Compression Behavior and Phase Equilibria of FeS

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High pressure and temperature behavior of stoichiometric FeS (troilite) was studied up to 16GPa and 800°C, and the phase diagram of FeS was determined. There were found four stable phases; the troilite phase, the hexagonal phase, the NiAs type phase and the high pressure phase with a monoclinic cell. Some remarkable phenomena were also observed in the stable region of the hexagonal phase near the phase transition to the monoclinic phase; convergence of iso *c/a* curves to the boundary, an inflection in the compression curve at 300°C, and a very small coefficient of cubical expansion. These results suggested an electronic transition of the hexagonal phase between 6 and 8GPa. The transition could explain an anomaly in the boundary between the hexagonal phase and the monoclinic high pressure phase. [FeS, phase transition, X-ray diffraction, synchrotron radiation]

1. Introduction

Since a discovery of a structure-unknown high pressure phase by Taylor & Mao (1970) [1], high pressure behavior of stoichiometric FeS (troilite) has been investigated from the viewpoints of space science, solid state physics, and crystal chemistry. Because natural troilite has an origin of meteorites, it is an important material for the earth and space science. Iron sulfides including troilite also show a variety of magnetic properties and crystal structures. At ambient pressure condition, troilite has a superstructure of the NiAs type structure with a hexagonal cell with $\sqrt{3}a_f$ and $2c_f$ where a_f and c_f are cell parameters of the fundamental NiAs type cell [2]. Troilite has a large c_f/a_f value because of peculiar Fe-Fe chemical bonds within the basal plane in the structure.

Fei *et al.* [3] proposed a P-T phase diagram of FeS with five phases (the troilite phase, the NiAs type phase, a hexagonal phase, the MnP type phase and a structure unknown phase), in which they showed an extremely curved boundary between the simple NiAs type phase and the hexagonal phase. They suggested an electronic transition of the hexagonal phase at about 6GPa for an explanation for the curved boundary, however the details of the electronic transition was not described. On the other hand, we first successfully explained the high pressure phase by a monoclinic cell ($a=8.044(3)\text{\AA}$, $b=5.611(2)\text{\AA}$, $c=6.433(4)\text{\AA}$, $\beta=93.11(4)^\circ$ and $Z=12$ at 10.3GPa and 27°C) with a NiAs type superstructure, and proposed that iron atoms have a low-spin state in the high pressure phase based on a large volume decrease at the phase transition [4]. We also demonstrated that the phase boundary between the NiAs type phase and the hexagonal phase could be described by a simple straight line [5].

The aim of the present study is to determine phase equilibria of FeS under high pressure and temperature conditions and to observe a compression behavior and a thermal expansion of the

hexagonal phase carefully with keeping the electronic transition in mind.

2. Experiments

Powdered specimen of FeS (troilite) for this study was synthesized by an evacuated glass tube method. From the *d*-spacing of the 114 diffraction line, chemical formula of the specimen was estimated to be Fe_{0.998}S.

High pressure and high temperature experiments up to 16GPa and 800°C were carried out using DIA type cubic anvil apparatus "MAX80" and "MAX90" installed at Photon Factory, Institute for Materials Structure Science, High Energy Accelerator Research Organization. X-ray diffraction patterns under high pressure were taken by an energy dispersive method using white X-rays from a synchrotron radiation source. Diffraction lines with *d*-spacings larger than 3Å were carefully observed, because phase identification was easily made by paying attention to such diffraction lines. Every X-ray patterns were taken after heating to 300°C or higher, in order to reduce strain effects of the sample and NaCl as a pressure marker. Temperature was measured by an R type thermocouple encased at the center of a pressure medium. Pressure was calculated based on the Decker scale of NaCl. An error of pressure determination was less than ±0.3GPa. Details of the X-ray observation procedure was described in our previous reports [4-6].

3. Results and Discussion

Pressure and temperature phase diagram of FeS

In the present study, phase transitions of FeS were examined up to 16GPa and 800°C. We observed four phases; the troilite phase, the simple NiAs type phase, the hexagonal phase and the monoclinic high pressure phase, as shown in Fig. 1. All of them were explained to have a common subcell, which was just the NiAs type cell itself, as shown in Fig. 2. The results of

Fig. 1. Typical energy dispersive type X-ray diffraction patterns of FeS taken at $3\theta=3.0^\circ$, a) the troilite phase, b) the NiAs type phase, c) the hexagonal phase, and d) the monoclinic phase.

Fig. 3. Pressure and temperature phase diagram of FeS with iso c/a ratio curves of the fundamental NiAs type structure.

phase equilibria are summarized in Fig. 3. As the stable phases except the monoclinic phase have a common hexagonal fundamental cell with parameters of a_f and c_f [5], iso c/a curves are also shown in Fig. 3.

The present P-T diagram has two different points from Fei's diagram [3]; One is the straight phase boundary between the NiAs type phase and the hexagonal phase up to 11 GPa, and the other is no stable region of the orthorhombic MnP type phase. Our P-T diagram also shows two remarkable points; an inflection of the phase boundary between the hexagonal phase and the monoclinic phase at 8 GPa, and a convergence of iso c/a curves to the phase boundary in the stable region of the hexagonal phase. In other words, temperature dependence of c/a ratio drastically changed near the phase transition: In the lower pressure region, the c/a value steeply decreases with elevating temperature, and the c/a value is nearly equal to the ideal value (1.633) and slightly increases by elevating temperature in the higher pressure region.

Fig. 2. Schematic illustration of the simple NiAs-type structure, the troilite structure, the hexagonal structure, and the monoclinic structure (from left to right) in the NiAs-type structure projection along the c -axis. Solid small circles show Fe atoms at $z=0$ and $z=1/2$. Open large circles show S atoms; thin circles indicate $z=1/4$, and thick circles indicate $z=3/4$.

Electronic transition around 6-8 GPa

Compression behavior of FeS at 300°C is shown in Fig. 4, which has two inflections at 3.8 GPa and 7.5 GPa. The inflection at 3.8 GPa just corresponds to the phase transition from the NiAs type phase and the hexagonal phase. The inflection at 7.5 GPa may be related to the electronic transition suggested by Fei *et al.* [3], because no differences of X-ray patterns were observed around the inflection. Bulk moduli of the NiAs type phase up to 3.8 GPa and the hexagonal phase in the pressure region high pressure higher than 7.5 GPa were calculated to be 43 ± 3 GPa and 49 ± 2 GPa, respectively, based on the Birch-Murnaghan equation with $K' = 4$.

Volume changes versus temperature are plotted in Fig. 5, where the vertical axis is normalized by the volume of the troilite phase at 0.1 MPa and 27°C. By fitting the data to a linear equation, thermal expansivities are calculated at each pressure condition, as shown in Fig. 6. An anomalously steep dip at 5.7 GPa were found, where the thermal expansivity is about a tenth as small as that at other pressure conditions.

Similar anomaly of the thermal expansion is observed in the invar type alloys near a phase transition. We consider that the current result is caused by the electronic transition similar to the invar type alloys. The assumption can explain the other remarkable phenomena in the stable region of the hexagonal phase around 6-8 GPa. The details of the discussion have been described elsewhere [6].

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Fig. 4. Compression curve of FeS at 300°C. Equation of state for the hexagonal phase was calculated from data higher than 8 GPa, indicated by solid marks.

Fig. 5. Thermal expansivities of FeS

Fig. 6. Pressure dependence of thermal expansivity of FeS. A broken line indicates the phase transition pressure to the monoclinic phase at 27°C.

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