Correlation between structural and optical properties in proton-exchanged $LiNbO_3$

Wei-Yung Hsu,[a] Gabriel Braunstein, Venkatraman Gopalan,[a] Craig S. Willand, and Mool C. Gupta
Corporate Research Laboratories, Eastman Kodak Company, Rochester, New York 14650-2017

(Received 23 July 1992; accepted for publication 23 October 1992)

We present a correlation of the structural characterization of proton-exchanged $LiNbO_3$ provided by ion beam and x-ray analysis with the optical characterization provided by refractive index and second-harmonic generation measurements. The process of proton exchange induces disorder in the crystal lattice of $LiNbO_3$. Subsequent thermal annealing removes only partially the lattice disorder and, in particular, the near surface region of the samples generally remains highly distorted. Results of x-rays studies indicate that the proton exchange induces a strain in the lattice and thermal annealing partially recovers it.

Recently,[1] frequency doubling of semiconductor diode laser radiation to obtain blue wavelength has generated a lot of interest. Efficient second-harmonic conversion has been obtained using waveguide structures in $LiNbO_3$,[2,3] $LiTaO_3$,[4] and KTP[5] in which phase matching is achieved by periodic domain reversal. However, the experimental conversion efficiencies are lower than the predicted theoretical efficiencies.[2] One possible reason is that there may be a degradation of the nonlinear optical properties during the waveguide fabrication process using proton exchange. Suhara *et al.*[6] and Cao *et al.*[7] have reported a 50% reduction in the nonlinear coefficient of $LiNbO_3$ after proton exchange in benzoic acid. Cao *et al.*[7] also reported essentially a complete recovery of the nonlinear coefficient after thermal annealing. Laurell *et al.*[8] have reported very recently a 30-fold reduction in the optical nonlinearity for $LiNbO_3$ but contrary to previous reports, they find that the optical nonlinearity cannot be effectively restored by thermal annealing. Bortz *et al.*[9] have measured the d_{33} nonlinear coefficient in proton-exchanged $LiNbO_3$ and observed a reduction to $<1\%$ of the bulk $LiNbO_3$ value. Bortz *et al.*[9] suggest that the differences between their results and those of Cao *et al.*[7] are due to neglect of the reflected second-harmonic intensity on both the d_{33} discontinuity at the film substrate interface and the angular dependence of the nonlinear polarization. Hsu *et al.*[10] have reported a similar degradation in the nonlinear coefficient of $LiNbO_3$ and $LiTaO_3$ after proton exchange using benzoic acid or pyrophosphoric acid. Very limited recovery of the nonlinear coefficient upon thermal annealing was observed in samples that underwent proton exchange for relatively short periods of time (0.5 h at 180 °C).

Several studies have been reported on the structural characterization of $LiNbO_3$. Rice[11] reported an approximate phase diagram for the stoichiometric $LiNbO_3$-$HNbO_3$ system. Depending upon composition, samples undergo one, two, or three phase transitions with temperature. Canali *et al.*[12] reported results of structural analysis of proton-exchanged lithium niobate optical waveguides fabricated in X, Y, and Z cut substrates immersed in pure benzoic acid. They measured atomic composition profiles and noted the marked lattice distortion. H and Li concentration measurements indicated an exchange of about 70% of the Li atoms. The hydrogen depth profile measurements showed a steplike shape in agreement with the refractive index profile measured optically. They concluded that exchange induces a large crystal distortion strongly correlated to the presence of protons. Lee *et al.*[13] studied structural phase changes in proton-exchanged $LiNbO_3$ waveguides using transmission electron microscopy. Regions of diffuse intensity within the single crystal electron diffraction patterns of $LiNbO_3$ were observed. Minakata *et al.*[14] measured the lattice constants and electro-optic constants of Z-cut proton-exchanged $LiNbO_3$ crystals by means of the x-ray rocking curve method and the phase modulation technique. They found that the strain along the c axis, $\Delta c/c$, was extremely large ($+0.45\%$) while the strain perpendicular to the c axis, $\Delta a/a$, was negligibly small in proton-exchanged $LiNbO_3$ single crystals (where c is lattice constant along c axis and a is lattice constant along the a axis). The electro-optic coefficient value in the layer reduced to one-tenth of the bulk crystal value. Vohra *et al.*[15] measured the concentration profiles of proton and lithium in proton-exchanged $LiNbO_3$ crystals using secondary ion mass spectroscopy and found proton concentration profiles nearly rectangular in shape. Recently Loni *et al.*[16] reported, using secondary ion mass spectrometry (SIMS) and an optical method, a direct comparison of hydrogen depth distributions and refractive index profiles in annealed proton-exchanged Z-cut $LiNbO_3$ waveguides. Novak and Matthews[17] have reported SIMS depth profile measurements of H, Li, Nd, and Er in $LiNbO_3$ and $LiTaO_3$. The above discussion indicates that extensive studies have been carried out on the characterization of the proton exchange process. Some results have also been reported on the degradation of the electro-optic coefficient. To our knowledge no results have been reported correlating the degradation of the nonlinear coeffi-

[a]Permanent address: Department of Materials Science and Engineering, Cornell University, Ithaca, NY 14853.

 0003-6951/92/513083-03$06.00

cient to its structural aspects. In this letter we report results of x-ray rocking curve studies as well as depth profiles of H and Li and ion channeling measurements using forward recoil spectrometry (FRES), the ion-induced nuclear reaction $Li^7(p,\alpha)He^4$ and Rutherford backscattering (RBS) techniques, respectively, that provide some structural characterization of proton-exchanged and annealed $LiNbO_3$ samples. These measurements are correlated with optical measurements of the refractive index and second-harmonic generation.

Proton exchange in X-cut $LiNbO_3$ was carried out using benzoic acid at 180 °C for different times. Thermal annealing was done at 350 °C in air for various times. The ion beam analysis was carried out using a 1.7 MeV tandetron accelerator. The hydrogen profile was determined by FRES using a 3 MeV He incident beam. The Li profile was determined by means of the $Li^7(p,\alpha)He^4$ nuclear reaction induced by a 1.2 MeV H beam. Disorder in the $LiNbO_3$ lattice was monitored by RBS combined with channeling using a 2 MeV He beam. X-ray rocking curve analysis was carried out using a Phillips MPD 1180/HR x-ray diffractometer, where the monochromatic Cu$K\alpha$ line is selected and collimated by using four Ge (220) single crystals.

Figure 1(a) shows the Li profiles for a bulk $LiNbO_3$ crystal, a proton-exchanged crystal and an annealed sample. These results indicate a significant loss of Li from the surface upon proton exchange and recovery of it after thermal annealing (although a region of about 0.1 μm in thickness still remains Li deficient). Figure 1(b) shows the hydrogen profiles of the same set of samples. The hydrogen peak at the surface of the untreated $LiNbO_3$ crystal could be due to the moisture present at the surface. The simulation results using the RUMP program[18] indicate a steplike profile of hydrogen after proton exchange in agreement with literature data.[16] After annealing the hydrogen concentration falls below our detection sensitivity except for a small peak in the near surface region of the sample. The RBS channeling results presented in Fig. 1(c) show that the proton exchange induces disorder in the Nb sublattice extending from the surface of the sample to a depth of approximately 0.7 μm. This disordered region coincides with the Li-depleted and hydrogen-occupied regions shown in Figs. 1(a) and 1(b), respectively. Upon thermal annealing most of the lattice disorder is recovered except for a narrow region, approximately 0.1-μm thick close to the surface of the sample. Figures 1(a) and 1(b) show that this region is also Li deficient and presumably, H rich, respectively. In the second-harmonic reflectance technique used by Laurell *et al.*,[8] Bortz *et al.*,[9] and Hsu *et al.*,[10] the second-harmonic signal is obtained only from the front surface since the skin depth for the wavelength employed is order of 0.1 μm. This implies that the reflectance technique does not provide a full characterization of the degradation in waveguides that are typically 1-μm deep. Also, since there is a marked recovery in deeper regions of sample, efficient second-harmonic generation is possible in $LiNbO_3$, although conversion efficiencies smaller than theoretical values can be expected. This explains the results obtained by Suhara *et al.*[6] and Cao *et al.*,[7] who used probing techniques that were more sensitive to the bulk of the samples than to their respective surfaces.

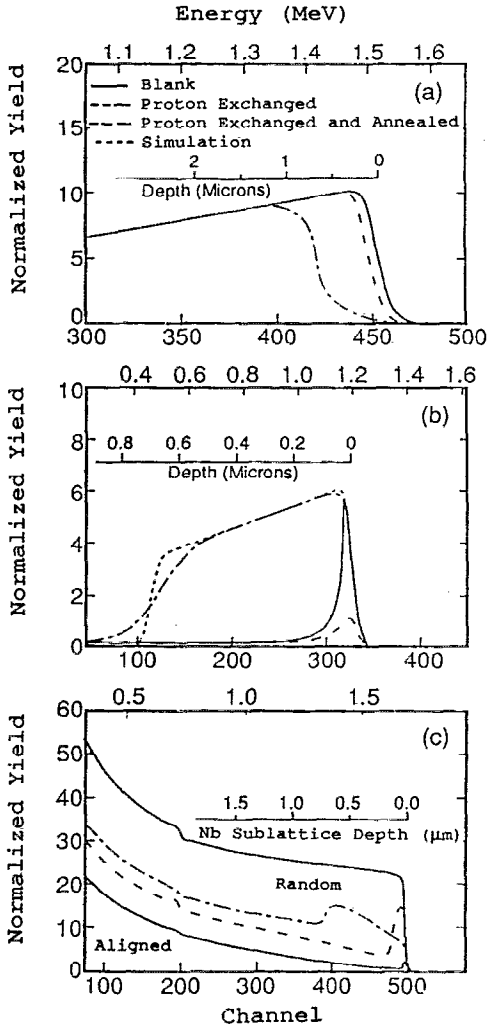

FIG. 1. Li depth profiles (a) H depth profiles (b) and ion channeling results (c) for X-cut $LiNbO_3$ blank, after proton exchange in benzoic acid at 180 °C for 1 h, and after thermal annealing in air at 350 °C for 10 h.

The RBS channeling results of a X-cut $LiNbO_3$ sample that was proton exchanged in benzoic acid for 30 min at 180 °C and subsequently annealed in air for 2 h at 350 °C, revealed disorder in the crystal lattice after proton exchange to a depth of about 0.35 μm. However, in this case (short p-exchange time) there is almost complete recovery after thermal annealing. Indeed, SHG signal was observed after thermal annealing but not after proton exchange. Also, the prism coupling method indicated a waveguide in the sample after thermal annealing but no waveguide was observed after proton exchange. The RBS channeling results of a X-cut $LiNbO_3$ sample that was proton exchanged for 30 min at 230 °C in pyrophosphoric acid and subsequently annealed in air for 1 h at 350 °C, indicated disorder in the crystal lattice after proton exchange extending to a depth of 1.8 μm, which partially recovers upon thermal annealing. No SHG signal was observed after proton exchange or thermal annealing. Therefore, proton exchange with pyrophosphoric acid produces similar lattice disorder

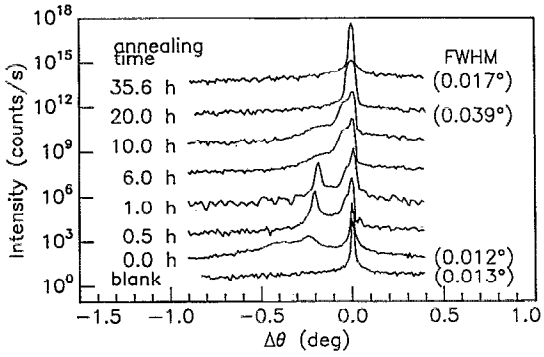

FIG. 2. X-ray rocking curve analysis for X-cut $LiNbO_3$ after exchange in benzoic acid at 180 °C for 1 h and thermal annealing in air at 350 °C for various times.

as proton exchanged with benzoic acid.

In Fig. 2 we present x-ray rocking curve results for a X-cut $LiNbO_3$ crystal that was proton exchanged in benzoic acid at 180 °C for 1 h and subsequently annealed for various times at 350 °C. Figure 2(a) shows that besides the substrate peak, there are two satellite peaks on the lower angle side of the substrate peak. These results are in agreement with some of the previously reported work.[19,20] From the satellite peak positions strains along the a axis were calculated as 0.86% and 0.63%. Of the two satellite peaks one could be due to surface strain, which is graded, as this peak has broader distribution, and other peak could be due to the deeper region where strain appears to be more uniform. Upon thermal annealing the strain decreases with increase in annealing time. However, even after 36 h of annealing, the x-ray peak shows significant broadening, indicating that the structure does not fully recover.

The refractive index was measured for X-cut $LiNbO_3$ after proton exchange and for various annealing times and the index profile was obtained using the IWKB[21] method. Proton exchange was carried out using benzoic acid at 180 °C for 1.5 h followed by annealing at 350 °C for 17 h. The hydrogen profile results for proton-exchanged samples indicate a steplike hydrogen concentration [Fig. 1(b)]. It is interesting to note that after thermal annealing there was no detectable hydrogen concentration. However, the waveguide was still present.

The large refractive index of $LiNbO_3$ is a result of the extreme polarizability of the Nb—O bonds. The proton exchange process induces a distortion of the crystal lattice and hence a distortion of the Nb—O bonds. This change on the niobate structure appears to cause the index increase. This effect appears to be also the source of the decrease in the nonlinear optical coefficient, a property that is also related to the polarizability of the Nb—O bond. Therefore, it appears that it is not the presence of the protons, but rather their effect on the Nb-O lattice, that affects the optical properties. Full recovery of the optical properties does not occur by removing the protons, but rather by restoring the crystal lattice.

In conclusion, our results indicate that the process of proton exchange creates a high disorder in the crystal lattice, which has a significant impact on the linear and nonlinear optical properties of the material. Thermal annealing recovers some of the disorder in the lattice except near the surface. Our results indicate that the 532 nm SHG experiments on proton-exchanged and subsequently annealed $LiNbO_3$ samples gave good information about the degradation in nonlinear properties near the surface, but nothing about the deeper parts of the waveguide region. SHG experiments with longer wavelength than 532 nm should provide information about deeper regions. Samples proton exchanged for short periods of time and subsequently thermal annealed showed almost complete recovery of lattice disorder and exhibited second-harmonic light generation. The x-ray studies indicate that the proton exchange process induces a strain in the lattice and long periods of thermal annealing are needed to remove the strain induced by the proton exchange.

[1] W. P. Risk, Optics and Photonics News, May 1990, p. 10.
[2] E. J. Lim, M. M. Fejer, and R. L. Byer, Electron. Lett. **25**, 731 (1989).
[3] J. Webjorn, F. Laurell, and G. Arvidsson, IEEE Photon. Tech. Lett. **1**, 316 (1989).
[4] K. Mizuuchi, K. Yamamoto, and T. Taniuchi, Appl. Phys. Lett. **58**, 2732 (1991).
[5] J. D. Bierlein, D. B. Laubacher, J. B. Brown, and C. J. van der Poel, Appl. Phys. Lett. **56**, 1725 (1990).
[6] T. Suhara, H. Tazaki, and H. Nishihara, Electron. Lett. **25**, 1326 (1989).
[7] X. Cao, R. Srivastava, R. Ramaswamy, and J. Natour, IEEE Photon. Tech. Lett. **3**, 25 (1991).
[8] F. Laurell, M. G. Roelofs, and H. Hsiung, Appl. Phys. Lett. **60**, 301 (1992).
[9] M. L. Bortz and M. M. Fejer, Opt. Lett. **17**, 704 (1992).
[10] W. Y. Hsu, C. S. Willand, V. Gopalan, and M. C. Gupta, Appl. Phys. Lett. **61**, 2263 (1992).
[11] C. E. Rice, J. Solid State Chem. **64**, 188 (1986).
[12] C. Canali, A. Camera, G. Della Mea, P. Mazzoldi, S. M. Al Shukri, A. C. G. Nutt, and R. M. De La Rue, J. Appl. Phys. **59**, 2643 (1986).
[13] W. E. Lee, N. A. Sanford, and A. H. Heuer, J. Appl. Phys. **59**, 2629 (1986).
[14] M. Minakata, K. Kumagai, and S. Kawaakami, Appl. Phys. Lett. **49**, 992 (1986).
[15] S. T. Vohra, A. R. Mickelson, and S. E. Asher, J. Appl. Phys. **66**, 5161 (1989).
[16] A. Loni, R. M. De La Rue, J. M. Zavada, R. G. Wilson, and S. W. Novak, Electron. Lett. **27**, 1245 (1991).
[17] S. W. Novak, P. Matthews, W. Young, and R. Wilson, *Proceedings of SIMS VII International Conference on SIMS*, edited by A. Benninghoven, K. Janssen, J. Tumpner, and H. Werner (Wiley, Chichester, England, 1992), pp. 471-474.
[18] L. Doolittle, Ph.D. thesis, Cornell University, 1987.
[19] V. G. Ganshin, Y. N. Korkishko, and T. X. Morzova, Phys. Status Solidi A **110**, 398 (1988).
[20] W. X. Hou, W. X. Hua, Y. X. Zhang, H. L. Tan, and J. Y. Chen, Ferroelectrics **119**, 1 (1991).
[21] J. M. White and P. F. Heidrich, Appl. Opt. **15**, 151 (1976).