

Phase composition and electro-optic properties of channel proton-exchanged LiNbO₃ waveguides

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ABSTRACT

Micro-Raman spectroscopy and Raman data calibration are proposed for quantitative study of the proton-exchanged LiNbO₃ channel waveguides, which contain the different H_xLi_{1-x}NbO₃ phases, depending on the fabrication conditions. The spectroscopic parameters, phase composition and electro-optic properties of these waveguides have been found to be depending on the small variation of stoichiometry in the near-congruent lithium niobate substrates used for waveguides fabrication.

Keywords: proton exchange, lithium niobate, waveguide, micro-Raman spectra, electro-optic coefficient.

1. INTRODUCTION

Today proton exchange (PE) is a firmly established technology for producing integrated optics devices based on LiNbO₃ crystal, since it makes it possible to design the waveguides with low optical losses and high electro-optic (EO) efficiency [1, 2]. However, the dependence of the main waveguide parameters on the stoichiometry of virgin crystals has been established at variation of a mol fraction of Li₂O within wide range: from congruent to stoichiometric composition [3]. This dependence may be assumed to be one of important source of the problem with the technological reproducibility of PE waveguides fabrication in the so-called congruent lithium niobate crystals [6]. Note that the congruent crystals are used primary for fabrication of the industrial integrated-optical devices [1, 2]. Therefore, the possible influence of these small stoichiometry variations on parameters of the PE waveguides has been subjected to our study.

At the same time, there is the need to develop a nondestructive method for determining the phase composition and estimating the EO coefficients for channel PE LiNbO₃ waveguides consisting of various devices, e.g. a multifunction integrated-optical chip (MIOC) [2]. In order to solve this problem, we propose to use the micro-Raman spectroscopy, since the use of a confocal Raman microscope provides the high spatial resolution (~1 μm), which is enough for a detailed study of channel waveguides.

2. EXPERIMENTAL

Planar and channel optical waveguides were prepared on plates of Z-cut LiNbO₃ crystal by PE, using benzoic acid. In order to obtain waveguides of different phase compositions, the processing conditions were varied over a broad range [2]. Several sets of planar and channel waveguides were fabricated on two types of the near-congruent LiNbO₃ substrates supplied by the different manufacturers. Division of substrates for these two types was made by us in accordance with a mol fraction of Li₂O [3]: [Li₂O] = 48.38 mol% for type I and [Li₂O] = 48.5–48.6 mol% for type II.

To determine the phase composition and estimate EO properties of PE waveguides, we use micro-Raman spectroscopy, as an each H_xLi_{1-x}NbO₃ phase has a specific spectrum [4]. Raman spectroscopy was performed on planar and channel waveguides with the aid of an Jobin Yvon LabRam spectrometer operating at excitation wavelengths of 514.5 and 632.8 nm. In the setup, a linearly polarized laser beam was focused to ~1.0 μm spot on the surface of a sample.

3. EXPERIMENTAL RESULTS AND DISCUSSION

The channel PE waveguides have found the greatest application in MIOCs with LiNbO₃ crystals [1, 2]. The evaluation of phase composition of these waveguides is an important step in design and optimization of such MIOCs. However, the X-ray diffraction, m-line mode analysis, UV- and IR-spectroscopy, which are the effective methods for study of the planar waveguides [3-5], don't allow to study the optical channel PE waveguides due to their small size (in our case, the channel width was 5.6 – 6.8 μm).

The most widely used approach is to apply the test samples of planar waveguides, i.e., these test samples and the channel waveguides are simultaneously treated to the PE processing and post-exchange annealing [4]. This approach is based on assumption that the channel waveguide has the same phase composition as the planar waveguides on the test samples. Indeed, the phase composition of the planar waveguides may be evaluated by the standard methods mentioned above. However, in the case of a narrow channel waveguide, the proton concentration x ($H_xLi_{1-x}NbO_3$) is different comparative to the etalon sample of planar waveguide, so the phase compositions of the channel waveguides may be other one [5]. In fact, the micro-Raman data confirm this finding and show that the Raman spectra of different phases are different from each other. Besides, a confocal microscope of micro-Raman spectrometer provides the high spatial resolution ($\sim 1 \mu m$), enough for the detailed study of channel waveguides, Fig. 1.

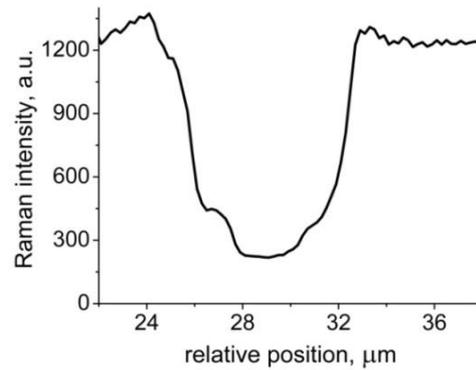


Figure 1. Micro-Raman profile of MIOC for the band at 871 cm^{-1} in direction transverse to a channel waveguide containing the κ_1 -phase. He-Ne laser ($\lambda = 632.8 \text{ nm}$), polarization geometry - (XX).

For calibration of the micro-Raman data, we used so-called “etalon” samples of the planar waveguides those phase compositions and values of the EO coefficient r_{13} were determined by the IR and UV spectroscopy methods with the aid of approach developed by us [4]. This lets us establish clear correlations between the parameters of the micro-Raman spectra and the phase composition, which we used to optimize the fabrication of EO phase modulators based on PE $LiNbO_3$ channel waveguides. However, this approach is based on micro-Raman spectra measurements within the lattice vibrations range ($150 - 1000 \text{ cm}^{-1}$) of the $LiNbO_3$ phonon spectrum [4]. Because of the strong overlapping of micro-Raman signals from the PE waveguide and a near-surface part of $LiNbO_3$ bulk, the identification of phase composition of the annealed channel PE waveguides requires the extra efforts for separation of these signals in an integral micro-Raman spectrum.

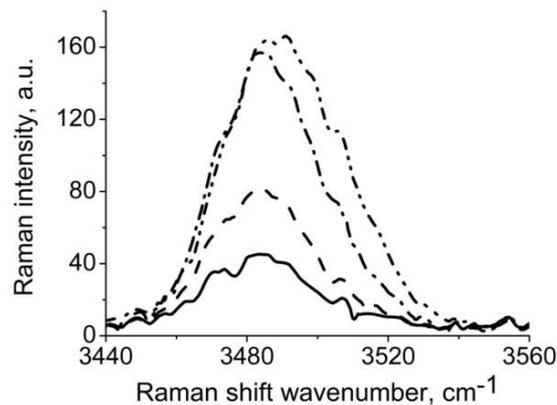


Figure 2. Micro-Raman spectra measured in the frequency range of stretching OH-band in the substrates and channel waveguides: type I substrate, type II substrate, α^* -phase waveguide in type I substrate, and α^{**} -phase waveguide in type II substrate. This samples order corresponds to spectra sequence from bottom to top at 3507 cm^{-1} . Ar⁺-laser ($\lambda = 514.5 \text{ nm}$), polarization geometry - (XX).

Our novel finding consists of the fact, that micro-Raman measurements within the stretching OH-band near 3500 cm^{-1} (Fig. 2) give the more detailed information about phase composition of the annealed PE waveguides. It was established that PE tends to generate an OH-band at 3507 cm^{-1} , while various dopants tend to produce peaks at slightly higher wave numbers [6]. According to this finding, the 3507 cm^{-1} band is due to stressed material created by PE, while our optimal annealing process reduces the proton concentration and leaves the crystal lattice in a low stress resulting in the 3484 cm^{-1} peak position.

It has been established that the micro-Raman spectra of the PE waveguides depend on small stoichiometry variation in near-congruent lithium niobate substrates. For example, micro-Raman study demonstrates the marked difference between the PE channel waveguides fabricated in the type I and type II substrates, Fig. 2. Therefore it can be expected, that some correction of MIOC optimization procedure, which is based on spectroscopic data, would be necessary to perform. The spectra shown in Fig.2 were measured for the PE waveguides annealed at the conditions (360 °C, 6 hours), which are optimal for the type I substrates. The extra annealing of waveguides in the type II substrates reduces the high-frequency shoulder of OH-band, that allows to assume a homogeneous α^* -phase composition of waveguides in the type II substrates, similar to the type I substrates, Fig. 2. Assignment of the phase composition of the channel PE waveguides to α^* or α^{**} phases (Table 1) was based on micro-Raman data on OH-band, according to definition of phase compositions made with Raman- and IR-spectroscopy data for OH-band in the planar PE waveguides [4, 5].

TABLE 1. PARAMETERS OF PE CHANNEL WAVEGUIDES WITH THE DIFFERENT PHASE COMPOSITIONS.

Substrate type	phase	I_{LO}/I_{TO}^*	r_{13}/r_{13}^{0**}
I	α^*	3.3–3.5	0.90–0.94
II	α^{**}	3.0–3.4	0.82–0.92
I and II	κ_1	1.1–1.5	0.19–0.26

*- I_{LO} is the intensity of $A_1(LO)$ -phonon line observed at $\nu = 871 \text{ cm}^{-1}$ (Fig. 1); I_{TO} is the intensity of $E(TO)$ -phonon line at 580 cm^{-1} ;

** - normalized values of the EO coefficient r_{13}/r_{13}^0 were calculated from micro-Raman data, where r_{13}^0 is the value for a virgin LiNbO_3 .

The experimental data obtained by us indicate the significant reduction of r_{13} immediately after the PE process (β_i -phases [4, 7]). However, after appropriate annealing the value of r_{13} are almost re-established and arrive at values approximately 3/4 of the corresponding bulk LiNbO_3 values, Table 1.

Optical measurements showed that Li depletion leads to lower values of Δn_e induced by PE [3]. This fact underlines the importance of crystal stoichiometry for obtaining reproducible results and high performance of the waveguiding devices. For example, only a few percent changes of the effective refractive index in the channels of a directional coupler can break down its action [3]. At the other hand, the dependence of micro-Raman spectra of the PE waveguides on a small variation of the substrate stoichiometry could be used for quick identification of crystals of the same stoichiometry which is very important for reproducible technological results.

4. CONCLUSIONS

This study allows for developing the new method for evaluation of phase composition and EO properties of the narrow PE waveguides in lithium niobate. This method is based on combination of the micro-Raman technique and special calibration procedure using the etalon samples of the planar PE waveguides. The methods used could contribute to the improvement of the PE technology towards a strict control of the phase composition, i.e. of the waveguide characteristics and quality.

REFERENCES

- [1] M. Bazzan, C. Sada: Optical waveguides in lithium niobate: Recent developments and applications, *Applied Physics Reviews*, vol. 2, 040603, Oct. 2015.
- [2] Yu.N. Korkishko, et al.: Proton-exchanged LiNbO_3 and LiTaO_3 optical waveguides and integrated optic devices, *Microelectron. Eng.*, vol. 69, pp. 228-236, Jun. 2003.
- [3] M. Kuneva, S. Tonchev: Spectroscopy of optical waveguiding layers, *Bulgarian Chemical Communications*, vol. 43, pp. 276-287, Apr. 2011.
- [4] S.M. Kostritskii, et al.: Subsurface disorder and electro-optical properties of proton-exchanged LiNbO_3 waveguides produced by different techniques, *J. Europ. Opt. Soc. Rap. Public.*, vol. 9, 14055, Dec. 2014.
- [5] S.M. Kostritskii, et al.: Leakage of a guided mode caused by static and light-induced inhomogeneities in channel HTPe- LiNbO_3 waveguides, *Proc. SPIE*, vol. 4944, pp. 346-352, Apr. 2003.
- [6] J.M. Cabrera, et al.: Hydrogen in LiNbO_3 , *Adv. Phys.*, vol. 45, pp. 349-394, 1996.
- [7] A. Mendez, et al.: Comparison of the electro-optic coefficient r_{33} in well-defined phases of proton exchanged LiNbO_3 waveguides, *Appl. Phys. B*, vol. 73, pp. 485-488, Oct. 2001.