The Phase Transition of Calcium Sulfide Under High Pressure

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Abstract. We carried out the accurate in situ angle derisive x-ray diffraction experiments and the electrical resistivity in CaS under high pressure. The result shows the pressure-induced phase transition of CaS from Na Cl-type structure (the space group Fm3m, phase I) to Cs Cl-type structure (the space group Pm3m, phase II) is reversible and the transition point is around 40.0 GPa; in the meantime, the electrical resistivity and light permeability decrease as the pressure increases and occur obvious discontinuities at the corresponding phase transition point; the result of the first-principles calculations is in concordance with the measurement results.

1. Introduction
Calcium sulphide (CaS) is an important binary alkaline earth metal compound semiconductor crystallizing into typical face-centered cubic structure (Na Cl-type structure)[1] as shown in Figure 1(a) and (b). In the crystal structure of CaS, the octahedron complementary to every six Ca^{2+} ions surround one S^{2−}, and every six S^{2−} ions surrounds one Ca^{2+} ion. Calcium sulphide, with doping rare earth elements, has excellent luminescent properties and has been investigated and applied widely[2-4]. After the phase transition under high pressure, the crystal of calcium sulfate is transformed to a Cs Cl-type structure. Figure 1a,b show the structure of CaS before and after phase transition, respectively.

![Figure 1](image-url)

Figure 1. (a) the space group Fm3m of CaS (Na Cl-type structure, phase), (b) the space group Pm3m of CaS (Cs Cl-type structure, phase II), (c) The comparison diagram of XRD diffraction spectra of CaS at 2.0 GPa and JCPDS 65-7852.
CaS is an insulator with the band gap range from 2.5 to 4.5 eV at ambient pressure which has a feature in electric band structure is that there exist no d electrons in the valance band. Previously reported studies mainly focused on preparation or optimizing the performance of CaS at ambient pressure, but few reports involve on the structure and electronic characteristics under high pressure, an effective approach to tune the physical properties of materials. Recently published X-ray diffraction (XRD) studies on CaS demonstrated that phase Fm3m transformed to phase Pm3m to at 40.0 GPa.[3, 5] But Z.J.Chen forecaster that the Na Cl-type structure of CaS transformed to Cs Cl-type structure at 36.5 GPa by a method based on plane-wave potentiality density functional theory[4, 6-7]. There are some different between the results of theoretical and experimental. In the meantime, the structure transition under compression is often accompanied by the changing of physical properties. Therefore, it makes most sense to study physical characteristics of CaS under high pressure.

In this paper, by combing the XRD, the electrical resistivity measurements, the light permeability measurements and the first-principles calculations, we conducted a comprehensive study on the structural, electrical transport and optical characteristics of CaS powders under compression.

2. Experiments and Theoretical Calculation
The sample was powder CaS (99.999%, from Alfa Aesar Company). Figure 1(c) shows the structure of obtained sample matches well with previous publication (JCPDS 65-7852). A diamond anvil cell (DAC) was used, generating high pressure with the per-indented rhenum as the gasket. The pressure transmitting medium consists of a liquid mixture of CH3OH, C2H5OH and H2O (16:3:1). Pressure calibration was conducted by use of the wave number shift of the R1 line of a ruby (~5 μm)[5,8]. One-dimensional strength versus diffraction angle 2θ patterns was obtained by integrating Bragg diffraction images with FIT2D software [6, 9]. The XRD pattern obtained from the experiment was refined by using the software package of GSAS.

By using angular dispersion source (λ = 0.6199 Å), In situ high-pressure XRD experiments were conducted at beam line 15U1 of Shanghai Synchrotron Radiation Facility (SSRF) and beam line 4W2 of Beijing Synchrotron Radiation Facility (BSRF).

By using the Van der Pauw method, the electrical resistivity was measured by a four-electrode microcircuit.[7, 10, 11] The insulation method between gasket and film electrode and the fabrication of thin film microcircuit used in this experiment is consistent with the method reported previously.[8 12-14] A Keithley 2400 Source Meter provided the measuring current, generally 100mA, a Keithley 2700 multi meter measuring the voltage. A Keithley Kusb-488 interface adapter and a general purpose interface bus were utilized to connect all instruments with a computer. On the basis of the Van der Pauw method, the measurement process was automatically performed.

3. Results and Discussion
3.1. In Situ High-pressure XRD Measurements.
The high-pressure XRD experiments on CaS powders up to 50.2 GPa were firstly conducted to compare with previous studies conveniently. Figures2 (a) and (b) display the XRD patterns of CaS at compress and decompress processes, respectively. In the compression process, all diffraction peaks were moving to relatively large angles with increasing pressure, and the strength of the diffraction peaks was growing smaller. This trend indicates that the inter-planar spacing decreases with the pressure increases, and also that the crystal structure becomes denser under pressure. In this figure, the angle of the (400) diffraction peak exceeds the maximum measurement range of the experiment under a pressure of 21 GPa, and the (300) diffraction peak weakens with the pressure increases, but it always exists until a maximum pressure is reached. At 40.5 GPa, a new peak phaseII (110) appeared at 2θ=16.2°, which indicated that CaS began to transit from phase Fm3m to phase Pm3m. Under continuous pressure, both phasesI and phaseIIcoexist, but the phaseII completely transformed into the phaseIIat 45.5 GPa. After this point, there was no phase transition observed until the pressure increased to 50.2 GPa. Under decompression, starting with the maximum pressure 50.2 GPa, there was
no significant change in the diffraction spectra of CaS, as shown in Figure 2(b). After the pressure was reduced to 34.9 GPa, the diffraction maximum at (110) of phase II disappeared, which indicated a return to the Na Cl-type structure. The disappearing (400) diffraction peak of the phase II in the compression process returns to its original position when the pressure is decreased continuously to 0.3 GPa (approximately atmospheric pressure). Thus, we confirm that the phase transition of CaS under high pressure from phase I to phase II is reversible. Comparing to the compression curve, the decompression curve has an approximately 5.0 GPa hysteresis effect. This is because the symmetry of the crystal structure of CaS suffered some damage in the compression process. So CaS must overcome a barrier, if it wants to revert back to the original structure. Through the above analysis, the conclusions of the previous experiment are verified using a high-pressure XRD experiment. Specifically, it is observed that the phase transition of CaS from phase I to phase II is reversible, with the phase transition occurring around 40.0 GPa.

Figure 2. XRD diffraction spectra of CaS at a few representative pressures, (a) compress process, (b) decompress process.

3.2. In-situ Resistivity Measurement Under High Pressure

Figure 3 shows that during the compression, the pressure dependence of the electrical resistivity at room temperature. In the initial state, CaS has a very high resistance value greater than $1 \times 10^{11} \Omega$ and hence is demonstrated characteristics of an insulator. As the pressure increased, the resistance value of CaS declined slowly. Around 40.0 GPa, an abrupt resistivity decrease was observed, which reflects the structural transition from the phase I (Na Cl-type) to the phase II (Cs Cl-type). At this point, the stability in the energy band of CaS with Na Cl-structure was destroyed, and the band gap began to shrink. The phase transition of CaS from the six-coordinate structure (Na Cl-type) to the eight-coordinate structure (Cs Cl-type) was achieved when the pressure increased to 51.1 GPa. After that, the resistance value was reduced almost seven orders of magnitude compared to the previous phase change. In addition, during the decompression process we also detected what has changed in electrical transport properties of CaS, where the resistance values rose to the previous values when the pressure fell to 34.1 GPa from the maximum pressure 51.1 GPa. This illustrates once again that the phase transition is reversible.

4. Conclusions

In the present study, the in situ angle disperse x-ray diffraction experiments have been performed, the electrical resistivity measurements in CaS under high pressure. The data from these two methods are consistent with each other. The results of the two methods above confirmed that the pressure-induced phase transition of CaS from Fm3m (phase I) structure to a Pm3m (phase II) structure is reversible, and that the phase transition pressure of CaS transforming from phase I to phase II is around 40.0 GPa. In our electrical resistivity measurement experiment, the electrical resistivity of CaS decrease with the...
pressure increases. After the phase transition, the reduction of the electrical resistivity is exacerbated. These data provide some reference for future applications under high pressure.

Figure 3. Measurement results of CaS electrical resistivity at room temperature under high pressure.

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