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Abstract

The high-pressure and high-temperature behaviors of anhydrite ($CaSO_4$) are studied up to 53.5 GPa and 1800 K using double-sided laser heating Raman spectroscopy and x-ray diffraction in diamond anvil cells. The evidence of phase transition from an anhydrite structure to the monazite type was observed at about 2 GPa under cold compression. Another phase transition and a change in color of the sample from transparent to black have been also observed at a pressure of 33.2 GPa after laser heating. The new phase after laser heating persists to 53.5 GPa and 1800 K.

1. Introduction

Anhydrite ($CaSO_4$) is one of the most common sulfate minerals in the Earth's crust. It has an orthorhombic structure with the lattice constants $a = 6.992$ Å, $b = 6.999$ Å, $c = 6.240$ Å and belongs to the space group $Cmcm$(63). The anhydrite formed from the dehydration of gypsum ($CaSO_4 \cdot 2H_2O$) is known to absorb water from the environment and to be converted into hydrates. The phase transitions are construed to be controlled by rehydration and dehydration processes [1]. From a geologic perspective, the hydration–dehydration reactions of gypsum have been extensively studied and indicate that molecular water begins to be removed from this structure at temperatures above about 333 K [2]. Prasad [3] and Sarma [4] reported in detail the process of the stepwise dehydration of gypsum using Raman spectroscopy and demonstrated the gypsum–bassanite–anhydrite phase transition sequence up to 550 K at ambient pressure. The different phases, gypsum, bassanite and anhydrite, have been widely studied by a variety of experimental techniques such as neutron diffraction [5], x-ray diffraction [6], Raman spectroscopy and infrared [7–9].

In contrast to the extensive work that has been conducted on the effect of temperature on the dehydration process of gypsum [10–20] and characterizing the structure of individual

phases, the high-temperature and high-pressure behavior of anhydrite has been the subject of fewer studies. Due to rapid graphitization of diamond and the loss of strength of the diamond support, studies under simultaneous high-pressure and high-temperature conditions are still limited. The diamond anvil might be damaged at high temperature even with inert gas protection. In a recent study using x-ray diffraction techniques and Raman spectroscopy in the DAC, it was reported that anhydrite at 21 GPa after laser irradiation transformed to a new high-pressure modification with an orthorhombic cell [21]. But they do not give the data of anhydrite at high pressure and room temperature.

In recent years, the laser heated diamond anvil cell (LHDAC) combined with analytical techniques has been widely used for high-pressure and temperature (P–T) studies to reach ultrahigh static P–T conditions [22–26]. Our previous work has developed a Raman scattering system and a Brillouin scattering system for *in situ* measurements under high pressure and high temperature (HPHT) [25, 26]. The Raman scattering system integrates micro-Raman spectroscopy equipment with a double-sided laser heating system for a diamond anvil cell (DAC). In the present study we report new data of anhydrite for the first time in the DAC using this system under ultrahigh-P–T conditions. The interesting behavior of anhydrite is discussed.

2. Experimental details

The anhydrite was obtained by heating the calcium sulfate dihydrate ($CaSO_4 \cdot 2H_2O$), which was purchased with a purity greater than 99%, at 550 °C for 2 h. Raman spectroscopy of the recovered sample at ambient condition is in good agreement with that of anhydrite [4] and showed the lack of the OH mode around 3500 cm^{-1}. In the *in situ* high-pressure Raman scattering experiment, we use a DAC with anvil face diameter of 400 μm. A T301 stainless steel gasket was pre-indented to a thickness of 60 μm and a hole of 100 μm was drilled in the center of the pre-indented area. Powdered anhydrite was loaded into the hole together with a small chip of ruby. The pressure in the DAC was calibrated by the well known ruby fluorescence method [27]. The excitation laser is a 150 mW Ar$^+$ ion laser at 514.5 nm. The scattered light was collected in backscattering geometry. We do not use a pressure medium in the present experiment, so as to avoid rehydration and possible reactions between the anhydrite and the pressure medium.

For laser heating experiments, the experimental samples consist of anhydrite powder mixed with Pt, which acts as an absorber of the laser beam for heating. Furthermore, a thermal insulator is necessary during the laser heating process under high pressure because diamond is a good thermal conductor. NaCl was used as the thermal insulation blanket to reduce the heat loss through the anvils. For the sample loading method, we adopt a traditional loading method: the sample was sandwiched between thermal insulator (NaCl or MgO powder). Anhydrite was loaded in the gasket hole near the middle of a NaCl flake and then covered by another NaCl flake. Using this loading method, we also efficiently prevented the DAC from being damaged by the heating laser.

The sample was heated up on both sides in the DAC using a 55 W Nd:YLF laser with a 1053 nm wavelength and TEM$_{01}$ mode on an *in situ* HPHT Raman scattering system with the 514.5 nm line of an Ar$^+$ laser as the excitation source. Temperatures are evaluated by fitting the thermal radiation spectrum to the Planck radiation function [25]. The temperature and pressure dependence of the ruby fluorescence are assumed to be independent of each other [28]. The high-pressure x-ray diffraction experiments were carried out in the DAC at room temperature on a Bruker three-circle diffractometer with a Smart Apex 4 K CCD area detector. The x-ray diffraction data were treated with Materials Studio from Accelrys.
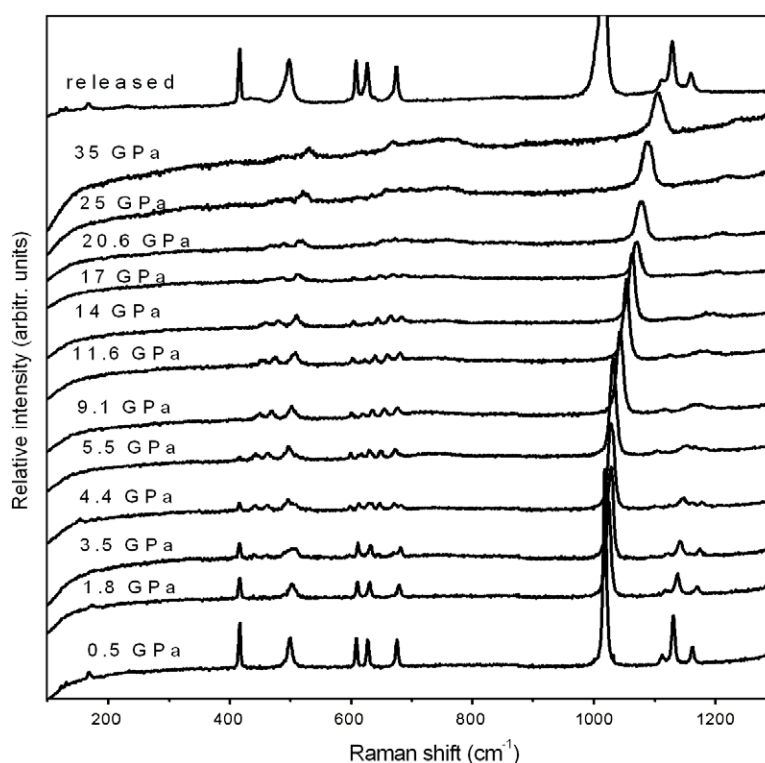
Figure 1. Raman spectra of the anhydrite obtained during compression at ambient temperature.

3. Results and discussion

3.1. Phase transition under cold compression

According to factor group analysis [18], the irreducible representation corresponding to the anhydrite lattice is

$$\Gamma = 6A_g + 5B_{1g} + 5B_{2g} + 2B_{3g} + 2A_u + 5B_{1u} + 5B_{2u} + 6B_{3u}$$

where A_g, B_{1g}, B_{2g} and B_{3g} modes are Raman active and A_u, B_{1u}, B_{2u} and B_{3u} modes are infrared active. The symmetry and assignment of the bands in the anhydrite are presented in table 1. Raman spectra were measured to 35 GPa at ambient temperature without heating. Figure 1 shows the Raman spectrum of anhydrite at selected pressure and room temperature. The spectrum is dominated by a strong A_g band at 1016 cm^{-1} (in ambient conditions) due to the mode derived from the symmetric stretching vibration (v_1) of the SO$_4$ tetrahedra. Observed band positions are in good agreement with those reported in the literature [29].

During the compression study, at pressure around 1.8 GPa three new bands appear at 491, 644 and 667 cm^{-1}. Furthermore, another three peaks emerge at 440, 458 and 596 cm^{-1} with increasing pressure to 3.5 GPa, (marked with asterisks in figure 2). These bands show a pressure-induced increase in intensity and shift, and simultaneously the bands assigned to the anhydrite weaken and disappear gradually, so we suggest the occurrence of the phase transitions.

Pressure shifts for all bands were obtained and the Raman frequencies are plotted as a function of pressure in figure 3. All bands, including new bands, exhibit a linear increase in frequency with increasing pressure, as expected, but the B_{3g} mode observed at 416 cm^{-1}
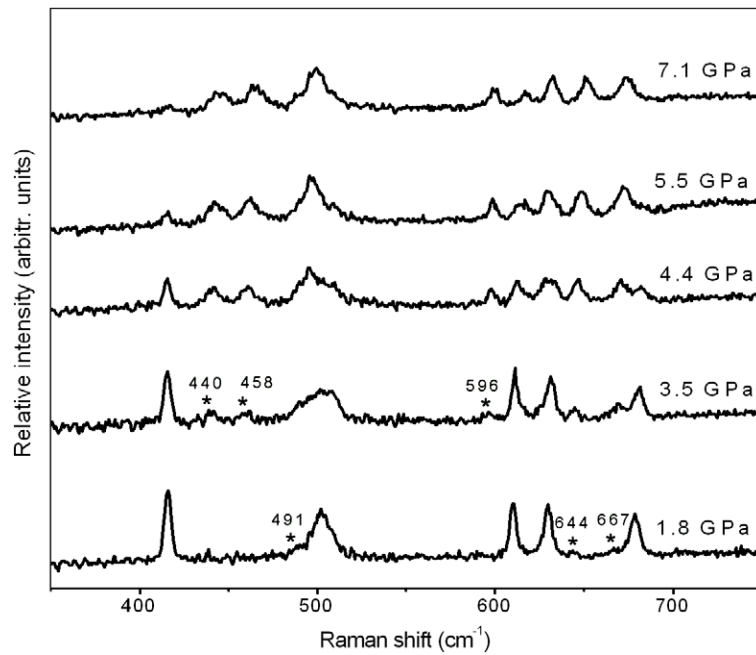
Figure 2. Raman spectra of the anhydrite obtained during compression at ambient temperature in the range 350–750 cm^{-1}. New peaks observed around 1.8 GPa are indicated by asterisks.
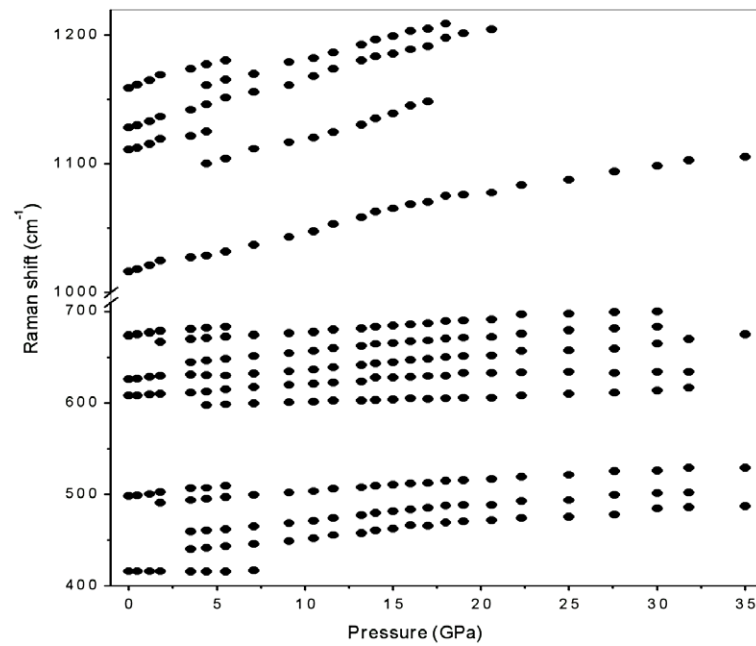

Figure 3. Pressure shift of Raman modes during compression at ambient temperature.

under ambient conditions is insensitive to pressure changes. When the pressure was released to ambient conditions, the new band disappears and the anhydrite bands return to their initial frequencies (figure 1 in top). Therefore, the phase transitions are fully reversible.
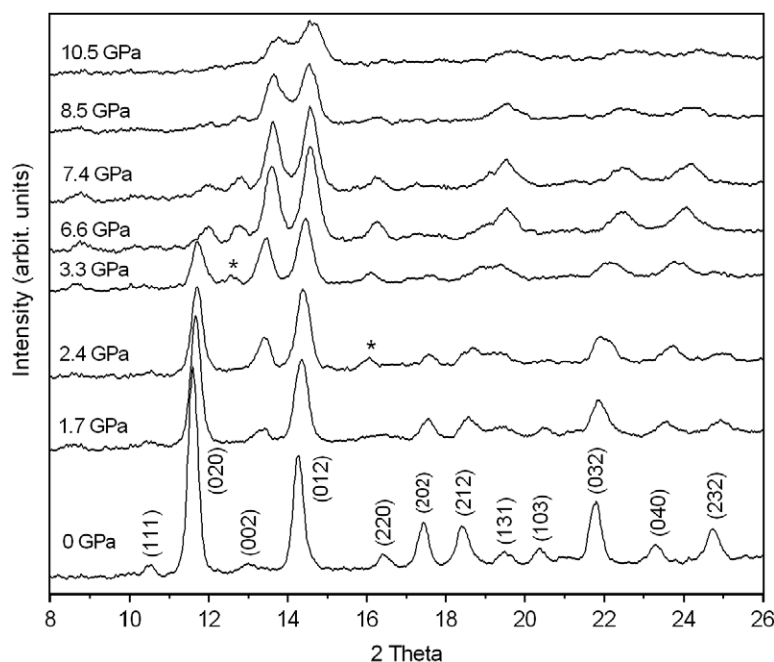
Figure 4. X-ray diffraction patterns during compression of the CaSO$_4$ at ambient temperature. The stars indicate new peaks.

Table 1. Experimental and calculated [29] ambient Raman frequencies (cm^{-1}), their symmetries and assignments and pressure dependence of the anhydrite (SO$_4$)$^{-2}$ group vibrations. (Note: R = rotational lattice mode; T = translational lattice mode; v_1, SO$_4$ symmetric stretch; v_2, SO$_4$ symmetric bend; v_3, SO$_4$ anti-symmetric stretch; v_4, SO$_4$ anti-symmetric bend.)

Mode symmetries	Assignments	v (cm^{-1}) (calculated)	v (cm^{-1}) (measured)	dv/dP (cm^{-1} GPa^{-1})
B$_{2g}$	T_z (SO$_4$, Ca)	67	—	
B$_{2g}$	R_y (SO$_4$), T_z (Ca)	98	—	
A$_g$	T_x (Ca, SO$_4$)	130	123	
B$_{1g}$	T_y (Ca, SO$_4$)	148	131	
B$_{3g}$	R_x (SO$_4$)	179	168	
B$_{1g}$	R_z (SO$_4$), T_y (Ca)	193	—	
A$_g$	T_x (SO$_4$, Ca)	222	—	
B$_{2g}$	T_z (SO$_4$, Ca)	240	235	
B$_{1g}$	T_y (SO$_4$, Ca)	253	—	
B$_{3g}$	v_2	411	416	0.038
A$_g$	v_2	490	498	2.171
B$_{1g}$	v_4	618	608	0.950
B$_{2g}$	v_4	619	626	1.365
A$_g$	v_4	673	674	1.635
A$_g$	v_1	1023	1016	2.722
B$_{2g}$	v_3	1110	1111	3.226
B$_{1g}$	v_3	1130	1128	3.780
A$_g$	v_3	1159	1159	3.888

In situ x-ray diffraction patterns were recorded up to 10.5 GPa (figure 4). A large change in the diffraction patterns was observed to occur beginning at pressure above 2 GPa, with the appearance of additional peaks indicating occurrence of a phase transition. This clearly shows
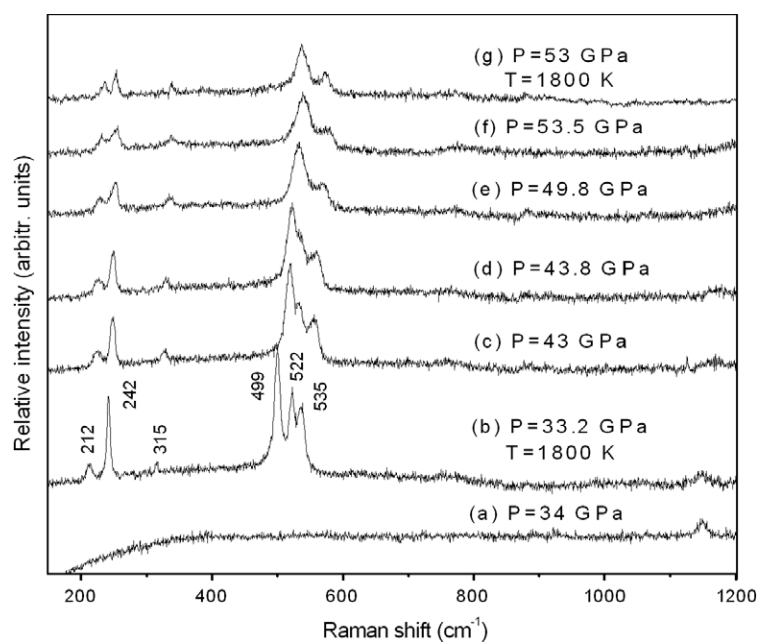
Figure 5. High-pressure Raman spectra of anhydrite measured after laser heating (a), (f) and under compression of the laser-heated sample (b)–(e). The Raman spectrum without laser heating measured at 34 GPa is shown for comparison.
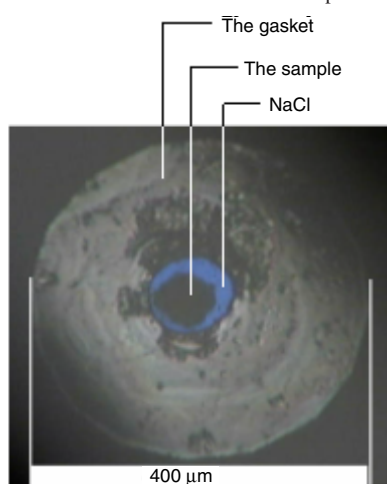

Figure 6. The photograph of the sample in the DAC at 33.2 GPa after laser heating.

(This figure is in colour only in the electronic version)

that the first phase transition starts from 2 GPa and is completed around 5 GPa. The phase transitions are fully reversible. This is in agreement with the Raman data presented above. The new diffraction pattern could be indexed within the $P21/n$ space group expected for the monazite structure with monoclinic structure. The lattice parameters refined within this space group for the new phase at 10.5 GPa were $a = 6.829$ Å, $b = 7.134$ Å, $c = 6.228$ Å and $\beta = 104.394°$.
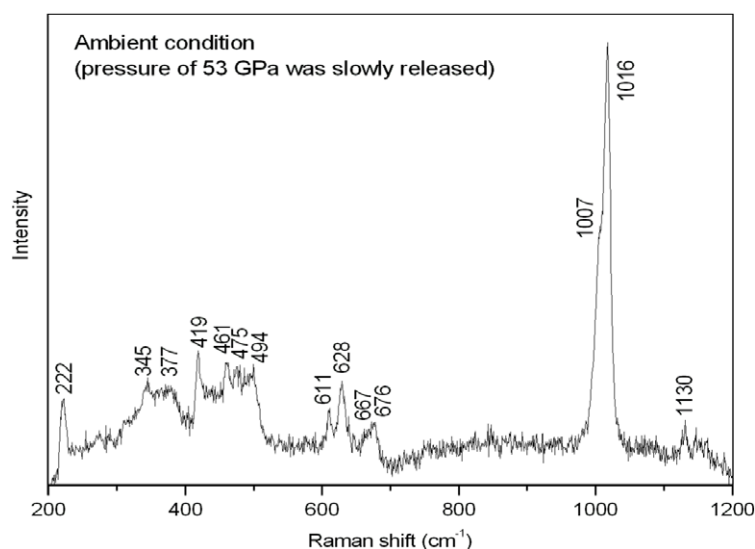
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Figure 7. Raman spectrum obtained after decompression of the laser-heated sample.

Previous shock-wave experiments on $CaSO_4$ have indicated a phase transition between 360 and 540 kbar [30]. In addition, on the basis of x-ray diffraction data, $CaSO_4$ undergoes a phase transition from its ambient anhydrite structure to the monazite type at 11.8 GPa and room temperature [31]. Our x-ray diffraction and Raman scattering results on $CaSO_4$ clearly indicate that a pressure-induced phase transformation occurs at about 2 GPa, which is comparable with Borg's result [32].

3.2. Phase transition about 33.2 GPa and 1800 K

Raman spectra of anhydrite acquired by the LHDAC Raman scattering system at various pressures and temperatures are shown in figure 4. Figure 4(a) displays the Raman spectrum without laser heating measured at 34 GPa for comparison. The Raman spectrum of the same sample as figure 4(a) at 33.2 GPa and 1800 K is shown in figure 4(b). From figure 4(b) we can see that the spectra have drastic changes. New Raman bands appear at 212, 242, 315, 499, 522 and 535 cm^{-1} and intensities of Raman scattering increase obviously. These new bands are neither the Raman bands of anhydrite nor the bands of the high-pressure phase of anhydrite at 1.8 GPa, indicating that the structure of anhydrite underwent change again. In addition, the change in color of the sample from transparent to black has been also observed at pressure of 33.2 GPa after laser heating.

Figure 6 shows the photograph of the sample in the DAC at 33.2 GPa after laser heating. NaCl was loaded around the sample in order to insulate the sample from the gasket to avoid heat loss. NaCl was also used as a pressure medium. With further increase of pressure at room temperature, the observed bands after laser heating blueshift gradually, and persist to 53.5 GPa (figures 5(c)–(f)). When the sample was heated to 1800 K at 53.5 GPa (figure 5(g)), the pressure released to 53 GPa after the quenching and the Raman spectrum does not have any obvious change, suggesting the structure of the new high-pressure phase is stable.

When samples were decompressed slowly, there were not only peaks of anhydrite, but also peaks of the new phase in the Raman spectrum (figure 7). Recently, a study using x-ray diffraction techniques and Raman spectroscopy in the DAC has pointed out that anhydrite transformed to a new high-pressure modification with an orthorhombic structure quenched from 21 GPa and 1000 °C [21]. Crichton *et al* [31] have observed and positively identified

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three structure types of CaSO$_4$ at HPHT, the monazite type, the barite type, and its distorted-AgMnO$_4$ variant, using *in situ* x-ray powder diffraction data and combining laser heating with a DAC. Moreover, the position of Raman peaks for the high-pressure modification at 21 GPa after laser irradiation is not the same as our results for the new high-pressure phase quenched from 1800 K. In order to obtain the structure of the new phase in our experiments, *in situ* HPHT study on anhydrite using x-ray diffraction should be carried out in the future.

4. Conclusion

The compressional behavior of anhydrite at high temperatures and at high pressures up to 53.5 GPa and 1800 K using double-sided laser heating Raman spectroscopy and x-ray diffraction in the diamond anvil cells has been reported. It has been found that the structure changes from an anhydrite to the monazite type at about 2 GPa under cold compression. Another phase transition and a change in color of the sample from transparent to black have been also observed at a pressure of 33.2 GPa after laser heating. The new phase after laser heating persists to 53.5 GPa and 1800 K.

Acknowledgments

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