

## KFM 13: Polar Oxide Crystals and Solid Solutions I

Chair: Prof. Dr. Holger Fritze (TU Clausthal)

Time: Thursday 10:00–12:35

Location: POT 106

KFM 13.1 Thu 10:00 POT 106

**Polaronic structures in LiNbO<sub>3</sub> and LiTaO<sub>3</sub> modelled from first principles** — ●NILS ANDRE SCHÄFER and SIMONE SANNA — Institute for Theoretical Physics, Justus Liebig University Giessen, Germany

Polaronic defects impact among other properties the optical response of LiNbO<sub>3</sub> (LN). Changes in their optical properties are of interest for the applications of LN in optoelectronics. These are relatively well known in LN but in LiTaO<sub>3</sub> (LT) less so. In order to improve our knowledge of polaronic structures in LT, we modeled polarons in LN and LT from first principles using the DFT+U method as implemented in VASP.

We explore different microscopic polaronic structures in both polar oxides with respect to changes in their electronic band structures and optical properties, especially with respect to Jahn-Teller distortions. Similarities and differences between different polaronic defects and both compounds are discussed as well.

KFM 13.2 Thu 10:20 POT 106

**Crystal growth and thermal analysis of Li(Nb,Ta)O<sub>3</sub> solid solutions** — ●UMAR BASHIR GANIE — IKZ, Berlin

This work presents the growth and thermal analysis of Lithium Niobate Tantalate (Li(Nb,Ta)O<sub>3</sub>, LNT) single crystals for different LiTaO<sub>3</sub> (LT) mole fractions (xLT), ( $xLT = nLT/(nLT+nLN)$ ). Our crystal growth experiments show that growth of LNT single crystal over the entire LT mole fraction is not only possible but can be achieved with weaker constituent segregation and therefore higher degree of homogeneity than considered previously. Our differential thermal analysis (DTA) measurements show that the melting temperature increases with increasing fraction of LT and follow the behavior of a (pseudo)binary phase diagram as published previously [1]. Thorough evaluation of the DTA results allows to propose an improved version of the LN-LT phase diagram that is not only thermodynamically stringent but also allows to explain the component distribution observed in LNT single crystals and to design growth experiments yielding crystals of higher homogeneity. We also performed specific heat capacity measurements of single crystals of LNT solid solutions. The aim was to investigate the variation of ferroelectric Curie temperature with composition. We observed that the ferroelectric Curie temperature decreases linearly with growing Ta composition in the LNT solid solution crystals.

KFM 13.3 Thu 10:40 POT 106

**Hydrogen Diffusion in LiNbO<sub>3</sub> and LiTaO<sub>3</sub>** — ●KOFAHL CLAUDIA<sup>1</sup>, DÖRRER LARS<sup>1</sup>, SUHAK YURIY<sup>2</sup>, YAKHNEVYCH ULIANA<sup>2</sup>, FRITZE HOLGER<sup>2</sup>, and SCHMIDT HARALD<sup>1,3</sup> — <sup>1</sup>Institut für Metallurgie, AG Festkörperkinetik, TU Clausthal, Germany — <sup>2</sup>Institut für Energieforschung und Physikalische Technologien, TU Clausthal, Germany — <sup>3</sup>Clausthaler Zentrum für Materialtechnik, TU Clausthal, Germany

LiNbO<sub>3</sub> and LiTaO<sub>3</sub> crystals are technologically important polar metal oxides with exceptional combinations of ferroelectric, piezoelectric, acoustic, optical and ion conductivity properties. The presence and diffusion of H in these materials has an important influence on the materials properties, reducing optical damage, increasing optical birefringence and changing ionic conductivity. The diffusion mechanism is unclear up to now. Therefore, it is of particular interest to study the diffusion of hydrogen. For this purpose, we use two different analytical methods, SIMS (Secondary Ion Mass Spectroscopy) and IRS (Infrared Spectroscopy). For the SIMS measurements, the crystals are loaded with high amounts of H by means of proton-exchange and the redistribution of H is monitored after post-annealing. In contrast, for the IRS experiments, only hydrogen of about 300 ppm, which is introduced by crystal growth in air, is replaced by deuterium during exchange anneals in D<sub>2</sub>O. The measured diffusion coefficients of the two methods differ from each other, but are higher than Li diffusivities as given in literature. The activation energies are similar. Possible reasons for the differences are discussed.

KFM 13.4 Thu 11:00 POT 106

**Acoustic loss in Lithium Niobate-Lithium Tantalate solid solutions with different Nb/Ta ratios at temperatures up to 900°C** — ●ULIANA YAKHNEVYCH<sup>1</sup>, CLAUDIA KOFAHL<sup>2</sup>, STEPAN HURSKYY<sup>1</sup>, STEFFEN GANSCHOW<sup>3</sup>, YURIY SUHAK<sup>1</sup>, HARALD SCHMIDT<sup>2</sup>, and HOLGER FRITZE<sup>1</sup> — <sup>1</sup>Institute of Energy Research and Physical Technologies, Clausthal University of Technology, Germany — <sup>2</sup>Institute of Metallurgy, Clausthal University of Technology, Germany — <sup>3</sup>Leibniz-Institut für Kristallzüchtung, Berlin, Germany

Lithium niobate-lithium tantalate solid solutions (LNT) are poorly studied materials in modern materials science, which must be seen in the light that they can combine the advantages of the edge compounds lithium niobate (LN) and lithium tantalate (LT). These crystals are expected to exhibit high piezoelectric coefficients and thermal stability. This work focuses on comparing the Q-factor of LN, LT, and LNT as well as on the analysis of loss contributions in samples. Electromechanical losses of the samples were determined using two different approaches, namely noncontacting resonant ringdown spectroscopy and resonant piezoelectric spectroscopy using Pt electrodes. LNT thickness-shear mode (TSM) acoustic resonators exhibit significantly lower loss than LN. The study of the acoustic loss in LNT resonators operated in the TSM showed strong frequency dependent loss increases at temperatures above 450°C. The loss was modelled using independent materials data. Based on the modelling, the above-mentioned loss above 450°C is associated with a conductivity-induced piezoelectric/carrier relaxation mechanism governed by Li migration.

15 min. break

KFM 13.5 Thu 11:35 POT 106

**High-temperature stability of electrical and acoustic properties of congruent and near stoichiometric single crystalline LiNbO<sub>3</sub>, LiTaO<sub>3</sub> and LiNb<sub>0.94</sub>Ta<sub>0.06</sub>O<sub>3</sub>** — ●YURIY SUHAK<sup>1</sup>, STEPAN HURSKYY<sup>1</sup>, ULIANA YAKHNEVYCH<sup>1</sup>, FATIMA EL AZZOUI<sup>1</sup>, CLAUDIA KOFAHL<sup>2</sup>, HARALD SCHMIDT<sup>2</sup>, STEFFEN GANSCHOW<sup>3</sup>, KLAUS-DIETER BECKER<sup>4</sup>, and HOLGER FRITZE<sup>1</sup> — <sup>1</sup>Institute for Energy Research and Physical Technologies, Clausthal University of Technology, Goslar, Germany — <sup>2</sup>Institute of Metallurgy, Clausthal University of Technology, Clausthal-Zellerfeld, Germany — <sup>3</sup>Leibniz Institut für Kristallzüchtung, Berlin, Germany. — <sup>4</sup>Braunschweig University of Technology, Braunschweig, Germany

It is known that the intrinsic properties of LiNbO<sub>3</sub>, LiTaO<sub>3</sub> and, consequently, of Li(Nb,Ta)O<sub>3</sub> solid solutions are strongly dependent on lithium stoichiometry. In current work the electrical and acoustic properties of congruent and near-stoichiometric single crystalline Li(Nb,Ta)O<sub>3</sub> are studied as a function of temperature by means of impedance spectroscopy and resonant piezoelectric spectroscopy, respectively. The preparation of near-stoichiometric samples was performed by vapor transport equilibration technique (VTE). It is shown, that VTE-treated samples generally exhibit lower conductivity and lower acoustic loss, which implies better thermal stability. The latter was examined by a long-term measurement of electrical conductivity at 500 °C in air. After about 330 hours of uninterrupted thermal treatment the conductivity of a congruent LiNb<sub>0.94</sub>Ta<sub>0.06</sub>O<sub>3</sub> specimen was found to decrease only for about 3 %.

KFM 13.6 Thu 11:55 POT 106

**A high-temperature optical spectroscopy study of lithium niobate, LiNbO<sub>3</sub>** — ●KLAUS-DIETER BECKER<sup>1</sup>, JIANMIN SHI<sup>1</sup>, PIOTR GACZYNSKI<sup>1</sup>, MISHA SINDER<sup>2</sup>, ULIANA YAKHNEVYCH<sup>3</sup>, NATALIA SYVOROTKA<sup>3</sup>, YURIY SUHAK<sup>3</sup>, STEFFEN GANSCHOW<sup>4</sup>, and HOLGER FRITZE<sup>3</sup> — <sup>1</sup>Institute of Physical and Theoretical Chemistry, TU Braunschweig, Braunschweig, Germany — <sup>2</sup>Materials Engineering Department, Ben Gurion University of the Negev, Beer-Sheva, Israel — <sup>3</sup>Institute for Energy Research and Physical Technologies, TU Clausthal, Goslar, Germany — <sup>4</sup>Leibniz Institut für Kristallzüchtung, Berlin, Germany

Optical absorption spectra of chemically reduced LiNbO<sub>3</sub> (LN) show broad bands in the vis and NIR region which have been attributed to various types of electron small polarons. At 1000°C, spectra are dominated by an absorption band at 0.9 eV due to free small polarons,

i.e. to electrons localized on niobium ions on regular sites. Band intensity has been found to follow a power-law dependence on oxygen partial pressure  $P_{O_2}$  of the form  $(P_{O_2})^m$  with  $m = -0.23(+/-)0.02$ . This  $m$ -value is in excellent agreement with the value of  $-1/4$  predicted from point defect thermodynamics of the chemical redox model of LN. The experimental kinetics of reduction and oxidation following a rapid change in oxygen partial pressure have been found to provide a novel route to diffusion of lithium vacancies at high temperatures as well as to that of lithium ions in LN.

KFM 13.7 Thu 12:15 POT 106

**Looking undercover - Probing subsurface properties by Piezoresponse force microscopy (PFM)** — •MATTHIAS ROEPER<sup>1</sup>, SAMUEL D. SEDDON<sup>1</sup>, LILI DING<sup>1</sup>, MICHAEL RÜSING<sup>1</sup>, and LUKAS M. ENG<sup>1,2</sup> — <sup>1</sup>Institut für Angewandte Physik, TU Dresden, Nöthnitzer Straße 61, 01187 Dresden, Germany — <sup>2</sup>ct.qmat: Dresden-Würzburg Cluster of Excellence - EXC 2147, TU Dresden, 01062 Dresden, Germany

Piezoresponse force microscopy (PFM) is one of the most widespread methods for investigating and visualizing ferroelectric domain structures at the nanometer length scale, even along all 3 dimensions (3D) [1]. PFM couples to the local dielectric displacement that is present near the sample surface, and hence is also sensitively probing into the bulk of the sample under investigation, i.e. into a subsurface volume with penetration  $d$  [2]. In this work, we systematically analyze in both theory and experiment, the contrast and depth resolution capabilities of PFM as a function of the various relevant experimental parameters. PFM tool properties such as the tip radius, ac driving voltage, and ac frequency were optimized, while equally dedicated sample structures incorporating (known) buried features, i.e. ferroelectric domain walls, fabricated into the bulk host at a distance  $d$  below the surface, were analyzed. Our findings allow to accurately adjust the image contrast to a certain penetration depth  $d$ , and thus quantify those local features with high precision.

[1] L. M. Eng et al., Appl. Phys. Lett. 74, 233 (1999) [2] F. Johann et al., Appl. Phys. Lett. 94, 172904 (2009)