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INVESTIGATIONS OF NONLINEAR OPTICAL PROPERTIES OF LITHIUM NIOBATE CRYSTALS

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The article is devoted to nonlinear effects in lithium niobate crystals. The possibility of using digital holographic interferograms obtained with the help of laser radiation of different duration at different moments of time for the reconstruction of dynamic phase changes is shown. Holograms were recorded on lithium niobate crystals doped with iron ions in various concentrations using He-Ne and He-Cd lasers, and the diffraction efficiency was calculated. Also, the effect of gamma radiation on the optical properties of $LiNbO_3$ and $LiNbO_3$:Fe crystals was studied. At the same time, it was determined that the band gap of the samples decreases, as a result of which the refractive index, absorption coefficient and photorefractive sensitivity increase several times.
Keywords: *Ferroelectric crystals; Digital holographic interferometry; Diffraction efficiency; Photorefractive sensitivity*
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INTRODUCTION

Among promising recording materials for creating holographic systems for optical information processing, a special place is occupied by ferroelectric crystals, for example, $LiNbO_3$ doped with iron ions in various concentrations [1–3]. Recording information in $LiNbO_3$:Fe crystals is possible due to the photorefractive effect, which is interpreted mainly by the impurity photovoltaic mechanism, the change in the refractive index responsible for recording dynamic gratings that repeat the light grating, due to which the space charge grating is formed [4,5]. One of the promising directions for the practical use of doped photorefractive crystals is their use as optical memory elements based on local holographic gratings recorded by a laser, which can be repeatedly rewritten and stored.

If ordinary holography is a method of recording the wave front of an electromagnetic wave in an industrial form (on a photographic plate, thermoplastic, photorefractive material), then digital holography is a method of recording a wave front in digital form, followed by its restoration, storage, and transformation using computer programs.

Pure ferroelectric crystals are not highly sensitive to optical radiation. However, doping with transition metals, in particular iron ions, significantly increases their photosensitivity. The effect of doping on the sensitivity of $LiNbO_3$ crystals is described in detail in [6-8]. The use of transition metals as dopants is associated with their ability to reversibly donate electrons to the conduction band under the action of light [9–11]. An increase in the diffraction efficiency during the recording of holograms in a pure $LiNbO_3$ crystal and in crystals with various additives was shown in [6]. It can be said that there is a correlation between the absorption spectra and the recording sensitivity of crystals with various additives.

The sensitivity to an optically induced refractive index change can be expressed in terms of material parameters as follows.

$$\frac{dn_e}{dJ} = el(\frac{n_e^3}{2}\cdot\frac{r_{33}}{\varepsilon_0\varepsilon_{33}})\frac{\alpha\beta}{\hbar\omega}, \tag{1}$$

where dn_e/dj is the energy sensitivity, el is the change in the electric dipole moment, the mechanism of which is different for different materials and experimental conditions.

For the most common case, the drift of photoexcited electrons in an internal or external electric field, the drift electron path length is $l = \mu\tau E_0$. The expression in brackets is due to the electro-optical effect. The expression $\alpha\beta/\hbar\omega$ gives the number of excited centers or the number of photoelectrons in the conduction band. Alloying with transition metals, violation of stoichiometry, annealing in a reducing atmosphere, irradiation with γ-rays, application of an electric field makes it possible to significantly increase their photosensitivity. In addition, lithium niobate crystals make it possible to obtain new types of heterostructures due to their unique electro-optical properties [12].

The systematic study of radiation effects in lithium niobate began, in practice, from the moment the specific properties of photorefractive crystals were discovered. Especially, they appear in crystals doped with transition metals.

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Doping with $LiNbO_3$ leads to a variety of radiation-induced effects, which include both bulk effects and effects arising during the formation of the component structure [13]. These effects can be used in lithium niobate-based thin-film optical devices as well as bulk acousto-optic modulators, which illustrate widely varying responses caused by radiation. The radiation sensitivity of $LiNbO_3$ has been determined both in pure and doped states. Depending on the field of application, $LiNbO_3$ can play the role of a sensitive radiation sensor or a radiation-resistant material used under radiation conditions [14].

EXPERIMENTAL PART

In 2-exposure digital holographic interferometry, 2 wave fronts reconstructed from 2 digital holograms G1 and G2 are compared. G1 is a hologram of an unperturbed object and G2 is a hologram of an object with induced optical inhomogeneities. As a result of the addition of wave fronts, an interferogram is obtained, the position and curvature of the fringes of which makes it possible to control the phase changes of the object under study. Fig. 1. below shows the experimental scheme. Holograms were recorded digitally with a Nikon E885 digital camera. The lens was removed from the camera and the recording took place directly on the area of the CCD matrix with the number of pixels 1000×1000. The size of one pixel is 9×9 microns. The electronic shutter of the camera provided a minimum shutter speed of 1/12000 sec and was synchronized with the operation of the laser. The studies were carried out in the radiation of a ruby laser with Q-switching, pulse duration 60 ns, radiation energy per pulse 0.5 mJ.

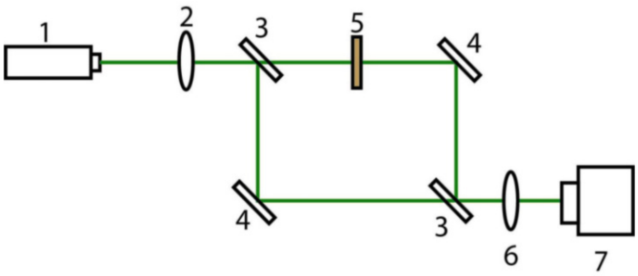


Figure 1. Optical scheme of the study. 1 - laser photograph input, 2 – focusing lens, 3 - beam splitter, 4 – mirror, 5 – sample, 6 - output lens, 7 – digital camera

Also, in experiments on the study of holographic recording in a $LiNbO_3$:Fe crystal, the scheme presented in [15,16] was used.

Information was recorded using helium-cadmium (He-Cd, λ = 440 nm) and helium-neon (He-Ne, λ = 630 nm) lasers. The optical sensitivity of the crystal for a wavelength of λ=440 nm is very high. Reading information was carried out using a low-intensity helium-neon laser. The optical sensitivity of the crystal for a wavelength of λ = 630 nm is very low, so the hologram does not disappear when information is read. As a result of the superposition of two plane waves in a crystal, an interference pattern appears in the form of light and dark lines. The γ-radiation power was ~106 R/s. The crystals were irradiated using a ^{60}Co facility (Institute of Nuclear Physics, Academy of Sciences of the Republic of Uzbekistan). The absorption spectra were studied using a Shimadzu UV 3600 spectrometer. The surface morphology and elemental composition of the samples were studied using an EVO MA10 SEM (Carl Zeiss).

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 [17]. On Fig. 2 shows an image of a pure lithium niobate crystal obtained using a scanning electron microscope and the results of elemental analysis.

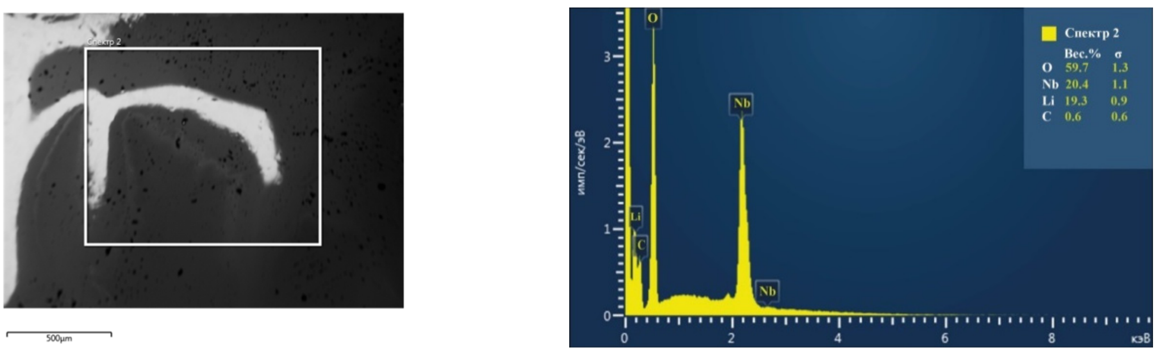
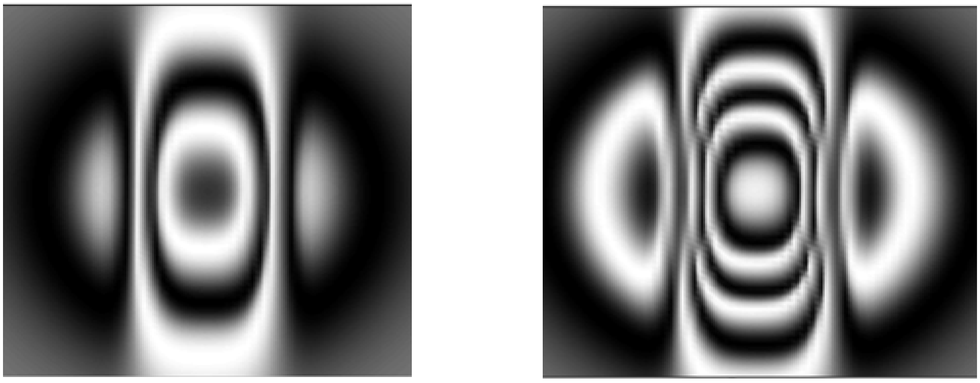


Figure 2. SEM image of a pure lithium niobate crystal and elemental analysis results

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 fully consistent with the above opinion.

Plates made of a photorefractive crystal $LiNbO_3$:Fe (0.01%) were used as objects of photography. Based on the recorded multicolor holograms, digital two-exposure interferometry methods were used to obtain digital interferograms of various stages of relaxation of the phase inhomogeneity recorded in the volume of a photorefractive $LiNbO_3$:Fe crystal. Based on the obtained interferograms, phase fronts were reconstructed, carrying quantitative information about changes in the samples under study.



a **b**

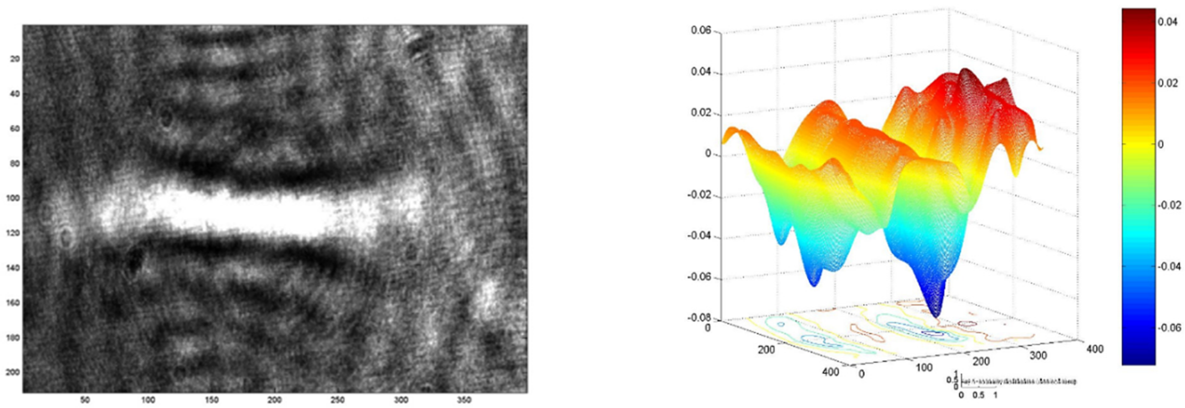
Figure 3. Changes in interference patterns at different exposures on photorefractive ones in $LiNbO_3$:Fe crystals

Phase inhomogeneity arising under the action of laser radiation in a photorefractive crystal is determined by the intensity of laser radiation I(t), exposure time τ, photorefractive sensitivity of the material K and absorption coefficient α. Fig. 3 shows images of phase inhomogeneity in a photorefractive $LiNbO_3$:Fe crystal at different exposure times, corresponding to interference patterns in digital format, while the spatial distribution of laser radiation intensity is assumed to be Gaussian. The exposure time of the image shown in Fig. 3b, 3 times longer than the exposure time of the image shown in Fig. 3a. It can be seen that with increasing exposure time, the image of the phase inhomogeneity becomes more complicated, which manifests itself in the form of an increase in the number of interference fringes.

The algorithm for reconstructing digital interferograms from recorded holograms was as follows. If I(x,y) the intensity distribution in the hologram recording plane (x,y) is determined by the square of the modulus of the sum of the complex amplitudes of the object O(x,y) and reference R(x,y) waves, namely:

$$I(x,y) = |R(x,y)|^2 + |O(x,y)|^2 + R(x,y)\,O^*(x,y) + R^*(x,y)\,O(x,y) \tag{2}$$

Then the last two terms of equation (2) contain information corresponding to the amplitude and phase of the object wave. This information can be extracted using the Fourier transform method. After the transformation, we obtain the Fourier spectrum of the hologram with four localized spectra of spatial frequencies, which correspond to the terms of equation (2). The first two terms in (2) form the zeroth order of the spectrum, which is localized at the center of the two-dimensional Fourier plane. The third and fourth terms of Equation (2) form two conjugate spectra localized symmetrically with respect to the center. If one of the regions of the localized spectrum is selected (filtered) and then the inverse Fourier transform is applied, then the phase front of the object wave will be restored. In accordance with this algorithm, the hologram G1 (of the unperturbed object) is taken in the first laser pulse, then the hologram G2 (of the perturbed object) is taken in the next pulse, and an interferogram is constructed. Next, a phase unfolding algorithm similar to [16] is used, and the surface of the perturbed phase is reconstructed from the interferogram. Fig. 4a shows the obtained interferogram, and in Fig. 4b is a three-dimensional picture of the phase inhomogeneity recorded in the $LiNbO_3$:Fe (0.01%) crystal after 10 laser flashes. In this case, the crystal was at a distance of 2 cm from the focus of lens 2. The recorded inhomogeneity was gradually erased, and this relaxation process can be repeated.



a **b**

Figure 4. Interferogram and phase reconstruction of a photorefractive structure

Due to the presence of nonlinear effects in the lithium niobate crystal, this crystal can be used as a memory element. One of the requirements for a memory element is diffraction efficiency and photorefraction. The diffraction efficiency is experimentally defined as the ratio of the intensity of the diffracted readout beam to the intensity of the beam that has passed through the crystal when the hologram is not recorded in the crystal.

It is known that the use of transition metals as dopants is associated with their ability to reversibly donate d-electrons to the conduction band under the action of radiation. When a crystal is doped with Fe^{3+} ions, the absorption of light in it is caused by ionization. The light sensitivity of crystals doped with iron is determined by the concentration of Fe^{2+} ions. Upon photoexcitation, Fe^{2+} donates a photoelectron to the conduction band, which is captured by the Fe^{3+} ion in the unilluminated region during diffusion. Consequently, as the concentration of Fe^{2+} increases, the absorption at the wavelength λ, at which information is recorded, increases, which increases the sensitivity of the crystal to light.

Fig. 5 and Fig. 6 show experimental studies of the dependence of the influence of various concentrations of iron ions in $LiNbO_3$ on the diffraction efficiency of holograms - η, recorded by a helium-neon laser – λ = 630 nm and a helium-cadmium laser – λ = 440 nm in the form of a plane wave front (sample 1 – 0.003 wt.% Fe, sample 2 - 0.005 wt.% Fe). Erasing was carried out with a helium-cadmium laser (λ=440 nm), since lithium niobate crystals doped with iron ions have high absorption in the blue frequency range. With an increase in the concentration of iron ions, as shown in Fig. 5 and Fig. 6, the photosensitivity of the crystal increases significantly.

As can be seen from Fig. 6, the photosensitivity in sample 2 is 7 times greater than in sample 1, and almost 2 times greater than in sample 1 when recording information at λ = 630 nm, Fig. 5. For a wave with a wavelength of λ = 630 nm obtained DE η = 31%, and for the wavelength λ = 440 nm – η = 34%.

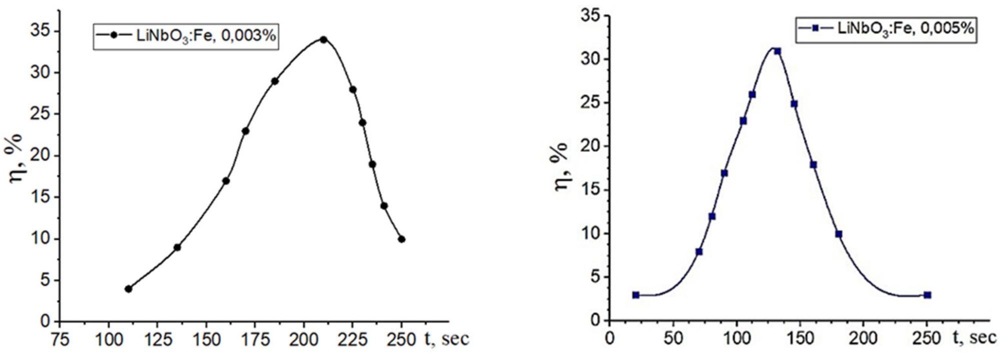


Figure 5. Experimental dependences of the diffraction efficiency of holograms on exposure: λ=630 nm (He-Ne)

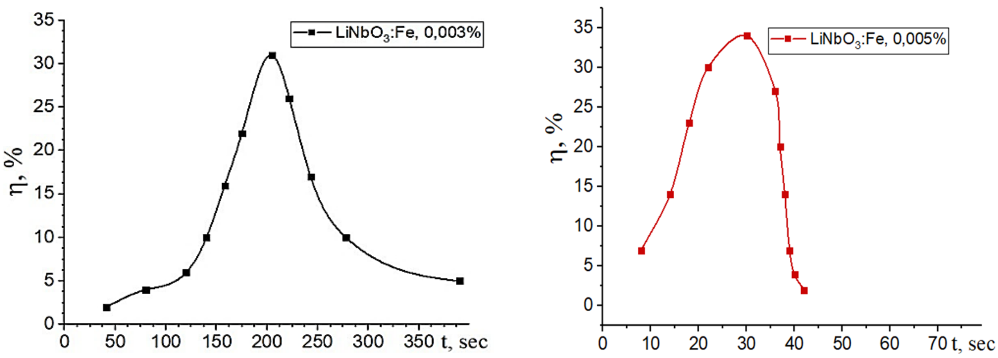


Figure 6. Experimental dependences of the diffraction efficiency of holograms on exposure: λ=440 nm (He-Cd)

In addition, when comparing the results obtained with He-Ne and He-Cd lasers, the photosensitivity for the first sample $LiNbO_3$:Fe 0.003 wt.% practically does not change. But with an increase in the concentration of iron ions in lithium niobate to 0.005 wt.%, the light sensitivity of the crystal increases by almost 3 times, which leads to a decrease in the erasure time by almost 5 times.

The formed spatial interference pattern modulates the refractive index of the crystal, as a result of which a phase diffraction grating appears. Modulation of the refractive index is caused by the space charge field, through the electro-optical effect [1]. The appearance of a spatially inhomogeneous charge is associated with the redistribution of photoexcited carriers between impurity centers with a long capture time. Such a redistribution can be caused by the photovoltaic effect [5] and diffusion of carriers from the illuminated region of the crystal to the unilluminated one [6].

Next, we investigated the effect of laser and radiation, especially γ-radiation, on the photorefractive properties of $LiNbO_3$ and $LiNbO_3$:Fe 0.03 wt.% crystals. To study the effect of radiation, the samples were irradiated with γ-radiation with a dose in the range of 10^3–10^8 R. However, for $LiNbO_3$ and $LiNbO_3$:Fe crystals at doses of 10^3 and 10^8 R, no spectral changes were observed, but with an increase in the irradiation dose, the optical absorption edge shifted towards long waves. The band gap and absorption coefficients of the samples were calculated from the absorption spectra. The calculations showed that the band gap for the $LiNbO_3$ crystal was within 3.25–3.39 eV, and for the $LiNbO_3$:Fe crystal it was 3.04-3.17 eV. The absorption coefficients were 0.32 ÷ 2.06 mm^{-1} for the $LiNbO_3$ crystal, and for the $LiNbO_3$:Fe crystal they were 2.03 ÷ 6.68 mm^{-1}. Another important parameter is the change in the refractive indices, which were: 2.297 – 2.3182 for the $LiNbO_3$ crystal and 2.3285 – 2.3561 for the $LiNbO_3$:Fe crystal. Calculations of the photorefractive sensitivity of materials - K show an increase of 9 times for the $LiNbO_3$ crystal and almost 2 times for the $LiNbO_3$:Fe crystal.

CONCLUSIONS

An analysis of the results shows the promise of using two-exposure digital holographic interferometry for direct dynamic measurement of phase inhomogeneities that arise in a strong laser field, and, consequently, for measuring the nonlinear refractive index, the photorefractive index of a material. An increase in the iron impurity content leads to a reduction in the erasing time of the holograms.

It has been established that the maximum diffraction efficiency of lithium niobate crystals doped with iron ions of various concentrations is η = 31% for a wavelength of λ = 630 nm and η = 34% for a wavelength of λ = 440 nm, and the photosensitivity increased by 3-7 once.

It was also found that the photorefractive sensitivity of the $LiNbO_3$ and $LiNbO_3$:Fe samples depends on the concentration of the introduced impurity and the irradiation dose, and the photorefractive sensitivity of the crystals increases by a factor of 9, and the band gap varies from 3.04 to 3.39 eV in the dose range γ -irradiation $10^4 \div 10^7$ R.

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ДОСЛІДЖЕННЯ НЕЛІНІЙНО-ОПТИЧНИХ ВЛАСТИВОСТЕЙ КРИСТАЛІВ НІОБАТУ ЛІТІЮ

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Стаття присвячена нелінійним ефектам у кристалах ніобату літію. Показано можливість використання цифрових голографічних інтерферограм, отриманих за допомогою лазерного випромінювання різної тривалості в різні моменти часу, для реконструкції динамічних фазових змін. За допомогою He-Ne і He-Cd лазерів на кристалах ніобату літію, легованих іонами заліза в різних концентраціях, записували голограми та розраховували дифракційну ефективність. Також досліджено вплив гамма-випромінювання на оптичні властивості кристалів $LiNbO_3$ та $LiNbO_3$:Fe. При цьому встановлено, що ширина забороненої зони зразків зменшується, внаслідок чого показник заломлення, коефіцієнт поглинання та фоторефрактивна чутливість зростають у кілька разів.

Ключові слова: *сегнетоелектричні кристали; цифрова голографічна інтерферометрія; ефективність дифракції; фоторефрактивна чутливість*