

Spatially resolved second-harmonic-generation investigations of proton-induced refractive-index changes in LiNbO₃

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Doping profiles generated by electric-field-assisted proton diffusion in LiNbO₃ bulk material are investigated, spatially resolved by absorption and by second-harmonic-generation measurements. The results allow a direct correlation of the refractive-index changes with the local proton density. It is shown that protons are the only mobile ions under the experimental conditions applied (600 °C, 100 V/cm), whereas lithium ions do not move under these conditions. Similar results were obtained for samples doped with deuterium.

I. INTRODUCTION

Impurities like hydrogen or 3d ions play an important role in LiNbO₃ crystals for their piezo- and electro-optical properties. The behavior of hydrogen in LiNbO₃ has been the subject of a large number of investigations, mainly in connection with optical applications of this material. It was found that treatment at about 700 °C for ½ h with an applied electric field of 250 V/cm decreases the susceptibility to laser-induced refractive-index changes ("optical damage") in LiNbO₃, as well as in LiTaO₃.¹ Smith *et al.*² suggested that the impurity ions that diffuse under the influence of the electric field and cause the improved radiation resistance are protons. The presence of hydrogen in LiNbO₃ can be detected by measuring the IR-absorption of the OH stretching vibration at 3485 cm⁻¹.³ A detailed description of the spectroscopic parameters of the OH and OD oscillators in LiNbO₃ is given in Ref. 4.

OH-absorption measurements were also used to investigate the role of protons during the thermal fixing process of volume-phase holograms in LiNbO₃.⁵ It was concluded that electric space-charge fields built up during the writing process of holograms are compensated by proton migration at temperatures of about 150 °C, thereby stabilizing the holograms against erasure during readout at room temperature.⁶ Refractive-index changes due to an increase of the hydrogen content in LiNbO₃ were also of interest concerning waveguide applications.⁷ Optical waveguides in LiNbO₃ surface layers could be realized by proton exchange during a treatment in benzoic acid at 200 °C.^{8,9} In this case a large amount of protons diffuses into the surface layer, partially replacing Li ions.

The absorption coefficient of the OH stretching vibration goes up to values of about 1500 cm⁻¹.¹⁰ Such a strong incorporation of hydrogen should also contribute to the refractive-index changes of about 0.12 in the surface layer¹¹ achieved by this treatment. The hydrogen content in LiNbO₃ bulk material grown with the Czochralski method in air is relatively small ($\alpha_{\text{OH}} < 1 \text{ cm}^{-1}$) and variations of the refractive indices, especially of the extraordinary one, are mainly determined by the Li:Nb ratio in the crystal.¹² Up to now no quantitative analysis of the influence of additional proton doping on the refractive indices in LiNbO₃ has been carried out.

II. EXPERIMENT

Methods to measure variations of the refractive indices include optical interferometry and optical second-harmonic generation (SHG), using the possibility of noncritical phase matching for Nd-YAG laser wavelengths in LiNbO₃ (YAG denotes yttrium aluminum garnet).^{13,14} By interferometry spatial changes in both the ordinary and extraordinary indices of refraction can be measured independently¹⁵; SHG can be used as a highly accurate method to determine small changes in their difference measuring the birefringence responsible for phase matching. The sensitivity for refractive-index and composition changes depends on the accuracy of the measured phase-matching temperature¹⁵:

$$n_e = -9.12 \times 10^{-5} T_{\text{PM}} + 2.2077, \quad (1)$$

$$x_c = 7.14 \times 10^{-3} T_{\text{PM}} + 48.571 \quad (2)$$

(x_c is the Li₂O mole percentage in the crystal and T_{PM} is the phase-matching temperature in °C).

Spatially resolved second-harmonic generation (SRSHG) has been used earlier to check the homogeneity and composition of LiNbO₃ samples and to investigate refractive-index profiles, for instance, generated by Li out-diffusion.¹⁶ In this work we measured interferometrically which of the refractive indices is changed by additional proton doping, and SRSHG was used to determine the size of the refractive-index change. The hydrogen content of the samples was increased by annealing them under an applied electric field in a humid atmosphere (air or oxygen). Since reports stated a Li-ion mobility under the influence of an electric field at temperatures of 50–300 °C,¹⁷ we had to find a way to distinguish whether only protons or Li ions also are mobile under our experimental conditions. This was achieved by a combination of the SRSHG method with IR-absorption measurements together with appropriate annealing steps.

The absorption measurements of the OH-stretching vibration were carried out with a Perkin-Elmer IR spectrometer moving the samples perpendicular to a fixed slit of 1 mm width. For the SRSHG measurements the second-harmonic signal generated by the crystal from an expanded Nd-YAG laser beam was detected, spatially resolved by means of an optical multichannel analyzer (Fig. 1). The sample tem-

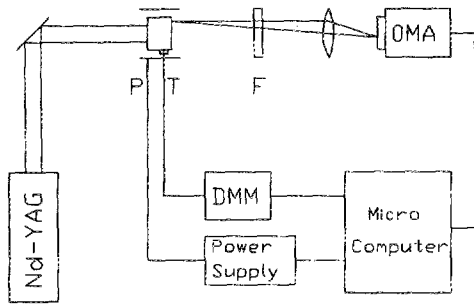


FIG. 1. Experimental setup for SRSHG. P, Peltier cooling; T, thermocouple; F, optical filter for separating the generated harmonic light from the fundamental wave; DMM, digital multimeter; OMA, optical multichannel analyzer. The Nd-YAG laser was driven in pulsed mode with a peak power of about 5 kW and a repetition rate of 1 kHz.

perature was controlled by Peltier cooling. Interferometric measurements were done in a Mach-Zehnder interferometer.

For our measurements we used congruent LiNbO_3 samples. To increase the hydrogen content of the samples, they were heated to about 650°C in a humid atmosphere with an applied electric field of 100 V/cm . The samples were held at this temperature for $\frac{1}{2}$ h.

III. RESULTS AND DISCUSSION

A. Proton doping

During the heating and cooling process, temperature-dependent conductivity measurements were carried out to determine the activation energy for the ionic charge transport (Fig. 2). The measured value of 1.08 eV agrees with the results of Ref. 10 for proton diffusion in LiNbO_3 : H waveguides.

The field treatment leads to an increase of the proton concentration at the anode and alters the refractive indices and therefore the phase-matching conditions. A typical phase-matching temperature (PMT) profile as measured by spatially resolved second-harmonic generation (SRSHG) is shown in Fig. 3 (dashed line). After the field treatment the sample was cut into two pieces, separating the part with both the main amount of protons and the decreased PMT from the rest. Both pieces were annealed at 850°C in a dry atmosphere for about 3 h. Under these annealing conditions the

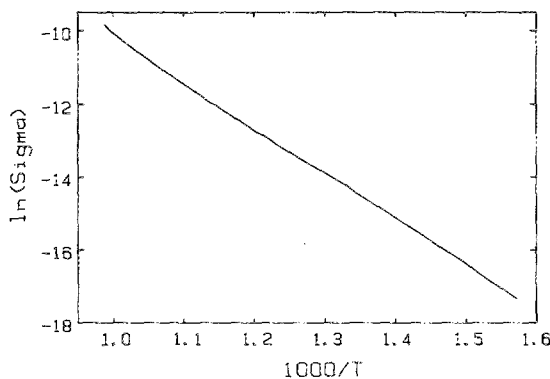


FIG. 2. Arrhenius plot of the ionic conductivity in LiNbO_3 during field doping with protons (data taken during cooling).

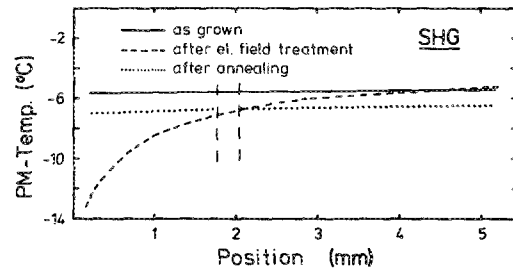


FIG. 3. Spatially resolved measurement of the phase-matching temperature in LiNbO_3 (solid line, as grown; dashed line, after field-assisted proton diffusion; dotted line, after cutting at the vertical dashed lines and annealing the sample at 850°C in a dry atmosphere).

additional hydrogen leaves the crystal completely. This was checked by absorption measurements. With a very small and equal hydrogen concentration in both pieces established, any remaining variations of the PMT could only be due to field-induced concentration changes of Li ions. However, after annealing, both pieces did show the same constant phase-matching temperature, nearly identical to that of the sample in the as-grown state. This means that the local Li:Nb ratio was not changed by the above treatments. From this fact it can be concluded that the measured PMT profile is due to a variation of the proton concentration only and that only protons are mobile under our experimental conditions.

To determine the refractive-index change induced by protons, the PMT profiles from SRSHG measurements were correlated with spatially resolved measurements of the OH absorption (Fig. 4). Figure 5 shows the variation of the phase-matching temperature with the OH absorption coefficient α (peak value in cm^{-1}) for several samples with different proton concentration profiles. A linear approximation yields a slope of

$$\Delta T_{\text{PM}} / \Delta \alpha_{\text{H}} = 0.5 \pm 0.1 \text{ K cm.} \quad (3)$$

The additional interferometric measurements showed that a shift of the interference pattern in samples with high

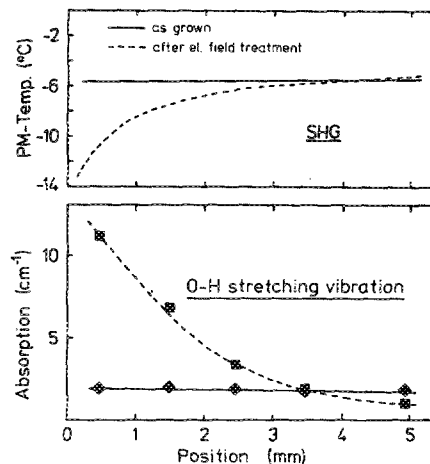


FIG. 4. Spatially resolved measurements of the phase-matching temperature (upper) and absorption in the OH-stretching vibration line (lower) before (solid line) and after field doping with protons (dashed line).

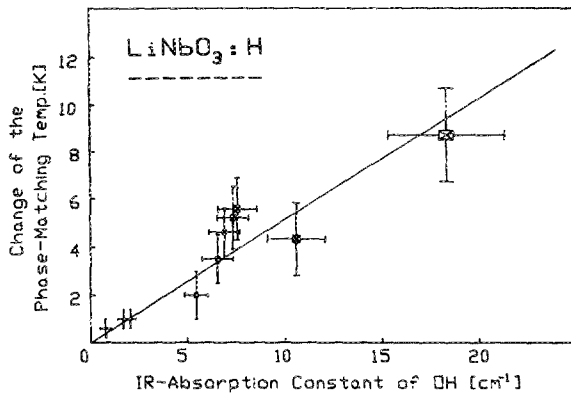


FIG. 5. Change of the phase-matching temperature vs the IR-absorption constant of the OH-stretching vibration from different LiNbO₃ samples doped with protons.

proton concentration near the anode occurs only for extraordinary light polarization. This means that only the extraordinary index is influenced by proton doping. Using Eq. (1) to correlate the change, the extraordinary index with the change of the phase-matching temperature leads to the proton-induced refractive-index change in LiNbO₃:

$$\Delta n_e / \Delta \alpha_H = (4.7 \pm 1.0) \times 10^{-5} \text{ cm.} \quad (4)$$

For a comparison of the proton-induced refractive-index change with those induced by other defects, the refractive-index change per proton concentration rather than that per absorption strength must be calculated. To achieve this, the absorption strength can be converted to concentration values using the integral absorption and the oscillator strength for the respective ion. With the experimental results of Bollmann, Schlothauer, and Zogal¹⁸ for LiNbO₃ which are in good agreement with results for KTaO₃,¹⁹ we derived the refractive-index change per proton concentration to be

$$\Delta n_e / \Delta c_H = (1.6 \pm 0.8) \times 10^{-24} \text{ cm}^3 \quad (5)$$

(c_H is the number of protons per cm³).

To get a rough estimate for the magnitude, this value can be compared with the corresponding value for Li, computed from Eqs. (1) and (2), which is $3.4 \times 10^{-23} \text{ cm}^3$. Both values apply only for small doping concentrations in the case of hydrogen and small concentration changes in the case of Li, respectively. Very high concentration changes cause shifts in the refractive indices that cannot be extrapolated from these values. For proton-exchanged optical waveguides, a deficit of Li atoms of about $1.5 \times 10^{22} \text{ cm}^{-3}$ and a refractive-index change of 0.12 in the surface layer were reported.²⁰ An extrapolation with the "small variation value" for Li would yield a refractive-index change three times higher. This indicates that the dependence between Li concentration and the refractive-index change should not be linear any longer for stronger variations of the Li concentration. Assuming a similar relation between the magnitudes of the refractive-index changes caused by Li and H as for small concentration changes, the direct influence of hydrogen on the refractive-index shift in the proton-exchanged surface layer of an optical waveguide would be negligible compared to that of Li.

B. Deuterium doping

Treatments with an applied electric field of LiNbO₃ crystals similar to the hydrogen doping described above were also carried out in a D₂O instead of H₂O vapor atmosphere. The resulting deuterium-doping profiles were detected by measuring the IR absorption of the OD stretching vibration at about 2560 cm⁻¹ and the shift of the PMT due to the spatially varying deuterium concentration. The measured activation energies for deuterium migration were equal to those for protons within the experimental uncertainty, which was estimated to be 0.05 eV. Plotting the change of the PMT versus the change of the IR absorption yields a slope slightly higher than that for protons:

$$\Delta T_{PM} / \Delta \alpha_D = 0.7 \pm 0.1 \text{ K cm.} \quad (6)$$

Again, the refractive-index change per absorption strength can be calculated:

$$\Delta n_e / \Delta \alpha_D = (6.6 \pm 1.0) \times 10^{-5} \text{ cm.} \quad (7)$$

Taking the ratio for the oscillator strengths of hydrogen and deuterium from Ref. 21, the refractive-index change per deuterium concentration can be derived:

$$\Delta n_e / \Delta c_D = (1.8 \pm 0.9) \times 10^{-24} \text{ cm}^3 \quad (8)$$

(c_D is the number of deuterons per cm³). Within the experimental error, this value corresponds to that for protons.

IV. CONCLUSION

Electric field doping experiments with protons and deuterons in LiNbO₃ show that under our experimental conditions Li ions are immobile and only protons or deuterons move under the influence of an electric field. The proton and deuterium-induced refractive-index changes were measured to be 1.6×10^{-23} and $1.8 \times 10^{-24} \text{ cm}^3$, respectively. These values show that the influence of protons and deuterons on the extraordinary index of refraction is only about 5% compared to that of Li. This seems to indicate that the local symmetry (which, among other parameters, determines the birefringence) is much more changed by a variation of the Li concentration than by doping with hydrogen or deuterium.

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