SPINELS RENAISSANCE: THE PAST, PRESENT, AND FUTURE OF THOSE UBIQUITOUS MINERALS AND MATERIALS

New structure of high-pressure body-centered orthorhombic Fe2SiO4†

TAKAMITSU YAMANAKA1,*, ATSUSHI KYONO1,3, YUKI NAKAMOTO1,4, SVETLANA KHALAMOVA1, VIKTOR V. STRUZHKIN1, STEPHEN A. GRAMSch1, HO-KWANG MAO1,2 AND RUSSELL J. HEMLEY1

1Geophysical Laboratory, Carnegie Institution of Washington, Washington, D.C. 20015, U.S.A.
2High Pressure Collaborative Access Team, Geophysical Laboratory, Carnegie Institution of Washington, Argonne, Illinois 60439, U.S.A.
3Division of Earth Evolution Sciences, Graduate School of Life and Environment Sciences, University of Tsukuba, Tsukuba Ibaraki, 305-8572, Japan
4Center for Quantum Science and Technology Under Extreme Conditions, Osaka University, Toyonaka Osaka, 560-8531, Japan

ABSTRACT

A structural change in Fe2SiO4 spinel (ringwoodite) has been found by synchrotron powder diffraction study and the structure of a new high-pressure phase was determined by Monte-Carlo simulation method and Rietveld profile fitting of X-ray diffraction data up to 64 GPa at ambient temperature. A transition from the cubic spinel structure to a body centered orthorhombic phase (I-Fe2SiO4) with space group Imaa and Z = 4 was observed at approximately 34 GPa. The structure of I-Fe2SiO4 has two crystallographically independent FeO octahedra. Iron resides in two different sites of sixfold coordination: Fe1 and Fe2, which are arranged in layers parallel to (101) and (011) and are very similar to the layers of FeO octahedra in the spinel structure. Silicon is located in the sixfold coordination in I-Fe2SiO4. The transformation to the new high-pressure phase is reversible under decompression at ambient temperature. A martensitic transformation of each slab of the spinel structure with translation vector <1/8 1/8 1/8> generates the I-Fe2SiO4 structure. Laser heating of I-Fe2SiO4 at 1500 K results in a decomposition of the material to rhombohedral FeO and SiO2 stishovite.

FeKβ X-ray emission measurements at high pressure up to 65 GPa show that the transition from a high spin (HS) to an intermediate spin (IS) state begins at 17 GPa in the spinel phase. The IS electron spin state is gradually enhanced with pressure. The Fe2+ ion at the octahedral site changes the ion radius under compression at the low spin, which results in the changes of the lattice parameter and the deformation of the octahedra of the spinel structure. The compression curve of the lattice parameter of the spinel is discontinuous at ~20 GPa. The spin transition induces an isostructural change.

Keywords: New high-pressure structure, Fe2SiO4, ringwoodite, X-ray emission spectra, spin transition, martensitic transition

INTRODUCTION

A great deal of attention has been paid to the high-pressure structural transitions of the many spinel phases present in the Earth’s crust due to their geophysical importance (Akimoto and Fujisawa 1967; Bassett and Ming 1972; Ito and Takahashi 1987; Irifune et al. 1998). One of the major minerals in the crust, (Mg,Fe)2SiO4 olivine (α-phase), transforms to wadsleyite (β-phase, modified spinel) and further to ringwoodite (γ-phase, spinel). These transitions were proposed for the origin of the seismic discontinuity of the transition zone from 410 to 660 km depth (Ringwood and Irifune 1988). These high-pressure transformations have been studied from various viewpoints, including the electronic and elastic properties of participating phases (Kiefer et al. 1997; Li et al. 2007) and continue to provide significant information for seismic interpretation (Leven et al. 1981; Burnley et al. 1991; Shim et al. 2001).

Recently, the Fe2SiO4 phase with spinel structure was found in meteorite, and silicate spinels of transition elements are investigated for their influence on the magnetic and electrical properties of the Earth’s crust and mantle. Their phase stabilities and structures under high-pressure and high-temperature conditions have been intensively studied. Phase relations in the Mg2SiO4-Fe2SiO4 ringwoodite solid solution system have been investigated in numerous high-pressure studies (Katsura and Ito 1989; Ito and Takahashi 1989; Fei et al. 1999; Matsuzaka et al. 2000). Mechanisms for the polymorphic transformations of the α, β, and γ phases of (Mg, Fe, Co, Ni) have been discussed in terms of the observation of dislocations by TEM (Price et al. 1982; Madon and Poirier 1983). Structures of silicate spinels Mg2SiO4 (M = Mg, Fe, Co, Ni) have been refined from X-ray diffraction data at ambient conditions (Yagi et al. 1974; Morimoto et al. 1970, 1974; Ma 1975; Marumo et al. 1974, 1977). (1981). End-member of ringwoodite solid solution, Fe2SiO4, undergoes transitions at 6.4 GPa at 1700 °C (Yagi et al. 1987). Further experimental studies have been undertaken by Fei et al. (1991) and Matsuzaka (2000).

Significant work is also focused on the physical properties of iron-bearing spinels to understand their strong electronic