

Refinement of the structure of celestite SrSO_4 *

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Auszug

Die Struktur von Celestin wurde mittels Ausgleichsrechnung auf Grund dreidimensionaler Diffraktometerdaten verfeinert. Die Ergebnisse stimmen im allgemeinen mit denen für die isomorphen Minerale Baryt BaSO_4 und Anglesit PbSO_4 überein.

Abstract

A least-squares refinement of the structure of celestite has been carried out using three-dimensional counter-diffractometer data. The results agree, in general, with those for the isotypic minerals barite (BaSO_4) and anglesite (PbSO_4).

Introduction

As part of a study on cleavage in crystals, a detailed study of the cleavages of the isotypic minerals celestite (SrSO_4), barite (BaSO_4), and anglesite (PbSO_4), and synthetic compounds of this structure type is being carried out in this laboratory. Accurate atom parameters of these compounds are needed for the computation of cleavage strengths. The structure of celestite was determined in 1925 by JAMES and WOOD¹. In this study the positions of oxygen ions were approximately determined chiefly through geometrical assumptions.

SAHL² published refinements of the structures of barite and anglesite while this study of the celestite structure was in progress. Although these compounds are isotypic with celestite we have con-

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¹ R. W. JAMES and W. A. WOOD, The crystal structure of barytes, celestine and anglesite. Proc. Roy. Soc. [London] **109** (1925) 598—620.

² K. SAHL, Die Verfeinerung der Kristallstrukturen von PbCl_2 (Cotunnit), BaCl_2 , PbSO_4 (Anglesit) und BaSO_4 (Baryt). Beitr. Min. Petr. **9** (1963) 111—132.

tinued with this work since it is of interest to determine structural variations in this isotopic series. This work also was carried out using the more accurate three-dimensional counter-diffractometer data, rather than two-dimensional film data.

Composition, space group and unit cell

The celestite used for the refinement was a fragment from a colorless, transparent crystal which was collected by one of us (D. G.) in the France Stone Company's quarry near Waterville, Ohio. An emission spectrographic analysis of a portion of the crystal gave the following results: BaO between 1.0 and 0.5% and CaO, MgO, SiO₂ each less than 0.002%. No other impurities were detected in measurable amounts.

JAMES and WOOD¹, RINNE, HENTSCHEL and SCHIEBOLD³, WYCKOFF and MERWIN⁴, BASCHE and MARK⁵, and SAHL² have studied natural members of this series and have concluded that the space group is *Pnma*. Form development, etch figures, and lack of pyroelectricity (this study) eliminate the only other space group with the observed diffraction symmetry. The unit-cell dimensions were determined from a powder-diffractometer trace using halite as an internal standard. They are $a = 8.377 \pm 0.006 \text{ \AA}$, $b = 5.350 \pm 0.004 \text{ \AA}$, and $c = 6.873 \pm 0.004 \text{ \AA}$.

Intensity data

The specimen used for the intensity measurements was an irregular fragment approximately 0.47 mm long parallel to *c*, 0.15 mm parallel to *a*, and 0.05 mm parallel to *b*. The exact shape was measured to the nearest micron. Intensities were determined using an equi-inclination counter-diffractometer with copper radiation and a proportional detector. All observations were recorded both graphically and by a direct-count method. Due to mechanical limitations of the equipment only 321 peaks out of the theoretical 389 in one octant of the reciprocal sphere were recorded. Approximately 200 intensity values were determined twice. In general the agreement is excellent and within calculated standard deviations.

³ F. RINNE, H. HENTSCHEL und F. SCHIEBOLD, Zum Feinbau von Anhydrit und Schwerspat. *Z. Kristallogr.* **61** (1925) 164–176.

⁴ R. W. G. WYCKOFF und H. E. MERWIN, Die Raumgruppe des Baryt (BaSO₄). *Z. Kristallogr.* **61** (1925) 452–462.

⁵ W. BASCHE und H. MARK, Über die Struktur von Verbindungen des Typus MeXO₄. *Z. Kristallogr.* **64** (1926) 1–70.

Intensity values were computed from the measurements of background on both sides of each peak and values obtained by scanning through the peak. They were corrected for background and absorption by use of modified IBM programs DFSET 4⁶ and ABSRB⁷. Weights for use in least-squares refinement were based on calculations of standard deviations in F values using standard counting statistics.

Refinement

The refinement of the atom parameters was carried out with a modified version of the least-squares program SFLSQ3⁸ which utilizes the full matrix. All atoms were assumed half ionized in computations of scattering functions, and the initial individual isotropic temperature factors were given values of 0.5. The initial coordinates used for Sr and S were those of JAMES and WOOD¹, and the oxygen parameters were modified from those listed in WYCKOFF⁹ for KClO₄ (see Table 1). A rejection test was initially employed which rejected all reflections for which $F_o - F_c$ was large.

The initial parameters gave a value of 23.0% for the unweighted discrepancy factor, R , and a value of 23.8% for the weighted R . This cycled to values of 17.0% and 13.2% respectively, with simultaneous refinement of coordinates and a single scale factor. A two-dimensional Fourier synthesis was computed which showed atom O_{III} as lying on a steep gradient. Its position was recomputed, in part, from the assumption that the oxygen atoms in the sulfur-coordination polyhedron were at the corners of a perfect tetrahedron. In the next cycles the R factors decreased to 14.1% and 11.4% respectively. A check of the original data eliminated three questionable reflections showing primary extinction and one whose observed intensity profile was diffuse. Corrections in the weighting function were also made. The unweighted R then converged to 13.5% and the weighted R to 9.5%. At this stage the rejection tests for F_o were

⁶ C. T. PREWITT, The parameters γ and φ for equi-inclination, with application to the single crystal diffractometer. *Z. Kristallogr.* **114** (1960) 355–360.

⁷ C. W. BURNHAM, Absorption corrections for prismatic crystals and evaluation of end effect. Abstract, 1962 Meeting of the American Crystallographic Society, 19.

⁸ C. T. PREWITT, SFLSQ2, an IBM program for least-squares refinement. Ph.D. thesis, M.I.T. (1962).

⁹ R. W. G. WYCKOFF, *Crystal Structure*, Vol. II, Chapt. VIII, Table page 23, Interscience.

removed. The final coordinate refinement gave an unweighted R of 10.4% and a weighted R of 7.7%.

A series of isotropic temperature factor refinements gave a final unweighted R of 9.5% and weighted R of 7.2%. Although initially some of the temperature factors became negative, all the factors refined to positive values. Refinement of anisotropic temperature factors was attempted, but since six values remained negative it was assumed that the accuracy of the data was being exceeded, and the refinement was discontinued. As a check on the weighting function,

Table 1. *Coordinates and isotropic temperature factors for SrSO₄, BaSO₄ and PbSO₄*

	BaSO ₄ (SAHL ²)	PbSO ₄ (SAHL ²)	SrSO ₄ (initial)	SrSO ₄ (final)	SrSO ₄
	Ba	Pb	Sr	Sr	σ
x	.1844	.1882	.179	.1836	.0006
y	1/4	1/4	1/4	1/4	0
z	.1587	.1670	.161	.1583	.0006
B	1.30	(1.25)*	.5	.53	.06
	S				
x	.436	.437	.443	.438	.002
y	3/4	3/4	3/4	3/4	0
z	.190	.186	.195	.188	.002
B	.85	(.95)*	.5	.15	.14
	O _I				
x	.592	.595	.557	.603	.004
y	3/4	3/4	3/4	3/4	0
z	.112	.100	.100	.093	.004
B	1.65	1.60	.5	.64	.61
	O _{II}				
x	.313	.319	.343	.305	.005
y	3/4	3/4	3/4	3/4	0
z	.043	.043	.050	.033	.004
B	1.65	1.60	.5	1.52	.68
	O _{III}				
x	.421	.415	.437	.420	.003
y	.966	.974	.958	.979	.004
z	.313	.306	.319	.312	.003
B	1.65	1.60	.5	.21	.29

* average of $h0l$ and $hk0$ data.

Table 2. Observed and final calculated structure factors of celestite

h k l	F _o	F _c	h k l	F _o	F _c	h k l	F _o	F _c	h k l	F _o	F _c
4 0 0	73.89	-74.03	1 4 1	3.54	8.35	3 5 2	97.09	101.31	8 0 4	72.93	64.86
6	40.36	37.05	2	33.33	-33.98	4	17.29	10.79	1 1 4	102.77	88.24
8	188.80	-211.08	3	65.81	-66.17	5	81.80	-80.41	2	74.34	61.56
10	57.46	46.94	4	163.04	189.21	6	41.52	42.03	3	82.62	-76.08
4 1 0	160.12	168.83	5	61.17	60.59	0 6 2	51.39	52.24	4	109.22	-101.84
6	163.09	-172.60	6	17.32	-17.58	1	101.16	108.49	5	83.64	80.37
8	37.47	-32.10	7	7.79	1.27	2	8.26	-8.73	6	62.69	52.86
10	135.74	128.16	8	21.44	-28.24	3	5.39	3.14	7	54.70	-55.84
2 2 0	147.07	149.98	0 5 1	23.59	-31.95	1 0 3	91.98	-89.35	8	25.40	23.70
4	18.60	10.09	1	51.31	-59.20	2	89.30	-86.62	0 2 4	154.06	115.73
6	123.07	-119.13	2	111.24	119.64	3	204.77	218.38	1	162.66	-156.71
8	171.56	157.53	3	20.19	15.96	4	57.84	-40.99	2	69.83	-60.60
2 3 0	139.42	134.77	4	3.94	-2.45	5	149.37	-143.15	3	95.15	-81.04
4	170.26	-148.55	5	39.29	43.64	6	14.82	-12.15	4	23.56	-22.60
6	158.22	144.28	6	111.02	-120.93	7	19.97	22.12	5	31.90	-21.92
8	42.69	40.36	1 6 1	14.78	9.30	8	13.10	14.14	6	59.86	58.70
2 4 0	48.74	-50.59	2	48.90	58.92	9	38.06	26.92	7	94.17	-80.79
4	31.41	-38.83	3	51.62	53.41	0 1 3	6.74	-10.97	8	77.07	-62.16
6	36.27	31.33	4	103.17	-108.34	1	209.28	193.61	1 3 4	109.09	-98.65
8	153.59	-166.01	1 0 2	175.42	-180.43	2	5.86	-5.35	3	65.25	64.24
2 5 0	135.41	-147.43	2	45.24	-39.22	3	118.67	-112.52	4	93.37	88.33
4	66.37	69.95	3	112.62	105.68	4	13.73	-13.69	5	56.45	-54.78
6	107.04	-114.92	4	21.98	21.04	5	134.42	-127.68	6	56.85	-46.77
0 6 0	148.47	-161.75	5	66.45	57.59	6	14.44	-9.52	7	60.84	65.75
2	51.34	55.55	6	13.41	11.43	7	120.08	110.24	0 4 4	100.56	-90.68
4	9.12	7.50	7	157.67	-173.02	8	33.76	39.61	1	93.97	93.49
1 0 1	7.29	6.77	8	92.48	96.17	9	97.37	-83.69	2	53.49	51.06
2	28.79	-34.87	9	86.71	75.35	1 2 3	36.53	-23.21	3	9.79	1.75
3	83.58	-78.45	1 1 2	185.90	-169.86	2	35.02	36.68	4	16.12	16.42
5	81.96	76.91	2	111.72	103.64	3	210.74	-200.60	5	9.56	-11.33
6	28.77	-25.29	3	178.22	179.72	4	11.19	3.45	6	49.68	-50.92
7	6.83	-0.13	4	26.98	3.70	5	198.40	194.94	1 5 4	55.11	55.07
8	31.63	-39.01	5	122.01	-111.81	6	10.55	9.91	2	52.37	44.32
9	30.44	-30.68	6	59.68	49.37	7	36.35	37.64	3	51.97	-51.78
10	37.49	21.53	7	78.42	66.20	8	0.00	5.43	4	65.73	-70.40
0 1 1	78.26	-76.05	8	9.05	8.31	0 3 3	4.63	10.28	1 0 5	21.82	16.90
1	100.46	-93.46	9	89.53	81.32	1	137.02	-138.09	2	100.89	90.20
2	178.01	194.57	0 2 2	54.73	40.60	2	2.92	-1.05	3	57.85	-56.02
3	10.82	9.68	1	204.48	208.40	3	126.10	116.58	4	185.91	-186.66
4	4.58	0.89	2	40.78	-25.40	4	12.26	13.81	5	9.12	-0.74
5	63.36	67.88	3	3.63	-0.40	5	142.72	122.37	6	71.69	67.54
6	154.36	-157.95	4	15.13	13.43	6	19.73	13.73	7	6.76	9.83
7	46.60	-42.69	5	19.00	-14.04	7	110.44	-101.07	8	23.55	26.43
8	62.40	56.89	6	49.47	46.73	8	23.57	-32.74	0 1 5	215.37	152.60
9	51.95	42.32	7	152.70	141.19	1 4 3	32.67	-39.75	1	6.53	1.20
10	74.23	-68.88	8	57.91	-63.93	2	48.32	-33.17	2	143.88	-127.72
1 2 1	58.63	45.66	9	116.11	-110.40	3	151.40	153.46	3	79.42	68.20
2	159.41	155.36	1 3 2	151.91	140.94	4	29.89	-24.79	4	10.51	-13.57
3	90.41	80.40	2	63.27	-68.15	5	120.53	-110.67	5	61.98	58.43
4	158.42	-155.81	3	138.40	-139.74	6	13.79	-13.71	6	122.77	111.88
5	109.38	-100.71	4	24.62	12.68	7	7.60	8.83	7	19.08	-15.79
6	45.30	31.03	5	99.35	82.34	0 5 3	24.41	-28.73	1 2 5	61.62	56.01
7	31.79	-25.67	6	56.41	-45.30	1	109.95	112.21	2	122.96	-107.91
8	9.73	-10.72	7	86.97	-69.79	2	7.95	-6.71	3	67.84	56.74
9	24.94	24.70	8	14.18	-15.73	3	67.25	-62.82	4	178.30	149.27
0 3 1	100.25	97.79	0 4 2	134.44	-108.46	4	4.73	-3.94	5	58.42	-51.90
1	61.80	70.58	1	131.43	-125.79	5	83.82	-83.89	6	74.88	-65.02
2	124.35	-134.91	2	15.73	-11.51	1 6 3	14.49	-12.37	7	49.85	-58.61
3	37.49	-30.18	3	40.72	47.07	1 0 4	120.82	118.50	0 3 5	148.07	-133.92
4	22.88	-12.61	4	11.76	11.81	2	72.35	66.17	1	8.09	-8.61
5	71.30	-63.19	5	34.29	34.83	3	6.39	-10.52	2	118.69	105.78
6	136.30	118.98	6	6.59	5.63	4	27.07	24.82	3	83.55	-77.33
7	48.61	41.92	7	122.87	-131.18	5	19.18	-25.26	4	16.33	14.64
8	61.38	-56.93	1 5 2	81.64	-81.01	6	61.86	-65.14	5	63.38	-62.28
9	34.84	-33.24	2	72.44	75.25	7	104.18	110.20	6	98.07	-94.12

Table 2. (Continued)

h k l	F _o	F _c	h k l	F _o	F _c	h k l	F _o	F _c	h k l	F _o	F _c
1 4 5	6.36	0.12	1 1 6	15.32	-16.05	2 3 6	121.49	114.90	2 1 7	76.99	75.25
2	72.42	67.30	2	135.26	-142.22	3	40.49	43.16	3	34.15	17.38
3	44.00	-45.45	3	46.23	-46.41	4	77.22	-77.19	4	14.61	15.57
4	149.35	-141.23	4	77.58	78.19	5	31.56	-36.34	5	22.47	22.94
5	16.12	7.16	5	26.78	29.41	0 4 6	152.68	148.76	1 2 7	74.90	-71.73
0 5 5	86.61	89.84	6	89.18	-83.02	1	15.63	17.54	2	24.95	50.59
1	8.85	-6.73	0 2 6	163.78	-150.04	2	42.24	-41.73	3	90.38	75.66
2	97.38	-87.99	1	8.40	3.04	3	21.45	-23.31	4	95.54	-83.84
1 0 6	22.05	22.94	2	82.32	76.34	1 0 7	52.85	52.84	0 3 7	36.19	36.34
2	58.17	-55.49	3	71.08	69.29	2	17.07	17.06	1	92.19	82.60
3	20.55	-21.37	4	7.00	-9.53	4	121.64	136.14	2	65.79	-62.18
4	16.09	-9.79	5	60.47	60.96	5	72.01	68.70			
5	32.46	-37.34	6	87.38	-86.50	0 1 7	29.53	-27.35			
6	59.28	51.92	1 3 6	26.84	26.23	1	104.44	-88.96			

all reflections were given equal weights and refinement was carried through to convergence. As expected, the final R value was higher than is noted above. The initial and final parameters are given in Table 1 with SAHL's² parameters for BaSO₄ and PbSO₄. The calculated and observed structure factors are listed in Table 2.

Results

The strontium-oxygen polyhedron is quite irregular but shows 12-fold coordination (Table 3). The Sr—O distances vary from 2.48 Å to 3.25 Å, with O_D at a distance of 3.83 Å, the closest oxygen ion not included in the polyhedron. A schematic drawing of the polyhedron for BaSO₄ and PbSO₄, which is also applicable to this structure, is given by SAHL². It consists approximately of parallel five- and six-membered rings of oxygen ions, with the remaining oxygen ion lying slightly above the center of the six-membered ring.

The sulfur-oxygen tetrahedron is close to ideal (Table 3), with the maximum differences in S—O distances of 3% and bond-angle variances from the ideal of 2 degrees or less. The S—O lengths and the isotropic temperature factors both decrease in the order O_{II} to O_I to O_{III}, suggesting that the S—O bond strength is greatest for O_{III} and least for O_{II}. Five of the six tetrahedron edges are shared with a strontium polyhedron. The sixth, between O_I and O_{II}, is shared with two, and, as expected, this is the longest edge. All oxygen ions are coordinated to one sulfur ion and three strontium ions.

As can be seen from Tables 1 and 3 the results of the present work agree well with those of SAHL's². Average cation-oxygen distances increase from strontium through barium, in very good agreement with standard ionic radii for these cations. The sulfur-oxygen distances vary in a random way for the three structures, although it should be

Table 3. *Interatomic distances and angles for celestite, barite, and anglesite*

	SrSO ₂	PbSO ₄ (SAHL ²)	BaSO ₄ (SAHL ²)
Sr polyhedron			
Sr—O _I	3.25 Å	3.25 Å	3.30 Å
O _I	2.48	2.63	2.78
2O _{II}	2.99	3.05	3.08
O _{II}	2.58	2.63	2.76
2O _{III}	2.66	2.63	2.84
2O _{III}	2.65	2.77	2.82
2O _{III}	2.81	2.93	2.91
average	2.83	2.88	2.95
S tetrahedron			
S—O _I	1.53	1.47	1.50
O _{II}	1.55	1.42	1.52
2O _{III}	1.50	1.48	1.48
average	1.52	1.46	1.50
O _I —O _{II}	2.53	2.38	2.54
O _I —O _{III}	2.47	2.43	2.41
O _{II} —O _{III}	2.47	2.35	2.47
O _{III} —O _{III}	2.46	2.42	2.36
average	2.48	2.39	2.44
O _I —S—O _{II}	111°	108°	114°
O _I —S—O _{III}	110	111	108
O _{II} —S—O _{III}	108	111	111
O _{III} —S—O _{III}	110	110	106

expected that the geometry of the sulfur coordination tetrahedron should be relatively invariant within this isotopic series. This indicates that a further refinement of these structures is desirable for the purpose of defining detailed structural variations within this series, at least for BaSO₄ and PbSO₄, where only two-dimensional film data has been used.

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