Optical and structural characterization of annealed proton exchange waveguides in Y-cut MgO:LiNbO$_3$

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Abstract

In this paper, studies are presented on proton exchanged (PE) and annealed proton exchanged (APE) waveguides in Y-cut magnesium doped lithium niobate based on our systematic fabrication and characterizations. The analysis is focused on the optical and structural properties from the measurements of prism coupler, X-ray diffraction and infrared absorption. The evolution of the index profile with annealing is studied. Unlike the Gaussian index profile for the APE waveguides in pure LiNbO$_3$, the index profile of APE waveguides in MgO:LiNbO$_3$ still keeps the characteristics of step-like profile though with a long index tail. From the measurement results of X-ray diffraction, the strain induced by proton exchange depends on the exchange condition in Y-cut MgO:LiNbO$_3$. The lattice distortion in the guiding layer of an as-exchanged waveguide in Y-cut MgO:LiNbO$_3$ can be up to +0.73%, which can be restored to +0.20% by annealing for a short time. The proton exchange causes more serious non-uniformity of the strain in Y-cut MgO:LiNbO$_3$ than that in pure LiNbO$_3$ in our study. It was also found that HNbO$_3$ phase of high hydrogen concentration can be formed more easily in Y-cut MgO:LiNbO$_3$ by proton exchange from the analysis of 3300 cm$^{-1}$ peak in the IR spectra. The intensity of the infrared absorption peak at 3500 cm$^{-1}$ decreases and the broad peak at 3300 cm$^{-1}$ disappears after annealing in Y-cut MgO:LiNbO$_3$ waveguides.

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1. Introduction

It has been shown that LiNbO$_3$ doped with 5-mol% or more MgO exhibits a remarkably reduced photorefractive response as compared with undoped LiNbO$_3$ [1,2]. Optical waveguides formed with such a material are characterized by high optical damage threshold and thus have important applications in nonlinear and integrated optics [3,4]. Like undoped LiNbO$_3$, proton exchange has been shown to be an efficient method for fabricating waveguides in MgO:LiNbO$_3$ [5,6]. Annealing provides a means of controlling the index profile of the guiding layer and influences the crystal structure and the optical properties of the waveguides. In order to fabricate MgO:LiNbO$_3$ waveguides of high quality, it is important to understand the lattice structural changes induced by the proton exchange and the subsequent annealing.

Structural characteristics of PE waveguides on Li-NbO$_3$ have been reported systematically [7–9]. Several different crystallographic phases of H$_x$Li$_{1-x}$NbO$_3$ have been identified according to the relation between increment in extraordinary index and the surface strain value.
normal to the surface plane of PE waveguide. However, little has been done for fundamental or systematic research on the PE waveguides in MgO:LiNbO$_3$ and the effect of annealing on structural changes of the PE layers. Only recently, Korkishko studied the phase diagram and reported that MgO:H$_2$Li$_{1-x}$NbO$_3$ PE layer exhibit very complex structural chemistry [10]. It was also found that annealing leads to crystal structure disorder in the sub layer of the surface region.

In the present paper, we give a crystal structure analysis of Y-cut MgO:LiNbO$_3$ PE waveguides by the X-ray diffraction and infrared spectroscopy methods, with an emphasis on the effects of annealing on the structural changes and optical properties of the waveguides. The optical and structural characteristics of PE and APE waveguides in MgO:LiNbO$_3$ and LiNbO$_3$ are compared.

2. Experimental

2.1. Fabrication of PE and APE waveguides

The substrates were single-crystal Y-cut 5-mol% MgO:LiNbO$_3$ (polished to optical-grade) with dimensions of $12 \times 10 \times 1$ mm. Benzoic acid was used as the proton source and contained in a glass tube. The cleaned substrate was put in the tube but does not contact with the substrate till they were heated in an oven to a predetermined exchange temperature. Then the substrates were immersed into the benzoic acid by turning the handle of the tube. The glass container was kept sealed during proton exchange process. After exchange for a certain time, the sample was separated from the molten benzoic acid and then cooled down naturally. Acetone was used to remove the residual acid. In our experiment the PE waveguides were fabricated at three temperatures (200°C, 220°C and 240°C) for 4.5h–33 h to obtain multi-moded planar waveguides. The fabricated waveguides in Y-cut MgO:LiNbO$_3$ don’t have the surface damage phenomenon, which usually occurs on Y-cut LiNbO$_3$ (without MgO doping) when benzoic acid is used as proton source [11,12]. After proton exchange, annealing process was carried out in air at three different temperatures (300°C, 350°C and 400°C) with a total duration ranging from 10min to more than 20h.

2.2. Measurements

The effective indices for the guided modes of the PE or APE waveguides were measured by means of the conventional prism-coupler technique with a single-crystal rutile prism. Only extraordinary light can be coupled into the waveguides, and this indicates that the proton exchange process can increase only the extraordinary index in the guiding layers of Y-cut MgO:LiNbO$_3$. All the measurements were made at $\lambda = 633$ nm.

X-ray diffraction method was employed to determine the lattice constant changes in the PE layer before and after annealing. X-ray diffraction was carried out using a Shinadzu XD-3A diffractometer. There are two characteristic wavelengths $K_{2\alpha}$ and $K_{2\beta}$ of the copper cathode. The principle of the X-ray diffraction is based on the well-known Bragg equation

$$2d \sin \theta = n \lambda$$

The lattice spacing $d$, the lattice constant $a$ and the strain $\Delta a/a$ in the $a$-axis (perpendicular to the surface of substrate) can be deduced by the angular position $\theta$ of the diffraction peaks for PE and APE waveguides on polished Y-cut MgO:LiNbO$_3$ (300).

The H$^+$ concentration and related structural information are deduced by IR absorption spectra. The evolution of OH$^-$ absorption spectra with annealing indicates the effect of annealing on H$^+$ concentration and related structural changes. The infrared absorption spectra of the PE and APE waveguide samples were measured with a Perkin Elmer Paragon 1000 spectrometer. The sharp peak around 3500 cm$^{-1}$ and the broad peak around 3300 cm$^{-1}$ are analyzed.

3. Results and discussion

3.1. Index profile

The index profile (including the surface index and the guide depth of the guiding layer) was reconstructed with an IWKB fitting procedure [13] from the measured effective indices for the guided modes of as-exchanged and annealed waveguides. The results are shown in Fig. 1.

The surface index increase $\Delta n_e$ of about 0.127 was achieved for an as-exchanged waveguide fabricated at 220°C for 11.5h and this $\Delta n_e$ can be reduced by post annealing.

![Fig. 1. Typical evolution of the index profile for a PE waveguide (sample M05; fabricated at 220°C for 11.5h) as the annealing time $t_a$ increases. The annealing temperature $T_a$ is 350°C.](image-url)
thermal annealing (see Fig. 1), such as after annealing at 350°C for 20h, the surface value of $\Delta n_e$ has been reduced by about 33%. The index profile becomes gradient-like after annealing due to the appearance of an index tail near the interface between the guiding layer and the substrate. With further annealing, the index tail becomes longer and the guiding layer deepens into the substrate. After long time annealing, unlike the Gaussian index profile for APE waveguides in LiNbO$_3$ [14,15], the index profile for MgO:LiNbO$_3$ APE waveguides still keeps the characteristics of step-like profile (though with a long index tail) even after annealing for 20h (at annealing temperature of 350°C), as shown in Fig. 1.

3.2. Analysis with X-ray diffraction

The lattice spacing $d$, the lattice constant $a$ and the strain $\Delta a/a$ in the $a$-axis (perpendicular to the surface of substrate) can be deduced by the angular position $\theta$ of the diffraction peaks for PE and APE waveguides on polished Y-cut MgO:LiNbO$_3$ (300). Fig. 2 shows the X-ray diffraction curves for a virgin crystal, the PE and APE waveguides of Y-cut MgO:LiNbO$_3$. Fig. 2(a) gives a typical (300) diffraction from the virgin single-crystal Y-cut MgO:LiNbO$_3$. The two close sharp peaks are due to the diffractions of $K_{a1}$ and $K_{a2}$ copper cathode characteristic wavelengths. Here we only analyse the diffraction peak from $K_{a1}$ ($\lambda = 1.54051\,\text{Å}$) since its intensity is much stronger than that of $K_{a2}$.

From the diffraction angle 62.38° of the virgin Y-cut MgO: LiNbO$_3$ (see Fig. 2(a)), the lattice constant along the $b$-axis was deduced to be 5.1522 Å, which is different from the corresponding value for congruent LiNbO$_3$ (5.148 Å). This slight difference may be indicative of the slightly different material structure caused by the doping of MgO. Compared to Fig. 2(a), the diffraction for the PE waveguides (shown in Fig. 2(b) and (c)) has a satellite peak to the left (with angle deviation $2\Delta \theta$) of the substrate $K_{a1}$ peak. This indicates that the lattice structure of the PE layer expands and exhibits a positive strain. The (angle) distance between the satellite peak and the substrate peak indicates the magnitude of the strain. It can be used to calculate the lattice structural modification (strain) induced by proton exchange, which is +0.59% for M01 (exchanged at 200°C for 4.5h) and +0.73% for M05 (exchanged at 220°C for 11.5h). The lattice constant of the PE layer depends on the proton exchange condition, and the strain is stronger for the sample exchanged at a higher temperature or for a longer time. This is different from the case of Z-cut LiNbO$_3$ (without MgO doping) for which $\Delta c/c$ is almost constant and influenced little by exchange conditions (see e.g. [16]) and is also different from the study by Korshiko on X-cut MgO: LiNbO$_3$ PE waveguides that during the proton exchange process the surface value of strain is constant even with variation of the proton exchange time [10].

M05 has a broader satellite peak than M01 (a broader satellite peaks indicates a less uniform modification of the lattice). Note that unlike the substrate peaks the satellite peak in Fig. 2(b) or (c) does not have double peaks. This is because the satellite peak is too broad and $K_{a2}$ is much weaker in intensity than $K_{a1}$ (Satellite

Fig. 2. X-ray diffraction for Y-cut MgO:LiNbO$_3$: (a) Virgin Y-cut MgO:LiNbO$_3$; (b) M01 (exchanged at 200°C for 4.5h); (c) M05 (exchanged at 220°C for 11.5h); and (d) M05A3 (by annealing M05 at 350°C for 1h).
peak of $K_{a2}$ is covered by that of $K_{a1}$). By comparing with the corresponding experimental results of X-ray diffraction for Z-cut LiNbO$_3$ (without MgO doping), we found that the proton exchange causes more serious non-uniformity of the strain in MgO:LiNbO$_3$ PE waveguides since the satellite peaks of $K_{a1}$ and $K_{a2}$ are sharper and clearly separated in all LiNbO$_3$ (without MgO doping) PE waveguides under similar fabrication conditions. The relative intensities of the satellite and substrate peaks depend on the waveguide fabrication conditions. For example, relative intensity of the satellite peak of M05 is higher than that of M01 (see Fig. 2), which shows M05 has a deeper PE thickness. The reason for the different behaviour of the lattice modifications for M01 and M05 is that the lattice structural modification is related to the hydrogen concentration incorporated into the PE layer, which depends on the proton exchange conditions such as the exchange temperature and time.

Fig. 2(d) shows the diffraction of sample M05A3 annealed at 350$^\circ$C for 1 h. Compared to Fig. 2(c), the satellite peak in Fig. 2(d) moves closer to the substrate peak after annealing, which indicates the lattice expansion has been restored partially and the lattice constant of the PE layer becomes closer to that of the substrate. The angle deviation $2\Delta \theta$ decreases from 0.5$^\circ$ (for PE waveguide M05) to 0.16$^\circ$ (for M05A3) after annealing, which corresponds to a relief of the strain from +0.73% to +0.20% after annealing at 350$^\circ$C for 1 h. Useful diffraction information of the angle deviation and strain for the virgin crystal, PE and APE waveguides of Y-cut MgO:LiNbO$_3$ is shown in Table 1. Our experiments have also shown that after annealing M05 for over 20 h, the satellite peak is not distinguishable from the substrate peak (indicating that the lattice constant of the guiding layer is very close to that of the substrate). The intensity of the satellite peak becomes stronger after annealing since hydrogens diffuse further into the substrate and the depth of the guiding layer increases. The shape of satellite peak becomes sharper, which indicates that annealing makes the lattice better ordered and then improves the guiding properties.

The above measurements and analysis show that annealing has a restoration effect on the structural modification induced by proton exchange. Annealing makes the lattice constant of a PE layer closer to that of the substrate since it can transform cubic perovskite HNbO$_3$ or H-rich rhombohedral H$_3$Li$_{1-x}$NbO$_3$ into near-Li$_2$NbO$_3$ rhombohedral structure [17]. The restoration effect of annealing on the lattice structure of the guiding layer can improve the waveguide quality, such as the transmission loss and the electro-optic effect, etc.

### 3.3. Analysis of infrared spectra

The characteristic OH absorption bands were observed in the infrared spectra of all the PE waveguides in Y-cut MgO:LiNbO$_3$. The virgin crystal exhibits a very weak IR absorption peak centred around a wave number of 3530 cm$^{-1}$ (see Fig. 3(a)) due to some hydrogens incorporated during the crystal growth. After the proton exchange, the peak shifts to a lower wave number position of 3500 cm$^{-1}$ (see Fig. 3(b) and (d)), and this is in agreement with the result reported by Loni et al. for PE waveguides on Z-cut 4.5-mol% MgO-doped LiNbO$_3$ [18]. Our experimental results for Z-cut LiNbO$_3$ (without MgO doping) show that the IR absorption peak of virgin OH band is centred around 3485 cm$^{-1}$ and it shifts to a higher wave number of 3505 cm$^{-1}$ after proton exchange. The differences in these wave numbers of IR absorption peaks for the cases with and without MgO doping indicate the differences in the material structure between LiNbO$_3$ and MgO:LiNbO$_3$. The sharp peak at 3500 cm$^{-1}$ is due to the free OH group, which is connected to moderate polarized hydrogen bonds in perovskite rhombohedral structure of H$_3$Li$_{1-x}$NbO$_3$. The broad absorption peak at 3300 cm$^{-1}$ is polarization-independent and usually assigned to stretching OH$^-$ vibrations induced by strong hydrogen bondings [19]. The peak at 3300 cm$^{-1}$ is much broader than that at 3500 cm$^{-1}$ since the position of interstitial hydrogen in the cubic perovskite structure of HNbO$_3$ phase is not stable. The random distribution of interstitial hydrogen in the PE layer leads to the broadening of the IR absorption peak at 3300 cm$^{-1}$, which is consistent to our previous X-ray diffraction result that the diffraction (satellite) peak of the exchanged layer is much broader than the substrate peak.

Note that the broad peak (at 3300 cm$^{-1}$) of M01 in Fig. 3(b) is not as strong as that of M05 in Fig. 3(d). This indicates that the HNbO$_3$ phase, to which the broad peak at 3300 cm$^{-1}$ is attributed [20], does not form in a short exchange time since it needs enough amount of hydrogen incorporated into the crystal during the proton exchange process. This is consistent to the previous result that no broad peak at 3300 cm$^{-1}$ was observed for those samples fabricated at 200$^\circ$C with exchange time less than 1 h [21]. Compared to our

<table>
<thead>
<tr>
<th>Sample</th>
<th>Process</th>
<th>$2\Delta \theta$ ($^\circ$)</th>
<th>$\Delta a/a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>M01</td>
<td>Exchanged at 200$^\circ$C for 4.5 h</td>
<td>$-0.4$</td>
<td>+0.59%</td>
</tr>
<tr>
<td>M01A1</td>
<td>Annealing M01 at 350$^\circ$C for 0.5 h</td>
<td>$-0.22$</td>
<td>+0.32%</td>
</tr>
<tr>
<td>M01A6</td>
<td>Annealing M01 at 350$^\circ$C for 2.5 h</td>
<td>$-0.12$</td>
<td>+0.17%</td>
</tr>
<tr>
<td>M05</td>
<td>Exchanged at 220$^\circ$C for 11.5 h</td>
<td>$-0.5$</td>
<td>+0.73%</td>
</tr>
<tr>
<td>M05A3</td>
<td>Annealing M05 at 350$^\circ$C for 1 h</td>
<td>$-0.16$</td>
<td>+0.20%</td>
</tr>
</tbody>
</table>

The diffractograms for virgin Y-cut MgO:LiNbO$_3$ PE waveguides M01, M05 and APE waveguide M05A3 are shown as Fig. 2(a)–(d) respectively.
corresponding experimental results for Z-cut LiNbO$_3$ (without MgO doping), HNbO$_3$ phase of high hydrogen concentration can be formed more easily in MgO:LiNbO$_3$ by proton exchange since the intensity of the 3300 cm$^{-1}$ peak in the IR spectra of MgO:LiNbO$_3$ waveguides is much stronger than that of LiNbO$_3$ waveguides exchanged at similar conditions. This can partially explain why in the X-ray diffractogram the intensity of the satellite peak of the MgO:LiNbO$_3$ PE layer increases much more dramatically after annealing than that of LiNbO$_3$ PE layer (the hydrogens in HNbO$_3$ phase diffuse further into the substrate and this causes the increase of the satellite peak for the PE layer).

The effect of annealing on OH absorption spectra is shown in Fig. 3(c) and (d). The broad band at 3300 cm$^{-1}$ in Fig. 3(b) for PE sample M01 quickly disappears after annealing at 350$^\circ$C for 2h (see Fig. 3(c) for sample M01A5). This phenomenon is also clearly shown in Fig. 3(d) for the IR absorption spectra of PE sample M05 (solid line) and APE sample M05A3 (dashed line; by annealing M05 at 350$^\circ$C for 1h). The disappearance of the broad band at 3300 cm$^{-1}$ is due to the fact that the hydrogen ions of the high concentration region in the PE layer diffuse further into the substrate (this leads to the disappearing of the H NbO$_3$ phase at the waveguide surface and the deepening of the guiding layer). At the same time, Li$^+$ at the boundary between the waveguide and the substrate move to the exchanged layer, and the crystal structure in the guiding layer can be reverted to the original rhombohedral structure. This conclusion is consistent with our previous X-ray measurement result that crystal lattice in the waveguide becomes closer to the substrate crystal lattice after annealing.

On the other hand, the hydrogen-bonded OH$^-$ decomposes into O$_2$ and H$_2$O, which vaporises and causes the loss of hydrogen from the guiding region during annealing. This is the reason why the intensity of the infrared absorption peak at 3500 cm$^{-1}$ decreases after the annealing. The loss of hydrogen in the guiding region may also lead to the formation of polymorphs Nb$_2$O$_5$ or LiNb$_3$O$_8$ or small cavities [22], which brings some complicity to the crystal structure in the guiding layer and is not good for guiding properties. In fact, it was found in our prism-coupling measurement that guiding modes could not be observed in some waveguides annealed in dry air for a too long time (such as at 350$^\circ$C for 22h). Therefore, a limited but long enough annealing is necessary to avoid the formation of polymorph and small cavities in the waveguides and at same time improve the guiding properties.

4. Conclusions

In conclusion, PE and APE waveguides in Y-cut MgO:LiNbO$_3$ have been fabricated and the as-exchanged waveguides have a steplike profile for the refractive index. Unlike the Gaussian index profile for annealed waveguides in LiNbO$_3$, the index profile for MgO:LiNbO$_3$ APE waveguide still keeps the characteristics of step-like profile (though with a long index tail) even after long time annealing. The lattice distortion induced by proton exchange depends on the exchange condition in Y-cut MgO:LiNbO$_3$ and the proton exchange causes more serious non-uniformity of the strain in Y-cut MgO:LiNbO$_3$ than that in undoped LiNbO$_3$. After annealing, it was found that the X-ray diffraction
peak related to the PE layer becomes sharper, stronger and closer to the unperturbed substrate peak. This indicates that annealing improves the lattice crystal structure while deepening the guiding layer. The IR absorption spectra, including the broad and sharp peaks, depend on the waveguide fabrication condition. A higher exchange temperature and a longer exchange time will ease the formation of the HNbO$_3$ phase, which is represented by the broad peak at 3300 cm$^{-1}$. After annealing the broad peak at 3300 cm$^{-1}$ disappears and the strength of the sharp peak decreases since the high concentration hydrogens in the exchanged layer diffuse further into the substrate during the annealing. The restoration effect of annealing on the lattice structure in the guiding layer leads to the improvement of the waveguide quality.

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