Phase Transition and EOS of Marmatite ($Zn_{0.76}Fe_{0.23}S$) up to 623 K and 17 GPa *

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In situ energy dispersive x-ray diffraction for natural marmatite ($Zn_{0.76}Fe_{0.23}S$) is performed up to 17.7 GPa and 623 K. It is fitted by the Birch–Murnaghan equation of state (EOS) that K_0 and α_0 for marmatite are 85(3) GPa and 0.79(16)$\times 10^{-4}\,K^{-1}$, respectively. Fe^{2+} isomorphic replacing to Zn^{2+} in natural crystal is responsible for high bulk modulus and thermal expansivity of marmatite. Temperature derivative of bulk modulus $(\partial K/\partial T)_P$ for marmatite is fitted to be $-0.044(23)\,GPaK^{-1}$. The unambiguous B3–B1 phase boundaries for marmatite are determined to be $P_{\rm upper}(GPa) = 15.50 - 0.016T(^\circ C)$ and $P_{\rm lower}(GPa) = 9.94 - 0.012T(^\circ C)$ at 300–623 K.

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ZnS will suffer the B3–B1 phase transition at about 15 GPa and room temperature[1–8] and the B3–B4 phase transition at about 1000°C and ambient pressure.[9,10] Fe^{2+} replacing Zn^{2+} is an important isomorphic replacement in ZnS crystal and then it is called marmatite. FeS crystal will suffer four phase changes at 0–20 GPa and high temperature[11–13] and the physical properties of $Zn_{1-x}Fe_xS$ solid solution will vary with the proportion of Fe at ambient condition.[14–17] However, we know few of the correlation between Fe content and physical properties of marmatite under high pressure and high temperature. Here, we study the phase transition and the equation of state (EOS) of marmatite ($Zn_{0.76}Fe_{0.23}S$) up to 17.7 GPa and 623 K, which are helpful for understanding physical changes brought by Fe^{2+} isomorphic replacing Zn^{2+} in marmatite crystal.

Marmatite was excavated from Gejiu tin deposits, China, and separated by electromagnetic method (purity > 99.5%). Chemical composition of specimen was determined by electron probe, and chemical formula of the crystal was calculated to be $(Zn_{0.759}Fe_{0.233}Mn_{0.009}Cd_{0.006}Ga_{0.006}In_{0.003}Ge_{0.002}Tl_{0.002})_{1.020}S$. From the chemical formula, except for Zn and Fe, other isomorphic replacements are less than 1%, so we ignore those elements when experimental results are discussed. X-ray diffraction measurement by using diamond anvil cell (DAC) is an important method for investigating the properties of mineral under high pressure.[18] In-situ x-ray diffraction analysis of marmatite was carried out on the High Pressure Experiment Station, Beijing Synchrotron Ray Fitting (BSRF), China. A diamond anvil cell (DAC) with exterior-heating instrument was used to supply static pressure. The pressure medium was a mixture of methanol and ethanol and water with 4:4:1. The energy diffusion x-ray diffraction (EDXD) method was adopted to investigate the structure of marmatite under high pressure and high temperature. The fixed 2θ angle was $15.9295 \pm 22^\circ$, which was calibrated by diffractive peaks of Au. Experimental pressure was calculated from the EOS of Au and its error was ± 0.3 GPa.[19] In the exterior-heating system surrounding the DAC, we adjusted the current across through thermocouple (NiCr thread) to control temperature of the whole DAC and its error is $\pm 2^\circ$C. Temperature was kept for about 10 min before spectrum was selected. The P–T path of the run is shown in Fig. 1. Typical spectra at selected pressures and temperatures are shown in Fig. 2. We read the energy E_{hkl} coupled with every peak by Maestro software and calculated the distance d_{hkl} using the energy diffusion formula ($E_{hkl} \times d_{hkl} = 6.199/\sin\theta$). Then, the cell parameters (in Table 1) of marmatite were calculated by Unitcell process.[20]

When pressure is higher than about 8 GPa, the peaks of B3 and B1 phase coexist in x-ray diffraction patterns, which will bring large errors for calculating cell parameters. Thus we fit only these more linear data collected under lower pressure (< 8 GPa) to the EOS of B3 phase marmatite. The P–V data at room temperature were fitted by the Birch–Murnaghan EOS:

$$P = (3/2)K_0[(V_0/V)^{7/3} - (V_0/V)^{5/3}]$$

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$$\cdot \{1 - (3/4)(4 - K_0')[(V_0/V)^{2/3} - 1]\}, \quad (1)$$

where V_0, K_0, and K_0' are the volume, the isothermal bulk modulus and its pressure derivative, respectively, under ambient conditions. We assume $K_0' = 4$ and fit that $V_0 = 158.25(31)$ Å^3 and $K_0 = 85(3)$ GPa for marmatite ($Zn_{0.76}Fe_{0.23}S$) at room temperature.

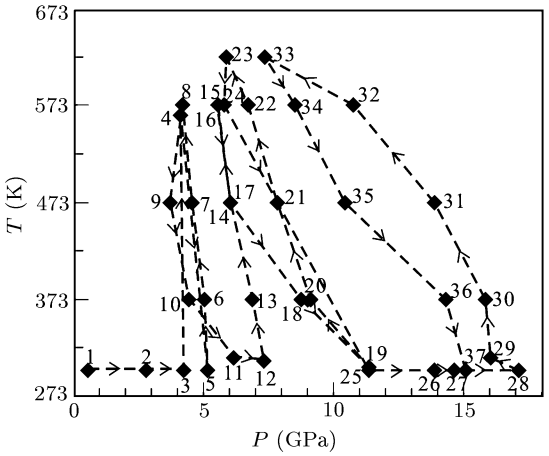

Fig. 1. P–T path of the run.

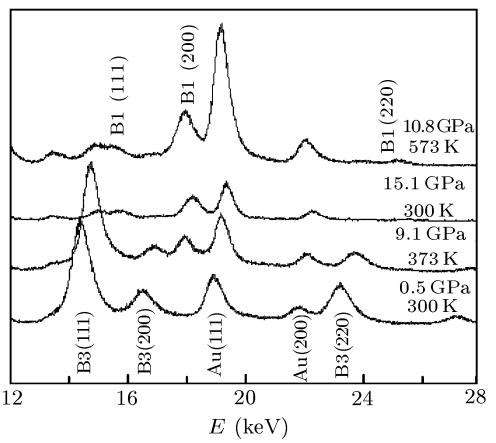

Fig. 2. X-ray diffraction spectra of marmatite ($Zn_{0.76}Fe_{0.23}S$) under different pressures and temperatures.

Two different approaches were used to analyse the P–V–T data of B3 structure of marmatite (shown in Fig. 3): (1) treating the whole dataset with a high-temperature version of the Birch–Murnaghan EOS; (2) independently analysing the data for each temperature level.

(1) High-temperature Birch–Murnaghan EOS. Because of lower experimental temperature, it is considered that bulk modulus is linearly dependent on temperature in this study,

$$K_T = K_0 + (\partial K/\partial T)_P(T - T_0). \quad (2)$$

The effect of temperature on cell volume could be given by

$$V_T = V_0\Big[\exp\Big(\int_{300}^{T} \alpha(T)dT\Big)\Big], \quad (3)$$

where $\alpha(T)$ is the volume thermal expansivity coefficient and it can be expressed as $\alpha(T) = \alpha_0 + \alpha_1(T)$. A high-temperature Birch–Murnaghan EOS can be given by taking the temperature dependences (2) and (3) into Eq. (1). During fitting the whole dataset to the high-temperature modification of Eq. (1), we assume that $\alpha_1 = 0$ and $K_T'(0) = 4$ and they are independent of temperature. It is obtained that $V_0 = 158.29(30)$ Å^3, $K_0 = 86(3)$ GPa, $\alpha_0 = 0.79(16) \times 10^{-4}$K^{-1}, and $(\partial K/\partial T)_P = -0.044(23)$ GPaK^{-1}.

Table 1. Marmatite ($Zn_{0.76}Fe_{0.23}S$) cell volume V as functions of P and T.

P (GPa)	T (K)	V (Å^3)	P (GPa)	T (K)	V (Å^3)
B3-type phase			5.5	573	151.41 (43)
0.5	300	157.14 (31)	5.6	573	151.32 (25)
2.8	300	153.65 (37)	6.0	473	150.18 (27)
4.2	300	151.31 (49)	6.7	573	149.54 (24)
4.1	563	153.36 (27)	5.8	573	151.16 (35)
5.1	300	150.02 (30)			
5.0	373	150.78 (43)	B1-type phase		
4.6	473	152.09 (24)	17.1	300	115.78 (54)
4.2	573	153.63 (22)	16.0	313	116.61 (60)
3.7	473	153.63 (22)	15.8	373	116.85 (54)
4.4	373	151.86 (26)	13.9	473	119.19 (30)
7.3	309	146.89 (22)	10.8	573	122.77 (56)
6.9	373	148.19 (26)	14.3	373	118.42 (27)
6.0	473	150.24 (38)	15.1	300	117.32 (42)

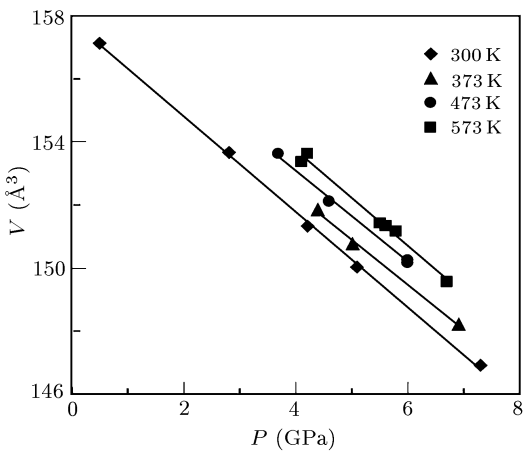

Fig. 3. P–V–T data of marmatite ($Zn_{0.76}Fe_{0.23}S$). The solid lines are isothermal Birch–Murnaghan fits at temperatures 300, 373, 473, and 573 K, respectively.

(2) Independent high-temperature analysis. Each isothermal set of pressure–volume measurements was individually fitted to the Birch–Murnaghan EOS, yielding the values of K_{T0} and V_{T0} at each temperature level. According to these fitting results, we estimated that the average values of α_0 and $(\partial K/\partial T)_P$ are 0.73×10^{-4} K^{-1} and -0.034 GPaK^{-1} in the temperature range studied, respectively.

These results obtained by the two approaches are in good agreement with each other. As shown in Table 2, K_0 of marmatite (ZnFeS) is larger than that of sphalerite (ZnS). For those iron sulfides, although their crystal structures are different from marmatite, the bulk moduli of these sulfides are far larger than those of marmatite.[21] Thus it is believed that in the crystal of marmatite, Fe^{2+} isomorphic replacing Zn^{2+} can increase its bulk modulus. In $Zn_{1-x}Fe_xS$ solid solution, Fe^{2+} isomorphic replacing Zn^{2+} will result in the augment of cell volume.[15–17] Fitting the P–V–T data of marmatite to the Birch–Murnaghan EOS, we obtain $V_0 = 158.29(30)$ Å^3, which is larger than that of sphalerite. However, this V_0 for marmatite is slightly smaller than those volumes in previous studies, which are measured on $Zn_{1-x}Fe_xS$ systems with comparable Fe content. We attribute this difference to those errors in fitting P–V–T data and other ions isomorphic replacing Zn^{2+} and Fe^{2+} in marmatite crystal. For volume thermal expansivity, marmatite is higher than sphalerite ($\alpha_0 = 0.28\times10^{-4}\,K^{-1}$).[22] Urakawa *et al.*[11] have proven that at 0–20 GPa, FeS transforms to FeS IV and then to FeS V with increasing temperature and the thermal expansivities of two new phases are very high ($0.716\times10^{-4}+0.608\times10^{-7}\,T$ for FeS IV and 1.042×10^{-4} for FeS V, respectively). Therefore, it is possible that for marmatite, Fe^{2+} isomorphic replacing Zn^{2+} enlarges the volume thermal expansivity of crystal. Previous parameters are compiled in Table 2.

Table 2. Previous data of V_0 and K_0 for zinc and/or iron sulfide.

Reference	Sample	V_0 (Å^3)	K_0 (GPa)	K_0'
Pan (1993)[17]	ZnS	157.464[a]		
	$Zn_{1-x}Fe_xS$ ($x = 0.262$)	161.879[a]		
Barton *et al.* (1966)[16]	ZnS	~ 158.253[a]		
	$Zn_{1-x}Fe_xS$ ($x = 0.20$)	~ 159.132[a]		
Lepetit *et al.* (2003)[15]	$Zn_{1-x}Fe_xS$ ($x = 0.20$)	~ 159.220[a]		
		~159.132[a] (different sulfur fugacity)		
Uchino *et al.* (1999)[5]	ZnS	157.989[a]	64.2	
Qadri *et al.* (2001)[2]	ZnS	157.989[a]	60.0	4
Lee *et al.* (1995)[8]	ZnS		84.5[b]	
Desgreniers *et al.* (2000)[3]	ZnS		79.5	4
Knittle (1995)[21]	ZnS		76.5	4.49
	FeS (troilite)		82 ± 7	-5 ± 4
	FeS_2 (pyrite)		143	4
	FeS_2 (marcasite)		146.5 ± 0.6	4.9

[a] Volumes are calculated with a learned from literatures.
[b] It is a calculated modulus for ZnS.

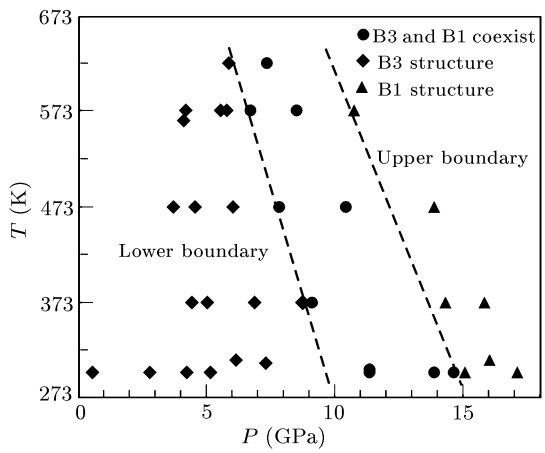

Fig. 4. Phase transition of marmatite ($Zn_{0.76}Fe_{0.23}S$) up to 623 K and 17 GPa. The dashed curves are fitting boundaries for unambiguous B3–B1 transition.

Desgreniers *et al.*[3] have indicated that ZnS can transit from B3 to B1 structure at 8 GPa, then B3 and B1 phases coexist up to 13 GPa, and phase transition is completed at 13 GPa. The unambiguous transition is also shown in this study on marmatite. Typical x-ray diffraction patterns (Fig. 2) show that peak (200) of B1 phase can be found at 9 GPa and 373 K, which indicates the onset of B3–B1 transition. Elevating the pressure and the temperature is followed by the augmentation of B1 peaks accompanied diminishment of B3 peak. The B3 and B1 phases coexist up to 15.1 GPa at ambient temperature, and the transition from B3 to B1 is completed. Iron sulfide will undergo several phase transitions up to 25 GPa and between 300 and 1000 K,[11] whereas this procedure indicates that for the B3–B1 phase transition of ZnS crystal, a little change will be brought by the impurity of Fe. From Fig. 2, it is obvious that transition pressure of marmatite is falling with elevating temperature. The boundaries for B3–B1 transitions are determined by fitting transition pressures of marmatite under high temperature. They are fitted linearly to be $P_{\rm upper}$(GPa)= 15.50 − 0.016T(°C) for upper boundary and $P_{\rm lower}$(GPa)= 9.94 − 0.012T(°C) for lower boundary at 300–623 K. Phase diagram of marmatite ($Zn_{0.76}Fe_{0.23}S$) up to 623 K and 17 GPa is shown in Fig. 4. In previous works, we have not found the study on properties of sphalerite (ZnS) under high pressure and high temperature. According to this work, it can be deduced that the B3–B1 transition pressure of ZnS

will decrease with increase of temperature. When the phase transition of ZnS is used to calibrate experimental pressure for high-pressure apparatus, it must be paid attention that the unambiguous transition and lower transition pressure can be induced by high temperature.

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