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, $LiNb_{1-x}Ta_xO_3$) 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_1, TO_2 and TO_4-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 $R\bar{3}c$). 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 $LiNb_{1-x}Ta_xO_3$ 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 2×1×1 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 4×4×4 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]. This

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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]

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

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 lattice parameters a and c can be observed. This in agreement with recent X-ray diffraction measurements [2] and existing data [11].

In a second step, the phonon modes are calculated for the calculated equilibrium geometries. In the end compounds LN and LT, the Γ-TO modes are split by symmetry into four A_1, five A_2 and nine E modes. The A_2 modes are not Raman active and will not be discussed in this work. An analysis of the phonon eigenvectors allows to classify the calculated modes as A_1 (if the mode preserves the full crystal symmetry), as A_2 (symmetry preserved, the ions of the same type vibrate in antiphase) and E modes (the crystal symmetry is not preserved, the mode is doubly degenerate).

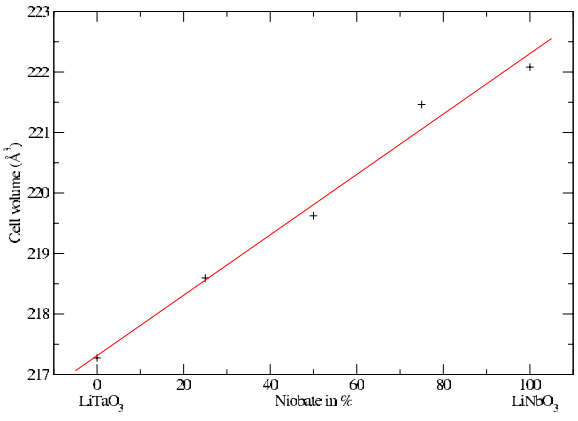

Table 1. Calcuated $LiNb_xTa_{1-x}O_3$ unit cell volume as a function of the Nb concentration. The volume grows almost linearly from $LiTaO_3$ to $LiNbO_3$.

Table 2. Calculated zone center phonon frequencies (in cm^{-1}) for lithium niobate-tantalate crystals with different compostions. Of the four TO-modes, only TO_3 becomes harder with increasing Ta content.

Mode	Composition				
	LN	$LN_{.75}T_{.25}$	$LN_{.50}T_{.50}$	$LN_{.25}T_{.75}$	LT
TO_1	240	233	221	212	203
TO_2	286	275	269	264	258
TO_3	353	357	362	365	368
TO_4	611	602	594	587	581

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].

The frequencies of the A_1 modes for the mixed crystals are listed in table 1. The Ta atomic mass (180.95 amu) is twice the Nb atomic mass (92.906 amu). Therefore, one would expect much harder phonon modes for LN than for LT. Furthermore, depending on the participation of Nb,Ta to the different modes, the frequency dependence of the four phonons is expected to be different. However, while TO_1, TO_2 and TO_4 become harder with increasing Nb concentration, TO_3 softens continuously from $LiTaO_3$ to $LiNbO_3$. This behavior cannot be explained by the different atomic mass. Indeed, it has been attributed by Caciuc and Postnikov [14] to a comparatively harder oxygen rotation in $LiTaO_3$. The TO_3 mode shows, however, a less pronounced dependency on the composition with respect to the other TO phonos. Because of their composition dependency, the TO modes, are true fingerprints of the crystal stoichiometry. In particular TO_1 and TO_4 can be used to identify the crystal composition by Raman measurements.

IV. Conclusions

The structural and vibrational properties of $LiNb_{1-x}Ta_xO_3$ mixed crystals have been investigated from first principles. The crystal volumes grows 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

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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REFERENCES

[1] R. S. Weis and T. K. Gaylord, „Lithium-niobate - summary of physical-properties and crystal-structure“, Appl. Phys. A, vol. 37, pp. 191-203, March 1985.

[2] A. Bartasyte, A. M. Glazer, F. Wondre, D. Prabhakaran, P. A. Thomas, S. Huband, D. S. Keebl, and S. Margueron, “Growth of $LiNb_{1-x}Ta_xO_3$ solid solution crystals”, Mat. Chem. and Phys., vol. 134, pp. 728–735, June 2012.

[3] I. G. Wood, P. Daniels, R. H. Brown, and A. M, Glaze, “Optical bire-fringence study of the ferroelectric phase transition in lithium niobate tantalate mixed crystals: $LiNb_{1-x}Ta_xO_3$”, J. Phys.: Condens. Matter, vol. 20, pp. 235237-235242, May 2008.

[4] D. Xue, K. Betzler, and H. Hesse, “Dielectric properties of lithium niobate–tantalate crystals“, Sol. Stat. Comm., vol. 115, pp. 581-585, Aug. 2000.

[5] J. P. Perdew and Y. Wang, “Accurate and simple density functional for the electronic exchange energy: Generalized gradient approximation”, Phys. Rev. B, vol. 33, pp. 8800-8802, June (1986).

[6] G. Kresse and J. Furthmüller, “Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set”, Phys. Rev. B, vol. 54, pp. 11169-11186, Oct. 1996.

[7] P. E. Blöchl, “Projector augmented-wave method”, Phys. Rev. B, vol. 50, pp. 17953-17979, Dec. 1994.

[8] W.G. Schmidt, M. Albrecht, S. Wippermann, S. Blankenburg, E. Rauls, F. Fuchs, C. Rödl, J. Furthmüller, and A. Hermann, “$LiNbO_3$ ground- and excited-state properties from first-principles calculations, Phys. Rev. B, vol. 77, pp. 035106-035112, Jan. 2008.

[9] W. G. Schmidt, F. Bechstedt, and G. P. Srivastava, “III-V(110) surface dynamics from an ab initio frozen-phonon approach”, Phys. Rev. B, vol. 52, pp. 2001-2007, July 1995,

[10] F. D. Murnaghan, “The compressibility of media under extreme pressures”, Proc. Nat. Acad. Sci. USA vol. 30, pp. 244-247, Sept. 1944.

[11] F. Shimura, Y. Fujino, Crystal growth and fundamental properties of $LiNb_{1-y}Ta_yO_3$“, J. Cryst. Growth, vol. 38, pp. 293-301, June 1977, and references therein.

[12] S. Sanna, G. Berth, W. Hahn, A. Widhalm, A. Zrenner and W. G. Schmidt, “Vibrational properties of the $LiNbO_3$ z-surfaces”, IEEE Transactions on ultrasonics, ferroelectrics and frequency control, vol. 58, pp. 1751-1756, September 2011.

[13] C. Rapitis, “Assigment and temperature dependence of the Raman modes of $LiTaO_3$ studied over the ferroelectric and paraelectric phases”, Phys. Rev. B, vol. 38, pp. 10007-10019, Nov. 1988.

[14] V. Caciuc and A.V. Postnikov, “Ab initio zone center phonons in $LiTaO_3$: Comparison to $LiNbO_3$”, Phys. Rev. B, vol. 64, pp. 224403-224409, Nov. 2001.

[15] A. Ridah, M. D. Fontana, and P. Bourson, “Temperature dependence of the Raman modes in $LiNbO_3$ and mechanism of the phase transition”, Phys. Rev. B, vol. 56, pp. 5967–5973, Sep. 1997.