

KFM 9: Focus: Polar oxide crystals and solid solutions

Time: Wednesday 9:30–13:30

Location: TOE 317

KFM 9.1 Wed 9:30 TOE 317

On the Growth of Lithium Niobate-Tantalate Solid Solution Single Crystals — ●STEFFEN GANSCHOW¹, DETLEF KLIMM¹, MICHAEL RÜSING², BENJAMIN KIRBUS², ZEESHAN AMBER², and LUKAS M. ENG² — ¹Leibniz-Institut für Kristallzüchtung, Max-Born-Straße 2, 12489 Berlin, Germany — ²Institut für Angewandte Physik, Technische Universität Dresden, Nöthnitzer Str. 61, 01187 Dresden, Germany

Lithium niobate (LiNbO₃, LN) and lithium tantalate (LiTaO₃, LT) belong to the most widely used ferroelectric materials, with applications that range from novel electronic and micro-mechanical devices to (integrated, nonlinear) optics. Recently, lithium niobate-tantalate solid-solution (LiTa_xNb_{1-x}O₃, LNT) single crystals have been demonstrated. LNT potentially might outperform pure LN and LT applications, since offering superior material properties such as the tailored birefringence combined with large temperature stability.

Crystallization of LNT solid solutions from the melt is characterized by a strong segregation leading to a pronounced macro-distribution of components and, occasionally, to cellular growth [1,2]. In this contribution here, we critically review previous attempts to manufacture LNT single crystals, and discuss novel approaches that promise LNT single crystals of enhanced chemical homogeneity. A phase diagram of the quasi-binary system based on a thermal analysis will be presented along with the results of our first crystal growth experiments.

[1] T. Fukuda and H. Hirano, *J. Crystal Growth* 33, 127 (1976).

[2] A. Bartasyte et al., *Mater. Chem. Phys.* 134, 728 (2012).

KFM 9.2 Wed 9:50 TOE 317

Poling of lithium niobate tantalate mixed crystals: Lessons learned from lithium niobate and tantalate — ●LUKAS M. ENG¹, STEFFEN GANSCHOW², HENRIK BECCARD¹, EKTA SINGH¹, ZEESHAN AMBER¹, BENJAMIN KIRBUS¹, and MICHAEL RÜSING¹ — ¹Institut für Angewandte Physik, Technische Universität Dresden, Nöthnitzer Str. 61, 01187 Dresden, Germany — ²Leibniz-Institut für Kristallzüchtung, Max-Born-Straße 2, 12489 Berlin, Germany

The ability to structure ferroelectric domains is the key ability for the functionalization of ferroelectric materials leading to their broad palette of applications, ranging from novel electronics, micro-mechanical devices, to (integrated, nonlinear) optics. Lithium niobate (LiNbO₃, LN) and lithium tantalate (LiTaO₃, LT) belong to the most widespread used materials for these applications. Recently, lithium niobate-tantalate (LiTa_xNb_(1-x)O₃, LNT) mixed crystals have been fabricated, that potentially promise advantages over the boundaries of bare LN or LT, such as an improved temperature stability, or the tailoring of material properties such as the birefringence. Furthermore, LNT presents a model system for testing the impact and relevance of several effects (doping, poling, temperature, etc.) on their technological performance. In this work we discuss and analyze the poling of the model systems LN and LT and present first observations of domains in this mixed crystal system. The fabrication and analysis of poled domains in the model system LNT presents a key step towards realizing novel devices for a broader range of applications.

KFM 9.3 Wed 10:10 TOE 317

High fidelity periodic poling of x-cut thin film lithium niobate for integrated optics analyzed with second harmonic microscopy — ●MICHAEL RÜSING¹, JIE ZHAO², SHAYAN MOOKHERJEA², and LUKAS M. ENG¹ — ¹Institut für Angewandte Physik, Technische Universität Dresden, Nöthnitzer Str. 61, 01187 Dresden, Germany — ²University of California, San Diego, 9500 Gilman Dr, La Jolla, CA-92093-0407, USA

Nonlinear optics in periodically-poled thin film lithium niobate (TFLN) promises superior performance and conversion efficiencies compared to their bulk counterparts. The keys to high nonlinear conversion efficiency are high fidelity periodic poling of waveguides with a homogenous domain duty cycle, and long poling length (at least for several mm). Recently observed conversion efficiencies are limited by poling length or by inhomogeneous domain duty cycles. In this work we demonstrate periodic poling of TFLN using a single poling pulse with a tailored waveform. The poling process is analyzed in detail with Second Harmonic (SH) microscopy which provides nondestructive information about the poling quality, such as the poling depth of inverted

domains measured with a 10 nm depth resolution. This enables us to produce near-perfect poling of domains over the entire length of up to 5 mm with a periodicity as small as 3 μm. Such devices are shown to possess a high SH conversion efficiency, as well as high-quality and narrow-band entangled photon-pair generation at telecommunication wavelengths.

KFM 9.4 Wed 10:30 TOE 317

Ion Transport in LiNbO₃ - An Overview — JOHANNA UHLENDORF¹, PETER FIELTIZ¹, ERWIN HÜGER^{1,2}, LARS DÖRRER^{1,2}, STEFFEN GANSCHOW³, KLAUS-DIETER BECKER⁴, HOLGER FRITZE⁵, GÜNTER BORCHARDT¹, and ●HARALD SCHMIDT^{1,2} — ¹TU Clausthal, Institut für Metallurgie — ²TU Clausthal, Clausthaler Zentrum für Materialtechnik — ³Leibniz-Institut für Kristallzüchtung, Berlin — ⁴TU Braunschweig, Institut für Physikalische und Theoretische Chemie — ⁵TU Clausthal, Institut für Energieforschung und Physikalische Technologien

Lithium niobate (LN) is one of the most technologically important polar metal oxides with an extraordinary combination of ferroelectric, piezoelectric, acoustic, optical as well as ion conducting properties. The self-diffusion of the ionic constituents and the underlying point defects of LN are of high importance for the overall conductivity, structural disorder, stability of defect clusters, ferroelectric domain wall pinning, high temperature stability and optical applications. We present a comprehensive overview of the state-of-the-art knowledge on the diffusion of Li, Nb, and O in LN as investigated in our laboratories during the last years. The experiments were carried out with stable tracers in combination with secondary ion mass spectrometry, neutron reflectometry and high-temperature optical spectroscopy.

10 min. break

KFM 9.5 Wed 11:00 TOE 317

Oxygen transport in single crystalline Li(Nb,Ta)O₃ solid solutions at high temperatures — ●BUJAR JERLIU¹, YURIY SUHAK¹, DMITRY ROSHCHUPKIN², BORIS RED'KIN², STEFFEN GANSCHOW³, HARALD SCHMIDT¹, GÜNTER BORCHARDT¹, KLAUS DIETER BECKER⁴ und HOLGER FRITZE¹ — ¹Clausthal University of Technology, Goslar, Germany — ²Institute of Microelectronics Technology and High Purity Materials, RAS, Chernogolovka, Russia — ³Leibniz Institute for Crystal Growth, Berlin, Germany — ⁴Braunschweig University of Technology, Braunschweig, Germany

Single crystalline lithium niobate-tantalate (LiTa_xNb_(1-x)O₃, LNT) solid solutions are expected to overcome the problems of thermal instability of lithium niobate (LiNbO₃, LN) and low Curie temperature of lithium tantalate (LiTaO₃, LT). This work focuses on study of transport mechanisms in LNT crystals with different Nb/Ta ratio, grown by the Czochralski technique. The oxygen transport kinetics are investigated in the temperature range from 850 °C to 1200 °C using the stable isotope ¹⁸O as the tracer. Subsequently, the diffusion profiles are acquired by secondary ion mass spectrometry. The oxygen diffusion coefficients for LiNb_{0.88}Ta_{0.12}O₃ single crystals at annealing temperatures of 850 °C and 1000 °C equal about 4.5 x 10⁻¹⁸ m²/s and 1.5 x 10⁻¹⁶ m²/s, respectively. Our previous ¹⁸O tracer experiments carried out on stoichiometric LN revealed a local maximum on the depth profiles, which was explained by the Li-diffusion out of the crystal structure. Such a maximum is not observed for LNT compound, which could possibly indicate an improved stability of the material.

KFM 9.6 Wed 11:20 TOE 317

Electrical and electromechanical properties of single crystalline Li(Nb,Ta)O₃ solid solutions at elevated temperatures — ●YURIY SUHAK¹, BUJAR JERLIU¹, DMITRY ROSHCHUPKIN², BORIS RED'KIN², STEFFEN GANSCHOW³, GÜNTER BORCHARDT¹, KLAUS-DIETER BECKER⁴, and HOLGER FRITZE¹ — ¹Clausthal University of Technology, Goslar, Germany — ²Institute of Microelectronics Technology and High Purity Materials, Chernogolovka, Russia — ³Leibniz Institute for Crystal Growth, Berlin, Germany — ⁴Braunschweig University of Technology, Braunschweig, Germany

Piezoelectric materials with high piezoelectric coefficients that can be operated above 500 °C are in high demand for industrial actuating applications. Lithium niobate (LiNbO₃) and lithium tantalate

(LiTaO₃) possess high piezoelectric coefficients, however their usage is limited by thermal instability (LiNbO₃) and low Curie temperature (LiTaO₃). This work focuses on the electrical and electromechanical properties of Li(Nb,Ta)O₃ crystals that are expected to overcome the mentioned restrictions of individual compounds. The electrical and electromechanical properties are investigated by means of impedance spectroscopy and resonant ultrasound spectroscopy, respectively. The experiments are performed in a gas-tight tube furnace, which allows working temperatures up to 1000 °C. The investigations revealed, that Li(Nb,Ta)O₃ solid solutions show lower conductivity than LiNbO₃ at high temperatures and low oxygen partial pressures (pO₂). At 930 °C and pO₂ of 10-15 bar the conductivity of LiNb_{0.29}Ta_{0.71}O₃ sample is almost two orders of magnitude lower than that of LiNbO₃.

KFM 9.7 Wed 11:40 TOE 317

Photoconductivity of strontium barium niobate revisited: spectral features, long-term relaxation, current-voltage hysteresis — ●ELKE BEYREUTHER¹, JULIUS RATZENBERGER¹, LIUDMILA I. IVLEVA², PAVEL A. LYKOV², and LUKAS M. ENG^{1,3} — ¹Institute of Applied Physics, Technische Universität Dresden, 01062 Dresden, Germany — ²Prokhorov Institute of General Physics, Russian Academy of Sciences, Moscow, Russia — ³Cluster of Excellence 2147 – Complexity and Topology in Quantum Matter (ct.qmat)

Here, we report on the large photoconductive response (PCR) of strontium barium niobate (Sr_{0.61}Ba_{0.39}Nb₂O₆, SBN61) single-crystals grown by the modified Stepanov technique. We analyzed the PCR for both z- and x-cut SBN61 samples, using two different electrical wiring setups for each, by gradually varying the intensity and spectral composition of the incident photons. The crystals show a pronounced PCR already under diffuse daylight. Apart from a huge resistance decrease by three orders of magnitude upon super-bandgap illumination (370 nm), we observe in all four samples (i) distinct spectral features upon sub-bandgap excitation (800-390 nm) that clearly hint towards in-gap states beyond the one- and two-center models discussed in conjunction with doped SBN61 so far, as well as (ii) an extremely slow long-term relaxation for both light-on and light-off transients in the range of hours (after sub-bandgap excitation) and days (after super-bandgap excitation). Moreover, a strong phototunable I-V hysteresis (tested with 500-nm and 380-nm illumination) along the polar axis of the z-cut sample is measured.

KFM 9.8 Wed 12:00 TOE 317

Superposed picosecond luminescence kinetics in lithium niobate — ●ANDREAS KRAMPF, SIMON MESSERSCHMIDT, and MIRCO IMLAU — University of Osnabrueck, Department of Physics, Barbarastrasse 7, 49076 Osnabrueck, Germany

Various manifestations of small polarons strongly affect the linear and nonlinear optical properties in the oxide crystal lithium niobate (LiNbO₃, LN). Whereas related transient-absorption phenomena in LN have been studied extensively in the last decades, a sound microscopic picture describing the blue-green (photo)luminescence of lithium niobate single crystals is still missing. In particular, nearly nothing is known about: (i) the luminescence build-up and (ii) its room temperature decay. We here present the results of our systematic experimental study using nominally undoped and Mg-doped LN crystals with different Mg concentration. Picosecond luminescence was detected by means of femtosecond fluorescence upconversion spectroscopy (FLUPS) extended to the inspection of oxide crystals in reflection geometry.

Taking the recently proposed microscopic model into account, which describes luminescence decay in LN by local radiative self-trapped exciton recombination and/or migration and subsequent pinning on defect sites, a detailed analysis of the kinetic traces reveals, that the picosecond luminescence decay represents the superposition of exponential and stretched-exponential decay paths.

We critically discuss the data considering the interplay with small polaron transport. Financial support by the DFG (IM37/11-1, INST 190/165-1 FUGG) is gratefully acknowledged.

10 min. break

KFM 9.9 Wed 12:30 TOE 317

A high-temperature optical spectroscopy study of lithium niobate, LiNbO₃ — ●KLAUS-DIETER BECKER¹, JIANMIN SHI¹, HOLGER FRITZE², GÜNTER BORCHARDT², and STEFFEN GANSCHOW³ —

¹TU Braunschweig, Institute of Physical and Theoretical Chemistry, 38106 Braunschweig, Germany — ²Clausthal University of Technology, 38640 Goslar, Germany — ³Leibniz Institute for Crystal Growth, 12489 Berlin

Optical absorption spectra of chemically reduced LN are dominated by broad bands in the visible and NIR region which have been attributed to various types of electron small polarons, see e.g. Ref. [1]. At 1000 °C, spectra measured under such conditions are dominated by an absorption band centered at about 0.9 eV due to free small polarons, i.e. due 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_{O₂} of the form (P_{O₂})^m with m = 0.23 ± 0.01. This m-value is in excellent agreement the value of 1/4 predicted on the basis of point defect thermodynamics for the proposed chemical reduction model of LN. The experimental kinetics of reduction and oxidation processes upon oxygen activity jumps have been found to provide a non-conventional route to diffusion of lithium vacancies as well as to lithium ions in c-LN.

[1] O.F. Schirmer, M. Imlau, C. Merschjann, B. Schoke, J. Phys. Condens. Matter, 21 (2009) 123201.

KFM 9.10 Wed 12:50 TOE 317

Tunable conductive domain wall switches in 200-μm-thick lithium niobate single crystals — ●HENRIK BECCARD, BENJAMIN KIRBUS, EKTA SINGH, ZEESHAN AMBER, MICHAEL RÜSING, ELKE BEYREUTHER, and LUKAS M. ENG — Institut für Angewandte Physik, Technische Universität Dresden, Nöthnitzer Str. 61, 01187 Dresden, Germany

In the ferroelectric model material lithium niobate (LNO), state-of-the-art techniques allow the targeted poling of ferroelectric domains, as well as the robust enhancement of domain wall (DW) conductivity over several orders of magnitude [1]. Imaging and analyzing these properties can be elegantly performed with piezoresponse force microscopy (PFM) and confocal 3D second harmonic generation (SHG) microscopy [2]. The correlation between DW geometry and electrical DW conductivity is well established both theoretically and experimentally. Moreover, it can be adequately simulated e.g. using a resistor network model [3].

Therefore, an increasing focus in the ferroelectrics community is set on the realization of DW-based nanoelectronic devices. Recently, tunable DW switches have been reported for LNO thin films [4]. On the contrary, we report on tunable DW switches inside of 200-μm-thick LNO single crystals, relying purely on solid electrodes [5].

- [1] C. Godau et al. ACS Nano 11, 4816 (2017)
- [2] T. Kämpfe et al. Phys. Rev. B 8, 035314 (2014)
- [3] B. Wolba et al. Adv. Electron. Mater. 4, 1700242 (2018)
- [4] H. Lu et al. Adv. Mater. 1902890 (2019)
- [5] B. Kirbus et al. ACS Appl. Nano Mater. 2, 5787 (2019)

KFM 9.11 Wed 13:10 TOE 317

LiNbO₃: Model ferroelectric oxide or unique compound? — ●SIMONE SANNA³, ANDREAS KRAMPF¹, YURIY SUHAK², MIRCO KAI IMLAU¹, and HOLGER FRITZE² — ¹Universität Osnabrück — ²Technische Universität Clausthal — ³Justus-Liebig-Universität Gießen

After five decades of dedicated research, LiNbO₃ has become one of the most intensively investigated ferroelectrics. The effort of the ferroelectric community has led to unprecedented deep insight (and open issues) in the physical mechanisms that determine the materials properties. It is however still to be settled whether the knowledge collected on LiNbO₃ is generally valid, or strictly material specific. In order to answer this question, we investigate and compare (theoretically and experimentally) fundamentally different aspects of LiTaO₃ and LiNbO₃. First principles calculations reveal the existence of point defects in LiTaO₃ compatible with the polaronic picture established in LiNbO₃. Luminescence and absorption spectroscopy measurements show very similar dynamics and spectral features in LiNbO₃ and LiTaO₃. Electrical conductivity measurements demonstrate the existence of a low temperature and a high temperature regime for the two materials, from which rather similar activation energies can be extrapolated. The results suggest that the knowledge of the physical mechanisms gathered on LiNbO₃ can be transferred to other ferroelectric oxides such as LiTaO₃ and related solid solutions.