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Editorial

New Trends in Lithium Niobate: From Bulk to Nanocrystals

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Abstract: The recent Special Issue on lithium niobate ($LiNbO_3$) is dedicated to Prof. Schirmer and his topics and contains nineteen papers, out of which seven review various aspects of intrinsic and extrinsic defects in single crystals, thin films, and powdered phases; six present brand-new results of basic research, including two papers on $Li(Nb,Ta)O_3$ mixed crystals; and the remaining six are related to various optical and/or thin film applications.

Keywords: lithium niobate; bulk crystals; thin films; nanocrystals

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This Special Issue was originally planned to celebrate the forthcoming 85th anniversary of Prof. Ortwin F. Schirmer, but his unexpected passing in 2020 made the occasion painfully more personal. A considerable number of his colleagues, students, and observers and followers of his fundamental lifework responded to the call, which resulted in a clarifying new synopsis of his topics.

1. Reviews on Defects in $LiNbO_3$

A general review on lithium niobate ($LiNbO_3$, LN) single crystals, as well as powders, which have been given a new emphasis, is presented in two parts by Sánchez-Dena et al. [1,2]. They discuss the crystal structure, the methods for the determination of chemical composition, the defect structures induced by the incorporation of hydroxyl ions, and the so-called optical damage resistant ions (e.g., Mg^{2+}), also discussing the origins of ferroelectricity, together with its possible association with ferromagnetism in $LiNbO_3$ doped with paramagnetic *3d* cations.

Extrinsic and intrinsic paramagnetic point defects in LN and lithium tantalate ($LiTaO_3$, LT) crystals have been reviewed by Grachev and Malovichko [3] based on electron paramagnetic resonance (EPR) and electron nuclear double resonance (ENDOR) studies. They focus on transition metal and rare-earth ions and give detailed information about the structures of impurity defects in LN crystals with various Li/Nb composition ratios (charge state, point symmetry, hyperfine interactions with neighboring nuclei, with corollaries for incorporation sites and charge compensation mechanisms).

A similar detailed review on defects in LN and LT crystals studied by nuclear methods has been presented by Kling and Marques [4]. They focus on ion beam methods under channeling conditions for the direct determination of the lattice site of dopants and intrinsic defects. Results of perturbed angular correlation measurements probing the local environment of dopants in the host lattice are also included in the analysis, yielding independent and complementary information.

The editors also initiated the clarification of the highly disputed issue of defects in the anionic sublattice of LN, but this only resulted in a repetition of earlier unconfirmed or refuted interpretations based on a superficial comparison disregarding the deep constitutional differences between LN and $SrTiO_3$ such as the extreme instability of the Li positions compared to the rigid Sr sublattice [5]. This forced the editors to present a review of their own on defect generation and annealing mechanisms in LN [6]. The oxygen sublattice of the LN bulk was demonstrated to play an essentially passive role, with oxygen loss and

Li_2O segregation mostly taking place in external or internal surface layers of a thickness of a few nanometers. Processes during thermo- and mechano-chemical treatments and irradiations of various types in LN were instead shown to be governed by as-grown and freshly generated Nb_{Li} antisite defects as traps for small polarons and bipolarons, while highly mobile lithium vacancies, also acting as hole traps, were shown to provide flexible charge compensation required for the stability of the defects just formed. The close relationship between $LiNbO_3$ and the Li battery materials $LiNb_3O_8$ and Li_3NbO_4 has also been pointed out.

A concise gap-filling review on the epitaxial growth of $LiNbO_3$ thin films has been published by Zivasatienraj et al. [7]. This review demonstrates that the highest crystalline quality obtainable by halide-based molecular beam epitaxy is comparable to that of bulk $LiNbO_3$ crystals while admitting that the slow growing rate presently limits most practical applications requiring substantial thicknesses. Research studies using the competing LNOI technology (LN On Insulator) based on ion-sliced LN films bonded on insulator substrates are addressed in the final part of this editorial.

2. Basic Research on Small Polarons and Optical, Electronic, and Acoustic Properties

Small polarons are the main topic of three recent research papers [8–10] published in this Special Issue, while the other papers are also at least indirectly concerned with transfers of polaronic charges or Li ions. Messerschmidt et al. [8] studied the laser-pulse-induced transient absorption of Nb^{4+}-type free polarons in heavily Mg-doped LN crystals. Their decay, attributed to polaron hopping leading to recombination with O^--type hole polarons, was found to be strongly temperature dependent between 45 K and 225 K. The Arrhenius-type behavior of the decay rate at high temperature and the non-Arrhenius one at low temperature could be coherently described by earlier theories of one of the co-authors (D. Emin), yielding good agreement for reasonable values of the hopping activation energy and the material's characteristic phonon frequency.

Using the same theoretical framework, Vittadello et al. [9] carried out Monte Carlo simulations of similar small-polaron-hopping processes for Fe-doped LN crystals, where, in addition to deep ${Fe_{Li}}^{3+}$ traps, shallow traps, also represented by ${Nb_{Li}}^{5+}$ antisite defects on Li sites, have to be taken into account. Decay regimes for fast direct trapping on Fe^{3+} for polarons generated in the vicinity of the dopant and slow hopping-governed trapping for others could be discerned, with the transition between both regimes depending on the concentrations of the traps and the temperature.

Schmidt et al. [10] further developed their first-principles calculations on intrinsic free and trapped-electron small-polaron and bipolaron states based on density-functional theory. Improved calculation of the electron–electron and electron–hole interactions allowed reliable comparisons with optical absorption spectra and other properties of various selected defect species. Special attention was given to symmetry-breaking distortions that further lower the total energy.

Luminescence of $LiNbO_3$ crystals single-doped with various rare-earth ions (Sm^{3+}, Dy^{3+} or Tb^{3+}) and $LiTaO_3$ doped only with Tb^{3+} was studied in a wide temperature range by Lisiecki et al. [11]. Following an initial temperature-independent stage, the luminescence lifetimes showed a steep decrease with increasing temperature with the onset at about 700, 600, and 150 K for Sm^{3+}, Dy^{3+}, and Tb^{3+} ions in LN, respectively, which was interpreted by a phenomenological temperature-dependent charge-transfer model. It was concluded that LN:Sm^{3+} is suitable as an optical sensor between 500–750 K, while LN:Dy^{3+} offers the highest sensitivity between 300–400 K.

Electrical conductivity and acoustic loss of single crystalline $Li(Nb,Ta)O_3$ solid solutions (LNT) were studied as a function of temperature and compared to those in LN and LT crystals by Suhak et al. [12]. The dominant transport mechanism in LNT in the range of 400–700 °C was identified as lithium-ion migration via lithium vacancies, as found in LN. It was also shown that the acoustic loss in LNT strongly increases at elevated temperatures, originating from a conductivity-related relaxation mechanism. LNT bulk acoustic resonators were found to exhibit significantly lower loss as compared to LN crystals.

Nanocrystalline $LiNb_{1-x}Ta_xO_3$ samples with x between 0 and 1 were synthesized by high-energy ball milling and subsequent high-temperature annealing by Vasylechko et al. [13]. The milling and annealing parameters were optimized to obtain single-phase LNT nanopowders checked by X-ray diffraction. In the Raman spectra of non-optimal milling and annealing runs, bands typical for the $Li(Nb,Ta)_3O_8$, Nb_2O_5, and/or Ta_2O_5 parasitic phases were observed. The Arrhenius-plots of the electrical conductivity measurements performed up to 820 °C revealed activation energies between 0.86 and 1.09 eV.

3. Applications of $LiNbO_3$

Among the contributions dealing with nonlinear optical applications of LN and LT in this Special Issue, papers using both traditional bulk crystals [14–16] and thin films on LNOI platform [17–19] can be found. All are concerned with internal electric fields resulting in nonlinear response, another topic of Prof. Schirmer.

In the paper by Zhao et al. [14], a laser-damage-resistant MgO-doped LN crystal is used as a nonlinear optical mirror to realize a high-power wavelength-tunable mode-locked picosecond $Yb:CaGdAlO_4$ laser. The tunable range was between 1039 and 1062 nm, the maximum output power reached at 1049 nm was 1.46 W, and the output pulse duration was about 8 ps, with a repetition rate and bandwidth of 115.5 MHz and 1.7 nm, respectively.

Due to its high second-order nonlinear-optical coefficients, high transparency, and large Pockels coefficients, LN is an excellent material for whispering gallery resonators (WGR), allowing for optical parametric oscillation and frequency comb generation. Minet et al. [15] studied the average strength of the electric field along the z-direction inside the region of the optical mode for different configurations and geometries of the LN WGR using the finite element method. Their simulations may be useful for the optimal design of similar resonators in future applications.

The generation of entangled photon pairs based on spontaneous parametric down-conversion was investigated theoretically and numerically by Kim et al. [16] in undoped and Mg-doped LN for non-poled and periodically poled cases. The spectral positions of the generated photon pairs fall into the mid-infrared range and are expected to find important applications for free-space quantum communications, spectroscopy, and high-sensitivity metrology.

Taking into account the enormous potential of LN thin films for integrated quantum photonics produced by the LNOI technology and comparable only to silicon-based photonics, progress in this field is of utmost interest. The contribution of Gainutdinov and Volk [17] addresses the problem of understanding and influencing the unique properties of nanodomains written by AFM-tip voltages in LN films formed on insulator structures where the electrical conductivity is essentially due to polaronic charges trapped by nanodomain walls.

Various nanometer-to-micrometer-scale imaging techniques required for optimizing performance parameters of periodically poled thin-film devices on LNOI platforms were compared by Reitzig et al. [18]. Piezoresponse force microscopy (PFM), second-harmonic generation (SHG), and Raman spectroscopy (RS) were found to monitor differently relevant sample properties. For standard imaging, SHG was found to be best-suited, in particular when investigating the domain poling process in x-cut thin films.

Modeling of a thin film device on lithium tantalate has been carried out by Yao et al. [19] by using a full-vectorial finite difference method. Design, simulation, analysis, and optimization of optical microring resonators on a lithium tantalate on insulator (LTOI) platform operating near 1.5 μm has been presented.

Conflicts of Interest: The authors declare no conflict of interest.

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