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P–V–T equation of state of molybdenite (MoS_2) by a diamond anvil cell and *in situ* synchrotron angle-dispersive X-ray diffraction

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ABSTRACT

The pressure–volume–temperature (P–V–T) equation of state (EoS) of a natural molybdenite (MoS_2) has been measured at high temperature up to 700 K and high pressures up to 18.26 GPa, by using *in situ* angle-dispersive X-ray diffraction and diamond anvil cell. Analysis of room-temperature P–V data to a third-order Birch–Murnaghan EoS yields: $V_0 = 107.0 \pm 0.1$ Å^3, $K_0 = 67 \pm 2$ GPa and $K'_0 = 5.0 \pm 0.3$. With K'_0 fixed to 4.0, we obtained: $V_0 = 106.7 \pm 0.1$ Å^3 and $K_0 = 74.5 \pm 0.8$ GPa. Fitting of our P–V–T data by means of the high-temperature third order Birch–Murnaghan equations of state, gives the thermoelastic parameters: $V_0 = 107.0 \pm 0.1$ Å^3, $K_0 = 69 \pm 2$ GPa, $K'_0 = 4.7 \pm 0.2$, $(\partial K/\partial T)_P = -0.021 \pm 0.003$ GPa K^{-1}, $a = (2.2 \pm 0.7) \times 10^{-5}$ K^{-1} and $b = (2.9 \pm 0.8) \times 10^{-8}$ K^{-2}. The temperature derivative of the bulk modulus and thermal expansion coefficient of MoS_2 are obtained for the first time. Present results are also compared with previously studies determined the elastic properties of MoS_2 and WS_2.

1. Introduction

Molybdenite is a mineral of molybdenum disulfide, MoS_2. It is the essential ore mineral of the molybdenum industry for the production of molybdenum, ferromolybdenum and pure chemical molybdenum compounds, mainly molybdenum trioxide, ammonium paramolybdate, and sodium and calcium molybdate [1–3]. In addition, the transition-metal dichalcogenide semiconductor MoS_2 has attracted great interest because of its distinctive electronic, optical, and catalytic properties, as well as its importance for dry lubrication [4–9]. Monolayer molybdenite shows good charge carrier mobility and can be used to create small or low-voltage transistors possibly more easily than using graphene [10]. Furthermore, recent studies show that MoS_2 can be used as potential shock absorbing material, which has resulted in recent extensive studies on structural stability under the influence of high pressure [11].

To date, most previous experimental studies focused on the room temperature and high pressure properties of MoS_2. Bagnall et al. [12] measured the frequencies of the Raman active A_{1g} and E^1_{2g} phonon modes of 2H–MoS_2 at high pressure up to 5 GPa using an opposed diamond anvil cell. Afterwards, Sugai and Ueda [13] also investigated the lattice vibration of the 2H–MoS_2 by the Raman spectroscopy, and increase the pressure up to 18 GPa. Aksoy et al. [14] investigated the high pressure behavior of MoS_2 using an energy dispersive synchrotron X-ray diffraction method in a diamond anvil cell to 38.8 GPa at room temperature, and reported the bulk modulus of MoS_2 is 53.4 GPa. Recently, Bandaru et al. [15] also studied the crystal structure and spectral properties of MoS_2 at high pressures up to 51 GPa using a diamond anvil cell with synchrotron radiation in addition to high temperature X-ray diffraction and high pressure Raman spectroscopic analysis and given the bulk modulus of MoS_2 is 70 GPa which is obvious different with the results reported by Aksoy et al. [14]. Furthermore, up to now, all of the studies on MoS_2 have been limited to either at high pressure and room temperature or at high temperature and ambient pressure. There are no reports in the literature about the thermoelasticity of molybdenite (MoS_2) at simultaneously high pressure and high temperature. Therefore, in this study, we have investigated the P–V–T relations of a natural molybdenite (MoS_2) at high pressure and high temperature, using a diamond anvil cell combined with *in situ* synchrotron radiation angle-dispersive X-ray diffraction. The thermoelastic property of molybdenite (MoS_2) is obtained by the fitting of the present P–V–T data to the high temperature Birch–Murnaghan (HTBM) EoS. Our results are also discussed with respect to previous reports of molybdenite (MoS_2) and tungstenite (WS_2).

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2. Sample and experiment

The natural molybdenite sample used in this study was collected from Zhongdian region of Yunnan Province, China. Table 1 presents the results of SEM-EDX analysis, and the chemical formulas of the crystals was calculated to be MoS_2. The pure molybdenite mineral grains were selected by hand under a microscope, and then grounded in an agate mortar for 4–6 h to obtain an average grain size of ~ 10 μm. The ground samples were examined using the conventional powder X-ray diffraction method, after being heated at 50 °C in a constant temperature furnace for 2 h to eliminate the absorbed water. The ambient X-ray diffraction data were collected using a D/Max-2200 X-ray diffractometer with graphite crystal monochromator and Cu $K\alpha$ radiation. The ambient X-ray spectrum of molybdenite sample was indexed according to the standard spectra (JCPDS87-2416), confirming that the structure of the natural molybdenite sample is hexagonal, and belongs to the $P6_3/mmc$ space group.

High pressure and high temperature experiments were carried out by using a modified Merrill–Bassett type diamond-anvil cell (DAC). A pair of 500 μm culet-size diamond anvil was used. Gaskets made from stainless steel foil (type T301), pre-indented to a thickness of ~ 50 μm and then drilled to a diameter of 200 μm, served as the sample chamber. The molybdenite sample powders were slightly pressed between two opposing diamond anvils to form an approximately 25 μm thick disk, and a piece of molybdenite sample about 100 μm in diameter was loaded into the sample chamber. The cell pressure was determined using the equation of state of gold (pressure marker) as proposed by Fei et al. [16]. The pressure transmitting medium was a 16:3:1 mixture ethanol–methanol–water. Heating was carried out by using a resistance-heating system, and the temperature was measured by a $Pt_{90}Rh_{10}$–Pt_{100} thermocouple, which was attached to the pavilion of the diamond. The spectrums were selected after the experiment temperature was kept for ~ 600 s. Typical exposure times for collecting diffraction patterns of the sample and the pressure marker were 600 s. Details of the experimental setup and cell assembly were described in Fan et al. [17].

In situ high pressure and high temperature angle-dispersive X-ray diffraction experiments were conducted at the 4W2 beamline of the Beijing Synchrotron Radiation Facility (BSRF). An image plate detector (MAR-345) was used to collect diffraction patterns. The wavelength of the monochromatic X-ray beam is 0.6199 Å calibrated by scanning through the Mo metal K-absorption edge. The distance between was focused to a beam size of 20×30 μm^2 full-width at half maximum (FWHM) by a pair of Kirkpatrick–Baez mirrors. The tilting and rotation of the detector relative to the incident X-ray beam were calibrated using cerium dioxide (CeO_2) powder as the X-ray diffraction standard. The sample-detector distance was calculated from the powder CeO_2 diffraction pattern at ambient conditions. The diffraction patterns were integrated to generate the conventional one-dimensional profiles using the Fit2D program [18]. Analyzes of all the patterns were carried out by means of the full profile-fitting technique implemented in the EXPGUI/GSAS software package [19,20]. Refinement of peak positions and extraction of cell parameters were achieved by reducing full diffraction patterns following the Le Bail method [21]. Precision upon the volume for molybdenite was estimated from the full spectrum fitting (Le Bail refinement) of X-ray diffraction profiles. X-ray diffraction patterns for the molybdenite sample collected at the present experiment pressure and temperature conditions showed that no phase transformation and other phases were observed throughout these experiments. Fig. 1 shows representative synchrotron powder X-ray diffraction patterns at various pressures and temperatures for molybdenite.

Table 1
Chemical composition of molybdenite (MoS_2).

Chemical (wt%)	Molybdenite (MoS_2) (10)[a]
Fe	0.04(1)
Ni	0.07(2)
Cu	0.08(2)
Sn	0.01(1)
Au	0.05(2)
Re	0.02(1)
Mo	59.83(40)
S	39.96(29)
Se	0.01(1)
Pb	0.00(0)
Te	0.00(0)
Total	100.07(42)

Data in the parentheses of compositions represent standard deviation.

[a] Number of electron microprobe analyses in parentheses.

3. Result and discussion

Unit-cell volumes of molybdenite at various pressures and temperatures conditions are shown in Table 2. The results of conventional X-ray diffraction collected at ambient condition gives the unit-cell volume $V_0 = 106.92 \pm 0.55$ Å^3 for molybdenite in this study, which is in good agreement with the results reported by Bronsema et al. [22] (i.e., $V_0 = 106.33$ Å^3). To derive thermoelastic parameters from the measured P–V–T data, we first fitted the compression P–V data at the 300 K isotherm to the Birch–Murnaghan equation of state (EoS), and then applied another commonly employed method, the high-temperature Brich–Murnaghan (HTBM) EoS approach.

3.1. Pressure–volume data at room temperature

The pressure–volume (P–V) relations have been determined by fitting the present room-temperature data to a third order Birch–Murnaghan (III-BM) EoS, which is represented as follows:

$$P = (3/2)K_0[(V_0/V)^{7/3} - (V_0/V)^{5/3}] \times \{1 + (3/4)(K'_0 - 4)[(V_0/V)^{2/3} - 1]\} \quad (1)$$

where V_0, K_0, K'_0 are the unit-cell volume, isothermal bulk modulus and its pressure derivative at ambient condition,

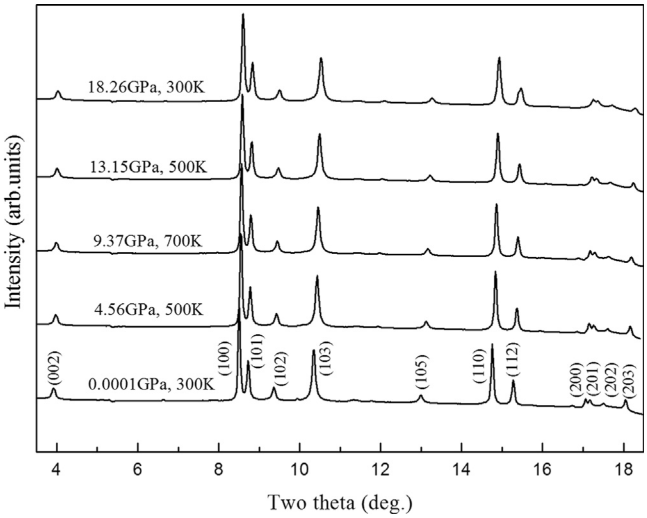

Fig. 1. Typical X-ray diffraction patterns of MoS_2 at high pressure and high temperature.