Stress in LiNbO$_3$ proton-exchanged waveguide layers

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Abstract. Penetration of hydrogen ions in the crystal lattice of LiNbO$_3$ certainly causes stress in the proton-exchanged region, especially when the level of doping is high. In the present study, a correlation between stress and the level of doping (respectively, between stress and the phase composition of the measured layer) has been obtained. Proton-exchanged waveguide layers in X, Y and Z-cut LiNbO$_3$ have been produced at different technological conditions. These layers have been studied by spectroscopic methods for analyzing their phase composition and by the optical integral method for stress measurements. The intrinsic stress which contributes to the better characterization of such optical waveguides was calculated. An attempt to indicate stress correlation to the relative quota of the different phases in the proton exchanged layer is made.

1. Introduction

The easy and fast obtaining of optical waveguides in the electro-optical crystal LiNbO$_3$ by proton exchange (PE) [1] has motivated the attempts to adjust the technology for producing high quality waveguides. The surface layer modified by hydrogen diffusion has a large extraordinary index change ($\Delta n_e$) and thus, a strong waveguide and polarizing effect. The Li$_{1-x}$H$_x$NbO$_3$ layer formed by Li-H ion exchange shows complex phase behavior (up to seven different crystallographic phases - $\alpha$, $\kappa_1$, $\kappa_2$, $\beta_1$, $\beta_2$, $\beta_3$ and $\beta_4$) depending on the hydrogen concentration (value of x) [2] and PE layers may show significant optical losses, instabilities and decrease of the electro-optical coefficient. The number and the type of different phase modifications in crystal solid solutions Li$_{1-x}$H$_x$NbO$_3$, what actually is the proton-exchanged lithium niobate, are determined by the crystallographic orientation and the rate of substitution of Li$^+$ by H$^+$ (x). Each phase originates as an individual sub-layer undergoing phase jumps with gradual change of x. In every single 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 leap.

Infrared spectroscopy has proved its ability to characterize PE layers in LiNbO$_3$ since the Li-H substitution dramatically increases the presence of OH groups in the exchanged layer. IR absorption in the range of OH stretching vibrations (2700-3700 cm$^{-1}$) has been widely used for estimation of the phase composition [3, 4, 5, 6]. The spectra show several bands (at 3488 cm$^{-1}$, 3500 cm$^{-1}$, 3512 cm$^{-1}$, 3250-3280 cm$^{-1}$) which could be attributed to different phases forming the PE layers [3].

An optical integral method contributes to the characterization of the waveguide film from mechanical stress (MS) point of view. 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. Up to now the stress characterization of PE LiNbO$_3$ layers is poorly studied. The purpose of this study is to explore the relation between phase composition and mechanical stress. In this sense proton exchanged (PE) waveguide layers in X-, Y- and Z-cut LiNbO$_3$ have been studied by spectroscopic
methods for analyzing their phase composition and by the optical integral method for stress measurements.

2. Experimental

Proton-exchanged waveguide layers were obtained at the technological conditions described in table 1.

Mode spectra were measured with resolution of ~10⁻⁶ at λ=633 nm by using prism coupling, and the inverse WKB method [7] was used for refractive index profile reconstruction. In cases of single-mode waveguides, the depth and surface index change were calculated by sequential iterations when assuming a steplike profile.

### Table 1. Technological and waveguide parameters of the proton-exchanged waveguides: (T – temperature, t – duration of the PE process, T_a and t_a – temperature and duration of the annealing, M - number of waveguide modes at λ = 633 nm, Δn_e – extraordinary refractive index change, d – waveguide depth)

| Sample | Sample environment | T (°C) | t (h) | M  | Δn_e | d (μm) | Phase composition (Spectroscopic evidence) |
|--------|--------------------|--------|-------|----|------|--------|------------------------------------------|
|        |                    |        |       |    |      |        | Mode                                      |
| Z-1    | LiHSO_4 (vapors)   | 250    | 3.50  | 6  | 0.1491 | 2.66   | β₁,β₂,β₃, β₁,β₂,β₄, κ₁/κ₂ (α)            |
| Z-2    | LiHSO_4 (vapors)   | 160    | 2.00  | 1* | 0.1529 | 0.18   | β₁ (i=1-4), β₁ (i=1-4), κ₁/κ₂ (α)        |
| Z-3    | LiHSO_4 (vapors)   | 160    | 4.00  | 1  | 0.1480 | 0.28   | β₁,β₂, β₁,β₂,(β₁), κ₁/κ₂ (α)             |
| Z-4    | LiHSO_4 (melt)     | 160    | 7.00  | 1  | 0.1463 | 0.33   | β₁,β₂, β₁,β₂, κ₁/κ₂ (α)                  |
| Z-7    | LiHSO_4 (vapors)   | 180    | 5.00  | 1  | 0.1384 | 0.54   | β₁,β₂, β₁,β₂,(β₁), κ₁/κ₂ (α)             |
| ZN-1   | NH₄HSO_4 (melt)    | 230    | 3.33  | 9  | 0.1508 | 2.47   | β₁,β₂,β₃, β₁,β₂,β₃, κ₁/κ₂ (α)            |
| ZN-5   | LiHSO_4 (melt)     | 175    | 1.50  | 1  | 0.1222 | 0.62   | β₁,β₂,β₃, κ₁/κ₂ (α)                      |
| X-2    | LiHSO_4 (vapors)   | 160    | 2.00  | 1  | 0.0999 | 0.37   | β₁,β₂, β₁,β₂, κ₁/κ₂ (α)                  |
| X-3    | LiHSO_4 (vapors)   | 160    | 4.00  | 1  | 0.1234 | 0.52   | β₁,β₂, β₁,β₂, κ₁/κ₂ (α)                  |
| X-4    | LiHSO_4 (vapors)   | 160    | 7.00  | 1  | 0.1090 | 0.70   | β₁,β₂, β₁,β₂, κ₁/κ₂ (α)                  |
| Y-1    | 1)Benzoic acid     | 230    | 0.50  | 3  | 0.1360 | 2.75   | β₁,(i=1-3), kᵢ/k₂ (α)                     |
|        | 2) Air             | 350    | 1.00  | 3  | 0.1360 | 2.75   | β₁,(i=1-3), kᵢ/k₂ (α)                     |
|        | 3)Benzoic acid     | 230    | 0.17  | 3  | 0.1360 | 2.75   | β₁,(i=1-3), kᵢ/k₂ (α)                     |
| Y-2    | Benzoic acid + 0.5% Lithium benzoate | 230 | 3.00  | 3  | 0.1134 | 1.56   | β₁, kᵢ/k₂ (α)                           |
| Y-3    | Benzoic acid + 1% Lithium benzoate | 230 | 7.00  | 4  | 0.1113 | 2.85   | β₁, kᵢ/k₂ (α)                           |
| Y-4    | 1) Cinnamic acid vapors | 300 | 0.50  | 3  | 0.1410 | 1.52   | β₁,(i=1-3), kᵢ/k₂ (α), β₁,(i=1-3), kᵢ/k₂ (α) |
|        | 2) Cinnamic acid melt | 230 | 0.08  | 3  | 0.1410 | 1.52   | β₁,(i=1-3), kᵢ/k₂ (α), β₁,(i=1-3), kᵢ/k₂ (α) |

* at λ = 458 nm
IR absorption spectra were recorded in the wavenumber range of 2700-3700 cm\(^{-1}\) of OH stretching modes with FTIR spectrometer (Brucker LFS-113 V) with a resolution of 1 cm\(^{-1}\). A Gaussian-Lorentzian decomposition procedure was applied to them. Figure 1 illustrates the distribution of peak frequencies and integrated intensities of the spectral components. Since the component due to the substrate \(\alpha\)-phase was extracted from the spectra after the deconvolution, only the components of the layers’ spectra are present in the histograms. The results allow the relative quota of each band to be calculated in \% (table 2).

**Table 2.** The relative quota of the waveguide layer IR spectral bands (corresponding phase quota respectively) compared to the stress measured.

| SAMPLE | IR BAND INTENSITY [%] | \(\sigma \times 10^9\) [N/m\(^2\)] |
|--------|----------------------|-------------------------------|
|        | 3280 cm\(^{-1}\) | 3480 cm\(^{-1}\) | 3500 cm\(^{-1}\) | 3512 cm\(^{-1}\) |
| Z-1    | 16.39                | 9.12                        | 55.83             | 18.77             | -0.95      |
| Z-2    | 27.33                | 11.65                       | 25.54             | 35.39             | -19.83     |
| Z-3    | 20.74                | 22.00                       | 57.14             | -                  | -4.21      |
| Z-4    | 18.48                | 21.75                       | 59.89             | -                  | -6.43      |
| Z-7    | 17.42                | 57.96                       | 13.91             | 10.68             | -2.17      |
| ZN-1   | 23.32                | 6.69                        | 57.22             | 11.92             | -2.45      |
| ZN-5   | 30.66                | 16.94                       | 52.30             | -                  | -1.17      |
| X-2    | 48.55                | 36.30                       | 15.12             | -                  | -12.3      |
| X-3    | 48.95                | 33.95                       | 17.00             | -                  | -0.45      |
| X-4    | 61.72                | 22.95                       | 15.31             | -                  | 1.15       |
| Y-1    | 0.20                 | 58.11                       | 23.89             | 17.84             | -0.01      |
| Y-2    | 0.05                 | 26.60                       | 71.48             | 1.85              | -0.54      |
| Y-3    | 0.08                 | 15.53                       | 69.44             | 1.76              | -0.29      |
| Y-4    | 0.09                 | 37.78                       | 38.81             | 23.23             | -0.27      |

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 lithium niobate with no waveguide on it for each orientation – X, Y and Z. Since the deformation of the waveguide follows that of the corresponding cut substrates, the elastic parameters, Young modulus and Poison’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 vapor temperature during the process of proton exchange is low, the thermal component of the 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 bulk. Besides, the nature of the stress is determined by its sign. If the sign is minus, the stress is compressive; the sign plus corresponds to tensile stress.
Figure 1. Schematic presentation of frequency position and intensity of the components in spectra of Z-cut (a), X-cut (b) and Y-cut (c) samples.
3.1. M-line spectroscopy

The values of extraordinary refractive index change $\Delta n_e=0.15$ for Z-1 and ZN-1 and its gradual change to 0.12 on the optical profiles of the waveguide lead to the suggestion that these waveguides should contain the $\beta_1$-phase which is characterized by a higher level of proton doping compared to monocrystalline $\text{H}_x\text{Li}_{1-x}\text{NbO}_3\ (0.65\leq x\leq0.7)$ [2]. The $\beta_4$-phase can exist only in $Z$-cut proton-exchanged lithium niobate and only together with the $\beta_1$ and $\beta_1$-phases of lower value of $x$: 0.53$\leq x\leq0.65$ for the $\beta_3$-phase and 0.44$\leq x\leq0.52$ for the $\beta_1$-phase. Thus, the waveguides Z-1 and ZN-1 consist of at least three $\beta_i$-phases: $\beta_1$, $\beta_3$ and $\beta_4$. The other Z-cut single-mode waveguides should be in $\beta_1$, $\beta_1+\beta_2$ or $\beta_1+\beta_3+\beta_4$ – phase since the value of $\Delta n_e$ exceeds 0.12, indicating that $\beta_i$-phase or phases have been formed during the PE process [2].

The same considerations applied to the X- and Y-cut samples lead to the conclusion that X-3 contains a $\beta_3$-phase [2], which can be found only together with a $\beta_1$-phase. The $\beta_4$-phase could not be formed in X-cut LiNbO$_3$ [3]. The lower values of $\Delta n_e$ for X-2 and X-4 mean that these layers could contain $\beta_1$ or $\beta_1+\beta_2$ phases. The shape of the optical profile could not be followed since the waveguides are single-mode. The optical profiles of Y-1 and Y-4 and the high surface refractive index change are characteristic for waveguides consisting of highly protonated $\beta_i$-phases ($i=1$-$3$) (0.56$\leq x\leq0.65$) and a layer of $\alpha$-phase (0$\leq x\leq0.12$) or $\kappa_1/\kappa_2$ phases (0.12$\leq x\leq0.56$) between them and the substrate. The optical parameters of Y-2 and Y-3 correspond to the coexistence of $\beta_1$ and $\kappa_1/\kappa_2$ phases. Y-2 has a steplike optical profile with a maximal index change of $\Delta n_e=0.11$. Thus, that waveguide should contain the $\beta_1$-phase - the only one which could be obtained by low-temperature direct proton exchange in Y-cut LiNbO$_3$ [10]. The profile shape of Y-4 shows [11] that the layer should consist of a $\beta_1$-phase together with $\kappa_1/\kappa_2$ or $\alpha$-phase which is due to the higher percent of lithium benzoate in the melt compared to the case of Y-2.

3.2. IR-spectra

As it was discussed earlier [3, 4], a band centered at 3488 cm$^{-1}$ in the IR spectra is attributed to the $\alpha$-phase. All other bands could be assigned to the phases formed by PE: the broad band centered at 3250-3280 cm$^{-1}$ - to the $\beta_3$, $\beta_3$ and $\beta_4$ phases, the band at 3500 cm$^{-1}$ - to the $\beta_4$, $\kappa_1$ and $\kappa_2$ produce peaks between 3488 cm$^{-1}$ and 3500 cm$^{-1}$ (intermediate values between the $\alpha$-phase and the $\beta_1$-phase) and are spectroscopically indistinguishable. For the strongly protonated samples, a fourth additional component emerges at about 3512 cm$^{-1}$ which could be attributed to phases with higher degree of doping (the $\beta_4$ only in case of Z-cut samples). Thereby the evolution of the bands assigned to different phases versus the variations in the technological parameters could be followed. Thus, the histograms show that all samples consist of $\alpha/\kappa_1/\kappa_2$, $\beta_1$ and $\beta_4$ phases, but the technological regime chosen reflects on the thickness of sublayers formed by these phases. The contribution of the $\beta_3$-phase is stronger in samples with higher $\Delta n_e$, i.e. higher level of proton doping. The contribution of $\alpha/\kappa_1/\kappa_2$ is stronger in samples obtained at regime including annealing (Y-1) or annealing-like step (Y-4). The contribution of $\beta_1$ is stronger for samples obtained by direct proton exchange (Y-2 and Y-3). It should also be noted that all the peaks except of a large shoulder at 3280 cm$^{-1}$ are polarized showing that OH bonds lay in the oxygen planes of the crystal. The unpolarized band indicates the presence of hydrogen in interstitial positions out of the oxygen planes, which usually means a higher level of doping.

3.3. Stress measurements

All but one samples studied show compressive stress regardless of crystal orientation. Such a behavior is not surprising. The network of bonds is distorted by the substitution of $\text{H}^+$ for $\text{Li}^+$ in the LiNbO$_3$ lattice. The ionic radius of $\text{Li}^+$ (1.55 Å) is higher than that of $\text{H}^+$ (0.46 Å). For all crystal orientations of the substrate, balancing forces are required to sustain equilibrium acting in compression to adjust the structure to the smaller-sized component. One of the samples (X-4) shows tensile stress. According to
It could be seen that the most stressed is the layer with the largest quota of the 3512 cm$^{-1}$ band (Z-2) and the least stressed is the Y-1 waveguide, where the band at 3480 cm$^{-1}$ ($\alpha$ or $\kappa$, phases) has largest quota. X-2 is stressed higher than other samples although it does not have the component at 3512 cm$^{-1}$. It seems that the main role in mechanical stress here is played by the quota of low-protonated phases (alpha or $\kappa$) – it is lower than the quota of the 3280 cm$^{-1}$ shoulder, which usually is related to interstitial hydrogen, the situation when the lattice is sufficiently disturbed. The only sample with positive stress is X-4, which has the largest shoulder centered at 3280 cm$^{-1}$ indicating the stronger presence of interstitial hydrogen. From 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 (Z-1 and X-2). It is quite possible (especially at higher temperatures, i.e. 250°C) that the kinetic energy of the substituting element transforms into energy of lattice deformation. In spite of the lower temperature (X-2), the larger diffusion coefficient for X-cut lithium niobate leads to the same effect. A longer diffusion when the temperature and proton source are the same decreases the MS (samples X-3 an X-4), probably due to the simultaneous process of annealing when a relaxation redistribution of the diffused protons takes place. Such low-temperature annealing (160°C) does not cause phase transitions and transformations, but probably causes homogenization of the existing phases, this way decreasing the MS in the layer.

As it could be expected, the lowest values of the magnitude of intrinsic stress were obtained with Y-cut samples. This is due to the optimization of technological conditions for obtaining of deep waveguides with high extraordinary index change in so oriented crystals. It is well known that in case of Y-cut substrates, PE leads to a fast damage of their surface exactly because of the higher MS arising under longer diffusion. Low values of MS in our case correlate with the absence of shoulders in the IR absorption spectra of these layers (figure 1-c). The appearance of 3512 cm$^{-1}$ component means only a high value of x (as it could be seen from the optical measurements), but not the presence of interstitial hydrogen. The shoulder at 3280 cm$^{-1}$ suggests both high value of x ($H^+$ at Li$^+$ positions) and interstitial hydrogen (figure 1-a, b). At high values of x, the lattice should be compressed, but the interstitial hydrogen stretches the lattice, so when the MS is positive, we could suggest that the balance is disturbed in favor of the interstitial instead of the substituting one.

Since LN is an anisotropic crystal, it should be expected that the stress is different along different directions, i.e. the bending should be different along each of the crystallographic directions. It is important to note that no elliptic interference fringes were observed during stress measurements. This means that the layer has lost its anisotropy which indeed corresponds to the total loss of electro-optical properties at high level of doping. Such kind of quasi-amorphization (paraelectric state) has been observed when Raman spectroscopy was applied for waveguide characterization showing that all $\beta_i$-phases ($i$=1-4) are paraelectric [13]. Actually, it is well known that at higher values of x the lattice changes from perovskite to cubic one [14].

**Conclusions**

The phase composition of proton-exchanged waveguides was studied by mode spectroscopy, IR absorption spectroscopy and mechanical stress measurements. The methods used independently gave information for the phase composition of the waveguide layer of multiphase proton-exchanged waveguides in LiNbO$_3$, and for the relative contribution of each of them.

It is demonstrated that a correlation exists between mechanical stress and the phase composition/hydrogen presence in the proton-exchanged layer as well as that the stress depends substantially on the technological regimes for obtaining waveguides. It has been shown that highly protonated phases and deep waveguides with very low mechanical stress could be obtained in Y-cut LiNbO$_3$ at specific technological conditions.

The substitution-interstitial proton ratio could be estimated from the sign and the magnitude of the mechanical stress calculated. There should be suitable fabrication conditions for obtaining a phase composition corresponding to a minimal stress in the waveguide layer.

The measurements confirm the paraelectric state of highly protonated ($\beta_i$, $i$=1-4) phases since such layers had lost their anisotropy.

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