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Influence of features of localization of hydrogen atoms in lithium niobate crystals on the form of oxygen-octahedral clusters of the structure

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Based on the IR absorption spectra in the region of OH^-–group stretching vibrations, it was established that the oxygen-octahedral clusters MeO6 (Me — Li, Nb, vacant octahedron V, impurity ion) in the structure of the $LiNbO_3$:Er(3.1 wt%) crystal and the nominally pure highly perfect $LiNbO_3$ crystal of stoichiometric composition (R=[Li]/[Nb]=1) have a shape close to the shape of a regular octahedron and at the same time there are practically no deep electron traps - point defects Nb_{Li}, responsible for the crystal's resistance to optical damage. In the IR spectrum of these crystals, only one line is observed, corresponding to the stretching vibrations of hydrogen atoms linked by hydrogen bonds with oxygen atoms oscillating along the polar axis of the crystal in the Me-O-Me bridge (Me — Li, Nb, vacancy, impurity metal). This vibration changes the dipole moment of the unit cell of the crystal and is active in the IR absorption spectrum. The vibration frequency is determined by the crystal composition. The stretching vibrations of the remaining hydrogen atoms of the hydroxyl groups OH of the highly symmetric oxygen-octahedral clusters MeO_6 of $LiNbO_3$ crystals do not change the dipole moment of the unit cell and are not active in the IR absorption spectrum. In the structure of non-stoichiometric $LiNbO_3$ crystals, there are two or more nonequivalent positions of OH^-- groups and more than two lines in the frequency range $3450-3550\,cm^{-1}$ are observed in their IR absorption spectrum.

Keywords: lithium niobate single crystal, stoichiometry, erbium doping, point defects, OH^-– groups, materials for active nonlinear laser media and laser radiation conversion, IR absorption spectra.

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Introduction

Currently, the development of technologies for highly perfect nonlinear-optical lithium niobate ($LiNbO_3$) single crystals of various compositions, both nominally pure and doped with metals, suitable for creating functional elements for various electronic devices, is a relevant task [1–4]. For the development of functional elements for active nonlinear laser media, for converting and modulating laser radiation, it is important to obtain highly perfect non-photorefractive doped $LiNbO_3$ single crystals and nominally pure single crystals of stoichiometric composition, in which the value R = [Li]/[Nb] = 1 and there are no point defects of the cation sublattice Nb_{Li} (ion located in the Li ion position of an ideal stoichiometric structure) and defects in the form of neighboring identical cations. A pressing task necessary for supporting the technologies of producing such materials is the development of methods to study and control the structural perfection of single crystals. Usually, laser conoscopy in highly divergent laser beams and Raman scattering spectroscopy (RRS) in the frequency range of fundamental lattice vibrations and two-phonon acoustic vibration states with zero total wave vector are used as control methods for highly perfect $LiNbO_3$ single crystals of various compositions [5–7].

A significant feature of $LiNbO_3$, crystals grown in an air atmosphere is the presence in the structure of complex defects caused by the presence of hydroxyl groups OH [8–10]. The heterodecomposed $LiNbO_3$ crystal consists of oxygen-octahedral clusters MeO_6 (Me — Li, Nb, vacancy V, impurity metal) and is characterized by the following types of interactions between its structural units: covalent bond, electrostatic bond, hydrogen bond [8,10]. Since the quasi-elastic constant of the hydrogen bond and the peculiarities of the localization of hydrogen atoms in the structure are much more sensitive to changes in the crystal field than analogous parameters of the much stronger covalent and electrostatic bonds, vibrational spectroscopy (Raman scattering spectroscopy and IR absorption spectroscopy) in the frequency range of valence vibrations of hydrogen atoms bonded by hydrogen bonds with oxygen atoms of oxygen-octahedral clusters MeO_6can be a promising method for controlling crystal growth technologies and determining their structural perfection. IR absorption spectroscopy has significant advantages over RRS due to its much higher sensitivity to the presence of OH groups in the crystal structure.

IR absorption spectra of $LiNbO_3$ crystals of different compositions and growth technologies in the valence vibration region of hydrogen atoms of hydroxyl groups OH have been extensively studied in the literature; reviews are given in works [8–11]. In the IR absorption and RRS spectra of $LiNbO_3$ crystals of different compositions, lines corresponding to valence vibrations of hydrogen atoms of OH^--groups appear in the frequency range $3450-3550\,cm^{-1}$. With changes in the composition of $LiNbO_3$ crystals, significant changes occur in the spectra: the number of lines, their frequency, width, and intensity change. Changes in line frequency indicate changes in the quasi-elastic constants of hydrogen bonds in OH groups. A decrease in line width indicates an increase in the structural perfection of the crystal. However, the question of the reasons for the changes in the number of lines corresponding to valence vibrations of hydrogen atoms in hydroxyl groups OH in the IR absorption spectra when changing the composition and structural perfection of $LiNbO_3$ single crystals of different compositions and growth technologies has not yet been clarified. This work is devoted precisely to this question.

This article discusses the results of studies of IR absorption spectra in the stretching vibration region of hydrogen atoms of hydroxyl groups OH in nominally pure $LiNbO_3$ single crystals with compositions close to stoichiometric ($R \approx 1$) and LiNbO3 single crystals $_3$ doped with magnesium ($LiNbO_3$:Mg) and erbium ($LiNbO_3$:Er) over a wide concentration range including concentration thresholds. The congruent composition $LiNbO_{3cong}$ single crystal was used as a comparison sample. Stoichiometric single crystals $LiNbO_3$ and $LiNbO_3$:Mg single crystals with high magnesium concentration (≈ 5.0 mol.%) are used to create nonlinear-optical materials for converting and modulating laser radiation [12–14]. $LiNbO_3$:Er single crystals are promising as active nonlinear laser media. The Er^{3+} ion in the $LiNbO_3$ crystal matrix is a very efficient emitter in the visible and infrared (IR) spectral regions. The Er^{3+} ion has several laser generation lines, of which the transition $^4I_{13/2} \rightarrow {}^4I_{15/2}$ (wavelength $1.55\,\mu$m) and the transition $^4I_{11/2} \rightarrow {}^4I_{13/2}$ (wavelength $2.9\,\mu$m) are of greatest interest [15–20]. In the nonlinear-optical $LiNbO_3$:Er crystal, self-frequency conversion of laser radiation is possible, where under pumping, laser generation occurs at a certain frequency, and due to the nonlinear properties of the $LiNbO_3$ crystal matrix, frequency conversion of this radiation from the IR range to the visible range occurs simultaneously.

Experimental Part

$LiNbO_{3cong}$, $LiNbO_3$:Mg and $LiNbO_3$:Er single crystals were grown by the Czochralski method from melt in an air atmosphere from a platinum crucible under relatively low ($2-4$ grad/cm) axial temperature gradient along the polar Z-axis at constant rotation speeds (16 turn/min) and pulling rates (0.8 mm/h). $LiNbO_{3st}$(4.5 wt% K_2O) and $LiNbO_{3st}$(4.5 and 6.0 wt% K_2O) single crystals were obtained by the Czochralski method using the HTTSSG (High Temperature Top Speed Solution Growth) technology from a congruent melt ($R = 0.946$ in the charge) with additions of K_2O flux. The crystallization front was planar during crystal growth. High-purity, chemically uniform, single-phase granulated congruent composition lithium niobate charge (R=[Li]/[Nb]=48.6 mol.% Li_2O) with high bulk density, developed at ICT KSC RAS (TU 0.027.039) was used [21]. Doping elements in the form of MgO and Er_2O_3 oxides were added to the charge immediately before crucible melting. The melt was homogenized for 6 hours under overheating by 150 °C above the melting point of the crystal before growth start. The grown single crystal was annealed at 1200 °C for 5 h. All grown crystals were monodomain by high-temperature electrodiffusion annealing under constant electric voltage applied during cooling at a rate of 20 grad/h in the temperature interval $1240-890$ °C. The details of single crystal growth are given in works [4,22,23]. Concentrations of elements Mg^{2+} and Er^{3+} as well as trace (uncontrolled) amounts of impurity metals in the crystals, were determined by emission spectrometry using a Shimadzu ICPS-900 spectrometer. The concentrations of trace impurities in the studied crystals were: Zr, Si, Ca, Fe, Sb, Al, Te $< 1 \cdot 10^{-3}$; Ti, Co, Bi, Mo, Mn, Mg, Pb, Sn, Ni, Cr, V, Cu$< 4 \cdot 10^{-4}$ wt%.

To identify hydrogen atoms localized in the $LiNbO_3$ crystal structure as hydroxyl groups OH, IR absorption spectroscopy in the stretching vibration region of OH^--groups was used. IR absorption spectra were recorded using a Bruker IFS 66 v/s Fourier spectrometer. Measurements were carried out at room temperature along the Zaxis, in vacuum, with non-polarized infrared radiation on monodomain $LiNbO_{3cong}$, $LiNbO_3$:Mg and $LiNbO_3$:Er single crystals cut in the shape of parallelepipeds ($8 \times 6 \times 10\,mm^3$), whose edges coincided with crystallographic axes ($X \times Y \times Z$, Z — the polar axis of the crystal). The crystal facets were carefully polished.

Results and Discussion

Lithium niobate is a non-stoichiometric phase of variable composition with a wide homogeneity range on the phase diagram ($44.5-50.5$ mol.% Li_2O at 1460 K), which strongly narrows with decreasing temperature [4,24]. The crystal structure of $LiNbO_3$ of any composition consists of oxygen-octahedral clusters MeO_6 (Me — Li^+, Nb^{5+}, vacant octahedron V, impurity ion), connected by facets and edges [25,26] (Fig. 1). At the same time, only two-thirds of the MeO_6 clusters are occupied by main (Li^+ and Nb^{5+}) and impurity elements, while one-third of the MeO_6 clusters remain vacant. Non-stoichiometric $LiNbO_3$ crystals (R=[Li]/[Nb]$\neq 1$), including $LiNbO_3$:Mg and $LiNbO_3$:Er crystals, are characterized by a complex spectrum of point and volumetric (complex) structural defects that create a complicated and difficult-to-model structural disorder in the real crystal [4,7,8,22,27,28]. The main defects of the $LiNbO_3$ crystal structure of any composition are point defects in the form of main ions (Li^+, Nb^{5+}) located in MeO_6 clusters not in their proper positions, impurity metal

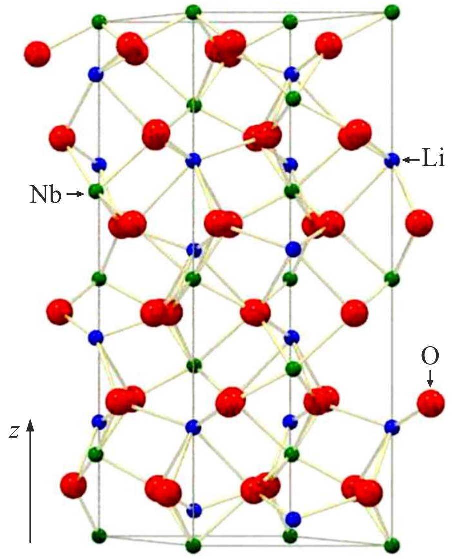

Figure 1. Three-dimensional model of the $LiNbO_3$ crystal structure [11].

ions, as well as microinclusions of impurity phases of other lithium niobates and various complex defects, including complex defects caused by the presence of hydrogen bonds. In $LiNbO_3$:Mg and $LiNbO_3$:Er crystals, clearly expressed concentration thresholds exist at about ≈ 5.5 mol.% MgO and 2.5 wt% Er respectively, beyond which the bond lengths between structural units of the crystal, the incorporation features of impurity and base metals (Li, Nb), and the defect state of the crystal change abruptly [22,23,27]. Meanwhile, the space symmetry group characterizing the unit cell of the crystal and the number of formula units in the unit cell remain unchanged.

Figs. 2–4 show dependencies of the IR absorption spectra in the valence vibration region of hydrogen atoms of OH^--groups on the composition of the studied $LiNbO_3$ crystals. In the spectrum of the nominally pure congruent $LiNbO_{3\mathrm{cong}}$ ($R = 0.946$) crystal, three lines at frequencies 3470, 3483and 3486 cm^{-1} are observed, corresponding to the stretching vibrations of hydrogen atoms in different MeO_6 clusters (Fig. 2, curve *1*). Spectra of crystals with magnesium and erbium concentrations away from the concentration threshold in terms of the number of lines correspond to spectra of the nominally pure congruent $LiNbO_{3\mathrm{cong}}$ (Fig. 2, curves *2–4*, Fig. 2, curves *2, 3*). At the same time, in the spectra of $LiNbO_3$:Mg crystals, the number of lines experimentally observed at magnesium concentrations both below and above the concentration threshold at 5.5 mol.% MgO is the same (Fig. 2). These features of the spectra of $LiNbO_3$:Mg crystals below the threshold indicate the same number of nonequivalent positions occupied in the crystal by hydrogen atoms bonded by hydrogen bonds with oxygen atoms.

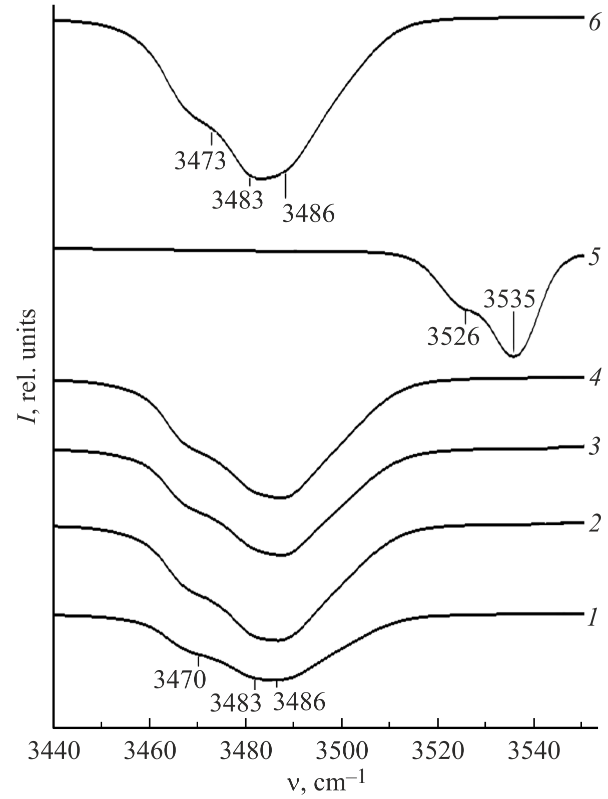

Figure 2. IR absorption spectra in the valence vibration region of hydrogen atoms of OH^--groups of single crystals: *1* — $LiNbO_{3\mathrm{cong}}$, *2* — $LiNbO_3$:Mg(1.53 mol.% MgO), *3* — $LiNbO_3$:Mg(2.13), *4* — $LiNbO_3$:Mg(3.02), *5* — $LiNbO_3$:Mg(5.29), *6* — $LiNbO_3$:Mg(5.91). $T = 293$ K.

From Figs. 2–4 it is seen that when the composition of doped $LiNbO_3$:Mg and $LiNbO_3$:Er crystals approaches the concentration threshold and the nominally pure $LiNbO_3$ crystals approach the stoichiometric composition (R = [Li]/[Nb] = 1), a significant transformation of the spectra occurs: the number of lines in the spectrum, their frequency, and intensity change. The change in line frequency indicates a change in the quasi-elastic constants of hydrogen bonds in OH groups due to the rearrangement of the defect structure with the change in crystal composition and the formation of new complex hydrogen-bond-related defects: V_{Li}-OH, Me_{Nb}-OH, Me_{Li}-OH-Me_{Nb} etc.

In congruent $LiNbO_3$ crystals, there exist about 1 wt% point defects Nb_{Li} (Nb located in a lithium octahedron) and 4 wt% point defects V_{Li} (vacant lithium octahedron) [8,27]. The defects Nb_{Li} are deep electron traps and strongly affect the photorefractive properties of $LiNbO_3$crystals. The Nb_{Li} point defect carries an effective charge of +4 relative to the lattice. The V_{Li} point defect has a negative charge -1, due to which hydrogen atoms are attracted to it forming a complex defect V_{Li}-OH [9–11]. Absorption lines at 3483 and 3486 cm^{-1}in the IR absorption spectrum of the congruent $LiNbO_3$ crystal correspond to this complex defect. The frequencies of these absorption lines significantly depend on stoichiometry (value of R=[Li]/[Nb]) and the concentration of the doping impurity in the crystal [8,29,30].

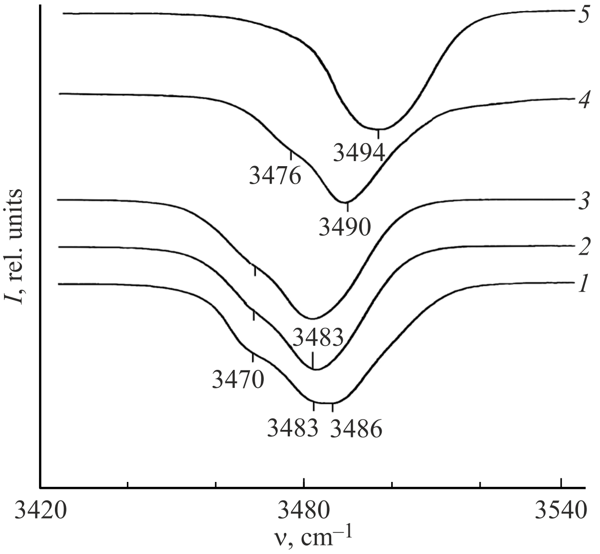

Figure 3. IR absorption spectra in the valence vibration region of hydrogen atoms of OH^--groups of single crystals: *1* — $LiNbO_{3cong}$, *2* — $LiNbO_3$:Er(0.16 wt%), *3* — $LiNbO_3$:Er(2.0), *4* — $LiNbO_3$:Er(2.5), *5* — $LiNbO_3$:Er(3.1). $T = 293$ K.

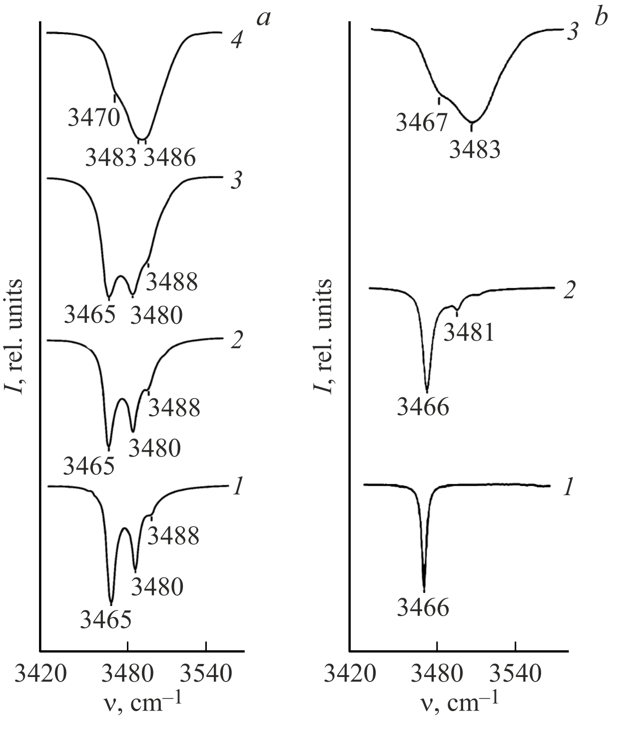

Figure 4. IR absorption spectra in the valence vibration region of hydrogen atoms of OH^--groups of single crystals. (*a*): *1* — $LiNbO_{3stex}$, *2* — $LiNbO_{3stex}$(6.0 mol.% K_2O), *3* — $LiNbO_{3stex}$(4.5 mol.% K_2O), *4* — $LiNbO_{3cong}$(48.6 mol.% Li_2O); (*b*): data from work [11] $LiNbO_{3stex}$, *1* — $LiNbO_{3stex}$(12.1 mol.% K_2O), *2* — $LiNbO_{3stex}$(9.35), $LiNbO_{3cong}$(48.7 mol.% Li_2O). $T = 293$ K.

Approaching the magnesium concentration threshold at about ≈ 5.5 mol.% MgO causes replacement of niobium ions located in lithium octahedra by magnesium ions. At the magnesium concentration threshold of ≈ 5.5 mol.% MgO the $LiNbO_3$:Mg crystal structure undergoes a sharp almost complete disappearance of Nb_{Li} and V_{Li} point defects and, correspondingly, of the complex V_{Li}-OH defects [29,30]. In the IR absorption spectrum, this abrupt change in the inclusion mechanism of magnesium ions at the concentration threshold ≈ 5.5 mol.% MgO is manifested by an abrupt shift of the stretching vibration frequencies of hydrogen atoms into the high-frequency region by more than 60 cm^{-1} (fig. 2, curve *5*). Magnesium ions in the $LiNbO_3$:Mg crystal at the concentration threshold occupy the basic Li, Nb ion positions, forming point defects Mg_{Li} and Mg_{Nb}. These point defects are a self-compensating pair Mg_{Li}-Mg_{Nb}, to which hydrogen atoms are attracted, forming new complex defects Mg_{Nb}-OH and Mg_{Li}-OH-Mg_{Nb}. These defects in the crystal's $LiNbO_3$:Mg absorption spectrum correspond to the absorption bands at 3526 and 3535 cm^{-1} (Fig. 2, curve *5*).

A completely different situation with composition change is observed for $LiNbO_3$:Er crystals and nominally pure $LiNbO_3$crystals close to stoichiometric composition grown by HTTSSG technology using K_2O flux. Figures 3 and 4 show that as the composition of $LiNbO_3$:Er crystals approaches the concentration threshold at about ≈ 2.5 wt% Er, and for $LiNbO_3$:K_2O crystals approaches the stoichiometric composition $(R \to 1)$ the number of lines in the IR absorption spectrum in the valence vibration region of hydrogen atoms of OH^--groups decreases. That is, with changes in crystal composition, the intensity of some lines tends to zero. In the spectrum of the stoichiometric $LiNbO_{3st}$ $(R = 1)$ crystal and in the spectrum of $LiNbO_3$:Er crystal with erbium concentration above the concentration threshold at ≈ 2.5 wt% Er only one line remains at frequencies 3466 and 3494 cm^{-1} respectively. Moreover, the width of this line ($\approx 20\,cm^{-1}$) in the spectrum of $LiNbO_3$:Er(3.1 wt%) crystal is significantly larger than in the spectrum of the stoichiometric crystal ($\approx 3.0\,cm^{-1}$) indicating a greater disordering of hydrogen bonds in the $LiNbO_3$:Er(3.1 wt%), crystal structure compared to the highly perfect stoichiometric crystal obtained in work [11].

The formation of hydrogen bonds in the $LiNbO_3$ crystal of any composition leads to a noticeable change in the wave functions of the outer electronic orbitals of oxygen ions and their electronic polarizability [10], influences the interaction of oxygen ions with lithium, niobium, and impurity ions, which inevitably causes significant distortion of the oxygen-octahedral clusters MeO_6 (Me — Li^+, Nb^{5+}, vacant octahedron V, impurity ion). The number of lines corresponding to valence vibrations of hydrogen atoms in hydroxyl groups OH in the $LiNbO_3$ crystal spectrum should, in the most general case, be equal to the number of hydrogen bonds in each oxygen-octahedral cluster MeO_6 of the crystal structure. However, many quasi-elastic constants of hydrogen bonds coincide. Accordingly, the frequencies corresponding to valence vibrations of hydrogen atoms in hydroxyl groups OH also coincide. Therefore, in the real vibrational spectrum of a crystal with composition close to stoichiometric, and in the stoichiometric crystal itself, significantly fewer lines are observed than in non-stoichiometric crystals ($R \neq 1$) (Fig. 4).

Thus, the more perfect (symmetric) the oxygen-octahedral cluster MeO3 $_6$ cluster of the $LiNbO_3$ crystal, the closer its shape to a regular octahedron, the less difference there will be between the O–O and O–H bond lengths in MeO_6, clusters, and consequently, the smaller the differences in the valence vibration frequencies of hydrogen atoms of OH^--groups. In the limiting case of a highly perfect ideal stoichiometric $LiNbO_3$, crystal, in which the oxygen octahedra O_6 of the structure are equivalent, all OH^--groups and lengths of hydrogen bonds O-H, except for the OH^--group involved in the valence bridging vibration of oxygen atoms Me–O–Me along the polar axis of the crystal, will be equivalent, and only one line will be observed in the IR absorption spectrum (Fig. 4, *b*). Only this valence vibration of hydrogen atoms, hydrogen-bonded to an oxygen atom oscillating along the polar axis of the crystal in the Me–O–Me bridge (Me — Li, Nb, vacancy, impurity metal [27]), causes a change in the dipole moment of the crystal's unit cell and therefore is active in the IR absorption spectrum. The stretching vibrations of the other hydrogen atoms of hydroxyl groups OH in the high-symmetry oxygen octahedra LiO_6, NbO_6 and VO_6 of the stoichiometric $LiNbO_3$ crystal with a high degree of structural perfection do not cause a change in the dipole moment of the crystal's unit cell and are inactive in the IR absorption spectrum. In the structure of real non-stoichiometric $LiNbO_3$ crystals, several nonequivalent positions for OH^--groups exist, and more than two lines are observed in their IR absorption spectrum in the frequency range $3450-3550\,cm^{-1}$ (Fig. 2–4).

This experimental fact may be of great importance for monitoring the technologies for producing highly perfect $LiNbO_3$ crystals. It is pertinent to note the following: a single line at $3466\,cm^{-1}$ was previously observed only in the IR absorption spectrum of a strictly stoichiometric $LiNbO_3$ crystal of high structural perfection grown by the HTTSSG technology [11], in which R=[Li]/[Nb]=1 and point defects Nb_{Li}, which are deep electron traps responsible for the photorefractive (optical damage) effect, are absent. Accordingly, in such a highly perfect stoichiometric $LiNbO_3$ crystal, complex (Nb_{Li})-OH defects associated with Nb_{Li}point defects are also absent [11]. At the same time, in the nominally pure $LiNbO_3$ crystals with composition close to stoichiometric grown by the same HTTSSG method studied by us, several lines are observed in the IR absorption spectrum in the valence vibration region of hydrogen atoms of OH^--groups (Fig. 4, *a*). That is, the stoichiometric composition of the $LiNbO_3$ crystal has not been achieved here. The presence in the IR absorption spectrum of the $LiNbO_3$:Er^{3+}(3.1 wt%) crystal of only one broad line, corresponding to valence vibrations of hydrogen atoms in OH^--groups of different oxygen-octahedral clusters MeO_6 in the crystal structure (Fig. 3), indicates that the MeO_6clusters in the $LiNbO_3$:Er^{3+}(3.1 wt%),crystal structure, as well as MeO_6clusters (Me — Li, Nb, vacancy V) of the high-quality stoichiometric crystal [11], have a shape close to that of a regular octahedron, i.e., are practically undistorted. Thus, the technology for producing highly perfect stoichiometric $LiNbO_3$ crystals can be controlled by the number of lines corresponding to valence vibrations of hydrogen atoms of OH^--groups. The more perfect the $LiNbO_3$, crystal and the closer the shape of oxygen octahedra O_6 is to a regular octahedron, the fewer lines corresponding to valence vibrations of hydrogen atoms of OH^--groups will be present in the IR absorption spectrum.

This conclusion, drawn from IR absorption spectroscopy data, is supported by literature data of X-ray structural analysis obtained for $LiNbO_3$:Er^{3+}crystals with different erbium concentrations. In work [22], the Rietveld full-profile X-ray structural analysis method was used to determine bond lengths and site occupancy factors (G) for positions: Nb_{Li}, Nb_V, Er_{Li}, Er_V in the oxygen-octahedral clusters MeO_6 of $LiNbO_3$:Er^{3+} crystals of varying erbium concentration. It was shown that with increasing Er^{3+} concentration in $LiNbO_3$:Er crystals, the dispersion of bond angles decreases, and already at an Er $\geq$ concentration of 2.8 wt% the Nb_{Li}defects are completely absent in the crystal structure. This fact indicates that the shape of the oxygen-octahedral clusters MeO_6 becomes more perfect and approaches that of a regular octahedron as the $_3$ concentration in the LiNbO crystal increases.

Thus, it can be asserted that in the $LiNbO_3$:Er^{3+}(3.1 wt%) crystal, whose IR absorption spectrum in the valence vibration region of hydrogen atoms of OH^--groups shows only one line (Fig. 3), the value R=[Li]/[Nb]$\approx$1 and the shape of the oxygen-octahedral clusters MeO_6 are close to a regular octahedron, i.e., close to that of a stoichiometric crystal. However, compared with the nominally pure highly perfect strictly stoichiometric $LiNbO_3$:Er^{3+}(3.1 wt%) crystal, the $LiNbO_{3st}$ crystal exhibits chaotic disordering of hydrogen atoms hydrogen-bonded to oxygen atoms. This is evidenced by the significantly greater broadening of the line at $3494\,cm^{-1}$ in the IR absorption spectrum of $LiNbO_3$:Er^{3+} (3.1 wt%) (Fig. 3) compared to the $3466\,cm^{-1}$ line in the IR absorption spectrum of the stoichiometric crystal (Fig. 4, *b*). The value of R=[Li]/[Nb] in $LiNbO_3$:Er^{3+}(3.1 wt%) is expected to be close to unity.

Therefore, if in $LiNbO_3$:Er the value R=[Li]/[Nb]$\approx$1 (close to stoichiometric composition), then in the crystal structure, point defects Nb_{Li}, which are deep electron traps responsible for the photorefractive effect, should be practically absent, and Er^{3+} ions will occupy not one but two positions in the cation sublattice. Moreover, according to works [22,23], one of these positions is the main one (Er_{Li}) and is occupied significantly more than the other (Er_V). In addition, according to X-ray structural analysis data, the concentration of $LiNbO_3$:Er^{3+} point defects decreases in Er_V [22,23], crystals, which also leads to a more perfect shape of the oxygen-octahedral clusters MeO_6. From the obtained results, it also becomes clear why, according to work [23], the $LiNbO_3$:Er^{3+}(3.1 wt%) crystal exhibits a low photorefractive effect — it has a low concentration of Nb_{Li}, defects responsible for the photorefractive effect.

Conclusion

From the IR absorption spectra in the stretching vibration region of OH^--groups, it was established that the oxygen-octahedral clusters MeO_6 (Me — Li^+, Nb^{5+}, vacant octahedron V, impurity ion) in the structure of the $LiNbO_3$:Er^{3+}(3.1 wt%), crystal, as well as the oxygen-octahedral clusters MeO_6 of a highly perfect compositionally homogeneous stoichiometric crystal (R=[Li]/[Nb]=1), have a shape close to that of a regular octahedron. This conclusion is supported by literature data from X-ray structural analysis [22,23]. It was also confirmed that the concentration of $LiNbO_3$:Er^{3+}(3.1 wt%) point defects responsible for the photorefractive effect is low in the structure of Nb_{Li}, crystals. Thus, hydrogen atoms bonded by hydrogen bonds to oxygen atoms are more ordered in the structure of $LiNbO_3$:Er^{3+}(3.1 wt%), crystals —where the erbium concentration is above the threshold value of about ≈ 2.5 wt% Er, than in crystals with sub-thresholdEr^{3+}, concentrations, which is unusual. This fact can be used for the development of highly perfect functional elements of optical devices with nonlinear-optical conversion of laser and broadband radiation. It should also be noted that due to the rapidity of spectrum registration, IR spectroscopy in the valence vibration region of hydrogen atoms of hydroxyl OH-groups can serve as a rapid method for determining the structural perfection of oxygen-octahedral clusters MeO_6 in $LiNbO_3$crystals, both nominally pure and doped, produced by different technologies. In the IR absorption spectra of $LiNbO_3$crystals characterized by highly perfect oxygen-octahedral clusters MeO_6, whose shape is close to a regular octahedron, only one line must be observed in the valence vibration region of hydrogen atoms of OH^--groups. The frequency and width of this line are determined by the crystal composition.

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Conflict of interest

The authors declare that they have no conflict of interest.

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