

DF 11: Small Polarons in LiNbO<sub>3</sub>

Small polarons determine a variety of optical and electrical features of lithiumniobate, LiNbO<sub>3</sub>, and can be used, e.g., to interpret the bulk photovoltaic effect on a microscopic level. In this session, excitation, lattice deformation, phonon-coupling, transport and recombination mechanisms of small free and bound polarons are discussed considering results of a broad range of modern experimental techniques as well as theoretical calculations and numerical modeling.

Organizer: Mirco Imlau (Universität Osnabrück)

Time: Wednesday 9:30–13:00

Location: EB 133C

DF 11.1 Wed 9:30 EB 133C

**Two-photon absorption in presence of small polaron formation in lithiumniobate** — ●MIRCO IMLAU, HOLGER BADORRECK, STEFAN NOLTE, FELIX FREYTAG, and JAVID SHIRDEL — Department of Physics, Osnabrueck University, D-49069 Osnabrueck

Two-photon absorption (TPA) appears in nominally undoped lithiumniobate with photon energies below the band gap energy of 3.8 eV and intensities of a few PW/m<sup>2</sup>; it is commonly studied by means of the *z*-scan technique. However, using ultrashort laser pulses with durations below 100 fs, the transmission signal is additionally affected by optically excited free carriers (FCA) and subsequently formed small polarons that have rise times of 50–100 fs (Nb<sub>Nb</sub><sup>4+</sup> [Qiu et al. *phys. stat. sol. c* **2**, 232 (2005)]) and below 400 fs (Nb<sub>Li</sub><sup>4+</sup> [Beyer et al. *Appl. Phys. B* **83**, 527 (2006)]). We applied the *z*-scan technique with 100 fs laser pulses at 2.5 eV to study the composed transmission loss that is given by TPA, FCA, and small polaron absorption. For data analysis, the well-known theory of Sheik-Bahae (*IEEE J. Quantum Electron.* **26**, 760 (1990)) is modified by contributions from absorption centers within the band gap [Shanmugavelu, *J. Appl. Phys.* **114**, 243103 (2013)]. The results of our analysis is experimentally verified by systematic *z*-scan studies using stretched pulses with durations up to 1.000 fs. We discuss the possibility to determine risetime and absorption cross section of optically excited hot carriers and present a refined model for the small polaron formation path in lithiumniobate. Financial support by the DFG (IM37/5-2, INST 190/165-1 FUGG) is gratefully acknowledged.

DF 11.2 Wed 9:50 EB 133C

**Density functional theory investigation of iron small bound polarons** — ●SIMONE SANNA and WOLF GERO SCHMIDT — Lehrstuhl für Theoretische Physik, Universität Paderborn

Iron doped lithium niobate is one of the most prominent photorefractive materials and is vastly employed, among others, for holographic data storage and optical filters. The dominant charge transport mechanism initiating photorefractive effect is the bulk photovoltaic effect, which is currently interpreted on the basis of Fe<sup>2+/3+</sup> small bound polarons [1]. In this work, we present a quantitative microscopic description of Fe<sup>2+/3+</sup> polaronic centers. Spin-polarized density functional theory with Hubbard corrections is employed to investigate the atomic structure around Fe<sub>Li</sub> centers. The theoretical models are compared with available experimental results [2,3], providing clear evidence for the polaronic distortion upon Fe<sup>2+/3+</sup> charge transition. The calculated atomic and electronic structures allow for a detailed consideration of the microscopic processes leading to the optical absorption, as well as the extrapolation of data that can be employed in the classic polaronic theory.

[1] O. F. Schirmer et al., *Phys. Rev. B* **83**, 165106 (2011)

[2] T. Vitova et al., *J. Appl. Phys.* **105**, 013524 (2009)

[3] A. Sanson et al., Submitted to *Phys. Rev. B* (2014)

DF 11.3 Wed 10:10 EB 133C

**Direct measurement of the Fe-polaron deformation in Fe:LiNbO<sub>3</sub>** — ●MARCO BAZZAN, ANDREA SANSON, ANNAMARIA ZALTRON, NICOLA ARGIOGLAS, and CINZIA SADA — Università di Padova, Padova, Italy

In this talk some recent experimental results on the structural characterization of the Fe small polarons in iron doped lithium niobate will be discussed.

On one hand, High Resolution X-rays Diffraction shows a bulk average strain appearing in the crystal as a consequence of the reduction process Fe<sup>3+</sup> + e → Fe<sup>2+</sup>. It will be shown that this effect has to be attributed to strain dipoles located at the Fe centers, with a magnitude dependent on the charge state of the Fe ion.

These findings are definitely confirmed using X-Ray Absorption Fine

Structure Spectroscopy at the Fe edge: upon oxidation or reduction the oxygen cage surrounding the Fe impurity is more or less compressed with respect to the regular LiNbO<sub>3</sub> structure.

Those results give a quantitative picture of the polaronic lattice deformation associated to the localization of an electronic charge at the Fe impurity.

DF 11.4 Wed 10:30 EB 133C

**Polarons trapped at Ti centres in LiNbO<sub>3</sub>** — ●GÁBOR CORRADI — Wigner Research Centre for Physics, Budapest, Hungary

Ti in LiNbO<sub>3</sub> is a well known dopant on Li-site changing the refractive index which can be used e.g. for producing waveguiding surface layers by Ti in-diffusion. The index change can be attributed to the existence of 3d-type Ti<sup>4+/3+</sup> donor polaron states in the gap which are similar to antisite Nb<sup>5+/4+</sup> polaron states with homologous 4d-type electron structure, the Ti level being only 0.11 eV deeper than the Nb<sup>5+/4+</sup> one. Mg co-doping can be used, similarly to the case of Nb(Li) antisites, also for the elimination of Ti(Li) centres, resulting in the appearance of Ti on Nb site. All four trapped-polaron d1 centres Ti(Li)<sup>3+</sup>, Ti(Nb)<sup>3+</sup>, Nb(Li)<sup>4+</sup>, and Nb(Nb)<sup>4+</sup> show absorption bands due to charge transfer to states inside the conduction band with slightly stronger local admixture for Ti than for Nb. As shown by the analysis of the EPR spectra, all four centres are subjected to Jahn-Teller distortion with increasing JT energy as one goes from Nb<sup>4+</sup> to Ti<sup>3+</sup> centres, or from Li to Nb substitution. The systematically shifted properties can be used for fine tuning polaronic effects by Ti and Mg doping and appropriate levels of reduction treatments.

### 30 min break with Posters (DF 1.5)

DF 11.5 Wed 11:20 EB 133C

**Polar niobate-nanocrystals: Synthesis and nonlinear optical analysis** — ●ANKE DÜTTMANN<sup>1</sup>, CHRISTIAN KIJATKIN<sup>1</sup>, KARSTEN KÖMPE<sup>2</sup>, JAVID SHIRDEL<sup>1</sup>, and MIRCO IMLAU<sup>1</sup> — <sup>1</sup>Dept. of Physics, Osnabrueck University, D-49069 Osnabrueck — <sup>2</sup>Institut. of Chemistry, Osnabrueck University, D-49076 Osnabrueck

Niobate-nanocrystals can be used as light emitters on the nanoscale by means of second harmonic generation (SHG). They are of interest as markers in high-resolution nonlinear optical microscopes for cell biology and tumor visualization as they offer a tremendous contrast in comparison to fluorescent markers. Although, however, the growth of KNbO<sub>3</sub> or LiNbO<sub>3</sub> single crystals is well established, almost nothing is known about respective nanocrystals synthesis with homogeneous size distribution and diameters in the range from 5–50 nm. In this contribution, we present our results on size-controlled synthesis of niobate-nanocrystals and their nonlinear optical analysis by means of SHG-microscopy. By choosing suitable oxidic precursors and their stabilization, we succeeded in a targeted synthesis of KNbO<sub>3</sub> and NaNbO<sub>3</sub> (20–80 nm). The dispersion properties of the SHG signal verify the polar nature of the nanocrystals and the possibility to induce a polarization wave in crystals with diameters smaller than the wavelength. Studies as a function of nanocrystal diameter follow the behavior expected from coupled wave theory such that signals detection of particles below 10 nm becomes possible. Financial support by the DFG (INST 190/165-1 FUGG) is gratefully acknowledged.

DF 11.6 Wed 11:20 EB 133C

**Light-induced polaron transport in 1, 2, and 3-dimensional systems** — ●CHRISTOPH MERSCHJANN<sup>1,2</sup> and STEFAN LOCHBRUNNER<sup>1</sup> — <sup>1</sup>Institut für Physik, Universität Rostock, D-18051 Rostock, Germany — <sup>2</sup>Freie Universität Berlin, D-14195 Berlin, Germany

Transient optical spectroscopy of functional materials is frequently used to extract important electronic quantities, such as the nature

of the photoexcitations (e.g., excitons or separated charge carriers, polarons, etc.), their concentrations, and mobilities. This is especially helpful for powders or microcrystalline samples which do not allow for macroscopic investigations like, e.g., standard conductivity measurements. The most prominent experimental techniques are pump-probe transient-absorption measurements and time-resolved fluorescence investigations. Very often, non-exponential decays of the transient spectra are observed, which are too frequently left unexplained or misinterpreted.

We apply a random-walk approach to model diffusion-type transports of light-induced charge carriers (e.g., small polarons). The obtained set of rate equations reveals distinct power-law behaviors for the decays of transient absorption and fluorescence. Typical phenomena like geminate and bimolecular recombination are clearly distinguishable. From the characteristics, one is able to directly deduce not only the dimensionality of the transport, but also mobilities and concentrations of the involved carriers.

DF 11.7 Wed 11:40 EB 133C

**Temperature dependence of polaron relaxation in iron-doped congruent lithium niobate: a Monte-Carlo simulation** — ●LAURENT GUILBERT and IMED MHAOUËCH — Laboratoire Matériaux Optiques, Photonique et Systèmes, Université de Lorraine et Supélec, 2, Rue E. Belin 57070 Metz (France)

The three elementary processes involved in the relaxation of bound polarons  $\text{NbLi}^{4+}$  in iron-doped lithium niobate (trapping at  $\text{Fe}^{3+}$  ions, hopping on Nb antisites and spontaneous conversion to the free polaron state  $\text{NbNb}^{4+}$ ) are simulated in a Monte-Carlo loop. Simulated decays match more or less the Kohlrausch-William-Watts law,  $\exp[-(t/\tau)^b]$ , similarly to experimental decays recorded by light-induced absorption (LIA) and reported in the literature. We focus here on the temperature dependence of the decays. As expected, the Arrhenius plots  $\log(\tau)$  or  $\log(\langle \tau \rangle)$  (average lifetime) versus  $1/T$  evidence three regimes. Their activation energies reflect, but are however not strictly equal to, the energy barriers of the elementary processes. As far as  $b$  is concerned, a low- $T$  limit is found. It corresponds to the trapping regime in which most of the bound polarons are trapped in a single hop. The limit value of  $b$  depends mainly on the  $\text{Fe}^{3+}$  trap concentration and on the orbital parameter  $c$  involved in the distance dependence of the trapping time in  $\exp(r/c)$ . The sharp increase of  $b(T)$  above 300 K, experimentally evidenced but poorly explained in previous models, now appears as a natural consequence of a trap size effect.

DF 11.8 Wed 12:00 EB 133C

**Temperature dependence of small polaron transport in Fe-doped lithium niobate** — ●SIMON MESSERSCHMIDT, FELIX FREYTAG, HOLGER BADORRECK, and MIRCO IMLAU — Department of Physics, Barbarastrasse 7, 49069 Osnabrück

Small bound  $\text{Nb}_{\text{Nb}}^{4+}$ ,  $\text{Nb}_{\text{Li}}^{4+}$  electron and  $\text{O}^-$  hole polarons are generated by single ns-laser pulses (2.5 eV) in Fe-doped lithiumniobate,  $\text{LiNbO}_3$  (source: Univ. Padova, Italy), thus, inducing a pronounced change of the macroscopic absorption  $\alpha_{ij}$ . Inspection of the temporal decay  $\alpha_{ij}(t)$  at photon energies characteristic for the specific polaron species allows to get insight to small polaron transport features and mutual recombination processes. Although, however, comprehensive studies on hopping processes at room and elevated temperature are available (270 – 400 K, Merschjann et al. Phys. Rev. Lett. **96**, 186404 (2006) and Refs. therein), studies of  $\alpha_{ij}(t)$  at low temperatures are missing. The temperature range between 20 – 300 K particularly is of inter-

est for transport studies as freezing of small polaron hopping accompanied by a predominance of tunneling is to be expected. We here present our systematic study in this temperature range by means of transient absorption spectroscopy and discuss our findings, i.e. pronounced changes in the recombination lifetime as well as of the shape of  $\alpha_{ij}(t)$ , using the Holstein model, Emin's polaron theory and established recombination models in presence of Fe-doping (Herth et al., Phys. Rev. B **71**, 125128 (2005)). Financial support by the DFG (IM37/5-2, INST 190/165-1 FUGG) is gratefully acknowledged.

DF 11.9 Wed 12:20 EB 133C

**Protons in doped  $\text{LiNbO}_3$  crystals resistant to photorefractive damage** — ●KRISZTIÁN LENGYEL, LÁSZLÓ KOVÁCS, VIKTOR SZALAY, and GÁBOR CORRADI — Wigner Research Centre for Physics, Budapest, Hungary

Protons are common impurities in  $\text{LiNbO}_3$  forming  $\text{OH}^-$  ions in the lattice. The characteristic spectrum in the 3400–3600  $\text{cm}^{-1}$  wavenumber range due to stretching vibrations of O–H is very sensitive to neighbouring defects (e.g. antisite  $\text{Nb}_{\text{Li}}$ , various dopants, polarons, etc). Studying the details of  $\text{OH}^-$  incorporation is also helpful for understanding the behavior of neighboring defects. Proton dynamics can be investigated by the SIESTA quantum chemical software package as already successfully demonstrated for undoped stoichiometric and congruent  $\text{LiNbO}_3$ . Dopants like Mg, Zn, Sc, In, Hf, Zr or Sn leading to photorefractive optical damage resistance (ODR ions) can change the polaronic behavior of  $\text{LiNbO}_3$  crystals as well. ODR-doping of  $\text{LiNbO}_3$  crystals above a threshold concentration also leads to substantially modified OH absorption bands which can be explained by assuming the existence of  $\text{ODR}_{\text{Nb}}^{n+}\text{-OH}$  defect complexes. In the present work this model will be discussed using the results of theoretical calculations of  $\text{OH}^-$  ions incorporated into ODR-doped  $\text{LiNbO}_3$  crystals. This project has been supported by the Hungarian Scientific Research Fund (OTKA) K83390.

DF 11.10 Wed 12:40 EB 133C

**Light induced changes in the  $\text{OH}^-$ -stretching bond by frequency-resolved femtosecond infrared absorption spectroscopy in congruent  $\text{LiNbO}_3$**  — ●FELIX FREYTAG, PHILLIP BOOKER, and MIRCO IMLAU — Department of Physics, Osnabrueck University, D-49069 Osnabrueck

The light induced generation of polarons in  $\text{LiNbO}_3$  is well studied by observing the absorption changes in the VIS/NIR spectral range. However, time-resolved measurements of the generation and relaxation of polarons in the MIR spectral range are missing.  $\text{LiNbO}_3$  crystals contain defects from  $\text{OH}^-$ -ions with a concentration of  $c_{\text{OH}^-} \approx 10^{18} \text{ cm}^{-3}$ . Due to protons coupling these ions attach to the  $\text{O}^{2-}$ -ions in the lattice at four different positions [Lengyel et al., Ferroelectrics **257**, 255 (2001)]. Polarons change the environment of  $\text{OH}^-$ -ions and therefore their vibrational resonance. Here we show data of a frequency-resolved femtosecond infrared spectroscopy experiment of the  $\text{OH}^-$ -stretching bond ( $\lambda \approx 2870 \text{ nm}$ ) in congruent  $\text{LiNbO}_3$  consisting of four components (due to slightly different positions in the crystal lattice). The transmission of mid-infrared pulses ( $\tau \approx 230 \text{ fs}$ ) is detected by two multichannel HgCdTe detectors as a function of a variable time delay to an intense VIS pump pulse of  $\tau \approx 100 \text{ fs}$  duration. We discuss the light-induced changes in the optical density of the  $\text{OH}^-$ -stretching bond. Financial support by the DFG (IM 37/5-2, INST 190/165-1 FUUG) is gratefully acknowledged.