Optik 126 (2015) 1081–1089

Contents lists available at ScienceDirect

Optik

journal homepage: www.elsevier.de/ijleo

Integrated research of structural and optical homogeneities of the lithium niobate crystal with low photorefractive effect

N.V. Sidorov[a], A.A. Kruk[a], O.Y. Pikoul[b,*], M.N. Palatnikov[a], N.A. Teplyakova[a], A.A. Yanichev[a], O.V. Makarova[a]

[a] Federal State Budget Institution of Science Institute of Chemistry and Technology of Rare Elements and Mineral Raw Materials, Kola Scientific Center (ICTREMRM KSC), Russian Academy of Sciences, Akademgorodok, 26a, 184209 Apatity, Russia
[b] Federal State Budget Institution of Education Far Eastern State Transport University, Seryshev str., 47, 680021 Khabarovsk, Russia

ARTICLE INFO

Article history:
Received 19 February 2014
Accepted 4 March 2015

Keywords:
Lithium niobate single crystals
Conoscopic patterns
Optical homogeneity
Optical damage

ABSTRACT

Stoichiometric (Li/Nb = 1) and congruent (Li/Nb = 0.946) single crystals of lithium niobate ($LiNbO_3$) doped with cations of Mg^{2+}, Zn^{2+}, Cu^{2+}, B^{3+}, Gd^{3+}, Y^{3+}, Fe^{3+}, Ta^{5+} were investigated by means of photoinduced light scattering (PILS), Raman spectroscopy (RS), electron spectroscopy and laser conoscopy. It was established that investigated specimens can be divided into three groups depending on the type of PILS painting. The first group includes crystals that manifest small photorefractive effect. PILS indicatrix of the third group crystals opens in first few seconds after laser irradiation and for the second group – after about a minute. First group of crystals is characterized by the steep rise of transmission edge in comparison with other crystals, which indicates high volume homogeneity of these specimens. Anomalous behavior of an edge transmission is typical for the $LiNbO_3$:Cu (0.015 wt.%) crystal which indicates its high optical inhomogeneity. The edge position of the optical transmission of the third group crystals ($LiNbO_3$:Y (0.46 wt.%) and $LiNbO_3$:Y(0.24 wt.%):Mg(0.63 wt.%)) is in a good agreement with the crystals of the first group, but the slope of the curve to the *x*-axis is substantially less. It is shown that asymmetry of PILS patterns and Raman spectra of photorefractive lithium niobate crystals in scattering geometries is due to the birefringence of the exciting laser radiation propagating perpendicular to the polar axis of the crystal.

1. Introduction

Ferroelectric single crystal of lithium niobate is one of the most important and sought-after photorefractive nonlinear optical materials [1–6]. Lithium niobate is a phase of variable composition with a wide homogeneity region of the phase diagram that effectively allows altering physical characteristics of the crystal by doping and stoichiometry changing [3,4]. Photorefractive effect and photoinduced light scattering cause severe degradation of the laser beam in a lithium niobate crystal and appear to be hindering factors for holography, the generation and radiation conversion [1,2]. For this reason researches that aimed at optimizing the photorefractive properties of lithium niobate crystal are currently the most relevant for the purposeful creation of materials with desired characteristics [4–6]. Regardless to $LiNbO_3$ crystals' composition photovoltaic mechanism is the predominant one and caused by the linear electro-optical effect [3–6]. Therefore crystal's photorefractive properties are largely determined by the presence of charged impurities and structural defects with localized electrons. The magnitude of the electro-optical effect determines the value of the disclosing angle of the PILS indicatrix that occurs mainly along the polar axis [1,2]. The magnitude and speed of the opening of an angle of the PILS indicatrix determine the sensitivity of electrooptical modulators, valves and the speed of holographic information recording. In addition to great practical significance PILS experimental studies in lithium niobate crystals are also important for understanding the nature of structural changes and optical processes occurring in the interaction of laser radiation with a photorefractive crystal. However PILS method gives information about photorefractive properties and provides no information about the features of the crystal structure and defects, determining these properties. An informative method of studying of the fine features of crystal structure and the state of its defectiveness is Raman spectroscopy [4]. Raman spectra are highly sensitive to changes of interactions between the structural units of the crystal and hence to various kinds of defects and features of the structure disordering. An important advantage of Raman spectroscopy is the ability

* Corresponding author. Tel.: +7 4212564729.
E-mail addresses: sidorov@chemy.kolasc.net.ru (N.V. Sidorov), pikoul2008@gmail.com (O.Y. Pikoul).

http://dx.doi.org/10.1016/j.ijleo.2015.03.018
0030-4026/

to study the photorefractive effect, fine structural features of the different sublattices of the crystal, local inhomogeneities in the structure and defects simultaneously [4]. In this paper structural features and photorefractive properties of series of nominally pure lithium niobate crystals of congruent and stoichiometric compositions, as well as congruent crystals doped by cations of Mg^{2+}, Zn^{2+}, Cu^{2+}, B^{3+}, Gd^{3+}, Y^{3+}, Fe^{3+}, Ta^{5+} were studied by means of PILS, Raman spectroscopy, electron spectroscopy and laser conoscopy. These crystals are promising as nonlinear optical materials with small photorefractive effect, and low-photoinduced scattering and are convenient model objects for studies of disorder in the crystal. In crystals with high photorefractive effect under laser radiation a significant change in the refractive index and strong laser beam degradation take place. This cause "smearing" of some optical effects associated with the passage of laser radiation through the crystal. Double doping is promising for producing optically durable lithium niobate crystals. Raman spectra and PILS pictures of lithium niobate crystals of stoichiometric composition, as well as congruent crystals doped with cations listed above were investigated earlier in Refs. [2,4,7–14]. Optical quality control and structural homogeneity of the grown crystals were carried out by laser conoscopy and electron spectroscopy.

2. Experimental technique

All crystals were grown from the melt of congruent composition (Li/Nb = 0.946) on the "Krystall-2" installation in air by Czochralski method using the one methodology. The original granular blend with high bulk density allowing to obtain "water white" nominally pure single crystals of lithium niobate synthesized in ICTREMRM KSC was used [15]. The technique of crystal growth and batch preparation are described in [15,16]. Photorefractive effect in nominally pure and doped with nonphotorefractive cations lithium niobate crystals is defined by the intrinsic defects with localized electrons and trace amounts of multiply charged photorefractive cations (Fe, Rh, Cu, etc.) [3–6]. Table 1 shows the trace concentrations of cationic impurities in lithium niobate crystal of congruent composition, determined by spectral analysis. Table 1 shows that the crystals are characterized by high uniformity along the axis of growth and the composition of the main components and impurities, which is particularly evidenced by the fact that the Curie temperature (T_C) of the upper and lower portions of the boule are the same. Similar results were obtained for concentrations and associated impurities of doped lithium niobate crystals.

Crystalline samples for research had cuboid size ≈ 7 mm × 6 mm × 5 mm with edges coincident with the directions of crystallophysical axes *X*, *Y*, *Z*, where *Z* is a polar axis of the crystal. Verges of parallelepipeds were carefully polished.

Table 1
The results of spectral analysis of wafers cut from the top and tail of the nominally pure congruent lithium niobate crystal.

Impurity	Impurity content, wt.%	
	Top	Tail
Zr	$<1 \times 10^{-3}$	$<1 \times 10^{-3}$
Mo	$<1 \times 10^{-3}$	$<1 \times 10^{-3}$
Ca	$<1 \times 10^{-3}$	$<1 \times 10^{-3}$
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	$<5 \times 10^{-4}$	$<5 \times 10^{-4}$
T_C, °C	1142.0	1142.0

PILS was excited by MLL-100 on the Y:Al-garnet laser (λ = 530 nm, *P* = 160 mW). In PILS experiments laser beam is directed along *Y* axis and the vector of the electric field strength *E* of the laser radiation is parallel to *Z*. In this scattering geometry the photorefractive effect manifests most vividly. Scattered radiation falls on a translucent screen placed behind the crystal and recorded with a digital camera. Metric ruler placed on the screen was used for determination of geometric size of the PILS indicatrix. Based on the geometry of the experiment (the distance from the crystal to the screen – *b*, distance between two brink points of the speckle pattern – *a*), scattering angle θ was calculated by the formula $\theta = arctg(a/b)$. Since the shape of the indicatrix of the scattered radiation can be varied and multiple [1,17] the outermost point of the PILS picture at which the scattering angle is determined was taken. It is the point at which the intensity of scattered radiation decreases tenfold.

Raman scattering line of 514.5 nm was excited with argon laser Spectra Physics (model 2018-RM) and recorded with T64000 spectrograph manufactured by Horiba Jobin Yvon using a confocal microscope. To eliminate the influence of photorefractive effect on the Raman spectrum the spectra were excited with low power. Power of the exciting laser radiation under the microscope did not exceed 3 mW. All spectra were recorded with a resolution of 1.0 cm^{-1} at room temperature. Absorption and transmission spectra were measured with SF-256 UWI spectraphotometer.

Structural distortions control of the crystals was carried out by laser conoscopy which allows to observe conoscopic pattern of large-scale and high-resolution. Technique is described in detail in [18,19]. Laser conoscopy unlike microscopic conoscopy allows to perform a detailed analysis of subtle features of the structural distortions of crystals in the center of the field of view and on the periphery of the conoscopic patterns. This is important for the detection of micro- and nanostructures unavoidably presented in doped single crystals due to the irregular occurrence of dopant into the structure as well as distortions arising from the laser beam radiation in photorefractive single crystals [4,20]. Conoscopic pattern of crystals were excited by a He–Ne laser (λ = 632.8 nm) of low power (*P* = 1 mW) and MLL-100 laser with Y:Al-garnet (λ = 532 nm, *P* = 90 mW). Excited with 632.8 nm (*P* = 1 mW) laser beam photorefractive effect and hence PILS of the most of investigated crystals do not appear. Before conducting the experiment conoscopic monocrystalline sample was mounted on a movable XY optical table that allows to scan the entire plane of laser beam entrance face and get a lot of conoscopic patterns corresponding to different portions of the cross-section of the test sample. The transmission axis of the polarizer and analyzer were oriented perpendicular to each other, the transmission axis of the polarizer was 45° angle with the vertical. Axis of the laser beam coincided with the optical (polar) axis of the crystal and was perpendicular to its front face. Conoscopic patterns of samples were recorded on a translucent screen using digital camera.

3. Results and discussion

3.1. Photorefractive light scattering in lithium niobate crystals

PILS time dependences paintings obtained with power of the exciting laser radiation (λ = 532 nm) of 160 mW are shown in Fig. 1a–c. The results obtained confidently allow to divide studied samples into three groups depending on the scattering pattern. To the first and largest group (Fig. 1a) can be attributed with crystals which PILS picture practically does not change in time or changes very little. For these crystals even with exciting radiation power of 160 mW photorefractive response cannot be registered and PILS indicatrix is not disclosed. Instead there is only a