

Article

First- and Second-Order Raman Scattering and Photorefraction in Nonlinear Optical Crystal $\text{LiNbO}_3:\text{Y}^{3+}$ (0.46 wt%)

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Abstract

It is found that the speckle structure of the photoinduced light scattering indicatrix of the $\text{LiNbO}_3:\text{Y}^{3+}$ (0.46 wt%) crystal and its behavior with the time of crystal irradiation with a laser undergo an atypical behavior caused by the features of the dissipation processes of laser-induced defects in the crystal. In the frequency range of $100\text{--}4000\text{ cm}^{-1}$, the Raman spectra of the $\text{LiNbO}_3:\text{Y}^{3+}$ (0.46 wt%) single crystal were recorded upon excitation by visible (532 nm) and near-IR (785 nm) laser radiation. Five second-order Raman scattering lines were detected in the frequency range of $1000\text{--}2100\text{ cm}^{-1}$, with the frequencies of two of them (of about 1790 cm^{-1} and 1940 cm^{-1}) somewhat exceeding the doubled value of the frequencies of fundamental vibrations of the $4A_1(z)\text{LO}$ (longitudinal optical) and $9E(x,y)$ symmetry types, which allows us to attribute these lines to the overtones of the fundamental vibrations of $4A_1(z)\text{LO}$ and $9E(x,y)$. It is found that only one Raman scattering line is observed in the region of stretching vibrations of OH-groups ($3200\text{--}3800\text{ cm}^{-1}$). The frequency of this line is found to depend on the scattering geometry, varied within $3431\text{--}3438\text{ cm}^{-1}$, and to be shifted to the low-frequency region by about $30\text{--}50\text{ cm}^{-1}$ relative to the frequencies in the IR absorption spectrum. This finding may be due to the alternative prohibition rule due to the presence of the center of symmetry of the oxygen octahedra O_6 of the crystal structure.

Keywords: lithium niobate; yttrium doping; Raman scattering; second order Raman spectra; OH-group; stretching vibration



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1. Introduction

Yttrium-containing crystals are extensively used as functional materials for various purposes: scintillators [1–4], highly efficient catalysts [5,6], wear-resistant electrodes [7], and gas sensors [8,9]. The transition element yttrium is considered most suitable for creating various nonlinear optical and laser materials as an element of the main matrix and activator [10,11], including as an activator in the matrix of the nonlinear optical crystal lithium niobate (LiNbO_3), which has exceptionally high values of nonlinear optical coefficients ($d_{33} = 37.8 \times 10^{-12}\text{ m/V}$, $d_{31} = 5.18 \times 10^{-12}\text{ m/V}$, $d_{22} = 2.468 \times 10^{-12}\text{ m/V}$) and quite high radiation resistance [11,12]. It should be noted that the LiNbO_3 single crystal is transparent in the range of $0.25\text{--}5.3\text{ }\mu\text{m}$, which allows the use of materials based on it in the visible, near-, and mid-IR (infrared) ranges. $\text{LiNbO}_3:\text{Y}^{3+}$ crystals are also promising

materials for nonlinear optical conversion of laser radiation [13–21], generation of THz radiation [22,23], recording of reflective gratings [24,25], and so on.

LiNbO₃ single crystals of any composition exhibit the photorefractive effect—the effect of photoinduced change in refractive indices (optical damage) [25–27]. The photorefractive effect limits many applications of LiNbO₃ single crystals in optics. With the photorefractive effect, quite strong destruction of the laser beam in the crystal occurs, and photoinduced light scattering (PILS) appears. As a result, these phenomena cause distortion of the laser beam wavefront, which leads to distortion of the converted radiation and to instability of the solid-state laser. If the Raman scattering and photorefractive effect are excited by the same laser radiation, then photorefractive effect leads to the appearance in the Raman spectrum of lines that are forbidden by the selection rules for this scattering geometry. The Raman spectra of the LiNbO₃:Y³⁺ crystal were previously analyzed in a number of studies [27–30]. In Ref. [27], the Raman spectra in the ranges of 40–160 and 500–800 cm^{−1} are investigated for the first time. A line with a frequency of 120 cm^{−1} was recorded, corresponding to two-particle states of acoustic phonons with a total wavevector equal to zero, and in the scattering geometry x(zx)y, lines of 580 cm^{−1} and 635 cm^{−1} were observed. Moreover, the fully symmetric line A₁(TO) (transverse optical) with a frequency of 635 cm^{−1} is forbidden for observation in the Raman spectrum in the scattering geometry x(zx)y and appears in it due to the presence of the photorefractive effect in the crystal. Also, the Raman spectra in the range of 500–700 cm^{−1} in the scattering geometry z(xz)y have been analyzed. A fundamental Raman line with a frequency of 577 cm^{−1} and two broad maxima with frequencies of 602 cm^{−1} and 620 cm^{−1} were observed on its wing. In the region of totally symmetric (A₁(TO)) vibrations of Li⁺ and Nb⁵⁺ ions located in the O₆ oxygen octahedra of the LiNbO₃ crystal structure (150–350 cm^{−1}), overlapping fundamental Raman lines with frequencies of 254 cm^{−1} and 275 cm^{−1}, corresponding to the 1A₁(z) and 2A₁(z) modes, as well as a weak line with a frequency of 334 cm^{−1} were recorded. In the frequency range of stretching bridge vibrations of oxygen atoms Nb–O–Nb (800–960 cm^{−1}), an asymmetric fundamental Raman line with a maximum near 873 cm^{−1} and a broad wing with a maximum at about 900 cm^{−1} was detected. In the scattering geometries y(zx)z and z(xz)y in the ranges of 130–170 and 500–750 cm^{−1}, the presence of fundamental Raman lines with frequencies of 150 cm^{−1} and 578 cm^{−1} was detected, and lines with frequencies of 172 cm^{−1} and 605 cm^{−1} manifested in the spectrum due to the effect of photorefractive effect [28,29]. In the scattering geometry x(zx)y, the intensity of the Raman lines at 580 cm^{−1} and 628 cm^{−1} turned out to be practically identical. Also, in the LiNbO₃:Y³⁺(0.46 wt%) crystal in the scattering geometries y(zz)y and x(yy)x, a Raman component with a frequency of about 695 cm^{−1} has been detected [30], the origin of which is quite ambiguous and is discussed in Refs. [31,32]. A double-doped LiNbO₃:Y:Mg single crystal grown from a congruent melt has been studied by Raman spectroscopy in Ref. [33]. In the scattering geometry z(yy)z, a number of fundamental Raman lines corresponding to the A₁(LO)- and E(TO)-modes were recorded.

Based on a brief review of the existing literature, it should be noted that the Raman spectra of the LiNbO₃:Y³⁺(0.46 wt%) single crystal earlier have been investigated only in the frequency range of 50–1000 cm^{−1}, in which mainly fundamental vibrations of the crystal lattice are manifested. However, the literature completely lacks studies of the Raman spectra of the LiNbO₃:Y³⁺(0.46 wt%) single crystal in the frequency range (1000–4000 cm^{−1}), in which second-order Raman spectra corresponding to bound states of fundamental vibrations of the crystal lattice have been obtained for LiNbO₃ crystals of other compositions [34–38]. In addition, earlier studies of the Raman spectra of the LiNbO₃:Y³⁺(0.46 wt%) single crystal have been performed only under excitation by a visible laser source with a wavelength of 514.5 nm and a relatively high power (200 mW),

causing a strong photorefractive effect [27]. It should be noted that, due to photorefractive, lines forbidden by the selection rules for the scattering geometry under study appear in the Raman spectrum, as well as spectral components caused by laser-induced defects. In order to obtain information on the state of the intrinsic defect structure of the crystal, undistorted by photoinduced processes, of considerable interest is to study the Raman spectra of the $\text{LiNbO}_3:\text{Y}^{3+}$ (0.46 wt%) single crystal in a wider frequency range (1000–4000 cm^{-1}) without the influence of the photorefractive effect on the Raman spectrum. To this end, it is necessary to excite the Raman scattering with laser radiation in the near- or mid-IR ranges that does not cause the photorefractive effect.

In this paper, comparative studies of the first-order (corresponding to fundamental vibrations of the crystal lattice) and second-order Raman spectra of a $\text{LiNbO}_3:\text{Y}^{3+}$ (0.46 wt%) single crystal in the frequency range of 100–4000 cm^{-1} , including the previously virtually unexplored frequency range of 1000–4000 cm^{-1} , in which overtone processes and bound states of fundamental vibrations may occur in LiNbO_3 crystals of different compositions [34–38], are performed for the first time under excitation by laser radiation in the visible ($\lambda_0 = 532$ nm wavelength) and near-IR ($\lambda_0 = 785$ nm) ranges. The use of laser sources with wavelengths of 532 nm and 785 nm in the current study is due to the observation that the photorefractive effect in a LiNbO_3 crystal depends on the wavelength of the exciting radiation. The photorefractive effect is maximal when the Raman spectra are excited by laser radiation in the visible range with a wavelength of 532 nm and is already absent when the Raman spectra are excited by laser radiation in the near-IR range with a wavelength of 785 nm.

2. Obtaining a $\text{LiNbO}_3:\text{Y}^{3+}$ (0.46 wt%) Single Crystal

To grow a $\text{LiNbO}_3:\text{Y}^{3+}$ (0.46 wt%) single crystal, we used a granulated batch (TU 0.027.039) synthesized in the ICT KSC RAS. The batch preparation is described in detail in Ref. [39]. The batch composition corresponded to the congruent melting composition (48.6 mol% Li_2O). The $\text{LiNbO}_3:\text{Y}^{3+}$ (0.46 wt%) single crystal was grown using a platinum crucible in an air atmosphere by the Czochralski method under conditions of a small (approximately 2 $^\circ\text{C}/\text{cm}$) axial temperature gradient on a Crystal-2 setup (Voroshilovgrad Electronic Machine Manufacturing Plant, Voroshilovgrad, USSR) equipped with an automatic weight control system, which makes it possible to maintain constant conditions during the crystallization of various samples and, consequently, to grow them with sufficiently reproducible characteristics. Direct doping of the melt with yttrium oxide (Y_2O_3 , 99.99% purity) has been performed. The single crystal was grown in the direction of the polar axis (Z-cut) at a rotation speed of 16 rpm and a travel speed of 0.8 mm/h. The growth rate was 1.08 mm/h. The process was completed when the crystal mass reached 130 g, with no more than 15% of the melt mass crystallizing. The crystal parameters were as follows: cone length—17 mm, cylindrical part length—30 mm, crystal diameter—30 mm, inverse cone length—5 mm. The yttrium concentration was determined directly in the crystal and is 0.46 wt%. The $\text{LiNbO}_3:\text{Y}^{3+}$ crystal was analyzed by X-ray fluorescence analysis (XRF) on a Spectroscan MAK-S-GV (Spectron, St. Petersburg, Russia) instrument. The distribution coefficient is $K_D(\text{Y}) \sim 0.89$. Accordingly, the yttrium concentration in the melt is about 0.52 wt%. The impurity concentration in the single crystal, determined by spectral analysis, is given in Table 1.

Immediately before growing the $\text{LiNbO}_3:\text{Y}^{3+}$ (0.46 wt%) single crystal, the melt was overheated and held in the overheated state for two hours at a temperature significantly (about 200 $^\circ\text{C}$) higher than the melting point in order to increase the homogeneity of the melt and eliminate gas inclusions. Overheating the melt promotes the destruction of associative bonds, which in turn allows for achieving the required homogeneity of the

single crystal. Then the melt was gradually cooled to the seeding temperature. Crystal seeding was performed no earlier than 5–7 h after obtaining the melt.

Table 1. Concentration of trace amounts of foreign cationic metal impurities and the Curie temperature ($T_C = 1145\text{ }^\circ\text{C}$) in the upper (cone) and lower parts of the $\text{LiNbO}_3:\text{Y}^{3+}$ (0.46 wt%) single crystal.

Impurity	Impurity Content, wt%	
	Top	Bottom
Zr	$<1 \times 10^{-2}$	$<1 \times 10^{-2}$
Mo	$<1 \times 10^{-3}$	$<1 \times 10^{-3}$
Ca	$<5 \times 10^{-3}$	$<5 \times 10^{-3}$
Fe	$<1 \times 10^{-3}$	$<1 \times 10^{-3}$
Ti	$<1 \times 10^{-3}$	$<1 \times 10^{-3}$
Si	$<1 \times 10^{-3}$	$<1 \times 10^{-3}$
Pb, Ni, Cr, Co	$<1 \times 10^{-3}$	$<1 \times 10^{-3}$
Al	$<5 \times 10^{-4}$	$<5 \times 10^{-4}$
Cu	$<5 \times 10^{-4}$	$<5 \times 10^{-4}$
Mn, V, Mg, Sn	$<5 \times 10^{-4}$	$<5 \times 10^{-4}$

In the zone of post-growth annealing of the single crystal, a virtually isothermal region with a temperature of $1205\text{ }^\circ\text{C}$ was formed. The grown single crystal was maintained at this temperature for two hours in order to relieve thermoelastic stresses in the crystal. Then, the crystal was cooled to room temperature at a rate of $50\text{ }^\circ\text{C/h}$. The single crystal grown and cooled to room temperature was subjected to additional annealing in a «Lanthan» (Voroshilovgrad Electronic Machine Manufacturing Plant, Voroshilovgrad, USSR) furnace at $1200\text{ }^\circ\text{C}$, after which it was cooled at a rate of $20\text{ }^\circ\text{C/h}$ to a temperature of $1000\text{ }^\circ\text{C}$. In the process of cooling, a constant voltage was applied to the crystal in order to make it monodomain. The monodomain nature of the crystals was controlled by an electroacoustic method based on measuring the electrical impedance using a technique developed by some of the authors [40]. It should be noted that during monodomainization, not only is a monodomain state formed, but also there is a significant reduction in macro-, meso-, and microdefects in the crystal.

The homogeneity of the composition of the $\text{LiNbO}_3:\text{Y}^{3+}$ (0.46 wt%) single crystal was controlled by the chemical composition of impurities and by the Curie temperature value measured by differential thermal analysis for plates cut from the upper and lower parts of the single crystal boule. Table 1 shows that the $\text{LiNbO}_3:\text{Y}^{3+}$ (0.46 wt%) crystal is characterized by high homogeneity along the growth axis by the composition of impurities and main components, as evidenced by the coincidence of the Curie temperatures of the upper and lower parts of the boule. The optical homogeneity of the $\text{LiNbO}_3:\text{Y}^{3+}$ (0.46 wt%) crystal was also controlled by conoscopic and PILS patterns. A single crystal sample in the form of a carefully polished plate or rectangular parallelepiped, the edges of which coincided in direction with the main crystallographic axes x , y , and z (z is the polar axis of the crystal), was mounted on a movable two-coordinate optical stage. This made it possible to scan the entire plane of the input face with a laser beam and obtain a multitude of conoscopic and PILS patterns corresponding to different sections of the cross section of the sample under study. The scanning step was 0.5 mm .

The samples for the studies of Raman spectra were prepared in the form of a rectangular parallelepiped (size $5 \times 6 \times 7\text{ mm}^3$). The axes of the Cartesian coordinate system were selected in accordance with IEEE standard 176-1987 [41]. The faces of the parallelepiped were carefully polished. The samples for the studies of conoscopic and PILS patterns were prepared in the form of carefully polished plates of 1 mm thickness.

3. Registration of Conoscopic and PILS Patterns, Raman and IR Absorption Spectra of $\text{LiNbO}_3\text{:Y}^{3+}$ (0.46 wt%) Crystal

To study the conoscopic and PILS patterns in this paper, we used the original experimental setups and techniques described in Refs. [42,43]. We used a YAG:Nd³⁺ laser MLL-100 (Changchun New Industries Optoelectronics Tech. Co., Ltd., Changchun, China) with a radiation wavelength of 532 nm and a laser beam diameter of 3 mm. The conoscopic and PILS patterns of the sample under study were recorded on a translucent screen using a digital camera. The conoscopic patterns were obtained at a laser radiation power of 1 and 90 mW, and the PILS patterns were obtained at a laser radiation power of 160 mW. At a low laser radiation power of 1 mW, the photorefractive effect is exceptionally small, so that no opening of the PILS indicatrix was observed. At such a low laser radiation power, the conoscopic pattern reflects only the state of the intrinsic structural defects of the crystal, since in this case there are no laser-induced defects or defects caused by the photorefractive effect. When excited by the radiation of the MLL-100 laser with a power of 90 mW, the conoscopic images showed both the intrinsic defects of the crystal (determined by the composition and technology of obtaining the crystal) and the defects induced in the crystal by the laser radiation, as well as the defects caused by the effect of photorefractive effect.

Raman spectra were recorded using BWS465-532S and BWS465-785H i-Raman Plus spectrometers (B&W Tek, Plainsboro Township, NJ, USA) using the known technique [35]. The laser spot diameter at focus was 85 μm . When recording the Raman spectra, the laser radiation power was selected so as not to cause local heating of the sample by laser radiation. Due to the presence of the photorefractive effect in the $\text{LiNbO}_3\text{:Y}^{3+}$ (0.46 wt%) crystal, the value of which can change with the time of irradiation of the crystal by laser radiation, all spectra were recorded at least 10 min after the action of laser radiation on the crystal, after which the photorefractive effect in the crystal no longer changes. IR absorption spectra in the region of stretching vibrations of OH-groups were recorded using a Bruker VERTEX 70x spectrometer (Bruker, Karlsruhe, Germany) using the known technique [38].

4. Photorefractive Properties of $\text{LiNbO}_3\text{:Y}^{3+}$ (0.46 wt%) Crystal

We have investigated the photorefractive properties of the $\text{LiNbO}_3\text{:Y}^{3+}$ (0.46 wt%) crystal using laser conoscopy and PILS. The conoscopic patterns of the $\text{LiNbO}_3\text{:Y}^{3+}$ (0.46 wt%) crystal obtained by irradiation with laser radiation with a wavelength of $\lambda_0 = 532 \text{ nm}$ and a power of 1 mW and 90 mW are shown in Figure 1. One can see from Figure 1 that at a laser radiation power of 1 mW, the conoscopic pattern of the $\text{LiNbO}_3\text{:Y}^{3+}$ (0.46 wt%) crystal completely corresponds to a uniaxial crystal with a high degree of structural perfection. However, with an increase in the laser radiation power to 90 mW, due to an increase in the photorefractive effect, distortions characteristic of weak optical biaxiality of the crystal appear in the conoscopic pattern. Namely, the circular symmetry of the image is broken, the “Maltese cross” is deformed in the vertical direction without enlightenment in the center, and the angles between its branches differ from right angles. At the same time, the isochromes effect retain the shape of concentric circles, characteristic of uniaxial crystals.

A direct consequence of the photorefractive effect in a photorefractive crystal is the photoinduced scattering of laser radiation by laser-induced microdefects, the refractive index of which differs from the refractive index of the crystal in the absence of the photorefractive effect [42,43]. Figures 2 and 3 show the dynamics of the time change of the speckle structure of the PILS indicatrix and the opening angle of the speckle structure of the PILS indicatrix of the $\text{LiNbO}_3\text{:Y}^{3+}$ (0.46 wt%) crystal, obtained using exciting laser ra-

diation with a wavelength of $\lambda_0 = 532$ nm and a power of 160 mW. It should be noted that the speckle structure of the PILS indicatrix of the $\text{LiNbO}_3:\text{Y}^{3+}$ (0.46 wt%) crystal is atypical from the speckle structures of other LiNbO_3 crystals of different compositions [43]. The dependences of the speckle structure of the PILS indicatrix and the opening angle θ of the speckle structure of the PILS indicatrix on the crystal laser irradiation time are also atypical (Figures 2 and 3). The time behavior of the angle θ and the type of the speckle structure of the PILS indicatrix (Figures 2 and 3) differ significantly from the time behavior of similar parameters of LiNbO_3 crystals of other compositions, characterized by different values of the photorefraction effect [42,43]. As an example for comparison, Figure 2b shows the PILS pattern of a highly perfect $\text{LiNbO}_3:\text{B}^{3+}$ (0.83 mol% B_2O_3 in the batch) crystal obtained under the same experimental conditions and the dynamics of its development over time. The influence of the non-metallic element boron on the structural and optical perfection of lithium niobate crystal is described in detail in a number of papers [44–47]. From Figure 2, one can see that a three-layer PILS pattern is observed for both crystals, which is characteristic of LiNbO_3 crystals of different compositions and production technologies [42,43]. However, for the $\text{LiNbO}_3:\text{Y}^{3+}$ (0.46 wt%) crystal, the speckle structure of the PILS indicatrix has the form of an ellipse, and for the $\text{LiNbO}_3:\text{B}^{3+}$ (0.83 mol% B_2O_3 in the batch) crystal, it has the form of a well-visible figure eight. In addition, the PILS pattern of the $\text{LiNbO}_3:\text{B}^{3+}$ (0.83 mol% B_2O_3 in the batch) crystal distinctly shows the birefringence of the laser beam (Figure 4), while the PILS pattern of the $\text{LiNbO}_3:\text{Y}^{3+}$ (0.46 wt%) crystal does not pronounce a birefringence (Figure 2). That is, the figure-eight appearance of the PILS pattern is due to the more pronounced and stronger birefringence of the laser beam in the $\text{LiNbO}_3:\text{B}^{3+}$ (0.83 mol% B_2O_3 in the batch) crystal compared to the $\text{LiNbO}_3:\text{Y}^{3+}$ (0.46 wt%) crystal.

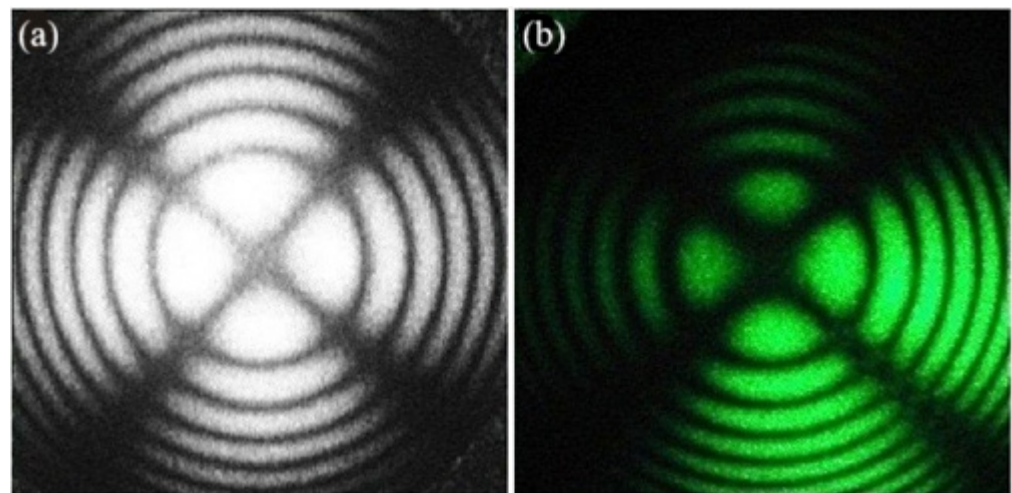


Figure 1. Conoscopic patterns of the $\text{LiNbO}_3:\text{Y}^{3+}$ (0.46 wt%) crystal obtained at $\lambda_0 = 532$ nm and laser radiation power P of (a) 1 mW and (b) 90 mW.

One can see from Figures 2 and 3 that the speckle structure of the PILS indicatrix in the $\text{LiNbO}_3:\text{Y}^{3+}$ (0.46 wt%) crystal appears almost instantly, during the first second of laser irradiation of the crystal. At the same time, under similar experimental conditions ($\lambda_0 = 532$ nm, power $P = 160$ mW), the disclosure of the speckle structure of the PILS indicatrix in the $\text{LiNbO}_3:\text{B}^{3+}$ (0.83 mol% B_2O_3 in the batch) crystal occurs within about 60 s after the start of laser irradiation of the sample (Figure 3).

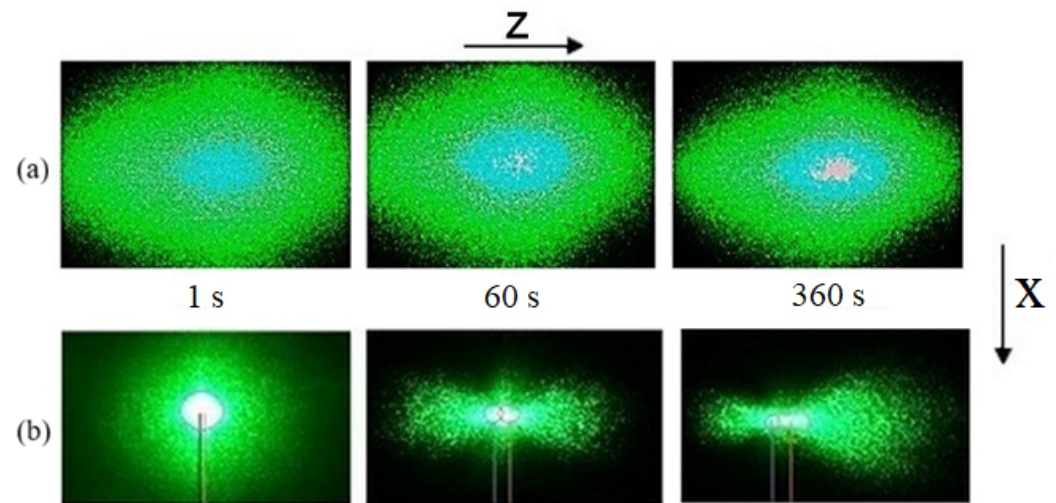


Figure 2. PILS patterns of $\text{LiNbO}_3:\text{Y}^{3+}$ (0.46 wt%) (a) and $\text{LiNbO}_3:\text{B}^{3+}$ (0.83 mol% B_2O_3 in the batch) (b) crystals, obtained with excitation by laser radiation with a wavelength of $\lambda_0 = 532$ nm and a power of 160 mW, and the dynamics of their development over time, as indicated. The exciting laser radiation is directed perpendicular to the polar Z-axis and polarized along the crystallographic X-axis. The polarization of the ordinary beam coincides with the direction of the X-axis, and the polarization of the extraordinary beam coincides with the direction of the Y-axis.

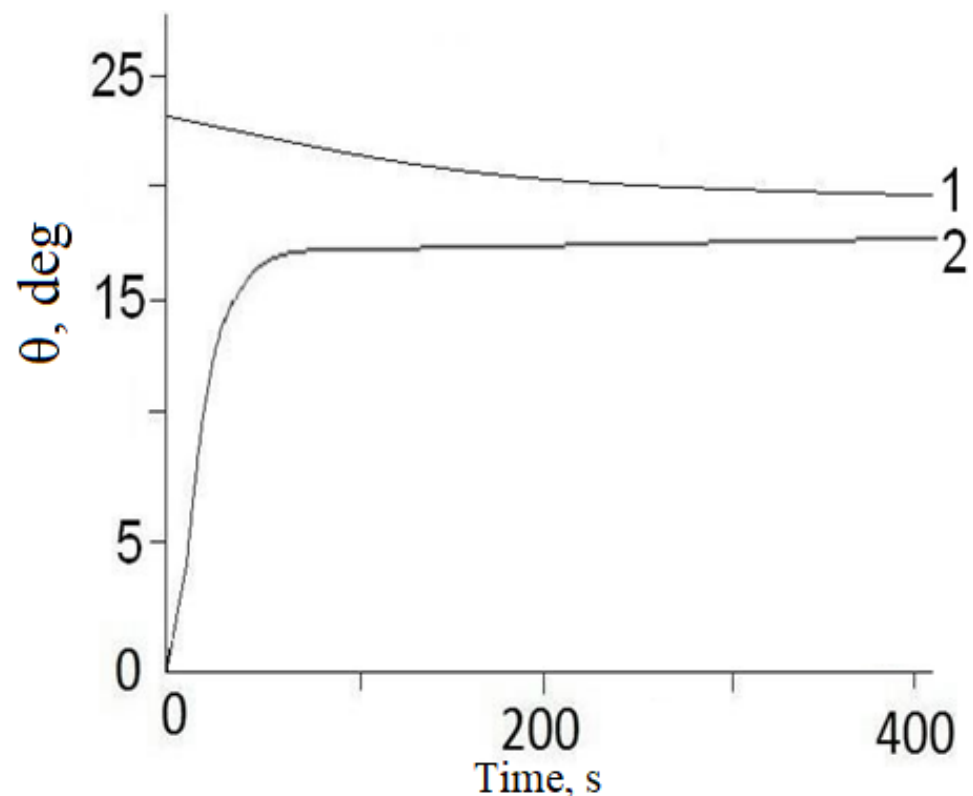


Figure 3. Time dependences of the opening angle θ of the speckle structure of the PILS indicatrix in $\text{LiNbO}_3:\text{Y}^{3+}$ (0.46 wt%) (1) and $\text{LiNbO}_3:\text{B}^{3+}$ (0.83 mol% B_2O_3 in the batch) crystals (2). $\lambda_0 = 532$ nm, $P = 160$ mW.

It is also noteworthy that for the $\text{LiNbO}_3:\text{Y}^{3+}$ (0.46 wt%) crystal, the central layer (laser spot) is absent in the speckle structure of the PILS indicatrix for more than 60 s of irradiation, Figure 2a, which is characteristic of the $\text{LiNbO}_3:\text{B}^{3+}$ (0.83 mol% B_2O_3 in the batch) crystal and of LiNbO_3 crystals of other compositions studied in the literature [43]. This finding indicates quite a strong dissipation of the laser radiation energy by laser-

induced defects of the $\text{LiNbO}_3:\text{Y}^{3+}$ (0.46 wt%) crystal and can be associated with the redistribution of energy between the ordinary and extraordinary rays. During the first 60 s of irradiation, the laser beam, experiencing birefringence when propagating perpendicular to the polar z axis, is divided into two closely spaced beams of different polarization (ordinary and extraordinary), which do not create their own laser track, since a significant part of the beam energy scattered by laser-induced defects dissipates into the volume of the crystal. The central layer (considerably weak) in the PILS pattern of the $\text{LiNbO}_3:\text{Y}^{3+}$ (0.46 wt%) crystal appears only after about 60 s of irradiation of the crystal with the laser beam (Figure 2), after the second and third layers of the speckle structure of the PILS indicatrix have already formed. In this case, the central layer of the speckle structure of the $\text{LiNbO}_3:\text{Y}^{3+}$ (0.46 wt%) crystal is presented in the form of separate dots (Figure 2), while for the $\text{LiNbO}_3:\text{B}^{3+}$ (0.83 mol% B_2O_3 in the batch) crystal and photorefractive LiNbO_3 crystals of other compositions, the central layer exists in the form of a single bright spot [43]. It can be assumed that this phenomenon is a consequence of the peculiarities of the interaction of laser radiation with laser-induced defects in the structure of the photorefractive $\text{LiNbO}_3:\text{Y}^{3+}$ (0.46 wt%) crystal. After 360 s, the laser beam in the $\text{LiNbO}_3:\text{Y}^{3+}$ (0.46 wt%) crystal can already be observed as a single bright spot. This behavior of the laser beam in the crystal indicates that the $\text{LiNbO}_3:\text{Y}^{3+}$ (0.46 wt%) crystal, after more than 360 s of laser irradiation, is no longer able to dissipate the entire laser radiation energy flux into the crystal volume. The unusual features of the photorefractive properties of the $\text{LiNbO}_3:\text{Y}^{3+}$ (0.46 wt%) crystal are reflected in its Raman spectrum.

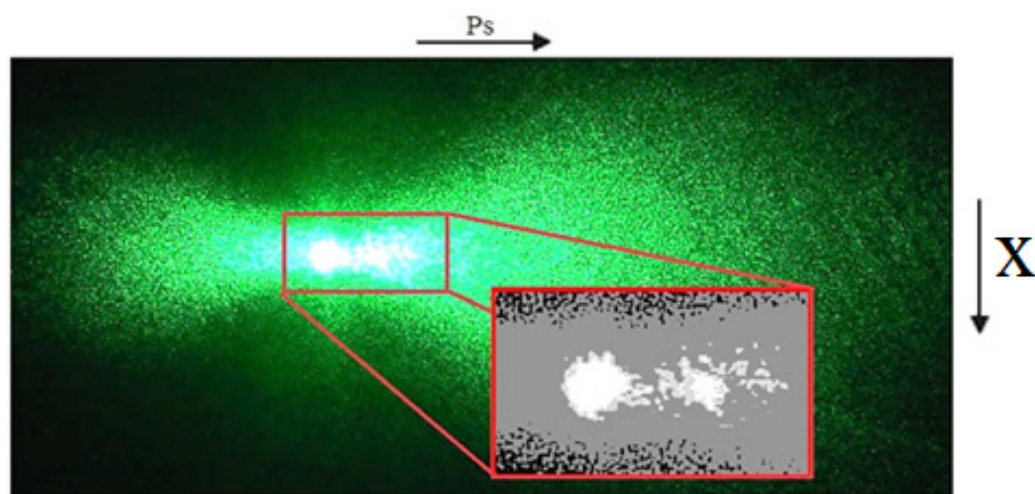


Figure 4. Birefringence of a laser beam in a $\text{LiNbO}_3:\text{B}^{3+}$ (0.83 mol% B_2O_3 in the batch) crystal. The central layer of the PILS indicatrix is highlighted in red and converted to black and white to enhance contrast. Two beams (ordinary and extraordinary) are quite well visible on the output face of the crystal as two round white spots. $\lambda_0 = 532$ nm, $P = 160$ mW. The exciting laser radiation is directed perpendicular to the polar Z-axis and polarized along the crystallographic X-axis. The polarization of the ordinary beam coincides with the direction of the X-axis, and the polarization of the extraordinary beam coincides with the direction of the Y-axis.

5. First- and Second-Order Raman Spectra of $\text{LiNbO}_3:\text{Y}^{3+}$ (0.46 wt%) Crystal

The photorefraction effect, laser-induced defects, and PILS can have a noticeable effect on the Raman spectrum of a crystal in polarized radiation. Raman spectroscopy can be an effective method for studying the photorefractive effect and photoinduced processes in crystals. In addition, it should be taken into account that under the action of the electric field of laser radiation in ferroelectric crystals, a change in the effective charge of longitudinal

(LO) optical phonons can occur, which should manifest itself in a change in the intensities of light scattering on longitudinal phonons [48]. The effective cross-section of scattering on transverse (TO) phonons indeed does not depend on the value of the effective transverse charge, and therefore it should not change with a change in the concentration of multiply charged dopants responsible for the photorefractive effect.

Figure 5 shows the Raman spectra of the $\text{LiNbO}_3:\text{Y}^{3+}$ (0.46 wt%) crystal excited by laser radiation with $\lambda_0 = 532$ nm, causing the photorefractive effect. Figure 6 illustrates the Raman spectra of the $\text{LiNbO}_3:\text{Y}^{3+}$ (0.46 wt%) crystal excited by laser radiation with $\lambda_0 = 785$ nm, which does not cause the photorefractive effect. The experimentally observed frequencies of the Raman lines of the $\text{LiNbO}_3:\text{Y}^{3+}$ (0.46 wt%) crystal upon excitation of the Raman spectra by the 532 nm and 785 nm laser lines and their assignment to the fundamental vibrations of the crystal lattice are given in Table 2. In the absence of the photorefractive effect in the Raman spectrum of the LiNbO_3 crystal in the scattering geometries $x(\text{zz}, \text{zy})\bar{x}$ and $y(\text{zz}, \text{zx})\bar{y}$, according to the selection rules, TO and LO polar fundamental vibrations of the $A_1(z)$ and $E(x,y)$ symmetry types appear. When using the scattering geometry $z(\text{xx}, \text{yy}, \text{xy})\bar{z}$, only LO polar vibrations of the $A_1(z)$ symmetry type appear in the Raman spectrum.

Table 2. Experimentally observed frequencies (cm^{-1}) of Raman lines of the $\text{LiNbO}_3:\text{Y}^{3+}$ (0.46 wt%) single crystal and their assignment based on polarization measurements performed in Refs. [49,50] for two values of the exciting laser radiation wavelength λ_0 and different scattering geometries.

$\lambda_0 = 532$ nm			$\lambda_0 = 785$ nm			Attribution
$x(\text{zz}, \text{zy})\bar{x}$	$y(\text{zz}, \text{zx})\bar{y}$	$z(\text{xx}, \text{yy}, \text{xy})\bar{z}$	$x(\text{zz}, \text{zy})\bar{x}$	$y(\text{zz}, \text{zx})\bar{y}$	$z(\text{xx}, \text{yy}, \text{xy})\bar{z}$	
123		118	119	117	115	
149	149	152	152	152	152	1E(x,y)TO
199	184	185	184	181	189	
235	235	235	238	238	238	2E(x,y)TO (2E(x,y)LO)
250	250		253	253		1A ₁ (z)TO
265		265			266	3E(x,y)TO 1A ₁ (z)LO (2A ₁ (z)TO)
	271		272	272		
321	321	327	322	322	328	4E(x,y)TO
365	365	359	367	365	361	5E(x,y)TO
432	432	429	433	433	431	6E(x,y)LO (7E(x,y)TO)
581	578	578	580	582	578	8E(x,y)TO
632	632	624	633	631		4A ₁ (z)TO
					669	
690	690		691	698		
875	875	872	876	876	871	4A ₁ (z)LO (9E(x,y)LO)

As an analytical line in the study of the photorefractive effect in LiNbO_3 crystals of different compositions, it is convenient to use the 4A₁(z)TO line with a frequency of about 630 cm^{-1} , corresponding to the fully symmetric vibrations of the oxygen atoms of the O₆ oxygen octahedra of the crystal structure [27]. This line is allowed by the selection rules in the scattering geometries $x(\text{zz}, \text{zy})\bar{x}$ and $y(\text{zz}, \text{zx})\bar{y}$ and is forbidden by the selection rules in the $z(\text{xx}, \text{yy}, \text{xy})\bar{z}$ scattering geometry. From a comparison of Figures 5c and 6c it is evident that when the Raman spectrum of the $\text{LiNbO}_3:\text{Y}^{3+}$ (0.46 wt%) crystal is excited by laser radiation with a wavelength of 785 nm, which does not cause the photorefractive effect, the 4A₁(z)TO line with a frequency of about 630 cm^{-1} is absent from the spectrum in the

$z(xx, yy, xy)\bar{z}$ scattering geometry. At the same time, this line reliably appears in the Raman spectrum in scattering geometries $z(xx, yy, xy)\bar{z}$ upon excitation of the spectrum by a laser line with a wavelength of 532 nm, causing the photorefractive effect. From a comparison of Figures 5 and 6, one can see that the frequencies of the lines in the Raman spectra of the $\text{LiNbO}_3:\text{Y}^{3+}$ (0.46 wt%) crystal, recorded in the same polarization scattering geometries, differ upon excitation by the lines of 532 nm (the photorefractive effect is present) and 785 nm (the photorefractive effect is absent). In addition, in addition to the lines corresponding to fundamental vibrations of the lattice (the first-order Raman spectrum), a number of low-intensity lines related to the second-order spectrum are observed in the Raman spectrum of the $\text{LiNbO}_3:\text{Y}^{3+}$ (0.46 wt%) crystal in the frequency range of 100–900 cm^{-1} . Thus, the lowest frequency of the registered Raman lines (115 cm^{-1}) observed by us is additional: it does not correspond to either the fundamental optical vibrations of the $A_1(z)$ and $E(x,y)$ symmetry types or the pseudoscalar optical vibrations of the A_2 symmetry type prohibited by the selection rules. The Raman line with a frequency of about 690 cm^{-1} was previously observed in congruent ($R = [\text{Li}]/[\text{Nb}] = 0.946$) and close to stoichiometric ($R \approx 1$) LiNbO_3 crystals [31,32,51–53]. However, no unambiguous assignment of this spectral component by the symmetry type and the nature of the atomic motion was revealed. Earlier, a line with a frequency of 199 cm^{-1} has been observed in the IR absorption spectrum of a congruent lithium niobate crystal [51]. This spectrum component is close to the calculated value for the $E(x,y)\text{LO}$ mode [54,55]. In $\text{LiNbO}_3:\text{Er}$ and $\text{LiNbO}_3:\text{Er}:\text{Ti}$ crystals, a Raman line with a frequency of 182 cm^{-1} , were recorded, which was attributed to the $2E(x,y)$ mode [56]. The Raman line with a frequency of 669 cm^{-1} was attributed to the second-order Raman spectrum [57].

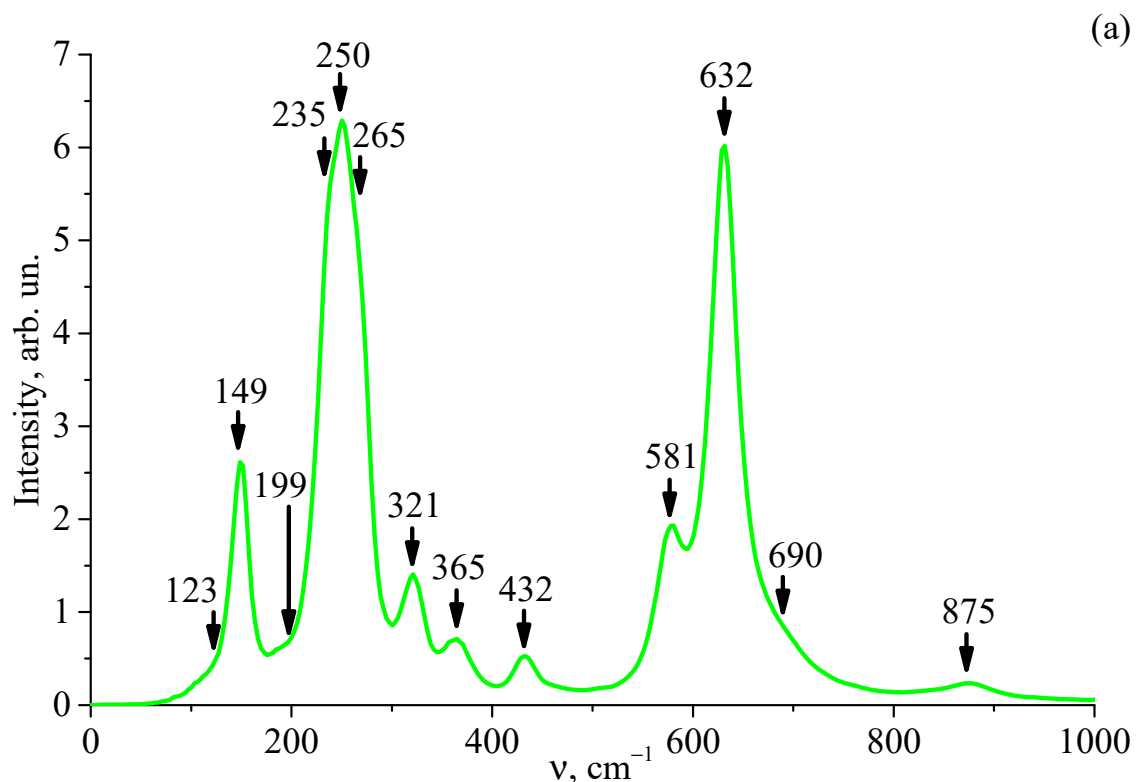


Figure 5. Cont.

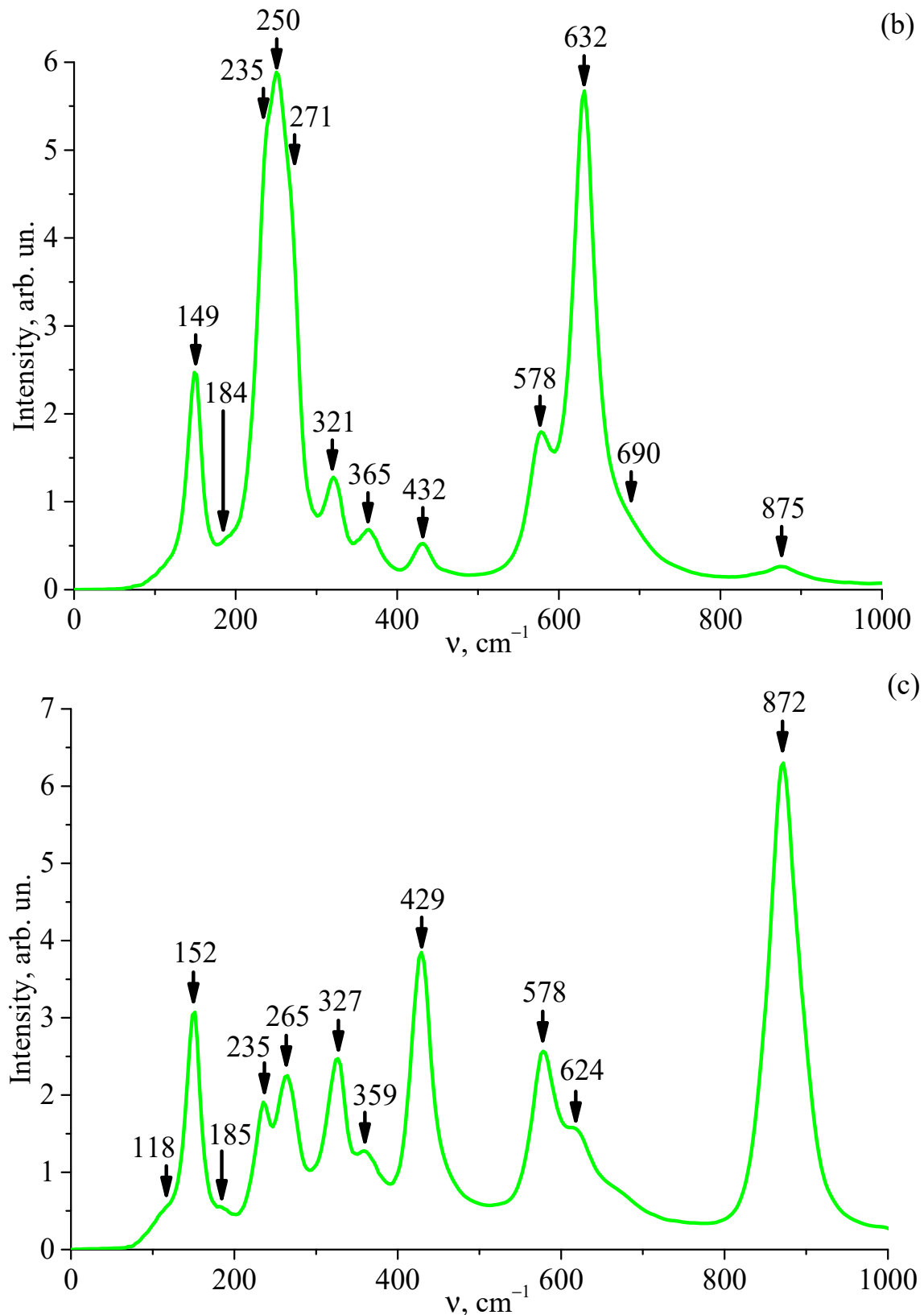


Figure 5. Raman spectra of the $\text{LiNbO}_3:\text{Y}^{3+}$ (0.46 wt%) crystal in scattering geometries $x(zz, zy)x$ (a), $y(zz, zx)y$ (b) and $z(xx, yy, xy)z$ (c). $\lambda_0 = 532 \text{ nm}$.

In the frequency range of $1000\text{--}2100 \text{ cm}^{-1}$, five second-order Raman lines are observed, the intensity of which is significantly lower than the intensity of the Raman lines corresponding to the fundamental vibrations of the lattice. In this case, two lines are visible

with frequencies of about 1790 cm^{-1} and 1940 cm^{-1} , somewhat exceeding the doubled value of the frequencies of the fundamental vibrations $4A_1(z)\text{LO}$ and $9E(x,y)\text{LO}$. That is, the lines with frequencies of about 1790 and 1940 cm^{-1} can be overtones of the fundamental vibrations $4A_1(z)\text{LO}$ and $9E(x,y)$ of the oxygen atoms of the oxygen octahedra O_6 . Previously, we have observed similar second-order Raman spectra in a number of LiNbO_3 and LiTaO_3 crystals of different compositions in the frequency range of $1000\text{--}2100\text{ cm}^{-1}$ [34–38].

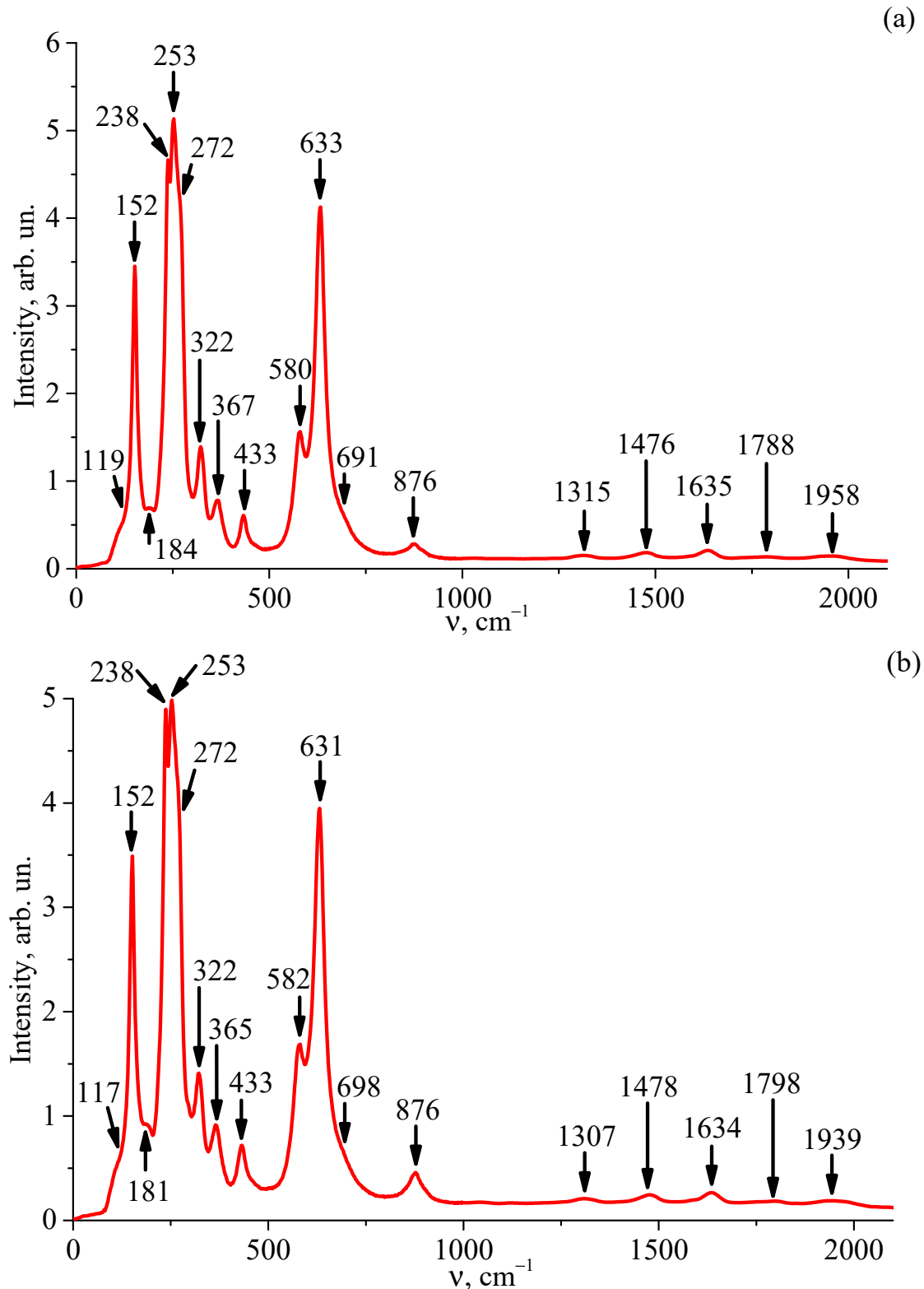


Figure 6. Cont.

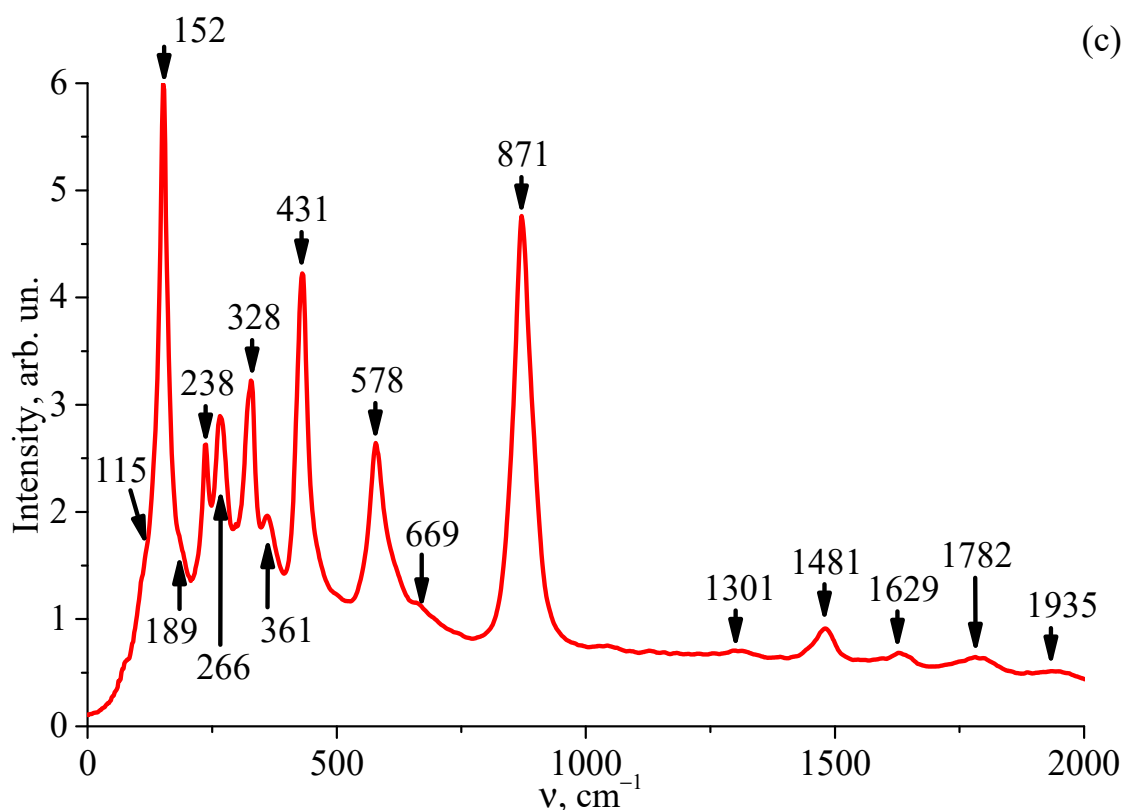


Figure 6. Raman spectra of the $\text{LiNbO}_3:\text{Y}^{3+}$ (0.46 wt%) crystal in scattering geometries $x(\text{zz}, \text{zy})\bar{x}$ (a), $y(\text{zz}, \text{zx})\bar{y}$ (b) and $z(\text{xx}, \text{yy}, \text{xy})\bar{z}$ (c). $\lambda_0 = 785 \text{ nm}$.

6. Raman and IR Absorption Spectra of $\text{LiNbO}_3:\text{Y}^{3+}$ (0.46 wt%) Crystal in the Region of Stretching Vibrations of OH-Groups

A basic type of defect that is formed in the LiNbO_3 crystal during growth by the Czochralski method in an air atmosphere is defects in the form of OH-groups [58–64]. In the ideal structure of the LiNbO_3 crystal of strictly stoichiometric composition ($R = 1$), there are no Nb_{Li} point defects, and the placement of hydrogen atoms is impossible [61]. The arrangement of hydrogen atoms in the structure of real LiNbO_3 crystals changes depending on the value of the R ratio, concentration, and type of dopant [58–64]. In this case, the configuration of the oxygen-octahedral clusters of the LiO_6 , NbO_6 , and MeO_6 structure is disrupted (Me is an impurity metal or a V, vacancy). The presence of hydrogen in the structure of the LiNbO_3 crystal also leads to the formation of complex defects: $\text{V}_{\text{Li}}\text{-OH}$, $\text{Nb}_{\text{Li}}\text{-OH}$, Me-OH , Me-OH-Me , etc. The presence of such defects results in a change in the nonlinear optical and ferroelectric characteristics of the crystal and affects such practically significant properties of LiNbO_3 as photoluminescence, photorefractive thermal fixation, dark conductivity, and photorefractive sensitivity [58]. It is natural to expect the manifestation of a defect in the form of OH-groups in the vibrational spectra.

Figure 7 shows a comparison of the recorded IR absorption and Raman spectra in the region of stretching vibrations of OH-groups.

The Raman lines with frequencies of 3431 cm^{-1} and 3438 cm^{-1} in the Raman spectrum and the lines with frequencies of 3489 cm^{-1} , 3527 cm^{-1} , and 3536 cm^{-1} in the IR absorption spectrum are related to the stretching vibrations of OH-groups. When entering the crystal lattice, the yttrium cation forms complex defects $\text{Y}_{\text{Nb}}^{3+}\text{-OH}$ and $\text{Y}_{\text{Li}}^{3+}\text{-OH-Y}_{\text{Nb}}^{3+}$, which correspond to the IR absorption lines of 3527 cm^{-1} and 3536 cm^{-1} . It should be noted that in the region of stretching vibrations of OH-groups, the frequencies in the Raman spectrum and in the IR absorption spectrum of the $\text{LiNbO}_3:\text{Y}^{3+}$ (0.46 wt%) crystal differ significantly,

and the Raman spectrum as a whole is shifted to the low-frequency region relative to the IR absorption spectrum by more than 50 cm^{-1} . In addition, for the $\text{LiNbO}_3\text{:Y}^{3+}(0.46\text{ wt}\%)$ crystal, the Raman line frequency ($3431\text{--}3438\text{ cm}^{-1}$) is shifted by about 40 cm^{-1} to the low-frequency region relative to the frequency of the 3482 cm^{-1} line in the IR absorption spectrum of the nominally pure congruent $\text{LiNbO}_{3\text{cong}}$ crystal ($R = 0.946$) and by about 30 cm^{-1} relative to the frequency of the 3466 cm^{-1} line in the IR absorption spectrum of the nominally pure stoichiometric LiNbO_3 crystal ($R = 1$) with a high degree of structural perfection, studied in [59,60]. It is also unexpected that in the Raman spectrum in the region of stretching vibrations of OH-groups, only one line is reliably observed. At the same time, several lines (at least three) are observed in the IR absorption spectrum in the region of stretching vibrations of OH-groups of non-stoichiometric ($R < 1$) LiNbO_3 crystals of different compositions [58–62]. Moreover, the number of lines in the IR absorption spectrum depends on the composition of the crystal. However, in the IR absorption spectrum of a LiNbO_3 crystal of strictly stoichiometric composition ($R = 1$) with a high degree of structural perfection, only one narrow line with a frequency of 3466 cm^{-1} has been observed [61]. The reasons for such a strong difference in the frequencies of the lines corresponding to stretching vibrations of OH-groups in the IR absorption spectra and Raman spectra currently remain unknown. One of the reasons may be the feature that the oxygen octahedra O_6 of the $\text{LiNbO}_3\text{:Y}^{3+}(0.46\text{ wt}\%)$ crystal structure have a shape close to the shape of a regular octahedron, i.e., they are centrosymmetric, and at the same time the vibrations of the OH-groups distort the shape of the O_6 octahedron negligibly little. For centrosymmetric structures, the rule of alternative prohibition applies: vibrations active in the IR absorption spectrum are prohibited in the Raman spectrum, and vice versa.

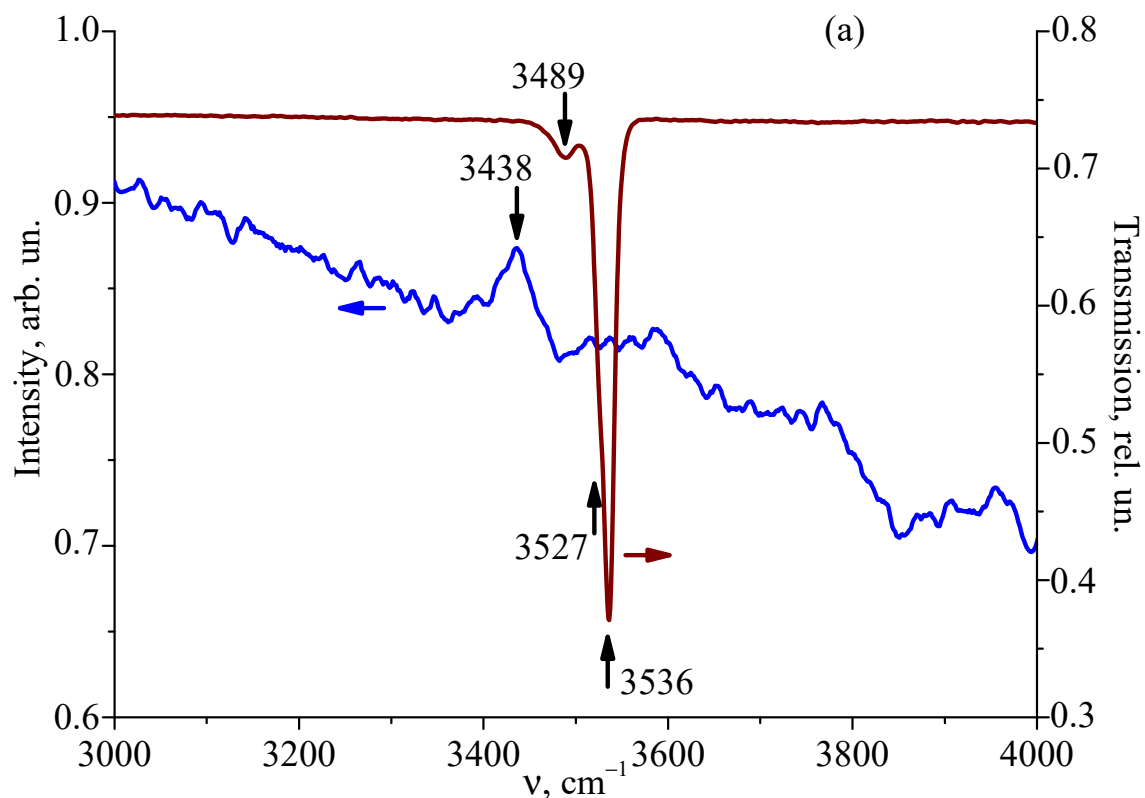


Figure 7. Cont.

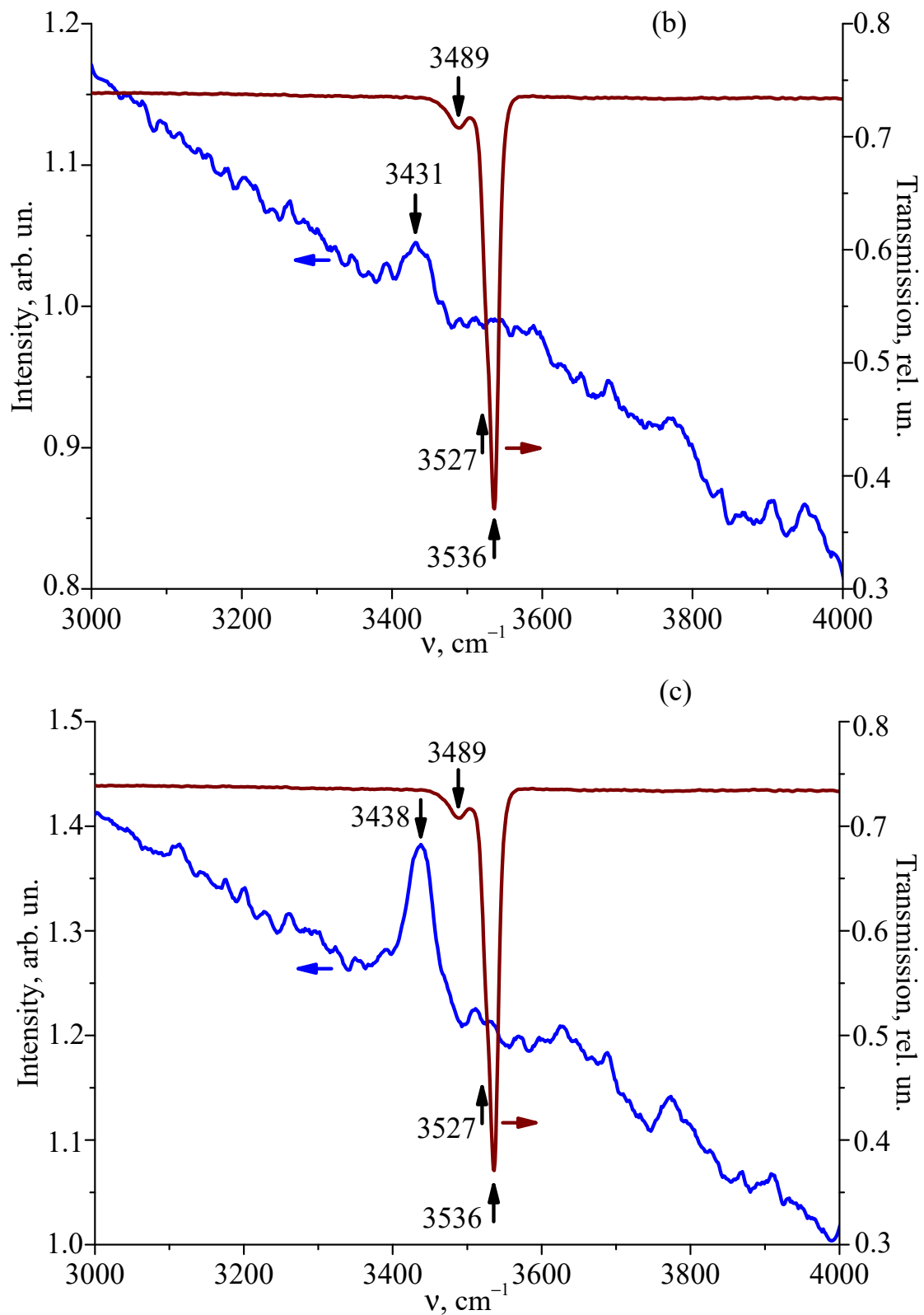


Figure 7. Comparison of IR absorption (dark red) and Raman spectra (blue) of the $\text{LiNbO}_3:\text{Y}^{3+}$ (0.46 wt%) crystal in the region of stretching vibrations of OH-groups in scattering geometries: $x(\text{zz}, \text{zy})\bar{x}$ (a), $y(\text{zz}, \text{zx})\bar{y}$ (b), $z(\text{xx}, \text{yy}, \text{xy})\bar{z}$ (c). Raman spectra were recorded upon excitation by a laser line with a wavelength of 532 nm.

7. Conclusions

In this paper, comparative studies of Raman spectra of photorefractive $\text{LiNbO}_3:\text{Y}^{3+}$ (0.46 wt%) single crystal excited by visible (532 nm) and near-IR (785 nm) laser sources in a wide frequency range ($100\text{--}4000\text{ cm}^{-1}$) are performed for the first time, and their interpretation is given taking into account the photorefractive effect (optical damage). It is found that the speckle structure of the photoinduced light scattering indicatrix of $\text{LiNbO}_3:\text{Y}^{3+}$ (0.46 wt%) crystal, in contrast to the speckle structure of LiNbO_3 crystals of other compositions, opens unexpectedly quickly—within the first second of laser radiation exposure to the crystal. With the irradiation time, the speckle structure of the PILS indicatrix is also found to exhibit atypical behavior caused by the peculiarities of the dissipation processes of laser-induced defects in the crystal. In the frequency range of $1000\text{--}2100\text{ cm}^{-1}$, five second-order Raman scattering lines have been detected for the first time, and the frequencies of two of them (about 1790 cm^{-1} and 1940 cm^{-1}) slightly have been observed to exceed the doubled value of the frequencies of fundamental vibrations of the $4\text{A}_1(\text{z})\text{LO}$ and $9\text{E}(\text{x},\text{y})$ symmetry types. That is, the lines with frequencies of about 1790 cm^{-1} and 1940 cm^{-1} may represent overtones of the fundamental vibrations of $4\text{A}_1(\text{z})\text{LO}$ and $9\text{E}(\text{x},\text{y})$. It is found that in the region of stretching vibrations of OH-groups ($3200\text{--}3800\text{ cm}^{-1}$) in the Raman spectrum of the $\text{LiNbO}_3:\text{Y}^{3+}$ (0.46 wt%) crystal, only one line with a frequency of about $3431\text{--}3438\text{ cm}^{-1}$ is observed. At the same time, in the IR absorption spectrum in the region of stretching vibrations of OH-groups of the $\text{LiNbO}_3:\text{Y}^{3+}$ (0.46 wt%) crystal and numerous non-stoichiometric ($R < 1$) LiNbO_3 crystals of different compositions studied in the literature [58–62], several lines (at least three) are observed. In this case, for the $\text{LiNbO}_3:\text{Y}^{3+}$ (0.46 wt%) crystal, the Raman spectrum as a whole is found to be shifted to the low-frequency region relative to the IR absorption spectrum by more than 50 cm^{-1} . It should be noted that in the IR absorption spectrum of the LiNbO_3 crystal of strictly stoichiometric composition ($R = 1$) with a high degree of structural perfection, as well as in the Raman spectrum of the $\text{LiNbO}_3:\text{Y}^{3+}$ (0.46 wt%) crystal, only one narrow line with a frequency of 3466 cm^{-1} was observed [59]. The reasons for such a strong enough difference in the frequencies of the lines corresponding to the stretching vibrations of OH-groups in the IR absorption spectra and Raman spectra currently remain unknown. It can be assumed that the oxygen octahedra O_6 of the $\text{LiNbO}_3:\text{Y}^{3+}$ (0.46 wt%) crystal structure has a shape close to the shape of a regular octahedron, i.e., are centrosymmetric. For centrosymmetric structures, the alternative prohibition rule applies: vibrations active in the IR absorption spectrum are prohibited in the Raman spectrum, and vice versa.

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References

1. Zapadlík, O.; Pejchal, J.; Babin, V.; Jary, V.; Vaněček, V.; Kučerková, R.; Jurek, K.; Beitlerová, A.; Nikl, M. GSAG:Ce scintillator: Insights from yttrium admixture. *RSC Adv.* **2025**, *15*, 2140–2151. [\[CrossRef\]](#)
2. Ermochenkova, I.M.; Zavartsev, Y.D.; Zagumennyi, A.I.; Yurasova, O.V.; Morozov, I.V.; Serebryakov, D.V. Scintillation $\text{Lu}_2\text{SiO}_5\text{-z}:\text{Y}^{3+}:\text{Ce}^{3+}:\text{Ca}^{2+}$ crystal for positron emission tomography. *Bull. Lebedev Phys. Inst.* **2024**, *51*, 25–29. [\[CrossRef\]](#)
3. Belov, M.V.; Zavartsev, Y.D.; Zavertyaev, M.V.; Zagumennyi, A.I.; Kozlov, V.A.; Kutovoi, S.A.; Pestovskii, N.V.; Savinov, S.Y. Scintillation properties of large $\text{Lu}_2\text{SiO}_5\text{-z}:\text{Y}^{3+}:\text{Ce}^{3+}:\text{Ca}^{2+}$ crystals. *Bull. Lebedev Phys. Inst.* **2022**, *49*, 121–124. [\[CrossRef\]](#)
4. Belov, M.V.; Vlasov, V.I.; Zavartsev, Y.D.; Zavertyaev, M.V.; Zagumennyi, A.I.; Kozlov, V.A.; Pestovskii, N.V.; Savinov, S.Y.; Tskhay, V.S. New scintillation crystals $\text{YAG}:\text{Yb}^{3+}:\text{Mg}^{2+}$ and $\text{YAG}:\text{Yb}^{3+}:\text{Ca}^{2+}:\text{Mg}^{2+}$ with a short decay time. *Bull. Lebedev Phys. Inst.* **2024**, *51*, 290–293. [\[CrossRef\]](#)
5. Wang, T.; Wang, Y.; Weng, Y.; Lv, L.; Guo, S.; Ding, C.; Liu, F.; Li, T.; Wang, B.; Peng, Z. Effect of yttrium doping on the properties of Nickel-Iron multiphase heterostructures at high current conditions. *Chem. Eng. Sci.* **2025**, *302*, 120859. [\[CrossRef\]](#)
6. Huang, Y.; Li, J.; Bai, L.; Chen, X.; Chen, S.; Zhang, H. Synthesis of magnetically recyclable cauliflower-like sonocatalyst yttrium doped ZrO_2 and sonocatalytic degradation of organic dye. *Desalin. Water Treat.* **2025**, *321*, 101049. [\[CrossRef\]](#)
7. Jiang, Y.; Zhu, L.; Tian, J.; Miao, H.; Tan, R.; Tian, Z.; Li, X.; Liu, Y. A high rate and stability O_3 -type cathode material based on a Y-doped $\text{NaNi}_{1/3}\text{Fe}_{1/3}\text{Mn}_{1/3}\text{O}_2$ matrix. *Mater. Today Commun.* **2025**, *46*, 112523. [\[CrossRef\]](#)
8. Luo, Q.; Wan, Y.; Wang, Z.; Gao, S.; Chen, Y.; Feng, C. Excellent-performing gas sensor based on Yttrium-doped ZnFe_2O_4 nanofibers for detection of n-Butanol. *J. Alloys Compd.* **2025**, *1027*, 180605. [\[CrossRef\]](#)
9. Wang, J.; Sun, C.; Bao, J.; Yang, Z.; Zhang, J.; Huang, X. Yttrium doping of perovskite oxide $\text{La}_2\text{Ti}_2\text{O}_7$ nanosheets for enhanced proton conduction and gas sensing under high humidity levels. *Sensors* **2025**, *25*, 901. [\[CrossRef\]](#)
10. Vatnik, S.M.; Osipov, V.V.; Luk'yashin, K.E.; Kravchenko, V.B.; Kopylov, Y.L.; Vedin, I.A.; Kurbatov, P.F. Multiwatt lasing of Nd:YAG laser ceramics containing 0.8 % and 1 % of Nd. *Quantum Electron.* **2014**, *44*, 585–587. [\[CrossRef\]](#)
11. Kaminskii, A.A. Laser crystals and ceramics: Recent advances. *Laser Photon. Rev.* **2007**, *1*, 93–177. [\[CrossRef\]](#)
12. Prokhorov, A.M.; Kuz'minov, Y.S. *Physics and Chemistry of Crystalline Lithium Niobate*; Adam Hilger: New York, NY, USA, 1990.
13. Aleksandrovskii, A.L.; Naumova, I.I.; Tarasenko, V.V.; Kholodnykh, A.I.; Yakovleva, G.I. Quasiphase-matched ee–e frequency conversion of light in $\text{LiNbO}_3:\text{Y}$ crystals with a regular domain structure. *Sov. J. Quantum Electron.* **1989**, *19*, 1343–1345. [\[CrossRef\]](#)
14. Volkov, V.V.; Laptev, G.D.; Morozov, E.Y.; Naumova, I.I.; Chirkin, A.S. Consecutive quasi-phase-matched generation of the third harmonic of the radiation from an Nd:YAG laser in a periodically poled $\text{Y}:\text{LiNbO}_3$ crystal. *Quantum Electron.* **1998**, *28*, 1020–1021. [\[CrossRef\]](#)
15. Kornienko, V.V.; Kitaeva, G.K.; Naumova, I.I.; Tuchak, A.N.; Penin, A.N.; Yakunin, P.V. Evaluating the spectral sensitivity of the nonlinear-optical terahertz wave radiation detectors via spontaneous parametric down-conversion spectra. *Opt. Spectrosc.* **2014**, *116*, 520–528. [\[CrossRef\]](#)
16. Goul'Kov, M.; Odoulov, S.; Naumova, I.; Agulló-López, F.; Calvo, G.; Podivilov, E.; Sturman, B.; Pruneri, V. Degenerate parametric light scattering in periodically poled $\text{LiNbO}_3:\text{Y}:\text{Fe}$. *Phys. Rev. Lett.* **2001**, *86*, 4021–4024. [\[CrossRef\]](#) [\[PubMed\]](#)
17. Barilov, D.; Shumelyuk, A.; Hesselink, L.; Sturman, B.; Odoulov, S. Coupling of orthogonally polarized waves and vectorial coherent oscillation in periodically poled $\text{LiNbO}_3:\text{Y}:\text{Fe}$. *J. Opt. Soc. Am. B* **2003**, *20*, 1649–1655. [\[CrossRef\]](#)
18. Aleksandrovskii, A.L.; Ershova, G.I.; Kitaeva, G.K.; Kulik, S.P.; Naumova, I.I.; Tarasenko, V.V. Dispersion of the refractive indices of $\text{LiNbO}_3:\text{Mg}$ and $\text{LiNbO}_3:\text{Y}$ crystals. *Sov. J. Quantum Electron.* **1991**, *21*, 225–227. [\[CrossRef\]](#)
19. Chirkin, A.S.; Volkov, V.V. Consecutive Quasi-phase-matched interactions of light waves in periodically poled nonlinear optical crystals. *J. Russ. Laser Res.* **1998**, *19*, 409–426. [\[CrossRef\]](#)
20. Aleksandrovski, A.L.; Naumova, I.I.; Tarasenko, V.V. Lithium niobate with laminar domains for frequency tripling of Nd: YAG laser radiation. *Ferroelectrics* **1993**, *141*, 147–152. [\[CrossRef\]](#)
21. Bihan, R.L.; Averty, D.; Pain, D.; Aleksandrovski, A.L.; Naumova, I.I. Study of lithium niobate with periodically reversed domains. *Ferroelectrics* **1995**, *172*, 181–186. [\[CrossRef\]](#)
22. Kornienko, V.V.; Kitaeva, G.K.; Sedlmeir, F.; Leuchs, G.; Schwefel, H.G.L. Towards terahertz detection and calibration through spontaneous parametric down-conversion in the terahertz idler-frequency range generated by a 795 nm diode laser system. *APL Photonics* **2018**, *3*, 051704. [\[CrossRef\]](#)
23. Ma, G.H.; Tang, S.H.; Kitaeva, G.K.; Naumova, I.I. Terahertz generation in Czochralski-grown periodically poled $\text{Mg}:\text{Y}:\text{LiNbO}_3$ by optical rectification. *J. Opt. Soc. Am. B* **2006**, *23*, 81–89. [\[CrossRef\]](#)
24. Odoulov, S.; Shumelyuk, A.; Thien, R.; von Bally, G. Reflection hologram recording in periodically poled $\text{LiNbO}_3:\text{Y}:\text{Fe}$. *J. Opt. A* **2004**, *6*, 224–228. [\[CrossRef\]](#)
25. Odoulov, S.; Tarabrova, T.; Shumelyuk, A.; Naumova, I.I.; Chaplina, T.O. Photorefractive properties of bulk periodically poled $\text{LiNbO}_3:\text{Y}:\text{Fe}$. *Opt. Mater.* **2001**, *18*, 65–68. [\[CrossRef\]](#)
26. Odoulov, S.; Tarabrova, T.; Shumelyuk, A.; Naumova, I.I.; Chaplina, T.O. Photorefractive response of bulk periodically poled $\text{LiNbO}_3:\text{Y}:\text{Fe}$ at high and low spatial frequencies. *Phys. Rev. Lett.* **2000**, *84*, 3294–3297. [\[CrossRef\]](#)

27. Sidorov, N.V.; Serebryakov, Y.A. The structural ordering and photorefraction in lithium niobate admixed crystals. *Ferroelectrics* **1994**, *160*, 101–105. [CrossRef]
28. Sidorov, N.V.; Chufyrev, P.G.; Palatnikov, M.N.; Mel'nik, N.N.; Zhelezov, Y.A.; Khomich, V.Y. Manifestation of a photorefractive effect in Raman spectra of lithium niobate crystals of different compositions. *Quantum Electron.* **2004**, *34*, 1177–1179. [CrossRef]
29. Sidorov, N.V.; Chufyrev, P.G.; Palatnikov, M.N.; Kalinnikov, V.T.; Mel'nik, N.N. Doping effect on the Raman spectrum and photorefractive properties of LiNbO₃ crystals. *Inorg. Mater.* **2005**, *41*, 164–171. [CrossRef]
30. Chufyrev, P.G.; Sidorov, N.V.; Palatnikov, M.N.; Yanichev, A.A. Manifestation of the specific structural features of lithium niobate single crystals of different composition in their Raman spectra. *Opt. Spectrosc.* **2008**, *105*, 913–918. [CrossRef]
31. Voron'ko, Y.K.; Kudryavtsev, A.B.; Osiko, V.V.; Sobol', A.A.; Sorokin, E.V. Raman scattering study of phase transitions in lithium niobate and tantalate. *Sov. Phys. Solid State* **1987**, *29*, 771–775.
32. Voron'ko, Y.K.; Kudryavtsev, A.B.; Sobol', A.A.; Sorokin, E.V. High-temperature Raman spectroscopy: A tool for probing phase transformations of laser crystals. *Trydy Inst. Obsch. Fiz. AN SSSR [Proc. Gen. Phys. Inst. AS USSR]* **1991**, *29*, 50–100. (In Russian)
33. Lengyel, K.; Szaller, Z.; Péter, Á.; Polgár, K.; Kovács, L. Microscopic and Raman spectroscopic investigation of the domain structures in LiNbO₃:Y:Mg crystals. *Ferroelectrics* **2008**, *368*, 3–11. [CrossRef]
34. Gorelik, V.S.; Abdurakhmonov, S.D. Overtone Raman scattering in lithium niobate single crystal doped with terbium. *Crystallogr. Rep.* **2022**, *67*, 252–255. [CrossRef]
35. Sidorov, N.V.; Pyatyshev, A.Y.; Stroganova, E.V.; Galutskiy, V.V.; Skrabatun, A.V. Features of Raman scattering in LiNbO₃:Er³⁺ crystal with erbium gradient. *J. Raman Spectrosc.* **2025**, *56*, 1100–1113. [CrossRef]
36. Sidorov, N.; Palatnikov, M.; Pyatyshev, A.; Sverbil, P. Second-order Raman scattering in ferroelectric ceramic solid solutions LiNb_xTa_{1-x}O₃. *Crystals* **2022**, *12*, 456. [CrossRef]
37. Sidorov, N.V.; Pyatyshev, A.Y.; Galutskiy, V.V.; Stroganova, E.V.; Skrabatun, A.V. Features of the defect structure of a lithium-gradient nonlinear optical single crystal LiNbO₃ and their manifestation in the Raman spectra. *Spectrochim. Acta A* **2025**, *327*, 125340. [CrossRef]
38. Sidorov, N.; Pyatyshev, A.; Stroganova, E.; Galutskiy, V.; Bushunov, A.; Tarabrin, M. Features of the defect structure of the compositionally homogeneous crystal LiNbO₃:Er³⁺ (3.1 wt%) and the gradient crystal LiNbO₃:Er³⁺ and their manifestation in the IR transmission spectra in the region of stretching vibrations of hydrogen atoms of OH⁻-groups. *Materials* **2025**, *18*, 579. [CrossRef]
39. Palatnikov, M.N.; Sidorov, N.V.; Biryukova, I.V.; Shcherbina, O.B.; Kalinnikov, V.T. Granulated charge for lithium niobate single crystals growth. *Perspekt. Mater. [Perspect. Mater.]* **2011**, *2*, 93–97. (In Russian). Available online: <https://j-pm.tilda.ws/page54744501.html> (accessed on 13 March 2026). [CrossRef]
40. Palatnikov, M.N.; Sandler, V.A.; Sidorov, N.V.; Efremov, I.N.; Makarova, O.V. Methods for controlling the degree of unipolarity of large LiNbO₃ crystals. *Instrum. Exp. Tech.* **2020**, *63*, 383–387. [CrossRef]
41. ANSI/IEEE Std 176-1987; Standard on Piezoelectricity. The Institute of Electrical and Electronics Engineers, Inc. (IEEE): New York, NY, USA, 1998. [CrossRef]
42. Maksimenko, V.A.; Syui, A.V.; Karpets, Y.M. *Photoinduced Processes in Lithium Niobate Crystals*; FIZMATLIT: Moscow, Russia, 2008. (In Russian)
43. Sidorov, N.V.; Pikoul', O.Y.; Teplyakova, N.A.; Palatnikov, M.N. *Laser Conoscopy and Photoinduced Light Scattering in Research of Properties of Optically Nonlinear Lithium Niobate Crystal*; RAS: Moscow, Russia, 2019. (In Russian). Available online: <https://new.ras.ru/work-new/publishing/monographs/lazernaya-konoskopiya-i-fotoindutsirovannoe-rasseyanie-sveta-v-issledovaniyakh-svoystv-nelineynno-opt/> (accessed on 13 March 2026).
44. Atsuo, Y.; Hitoshi, T.; Masaki, S. Liquid phase epitaxial growth of LiNbO₃ thin film using Li₂O-B₂O₃ flux system. *J. Cryst. Growth* **1993**, *132*, 48–60. [CrossRef]
45. Can, H.; Shichao, W.; Ning, Y. Subsolidus phase relations and the crystallization region of LiNbO₃ in the system Li₂O-B₂O₃-Nb₂O₅. *J. Alloys Compd.* **2010**, *502*, 211–214. [CrossRef]
46. Palatnikov, M.; Sidorov, N.; Kadetova, A.; Titov, R.; Biryukova, I.; Makarova, O.; Manukovskaya, D.; Teplyakova, N.; Efremov, I. Growing, structure and optical properties of LiNbO₃:B crystals, a material for laser radiation transformation. *Materials* **2023**, *16*, 732. [CrossRef]
47. Titov, R.; Kadetova, A.; Tokko, O.; Sidorov, N.; Palatnikov, M.; Teplyakova, N.; Masloboeva, S.; Biryukova, I.; Efremov, I.; Manukovskaya, D. Influence of doping technology on the stoichiometry and features of the localization of B³⁺ cations in LiNbO₃:B single crystals. *Crystals* **2023**, *13*, 1245. [CrossRef]
48. Anderson, A. (Ed.) *The Raman Effect. Volume 2: Applications*; Marcel Dekker, Inc.: New York, NY, USA, 1973.
49. Sanna, S.; Neufeld, S.; Rüsing, M.; Berth, G.; Zrenner, A.; Schmidt, W.G. Raman scattering efficiency in LiTaO₃ and LiNbO₃ crystals. *Phys. Rev. B* **2015**, *91*, 224302. [CrossRef]
50. Margueron, S.; Bartasyte, A.; Glazer, A.M.; Simon, E.; Hlinka, J.; Gregora, I.; Gleize, J. Resolved E-symmetry zone-centre phonons in LiTaO₃ and LiNbO₃. *J. Appl. Phys.* **2012**, *111*, 104105. [CrossRef]

51. Barker, A.S., Jr.; Loudon, R. Dielectric properties and optical phonons in LiNbO₃. *Phys. Rev.* **1967**, *158*, 433–445. [[CrossRef](#)]
52. Ridah, A.; Bourson, P.; Fontana, M.D.; Malovichko, G. The composition dependence of the Raman spectrum and new assignment of the phonons in LiNbO₃. *J. Phys. Cond. Matter* **1997**, *9*, 9687–9693. [[CrossRef](#)]
53. Savova, I.; Savatinova, I.; Liarokapis, E. Phase composition of Z-cut protonated LiNbO₃: A Raman study. *Opt. Mater.* **2001**, *16*, 353–360. [[CrossRef](#)]
54. Friedrich, M.; Riefer, A.; Sanna, S.; Schmidt, W.G.; Schindlmayr, A. Phonon dispersion and zero-point renormalization of LiNbO₃ from density-functional perturbation theory. *J. Phys. Cond. Matter* **2015**, *27*, 385402. [[CrossRef](#)]
55. Repelin, Y.; Husson, E.; Bennani, F.; Proust, C. Raman spectroscopy of lithium niobate and lithium tantalate. Force field calculations. *J. Phys. Chem. Solids* **1999**, *60*, 819–825. [[CrossRef](#)]
56. Zhang, D.; Chen, X.; Jin, Y.; Cao, X.; Zhu, D.; Wang, Y.; Ding, G.; Cui, Y.; Chen, C.; Wu, Z.; et al. Raman study on vapor-phase equilibrated Er:LiNbO₃ and Er:Ti:LiNbO₃ crystals. *Appl. Phys. A* **2001**, *72*, 95–102. [[CrossRef](#)]
57. Yang, X.; Lan, G.; Li, B.; Wang, H. Raman spectra and directional dispersion in LiNbO₃ and LiTaO₃. *Phys. Status Solidi b/Basic Sol. State Phys.* **1987**, *142*, 287–300. [[CrossRef](#)]
58. Volk, T.; Wöhlecke, M. *Lithium Niobate: Defects, Photorefractive and Ferroelectric Switching*; Springer: Berlin/Heidelberg, Germany, 2009. [[CrossRef](#)]
59. Lengyel, K.; Péter, Á.; Kovács, L.; Corradi, G.; Pálfi, L.; Hebling, J.; Unferdorben, M.; Dravecz, G.; Hajdara, I.; Szaller, Z.; et al. Growth, defect structure, and THz application of stoichiometric lithium niobate. *Appl. Phys. Rev.* **2015**, *2*, 040601. [[CrossRef](#)]
60. Cabrera, J.M.; Olivares, J.; Carrascosa, M.; Rams, J.; Müller, R.; Diéguez, E. Hydrogen in lithium niobate. *Adv. Phys.* **1996**, *45*, 349–392. [[CrossRef](#)]
61. Wöhlecke, M.; Kovács, L. OH[−] ions in oxide crystals. *Crit. Rev. Solid State Mater. Sci.* **2001**, *26*, 1–86. [[CrossRef](#)]
62. Kovács, L.; Rebouta, L.; Soarest, J.C.; da Silva, M.F.; Hage-Ali, M.; Stoquert, J.P.; Siffert, P.; Sanz-Garcia, J.A.; Corradi, G.; Szaller, Z.; et al. On the lattice site of trivalent dopants and the structure of Mg²⁺-OH[−]-M³⁺ defects in LiNbO₃:Mg crystals. *J. Phys. Cond. Matter* **1993**, *5*, 781–794. [[CrossRef](#)]
63. Köhler, T.; Zschornak, M.; Röder, C.; Hanzig, J.; Gärtner, G.; Leisegang, T.; Mehner, E.; Stöcker, H.; Meyer, D.C. Chemical environment and occupation sites of hydrogen in LiMO₃. *J. Mater. Chem. C* **2023**, *11*, 520–538. [[CrossRef](#)]
64. Savelyev, E.; Akhmatkhanov, A.; Tronche, H.; Doutre, F.; Lunghi, T.; Baldi, P.; Shur, V. Kinetics of the domain structure in uniform electric field in LiNbO₃ with surface layer modified by soft proton exchange. *Phys. Status Solidi rrl/Rapid Res. Lett.* **2024**, *18*, 2300420. [[CrossRef](#)]

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