

# Crystal-structure analysis of four mineral samples of anhydrite, CaSO<sub>4</sub>, using synchrotron high-resolution powder X-ray diffraction data

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The crystal structures of four samples of anhydrite, CaSO<sub>4</sub>, were obtained by Rietveld refinements using synchrotron high-resolution powder X-ray diffraction (HRPXRD) data and space group *Amma*. As an example, for one sample of anhydrite from Hants County, Nova Scotia, the unit-cell parameters are  $a = 7.00032(2)$ ,  $b = 6.99234(1)$ ,  $c = 6.24097(1)$  Å, and  $V = 305.487(1)$  Å<sup>3</sup> with  $a > b$ . The eight-coordinated Ca atom has an average  $\langle \text{Ca-O} \rangle$  distance of 2.4667(4) Å. The tetrahedral SO<sub>4</sub> group has two independent S-O distances of 1.484(1) to O1 and 1.478(1) Å to O2 and an average  $\langle \text{S-O} \rangle$  distance of 1.4810(5) Å. The three independent O-S-O angles [ $108.99(8) \times 1$ ,  $110.38(3) \times 4$ ,  $106.34(9)^\circ \times 1$ ; average  $\langle \text{O-S-O} \rangle [6] = 109.47(2)^\circ$ ] and S-O distances indicate that the geometry of the SO<sub>4</sub> group is quite distorted in anhydrite. The four anhydrite samples have structural trends where the  $a$ ,  $b$ , and  $c$  unit-cell parameters increase linearly with increasing unit-cell volume,  $V$ , and their average  $\langle \text{Ca-O} \rangle$  and  $\langle \text{S-O} \rangle$  distances are nearly constant. The grand mean  $\langle \text{Ca-O} \rangle = 2.4660(2)$  Å, and grand mean  $\langle \text{S-O} \rangle = 1.4848(3)$  Å, the latter is longer than 1.480(1) Å in celestite, SrSO<sub>4</sub>, as expected. © 2011 International Centre for Diffraction Data. [DOI: 10.1154/1.3659285]

Key words: anhydrite, CaSO<sub>4</sub>, Rietveld refinement, HRPXRD, crystal structure

## I. INTRODUCTION

The crystal structure of anhydrite was investigated by Wasastjerna (1925) and by Dickinson and Binks (1926). Later works by Höhne (1961, 1962) and Cheng and Zussman (1963) confirmed the structure proposed by Wasastjerna (1925). Single-crystal X-ray diffraction studies were reported by Morikawa *et al.* (1975), Hawthorne and Ferguson (1975), and Kirfel and Will (1980). Swanson *et al.* (1955) reported unit-cell parameters of  $a = 6.991$ ,  $b = 6.996$ , and  $c = 6.238$  Å for anhydrite; the  $a$  and  $b$  parameters are slightly different from each other. Höhne (1962) and Cheng and Zussman (1963) assigned the space group *Amma* and adopted the unit-cell values of Swanson *et al.* (1955). Morikawa *et al.* (1975) pointed out that their labelling of  $a$  and  $b$  should be interchanged for space group *Amma*, so that  $a > b$ , whereas for space group *Bmmb*,  $b > a$ . Hartman (1989) also observed contradictions in unit-cell dimensions for anhydrite; the powder data of the JCPDS card 6-226 and the unit-cell data of Hawthorne and Ferguson (1975) gave contradictory results. The relevant data are given in Table I. Based on data available in the literature, Hartman (1989) calculated an average structure for anhydrite. On the basis of the contradictory unit-cell parameters, further work on anhydrite is necessary.

Hartman (1989) chose space group *Bmmb* because the slice (200) has a zircon-like arrangement of Ca and SO<sub>4</sub> that also occurs in the (200) slice of monoclinic monazite, with a slight deformation. In addition, the Ca and S atoms are nearly linearly arranged in [100] and [001] directions, giving the (020) slice a NaCl-like appearance, which also holds with larger deformation for the (020) slice of monazite. Hawthorne and Ferguson (1975) and Kirfel and Will (1980) used the *Amma* setting and showed the relation between

anhydrite and gypsum, CaSO<sub>4</sub>·2H<sub>2</sub>O, which also accounted for the orientated nature of the high-temperature dehydration of gypsum to anhydrite (Atoji, 1959). Structural data in space group *Amma* can be transformed to *Bmmb*.

Jacobsen *et al.* (1998) refined the structures for the isostructural minerals celestite (SrSO<sub>4</sub>), anglesite (PbSO<sub>4</sub>), and barite (BaSO<sub>4</sub>). They concluded that the average  $\langle \text{M-O} \rangle$  distance increases linearly with unit-cell volume, but SO<sub>4</sub> behaves as rigid group with an average  $\langle \text{S-O} \rangle$  distance of 1.476 Å, which is constant across the series. Miyake *et al.* (1978) indicated a possible systemic variation in the SO<sub>4</sub> tetrahedron with field strength of the M<sup>2+</sup> cation across the isostructural series, but their SO<sub>4</sub> geometry was statistically identical, as pointed out by Jacobsen *et al.* (1998). The CO<sub>3</sub> and SiO<sub>4</sub> groups are often considered as rigid groups, but Antao *et al.* (2008) and Antao and Hassan (2009) have shown that their geometries do vary in a systematic way. Therefore, systematic variation in the geometry of the SO<sub>4</sub> group is expected as the M<sup>2+</sup> cation changes.

This study examines trends in the unit-cell parameters and the geometry of the SO<sub>4</sub> group in anhydrite. The Rietveld structure refinements were carried out in space group *Amma* and data from the literature in space group *Bmmb* were transformed to *Amma* for comparison (Table I).

## II. EXPERIMENTAL

### A. Sample characterization

The four anhydrite samples used in this study are from: (1) Hants County, Nova Scotia (UC8215); (2) Naica, Mexico; samples (3) and (4) are from the Baldonnel sedimentary formation in west-central Alberta. These two samples are from two different drill cores and the crystals occur at depths of 1190 (Baldonnel-1) and 1135 (Baldonnel-2) meters below sea level.

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TABLE I. Unit-cell parameters (Å) and average bond distances (Å) for anhydrite in space group *Amma*.

Source	<i>a</i>	<i>b</i>	<i>c</i>	<i>V</i>	<Ca-O>	<S-O>
JCPDS # 6-226	<i>6.991</i>	<i>6.996</i>	6.238	305.09		
Chen and Zussman (1963)	<i>6.991</i>	<i>6.996</i>	6.238	305.09		
<sup>a</sup> Morikawa <i>et al.</i> (1975)	6.999(1)	6.992(1)	6.240(1)	305.37	2.468	1.475
Hawthorne and Ferguson (1975)	<i>6.993(2)</i>	<i>6.995(2)</i>	6.245(2)	305.48	2.470	1.473
Kirfel and Will (1980)	7.006(1)	6.998(1)	6.245(1)	306.2(1)	2.470	1.4745(7)
<sup>a</sup> Hartman (1989)	6.998	6.992	6.238	305.23	2.468	1.473
This work <sup>b</sup>	7.00032(2)	6.99234(1)	6.24097(1)	305.487(1)	2.4667(4)	1.4810(5)

<sup>a</sup>data were transformed from *Bmmb* to *Amma*. Values for *a* and *b* given in italic have *a* < *b*, which are incorrect for space group *Amma*.

<sup>b</sup>Sample from Nova Scotia.

The samples were analyzed using a JEOL JXA-8200 electron microprobe and the standard JEOL operating program on a Solaris platform. The wavelength-dispersive operating conditions were 15-kV accelerating voltage, 10-nA beam current, a beam diameter of 5 μm, and using various standards. The chemical compositions of the samples are given (Table II). The samples are homogeneous based on optical observations and microprobe analyses of at least eight spots. Based on the chemical analyses, the four samples are chemically similar, and the pure CaSO<sub>4</sub> formula was used in the structure refinements.

## B. HRPXRD

The anhydrite samples at 23 °C were studied by high-resolution synchrotron powder X-ray diffraction (HRPXRD) experiments performed at Beam-line 11-BM, Advanced Photon Source (APS), and Argonne National Laboratory (ANL). The samples were crushed to fine powders using an agate mortar and pestle. The samples were loaded into Kapton capillaries and rotated during the experiment at a rate of 90 rotations per second. The data were collected to a maximum 2θ of about 43° with a step size of 0.001° and a step time of 0.1 s per step. The HRPXRD traces were collected with twelve silicon (111) crystal analyzers that increase de-

TABLE II. Electron microprobe analysis (EMPA) of four anhydrite samples.

	Nova Scotia	Mexico	Baldonnel 1	Baldonnel 2
Wt. % Oxide				
CaO	40.17	41.44	41.27	41.40
MgO	0.03	0.01	0.01	0.02
FeO	0.00	0.05	0.00	0.05
MnO	0.02	0.00	0.02	0.00
SrO	0.00	0.00	0.33	0.18
SO <sub>3</sub>	56.20	57.60	58.80	57.86
Total	96.42	99.10	100.43	99.51
<sup>a</sup> <i>apfu</i>				
Ca	1.009	1.013	0.998	1.002
Mg	0.001	0.000	0.000	0.000
Fe	0.000	0.001	0.000	0.000
Mn	0.000	0.000	0.000	0.001
Sr	0.000	0.000	0.004	0.000
S	0.989	0.986	0.996	0.995

<sup>a</sup>Atoms per formula unit.

TABLE III. Unit-cell parameters and Rietveld refinement statistics for anhydrite in space group *Amma*.

Sample	Nova Scotia	Mexico	Baldonnel 1	Baldonnel 2
<i>a</i> (Å)	7.00032(2)	7.00071(3)	7.00121(2)	7.00136(3)
<i>b</i> (Å)	6.99234(1)	6.99274(4)	6.99323(2)	6.99339(3)
<i>c</i> (Å)	6.24097(1)	6.24125(2)	6.24160(2)	6.24171(2)
<i>V</i> (Å <sup>3</sup> )	305.487(1)	305.535(2)	305.595(2)	305.615(2)
λ (Å)	0.41220(2)	0.41399(2)	0.41400(2)	0.41400(2)
<sup>a</sup> R <sub>F</sub> <sup>2</sup>	0.0661	0.0630	0.0599	0.0543
R <sub>p</sub>	0.1049	0.0974	0.0927	0.0897
R <sub>wp</sub>	0.1346	0.1291	0.1224	0.1174
N <sub>obs</sub>	521	548	548	556

<sup>a</sup>R<sub>F</sub><sup>2</sup> = R-structure factor based on observed and calculated structure amplitudes = [∑(F<sub>o</sub><sup>2</sup> - F<sub>c</sub><sup>2</sup>)/∑(F<sub>o</sub><sup>2</sup>)]<sup>1/2</sup>. N<sub>obs</sub> = number of observed reflections. The number of data points for each trace is 39499 and the 2θ data range was 3.5 to 43°.

tector efficiency, reduce the angular range to be scanned, and allow for rapid acquisition of data. A silicon and alumina NIST standard (ratio of 1/3 Si : 2/3 Al<sub>2</sub>O<sub>3</sub>) was used to calibrate the instrument and to determine and refine the monochromatic wavelength [e.g., k<sup>1</sup>/<sub>4</sub> 0.41220(2) Å] used in the experiment (Table III). Additional details of the

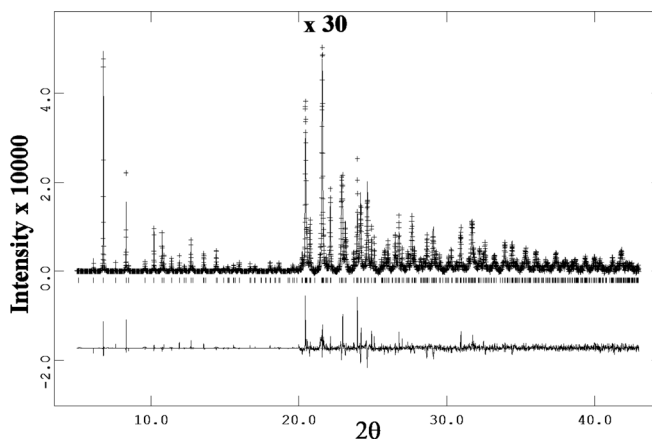


Figure 1. The HRPXRD trace for anhydrite from Nova Scotia together with the calculated (continuous line) and observed (crosses) profiles. The difference curve (*I*<sub>obs</sub> - *I*<sub>calc</sub>) is shown at the bottom and has the same scale as that for intensity. The short vertical lines indicate allowed reflection positions. The intensities and difference curve beyond 20° 2θ are scaled by a factor of ×30.

TABLE IV. Atom positions and isotropic displacement parameters ( $\times 100 \text{ \AA}^2$ ) for anhydrite in space group *Amma*.

Atom		Nova Scotia	Mexico	Baldonnel-1	Baldonnel-2	
Ca	<i>x</i>	3/4	3/4	3/4	3/4	
	<i>y</i>	0	0	0	0	
	<i>z</i>	0.34673(8)	0.34637(9)	0.34657(8)	0.34631(9)	
	<i>U</i>	0.62(1)	0.81(1)	0.82(1)	0.81(1)	
	<i>S</i>	1/4	1/4	1/4	1/4	
S	<i>y</i>	0	0	0	0	
	<i>z</i>	0.1557(1)	0.1554(1)	0.1557(1)	0.1551(1)	
	<i>U</i>	0.71(1)	0.71(2)	0.71(1)	0.75(2)	
	O1	<i>x</i>	1/4	1/4	1/4	1/4
		<i>y</i>	0.1728(1)	0.1733(2)	0.1730(1)	0.1721(1)
<i>z</i>		0.0176(1)	0.0164(2)	0.0165(1)	0.0159(1)	
<i>U</i>		0.81(2)	0.79(3)	0.97(3)	0.88(3)	
O2		<i>x</i>	0.0811(2)	0.0797(2)	0.0796(2)	0.0798(2)
	<i>y</i>	0	0	0	0	
	<i>z</i>	0.2976(2)	0.2967(2)	0.2966(2)	0.2976(2)	
	<i>U</i>	1.08(2)	0.77(2)	1.01(2)	0.91(2)	

experimental set-up are given elsewhere (Antao *et al.*, 2008b; Lee *et al.*, 2008; Wang *et al.*, 2008).

### C. Rietveld structure refinements

The HRPXRD data were analyzed by the Rietveld method (Rietveld, 1969), as implemented in the *GSAS* program (Larson and Von Dreele, 2000), and using the *EXPGUI* interface (Toby, 2001). Scattering curves for neutral atoms were used. Initial atom coordinates and unit-cell parameters were taken from Kirfel and Will (1980) for space group *Amma*. The background was modeled using a Chebyshev polynomial (12 terms). Each reflection-peak profile was fitted using a type-3 profile in the *GSAS* program. Full-matrix least-squares refinements were carried out by varying the parameters in the following sequence: scale factor, unit-cell parameters, atom coordinates, and

TABLE V. Selected bond distances<sup>a</sup> ( $\text{\AA}$ ) and angles ( $^\circ$ ) for anhydrite in space group *Amma*.

Bonds		Nova Scotia	Mexico	Baldonnel 1	Baldonnel 2
Ca-O1	$\times 2$	2.5748(10)	2.5678(10)	2.5690(10)	2.5616(10)
Ca-O1	$\times 2$	2.4395(10)	2.4399(10)	2.4414(10)	2.4487(10)
Ca-O2	$\times 2$	2.3377(10)	2.3289(11)	2.3289(10)	2.3289(10)
Ca-O2	$\times 2$	2.5149(11)	2.5264(11)	2.5264(10)	2.5219(10)
<Ca-O> [8]		2.4667(4)	2.4658(4)	2.4664(4)	2.4653(4)
S-O1	$\times 2$	1.4844(10)	1.4905(10)	1.4890(10)	1.4847(10)
S-O2	$\times 2$	1.4775(10)	1.4831(10)	1.4820(10)	1.4870(10)
<S-O> [4]		1.4810(5)	1.4868(5)	1.4855(5)	1.4859(5)
O1-S-O1	$\times 1$	108.99(8)	108.79(9)	108.65(8)	108.36(9)
O1-S-O2	$\times 4$	110.38(3)	110.26(3)	110.25(2)	110.49(2)
O2-S-O2	$\times 1$	106.34(9)	107.00(9)	107.18(9)	106.54(9)
<O-S-O> [6]		109.47(2)	109.47(2)	109.47(2)	109.47(2)

<sup>a</sup>For the four samples, the grand mean for <Ca-O> and <S-O> are 2.4660(2) and 1.4848(3)  $\text{\AA}$ , respectively.

isotropic displacement parameters. Toward the end of the refinement, all the parameters were allowed to vary simultaneously, and the refinement proceeded to convergence. A HRPXRD pattern for the anhydrite sample from Nova Scotia is shown in Figure 1.

The unit-cell parameters and the Rietveld refinement statistics are listed in Table III. Atom positions and isotropic displacement parameters are given in Table IV. Bond distances and angles are given in Table V.

### III. RESULTS AND DISCUSSION

In the anhydrite structure, parallel to the *c* direction, alternating  $\text{CaO}_8$  dodecahedra and  $\text{SO}_4$  tetrahedra share

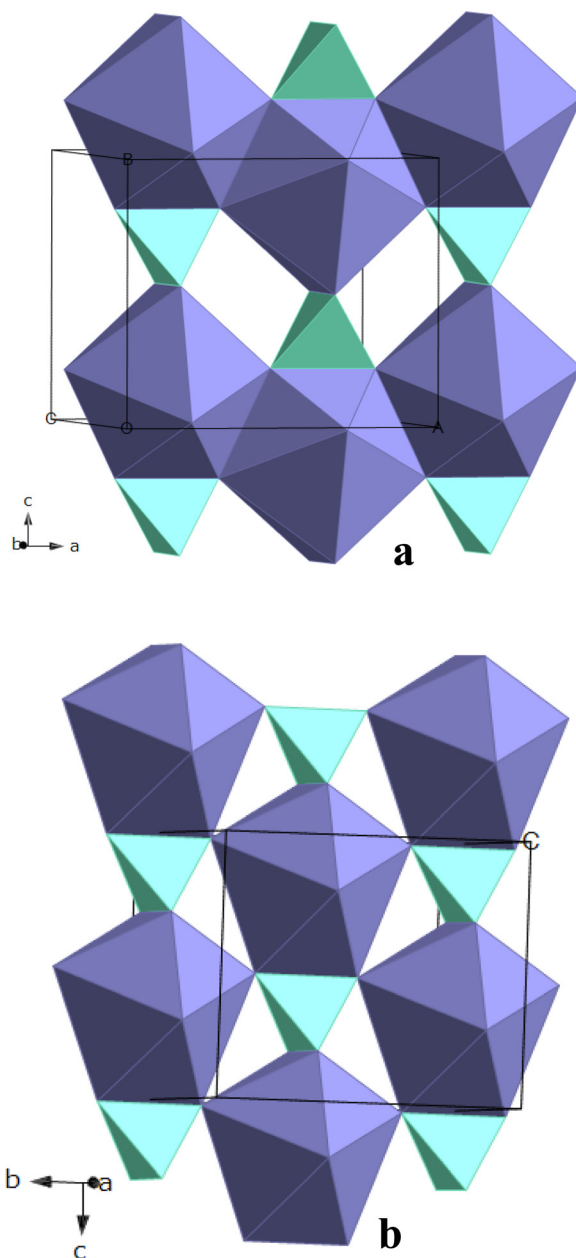


Figure 2. (Color online) Projection of the structure of anhydrite down: (a) close to the *b* axis showing edge-sharing between  $\text{CaO}_8$  dodecahedra and  $\text{SO}_4$  tetrahedra, and (b) close to the *a* axis showing the Ca dodecahedra and S tetrahedra sharing corners.

edges and form a chain (Figure 2). In the *a* direction, the chains are connected by edge-shared CaO<sub>8</sub> dodecahedra [Figure 2(a)], and in the *b* direction by corner-shared CaO<sub>8</sub> dodecahedra and SO<sub>4</sub> tetrahedra [Figure 2(b)]. The anhydrite structure is related to the structures of gypsum, zircon, monazite, and halite (Atoji, 1959; Robinson *et al.*, 1971; Wyckoff, 1965; Hartman, 1989).

The unit-cell parameters for anhydrite are in the sequence indicated by Morikawa *et al.* (1975) and Hartman (1989): *a* > *b* for space group *Amma* (Tables I and III). HRPXRD data have a large 2θ range and a large number of data points, which enables unit-cell parameters to be determined reliably. The precision and internal consistency of the structural data can be seen from the errors reported (Table I).

Values of the *a*, *b*, and *c* unit-cell parameters increase linearly with increasing unit-cell volume, *V* [Figures 3(a) and 3(b)]. Such linear relations were not previously observed. These linear trend lines are derived from the four samples that have quite similar chemical composition and nearly identical structural parameters. The large and small unit-cell data from Kirfer and Will (1980) and Morikawa *et al.* (1975), respectively, fall close to the extension of the linear least-squares lines that represent the data from this study [Figures 3(a) and 3(b)]. The trend lines representing the variations of the *a* and *b* parameters are parallel to each other and indicate that *a* and *b* parameters differ by about 0.008 Å in anhydrite [Figure 3(a)]. The unit-cell data from Hawthorne and Ferguson (1975) do not fall on the observed trend lines because their data are incorrect, as pointed out by

Hartman (1989). The anhydrite sample studied by Kirfel and Will (1980) is quite interesting, as it has the largest unit-cell parameters [Figures 3(a) and 3(b)]. Unfortunately, a modern chemical analysis is not available for this sample, so the reason for their large unit-cell parameters is not known. The reason for the linear relations may be related to the trace element contents in anhydrite, such as Mg and Sr replacing Ca atoms to some extent.

For eight-coordinated Ca, the grand mean <Ca-O> distance is 2.4660(2) Å for the four anhydrite samples [Figure 3(b); Table V], which is comparable with 2.470 Å obtained by Hawthorne and Ferguson (1975) and Kirfel and Will (1980), and 2.468 Å reported by Morikawa *et al.* (1975) and Hartman (1989) [Table I]. Based on ionic radii (Ca<sup>2+</sup> [8] = 1.12 Å and O<sup>2-</sup> [3] = 1.36 Å; Shannon, 1976), Ca-O = 2.48 Å. In gypsum, CaSO<sub>4</sub>·2H<sub>2</sub>O, the average <Ca-O> [8] is 2.458 Å (Cole and Lancucki, 1974), which is similar to the grand mean <Ca-O> = 2.4660(2) Å in anhydrite. The average <Ca-O> distances are closer to the data of Morikawa *et al.* (1975), but do not match those of Hawthorne and Ferguson (1975) or Kirfel and Will (1980; Figure 3(c)).

The anhydrite sample from Nova Scotia has tetrahedral SO<sub>4</sub> group with two independent S-O distances of 1.484(1) to O1 and 1.478(1) Å to O2 (Table V). These distances are different from each other, and their average <S-O> distance is 1.4810(5) Å, which is slightly different from values previously reported in the literature that are typically about 1.475 Å (Table I). The three independent O-S-O angles

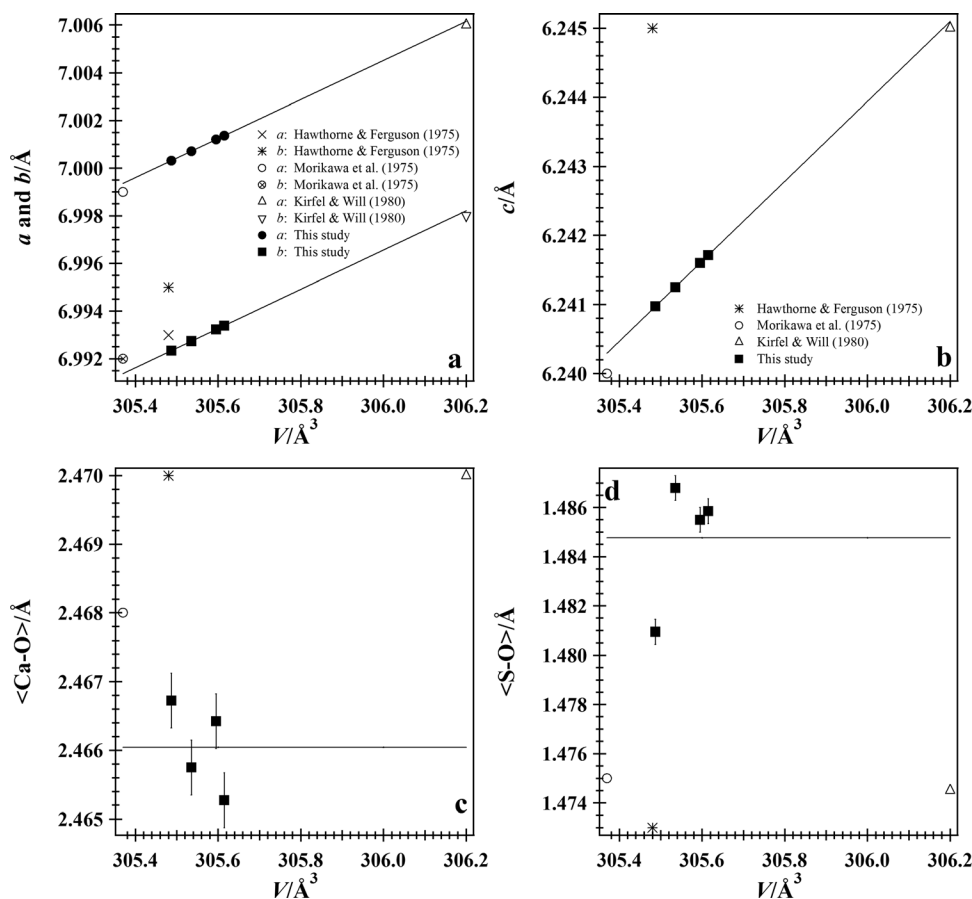


Figure 3. Structural variations in anhydrite (space group *Amma*). The *a* and *b* unit-cell parameters in (a) and *c* parameter in (b) increase linearly with increasing *V*. Data from the literature are included for comparison, but are not fitted to the trend lines. Errors in (a) and (b) are smaller than the symbols. The average <Ca-O> distances and their grand mean (horizontal line) are shown in (c), whereas the average <S-O> distances and their grand mean (horizontal line) are shown in (d).

[108.99(8) × 1, 110.38(3) × 4, 106.34(9)° × 1] and the S-O distances indicate that the geometry of the SO<sub>4</sub> group is quite distorted in CaSO<sub>4</sub>. In gypsum, CaSO<sub>4</sub>·2H<sub>2</sub>O, the S-O distances are 1.457 and 1.461 Å, and the average <S-O> distance of 1.459 Å is shorter than the present values for anhydrite (Cole and Lancucki, 1974). For the isostructural minerals celestite (SrSO<sub>4</sub>), anglesite (PbSO<sub>4</sub>), and barite (BaSO<sub>4</sub>), the SO<sub>4</sub> behaves as a rigid group with an average <S-O> distance of 1.476 Å, which is constant across the series (Jacobsen *et al.*, 1998). The four anhydrite samples in this study have a grand mean <S-O> distance of 1.4848(3) Å, which is larger than those in the isostructural series because the eight-coordinated Ca has a smaller size than the other twelve-coordinated M<sup>2+</sup> (= Sr, Pb, and Ba) cations. The Ca atom satisfies the charge on the O atoms more effectively, thereby allowing the S-O distance to be larger in anhydrite. The <S-O> distance in anhydrite can be compared with an average <S-O> distance of 1.49 Å in other inorganic structures (*International Tables of X-Ray Crystallography*, 1962).

The geometry of the SO<sub>4</sub> group should vary in a regular manner as the M<sup>2+</sup> (= Ca, Sr, Pb and Ba) cation changes, as proposed by Miyake *et al.* (1978). That is, the <S-O> distance is longest in CaSO<sub>4</sub> and shortest in BaSO<sub>4</sub>; it should change in the following sequence: CaSO<sub>4</sub> > SrSO<sub>4</sub> > PbSO<sub>4</sub> > BaSO<sub>4</sub> because as the M<sup>2+</sup> cation radius increases, the effective charge decreases (Antao, 2012).

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