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Pressure-induced ferroelectric to paraelectric transition in LiTaO₃ and (Li,Mg)TaO₃

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X-ray powder diffraction and Raman scattering of LiTaO₃ (LT) and (Li,Mg)TaO₃ (LMT) have been measured under pressure up to 46 GPa. Above 30 GPa, the ferroelectric rhombohedral phase (R₃c, Z = 6) of LiTaO₃ transforms to a paraelectric orthorhombic phase (Pnma with Z = 4) with a large hysteresis. Rietveld profile fitting analysis shows that the Li-O bond is compressed and approaches that of Ta-O with pressure. The cation distribution analysis of the orthorhombic perovskite structure shows that Li and Ta are located in the octahedral 8-fold coordination sites. Difference Fourier \([F_{\text{obs}}(hkl)] - [F_{\text{cal}}(hkl)]\) maps of LiTaO₃ and (Li,Mg)TaO₃ indicate polarization in the c axis direction and a more distinct electron density distribution around the Ta position for (Li,Mg)TaO₃ compared to LiTaO₃. The observed effective charges indicate that for (Li,Mg)TaO₃ without vacancies Ta⁵⁺ becomes less ionized as a function of Mg substitution. Considering both site occupancy and effective charge analysis, Ta⁵⁺ is reduced to Ta⁴⁺. Mg²⁺ and O²⁻ change to Mg¹⁺ and O¹⁻, respectively. The space- and time-averaged structures of the dynamical vibration of atoms can be elucidated from the electron density analysis by difference Fourier and temperature factors \(T(hkl)\) in the structure refinement. The refinement of the temperature factor is consistent with the cation distribution assuming full stoichiometry. The residual electron density induced from the excess electron in (Li,Mg)TaO₃ indicates more electrons around the Ta site, as confirmed by the effective charge analysis. Raman spectra of LiTaO₃ and (Li,Mg)TaO₃ show notable changes over the measured pressure range. Raman peaks centered at 250 cm⁻¹ and 350 cm⁻¹ at ambient pressure merge above 8 GPa, which we associate with the diminishing of difference in distances between Li-O and Ta-O bonds with pressure in both materials. Raman spectra show significant changes at 28 GPa and 33 GPa for LT and LMT, respectively, due to the structural transition from R₃c to Pnma consistent with the x-ray diffraction results. © 2016 AIP Publishing LLC.

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I. INTRODUCTION

LiTaO₃ is an important optical material with excellent photorefractive, nonlinear, and electro-optic effects, ferroelectric and piezoelectric devices. The ferroelectric bulk crystals are widely used in optoelectronic devices. Indeed, along with LiNbO₃ and KNbO₃, LiTaO₃ is among the most important lead-free A⁺B⁵⁺O₄ ferroelectric materials. LiTaO₃ determined by x-ray¹⁻³ and neutron¹⁻⁶ diffraction has a LiNbO₃-type rhombohedral R₃c structure, where Li and Ta atoms are displaced from the center of octahedral along the trigonal c axis, which induces the ferroelectric properties. Dielectric, thermal, and pyroelectric properties of ferroelectric LiTaO₃ have been investigated,⁷ and many structures of the Curie temperature of the stoichiometric LiTaO₃, as well as LiNbO₃, have been reported (e.g., Refs. 8 and 9). The Curie temperature \(T_c\) of LiTaO₃ (917–948 K) is much lower than that of LiNbO₃ (1475–1486 K). It has also been reported that the high temperature paraelectric phase is rhombohedral but has a centrosymmetric space group \(R\bar{3}c\). Moreover, the elastic properties, dielectric susceptibilities, and electrical conductivity of LiTaO₃ have been measured over a broad temperature range up to 1200 K.¹⁰ An order-disorder model for the oxygen atoms has been proposed as the driving mechanism for the ferroelectric instability and a large hybridization between the oxygen and the transition-metal atoms.¹¹ It has also been shown that the physical properties of LiTaO₃ and the solid solution (Li,Mg)TaO₃ are sensitive to the existence of intrinsic and extrinsic defects.⁷,¹¹⁻¹³

The transition temperature \(T_c\) depends on doping by Mg.¹⁴ Indeed, the effect of Mg substitution on the electrical conductivity is an important topic for understanding ferroelectricity in LiTaO₃ based materials.¹⁵

High-pressure behavior of LiTaO₃ has also been investigated by x-ray diffraction and Raman scattering.¹³,¹⁶ In order to gain further insight into these materials, we examine the effect of pressure on the structure of LiTaO₃ (LT) and (Li,Mg)TaO₃ (LMT) from ferroelectric rhombohedral phase (R₃c, Z = 6) to the paraelectric orthorhombic perovskite phase (Pnma, Z = 4). In order to further understand the driving force of the transition, dynamical atomic thermal
vibration is examined on compression and decompression. A charge transfer model of cations is used to interpret the mechanism of substitution of Mg$^{2+}$ in LMT, and the effective charges of the cations are analyzed using the electron densities determined by the x-ray diffraction refinements.

**II. EXPERIMENTAL METHODS**

Single crystals of stoichiometric LT and LMT with the Mg substitution of 7 mol.% were supplied from Oxide Co. The detailed crystal growth procedure and their chemical homogeneity and crystallinity have been described.\(^{17}\) Angle-dispersive powder x-ray diffraction was measured with special attention paid to the precise measurement of diffraction pattern on compression and decompression to 46 GPa. The diffraction was measured using synchrotron radiation with a wavelength of 0.4262 Å, at beam lines 13-BM-D and 16-IDB (0.3115 Å and 0.3956 Å) of the Advanced Photon Source (APS), Argonne National Laboratory (ANL). A focused x-ray beam with 30 μm in diameter was aligned with the center of the sample chamber in symmetric diamond-anvil cells (DACs). The diffraction patterns were recorded with an imaging plate MAR-345 and processed with FIT2D software. The lattice parameters of the samples were determined by Rietveld profile fitting from the observed diffraction peaks. The DACs were prepared with a 200 μm culets and a 450 μm diameter tables. The sample chamber was created from a 100 μm hole drilled in a Re gasket preindented to 60 μm from the initial thickness of 200 μm. Fine powder sample and ruby chip for a pressure marker were loaded in the sample chamber. Ne is used for the pressure medium, and pressure was determined from the ruby luminescence method.\(^{18,19}\)

Rietveld profile fitting analyses at various pressures were conducted from the powder diffraction patterns with increasing pressure. Since LT has a non-centric structure of R$^{3c}$, the atomic position of Ta is fixed to (0 0 0) at a crystallographic special position. Li and oxygen have variable positional parameters of (0 0 z) and (x, y, z), respectively. Rietveld profile fitting of powder diffraction pattern was performed with the program RIETAN-2000.\(^{20}\) The background intensity distribution was first adjusted for the refinement, and the lattice parameters, atomic positional coordinates, and temperature factors were treated as variable parameters. Subsequently, profile parameters (full width at half maximum, asymmetry parameters, and angular decay parameter) were varied in the refinement, and preferred orientation correction was made. Finally, a full matrix, least-squares refinement was conducted.

Single-crystal structure refinements of both LT and LMT at ambient pressure were performed using a four-circle x-ray diffractometer at synchrotron beamline BL-10 A KEK Tsukuba.\(^{21}\) To determine effective charges of constituent atoms, a conventional structural refinement using single-crystal diffraction intensities was carried out by the full matrix least-squares program RADY.\(^{22}\) A diamond absorption correction was applied during the analyses. Observed intensities were converted to structure factors after correction for x-ray absorption, x-ray extinction, and Lorentz and polarization effects. Structure factors $F(h)$ for reflections $hkl$ were calculated from the atomic position $(x_h, y_h, z_h)$ of s atom and atomic scattering factor $f_j$ of element $j$ together with temperature factor $T_j(h)$, where $h$ is a scanning vector. Calculated structure factors are expressed by

$$F_{\text{cal}}(h) = K \sum_j a_j f_j(h) \sum T_j(h) \exp \{2\pi i(hx_j + ky_j + lz_j)\},$$

(1)

where $K$ is a scaling factor, $a_j$ is the site occupancy of $j$ atoms, and $f_j$ is the atomic scattering factor of $i$ ion. $T_j(h)$ is the thermal vibration parameter. Least-squares refinement was conducted by minimization of

$$\Delta = \sum_h w(h) \left[ |F_{\text{obs}}(h)| - |F_{\text{cal}}(h)| \right]^2.$$

(2)
Atomic coordinates, site occupancy parameters, anisotropic temperature factors, and isotropic extinction parameters were chosen as the variable parameters and results were presented in Table I. Since ferroelectric phases have a noncentric symmetry, the origin of the structure was fixed at Ta(0 0 0) in LT and LMT rhombohedral structures.

For the Raman measurements, we loaded crystals in a DAC with Ne as the pressure medium. The measurements were performed in a backscattering geometry. The measured spectra represent the sum of both polarized and depolarized components.

III. RESULTS AND DISCUSSION

A. Ta effective charges in (Li,Mg)TaO₃

The space- and time-averaged structures of the dynamical vibration of the constituent atoms of ferroelectrics can be elucidated from the electron density (ED) analysis. In the analysis, the cation site occupancy was a variable parameter in the least-square refinement, and the effective charges were evaluated from the single-crystal x-ray data. The atomic displacement due to dynamical vibration of atoms of ferroelectric materials was clarified by the refinement. Structure factor $F_i(hkl)$ in Eq. (1) was derived from the site occupancy $a_i$, atomic scattering factors $f_i$, anisotropic temperature factors $T_i(hkl)$, and isotropic extinction parameters together with atomic position $(x_i, y_i, z_i)$ of atom $i$. The converged structure parameters from the refinement are presented in Tables II & III.

Here, the atomic scattering factors $f_i$ of Mg, Ta, and O are used as variable parameters in the least-square refinement in order to evaluate the effective charges of these cations. The effective charges are determined by the monopole refinement from observed $F(hkl)$ data. Atomic scattering factors $f_i$ used in the conventional structure analysis are obtained from the wave function based on the Hartree-Fock approximation, and these factors are presented in Ref. 24. Note that the calculation using the isolated atom model gives an ideally spherical electron density distribution without any interaction with adjacent atoms. The $\kappa$-parameter\textsuperscript{25,26} was applied in the atomic scattering factor, which is an indicator of the radial distributions of electron. Effective charges of atoms are obtained from the following equation in the least-squares calculation using the shell model in which the core and valence electrons are separated as follows:

$$f(s/2) = f_{i,\text{core}}(s/2) + P_{j,\text{valence}} f_{j,M-\text{core}}(k_j s/2) + f_j'' + i f_j''' , \quad (3)$$

where \(s/2 = \sin \theta/2\), and $P_{j,\text{valence}}$ is a population of valence electron of $j$ atom. $f_j''$ and $f_j'''$ are anomalous dispersion factors.

<table>
<thead>
<tr>
<th>Press (GPa)</th>
<th>0.0001</th>
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<th>8.82</th>
<th>13.1</th>
<th>17.6</th>
<th>21.9</th>
<th>26.6</th>
<th>28.5</th>
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<td>4.34</td>
<td>2.38</td>
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<td>8.34</td>
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<tr>
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<td>15.86</td>
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<td>12.76</td>
<td>4.75</td>
<td>6.84</td>
<td>12.54</td>
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<td>5.0095(5)</td>
<td>4.9722(5)</td>
<td>4.9307(5)</td>
<td>4.969(2)</td>
<td>4.8649(2)</td>
<td>4.8504(2)</td>
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<tr>
<td>$\text{Vol}(Å^3)$</td>
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<td>299.7(8)</td>
<td>293.8(7)</td>
<td>285.7(2)</td>
<td>281.6(3)</td>
<td>273.1(7)</td>
<td>266.9(5)</td>
<td>265.0(3)</td>
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<table>
<thead>
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</thead>
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<td>y</td>
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<tr>
<td>z</td>
<td>0.0</td>
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<tr>
<td>y</td>
<td>0.3325(12)</td>
</tr>
<tr>
<td>z</td>
<td>0.0870(2)</td>
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<tr>
<td>$B_{iso}$</td>
<td>0.59(6)</td>
</tr>
</tbody>
</table>

| d(Li-O) x3Å | 2.0510(5)| 1.981(9)| 1.987(4)| 1.945(9)| 1.945(8)| 1.950(6)| 1.927(8)| 1.914(13)|
| d(Ta-O) x3Å | 2.203(5)| 2.118(9)| 2.102(7)| 2.105(9)| 2.045(8)| 2.034(6)| 2.028(9)| 2.004(13)|

<table>
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<th>1.074</th>
<th>1.0691</th>
<th>1.0576</th>
<th>1.0822</th>
<th>1.0514</th>
<th>1.0430</th>
<th>1.0524</th>
<th>1.0470</th>
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<td>av (Å)</td>
<td>2.1357(5)</td>
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<td>2.044(7)</td>
<td>2.025(9)</td>
<td>1.995(8)</td>
<td>1.992(6)</td>
<td>1.978(9)</td>
<td>1.959(13)</td>
</tr>
<tr>
<td>d(Ta-O) x3Å</td>
<td>1.9763(7)</td>
<td>1.976(8)</td>
<td>1.917(9)</td>
<td>1.875(8)</td>
<td>1.905(8)</td>
<td>1.906(9)</td>
<td>1.866(8)</td>
<td>1.838(12)</td>
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<tr>
<td>d(Ta-O) x3Å</td>
<td>2.0287(8)</td>
<td>1.997(8)</td>
<td>2.058(8)</td>
<td>2.074(8)</td>
<td>2.033(8)</td>
<td>1.993(8)</td>
<td>2.006(8)</td>
<td>2.043(12)</td>
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<th>1.0736</th>
<th>1.1061</th>
<th>1.0672</th>
<th>1.0437</th>
<th>1.0750</th>
<th>1.1153</th>
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<td>av (Å)</td>
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<td>1.986(8)</td>
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<td>1.975(8)</td>
<td>1.969(8)</td>
<td>1.941(8)</td>
<td>1.936(8)</td>
<td>1.940(12)</td>
</tr>
<tr>
<td>$d(\text{Li-O})/\text{do}$</td>
<td>1.000</td>
<td>0.9594</td>
<td>0.9571</td>
<td>0.9482</td>
<td>0.9341</td>
<td>0.9327</td>
<td>0.9262</td>
<td>0.9173</td>
</tr>
<tr>
<td>$d(\text{Ta-O})/\text{do}$</td>
<td>1.000</td>
<td>0.9917</td>
<td>0.9922</td>
<td>0.9862</td>
<td>0.9833</td>
<td>0.9693</td>
<td>0.9668</td>
<td>0.9688</td>
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</tbody>
</table>
Detailed discussion of the derivation of the core $f_{core}$ and $f_{valence}$ have been described previously. Under ambient conditions, $P_{Ta,valence}$ and $\kappa$-parameter are observed from the structure refinement. $P_{Pb,valence}$, $P_{Mg,valence}$, $O_{a,valence}$, $\kappa_{Ta}$, $\kappa_{Mg}$, and $\kappa_{O}$ of Ta and Mg are variable parameters in the calculation. The population parameter ($P$) of the valence electrons in Eq. (3) defines the effective charge. The $\kappa$-parameters and valence electrons are presented in Table IV. In order to estimate the electron density deformation by the $\kappa$-parameter, the residual factor $R_{\kappa}$ was minimized with the $\kappa$-parameter. The population parameter was optimized together with the $\kappa$-parameter. In the refinement, the charges of all ions are constrained to be neutral in the bulk crystal.

The $\kappa$-parameters for cations in LMT are $\kappa_{Li} = 1.04$, $\kappa_{Mg} = 1.06$, and $\kappa_{Ta} = 0.91$, in the case where the total number of valance electrons is constraint. Those in LT are $\kappa_{Li} = 1.07$ and $\kappa_{Ta} = 0.95$. The electron distributions on their M-O bonds are more localized, when more ionic with increase in the atomic number. A more bonding electron distribution in the covalent-bonded structure indicates a smaller $\kappa$-parameter. (A cation with $\kappa = 1.0$ has the same atomic scattering of $\sin h/k$ with a formal charge as the Hartree-Fock calculation.)

Granting that the effective charge $q$ does not change over the measured pressure range in spite of larger electron localization at higher pressure, the static dipole moment can be obtained using the observed $q$ and $\Delta r_i$.

### Table III. Rietveld analysis of the high-pressure LiTaO₃ perovskite phase.

<table>
<thead>
<tr>
<th>Pressure (GPa)</th>
<th>32.0</th>
<th>35.3</th>
<th>38.7</th>
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<td>$\gamma F$</td>
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<td>0.92</td>
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<td>$wF_p$</td>
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<td>4.64</td>
<td>4.36</td>
<td>14.36</td>
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<tr>
<td>$a$ (Å)</td>
<td>5.06(9)</td>
<td>5.058(9)</td>
<td>5.053(9)</td>
<td>5.035(9)</td>
<td>5.038(6)</td>
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<tr>
<td>$b$ (Å)</td>
<td>6.62(9)</td>
<td>6.585(9)</td>
<td>6.553(9)</td>
<td>6.527(9)</td>
<td>6.486(9)</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>4.55(9)</td>
<td>4.5516(9)</td>
<td>4.4884(9)</td>
<td>4.4576(9)</td>
<td>4.447(7)</td>
</tr>
<tr>
<td>Vol (Å³)</td>
<td>152.6(9)</td>
<td>150.4(9)</td>
<td>148.7(9)</td>
<td>147.0(9)</td>
<td>145.6(9)</td>
</tr>
<tr>
<td>Li Occupancy</td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>$x$</td>
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<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>$y$</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
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<tr>
<td>$z$</td>
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<td>0.5</td>
<td>0.5</td>
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<tr>
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<td>0.96(3)</td>
<td>1.96(3)</td>
<td>0.96(3)</td>
<td>1.14(3)</td>
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<td>$x$</td>
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<td>0.10(9)</td>
<td>0.10(9)</td>
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<td>0.105(9)</td>
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<td>0.25</td>
<td>0.25</td>
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<tr>
<td>$z$</td>
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<tr>
<td>$B_{iso}$</td>
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<td>0.77(4)</td>
<td>0.41(5)</td>
<td>0.77(5)</td>
<td>0.54(5)</td>
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<td>$x$</td>
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<td>0.466(6)</td>
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<td>0.096(5)</td>
<td>0.086(6)</td>
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<tr>
<td>$B_{iso}$</td>
<td>3.10(6)</td>
<td>1.41(6)</td>
<td>1.02(6)</td>
<td>1.41(6)</td>
<td>0.86(6)</td>
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<td>O2 Occupancy</td>
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<tr>
<td>$x$</td>
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<td>0.419(7)</td>
<td>0.679(7)</td>
<td>0.336(7)</td>
<td>0.331(7)</td>
</tr>
<tr>
<td>$y$</td>
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<td>0.008(7)</td>
<td>0.08(7)</td>
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<tr>
<td>$z$</td>
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<td>0.719(7)</td>
<td>0.685(9)</td>
<td>0.667(5)</td>
<td>0.655(9)</td>
</tr>
<tr>
<td>$B_{iso}$</td>
<td>5.05(6)</td>
<td>1.066(6)</td>
<td>1.07(7)</td>
<td>3.05(7)</td>
<td>1.12(7)</td>
</tr>
<tr>
<td>d(Li-O1) x3(Å)</td>
<td>1.712(3)</td>
<td>1.701(4)</td>
<td>1.693(4)</td>
<td>1.696(6)</td>
<td>1.681(6)</td>
</tr>
<tr>
<td>d(Li-O1) x3(Å)</td>
<td>1.861(2)</td>
<td>1.850(3)</td>
<td>1.855(4)</td>
<td>1.865(8)</td>
<td>1.893(5)</td>
</tr>
<tr>
<td>d(Li-O2) x3(Å)</td>
<td>1.769(2)</td>
<td>1.757(3)</td>
<td>1.748(4)</td>
<td>1.741(6)</td>
<td>1.714(6)</td>
</tr>
<tr>
<td>av (Å)</td>
<td>1.781(3)</td>
<td>1.772(3)</td>
<td>1.765(4)</td>
<td>1.758(6)</td>
<td>1.738(6)</td>
</tr>
<tr>
<td>d(Ta-O1) (Å)</td>
<td>1.948(2)</td>
<td>1.946(3)</td>
<td>1.944(4)</td>
<td>1.865(8)</td>
<td>1.893(5)</td>
</tr>
<tr>
<td>d(Ta-O1) (Å)</td>
<td>2.085(2)</td>
<td>2.069(3)</td>
<td>2.057(4)</td>
<td>2.033(8)</td>
<td>2.027(5)</td>
</tr>
<tr>
<td>d(Ta-O2) x2(Å)</td>
<td>2.396(2)</td>
<td>2.383(3)</td>
<td>2.373(3)</td>
<td>2.398(7)</td>
<td>2.357(5)</td>
</tr>
<tr>
<td>d(Ta-O2) x2(Å)</td>
<td>2.095(3)</td>
<td>2.086(3)</td>
<td>2.099(3)</td>
<td>2.199(7)</td>
<td>2.215(5)</td>
</tr>
<tr>
<td>av (Å)</td>
<td>2.133(3)</td>
<td>2.122(3)</td>
<td>2.113(3)</td>
<td>2.108(7)</td>
<td>2.106(6)</td>
</tr>
<tr>
<td>Tolerance factor</td>
<td>0.847</td>
<td>0.847</td>
<td>0.847</td>
<td>0.848</td>
<td>0.857</td>
</tr>
<tr>
<td>Vol(LiO6) (Å³)</td>
<td>7.432</td>
<td>7.321</td>
<td>7.238</td>
<td>7.004</td>
<td>6.802</td>
</tr>
<tr>
<td>d(Li-O)/do</td>
<td>1.0000</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>d(Ta-O)/do</td>
<td>1.0000</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*RF and $wR_F$ are expressed the following equations: $R_F = \frac{\sum|F_{obs}|-|F_{cal}|}{\sum|F_{obs}|}$, $wR_F = \left(\frac{\sum w_i |F_{obs}|-|F_{cal}|^2}{\sum w_i F_{obs}^2}\right)^{1/2}$, where $F$ indicate the structure factor, $y_i$ is the observed diffraction intensity at the $i$-th position in $2\theta$, and $f(x)$ is the calculated intensity. A variable $w$ is a weight for each data points.
in the direction of the $c$ axis with increasing pressure; the classical definition moment $\Delta r$, is lowered in the rhombohedral phase.

The inverse Fourier of $F(h)$ gives electron density $r(xyz)$ at position $(xyz)$ in the real space by

$$q_{xyz} = \frac{1}{V} \sum_h \sum_k \sum_l \left( |F_{\text{obs}}(h)| - |F_{\text{calc}}(h)| \right) \exp \left\{ -2\pi i (hx + ky + lz) \right\}. \tag{4}$$

The polarization and dipole moment are related to dielectric susceptibility, elastic properties, and strain and stress tensors. The definite orientation and anisotropy in the dynamical phenomena arise from the elasticity of the crystal. A harmonic oscillation model is a good approximation in most cases using the ellipsoidal vibration represented by ellipsoidal second-rank anisotropic thermal parameters $\alpha_{ij}$ (Table II).

The calculated structure factors $F_{\text{calc}}(hkl)$ for the difference Fourier $|F_{\text{obs}}(hkl)| - |F_{\text{calc}}(hkl)|$ of LT and LMT at ambient conditions are derived in comparison with the fully ionized model (i.e., Li$^+$, Mg$^{2+}$, and Ta$^{5+}$). DF maps of LT and LMT are the projections on (010) plane at the section of $y = 0.0$ in the region from $-2 \text{e}/\text{Å}^3$ to $2 \text{e}/\text{Å}^3$ (Fig. 1). The maps show the residual electron density distribution indicating the polarization in the direction of $[001]$. However, the maps projected on (001) in the section $z = 0.0$ and $z = 0.3$ indicate no polar character in the direction of $[100]$ and $[010]$ (Fig. 2). The DF map of LMT compared with LT shows a more distinct ED distribution in the direction of the $c$ axis around the Ta position than that of Li atomic position. The plausible fully ionized Ta$^{5+}$ induces the residual electron density from the excess electron.
changed to Mg1.643

electron density with a height of 0.7 e/A³ is found in the evident by DF map on the plane (010) (Fig.1). Residual density around the cation sites is probably induced from the metal position. The non-spherical residual electron p

Ta-O bond in the fi

deformation nor obvious residual electron density and is almost spherical.

because Ta is less ionized to Ta⁴⁺ with more electrons. This is consistent with the result of the structure refinement, which is indicated by the highest reliable factor with the cation distribution of stoichiometric model. The cation distribution of (Li₀.₉₀₇₅Mg₀.₀₉₂₅)Ta₁.₀O₃ is confirmed by the calculation of LMT. In consideration of both site occupancy and effective charge analysis, Ta⁵⁺ is reduced to Ta¹₂⁺ and Mg²⁺ is changed to Mg⁴⁺. The present structure refinement of LMT thus gives (Li¹⁻₅ₓ₃₀⁻₃ᵧ Mg⁴ᵧ₃-Ta¹₈ᵧ₃ V₁₉ₓ₄₅/₄]O₃ for non-stoichiometric with x < 0, and [Li¹⁻₅ₓ₃₀⁻₃ᵧ Mg⁴ᵧ₃Ta⁴ᵧ₅ V₄ₓ₅₄/₄₅]O₃ for non-stoichiometric with x > 0, where V denotes the vacancy.

If we apply effective charges instead of the formal charges, the stoichiometry can be preserved without vacancies in order to maintain neutrality of the bulk crystal. We test the cation distribution using the structure refinement. Site occupancy aᵢ in the least-square calculation in Eq. (1) is a variable parameter. Generally, Mg in these oxides is preferentially located in the octahedral site (owing to its ion radius of 0.72 Å).⁶⁻ Li and Mg are placed in the octahedral B site in the AVIIIBVIO₃ orthorhombic perovskite. The following cation distribution model is obtained from the least-square calculation:

\[(Li^{+}_{1-5x3y} Mg^{+}_{4y/3}) Ta^{+}_{1-8y/3} Mg^{+}_{8y/3}) O_3\]

The converged site occupancies in the least-square calculation are presented in Table IV.

C. Rhombohedral LiTaO₃

Li and Ta octahedra in LT are alternately located in the same layer and share the plane perpendicular to the c axis, while they are connected with shared edges in the direction parallel to the c axis. LiO₆ and TaO₆ octahedra have antiparallel di-trigonal pyramids. Powder diffraction patterns with increasing pressure up to 46.2 GPa are presented in Fig. 3, those with decreasing pressure in Fig. 4. From ambient pressure to 28.5 GPa, the rhombohedral LT phase with R₃c was found to and persist other phases were detected. Above that pressure, a structured transition to a high-pressure phase was found. The phase was found to be the orthorhombic perovskite structure (Pnma).⁶ For comparison, in Fig. 5, we show x-ray diffraction patterns at selected pressures for both LT and LMT. The spectra before and after the transitions are also shown in Fig. 5.

The significant difference in x-ray scattering power of Li (atomic number 3) and Ta (atomic number 73) complicates the diffraction measurements for LT. The powder diffraction intensity is strongly affected by the Ta atomic position. The atomic positions of LiNbO₃-type structure (R₃c, Z = 6) were taken for the initial model of the least
TABLE IV. Occupancy, effective charge, and $\kappa$-parameter of the R3c ferroelectric phase.

<table>
<thead>
<tr>
<th></th>
<th>LiTaO$_3$</th>
<th>Li$<em>{0.93}$Mg$</em>{0.07}$TaO$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Occupancy</td>
<td>Li</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>Mg</td>
<td>0.0925</td>
</tr>
<tr>
<td></td>
<td>Ta</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>3.0</td>
</tr>
<tr>
<td>$\kappa$-parameter</td>
<td>$\kappa$(Li)</td>
<td>1.07</td>
</tr>
<tr>
<td></td>
<td>$\kappa$(Mg)</td>
<td>0.95</td>
</tr>
<tr>
<td></td>
<td>$\kappa$(Ta)</td>
<td>0.95</td>
</tr>
<tr>
<td>Effective charge</td>
<td>Li</td>
<td>1.0$^+$ (fix)</td>
</tr>
<tr>
<td></td>
<td>Mg</td>
<td>1.643$^+$</td>
</tr>
<tr>
<td></td>
<td>Ta</td>
<td>4.129$^+$</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>2.0$^+$ (fix)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.732$^+$</td>
</tr>
</tbody>
</table>

D. Orthorhombic LiTaO$_3$ above 30 GPa

Above 30 GPa, the ferroelectric rhombohedral phase of LT transforms to a high-pressure phase of paraelectric orthorhombic perovskite $Pnma$ structure. This structural transition has been reported at 33 GPa. In the conventional orthorhombic ABO$_3$ perovskite, a large cation occupies the 8-fold coordinated A site and a small cation is located in the octahedral B site. The present refinement was used to test the cation distribution in the sites of $A(x \ y \ 1/4)$ and $B(0 \ 1/2 \ 0)$ in the orthorhombic perovskite structure. The test proves that Li is located in the crystallographical special-position of Li(0 1/2 0), which is the smaller B site and Ta is in the variable position of $A(x \ y \ 1/4)$ referring to the reliable factor $R_F$ and $wR_F$. Oxygen has two positions, $O_1(\ x \ y \ 1/4)$ and $O_2(\ x \ 1/2 \ y)$. The observed orthorhombic structure is shown in Fig. 8.
The observed radii differ from those determined at ambient pressure. Bond distances of Li-O and Ta-O with increasing pressure are shown in the table. Li-O distance in the rhombohedral structure contracts from 2.4 Å at ambient conditions to 1.96 Å at 28.5 GPa. The LiO$_6$ octahedra become more regular as indicated by bond ratio (Table II). The average octahedral Li-O distance of the perovskite structure is compressed to 1.78 Å at 32 GPa (Table III). The Ta site changes its coordination from 6-fold in $R3c$ to 8-fold in $Pnma$. The average Ta-O bond distance in the perovskite

FIG. 5. Powder x-ray diffraction patterns of LiTaO$_3$ and (Li,Mg)TaO$_3$ at selected pressures for comparison.

FIG. 6. Relative unit cell volumes ($V/V_0$) of both ferroelectric rhombohedral and paraelectric orthorhombic phases as a function of pressure.
structure is much larger than that in the rhombohedral structure because of the different coordination. On further compression up to 46.2 GPa, Li-O bond is more compressed than Ta-O bond. However, the tolerance factor $t = \frac{(r_A + r_O)}{\sqrt{2}(r_B + r_O)} \approx \frac{d_{(Ta-O)}}{\sqrt{2}d_{(Li-O)}}$ is $t = 0.85$ in all pressure range.

E. Thermal factors

The asymmetric polarization and conductivity of LT have been confirmed by systematic time-temperature measurements. The anisotropic atomic vibration is observed as positional disorder and thermal vibration of atoms. Our electron deformation analysis in the pressure dependence of the anisotropy in electric conductivity of ilmenite FeTiO$_3$ by the DF map shows the noticeable anisotropic residual electron density. The anisotropic atomic vibration can be evaluated by the anisotropic temperature $T(hkl)$ [Eq. (1)].

The features of the ED maps on (010) and (001) projections (Figs. 2 and 3) are interpreted in two ways: one is static positional disorder (lattice average) and the other is dynamical disorder (time average) of the atomic vibration in the crystal structure. The overall temperature factor $B_{iso}$ and anisotropic temperature factors $u_{ij}$ in $T(hkl)$ are indicators of the thermal vibrations of atoms and atomic positional disorder by the following second rank anisotropic temperature factors $u_{ij}$:

$$T(hkl) = \exp \left\{ -2\pi^2(u_{11}h^2a^2 + u_{22}k^2b^2 + u_{33}l^2c^2 + 2u_{12}hka^*b^* + 2u_{13}hla^*c^* \cos \gamma + 2u_{23}kib^*c^* \cos \alpha) \right\},$$

where $u_{ij}$ is a mean square displacement of the amplitude of atomic thermal motion. Since the site symmetry of Li and Ta site is $3m$ and that of O is 2 in the space group $R3c$, the following constraint in $u_{ij}$ is applied in the least-square calculation: for Li and Ta: $u_{11} = u_{22}$, $u_{33} = u_{12} = u_{11}/2$, $u_{11} = u_{11} = 0$, and for O: $u_{11} = u_{22}$, $u_{33} = u_{12} = u_{13} = u_{23}$.

The light atom Li has a larger $B_{iso}$ relative to the Ta in both LT and LMT and $u_{33}$ of the both atoms in LMT along the $c$ axis is much larger than $u_{11} (= u_{22})$ along the $a$ and $b$ axes. The elongation of ED in the DF map (Fig. 1) is in a good agreement with $u_{ij}$ observed in the refinement. The anisotropy of thermal vibration of Ta is distinguished by the large $u_{33}$. The residual electron density induced from the excess electron along the $c$ axis in LMT indicates more electrons around the Ta site, as confirmed by the effective charge analysis. On the other hand, LT displays an obvious anisotropy of Li, which may be the evidence of the ferroelectricity of LiTaO$_3$. The refinement of the temperature factors is
consistent with the residual electron density presented by DF map.

The isothermal bulk modulus $K_0$ and its pressure derivative $K_0'$ determined from second-order Birch-Murhagham equation of state fits of the cell volumes with pressure give

LT: $K_0 = 95(5)$ GPa $K_0' = 5.9(0.7)$

LMT: $K_0 = 103(9)$ GPa $K_0' = 6.1(1.4)$.

The two materials show the different transition pressures: 28 GPa for LT and 33 GPa for LMT.

Xiang et al. reported $K_0 = 116$ GPa and $K_0' = 6.6$ for LT based on a Birch-Murnaghan equation of state fit. The slightly larger $K_0$ reported by Xiang et al. may be associated with the stiffer pressure transmitting medium (silicon oil) used in those experiments.

F. Raman scattering

Figures 9 and 10 show the results of Raman measurements for the two materials. Representative Raman spectra for LT at selected pressures are shown in Fig. 9(a), and a comparison LT and LMT at 7 GPa is shown in Fig. 9(b). The spectra of the two measurements are almost identical. In its ferroelectric phase, the point group symmetry of LT is $C_{3v}$. Thus, the irreducible representations of optical vibrational modes are

$$\Gamma_{opt} = 4A_1(Z) + 9E(X, Y) + 5A_2,$$

where $A_1$ and $E$ are Raman, infrared, and hyper-Raman active, whereas the silent $A_2$ modes are only hyper-Raman active. Assuming each excitation to be represented by a Lorentzian function (e.g., Fig. 10(a)), we assign peaks (ambient pressure frequencies) at 215 cm$^{-1}$, 231 cm$^{-1}$, 326 cm$^{-1}$, 609 cm$^{-1}$, to $A_1$ (TO) modes and peaks at 148 cm$^{-1}$, 272 cm$^{-1}$, 294 cm$^{-1}$, 378 cm$^{-1}$, 412 cm$^{-1}$, 472 cm$^{-1}$, to $E$ (TO) modes (Fig. 9(a)). We also observed three peaks from silent $A_2$ (TO) mode. We did not attempt polarization experiments because stressed diamond anvils tend to scramble the polarization of the light. Our focus is on the pressure dependencies of the more intense Raman bands.

Figure 10(b) shows the pressure dependencies of each Raman mode obtained by a multipeak fitting procedure. We found that most peaks harden on compression and several peaks show non-linear dependencies with pressure. In particular, peaks at 272 and 294 cm$^{-1}$ merge together above 8 GPa; this is accompanied by the appearance of a peak at 256 cm$^{-1}$ and 550 cm$^{-1}$. This behavior is similar to that of PbTiO$_3$ (PT) and Pb-based relaxors. For example, in PbTiO$_3$, two peaks merge around 11 GPa, which correspond to the
ferroelectric to paraelectric transitions.\textsuperscript{32} In relaxor materials, PMN-PT\textsuperscript{33,34} or PZN-PT,\textsuperscript{35} merging of two peaks are accompanied with the appearance of a new peak near 370 cm\textsuperscript{-1}, and transitions occur between 4 and 7 GPa. The similar behavior occurs at 8 GPa in both LT and LMT. However, it should be noted that because of the difference distance between Li-O and Ta-O bonds is approaching each other under pressure; thus, these two modes approach each other with pressure. In addition, to verify whether the pressure-induced structural transitions in LT and LMT were associated with soft optical phonon, we investigated the pressure dependence of the lowest phonon mode and shown in Fig. 11; however, we found no soft optical involved in this transition.

Other changes in Raman spectra occur around 20 GPa. Two Raman peaks between 350 and 450 cm\textsuperscript{-1} merge above 20 GPa. At this stage, we do not know the origin for this change, but these two peaks show different pressure dependencies, the lower one shows a linear pressure dependence and increases with pressure linearly, whereas the higher frequency one shows non-linear behavior with pressure, first increasing with pressure and then becoming flat with pressure above 20 GPa. These two peaks thus crossover around 20 GPa, and because no other changes were observed up to 28 GPa, we do not associate this with a structural transition.

Additional changes in the Raman spectra occur at higher pressure. The Raman spectra show major changes above 28 GPa for LT and 33 GPa for LMT, respectively. The Raman spectra features of LT are completely different below 28 GPa for LT and 33 GPa for LMT, respectively. The pressure. The Raman spectra show major changes above 28 GPa, we do not associate this with a structural transition.

Changes in the Raman spectra are accompanied with a large volume collapse consistent with the structural transformation from the R3c to Pnma phase.

A combination of Raman scattering and x-ray diffraction was further employed to investigate the behavior of LT and LMT up to 50 GPa at 300 K. The Raman spectra show drastic changes indicating of a structural transition for both LT and LMT. Our x-ray diffraction results reveal that structural transition is first-order, from a rhombohedral R3c to orthorhombic Pnma. We also find that Mg doping specimen has a minimal effect on the phase transition.

IV. CONCLUSIONS

Both x-ray powder diffraction and Raman scattering experiments indicate LF ferroelectric rhombohedral phase of R3c with Z = 6 transforms to paraelectric orthorhombic perovskite structure of Pnma with Z = 4 at 30 GPa. The bond length of Li-O is enormously compressed to the close values of Ta-O with increasing pressure. In the high-pressure perovskite, Li is located in the smaller octahedral site than Ta site with the 8-fold coordination. The Mg-doped sample (LMT) enhances the property of nonlinear optics and efficiency of ferroelectricity. Difference Fourier of LT and LMT shows the noticeable residual electron density distribution, indicating the polarization in the direction of the c axis and a more distinct electron density distribution around the Ta position in LT in comparison with that of LT.

The deformation of ED distributions discloses that ferroelectric property of LT is mainly caused by the deformation of the light element of Li. On the other hand, in the Mg-doped LMT with the high efficiency of ferroelectricity, ED around Ta atom shows a noticeable deformation and obvious residual electron density and confirms the Mg replacement at the Li site.

The effective charges analysis of LMT by the monopole refinement from observed $F(hkl)$ data shows Ta\textsuperscript{4.128+}, Mg\textsuperscript{1.643+}, and O\textsuperscript{1.729−}, indicating a stoichiometric (Li\textsuperscript{1.008}Mg\textsuperscript{1.643+}Ta\textsuperscript{4.128+})O\textsuperscript{1.729−}. The present result is strikingly different from the previous discussion of the enhancement of the ferroelectric property of LMT based on the fully ionized cations’ model of the nonstoichiometric structure with vacant sites. LMT is composed of not fully ionized and the present difference Fourier is consistent with the view that the non-spherical residual electron density around the cation sites is induced from d–p bonding between 5d_{z^2} and 5d_{x^2−y^2} orbitals of Ta and 2p_x and 2p_y orbitals of oxygen. Anisotropic temperature factors $\tilde{u}_{ij}$ of $T(hkl)$ in the single crystal structure refinement elucidates the space- and time-averaged structures of the dynamical vibration of atoms. The refinement of temperature factor is consistent with the cation distribution of deformation of electron cloud along the c axis in the rhombohedral ferroelectric phase.

We assigned all peaks observed at ambient pressure to $A_1$ (TO) modes and to E (TO) modes. The pressure dependencies of each Roman mode were obtained by a multipeak fitting procedure. Raman spectra show drastic change at 28 GPa for LT and 33 GPa for LMT due to the structural transition from R3c to Pnma and consistent with the x-ray

FIG. 11. Representative low-frequency Raman spectra of Mg\textsubscript{0.07}Li\textsubscript{0.093}TaO\textsubscript{3} at selected pressures.
diffraction results. Raman scattering of LT and LMT reveal the anomalous changes in several Raman peaks. The two Raman peaks centered at 250 cm$^{-1}$ and 350 cm$^{-1}$ at ambient pressure merge together above 8 GPa due to the diminishing distance difference between Li-O and Ta-O bonds with pressure in both LT and LMT.

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