

Revision 1

A new $(\text{Mg}_{0.5}\text{Fe}^{3+}_{0.5})(\text{Si}_{0.5}\text{Al}^{3+}_{0.5})\text{O}_3$ LiNbO₃-type phase synthesized at lower mantle conditions

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Abstract

A new $(\text{Mg}_{0.5}\text{Fe}^{3+}_{0.5})(\text{Si}_{0.5}\text{Al}^{3+}_{0.5})\text{O}_3$ 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 ($B = \text{Si}_{0.5}\text{Al}^{3+}_{0.5}$) octahedra is 1.6 times higher than that of AO₆ ($A = \text{Mg}_{0.5}\text{Fe}^{3+}_{0.5}$) 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

31 INTRODUCTION

32 Phase compositions of ABO_3 compounds are of great significance in physics, chemistry, and
33 geoscience. Among ABO_3 compounds, $LiNbO_3$ (LN)-type compounds exhibit remarkable
34 physical properties because of their noncentrosymmetric structure (space group: $R3c$) and
35 capacity to adopt a multitude of distortions between BO_6 and AO_6 octahedra (Navrotsky et al.,
36 1998). Some LN -type oxides such as $LiNbO_3$ and $LiTaO_3$ can be prepared at ambient conditions
37 (Megaw, 1968; Abrahams and Bernstein, 1967), whereas the majority of LN -type oxides have been
38 regarded as a metastable quench phase formed from high-pressure stable orthorhombic
39 perovskite by a diffusionless transformation upon decompression (e.g., Ross et al., 1989;
40 Leinenweber, 1991; Navrotsky et al., 1998; Ishii et al. 2017). Natural LN -type $FeTiO_3$ was also
41 discovered in shocked gneiss from the Ries impact crater, southern Germany (Dubrovinsky et al.,
42 2009), and can be used an indicator for shock conditions (Akaogi et al., 2016). Consequently,
43 synthesis of new LN -type compounds and exploration of the novel functionalities related to their
44 structures are important in Earth and planetary science as well as and physics and material
45 science.

46 $MgSiO_3$ perovskite (bridgmanite) is one of the most common ABO_3 phases in the Earth's
47 mantle, and can contain a large amount of Fe^{3+} in the presence of Al^{3+} (McCammon, 1997; Frost
48 and Langenhorst, 2002). The incorporation of Fe^{3+} and Al^{3+} would great change the physical and
49 chemical properties of bridgmanite such as elasticity (e.g., Boffa Ballaran et al., 2012), electrical
50 conductivity (e.g., Yoshino et al., 2016), and Mg-Fe partitioning in the lower-mantle phases
51 (Frost and Langenhorst, 2002). Several studies have found that $MgSiO_3$ bridgmanite with the
52 Al_2O_3 contents above 25 mol% would transform to the LN -type phase upon releasing pressure
53 (Funamori et al., 1997; Miyajima et al., 1999; Liu et al., 2016, 2017a; Ishii et al., 2017). The

54 presence of Al^{3+} can also enhance the incorporation of Fe^{3+} to form the charge-coupled FeAlO_3
55 component in bridgmanite through the following reaction: $\text{Al}_2\text{O}_3 + 3\text{Fe}^{2+}\text{O} = 2\text{Fe}^{3+}\text{AlO}_3 + \text{Fe}^0$
56 (Frost and Langenhorst, 2002). The effective ionic radius of Fe^{3+} (0.645 Å) in six-fold
57 coordination is significantly larger than that of Al^{3+} (0.535 Å) and Si^{4+} (0.40 Å) but close to that
58 of Mg^{2+} (0.72 Å) (Shannon, 1976). In principle, Fe^{3+} preferentially substitutes on the *A* (Mg^{2+})
59 site rather than the *B* (Si^{4+}) site due to comparable cation sizes. It is thus expected that FeAlO_3 -
60 bearing *LN*-type phases can be synthesized at lower mantle conditions and exhibit similar or
61 distinct physical and chemical properties with only Al-bearing *LN*-type phases. However, such
62 issues remain poorly understood.

63 Here, we report a new *LN*-type compound $(\text{Mg}_{0.5}\text{Fe}^{3+}_{0.5})(\text{Si}_{0.5}\text{Al}^{3+}_{0.5})\text{O}_3$ with *R3c*
64 symmetry synthesized at 27 GPa and 2000 K in a multi-anvil press. We investigate the crystal
65 structure of the *LN*-type phase by means of single crystal X-ray diffraction, electron probe
66 microanalyzer, and Mössbauer spectroscopy. Finally, we discuss the crystal chemistry of the *LN*-
67 type phase and its implications for the mineralogy of the lower mantle and the pressure and
68 temperature conditions of shocked meteorites.

69

70 **EXPERIMENTAL METHODS**

71 A fine-grained oxide mixture with a bulk composition 50 mol% MgSiO_3 plus 50 mol%
72 FeAlO_3 was used as the starting material, which was prepared from reagent-grade oxide powders
73 of MgO , SiO_2 , Al_2O_3 , and Fe_2O_3 with a grain size smaller than 1 μm . The starting material was
74 loaded into a platinum capsule, heated at 800 K for one hour, and then welded. This procedure is
75 expected to maintain $\text{Fe}^{3+}/\sum\text{Fe} = 100\%$ and minimize absorbed water. Quench experiments were

76 performed at 27 GPa and 2000 K for 20 hours using a Cr₂O₃-doped MgO octahedron with a 7-
77 mm edge length and LaCrO₃ sleeve for heating in combination with tungsten carbide cubes with
78 3-mm truncated edge lengths in a Kawai-type multi-anvil apparatus (IRIS-15) with a press load
79 of 15 MN at the Bayerisches Geoinstitut, University of Bayreuth (Ishii et al., 2016; Liu et al.
80 2017b).

81 Phases in recovered samples were initially identified using a micro-focused X-ray
82 diffraction (MXRD) with a Co anode operated at 40 kV and 500 mA. Back-scattered electron
83 (BSE) images were obtained using a LEO1530 scanning electron microscope (SEM). Phase
84 compositions were analyzed using a JEOL JXA-8200 electron probe microanalyzer (EPMA)
85 operating at an acceleration voltage of 15 kV and a beam current of 5 nA with standards of
86 enstatite for Mg and Si and corundum for Al. A high-quality single crystal of ~0.04 mm in
87 diameter was selected for single crystal X-ray diffraction (SXRD) and the data were collected at
88 ambient conditions using a three-circle diffractometer equipped with a SMART APEX CCD
89 detector and a high-brilliance I μ s 3.0 microfocus anode (Ag radiation). The exposure time was
90 10 s per frame. Lorentz and polarization corrections as well as an analytical absorption
91 correction based on the crystal shape were taken into account for the correction of the reflection
92 intensities using the CrysAlis package (Oxford Diffraction 2017). All crystallographic data
93 refinements were performed based on F^2 using the SHELX97 program package (Sheldrick, 2008)
94 in the WinGX System (Farrugia, 1999). The Fe³⁺/ Σ Fe ratio was measured using Mössbauer
95 spectroscopy on one the same single crystal, which was conducted in transmission mode on a
96 constant acceleration Mössbauer spectrometer with a nominal 370 MBq ⁵⁷Co point source in a 12
97 mm Rh matrix. The velocity scale was calibrated relative to α -Fe. Detailed information can be
98 found in McCammon (1994).

100 RESULTS AND DISCUSSIONS

101 The MXRD pattern of the recovered sample indicates that all diffraction peaks can be
102 matched to those of an *LN*-type phase (Fig. 1a). A BSE image further confirms that the run
103 product consists of only a single phase with grain sizes on the order of 0.2-0.3 mm (Fig. 1b).
104 Optical microscope observations show that the crystals are translucent, maroon in color, and free
105 of visible imperfections (Fig. 1c). The room temperature Mössbauer spectrum of the sample (Fig.
106 1d) can be fit to one doublet. The hyperfine parameters, center shift (CS) and quadruple splitting
107 (QS), are 0.34 ± 0.01 and 0.91 ± 0.01 mm/s, respectively. These values are in good agreement
108 with Fe^{3+} in silicate perovskite with CS of ~ 0.3 mm/s and QS of 0.73–0.94 mm/s (McCammon,
109 1997; Lauterbach et al. 2000). However, a doublet with high CS and QS characteristic of Fe^{2+} in
110 silicate perovskite is not observed. The $\text{Fe}^{3+}/\Sigma\text{Fe}$ value is thus 100% within analytical uncertainty,
111 suggesting a pure Fe^{3+} -bearing *LN* phase. EPMA shows that the *LN*-type phase has a
112 composition of $(\text{Mg}_{0.49} \pm 0.01\text{Fe}^{3+}_{0.49} \pm 0.01\text{Al}^{3+}_{0.02} \pm 0.01})(\text{Si}_{0.50} \pm 0.01\text{Al}^{3+}_{0.50} \pm 0.01)\text{O}_{3.01} \pm 0.01$. Because
113 the effective ionic radius of Fe^{3+} (0.645 Å) in six-fold coordination is closer to that of Mg^{2+} (0.72
114 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+} ,
115 Fe^{3+} , and Al^{3+} are expected to substitute for Mg^{2+} (*A* site) and Si^{4+} (*B* site), respectively, through
116 a charge-coupled substitution (Fe^{3+} (*A*) + Al^{3+} (*B*) = Mg^{2+} (*A*) + Si^{4+} (*B*)). But we note that a small
117 fraction of Al^{3+} may be present on the *A* site (within the uncertainty of the measurements) due to
118 an excess of Al. These results will be discussed below based on the results of SXRD refinement.

119 Crystallographic data for the *LN*-type $(\text{Mg}_{0.5}\text{Fe}^{3+}_{0.5})(\text{Si}_{0.5}\text{Al}^{3+}_{0.5})\text{O}_3$ phase from the SXRD
120 refinement can be found in the deposited CIF. The lattice parameters and volume are $a = b =$
121 4.8720 (6) Å, $c = 12.898$ (2) Å, and $V = 265.14$ (8) Å³, which are substantially larger than those

122 reported for the $\text{Mg}_{0.75}\text{Al}_{0.5}\text{Si}_{0.75}\text{O}_3$ LN-type phase ($a = b = 4.8194(3) \text{ \AA}$, $c = 12.6885(8) \text{ \AA}$, $V =$
123 $255.23(3) \text{ \AA}^3$; Ishii et al., 2017). More than 900 unique reflections were collected and indexed in
124 the space group $R3c$ (#161) with $R_{\text{int}} = 2.9\%$. A structure solution based on the single crystal data
125 was further refined in an anisotropic approximation for all atoms to $R_1 = 5.9\%$. The scattering
126 factors of Mg, Al, and Si are similar, but very different to those of Fe. By assuming that both
127 cation sites are fully occupied, we found that Fe^{3+} is located only in A site together with Mg.
128 These results are in agreement with the Mössbauer spectroscopy data. Free refinement of the A-
129 site occupancy yielded 0.48 (5) and 0.52 (5) for Mg and Fe^{3+} , respectively, which agrees with
130 results of the chemical analysis. These two occupancies are indistinguishable from 0.5 within the
131 uncertainties of this method. In the final structural refinement, we fixed the occupancies of Fe^{3+}
132 and Mg in the A-site to 0.5. Since Si and Al in the B site cannot be distinguished by SXRD, their
133 occupancies were also fixed to 0.5 based on the composition.

134 As shown in Figure 2, the $\text{Mg}_{0.5}\text{Fe}^{3+}_{0.5}$ and $\text{Si}_{0.5}\text{Al}^{3+}_{0.5}$ atoms occupy six-coordinated A-
135 and B-sites to form AO_6 and BO_6 octahedra, respectively, which are interpenetrated via edge-
136 sharing octahedral dimers in the ab -plane and face-sharing octahedral pairs along the c -axis. The
137 size of the AO_6 octahedron ($\sim 10.3 \text{ \AA}^3$) is significantly larger than that of the BO_6 octahedron
138 ($\sim 8.6 \text{ \AA}^3$) because AO_6 and BO_6 octahedra are occupied by larger (Mg^{2+} and Fe^{3+}) and smaller
139 (Si^{4+} and Al^{3+}) cations, respectively. Noticeable structural features include the distortions of AO_6
140 and BO_6 octahedra as a result of shifts of A and B cations from the geometrical centers of face-
141 sharing octahedra by 0.2 and 0.3 \AA , respectively (see deposited CIF). The average bond lengths
142 of two types of $\langle \text{Mg/Fe-O} \rangle$ are 1.975 ± 0.006 and $2.090 \pm 0.008 \text{ \AA}$, which are significantly
143 larger than those of $\langle \text{Si/Al-O} \rangle$ (1.939 ± 0.008 and $1.802 \pm 0.006 \text{ \AA}$). We estimated the
144 octahedral distortion using the above bond lengths by the following equation:

145
$$\Delta = \frac{1}{6} \sum_i \left\{ \frac{(d_i - d_{ave})}{d_{ave}} \right\}^2, \quad (1)$$

146 where d_i is the individual bond length and d_{ave} is the average bond length. Values of Δ are 8×10^{-4}
147 and 13×10^{-4} for $(Mg_{0.5}Fe^{3+}_{0.5})O_6$ and $(Si_{0.5}Al^{3+}_{0.5})O_6$ octahedra, respectively, confirming a
148 weaker distortion of AO_6 than BO_6 . Furthermore, the distortion of BO_6 octahedra in the present
149 phase is significantly larger than that of $MgSiO_3$ bridgmanite (1.6×10^{-5}) by a factor of 86.

150 We also use the Goldschmidt tolerance factor (t) for LN -type or perovskite ABO_3
151 compounds to express the geometric stability and crystal structure distortions in terms of
152 constituent ionic packing (Goldschmidt, 1926). The parameter t is defined by the ratios of
153 constituent ionic radii of A , B and O as $t = (r_A + r_O) / \sqrt{2}(r_B + r_O)$, where r_A , r_B , and r_O are
154 the ionic radii of A and B in six-fold coordination and O , respectively. As shown in Figure 3, we
155 obtained $t = 0.79$ for $(Mg_{0.5}Fe^{3+}_{0.5})(Si_{0.5}Al^{3+}_{0.5})O_3$ ($r_{Mg^{2+}} = 0.72 \text{ \AA}$; $r_{Al^{3+}} = 0.535 \text{ \AA}$; $r_{Fe^{3+}} = 0.645$
156 \AA ; $r_O = 1.4 \text{ \AA}$) in the present study, which is comparable with that of LN -type $MnTiO_3$ ($t = 0.79$,
157 Ross et al., 1989), $Mg_{0.75}Al_{0.5}Si_{0.75}O_3$ ($t = 0.80$, Liu et al., 2016, 2017a; Ishii et al., 2017) but
158 significantly higher than that of $FeTiO_3$ ($t = 0.77$, Leinenweber et al., 1991). All of these values
159 are significantly lower than those for stable perovskite of $CaSiO_3$ ($t = 0.95$, Liu and Ringwood,
160 1975) and $MgSiO_3$ ($t = 0.83$, Ito and Matsui, 1978). In summary, t decreases with increasing B
161 cation radius relative to that of the A cation as a result of the increasing degree of cell distortion.

162

163 **IMPLICATIONS**

164 Most LN -type phases are generally accepted as a quenchable phase that back-transforms
165 from a high-pressure stable perovskite phase by a diffusionless transition because of the

166 displacement of A cations and distortion of BO_6 octahedra resulting from cation substitution
167 upon decompression (e.g., Navrotsky et al., 1998; Ross et al., 1989; Leinenweber, 1991; Ishii et
168 al., 2017). It is noted that the charge-coupled FeAlO_3 component dominates in bridgmanite,
169 especially Fe^{3+} - and Al^{3+} -rich bridgmanite, although trace amounts of the oxygen vacancy
170 substitution may exist in Fe^{3+} - and Al^{3+} -poor bridgmanite in the $(\text{Mg}, \text{Fe}^{2+})\text{O}-\text{Fe}^{3+}\text{AlO}_3-\text{SiO}_2$
171 ternary system (Fig. 4) (McCammon, 1997; Lauterbach et al. 2000; Frost and Langenhorst, 2002;
172 Nishio-Hamane et al., 2005; Saikia et al., 2009; Boffa Ballaran et al. 2012; Yoshino et al., 2016).
173 The Al_2O_3 content (25 mol%) in the present phase is also considerably higher than that in the Fe-
174 free bridgmanite (12 mol%, Liu et al., 2016; 2017a). Therefore, the Al_2O_3 content in bridgmanite
175 could be highly enhanced in the presence of Fe^{3+} because of the formation of the charge-coupled
176 $\text{Fe}^{3+}\text{AlO}_3$ composition. In the present study, bridgmanite can incorporate the FeAlO_3 content up
177 to 50 mol% at 27 GPa and 2000 K, which is beyond solubility limit in both pyrolite (~6
178 mol%) and MORB (mid-ocean ridge basalt) (~25 mol%) and previously reported value (37
179 mol%, Boffa Ballaran et al., 2012). Bridgmanite would thus be the major phase for Fe^{3+} and
180 Al^{3+} for the pyrolite and MORB lower mantle.

181 Furthermore, the pressure at which the present phase forms (27 GPa) is significantly
182 lower than that of the pyropic ($\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ pyrope) *LN*-type phase (45 GPa, Liu et al., 2016;
183 2017a). This observation may be explained by a reduction of the ionic radius ratio between the
184 A-site cation and oxygen because of the smaller Fe^{3+} in A (Mg) site and larger octahedral
185 distortion than found in the pyropic *LN*-type phase. Our results together with that obtained by
186 Boffa Ballaran et al. (2012) suggest that bridgmanite with the FeAlO_3 content above ~37 mol%
187 would transform into the *LN*-type phase upon decompression from lower mantle conditions.

188 The formation of the *LN*-type phase is a useful indicator for constraining the pressure and
189 temperature conditions for shocked meteorites (Sharp et al., 1997; Xie et al., 2006; Tomioka and
190 Fujino 1997; Ishii et al., 2016). Dubrovinsky et al. (2009) found a natural *LN*-type FeTiO₃ phase
191 from the Ries Crater, Germany, which is considered to be recovered from perovskite at 15-28
192 GPa after shocking (Akaogi et al., 2016). The presence of the Fe³⁺-and Al³⁺-rich *LN*-type phase
193 can therefore be used to constrain the formation conditions of shocked meteorites.

194

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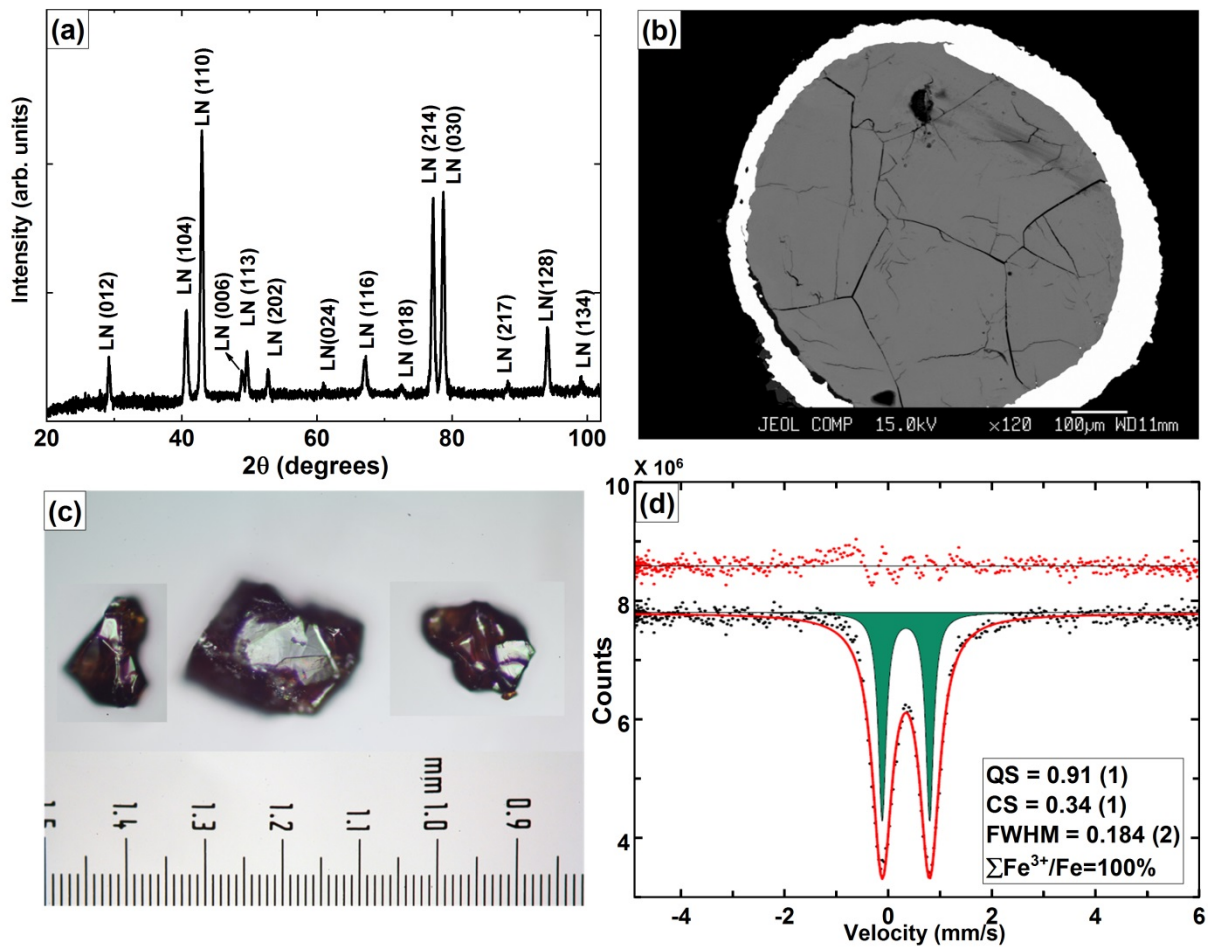
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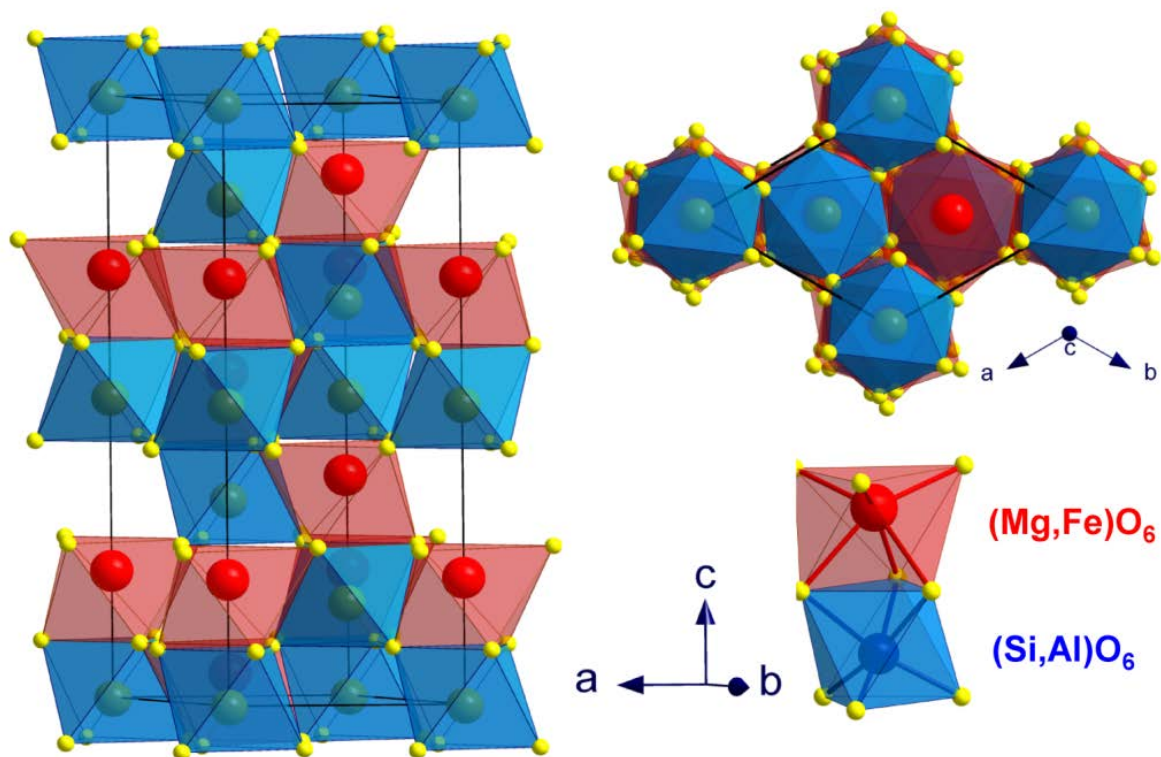
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295 **Figures and Tables**



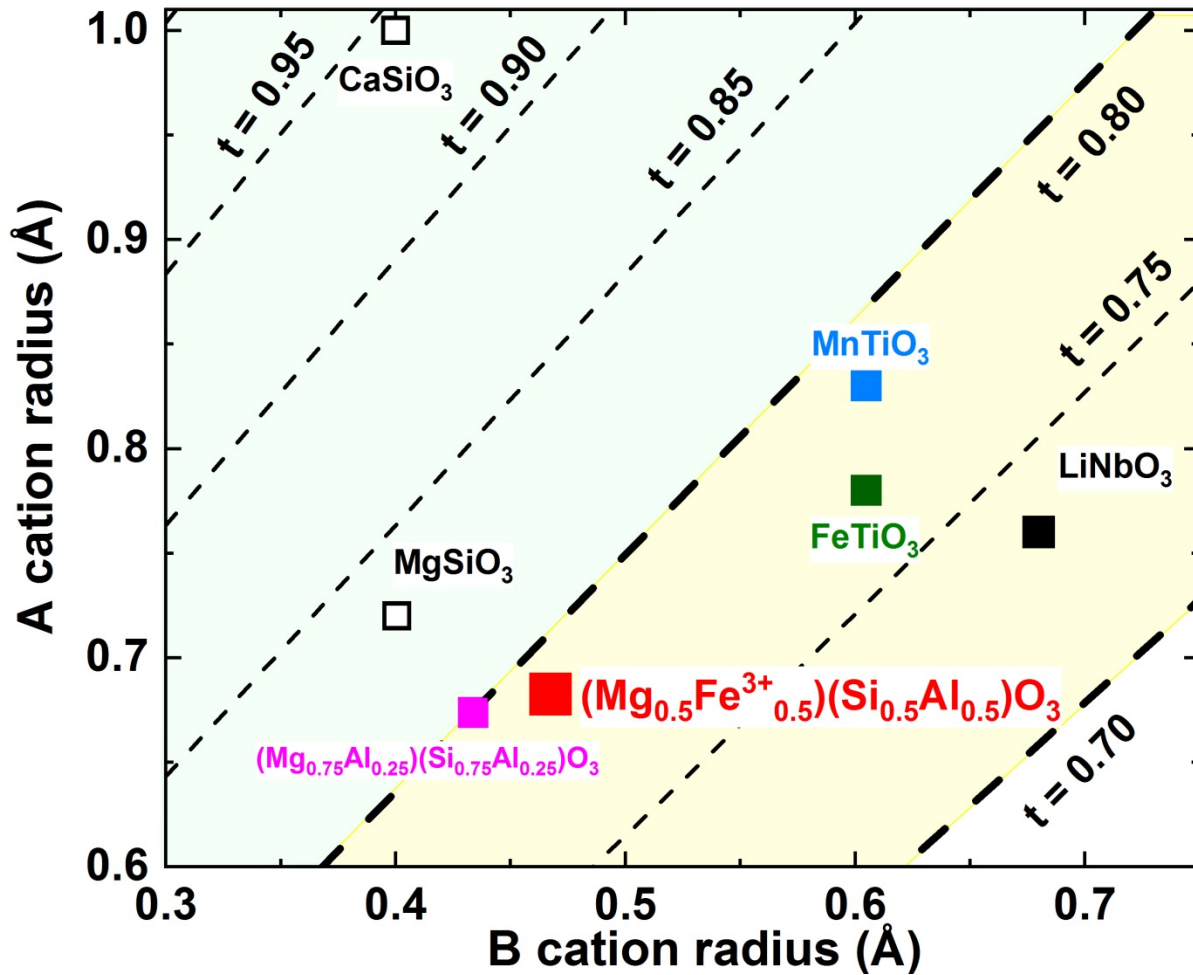
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297 **FIGURE 1.** Characteristics of the $(\text{Mg}_{0.5}\text{Fe}^{3+}_{0.5})(\text{Si}_{0.5}\text{Al}^{3+}_{0.5})\text{O}_3$ LN-type phase: (a) MXRD
298 profile, (b) BSE image, (c) photograph of selected single crystals, and (d) Mössbauer spectrum.
299 Black dots indicate experimental data, while the red line shows the fitted curve. Red dots
300 indicate the residual, i.e., the difference between calculated and experimental results. The small
301 deviations in the residual are likely due to slight deviation from Lorentzian lineshape due to
302 next-nearest-neighbor effects in the solid solution. Abbreviations: CS: center shift, QS:
303 quadruple splitting, FWHM: Full width at half maximum.



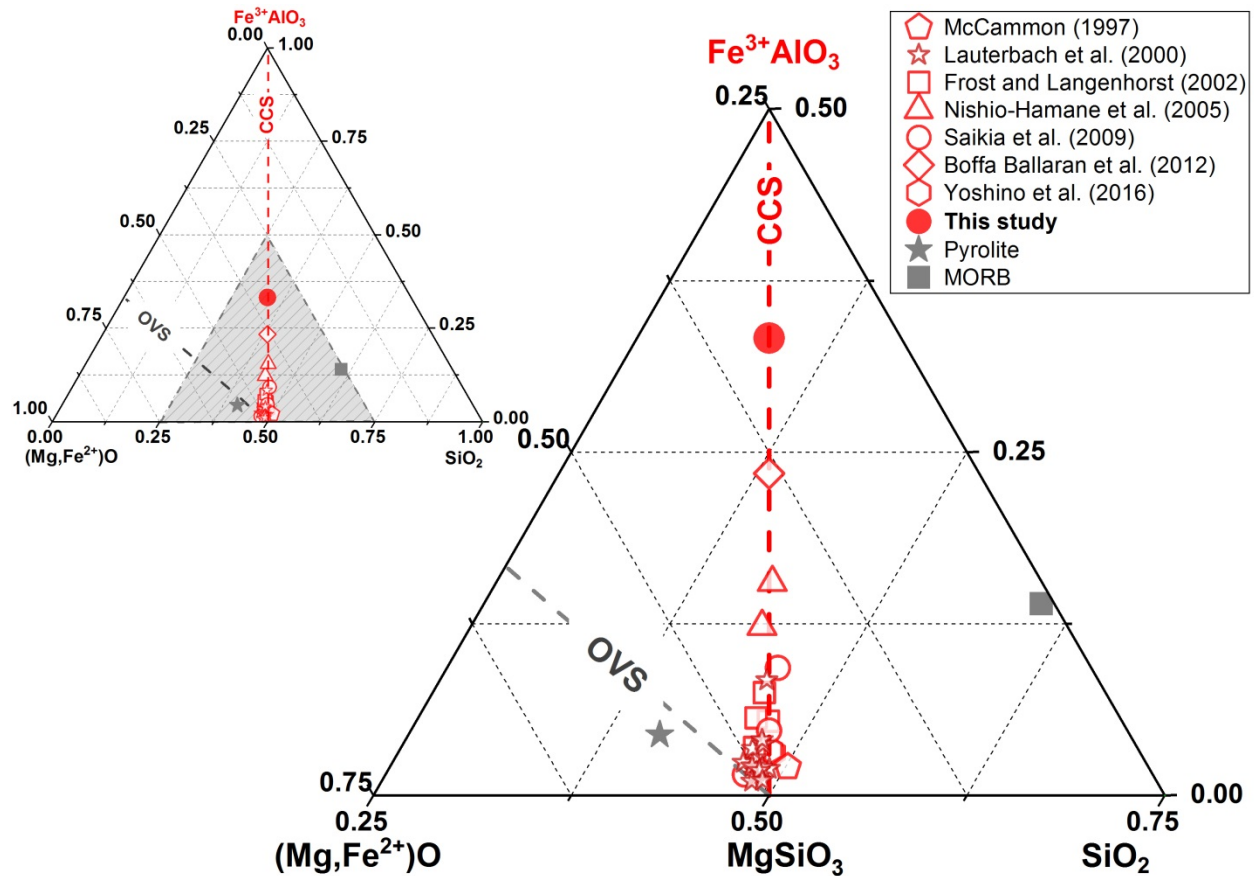
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FIGURE 2. Crystal structure of the $(\text{Mg}_{0.5}\text{Fe}^{3+}_{0.5})(\text{Si}_{0.5}\text{Al}^{3+}_{0.5})\text{O}_3$ LN-type phase and AO_6 ($A = \text{Fe}^{3+}_{0.5}\text{Mg}_{0.5}$) and BO_6 ($B = \text{Al}^{3+}_{0.5}\text{Si}_{0.5}$) octahedra. Yellow spheres are oxygen, blue spheres are Si/Al³⁺, and red spheres are Mg/Fe³⁺.



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309 **FIGURE 3.** Goldschmidt diagram for selected ABO_3 perovskite and the LN -type compounds (yellow
310 shading). Dotted lines are contours of the Goldschmit tolerance factor. Open symbols: perovskite-forming
311 compounds ($CaSiO_3$; Liu and Ringwood, 1975; $MgSiO_3$; Ito and Matsui, 1978). Solid symbols: LN -type
312 quenched products, $(Mg_{0.5}Fe^{3+}_{0.5})(Si_{0.5}Al_{0.5})O_3$ (this study), $Mg_{0.75}Al_{0.5}Si_{0.75}O_3$ (Liu et al., 2016, 2017a;
313 Ishii et al., 2017), $FeTiO_3$ (Akaogi et al., 2016), $MnTiO_3$ (Ko and Prewitt, 1988), and $LiNbO_3$ (Megaw,
314 1968).



315
 316 **FIGURE 4.** Ternary phase diagram of the $(\text{Mg}, \text{Fe}^{2+})\text{O}-\text{Fe}^{3+}\text{AlO}_3-\text{SiO}_2$ system for showing the
 317 compositions of Fe and Al-bearing bridgmanite in previous and present studies. The grey shadow is the
 318 magnified region from the whole ternary phase relations. The black star represents the composition of
 319 pyrolite by assuming the amount of $\text{Fe}^{3+}/\Sigma\text{Fe}$ of 50-60% under the reduced conditions (McCammon,
 320 1997; Frost and Langenhorst, 2002), while the square represents that of MORB. Abbreviation: CCS,
 321 charge-coupled substitution ($\text{Mg}^{2+}(\text{A}) + \text{Si}^{4+}(\text{B}) = \text{M}^{3+}(\text{A}) + \text{M}^{3+}(\text{B})$, where M represent Fe^{3+} or Al^{3+});
 322 OVS, oxygen vacancy substitution ($2\text{Si}^{4+}(\text{B}) + \text{O}^{2-} = 2\text{M}^{3+}(\text{B}) + \text{V}_\text{o}$, where V_o is the oxygen vacancy).

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