Conference materials
UDC 535.3, 544.015
DOI: https://doi.org/10.18721/JPM.183.112

Annealed proton-exchange waveguides in mixed lithium niobate-tantalate solid solutions

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Abstract. Annealed proton-exchange (APE) waveguides in lithium niobate are widely used in integrated photonics for navigation, telecommunications and electric field sensors. In this paper, we analyze the characteristics of planar APE waveguides in new mixed single crystals of lithium niobate-tantalate solid solution by various methods (prism coupling, XRD and IR spectroscopy). The elemental composition (ratio Nb/Ta) of Z-cut mixed lithium niobate-tantalate samples gives a good uniform distribution over the all-surface area by X-ray fluorescence method. APE waveguides in mixed lithium niobate-tantalate single crystals are characterized by a lower value of refractive index increment due to Ta atoms and higher proton diffusion coefficients due to lattice disordering. High diffusion coefficients provide a deeper APE waveguide layer and rapid recovery of the crystal lattice during post-exchange annealing. These results expand the understanding of the proton exchange process in mixed lithium niobate-tantalate solid solutions for the creation of single-mode APE waveguides.

Keywords: optical materials, lithium niobate-tantalate, APE waveguides

Funding: This work was funded by Ministry of Education and Science of the Perm Region [grant number C-26/37], experimental samples were created by state task [FSME-2023-0003 and 075-00295-25-00]. XRF was carried out whithin thestate assignment of NRC "Kurchatov Institute". We used a proton exchange reactor AN-0034 manufactured by Concept-Lab LLC (Moscow).

Citation: Sosunov A.V., Petukhov I.V., Kornilicyn A.R., Mololkin A.A., Umylin V.E., Fakhrtdinov R.R., Kulikov A.G., Annealed proton-exchange waveguides in mixed lithium niobate-tantalate solid solutions, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 18 (3.1) (2025) 71–76. DOI: https://doi.org/10.18721/JPM.183.112

Материалы конференции
УДК 535.3, 544.015
DOI: https://doi.org/10.18721/JPM.183.112

Отожженные протонообменные волноводы в смешанных кристаллах твердого раствора ниобата-танталата лития

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Аннотация. Отожженные протонообменные волноводы в ниобате лития широко используются в интегральной фотонике для навигации, телекоммуникаций и датчиков электрического поля. В данной работе мы анализируем характеристики планарных волноводов в новых смешанных монокристаллах твердого раствора ниобата-танталата лития с помощью различных методов (призменный элемент связи, рентгеновская дифракция, ИК-спектроскопия, рентгенофлуоресцентный анализ). Элементный состав (соотношение Nb/Ta) исследуемых образцов Z-среза демонстрирует однородное распределение по всей площади поверхности. Оптические волноводы характеризуются более низким значением приращения показателя преломления из-за присутствия атомов Ta (7%) и более высокими коэффициентами диффузии протонов из-за разупорядочения кристаллической решетки по сравнению с ниобатом лития. Высокие коэффициенты диффузии обеспечивают более глубокий волноводный слой и быстрое восстановление кристаллической решетки при постобменном отжиге. Полученные результаты расширяют понимание процесса протонного обмена в смешанных твердых растворах ниобата-танталата лития для создания одномодовых оптических волноводов.

Ключевые слова: оптические материалы, ниобат-танталат лития, волновод, протонный обмен

Финансирование: Работа выполнена при финансовой поддержке Министерства образования и науки Пермского края [грант № С-26/37], экспериментальные образцы получены при финансовой поддержке госзадания [FSME-2023-0003 и 075-00295-25-00]. Результаты РФЭС получены в рамках выполнения государственного задания НИЦ «Курчатовский институт».

Ссылка при цитировании: Сосунов А.В., Петухов И.В., Корнилицын А.Р., Мололкин А.А., Умылин В.Е., Фахртдинов Р.Р., Куликов А.Г. Отожженные протонообменные волноводы в смешанных кристаллах твердого раствора ниобата-танталата лития // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2025. Т. 18. № 3.1. С. 71–76. DOI: https://doi.org/10.18721/JPM.183.112

Introduction

Integrated photonics and nonlinear optics are rapidly growing scientific and practical areas. Integrated optical circuits allow the production of navigation systems [1], telecommunication systems [2] and sensors [3]. The key position of lithium niobate (LN) and lithium tantalate (LT) for optoelectronics is due to their high electrooptical coefficients, excellent piezoelectric and acousto-optic features, strong birefringence and nonlinearity, suitability for industrial manufacturing, etc.

The mixed $LiNb_xTa_{1-x}O_3$ (LNT) crystal attracts the attention since its physical, optical and electrooptical properties can be tuned by varying the crystal composition (changing x from 0 (LT) to 1 (LN)). LNT to combine the best properties of LN (e.g. high electrooptical coefficients and high Tc and thermal stability) and LT (e.g. high photorefractive damage resistance). The possibility of controlling the crystal composition makes it possible to control birefringence and, in the future, to obtain crystals without birefringence at all.

Recently, the production of single-domain LNT crystals with isomorphic substitution of Nb by Ta in the cationic sublattice, with a Curie temperature of 1105 °C, close to the Tc of lithium niobate (1140 °C), was demonstrated [4]. It is shown that the change in the unit cell parameters depends linearly on the composition of the crystals. The LNT solid crystal solutions seem to be promising functional materials for integrated optics.

One of the main passive elements in photonics is an optical waveguide. Diffuse waveguides are obtained either by annealed proton exchange (APE) or by Ti diffusion [5]. APE waveguides are characterized by a complex phase composition, but they are easy to manufacture. Description of structural-phase transformations during proton exchange and annealing in LNT crystals is given in [6, 7].

The aim of this work is to produce a planar APE waveguide in Z-cut LNT single-crystal and study its characteristics in comparison to these of a waveguide in LN produced at the same technological parameters.

Materials and Methods

The crystals of LNT solid solution with composition $LiNb_{0.93}Ta_{0.07}O_3$ were grown by the Czochralski method in NIKA-3M apparatus with induction heating and automatic control of crystal diameter at the Institute of Microelectronics Technology and High Purity Materials, Russian Academy of Sciences. The crystal was drawn along the polar Z axis. The experimental samples had size 10×12×1 mm and double-side polished. The single-domain state analysis, the phase diagram and the description of the growth effects were also previously reported in [4, 8–9].

X-ray fluorescence (XRF) method was used to analyze the Nb/Ta atomic ratio on the LNT surface (Fig. 1). XRF was performed by ORBIS micro-XRF setup (USA) with a rhodium (Rh) X-ray tube, a probe beam of 30 μm, an accelerating voltage of 40 kV, and a cathode filament current of 400 μA. Two-dimensional maps were obtained. The mapping grid resolution was 256×200 points. The spectral accumulation time at each point was 700 ms in the Live time mode. The "dead time" in the experiment did not exceed 24%. The intensity of the regions of the spectrum corresponding to the NbK (16.6 keV) and TaL (8.1 keV) series lines was analyzed. The percentage ratio of the specified chemical elements was determined by the ratio of the total intensities of all lines included in the specified series.

XRF analysis over the entire LNT sample area shows a fairly uniform distribution of Ta atoms (X and Y axes). We did not observe loci of frontal segregation. This is very important for the stable PE process.

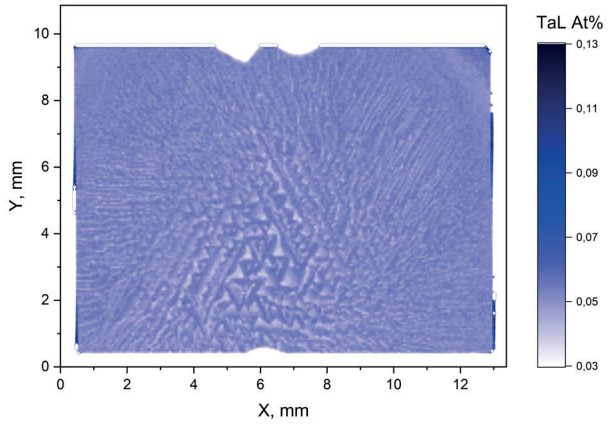

Fig. 1. XRF image of LNT sample

APE waveguides were created in a closed zirconium reactor containing a benzoic acid melt at a temperature of 190 °C for 2 hours and annealed in air at a temperature of 350 °C for 5 hours. APE planar waveguides were obtained in LN and LNT under identical conditions.

The structure of the APE waveguides was studied by X-ray diffraction (XRD) and IR absorption spectroscopy. XRD was carried out using a double-crystal spectrometer. A single crystal of dislocation-free Si was used as a monochromator, set to the reflecting position of the K_β-line of Co-emission (λ = 1.62075 Å) from the crystallographic plane (111). XRD spectra were obtained from the crystallographic plane (006) for Z-cut samples. The deformations ε_{33} (deformations in the direction normal to the surface of the sample) of the crystal lattice of LNT samples were determined by the shift of lines in the spectrum. Deformations $\varepsilon_{33} = \Delta d/d$ were calculated from the Wulff-Bragg equation:

$$d = \frac{\lambda}{2\sin\theta}, \quad (1)$$

where λ is the wavelength, d is the interplanar distance, θ is the Bragg reflection angle, $n = 1$ is the order of reflection.

IR spectroscopy was carried out using a Spectrum Two Fourier transform spectrometer (PerkinElmer) in the range valence vibrations of 2800–4000 cm^{-1} with a resolution of 1.0 cm^{-1}. The decomposition of the IR and XRD spectra was done using the Fityk program.

Integrated-optical parameters of APE waveguides were determined by prism coupling method at a wavelength $\lambda_{He\text{-}Ne} = 632$ nm. Numerical method for reconstruction of the refractive index profile of diffused APE waveguides was used [10].

Results and Discussion

APE waveguide profile. APE waveguides have a gradient profile (Fig. 2). However, we observe a decrease in the refractive index increment (waveguide contrast) for LNT crystal. The decrease in the refractive index increment Δn_e can be explained by the increase in diffusion coefficients $D_z(T)$, which are caused by a more disordered crystal lattice, which allows protons to penetrate deeper into the LNT crystal faster. The diffusion coefficients were calculated from the root equation, where the waveguide depth X is proportional to the square root of time [11]. This equation allows a comparative assessment of the diffusion coefficient (Table):

$$X = 2\sqrt{D_z \cdot t}, \quad (2)$$

where t – annealing time. According to equation (2), the proton penetration depth and diffusion coefficient increase for LNT, respectively. The results of the optical properties of the APE waveguides in LNT crystals are well explained by the results of structural studies, which are given in the next section B.

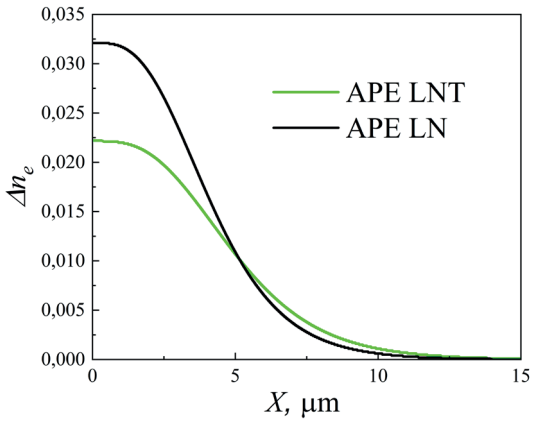

Fig. 2. APE waveguide profile

Table

Optical and diffusion parameters of APE waveguides

Sample	T, °C	t, h	Δn_e	X, μm	$D_z(T)$, $\mu m^2/h$
APE LN	350	5	0.032	4.8	0.61
APE LNT	350	5	0.022	5.7	0.88

Structure. The phase analysis of the experimental samples is shown in Fig. 3. The IR spectra indicate the formation of the α-phase for APE LNT crystals (Fig. 3, *a*, inset, 3489 cm^{-1} [6]). This is consistent with the contrast of the refractive index, since for the α-phase it is less than ≤ 0.025. At the same time, for APE LN, the phase analysis shows the presence of the κ_1-phase (Fig. 3, *a*, 3494 cm^{-1}).

This means that the annealing time was insufficient for the formation of the α-phase. Also, the integral intensity of the OH-group band in the IR spectrum of APE LNT is lower than for APE LN, which corresponds to a lower proton concentration and faster relaxation of the crystal lattice during post-annealing. This is also confirmed by the XRD results (Fig. 3, *b*). Relative deformations of the crystal lattice show the formation of the κ_1-phase for APE LNT and the α-phase for APE LN. The APE waveguides in LN are characterized by a refractive index increment of ≤ 0.025 and have the so-called stable α-phase [12]. The proton exchange and annealing time allowed us to form such waveguides in mixed LNT solid solutions. However, for LN crystals, an intermediate κ_1-phase is formed, which requires additional annealing time. This means that higher proton diffusion coefficients lead to rapid relaxation of the structure during annealing, which is shown in Section A. Our results show the fundamental possibility of obtaining planar waveguides in new mixed LNT solid solutions.

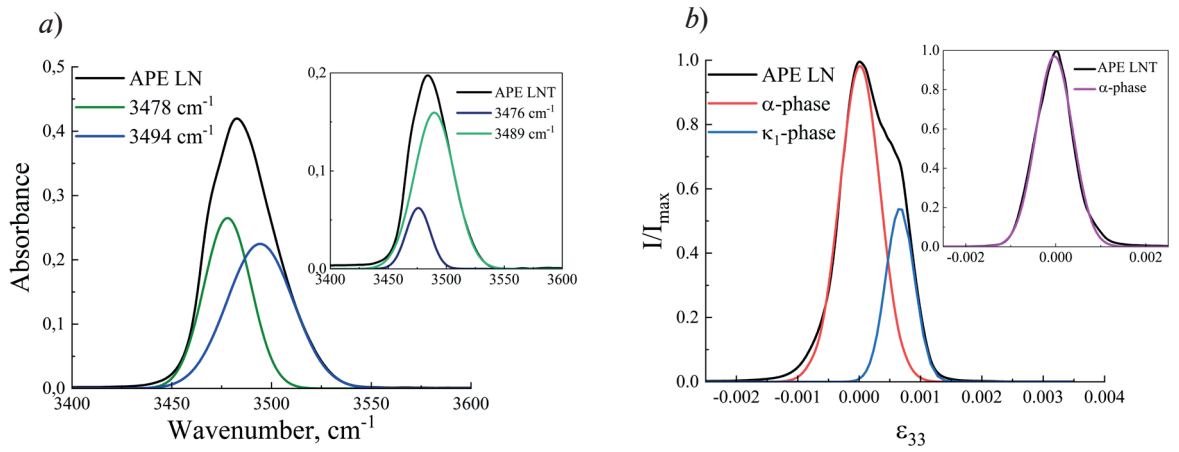

Fig. 3. Structure of APE waveguides: IR spectra of valence vibrations OH groups for APE LN and APE LNT (insert right) (*a*), relative deformations for APE LN and APE LNT (insert right) (*b*)

Conclusion

We have obtained and characterized planar proton-exchange waveguides in mixed crystals of LNT solid solution for the first time. They have higher diffusion coefficients, which lead to rapid relaxation of deformations of the LNT crystal lattice. Our results open up the possibility of using new mixed LNT crystals for the problems of integrated and nonlinear photonics.

Further, it is planned to study the characteristics of channel waveguides and establish the relationship between structure and optical losses.

Acknowledgments

XRF measurements was made of NRC "Kurchatov Institute" using the equipment of the Shared Research Center "Structure diagnostics of materials". We used a proton exchange reactor AN-0034 manufactured by Concept-Lab LLC (Moscow).

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Received 11.08.2025. Approved after reviewing 09.09.2025. Accepted 09.09.2025.