A new (Mg₀.₅Fe³⁺₀.₅)(Si₀.₅Al³⁺₀.₅)O₃ LiNbO₃-type phase synthesized at lower mantle conditions

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Abstract

A new (Mg₀.₅Fe³⁺₀.₅)(Si₀.₅Al³⁺₀.₅)O₃ LiNbO₃-type phase was synthesized at 27 GPa and 2000 K under highly oxidized conditions using an advanced multi-anvil apparatus. Single crystals for this phase are 0.2-0.3 mm in dimension and maroon in color. They crystallize in a noncentrosymmetric structure with space group R3c and lattice parameters of a = b = 4.8720 (6) Å, c = 12.898 (2) Å, and V = 265.14 (8) Å³. Fe³⁺ and Al³⁺ cations substitute into A (Mg²⁺) and B (Si⁴⁺) sites through charge-coupled substitution mechanism, respectively. The distortion of BO₆ (B = Si₀.₅Al³⁺₀.₅) octahedra is 1.6 times higher than that of AO₆ (A = Mg₀.₅Fe³⁺₀.₅) octahedra. This phase is probably recovered from bridgmanite at lower-mantle conditions by a diffusionless transition because of the displacement of A cations and distortion of BO₆ octahedra on releasing pressure. Bridgmanite can thus contain the FeAlO₃ component (50 mol%) beyond previously reported solubility limit (37 mol%). The present study shows that the Earth’s most abundant elements form a new Fe³⁺- and Al³⁺-rich LiNbO₃-type compound from bridgmanite at lower mantle conditions. This new compound provides a new insight into the complicated crystal chemistry of LiNbO₃-type phase/bridgmanite and constrains the pressure and temperature conditions for shocked meteorites.

Keywords: LiNbO₃-type, single crystals, bridgmanite, crystal chemistry, lower mantle
INTRODUCTION

Phase compositions of $ABO_3$ compounds are of great significance in physics, chemistry, and geoscience. Among $ABO_3$ compounds, LiNbO$_3$ ($LN$)-type compounds exhibit remarkable physical properties because of their noncentrosymmetric structure (space group: $R\bar{3}c$) and capacity to adopt a multitude of distortions between $BO_6$ and $AO_6$ octahedra (Navrotsky et al., 1998). Some $LN$-type oxides such as LiNbO$_3$ and LiTaO$_3$ can be prepared at ambient conditions (Megaw, 1968; Abrahams and Bernstein, 1967), whereas the majority of $LN$-type oxides have been regarded as a metastable quench phase formed from high-pressure stable orthorhombic perovskite by a diffusionless transformation upon decompression (e.g., Ross et al., 1989; Leinenweber, 1991; Navrotsky et al., 1998; Ishii et al. 2017). Natural $LN$-type FeTiO$_3$ was also discovered in shocked gneiss from the Ries impact crater, southern Germany (Dubrovinsky et al., 2009), and can be used an indicator for shock conditions (Akaogi et al., 2016). Consequently, synthesis of new $LN$-type compounds and exploration of the novel functionalities related to their structures are important in Earth and planetary science as well as and physics and material science.

MgSiO$_3$ perovskite (bridgmanite) is one of the most common $ABO_3$ phases in the Earth’s mantle, and can contain a large amount of Fe$^{3+}$ in the presence of Al$^{3+}$ (McCammon, 1997; Frost and Langenhorst, 2002). The incorporation of Fe$^{3+}$ and Al$^{3+}$ would great change the physical and chemical properties of bridgmanite such as elasticity (e.g., Boffa Ballaran et al., 2012), electrical conductivity (e.g., Yoshino et al., 2016), and Mg-Fe partitioning in the lower-mantle phases (Frost and Langenhorst, 2002). Several studies have found that MgSiO$_3$ bridgmanite with the Al$_2$O$_3$ contents above 25 mol% would transform to the $LN$-type phase upon releasing pressure (Funamori et al., 1997; Miyajima et al., 1999; Liu et al., 2016, 2017a; Ishii et al., 2017).
presence of Al\textsuperscript{3+} can also enhance the incorporation of Fe\textsuperscript{3+} to form the charge-coupled FeAlO\textsubscript{3} component in bridgmanite through the following reaction: \( \text{Al}_2\text{O}_3 + 3\text{Fe}^{2+}\text{O} = 2\text{Fe}^{3+}\text{AlO}_3 + \text{Fe}^0 \) (Frost and Langenhorst, 2002). The effective ionic radius of Fe\textsuperscript{3+} (0.645 Å) in six-fold coordination is significantly larger than that of Al\textsuperscript{3+} (0.535 Å) and Si\textsuperscript{4+} (0.40 Å) but close to that of Mg\textsuperscript{2+} (0.72 Å) (Shannon, 1976). In principle, Fe\textsuperscript{3+} preferentially substitutes on the \( A \) (Mg\textsuperscript{2+}) site rather than the \( B \) (Si\textsuperscript{4+}) site due to comparable cation sizes. It is thus expected that FeAlO\textsubscript{3}-bearing LN-type phases can be synthesized at lower mantle conditions and exhibit similar or distinct physical and chemical properties with only Al-bearing LN-type phases. However, such issues remain poorly understood.

Here, we report a new LN-type compound (Mg\textsubscript{0.5}Fe\textsubscript{3+0.5})(Si\textsubscript{0.5}Al\textsubscript{3+0.5})O\textsubscript{3} with \( R3c \) symmetry synthesized at 27 GPa and 2000 K in a multi-anvil press. We investigate the crystal structure of the LN-type phase by means of single crystal X-ray diffraction, electron probe microanalyzer, and Mössbauer spectroscopy. Finally, we discuss the crystal chemistry of the LN-type phase and its implications for the mineralogy of the lower mantle and the pressure and temperature conditions of shocked meteorites.

**EXPERIMENTAL METHODS**

A fine-grained oxide mixture with a bulk composition 50 mol\% MgSiO\textsubscript{3} plus 50 mol\% FeAlO\textsubscript{3} was used as the starting material, which was prepared from reagent-grade oxide powders of MgO, SiO\textsubscript{2}, Al\textsubscript{2}O\textsubscript{3}, and Fe\textsubscript{2}O\textsubscript{3} with a grain size smaller than 1 µm. The starting material was loaded into a platinum capsule, heated at 800 K for one hour, and then welded. This procedure is expected to maintain \( \text{Fe}^{3+}/\sum \text{Fe} = 100\% \) and minimize absorbed water. Quench experiments were
performed at 27 GPa and 2000 K for 20 hours using a Cr$_2$O$_3$-doped MgO octahedron with a 7-
mm edge length and LaCrO$_3$ sleeve for heating in combination with tungsten carbide cubes with
3-mm truncated edge lengths in a Kawai-type multi-anvil apparatus (IRIS-15) with a press load
of 15 MN at the Bayerisches Geoinstitut, University of Bayreuth (Ishii et al., 2016; Liu et al.
2017b).

Phases in recovered samples were initially identified using a micro-focused X-ray
diffraction (MXRD) with a Co anode operated at 40 kV and 500 mA. Back-scattered electron
(BSE) images were obtained using a LEO1530 scanning electron microscope (SEM). Phase
compositions were analyzed using a JEOL JXA-8200 electron probe microanalyzer (EPMA)
operating at an acceleration voltage of 15 kV and a beam current of 5 nA with standards of
enstatite for Mg and Si and corundum for Al. A high-quality single crystal of ~0.04 mm in
diameter was selected for single crystal X-ray diffraction (SXRD) and the data were collected at
ambient conditions using a three-circle diffractometer equipped with a SMART APEX CCD
detector and a high-brilliance Iµs 3.0 microfocus anode (Ag radiation). The exposure time was
10 s per frame. Lorentz and polarization corrections as well as an analytical absorption
correction based on the crystal shape were taken into account for the correction of the reflection
intensities using the CrysAlis package (Oxford Diffraction 2017). All crystallographic data
refinements were performed based on $F^2$ using the SHELX97 program package (Sheldrick, 2008)
in the WinGX System (Farrugia, 1999). The Fe$^{3+}$/ΣFe ratio was measured using Mössbauer
spectroscopy on one the same single crystal, which was conducted in transmission mode on a
constant acceleration Mössbauer spectrometer with a nominal 370 MBq $^{57}$Co point source in a 12
mm Rh matrix. The velocity scale was calibrated relative to α-Fe. Detailed information can be
found in McCammon (1994).
RESULTS AND DISCUSSIONS

The MXRD pattern of the recovered sample indicates that all diffraction peaks can be matched to those of an \( LN \)-type phase (Fig. 1a). A BSE image further confirms that the run product consists of only a single phase with grain sizes on the order of 0.2-0.3 mm (Fig. 1b). Optical microscope observations show that the crystals are translucent, maroon in color, and free of visible imperfections (Fig. 1c). The room temperature Mössbauer spectrum of the sample (Fig. 1d) can be fit to one doublet. The hyperfine parameters, center shift (CS) and quadruple splitting (QS), are \( 0.34 \pm 0.01 \) and \( 0.91 \pm 0.01 \) mm/s, respectively. These values are in good agreement with \( Fe^{3+} \) in silicate perovskite with CS of \( \sim 0.3 \) mm/s and QS of \( 0.73-0.94 \) mm/s (McCammon, 1997; Lauterbach et al. 2000). However, a doublet with high CS and QS characteristic of \( Fe^{2+} \) in silicate perovskite is not observed. The \( Fe^{3+}/2Fe \) value is thus 100% within analytical uncertainty, suggesting a pure \( Fe^{3+} \)-bearing \( LN \) phase. EPMA shows that the \( LN \)-type phase has a composition of \( (Mg^{0.49 \pm 0.01}Fe^{3+^{0.49 \pm 0.01}}Al^{3+^{0.02 \pm 0.01}})(Si^{0.50 \pm 0.01}Al^{3+^{0.50 \pm 0.01}})O^{3.01 \pm 0.01} \). Because the effective ionic radius of \( Fe^{3+} \) (0.645 Å) in six-fold coordination is closer to that of \( Mg^{2+} \) (0.72 Å) rather than to that of \( Si^{4+} \) (0.40 Å), and the radius of \( Al^{3+} \) (0.535 Å) is closer to that of \( Si^{4+} \), \( Fe^{3+} \), and \( Al^{3+} \) are expected to substitute for \( Mg^{2+} \) (\( A \) site) and \( Si^{4+} \) (\( B \) site), respectively, through a charge-coupled substitution (\( Fe^{3+} \) (\( A \)) + \( Al^{3+} \) (\( B \)) = \( Mg^{2+} \) (\( A \)) + \( Si^{4+} \) (\( B \))). But we note that a small fraction of \( Al^{3+} \) may be present on the \( A \) site (within the uncertainty of the measurements) due to an excess of \( Al \). These results will be discussed below based on the results of SXRD refinement.

Crystallographic data for the \( LN \)-type \( (Mg_{0.5}Fe^{3+}_{0.5})(Si_{0.5}Al^{3+}_{0.5})O_3 \) phase from the SXRD refinement can be found in the deposited CIF. The lattice parameters and volume are \( a = b = 4.8720 \) (6) Å, \( c = 12.898 \) (2) Å, and \( V = 265.14 \) (8) Å\(^3\), which are substantially larger than those
reported for the Mg$_{0.75}$Al$_{0.5}$Si$_{0.75}$O$_3$ LN–type phase ($a = b = 4.8194(3)$ Å, $c = 12.6885(8)$ Å, $V = 255.23(3)$ Å$^3$; Ishii et al., 2017). More than 900 unique reflections were collected and indexed in the space group $R3c$ (#161) with $R_{int} = 2.9\%$. A structure solution based on the single crystal data was further refined in an anisotropic approximation for all atoms to $R_1 = 5.9\%$. The scattering factors of Mg, Al, and Si are similar, but very different to those of Fe. By assuming that both cation sites are fully occupied, we found that Fe$^{3+}$ is located only in A site together with Mg. These results are in agreement with the Mössbauer spectroscopy data. Free refinement of the A-site occupancy yields 0.48 (5) and 0.52 (5) for Mg and Fe$^{3+}$, respectively, which agrees with results of the chemical analysis. These two occupancies are indistinguishable from 0.5 within the uncertainties of this method. In the final structural refinement, we fixed the occupancies of Fe$^{3+}$ and Mg in the A-site to 0.5. Since Si and Al in the B site cannot be distinguished by SXRD, their occupancies were also fixed to 0.5 based on the composition.

As shown in Figure 2, the Mg$_{0.5}$Fe$_{3+0.5}$ and Si$_{0.5}$Al$_{3+0.5}$ atoms occupy six-coordinated A- and B-sites to form $AO_6$ and $BO_6$ octahedra, respectively, which are interpenetrated via edge-sharing octahedral dimers in the $ab$-plane and face-sharing octahedral pairs along the $c$-axis. The size of the $AO_6$ octahedron (~10.3 Å$^3$) is significantly larger than that of the $BO_6$ octahedron (~8.6 Å$^3$) because $AO_6$ and $BO_6$ octahedra are occupied by larger (Mg$^{2+}$ and Fe$^{3+}$) and smaller (Si$^{4+}$ and Al$^{3+}$) cations, respectively. Noticeable structural features include the distortions of $AO_6$ and $BO_6$ octahedra as a result of shifts of $A$ and $B$ cations from the geometrical centers of face-sharing octahedra by 0.2 and 0.3 Å, respectively (see deposited CIF). The average bond lengths of two types of $<Mg/Fe-O>$ are 1.975 ± 0.006 and 2.090 ± 0.008 Å, which are significantly larger than those of $<Si/Al-O>$ (1.939 ± 0.008 and 1.802 ± 0.006 Å). We estimated the octahedral distortion using the above bond lengths by the following equation:
\[
\Delta = \frac{1}{6} \sum_i \left( \frac{(d_i - d_{\text{ave}})}{d_{\text{ave}}} \right)^2 ,
\]

where \(d_i\) is the individual bond length and \(d_{\text{ave}}\) is the average bond length. Values of \(\Delta\) are \(8 \times 10^{-4}\) and \(13 \times 10^{-4}\) for \((\text{Mg}_{0.5}\text{Fe}^{3+}_{0.5})\text{O}_6\) and \((\text{Si}_{0.5}\text{Al}^{3+}_{0.5})\text{O}_6\) octahedra, respectively, confirming a weaker distortion of \(\text{AO}_6\) than \(\text{BO}_6\). Furthermore, the distortion of \(\text{BO}_6\) octahedra in the present phase is significantly larger than that of \(\text{MgSiO}_3\) bridgmanite \((1.6 \times 10^{-5})\) by a factor of 86.

We also use the Goldschmidt tolerance factor \((t)\) for LN-type or perovskite \(\text{ABO}_3\) compounds to express the geometric stability and crystal structure distortions in terms of constituent ionic packing (Goldschmidt, 1926). The parameter \(t\) is defined by the ratios of constituent ionic radii of \(A\), \(B\) and \(O\) as \(t = \frac{(r_A + r_O)}{\sqrt{2}(r_B + r_O)}\), where \(r_A\), \(r_B\), and \(r_O\) are the ionic radii of \(A\) and \(B\) in six-fold coordination and \(O\), respectively. As shown in Figure 3, we obtained \(t = 0.79\) for \((\text{Mg}_{0.5}\text{Fe}^{3+}_{0.5})\text{(Si}_{0.5}\text{Al}^{3+}_{0.5})\text{O}_3\) \((r_{\text{Mg}^{2+}} = 0.72 \, \text{Å}; r_{\text{Al}^{3+}} = 0.535 \, \text{Å}; r_{\text{Fe}^{3+}} = 0.645 \, \text{Å}; r_O = 1.4 \, \text{Å})\) in the present study, which is comparable with that of LN-type \(\text{MnTiO}_3\) \((t = 0.79, \text{Ross et al., 1989})\), \(\text{Mg}_{0.75}\text{Al}_{0.5}\text{Si}_{0.75}\text{O}_3\) \((t = 0.80, \text{Liu et al., 2016, 2017a; Ishii et al., 2017})\) but significantly higher than that of \(\text{FeTiO}_3\) \((t = 0.77, \text{Leinenweber et al., 1991})\). All of these values are significantly lower than those for stable perovskite of \(\text{CaSiO}_3\) \((t = 0.95, \text{Liu and Ringwood, 1975})\) and \(\text{MgSiO}_3\) \((t = 0.83, \text{Ito and Matsui, 1978})\). In summary, \(t\) decreases with increasing \(B\) cation radius relative to that of the \(A\) cation as a result of the increasing degree of cell distortion.

**IMPLICATIONS**

Most LN-type phases are generally accepted as a quenchable phase that back-transforms from a high-pressure stable perovskite phase by a diffusionless transition because of the
displacement of A cations and distortion of BO$_6$ octahedra resulting from cation substitution upon decompression (e.g., Navrotsky et al., 1998; Ross et al., 1989; Leinenweber, 1991; Ishii et al., 2017). It is noted that the charge-coupled FeAlO$_3$ component dominates in bridgmanite, especially Fe$^{3+}$- and Al$^{3+}$-rich bridgmanite, although trace amounts of the oxygen vacancy substitution may exist in Fe$^{3+}$- and Al$^{3+}$-poor bridgmanite in the (Mg, Fe$^{2+}$)O-Fe$^{3+}$AlO$_3$-SiO$_2$ ternary system (Fig. 4) (McCammon, 1997; Lauterbach et al. 2000; Frost and Langenhorst, 2002; Nishio-Hamane et al., 2005; Saikia et al., 2009; Boffa Ballaran et al. 2012; Yoshino et al., 2016). The Al$_2$O$_3$ content (25 mol%) in the present phase is also considerably higher than that in the Fe-free bridgmanite (12 mol%, Liu et al., 2016; 2017a). Therefore, the Al$_2$O$_3$ content in bridgmanite could be highly enhanced in the presence of Fe$^{3+}$ because of the formation of the charge-coupled Fe$^{3+}$AlO$_3$ composition. In the present study, bridgmanite can incorporate the FeAlO$_3$ content up to 50 mol% at 27 GPa and 2000 K, which is beyond solubility limit in both pyrolite (~6 mol%) and MORB (mid-ocean ridge basalt) (~25 mol%) and previously reported value (37 mol%, Boffa Ballaran et al., 2012). Bridgmanite would thus be the major phase for Fe$^{3+}$ and Al$^{3+}$ for the pyrolite and MORB lower mantle.

Furthermore, the pressure at which the present phase forms (27 GPa) is significantly lower than that of the pyropic (Mg$_3$Al$_2$Si$_3$O$_{12}$ pyrope) LN-type phase (45 GPa, Liu et al., 2016; 2017a). This observation may be explained by a reduction of the ionic radius ratio between the A-site cation and oxygen because of the smaller Fe$^{3+}$ in A (Mg) site and larger octahedral distortion than found in the pyropic LN-type phase. Our results together with that obtained by Boffa Ballaran et al. (2012) suggest that bridgmanite with the FeAlO$_3$ content above ~37 mol% would transform into the LN-type phase upon decompression from lower mantle conditions.
The formation of the LN–type phase is a useful indicator for constraining the pressure and temperature conditions for shocked meteorites (Sharp et al., 1997; Xie et al., 2006; Tomioka and Fujino 1997; Ishii et al., 2016). Dubrovinsky et al. (2009) found a natural LN–type FeTiO$_3$ phase from the Ries Crater, Germany, which is considered to be recovered from perovskite at 15-28 GPa after shocking (Akaogi et al., 2016). The presence of the Fe$^{3+}$-and Al$^{3+}$-rich LN–type phase can therefore be used to constrain the formation conditions of shocked meteorites.

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References


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FIGURE 1. Characteristics of the (Mg$_{0.5}$Fe$^{3+}_{0.5}$)(Si$_{0.5}$Al$^{3+}_{0.5}$)O$_3$ LN-type phase: (a) MXRD profile, (b) BSE image, (c) photograph of selected single crystals, and (d) Mössbauer spectrum. Black dots indicate experimental data, while the red line shows the fitted curve. Red dots indicate the residual, i.e., the difference between calculated and experimental results. The small deviations in the residual are likely due to slight deviation from Lorentzian lineshape due to next-nearest-neighbor effects in the solid solution. Abbreviations: CS: center shift, QS: quadruple splitting, FWHM: Full width at half maximum.
FIGURE 2. Crystal structure of the (Mg$_{0.5}$Fe$^{3+}_{0.5}$)(Si$_{0.5}$Al$^{3+}_{0.5}$)O$_3$ LN–type phase and $AO_6$ ($A$ = Fe$^{3+}_{0.5}$Mg$_{0.5}$) and $BO_6$ ($B$ = Al$^{3+}_{0.5}$Si$_{0.5}$) octahedra. Yellow spheres are oxygen, blue spheres are Si/Al$^{3+}$, and red spheres are Mg/Fe$^{3+}$. 
FIGURE 3. Goldschmidt diagram for selected ABO₃ perovskite and the LN-type compounds (yellow shading). Dotted lines are contours of the Goldschmit tolerance factor. Open symbols: perovskite-forming compounds (CaSiO₃: Liu and Ringwood, 1975; MgSiO₃: Ito and Matsui, 1978). Solid symbols: LN-type quenched products, (Mg₀.₅Fe³⁺₀.₅)(Si₀.₅Al³⁺₀.₅)O₃ (this study), Mg₀.₇₅Al₀.₅Si₀.₇₅O₃ (Liu et al., 2016, 2017a; Ishii et al., 2017), FeTiO₃ (Akaogi et al., 2016), MnTiO₃ (Ko and Prewitt, 1988), and LiNbO₃ (Megaw, 1968).
FIGURE 4. Ternary phase diagram of the (Mg, Fe^{2+})O-Fe^{3+}AlO_3-SiO_2 system for showing the compositions of Fe and Al-bearing bridgmanite in previous and present studies. The grey shadow is the magnified region from the whole ternary phase relations. The black star represents the composition of pyrolite by assuming the amount of Fe^{3+}/ΣFe of 50-60% under the reduced conditions (McCammon, 1997; Frost and Langenhorst, 2002), while the square represents that of MORB. Abbreviation: CCS, charge-coupled substitution (Mg^{2+} (A) + Si^{4+} (B) = M^{3+} (A) + M^{3+} (B), where M represent Fe^{3+} or Al^{3+}); OVS, oxygen vacancy substitution (2 Si^{4+} (B) + O^{2-} = 2M^{3+} (B) + V_o, where V_o is the oxygen vacancy).