

MEASUREMENT OF THE ENTHALPY OF PHASE TRANSITION FOR IRON CHEVREL PHASE SULPHIDE IN THE TEMPERATURE RANGE FROM 300 TO 500 K

H. Honda, A. Oshima, H. Hinode and M. Wakihara

DEPARTMENT OF CHEMICAL ENGINEERING, TOKYO INSTITUTE OF TECHNOLOGY, MEGURO-KU, TOKYO 152, JAPAN

Enthalpy increment $H_T - H_{289\text{ K}}$ measurements have been made on iron Chevrel phase sulphide $\text{Fe}_2\text{Mo}_6\text{S}_{7.8}$, in the temperature range 300 to 500 K by the drop method using a high-temperature Calvet-type twin calorimeter. The first-order phase transition of this sulphide from a triclinic (low-temperature phase) to a rhombohedral (high-temperature phase) occurred at 375 K, and the enthalpy was evaluated to be 6.0 kJ/mol. The heat capacities of iron Chevrel phase sulphide $\text{Fe}_2\text{Mo}_6\text{S}_{7.8}$ were also calculated before and after the phase transition.

Keywords: enthalpy of phase transition, iron Chevrel phase sulphide

Introduction

Ternary molybdenum chalcogenides, $\text{M}_x\text{Mo}_6\text{X}_{8-y}$ ($M = \text{metal}$, $X = \text{S, Se, Te}$), generally called Chevrel phase compounds have attracted attention because of their structures and physical properties like their high superconducting critical temperatures and high critical fields. However, much less attention has been paid to their thermal properties except for the specific heat capacity measurement at extremely low temperatures.

The majority of these compounds which contain building blocks with the formula Mo_6S_8 , generally crystallize in rhombohedral (or hexagonal) structure. However, there also exist triclinic Chevrel phase compounds, such as $\text{Ni}_{0.33}\text{Mo}_3\text{Se}_4$ [1], MMo_3S_4 ($M = \text{Fe, Mn and Cr}$) [2] and the low temperature modification of $\text{Cu}_{1.8}\text{Mo}_6\text{S}_8$ [3]. These triclinic deformations usually depend on their metal or sulphur contents or the temperature.

Wada *et al.* [4] have determined the single-phase field and phase relations of $\text{Fe}_y\text{Mo}_6\text{S}_{8-z}$ at 1000°C (Fig. 1). The single-phase of triclinic iron Chevrel phase sulphides is denoted by solid triangles in the diagram. According to Yvon *et al.* [5], the triclinic $\text{Fe}_2\text{Mo}_6\text{S}_8$ transforms into the rhombohedral modification at a

temperature above 473 K owing to the order-disorder transition of the iron atoms. Wada *et al.* [4] reported that this order-disorder transition was reversible, since the quenched sample of $\text{Fe}_2\text{Mo}_6\text{S}_8$ revealed only the triclinic phase. Hence, the rhombohedral high temperature phase might not be quenchable.

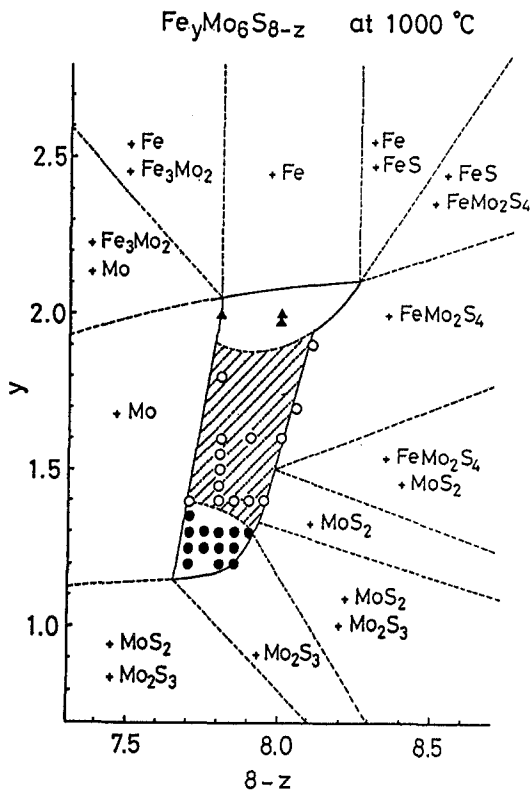


Fig. 1 Relationship between y and $8-z$ of $\text{Fe}_y\text{Mo}_6\text{S}_{8-z}$ at 1000°C. The single phase region corresponds to the area surrounded by solid lines. Δ : $\text{Fe}_2\text{Mo}_6\text{S}_8$ (triclinic phase), \bullet : $\text{Fe}_y\text{Mo}_6\text{S}_{8-z}$ (rhombohedral phase), \circ : $\text{Fe}_2\text{Mo}_6\text{S}_8$ and $\text{Fe}_y\text{Mo}_6\text{S}_{8-z}$ (non-quenchable phase) Redrawn from ref. 3.

In this paper, we present the molar enthalpy, temperature of the phase transition and heat capacity of iron Chevrel phase sulphide $\text{Fe}_2\text{Mo}_6\text{S}_{7.8}$ measured by the drop method using a Calvet-type calorimeter. At the same time, the structural modification of the triclinic structure and the rhombohedral structure of $\text{Fe}_2\text{Mo}_6\text{S}_{7.8}$ are investigated by high-temperature X-ray powder diffraction analysis ($\text{CuK}\alpha$ radiation) at ambient pressure.

Experimental

Sample preparation

Iron disulphide powder (Hanaoka mine 99.9%), molybdenum powder (Wako Pure chemical Industries Ltd.) distilled sulphur powder (Yoneyama Chemical Industries Ltd.) were used for the preparation of iron Chevrel phase sulphide. In order to make samples with composition $\text{Fe}_2\text{Mo}_6\text{S}_{7.8}$, the elements were mixed in the desired ratio to an accuracy of 0.01 mg.

The mixture in a vacuum-sealed ampoule was heated at 400°C for 24 h and then maintained at 1000°C for about 3 days followed by quenching. After grinding, the sample was sealed again under vacuum and was heated to 1000°C and maintained for 2 days followed by quenching. The $\text{Fe}_2\text{Mo}_6\text{S}_{7.8}$ phase was identified by X-ray powder diffractometry using nickel-filtered $\text{Cu-K}\alpha$ radiation, and no impurity could be observed.

High-temperature X-ray powder diffraction analysis

A high-temperature X-ray diffractometer attachment was used for the observation of in-site phase transition of $\text{Fe}_2\text{Mo}_6\text{S}_{7.8}$. The Geigerflex D/max-RA X-ray diffractometer system (ROTAFLEX RU-200 powerful rotating anode X-ray generator, Rigaku Co.) was applied for the X-ray studies. The powder sample (Ca. 400 mg) was ground in an agate mortar with propyl alcohol to a paste. It was then applied to the sample slate made of Pt and the surface made flat by pressing. The sample set on the device was heated from 298 to 402 K discontinuously under an oxygen-free dried nitrogen atmosphere, at ambient pressure. The experimental temperature increment over the entire temperature range in a series of consecutive experiments was 20–30 K for each X-ray powder diffraction measurement. It took a few hours to attain thermal equilibrium.

Apparatus and procedure

The Calvet-type twin calorimeter designed for operation at temperatures up to 650°C [6, 7] was used for the drop calorimetry of $\text{Fe}_2\text{Mo}_6\text{S}_{7.8}$. In this calorimeter, the thermal effect was detected as electrical output with a thermocouple. The electrical signal was amplified by a microvolt amplifier and integrated to obtain the enthalpy change by an on-line computer.

Since this sulphide is oxidized at high temperature under an air atmosphere, each sample (about 100 mg) was sealed under vacuum in a quartz ampoule (2 mm diameter and 15 mm to 20 mm long). This ampoule was dropped at room temperature ($25\pm 1^\circ\text{C}$) into the calorimeter, and the temperature was kept constant at above room temperature. Measurements of the variation of $H_T - H_{298\text{ K}}$ values

were carried out at temperatures from 300 to 500 K. The optimum experimental conditions were fixed for the present study as summarized in Table 1.

Table 1 Conditions for the experiments with $\text{Fe}_2\text{Mo}_6\text{S}_{7.8}$

Temperature of calorimeter	320 – 450 (K)
Particle size of sample	~ 80 (μm)
Amount of sample	90 – 120 (mg)
Weight of quartz ampoule	180 – 220 (mg)

Calibration of the calorimeter was performed by measuring the enthalpy increment $H_T - H_{298\text{ K}}$ of quartz at several temperatures (Fig. 2).

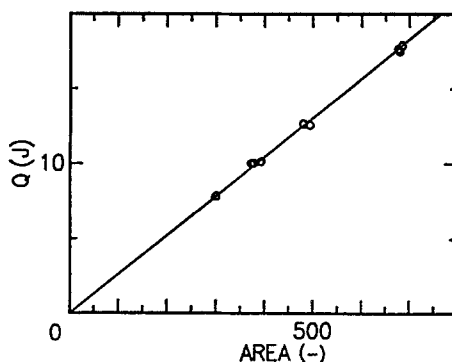


Fig. 2 Calibration at 397 K by drops of quartz

Results and discussion

Phase transition of $\text{Fe}_2\text{Mo}_6\text{S}_{7.8}$

High-temperature X-ray powder diffraction patterns of triclinic (room-temperature phase) and rhombohedral (high-temperature phase) of the $\text{Fe}_2\text{Mo}_6\text{S}_{7.8}$ are shown in Fig. 3. The $\text{Fe}_2\text{Mo}_6\text{S}_{7.8}$ revealed only the triclinic phase at room temperature, while it has transformed into the rhombohedral modification above 402 K. Accordingly, the transition of the $\text{Fe}_2\text{Mo}_6\text{S}_{7.8}$ from the triclinic phase to the rhombohedral phase occurred in the temperature range from 298 K to 402 K. The data reported by Yvon *et al.* [5] was used as reference for the lattice parameters of the Chevrel phase.

Thermal analysis

The enthalpy increment $H_T - H_{298\text{ K}}$ obtained in the present study is given in Table 2. The results are plotted graphically in Fig. 4. It can be seen from the plots of temperature vs. $H_T - H_{298\text{ K}}$ in Fig. 4 that there exists a discontinuity, which indicates the first-order phase transition of $\text{Fe}_2\text{Mo}_6\text{S}_{7.8}$.

Table 2 Dependence of the enthalpy increment on temperature for $\text{Fe}_2\text{Mo}_6\text{S}_{7.8}$

T / K	$H_T - H_{298} / \text{kJ/mol}$
298	0
328	15.4 ± 0.3
339	19.8 ± 1.0
357	27.6 ± 0.8
366	32.0 ± 0.8
370	33.0 ± 0.6
375	transition
379	43.4 ± 1.7
397	50.0 ± 1.2
414	58.7 ± 2.0
437	67.4 ± 1.4
449	73.0 ± 2.3

The enthalpy increment of $\text{Fe}_2\text{Mo}_6\text{S}_{7.8}$ is fitted to a linear function of temperature before and after the phase transition by the least-squares method. The differentiation of these equations with respect to temperature should yield the molar heat capacity. The temperature of the phase transition is determined from the mean value of the adjacent temperature at which the discontinuity occurred, and the molar enthalpy of phase transition is estimated by substituting temperatures of phase transition into the fitted equations.

Table 3 Heat capacities of triclinic and rhombohedral $\text{Fe}_2\text{Mo}_6\text{S}_{7.8}$, and temperature, enthalpy and entropy changes of phase transition

	Triclinic (room temp.)	Rhombohedral (high temp.)
$C_p / \text{kJ/mol}\cdot\text{K}$	0.432	0.428
ΔH_T (Tri - Rho)		$6.0 / \text{kJ/mol}$
ΔS_T (Tri - Rho)		$16 / \text{J/mol}\cdot\text{K}$
T_L / K		375 ± 4

Values estimated in this way are summarized in Table 3. From these results, we realize that the values of the molar enthalpy or molar entropy changes for the

phase transition from the triclinic to the rhombohedral structure of iron Chevrel phase sulphide $\text{Fe}_2\text{Mo}_6\text{S}_{7.8}$ is positive.

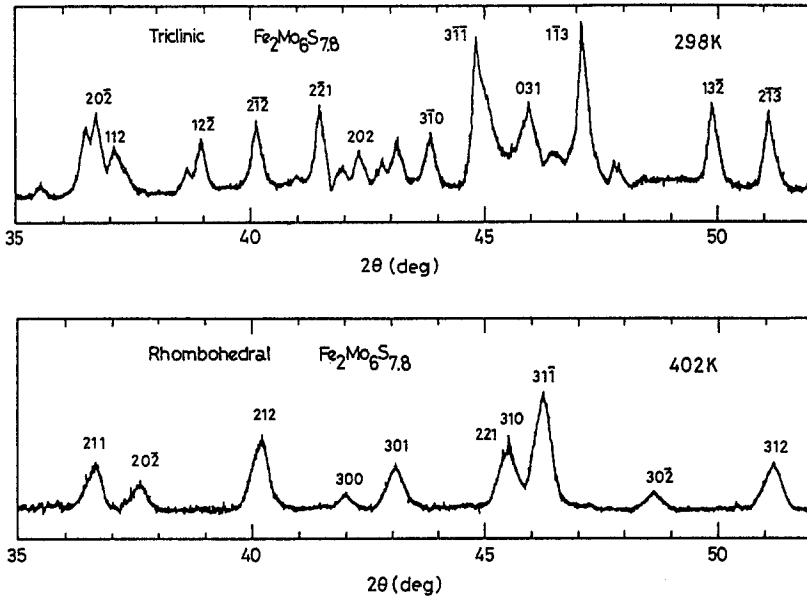


Fig. 3 Typical X-ray diffraction patterns of triclinic and rhombohedral $\text{Fe}_2\text{Mo}_6\text{S}_{7.8}$, using high-temperature X-ray apparatus

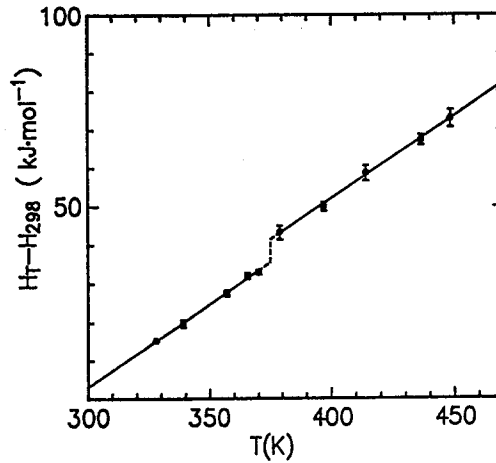


Fig. 4 Dependence of enthalpy increment on temperature for $\text{Fe}_2\text{Mo}_6\text{S}_{7.8}$

The main difference of these structures depends on the distribution of Fe atoms. In the triclinic room temperature modification, Fe atoms occupy only one lattice site, which represents two symmetry-equivalent point positions. On the other hand, in the rhombohedral structure the Fe atoms are distributed over 12 different available lattice sites [5]. Therefore the Fe atoms are ordered and form pairs in the triclinic cell, but after the phase transition occurs, they are disordered in the rhombohedral cell. Hence, we assume that the positive molar enthalpy or molar entropy changes refer to the absorption of energy into the crystal lattice sites from the surrounding parts of the cell.

Reference

- 1 O. Bars, J. Guillevic and D. Grandjean, *J. Solid State Chem.*, 6 (1973) 335.
- 2 R. Chevrel, M. Sergent and J. Prigent, *J. Solid State Chem.*, 3 (1971) 515.
- 3 R. Baillif, K. Yvon, R. Flükiger and J. Müller, *J. Low Temp. Phys.*, 37 (1979) 231.
- 4 H. Wada, M. Onoda, H. Nozaki and I. Kawada, *J. Less-Common Met.*, 113 (1985) 53.
- 5 K. Yvon, R. Chevrel and M. Sergent, *Acta Cryst.*, B36 (1980) 685.
- 6 M. Nishio, K. Kuwata, H. Hinode, M. Wakihara and M. Taniguchi, *Thermochim. Acta*, 88 (1985) 101.
- 7 A. Oshima, E. Ike, H. Hinode and M. Wakihara, *Thermochim. Acta*, 191 (1991) 341.

Zusammenfassung — Nach der Tropfenmethode wurden mittels eines Hochtemperaturdoppelkalorimeters vom Typ Calvet im Temperaturbereich 300-500 K an $\text{Fe}_2\text{Mo}_6\text{S}_{7.8}$ Messungen der Enthalpieinkremente $H_T - H_{298K}$ durchgeführt. Die Phasenumwandlung erster Ordnung bei diesem Sulfid von der triklinen (Niedertemperaturphase) in die rhomboedrische (Hochtemperaturphase) erfolgt bei 375 K und die Enthalpie erhielt man mit einem Wert von 6.0 kJ/mol. Die Wärmekapazitäten für $\text{Fe}_2\text{Mo}_6\text{S}_{7.8}$ wurden sowohl vor als auch nach der Phasenumwandlung berechnet.