



Magnesium silicate perovskite and effect of iron oxidation state on its bulk sound velocity at the conditions of the lower mantle



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ABSTRACT

A comprehensive understanding of the iron- and aluminum-bearing magnesium silicate perovskite (Pv) crystal structure and its evolution under pressure is vital for our understanding of the deep Earth's lower mantle physics and chemistry as well as for correct interpretation of seismic data. In this study we investigate material with composition relevant to subducted oceanic crust, by means of single crystal X-ray diffraction at high pressure and high temperature conditions. We found that (a) there is no spin state crossover in ferric iron occupying the bicapped trigonal prism (“A”) crystallographic site, and (b) ferric iron does not enter the octahedral (“B”) site at any conditions of our experiments. We constrain the thermal equation of state for Pv with variable content of iron and aluminum. For compositions of Pv relevant for Earth's lower mantle, variation of $\text{Fe}^{3+}/\Sigma\text{Fe}$ can lead to significant changes of Pv bulk sound velocity (over 1%), demonstrating the importance of iron oxidation state to the interpretation of seismic tomography data.

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1. Introduction

Iron- and aluminum-bearing magnesium silicate perovskite ($\text{Mg, Fe}(\text{Si, Al})\text{O}_3$ (FeAlPv) is believed to be the most abundant phase of the Earth's lower mantle and thereby of the entire Earth. For planetary geophysics and geochemistry, the importance of iron (~5–15 mole % for the Earth's lower mantle composition) goes beyond the role of an ordinary impurity. The valence and spin state of iron in major phases of the lower mantle, namely, silicate perovskite and ferropervicite (Fp), are key factors affecting density, sound velocity, rheology, heat transfer, element partitioning, oxygen fugacity, and ultimately the dynamics of the Earth's mantle (Irifune et al., 2009; Lin et al., 2005; McCammon, 2005; Wicks et al., 2010; McCammon et al., 2013; Lin et al., 2013).

The structure of FeAlPv is different from the ideal cubic ABX_3 perovskite (space group $Pm\bar{3}m$). FeAlPv has space group $Pbnm$ (Horiuchi et al., 1987) (see Supplementary Fig. S1) and the struc-

ture comprises a three-dimensional network of tilted corner-sharing octahedra (B-sites). Cavities between the octahedra form sites in the shape of bicapped trigonal prisms (A-sites) which can be occupied by Mg_A^{2+} or $\text{Fe}_A^{2+/3+}$ (Horiuchi et al., 1987; McCammon et al., 1992). The smaller octahedral B-sites can be occupied by Si_B^{4+} , Al_B^{3+} or probably Fe_B^{3+} cations. It is generally accepted that the unusual crystal chemistry of silicate perovskite is the underlying reason for the stability of ferric iron in Pv, even under the reducing conditions of the lower mantle (Lauterbach et al., 2000; McCammon, 2005).

While the implications of different spin and valence states of iron in Fp and Pv for geophysics and geochemistry are still intensively debated, there is an emerging consensus that spin-state crossover of ferrous iron (high spin to intermediate spin state) has a negligible effect on the compressibility of the perovskite phase supported by the experimental evidence (Lundin et al., 2008; McCammon et al., 2008; Boffa Ballaran et al., 2012). It should be noted, that most recent first principle calculations challenge the possibility for this transition to occur at conditions of the lower mantle (Hsu et al., 2010, 2011; Metsue and Tsuchiya, 2012). Still, any changes of $\text{Fe}_{A/B}^{3+}$ spin state should cause a noticeable volume reduction accompanied by significant softening of the bulk modu-

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lus (Lin et al., 2013; McCammon et al., 2013), and ultimately seismic velocity anomalies in the lower mantle (Houser et al., 2008; Stackhouse et al., 2007). However experimental results regarding the effect of ferric iron and aluminum and their implications for the lower mantle are very limited.

The lower mantle perovskite phase is believed to contain more than half of its iron as ferric (Fe^{3+}), which can be incorporated through different substitution mechanisms, for example by charge coupling with Al_B^{3+} (FeAl coupling) or with Fe_B^{3+} (FeFe coupling). The addition of aluminum stabilizes Fe^{3+} in FeAlPv and leads to higher values of the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio (Lauterbach et al., 2000). For Al-free Pv, theoretical studies have predicted high-spin (HS) to low-spin (LS) crossover of Fe_A^{3+} with spin number S changing from 5/2 to 1/2 at 105–130 GPa (Stackhouse et al., 2007). HS–LS spin crossover of Fe_B^{3+} was estimated in the same study to occur at 60–150 GPa. More recent calculations report that Fe_B^{3+} undergoes HS–LS crossover at 40–70 GPa, while Fe_A^{3+} remains in the HS state at all pressures relevant for the Earth's lower mantle (Hsu et al., 2011). In contrast to theoretical predictions, some experimental data have suggested that the transition of Fe_A^{3+} to the LS state is complete by 70 GPa (Jackson et al., 2005). A more recent combined X-ray powder diffraction, nuclear forward scattering (NFS), and X-ray emission spectroscopy (XES) study of iron-containing Pv with all iron inferred to be ferric reported that the abundance of LS Fe_B^{3+} gradually increased above 40 GPa, with all Fe_B^{3+} being in the LS state above 50–60 GPa (Catalli et al., 2010). The same study suggested that Fe_A^{3+} remains in the HS state up to at least 136 GPa. Among the uncertainties, however, is the effect of Al, which is known to be present in lower mantle perovskite. The presence of aluminum should affect the elastic properties and may lead to additional effects, for example, $\text{Fe}_A^{3+} \leftrightarrow \text{Al}_B^{3+}$ redistribution at high pressure and high temperature (Catalli et al., 2010, 2011).

In order to evaluate the influence of ferric iron (FeAl coupling) on the structure and elastic properties of lower mantle perovskite at conditions along the lower mantle geotherm, we studied $\text{Mg}_{0.60}\text{Fe}_{0.40}\text{Si}_{0.63}\text{Al}_{0.37}\text{O}_3$ synthesized in a multi-anvil apparatus at 25 GPa and 1300 K (see Methods).

2. Methods

2.1. Synthesis and characterization

The perovskite sample was synthesized from a ground mixture of oxides and hydroxides (13.6 wt% Al_2O_3 , 21.6 wt% Fe_2O_3 , 33 wt% SiO_2 , 31.8% $\text{Mg}(\text{OH})_2$) with a bulk composition similar to that used in experiments on mid-ocean ridge basalt compositions. The prepared mixture was loaded into a platinum capsule which was welded closed and placed into an octahedral multi-anvil pressure assembly together with a W_{97}Re_3 – $\text{W}_{75}\text{Re}_{25}$ thermocouple and LaCrO_3 furnace. The assembly was compressed in a multi-anvil press to approximately 25 GPa and then heated to 1300 °C for 30 minutes. The run products comprised magnesium silicate perovskite co-existing with quenched crystallized melt and small (<10 μm) crystals of an Al-rich hydrous phase. The composition of several perovskite crystals was determined by electron microprobe analysis to be the following (wt%): 16.4 (3)% Al_2O_3 , 26.1 (4)% FeO, 33.6 (5)% SiO_2 , 21.6 (3)% MgO. We determined the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio to be 0.93 ± 0.3 using Mössbauer spectroscopy on a powdered sample from the same experimental charge. The crystallographic site occupancy of iron was derived from structural refinements of single-crystal intensity data collected at ambient conditions using an XCalibur single-crystal X-ray diffractometer equipped with a Mo $K\alpha$ radiation and a CCD detector and provided unambiguous evidence that ferric and ferrous iron ions occupy exclusively the A-sites (Fig. S1).

2.2. High pressure X-ray diffraction

Small single crystals of the prepared material ($\sim 10 \times 15 \times 5 \mu\text{m}^3$) were loaded together with ruby chips (pressure marker at ambient temperature) into the sample chambers of membrane diamond anvil cells (DACs) available at the European Synchrotron Radiation Facility (ESRF). We installed Boehler–Almax design diamonds into Chervin-type DACs (Chervin et al., 1995). This setup allows to collect high pressure data in range of $2\theta \approx 60^\circ$. The sample chamber was prepared by drilling a hole in a pre-indented rhenium gasket, and the hole was filled with the sample material, small spheres of ruby for ambient temperature pressure measurement, and the quasi-hydrostatic pressure medium, Ne, which was also used as thermal insulation during laser annealing as well as an independent ambient and high-temperature pressure standard (Fei et al., 2007a).

The single crystal X-ray diffraction experiments were carried out at beamline ID09a, ESRF, Grenoble, France (Merlini and Hanfland, 2013). We used a MAR555 flat panel detector installed at the beamline, and the X-ray wavelength was 0.415 Å. At ambient temperature the data were collected during ω rotation scans of $\pm 30^\circ$ with a 0.5° step. Due to space restrictions imposed by the beamline, the limits of the ω rotation scans collected at high temperature were lower ($-28 \rightarrow 20^\circ$). However, in order to improve the number of unique reflections from the sample and, consequently, the quality of the data, we collected diffraction at high temperature in two different sample orientations by rotating the DAC by 90° along the X-ray beam propagation axis. The 2D diffraction images (Fig. S1.1) were first analyzed using Oxford Diffraction CrysAlis software (CrysAlis RED, 2006) with consequent structural refinements of integrated intensities using SHELXL-97, WinGX version (Farrugia, 1999; Sheldrick, 2008). Atomic scattering factors were used and all atoms were refined isotropically. The occupancy of Mg at the A site was constrained to be equal to the value obtained from the chemical analysis, whereas the occupancy of Fe at the A site and of Si at the B was allowed to vary. This refinement procedure was chosen in order to investigate the variation of mean electronic number at the two sites which give insights on possible Al/Fe disorder at high-pressure and temperature. The parameters obtained from the structural refinements are summarized in Table T1.

In order to create high temperature conditions, we used an enhanced version of the portable laser setup described previously and adjusted for the requirements of ID09a (Dubrovinsky et al., 2010, 2009). The setup consisted of the SPI laser system (SPI100, wavelength 1064 nm, 100 W) coupled by an optical fiber to the UniHead system, which allows simultaneous visual observation of the sample, laser heating and evaluation of temperature. In order to ensure homogeneous heating of the small single crystal samples, a laser spot with a diameter of about 50 μm was used. In order to guarantee homogeneous heating we flattened the power profile of the laser beam using a special optical device (π -shaper) mounted on the UniHead. As was shown previously (Sinmyo and Hirose, 2010), homogeneous heating prevents Soret diffusion effects and formation of chemical heterogeneities. Thermal radiation coming from the heated sample was collected by an Ocean Optics QE65000 spectrometer, and the resulting spectra were fitted to the Planck radiation function. Laser heating was conducted in continuous laser operation mode, and prior to data collection, the samples were annealed at 1100–1300 K for ~ 10 –15 minutes at each pressure point. Duration of data collection with *in situ* laser heating was ~ 10 –20 minutes.

Additional information on the data analysis can be found below.

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