Earth and Planetary Science Letters 312 (2011) 422–428

Contents lists available at SciVerse ScienceDirect

Earth and Planetary Science Letters

journal homepage: www.elsevier.com/locate/epsl

Synthesis and equation of state of post-perovskites in the $(Mg,Fe)_3Al_2Si_3O_{12}$ system

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ARTICLE INFO

Article history:
Received 18 April 2011
Received in revised form 12 September 2011
Accepted 29 September 2011
Available online 24 November 2011

Editor: L. Stixrude

Keywords:
low mantle
D″ layer
post-perovskite
perovskite
iron content
Al_2O_3

ABSTRACT

The formation and properties of the post-perovskite ($CaIrO_3$-type) phase were studied in Fe-rich compositions along the pyrope–almandine ($(Mg,Fe)_3Al_2Si_3O_{12}$) join. Natural and synthetic garnet starting materials with almandine fractions from 38 to 90 mol% were studied using synchrotron X-ray diffraction in the laser-heated diamond anvil cell. Single-phase post-perovskite could be successfully synthesized from garnet compositions at pressures above 148 GPa and temperatures higher than 1600 K. In some cases, evidence for a minor amount of Al_2O_3 post-perovskite was observed for Alm38 and Alm54 compositions in the perovskite + post-perovskite two-phase region. Pressure–volume data for the post-perovskite phases collected during decompression show that incorporation of Fe leads to a systematic increase of unit cell volume broadly similar to the variation observed in the $(Mg,Fe)SiO_3$ system. The presence of Al_2O_3 increases the stability of perovskite relative to post-perovskite, requiring higher pressures (> 148 GPa) for synthesis of pure post-perovskites. Our data together with those of Tateno et al. (2005) also suggest that in the Al-rich system the presence of Fe has no strong effect on the pressure required to synthesize the pure post-perovskite phase, but the two-phase perovskite and post-perovskite region may be broad and its width dependent on Fe content. Our results suggest that any regions highly enriched in Al_2O_3 may consist of either the perovskite phase or a mixture of perovskite and post-perovskite phases throughout the entire thickness of the D″ region. The observed synthesis pressures (> 148 GPa) for a pure post-perovskite phase are beyond that at the Earth's core–mantle boundary (~135 GPa).

1. Introduction

The Earth's core–mantle boundary (the D″ layer) is expected to be a complex region of structural heterogeneity and thermal variability (Hirose, 2006; Shim, 2008). The discovery and investigation of the transformation of the $MgSiO_3$ perovskite phase (Pv) to a post-perovskite phase ($CaIrO_3$-type) (pPv) has dramatically altered our understanding of the region (Iitaka et al., 2004; Murakami et al., 2004; Oganov and Ono, 2004; Shim et al., 2004; Wentzcovitch et al., 2006; Wookey et al., 2005). Perovskites and post-perovskites in the deep lower mantle are expected to be chemically complex, and the behavior of post-perovskites across a range of mantle-relevant compositions needs to be investigated in detail to properly interpret seismic data for the deep Earth.

Aluminum is an important chemical constituent of the lower mantle that may be enriched locally in particular regions such as those containing subducted basaltic remnants. In experiments using pyrope ($Mg_3Al_2Si_3O_{12}$) starting material, it was found that a perovskite phase (i.e., $(Mg_{0.75}Al_{0.25})(Al_{0.25}Si_{0.75})O_3$) was stable to 140 GPa, and a single-phase post-perovskite was formed above 170 GPa (Tateno et al., 2005). When compared with $MgSiO_3$, this indicates that the presence of aluminum expands the stability field of perovskite relative to post-perovskite. Other experimental studies of Al-bearing $MgSiO_3$ compositions (with and without Fe) also conclude that the presence of Al^{3+} will broaden and deepen the perovskite to post-perovskite boundary (Andrault et al., 2010; Catalli et al., 2009; Kubo et al., 2007; Nishio-Hamane et al., 2007). Thus, the abundance of aluminum may have important consequences for the D″ region and interpretation of its seismic structure (Andrault et al., 2010; Catalli et al., 2009).

There have been a number of theoretical studies of post-perovskites in the $MgSiO_3$–Al_2O_3 system. Using density functional theory calculations, Tsuchiya and Tsuchiya (2008) examined the $MgSiO_3$–Al_2O_3 system and found that the addition of moderate amounts of Al_2O_3 slightly reduced the Pv–pPv transition pressure and produced a relatively narrow coexistence region for perovskite and post-perovskite. At higher Al_2O_3 contents, an Rh_2O_3-II-type perovskite phase was stabilized at lower pressures, and an Al_2O_3-rich post-perovskite was formed at higher pressures. Other theoretical studies have found a slight increase in the Pv–pPv transition pressure due to addition of Al^{3+} to $MgSiO_3$ (Caracas and Cohen, 2005a,b; Ono and Oganov, 2005; Zhang and Ogonov, 2007). These results stand in

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doi:10.1016/j.epsl.2011.09.054

contrast to the experimental studies discussed above which suggest a much stronger effect of aluminum on the phase boundary. However, one earlier theoretical study found that incorporation of Al^{3+} into $MgSiO_3$ pPv would lead to a large increase in transition pressure and coexistence of Pv and pPv over a wide pressure range (Akber-Knutson et al., 2005).

There has also been considerable investigation into the Pv–pPv transition in Fe-containing systems. Features of the deep lower mantle such as large, low-shear velocity provinces, ultra-low velocity zones, subducted slab materials, dense primordial remnants, and core–mantle reaction products (e.g. Garnero and McNamara, 2008; Mao et al., 2005; Nakagawa et al., 2010) could potentially exhibit varying degrees of iron enrichment. In addition to applications to Earth's mantle, the amount of Fe that post-perovskite can accommodate is also relevant to understanding the limits of core sizes in possible super-Earth extrasolar planets (Valencia et al., 2009). Some experimental studies in the $(Mg,Fe)SiO_3$ system suggest that Fe prefers post-perovskite over perovskite thereby reducing the transition pressure and producing a wide Pv–pPv phase loop (Caracas and Cohen, 2005a,b; Mao et al., 2004; Stackhouse et al., 2006) whereas others report a much narrower loop more consistent with a sharp seismic discontinuity (Murakami et al., 2005; Tateno et al., 2007). Variations in Fe oxidation state and also potentially its spin state as well as coupled behavior between Fe and Al add complexity to understanding this chemical component (Catalli et al., 2010a,b; Jackson et al., 2009; Lin et al., 2008; Mao et al., 2010; Sinmyo et al., 2006).

The pyrope–almandine system $(Mg,Fe)_3Al_2Si_3O_{12}$ is Al_2O_3-rich (25 mol%) and exhibits complete Mg–Fe solid solution. Natural and synthetic samples with a wide range of Mg# (= Mg/(Mg + Fe)) are available (Hofmeister, 2006; Hofmeister et al., 1998). Here we report an examination of such compositions at deep mantle pressures to provide new insights into the behavior of post-perovskites enriched in both aluminum and iron.

2. Experimental method

Three natural garnets with compositions close to the pyrope–almandine join (designated as Alm38, Alm54, and Alm73) (Hofmeister, 2006; Hofmeister et al., 1998) and one synthetic garnet glass (Alm90) were used as starting materials (Table 1). Note that the Alm90 glass contains excess Al_2O_3. The natural samples have total grossular and spessartine components of 4–6 mol%. While the amount of ferric iron was not directly measured, the microprobe data suggest the amount of ferric iron in the starting material is small.

The samples were each ground to a fine powder and mixed with ~10 wt.% platinum or gold for use as a pressure calibrant. High pressure and temperature experiments were conducted using laser-heated diamond anvil cells. The sample mixtures were loaded in the 25–35 μm hole of a rhenium gasket, together with NaCl or argon as a pressure medium and sample insulator. Neon gas was loaded for one Alm54 sample with the GSECARS/COMPRES high-pressure gas loading system. In situ high-pressure and high-temperature synchrotron X-ray diffraction experiments were conducted at beamline 13-ID-D of the GSECARS sector, Advanced Photon Source. Double-sided laser heating was used to achieve high temperatures with minimal temperature gradients (Prakapenka et al., 2008; Shieh et al., 2006). Temperatures were measured from both sides of the sample by spectroradiometry. The samples were probed with a monochromatic X-ray beam (wavelength 0.3344 Å) focused to about $5 \times 5\ \mu m^2$ using Kirkpatrick–Baez mirrors. Prior to data collection, the X-ray beam, the center of the heating spot, and the optical paths of the temperature measurement system were carefully aligned using fluorescence generated by the X-rays as they passed through the sample. Two-dimensional X-ray diffraction images were collected at both ambient and high temperatures with a MAR CCD detector. CeO_2 powder was used to calibrate the sample-to-detector distance and orientation of the detector. The images were reduced to one-dimensional spectra using the Fit2D program (Hammersley et al., 1996). Diffraction peaks were fit to Voigt lineshapes after background subtraction. The unit cell parameters were obtained by least-squares fit with the UnitCell program. The pressure was determined from the measured *d*-spacings of Pt and Au using their equations of state (Pt) (Fei et al., 2007) and (Au) (Dewaele et al., 2004).

3. Results and discussions

Samples were first compressed at room temperature to pressures in excess of 110 GPa. At these conditions, diffraction peaks for all the garnet samples were weak and broad. For each composition, several experiments using different samples (designated as A, B, C, etc.) were carried out. The samples were heated for time periods ranging from 38 to 264 min, and diffraction patterns were collected at both high and room temperatures (Table 2). Note that the pressures listed in the Table 2 represent the maximum pressure achieved during heating in each run and therefore the thermal pressures are considered. In general, due to the high iron contents of the silicate samples, the heating was quite stable and only ~10–40% of the total laser power (100 W) was adequate to heat the sample to 1300–2600 K range. After heating, additional diffraction patterns were recorded both at the heated spot and nearby locations (±6–10 μm). Depending on heating conditions, the CCD images contained relatively smooth or more spotty and heterogeneous rings. Absorption changes accompanying the phase transition sometimes led to runaway heating which resulted in spottier diffraction patterns.

We found that single-phase post-perovskite can be successfully synthesized from all studied garnet compositions at pressures above 148 GPa and temperatures higher than 1600 K (Figs. 1 and 2). Our results demonstrate that the pPv phase can simultaneously accommodate both high aluminum and high iron contents. However, a separate Al_2O_3-rich pPv phase was also observed under certain conditions (particularly with heating at 2050 K and below) during some runs for Alm54 and Alm38.

For Alm38A, the sample was compressed to 148 GPa and heated at 1490–1830 K for 60 min. Our results showed that the post-perovskite phase emerged after about 33 min heating, and after temperature quenching the pressure was determined to be ~160 GPa (Fig. 2a). In a separate run, Alm38B was compressed to 160 GPa and heated to 1760–2050 K. The pPv phase was observed during the initial heating

Table 1
Chemical compositions of garnet starting materials as determined by electron probe microanalysis.

	MgO (wt.%)	FeO (wt.%)	Al_2O_3 (wt.%)	SiO_2 (wt.%)	CaO (wt.%)	MnO (wt.%)	TiO_2 (wt.%)	Cr_2O_3 (wt.%)	Composition
Alm38	15.88	18.46	23.23	39.93	1.13	0.90	0.01	0.02	Alm38Pyr58Grs3Sps2 $(Mg_{0.44}Fe_{0.29}Al_{0.24}Ca_{0.02}Mn_{0.01})(Si_{0.74}Al_{0.26})O_3$
Alm54	11.61	26.14	22.75	39.37	0.96	0.28	0.02	0.02	Alm54Pyr43Grs3Sps1 $(Mg_{0.33}Fe_{0.41}Al_{0.24}Ca_{0.02})(Si_{0.74}Al_{0.26})O_3$
Alm73	5.28	32.84	20.47	38.86	1.65	0.61	0.02	–	Alm73Pyr21Grs5Sps1 $(Mg_{0.16}Fe_{0.55}Al_{0.25}Ca_{0.03}Mn_{0.01})(Si_{0.77}Al_{0.23})O_3$
Alm90	2.38	37.39	24.72	35.50	–	–	–	–	Alm90Pyr10 $(Mg_{0.07}Fe_{0.63}Al_{0.3})(Si_{0.71}Al_{0.29})O_3$

Alm = almandine, Pyr = pyrope, Grs = grossular, Sps = spessartine. Compositions are given both as endmember proportions in the pyrope–almandine–grossular–spessartine quaternary as well as a recalculation based on the ABO_3 stoichiometry of the $CaIrO_3$-type structure. Refs: Alm38 (#36, Table 1, Hofmeister et al., 1998), Alm54 (#40, Table 1, Hofmeister et al., 1998), Alm73 (Al-3, Table 1, Hofmeister, 2006). The Alm90 glass was synthesized in the laboratory of H. O'Neill (Australian National University).