Raman scattering efficiency in LiTaO$_3$ and LiNbO$_3$ crystals

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LiTaO$_3$ and LiNbO$_3$ crystals are investigated here in a combined experimental and theoretical study that uses Raman spectroscopy in a complete set of scattering geometries and corresponding density-functional theory calculations to provide microscopic information on their vibrational properties. The Raman scattering efficiency is computed from first principles in order to univocally assign the measured Raman peaks to the calculated eigenvectors. Measured and calculated Raman spectra are shown to be in qualitative agreement and confirm the mode assignment by Margueron et al. [J. Appl. Phys. 111, 104105 (2012)], thus finally settling a long debate. While the two crystals show rather similar vibrational properties overall, the E-TO$_3$ mode is markedly different in the two oxides. The deviations are explained by a different anion-cation bond type in LiTaO$_3$ and LiNbO$_3$ crystals.

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I. INTRODUCTION

LiTaO$_3$ and LiNbO$_3$ are related ferroelectric oxides. At room temperature, they both crystallize in a ferroelectric structure belonging to the space group $R3c$ [1]. Starting from the 1970s up to now, both materials have been widely employed for the fabrication of electro-optic [2,3] and acousto-optic devices [4]. Accordingly, the two oxides have been intensively investigated by several experimental techniques [5,6]. Raman spectroscopy is one of the foremost tools for the analysis of the vibrational properties of molecules and solid-state systems [7]. It is commonly employed to characterize samples, as it leads to information about crystallinity, stoichiometry [8], strain [9], doping [10,11], etc. In particular, in combination with theoretical approaches yielding phonon eigenvectors such as the density functional theory (DFT), it is possible to assign a displacement pattern to each Raman peak and attain structural information from the peak modifications with temperature and composition. Thus, Raman spectroscopy has been used to investigate phase transitions [12,13], visualize ferroelectric domains [14–16], and even to establish the surface polarity [17].

Yet, the assignment of the phonon modes in LiTaO$_3$ and LiNbO$_3$ remained under discussion for a long time, as intrinsic and extrinsic defects, as well as the presence of modes with similar frequency or low Raman intensity, complicated the investigations [18]. Existing first-principles calculations did not clarify these controversies, as the assignment of the peaks was based only on the mode energy [19,20]. This procedure is not always reliable. In large systems with many vibrational modes, the mode assignment is not unambiguous, as many calculated phonons might have frequencies compatible with a given Raman peak. Furthermore, some of the calculated modes might have vanishing Raman intensity, which complicates the identification of the phonons. On the other side, modes which are not expected to be Raman active might appear in the recorded spectra, if a perturbation softens the selection rules (e.g., the presence of domain boundaries).

In this respect, the ab initio calculation of the Raman intensities [21–24] might be useful. Hermet et al., e.g., have calculated for selected scattering configurations the nonresonant Raman scattering spectra of the ferroelectric phase of lithium niobate from first principles, with an implementation based on the nonlinear response formalism and taking advantage of the $2n + 1$ theorem [25]. This allowed for a different assignment of the $E$ modes. Later, Margueron et al. presented a complete assignment of the $E$ modes in LiTaO$_3$ and LiNbO$_3$ by comparing Raman and infrared data [26].

In this work we combine $\mu$-Raman measurements and DFT calculations to identify the controversial phonon modes. We systematically measure and calculate the Raman spectra of LiTaO$_3$ and LiNbO$_3$ for all possible polarization configurations of incoming and scattered photons. The calculation of the Raman intensities allows for the conclusive assignment of the measured Raman peaks to the calculated phonon eigenvectors. The Raman intensities are calculated with an approach similar to the calculations of Ref. [25]. However, instead of using the density functional perturbation theory, the calculations are performed based on ground-state DFT calculations for frozen phonons [27].

Our results confirm the assignment proposed in Refs. [25,26], and thus resolve the long-standing debate concerning in particular the assignment of the $E$ modes. The $E$ TO$_3$ phonon mode, whose oscillator strength strongly differs in LiTaO$_3$ and LiNbO$_3$, is examined in some detail. The theoretical modeling of the scattering efficiencies is crucial for the assignment of phonon modes in complex systems, with a large number of modes or where selection rules are relaxed by the system morphology.

The paper is structured as follows: Sec. II describes the theoretical foundations of the Raman susceptibility calculations and computational details. The sample preparation and characterization together with the experimental details are given in Sec. III. In Sec. IV the results of this combined investigation are exposed and discussed. Finally, the main results of this work are summarized in Sec. V.

II. THEORY

A. Raman susceptibility

The Raman scattering efficiencies of zone center optical phonons can be calculated from first principles. The main
The scattering geometry of the experiment performed in this work is described within the Porto notation $\mathbf{k}_0(\mathbf{e}_0, \mathbf{e}_3)\mathbf{k}_S$, where
TABLE I. Selection rules and Raman tensor elements for all investigated backscattering geometries. X, Y, Z refer to the orthogonal reference system for tensor properties. TO and LO label transverse and longitudinal optical modes, respectively.

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Symmetry</th>
<th>Eff. TO</th>
<th>Eff. LO</th>
</tr>
</thead>
<tbody>
<tr>
<td>$X(Y,Y)X$</td>
<td>A1; TO, E TO</td>
<td>$a^2 + c^2$</td>
<td></td>
</tr>
<tr>
<td>$X(Y,Z)X$</td>
<td>E TO</td>
<td></td>
<td>$d^2$</td>
</tr>
<tr>
<td>$X(Z,Z)X$</td>
<td>A1; TO</td>
<td></td>
<td>$b^2$</td>
</tr>
<tr>
<td>$Y(X,X)Y$</td>
<td>A1; TO, E LO</td>
<td>$a^2$</td>
<td>$c^2$</td>
</tr>
<tr>
<td>$Y(X,Z)Y$</td>
<td>E TO</td>
<td></td>
<td>$d^2$</td>
</tr>
<tr>
<td>$Z(X,Z)Y$</td>
<td>A1; TO</td>
<td></td>
<td>$b^2$</td>
</tr>
<tr>
<td>$Z(X,Y)Z$</td>
<td>E TO</td>
<td></td>
<td>$c^2$</td>
</tr>
<tr>
<td>$Z(Y,Y)Z$</td>
<td>A1; LO, E TO</td>
<td>$c^2$</td>
<td>$a^2$</td>
</tr>
</tbody>
</table>

$k_0, k_5$ are the propagation directions of incoming and scattered photons and $e_0, e_5$ are their polarization. The Porto notation refers to the orthogonal coordinate system $XYZ$ commonly used for tensor properties. Thereby $Z$ is parallel to the crystal $c$ axis, $X$ corresponds to one of the equivalent axis of the hexagonal structure and is therefore perpendicular to a mirror symmetry plane, and $Y$ is chosen such that the system is right handed. Within the orthogonal coordinate system, the matrices for the components of the Raman tensor for the irreducible representations of the $3m$ point group are [36]

$$A_1(\mathbf{z}) = \begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{pmatrix}, \quad (4)$$

$$E(\mathbf{y}) = \begin{pmatrix} c & 0 & 0 \\ 0 & -c & d \\ 0 & d & 0 \end{pmatrix}, \quad (5)$$

$$E(-\mathbf{x}) = \begin{pmatrix} 0 & -c & -d \\ -c & 0 & 0 \\ -d & 0 & 0 \end{pmatrix}. \quad (6)$$

The Raman tensor describes the contribution to the scattering intensity depending on the polarization direction of the incoming and scattered light, i.e., the selection rules. Depending on the scattering geometry $A_1$ or $E$ modes as well as longitudinal or transversal modes can be observed. The $A_1$ tensor describes the scattering process in which the polarization of the incoming and scattered photons are parallel, while the $E$ tensor describes the case in which the polarization of incoming and scattered photons is perpendicular. The modes observed for a given scattering geometry are compiled in Table I.

III. EXPERIMENT

The experiments have been carried out on a $\mu$-Raman setup at room temperature in back-scattering geometry as described in Refs. [16,17]. The excitation source was provided by a frequency-doubled 532-nm Nd:YAG laser with 50 mW output power, while the spectral analysis was carried out on a spectrometer with an integrated notch filter and holographic grating (KOSI Holospec /1.8i) with an attached Andor Newton Charge-coupled Device (CCD) camera and an overall spectral resolution of about 2.5 cm$^{-1}$. Additionally, polarizers have been added in the excitation and detection path, which allows for defined scattering geometries. In contrast to previous work, no confocal pinhole was applied [16,17]. The neglect of a depth-resolved analysis ensures a large scattering and detection volume. Hence, nearly exclusively bulk phonons, which are the focus of this investigation, will contribute to the spectra. The importance of measuring stoichiometric samples has been outlined by Ridah et al., as in congruent specimens broader and less resolved Raman bands appear [18]. Furthermore, defect bands could lead to a misleading mode assignment. The studied samples were both commercially available stoichiometric LiTaO$_3$ (DÖRER Elektrooptik GmbH and partner Deltronic Crystal Inc.) and stoichiometric LiNbO$_3$ (Roditi International Corporation), with lattice parameters as indicated in Sec. II B. The samples have been polished on the $X, Y$ and $Z$ faces for a smooth surface. Congruent lithium niobate and lithium tantalate are not object of this investigation.

In the experiment, Raman spectra have been obtained in the range from 100 to 1000 cm$^{-1}$ in the scattering geometries summarized in Table I. There is neither experimental nor theoretical evidence of LiNbO$_3$- or LiTaO$_3$-related phonon modes at lower or higher frequencies. The main goal of this work is the identification and assignment of the zone center TO phonon modes. Therefore, not only the knowledge of the phonon frequencies at $\Gamma$ but also the relative intensities in each spectrum are necessary. The spectral signatures of all detected phonons have been fitted with Lorentzian functions to obtain peak intensities (peak areas), FWHM, and peak frequencies. Following the usual procedure, the spectra have been recalculated based on the obtained values. This method is illustrated in Fig. 2 using the LiNbO$_3$ spectra recorded within the $X(Y,Y)X$ geometry between 100 and 500 cm$^{-1}$ as an example. The raw data (black curve) are best fitted by the 10 Lorentzian functions shown in light blue (gray). The sum of the single functions is the fitted spectrum, shown in the picture as a blue (gray) curve. The minor peak indicated at 194 cm$^{-1}$ is a spectral feature which cannot be assigned to any first order scattering process (see, e.g., Ref. [26] and the discussion in the next section) and does not appear in the calculated spectra. Removing the corresponding Lorentzian from the spectrum yields the corrected spectrum shown in the picture as a dark blue (gray) curve, which can be readily compared with the DFT calculations. With this procedure the spectra are corrected for those peaks that could be assigned without ambiguity to multiphonon processes. Also, LO phonons were removed from the spectra for a direct comparison with the calculated values. If peaks did show a unsolvable overlap, both peaks have been fitted with a single Lorentzian. This was the case for the $E$ TO$_3$ and $E$ TO$_5$ in all geometries or the $E$ TO$_3$ and $A_1$ TO$_4$ in LiTaO$_3$ in the $X(Y,Y)X$ geometry. The measured spectra are renormalized with respect to the highest peak, so that the intensity of the following spectra are expressed in arbitrary units. The relative peak intensity and not the absolute value is thus relevant.
IV. RESULTS

As LiTaO$_3$ and LiNbO$_3$ are very similar in many aspects, we employ the same procedure to investigate the two materials. The first step is the assignment of the $A_1$ TO modes. Relying on the selection rules shown in Table I, most modes can be assigned without uncertainty. The $A_1$ TO modes can be relatively easily identified within the $\tilde{X}(Y,Y)X$ scattering configuration, as they are the only active modes in this geometry. The $E$ TO modes can be detected within the $\tilde{Z}(Y,X)Z$ setup instead. Unfortunately, only 8 of 9 modes can be detected in our experiment. The resulting data are shown in Tables II and III. From the comparison with other scattering geometries, e.g., $\tilde{Z}(X,X)Z$, the $A_1$ longitudinal modes can be identified. For both LiTaO$_3$ and LiNbO$_3$ the experimentally detected LO and TO $A_1$ modes are in good agreement with the literature [18–20,37–41] and shall not be further discussed at this point.

For the assignment of the $E$ modes, a comparison between calculated and measured Raman intensity is indeed necessary. In this respect, a word of caution is in order. While the measured peak width provides information, e.g., about stoichiometry, the peak form is chosen to be Lorentzian with a constant width of 12 cm$^{-1}$ for all the calculated Raman spectra shown in the following [42]. This might introduce some deviation from the experiment whereas broad peaks overlap with minor peaks, resulting in an increased apparent intensity of the minor peak.

The dielectric permittivity is a symmetric tensor. Therefore no differences in the calculated spectra are observed by swapping the polarization of incoming and scattered photon: $(X,Y) = (Y,X)$. Furthermore, the propagation direction (wave vector) of the incoming and scattered vectors do not enter in the calculation. All the spectra are calculated for an incoming photon frequency of 532 nm, which corresponds to the energy of the laser employed in the experiment.

Since the longitudinal modes are not considered within our computational approach, the measured Raman peaks assigned to the longitudinal modes are removed from the spectra during the fitting procedure described in Sec. III. This only affects the $E$ modes appearing in the $\tilde{Y}(X,Y)Y$ configuration and the $A_1$ modes according to Table I. This procedure does not introduce any uncertainty in our approach, as all appearing longitudinal modes can be unambiguously identified.

A. LiNbO$_3$

Table II shows the measured and calculated frequencies of the optical transverse and longitudinal modes in LiNbO$_3$. The measured values are given within a small range due to minor

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>Mode</th>
<th>Theory</th>
<th>Exp.</th>
<th>Mode</th>
<th>Exp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</td>
<td>TO$_1$</td>
<td>239</td>
<td>252–255</td>
<td>LO$_1$</td>
<td>274</td>
</tr>
<tr>
<td>$A_1$</td>
<td>TO$_2$</td>
<td>289</td>
<td>275–276</td>
<td>LO$_2$</td>
<td>330</td>
</tr>
<tr>
<td>$A_1$</td>
<td>TO$_3$</td>
<td>353</td>
<td>333–334</td>
<td>LO$_3$</td>
<td>422</td>
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<tr>
<td>$A_1$</td>
<td>TO$_4$</td>
<td>610</td>
<td>633</td>
<td>LO$_4$</td>
<td>871</td>
</tr>
<tr>
<td>$E$</td>
<td>TO$_1$</td>
<td>148</td>
<td>150–151</td>
<td>LO$_1$</td>
<td>192</td>
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<tr>
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<td>TO$_2$</td>
<td>216</td>
<td>237</td>
<td>LO$_2$</td>
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<td>TO$_3$</td>
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<td>262–263</td>
<td>LO$_3$</td>
<td>297</td>
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<tr>
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<td>TO$_4$</td>
<td>323</td>
<td>320–321</td>
<td>LO$_3$</td>
<td>–</td>
</tr>
<tr>
<td>$E$</td>
<td>TO$_5$</td>
<td>380</td>
<td>367–369</td>
<td>LO$_3$</td>
<td>369</td>
</tr>
<tr>
<td>$E$</td>
<td>TO$_6$</td>
<td>391</td>
<td>367–369</td>
<td>LO$_6$</td>
<td>428</td>
</tr>
<tr>
<td>$E$</td>
<td>TO$_7$</td>
<td>423</td>
<td>432</td>
<td>LO$_7$</td>
<td>456</td>
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<tr>
<td>$E$</td>
<td>TO$_8$</td>
<td>579</td>
<td>580–581</td>
<td>LO$_8$</td>
<td>–</td>
</tr>
<tr>
<td>$E$</td>
<td>TO$_9$</td>
<td>667</td>
<td>664</td>
<td>LO$_9$</td>
<td>877</td>
</tr>
</tbody>
</table>

TABLE II. Calculated and measured frequencies of the Raman active phonon modes in LiNbO$_3$. $E$ TO$_5$ and $E$ TO$_6$ have similar frequencies and cannot be resolved within Raman spectroscopy. All frequencies are in cm$^{-1}$.

B. LiTaO$_3$

TABLE III. Calculated and measured frequencies of the Raman active phonon modes in LiTaO$_3$. $E$ TO$_5$ and $E$ TO$_6$ have similar frequencies and cannot be resolved within Raman spectroscopy. All frequencies are in cm$^{-1}$.
FIG. 3. (Color online) Calculated (left-hand side) and measured (right-hand side) LiNbO₃ Raman spectra for all different scattering geometries. The Raman intensity is expressed in arbitrary units.

The differences observed for different scattering geometries. The calculated modes show a mean deviation of 10.7 cm⁻¹ from the measured values and can be considered in good agreement with the experiment. The largest deviation occurs for the A₁ TO₄ and amounts to 23 cm⁻¹. Both calculated and measured values are also in agreement with the results available in the literature [18,20].

The Raman spectra of LiNbO₃ measured and calculated for all different scattering configurations are compared in Fig. 3. Within X(Z,Z)X [Fig. 3(f)], both the incoming and scattered photons are polarized along the Z direction. Thus, only A₁ TO modes have a nonvanishing scattering efficiency in this configuration. All four TO modes are correctly predicted from the theory, both in position and intensity. We observe that while TO₁, TO₂, and TO₄ have similar, strong Raman intensity, TO₃ appears both in the measured and calculated spectra as a very small-sized peak. This can be readily understood on the basis of the mode eigenvector. A₁ TO₃ is a rigid rotation of the oxygen octahedra around the crystal c axis [see Fig. 4(a)]. The atomic displacement preserves the crystal symmetry and does not modify the cation-anion distances. It thus results in a minor modification of the crystal polarization and therefore in strongly reduced Raman intensity. While the strong intensity difference between the A₁ TO₁, TO₂, and the A₁ TO₃ bands is correctly reproduced in our calculations, TO₂ appears in the calculation slightly stronger than TO₁, in contrast to the measurements. However, this does not mean that the two bands are inverted in our theoretical model, as the comparison of the phonon eigenvectors with the descriptions available in the literature readily confirms the assignment in Fig. 3(f). Moreover, the relative intensity of A₁ TO₁ and TO₂ is correctly predicted for the (X,Z) and (Y,Y) scattering geometries. A detailed description of the phonon eigenvectors of the A₁ TO modes can be found in our previous work [43].

The A₁ modes can be also detected with the Y(X,X)Y [Fig. 3(a)] configuration. Within this geometry the dominant peak is the TO₄. This mode consists of a rotation of the oxygen octahedra around the crystal c axis combined with an expansion of the cage itself [see Fig. 4(b)]. Having both displacement in the X-Y plane as well as along Z, the mode can be efficiently excited in the X(Z,Z)X, Y(X,X)Y, and in the X(Y,Y)X [Fig. 3(d)] configuration as well. The E modes can be also observed with the remaining configurations Z(X,Y)Z, X(Z,Y)X, and X(Z,Z)Z.

The latter scattering geometry allows for the simultaneous detection of the E modes. Unfortunately, none of the configurations allows for the detection of all 9 E TO modes, as only 7 or 8 peaks appear in the spectra. For this reason many contradictory assignments can be found in the literature, which is therefore no real help in the mode assignment. In particular, several inconsistent assignment of the two “missing” modes have been proposed. The oldest assignment date back to the works of Kaminow [37] and Barker [38] (both 1967). The first proposed modes at 92 and 630 cm⁻¹ and the second at 180 and 610 cm⁻¹, which were interpreted as mixed modes, though. Claus [39] (1972) reported modes at 668 and 743 cm⁻¹. Yang and coworkers [40] (1987) interpreted the modes at 670 and 743 cm⁻¹ as combination bands, suggesting the presence of...
modes at 152 and 530 cm$^{-1}$. Ridah [18] and Repelin [41] (1997 and 1999) agree about the presence of regular modes at 180 and 610 cm$^{-1}$, which were previously interpreted by Barker as mixed modes. More recently, Margueron [26] (2012) suggested that the $E$ TO$_5$ and TO$_6$ have close frequencies and that TO$_6$ has vanishing oscillator strength. From the theoretical point of view, the two missing modes were predicted by Parlinski [19] and Caciuc [20] (both 2000) at 423 and 690 cm$^{-1}$, and at 167 and 617 cm$^{-1}$, respectively. Hermet [25] (2007) suggested that the TO$_3$ and TO$_6$ modes are not the same experimental Raman mode but are two different $E$ TO modes, the first mode only being visible by infrared spectroscopy and the second only being visible by Raman spectroscopy.

Our assignment of the $E$ modes can be best understood from the spectra recorded with the $Z(Y,X)Z$ [Fig. 3(b)] configuration. In this configuration 8 modes can be easily assigned to the calculated eigenvectors, the only uncertainty regarding TO$_3$ and TO$_6$. A comparison with the calculated spectra reveals that the TO$_3$ and TO$_6$ are two distinct modes that always appear in Raman as a single peak, due to their closeness in energy (calculated $|\Delta \nu|$ value 9 cm$^{-1}$) and relative broad peaks. This is in agreement with the assignment previously proposed by Hermet [25]. However, depending on the scattering configuration, the TO$_3$ might have higher Raman intensity than the TO$_6$. The TO$_6$ has higher Raman intensity within the ($X,Z$) and ($Y,Z$) scattering geometry, while TO$_3$ is stronger in ($X,Y$) (see Fig. 5). In the ($Y,Y$) scattering geometry both modes have vanishing intensity. The theoretical predictions are corroborated by the Raman measurements. Indeed, while it is not possible to discriminate between the peaks in the experiment, which are fitted by a single Lorentzian, the fit is centered at 367 cm$^{-1}$ within the ($X,Y$) and ($Y,Y$) scattering configurations, while it is shifted to somewhat higher frequencies (i.e., centered at 369 cm$^{-1}$) within the ($X,Z$) and ($Y,Z$) scattering configurations. This suggests that in the first case the TO$_3$ mode has a higher intensity than the TO$_6$, while in the second case TO$_6$ becomes dominant, as predicted from the theory. Our assignment of the $E$ modes thus confirms the most recent assignment proposed by Hermet [25] and Margueron [26].

The $Z(Y,X)Z$ configuration is furthermore particularly interesting, as it is the only configuration that allows for the detection of the $E$ TO$_5$. E TO$_5$ has a small scattering efficiency both in the calculated and measured spectra and can only be observed with very low intensity. However, the comparison of the calculated spectra with the records of the $Z(Y,X)Z$ backscattering configuration shows that the peak at 664 cm$^{-1}$ is a regular Raman mode and not a second-order process.

Summarizing, as in the case of the $A_1$ modes, also in the case of the $E$ modes the overall agreement between theory and experiment is noticeably good, both concerning peak position and intensity. As a general feature, the intensity of the calculated low-frequency peaks slightly underestimates the experimental value.

### B. LiTaO$_3$

Table III shows the measured and calculated frequencies of the optical transverse modes in LiTaO$_3$. With a mean deviation of 10.8 cm$^{-1}$ from the measured values, the calculated frequencies have accuracy similar to that in the case of LiNbO$_3$. The agreement of measured and calculated phonon energies can be considered satisfactory. Available data from the literature [26,40,41,44–47], are in agreement with both the measured and calculated frequencies.

In analogy with LiNbO$_3$ the comparison of the measured and calculated spectra in the scattering configurations $Z(Y,Y)Z$ [Fig. 6(f)] and $Z(X,Y)Z$ [Fig. 6(b)] yields the assignment of all transversal modes of $A_1$ and $E$ symmetry, respectively. Exactly as in the case of LiNbO$_3$, the TO$_3$ and TO$_6$ bands appear in the experiment as a single broad peak. Their frequency is indeed very close (calculated value $|\Delta \nu| = 11$ cm$^{-1}$). Depending on the scattering configuration either TO$_3$ or TO$_6$ outweighs the other mode, resulting in a single detectable band. The calculated intensity of the Raman spectra for all investigated polarization directions is in very good agreement with the measured values, apart from the underestimation of the intensity of the experimental peak assigned to the $A_1$ TO$_4$ + $E$ TO$_5$ in the $X(Y,Y)X$ [Fig. 6(d)]. This is due to the fact that the intensity of the two modes sums up in the experiment, while this is not the case for the calculated spectra.

The Raman spectra of LiTaO$_3$ and LiNbO$_3$ are overall rather similar, with one single but relevant difference: the $E$ TO$_5$ band. The Raman behavior of this mode in the two oxides is strikingly different, as the mode is hardly detectable in LiNbO$_3$, while it is one of the strongest modes in LiTaO$_3$. While pronounced differences are expected for modes involving Ta and Nb, respectively, it is surprising to observe large differences in modes that only involve the oxygen sublattice. Indeed, the eigenvector of this mode represents a distortion of the oxygen cage, precisely the elongation along one of the three equivalent $XZ$ planes (see Fig. 7). The $E$ TO$_5$ mode is thus a pure oxygen mode and its frequencies in LiTaO$_3$ and LiNbO$_3$ are therefore very similar. As the phonon eigenvectors in the two materials are nearly identical, the reasons for the mode quenching in LiNbO$_3$ have to be searched for in the local environment around oxygen atoms, which is different in the two materials.
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FIG. 6. (Color online) Calculated (left-hand side) and measured (right-hand side) LiTaO₃ Raman spectra for all different scattering geometries. The Raman intensity is expressed in arbitrary units.

FIG. 7. (Color online) Eigenvectors of the $E_{\text{vibrational transversal branch TO}_9$ of LiTaO₃ and LiNbO₃. The undistorted oxygen octahedron (b) is stretched along the $XZ$ plane [(a), (d)]. In both materials the mode only concerns displacements of the oxygen sublattice. Arrows represent the distortion direction.

FIG. 8. (Color online) Calculated Raman intensity of the LiNbₓTa₁₋ₓO₃ mixed crystals with $x = 0$, 0.5, and 1 for the $(X,Y)$ and $(Y,Z)$ tensor components.

for in the polarizability differences of the respective bonds involved in the two crystals. One possible explanation might be given by the different Nb-O and Ta-O bond lengths and strengths in the two systems. As Nb and Ta have exactly identical ionic radii [48], the average calculated Nb-O bond length in LiNbO₃ of 2.02 Å corresponds to a weaker Nb-O bond than the average Ta-O bond with a calculated length of 1.99 Å in LiTaO₃. Thus, the TO₉ phonon distortion results in a larger relative deformation of the Ta-O bond in LiTaO₃ than of the Nb-O bond in LiNbO₃, with corresponding larger modification of the polarizability. This possible explanation is in agreement with the fact that also the other phonon bands involving solely a displacement of the oxygen ions (e.g., $A_1$ TO₃ and TO₄) have a stronger relative intensity in LiTaO₃ than in LiNbO₃. In order to verify our assumption, we have calculated the Raman intensity for ordered LiNbₓTa₁₋ₓO₃ mixed crystals with $x = 0$.5. Modeling mixed crystals as ordered alloys is certainly an approximation, which, however, suffices for our test purposes. The average Nb,Ta-O distance in these crystals amounts to 2.00 Å and is thus in between the two end compounds. The results of our calculation are shown in Fig. 8 for the Raman tensor components $(X,Y)$ and $(Y,Z)$. As expected, the calculated intensity of the $E\,\text{TO}_9$ mode for the mixed crystals is between the mode intensity in LiTaO₃ and in LiNbO₃. In further agreement with Ref. [26], we find the Raman intensity of the $E\,\text{TO}_9$ mode in LiNbₓTa₁₋ₓO₃ mixed crystals to be a sublinear function of the Ta concentration.

V. CONCLUSIONS

The vibrational properties of bulk LiTaO₃ and LiNbO₃ were addressed here by combining nonresonant $\mu$-Raman spectroscopy with scattering efficiency calculations within density-functional theory for all possible scattering geometries. A generally very good agreement between measured and calculated peak positions and intensities has been achieved that allowed for a conclusive assignment of the TO phonon modes. In particular, all $A_1$ and $E$ transversal optical modes, which have been controversially discussed for many decades, could be unambiguously identified.

Furthermore, the intensity of the measured Raman peaks could be understood on the basis of the atomic displacement of the corresponding phonon mode. In particular, it is shown
that the TO$_5$ and TO$_6$ are very close in energy and appear as a single Raman peak both in LiTaO$_3$ and LiNbO$_3$. Depending on the scattering geometry, either TO$_5$ or TO$_6$ can be detected; however, depending on the particular configuration, one mode dominates over the other, resulting in a single Raman band. This shows the importance of an approach capable of reliable prediction of the Raman scattering efficiency for a given configuration setup. Indeed, Raman scattering efficiencies for piezoelectric crystals and their angular variations are dependent upon whether electrostatic forces predominate over anisotropy in the short-range interatomic forces or vice versa and are thus hard to predict.

The E TO$_6$ mode has a different behavior in LiTaO$_3$ and LiNbO$_3$. While it is only detectable with a very low intensity in the Z(Y,X)Z scattering geometry in LiNbO$_3$, it appears as a strong Raman peak in several configurations in LiTaO$_3$. The difference is tentatively explained by the larger relative distortion of the Ta-O bond in LiTaO$_3$ than of the Nb-O bond in LiNbO$_3$.

The combination of theoretical and experimental Raman spectroscopy employed here to clarify the assignment of bulk phonon modes is expected to be very helpful to investigate the Raman intensity modulation at extended defects or domain walls in ferroelectric materials [16].

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[42] This value has been chosen as the measured peaks have a width between 10 and 15 cm$^{-1}$.


