



Real structure influencing the hydrogen defect chemistry in congruent LiNbO_3 and LiTaO_3



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ABSTRACT

Hydrogen incorporation into lithium niobate and lithium tantalate during crystal growth has attracted research interest for a long time, but the diffusion paths and defect sites within the materials are only partially understood. In the present study, the hydrogen defect is investigated by crystal orientation and light polarization resolved FT-IR spectroscopy. The OH⁻ absorption band is splitting in two sub-bands, which are significantly affected by intrinsic defects. We attribute the line broadening of both band components to the antisite defect cluster, which is decorated by hydrogen. LiNbO_3 and LiTaO_3 although, isomorphous in crystal and defect structure, differ significantly in their antisite defect cluster concentration and, as we show, also in the occupation of hydrogen bonding sites in the structure.

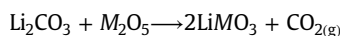
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1. Introduction

Lithium niobate (LiNbO_3) and lithium tantalate (LiTaO_3) are functional oxides, as they are ferroelectric, piezoelectric, pyroelectric, photorefractive and optical non-linear materials [1]. This variety of physical properties results in many applications in the fields of optics, electro-optics and acoustics, such as motion sensors [1], holographic storage devices [2], radiation detectors [3], optical waveguides [4], frequency doubling setups [5], optical phase and amplitude modulators [1], acoustic filters [6], Q-switches [7], and many more. The materials are also known for their low acoustic losses and are therefore suitable for surface acoustic wave (SAW) devices [8]. Novel interesting applications for LiNbO_3 and LiTaO_3 are the water disinfection and the generation of reactive oxygen species (ROS) employing the pyroelectric effect [9,10].

The synthesis of single crystals is carried out from the melt by the CZOCHRALSKI method [11]. For over 50 years numerous reports have been published on the influence of the composition of the melt on the properties of the crystals [1,12–19]. The commercial growth of crystals uses a melt of lithium carbonate (Li_2CO_3) and niobium or tantalum pentoxide (Nb_2O_5 or Ta_2O_5). The reaction

equation is given by BRICE [20] (with $M=\text{Nb}$ or Ta):



For a congruent composition (C- LiMO_3) a Li/Nb ratio of 48.5/51.5 and a Li/Ta ratio of 48.75/51.25 are used, respectively [21,22]. For the stoichiometric composition (S- LiMO_3) the double-crucible CZOCHRALSKI method is applied [23]. The properties, such as melting temperature [24], CURIE temperature [24,25], lattice parameters [26,27], band gap [28,29] and pyroelectric coefficient [30–32] depend on the chemical composition.

Hydrogen is incorporated in all air-grown LiMO_3 crystals stemming either from the starting material and/or incorporation from the atmosphere during the growth process [33]. The protons form OH⁻ ions in the materials [34]. These hydroxyl ions show up in infrared spectroscopy as absorption bands, which arise from the OH⁻ stretching vibration. The present paper investigates the crystallographic orientation of the hydrogen defects and their dependence on the real structure of the congruent composition using polarized FT-IR spectroscopy.

2. Crystallography and defect chemistry

2.1. Crystal structure

The two material systems LiNbO_3 and LiTaO_3 are isomorphous, i.e. they are identical in their structure and only the metal M -site cation is different. However, the two materials are often dissimilar

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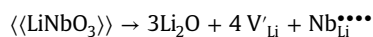
in their physical properties (see Suppl., Table S1), which makes them relevant objects of systematic solid state research [75–79].

The pseudo-ilmenite structure [8] of the two materials, below T_C , is trigonal with point group 3m and space group R3c [1,35]. The oxygen octahedra are filled by one-third of lithium atoms, one-third of transition metal atoms M and one-third of vacancies. In $+c$ direction the sequence in the oxygen octahedra is: Li^+ , M^{5+} , vacancy, Li^+ , M^{5+} , vacancy, ... [35].

The tensor properties, e.g. pyroelectricity, piezoelectricity and permittivity, are described in a cartesian coordinate system: the z axis is chosen parallel to the c axis, the x axis parallel to any of the three equivalent hexagonal a axes, the y axis lies in a mirror plane and forms a right-handed x, y, z system [36].

2.2. Intrinsic defects

The defect models will be presented for LiNbO_3 since LiTaO_3 is isomorphic and an analogous defect structure is expected. The growth of a congruent composition with the CZOCHRALSKI method leads to an excess of Nb_2O_5 and, hence, to the formation of defects in the structure. The structure of C- LiNbO_3 has a deficiency of Li atoms, where the lattice has approximately 6% free Li sites [37]. In order to ensure charge neutrality, a combination of several defects is necessary. The most common model in the literature is summarized by the following equation (in KRÖGER-VINK notation [38]):



Here, V_{Li} is a lithium vacancy and $\text{Nb}_{\text{Li}}^{\bullet\bullet\bullet}$ is a Nb atom on a regular Li lattice site, the so-called Nb antisite defect. This model is supported through studies by X-ray and neutron diffraction of LiNbO_3 [21] and LiTaO_3 [39,40]. These data show that only 1% of Li positions is occupied by Nb^{5+} , i.e. 4% V_{Li} are required for charge neutrality [21,40]. Also theoretical calculations of Xu [41] confirm this mechanism. Kim [42] reported a plausible structure of the defect complex with the niobium antisite defect surrounded by three lithium vacancies in the nearest neighbourhood and another independent lithium vacancy. This fourth V_{Li} is shifted, with respect to the other three V_{Li} , along the polar c axis [42].

2.3. Hydrogen defects

The model of interstitial hydrogen distribution is presented in Fig. 1, which is a schematic representation of the nearest neighbors for the O^{2-} anions in LiMO_3 [43–46]. HERRINGTON [43] showed that the OH^- band is polarized perpendicular to the c axis and assumed that the band consists of at least two components. From structure data of ABRAHAMS [35], HERRINGTON concluded that the OH^- bond is aligned parallel to the two shortest distances of 2.73 Å between two oxygen atoms. These two distances (positions 1 and 2 in Fig. 1) are equal in length, but they are not equal to those O–O distances to the left and right (3–6 in Fig. 1); this results in small differences in the OH^- stretching vibration and thus leads to two band components [43].

As laid down by Kovács [44,45], three different triangular positions exist in the oxygen plane. The proton positions 1–2, 3–4 and 5–6 in Fig. 1 can be regarded as equivalent, respectively. It is assumed that the longest O–O connection line is not decorated with hydrogen. In other ABO_3 materials with an OH^- stretching vibration near 3500 cm^{-1} , the O–O distance is approximately 2.8 Å [33], which corresponds well to the bonds 1–4, however, not 5–6. Therefore, it is assumed that these four contributions on the two shortest O–O distances are responsible for the OH^- absorption band in LiMO_3 [33].

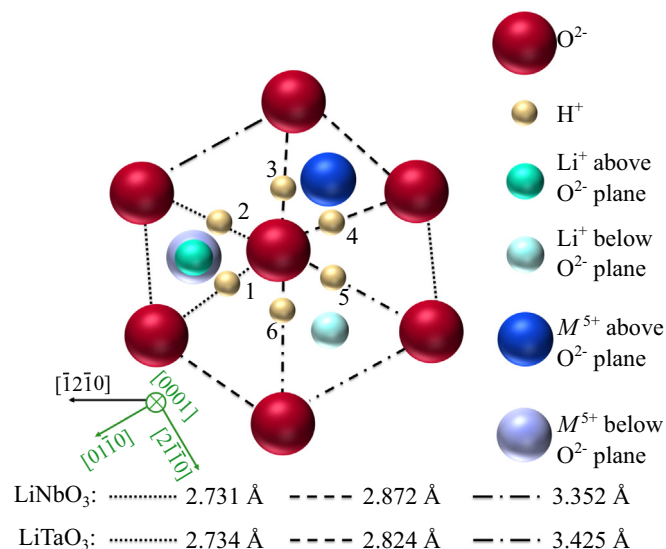


Fig. 1. Schematic representation of possible interstitial proton positions (numbered yellow spheres) in the oxygen plane (red spheres) at $z \sim 0.56$ perpendicular to the c axis in LiMO_3 . Bright green and blue spheres indicate the ions below and dark green and blue above the oxygen plane. Blue spheres denote Nb^{5+} ions and green spheres Li^+ ions (after Kovács [45]). Distances between oxygen atoms are differing as given by the different connection lines. The green coordinate system shows the cube cut. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3. Materials and methods

3.1. Crystals and FT-IR spectroscopy

For all measurements congruent (C-) LiMO_3 crystals of $5\text{ mm} \times 5\text{ mm} \times 5\text{ mm}$ were applied. The crystal cubes were cut in the $[0001]$, $[2\bar{1}\bar{1}0]$ and $[01\bar{1}0]$ directions and were obtained from CrystTec GmbH, Berlin.

For the presentation of the results, the following convention is used to describe the crystal orientations (see Fig. 2): Crystallographic directions $[2\bar{1}\bar{1}0]$, $[01\bar{1}0]$ and $[0001]$ shall correspond to x , y , and z . A letter triplet determines the transmission direction relative to the orientation of the crystal cube. For example Fig. 2 shows the cube in xyz position: the first position denotes the direction parallel to the beam, here $[2\bar{1}\bar{1}0]$. The second letter gives

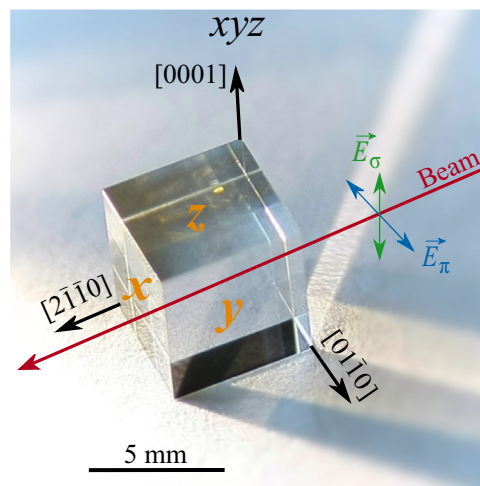


Fig. 2. Nomenclature for spectroscopy on crystal cubes. The crystallographic directions $[2\bar{1}\bar{1}0]$, $[01\bar{1}0]$ and $[0001]$ are abbreviated by x , y , and z . The xyz coordinate triplet describes the orientation of the crystal relative to the IR beam: x is parallel to the beam, $y \parallel \vec{E}_\pi$ and $z \parallel \vec{E}_\sigma$.

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