Proton-exchanged optical waveguides in LiTaO$_3$: phase composition and stress

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Abstract. Planar optical waveguide layers were obtained in Z-cut LiTaO$_3$ crystal substrates via proton exchange. Two different media were used as proton sources: benzoic acid melt and lithium hydrosulphate vapors, controlling the thickness of the waveguides by duration and temperature of the proton exchange process and also by post-exchange annealing. The intrinsic stress caused by the penetration of the hydrogen ions into the crystal lattice was estimated by the optical integral method. The phase composition of proton-exchanged layers was analyzed based on the mode and IR-absorption spectra. An attempt to relate the level of stress to the level of proton doping has been made.

1. Introduction
Lithium tantalate (LT) is one of the attractive ferroelectric materials for integrated optics due to its strong nonlinearity, high electro-optical coefficients and optical resistivity, as well as to the transparency to shorter wavelengths compared to the most popular lithium niobate (LN).

The proton exchange (PE) method [1, 2] has been widely studied because of the easy and fast obtaining of waveguides with strong waveguide effect in electrooptical crystals like LiNbO$_3$ and LiTaO$_3$. The surface layer modified by hydrogen diffusion has a large extraordinary index change ($\Delta n_e$) and thus, a strong waveguide and polarizing effect. PE is a low-temperature process, compared to other technological methods of producing waveguides and is especially appropriate for LT, whose Curie temperature is lower. The Li$_{1-x}$H$_x$TaO$_3$ layers formed by Li-H ion exchange show complex phase behavior depending on the hydrogen concentration (value of $x$) [3, 4]. Studies have shown the presence of up to six different phases in PE LT [4, 5] originating as individual sublayers of several hundred nm thickness or less. In each of them one of them $\Delta n_e$ is a linear function of proton concentration. Within a phase transition, the value of $\Delta n_e$ and/or of the deformations perpendicular to the surface change by a leap.

Since the development of the PE technology, the main efforts have been directed to the study of phases coexisting in such waveguides and how technological conditions effect their formation. The proton presence causes changes in crystal lattice parameters which reflect on the vibrational spectra of exchanged layers. Using the results of optical profiles and IR-absorption spectra we could perform an analysis of the phase content of PE layers. The use of a combination of different methods to confirm the presence of a different phase or set of phases has been reported recently [6].
It is well known that PE is accompanied by accumulation and relaxation of internal strain [7]. An optical integral method [8] contributes to the characterization of the waveguide film from the point of view of mechanical stress (MS). Since the MS is a function of the film structure, by its change due to different film composition, an additional picture for the building units of the film could be gained.

2. Experimental

Proton-exchanged waveguide layers were obtained in Z-cut substrates of LT at the technological conditions described in table 1. Two technological methods were applied: PE in vapors (one-step process) and PE in a melt followed by annealing (APE two-step process). The LT substrates used in each method were of identical stoichiometry. The cooling after diffusion was slow (10 deg/min), so avoiding metastable phase formation and short-time instability of the waveguides as well.

| Sample | Proton source | T [°C] | t [h] | T_a [°C] | t_a [h] | M | d [µm] | Δn_e | Phase composition | σ x10^9 [N/m²] |
|--------|---------------|-------|------|----------|--------|---|--------|------|-------------------|----------------|
| TZ-1   | LiHSO_4 (vapors) | 250   | 10   | -       | -      | 1 | 0.89   | 0.0186 | α, κ, δ           | +22.80         |
| TZ-2   | LiHSO_4 (vapors) | 250   | 20   | -       | -      | 1 | 1.23   | 0.0162 | α, κ, δ           | +3.41          |
| TZ-3   | LiHSO_4 (vapors) | 220   | 48   | -       | -      | 1 | 1.44   | 0.0101 | α, κ, δ           | +2.50          |
| TZ-4   | LiHSO_4 (vapors) | 200   | 72   | -       | -      | 1 | 2.09   | 0.0058 | α, κ, δ           | +23.00         |
| T-1    | Benzoic acid   | 240   | 8    | 265     | 295    | 1 | 1.5    | 2.18  | 0.0213 | β(γ)            | +2.10          |
| T-2    | Benzoic acid   | 240   | 31   | 400     | 2      | 5 | 9.45   | 0.0155 | α                | -2.10          |
| Z-1    | Benzoic acid   | 240   | 8    | 295     | 350    | 1 | 1      | 4.25  | 0.0189 | α, κ             | +3.86          |

The refractive index profiles (figure 1) were reconstructed by an inverse WKB method after mode spectra measurements at a wavelength of λ=633 nm. For single-mode waveguides, the optical measurements were performed in two media, air and water, and two values of the effective mode index n_eff were obtained, allowing two mode-propagation equations to be written by assumption of a step-like optical profile. Then the depth and surface index change were calculated from both equations for the individually determined n_eff.

The IR absorption spectra (figure 2a) of protonated in vapors and as-grown LT samples were recorded in the wavenumber range of 2700-3700 cm⁻¹ of OH-stretching modes with a Brucker LFS-113 V FTIR spectrometer with a resolution of 1 cm⁻¹. After measuring the IR-absorption spectra, a Gaussian-Lorentzian decomposition procedure was performed. The substrate spectrum (TZ-ref) is extracted from the spectra of protonated samples, so only spectra of PE-layers are present on the histograms. The results are shown in figure 2b.

The quantitative calculations of layer stress have been performed by an ex situ optical interference technique [8, 9]. The role of the substrate is assumed to be of LT with no waveguide on it. Since the deformation of the waveguide follows that of the substrate, the elastic parameters, Young modulus and Poisson’s ratio are taken for the substrates. The change in the interference fringe patterns between the substrate and an optical flat is used to measure the deformation of the layer-substrate system. The
radius of curvature is actually the substrate radius. The error in the radii determined by curvature measurements was 10%. Since the temperature during the process of proton exchange is low, the thermal component of stress is negligible. Thus, the calculated stress is the intrinsic stress for the waveguide layers. It has to be noted that this method for determining stress gives an integral value over the waveguide thickness. Besides, the nature of the stress is determined by its sign. If the sign is negative, the stress is compressive whereas a positive sign corresponds to tensile stress.

3. Discussion

It was established earlier that the profile of the extraordinary index change $\Delta n(z)$ in H:LiTaO$_3$ layers has a step-like form preserved even after annealing at temperatures of up to 320-350 °C [10], so the shape of the optical profile could not be used for phase composition evaluation. An exception is the profile of single-$\alpha$-phase waveguide which tends to a graded shape. The $\alpha$ phase which is the most important for different applications requiring preserving or restoration of the electro-optical properties could be obtained only by annealing of the waveguides obtained in $\beta$, $\gamma$, and $\delta$ phase.

Some results were reported for $\alpha$-phase waveguides obtained in LT by direct proton exchange in benzoic acid vapors at 350 °C [11]. The essential detail of that experiment is the vapor temperature since the transition from high-protonated phases in LT to the lower-protonated $\alpha$-phase starts at about
320 °C [10]. This way the diffusion temperature does not allow other phases other than the α-phase to be formed and the diffusion due to the annealing at such a temperature seems to be a reason for the decrease in $\Delta n$ when the duration of PE is increased [11]. When PE in vapors (PEV) is used at an appropriate temperature instead of in liquid acid, it allows an annealing to be performed simultaneously at a vapor temperature higher than 350 °C, when phase transition to α phase takes place, and high-quality waveguides could be obtained by a one-step technological process. Since in the experiment described here we used vapor temperatures lower than 350 °C for obtaining waveguides by PEV, we could expect that the phase composition of the PE-layers is complex and contains phases with strongly differing lattice parameters. However, we believe that by using higher temperatures of LiHSO$_4$ vapors, α-phase waveguides could also be obtained.

A preliminary evaluation of the possible phases existing in the waveguide layers could be made on the basis of optical profiles of the investigated samples. The considerations performed are based on the phase model for Z-cut Li$_{1-x}$H$_x$TaO$_3$ suggesting that 5 different crystallographic phases could be formed in the PE-layer [4]. According to the phase diagram presented in [4], the determined values of $\Delta n$, for samples obtained by PEV correspond to $\delta$ – phase ($\Delta n = 0.01 – 0.02$) except of TZ-4 having a value of $\Delta n$, lower than 0.01, which corresponds to the α-phase. Since α-phase waveguides cannot be obtained by direct proton exchange [4], when the diffusion temperature is below 350 °C (350 °C is the temperature at which phase transition to α-phase takes place [10]) we could expect the waveguides TZI-3 to have $\delta$- or $\kappa$-phase as well. The fact that $\Delta n$ decreases with increasing proton exchange duration (proton concentration respectively) also confirms the presence of the $\delta$-phase. The other two possible phases (β and γ) require larger values of $\Delta n$. Therefore, the determination of the crystallographic phase of the waveguide could not be performed on the basis of the extraordinary index change only, since it could correspond to both $\kappa$- and $\delta$-phases [4].

The mobility of Li ions and their ability to be exchanged by protons in the lattice of LT is quite a bit lower than in the lattice of the widely used LN [12]. The amount of protons and the depth of their penetration is less than in the case of LN. That is why the PE-waveguides in LT obtained by direct PE are shallow and usually do not support more than one mode and need to be annealed.

Direct proton exchange in pure acid melts (benzoic, pyrophosphoric etc.) provides waveguides in the $\delta$-phase, characterized by strongly reduced nonlinear coefficients in the waveguide region, and post-exchange annealing needs to be performed to restore the electro-optical and nonlinear properties when the $\alpha$-phase is reached [13]. Samples obtained by APE treated over 350 °C undergo phase transformation to $\alpha$ phase (sample T-2), but sample T1 annealed at lower temperatures demonstrates a higher value of $\Delta n$, characteristic for the $\beta$- and $\gamma$-phases.

The IR-absorption spectra (figure 2) show three well-defined bands: at 3488 cm$^{-1}$, polarized perpendicularly to the Z-axis ($\alpha$-phase), at 3500 cm$^{-1}$ with the same polarization ($\beta$- or $\gamma$-phase), and a large unpolarized band at 3200 cm$^{-1}$, which can be assigned to the much higher degree of substitution of Li$^+$ by H$^+$ [14] characteristic for the $\delta$-phase. The shoulder at 3200 cm$^{-1}$ suggests both high value of x (H$^+$ at Li$^+$ positions) and interstitial hydrogen.

The spectra deconvolution (figure 2b) allows some conclusions to be made about the rate of creation of the different monophase sublayers, as well as about the relative quota of each phase to the whole multiphase PE-layer. The fact that the band area of the $\alpha$-phase is the largest proves the dominance of the $\alpha$-phase in the waveguides obtained by PEV in LiHSO$_4$. The analysis of the phase composition confirms this way the presence of more than one phase in the waveguides obtained by PE in LiHSO$_4$ vapors at temperatures lower than 350 °C.

It is well known that the change in the refractive index of ferroelectric materials with doping is due to the changes in molecular refraction, in spontaneous polarization and to elastic deformations in the crystal [15]. When the proton concentration increases, the lattice extends in the direction normal to the surface in order to satisfy the boundary conditions, so in the horizontal plane the PE-layer and the substrate should have identical lattice parameters [16]. This way the deformations introduced by the dopant contribute to the change of the refractive index through the elasto-optic effect. In our case (Z-
cut substrates) deformations should be parallel to the optical axis, and at high values of $x$ the lattice should be under tensile stress, which is confirmed by stress measurements.

Phase identification by measurement of crystal lattice deformations of Z-cut samples in the optical axis direction was performed in [4, 17]. It has been shown that for each phase there is a linear dependence between the increase of the refractive index change and the deformations (the proton concentration respectively), but the coefficient of proportionality is different for each phase. The coefficient changes when a phase transition takes place.

It would be logical to assume that the higher level of the dopant causes stronger deformations of the lattice and therefore stronger mechanical stresses in the PE-layer. The authors of [18] have established that the most strained PE layers are those with a higher level of substitution when the surface damage takes place. The smallest internal stress calculated (table 1) is characteristic for homogeneous and less disturbed layers such as the $\alpha$-phase (T-2) or single-phase ones (T-1).

From a technological point of view, it is interesting to note that the most strained layers have been obtained in two of the cases when PE was performed in vapors (TZ-1 and TZ-4). It is quite possible (especially at higher temperatures and short exchange times) that the kinetic energy of the substituting element transforms into energy of the lattice deformation. Longer diffusion (the temperature and proton source being the same, TZ-2) allows a redistribution of the diffused protons and lattice relaxation. Such low-temperature annealing does not lead to phase transitions and transformations, but probably causes homogenization of the existing phases, this way decreasing the MS in the layer [19]. In the case of TZ-4 the highest stress value is due to longer diffusion at lower temperature when a relatively thick multiphase layer is formed.

The only sample with compressive stress is T-2. It is the $\alpha$-phase layer with the lowest value of MS measured. As it was discussed above, the strain introduced in the lattice after PE should be tensile and directed perpendicularly to the layer’s surface. In the case of Z-cut samples, the Z direction coincides with the optical axis and it is quite possible that the sign “+” or “−” depends on the orientation of the optical axis towards the layer, probably due to the different orientation of the ferroelectric domains in the crystal.

It can be seen in table 2 that there should be a thickness $d_s$ of the sublayer, responsible for the 3200 cm$^{-1}$ band, at which the mechanical stress is minimal. As in the case of LN [19], that thickness is about 0.35 µm.

**Table 2.** The relative quota of the IR spectral bands of the multiphase waveguide layers and the thicknesses of the phase sublayers (corresponding phase quota respectively) compared to the measured stress.

| SAMPLE | IR BAND INTENSITY [%] / PHASE-SUBLAYER THICKNESS [µm] | $\sigma \times 10^9$ [N/m$^2$] |
|-------|------------------------------------------------------|-------------------------------|
|       | 3200 cm$^{-1}$ | 3480 cm$^{-1}$ | 3500 cm$^{-1}$ |                                   |
| TZ-1  | 16.67/0.148  | 62.50/0.556    | 20.83/0.185    | +22.80                           |
| TZ-2  | 22.00/0.271  | 58.00/0.713    | 20.00/0.246    | +3.41                            |
| TZ-3  | 27.40/0.394  | 58.90/0.848    | 13.70/0.197    | +2.50                            |
| TZ-4  | 28.30/0.591  | 62.28/1.302    | 9.43/0.197     | +23.00                           |

The phase model we referred to [4] is based on the fact that each phase has its own specific dependence of the refractive index on proton concentration, which is proportional to the lattice strain $\varepsilon_{33}$ of the proton-exchanged layer [20]. The authors of [20], who have studied the electro-optical
properties of all possible \(H_xLi_{1-x}TaO_3\) phases have observed that the electro-optical effect (the value of the \(r_{33}\) coefficient respectively) decreases monotonically with the rise of mechanical stress (increase of \(x\)), but the authors of [21] have established that the electro-optical coefficient \(r_{33}\) has a minimal value at an intermediate value of \(x\), corresponding to the \(\kappa\)- or \(\beta\)-phase. This contradiction could be explained to some extent through the existence of \(d_s\): by varying the highly protonated sublayer’s thickness we could tune the internal stress and \(r_{33}\), respectively, not changing the value of \(x\) (for given value of \(x\)).

4. Conclusions

In summary, it could be concluded that the independent study of the phase composition of multiphase proton-exchanged waveguides by mode spectroscopy, IR absorption spectroscopy and mechanical stress measurements show that a correlation exists between mechanical stress and the phase composition (hydrogen presence) in the proton-exchanged layer. The stress depends substantially on the technological conditions for obtaining waveguides.

The use of various kinds of melts and technological regimes makes it possible to control to some extent the phase status of the layer obtained, which determines its quality in respect of optical losses and electro-optical properties. Thus, with an appropriate arrangement of the technology it is possible to avoid undesired effects such as phase mixture and formation of highly distorted layers.

The thickness of the phase sublayers having their own bands in the IR spectra could be assessed by spectral deconvolution and optical profile reconstruction. There is a certain thickness of the strongly protonated sublayer corresponding to a minimal stress for the entire PE layer.

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