

# EFFECT OF THE ANNEALING PROCESS ON ACTIVE PROPERTIES OF PROTON-EXCHANGED OPTICAL WAVEGUIDES IN ERBIUM-DOPED LITHIUM NIOBATE

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*We report about our study of the annealing effect on the resultant chemical composition of the APE (Annealed Proton Exchange) layers and their optical properties, with emphasis on their potential active function. The samples were annealed at various conditions and characterised by a number of nuclear analytic methods (NDP; ERDA; HIERDA) to investigate concentration profiles of the exchanged ions. The content of OH groups, which are undesirable in the active waveguiding layers owing to their effect of erbium excited state lifetimes shortening, was studied by IR absorption spectrometry. The waveguiding properties (number of guided modes, refractive index vs. depth profile) were measured by mode spectroscopy at 632.8 nm. We found out that hydrogen introduced to the surface layers of LiNbO<sub>3</sub> by PE (Proton Exchange) moves deeper into the substrate during A (Annealing), lowering thus total refractive index increment. Consequently, the crystallographic phase of the exchanged layers changes towards the  $\alpha$ -phase. The lowest amounts of OH groups were found when highest annealing temperatures were used; however, a limitation exists there as temperatures above 400°C cause degradation of the waveguiding properties.*

## INTRODUCTION

Among optical crystals, lithium niobate (LN) is considered as one of the most popular materials for construction of various devices, as couplers, modulators, switches and oscillators or tuneable lasers. In the past few years a considerable interest has grown about the possibility to realize active optical devices based on erbium doped lithium niobate (Er:LN), which would allow integration of both passive and active function of the component on the same substrate [1].

The use of proton exchanged (PE) or annealed proton exchanged (APE) waveguides in lithium niobate has been known for some time (e.g. [2 - 6] and references therein). Annealed Proton Exchange is commonly used two-step technique of waveguide fabrication in this material: firstly, ion exchange (PE)  $H^+ \leftrightarrow Li^+$  occurs, when the crystalline wafers (X- or Z- crystallographic cut) are immersed into the proton source, in our case melt of environmental friendly adipic acid. Secondly, the post-exchange annealing (A), i.e. heating of the as-exchanged samples at desired conditions, follows to improve stability and optical properties of the fabricated waveguides.

The APE waveguides in Er-doped lithium niobate are extremely useful for fabrication of high-refractive-index waveguides or for use as polarizers, where advantage is made of the fact, that the PE and APE waveguides will only guide radiation of one polarization depending on the orientation of the substrate wafer (X or Z-cuts). However, presence of the OH groups arising from the hydrogen ions introduced into the waveguiding layer by the proton exchange has caused so far serious problems in shortening the  $Er^{3+}$  excited states lifetimes. Here we present our study of exploiting one of the fabrication steps - the annealing - to lower the amount of the undesired OH groups in the waveguiding region without damaging the waveguiding properties. The results of the study of the planar guides were then applied to design fabrication conditions for obtaining single-mode channel waveguides suitable for coupling to optical fibres.

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## EXPERIMENTAL

X and Z crystallographic cuts of erbium-doped (5000 ppm) congruent LiNbO<sub>3</sub> were used in the experiments; the polished substrates were provided by AVTEX, Czech Republic. The one side polished wafers were pre-cleaned in acetone and the ion exchange process occurred after their immersing into reaction melt, which was buffered proton source (adipic acid with addition of lithium carbonate).

Experimental conditions of proton exchange (PE) were: temperature 213°C and duration 1–3 hrs. Residuals of the reaction melt were removed after the reaction by immersing the samples into distilled water and isopropyl alcohol. The as-exchanged samples were stabilized by annealing in air at 300, 350, 375 and 400°C while duration of heating varied from 0.5 to 50 hrs.

The optical (waveguiding) properties of the fabricated samples, i.e. number and spectra of the guided extraordinary modes, were characterized by mode spectroscopy at 632.8 nm (prism coupling set-up). The refractive index vs. depth profiles were reconstructed from the mode spectra by means of inverse WKB (Wentzel-Kramers-Brillouin) approximation.

Changes in the chemical composition of the surface layers were determined by a number of nuclear analytical methods. Neutron Depth Profiling (NDP) was used to study concentration depth profiles of lithium ions (<sup>6</sup>Li isotope) in the waveguiding region; the measurement was performed in the cooperation with the Institute of Nuclear Physics of Czech Academy of Sciences. ERDA (Elastic Recoil Detection Analysis) and HIERDA (High Energy Ion Elastic Recoil Detection Analysis) were employed to obtain information on hydrogen and simultaneous hydrogen-lithium concentration profiles, respectively. ERDA analysis was carried out at electrostatic accelerator in the Nuclear Physics Institute in Rez. The measurement was performed in a glancing geometry using alpha particle beam (2.68 MeV); the recoiled protons were registered under the angle of 300 with a surface barrier detector covered with 12 μm thick Mylar stopping foil. The obtained ERDA spectra were evaluated using the computer code SIMNRA [7]. HIERDA was applied using 30 MeV Cl-ions from the 5 MV Tandem accelerator of the Research Center Rossendorf [8]. The scattered ions and the light recoils (without hydrogen) were detected by a Bragg Ionisation Chamber located under a scattering angle of 30°, the hydrogen recoils were detected with a Si-detector covered by a 18 μm thick Al foil to stop all other recoils and scattered ions. The energy spectra of separated elements were converted into concentration versus depth profiles by means of a computer code [9] using the stopping power data from Ziegler et al. [10].

The relative amounts of the OH groups in the PE and APE layers were determined by FT-IR spectrometer BRUKER IFS66/V with microscope HYPERION (magnification 15×). The spectra in the region of 4000

to 600 cm<sup>-1</sup> were collected in the reflection mode (the total number of scans is 2048), modified by Kramers-Krönig correction and converted into KMU (Kubelka-Munk units).

## RESULTS AND DISCUSSION

### Optical properties of the fabricated layers

Firstly, effect of the annealing on the waveguiding function of the samples was investigated. The large set of the samples annealed at different conditions was fabricated. We observed similar effect of increasing time of the annealing as typical for prolonged duration of proton exchange: both, depth of the fabricated optical layers and number of guided modes increased. Shape of the refractive index vs. depth profiles changed from the step-like towards the graded ones (see figure 1) and consequently the total refractive index increment decreased with longer times of the annealing.

Temperature of the annealing affected the refractive index vs. depth dependencies in a similar way; shape of the profiles changed towards the graded ones after annealing of the samples at 350–400°C. When using higher temperatures (above 400°C) the waveguiding function of the fabricated APE layers was degraded.

In the case of channel optical waveguides we observed strong limitation of the annealing conditions. Temperature of A should not exceed 375°C and duration of A should be 30 hrs at most to preserve waveguiding properties of the samples (i.e. to form single-mode channels at 1500 nm). When temperature and/or duration of the annealing were exceeded the total refractive index increment decreased to such extent that the APE layer was not able to support any mode.

### Chemical composition of the optical layers

When searching into the role of the exchanged ions in formation of the waveguiding layers we found out that the resultant optical properties are mostly dependent on the hydrogen ions distribution and that protons migration in the matrix is almost unaffected by lithium ions migration. This fact can be well demonstrated by the following series of figures (figure 2a, b), where the example of behaviour of the PE samples that were annealed at the lowest temperature is presented. When comparing hydrogen distribution in these samples, the significant difference was observed: surface hydrogen concentration after 50 hrs of A decreased to 7 atomic % while the concentration of protons after the shortest (0.5 hr) annealing was 19 atomic % (the hydrogen ions diffused deeper into the substrate). At the same time the optical layers were significantly deepened as showed in figure 2a. However, the lithium ions distribution in these samples was almost unchanged (see figure 2b).

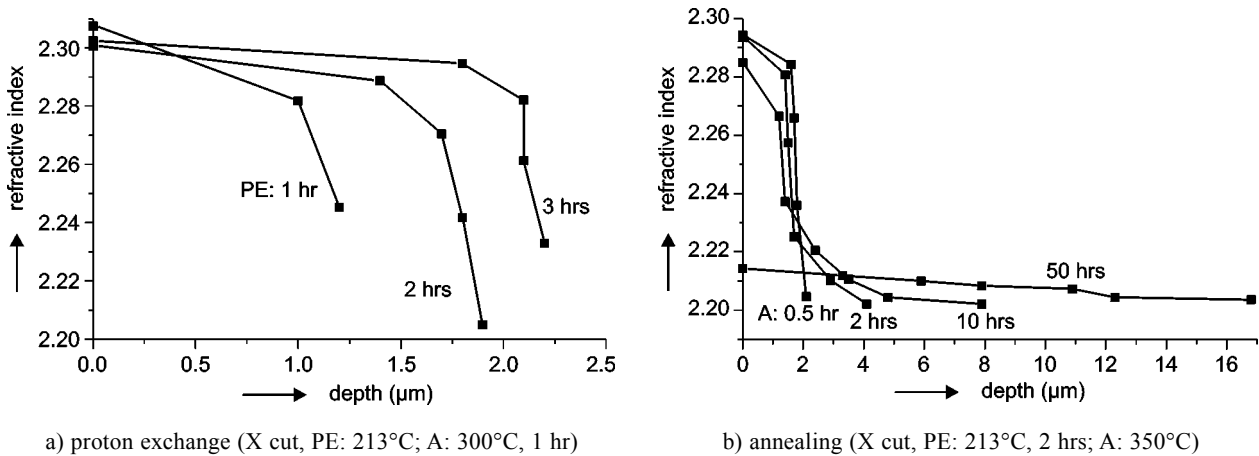


Figure 1. Effect of duration of PE and A on the optical properties of the fabricated layers.

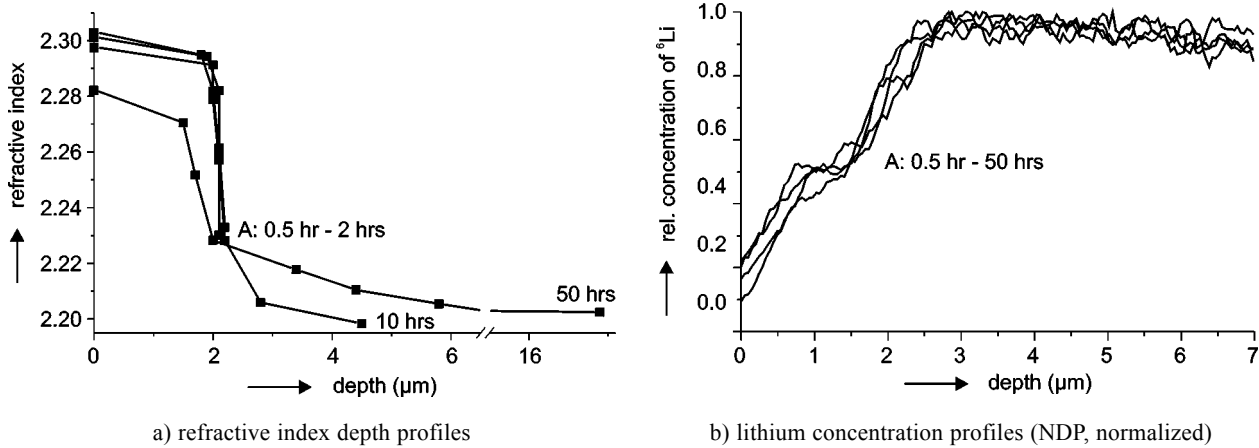


Figure 2. Effect of the annealing process on the optical properties and lithium distribution in the samples. (X cut, PE: 213°C, 3 hrs; A: 300°C).

Results of ERDA and NDP measurement showed progression of the proton and lithium concentration profiles (table 1 and figure 3), respectively, during the annealing at higher temperatures (effect is very similar within 350–400°C region). It is clear that this time the profiles were in a good agreement with the ion exchange process conception. Lithium ions depletion caused by the first fabrication step (PE) was being levelled and the surface depletion was only approx. 60–40 % of the bulk value compared with depletion of 90–80 % observed in the case of annealing at the lower temperature.

It is also evident from both types of the concentration profiles that optical layers in various crystallographic phases were formed. The distribution of the exchanged ions in the "short time annealed" and "long time annealed" samples exhibited strong difference (also observed in collected IR spectra - see below); therefore the existence of two different crystallographic phases is a reasonable explanation.

The HIERDA measurement gave detailed information on behaviour of the particular crystallographic cuts of the substrates, providing the simultaneous concentration profiles of  $\text{Li}^+$  and  $\text{H}^+$  ions in the thin surface APE layers (in lithium niobate up to 500 nm, quantitatively equal to ERDA results). Figure 4 shows that at the beginning, i.e. after only a short annealing, concentration profiles of the exchanged ions in the particular cuts differ minimally (at the same level as the measurement error); for comparison there is also given concentration profile of the sample annealed for 10 hrs at 350°C. Effect of the crystallographic cuts was significant when comparing long time annealed samples - the surface hydrogen concentration decreased more quickly in the case of the X cuts (indicating faster migration through the crystal matrix). Surprisingly, lithium distribution in the APE layers on the other hand changed more excessively in the case of the Z cuts. This interesting phenomenon will be further investigated.

FT-IR Spectrometry (O-H bonding)

Small amounts of hydrogen ions (i.e. OH groups) are initially present in the surface of the virgin crystals (up to approx. 50 nm). However, most of the finally found OH groups are formed in the waveguiding layers by protons incorporated during the proton exchange. This type of bonding is undesirable in the waveguides fabricated in Er:LiNbO<sub>3</sub> from the point of view of their potential amplifying function as it causes decreasing of the excited state lifetimes of the laser-active Er<sup>3+</sup> ions (i.e. decreases efficiency of the erbium emission at 1.5 μm). The reason for that is that the OH overtone vibrations absorb at wavelength of 1.45 μm (6900 cm<sup>-1</sup>), which is very close to the wavelength emitted by the laser-active Er<sup>3+</sup> ions, which is being exploited; fundamental vibrations of OH groups are located at 2.86 μm (3500 cm<sup>-1</sup>).

Since the overtone vibration band at 6900 cm<sup>-1</sup> was out of the measured range, intensity of the fundamental vibration band at 3500 cm<sup>-1</sup> was measured and evaluated instead. Intensity of the absorption band in standard FT-IR spectrometry was quite low and that is the reason why spectrometer with microscope was employed in this work. Significant decrease of the OH absorption band intensity with increasing duration of the annealing (to approx. 20 % of the primary value) is obvious from the obtained IR absorption spectra (given in figure 5) as well as the difference between "the short time" and "the long time annealed" samples. Idea of formation of the different crystallographic phases (different crystalline structures) is supported by the fact, that there is a slight shift of the absorption band to the lower frequencies observed, which indicates prolonging of the O-H bonds lengths. This prolonging is probably a consequence of the volume expansion of the exchanged layer during the fabrication process.

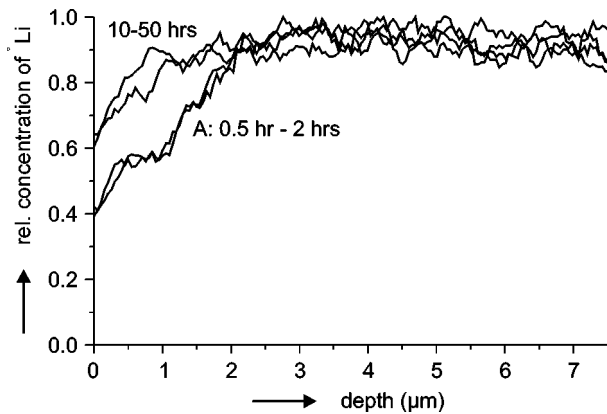


Figure 3. Changes in distribution of lithium ions in the X cut samples caused by annealing at 350°C. (NDP measurement, normalized).

Table 1. Changes in distribution of hydrogen ions in the X cut samples caused by annealing process at 350°C (ERDA measurement, d.l. = detection limit ≅ 0.5 μm).

Duration of A (hrs)	Depth (nm)	Conc. of hydrogen (atomic %)
0.5	0 - 70	19
	70 - d.l.	13
2	0 - 120	15
	120 - d.l.	13
10	0 - 95	7
	95 - d.l.	4
50	0 - 70	6
	70 - d.l.	2

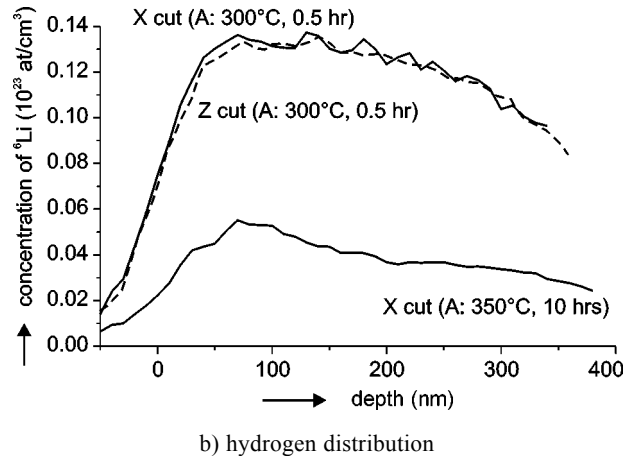
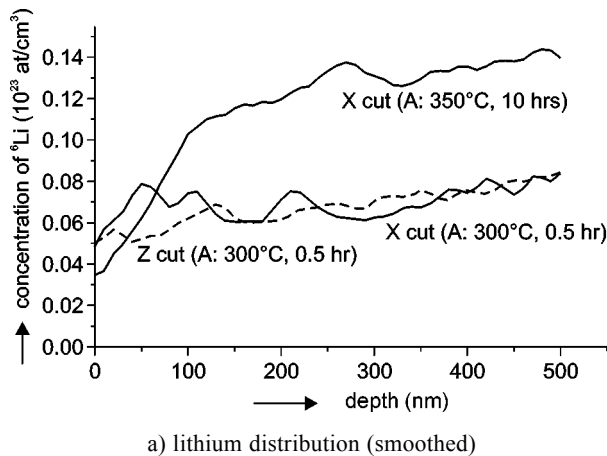


Figure 4. HIERDA measurement of the samples fabricated in various crystallographic cuts (PE: 213°C, 2 hrs; A: 350°C).

## CONCLUSIONS

To improve active function of the APE waveguides in Er:LiNbO<sub>3</sub>, the amount of OH groups present in the waveguiding layers has to be substantially decreased. The annealing process is a useful tool in this problem; the higher temperatures and/or longer duration of the annealing would result in more significant decrease of the intensity of OH absorption bands. We have found out that using longer annealing times for increasing the APE layers' depth would cause simultaneous decrease of the total refractive index increment and we are then able to fabricate samples of various crystallographic phases (approaching the desired alpha phase).

However, a limitation of the annealing conditions exists: in the case of planar waveguides the annealing temperature should not exceed 400°C (and similarly in the case of channel waveguides there is limitation for both annealing temperature 375°C and duration 30 hrs) or the waveguiding capability of the fabricated APE layers would be lost. To preserve the waveguiding properties of the APE layers it is possible to decrease the surface hydrogen concentration maximally to 25 % of the original value.

## Acknowledgement

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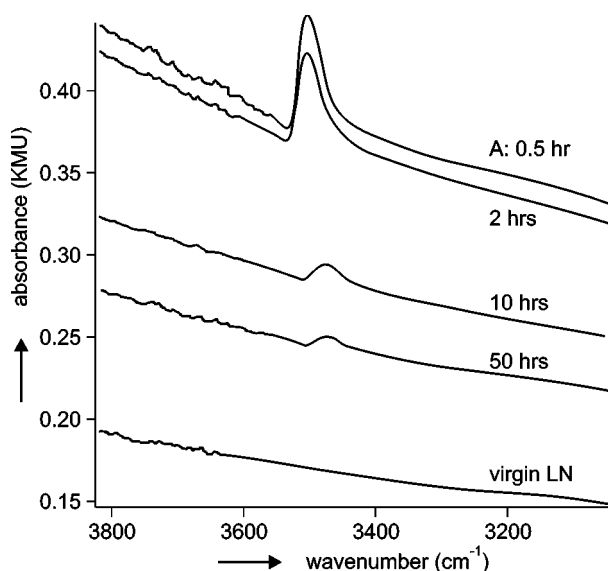


Figure 5. Changes in intensity of OH absorption band with increasing time of annealing determined by FT-IR spectrometer with microscope (Z cut, PE: 213°C, 2 hrs; A: 350°C); absorption is given in Kubelka-Munk units.

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Vliv žíhání na aktivní vlastnosti APE  
optických vlnovodů v erbiem dovovaném  
niobičnanu lithném

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Studovali jsme vliv žíhání na chemické složení a optické vlastnosti vrstev připravených protonovou výměnou (APE) s důrazem na jejich potenciální aktivní funkci. Vzorky byly žíhány za různých podmínek a následně charakterizovány celou řadou nukleárních analytických metod (NDP; ERDA; HIERDA) pro stanovení koncentračního profilu vyměněných iontů. Obsah OH skupin, které jsou nežádoucí pro aktivní vlnovodné vrstvy díky jejich vlivu na zkrácení doby života excitovaných stavů iontů erbia, byl sledován IČ absorpční spektroskopii. Vlnovodné vlastnosti (počet vidů, hloubkový profil indexu lomu) byly měřeny vidovou spektroskopií na 632,8 nm. Zjistili jsme, že vodík vnesený do povrchové vrstvy LiNbO<sub>3</sub> protonovou výměnou (PE) se během žíhání (A) pohybuje hlouběji do substrátu, čímž dochází ke snížení celkového přírůstku indexu lomu. Díky tomu se složení připravených vrstev mění směrem k α-fázi. Nejvyšší množství OH skupin bylo zjištěno ve vzorcích žíhaných na nejvyšší teplotu, existuje zde ovšem omezení, protože žíhání při teplotě nad 400°C způ-