Available online at www.sciencedirect.com

Optical Materials 28 (2006) 1292–1295

www.elsevier.com/locate/optmat

Characterization of erbium doped lithium niobate crystals and waveguides

M. Mattarelli [a,*], S. Sebastiani [b], J. Spirkova [c], S. Berneschi [b], M. Brenci [b], R. Calzolai [b], A. Chiasera [d], M. Ferrari [d], M. Montagna [a], G. Nunzi Conti [b], S. Pelli [b], G.C. Righini [b]

[a] Physics Department, University of Trento, CSMFO Group, Via Sommarive 14, I-38050 Povo, Trento, Italy
[b] IFAC-CNR, "Nello Carrara" Institute of Applied Physics, Via Panciatichi 64, I-50127 Firenze, Italy
[c] Department of Inorganic Chemistry, Institute of Chemical Technology Prague Technicka 5, 16628 Prague, Czech Republic
[d] IFN-CNR, Institute of Photonics and Nanotechnologies, CSMFO Group, Via Sommarive 14, I-38050 Povo, Trento, Italy

Received 5 September 2005; received in revised form 21 December 2005; accepted 11 January 2006
Available online 11 May 2006

Abstract

Optical planar waveguides have been fabricated by the titanium in-diffusion process in lithium niobate crystals activated with erbium ions. The waveguides were studied by *m*-line technique in order to recover the index profile. The effect of the Ti in-diffusion on the structural and spectroscopic properties of the lithium niobate crystals was investigated by Raman and photoluminescence spectroscopies. The presence of titanium has only minor effects on the vibrational properties of the crystal, and no change in the emission properties of the erbium ions is observed.

PACS: 42.82.Et; 78.66.Nk; 78.55.Hx

Keywords: Lithium niobate; Erbium; Optical amplification

1. Introduction

Lithium niobate is one of the most popular materials for integrated optics, mainly due to its electro-optical and non-linear properties that are exploited in commercial and research devices [1–6]. Other effects are also being exploited, such as the strain-optic effect to implement wavelength-tunable polarization converters [7]. In the recent years there has been an increasing interest for massive or local doping of lithium niobate in order to extend its functionality. Integrated optical lasers and amplifiers were made possible by doping with rare earths (e.g. with Nd, Yb and Er) [8–12] or with chromium [13]. Combining the lithium niobate host properties with the spectroscopic properties of the dopants, higher component integration may be achieved; this, of course, is imposing increasingly demanding conditions to the materials and fabrication techniques. Let us limit ourselves to consider the case of Er-doped waveguides: generally, the waveguide is fabricated by Ti in-diffusion using either a homogeneously-doped crystalline wafer substrate or a high-quality commercial wafer where selective doping of the surface had been performed. Homogeneous doping can be achieved during crystal growth from an Er-doped melt; selective doping can be obtained by implantation and annealing or by in-diffusion of deposited thin erbium layers [8]. Often, however, it is said that it is difficult to achieve high-quality homogeneously-doped crystals, because the introduction of erbium ions tends to increase the number of domains in the crystal [14]. Thus, we considered worth to investigate the optical and spectroscopic properties of Ti in-diffused planar waveguides fabricated in Er^{3+}-doped niobate crystals,

---

[*] Corresponding author. Tel.: +39 0461 881543/695; fax: +39 0461 881696/680.
E-mail address: mattarel@science.unitn.it (M. Mattarelli).

0925-3467/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.optmat.2006.01.030

and to assess the change of the structural and spectroscopic properties after the formation of waveguides by titanium in-diffusion.

2. Experimental

The crystals were grown by Czochralski method in air using Pt crucible and resistance heating. An exact value of the growth rate cannot be indicated, because it depends on many parameters, such as the size of the crucible, the decreasing of the level of the melt etc.; the pulling rate was 2.8×10^{-7} m s^{-1}. The rotation rate was changed during the growth process, in the range from approximately 25×10^{-2} s^{-1} to 8×10^{-2} s^{-1} revolutions: starting from the maximum value, it was decreased quickly at the beginning of the pulling, then it was kept constant for some time and later decreased again, to reach the minimum value. The exact rotation regime is important for keeping the melt – crystal interface flat (to avoid "heap" on the lower end of the pulled crystal). The optimal regime has to fit to the particular experimental procedure and set-up, taking into account the type of the oven, the temperature gradient etc.

The melt consisted of lithium carbonate, niobium oxide and, in some batches, an appropriate amount of erbium oxide. Congruent composition of the undoped melt consisted of 48.6 mol% of Li_2O and 51.4 mol% of Nb_2O_5. For doped crystals, 5000 ppm of erbium were also added to the melt. The analysis of the melt, however, showed a value about 18% lower: this apparent lower concentration was probably a consequence of a non-precise homogeneity of the Er in the melt at the moment of removing the sample for the analysis. It has also to be taken into account that measurements' uncertainty was of the order of ±200 ppm. Subsequently, the crystal composition was analyzed by a specialized firm (Analytica s.r.o.) by using ICP/MS (Ion Coupling Photoemission/Mass Spectroscopy) methods. The results of the analysis confirmed that the distribution coefficient of Er^{3+} in $LiNbO_3$, defined as the ratio between the Er^{3+} concentration in the crystal over the Er^{3+} concentration in the melt, was close to 1.

Finally, the crystal was poled. For that purpose, both ends of the crystal were cut to be flat and were covered with powdered lithium niobate. Pt-electrodes were clung to both the ends and connected to a direct current power supply. The crystal was heated slightly above the Curie temperature, then an electric field was applied for a few hours; after that, the temperature was decreased linearly to approx. 900 °C: when such a value was reached, the electric field was switched off.

The mono-domain structure of the crystals was also checked, by using a standard procedure [15] which involved the etching of the crystal with a mixture of HF and HNO_3 (volume ratio 1:2) at 100 °C. No presence of micro-domains was found.

Optical waveguides were fabricated by the Ti in-diffusion process [16,17], by depositing a 100 nm thick Ti layer by RF-sputtering on 1 mm thick *x*- and *z*-cut slices of the doped and undoped $LiNbO_3$ crystals grown as specified (Table 1). In order to obtain single-mode waveguides at 1.5 μm, the diffusion temperature was set at 1060 °C and the diffusion time was 7.5 h.

Table 1
Specifications of the lithium niobate samples where waveguides were produced by Ti in-diffusion process

Sample	Er^{3+} concentration (mol%)	Crystal cut
LNX0	0	*x*-cut
LNX1	0.5	*x*-cut
LNZ1	0.5	*z*-cut

The index profiles of the waveguides were measured for both transverse electric (TE) and transverse magnetic (TM) polarization by an *m*-line apparatus based on the prism coupling technique. We used a rutile prism with a refractive index of 2.8659 (TE) and 2.5839 (TM) at 632.8 nm. The apparatus was equipped with a Si detector, and the measurements were made at two wavelengths, using two He–Ne lasers, emitting at 632.8 and 543.5 nm, respectively. The resolution in the determination of the angles synchronous to the propagation modes was 0.0075°.

The Raman spectra were collected upon excitation by an Ar^+ ion laser, operating at 488 nm in order to avoid the superposition between Raman and luminescence lines. The measurements were performed both in bulk and in waveguides, exciting the TE_0 mode. The signal, collected at 90° from the exciting beam, was selected by a double monochromator, after passing through a polarization analyzer and a scrambler to remove the polarizing effect of the monochromator, and collected by a photon-counting system. The resolution was set at 2 cm^{-1}.

Photoluminescence (PL) spectroscopy in the region of the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition of Er^{3+} ions was performed using the 514.5 nm line of an Ar^+ ion laser as excitation source. The luminescence was dispersed by a 320 mm single-grating monochromator with a resolution of 2 nm. The light was detected using an InGaAs photodiode and the standard lock-in technique. All the measurements were performed at room temperature.

3. Results and discussion

In an uniaxial crystal, such as lithium niobate, the refractive index depends on the angle ϑ between the electric field of the propagating beam and the optical axis [18]

$$\frac{1}{n_{\mathrm{eff}}^2(\vartheta)} = \frac{\sin^2(\vartheta)}{n_0^2} + \frac{\cos^2(\vartheta)}{n_{\mathrm{e}}^2}.$$

The refractive index measured by *m*-line technique, therefore, changes with the propagating direction and, for TM modes, also with the incidence angle. Consequently, in order to reliably measure the index profile, TE polarization was preferred. In *x*-cut waveguides, TE guided beams, depending on the direction, scan both ordinary and extraordinary indices, while for *z*-cut waveguides TE modes sense only the ordinary refractive index. The doped waveguides present four confined modes at 543.5 nm and three at 632.8 nm for both TE and TM, while the undoped waveguide shows one more mode (for the same diffusion time).

From the effective indices of the modes it is possible to reconstruct the index profile by means of the inverse Wentzel–Kramer–Brillouin (IWKB) method [19]. The results for the ordinary index profile obtained from the TE modes at 632.8 nm are shown in Fig. 1, where it has to be considered that the increase of the substrate refractive index due to the erbium doping is 0.002 (for undoped lithium niobate, the ordinary index is 2.2865 and the extraordinary index is 2.2024 [20]). The surface-to-substrate index change induced by in-diffusion is $\Delta n_0 = 0.0075$. The extraordinary index profile, measured only in the *x*-cut waveguides, presents the same complementary error function shape, typical of diffusion processes, but the Δn between surface and substrate is 0.015.

It is evident that the effects of the Ti in diffusion process are strongly anisotropic and, as reported also elsewhere [21], the diffusion in the *z*-direction is less efficient that in the *x* (or *y*)-direction, giving rise to a lower refractive index change ($\Delta n_0 =$ 0.006). Unfortunately, in our experiments, while the waveguides produced from the *x*-cut samples show good propagating properties, the surface of the LNZ1 sample appears damaged, and propagation of the light turns out to be very lossy. This damage has to be attributed to an error in the process, due to a fault in the gas supply line during the diffusion process.

The titanium in-diffusion does not appear to be affected by the presence of the erbium, at least at these concentrations, and the refractive index change in the doped and undoped *x*-cut waveguides is the same.

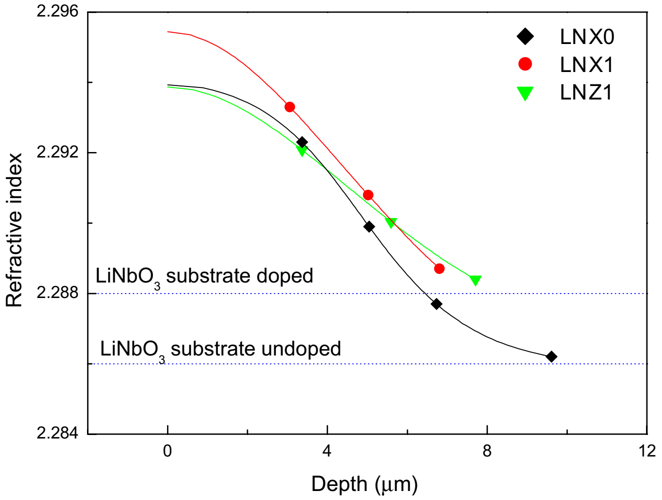

Fig. 1. Ordinary refractive index profile of the lithium niobate waveguides reconstructed from TE modal measurements at 632.8 nm. The effective indices of the guided modes for LNX0 (◆), LNX1 (●) and LNZ1 (▼) are reported.

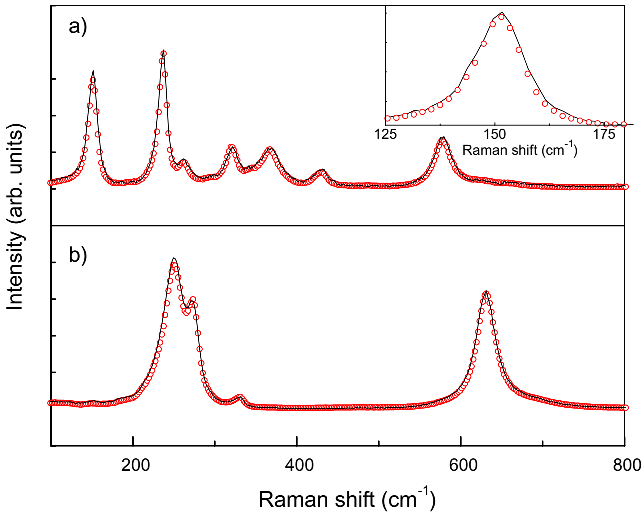

Fig. 2. Comparison of the Raman spectra of LNX1 waveguides (–) and substrate (○) in the Y(ZY)X (a) and Y(ZZ)X configuration (b). In the inset the 155 cm^{-1} *E*-line, suitably magnified, is shown. The excitation wavelength was set at 488 nm.

Fig. 2 shows, as an example, the comparison of the Y(ZY)X and Y(ZZ)X spectra (designated according to Porto notation [22]) for LNX1 bulk and waveguide samples, where we can distinguish the Raman lines related to *E* and *A*1 vibrational modes, respectively.

The positions and widths of the peak have been compared with the values reported by Ridah et al. [23] for nearly stoichiometric $LiNbO_3$. Both for bulk and for waveguides, it appears that the peak positions are very close, but, nearly ever, slightly lower with respect to the nearly stoichiometric $LiNbO_3$, and the widths are larger. Widening and red-shift of the lines are associated to the increase of stoichiometry defects, in particular to a reduction of the [Li]/[Nb] ratio [23,24]. The high number of defects detected in the analyzed samples, which are present in LNX0 too, is probably connected to the growing technique. Yet, the Ti in-diffusion results in a further, but slight, increase of the defects, as the widening and the red-shift of Raman lines is more accentuated in the waveguides than in the bulk (see inset). The Raman scattering features, however, remain basically unchanged with respect to the pure crystal one, indicating a negligible effect of the erbium and titanium doping on the lattice structure, at least at this concentration. Similar conclusion can be drawn from the comparison of the spectra of LNX0 and LNZ1, not shown here.

Fig. 3 shows σ ($E \perp z$)- and π ($E \| z$)-polarized photoluminescence spectra of the $^4I_{13/2} \rightarrow {^4I_{15/2}}$ Er^{3+} transition, which is the most important one for telecommunications applications, obtained in waveguide configuration from LNX1 sample. The σ- or π-polarization was selected by a polarizer placed before the collecting lens, while the polarization of the exciting radiation is not relevant because, after that the ions have been excited, there is a fast (compared with lifetime) redistribution of energy among the

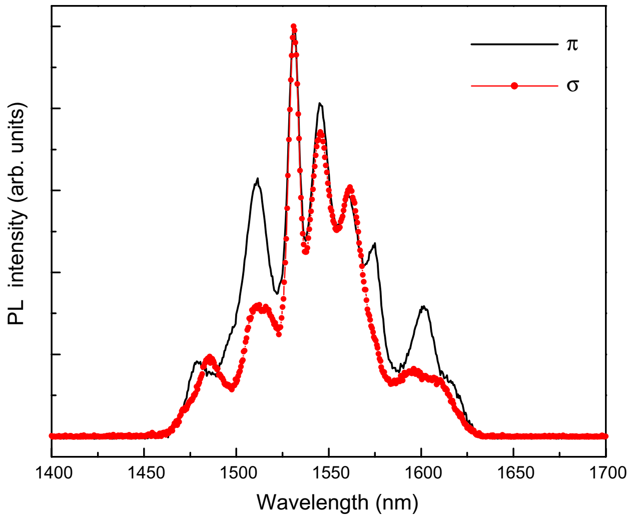

Fig. 3. σ- and π-polarized photoluminescence spectra of the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition of the Er^{3+} ions in the LNX1 waveguide upon excitation at 514.5 nm.

various Stark levels until reaching the thermal equilibrium, according to the Boltzmann law. In order to assess the effect of the titanium on the spectroscopic properties of the erbium ions, we measured the polarized PL spectra of the LNX1 substrate. The spectra completely matched, showing that the in-diffusion process does not influence the emission features.

4. Conclusions

Lithium niobate crystals, either doped with erbium or undoped, have been grown by the Czochralski method. High-quality optical planar waveguides have been fabricated by titanium in-diffusion process in *x*-cut lithium niobate wafers. The titanium in-diffusion does not result affected by the presence of the erbium, and the refractive index change ($\Delta n_0 = 0.0075$, $\Delta n_e = 0.015$) in the doped and undoped waveguides is the same. In the *z*-cut wafer the in-diffusion process is not equally efficient, and the ordinary index change is lower ($\Delta n_0 = 0.006$).

Apart from a slight increase of stoichiometry defects, the Raman spectra showed that the titanium does not modify neither the crystal structure of lithium niobate nor the spectroscopic properties of erbium. This result is in agreement with a site-selective spectroscopy investigation carried out on lithium niobate samples locally doped by erbium metal layer diffusion [25].

In conclusion, the use of homogeneously doped lithium niobate crystals is confirmed to be fully suitable for the fabrication of devices integrating several functionalities.

Acknowledgements

This work was partially supported by MIUR, Italy, through the FIRB projects "Miniature systems for electronics and photonics" and "Microdevices in lithium niobate", and the MIUR-PRIN 2004 (2004–2005) project, and by a bilateral CNR-AVCR (Firenze–Prague) collaboration. The authors are grateful to Dr. O. Jarolimek (Crytur Ltd.) for useful comments and information.

References

[1] B.C. Thomsen, D.A. Reid, R.T. Watts, L.P. Barry, J.D. Harvey, IEEE Trans. Instrum. Measur. 53 (2004) 186.
[2] D. Caccioli, A. Paoletti, A. Schiffini, A. Galtarossa, P. Griggio, G. Lorenzetto, P. Minzioni, S. Cascelli, M. Guglielmucci, L. Lattanzi, F. Matera, G.M. Tosi Beleffi, V. Quiring, W. Sohler, H. Suche, S. Vehovc, M. Vidmar, IEEE J. Sel. Top. Quantum Electron. 10 (2004) 356.
[3] A.-C. Chiang, T.-D. Wang, Y.-Y. Lin, C.-W. Lau, Y.-H. Chen, B.-C. Wong, Y.-C. Huang, J.-T. Shy, Y.-P. Lan, Y.-F. Chen, P.-H. Tsao, IEEE J. Quantum Electron. 40 (2004) 791.
[4] G.L. Li, P.K.L. Yu, J. Lightwave Technol. 21 (2003) 2010.
[5] S. Caponi, M. Dionigi, D. Fioretto, M. Mattarelli, L. Palmieri, G. Socino, Rev. Sci. Instrum. 72 (2001) 198.
[6] E.L. Wooten, K.M. Kissa, A. Yi-Yan, E.J. Murphy, D.A. Lafaw, P.F. Hallemeier, D. Maack, D.V. Attanasio, D.J. Fritz, G.J. McBrien, D.E. Bossi, IEEE J. Sel. Top. Quantum Electron. 6 (2000) 69.
[7] T.-J. Wang, J.-S. Chung, IEEE Photon. Technol. Lett. 16 (2004) 2275.
[8] I. Baumann, S. Bosso, R. Brinkmann, R. Corsini, M. Dinand, A. Greiner, K. Schäfer, J. Sochtig, W. Sohler, H. Suche, R. Wessel, IEEE J. Sel. Top. Quantum Electron. 2 (1996) 355.
[9] D. Jaque, J.A. Sanz Garcia, J. Garcia Solé, Appl. Phys. Lett. 85 (2004) 19.
[10] C. Becker, T. Oesselke, J. Pandavenes, R. Ricken, K. Rochhausen, G. Schreiber, W. Sohler, H. Suche, R. Wessel, S. Balsamo, I. Montrosset, D. Sciancalepore, IEEE J. Sel. Top. Quantum Electron. 6 (2000) 101.
[11] J. Capmany, J.A. Pereda, A. Coves, V. Bermudez, E. Dieguez, in: Proc. CLEO/Europe 2003, p. 228.
[12] M.O. Ramirez, D. Jaque, L.E. Bausa, J.A.S. Garcia, J.G. Sole, in: Proc. CLEO/Europe 2003, p. 80.
[13] J.M. Almeida, G. Boyle, A.P. Leite, R.M. Delarue, C.N. Ironside, F. Caccavale, P. Chakraborty, I. Mansour, J. Appl. Phys. 78 (1995) 2193.
[14] N.F. Evlanova, L.N. Rashkovich, Sov. Solid State Phys. 13 (1971) 223.
[15] K. Nassau, H.J. Levinstein, G.M. Loiacono, Appl. Phys. Lett. 6 (1965) 228.
[16] R.V. Schmidt, I.P. Kaminow, Appl. Phys. Lett. 25 (1974) 458.
[17] M.N. Armenise, Proc. IEE 135 (1988) 85.
[18] A. Yariv, Optical Electronics, Saunders College Publishing, London, 1991.
[19] K.S. Chiang, J. Lightwave Technol. LT-3 (1985) 385.
[20] See, for instance, the data on the web page <http://www.almazoptics.com/LiNbO3.htm>.
[21] S. Padovani, F. D'Acapito, C. Sada, E. Cattaruzza, F. Gonella, N. Argiolas, M. Bazzan, C. Maurizio, P. Mazzoldi, Eur. Phys. J. B 32 (2003) 157.
[22] D.A. Long, Raman Spectroscopy, McGraw-Hill, New York, NY, 1977.
[23] A. Ridah, P. Bourson, M.D. Fontana, G. Malovichko, Condens. Matter 9 (1997) 9687.
[24] M.-L. Hu, C.-T. Chia, J.Y. Chang, W.-S. Tse, J.-T. Yu, Mater. Chem. Phys. 78 (2002) 358.
[25] V. Dierolf, A.B. Kutsenko, A. Ostendorf, W. von der Osten, W. Sohler, H. Suche, Appl. Phys. B 72 (2001) 803.