In situ determination of the spinel–post-spinel transition in Fe₃O₄ at high pressure and temperature by synchrotron X-ray diffraction

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ABSTRACT

The position of the spinel–post-spinel phase transition in Fe₃O₄ has been determined in pressure-temperature space by in situ measurements using a multi-anvil press combined with white synchrotron radiation. Pressure measurement using the equation of state for MgO permitted pressure changes to be monitored at high temperature. The phase boundary was determined by the first appearance of diffraction peaks of the high-pressure polymorph (h-Fe₃O₄) during pressure increase and the disappearance of these peaks on pressure decrease along several isotherms. We intersected the phase boundary over the temperature interval of 700–1400 °C. The boundary is linear and nearly isobaric, with a slightly positive slope.

Post-experiment investigation by TEM confirms that the reverse reaction from h-Fe₃O₄ to magnetite during decompression leads to the formation of microtwin on the (311) plane in the newly formed magnetite. Observations made during the phase transition suggest that the transition has a pseudomartensitic character, explaining in part why magnetite persists well within the stability field of h-Fe₃O₄, even at high temperatures. This study emphasizes the utility of studying phase transitions in situ at simultaneously high temperatures and pressures since the reaction kinetics may not be favorable at room temperature.

Keywords: Magnetite, post-spinel, phase transition, synchrotron experiment

INTRODUCTION

Magnetite (Fe₃Fe₂O₁₀) belongs to the large group of spinel-structured minerals with the general formula AB₂O₄. It is an important accessory mineral in many magmatic and metamorphic rocks and occurs as a component in spinels of the spinel peridotite facies of the upper mantle (e.g., Wood and Virgo 1989), as well as in (Mg,Fe)₂SiO₄ ringwoodite, which is expected to be stable in the mantle transition zone (e.g., O’Neill et al. 1993). Nearly pure magnetite has also been found as inclusions in diamonds (Meyer 1987; Stachel et al. 1998). Hence the stability and high-pressure properties of Fe₃O₄ have direct relevance to geochemical processes in the deep earth as magnetite and its polymorphs provide important structural models for understanding the behavior of Fe²⁺-bearing components in the mantle. Further knowledge about its high-pressure behavior is fundamental for the understanding of the phase relations in the simple Fe-O system. For these reasons, magnetite has been the subject of many studies over the years. Magnetite is known to undergo an unquenchable phase transition at ~21 GPa at room temperature to a high-pressure polymorph (hereafter denoted as h-Fe₃O₄) (Mao et al. 1974; Huang and Bassett 1986; Pasternak et al. 1994; Fei et al. 1999).

The h-Fe₃O₄ polymorph was found by Fei et al. (1999) to have space group Pbcm (CaMn₂O₄-type structure) with cell parameters a = 2.7992(3), b = 9.4097(15), and c = 9.4832(9) Å at 24 GPa and 650 °C. However, more recent studies suggest that a CaTi₂O₄-type structure (with space group Bbmm) is more consistent with the available diffraction data from room-temperature experiments between 21.8 and 43 GPa (Haavik et al. 2000) or experiments up to 930 °C and 60 GPa (Dubrovinsky et al. 2003). The unquenchable nature of h-Fe₃O₄ complicates direct crystallographic analysis of this phase. A further difficulty in studying this transition is the apparent sluggishness of the reaction and the persistence of magnetite at pressures significantly above that where h-Fe₃O₄ first appears (e.g., Huang and Bassett 1986). In addition, there is a large hysteresis in the back-reaction to magnetite, even at temperatures up to ~800 °C (e.g., Huang and Bassett 1986; Woodland et al. 2001). For these reasons, the actual position and slope of the phase boundary in P-T space remains poorly constrained. In this contribution we report the results of in situ diffraction measurements at high pressures and temperatures using synchrotron radiation that provide further important constraints on the position of the magnetite–h-Fe₃O₄ phase boundary. Our new experiments significantly expand the temperature range investigated by earlier studies. The current