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Features of increasing the volume concentration of hydrogen in $LiNbO_3$ crystals

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The features of increasing the volume concentration of hydrogen in $LiNbO_3$ crystals of congruent composition using a previously proposed method have been studied. After a single treatment of a $LiNbO_3$ crystal of congruent composition in adipic acid and subsequent annealing in humid air at $T = 973\,K$, a satisfactory inhomogeneity of the hydrogen distribution throughout the volume of the sample with dimensions of $5.9 \times 5.8 \times 5.8$ mm, which should significantly improve when the annealing temperature is increased to 1023 K. It has been established that repeated treatments lead to a progressive increase in the volume concentration of hydrogen in the sample, but this process is not linear due to an increase in the reverse diffusion of hydrogen from the surface modified layers into the surrounding air. It has been shown that the value of the volume concentration of hydrogen c_H affects the structure of the IR absorption spectrum of OH^-- groups in $LiNbO_3$ crystals of congruent composition, and with increasing c_H the probability of localization of H^+ ions in undistorted $Nb_{Nb}O_6$ octahedra increases.

Keywords: $LiNbO_3$, hydrogen, diffusion, IR spectroscopy.

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Introduction

The ferroelectric crystals of lithium niobate $LiNbO_3$ (LN) lithium tantalate $LiTaO_3$ (LT) are widely used in modern optoelectronic devices [1]. Nonstoichiometry of LN and LT and impurities contained therein substantially affect many physical properties of these crystals, which are important when manufacturing specific products based thereon. In particular, narrow-band holographic interference filters are based on LN [2]. For this purpose, a volume phase hologram (VPH) with given parameters is recorded inside the crystal (which is usually LN with Fe impurity) to be followed by a procedure of its thermal fixation [3], which dramatically increases the VPH relaxation time and correspondingly enhances long-term stability of the filter properties.

The main role in the thermal fixing process is played by impurity H^+hydrogen ions [4], so their volume concentration affects the quality and stability of the VPH. A review of the main methods of increasing of the hydrogen concentration in the LN crystals is given in [5]. Another method has been proposed and tested [6], which consists of placing the LN sample at the first stage for several hours into heated acid with a high boiling temperature (benzoic, adipic, stearic, etc.). By chemical exchange ($Li^+ \leftrightarrow H^+$), all the sample surfaces exhibit formation of the $H_{1-x}Li_xNbO_3$ compound, where $x \sim 0.7$ [7]. After that the sample is undergoes normal processing in the atmosphere of humid air or humid oxygen at the temperatures above 873 K [8,9].

It has been shown that as a result the H^+ ions are redistributed from the subsurface layers across the entire sample volume, and their volume concentration was and $c_H = (15.7 \pm 2.1) \cdot 10^{18}\,cm^{-3}$ with the sample thickness of 2.7 mm, whereas there was not any observed diffusion of the H^+ ions from the sample. Based on the obtained results of measurement of static electrical conductivity and impedance, the work [6] has concluded that there is hydrogen distribution across the z-cut wafer with the thickness of ~ 2.7 mm, which is close to the homogeneous distribution.

This gives reason to believe that by this repeated treatment of the same sample it is possible to obtain substantially higher values of c_H than by the other methods. Among other things, producing of the $LiNbO_3$ volume samples with a high value of c_H allows more correct studies of localization of the H^+ ions in the LN structure by means of nuclear magnetic resonance (NMR) of the ^1H nuclei as compared with previous works on the polycrystalline samples [10,11].

Let us note that now c_H is measured using analysis of the IR absorption spectrum of the OH^--groups with applying the calibration relationship $A_{int}/c_H = (2.1 \pm 0.32) \cdot 10^{-17}$ cm, where A_{int} — is the integral intensity of absorption of the OH^--groups [12]. Nevertheless, this relationship is an estimated one and is not based on exact measurements of c_H in the samples, for which the IR spectra were analyzed.

It is well known that the spectrum composition of IR absorption in the LN crystals heavily depends on nonstoichiometry of the sample, thereby making it possible to use this method for determining the Li/Nb ratio in the sample [13,14]. However, after proton exchange, in the isostructural LN crystals of the LT congruent composition there is also transformation of the IR absorption spectra [15]. The presence of such a defect has been confirmed in the work [16], which also discusses its possible causes.

Presumably, such the effect can also be in the LN crystals as the IR absorption spectra of the OH^--groups were previously analyzed in detail only for samples with relatively low volume concentration of hydrogen [13,4].

The main aim of the present work was to check efficiency of the previously proposed method of increasing the volume concentration of hydrogen in the LN crystals by a repeated procedure proposed in [6], and to additionally analyze nonuniformity of distribution of the H^+ ions across the sample volume.

The second aim was to study possible transformation of the IR absorption spectra of the OH^--groups when increasing the hydrogen content in the lithium niobate samples of congruous composition (CLN).

1. Samples and experimental method

The basic series of the experiments for increasing c_H included use of the same mono-domained sample S1 of nominally undoped CLN as the wafer of the polar z-transection of the thickness of ~ 2.7 mm. The volume concentration of hydrogen was increased in a procedure of the previously proposed algorithm [6]. The first stage included preliminary proton exchange by immersing the sample into adipic acid at the temperature $T = 473$ K, where the sample was kept for 5 h. The final thermochemical treatment was in the atmosphere of humid air at $T = 973$ K for 5 h. After the optical and infrared measurements this cycle was repeated many times for further increase of the hydrogen content in the sample.

The increase volume concentration of H^+ can be also achieved by increasing the time of treatment in adipic acid. However, the total number of the H^+ ions(N) inside the processed sample increases in the first approximation by the law $N \propto \sqrt{t}$, where t — the treatment time. Thus, in order to increase N in two times, the treatment time increases in four times. With our selected time algorithm of crystal treatment, the same time may include two treatments in the acid followed by subsequent annealings in humid air. In doing so, the first annealing in humid air already has the first „batch“ of the H^+ ions redistributed across the sample volume. Thus, after the second cycle of treatment, the total value of N will be the same, but nonuniformity of distribution of hydrogen across the sample volume will be obviously less with the same total time of crystal treatment.

In order to study distribution of hydrogen across the crystal volume, the sample S2 of the nominally undoped CLN with the sizes $5.9 \times 5.8 \times 5.8$ mm, was manufactured and once treated in the same conditions except for the time of treatment in acid, which was ~ 3 h.

Another sample S3 of nominally undoped CLN with the sizes $5.9 \times 5.3 \times 5.7$ mm was annealed in the atmosphere of saturated vapor of H_2O at $T = 773$ K for 5 h under pressure of $\sim 10^5$ Pa in accordance with the method used in the work [17].

For analysis of the IR absorption spectrum composition of the OH^--groups, other nominally undoped CLN crystals with various values of c_H were also used — including the samples without postgrowth thermochemical treatments and the samples that have undergone the procedure of increase of the hydrogen content as per various methods including the above-described one.

The preliminary proton exchange in adipic acid was performed in the muffle furnace SNOL 58/350, while the final thermochemical treatment was carried out in the leaky tubular heater with a low spatial temperature gradient. Preheated water vapor was supplied into the working region of the heater. After the thermochemical treatment the polar surfaces of the sample were polished to optical quality and the optical and infrared measurements were carried out. Further on, this cycle was repeated many times.

The optical absorption coefficient in the visible spectrum region and the infrared absorption spectra of the OH^--groups were recorded using the same equipment as in the previous work [6].

It is well known that in the volume of the $LiNbO_3$ and $LiTaO_3$ crystals the H^+ ions can not be localized in positions of the Li^+ ions, and they exist only in the composition of the OH^--groups [18], so the volume concentration of the H^+ ions within the crystal volume identically coincides with the volume concentration of the OH^--groups.

The spatial distribution of the OH^--groups in the sample was analyzed by scanning the sample along the nonpolar axes x and y in the directions that pass through a crystal center by a narrow (the diameter of 0.7 mm) beam of non-polarized infrared radiation that is directed along the polar axis of the z crystal. The experimental setup is shown in Fig. 1.

2. Results and discussion

After treatment of the CLN sample in the acid with the high boiling temperature, there is the $H_xLi_{1-x}NbO_3$ compound formed on the surface, which is the multi-phase one, whereas a type of the phase and the phase ratio depend on the value of x [19]. During high-temperature annealing in humid air the H^+ ions diffuse from the surface layer inside the sample with dilution of the initial concentration profile and, correspondingly, with abrupt reduction of the x in the surface layers even at quite low temperatures of annealing [20]. It results in destruction of „classic“ $H_xLi_{1-x}NbO_3$ phases on the surface and after annealing of the sample in humid air there are the recorded IR spectra of the OH^--groups which are typical for „as grown“ $LiNbO_3$ crystals, while the other components are not observed.

Fig. 1 shows the results of measurement of integral intensity A_{int} of the infrared absorption within the range $(3400-3600)\,cm^{-1}$ while scanning the sample S2 when

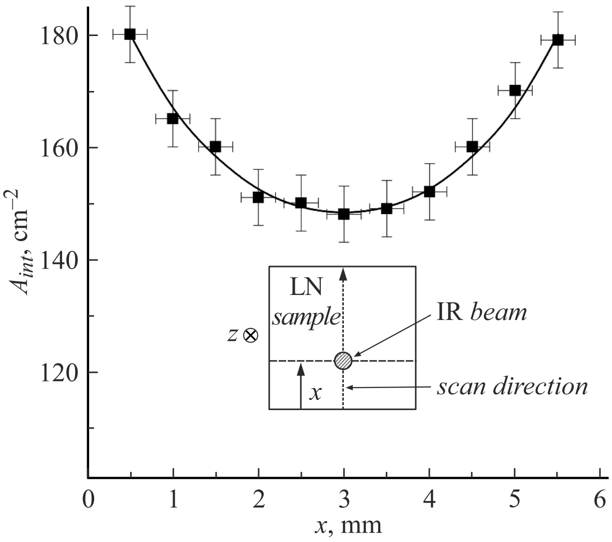

Figure 1. Results of infrared scanning of the CLN sample in the central plane along the direction x.

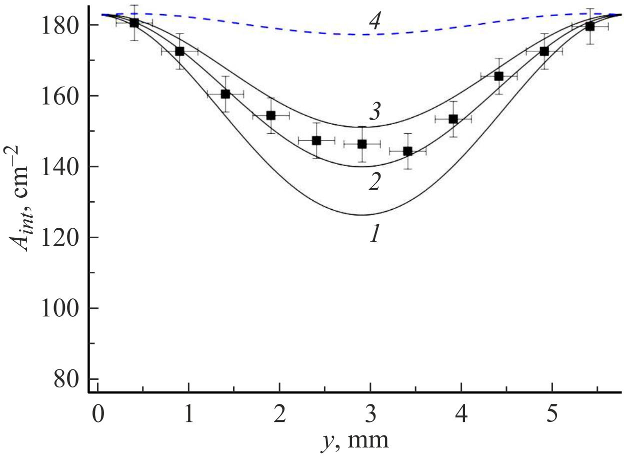

Figure 2. Results of IR scanning of the CLN sample in the central plane along the direction y and results of its modeling at: *1* — $D_0 = 0.12\,\mathrm{cm^2/s}$, $T = 973\,\mathrm{K}$; *2* – $D_0 = 0.15\,\mathrm{cm^2/s}$, $T = 973\,\mathrm{K}$; *3* — $D_0 = 0.18\,\mathrm{cm^2/s}$, $T = 973\,\mathrm{K}$; *4* — $D_0 = 0.16\,\mathrm{cm^2/s}$, $T = 1023\,\mathrm{K}$.

moving the beam from the lower to the upper non-polar facet of the sample along the direction x. Scanning the sample S2 in the direction y, whose results are shown in Fig. 2, qualitatively and within the measurement error correspond to the data of Fig. 1.

These results indicate isotropy of mobility of the H^+ ions within the plane xy of the CLN crystals and based on their analysis, it is possible to obtain additional information about diffusion of the H^+ions and quite good uniformity of distribution of hydrogen across the crystal volume.

The diffusion of hydrogen from the subsurface layers inside the crystal is diffusion from a limited source. Its closest analogue is dissipation of the impurity in the semiconductors which is described by the Gaussian function:

$$c(x,t) = \frac{N}{\sqrt{\pi D(T)t}} \exp\left(-\frac{x^2}{4D(T)t}\right), \qquad (1)$$

where N — the density of atoms of the impurity under a unit area of the surface, which is invariable at any moment of diffusion; x — the depth corresponding to this concentration; $D(T)$ — the impurity diffusion constant; t — duration of the diffusion process [21]. In turn, the diffusion constant depends on the temperature and is described as follows:

$$D(T) = D_0 \exp\left(-\frac{E_a}{k_0 T}\right),$$

where D_0 — the constant, E_a — the activation energy, k_0 — the Boltzmann constant.

During treatment of the CLN crystals in acids with the high boiling temperature the chemically-modified layer of the $H_{1-x}Li_xNbO_3$ compound is formed on each PELN (proton-exchanged lithium niobate) facet of the sample. According to [22], with the same conditions of treatment the depth of the chemically-modified layer of the CLN wafers of the x-transection (d_x) is higher than that of the z-transection (d_z) — approximately in 1.15 times. The similar conclusion was made in the work [23], which additionally noted that the ratio $\frac{d_x}{d_z}$ increased upon introduction of some amount of lithium salts (buffering).

While annealing the PELN sample in the atmosphere of humid air, hydrogen diffuses simultaneously from three superficially-modified pairs of the facets, so it is quite difficult to analytically solve such a problem. However, it is obvious that diffusion contribution from the polar facets and from the second pair of the non-polar facets will be in the first approximation the same for each experimental point of Fig. 1 and 2.

That is why the observed changes of A_{int}, which are proportional to the change of the average volume concentration of hydrogen c_H in an illuminated area of the crystal correspond to the change of the contribution of hydrogen introduced only from the pair of the facet, whose normal coincides with the direction x (Fig. 1) or y (Fig. 2). Therefore, the profile of hydrogen distribution $i = x, y$ along the scanning direction can be presented as follows:

$$A_{int}(i) = A' + A_0 + \frac{N}{\sqrt{\pi D(T)t}} \left[\exp\left(-\frac{i^2}{4D(T)t}\right) + \exp\left(-\frac{(l_i - i)^2}{4D(T)t}\right)\right], \qquad (2)$$

where l_i — the length of the corresponding facet, t — the time of crystal annealing, A_0 — contribution to the integral intensity by diffusion of hydrogen from other pairs of the facets, A' — the initial value A_{int} before proton treatment, which was $41\,\mathrm{cm^{-2}}$ for this sample.

In the approximation of isotropy of diffusion of the H^+ ions, using (2), it is possible to simulate the results of

IR scanning of the sample along the non-polar directions. Unfortunately, the references contain no data on the value of D of the H^+ in CLN for the temperature $T = 973$ K, at which the samples were annealed in humid air. At the same time, the analysis of the known data on diffusion of hydrogen in CLN [9,24–29] shows that the previously found values of D_0 stay within the range $(1.4 \cdot 10^{-3} - 6)$ cm^2/s, and the activation energy E_a varies from 0.98 to 1.24 eV. That is why it has been simulated at the most probable value of the activation energy of mobility of the ions H^+ $E_a = 1.03$ eV [30] and at variation of the values of D_0. The results of modelling of IR absorption during scanning the sample along the direction y are shown in Fig. 2. It is clear that at $D_0 \cong 0.16$ cm^2/s we shall observe quite good compliance of the calculated and the experimental data. It is natural that the obtained combination of the values of D_0 and E_a is an estimated one, since the modelling process included a number of approximations and the process of diffusion of the H^+ ions in CLN requires separate additional study.

Simulation of the profile of IR absorption at $E_a = 1.03$ eV, $D_0 = 0.16$ cm^2/s, but with the annealing temperature $T = 1023$ K, has shown that these conditions shall provide almost uniform distribution of hydrogen in the xy-planes of the studied sample. The corresponding results are shown in Fig. 2. Thus, when using this method of increase of the volume content of oxygen, the optimal temperature for annealing the CLN sample in humid air is 1023 K or higher

It is obvious that with isotropy of diffusion of the H^+ ions the same pattern would be observed when studying the profile of IR absorption along the axis z, which would indicate quite high uniformity of distribution of H^+ across the sample volume. However, in accordance with some data, diffusion of the H^+ ions in CLN is substantially anisotropic and the values of the diffusion constant for the polar direction $(D_0)_z$ can be in (1.5−2) times less than for the non-polar $(D_0)_x$ [31] and it will result in increase of spatial non-uniformity of distribution of c_H. But with our selected geometry of the sample S1 (the size along the axis z is in two times less than for S2) in the same conditions of treatment the uniformity of distribution of H^+ across the sample volume will be obviously better than in the cubic sample S2.

Fig. 3 shows the results that illustrate the change of the optical absorption coefficients of the same sample S1 in the visible range depending on the number of performed treatement cycles N. These results are quite predictable — the increased absorbance of LN crystals in the visible range when annealing in the humid air is caused by increase of the volume concentrations of oxygen vacancies V_0 c_{V_0}, thus the crystal gets a grey hue [9]. It is obvious that with the fixed partial pressure of water vapor P_{H_2O} and the fixed annealing temperature the value of c_{V_0} shall linearly depend on the annealing time, i.e. the number of treatement cycles, as can be observed in the experiment. Additionally, these results indicate that the partial pressure of water vapor in each annealing cycle was approximately the same.

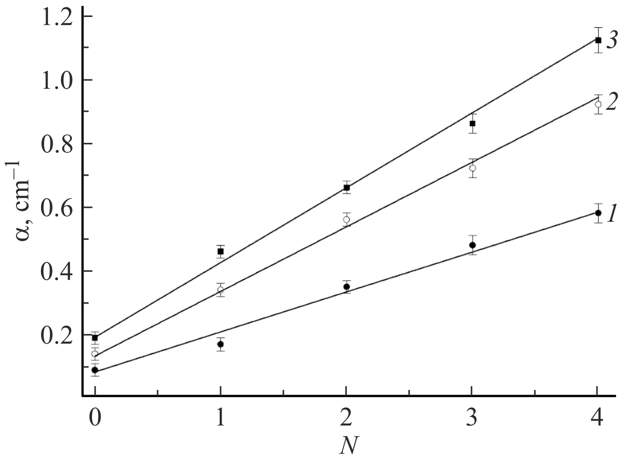

Figure 3. Dependences of the optical absorption coefficients on the number of cycles of the sample treatment N at λ, nm: *1* — 635, *2* — 525, *3* — 465.

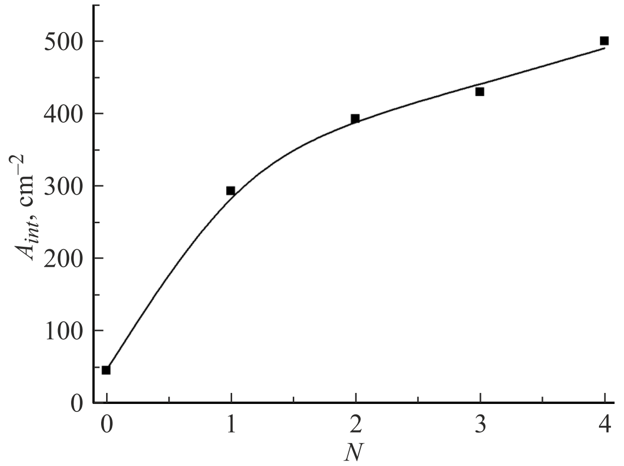

Figure 4. Dependence of A_{int} of the IR absorption spectrum of the OH^--groups on the number of treatment cycles for the same CLN sample.

Fig. 4 shows dependence of the integral intensity A_{int} of the IR absorption spectrum of the OH^--groups on the number of treatment cycles N for the sample of the thickness of ~ 2.7 mm. In accordance with the calibration relationship $A_{int}/c_H = (2.1 \pm 0.32) \cdot 10^{-17}$ cm [12], the maximal value obtained $c_H = (24 \pm 4) \cdot 10^{18}$ cm^{-3}.

It is obvious that with each subsequent treatment of the crystal in adipic acid the thickness of generated surface chemically modified layers will be the same. Nevertheless, with each subsequent cycle of treatment the crystal volume additionally gets less and less the H^+ions. This indicates reverse diffusion of hydrogen from the chemically-modified subsurface layers of the crystal at the high-temperature stage of crystal treatment and its intensification with increase of c_H.

Qualitatively, the process of Fig. 4 looks like dependence of A_{int} in CLN on time in long-time thermochemical treatment of the sample in humid air with $T = 1173\,\mathrm{K}$ [8]. In accordance with [9], this process is well described by the second Fick's law for diffusion from an unlimited source, wherein the limit value of c_{H} heavily depends on the process temperature [9] and probably on the partial pressure of vapor of H_2O.

The role of impact by the partial pressure of vapor H_2O is indicated by the following experiment. Fig. 5 shows the IR absorption spectra of the OH^--groups of the sample S3 before and after annealing in the atmosphere of pure vapor of H_2O with $T = 773\,\mathrm{K}$ for 5 h and under pressure $\sim 10^5\,\mathrm{Pa}$. In doing so, the value of A_{int} increased from 43 to $88\,\mathrm{cm}^{-2}$, which corresponds to increase of c_{H} in 2 times. At the same time, annealing of the CLN sample in the atmosphere of humid air (the partial pressure of vapor of H_2O was not controlled) at the same temperature $T = 773\,\mathrm{K}$ within the measurement error does not affect the value of c_{H} [9], while annealing of CLN in the atmosphere of dry oxygen or dry air at $T = 873\,\mathrm{K}$ results in substantial loss of hydrogen in the sample [32].

Thus, increase of the partial pressure of vapor H_2O during annealing of CLN in the atmosphere of humid air shall increase the efficiency of proton exchange due to decrease of the reverse diffusion of hydrogen from the sample the sample in our used process. However, increase of the partial pressure of vapor of H_2O also results in progressing loss of oxygen by the sample and increase of optical dencity of the crystal [17].

Additional information about peculiarities of proton exchange in CLN can be obtained from analysis of the IR absorption spectral composition of the OH^--groups. More or less unambiguous decomposition of these spectra can be made only in the LN crystals with the composition close to the stoichiometric one, when all three main spectrum components have quite good resolution by decreasing their width [14].

In the CLN crystals, the IR absorption spectrum consists of at least three lines with weak resolution [26,33] and its decomposition is associated with a number of problems. Since an individual form of each spectrum component is initially unknown, then the most reliable method is modeling of each experimental spectrum. Generally, the form of each line is described by pseudo Voight distribution (pseudo Voight, PV) [8], which is a linear combination of the Lorentz distribution $L(\overline{\nu})$ and the Gaussian distribution $G(\overline{\nu})$:

$$PV(\overline{\nu}) = \eta L(\overline{\nu}) + (1-\eta)G(\overline{\nu}),$$

where the parameter η — varies from 0 to 1, wherein the values of the line width at the half's height can be different for the distributions $L(\overline{\nu})$ and $G(\overline{\nu})$. At the same time, both uniform and non-uniform broadening of the line can be taken into account.

Accuracy of approximation can be estimated by considering the difference function $\Delta\alpha(\overline{\nu}) = \alpha_{\mathrm{exp}}(\overline{\nu}) - \alpha_{\mathrm{calc}}(\overline{\nu})$ using the expression

$$\mu = \frac{\sum\limits_{i=1}^{k} |\Delta\alpha_i|}{\sum\limits_{i=1}^{k} (\alpha_i)_{\mathrm{exp}}}, \tag{3}$$

where $(\alpha_i)_{\mathrm{exp}}$ — the experimental (without taking into account noises) and $(\alpha_i)_{\mathrm{calc}}$ — the calculated value of the IR absorption coefficient in the i-th point of the spectrum within the range from 3405 to $3555\,\mathrm{cm}^{-1}$. Previously, this approach was successfully used when analyzing the IR spectra of the LN crystals with different stoichiometry [34].

It has turned out during modeling that due to heavy overlapping of the second and third IR spectrum components the same quality of approximation ($\mu \leq 1.0\,\%$) can be achieved with substantially different parameters which characterize each line of the spectrum. The table provides possible variants of IR spectrum decomposition of one of the studied samples. It also includes average values of the respective parameters.

As will be shown below, special meaning is paid to the relationship $K = A_1/(A_2 + A_3)$, where A_1, A_2 and A_3 — are the integral intensities of the first, second and third spectrum

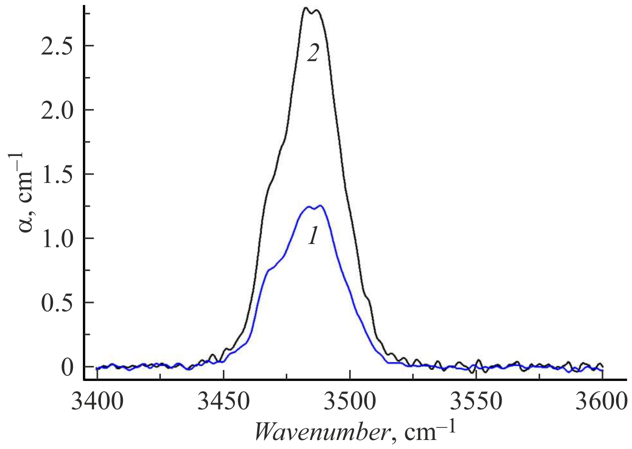

Figure 5. IR spectra of absorption of the CLN sample before (*1*) and after (*2*) thermochemical treatment in the atmosphere of pure H_2O when $T = 773\,\mathrm{K}$.

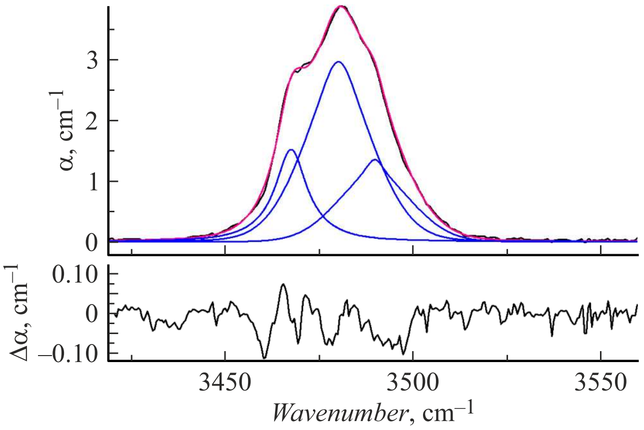

Figure 6. Typical results of IR spectrum absorption decomposition of the OH^--groups of one of the studied samples.

Variants of decomposition (V1–V8) of the IR absorption spectrum of the OH^--groups of one of the studied CLN samples

variants	$\overline{\nu}_1$ cm^{-1}	$\overline{\nu}_2$ cm^{-1}	$\overline{\nu}_3$ cm^{-1}	A_1, cm^{-2}	A_2, cm^{-2}	A_3, cm^{-2}	K	μ, %
V1	3467.6	3480.6	3490.5	21.8	70.8	26.9	0.22	1.1
V2	3467.4	3480.6	3490.5	19.6	76.9	22.8	0.20	1.1
V3	3467.4	3480.8	3490.9	26.9	64.5	28	0.29	1.0
V4	3467.4	3480.6	3490.5	20.3	76.9	22.8	0.20	1.0
V5	3467.4	3480.6	3490.5	25.6	65.5	28.9	0.27	1.0
V6	3467.6	3480.2	3489.9	23.3	67.7	29.1	0.24	1.0
V7	3467.6	3480.0	3489.6	21.2	68.9	29.3	0.22	1.0
V8	3467.8	3480.2	3489.4	17.2	77.9	23.9	0.17	1.0
Average	3467.5 ± 0.2	3480.5 ± 0.3	3490.2 ± 0.5	22.0 ± 3.2	71.1 ± 5.4	26.5 ± 2.9	0.23 ± 0.03	1.0

components, respectively. The typical results of IR spectrum decomposition of the same sample are shown in Fig. 6.

Similar analysis was performed for the samples with another value of A_{int} and the obtained dependence of K on A_{int} is shown in Fig. 7. It is clear that the results can be approximated with the linear dependence $K = K_0 + bA_{int}$, where $K_0 = (0.184 \pm 0.011)$, $b = (11 \pm 3) \cdot 10^{-5}\,cm^2$.

The line with the maximum at $\overline{\nu}_1 \approx 3467\,cm^{-1}$ is present in the IR spectrum of the LN crystals of any stoichiometry [8,13,14] and therefore, it corresponds to the OH^--groups associated with oxygen ions contained in the undistorted $Nb_{Nb}O_6$ octahedron. The sources of the lines with the wave numbers $\overline{\nu}_2 \approx 3480\,cm^{-1}$ and $\overline{\nu}_3 \approx 3490\,cm^{-1}$ are the OH^--groups associated with the $Nb_{Li}O_6$ or $V_{Li}O_6$ oxygen octahedrons, where V_{Li} — the lithium vacancy.

Let us consider probabilities of localization of the H^+ ion (if it is contained in the crystal) in the NbO_6 $w_1(c_1)$ octahedron and in two other positions: $w_2(c_2)$ and $w_3(c_3)$, where c_1, c_2 and c_3 — the volume concentration of the H^+ ions in respective positions. Then the following expression may be used to describe the association between the change of the integral intensity of the IR spectrum lines dA_1, dA_2 and dA_3 for the time dt during redistribution of the H^+ ions from the surface layers across the crystal volume

$$\frac{dA_1}{dA_2 + dA_3} = \frac{w_1(c_1) \cdot (c_{Nb_{Nb}} - c_1)}{w_2(c_2) \cdot (c_{Nb_{Li}} - c_2) + w_3(c_3) \cdot (c_{V_{Li}} - c_3)}, \tag{4}$$

where $c_{Nb_{Nb}}$ — the volume concentration of the Nb^{5+} ions in the regular positions, $c_{Nb_{Li}}$ — the volume concentration of the antistructure Nb ions, $c_{V_{Li}}$ — the volume concentration of the lithium vacancies, $w_i(c_i)$ — probabilities of localization of the H^+ ion in respective positions.

The structure formula of CLN is written as $[Li_{1-5x}Nb_xV_{4x}][Nb]O_3$, where, in accordance with [35], $x \cong 0.0118$. The volume of the CLN lattice cell at the room temperature is $V = 318.4\,Å^3$ [36], and therefore, $c_{Nb_{Nb}} \cong 1.88 \cdot 10^{22}\,cm^{-3}$, while $c_{Nb_{Li}} \cong 2.22 \cdot 10^{20}\,cm^{-3}$. Since $c_{V_{Li}} = 4c_{Nb_{Li}}$, and the value of c_H is almost by an order less than $c_{Nb_{Li}}$, the expression (4) can be simplified

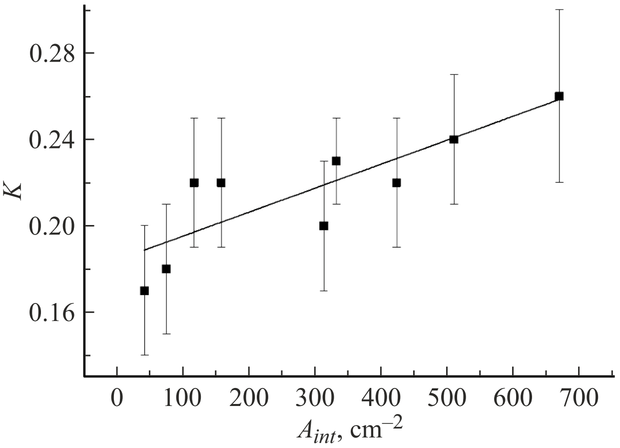

Figure 7. Dependence of the relationship of the integral intensities of the components K of the IR absorption spectrum of the OH^--ions in CLN on A_{int}.

$$\frac{dA_1}{dA_2 + dA_3} \cong \frac{w_1(c_1) \cdot c_{Nb_{Nb}}}{[w_2(c_2) + 4 \cdot w_3(c_3)] \cdot c_{V_{Li}}}$$

$$\cong 84 \frac{w_1(c_1)}{[w_2(c_2) + 4 \cdot w_3(c_3)]}. \tag{5}$$

The form of the IR absorption spectrum distribution during with increase of c_H will be kept provided that $dA_1 = K_0(dA_2 + dA_3)$, where K_0 — the value of K at the small (initial) concentration of hydrogen. In this case, the total probability of appearance of the additional OH^--groups in the defect $Nb_{Li}O_6$ or $V_{Li}O_6$ octahedrons would be in ~ 5 times higher than in the ideal NbO_6 octahedrons. Probably, it is related to different energies of formation of the OH^--groups in the respective positions. The increase of the value of K with growth of c_H can indicate decrease of probability of localization of the H^+ ions in the distorted $Nb_{Li}O_6$ octahedrons as these positions are filled.

Conclusion

It is found that repeated performance of thermochemical treatments of the CLN crystals in accordance with the method proposed in [6] results in progressing increase of the volume concentration of the H^+ and allows to obtain the high volume concentration of hydrogen in the sample of the thickness of ~ 2.7 mm. However, with the second and subsequent treatment this process is accompanied by loss of the substantial part of hydrogen by the sample from the chemically-modified surface layers. The reverse diffusion can be probably decreased by increasing the partial pressure of water vapor during the second and subsequent thermochemical treatment.

It is concluded that it is possible to obtain almost uniform distribution of the H^+ ions across the CLN sample with the sizes $\sim 6 \times 6 \times 3$ mm at the temperature of annealing in humid air about 1023 K.

It is shown that the ratio between the integral intensities of the IR absorption spectrum components for the OH^--groups and its form in the CLN crystals depends on the volume concentration of hydrogen in the sample, but not to the same extent as in the CLT crystals.

Conflict of interest

The authors declare that they have no conflict of interest.

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