Optical and Structural Properties of Proton Exchanged MgO:LiNbO$_3$ waveguides

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We show that proton exchanged MgO:LiNbO$_3$ optical waveguides exhibit complex structural chemistry which is different from known for congruent material. It’s shown that Annealing Proton Exchange process leads to strong degradation of surface region of waveguides, but Soft Proton Exchange preserves the crystal structure of MgO:LiNbO$_3$.

Keywords: proton exchange, magnesium doped lithium niobate, waveguide, crystal structure.

Introduction

Lithium niobate, LiNbO$_3$, is very important ferroelectric crystal with various acoustical, integrated optical and optoelectronic applications. Integrated optical devices require material improvements in optical homogeneity and optical damage resistance. It is known [1-3], that resistance to optical damage in LiNbO$_3$ is effectively improved if more than 4.5 mol.% MgO is added to the melt.

One of basic methods to make optical waveguides in LiNbO$_3$ crystals is proton exchange (PE) [4]. Despite the simplicity of the proton exchange technique, the PE LiNbO$_3$ waveguides exhibit very complex structural chemistry. Our works [5,6] have allowed us to identify seven different crystallographic phases, $\beta_4$, $\beta_3$, $\beta_2$, $\beta_1$, $\kappa_2$, $\kappa_1$ and $\alpha$- $\mathrm{H}_x\mathrm{Li}_{1-x}\mathrm{NbO}_3$, which can be realized in the PE LiNbO$_3$ waveguides. Annealing is an important parameter in the fabrication of PE waveguides. Actually, most of the published results were obtained using PE waveguides, whose index profiles indicate that they are in the $\alpha$-phase. These waveguides can be fabricated by two step process, including proton exchange and subsequent annealing (APE waveguides [7]) or by one step process, so-called Soft Proton Exchange (SPE) [8,9]. In contrast to APE LiNbO$_3$, the SPE LiNbO$_3$ waveguides preserve nonlinear coefficients of bulk material [10].

Several fundamental issues in the fabrication of waveguides by proton exchange in MgO:LiNbO$_3$ have not been addressed to date. Previously published investigations of PE MgO:LiNbO$_3$ waveguides have been incomplete and restricted to particular fabrication process [11-15].

Up to date, there are no reports about crystallographic study on proton exchange layers in Mg:LiNbO$_3$. In the present paper we shall show that structural and optical properties of the different types of PE MgO:LiNbO$_3$ waveguides depend strongly on fabrication conditions.

Preparation of samples and their characterization

PE waveguides were fabricated in optical grade X-cut MgO:LiNbO$_3$ substrates, containing 5.5 mol.% of MgO, supplied by Crystal Technology, Inc.

As the source of PE we used benzoic acid whose acidity can be reduced by adding up to 5 wt.% of lithium benzoate. Postexchange annealing at 330$^\circ$C was used to modify the parameters of the waveguides. HTPE process [9] has been performed in the mixture of stearic acid and lithium stearate. Soft Proton Exchange process has been realized by HTPE in melts with lithium stearate concentration higher than the threshold value. In this case uniform $\alpha$-phase waveguides are formed.

In order to find modes effective indices, we measured excitation angles of dark m-lines of modes with one prism coupler setup at the 633 nm wavelength. The refractive index profiles throughout the guide depth were reconstructed by the IWKB technique [16]. The strains perpendicular to the substrate surface, $\varepsilon_{33}$, were calculated from rocking curves on plane (220) obtained by double-crystal X-ray diffractometer DRON-3 (Cu K$_{\alpha_1}$ radiation, Si (311) monochromator):
\[ \varepsilon''_{33} = -\Delta \theta_{hkl} \cdot \cot \theta_{hkl} \]  \hspace{1cm} (1)

where \( \theta_{hkl} \) is the Bragg angle of the reflected surface plane for stress-free substrate.

**Experimental results**

Fig.1 shows the surface extraordinary index increase, \( \Delta n_e \) as a function of strain \( \varepsilon''_{33} \) for X-cut MgO:LiNbO\(_3\) substrates. One can see that this structural phase diagram is absolutely different from such diagram, obtained for congruent material [6]. No doubt that some MgO:H\(_x\)Li\(_{1-x}\)NbO\(_3\) phases exist, however, in contrast to structural phase diagram for congruent material [6], the possible phase transitions for PE MgO:LiNbO\(_3\) are not so evident.

![Fig.1](image1.png)

**Fig.1**. Dependence of the extraordinary index variation \( \Delta n_e \) measured at \( \lambda = 633 \) nm versus the surface value of deformation \( \varepsilon''_{33} \) normal to surface plane.

![Fig.2](image2.png)

**Fig.2** Refractive index change (rectangular dots, solid curve) and strains \( \varepsilon''_{33} \) (circular dots, dotted curve) as a function of melt composition in stearic acid + lithium stearate melts at 370°C.

![Fig.2](image2.png)

**Fig.2** shows the variation of the MgO:H\(_x\)Li\(_{1-x}\)NbO\(_3\) surface value refractive index increment, \( \Delta n_e \) and deformations \( \varepsilon''_{33} \) as a function of the LS content for HTPE at 370°C. The two regions can be clearly recognized. These regions correspond to, at least, two different phases. The \( \Delta n_e \) and \( \varepsilon''_{33} \) are found to be largely independent of melt composition for dilution up to threshold value, \( \rho_0 \) (Fig.2). The \( \alpha\)-phase MgO:H\(_x\)Li\(_{1-x}\)NbO\(_3\) fabricated at \( \rho > \rho_0 \) is characterized by low index increment and deformations.

The rocking curves on plane (220) and refractive index profiles for X-cut PE MgO:LiNbO\(_3\) samples obtained under different exchange and annealing conditions are presented in Fig. 3.

As exchanged waveguides, similar to PE waveguides in congruent LiNbO\(_3\), are characterized by positive deformations \( \varepsilon''_{33} \). Three peaks can be clear recognized at X-ray rocking curve (Fig.3a). Most probably, these three peaks correspond to three different phases in PE MgO:LiNbO\(_3\). However, after some time of annealing, \( \varepsilon''_{33} \) becomes negative. It is possible to obtain waveguide with large index increment (\( \Delta n_e = 0.1 \)) and with zero deformation \( \varepsilon''_{33} \) (Fig.3b). Future annealing leads to increasing of absolute value of negative deformation.
It is very surprising that well annealed APE Mg:LiNbO₃ waveguides contain distorted layer with deformations $\varepsilon''_{33} \approx -3 \cdot 10^{-3}$. Rocking curves for APE samples with $\Delta n_e < 0.1$ show broad additional peak (Fig. 3c). Precise polishing shows that thickness of this layer is very close to thickness of initial as-exchanged layer.

It was obtained that this distorted layer is not been removed even after long reverse proton exchange process in LiNO₃-KNO₃-NaNO₃ melt. IR spectral measurements show that after RPE process at 330°C during 15 h, the intensity of $\nu$-OH absorption at 3485 cm⁻¹ becomes similar to one for initial MgO:LiNbO₃ crystal, however the rocking curve shows additional peak (Fig. 4) with even larger deformation that for initial APE sample.

Therefore, one can conclude that APE process leads to structural damage of surface layer, that can be a reason of additional scattering of light in APE MgO:LiNbO₃ waveguides.

Fig. 3c shows the X-ray rocking curve for HTPE MgO:LiNbO₃ sample fabricated at 370°C for 5 h at the melt with $\rho=0.7\%$. One can see, that in contrast to $\alpha$-phase MgO:HₓLi₁₋ₓNbO₃ fabricated by APE technology (Fig.3c), the $\alpha$-phase MgO:HₓLi₁₋ₓNbO₃ prepared by HTPE technology characterized by absence of distorted surface layer. Therefore, the HTPE process preserves the crystal structure of $\alpha$-phase MgO:LiNbO₃ waveguides. It is expected that such waveguides would show lower optical losses than APE waveguides.

**Conclusion**

The crystal structure and optical properties of PE MgO:LiNbO₃ structures are strongly depended on proton exchange and annealing conditions. Some crystal phases MgO:HₓLi₁₋ₓNbO₃ can be generated on surface of MgO:LiNbO₃ single crystals depending on exchange and annealing conditions. It has been shown that traditional for congruent LiNbO₃ crystals APE technology leads to formation of distorted layer at the surface of MgO:LiNbO₃. It is expected that it would drastically increase the optical losses in APE MgO:LiNbO₃ waveguides. In contrast, the HTPE MgO:LiNbO₃ waveguides do not contain any distorted layer at the surface region. Therefore, such waveguides should show lower propagation losses.
References


Fig. 4 X-ray rocking curve for PE MgO:LiNbO3 sample, fabricated at benzoic acid melt at 220°C for 6 h then annealed at 330°C for 552 h and treated at the melt LiNO3-KNO3-NaNO3 at 320°C for 24 h.

Fig. 5. X-ray rocking curve for HTPE MgO:LiNbO3 sample fabricated at 370°C for 5 h at the melt with ρ=0.7%.