RUSSELL, *Met. Trans.* 2 (1971) 189.
9. M. K. THOMAS and R. E. TRABOCCO, Proceedings of the Conference "*In Situ*-Grown Composites", Lakeville, Connecticut (1972) p. 301.
10. A. MAGNELL, L. E. EDSHAMMAR and T. DAGGERMANN, Final technical Report No. 1 under contract DA-91-591-EUC-2734 (AD 426927) (1963) p. 46.
11. C. McL. ADAM, I. O. SMITH and L. M. HOGAN, as for [9], p. 309.

Received 28 November 1978
and accepted 23 March 1979.

G. PIATTI
G. PELLEGRINI
Materials Science Division,
CEC, Joint Research Centre,
Ispra Establishment,
I-21020 Ispra (Va), Italy

The effect of powdering on the polytypic crystal structures of tin disulphide

During a study of polytypism in single crystals of tin disulphide grown by the iodine vapour transport method, single crystal X-ray diffraction studies brought to light several instances of polytypic structure, and in one or two cases revealed hitherto unreported polytypes. A full account of this work is to appear elsewhere [1]. A parallel study of similar samples by means of powder X-ray diffraction failed to reveal any indication of polytypes other than the 2H form [2].

In view of this, it was thought that the process of crushing and grinding in an agate mortar, adopted for the preparation of powder specimens, might be affecting the atomic structure of the resulting samples, possibly by the introduction of numerous stacking faults and dislocations to alter the structure of the higher order polytypes. The structure of tin disulphide is isomorphous with cadmium iodide, and is characterized by easy cleavage and glide parallel to the basal plane of the trigonal crystals.

To test this hypothesis, three SnS_2 crystals were carefully examined by single crystal diffraction methods to discover their polytype structures, and they were then crushed to make powder specimens. The powder diffraction data were then compared with those from the single crystals to determine whether the same polytypes were still present.

The powder data derived from a crystal known from single crystal studies to consist entirely of the 2H polytype ($P\bar{3}ml$; Zhdanov symbol [11], $a = b = 3.643 \pm 0.002$ Å, $c = 5.894 \pm 0.005$ Å) were in excellent agreement with those calculated for the 2H structure. The comparison is made in Table I. Absorption and temperature factor corrections have not been applied, and the relative intensities only of diffraction lines which are fairly close together may be quantitatively compared. The structure of this crystal is therefore unaffected by the powdering process.

TABLE I A comparison of the experimentally observed powder data for SnS_2 crystal no. 1 (2H polytype) with values calculated on the basis of the 2H structure (CuKα radiation)

Reflection *hkl*	θ_{obs} (deg)	θ_{calc} (deg)	d_{calc} (Å)	I_{calc} (normalized)	I_{obs}
0 0 1	7.48	7.51	5.894	94.7	vvs
1 0 0	14.10	14.14	3.155	31.6	ms
0 0 2	15.05	15.16	2.947	3.1	vvw
1 0 1 $1 0 \bar{1}$	16.07	16.09	2.782	11.5 100.0	vvs
1 0 2	20.93	20.97	2.154	69.5	ms
0 0 3	23.10	23.10	1.965	5.4	vw
1 1 0	24.98	25.04	1.822	29.8	m
1 1 1	26.25	26.29	1.740	22.0	mw
1 0 3 $1 0 \bar{3}$	27.46	27.53	1.668	20.2 2.8	mw
2 0 0	29.17	29.25	1.577	4.3	vw
1 1 2	29.85	29.84	1.549	3.4	vvw
2 0 1 $2 0 \bar{1}$	30.32	30.30	1.524.	14.9 2.1	mw
0 0 4	31.42	31.55	1.473	4.8	vw
2 0 2	33.54	33.66	1.391	16.4	mw
1 1 3 1 0 4	35.21	35.25 35.27	1.336 1.335	9.0 4.9	w
2 0 3 $2 0 \bar{3}$	38.75	38.81	1.230	1.0 7.2	vw–w
2 1 0	40.16	40.28	1.192	3.3	vw
0 0 5	40.68	40.84	1.179	1.0	vvw
1 2 1 2 1 1	41.16	41.27	1.169	12.4 1.7	mw
1 1 4	42.21	42.29	1.146	12.9	w
2 1 2 1 0 5 $1 0 \bar{5}$	44.09	44.22 44.28 44.28	1.105 1.104 1.104	16.0 0.7 5.3	m

0022–2461/79/102516–04 $02.40/0

A crystal consisting almost entirely of 4H prior to crushing was also examined. The crystal contained a very small region of 40H polytype, of undetermined stacking sequence. Powder data obtained from this crystal are compared in Table II with those calculated on the basis of the 4H structure ($P6_3mc$, Zhdanov symbol [22]; $a = b = 3.643 \pm 0.002$ Å, $c = 11.79 \pm 0.01$ Å).

The level of agreement between the two sets of data is poor. In particular, the observed intensity of the 1 0 . 0 reflection is very high compared with the corresponding calculated value, whilst the 1 0 . 2 and 1 0 . 5 reflections, although theoretically expected to be of fairly high intensity, could not be detected experimentally.

The possibility that the intensity discrepancies might be explicable by preferred orientation in the sample is discounted. To fabricate a powder specimen in which preferred orientation did not occur the crystal was powdered. The powder was then mixed with Canada balsam and allowed to dry. The dried sample was then re-powdered before rolling the equi-axed granular material on to a fine glass fibre. No arcing characteristic of preferred orientation was visible on the powder photographs.

TABLE II A comparison of the experimentally observed powder data for SnS_2 crystal no. 2 (predominantly 4H polytype) with values calculated on the basis of the 4H structure (CuKα radiation)

Reflection hkl	θ_{obs} (deg)	θ_{calc} (deg)	d_{calc} (Å)	I_{calc} (normalized)	I_{obs}
0 0 2	7.53	7.51	5.894	100.0	vvs
1 0 0	14.19	14.14	3.155	8.3	ms
1 0 1	14.69	14.65	3.048	61.3	m
0 0 4	–	15.16	2.947	3.3	abs
1 0 2	–	16.08	2.782	41.0	abs
1 0 3	18.11	18.26	2.460	74.0	vw
1 0 4	–	20.97	2.154	18.3	abs
0 0 6	–	23.10	1.965	5.7	abs
1 0 5	–	24.09	1.889	32.8	abs
1 1 0	25.05	25.04	1.822	31.5	m
1 1 2	26.27	26.29	1.740	23.2	mw
1 0 6	–	27.53	1.668	8.2	abs
2 0 0	–	29.25	1.577	1.1	abs
{2 0 1	29.60	29.54	1.564	8.5	vvw
1 1 4}		29.84	1.549	3.6	
2 0 2	–	30.39	1.524	6.0	abs
1 0 7	–	31.26	1.486	7.2	abs
{0 0 8	31.71	31.54	1.474	5.1	vvw
2 0 3}		31.78	1.464	14.0	
2 0 4	–	33.66	1.391	4.3	abs
{1 1 6	35.29	35.25	1.336	9.5	vvw
1 0 8}		35.27	1.335	1.3	
2 0 5	36.04	36.01	1.311	9.6	vvw
2 0 6	–	38.81	1.230	2.9	abs
1 0 9	–	39.59	1.210	3.6	abs
2 1 0	–	40.28	1.192	0.9	abs
2 1 1	–	40.52	1.186	6.7	abs
0 0 . 10	–	40.84	1.179	1.0	abs

The influence of possible polytype transformations induced by the powdering process was therefore considered. A comparison of Tables I and II shows that the strong 1 0 . 0 reflection of the 2H polytype overlaps the weaker 1 0 . 0 reflection of the 4H polytype, and could give rise to an increase in the observed intensity. However, other strong 2H reflections, such as 1 0 . 1 and 1 0 . $\bar{1}$ are not observed. Intensity comparisons were calculated for a number of differing polytypes and polytype mixtures, but without acceptable agreement.

The results obtained, therefore, show that the structure of the 4H polytype was indeed influenced by the crushing process, but in a way which cannot be explained simply in terms of the formation of alternative polytypes.

A crystal containing the 4H, 6H and 18R polytypes prior to crushing was examined. The data relating to each type are as follows:

4H $P6_3mc$, Zhdanov symbol [22]; $a = b = 3.643 \pm 0.002$ Å, $c = 11.79 \pm 0.01$ Å.

6H (Stacking sequence not positively identified). Either $P\bar{3}ml$, Zhdanov symbol [33] or $P3ml$, Zhdanov symbol [2211]; $a = b = 3.643 \pm 0.002$ Å, $c = 17.683$ Å.

18R $P\bar{3}ml$, Zhdanov symbol $[1212]_3$; $a = b = 3.643$ Å, $c = 53.05$ Å.

The X-ray powder intensity data obtained from this sample are presented in Table III, where again a poor level of agreement exists between the experimentally observed and theoretically derived powder intensities. A number of X-ray reflections which were computed to possess high intensities, e.g. the 1 0 . 3 reflection of the 4H polytype, the 1 0 . 4 and the 1 0 . 5 of the 6H polytype, and the 1 0 . 7 and the 1 0 . 16 reflections from the 18R polytype, were in fact absent from the powder photograph. Additionally, the powder data are not in exact agreement with any mixture of the individual polytypes, nor of the 2H modification. It is clear that the structure of this sample has also

TABLE III A comparison of the experimentally observed powder data for SnS_2 crystal sample no. 3 with values computed on the basis of the 4H, 6H and 18R polytypes (CuKα radiation)

θ_{obs}	[22]; 4H structure			6H structures				$[1212]_3$; 18R structure			I_{obs}
(deg)	Reflection	θ_{calc} (deg)	I_{calc} (norm)	Reflection	θ_{calc} (deg)	I_{calc} (norm) [2211]	I_{calc} (norm) [33]	Reflection	θ_{calc} (deg)	I_{calc} (norm)	
7.46	0 0 2	7.51	100.0	0 0 3	7.51	100.0	100.0	0 0 9	7.51	100.0	vvs
14.24	1 0 0	14.14	8.3	1 0 0	14.14	11.1	0.0				ms
								1 0 1	14.17	5.7	
								1 0 2	14.24	22.1	
				1 0 1	14.37	12.3	1.8				
				$1 0 \bar{1}$	14.37	12.3	44.1				
–								1 0 4	14.55	4.8	abs
–	1 0 1	14.65	61.3								abs
–								$1 0 \bar{5}$	14.77	12.0	abs
–				1 0 2	15.04	15.0	28.7				abs
–				$1 0 \bar{2}$	15.04	15.0	4.7				abs
–	0 0 4	15.16	3.3	0 0 6	15.16	3.3	3.3	0 0 . 18	15.16	3.3	abs
–								1 0 7	15.35	38.2	abs
–								$1 0 \bar{8}$	15.70	1.8	abs
16.19	1 0 2	16.09	41.0	1 0 3	16.09	9.2	5.1				vw
				$1 0 \bar{3}$	16.09	40.3	5.1				
–								1 0 . 10	16.52	26.3	abs
–								$1 0 . \overline{11}$	16.98	29.2	abs
–				1 0 4	17.47	17.2	3.0				abs
				$1 0 \bar{4}$	17.47	17.2	62.2				abs
–								1 0 . 13	17.99	7.0	abs
–	1 0 3	18.26	74.0								abs
								$1 0 . \overline{14}$	18.54	12.0	abs
–				1 0 5	19.11	15.3	39.7				abs
–				$1 0 \bar{5}$	19.11	15.3	0.7				abs
–								1 0 . 16	19.71	32.2	abs
–								1 0 . 17	20.33	2.1	abs
–	1 0 4	20.97	18.3	1 0 6	20.97	24.5	0.0				abs
–								1 0 . 19	21.63	1.8	abs
22.25								$1 0 . \overline{20}$	22.31	22.3	vvw
–				1 0 7	23.01	8.8	0.4				abs
–				$1 0 \bar{7}$	23.01	8.8	23.1				abs
–	0 0 6	23.10	5.7	0 0 9	23.10	5.7	5.7	0 0 . 27	23.10	5.7	abs
–								1 0 . 22	23.73	5.8	abs
–	1 0 5	24.09	32.8								abs
–								$1 0 . \overline{23}$	24.46	2.9	abs
24.84	1 1 0	25.04	31.5	1 1 0	25.04	31.5	31.5	1 1 0	25.04	31.5	s
–				1 0 8	25.20	5.9	21.1				abs
				$1 0 \bar{8}$	25.20	5.9	0.9				
–								$1 0 . \overline{25}$	25.96	8.6	abs
26.26	1 1 2	26.29	23.2	1 1 3	26.29	23.2	23.2	1 1 9	26.29	23.2	m

been influenced by the powdering process. Intensities calculated on the assumption that polytype transformation had taken place failed to give improved correlation between observed and calculated data.

It is thought that the grinding process used to prepare X-ray powder specimens influences the structures, except for the 2H modification, of polytypic crystals of SnS_2. The effect is not satisfactorily explained by polymorphic phase changes to other tin–sulphur compounds (such phase changes would in any case normally require the application of high temperatures). Nor is the effect explained fully by the formation of alternative polytypes.

For the polytypic crystals examined, powder lines of notable intensity from higher polytypes are usually overlapped by strong 2H reflections, the only exception being the 1 0 . 1 reflection from the 4H structure. This is probably why only one SnS_2 polytype other than the basic 2H modification has ever been reported from powder studies alone, this latter being the 4H polytype observed by Guenter and Oswald [3]. Ishizawa and Fujiki [4–6] have also examined polytypes of SnS_2 by powder and Weissenberg techniques and infer in their work that single crystal X-ray examination is to be preferred if reliable structure analysis is to be achieved. Terhell and Lieth [7] have reported structural alterations similar to those described above in their studies of GaSe layer crystals.

Acknowledgements

The authors are indebted to Dr N. Pentland OBE, Head of the Department of Applied Physics at Brighton Polytechnic, for research facilities and to Dr E. A. Kellett, now at the Hosiery and Allied Trades Research Association, Nottingham, for most useful discussions.

References

1. C. R. WHITEHOUSE and A. A. BALCHIN, *J. Crystal Growth* (in press).
2. R. W. G. WYCKOFF, "Crystal Structures", Vol 1, 2nd edn (Interscience, New York, 1962).
3. J. R. GUENTER and H. R. OSWALD, *Naturwissenschaften* 55 (1968) 177.
4. Y. ISHIZAWA and Y. FUJIKI, *J. Phys. Soc. Japan.* 35 (1973) 1259.
5. *Idem, Mineral. J. Japan* (1972) 498.
6. R. S. MITCHELL, Y. ISHIZAWA and Y. FUJIKI, *Nature* 247 (1974) 537.
7. J. C. J. M. TERHELL and R. M. A. LIETH, *Phys. Stat. Sol. (a)* 10 (1972) 529.

Received 31 January
and accepted 12 March 1979.

C. R. WHITEHOUSE*
A. A. BALCHIN
Crystallography Laboratory,
Department of Applied Physics,
Brighton Polytechnic,
Moulsecoomb, Brighton, Sussex, UK

---

*Present address: The Department of Electrical and Electronic Engineering, University of Newcastle-upon-Tyne, NE1 7RU, UK.

Optical absorption of transition metals in alkali lime germanosilicate glasses

The absorption loss in alkali lime germanosilicate optical fibres, made by the double crucible method, is due in general to the presence in the glass of OH groups and transition metals, in concentrations in the p.p.m. and p.p.b. range respectively [1, 2]. In the course of an investigation aimed at lowering the loss of these optical fibres, the absorption spectra of the different transition metal ions in alkali lime germanosilicate glass were measured.

Typical core glasses of molar composition 0.44 SiO_2 0.29 GeO_2 0.02 Al_2O_3 0.10 CaO 0.14 Na_2O 0.1 K_2O with 0.05% As_2O_3 acting as a fining agent were melted in Pt–10% Rh crucibles in a resistance furnace. Very pure starting materials* with transition metal impurities below 0.01 p.p.m. were used. Transition metal compounds were added to the batch to give a concentration of 20 p.p.m. (V, Cr, Co, Ni, and Cu) or 200 p.p.m. (Ti, Mn and Fe). The melt was bubbled for one hour at 1400° C after which the melt was allowed to stand for one hour at 1300° C for fining. The bubble free melt was poured into graphite moulds and annealed at 620° C for one hour. This melting procedure was chosen because it had previously proved possible to minimize the absorption loss of optical fibres by using pure glasses prepared in this manner in fused silica crucibles [2]. The absorption spectra were recorded from 350 to 1500 nm with a Cary 17 spectrophotometer on 5 to 10 cm polished rods. This range incorporates the wavelengths at which it is proposed to use optical fibres (800 to 1300 nm)

---

*SiO_2, $CaCO_3$, Na_2CO_3, K_2CO_3 and As_2O_3 (Merck, FO Optipur), GeO_2 (Hoboken-Belgium extra pure) and Al_2O_3 (J. T. Baker, Ultrex).

0022–2461/79/102519–03 $02.30/0