# INVESTIGATION OF OPTICAL HETEROGENEITY OF LITHIUM NIOBATE CRYSTAL UNDER RADIATION EXPOSURE

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**Abstract**

This article investigated the effect of gamma radiation on the optical heterogeneity of the photorefractive crystal of lithium niobate. The results show that the ordinary and unusual refractive indices increase with an increase in the radiation dose and practically do not change after a dose of $10^7$ R. The optical absorption edge is shifted towards the long waves according to the dose. When studying the combined scattering spectra, a new peak was found in the range of 1300÷1600 $cm^{-1}$.

**Keywords:** niobate lithium, refractive index, optical absorption edges, gamma radiation, Raman spectra.

## 1. INTRODUCTION

The study of radiation effects in lithium niobate ($LiNbO_3$) began almost from the moment the specific properties of photorefractive crystals were discovered. The radiation effects responsible for the mechanisms of their manifestation are discussed in two separate areas: radiation responses inherent in bulk materials, and responses arising from the effects of component geometry. Effects in $LiNbO_3$-based technologies such as thin-film integrated optical devices and volumetric acousto-optic modulators illustrate the widely differing radiation-induced responses that can occur in current component technologies. The radiation sensitivity of the $LiNbO_3$ was determined as in a clean state. Depending on the application, the $LiNbO_3$ may act as a sensitive radiation sensor or material sufficiently resistant to radiation [1].

Scattering of laser radiation by laser-induced fluctuating defects in micro and nanostructures is called photorefractive light scattering [2]. Photorefractive light scattering is a dynamic process: it interferes with laser light and causes a strong change in the laser beam emerging from the crystal. Along with the disordering of the crystal lattice and the appearance of defects, photorefractive light scattering is one of the most significant factors that deteriorates the quality of holograms, grids and converters of frequency parameters of laser radiation [3]. The study of the dependence of photorefractive scattering of light in real single crystals depends on the characteristics of the composition and structure of the crystal and is of great interest for the creation of materials with specified photorefractive properties. In this regard, studies carried out to optimize photorefractive properties are of great relevance. Increasing the sensitivity and speed of recording holographic information can be achieved by changing the composition of the crystal and the features of its structure. Its most interesting part is the influence of the order of units of the cationic sublattice along the polar axis on the properties of the photorefractive effect and photorefractive light scattering. Note that the order of the units of the cationic sublattice determines the magnitude of spontaneous polarization in optically nonlinear crystals with an oxygen-octahedral structure, as noted in [1].

Numerous studies have been reported on the Raman spectra of the ferroelectric phase of undoped $LiNbO_3$ [4-6]. Although there was some ambiguity in the early work on Raman scattering, the assignments and approximate wavenumbers of Sidorov et al. [7] are listed. Additional lines, typically found near 95, 630, 668 and 740 $cm^{-1}$, are most likely due to crystal growth, structure and chemistry deviating from the ideal crystal, including point and extended defects (intrinsic and impurities), as well as ilmenite stacking defects [8].

Other Raman studies of undoped lithium niobate have emphasized the angular dependences and asymmetries of scattering cross sections with respect to scattering geometry [9], general properties of polaritons [10], precision cross-section measurements [11], asymmetries [12], and the dependence of phonon frequencies on temperature and pressure [13 ].

The purpose of this work is to study the influence of radiation effects (γ-irradiation) on the optical properties (ordinary $n_o$ and extraordinary $n_e$ refractive indices, optical absorption edges, and Raman scattering) of lithium niobate single crystals

## 2. MATERIALS AND METHODS

The work carried out comparative studies of the spectral characteristics of unirradiated and irradiated $LiNbO_3$ crystals with γ-radiation. The samples for research were made from nominally pure $LiNbO_3$ crystals in the form of parallelepipeds with dimensions of 2×3×10 mm, the edges of which were oriented along the direction of the crystallographic axes. $LiNbO_3$ single crystals were grown by the Czochralski method in an air atmosphere. The methodology for crystal growth and batch preparation is described in detail in [14]. The γ-radiation power was ~ 106 R/s. The crystals were irradiated using the $Co^{60}$ installation (Institute of Nuclear Physics, Academy of Sciences of the Republic of Uzbekistan). To study the effect of radiation, the samples were irradiated with γ-radiation with a dose in the range of $10^3 \div 10^8$ R. However, for $LiNbO_3$ crystals at doses of $10^3$ and $10^8$ R, no spectral changes were observed. Absorption spectra were studied using a Shimadzu UV 3600 spectrometer. Measurements were carried out in the range of 320-1100 nm with a step of 1 nm. Raman spectra were obtained on an Ocean Optics QEPro spectrometer with a 785 nm laser and an integration time of 500 ms. The spectra were processed using the Origin 8.1 software package. Studies of the surface morphology and elemental composition of the samples were carried out using an EVO MA10 SEM (Carl Zeiss). Refractive index measurements were carried out using the prism method using the angle of smallest deviation using a G5 goniometer. The error in measuring refractive indices was $10^{-5}$.

## 3. RESULTS AND DISCUSSION

The structure of a pure lithium niobate crystal is formed by $O_6$ oxygen octahedral, which are connected to each other in such a way that they have common edges and sides [15]. On Fig. 1 shows an image of a pure lithium niobate crystal obtained using a scanning electron microscope and the results of elemental analysis.

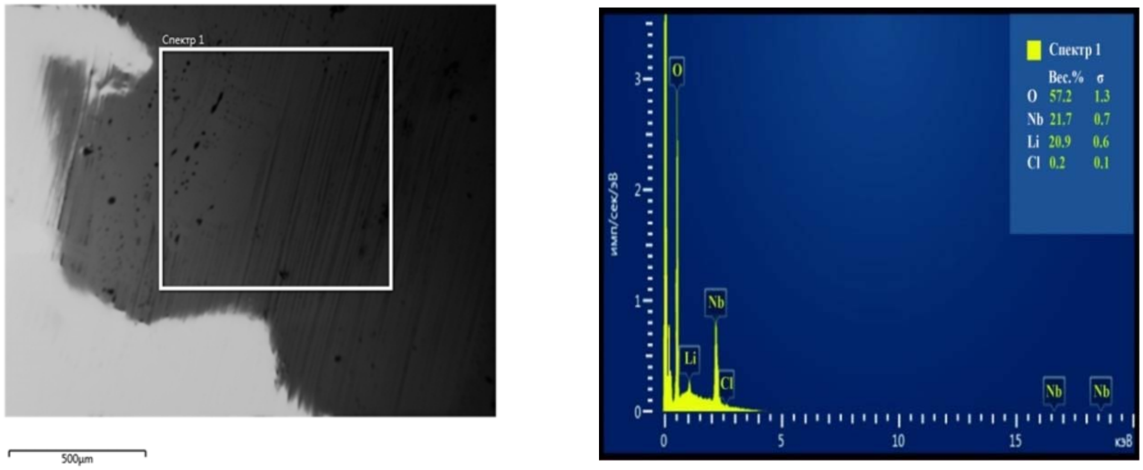



**Fig. 1.** SEM image of a pure lithium niobate crystal and elemental analysis results

Elemental analysis results show that the amount of oxygen in the crystal is almost three times higher than that of niobium and lithium. This is completely consistent with the above opinion.

In the absorption spectra of γ-irradiated samples (Fig. 2) of nominally pure $LiNbO_3$ single crystals, a wide absorption band is observed at ~ 400; it is clear that the spectra do not change shape and are located above each other, according to the irradiation doses, indicating an increase in optical density. To clarify the properties of radiation centers and their influence on photorefraction, studies of the polarized absorption spectra of $LiNbO_3$ crystals were carried out.

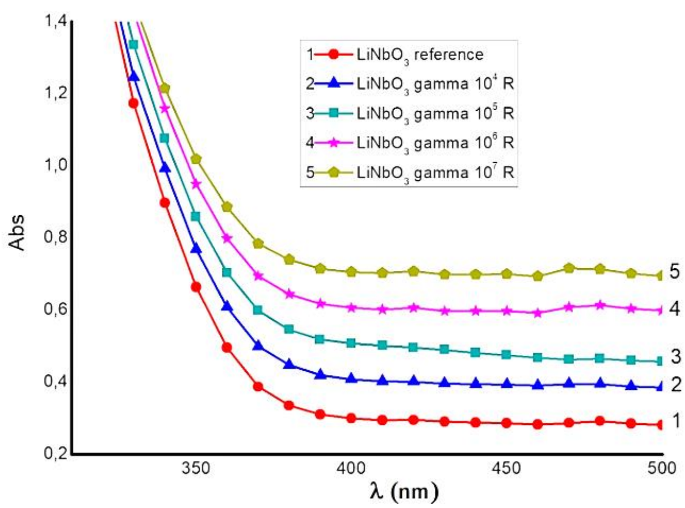



**Fig. 2.** Absorption spectrum of irradiated and non-irradiated $LiNbO_3$

From the presented spectra it is clear that gamma irradiation leads to the appearance of a broad absorption band in the visible region of the spectrum. At the same time, radiation coloring has a different character in pure crystals. Analysis of the changes occurring in the spectra shows that gamma irradiation of crystals leads to a significant change in absorption, mainly in the region of 350-400 nm.

Color centers in $LiNbO_3$ crystals induced by irradiation with γ-radiation and electrons or heat treatment in various atmospheres have been studied previously [16, 17]. However, at present there is no consensus on the nature and mechanisms of formation of color centers. The presence of different models of color centers is assumed: F-type centers and the transition of niobium ions to a lower valence state; hole centers $O^-$ are localized near defects in cation sublattices; bipolarons, as well as charge exchange of doping ions or complex associates consisting of an oxygen vacancy and an impurity. Saturation of dose dependences in $LiNbO_3$ under γ-irradiation indicates the predominance of radiation mechanisms for recharging growth defects.

Based on the model of the x-ray refractive effect, a slight decrease in refractive indices after irradiation can be associated with the relaxation of internal fields formed during irradiation. When $LiNbO_3$ single crystals are γ-irradiated, a photochromic effect is observed, which disappears when the crystals are annealed [13]. The change in the refractive index of the sample with respect to the ordinary and extraordinary laser beam is shown in Fig. 3, it can be seen that the refractive indices increase nonlinearly with increasing radiation dose.

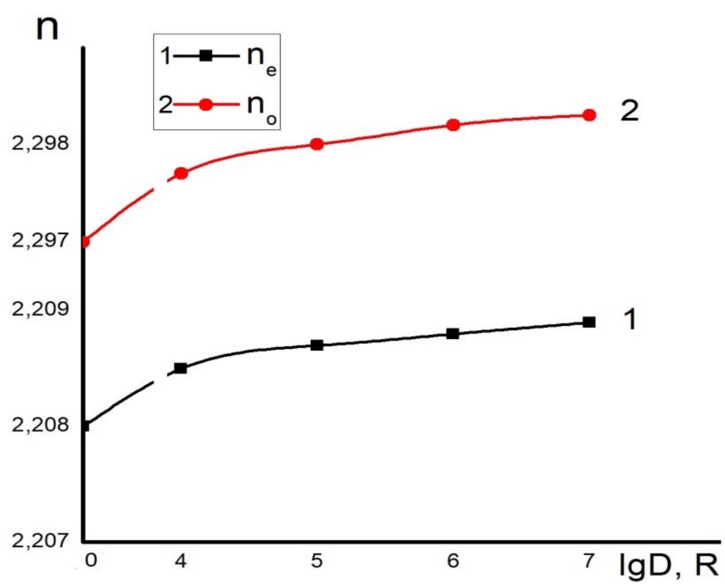



**Fig. 3.** Dependences of $n_e$ and $n_o$ on the dose of γ-radiation for $LiNbO_3$ crystals

It has been established that irradiation leads to an increase in the refractive indices of $LiNbO_3$ single crystals. The values of $n_o$ and $n_e$ increase with increasing dose of γ-irradiation and reach saturation at a dose of $10^7$ R.

In the literature on the influence of γ-radiation there is a lot of data on changes in the optical absorption edge, refractive indices, and sensitivity of photorefractive crystals, but little has been studied on Raman scattering from these crystals. Raman spectra of single-crystal samples of unirradiated and irradiated $LiNbO_3$ crystals are presented in Fig. 4 and 5. It can be assumed that the displacements of Li cations affect only frequencies in the range of 270–400 $cm^{-1}$, as evidenced by peaks in the low-frequency part of the spectrum. The range 550–670 $cm^{-1}$ is assigned to the Nb–O stretching modes, which mainly include shifts of oxygen atoms; O–Nb–O bending modes appear at 432 $cm^{-1}$ and below, thus it is clear that the bending modes are strongly coupled to both the Li–O stretching modes and the O–Li–O bending modes. The highest intensity at 245 $cm^{-1}$ is mainly due to the deformation of the Nb-O framework. When taking Raman scattering spectra from γ-irradiated crystals, in the low-frequency part of the spectrum the peak locations at frequencies of 250 $cm^{-1}$ and 600 $cm^{-1}$ did not change, and in the high-frequency part of the spectrum at a frequency of 1375 $cm^{-1}$ peaks appear in Fig. 5.

**Fig. 4.** Raman spectra of lithium niobate

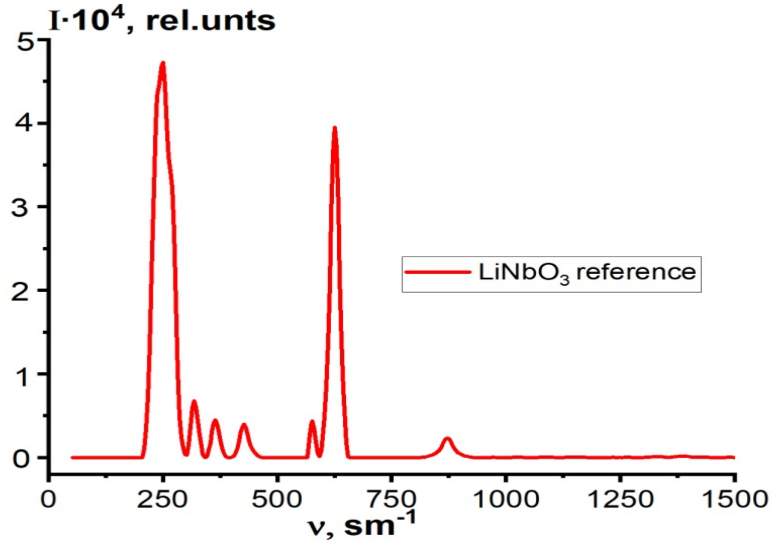
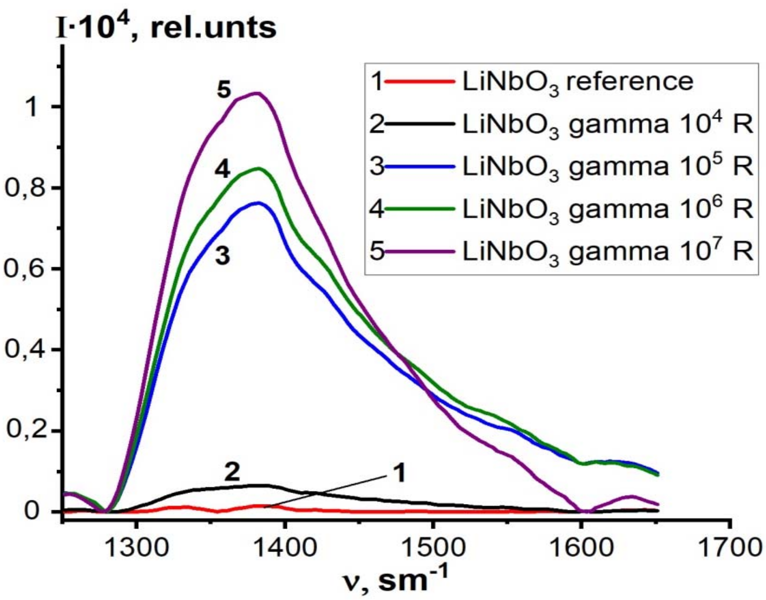



**Fig. 5.** Raman spectra of lithium niobate




From the spectra it is clear that in the range of 1300 ÷ 1600 $cm^{-1}$ with γ-irradiation at a frequency of 1375 $cm^{-1}$ peaks appear, the height of which increases according to the increase in the dose of γ-irradiation (the low-frequency part of the spectrum, due to its identity with the spectrum of Fig. 4, in Fig. .5 not shown). We believe that the appearance of these peaks is caused by radiation defects, centers of changes in Raman frequencies that arise under the influence of γ-radiation, and this causes changes in the optical properties of lithium niobate crystals.

## 4. CONCLUSION

In all considered areas of electromagnetic radiation, an increase in the relative dose of γ-irradiation leads to an increase in absorption;

Lithium niobate crystals can be used as materials for memory elements that provide optically high sensitivity in a certain range of γ-radiation doses, convenient for recording and storing information;

For the first time, when studying a lithium niobate crystal irradiated with γ-rays by combinatorial scattering, a peak with maximum intensity corresponding to a frequency of 1375 $cm^{-1}$ was determined in the range of 1300÷1600 $cm^{-1}$.

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