Characterization of High-pressure Iron-Sulfur Compounds

M. Frank,[1] Y. Fei,[2] H. Watson[3]
[1]Northern Illinois University, DeKalb, IL, U.S.A.
[2]Carnegie Institution of Washington, Washington, DC, U.S.A.
[3]Rensselaer Polytechnic Institute, Troy, NY, U.S.A.

Introduction

It has long been hypothesized that iron and sulfur are important contributors to the cores of terrestrial planets such as Earth and Mars [1, 2]. Compositional models, based on elemental trends observed in SNC meteorites, suggest that the core of Mars may contain elevated concentrations of sulfur (>10 wt%; [3]). Further, at the time, the lack of high-pressure data in the Fe-S system required that Fe and FeS be considered end-member compositions. Recent high-pressure experiments conducted by using a multianvil apparatus were able to determine the presence of high-pressure iron-sulfur compounds at 14 and 21 GPa, respectively [4, 5]. The melting relations and bulk mineralogy in the Fe-FeS system at 21 GPa were outlined for temperatures ranging from 950 to 1400°C [5]. These high-pressure experiments revealed that at least three new iron-sulfur compounds — Fe_3S_2, Fe_2S, and Fe_3S — were formed at pressures greater than approximately 14 GPa (Fig. 1).

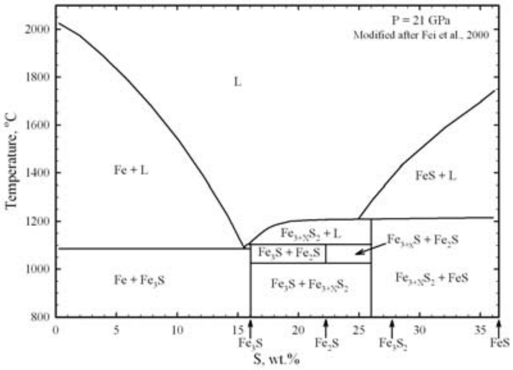

FIG. 1. Schematic representation of the Fe-FeS system at a pressure of 21 GPa (modified from Ref. 5).

The possible presence of light elements in the cores of terrestrial planets requires that the properties of sulfur-rich high-pressure phases be well understood [6]. Specifically, Fe_3S is important because it is the sulfur-bearing component that will be in equilibrium with metallic Fe for cores with sulfur concentrations of <16.1 wt%. To date, only the structure and pressure-density relation of Fe_3S have been determined at 300K [5]. A recent study noted that Fe_3S is the only quenchable phase in the system, whereas Fe_3S_2 and Fe_2S were unstable at ambient conditions [7]. The absence of structure and pressure-density data for the Fe_3S_2 and Fe_2S phases, plus the lack of any data for the three phases at elevated temperatures and pressures, limit the ability to accurately model the density profile of a sulfur-bearing iron core. Therefore, it is essential to determine the properties of these phases at elevated temperatures and pressures to place constraints on models of terrestrial core formation.

Methods and Materials

Although Fe_3S_2 and Fe_2S are not quenchable, samples with their bulk mineralogy were synthesized in a multianvil apparatus at 25 GPa and 1220K and 1370K, respectively. The synthesized starting compositions were compressed in a Mao-Bell-type diamond anvil cell with flat anvils (300 μm). Rhenium gaskets were preindented to ~25 GPa, and 70 to 150 μm holes were drilled in the compressed regions by using an erosion drill. The Fe-S starting material and gold (internal pressure calibrant) were loaded into the sample chamber.

High temperatures were obtained by using a small Mo-wire resistance heater placed around the diamond anvils and a $Ni_{0.8}Cr_{0.2}$ heater placed around the body of the cell. The temperature of the experiment was monitored by placing a $Pt\text{-}Pt_{0.9}Rh_{0.1}$ thermocouple between the diamond anvil and Re gasket, directly against the surface of the diamond. Temperatures were kept constant to ±3K during data collection, whereas the uncertainty associated with the thermocouple itself is ±2K over the range of temperatures in this study.

Synchrotron radiation was used to monitor the unit cells of Fe_3S_2, Fe_2S, Fe_3S, and gold. The experiments were conducted at GSECARS beamline station 13-ID-D at the APS by using the on-line imaging plate system. Data were analyzed by using the FIT2D software [8]. CeO_2 was used to calibrate the sample-to-detector distance, coordinates of the directed beam on the detector, and angle and tilt of the detector. The unit cell of gold determined from the diffraction lines was used in conjunction with a previously established pressure-volume temperature (PVT) equation of state [9] to calculate the experimental pressure.

Results

X-ray diffraction data were collected from 300K to 1000K at pressures of >16 GPa. Table 1 lists the experimental pressures and temperatures at which the diffraction data were collected for Fe_3S and Fe_2S. The data presented here concentrate on the properties of Fe_3S.

TABLE 1. Pressures, temperatures, and phases present in the experiments.

Temperature (K)	Pressure (GPa)	Phases
300	19	$Fe_3S + Fe_2S$
300	23	$Fe_3S + Fe_2S$
300	30	$Fe_3S + Fe_2S$
450	26	$Fe_3S + Fe_2S$
700	21	$Fe_3S + Fe_2S$
700	28	$Fe_3S + Fe_2S$
800	20	$Fe_3S + Fe_2S$
850	21	$Fe_3S + Fe_2S$
900	16	$Fe_3S + Fe_2S$
900	28	$Fe_3S + Fe_2S$
950	16	$Fe_3S + Fe_2S$
950	22	$Fe_3S + Fe_2S$
1000	19	$Fe_3S + Fe_2S$

Some typical x-ray data, presented as a function of 2 theta, are displayed in Fig 2. Generally, the spectra would sharpen as the temperature was increased; however, no new phases were observed over the range of conditions in this study. Fe_3S was found to be isostructural with Fe_3P (space group $I\bar{4}$), confirming the work of others [5, 7]. At 300K and pressures between 23 and 30 GPa, a new peak was observed in samples containing Fe_3S that could not be attributed to the $I\bar{4}$ space group. The main peaks associated with Fe_3S were unchanged, however. We are presently evaluating this "new" peak, and further experiments will probably be required.

The unit cell dimensions of Fe_3S were calculated from the 321, 330, 141, and 420 diffraction lines. Our results are generally consistent with those of previous studies [5, 7] at 300K. Preliminary data analysis indicates that thermal expansion of the Fe_3S phase is broadly consistent with that of similar compounds. Our results suggest that the volume of Fe_3S at 1000 and 19 GPa is ~6% greater than the volume at 300K and equivalent pressure.

Previous models of sulfur-bearing cores used FeS as an end-member to estimate the density of the Martian core [6]. The density of the Martian core should be modeled by using Fe_3S as an end-member in light of the finding of these new Fe-S compounds at high pressures. Our results present the first data on Fe_3S at elevated pressures and temperatures and should provide for more accurate density models for the Martian core.

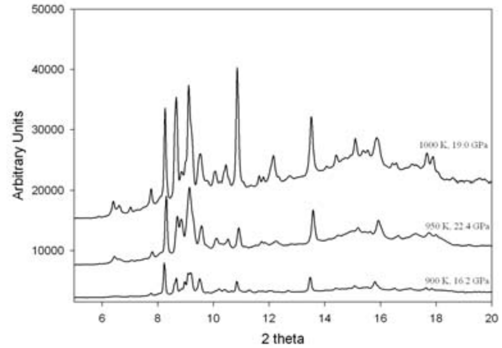

FIG. 2. Representative diffraction patterns of the bulk sample and gold (the internal pressure calibrant) as a function of the diffraction angle (2 theta).

The thermal expansivity of Fe_3S is of great importance in understanding the effects of temperature on the molar density and volume on Fe_3S under conditions analogous to terrestrial bodies. Thermal expansivity (α) is defined here as follows:

$$\alpha = \frac{1}{V_0}\left(\frac{\partial V}{\partial T}\right)_P \quad ,$$

where V_0 is the zero pressure volume and $\partial V/\partial T$ is the temperature derivative of the volume. The results indicate that Fe_3S has a thermal expansivity on the order of $\sim 1 \times 10^{-6}$, broadly consistent with similar materials. The density profile for Fe_3S has been calculated as a function of pressure for the 300K isotherm. Our results suggest the volume of Fe_3S at 1000K and 19 GPa is ~6% greater than the volume at 300K and equivalent pressure. Further experiments will be conducted to additionally constrain the thermal expansivity of Fe_3S, so that more accurate modeling can be accomplished at high pressures and temperatures.

Discussion

We conducted experiments in the Fe-S system at elevated pressures and temperatures to evaluate the PVT relations of Fe_3S. Fe_3S is the sulfur-bearing end-member phase in the iron-rich regime of the Fe-S system at high pressures. We provided new density data on Fe_3S that are applicable to density models of the Martian core. Thus, previous models of core formation that used FeS as an end-member should be reevaluated by using the data presented here. We have also observed a "new" peak at 300K and at pressures between 23 and 30 GPa in samples of Fe_3S that could not be attributed to the $I\bar{4}$ space group. We are presently assessing this peak and will conduct further experiments to characterize it.

Acknowledgements

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