

Pressure Dependence and Nonstoichiometric Effect on the B1-B8 Phase in FeO

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Introduction

The Earth's outer core is believed to be about 10% lighter than molten pure iron. Since oxygen is one of the most abundant elements in both the solar system and the Earth's mantle, it is an important candidate for being a light element in the Earth's core. Even though the miscibility of oxygen into molten iron is limited at ambient pressure, it could increase with increasing pressure and temperature, especially when this is associated with metallization of FeO under conditions corresponding to conditions in the Earth's core. It is thus important to understand the behavior of FeO at high pressures and temperatures.

Fe_{0.94}O transforms to a high-density phase beginning at 70 GPa in shock wave experiments [1, 2]. In addition, low electrical resistivity was observed over 70 GPa in shock wave experiments [3]. The high-pressure phase of Fe_{0.94}O was considered to be metallic. But no structural information was obtained from these shock wave experiments. Instead, the structure of the high-pressure phase of Fe_{0.98}O was observed in an external heated diamond anvil cell (EHDAC) [4]. The observed phase was assigned as a normal B8 phase. However, Mazin et al. [5] interpreted this same x-ray diffraction pattern as a stacking of the normal and inverse B8 phases. In addition, theoretical calculations on stoichiometric FeO showed that the inverse B8 phase is more stable than the normal B8 phase in the ground state (e.g., Refs. [6 and 7]). The inverse B8 phase is predicted to be an insulator, and the normal B8 phase is predicted to be metallic [5].

We previously conducted continuous high-pressure and high-temperature experiments in Fe_{0.91}O. The B8 phase appeared at 136 ± 7 GPa and 1500 ± 150K. We performed similar experiments but decreased the pressure gradually. The B8 phase disappeared at 120 ± 7 GPa and 1500 ± 150K. The B1-B8 phase boundary observed in our experiments is not consistent with the density discontinuity observed in the shock wave experiments. In this study, we conducted experiments on Fe_{0.95}O. No B1-B8 transformation was observed for FeO with this stoichiometry up to 143 GPa, above which the anvils failed.

Methods and Materials

A diamond anvil cell, beveled with a small culet size of 150 μm from a culet of 300 μm, and a stainless-steel guided boron gasket were used for generating high-pressure conditions. The sample was synthetic Fe_xO with $x = 0.952$ (hereafter denoted as Fe_{0.95}O, provided by Dr. Fei [4]), estimated from the cell parameter of 4.311 ± 0.002 Å. NaCl was used as a pressure medium and thermal insulating layer for laser heating. The NaCl powder was dried in a vacuum oven to eliminate any moisture. Sample loading was performed in an argon atmosphere in a glove bag. Angle dispersive x-ray diffraction experiments under *in situ* high pressure and temperature were performed at GSECARS beamline station 13-ID-D at the APS. A double-sided yttrium lithium fluoride (YLF) laser heating system [8] was used for the experiments. The laser heating spot size at the sample position was about 20 to 30 μm in diameter. A monochromatic x-ray beam (energy of 30.491 keV) was produced by a channel-cut crystal of silicon (220). The x-ray beam size was controlled by a slit system to 150 × 150 μm² and subsequently focused by Kirkpatrick-Baez mirrors to a beam size of 7 μm (vertical) × 10 μm (horizontal) at full width half maximum (FWHM). A charge-coupled device (CCD) detector (Bruker-2k) and an imaging plate (IP) detector (Mar345) were used for diffraction measurements. The exposure time for both detectors was 2 minutes. Pressures were determined from the lattice parameters of the NaCl B2 phase [10] after heating.

Results and Discussion

Our experimental procedure was to increase the pressure at room temperature to a desired point and then obtain x-ray diffraction patterns before, during, and after laser heating. The heating temperatures were fixed at 1500 ± 150K. Only the B1 phase was observed at 1500K up to 147 GPa. The experiment was stopped at that point because of an anvil failure. Combined with previous results on Fe_{0.91}O, the B1 phase was stable up to approximately 130 GPa at 1500K. It is not consistent with the rB1-B8 transformation in the EHDAC experiments, in

which the B8 phase was observed around 90 GPa. However, temperatures were different in these experiments. More experiments are needed to make the phase diagram of FeO clear under high pressure.

The modified Birch-Murnaghan equation of state (EoS) [9] does not require the zero pressure volume V_0 , and the fit can be made at any reference volume V_r . The fitting parameters (pressure P_r and bulk modulus K_r) are associated with those at the reference volume. Here, P_r was adjusted at almost zero by choosing suitable V_r ; in this way, a comparison with the result of the BM-EoS can be made. Results of the least square fits are $P_r = 0.0 \pm 1.1$ GPa and $K_r = 123.06 \pm 0.59$ GPa with $V_r = 12.74 \text{ cm}^3 \text{ mol}^{-1}$ for $\text{Fe}_{0.95}\text{O}$. The bulk moduli at 1500K are smaller than those at room temperature (140-155 GPa of $\text{Fe}_{0.91-0.95}\text{O}$) [10], which is reasonable at high temperature.

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