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A Variant of the NaCl Structure Type: BaSnS₂*

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A structural analysis based on three-dimensional X-ray data has been carried out for BaSnS₂. The space group is $P2_1/c$, $a = 6\cdot0848$ (3), $b = 12\cdot1396$ (8), $c = 6\cdot2356$ (2) Å, $\beta = 97\cdot058$ (4)°. The least-squares refinement of the parameters gave $R = 0\cdot0574$ for 1049 intensities. The structure is a distortion of the NaCl structure and can be considered as a composite of the BaS and SnS structures, both of which are based on the NaCl motif. Ba is in sixfold coordination in a slightly distorted octahedron. Sn is in a distorted octahedral void but is very close to a triangular face of S ions so that it is bonded to 3 sulfur atoms only. In this polar arrangement Sn can be considered to have a tetrahedral environment in which a lone pair of electrons occupies one vertex. The cations are ordered so that Ba layers alternate with Sn layers in the overall NaCl type architecture.

Introduction

Several ternary sulfides containing Ba and Sn have been recently reported (Hervieu, Perez & Hagenmuller, 1967; Susa & Steinfink, 1971; Yamaoka & Okai, 1970; Jumas, Ribes, Philippot & Maurin, 1971). As a result of an attempt to prepare substitutional solid solutions in the Ba–Fe–Sn–S system, we became interested in the crystal structure of one of the possible end members of the series, BaSnS₂. BaSnS₂ has been prepared by Hervieu, Perez & Hagenmuller (1967), hereafter referred to as HPH. They found the compound to be a black powder with an orange-red color upon grinding. The powder pattern (reported also on card 20–150 of the Joint Committee on Powder Diffraction Standards) was indexed in terms of an orthorhombic lattice with parameters $a = 12\cdot000$ (4), $b = 8\cdot381$ (8), $c = 4\cdot606$ (10) Å with systematic absences compatible with the space

groups *Pnma* and *Pn2₁a*. No indication is given as to how the standard deviations of the lattice parameters were estimated but it is unusual that the *c* axis, which is the shortest, has the greatest standard deviation, a result not common when least-squares refinement of parameters is employed.

Experimental

Since HPH report that the same powder pattern is obtained for BaSnS₂ prepared at 800°C or at 650°C, and that long annealing at 650°C failed to indicate any low-temperature modification, we prepared the material from a 1:1 mixture of BaS and SnS fired at 750°C for two weeks, cooling it by cutting off power to the furnace. The material appeared as yellow–orange plate-like crystals with some metallic luster. The main peaks in the powder pattern approximately matched those in the pattern reported by HPH. Several single crystals were selected and oscillation, zero and upper-level Weissenberg and zero-level precession photographs were taken. The diffraction symmetry observed was $2/m$ and the systematic absences were $h0l$, $l = 2n + 1$

and $0k0$, $k = 2n + 1$. These results uniquely characterize the space group as $P2_1/c$ (No. 14). The best crystal was transferred to a three-circle single-crystal diffractometer and 22 reflections with 2θ ranging between 40 and 54° were accurately centered on the Mo $K\alpha_1$ and Mo $K\alpha_2$ radiation peaks ($\lambda_1 = 0\cdot70926$ Å, $\lambda_2 = 0\cdot71354$ Å), with the instrument set at a take-off angle of 1° and a 0·05° slit in front of the scintillation counter aperture. The 2θ values, measured at room temperature, $20 \pm 0\cdot5$°C, were used in a least-squares refinement of the lattice parameters $a = 6\cdot0848$ (3), $b = 12\cdot1396$ (8), $c = 6\cdot2356$ (2) Å, $\beta = 97\cdot058$ (4)°.

Three-dimensional intensity data to $\sin\theta/\lambda = 0\cdot65$ were collected with Mo $K\alpha$ radiation, using balanced filters and the stationary-crystal stationary-counter technique, with the diffractometer set at a 5° take-off angle, no slit between the receiving collimator and the counter window, and the channel width of the pulse-height analyzer set to accept 85% of the incident power. Preliminary ω scans performed under these conditions for several reflections had shown peak widths less than 0·75° measured at the base of the peaks. Intensities were counted for 20 sec with a Zr filter, and then background was measured for the same length of time with an Y filter. A total of 1049 independent reflections were measured of which 878 were considered observed on the basis that the peak count exceeded the background by 8 counts in 20 sec. The measured intensities were transformed into structure-factor amplitudes after application of Lorentz, polarization and absorption corrections.
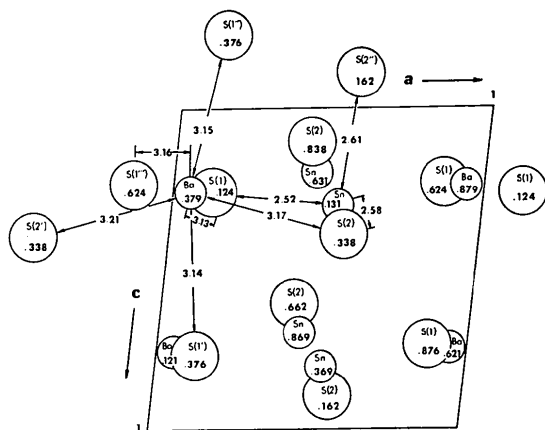
For the absorption correction the shape of the crystal, approximately $0\cdot09 \times 0\cdot09 \times 0\cdot06$ mm, was described by six planes, and the calculated transmission factors ranged from $0\cdot234$ to $0\cdot382$; $\mu_1 = 149$ cm^{-1}, calculated on the assumption of having 4 formula units of $BaSnS_2$ per unit cell, $\rho_x = 4\cdot65$ g cm^{-3}. The expression (Evans, 1961)

$$\sigma(|F|) = \tfrac{1}{2}\left[K\cdot\frac{1+b}{1-b}\right]^{\frac{1}{2}}$$

was used to estimate the standard deviation of the observed structure amplitudes, where $b = I_Y/I_{Zr}$ is the background to peak ratio, and K is the product of the absorption, Lorentz and polarization corrections. For unobserved reflections, the standard deviation was set at $|F|/\sqrt{2}$ and $|F|$ was computed by assuming the intensity to be 4 counts in 20 sec, half the limit value considered observable, and applying to this intensity the corresponding corrections.

Structure determination

The structure was solved from the three-dimensional Patterson function which yielded the heavy-atom positions. They were used to calculate a three-dimensional electron-density map which yielded the positions of the other atoms.

The structure was refined by least squares with the exclusion of the unobserved reflections. Ten reflections with intensity higher than 6000 counts were also excluded in order to minimize the influence of extinction. Since Ba and Sn are not very different in scattering power the following models were refined varying all positional, anisotropic thermal parameters and scale factor:

Hypothesis	Heavy-atom position 1	Heavy-atom position 2	R	wR
I	Ba	Sn	0·0373	0·0455
II	Sn	Ba	0·0590	0·0796
III	$\tfrac{1}{2}$Ba$+\tfrac{1}{2}$Sn	$\tfrac{1}{2}$Ba$+\tfrac{1}{2}$Sn	0·0432	0·0557

$(R = \sum||F_o| - |F_c||/\sum|F_o|$, $wR = [\sum w(F_o - F_c)^2/\sum wF_o^2]^{1/2}$, function minimized $\sum w||F_o| - |F_c||)$.

Hypotheses II and III can be rejected on the basis of a statistical test (Hamilton, 1965) at least at the 0·005 significance level. The choice of hypothesis I will be seen to be further supported by chemical evidence. The scattering factors for the neutral atoms uncorrected for dispersion were used in the calcula

Fig. 1. Projection of the structure on (010). The numbers denote the y parameter; distances are in Å.

Table 1. *Atomic parameters for* $BaSnS_2$ *and standard deviations* (*in parentheses*) $\times 10^4$

The temperature factor is $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ba	567 (1)	3796 (1)	2589 (1)	106 (2)	24 (1)	54 (2)	11 (1)	22 (2)	4 (1)
Sn	5412 (1)	1307 (1)	3018 (1)	65 (3)	31 (1)	81 (2)	7 (1)	6 (2)	10 (1)
S(1)	1249 (5)	1239 (3)	2668 (5)	68 (8)	22 (2)	43 (7)	− 4 (3)	20 (6)	−1 (3)
S(2)	5699 (6)	3381 (3)	3916 (5)	68 (9)	32 (2)	71 (8)	−10 (4)	26 (7)	− 6 (3)

tions (*International Tables for X-ray Crystallography*, 1962). The standard deviation of a reflection of unit weight $[\sum w(|F_o|-|F_c|)^2/(n_o-n_v)]$ is 1·201. In the final cycle of refinement the parameter shifts were all less than 5% of the corresponding standard deviations.

The final atomic parameters are listed in Table 1. A structure-factor calculation with these parameters fixed and including all 1049 measured reflections gave $R=0·0574$. The observed and calculated structure factor amplitudes are listed in Table 2. A difference-electron-density map showed no peaks higher than 0·55 e Å^{-3}.

Discussion of the structure

A projection of the structure on the (010) plane is shown in Fig. 1. The important interatomic distances and angles are tabulated in Table 3.

The structure can be described as a mixture of the structures of BaS and SnS and, insofar as BaS has the NaCl structure and the SnS is usually considered a distortion of the same type, the structure of $BaSnS_2$ can be also considered as a distortion of the NaCl

Table 3. *Interatomic distances and angles for* $BaSnS_2$

Standard deviations in parentheses

Ba–S(1)	3·131 (6) Å	Sn–S(1)	2·517 (6) Å
Ba–S(1′)	3·144 (6)	Sn–S(2)	2·580 (6)
Ba–S(1″)	3·147 (6)	Sn–S(2″)	2·612 (6)
Ba–S(1‴)	3·162 (6)	Sn–S(1^{iv})	3·586 (6)
Ba–S(2)	3·171 (6)	Sn–S(2‴)	3·680 (6)
Ba–S(2′)	3·212 (6)	Sn–S(2^{iv})	3·786 (6)

S(1) —Ba–S(1′)	88·3 (1)°	S(1)–Sn–S(2)	95·3 (2)°
S(1) —Ba–S(1″)	88·2 (1)	S(1)–Sn–S(2″)	96·2 (2)
S(1) —Ba–S(1‴)	167·3 (1)	S(2)–Sn–S(2″)	93·5 (2)
S(1) —Ba–S(2)	73·4 (1)		
S(1) —Ba–S(2′)	88·0 (1)		
S(1′)—Ba–S(1″)	164·9 (1)		
S(1′)—Ba–S(1‴)	93·8 (1)		
S(1′)—Ba–S(2)	74·4 (1)		
S(1′)—Ba–S(2′)	75·5 (1)		
S(1″) –Ba–S(1‴)	92·9 (1)		
S(1″) –Ba–S(2)	90·5 (1)		
S(1″) –Ba–S(2′)	119·0 (1)		
S(1‴)–Ba–S(2)	119·3 (1)		
S(1‴)–Ba–S(2′)	80·4 (1)		
S(2) —Ba–S(2′)	144·8 (1)		

Table 2. *Observed and calculated structure factors for* $BaSnS_2$

* Denotes unobserved reflection.
† Denotes reflection subject to extinction.

Table 4. *Observed and calculated powder pattern for* $BaSnS_2$ ($\lambda = 1·5405$ Å)

d_{HPH}	d_{obs}	d_{calc}	I_{obs}	I_{calc}	I_{HPH}	hkl
	4·26	4·281	6	3		120
	3·85	3·866	11	6		111
3·65	3·66	3·674	79	83	80	12$\bar{1}$
3·35	3·38	3·385	53	69	80	121,031
3·04	3·09	3·094	40	47	50	002
3·00	3·03	*{ 3·035	100	100	100	040
		{ 3·019				200
	2·99	2·998	16	12		01$\bar{2}$
	2·93	2·930	37	28		210
2·88	2·88	2·873	4	2	50	131
2·80	2·81	2·823	13	11	20	11$\bar{2}$
	2·64	*{ 2·626	4	3		102
		{ 2·618				12$\bar{2}$
	2·44	2·458	4	3		032
2·403	2·415	2·420	18	13	20	230
2·296	2·302	2·307	13	20	20	20$\bar{2}$
2·155	2·168	2·166	51	33	50	042
2·129	2·139	2·140	45	24	50	240
2·000	2·013	2·011	15	16	20	212
1·950					20	
1·913	1·925	1·920	12	15	20	12$\bar{3}$
1·883	1·888	*{ 1·892	16	16	20	250
		{ 1·888				32$\bar{1}$
1·841	1·852	1·853	13	15	20	16$\bar{1}$
	1·836	1·837	13	17		24$\bar{2}$
1·828	1·821	*{ 1·827	11	13	20	311
		{ 1·821				232
	1·812	1·812	8	10		161
1·805	1·799	1·798	8	9	20	123
1·761	1·769	*{ 1·772	9	8	20	31$\bar{2}$
		{ 1·768				321
	1·705	1·707	4	3		133
1·675	1·680	1·681	4	4	20	331
1·626					20	
1·562	1·560	1·562	6	7	20	252
1·534					20	
1·512	1·516	1·517	9	6	20	080

* Unresolved doublet

structure. Both Ba and Sn retain the same coordination polyhedron which they have in their corresponding monosulfides. Ba is in sixfold coordination with Ba–S distances ranging from 3·13 Å to 3·21 Å forming a distorted octahedron. The Sn atom is also in a distorted octahedral void, but instead of being in the center of the octahedron it moves very close to one of the triangular faces so as to become bonded to 3 S atoms, Sn–S distances of 2·52, 2·58 and 2·61 Å, and is very far from the other 3 S atoms, Sn–S distances of 3·59, 3·68 and 3·79 Å. This kind of polar environment is usually expected for ions with s^2 configuration (Jellinek, 1968) in which one of the sp^3 hybrid orbitals is occupied by the lone pair and the other three are filled by electrons donated by the sulfur ions. Thus the Sn polyhedron can be described as a tetrahedron with one corner occupied by a lone pair of electrons.

As previously mentioned, the structure can be considered as a distortion of the NaCl structure if one considers both metal sites as equivalent. The cations are ordered in slightly puckered layers parallel to (100) in such a way that Ba layers alternate with Sn layers following the overall architecture of the NaCl structure.

Our observed powder pattern does not match HPH's except in a qualitative manner, Table 4. There is substantial agreement for the six strongest lines, but the line we observe at 2·93 Å is not present in HPH's pattern or else it corresponds to the one at 2·88 Å. For the weaker reflections there is qualitative agreement in

intensity between our pattern and theirs, but the positions of the lines do not agree very well. We thought that a monoclinic polymorph of $BaSnS_2$ exists and that HPH had synthesized an orthorhombic one. However, they report the same phase at 800°C and at 650°C and the existence of a different modification at 750°C seems improbable. We repeated HPH's preparation of $BaSnS_2$ by heating BaS:SnS at 800°C for three days and obtained the same powder pattern that we found in the first preparation at 750°C which had been heated for two weeks. The possibility that there is, indeed, an orthorhombic polymorph seems remote.

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The Crystal Structure of an Anorthoclase: an Intermediate Alkali Feldspar

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The results of a structure analysis of an anorthoclase (Or 29%, Ab 65%, An 6%) are reported. By use of three-dimensional difference Fourier and least-squares techniques, parameters have been refined to give $R = 7·7\%$. The structure appears to be completely disordered with respect to Al and Si distribution. The anisotropy of the electron densities for the Na/K atom is discussed.

Introduction

Potassium feldspars display a number of different crystal structures which have been studied by many authors. We may mention, in this connexion, the determination and refinement of two sanidine structures obtained by heating orthoclase (Cole, Sörum & Kennard, 1949; Ribbe, 1963), of natural sanidine (Onorato, Penta & Sgarlata, 1963), of an orthoclase (Jones & Taylor, 1961; Colville & Ribbe, 1968), of an adularia (Colville & Ribbe, 1968), of an intermediate microcline (Bailey & Taylor, 1955), and of two maximum micro-

clines (Brown & Bailey, 1964; Finney & Bailey, 1964). In addition, the high and low albite structures are well known (Ferguson, Traill & Taylor, 1958; Ribbe, Megaw & Taylor, 1969). It would appear, therefore, that apart from some as yet unresolved details the end-members of the alkali feldspar series are well determined. On the other hand, absolutely nothing is known about the structures of the intermediate members.

In this paper we wish to report the results of a structure analysis of one of these intermediate members, a natural anorthoclase (Or 29%, Ab 65% An 6%). The