

Article

Some Optical Properties of $\text{LiNbO}_3\text{:Gd}^{3+}(0.003)\text{:Mg}^{2+}(0.65 \text{ wt } \%)$ Single Crystal: A Promising Material for Laser Radiation Conversion

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Abstract: A nonlinear optical double-doped single-crystal $\text{LiNbO}_3\text{:Gd:Mg}$ (Gd concentration is 0.003, Mg—0.65 wt % in the crystal) has been researched by several optical methods: laser conoscopy, photoinduced light scattering (PILS), optical spectroscopy, and Raman scattering. The crystal has been shown to have no photorefractive effect and a high optical uniformity. Fine features of the crystal structure have been studied via Raman spectra. Spectra have been registered in the first and second orders, they have been excited by visible (532 nm) and near-IR (785 nm) lasers. Registered Raman spectra have the fundamental vibrations of the crystal lattice of the $A_1(\text{TO,LO})$ - and $E(\text{TO,LO})$ -type symmetry located in the range of $150\text{--}900 \text{ cm}^{-1}$. A number of low-intensity Raman bands in the $900\text{--}2000 \text{ cm}^{-1}$ region have been determined to correspond to the second-order Raman spectrum. These bands are polarized and appear only in certain polarization-scattering geometries. They appear in the spectrum excited by visible radiation, but their number and intensity are much lower than those excited by near-IR lasers. Oxygen-octahedral MeO_6 clusters in our case can contain Li, Nb, Gd, or Mg in the Me site. The clusters in the $\text{LiNbO}_3\text{:Gd:Mg}$ crystal structure are slightly distorted compared with similar clusters in the nominally pure LiNbO_3 crystal. It has been established that the value $R = [\text{Li}]/[\text{Nb}]$ in the studied crystal is ≈ 1 . Such a ratio usually characterizes a nominally pure stoichiometric crystal.

Keywords: lithium niobate; single crystal; double doping; photorefractive; laser conoscopy; photoinduced light scattering; Raman scattering; second order spectra



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1. Introduction

Modern physical materials science is highly interested in the development of optical materials with a low photorefractive effect (also known as optical damage). Such materials can be based on a nonlinear optical single crystal of lithium niobate (LN, LiNbO_3). LN in a crystal state has high nonlinear optical coefficients, which is crucial for the development of functional materials. Laser radiation can be generated, converted, and modulated using such materials [1–6]. In this case, an important requirement in the conversion of both laser and broadband radiation is minimization of various distortions that are inevitably present in the crystalline matrix. There are a number of factors that significantly limit the possibilities of creating highly advanced optical materials for various purposes [6–11] based on LiNbO_3 . The optical damage phenomenon is an effect of a photoinduced change in the refractive indices. It is the most important factor, since it causes strong distortions of photoluminescence and destroys the laser radiation wavefront passing through the LiNbO_3 crystal. We should also expect such compositional non-uniformities as microstructures

(clusters) in the structure of the LiNbO_3 crystal; they have various sizes and their structure differs from that of the crystalline matrix.

$\text{LiNbO}_3\text{:Mg}$ (5.0 mol % or 0.85 wt %) is LiNbO_3 single-crystal-based optically highly perfect and compositionally uniform material. It has a low photorefractive effect and it is currently used for optical frequency conversion in the phase quasi-phase-matching mode on regular domain structures (PPLN—periodically-poled LiNbO_3) [12–15]. However, such a strong doping decreases compositional and optical uniformity of a single-doped crystal compared with a nominally pure congruent crystal. The decrease is caused by the closeness of the magnesium concentration in the $\text{LiNbO}_3\text{:Mg}$ (0.85 wt %) crystal to the threshold value of the magnesium concentration in LN (0.935 wt % or 5.5 mol %). Dopants tend to incorporate into certain positions of LN structure. The threshold changes abruptly the incorporation mechanism of the dopant [16]. Thus, it is interesting to investigate the possibilities of double doping of the LN crystal. Double and triple doping can create highly perfect LN single crystals with an improved compositional uniformity [17]; the magnesium concentration is expected to be significantly lower than the threshold concentration. Double doping provides finer control than single doping. Doping controls many properties of an LN crystal. The most important ones are the alteration of the cations along the LN crystal polar axis and the polarizability of MeO_6 clusters. Me sites in general can be occupied with Li, Nb, vacancy, impurity, or doping metal. The alteration of cations determines the magnitude of spontaneous polarization, and the MeO_6 cluster polarizability determines the nonlinear optical properties of the crystal. Doping (including double and multiple doping) also influences the type and concentration of defects in a crystal. Defects can be both point and complex (extended). These defects produce deep and shallow energy levels in the LN band gap, which significantly affects the magnitude of the photorefractive effect and the optical damage resistance of the crystal [6]. Nonlinear optical coefficients are higher in perfect double-doped LiNbO_3 crystals, including those co-doped with magnesium, compared with single-doped crystals [18,19].

Important information about the structural perfection, compositional uniformity, and optical damage resistance of LN crystals can be obtained using a set of methods: laser conoscopy, photoinduced light scattering (PILS), and Raman spectroscopy of the first and second orders. The Raman spectra are sensitive to the slightest rearrangements in the structural units of the LN crystal [7,8,10,20–22]. Second-order spectra are especially sensitive and informative because they are absent from highly perfect crystals. Second-order Raman spectra exist only because of two factors: the disordering of the crystal structure and the anharmonic interaction between the structural units of the crystal [10,23–25]. Thus, the more perfect the crystal structure is, the less intense and less “rich” the second-order Raman spectrum should be. The Raman spectra of various substances obtained upon excitation in the visible and near IR regions can noticeably differ from each other [26,27]. This may be caused by several reasons: different sensitivities of their secondary structures, structural disorder, and anharmonicity, which inevitably exist in different crystals. By the secondary structure we mean micro- and macrostructures, clusters, and point defects. Point defects can be caused by irregularly located intrinsic, doping, and impurity atoms.

In this work, the features of the defect structure, compositional uniformity, and photorefractive properties are investigated in a double-doped $\text{LiNbO}_3\text{:Gd:Mg}$ (Gd concentration is 0.003, Mg—0.65 wt % in the crystal) single crystal. We investigated Raman spectroscopy in the frequency range $50\text{--}2000\text{ cm}^{-1}$, and spectra were excited in the visible and near-IR region. Optical spectroscopy, laser conoscopy, and PILS were also applied in the study. The compositional uniformity and photorefractive properties of the $\text{LiNbO}_3\text{:Gd:Mg}$ crystal were controlled with those for nominally pure (undoped) crystals of congruent (CLN, $R = [\text{Li}]/[\text{Nb}] = 0.946$) and stoichiometric (SLN, $R = 1$) compositions. The Raman spectra of a series of doubly doped $\text{LiNbO}_3\text{:Gd:Mg}$ crystals of various compositions have been previously studied in [20]. The crystal structure of samples with relatively low concentrations of Gd^{3+} and Mg^{2+} are characterized by better ordering in the cation arrangement along the polar axis. However, in [20], only the Raman spectra of fundamental vibrations

of the crystal lattice have been studied in the frequency range 50–1000 cm^{-1} . Second-order Raman spectra (above 1000 cm^{-1}) have not been recorded in [20] due to the insufficient sensitivity of the spectrometers of that time. In addition, the $\text{LiNbO}_3\text{:Gd:Mg}$ crystal has not been previously studied by optical spectroscopy, laser conoscopy, and PILS. Doping Gd^{3+} and Mg^{2+} cations have different valencies and ionic radii. Both are non-photorefractive dopants. Doping affects the crystal defectivity, spontaneous polarization, the geometry of NbO_6 clusters, and the effect of photorefraction. The two different dopants have different influences on these factors. At the same time, additional Raman bands appear upon doping with magnesium > 3.0 wt %. The bands correspond to pseudoscalar fundamental lattice vibrations of the A_2 symmetry type, which are forbidden by the selection rules for the $R3c$ symmetry space group (SPGR) [28]. An increase in the magnesium concentration in single- and double-doped LN crystals increases the intensity of E-symmetry-type Raman vibrations without a noticeable frequency shift [29–31].

2. Materials and Methods

The creation of optically and compositionally uniform LN crystals with double doping by the Czochralski method is quite a difficult task. It becomes even more complex when the concentration of one of the dopants is significantly higher than the concentration of the other one. Mg and Gd have strongly different dopant distribution coefficients in LN: $K_{\text{DMg}} \approx 1.1$, $K_{\text{DGd}} \approx 0.25$ [20]. Consequently, the composition of the melt layer near the crystallization front during crystal growth can simultaneously have an excess of one dopant and a lack of the other. Thus, the composition of a doped crystal cone almost always fails to coincide with the composition of the bottom of the crystal; such a difference causes compositional and optical non-uniformity. Thus, different parts of the crystal will have substantially different characteristics. To minimize such shortcomings, it is necessary to experimentally select the optimal technological parameters of crystal growth and their combinations: temperature gradients in the melt and growth zones, and the speed of rotation and pulling of the crystal. The shortcomings are also eliminated by the effective technological methods: melt pre-treatment before crystal growth, a special design of the thermal unit, the use of low crystallization rates, long after-growth annealing, and appropriate conditions for electro-thermal treatment of the crystal [6,20].

The charge was synthesized using Nb_2O_5 ($<3 \times 10^{-4}$ wt % of each impurity, Solikamsk Magnesium Works, Solikamsk, Russia) prepared due to Russian technical standard 1763–025-00545484–2000 and Li_2CO_3 ($<3 \times 10^{-4}$ wt % of each impurity, Solikamsk Magnesium Works, Solikamsk, Russia). These components were mixed under certain conditions in order to prepare granulated congruent charge ($[\text{Li}_2\text{O}] = 48.6$ mol %). Ready charge of any composition had a high bulk density (~ 3.4 g/ cm^3). The preparation of the charge is described in detail in [6,32].

The congruent melt ($[\text{Li}]/[\text{Nb}] = 0.946$) was directly doped with Gd_2O_3 (not more than 10^{-3} of each impurity, Neva Reactiv, Russia) and MgO (not more than 10^{-4} of each impurity, Himkraft, Russia) oxides. Table 1 shows the concentration of basic impurities in the granular charge and the grown $\text{LiNbO}_3\text{:Gd:Mg}$ single crystal.

Table 1. Impurity concentrations (C, wt %) in the granular charge, in the cone and bottom parts of the $\text{LiNbO}_3\text{:Gd:Mg}$ crystal.

Impurity		Mn	Ni	Al	Fe	Cr, Cu, V	Pb, Sn	Bi	Mg	Si, Ti, Mo, Ca, Co	Sb	Zr
$C \cdot 10^{-3}$, wt %	Charge	<0.2	<0.3	<0.3	<0.3	0.3	<0.5	0.5	0.5	1	2.1	<10
	Crystal cone	<0.2	<0.3	<0.3	0.32	0.3	<0.5	0.5	0.53	1	1.7	10
	Crystal bottom	<0.2	<0.3	1	0.38	0.3	<0.5	0.5	0.58	1	2	10

The melt was overheated for 8–11 h by 180–200 °C relative to the regular LN melting temperature ($T_{\text{melt}} = 1263$ °C) before the seeding. This procedure homogenizes the impurities in the melt.

An $\text{LiNbO}_3\text{:Gd:Mg}$ single crystal was grown in air from a melt by the Czochralski method. Platinum crucibles, 75 mm in diameter, were used during growth. Crystals were grown at a low axis gradient (~ 2.5 deg/cm). According to the Czochralski method, pulling was carried out along the polar axis (Z-cut, (001)). The rotation speed was 16–18 rpm and the speed of crystal pulling was 0.7 mm/h. The crystal increment rate was 1.02–1.04 mm/h. Growth was carried out at the Kristall-2 facility (Voroshilovgradsky zavod electronnogo mashinostroeniya, Voroshilovgrad, USSR) equipped with automatic crystal diameter control. The $\text{LiNbO}_3\text{:Gd:Mg}$ growth parameters of the crystal were selected based on the need to obtain a flat crystallization front, which should ensure a sufficiently high structural perfection of the crystal. The growth was considered finished when the $\text{LiNbO}_3\text{:Mg:Gd}$ crystal achieved ≤ 275 g; a growth unit weight sensor determined the crystal weight. An exact weight of the $\text{LiNbO}_3\text{:Gd:Mg}$ crystal was determined after extraction of the crystal seed. Approximately 25% of the total melt weight transferred into the crystal. The grown crystal had a flat crystallization front and the following geometric dimensions: diameter ($\varnothing$) ≈ 38 mm, length of the cylindrical part $L_c \approx 40$ mm. To relieve thermoelastic stresses, the grown crystal was subjected to heat treatment in an air atmosphere at 1500 K for 15 h in a high-temperature annealing furnace «Lantan» (Voroshilovgradsky zavod electronnogo mashinostroeniya, Voroshilovgrad, USSR). The design of the thermal unit used had a double “insulation”, it is described in [33]. The thermal unit creates an isothermal zone in the bulk of the platinum screen. The zone serves for postgrowth annealing of the crystal. It also provides a small temperature gradient at the crystallization front during crystal growth.

After growth, the $\text{LiNbO}_3\text{:Gd:Mg}$ crystal was not cooled immediately; it was annealed at 1200 °C in a growth facility for 10 h and only then cooled at a controlled rate of ~ 50 °C/h. The prolonged post-growth annealing was carried out in the isothermal zone under the platinum screen. This step homogenizes the composition of the doped crystal and relieves possible thermal and mechanical stresses.

Control CLN and SLN single crystals were grown using a similar sequencing: CLN from a congruent melt ($R = 0.946$) and SLN from a melt with 58.5 mol % Li_2O .

As-grown CLN, SLN, and $\text{LiNbO}_3\text{:Gd:Mg}$ crystals are not strictly single domains. All LN crystals are supposed to be turned to a single domain state; the procedure is called high-temperature electrodiffusion annealing: a constant electric voltage is applied to the polar cuts of the LN crystal during its cooling at a slow rate of 20 °C/h in the temperature range ~ 1230 –870 °C.

The distribution of a dopant concentration in the charge and $\text{LiNbO}_3\text{:Gd:Mg}$ crystal was determined by an analysis of plates cut from the top (closest to the cone) and bottom parts of the boule. The concentrations of different dopants in the milled samples were determined by different methods. Inductively coupled plasma atomic emission spectroscopy was used to study Mg concentration (ICP AES) on an Optima 8300 ICP-OES spectrometer (PerkinElmer, Hopkinton, MA, USA). Atomic absorption spectrometry (AAS) was used to study Gd concentration on a Kvant-FA instrument (GRANAT, Russia, Moscow).

The samples for investigations by Raman spectroscopy, optical spectroscopy, laser conoscopy, and PILS were parallelepipeds. Pieces were cut from the boule bulk. Their dimensions were $4.93 \times 5.98 \times 8.41$ mm³, and the ribs of the samples coincided with the directions of the principal LN crystallophysical axes. Careful polishing was applied to the faces of the parallelepipeds.

Experimental setups for recording conoscopic patterns by laser conoscopy and PILS patterns are described in the book [32]. Conoscopic patterns were excited by a laser radiation with a wavelength of 532 nm and powers of 1 and 90 mW. The optical transmission spectra of the single crystal were recorded on a UNICO 2800 UV/VIS spectrophotometer (United Products & Instruments, Dayton, NJ, USA). The range of detection was 190–1100 nm with a resolution of 0.2 nm. A BWS465-532S spectrometer (B&W Tek, Plains-

boro Township, NJ, USA) was used while recording the Raman spectra in the visible region. This setup is able to fix spectra in the range of 50–4000 cm^{-1} with a resolution of 4.5 cm^{-1} . A BWS465-785H spectrometer (B&W Tek, Plainsboro Township, NJ, USA) recorded the Raman spectra in the near-IR region in the range of 50–2850 cm^{-1} with a resolution of 3.5 cm^{-1} . To excite the Raman spectrum in the visible and near-IR regions, cw lasers with a wavelength of 532 nm and 785 nm were used. The power of green laser radiation ($\lambda_0 = 532$ nm) during registration of Raman spectra was 30 mW, and the power of radiation in the near-IR region ($\lambda_0 = 785$ nm) was 340 mW. In all cases, the numerical aperture of the focusing system was 0.22. The size of the laser spot at the focus was 85 μm . All Raman spectra were recorded at room temperature. The geometry in all cases was backscattering. The use of long-wavelength (785 nm) exciting laser radiation ensured suppression of the photorefraction effect observed in LN crystals when illuminated with shorter-wavelength radiation.

3. Results and Discussion

3.1. Transmission Spectra of the $\text{LiNbO}_3\text{:Gd:Mg}$ Crystal

Figure 1 shows the transmission spectrum of a $\text{LiNbO}_3\text{:Gd:Mg}$ crystal.

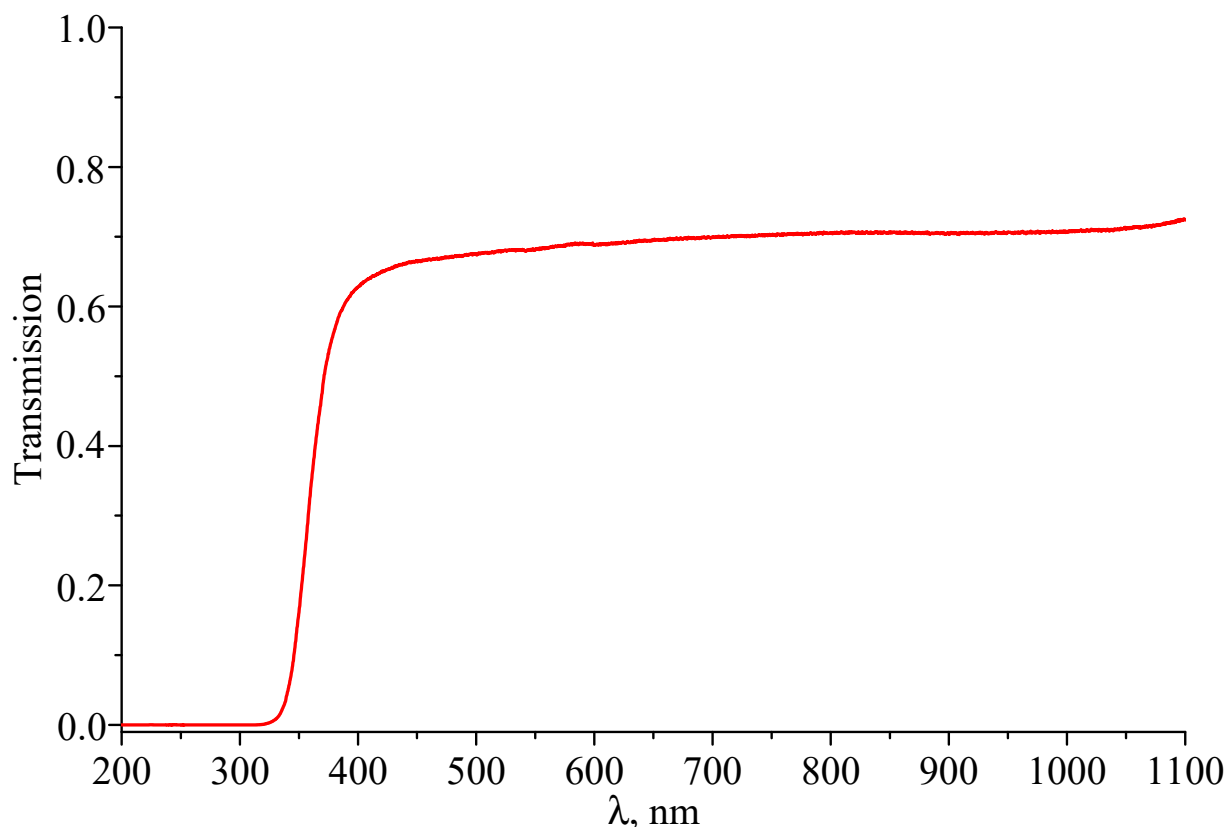


Figure 1. Transmission spectrum of a $\text{LiNbO}_3\text{:Gd:Mg}$ crystal.

Figure 1 demonstrates that the crystal under study has a fairly high and stable transmittance in the spectral range of 450–1100 nm.

The bandgap width was determined according to the formula $\Delta E_g = hc/\lambda$, where λ is the wavelength corresponding to the fundamental absorption edge, h is Planck's constant, and c is the speed of light in vacuum. The accuracy of determining the boundary of the fundamental absorption edge was ± 1.0 nm. The band gap in the $\text{LiNbO}_3\text{:Gd:Mg}$ crystal is ~ 3.62 eV. The band gap has an intermediate value between the values of CLN ~ 3.72 eV and SLN ~ 3.48 eV [32]. The electrical conductivity of a CLN crystal is $\sim 10^{-16}$ – 10^{-15} ($\Omega \text{ cm}$) $^{-1}$ [34]. The smaller value of the band gap in the SLN crystal indicates a higher density of small energy levels (“sticking levels”) in the band gap, which increases the photorefractive effect and the electrical conductivity of the crystal.

3.2. Laser Conoscopy of the $\text{LiNbO}_3\text{:Gd:Mg}$ Crystal

Figure 2 illustrates conoscopic patterns of the $\text{LiNbO}_3\text{:Gd:Mg}$ crystal. The patterns were obtained upon excitation by a laser radiation with a wavelength of 532 nm and powers of 1 and 90 mW. For comparison, conoscopic patterns of nominally pure CLN, SLN crystals are also given in Figure 2.

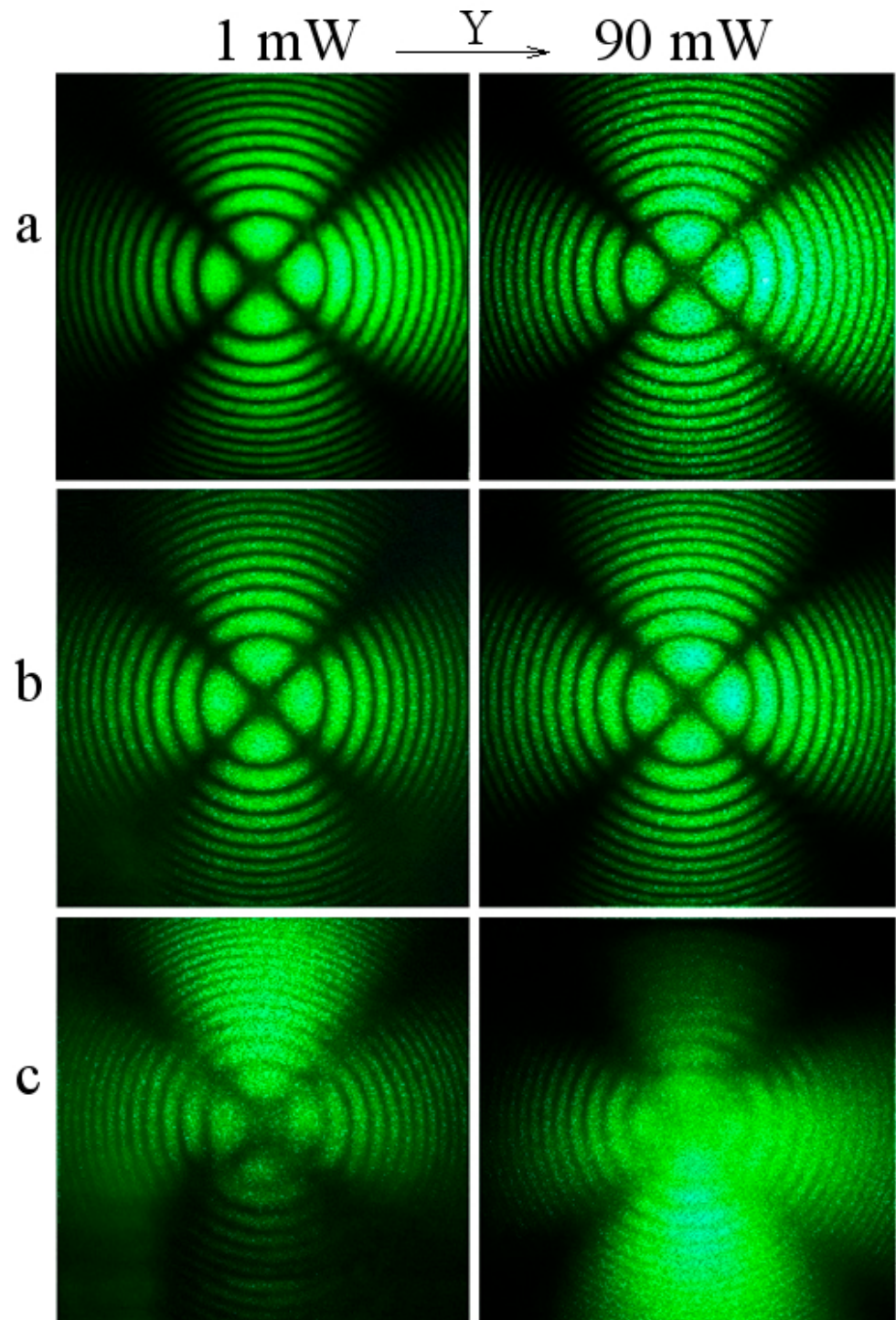


Figure 2. Conoscopic patterns of the crystals: (a)— $\text{LiNbO}_3\text{:Gd:Mg}$; (b)—CLN; (c)—SLN, $\lambda_0 = 532$ nm, $P = 1$ and 90 mW.

Conoscopic patterns obtained at a laser power of 1 mW for $\text{LiNbO}_3\text{:Gd:Mg}$ and CLN crystals correspond to uniaxial crystals. Moreover, such a low power of laser radiation

(1 mW) fails to excite the photorefractive effect; thus conoscopic patterns characterize only the structural defectiveness of crystals. The conoscopic patterns of $\text{LiNbO}_3\text{:Gd:Mg}$ and CLN crystals are ideal patterns for a uniaxial crystal. The conoscopic patterns have the background of concentric isochrome rings. The branches of the Maltese cross are formed by two isogyres of minimum intensity. Branches intersect in the center of the field of view; they are perpendicular to each other, and coincide with the transmission axes of the polarizer and analyzer. This type of conoscopic pattern indicates the high optical uniformity of the CLN and $\text{LiNbO}_3\text{:Gd:Mg}$ crystals and their high optical quality. Scanning with a laser beam along the input face of these crystals also confirms that the optical uniformity over the volume of the $\text{LiNbO}_3\text{:Gd:Mg}$ crystal is high, coincides with that for the CLN crystal, and is much higher than the optical uniformity of the SLN crystal. It is a known fact that congruent LN crystals are distinguished by the maximum optical homogeneity among all nominally pure (with different Li/Nb ratios) and doped with different metals LN single crystals [32].

Figure 2 reveals that the conoscopic patterns of the SLN crystal differ significantly from those of the $\text{LiNbO}_3\text{:Gd:Mg}$ and CLN crystals. SLN conoscopic patterns contain signs of anomalous optical biaxiality: a noticeable deformation of the optical indicatrix of the crystal in the direction corresponding to the direction of the shift of the parts of the Maltese cross. The isochromes are stretched in the direction of displacement of the cross fragments and take the form of ellipses. The conoscopic pattern itself is significantly blurred (Figure 2). The detected anomalies in the conoscopic patterns mean that the SLN crystals are optically non-uniform.

With an increase in the laser radiation power to 90 mW, both the intrinsic defectiveness of the crystal (determined by the composition and conditions of crystal growth) and the imperfections induced by laser radiation appear in the conoscopic patterns. To study the effect of PILS on conoscopic patterns, the crystals were preliminarily irradiated with ~160 mW laser radiation. Increasing the laser power to 90 mW leads to a certain enhancement of the contrast and clarity of the image; however, no additional distortions appear in the conoscopic patterns of $\text{LiNbO}_3\text{:Gd:Mg}$ and CLN crystals (Figure 2a,b). The absence of a photorefractive response of these crystals might be the reason for such behavior (Figure 3a,b, see Section 3.3). The anomalies of the conoscopic patterns of the SLN crystal increase with an increase in the laser radiation power; the contrast and sharpness of the image generally decrease; and the branches of the Maltese cross noticeably blur (Figure 2c). A significant distortion of the conoscopic patterns for the SLN crystal with an increase in the laser radiation power to ~90 mW is obviously associated with the presence of a significant photorefractive response. The response is confirmed by the data of PILS (Figure 3c). In this case, the effect of photorefraction is due to the capture of photoelectrons by deep traps in the bandgap; photoelectrons drift in the electric field when the crystal is illuminated due to the manifestation of the photovoltaic effect.

3.3. PILS of the $\text{LiNbO}_3\text{:Gd:Mg}$ Crystal

Figure 3 demonstrates the PILS patterns of $\text{LiNbO}_3\text{:Gd:Mg}$, CLN, and SLN crystals, obtained upon excitation by a laser radiation with a wavelength of 532 nm and a power of 160 mW. The PILS speckle structure in LN crystals of different compositions predominantly opens along the polar axis of the crystal [32]. In our case, the exciting laser radiation is directed perpendicularly to the polar axis. Figure 3 shows that the PILS patterns of $\text{LiNbO}_3\text{:Gd:Mg}$ and CLN crystals stay the same regardless of the time of laser radiation exposure to the crystal. Moreover, for these crystals, even after exposure to laser radiation with wavelength $\lambda_0 = 532$ nm and power of 160 mW for 360 s, the indicatrix of the PILS speckle structure is not revealed, and only circular scattering by static structural defects is observed (Figure 3a,b). This fact indicates the absence of photoinduced defects in the $\text{LiNbO}_3\text{:Gd:Mg}$ and CLN crystals exposed to laser radiation with a wavelength of 532 nm and a power of 160 mW.

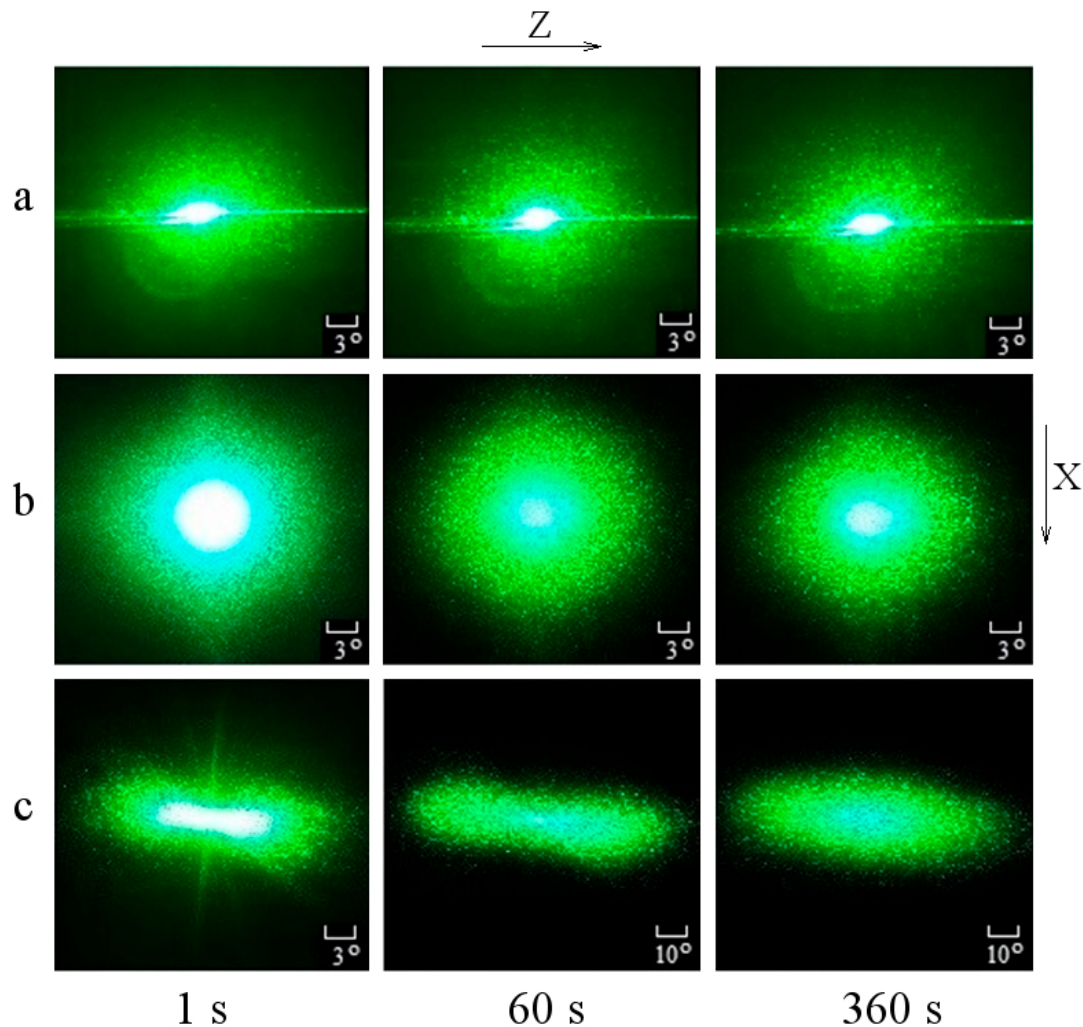


Figure 3. PILS patterns of the crystals: (a)—LiNbO₃:Gd:Mg; (b)—CLN; (c)—SLN, $\lambda_0 = 532$ nm, $P = 160$ mW.

For the SLN crystal, the speckle structure of the PILS indicatrix is completely opened. Moreover, the dynamics of its disclosure over time is unusual. The PILS indicatrix opens up very quickly, during the first second of exposure of the crystal to laser radiation. Subsequently, the central layer of the speckle structure, corresponding to the cross section of the laser beam at the exit from the crystal, almost completely disappears during the first 60 s of crystal irradiation. Then the central layer appears again, but it has a much lower brightness than at the first seconds of irradiation of the crystal. This indicates that the energy of the laser beam after the first seconds of impact begins to dissipate significantly on structural defects in the bulk of the crystal. The energy of the laser beam also dissipates on structural defects of CLN crystal, but much less, and the dissipation is not accompanied by the opening of the speckle structure of the PILS indicatrix (Figure 3). No energy dissipation is observed for the LiNbO₃:Gd:Mg crystal, which also indicates a small number of structural defects (Figure 3a).

The differences found in the features of PILS in LiNbO₃:Gd:Mg, SLN, and CLN crystals indicate the following: the band gap of the SLN crystal has a high density of shallow energy levels (sticking levels [9]) near the bottom of the band gap. Shallow levels are added to deep energy traps. Shallow levels are caused by shallow electron traps in the form of defects V_{Li} , V_{Nb} , Cu_V , etc., which significantly increase the diffusion photoelectric fields that determine the features of the dynamics of the opening of the speckle structure of the PILS indicatrix in time. At the same time, the CLN crystal is distinguished by a high concentration

(≈ 5 wt %) of deep electron traps in the form of Nb_{Li} point defects [6,20]. However, CLN has much fewer of such shallow electron traps, and, therefore, the fraction of the photovoltaic mechanism in the formation of the photorefractive effect is much larger. Indeed, the values of the photoelectric fields (diffusion E_d and photovoltaic E_{pv}) excited in certain conditions ($\lambda_0 = 532$ nm, $P = 160$ mW (6.29 W/cm²)) were: $E_{\text{pv}} = 3178$ V/cm, $E_d = 1360$ V/cm for SLN crystal; $E_{\text{pv}} = 5620$ V/cm, $E_d = 104$ V/cm for CLN crystal; $E_{\text{pv}} = 3700$ V/cm, $E_d = 735$ V/cm for $\text{LiNbO}_3:\text{Gd}^{3+}(0.003):\text{Mg}^{2+}(0.65$ wt %) crystal. The values of the band gap ΔE_g were 3.48, 3.72, and 3.62 eV, respectively, for SLN, CLN, and $\text{LiNbO}_3:\text{Gd}^{3+}(0.003):\text{Mg}^{2+}(0.65$ wt %) crystals [35].

Thus, the data show an increase in the diffusion field (104, 745, and 1360 V/cm) in the series of CLN, $\text{LiNbO}_3:\text{Gd}:\text{Mg}$, SLN crystals. At the same time, the band gap decreases. The predominant mechanism of photorefractive effect in all studied crystals is photovoltaic, since the value of the photovoltaic field is much greater than that of the diffusion field. The number of deep electron traps caused by multiply charged transition metal impurity cations (Fe, Cu, etc.), which affect the photorefractive effect and PILS, is the same in all the crystals under study since single crystals were grown using the same granular charge with the same composition and concentration of trace metal impurities (Table 1).

Deep electron traps in LN are usually Nb_{Li} point defects and impurities of multiply charged transition metal cations Fe, Cu, etc.; shallow electron traps are formed by point defects V_{Li} , V_{Nb} , Cu_V , etc. The presence of both can also lead to a high dissipation of the absorbed energy on lattice phonons, which should show up in the vibrational spectrum of the crystal. The magnitude of the photorefractive effect depends on the wavelength of the laser radiation. Thus, there should be noticeable differences in the spectra when excited by the visible laser radiation ($\lambda_0 = 532$ nm when the photorefractive effect is present) and the near-IR ($\lambda_0 = 785$ nm when there is no photorefractive effect).

3.4. Raman Spectra of the $\text{LiNbO}_3:\text{Gd}:\text{Mg}$ Crystal

Figure 4 shows the Raman spectra of the $\text{LiNbO}_3:\text{Gd}:\text{Mg}$ crystal in scattering geometries: $x(\text{zz}, \text{zy})\bar{x}$ and $z(\text{xx}, \text{yy}, \text{xy})\bar{z}$, recorded in the range 50–1000 cm^{−1}. The spectra in Figure 4 were excited by lasers with wavelengths of 532 and 785 nm.

Figure 4 shows that the spectra contain intense bands with frequencies 253–256 and 627–629 cm^{−1}, attributed to fundamental phonons of $A_1(\text{TO})$ symmetry type along the polar Z axis; bands with frequencies 295–296, 615, and 875–876 cm^{−1}, attributed to fundamental phonons of $A_1(\text{LO})$ symmetry type; and all 9 bands with frequencies 152, 237, 262, 328, 363, 429, and 580 cm^{−1}, attributed to fundamental doubly degenerate phonons of $E(\text{TO})$ symmetry type; these phonons vibrate perpendicularly to the polar Z axis.

A weak band with a frequency 186 cm^{−1} was detected in $x(\text{zz}, \text{zy})\bar{x}$ scattering geometry and 188 cm^{−1} in $z(\text{xx}, \text{yy}, \text{xy})\bar{z}$ geometry upon excitation of Raman spectra with the 785 nm laser. According to [36–39], these bands are attributed to a fundamental line $1E(\text{LO})$. The $z(\text{xx}, \text{yy}, \text{xy})\bar{z}$ geometry contains a wide Raman band with a frequency of 732 cm^{−1}. The attribution of the band is still discussed today. In [40], this band is attributed to the ilmenite phase. In article [41], the authors believe that it corresponds to the second-order Raman line. Finally, in a number of works [42,43], this band is assigned to the fundamental mode $E(\text{TO})$.

The Raman spectrum of a LN single crystal of any composition (both nominally pure with different [Li]/[Nb] ratios and doped) is distinguished by an abundance of low-intensity bands not provided by the selection rules for fundamental phonons for the SPGR $R3c$ (C_{3v}^6). This SPGR describes the unit cell symmetry of a LN crystal with the exact composition LiNbO_3 and two formula units in it. Such bands are called “extra bands”. According to numerous studies in the literature, the number of extra low-intensity bands in the Raman spectrum only in the range of 50–1000 cm^{−1} is approximately equal to the number of bands (26) corresponding to fundamental phonons [6,8,10,20,24–26,28].

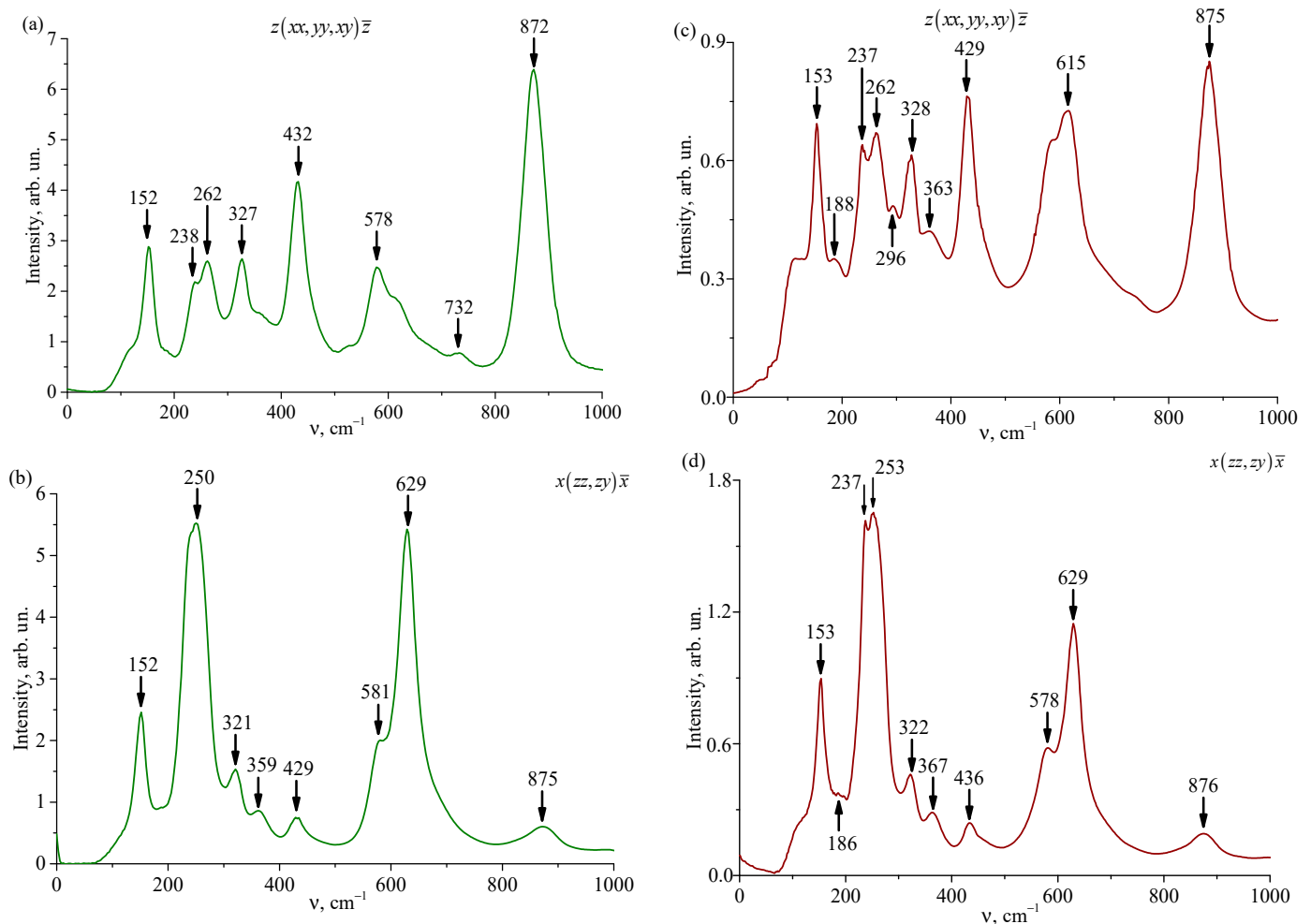


Figure 4. Raman spectra of a LiNbO₃:Gd:Mg crystal. Spectra were recorded in scattering geometries $x(zz,zy)\bar{x}$ and $z(xx,yy,xy)\bar{z}$ and excited by a laser line with a wavelength of (a,b) 532 nm and (c), (d) 785 nm in the range 0–1000 cm⁻¹.

The Raman spectra of the LiNbO₃:Gd:Mg and SLN crystals did not contain a low-intensity band with a frequency of 120 cm⁻¹ of the A₁(TO) symmetry type. The band corresponds to two-particle states of acoustic phonons with a total wave vector equal to zero. It is usually observed in the involved scattering geometries in the spectra of all nonstoichiometric LN crystals [6,8,10,20,24,25]. It was experimentally shown in [6,8,10,20,24,25] that the Raman spectrum of a highly perfect stoichiometric LiNbO₃ crystal has no bands in the range of 110–130 cm⁻¹. The absence of Raman bands in the range of 110–130 cm⁻¹ of a highly perfect SLN crystal was first noted in a theoretical work [44]. It was explained by the fact that acoustic phonons with frequencies of 110–130 cm⁻¹ are not active in the Raman spectrum since their wave vector is not equal to zero. Thus, if a 120 cm⁻¹ A₁(TO) band is absent from the Raman spectrum, then the $R = [\text{Li}]/[\text{Nb}]$ value in the LiNbO₃:Gd:Mg crystal approaches unity. Such an R value is usually characteristic of a nominally pure stoichiometric LiNbO₃ crystal [6,20,24,25,44]. The 110–130 cm⁻¹ Raman bands in the spectrum of nonstoichiometric LN crystals of various compositions indicates a strong anharmonic interaction of the lowest-frequency fundamental phonons of the A₁(TO) symmetry type (quasi-soft mode) with the acoustic continuum [20,24,25]. In this case, if two acoustic phonons with oppositely directed wave vectors interact with each other in such a way that they form a quasiparticle (biphonon) whose wave vector is equal to zero, then such an acoustic biphonon will be active in the Raman scattering of light. Moreover, the intensity of the band in the Raman spectrum corresponding to this acoustic biphonon

will be proportional to the interaction energy due to the Fermi resonance of the biphonon with low-frequency optical fundamental phonons of the $A_1(\text{TO})$ symmetry type.

In the Raman spectrum of the $\text{LiNbO}_3\text{:Gd:Mg}$ crystal, we also did not find extra bands found in the spectrum of LN crystals heavily doped with magnesium (>4.0 mol %) [28]. The bands can be explained in the Raman spectrum by a decrease in the local crystal symmetry SPGR from C_{3V} to C_3 due to the distortion of MeO_6 clusters by doping cations [8,20]. For the point symmetry group C_3 , the optical representation has the form $9A(z) + 9E(x,y)$ [20]. Thus, pseudoscalar phonons of the A_2 symmetry type transfer into phonons of the $A(z)$ symmetry type. Phonons of the A_2 symmetry type are forbidden in the Raman spectrum for the C_{3V} symmetry group by the selection rules, but phonons of the $A(z)$ symmetry type are allowed. Thus, if phonons of the A_2 symmetry type are absent, then co-doping with Gd^{3+} and Mg^{2+} cations has little effect on the geometry of oxygen-octahedral MeO_6 clusters in the $\text{LiNbO}_3\text{:Gd:Mg}$.

Figure 5 shows fragments of the second-order Raman spectra of the $\text{LiNbO}_3\text{:Gd:Mg}$ crystal in the scattering geometries $x(\text{zz}, \text{zy})\bar{x}$, $y(\text{zz}, \text{zx})\bar{y}$, and $z(\text{xx}, \text{yy}, \text{xy})\bar{z}$, recorded in the range $1000\text{--}2000\text{ cm}^{-1}$, excited by both laser lines.

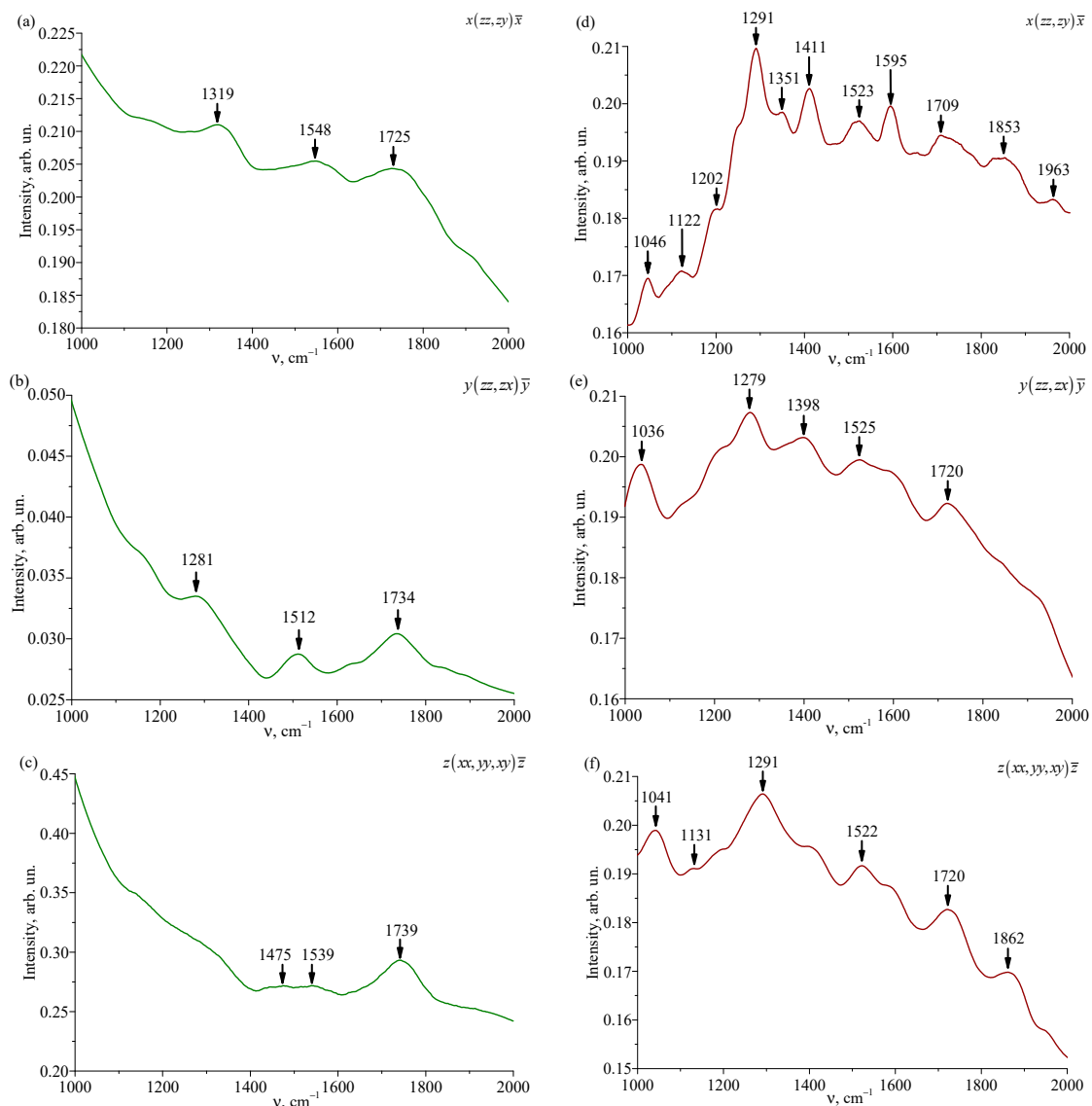


Figure 5. Fragments of the Raman spectra (on an enlarged scale) of the $\text{LiNbO}_3\text{:Gd:Mg}$ crystal, obtained in scattering geometries $x(\text{zz}, \text{zy})\bar{x}$, $y(\text{zz}, \text{zx})\bar{y}$, and $z(\text{xx}, \text{yy}, \text{xy})\bar{z}$, excited by laser radiation (a–c) 532 nm and (d–f) 785 nm in the range $1000\text{--}2000\text{ cm}^{-1}$.

As is known, LN is a uniaxial crystal. Despite this, we have discovered that the second-order Raman spectra are polarized; for two orientations perpendicular to the polar axis, they differ noticeably. A number of broad bands appear in the range of 1000–2000 cm^{-1} , the frequencies of which do not correspond to the fundamental phonons of the crystal lattice (Figures 4 and 5). The intensity of these extra low-intensity bands is almost two orders of magnitude less than the intensity of the strongest bands corresponding to the fundamental phonons of the lattice. Figure 5 also shows that, upon excitation by the visible laser line (532 nm), three second-order Raman lines bands were recorded; the frequencies of the bands do not exceed the exact value of the doubled frequency of the overtone of the fully symmetric fundamental mode $4A_1(z)\text{LO}$ (875 cm^{-1} , Figure 4b). When excited by near-IR laser radiation, significantly more second-order Raman bands were recorded (Figure 5a–c). The frequencies of two second-order Raman bands significantly exceed the exact value of the doubled frequency of the overtone of the fully symmetric fundamental mode $4A_1(z)\text{LO}$ (876 cm^{-1} , Figure 4d).

In the Raman spectra of nominally pure LiNbO_3 and LiTaO_3 single crystals, according to the data of numerous studies by different authors carried out over decades, no bands were found at all in the range of 900–2000 cm^{-1} . Quite intense bands were observed in the range of 900–2500 cm^{-1} [23,45–47] in the spectra of single crystals and ceramics of single and double doping $\text{LiNbO}_3\text{:Tb}^{3+}$ (2.24 wt %), $\text{LiTaO}_3\text{:Cr}^{3+}$ (0.005 wt %), $\text{LiTaO}_3\text{:Cr(0.2):Nd(0.45 wt \%)}$, and $\text{LiNb}_x\text{Ta}_{1-x}\text{O}_3$. The bands are attributed to the second-order Raman spectrum. These samples have strongly disordered cationic sublattices. Their MeO_6 clusters are noticeably distorted compared with the MeO_6 clusters of a congruent and stoichiometric crystal. The reasons for the appearance in the range of 900–2000 cm^{-1} of low-intensity bands in the Raman spectrum of LiNbO_3 and LiTaO_3 single crystals and ceramics of various compositions remain unclear at present. The most probable is the attribution of these extra bands to the second-order spectrum, which arises in disordered and highly anharmonic crystals and ceramics. It is also unclear why the intensity of the extra bands is higher when the Raman spectrum is excited by laser radiation in the near-IR region (785 nm) than when it is excited in the visible region (532 nm). The currently existing methods for calculating spectra and theories do not yet allow us to explain this fact.

4. Conclusions

Optical transmission, conoscopy, PILS, optical spectroscopy, and Raman spectroscopy were used to study nonlinear optical single crystals of double doping $\text{LiNbO}_3\text{:Gd:Mg}$ (Gd concentration is 0.003, Mg—0.65 wt % in the crystal).

The absence of distortion of the conoscopic patterns of $\text{LiNbO}_3\text{:Gd:Mg}$ was established, which demonstrates the high optical uniformity of this crystal. When the crystal under study was irradiated for 360 s with laser radiation with a wavelength of 532 nm and a power of 160 mW, the PILS speckle structure did not open. During this time, only circular scattering by static structural defects was observed. These facts indicate the absence of photoinduced defects in the $\text{LiNbO}_3\text{:Gd:Mg}$ crystal.

According to the Raman spectra of the first and second orders obtained in the range of 50–2000 cm^{-1} upon excitation by lasers with wavelengths of 532 and 785 nm, it was shown that the structures of the $\text{LiNbO}_3\text{:Gd:Mg}$ MeO_6 clusters are slightly distorted compared with those of the nominally pure crystal and, in addition, the value of $R = [\text{Li}]/[\text{Nb}]$ is increased compared with that for a congruent crystal. This indicates an increase in the stoichiometry of LiNbO_3 with its double doping with magnesium and gadolinium. The increase in stoichiometry is also confirmed by the fact that the Raman spectrum of the $\text{LiNbO}_3\text{:Gd:Mg}$ crystal lacks a low-intensity band with a frequency of 120 cm^{-1} ($A_1(\text{TO})$). This band corresponds to two-particle states of acoustic phonons with a total wave vector equal to zero. Its absence in the spectrum also indicates a small anharmonic interaction of the lowest-frequency fundamental vibration $A_1(\text{TO})$ of the symmetry type (quasi-soft mode) with the acoustic continuum. A low-intensity band with a frequency of 120 cm^{-1} ($A_1(\text{TO})$) is definitely observed in the spectra of non-stoichiometric LiNbO_3 crystals, nom-

inally pure and doped, and it is absent from the Raman spectrum of a stoichiometric crystal [6,20,24,25,35]. The results obtained indicate a high structural perfection of the crystal. The results allow us to claim that the LiNbO₃:Gd:Mg crystal is close in some of its properties to the stoichiometric LiNbO₃ crystal. One such property of stoichiometric and magnesium-doped LiNbO₃ crystals, which are important for creating materials for laser radiation conversion on periodically polarized submicron-sized domains with flat boundaries [14], is a low value of the coercive field (≈ 2.3 kV/cm). In a congruent LiNbO₃ crystal, the coercive field is much higher, ≈ 23.0 kV/cm. At the same time, the LiNbO₃:Gd:Mg crystal has a much higher optical uniformity than the stoichiometric crystal and is also distinguished by the absence of the photorefractive effect.

It was found that, upon excitation of the Raman spectrum of LiNbO₃:Gd:Mg by a laser line with a wavelength of 785 nm, the spectrum manifests itself as a number of bands corresponding to the fundamental vibrations of the crystal lattice A₁(TO,LO)- and E(TO,LO)-type symmetry, as well as bands corresponding to the second-order Raman spectrum with frequencies of 1046, 1122, 1202, 1291, 1291, 1351, 1411, 1523, 1595, 1709, 1853, and 1963 cm⁻¹. Simultaneously, when the Raman spectrum of the LiNbO₃:Gd:Mg crystal is excited by a laser line with a wavelength of 532 nm, the intensity and number of bands corresponding to the second-order spectrum are significantly (by an order of magnitude or more) reduced. At the same time, in the Raman spectrum in the region below 900 cm⁻¹, no bands were found corresponding to the second-order spectrum, as well as bands with frequencies of 209, 230, 298, and 880 cm⁻¹ of disordered LiNbO₃:Mg crystals [28].

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