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Fabrication of optical waveguides $LiNbO_3$ by proton-exchange in molten adipin acid

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The fabrication and characterization of optical waveguides formed in $LiNbO_3$ by proton exchange method in adipic acid melts for *x*-cut and *y*-cut crystals have been reported. For the TE modes the variation of the refractive index of *x*-cut substrates was found to be $\Delta n_{ex} = 0.139$ ($\lambda = 632.8$ nm). This is the heighest increase of refractive index obtained to date for $LiNbO_3$ by proton-exchange. The measured optical propagation losses in single-mode waveguide at 632.8 nm wavelength ranged between 3.5 dB/cm and 5 dB/cm.

1. Introduction

The proton-exchange method developed in the past few years appeared to be a very promising method for fabrication of optical waveguides on $LiNbO_3$. Proton-exchange in commonly used molten benzoic acid is a low-temperature process in which the increase ($\Delta n = 0.12$ at $\lambda = 632.8$ nm) of the extraordinary refractive index is larger than that produced by conventional Ti in-diffusion ($\Delta n = 0.02$ at the same wavelength) [1]. Although in *y*-cut the proton exchange process produces surface damage [2], it is readily used in *x*-cut and *z*-cut $LiNbO_3$. Recently, several attempts have been made to apply the process successfully even on *y*-cut substrates [3]–[5]. This simple technique has been demonstrated for different cuts $LiNbO_3$ crystals to fabricate various types of waveguide devices, e.g., high efficiency beam deflectors [6], second harmonic generators [7], polarizers [8], ring resonators [9], π-arc waveguide interferometer [10], optical frequency translator [11] and acoustooptic modulators [12], [13].

A variety of protonic sources may be used to fabricate optical waveguides, but the presence of a significant concentration of solved H^+ in the exchange medium is the main requirement. The analysis of all known doping melts indicates that they can be classified into two types. Melts of type I are those that make possible the formation of *y*-cut $LiNbO_3$ more than one mode waveguides without surface destruction (e.g., stearic acid [14] and mixture of benzoic acid lithium benzoate [15]). Type II includes strongly acidic melts with a high intensity of PE (as mentioned previously benzoic acid). Direct *y*-cut waveguide formation in these melts is impossible because of high H^+ saturation of the surface and its destruction. Unfortunately, some important problems have been found when waveguides were exchanged in strong acids. These, in particular, include degradation of electro-optic activity [13], short and long term instability of waveguide refractive index [16]. Nevertheless, there exists the possibility to remove these drawbacks by subsequent annealing of samples or by treating them in Li^+-containing melts after PE [17]. However, strong acids give the possibility to form waveguides with extremely high changes of refractive index, for example, Taniuchi and Yamanoto have reported the index changes $\Delta n_{ex} = 0.137$ using phosphoric acid [18].

This paper presents the results of proton-exchanged lithium niobate optical waveguide fabrication in *x*-cut and *y*-cut substrates immersed in pure adipic acid. Adipic acid used as a protonic source can be classified into the melts of type II. The changes of refractive index obtained in *x*-cut crystals are the highest reported, recently.

2. Experimental details

Waveguide slabs were formed using *x*-cut and *y*-cut $LiNbO_3$ substrate. Well polished substrates have been supplied by the Institute for Technology of Electronic Materials, Warsaw*. The proton exchange process was carried out in an open stainless steel beaker containing molten analar adipic acid. The beaker was kept in resistively heated furnace, the temperature of which was controlled within $\pm 0.5°C$. The bath temperature ranged from 170°C to 250°C. Although thermal shock does not seem to be a problem for *x*-cut crystals, but all specimens, before being immersed in melted acid and after their removal were kept, for 1 to 2 minutes over the hot acid surface in the furnace. After the exchange process the slabs were washed in methanol to remove the excess to adipic acid. The exchange beaker was covered to provide a well-isolated temperature-stable environment. The content of the beaker was renewed after each exchange run.

It was observed that after the proton exchange the surfaces of *x*-cut substrates were without any destruction, but *y*-cut samples after few minutes of the exchange process have shown a surface damage. Because of this effect the *y*-cut waveguides have been made by a short time proton-exchange (1–10 minutes) and and annealed at 350°C for 30 minutes.

The *x*-cut samples after PE were stored for a period long enough (typically for three weaks, at least) enabling the refractive index of the waveguide region to relax to a stable value [16].

3. Results

The mode structures of the optical waveguides were measured by means of the conventional prism-coupler technique with crystal rutile prism at $\lambda = 632.8$ nm [19].

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* Those substrates were for electroacoustic applications.

It has been confirmed experimentally that in waveguides formed in *x*-cut and *y*-cut $LiNbO_3$ by the proton exchange in the molten adipic acid, only TE modes excited.

x-cut

All the measurements were carried out in the light propagation direction in accordance with the *y*-axis. For multi-mode waveguides (> 4 modes) the values of the effective refractive indices of each observed mode were used as a data input for a computer program based on the WKB approximation [20], [21] which estimates the shape of refractive index profile. The program calculates the surface refractive index and waveguide depth at which the n_{eff} value becomes equal to the local refractive index. Figure 1 shows the step-like refractive index profile ($\Delta n_{cx} = 0.139$) of *x*-cut $LiNbO_3$ waveguide at 250°C. In general, all the waveguides formed in adipic acid were found to have step-index profiles.

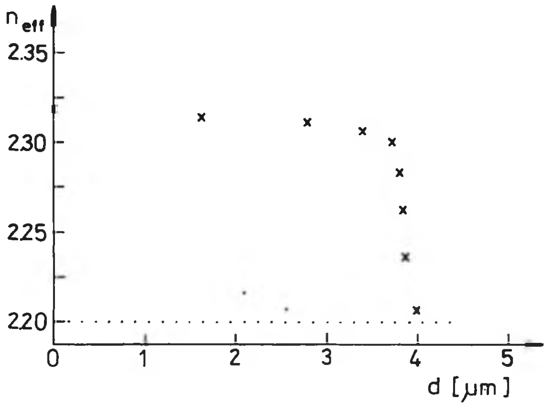

Fig. 1. Index profile for *x*-cut sample exchanged in adipic acid for 5 hours at 250°C

The assumption of the step-like profile for the *x*-cut waveguides permitted us to use the quick method of JAUSSAUD and CHARTIER [22] to obtain the depth of the few-mode (< 4 modes) planar waveguides.

The diffusion depth versus square root of time is plotted in Fig. 2. The values of the diffusion coefficient $D(T)$ for the exchange process at different temperatures were calculated from the following relation:

$$d = 2\sqrt{t \times D(T)} \quad (1)$$

where d is the diffusion depth, t — the exchange time, and T — the temperature of the exchange process.

The exchange process is very rapid. For example, at 250°C the diffusion coefficient $D(T)$ for diffusion in the *y*-direction is 1.46 μm²/h, $D(210°C) = 0.295$ μm²/h and $D(170°C) = 0.46$ μm²/*h*.

By plotting $D(T)$ versus T^{-1}, as shown in Fig. 3, we are able to calculate the usual temperature dependence for $D(T)$ in accordance with the Arrhenius law

$$D(T) = D_0 = \exp(-Q/RT) \quad (2)$$

where D_0 is the exchange process constant, R — the universal gas constant, and Q — the activation energy for the exchange process. The values observed in the present investigation were $D_0 = 1.03 \times 10^9$ μm²/h and $Q = 88.5$ J/mol.

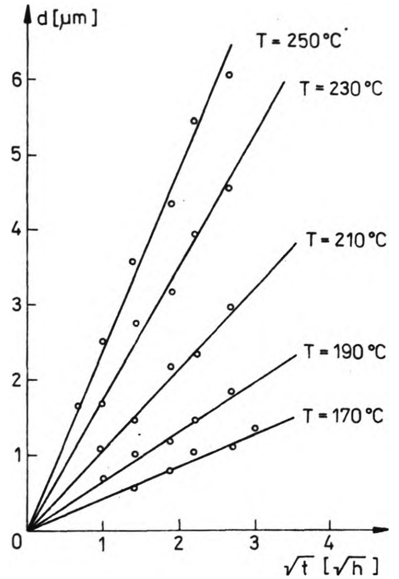

Fig. 2. Diffusion depth versus square root of time for x-cut waveguides exchanged in adipic acid

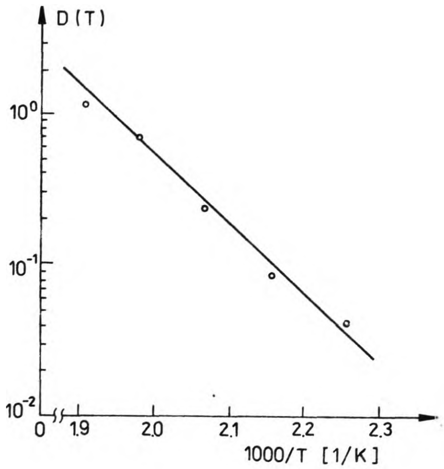

Fig. 3. Plot of In(D) versus $1/T$

The measurements of propagation losses by using two-prism method were made on various single-mode samples fabricated at different temperatures. The measured losses were between 3.5 and 5 dB/cm, and they were approximately the same as losses obtained with the benzoic acid on the similar material [23]. No clear relationship between the propagation losses and fabrication conditions has been found.

y-cut

The exchange process in the adipic acid, though very effective for *x*-cut, produces a damage in *y*-cut $LiNbO_3$ surface, if the exchange is allowed to proceed for more than few minutes. This effect is similar to the cleavage surface *y*-cut plates obtained by the proton-exchange in the benzoic acid and is associated with high proton concentration near the crystal surface which results in large changes in lattice dimensions. This is why the *y*-cut $LiNbO_3$ waveguides were fabricated by short (< 10 minutes) period of the proton exchange followed by annealing in air. It was noticed that the quality of the waveguides estimated by measured optical propagation losses was much better after annealing.

In the present investigation three series of the specimens have been made, i.e., at 190°, 210°, and 230°C. In each series ten samples have been fabricated for 1–10 minutes. After the exchange process all the specimens were annealed at 350°C for 30

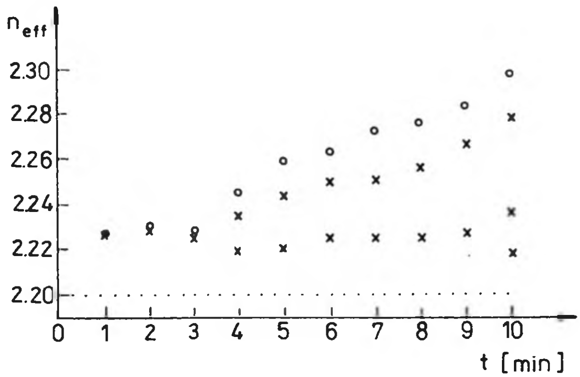

Fig. 4. Values of the effective refractive index n_{eff} at different exchange times for *y*-cut waveguides exchanged at 210°C, before and after annealing (annealing 350°C, 30 min). o — before annealing, × — after annealing

Comparison of the parameters of waveguides before and after annealing (annealing 350°C, 30 min). The columns show number of samples which supported given number of modes. In the brackets time of the exchange process is presented

Exchange temperature [°C]	Ion-exchange			Ion-exchange + annealing		
	number of samples			number of samples		
	0-mode	1-mode	2-mode	1-mode	2-mode	3-mode
230	–	5 (1–5 min)	5 (6–10 min)	1 (1 min)	4 (2–5 min)	5 6–10 min)
210	1 (1 min)	9 (2–10 min)	–	3 (1–3 min)	6 (4–9 min)	1 (10 min)
190	2 (1–2 min)	8 (3–10 min)	–	2 (1–2 min)	8 (3–10 min)	–

minutes. In the samples made at 230°C during the time longer than 6 minutes a slight surface damage could be observed. After annealing the surface damage, seen be the naked eye, vanished (except for the sample made for 10 min). Figure 4 shows the values of the effective refractive index n_{eff} at different exchange times for waveguides exchanged at 210°C before and after annealing. Summarized results of the exchange process for *y*-cut $LiNbO_3$ samples are presented in the Table. It contains information about the number of the samples which can support different numbers of the waveguide modes depending on the exchange temperature as well as the exchange time, before and after annealing.

Measured first mode losses on various *y*-cut samples were between 4 and 5 dB/cm.

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References

[1] JACKEL J. L., RICE C. E., VESELKA J. J., Appl. Phys. Lett. **41** (1982), 607.
[2] GOODWIN M., STEWART C., Electron. Lett. **19** (1983), 223.
[3] DAWAR A. L., AL-SHUKRI S. M., DE LA RUE R. M., Appl. Phys. Lett. **48** (1986), 1579.
[4] DE MICHELI M., BOTINEAU J., SIBILLOT P., OSTROWSKY D. B., PAPUCHON M., Optics Commun. **42** (1982), 101.
[5] JACKEL J. L., RICE C. E., VESELKA J. J., Electron. Lett. **19** (1983), 387.
[6] PUN E. Y., WONG K. K., ANDONOVIC I., LAYBOURN P. J., DE LA RUE R. M., Electron. Lett. **18** (1982), 740.
[7] DE MICHELI M., BOTINEAU J., NEVEU S., SIBILLOT P., OSTROWSKY D. B., PAPUCHON M., Opt. Lett. **8** (1983), 116.
[8] PAPUCHON M., VATOUX S., Electron. Lett. **19** (1983), 612.
[9] MAHAPATRA A., ROBINSON W. C., Appl. Opt. **24** (1985), 2285.
[10] HARUNA M., NAKAJIMA H., NASHIHARA H., Appl. Opt. **24** (1985), 2483.
[11] WONG K. K., DE LA RUE R. M., WRIGHT S., Opt. Lett. **7** (1982), 546.
[12] SAIGA N., ICHIOKA Y., J. Appl. Phys. **61** (1987), 1230.
[13] BECKER R A., Appl. Phys. Lett. **43** (1983), 131.
[14] JACKEL J. L., RICE C. E., Proc. SPIE **460** (1984), 43.
[15] WONG K. K., GEC J. Research **3** (1985), 243.
[16] YI-YAN A., Appl. Phys. Lett. **42** (1983), 633.
[17] KORKISHKO Y. N., GANSHIN V. A., Zh. Tekh. Fiz. **58** (1988), 692.
[18] TANIUCHI T., YAMAMOTO K., Proc. SPIE **864** (1988), 36.
[19] TIEN P. K., ULRICH R., J. Opt. Soc. Am. **60** (1970), 1325.
[20] WHITE J. M., HEIDRICH P. F., Appl. Opt. **15** (1976), 151.
[21] CHIANG K. S., J. Lightwave Techn. LT-3 (1985), 385.
[22] CHARTIER G. H., JAUSSAUD P. C., J. Appl. Phys. **49** (1978), 91.
[23] MACIAK T., SOKOŁOWSKI M., Opt. Appl. **19** (1989), 461.

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Производства оптических волноводов $LiNbO_3$ путем протонного обмена в расплаве адипиновой кислоты

В работе представлен метод производства оптических волноводов $LiNbO_3$ на *x*- и *y*-срезе путем протонного обмена в расплаве адипиновой кислоты. В результате процесса получено максимальное изменение необыкновенного показателя преломления света $\Delta n_e = 0{,}139$ ($\lambda = 632.8$ нм.). Это высшее изменение покателя преломления света получено до сих пор в результате протонного обмена в $LiNbO_3$. Коэффициент затухания измерений в одномодных пробках заключался в границах от 3,5 до 5 дБ/см.