Bulgarian Chemical Communications, Volume 44, Proceedings of the IIIrd National Crystallographic Symposium (pp. 98–108) 2012

Rare-earth doped optical waveguides in $LiNbO_3$

M. Kuneva

Institute of Solid State Physics – Bulgarian Academy of Sciences,
72 Tzarigradsko Chaussee Blvd, Sofia 1784, Bulgaria

Received February 15, 2012; Revised March 26, 2012

Doping of dielectric hosts with laser-active ions, such as the rare earth ones, is widely researched recently. The great interest has been provoked by the miniature waveguide solid state lasers obtained that way, and the opportunity for monolithic integration of these lasers and other elements on a common substrate.

The present article is a data review on the doping of $LiNbO_3$ with ions of rare-earth elements. Here, an attempt is made to summarize the most important results on technologies for doping with rare earths of optical waveguides in $LiNbO_3$ substrates and for obtaining of optical waveguides in rare-earth doped $LiNbO_3$. The sequence of the technological steps depends on the methods of doping and particularly on the temperature. The main methods of doping are described: ion implantation, diffusion from a layer deposited on the $LiNbO_3$ crystal substrate, diffusion from a melt. The main points of consideration are the effect of substrate orientation and of the initial doping on the subsequent diffusion processes, mechanism of rare-earth ion penetration and the possible positions they occupy in the lattice, structural changes due to the doping versus technological parameters, etc. A special attention is paid to the low-temperature methods of diffusion; they imply ion exchange or diffusion without ion exchange when the doping ions are situated in existing vacations of the host. The influence of the melt composition, temperature and duration of the diffusion on the concentration of the dopant in the waveguide is discussed, as well as the conditions at which that kind of anisotropic diffusion process becomes self-restricted.

Key words: Rare earths, Optical waveguides, $LiNbO_3$

INTRODUCTION

Being a crystal with strong electro-optical and non-linear properties, lithium niobate (LN) is one of the main materials having application in integrated optics. Of particular interest in recent years are the possibilities to obtain waveguide lasers based on LN doped with rare-earth elements, since the lifetime of their excited states in crystal matrices vary from 1 to 23 ms – a time sufficient for inverse population to appear [1]. The integrated-optical technologies based on the use of LN make possible the monolithic integration of waveguide lasers with other functional elements on a common substrate. An entire family of waveguide lasers already exists [2, 3–5] having excellent parameters, mainly based on erbium-doped LN, and emitting in the range 1530 nm < λ < 1610 nm. This range belongs to the third telecommunication spectral window, in which the losses in fiber-optical cables are the lowest. It is also important to note that, unlike rare-earth-doped glass fibers, the dopant positions occupy particular sites in the crystal lattice, which reduces band broadening due to inhomogeneities, i.e. the pumping and amplification efficiencies are increased [6].

The obtaining of waveguide lasers consists of two technological steps: (1) doping with a rare-earth element, and (2) obtaining of a waveguide.

METHODS OF RARE EARTH CRYSTAL DOPING

Doping during crystal growth (Nd^{3+}, Er^{3+}, Yb^{3+}, $Er^{3+}+Yb^{3+}$, $Yb^{3+}+Pr^{3+}$)

The doping takes place by adding the activating compound – usually an oxide (e.g. Er_2O_3 for erbium doping [7]) – to the melt, in which the growth of the crystal starts (usually a congruent melt composition with Li^+ to Nb^{5+} concentration ratio of the order of 0.945). The congruent melt gives rise to Li-defficient crystals that need intrinsic defects to satisfy the overall charge compensation.

---

* To whom all correspondence should be sent:
E-mail: kuneva@issp.bas.bg

The doping of LN with erbium is the most extensively studied one. The erbium concentration changes the parameters of the lattice and the intensity of the absorption band. Erbium-doped LN crystals with an erbium concentration of 0.5 to 8 mol% have been grown by Czochralski's method in order to study the integration of erbium in the lattice of LN [7]. It was observed that the erbium concentration in the crystal changes linearly depending on the melt concentration up to a concentration which remains constant, independent of the increase of the dopant concentration in the melt. The maximal amount of erbium ions integrated in the lattice is about 3 mol%. This value should correspond to the concentration limit of presence of erbium in LN. The research of other authors indicates that the rare-earth component occupies random places in LN's lattice and that, when the concentration limit is reached (the limit of solubility of the dopant in the crystal, corresponding to non-clustered or axially-positioned erbium ions), the possibility appears that chaotically positioned clusters or precipitates form [8, 9]. Their formation is stimulated also by the large ion radius of rare-earth elements. As shown in [8], the clusters formed above the saturation point cause distortions of the lattice and change the matrix's crystallography. The presence of clusters is proven experimentally in [10, 11]. When the erbium concentration increases, radiation trapping effect of the emission at 1.5 μm is observed, which decreases the lifetime of the excited states.

The doping of LN with ytterbium is also well-studied experimentally [6, 12] and theoretically [13] regarding the concentration and the sites occupied by the dopant in the lattice during the crystal growht, which is of particular importance, as it was shown above. The concentrations of the dopant considered in this case are relatively low (1.0 wt.% and 0.8 wt.% for LN: Yb, and LN: Yb, Pr, respectively [14]). The results show that the rare-earth ions occupy mainly Li^+ sites, and when co-doping with another element takes place (e.g. Pr), Yb^{3+} ions may also occupy Nb^{5+} sites [13] or form Yb^{3+} pairs in an LN matrix with one Yb^{3+} ion placed at the Li^+ site and another one at the Nb^{5+} site, while the rest of the Yb^{3+} ions are randomly distributed over the Li^+ sites [15, 16].

More research is also needed to clarify the influence of rare-earth elements on the crystal of the incongruent LN [7].

Since the domain structure also strongly depends on the concentration of the dopant in the crystal, the concentration of Er and Yb influences the formation of PPLN (periodically poled LN). The best PPLN structures are formed by doping with 0.5 mol% with erbium as well as ytterbium. Below 0.5 mol%, a regular domain structure is observed, whereas at dopant concentrations over 1 mol% the domain structure is distorted and becomes non-periodic [7].

A very important conclusion from the technological point of view is the one that at very low concentrations of the rare-earth element (below 0.1 at.%) the doping does not lead to luminescent activation of the crystal, and at higher concentrations (above 0.6 at.%) effects appear which lead to quenching of the luminescence. Due to these reasons, the most effective concentration of the rare-earth element happens to be in the range from 0.1 to 0.6 at.%.

The simultaneous doping of LN with more than one rare-earth element is used to avoid effects harmful to optical amplifiers and lasers such as photorefraction and luminescence quenching. Also, at co-doping with erbium and ytterbium, the Yb^{3+} ions act as sensitizers of the Er^{3+} luminescence, absorbing the pumping light and effectively transmitting it to the erbium which then emits it [17]. With this co-doping, compact and highly efficient waveguide lasers and amplifiers are obtained. The proportions in the quantity of co-doping elements for growing $LiNbO_3:Er^{3+}/Yb^{3+}$ and the parameters of the growing process are also described elsewhere [18]. The structural analysis performed by these authors shows that both types of rare-earth ions occupy sites in the crystal lattice slightly shifted towards lithium sites (ca. 0.25 Å). The doping with both ion types changes the refractive indices of the crystal so that their values are maximal at concentration of 1.1–1.2 mol% in the crystal.

However, it has to be emphasized that it is not at all easy to dope the crystal homogeneously during its growth, especially when a low concentration of the dopant is required (e.g. 0.5 mol%), since in that case the relative inhomogeneity reaches high values. Besides, the doping of the bulk material is not the best solution for waveguide integrated optics, because, at excitation, all parts of the waveguide will absorb. The integrated-optical devices are thin-layer ones and they do not require bulk doping. Therefore, the methods for local doping of LN are preferred [19]. The bulk-doped crystals are of interest mainly with regard to the construction of high-gain-switched lasers; they operate at concentrations up to 2%, which cannot be reached with the methods for local doping (indiffusion).

Ion implantation followed by annealing (Nd^{3+}, Eu^{3+}, Er^{3+})

The attractiveness of ion implantation as a method for local doping is mainly due to the fact that it provides the possibility to adjust better the obtained profile of the dopant in the layer with the profile of the optical waveguide which is obtained thereafter [20]. High-energy (MeV) ion implantation is used for doping of LN with erbium ions at ion beam energy of 2.0 or 3.5 MeV and surface density of the beam of 2×10^{14} and 7.5×10^{15} cm^{-2}. The obtained doped layers after annealing do not differ in their optical properties from bulk-doped LN. The erbium ions occupy optically active sites, so the photoluminescent spectra and the lifetime of the $I_{13/2}$ level are the same. No luminescence quenching is observed at erbium ion concentrations up to 0.12 at.% in the layer, which is the maximal concentration obtained under these conditions. Ion implantation could be used also for the modification of already obtained waveguides in order to introduce laser/amplifier-active ions such as Er^{3+} which offers attractive possibilities for new devices.

Since the ion beam damages the structure of the crystal close to the surface and causes amorphization of the 50–60 nm thick subsurface layer, the implantation always requires subsequent annealing for recrystallization. The recrystallization may not always be complete. It takes place at high temperatures (800–1250 °C), close to the Curie temperature for LN, so the electro-optical properties of the material may be lost. At the annealing, along with recrystallization, the diffusion of the rare-earth element in depth also continues, and the profile of its distribution changes from steplike to Gaussian [21]. This ensures a better overlap of the doped region and the field in the optical waveguide formed thereafter. On the other hand, the amorphized region provides higher mobility for the dopant ions and hence, at the thermal treatment, they migrate more to the surface and less in the depth of the crystal, so that the effective doping does not coincide with the field of the optical mode propagating in the waveguide. This increases the losses of erbium fluorescence. Also, the annealing requires special attention since the higher concentrations of the doping element combined with the higher temperatures raise the risk of formation of nano-sized atomic metal clusters of the dopant, which leads to luminescence quenching [2]. This makes ion implantation not only an expensive method, but also a risky one [22].

Indiffusion

The doping by diffusion allows avoiding the use of expensive equipment for doping during crystal growth as well as the high energy in ion implantation. It allows local control of the doping element concentration by using photolithographic techniques and the obtaining of a large variety of integrated-optical devices in any combination on a common substrate at a higher rate of integration.

a) Thermal diffusion from a metal layer deposited onto LN substrate (Nd^{3+}, Er^{3+}, Tm^{3+}, Yb^{3+})

The doping by diffusion of rare-earth ions from a metal layer deposited on the crystal surface takes place at high temperatures (1050–1130 °C) for a quite long time (50–250 h depending on the crystal orientation of the substrate) in a flow of dry oxygen. These high temperatures and time are required due to the relatively large ion radii of rare-earth elements and their harder entry into the LN crystal. Since the Curie temperature (T_c = 1142 °C for congruent LN) is close to the diffusion one, the risk exists that during the diffusion the crystal loses its ferrooelectric and electro-optical properties. The diffusion creates a homogeneously doped but very thin surface layer (nm) in the substrate, so additional annealing is required for the dopant to enter deeper into the crystal. At the beginning of the process, while the source is not yet exhausted, the distribution of the dopant from the surface to the depth of the crystal has the shape of an erfc-function. After that, at further thermal treatment after the diffusion of the layer, the profile transforms to a Gaussian one [23, 24]. In an aerial atmosphere the metal oxidizes and forms a hard matte layer. It worsens the optical quality of the crystal. In that case, either the diffusion should be continued until the metal oxide transfers entirely to the substrate, or the crystal surface should be polished carefully to minimize the losses from surface scattering in the optical waveguide to be obtained thereafter in the rare-earth-doped layer [23]. Due to the low mobility of the ions of rare earth elements, the doping with them is always the first step of the obtaining of doped waveguides. The above discussed shows that the thermal diffusion from a layer deposited on the surface is also a process quite difficult from the technological point of view. Nevertheless, this method has a number of advantages which will be discussed below with the example of the thermal diffusion of erbium ions from a thin vacuum-deposited metal layer.

Besides having the most appropriate emission spectrum for optical communications, erbium is also the rare-earth element most frequently used for diffusion due to its low ion diameter compared to other rare-earth elements which provides it with a relatively good mobility during the diffusion process [25]. The electron transitions of Er^{3+}:LiNbO$_3$ used for laser generation with a wavelength of 1550 nm are a quasi three level system with ground state absorption. Therefore the erbium doping has to be limited to these regions of the integrated-optical device for the function of which pumping is required; otherwise strong absorption takes place and the efficiency of the device decreases strongly. Such selective doping cannot be performed during the crystal growth but only by indiffusion from a structured vacuum-deposited layer [23]. This method allows avoiding the clustering of erbium ions in the matrix and is compatible with the diffusion methods for obtaining of waveguides. It allows concentration values to be reached close to the solubility limit for a solid solution (ca. 0.18 at.% at 1060 °C) without fluorescence quenching [21]. This is a prerequisite for a significant optical amplification in a short distance (experimentally achieved up to 2 dB/cm). For example, the diffusion of an erbium layer (23 Å thick) for 40 h at 1060 °C results in a subsurface layer with erbium concentration of 3.6×10^{19} cm^{-3} [26].

To understand the physical mechanisms behind the optical properties of the doped LN, it is necessary to be known which sites the dopant occupies in that pseudo-perovskite matrix. The authors of [27] have found that in the diffusion from a metal layer, the Er atoms occupy sites located at 0.46 Å from the lithium sites in a ferroelectric state directed along the optical axis; at higher erbium concentrations the diffusion resembles an exchange, where Li and Nb ions are replaced by erbium ions, thus changing considerably the structure of the crystal. It remains well-ordered, with strongly coherent fractions of erbium and niobium atoms located in the respective positions as in [27].

Varioius waveguide lasers have been obtained by thermal diffusion from a metal layer: Distributed Bragg Reflector (DBR) laser [3], Distributed Feedback (DFB) laser [4], DFB-DBR coupled cavity laser [5], etc.

b) Diffusion from a melt (Er^{3+})

Although the methods described above allow the obtaining of high-quality doped waveguides, they are time-consuming, require high temperatures or high energy and are risky and technologically complicated. Very promising seems the doping by diffusion from melts of eutectic mixtures of nitrates [28] or sulphates [29], where the diffusion quite probably takes the form of an ion exchange. The process takes place by dipping the substrate in the doping mixture at relatively low temperatures (a few hundred degrees). Until now this technology has been studied and applied only for doping of LN with erbium. It has to be noted that the diffusion coefficient of erbium with this method is twice higher than with diffusion from a metal layer [30]. Melts with the following composition have been proposed (I–III):

$$76\ CsNO_3 + 14\ Ba(NO_3)_2 + 10\ Er(NO_3)_3\ [28] \qquad (I)$$

The diffusion takes place at a temperature of about 400 °C and for about 5 h. This way, a very thin doped surface layer is obtained having an erbium concentration of up to 9 wt%. The post-diffusion annealing at 400 °C for 20–40 hours increases the depth of the doped region and lowers the dopant concentration in the subsurface layer. The temperature should not exceed 500 °C since higher temperatures cause microcracks to appear on the sample surface, probably due to the too fast relaxation of the tensions in the diffused region [28]. The best results are obtained for X-cut samples.

$$90\ KNO_3 + 10\ Er(NO_3)_3\ [28] \qquad (II)$$

The diffusion lasts about 5 hours at a temperature of 350–400 °C in a platinum crucible. Under these conditions, in X-cut samples, a thin (50 nm) doped layer is obtained having a dopant concentration up to 20 at.%. Erbium ions have a homogeneous (step-like) distribution. The erbium concentration in the different cuts differs significantly – from ca. 3 at.% for Y- and Z-cut to 20 at.% for X-cut. Erbium ions may diffuse into the crystal when additional annealing is applied at 350 °C, and their distribution becomes Gaussian [28].

The change in lithium concentration in the doped layer (i.e. lithium decrease) is studied by the Neutron Depth Profiling (NDP) method. The distribution of the integrated erbium atoms is determined using Rutherford Backscattering Spectrometry (RBS) [19]. The RBS spectrum shows that erbium ions are located in a ca. 100 nm thick layer (after annealing) on the surface of the crystal, and that there is a strong anisotropy when doping substrates having different crystal orientations. While with Y- and Z-cut substrates the erbium concentration does not exceed 5 at.%, in the cases of an X-cut it could easily reach 20 at.%. This may be explained, to some extent, as owing to the known different wettability of the Z-cut compared to the X- and Y-cut by the melt. The wettability of Z-cuts by the melt is impeded most probably due to the pyroelectric effect (the pyroelectric axis of LN is perpendicular to the Z-cut substare). This cannot, however, explain the different behaviour of X- and Y-cuts.

The study on concentration profiles of lithium shows that no lithium decrease is observed in the doped layer, therefore erbium ions do not occupy lithium sites during low-temperature doping, and it does not take the form of an exchange, but of an interstitial diffusion. Erbium ions most probably occupy the majority of vacancies, which explains the higher concentration of erbium ions in the X-cut samples [28].

Other authors have an interpretation slightly opposing the above – they assume that the diffusion has the form of an ion exchange [30]. These authors use sulphate melts instead of nitrate ones (III) [29]. Ion exchange is a transfer of different types of ions between phases brought to a contact. The gradient in chemical potential at their interface leads to movement and exchange of the different ion types, so that electrical neutrality is preserved. When ion exchange is not isovalent, the diffusion coefficient depends on many parameters and it is not easy to predict the profile of the doping element (i.e. of its distribution in depth). Within this exchange, a complex rearrangement of the crystal structure takes place, for which no thorough model has been created yet [31].

$$19.4K_2SO_4+9.9Na_2SO_4+70.7Li_2SO_4 +0.125\text{ wt.\% } Er_2(SO_4)_3 \text{ [29]} \qquad \text{(III)}$$

The diffusion lasts 24 hours at 680 °C. The exchange takes place at temperatures of 560–700 °C. The profile of erbium distribution depends on the speed of melt heating – fast (300 °C/h) or slow (150 °C/h). The diffusion time varies from 4 to 24 hours. Additional annealing at 900 °C for 15 h is also performed. By varying the amount of erbium sulphate in the melt from 0.002 wt.% to 5 wt.%, it has been found that below 0.002 wt.% the exchange is inefficient even at longer times and higher temperatures. Above 5 wt.% the thickness of the ion-exchange layer decreases. A thickness of a few micrometers is achievable at a concentration of 0.6 %, time below 10 hours and temperature about 600 °C. At concentrations of erbium sulphate between 0.1–0.6 wt.% the luminescence intensity increases linearly with concentration, i. e. within this range there is still no luminescence quenching. The systematic study done by these authors to establish the dependence of erbium profile on diffusion parameters shows that it is preferable to use lower temperatures and shorter times, since the process seems to be self-limiting. The authors state that, due to the higher mobility of lithium compared to erbium, a local unbalanced charge appears which limits the further diffusion of erbium into the matrix. The gradient in ion concentration leads to the formation of a barrier layer which blocks the diffusion of ions involved in the process. As a possible explanation for the fact that in X-cut samples the exchange layer is thicker than in Z-cut ones, these authors also point out the better wettability of X-cut substrates. It is harder in terms of energy for erbium to enter Z-cut substrates due to its lower concentration on the surface.

The analysis of concentration profiles using SIMS and RBS shows complete lithium depletion of the subsurface layer, and a stoichiometry close to $Er_1Nb_1O_{4.5}$ which corresponds to a mixture of erbium and niobium oxides. Under the subsurface layer, a multivalent Er^{3+}-$3Li^+$ exchange takes place. Thicker layers are formed in X-cut substrates than in Z-cut ones, i.e. these authors also find anisotropy of diffusion. Moreover, they also find that in the case of X-cut samples, both surfaces of the sample dipped in the melt are equally and homogeneously doped, whereas with Z-cut, active erbium agglomerates are formed, probably due to the different orientation of the ferroelectric domains in the crystal, which results in doping with active erbium ions of only one surface of the substrate.

Ion exchange in a salt melt is the most convenient technology for local doping, if no co-doping with another element is needed. With this method the thermal stress upon the crystal is minimal and the risk of depolarization and loss of electro-optical properties is avoided.

To use rare-earth doped substrates in integrated-optical circuits, after the doping it is necessary to obtain high-quality optical waveguides.

WAYS FOR OBTAINING ACTIVE WAVEGUIDES

Creation of the the waveguide by the doping itself

It has been found with erbium diffusion from nitrate melts [28], that all samples regardless of their crystal orientation have waveguiding properties stemming from a change in the extraordinary refractive index in the range 0.003–0.005 for wavelength of 0.633 μm. The waveguides obtained this way are quite thick – up to 9 μm [19]. This waveguide effect of the diffused layer results solely from the presence of erbium ions. However, due to a number of reasons, the waveguides so obtained do not have a practical application.

Creation of an optical waveguide in a rare-earth doped crystal

For the formation of optical waveguides in LN previously doped with rare-earth elements, ion implantation, diffusion from a metal layer, and proton exchange have been used. It has to be mentioned that the rare-earth doping also changes the refractive index, and if it is a local one, it also creates a waveguide itself.

The two widely accepted technologies for obtaining of optical waveguides in LN by diffusion are titanium diffusion and proton exchange. Proton exchange has the advantage of increasing the photorefractive resistance and the generation of a strong waveguide effect, but the obtained waveguides maintain only one polarization, since only the extraordinary refractive index rises. This makes some authors state that the waveguides obtained by proton exchange are not suitable for laser action, since the fluorescence of the system La^{3+}:LN has both polarizations [32]. Many authors however consider proton-exchanged waveguides as a good alternative to titanium ones for the obtaining of integrated-optical lasers [28, 33].

a) In-diffusion of Ti or Zn from a metal layer

The most frequently used and approved technology is the diffusion of Ti in LiNbO$_3$. Until now, this is the technology providing the highest quality of waveguides formed in LN previously doped with rare-earth ions. A thin layer of titanium with a thickness of 20-200 nm is deposited onto a crystal substrate and after that, the thermal diffusion takes place at ca. 950–1100 °C for several (5–20) hours in flowing Ar gas atmosphere (to prevent oxidation of the metal) replaced by O$_2$ during cool-down to allow reoxidation. If the diffusion takes place in an argon atmosphere, the ions directly enter the substrate and diffuse from the metal layer until its exhaustion. If the diffusion is carried out in an oxygen atmosphere, the layer is first oxidized to TiO$_2$ or ZnO$_2$ respectively, and the metal ions enter the substrate from the oxide layer. In this case, as with the rare-earth activation from a metal layer deposited onto the crystal surface, it is very important that the diffusion of Ti/Zn is complete. If the metal layer diffuses incompletely, it is necessary to polish the surface in order to obtain a high-quality, low-loss waveguide.

Diffusion gives a profile which is typically half-Gaussian or error-function in shape, with a maximal change at the surface.

The formation of the waveguide structure is performed by photolithography, followed by deposition of a Ti layer and thermal diffusion. Due to the high losses and the instability of the obtained waveguides, additional annealing in an oxygen atmosphere or periodic poling is needed [32]. The obtained optical waveguide overlaps the rare-earth doped region. Since the diffusion temperature and the duration of the process of waveguide formation also allow the rare-earth element to enter deeper into the crystal, it is best to consider this process as an additional annealing of the doped layer when calculating the final diffusion depth of the rare-earth element. At the same time, titanium has a faster diffusion (due to its shorter ion radius) and this way it provides the necessary larger width of the waveguide channel compared to the width of the rare-earth region.

In Figure 1, the transverse section of a crystal is shown, surface-doped with a rare-earth element surrounded by a stripe waveguide, obtained by titanium diffusion or proton exchange. The rare-earth doped area has a smaller width than the waveguide and a smaller doping depth than the waveguide channel depth. The maximal concentration of the rare-earth dopant is located in the center below the surface of the crystal.

A good combination of the technologies for obtaining of erbium-doped LN and for the formation of optical waveguides by titanium diffusion is demonstrated by the authors of [34-36], as well as optical amplifiers and lasers based thereon [2].

The obtaining of waveguides by diffusion of titanium or zinc in the activated systems (Nd/Er/Tm/Yb):LiNbO$_3$ has been described [37]. Single-mode waveguides are formed by diffusion of 7 μm wide, 100 nm thick Ti-stripes for 9 hours at 1060 °C. The crystal orientation of the substrates is selected with regard to the type of laser device to be obtained: for DBR/DFB lasers or for acoustooptically tunable lasers, X-cut substrates are used, and a propagation of the light beam along Z in the first case, and along Y in the second one. For the obtaining of Q-switched and modelocked lasers, Z-cut substrates are selected and a propagation of the light beam along X, in order to use the highest value of the electro-optical coefficient for more efficient modulation.

The main advantages of the formation of optical waveguides by thermal indiffusion of a metal layer in LN are: high reproducibility, increase of both ordinary and extraordinary refractive indices, high stability of waveguide parameters and low losses in the obtained waveguides. As disadvantages,

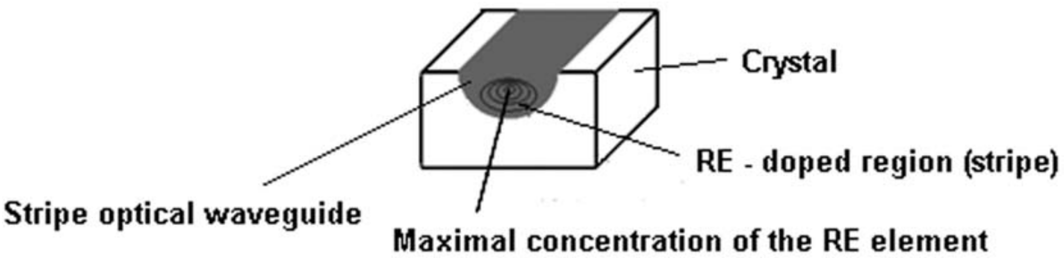

Fig. 1. A transverse section of a rare-earth doped waveguide channel in LN

the following may be cited: the high temperature required and the parasitic waveguides formed by out-diffusion, as well as the 100-fold reduction in the optical damage threshold power density from the bulk value.

b) Proton exchange

Proton exchange (PE) takes place in a surface layer of a substrate immersed in an appropriate acidic melt [38]. PE modifies the surface layer (several μm in depth) by Li-H ion exchange at a relatively low temperature (160–250 °C) causing a large extraordinary index change Δn_e ($\Delta n_e \cong 0.12$ at 0.633 μm). The PE layers show complex phase behavior depending on the hydrogen concentration. Strong protonation considerably worsens electro-optical properties of the waveguiding layer [39] and causes higher losses (2 to 5 dB/cm) [40] and some instability of the parameters over time. However, taking into consideration that other methods (melt buffering and/or annealing) exist for the adjustment of phase composition [41], these drawbacks can be corrected or even turned into advantages for the possibility to modify the electro-optical properties. These can also be avoided by using the methods for optimization of proton concentration [42]. Waveguide fabrication by PE has multiple variations, including post-exchange annealing (APE) [42]. Proton-exchanged LN waveguide devices are preferred over Ti-diffused LN ones in cases where high optical powers are to be transmitted and/or single polarization operation is desired.

Considering proton exchange of rare-earth doped LN, it should be taken into account that radiative lifetime reduction and strong fluorescence quenching occur because of the coupling to OH-phonons [43, 44]. Due to these reasons, some authors do not find the combination of rare-earth doping with subsequent obtaining of the optical waveguide by proton exchange a good one for waveguide lasers, since the presence of hydrogen has a killing effect on the excited erbium electrons, shortening their lifetimes, which then results in a drastically reduced optical gain [2, 24, 36, 44, 45]. Promising results have been obtained with selection of appropriate conditions for carrying out proton exchange with subsequent annealing for the formation of the optical waveguide [19, 28, 29], or with using reverse proton exchange (RPE) [46]. Waveguide lasers have been described based on stripe waveguides obtained in erbium-doped LN by proton exchange for 2 h in benzoic acid buffered with 1 mol% lithium benzoate at 200 °C, with subsequent annealing for 3–4 hours at 350 °C [47]. Continuous-wave laser action at 1084.5° nm at room temperature in $LiNbO_3:Nd^{3+}$ channel waveguides, fabricated by RPE, is reported.[46]. Yb-diffused $LiNbO_3$ annealed/proton-exchanged waveguide lasers are also demonstrated. A Fabry-Pérot waveguide laser of 3-cm length is fabricated and characterized. For optical pumping at 918-nm wavelength, stable continuous-wave laser oscillation is achieved at 1061 nm with a threshold power of 40 mW. [33]. It has been demonstrated that Er-doped optical waveguides produced by a moderate temperature process (APE, for example) are quite effective [19]. With appropriately chosen parameters of the APE technology [43], the hydrogen content in the waveguides could be decreased to a level not causing photoluminescent quenching, so that such waveguides could be used in active integrated-optical structures.

The results of the study of APE layers in LN doped with erbium or erbium+ytterbium show also that during the APE process, no loss of rare-earth elements from the substrate previously doped with them is observed. The waveguide properties and the PE process itself in doped samples do not differ from those of non-doped ones. The presence of doping ions (rare-earth as well as hydrogen ones) leads to worsening of the electro-optical properties of LN, but a carefully designed APE technology may restore them almost to the degree of a non-doped LN. This may be done by modeling the distribution of lithium in the waveguide area, since a correlation between the uniform distribution of lithium and the high values of the electro-optical coefficient r_{33} has been found. A homogeneous distribution of lithium and a very low content of hydrogen has been obtained in the long-time-annealed waveguiding layers [48].

It has to be mentioned that the problems with luminescence quenching are observed only with protonation of erbium-doped LN, whereas, for example, after protonation of a neodymium-doped LN, a very effective luminescence has been registered around 1 μm wavelength and no quenching problems are reported [44, 49]. Besides, luminescence quenching after the proton exchange has not always been observed in the case of erbium activation of LN. This effect has been reported when the doping has been performed either during crystal growth by ion implantation, or by diffusion from a metal layer [2, 24, 44, 45] and does not take place when the doping has been performed with a low-temperature process in a melt [19, 28–29, 50–52].

The advantages of proton exchange as a method for obtaining of optical waveguides in LN are: a fast and simple waveguide formation procedure; non-toxicity and lower cost; possibility of thermal tuning of the refractive index; a strong waveguiding effect; an increased photorefractive resistance; flexibility and compatibility with other technologies; a large variety of optimization steps. Its main disadvantages are: multiphase composition of the waveguide layer; deterioration of electro-optical properties in strongly protonated layers; some instability over time.

Doping of a previously obtained optical waveguide with laser-active ions (rare earths)

Since for the formation of laser-active waveguides the opposite procedure is also generally possible – proton exchange and subsequent diffusion of a rare-earth element – the influence of proton exchange on the following erbium-ion doping has been studied, in the case that the obtaining of the optical waveguide is chosen as the first step in the fabrication of the waveguide light amplifier or laser [19, 28]. It has been found that with the diffusion of erbium the amount of diffused erbium depends not only on the crystal orientation but also on the history of the substrate – untreated or previously proton-exchanged. This dependence is strongest with X-cut samples, in which the proton exchange lowers about 15 times the amount of erbium ions compared to that in non-protonated subtstrates under identical conditions [28]. This is most probably due to the gradual transition of the structure of LN towards monocline one after PE. Although the lattice parameters do not change significantly, that suppresses the diffusion of erbium ions. Due to these reasons, the erbium doping should be performed before the APE process, since the completely changed structure of APE layers impedes the process of rare-earth doping [19].

In Figure 2-A, the steps for the obtaining of a stripe optical waveguide activated by a rare-earth element are schematically shown. The first step is the deposition of structured photoresist (PR) onto the crystal surface, thereby obtaining photoresist-free channels in the area subjected to rare-earth doping. The second step is the deposition of the rare-earth element (RE) by sputtering or vaccum evaporation in the form of a metal or a metal oxide, after which the photoresist (PR) together with the overlying layer are removed by the lift-off technique. This results in a small rare-earth stripe (RE) deposited onto the surface of the crystal substrate (S); the stripe would diffuse in S in the next step. This diffusion takes place during the first thermal treatment (T1) in an atmosphere of Ar-O$_2$, the temperature and duration being so chosen that a controlled diffusion depth is achieved which has to be smaller than the depth of the waveguide channel, which should be inserted thereafter. It has been shown, for example [49] that with Z-cut substrates, an average diffusion depth of 5 μm is reached after 100 h at 1050 °C, and at 1080 °C the depth is 7.2 μm. The diffusion depth is defined as 1/e of the surface concentration. The next step is the deposition of silica-gel (sol-gel) (SG) onto the crystal surface, followed by the second thermal treatment (T2) which leads to partial out-diffusion of the dopant close to the surface through the sur-

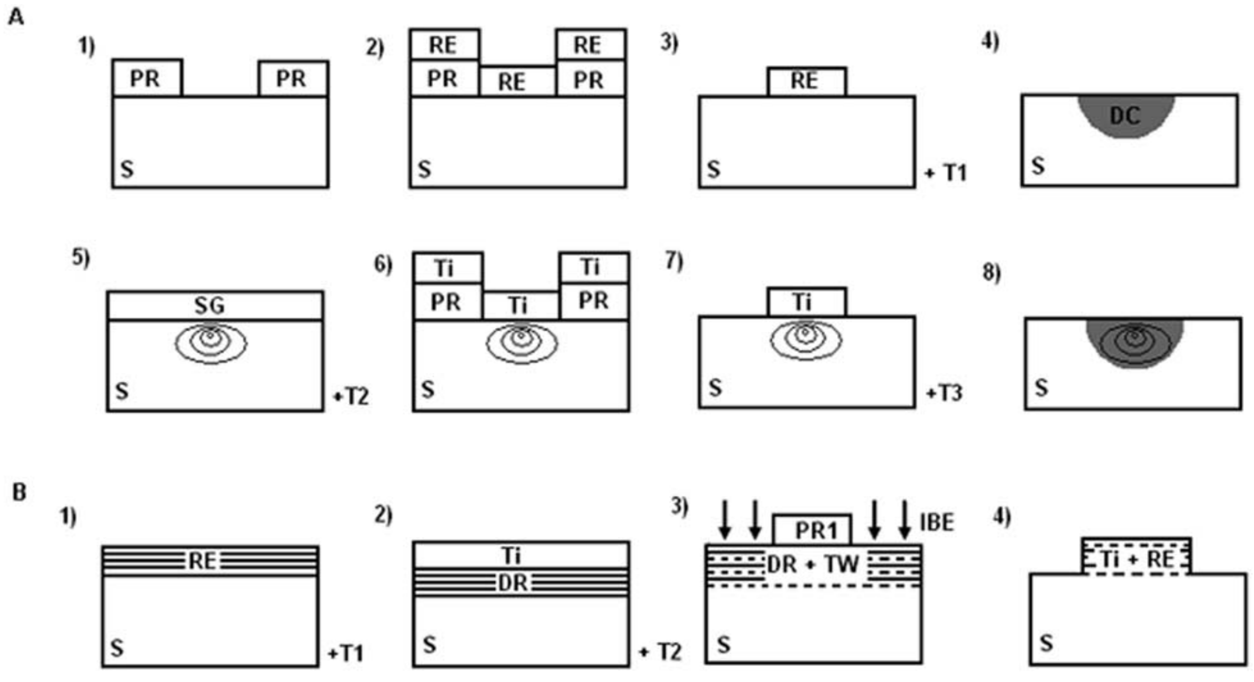

Fig. 2. Scheme of the technological steps for obtaining an active waveguide

face in the gel. This way, an area with a maximal dopant concentration is formed under the surface of the crystal. At the same time, the rare-earth doped area becomes deeper. The next step is the deposition of titanium (Ti) onto the structured photoresist (PR) onto the surface of S and its diffusion in the crystal during the third thermal treatment (T3), again in an atmosphere of $Ar-O_2$. A titanium stripe is deposited over the center of the rare-earth doped area, and as a result, the axis of the waveguide channel is parallel to that of the rare-earth channel. With a 95 nm thick titanium layer and a diffusion of 10 h at 1050 °C, a single-mode waveguide is obtained.

In Figure 2-B, another method is shown for the formation of the lateral borders of the waveguide channel. This process comprises an initial deposition of a rare-earth layer (RE) onto a wide area of the crystal substrate (S) and its diffusion during the first thermal treatment (T1). After that, again over a wide area, a waveguide is formed by Ti diffusion or PE. The next step is the deposition of photoresist (PR) onto the doped area (DR), the photoresist being so structured that a small stripe of photoresist (PR1) remains where the waveguide channel should be formed. In the following step, the surplus doped material at both sides of the stripe is etched by ion etching, and the photoresist is removed in the next step. This way a small stripe – a narrow stripe waveguide doped with a rare-earth element – stays on the crystal.

Ion implantation (He^+, Ne^+)

Ion implantation is performed usually at energies from 7 keV to 2 MeV. The change of the refractive index depends on the ion energy and is relatively large – from 0.02 to 0.08 [53]. After the implantation, annealing is always performed to restore the crystal structure [2, 25]. The implantation of H^+ in erbium-doped LN easily leads to chemical reactions, for example formation of OH-groups, and they are important centers of luminescence quenching [2]. In this case, for ion-implanted waveguides, co-doped LN substrates are used, for example with MgO, which avoids the quenching by OH-groups. Waveguides with a high optical quality have been obtained with implantation of H^+ in $LiNbO_3$ bulk-doped with Eu^{3+} and MgO [54]. There, no luminescence quenching is observed and the fluorescence in the waveguide is the same as bulk fluorescence.

The method has the advantages of preserving the bulk material properties, depth control and possibility for obtaining multilayer structures, as well as an opportunity of writing optical circuits by ion beam. However, it is a very expensive method and some instability of waveguide parameters over time has been demonstrated.

CONCLUSIONS

- The choice of technological conditions for rare-earth doping of LN affects the dopant penetration and location as well as the structural changes of the doped layers.
- The concentration of the dopant and the sites its ions occupy in the crystal lattice of the LN matrix are crucial for both the dopant's luminescent activation and its optical properties.
- The local doping of $LiNbO_3$ exhibits strong anisotropy.
- In many cases lasing efficiency and optical properties of the waveguides obtained could be improved by co-doping.
- The most convenient and promising methods for obtaining waveguide lasers are the diffusion ones – for rare-earth doping as well as for the subsequent fabrication of the optical waveguides.
- Better results are achieved when the doping with rare-earth ions precedes the fabrication of the optical waveguides, although in some cases the reverse procedure is also possible.

REFERENCES

1. L. Tsonev,*Optical Materials*, **30**, 892 (2008).
2. Ch. Buchal, S. P. Withrow, C. W. White, D. B. Poker, *Annual Revue of Materials Science*, **24**, 125 (1994).
3. B. K. Das, H. Suche, W. Sohler,*Appl. Phys. B*, **73**, (2001).
4. B. K. Das, R. Ricken, W. Sohler, *Appl. Phys. Lett.*, **l82**, 1515 (2003).
5. B. K. Das, R. Ricken, V. Quiring, H. Suche,W. Sohler, *Opt. Lett.*, **29**, 165 (2004).
6. G. Burns, D. F. O'Kane, R. S. Title, *Phys. Rev.,* **167**, 314 (1968).
7. V. Bermudez, M. D. Serrano, J. Torento, E. Diegues, *Solid State Communications*, **112**, 699 (1999).
8. L. Rebouta, M. F. Da Silva, J. C. Soares, D. Serrano, E. Diéguez, F. Agulló-López, J. Tornero. *Appl. Phys. Lett.* **70**, 1070 (1997).
9. B. Herreros, PhD Thesis, UAM, Madrid, Spain, 1997.
10. L. Nuñez, R. Duchowicz, M. Voda F. Cussó, *J. Physique IV*, **4**, C4–443 (1994).
11. D. M. Gill, J. C. Wright and L. McCaugan, *Appl. Phys. Lett.* **64**, 2483 (1994).
12. C. Bonardi, C. J. Magon, E. A. Vidoto, M. C. Terrile, L. E. Bausa, E. Montoya, D. Bravo, A. Martin, F. J. Lopez, *J. Alloy Comp.*, **323-324**, 340 (2001).
13. H.-N. Dong, S.-Y. Wu , W.-C. Zheng, *J. Phys. Chem. Solids*, **64**, 695 (2003).
14. I. Pracka, M. Malinowski, A. L. Bajor, B. Surma, Z. Galazka, M. Swirkowicz, M. Mozdzonek, *Proc. SPIE*, **3178**, 295 (1997).
15. E. Montoya, O. Espeso, L. E. Bausa, *J. Lumin.*, **87-89**, 1036 (2000).
16. E. Montoya, L. E. Bausa, B. Schaudel , P. Goldner, *J. Chem. Phys.*, **114**, 3200 (2001).

17. C. Huang, L. McCaughan, *IEEE Photonics Technology Letters*, **9**, 599 (1997)
18. V. A. Fedorov, Yu. Korkishko, J. A. Sanz-Garcia, E. Cantelar, R. Nevado, G. Lifante, F. Gusso, in: Proc. ECIO'01, Padeborn, April 2001, 297 (2001).
19. V. Perina, J. Vacik, V. Hnatovicz, J. Cervena, P. Kolarova, J. Spirkova-Hradilova, J. Schröfel, *NIM-B*, **139**, 208 (1998).
20. M. Fleuster, Ch. Buchal, H. Holzbrecher, E. Snoeks, A. Polman, *J. Appl. Phys.*, **75**, 173 (1994).
21. M. Fleuster, Ch. Buchal, E. Snoeks,A. Polman, *Appl. Phys. Lett.*, **65**, 225(1994).
22. P. Moretti, B. Canut, S. M. M. Ramos, P. Thevenard, D. Poker, J. B. M. Da Cunha, L. Amaral, A. Vasquez, *J. Mater. Res.,* **8**, 2679 (1993).
23. I. Baumann, R. Brinkmann, M. Dinand, W. Sohler, L. Beckers, Ch. Buchal, M. Fleuster, H. Holzbrecher, H. Paulus, K.-H. Müller, Th. Gog, G. Materlick, O. Witte, H. Stolz, W. von der Osten, *Appl. Phys. A*, **A64**, 33 (1997).
24. I. Baumann, S. Bosso, R. Brinkmann, R. Corsini, M. Dinand, A. Greiner, K. Schäfer, J. Söchtig, W. Sohler, H. Suche, R. Wessel, *IEEE J. Select. Topics in Quantum Electron*, **2**, 355 (1996).
25. W. Sohler, B. K. Das, D. Dey, S. Reza, H. Suche, R. Ricken,*IEICE Trans. Electron.*, **E88–C**, 990 (2005).
26. I. Baumann, R. Brinkmann, Ch. Buchal, M. Dinand, M. Fleuster, H. Holzbrechel, W. Sohler, H. Suche, in: Proc. ECIO'93, Neuchatel, 1993, p. 3.
27. Th. Gog, M. Griebenow and G. Materlik, *Physics Letters A*, **181**, 417 (1993).
28. J. Hradilova, P. Kolarova, J. Schröfel, J. Ctyroky, J. Vacik, V. Perina, *Proc. SPIE*, **2775**, 647 (1996).
29. C. Sada, E. Borsella, F. Caccavale, F. Gonella, F. Segato, Yu. N. Korkishko, V. A. Fedorov, T. M. Morozova, G. Battaglin, R. Polloni, *Appl. Phys. Lett.*, **72**, 3431 (1998).
30. F. Caccavale, C. Sada, F. Segato, B. Allieri, L. E. Depero, L. Sangaletti, V. A. Fedorov, Yu. N. Korkishko, T. V. Morozova, *J. Non- Cryst. Solid*s, **280**, 156 (2001).
31. F. Caccavale, C. Sada, F. Segato, in: Properties of Lithium Niobate, K. K. Wong (ed.), INSPEC Inc., 2002, p. 300.
32. J. K. Jones, J. P. de Sandro, M. Hempstead, D. P. Shepherd, A. C. Large, A. C. Tropper, J. S. Wilkinson, *Optics Letters*, **20**, 1477 (1995).
33. M. Fujimura, H. Tsuchimoto, T. Suhara, *Photonics Technology Letters, (IEEE 17)*, 130 (2005).
34. A. Lorenzo, L. E. Bausa, J. Garcia-Sole, *Phys. Rev. B*, **51**, 16643 (1995).
35. K.A. Winick, *Proc.SPIE*, **3280**, 88 (1998).
36. A. Fukumi: PhD Thesis, Hiroshima University, June 2002.
37. E. Cantelar, R. Nevado, G. Martin, J. A. Sanz-Garcia, G. Lifante, F. Cusso, M. J. Hernandez, P. L. Pernas, *J. Luminesc.*,**87/ 89**, 109 (2000).
38. J. Jackel, C. Rice, J. Veselka, *Appl. Phys. Lett.*, **41**, 607 (1982).
39. M. Rottschalk, A. Rash, W. Karthe, *J. Opt. Commun*., **9**, 19 (1988).
40. A. Loni, R. De La Rue, J. Winfield, in: Technical Digest Series 5 (Proc. Topical Meeting on Integrated & Guided Wave Optics, March 28-30, Santa Fe, New Mexico), 1988, p. 84.
41. K. Wong , *Gec. J. Research*, **3**, 243 (1985).
42. S. M.Al-Shukri, S., A. Dawar, R. De La Rue, A. Nutt, M. Taylor, J. Tobin, in: Proc. 7th Top. Meet. on Integrated and Guided Wave Optics, Florida, April 1984, PD7/1.
43. J. K. Jones, J. P. De Sandro, M. Hempstead, D. P. Shepherd, A. C. Tropper, J. S. Wilkinson, in: Proc. Symp. on Materials for Advanced Solid State Lasers, Boston, 1993, publ. by, Materials Research Society, Pittsbourgh, PA, 1994, p. 233.
44. Marc P. De Micheli, *Proc. SPIE*, **2996**, 62 (1997).
45. A. C. Cino, S. Riva Sanseverino, M. P. De Micheli, K. El Hadi, F. Cusso, G. Lifante, *Proc. SPIE*, **3280,** 152 (1998).
46. E. Cantelar, G. Lifante, F. Cussó, M. Domenech, A. Busacca, A. Cino, S. Riva-Sanseverino, *Optical Materials*, **30**, 1039 (2008).
47. W. Sohler, H. Suche,*US Patent* 5 473 722 (1995).
48. P. Nekvindova, J. Cervena, P. Capek, A. Mackova, V. Perina, J. Schröfel, J. Spirkova, *Optical Materials*, **24**, 527 (2003).
49. M. Hempstead, J. S. Wilkinson, L. Reekie, *IEEE Photon. Technol. Lett.*, **4**, 852 (1992).
50. P. Nekvindova, J. Spirkova-Hradilova, J. Schroefel, M. Slunecko, V. Perina, J. Vacik, *Proc. SPIE*, **3858**, 180(1999).
51. F. Zhou, Y. Zhou, *Singapore J. Phys*. **12**, 21 (1996).
52. J. Spirkova-Hradilova, P. Nekvindova, J. Vacik, J. Cervena, V. Perina, A. Mackova, J. Schroefel, M. Budnar, A. Raspet, B. Zorko, P. Pelicon, *Proc. SPIE*, **4277**, 200 (2001).
53. A. Polman, E. Snoeks, G. N. van den Hoven, M. L. Brongersma, R. Serna, J. H. Shin, P. Kik, E. Radius, *Nucl. Instr. Meth. Phys. Res. B*, **106**, 393 (1995).
54. C. Mignotte, P. Moretti, K.E. Lipinska-Kalita, G. Boulon, J. Mugnier, *J. Optics*, **27**,259 (1996).

ОПТИЧНИ ВЪЛНОВОДИ В ЛИТИЕВ НИОБАТ, ДОТИРАН С РЕКОЗЕМНИ ЕЛЕМЕНТИ

М. Кънева

Институт по физика на твърдото тяло „Акад. Г. Наджаков“ – Българска академия на науките,
бул. „Цариградско шосе“ № 72, София 1784, България

Постъпила на 15 февруари, 2012 г.; приета на 26 март, 2012 г.

(Резюме)

Дотирането на диелектрици с лазерно-активни йони, каквито са йоните на редкоземните елементи, е предмет на широко изследване през последните години. Големият интерес се дължи на възможността за получаване по този начин на миниатюрни твърдотелни лазери и за монолитно интегриране на тези лазери и други елементи върху обща подложка.

Настоящата публикация представлява обзор на по-важните изследвания в областта на дотирането на литиев ниобат с йони на редкоземни елементи. Направен е опит за обобщаване на резултатите по отношение на технологиите за дотиране на $LiNbO_3$ с лазерно-активни йони и за получаване на оптични вълноводи в дотираните с редкоземни елементи подложки от $LiNbO_3$. Основните методи за дотиране са: въвеждане на примеса при израстването на кристала, йонна имплантация, дифузия от слой, отложен върху кристалната подложка, дифузия от стопилка. Разгледано е влиянието на ориентацията на подложката върху дотирането, влиянието на дотирането върху следващи дифузионни процеси, възможните позиции на примесните йони в решетката на $LiNbO_3$-матрица, структурните промени в нея и зависимостта им от технологичните параметри на дифузионния процес и т.н. Специално внимание е отделено на нискотемпературните методи за дифузия, при които се извършва йонен обмен или дифузия без йонен обмен, при която дотиращите йони се разполагат в съществуващите ваканции в кристалната решетка на $LiNbO_3$. Обсъдено е влиянието на състава на стопилката, температурата и продължителността на дифузията върху концентрацията на дотиращия елемент, както и условията, при които анизотропната дифузия става самоограничаващ се процес.