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Ion Exchange Model for α Phase Proton Exchange Waveguides in $LiNbO_3$

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***Abstract*—An H^+/Li^+ exchange model is found to be applicable to describe the diffusion of protons when optical waveguides are formed in $LiNbO_3$ by proton exchange methods where the proton doped crystal structure stays in the pure α phase. The H^+ and Li^+ self-diffusion coefficients in the ion exchange model are determined as a function of the proton exchange temperature both for x-cut and z-cut $LiNbO_3$. In this way a very useful tool for predicting the proton concentration profiles and hence the refractive index profiles of α phase proton exchange $LiNbO_3$ waveguides is achieved.**

***Index Terms*— Diffusion processes, modeling, optical waveguides.**

I. Introduction

THE proton exchange (PE) method [1] has been used for several years to form optical waveguides at the surface of $LiNbO_3$ crystals. Exchanging lithium ions with protons in a proton source such as benzoic acid, typically at temperatures of $T = 200$ °C, induces an increase of the $LiNbO_3$ extraordinary refractive index of ~0.12 at the 632.8 nm wavelength while a decrease in the ordinary refractive index is observed. The crystalline structure of proton doped $LiNbO_3$ depends on the exchange conditions, and several phases can be induced in the crystal [2]. Original $LiNbO_3$ qualities such as optical nonlinear properties are reduced due to such phase changes [3]–[5]. However, for proton concentrations (normalized to the initial lithium concentration, in the following just referred to as proton concentration c) below 0.12 the PE $LiNbO_3$ stays in a crystal phase denoted as the α phase where no significant changes of the normal $LiNbO_3$ crystal are observed [2]. A method to form waveguides with only this α phase induced are the dilute melt proton exchange [6]–[9] (DMPE) method typically using exchange temperatures of $T = 200$–300 °C. Using this exchange method with the appropriate exchange melt composition, PE waveguides with proton concentrations below 0.12 can be directly achieved. Waveguides formed in this way have optical second order nonlinearities close to the values of untreated $LiNbO_3$ [10]. As another example it was found in [11] that regions in $LiNbO_3$ crystals with periodic inversion of the ferroelectric domains, useful for optical frequency doubling by the quasiphasematching method [12]–[14], are unaffected by the fabrication of a waveguide with relatively low proton concentrations using the so-called graded proton exchange (GPE) [15]. According to [11] this is not necessarily the case when the waveguide is fabricated by the annealed proton exchange method (APE) where high refractive indexes and hence high proton concentrations are induced during the waveguide formation process.

The paper presented here is concerned with the proton diffusion properties when α phase optical waveguides are formed in $LiNbO_3$ by a method such as DMPE. Detailed knowledge of these diffusion properties is an important tool for the optimization of optical waveguide design.

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II. Ion Exchange Model

While the general description of proton diffusion in waveguides made by PE is a complicated task, related to the seven different crystal phases that can be induced [2], we assume that the protonic diffusion in PE $LiNbO_3$ staying in the pure α phase region can be estimated by an H^+/Li^+ exchange model [16]–[18]. Assuming this to be correct, the proton concentration profile can be found by solving the diffusion equation with a proton concentration dependent diffusion coefficient. In the case of planar waveguides the one-dimensional (1-D) diffusion equation then is [16]

$$\frac{dc}{dt} = \frac{d}{dx}\left(\frac{D_{\mathrm{H}}}{1 - \left(1 - \frac{D_{\mathrm{H}}}{D_{\mathrm{Li}}}\right)c} \frac{dc}{dx} \right) \tag{1}$$

where D_{H} and D_{Li} are the self-diffusion coefficients for the protons and lithium ions, respectively. The quantity x is waveguide depth position whereas t is the exchange time. D_{H} and D_{Li} are expected to follow an exponential activation law of the form $D_i(T) = D_{\infty,i} \exp(-T_{o,i}/T), i = \mathrm{H}, \mathrm{Li}$. Having determined $D_{\mathrm{H}}(T)$ and $D_{\mathrm{Li}}(T)$, (1) then can be solved at any temperature to predict the induced proton concentration profile for waveguides in the α phase region. In the case of channel waveguide formation the corresponding two-dimensional (2-D) diffusion equation can be applied if the self-diffusion coefficients are determined for both x- and z-cut planar PE waveguides.

III. Experimental

We have estimated experimentally $D_{\mathrm{H}}(T)$ and $D_{\mathrm{Li}}(T)$ from annealing treatments of PE planar waveguides both made in x- and z-cut $LiNbO_3$ in the following way. The PE optical waveguides were fabricated in an exchange melt consisting of 1 g $KHSO_4$ dissolved in 100 mL glycerol [19] at an exchange temperature of $T = 230$ °C. The exchange times were 2.5

h (x-cut) and 6 h (z-cut). Different waveguides were then annealed in air at temperatures in the range $T = 280$–375 °C. This was done to diffuse the protons deeper into the crystal to obtain the α phase structure there. For each annealed PE waveguide the annealing treatment was divided into several steps. Between each annealing step the optical waveguide mode indexes were measured with a prism coupler setup at the 632.8 nm wavelength (in the following the optical properties discussed of the $LiNbO_3$ waveguides are at 632.8 nm and the refractive index always refers to the extraordinary refractive index). From the measured mode indexes, the profile of the refractive index was estimated by the inverse WKB method by White *et al.* [20]. To have some approximate relation between the change of the refractive index (Δn) and the proton concentration, the expression suggested in [9], based on the structural behavior of powder $LiNbO_3$ with proton concentration [21], was found to give fairly consistent results in our calculations

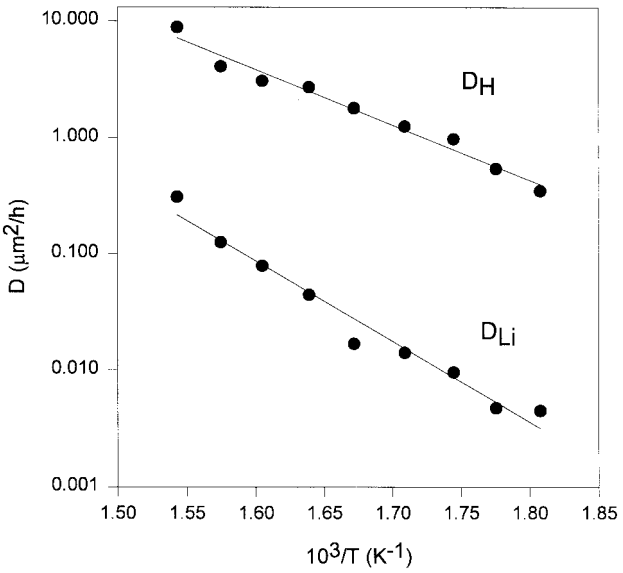
$$\begin{aligned} c \le 0.12\text{: } \Delta n(c) &= 0.1623c \\ 0.12 < c \le 0.56\text{: } \Delta n(c) &= -0.2656c^2 + 0.3636c - 0.0203 \\ c > 0.56\text{: } \Delta n(c) &= 0.0833c + 0.0533. \end{aligned} \tag{2}$$

Using this relation both for x- and z-cut $LiNbO_3$, the proton concentration before and after each annealing step thus could be determined. The values of D_{H} and D_{Li} for a certain temperature were then obtained as follows. For each annealing step (1) was used to calculate the proton concentration profile after this annealing step. When solving (1) the measured concentration profile before the annealing step was used as the initial proton profile. The calculated and measured proton profile after the annealing step were then compared via the expression

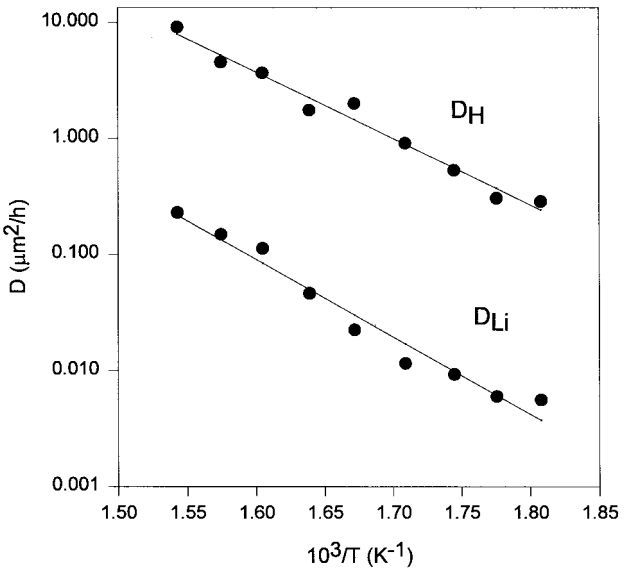
$$S = \frac{1}{N} \sum_{i=0}^{N-1} \frac{(c(x_i) - \underline{c}(x_i))^2}{c(x_i)^2}. \tag{3}$$

The quantities $c(x_i)$ and $\underline{c}(x_i)$ are the measured and calculated proton concentrations taken in a number N of equally spaced waveguide depth positions x_i. For each annealing temperature the values of D_{H} and D_{Li} were determined by minimizing S averaged over all annealing steps.

The main advantage of using APE waveguides to determine D_{H} and D_{Li}, is that it is easy to achieve waveguides with many modes over a relatively large temperature interval. Therefore, detailed information on the waveguide proton concentration profile from mode index measurements can be obtained in this temperature interval. Though a more complicated description than a simple ion exchange model must be included when describing the formation of the PE waveguides formed with the above mentioned conditions [22], we prefer to calculate the α phase self-diffusion coefficients from the corresponding APE waveguides as a simple approximation assuming that diffusion mainly takes place as in the α phase. This approximation is probably good since the waveguides contained regions with relatively low proton concentrations and since the function in (3) due to the weight parameter $c(x_i)^2$ emphasizes the α phase region where $c(x_i)^2$ is small.



(a)



(b)

Fig. 1. Relation between D_{H} and T (upper curve) and D_{Li} and T (lower curve) for (a) x-cut $LiNbO_3$ and (b) z-cut $LiNbO_3$.

The values determined for D_{H} and D_{Li} as a function of temperature are shown by the dots in Fig. 1 and compared to the expected $D(T) = D_{\infty,i} \exp(-T_{o,i}/T), i = \mathrm{H}, \mathrm{Li}$, dependence. The agreement is excellent. Hence, the diffusion model in (1) seems to be confirmed. From the data shown in Fig. 1, the values of $D_{\infty,i}$ and $T_{o,i}$ were determined to be $D_{\infty,\mathrm{H}} = \exp(18.82)\ \mu\mathrm{m}^2/\mathrm{h}, T_{o,\mathrm{H}} = 10.92 \cdot 10^3$ K and $D_{\infty,\mathrm{Li}} = \exp(23.05)\ \mu\mathrm{m}^2/\mathrm{h}, T_{o,\mathrm{Li}} = 15.93 \cdot 10^3$ K for x-cut $LiNbO_3$. For z-cut $LiNbO_3$ the values were determined to be $D_{\infty,\mathrm{H}} = \exp(22.39)\ \mu\mathrm{m}^2/\mathrm{h}, T_{o,\mathrm{H}} = 13.17 \cdot 10^3$ K and $D_{\infty,\mathrm{Li}} = \exp(22.11)\ \mu\mathrm{m}^2/\mathrm{h}, T_{o,\mathrm{Li}} = 15.32 \cdot 10^3$ K.

To further verify the ion exchange model with the self-diffusion coefficients determined by the above described procedure, we calculated the proton concentration profile and

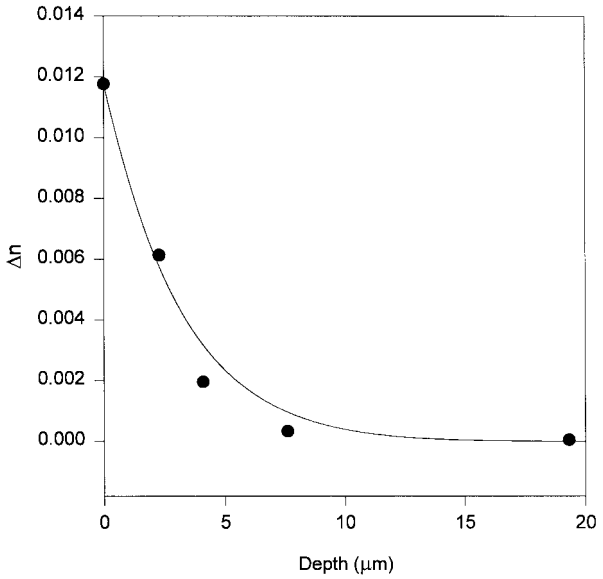


Fig. 2. Experimentally determined refractive index profile for a z-cut GPE waveguide (dots) taken from [11] and calculated profile using (1) [solid curve].

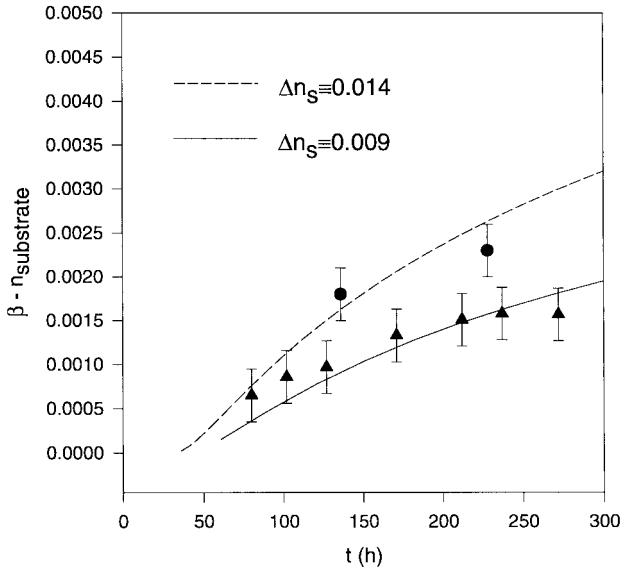


Fig. 3. Calculated and measured dependence of fundamental mode refractive index β on exchange time for z-cut waveguides formed by the DMPE method in [9].

hence the refractive index profile of a waveguide in z-cut $LiNbO_3$ from [11] fabricated by GPE at an exchange temperature of $T = 400$ °C. The experimentally determined profile of the refractive index is taken from Fig. 8 in [11] and is shown here by the dots in Fig. 2. The solid line shown in this figure is the refractive index profile calculated from the ion exchange model with the values determined for $D_{\mathrm{H}}(T)$ and $D_{\mathrm{Li}}(T)$ at $T = 400$ °C using the parameters found above. The diffusion equation was solved assuming that the value of the proton concentration at the $LiNbO_3$ crystal surface is kept constant during the exchange process.

We also applied the ion exchange model to DMPE optical waveguides. The waveguides were made in z-cut $LiNbO_3$ by the DMPE method from [9] using a system of glycerol, $KHSO_4$ and lithium benzoate at an exchange temperature of $T = 230$ °C. Fig. 3 shows how the fundamental waveguide mode index β evolves with the exchange time. The values of the mode index β, determined experimentally from prism coupler measurements, are shown by the points while the solid lines represent the values of β determined from the proton profile solution obtained from (1) at $T = 230$ °C. The error bars in Fig. 3 are the uncertainty in the mode index determination using the prism coupler, the value estimated to be ± 0.0003. When solving the diffusion equation it was assumed that the surface refractive index and hence surface proton concentration is kept constant during the exchange process. The two curves correspond to different exchange melt compositions which determine the surface refractive index change Δn_s. The calculated refractive index profile was subdivided into a number of step layer profiles, and the method by Offersgaard [23] was then used for calculating β. In the calculation of β it was assumed that the ratio between the ordinary and extraordinary refractive index change was -0.32 [23]. Both in Figs. 2 and 3, we see a very good agreement between experimental data and predicted data using (1) for, respectively, GPE and DMPE waveguides.

IV. Summary

In conclusion, it can be stated that we have shown that it is possible to use an H^+/Li^+ exchange model to describe the diffusion of protons in waveguides with proton concentrations that correspond to the α phase, when these waveguides are formed in $LiNbO_3$ either by the graded proton exchange or the dilute melt proton exchange method. The values of the proton and lithium self-diffusion coefficients have been determined as a function of temperature for x- and z-cut $LiNbO_3$. In this way any α phase proton profile of proton exchange planar or channel optical waveguides in $LiNbO_3$ can be predicted at any fabrication temperature. This is an extremely useful tool in the optimization procedure of the optical properties of α phase waveguide designs.

References

[1] J. L. Jackel, C. E. Rice, and J. J. Veselka, "Proton exchange for high-index waveguides in $LiNbO_3$," *Appl. Phys. Lett.*, vol. 41, pp. 607–608, 1982.

[2] Yu. N. Korkishko, and V. A. Fedorov, "Structural phase diagram of $H_xLi_{1-x}NbO_3$ waveguides: The correlation between optical and structural properties," *IEEE J. Select. Topics Quantum Electron.*, vol. 2, pp. 187–196, 1996.

[3] M. L. Bortz, L. A. Eyres, and M. M. Fejer, "Depth profiling of the d_{33} nonlinear coefficient in annealed proton exchanged $LiNbO_3$ waveguides," *Appl. Phys. Lett.*, vol. 62, pp. 2012–2014, 1993.

[4] R. W. Keys, A. Loni, and R. M. De La Rue, "Measurement of the increase in the SHG coefficient of proton exchanged after annealing using a grating diffraction technique," *Electron. Lett.*, vol. 26, pp. 624–626, 1990.

[5] T. Suhara, H. Tazaki, and H. Nishihara, "Measurement of reduction in SHG coefficient of $LiNbO_3$ by proton exchanging," *Electron. Lett.*, vol 25, pp. 1326–1328, 1989.

[6] P. G. Suchoski, T. K. Findakly, and F. J. Leonberger, "Stable low-loss proton-exchanged $LiNbO_3$ waveguide devices with no electro-optic degradation," *Opt. Lett.*, vol. 13, pp. 1050–1052, 1988.

[7] M. M. Abouelleil and F. J. Leonberger, "Waveguides in lithium niobate," *J. Amer. Ceram. Soc.*, vol. 72, pp. 1311–1321, 1989.

[8] M. J. Li, M. De Micheli, D. Ostrowsky, and M. Papuchon, "Réalization sur $LiNbO_3$ de guides d'ondes présentant une forte variation d'indice et de très faibles pertes," *Ann. Télécommun.*, vol. 43, pp. 73–77, 1988.
[9] T. Veng and T. Skettrup, "Diluted melt proton exchange slab waveguides in $LiNbO_3$: A new fabrication and characterization method," to be published in *Applied Optics*.
[10] T. Veng, T. Skettrup, and K. Pedersen, "Second-order optical nonlinearities in dilute melt proton exchange waveguides in z-cut $LiNbO_3$," *Appl. Phys. Lett.*, vol. 69, pp. 2333–2325, 1996.
[11] J. Webjörn, "Structural influence of proton exchange on domain-inverted lithium niobate revealed by means of selective etching," *J. Lightwave Technol.*, vol. 11, pp. 589–594, 1993.
[12] J. Webjörn, F. Laurell, and G. Arvidson, "Blue light by frequency doubling of laser diode light in a lithium niobate channel waveguide," *IEEE Photon. Technol. Lett.*, vol. 1, pp. 316–318, 1989.
[13] E. J. Lim, M. M. Fejer, and R. L. Byer, "Second-harmonic generation of green light in periodically poled planar lithium niobate waveguide," *Electron. Lett.*, vol. 25, pp. 174–175, 1989.
[14] T. Yamada, N. Nada, M. Saitoh, and K. Watanabe, "First-order quasiphase matched $LiNbO_3$ waveguide periodically poled by applying an external field for efficient blue second-harmonic generation," *Appl. Phys. Lett.*, vol. 62, pp. 435–436, 1993.
[15] V. A. Ganshin and Yu. N. Korkishko, "Proton exchange in lithium niobate and lithium tantalate single crystals: Regularities and specific features," *Phys. Stat. Sol. (a)*, vol. 119, pp. 10–25, 1990.
[16] J. Crank, "The mathematics of diffusion," Oxford University Press, 2nd ed., 1975.
[17] D. F. Clark, A. C. G. Nutt, K. K. Wong, P. J. R. Laybourn, and R. M. De La Rue, "Characterization of proton-exchange slab optical waveguides in z-cut $LiNbO_3$," *J. Appl. Phys.*, vol. 54, pp. 6218–6220, 1983.
[18] S. T. Vohra, A. R. Mickelson, and S. E. Asher, "Diffusion characteristics and waveguiding properties of proton-exchanged and annealed $LiNbO_3$ channel waveguides," *J. Appl. Phys.*, vol. 66, pp. 5161–5174, 1989.
[19] V. A. Ganshin and Yu. N. Korkishko, "Stress and strain in H:$LiNbO_3$ optical waveguides," *Sov. Phys. Tech. Phys.*, vol. 37, pp. 49–54, 1992.
[20] J. M. White and P. F. Heidrich, "Optical waveguide refractive index profiles determined from measurements of mode indices: A simple analysis," *Appl. Opt.*, vol. 15, pp. 151–155, 1976.
[21] C. E. Rice, "The structure and properties of $Li_{1-x}H_xNbO_3$," *J. Solid State Chem.*, vol. 64, pp. 188–199, 1986.
[22] V. A. Ganshin and Yu. N. Korkishko, "Kinetic model of proton-lithium exchange in $LiNbO_3$ and $LiTaO_3$ crystals: The role of cation vacancies," *Solid State Ionics*, vol. 58, pp. 23–32, 1992.
[23] J. F. Offersgaard, "Waveguides formed by multiple layers of dielectric, semiconductor, or metallic media with loss and anisotropy," *J. Opt. Soc. Amer. A*, vol. 12, pp. 2122–2128, 1995.

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