)	$2\theta_{calc}$ (deg)	d_{obs} (Å)	I_{obs}
200	9.057	9.040	9.76	31
210	10.125	10.110	8.73	100
211	11.092	11.077	7.97	92
222	15.701	15.690	5.64	14
320	16.343	16.335	5.42	28
321	16.967	16.956	5.22	17
400	18.142	18.137	4.886	41
410	18.696	18.700	4.742	<1
330	19.250	19.247	4.607	23
421	20.807	20.806	4.266	36
332	21.294	21.301	4.169	11
422	22.260	22.260	3.990	26
430	22.724	22.725	3.910	<1
510	23.182	23.181	3.834	24
520	24.504	24.502	3.630	71
521	24.932	24.927	3.568	10
440	25.764	25.758	3.455	11
530	26.568	26.566	3.353	28
600	27.352	27.350	3.258	13
611	28.121	28.115	3.171	11
541	29.599	29.590	3.016	5
622	30.305	30.303	2.947	8
630	30.657	30.653	2.914	27
631	31.005	31.001	2.882	3
444	31.687	31.685	2.821	35
550	32.358	32.356	2.764	12
720	33.343	33.340	2.685	7
721	33.665	33.662	2.660	6
642	34.300	34.299	2.612	8
650	35.849	35.847	2.503	11
651	36.151	36.150	2.4826	9
800	36.749	36.749	2.4436	1
741	37.340	37.339	2.4063	9
820	37.915	37.922	2.3711	1
821	38.212	38.211	2.3533	3
750	39.629	39.627	2.2724	4
662	40.182	40.181	2.2424	15
832	40.453	40.456	2.2280	7
752	40.727	40.730	2.2136	4
920	42.600	42.603	2.1205	11
761	42.867	42.865	2.1080	17
664	43.387	43.386	2.0839	<1
930	43.902	43.901	2.0606	1
852	44.665	44.666	2.0272	2
932	44.922	44.918	2.0162	2
770	45.906	45.918	1.9752	2
860	46.407	46.411	1.9551	7
1010	46.656	46.656	1.9452	16
1011	46.899	46.900	1.9357	4
950	47.866	47.867	1.8988	2
1022	48.347	48.345	1.8810	1
1030	48.574	48.583	1.8728	1
1031	48.820	48.820	1.8639	2
871	49.756	49.759	1.8310	<1

from a high-resolution instrument using the parafocusing Bragg–Brentano geometry (Siemens D500).[12] The alignment of the diffractometer was checked by means of standard reference materials. The zero error was measured as less than 0.005°(2θ). The powder sample, mounted in a top-loaded sample holder, was completely illuminated at 15°(2θ). The diffraction pattern was scanned to 115°(2θ), with a step length of 0.02°(2θ) and a counting time of 23 s step^{-1}. To have better accuracy of reflection intensities at low angles, particularly below 15°(2θ), a second data set was collected with a diffractometer using a curved position sensitive detector (INEL CPS120) and Debye–Scherrer geometry.[13] The sample was contained in a rotating 0.5-mm-diameter capillary and data were collected for 15 h. The calibration of the detector was performed by using peak positions measured from the first data set.

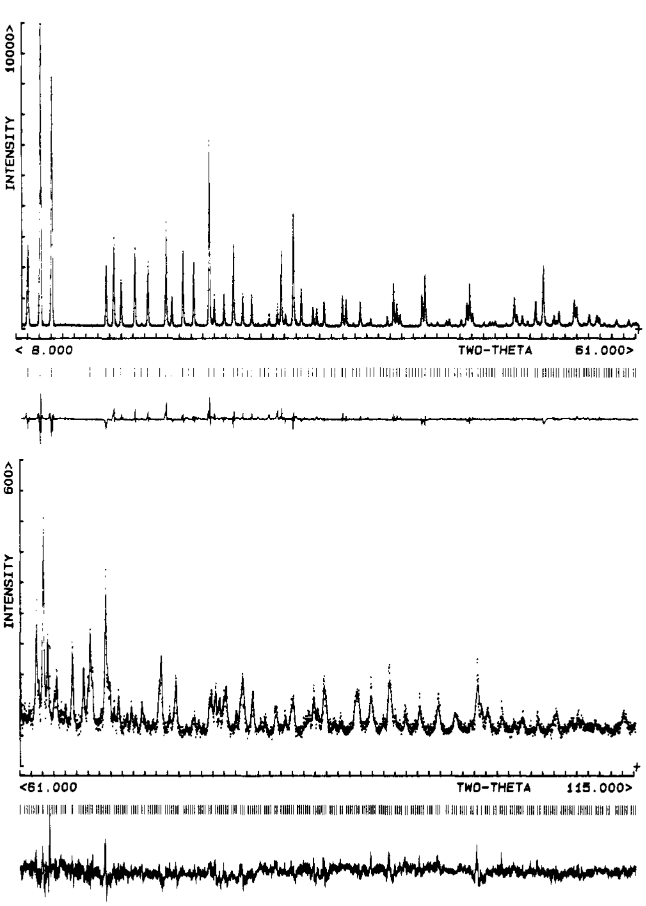

Figure 1. Final Rietveld difference plot of $[(CH_3)_4N]_4Ge_4S_{10}$. The upper trace shows the observed data as dots and the calculated pattern is shown by the solid line. The lower trace is a plot of the difference: observed minus calculated. The vertical markers show positions calculated for Bragg reflections. Note the expanded scale used for the high-angle range.

Table 2. Crystallographic Data and Details of the Rietveld Refinement for $[(CH_3)_4N]_4Ge_4S_{10}$

formula weight (g)	907.44
crystal system and space group	cubic $P\bar{4}3n$
Z	8
a (Å)	19.5490(4)
V (Å^3)	7470.9
wavelength (Å)	1.540 598
step increment (deg 2θ)	0.02
2θ range (deg)	8–115
no. of reflections	958
no. of structural parameters	37
no. of profile parameters	13
no. of non-hydrogen atoms	15
$R_F = \sum\lvert I(\text{"obs"})^{1/2} - I(\text{calc})^{1/2}\rvert/\sum I(\text{"obs"})^{1/2}$	0.06
$R_B = \sum\lvert I(\text{"obs"}) - I(\text{calc})\rvert/\sum I(\text{"obs"})$	0.07
$R_P = \sum\lvert y_i(\text{obs}) - (1/c)y_i(\text{calc})\rvert/\sum y_i(\text{obs})$	0.09
$R_{wp} = \{\sum w_i[y_i(\text{obs}) - (1/c)y_i(\text{calc})]^2/\sum w_i[y_i(\text{obs})]^2\}^{1/2}$	0.12

Results and Discussion

Structure Determination. Indexing of the pattern by the successive dichotomy method[14] gave a cubic unit cell with a = 19.5490(4) Å [M_{20} = 60, F_{30} = 112(0.0051, 52)] with systematic absences (hhl, l = 2n + 1), consistent whith space group $P\bar{4}3n$ or $Pm3n$. A list of observed and calculated peak positions is given in Table 1. The structure solution subsequently demonstrated the noncentrosymmetric space group to be the correct one. Integrated intensities (PSD data set) were obtained by an iterative

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Table 3. Final Refined Atomic Parameters and Selected Bond Distances and Angles for $[(CH_3)_4N]_4Ge_4S_{10}$

Atomic Parameters[a]

	x	y	z	B_{iso} (Å^2)
Ge1	0.3165(3)	0.4314(2)	0.0616(2)	0.9(3)
Ge2	0.0658(3)	0.0658(3)	0.0658(3)	0.9(3)
S1	0.2494(6)	0.3677(6)	−0.0058(5)	1.6(3)
S2	0.3765(4)	0.3613(3)	0.1201(6)	1.6(3)
S3	0.3826(8)	0.5	0.0	1.6(3)
S4	0.0	0.1316(8)	0.0	1.6(3)
S5	0.1313(6)	0.1313(6)	0.1313(6)	1.6(3)
N1	0.337(1)	0.337(1)	0.337(1)	
N2	0.417(1)	0.350(1)	0.834(1)	
C1	0.413(1)	0.311(2)	0.322(2)	
C2	0.295(1)	0.295(1)	0.295(1)	
C3	0.425(1)	0.338(1)	0.910(1)	
C4	0.349(1)	0.347(2)	0.825(1)	
C5	0.443(2)	0.412(1)	0.825(2)	
C6	0.450(2)	0.301(1)	0.790(1)	
	Selected Bond Distances (Å) and Angles (deg)			
Ge1	S1 (×2)	2.24(1)	S1–Ge1–S1	109.2(9)
	S2	2.14(1)	S1–Ge1–S2	106.3(8)
	S3	2.22(1)	S1–Ge1–S3	111.0(9)
			S1–Ge1–S2	109.6(8)
			S1–Ge1–S3	109.7(9)
			S1–Ge1–S3	111.0(7)
Ge2	S4 (×3)	2.23(1)	S4–Ge2–S4 (×3)	109.5(9)
	S5	2.22(1)	S4–Ge1–S5 (×3)	109.5(9)
N1	C1 (×3)	1.59(4)	C1–N1–C1 (×3)	113(4)
	C2	1.42(4)	C1–N1–C2 (×3)	113(4)
N2	C3	1.51(4)	C3–N2–C4	104(4)
	C4	1.34(3)	C3–N2–C5	103(4)
	C5	1.34(4)	C3–N2–C6	116(5)
	C6	1.43(4)	C4–N2–C5	113(5)
			C4–N2–C6	110(4)
			C5–N2–C6	110(5)

[a] B_{iso} were constrained to be the same for Ge atoms and also for S atoms. For C and N atoms an overall B parameter (0.47 Å^2) was refined.

fitting procedure,[15] available in the Rietveld refinement program FULLPROF.[16] Several sets of observed structure factors were generated for different sin θ/λ limits, using an equipartition of the overall intensity F_{obs}^2 for exact overlapping reflections. These were used as input for the direct-methods program SHELXS-86.[17] Most of the E maps revealed small fragments of the structure, but not enough to be convincing except for the data set 8.5–80°-(2θ) (436 independent reflections), from which a model was obtained, except for TMA groups. This structure solution involved an estimate of 110 phases for E values greater than 1.2 and used 6848 unique triplets and 69 negative quartets (CFOM = 0.426). Examination of this solution showed that 8 of the 26 peaks listed were likely to be correct, taking into consideration the known tetrahedral configuration of the GeS_4 group.

The solution was input to FULLPROF, and the refinement converged to an R_F factor of 0.25, but no additional structure fragment was obtained from difference Fourier maps. Accordingly, the data set collected with the focusing diffractometer, characterized by better resolution at high angles, was used to further the analysis. The eight atomic positions previously found were used to generate a difference Fourier map from the complete data set (958 independent reflections). The dominant peaks completed the structure model, except for one C atom, of which the coordinates were calculated from the well-known tetrahedral configuration of TMA groups. The complete model with 15 atoms in the asymmetric unit was refined by the Rietveld method (R_F = 0.06). A Pearson VII function was used to describe the peak shape and the angular dependence of half-widths was represented by the usual quadratic form in tan θ. Five coefficients were refined to define the functional dependence of the background. The conditions of the refinement are listed in Table 2. Figure 1 shows the final fit between calculated and observed patterns. Atomic positions and selected distances and angles are given in Table 3.

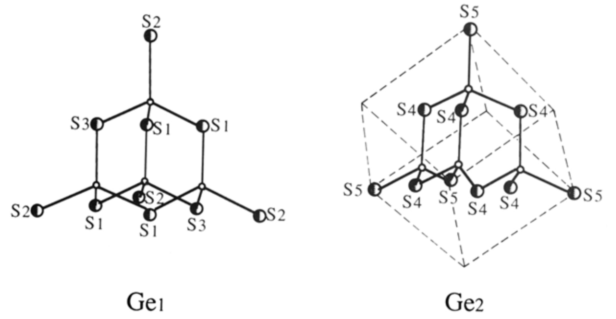

Figure 2. The two independent $Ge_4S_{10}^{4-}$ groups.

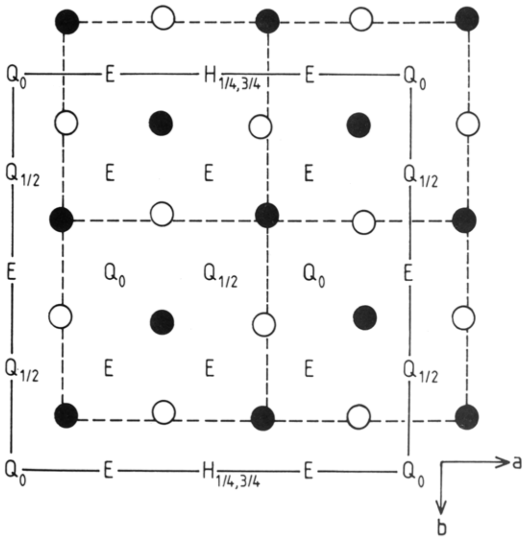

Figure 3. Fcc arrangement of the S_a atoms in projection on the (001) plane showing the filling of the tetrahedral sites by the Ge_4S_6 moieties. Closed circles: S_a in the base faces. Open circles: S_a in the middle of the lateral faces of the subcells $a' = a/2$. Dotted lines emphasize the subcells $a' = a/2$; bold lines emphasize the true unit cell. $H_{1/4,3/4}$ means half the tetrahedral sites are filled by Ge_4S_6 at height $z = {}^1/_4, {}^3/_4$; $Q_{0,1/2}$ means quarter of tetrahedral sites occupied in z = 0 and $^1/_2$, E means empty sites.

Description of the Structure. The structure of $TMA_4Ge_4S_{10}$ is a new structure type. It consists of isolated condensed thioanions $Ge_4S_{10}^{4-}$ with tetrahedral $(CH_3)_4N^+$ cations as positive counterparts. Two independent $Ge_4S_{10}^{4-}$ anions (Ge1 and Ge2 atoms) occur in the structure (Figure 2). The atomic distances for these anions agree well with those previously reported for related compounds.[18–21] The $Ge_4S_{10}^{4-}$ thioanion results from the condensation of four

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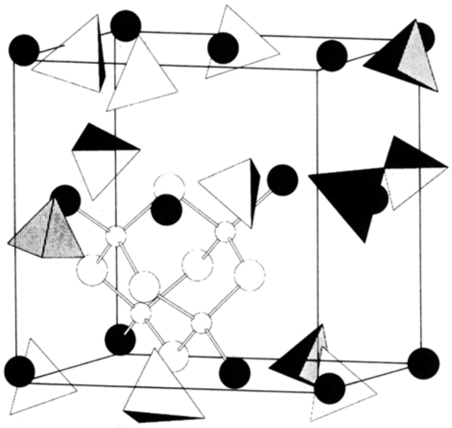

Figure 4. Perspective view of one subcell $a' = a/2$ showing the tetrahedral TMA^+ ions located approximately in the octrahedral sites and the Ge_4S_6 adamantine unit in one tetrahedral site. The content of a subcell is $[Ge_4S_{b6}]_{tetra}\square_{7tetra}[TMA]_{4octa}S_{a4}$.

GeS_4^{4-} tetrahedra sharing apices with an average S–Ge–S bond angle, for the two anions, of 109.50°, which is close to the ideal value. It consists of six bridging S_b atoms (S1, S3 for Ge1 and S4 for Ge2) and four apical S_a atoms (S2 for Ge1 and S5 for Ge2). The Ge–S_b and Ge–S_a distances are homogeneous in the range 2.22–2.25 Å for the two independent Ge atoms, except for the Ge1–S_a distance [2.14(1) Å]. Such a shortening of bonds is well-known for isoelectronic M_4X_{10} units and is explained by π-transfer.[1,22] The $Ge_4S_{10}^{4-}$ thioanion can be inscribed in a cube as shown in Figure 2, with S_a atoms located at half the corners, S_b in the center of the faces, and Ge in half the tetrahedral sites.

Owing to the high volume of the unit cell, the packing of the structure is not easy to describe. However, a simple representation of the structure can be made by considering the quasi perfect fcc arrangement of the S_a atoms (Figure 3). In this description, all octahedral voids are filled by the TMA^+ ions while only one-eighth of the tetrahedral voids are occupied by the adamantine-like Ge_4S_6 moieties (Figure 4). The compound can then be formulated as $[Ge_4S_{b6}]_{1tetra}\square_{7tetra}[TMA]_{4octa}S_{a4}$, which demonstrates that the space filling is small, as shown by the density (ρ_{obs} = 1.72 g cm^{-3}, ρ_{calc} = 1.61 g cm^{-3}). Eight similar subcells with different locations of the adamantine group generate the complete crystal structure with the Ge_4S_6 units distributed in the tetrahedral voids, as shown in Figure 3. Only van der Waals interactions occur between the TMA^+ ions and $Ge_4S_{10}^{4-}$, since no distances shorter than 3.57 Å have been encountered. All the results obtained from analytical methods to characterize this new phase agree with the structure solution, e.g., thermogravimetric weight loss of 33% corresponding to the departure of TMA groups and chemical analyses. Moreover, IR absorption and Raman scattering spectra have shown the vibrational modes of the $Ge_4S_{10}^{4-}$ anion[19,23] at 460, 392, 341, 200, and 122 cm^{-1}. Both spectra are simple, nevertheless the broadening of the lines in the high-frequency region (460 and 392 cm^{-1}) is indicative of some deviation from the ideal T_d point group.

This *ab initio* structure determination demonstrates that reliable information on high-symmetry materials with large unit cells can be obtained from powder diffraction data. It is worth noting that the result has been obtained with a high-resolution system using a conventional X-ray source. It is the first complete determination of the crystal structure of a thiogermanate compound containing an organic counterion. This novel cubic structure sheds new light on the chemistry of materials based on the condensation of monomeric GeS_4 moieties.

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