JOURNAL OF MATERIALS SCIENCE 31 (1996) 6507–6510

On the structure of stibnite (Sb_2S_3)

P. ARUN, A. G. VEDESHWAR
Department of Physics and Astrophysics, Delhi University, New Delhi, 110007, India

A new crystal structure is found to exist for stibnite which is orthorhombic, Pmmm. In this structure all the antimony and sulphur atoms have only one type of coordination, namely, trivalent and diavalent, respectively. They form a honey-comb-like planar network which is parallel to the *xz*-plane and stacked along the *y*-axis with the middle plane slightly displaced along the plane with respect to the top or bottom layer. The structural analysis based on the observed reflections in the diffraction pattern shows that the proposed structure is correct. We feel that stibnite can also crystallize and exist in this proposed new structure which is entirely different from the existing structure. The present structure can also account for the fact that this compound can transform easily from amorphous to crystalline state.

1. Introduction

The crystal structure of stibnite, the mineral form of antimony trisulphide, was first reported by Hofmann [1]. It is known to be orthorhombic (Pbnm-D_{2h}^{16}) with $a = 1.120$ nm, $b = 1.128$ nm and $c = 0.383$ nm. This was refined by Scavnicar [2] slightly. The latest refinement of the structure was carried out by Bayliss and Nowacki [3] which also shows stibnite is orthorhombic (Pnma-D_{2h}^{16}) with $a = 1.13107$ nm, $b = 0.38363$ nm and $c = 1.12285$ nm. However, in all these proposed structures both antimony and sulphur atoms exhibit two different types of coordination with one half of the antimony atoms surrounded by five sulphur atoms. This environment of one half of the Sb atoms is rather unsatisfactory according to Wells [4]. Surprisingly, none of the indexed diffraction patterns of commercial Sb_2S_3 from different companies reported by Mady *et al.* [5] tallies with the earlier reports. However, Mady *et al.* did not calculate the cell dimensions or do any structural analysis. This motivated us to re-examine the structure of stibnite. We found the cell dimensions were entirely different from earlier reports when we indexed all the lines of the diffraction pattern of naturally occurring single crystal stibnite. This led us to propose a new structure in which stibnite can crystallize and exist because it is well known that some materials exhibit more than one structure.

2. Experimental details

The naturally occurring mineral stibnite (Sb_2S_3) was collected from Andra Pradesh, India. It was in the form of a single crystal having a needle-like structure along the larger dimension. It cleaves along the direction of the needle structure. It had a shiny dark grey colour. Both chemical analysis and ESCA with depth profile confirmed the stoichiometry of the sample. The X-ray diffraction was recorded using a diffractometer, Philips PW1840, using Bragg–Bentano focusing. A thin slice of the single crystal stibnite (1 cm × 1.2 cm × 0.1 cm) was used. Many pieces of various orientations were tried to obtain the maximum number of reflections. However, we could obtain only fifteen reflections which are sufficiently reproducable. The pattern also shows the same reflections. The indexed powder diffraction pattern of stibnite is shown in Fig. 1. Initial indexing was done using a computer program in Turbo-BASIC developed by us. However, refinement of the cell dimensions, $\delta 2\theta$, space group analysis etc., were performed using a software developed by Charles W. Burnham, Department of Earth and Planetary Sciences, Harvard University.

3. Results

To our surprise, we obtained the cell dimensions $a = 1.420$ nm, $b = 1.147$ nm and $c = 0.747$ nm which are completely different from the earlier reports. Therefore, we carried out the structural analysis. Unlike earlier reports, we assumed only one type of coordination for both Sb and S atoms for our trial structure. This leads to the formation of bases consisting of a Sb–S–Sb linear chain to which another two S atoms are bonded at an angle of 120° to each other (Fig. 2). This forms a planar honey-comb-like structure similar to graphite. Such planes (parallel to the *xz*-plane) are stacked along the y-axis. There are three such planes in a unit cell. However, the middle plane in the unit cell is slightly displaced along the plane with respect to the upper and bottom planes so that the sulphur atoms of this plane face the antimony atoms of the next plane. This accounts for a more stable layer structure with partial Coulombic forces between the layers due to the slightly displaced configuration of the covalent bonds arising due to the difference between the electron affinity of the two atoms (Fig. 3).

The structural analysis was carried out with the usual corrections for polarization and Lorentz factors. The initial discrepancy factor obtained was $R = 0.26$.

0022–2461 © *1996 Chapman & Hall*

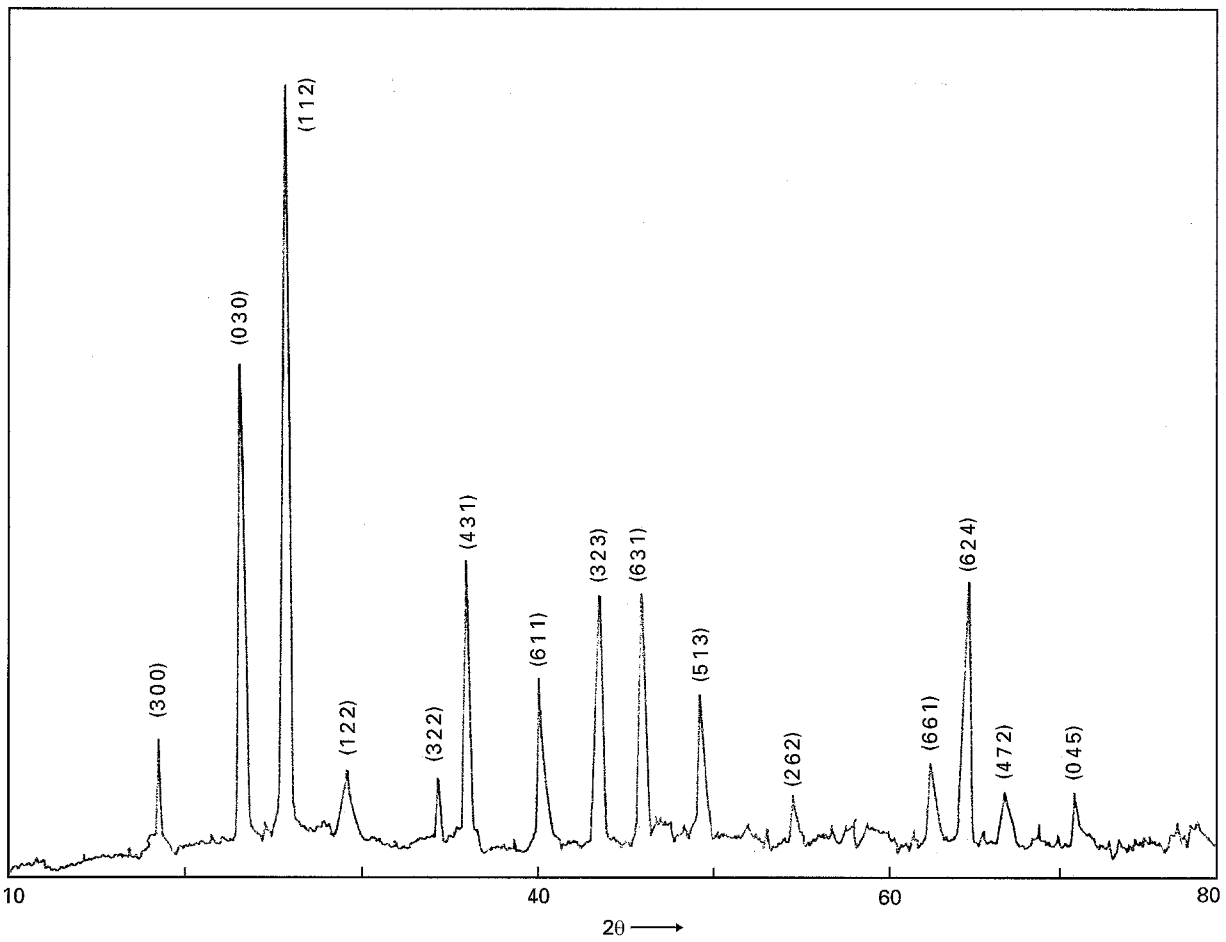
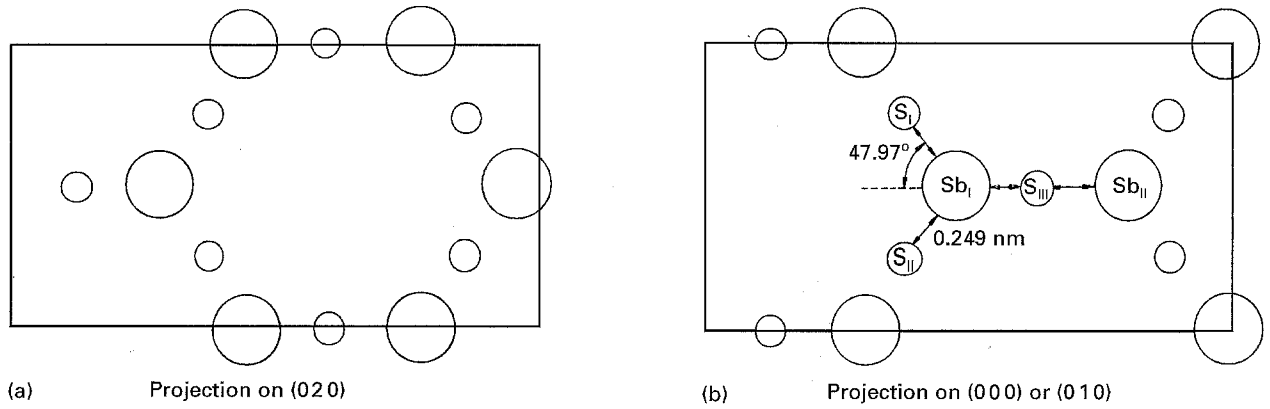


Figure 1 X-ray diffraction pattern of single crystal stibnite.



(a) Projection on (020)

(b) Projection on (000) or (010)

Figure 2 Arrangements of antimony and sulphur atoms on the plane (a) (020) and (b) (000) or (010) of the proposed structure.

On further refinement of the atomic positions and taking into account the anisotropic temperature factor we obtained $R = 0.16$. This is of a sufficiently low value to accept the proposed structure as correct [6]. We have not tried further refinement. We have given the necessary and relevant data for all the reflections observed in Table I. The atomic positions of all the atoms in the unit cell are given in Table II. Interatomic bond distances are listed in Table III. The anisotropic temperature factors have been listed in Table IV.

4. Conclusions

In conclusion, the proposed structure is a possible new stable structure in which stibnite can exist. Further

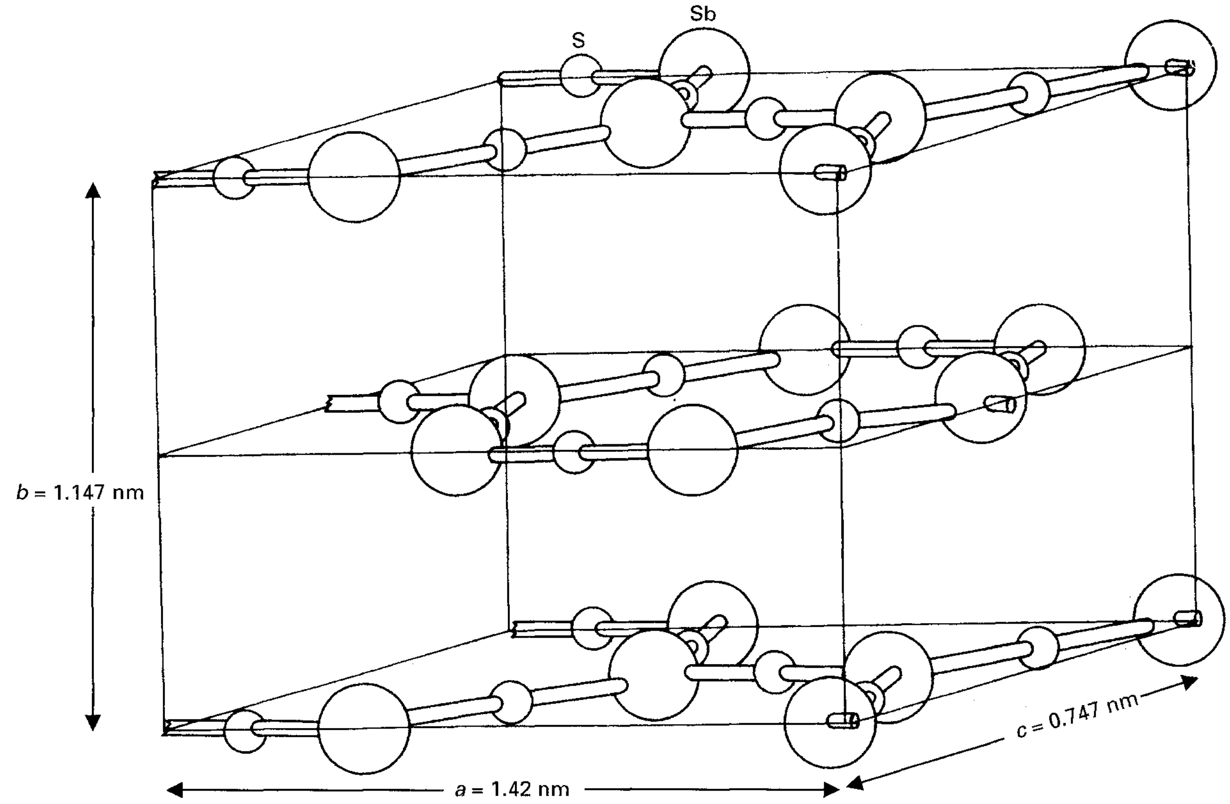


Figure 3 Proposed structure of stibnite.

TABLE I Details of the observed reflections of diffraction pattern

S no.	2θ	I_{rel}	*hkl*	δ2θ	F_o	F_c
1.	18.72	15.24	300	− 0.004	3.23	3.68
2.	23.23	63.81	030	0.009	8.28	9.79
3.	25.94	100.00	112	0.14	5.82	5.41
4.	29.25	9.05	122	0.09	1.99	2.43
5.	34.28	8.57	322	− 0.002	2.3	1.77
6.	36.47	38.57	431	− 0.044	5.21	5.00
7.	40.69	22.85	611	− 0.013	4.53	5.29
8	43.92	33.81	323	− 0.003	6.00	5.29
9.	46.67	33.81	631	− 0.008	6.43	4.99
10.	49.21	18.57	513	− 0.007	5.06	7.33
11.	55.43	6.66	262	0.017	3.47	3.94
12.	63.69	12.38	661	− 0.009	5.53	3.36
13.	65.59	36.2	624	− 0.006	9.76	10.16
14.	67.66	7.62	472	− 0.001	4.62	4.75
15.	70.97	7.62	045	− 0.004	6.87	5.83

TABLE II Coordinate of antimony and sulphur atoms

Antimony atoms				Sulphur atoms			
S no.	X	Y	Z	S no.	X	Y	Z
1.	0.29	0.5	0.5	1.	0.114	0.5	0.5
2.	0.29	0.5	− 0.5	2.	0.114	0.5	− 0.5
3.	0.464	0.5	0.0	3.	0.377	0.5	0.25
4.	0.815	0.5	0.0	4.	0.377	0.5	− 0.25
5.	0.989	0.5	0.5	5.	0.639	0.5	0.0
6.	0.989	0.5	− 0.5	6.	0.902	0.5	0.25
7.	0.29	− 0.5	0.5	7.	0.902	0.5	− 0.25
8.	0.29	− 0.5	− 0.5	8.	0.114	− 0.5	0.5
9.	0.464	− 0.5	0.0	9.	0.114	− 0.5	− 0.5
10.	0.815	− 0.5	0.0	10.	0.377	− 0.5	0.25
11.	0.815	− 0.5	0.5	11.	0.377	− 0.5	− 0.25
12.	0.989	− 0.5	− 0.5	12.	0.639	− 0.5	0.0
13.	0.318	0.0	0.0	13.	0.902	− 0.5	0.25
14.	0.49	0.0	0.5	14.	0.902	− 0.5	− 0.25
15.	0.49	0.0	− 0.5	15.	0.144	0.0	0.0
16.	0.838	0.0	0.5	16.	0.404	0.0	0.25
17.	0.838	0.0	− 0.5	17.	0.404	0.0	− 0.25
18.	0.97	0.0	0.0	18.	0.664	0.0	0.5
				19.	0.664	0.0	− 0.5
				20.	0.924	0.0	0.25
				21.	0.924	0.0	− 0.25

TABLE III Interatomic bond length and angles suspended between atoms

	(nm)	(°)
Neighbouring atoms		
1. Sb–S	0.249	
Angles		
1. S(I)–Sb(I)–S(II)		95.94
2. S(I)–Sb(I)–S(II)		132.03

TABLE IV Anisotropic temperature factors

Atom	B_{xx} (nm^2)	B_{xx} (nm^2)	B_{xx} (nm^2)	B_{yy} (nm^2)	B_{xy} (nm^2)	B_{yx} (nm^2
Sb	0	0.00008	0.000002	0.000003	0	0
S (at $z = 0.25$)	0	0	0	0.00016	0	0
S (remaining)	0	0	0.00002	0	0	0

studies on the correlation of the structure with some of its physical properties are underway and will be published elsewhere soon.

Acknowledgements

We would like to thank Professor G. K. Chadha, Department of Physics, Delhi University, for allowing us to carry out the X-ray diffraction studies on the Philips PW 1840 diffractometer. Also we would like to thank Dr. P. K. Verma, Department of Geology, Delhi University, for providing us the software package. LCLSQ8N developed by Charles W. Burnham. We are very grateful to Professor A. Mansingh for his constant encouragement. The financial assistance of UGC in the form of a fellowship to one of the autho (P. A.) is gratefully acknowledged.

References

1. W. HOFMANN, *Z. Kristalogr.* **86** (1993) 225.
2. S. SCAVNICAR, *ibid.* **114**, (1960) 85.
3. P. BAYLISS and W. NOWACKI, *ibid* **135** (1972) 308
4. A. F. WELLS, "Structural Inorganic Chemistry", 2nd Ed (Un versity Press, Oxford, 1950).
5. KH. A. MADY, S. M. HAMMAD and W. Z. SOLIMA *J. Mater. Sci.* **22** (1987) 4153.
6. L. S. DENT GLASSER, "Crystallography and its Applic tions", (Van Nostrand Reinhold Company Ltd, 1977) p. 153

Received 30 August 1995
and accepted 13 June 1996