

## Surface phase detection of proton-exchanged layers in LiNbO<sub>3</sub> and LiTaO<sub>3</sub> by IR reflection spectroscopy

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The proton exchange (PE) technology has focused scientists' attention for the last 30 years because of the easy and fast obtaining of waveguides with strong waveguiding effect in electro-optical crystals like LiNbO<sub>3</sub> (LN) and LiTaO<sub>3</sub> (LT). The Li<sub>1-x</sub>H<sub>x</sub>NbO<sub>3</sub>/Li<sub>1-x</sub>H<sub>x</sub>TaO<sub>3</sub> layer, formed by Li-H ion exchange, shows complex phase behavior depending on the hydrogen concentration (value of x). Up to seven phases exist in PE-LN and up to five – in PE-LT. Each phase forms its own sublayer in the protonated region, the one with the highest value of x being on the top. That is why the recognition of the top sublayer phase in many cases could be used for some conclusions about the phases building the rest of the whole layer or for the optical and electro-optical quality of the optical waveguiding layer. It has been established that IR reflection spectra of proton-exchanged layers contain new bands within the range 850–1050 cm<sup>-1</sup> and each phase has its own reflection spectrum. This way, IR reflection spectra in low-frequency range could determine the top-layer phase status. The samples investigated were obtained at different technological conditions and the analysis performed contributes to the accumulation of knowledge about the technological control of the phase composition of proton-exchanged waveguide layers in LN and LT.

**Key words:** LiNbO<sub>3</sub>, LiTaO<sub>3</sub>, optical waveguides, proton exchange, phase composition.

### INTRODUCTION

Lithium niobate and lithium tantalate are among the most attractive ferroelectric crystals for integrated optics. Being an alternative of the most popular technology for obtaining optical waveguides in LiNbO<sub>3</sub> – Ti-indiffusion, proton exchange (PE) [1, 2] has undergone a strong development in the last two decades. PE represents a chemical reaction (diffusion and Li-H ion exchange) which takes place in the surface layer of a crystal immersed in an appropriate melt.

Going by the scheme:



PE modifies the surface layer (several μm in depth) by Li-H ion exchange causing a large extraordinary index change Δn<sub>e</sub> (Δn<sub>e</sub> ≅ 0.12 for LiNbO<sub>3</sub>

and ≅ 0.02 for LiTaO<sub>3</sub> at 0.633 μm). The PE layers show complex phase behaviour depending on the hydrogen concentration (value of x) and causing significant decrease in electro-optical coefficients and increase in optical losses and instabilities.

The phase model developed by Korkishko et al. [3, 4], on which contemporary ideas on phase formation in monocrystalline layers of Li<sub>1-x</sub>H<sub>x</sub>MO<sub>3</sub> are based, suggests that each phase originates as an individual sublayer of several hundred nm or less. In every single one of them Δn<sub>e</sub> is a linear function of concentration. The lattice parameters vary among phases. Within each phase, the change of the extraordinary refractive index Δn<sub>e</sub> is proportional to x; within a phase transition, the value of Δn<sub>e</sub> and/or of the deformations perpendicular to the surface change by leap. Up to 7 phases could be formed in LiNbO<sub>3</sub> (α, κ<sub>1</sub>, κ<sub>2</sub>, β<sub>1</sub>, β<sub>2</sub>, β<sub>3</sub>, β<sub>4</sub>), and up to 5 – in LiTaO<sub>3</sub> (α, κ, β, γ, δ).

The complicated phase composition of the proton-exchanged layers, determined by the degree of H<sup>+</sup>-Li<sup>+</sup> substitution, has oriented the main efforts since the beginning of the technology to the ways for controlling the phase composition and to methods for waveguide phase characterization.

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**Table 1.** Technological and waveguide parameters of the proton-exchanged waveguides: (T – temperature, t – duration of the PE process, T<sub>a</sub> and t<sub>a</sub> – temperature and duration of the annealing, M – number of waveguide modes at λ = 633 nm, Δn<sub>e</sub> – extraordinary refractive index change, d – waveguide depth)

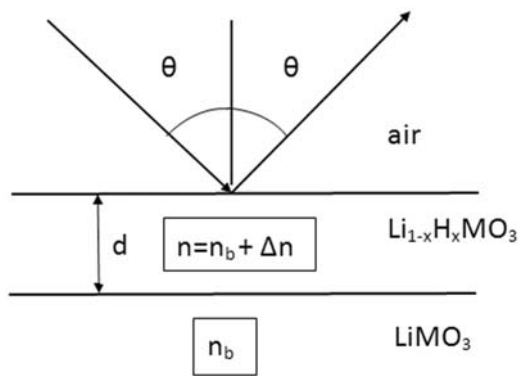
Material	Sample	Proton source	T [°C]	t [h]	T <sub>a</sub> [h]	t <sub>a</sub> [h]	M	d [μm]	Δn <sub>e</sub>	Possible phase composition	Surface phase
LiTaO <sub>3</sub>	TZ-2	LiHSO <sub>4</sub> (vapors)	250	20	–	–	1	1.23	0.0162	α, κ, δ	δ
LiTaO <sub>3</sub>	TZ-3	LiHSO <sub>4</sub> (vapors)	220	48	–	–	1	1.44	0.0101	α, κ, δ	δ
LiTaO <sub>3</sub>	TZ-4	LiHSO <sub>4</sub> (vapors)	200	72	–	–	1	2.09	0.0058	α, κ, δ	δ
LiTaO <sub>3</sub>	T-1	Benzoic acid	240	8	265 295	1 1.5	2	2.18	0.0213	β(γ)	γ
LiTaO <sub>3</sub>	T-2	Benzoic acid	240	31	400	2	5	9.45	0.0155	A	α
LiTaO <sub>3</sub>	Z-1	Benzoic acid	240	8	295 350	1 1	4	4.25	0.0189	α, κ	α, κ
LiNbO <sub>3</sub>	LZ-1	LiHSO <sub>4</sub> (vapors)	250	3.5	–	–	6	2.66	0.1491	β <sub>1</sub> , β <sub>3</sub> , β <sub>4</sub>	β <sub>4</sub>
LiNbO <sub>3</sub>	NM-1	NH <sub>4</sub> HSO <sub>4</sub> (melt)	230	3.3	–	–	9	2.47	0.1508	β <sub>1</sub> , β <sub>3</sub> , β <sub>4</sub>	β <sub>4</sub>
LiNbO <sub>3</sub>	NM-5	LiHSO <sub>4</sub> (melt)	175	1.5	–	–	1	0.62	0.1222	β <sub>1</sub> , β <sub>2</sub> , β <sub>3</sub>	β <sub>1</sub>

## EXPERIMENTAL

Proton-exchanged optical waveguides in Z-cut LiNbO<sub>3</sub> and Z-cut LiTaO<sub>3</sub> were obtained by different technology conditions described in Table 1.

The phase analysis based on mode and IR absorption spectra was performed and reported earlier [5–8], the results being presented also in Table 1. In addition, infrared reflection spectra were registered in order to confirm the phase composition as well as to give some indications about the distribution of the different phases within the proton-exchanged layers.

IR reflection spectra were recorded at angle of incidence θ = 70° (measured from the normal to the surface) as shown in Fig. 1. The spectrometer accessories for specular reflectance were fixed-angle ones (for 20° and 70°). Since the penetration depth depends on the angle of incidence, at smaller angles (closer to the normal incidence) deeper penetration



**Fig. 1.** Schematic sketch of IR reflection measurements

takes place and the measured spectra are affected by the presence of the various phases forming the waveguide. It was established [9] that at 70° the spectrum of the surface layer is separated from those of deeper situated layers in multiphase guides. This way only the surface phase could contribute to the reflection spectra of multiphase waveguides and the IR reflection spectroscopy allows the surface phase to be recognized.

## RESULTS AND DISCUSSION

### LiNbO<sub>3</sub>

The IR reflection spectra for LN samples are presented in Fig. 2.

The reflection IR spectra of protonated LN crystals have new bands compared to the spectra of virgin crystal (LZ-ref) or α-phase PE-LiNbO<sub>3</sub> [9]. These bands appear at frequencies in the range of 890–1010 cm<sup>-1</sup>, each phase having its own spectrum. It has been found that the new bands which can be attributed to new phases are 975 cm<sup>-1</sup> for β<sub>1</sub> phase, 980 cm<sup>-1</sup> for β<sub>2</sub> and β<sub>3</sub> phases, 970 cm<sup>-1</sup> for β<sub>4</sub> phase [9, 10]. The new band at 890–985 cm<sup>-1</sup> appears after PE in addition to the lattice spectrum of LN.

The low-frequency edges of the band correspond to the TO phonons of the NbO<sub>6</sub> vibration mode. Less distorted NbO<sub>6</sub> octahedra without any non-bridging oxygen ions are present in the α, κ<sub>1</sub> and κ<sub>2</sub> phases, as well as in pure LN. The appearance of weak extra bands in the region of IR reflection spectra from 800 to 900 cm<sup>-1</sup> for all β<sub>i</sub> phases suggests the presence of more distorted NbO<sub>6</sub> octahedra with non-bridging oxygen ions. Each β<sub>i</sub> phase is marked by a very specific lattice vibration spectrum with unique charac-

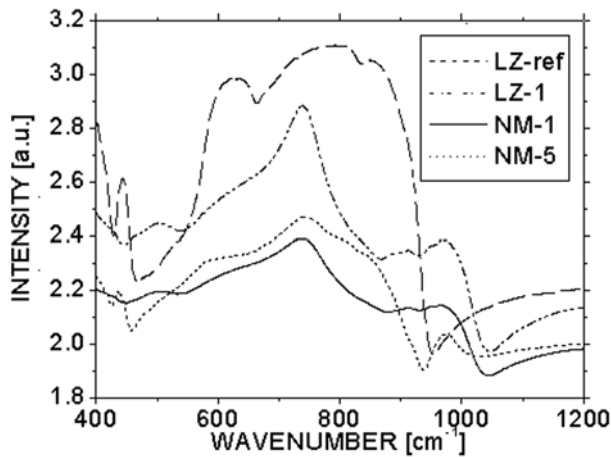


Fig. 2. IR reflection spectra measured at  $\theta = 70^\circ$  for the  $\text{LiNbO}_3$  proton exchanged layers

teristic bands. A significant difference between the crystalline structures of different  $\beta_i$  phases exists, which is introduced by the added chemical bonds with characteristic frequencies of vibration. This feature can be used for accurate identification of  $\beta_i$  phases in any  $\text{H}_x\text{Li}_{1-x}\text{NbO}_3$  waveguide.

Since the analysis based on mode and IR absorption spectroscopy suggests a particular phase composition, where the most strongly protonated phase is at the surface of the waveguide, particular changes in the reflection spectrum can be attributed to the respective phase. This way the analysis was made which allows a particular frequency band to be attributed to the presence of the definite phase on the surface.

The new bands which can be attributed to new phases are:  $955\text{ cm}^{-1}$  and  $970\text{ cm}^{-1}$  for  $\kappa_2$ -phase,  $965\text{ cm}^{-1}$  for  $\kappa_1$ -phase and  $965\text{ cm}^{-1}$  for  $\alpha$ -phase.

Thus, looking at the spectra in Fig. 2 we could conclude that  $\beta_1$  phase is present on the top of sample NM-5 while  $\beta_4$  phase forms the top of the waveguiding layers of samples NM-1 and LZ-1, which are really strongly protonated. Also, it is seen that the spectrum of NM-5 is closest to the shape of the virgin sample (LZ-ref), which suggests that the contribution of the  $\alpha$ -phase is larger than in the case of the other two samples. It could be seen that LZ-1 and NM-1 have almost the same spectra, confirming their equal phase composition determined by other methods, as it can be seen in Table 1.

In the case of analysis of the phase composition of the most weakly protonated waveguide, the reflection spectra give particularly important information since they show that the waveguide is a single-phase one. As it is known from the phase model, the single-phase layers form the layer in

such way that the value of  $x$  increases towards the surface (i. e. the most strongly protonated layer is at the surface). In our case the uppermost layer is of the  $\beta_1$  phase and therefore, according to the phase analysis based on mode and IR spectroscopy, the possible  $\beta_2$  and  $\beta_3$  phases are not present in the protonated layer. (Another possibility is that the layer is slightly “buried” but the technological conditions do not suggest such a result).

### LiTaO<sub>3</sub>

The IR reflection spectra for LT samples are presented in Fig. 3 and Fig. 4.

The main changes in the reflection spectra introduced by proton exchange in Z-cut  $\text{LiTaO}_3$  occur in the range of  $850\text{--}1050\text{ cm}^{-1}$ . They were compared to the spectra of X-cut PE- $\text{LiTaO}_3$  given in [10] and some correlations with lattice deformations and reflection minimums were made in order to assign the spectral changes to a definite phase. According to [10], the changes observed at  $899$ ,  $952$  and  $985\text{ cm}^{-1}$  in IR-reflection spectra of all samples could be assigned to the  $\beta$ - and  $\gamma$ -phases, and the change at about  $1000\text{ cm}^{-1}$  to the  $\delta$ -phase, respectively. Since in the case of the waveguides (Fig. 3) obtained by proton exchange in vapors (PEV) the second perturbation is much stronger, we should conclude that the surface phase of all investigated waveguides is  $\delta$  as their spectra are almost identical.

The phase composition of the annealed samples suggests the presence of  $\alpha$ - and  $\kappa$ -phases, so the new bands in their reflection spectra (Fig. 4) could be assigned to these two phases:  $960\text{ cm}^{-1}$  for the  $\kappa$ -phase,  $974\text{ cm}^{-1}$  for the  $\alpha$ -phase,  $891$  for both  $\alpha$ - and  $\kappa$ -phases. For the  $\beta$ - and  $\gamma$ -phases the

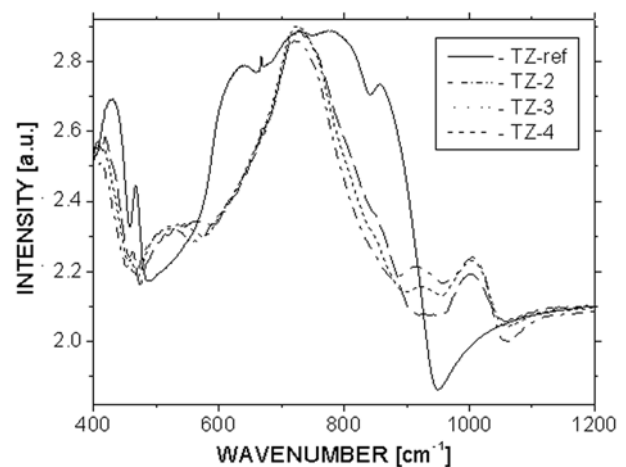


Fig. 3. Infrared reflection spectra measured at  $\theta = 70^\circ$  for the  $\text{LiTaO}_3$ -waveguides obtained in  $\text{LiHSO}_4$  vapors

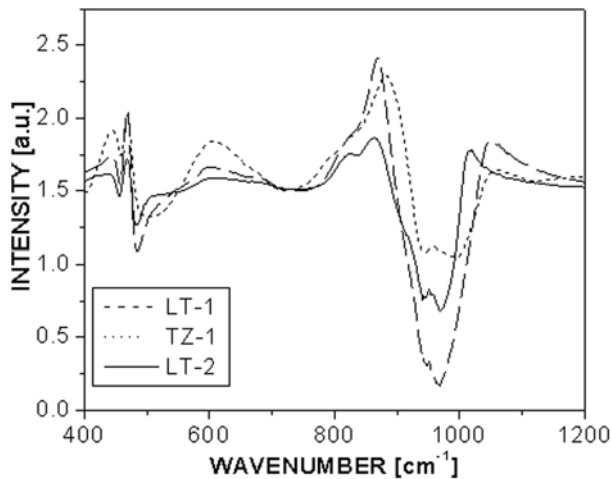


Fig. 4. Infrared reflection spectra measured at  $\theta = 70^\circ$  for the post-exchange annealed  $\text{LiTaO}_3$ -samples

band has three components at 890–915, 960 and 992  $\text{cm}^{-1}$ , which are shifted to lower frequencies compared to the bands for the  $\gamma$ - and  $\delta$ -phase of PEV waveguides.

The results of the IR-spectra analysis for the investigated LN and LT samples are shown in the rightmost two columns of Table 1. The information given by these spectra allows the determination to be made, which phase forms the uppermost layer of the waveguide. Thus, the information given by the analysis of the IR-reflection spectra allows us to be much more specific when determining which phases build the investigated waveguide layers.

## CONCLUSIONS

- The phase composition of the entire PE-layers was determined by combined mode and IR absorption spectroscopy.
- IR reflection spectra of proton-exchanged layers contain new bands within the range 890–1010  $\text{cm}^{-1}$  and each phase has its own reflection spectrum. This way, IR reflection spectra in the low-frequency range could determine the top-layer phase status.
- The low-frequency edges of the band correspond to the TO phonons of the  $\text{NbO}_6/\text{TaO}_6$  vibration mode. The appearance of weak extra bands in the region of IR reflection spectra from 800 to 900  $\text{cm}^{-1}$  suggests the presence of more distorted

$\text{NbO}_6/\text{TaO}_6$  octahedra with non-bridging oxygen ions. There is a significant difference between the crystalline structures of different phases, which is introduced by the added chemical bonds with characteristic frequencies of vibration.

- The phase-characteristic bands for  $\text{LiNbO}_3$  are at:

- 965  $\text{cm}^{-1}$  for both  $\alpha$ - and  $\kappa_1$ -phase;
- 955  $\text{cm}^{-1}$  for  $\kappa_2$ -phase;
- 975  $\text{cm}^{-1}$  for  $\beta_1$ -phase;
- 980  $\text{cm}^{-1}$  for  $\beta_2$ - and  $\beta_3$ -phases;
- 970  $\text{cm}^{-1}$  for  $\beta_4$ -phase.

- The new bands assigned to the definite phase in the case of  $\text{LiTaO}_3$  are:

- 960  $\text{cm}^{-1}$  for the  $\kappa$ -phase;
- 974  $\text{cm}^{-1}$  for the  $\alpha$ -phase;
- 890  $\text{cm}^{-1}$  for both  $\alpha$ - and  $\kappa$ -phases;
- 890–915, 960 and 992  $\text{cm}^{-1}$  for  $\beta$ - and  $\gamma$ -phases, the components of the first being shifted to lower frequencies compared to the bands of the second;
- 1000  $\text{cm}^{-1}$  for the  $\delta$ -phase.

- The presented results could contribute to the obtaining of waveguides with control of their phase composition and therefore of their optical and electro-optical properties.

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ОПРЕДЕЛЯНЕ НА ПОВЪРХНИННАТА ФАЗА  
НА ПРОТОННО-ОБМЕНЕНИ СЛОЕВЕ В LiNbO<sub>3</sub> И LiTaO<sub>3</sub>  
ЧРЕЗ ОТРАЖАТЕЛНА ИЧ СПЕКТРОСКОПИЯ

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(Резюме)

Протонният обмен (PE) е технология, която привлича вниманието на учените през последните 30 години поради лесното и бързо получаване на оптични вълноводи със силен вълноводен ефект в електрооптичните кристали LiNbO<sub>3</sub> (LN) и LiTaO<sub>3</sub> (LT). Слой  $\text{Li}_{1-x}\text{H}_x\text{NbO}_3/\text{Li}_{1-x}\text{H}_x\text{TaO}_3$ , получен чрез Li-H йонен обмен, има сложен фазов състав, зависещ от концентрацията на водорода (стойността на  $x$ ). До седем фази могат да съществуват в PE-LN и до пет – в PE-LT. Всяка фаза образува свой собствен подслой в протонираната област, като този с най-висока стойност на  $x$  се намира на повърхността. По тези причини от определянето на фазата на повърхнинния слой в много случаи може да се направят изводи и за фазите, изграждащи целия слой или за оптичните и електрооптичните качества на вълноводния слой. Установено е, че ИЧ отражателни спектри на протонно-обменените слоеве съдържат нови ивици в областта 850–1050 cm<sup>-1</sup> и всяка фаза има свой специфичен отражателен спектър. По този начин по ИЧ отражателни спектри в нискочестотната област може да се определи повърхнинната фаза. Тъй като изследваните проби са получени при различни технологични условия, проведенят анализ допринася за натрупване на знания по технологичен контрол на фазовия състав на протонно-обменени слоеве в LN и LT.