Conference Paper

Photoelectric Fields and Band Gap in Doped Lithium Niobate Crystals

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Abstract

Photorefractive effect was researched and band gap was determined in nominally pure congruent and stoichiometric lithium niobate crystals, and in a series of congruent $LiNbO_3$ crystals doped by Mg, Zn, B, Gd, Y, Er cations, and $LiNbO_3$ single crystals with double doping Mg:Gd, Mg:Fe, Mg:Y, Mg:Ta by photoinduced light scattering and optical spectroscopy methods.

Keywords: lithium niobate single crystal, doping, photorefractive effect, photoinduced light scattering, optical spectroscopy, band gap

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Received: 28 January 2018
Accepted: 15 March 2018
Published: 25 April 2018

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Selection and Peer-review under the responsibility of the PhIO Conference Committee.

1. Introduction

Researches aimed at creation of optically perfect ferroelectric materials with low photorefractive effect are highly topical for devices for transmission, storage and processing of information, frequency converters, electro-optical modulators and closures with optimal properties. Ferroelectric lithium niobate crystal ($LiNbO_3$) possesses high electro-optic, pyro-electric, optically nonlinear and piezoelectric coefficients and photorefractive effect. The value of the latter varies in wide range in dependence of the crystal compound [1-4].

Lithium niobate is a phase of variable composition. This allows us to change and finely vary physical characteristics of the crystal by doping and changing of the crystal stoichiometry [1, 3]. Unique properties of $LiNbO_3$ crystal are determined by particularities of its highly defective structure that strongly depends on the compound [1-4]. In addition to deep electron traps formed by point photorefractive centers

(mostly by Nb_{Li}defects – Nb^{5+} ions in Li^{+} sites of the perfect stoichiometric structure) the crystal contains great number of shallow electron traps that affect photorefractive effect [3-6]. Photo-excitation processes (drift and diffusion of electrons) occur in $LiNbO_3$crystal under the laser radiation. This leads to a spatial separation of the charge and appearance of an intrinsic electric field which causes photoinduced change of refractive indices [4-7]. The main photorefractive mechanism in a $LiNbO_3$crystal is a photovoltaic one. The value of a photovoltaic field (E_{pv}) is considerably higher than the value of a diffusion field (E_D) [6]. In addition, Rayleigh photoinduced (photorefractive) light scattering (PILS) occurs in a crystal under the laser radiation on laser-induced defects with changed refractive index [7, 8]. The opening angle value and the speckle-structure indicatrix opening velocity determine photorefractive sensitivity and speed of information recording. PILS, photo- and electroconductivity, photorefractive effect vary in a wide range in the dependence of the crystal compound [3, 4, 7-13]. Band gap should change at this. Band gap of a nominally pure congruent crystal is 3.72 eV. This value is characteristic for wide-gap semiconductors [6]. Reducing the width of the band gap could approximate the properties of the $LiNbO_3$ crystal to semiconductor. This opens a possibility to develop optical materials with cross-effects.

In this paper we have researched photorefractive effect and determined band gap in a series of $LiNbO_3$ single crystals doped by Mg^{2+}, Zn^{2+}, B^{3+}, Gd^{3+}, Y^{3+}, Er^{3+} cations, and $LiNbO_3$ single crystals with double doping Mg^{2+}:Gd^{3+}, Mg^{2+}:Fe^{3+}, Mg^{2+}:Ta^{5+}, Mg^{2+}:Y^{3+} by photoinduced light scattering and optical spectroscopy methods. These crystals are perspective materials for frequency converters, electro-optical modulators and closures, optical materials with micron and submicron periodical structures. We have compared obtained results with data on nominally pure congruent ($LiNbO_{3cong}$) and stoichiometric ($LiNbO_{3stoich}$) crystals. Optical absorption spectra, conductivity, PILS and photoelectric fields were previously researched for some of these $LiNbO_3$crystal compounds in papers [3, 12-19].

2. Method

Growth of $LiNbO_3$ single crystals was carried out by Czochralski on air [20]. Nominally pure congruent crystals were obtained from the congruent melt, stoichiometric – from the melt with 58.6 mol % Li_2O. Dopants were added as oxides with impurities less than 10^{-4} mol %. We have used lithium niobate charge prepared in ICTREMRM KSC RAS [21]. In the case of crystals $LiNbO_3$:Mg(0.86 wt. %):Fe(0.0036) and $LiNbO_3$:B(0.12 wt. %) dopants were added not directly to the melt, but at the charge synthesis, as a

homogeneously doped precursor Nb_2O_5:Mg:Fe and Nb_2O_5:B [22]. Samples had a shape of rectangular parallelepipeds ~ 7.6.5 mm^3 (± 2 mm) in size with edges coinciding with crystallographic axes *X*, *Y*, *Z*, where *Z* is a polar axis of a crystal. Faces of parallelepipeds were thoroughly polished.

The absorption edge was detected by a monochromator MDR-41. A transmission spectrum of a crystal was detected to find a band gap. The absorption spectrum was obtained as inversion of an intensity of the radiation that transmitted through the crystal. The radiation source was a deuterium lamp. The decreasing linear part of the absorption spectrum was approximated by a line to the intersection with the abscissa axis. The intersection point is a wavelength corresponding to the crystal absorption edge. The absorption edge value measure error is ±1.0 nm. The band gap was detected due to the formula $E = \frac{hc}{\lambda}$, where λ is a wavelength of the absorption edge, *h* is a Planck constant, *c* is a light speed in a vacuum. PILS was excited by Nd:YAG (MLL-100) laser, λ_o = 532 nm, *I* ~ 6.29 W/cm^2. The experimental setup and the PILS indicatrix parameters determining are described in detail in works [8, 12]. Using method suggested in [23] we have calculated intensity values of the photovoltaic and diffusion electric fields and induced birefringence due to the PILS indicatrix parameters and considering Sellmeier equation. The measurement error is 1.5-2.0 %. The equipment and the method for determination of photoelectric fields are described in detail in [16, 17].

3. Results and Discussion

The table contains results of the band gap calculation for $LiNbO_3$ crystals of different compound, values of photoelectric fields (photovoltaic E_{PV} and diffusion E_D ones) and PILS opening angle. Photoelectric fields and photorefractive effect (induced birefringence Δn) are minimal for crystals $LiNbO_3$:Er(3.1 wt. %), $LiNbO_3$:Mg(0.75):Gd(0.23), $LiNbO_3$:Y(0.46), $LiNbO_{3stoich}$, and maximal for the crystal $LiNbO_3$:Mg(0.35). The largest PILS opening angle is less than 15° for all doped crystals. However, PILS opening angle in the crystal $LiNbO_{3stoich}$, is much wider and reaches 56° [12]. This indicates higher photorefractive effect in this crystal comparing with other crystals. At the photovoltaic field of this crystal is higher than of other crystals and reaches ~ 3178 V/cm. Stoichiometric crystal is characterized by much higher order of cation lattice units, smaller amount of Nb_{Li} defects (which are the deepest electron traps) and higher amount of shallow electron traps [4, 12]. Obtained data demonstrate that band gap of researched crystals varies in the range 3.25÷3.84 eV. Crystals $LiNbO_3$:B(0.12

wt. %), $LiNbO_3$:Gd(0.26), $LiNbO_3$:Y(0.46), $LiNbO_3$:Mg(0.63):Y(0.24), $LiNbO_3$:Mg(0.86):Fe(0.0036), $LiNbO_3$:Mg(0.011):Ta(1.13) have the narrowest band gap, table. At this PILS indicatrix opens very fast in crystals $LiNbO_3$:Y(0.46 wt. %), $LiNbO_3$:Mg(0.63):Y(0.24). The opening occurs at firs seconds of the laser irradiation [24]. In other crystals PILS opens for approximately ~ 60 s. In crystals $LiNbO_3$:Y(0.46 wt. %) and $LiNbO_3$:Mg(0.63):Y(0.24) PILS opening dynamics in time is complex. it is caused by complex rearrangement of energy between ordinary and extraordinary rays [24]. Crystals $LiNbO_3$:Mg(0.75 wt. %):Gd(0.23) and $LiNbO_3$:Zn(2.05) have the widest band gaps: 3.84 and 3.83 eV, correspondingly (table). Congruent crystal band gap is close to the maximal one (3.72 eV). At this congruent crystal conductivity is $\approx 10^{-16}$-$10^{-15}(\Omega.cm)^{-1}$ [25]. Note that conductivity along the polar axis is lower than the conductivity perpendicular to Z [25, 26]. Due to our data (table) band gap of the stoichiometric crystal is intermediate (3.48 eV). We failed to find data on electric conductivity of the stoichiometric crystals. It is important to pay attention at the fact that in weakly colored crystals $LiNbO_3$:Mg(0.86 wt. %):Fe(0.0036) and $LiNbO_3$:Er(3.1) absorption bands of the dopant can influence the absorption edge [4, 27]. The closer these bands to the fundamental absorption edge are, the stronger this influence is.

Thus we have observed correlation between bang gap, photoelectric fields values, value and time dynamics of PILS for the researched crystals, table. Defects with localized electrons are responsible for the photorefractive effects in $LiNbO_3$crystal. Structure homogeneity is responsible for the state of the fundamental absorption edge. The structure homogeneity is higher in nominally pure congruent crystals than in doped congruent crystals [14, 15, 18, 19]. Nb_{Li} defects and shallow electron traps are the main defects in nominally pure and doped congruent crystals [3-6]. At this increase in the *R* = Li/Nb value leads to decrease in Nb_{Li} defects concentration and increase in shallow electron traps amount. Nb_{Li} defects are absent in a perfect stoichiometric crystal. Photorefractive effect in the crystal is caused by shallow electron traps. Amount of the latter in a stoichiometric crystal is much higher than in a congruent crystal. Obtained data also reveal (table) that the higher photoelectric fields are, the grater is the value of a photorefractive effect and the wider is a PILS indicatrix.

4. Conclusion

Absorption spectra and PILS were researched for $LiNbO_3$crystals. The position and behavior of the absorption edge were detected to depend on the dopant type. The band gap was calculated due to absorption edge parameters and photovoltaic

Table 1: Photoelectric parameters of PILS and band gap of lithium niobate crystals at t = 25 °C.

№	Crystal	λ, nm	ΔE_g, eV	λ = 532 nm, $I \sim 6.29$ W/cm ^{2}		
				E_{pv}, V/cm	E_D, V/cm	$\Delta n \cdot 10^{-5}$
1	$LiNbO_{3stoich}$	360.0	3.48±0.01	3178	1360	5.3
2	*$LiNbO_{3cong}$	334.2	3.72±0.011	5620	104	6.7
3	*$LiNbO_3$:Zn(2.05 wt. %)	323.0	3.83±0.012	4770	75	5.6
4	*$LiNbO_3$:Mg(0.35 wt. %)	341.0	3.65±0.011	7405	295	9.0
5	$LiNbO_3$:B(0.12 wt. %)	380.0	3.27±0.009	5374	99	6.4
6	*$LiNbO_3$:Gd(0.26 wt. %)	380.0	3.27±0.009	-	-	-
7	*$LiNbO_3$:Er(3.1 wt. %)	335.2	3.71±0.011	4400	81	5.2
8	$LiNbO_3$:Y(0.46 wt. %)	346.4	3.59±0.01	4340	237	5.3
9	$LiNbO_3$:Mg(0.63 wt. %):Y(0.24)	342.2	3.63±0.011	5440	98	6.5
10	*$LiNbO_3$:Mg(0.75 wt. %):Gd(0.23)	323.8	3.84±0.012	3800	745	5.3
11	*$LiNbO_3$:Mg(0.86 wt. %):Fe(0.0036)	382.4	3.25±0.009	4655	127	5.6
12	$LiNbO_3$:Mg(0.01 wt. %):Ta(1.13)	380.0	3.27±0.009	6052	115	7.1
*PILS indicatrix does not open for these crystals at $I \sim 6.29$ W/cm^2.						

and diffusion fields were detected due to PILS indicatrix parameters. The band gap was demonstrated to depend on the crystal defect structure state which also determines photorefractive effect and photo-fields. The narrowest band gap is characteristic of $LiNbO_{3stoich}$, $LiNbO_3$:B(0.12 wt. %), $LiNbO_3$:Y(0.46), $LiNbO_3$:Mg(0.011):Ta(1.13), $LiNbO_3$:Mg(0.63):Y(0.24) crystals.

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