

Synthesis and crystal structure of LiNbO₃-type Mg₃Al₂Si₃O₁₂: A possible indicator of shock conditions of meteorites

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ABSTRACT

LiNbO₃-type Mg_{2.98(2)}Al_{1.99(2)}Si_{3.02(2)}O₁₂ (py-LN) was synthesized by recovering a run product from 2000 K and 45 GPa to ambient conditions using a large volume press. Rietveld structural refinements were carried out using the one-dimensional synchrotron XRD pattern collected at ambient conditions. The unit-cell lattice parameters were determined to be $a = 4.8194(3)$ Å, $c = 12.6885(8)$ Å, $V = 255.23(3)$ Å³, with $Z = 6$ (hexagonal, $R3c$). The average A -O and B -O distances of the AO_6 and BO_6 octahedra have values similar to those that can be obtained from the sum of the ionic radii of the averaged A - and B -site cations and oxygen (2.073 and 1.833 Å, respectively). The present compound has the B -site cations at the octahedral site largely shifted along the c axis compared with other LiNbO₃-type phases formed by back-transition from perovskite (Pv)-structure, and as a result, the coordination number of this site is better described as 3+3. It appears therefore that the B -site cation in the octahedral position cannot be completely preserved during the back-transition because of the small size of Si and Al, which occupy usually a tetrahedral site at ambient conditions. The formation of py-LN can be explained by the tilting of BO_6 octahedra of the perovskite structure having the pyrope composition and formed at high P - T conditions. The tilting is driven by the decrease in ionic radius ratio between the A -site cation and oxygen during decompression. This also explains why there is no back-transition from the Pv-structure to the ilmenite-structure during decompression, since this is a reconstructive phase transition whose activation energy cannot be overcome at room temperature. Py-LN may be formed in shocked meteorites by the back-transformation after the garnet-bridgmanite transition, and will indicate shock conditions around 45 GPa and 2000 K.

Keywords: Bridgmanite, large volume press, Rietveld analysis, LiNbO₃, high pressure

INTRODUCTION

LiNbO₃ (LN)-structure (space group 161: $R3c$) crystallizes in the trigonal system and is very similar to the ilmenite (Ilm)-structure (space group: $R\bar{3}$), which has the same crystal system. LN- and Ilm-type ABO_3 compounds consist of two kinds of octahedra, referred as AO_6 and BO_6 in this paper. The larger cations are stored in the AO_6 octahedra, whereas the smaller ones are in the BO_6 octahedra. The two structures can be distinguished by the different arrangement of the AO_6 and BO_6 octahedra. The Ilm-structure has alternating layers of edge-sharing AO_6 and BO_6 octahedra normal to the c axis. On the other hand, each layer in the LN-structure consists of alternating edge-sharing AO_6 and BO_6 octahedra. The majority of LN-type ABO_3 compounds result from the back-transformation of perovskite (Pv)-type high-pressure polymorphs during decompression. The LN-type structure is non-centrosymmetric and therefore this kind of compounds is used as functional materials of nonlinear optics and piezoelectricity. Recently, it was suggested that the degree of polarity increases

with the distortion of the BO_6 octahedra (Inaguma et al. 2012). Therefore, efforts have been made to synthesize novel LN-type compounds, sometimes by applying high-pressure techniques, and to analyze their structures. Leinenweber et al. (1991) reported that MnSnO₃ and FeTiO₃ with the Ilm-type structure transform to the Pv-type structure at high pressure and temperature, and back-transform to the LN-type structure during decompression at room temperature. They interpreted this back-transition based on the tolerance factor for the Pv-structure, t , which is defined as $t = (r_A + r_O)/\sqrt{2}(r_B + r_O)$, where r_A , r_B , and r_O are the ionic radii of the A - and B -site cations and oxygen, respectively, and concluded that Pv-structured compounds with $t < 0.84$ transform to the LN-structure by pressure release.

In the field of Earth science, various kinds of ABO_3 compounds have been investigated as analog materials of MgSiO₃ with the orthorhombic Pv-structure (bridgmanite, Brg), because Brg is considered to be the most abundant mineral in the Earth's lower mantle. Brg can incorporate Al³⁺ by two possible substitution mechanisms [a charge-coupled substitution (Mg+Si for 2Al) and an oxygen vacancy substitution (2Si+O for 2Al+□_O)]. This incorporation shifts the stability field of Brg to higher pres-

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tures and changes its physical properties. For example, rigidity decreases and electrical conductivity increases (e.g., Kesson et al. 1995; Irifune et al. 1996; Xu et al. 1998; Walter et al. 2004; Murakami et al. 2012). It was also pointed out that the oxygen vacancy substitution may allow water incorporation (Navrotsky 1999) although it is still unclear whether aluminous Brg can incorporate significant amounts of water. Therefore, understanding the stability and Al-substitution mechanism in Brg is one of the important subjects in Earth science.

Funamori et al. (1997) using a laser-heated diamond-anvil cell (LH-DAC) discovered that $(\text{Mg},\text{Fe},\text{Ca},\text{Mn})_3\text{Al}_2\text{Si}_3\text{O}_{12}$ natural garnet directly transforms to the Pv-structure at high pressures, and then transforms to a metastable phase with the LN-structure during decompression. Miyajima et al. (1999) examined the Pv-LN transition using natural garnets with various compositions also using a LH-DAC. These authors suggested that Brg with Al_2O_3 contents larger than 25 mol% transforms to the LN-structure during decompression. However, the structures of these LN-type compounds were not analyzed in detail because only small amount of the LN-type material was obtained together with amorphous phases, which were also formed by back-transformations in DACs. Recently, Ishii et al. (2016) succeeded in synthesizing a bulk sample of the LN-type phase with the pyrope composition ($\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$) at pressures over 40 GPa using a multi-anvil press. Since this product is almost completely composed of the LN-type phase, it is suitable for the structural analysis by the Rietveld method.

In this paper, we report the crystal structure of the LN-type $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ determined by X-ray powder diffraction and Rietveld analysis. The transformation mechanism of the Pv-LN back-transition and implications for a possible natural occurrence of this compound are discussed.

EXPERIMENTAL METHODS

Sample synthesis and characterization

The $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ with LN-type structure was synthesized via the following three steps. First, a glass with a nominal composition of $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ (py-glass) was produced by quenching in water a mixture of MgO , Al_2O_3 , and SiO_2 with a 3:1:3 molar ratio melted at 1950 K for 1 h. The py-glass was then converted to a sintered aggregate of Ilm-type $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ (py-Ak) at 27 GPa and 1170 K for 1 h. The sintered py-Ak aggregate was then subjected to a press load of 15 MN and 2000 K for 3 h, quenched to ambient temperature, and then decompressed to ambient pressure. The recovered sample consisted of a sintered aggregate of LN-type $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ (py-LN) compound. The high P - T syntheses were conducted using a multi-anvil apparatus for ultrahigh-pressure generation, IRIS-15, at the Bayerisches Geoinstitut, University of Bayreuth, Germany. Details of the experimental setup are described in Ishii et al. (2016). Liu et al. (2016) reported that Brg with a pyrope composition (py-Brg) is stabilized at 45 GPa and 2000 K, and that py-LN formed by back-transition from py-Brg during decompression in a multi-anvil press installed at the BL04B1 in the synchrotron facility, SPring-8. Therefore, py-LN obtained in this study also has been likely formed by the back-transition from py-Brg during decompression from at least 45 GPa.

The phases present in the synthesis run products recovered from the second and the third final steps were identified using a laboratory micro-focused X-ray diffractometer (MF-XRD) (Bruker, D8 DISCOVER) with a two-dimensional solid-state detector (VANTEC500) and a micro-focus source ($\text{I}\mu\text{S}$) of $\text{CoK}\alpha$ radiation operated at 40 kV and 500 μA . The X-ray beam was focused to 50 μm beam using a IFG polycapillary X-ray mini-lens. The run products were also examined in backscattered electron (BSE) images by means of scanning electron microscopy (SEM) to determine whether minor phases were present. Compositional analysis was carried out using an electron microprobe with wavelength-dispersive spectrometers (JEOL, JXA-8200) and an accelerated voltage and probe current of 15 kV and 15 nA, respectively. Natural pyrope was used as standard material for Mg, Al, and Si.

Synchrotron X-ray diffraction and Rietveld refinement

Angle-dispersive powder X-ray diffraction was conducted at the beamline BL10XU of the synchrotron radiation facility SPring-8, Japan. The py-LN aggregate was crushed to a powder. The powdered sample was loaded into a hole with a diameter of 300 μm in a rhenium plate with a thickness of 20 μm . X-ray beams monochromatized with a Si double monochromator were collimated to 10–20 μm in diameter to irradiate the sample. The two-dimensional diffraction patterns were collected for 1 s on a flat panel detector (PerkinElmer). The X-ray wavelength ($\lambda = 0.41429$ Å) and detector distance from the sample were calibrated using a CeO_2 standard. Five one-dimensional diffraction profiles of the sample were obtained by integrating the two-dimensional profile at different azimuth angles using the software “IPAnalyzer” (Seto et al. 2010). The five one-dimensional diffraction patterns were combined for the Rietveld refinement.

Rietveld analysis was performed using the RIETAN-FP/VENUS package (Izumi and Momma 2007). The VESTA software (Momma and Izumi 2011) was used to draw crystal structures. The structure parameters of LN-type FeTiO_3 (Leinenweber et al. 1991) were used as an initial structure model. Unit-cell lattice parameters, scale factor, atomic coordinates and isotropic atomic displacement parameters (Table 1), and a split-type pseudo-Voigt fitting function formulated by Toraya (1990) were refined simultaneously. Since peaks of SiO_2 stishovite (St) were present in the synchrotron XRD, this phase was included in the Rietveld analysis, and the lattice parameters, the scale factor and the atomic coordinates were refined. A Legendre polynomial function with 12 parameters was used for fitting of the XRD background.

RESULTS AND DISCUSSION

Phase identification and sample composition

The compositions of py-glass, py-Ak, and py-LN were found to be $\text{Mg}_{2.93(2)}\text{Al}_{2.00(2)}\text{Si}_{3.04(2)}\text{O}_{12}$, $\text{Mg}_{2.99(2)}\text{Al}_{2.01(2)}\text{Si}_{3.01(1)}\text{O}_{12}$, and $\text{Mg}_{2.98(2)}\text{Al}_{1.99(2)}\text{Si}_{3.02(2)}\text{O}_{12}$, respectively, in agreement with the nominal composition and confirming that the high-pressure phases have a pyrope composition.

The MF-XRD patterns of py-Ak and py-LN are shown in Figure 1. Although both phases have similar structural features, their diffraction patterns show clear differences. For instance, the 003 peak is present in the pattern of py-Ak, but it is absent in the py-LN pattern, as required by the reflections conditions of the two different space groups ($R\bar{3}$ and $R3c$, respectively) in which these two materials crystallize. All peaks can be identified as belonging

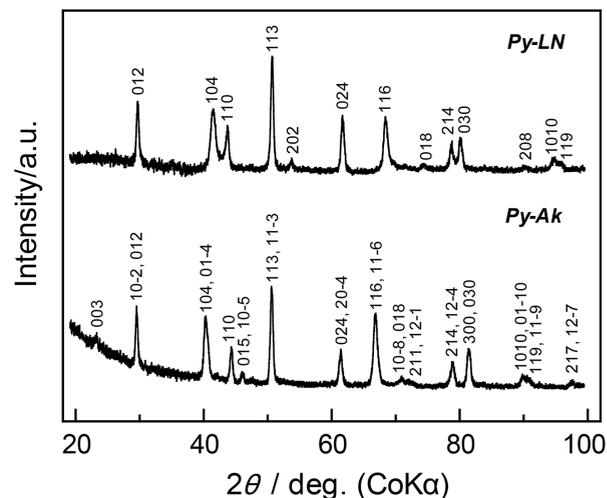


FIGURE 1. MF-XRD patterns of akimotoite (bottom) with the pyrope composition (py-Ak) synthesized at 27 GPa and 1170 K and LiNbO_3 -type phase (top) also with the pyrope composition (py-LN) obtained from recovering a sample from 2000 K and 45 GPa.

TABLE 1. Structural parameters of LiNbO₃ (LN)-type Mg_{2.98(2)}Al_{1.99(2)}Si_{3.02(2)}O₁₂ refined in space group R3c (#61)

Site	Wyckoff site	<i>g</i> (Mg or Si)	<i>g</i> (Al)	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} (Å ²)
A ^a	6 <i>a</i>	0.75 ^b	0.25 ^b	0	0	0	0.0089(7)
		0.75 ^b	0.25 ^b	0	0	0	0.0160(8)
B ^a	6 <i>a</i>	0.75 ^b	0.25 ^b	0	0	0.2154(1)	0.0038(8)
		0.75 ^b	0.25 ^b	0	0	0.2145(1)	0.0113(9)
O	18 <i>b</i>	–	–	0.3473(5)	0.0681(4)	0.1035(3)	0.0067 ^c
		–	–	0.3430(5)	0.0613(4)	0.1060(3)	0.0242(8)

Notes: For each atom the values obtained from the oxygen *U*_{iso}-fixed refinements are reported in the upper lines, whereas those obtained from the oxygen *U*_{iso}-free refinements are reported in the lower line.

For the oxygen *U*_{iso}-fixed refinements we obtained unit-cell lattice parameters: *a* = 4.8194(3) Å, *c* = 12.6885(8) Å, *V* = 255.23(3) Å³, *Z* = 6, *V_m* (molar volume) = 25.617(3) cm³/mol, and *D* = 3.934(1) g/cm³.

Discrepancy factors: *R*_{wp} = 4.108%, *R*_e = 3.253%.

LN phase: *R*_b = 1.188%, *R*_f = 0.506%.

SiO₂ stishovite: *R*_b = 1.420%, *R*_f = 1.020%.

For the oxygen-*U*_{iso}-free refinements we obtained unit-cell lattice parameters: *a* = 4.8194(3) Å, *c* = 12.6887(8) Å, *V* = 255.24(3) Å³, *Z* = 6, *V_m* = 25.618(5) cm³/mol, and *D* = 3.934(1) g/cm³.

Discrepancy factors: *R*_{wp} = 3.615%, *R*_e = 3.255%.

LN phase: *R*_b = 0.838%, *R*_f = 0.396%.

SiO₂ stishovite: *R*_b = 3.693%, *R*_f = 1.274%.

$$R_{wp} = \left[\frac{\sum_i w_i |y_i - f_i(x)|^2}{\sum_i w_i y_i^2} \right]^{1/2}, \quad R_b = \frac{\sum_K |I_o(h_k) - I(h_k)|}{\sum_K I_o(h_k)}$$

$$R_f = \frac{\sum_K |F_o(h_k) - |F(h_k)||}{\sum_K |F_o(h_k)|}, \quad R_e = \left[\frac{N - P}{\sum_i w_i y_i^2} \right]^{1/2}$$

where *y_i*, *w_i*, and *f_i(*x*)* are the intensity observed at step *i*, the statistical weight and theory intensity, respectively. *I_o(*h_k*)*, *I(*h_k*)*, *F_o(*h_k*)*, and *F(*h_k*)* are the observed and calculated intensities and structure factors for reflection *K*, respectively. *N* and *P* are number of all data points and refined parameters, respectively. *g*(*M*) = site occupancy of *M*.

^a A and B atom positions are occupied by Mg or Al and Si or Al, respectively.

^b Site occupancies are fixed.

^c Isotropic atom displacement parameter of oxygen is fixed to that of LiNbO₃ reported by Hsu et al. (1997).

to py-Ak (Fig. 1, bottom) or to py-LN (Fig. 1, top); however, some St and very small amounts of Al₂O₃ corundum (Crm) grains were identified in the BSE images taken for py-LN. The amounts of these minor phases appear to be below the detection limit of the Bruker diffractometer. These trace phases may have formed during heating to 2000 K for the synthesis of py-Brg. As mentioned in the experimental session, in the synchrotron XRD pattern of py-LN, only St was present but no peaks of Crm were observed.

Rietveld refinement of LiNbO₃-type Mg₃Al₂Si₃O₁₂

The results of Rietveld refinements of the synchrotron XRD pattern of py-LN are shown in Figure 2. Because the X-ray scattering factors of Mg, Al, and Si atoms are very similar, it is practically impossible to determine their site occupancies at the A and B sites. Thus, these were fixed by assuming 25% of Al at each site based on the compositional analysis and complete order of Mg-Si resulting in the following occupancies: Mg_{0.75}Al_{0.25} at the A site and Si_{0.75}Al_{0.25} at the B site. This assumption is based on the fact that no cation disorder has been reported either for Fe-bearing, Al-free or Fe-Al-bearing bridgmanites (e.g., Horiuchi et al. 1987; Vanpeteghem et al. 2006), thus the same cation distribution is likely retained in py-LN since it is formed by the back-transformation of py-Brg. During refinement, the isotropic atomic displacement parameter (*U*_{iso}) of oxygen converged toward a much larger value than the one generally observed for several structures (i.e., < ~0.013 Å²) (see Table 1). Therefore, we

TABLE 2. Interatomic distances and angles of LiNbO₃-type Mg_{2.98(2)}Al_{1.99(2)}Si_{3.02(2)}O₁₂

Al _{1.99(2)} Si _{3.02(2)} O ₁₂			
Bond length (Å)			
A-O ⁱ × 3	2.021(3)	B-O ⁱⁱⁱ × 3	1.587(2)
	2.031(3)		1.629(3)
A-O ⁱⁱ × 3	2.064(2)	B-O ^{vi} × 3	2.092(2)
	2.035(3)		2.056(3)
Average	2.043	Average	1.840
	2.033		1.843
BVS (A)	2.27	BVS (B)	4.23
	2.33		3.96
		^{iv} BVS (B) ^a	3.66
			3.33
<i>n_{c,A}</i>	5.98	<i>n_{c,B}</i>	3.13
	6.00		3.40
Bond angles (°)			
O ⁱ -A-O ⁱⁱⁱ	82.3(1)	O ⁱⁱ -A-O ^{iv}	105.9(1)
	82.1(1)		106.5(1)
O ^{vii} -B-O ^{viii}	102.3(2)	O-B-O ^j	89.0(1)
	101.0(2)		89.07(6)
A-O-B ^v	103.7(2)	A-O-B	83.27(1)
	101.5(2)		83.40(8)
A-O ^{vii} -A ^{iv}	117.6(1)	B-O ^{vii} -B ^{viii}	143.3(1)
	118.5(1)		143.0(2)

Notes: Symmetry codes: (i) $-y, x-y, z$. (ii) $-x+y+\frac{1}{2}, y+\frac{1}{2}$. (iii) $-x+y, -x, z$. (iv) $x+\frac{1}{2}, x-y+\frac{1}{2}, z+\frac{1}{2}$. (v) $-y+\frac{1}{2}, -x+\frac{1}{2}, z+\frac{1}{2}$. (vi) $x+\frac{1}{2}, x-y+\frac{1}{2}, z+\frac{1}{2}$. (vii) $-y+\frac{1}{2}, -x+\frac{1}{2}, z+\frac{1}{2}$. (viii) $-x+y+\frac{1}{2}, y+\frac{1}{2}, z+\frac{1}{2}$. (ix) $x+\frac{1}{2}, y+\frac{1}{2}, z+\frac{1}{2}$. The upper and lower lines reported for each site represent the oxygen *U*_{iso}-fixed and oxygen *U*_{iso}-free refinements, respectively. BVS = bond valence sum value. *n_c* = effective coordination number. ^a ^{iv}BVS (B) represents the value calculated with three shorter and one longer oxygen-B cation bond lengths.

also performed refinements with the *U*_{iso} of oxygen fixed to the value obtained for LiNbO₃ by means of single-crystal structural refinement (Hsu et al. 1997). Both refinement strategies, i.e., with oxygen *U*_{iso} fixed or free to vary resulted in very similar crystal structures (see Tables 1 and 2). In both cases, the discrepancy indexes converged to satisfactory values of less than 5% (Table 1). The CIF¹ is deposited.

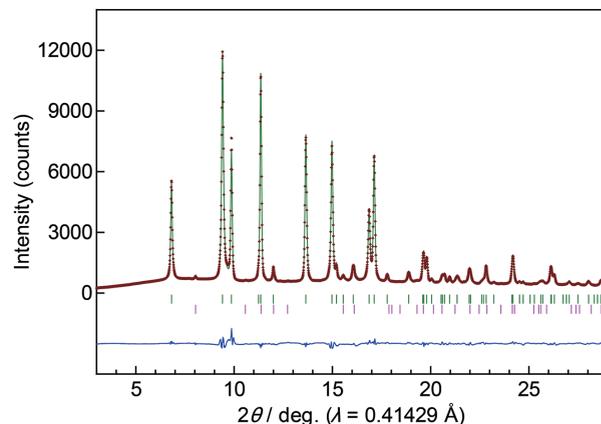


FIGURE 2. Rietveld refinement of LiNbO₃-type Mg₃Al₂Si₃O₁₂. The XRD pattern was collected at atmospheric pressure and room temperature. Data points and solid lines represent the observed and the calculated profiles, respectively, and the residual curve is shown at the bottom. Bragg peak positions are shown by small ticks. The upper and lower ticks are for LiNbO₃-type Mg₃Al₂Si₃O₁₂ and rutile-type SiO₂ (stishovite), respectively. (Color online.)

¹Deposit item AM-17-96027, CIF. Deposit items are free to all readers and found on the MSA web site, via the specific issue's Table of Contents (go to http://www.minsocam.org/msa/ammin/toc/2017/Sep2017_data/Sep2017_data.html).

TABLE 3. Volumes and densities of Mg₃Al₂Si₃O₁₂ compounds

	V_m (cm ³ /mol)	V (Å ³ /formula unit)	D (g/cm ³)	Reference
Pyrope	113.13(3)	46.959(3)	3.564(1)	Geiger et al. (1987)
py-Ak	104.63(5)	43.437(5)	3.853(1)	Akaogi et al. (2002)
py-LN	102.47(5)	42.538(5)	3.934(1)	This study
py-Brg ^a	99.5(7)	41.3(7)	4.06(3)	Liu et al. (2016)

Note: Py-Ak, py-LN, and py-Brg represent ilmenite, LiNbO₃, and perovskite phases with pyrope composition, respectively.

^a Unit-cell lattice parameters of Brg with Al₂O₃ content (~29 ± 5 mol%) from Liu et al. (2016).

The difference between the Ilm- and LN-structures can be described in terms of their c/a ratio (Funamori et al. 1997). The ranges of c/a ratios of Ilm- and LN-type phases are 2.76–2.87 and 2.58–2.69, respectively (e.g., Ko and Prewitt 1988; Leinenweber et al. 1991; Funamori et al. 1997; Hsu et al. 1997; Inaguma et al. 2010; Akaogi et al. 2002). The present py-LN has a c/a ratio of 2.63, which is within the range of the LN-type phases defined by Funamori et al. (1997), and is smaller than that of py-Ak reported by Akaogi et al. (2002) ($c/a = 2.80$). The unit-cell volumes and densities of the Mg₃Al₂Si₃O₁₂ compounds are summarized in Table 3. There is a volume increase for the py-Brg to py-LN transition at ambient conditions of ~3.0% and this value is in the range obtained for MnTiO₃, MnSnO₃, FeTiO₃, ZnGeO₃, and MgGeO₃ compounds (2.7–3.6%) (Leinenweber et al. 1991). The density of py-LN lies between those of py-Ak and py-Brg, which may explain the formation of py-LN and not py-Ak by back-transformation from py-Brg.

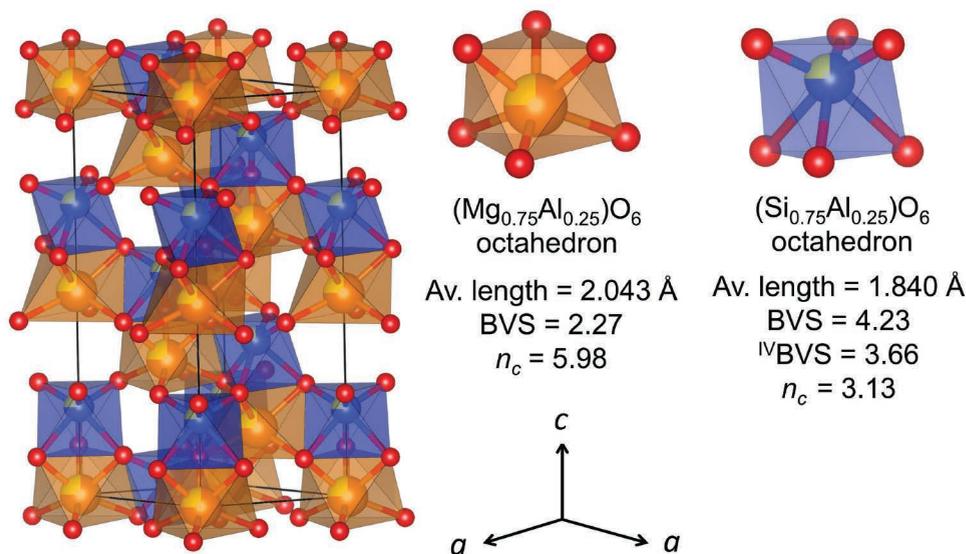
The crystal structure of py-LN is shown in Figure 3. The bond length, bond angles, and bond valence sum (BVS) (Brown and Altermatt 1985) and effective coordination numbers (n_c) (Hoppe 1979) calculated from the bond lengths of the py-LN are summarized in Table 3. Neighboring AO_6 octahedra ($A = \text{Mg}_{0.75}\text{Al}_{0.25}$) and neighboring BO_6 octahedra ($B = \text{Si}_{0.75}\text{Al}_{0.25}$) are corner-sharing, whereas AO_6 and BO_6 octahedra are edge-sharing in the a - b plane and share a face along the c -axis, resulting in A - B empty site periodicity along the c -axis (Fig. 3). The average A -O and B -O distances of the AO_6 and BO_6 octahedra are 2.033–2.043 and 1.840–1.843 Å, respectively. The ionic

radii of Mg²⁺, Al³⁺, Si⁴⁺, and O²⁻ in sixfold coordination are $r_{\text{Mg}} = 0.72$, $r_{\text{Al}} = 0.535$, $r_{\text{Si}} = 0.4$, and $r_{\text{O}} = 1.40$ Å, respectively (Shannon 1976). The average A -O and B -O distances calculated using these ionic radii for $0.75r_{\text{Mg}} + 0.25r_{\text{Al}} + r_{\text{O}}$ (2.073 Å) and $0.75r_{\text{Si}} + 0.25r_{\text{Al}} + r_{\text{O}}$ (1.833 Å), respectively, are very similar to those obtained from the structural refinement, hence supporting the assumption of complete order of Mg²⁺ and Si⁴⁺. The BVS value of the A site (Table 2) is slightly larger than 2 as expected due to the Al substitution, whereas the BVS value of the B site is still close to the value of 4 in spite of the presence of Al³⁺, which has a lower valence than Si⁴⁺. Moreover, the n_c value of the B -site cation (3.13–3.40) is much smaller than 6 (Table 2); this derives from the large difference between the two non-equivalent B -O lengths (0.427–0.505). The B -site cation is largely shifted from the position at the center of the octahedron along the c axis, reducing the coordination number to almost three. The n_c values of Ti⁴⁺ cations in LN-type FeTiO₃ and MnTiO₃ compounds (5.0–5.2) which formed by back-transition from the corresponding Pv-type phases are significantly larger (e.g., Ko and Prewitt 1988; Leinenweber et al. 1991; Hsu et al. 1997). This suggests that during the back-transformation from the py-Brg to the py-LN, the Si and Al cations tend to shift toward a tetrahedral coordination, given that this is their preferred coordination at ambient conditions. However, a complete reversion to such coordination is likely not possible at room temperature and the B site can therefore be seen as a 3+3 coordination site. The large off-set of the B atoms from the center of the octahedra is likely favored by the acentric space group in which the py-LN phase crystallizes. However, additional property tests (e.g., ferroelectric hysteresis measurement) need to be conducted to characterize the dielectric properties of py-LN phase, which likely may not present the ferroelectric behavior of many other LN-type structures.

Back-transformation mechanism from py-Brg to py-LN

This study shows that the investigated compound has the LN-type structure. Liu et al. (2016) reported that Brg with 25 mol% Al₂O₃ transforms to py-LN during decompression, whereas

FIGURE 3. Crystal structure of LiNbO₃-type Mg₃Al₂Si₃O₁₂ obtained using the oxygen- U_{iso} -fixed model (note that this structure is identical to that obtained from the oxygen- U_{iso} -free model). The solid line is the unit cell. Occupancies of Mg and Al at the A site and Si and Al at the B site are shown with areas of different colors in each sphere. Smaller spheres are oxygen. BVS and n_c represent the bond valence sum values and effective coordination numbers of each site, respectively (Table 2). (Color online.)



Brg with a lower Al_2O_3 content can be recovered. Bridgmanite has the orthorhombic perovskite structure that can be viewed as a result from the distortion of the cubic Pv-structure due to the too small ratio in ionic radii between the *A*-site cation and the 12-fold-coordinated anion. The ionic radius of the Mg^{2+} is too small for the oxygen packing in the ideal cubic Pv-structure. Distortion to the orthorhombic symmetry decreases the actual coordination number from 12 to 8+4, which changes the AO_{12} dodecahedral site to a AO_6 prism site with two longer *A*-site cation-oxygen bonds (bicapped prism site) with consequent reduction of the polyhedral volume. The substitution of Mg^{2+} by Al^{3+} makes the average ionic radius of the *A*-site cation even smaller. Accordingly, bridgmanite with pyrope composition has likely a much more distorted orthorhombic structure than pure MgSiO_3 bridgmanite and can be stabilized only at higher pressures, because at these conditions the relatively larger compressibility of the oxygen anions with respect to the cations favor the substitution of smaller atoms at the *A* site. By decreasing pressure, the oxygen atoms expand more than the *A*-site cations and the resulting *A*-site volume becomes too large for the small Mg and Al cations. This likely hinders the possibility of recovering the orthorhombic Pv-structure containing a large amount of Al (25 mol%) outside its stability field and favors the transformation to the LN-structure because of the reduction of the coordination number of the *A*-site cation to six.

A comparison among the orthorhombic Pv-structure (MgSiO_3 Brg), the LN-structure with pyrope composition and MgSiO_3 ,

akimotoite is given in Figures 4a, 4b, and 4c, respectively. The Pv- and LN-structures have a very similar BO_6 octahedral framework. The transformation from the orthorhombic Pv-structure to the LN-structure is caused by the change in the tilting of the BO_6 octahedra and by the shift of the *A*-site cations, as shown by the thick yellow and thin red arrows in Figure 4a. These changes correspond to the transformation from the [111] cubic closed-packing layer composed of oxygen and *A*-site cations in the orthorhombic Pv-structure to the [001] hexagonal closed-packing layer of oxygen with an interstitial *A*-site cations between two oxygen layers in the LN-structure. Red balls in Figures 4a and 4b represent the oxygen atoms coordinating the *A*-site cation in the Pv- and LN-structures. Due to the back-transformation, the *A*-site cation shifts closer to the octahedral framework giving rise to the octahedral coordination observed in the LN-structure (Fig. 4b).

The octahedral tilting can be described for the two structures in terms of *B-O-B* angles. These angles are all the same in the LN-structure and their value (143.0 – 143.3° , Table 2) is smaller than the two *B-O-B* angles (146.5° in the *c* direction and 147.0° in the *b* direction) of the MgSiO_3 Brg structure (Horiuchi et al. 1987). However, as already mentioned, the Al substitution in bridgmanite may give rise to a larger orthorhombic distortion (similar to what observed for Fe-Al-bearing bridgmanites, Vanpeteghem et al. 2006), resulting in *B-O-B* angles smaller than those observed for pure MgSiO_3 bridgmanite. It is very likely, therefore, that the Brg to LN transformation results in an increase of the *B-O-B* angle and hence a smaller octahedral tilting.

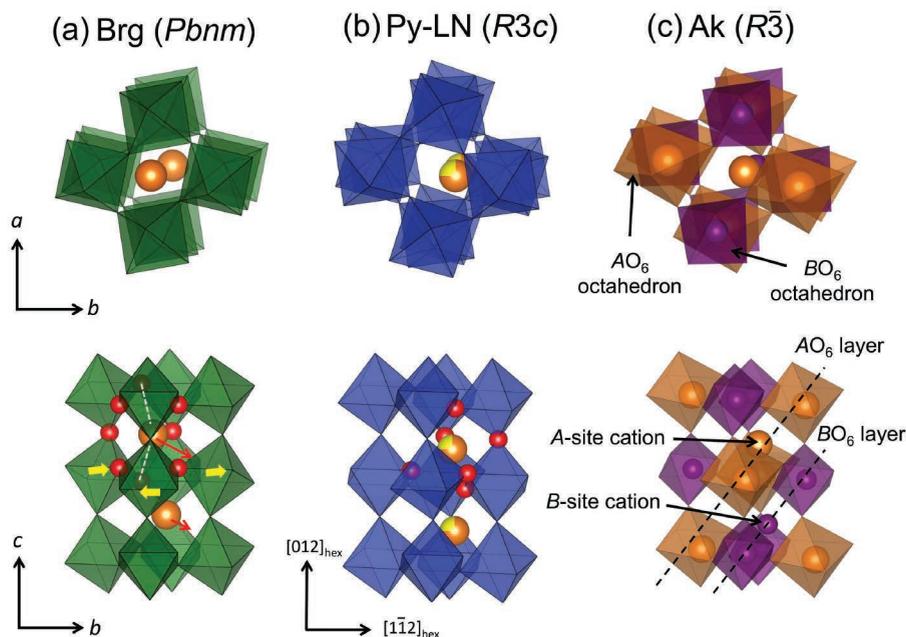


FIGURE 4. Structural relationship among (a) orthorhombic Pv-type MgSiO_3 (Brg), (b) LN-type $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ (py-LN), and (c) Ilm-type MgSiO_3 (Ak). Thick yellow and thin red arrows indicate the tilting directions of the octahedra and the shifting directions of the *A*-site cations during the Brg to LN transition, respectively. The structure of Brg is viewed down the *a* direction, whereas, for comparison, py-LN and Ak are viewed in the $[112]_{\text{hex}}$ and $[012]_{\text{hex}}$ plane. Red balls represent the oxygen atoms bonded to the *A*-site cations in Brg and py-LN. The two dashed white lines in Brg represent the two longer *A*-site cation-oxygen bonds of the AO_8 polyhedron. AO_6 and BO_6 octahedra are shown for Ak. Dashed lines in Ak indicate the directions of the alternating AO_6 and BO_6 layers. (Color online.)

Py-Brg does not transform to py-Ak, but to py-LN, even though the Ilm- and LN-structures are very similar. As shown in Figure 4c, the Ilm-structure has alternating layers of corner-sharing AO_6 and BO_6 octahedra. This arrangement cannot be obtained simply by tilting of BO_6 octahedra and displacement of the A -site cations of the Pv-structure, but requires a reconstructive transition whose activation energy cannot be overcome during the pressure release at room temperature.

IMPLICATIONS

A natural LN-type FeTiO₃ compound was recently discovered in a shocked gneiss from the Ries Crater, Germany (e.g., Dubrovinsky et al. 2009). Akaogi et al. (2016) constrained the shock pressure needed to obtain such material in the range of 14–28 GPa, based on the stability field of Pv-type FeTiO₃ that likely was formed during the shocking event and then back-transformed to the LN-type FeTiO₃ structure after the shock relaxation. Similarly, py-LN phases might form after quenching in shocked meteorites where the pressures may enrich the values needed for the transition from garnet to Brg. The recovery of such phase after a shock event depends on its thermal stability, however the py-LN phase may also be a good indicator of the formation of the Brg phase with pyrope garnet composition and can be used to constrain the P - T conditions of the relatively heavy shock event around 45 GPa and 2000 K at least in a similar manner to amorphous phases with the (Mg,Fe)SiO₃ Brg composition that have been used as evidence of the formation of Brg in meteorites (Sharp et al. 1997; Tomioka and Fujino 1997).

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