The composition is now $In_{40}S_{32}$, which corresponds to the unit-cell content.

Structural relationships

The In atom at the center of the In_2S_3 tetrahedron has an environment of three S and one In atom.

A similar coordination is found among other combinations of elements from the same groups, for instance GaS (Hahn & Frank, 1955). However, the building units in the layer structure of GaS are S_6 prisms with two Ga atoms inside.

Mixed tetrahedral coordination is also exhibited by 1:1 combinations of elements from the Groups IV and V such as SiAs (Wadsten, 1965) and SiP (Wadsten, 1975). The building units of these layer compounds are As_6 or P_6 octahedra surrounding two Si atoms.

The compound InS (Schubert *et al.*, 1954) can also be included as an example of mixed tetrahedral environment for the In atoms, but the structure can be visualized as being built up of corner-sharing In_2S_6 octahedra.

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Sulphides with the $GdFeO_3$ Structure

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Abstract

$CaZrS_3$, $SrZrS_3$, $BaZrS_3$, $BaUS_3$, $CaHfS_3$, $BaHfS_3$, $EuZrS_3$ and $EuHfS_3$ have been found to have the $GdFeO_3$ ($CaTiO_3$) structure, *Pnma*, with $Z = 4$. For the first four compounds, atomic positional parameters have been determined by neutron diffraction powder methods. [R_w values were 8·00, 7·51, 8·14 and 8·49 respectively.]

Introduction

We have investigated the crystal structures of ABS_3 type compounds with A = Ca, Sr, Ba and Eu, and B = Zr, Hf and U. This is part of a research programme on the structural relations of compounds ABX_3, where A represents an alkaline or an alkaline-earth metal, B a transition metal and X a halogen or S (van Loon & Verschoor, 1973; van Loon, 1974; Crama, Maaskant & Verschoor, 1978; Lelieveld & IJdo, 1978).

Single crystals of the ABS_3 compounds were not available, so we decided to use the neutron powder-profile-refinement technique (Rietveld, 1969) in order to obtain precise structural information for the Zr and U compounds. The ionic radii for Zr and Hf for six-coordination are 0·72 and 0·71 Å respectively; hence, the same structures for $AZrS_3$ and $AHfS_3$ can be expected. Moreover, for routine neutron powder-diffraction experiments samples of about 30 g are needed, so we limited ourselves to the Zr and U compounds. Neutron diffraction for Eu compounds is not useful because of the high absorption of Eu.

Hahn & Mutschke (1956) prepared $BaZrS_3$ and produced an X-ray powder diagram, which they indexed as a tetragonal deformed perovskite; they were unable to prepare $SrZrS_3$ and $CaZrS_3$. Clearfield (1963) published the X-ray powder diagrams of

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BaZrS$_3$, SrZrS$_3$ and CaZrS$_3$. From these he concluded BaZrS$_3$ to be a distorted perovskite of the GdFeO$_3$ type (Geller, 1956), and proposed a highly distorted multiple-cell perovskite structure for SrZrS$_3$ and CaZrS$_3$. Brochu, Padiou & Grandjean (1970) published the X-ray powder structure determination of BaUS$_3$ which is also isomorphous with GdFeO$_3$.

Experimental and interpretative work

We prepared the compounds by firing appropriate mixtures of alkaline-earth carbonates and transition-metal dioxides in a stream of hydrogen sulphide in an induction furnace with carbon crucibles at temperatures of about 1373 K for a week. EuZrS$_3$ and EuHfS$_3$ were prepared by heating the binary compounds in an evacuated silica tube at 1373 K.

The X-ray powder-diffraction patterns were obtained with a Philips PW 1050 diffractometer. The patterns could all be indexed without the doubling of axes reported by Clearfield (1963). The symmetry and systematic absences led to the space group *Pnma* or *Pn*2$_1$*a*. The lattice parameters were determined by means of a least-squares computer program (van Laar & IJdo, 1969).

The neutron diffraction diagrams were collected at 300 K on the powder diffractometer at the Petten High-Flux Reactor as described by van Laar, Rietveld & IJdo (1971). A wavelength of 2·57 Å from the (111) planes of a Cu monochromator was used. The complete range of data obtained ($5{\cdot}4° < 2\theta < 138°$) was used in the refinement. Absorption and extinction effects were small and no corrections were made. The samples were contained in thin-walled vanadium tubes.

Structure refinements were carried out using the Rietveld (1969) profile method by minimizing the residual function $\sum w\left[y_i(\text{obs.}) - \frac{1}{c}\, y_i(\text{calc.})\right]^2$, where y(obs.) and y(calc.) are the observed and calculated intensities per measuring point in a peak, w is the statistical weight and c the scale factor. For the trial model, the setting chosen was that which gave the space group as *Pnma*, with orthorhombic lattice parameters a, b, c, and atomic positions as follows: A in 4(c): $x,\frac{1}{4},z$; B in 4(b): $0,0,\frac{1}{2}$; S(1) in 4(c), and S(2) in 8(d): x,y,z. The atomic positional parameters of UCrS$_3$ (Noël, Padiou & Prigent, 1975), for which a different setting and origin had originally been used, were transformed to the present setting to give initial values for the model of CaZrS$_3$, and the refined values for CaZrS$_3$ in turn gave initial values for the other

Table 1. *Lattice parameters* (Å)

(a) Compounds studied in this work

Standard errors in the lattice parameters do not include errors in the neutron wavelengths, which were 2·5701 (4) for a, 2·5699 (4) for b and 2·5745 (3) Å for c. The X-ray wavelength was 1·54178 Å.

	a	b	c		
CaZrS$_3$	7·0300 (4)	9·5896 (6)	6·5366 (3)	Neutron diffraction	a
SrZrS$_3$	7·1085 (4)	9·7661 (5)	6·7350 (3)		b
BaZrS$_3$	7·0599 (8)	9·9813 (17)	7·0251 (12)		c
BaUS$_3$	7·4823 (5)	10·3801 (7)	7·2148 (5)		c
CaHfS$_3$	6·983 (3)	9·537 (4)	6·518 (3)	X-ray diffraction	
SrHfS$_3$	7·051 (4)	9·716 (4)	6·718 (3)		
BaHfS$_3$	7·002 (6)	9·915 (6)	6·995 (6)		
EuZrS$_3$	7·107 (2)	9·719 (2)	6·671 (2)		
EuHfS$_3$	7·057 (3)	9·678 (4)	6·661 (3)		

(b) Values from the literature

	a	b	c	
CaZrS$_3$	14·05	9·58	13·07	Clearfield (1963)
SrZrS$_3$	14·23	9·79	13·49	Clearfield (1963)
BaZrS$_3$	7·050	9·983	7·037	Clearfield (1963)
BaZrS$_3$	4·990 (6)	4·990 (6)	5·088 (6)	Hahn & Mutschke (1956)
BaUS$_3$	7·44	10·38	7·24	Brochu *et al.* (1970)
UCrS$_3$	7·163	8·851	6·095	Noël *et al.* (1975)

Table 2. *Atomic parameters*

(a) This work

	A		S(1)		S(2)		
	x	z	$-x$	z	x	$-y$	z
CaZrS$_3$	0·0903 (4)	0·0333 (7)	0·0345 (9)	0·6252 (9)	0·1897 (6)	0·0626 (4)	0·8185 (6)
SrZrS$_3$	0·0769 (3)	0·0228 (5)	0·0177 (8)	0·5987 (8)	0·1962 (6)	0·0477 (5)	0·8086 (6)
BaZrS$_3$	0·0376 (5)	0·0069 (16)	0·0045 (13)	0·5614 (21)	0·2155 (14)	0·0293 (9)	0·7869 (12)
BaUS$_3$	0·0593 (4)	0·0154 (9)	0·0212 (11)	0·5906 (10)	0·2003 (7)	0·0471 (6)	0·8004 (7)

(b) Values from the literature

Where necessary, parameter values have been transformed from the original setting (including choice of origin) used in the work quoted to the setting and origin adopted in the present work.

	A		X(1)		X(2)		
	x	z	$-x$	z	x	$-y$	z
BaUS$_3$^{a}	0·055	0	0·02	0·54	0·23	0·03	0·77
UCrS$_3$^{b}	0·1172 (9)	0·0518 (1)	0·0421 (6)	0·6406 (8)	0·1715 (4)	0·0590 (3)	0·8320 (5)
GdFeO$_3$^{c}	0·06284 (6)	0·01556 (5)	0·0328 (11)	0·6005 (10)	0·1984 (6)	0·0506 (4)	0·8043 (6)
SrZrO$_3$^{d}	0·025 (1)	0·001 (2)	0·015 (1)	0·573 (2)	0·215 (1)	0·035 (1)	0·784 (1)

References: (a) Brochu *et al.* (1970). (b) Noël *et al.* (1975). (c) Marezio *et al.* (1970). (d) Ahtee *et al.* (1976).

Table 3. *Isotropic temperature factors* (Å²) *and* R_w *values*

	Isotropic temperature factors				
	A	B	S(1)	S(2)	R_w
$CaZrS_3$	1·35 (11)	0·69 (7)	0·84 (17)	0·73 (11)	8·00
$SrZrS_3$	0·60 (7)	0·76 (7)	0·43 (17)	0·76 (12)	7·51
$BaZrS_3$	1·12 (9)	0·76 (6)	0·69 (33)	0·98 (18)	8·14
$BaUS_3$	1·45 (11)	0·50 (6)	0·47 (21)	0·95 (15)	8·49

Table 4. *Interatomic distances* (Å) *and angles* (°)

Distances marked with an asterisk occur in pairs.

	$BaZrS_3$	$SrZrS_3$	$CaZrS_3$	$BaUS_3$
A–S(1)	3·144 (18)	2·934 (4)	2·808 (7)	3·123 (9)
	3·269 (10)	2·996 (6)	2·835 (7)	3·231 (9)
A–S(2)*	3·426 (11)	3·354 (5)	3·383 (5)	3·609 (7)
*	3·185 (11)	2·994 (5)	2·836 (5)	3·158 (7)
*	3·430 (11)	3·196 (6)	3·016 (5)	3·450 (7)
A–S(1)a	3·857 (10)	4·305 (6)	3·967 (7)	4·410 (9)
a	3·907 (18)			4·194 (9)
–S(2)*a	4·147 (11)			
B–S(1)*	2·533 (3)	2·534 (2)	2·545 (2)	2·681 (2)
–S(2)*	2·542 (9)	2·546 (4)	2·544 (4)	2·680 (5)
*	2·522 (9)	2·558 (4)	2·555 (4)	2·709 (5)
S(1)–S(1)*	4·414 (7)	4·097 (6)	3·875 (5)	4·392 (7)
S(1)–S(2)*b	3·562 (12)	3·573 (6)	3·615 (5)	3·814 (7)
*b	3·580 (11)	3·603 (6)	3·589 (6)	3·804 (7)
*b	3·614 (14)	3·611 (6)	3·582 (6)	3·767 (8)
*b	3·569 (13)	3·597 (7)	3·623 (7)	3·819 (8)
*			4·201 (7)	
S(2)–S(2)*b	3·594 (4)	3·577 (3)	3·584 (4)	3·811 (4)
*b	3·568 (2)	3·641 (2)	3·627 (2)	3·811 (2)
	4·309 (18)	3·911 (9)	3·767 (9)	4·270 (11)
	4·406 (17)	3·952 (10)	3·594 (9)	4·213 (13)
B–S(1)–B	160·3 (6)	149·0 (2)	140·8 (2)	150·9 (3)
B–S(2)–B	159·1 (4)	147·2 (2)	140·6 (2)	149·3 (2)
S(1)–B–S(2)	89·2 (4)	89·4 (2)	90·5 (2)	90·7 (2)
	89·8 (4)	89·9 (2)	90·5 (2)	90·2 (2)
S(2)–B–S(2)	90·4 (1)	89·0 (1)	89·3 (1)	90·0 (1)

(*a*) Additional distance from the cuboctahedron, not belonging to the bicapped prism.
(*b*) Edges belonging to the BS_6 octahedra.

compounds. The variables in the refinement were: a scale factor, three half-width parameters defining the Gaussian line shape, the counter zero error, the unit-cell parameters, the atomic positional parameters, isotropic temperature factors and an asymmetry parameter. The coherent scattering lengths assumed were: Ca 4·7, Sr 6·9, Ba 5·2, Zr 7·1, U 8·5 and S 2·8 fm (Bacon, 1972). The R factor was calculated by

$$R_w = 100\left[\sum w|y(\text{obs.}) - \frac{1}{c}\,y(\text{calc.})\,|^2/\sum w|y(\text{obs.})|^2\right]^{1/2}$$

where w, y and c are as defined above. Repetition with a trial model using space group $Pn2_1a$ with the same initial parameters gave no significantly better results.

Results

The lattice parameters found here for all nine compounds are shown in Table 1(*a*) and the values from the literature are in Table 1(*b*). The atomic parameters for the four compounds studied in fuller detail are given in Table 2 along with the values from the literature.* Thermal parameters are given in Table 3. Calculated R_w factors are shown in the same table. Table 4 gives the interatomic distances and angles.

Discussion

From Table 1(*a*), it can be seen that in the series ABS_3, with increasing radius of A the b and c parameters increase, while the a parameter goes through a maximum. Table 4 shows that with decreasing radius of A the distances between the first-nearest S and A atoms decrease, but the distances between the second-nearest S and A atoms increase, resulting in decreasing coordination of A. The coordination polyhedron about A is in this way reduced from a cuboctahedron to a slightly distorted bicapped trigonal prism. In $BaZrS_3$ the four additional distances belonging to the cuboctahedron are still involved in the coördination. The same behaviour was reported by Marezio, Remeika & Dernier (1970) for several ternary oxides with the $GdFeO_3$ structure.

The facts above can be explained in terms of the tilting of octahedra in the ideal perovskite structure. The ideal perovskite structure, with general formula ABX_3, consists essentially of a framework of parallel BX_6 octahedra linked by their corners, with a large A atom occupying a void of about the same size as an X atom. If the radius of A is too small, the void is reduced in size by tilting of the octahedra. Megaw (1972), Glazer (1972) and O'Keeffe & Hyde (1977) analysed these tilts in terms of regular octahedra. Megaw's analysis for the $GdFeO_3$ ($CaTiO_3$)-type tilt system used two independent rotation angles, φ about [101] of the aristotype and ω about [010] of the aristotype, interactions between the two being negligibly small. The rotation angles can be calculated in two ways: (i) if the octahedra are assumed to be regular, they are deducible from the lattice parameters, (ii) when positional parameters are known, they can be found without any such assumption. O'Keeffe & Hyde postulated a rotation φ (hereafter called φ_O) about two or more $\langle 111 \rangle$ axes of the aristotype, their interactions creating a small rotation ψ about the [001] axis of the orthorhombic structure, and used this to study the effect of varying φ_O, for different combinations of $\langle 111 \rangle$ axes, in a wide variety of perovskites and related compounds, but did not test its validity for structures with *Pnma* symmetry. Like Megaw, they gave

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* A list of observed and calculated neutron profile intensities has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35326 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

expressions relating their φ's either to a,b,c or to the x,y,z values.

Using the cubic reference axes of the aristotype, it can be shown geometrically that, if small rotations p about [010] and q about [101] give a resultant r about [111], then

$$p:q:r = 1:\sqrt{2}:\sqrt{3}.$$

The fact noted by Megaw (1972) that for many compounds $\omega = \varphi_M/\sqrt{2}$ is thus evidence for the $\langle 111 \rangle$ direction of the tilt axes. Further evidence is provided in Table 5. It follows that $\varphi_O = \sqrt{3}\omega$. We must distinguish between values of tilt angles calculated from lattice parameters, $\omega(l)$ or $\varphi(l)$, and those calculated from atomic position parameters, $\omega(a)$ or $\varphi(a)$. Following Megaw and O'Keeffe & Hyde, we write

$$\omega_M(a) = \tfrac{1}{2}\tan^{-1}\{2[2z_{X(2)} - 1{,}5]c/a\} + \tfrac{1}{2}\tan^{-1}\{2[\tfrac{1}{2} - 2x_{X(2)}]a/c\},$$

$$\varphi_M(a) = \tan^{-1}\{-2y_{X(2)}b/\sqrt{[(\tfrac{1}{2}c)^2 + \{[\tfrac{1}{2} - 2x_{X(2)}]a\}^2]}\},$$

$$\varphi_O(a) = \tan^{-1}[-y_{X(2)}b\sqrt{48}] \simeq \frac{\sqrt{3}}{\sqrt{2}}\,\varphi_M(a).$$

For calculations from the lattice parameters we have

$$\omega(l) = \cos^{-1}(\sqrt{2}c/b), \quad \cos\varphi_M(l) = \cos^{-1}(c/a),$$

$$\varphi_O(l) = \cos^{-1}\left(\frac{\sqrt{2}c^2}{ab}\right),$$

thus $\cos\varphi_O(l) = \cos\omega(l)\cos\varphi_M(l)$.

In Table 5, values of the tilt angles have been calculated for the four compounds studied in the present work, and also for comparison for $UCrS_3$ (Noël, Padiou & Prigent, 1975), $GdFeO_3$ (Marezio, Remeika & Dernier, 1970) and $SrZrO_3$ (Ahtee, Ahtee, Glazer & Hewat, 1976). The following points may be noted: (i) a general near-equality of values in the first pair of columns, and again in the second pair, in agreement with the postulate of O'Keeffe & Hyde (1977); (ii) rather greater differences between the two pairs of columns, giving an indication of the distortion of the octahedra, in particular for $UCrS_3$ which has a Jahn–Teller distorted octahedron around Cr; (iii) with decreasing A radius and increasing B radius there are increasing tilts, which act to reduce the void available for A.

Table 5. *Tilt angles* (°)

	$\omega(l)$	$\varphi_M(l)/\sqrt{2}$	$\omega(a)$	$\varphi_M(a)/\sqrt{2}$
$BaZrS_3$	5·5	4·0	8·1	6·6
$SrZrS_3$	12·8	13·2	12·7	10·7
$CaZrS_3$	15·4	15·3	14·4	13·5
$BaUS_3$	10·6	10·9	11·3	10·5
$UCrS_3$	13·1	22·4	17·9	12·6
$SrZrO_3$	3·2	4·0	7·9	7·9
$GdFeO_3$	9·5	12·4	12·0	11·2

From the similarity in the lattice parameters of the remaining compounds in Table 1(a), and their dependence on A, it is concluded that they are isostructural with $GdFeO_3$.

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