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Effect of Fe on the equation of state of mantle silicate perovskite over 1 Mbar

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ABSTRACT

In order to investigate the effect of Fe on the equation of state (EOS), the volume of the perovskite (Pv) phases, $(Mg_{1-x}Fe_x)SiO_3$, with different Fe contents ($x = 0, 0.09, 0.15$), has been measured at high pressures up to 1 Mbar in an Ar or NaCl medium. A bulk modulus (K_0) ranging between 255 and 261 GPa is obtained when the Au scales consistent with the Pt scale are used and the data are fit to the second order Birch–Murnaghan (BM) equation. When the third order BM equation is used, we obtain $K_0 = 250–264$ GPa and $K'_0 = 3.7–4.5$, which is consistent with previous low-pressure X-ray diffraction and Brillouin measurements. Within experimental uncertainties (0.5% in volume and 6% in bulk modulus), we do not resolve differences in the EOS between Fe-bearing (up to 15%) and Fe-free Pv to 1 Mbar (2600-km depth in the mantle). This is in contrast with the much larger effect of the Fe spin transition for the EOS of ferropericlase (Fp) reported recently. This is perhaps due to much more diverse states of Fe (e.g., oxidation, coordination, and spin states) in Pv than in Fp.

1. Introduction

Iron is the most abundant transition metal in the mantle and enters the crystal structures of the dominant mantle phases, silicate perovskite (Pv) and ferropericlase (Fp) (e.g., Kesson et al., 1998). The effect of Fe on the equation of state (EOS) of these mantle phases is fundamental for constraining the chemical composition of the lower mantle combined with seismic models (Stixrude et al., 1992).

It has been predicted that Fe in the mantle phases undergoes a magnetic collapse at pressure relevant for the lower mantle (Cohen et al., 1997). Recent spectroscopic measurements have found that the spin state of Fe in Pv and Fp changes at mantle pressures (Badro et al., 2003, 2004; Li et al., 2004; Speziale et al., 2005; Jackson et al., 2005). Moreover, the spin transition in Fp affects the pressure (P)–volume (V) relations (Lin et al., 2005; Speziale et al., 2005; Fei et al., 2007), which has been further supported by first-principles calculations (Tsuchiya et al., 2006; Persson et al., 2006).

However, no systematic EOS measurements have been performed for Pv, which is the dominant phase in the lower mantle, by varying the content of Fe at mantle pressures. An earlier study (Mao et al., 1991) investigated the effect of Fe and concluded that Fe does not change the EOS of Pv. Yet the data were collected only up to 29 GPa which is much lower than the reported spin transition pressure in Pv, 70–120 GPa (Badro et al., 2004; Li et al., 2004). Although the EOS of Pv with different Fe contents have been measured to higher pressures by some investigators (e.g., Knittle and Jeanloz, 1987), it is difficult to reliably extract the effect of Fe by combining these data, because of the use of different pressure scales and pressure transmitting media in these measurements. Furthermore, even for the Pv phase in $MgSiO_3$, the most studied system, P–V relations have been measured without pressure medium above 50 GPa. Therefore, it is necessary to investigate the effect of Fe on Pv at mantle pressures under improved stress conditions using the same pressure scale in order to facilitate comparison among the Pv phases with different Fe contents.

First-principles studies (Zhang and Oganov, 2006; Stackhouse et al., 2007) and experimental measurements (Badro et al., 2004; Li et al., 2004; Jackson et al., 2005) are in agreement in that the spin transition occurs over a wide pressure range in Pv. Also the computational studies have suggested that the transition occurs gradually in Pv. In other words, if the spin transition indeed affects density of Pv, it likely happens gradually over a wide pressure range. Therefore, the effect of the spin transition may be recognized from differences in compressibility between Fe-bearing and Fe-free Pv, rather than by a discrete change (or a change over a narrow P range)

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in density as found in Fp (Lin et al., 2005; Speziale et al., 2005; Fei et al., 2007).

We report the P–V relations of $(Mg_{1-x}Fe_x)SiO_3$-Pv ($x = 0$, 0.09, 0.15) over 1 Mbar. In order to resolve differences in the EOS among different composition systems, we use the same pressure scale (Au) throughout the measurements and the same pressure medium (Ar) for most of the data up to 1 Mbar.

2. Experimental methods

Natural pyroxene samples $[(Mg_{1-x}Fe_x)SiO_3]$ with $x = 0.00$, 0.09, and 0.15 are used as starting materials. The chemical compositions of the samples were examined using electron microprobe at MIT. No significant amounts of other minor elements are detected for the starting materials. The starting materials were ground to powders and mixed with 10 wt% Au which serves as an internal pressure standard and laser coupler. The mixtures were pressed to 5-μm thick foils. Each foil was loaded in a hole in a preindented Re gasket and then the assemblage was sandwiched between diamond anvils in a symmetric type diamond-anvil cell. For most of our measurements, we cryogenically loaded Ar as a pressure transmitting and insulation medium in the sample chamber. A few grains of the sample materials were placed below and above the sample foil in order to allow liquid Ar to flow in between the foil and diamond anvils. The diffraction lines of Ar are well resolved up to our maximum pressure, confirming that a significant amount of the pressure medium surrounds our samples (Fig. 1). In some measurements for the sample with $x_{Fe} = 9$ mol%, a sample foil was sandwiched between two foils of NaCl which serves as an insulation and pressure medium.

We used a culet size of 200 μm for measurements up to 80 GPa. Beveled anvils with 150 μm culets were used for measurements at pressures above 80 GPa. In order to examine reproducibility, we conducted at least 3 different runs for each compositional system with pressure ranges overlapping at least 10 GPa.

X-ray diffraction (XRD) measurements were conducted at the GSECARS sector and the HPCAT beamline of Advanced Photon Source (APS) and the 12.2.2 beamline of Advanced Light Source (ALS). A monochromatic X-ray beam with an energy of 30 keV was focused to a size smaller than 10 μm × 20 μm. Two-dimensional diffraction images were collected using a Mar345 imaging plate or a MarCCD detector. Diffracted beams were measured through X-ray semi-transparent (40–60% transmittance for a 30-keV X-ray beam) cBN backing plates, which extends measurable d-spacings to 1.1 Å. This is particularly helpful for accurate determination of volume for Pv and Au. A total of 9–25 diffraction lines are used to constrain the volume of Pv. For Au, we use 3–5 diffraction lines.

In order to synthesize the Pv phases, the sample in the diamond-anvil cell was heated with an Nd:YLF laser beam to 1500–2000 K at pressures higher than 35 GPa for at least 20 min. Laser heating was conducted at MIT, APS, and ALS. The samples were also scanned with the laser before each diffraction measurement in order to anneal the deviatoric stresses.

One of the key requirements for the determination of EOS is the accuracy of the pressure scale. Recent studies have shown that the popular X-ray pressure scales, such as Pt, Au, and MgO, are not consistent with each other (Irifune et al., 1998; Shim et al., 2001a; Fei et al., 2004; Dewaele et al., 2004; Hirose et al., 2006). Although less discrepancy exists among the different Pt scales (Jamieson et al., 1982; Holmes et al., 1989), the existing Pt scales are constrained only by shock-wave measurements in which the temperature effect is difficult to separate. The EOS of Au has been much more extensively studied (e.g., Takemura, 2001; Shim et al., 2002; Dewaele et al., 2004; Tsuchiya, 2003; Akahama et al., 2002; Fei et al., 2004). However, the existing Au scales predict pressures that differ by as much as 20 GPa at 1.2 Mbar. Yet, as pointed out by Jamieson et al. (1982), Au is preferred to Pt as a pressure scale due to its higher compressibility. In addition, Au can couple with infrared laser beams for heating like Pt. In this study, we use the Au scales (Tsuchiya, 2003; Dewaele et al., 2004) which are known to be more consistent with the Pt scales (Jamieson et al., 1982; Holmes et al., 1989) in order to facilitate the comparison of our data with previous X-ray studies as most of them used the Pt scales.

3. Result

In order to synthesize the Pv phase at the stable P–T conditions, we compressed the starting materials directly to 35–50 GPa. Synthesis of the Pv phase was confirmed during or after heating at 2000 K (Fig. 1). The diffraction lines from the Pv phase are fit well to an orthorhombic unit cell (space group: *Pbnm*). The Pv phase was observed up to 108 GPa, confirming its stability in the lower mantle (Knittle and Jeanloz, 1987; Serghiou et al., 1998; Shim et al., 2001b).

The postperovskite (PPv) transition has been reported at 100–120 GPa in $(Mg,Fe)SiO_3$(Murakami et al., 2004; Mao et al., 2005; Shieh et al., 2006; Hirose et al., 2006; Shim et al., 2008). Furthermore, it has been shown that Fe does not partition into Pv and PPv with equal amounts (Murakami et al., 2005; Kobayashi et al., 2005). Therefore, we exclude data points with any sign of the PPv transition. It is notable that in our measurements on $x_{Fe} = 15$ mol% the PPv transition was detected above 110 GPa after heating. If thermal pressure is included, the transition pressure would be approximately 120 GPa, which is more consistent with a small effect of Fe on the PPv transition as reported by Hirose et al. (2006).

For some samples, we observed a weak diffraction line at 2.6–2.8 Å which has been also documented in previous measurements (e.g., O'Neill and Jeanloz, 1994). In diffraction images, the line consists of only a few dots indicating that the diffraction line is from a highly preferred oriented phase. This line can be assigned to the most intense line of stishovite (or $CaCl_2$-type SiO_2), although it is the only line that can be uniquely assigned to SiO_2. If the appearance of SiO_2 would be a result of $(Mg,Fe)SiO_3 \rightarrow (Mg,Fe)O + SiO_2$, we should have seen lines from Fp. However, we did not observe any lines that can be exclusively assigned to Fp.

This line was more frequently observed in the Fe-bearing samples. McCammon (1997) reported that significant amount of Fe is Fe^{3+} in $(Mg,Fe)SiO_3$-Pv synthesized from Fe^{3+}-free starting materials. Frost et al. (2004) proposed that Fe^{3+} in $(Mg,Fe)SiO_3$-Pv is due to a charge disproportionation ($3Fe^{2+} \rightarrow 2Fe^{3+} + Fe^0$). Therefore, some amount of SiO_2 could form through this reaction. However, we could not detect any line which can be assigned to metallic Fe.

This line was also observed in one of the two different samples of Mg endmember, although the intensity is very low (Fig. 1b). The Pv phase in Fig. 1b was synthesized at 42 GPa. When it was synthesized, we found the 2.8 Å peak. Therefore, the peak observed at 89 GPa can be from a small amount of SiO_2 formed during synthesis at low pressure. However, in the run where Pv was first synthesized at 78 GPa, we did not observe the 2.8 Å peak.

In a separate run, we first synthesized pure Pv without the 2.8 Å line at 54 GPa (Fig. 1a) and then heated while the sample was decompressed. The 2.8 Å peak appeared when the sample was heated at 25 GPa. This observation may indicate that SiO_2 may form below 42 GPa in $MgSiO_3$. If this is the case, $MgSiO_3$-Pv synthesized at low pressure may have some amount of defects in the structure. Interestingly, the P–V relation measured during the decompression is distinct from that at higher pressures. This could also be due to the fact that we did not anneal the sample during decompression in order to prevent back transformation to low-pressure phases.