Determination of high-pressure phase equilibria of Fe$_2$O$_3$, using the Kawai-type apparatus equipped with sintered diamond anvils

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ABSTRACT

Phase equilibria of Fe$_2$O$_3$, have been studied up to 58 GPa and 1400 K using the Kawai-type multi anvil apparatus equipped with sintered diamond anvils. Identification of phases and pressure determination has been carried out by means of in situ X-ray observation using synchrotron radiation at SPring-8. Hematite (phase I) successively transforms to the Rh$_2$O$_3$(II)-type structure (phase II) and then to an orthorhombic structure (phase III) with increasing pressure. The transformations of hematite into high-pressure phases have been observed only at temperatures higher than 500 K, which is not concordant with previous results obtained by using the diamond anvil cell. Volume changes accompanied by the I-II and II-III transformations are calculated to be –2.8 and –5.0%, respectively. The phase boundary between I and II phases and that between II and III have been proposed to be $P$(GPa) = –0.015 $T$(K) + 44.2 and $P$(GPa) = –0.005 $T$(K) + 48.7, respectively. Possible correlation between a Mott transition and the phase stabilities may be concealed at room temperature due to slow reaction kinetics of the structural transformations.

Keywords: High-pressure phase equilibria, Fe$_2$O$_3$, Kawai-cell, sintered diamond, in situ X-ray observation

INTRODUCTION

Hematite Fe$_2$O$_3$, a typical trivalent transition metal oxide, crystallizes with the corundum structure and is a wide-gap antiferromagnetic insulator at ambient conditions. From the importance of hematite in materials science and Earth science, extensive studies have been carried out to clarify its structural, magnetic, and electronic properties under high pressures.

Existence of a denser phase of Fe$_2$O$_3$ at high pressure was first indicated by shock-compression in the 1960s (McQueen and Marsh 1966). Goto et al. (1982) reported the shock-induced spin-pairing transformation of hematite at ~50 GPa. Since the early 1980s, on the other hand, many static compression studies have been carried out using the diamond anvil cell (DAC). The isostructural low spin state at higher than 55 GPa was first supported by Yagi and Akimoto (1982). However, a simple high-spin–low-spin (HS–LS) transformation was later suspected based on Mössbauer spectroscopy measurement by Syono et al. (1984) and Suzuki et al. (1985). Recently transformations to the Rh$_2$O$_3$ II type structure (Rozenberg et al. 2002; Liu et al. 2003) or the orthorhombic perovskite type (Ono et al. 2004) at about 50 GPa have been proposed. It has also been noted that both the Rh$_2$O$_3$(II)-type and the perovskite structures exhibit very similar powder X-ray diffraction patterns, and the discrimination is somewhat subtle based on crystal-chemical assessment or ab initio calculations (Rozenberg et al. 2002; Liu et al. 2003; Ono and Ohishi 2005). Moreover, Ono and Ohishi (2005) reported that the CaIrO$_3$-type structure (space group Cmcm) is stabilized at pressures higher than 60 GPa and at temperatures in the 1200–1800 K range. In both the orthorhombic perovskite and the CaIrO$_3$-type structures, iron ions have to be accommodated in both the sixfold and higher coordinated sites, and thus the disproportionation $2Fe^{3+} \rightarrow Fe^{2+} + Fe^{4+}$ or the spin transition, $2Fe^{3+}$(high spin) $\rightarrow Fe^{2+}$(high spin) + $Fe^{4+}$(low spin), is anticipated. On the other hand, Liu et al. (2003) observed a new orthorhombic phase at 22 GPa after laser heating to ~3500 K. Therefore, high-pressure and high-temperature stability relations in Fe$_2$O$_3$ have not been well clarified.

Recently Ono et al. (2005) and Ono and Ohishi (2005) proposed the phase boundary between hematite and the orthorhombic perovskite or the Rh$_2$O$_3$(II)-type structure and that between the later and the CaIrO$_3$-type structure, respectively. Their conclusions were based on in situ X-ray experiments using the laser-heated diamond anvil cell (LHDAC). We have also studied the high-pressure stability relations of Fe$_2$O$_3$ up to ~58 GPa and 1400 K by means of in situ X-ray observation using the Kawai-type multi-anvil apparatus equipped with sintered diamond (SD) anvils. The phase relations obtained in our study are in marked contrast to those of Ono et al. (2005) and Ono and Ohishi (2005). The purpose of the present paper is to report the analyses on the high-pressure phases and to propose a new high P-T phase diagram of Fe$_2$O$_3$. 

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