High-pressure structural behavior of $\alpha$-Fe$_3$O$_3$ studied by single-crystal X-ray diffraction and synchrotron radiation up to 25 GPa

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ABSTRACT

In situ X-ray diffraction experiments were carried out at pressures up to 25 GPa on a synthetic hematite ($\alpha$-Fe$_3$O$_3$) crystal using synchrotron radiation in an angle-dispersive setup. Experiments were performed in diamond-anvil cells using neon as a pressure-transmitting medium. Single-crystal diffraction data were collected from omega scans and structural refinements were carried out for 10 pressure points. Bulk and linear incompressibilities were obtained from least-squares fits of refined data to the Eulerian strain based Birch-Murnaghan equation of state. Finite strain analysis suggests a truncation at second order, yielding results of $K_a = 207(3)$, $K_{0a} = 751(17)$, and $K_{0c} = 492(8)$ for bulk and axial moduli, respectively. The a-axis is about 1.5 times stiffer than the c-axis. Compression of the main structural feature, the FeO$_6$ octahedra, is quite uniform, with just slight changes of distortion parameters at higher pressures.

Keywords: Compressibility, diamond-anvil cell, hematite, axial anisotropy, neon pressure medium

INTRODUCTION

The majority of transition metal sesquioxides (M$_2$O$_3$; M = Al, Ti, V, Cr, Fe) adopt the corundum structure (space-group symmetry $R3c$), forming compounds with great importance in mineralogy and technology due to their electric and magnetic properties. Among these, Fe$_3$O$_3$ is particularly relevant to geosciences and solid-state physics as it can be considered an archetype Mott-insulator (Pasternak et al. 1999) and is antiferromagnetic between the Morin temperature (260 K) and the Néel temperature (955 K). Considering that iron is one of the most abundant elements in the Earth’s mantle, it is essential to understand in detail the high-pressure as well as high-temperature behavior of iron-bearing compounds as well as that of trivalent iron in general. So far, numerous studies have been conducted on the behavior of Fe$_3$O$_3$ at P-T ranges corresponding to mantle conditions, focusing in particular on elucidating the nature of the phase transition and of the controversially discussed high-pressure phase of hematite (Shim et al. 2008; Ono et al. 2004; Ono and Ohishi 2005; Liu et al. 2003; Badro et al. 2002; Rozenberg et al. 2002; Pasternak et al. 1999; Olsen et al. 1991). Less attention has been paid to the detailed structural evolution of the $\alpha$-phase of Fe$_3$O$_3$ (hematite). The existing compressibility studies have been confined to powder diffraction (Rozenberg et al. 2002; Liu et al. 2003) or to the low-pressure regime investigated by single-crystal diffraction in DACs (Wilburn and Bassett 1978; Finger and Hazen 1980; Sato and Akimoto 1979).

Bulk and axial compressibilities have been reported by means of XRD up to 60–70 GPa (Sato and Akimoto 1979; Olsen et al. 1991; Rozenberg et al. 2002; Liu et al. 2003). However, structural high-pressure data were only included by Sato and Akimoto (1979) and Rozenberg et al. (2002), both these studies having been done on powders. Furthermore, it may be questioned if the pressure media used, liquid argon or 4:1 methanol-ethanol mixture, are actually appropriate for the investigated pressure ranges, especially as powder samples respond more sensitively to non-hydrostatic environments and thus generate local stresses. Surprisingly, the only structural single-crystal data on $\alpha$-Fe$_3$O$_3$ at high pressure known to us are those of Finger and Hazen (1980), which were restricted to 5.2 GPa.

The aim of this work is to study the structural evolution of Fe$_3$O$_3$ by means of single-crystal X-ray diffraction in the quasi-hydrostatic pressure range of liquid neon, below the phase transition to the Rh-O$_3$-II type structure, which has been addressed in another paper (Dubrovinsky et al. 2010). The results are discussed and compared to earlier single-crystal data and powder-diffraction data.

EXPERIMENTAL METHODS

Single crystals of $\alpha$-Fe$_3$O$_3$ used in this study were grown by slow oxidation of pure (99.999%) iron at 1200 °C in a gas-mixing furnace following the procedure given by Chase and Morse (1973). Pressure was generated using a diamond-anvil cell with a half opening angle of 35°, diamond anvils with culet sizes of 300 μm, tungsten carbide seats as backing plates and a rhenium gasket, preindented to 50 μm with an initial hole-diameter of 150 μm. For high-pressure experiments, small crystals of approximate dimensions $15 \times 15 \times 15$ μm$^3$ were selected and tested for their quality using an Oxford Diffraction Xcalibur diffractometer. The chosen sample was then placed in the pressure chamber together with ruby spheres as pressure sensor. Neon was loaded at 1.4 kbar as pressure-transmitting medium to provide quasi-hydrostaticity throughout the pressure range investigated.

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