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Investigation of Optical and Pyroelectric Properties of Lithium Niobate Single Crystals Caused by Metal Ions Diffusion

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Spatial changes of optical and pyroelectric properties of doped $LiNbO_3$ single crystals were investigated. Doping with Cu and Fe was performed after crystal growth by thermal diffusion at elevated temperatures. The crystals were all-side-covered by corresponding metal oxide powder before annealing. In order to reveal the role of various types of diffusion sources in the formation of the modified layers of $LiNbO_3$, the same investigations were performed on the samples covered by copper films before annealing. The optical absorption spectra of the samples were recorded in a direction perpendicular to the direction of diffusion at different distances from the crystal surface. The intensities of the absorption bands of Cu^+ (400 nm), Cu^{2+} (1000 nm) and Fe^{3+} (480 nm) ions were analyzed depending on the annealing temperature and the distance from the source of diffusion. The maxima were obtained on the depth profiles of additional absorption for all samples. The concentrations of Cu and Fe ions were calculated in accordance with the Smakula-Dexter formula. For the determination of correlation of the changes of optical and pyroelectric properties, the profiles of pyroelectric coefficient in the doped crystals were investigated by the laser intensity modulation method. To avoid the measurement uncertainty of thermal wave method that increases with increasing depth, the pyroelectric current was registered under excitation from both the front and the back sides of the sample. The averaged pyroelectric coefficients were also determined for calibration of the results. Here, a Peltier stage provided a sinusoidal modulation of the sample temperature at a frequency of 0.1 Hz. It is shown that diffusion doping affects the pyroelectric properties of lithium niobate crystals.

Keywords: $LiNbO_3$ single crystals, Dopant diffusion depth profile, Pyroelectric coefficient depth profile.

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1. INTRODUCTION

The development of novel optical and electronic devices requires a detailed study and an improvement of material properties. Lithium niobate ($LiNbO_3$, LN) single crystals possess an outstanding multi-functionality with wide applications in waveguides, second harmonic generation, modulators, high-density optical data storage, etc. [1].

One way of improving device performance by influencing the defect state of the LN subsystem is high-temperature annealing of crystals under different conditions (oxidizing, reducing, in the presence of metal ions, etc.). High-temperature annealing in the presence of metal ions is used to increase the photorefractive sensitivity of LN in optical recording devices [2]. In this case, metal ions that can change their valence under the influence of light and thermochemical treatments (Fe, Mn, Cu, combinations thereof, as well as combinations with other impurities) are used as dopants [3]. Usually, doping is carried out during the crystal growth [4, 5]. On the other hand, also diffusion doping is widely used for the fabrication of thin layers. Here, impurities are incorporated into crystals during high-temperature annealing in an environment containing the corresponding ions [6, 7]. Diffusion doping of LN crystals by copper and iron ions allows to increase the photosensitivity of these crystals and to obtain the diffusion layers with modified refractive index for integral optics applications [6-9].

The objective of our work is to determine the spatial distributions of Cu and Fe ions incorporated during annealing at elevated temperatures into LN bulk single crystals. Copper was selected as a preferential diffusion agent since, first, the diffusion coefficient of copper in $LiNbO_3$ is about 500 times larger than the one of iron under the same conditions [10], and, second, the two different valence states of copper ions in LN (Cu^+ and Cu^{2+}) are easily detected by their optical absorption bands well separated in energy [4, 11-13]. For this reason, we study the dopant and pyroelectric depth profiles by optical spectrometry [14] and an approximate laser intensity modulation method (LIMM) [15].

2. EXPERIMENTAL DETAILS

2.1 Optical spectrophotometry

$LiNbO_3$ crystals of the congruent composition were obtained in the SRC 'Electron-Carat' by Czochralski technique in platinum crucibles in air according to the technology described in [16]. Crystal growth was carried out in the crystallographic direction Z. The single domain state of the crystals was ensured by a special after-growth high-temperature treatment in the presence of an electrical field. Samples for annealing were cut from a single ingot in the form of oriented parallelepipeds with dimensions of 7 mm (X) × 15 mm (Y) × 32 mm (Z). The faces of these parallelepipeds were polished. Annealing of the samples was carried out in an industrial furnace (Nabertherm GmbH, Germany). Here, the samples were all-side-covered by corresponding metal oxide powder. The thickness of the metal oxide powder layer between the sample and the crucible walls as well as on the top of the sample was at least 5 mm.

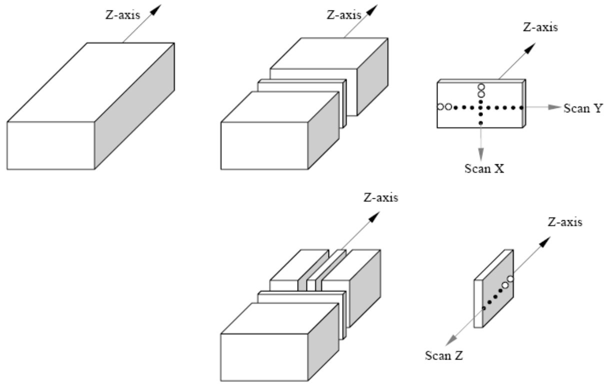

Fig. 1 – Scheme of cutting the annealed sample to study the diffusion depth profile

Additionally, for comparison, we also investigated the diffusion from 650 nm thick copper films which were deposited on the surface of the crystals before annealing. In all cases, annealing was performed in air at a temperature of 1073 K during a few up to a few tens of hours. The heating (cooling) rate amounted to 5 K/min. After cooling down, the annealed LN samples were cut into 1 mm thick crystallographic oriented plates (Fig. 1) which were grinded and polished. These plates were used for further optical measurements, particularly, for scanning the changes of the optical absorption along certain crystallographic directions.

The absorption and transmission spectra were recorded in the range from 300 to 1500 nm by a UV3600 Shimadzu spectrophotometer. A special, moveable platform with a micrometer screw was placed inside the spectrometer chamber. It allowed scanning of the light beam with 20 μm steps through the aperture with 100 μm in diameter and studying the colour changes at different distances from the crystal surface. The difference absorption spectra were calculated for each measured point and related to the optical absorption in the central part of the plate, where the optical absorption was practically unchanged. The dopant-related additional (or induced) absorption is then given by

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

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

The concentrations of dopant ions were estimated calculating the integrated absorption intensities of the corresponding absorption bands, i.e., of the bands in the region of 480 nm (Fe^{3+} ions) [17], 400 nm (Cu^{+} ions), and 1000 nm (Cu^{2+} ions) [18] by using the Smakula-Dexter formula [19].

2.2 Pyroelectric profiling

For pyroelectric profiling by means of LIMM, the samples were cut perpendicular to the diffusion direction. The thickness of the plates was about 1.8 mm. The plates were polished and spray-coated with a graphite-based layer (Graphite 33, Kontakt Chemie, CRC Industries Group) enhancing laser absorption. It has to be noted that the electrodes have been applied here in a way that the measurements took place along the direction of diffusion.

Averaged pyroelectric coefficients were determined for calibration. A Peltier stage provided a sinusoidal modulation of the sample temperature at a frequency of 0.1 Hz. The temperature of the stage was monitored and controlled by a Pt100 platinum temperature sensor (Heraeus Sensor Technology GmbH). The pyroelectric current was recorded by the current input of a SR850 lock-in amplifier (Stanford Research, USA).

For LIMM measurements, the samples were periodically heated by a laser diode (LCU98A041A, Laser Components GmbH, Olching, Germany) at a wavelength of 980 nm with a power of 12 mW, square-wave-modulated in the frequency range from 100 mHz up to 1 kHz. The complex pyroelectric current was determined by an impedance/gain-phase analyzer (Solartron 1260, Solartron Analytical, Farnborough, UK) with DC coupling. In order to reduce noise, 30 measurement repetitions were used for averaging. Since the measurement uncertainty of thermal wave methods increases with sample depth, the pyroelectric current was recorded from both the front and the back sides of the sample. The measured values of the pyroelectric current were converted into a depth profile of the pyroelectric coefficient following the approach described in detail in [15]. Fig. 2 illustrates the pyroelectric coefficient depth profile of an undoped LN single crystal.

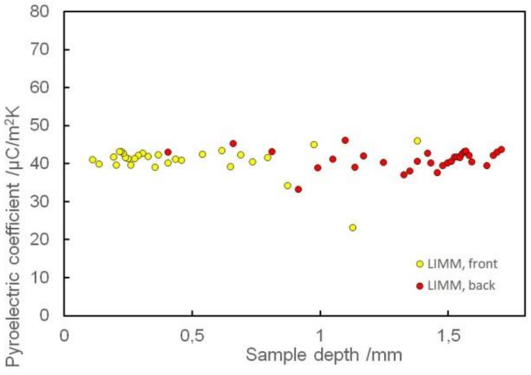

Fig. 2 – Pyroelectric depth profile of an undoped LN sample

3. RESULTS AND DISCUSSION

The LN parallelepipeds, which were annealed in the presence of CuO powder or Cu film, have gotten an orange colour, whereas the samples annealed in Fe_2O_3 powder were yellow-green coloured. As expected, the coloration was maximal near the surfaces, which were in contact with the diffusion source and it decreases towards the centre of the crystal.

In the spectra of the annealed parallelepipeds (light propagation in the direction of diffusion), a shift of the absorption edge to higher wavelengths was observed.

For example, the absorption spectra of the parallelepipeds annealed at $T = 1073$ K are shown in Figs. 3-4. In addition, annealing in the presence of copper ions leads to additional absorption bands in the range of 400 and 1000 nm (Fig. 3), and high temperature treatment in the Fe_2O_3 powder causes the appearance of bands in the 480 and 650 nm region (Fig. 4). This observation is in general coincident with the data given in [8, 16].

Following the results of [5, 8, 11-13, 18], we attribute the 400 nm band observed in LN doped with copper (see Fig. 3) to the intervalence transition $Cu^+ \rightarrow Nb^{5+}$, whereas the band in the vicinity of 1000 nm is assigned to an intracenter absorption transition in the Cu^{2+} ion. The absorption band near 480 nm observed in LN doped with iron (Fig. 4) is associated with the spin-forbidden *d*–*d*-transitions in the Fe^{3+} ions.

Analysis of the excess absorption bands caused by Cu^+, Cu^{2+} and Fe^{3+} ions which are obtained at different distances from the surface of the plates allows to calculate the concentration of dopants and to determine their distributions along different LN crystallographic directions. This calculation was carried out by means of the Smakula-Dexter formula, derived considering the interactions of an impurity atom with its neighbours in an idealized solid [19]. In the case of a Gaussian shape of the absorption band, this formula yields:

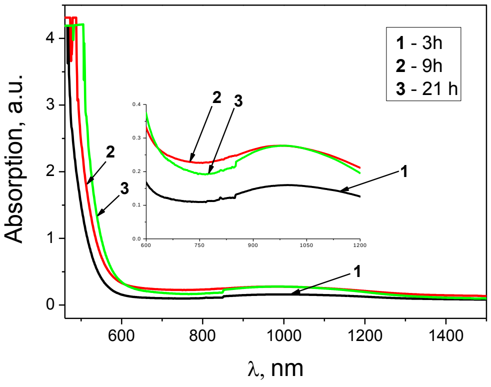

Fig. 3 – Absorption spectra of $LiNbO_3$ after annealing in CuO at 1073 K (light propagates along the Z-direction). Parameter: annealing time. The inset is a zoom of the region of lower wavelengths

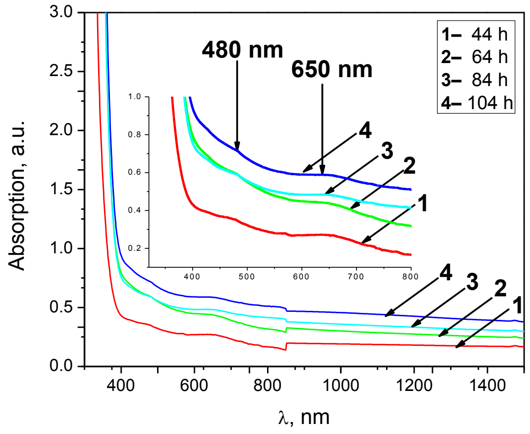

Fig. 4 – Absorption spectra of $LiNbO_3$ after annealing in Fe_2O_3 at 1073 K (light propagates along the Z-direction). Parameter: annealing time. The inset is a zoom of the region of lower wavelengths

$$N_i = 0.87\times10^{17}\,\mathrm{cm}^{-3}\,\frac{n_i}{\left[n_i^2+2\right]^2}\,\frac{1}{f}\,\mu_i^{\max}\Delta E_i. \qquad (2)$$

Here μ_i^{max} is the maximal value of the absorption coefficient in cm^{-1} of the *i*-th band of impurity, ΔE_i is the width of the corresponding absorption band in eV, n_i is the refractive index at the wavelength corresponding to the maximum absorption coefficient, and f is the oscillator strength. Eq. (2) applies to the case of sufficiently low concentrations where the interaction between impurities is negligible.

The values of μ_i^{max} and ΔE_i can be determined experimentally from the absorption spectra obtained at different distances from the surfaces of the crystals.

The refractive index n_i was calculated in accordance with the three-oscillator Sellmeier equation [20]:

$$n_i^2 - 1 = \frac{2.6734\lambda_i^2}{\lambda_i^2 - 0.01764} + \frac{1.229\lambda_i^2}{\lambda_i^2 - 0.05914} + \frac{12.614\lambda_i^2}{\lambda_i^2 - 474.6}, \qquad (3)$$

where λ_i is the wavelength in μm corresponding to the maximum of the absorption coefficient for the *i*-th band.

The oscillator strengths for the Cu^+ and Cu^{2+} bands amount to $f_{Cu^{2+}} = 4\cdot10^{-2}$ ($^2Eg \rightarrow {}^2T_{2g}$ transition) and $f_{Cu^+} = 2\cdot10^{-4}$ (intervalence $Cu^+ \rightarrow Nb^{5+}$ transition), respectively [18], and to $1.3\cdot10^{-2}$ for the Fe^{3+} band (spin-forbidden *d*–*d*-transition) [17].

It should be noted that the $LiNbO_3$ crystal is trigonal. Therefore, one can expect that the values of oscillator strengths should be different for different directions. However, there is no information given at all regarding the anisotropy of these values in LN. Moreover, formula (2) is obtained for cubic crystals, so the anisotropy of the crystal is neglected in our calculations.

The dopant concentration dependencies on the distance from the crystal surface were built based on equations (2), (3).

Fig. 5 shows the dopant concentration depth profiles of the Cu^+ and Cu^{2+} ions in the Z direction after annealing in CuO at a temperature of 1073 K for one hour. In the same figure, the depth profile of the pyroelectric coefficient obtained by LIMM in the same sample is given for comparison. Near the surface, the pyroelectric coefficient of LN of the Cu-doped sample has about twice the value of the undoped sample (cf. Fig. 2). In the bulk of the sample, the value of the pyroelectric coefficient is slightly higher, but close to the values of 45-50 μC/m²K of the crystal that was not subjected to diffusion treatment.

In order to compare the role of various types of diffusion sources of metal ions in the process-modified layers in crystals, the same investigations were performed with the samples covered by copper films before annealing (Fig. 6). In this case, the peak concentration of copper ions of both charge states increases in comparison to the crystals which were annealed in the presence of a copper oxide powder.

At the same time, the depth profile of the pyroelectric coefficient does not show a pronounced peak near the surface of the sample. On the other hand, the averaged pyroelectric coefficient is also slightly higher than for the undoped crystal.

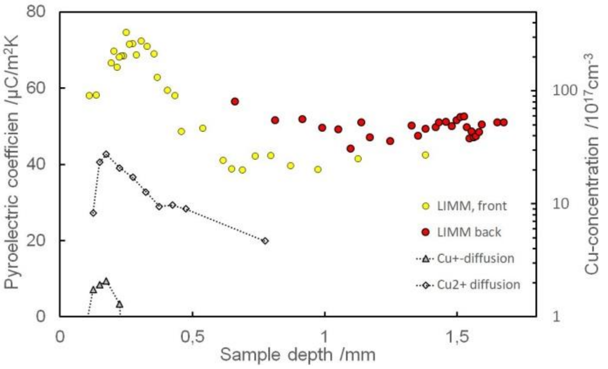

Fig. 5 – Comparison of the concentration and pyroelectric coefficient depth profiles of $LiNbO_3$:Cu covered by CuO and annealed at 1073 K for 1 h

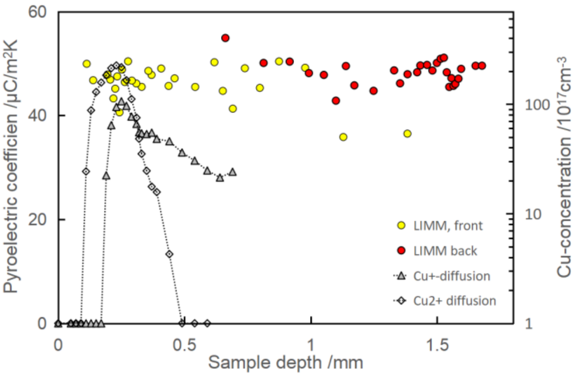

Fig. 6 – Comparison of the depth profiles of both the concentration and pyroelectric coefficient of $LiNbO_3$:Cu covered by Cu-film and annealed at 1073 K for 1 h

Almost identical results were obtained in previous experiments of similar long-time Cu and Fe diffusion doping procedures [21]. The value of the pyroelectric coefficient of LN:Fe increases in comparison to the undoped crystal. Here, we did not observe an increase of the pyroelectric coefficient of LN:CuO after long-term annealing. Annealing in the presence of CuO at 1073 K in air for 21 h produced a maximal Cu^{2+} concentration of ions of $8{\cdot}10^{19}\ cm^{-3}$ at a depth of 0.3-0.4 mm. The maximal Cu^+ concentration was about one order of magnitude lower. Diffusion doping in the presence of Fe_2O_3 powder at 1073 K in air for 104 h led to a maximum Fe^{3+} concentration of ions of $10^{19}\ cm^{-3}$ peaked at a depth of about 0.25 mm. In this work, annealing in the presence of Cu film or CuO powder at 1073 K in air for 1 h provided a maximal Cu^{2+} concentration of ions of $20\text{-}27{\cdot}10^{18}\ cm^{-3}$ at a depth of 0.17-0.25 mm. The maximal Cu^+ concentration was also about one order of magnitude lower than that of Cu^{2+}.

4. CONCLUSIONS

Diffusion doping of lithium niobate crystals by metal ions at a temperature of 1073 K leads to changes in their optical properties due to the introduction of impurities in the structural positions of the crystal. This is manifested by the occurrence of characteristic absorption bands of impurity ions (Cu^+, Cu^{2+}, Fe^{3+}) in the spectra of crystals.

It was established that the values of the pyroelectric coefficients in crystals subjected to heat treatment in the presence of copper and iron ions were increased. This opens the way to modify the pyroelectric properties of lithium niobate crystals with respect to particular requirements.

There is no direct correlation between the distribution profiles of the ion impurities introduced to the lithium niobate crystal by diffusion and the depth profile of their pyroelectric coefficients. Nevertheless, at the same time, there is evidence that there are heat treatment conditions (source of diffusion, duration and temperature of annealing) in which profiles of impurity concentrations and of the pyroelectric coefficient might be correlated. However, the search for such conditions requires additional studies which are in progress now.

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Дослідження оптичних і піроелектричних властивостей монокристала ніобата літію, викликаних дифузією іонів металів

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Досліджено просторові зміни оптичних і піроелектричних властивостей монокристалів $LiNbO_3$, легованих іонами Cu і Fe шляхом дифузії за високих температур. Перед відпалом кристали були повністю покриті відповідним порошком оксиду металу. Для визначення ролі різних типів дифузійних джерел іонів металів у формуванні модифікованих шарів $LiNbO_3$ аналогічні дослідження були виконані і для зразків, покритих перед відпалом плівками Cu. Оптичне поглинання зразків реєстрували в напрямку, перпендикулярному напрямку дифузії на різних відстанях від поверхні кристала. Інтенсивність смуг поглинання іонів Cu^{+} (400 нм), Cu^{2+} (1000 нм) і Fe^{3+} (480 нм) аналізували залежно від температури відпалу та відстані від джерела дифузії. На залежностях змін додаткового поглинання з глибиною у всіх зразках спостерігались максимуми. Концентрації іонів Cu та Fe розраховували за формулою Смакули-Декстера. Для встановлення кореляції змін оптичних і піроелектричних властивостей методом модуляції інтенсивності лазерного випромінювання були досліджені профілі піроелектричного коефіцієнта у легованих кристалах. Для запобігання невизначеності вимірювань методом теплових хвиль, яка збільшується з глибиною зразка, піроелектричний струм реєструвався під час збудження кристала як з передньої, так і задньої площини пластини. Для калібрування результатів також були виміряні усереднені піроелектричні коефіцієнти. Синусоїдальна модуляція температури зразка з частотою 0.1 Гц забезпечувалась за допомогою модуля Пельтьє. Встановлено, що дифузійне легування впливає на піроелектричні властивості кристалів ніобату літію.

Ключові слова: Монокристали $LiNbO_3$, Профілі глибини дифузії домішок, Профілі піроелектричного коефіцієнта