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Phase transformation of ferric-iron-rich silicate in Earth's mid-mantle

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ABSTRACT

The incorporation of ferric iron in mantle silicates stabilizes different crystal structures and changes phase transition conditions, thus impacting seismic wave speeds and discontinuities. Recent experiments of $MgSiO_3$-Fe_2O_3 mixtures indicate the coexistence of fully oxidized iron-rich $(Mg_{0.5}Fe^{3+}_{0.5})(Fe^{3+}_{0.5}Si_{0.5})O_3$ with Fe-poor silicate (wadsleyite or bridgmanite) and stishovite at 15 to 27 GPa and 1773 to 2000 K, conditions relevant to subducted lithosphere in the Earth's transition zone and uppermost lower mantle. X-ray diffraction (XRD) shows that $(Mg_{0.5}Fe^{3+}_{0.5})(Fe^{3+}_{0.5}Si_{0.5})O_3$ recovered from these conditions adopts the $R3c$ $LiNbO_3$-type structure, which transforms to the bridgmanite structure again between 18.3 and 24.7 GPa at 300 K. XRD data are used to obtain the equation of state of the $LiNbO_3$-type phase up to 18.3 GPa. Combined with multi-anvil experiments, these observations suggest that the stable phase of $(Mg_{0.5}Fe^{3+}_{0.5})(Fe^{3+}_{0.5}Si_{0.5})O_3$ is bridgmanite at 15–27 GPa, which transforms on decompression to $LiNbO_3$-type structure. Our calculation revealed that ordering of the ferric ion reduces the kinetic energy barrier of the transition between $(Mg_{0.5}Fe^{3+}_{0.5})(Fe^{3+}_{0.5}Si_{0.5})O_3$ $LiNbO_3$ structure and bridgmanite relative to the $MgSiO_3$ akimotoite-bridgmanite system. A dense Fe^{3+}-rich bridgmanite structure is thus stable at substantially shallower depths than $MgSiO_3$ bridgmanite and would promote subduction.

Keywords: $LiNbO_3$, bridgmanite, ferric iron, transition zone, lower mantle, phase transition, equation of state

INTRODUCTION

Mineralogical differences due to chemical heterogeneity in the mantle are crucial for understanding the dynamics of mantle convection and driving forces for plate tectonics (Stixrude and Lithgow-Bertelloni 2012; Faccenda and Dal Zilio 2017). The average oxygen fugacity of the upper mantle has been underestimated (Cottrell and Kelley 2011), and orders of magnitude heterogeneity in mantle oxygen fugacity suggest that both subduction and plumes oxidize the mantle (Cottrell and Kelley 2013; Moussallam et al. 2019; Cottrell et al. 2021). Local iron enrichment and high oxygen fugacity may also be found in regions containing subducted basalt and hematite-rich sediment. These variations in mantle oxidation may impact the stability and equilibrium composition of major mantle minerals (e.g., Gu et al. 2016), with corresponding effects on seismic velocities and dynamics of downwelling slabs and upwelling plumes.

Recent experiments (Wang et al. 2021; Chanyshev et al. 2023) indicate that under oxidizing conditions in the transition zone and uppermost lower mantle, Fe^{3+} may partition out of dominant silicates wadsleyite, ringwoodite, and bridgmanite into a separate dense phase. In bulk compositions with 90–93% $MgSiO_3$ and 7–10% Fe_2O_3, experiments at 15–27 GPa and 1773–2000 K produce $(Mg_{0.5}Fe^{3+}_{0.5})(Fe^{3+}_{0.5}Si_{0.5})O_3$ coexisting with wadsleyite and stishovite or bridgmanite and stishovite. Because the Fe^{3+}-rich phase forms within a much less Fe-rich bulk composition, it could be found in oxidized natural lithologies. However, these studies did not observe the structure of $(Mg_{0.5}Fe^{3+}_{0.5})(Fe^{3+}_{0.5}Si_{0.5})O_3$ in situ at high pressure and temperature. Identifying this phase and its stability range and physical properties is important to determine the mineralogy of oxidized mantle and its impact on geophysics.

$(Mg_{0.5}Fe^{3+}_{0.5})(Fe^{3+}_{0.5}Si_{0.5})O_3$ recovered from lower mantle pressures exhibits a structure within the corundum family, a group of minerals with related structures and multiple possible cation orderings including corundum Al_2O_3 and hematite Fe_2O_3 (space group $R\bar{3}c$), hemleyite $FeSiO_3$ and ilmenite $FeTiO_3$ (space group $R\bar{3}$), $LiNbO_3$-type wangdaoite $FeTiO_3$ (space group $R3c$) (Navrotsky 1998; Dubrovinsky et al. 2009; Bindi et al. 2017; Xie et al. 2020), and an $R3$ modified corundum structure similar to the

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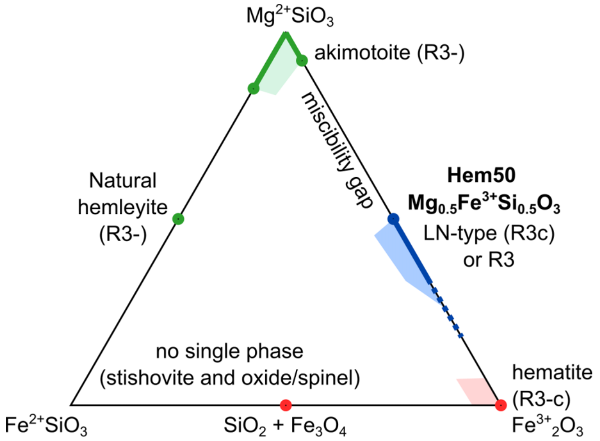

FIGURE 1. Schematic diagram summarizing known compositions and structures of compounds in the $MgSiO_3$-$Fe^{2+}SiO_3$-$Fe^{3+}_2O_3$ system at ~20–24 GPa. For $MgSiO_3$ and Fe_2O_3 end-members, stable structures at subducted slab conditions are $R\bar{3}$ akimotoite and $R\bar{3}c$ hematite, respectively. For compositions at or near the $FeSiO_3$ end-member, experiments at deep transition zone conditions produce a mixture of stishovite and wüstite, magnetite, or ringwoodite (Tateno et al. 2007; Ismailova et al. 2015). Maximum observed solubility of $FeSiO_3$ in $R\bar{3}$ $MgSiO_3$ akimotoite (green area) is based on experiments at 1100 °C and 24 GPa by Ito and Yamada (1982). Natural $R\bar{3}$ hemleyite (green dot) was characterized with higher Fe^{2+}-content than the experimental solubility limit (Bindi et al. 2017). Composition of Fe^{3+}-bearing LN-type phase (blue area) coexisting with bridgmanite is obtained from experiments at 1873 K, 20–24 GPa as reported in Wang et al. (2021). The blue dot represents hem50-LN (50% hematite, 50% enstatite) investigated in this study and others (Chanyshev et al. 2023; Koemets et al. 2023). (Color online.)

$LiNbO_3$-type structure (Koemets et al. 2023) (Fig. 1). Both $LiNbO_3$-type and ilmenite-type structures have two octahedral cation sites with different sizes, denoted as AO_6 (A site) and BO_6 (B site), respectively. Cation ordering, as in $LiNbO_3$, makes this structure approach a distorted perovskite and thus promotes its transition to bridgmanite (orthorhombic perovskite) with a very low energy barrier (Navrotsky 1998). The synthesis and phase transition of $LiNbO_3$-type $(Mg_{0.5},Fe^{3+}_{0.5})(Si_{0.5},Al^{3+}_{0.5})O_3$ has also been reported (Liu et al. 2019; Zhu et al. 2020; Koemets et al. 2023). Fe^{3+} can simultaneously substitute for Mg^{2+} and Si^{4+} in compositions along the $MgSiO_3$–Fe_2O_3 join. In contemporary experiments to this work, $(Mg_{0.5}Fe^{3+}_{0.5})(Fe^{3+}_{0.5}Si_{0.5})O_3$ was identified with the $R3c$ $LiNbO_3$-type structure (Chanyshev et al. 2023), but additional single-crystal diffraction suggests reassigning this material to the $R3$ structure (Koemets et al. 2023). Analysis of natural akimotoite and hemleyite in chondritic meteorites (Sharp et al. 1997; Tomioka and Fujino 1997) demonstrates incorporation of Fe and Al in the ilmenite-structured silicate up to at least 50% Fe^{2+} substituting for Mg^{2+} on the A site, above the solubility limit determined by experiment (Ito and Yamada 1982). Pressure can drive cation reordering transitions between the ilmenite and $LiNbO_3$-type structures (Ko and Prewitt 1988), and the closely related structures may be difficult to distinguish with diffraction techniques.

The $R3c$ $LiNbO_3$-type or modified $R3$ corundum structure in $(Mg_{0.5}Fe^{3+}_{0.5})(Fe^{3+}_{0.5}Si_{0.5})O_3$ is inferred to result from back-transformation from bridgmanite or a related double perovskite structure on decompression from 24–27 GPa (Wang et al. 2021; Chanyshev et al. 2023; Koemets et al. 2023). The $LiNbO_3$-type structure is known to readily transform to a perovskite-type structure and back in several compounds (Ross et al. 1989; Funamori et al. 1997; Linton et al. 1997; Inaguma et al. 2014; Akaogi et al. 2017; Zhu et al. 2020; Koemets et al. 2023). However, the range of conditions under which Fe^{3+}-bearing bridgmanite is stable is unknown. Furthermore, the separate Fe^{3+}-rich phase was also observed upon recovery from transition zone conditions of 15 GPa and 1773 K (Wang et al. 2021). This synthesis pressure is lower than the stable pressure range not only for $MgSiO_3$ bridgmanite, expected to be stable above 20–24 GPa, but also for $MgSiO_3$ akimotoite, stable above ~18–22 GPa (Ishii et al. 2011; Kulka et al. 2020). Experimental observations could be consistent with Fe^{3+}-rich majorite garnet or stabilization of Fe^{3+}-rich $LiNbO_3$-type silicate or bridgmanite at transition zone depths. In this study, we performed powder and single-crystal X-ray diffraction (XRD) measurements on Fe^{3+}-rich $(Mg_{0.46},Fe^{3+}_{0.53})(Si_{0.49},Fe^{3+}_{0.51})O_3$ at ambient conditions and high pressures as well as first-principles calculations to reveal its crystal structure, compressibility, and the mechanism of its phase transition to bridgmanite.

MATERIALS AND METHODS

Experimental methods

Synthesis and compositional characterization of the Fe^{3+}-rich starting material used in this work is described by Liu et al. (2018) and Dorfman et al. (2020). Electron microprobe analysis shows that the sample is chemically homogeneous with a composition of $Mg_{0.46(2)}Fe_{1.04(1)}Si_{0.49(1)}O_3$ (Liu et al. 2018), and conventional Mössbauer spectroscopy results indicate 100% Fe^{3+}/total Fe (Dorfman et al. 2020). Hence, the stoichiometric chemical formula of the sample is determined to be $(Mg_{0.46},Fe^{3+}_{0.53})(Si_{0.49},Fe^{3+}_{0.51})O_3$. Crystals used in single-crystal diffraction measurements were ~200 × 200 × 200 μm^3, while polycrystalline aggregate grains a few micrometers in size were used for powder diffraction measurements.

Single-crystal X-ray diffraction (XRD) was carried out at ambient conditions at the GSECARS facility at APS, Argonne National Laboratory, station 13BM-C. A silicon (311) monochromator was used to select X-rays at 28.6 keV (0.434 Å) with 1 eV bandwidth. Kirkpatrick-Baez mirrors focused the beam to vertical × horizontal focus spot size of 15 × 15 μm, measured as full-width at half maximum (FWHM). The MAR165 charge-coupled device (CCD) detector (Rayonix) was placed about 200 mm from the sample. LaB_6 powder standard was used to calibrate the distance and orientation of the detector. A ~200 × 200 × 200 μm^3 crystal of $(Mg_{0.46},Fe^{3+}_{0.53})(Si_{0.49},Fe^{3+}_{0.51})O_3$ was mounted onto a polymer micromesh sample holder (MiTeGen) for room-pressure measurement. The sample was centered at the rotation axis of the diffractometer and aligned with an optical microscope. At room pressure, a series of 10° wide segment rotation exposures covered the angular range from $\varphi = -90°$ to 90°, followed by a series of step φ-exposures, each covering 1° scan width. The typical exposure time was 1 s/°. At zero diffractometer position, the φ scan rotation axis for the 13BM-C diffractometer is in the instrument's horizontal plane, perpendicular to the incident X-ray direction. The diffraction images were analyzed using the GSEADA/RSV software package (Dera et al. 2013). SHELXL software was used for refinement (Sheldrick 2015). We used isotropic atomic displacement parameters (U_{iso}) for all atoms due to the lack of independent reflections.

A symmetric diamond-anvil cell (DAC) with 300 μm flat diamonds was used for high-pressure experiments at ambient temperature. A 250 μm thick rhenium gasket was pre-indented to ~30 μm, and a hole with a 150 μm diameter was drilled in the center using the laser drilling system at HPCAT (Sector 16) of the Advanced Photon Source (APS), Argonne National Laboratory (ANL) (Hrubiak et al. 2015). A polycrystalline sample aggregate sized ~20 × 20 × 7 μm^3 was loaded into the sample chamber, and then Ne was loaded as a hydrostatic pressure medium using the COMPRES/GSECARS gas-loading system (Rivers et al. 2008). Au powder was spread on top of the sample, serving as the pressure standard with a minimal pressure gradient between the sample and Au (Liu et al. 2018). Pressure was calculated from the Au (111) peak using the equation of state (Fei et al. 2007).

The crystal structure during compression in the DAC was determined by angle-dispersive synchrotron XRD measurements performed at beamline 13-BM-C of the APS, ANL with beam characteristics and detector position calibration as described above. On compression at 1–2 GPa intervals, XRD images of the samples were recorded for an exposure time of 60 s. The XRD images were integrated using the software DIOPTAS (Prescher and Prakapenka 2015). Crystal structures were examined using full spectrum Le Bail fitting implemented in the EXPGUI/GSAS software package (Toby 2001), and the unit-cell parameters were extracted based on five diffraction lines (012, 104, 110, 113, 024, 116) using the program PDIndexer (Seto et al. 2010).

First-principles calculations of the phase transition pathway

To determine the effects of compositional and structural differences between $MgSiO_3$ and $(Mg_{0.5}Fe_{0.5})(Fe_{0.5}Si_{0.5})O_3$ on the phase transition path and energy barrier for formation of bridgmanite, we performed calculations using the stochastic surface walking (SSW) method integrated with density functional theory (DFT). SSW has successfully been used to predict the low-energy pathways of crystal phase transitions (e.g., Zhu et al. 2019). Calculations employed the Vienna ab initio simulation package (VASP) for plane-wave DFT. Electron-ion interactions for all atoms were represented in VASP using the projector augmented wave (PAW) scheme. The exchange-correlation function is described by the generalized gradient approximation in the Perdew-Burke-Ernzerhof parameterization. The pathway sampling was carried out in a 20-atom lattice (4 $MgSiO_3$ units per cell) for akimotoite, $LiNbO_3$-type phase, and bridgmanite. Through SSW sampling, a large set ($\sim 10^2$) of initial/final state pairs was collected at 24 GPa. The transition state (TS) was located using double-ended surface walking. The lowest energy pathway was found by sorting the heights of computed energy barriers. Then, the lowest candidate pathway was refined by solid-state NEB (ssNEB) method. To speed up the sampling, the Monkhorst-Pack *k*-point mesh of ($4 \times 4 \times 4$) set for sampling and energy barrier scan is $2 \times 2 \times 2$, while for barrier refinement the Monkhorst-Pack k-point mesh is set to $4 \times 4 \times 4$. The kinetic energy plane-wave cutoff is 500 eV. For all the structures, both lattice and atomic positions were fully optimized until the maximal stress component was below 0.1 GPa and the maximal force component was below 0.01 eV/Å.

RESULTS AND DISCUSSION

$LiNbO_3$-structured $(Mg_{0.5}Fe_{0.5})(Fe_{0.5}Si_{0.5})O_3$

At ambient conditions, single-crystal and powder XRD indicate that $(Mg_{0.5}Fe_{0.5})(Fe_{0.5}Si_{0.5})O_3$ recovered from synthesis at 24 GPa and 1873 K adopts the $LiNbO_3$-type structure (Fig. 2). We attempted to fit each data set using the $R\bar{3}$ ilmenite-type structure, $R3c$ $LiNbO_3$-type structure, and corundum-derivative $R3$ structure proposed by Koemets et al. (2023) based on contemporaneous experiments. The $R\bar{3}$ ilmenite-type structure and $R3c$ differ only in ordering the two cation sites (Online Materials[1] Fig. S1). $R3$ is nearly identical to $R3c$ but has lower symmetry. For the single-crystal XRD data, fits to the $R\bar{3}$ ilmenite and $R3$ structures do not converge. Additional peaks expected for the $R\bar{3}$ ilmenite structure are not present. Due to the group-subgroup relationship between the $R3$ and $R3c$ structures, it is possible to describe the observed peaks with the $R3$ structure, and failure to converge may be due to the higher number of degrees of freedom in the fit and completeness of the data set. The fit to the $R3c$ $LiNbO_3$-type structure converges with an R1 value of 7.11% and goodness-of-fit of 1.423. Refinement details, fractional coordinates, and atomic displacement parameters are given in Online Materials[1] Tables S1 and S2. Powder XRD peaks are also consistent with the $R3c$ $LiNbO_3$-type structure.

The ratio of *c* and *a* lattice parameters for the $(Mg_{0.5}Fe_{0.5})(Fe_{0.5}Si_{0.5})O_3$ is also more consistent with previous observations of $LiNbO_3$-type compounds than ilmenites. Refined lattice parameters for $(Mg_{0.5}Fe_{0.5})(Fe_{0.5}Si_{0.5})O_3$ at 1 bar yield a *c*/*a* ratio of 2.69 in both this study and Koemets et al. (2023). This value is near the upper end of the 2.61–2.70 range reported for silicate, titanate, niobate, stannate, and other compounds with $LiNbO_3$ type ordering (Leinenweber et al. 1995; Linton et al. 1999; Aimi et al. 2011) and lower than the 2.74–2.94 range reported for ilmenite type ordering (Wechsler and Prewitt 1984; Kumada et al. 1990; Baraton et al. 1994). Among ilmenite-structured silicates, $R\bar{3}$ $MgSiO_3$ akimotoite exhibits a *c*/*a* ratio of 2.87, and the ratio for $R\bar{3}$ $FeSiO_3$ hemleyite is 2.88 (Bindi et al. 2017). For Fe^{3+}- and Al^{3+}-bearing $(Mg_{0.5}Fe_{0.5})(Al_{0.5}Si_{0.5})O_3$, the *c*/*a* ratio is much lower at 2.65–2.67, and XRD data was consistent with the $LiNbO_3$-type structure (Zhu et al. 2020; Koemets et al. 2023). The charge-coupled substitution of Fe^{3+}, $Mg^{2+}_A + Si^{4+}_B = Fe^{3+}_A + Fe^{3+}_B$, distributes Fe^{3+} evenly between the AO_6 and BO_6 octahedra and effectively homogenizes these two sites. Fe^{3+}-rich silicates are thus close to the stability boundary between these two similar structures.

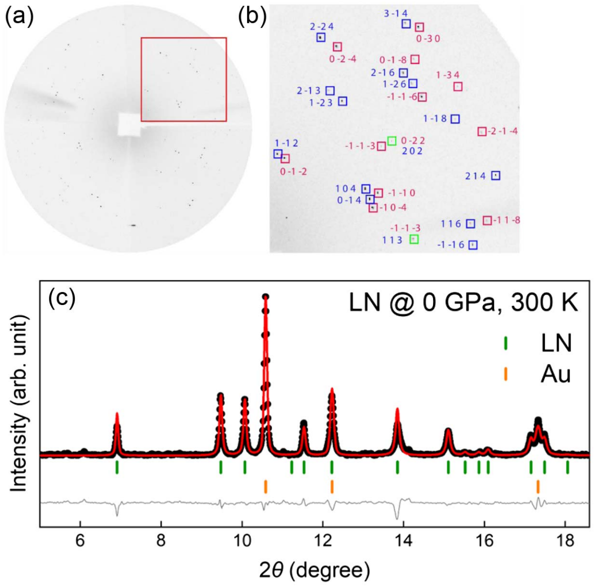

FIGURE 2. Single-crystal and powder XRD patterns (λ = 0.434 Å) and fits for synthetic $(Mg_{0.46},Fe^{3+}_{0.53})(Si_{0.49},Fe^{3+}_{0.51})O_3$ at 0 GPa and 300 K. (**a** and **b**) Single-crystal XRD pattern viewed along (100) direction with peaks identified corresponding to the hexagonal $R3c$ crystal structure. The red and blue boxes indicate diffraction peaks from two grains of the Hem50-LN, and the green boxes indicate the overlapped peaks from the two grains. Unit-cell parameters obtained from this fit are $a = 4.9496(5)$ Å, $c = 13.3138(19)$ Å, and $V = 282.47(6)$ Å^3. (**c**) Le Bail fitting applied to background-subtracted powder XRD pattern: red solid curve represents the fitted profile, and green and orange vertical ticks indicate the $LiNbO_3$-type structure and Au, respectively. Refined unit-cell parameters are $a = 4.950(5)$ Å, $c = 13.323(2)$ Å, and $V = 282.8(6)$ Å^3. (Color online.)

$LiNbO_3$-type (LN) $(Mg_{0.5}Fe_{0.5})(Fe_{0.5}Si_{0.5})O_3$ (50% hematite, 50% enstatite, called Hem50 hereafter) diffraction peaks are observed from 1 bar to 18.3(1) GPa at 300 K. XRD patterns of sample assemblages showed diffraction peaks from Hem50-LN, Au calibrant, and Ne medium (Online Materials[1] Fig. S2). We observe no evidence of peak splitting, broadening, dissociation, or transition of the LN structure up to 18.3(1) GPa.

Equation of state

The compression properties of Hem50-LN were obtained based on volumetric compression measurements from 0 to 18.3(1) GPa (Online Materials[1] Table S3; Fig. 3). Pressure-volume (P-V) data for Hem50-LN were fit to a second-order Birch Murnaghan equation of state (BM EoS). The resulting parameters are listed with literature values in Online Materials[1] Table S4. The slope of normalized stress Eulerian strain (F f) fitting is flat (Online Materials[1] Fig. S3), supporting the validity of fixing $K_0^{'}$ to 4. The V_0 for Hem50- LN is consistent with 50% linear mixing between that of $MgSiO_3$ akimotoite (Wang et al. 2004) and Fe_2O_3 hematite (Bykova et al. 2016), although the crystal structures of the two end-members are different. Observed volumes are consistent with measurements obtained by Koemets et al. (2023), although they do not report equation of state for the modified corundum structure for this composition. $MgSiO_3$ akimotoite K_0 and $K_0^{'}$ values have recently been constrained by Brillouin spectroscopy, ultrasonic, powder XRD measurements (Wang et al. 2004; Zhou et al. 2014; Siersch et al. 2021) and theoretical calculations (Hao et al. 2019) to pressure range between 205–210 GPa and 4.2–4.8, respectively. Comparison between Hem50-LN and $MgSiO_3$ akimotoite indicates incorporation of Fe^{3+} through substitution of (Mg^{2+}+Si^{4+}) on both A-site and B-site decreases the incompressibility of $MgSiO_3$ akimotoite (Fig. 3). The equation of state parameters of $FeSiO_3$ akimotoite compiled by Stixrude and Lithgow-Bertelloni (2012) show a similar increase in K_0 due to incorporation of Fe^{2+} on A-site.

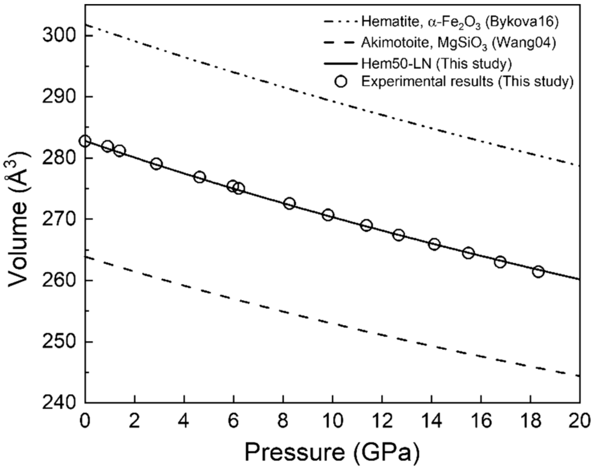

FIGURE 3. P-V plots for Hem50-LN, $MgSiO_3$ akimotoite (Wang et al. 2004), and Fe_2O_3 hematite (Bykova et al. 2016).

Transition to perovskite-type structure

At pressures higher than 18.3 GPa, new peaks corresponding to orthorhombic bridgmanite (space group *Pnma*, hereafter Hem50-Bdg) gradually replace Hem50-LN (Fig. 4). The Hem50-LN to Hem50-Bdg polymorphic transition was completed at 24.7(1) GPa. Full-profile Le Bail refinement of the XRD pattern at 18.3 GPa compared to the pattern at 24.7 GPa confirms the Hem50 LN-to-Bdg transition and pressure range. In conjunction with the previously reported 300 K equation of state parameters of Hem50-Bdg, $MgSiO_3$ Aki, and Bdg, we can calculate that the unit-cell volume decreases 3.5% across Hem50-LN to Bdg transition at 20 GPa. This contrast is relatively smaller than the volume contrast of 5.9% across $MgSiO_3$ Aki and Bdg transition at 24 GPa.

The transition from Hem50-LN to Hem50-Bdg occurred at 300 K without heating, which implies a low kinetic barrier between the two Fe^{3+}-rich phases along the $MgSiO_3$-Fe_2O_3 join. In contrast to the observed low kinetic energy barrier between Hem50-LN and Hem50-Bdg, the $MgSiO_3$ Aki-Bdg transition has been documented to require high temperature to overcome a high energy barrier (Ono et al. 2001). However, the $LiNbO_3$-type structure transforms to orthorhombic perovskite at room temperature on compression and the reverse on decompression for several compositions including (Mg,Mn, Fe,Zn)TiO_3 (Ross et al. 1989; Linton et al. 1997; Inaguma et al. 2014; Akaogi et al. 2017), ($Mg_{0.37}Fe_{0.22}Ca_{0.16}Mn_{0.01}Al_{0.25}$)($Al_{0.25}Si_{0.75}$)$O_3$ (Funamori et al. 1997), and ($Mg_{0.5}$,$Fe^{3+}_{0.5}$)($Si_{0.5}$,$Al^{3+}_{0.5}$)O_3 (Zhu et al. 2020; Koemets et al. 2023). The favorable kinetics of this transition is attributed to the ordering of cations in the $LiNbO_3$-type structure that matches the perovskite ordering (Ross et al. 1989) and further promoted by interchangeable ions on both cation sites. The octahedral (Fe^{3+},Si) site can rotate to form the BO_6 octahedral network of the perovskite structure without breaking bonds (Megaw 1968). In addition, for ($Mg_{0.5}$,$Fe^{3+}_{0.5}$)($Si_{0.5}$,$Fe^{3+}_{0.5}$)O_3 LN, Fe^{3+} ions in either A or B sites can become Fe^{3+} in either A or B sites in

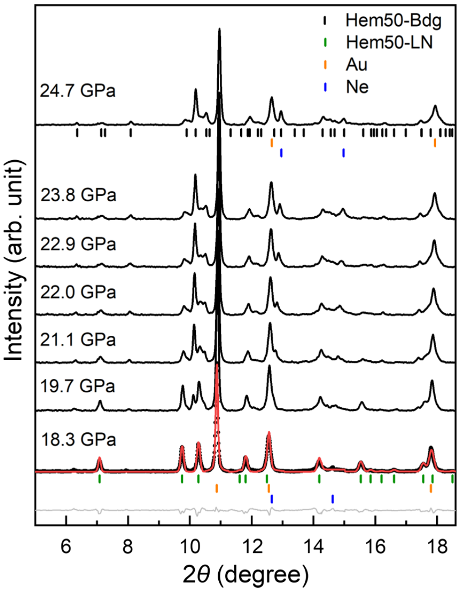

FIGURE 4. Representative powder X-ray diffraction patterns of ($Mg_{0.46}$,$Fe^{3+}_{0.53}$)($Si_{0.49}$,$Fe^{3+}_{0.51}$)O_3 at 18.3–24.7 GPa and 300 K show a phase transition from $LiNbO_3$-type structure to bridgmanite. Le Bail fitting is applied to interpret the pattern at 18.3 GPa. The red solid curve represents the refined profile, the gray curve represents the misfit, and the vertical ticks represent $LiNbO_3$-type structure (green), Au (orange), and Ne (blue). At 24.7 GPa, the vertical ticks represent bridgmanite (black), Au (orange), and Ne (blue). The wavelength of the incident X-ray beam is 0.434 Å. (Color online.)

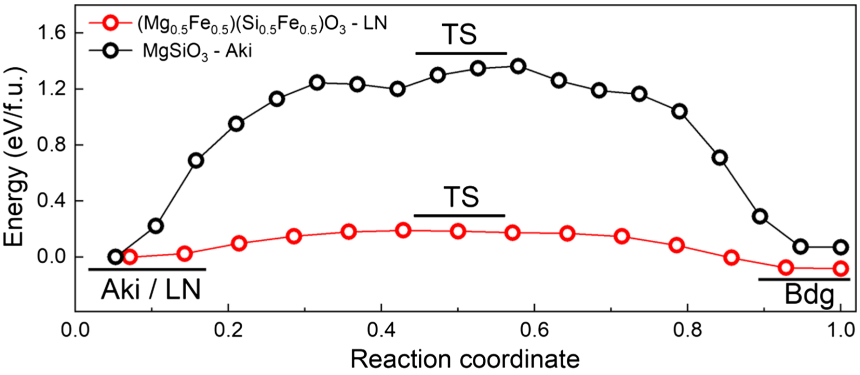

FIGURE 5. Potential energy profile connecting $(Mg_{0.5},Fe^{3+}_{0.5})(Si_{0.5},Fe^{3+}_{0.5})O_3$ $LiNbO_3$-type structure and bridgmanite (red dot line) compared to $MgSiO_3$ akimotoite and bridgmanite (black dot line), obtained by first-principles free-energy landscape sampling methods. A transition state (TS) can be located along the pathway. (Color online.)

$(Mg_{0.5},Fe^{3+}_{0.5})(Si_{0.5},Fe^{3+}_{0.5})O_3$-bridgmanite, facilitating rearrangement of sites without diffusing atoms during the phase transition. Thus, $MgSiO_3$ akimotoite and $(Mg_{0.5},Fe^{3+}_{0.5})(Si_{0.5},Fe^{3+}_{0.5})O_3$ LN have different atom-to-atom correspondence pathways, and consequently, more energy is needed to transform the akimotoite to correctly A/B sorted bridgmanite.

We confirm the phase transition mechanism of Hem50-LN to Hem50-Bdg and the effects of incorporation of Fe^{3+} on the energy barrier via theoretical simulations. We investigated the structural transformations from Hem50-LN to Hem50-Bdg and from $MgSiO_3$ Aki to Bdg, and identified their lowest energy pathways, respectively (Fig. 5). The mechanism of the transformation between these related structures (Online Materials[1] Fig. S1) is octahedral tilting. The enthalpy barrier of the Hem50-LN to Hem50-Bdg transition is 0.19 eV/formula unit (fu) (18.33 kJ/mol), which is only 14% of the 1.36 eV/fu (131.22 kJ/mol) barrier for Fe-free Aki to Bdg transition. The low enthalpy barrier between Hem50-LN and Hem50-Bdg explains our observation that the transition can proceed even at ambient temperature. As a comparison, the activation energy for post-spinel transformation in Mg_2SiO_4 was estimated as 355 kJ/mol (Kubo et al. 2002a), which requires overpressure of more than ~1 GPa at the transformation at 700 km depth in cold slabs. Growth of majoritic garnet (van Mierlo et al. 2013) and transformation from garnet to bridgmanite (Kubo et al. 2002b) have also been argued to be delayed by kinetics in cold slabs. In contrast, the ilmenite/$LiNbO_3$-type structure to Bdg transition would be more kinetically favorable than the post-spinel or post-garnet transition.

The transition from LN-type phase to Bdg observed for our Fe^{3+}-rich composition started on compression between 18.3–19.7 GPa at 300 K. The onset of the transition is similar to the 18 GPa transition observed for LN-type $(Mg_{0.5},Fe^{3+}_{0.5})(Si_{0.5},Al_{0.5})O_3$ powder (Zhu et al. 2020). However, experiments on single crystals of LN-type $(Mg_{0.5},Fe^{3+}_{0.5})(Si_{0.5},Al_{0.5})O_3$ and modified corundum *R*3 structure of $(Mg_{0.5},Fe^{3+}_{0.5})(Si_{0.5},Fe^{3+}_{0.5})O_3$ indicate transitions to Bdg or a novel double perovskite at lower pressures, 8(2) and 12(2) GPa, respectively (Koemets et al. 2023). The difference in the observed transition pressures could be due to structure/compositional variance between the samples or differences in stress conditions in single crystal vs. powder (although all studies employed neon quasi-hydrostatic pressure-transmitting medium). This difference in transition conditions could also indicate the metastability of the LN-type phase. If hysteresis is observed in the transition, the conditions at which the Gibbs free energy of the bridgmanite phase becomes lower than the LN-type phase, whether or not this is the minimum energy (equilibrium) state, should be between the minimum observed transition pressure on compression and maximum transition pressure on decompression.

If 12(2) GPa is an upper bound on the LN or modified corundum *R*3 structure to (single or double) perovskite transition, this would be consistent with crystallization as perovskite-type phase at 15–27 GPa in all experiments by Wang et al. (2021), Chanyshev et al. (2023), and Koemets et al. (2023) and transformation to the *R*3*c* or *R*3 structure on decompression. These studies do not have in situ characterization to confirm the structure formed at 15–27 GPa. Because synthesis experiments performed in the bridgmanite stability field yielded a $LiNbO_3$-type phase upon quenching to ambient pressures, we infer that the reverse transition during decompression proceeds without heating as well (Liu et al. 2018; Wang et al. 2021). In addition, if the Clapeyron slope of the conditions of the LN-Bdg transition is negative (like the Aki-Bdg transition), the LN-Bdg transition could occur at even lower pressures at high temperatures. These results point to Fe^{3+} stabilizing the perovskite structure within the Earth's transition zone.

GEOPHYSICAL IMPLICATIONS

Differences in the stability of corundum-family and bridgmanite structures due to composition may impact the dynamics of subducting slabs. $MgSiO_3$ akimotoite in subducting slabs is thought to impede subduction at 660 km depth due to the Aki-Bdg transition with a negative Clapeyron slope and low density (e.g., Chanyshev et al. 2022). Incorporation of up to ~10% $Fe^{2+}SiO_3$ in ilmenite-structured akimotoite was observed to have no effect on the transition from akimotoite to bridgmanite or possibly slightly increase the transition pressure based on observed compositions of coexisting phases (Ito and Yamada 1982), further impeding subduction. In contrast, dense Fe^{3+}-bearing bridgmanite may be stable within the $MgSiO_3$ akimotoite stability field in an oxidized Fe-bearing system. Crystallization of this dense phase within oxidized subducting lithosphere at transition zone pressures may facilitate subduction.

Whether phase transitions from akimotoite or spinel to bridgmanite result in a seismic discontinuity depends on the depth range of coexisting low- and high-pressure phases. Incorporation of Al in $MgSiO_3$ bridgmanite is predicted to broaden the transition pressure range by ~1 GPa and increase the Aki-Bdg transition pressure by ~2–3 GPa along a cold slab geotherm (Ita and Stixrude 1992; Vacher et al. 1998; Akaogi et al. 2002). For compositions enriched in Al^{3+}, this breadth suggests that a transition from the Aki to Bdg would not be observable globally as a sharp seismic discontinuity. The 660-km discontinuity can be explained by the post-spinel transition in both pyrolite (Ishii et al. 2011) and harzburgite (Irifune and Ringwood 1987) not only due to its steep Clapeyron slope but also the extremely narrow transition pressure interval (Ito and Takahashi 1989; Ishii et al. 2019). In the $MgSiO_3$-Fe_2O_3 system investigated by Wang et al. (2021) and Chanyshev et al. (2023), most of the Fe_2O_3 component partitions into the Fe^{3+}-rich phase, leaving relatively Fe^{3+}-depleted spinel and bridgmanite. This partitioning can be expected to further sharpen the post-spinel phase boundary at 660 km. Because the $LiNbO_3$-type phase does not appear stable and bridgmanite would replace akimotoite, no discontinuity would be associated with the akimotoite-bridgmanite transition in oxidized Fe-bearing mantle.

The stability of Fe^{3+}-rich bridgmanite in the transition zone depends on sufficient iron and high oxygen fugacity. Mantle lithologies exhibit widely ranging oxygen fugacity (Cottrell et al. 2021), and upwelling plumes may also be relatively oxidized (Moussallam et al. 2019). Self-disproportionation of Fe^{2+} may elevate the concentration of Fe^{3+} in the transition zone, as in the lower mantle for the mineral bridgmanite (Frost et al. 2004; Rohrbach et al. 2007; Chanyshev et al. 2023). As a minor phase, Fe^{3+}-bearing bridgmanite in the transition zone would not dominate seismic properties but could have a significant effect on the density, composition, and seismic properties of the overall phase assemblage.

The $LiNbO_3$-type structure has also been observed in natural materials that have been shocked to high pressures during planetary impacts and inferred to represent back-transformation from the perovskite structure. $LiNbO_3$-structured $FeTiO_3$, now named wangdaoite, was documented in the Ries impact crater (Dubrovinsky et al. 2009) and the Suizhou chondritic meteorite (Xie et al. 2020). In these samples, coexisting minerals suggest shock pressures estimated in the 16–28 GPa range, corresponding to the $FeTiO_3$ perovskite stability field. Shock veins in chondrites also contain $R\bar{3}$ $FeSiO_3$ hemleyite (Bindi et al. 2017), $MgSiO_3$ akimotoite (Tschauner et al. 2018), *Pnma* $FeSiO_3$ hiroseite (Bindi et al. 2020), and $MgSiO_3$ bridgmanite (Tschauner et al. 2014). In contrast to natural hemleyite, which was reported to contain no significant ferric iron, natural hiroseite was observed with Fe^{3+}/Fe total ~19%, supporting the importance of crystal chemistry of Fe^{3+} in perovskites. However, the interpretation of $R\bar{3}c$ hematite in meteorites is complicated by the many mechanisms through which this phase forms, including weathering and low-pressure, high-temperature decomposition of silicates (e.g., Kuchka et al. 2017). The results of this work provide constraints on interpreting intermediate $MgSiO_3$-Fe_2O_3 phases transformed during shock impacts.

CONCLUDING REMARKS

We performed high-pressure XRD measurements on synthetic $LiNbO_3$-type $(Mg_{0.46},Fe^{3+}_{0.53})(Si_{0.49},Fe^{3+}_{0.51})O_3$ (Hem50-LN), and we observed the Hem50-LN to Bdg transition occurring between 18.3 and 24.7 GPa at 300 K. We investigated the phase transition mechanism of akimotoite and $LiNbO_3$-structured phases to bridgmanite with compositions of both $MgSiO_3$ and $(Mg_{0.5},Fe^{3+}_{0.5})(Si_{0.5},Fe^{3+}_{0.5})O_3$ via first-principles calculation and determined that accommodating Fe in LN-phase results in a lowered kinetic energy to transform to bridgmanite relative to transforming to bridgmanite from akimotoite. Our experiments and calculations confirm that accommodating Fe^{3+} in LN can significantly decrease the kinetic energy barrier to crystallize bridgmanite. Due to the enrichment of Fe^{3+}, this dense phase may play an important role in slab dynamics and localized geochemical anomalies.

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