Earth and Planetary Science Letters 418 (2015) 11–19

Contents lists available at ScienceDirect

Earth and Planetary Science Letters

www.elsevier.com/locate/epsl

The structure of Fe–Si alloy in Earth's inner core

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ARTICLE INFO

Article history:
Received 3 September 2014
Received in revised form 22 January 2015
Accepted 10 February 2015
Available online 9 March 2015
Editor: J. Brodholt

Keywords:
inner core
high pressure
iron–silicon alloy
diamond–anvil cell

ABSTRACT

Phase relations of iron–silicon alloy (Fe–6.5 wt.% Si and Fe–9 wt.% Si) were investigated up to 407 GPa and 5960 K in a laser-heated diamond–anvil cell, which likely covers the entire pressure and temperature conditions of the Earth's inner core. Synchrotron X-ray diffraction measurements show that Fe–9 wt.% Si with a hexagonal close-packed (hcp) structure is stable to 4800 K at 330 GPa, corresponding to the pressure at the inner/outer core boundary, and decomposes into a mixture of Si-poor hcp and Si-rich CsCl-type (B2) phases at higher temperatures. We also found that the solubility of silicon in solid iron is relatively insensitive to temperature, decreasing from 9 to >6.5 wt.% over a range of 1500 K at 70 GPa. These suggest that the inner core is composed solely of the hcp phase, when the silicon content is up to 7 wt.% that likely accounts for the inner core density deficit as well as for the Mg/Si ratio and the Si isotopic composition of the mantle. Additionally, the present experiments demonstrate that the incorporation of silicon in iron expands the stability of hcp with respect to that of fcc.

1. Introduction

Crystal structure in the Earth's inner core is of great importance to understand its elastic and transport properties, and dynamics (de Koker et al., 2012; Pozzo et al., 2012; Gomi et al., 2013). While a variety of different crystal structures have been proposed for iron at high pressure and temperature (P–T) (Saxena et al., 1995; Belonoshko et al., 2003; Mikhaylushkin et al., 2007), recent static experiments (Tateno et al., 2010) revealed that the hcp structure is a stable form of iron up to 377 GPa and 5700 K. Such experimental result is also supported by the most recent ab initio calculations (Stixrude, 2012). Nevertheless, the terrestrial core is not pure iron. Silicon is likely to be a major light component in the core (~6 wt.%, Hirose et al., 2013), which is strongly favored by cosmochemical and geochemical arguments based on 1) the depletion in silicon in the Earth's mantle relative to solar abundance and primitive meteorites (e.g., Allègre et al., 1995) and 2) the difference in ^{30}Si/^{28}Si ratio between meteorites and terrestrial rocks (Georg et al., 2007; Fitoussi et al., 2009; Shahar et al., 2009; Ziegler et al., 2010). Such high concentration of silicon in the core has been supported by metal–silicate partitioning experiments (Takafuji et al., 2005; Sakai et al., 2006; Ozawa et al., 2009; Rubie et al., 2011), although some experimental and theoretical studies argued for a subordinate role of silicon (<4.5 wt.%) (Antonangeli et al., 2010; Siebert et al., 2013; Badro et al., 2014). Since only small fractionation of silicon is known to occur between liquid and solid iron, the inner core may possess similar amount of silicon to that in the bulk core (Kuwayama and Hirose, 2004; Alfè et al., 2002; Fischer et al., 2013). Indeed, previous density and sound velocity measurements of Fe and Fe–Si alloy at high pressure suggested that iron alloyed with silicon can explain seismic observations in the inner core (Badro et al., 2007; Mao et al., 2012).

Phase relations in Fe–Si alloys, however, have been examined by earlier experiments only to 257 GPa and 2400 K (Asanuma et al., 2008), while the inner core is under >330 GPa and ~5000 K. The phase diagram of Fe–9 wt.% Si was extensively studied under pressure in a DAC (Kuwayama et al., 2009; Lin et al., 2009; Fischer et al., 2013). These previous experiments consistently demonstrated that hcp-Fe containing 9 wt.% silicon decomposes into a mixture of hcp and B2 phases with increasing temperature. It suggests a possibility of two-phase mixture in the inner core (Brosh et al., 2009; Fischer et al., 2013), although the boundary between hcp and hcp + B2 has never been constrained above 240 GPa. On the other hand, ab initio calculations argued that the incorporation of small amount of silicon in iron stabilizes body-centered cubic (bcc) or fcc phase with respect to the hcp phase (Vočadlo et al., 2003; Côté et al., 2008a, 2010), but it has never been verified by experiments.

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http://dx.doi.org/10.1016/j.epsl.2015.02.008
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In this study, we examine the phase diagram and the equation of state (EoS) of Fe–Si alloys at multimegabar pressures by a combination of laser-heated diamond–anvil cell (DAC) techniques and synchrotron X-ray diffraction (XRD) measurements. The phase relation in Fe–9 wt.% Si ($Fe_{0.84}Si_{0.16}$ in atomic ratio) was determined up to 407 GPa and 5960 K, the highest static P–T ever reported. The pressure–volume data for hcp Fe–9 wt.% Si was also obtained to 305 GPa at 300 K. In addition, the stabilities of hcp and fcc Fe–6.5 wt.% Si ($Fe_{0.88}Si_{0.12}$ in atomic ratio) were examined up to melting temperature at relatively low pressures (<70 GPa). Based on these new data, we discuss the stable crystal structure of Fe–Si alloy in the Earth's inner core.

2. Experimental methods

2.1. High-P/room-T experiments for Fe–9 wt.% Si

High-pressure/room-temperature experiments were performed in a DAC to obtain the EoS of hcp Fe–9 wt.% Si (runs #1–4) (Table S1). We used a powder sample (*Goodfellow*) as starting material. We examined unheated portion of a recovered sample under scanning transmission electron microscope and confirmed the starting composition and the chemical homogeneity at micrometric scale. It was loaded into a hole in a pre-indented rhenium gasket together with MgO (pressure standard) and pressure medium (Ar or SiO_2 glass). Pressure–volume data were collected with thermal annealing using laser each time after pressure increment except run #4 using Ar performed in a low-pressure range. We therefore loaded such sample assembly as MgO/SiO_2-glass/Fe-Si-alloy/SiO_2-glass so that MgO was detached from an iron sample, in order to avoid possible chemical reaction at high temperature. The sample assembly was then dried leaving the cell in a vacuum oven at 393 K for >1 h prior to pressurizing and flushed with argon gas when the oven was opened. Subsequently the sample was compressed to high pressure in an argon atmosphere in a glove box when using the SiO_2 glass (runs #1–3). In case of argon pressure medium (run #4), it was cryogenically introduced into a sample chamber. Diamond–anvils with a culet size of 300, 120, or 40 μm in diameter were employed depending on a target pressure.

Angle-dispersive XRD measurements conducted at BL10XU, SPring-8 (Ohishi et al., 2008). The XRD patterns were collected at room T on an imaging plate (*Rigaku R-AXIS IV*). Typical exposure time was 3 min. A monochromatic incident X-ray beam was focused by stacked compound refractive lenses and collimated to approximately 6 μm area (full-width at half maximum, FWHM) at sample position. Thus, around 80% of diffraction signal was derived from this area. The wavelength varied slightly between different beamtimes and was determined using CeO_2 as standard; 0.4134–0.4147 Å (∼30 keV). Two-dimensional XRD images were integrated over the Debye–Scherrer rings, using the IP Analyzer program (Seto et al., 2010), in order to produce a conventional one-dimensional diffraction pattern as a function of two-theta angle. Three to seven and two to four diffraction lines were used to obtain the lattice parameters for hcp Fe–9 wt.% Si and MgO, respectively. Pressure was determined by using the EoS of MgO (Wu et al., 2008).

2.2. High P–T experiments for Fe–9 wt.% Si

Ultrahigh P–T experiments were conducted using laser-heated DAC techniques to determine the phase relations in Fe–9 wt.% Si (runs #1, 5–7) (Table S2). A single coarse grain of Fe–9 wt.% Si (*Goodfellow*) was used as a starting material. It was loaded together with SiO_2 glass (thermal insulator) except in run #1 (see above) and then sealed in the similar way described above. Double-beveled diamond anvils with 60, 40, or 30 μm culets were used for compression.

Heating was performed from both sides of the sample by employing a couple of 100 W single-mode Yb fiber lasers (*SPI*). The laser-heated spot was 15 to 20 μm across. Temperature was measured by a spectroradiometric method (Ohishi et al., 2008) (Fig. S1). In order to reduce radial temperature gradient, we used beam shapers (*New focus*) that convert a beam with a Gaussian intensity distribution to the one with a flat-top distribution. Sample temperatures reported in this study are the average in 6 μm region probed by X-rays around the hot spot. Temperature variations within such 6 μm spot were less than ±10% below 5000 K and ±15% at higher temperatures as shown in supplementary Fig. S2 (Tateno et al., 2010, 2012). It is noted that the peak temperature rather than the average temperature might be important for the appearance of the B2 phase.

The angle-dispersive XRD patterns were collected at high T on a CCD detector (*Bruker APEX*). Typical exposure time was 10 s. The wavelength was 0.4179–0.4191 Å. Visible fluorescence light from diamond excited by X-rays was used to align both laser-heated spot and position of temperature measurement with the X-ray beam. We obtained one-dimensional diffraction pattern in the same manner as that for room-T experiments.

An internal pressure standard was not used in order to avoid possible chemical reaction with the sample. We determined sample pressures from the unit-cell volume of hcp Fe–9 wt.% Si using both 100 and 101 reflections and its P–V–T EoS obtained in this study (runs #1–4, see above). The ±15% uncertainty in temperature led to about ±3% errors in pressure (for example, 407 ± 12 GPa at 5960 K).

2.3. High P–T experiments for Fe–6.5 wt.% Si

The experimental setup for the Fe–6.5 wt.% Si sample was similar to that for Fe–9 wt.% Si (runs #8–10) (Table S3). A foil starting material (*Rare Metallic*) was embedded between SiO_2 glass layers. An X-ray beam was focused to about 2 μm in diameter (FWHM), much smaller than a laser-heated spot size (20–30 μm). Sample temperatures are the averages in 2 μm region probed by X-rays. Temperature variations in such 2 μm area were only less than ±3%, at least in radial direction. The exposure time for XRD measurement was 1 s using a CCD detector. Sample pressure was calculated from the estimated EoS of hcp Fe–6.5 wt.% Si (bulk modulus $K_0 = 166.7$ GPa, its pressure derivative $K'_0 = 5.47$, and volume at ambient condition $V_0 = 11.312$ Å^3/atom), whose volumes were obtained by linear interpolation between those of pure hcp Fe (Dewaele et al., 2006) and hcp Fe–9 wt.% Si (this study). When the fcc phase was present, the pressure was obtained by assuming constant thermal pressure per given temperature increase in each heating cycle.

3. Results

3.1. Equation of state of hcp Fe–9 wt.% Si

Four separate sets of experiments were performed to determine the EoS of hcp-structured Fe–9 wt.% Si at 300 K between 13 and 305 GPa (runs #1–4). The observed unit-cell parameters and volumes of hcp Fe–9 wt.% Si and MgO are summarized in Table S1. A representative XRD pattern collected at 305 GPa at room temperature is shown in Fig. 1a, in which the diffraction peaks from hcp Fe–9 wt.% Si and NaCl-type (B1)-MgO were found. The diffraction peaks of SiO_2 were not observed through the present experiments; crystallization from SiO_2 glass is known to be quite sluggish even at relatively low pressures (Komabayashi et al., 2009, 2012) and