



Phase transition and thermoelastic behavior of barite-group minerals at high-pressure and high-temperature conditions

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Abstract

Experimental studies on the phase transition and thermoelastic behavior of barite-group minerals are crucial to understand the recycle of sulfur in Earth's interior. Here, we present a high-pressure and high-temperature (high P – T) study on two barite-group minerals—barite (BaSO_4) and celestite (SrSO_4) up to ~ 59.5 GPa 700 K and ~ 22.2 GPa, 700 K, respectively, using in situ synchrotron-based X-ray diffraction (XRD) combined with diamond anvil cells (DACs). Our results show that BaSO_4 undergoes a pressure-induced phase transition from $Pbnm$ to $P2_12_12_1$ at ~ 20.3 GPa, which is different from the previous results. Upon decompression, the high-pressure phase of BaSO_4 transforms back into its initial structure, which indicates a reversible phase transition. However, no phase transitions have been detected in SrSO_4 over the experimental P – T range. In addition, fitting a third-order Birch–Murnaghan equation of state to the pressure–volume data yields the bulk moduli and their pressure derivatives of BaSO_4 and SrSO_4 . Simultaneously, the thermal expansion coefficients of BaSO_4 and SrSO_4 are also obtained, by fitting the temperature–volume data to the Fei-type thermal equation of state. Furthermore, the compositional effects on the phase transformation and thermoelastic behavior of barite-group minerals are also discussed, and the results suggest that the bond length of $\langle M\text{--O} \rangle$ ($M=\text{Ba}, \text{Sr}, \text{Pb}$) is an important factor that causes the phase transition pressure of SrSO_4 to be the largest, PbSO_4 is the second, and BaSO_4 is the lowest.

Keywords Sulfate · High temperature and high pressure · Synchrotron · X-ray diffraction · Equation of state · Diamond anvil cell

Introduction

As an abundant environment-influencing element, sulfur is not only vital in the evolution of life, but also a basic component of the ore-forming systems associated with subduction (Richards 2011; Tomkins and Evans 2015). Sulfur is transported into the deep Earth by the effective carrier of fluids or melts liberated from the subducted crust, while released into the atmosphere by magma degassing, dynamics of volcanic eruption, and redox evolution of magma (Evans 2012; Jégo and Dasgupta 2013, 2014; Wang et al. 2014; Tomkins and Evans 2015). Therefore, the recycling of sulfur in subduction zone is particularly important for biogeochemical cycles, the history of degassing of magmas, and the migration of ore metals (Canil and Fellows 2017). Sulfur exists in the forms of sulfide, sulfate minerals, sulfur-bearing fluids and melt in Earth's interior (Jégo and Dasgupta 2013). Some studies have suggested that the remarkable oxidized state of the mantle wedge originates from slab-derived sulfate

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species (SO_4^{2-}) (Mungall 2002; Kelley and Cottrell 2009), indicating the importance of sulfate. Obviously, as common crust minerals and important sulfur-bearing minerals, the structural variation and thermoelastic properties of sulfates at high P – T conditions are necessary to improve our understanding on the existing forms of sulfur in Earth's interior (Kuang et al. 2017; Li et al. 2018).

Typical sulfate minerals in the deep Earth are anhydrite (CaSO_4), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), barite (BaSO_4), celestite (SrSO_4), and anglesite (PbSO_4) (Gracia et al. 2012; Lee et al. 2013). Anhydrite and gypsum are not only the most important sulfate minerals, but also important component minerals in the crust. To date, the phase transformation characteristics of CaSO_4 have been extensively studied by experiment (e.g., XRD, Raman spectroscopy) and theoretical calculation (e.g., density functional theory) (e.g., Borg and Smith 1975; Crichton et al. 2005; Gracia et al. 2012; Fujii et al. 2016). Besides CaSO_4 , barite-group minerals (celestite, barite, and anglesite) are also widely distributed in the crust (Lee et al. 2013). At ambient conditions, barite-group minerals are orthorhombic structure ($Pbnm$) and characterized by SO_4 tetrahedra and MO_{12} polyhedra ($M=\text{Sr}$, Pb , Ba). Each M atom coordinates with 12 oxygen atoms of six neighboring SO_4 groups to form a MO_{12} polyhedron, and SO_4 tetrahedra and MO_{12} polyhedra share edges (Fig. 1) (Garske and Peacor 1965; Miyake et al. 1978).

To date, a considerable number of experimental and theoretical investigations have been conducted to explore the structural phase transition of barite-group minerals. Previous synchrotron XRD studies show that BaSO_4 exists

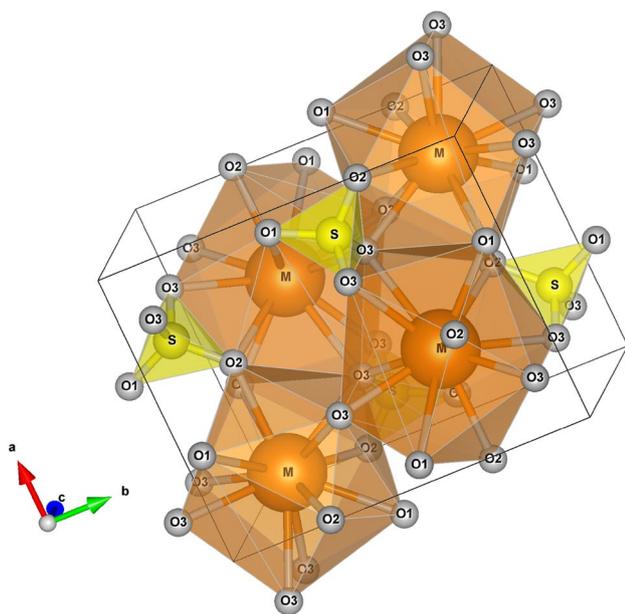


Fig. 1 Crystal structure of barite-group minerals at ambient pressure and room temperature (in $Pbnm$)

a pressure-induced phase transition at different pressures using different pressure media (Lee et al. 2003; Santamaría-Pérez et al. 2011). Simultaneously, Lee et al. (2003) also conducted the high-pressure Raman spectroscopic measurements on BaSO_4 and confirmed the pressure-induced phase transition by synchrotron XRD. Moreover, the theoretical calculation further indicated that the crystal structure of the high-pressure phase for BaSO_4 is also orthorhombic structure ($P2_12_12_1$) (Santamaría-Pérez et al. 2011). In contrast, Crichton et al. (2011) have not observed any pressure-induced phase transition of BaSO_4 to 21.5 GPa by Raman spectroscopic method. Therefore, experimental results of the pressure-induced phase transition of BaSO_4 are controversial. As an isostructural material with BaSO_4 , the phase transition of SrSO_4 is controversial as well. Chen et al. (2010) observed a pressure-induced phase transition of SrSO_4 at ~ 12 GPa by Raman spectroscopic method. However, Kuang et al. (2017) have not observed any phase transition of SrSO_4 using in situ angle-dispersive XRD method to a maximum pressure of 15 GPa. Moreover, the previous studies of SrSO_4 are conducted under relatively poor hydrostatic conditions, which can significantly influence the structural phase transition. Hence, considering the controversy about the phase transition of SrSO_4 , further experimental studies under better hydrostatic conditions are still essential to clarify its phase transition processes.

Insofar, the thermoelastic behavior of barite-group minerals has been the subject of several previous studies, but these experimental studies about the axial compression anisotropies of BaSO_4 and SrSO_4 are still controversial (Lee et al. 2003; Chen et al. 2010; Santamaría-Pérez et al. 2011; Kuang et al. 2017). In addition, the previous XRD studies on BaSO_4 were carried out at high temperatures, but have not provided the thermal expansion coefficient directly (Sawada and Takéuchi 1990). Furthermore, to the authors' knowledge, there are still no any existing relevant studies about the thermal properties of SrSO_4 at high temperatures. From the above, studying the compressibility and expansion of BaSO_4 and SrSO_4 at high P – T conditions are still needed to understand the thermoelastic behavior of barite-group minerals.

In this study, we have investigated the phase transition, compressibility, and thermal expansion of BaSO_4 and SrSO_4 at high-pressure/temperature conditions up to ~ 59.5 GPa and 700 K, ~ 22.2 GPa and 700 K, respectively, using the DACs combined with in situ angle-dispersive synchrotron XRD method. We find that BaSO_4 undergoes a pressure-induced phase transition, but no phase transition occurs in SrSO_4 over the current P – T range. We also obtain the compressibility and expansivities of BaSO_4 and SrSO_4 . Moreover, combined with the previous results of PbSO_4 , we also discuss the phase transitions, compressibility, and thermal expansion of barite-group minerals MSO_4 ($M=\text{Ba}$, Pb , and Sr).

Samples and experiments

Samples

The high-purity BaSO₄ and SrSO₄ samples (99.999%) in this study were purchased from Alfa Aesar Corporation. Both of them were ground in the agate mortar to an average size of 5 μm, and then were heated at 100 °C in the constant temperature furnace for 2 h to eliminate the absorbed water. The XRD pattern of samples under ambient conditions was obtained from the conventional power X-ray diffraction method with a D/Max-2200 X-ray diffractometer using graphite crystal monochromator and Cu Kα radiation. The ambient XRD spectrum of BaSO₄ and SrSO₄ was indexed according to the standard spectra of JCPDS83-1718 and JCPDS83-1719, respectively, confirming that the crystal structure of BaSO₄ and SrSO₄ is orthorhombic, and with *Pbnm* space group. In this study, to solve the controversy about the pressure-induced transition of BaSO₄ and SrSO₄ and obtain the thermal expansion coefficient accurately, the in situ synchrotron XRD experiments consist of two parts: ambient-temperature and high-pressure, and ambient-pressure and high-temperature experiments.

High-pressure experiments

Ambient-temperature and high-pressure experiments of BaSO₄ and SrSO₄ were carried out using symmetric piston cylinder DACs with pairs of 300 μm and 500 μm culet-size diamond anvils, respectively. The rhenium gaskets pre-indented to a thickness of ~45 μm and ~50 μm with a hole of 180 μm and 300 μm in diameter were used as the sample chamber for BaSO₄ and SrSO₄, respectively. In both experiments, a piece of sample disk was loaded into the sample chamber with a gold tablet as the pressure calibrant (Fei et al. 2007). The XRD patterns of gold were collected before and after sample data collection for each pressure, and the average pressure values were used for equation of state (EoS) calculation. Neon gas was used as the pressure-transmitting medium (Hemley et al. 1989), by the gas-loading system at Center for High-Pressure Science and Technology Advanced Research (HPSTAR), China.

In situ ambient-temperature and high-pressure synchrotron XRD experiments were carried out at the BL15U1 beamline of Shanghai Synchrotron Radiation Facility (SSRF). The incident wavelength of the monochromatic beam was 0.6199 Å and the X-ray beam was focused to a beam size of 2 × 3 μm². The sample-to-detector distance and the geometrical parameters of the detector were

calibrated with cerium dioxide (CeO₂). Diffraction data of the samples were collected by a MAR-165 charge-coupled device (CCD) detector, and then were integrated as a function of 2θ using the Fit2D program (Hammersley et al. 1996). Further analyses and refinements of high-pressure XRD patterns were performed by means of the profile-fitting technique implemented in the EXPGUI/GSAS software package (Larson and Von Dreele 2004). Refinement of peak positions and extraction of unit-cell parameters were analyzed by the Le Bail method (Le Bail et al. 1988). The initial unit-cell parameters, unit-cell coordinates, and space group were stemmed from Miyake et al. (1978). The sequence of the full-matrix least-squares fitting was refined by changing the unit-cell parameters, background, and profile function parameters. Until the end of the refinement, all the unit-cell parameters should be changed simultaneously, and the refinement approached convergence.

High-temperature experiments

Ambient-pressure and high-temperature experiments were carried out using an externally heating DAC (Fan et al. 2010, 2014) equipped with two pairs of 400 μm and 500 μm culet-size diamond anvils for BaSO₄ and SrSO₄, respectively. The pre-indented T301 stainless steel foil gaskets with thickness of 60–80 μm were drilled with diameter of 280–300 μm holes as the sample chambers. Heating was carried out using NiCr resistor wire with a diameter of 0.3 mm as an external heating device. The experimental temperature was measured by a Pt₉₀Rh₁₀–Pt₁₀₀ thermocouple attached to the pavilion of the diamond anvil, and its precision was ± 2 °C. The BaSO₄ and SrSO₄ powders were slightly formed approximately 50-μm-thick disks, and a piece of sample about 200 μm in diameter was loaded into the sample chamber without any pressure-transmitting medium. The ambient-pressure and high-temperature experimental process is as follows. The temperature was first increased from ambient-temperature to the maximum temperature of 700 K, and then, temperature was kept for ~600 s to relax the sample before collection of the XRD spectrum. Then, the temperature was dropped to 320 K in 30 K steps. For each temperature point, an XRD pattern was collected, and the typical exposure time for collecting these XRD patterns of samples was 300 s. Additional details of the experimental setup and DAC assembly were given in Fan et al. (2010).

The ambient-pressure and high-temperature synchrotron XRD experiments were conducted at the 4W2 beamline of Beijing Synchrotron Radiation Facility (BSRF). Diffraction patterns were collected using an image plate detector (MAR-345). The incident X-ray beam was monochromatized to a wavelength of 0.6199 Å and the beam size was collimated to 20 × 30 μm². CeO₂ was used as the diffraction standard. The

process of integrate diffraction patterns and further analysis of high-temperature XRD data were the same as ambient-temperature and high-pressure XRD experiments.

Results

Figure 2 shows the typical pressure evolution of the XRD patterns of BaSO_4 , where all of the peaks shift to higher 2θ angle and the intensity of some peaks become slightly weak and broad with increasing pressure. However, a new peak appears at $2\theta = 10.086^\circ$ when pressure increases to ~ 20.3 GPa. Further increase pressure to ~ 26.6 GPa, another new peak appears at $2\theta = 12.037^\circ$. These significant changes indicate that BaSO_4 undergoes a pressure-induced phase transition. In addition, with continuous increasing pressure, the intensity of these new peaks increases and obviously split. These new diffraction peaks from the new high-pressure phase are stable up to the maximum pressure (59.5 GPa) in this study, which indicates that there is no further phase transition of BaSO_4 . Upon decompression, the high-pressure phase of BaSO_4 transforms back to its original structure (on the top of Fig. 2), which demonstrates that BaSO_4 undergoes a reversible phase transition at ~ 20.3 GPa. Previous experimental and theoretical results show that the crystal structure of the new high-pressure phase of BaSO_4 is $P2_12_12_1$ structure (Santamaría-Pérez et al. 2011). Hence, it is reasonable to infer that $P2_12_12_1$ structure is the most possible high-pressure phase of BaSO_4 . We thus fit the XRD patterns of the high-pressure phase using the

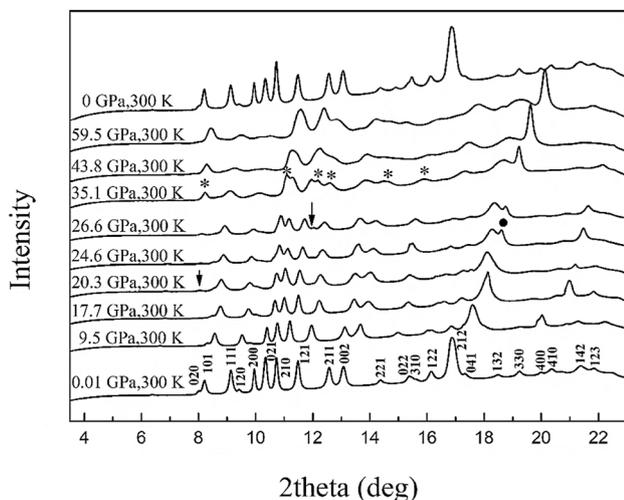


Fig. 2 Representative X-ray diffraction patterns of BaSO_4 obtained in this study up to 59.5 GPa at room temperature. The appearance of new peaks for BaSO_4 has been observed in the experimental process at 20.3 GPa and 26.6 GPa, respectively. Asterisks indicate the peak indices of $P2_12_12_1$ phase, which are (011), (021), (121), (201), (031), and (112). Black solid dot indicates diffraction peaks from the pressure-transmitting medium Neon

$P2_12_12_1$ structure, but the fitting results are unsatisfactory. Nevertheless, we obtain excellent fitting results using the $P2_12_12_1 + Pbnm$ structure to fit the XRD patterns of the high-pressure phase. The Le Bail refinements show an excellent agreement between calculated and experimental results using GSAS program (Fig. 3), and give satisfying fitting results with $R_{wp} = 0.9\%$ and $R_p = 0.54\%$. Therefore, we infer that BaSO_4 undergoes a pressure-induced phase transition from $Pbnm$ to $P2_12_12_1$, but this phase does not completely immediately and there is a two-phase coexistence zone at pressures above 20 GPa. Moreover, up to the maximum pressure (59.5 GPa) in this study, we still obtain better fitting results using $P2_12_12_1 + Pbnm$ structures than only using $P2_12_12_1$ structure, which means that the two phases of $Pbnm$ and $P2_12_12_1$ may still coexist at pressures up to ~ 60 GPa.

Moreover, typical XRD patterns of SrSO_4 at high pressure are also shown in Fig. 4. With increasing pressure, all peaks just shift toward higher 2θ angles and become slightly broad and weak. It is noteworthy that a new peak appears at 12.4 GPa in the region of 17° – 19° , which is confirmed to be a peak of Neon pressure medium at this pressure condition. However, besides this Neon peak, neither the disappearance of peaks nor appearance of other new peaks has been observed in the pressure range of this study. Therefore, SrSO_4 does not undergo phase transition under the pressure range in this study. The typical refinement results of SrSO_4 at high pressure are shown in Fig. 5.

The typical temperature evolution of the XRD patterns for BaSO_4 and SrSO_4 is shown in Fig. 6, where all the peaks for BaSO_4 and SrSO_4 shift toward lower 2θ angle with increasing temperature from 315 to 320 K to 700 K at ambient pressure. Neither the disappearance of peaks nor appearance of new peaks has been observed in the temperature range of these experiments, indicating that BaSO_4 and SrSO_4 remain stable without any temperature-induced phase transition. The typical refinement results of BaSO_4 and SrSO_4 at high temperature are shown in Fig. 7.

The unit-cell parameters of BaSO_4 and SrSO_4 at high-pressure conditions are shown in Tables 1 and 2, respectively. The P – V data are fitted with the third-order Birch–Murnaghan EoS to obtain the elastic parameters (Birch 1947):

$$P = \left(\frac{2}{3}\right)K_0 \left[\left(\frac{V_0}{V}\right)^{7/3} - \left(\frac{V_0}{V}\right)^{5/3} \right] \times \left\{ 1 + (3/4)(K_0' - 4) \left[\left(\frac{V_0}{V}\right)^{2/3} - 1 \right] \right\},$$

where V_0 , V , K_0 , and K_0' are the zero-pressure unit-cell volume, and high-pressure unit-cell volume, isothermal bulk modulus, and its pressure derivative at ambient conditions, respectively. The results obtained from least-squares fitting by Eos-Fit program (Gonzalez-Platas et al. 2016) are

Fig. 3 La Bail profile fit of the diffraction profile of BaSO₄ at 17.7 GPa (a) and Rietveld profile fit of the diffraction profile at 45.4 GPa at room temperature (b). Observed spectra (black line), fitted spectra (red solid line), difference plot (blue solid line), and Bragg peak positions (tick marks) are shown

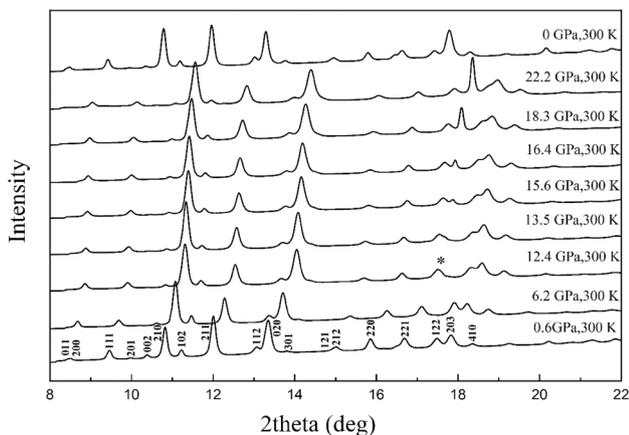
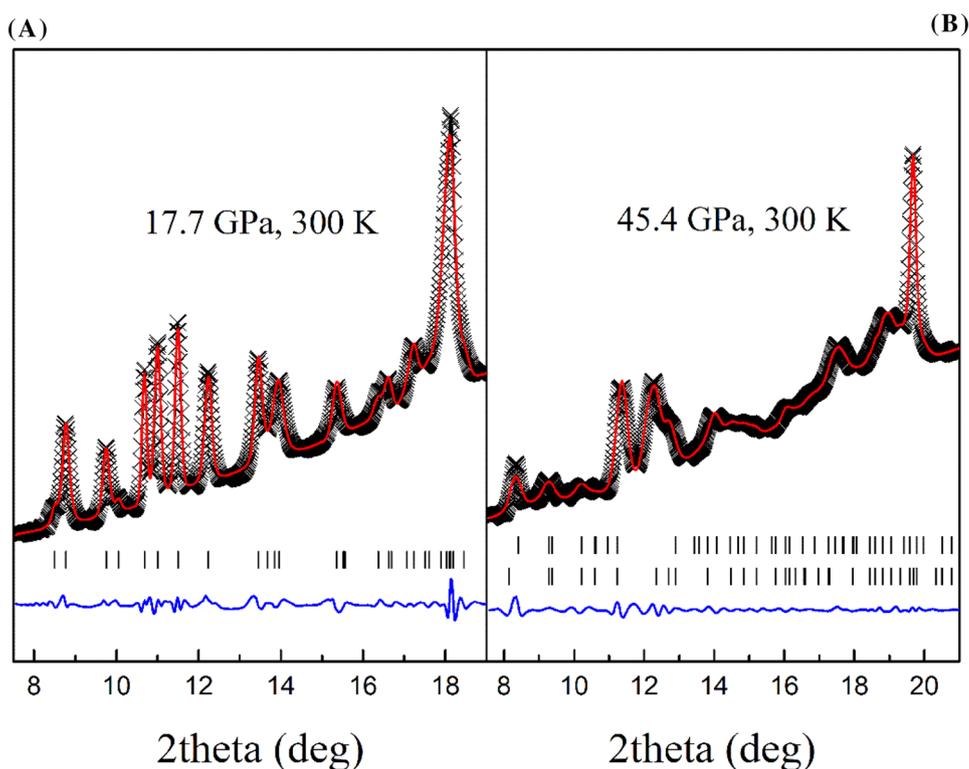


Fig. 4 Representative X-ray diffraction patterns of SrSO₄ obtained in this study up to 22.2 GPa at room temperature. Asterisk indicates diffraction peaks from the pressure-transmitting medium Neon

$V_0 = 344.173(1) \text{ \AA}^3$, $K_0 = 58(2) \text{ GPa}$, $K_0' = 4.2(4)$ of BaSO₄ and $V_0 = 306.846(1) \text{ \AA}^3$, $K_0 = 64(2) \text{ GPa}$, $K_0' = 4.8(4)$ of SrSO₄. When fix $K_0' = 4$, the fitting results yield $K_0 = 60(1) \text{ GPa}$ and $K_0 = 68(1) \text{ GPa}$ of BaSO₄ and SrSO₄, respectively. The unit-cell volume variation of BaSO₄ and SrSO₄ as a function of pressure and the compression curve calculated by these fitted parameters are plotted in Fig. 8, where only the data before the phase transition of BaSO₄ are selected for fitting. To evaluate the quality of the third-order

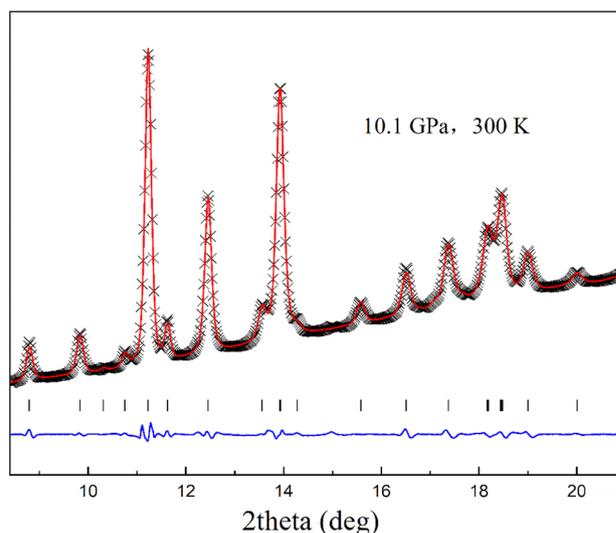


Fig. 5 La Bail profile fit of the diffraction profile of SrSO₄ at 10.1 GPa at room temperature. Observed spectra (black line), fitted spectra (red solid line), difference plot (blue solid line), and Bragg peak positions (tick marks) are shown

Birch–Murnaghan EoS fitting, the relationship between the Eulerian strain ($f_E = [(V_0/V)^{2/3} - 1]$) and normalized pressure ($F_E = P/[3f_E(2f_E + 1)^{5/2}]$) (Angel 2000) of BaSO₄ and SrSO₄ are plotted and shown in Fig. 9. Both sets of data show a slightly positive slope (Fig. 9) which

Fig. 6 Representative X-ray diffraction patterns of BaSO₄ (a) and SrSO₄ (b) obtained in this study up to 700 K at ambient pressure

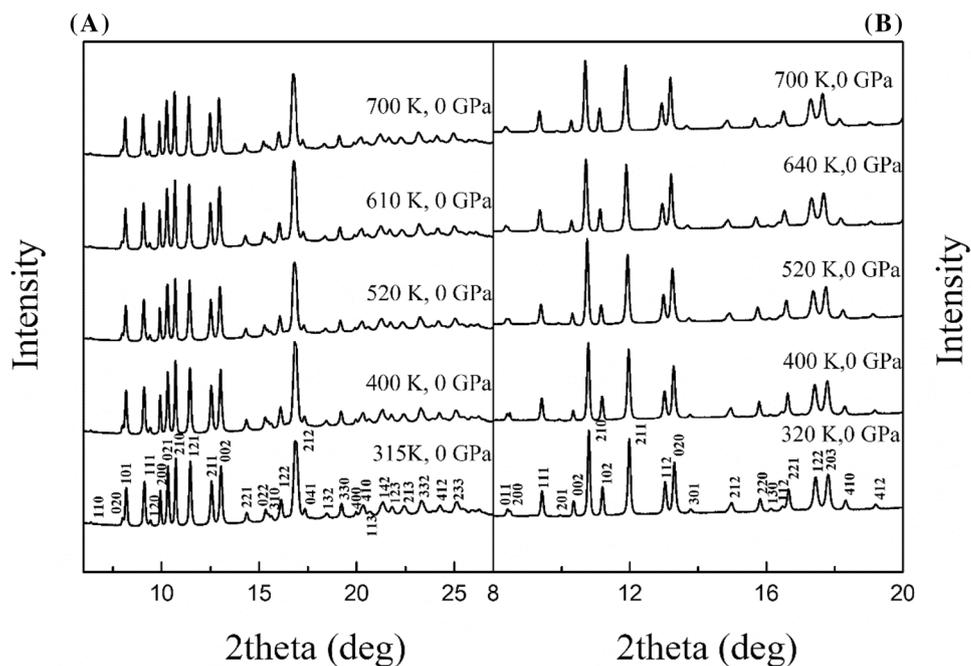
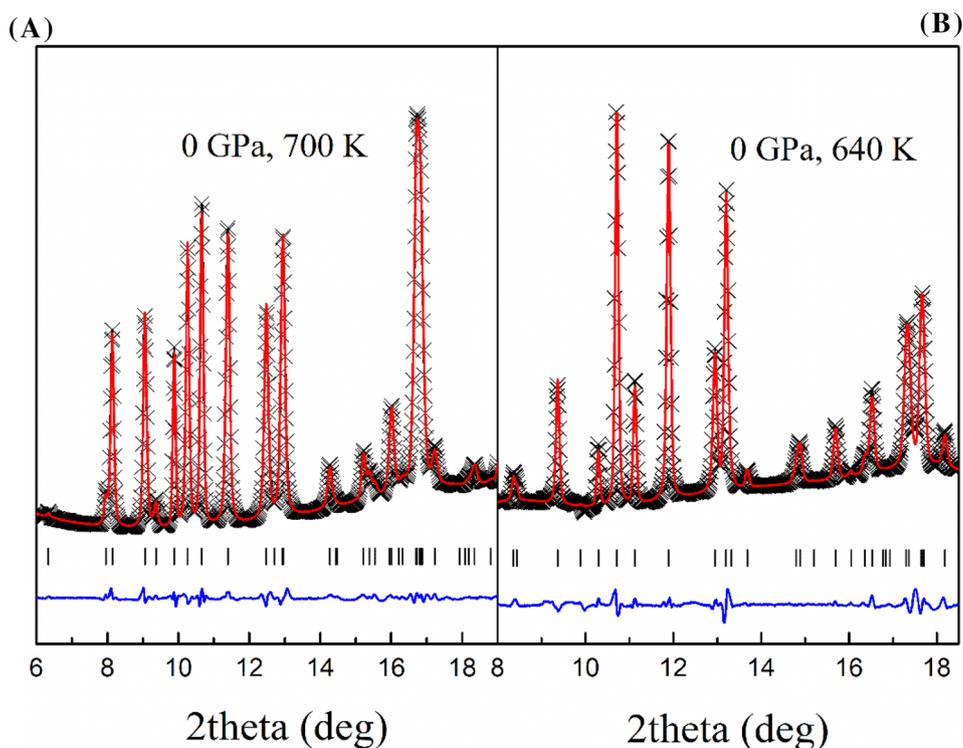


Fig. 7 La Bail profile fit of the diffraction profile of BaSO₄ at 700 K at ambient pressure (a) and SrSO₄ at 640 K at ambient pressure (b). Observed spectra (black line), fitted spectra (red solid line), difference plot (blue solid line), and Bragg peak positions (tick marks) are shown



indicates that the pressure derivative of the bulk modulus (K_0') is higher than 4. In addition, the weighted linear regression through the data points yields the intercept value, $F_E(0) = 58$ (1) GPa for BaSO₄ and $F_E(0) = 64$ (1) GPa for SrSO₄, which is absolutely consistent with the isothermal

bulk modulus $K_0 = 58$ (2) GPa and $K_0 = 64$ (2) GPa obtained by the third-order Birch–Murnaghan EoS fitting, respectively. Therefore, the third-order Birch–Murnaghan EoS is reasonable to describe the P – V data for BaSO₄ and SrSO₄ in this study.

Table 1 Unit-cell parameters in BaSO₄ at ambient temperature and high pressure

<i>P</i> (GPa)	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	<i>V</i> (Å ³)
0.0001	7.1371 (2)	8.8656 (4)	5.4384 (3)	344.11 (3)
0.7	7.1117 (2)	8.8384 (6)	5.4170 (3)	340.49 (3)
1.8	7.0695 (2)	8.7929 (4)	5.3800 (3)	334.43 (3)
2.7	7.0341 (2)	8.7513 (5)	5.3511 (3)	329.40 (3)
3.9	6.9907 (3)	8.7075 (6)	5.3180 (4)	323.68 (4)
4.6	6.9816 (2)	8.6974 (6)	5.3077 (3)	322.29 (3)
4.9	6.9651 (2)	8.6790 (4)	5.2967 (2)	320.19 (2)
5.9	6.9307 (2)	8.6409 (5)	5.2726 (3)	315.76 (3)
7.3	6.8898 (3)	8.6019 (8)	5.2410 (4)	310.60 (4)
7.5	6.8868 (2)	8.5985 (6)	5.2409 (3)	310.34 (3)
7.8	6.8787 (2)	8.5917 (6)	5.2310 (4)	309.16 (3)
8.7	6.8533 (2)	8.5663 (5)	5.2157 (3)	306.20 (3)
9.5	6.8359 (3)	8.5407 (7)	5.2069 (3)	304.00 (3)
10.5	6.8024 (3)	8.5109 (7)	5.1817 (4)	300.00 (4)
11.6	6.7771 (3)	8.4839 (7)	5.1690 (5)	298.20 (4)
13.2	6.7519 (3)	8.4628 (7)	5.1483 (4)	294.18 (4)
13.8	6.7410 (2)	8.4324 (6)	5.1288 (4)	291.54 (3)
14.5	6.7202 (3)	8.4192 (9)	5.1194 (6)	289.65 (5)
15.9	6.7045 (3)	8.3669 (9)	5.0934 (7)	285.72 (5)
17.7	6.6897 (3)	8.3518 (8)	5.0715 (5)	283.35 (4)

Numbers in parenthesis represent standard deviations

The axial compressibility of BaSO₄ and SrSO₄ as functions of pressure are plotted in Fig. 10. Fitting the unit-cell parameters at room temperature by a “linearized” third-order Birch–Murnaghan EoS with Eos-Fit program (Gonzalez-Platas et al. 2016) obtain the unit-cell parameters and the axial elastic parameters of BaSO₄ and SrSO₄. The unit-cell parameters of BaSO₄ and SrSO₄ are *a*₀ = 7.138 (1) Å, *b*₀ = 8.866 (1) Å, *c*₀ = 5.439 (1) Å and *a*₀ = 6.864 (1) Å, *b*₀ = 8.358 (1) Å, *c*₀ = 5.348 (1) Å and the refined axial moduli of BaSO₄ and SrSO₄ are *K*_{a0} = 169 (2) GPa, *K*_{b0} = 203 (2) GPa, *K*_{c0} = 164 (2) GPa and *K*_{a0} = 214 (2) GPa, *K*_{b0} = 237(3) GPa, *K*_{c0} = 167 (2) GPa, respectively, at ambient pressure. According to the following form of ambient-pressure axial compressibility β_{*i*} (Xia et al. 1998; Fan et al. 2010, 2015):

$$\beta_i = \frac{1}{(3M_i)}$$

The ambient-pressure axial compressibility of *a*-, *b*-, and *c*-axes are 1.97 (2) × 10⁻³, 1.64 (2) × 10⁻³, 2.03 (2) × 10⁻³ GPa⁻¹ for BaSO₄ and 1.56 (2) × 10⁻³, 1.41 (3) × 10⁻³, and 2.00 (2) × 10⁻³ GPa⁻¹ for SrSO₄. This clearly shows that both BaSO₄ and SrSO₄ have axial compressive anisotropy. For BaSO₄, *b*-axial is the most

Table 2 Unit-cell parameters in SrSO₄ at ambient temperature and high pressure

<i>P</i> (GPa)	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	<i>V</i> (Å ³)
0.6	6.8479 (2)	8.3379 (2)	5.3322 (1)	304.45 (1)
0.6	6.8440 (3)	8.3323 (2)	5.3282 (1)	303.84 (2)
1.0	6.8315 (3)	8.3204 (2)	5.3156 (1)	302.14 (2)
1.7	6.8083 (2)	8.2904 (2)	5.2936 (1)	298.80 (1)
2.5	6.7858 (2)	8.2641 (2)	5.2733 (1)	295.72 (1)
3.6	6.7608 (2)	8.2341 (2)	5.2500 (1)	292.27 (1)
4.8	6.7330 (3)	8.1953 (3)	5.2198 (2)	288.02 (2)
5.6	6.7145 (4)	8.1804 (3)	5.2022 (2)	285.75 (2)
6.2	6.7011 (3)	8.1680 (2)	5.1901 (1)	284.08 (2)
6.8	6.6835 (3)	8.1493 (2)	5.1742 (1)	281.82 (2)
7.2	6.6738 (4)	8.1382 (3)	5.1671 (2)	280.64 (2)
7.9	6.6576 (5)	8.1204 (3)	5.1523 (2)	278.54 (3)
8.7	6.6449 (4)	8.1055 (4)	5.1359 (4)	276.62 (3)
9.4	6.6239 (3)	8.0867 (5)	5.1215 (4)	274.34 (3)
10.1	6.6082 (4)	8.0712 (3)	5.1059 (2)	272.33 (2)
10.9	6.5900 (5)	8.0483 (3)	5.0903 (2)	269.98 (2)
11.5	6.5758 (5)	8.0346 (3)	5.0789 (2)	268.34 (2)
12.4	6.5593 (6)	8.0187 (3)	5.0616 (2)	266.22 (3)
13.5	6.5449 (5)	8.0019 (3)	5.0477 (2)	264.36 (3)
14.2	6.5335 (5)	7.9919 (3)	5.0384 (2)	263.08 (3)
14.9	6.5202 (7)	7.9788 (4)	5.0278 (2)	261.56 (3)
15.6	6.5122 (6)	7.9646 (3)	5.0202 (1)	260.38 (3)
16.4	6.4962 (8)	7.9453 (3)	5.0080 (2)	258.48 (4)
17.0	6.4901 (6)	7.9388 (2)	5.0043 (1)	257.84 (3)
17.6	6.4809 (6)	7.9305 (3)	4.9942 (2)	256.68 (3)
18.3	6.4682 (6)	7.9164 (2)	4.9834 (1)	255.17 (2)
19.3	6.4519 (6)	7.9006 (2)	4.9705 (1)	253.37 (3)
19.9	6.4455 (6)	7.8885 (2)	4.9630 (1)	252.35 (6)
20.6	6.4356 (9)	7.8801 (3)	4.9554 (2)	251.30 (4)
21.1	6.4269 (6)	7.8711 (3)	4.9471 (1)	250.26 (3)
22.2	6.4148 (7)	7.8599 (3)	4.9372 (1)	248.93 (3)

Numbers in parenthesis represent standard deviations

incompressible and the compressibility along *a*-axis and *c*-axis is almost equivalent (Fig. 10). Meanwhile, the compressibility of SrSO₄ along *c*-axis is the most, followed by *a*-axis and *b*-axis (Fig. 10). There is a good consistency of *b*-axis compressibility between BaSO₄ and SrSO₄.

Thermal expansion coefficients of BaSO₄ and SrSO₄ are obtained from the *T*–*V* data (Tables 3, 4) up to 700 K at ambient pressure. The thermal expansion expression proposed by Fei (1995) is fitted to calculate our ambient-pressure and high-temperature data with the following form:

$$V_{0T} = V_0 \exp \left(\alpha_0 (T - T_{ref}) + \frac{1}{2} \alpha_1 (T^2 - T_{ref}^2) - \alpha_2 \left(\frac{1}{T} - \frac{1}{T_{ref}} \right) \right),$$

where *V*₀ represents the unit-cell volume at room temperature, and α₀, α₁, and α₂ are the parameters for the thermal

Fig. 8 Comparison of P – V data of BaSO_4 (a) and SrSO_4 (b) at room temperature with predecessors

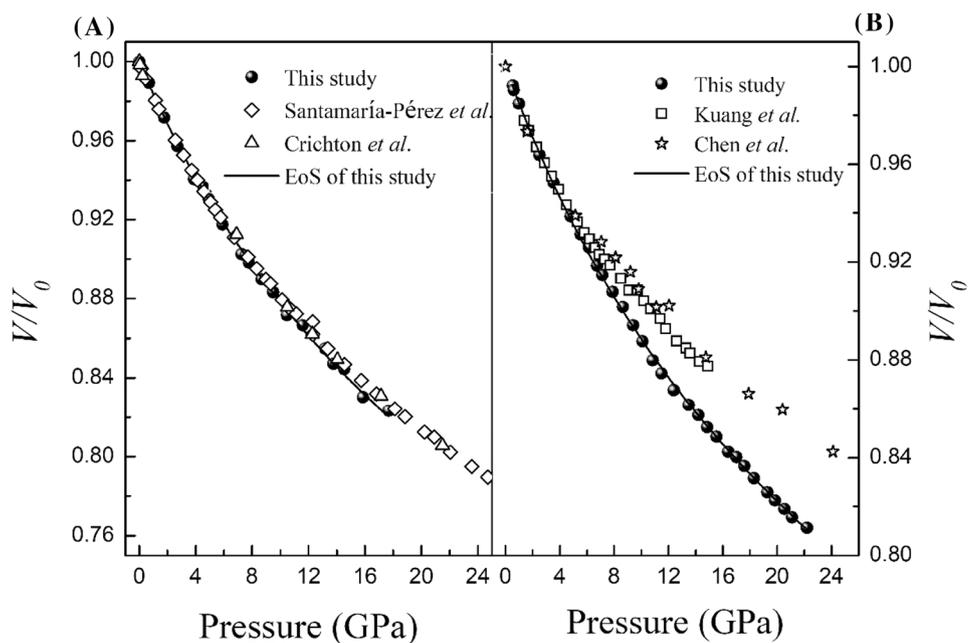
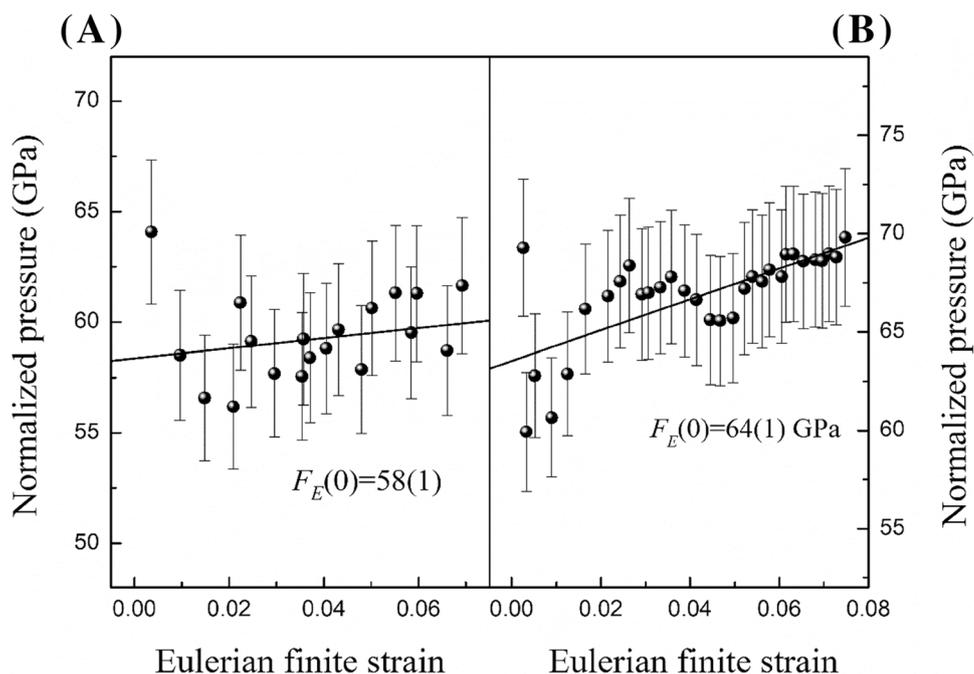


Fig. 9 Eulerian finite strain-normalized pressure (F_E - f_E) plot of BaSO_4 (a) and SrSO_4 (b). The solid lines represent the linear fit through the data



expansion α as a function of temperature $a = a_0 + a_1 T + a_2 T^{-2}$. Considering the limited data at high temperatures, we use the simplified form $a = a_0 + a_1 T$. Using the above equations to fit our high-temperature data with the Eos-Fit program (Gonzalez-Platas et al. 2016), the volumetric thermal expansion coefficients for BaSO_4 and SrSO_4 are $a_V = 2.52(24) \times 10^{-5} + 5.25(54) \times 10^{-8} \times T$, and $a_V = 2.52(24) \times 10^{-5} + 8.48(51) \times 10^{-8} \times T$ within 300–700 K, where the volumetric thermal expansion coefficients at

ambient conditions are $4.091 \times 10^{-5} \text{ K}^{-1}$ for BaSO_4 and $5.061 \times 10^{-5} \text{ K}^{-1}$ for SrSO_4 , respectively (Fig. 11). Simultaneously, the axial thermal expansion coefficients of BaSO_4 along a -, b -, and c -axes are $a_a = 0.66(6) \times 10^{-5} + 1.75(12) \times 10^{-8} \times T$, $a_b = 0.92(10) \times 10^{-5} + 1.50(23) \times 10^{-8} \times T$, and $a_c = 1.25(11) \times 10^{-5} + 1.43(24) \times 10^{-8} \times T$, respectively. At ambient conditions, $a_{a0} = 1.18 \times 10^{-5} \text{ K}^{-1}$, $a_{b0} = 1.36 \times 10^{-5} \text{ K}^{-1}$, and $a_{c0} = 1.67 \times 10^{-5} \text{ K}^{-1}$ for BaSO_4 along a -, b -, and c -axes (Fig. 12a). The obtained

Fig. 10 Pressure dependence of the unit-cell parameters *a*, *b*, and *c* of BaSO₄ (a) and SrSO₄ (b) at room temperature

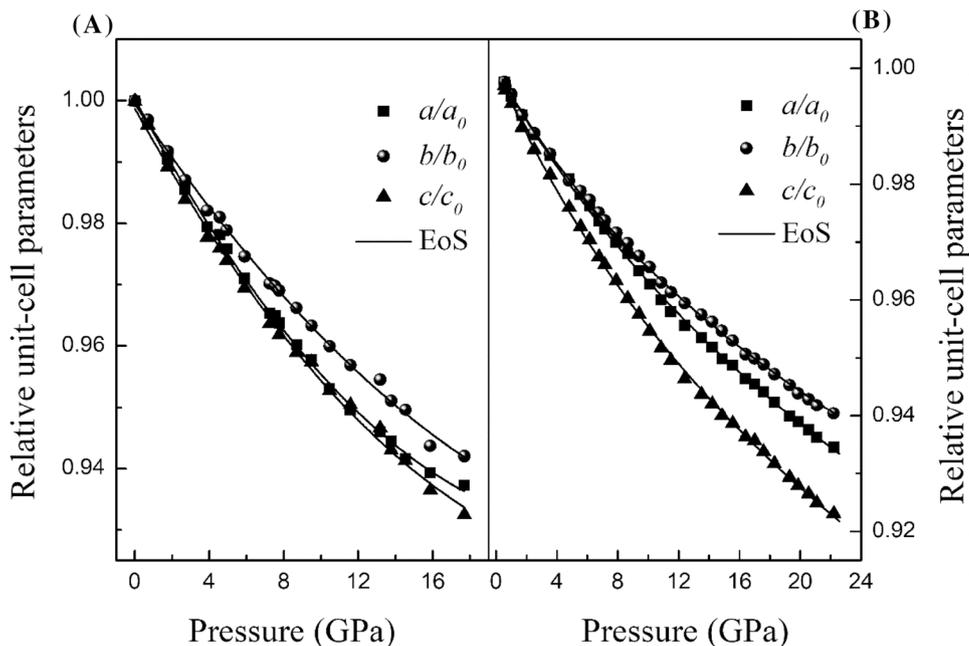


Table 3 Unit-cell parameters in BaSO₄ at high temperature and room pressure

<i>T</i> (K)	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	<i>V</i> (Å ³)
315	7.1449 (1)	8.8683 (3)	5.4501 (1)	345.33 (2)
340	7.1472 (1)	8.8712 (3)	5.4528 (1)	345.73 (1)
370	7.1499 (1)	8.8753 (3)	5.4556 (1)	346.20 (2)
400	7.1526 (1)	8.8785 (3)	5.4585 (1)	346.64 (2)
430	7.1550 (1)	8.8811 (3)	5.4601 (2)	346.95 (2)
460	7.1584 (2)	8.8876 (4)	5.4641 (2)	347.63 (2)
490	7.1624 (2)	8.8907 (4)	5.4665 (2)	348.10 (2)
520	7.1655 (2)	8.8966 (2)	5.4712 (1)	348.78 (2)
550	7.1690 (1)	8.9012 (3)	5.4743 (1)	349.33 (2)
580	7.1720 (1)	8.9056 (4)	5.4771 (2)	349.83 (2)
610	7.1758 (1)	8.9101 (3)	5.4812 (1)	350.45 (2)
640	7.1798 (2)	8.9148 (3)	5.4880 (2)	350.99 (2)
670	7.1838 (1)	8.9207 (4)	5.4883 (2)	351.71 (2)
700	7.1873 (1)	8.9250 (3)	5.4914 (2)	352.25 (2)

Numbers in parenthesis represent standard deviations

axial thermal expansion coefficients of SrSO₄ along *a*-, *b*-, and *c*-axes are $a_a = 1.14 (11) \times 10^{-5} + 1.45 (23) \times 10^{-8} \times T$, $a_b = -0.06 (11) \times 10^{-5} + 5.25 (24) \times 10^{-8} \times T$, and $a_c = 1.49 (15) \times 10^{-5} + 1.63 (31) \times 10^{-8} \times T$, respectively. These values at ambient conditions are $a_{a0} = 1.57 \times 10^{-5} \text{ K}^{-1}$, $a_{b0} = 1.52 \times 10^{-5} \text{ K}^{-1}$, and $a_{c0} = 1.98 \times 10^{-5} \text{ K}^{-1}$ for SrSO₄ along *a*-, *b*-, and *c*-axes (Fig. 12b). The ratios of axial thermal expansion coefficients at 300K of BaSO₄ and SrSO₄ are

Table 4 Unit-cell parameters in SrSO₄ at high temperature and room pressure

<i>T</i> (K)	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	<i>V</i> (Å ³)
320	6.8603 (4)	8.3494 (4)	5.3465 (2)	306.24 (3)
340	6.8625 (4)	8.3527 (4)	5.3481 (2)	306.56 (3)
370	6.8657 (4)	8.3574 (4)	5.3507 (2)	307.02 (3)
400	6.8686 (5)	8.3612 (5)	5.3542 (3)	307.49 (3)
430	6.8718 (5)	8.3672 (2)	5.3573 (2)	308.03 (3)
460	6.8765 (5)	8.3729 (5)	5.3614 (3)	308.69 (3)
490	6.8809 (6)	8.3801 (6)	5.3654 (3)	309.38 (4)
520	6.8838 (6)	8.3863 (6)	5.3688 (3)	309.94 (4)
550	6.8874 (6)	8.3924 (6)	5.3733 (3)	310.58 (4)
580	6.8919 (6)	8.3984 (6)	5.3780 (4)	311.28 (4)
610	6.8974 (6)	8.4062 (6)	5.3821 (3)	312.06 (4)
640	6.9023 (6)	8.4149 (6)	5.3862 (3)	312.84 (4)
670	6.9045 (3)	8.4261 (3)	5.3880 (1)	313.51 (2)
700	6.9090 (2)	8.4329 (2)	5.3929 (1)	314.20 (2)

Numbers in parenthesis represent standard deviations

1.00:1.15:1.42 and 1.03:1.00:1.30, respectively. The axial thermal expansion of BaSO₄ and SrSO₄ is slightly anisotropic, where the *c*-axis of BaSO₄ exhibits a much larger thermal expansion coefficient than those along *a*-, and *b*-axes, but *b*-axis of SrSO₄ has larger thermal expansion coefficient than those along *a*- and *c*-axes. It is worth noting that *c*-axis of BaSO₄ has the most compressibility as well as thermal expansivity.

Fig. 11 T - V data of BaSO_4 (a) and SrSO_4 (b) at ambient pressure

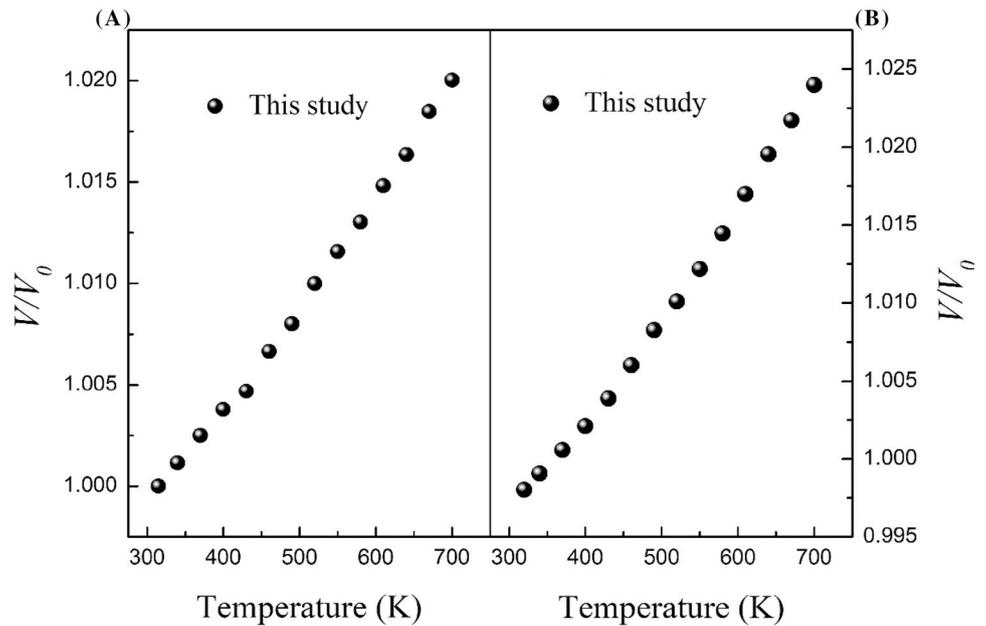
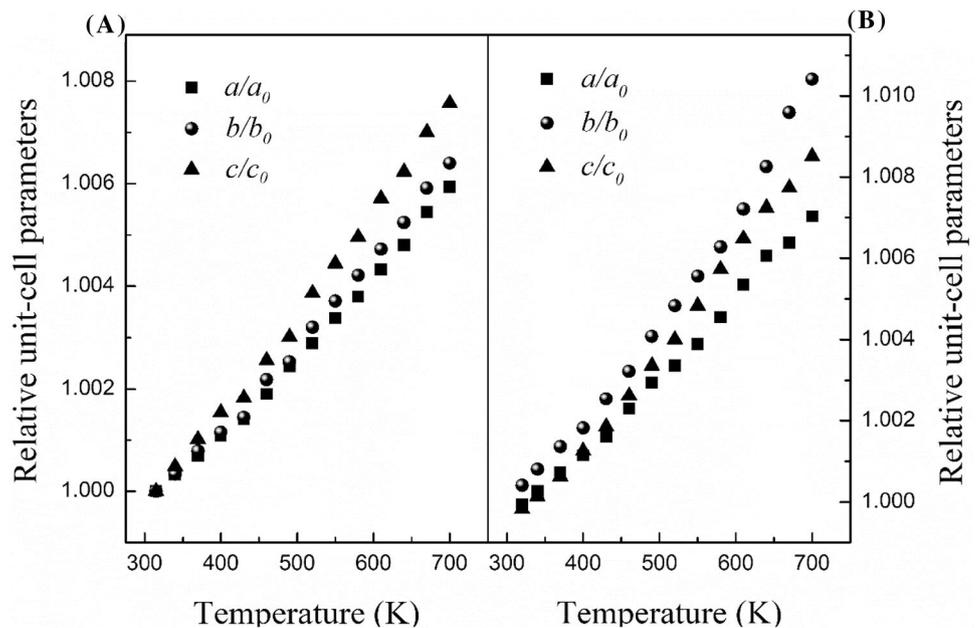


Fig. 12 Temperature dependence of the unit-cell parameters a , b , and c of BaSO_4 (a) and SrSO_4 (b) at ambient pressure



Discussion

Pressure-induced phase transition of barite-group minerals

BaSO_4

Our results confirm that BaSO_4 exists a pressure-induced reversible phase transition from $Pbnm$ to $P2_12_12_1$ at ~ 20.3 GPa. A comparison of our results with the previous results shows that BaSO_4 undergoes a pressure-induced

phase transition, but the phase transition pressure is still inconclusive. Santamaría-Pérez et al. (2011) obtained the phase transition pressures were ~ 17 GPa, ~ 19 GPa, and ~ 27 GPa using different pressure-transmitting mediums (methanol–ethanol mixture, silicone oil, and He, respectively) by synchrotron XRD. Similarly, Lee et al. (2003) also observed a reversible phase transition of BaSO_4 at ~ 10 GPa without any pressure-transmitting medium (Lee et al. 2003). On the contrary, Crichton et al. (2011) have not observed any phase transition of BaSO_4 by XRD and Raman spectroscopy methods up to 21.5 GPa using He as

pressure-transmitting medium. From the above analysis, we can conclude that the hydrostatic environment provided by different pressure-transmitting media can result in the different phase transition pressures of BaSO₄. The better hydrostatic environment may drive the phase transition to occur at higher pressures.

SrSO₄

Until now, it is still controversial about whether SrSO₄ exists the pressure-induced phase transition. Chen et al. (2010) concluded relevant Raman spectroscopy and XRD measurements of SrSO₄ at high pressure. They observed a discontinuity in the slope ($d\nu_1/dp$) of vibration and a disappearance of the (201) diffraction peak at ~11–12 GPa, and they inferred that SrSO₄ exists a pressure-induced phase transition. However, the discontinuity in the slope ($d\nu_1/dp$) of Raman vibration showed in the study of Chen et al. (2010) was not clear. In addition, Chen et al. (2010) used 4:1 methanol–ethanol mixture as a pressure-transmitting medium that could result in relatively low quality of experimental data. Therefore, we estimate that there is not enough evidence to prove that SrSO₄ has undergone a pressure-induced phase transition. Recently, Kuang et al. (2017) conducted the in situ synchrotron XRD measurements of SrSO₄ up to 15 GPa at ambient temperature without observing any phase transition that is consistent with this study. However, the pressure-transmitting medium used in the previous studies were 4:1 methanol–ethanol mixture or 16:3:1 methanol–ethanol–water mixture, which could not maintain a good hydrostatic environment and cause nonhydrostatic stress in the sample chambers at pressures above 10 GPa. Furthermore, by coupling with the spontaneous strain, nonhydrostatic stresses can promote or suppress phase transitions (Decker et al. 1979; Resel et al. 2004), indicating that the previous studies cannot provide an adequate explanation about the structural characteristics of SrSO₄ at high pressures. In this study, neon is chosen as pressure-transmitting medium which provides a better hydrostatic environment in the sample chambers at pressures above 10 GPa. Even so, there is still no pressure-induced transition of SrSO₄ occurred within the pressure range in this study. These results clearly show that the crystal structure of SrSO₄ is stable at least at pressures lower than ~22.2 GPa. Furthermore, the previous studies have not observed any pressure-induced phase transition of PbSO₄ at pressures up to 35 GPa and 21.6 GPa, respectively (Lee et al. 2003; Li et al. 2018). Therefore, for better understanding the phase transition behavior of the barite-group minerals, future further investigations of SrSO₄ and PbSO₄ are highly needed at higher pressure.

Factors on the pressure-induced phase transition

From the above analysis, our results indicate that BaSO₄ undergoes a pressure-induced phase transition from *Pbnm* to *P2₁2₁2₁* at ~20.3 GPa. However, the existing data show no pressure-induced phase transitions of SrSO₄ and PbSO₄ up to 22.2 GPa and 35 GPa, respectively. The bond length may be the most important factor on the phase transition pressure of barite-group minerals. In the crystal structure of barite-group minerals, each M²⁺ coordinates with 12 oxygen atoms, and each S atom is surrounded by four oxygen atoms to form SO₄ tetrahedron (Miyake et al. 1978). The radii of Sr²⁺, Pb²⁺, and Ba²⁺ are 1.44 Å, 1.49 Å, and 1.61 Å, respectively (Shannon 1976). The average <M–O> distance increases with increasing ionic radius, and the corresponding average <M–O> distances for SrSO₄, PbSO₄, and BaSO₄ are 2.827 Å, 2.856 Å, and 2.953 Å (Antao 2012), respectively. Hence, the <Sr–O> distance is the shortest and the <Ba–O> distance is the longest, and the bonding force of <Sr–O> is the strongest, followed by those of <Pb–O> and <Ba–O>. In addition, the corresponding average <S–O> distances are 1.480 Å, 1.477 Å, and 1.471 Å (Miyake et al. 1978). Although the <S–O> distance decreases linearly with increasing cation ionic radius, the magnitude of the <S–O> distance variation is smaller than that of <M–O> distance variation, and the average of <S–O–S> angles of three barite-group minerals are nearly constant (109.5° for SrSO₄, 109.4° for PbSO₄, and 109.46° for BaSO₄). Therefore, <S–O> distances and <S–O–S> angles are less insensitive to pressure increase than that of <M–O> distances in the structure. When SrSO₄ is compressed, it needs to overcome more energy of <Sr–O> to convert into another more stable structure. Consequently, SrSO₄ may undergo a phase transition at a relatively higher pressure. The conjecture is consistent with the existing experimental results, where the phase transition pressure of BaSO₄ is ~20.3 GPa using neon as pressure-transmitting medium and the phase transition pressure of PbSO₄ is higher than ~35 GPa. However, the phase transition pressure of SrSO₄ may be even higher than that of PbSO₄. Therefore, among BaSO₄, PbSO₄, and SrSO₄, SrSO₄ has the highest phase transition pressure, and then, PbSO₄, and BaSO₄ has the lowest phase transition pressure.

Thermoelastic of barite-group minerals

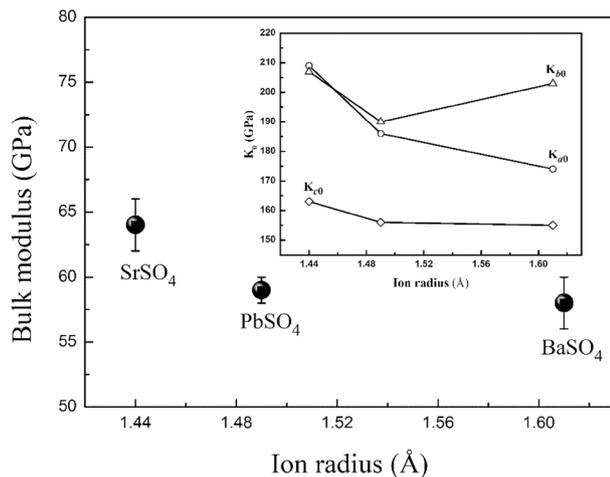
Bulk modulus

The bulk moduli and their pressure derivatives of BaSO₄ and SrSO₄ in this study are 58 (2) GPa, 4.2 (2) and 64 (2) GPa, 4.8 (4), respectively. The bulk moduli of barite-group minerals under different pressure-transmitting media are summarized in Table 5 and the variation of bulk modulus with

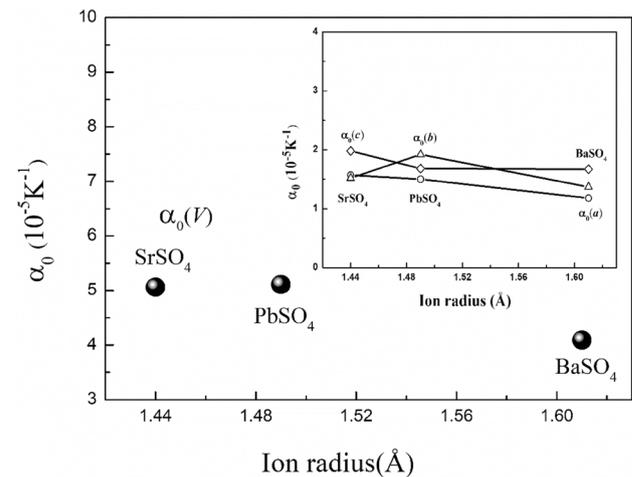
Table 5 Elastic parameters of barite-group minerals

Samples	K_0 (GPa)	K'_0	References
Barite (He)	58.6 (2)	4.82 (4)	Santamaría-Pérez et al. (2011)
Barite (Silicone oil)	62 (1)	7.3 (4)	Santamaría-Pérez et al. (2011)
Barite (M:E = 4:1)	60.3 (9)	6.3 (2)	Santamaría-Pérez et al. (2011)
Barite (Theory)	62 (2)	4.5 (3)	Santamaría-Pérez et al. (2011)
Barite (No medium)	63 (2)	4 (fixed)	Lee et al. (2003)
Barite (He)	58.5 (20)	4.9 (3)	Crichton et al. (2011)
Barite (Neon)	58 (2)	4.2 (4)	This study
Barite (Neon)	60 (1)	4 (fixed)	This study
Celestite (Neon)	64 (2)	4.8 (4)	This study
Celestite (Neon)	68 (1)	4 (fixed)	This study
Celestite (M:E = 4:1)	87 (3)	4 (fixed)	Chen et al. (2010)
Celestite (M:E:W = 16:3:1)	62 (5)	11 (1)	Kuang et al. (2017)
Celestite (M:E:W = 16:3:1)	98 (2)	4 (fixed)	Kuang et al. (2017)
Anglesite (Neon)	59 (1)	5.3 (4)	Li et al. (2018)
Anglesite (Neon)	63.8 (7)	4 (fixed)	Li et al. (2018)

Numbers in parenthesis represent standard deviations

**Fig. 13** Variations of the bulk modulus and linear modulus of barite-group minerals against ionic radius

effective size of ionic radius is shown in Fig. 13. Considering that neon can maintain a good hydrostatic environment, we chose the bulk moduli of BaSO₄ and SrSO₄ obtained in this study and the bulk modulus of PbSO₄ obtained by Li et al. (2018) for comparison. From Fig. 13, the bulk modulus of SrSO₄ is slightly higher than those of BaSO₄ and PbSO₄, where their bulk moduli are almost equal each other. In fact, the influencing factors on the compressibility of minerals are many and complicated. The effective size of M²⁺ cation, the bond length, the polarizability of the M element, the electronegativity, and the chemical valence are believed to be the factors on the compressibility of barite-group minerals (Zhang 1999; Liu et al. 2008; Fan et al. 2011, 2013; Li et al. 2018). The factors affecting the compressibility of

**Fig. 14** Variation of the linear and volume thermal expansion coefficients of barite-group minerals with ion radius

barite-group minerals have been summarized by Li et al. (2018). In the light of the complexity of its impact, we believe that both geometrical and chemical factors actually influence the compressibility of barite-group minerals.

Volumetric thermal expansion

The volumetric thermal expansion coefficients at 300 K of BaSO₄ and SrSO₄ obtained in this study are $4.09 \times 10^{-5} \text{K}^{-1}$ and $5.06 \times 10^{-5} \text{K}^{-1}$, respectively (Fig. 11). However, among the previous studies, only Fei (1995) recalculated the volumetric thermal expansion coefficient of BaSO₄ based on the data obtained from Sawada and Takéuchi (1990) and yielded $\alpha_V = 5.48 \times 10^{-5} \text{K}^{-1}$, which is inconsistent with this

study. Meanwhile, there are still no reports about the volumetric thermal expansion of SrSO₄. In addition, Li et al. (2018) also reported the volumetric thermal expansion coefficient of PbSO₄ at high temperatures. However, to ensure the reliability of comparison, we recalculate the volumetric thermal expansion coefficients of PbSO₄ using the data from Li et al. (2018) based on the expression proposed by Fei (1995) and obtain the $\alpha_v = 5.11 \times 10^{-5} \text{ K}^{-1}$. Figure 14 shows the relationship between the volumetric thermal expansion coefficients and the effective size of ionic radius of barite-group minerals, which suggests that the volumetric thermal expansion coefficients seem to be decreasing within increasing ionic radius. The effective ionic radii of Sr²⁺, Pb²⁺, and Ba²⁺ are 1.44 Å, 1.49 Å, and 1.61 Å, respectively (Shannon 1976) and the corresponding average <M–O> distances for SrSO₄, PbSO₄, and BaSO₄ are 2.827 Å, 2.856 Å, and 2.953 Å (Antao 2012). Therefore, we infer that bond length may be a major factor affecting the volumetric thermal expansion of barite-group minerals.

Axial compressibility

The axial compressibility of BaSO₄ and SrSO₄ is also obtained in this study (Table 6). The variations of lattice parameters *a*, *b*, and *c* of BaSO₄ and SrSO₄ with pressure are shown in Fig. 10. These results clearly indicate that there is a different axial compression anisotropy between BaSO₄ and SrSO₄. The *b*-axis in both BaSO₄ and SrSO₄ is the most incompressible, and the axial compressibility of BaSO₄ along *a*- and *c*-axes is almost equivalent, but the axial compressibility of SrSO₄ along *c*-axis is higher than *a*-axis. Moreover, the minimal axial compressibility of all three barite-group minerals (SrSO₄, BaSO₄, and PbSO₄) is along the *b*-axis (Table 6). This phenomenon may be

caused by the different bonding distances between M and SO₄ among the three crystallographic axes. The *b*-axis is the longest crystallographic axis in the barite-group minerals, but the distance between M and SO₄ is minimal, and then results in the maximum bonding force between M and SO₄. Therefore, when external force like pressure is applied to these minerals, the *b*-axis reflects the minimum axial compressibility.

In addition, Fig. 13 shows a comparison of the relationship between axial compressibility and ionic radius among the barite-group minerals. The axial moduli of *a*-axis and *c*-axis for the barite-group minerals decrease with increasing ionic radius; however, the variation tendency of *b*-axis with ionic radius is different, where the *b*-axis of PbSO₄ is the least compared with SrSO₄ and BaSO₄.

Axial thermal expansion

The axial thermal expansion coefficients of BaSO₄ and SrSO₄ at ambient conditions are also obtained in this study, $1.18 \times 10^{-5} \text{ K}^{-1}$, $1.37 \times 10^{-5} \text{ K}^{-1}$, $1.67 \times 10^{-5} \text{ K}^{-1}$ and $1.57 \times 10^{-5} \text{ K}^{-1}$, $1.52 \times 10^{-5} \text{ K}^{-1}$, $1.98 \times 10^{-5} \text{ K}^{-1}$ along *a*-, *b*-, and *c*-axes, respectively. Moreover, we also calculate the axial thermal expansion coefficients of BaSO₄ using the data of Sawada and Takéuchi (1990) as well and obtain $\alpha_a = 1.39 \times 10^{-5} \text{ K}^{-1}$, $\alpha_b = 1.09 \times 10^{-5} \text{ K}^{-1}$, and $\alpha_c = 2.49 \times 10^{-5} \text{ K}^{-1}$ at ambient conditions, which are inconsistent with this study. Too large temperature interval and too few data points in the previous work may cause the difference. From Fig. 12, we conclude that the axial thermal expansion of BaSO₄ and SrSO₄ is slightly anisotropic. The axial thermal expansion along *c*-axis of BaSO₄ exhibits larger than those along *a*- and *b*-axes, but the *b*-axis of SrSO₄ has larger thermal expansion coefficient than those along *a*- and *b*-axes. Moreover, the compressibility and thermal expansion coefficient of BaSO₄ along *c*-axis are both largest, which is consistent with the result of Lee et al. (2003).

In addition, Table 7 summarizes the axial thermal expansivities of the barite-group minerals and Fig. 14 shows the variation of axial thermal expansion at 300 K with ionic radius. Obviously, the variation of the axial thermal expansions with ionic radius of these three barite-group minerals is different. The axial thermal expansion along *a*-axis of SrSO₄ and PbSO₄ is similar, but both of them are larger than that of BaSO₄. In addition, the axial thermal expansion along *b*-axis of PbSO₄ is also larger than that of SrSO₄ and BaSO₄. Moreover, the axial thermal expansion along *c*-axis of BaSO₄ and PbSO₄ is almost identical and smaller than that of SrSO₄. In a word, the axial thermal expansion of barite minerals is insensitive to ionic radius and there is no good correlation between the axial thermal expansion behavior and the axial compressibility of the barite-group minerals.

Table 6 Axial compressibility moduli along *l*-axial (*l*=*a*, *b*, *c*) of barite-group minerals at room temperature

	<i>l</i> ₀ (Å)	<i>K</i> ₀ (GPa)	<i>K</i> ₀ '	References
Celestite				
<i>a</i>	6.864 (1)	209 (7)	13 (1)	This study
<i>b</i>	8.358 (1)	207 (7)	18 (2)	
<i>c</i>	5.348 (1)	163 (4)	13 (1)	
Barite				
<i>a</i>	7.1375 (2)	174 (5)	11 (1)	This study
<i>b</i>	8.8661 (4)	203 (5)	12 (1)	
<i>c</i>	5.4388 (3)	155 (4)	14 (1)	
Anglesite				
<i>a</i>	6.9493 (3)	186 (4)	13 (1)	Li et al. (2018)
<i>b</i>	8.4681 (4)	190 (5)	17 (1)	
<i>c</i>	5.3931 (2)	156 (4)	17 (1)	

Numbers in parenthesis represent standard deviations

Table 7 Axial thermal expansivities along *l*-axial (*l* = *a*, *b*, *c*) of barite-group minerals at ambient pressure

	l_0	$\text{alph}_0 (\times 10^5)$	$\text{alph}_1 (\times 10^4)$	$\text{Alpha} (\times 10^5)$	References
Celestite					
<i>a</i>	6.858 (1)	1.14 (11)	1.45 (23)	1.57	This study
<i>b</i>	8.347 (1)	−0.06 (11)	5.25 (24)	1.52	
<i>c</i>	5.343 (1)	1.49 (15)	1.63 (31)	1.98	
<i>V</i>	305.85 (4)	2.52 (24)	8.48 (51)	5.06	
Barite					
<i>a</i>	7.143 (1)	0.66 (6)	1.75 (12)	1.18	This study
<i>b</i>	8.866 (1)	0.92 (10)	1.50 (23)	1.37	
<i>c</i>	5.447 (1)	1.25 (11)	1.43 (24)	1.67	
<i>V</i>	345.10 (5)	2.52 (25)	5.25 (54)	4.09	
Anglesite					
<i>a</i>	6.948 (1)	1.31 (5)	0.63 (11)	1.50	Li et al. (2018)
<i>b</i>	8.468 (1)	1.15 (6)	2.60 (14)	1.92	
<i>c</i>	5.391 (1)	1.34 (8)	1.13 (19)	1.68	
<i>V</i>	317.20 (2)	3.82 (15)	4.31 (33)	5.11	

Numbers in parenthesis represent standard deviations

Conclusion

The phase transition and thermoelastic behavior of BaSO₄ and SrSO₄ have been investigated in the *P*–*T* range of 59.5 GPa, 700 K and 22.2 GPa, 700 K, respectively, using in situ synchrotron XRD combined with DACs. Our results confirm that BaSO₄ undergoes a pressure-induced phase transition at ~20.3 GPa from *Pbnm* to *P2₁2₁2₁*, but SrSO₄ does not in the *P*–*T* ranges. The bulk moduli and their pressure derivatives of BaSO₄ and SrSO₄ are derived from the *P*–*V* data. While their volumetric thermal expansion coefficients are derived from the *T*–*V* data. Our results show that SrSO₄ has anisotropic axial compressibility and axial thermal expansivity, but BaSO₄ has almost the same axial compressibility along *a*-axis and *c*-axis and relatively weak axial thermal expansivity. Furthermore, the influencing factors on the phase transition pressure of barite-group minerals are also discussed. The bond length of <M–O> may be the main factor which results in the maximum phase transition pressure of SrSO₄, compared with PbSO₄ and BaSO₄. Our results also show that geometrical and chemical factors influence the compressibility of barite-group minerals together and bond length may be the major factor affecting the volumetric thermal expansion of barite-group minerals. In addition, there is no good correlation between the axial thermal expansion behavior and the axial compressibility of the barite-group minerals.

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References

- Angel RJ (2000) Equations of state. *Rev Miner Geochem* 41:35–59. <https://doi.org/10.2138/rmg.2000.41.2>
- Antao SM (2012) Structural trends for celestite (SrSO₄), anglesite (PbSO₄), and barite (BaSO₄): confirmation of expected variations within the SO₄ groups. *Am Miner* 97:661–665. <https://doi.org/10.2138/am.2012.3905>
- Birch F (1947) Finite elastic strain of cubic crystals. *Phys Rev* 71:809–824. <https://doi.org/10.1103/PhysRev.71.809>
- Borg IY, Smith DK (1975) A high pressure polymorph of CaSO₄. *Contrib Miner Petrol* 50:127–133. <https://doi.org/10.1007/BF00373332>
- Canil D, Fellows SA (2017) Sulphide–sulphate stability and melting in subducted sediment and its role in arc mantle redox and chalcophile cycling in space and time. *Earth Planet Sci Lett* 470:73–86. <https://doi.org/10.1016/j.epsl.2017.04.028>
- Chen YH, Yu SC, Huang E, Lee PL (2010) Raman spectroscopy and X-ray diffraction studies on celestite. *Phys B Condens Matter* 405:4386–4388. <https://doi.org/10.1016/j.physb.2010.08.001>
- Crichton WA, Parise JB, Antao SM, Grzechnik A (2005) Evidence for monazite-, barite-, and AgMnO₄ (distorted barite)-type structures of CaSO₄ at high pressure and temperature. *Am Miner* 90:22–27. <https://doi.org/10.2138/am.2005.1654>
- Crichton WA, Merlini M, Hanfland M, Muller H (2011) The crystal structure of barite, BaSO₄, at high pressure. *Am Miner* 96:364–367. <https://doi.org/10.2138/am.2011.3656>
- Decker DL, Petersen S, Debray D, Lambert M (1979) Pressure-induced ferroelastic phase transition in Pb₃(PO₄)₂: a neutron-diffraction

- study. *Phys Rev B* 19:3552–3555. <https://doi.org/10.1103/PhysRevB.19.3552>
- Evans KA (2012) The redox budget of subduction zones. *Earth Sci Rev* 113:11–32. <https://doi.org/10.1016/j.earscirev.2012.03.003>
- Fan D, Zhou W, Wei S et al (2010) A simple external resistance heating diamond anvil cell and its application for synchrotron radiation X-ray diffraction. *Rev Sci Instrum* 81:053903. <https://doi.org/10.1063/1.3430069>
- Fan D, Wei S, Liu J et al (2011) High pressure X-Ray diffraction study of a grossular—andalusite solid solution and the bulk modulus variation along this solid solution. *Chin Phys Lett* 28:076101. <https://doi.org/10.1088/0256-307X/28/7/076101>
- Fan D, Ma M, Wei S et al (2013) In-situ synchrotron powder X-ray diffraction study of vanadinite at room temperature and high pressure. *High Temp High Press* 42:441–449
- Fan D, Xu J, Liu J et al (2014) Thermal equation of state of natural stibnite up to 25.7. *High Temp High Press* 43:351–359
- Fan D, Xu J, Kuang Y et al (2015) Compressibility and equation of state of beryl ($\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$) by using a diamond anvil cell and in situ synchrotron X-ray diffraction. *Phys Chem Miner* 42:529–539. <https://doi.org/10.1007/s00269-015-0741-1>
- Fei Y (1995) Thermal expansion. In: Ahrens TJ (ed) *Mineral physics & crystallography: a handbook of physical constants*. American Geophysical Union, Washington, DC, pp 29–44
- Fei Y, Ricolleau A, Frank M et al (2007) Toward an internally consistent pressure scale. *Proc Natl Acad Sci* 104:9182–9186. <https://doi.org/10.1073/pnas.0609013104>
- Fujii T, Ohfuji H, Inoue T (2016) Phase relation of CaSO_4 at high pressure and temperature up to 90 GPa and 2300 K. *Phys Chem Miner* 43:353–361. <https://doi.org/10.1007/s00269-016-0799-4>
- Garske D, Peacor DR (1965) Refinement of the structure of celestine SrSO_4 *. *Zeitschrift für Krist* 121:204–210. <https://doi.org/10.1524/zkri.1965.121.2-4.204>
- Gonzalez-Platas J, Alvaro M, Nestola F, Angel R (2016) EosFit7-GUI: a new graphical user interface for equation of state calculations, analyses and teaching. *J Appl Crystallogr* 49:1377–1382. <https://doi.org/10.1107/S1600576716008050>
- Gracia L, Beltrán A, Errandonea D, Andrés J (2012) CaSO_4 and its pressure-induced phase transitions. A density functional theory study. *Inorg Chem* 51:1751–1759. <https://doi.org/10.1021/ic202056b>
- Hammersley AP, Svensson SO, Hanfland M et al (1996) Two-dimensional detector software: from real detector to idealised image or two-theta scan. *High Press Res* 14:235–248. <https://doi.org/10.1080/08957959608201408>
- Hemley RJ, Zha CS, Jephcoat AP et al (1989) X-ray diffraction and equation of state of solid neon to 110 GPa. *Phys Rev B* 39:11820–11827. <https://doi.org/10.1103/PhysRevB.39.11820>
- Jégo S, Dasgupta R (2013) Fluid-present melting of sulfide-bearing ocean-crust: experimental constraints on the transport of sulfur from subducting slab to mantle wedge. *Geochim Cosmochim Acta* 110:106–134. <https://doi.org/10.1016/j.gca.2013.02.011>
- Jégo S, Dasgupta R (2014) The fate of sulfur during fluid-present melting of subducting basaltic crust at variable oxygen fugacity. *J Petrol* 55:1019–1050. <https://doi.org/10.1093/petrology/egu016>
- Kelley KA, Cottrell E (2009) Water and the oxidation state of subduction zone magmas. *Science* 325:605–607. <https://doi.org/10.1126/science.1174156>
- Kuang Y, Kuang J, Zhao D et al (2017) The high-pressure elastic properties of celestine and the high pressure behavior of barite-type sulphates. *High Temp High Press* 46:481–495
- Larson AC, Von Dreele RB (2004) General structure analysis system (GSAS). Los Alamos Natl Lab LAUR 86–748:1–179
- Le Bail A, Duroy H, Fourquet JL (1988) Ab-initio structure determination of LiSbWO_6 by X-ray powder diffraction. *Mater Res Bull* 23:447–452. [https://doi.org/10.1016/0025-5408\(88\)90019-0](https://doi.org/10.1016/0025-5408(88)90019-0)
- Lee PL, Huang E, Yu SC (2003) High-pressure Raman and X-ray studies of barite, BaSO_4 . *High Press Res* 23:439–450. <https://doi.org/10.1080/0895795031000115439>
- Lee PL, Huang E, Yu SC, Chen YH (2013) High-pressure raman study on anglesite. *World J Condens Matter Phys* 03:28–32. <https://doi.org/10.4236/wjcmp.2013.31005>
- Li B, Xu J, Chen W et al (2018) Compressibility and expansivity of anglesite (PbSO_4) using in situ synchrotron X-ray diffraction at high-pressure and high-temperature conditions. *Phys Chem Miner* 45:883–893. <https://doi.org/10.1007/s00269-018-0970-1>
- Liu X, Shieh SR, Fleet ME, Akhmetov A (2008) High-pressure study on lead fluorapatite. *Am Miner* 93:1581–1584. <https://doi.org/10.2138/am.2008.2816>
- Miyake M, Minato I, Morikawa H, Iwai S (1978) Crystal structures and sulphate force constants of barite, celestite, and anglesite. *Am Miner* 63:506–510
- Mungall JE (2002) Roasting the mantle: Slab melting and the genesis of major Au and Au-rich Cu deposits. *Geology* 30:915. [https://doi.org/10.1130/0091-7613\(2002\)030%3C0915:RTMSMA%3E2.0.CO;2](https://doi.org/10.1130/0091-7613(2002)030%3C0915:RTMSMA%3E2.0.CO;2)
- Resel R, Oehzelt M, Shimizu K et al (2004) On the phase-transition in anthracene induced by high pressure. *Solid State Commun* 129:103–106. <https://doi.org/10.1016/j.ssc.2003.09.019>
- Richards JP (2011) Magmatic to hydrothermal metal fluxes in convergent and collided margins. *Ore Geol Rev* 40:1–26. <https://doi.org/10.1016/j.oregeorev.2011.05.006>
- Santamaría-Pérez D, Gracia L, Garbarino G et al (2011) High-pressure study of the behavior of mineral barite by X-ray diffraction. *Phys Rev B* 84:054102. <https://doi.org/10.1103/PhysRevB.84.054102>
- Sawada H, Takéuchi Y (1990) The crystal structure of barite, $\beta\text{-BaSO}_4$, at high temperatures. *Zeitschrift für Krist Cryst Mater* 191:161–171. <https://doi.org/10.1524/zkri.1990.191.3-4.161>
- Shannon RD (1976) Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallogr Sect A* 32:751–767. <https://doi.org/10.1107/S0567739476001551>
- Tomkins AG, Evans KA (2015) Separate zones of sulfate and sulfide release from subducted mafic oceanic crust. *Earth Planet Sci Lett* 428:73–83. <https://doi.org/10.1016/j.epsl.2015.07.028>
- Wang J, Bass JD, Kastura T (2014) Elastic properties of iron-bearing wadsleyite to 17.7 GPa: Implications for mantle mineral models. *Phys Earth Planet Inter* 228:92–96. <https://doi.org/10.1016/j.pepi.2014.01.015>
- Xia X, Weidner DJ, Zhao H (1998) Equation of state of brucite; single-crystal Brillouin spectroscopy study and polycrystalline pressure-volume-temperature measurement. *Am Miner* 83:68–74. <https://doi.org/10.2138/am-1998-1-207>
- Zhang J (1999) Room-temperature compressibilities of MnO and CdO: further examination of the role of cation type in bulk modulus systematics. *Phys Chem Miner* 26:644–648. <https://doi.org/10.1007/s002690050229>
- Zhang J (2009) High-pressure Raman and X-ray studies of barite, BaSO_4 . *High Press Res* 23:439–450. <https://doi.org/10.1080/0895795031000115439>