trary, the present crystallographic results – acceptably low R index, small residual electron density in the difference synthesis, and in particular a good agreement between observed and calculated densities – rather support an anhydrous character for the body-centered tetragonal phase. (A 10% weight loss, if due to loss of water, would correspond to an original formula of $ThCl_4 . 2H_2O$; the calculated density for such a formulation would, of course, be about 10% higher than observed.) Moreover, an examination of a model of the structure discloses that while there are channels between Cl atoms (extending along the fourfold screw axes), the centers of the largest cavities within these channels are only about 2·3 Å away from Cl atoms. Hence, these channels are too small to house water molecules. (Incidentally, the pronounced anisotropic thermal motion observed for Cl can be interpreted as being due to easy vibrations in and out of these channels; vibrations of the Th atoms, by way of contrast, are isotropic within limits of error.)

As far as the reported second form of $ThCl_4$ is concerned, we have no evidence of its existence under the present preparative conditions. Furthermore, we have grave doubts about the correctness of the unit cell information. The orthorhombic cell ($a=11·18$, $b=5·93$ and $c=9·09$ Å) proposed by Takeuchi & Obata (1966*a,b*) leads to a calculated density of 4·12 g.cm^{-3}, a value which is almost certainly too low. It would seem that either the unit-cell parameters are incorrect or that the material is not $ThCl_4$. Evidently, further work is required.

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References

Brown, D., Petcher, T. J. & Smith, A. J. (1968). *Nature, Lond.* **217**, 737.
Elson, R. E., Fried, S., Sellers, P. & Zachariasen, W. H. (1950). *J. Amer. Chem. Soc.* **72**, 5791.
Furnas, T. C. (1957). *Single Crystal Orienter Instruction Manual.* Milwaukee: General Electric Company.
Handbook of Chemistry and Physics (1964). Cleveland: The Chemical Rubber Publishing Company.
Hoard, J. L. & Silverton, J. V. (1963). *Inorg. Chem.* **2**. 235.
Hoard, J. L., Silverton, E. W. & Silverton, J. V. (1968). *J. Amer. Chem. Soc.* **90**, 2300.
International Tables for X-ray Crystallography (1952). Vol. I. Birmingham: Kynoch Press.
International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.
Mooney, R. C. L. (1949). *Acta Cryst.* **2**, 189.
Mucker, K., Smith, G. S. & Johnson, Q. (1968). *Acta Cryst.* B**24**, 874.
Takeuchi, S. & Obata, N. (1966*a*). *Nippon kink. Gakk.* **30**, 941. (In Japanese.) Reported also in *Nuclear Sci. Abstr.* **21**, 856 (1967).
Takeuchi, S. & Obata, N. (1966*b*). *Nippon kink. Gakk.* **30**, 946. (In Japanese.) Reported also in *Nuclear Sci. Abstr.* **21**, 856 (1967).
Wyckoff, R. G. W. (1964). *Crystal Structures.* Vol. 2, 2nd Ed. New York: Interscience.

Acta Cryst. (1969). B**25**, 2365

Remeasurement of the Structure of Piezoelectric $BaS_4.H_2O$

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The remeasured lattice constants of orthorhombic $BaS_4.H_2O$ are $a=9·691\pm0·001$, $b=8·017\pm0·001$ and $c=7·828\pm0·001$ Å at 298°K, in space group $P2_12_12$. A total of 7747 structure factors, within a reciprocal lattice hemisphere of radius $(\sin\theta)/\lambda=1·02$ Å^{-1} were measured with PEXRAD. The 894 independent F_{meas} above background were used to refine the coordinates determined in 1954 (Abrahams, S.C., *Acta Cryst.* **7**, 423), by the method of least-squares. All atoms vibrate anisotropically. The final agreement index R was 0·0322. The two crystallographically independent tetrasulfide anions are dimensionally equivalent. The four independent S–S bond distances are not significantly different from their mean value of 2·069 ± 0·002 Å. The mean S–S–S bond angle is 104·1 ± 0·1 °, the mean SSS/SSS dihedral angle in the tetrasulfide anion is 76·4 ± 0·2°. The absolute configuration of the atomic arrangement, which may be related to the sense of the piezoelectric polarization induced by compressive stress, has been determined.

Introduction

The crystal structure of piezoelectric $BaS_4.H_2O$ was first studied fifteen years ago as part of an investigation of the properties of subgroup VIB of the periodic table (Abrahams, 1956). This work (Abrahams, 1954) showed the S_4^{2-} anion to be nonbranched and nonplanar, with C_2 symmetry and a dihedral SSS/SSS angle of about

Table 1. *Measured and calculated* $BaS_4.H_2O$ *structure factors at* 298 °K *and the standard deviation in the measured structure factor,* σF_m

h	k	l	F_{meas}	σF_m	F_{calc}
2	0	0	41.7	1.6	39.1
4	0	0	156.3	5.4	169.3
6	0	0	33.9	1.3	32.2
8	0	0	74.8	2.8	72.6
10	0	0	39.0	1.5	41.3
12	0	0	34.5	1.4	34.3
14	0	0	40.8	1.7	40.2
16	0	0	18.9	0.9	17.7
1	1	0	5.4	0.4	5.8
2	1	0	125.1	5.7	129.8
3	1	0	49.8	1.9	49.3
4	1	0	55.0	2.1	56.5
5	1	0	37.5	1.5	37.4
6	1	0	152.5	5.5	158.1
7	1	0	16.4	0.8	16.3
8	1	0	58.8	2.3	57.7
9	1	0	23.5	1.3	23.6
10	1	0	75.8	2.9	77.3
11	1	0	18.7	1.0	19.0
14	1	0	32.2	2.1	32.0
0	2	0	104.5	4.4	110.8
1	2	0	21.8	0.8	20.8
2	2	0	26.3	2.1	21.3
3	2	0	50.0	1.9	47.9
4	2	0	138.7	5.5	140.4
5	2	0	16.5	0.7	16.5
6	2	0	16.3	0.9	16.9
7	2	0	12.8	0.6	12.9
8	2	0	74.3	2.8	73.5
9	2	0	24.4	1.2	24.1
12	2	0	44.8	2.1	45.8
16	2	0	15.8	1.4	17.8
17	2	0	7.7	1.3	7.1
1	3	0	68.4	3.4	66.9
2	3	0	199.0	13.1	197.4
4	3	0	20.2	0.8	21.4
5	3	0	10.5	0.6	10.3
6	3	0	68.0	2.6	65.5
7	3	0	7.7	0.9	7.3
8	3	0	14.7	2.2	13.7
10	3	0	47.8	1.9	48.1
12	3	0	27.5	1.4	27.8
14	3	0	29.3	1.4	29.0
18	3	0	14.9	1.8	15.3
0	4	0	94.7	3.5	92.1
1	4	0	10.6	0.5	9.3
2	4	0	38.4	1.5	37.2
3	4	0	26.0	1.3	25.0
4	4	0	133.2	5.3	136.1
5	4	0	11.5	0.6	12.1
6	4	0	70.4	2.7	69.7
7	4	0	27.2	1.6	27.3
8	4	0	120.9	4.5	118.9
10	4	0	33.6	1.5	34.8
12	4	0	42.0	1.7	41.7
1	5	0	31.7	1.7	31.3
2	5	0	174.3	6.3	180.5
3	5	0	25.9	1.1	24.9
4	5	0	18.2	0.8	12.1
5	5	0	18.5	1.1	17.3
6	5	0	87.4	3.5	84.4
10	5	0	46.2	2.2	46.5
11	5	0	7.1	1.2	8.0
12	5	0	28.0	1.2	28.4
14	5	0	19.0	1.4	17.7
16	5	0	16.5	1.2	15.6
0	6	0	106.5	3.9	100.4
1	6	0	6.1	0.9	6.8
4	6	0	94.7	3.8	90.1
5	6	0	12.8	1.1	14.1
6	6	0	13.3	1.1	13.2
7	6	0	31.2	1.5	32.5
8	6	0	50.2	3.6	48.0
9	6	0	21.2	0.9	21.3
10	6	0	13.8	0.9	14.5
12	6	0	36.4	1.5	36.4
14	6	0	10.1	1.2	11.6
1	7	0	18.8	1.2	18.8
2	7	0	51.2	2.2	48.9
3	7	0	7.0	0.7	6.9
4	7	0	16.4	0.9	13.9
5	7	0	19.5	1.2	19.1
6	7	0	85.4	3.7	82.4
8	7	0	16.8	0.7	17.4
9	7	0	14.1	1.1	14.7
10	7	0	43.0	1.7	43.9
14	7	0	19.9	1.6	20.3
0	8	0	132.3	4.9	131.1
1	8	0	30.1	1.2	29.7
2	8	0	11.6	1.2	12.6
4	8	0	61.7	2.4	63.0
5	8	0	14.8	0.9	14.1
6	8	0	14.3	1.0	14.0
8	8	0	38.2	1.7	39.2
9	8	0	12.7	0.7	12.4
10	8	0	13.0	0.8	11.6
12	8	0	23.4	1.7	23.4
16	8	0	14.3	1.7	12.1
1	9	0	6.9	1.0	7.2
2	9	0	66.1	3.3	67.5
4	9	0	16.6	0.7	14.9
6	9	0	65.8	2.9	64.1
8	9	0	29.8	1.5	30.0
10	9	0	34.4	2.1	34.1
14	9	0	19.0	1.1	17.7
0	10	0	51.4	2.0	52.0
3	10	0	16.2	0.9	16.2
4	10	0	58.9	2.7	59.0
6	10	0	14.4	1.3	15.0
8	10	0	37.4	1.7	36.8
12	10	0	17.5	0.9	17.5
2	11	0	47.2	2.5	47.0
5	11	0	13.9	1.0	14.2
6	11	0	22.5	1.7	21.6
10	11	0	20.8	1.0	20.3
12	11	0	8.5	0.9	9.0
4	12	0	33.5	1.5	33.0
8	12	0	28.4	1.3	27.1
12	12	0	14.8	1.0	13.6
2	13	0	34.7	1.5	35.8
6	13	0	25.5	1.2	24.5
10	13	0	16.5	1.5	16.7
0	14	0	28.6	2.3	29.2
4	14	0	23.8	1.9	24.2
2	15	0	16.0	1.2	17.1
6	15	0	17.7	1.6	18.0
1	1	1	125.6	5.9	129.0
2	1	1	25.5	1.0	24.9
4	1	1	43.0	1.8	43.2
5	1	1	56.6	2.5	53.7
6	1	1	21.0	0.9	22.8
7	1	1	87.4	4.2	87.7
8	1	1	19.2	1.7	19.0
9	1	1	55.2	3.0	55.0
10	1	1	12.8	0.7	12.4
11	1	1	58.5	3.1	60.8
13	1	1	22.6	1.0	23.7
15	1	1	24.6	1.6	26.2
0	2	1	50.4	1.9	49.8
1	2	1	171.2	8.8	175.7
2	2	1	26.4	1.1	25.6
3	2	1	114.5	4.3	118.6
4	2	1	32.2	1.9	33.2
5	2	1	130.4	5.3	137.6
6	2	1	20.4	0.9	20.4
7	2	1	83.0	6.0	83.5
8	2	1	7.8	0.7	7.1
9	2	1	80.3	3.4	77.7
10	2	1	14.1	0.9	14.9
11	2	1	19.5	1.1	20.3
13	2	1	43.4	2.3	43.3
17	2	1	16.5	1.0	15.6
0	3	1	44.6	1.7	44.1
1	3	1	141.4	5.4	147.4
2	3	1	30.1	1.2	30.8
3	3	1	110.6	4.2	110.3
4	3	1	28.6	1.2	29.2
5	3	1	110.0	4.2	109.2
6	3	1	13.3	0.8	12.9
7	3	1	92.4	3.7	90.2
9	3	1	26.7	1.0	25.7
10	3	1	12.1	0.7	13.6
11	3	1	44.8	1.7	44.8
13	3	1	8.9	1.1	9.0
15	3	1	27.6	1.7	27.7
0	4	1	40.8	1.6	40.3
1	4	1	114.3	4.2	112.6
2	4	1	34.8	1.5	34.6
3	4	1	40.3	3.6	38.9
5	4	1	79.9	3.1	76.4
7	4	1	56.4	2.5	54.4
8	4	1	8.7	0.7	9.2
11	4	1	36.9	1.7	36.5
13	4	1	30.7	1.3	31.2
0	5	1	37.0	1.5	37.4
1	5	1	91.0	4.8	91.9
2	5	1	15.4	0.8	15.3
3	5	1	69.8	3.0	67.5
4	5	1	12.7	1.1	13.9
5	5	1	89.9	4.0	90.1
6	5	1	15.9	1.2	15.3
7	5	1	59.8	3.5	60.0
8	5	1	22.5	1.3	23.4
9	5	1	28.3	1.1	28.5
11	5	1	32.6	2.3	30.9
13	5	1	14.9	0.7	15.2
0	6	1	15.0	1.0	15.2
1	6	1	97.4	5.2	96.4
2	6	1	17.9	1.4	17.3
3	6	1	80.3	4.1	77.3
5	6	1	77.7	2.9	77.7
7	6	1	41.9	2.9	38.9
8	6	1	22.2	0.9	23.2
9	6	1	51.5	2.6	52.3
11	6	1	15.5	0.9	15.6
13	6	1	33.8	1.3	35.5
1	7	1	69.5	3.1	68.5
2	7	1	22.9	0.9	23.3
3	7	1	96.0	4.0	92.9
4	7	1	17.8	1.2	17.8
5	7	1	33.4	1.3	33.3
7	7	1	60.1	2.4	62.1
9	7	1	34.3	1.7	34.1
11	7	1	40.5	1.6	40.9
15	7	1	17.9	1.4	15.5
0	8	1	15.2	0.8	15.7
1	8	1	50.4	3.2	51.8
2	8	1	11.3	0.7	11.3
3	8	1	64.4	3.9	65.0
5	8	1	50.3	2.0	51.4
6	8	1	13.7	0.8	12.7
7	8	1	28.9	1.6	28.7
9	8	1	36.6	1.4	36.8
11	8	1	10.6	0.8	11.4
13	8	1	18.9	1.3	17.6
0	9	1	16.2	1.3	16.8
1	9	1	39.9	2.2	38.8
2	9	1	21.5	1.5	23.6
3	9	1	45.4	2.0	45.8
5	9	1	25.3	1.6	25.4
7	9	1	28.1	1.2	30.3
9	9	1	24.1	1.8	23.7
11	9	1	25.0	1.1	26.0
13	9	1	10.7	1.0	11.5
0	10	1	10.7	0.7	12.7
1	10	1	38.8	1.8	39.0
2	10	1	14.6	1.0	14.8
3	10	1	31.3	1.5	31.2
5	10	1	37.9	1.7	38.0
6	10	1	13.2	0.7	12.0
7	10	1	27.7	1.1	28.2
9	10	1	26.5	1.4	26.7
11	10	1	10.9	1.1	13.0
1	11	1	36.5	1.4	39.2
3	11	1	33.6	1.9	34.2
4	11	1	11.6	1.4	12.3
5	11	1	28.5	1.5	29.6
7	11	1	32.8	2.0	34.3
11	11	1	18.8	1.8	18.7
1	12	1	35.7	2.7	35.8
3	12	1	16.6	1.6	16.6
5	12	1	25.8	1.5	26.7
7	12	1	15.9	1.5	15.3
9	12	1	21.4	2.1	20.9
11	12	1	8.3	1.1	8.0
1	13	1	19.2	1.6	19.3
3	13	1	18.8	1.2	18.9
5	13	1	17.9	1.9	16.9
7	13	1	17.4	1.7	18.7
1	14	1	17.0	1.6	15.6
3	14	1	17.8	1.2	16.3
5	14	1	14.8	1.3	15.3
1	15	1	13.9	1.1	14.1
1	0	2	4.8	0.2	4.6
2	0	2	38.9	1.5	42.6
3	0	2	48.9	2.2	48.5
4	0	2	136.1	4.8	144.5
5	0	2	58.1	2.7	57.7
6	0	2	65.6	2.5	66.8
8	0	2	105.0	4.6	104.7
9	0	2	19.8	0.8	18.9
10	0	2	14.3	0.7	15.0
11	0	2	11.2	0.8	11.4
16	0	2	15.6	1.4	12.7
0	1	2	47.0	4.6	48.1
1	1	2	14.1	0.6	13.4
2	1	2	224.1	10.5	225.4
3	1	2	22.1	0.9	21.7
4	1	2	20.6	0.9	18.2
5	1	2	23.4	0.9	23.2
6	1	2	111.9	4.7	115.5
7	1	2	10.7	1.0	10.5
8	1	2	36.1	2.6	34.9
10	1	2	45.9	1.9	47.9
11	1	2	14.8	1.4	14.1
12	1	2	25.2	1.8	24.7
14	1	2	27.9	1.2	26.9
16	1	2	12.7	1.3	14.6
18	1	2	12.8	2.1	13.1
1	2	2	24.0	0.9	24.0
2	2	2	52.7	2.3	49.6
4	2	2	132.1	5.6	132.6
5	2	2	34.9	1.5	34.7
6	2	2	18.3	1.1	19.3
8	2	2	88.6	3.6	86.0
9	2	2	17.3	0.8	17.6
10	2	2	39.5	1.9	40.7
12	2	2	42.2	1.6	42.2
0	3	2	52.3	2.1	52.4
1	3	2	28.9	1.1	27.0
2	3	2	123.4	5.0	126.0
3	3	2	26.7	1.2	27.1
4	3	2	58.5	2.5	59.1
5	3	2	14.9	0.9	15.0
6	3	2	110.6	4.6	107.9
7	3	2	13.2	0.6	13.7
8	3	2	23.6	1.2	23.7
10	3	2	74.4	5.9	73.6
11	3	2	13.1	0.8	13.9
12	3	2	15.1	1.0	14.5
14	3	2	26.9	1.3	26.2
0	4	2	161.0	5.7	164.3
1	4	2	54.1	2.2	53.4
2	4	2	39.8	1.6	37.9
3	4	2	14.1	1.0	13.9
4	4	2	138.5	5.8	139.6
5	4	2	6.8	0.9	7.1
8	4	2	53.4	2.7	53.9
9	4	2	11.4	1.2	11.9
10	4	2	17.2	1.6	18.3
12	4	2	29.8	1.2	29.6
13	4	2	15.2	1.2	15.2
14	4	2	21.3	1.5	19.7
16	4	2	17.5	2.0	17.3
0	5	2	29.9	1.2	31.0
1	5	2	22.6	0.9	24.1
2	5	2	105.6	4.5	107.6
3	5	2	11.4	0.9	11.5
4	5	2	40.8	2.0	39.9
5	5	2	24.3	1.0	24.1
6	5	2	88.3	3.4	85.4
7	5	2	19.2	1.0	19.1
8	5	2	24.9	1.3	27.0
9	5	2	12.9	0.8	13.3
10	5	2	60.7	2.5	59.7
12	5	2	15.4	0.8	16.2
14	5	2	24.9	1.4	26.1
0	6	2	111.5	4.7	109.9
1	6	2	16.2	1.1	16.9
2	6	2	18.3	1.7	18.0
3	6	2	16.4	0.7	16.9
4	6	2	101.1	4.5	101.8
5	6	2	10.1	0.6	10.2
6	6	2	9.4	0.9	9.5
8	6	2	62.8	4.7	66.4
10	6	2	24.6	1.4	26.4
12	6	2	28.3	1.2	29.2
16	6	2	10.0	1.2	12.5
2	7	2	102.8	4.0	97.6
3	7	2	18.0	0.7	18.1
4	7	2	15.1	1.6	13.5
6	7	2	61.9	2.6	61.1
7	7	2	27.0	1.6	29.2
8	7	2	17.9	1.3	15.0
10	7	2	30.9	1.3	31.2
12	7	2	15.2	1.1	17.4
14	7	2	20.5	1.9	20.4
1	8	2	18.1	1.0	18.9
2	8	2	18.8	1.2	18.9
3	8	2	15.1	1.1	16.6
4	8	2	63.0	3.2	65.2
5	8	2	13.5	0.9	12.0
6	8	2	26.1	1.9	27.4
8	8	2	50.2	2.2	51.5
12	8	2	31.6	1.8	30.5
2	9	2	71.2	3.7	74.0
3	9	2	19.2	1.1	18.9
4	9	2	9.7	0.9	11.6
6	9	2	49.5	2.5	50.9
8	9	2	12.7	1.0	12.7
10	9	2	26.4	1.3	25.3
0	10	2	56.6	2.2	57.2
1	10	2	10.7	0.7	9.6
2	10	2	12.7	0.7	12.1
4	10	2	46.3	2.6	44.6
8	10	2	33.5	1.6	34.0
10	10	2	16.4	0.9	14.7
12	10	2	17.4	1.1	19.1
2	11	2	40.4	1.8	40.1
6	11	2	34.6	1.9	35.9
10	11	2	24.1	1.7	24.3
0	12	2	37.9	1.5	37.3
2	13	2	29.8	1.8	28.0
6	13	2	22.2	1.5	22.0
10	13	2	18.5	1.0	15.7
8	14	2	16.2	1.0	17.0
2	15	2	18.1	1.3	18.4
1	1	3	178.3	5.9	166.6
3	1	3	104.7	4.0	108.8
4	1	3	35.5	1.7	34.8
5	1	3	102.8	3.9	103.1
6	1	3	20.6	0.8	21.2
8	1	3	15.4	1.3	14.5
9	1	3	24.9	1.0	24.3
11	1	3	39.4	1.5	39.8
15	1	3	30.4	1.3	29.1
0	2	3	26.5	1.1	26.2
1	2	3	112.7	4.3	112.1
2	2	3	16.1	1.3	15.0
3	2	3	72.6	3.0	69.6
4	2	3	25.3	1.0	24.3
5	2	3	75.0	4.1	70.0
6	2	3	23.3	1.1	23.2
7	2	3	53.6	2.8	54.9
8	2	3	10.3	1.0	10.7
9	2	3	57.8	2.6	61.6
10	2	3	11.7	0.9	12.5
11	2	3	22.1	1.4	21.0
13	2	3	30.3	1.7	30.3
0	3	3	12.9	0.6	14.3
1	3	3	56.3	2.3	51.4
2	3	3	30.4	1.4	29.5
3	3	3	104.8	3.8	106.4
4	3	3	19.5	1.0	19.0
5	3	3	38.5	2.3	36.8
6	3	3	14.8	0.7	15.8
7	3	3	88.9	3.3	87.1
9	3	3	51.8	2.1	52.6
11	3	3	48.9	3.0	45.8
13	3	3	21.3	1.2	21.7
15	3	3	13.7	1.0	14.0
0	4	3	35.9	1.4	35.5
1	4	3	101.9	4.0	100.4
2	4	3	39.1	1.5	38.9
3	4	3	141.0	5.6	141.0
4	4	3	13.3	1.0	13.9
5	4	3	73.7	2.9	73.0
7	4	3	39.6	2.2	38.2
9	4	3	37.5	1.8	38.0
13	4	3	35.6	1.7	35.3
17	4	3	17.3	1.4	18.8
0	5	3	31.1	1.5	31.1
1	5	3	64.9	2.4	63.5
2	5	3	13.1	0.6	13.1
3	5	3	101.4	5.3	97.4
5	5	3	32.6	1.5	34.4
6	5	3	16.6	1.2	16.2
7	5	3	78.3	3.2	79.8
8	5	3	13.1	1.1	13.9
9	5	3	31.6	1.3	31.6
10	5	3	12.2	1.0	12.0
11	5	3	48.7	2.2	51.0
13	5	3	17.0	1.8	13.8
15	5	3	16.8	1.0	17.5
0	6	3	19.7	0.8	20.7
1	6	3	74.4	2.8	72.4
2	6	3	9.7	0.7	10.6
3	6	3	51.3	3.0	54.1
5	6	3	62.7	2.4	62.9
6	6	3	17.5	1.3	17.4
7	6	3	43.1	1.7	44.0
9	6	3	43.6	1.8	45.5
11	6	3	20.8	1.2	22.7
13	6	3	18.1	1.0	17.5
0	7	3	11.5	0.9	10.8
1	7	3	70.9	2.7	70.3
2	7	3	15.5	0.9	15.8
3	7	3	43.1	2.0	43.5
5	7	3	52.7	2.0	52.7
6	7	3	20.4	1.1	21.2
7	7	3	29.3	1.4	29.6
11	7	3	24.5	1.5	25.9
15	7	3	19.0	2.2	19.4
1	8	3	47.8	2.2	48.3
2	8	3	15.6	1.1	15.7
3	8	3	25.3	1.8	28.5
4	8	3	21.4	1.0	22.5
5	8	3	60.2	3.6	60.0
7	8	3	24.8	1.0	24.5
9	8	3	40.6	1.8	40.5
11	8	3	22.3	1.0	23.3
13	8	3	20.8	2.2	21.4
1	9	3	51.9	2.2	51.3
3	9	3	49.1	2.1	48.9
4	9	3	13.1	1.5	14.3
5	9	3	39.3	2.4	39.9
7	9	3	38.7	2.1	38.7
9	9	3	13.5	1.1	13.7
15	9	3	16.2	0.9	13.3
1	10	3	40.7	2.3	42.9
3	10	3	30.6	1.3	31.7
5	10	3	31.0	1.8	30.7
7	10	3	18.3	1.4	19.7
9	10	3	27.2	1.3	27.6
1	11	3	21.3	0.9	22.0
2	11	3	14.2	1.5	13.2
3	11	3	29.5	1.5	30.9
5	11	3	17.0	0.8	15.5
7	11	3	26.1	1.6	25.5
9	11	3	16.5	1.2	17.0
1	12	3	21.4	1.7	21.0
3	12	3	27.8	1.4	27.8
4	12	3	11.1	1.0	10.3
5	12	3	21.5	2.2	21.3
7	12	3	13.4	1.2	13.0
1	13	3	20.2	1.1	21.2
3	13	3	22.0	2.0	22.2
5	13	3	7.4	1.2	11.7
9	13	3	8.5	1.1	7.8
1	14	3	20.5	1.0	18.7
5	14	3	18.0	0.9	17.7
1	15	3	13.5	1.0	12.9
5	0	4	9.2	0.6	7.9
6	0	4	8.8	0.5	8.2
7	0	4	24.7	2.3	12.0
9	0	4	10.1	0.9	11.5
10	0	4	7.6	0.7	7.8
16	0	4	23.6	1.0	26.0
3	1	4	34.2	1.5	33.5
4	1	4	30.5	2.2	30.5
5	1	4	30.1	1.7	28.8
6	1	4	77.3	3.7	77.0
8	1	4	26.4	2.0	25.8
9	1	4	19.8	1.1	17.5
10	1	4	59.6	2.9	58.8
12	1	4	18.5	1.4	17.7
14	1	4	30.2	3.2	26.7
2	2	4	51.2	2.1	51.3
3	2	4	27.3	1.0	26.9
4	2	4	139.3	5.6	142.5
6	2	4	39.4	1.7	41.2
8	2	4	80.4	3.0	77.8
10	2	4	33.6	1.8	32.0
12	2	4	39.9	3.8	39.9
16	2	4	14.2	1.1	15.1
0	3	4	54.4	2.8	51.2
1	3	4	37.8	1.8	36.3
2	3	4	122.6	4.4	123.2
3	3	4	15.4	1.1	12.9
6	3	4	115.0	7.3	110.7
8	3	4	36.1	2.9	35.7
9	3	4	14.3	0.7	14.3
10	3	4	44.2	1.7	44.2
12	3	4	16.4	1.5	16.6
14	3	4	22.6	1.4	23.2
0	4	4	125.8	5.2	121.8
1	4	4	21.8	1.7	22.0
2	4	4	26.0	1.7	23.8
3	4	4	16.3	0.9	16.0
4	4	4	68.2	2.6	65.4
6	4	4	8.9	0.5	8.4
7	4	4	13.7	1.4	14.6
8	4	4	55.2	2.5	54.7
12	4	4	38.6	2.5	36.5
16	4	4	13.6	1.6	13.7
0	5	4	42.9	2.1	43.8
1	5	4	27.3	1.0	25.4
2	5	4	76.4	4.1	76.0
3	5	4	11.3	1.2	11.2
6	5	4	79.1	7.3	76.3
7	5	4	16.0	1.4	16.8
10	5	4	34.9	1.4	34.9
14	5	4	22.3	1.9	21.5
0	6	4	95.8	4.4	91.4
1	6	4	13.0	1.2	11.9
2	6	4	31.1	1.5	31.7
3	6	4	20.7	1.0	20.7
4	6	4	91.0	7.9	85.1
6	6	4	23.8	2.3	24.5
7	6	4	22.1	1.0	20.7
8	6	4	57.6	4.4	54.6
10	6	4	18.3	1.7	17.7
12	6	4	29.8	1.2	29.1
0	7	4	14.7	0.7	15.2
2	7	4	98.8	3.9	96.2
3	7	4	14.2	1.2	12.9
4	7	4	23.2	2.8	22.5
6	7	4	58.4	4.2	56.7
8	7	4	15.1	1.4	14.7
10	7	4	40.3	1.9	39.0
12	7	4	18.1	1.8	18.5
16	7	4	7.7	1.3	8.6
0	8	4	50.9	1.9	52.2
3	8	4	11.0	1.0	11.7
4	8	4	67.8	4.5	64.3
8	8	4	41.2	2.7	39.3
0	9	4	15.3	0.8	14.6
1	9	4	18.5	0.8	18.1
2	9	4	45.8	1.8	45.6
6	9	4	30.1	1.2	31.0
10	9	4	28.2	1.4	27.7
3	10	4	18.1	1.6	18.1
4	10	4	42.5	3.6	41.1
5	10	4	11.1	0.9	10.5
8	10	4	29.6	1.2	29.7
12	10	4	16.4	1.5	16.6
2	11	4	39.5	2.0	40.4
5	11	4	8.2	1.0	8.0
6	11	4	38.6	1.6	37.6
10	11	4	16.9	1.3	18.1
0	12	4	41.8	1.6	41.7
4	12	4	27.8	1.9	27.0
8	12	4	20.8	1.7	20.8
2	13	4	23.1	1.3	21.9
6	13	4	21.7	1.5	20.3
0	14	4	18.4	1.4	17.2
4	14	4	17.9	0.9	17.5
1	1	5	50.1	1.9	51.3
2	1	5	14.6	0.6	15.0
3	1	5	84.9	3.4	85.6
4	1	5	25.6	1.4	25.4
5	1	5	48.8	2.1	48.8
6	1	5	20.3	1.2	20.5
7	1	5	100.5	4.3	97.6
9	1	5	25.2	1.0	25.4
10	1	5	19.3	1.0	19.4
11	1	5	40.1	2.1	39.2
15	1	5	17.5	1.6	15.4
0	2	5	11.7	0.5	11.5
1	2	5	56.7	3.3	54.5
2	2	5	22.6	1.0	22.9
3	2	5	70.7	3.1	68.9
4	2	5	18.4	0.7	18.4
5	2	5	66.0	2.9	65.9
7	2	5	43.4	2.6	41.3
8	2	5	18.2	0.9	17.3
10	2	5	11.0	0.8	9.0
13	2	5	23.7	1.7	25.0
1	3	5	100.4	3.7	96.1
2	3	5	14.0	0.8	14.2
3	3	5	69.7	3.1	69.2
5	3	5	55.2	2.3	54.1
7	3	5	20.0	0.8	20.9
9	3	5	29.0	1.6	29.8
11	3	5	35.7	1.5	35.8
15	3	5	21.5	2.6	21.6
1	4	5	51.5	2.1	52.7
2	4	5	10.9	1.1	9.1
3	4	5	40.0	2.5	39.2
4	4	5	19.5	1.9	20.5
5	4	5	100.8	4.4	98.9
6	4	5	11.0	0.9	9.5
7	4	5	34.3	1.6	34.1
8	4	5	13.8	0.9	13.4
9	4	5	72.5	2.8	71.5
11	4	5	19.3	1.2	17.2
13	4	5	16.9	2.0	18.2
15	4	5	10.6	2.3	10.6
0	5	5	19.4	1.8	18.6
1	5	5	92.1	3.8	88.4
2	5	5	24.5	1.1	23.7
3	5	5	81.6	3.3	79.5
5	5	5	48.8	2.8	47.6
6	5	5	12.7	0.8	12.0
7	5	5	36.3	1.4	37.0
8	5	5	12.8	0.7	12.3
9	5	5	20.1	0.9	22.2
11	5	5	32.1	1.3	32.3
15	5	5	14.4	0.9	17.5
3	6	5	49.2	2.0	48.5
5	6	5	43.7	1.7	45.2
6	6	5	17.1	0.8	17.5
7	6	5	24.0	2.0	22.9
8	6	5	22.0	1.1	22.5
9	6	5	32.2	1.3	31.3
11	6	5	15.1	1.2	14.3
13	6	5	24.4	1.7	24.4
0	7	5	19.4	1.5	19.8
1	7	5	23.1	1.3	24.7
3	7	5	37.9	2.3	36.4
5	7	5	33.1	1.8	33.8
7	7	5	50.1	1.9	50.2
9	7	5	20.8	1.3	21.4
11	7	5	19.7	1.1	18.2
1	8	5	68.8	2.0	67.3
2	8	5	19.8	1.1	19.7
3	8	5	38.3	1.8	37.1
5	8	5	22.3	1.2	22.7
7	8	5	26.4	1.7	27.4
9	8	5	21.7	1.1	23.2
13	8	5	19.5	1.3	19.9
1	9	5	32.2	1.7	31.6
2	9	5	17.1	0.8	16.8
3	9	5	38.7	1.9	39.5
5	9	5	24.6	1.5	24.0
7	9	5	44.5	2.0	44.2
11	9	5	24.2	2.1	23.5
1	10	5	26.9	1.1	28.5
2	10	5	12.1	0.8	13.0
3	10	5	28.4	1.2	28.4
5	10	5	36.4	1.4	35.2
9	10	5	17.8	1.7	18.9
11	10	5	11.3	1.1	9.4
13	10	5	9.0	1.2	10.5
1	11	5	27.2	2.6	26.9
3	11	5	22.2	1.0	22.7
5	11	5	12.5	0.9	14.3
9	11	5	13.1	0.9	11.2
11	11	5	10.2	1.2	14.9
1	12	5	12.9	1.3	13.1
5	12	5	23.7	1.5	21.1
7	12	5	12.7	1.2	11.8
9	12	5	17.6	1.5	17.7
1	13	5	20.0	1.2	19.3
3	13	5	21.4	1.6	20.8
1	14	5	14.1	1.0	15.5
2	0	6	24.8	1.1	25.1
3	0	6	9.7	0.8	10.7
4	0	6	91.8	3.8	93.0
5	0	6	23.2	0.9	22.0
7	0	6	11.6	1.3	11.0
8	0	6	39.9	1.8	40.3
9	0	6	16.6	0.8	16.2
10	0	6	17.0	0.8	17.6
11	0	6	10.9	0.9	10.1
12	0	6	21.1	1.4	20.8
14	0	6	12.1	1.2	11.6
16	0	6	18.9	1.6	18.8
0	1	6	39.8	1.5	46.3
2	1	6	79.9	3.0	81.2
3	1	6	8.8	0.5	9.1
4	1	6	39.8	1.7	40.4
5	1	6	15.6	0.8	16.4
6	1	6	71.3	2.9	70.6
7	1	6	12.1	1.0	11.8
8	1	6	17.0	1.7	14.9
10	1	6	54.3	2.2	54.2
0	2	6	95.1	3.6	96.3
1	2	6	22.8	0.9	23.0
2	2	6	21.9	1.5	22.8
3	2	6	15.3	1.1	15.1
4	2	6	90.8	3.9	89.5
5	2	6	18.3	0.9	18.9
6	2	6	31.0	1.9	28.7
7	2	6	9.8	0.9	11.0
8	2	6	60.1	3.3	61.2
12	2	6	28.9	1.2	28.9
0	3	6	20.3	1.0	20.2
1	3	6	14.7	1.3	15.5
2	3	6	100.2	3.9	102.2
3	3	6	22.6	1.7	22.1
4	3	6	24.2	1.2	24.2
6	3	6	69.6	4.4	67.9
8	3	6	18.8	1.1	19.9
10	3	6	26.4	1.4	27.1
12	3	6	16.4	1.2	16.1
14	3	6	20.1	2.2	19.2
0	4	6	67.7	2.5	69.5
1	4	6	28.4	1.7	27.4
2	4	6	33.2	1.4	34.2
4	4	6	55.3	2.1	55.3
6	4	6	22.0	1.5	21.4
8	4	6	61.7	2.5	61.5
12	4	6	32.7	1.3	33.0
0	5	6	19.1	2.4	19.0
1	5	6	15.0	1.1	15.5
2	5	6	77.5	3.4	76.5
4	5	6	16.9	1.0	17.5
6	5	6	58.9	2.8	58.1
7	5	6	19.6	1.5	19.0
8	5	6	14.7	1.1	12.2
10	5	6	25.8	2.0	26.3
0	6	6	69.5	2.7	70.5
2	6	6	30.2	1.2	29.2
4	6	6	61.9	2.9	62.9
6	6	6	13.6	1.2	12.1
7	6	6	8.4	0.9	8.8
8	6	6	35.8	1.9	34.8
9	6	6	10.8	0.9	10.3
10	6	6	11.2	1.1	13.7
12	6	6	23.9	2.4	23.1
0	7	6	18.0	2.0	16.4
2	7	6	53.7	2.6	53.6
4	7	6	23.8	1.2	24.8
6	7	6	46.1	2.0	45.6
7	7	6	11.7	1.1	12.2
10	7	6	35.8	1.5	35.4
0	8	6	56.0	2.3	55.0
1	8	6	14.8	0.8	14.7
2	8	6	12.4	2.4	12.2
4	8	6	49.3	1.9	50.0
8	8	6	27.1	1.9	26.1
12	8	6	12.4	1.2	14.4
1	9	6	12.4	1.2	13.6
2	9	6	38.5	2.0	38.8
6	9	6	31.2	2.3	30.5
10	9	6	24.3	2.6	23.3
0	10	6	35.0	1.8	35.2
4	10	6	33.1	1.8	33.9
6	10	6	11.9	1.8	11.8
8	10	6	27.8	1.4	25.8
2	11	6	34.3	2.0	33.0
6	11	6	25.3	2.5	25.1
0	12	6	25.8	3.1	27.0
4	12	6	19.6	1.9	19.9
8	12	6	16.2	1.6	17.6
2	13	6	20.6	1.6	20.1
0	14	6	15.4	1.0	16.5
3	1	7	64.1	3.4	62.2
5	1	7	48.5	2.2	46.9
6	1	7	10.3	0.9	9.7
7	1	7	38.0	1.8	39.7
9	1	7	26.4	1.9	25.5
11	1	7	26.4	1.8	27.0
15	1	7	15.0	2.3	15.0
0	2	7	3.1	0.5	3.3
1	2	7	71.6	2.8	73.2
2	2	7	9.6	0.6	11.3
3	2	7	47.1	2.2	47.4
5	2	7	62.8	2.8	64.2
6	2	7	12.1	0.7	12.4
7	2	7	31.4	1.8	31.7
9	2	7	48.8	2.4	45.6
13	2	7	23.6	2.4	21.7
0	3	7	11.7	0.7	12.8
1	3	7	49.4	2.2	50.5
3	3	7	63.7	2.5	61.8
5	3	7	32.5	1.7	32.3
6	3	7	13.5	1.1	13.8
7	3	7	50.7	1.9	48.8
9	3	7	18.9	1.2	19.7
11	3	7	33.9	1.8	34.4
15	3	7	14.9	1.4	13.8
0	4	7	33.4	1.4	31.0
1	4	7	49.0	1.9	47.9
2	4	7	15.3	0.8	16.2
3	4	7	51.6	2.0	51.4
5	4	7	40.2	1.6	40.9
7	4	7	25.5	1.1	25.2
9	4	7	22.6	2.4	25.2
1	5	7	32.9	1.6	33.6
2	5	7	14.0	1.7	16.1
3	5	7	47.1	2.2	49.8
4	5	7	8.2	0.9	8.4
5	5	7	25.6	1.3	26.1
6	5	7	14.3	0.8	13.9
7	5	7	38.7	2.6	37.9
9	5	7	16.0	1.6	17.0
11	5	7	27.6	1.1	25.1
1	6	7	49.3	2.1	48.8
3	6	7	39.1	1.8	36.8
5	6	7	41.7	2.1	38.5
6	6	7	6.7	1.2	6.8
7	6	7	28.3	1.4	25.8
9	6	7	32.1	1.5	30.6
13	6	7	15.5	1.1	15.6
1	7	7	41.0	1.9	38.8
3	7	7	43.4	1.8	42.8
5	7	7	27.3	1.3	27.3
7	7	7	31.6	1.5	31.7
11	7	7	21.5	1.6	19.9
1	8	7	27.8	1.1	28.2
2	8	7	13.5	0.7	11.4
3	8	7	25.9	1.7	24.7
4	8	7	10.0	1.0	10.4
5	8	7	33.9	1.4	33.7
9	8	7	24.5	1.9	22.7
1	9	7	27.4	1.9	27.9
3	9	7	30.2	1.7	29.8
5	9	7	19.0	1.5	19.7
7	9	7	18.2	1.3	18.4
5	10	7	19.4	1.9	23.2
1	11	7	19.4	1.1	18.7
3	11	7	22.9	1.0	20.6
1	12	7	18.8	1.6	17.5
1	13	7	12.7	1.1	11.9
6	0	8	38.7	2.2	37.2
8	0	8	57.2	2.2	55.2
12	0	8	32.4	1.5	31.2
2	1	8	68.4	3.1	80.5
4	1	8	11.9	0.5	12.8
5	1	8	19.9	1.6	19.3
6	1	8	51.3	2.2	49.8
10	1	8	17.5	1.6	19.5
0	2	8	49.8	2.5	57.9
4	2	8	40.8	1.8	42.9
8	2	8	36.2	1.7	36.2
12	2	8	19.4	1.2	20.1
1	3	8	10.1	0.5	10.8
2	3	8	41.0	1.7	42.1
4	3	8	23.8	1.8	24.3
6	3	8	43.4	1.7	43.6
9	3	8	11.8	0.7	10.5
10	3	8	37.9	1.9	37.0
0	4	8	75.3	3.1	75.1
2	4	8	16.6	0.9	18.4
3	4	8	13.9	1.2	14.7
4	4	8	72.3	3.1	69.9
8	4	8	24.5	2.3	23.8
1	5	8	11.5	1.2	11.8
2	5	8	52.7	2.1	50.5
4	5	8	25.5	1.6	24.0
6	5	8	42.8	1.8	41.1
8	5	8	14.4	1.2	15.1
10	5	8	34.2	2.5	32.7
0	6	8	44.9	1.8	44.4
4	6	8	38.9	1.8	37.5
8	6	8	31.7	2.2	30.8
12	6	8	13.6	1.3	13.2
2	7	8	39.4	2.2	40.3
4	7	8	11.1	0.7	10.3
6	7	8	25.3	1.9	26.0
10	7	8	11.3	0.9	12.1
0	8	8	31.5	1.3	30.4
4	8	8	28.2	2.4	28.8
8	8	8	28.0	2.5	26.6
2	9	8	38.7	2.5	37.8
4	9	8	32.3	2.1	29.9
0	10	8	33.9	1.9	30.7
4	10	8	21.3	3.2	22.1
8	10	8	16.2	1.2	17.2
4	12	8	18.6	2.1	18.7
2	13	8	14.8	1.2	16.6

75·6°. The inner S–S bond length was found to be $2{\cdot}06_7 \pm 0{\cdot}02_8$ Å and the outer S–S bond length to be $2{\cdot}02_6 \pm 0{\cdot}02_8$ Å. A later study by Blank, Donohue & Abrahams (1965), with the intensities visually estimated in 1954 but corrected for absorption and anomalous dispersion, resulted in unacceptable atomic temperature factors ($B_{\text{Ba}}=1{\cdot}2$ Å^2, B_{S} ranging from 0·5 to 2·1 Å^2, $B_{\text{O}}=0{\cdot}8$ and 8·8 Å^2).

The $BaS_4.H_2O$ structure has been remeasured, both to examine the earlier report of possible bond-length variation in the S_4^{2-} anion, and because of our continuing interest in piezoelectric materials.

Experimental

A sphere of radius 0·126 ± 0·005 mm was ground from one of the prismatic crystals used in the 1954 X-ray study. It was necessary to protect the crystal from the atmosphere, since on removal from the sealed vial in which the crystal had been stored, rapid decomposition took place: Ambroid* proved a satisfactory protectant. The sphere was mounted on a Pyrex capillary of 0·196 mm outside diameter and 0·120 mm inside diameter, with the *c* axis parallel to the capillary axis. All measurements of integrated intensity were made with this sphere, by the use of our programmed electronic X-ray automatic diffractometer PEXRAD (Abrahams, 1962, 1963). The basic experimental conditions have been described elsewhere (Abrahams & Bernstein, 1965; Abrahams & Reddy, 1965). The profile through each reciprocal lattice point was determined, for each member of the balanced pair of filters, at 81 values of ω differing successively by 0·05°. A total of 7747 reflections were measured, with Mo $K\alpha$ radiation, within a reciprocal hemisphere of radius $(\sin\theta)/\lambda=1{\cdot}02$ Å^{-1}.

Structure factors (F_{meas}) together with the corresponding standard deviations (σF_{meas}) were computed directly from the PEXRAD magnetic tape output, with programs similar to those of Cetlin & Abrahams (1963). The integrated intensities were corrected for Lorentz and polarization factors and for absorption. The constant term for the variance resulting from systematic isotropic sources of error (Abrahams, 1964) was 57×10^{-4} $(F_{\text{meas}})^4$. A correction for extinction was made by Zachariasen's (1963) method, the parameter C having a value of $0{\cdot}513\times10^{-5}$ on the absolute scale. The resulting maximum change in $|F_{\text{meas}}|$ is 22·3 per cent, for $F(212)$. The 894 independent values of F_{meas} and σF_{meas} used in this study are given in Table 1 on the final least-squares derived absolute scale ($K=0{\cdot}1251$).

Crystal data

Barium tetrasulfide monohydrate, $BaS_4.H_2O$ has a formula weight (F.W.) of 283·611. The lattice constants of this orthorhombic crystal are $a=9{\cdot}691\pm1$, $b=8{\cdot}017$ ±1 and $c=7{\cdot}828\pm1$ Å† at 298°K, measured by Abrahams & Reddy's (1965) method with Cu $K\alpha_1$ radiation [$\lambda=1{\cdot}54056$ Å, Bearden (1964)]. Each of these values is about 0·2 per cent greater than the 1954 constants; these differences correspond to a single pooled standard deviation. The unit-cell volume, V, is $608{\cdot}18\pm22$ Å^3. $D_m=3{\cdot}11\pm5$ g.cm^{-3} (Abrahams, 1954): $Z=4$ F.W. per unit cell; $D_x=3{\cdot}097$ g.cm^{-3}. The absorption coefficient for Mo $K\alpha$ radiation is 7·88 mm^{-1}; for the sphere used, $\mu R=0{\cdot}989$. $F(000)=520e$.

The only reflections systematically absent are $h00$ for $h=2n+1$ and $0k0$ for $k=2n+1$, consistent with the 1954 space group assignment of $P2_12_12$ (D_2^3).

Refinement of the structure

The 1954 coordinates for $BaS_4.H_2O$ were taken as initial values for refinement by the method of least-squares; Busing, Martin & Levy's (1962) *ORFLS* program, modified by W. C. Hamilton and by B. B. Cetlin, was used for the calculations. Scattering factors based on relativistic Dirac–Slater wave functions (Cromer & Waber, 1965) for neutral Ba, S and O were used, relevant corrections for anomalous dispersion with Mo $K\alpha$ radiation being made with Cromer's (1965) values for $\Delta f'$ and $\Delta f''$.

An initial scale factor that placed the F_{meas} on a scale within 2·5 per cent of absolute, together with F_{calc} based on the 1954 coordinates, resulted in the conventional residual $R=0{\cdot}341$. Three models were used in refinement:

(*a*) all atoms isotropically vibrating;

(*b*) Ba vibrating anisotropically, S and O isotropically;

(*c*) all atoms anisotropically vibrating.

All three models converged rapidly, with $wF_{\text{meas}}=1/\sigma^2F_{\text{meas}}$ as weights, to give parameter shifts less than 0·1 standard deviations. The corresponding accuracy indicators, for these models, are:

$$\begin{aligned}(a)\;& R=0{\cdot}0556,\; wR=0{\cdot}0801,\; S=1{\cdot}566\,,\\ (b)\;& R=0{\cdot}0447,\; wR=0{\cdot}0717,\; S=1{\cdot}405\,,\\ (c)\;& R=0{\cdot}0322,\; wR=0{\cdot}0498,\; S=0{\cdot}991\,,\end{aligned}$$

where wR is the weighted 'reliability' index and S is the standard deviation of an observation of unit weight.

In comparison with model (*c*), models (*a*) and (*b*) can clearly be rejected as inferior. With Hamilton's (1965) $\mathscr{R}$-ratio as criterion $wR(b)/wR(c)$ for example is 1·440 experimentally, compared with $\mathscr{R}_{25,839,0\cdot005}=1{\cdot}028$. Hence the best atomic coordinates are those obtained by the use of model (*c*): the position coordinates for the final model are given in Table 2, and the corresponding anisotropic temperature coefficients in Table 3.

The final value of S may conveniently be examined in terms of the indicator $\mathscr{U}_\alpha$ (Abrahams, 1969). Correct assignment of σF_{meas}, on the original experimental scale,

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* Ambroid Company, Inc., Boston, Massachusetts.

† Error values here, and later in this paper, without decimal point correspond to the least significant digit in the function value.

Table 2. *Final position coordinates of* $BaS_4.H_2O$ *at* 289°K

	x	y	z
Ba	0·11997±4	0·25025±5	0·24855±5
S(1)	0·1036±2	0·4703±2	0·6329±3
S(2)	0·3167±2	0·1063±2	0·5690±4
S(3)	0·3291±2	0·3635±2	0·9408±3
S(4)	0·4678±2	0·3774±2	0·1429±4
O(1)	0	0	0·4471±14
O(2)	0	½	0·0557±14

would result in a $\mathscr{U}_\alpha$ range corresponding to a confidence interval of 100(1–2α) per cent encompassing the value of unity. At the one per cent level, $\mathscr{U}_{0\cdot01}$ ranges from 0·932 to 1·057, indicating both an entirely satisfactory model and an accurate assignment of σF_{meas}.

Absolute configuration

Since all the $BaS_4.H_2O$ structure factors within a complete hemisphere of reciprocal space have been measured, it is possible to determine the absolute configuration of the atomic arrangement in this piezoelectric crystal, with violations of Friedel's law caused by the anomalous scattering of the Ba and S atoms as indicators. Instead of reversing the signs of all Miller indices and comparing the results of the ensuing least-squares refinement with those in the preceding section, it is simpler to replace each xyz coordinate in Table 2 by $\bar{x}\bar{y}\bar{z}$. The value of wR corresponding to Table 2 is 0·04980, and that corresponding to refinement with $\bar{x}\bar{y}\bar{z}$ coordinates is 0·05343, on convergence.

The ratio $wR(\bar{x}\bar{y}\bar{z})/wR(xyz)=1{\cdot}073$ greatly exceeds Hamilton's (1965) $\mathscr{R}$-ratio for the one-dimensional hypothesis with 839 degrees of freedom, for which $\mathscr{R}_{1,839,0\cdot005}=1{\cdot}005$. The hypothesis that the xyz coordinates in Table 2 should be replaced by corresponding $\bar{x}\bar{y}\bar{z}$ values may hence be rejected.

Interatomic distances and angles

The position coordinates in Table 2, together with the lattice constants given under *Crystal data*, were used to derive the interatomic distances and angles of Tables 4 and 5 by means of Busing, Martin & Levy's (1964) *ORFFE* program. Corrections for the effects of thermal vibration have not been made on these distances and angles, nor have the associated variances been used in calculating the standard deviations given in Tables 4 and 5.

Thermal vibrations

In the *Refinement* section, it was shown that the model with all atoms vibrating anisotropically was more acceptable than the alternatives [models (*a*) and (*b*)] considered. The root-mean-square amplitudes corresponding to the principal axes of the ellipsoid of vibration for each atom are given in Table 6 and the equivalent radial displacements in Table 7. The differences among these amplitudes confirm that Ba and the four S atoms have very significantly anisotropic motion. The vibrations for the oxygen atoms, in contrast, are essentially isotropic.

Table 5. *Tetrasulfide anion bond and dihedral angles*

S(1)–S(1)–S(2)	104·0±0·1°
S(4)–S(4)–S(3)	104·3±0·1
S(2)S(1)S(1)/S(1)S(1)S(2)	76·2±0·2
S(3)S(4)S(4)/S(4)S(4)S(3)	76·5±0·2

Table 3. *Final temperature coefficients* for* $BaS_4.H_2O$ ($\times 10^5$)

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	B†
Ba	527±4	589±4	875±11	5±4	−5±5	−2±7	1·74±1Å²
S(1)	503±16	811±24	1019±35	92±17	−123±25	91±28	2·01±5
S(2)	468±16	766±23	1081±44	70±17	−30±23	−19±30	1·91±5
S(3)	527±18	836±23	916±37	−117±17	65±24	−38±31	2·02±5
S(4)	602±17	648±23	900±38	50±17	11±23	126±25	1·97±5
O(1)	572±78	1112±127	807±163	65±73	0	0	2·2±2
O(2)	606±78	733±99	1080±169	21±65	0	0	2·2±2

* Based on the factor $\exp\{-[h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23}]\}$. Symmetry requires that $\beta_{13}=\beta_{23}=0$ for O(1) and O(2).

† The Debye–Waller temperature factors from the final isotropic temperature coefficient least-squares refinement of model (*a*), see text.

Table 4. *Interatomic distances in* $BaS_4.H_2O$

S(1)–S(2)	$2{\cdot}069_0\pm3_5$ Å	O(1)–S(3)	3·628±10 Å
S(1)–S(1)	$2{\cdot}063_3\pm3_8$	O(1)–S(4)	3·371±11
S(3)–S(4)	$2{\cdot}079_3\pm3_3$	O(2)–S(1)	3·467±11
S(4)–S(4)	$2{\cdot}062_4\pm3_6$	O(2)–S(2)	3·537±9
Ba–O(1)	2·792±6	Ba–O(2)	2·764±6
Ba–S(1)	3·491±3	Ba–S(3)	3·277±2
Ba–S(2)	3·250±2	Ba–S(3)	3·313±2
Ba–S(2)	3·356±2	Ba–S(3)	3·472±2
Ba–S(2)	3·464±2	Ba–S(4)	3·552±3
		Ba–S(4)	3·618±2

Table 6. *R.m.s. amplitudes of thermal vibration in* $BaS_4.H_2O$ *at* 298°K*

	1	2	3
Ba	$0{\cdot}1384\pm5$ Å	$0{\cdot}1583\pm6$ Å	$0{\cdot}1648\pm10$ Å
S(1)	$0{\cdot}138\pm3$	$0{\cdot}170\pm3$	$0{\cdot}185\pm3$
S(2)	$0{\cdot}143\pm3$	$0{\cdot}163\pm3$	$0{\cdot}184\pm4$
S(3)	$0{\cdot}146\pm3$	$0{\cdot}165\pm4$	$0{\cdot}180\pm3$
S(4)	$0{\cdot}138\pm3$	$0{\cdot}168\pm3$	$0{\cdot}175\pm3$
O(1)	$0{\cdot}16\pm2$	$0{\cdot}16\pm1$	$0{\cdot}19\pm1$
O(2)	$0{\cdot}15\pm1$	$0{\cdot}17\pm1$	$0{\cdot}18\pm1$

* The amplitudes are given along the principal axes of vibration.

Table 7. *Equivalent r.m.s. radial displacement**

	Displacement
Ba	$0{\cdot}1543\pm5$ Å
S(1)	$0{\cdot}165\pm1$
S(2)	$0{\cdot}164\pm1$
S(3)	$0{\cdot}164\pm1$
S(4)	$0{\cdot}161\pm1$
O(1)	$0{\cdot}17\pm1$
O(2)	$0{\cdot}17\pm1$

* Based on the anisotropic temperature factors in Table 3, and given by the root-mean-square of the amplitudes in Table 6.

Discussion

The two principal features of interest that led to the present restudy of $BaS_4.H_2O$, namely the detailed atomic arrangement within the S_4^{2-} anion and the piezoelectric properties of the crystal, are considered in this section, together with a brief account of the crystal structure in relation to other compounds.

In the 1954 study, the inner S–S bond of the helical S_4^{2-} anion was reported to differ in length from the outer S–S bond (the anion has C_2 symmetry) by about 0·04 Å. The standard deviation for each S–S bond length was estimated at about 0·04 Å; however, a similar bond length difference in both crystallographically independent S_4^{2-} anions was taken as evidence that this difference might indeed be real. The distances and angles given in Tables 4 and 5 may now be examined to determine (1) whether the two independent S_4^{2-} anions differ significantly in dimension, and (2) whether the inner S–S bond length differs significantly from that of the outer bond.

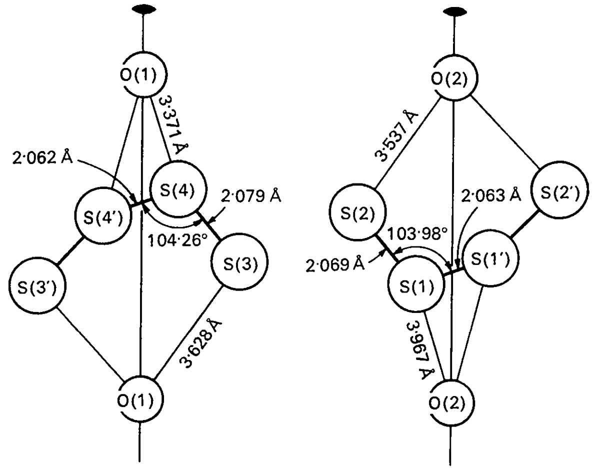

Fig. 1. Diad symmetry and dimensions of the tetrasulfide anion and neighboring water molecule.

Considering question (1), the lengths of the two inner bonds S(1)–S(1) and S(4)–S(4) are $2{\cdot}063_3\pm3_8$ and $2{\cdot}062_4\pm3_6$ Å respectively. With a pooled standard deviation of $0{\cdot}005_2$ Å, these two bonds lengths are clearly not significantly different: the mean length of the inner bond is thus $2{\cdot}062_9\pm2_6$ Å. The lengths of the two outer bonds S(1)–S(2) and S(3)–S(4) are $2{\cdot}069_0\pm3_5$ and $2{\cdot}079_3\pm3_3$ Å respectively. The outer bond pooled standard deviation is $0{\cdot}004_8$ Å and the difference between the two bonds is 2·15 pooled standard deviations. Hence it is most likely that the two outer S–S bond lengths are not significantly different: the mean bond length is thus $2{\cdot}074_2\pm2_4$ Å. The bond angles S(4)–S(4)–S(3) and S(1)–S(1)–S(2) differ by 2·0 pooled standard deviations, a difference of low significance. Similarly, the dihedral angle in the two anions differs by less than two pooled standard deviations. The two independent S_4^{2-} anions may therefore be confidently regarded as being dimensionally equivalent.

In considering question (2), the following relationships are relevant:

(*a*) inner bond S(1)–S(1) differs in length from outer bond S(1)–S(2) by 1·1 pooled standard deviations;

(*b*) inner bond S(4)–S(4) differs in length from outer bond S(3)–S(4) by 3·5 pooled standard deviations;

(*c*) the mean inner and outer S–S bonds differ in length by 3·2 pooled standard deviations;

(*d*) the individual S–S bonds differ in length from the mean value of $2{\cdot}069_1$ Å by the following number of standard deviations: 1·5 for S(1)–S(1), 0 for S(1)–S(2), 1·9 for S(4)–S(4) and 3·1 for S(3)–S(4).

In terms of the null hypothesis, statistical theory gives the probability of these observed deviations occurring as 27 per cent for case (*a*), 0·05 per cent for (*b*) and 0·14 per cent for (*c*). For case *d*, the smallest probability is 0·2 per cent, for the S(3)–S(4) bond. It has now been established (*e.g.* Hamilton & Abrahams, 1969) that if systematic error is present in the diffraction experiment, the least-squares derived standard deviations in the variables may be appreciably reduced in absolute value. If the computed standard deviations above are too small by as little as 20 per cent, the least likely event as represented by case *b* becomes one with an 0·5 per cent chance of occurring. In view of this uncertainty, the hypothesis that the inner S–S bonds are equivalent in length to the outer S–S bonds should not be rejected.

The absolute configuration of the atomic arrangement in $BaS_4.H_2O$ may be related to the piezoelectric polarization if crystals large enough to permit measurement of the sense of the piezoelectric response with respect to the crystal orientation become available. An attempt to grow such crystals is now being made by Remeika (1968). The absolute orientation may then be recognized by measurement of the ratio $A = I(hhh)/I(\bar{h}\bar{h}\bar{h})$. With Mo $K\alpha$ radiation, the following A-ratios are expected: for $h=1$, $A=1{\cdot}10$; $h=2$, $A=1{\cdot}04$; $h=3$, $A=0{\cdot}94$; $h=4$, $A=0{\cdot}97$; $h=5$, $A=0{\cdot}91$ and for $h=6$, $A=0{\cdot}83$. On completion of this configurational experiment, it may become possible to determine the atomic mechanism giving rise to the piezoelectricity in $BaS_4.H_2O$.

The present study, as shown above, indicates no significant variation among the S–S bond lengths in the tetrasulfide anion. The resulting mean S–S bond length of 2·069 ± 2 Å compares very closely with the S–S distances reported in the three allotropes of elementary sulfur that have now been accurately measured. A review by Donohue (1965) gives the S–S bond length in α-S_8 as 2·060 ± 2 Å, in β-S_8 as 2·063 ± 17 Å and in ϱ-S_6 as 2·057 ± 18 Å. Hence the additional two-thirds of an electron associated with each S–S bond in the tetrasulfide ion has very little effect on the interatomic separation.

The role of the hydrogen atoms of the water molecules in this crystal is not clear: careful examination of the final three-dimensional Fourier series revealed no signs of these atoms. Hydrogen bonding, as evidenced by short oxygen–oxygen or oxygen–sulfur contacts, apparently is not important in $BaS_4.H_2O$. Fig. 1 illustrates the separation between the S_4^{2-} anions and the water molecules lying on common diad axes.

Donohue (1968) has pointed out that the S_4^{2-} helices S(2)–S(1)–S(1)–S(2) and S(3)–S(4)–S(4)–S(3) are of opposite chirality. The relative sense of these independent helices is not determined by the symmetry operators, unlike the case in Cs_2S_6 (Abrahams & Grison, 1953) where inversion centers require pairs of related S_6^{2-} helices to be of opposite chirality.

The barium atom in $BaS_4.H_2O$ has eleven nearest neighbors, at distances listed in Table 4. The two independent Ba–O distances differ only by 3·2 pooled standard deviations, and in terms of the above discussion are probably equivalent. The average Ba–O distance of 2·778 ± 4 Å is comparable to the value in BaO of 2·769 Å (Zollweg, 1955), but longer than the shortest observed values for this contact; a review of such distances was recently given by Jamieson, Abrahams & Bernstein (1968). The barium atom coordination polyhedron may be described as a distorted square antiprism, if bonded pairs of sulfur atoms are regarded as single nearest neighbors. There are two such S(3)–S(4) pairs and one S(1)–S(2) pair. The resulting eight effective nearest neighbors are arranged such that the basal faces of the distorted square antiprism are approximately normal to the crystallographic c axis.

It is a pleasure to thank Professor Jerry Donohue for his observations on the chirality of polysulfide anions.

References

Abrahams, S. C. (1954). *Acta Cryst.* **7**, 423.

Abrahams, S. C. (1956). *Quart. Rev. Chem. Soc. London,* **10**, 407.

Abrahams, S. C. (1962). *Rev. Sci. Instrum.* **33**, 973.

Abrahams, S. C. (1963). *Rev. Sci. Instrum.* **34**, 1279.

Abrahams, S. C. (1964). *Acta Cryst.* **17**, 1327.

Abrahams, S. C. (1969). *Acta Cryst.* **A25**, 165.

Abrahams, S. C. & Bernstein, J. L. (1965). *Acta Cryst.* **18**, 926.

Abrahams, S. C. & Grison, E. (1953). *Acta Cryst.* **6**, 206.

Abrahams, S. C. & Reddy, J. M. (1965). *J. Chem. Phys.* **43**, 2533.

Bearden, J. A. (1964). *X-ray Wavelengths,* U.S. Atomic Energy Commission, Oak Ridge, Tennessee.

Blank, J. S., Donohue, J. & Abrahams, S. C. (1965). American Crystallographic Association Meeting, Gatlinburg, Tennessee, Paper M4.

Busing, W. R., Martin, K. O. & Levy, H. A. (1962). ORNL Report TM-305. Oak Ridge National Laboratory, Tennessee.

Busing, W. R., Martin, K. O. & Levy, H. A. (1964). ORNL Report TM-306. Oak Ridge National Laboratory, Tennessee.

Cetlin, B. B. & Abrahams, S. C. (1963). *Acta Cryst.* **16**, 943.

Cromer, D. T. (1965). *Acta Cryst.* **18**, 17.

Cromer, D. T. & Waber, J. T. (1965). *Acta Cryst.* **18**, 104.

Donohue, J. (1965). In *Elemental Sulfur,* Ed. B. Meyer, Ch. 2. New York: Interscience Publishers.

Donohue, J. (1968). Private communication.

Hamilton, W. C. (1965). *Acta Cryst.* **18**, 502.

Hamilton, W. C. & Abrahams, S. C. (1969). To be published.

Jamieson, P. B., Abrahams, S. C. & Bernstein, J. L. (1968). *J. Chem. Phys.* **48**, 5048.

Remeika, J. P. (1968). Private communication.

Zachariasen, W. H. (1963). *Acta Cryst.* **16**, 1139.

Zollweg, R. J. (1955). *Phys. Rev.* **100**, 671.