Earth and Planetary Science Letters 434 (2016) 91–100

Contents lists available at ScienceDirect

Earth and Planetary Science Letters

www.elsevier.com/locate/epsl

Spin transition of ferric iron in the NAL phase: Implications for the seismic heterogeneities of subducted slabs in the lower mantle

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ARTICLE INFO

Article history:
Received 13 July 2015
Received in revised form 14 October 2015
Accepted 10 November 2015
Available online 2 December 2015
Editor: J. Brodholt

Keywords:
NAL phase
spin transition
subducted slabs
lower mantle
seismic heterogeneities

ABSTRACT

Al-rich phases (NAL: new hexagonal aluminous phase and CF: calcium–ferrite phase) are believed to constitute 10∼30 wt% of subducted mid-ocean ridge basalt (MORB) in the Earth's lower mantle. In order to understand the effects of iron on compressibility and elastic properties of the NAL phase, we have studied two single-crystal samples (Fe-free $Na_{1.14}Mg_{1.83}Al_{4.74}Si_{1.23}O_{12}$ and Fe-bearing $Na_{0.71}Mg_{2.05}Al_{4.62}Si_{1.16}Fe^{2+}{}_{0.09}Fe^{3+}{}_{0.17}O_{12}$) using synchrotron nuclear forward scattering (NFS) and X-ray diffraction (XRD) combined with diamond anvil cells up to 86 GPa at room temperature. A pressure-induced high-spin (HS) to low-spin (LS) transition of the octahedral Fe^{3+} in the Fe-bearing NAL is observed at approximately 30 GPa by NFS. Compared to the Fe-free NAL, the Fe-bearing NAL undergoes a volume reduction of 1.0% (∼1.2 Å^3) at 33∼47 GPa as supported by XRD, which is associated with the spin transition of the octahedral Fe^{3+}. The fits of Birch–Murnaghan equation of state (B–M EoS) to P–V data yield unit-cell volume at zero pressure $V_0 = 183.1(1)$ Å^3 and isothermal bulk modulus $K_{T0} = 233(6)$ GPa with a pressure derivative $K'_{T0} = 3.7(2)$ for the Fe-free NAL; $V_{0\text{-}HS} = 184.76(6)$ Å^3 and $K_{T0\text{-}HS} = 238(1)$ GPa with $K'_{T0\text{-}HS} = 4$ (fixed) for the Fe-bearing NAL. The bulk sound velocities (V_Φ) of the Fe-free and Fe-bearing NAL phase are approximately 6% larger than those of Al, Fe-bearing bridgmanite and calcium silicate perovskite in the lower mantle, except for the spin transition region where a notable softening of V_Φ with a maximum reduction of 9.4% occurs in the Fe-bearing NAL at 41 GPa. Considering the high volume proportion of the NAL phase in subducted MORB, the distinct elastic properties of the Fe-bearing NAL phase across the spin transition reported here may provide an alternative plausible explanation for the observed seismic heterogeneities of subducted slabs in the lower mantle at depths below 1200 km.

1. Introduction

Mid-ocean ridge basalt (MORB) is generated by means of partial melting of the upper-mantle peridotite along mid-ocean ridges, enriching aluminum, iron, and other incompatible elements (Green et al., 1979; Hofmann, 1997). The MORB, in turn, can be transported back into the Earth's interior via subduction of slab materials at plate convergence regions, supplying the mantle with chemically distinct and heterogeneous materials. Due to differences in temperature, chemical composition and mineral constituent between subducted slabs and normal mantle peridotite, subducted slabs exhibit higher seismic velocities than peridotite in the Earth's mantle (Bina and Helffrich, 2014; Fukao et al., 2009). Furthermore, seismic anomalies observed in the mantle, such as seismic scatterers and mid-lower mantle discontinuities, are generally suggested to be related to subducted slabs (Kaneshima, 2013; Kawakatsu and Niu, 1994). Therefore, in order to have a better un-

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http://dx.doi.org/10.1016/j.epsl.2015.11.011

derstanding of the geochemical and geophysical properties of the deep Earth, it is essential to have a thorough understanding of the thermal elastic properties of the minerals potentially present in the slabs.

MORB assemblage is generally expected to have distinct chemical compositions that contain more aluminum than the bulk mantle (Green et al., 1979; Sun, 1982). These basaltic materials have been reported to transform into an assemblage of magnesium silicate perovskite (Mg–Pv, named bridgmanite), calcium silicate perovskite (Ca–Pv), stishovite, and aluminous-rich phases in the lower mantle (Hirose et al., 2005; Irifune and Ringwood, 1993; Ohta et al., 2008; Ricolleau et al., 2010). An aluminous phase with calcium–ferrite (CF) structure (*Pbnm*, $Z = 4$) was found in subducted oceanic crust at pressures above 25 GPa and temperatures above 1200 °C (Irifune and Ringwood, 1993). Following this pioneering work, another aluminous phase, named "new hexagonal aluminous phase (NAL)", was subsequently observed in the garnet-to-perovskite transformation and the $MgAl_2O_4$–$CaAl_2O_4$ system at relevant conditions of the lower mantle (Akaogi et al., 1999; Miyajima et al., 1999). Recently, studies on mineral inclusions in diamonds from Juina-5 kimberlite indicate that these mineral inclusions have compositions consistent with the phase assemblage expected to crystallize from basaltic materials at lower-mantle conditions, comprising of Mg–Pv, Ca–Pv, NAL, CF, and SiO_2 phases (Walter et al., 2011). These results provide direct petrological evidence for the existence of the NAL and CF phases in subducted MORB assemblage in the lower mantle. NAL and CF phases therefore have been considered as the main hosts of aluminum accounting for 10∼30 wt% of the subducted basalt in the lower mantle (Ricolleau et al., 2010).

The NAL phase with a chemical formula of $AB_2C_6O_{12}$ has a hexagonal crystal structure with the space group of $P6_3/m$. (Fig. S1) (Miura et al., 2000). The A site, located on a tunnel with a hexagonal cross-section in the projection of the *c*-axis direction, is partially occupied by a large monovalent or divalent cation (Na^+, K^+, or Ca^{2+}). The B site has a di-trigonal cross-section and is occupied by a smaller cation (Mg^{2+} or Fe^{2+}) to form a trigonal prismatic coordination polyhedron with surrounding oxygen atoms. The C site, an octahedral site, is occupied by Al^{3+}, Fe^{3+}, and/or Si^{4+}. Edge-sharing CO_6 octahedra are arranged along the *c*-axis direction to form a chain framework structure. By sharing corners in the *ab* plane, three edge-sharing double chains form two kinds of tunnels for A and B sites, respectively (Miura et al., 2000). The CF phase with a chemical formula of $B_3C_6O_{12}$ has a chain framework structure along the *c*-axis direction similar to the NAL phase, but it only forms one kind of tunnel with a di-trigonal cross-section in the *ab* plane for the B-site cation (Yamada et al., 1983).

The high amount of Al-rich phases in the subducted MORB assemblage has motivated extensive studies of their phase stabilities and physical properties as they can relate to the properties of subducted slabs in the lower mantle (Dai et al., 2013; Guignot and Andrault, 2004; Imada et al., 2011; Kawai and Tsuchiya, 2012; Ono et al., 2009). High pressure–temperature (P–T) X-ray diffraction (XRD) and transmission electron microscopy studies on a natural MORB assemblage indicate that the NAL and CF phases coexist up to ∼50 GPa, beyond which only the CF phase is observed (Ricolleau et al., 2010), and results on phase relations of the $NaAlSiO_4$–$MgAl_2O_4$ system show that the CF phase is identified as the high pressure form of the NAL phase (Imada et al., 2011; Ono et al., 2009). Studies on the MORB assemblage further show that the NAL phase is more enriched in potassium than the coexisting CF phase such that the NAL phase is stabilized to higher pressures (Guignot and Andrault, 2004; Kato et al., 2013). On the other hand, Brillouin light scattering studies on polycrystalline samples and theoretical calculations have suggested that the change in the shear wave anisotropy across the NAL to CF phase transition is significant enough to be seismically detectable (Dai et al., 2013; Kawai and Tsuchiya, 2012), affecting our understanding of seismic signatures of the subducted slabs in the lower mantle.

The NAL and CF phases contain a certain amount of iron (Ricolleau et al., 2010), which can potentially affect physical and chemical properties of the host minerals at extreme P–T conditions. The spin and valence states of iron in various crystallographic sites of the candidate lower-mantle phases have been investigated using synchrotron X-ray and spectroscopic techniques as well as first-principle calculations (Lin et al., 2013 and references therein). Electronic high-spin (HS) to low-spin (LS) transitions of iron have been reported to occur in a number of candidate mantle minerals, including ferropericlase, bridgmanite, ferromagnesite, and Phase D (Chang et al., 2013; Lin et al., 2012, 2005; Liu et al., 2014). In ferropericlase (Mg,Fe)O, octahedral Fe^{2+} undergoes a spin transition at approximately 40 to 50 GPa (Lin et al., 2005). In ABO_3-type bridgmanite, Fe^{2+} predominantly occupies the pseudo-dodecahedral A site, whereas Fe^{3+} occupies both the A and octahedral B sites (Lin et al., 2012). The current consensus for the spin and valence states of iron in bridgmanite is that the octahedral Fe^{3+} undergoes a spin transition at pressures of the uppermost lower mantle, while Fe^{2+} and Fe^{3+} in the pseudo-dodecahedral site remain in the high-spin state throughout the entire lower mantle (Lin et al., 2013). Studies on the aforementioned Al-rich phases so far have been mostly focused on their phase stabilities and equation of state (EoS) parameters, while the influence of iron on elastic properties has yet to be investigated. Since the NAL phase likely contains up to 12 mol% iron (Ricolleau et al., 2010), the valence and spin states of iron in the NAL phase can potentially affect its elasticity which in turn can affect our understanding of the mineral physics of the MORB assemblage in the lower mantle (Lin et al., 2013).

Here we have studied two single-crystal samples of the NAL phase, Fe-free and Fe-bearing, to investigate the spin and valence states of iron in the NAL phase and the effects of iron on EoS parameters of the NAL phase using nuclear forward scattering (NFS) and XRD in conjunction with diamond anvil cells (DAC). A spin transition in the octahedral Fe^{3+} of the Fe-bearing NAL phase is observed at approximately 30 GPa from the NFS, and it can be associated with changes in the lattice parameters evaluated from the XRD measurements. These results are compared to other candidate minerals in the MORB assemblage and applied to understand their influences on the seismic profiles of the lower mantle.

2. Experimental methods

2.1. Sample synthesis and characterization

Single crystals of the Fe-free and Fe-bearing NAL phases were synthesized using the 5000-ton Kawai-type multi-anvil apparatus (USSA-5000) at the Institute for Study of the Earth's Interior (ISEI), Okayama University at Misasa. $NaAlSiO_4$ (nepheline, $P6_3$) was firstly synthesized by heating stoichiometric mixtures of $NaCO_3$, Al_2O_3 and SiO_2 at 1200 °C for 12 hrs. Subsequently, a mixture of $NaAlSiO_4$, MgO and Al_2O_3 in a molar ratio of 0.4 : 0.6 : 0.6 was used as the starting materials for synthesizing the Fe-free NAL phase. 2 wt% H_2O in the form of $Mg(OH)_2$ was added into the mixture in order to promote the growth of single crystals and the MgO proportion in the starting materials was slightly adjusted accordingly. The mixture was loaded into a platinum capsule 2 mm in diameter and 3 mm in length. This assemblage was then compressed to 20 GPa and heated at 1600 °C for 1 hr, and then cooled to 1300 °C keeping for 2 hrs (RUN #: 5K2283).

For the ^{57}Fe-bearing NAL sample, the starting materials was prepared using the same procedure for the Fe-free sample, but