

Rhombohedral FeO at high pressures and temperatures

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Introduction

Iron oxides are of great interest in materials science because they display many diverse electric, magnetic, and optical properties. The spin transition of iron in iron-bearing magnesium oxide and silicate is now under intense study and debate. The ferrous iron oxide, wüstite (Fe_{1-x}O), is paramagnetic, and crystallizes with a NaCl-type (B1) structure under ambient conditions. As the pressure increases, the NaCl-type structure starts to distort into a rhombohedral structure as observed in diamond anvil cell study using the X-ray diffraction method. Recently, the magnetic properties of FeO above 100 GPa at room temperature have been investigated by X-ray emission spectroscopy, and by Mössbauer spectroscopy. However, there is a significant discrepancy contradiction between previous experimental studies. In this study, the pressure-induced structural change in FeO was investigated using a laser-heated diamond anvil cell combined with a synchrotron X-ray diffraction method.

Experimental

Powdered Fe_{1-x}O with purity 99.9% was used as the starting material. It is known that wüstite, Fe_{1-x}O , is a non-stoichiometric compound with a cation deficiency. Before the experiments, the cell parameter of the starting material was measured, and x was confirmed to be 0.10. High-pressure X-ray diffraction experiments were performed using a laser-heated diamond anvil cell high-pressure apparatus. The sample was loaded into a 100 μm diameter holes that were drilled into a rhenium gasket. NaCl was used as pressure reference [1]. The samples were heated with a YAG laser. The samples were probed using an angle-dispersive X-ray diffraction technique at the synchrotron beam lines BL13A, Photon Factory in Japan [2]. A monochromatic incident X-ray beam was used. The X-ray beams were collimated to a diameter of 15-30 μm , and the angle-dispersive X-ray diffraction patterns were obtained on an imaging plate.

Results and Discussion

In the first set of experiments, the pressure was increased directly to 45 GPa, at room temperature. After the desired pressure was achieved, the sample was heated to ~1500 K to relax the differential stress. After heating, the sample pressure decreased to 41 GPa, due to stress relaxation in the sample chamber. Moreover, the sample was compressed gradually to 61 GPa. The volume of rhombohedral FeO decreased continuously as the pressure increased (Figure 1). In the next run, the initial pressure was increased to 60 GPa, and X-ray diffraction

of the rhombohedral FeO was recorded at each pressure increment as the pressure increased gradually up to 97 GPa. No change in the X-ray diffraction pattern was observed. This indicated that there was no structural phase transition in this pressure range. However, a significant discontinuity in the volume change, of 1.6%, was observed (Figure 1). In the third run, the sample was investigated from 97 to 142 GPa. No volume discontinuity or structural change was observed over the higher pressure range. A possible explanation for these features is that a pressure-induced magnetic spin transition in iron occurs in rhombohedral FeO. It is known that the HS to LS transition of iron occurs in some iron-bearing materials. When the HS to LS transition occurs, the effective ionic radius of iron decreases. This decrease in the ionic radius can induce the discontinuous volume reduction without any crystallographic phase transition.

References

- [1] Ono et al., Solid State Commun. 137, 517 (2006).
 - [2] Ono et al., J. Appl. Phys. 97, 073523 (2005).
 - [3] Ono et al., J. Phys. Condens. Matter 19, 036205 (2007).
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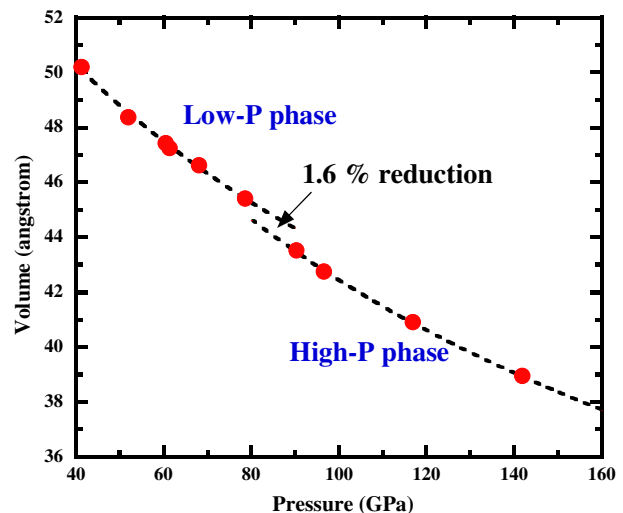


Figure 1. Pressure-volume data for rhombohedral FeO at 300 K. Dashed lines are the Birch-Murnaghan equation fits for volumes of each phase. The transition pressure was 85 GPa.