Thermoelastic property and high-pressure stability of Fe$_3$C$_3$: Implication for iron-carbide in the Earth’s core

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ABSTRACT

To investigate the physical property of Fe$_3$C$_3$, we carried out in situ X-ray diffraction experiments using a Kawai-type multi-anvil apparatus and a diamond anvil cell up to 71.5 GPa and 1973 K. The carbide was found to be stable under these experimental conditions. However, we found anomalous behavior in its isothermal compression and thermal expansivity. These anomalies could be due to the magnetic phase transition in Fe$_3$C$_3$ from a ferromagnetic (fm) to a paramagnetic (pm) phase. The Curie temperature of 523 K at 1 bar (Tsuzuki et al. 1984) decreases with pressure, and the pressure-induced magnetic transition is estimated to occur at ~18 GPa and 300 K. The pressure-volume-temperature (P-V-T) data set for the pm-Fe$_3$C$_3$ was fitted by the Mie-Grüneisen-Debye (MGD) equation of state (EOS) and the following parameters were obtained: unit-cell volume $V_0 = 184.2 \pm 0.3$ Å$^3$, bulk modulus $K_0 = 253 \pm 7$ GPa, the pressure derivative of bulk modulus $K'_0 = 3.6 \pm 0.2$, Grüneisen parameter $\gamma_0 = 2.57 \pm 0.05$, Debye temperature $\theta_0 = 920 \pm 140$ K, and $\gamma = 2.2 \pm 0.5$, respectively, at zero pressure. The calculated density for Fe$_3$C$_3$ provides a good explanation for the density of the Earth’s inner core obtained from seismological observations.

Keywords: Fe$_3$C$_3$, Earth’s inner core, equation of state, in situ XRD measurement

INTRODUCTION

The chemical composition of the Earth’s core is key to understanding Earth’s formation, chemical evolution, thermal regime, and core dynamo. It is widely accepted that the Earth’s core consists mainly of iron. Geophysical observations indicate that the density of the core is lower than that of iron at core pressures. This is likely due to the presence of lighter elements in the Earth’s core. The density deficit is estimated to be ~10% for the outer core (Birch 1952, 1964; Brown and McQueen 1986; Anderson and Ahrens 1994) and 2–5% for the inner core (Mao et al. 1990; Dubrovinsky et al. 2000). These studies indicate that the light elements are present in both the outer- and inner-core. The possible candidates of the light elements are H, C, O, Si, and S (see reviews by Poirier 1994; Li and Fei 2003). The nature of the light elements, however, is controversial. Hence, it is crucial to investigate the thermo-physical properties of the iron alloys with light elements at high pressure to understand the constituents of the Earth’s core.

Carbon is one of the likely candidates for the light elements in the core. Based on thermodynamic calculations, Wood (1993) suggested that an iron-carbide Fe$_3$C might be a constituent of the Earth’s inner core that solidified from the carbon-rich liquid outer core. However, recent high-pressure experiments on the Fe-C system have shown that Fe$_3$C rather than FeC might be stabilized under core pressures and temperatures (Nakajima et al. 2009; Lord et al. 2009). Nakajima et al. (2009) observed the Fe$_3$C$_3$ phase as the liquidus phase for the Fe$_3$C composition (Fe-6.7 wt% C) up to at least 30 GPa. Lord et al. (2009) measured the melting temperatures of the Fe-C eutectic, FeC and Fe$_3$C$_3$, up to 70 GPa, and proposed that Fe-C$_3$, instead of FeC$_3$, would form a eutectic relation with Fe above 135 GPa. Based on both of these results, Fe$_3$C$_3$ would crystallize from liquid outer core and is a likely constituent of the solid inner core, if the outer core contains carbon. Therefore, the thermoelastic properties of the Fe$_3$C$_3$ phase are crucial for understanding the chemistry of Earth’s inner core.

In this study, we have investigated the thermoelastic property and stability of Fe$_3$C$_3$. We have conducted in situ X-ray diffraction (XRD) measurements using a Kawai-type multi-anvil apparatus (KMA) and diamond-anvil cell (DAC) for higher pressures.

EXPERIMENTAL METHODS

Starting material

The starting material for the in situ XRD measurements were polycrystalline Fe$_3$C$_3$ synthesized from a powdered mixture of iron and graphite. The starting material was synthesized at 12 GPa and 1473 K using a Kawai-type multi-anvil apparatus (SPI-1000) at the Magma Factory, Tokyo Institute of Technology. The chemical composition and present phase of synthesized iron-carbide Fe$_3$C$_3$ was confirmed using electron microprobe analysis (EMPA) and X-ray diffraction.

DAC experiments

In situ XRD measurements were conducted in a DAC at a beamline BL10XU at the SPring-8 synchrotron facility, Japan. The experimental method is described...