Editorial

Recent Progress in Lithium Niobate

Robert A. Jackson [1,*] and **Zsuzsanna Szaller [2,*]**

[1] Lennard-Jones Laboratories, School of Chemical and Physical Sciences, Keele University, Keele, Staffordshire ST5 5BG, UK

[2] Institute for Solid State Physics and Optics, Wigner Research Centre for Physics, Konkoly-Thege Miklós út 29-33, 1121 Budapest, Hungary

[*] Correspondence: r.a.jackson@keele.ac.uk (R.A.J.); szaller.zsuzsanna@wigner.hu (Z.S.)

check for updates

Abstract: This special issue features eight papers which cover the recent developments in research on lithium niobate. Papers are divided into three groups based on their topic.

1. Photorefractive Properties and Defect Structure

The photorefractive properties of lithium niobate (LN): Mo,Zn crystals with different doping concentrations were investigated in paper [1]. Zinc can shorten the response time and improve the photorefractive sensitivity of the LN:Mo,Zn crystal. Valence states of Mo ions were identified by XPS. Three valences (+6, +5, +4) were identified in the crystal and one (+6) in the residue. In the LN:Mo,Zn 7.2 crystal the Mo_{Nb}^+ and $Mo_{Li}^{3+/4+}$ defects served as the photorefractive centre for fast photorefraction. Potential material for fast response holographic storage are 7.2 mol% Zn and 0.5 mol% Mo co-doped $LiNbO_3$ crystals.

Vanadium and molybdenum ions are of interest in enhancing the photorefractive properties of $LiNbO_3$. Paper [2] presents a computer modelling study of V^{2+}, V^{3+}, V^{4+} and V^{5+} as well as Mo^{3+}, Mo^{4+}, Mo^{5+} and Mo^{6+} in $LiNbO_3$ using interatomic potentials. It was found that divalent (V^{2+}), trivalent (V^{3+}, Mo^{3+}) and tetravalent (V^{4+}) ions are incorporated at the Li and Nb sites through the self-compensation mechanism. However, the tetravalent (Mo^{4+}) ion is more favourably incorporated at the niobium site, compensated by an oxygen vacancy. The pentavalent ions (V^{5+}, Mo^{5+}) and hexavalent (Mo^{6+}) ions substitute Nb. No charge compensation is found for pentavalent ions, but there is charge compensation with a lithium vacancy for the Mo^{6+} ion.

2. $LiNbO_3$ Preparation Techniques

Lithium niobate nanocrystals were prepared by high-energy ball-milling of the residue of a Czochralski grown congruent single crystal which depend on different types of vials, milling parameters as described in paper [3]. Characterisation of LN nanocrystals and mechanochemical reactions of lithium niobate such as decomposition and the redox processes induced by high-energy ball-milling were studied. During the milling process, the formation of the $LiNb_3O_8$ phase taking place and the reaction can be described as

$$3 \; LiNbO_3 \rightarrow LiNb_3O_8 + Li_2O \tag{1}$$

where lithium oxide is a volatile by-product. The material undergoes partial reduction that leads to a balanced formation of bipolarons and polarons yielding a grey colour together with Li_2O segregation on the open surfaces.

In paper [4], determination of chemical composition between congruent and stoichiometric LiNbO$_3$ powders was worked out by four analytical techniques. Sample preparations were done by mechanosynthesis.

In paper [5], Ø2″ LN crystals doped with 0.3 mol% and 5 mol% Mg concentrations with high homogeneity were grown by the Bridgman method using a systematically optimised scheme with careful thermal field design. LN:Mg polycrystalline powders were synthesised by a wet chemistry method to avoid scattering particles and inclusions in the crystal. The homogeneity of LN:Mg crystals was also checked. The extraordinary refractive index gradient was as small as 2.5×10^{-5}/cm.

3. Applications of Lithium Niobate Waveguides

Titanium-diffused lithium niobate waveguide devices are suitable for electric-field detection since their sensors will not perturb the field to be measured. Paper [6] studied photonic electric-field sensors using a 1×2 Y-fed balanced-bridge Mach-Zehnder interferometer modulator composed of two complementary outputs and a 3 dB directional coupler based on the electro-optic effect and titanium diffused lithium niobate optical waveguides.

Proton-exchange (PE) is one of the waveguide fabricating techniques. In the research in paper [7], authors simulated and analysed a proton-exchanged E-O Mach-Zehnder interferometer in an x-cut lithium niobate on insulator, LNOI. Based on the full-vectorial finite-difference method, the single-mode conditions, mode size, and optical power distribution of PE waveguides were investigated. The bending losses the Y-branch structures were analysed and propagation losses of the PE waveguides with different separation distances between electrodes were simulated. The half-wave voltages of the devices were calculated using the finite difference beam propagation method (FD-BPM).

In paper [8] it was confirmed that the nano-domains in lithium niobate thin films are thermally unstable even at a temperature of the order of ~100 °C, which can be easily reached due to light absorption. The thermal instability of nano-domains could be very detrimental to practical applications, such as periodically poled lithium niobate (PPLN) microcavities, PPLN ridge waveguides, and ferroelectric domain memories. Thermal stability of nano-domains can be greatly improved when the lithium niobate thin film undergoes a pre-heat treatment before the fabrication of nano-domains. This thermal stability improvement is attributed to the generation of a space charge field during the pre-heat treatment, which is parallel to the spontaneous polarisation of nano-domains.

The wide range of topics covered by the papers in this special issue shows that the field of lithium niobate research is very much alive and that we can continue to expect new developments in this research area.

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

References

1. Xue, L.; Liu, H.; Zheng, D.; Saeed, S.; Wang, X.; Tian, T.; Zhu, L.; Kong, Y.; Liu, S.; Chen, S.; et al. The Photorefractive Response of Zn and Mo Codoped LiNbO$_3$ in the Visible Region. *Crystals* **2019**, *9*, 228. [CrossRef]
2. Araujo, R.; dos Santos Mattos, E.; Valerio, M.; Jackson, R. Computer Simulation of the Incorporation of V^{2+}, V^{3+}, V^{4+}, V^{5+} and Mo^{3+}, Mo^{4+}, Mo^{5+}, Mo^{6+} Dopants in LiNbO$_3$. *Crystals* **2020**, *10*, 457. [CrossRef]
3. Kocsor, L.; Péter, L.; Corradi, G.; Kis, Z.; Gubicza, J.; Kovács, L. Mechanochemical Reactions of Lithium Niobate Induced by High-Energy Ball-Milling. *Crystals* **2019**, *9*, 334. [CrossRef]
4. Sánchez-Dena, O.; Villagómez, C.; Fierro-Ruíz, C.; Padilla-Robles, A.; Farías, R.; Vigueras-Santiago, E.; Hernández-López, S.; Reyes-Esqueda, J. Determination of the Chemical Composition of Lithium Niobate Powders. *Crystals* **2019**, *9*, 340. [CrossRef]
5. Yan, X.; Tian, T.; Wang, M.; Shen, H.; Zhou, D.; Zhang, Y.; Xu, J. High Homogeneity of Magnesium Doped LiNbO$_3$ Crystals Grown by Bridgman Method. *Crystals* **2020**, *10*, 71. [CrossRef]

6.   Jung, H. An Integrated Photonic Electric-Field Sensor Utilizing a 1 × 2 YBB Mach-Zehnder Interferometric Modulator with a Titanium-Diffused Lithium Niobate Waveguide and a Dipole Patch Antenna. *Crystals* **2019**, *9*, 459. [CrossRef]

7.   Han, H.; Xiang, B.; Lin, T.; Chai, G.; Ruan, S. Design and Optimization of Proton Exchanged Integrated Electro-Optic Modulators in X-Cut Lithium Niobate Thin Film. *Crystals* **2019**, *9*, 549. [CrossRef]

8.   Jiao, Y.; Shao, Z.; Li, S.; Wang, X.; Bo, F.; Xu, J.; Zhang, G. Improvement on Thermal Stability of Nano-Domains in Lithium Niobate Thin Films. *Crystals* **2020**, *10*, 74. [CrossRef]