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The Synthesis and Crystal Structures of some Alkaline Earth Titanium and Zirconium Sulfides

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Barium titanium sulfide ($BaTiS_3$) and calcium, strontium and barium zirconium sulfides ($CaZrS_3$, $SrZrS_3$ and $BaZrS_3$) have been synthesized by the reaction of CS_2 with the respective ternary oxides at elevated temperatures. Barium titanium sulfide is hexagonal but its sulfur content decreases with increasing temperature of preparation. This results in a variation of unit cell dimensions from $a=6·752$, $c=5·810$ Å when prepared at 700 °C. to $a=6·77$, $c=5·74$ Å when prepared at 1100 °C. $BaTiS_3$ containing a stoichiometric or near stoichiometric equivalence of sulfur has the barium nickelate structure. As the sulfur content decreases the structure becomes increasingly disordered. $BaZrS_3$ is orthorhombic with $a=7·037$, $b=9·983$, $c=7·050$ Å and has a distorted perovskite structure. $SrZrS_3$ and $CaZrS_3$ have even more highly distorted perovskite structures and require orthorhombic unit cells with $a=13·49$, $b=9·79$, $c=14·23$ Å for $SrZrS_3$ and $a=13·07$, $b=9·58$, $c=14·05$ Å for $CaZrS_3$.

Introduction

Hahn & Mutschke (1956) prepared $SrTiS_3$, $BaTiS_3$ and $BaZrS_3$ by heating mixtures of the binary sulfides in sealed evacuated tubes for several weeks. The strontium and barium titanium sulfides were isomorphous and could be indexed by means of hexagonal, orthorhombic or tetragonal unit cells. These compounds were tentatively assigned the hexagonal $BaNiO_3$ structure (Lander, 1951). However, some serious discrepancies between the calculated and observed intensities were obtained. Barium zirconium sulfide was found to be dimorphic. The allotrope prepared below about 800 °C. was found to be tetragonal with $a=4·990$, $c=5·088$ Å and to have a perovskite structure. The high temperature form could not be indexed.

This paper describes the preparation of alkaline earth titanium and zirconium sulfides by the action of CS_2 on the corresponding ternary oxides together with additional observations on their structure.

Experimental

All of the titanates and zirconates used were c.p. grade (TAM Division, National Lead Company) and contained less than 0·2% total metallic impurities. Powder patterns of the ternary oxides showed the presence of only the desired phase. The sulfiding procedure was similar to that used for the preparation of ZrS_2 (Clearfield, 1958). Argon was bubbled through a tower containing CS_2 and the resultant gas mixture then led into a zircon combustion tube containing 10 g. of the ternary oxide in a carbon boat. The flow rate of the argon was fairly constant so that the amount of CS_2 entering the combustion tube was roughly proportional to the reaction time. Powder patterns were obtained with a G. E. XRD-3 X-ray unit and diffractometer using filtered Cu $K\alpha$ radiation. Aluminum powder and aluminum oxide were used as internal standards for the determination of accurate unit cell dimensions.

Barium titanium sulfide

The preparation of $BaTiS_3$ was carried out at one hundred degree intervals in the temperature range 400–1100 °C. Only small amounts (up to 30%) of sulfide were obtained in 4 hours time below 700 °C. However, the products obtained in 4 hours reaction time at 700 to 1000 °C. showed only the presence of the single phase $BaTiS_3$. The powder patterns of the 1100 °C. preparations contained some new reflections. Reaction times in the order of 24 hours were required to eliminate or reduce to low values the intensities of these reflections.

The powder patterns could be indexed on the basis of either an orthorhombic or hexagonal unit cell. However, the unit cell dimensions changed slightly with temperature of preparation. This is shown in Fig. 1 by the increased resolution of the (200), (002) doublet (hexagonal indexing) as a function of temperature of preparation. In all of the $BaTiS_3$ samples the a axis of the orthorhombic unit cell equaled $\sqrt{(3)}c$ and the a–c diagonal equaled $2c$ and made an angle of 60° with the c axis. Thus, the true unit cells are most probably hexagonal with the dimensions given in Table 1. The values reported by Hahn & Mutschke are included for comparison.

Table 1. *Hexagonal unit-cell dimensions of* $BaTiS_3$

Sample no.	Temp. of preparation	a (Å)	c (Å)
2	700 °C.	$6{\cdot}752 \pm 0{\cdot}006$	$5{\cdot}810 \pm 0{\cdot}005$
3	1000	$6{\cdot}758 \pm 0{\cdot}008$	$5{\cdot}778 \pm 0{\cdot}006$
5	1100	$6{\cdot}77 \pm 0{\cdot}01$	$5{\cdot}74 \pm 0{\cdot}01$
Hahn & Mutschke		6·730	5·829

Analytical data for a number of $BaTiS_3$ preparations are given in Table 2. Each of the products also contained 0·1 to 0·3% insolubles (carbon, silica). The fact that the elemental composition of each sample totaled less than 99·7% indicates that oxygen was incompletely replaced by sulfur. Also, the sulfur deficiency increased with increasing temperature of preparation. Thus, the variation in unit cell dimensions appears to be related to the sulfur content of the products.

The unit cell volumes of all the preparations listed in Table 1 are practically identical and contain 2 molecules of $BaTiS_3$ based on Hahn & Mutschke's observed density of 4·00 g.cm.$^{-3}$. Integrated intensities were obtained for preparations No. 2 (700°) and No. 3 (1000°) by counting the area under the peaks for the first 6 reflections using the scaler. The intensities for the remaining reflections were estimated by comparison with the measured reflections. Intensity calculations were first made assuming the barium nickelate structure, space group C_{6v}^4–$P6_3mc$,

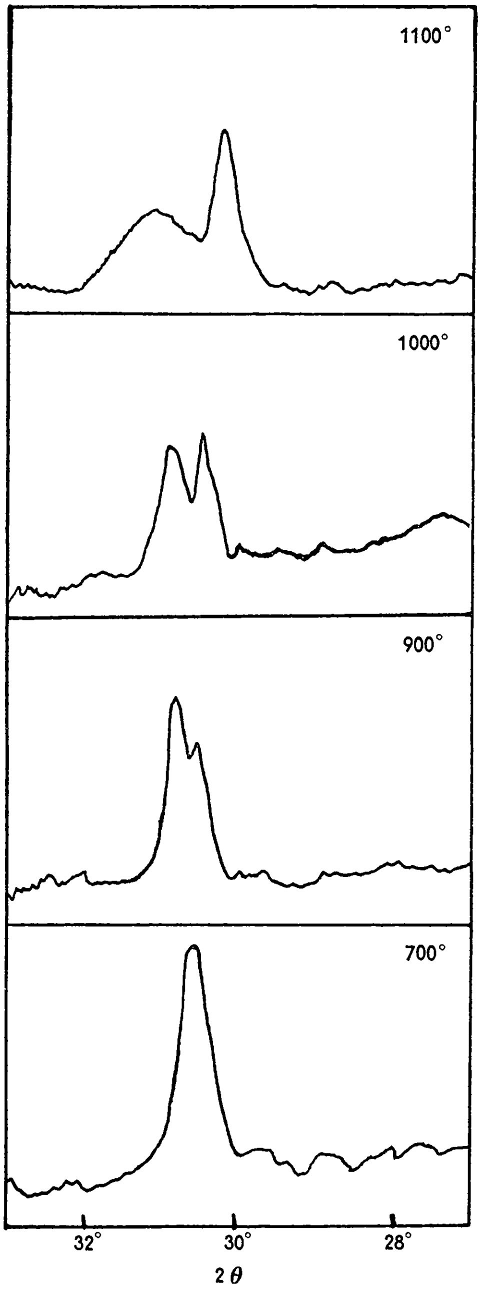

Fig. 1. Effect of temp. of preparation of $BaTiS_3$ upon the intensity and resolution of (200), (002) doublet.

Table 2. *Analytical data for* $BaTiS_3$

Sample no.	Reaction temp. (°C.)	Reaction time (hr.)	% Ba	% Ti	% S	S/Ti	S/Ba
1	700	4	—	—	33·5	—	—
2	700	24	48·25	17·01	34·4	3·02	3·06
3	1000	4	47·82	17·22	33·46	2·90	3·00
4	1000	4	48·65	17·12	33·90	2·96	2·98
5	1100	24	49·78	16·81	32·89	2·88	2·79
	Required for $BaTiS_3$		48·80	17·02	34·18	3·00	3·00

Table 3. *Structure data for* BaTiS$_3$ *prepared at* 700 °C.

hkl	d_o	d_c	$I_c\times10^{-4}$	$\Sigma I_c\times10^{-4}$	$I_o\times10^{-4}$
100	—	5·848	0·5	0·5	0
001	—	5·810	0	0	0
101	4·128	4·122	244	244	237
110	3·387	3·377	210	210	215
111		2·920	0	0	0
200	2·924	2·924	39·2	123	110
002	2·906	2·905	84		
201	2·614	2·612	415	499	473
102		2·602	84		
210	2·201	2·210	0·4	19·9	19·4
112		2·202	19·5		
211	2·063	2·066	68	172	161
202		2·061	104		
300	1·949	1·949	37	37	37
003	—	1·937	0	0	0
301	—	1·848	0	0	0
103	1·836	1·839	22·4	22·4	19
212	1·758	1·759	43	43	30
113	—	1·680	0	0	0
220	1·688	1·688	67	67	77
310	—	1·622	0·2	0·2	0
221		1·621	0		
302	1·613	1·619	6·1	65·6	57
203		1·615	59·5		
311	1·565	1·562	21	21	17·6
400	1·459	1·462	2·4	61·9	54
222		1·460	33·3		
213		1·457	14·9		
004		1·452	11·3		
401	1·417	1·418	31·8	45·8	41·4
312		1·416	14·0		
104	—	1·410	0·1	0·1	0
303	—	1·374	0	0	0
320	—	1·342	0·1	0·1	0
114	1·333	1·334	12·2	12·2	5·8
321	1·307*B*	1·307	8·9	25	26
402		1·306	13·2		
204		1·302	2·9		
410	1·277	1·276	10	10	13
223	—	1·273	0	0	0
411	1·244	1·247	0	6·7	5·2
313		1·244	6·7		
322	1·217	1·218	6·7	6·8	5·2
214		1·214	0·1		
500	1·168*B*	1·170	0	21·6	22·8
412		1·168	2·5		
403		1·167	12·7		
304		1·165	6·4		
005	—	1·162	0	0	0
501	1·147	1·147	2·3	4·6	4
105	1·139	1·140	2·3		
330	1·125	1·125	2·7	2·7	3·5
420	1·102*B*	1·105	1·4	23·2	17
331		1·105	0		
323		1·103	4·0		
224		1·101	17·8		
115		1·099	0		
421	1·086*B*	1·086	18·4	29·6	41
502		1·086	1·9		
314		1·082	0·1		
205		1·080	9·2		
413	—	1·066	0	0	0
510	—	1·050	0	0·8	0
332	—	1·049	0·8		
511	1·034*B*	1·034	3·0	15·9	16·6
422		1·033	9·0		
404		1·030	1·0		
215		1·029	2·9		
503	—	1·001	1·6	1·6	0
305	—	0·9981	0	0	0
512	—	0·9878	2·7	2·7	0
324	—	0·9855	0·05	0·05	0
600	0·9749	0·9744	5·6	5·6	9·0
333	—	0·9731	0	0	0
006	—	0·9683	0·9	0·9	0
430	—	0·9614	0·1	0·1	0
601	—	0·9613	0	0	0
423	0·9594*B*	0·9599	12·5	18·1	14·6
414		0·9587	5·6		
225	—	0·9572	0	0	0
106	—	0·9553	1·3	1·3	0
431	—	0·9485	2·4	2·4	0
315	—	0·9446	2·4	2·4	0
520	0·9368	0·9364	2·9	2·9	4
116	—	0·9308	0·6	0	0
521	—	0·9246	0	0	0
602	0·9237*B*	0·9241	4·8	7·0	8·5
513		0·9233	2·2		
206	—	0·9192	3·3	3·3	0
432	—	0·9127	0·5	0·5	0
504	—	0·9110	0	0	0
405	—	0·9097	5·8	5·8	0
610	—	0·8918	0·02	0·02	0
522	—	0·8913	1·1	1·1	0
334	—	0·8896	2·7	2·7	0
216	—	0·8866	2·2	2·2	0
611	—	0·8815	2·0	2·0	0
424	—	0·8795	1·4	1·4	0
325	—	0·8783	2·1	2·1	0
603	—	0·8703	0	0	0
306	—	0·8672	0·02	0·02	0
433	—	0·8611	2·1	2·1	0
415	—	0·8592	0	0	0
612	—	0·8526	2·1	2·1	0
514	—	0·8511	0·02	0·02	0
440	0·8445	0·8441	4·5	4·5	3·5
523	—	0·8430	0	0	0
226	—	0·8399	4·6	4·6	0
530	—	0·8354	0·01	0·02	0
700	—	0·8353	0·01		
441	—	0·8353	0		
316	—	0·8314	2·3	2·3	0
007	—	0·8300	0	0	0
531	—	0·8269	2·2	3·3	0
701	—	0·8269	1·1		
505	—	0·8243	1·1	1·1	0
107	—	0·8218	1·0	1·0	0
620	0·8095*B*	0·8110	0·7	21·9	22·7
442		0·8106	4·9		
613		0·8101	2·4		
604		0·8094	10·3		
335		0·8084	0		
406		0·8073	3·6		
117	—	0·8060	0	0	0
621	0·8036*B*	0·8034	11·7	30·6	38·3
702		0·8029	1·3		
532		0·8029	1·2		
434		0·8017	0		
425		0·8008	11·1		
207		0·7985	5·3		

and the same atomic positions chosen by Hahn & Mutschke (1956). This calculation confirmed the discrepancies noted earlier by these authors. However, when the barium atom parameters were changed to $\frac{2}{3}, \frac{1}{3}, \frac{1}{4}; \frac{1}{3}, \frac{2}{3}, \frac{3}{4}$ the discrepancies disappeared.

Plots of log I_o/I_c versus $(\sin\theta/\lambda)^2$ were made for both the 700° data and the 1000° data. Intensities were then calculated from the equations

$$I_c = m \times LP \times |F_c|^2 \exp -2B\,(\sin\theta/\lambda)^2$$
$$I_c = S \times I_o$$

where

m = multiplicity
LP = Lorentz and polarization factor
S = scale factor.

The values of S and B were $4{\cdot}73 \times 10^4$ and 2·61 for sample No. 2 (700° data) and $4{\cdot}35 \times 10^4$ and 3·53 for sample No. 3 (1000° data). A comparison of the observed and calculated intensities for sample No. 2 is given in Table 3. The reliability index, $R = \Sigma(\sqrt{I_o} - \sqrt{I_c})/\Sigma\sqrt{I_o}$, was 0·11 for the 700° data and 0·16 for the 1000° data. R was calculated using half the least observable value of I_o for the unobserved reflections.

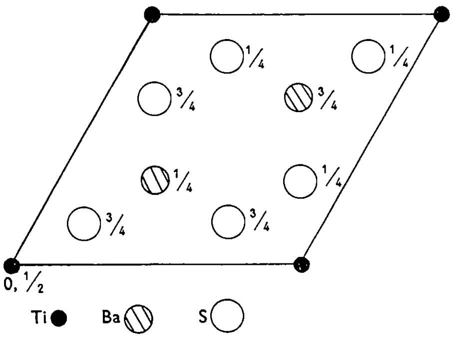

Fig. 2. Unit cell of $BaTiS_3$ projected onto (001) plane.

A projection of the unit cell onto the (001) plane is shown in Fig. 2. Each titanium atom is octahedrally coordinated by sulfur atoms. Each barium atom is surrounded by 12 sulfur atoms in a hexagonal close packed arrangement. The interatomic distances for the 700° preparation are given in Table 4. The primed sulfur atoms refer to those lying in planes above and below the barium atom while the unprimed ones lie in the same plane as the barium atom.

Table 4. *Interatomic distances in* $BaTiS_3$

6 Ti–S	2·43 Å
6 Ba–S	3·38
6 Ba–S^1	3·49

Table 5. *Variation in intensities of* $BaTiS_3$ *with temperature of preparation*

	I_o		
hkl	Prep. no. 2 (700°)	Prep. no. 3 (1000°)	Prep. no. 5 (1100°)
101	237	234	207*B*
200	44	42	38
002	66	45	42*B*
201 102	473	430	398
103	19	26	33
220	77	75	64
302 203	57	50	34*B*
114	5·8*B*	—	—
412 403 304	22·8*B*	10*B*	6*B*

B denotes broadened reflections.

The reason for the poorer agreement obtained with the higher temperature data became apparent upon examination of the differences in the powder patterns of the several preparations. Many reflections for which l is not zero become broadened and undergo large

Table 6. *Products obtained on reacting* $BaZrO_3$ *with* CS_2 *at several different temperatures*

				% Composition of product		
Reaction temp. (°C.)	Reaction time (hr.)	Color of product	Sulfur content (%)	$BaZrO_3$	$BaZrS_3$	Unknown phase
500	4	light orange	—	100	—	—
500	12	orange	—	85	15	0
600	4	orange	2·45	100	0	0
600	12	red	7·05	80	20	0
700	4	orange	4·18	88	12	0
750	4	red	9·65	68	25	7
750	18	violet	—	15	75	10
800	4	maroon	15·3	40	40	15
900	4	violet	21·18	20	70	10
1000	4	grey-black	27·10	0	100	0
1050	4	blue-black	28·60	0	100	0
1050	24	blue-black	29·60	0	100	0
Required for $BaZrS_3$			29·52			

Table 7. *Analytical data for alkaline earth zirconium sulfides*

					Found			Required	
Compound	Reaction temp. (°C.)	Reaction time (hr.)	Color	A^{2+}	Zr	S	A^{2+}	Zr	S
$BaZrS_3$	1050	4	Blue-black	42·10	28·10	28·60	42·16	28·32	29·52
$SrZrS_3$	1000	24–30	Violet	31·66	33·45	33·75	31·74	33·41	34·84
$CaZrS_3$	1150	24	Black	17·7	39·5	42·0	17·54	40·37	42·09

changes in relative intensity with increased temperature of preparation. However, the *hk*0 reflections remain sharp, and their intensities change only slightly. This is shown in Fig. 1 for the (200) and (002) reflections and by the data in Table 5. The intensities were placed on the same scale by assuming that the intensity of the (110) reflection was constant in all the patterns.

Symmetry requirements permit only variations in the *x* and *z* parameters of the sulfur atoms and the *z* parameters of the other atoms. The intensity data indicate that only changes in the *z* parameters need be considered. The origin was fixed at a titanium atom and the effect of variations in the *z* parameters of the barium and sulfur atoms upon the calculated intensities was ascertained. The intensity changes listed in Table 5 could not be accounted for, even qualitatively, unless it was assumed that the *B* component of the structure factors was greatly decreased. This observation and the broadening of the reflections for which *l* is not zero suggests that the structure becomes increasingly disordered with increasing temperature of preparation, *i.e.* with increasing sulfur deficiency.

Alkaline earth zirconium sulfides

Barium zirconate was allowed to react with CS_2 in the temperature range 500–1350 °C. for different lengths of time. Below 1000 °C. highly colored products of varying sulfur content were obtained. These products consisted of mixtures of $BaZrO_3$, $BaZrS_3$ and an unidentified phase in the proportions shown in Table 6. The per cent composition of each product was determined by comparing the intensities of several reflections of pure $BaZrO_3$ and $BaZrS_3$ with their values in the mixtures.

Samples of $BaZrS_3$ prepared in the temperature range 950–1200 °C. and 4 to 24 hours reaction time gave identical X-ray diffraction patterns although their sulfur contents varied from 27% to 29·6%. The powder pattern (Table 8) was indexed on the basis of an orthorhombic unit cell with

$$a = 7{\cdot}037,\quad b = 9{\cdot}983,\quad c = 7{\cdot}050\ \text{Å}\,.$$

Table 8. *Powder patterns of the alkaline earth zirconium sulfides*

$BaZrS_3$			
hkl	d_o	d_c	I/I_0
111	4·461	4·457	4
121	3·528 ǂ	3·526	100
002		3·525	
200		3·519	
012	3·325	3·325	4
102	3·149	3·151	2
201		3·148	
130	2·998	3·008	5
112		3·005	
211		3·003	
022	2·874 ǂ	2·879	18
220		2·876	
131	2·768	2·767	4
122	2·668	2·665	3
221		2·663	
040	2·495 ǂ	2·496	60
202		2·490	
032	2·419	2·420	5
212		2·416	
132	2·286	2·288	1
231		2·287	
310		2·284	
141	2·234 ǂ	2·232	1
103		2·229	
222		2·228	
301		2·225	
113	2·177	2·176	5
311		2·173	
042	2·036 ǂ	2·037	50
240		2·036	
123		2·036	
321		2·033	
150	1·918	1·921	1
213		1·918	
330		1·917	
312		1·916	

	$SrZrS_3$				$CaZrS_3$		
hkl	d_o	d_c	I/I_0		d_o	d_c	I/I_0
200	—	—			6·53	6·53	14
201	—	—			5·83	5·92	12
012	5·84	5·76	5		—	—	
020	4·901	4·894	12		4·795	4·790	80
202		4·898				4·785	
120	4·548*B*	4·601	4		—	—	
300		4·497			—	—	
121	4·382	4·378	15		4·282	4·282	6
212		4·380				4·280	
004	3·561	3·560	23		3·512	3·512	25
222	3·463	3·463	100		3·386	3·386	100
400	3·373	3·373	30		3·274	3·267	25
014	3·343	3·346	10		—	—	
401	—	—			3·160	3·183	18
130	3·168	3·172	4		3·090	3·102	4
204		3·150				3·093	
410		3·189				3·092	
402	3·050	3·050	3		2·961	2·963	8
214	2·998	2·995	3		2·946	2·944	8
230	2·927	2·937	20		2·868	2·869	22
412	2·912	2·910	20		2·826	2·831	80
132		2·896				2·837	
024	2·877	2·879	2			2·833	
231		2·876					
124	—	—			2·763	2·768	20
304	2·791	2·792	10		—	—	
420	2·781	2·777	10		—	—	
323	2·712	2·717	12		2·655	2·655	15
232		2·715				2·656	
115	2·677	2·681	6		—	—	
500	—	—			2·614	2·614	5
224	2·647	2·649	6		2·596	2·599	14
413		2·647			—	—	
	—	—					
422	2·587	2·587	5		2·520	2·520	8
510	—	—				2·521	
215	2·532	2·535	7		—	—	
040	2·447	2·447	70		2·393	2·395	66
404		2·448				2·393	

Table 8 (*cont.*)

BaZrS$_3$			
hkl	d_o	d_c	I/I_0
151	1·855	1·853	3
133		1·852	
331		1·850	
242	1·763ǂ	1·763	28
004		1·762	
400		1·759	
052	1·738	1·737	2
014		1·735	
152	1·684	1·687	3
251		1·686	
233		1·685	
114		1·685	
332		1·684	
411		1·682	
313	1·638	1·638	2
161	1·576ǂ	1·578	15
204		1·576	
323		1·575	
402		1·574	
252	1·557	1·558	4
034		1·557	
214		1·556	
412		1·555	
153	1·485	1·487	4
351		1·486	
333		1·485	
044	1·439ǂ	1·439	8
440		1·438	
234	1·424	1·424	3
432		1·423	
115	1·370	1·372	2
171		1·371	
511		1·367	
125	1·331ǂ	1·334	18
361		1·333	
163		1·333	
244		1·332	
442		1·331	
521		1·330	
135	1·277	1·279	1
353		1·277	
531		1·275	
080	1·245ǂ	1·248	2
404		1·245	
082	1·175ǂ	1·176	8
280		1·176	
325		1·176	
363		1·175	
006		1·175	
523	1·173ǂ	1·174	8
600		1·173	
282	1·116	1·116	4
206	1·114ǂ	1·114	5
444		1·114	
602	1·112ǂ	1·113	4
074	1·108	1·108	2
036		1·108	
216		1·107	
345	1·088	1·089	1
183		1·089	
381		1·088	
226		1·088	
543		1·087	
622		1·086	

	SrZrS$_3$			CaZrS$_3$		
hkl	d_o	d_c	I/I_0	d_o	d_c	I/I_0
041				2·361	2·361	12
305					2·361	
034	2·402	2·405	13		2·363	
140		2·408				
141	2·373	2·374	13	2·320	2·324	12
414		2·376			2·320	
006		2·373			—	
234	2·266	2·266	2	—	—	
241		2·266		—	—	
206	2·236	2·240	15	2·204	2·204	32
600	—	—		2·173	2·178	4
432	—	—			2·172	
216	2·183	2·183	25	2·144	2·148	55
424		2·190			2·141	
242		2·189			2·142	
602	2·147	2·145	5	2·082	2·081	5
612	2·089	2·095	5	—	—	
530		2·080		—	—	
342	2·060	2·058	2	—	—	
531		2·058		1·998	2·002	50
226	2·030	2·036	10		2·002	
007		2·035			2·001	
603		2·032		1·980	1·975	25
004	2·011	2·016	15		1·979	
107		2·012			1·984	
620	—	—			1·983	
117	1·975	1·971	20			
440		1·981		1·933	1·932	15
613					1·935	
622	1·959	1·962	45	1·908	1·908	50
441		1·962			1·914	
434		1·959			1·915	
343		1·958			1·915	
050		1·957			1·916	
505		1·595			1·914	
406					1·903	
	1·879		7	1·847		2
	1·843		2	1·829		3
	1·748		4	1·816		3
	1·727		20	1·801		4
	1·685		4	1·755		3
	1·662*B*		5	1·743		3
	1·647		10	1·694		20
	1·545		13	1·649		7
	1·524		7	1·630		14
	1·496		5	1·623		14
	1·415		5	1·609		4
	1·388		6	1·580		5
	1·373		2	1·544		7
	1·320		3	1·520		7
	1·316		4	1·515		12
	1·314		4	1·495		4
	1·297		7	1·476		4
	1·296		8	1·471		10
	1·293		7	1·414		12
	1·278		7	1·392		4
	1·275		4	1·380		4
	1·209		6	1·374		3
	1·205		3	1·328		4
	1·201		5	1·266		5
	1·199		3	1·262		10
	1·185		3	1·152		4
	1·183		4	1·138		3
	1·154		4	1·134		3
	1·152		7	1·129		3
	1·148		6	1·125		3
	1·139		5	1·116		2

Table 8 (*cont.*)

$BaZrS_3$			
hkl	d_o	d_c	I/I_0
373	1·080	1·082	1
191		1·083	
165	1·061ǂ	1·064	5
046		1·063	
561		1·062	
640		1·061	
092	1·058	1·058	5
472		1·057	
274		1·057	
454		1·056	
553	1·032	1·033	1
265		1·030	
084	1·017ǂ	1·018	4
480		1·018	
246		1·018	
642	1·015ǂ	1·016	4
292	1·013	1·013	4
056		1·012	
0,10,0	0·9982	0·9983	1
175	0·9933	0·9933	2
193		0·9930	
391		0·9928	
117	0·9918	0·9921	2
515		0·9921	
571		0·9918	
1,10,1	0·9784*B*ǂ	0·9789	7
365		0·9785	
284		0·9782	
482		0·9778	
127		0·9777	
525		0·9777	
563	0·9768*B*ǂ	0·9773	10
406		0·9770	
604		0·9762	
256	0·9738	0·9732	8
652	0·9720	0·9716	
185	0·9271	0·9270	1
2,10,2		0·9266	
545	0·9256	0·9259	1
266		0·9259	
581		0·9256	
307		0·9254	
662		0·9250	
375	0·9224	0·9226	1
393		0·9222	
1,10,3	0·9110	0·9111	4
3,10,1		0·9109	
446	0·9083	0·9098	5
644		0·9092	
723		0·9088	
294		0·9070	
3,10,3	0·8558	0·8555	4
086		0·8554	
565		0·8552	
167		0·8552	
802	0·8532	0·8535	5
2,11,2		0·8527	
0,12,0	0·8319	0·8319	2
840	0·8293	0·8296	3
494	0·8285	0·8281	3
575	0·8166	0·8171	3
717		0·8171	
593		0·8168	
715		0·8163	
0,12,2	0·8094	0·8097	4
2,12,0		0·8096	
842	0·8072	0·8075	6
0,11,4		0·8068	
2,12,2	0·7888	0·7890	2
804	0·7866	0·7870	3

$SrZrS_3$			
hkl	d_o	d_c	I/I_0
	1·131		4
	1·123		3
	1·093		3
	1·090		4
	1·078		4
	1·043		2
	1·029		3
	1·004		3
	1·000		2
	0·9781		3
	0·9761		3
	0·9748		2
	0·9557		3
	0·9554		2
	0·9526		2
	0·9503		5
	0·9482		3
	0·9369		3
	0·9358		3
	0·9319		2
	0·9289		4
	0·9266		2
	0·9216		2
	0·9179		3
	0·8885		2

$CaZrS_3$		
d_o	d_c	I/I_0
1·111		7

The unit cell contains 4 $BaZrS_3$ units based on the density of 4·23 g.cm.$^{-3}$ reported by Hahn & Mutschke for their preparation. The systematic absences are ($hk0$) for $h+k$ odd and ($0kl$) for l odd. Thus, the space group is either D_{2h}^{16}–$Pnmc$ or C_{2v}^{9}–$Pnc2_1$. The reflections marked with an ǂ in Table 8 can be indexed on the basis of a tetragonal cell with $a \cong \frac{1}{2}\sqrt{(2)}a_t \cong \frac{1}{2}\sqrt{(2)}c_t$ and $c=\frac{1}{2}b_t$, where the subscript t refers to the true unit cell dimensions. These reflections correspond very nearly in position and intensity to those expected for an ideal perovskite structure. Thus, barium zirconium sulfide must have a distorted perovskite structure probably similar to that of $CaTiO_3$ (Kay & Bailey, 1957) or $GdFeO_3$ (Geller, 1956). The difference in structure between the barium zirconium sulfide obtained in this study and that reported by Hahn & Mutschke may again be due to a sulfur deficiency resulting from the present method of synthesis.

Attempts to obtain a high temperature modification of $BaZrS_3$ were unsuccessful. Only mixtures of BaS, ZrS_2 and the $BaZrS_3$ phase described above were obtained when the reaction was carried out above 1200 °C.

Strontium and calcium zirconium sulfides were prepared from the corresponding ternary oxides at 1000–1200 °C. Below 1000 °C. mixtures of binary oxides and sulfides together with small amounts of ternary oxide and sulfide phases were obtained. Usually, complete reaction was achieved in 24 hours as shown by the analyses in Table 7 and the constancy of the X-ray patterns on longer reaction. The powder patterns are given in Table 8. It was possible to index the patterns on the basis of orthorhombic unit cells with the following dimensions:

	a	b	c
$SrZrS_3$	13·49 Å	9·79 Å	14·23 Å
$CaZrS_3$	13·07	9·58	14·05

The unit cells contain 16 molecules based on measured densities of 3·85 g.cm.$^{-3}$ for $SrZrS_3$ and 3·33 g.cm.$^{-3}$ for $CaZrS_3$. The space groups of these compounds could not be determined because the large unit cell dimensions do not permit unambiguous indexing. However, the similarity of the powder patterns to that of barium zirconium sulfide indicates that $SrZrS_3$ and $CaZrS_3$ have highly distorted multiple-cell perovskite structures.

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A Rapid Method of Obtaining the Third Set of Coordinates in a Crystal Structure Analysis

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When two of the coordinates of the atoms in the unit cell of a centrosymmetric crystal have been obtained by finding the projection of the electron density down one of the principal axes, the coordinates in the third direction are sometimes difficult to obtain without a tedious trial-and-error process. The following paper gives a simple method of determining the signs of the larger structure factors for a second projection and hence obtaining the third set of coordinates. The method appears to be useful as long as the number of atoms in the unit cell is no more than fifty to sixty.

Theory

In a centrosymmetric crystal, any structure factor has the form

$$F(h,k,l)=2\sum_{j=1}^{N/2} f_j(h,k,l)\cos 2\pi(hx_j+ky_j+lz_j)\,. \quad (1)$$

In two dimensions and more suitable form, it becomes

$$F(h,k,0)=2\sum_{j=1}^{N/2} f_j(h,k,0)\,(\cos 2\pi hx_j \cos 2\pi ky_j - \sin 2\pi hx_j \sin 2\pi ky_j)\,. \quad (2)$$

If the x_j coordinates are as yet undetermined but the y_j coordinates are known, $|F(h,k,0)|$ and the factors $f_j(h,k,0)\cos 2\pi ky_j$ and $f_j(h,k,0)\sin 2\pi ky_j$ are known quantities. A series of simultaneous equations is ob-