Vibrational fingerprints of LiNbO$_3$-LiTaO$_3$ mixed crystals

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Abstract — The structural and vibrational properties of lithium niobate (LN) – lithium tantalate (LT) mixed crystals (LNT, LiNb$_{1-x}$Ta$_x$O$_3$) are investigated over the whole composition range by first-principles simulations. The crystal volume grows roughly linearly from LT to LN, whereby the lattice parameters $a$ and $c$ show minor deviations from the Vegard behavior between the end-compounds, LiNbO$_3$ and LiTaO$_3$. Our calculations in the framework of the density functional theory show the TO$_3$, TO$_2$ and TO$_3$-modes to become harder with increasing Nb concentration. TO$_3$ becomes softer with increasing Nb content, instead. The frequency shifts of the zone center A$_1$-TO phonon modes for crystals with different compositions are found to be as large as 30 cm$^{-1}$. Raman spectroscopy, which is sensitive to the A$_1$ modes, can be therefore employed to determine the crystal composition.

Keywords: Ferroelectrics; Vibrational properties; LiNbO$_3$; LiTaO$_3$; Mixed Crystals

I. INTRODUCTION

Lithium niobate and lithium tantalate are two isomorphic ferroelectric materials belonging to the R3c space group. Besides the structure, the two crystals share several common physical and chemical properties, including a high temperature phase transition to the paraelectric phase (space group R3c). However, while LN is the most important electro-optic material and is widely used for a variety of applications, ranging from optical modulators to frequency doubling, LT is mainly employed as a LN replacement for shorter wavelength applications [1].

Mixed crystals have recently attracted the attention of the scientific community, as they offer the possibility to tune the physical properties by varying the composition. Lithium niobate-tantalate (LNT) is one of the simplest ferroelectric mixed crystals, which shows quite unusual physical properties. In particular, the existence of a composition with zero birefringence at room temperature is unique in ferroelectric nonlinear-optical materials. Indeed within this composition the crystal is optical isotropic and yet electrically polar [2,3].

Despite the huge potential in electro-optic and acousto-optic devices and the extensive use of the end-compounds LN and LT, relatively few is known about the mixed crystals [4]. This is mainly to the difficulty to grow compositionally homogeneous crystals with traditional methods such as the Czochralski growth from a lithium rich melt. In fact, despite the isomorphism of the end compounds and the similar radii and valence of Ta and Nb, the large separation of the solid-liquid lines in the LN-LT phase diagram makes the crystal growth across the composition range a technically demanding task. However, the growth of homogeneous crystals by several techniques has been demonstrated recently [2].

In this contribution, we investigate the structural and vibrational properties of LiNb$_{1-x}$Ta$_x$O$_3$ over the whole composition range by first-principles simulations. To our knowledge, our work represents the first theoretical modeling of LNT mixed crystals.

II. METHODOLOGY

Total energy density functional calculations have been performed within the PW91 formulation of the generalized gradient approximation (GGA) [5] as implemented in the VASP simulation package [6]. PAW potentials [7] with projectors up to $l = 3$ for Nb, Ta and $l = 2$ for Li, O have been used for the calculations. The electronic wave functions are expanded into plane waves up to a kinetic energy of 400 eV. Our work is therefore on the same footing of previous calculations on LN bulk crystals [8]. This approach yields lattice parameters $a$ and $c$ as well as internal parameter $z$, $u$, and $w$ for the end compounds LiNbO$_3$ and LiTaO$_3$ within 1-2% of the experimental values. Rhombohedral supercells containing 20 atoms (i.e. a 2x1x1 repetition of the LN primitive cell) were used in order to model Ta concentrations of 0%, 25%, 50%, 75% and 100%. Our calculations refer to stoichiometric, compositionally homogeneous crystals: the investigation of the commonly used congruent materials is beyond the goals of this work. A Γ-centered 4x4x4 k-point mesh was used to carry out the integration in the Brillouin zone. The atomic positions were allowed to relax until the forces acting on each atom were lower than 10 meV/Å. The phonon modes and frequencies are calculated using the frozen-phonon approach [9].

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approach does not include the long-range electric fields that accompany longitudinal phonons. For this reason, we restrict ourselves to the transverse modes.

III. RESULTS

In a first step the equilibrium lattice parameters are calculated for all the investigated concentrations. Thereby, atomic positions and primitive vectors are optimized at fixed volume for a set of 15 different volumes in the range of ±5% of the LN volume. The total energy as a function of the cell volume is then fitted to the Murnaghan state equation [10]

\[ E(V) = V_0 \frac{B}{B'} \left[ \frac{1}{2} \left( \frac{V_0}{V} \right)^{(B'-1)/(B-1)} - 1 \right] \frac{V}{V_0} + \text{const.} \]  

(1)

where \( B \) is the bulk modulus, \( B' \) its first derivative and \( V_0 \) the equilibrium volume, in order to find the equilibrium volume. A further calculation is then performed at the Murnaghan minimum in order to find the equilibrium total energy. The results of this procedure are reported in Fig. 1. The Murnaghan state equation also yields information about the crystal response to external pressure (the bulk moduli \( B \) and \( B' \)), which however is not discussed in this work. The supercell volume grows almost linearly from LT to LN (Vegard behavior), while minor deviations from the linearity of the volume grows almost linearly from LT to LN (Vegard response to external pressure (the bulk moduli \( B \) and \( B' \)).

Within the DFT calculations, the LN \( A_1 \) modes are found at 240, 286, 353, and 611 cm\(^{-1}\), and the corresponding LN modes at 203, 258, 368, and 581 cm\(^{-1}\). The eigenvectors of the four \( A_1 \) modes (labeled by TO\(_1\) to TO\(_4\)) are represented in Fig. 5. TO\(_1\) is essentially a \( z \)-vibration, with the Nb,Ta ions vibrating in antiphase with the oxygen octahedra TO\(_2\) is a \( z \)-vibration as well, in which only the Li ions are displaced from the equilibrium positions. TO\(_3\) and TO\(_4\) essentially involve the oxygen octahedra and the ionic displacements take place in the \( xy \)-plane. While TO\(_3\) consists of an almost rigid rotation of the whole octahedra, in TO\(_4\) the displacement pattern is more complex. The ions in one oxygen plane rotate about the trigonal axis as in TO\(_3\), while the ions of the other plane show a typical breathing movement. The oxygen octahedra are thus distorted. For a thorough description of the TO-mode eigenvectors see, among others, [12]. The description of the eigenvectors of the \( E \) modes is beyond the goals of this study. Within deviations of at most 30, but typically about 10 cm\(^{-1}\) (which is mainly due to anharmonicity effects), the calculated frequencies match the experimental findings, both for LN and LT [13-15]. The accuracy of our calculations is thus comparable to earlier frozen-phonon calculations [9,12].

Table 2. CALCULATED ZONE-CENTER PHONON FREQUENCIES (IN CM\(^{-1}\)) FOR LITHIUM NIOBATE-TANTALATE CRYSTALS WITH DIFFERENT COMPOSITIONS. OF THE FOUR TO-MODES, ONLY TO\(_1\) BECOMES HARDER WITH INCREASING Ta CONTENT.

<table>
<thead>
<tr>
<th>Mode</th>
<th>Composition</th>
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<tbody>
<tr>
<td></td>
<td>LN</td>
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<tr>
<td>TO(_1)</td>
<td>240</td>
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<tr>
<td>TO(_2)</td>
<td>286</td>
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<tr>
<td>TO(_3)</td>
<td>353</td>
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<tr>
<td>TO(_4)</td>
<td>611</td>
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</tbody>
</table>

IV. CONCLUSIONS

The structural and vibrational properties of LiNb\(_{1-x}\)Ta\(_x\)O\(_3\) mixed crystals have been investigated from first principles. The crystal volumes grow almost linearly from LiTaO\(_3\) to LiNbO\(_3\), while the lattice parameters \( a \) and \( c \) of the rhombohedral structure show small deviations from a linear dependence on

![Graph](image_url)

Table 1. Calculated LiNb\(_{1-x}\)Ta\(_x\)O\(_3\) unit cell volume as a function of the Nb concentration. The volume grows almost linearly from LiTaO\(_3\) to LiNbO\(_3\).
the composition. The zone center phonon modes have been calculated with the frozen phonon approach. A dependence on the composition of the four TO modes has been predicted. According to our calculation, Raman spectroscopy measurements, can be used to identify the crystal composition on the basis of their vibrational properties.

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