High-pressure phase transformation in CaSO$_4$

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Abstract

Raman spectroscopic study of anhydrite (CaSO$_4$) at $P > 140$ kbar (after being heated to $\sim 1000°$C by laser irradiation, and then cooled to room temperature) revealed that anhydrite transformed to a new high-pressure modification. Depending on the rate of pressure release, the high-pressure modification can only be partially preserved at ambient condition, if the pressure is slowly released. X-ray diffraction study of the partially preserved high-pressure modification at ambient condition revealed 15 diffraction lines for the new phase. The d-spacings for these new lines can be reasonably fitted by an orthorhombic cell with $a = 6.602 \pm 0.005$, $b = 7.759 \pm 0.007$, $c = 5.970 \pm 0.007$ Å. If $Z = 4$ is assumed, the calculated volume of the new phase is 0.2% *greater* than that of anhydrite at ambient condition. The fitting is non-unique, however. The new phase has also been fitted by other possible candidate structures, such as sheelite, monazite and barite, but without success. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

For isometric compounds, the structure of larger-cation compounds at atmospheric pressure is usually considered as a model structure of the high-pressure polymorph of smaller-cation compounds in the study of high-pressure phase transformations [1]. Table 1 lists the well-known example of the aragonite and calcite structures of carbonates. The larger-cation carbonates all crystallize in the aragonite structure and the smaller-cation carbonates in the calcite structure at ambient conditions. In nature, the size of Ca^{2+} can fit the structures of both aragonite and calcite. Following this empirical rule, Liu and Lin [2] have demonstrated that the calcite-type CdCO$_3$ (otavite) transforms to the aragonite-type structure at high pressures. Table 1 also shows that the larger-cation sulfates crystallize in the barite structure and the smaller-cation sulfate in the anhydrite structure in nature. Thus, following the previous example of the carbonates, one would expect that anhydrite (CaSO$_4$) should adopt the barite structure at high pressures. We attempt to explore this phase transition at high pressures and/or high temperatures in the present study.

Shock-wave experiments on CaSO$_4$ are available up to 1.06 Mbar by Simakov et al. [3], who have demonstrated that there exists a high-pressure phase transition in CaSO$_4$ between 360 and 540 kbar.

2. Samples and experimental procedures

Calcium sulfate dihydrate (CaSO$_4$·2H$_2$O) with a purity greater than 99% was purchased from Merck Ltd and heated at 500°C for 4 h. Raman spectroscopic study of the recovered sample at ambient condition showed the lack of the OH stretching mode around 3500 cm^{-1}, and the spectrum at <1200 cm^{-1} is identical to that of anhydrite [4]. The sample was then intimately mixed with a trace amount of graphite, which served to absorb the laser radiation and thus to heat the sample under compression. Samples thus prepared were compressed in a diamond-anvil press and irradiated by a continuous YAG laser. Sample temperatures were estimated on the basis of the intensity of incandescent light emitted from the sample and thus subject to broad uncertainty. In some experiments, a hardened stainless steel gasket with a hole of ~ 150 μm in diameter and 20–50 μm in depth was used to confine the sample at high pressures. But, in some experiments, no metal gasket was used at all.

No pressure medium was used in the present experiment,

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Table 1
Carbonates (ACO_3) crystallized in the aragonite and calcite structures and sulfates (ASO_4) crystallized in the barite and anhydrite structures are listed according to the size of the A cation (increases from left to right)

Aragonite					$[CdCO_3]^a$	$CaCO_3$	$SrCO_3$	$PbCO_3$	$BaCO_3$
Calcite	$NiCO_3$	$MgCO_3$	$FeCO_3$	$MnCO_3$	$CdCO_3$	$CaCO_3$			
Barite						?	$SrSO_4$	$PbSO_4$	$BaSO_4$
Anhydrite		$(MgSO_4)^a$				$CaSO_4$			

[a] The compound listed inside the brackets was made in high-pressure experiment by Liu and Lin [2], and that listed inside the parentheses has the $ZnSO_4$-type structure, but is listed for reference.

so as to avoid rehydration and possible reactions between anhydrite and pressure medium. The frequency of the most intense Raman band of anhydrite at $1016 \pm 1 \text{ cm}^{-1}$ was first calibrated against pressure using the ruby-fluorescence technique (Fig. 1). Thus, the sample pressure was determined by directly measuring Raman frequency of the sample.

Besides calibrating the sample pressures in the diamond-anvil cell, Raman spectroscopy was also utilized to determine the phase transformations of anhydrite at high pressures. Raman spectra were obtained by a RENISHAW micro-optical spectrometer system at room temperature. The excitation source was 514.5 nm radiation from an argon-ion laser and the spectrum was recorded in a back-scattering geometry. Raman frequency was recorded in the range of $200–1200 \text{ cm}^{-1}$ for the samples at both high pressures and at ambient condition. The resolution is accurate to $\pm 1 \text{ cm}^{-1}$.

If a new high-pressure phase of anhydrite, after being subjected to high pressure and high temperature, was
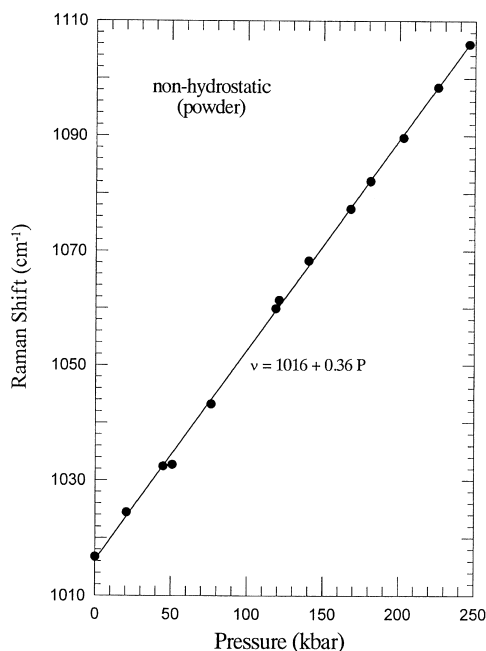

Fig. 1. The variation of frequency of the most intense Raman band of anhydrite with pressure at room temperature.

identified by Raman spectroscopic study, then the pressure of the sample was slowly released at room temperature. Samples thus obtained were transferred to a modified 57.3 mm diameter Debye–Scherrer camera for X-ray diffraction study using $CoK\alpha$ radiation at 40 kV and 20 mA. The total exposure time was about 240 h for each run.

3. Raman spectra of $CaSO_4$

Raman spectra of $CaSO_4$ obtained at various conditions are shown in Fig. 2. Fig. 2(a) displays the ambient Raman spectrum of anhydrite [4,5], and Fig. 2(b) the Raman spectrum of anhydrite at 210 ± 10 kbar and room temperature. The Raman spectrum of the same sample of Fig. 2(b) after laser heating and then air cooling to room temperature is shown in Fig. 2(c). As can be seen, not only the frequency of the $\nu_1 (SO_4)$ mode dropped from 1092 to 1084 cm^{-1}, but there appeared two strong Raman bands at 495 and 462 cm^{-1} and other weak modes at, e.g. 209 cm^{-1}. The Raman bands at $<1000 \text{ cm}^{-1}$ shown in Fig. 2(c) do not correspond to any of the Raman bands of anhydrite shown in Fig. 2(a) and (b). Thus, it was concluded that the Raman spectrum of Fig. 2(c) represented a new high-pressure phase of $CaSO_4$. This change was observed in all the samples of anhydrite subjected to pressures greater than ~ 140 kbar and heated by laser irradiation.

Unfortunately, the new high-pressure phase is difficult to preserve after release of pressure. It is particularly sensitive to the rate of the pressure being released. If the pressure was released too fast, a Raman spectrum identical to that of Fig. 2(a) was obtained. If the pressure was released slowly, the general feature of Fig. 2(c) can be maintained (except that the Raman frequencies decrease with decreasing pressure) until near ambient pressure. A Raman spectrum corresponding to anhydrite appeared only when pressure was completely released. In this case, the strong 495 cm^{-1} band shown in Fig. 2(c) can still be preserved at the ambient condition (see the 458 cm^{-1} band in Fig. 2(d)). Another strong 462 cm^{-1} band in Fig. 2(c) may be superimposed by the 416 cm^{-1} band in Fig. 2(d). In addition, there are also other bands such as those at 374 and 338 cm^{-1} shown in Fig. 2(d), which do not belong to anhydrite but to the new phase. By extrapolation, the ambient frequency of the $\nu_1 (SO_4)$ mode for the new phase was
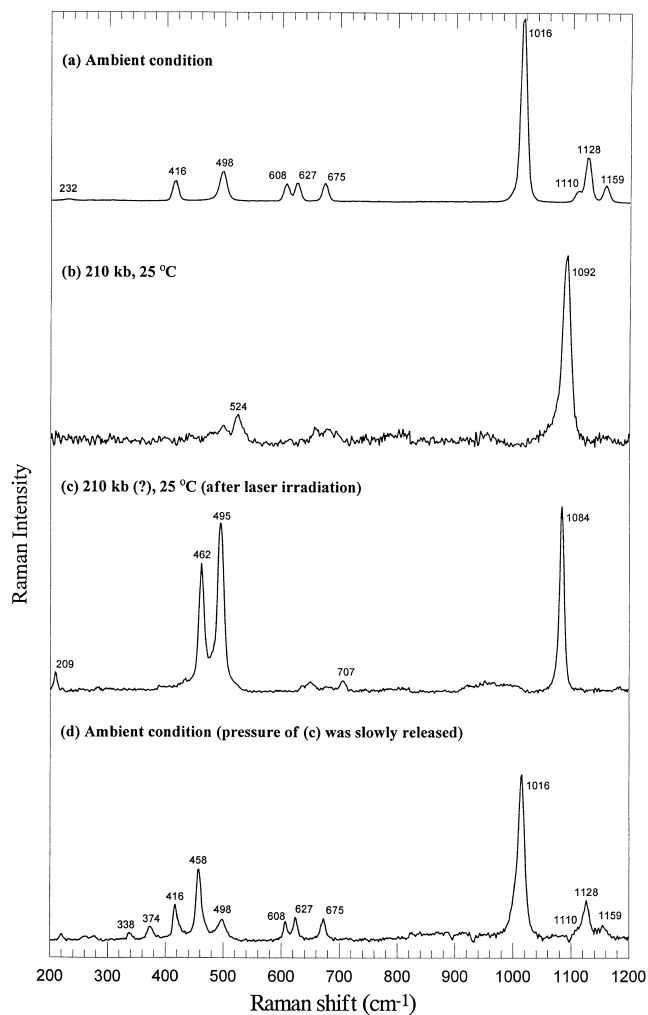
Fig. 2. (a) Raman spectrum of the starting sample of anhydrite (CaSO$_4$) at ambient condition. (b) Raman spectrum of the same sample as in (a), but at 210 ± 10 kbar and room temperature. (c) Raman spectrum of the same sample as in (b), but heated to ~ 1000°C and then cooled to room temperature. (d) Raman spectrum of the same sample as in (c), but the pressure was released *slowly* to atmospheric pressure.

found to be 1009 ± 2 cm^{-1}, which is significantly lower than 1016 ± 1 cm^{-1} for anhydrite at ambient condition. Only the samples obtained by slow release of pressure were transferred to the Debye–Scherrer camera for X-ray diffraction study.

4. X-ray diffraction study

The X-ray powder diffraction data of the sample quenched from ~ 210 kbar and ~ 1000°C are given in Table 2. As already known from the Raman spectroscopic study, the X-ray diffraction data of the quenched samples are a mixture of the parent phase of anhydrite and the new high-pressure phase of CaSO$_4$, and the former is always more abundant than the latter. The appearance of anhydrite in the quenched samples is probably due to the unreacted

starting materials in the chill zones contacting directly with the diamond anvils and the product of the retrogressive reaction of the new phase after release of pressure. On the basis of the results of the Raman spectroscopic study, it is nearly certain that anhydrite in the quenched samples is most likely derived from the retrogressive reaction.

It is noticed that there are several diffraction lines that are spotty in character. All these spotty lines can be attributed to the new phase, some of which, of course, may be super-imposed by diffraction lines of anhydrite. The spotty lines must be produced from larger crystal grains in the quenched samples. It is possible that some of the new phase was preserved after quenching because of the larger crystal grains.

Table 2 shows that there are 15 new diffraction lines, which do not correspond to those of anhydrite. The

Table 2
Ambient X-ray diffraction data for $CaSO_4$ quenched from ~210 kbar and ~1000°C

Observed[a]		Anhydrite[b]		High-pressure phase of $CaSO_4$[c]				
I/I_{100}	d (Å)	I/I_{100}	d (Å)	d (Å)	h	k	l	I/I_{100}
20	6.0			5.970	0	0	1	60
<5	4.7			4.732	0	1	1	5
15s	3.86	6	3.870					
100	3.49	100	3.490					
<5	3.39			3.345	1	2	0	5
30s	3.25			3.253	0	2	1	90
5s	3.11	4	3.110					
35sb	3.02			3.038	2	1	0	100
<5	2.93			2.918	1	2	1	5
40	2.847	35	2.849					
30	2.797	4	2.797	2.786	0	1	2	10
8s	2.704			2.707	2	1	1	25
10	2.560			2.567	1	1	2	30
15	2.477	8	2.473					
<5s	2.42			2.408	1	3	0	5
40	2.325	20	2.328	2.317	2	2	1	15
40s	2.206	20	2.208	2.201	3	0	0	15
10	2.179	8	2.183					
8	2.116			2.117	3	1	0	25
10	2.084	10	2.086					
25s	1.995	6	1.993	1.995	3	1	1	10
20	1.944	4	1.938	1.940	0	4	0	8
<5	1.92			1.914	3	2	0	5
25	1.869	16	1.869	1.861	1	4	0	10
10	1.845	4	1.852	1.845	0	4	1	5
40	1.748	{ 12	1.749					
		10	1.748					
5	1.703			1.704	2	0	3	15
20	1.654	14	1.648					
10s	1.637			1.627	0	4	2	30
15	1.567	6	1.564	1.560	2	2	3	5
20	1.526	4	1.525	1.534	1	3	3	8
15	1.493	6	1.490	1.493	0	0	4	5
15	1.426	{ 4	1.424	1.423	2	3	3	5
		2	1.418					
15	1.402	{ 4	1.398	1.404	2	5	0	5
		2	1.396					
25	1.322	4	1.319	1.320	5	0	0	10
5	1.305	2	1.296	1.302	5	1	0	2
10	1.287	6	1.277	1.289	5	0	1	5
5	1.248			1.250	5	2	0	15
15s	1.219	4	1.216	1.220	3	1	4	5
15	1.167	{ 4	1.166	1.168	1	6	2	5
		2	1.165					
10	1.153	2	1.148	1.153	5	2	2	5
15s	1.106	{ 6	1.106					
		4	1.104					
10	1.044			1.045	3	6	2	30

[a] X-ray data were collected using CoKα radiation. The letters b and s denote broad lines and spotty lines, respectively. The relative intensities were estimated visually.

[b] From JCPDS 6-226.

[c] d-Spacings were calculated from cell dimensions of $a = 6.602$, $b = 7.759$, $c = 5.970$ Å. Intensities of overlapped lines were estimated by assuming that 1/3 of the observed intensity was contributed from high-pressure phase of $CaSO_4$ (see text).
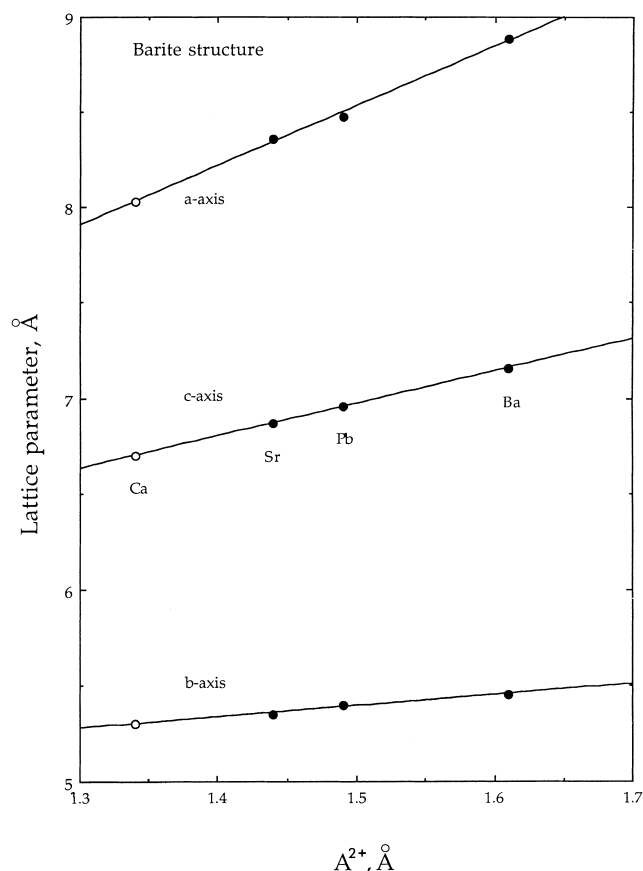
Fig. 3. Correlation between the lattice parameters and cation size in barite-type structure of $A^{2+}SO_4$ compounds. The data for the lattice parameters for $BaSO_4$, $PbSO_4$ and $SrSO_4$ are from the JCPDS card catalog, and the cation size from Shannon [8]. The lattice parameters for the hypothetical barite-type $CaSO_4$ were estimated by linear extrapolation.

measured d-spacings of these new lines were used to fit a barite-structure lattice. After many attempts, we have concluded that the new phase of $CaSO_4$ does not possess a typical barite structure. This conclusion is also consistent with the data revealed in the Raman spectroscopic study. As shown in Fig. 2(c), the Raman spectrum of the new phase is not similar to that of any of the barite structure compounds listed in Table 1. It is, however, found that these 15 new diffraction lines can be reasonably indexed by an orthorhombic lattice with $a = 6.602 \pm 0.005$, $b = 7.759 \pm 0.007$, $c = 5.970 \pm 0.007$ Å. If $Z = 4$ is assigned, the ambient molar volume of the new phase is calculated to be 46.04 ± 0.13 cm^3, which is about 0.2% *greater* than that of anhydrite. This is unusual, but not unique, for high-pressure phase transitions. The most well-known example is the pair of orthoenstatite and clinoenstatite. The latter is the high-pressure modification of the former, yet the volume for clinoenstatite is 0.22% *greater* than that for orthoenstatite at ambient condition.

The relative intensities of the diffraction lines for the new phase listed in Table 2 were estimated by assigning the

strongest 210 reflection of the new phase to be 100 and adjusting others accordingly. For lines superimposed by those of anhydrite, the intensities were estimated by assuming that 1/3 of the observed intensity was contributed from the new phase. This ratio was determined by the relative abundance of anhydrite to the new phase in the quenched products, which were approximately 70% anhydrite and 30% the new phase on the basis of their relative intensities of independent reflections. Then, the relative intensities of weak lines having observed intensities of <5 were denoted as 5 for the new phase.

5. Discussion

The high-pressure phase behavior of ABO_4 compounds has been reviewed by Liu and Bassett [1] and Bastide [6]. The possible well-known high-pressure crystal structures which may be adopted by anhydrite are scheelite, monazite, $BaWO_4$ (II) type and barite. We have previously ruled out the possible candidate of barite. W^{6+} in the $BaWO_4$ (II) type

structure is six-fold coordinated. On the basis of the Raman data, S^{6+} in the new phase most likely exists as the ν_1 (SO_4) mode. So, the $BaWO_4$ (II) type structure and any other structures requires the B atom in ABO_4 has more than four-fold coordination can also be ruled out as the possible candidate structures for anhydrite. We have also tried to fit the X-ray diffraction data of the new phase in terms of the scheelite and monazite structures, but without success.

In the study of various high-pressure phase transitions of perchlorates, Pistorius et al. [7] proposed that there may exist an $AgMnO_4$-type structure, a distorted barite structure, between anhydrite and barite. The $AgMnO_4$-type structure is monoclinic with $Z = 4$. One can fit all 15 diffraction lines of the new phase listed in Table 2 by a monoclinic lattice, e.g. with $a = 5.779 \pm 0.005$, $b = 9.342 \pm 0.009$, $c = 7.792 \pm 0.005$ Å and $\beta = 85.311 \pm 0.060°$ (thus the assignment of the new phase is non-unique). However, the calculated volume of the new phase is much greater than that of anhydrite, if $Z = 4$ is assumed.

A group theoretical analysis of the Raman active modes might shed light on the potential structure of the new high-pressure phase of $CaSO_4$. A potential structure can be precluded if the number of calculated Raman active modes is less than that of the observed ones. In general, the less symmetrical structure possesses more Raman active modes for a given Z number. Thus, we have chosen one of the most symmetric space groups, i.e. *Imma (74)*, among the potential orthorhombic and monoclinic structures to perform a factor group analysis of the Raman active modes. Depending upon the various positions occupied by the atoms of $CaSO_4$, the analysis yielded 14–18 Raman active modes for the chosen space group. This is much more than the observed number of Raman peaks for the high-pressure phase shown in Fig. 2(c). On the other hand, it is rather common that the observed number of Raman modes is less than that calculated by a factor group analysis for a known structure. Thus, this type of analysis does not seem to be able to resolve the structure of the high-pressure phase of $CaSO_4$ revealed in this study.

The ambient density of the high-pressure phase of $CaSO_4$ revealed in the shock-wave experiment of Simakov et al. [3] is about 24% greater than that of anhydrite. The molar volume of the hypothetical barite-type $CaSO_4$ can be estimated from the data shown in Fig. 3. The ambient molar volume of hypothetical barite-type $CaSO_4$ thus calculated is 42.9 ± 0.2 cm^3, which is 6.5% smaller than that of anhydrite. Thus, it is unlikely that the high-pressure phase of $CaSO_4$ revealed in the shock-wave experiment is related to the anhydrite $\rightarrow$ barite transition, or to the new phase discovered in the present study.

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