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Preparation and Crystal Structures of New Barium Zirconium Sulfides, Ba_2ZrS_4 and $Ba_3Zr_2S_7$

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New barium zirconium sulfides, Ba_2ZrS_4 and $Ba_3Zr_2S_7$, have been prepared by the reaction of CS_2 with mixture of $BaCO_3$ and $BaZrO_3$. The crystal structures of the compounds were refined on the powder X-ray diffraction data. The result showed that Ba_2ZrS_4 [tetragonal, *I4/mmm*, $a = 4.7852(1)$ Å and $c = 15.9641(3)$ Å] crystallizes in the K_2NiF_4 type structure, and $Ba_3Zr_2S_7$ [orthorhombic, *Cccm*, $a = 7.0697(2)$ Å, $b = 25.4923(7)$ Å and $c = 7.0269(2)$ Å] has a distorted variant of the $X_3Y_2Z_7$ type structure which is closely related to the perovskite structure.

Introduction

Ternary barium sulfides, Ba–*M*–S (*M* = metal), reveal various types of crystal structures. For example, $Ba_{1-x}Cr_2S_{4-x}$ (*1*) and $Ba_xFe_2S_4$ (*2*) crystallize in columnar composite crystals. The structures of $Ba_{16.5}Nb_9S_{42}$, Ba_2NbS_5 (*3*), $Ba_{16.5}Ta_9S_{39}$, and Ba_2TaS_5 (*4, 5*) are characterized by the existence of extra BaS_x layers in the $BaNiO_3$ structure. In the Ba–Ti–S system, Ba_2TiS_4 (*6*) and Ba_3TiS_5 (*7*) are isostructural with the corresponding oxides, Ba_2TiO_4 and Ba_3TiO_5.

This suggests that in the Ba–M–S system there are some unknown compounds that may have novel structures. For this reason, the preparation was attempted for the Ba–Zr–S system and resulted in the finding of new barium zirconium sulfides, Ba_2ZrS_4 and $Ba_3Zr_2S_7$. This paper reports the preparation and crystal structures of these sulfides.

In the Ba–Zr–S system, $BaZrS_3$ has been found (*8, 9*). It is isostructural with $GdFeO_3$, i.e., a distorted perovskite structure.

Experimental

(*1*) *Preparation of* Ba_2ZrS_4 *and* $Ba_3Zr_2S_7$

The starting materials, $BaCO_3$ (purity 99%) and $BaZrO_3$ (99.9%), were mixed in a 1/1 $BaZrO_3/BaCO_3$ ratio for Ba_2ZrS_4 and 2/1 for $Ba_3Zr_2S_7$. After mixing, they were placed in a furnace where CS_2 in N_2 carrier gas maintained a sulfiding atmosphere. To produce Ba_2ZrS_4 the mixture was kept at 750°C for 3 days. To prepare $Ba_3Zr_2S_7$ the mixture was kept at 750°C for 3 days followed by 1100°C for 20 min. After cooling to room temperature, the specimens were sealed in evacuated silica tubes and kept at a temperature of 1100°C for 5 hr. They were quenched in water.

(*2*) *Chemical Analysis*

A chemical analysis was performed for Ba, Zr, and S. The details are as follows.

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To determine Ba and Zr contents, about 0.2 g of the specimen was oxidized at 900°C for 15 min in a crucible. This oxide was fused with $K_2S_2O_7$ (4 g, purity G.R) at 500°C for 15 min. About 36 mol sulfuric acid (5 ml) was added to this solution to produce $BaSO_4$ precipitate. The precipitate was separated from the solution and ignited at 1000°C for 1 hr. The amount of Ba was determined from the weight of the precipitate. The amount of Zr was obtained by the EDTA titration of the solution separated from the $BaSO_4$. Xylenol orange (XO) was used as indicator.

To determine the sulfur content, the specimen (0.2 g) was dissolved in a solution consisting of 50 wt% NaOH (5 ml) and 30 wt% H_2O_2 (1 ml). Concentrated HNO_3 (10 ml) and Br_2 (1 ml) were added to the solution to oxidize the S to SO_4^{2-}. About 5 wt% $BaCl_2$ was added to the solution to produce $BaSO_4$. The sulfur content was calculated from the amount of precipitated $BaSO_4$.

Detailed experimental conditions of this chemical analysis will be published elsewhere (*10*).

(*3*) *Diffraction Data*

The X-ray and electron diffraction patterns of the specimen were measured to obtain information on their crystal structures. The powder X-ray diffraction data were collected with a step-scan procedure on a Rigaku-RAD-2B-type diffractometer using diffracted beam monochromatized Cu$K\alpha$ radiation. The measurement was performed from $2\theta = 5°$ to $100°$ with an interval of 0.02°. It took 35 sec to measure one point. The electron diffraction patterns were taken by rotating a single crystal around a principal axis, and using a 100 kV electron microscope (Hitachi-500 type).

(*4*) *Density*

Density was obtained by measuring the buoyancy in carbon tetrachloride. About 0.5 g of the specimen with fine particles was placed in a bottle, the volume of which was about 2 ml, and the weight of which was 1.5 g. The bottle was evacuated by an aspirator to remove the bubbles attached on the specimen and on the surface of the bottle. The buoyancy was obtained by measuring weights in air and in carbon tetrachloride at 25°C. The temperature was measured within ±0.1°C with a calibrated thermometer.

Results

Single phases of Ba_2ZrS_4 and $Ba_3Zr_2S_7$ were obtained at the starting Zr/Ba compositions of 1/2 and 2/3. The powder X-ray diffraction patterns of these compounds did not correspond to any known sulfides. The Ba_2ZrS_4 was contaminated with BaS at compositions richer in Ba than Zr/Ba = 1/2, and the $Ba_3Zr_2S_7$ was contaminated with $BaZrS_3$ at the composition richer in Zr than Zr/Ba = 2/3. Ba_2ZrS_4 is orange and $Ba_3Zr_2S_7$ is brown-black in color. They are insulators.

The chemical compositions obtained from two compounds listed in Table I resulted in the stoichiometries Ba_2ZrS_4 and $Ba_3Zr_2S_7$, respectively, within experimental error.

TABLE I

CHEMICAL COMPOSITIONS OF TWO SULFIDES

Ba_2ZrS_4			
Element	Ba(wt%)	Zr(wt%)	S(wt%)
Experimental values	55.2, 55.5, 55.6, 55.6, 55.9	18.4, 18.3, 18.4, 18.6, 18.1	24.9, 25.0, 25.1, 25.0, 25.0
Average	55.6(0.2)[a]	18.4(0.2)[a]	25.0(0.1)[a]
Calculated values for Ba_2ZrS_4	55.6	18.5	26.0
$Ba_3Zr_2S_7$			
Element	Ba(wt%)	Zr(wt%)	S(wt%)
Experimental values	50.5, 49.9, 49.8, 49.9, 50.5	22.4, 22.5, 22.5, 22.4, 22.1	27.3, 27.3, 27.3, 27.5, 27.2
Average	50.1(0.3)[a]	22.4(0.2)[a]	27.3(0.2)[a]
Calculated values for $Ba_3Zr_2S_7$	50.3	22.3	27.4

[a] Numerical values in parentheses give the standard deviations.

(1) *Electron Diffraction Spots and Powder X-Ray Diffraction Patterns*

The electron diffraction patterns of Ba_2ZrS_4 shown in Fig. 1 are indexable on the basis of the tetragonal cell with the lattice parameters of $a = 5$ Å and $c = 16$ Å. The spots satisfied the condition of $h + k + l = 2n$. All of the peaks of the powder X-ray diffraction pattern detected were also indexed on the basis of the tetragonal cell with the lattice parameters of $a = 4.7852(1)$ Å and $c = 15.9641(3)$ Å with the reflection condition of $h + k + l = 2n$.

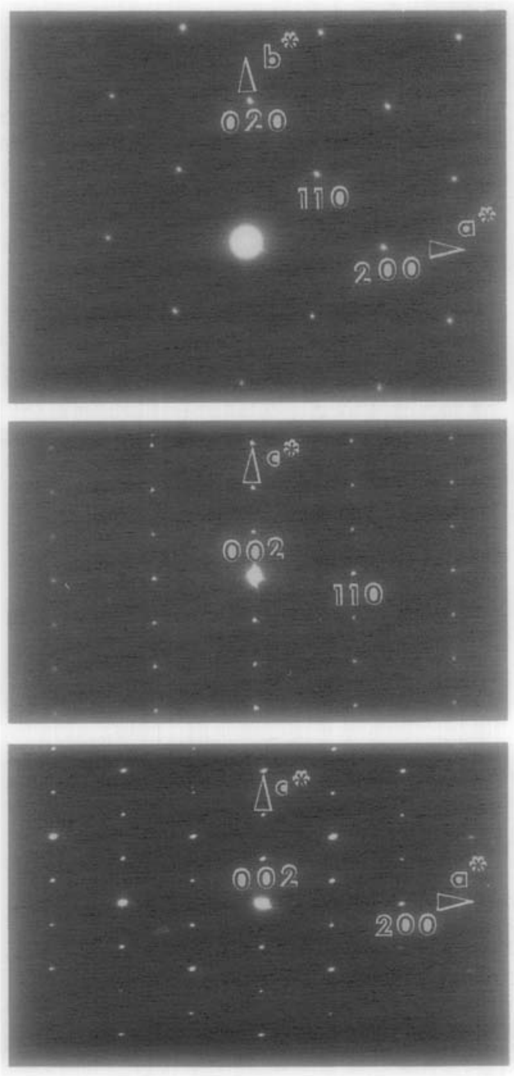


FIG. 1. Electron diffraction patterns of Ba_2ZrS_4.

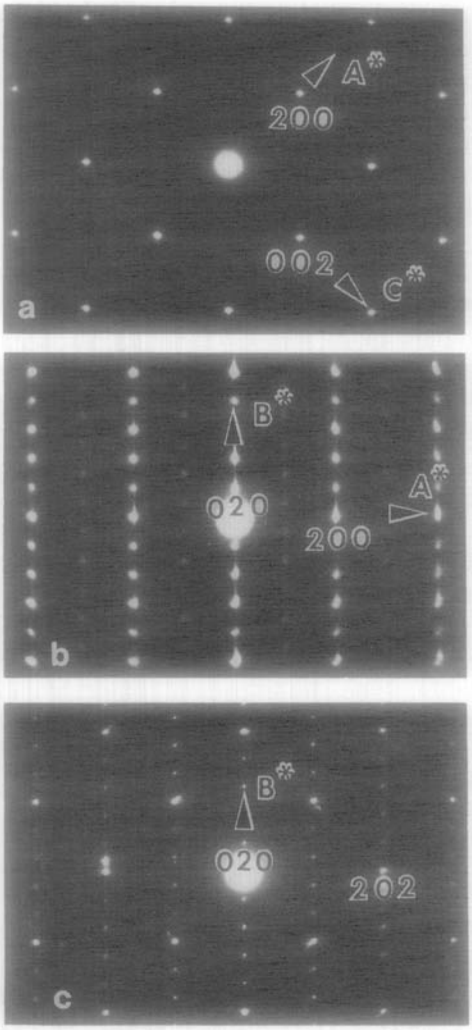


FIG. 2. Electron diffraction patterns of $Ba_3Zr_2S_7$.

The electron diffraction patterns of $Ba_3Zr_2S_7$ are given in Fig. 2. Weak super spots are observed (Fig. 2b). Ignoring these super spots the subcell belongs to the tetragonal cell with the lattice parameters of $a_T = 5$ Å and $c_T = 25$ Å. The patterns of Fig. 2 containing the super spots were indexed on the orthorhombic cell with the lattice param-

TABLE II

Structure Data of Oxides and Sulfides

Zr/Ba:	1	2/3	1/2	0
Oxide	$BaZrO_3$ Cubic a = 4.19 Å (Perovskite type)	$Ba_3Zr_2O_7$ Tetragonal a = 4.19 Å c =21.72 Å ($X_3Y_2Z_7$ type)	Ba_2ZrO_4 Tetragonal a = 4.18 Å c = 13.48 Å (K_2NiF_4 type)	BaO Cubic a = 5.83 Å (NaCl type)
Sulfide	$BaZrS_3$ Orthorhombic $a = 4.99 \times \sqrt{2}$ Å $b = 4.99 \times 2$ Å $c = 4.97 \times \sqrt{2}$ Å (Distorted Perovskite type)	$Ba_3Zr_2S_7$ Orthorhombic $a = 5.00 \times \sqrt{2}$ Å b = 25.49 Å $c = 4.97 \times \sqrt{2}$ Å (Distorted $X_3Y_2Z_7$ type)	Ba_2ZrS_4 Tetragonal a = 4.79 Å c = 15.96 Å (K_2NiF_4 type)	BaS Cubic a = 6.39 Å (NaCl type)

eters of $A = 5 \times \sqrt{2}$ Å $= \sqrt{2}a_T$, $B = 25$ Å $= c_T$ and $C = 5 \times \sqrt{2}$ Å $= \sqrt{2}a_T$ and with the reflection conditions $H + K = 2n$ (general) and $L = 2n$ ($H0L$). The powder X-ray diffraction pattern of $Ba_3Zr_2S_7$ was also indexed on the orthorhombic cell with the lattice parameters A = 7.0697(2) Å, B = 25.4923(7) Å, and C = 7.0269(2) Å.

The observed density of Ba_2ZrS_4 is 4.36 g/cm^3, the average of four measurements (4.36, 4.36, 4.36, and 4.37), compared with the calculated density of 4.49 g/cm^3 (V = 366 Å^3, Z = 2). The observed density of $Ba_3Zr_2S_7$ is 4.26 g/cm^3 (4.25, 4.25, 4.26, and 4.26), compared with the calculated one of 4.30 g/cm^3 (V = 1266.4 Å^3, Z = 4).

(2) *Crystal Structures*

Before considering the crystal structures of the sulfides previously described, the structure data of the corresponding oxides are given in Table II. As is seen in the table, the sulfides are isomorphous with the oxides at the composition of Zr/Ba = 1 and 0, i.e., $BaZrO_3$ crystallizes in the perovskite structure (*11*) and $BaZrS_3$ crystallizes in the distorted one (*8*, *9*), and both BaO and BaS have a NaCl type structure. This suggests that at the compositions Zr/Ba = 1/2 and 2/3, the sulfides are isomorphous with the corresponding oxides. From this point of view, it was assumed that Ba_2ZrS_4 and $Ba_3Zr_2S_7$ are isomorphous with their oxides (*12*). All features of powder X-ray and electron diffraction patterns support this assumption.

(*2.1*) *Ba_2ZrS_4*. The crystal structure of Ba_2ZrS_4 was refined on the powder X-ray diffraction data using positional parameters of K_2MgF_4 (*13*) with space group *I4/mmm* as a starting model. The total pattern fit program RIETAN (*14*) based on the Rietveld method (*15*) was used. The refinement was performed for regions from d = 4.4 Å to d = 1.0 Å with two positional parameters, three temperature factors, and one scaling factor. Those diffraction peaks whose d-values were larger than 4.4 Å were ignored because in this region the measured intensities were not correct. The calculated pattern with the correction of the preferred orientation was in good agreement with that observed (R_{wp} = 10.9%, R_p = 8.5%, R_I = 6.9%, R_F = 4.2%). The final values of the structure parameters are listed in Table III. The definitions of the reliability factors R_{wp}, R_p, R_I, and R_F, and the preferred orientation factor P are given in the footnote to Table III. Table IV gives the intensities I_{calc} calcu-

TABLE III

CRYSTAL DATA AND ATOMIC PARAMETERS OF Ba_2ZrS_4

Crystal data (tetragonal, space group *I*4/*mmm* (No. 139)) a = 4.7852(1) Å, c = 15.9641(3) Å, V = 365.55 Å^3, Z = 2 (according to the formula Ba_2ZrS_4)

Atom	Occupation	Atomic parameters x	 y	 z
Ba	1.0	0	0	0.3567(4)
Zr	1.0	0	0	0
S(1)	1.0	0	1/2	0
S(2)	1.0	0	0	0.164(1)

B(Ba) = 1.3(2) Å^2, B(Zr) = 4.2(4) Å^2, B[S(1)] = B[S(2)] = 3.1(4) Å^2

Note. R values (*16*):

$$R_{wp} = \left\{\frac{\Sigma\, W_i[Y_i(o) - (1/c)Y_i(c)]^2}{\Sigma\, W_i[Y_i(o)]^2}\right\}^{1/2}$$

$$R_p = \frac{\Sigma\, |Y_i(o) - (1/c)Y_i(c)|}{\Sigma\, Y_i(o)}$$

$$R_I = \frac{\Sigma\, |I_k(\text{`}o\text{'}) - I_k(c)|}{\Sigma\, I_k(\text{`}o\text{'})}$$

$$R_F = \frac{\Sigma |[I_k(\text{`}o\text{'})]^{1/2} - [I_k(c)]^{1/2}|}{\Sigma\, [I_k(\text{`}o\text{'})]^{1/2}},$$

where $1/c$ is a scaling factor, I's are integrated peak intensities, Y's are profile intensities after background substraction, and W's are weight. (o) and (c) represent the observed and calculated values.

Preferred orientation factor P (*16*):

$$P = p_1 + (1 - p_1)\exp[-p_2\theta^2]$$

$$p_1 = 0.594(6),\ p_2 = 2.52\ (9),$$

where θ is the acute angle in radians between the diffraction plane and the selected preferred plane.

lated on the atomic parameters without the preferred orientation correction and the observed integrated intensities I_{obs} obtained from the pattern. The calculated and observed diffraction profiles are given in Fig. 3.

The structure, therefore, can be described as isostructural with the corresponding oxide (*12*) (space group *I*4/*mmm*, K_2NiF_4 type structure). The structure of Ba_2ZrS_4 given in Fig. 4 is based on the stacking of the pervoskite unit cell, represented by P, and

TABLE IV

INDICES AND CALCULATED AND OBSERVED VALUES OF *d* SPACINGS AND INTENSITIES FOR Ba_2ZrS_4 (a = 4.7852(1), c = 15.9641(3) Å)

H	K	L	d_{obs}	d_{calc}	I_{obs}	I_{calc}
0	0	2	7.99	7.98	10	13
1	0	1	4.59	4.58	4	4
0	0	4	3.994	3.991	9	7
1	0	3	3.559	3.558	100	100
1	1	0	3.386	3.384	85	82
1	1	2	3.117	3.115	5	6
0	0	6	2.660	2.661	64	25
1	0	5		2.656		19
1	1	4	2.582	2.581	44	40
2	0	0	2.394	2.393	49	55
2	0	2	2.292	2.292	<1	1
2	1	1	2.122	2.121	2	2
1	1	6	2.092	2.092	26	20
1	0	7	2.054	2.059	14	7
2	0	4		2.052	48	5
0	0	8	1.996	1.996		5
2	1	3	1.986	1.986		36
2	0	6	1.780	1.779	22	24
2	1	5		1.778		9
1	1	8	1.720	1.719	5	4
2	2	0	1.693	1.692	14	16
1	0	9	1.664	1.663	2	1
0	0	10	1.597	1.596	2	1
2	1	7	1.561	1.561	9	6
2	2	4		1.558	15	2
2	0	8	1.533	1.533		7
3	0	3	1.529	1.528		7
3	1	0	1.514	1.513	10	11
3	1	2	1.487	1.487	1	1
1	1	10	1.445	1.444	7	6
2	2	6	1.428	1.428	11	9
3	0	5	1.424	1.427		1
3	1	4	1.415	1.415	12	10
1	0	11	1.390	1.389	11	7
2	1	9	1.366	1.366	1	1
2	0	10	1.328	1.328	4	2
3	2	1	1.325	1.323		1
3	1	6	1.316	1.315	7	6
3	0	7	1.308	1.307	2	2
2	2	8	1.291	1.291	9	3
3	2	3	1.288	1.288		6
3	2	5		1.226		2
3	1	8	1.206	1.206	1	2
2	1	1	1.202	1.201	7	9

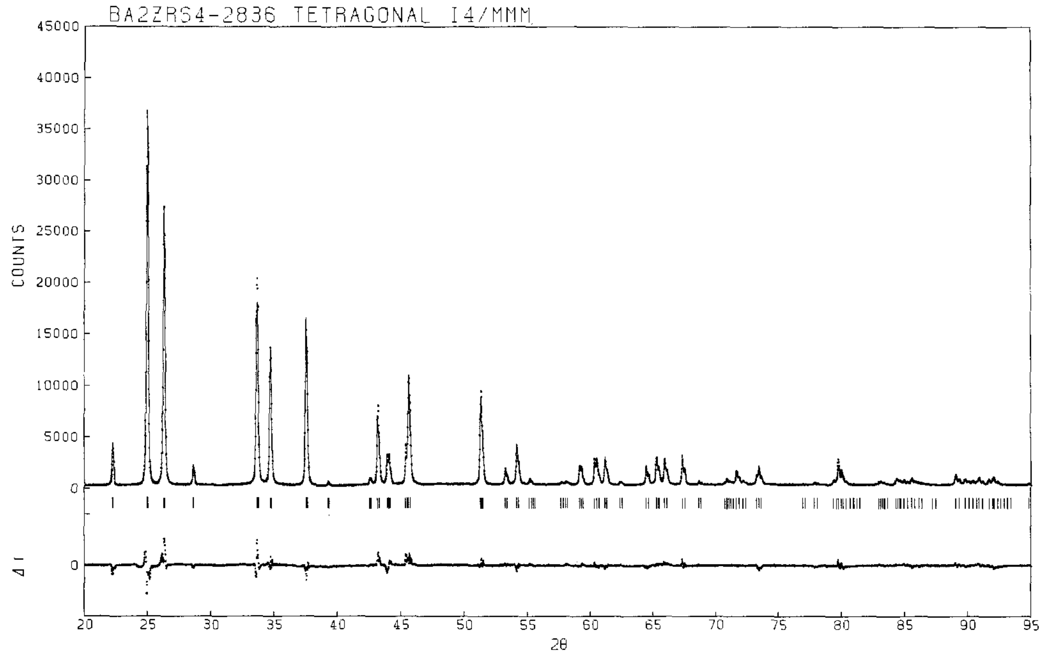


FIG. 3. Powder X-ray diffraction profile of Ba_2ZrS_4. The data profile is shown with the dotted line and the calculated one is the solid line. The difference curve at the bottom is on the same scale as the data. The tick marks indicate peak positions for the model.

BaS layer, represented by B, with sequence PBPB···.

(*2.2*) *$Ba_3Zr_2S_7$*. It was assumed that $Ba_3Zr_2S_7$ crystallizes with a distorted variant of the $X_3Y_2Z_7$ type structure (*13*) (that is, a distorted $Ba_3Zr_2O_7$ type structure), which is related to the perovskite structure, and that the space group of the distorted variant is *Cccm*. The structure of the sulfide was refined on the powder X-ray diffraction data using positional parameters which were obtained from the $X_3Y_2Z_7$ type (*13*) by translation from space group *I4/mmm* to the space group *Cccm*.

The refinement was performed for regions from d = 4.4 Å to d = 1.0 Å with eight positional parameters, three temperature factors, and one scaling factor. The calculated patterns with correction of preferred orientation gave good agreement with that observed (R_{wp} = 10.6%, R_p = 8.2%, R_I =

TABLE V

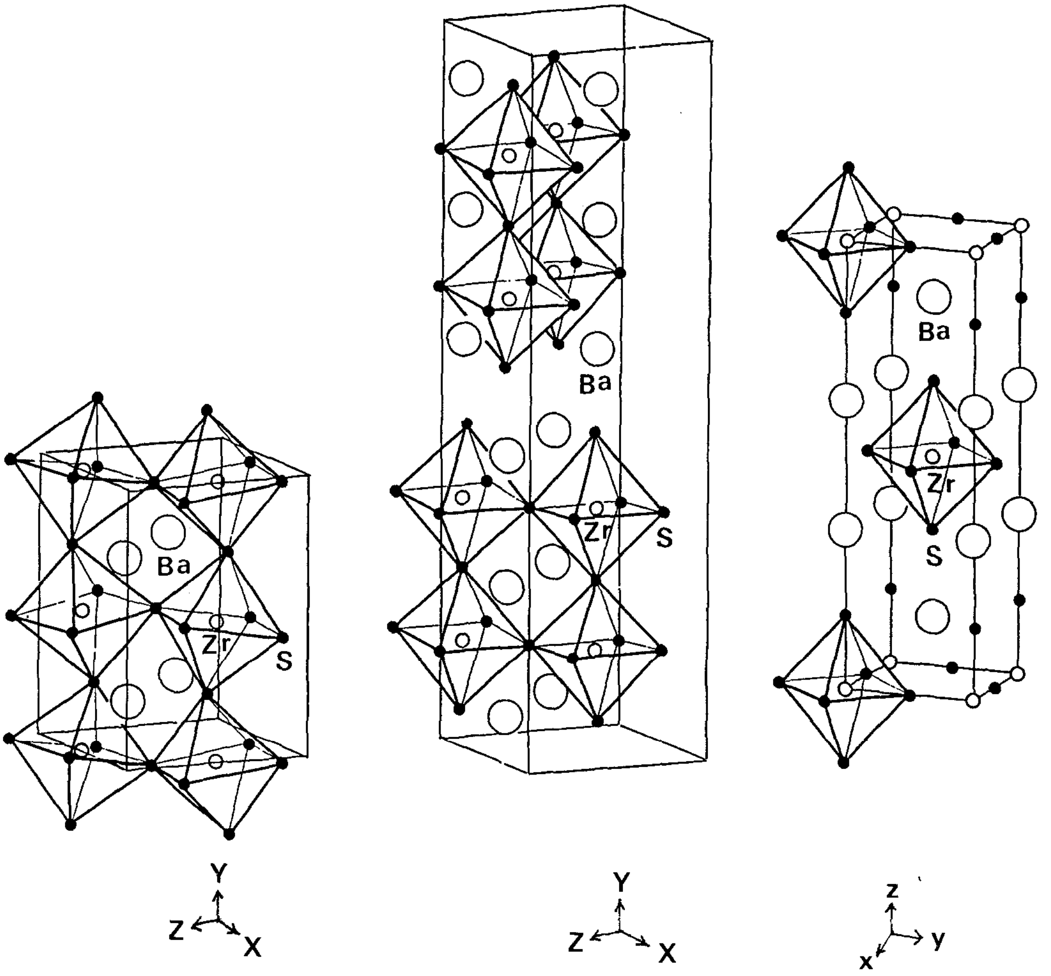
CRYSTAL DATA AND ATOMIC PARAMETERS OF $Ba_3Zr_2S_7$

Crystal data (orthorhombic, space group *Cccm* (No. 66) A = 7.0697(2) Å, B = 25.4923(7) Å, C = 7.0269(2) Å, V = 1266.4 Å^3, Z = 4 (according to the formula $Ba_3Zr_2S_7$)

		Atomic parameters		
Atom	Occupation	*x*	*y*	*z*
Ba(1)	1.0	1/4	3/4	0
Ba(2)	1.0	0.246(1)	0.9318(1)	0
Zr	1.0	0.261(2)	0.159(1)	0
S(1)	1.0	1/4	1/4	0
S(2)	1.0	0	0.159(1)	1/4
S(3)	1.0	0.219(4)	0.0520(5)	0
S(4)	1.0	0	0.350(1)	1/4

B[Ba(1)] = B[Ba(2)] = 2.20(9) Å^2, B(Zr) = 0.9(1) Å^2
B[S(1)] = B[S(2)] = B[S(3)] = B[S(4)] = 2.0(2) Å^2

Note. Preferred orientation factor P (*16*): $P = p_1 + (1 - p_1)\exp[-p_2\theta^2]$ p_1 = 0.865(5), p_2 = 2.7(3).



BaZrS3 Ba3Zr2S7 Ba2ZrS4

FIG. 4. Crystal structures of $BaZrS_3$ (9), Ba_2ZrS_4, and $Ba_3Zr_2S_7$. Barium atoms are indicated by the large open circles, zirconium atoms by small open circles, and sulfur atoms by small solid circles.

6.3%, $R_F = 4.0\%$). The final values of the structure parameters are listed in Table V. Figure 5 gives the experimental and the calculated profiles of the powder X-ray diffraction pattern. Table VI gives the d_{obs}, d_{calc}, I_{obs}, and I_{calc}. The refinement for the space group, *Ccc*2, did not give a better reliability factor compared with that of *Cccm*.

The structure, therefore, can be described as a distorted $Ba_3Zr_2O_7$ type structure (*12*). The structure given in Fig. 4 is based on the stacking of the pervoskite unit cell, represented by P, and BaS layer, represented by B, with sequence PPBPPB···. The selected interatomic distances of Ba_2ZrS_4 and $Ba_3Zr_2S_7$ are listed together in Table VII.

Conclusion

Two new barium zirconium sulfides,

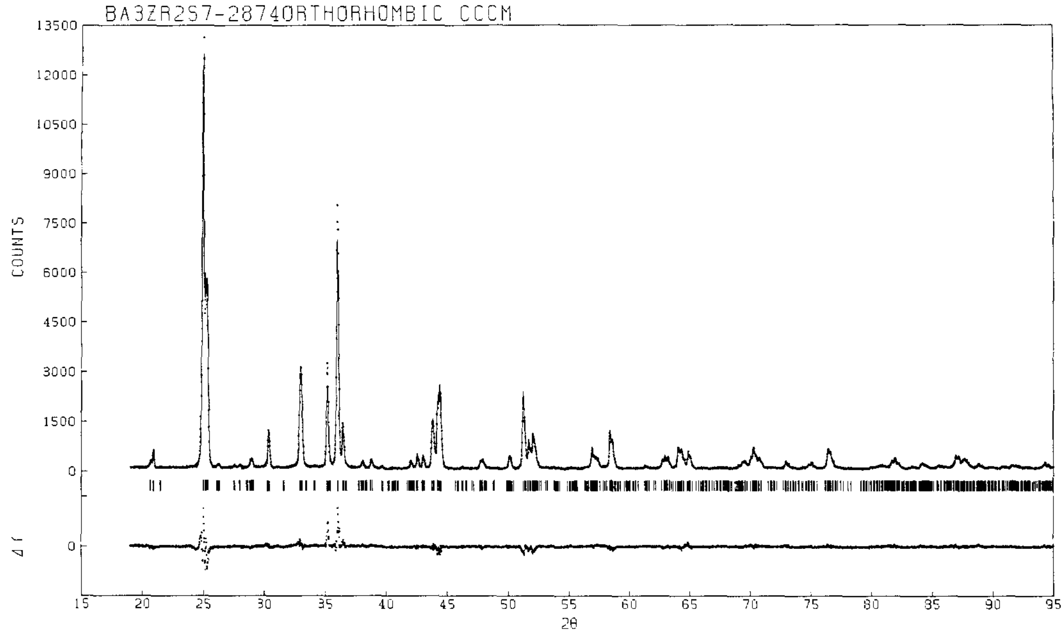


FIG. 5. Powder X-ray diffraction profile of $Ba_3Zr_2S_7$. The data profile is shown with the dotted line and the calculated one is the solid line. The difference curve at the bottom is on the same scale as the data. The tick marks indicate peak positions for the model.

TABLE VI

INDICES, CALCULATED, AND OBSERVED VALUES OF d SPACINGS AND INTENSITIES FOR $Ba_3Zr_2S_7$ (a = 7.0697(2), b = 25.4923(8), c = 70269(2) Å)

H	K	L	d_{obs}	d_{calc}	I_{obs}	I_{calc}
0	2	0	12.73	12.75	3	6
0	4	0	6.38	6.37	5	6
1	1	1	4.89	4.89	2	1
1	3	1	4.29	4.30	5	2
0	6	0	4.25	4.25		4
1	5	1	3.562	3.564	100	100
2	0	0	3.509	3.535	78	39
0	0	2		3.514		39
2	2	0	3.404	3.406	1	1
0	2	2	3.388	3.387		1
0	8	0		3.187	<1	1
2	4	0	3.081	3.091	<1	2
0	4	2		3.077	3	2
1	7	1	2.940	2.941	11	10
2	6	0	2.711	2.717	39	18
0	6	2		2.708		18
0	10	0	2.549	2.549	29	23
2	0	2	2.497	2.492	69	65
1	9	1	2.462	2.463	14	11
2	2	2		2.446		1
2	8	0	2.362	2.367	2	1
0	8	2		2.360		1
2	4	2	2.321	2.321	2	2
2	6	2	2.149	2.150	2	2
0	12	0	2.124	2.124	4	4
1	11	1	2.101	2.101	3	3
2	10	0		2.068	16	9
0	10	2	2.063	2.063		9
3	5	1	2.047	2.046	39	21
1	5	3	2.039	2.038		20
3	7	1	1.903	1.905	4	2
1	7	3	1.899	1.898		2
0	14	0	1.819	1.821	5	2
2	12	0		1.821		2
0	12	2		1.818		2
2	10	2	1.782	1.782	23	26
4	0	0	1.767	1.767	24	9
0	0	4	1.754	1.757		10
3	9	1		1.754		3
1	9	3		1.749		4
2	14	0		1.619	12	1
0	14	2	1.617	1.617		1
2	12	2		1.617		6
1	15	1	1.609	1.609		2
3	11	1		1.609		1
1	11	3	1.605	1.605		1

Ba_2ZrS_4 and $Ba_3Zr_2S_7$, were prepared. They have K_2NiF_4 and distorted $Ba_3Zr_2O_7$ type structures. These structure types had not been encountered previously in any sulfides, although they occur frequently in oxides and in halogenides.

TABLE VII

INTERATOMIC DISTANCES (Å)

	Ba_2ZrS_4
Ba—S1	4 × 3.310(5)
—S2	4 × 3.399(2)
—S2	1 × 3.08(2)
Zr—S1	4 × 2.393
—S2	2 × 2.61(2)
	$Ba_3Zr_2S_7$
Ba1—S1	2 × 3.535
—S1	2 × 3.514
—S2	4 × 3.42(2)
—S4	4 × 3.56(2)
Ba2—S2	2 × 3.38(2)
—S3	3.80(3)
—S3	3.543(2)
—S3	3.07(1)
—S3	3.32(3)
—S3	3.543(2)
—S4	2 × 3.24(2)
Zr—S1	2.538(5)
—S2	2 × 2.55(1)
—S3	2.53(1)
—S4	2 × 2.55(1)

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