Piezoresponse force microscopy on proton exchanged LiNbO₃ layers

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Abstract: We use piezoresponse force microscopy for high-resolution investigations on proton exchanged LiNbO₃ surfaces. We also quantify the reduction of the d_{33} nonlinear coefficient induced by proton exchange in congruent LiNbO₃ substrates with and without Mg-doping.

OCIS codes: (130.3730) Lithium Niobate; (180.0180) Microscopy; (160.2260) Ferroelectrics.

1. Introduction

The demand to engineer nonlinear optical materials at the micro- and nano-scale has opened up to a new range of challenges in material science, encompassing also structuring technologies and characterization techniques. LiNbO₃ is one of the most widely used and versatile nonlinear optical materials due to several attractive properties, e.g., high nonlinear coefficients, wide transparency range, availability of substrates of large size and high homogeneity [1]. Moreover, the use of chemical patterning techniques, such as proton exchange, has developed over the past years into a mature and reliable LiNbO₃ waveguide technology.

Proton exchange (PE) consists of the substitution of Li^+ ions with protons at the surface of the crystal, typically implemented by exposing the latter to an acid solution, with mild heating (~ 200 °C) to enhance diffusion. The process yields different crystallographic phases of $H_xLi_{1-x}NbO_3$, depending on the value of x , i.e., the Li^+-H^+ substitution ratio. The so-called β -phase is the one with the highest substitution ratio ($x \sim 70\%$) and is known to exhibit almost vanishing nonlinear and electro-optic coefficients, typically quantified via optical techniques [2, 3]. The latter involve indirect assessments of the nonlinearity through measurements of conversion efficiencies in waveguide configurations or by surface second-harmonic generation in reflection geometries [4]. However, despite their widespread use and reliability, such techniques do not lend themselves to nanoscale investigations of the properties of the PE layers.

Piezoresponse Force Microscopy (PFM) is a high-resolution scanning probe microscopy technique developed in the past decade for the study, manipulation, and imaging of ferroelectric domains [5]. As such, it has gained widespread use also in the investigation of periodically poled LiNbO₃ at sub-micrometric scales [6, 7].

Here, we applied PFM for the local characterization of PE-LiNbO₃ layers. The technique provided a quick and non-destructive analysis of $H_xLi_{1-x}NbO_3$ surfaces with nanoscale resolution. Furthermore, when systematically applied to selectively proton exchanged substrates, it allowed quantitative estimates for the nonlinearity reduction associated with PE to be extracted. For β -phase PE on undoped congruent LiNbO₃, the PFM measurements consistently indicated a reduction in the d_{33} nonlinear piezoelectric coefficient amounting to 81% of the original (non-PE) value. The remarkably good agreement of these results with previous reports relying on completely different (optical) characterizations [3], confirms the reliability of the PFM method. Moreover, we extended the PFM analysis to 5 mol% Mg-doped LiNbO₃ substrates, selectively proton exchanged under the same conditions as the undoped crystals, and could estimate the nonlinearity reduction in this case to amount to 44%.

2. Sample preparation and PFM technique

The preparation of the samples for PFM experiments consisted of two steps. We started with commercially available 0.5mm-thick z -cut congruent LiNbO₃ substrates (undoped or doped with 5 mol% MgO). In order to selectively proton exchange the crystal surface, we deposited a periodic titanium mask with a period of 6.9 μm and a 50% duty cycle. Then, a selective PE was performed by dipping the crystals in pure benzoic acid for 24 hours at 200 °C, yielding a depth of exchange $d_{PE} \sim 2.3$ μm [8]. The 1D PE surface chemical grating had a final duty cycle of $\sim 80\%$, due to lateral diffusion of protons under the Ti stripes. After the PE step, the Ti masking layers were removed by dipping the samples in hydrofluoric acid for a few seconds. In order to evaluate the influence of the polarization of the substrate, we prepared several samples, periodically exchanged on either $+z$ or on $-z$. The PE grating geometry is illustrated in Fig. 1a. In the top view (x - y plane) of each crystal (sampled by PFM) one can distinguish between two areas, namely: bare LiNbO₃ (grey regions in Fig.1a) and PE- LiNbO₃ (blue regions).

Fig. 1 *a)* 3D sketch of the 1D periodically proton exchanged substrates (blue regions). *b)* Top view (x - y plane) of the sample; detail of the area between the openings of the original titanium mask. *c)* and *d)* high resolution images of topographic structures due to direct proton exchange and the lateral diffusion under the titanium mask.

In a PFM system, a conductive cantilever (sketched on top of the sample in Fig. 1a) is usually coated with Ti-Pt and electrically connected to an external voltage power supply whereas the back side of the sample is grounded. The conductive tip is then biased with an AC voltage and the electromechanical response of the material is measured as the first harmonic component of the bias-induced tip deflection [6]. A piezoelectric crystal such as LiNbO₃ produces an electric charge when a mechanical stress is applied to it (*direct piezoelectric effect*). Conversely, the application of an electric field (as in Fig. 1) results in a mechanical deformation of the crystal (*inverse piezoelectric effect*), which can be recorded by the PFM system. The piezoresponse of the sample, due to the inverse piezoelectric effect, can be expressed as below:

$$S_{yz} = \sum_x d_{xyz} E_x$$

where S_{yz} is the deformation tensor, d_{xyz} is the piezoelectric tensor, whereas E_x signal is the electric field applied through the tip. Since we used z -cut crystals and the voltage was applied orthogonal to the surface via the tip, we can rewrite the previous equation as follows:

$$S_z = \alpha \cdot d_{33} E_z \propto \alpha \cdot d_{33} V_{AC} \quad (1)$$

where S_z is the signal obtained from the PFM system, α is a constant dependent on the cantilever, the calibration of the setup, d_{33} is the relevant nonlinear coefficient, and E_z is the electric field applied onto the sample. By measuring S_z as a function of the applied voltage (V_{AC}) in the experiments and then using Eq. 1, we characterized the behavior of the crystal and extrapolated the effect of PE on the optical nonlinearity (d_{33}). The scanning probe technique allowed us to perform such an analysis with extremely high spatial resolutions, i.e., down to the nanoscale (examples in Fig. 1b).

3. Results

On non-PE surfaces, the PFM experiments showed consistently the same value of d_{33} , regardless of the substrate polarity ($+z$ or $-z$). On the other hand, we could clearly observe a nonlinearity reduction associated to proton exchange, both for undoped and for Mg-doped substrates.

According to Eq. 1, the piezoresponse recorded by the cantilever (amplitude and phase) provides information on both the amplitude and the sign of the optical nonlinear coefficient d_{33} . For a quantitative assessment of the nonlinearity reduction in the PE regions, we performed a systematic analysis of the piezoresponse on the crystals as a function of the AC bias signal. Fig. 2a summarizes the results of one of such measurement, in which the cantilever was left scanning on the same line across periodically PE on the LiNbO₃ surface (along the x axis, cf Fig. 1 – i.e., slow axis scan disabled), while the applied AC bias was progressively raised in the range 0-10V by steps of 1V. The 2D map of Fig. 2a shows the signal obtained from the PFM setup (accounting for the deformation of the material, S_z) as a function of the scanning coordinate (x) and of the AC bias for a set of measurements across two PE stripes (darker vertical stripes).

From PFM scans such as the one reported in Fig. 2a, we could then reliably extrapolate the reduction of the nonlinear coefficient associated with the PE chemical treatment. This is further illustrated by the data plots in Fig. 2b and 2c, concerning CLN and Mg:CLN substrates, respectively.

Fig. 2 a) 2D map of the piezoresponse analysis of the Mg:CLN. **b)** and **c)** show a scan profile of image a) in the case of LiNbO₃ and MgO:LiNbO₃ respectively. The blue lines account for the piezoresponse of the virgin crystals whereas the green ones for the reduced-signal PE regions. The d_{33} coefficient is the first order derivative of the linear fitting.

Fig. 2b shows the variation of the recorded piezoresponse with the AC bias at two different locations (x-positions, highlighted by blue and green lines in Fig. 2a) on a CLN sample. The blue dots refer to measurements on a non-exchanged location (CLN), while the green ones to a PE location (PE:CLN). On the same graph, we plot also linear fits (solid lines) to the experimental data. Both the CLN and PE:CLN piezoresponse data exhibit a linear trend as function of the AC bias. The values of the d_{33} coefficients for PE versus non-PE regions can be extracted from the slope of the linear fits. The data of Fig. 2b yield: $d_{33}^{\text{PE:CLN}} = 0.81\% d_{33}^{\text{CLN}}$. The 81% nonlinearity reduction estimated by our PFM method closely matches previous reports (84%), obtained by nonlinear optical techniques [3].

By applying a similar procedure to the piezoresponse data from MgO:CLN substrates (Fig. 2c), we estimated the reduction in the d_{33} coefficient in the latter to amount to 44%. We are currently investigating, with complementary optical measurements, the origin of the observed difference between PE:MgO:CLN and PE:CLN, which may be ascribed to a different dynamics of the PE process on MgO-doped substrates.

3. Conclusions and acknowledgements

We characterized the effect of the proton exchange on the piezoelectric properties of lithium niobate. We were able to locally determine the nonlinearity reduction of the crystal and then directly compare the effect of the proton exchange on undoped and 5 mol% MgO-doped CLN. The percentage reduction of the nonlinear coefficient due to proton exchange was estimated to be 81% and 44% for the two cases, respectively. Our estimate for d_{33} in undoped CLN compares well with previous reports found in the literature (based on optical techniques), confirming the reliability of the proposed PFM technique to locally probe the nonlinear properties of PE layers. The results open the route to a new method for nanoscale characterizations of a key technological process (PE) for LiNbO₃ integrated optical devices.

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