THE PHOTOREFRACTIVE EFFECT IN LiNbO$_3$ CRYSTALS WITH VARIOUS DOPANTS

N. Tarjányi[1]**, I. Turek**

Department of Physics, Faculty of Electrical Engineering, University of Žilina,
Veľký diel, 010 26 Žilina, Slovakia

The photorefractive effect in various crystals of LiNbO$_3$ is investigated in the paper. The experiments were carried out at room temperature by means of set-up for holographic investigation of photorefractive effect. Results of the time dependence of intensity of diffracted beams measurements give information about creation process of the record. Such measurements at high exposures were carried out and their interpretation is presented in the paper. The results of such measurements on samples from different providers indicate the differences among samples with respect to impurities they contain.

1 Introduction

The photorefractive effect (formerly referred to as *optical damage*) has been widely used in a huge amount of applications in various fields of engineering since its first observation [1] in the beginning of the second half of 20$^{\text{th}}$ century. As examples, utilization of the effect for optical data storage [2–5] and construction of optical modulators [6] or filters [7,8] can be mentioned. In published works, this effect is described using a combination of photovoltaic and electrooptic effect [9]. According to this conception, optical properties of material are changed due to electrostatic field formed in the crystal as a result of redistribution of charged particles. This distribution is generated by illumination with inhomogeneous intensity [9]. It is generally accepted that charged particles which generate the electric field are captured at deep impurity centers. Even if the works that examined the influence of different dopants on photorefractive effect exist [10], to the best of our knowledge, there have been no studies published so far that treat in detail the influence of the dopants in a quantitative way. That is why this work is devoted to investigation of photorefractivity in various crystals of LiNbO$_3$ and to search for a relationship between properties of photorefractive effect and impurities in these crystals.

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[1]E-mail address: tarjanyi@fyzika.utc.sk

2   The fundamental model of photorefractivity

When describing the mechanism causing the photorefractivity of the crystal there is very often used the so-called one–level model, which can be considered as the classical model of photorefractivity, today. It is essential in the model that photorefractive material contains certain type of impurities or imperfections, which create allowed energy levels in the band gap. For the sake of simplicity, the model assumes that all these centers are of the same type and they are deep enough not to be ionized at the room temperature and in darkness [9]. Once again, for simplification, the model takes into account only one type of charge carriers – the most often models deal with electrons. In this case, the centers behave as donors that can be ionized (only once) by light with proper wavelength and an empty donor center is capable to catch a free electron. In this model, the process of ionization is assumed to be one-photon process. The fact that in the initial state only part of donor centers is occupied means that apart from the donors there are also acceptor impurities present in crystal and all of them are occupied at room temperature. Denoting the concentration of all donors as N_D and concentration of all acceptors as N_A, the initial concentration of electrons at donor (ground) level before starting optical recording is given by $n_{D_0} = N_D - N_A$.

Impact of radiation with the proper wavelength and spatial dependence $I(\vec{r})$ is that electrons are generated into the conduction band. The number of electrons generated per unit time in a unit volume depends on probability density of electron generation g_D, intensity of illumination in considered place and concentration of electrons at the donor level $n_D(t, \vec{r})$. Similarly, the number of electrons captured at donor level depends on count of empty centers $N_D - n_D(t, \vec{r})$, number of free electrons that are able to recombine $n_c(t, \vec{r})$ and probability density of capture r_D. These processes are described by the rate equation

$$\frac{\partial n_D(t, \vec{r})}{\partial t} = -g_D I(\vec{r}) n_D(t, \vec{r}) + r_D n_c(t, \vec{r})(N_D - n_D(t, \vec{r})). \tag{1}$$

The change of electron concentration in conduction band in time is described by equation

$$\frac{\partial n_c(t, \vec{r})}{\partial t} = -\frac{\partial n_D(t, \vec{r})}{\partial t} + \frac{1}{e}\nabla \vec{j}(t, \vec{r}), \tag{2}$$

where e is the elementary charge, $\vec{j}$ is the electric current density vector and the meaning of other symbols is apparent from previous text. The total electric current density $\vec{j}$ consists not only of diffusion current which is a consequence of free carriers concentration gradient but also of ohmic current caused by the electric field formed by displacement of electrons

$$\vec{j}(t, \vec{r}) = D\nabla n_c(t, \vec{r}) + \bar{\bar{\sigma}}\vec{E}(t, \vec{r}), \tag{3}$$

where D is the diffusion coefficient of free carriers in conduction band, $\bar{\bar{\sigma}}$ is the conductivity tensor of material and $\vec{E}(t, \vec{r})$ is the distribution of electric field intensity formed by spatial redistribution of charge. This field fulfils the Poisson's equation

$$\nabla \bar{\bar{\varepsilon}}\vec{E} = \rho(t, \vec{r}), \tag{4}$$

where upon $\rho(t, \vec{r}) = e(n_c(t, \vec{r}) + N_A + n_D(t, \vec{r}) - N_D)$ is the spatial distribution of the charge density due to illumination, $\bar{\bar{\varepsilon}}$ is the permitivity tensor of the medium. The electric field

(described by Eq. (4)) induces changes of refractive index due to electrooptical effect, which is considered a linear one. This change can be expressed by change of impermeability tensor $\bar{\bar{B}}$

$$\Delta\bar{\bar{B}}\left(t,\vec{r}\right) = \bar{\bar{r}}\vec{E}\left(t,\vec{r}\right), \tag{5}$$

where $\Delta\bar{\bar{B}}\left(t,\vec{r}\right) = \Delta\left(\frac{1}{(n(t,\vec{r}))^2}\right)_{ij}$ with $i, j = 1, 2, 3$ and $\bar{\bar{r}}$ is the tensor of electrooptical coefficients [9,11]. As the refractive index distribution $n\left(t,\vec{r}\right)$ is a result of distribution of illumination intensity $I\left(\vec{r}\right)$ and duration of its influence, one can consider the distribution of refractive index as the record of spatial distribution of illumination. Eqs. (1)–(5) then mathematically describe the model of creating such photorefractive record.

3 Experimental investigation of photorefractive record at high and repeated exposures

The experiments were performed using a set-up for holographic investigation of photorefractive effect [12,14]. To examine the effect we used to record the optical field formed by interference of two coherent beams of Argon ion laser ILA 120 operating at 488 nm. The beams intersected each other in the place of the crystal sample seating with small angle (about 0.004 rad). Due to the angle, laser beams form the optical field with harmonic dependence on coordinate with period about 300 μm. The optical axis of the crystal was parallel to direction of gradient of illumination $I(z)$. This optical field creates the phase diffraction grating (a region with spatially modulated refractive index), which can be considered as a record of this field. The information about process of the record formation can be obtained by measuring the time dependence of the diffraction maxima intensities that occur either due to self-diffraction of the light creating the record or due to diffraction of the light illuminating the record from another light source. To read the record we illuminated the crystal with He – Ne laser (633 nm) beam. The polarization of the reading beam was chosen to correspond to extraordinary beam. We chose small intensity of the reading beam to minimize its effect on record but at the same time, intensive enough to provide legible diffracted beams. Time dependencies of intensity of the beams diffracted on records created in different samples of LiNbO₃ crystals obtained experimentally at room temperature are shown in Fig. 1.

It is well known that the record is erased when it is read out by light with the same wavelength, or close one to that used at creation of the optical record. After simple manipulations with Eqs. (1) – (4) one can show that irradiation of the crystal by homogeneous light (this corresponds to situation of readout, or erasing of the record) for time long enough causes the homogeneous distribution of electrons in conduction band and donor level, as well. This will happen no matter what the distribution of electrons in crystal before an application of homogeneous illumination was. After turning this light off the crystal gets to the state when $n_D = n_{D_0} = N_D - N_A$ and it is valid for its whole volume. This state is identical with initial one in which the crystal had been before the record was created. It means that medium wherein processes described by the set of Eqs. (1) – (4) occur, can be used for repeated recording and the sensitivity at each particular recording process is the same.

By repeated recording and erasing of records in LiNbO₃ crystals we kept in our disposal, we indeed observed the possibility of repetition of the process but with the decrease of photosensitivity of the material. The amplitude of last records compared to amplitude of the first record was lower (Fig. 2). In some crystals, we observed as much as tenfold drop of amplitude. There
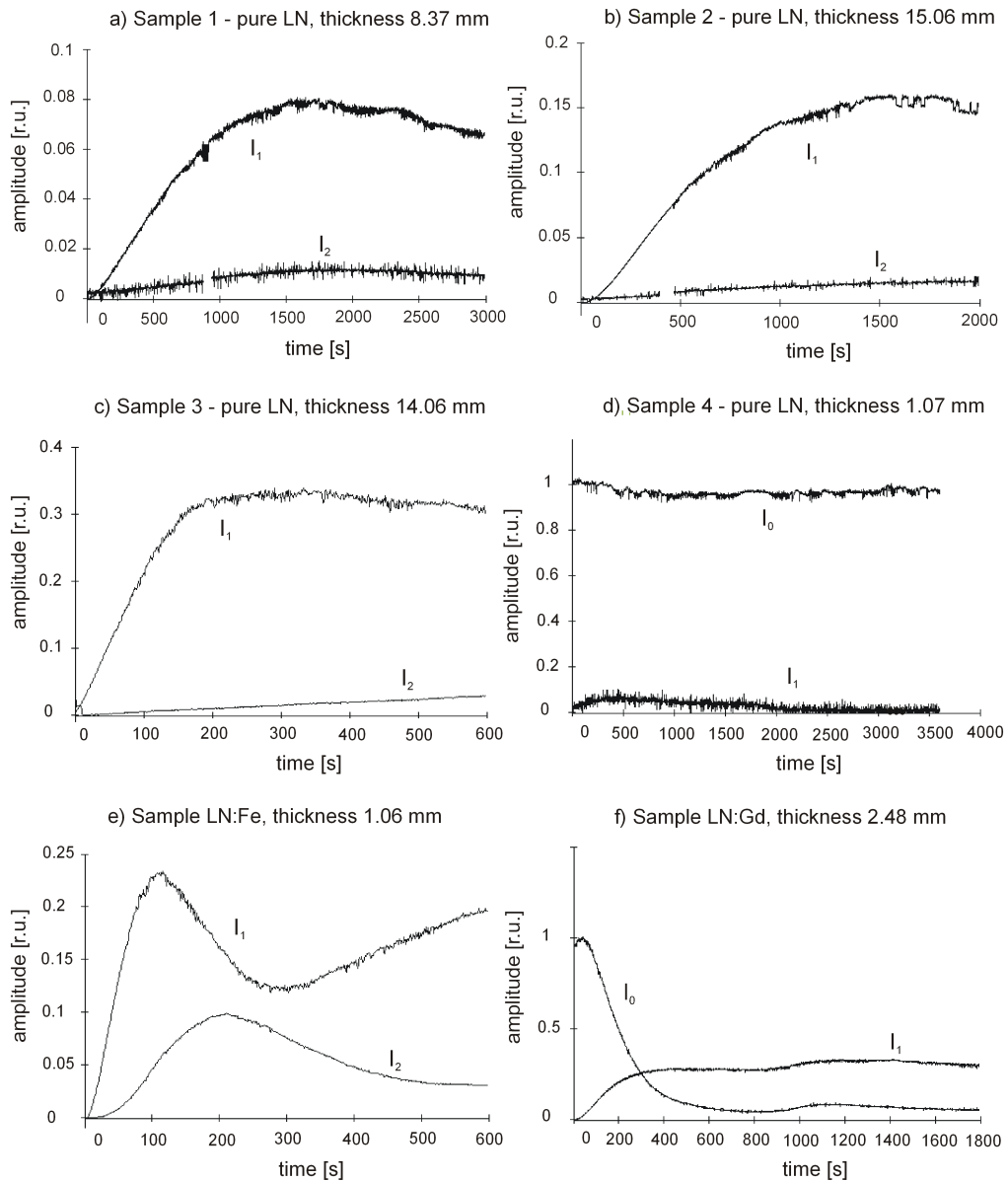
Fig. 1. The diffraction efficiency as the function of time. The part a), b), c), e) – intensity of the first (I_1) and the second (I_2) diffraction maximum. To see the second diffraction maximum well, values are multiplied by factor of 5 in a) and b) and by factor of 2 in c). The part d) and f) – intensity of the zero (I_0) and the first (I_1) diffraction maximum. In d) the values of the first diffraction maximum are multiplied by factor of 30.

is the contradiction between the result of our experiment and the result, which follows from rate equations for one-level model.
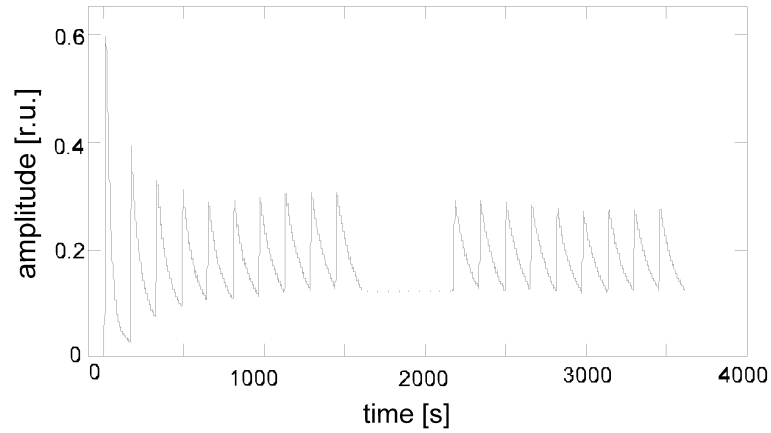

Fig. 2. Time dependence of relative intensities of diffracted beam during multiple recording and optical erasing of the optical field record in iron doped sample (denoted as sample LN:Fe in Fig. 1).
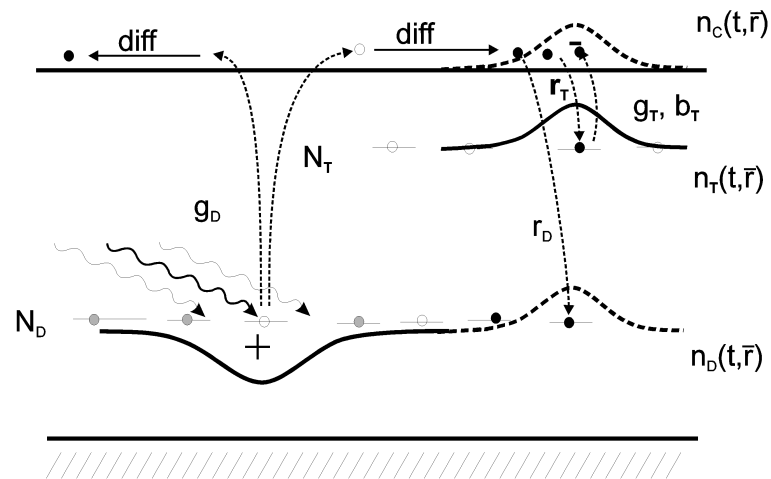

Fig. 3. A scheme of the two-level model.

To explain this contradiction one needs to modify the fundamental model. The modification lies in the assumption that there is another type of allowed centers beside donors in the band gap. These centers act as the deep traps even if their position in the band gap is shallower than the position of donors (Fig. 3). For the model, it is possible to write down similar rate equations as

we used for one–level model

$$\frac{\partial n_D\left(t,\vec{r}\right)}{\partial t} = -g_D I\left(\vec{r}\right) n_D\left(t,\vec{r}\right) + r_D n_c\left(t,\vec{r}\right)\left(N_D - n_D\left(t,\vec{r}\right)\right), \tag{6}$$

$$\frac{\partial n_T\left(t,\vec{r}\right)}{\partial t} = -\left(g_T I\left(\vec{r}\right) + \beta_T\right) n_T\left(t,\vec{r}\right) + r_T n_c\left(t,\vec{r}\right)\left(N_T - n_T\left(t,\vec{r}\right)\right), \tag{7}$$

$$\frac{\partial n_c\left(t,\vec{r}\right)}{\partial t} = -\frac{\partial n_D\left(t,\vec{r}\right)}{\partial t} - \frac{\partial n_T\left(t,\vec{r}\right)}{\partial t} + \frac{1}{e}\nabla\vec{j}\left(t,\vec{r}\right). \tag{8}$$

Equations (6) - (8) with addition of Eqs. (3) and (4) describe the modified model. However, in expression for the space charge $\rho\left(t,\vec{r}\right)$ we have to include also carriers captured at traps. The space charge distribution is then

$$\rho\left(t,\vec{r}\right) = e\left(n_c\left(t,\vec{r}\right) + n_T\left(t,\vec{r}\right) + n_D\left(t,\vec{r}\right) - n_{D_0}\right). \tag{9}$$

The meaning of all symbols in Eqs. (6) – (9) is the same as in Eqs. (1) – (4); only the subscript „T" specifies the traps. As we assume the existence of shallower traps, there is also higher probability of thermal excitation of electrons from traps into the conduction band. Hence, parameter β_T - the probability of thermal generation appears in Eq. (7).

With respect to number of levels in the band gap forming the record the model can be qualified as the two–level model. According to this model, the record is made by charge distribution at donor level and traps.

According to Eq. (9), the electric field that is the cause of the record is formed not only by trapped charges but also by free carriers. The distribution of trapped carriers after turning the recorded optical field off is quite stable. Consequently, any changes in intensity of diffracted beams in short time after turning off the light may be caused only by change of the free carriers distribution. This can be used to measure the contribution of free carriers to the record. Therefore, we investigated the influence the turning off the recorded field had on intensity of diffracted beams at constant intensity of read out beam. We did register no short-time change[2] in intensity of diffracted beams even if the optical field was turned off in different stages of record creation. Our equipment allowed us to measure short-time changes of the order of magnitude 10^{-3} of diffracted beams intensity. It indicates that the electric field is dominantly formed by captured carriers.

It is possible to explain the observed change in sensitivity of material that occurs when providing the multiple repeating of optical creating and erasure of the record by establishment of the following assumption. Let us assume that the probability density of donors and traps ionization for light used in experiment is not the same, i.e., $g_D \neq g_T$. To illustrate the situation, consider g_T close to zero for the light with given wavelength and at same time consider $N_T > n_{D_0}$. The results of experimentally examined thermal relaxation of the record [12] showed that the time decay constant of the record at room temperature is of the order of months. Hence, we can neglect the influence of thermal excitation of the traps at room temperature. Taking into account premises mentioned above, solving Eqs. (6) and (7) one can show that the sensitivity of medium in this extreme case will decline to zero.

Next, it follows from Eqs. (6) – (9) and (3) – (5) that at high exposures the growth of amplitude of the record gradually decelerates until it stops definitely. The reason of this can be

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[2]Up to few tents of seconds.

a) compensation of the diffusion current by the drift current $\vec{j}_{dif}\left(t,\,\vec{r}\right)=-\vec{j}_{ohm}\left(t,\,\vec{r}\right)$

b) or depletion of donor centers $n_D\left(t\to\infty,\,\vec{r}\right)\to0$.

Experiments show that time period needed to reach the steady state (at beam intensities used for the records) is of the order of hundreds seconds. Accordingly, it is feasible to assume that the time needed to reach the steady state of the free carriers concentration is of few orders shorter than the exposure duration needed for examination of time dependencies of the record creation. Hence, using Eqs. (6) – (8) and applying the assumption that there is no ionization of traps $(g_T\to0,\ \beta_T\to0)$ we can write down the expression for steady state value of electron concentration in conduction band. In first approach the steady state value is

$$n_c\left(t,\,\vec{r}\right)=\frac{g_D I\left(\vec{r}\right)n_D\left(t,\,\vec{r}\right)}{r_T N_T+r_D N_D}. \tag{10}$$

With reference to mentioned conditions it results from Eq. (6) that population of donor level $n_D\left(t,\,\vec{r}\right)$ is the exponential function of time

$$n_D\left(t,\,\vec{r}\right)=n_{D_0}\exp\left[-t/\tau\right] \tag{11}$$

with time constant τ dependent on intensity of illumination

$$\tau=\frac{1}{g_D I\left(\vec{r}\right)\left(1-\frac{r_D N_D}{r_D N_D+r_T N_T}\right)}. \tag{12}$$

In case that growth of the record will stop due to compensation of the diffusion and drift components of the current by each other, it follows from Eq. (3) (using expression (10) and assuming $I(z)=I_0+I_1\cos(Kz)$) that component of the electrostatic field that modulates the refractive index in illuminated region of crystal is

$$E_u\left(z\right)=\frac{DKI_1\sin\left(Kz\right)}{\mu\left(I_0+I_1\cos\left(Kz\right)\right)}, \tag{13}$$

where $E_u\left(z\right)$ is the component of the field in direction of the spatial frequency of the illumination, $\vec{K}$ and μ is the mobility of electrons.

It can be seen from Eq. (13) that for the case of $\mu I_1\cos\left(\vec{K}\vec{r}\right)<<I_0\mu$, the amplitude of the steady state value of the record is proportional to intensity of illumination. In case of $\mu I_1\cos\left(\vec{K}\vec{r}\right)$ comparable or greater than $I_0\mu$, the steady state value does not depend on intensity of illumination but shows heavy deviation from harmonic dependence. Finally, if the growth of the record is limited by the second mechanism (emptying the donor centers) the steady state amplitude of the record is not the function of illumination.

Comparison of measured temporal dependencies of diffracted beam intensities (Fig. 4) with values resulting from diffraction integral for harmonic grating [13]

$$I_{dif}\left(\vartheta,\,t\right)=\left(\frac{\sin\left(\frac{N\pi d\vartheta}{\lambda}\right)}{\sin\left(\frac{\pi d\vartheta}{\lambda}\right)}\right)^2\left(\left|\int_0^d\exp\left(-ik\Delta\varphi\left(t,x\right)\right)\exp\left(-ik\vartheta\xi\right)d\xi\right|\right)^2, \tag{14}$$
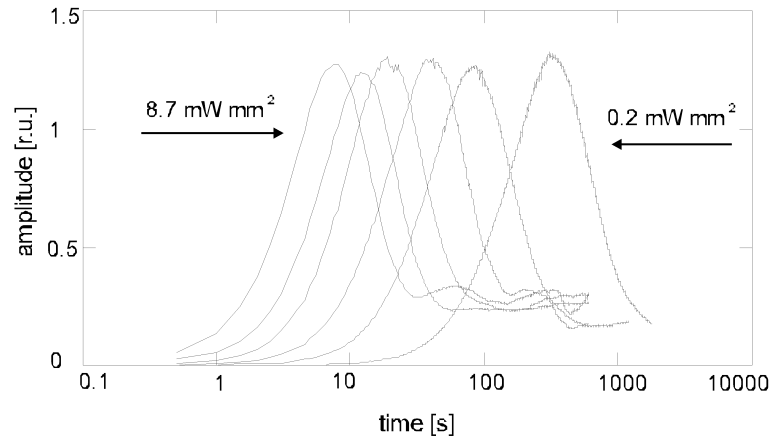
Fig. 4. Time dependences of relative intensities at different intensities of recorded field. The plotted curves are for following intensities: $8.7 \, \mathrm{mW \, mm^{-2}}$, $5.2 \, \mathrm{mW \, mm^{-2}}$, $3.5 \, \mathrm{mW \, mm^{-2}}$, $1.7 \, \mathrm{mW \, mm^{-2}}$, $0.9 \, \mathrm{mW \, mm^{-2}}$, $0.2 \, \mathrm{mW \, mm^{-2}}$.

shows that the steady state value of the record amplitude is independent on illumination intensity and the grating can be considered as harmonic one. According the previous paragraphs it means that existence of steady state of refractive index modulation at long exposure is caused by depletion of donor centers. In expression (14) $I_{dif}(\vartheta, t)$ denotes the distribution of intensity of diffracted beam in time t and direction assigned to diffraction angle ϑ, d is the grating constant, λ is the wavelength of the diffracted light, k is the magnitude of the wave vector and $\Delta\varphi(t, x)$ denotes the change of phase induced by change of refractive index.

To complete the information about crystal sensitivity changes, let us note that in investigated samples it is possible to achieve the restoration of an initial state, i.e. the state with previous relatively high sensitivity to optical record creation. The way to do it is the heating treatment of the crystal. Upon experimentally received thermal dependence of the time decay constant of the record, we know that this one will erase when heating crystal to the temperature of about $100°C - 110°C$ for several minutes. The sensitivity of the crystal after this treatment is approximately the same as in initial state. Tempering the crystal for shorter time, we observed only partial erasure of the record [12].

4   Time dependencies of the amplitude of records

Using expressions (10) and (11) one can find that also the amplitude of concentration of free carriers modulation is the exponential function of time. As a consequence, the concentration gradient and hence also the divergence of current density vector in the first approximation changes exponentially with time constant expressed by (12). The amplitude of the record can be then expressed by

$$\tilde{n} = \tilde{n}_{\max} \left(1 - \exp\left(-\frac{t}{\tau} \right) \right), \tag{15}$$

Tab. 1. Maximal amplitudes of refractive index modulation $\tilde{n}$ of records and corresponding time constants τ in investigated samples.

	Sample 1-pure	Sample 2-pure	Sample 3-pure	Sample 4-pure	Sample LN:Fe	Sample LN:Gd
$\tilde{n} \times 10^6$	11.35	9.497	20.51	13.02	754.7	121.0
$\tau[\mathrm{s}]$	490	460	110	100	220	150

where $\tilde{n}_{\max}$ is the steady state amplitude of the record and τ is the time constant of the process.

Because the investigated diffraction efficiency depends on amplitude of refractive index modulation and thickness of the sample, as well, the time dependence in Fig. 1 do not provide direct information about time evolution of amplitude of the record. Therefore we expressed the amplitude of phase modulation from measured values and after simple conversion, we got the amplitude of refractive index modulation. To be able to compare experimentally obtained dependencies with the features resulting from diffraction integral (14), we used (15) and after fitting the time constant, we got dependencies shown in Fig. 5.

Looking at the figure it is apparent that the maximal (the steady state) values of amplitude of the record are different for single crystals even though some of them are labeled as pure (i.e. undoped) crystals. The obtained curves showed that there was a difference among crystals not only in maximal amplitude of modulation (in the steady state) but also in time constant. The values obtained by fitting these parameters in the expression (15) are presented in Tab. 1.

Knowledge of the time constant τ is useful because it allows (in combination with measurement of absorption coefficient and using Eqs. (6), (11), and (12)) estimating the donor concentration in examined sample [15].

5   Anharmonicity of the record

The study of photorefractive effect by means of reading the intensity of beams originated on the record by diffraction, presented in the previous paragraphs is the natural and obvious way of the record investigation. This method gives semiquantitative agreement between measured diffracted beams intensities and those calculated from diffraction integral (14). It confirms that the record of the interference field represents the phase diffraction grating that is very close to harmonic one (Fig. 6).

Providing the examination of photorefractivity in crystals of LiNbO$_3$, we have also used another way of investigation that gives information about observed process independently on measuring the time dependencies of intensities in diffraction maxima. Its fundamental idea is to image the record. As the record represents the phase object, its image can be obtained using an interference imaging. For example, by using the interference of beams reflected from the front and rear surface of the crystal that contains the record. The registration of such interference pattern in different moments (different phases of the process of record creation) is shown in Fig. 7.

It is useful when the interference fringes are parallel to the gradient of the refractive index.
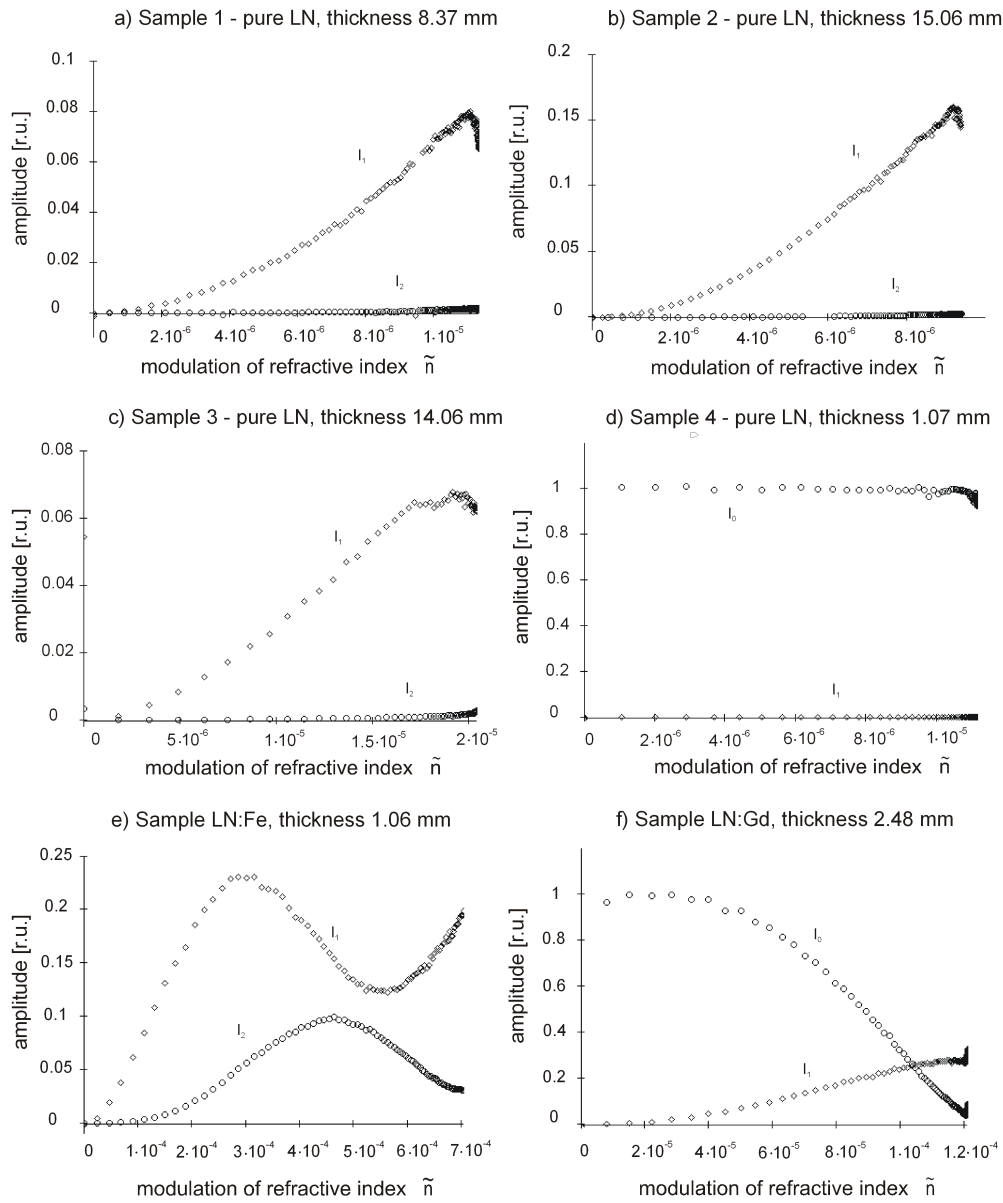
Fig. 5. Time dependences from Fig.1 converted into the refractive index modulation dependence.
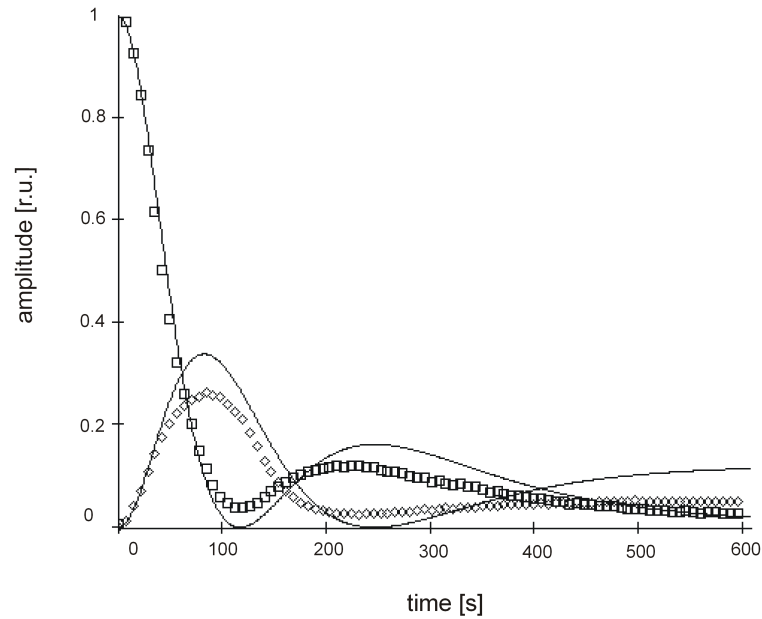
Fig. 6. Intensity of the zero -□- and the first -◇- diffraction maximum measured in sample LiNbO$_3$:Fe and – calculated from diffraction integral.

In this case, their shape directly shows the refractive index profile and the spatial period of the record can be directly read out from the interference pattern. The interferograms in Fig. 7 show that the spatial dependence of refractive index is close to periodic dependence and confirm that its value corresponds to period of the recorded optical field. It means that the distribution of refractive index modulation is not as anharmonic as it follows from the expression (13), which was derived assuming diffusion and drift current mutually compensate each other.

However, we observed some slight deviation from harmonicity when recording harmonic field. It occurred at considerably high exposures and it was manifested by observable asymmetry of the diffraction pattern (different intensities of maxima of higher diffraction orders on positive and negative side) [14].

6 Conclusion

Results of investigation of photorefractivity presented in this work show that examination of photorefractive effect in LiNbO$_3$ crystals at high exposures allows obtaining information about crystals under study. In particular, the repetition of the re-recording of the photorefractive records after their optical erasure indicates that besides the donor level there exists another level in the band gap. In addition, obtained results confirm relationship between time constant of the record creation (which is well measurable value) and material parameters r_T, r_D, N_D, N_T and g_D. The different time constants and different values of maximum amplitude of the record observed

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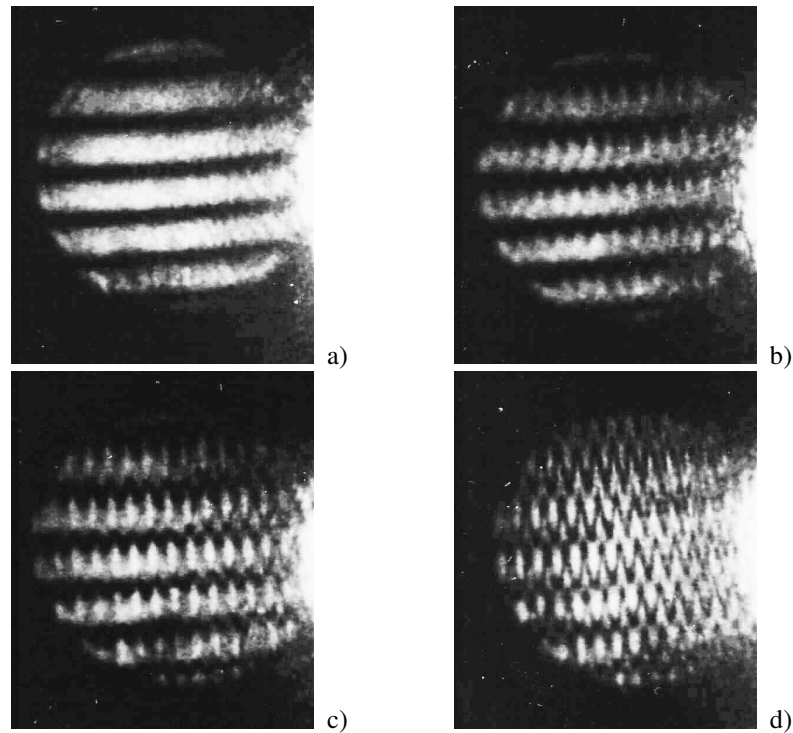

Fig. 7. The interference pattern of beams reflected from front and back surfaces of 1 mm thick sample of LiNbO$_3$:Fe in different stage of recording. The interference pattern created by two Ar laser beams (488 nm) making angle about 0.004 rad: a) before recording, b) after 40 seconds, c) after 100 seconds, d) after 200 seconds of recording. Diameter of illuminated spot is 1.5 mm.

in single crystals (shown in Table 1) suggest that there are significant differences among crystals. It is not surprising when comparing LiNbO$_3$: Fe and LiNbO$_3$: Gd crystals but it becomes interesting when examining crystals of various origin, though all labeled as pure (undoped) crystals. It is clear that differences are related to presence of impurities in used samples. This allows saying that the investigation of photorefractivity at high exposures can be used for approximate estimation of the concentration of impurities.

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