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FABRICATION AND CHARACTERIZATION OF PROTON EXCHANGED LITHIUM NIOBATE PLANAR OPTICAL WAVEGUIDES

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Abstract. Proton exchange process in benzoic acid with 1% lithium benzoate added is used to fabricate planar waveguides in LiNbO_3 . The surface quality of the waveguides obtained is compared with that of samples exchanged in pure benzoic acid. Planar waveguides in Z-cut substrates fabricated at three different temperatures: 210, 220 and 230°C for 7 hours were systematically studied. The diffusion constant D_{0z} and activation energy E_a in the diffusion equation were calculated from the measured effective indices n_{eff} and compared with those obtained by other authors in the case of TIPE process and for exchange in pure benzoic acid. The waveguide stability with time is investigated. IR-spectra of virgin LiNbO_3 as well as of exchanged layers were recorded and considered as an indicator of the waveguiding effect, waveguide optical quality and parameter stability.

Резюме. Протонным обменом в бензойной кислоте с добавлением 1% бензоата лития получены планарные оптические волноводы в LiNbO_3 . Качество поверхности полученных волноводов сравнено с качеством поверхности образцов X-среза, обработанных чистой бензойной кислотой. Проведено систематическое исследование волноводов в образцах Z-среза, полученных при трех температурах расплава — 210, 220, 230°C и продолжительности обмена 7 часов. Из измеренных значений эффективных показателей n_{eff} получены величины диффузионной константы D_{0z} и энергии активации E_a в уравнении диффузии, которые сравнены с величинами, полученными другими авторами в случаях обмена в чистой бензойной кислоте в TIPE. Исследована устойчивость волновода во времени. Регистрированы ИК-спектры необработанного образца и протонно-обменных слоев. Эти спектры рассмотрены в качестве индикатора наличия волноводного эффекта, качества волновода и устойчивости его параметров.

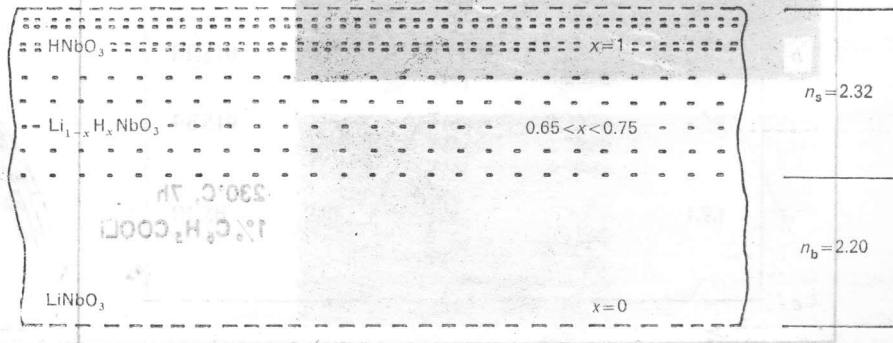
1. Introduction

In the present report we describe our first results in the field of a new very promising technology for fabrication of planar optical waveguides — proton exchange (PE) in LiNbO_3 . The process takes place when the crystal is immersed in a liquid medium — electrolyte, as protons source (usually acid or hydrate melt), which ensures exchange of Li-ions from the crystal with protons. One of the preferred sources of protons for the PE-process is benzoic acid, characterized by low acidity

and toxicity and low price. It is used as a melt (melting point is at 122°C, boiling point → at 249°C), the working temperature for proton diffusion being between 160–300°C. This makes the process more favourable for LiNbO₃ crystals than the high temperature Ti-diffusion in the conventional technology of Ti:LiNbO₃ waveguide fabrication. Li-ions in the crystal lattice are very movable and may be easily replaced by other cations (protons in the case considered). As a result of this two-directional diffusion process, Li⁺-H⁺ exchange occurs in the surface layer of the crystal (Fig. 1). Depending on the duration and temperature, the protons penetrate to different depths *d*. This exchanged layer of depth *d* is characterized by a strong waveguiding effect due to the much higher refractive index ($\Delta n_e = 0.12$ at $\lambda = 632.8$ nm, i. e. an order of magnitude higher than that in the case of Ti:LiNbO₃ waveguides [1, 2]). Another substantial feature of the waveguiding layers, fabricated by proton exchange, is the step-like profile of Δn , which lightens the waveguide connection to optical fibers.

The chemical composition of the exchanged layer is described as Li_{1-x}H_xNbO₃, where *x* expresses the degree of Li⁺-H⁺ exchange. Up to $x \approx 70\%$ the crystal structure of the layer is close to that of an as-grown crystal, which is rhombohedral. At $x = 1$ a cubic perovskite structure of HNbO₃ (with cell dimensions greater than those of the rhombohedral structure) is formed [3, 4]. However, full exchange is undesirable because it induces strains in the waveguiding layers and sometimes causes cracks on the crystal surface and in that way strongly deteriorating the waveguide properties. The HNbO₃ formation explains the main disadvantages of PE-waveguides — parameter instabilities with time (particularly of Δn) [5], decrease in electrooptical coefficients (~ 10 times) [6], relatively high losses and surface etching. The last is valid especially in the case of *Y*-cut waveguides prepared in pure benzoic acid — after about 10 min their surface is etched. That is why it is necessary to allow the protons to penetrate deeply enough into the crystal without full exchange of Li-ions. Recently a solution of this problem was suggested by adding small amounts (few weight percents) of lithium benzoate, which suppresses the Li⁺-H⁺ exchange process between crystal and melt [7]. Preliminary experiments [8] have shown that in this case partial exchange of about 65–75% takes place, which produces layers with a strong waveguiding effect and the crystal structure is not substantially affected. This allows to obtain waveguides with electrooptical parameters close to those of unchanged LiNbO₃ (about 2/3 of their value) [9], low losses and low photorefractive susceptibility (an order of magnitude lower than in the case of Ti:LiNbO₃-waveguides) [10, 11].

Fig. 1. Schematic cross-section of Li⁺ — H⁺ exchanged structure

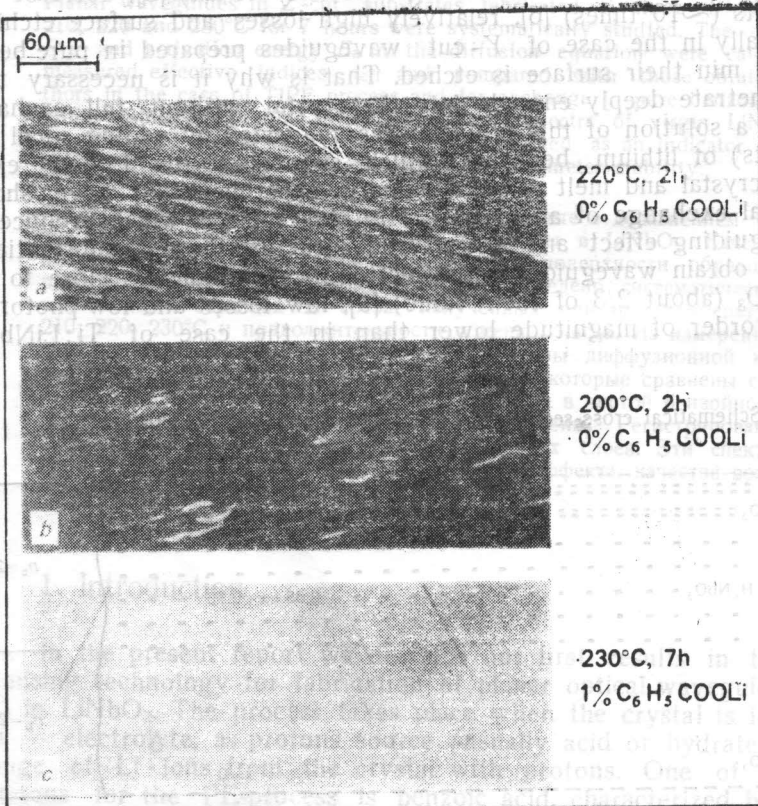


A similar effect on waveguide properties is shown by the combination of proton exchange in pure benzoic acid followed by temperature annealing. In such a case the protons penetrate deeper into the crystal and the strains relax in the crystal depth. However, annealing itself substantially decreases the change in refractive index Δn and influences its profile. Because of that the addition of lithium benzoate in the melt is more accessible for fabrication of stable planar waveguides of high Δn and good quality, especially if step-like profile is required. The combination of the two methods provides possibilities to strongly reduce the losses (up to 0.15 dB/cm) and for control of the Δn -profile [12].

2. Experiment

This paper presents a systematic study of optical waveguides in LiNbO_3 fabricated by the PE fabrication technique. An illustration of the situation described above is Fig. 2, which represents surface photographs of three waveguide layers in X-cut LiNbO_3 , fabricated by us in three different regimes leading to a different degree of exchange. The crystal surface was observed in a phase-contrast microscope

Fig. 2. Surface of X-cut LiNbO_3 substrates exchanged under different conditions. The photographs are made with a phase-contrast microscope (40 x)



under 40 times magnification. Taking into account the waveguide fabrication conditions, it is possible to assume $x \approx 1$ in the first case (Fig. 2a), $0.75 \leq x \leq 1$ in the second (Fig. 2b), and $x \leq 0.75$ in the third case (Fig. 2c). The first pattern is an example for drastic etching of the surface layer when full exchange takes place. The first and second samples were fabricated in pure benzoic acid at 220°C and 200°C, respectively, for 2 hours. The third sample was fabricated by immersing the crystal in benzoic acid with 1% lithium benzoate added during a time interval, that was long enough to obtain a PE-layer with the same depth as in the second pattern (1.5 μm) — 7 hours at 230°C. It is readily seen that the islands of initial cracks on the surface, which are observed with the second pattern, are absent in the third case; only some streaks can be seen which are due to bad polishing of the crystal. Thus the addition of small amounts of lithium benzoate in the melt prevents surface etching and as it is shown later, it leads to the fabrication of waveguides having time-stable parameters.

2. 1. Waveguide measurements

The essential part of our experiment includes fabrication and investigation of planar waveguides on Z-cut substrates using benzoic acid with 1% lithium benzoate added and treatment for the duration of 7 hours at three different melt temperatures: 210, 220 and 230°C. The experimental setup used is shown in Fig. 3. Thus three waveguides of different depths d and more numbers were fabricated for which the effective indices n_{eff} were measured* at $\lambda = 632.8$ nm (Table 1). Assuming a step-like index profile the increase in the refractive index of the substrates was estimated to be almost equal for the samples ($\Delta n_e \approx 0.11$). In Fig. 4 the theoretical dispersion curves (for layer depths up to 2.5 μm) are represented. Triangle marked points in the same curves represent measured values of n_{eff} . It is seen that they are situated very close to the theoretical curves.

The values for the diffusion coefficient $D_z(T)$ at 220°C and for the parameters in the diffusion equation — the diffusion constant D_{0z} and the activation energy E_a , which were estimated by us are summarized in Table 2. For comparison, the data from other authors calculated for substrates treated in pure benzoic acid, as well as for a process of Ti-in-diffusion followed by proton exchange (TIPE) are given, too. Apparently a small amount of lithium benzoate in the melt reduces considerably the

Table 1. Effective mode indices measured at $\lambda = 632.8$ nm and waveguiding layers depths for Z-cut PE-waveguides in LiNbO_3 fabricated for 7 h at different temperatures

Sample	Temperature, °C	Mode	n_{eff}	d , μm
PEZ10	210	TM_0	2.2891	0.82
		TM_1	2.2222	
PEZ19	220	TM_0	2.2999	1.10
		TM_1	2.2529	
		TM_2	2.2008	
PEZ6	230	TM_0	2.3016	1.23
		TM_1	2.2639	
		TM_2	2.2162	

* Accuracy of measurements is 5×10^{-4} .

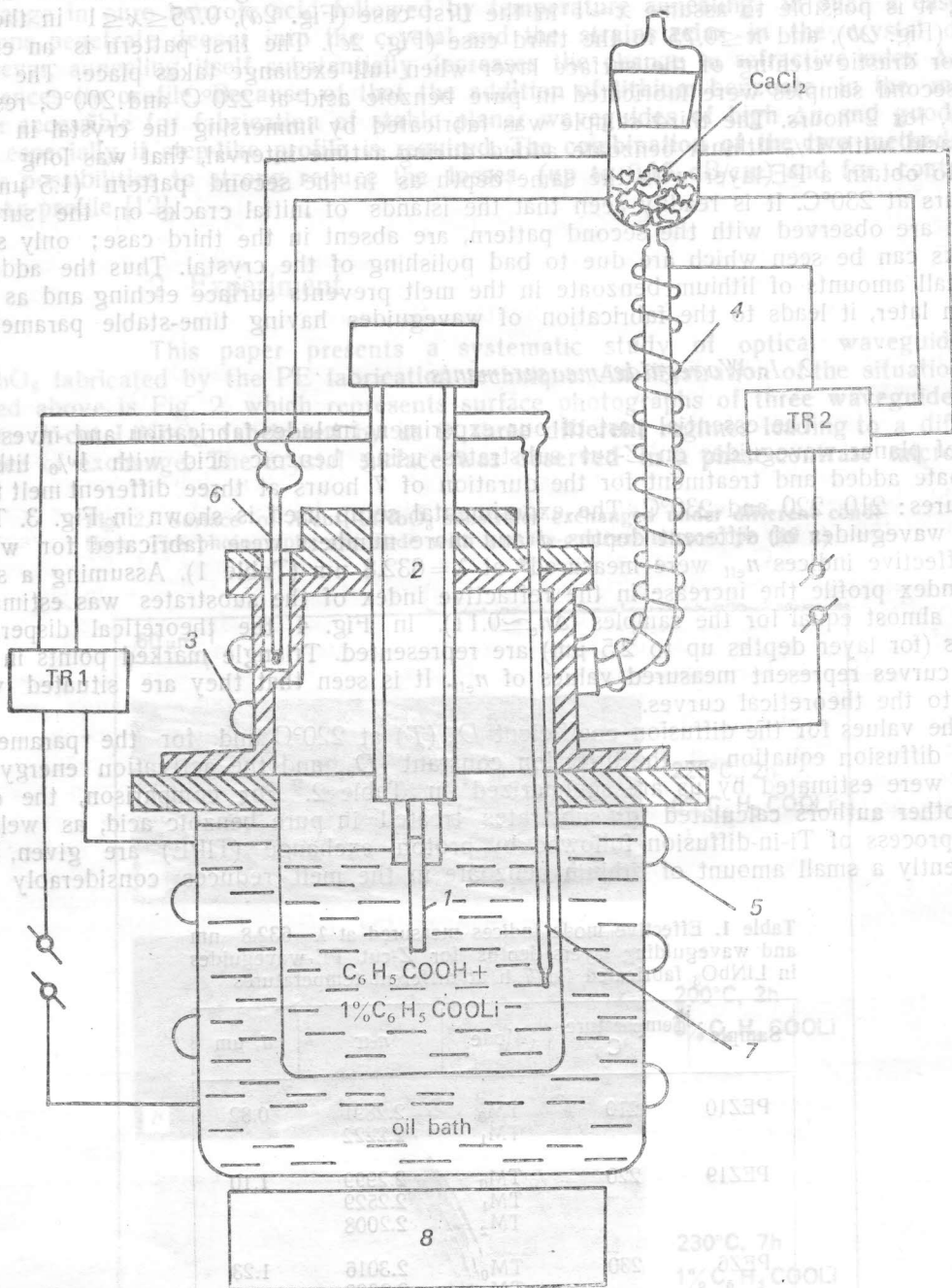


Fig. 3. Experimental set used for proton exchange: 1 — LiNbO_3 substrate, 2 — holder, 3, 4 — heating spirals, 5, 6 — thermocouples, TR1, TR2 — thermoregulators, 7 — heater

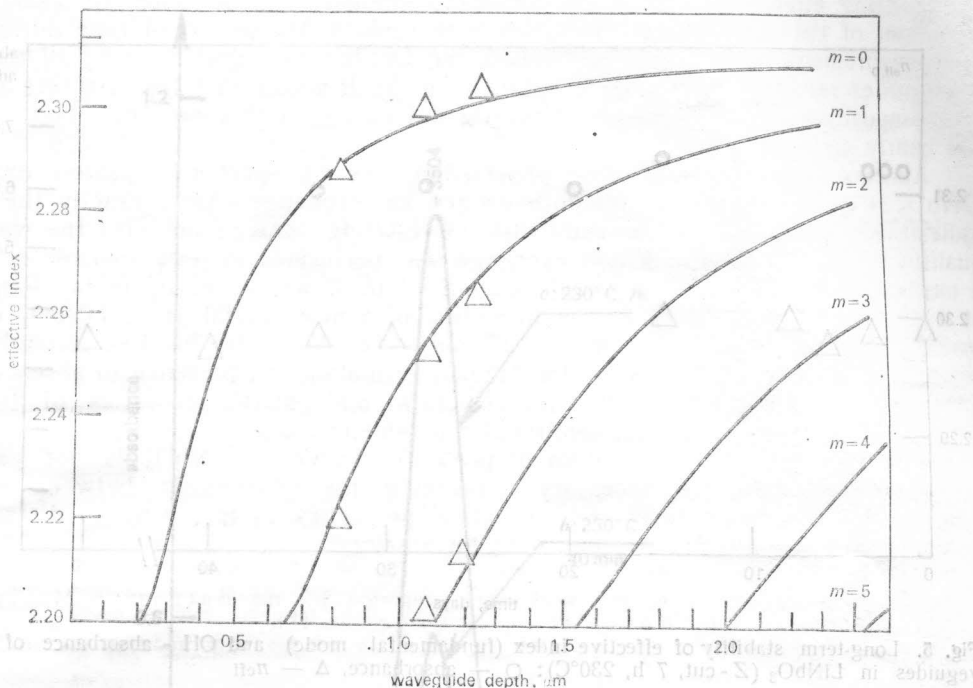


Fig. 4. Theoretical dispersion curves for PE LiNbO₃ - waveguides (Δ — experiments)

Table 2. Comparison of the diffusion coefficients $D_z(T)$ at 220°C, constant D_{Oz} and activation energy E_a for different proton exchange processes

Z-cut LiNbO ₃	PE in pure benzoic acid [2]	PE in benzoic acid with 1% lithium benzoate added [this work]	TIFE-process [16]
$D_z(220^\circ\text{C}), \mu\text{m/h}$	0.207	0.043	0.161
$D_{Oz}, \mu\text{m/h}$	1.84×10^9	0.547×10^9	0.542×10^9
E_a, J	1.57×10^{-19}	1.60×10^{-19}	1.50×10^{-19}

diffusion coefficient D_z . Also, D_z (and variations of $\Delta n, \delta n$) at room temperature are reduced. As a result stable waveguides can be produced.

Combining D_{Oz} , E_a and the dispersion curves from Fig. 3 we were able to prognosticate the process, i. e. to choose the duration and temperature of the process in order to produce waveguides supporting a desired number of modes (Δn and layer depth, respectively).

The next Figure (Fig. 5) illustrates the waveguide stability with time following n_{eff} of the fundamental mode. The effective indices were measured for 80 days after the guide layer was formed. Their IR-spectra have been recorded parallel to the index measurements and spectroscopic results are included, too. They will be discussed later. Usually the first two weeks after the proton exchange are considered to be critical for

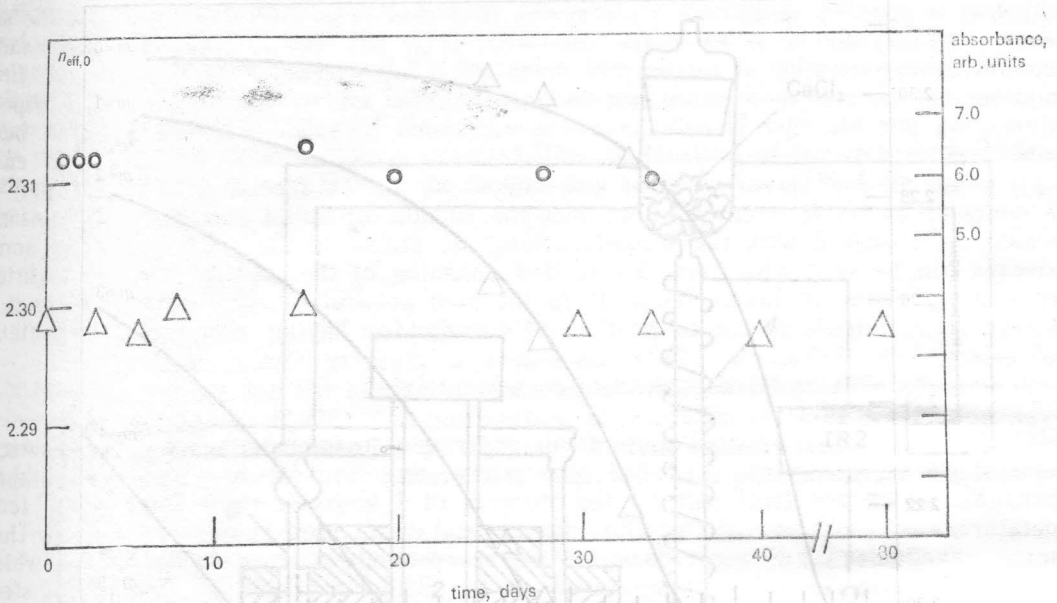


Fig. 5. Long-term stability of effective index (fundamental mode) and OH - absorbance of PE - waveguides in LiNbO_3 (Z - cut, 7 h, 230°C): \circ — absorbance, Δ — n_{eff}

the waveguide parameter variations. After this period their values remain constant for at least 8 months [8].

2. 2. IR-spectra

Another very sensitive indicator for optical quality and properties of the PE-waveguides are their IR-spectra. The IR-spectroscopy is a very convenient method for the investigation of the hydroxyl groups which are present in such a type of thin layers.

The IR-spectrum of LiNbO_3 in the range of OH vibrations exhibits a dependence of absorption on light polarization for virgin as well as for proton exchanged crystal. In both cases the main absorption is observed in the case when the polarization of incident light is in the plane perpendicular to the optical (Z) axis (Fig. 6). The structural studies of pure LiNbO_3 single crystals show that the oxygen anions are situated in these planes at three different distances from each other: 2.72, 2.88 and 3.36 Å. According to some authors [13] the hydrogen ions are positioned at the shortest distance to the oxygen ions. In the later works the OH-band structure in IR-spectrum of virgin LiNbO_3 is interpreted as due to three energetically different proton sites [14]. The central peak is attached to O-O distance of 2.88 Å. It should be noted that the ratio of the band intensity depends strongly on the crystal stoichiometry.

The OH-band of virgin crystals (Fig. 6a) consists of three lines at 3471, 3482 and 3487 cm^{-1} , which corresponds to a crystal grown from the nearly-stoichiometric melt. After proton exchange the appearance of a strong peak at 3504 cm^{-1} is observed (Fig. 6c) corresponding to at least one new type of O-H band. Namely, this hydroxyl group is connected with the waveguiding effect. For comparison IR-spectra of two waveguides produced at different temperatures and for different durations of proton exchange

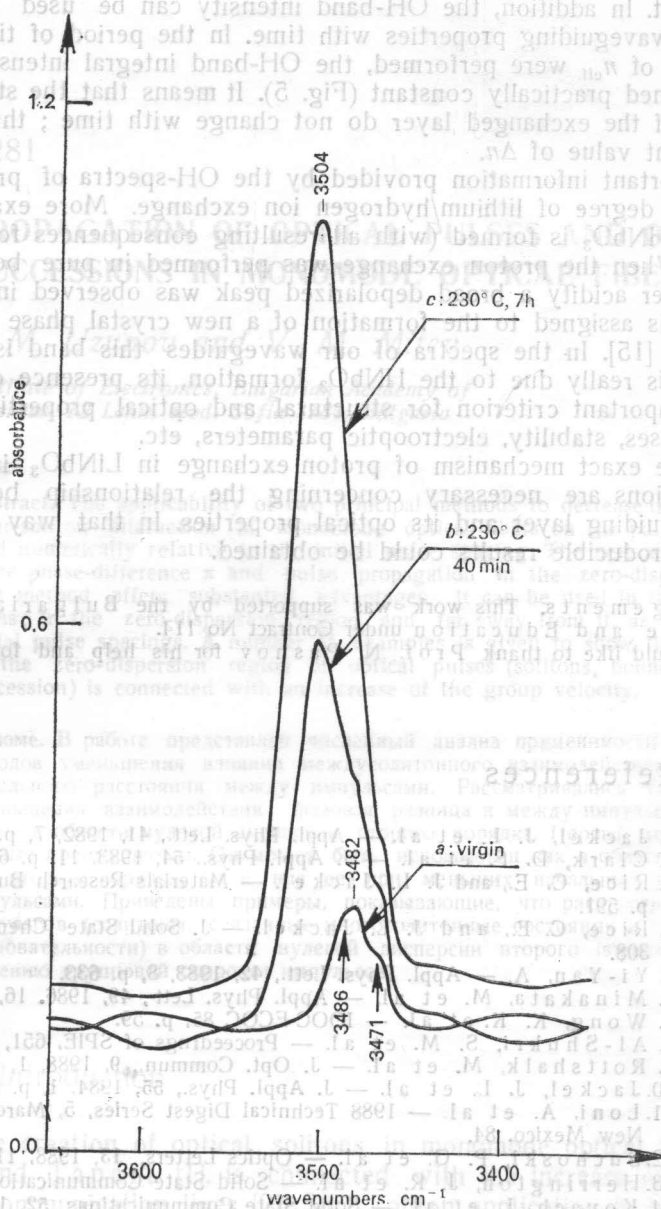


Fig. 6. OH — absorption spectra of Z-cut LiNbO₃ — samples: (a) virgin, (b) and (c) PE-samples

are shown in the Figure. Both spectra were recorded a month after the waveguide fabrication. The first waveguide, initially single-mode one (Fig. 6b) was found to be degraded but the second (initially three-mode), was unchanged (Fig. 6c). Apparently the amount of OH-groups in the first case is insufficient for lightguiding. Thus the integral intensity of the OH-band in PE-waveguides can be used as a criterion for the

waveguiding effect. In addition, the OH-band intensity can be used to examine the evolution of the waveguiding properties with time. In the period of time during which the measurements of n_{eff} were performed, the OH-band integral intensity of the stable waveguides remained practically constant (Fig. 5). It means that the structure and even the composition of the exchanged layer do not change with time; this fact supports the nearly constant value of Δn .

Another important information provided by the OH-spectra of proton exchanged LiNbO_3 is on the degree of lithium/hydrogen ion exchange. More exactly the spectra indicate whether HNbO_3 is formed (with all resulting consequences for the waveguide quality) or not. When the proton exchange was performed in pure benzoic acid or in a medium of higher acidity a broad depolarized peak was observed in the IR-spectrum at 3280 cm^{-1} . It is assigned to the formation of a new crystal phase HNbO_3 with perovskite structure [15]. In the spectra of our waveguides this band is strongly reduced. If this peak is really due to the HNbO_3 formation, its presence or absence in the spectrum is an important criterion for structural and optical properties of PE-waveguide layers — losses, stability, electrooptic parameters, etc.

Obviously the exact mechanism of proton exchange in LiNbO_3 is not yet clear. Further investigations are necessary concerning the relationship between structure changes of waveguiding layer and its optical properties. In that way predictable and high accuracy reproducible results could be obtained.

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