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Discussion

Synthesis and equation of state of perovskites in the $(Mg, Fe)_3Al_2Si_3O_{12}$ system to 177 GPa

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ABSTRACT

Natural and synthetic pyrope–almandine compositions from 38 to 100 mol% almandine (Alm38–Alm100) were studied by synchrotron X-ray diffraction in the laser-heated diamond anvil cell to 177 GPa. Single-phase orthorhombic $GdFeO_3$-type perovskites were synthesized across the entire examined compositional range at deep lower mantle pressures, with higher Fe-contents requiring higher synthesis pressures. The formation of perovskite with Alm100 ($Fe_3Al_2Si_3O_{12}$) composition at 80 GPa marks the first observation of a silicate perovskite in a Fe end-member. Fe-enrichment broadens and lowers the pressure range of the post-perovskite transition for intermediate compositions such as Alm54, but the more Fe-rich Alm100-composition perovskite remains stable to pressures as high as 149 GPa. Volume compression data for the Alm54 and Alm100 compositions were fit to the Birch–Murnaghan equation of state. The compressibility of perovskites synthesized from compositions along the pyrope–almandine join is not strongly sensitive to Fe-content. The compression curves were smooth over the entire measured range, and no evidence for a volume anomaly associated with a spin transition was observed.

In the Earth's deep lower mantle, seismic imaging has identified regions of high density and low shear wave speed as possible thermochemical piles (Garnero and McNamara, 2008). These large low shear velocity provinces (LLSVPs) on the scale of ~1000 km (Ishii and Tromp, 2004; Trampert et al., 2004) may be sequestered primitive mantle (Lee et al., 2010) or stagnating Fe,Al-rich subducted slabs (Williams and Garnero, 1996; McNamara and Zhong, 2005). In order to evaluate which hypotheses match geophysical constraints on the properties of the LLSVPs, this study explores how variations in Fe and Al content affect stability and observable physical properties of silicates stable under deep mantle conditions.

Garnet is the major Al-bearing mineral of the upper mantle and transition zone and a useful starting material for investigating the incorporation of Fe and Al in lower mantle silicates (Kesson et al., 1995). At 37–40 GPa, pyrope ($Mg_3Al_2Si_3O_{12}$) garnet transforms to the dominant phase of the lower mantle, orthorhombic (Mg, Al)(Al, Si)O_3 perovskite ($GdFeO_3$-type, *Pbnm*, $Z=4$) (Liu, 1974; Irifune et al., 1996; Ito et al., 1998; Kubo and Akaogi, 2000). Almandine ($Fe_3Al_2Si_3O_{12}$) garnet, however, has not been observed to form perovskite; it breaks down to a mixture of stishovite, wüstite, and corundum at 20–21 GPa and 1200–1600 °C (Conrad et al., 1996; Akaogi et al., 1998). In a previous study of the pyrope–almandine (Pyr–Alm) system, samples were heated at 55–70 GPa and examined *ex situ* at ambient pressure and temperature (Kesson et al., 1995). Quench products for compositions up to 75 mol% almandine, Alm75, consisted of rhombohedral perovskites. More Fe-rich compositions including Alm100 were observed to break down to a mixture of perovskite and oxides. This is similar to the reported behavior of compositions in the (Mg, Fe)SiO_3 system; although perovskites with as much as 75% $FeSiO_3$ are stable at deep lower mantle pressures (Tateno et al., 2007; Dorfman et al., in press), perovskite has not been synthesized from $FeSiO_3$, which has instead been observed to dissociate to FeO and SiO_2 from 20 to 150 GPa and ~1800−2100 K (Ming and Bassett, 1975; Mao et al., 2004; Fujino et al., 2009). While the limits of the solubility of Fe and Al components into perovskite have been studied extensively at pressures below 50 GPa (Fei et al., 1996; Mao et al., 1997;

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Akaogi et al., 1998; Kubo and Akaogi, 2000; Nishio-Hamane et al., 2005) they are not well-known at deep lower mantle conditions.

Previous findings on the effects of Fe and Al cation substitutions on physical properties of perovskite have been complex and/or inconsistent (Knittle and Jeanloz, 1987; Mao et al., 1991; Andrault, 2001; Andrault et al., 2007; Walter et al., 2004; Lundin et al., 2008; Nishio-Hamane et al., 2008; Catalli et al., 2010, 2011; Fujino et al., 2012; Boffa Ballaran et al., 2012). The different effects of Fe^{2+}, Fe^{3+}, and Al in the perovskite A- and B-sites on the bulk modulus are each controversial: incorporation of ferrous iron has been observed to increase the bulk modulus (Mao et al., 2011; Boffa Ballaran et al., 2012) or have no significant effect (Lundin et al., 2008; Dorfman et al., in press); ferric iron may decrease bulk modulus through a high-to-low electronic spin transition (Catalli et al., 2010, 2011; Fujino et al., 2012) or have no effect (Nishio-Hamane et al., 2008); aluminum may decrease (Zhang and Weidner, 1999; Kubo and Akaogi, 2000; Daniel et al., 2001; Walter et al., 2004; Catalli et al., 2011; Boffa Ballaran et al., 2012), increase (Andrault et al., 2001, 2007) or have no effect (Daniel et al., 2004; Walter et al., 2006) on the bulk modulus. Aluminum may also modify the chemistry and effects of iron incorporation (Fei, 1998; Frost and Langenhorst, 2002; Saikia et al., 2009; Fujino et al., 2012; Boffa Ballaran et al., 2012). However, direct comparison of these previous studies is hampered by differences between experimental conditions including pressure calibrant, calibrant equation of state, and pressure medium. By measuring samples with different compositions under consistent experimental conditions, the effects of Fe and Al on the equation of state and the possible effects of different oxidation states and spin states may become resolvable.

The post-perovskite phase ($CaIrO_3$-type, *Cmcm*, $Z=4$) observed in $MgSiO_3$ above 125 GPa and 2500 K (Murakami et al., 2004; Oganov and Ono, 2004) has been of much recent interest for its potential to explain seismic observations near the base of the lower mantle. The pressure range at which the post-perovskite transition occurs has been found to be raised, lowered, and/or broadened by changes in composition, depending on Fe and Al content and Fe oxidation state (Shim, 2008). Diamond anvil cell experiments (Mao et al., 2004, 2005, 2006; Tateno et al., 2007) and density functional theory (DFT) calculations (Caracas and Cohen, 2008) have found that ferrous iron stabilizes post-perovskite relative to perovskite and the two-phase mixture is stable over a wide pressure range. In Al-free, Fe^{2+}-rich compositions, post-perovskite has been found to coexist with perovskite at pressures as low as 82 GPa (Tateno et al., 2007; Dorfman et al., in press). However, for the pyrope composition (Fe-free, 25 mol% Al_2O_3), post-perovskite has not been observed below 140 GPa (Tateno et al., 2005). DFT calculations have reported conflicting results for the effect of Al on the transition, some giving a broad two-phase region at higher pressure (Akber-Knutson et al., 2005) and others yield a slightly lower transition pressure and a narrow two-phase interval (Tsuchiya and Tsuchiya, 2008). Paired substitution of ferric iron and Al has been seen to increase the post-perovskite transition pressure (Nishio-Hamane et al., 2007). The combined effect of direct Mg-Fe^{2+} and paired Mg+Si–Al+Al substitutions on the perovskite-post-perovskite transition is not well-constrained.

In this work, we investigate the phase diagram of Pyr–Alm compositions *in situ* to 177 GPa and temperatures as high as 3000 K with X-ray diffraction in the laser-heated diamond anvil cell. We investigate the synthesis conditions for single-phase perovskites and post-perovskites from these compositions. In addition, we examine the breakdown of Fe^{2+}, Al-rich perovskites at lower pressures and the perovskite-post-perovskite transition at higher pressures. We measure the equations of state of perovskites synthesized from Alm54 and Alm100 compositions under consistent experimental conditions as those in our previous work on Al-free compositions (Dorfman et al., in press).

1. Method

Fe-bearing samples with compositions close to the Pyr–Alm join were selected for study. These are the same materials used in the recent work by Shieh et al. (2011). Compositions were determined by electron microprobe analysis and are listed in Shieh et al. (2011). Microprobe analyses (Hofmeister, 2006) and energy-resolved Mössbauer spectroscopy indicated no detectable ferric iron in the starting materials. Samples with Fe# (Fe/(Fe+Mg+Ca+Mn) in mol%) 38, 54, and 73 (Alm38, Alm54 and Alm73) are natural samples containing minor amounts of Ca and Mn (Hofmeister et al., 1998; Hofmeister, 2006) while Fe# 90 and 100 materials (Alm90 and Alm100) are pure synthetic glasses. The Alm90 glass is richer in Al_2O_3 content than an ideal almandine by ~ 5 mol%.

Samples were ground into powders and mixed with 15 wt% Au powder as an internal pressure calibrant (Fei et al., 2007). Compacted powder mixtures were either sandwiched between NaCl or supported by NaCl and loaded in Ne as quasi-hydrostatic pressure medium. NaCl was kept in an oven at 110 °C until immediately prior to loading. Samples were loaded in holes drilled through Re gaskets preindented to 20−35 μm thickness. Symmetric piston-cylinder diamond anvil cells with either flat anvils of 200 μm diameter or beveled culets with inner diameters of 100 or 75 μm were used to generate pressures up to 177 GPa. Errors in pressure due to uncertainty in the calibrant lattice parameter and effects of differential stress are estimated to be 1–2 GPa for annealed samples.

Angle-dispersive X-ray diffraction with *in situ* laser heating was performed at beamlines 13-ID-D of the GSECARS sector and 16-ID-B of the HPCAT sector of the Advanced Photon Source (APS). At both facilities the X-ray beam was focused with a Kirkpatrick–Baez double mirror system to dimensions between $3–5\times4-10$ μm. Diffraction patterns were collected using a MarCCD detector. The position and orientation of the detector were calibrated using a CeO_2 standard. In various experimental runs, X-ray wavelengths were 0.3100–0.4116 Å.

Samples were heated with a Nd:YLF or Nd:YAG double-sided laser heating system (Meng et al., 2006; Prakapenka et al., 2008). Temperatures were measured from both sides by spectroradiometry (Shen et al., 2001). Observed temperatures typically varied by 100 K between upstream and downstream measurements and exhibited 100–400 K variations over 30 min heating times. In a typical synthesis experiment, *in situ* laser heating to 2000–3000 K was carried out for durations of 30–60 min. In addition, we heated to 1500–2000 K for 15–30 min at 5–10 GPa intervals for annealing during equation of state measurements.

Diffraction images were integrated to produce 1-D diffraction patterns using Fit2D software (Hammersley et al., 1996). To obtain peak positions, widths, and intensities, patterns were fit with background-subtracted Voigt lineshapes. Lattice parameters were refined using Unitcell (Holland and Redfern, 1997). Full-profile refinement of selected patterns was conducted using GSAS and EXPGUI software (Larson and Von Dreele, 2000; Toby, 2001).

2. Results

2.1. Heating experiments below 50 GPa

We performed laser heating on Alm100, Alm90, and Alm38 compositions over the range 26–50 GPa. After heating Alm100 glass at 2000 K for 50 min at a starting pressure of 27 GPa, we observed diffraction peaks of stishovite, wüstite, and corundum consistent with the breakdown reaction observed in other studies near 20 GPa (Conrad et al., 1996; Akaogi et al., 1998). No perovskite diffraction peaks were observed. In addition, the