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Aging of proton-exchanged optical waveguides in Y-cut $LiNbO_3$[♣]

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Optical waveguides in Y-cut $LiNbO_3$ were obtained in different technological regimes, resulting in a variety of phases composing the proton-exchanged layer. Mode spectra measurements, infrared absorption and Raman spectra recording were performed after creation of the samples, and also after a period of ten years. The phase composition was estimated, and some conclusions are made concerning the stability of such waveguides.

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1. Introduction

Proton exchange (PE) [1] is successfully used as an alternative to the more popular Ti-indiffusion technology for waveguide fabrication in $LiNbO_3$. Despite the advantages offered by PE in $LiNbO_3$, a significant problem is the fast surface etching of Y-cut crystals due to structural deformations introduced by PE, as well as the instability of $Li_{1-x}H_xNbO_3$-waveguides over time, due to their complicated phase composition. The PE layers can form up to seven different crystallographic phases determined by the degree of Li^+ to H^+ substitution (value of x) [2]. Recently, attempts were made to put under control the phase status of the waveguide layers, by the use of new proton sources or modifications of the technological regimes [3, 4]. This is why the methods for phase composition analysis of such layers are also strongly investigated. The short-term and long-term stability of PE waveguides also depends on the phase composition. The long-term stability is an important area of investigation, since it determines the constant parameters of the integrated optical element or device.

Table1. Technological and waveguide parameters of the proton-exchanged waveguides: as-exchanged (a) and after 10 years (b) (T – temperature, t – duration of the PE-process, Ta and t_a – temperature and duration of the annealing, M - number of waveguide modes at $\lambda = 633$ nm, Δn_e – extraordinary refractive index change, d – waveguide depth)

Sample	Technological Steps and Parameters					M		Δn_e		d [μm]	
	Sample environment	T [°C]	t [h]	T_a [°C]	t_a [h]	a	b	a	b	a	b
C1	1)Benzoic acid	230	0.05			4	3	0.13	0.136	2.7	2.75
	2) Air			350	1						
	3) Benzoic acid	230	0.17								
C2	Benzoic acid + 0.5% Lithium benzoate	230	3.00			3	3	0.11	0.104	1.56	1.56
C3	Benzoic acid + 1% Lithium benzoate	230	7.00			3	4	0.11	0.11	1.5	2.85
S1	1) Cinnamic acid	300	0.50			3	3	0.146	0.141	1.39	1.52

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	vapors										
	2) Cinnamic acid melt	230	0.08								

2. Experimental

The samples were prepared under the technological conditions described in Table I. Mode spectra were measured by a He-Ne laser at a wavelength λ=633 nm, and optical profiles were reconstructed (Fig. 1). The infrared (IR) absorption spectra were recorded in the range 2700-3700 cm^{-1} of the OH-stretching modes, with a Bruker Tensor 27 FTIR spectrometer at 1 cm^{-1} resolution, and a Gaussian decomposition procedure was performed (Fig. 2). The Ra scattering from the m=0 guide modes excited by an Ar laser (λ=514.5 nm) was registered with 1 cm^{-1} resolution (Fig. 3) using a scattering geometry which activates A1 type phonons - it was shown that the A1 Ra spectra are mainly affected by proton strains introduced by proton incorporation.

3. Results and discussion

3.1. Mode spectra

The profile shape and the maximal value of the index change allow a preliminary evaluation of the phase composition, according to the phase model [1, 5].

The optical profile of as-exchanged C1 is characteristic for waveguides consisting of highly protonated β_i-phases (i=1-3) ($0.56 \le x \le 0.65$) and a layer of α-phase ($0 \le x \le 0.12$) or κ_1/κ_2 phases ($0.12 \le x \le 0.56$) between them and the substrate. After ten years, C1 has an optical profile which resembles that of the κ_i-phases formed after annealing, but the surprisingly high surface value of Δn_e=0.136 could be attributed not only to the β_i (i=1-3) but even to the β_4-phase ($0.65 \le x \le 0.76$).

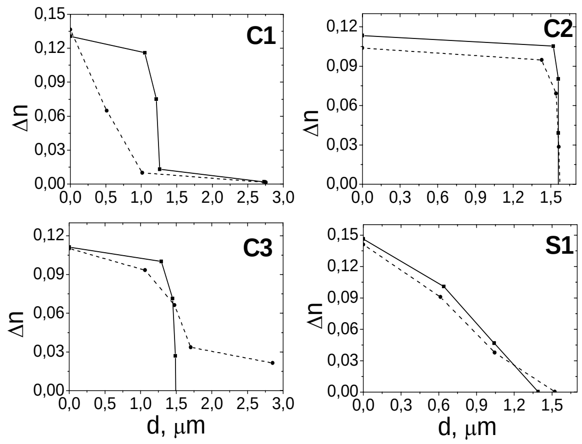

Fig.1. Optical profiles reconstructed from the measured mode spectra of as-exchanged samples (solid line) and after ten years (dashed line).

C2 has a steplike optical profile, with a maximal index change of Δn_e=0.11 which is changed to 0.104 after ten years. The depth and shape of the profile remain unchanged. Thus this waveguide has to contain the β_1-phase - the only one which could be obtained by low-temperature direct proton exchange in Y-cut $LiNbO_3$ [6].

The profile shape of C3 changes from truncated after PE to graded after aging, keeping a maximal value of Δn_e=0.11. It should consist of the β_1-phase, together with the α-phase which is due to the higher percentage of lithium benzoate in the melt compared to the case of C2**.**

The optical profile of sample S1 is similar to that of the aged C1, with an even higher value of Δn_e (Δn_e=0.14), and has been almost unaffected by the aging. The high degree of proton exchange confirmed by the surface refractive index change indicates the presence of the β_4-phase, but β_i–phases (i=1-3) could also be present.

During the aging, some redistribution probably has taken place between the co-existing phases and the substrate, which affects the waveguide depth and the optical field distribution and smoothes the transition between the substrate and the waveguide. Probably, the as-exchanged C3 and aged C1 had supported 4 modes, but due to the high optical losses in the inhomogeneous layers or at the waveguide-substrate interface, the last mode could not be measured.

3.2. Infrared spectra

As is known [2, 7], the main bands in the IR-absorption spectra of PE $LiNbO_3$ could be attributed to the different phases as follows: the band centred at 3488 cm^{-1} – to the α-phase, the broad band centred at 3250-3280 cm^{-1} – to the β_i -phases (i=2-4), 3250 cm^{-1} – to the β_1-phase, 3512 cm^{-1} – to the β_4-phase. κ_1 and κ_2 have peaks between 3488 and 3500 cm^{-1} (intermediate values between the α- and β_1-phases) and are spectroscopically undistinguishable. Since the component due to the substrate α-phase was extracted from the spectra after the deconvolution, only the components of the layers' spectra are present in the histograms (Fig. 2). Thereby, the evolution of the bands assigned to different phases versus the variations in the technological parameters and after aging could be followed. The histograms show that all samples consist of different phase combinations, but the chosen technological regime influences the thickness of the sublayers formed by these phases. The contribution of the β_4 phase is stronger in samples with higher Δn_e (S1 and C1), i.e. with a higher level of proton doping. The contribution of $\alpha/\kappa_1/\kappa_2$ is stronger in samples obtained in a regime including annealing (C1) or an annealing-like step (S1).

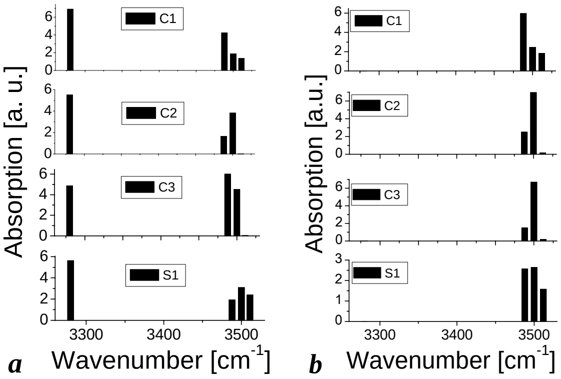

Fig. 2. Comparative scheme of the frequency positions and intensities of the Gaussian OH-components of the IR spectra:as-exchanged samples (a) and after ten years (b).

The contribution of β_1 is stronger for samples obtained by direct proton exchange (C2 and C3). The aging time influences most remarkably the large band at 3250-3280 cm^{-1}, which has completely disappeared after ten years, confirming the proton redistribution in the exchanged layer. Thus, the contribution of the α-phase and the κ_1/κ_2 phases increases after aging, as well as the contribution of the β_1-band at 3500 cm^{-1}. This is due to the diffusion of weaker bonded protons from the β_i-phases (i=2-4) responsible for the 3250-3280 cm^{-1} centred band; the protons are supposed to occupy interstitial positions in the lattice of PE LiNbO$_3$. It could be seen also that due to some proton redistribution in the exchanged layers of C1 and S1, the relative contribution of β_4 decreases after aging.

3.3. Raman spectra

The set of narrow peaks in the Ra spectra (Fig. 3) indicates high value of x [8]. A broad band in the range 520-780 cm^{-1} is observed, originating from a paraelectric-like phase, as well as the A1(TO) peak at 690 cm^{-1} and the bulk spectra intensity attenuation. The new peak which appears at 690 cm^{-1} is attributed to highly protonated phases having almost paraelectric properties (β_i phases, i=1-3), since it is characteristic of the paraelectric phase of LiNbO$_3$ [8]. Its relative intensity allows some estimation of the phase contribution to the PE layers to be made. Since it is higher for samples C2 and C3, this band could be attributed to the β_1 phase which is the only possible phase formed by direct proton exchange in Y-cut LiNbO$_3$ [6]. The spectra of C2 remain unchanged after ten years, since that waveguide consists only of a β_1-phase and no proton redistribution between different phases could take place.

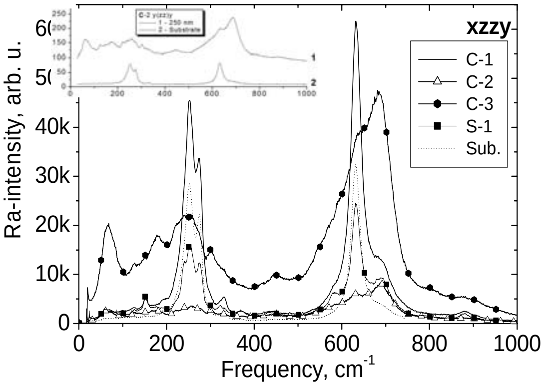

Fig. 3. Raman spectra – A1(TO)-mode for all samples after a 10-year period and for as-exchanged C2 (inserted).

The peak appearing at 878 cm^{-1} (samples C1, C3 and S1) comes from the E(LO) mode, excited due to the strong lattice perturbation introduced by PE at a high level of H$^+$ doping (β_1-phases, i=1-4). It can be seen that the spectrum of C1 contains the peaks characteristic of bulk LiNbO$_3$, in positions and in relative intensities as well. This shows that the α-phase has a strong contribution to the layer composition. The intensity increase of the band centred at 632 cm^{-1} could be due to the presence of the α- and κ_i-phases. The peak at 70 cm^{-1} is present only in PE LiNbO$_3$ and usually is used as an indicator for Li$^+$-H$^+$ exchange [9]. The spectra of C1 and S1 are quite similar, so we could conclude that S1 contains also some of the β_i phases, i=1-4, κ_i- phases (i=1-2) and α-phase.

The results of the phase content analysis performed are presented in Table 2.

Table 2. Phase composition according to the spectroscopy evidence, for as-exchanged samples (a) and after 10 years (b).

Sample	Phase composition: Spectroscopic evidence					
	Mode		IR		Ra	
	a	b	a	b	a	b
C 1	β_i (i=1-3) k_1/k_2	β_i (i=1-4) k_1/k_2	β_i (i=1-4) k_1/k_2 (α)	β_i (i=1-4) k_1/k_2 (α)	-	β_i (i=1-4) k_1/k_2 (α)
C 2	β_1	β_1	β_1 (α)	β_1 (α)	β_1	β_1
C 3	β_1 α	β_1 α	β_1 (α)	β_1 α	-	β_1

S1	β_i (i=1-4) k_1/k_2 α	β_i (i=1-4) k_1/k_2 α	β_i (i=1-4) k_1/k_2 (α)	β_i (i=1-4) k_1/k_2 (α)	-	β_i (i=1-4) k_1/k_2 α

4. Conclusions

The combined analysis based on mode, IR absorption and Ra spectra allows the identification of phases as well as the relative contribution of each of them to the composition of the waveguide layer of multiphase proton-exchanged waveguides in lithium niobate.

It has been shown that highly proton- exchanged phases and deep waveguides having a high extraordinary refractive index change could be obtained in Y-cut $LiNbO_3$ under specific technological regimes.

The analysis of the Ra spectra indicates that the band at 690 cm^{-1} could be attributed to the β_1-phase, which makes that phase already spectroscopically distinguishable.

The aging of proton-exchanged optical waveguides in $LiNbO_3$ influences the depth and the maximal value of the refractive index change, with the former increasing and the latter decreasing. In most cases, aging does not affect the area of the refractive index profile, i.e. the quantity of protons penetrated during the exchange. However, their redistribution from the highly-protonated phases to the ones with lower proton concentrations takes place. Thus, the redistribution of protons during the aging affects the optical field distribution in the PE waveguides, influencing their parameters.

The waveguides consisting of a single-phased layer demonstrate better long-term stability of their optical parameters.

Acknowledgements

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