

Concentration Dependence of Structural and Optical Properties of $\text{LiNbO}_3\text{:Zn}$ (0.03÷4.5 mol. %) Crystals

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Abstract— The comparative studies of structural and optical properties of $\text{LiNbO}_3\text{:Zn}$ (0.03÷4.5 mol. %) crystals were carried out by the photoinduced light scattering, Raman spectroscopy, laser conoscopy and fractal analysis. It was shown that photorefractive dependance on the concentration of Zn^{2+} in lithium niobate crystals is non-monotonic. The decrease of photorefractive effect is described by the structure ordering. The latter happens due to the reduce of defects with localized electrons, that form levels of energy close to the conduction band bottom (trapping levels) and due to radiative recombination of laser-induced photoelectrons. Structure order of the searched crystals also improves due to substitution of structure defects Nb_{Li} and Li by Zn^{2+} cations. The area of increased structure ordering was detected by Raman spectra. The ordering supposes the most right order of main cations, impurities and vacancies along the polar axis for the real crystal.

Index Terms— Photorefractive Effect, Optical Damage Resistance, Lithium Niobate Crystals

I. INTRODUCTION

NON-LINEAR photorefractive lithium niobate crystal (LiNbO_3) is one of the most perspective materials for the production of frequency converters, electro optical modulators, etc. Doping of congruent ($R=\text{Li}/\text{Nb}=0.946$) lithium niobate (LN) crystals with 'optical damage resistant' impurities Zn^{2+} , Mg^{2+} , Gd^{3+} et. al. is known to be an effective method to significantly decrease the photorefractive effect (PE) [1]-[6]. The greatest reduction of PE (two orders of magnitude) is achieved at high concentrations of "non-

photorefractive" impurities, when they are almost completely displace antisite defects Nb_{Li} (Nb^{5+} cations in the position of Li^+ cations). The defects form the most deep electron traps and are largely responsible for the PE [1], [5]. In particular Zn^{2+} cations completely displace Nb_{Li} antistructure defects at threshold concentrations higher than 7.5 mol. %, as well as Mg^{2+} ones do this at 5.5 mol. % and higher [1]-[5]. At Zn^{2+} and Mg^{2+} concentrations above threshold, PE almost doesn't change, as it is suppressed. However, the doping, especially at high concentrations close to threshold ones, may cause, besides the reduction of PE, oxygen octahedra deformation and strong structural and optical inhomogeneities. This results in forming of micro ranges, clusters and other spatial defects that worsen the quality of optical materials. So the selection of optimal impurities concentrations for crystals growth is a task of great interest. Furthermore the investigations of the connection between subtle features of structure, structural and optical homogeneity of LiNbO_3 crystals and PE, depending on the impurities concentrations are very important.

In this paper structural and optical characteristics of Zn doped LN crystals at 0.03÷4.5 mol. % concentration range were investigated by photoinduced light scattering (PILS), laser conoscopy, Raman spectroscopy, electron spectroscopy, fractal analysis.

II. EXPERIMENTAL

The crystals investigated in this paper were grown by Czochralski method by «Crystal-2» equipment. The impurities were added to melt as reagent ZnO oxide. The growth method is described in details in papers [7]-[11]. Since PE in LN crystals is defined by both the intrinsic defects with localized electrons and multiply charged impurities of transition metals ($\text{Fe}^{2+}\text{-Fe}^{3+}$, $\text{Cu}^+\text{-Cu}^{2+}$) [1], [2], [6], the trace concentrations of impurities in nominally pure congruent LN determined by the spectral analysis are given in table 1.

Table 1 shows that congruent crystal has a highly homogeneous structure along the growth axis and the composition of impurities. This is proved by the fact that the Curie temperature (T_C) of the upper and lower parts of same boule is constant. For growing of $\text{LiNbO}_3\text{:Zn}$ crystals similar charge is used, so similar results related to impurity concentrations were obtained for crystals $\text{LiNbO}_3\text{:Zn}$ (0.03 ÷ 4.5 mol.%).

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Table 1

The results of analysis of the plates cut from the top (closest to cone) and bottom (closest to the melt) parts of congruous nominally pure lithium niobate crystals.

Impurity	Amount of impurity, wt. %	
	top	bottom
Zr	$<1 \cdot 10^{-3}$	$<1 \cdot 10^{-3}$
Mo	$<1 \cdot 10^{-3}$	$<1 \cdot 10^{-3}$
Ca	$<1 \cdot 10^{-3}$	$<1 \cdot 10^{-3}$
Fe	$<1 \cdot 10^{-3}$	$<1 \cdot 10^{-3}$
Ti	$<1 \cdot 10^{-3}$	$<1 \cdot 10^{-3}$
Si	$<1 \cdot 10^{-3}$	$<1 \cdot 10^{-3}$
Pb, Ni, Cr, Co	$<1 \cdot 10^{-3}$	$<1 \cdot 10^{-3}$
Al	$<5 \cdot 10^{-4}$	$<5 \cdot 10^{-4}$
Cu	$<5 \cdot 10^{-4}$	$<5 \cdot 10^{-4}$
Mn, V, Mg, Sn	$<5 \cdot 10^{-4}$	$<5 \cdot 10^{-4}$
$T_c, ^\circ\text{C}$	1142.0	1142.0

Crystalline samples for research were in form of cuboids $7 \cdot 6 \cdot 5 \text{ mm}^3$ with edges coinciding with the crystallographic axes X, Y, Z, where axis Z is the polar axis of the crystal. The faces of the parallelepiped were carefully polished.

Optical absorption spectra and transmission spectra were measured by SF-256 UWI. PILS was exciting by laser MLL-100 on the Y: Al garnet ($\lambda_o = 530 \text{ nm}$). The equipment and the method of determining of PILS indicatrix opening angle are described in detail in [12], [13]. The radiation scattered by the crystal fell on translucent screen placed behind the crystal. The image was recorded by a digital foto-camera. The scattering angle θ was calculated according to the formulae $\theta = \arctg(a/b)$, where a – PILS indicatrix size along the polar axis, b – the distance between the crystal and the screen.

The shape of the PILS indicatrix is complicated and multi-layered [10], [11]. So for the farthest points of the PILS picture, which determined linear size of PILS, were taken the points where intensity of the scattered radiation reduced to one order. To assess the degree of asymmetry of the PILS indicatrix, the parameter $\gamma = \theta / b$ introduced in [13] was applied. In the formulae θ – the maximum angle of the scattered radiation in the positive direction of the polar axis of the crystal; b – the maximum angle of the scattered radiation in the negative direction of the polar axis of the crystal.

Raman spectra were excited by the 514.5 nm line of an argon laser Spectra Physics (model 2018-RM) and recorded by T64000 spectrograph manufactured by Horiba Jobin Yvon using a confocal microscope. To eliminate the influence of PE on the Raman spectrum, the spectra were excited by the radiation of low power ($P < 3 \text{ mW}$). All spectra were recorded with a resolution of 1.0 cm^{-1} at room temperature.

Conoscopic research technique is described in detail in [14], [15]. Laser MLL-100 on the Y: Al garnet radiation ($\lambda_o = 532.0 \text{ nm}$, $P = 1$ and 90 mW) was used. The sample was mounted on a movable optical XY table that has given numerous conoscopic patterns corresponding to different areas of the cross-section of sample. Conoscopic pattern was recorded on a translucent screen by the digital camera.

For fractal analysis each frame of PILS picture was treated in GIMP 2.6.12. Three PILS layers were separated by digital tools. Each layer image was treated by program Fractalyze 2.4.1. So the dependence of the fractal dimension of each PILS layer on time was obtained. The method was described in detail in [25].

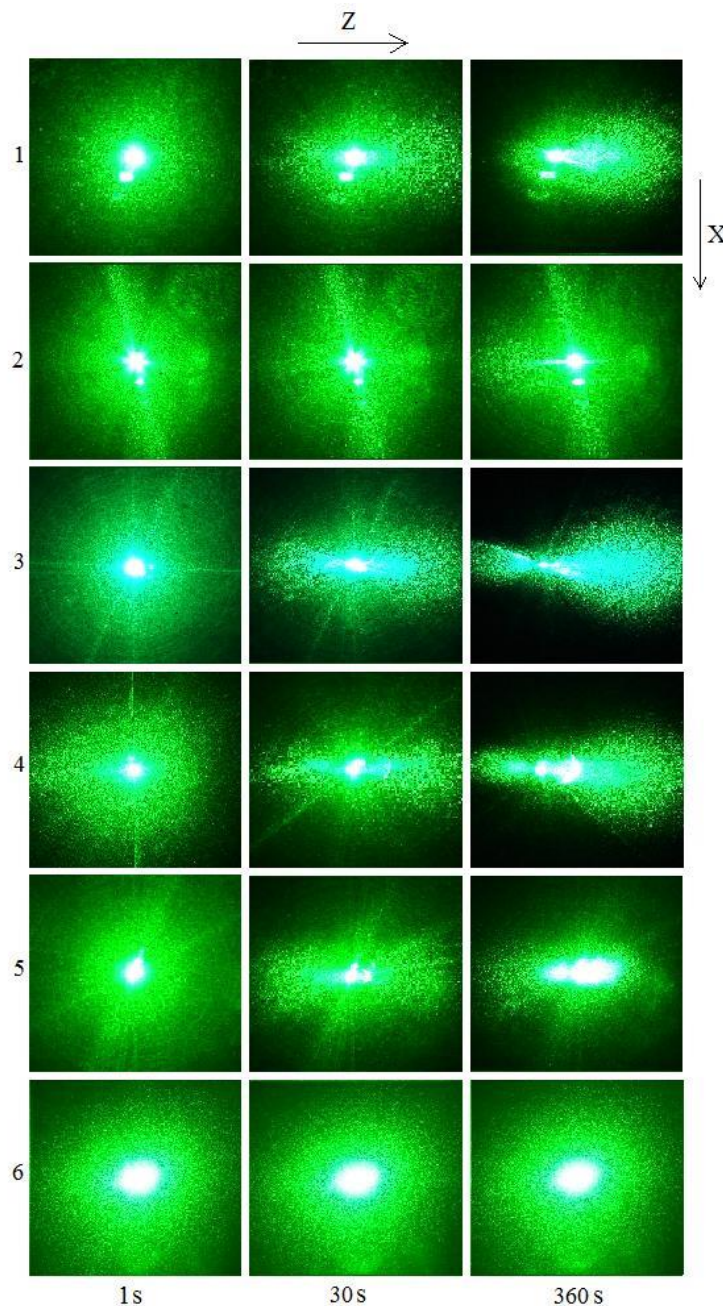


Fig. 1. PILS pictures of crystals $\text{LiNbO}_3:\text{Zn}^{2+}$: 1). 0.03; 2). 0.05; 3). 0.94; 4). 1.12; 5). 1.59; 6). 4.5 mol. %. $\lambda = 532 \text{ nm}$. $P = 160 \text{ m}$.

III. RESULTS AND DISCUSSION

Time dynamics of PILS pictures of crystals LiNbO₃: Zn (0.03 ÷ 4.5 mol.%) obtained at 160 mW of the exciting laser radiation ($\lambda_0 = 532$ nm), is shown on Fig. 1. Fig. 1 shows that the dynamics of change on PILS picture in time for the investigated crystals varies considerably. So, for crystals LiNbO₃: Zn (0.05 mol.%) and LiNbO₃: Zn (4.5 mol.%) the shape of the scattering pattern remains practically unchanged in time, Fig. 1 (2, 6). For these crystals even when the radiation power is 160 mW photorefractive response is absent, the PILS indicatrix doesn't expand, and there is only a circular scattering by static structural defects. The scattering angle is not more than 3 degrees. Scattering pattern keeps its shape close to a circle throughout the experiment. This temporal behavior of PILS pictures indicates a low value of PE in LiNbO₃: Zn (0.05 mol.%) and LiNbO₃: Zn (4.5 mol.%) crystals. At the same time the PILS pictures of LiNbO₃: Zn (0.05 mol.%) and LiNbO₃: Zn (4.5 mol.%) crystals were significantly different. LiNbO₃: Zn (4.5 mol.%) crystal is characterized by a much larger size of the central layer corresponding to the laser beam. Whole scattering pattern indicates a greater dispersibility of LiNbO₃: Zn (4.5 mol.%) crystal compared with the LiNbO₃: Zn (0.05 mol.%) crystal, Fig. 1 (2, 6). This means that it has significantly higher defect structure.

Unlike the circular scattering, PILS interferes with the exciting radiation. This forms a complex picture of the minima and maximums of intensity (speckle-picture). The form of speckle-picture is determined by the structure of the crystal and the peculiarities of its defect structure [12], [13]. The shape and characteristics of the speckle-picture of PILS indicatrix depend not only on the crystal structure, but also on the polarization of the radiation and the geometry of the experiment. Time and the angle of the PILS indicatrix opening governs performance of electro-optic modulators and gates. These characteristics of PILS are determined by the depth of the traps and the mobility of the electrons responsible for PE and characteristics of the interaction of laser radiation with the crystal [12].

PILS indicatrix asymmetry is caused by the redistribution of energy between the ordinary and extraordinary beams [16]. The laser beam that propagates perpendicular to the polar axis manifests birefringence. It is divided into two closely spaced beams of lower power, which often do not create a track. The latter happens due to the fact that much of the beam energy is dissipated by defects in the crystal volume. Fig. 2 shows time dependence of the opening of θ and of the asymmetry parameter γ of PILS indicatrix in crystals with PE.

LiNbO₃: Zn (0.03), LiNbO₃: Zn (0.94), LiNbO₃: Zn (1.12), LiNbO₃: Zn (1.59 mol.%) crystals had a three-layer structure of a PILS speckle-picture [17] that significantly changed over time, Fig. 1 (1, 3-5). In this case, the indicatrix of PILS of round shape (the first seconds of excitement PIS) eventually transformed first into an oval ("cometary") form, and then into an asymmetric "eight", oriented along the polar axis of the crystal. Over time, the bigger "petal" of the eight is extending in the positive direction of the polar axis, and the smaller "petal" - in the negative one. These crystals are also

characterized by a gradual "overflow" of the intensity of the different layers of PILS pictures in the direction of the polar axis of the crystal. It should be noted also that for LiNbO₃: Zn (0.94 mol.%) and LiNbO₃: Zn (1.12 mol.%) crystals a division of the central spot in two halves was observed, Fig. 1 (3, 4). That division is due, in our opinion, to birefringence, since in this case the laser radiation exciting the PILS, extends perpendicular to the polar axis of the crystal.

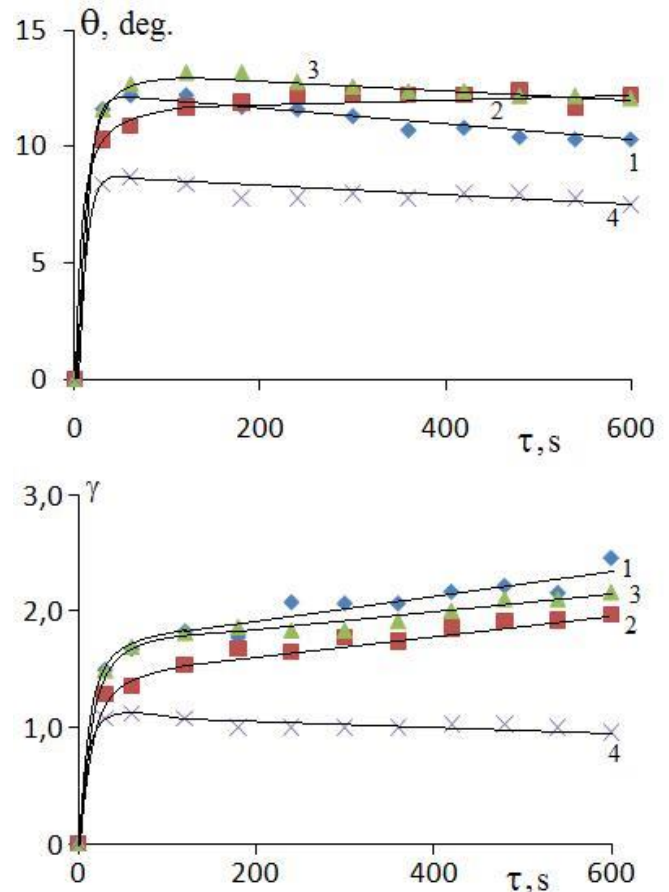


Fig. 2. Dependence of PILS indicatrix opening angle θ and PILS indicatrix asymmetry parameter γ on time in crystals LiNbO₃:Zn²⁺: 1). 0.03; 2). 0.94; 3). 1.12; 4). 1.59 mol. %. $\lambda = 532$ nm. $P = 160$ mW.

PILS indicatrix of LiNbO₃: Zn (0.03 mol.%), LiNbO₃: Zn (0.94 mol.%), LiNbO₃: Zn (1.12 mol.%), LiNbO₃: Zn (1.59 mol.%) crystals at laser power of 160mW expands in the first 30 seconds of irradiation, Fig. 2. Over time, a slight decrease of scattering angle due to a decrease of photorefraction caused by the heating of crystal by laser radiation was observed. In this case, the asymmetry parameter γ of LiNbO₃: Zn (0.03 mol.%), LiNbO₃: Zn (0.94 mol.%), LiNbO₃: Zn (1.12 mol.%) crystals increases with time, and for the LiNbO₃: Zn (1.59 mol.%) crystal, on the contrary, decreases slightly, Fig. 2.

According to [1]-[5] the doping of congruent LiNbO₃ crystal with Zn²⁺ cations at concentrations above the threshold ones should lead to the suppression of PE for at least two orders of magnitude, due to the almost complete displacement of antisite Nb_{Li} defects, which are the most deep electron traps, by Zn²⁺ cations. There are almost no Nb_{Li} crystal defects in LiNbO₃ at 5.2 mol. % concentrations of Zn²⁺[1], [4], [5]. So

a significant decrease of the PE in $\text{LiNbO}_3\text{:Zn}$ (4.5 mol.%) crystal can be explained by this way. However, in the $\text{LiNbO}_3\text{:Zn}$ (0.05 mol.%) crystal, where the concentration of defects Nb_{Li} is high (in pure congruent crystal $\approx 6\%$ [1]) reduction of the PE (Fig. 1 (2)) is due to some other reasons.

This may be given the following explanation. According to [1], [3], [18] at low concentrations Zn^{2+} cations displace not only antisite defects Nb_{Li} and $\text{Li}_{\square}$, but at the same time the cations Li^+ , located in their own states, and fill vacant octahedra. In this case, during the replacement of one defect Nb_{Li} three lithium vacancies disappear, and during the replacement of one defect $\text{Li}_{\square}$ or Li^+ cations in their proper position, on the contrary, one vacancy appears. Thus, small amounts of Zn^{2+} cations, displacing defects Nb_{Li} and $\text{Li}_{\square}$, put in order the alternation of major, impurity cations and vacancies along the polar axis and reduce concentration of defects in form of vacancies Li^+ .

Since electrons are localized on the defects, the decrease in crystal imperfection inevitably reduces the PE. There is a direct significant association between the ordering of the structural units and the state of the electron subsystem of the crystal [19]. Under the certain low concentrations of impurities in LiNbO_3 non-photorefractive impurities can form a substantial amount of small electron traps near the bottom of the conduction band (trapping levels). For example, in [20] was shown that non-photorefractive impurity in LiNbO_3 can form small electronic traps. At doping by Mg, “ Mg^+ complexes” which is an ion of Mg^+ in place of Li^+ with delocalized on a number of surrounding ions electron [21], form such levels.

At the same time PE is significantly reduced due to improving of the efficiency of radiative recombination of photo-excited carriers without their capture at deep levels (such as Nb_{Li} or Fe^{3+}). That is, when $\text{LiNbO}_3\text{:Zn}$ (0.05 mol.%) crystal is illuminated by laser radiation there are two competing processes. On the one hand, significant amount of deep trapping levels in the band gap (which are antisite defects Nb_{Li}) form uncompensated internal electric fields that affect the refractive index and determine the PE in the crystal. On the other hand, with an increase in the degree of structural perfection in the $\text{LiNbO}_3\text{:Zn}$ (0.05 mol.%) crystal, the number of shallow electron traps is significantly increased and, accordingly, this greatly increases the probability of radiative recombination of photo-excited carriers without their capture by deep traps. This explains the significant weakening of PE in $\text{LiNbO}_3\text{:Zn}$ (0.05 mol.%) crystal, even with the presence of significant amounts of deep trapping levels - antisite defects Nb_{Li} .

Values of the main parameters of the lines in the Raman spectra of the investigated $\text{LiNbO}_3\text{:Zn}$ crystals are given in Table 2. Increasing of the ordering of structural units of the $\text{LiNbO}_3\text{:Me}$ cation sublattice at low concentrations of cations $\text{Me} = \text{Mg}^{2+}$, Zn^{2+} , Gd^{3+} , etc. is confidently manifested in the Raman spectra [1], [18]. In this case, the widths of the lines corresponding to vibrations of Nb^{5+} and Li^+ cations of A_1 (TO, LO) type of symmetry (along the polar axis) decrease [1]. For crystals doped with Zn^{2+} the concentration dependence of the widths of most lines shows a distinct minimum in the $0.05 \div 0.94$ mol. % Zn^{2+} concentration area, that evidences the ordering of structural units of the cation sublattice, Fig. 3.

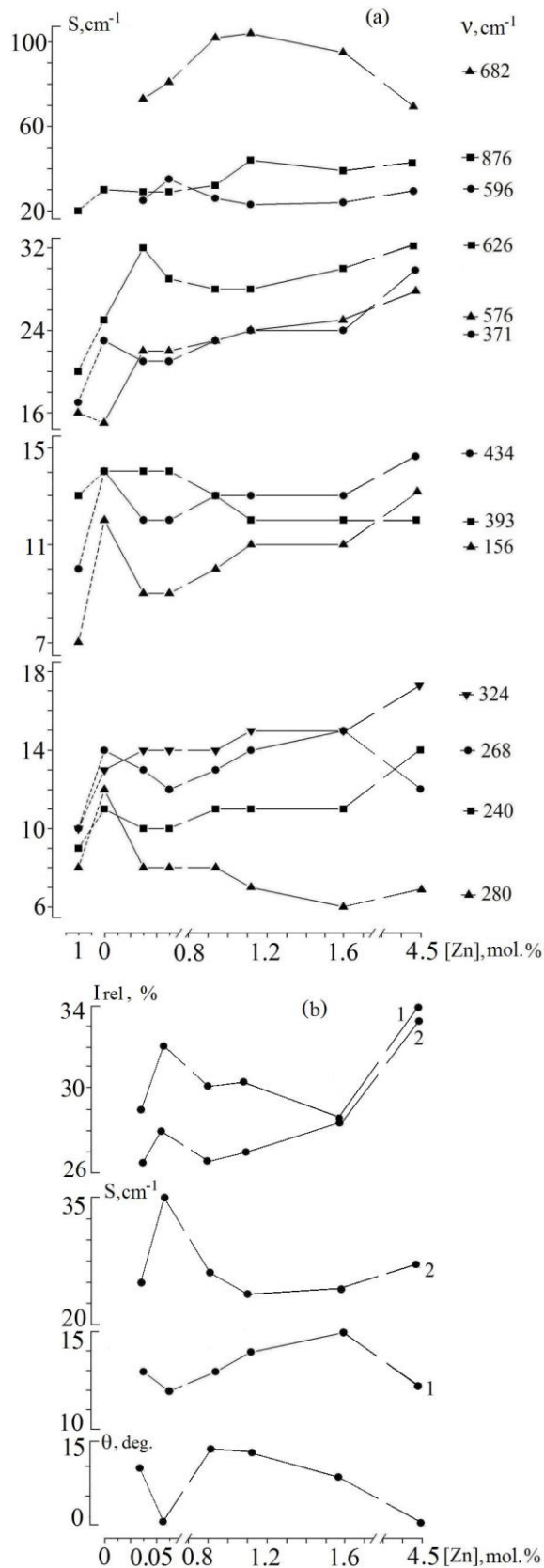


Fig. 3. Dependence of linewidth (S , cm^{-1}) in Raman spectra of $\text{LiNbO}_3\text{:Zn}$ on Zn^{2+} concentration. Dotted line shows linewidth change at going from stoichiometric crystal to congruous one (a); Dependence of PILS indicatrix opening angle θ , widths and relative intensities (I_{rel} , %) of lines 268 (1) and 596 (2) cm^{-1} in Raman spectra of $\text{LiNbO}_3\text{:Zn}$ crystals on Zn^{2+} concentration (b).

Table 2

Basic parameters of the lines corresponding to vibrations of E(TO) symmetry type in the Raman spectra of LiNbO₃:Zn [0.03 ÷ 4.5 mol. %] single crystals.

[Zn] = 0.03			[Zn] = 0.05			[Zn] = 0.94			[Zn] = 1.12			[Zn] = 1.59			[Zn] = 4.5		
ν	s	I_{rel}	ν	s	I_{rel}	ν	s	I_{rel}	ν	s	I_{rel}	ν	s	I_{rel}	ν	s	I_{rel}
156	9	71,77	155	9	81,78	155	10	75,75	155	11	80,95	155	11	68,83	154	13	143,92
240	10	84,59	240	10	95,83	240	11	90,39	240	11	95,81	240	11	89,94	244	14	141,01
268	13	29,03	268	12	32,1	268	13	30,18	268	14	30,23	268	15	28,4	271	12	34,29
280	8	11,47	280	8	13,28	279	8	12,89	280	7	12,55	279	6	12,74	280	7	17,17
324	14	47,96	324	14	52,85	324	14	50,36	324	15	55,67	324	15	57,18	328	18	87,02
371	21	28,9	371	21	30,59	371	23	29,81	371	24	30,74	370	24	29,76	372	29	37,58
393	14	9,89	393	14	10,27	394	13	9,46	394	12	10,14	394	12	10,13	394	12	14,09
434	12	22,73	434	12	22,66	434	13	23,73	435	13	23,96	435	13	23,36	436	15	23,66
576	22	100	576	22	100	576	23	100	576	24	100	576	25	100	573	28	100
596	25	26,53	597	35	28,11	598	26	26,63	598	23	27,22	598	24	28,42	596	30	33,41
626	32	17,07	625	29	19,25	625	28	19,63	625	28	21,1	625	30	21,81	624	32	21,12
682	73	5,15	682	81	5,5	666	102	6,5	662	104	7,9	668	95	7,64	679	66	6,73
876	29	1,35	874	29	1,54	873	32	1,39	876	44	1,7	874	39	1,67	876	34	2,02

At the same time there is a correlation in the concentration dependence of the indicatrix PILS angle (θ) opening, width (S) and relative intensities (I_{rel}) of lines with frequencies of 268 and 596 cm⁻¹ in the Raman spectrum, Fig. 3b. Fig. 3b shows that S and θ of the line with frequency of 268 cm⁻¹ are minimal, and the S of line with frequency of 596 cm⁻¹ and I of lines with frequencies of 268 and 596 cm⁻¹, on the contrary, are maximum at concentration of Zn²⁺ in 0.05 mol. %.

Such behavior of the widths and intensities of the lines corresponding to internal vibrations of oxygen octahedrons O₆ of E(TO) symmetry type and fluctuations of Nb⁵⁺ and Li⁺ cations in octahedrons O₆ shows the connection between the order of arrangement of cations along the polar axis, deformation of octahedrons, changing of their polarizability, concentration of defects with localized electrons and PE value. When changing the amount of Zn²⁺ in the crystal structure the anisotropic deformation and changes in the polarizability of the oxygen octahedrons occur. Octahedrons deformation is promoted by the fact that Zn²⁺ ion radius is larger than the ionic radii of Li⁺, and Nb⁵⁺. Anisotropic expansion of oxygen octahedrons when doping is also confirmed by a non-synchronous increase of a and c parameters of unit cell when the amount of Zn²⁺ increases [1], [22] and by the increase in width of line with frequency 876 cm⁻¹. This line corresponds to the stretching vibrations of the oxygen atoms in the octahedrons O₆ (Fig. 3) and is sensitive to clustering cations [1].

The anisotropic oxygen octahedrons (O₆) deformation described above is confirmed by the presence of minimum three Zn concentration at about 3 mol. % on the concentration dependence of coefficient of linear electro-optic effect. According to [3], [4] this concentration of Zn²⁺ matches significant substitution of Nb_{Li} defects and minimum of lithium vacancies concentration. Furthermore, it is necessary to take into consideration the existence of uncontrollable «photorefractive» impurities (table 1) that have important influence on photorefraction. Fe³⁺ ions in congruent LiNbO₃ crystal get in lithium positions [1]. Zn²⁺ ions at low concentrations replace simultaneously both the Nb_{Li} and Li_□ defects and Li⁺ cations in their own sites [1], [4]. Introducing of the Zn²⁺ ions into crystal structure certainly will cause the localization of Fe ions and will change the type of the trap that also have an impact on the magnitude of the PE [1].

We have investigated spatial structural defects, distortions of the optical indicatrix caused by mechanical stresses or compositional heterogeneity of the crystal, as well as static and fluctuating defects induced in photorefractive crystal by laser radiation, by laser conoscopy method at different laser power. In this case, at low laser power the differences of conoscopic patterns from ideal ones are due to the structural heterogeneity of crystals. Distortions of conoscopic patterns, appearing with the increase of laser power, will provide information on the structure of a photorefractive crystal distortions caused by the action of the laser beam.

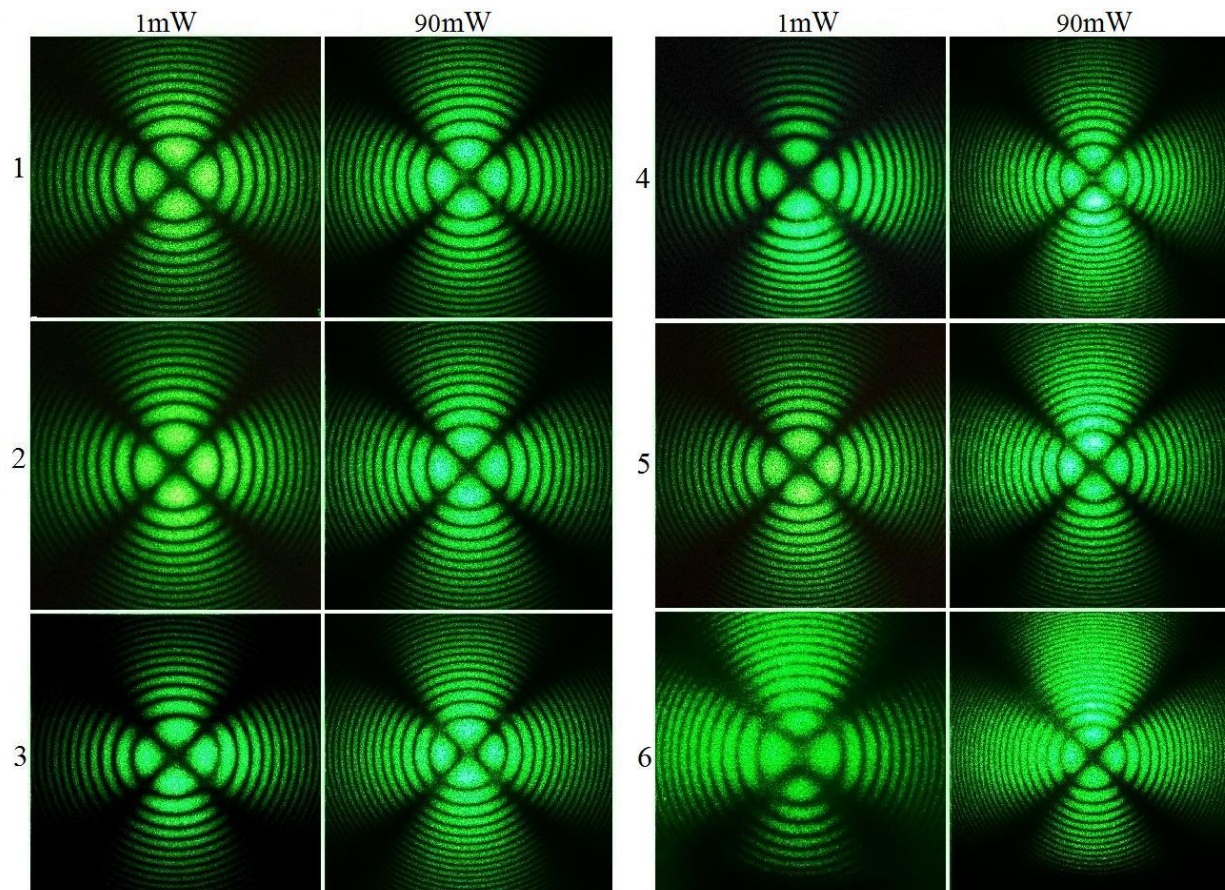


Fig. 4. Conoscopic pictures of crystals $\text{LiNbO}_3:\text{Zn}^{2+}$: 1). 0.03; 2). 0.05; 3). 0.94; 4). 1.12; 5). 1.59; 6). 4.5 mol. %. $\lambda = 532 \text{ nm}$. $P = 1$ and 90 mW.

Fig. 4 shows the conoscopic patterns of $\text{LiNbO}_3:\text{Zn}$ (0.03 ÷ 4.5 mol.%) crystal obtained at the radiation power of 1 and 90 mW. The patterns of $\text{LiNbO}_3:\text{Zn}$ (0.03 mol.%) and $\text{LiNbO}_3:\text{Zn}$ (0.05 mol.%) crystals at the laser power of 1 and 90 mW (Fig. 4 (1, 2)) are in good agreement with the picture of a uniaxial optically homogeneous crystal. Patterns have circular symmetry, "Maltese cross" preserves the integrity of the center of the visual field. However, at 90 mW at the pattern of $\text{LiNbO}_3:\text{Zn}$ (0.03 mol.%), Fig. 4 (1), there is the presence of additional interference fringes in the lower half, in the right branch of the "Maltese cross" between the first and fifth isochromes. In this case, there is a gap in the first isochrome and slight enlightenment in the "Maltese cross."

The conoscopic pattern of $\text{LiNbO}_3:\text{Zn}$ (0.94 mol. %) crystal at 1 mW of laser radiation matches completely to the uniaxial one, Fig. 4(3). However, at the exciting laser power 90 mW, there are signs of anomalous optical biaxiality, such as deformation of the "Maltese cross" in the center of the field of view with a shift of fragments in the horizontal direction from the center and the difference from 90° of angles between its branches. Isochromes gain weak ellipticity, maintaining regular geometric shape, Fig. 4 (3). In addition, in the upper left-hand branch of "Maltese cross", as well as in the lower half of the conoscopic interference pattern there are minor anomalies in the form of the gap in izochrome and the presence of additional interference fringes. In this case, the image

contrast in the upper left and lower branches of the "Maltese cross" is slightly reduced.

Such distortions of conoscopic pattern are undoubtedly caused by PE. But the appearance of anomalous optical biaxiality is, probably, due to the existence of local micro-areas and clusters in the crystal, which posses birefringence. This is supported by studies of PILS. Fig. 1 (3, 4) shows the division of the central spot of PILS pattern into two halves, which indicates the presence of birefringence.

The appearance of local micro-areas and clusters in the crystal at laser power of 90 mW can be explained by thermally stimulated birefringence, which manifestation in a conoscopic pattern in a lithium niobate crystal is discussed in detail in [23]. Anomalies that appear in the conoscopic patterns with increasing of laser power from 1 to 90 mW, were recorded earlier in our study of photorefractive $\text{LiNbO}_3:\text{steh.}$; $\text{LiNbO}_3:\text{Y}^{3+}$ (0.46 wt.%); $\text{LiNbO}_3:\text{Y}^{3+}$ (0.24 wt.%); Mg^{2+} (0.63 wt.%) crystals. The crystals are characterized by a fast photorefractive response so that the PILS indicatrix expands very quickly in the first few seconds of the irradiation of the crystal by laser radiation [24]. Obviously, the distortions of conoscopic patterns of investigated crystals are associated with the manifestation of structural rearrangements and optical processes occurring under the action of laser radiation.

The conoscopic pattern of $\text{LiNbO}_3:\text{Zn}$ (1.12 mol.%) at the laser power of 1 mW is also matches to uniaxial crystal, Fig. 4

(4). However, in the lower right-hand branch of "Maltese cross" the image contrast is reduced. There are some significant anomalies in conoscopic patterns at 90 mW, such as that observed for the $\text{LiNbO}_3\text{:Zn}$ (0.94 mol.%). Such anomalies indicate the optical inhomogeneity of the sample. However, signs of abnormal optical biaxiality, as observed for the crystal $\text{LiNbO}_3\text{:Zn}$ (0.94 mol.%) were not detected.

The conoscopic pattern of $\text{LiNbO}_3\text{:Zn}$ (1.59 mol.%) crystal matches uniaxial one both at 1 and 90 mW laser radiation, Fig. 4(5). However, at 90 mW there is a slight blur of "Maltese cross" and a reduction in image contrast in the upper left-hand branch. Significant distortions (caused by PE) inherent to $\text{LiNbO}_3\text{:Zn}$ (0.94 mol.%) and $\text{LiNbO}_3\text{:Zn}$ (1.12 mol.%) crystals were not found for the $\text{LiNbO}_3\text{:Zn}$ (1.59 mol.%) crystal, which agrees well with the PILS data.

The most interesting anomalies in the conoscopic patterns were observed for the $\text{LiNbO}_3\text{:Zn}$ (4.5 mol.%), Fig. 4 (6). Even at a power of 1 mW picture has features of anomalous optical biaxiality: deformation is observed in the center of a black "Maltese cross" in the form of a vertical displacement. The displacement corresponds to the direction of deformation of the optical indicatrix of the crystal. There is enlightenment in the central part of the black "Maltese cross", and the angles between its branches are different from 90° .

At the same time the isochromes preserve the integrity and regular geometric shape, but extended in the direction of displacement of fragments of the cross and take the form of ellipses, Fig. 4 (6). There is some blur of the picture that indicates optical inhomogeneity of sample. In addition, there are obvious anomalies in all the branches of "Maltese cross". Such distortions of conoscopic pattern is undoubtedly related to the structural heterogeneity of the crystal, probably due to the irregular entry (at such a high concentration) of Zn^{2+} cations to the structure during crystal growth. This conclusion is confirmed by the PILS and Raman spectra. The scattering ability for $\text{LiNbO}_3\text{:Zn}$ (4.5 mol.%) crystal was found to be

much larger than for other crystals (Fig. 1). In addition, Raman spectra revealed expression of line broadening corresponding to both internal vibrations of oxygen octahedra and fluctuations of Nb^{5+} and Li^+ cations in O_6 octahedrons, Fig. 3.

It is also unusual that at exciting laser power 90 mW standard conoscopic pattern of uniaxial crystal of high optical quality is observed for the crystal $\text{LiNbO}_3\text{:Zn}$ (4.5 mol.%) (Fig. 4 (6)). This pattern is significantly better than the one at power of 1 mW. There is a circular symmetry, black contrasting "Maltese cross" preserves the integrity of the center of the visual field, and isochromes are concentric circles centered at the output of the optical axis. Only in the left upper branch "Maltese cross" has a slight decrease in image contrast. This improvement in the optical quality of the crystal can be caused by appearance of "healing" defects at increase of laser radiation power. We have not found changes in the conoscopic pattern of the $\text{LiNbO}_3\text{:Zn}$ (4.5 mol.%) due to the PE. This correlates well with the data of PILS, according to which in the $\text{LiNbO}_3\text{:Zn}$ (4.5 mol.%) photorefractive response is absent even when the laser power is 160 mW, Fig. 1 (6).

It should be noted also that the edge of the optical transmission of the $\text{LiNbO}_3\text{:Zn}$ (4.5 mol.%) crystal is characterized by the steep rise. In the edge of the optical transmission of the crystal there also is a significant shift to shorter wavelengths in comparison with other crystals, Fig. 5 (6). This is associated with a significant decrease (near the threshold) of the number of Nb_{Li} defects. This leads to the decrease of probability of change in the charge state of the Nb_{Li} defects (which means appearance of Nb^{4+} cations) and the formation of local disturbances in the oxygen sublattice of the crystal, leading to the formation of charged centers, changing the character of the optical absorption of the crystal [1], [25].

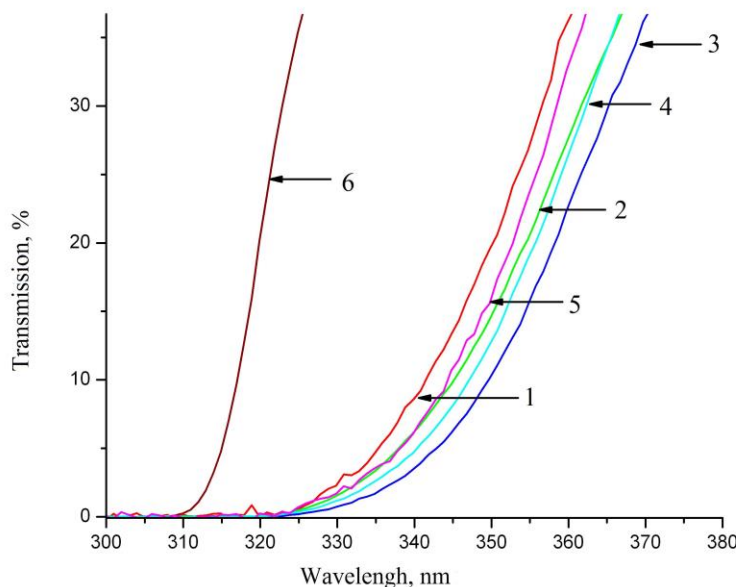


Fig. 5. Electronic transmission spectra of crystals $\text{LiNbO}_3\text{:Zn}^{2+}$: 1). 0.03; 2). 0.05; 3). 0.94; 4). 1.12; 5). 1.59; 6). 4.5 mol. %.

For all other crystals $\text{LiNbO}_3\text{:Zn}$ transmission edge shifted to longer wavelengths, and the rise was more gradual, Fig. 5. Our data agree well with the data obtained in [1], [5].

The PILS picture is self-similar and due to its finiteness in the space, it has fractional dimension different from the topological one [27]. Nevertheless, the methods of fractal analysis have never been applied to investigate PILS speckle pictures.

So the problem of developing methods of PILS pictures fractal analysis is of great interest. Such methods could reveal the character of dynamics and organization of laser-induced defects in the crystal. The methods are not developed yet although there are a lot of PILS models (see [12]).

Change of fractal dimension of any system means change of complicity of the system, or change in entropy production [28]. When fractal dimension rises, system becomes more complicated and entropy production rises, and vice versa. As long as in our case the system is all laser-induced defects that correspond to one PILS layer, the more complicated PILS layer contains more laser-induced defects.

The time dynamics of fractal dimension of PILS pictures three layers for Zn-doped LN crystals is shown on Fig. 6. $\text{LiNbO}_3\text{:Zn}$ (4.5 mol.%) was not considered because PILS does not appear in this crystal under searched laser power. For this method PILS was excited by laser power 160mW due to the fact that scattered light indicatrix is brighter and opens better. For the first PILS layer at least two maximums are observed for each concentration of impurity. It means that concentration of the laser-induced defects in the $\text{LiNbO}_3\text{:Zn}$ under laser radiation is not stable. We believe that these changes are the result of auto-wave processes connected with excitation and migration of laser-induced defects. Fig. 1 (1) clearly shows dependence between the concentration of Zn in LN crystals and time of the first maximum of fractal dimension in first PILS layer.

The structure of Zn^{2+} -doped LN crystals obviously depends on impurity cations concentration. Moreover, the area of highly ordered crystal structure is revealed in LN crystals doped by Zn in concentrations $0.05 \div 0.94$ mol. % by Raman spectra. So the processes that take place in PILS layers and that are revealed in fractal analysis of PILS pictures layers strongly depend on the crystal defectiveness and the cation order. Thus, as we can see on Fig. 6 (1), the most effective crystal is the one with the fastest response to laser radiation – i.e. $\text{LiNbO}_3\text{:Zn}$ (1.12 mol. %). Perhaps, order of cation in this crystal is the best. And, due to all previously described researches of this series of LN crystals, it means that dependence of PE on the Zn concentration is strongly nonlinear. Maybe it shows the best PE among all other searched crystals.

The excitements that we see in the first PILS layer (Fig. 6 (1)) are propagating to the third PILS layer (Fig. 6 (3)). And again we see that the maximum of the laser-induced defects concentration occurs faster for $\text{LiNbO}_3\text{:Zn}$ (1.12 mol. %) crystal.

Note that second PILS layer (Fig. 6 (2)) shows no response to the laser radiation. Perhaps it just transfers the wave of laser-induced defects from the first PILS layer to the third one, but doesn't change.

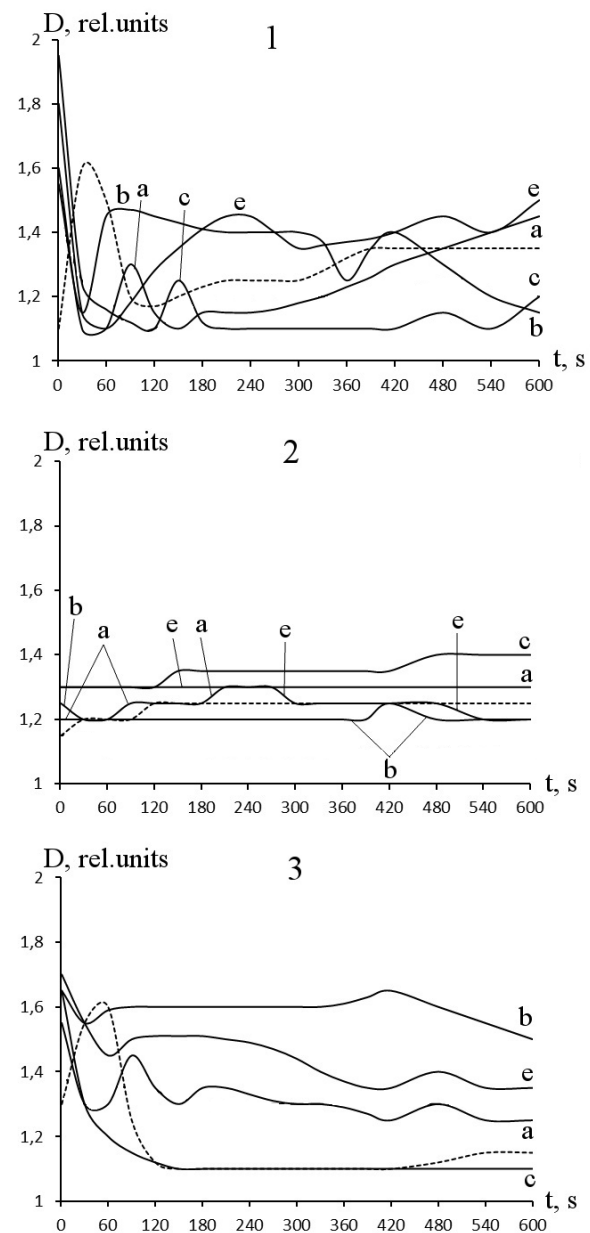


Fig. 6. Fractal dimension D time (t) dynamics of first (1), second (2) and third (3) layers of PILS speckle-picture of LiNbO_3 crystals doped by Zn in concentrations 0.03 mol. % - a, 0.05 mol. % - b, 0.94 mol. % - c, 1.12 mol. % - dotted line, 1.59 mol. % - e. Exciting laser radiation was 160 mW.

IV. CONCLUSION

$\text{LiNbO}_3\text{:Zn}$ (0.03 $\div$ 4.5 mol. %) crystals with a comparatively low PE were investigated by the methods of PILS, laser conoscopy, Raman spectroscopy, electron spectroscopy and fractal analysis. It was found that the PE depends non-monotonically on Zn^{2+} ion concentration in the crystal. The increase of photorefraction at 0.03; 0.94; 1.12 and 1.59 mol. % concentrations of Zn^{2+} in the crystal was found. Concentrations of 0.05 and 4.5 mol. % was found to have significantly decreased PE compared to the nominally pure congruent crystal. In this case, photorefraction is reduced

since the 1.59 mol. % concentration of Zn^{2+} and is virtually absent at a concentration of Zn^{2+} 4.5 mol. %. The range of increased structure order that reveals through the cation sublattice increased order of succession of basic, impurity cations and vacancies along the polar axis, was detected in Raman spectra in the range of Zn^{2+} concentrations of about $\sim 0.05 \div 0.94$ mol.%. Fractal analysis confirmed and specified these data. It revealed the fastest response of laser-induced defects under laser radiation for crystal $\text{LiNbO}_3\text{:Zn}$ (1.12 mol. %). At the same time appearance of abnormal optical biaxiality, especially noticeable when the laser power was 90 mW, revealed on the conoscope patterns of the crystals. However, the $\text{LiNbO}_3\text{:Zn}$ (4.5 mol.%) crystal at the laser power of 90 mW shows standard conoscope pattern of uniaxial crystal of high optical quality. That pattern is much better than the one at power of 1 mW, which is caused by "healing" of defect structure by laser radiation. The high optical quality of the $\text{LiNbO}_3\text{:Zn}$ (4.5 mol.%) is also indicated by a significant (compared to the rest of the investigated Zn doped crystals) shift of the optical transmittance in the short wavelength range.

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