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Stearic acid as a protonic source for fabrication of $LiNbO_3$ waveguides by proton exchange

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The fabrication and properties of optical waveguides formed in *x*-cut and *y*-cut $LiNbO_3$ by proton exchange method in stearic acid melts are reported. For the TE modes the refractive index variation was found to be $\Delta n_e = 0.130$ and $\Delta n_e = 0.128$, respectively, for *x*-cut and *y*-cut waveguides ($\lambda = 632.8$ nm). The measured losses in single-mode waveguide at 632.8 nm wavelength were close to the losses of the waveguides fabricated in the molten benzonic acid.

1. Introduction

The proton exchange (PE) process for waveguide fabrication in $LiNbO_3$ substrates has been extensively studied in recent years. It is a relatively low temperature process which creates in the $LiNbO_3$ substrates a large positive change (0.12 at $\lambda = 632.8$ nm) in the extraordinary refractive index with a near step-index profile [1]. Because of its advantages this simple technique has been used to fabricate various types of waveguide devices [2]. Unfortunately, some important practical disadvantages have been identified with PE mode waveguides using strong acid melts as, e.g., benzonic acid. In particular these include degradation of the electrooptic activity [3] and short- and long-term instability of waveguide refractive index [4]. Furthermore, the high hydrogen concentration introduced into the host lattice may cause large crystal distortions and the surface damage observed on *y*-cut plate. Some of these problems can be overcome by fabricating proton-exchange and benzonic acid [5] or by titanium indiffusion followed by proton exchange (TIPE process) [6]. Moreover, the high quality of *y*-cut few-mode (<3 modes) waveguides has been obtained by proton exchange carried for a very short period followed by annealing [7]. Besides strong acidic melts with a high intensity of the proton exchange in which direct *y*-cut waveguide formation is impossible, acid melts with a low concentration of H^+ in the exchange medium exist. Melts of that type make possible formation of *y*-cut $LiNbO_3$ multi-mode waveguides without surface destructions. They include melts with some organic acids as palmetic, stearic, lauric, myristic, etc., [8], [9]. However, these melts, like most other organic acids, decompose if they are exposed at higher temperatures. Thus, the useful range of the exchange temperatures and times is limited in these acids.

In this paper, the results of proton-exchanged lithium niobate optical waveguide fabrication in x-cut and y-cut substrates immersed in pure stearic acid are presented. The most useful range of the process parameters for the waveguides formation is found.

2. Experiment

A polished x-cut and y-cut $LiNbO_3$ substrates supplied by Institute of Technology of Electronic Materials (Warsaw) were immersed in a stainless steel beaker containing a molten analar stearic acid. The beaker was placed in a resistively heated furnace. This experimental arrangement supplies, at least qualitatively, the same data as the arrangement with a closed quartz ampoule [4]. Exchange temperatures and times ranged from 200 to 270°C and from 30 min to 8 h, respectively. The temperature was controlled within ± 0.5°C. After the process the substrates were cleaned in acetone to remove excess of stearic acid. The content of the beaker was renewed after each exchange run.

After the exchange process the surfaces of the x-cut samples were free from any surface damages. Unfortunately, the proton exchange is not ideal in the examined range. In the case of the y-cut samples exchanged for 5 h and 8 h at temperature of 200°C and for 8 h at temperature of 215°C small cracks running from the edges of the samples were observed with the naked eye. As it is known, the exchange process introduces the high-stress gradient into the $LiNbO_3$ lattice. In case of y-cut samples the process temperature is too low to cause the plastic relaxation of the crystal lattice stress. Thus, the lattice stress is relaxed by the formation of the surface cracks. Despite the cracks which occupied a part of the sample surface, the mode effective index measurement could be done except for the samples exchanged for longer than 3 h at 200°C.

On the other hand, a process longer than 5 h at temperature 270°C leads to the partial decomposition of acid and the waveguide irreproducibility. Furthermore, in a process longer than 5 h the waveguides became slightly brown.

After the proton exchange process the x-cut and y-cut samples were stored for about 3 weeks at the room temperature to relax the refractive index of the waveguide region to a stable value [4], and then measured.

3. Results

The optical properties of the planar waveguides were measured using a standard prism coupling technique at wavelength of 632.8 nm [10]. The measurement was done with accuracy of ± 1 min in the measured synchronous angle, corresponding to accuracy of $\pm 2 \times 10^{-4}$ in the measured effective index.

For multi-mode waveguides (>4 modes), the values of the effective refractive indices n_{eff} for each observed mode were used as a data input for a computer program based on the inverse WKB approximation [11] which estimates the shape

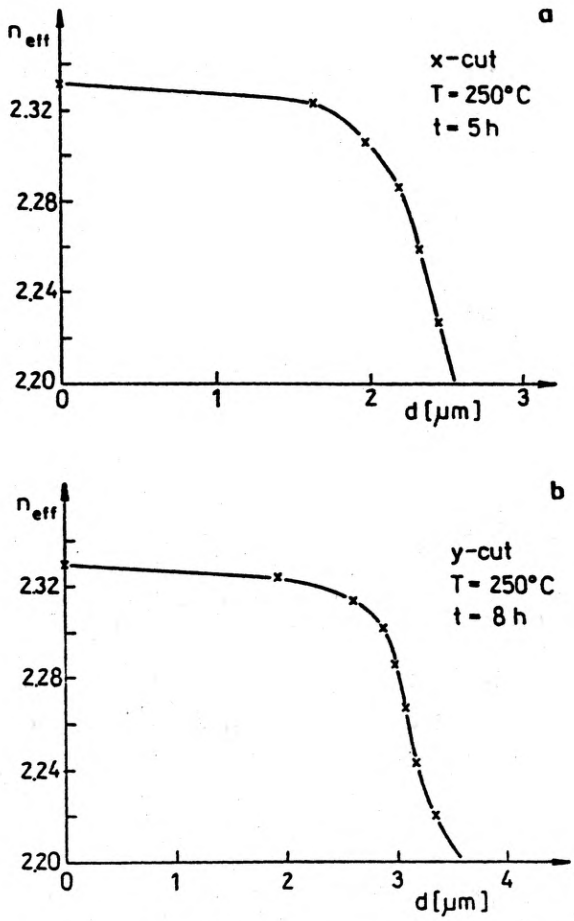

Fig. 1. Index profile for *x*-cut sample exchanged for 5 hours at 250°C (**a**). Index profile for *y*-cut sample exchanged for 8 hours at 250°C (**b**)

of refractive index profile. The program calculates the surface refractive index n_s and the waveguide depth d at which the n_{eff} value becomes equal to the local refractive index. Figure 1**a** shows the refractive index profile of *x*-cut $LiNbO_3$ waveguide at 250°C . We can see that the profile is step-like, with surface index change of 0.130 for extraordinary polarization. The result, i.e., that guides fabricated by using the proton-exchange process have a step-index profile, has been confirmed by secondary-ion mass spectroscopy analysis. In Fig. 2, for the same sample, the lithium ions depletion of the waveguiding layer is presented. A 3-μm diameter primary beam of Ar^+ at 4 keV was used. Similarly, as with the *x*-cut waveguides, the profiles of *y*-cut guides were step-like which is illustrated in Fig. 1**b** for samples exchanged for 8 h at 250°C. It was found that maximum extraordinary changes were 0.130 and 0.128 for *x*-cut and *y*-cut samples, respectively.

The assumption of the step-like profile for the *x*-cut waveguides, which was confirmed by our experiment, permitted the use of the method of CHARTIER and

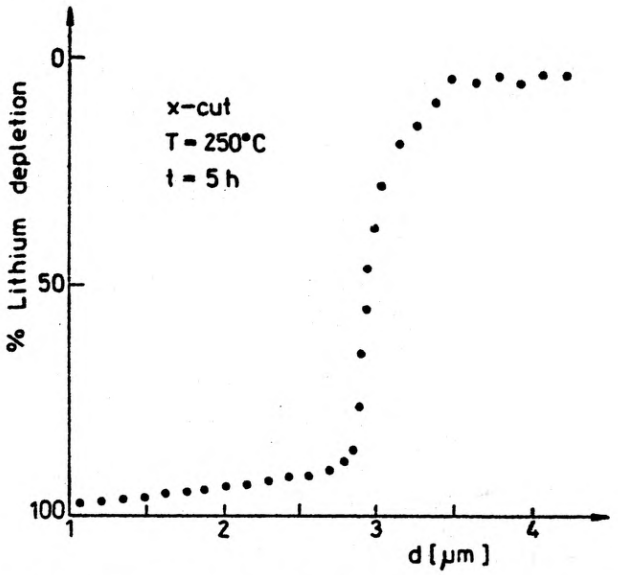

Fig. 2. Microprobe results for *x*-cut sample exchanged in stearic acid for 5 hours at 250°C. Li count normalized to that measured for the substrate $LiNbO_3$ is plotted vs the waveguide depth

JAUSSAUD [12] to obtain the values of the planar waveguide depth d, and the surface index n_s. According to this method the effective mode refractive index n_{eff} for a step-index profile can be expressed as

$$n_{eff}^2 = n_s^2 - \frac{\lambda^2 p^2}{4d^2} \tag{1}$$

where λ is the wavelength used and p is the mode order ($p = 1, 2, 3, \ldots$). A plot of n_{eff}^2 versus p^2 should give the value of n_s and d from the intercept and slope, respectively.

It was noticed that values of the diffusion depth estimated with IWKB are slightly samaller than those obtained by Chartier and Jaussaud method. This is due to the fact that for a real step-like refractive index profile, the IWKB procedure is not very accurate and it always underestimates surface index due to the inherent procedure of smoothing off the curves. An error is negligible for multi-mode waveguides but it becomes higher for few-mode waveguides. For example, the waveguide depth for the sample presented in Fig. 1a estimated by IWKB method is 2.43 μm. The waveguide depth for the same sample estimated by Chartier and Jaussaud method is 2.74 μm. The SIMS method gives the diffusion depth equal to 2.94 μm and it is quite close to the value obtained by Chartier and Jaussaud method.

Plots of the diffusion depth versus square root of time for *x-cut* and *y*-cut waveguides are shown in Fig. 3. From the curve gradient the diffusion coefficient $D(T)$ for different temperatures were calculated assuming that diffusion depth d varies as follows:

$$d(T,t) = 2\sqrt{t \times D(T)} \tag{2}$$

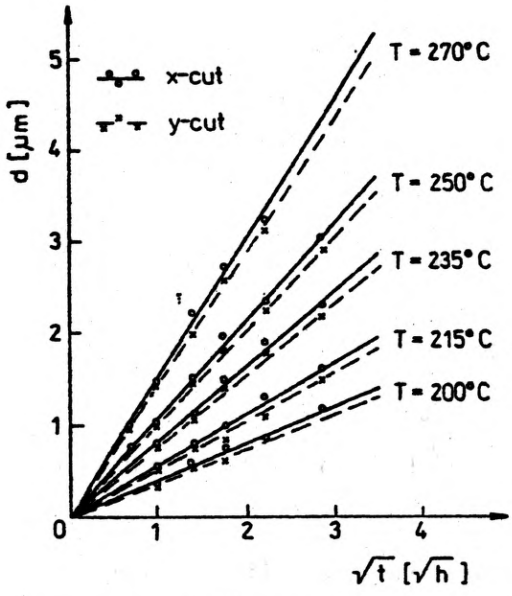

Fig. 3. Diffusion depth vs square root of the time for *x*-cut and *y*-cut waveguides exchanged in stearic acid

where t is the exchange time and T is the temperature of the exchange process.

The exchange process is two times slower compared to exchange in benzoic acid. The mean values of $D(T)$ are shown in the Table.

Plotting $D(T)$ versus T^{-1}, as shown in Fig. 4, allows one to find the usual temperature dependence for $D(T)$ in accordance with the Arrhenius' law

$$D(T) = D_0 \exp(-Q/RT) \tag{3}$$

where D_0 is the exchange process constant, R is the universal gas constant, and Q is the activation energy for the exchange process. Calculated values of the activation energy for the exchange process are the same for *x*-cut and *y*-cut and they are equal to 88.3 kJ/mol. The main difference is in the absolute value of D which appears larger for *x*-cut ($D_{0x} = 2.06 \times 10^8 \mu m^2/h$) and slightly lower for *y*-cut ($D_{0y} = 1.86 \times 10^8\ \mu m^2/h$).

The time stability of fabricated waveguides have been studied by measurement of effective mode indices n_{eff} versus time. The short time stability measurement was done every day for the period of three weeks. The waveguide samples were kept at

Diffusion coefficient of *x*-cut and *y*-cut waveguides for different temperatures

T[°C]	$D(T)[\mu m^2/h]$	
	x-cut	*y*-cut
200	0.040	0.037
215	0.078	0.070
235	0.172	0.155
250	0.215	0.265
270	0.581	0.530

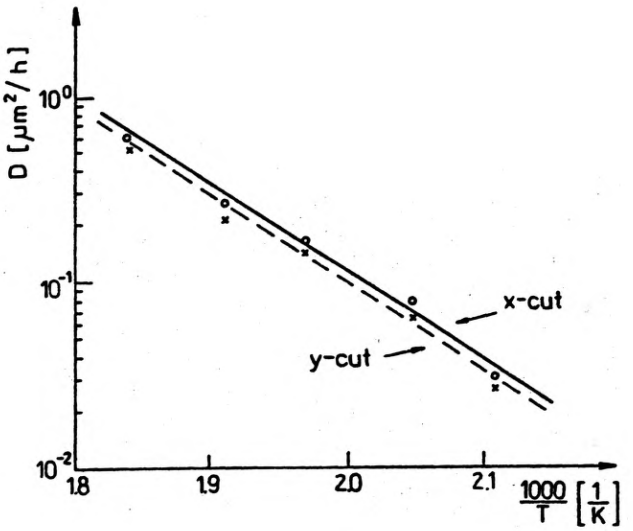

Fig. 4. Plot of ln (D) vs $1/T$

the room temperature. The measured effective mode indices demonstrated that the index profile is not stable but it evolves as a function of time. This effect is shown in Fig. 5 for one-mode and for multi-mode y-cut sample. The shape of effective mode indices variation can be described by a slow damping component superimposed on not well defined oscillating function. Generally, the amplitude of oscillation increases with the mode number. For the example presented in Fig. 5 the rate $\Delta N/\Delta n_e$, where ΔN is the mode oscillation amplitude and $\Delta n_e = 0.128$ corresponds with the increase of the effective index by the exchange process, was in the range from 1.5% to 6%. It was smaller than that for waveguides fabricated in benzoic acid [4]. It was noticed that for the x-cut samples the rate $\Delta N/\Delta n_e$ was by 3% to 5% greater than that calculated for y-cut samples.

The long-stability measurements of the fabricated waveguides were every month for the period of eleven months. We found that the average decrease of the effective mode indices in samples, including the first instability period, were about 5–10%. In the multi-mode waveguides, the index profile became more graded. This ageing effect is presented in Fig. 6 for the multi-mode y-cut sample.

Presented results suggested that observed oscillatory instability might be caused by a continuous migration of protons within the thickness of the waveguiding layer. This migration is connected with the high concentration gradient of the H^+ ions in the exchanged layer. The index instabilities effect occurs under normal laboratory conditions and has not been found to disappear completely throughout the examination period.

Measurements of propagation losses using two-prism method were made on various single-mode samples fabricated at different temperatures. Measured losses were between 3 and 5 dB/cm and were close to the losses of the waveguides fabricated in the molten benzoic acid. No clear relationship between propagation losses and the fabrication conditions could be identified.

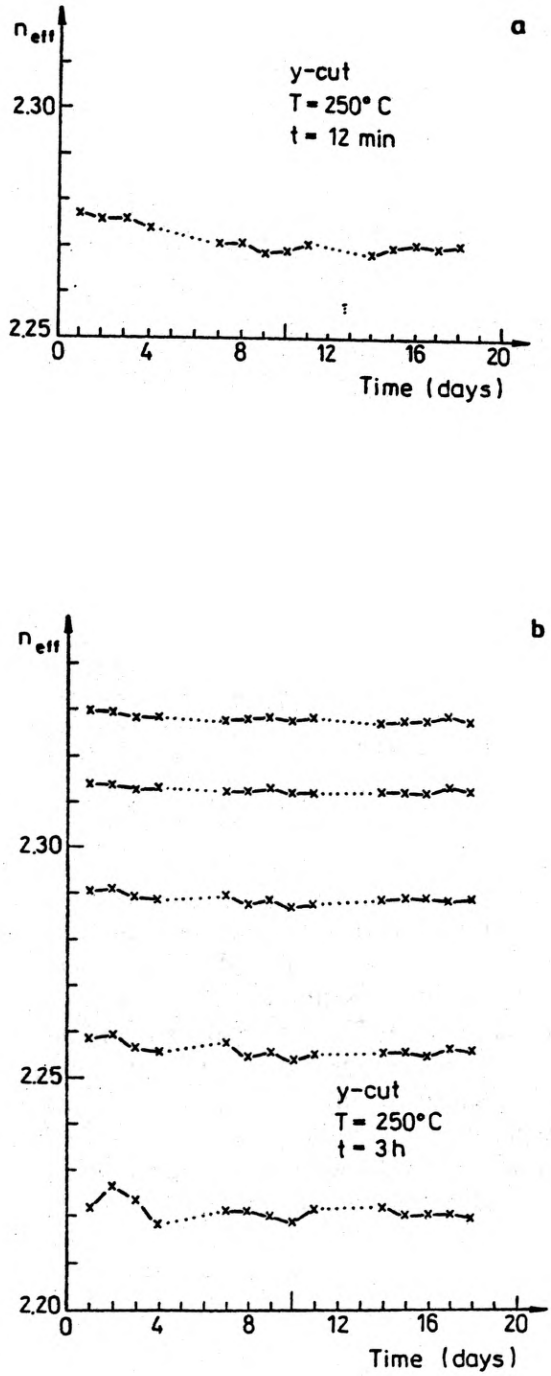

Fig. 5. Variation of the effective mode indices as a function of time for *y*-cut waveguides: **a** – one-mode, **b** – multi-mode. Accuracy of the measurement is about $\pm 2 \times 10^{-4}$

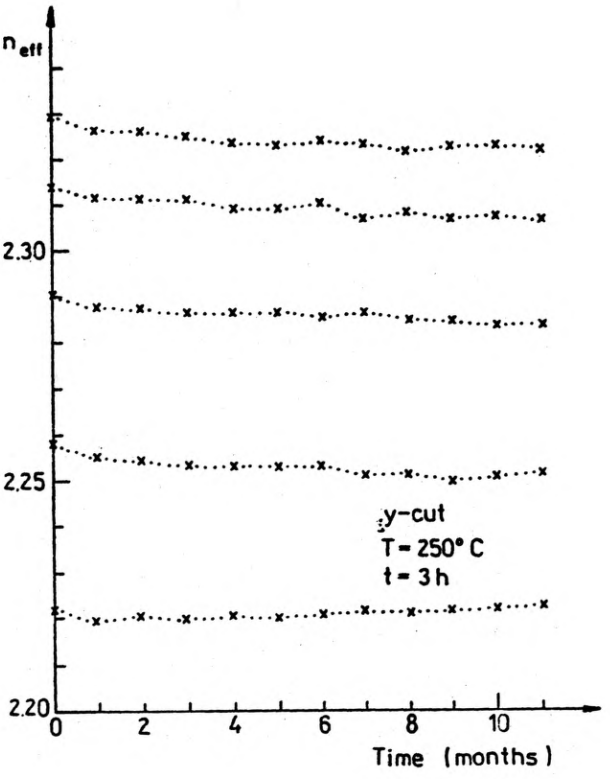

Fig. 6. Long-term refractive index stability for *y*-cut multi-mode waveguide. Accuracy of the measurements is about $\pm 2 \times 10^{-4}$

4. Conclusions

The results presented in this paper indicate that the stearic acid is subitable for *x*-cut and *y*-cut $LiNbO_3$ waveguides fabrication, but in the limited range of the temperatures and times. Generally, the exchange process should be carried out at temperatures below 270°C and should not exceed 5 h. This limitation is connected with the decomposition of the stearic acid during long exposition at higher temperatures. On the other hand, for the *y*-cut substrates the temperature lower limit exist. It results from the possibility of the plastic relaxation on the $LiNbO_3$ crystal interfaces. Finally, the low-rate exchange process provides waveguides more stable in time than those obtained in the benzoic acid exchange process.

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Стеариновая кислота как источник протонов в процессе формирования световодовых слоев $LiNbO_3$ методом ионообмена

В работе определены возможности получения световодовых слоев на x- и y-срезах $LiNbO_3$ посредством ионообмена в расплаве стеариновой кислоты. Было установлено, что максимальное изменение необыкновенного показателя преломления составляет $\Delta n_e = 0.130$ — для волноводов x-среза и $\Delta n_e = 0.128$ для волноводов y-среза ($\lambda = 632{,}8$ nm). Измеренные потери в одномодных волноводах были близки потерям в волноводах, полученных посредством ионообмена в расплаве бензойной кислоты.