



	Experiment title: Detection of Hydrogen in lithium niobate and lithium tantalate by means of resonant forbidden reflections	Experiment number: MA-2361
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Report:

In this project, we investigate the real-structure of the two crystallographically isomorphous, ferroelectric materials lithium niobate (LiNbO_3) and lithium tantalate (LiTaO_3). Both materials are interesting for many applications due to physical properties as pyroelectricity, piezoelectricity and ferroelectricity. Commonly grown via the Czochralski method, most crystals in use are not stoichiometric but congruent and, hence, show a Li deficiency. Therefore, crystals of both materials are expected to exhibit a variety of different defects or defect clusters. Many different defect models including lithium vacancies, niobium/tantalum vacancies, oxygen vacancies, and niobium/tantalum antisite have been discussed in the literature [1]. The inherent presence of hydrogen impurities increases the complexity of the real-structure and their interaction with other defects are not understood yet. Oxygen and hydrogen defects are commonly investigated by UV/VIS spectroscopy, infrared spectroscopy, and, for small perturbations, density-functional theory (DFT) calculations, etc. In our experiments, we used an alternative approach to study the real-structure of both congruent and near-stoichiometric LiMeO_3 using resonant X-ray diffraction (RXD). In particular, we recorded spectra of so called “forbidden” reflections which are non-zero only near the absorption edge of an element contained in the unit cell. This kind of reflections only exists due to an anisotropy of the atomic scattering amplitude with respect to the polarization and wave vector of both incident and scattered radiation [2]. While defects are hard to track by conventional X-ray absorption spectroscopy due to their low concentration, “forbidden” reflections are highly sensitive to displacement of the resonant atom and, hence, to defects and vibrations [3,4,5]. The obtained spectra can be modeled from first principles, using the structural information and defect models.

In order to isolate different defects, the starting point of our study was a characterization of near-stoichiometric LiMeO_3 crystals, representing the most ideal structure. This was followed by strategic sample treatment, which involves heat treatment under vacuum or oxygen atmosphere and an introduction of protons into the crystal structure, leading to the formation of OH^- bonds. As they are most widely used in application, a corresponding sample series was prepared for congruent crystals, that naturally show a Li-deficiency. The measurements were carried out for the 003 reflection which has zero intensity in conventional X-ray diffraction due to glide plane symmetries in space group 161 ($R3c$). Taking into account the anisotropy in resonant scattering, a contribution to the 003 reflection intensity is caused by two components of the mixed

dipole-quadrupole transition tensor. This results in a specific mapping of the overlap of p - d hybridized states with the core s states when measuring at the K -absorption edge and with the core p states when measuring at the L_3 edge resulting in different different excitation probabilities for the two cases. In the case of LiNbO_3 , the measurements were performed at the $\text{Nb-}K$ edge (18.99 eV) while at the $\text{Ta-}L_3$ edge (9.88 eV) in the case of LiTaO_3 . Spectra were obtained at different lower temperatures to isolate the thermal motion induced contribution to forbidden reflections. Recording the 003 reflection spectra was complicated by a strong and frequent occurrence of the Renninger effect. This required for each temperature a repeated measurement at many different azimuthal positions in a small 10° -range to collect redundant data which could be used to extract the clean spectra. Fig. 1 shows the obtained results for lithium tantalate samples. As a first step, we focussed our study on the untreated stoichiometric, the untreated congruent and the heat-treated (deprotonated) crystals.

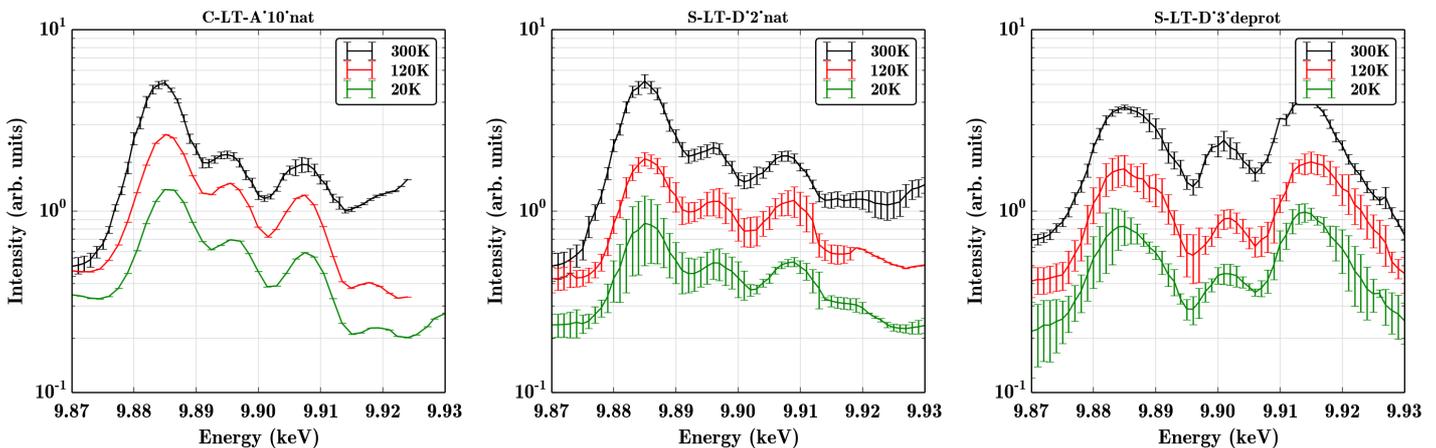


Figure 1: 003 reflection spectra of LiTaO_3 for the congruent (left), stoichiometric (middle) and stoichiometric heat-treated (right) sample for different temperatures. In case of the heat-treated sample, a shift of the second and third maximum as well as a strong increase of the third maximum can be observed. The spectra are scaled for clarity.

The spectra of as-grown near stoichiometric and congruent LiTaO_3 look very similar, while strong changes occur after moderate heat treatment in vacuum. These changes should be related to lithium and / or oxygen vacancies. The reason why they can't be observed in the congruent crystal may be that the lithium deficiency is compensated by Nb antisite defects. It should be noted that absorption spectra as well as the spectra obtained for LiNbO_3 do not show such clear trends. This might be due to the fact that different orbitals are involved when measuring at the $\text{Nb-}K$ edge. In future work, we want to clarify this question by mapping also the $\text{Ta-}L_1$ edge where the initial state of the virtual photoelectron has an s -character, as for the K -edge. A sophisticated modeling of the presented data on the basis of known defect structures has been started. A set of 13 defect structures based on models known from literature as well as own considerations has been relaxed with DFT and, on the basis of formation energy, the most probable candidates have been selected for the modeling. Meanwhile, a further exploration of the parameter space and the influence of the corresponding sample treatment is highly desired. In particular, we aim for a characterization of samples heated at higher temperatures and protonated samples, exhibiting oxygen vacancies and hydrogen impurities, respectively. This will be focussed on LiTaO_3 , since the influence of defects is more pronounced at the $\text{Ta-}L_3$ edge.

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