

Proceedings of the International Conference on Oxide Materials for Electronic Engineering, May 29–June 2, 2017, Lviv

Optical Investigation of the Cu Ions Diffusion into Bulk Lithium Niobate

D. SUGAK^{a,b,*}, I.I. SYVOROTKA^{a,b}, U. YAKHNEVYCH^a, O. BURYI^a, N. MARTYNYUK^a,
S. UBIZSKII^a, YA. ZHYDACHEVSKYY^{a,c}, A. SUCHOCKI^{c,d}, H. KUMAR^e,

V. JANYANI^e AND G. SINGH^e

^aLviv Polytechnic National University, Lviv, Ukraine

^bScientific Research Company “Electron–Carat”, Lviv, Ukraine

^cInstitute of Physics, PAS, Warsaw, Poland

^dInstitute of Physics, Kazimierz Wielki University, Bydgoszcz, Poland

^eDepartment of Electronics and Communication Engg. MNIT, Jaipur, India

Spatial changes of optical properties of bulk LiNbO₃ crystal were investigated after annealing in CuO powder. The incorporation of copper ions into the crystal was confirmed by registration of additional absorption spectra that revealed formation of the absorption bands of both Cu⁺ (400 nm) and Cu²⁺ (1000 nm) ions. The changes of optical absorption caused by thermal treatment were registered along the direction of diffusion by the probe beam perpendicular to this direction. The anisotropy of diffusion was revealed. The maxima were observed on the depth dependences of additional absorption both for the wavelengths of 400 and 1000 nm for all main crystallographic directions. The concentrations of copper ions were calculated in accordance with the Smakula–Dexter formula. The X-ray diffraction study revealed reflexes which probably belong to CuNb₂O₆, CuNbO₃ and CuO. The halo was observed on these diffraction patterns that confirms the formation of the scattering centers (about 1 nm in diameter) in the near-surface region.

DOI: [10.12693/APhysPolA.133.965](https://doi.org/10.12693/APhysPolA.133.965)

PACS/topics: 66.30.–h, 78.20.–e

1. Introduction

Lithium niobate crystal (LiNbO₃, LN) is one of the most frequently used optoelectronic materials [1]. The photorefractive properties of lithium niobate give possibility of its using for optical data storage [2]. Increase of LiNbO₃ photorefractive sensitivity can be achieved by doping with metal ions which can change their valence state under the influence of light or thermochemical treatment [3]. Usually doping is carried out during crystal growth [4–6]. The diffusion method is also used, at that the dopants incorporate into the crystal during high-temperature treatment in the appropriate environment containing metal ions. So far, doping of LiNbO₃ with use of the latter method by Mg, Sc, Ti, Cr, Fe, Cu, Zn, Ga, Zr, In, Sn, Hf, Nd, and Tm was investigated [7–19]. Particularly, the diffusion doping of lithium niobate by Cu is successfully used for increase of the photorefractive sensitivity of this crystal as well as for modification of the refractive indices in the near-surface layers for obtaining of integrated optics structures [20–30].

It should be mentioned that the diffusion doping of LiNbO₃ by copper ions can be realized in various ways. Particularly, the crystals were annealed after immersion into the copper salt melts (KCl–CuCl or Na₂SO₄–

CuSO₄) in [20, 21], the copper film was deposited on the crystal surface before the thermal treatment [26–28] or the crystals were covered by CuO-containing powders before annealing [22].

The authors of [21] investigated the changes in the composition and properties of LN layers that is caused by the diffusion of Cu ions by secondary ions mass spectroscopy (SIMS). The same problem was studied in [20] by scanning Auger microscopy (SAM). However, these methods allow studying the near-surface regions only (about few μm in depth). In both cases the studies are performed in the direction of diffusion.

Optical spectroscopy is very often used to characterize crystals containing impurities, particularly, in the investigations of LN doped by copper. These studies provide additional information about the composition and the uniformity of diffusion layers, allow determining the diffusion coefficients. The absorption spectra can be used for determination of the charge states of multivalent dopants, including copper ions, in the LN crystal. However, most studies of the optical absorption of LN crystals doped by Cu have been carried out in the longitudinal geometry when the direction of propagation of light coincides with the direction of diffusion (e.g. see [22]). Therefore, only the average picture of the changes of LN optical properties was obtained.

The depth dependences of optical absorption of Cu-doped LN crystal were studied only in [28]. The diffusion was carried out along *X*-axis of the crystal at that the copper film was formed on *YZ*-surfaces of 1 mm thick

*corresponding author; e-mail: dm_sugak@yahoo.com

plates. These plates were annealed in air at 1000 °C for 10 h. The absorption changes corresponding to changes of Cu ions concentration were determined at the one wavelength of 477 nm. The focused laser beam propagated perpendicularly to the direction of diffusion; during measurements the laser beam was scanned along X -axis of the crystal. One of the tasks of [28] was ensuring of the uniform distribution of dopant that was achieved due to high temperature (1000 °C) and long-term annealing (100 h) as well as the relatively small thickness of the plates (1 mm). The investigations of the copper diffusion layers in lithium niobate in the direction perpendicular to the diffusion one were also carried out by optical microscopy [26]. As is shown in this paper, the essential optical contrast is observed between the copper diffusion layers and the regions of the crystal where the diffusion did not occur.

Therefore, the systematic studies of spatial changes of LN optical properties caused by metal ions diffusion for the distances about several millimeters and deeper into the crystal were not performed. The anisotropy of diffusion of metal ions in lithium niobate is still the open question.

In our work we studied the copper diffusion because of two following considerations: (i) under the same conditions, the diffusion coefficient of copper in LiNbO_3 is about 500 times higher than the one, for example, of iron [24, 25]; (ii) the absorption bands caused by Cu^+ and Cu^{2+} ions in LN crystal are easy to distinguish by optical spectroscopy [4, 31–34].

Thus, the objective of this work is the determination of spatial distribution of copper ions by registration of the optical absorption in the directions perpendicular to the directions of diffusion (X , Y , or Z crystal-physics axes) in the case of the bulk congruent lithium niobate crystal annealed in the presence of CuO powder on its surfaces.

2. Experimental details

LiNbO_3 crystals of the congruent composition were grown at the SRC “Electron–Carat” by the Czochralski technique in the platinum crucibles in air according to the technology described in [35]. The growth was carried out in the crystallographic Z direction. The single domain state of the crystals was ensured by the special after-growth high temperature treatment in electrical field. The samples for investigations were cut from one crystal boule and have got the form of oriented parallelepipeds with dimensions 7 mm (X) \times 15 mm (Y) \times 32 mm (Z). All faces of these samples were polished. Two samples of the above sizes were used in our studies. They were covered by CuO powder on all sides and annealed in ceramic crucibles in the Nabertherm furnace (Germany). The thickness of the layer of the powder between the sample and the crucible walls as well as the layer over the sample is not lower than 5 mm. The scheme of the sample location in the crucible containing CuO powder is shown in Fig. 1a. The powder of copper(II) oxide that

was used in the experiments corresponds to the qualification OSCh. 9-2 (Russia) and to the Technical Conditions TU 6-09-02-391-85. The size of the grain in this powder is not standardized and is about units or tens of μm .

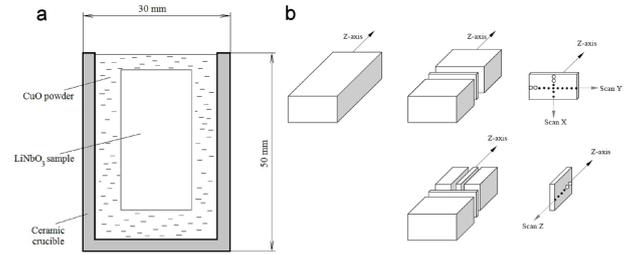


Fig. 1. (a) The scheme of the LN sample location in the crucible containing CuO powder; (b) the scheme of the LN annealed samples cutting for investigation of coloration depth after treatment.

The atmosphere of annealing was air and the heating rate was 5 K per min. The first sample was heated to $T = 973$ K and was annealed at that temperature for 1 h. The second sample was heated to $T = 1073$ K additionally in three stages: 3 + 6 + 12 h. After each stage of annealing, the transmission spectra of the sample were registered at room temperature. After completion of annealing the samples were cooled down in the furnace. After annealing and measurements which were carried out on whole LN samples, the 1 mm thick plates were cut from them in accordance with the scheme shown in Fig. 1b. The plates undergo polishing procedures and, thereafter, were used for investigation of optical absorption along certain crystallographic directions of the LN crystal.

The absorption and transmission spectra were measured by UV3600 Shimadzu spectrophotometer. For the uncut sample the transmission spectra were registered in the range of 300–1500 nm through the diaphragm with aperture of 3 mm. The plates were used for determination of the optical absorption changes at the different distances from the crystal surfaces that were in the direct contact with CuO powder during annealing (see Fig. 1). For this purpose the movable table with a micrometer screw was placed in the sample chamber of the spectrophotometer. This table allowed moving the plate in relation to the special 100 μm diaphragm. The spectra were recorded consecutively along the crystallographic directions X , Y , and Z (the diffusion directions) with the 20 μm step. The scanning beam propagated perpendicularly to the chosen crystallographic direction so the depth dependences of the optical absorption were registered. It should be noted that this method has been successfully used for investigation of the spatial distribution of LN coloration caused by high-temperature reducing annealing [36–38].

To characterize the coloration changes at the different distances from the crystal surface the sequential difference spectra were calculated for each measured point in

relation to the optical absorption in the central part of the plates where the optical absorption was practically unchanged. The additional absorption (AA) ΔK was determined as

$$\Delta K = \frac{1}{d} \ln \frac{T_c}{T_n}, \quad (1)$$

where d is the thickness of the sample, T_n is the transmission of the sample in the n point, T_c is the transmission in the central part of the sample.

The structural changes of the annealed samples were determined by the X-ray diffractometer DRON-3M (Russia). X-ray diffraction patterns were obtained in the reflection mode from the surface of the crystal that was in direct contact with the CuO powder during annealing and from the inner surface of the sample, which was formed after cutting of the parallelepiped.

The photos of surfaces of polished plates cut from the annealed samples were obtained by the Eclipse LV100 POL polarization microscope (Nikon, Japan) in the phase contrast mode.

3. Results and discussion

The uncut samples of LiNbO₃, annealed in the presence of CuO powder both at 973 and 1073 K have got an orange color (Fig. 2). The coloration is maximal near the surfaces that were in contact with the copper oxide powder. The coloration decreases toward the center of the crystal as it is seen from the photo of the plate (Fig. 2). Because the color of the crystal annealed at 1073 K is more intensive, the results for this sample will be considered as the first ones.

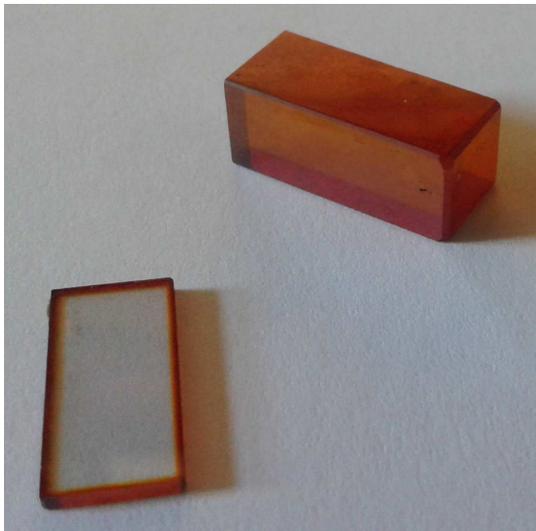


Fig. 2. The bulk sample of the LN single crystal after annealing in CuO at 1073 K and a plate that was cut from it.

In the spectra of the annealed uncut parallelepipeds measurements in the direction of diffusion the shift of the absorption edge to the region of higher wavelengths

and the weak broad band with a maximum near 1000 nm are observed (Fig. 3). This result is in agreement with the one of Ref. [22].

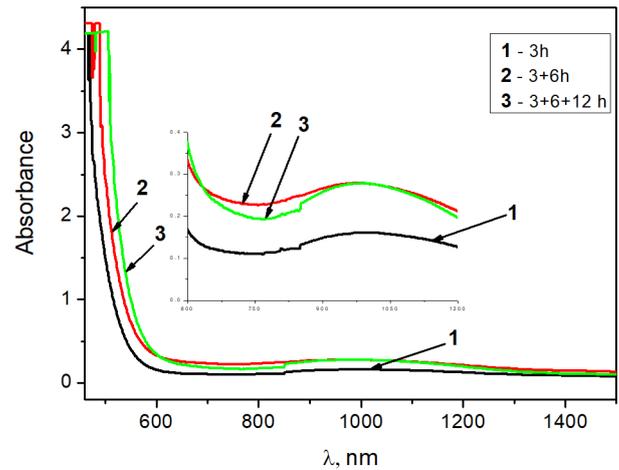


Fig. 3. Absorbance spectra of the LN after annealing in CuO at 1073 K (light propagates along Z -direction).

The additional absorption spectra of the annealed sample measured in the region of 300–850 nm at the different distances from the crystal edges and in the different crystallographic directions are shown in Fig. 4. In addition to the near-IR band (1000 nm) the band with a maximum near 400 nm was observed at these spectra. Based on the results of [23, 30, 32–35], we can give the following interpretation of these bands: 400 nm is the charge transfer transition $\text{Cu}^+ \rightarrow \text{Nb}^{5+}$; 1000 nm — $E_g \rightarrow {}^2T_{2g}$ intracenter transition in Cu^{2+} ion.

However, as it is seen from Fig. 4a, the additional absorption spectra in the visible region have got the complex character and look like a superposition of at least two absorption bands. Probably, the polaron centers that have got the absorption in this spectral region [39] make a contribution to AA spectra of the samples.

These absorption bands are distinctive of Cu^+ and Cu^{2+} ions which incorporate into LN crystal during crystal growth, when copper ions occupy the clear structural positions. Most of the works note that these are the positions of lithium.

As it is seen from the comparison of the AA spectra registered at different distances from the crystal edge (Fig. 4), the changes of optical absorption have got the complex character. At the distances about 100 μm and smaller from the crystal edge the optical absorption both by Cu^+ and Cu^{2+} ions is lower than the one at the depths of 300–500 μm . At these distances the optical absorption reaches the maximum and then falls to zero at distances larger than 800 μm from the crystal edges (see Fig. 5). This peculiarity is observed for diffusion in all main crystallographic directions. The maxima of the absorption are well distinguished for both wavelengths. The position of the maximum caused by Cu^{2+} absorption do not

reveal an essential dependence on the crystallographic direction: it is located near $300 \mu\text{m}$ in the case of X direction, near $250 \mu\text{m}$ for Y one and near $340 \mu\text{m}$ for Z one. Taking into account the accuracy of the measurements, one can argue that the maximum is observed at the distances about $300 \mu\text{m}$ for all directions. The max-

ima of the absorption caused by the presence of Cu^+ ions are higher than the one of Cu^{2+} and are observed at the essentially larger distances from the plate edge for different crystallographic directions: near $400 \mu\text{m}$ for X , near $500 \mu\text{m}$ for Y one and near $550 \mu\text{m}$ for Z one.

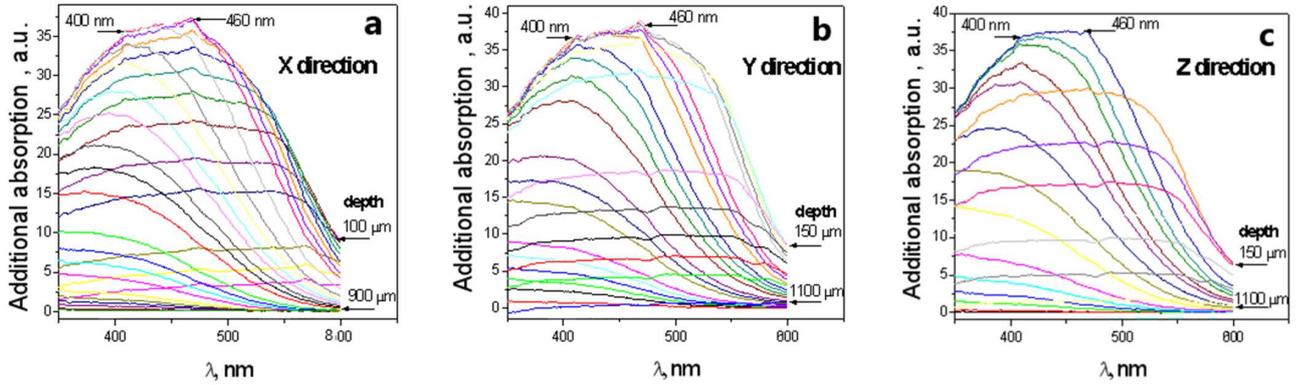


Fig. 4. Additional absorption spectra at the different distances from the crystal edges of LN after annealing in CuO at $T = 1073 \text{ K}$ additively in three stages — 3 h + 6 h + 12 h: (a) X direction, (b) Y direction, (c) Z direction.

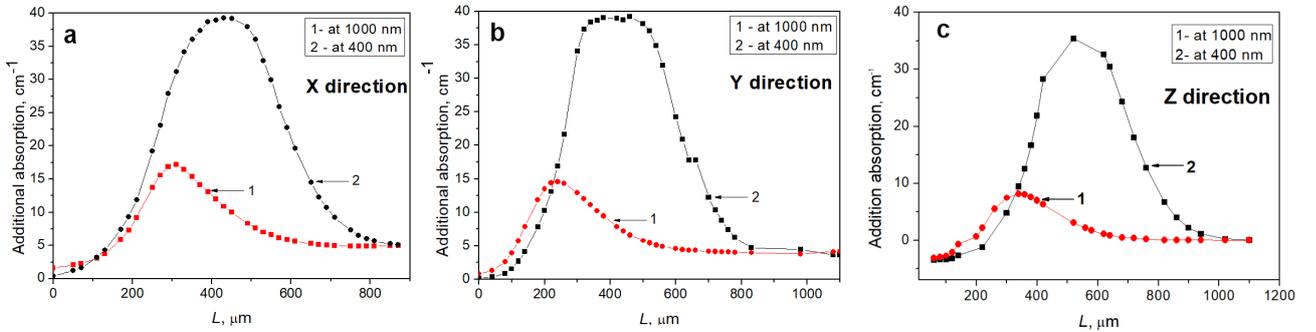


Fig. 5. The dependences of the absorption coefficient at 400 and 1000 nm on depth after treatment of the LN sample at $T = 1073 \text{ K}$ in CuO powder additively in three stages — 3 h + 6 h + 12 h: (a) X direction, (b) Y direction, (c) Z direction.

At the known spatial distributions of the absorption, the concentrations of Cu^+ and Cu^{2+} ions can be calculated in accordance with the Smakula–Dexter formula [40] under the assumption that the forms of absorption bands are close to Gaussian ones

$$N = 8.7 \cdot 10^{16} \frac{n}{(n^2 + 1)^2} \frac{1}{f_0} K_{max} \Delta E, \quad (2)$$

where n is the refractive index calculated in accordance with the Sellmeier formula for LiNbO_3 [41, 42], $f_0 = 4 \times 10^{-2}$ for Cu^+ (400 nm) and 2×10^{-4} for Cu^{2+} (1000 nm) are the oscillator strengths [30, 32], K_{max} is the measured peak absorption coefficient, ΔE is the width of absorption band at its half-maximum. The results of these calculations are shown in Fig. 6.

As is seen from Fig. 6, the forms of the calculated dependences of concentrations are qualitatively corresponding to the ones of the additional absorption curves (Fig. 5), particularly, they also reveal the maxima. However, despite the absorption caused by Cu^+ ions is higher than the one of Cu^{2+} , the concentration of Cu^{2+} ions

is essentially higher. Particularly, the concentrations of Cu^{2+} ions in maxima are about $(3.0\text{--}3.5) \times 10^{19} \text{ cm}^{-3}$ for different crystallographic directions, whereas for Cu^+ this value is about $5 \times 10^{18} \text{ cm}^{-3}$. Obviously, it is connected with lower value of the oscillator strength of transition ${}^2E_g \rightarrow {}^2T_{2g}$ in the Cu^{2+} ion in comparison with the one of $\text{Cu}^+ \rightarrow \text{Nb}^{5+}$ transition [30, 32]. The distances of the concentration maxima locations are slightly different from the distances of the corresponding AA maxima that are caused by relatively low accuracy of the determination of ΔE value at the different distances from the crystal edge. However, as well as in the case of AA dependences, the positions of the maxima of the concentration distributions are different for different crystallographic directions.

It should be emphasized that the observed decrease of the optical absorption and concentrations of copper ions in the near-surface region can not be caused by the light that passes beyond the crystal and gets into the diaphragm. Indeed, the distances of the maxima loca-

tions are several times greater than the diameter of the diaphragm ($100\ \mu\text{m}$).

On the other hand, this peculiarity cannot be explained by simple diffusion models which do not predict the non-monotonous of the spatial distribution. Only in the case of diffusion of two species (both positively and negatively charged) the maxima can be observed on spatial distribution of faster diffusant. However, this case is obviously not realized in our experiments. Indeed, we

observed the maxima of concentration for both Cu^+ and Cu^{2+} ions and not any other positive ions incorporated into the crystal. Of course, diffusion of copper ions should be accompanied by diffusion of electrons (probably, in the form of polarons) because of electrical neutrality condition. However, it cannot lead to the non-monotonous of spatial distributions because of opposite charges of electrons and copper ions.

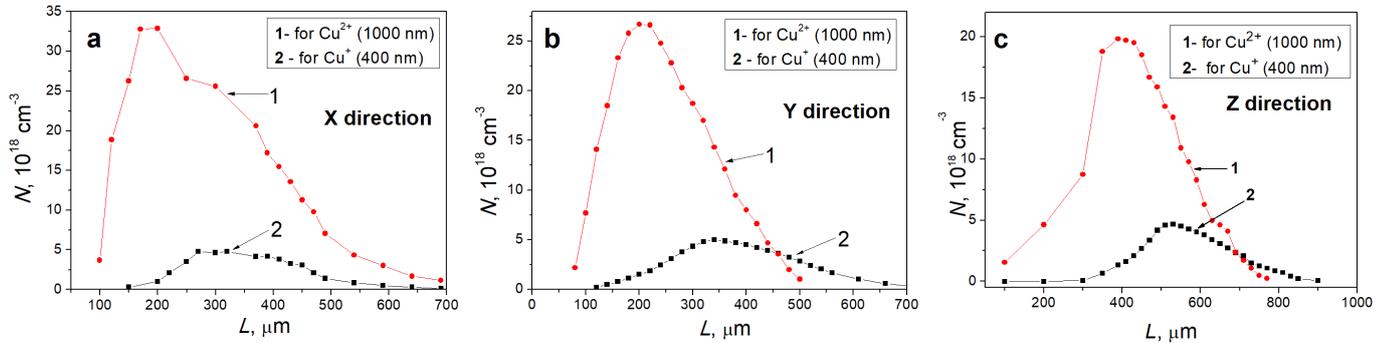


Fig. 6. The spatial distributions of Cu^+ and Cu^{2+} ions concentrations in LiNbO_3 for different crystal-physic directions after treatment of the LN sample at $T = 1073\ \text{K}$ in CuO powder additively in three stages — 3 h + 6 h + 12 h: (a) X direction, (b) Y direction, (c) Z direction.

We would like to stress that our measurements detect only Cu^+ and Cu^{2+} ions and they are not sensitive to the other Cu-related centers. Particularly, the copper ions may form the complexes that do not absorb in the investigated spectral range. Therefore the nature of these complexes cannot be determined from our investigations.

Significant decrease in absorption near the edge of the plate may indicate that copper in the near-surface layers of the crystal may be in the form of CuO particles (nanoparticles). Hence the absorption bands inherent in copper ions embedded in the structure of lithium niobate are not observed. The photographs of plate surfaces may be partial confirmation of it (Fig. 7).

As is seen from Fig. 7, the contrast limit is observed at a distance of about $300\ \mu\text{m}$, which also characterizes the process of copper entering into the crystal. At the same time, the intensity of the color of the region enriched with copper is the largest on the edge of the wafers. We have noted that at a distance of $300\ \mu\text{m}$ the maxima are also observed for the Cu^{2+} ions concentration (Figs. 5 and 6), whereas the maxima for the Cu^+ ions one are situated at the distances of $400\text{--}600\ \mu\text{m}$, i.e. in the regions that do not differ from the inner regions of the crystal on the photos.

In order to confirm the assumption about the change of copper ions state in the near-surface region, X-ray diffraction studies of the annealed samples were carried out. X-ray patterns were obtained from the regions which were in direct contact with the CuO powder as well as from the inner regions of the samples that were opened after sample cutting. This study has shown that only the reflexes inherent to the structure of lithium niobate are

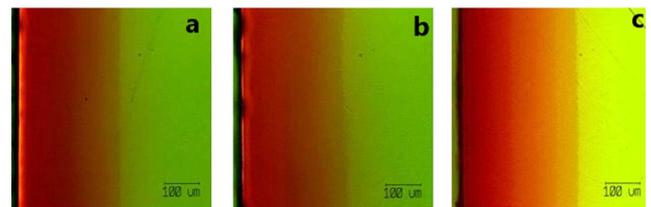


Fig. 7. The photos (50-fold increase) of the diffusion regions for different crystal-physic directions after treatment of the LN sample at $T = 1073\ \text{K}$ in CuO powder additively in three stages — 3 h + 6 h + 12 h: (a) X direction, (b) Y direction, (c) Z direction.

observed from the inner parts of the crystal. The additional reflexes which do not relate to the LiNbO_3 phase were observed in the X-ray diffraction pattern from the regions which were in the direct contact with CuO powder. These reflexes can belong to CuNb_2O_6 , CuNbO_3 , and CuO (Fig. 8).

The presence of additional reflexes was also observed in X-ray diffraction patterns obtained from surfaces of LN plates after their heating in a melt mixture of $\text{Na}_2\text{SO}_4\text{--CuSO}_4$ salts [21]. The authors of [21] assumed that the observed reflexes belong to CuNb_2O_6 , CuNbO_3 compounds or to $\text{Cu}_x\text{Li}_{1-x}\text{NbO}_3$ solution.

The attribution of the reflexes, that do not belong to the LiNbO_3 phase, requires a separate study that is foreseen for the future.

An important point to be noted consists in observation of the halo on the diffraction patterns from the sur-

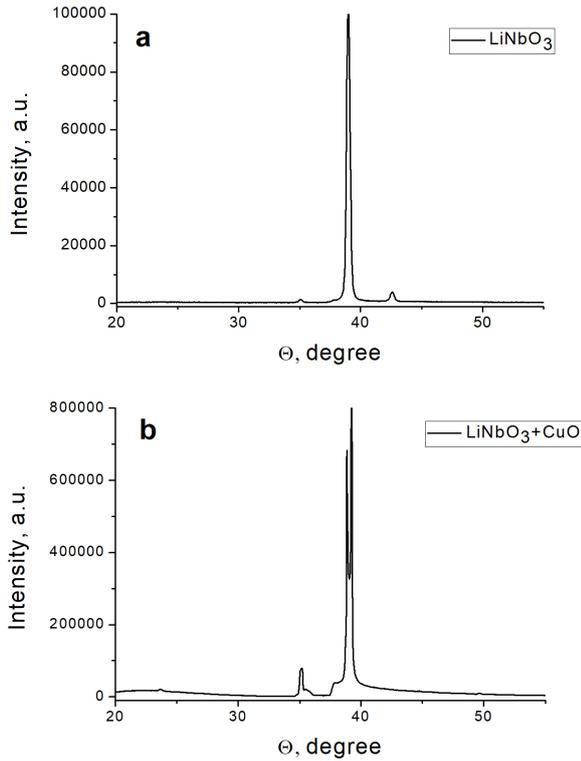


Fig. 8. Diffraction patterns of the LN Z surfaces before (a) and after (b) annealing in CuO powder at $T = 1073$ K additively in three stages — 3 h + 6 h + 12 h.

faces which were in the contact with CuO (Fig. 9). It can indicate the appearance of scattering centers in the structure of the surface layer after annealing. The size (diameter) of scattering centers was calculated according to the Scherrer formula [42] for different crystallographic planes. As it is followed from the calculations, the diameter of these centers for X plane is equal to 1.3 nm, for Y plane — to 0.6 nm and for Z one — to 1.1 nm. This result also points to the anisotropy of the Cu diffusion process in LN.

Similar complex of investigations was performed on a sample that was annealed into a copper oxide powder at 973 K for 1 h. These investigations have shown the similar results, particularly, the shapes of the depth dependences of absorption and concentration are the same as for the sample annealed at 1073 K. However, the value of the additional absorption is $0.6\text{--}5\text{ cm}^{-1}$, and the concentration of ions in the spatial distribution maxima is about $(3.0\text{--}3.5) \times 10^{18}\text{ cm}^{-3}$ for Cu^{2+} and $(0.3\text{--}1) \times 10^{18}\text{ cm}^{-3}$ for Cu^+ . The X-ray diffraction pattern obtained from Z plane has shown the presence of the scattering centers (1.1 nm in the diameter) on the surface that was in the contact with CuO.

Consequently, based on the obtained results, one can suppose that the transformation of compounds in the crystal volume containing copper ions occurs gradually: from CuO through CuNb_2O_6 to CuNbO_3 . The total copper concentration cannot be estimated from optical

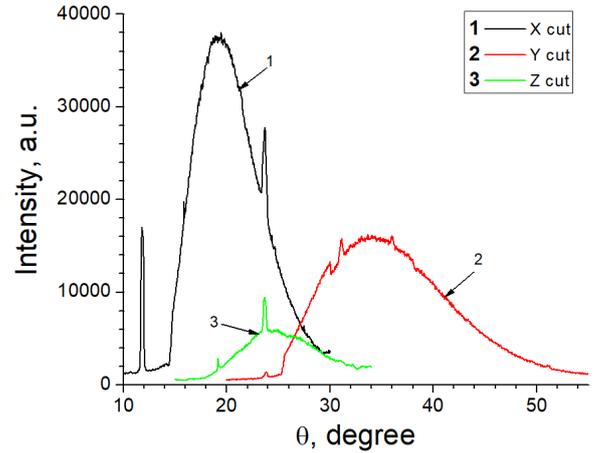


Fig. 9. Diffraction patterns in the halo region on X , Y , and Z surfaces of the LN crystal after annealing at $T = 1073$ K in CuO powder additively in three stages — 3 h + 6 h + 12 h.

absorption studies. The observed absorption and concentration curves of copper ions of different valences are the result of several processes, namely, the actual diffusion and quasi-chemical reactions of the formation of CuNb_2O_6 and CuNbO_3 compounds.

The participation of point defects in the processes revealed by our investigations are also possible. One of such defects is niobium ions in the positions of lithium ions [43] that is the typical defect in the congruent lithium niobate. The uneven extension of the AA band from the region of 400 nm to the larger wavelengths (Fig. 4) can be caused by the formation of bipolarons (bound pairs: Nb^{4+} in a regular structural position — Nb^{4+} in the position of Li), with a maximum absorption band of 500 nm [43].

Thus, we can conclude that there is only one aspect of the complex process of incorporation of copper ions into the lithium niobate crystal is revealed in our experiments. The obtained data allow determining the spatial distribution of copper ions of different valences embedded into the structural positions of cations in LiNbO_3 structure that is the final stage of complex process. However, the description of the previous stages of incorporation requires a separate research by other methods — SIMS, micro-Raman spectroscopy, micro-cathodoluminescence, etc.

4. Conclusions

The spatial changes of optical properties of bulk LiNbO_3 crystal were investigated after annealing in presence of CuO powder on the crystal surface.

The incorporation of copper ions into the crystal was confirmed by additional absorption spectra registration. Particularly, two absorption bands with the maxima in the regions 400 and 1000 nm were observed at these spectra. The first of them is due to $\text{Cu}^+ \rightarrow \text{Nb}^{5+}$ charge transfer transition, whereas the second one — due to ${}^2E_g \rightarrow {}^2T_{2g}$ intracenter transition in the Cu^{2+} ion.

For the first time, the studies of absorption changes of bulk LiNbO₃ crystals annealed in the presence of copper ions were carried out in the direction that is perpendicular to the diffusion one. The depths of copper ions incorporation is no more than 800 μm in our experiments and depend on the crystallographic directions. Particularly, the depth of copper incorporation is greatest in *Z* direction, and the lowest in *X* one. The maxima were observed on the depth dependences of additional absorption both for the wavelengths of 400 and 1000 nm for all crystallographic directions.

The changes in the concentration of copper ions with depth in different crystal-physical directions were calculated in accordance with the Smakula–Dexter formula. As well as the additional absorption spatial distributions, the depth dependences of copper ions concentrations reveal the maxima. The concentration of Cu²⁺ ions at the maximum of its distribution reaches a value of $3.5 \times 10^{19} \text{ cm}^{-3}$, whereas the maximum concentration of Cu⁺ ions is about $5 \times 10^{18} \text{ cm}^{-3}$ for the sample additively annealed for 21 h at 1073 K.

The presence of the maxima on spatial distributions of copper ions is indicated that the nature of the processes occurring during annealing is more complicate than the one predicted on the basis of simple diffusion models. Probably, such a behavior indicates that the additional processes accompany the copper ions diffusion, particularly, the formation of CuNb₂O₆ and CuNbO₃ compounds can occur. The quasichemical reactions with participation of point defects (antisite niobium ions) are also possible.

The magnitude of the changes of the optical absorption of lithium niobate samples annealed at 1073 K for 21 h is an order of magnitude higher than the ones for the samples annealed at 973 K for 1 h.

Comparative studies of X-ray diffraction in the reflection mode reveal the additional reflexes at diffraction pattern obtained for the near-surface region that was in the direct contact with CuO powder. These reflexes are probably belonging to CuNb₂O₆, CuNbO₃ and CuO. Moreover, the halo was observed on these diffraction patterns that confirms the formation of scattering centers (about 1 nm in diameter) in the near-surface region. It can be assumed that during heating of LiNbO₃ in the presence of CuO the copper is partially stored in the form of CuO nanoparticles or clusters near the crystal surface. CuNb₂O₆ compound is formed with increasing of the depth and then the CuNbO₃ ones forms during the diffusion process.

The final determination of copper diffusion mechanisms in LiNbO₃ crystal requires additional research.

Acknowledgments

This research was supported by Ministry of Education and Science of Ukraine in the frames of the projects EMSh (0116U004134) and MEZHA (0118U000273) and also the joint Ukrainian-Indian project M/122-2016

(0715U002471). The authors are grateful to Dr. Ivan Solskii (SRC “Electron–Carat”) for growth of the crystal for investigations and to Mr. Vasyi Baluk for XRD measurements. Ya. Zhydachevskyy and A. Suchocki acknowledge support of the EU within the European Regional Development Fund through the Innovative Economy grant (POIG.01.01.02-00-108/09).

References

- [1] *Properties of Lithium Niobate*, Ed. K.K. Wong, INSPEC, London 2002.
- [2] T. Volk, M. Wöhlecke, *Lithium Niobate: Defects, Photorefraction and Ferroelectric Switching*, Springer, Berlin 2009.
- [3] Y. Kong, S. Liu, J. Xu, *Materials* **5**, 1954 (2012).
- [4] L. Arizmendi, J. Cabrera, F. Agullo-Lopez, *J. Phys. C Solid State Phys.* **17**, 515 (1984).
- [5] I. Pracka, A. Bajor, S. Kaczmarek, M. Swirkowicz, B. Kaczmarek, J. Kisielewski, T. Lukaszewicz, *Cryst. Res. Technol.* **34**, 627 (1999).
- [6] T. Gebre, A.K. Batra, P. Guggilla, M. Aggarwal, R. Lal, *Ferroelectr. Lett.* **31**, 131 (2004).
- [7] D. Bryan, R. Gerson, H. Tomaschke, *Appl. Phys. Lett.* **44**, 847 (1984).
- [8] T. Volk, V. Pryalkin, N. Rubinina, *Opt. Lett.* **15**, 996 (1990).
- [9] M. Nakamura, S. Takekawa, Y. Liu, K. Kitamura, *J. Cryst. Growth* **281**, 549 (2005).
- [10] J. de Sandro, J. Jones, D. Shepherd, M. Hempstead, J. Wang, A. Tropper, *IEEE Photon. Technol. Lett.* **8**, 209 (1996).
- [11] K. Kasemir, K. Betzler, B. Matzas, B. Tiegel, T. Wahlbrink, M. Wöhlecke, *J. Appl. Phys.* **84**, 5191 (1998).
- [12] L. Razzari, P. Minzioni, I. Cristiani, V. Degiorgio, *Appl. Phys. Lett.* **86**, 131914 (2005).
- [13] Y. Kong, S. Liu, Y. Zhao, H. Liu, S. Chen, J. Xu, *Appl. Phys. Lett.* **91**, 081908 (2007).
- [14] L. Wang, S. Liu, Y. Kong, S. Chen, Z. Huang, L. Wu, R. Rupp, J. Xu, *Opt. Lett.* **35**, 883 (2010).
- [15] J. Almeida, G. Boyle, A. Leite, *J. Appl. Phys.* **78**, 2193 (1995).
- [16] G. Maggioni, G. Battaglin, V. Tarasova, N. Krasil'nikova, L. Bogomolova, S. Kostitskii, V. Fedorov, Y. Korkishko, P. Mazzoldi, N. Argiolas, E. Cattaruzza, M. Bazzan, C. Sada, *Mater. Sci. Eng. B* **118**, 155 (2005).
- [17] M. Hempstead, *J. Appl. Phys.* **74**, 5483 (1993).
- [18] W. Huang, W. Wang, *IEEE Photon. Technol. Lett.* **19**, 1679 (2007).
- [19] T. Nozawa, K. Noguchi, H. Miyazawa, K. Kawano, *Appl. Opt.* **30**, 1085 (1991).
- [20] V. Ivanov, V. Ganshin, Yu. Korkishko, *Vacuum* **43**, 317 (1992).
- [21] F. Caccavale, C. Sada, F. Segato, L. Bogomolova, N. Krasil'nikova, Yu. Korkishko, V. Fedorov, T. Morozova, *J. Mater. Res.* **15**, 1120 (2000).
- [22] S. Kar, K. Bartwal, *Mater. Lett.* **62**, 3934 (2008).

- [23] T. Kobayashi, K. Muto, J. Kai, A. Kawamori, *J. Magn. Res.* **34**, 459 (1979).
- [24] J. Hukriede, B. Gather, D. Kip, E. Krätzig, *Phys. Status Solidi A* **172**, R3 (1999).
- [25] D. Kip, B. Gather, H. Bendig, E. Krätzig, *Phys. Status Solidi A* **139**, 241 (1993).
- [26] O. Mikami, *Opt. Commun.* **30**, 11 (1974).
- [27] J. Noda, T. Saku, N. Uchida, *Appl. Phys. Lett.* **25**, 308 (1974).
- [28] K. Peithmann, J. Hukriede, K. Buse, E. Krätzig, *Phys. Rev. B* **61**, 4615 (2000).
- [29] K. Buse, F. Jermann, E. Krätzig, *Appl. Phys. A Solids Surf.* **58**, 191 (1994).
- [30] E. Krätzig, R. Orlowski, *Ferroelectrics* **27**, 241 (1980).
- [31] M. Clark, F. DiSalvo, A. Glass, G. Peterson, *J. Chem. Phys.* **59**, 6209 (1973).
- [32] A. Petrosyan, R. Khaghatryan, E. Sharoyan, *Phys. Status Solidi B* **122**, 725 (1984).
- [33] A. Matkovskii, P. Potera, D. Sugak, Ya. Zhydachevskii, V. Pankratov, D. Millers, L. Grigorjeva, I. Pracka, T. Lukasiewicz, *Cryst. Res. Technol.* **38**, 388 (2003).
- [34] P. Potera, S. Ubizskii, D. Sugak, T. Lukasiewicz, *Radiat. Measur.* **42**, 232 (2007).
- [35] I. Solskii, D. Sugak, M. Vakiv, *Acta Phys. Pol. A* **124**, 314 (2013).
- [36] D. Sugak, *Solid State Phenom.* **230**, 228 (2015).
- [37] D. Sugak, I. Syvorotka, O. Buryy, U. Yakhnevych, I. Solskii, N. Martynyuk, Yu. Suhak, G. Singh, V. Janyani, S. Ubizskii, *IOP Conf. Series Mater. Sci. Eng.* **169**, 012019 (2017).
- [38] D. Sugak, I. Syvorotka, O. Buryy, U. Yakhnevych, I. Solskii, N. Martynyuk, Yu. Suhak, A. Suchocki, Ya. Zhydachevskii, R. Jakiela, S. Ubizskii, G. Singh, V. Janyani, *Opt. Mater.* **70**, 106 (2017).
- [39] R. Jenkins, R. Snyder, *Introduction to X-ray Powder Diffractometry*, Wiley, 1996.
- [40] D. Dexter, *Phys. Rev.* **101**, 48 (1956).
- [41] D.E. Zelmon, D.L. Small, D. Jundt, *J. Opt. Soc. Am. B* **14**, 3319 (1997).
- [42] D.Yu. Sugak, A.O. Matkovskii, I.M. Solskii, B.N. Kopko, V.Ya. Oliinyk, I.V. Stefanskii, V.M. Gaba, V.V. Grabovskii, I.M. Zaritskii, L.G. Rakitina, *Cryst. Res. Technol.* **32**, 805 (1997).
- [43] O.F. Schirmer, M. Imlau, C. Merschjann, B. Schoke, *J. Phys. Condens. Matter* **21**, 123201 (2009).