



(Fe, Al)-bearing post-perovskite in the Earth's lower mantle



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ABSTRACT

The combined effects of Fe and Al on the electronic spin and valence states as well as the equation of state (EoS) of post-perovskite have been investigated using synchrotron X-ray diffraction and Mössbauer spectroscopy in high-pressure diamond anvil cells. Two post-perovskite samples ($\text{Mg}_{0.6}\text{Fe}_{0.15}\text{Al}_{0.5}\text{Si}_{0.75}\text{O}_3$ and $\text{Mg}_{0.66}\text{Fe}_{0.13}\text{Al}_{0.28}\text{Si}_{0.86}\text{O}_3$) were synthesized at approximately 165 GPa and 2200–2500 K, and were subsequently investigated for these properties at 114–170 GPa and 300 K. Analyses of the high-pressure Mössbauer spectra show that Fe^{2+} and Fe^{3+} occupy the large bipolar prismatic sites in both of our samples and remain in the high-spin state at ~165–168 GPa and 300 K. Combining the Mössbauer results with the obtained pressure–volume relationship from X-ray diffraction, we have found that the unit cell volume of post-perovskite can be significantly affected by the spin and valence states of Fe and the Al substitution. $\text{Mg}_{0.6}\text{Fe}_{0.15}\text{Al}_{0.5}\text{Si}_{0.75}\text{O}_3$ -PPv with the predominantly high-spin Fe^{2+} (~95%) and a greater amount of Al has a unit cell volume similar to that of $\text{Mg}_{0.66}\text{Fe}_{0.13}\text{Al}_{0.28}\text{Si}_{0.86}\text{O}_3$ -PPv in which ~65% of Fe is in the high-spin Fe^{3+} state. Our results are used together with previous results regarding the EoS parameters in Fe-bearing perovskite and post-perovskite to model the density and bulk sound velocity variation between perovskite and post-perovskite in the D'' layer, in which the enrichment of Fe and Al can produce an increase in density but substantially reduce the bulk sound velocity across the phase transition. That is, the combined effect of Fe and Al leads to an anti-correlation between the enhanced density and the reduced bulk sound velocity at the pressure condition of the lowermost mantle. Our results indicate that (Fe, Al)-rich silicate post-perovskite existing in the D'' region would be shown as a relatively high-density and low-velocity region in deep-mantle seismic observations.

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1. Introduction

The bottom 200–300 km of the lower mantle above the core-mantle boundary (CMB), which is typically referred as the D'' layer and characterized by a discontinuous increase in velocity, is one of the most seismically complex regions in the Earth (e.g. Garnero, 2000; Lay and Helmberger, 1983; van der Hilst et al., 2007). Various velocity anomalies, such as the ultra-low velocity zones (Garnero and Helmberger, 1995; Wen and Helmberger, 1998; Williams and Garnero, 1996), anomalous velocity gradient (e.g. He et al., 2006; Lay et al., 1998), velocity discontinuity (e.g. Sidorin et al., 1999; van der Hilst et al., 2007), and strong seismic velocity anisotropies (e.g. Lay et al., 1998; Panning and Romanowicz,

2004), have been identified in the region. In 2004, the discovery of the Mg-silicate perovskite (Pv) to post-perovskite (PPv) phase transition increased our understanding of the unusual characteristics of the D'' layer (Murakami et al., 2004; Oganov and Ono, 2004). In the last decade since its discovery, both experimental and theoretical studies have reported a wealth of exciting results pertaining to the physical properties of PPv, greatly contributing to our understanding of the structure, composition, and dynamic behavior of the lowermost mantle (e.g. Cobden et al., 2012; Dobson et al., 2013; Hirose, 2006; Lay et al., 2006; Mao et al., 2006; Shieh et al., 2006; Shim, 2008; van der Hilst et al., 2007; Zhang et al., 2013).

Of particular importance is the equation of state (EoS) of (Fe, Al)-PPv at relevant pressure–temperature–composition conditions of the D'' layer, which can provide crucial constraints on the density (ρ), elasticity, and bulk sound velocity (V_ϕ) of the

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lowermost mantle. However, experimental studies on the compositional effect, including the addition of Fe and Al, on the EoS of Mg-silicate PPv have so far been limited due to the challenging experimental pressure and temperature conditions along with the technical capability to reliably determine the spin and valence states of iron (Catalli et al., 2010a; Guignot et al., 2007; Lin et al., 2008; Mao et al., 2006; Nishio-Hamane and Yagi, 2009; Shieh et al., 2006). In Al-free PPv, previous studies have focused on the EoS of PPv with Fe content $[\text{Fe}/(\text{Fe} + \text{Mg})]$ up to 40% (Catalli et al., 2010a; Guignot et al., 2007; Mao et al., 2006; Shieh et al., 2006). Addition of Fe has been found to greatly increase the density of PPv, yet has a negligible effect on the isothermal bulk modulus (K_T) and V_ϕ when the amount of Fe is less than 10% (Catalli et al., 2010a; Guignot et al., 2007; Shieh et al., 2006) (for a recent review, please see Lin et al., 2013). Mao et al. (2006), on the other hand, has shown that the presence of 40% Fe can significantly increase the K_T by 39% at a pressure of 125 GPa and 300 K. Since there are no compression data for PPv with an Fe content between 10% and 40%, the question on how the substitution of Fe in PPv starts to affect its K_T remains open.

Studies on the net effect of Fe and Al on the EoS of PPv are even more scarce (Nishio-Hamane and Yagi, 2009; Shieh et al., 2011). Shieh et al. (2011) worked on the pressure–volume (P – V) relationship of (Fe, Al)-bearing PPv in the pyrope–almandine composition system, showing a linear increase in density with Fe content; however, the combined effect of Fe and Al on the K_T and V_ϕ was not addressed in Shieh et al. (2011) because they focused on the stability of Al-bearing PPv with a great amount of Fe. Studies by Nishio-Hamane and Yagi (2009) on the EoS of $\text{Mg}_{0.85}\text{Fe}_{0.15}\text{Al}_{0.15}\text{Si}_{0.85}\text{O}_3$ –PPv showed a great decrease in the K_T and V_ϕ because of the presence of the FeSiO_3 and FeAlO_3 components.

More interestingly, the D'' layer has been proposed to be chemically heterogeneous in previous studies (e.g. Buffett et al., 2000; Dobson and Brodholt, 2005; Mao et al., 2006; Williams and Garnero, 1996). Enrichment of Fe in the D'' layer may be caused by interaction between the lowermost mantle and the outer core or the subduction of slabs with mid-ocean ridge basalt (MORB) (e.g. Dobson and Brodholt, 2005; Knittle and Jeanloz, 1989, 1991; Mao et al., 2006; McNamara and Zhong, 2005; Otsuka and Karato, 2012). In addition, sinking slabs can deliver a great amount of Al to the lower mantle through the aluminous phase with the Ca-ferrite structure (Funamori et al., 2000; Hirose et al., 1999; Kesson et al., 1994). Therefore, experimental constraints on the combined effect for the enrichment of Fe and Al on the EoS of PPv would significantly enhance our understanding of the chemical heterogeneity and velocity anomalies in the Earth's D'' layer.

Previous studies on the spin and valence states of Fe in PPv have shown that Fe^{3+} in the bipolar prismatic sites (Mg) stays in the high spin (HS) state at lower mantle pressures, whereas it transforms into the low spin (LS) state in the octahedral sites (Catalli et al., 2010a). In Al-free PPv, theoretical calculations showed that Fe^{3+} enters PPv through the Fe^{3+} – Fe^{3+} coupled substitution (Zhang and Oganov, 2006). The spin transition of Fe has been known to significantly affect the EoS of candidate lower-mantle minerals (e.g. Catalli et al., 2011; Chang et al., 2013; Fei et al., 2007b; Komabayashi et al., 2010; Li et al., 2004; Lin et al., 2005, 2013; Mao et al., 2011a, 2011b). The HS to LS transition of Fe^{2+} in ferroperrichite and Fe^{3+} in perovskite have been observed to abruptly decrease the unit cell volume associated with an increase in density (Komabayashi et al., 2010; Lin et al., 2013; Mao et al., submitted for publication). Spin transition of Fe has also been shown to cause an anomalous softening in the elasticity and sound velocities (Crowhurst et al., 2008; Marquardt et al., 2009; Wentzcovitch et al., 2009; Wu et al., 2013).

The effect of Fe spin transition on the EoS of PPv has been explored recently (Catalli et al., 2010a). It has been shown that the presence of Fe^{2+} increases the volume of PPv while the presence of the LS Fe^{3+} does not produce an observable effect on the volume of PPv and thus effectively increases the density of PPv (Catalli et al., 2010a). Theoretical calculations further indicate that the addition of Al can enhance the substitution of Fe^{3+} into PPv through the Fe^{3+} – Al^{3+} coupled substitution (Yu et al., 2012). Metastable LS Fe^{3+} could be present in the octahedral sites at high pressure–temperature conditions (Caracas, 2010; Hsu et al., 2012). However, thus far, there is only one experimental study on the spin and valence states of Fe in (Fe, Al)-bearing PPv using X-ray emission spectroscopy (XES) which suggested the presence of LS Fe^{3+} in the octahedral sites (Fujino et al., 2013). We note that X-ray emission spectroscopic data alone cannot be used to distinguish different valence states of Fe^{2+} and Fe^{3+} , and that the disappearance of the $K\beta'$ satellite peak in XES spectra can also be a result of pressure-induced spectral broadening effect (Mao et al., 2014). As such, the spin and valence states of Fe in (Fe, Al)-bearing PPv and their potential effects on the EoS of PPv remain unclear.

Here we have conducted high-pressure synchrotron Mössbauer spectroscopy (SMS) and X-ray diffraction (XRD) experiments on PPv in two distinct compositions ($\text{Mg}_{0.60}\text{Fe}_{0.15}\text{Al}_{0.5}\text{Si}_{0.75}\text{O}_3$ and $\text{Mg}_{0.66}\text{Fe}_{0.13}\text{Al}_{0.28}\text{Si}_{0.86}\text{O}_3$) at pressures up to 170 GPa. We used SMS results to provide crucial constraints on the spin and valence states of Fe in PPv, while using our XRD to decipher the combined effects of Al and Fe on the EoS of PPv at lowermost-mantle pressures. These results are modeled using the Birch–Murnaghan (BM) EoS to understand the combined effect of Al and Fe, and then to understand the seismic profiles and potential chemical heterogeneity in the D'' region.

2. Experimental details

^{57}Fe -enriched glass, $\text{Mg}_{0.66}\text{Fe}_{0.13}\text{Al}_{0.28}\text{Si}_{0.86}\text{O}_3$ (labeled as 0.28Al–PPv13 hereafter), and single-crystal ^{57}Fe -enriched pyrope, $\text{Mg}_{0.60}\text{Fe}_{0.15}\text{Al}_{0.5}\text{Si}_{0.75}\text{O}_3$ (labeled as 0.5Al–PPv15 hereafter), were used as the starting samples for the syntheses of PPv, respectively. The glass sample was synthesized from the powders of MgO , $^{57}\text{Fe}_2\text{O}_3$, Al_2O_3 and SiO_2 mixed in the appropriate ratios, where the enrichment of ^{57}Fe in the samples was greater than 95%. The chemical composition of the starting glass has been determined using the electron microprobe analyses, and the starting pyrope crystal was examined using XRD and electron microprobe analyses to determine the crystal structure and chemical composition (Mao et al., 2014). The same batch of pyrope crystals was also studied using SMS to investigate the spin and valence states of Fe from ambient conditions to high pressures and temperatures (Mao et al., 2014).

The starting samples were polished down to approximately 10 μm in thickness and subsequently cut into pieces of 25 μm in diameter. The sample disk was sandwiched between two dried NaCl layers of approximately 5 μm in thickness which was used as the pressure medium, pressure calibrant and thermal insulator (Fei et al., 2007a). Each sample assemblage was loaded into a symmetric diamond cell equipped with a pair of beveled diamonds of 75/300 μm in culet size and a pre-indented Re gasket with a hole of 40 μm diameter and 25 μm thickness. Each loaded sample was directly compressed to ~ 160 GPa at 300 K, and then laser heated at 2200–2500 K for approximately 14 h to fully transform the starting material to PPv at GSECARS of the Advanced Photon Source (APS), Argonne National Laboratory (ANL). The synthesized PPv samples were confirmed by XRD.

SMS measurements for the PPv samples were performed at HP-CAT of the APS, ANL using an X-ray beam with a 2 meV energy

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