RADIATION AND OPTICAL PROPERTIES OF THE $LiNbO_3$ CRYSTALS DOPED WITH *d*- AND *f*-ELEMENTS

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The influence of gamma irradiation on optical properties of the $LiNbO_3$ crystals doped with *d*- and *f*-elements was studied. The origin of the induced absorption is discussed. A model of the genetic defects formation for these crystals is proposed.

Key words: lithium niobate, optical spectroscopy, gamma irradiation, additional absorption, crystal defects.

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I. INTRODUCTION

Lithium niobate (LN) because of its unique physical properties is widely used in various fields of science and engineering: acousto- and optoelectronics, quantum electronics and integral optics, optical recording, etc.

LN monocrystals doped with the rare-earth ions (REI) are prospective materials for solid state lasers due to the possibility of combining the nonlinear optical, acoustooptical and electrooptical properties of the crystal with laser properties of active dopands. But utilization of LN crystals as laser media was strongly restricted because of an optical damage. An interest in LN doped with REI was renewed after a demonstration that co-doping with MgO diminishes the optical damage in the crystal [1]. At present the possibility of integrated lasers on the basis of LN doped with Nd^{3+} and Er^{3+} have been reported [2–4]. These facts promoted the absorption and luminescence studies of various REI in LN [5–8].

Utilization of quantum electronics devices in extremal conditions, in particular under radiation, puts out special demands with respect to a safe acting of such devices and their individual elements. That is why a study of the influence of ionizing radiation on the optical properties of pure LN as well as LN doped with *d*- and *f*-elements is of interest. Besides, this study is necessary for understanding the mechanisms of radiation interaction with the LN crystal and the nature of induced and genetic defects in LN.

At present there is no universally shared opinion about the origin of optically active point defects (color centers) in LN. On the basis of various studies of photo-, thermo- and radiation induced changes of properties of LN different models of color centers (CC) are assumed [9–14], which include F-type centers, transition of niobium ions to a lower valent state, bipolarons, hole centers O^- localized near cation sublattice defects and also recharging of doping ions or complex associates consisted of an oxygen vacancy and impurity. The proposed models explain the data on some experiments but do not agree with others. This can be explained by the complexity of the defect structure of LN, that consists of intrinsic (non-stoichiometric) defects and extrinsic (produced by impurities) defects. The addition of the impurities with a changeable valent state, e.g. iron ions, makes the defect structure much more complicated for understanding.

There are many publications devoted to the investigation of the influence of various ionizing radiations on LN crystals [9, 11, 12, 14, 15]. In most cases nominally pure LN, LN–Fe and LN–Mg crystals are studied. Exactly these facts indicate the necessity of experimental study of the influence of radiation on some optical properties of LN doped with rare-earth and iron group elements, all the more the models of defect centers (color centers) in LN remain disputable.

II. EXPERIMENTAL PROCEDURE

The LN monocrystals were grown by the Czochralski method from the congruent melt. The crystal growth procedure was performed in the air from platinum crucibles using the equipments of PHYSITERM (France) and SPEXON (Poland) with high frequency heating and automatic boule diameter control by the weighing method [16, 17]. The dopants were added to the congruent melt in the form of oxides of dopant elements.

The following LN crystals were investigated: LN (nominally pure); LN–Mg (5 mol.%); LN–Nd (2 mol.%), Mg (6 mol.%); LN–Fe (0.2 mol.%); LN–Cr (0.1 mol.%); LN–Yb (1 mol.%); LN–Dy (1 mol.%); LN–Yb (0.8 mol.%), Pr (0.1 mol.%); LN–Tm (0.3 mol.%); LN–Er (0.3 mol.%); LN–Pr (1 mol.%). The dopants content corresponds to molar percentage in a charge. The samples were prepared as flat-parallel polished plates (thickness $0.9 \div 2.0$ mm) with the surface perpendicular to the z axis.

The optical absorption spectra in visible and IR region were measured by LAMBDA–2, FS 1725X and SPECORD M40 spectrophotometers at room temperature.

The irradiation with gamma-quanta was performed using a ^{60}Co source (the average energy 1.25 MeV) up to the absorbed doses $D = 1$ MGy and $D = 1.5$ MGy.

LN–Yb		
λ, nm	E, cm^{-1}	Multiplet
917.8	10896	$^2F_{5/2}$
938.5	10655	
943.6	10598	
955.2	10469	
979.7	10207	
1004.1	9960	
LN–Dy		
λ, nm	E, cm^{-1}	Multiplet
326.8	30600	$^4I_{9/2} + (^4F, ^4M)_{5/2}$
339.1	29489	
354.4	28217	$^6P_{7/2} + ^4I_{11/2}$
360.8	27716	
368	27174	$^6P_{5/2} + (^4P, ^6P)_{3/2} +$ $^4M_{19/2}$
378.6	26413	
389.8	25654	$^4F_{7/2} + ^4K_{17/2} +$ $^4I_{13/2} + ^4M_{21/2}$
391.8	25523	
395.6	25278	
427.5	23390	$^4G_{11/2}$
450.9	22173	$^4I_{15/2}$
455.2	21698	
470.5	21254	$^4F_{9/2}$
475.1	21047	
479	20877	
484.9	20623	
756.1	13215	$^4F_{3/2}$
777	12870	$^6F_{3/2} + ^6F_{5/2}$
806.7	12396	$^6F_{5/2}$
816.5	12247	
831.4	12028	
904.1	11061	$^6F_{7/2}$
913.4	10948	
942.7	10608	
955.1	10470	
979.7	10207	
1003.5	9965	$^6H_{5/2}$
1026.1	9746	
1097	9116	$^6H_{7/2} + ^6H_{9/2}$
1114.1	8976	
1288.3	7762	$^6H_{9/2} + ^6H_{11/2}$
1318	7587	
1328	7530	
1394	7174	
1663.7	6011	$^6H_{11/2}$
1692.6	6095	
1733	5770	

LN–Pr		
λ, nm	E, cm^{-1}	Multiplet
461.9	21650	$^1I_6 + ^3P_1 + ^3P_0 + ^1D_2$
486.5	20555	
501.3	19948	
514	19455	
606.5	16488	
615.9	16236	
1030.1	9708	$^1G_4$
1059.7	9437	
1074.8	9304	
1437.7	6956	$^3F_4$
1443.6	6927	
1469.9	6803	
1479.1	6761	
1570.7	6367	$^3F_4$
1575.8	6346	
1610.6	6209	
1673	5977	
1919.4	5210	$^3F_3$
1956	5113	
1996.9	5008	
2181	4585	$^3H_6$
2250.1	4444	
2307.1	4334	
2369	4221	

Table 1. Stark structure of energy transitions in LN–Yb, LN–Dy and LN–Pr.

The additional absorption ΔK induced by the irradiation was found as

$$\Delta K = K_2 - K_1,$$

where K_1 and K_2 are the optical absorption before and after irradiation respectively.

III. RESULTS AND DISCUSSION

LN crystals are transparent in the range of 350–5300 nm (30000–1900 cm^{-1}). At $\sim$ 3480 cm^{-1} the absorption peak due to the OH^- stretching vibration is observed. After doping with rare-earth ions some narrow bands of the REI intra-center absorption appear in the transparency range. The general absorption spectra of the LN–Yb, LN–Dy and LN–Pr crystals are presented in Fig. 1, and Stark structure of energy transitions of Yb^{3+}, Dy^{3+} and Pr^{3+} in LN is examined in Table 1.

Fig. 2 represents the additional absorption (AA) spectra of the LN crystals after gamma irradiation. As it is seen from the figure the AA spectrum structure is similar for all the crystals investigated. In these spectra one can distinguish two wide maxima near 26000 and 21000 cm^{-1}. The AA spectra for various samples differ one from the other only in the AA value and correlation of intensities of these two maxima. Similar observations were made in our earlier investigation of the influence of gamma and electron irradiation on optical properties of the LN crystals doped with Er and Tm and co-doped with Mg [14]. Similar but less intensive AA spectra for the LN–Fe and LN–Cr crystals were also obtained at the irradiation by gamma-quanta (energy 1.1 MeV) of a reactor contour [18].

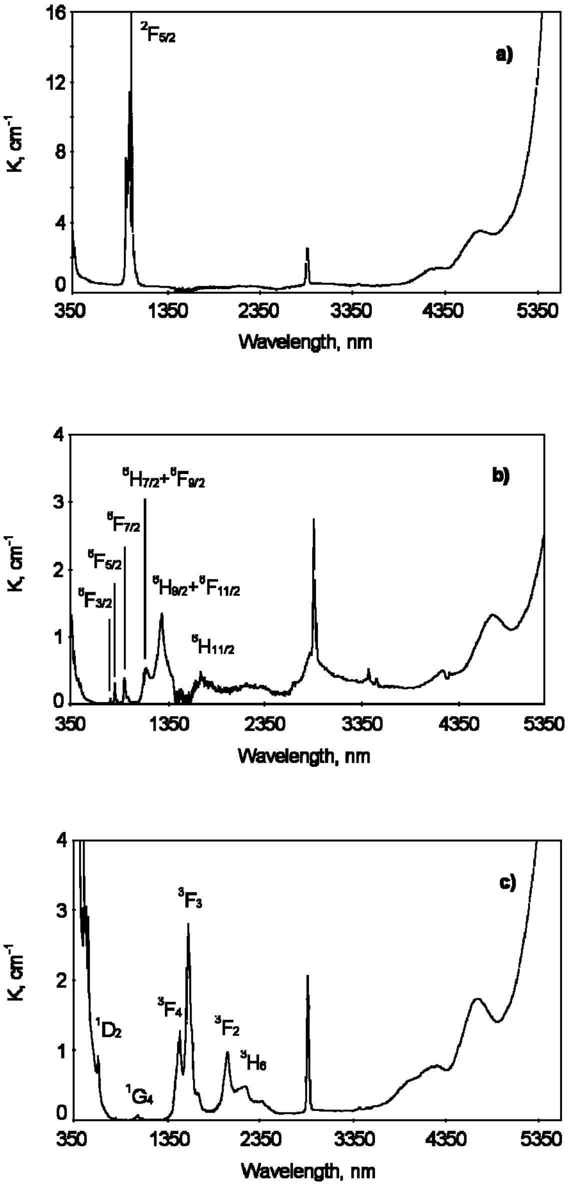

Fig. 1. Absorption spectra of LN crystals: (a) LN–Yb, (b) LN–Dy, (c) LN–Pr.

Comparing the value of induced absorption for various crystals (Fig. 2) it can be seen that the AA value for all doped crystals is greater than the corresponding value for nominally pure LN with the exception of the LN–Mg and LN–Nd, Mg crystals. It must be marked that the AA value for LN–Nd (2%), Mg (6%) is about 30% less than another one for nominally pure LN and that in accordance with [14] the AA value for LN–Er (0.2%), Tm (1.2%), Mg (5%) is two times greater than the corresponding value for nominally pure LN and only for LN–Er (0.2%), Tm (1.2%), Mg (10%) crystal the AA value is commensurable with the induced absorption in nominally pure LN at equal doses of irradiation.

According to [15] the influence of used gamma irradiation on oxide crystals consists mainly in the recharging of genetic structure defects.

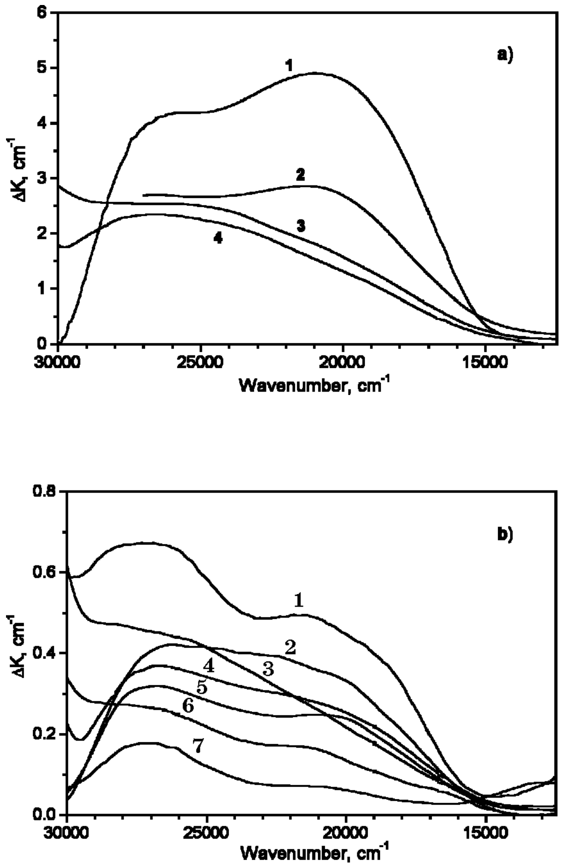

Fig. 2. The AA spectra of gamma irradiated crystals: (a) 1 — LN–Cr ($D = 1.5$ MGy); 2 — LN–Fe ($D = 1$ MGy); 3 — LN–Yb,Pr ($D = 1.5$ MGy); 4 — LN–Pr ($D = 1.5$ MGy). (b) 1 — LN–Dy ($D = 1$ MGy); 2 — LN–Yb ($D = 1$ MGy); 3 — LN–Er ($D = 1.5$ MGy); 4 — LN–Tm ($D = 1.5$ MGy); 5 — LN ($D = 1.5$ MGy); 6 — LN–Nd,Mg ($D = 1.5$ MGy); 7 — LN–Mg ($D = 1$ MGy).

Taking into account that in all the investigated crystals including the Mg-doped crystals a similar structure of AA is observed it can be concluded that color centers created in these crystals have the same origin. Doping with REI as a rule helps to increase the concentration of induced CC. Nd^{3+} ions are an exception from the number of REI elements: the presence of these ions does not increase the induced absorption or at least to leasser extent assists to rise of AA in comparison with other REI elements. The adding of Mg decreases considerably the CC's concentration in nominally pure LN crystals as well as in REI-doped crystals.

Many publications are concerned with the studying of optical properties of the LN–Fe crystals. It is known that iron ions can be present in a crystal in two valent states

— Fe^{2+} and Fe^{3+}. Some changes in the optical properties of LN–Fe induced by ionizing irradiation or thermal treatments in various atmospheres are considered to be related not only to the recharging of genetic defects but also to the charge transfer of the iron ions [11, 13].

It was demonstrated [13] that the vacuum annealing of LN–Fe causes the rise of AA in bands centered at ~ 28000, ~ 25500 and ~ 20000 cm^{-1} and simultaneously clearing in the band ~ 32500 cm^{-1}, and air annealing gives the opposite effect. It was supposed that the 32500 cm^{-1} band corresponds to the O^{2-}–Fe^{3+} charge transfer band and the 28000 cm^{-1} band is the Fe^{2+} photoionization band. In our LN–Fe sample (thickness $d = 0.9$ mm) bands at 32500 and 28000 cm^{-1} are not visible due to the short-wave absorption edge and bands at 26000 and 21000 cm^{-1} are similar to others observed in all the investigated crystals. On the basis of the latter observation we conclude that the absorption centered at 26000 and 21000 cm^{-1} is not connected directly with the iron ions.

In [19] it was found that chromium ions may be introduced into LN crystals in two valent states Cr^{3+} and Cr^{2+}, and 21000 cm^{-1} band corresponds to a charge transfer of Cr ions. The last assumption can explain the large value of induced absorption of our LN–Cr crystal.

As is known the ratio Li/Nb for congruent LN equals ~ 0.94. The excess of Nb_2O_5 in the crystal is provided by Nb ions occupying Li sites $(Nb_{Li})^{4+}$. The charge compensation of Nb_{Li} centers is considered to be occurring by vacancies in cation sublattice [10, 20]. Mg^{2+} ions in LN structure occupy Li sites, at that concentration of Nb_{Li} antisites decreases. Above the threshold concentration (~ 5 mol.%) Mg^{2+} ions simultaneously with Li sites occupy also Nb sites and concentration of cation vacancies decreases.

According to the studies by Rutherford backscattering and proton-induced X-ray emission channeling techniques [21] rare-earth ions occupy as a rule Li sites in LN structure and in accordance with [22] unlike Er^{3+}, Tm^{3+} and Gd^{3+} ions that occupy mainly Li sites, Nd^{3+} ions occupy both Li and Nb sites. Fe and Cr ions are considered to occupy both Li and Nb sites (see Ref. in [22]).

Considering the induced absorption in the range of 30000–15000 cm^{-1} is caused by CC created on the basis of oxygen vacancies we propose the mechanism of the genetic defects formation at doping of LN with REI elements. In accordance with this mechanism the incorporation of rare-earth ions into Li sites is accompanied by creation of oxygen vacancies. If the rare-earth ion incorporates into Nb site it does not promote to oxygen vacancy creation. The last statements can be comprehended from the following reasoning. The LN crystal grows in paraelectric structure and later after cooling through the Curie temperature the crystal transforms into the ferroelectric state. In the paraelectric state Li ions are located exactly in oxygen layer between two oxygen octahedra and Nb ions are located in central position of oxygen octahedra [23]. The distance from the top of oxygen triangle to its center (see Fig. 3) at $T = 1150$°C is equal 2.08 Å[24]. This distance is quite sufficient for location of Li^+ ion in the triangle, but it is insufficient for rare-earth ion location which ionic radius is 1.2 (for Yb^{3+}) $\div$1.5 (for Ce^{3+}) times larger then Li^+ radius. Taking into account this reasoning the formation of oxygen vacancies during the incorporation of rare-earth ions into Li sites is favorable. In the case of central-octahedral position (Nb-position) the room is quite enough for location of impurity ion without any perturbation of oxygen sublattice. The charge of the $(REI_{Li})^{2+}$–$(V_O)^{2+}$ complex that must be compensated is 4+. The charge compensation of such complex apparently takes place as in the case of $(Nb_{Li})^{4+}$ antisite by means of Li or Nb vacansies.

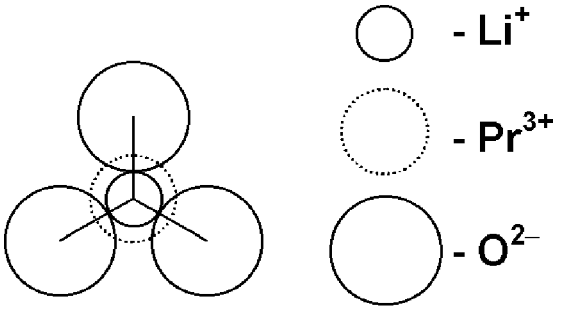

Fig. 3. Schematic representation of the lithium ion surrounding in paraelectric LN.

Assuming that the formation of $(Mg_{Li})^+$ centers compete with the $(V_O)^{2+}$ formation and at considerable concentration of magnesium the Mg_{Li} completely force out oxygen vacancies, it is easy to explain the stabilizing action of Mg on the optical properties of LN.

The proposed model of the genetic defects formation at doping with the REI elements explains:

- increasing of AA induced by ionizing irradiation in REI-doped LN due to the increasing of concentration of oxygen vacancies;
- lessing of AA of Nd-doped LN in comparison with other REI-doped crystals because a part of Nd ions occupy Nb sites;
- decreasing of induced absorption of Mg-doped LN.

For Fe and Cr ions the proposed mechanism is possible as well, but a considerable rise of the induced absorption in 30000–15000 cm^{-1} range for the LN–Fe and LN–Cr crystals can be explained by the charge transfer processes stimulated by ionizing radiation which include also recharging of these ions.

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РАДІЯЦІЙНО-ОПТИЧНІ ВЛАСТИВОСТІ КРИСТАЛІВ $LiNbO_3$, ЛЕҐОВАНИХ ЙОНАМИ *d*- ТА *f*-ЕЛЕМЕНТІВ

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Досліджено вплив гамма-опромінення на оптичні властивості кристалів $LiNbO_3$, леґованих йонами *d*- та *f*-елементів. Обговорено природу індукованого поглинання. Запропоновано модель утворення генетичних дефектів у цих кристалах.