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High-pressure X-ray diffraction and X-ray emission studies on iron-bearing silicate perovskite under high pressures

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Iron-bearing silicate perovskite is believed to be the most abundant mineral of the Earth's lower mantle. Recent studies have shown that Fe^{2+} exists predominantly in the intermediate-spin state with a total spin number of 1 in silicate perovskite in the lower part of the lower mantle. Here we have measured the spin states of iron and the pressure–volume relation in silicate perovskite $[(\text{Mg}_{0.6}, \text{Fe}_{0.4})\text{SiO}_3]$ at pressure conditions relevant to the lowermost mantle using *in situ* X-ray emission and X-ray diffraction in a diamond cell. Our results showed that the intermediate-spin Fe^{2+} is stable in the silicate perovskite up to ~ 125 GPa but starts to transition to the low-spin state at approximately 135 GPa. Concurrent X-ray diffraction measurements showed a decrease of approximately 1% in the unit cell volume in the silicate perovskite $[(\text{Mg}_{0.6}, \text{Fe}_{0.4})\text{SiO}_3]$, which is attributed to the intermediate-spin to the low-spin transition. The transition pressure coincides with the pressure conditions of the lowermost mantle, raising the possibility of the existence of the silicate perovskite phase with the low-spin Fe^{2+} across the transition from the post-perovskite to the perovskite phases in the bottom of the D'' layer.

Keywords: silicate perovskite; electronic spin transition; X-ray emission; equation of state; high pressure

1. Introduction

Based on a pyrolitic compositional model [1], the Earth's lower mantle consists of $\sim 33\%$ (by weight) ferropericlase $[(\text{Mg}, \text{Fe})\text{O}]$ and $\sim 62\%$ aluminous silicate perovskite $[\text{Al}-(\text{Mg}, \text{Fe})\text{SiO}_3]$, together with $\sim 5\%$ calcium silicate perovskite (CaSiO_3). Recent studies showed that silicate perovskite transforms to a post-perovskite structure just above the core–mantle region, the D'' layer [2]. Current consensus for the iron abundance and valence states in the lower-mantle minerals is that iron exists mainly as ferrous iron (Fe^{2+}) with a concentration level of approximately 20% ($\text{Fe}/(\text{Fe} + \text{Mg})$) in ferropericlase, whereas iron exhibits two main valence states, Fe^{2+} and

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ferric iron (Fe^{3+}), with a total concentration level of approximately 10% in silicate perovskite [3]. Enrichment of iron in silicate perovskite and post-perovskite may occur at the core–mantle boundary region [4]. Since silicate perovskite is the most abundant mineral in the lower mantle and perhaps at the bottom of the D'' layer [5], understanding the electronic spin and valence states of iron in perovskite at relevant pressure–temperature conditions of the lower mantle is of great importance to the deep-Earth research.

Electronic spin-pairing transitions of Fe^{2+} and/or Fe^{3+} have been recently reported to occur in iron-bearing silicate perovskite using X-ray emission spectroscopy (XES) [6–9], Mössbauer spectroscopy [8–11] and theoretical calculations [12–15]. Though these transitions appear to be more complex than that in ferroperricite and are likely due to the low-symmetry oxygen ligand field in perovskite [16], the consensus on recent experimental results is that a high-spin to an intermediate-spin transition of Fe^{2+} in perovskite occurs at the top of the lower mantle and the intermediate-spin Fe^{2+} remains stable throughout the bulk of the lower mantle [9,11]. Fe^{2+} in silicate post-perovskite is also observed to be in the intermediate-spin state under relevant pressure–temperature conditions of the lowermost mantle [9]. There is also some experimental evidence for the occurrence of a low-spin Fe^{2+} in the silicate perovskite [$(\text{Mg}_{0.9},\text{Fe}_{0.1})\text{SiO}_3$] at ~ 120 GPa [6].

The spin transition of Fe^{2+} results in significant changes in density, incompressibility, sound velocities, radiative thermal conductivity and electrical conductivity in lower-mantle ferroperricite [16–23]. In particular, a density increase of ~ 3 –4% is observed across the high-spin to low-spin transition in ferroperricite at ~ 50 GPa [16–20]. However, the effect of the spin transition on the pressure–volume (P – V) relation of silicate perovskite remains largely unknown. In order to understand the interplay between the iron spin states and the equation of state (EoS) of the silicate perovskite, here we have conducted *in situ* XES and X-ray diffraction experiments on silicate perovskite [$(\text{Mg}_{0.6},\text{Fe}_{0.4})\text{SiO}_3$] in a laser-heated diamond-anvil cell (DAC). XES spectra are used to derive the average spin moment of the sample, whereas concurrent X-ray diffraction patterns permit the evaluation of the influence of the iron spin states on the density of the silicate perovskite at high pressures.

2. Experiments

The starting samples, polycrystalline enstatite [$(\text{Mg}_{0.6},\text{Fe}_{0.4})\text{SiO}_3$], had been characterized and used in a previous study [9]. The high iron content in the sample allowed us to collect the XES spectra within a reasonable time frame and to enhance the compositional effect on the unit cell volume of the silicate perovskite. Mössbauer analyses of the starting sample showed that iron is mainly Fe^{2+} in the high-spin state and there is no evidence of Fe^{3+} in the sample [9]. Samples approximately 15 μm thick and 40 μm in diameter were loaded into DACs with 100–300 μm bevel diamonds, Be gaskets of 3 mm in diameter and cubic BN gasket inserts. Samples were sandwiched between dried NaCl layers in the DACs, and the NaCl was used as the thermal insulators, pressure medium and pressure calibrant [24] (Figure 1). Details of the sample preparation and syntheses can be found elsewhere [9].

In situ high-pressure XES and X-ray diffraction experiments were conducted at the GeoSoilEnviroCARS sector of the Advanced Photon Source (APS), Argonne National Laboratory (ANL) using a Rowland circle spectrometer configured vertically around the double-sided laser-heating system [9,25,26]. Two enstatite samples in the DACs were compressed to approximately 110 GPa and laser-heated at approximately 2000 K for at least 3 h to be fully transformed to the perovskite phase. Two diode-pumped ytterbium infrared fiber lasers were focussed down to flat-top shapes of 25 μm in diameter at the sample position and were used to laser-heat the sample from both sides

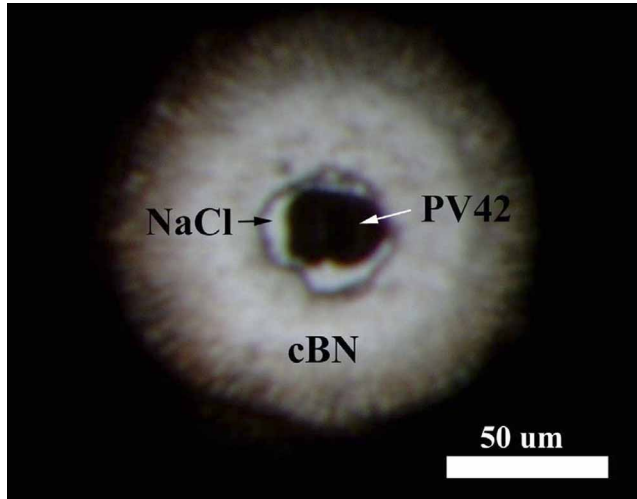


Figure 1. Image of the silicate perovskite (PV) $[(\text{Mg}_{0.6}, \text{Fe}_{0.4})\text{SiO}_3]$ sample at 115 GPa and 300 K. The image was taken in a transmitted light after the sample had been continuously laser-heated up to approximately 2000 K for a few hours. Cubic boron nitride (cBN) was used as the gasket insert with the Be gasket in order to maintain a sufficient sample thickness for laser-heating XES experiments at high pressure–temperature conditions over an extended period of time. The sample was sandwiched between two thin NaCl layers of $\sim 5 \mu\text{m}$ in the DAC, which served as the pressure calibrant [24] and thermal insulator.

of the DAC [26]. A monochromatic X-ray beam of 14 keV was focussed down to approximately $5 \mu\text{m}$ in diameter at the sample position in the XES experiments, whereas an X-ray source with a wavelength of 0.4959 \AA (approximately 25 keV) was used for the diffraction experiments by tuning the monochromatic X-ray beam from 14 to 25 keV [25]. The Fe $K\beta$ XES spectra were collected by a silicon detector through the Be gasket and a Si analyzer in the Rowland circle geometry, and the diffraction patterns were collected by a CCD (MAR165). A number of reference XES spectra, including high-spin enstatite and perovskite $[(\text{Mg}_{0.9}, \text{Fe}_{0.1})\text{SiO}_3]$, low-spin FeS_2 at ambient conditions and low-spin amorphous enstatite at 115 GPa, were collected and used for XES data analyses.

3. Results and discussion

Two silicate perovskite samples were synthesized at approximately 110 GPa and used for the *in situ* XES and X-ray diffraction experiments. X-ray diffraction patterns confirmed the occurrence of the silicate perovskite, without any sign of other phases (except the NaCl pressure standard) (Figure 2). Using the same starting sample and synthesis procedure, our previous study showed that iron exists predominantly as Fe^{2+} in the intermediate-spin state with a total spin number of 1, based on both XES and synchrotron Mössbauer analyses [9]. One of the samples was then used for XES and X-ray diffraction experiments in compression to 135 GPa and another for decompression measurements to 60 GPa.

Together with the reference XES spectra, the XES spectra of the samples were used to quantitatively derive the total local spin number of iron using integrated absolute difference (IAD) analysis [27]. The peak position of the Fe $K\beta$ peak, which is independent of the reference spectra and the IAD analysis, provides additional evidence for the total spin number of iron in the samples [27]. These analyses showed that the average spin momentum of iron is one in the samples at

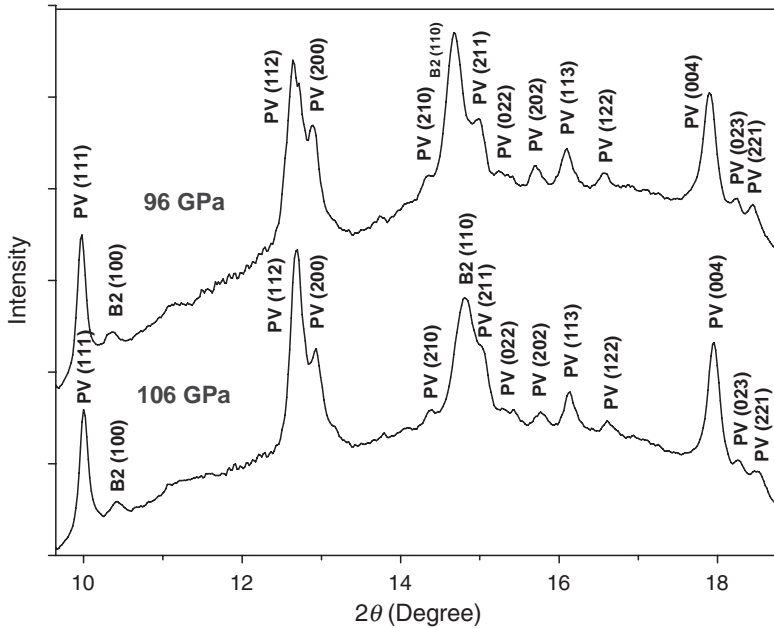


Figure 2. Representative X-ray diffraction patterns of the silicate perovskite (PV) $[(\text{Mg}_{0.6},\text{Fe}_{0.4})\text{SiO}_3]$ at high pressures and 300 K. The diffraction patterns were integrated with the FIT2D program, and the backgrounds were not subtracted. PV, perovskite; B2, NaCl thermal insulator and pressure calibrant in the B2 structural phase. Unit cell parameters of the perovskite were calculated and plotted in Figure 5. An X-ray source with a wavelength of 0.4959 \AA was used for the diffraction experiments.

approximately 116 GPa (Figures 2 and 3), consistent with previous studies that showed the occurrence of the predominant intermediate-spin Fe^{2+} in the silicate perovskite [9,11]. The derived spin number of iron increases from 1 at ~ 116 GPa to 1.24 at ~ 60 GPa, indicating some of the Fe^{2+} transitions to the high-spin state while other Fe^{2+} remains in the intermediate-spin state. A significant drop in the average spin momentum is observed to occur at approximately 135 GPa (Figure 4). Analyses of the peak position of the Fe $K\beta$ peak showed an energy shift of 0.4 eV from 116 to 135 GPa [9]. We note that an energy decrease of approximately 1.6 eV in the main $K\beta$ peak was observed across the high-spin to low-spin transition in ferroperricite [16,17]. Therefore, we conclude that the decrease in the average spin momentum indicates that approximately 50% of the Fe^{2+} in silicate perovskite transitions to the low-spin state at 135 GPa.

Concurrent X-ray diffraction measurements are used to study the P - V relation in the sample from 60 to 135 GPa (Figure 5). Within experimental uncertainties, the compression curve of our samples (with 40% iron ($\text{Fe}/(\text{Fe} + \text{Mg}))$) between 95 and 125 GPa, where the iron is predominantly in the intermediate-spin state (Figure 4), behaves similarly to that of iron-free and iron-bearing (up to 15%) silicate perovskite [28]. However, the P - V relation below 95 GPa deviates from this compression behavior, which could be due to the unreleased stress in the sample. Therefore, the decompression data below 95 GPa were not used for further EoS analyses. Because of the limited pressure range, our data do not permit us to derive reliable EoS parameters of the silicate perovskite. Since previous studies showed no resolvable differences in the EoS between Fe-bearing (up to 15%) and Fe-free PV to 100 GPa [28], we instead used the literature K_0 value of 256 GPa with a fixed K'_0 of 4 to construct a reference P - V relation for the $(\text{Mg}_{0.6},\text{Fe}_{0.4})\text{SiO}_3$ perovskite using the Birch-Murnaghan EoS [28,29] (Figure 5).

Comparison between the reference EoS and the experimental data shows that at 135 GPa the unit cell volume of $(\text{Mg}_{0.6},\text{Fe}_{0.4})\text{SiO}_3$ perovskite dropped to a value similar to that of

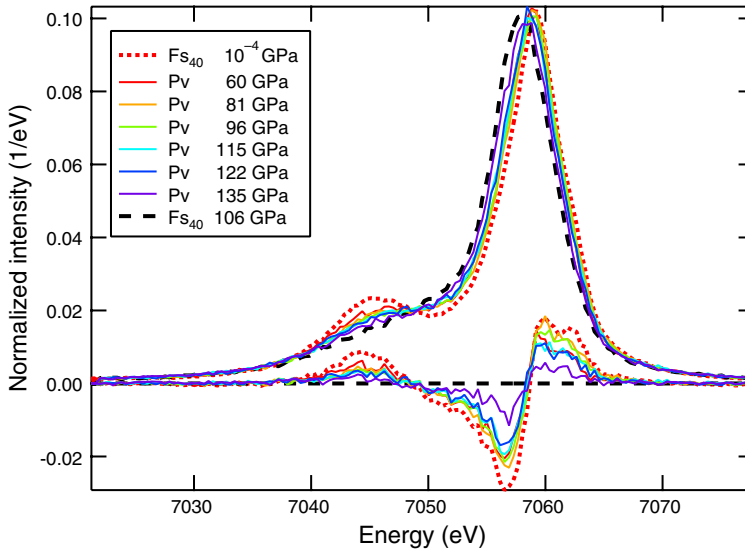


Figure 3. Representative X-ray emission spectra of iron in perovskite at high pressures. Similar to our previous study [9], reference spectra of the high-spin enstatite at ambient pressure (labeled as FS_{40} in red dotted line) [$(Mg_{0.6}, Fe_{0.4})SiO_3$] and the low-spin amorphous enstatite at 106 GPa [$(Mg_{0.6}, Fe_{0.4})SiO_3$] (black dotted line) are used for the integrated absolute difference analysis and to derive the average spin number of Fe^{2+} [27] (Figure 4). Energy shift in the main $K\beta$ emission peak is also used to derive the total spin number. Differences from the low-spin line shape are shown below the spectra (color online).

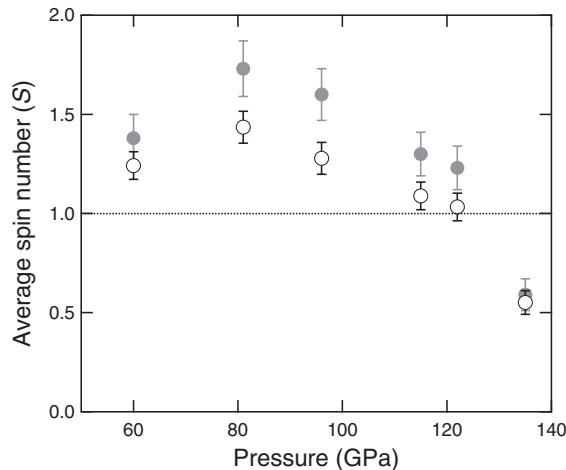


Figure 4. Average spin number of Fe^{2+} in silicate perovskite at high pressures. The average spin number (S) is derived from the integrated absolute difference (IAD) analysis of the XES spectra of the samples using high-spin enstatite (FS_{40}) at 1 bar and amorphous, low-spin enstatite (FS_{40}) at 106 GPa as the reference spectra (black symbols) or the shift of the $K\beta$ peak position (gray symbols) (see Figure 3 for details).

$(Mg_{0.85}, Fe_{0.15})SiO_3$. This visible decrease in the unit cell volume (approximately 1%) (Figure 5) took place at the same pressure at which XES analyses showed a significant drop in the total spin momentum (Figures 3 and 4). These XES and X-ray diffraction results thus strongly suggest that an intermediate-spin to low-spin transition of Fe^{2+} in silicate perovskite occurs at approximately 135 GPa and results in a volume collapse; a complete transition to the low-spin state should have even higher effect on the P - V relation of perovskite, with a likely 2% reduction in volume.

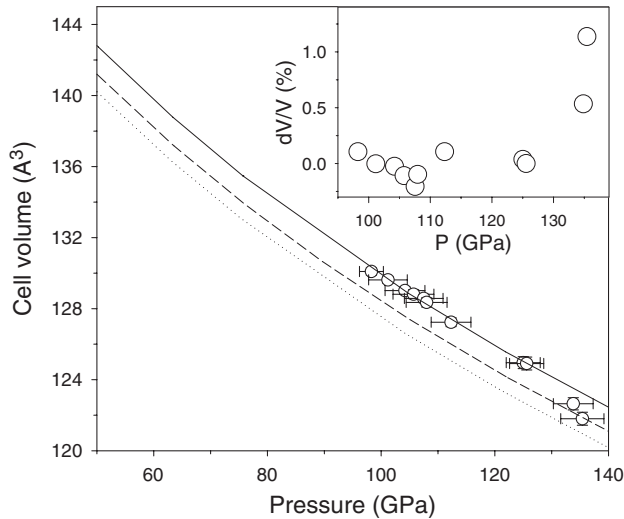


Figure 5. Unit cell volume of the silicate perovskite $[(\text{Mg}_{0.6}, \text{Fe}_{0.4})\text{SiO}_3]$ at high pressures. Our results (open circles) are compared with previous studies [28] on silicate perovskite with MgSiO_3 composition (dotted line) and $(\text{Mg}_{0.85}, \text{Fe}_{0.15})\text{SiO}_3$ composition (dashed line). The K_0 of 256 GPa with a fixed K'_0 of 4 are used to construct a reference P - V relation using the Birch–Murnaghan EoS [29] (black solid line); the fitted V_0 of 165 \AA^3 is consistent with the literature value [28] after taking the compositional effect into account. Insert: percentage of the volume difference calculated using the calculated EoS (black solid line) as the reference.

Addition of iron into MgO is well known to increase the density and unit cell volume in the high-spin ferropervicite under ambient conditions [30]. The electronic spin-pairing transition results in a smaller ionic radius of iron [31] and thus a bulk volume reduction of 2–4% in ferropervicite containing 17–20% iron ($\text{Fe}/(\text{Fe} + \text{Mg})$) as seen in recent high-pressure X-ray diffraction studies [16–21,25]. The spin transition thus enhances the compositional effect of the addition of FeO on the density of $(\text{Mg}, \text{Fe})\text{O}$; the volume collapse of 2–4% across the spin transition is equivalent to 3–5% variation in iron content in ferropervicite [16–21,25].

Our study indicates that the intermediate-spin to low-spin transition of Fe^{2+} has an appreciable effect on the volume of iron-bearing silicate perovskite (with 40% iron). The effect of the addition of iron to MgSiO_3 is to increase the density as well as unit cell volume in the silicate perovskite [28]. The spin transition, however, partially offsets the increase in unit cell volume and therefore enhances the compositional effect on density. The observed transition pressure of approximately 135 GPa coincides with the pressure conditions at the lowermost mantle. A double-crossing transition model, transition from perovskite to post-perovskite and then to perovskite, has been recently proposed to occur at the bottom of the D'' region in order to account for double seismic discontinuities observed in the lowermost part of the mantle [5]. When we take this model into account, our study here raises the possibility that silicate perovskite containing the low-spin Fe^{2+} may exist at the bottom of the D'' layer. Similar to the studies on the spin transition in ferropervicite, future multidisciplinary high pressure–temperature studies on silicate perovskite with various iron contents are needed to decipher the effects of the spin transition on physical, chemical and rheological properties of the deep lower mantle.

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