Experimental report

28/08/2017

Proposal: 7-03-159 **Council:** 10/2016

Title: Dynamics of Ion Conduction in congruent LiNbO3/LiTaO3

Research area: Materials

This proposal is a new proposal

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Samples: LiTaO3
LiNbO3

Instrument	Requested days	Allocated days	From	To
IN4	4	3	06/02/2017	09/02/2017
IN6	6	3	20/02/2017	23/02/2017

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. The impurities highly influence the properties of the material and often form the basis for important applications. Therefore, the underlying ionic migration processes not only of hydrogen are of high scientific interest, but those of lithium and oxygen as well. For these ionic species a complete set of kinetic parameters, such as diffusion barrier and diffusion coefficient, are not yet available. Consequently, we propose lattice dynamic measurements and determination of thermally activated ionic transport pathways via temperature dependent inelastic and quasi-elastic neutron scattering.

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Scientific Background

Lithium niobate (LNO) and lithium tantalate (LTO) are isomorphous crystalline materials and ferroelectric at room temperature. Therefore they are very interesting for many applications such as nonlinear optics, surface acoustic wave devices and optical wave-guides [1-4]. The congruent single crystals of these materials usually contain hydrogen, mainly in the form of OH- ions, as well as a Li deficiency as a result of the crystal growth process. Diffusion processes are rather well investigated using tracer or nuclear magnetic resonance (NMR) for LNO [5, 6] in comparison to LTO, where a similar behavior is expected. Reference 7 presents a comprehensive study of congruent LNO - exhibiting Li vacancies as migration paths for impurities - summarizing mobilities of different cations in LNO, and presenting a wide spread of diffusion coefficients with respect to Li (being the most mobile specie). Lattice dynamics is of a considerable interest here, we have therefore performed inelastic neutron scattering (INS), at the ILL, to gain new insights into mobility and temperature dependent defect formation. Up to now, neutron scattering has been primarily used in related work to investigate the phase transition of LTO, but its potential to monitor the dynamics of defects is yet untapped.

We have recently found that defect structures of LNO and LTO are not identical, as demonstrated by defect induced inhomogeneous broadening of the OH stretching mode [8] as well as NMR measurements. This refutes similar defect structures in these isomorphs [9]. Furthermore, kinetic investigations by means of reduction at high temperature, related to the introduction of oxygen vacancies, highlight different activation energies for both LNO and LTO.

INS Experiments

The INS measurements, subject of the present report, focused on the LTO sample under two powdered forms: as-grown $LiTaO_3$ powder (A1 and A2) and chemically reduced powder for 20 hours at 900°C (T1).

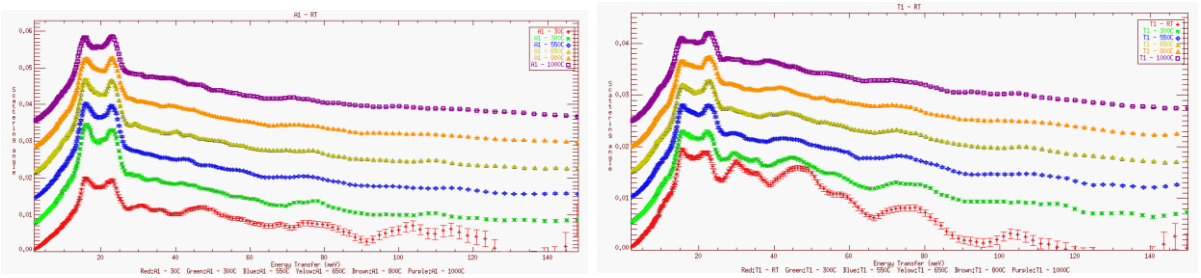

Fig. 1: Temperature dependence of phonon spectra for (a) as-grown LTO sample A1 and (b) annealed sample T1, using IN4C (vertically shifted for clarity).

We first collected data in the up-scattering mode, at 30, 300, 550, 650, 800 and 1000 °C, using IN4C, and selecting an incident neutron wavelength of 2.41 Å.

Fig. 1(a) shows the phonon temperature dependence of A1 and (b) of thermally pre-treated LTO (sample T1). It can clearly be seen that the phonon spectrum measured at room temperature exhibits the sharpest phonon bands. The structure of the phonon bands decreases with increasing temperature due to the temperature-induced broadening. A comparison of the two data sets shows significant differences in the range of 0-40 meV. For T1, the appearance of several low-energy

features around 10 meV is evident for high temperatures as well as in the range of 10–14 meV at room temperature, which are not observable in as-grown LTO (sample A1).

We then used IN6 to measure high-resolution phonon spectra in order to better resolve features in the phonon band 0-40 meV. The measurements were performed in the up-scattering mode at 30, 650 (above the Curie temperature of LTO) and 1000 °C, and using an incident neutron wavelength of 4.14 Å. The temperature points were limited to three because in the high-resolution setup of IN6, there is a considerable reduction of the flux, imposing a longer acquisition time.

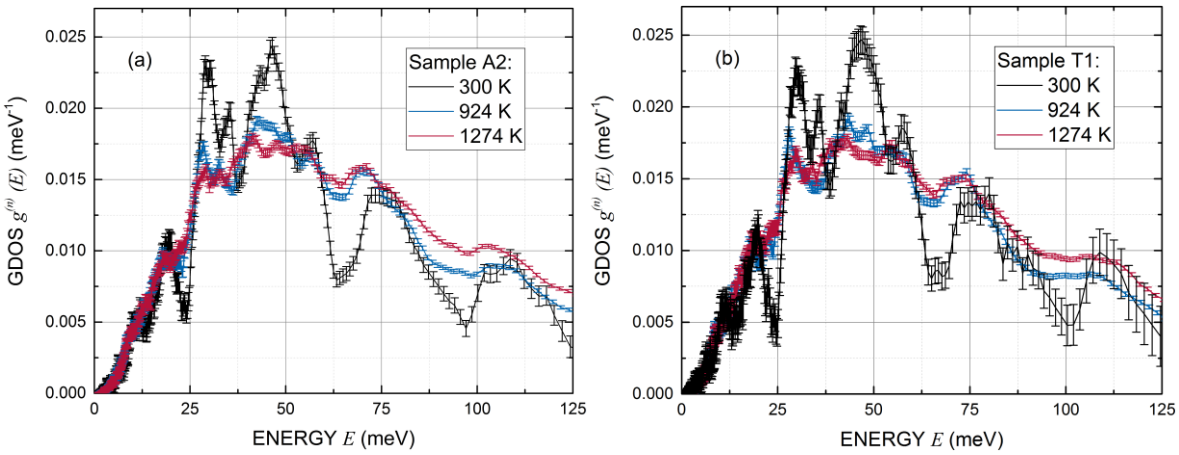

Fig. 2: Temperature dependence of phonon spectra for (a) as-grown LTO sample A1 and (b) annealed sample T1, using IN6.

Fig. 2(a) shows temperature dependence of phonon spectra of as-grown LTO (sample A2), and (b) of thermally pre-treated LTO (sample T1), from IN6 measurements. Here, a fresh as-grown sample was used, but the same thermally pre-treated LTO (T1) from IN4 measurements was used to collect data on IN6. It should be noted that T1 has additionally been thermally treated about 10 hours up to 1000°C during the measurements at IN4. It is clear that phonon spectra collected using IN6 exhibit a better energy resolution comparing to data using IN4C.Comparing A2 and T1, the phonon spectra point out that at 30 °C significant differences between both samples exist. With increasing temperatures A1 adopts more and more the fine-structure of T1. It should be noted that, in addition to the INS measurements, we also carried out Raman spectroscopy (RS) and far infrared (F-IR) spectroscopies. (see Fig.3). For both techniques, as-grown powder was used, and is represented with normalized intensities. It is visible, that the peak positions of RS and F-IR are comparable. Differences in intensity are attributed to different selection rules of RS and F-IR regarding excitation of the TO and LO vibrations. Further, our different measurements are accompanied by *ab-initio* modeling of stoichiometric LTO, by means of density functional theory (DFT). Figure 3 compares the DFT-derived phonon spectrum with spectra measured using INS, RS and F-IR. The ab-initio calculations agree very well with the measurements for as-grown LTO.

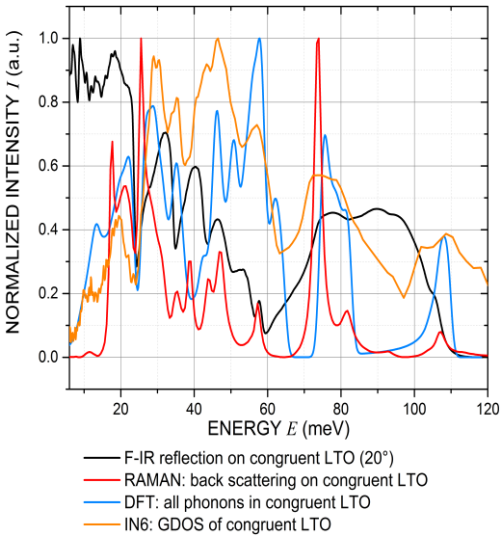

Fig. 3: Comparison of experimental phonon spectra from INS, F-IR and RAMAN with a DFT modeled spectrum for as-grown LTO.

Conclusion and outlook

Inelastic neutron scattering yields distinctive differences between as-grown and chemical reduced LTO, which is attributed to varying concentration and types of defects. Caused by the introduction of oxygen vacancies during temperature treatment TaO_6 octahedra are distorted, exhibiting additional features in the phonon spectra. Comparing room temperature data of as-grown LTO samples A1, A2 and thermally treated sample T1 clearly shows that different phonon vibrations occur. However, an increasing temperature leads for both samples to the appearance of similar phonon contributions, which is referred to the formation of a specific defect type. To get more insights into diffusion processes of individual atoms, quasi-elastic neutron scattering (QENS) experiments should be attempted. For the ionic species of interest, the diffusion coefficients are known: $D_{Li} = 4{,}7*10^{0}$ cm^2s^{-1} [5] and $D_O = 3{,}0*10^{-6}$ cm^2s^{-1} [10]. A cold-neutron TOF spectrometer like IN6 is therefore well adapted for such a QENS probe.

References:

[1] R. Weis, T. Gaylord, Applied Physics A, 37 (4) (1985), pp. 191–203.
[2] F.S. Chen, J.T. LaMacchia, D.B. Fraser, Applied Physics Letters, 13 (7) (1968), pp. 223–225.
[3] R. Whatmore, Ferroelectrics, 118 (1) (1991), pp. 241–259.
[4] L. Arizmendi, Physica Status Solidi (a) 201 (2) (2004) 253–283.
[5] Ptashnik, V. B., T. Yu Dunaeva, and I. V. Myasnikov, Inorg. Mater.(Engl. Transl.);(United States) 21.12 (1986).
[6] T. K. Halstead, The Journal of Chemical Physics 53.9 (1970), 3427-3435.
[7] D. P. Birnie III, Journal of Materials Science, 28 (2) (1993), 302–315.
[8] T. Köhler, E. Mehner, J. Hanzig, G. Gärtner, H. Stöcker, D. C. Meyer, Journal of Solid State Chemistry 244 (2016), 108-115.
[9] A. Vyalikh, M. Zschornak, T. Köhler, M. Nentwich, T.Weigel, J. Hanzig, R. Zaripov, E. Vavilova, S. Gemming, E. Brendler, D. C. Meyer, Journal of Functional Materials (2017), submitted
[10] P. J. Jorgensen, R. W. Bartlett, Journal of Physics and Chemistry of Solids 30.12 (1969), 2639-2648.