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Optical properties of lithium niobate crystals

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ABSTRACT

According to optical absorption spectra the width of the forbidden band of nominally pure congruent and stoichiometric lithium niobate crystals, as well as a series of congruent crystals doped with cations of Mg^{2+}(0.35 wt.%), Zn^{2+}(2.05), B^{3+}(0.12), Gd^{3+}(0.26, 0.44, 0.51), Y^{3+}(0.46), Gd^{3+}(0.23):Mg^{2+}(0.75), Mg^{2+}(0.86):Fe^{3+}(0.0036), Ta^{5+}(1.13):Mg^{2+}(0.01), Y^{3+}(0.24):Mg^{2+}(0.63), Er^{3+}(3.1) is determined. The photorefractive effect in crystals, their structural and optical homogeneity was studied by photo induced and Raman scattering methods, laser conoscopy.

1. Introduction

Nowadays the researches aimed at the optimal use of optical properties of materials in the devices for the transmission, storage and processing of information are relevant. The actively developing devices are the ones operating in the optical range (optical switches, modulators, etc.), in which nonlinear optical crystals are used [1,2]. The ferroelectric lithium niobate crystal ($LiNbO_3$) has high electro optical, pyro electric, nonlinear optical and piezoelectric coefficients [2–4]. The unique properties of the $LiNbO_3$ crystal are determined by its composition and the features of the deeply defect structure, which depends substantially on the composition [3,4]. The $LiNbO_3$ crystal is a material with a widely developed secondary structure [5]. In the crystal except deep electron traps created by point photorefractive centers (mainly by defects Nb_{Li} – ions Nb^{5+} located in Li^+ ion positions of an ideal stoichiometric structure), there are many small traps that affect the photo induced change in refractive index (photorefractive effect, optical damage) and electrical properties [4–6]. Besides, lithium niobate crystal is a phase of variable composition which by alloying and changing the stoichiometry both fundamentally change the properties and finely vary the physical characteristics of the crystal [3,4]. The number of Nb_{Li} defects and small traps depends on composition of the crystal [4]. In nominally pure crystals with an increase in the ratio R = Li/Nb the number of deep electron traps (Nb_{Li} defects) decreases, but at the same time the number of defects in the form of small electron traps increases [4,7].

When laser radiation is applied to the ferroelectric $LiNbO_3$ crystal, spatial separation of the charge occurs as a result of photo excitation processes (drift and diffusion of electrons) and an internal electric field arises that leads to a photo induced

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change in the refractive indices at the site of radiation [3,4,7,8]. In the $LiNbO_3$ crystal the photovoltaic mechanism is the predominant photo refraction mechanism that is the value of the magnitude of the photovoltaic field is much larger than the value of the diffusion field [4,7,8]. In addition under the action of laser radiation Rayleigh photo induced light scattering (PhILS) occurs on static and dynamic (fluctuating) defects with an altered refractive index induced by laser radiation [9,10]. At the same time, the value of the electro-optic effect determines the value of the opening angle of the PhILS indicatrix, which in the $LiNbO_3$ crystal occurs predominantly along the polar Z axis [9,10]. The magnitude and velocity of the opening angle of the PILS indicatrix are determined by the photorefractive sensitivity and the speed of photorefractive recording of information in electro-optical crystals [10,11]. Depending on the composition the magnitude of the photo refraction effect, photo- and electrical conductivity in the $LiNbO_3$ crystal vary widely [4,9–17]. In this case there should occur the change of the forbidden band width which is 3.72 eV for a nominally pure congruent crystal, that is close to the value characteristic for wide-gap semiconductors [8,11,18]. By reducing the width of the band gap, we can approximate the properties of the $LiNbO_3$ crystal to semiconductor crystals, which in principle allows us to develop materials with cross effects.

The investigated crystals have a relatively low photo refraction effect and are promising as the materials for frequency converters, electro-optical modulators and closures, optical materials with micron and submicron periodic structures. Double doping is promising for obtaining crystals of increased optical strength. By an alteration of the intrinsic absorption edge the band gap anomalies that arise when the crystal composition changes can be found out.

Optical absorption spectra, conductivity, Raman scattering spectra and PhILS, photoelectric fields of crystals of some compositions, as well as their optical and structural homogeneity, were partially investigated earlier in refs [4,19–43].

The purpose of this work is a comprehensive study of the band gap behavior, photorefractive and electrically conductive properties depending on the composition, structural features and the defect state of $LiNbO_3$ crystals obtained both from a single source and from different growing technologies.

2. Methods of the experiment

$LiNbO_3$ single crystals growth was carried out by the Chokhralsky method in the air atmosphere [44]. The doping additive was introduced directly into the melt in the form of the corresponding oxides of the ultrapure qualification. The charge of lithium niobate produced by I.V. Tananaev Institute of Chemistry and Technology of Rare Elements and Mineral Raw Materials of the Russian Academy of Sciences was used, its production technology is described in the work [45]. In the case of $LiNbO_3$: Mg^{2+} (0.86 wt.%): Fe^{3+} (0.0036), the doping additive was not introduced into the melt but in the synthesis of the lithium niobate charge as a homogeneously doped precursor of Nb_2O_5: Mg: Fe [46,47]. The crystalline samples for the studies had the form of rectangular parallelepipeds of dimensions ~7·6·5 mm^3 (±2 mm) with ribs coinciding in direction with the crystal-physical axes *X, Y, Z*, where the *Z*-axis is the polar axis of the crystal. The faces of the parallelepipeds were thoroughly polished. The determination of the absorption edge was carried out with the aid of the monochromator. To determine the width of the forbidden band the transmission spectrum of the crystal was recorded. According to the obtained dependence of the intensity of radiation passing through the crystal an inverted spectrum – the absorption spectrum was constructed. A deuterium lamp was used as the source of radiation. The obtained absorption spectrum in the decreasing linear part of the graph was approximated by a straight line till crossing with the abscissa axis. The intersection point of this line and the abscissa axis is the wavelength corresponding to the absorption edge of the crystal. The width of the band gap was determined from the formula $E = hc/\lambda$, where λ is the wavelength corresponding to the absorption edge, *h* is the Planck constant, and *c* is the speed of light in a vacuum. The accuracy of determining the border of the absorption edge is ±1.0 nm.

PhILS was excited by a laser Nd: YAG (MLL-100), l_O = 532 nm, I ~ 6.29 W/cm^2. The radiation scattered by the crystal laid on a translucent screen placed behind the crystal and was recorded by a digital video camera. The experimental setup and the procedure for determining the PhILS indicatrix are described in detail in the works [10,19]. In the PhILS experiments the laser beam is directed along the *Y* axis and the intensity vector *E* of the electric field of the laser radiation is parallel to the polar axis *Z* of the crystal. According to the parameters of the PhILS indicatrix in the studied crystals the values of the intensities of the photovoltaic and diffusion electric fields and also the induced birefringence, taking into account the Selmeyer formulae were determined. The installation and the technique for determining the photoelectric fields are described in detail in the works [38–40]. The error in calculating the photoelectric fields under the experimental conditions is 5–10%. The method of conoscopic researches is described in [29,33,41,42]. We used Nd: YAG (MLL-100) laser radiation (l_O = 532.0 nm, intensity up to 3.54 W/cm^2). In the PhILS experiments and in conoscopic studies the sample was mounted on a movable two-coordinate optical stage, which allowed obtaining many PhILS pictures and conoscopic patterns corresponding to different sections of the sample cross-section. The conoscopic picture was recorded on a translucent screen by a digital camera.

Raman scattering spectra were excited with a 514.5 nm line of the Spectra Physics argon laser (model 2018-RM) and recorded with a Horiba Jobin Yvon T64000 spectrograph using a confocal microscope. In this case the Raman scattering spectra were excited by low-power radiation (P < 3 mW) to exclude the impact of the photo refraction effect on the spectrum. All spectra were recorded at a resolution of 1.0 cm^{-1} at room temperature. The spectra were processed using Horiba LabSpec 5.0 and Origin 8.1 software. The accuracy of determining the frequencies, widths and line intensities is ±1.0, ± 3.0 cm^{-1} and 5% respectively.