On structural damages induced in photorefractive processes in LiNbO$_3$:Fe crystals

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Abstract

The temporal characteristics of the photorefractive diffraction efficiency were measured on LiNbO$_3$:Fe single crystal samples using a cw Argon-ion laser with power density of 1.5 W cm$^{-2}$. During successive writing-erasure cycles systematic changes were recorded in the time characteristics with increasing irradiation dose up to 3.2 × 10$^4$ J cm$^{-2}$. Though the used power density was much lower than the known pulse-laser induced damage threshold values (0.1–11 GW cm$^{-2}$), over a critical dose of about 1.5 × 10$^4$ J cm$^{-2}$ definite structural damages of samples could be observed by light- and scanning electron microscopy. The dose-dependent changes observed in the diffraction efficiency and the simultaneous cumulative structural damages are firstly described.

1. Introduction

Undoped and doped LiNbO$_3$ crystals are widely used materials because of their excellent dielectric and non-linear optical properties [1]. As known, laser-irradiations can cause different ‘damages’ in the materials [2]. Such a special damage, the photorefractive (PR) effect was initially recognized in LiNbO$_3$ [3]. Since then a lot of PR investigation has been carried out on this material as well as on other oxide crystals [1,4–6]. Fe-doped LiNbO$_3$ crystals have very favorable photorefractive behaviors for practical applications in holographic information storage due to their large PR sensitivity and slow dark decay [4,5,7]. A generally used method for investigations of photorefractive properties of materials is the measurement of four-wave-mixing (FWM) diffraction efficiency [4,5,8]. In these measurements, the power densities of the continuous wave (cw) laser beams (about 1 W cm$^{-2}$) are usually smaller by several orders of magnitude than the structural damage threshold values known for optical materials (from kW cm$^{-2}$ upto GW cm$^{-2}$) [2,9–11]. The small intensities used generally in PR measurements do not predict the occurrence of any structural damage in the samples. The real possibility of any cumulative type damages, however, can not be excluded.

In connection with low intensity photorefractive measurements the appearance of any definite structural damage has not been mentioned by other investigators to the best of our knowledge. Some hints have only been found that some paleness or slight opacities could be observed in the laser exposed...
regions of samples used in photorefractive investigations [12,13].

In the present work, the first results of a systematic study of irreversible cumulative structural damages will be reported which were observed by light- and scanning electron microscopic methods on LiNbO₃:Fe crystal samples previously used for photorefractive measurements. Such structural damages can be important factors limiting the usability of photorefractive materials as optical storage media.

2. Experiments

The crystal samples for investigations were prepared from a LiNbO₃:Fe single crystal boule grown by the balance-controlled Czochralski method from congruent melt. The average iron concentration within the crystal was \( C_s = 8.5 \times 10^{-2} \) mol% measured by atomic absorption spectroscopy [14]. The polished crystal samples were of \( 8 \times 1 \times 5 \) mm³ dimensions along the orthohexagonal \( X, Y \) or \( Z \) crystallographic axes, respectively. For providing the optimum photorefractive conditions the \( XZ \) surfaces of the samples were exposed in writing and testing. The photorefractive diffraction efficiency measurements were carried out at room temperature. The usual four-wave-mixing arrangement was used with the 488 nm output of an Ar-ion laser of 15 mW mm⁻² intensity. The gratings were written with a 23° beam crossing angle resulting in an interference fringe periodicity of (2.35 ± 0.05) \( \mu \)m. The intensities of the two writing beams were nearly the same in the 3 mm dia light spot. A He-Ne laser with 632.8 nm wavelength was used as the test beam, which was attenuated to 0.18 mW mm⁻². The red diffracted read beam was separated from any other light by a chopper, a lock-in amplifier and a filter, and it was detected by a photodiode. The samples were exposed in successive writing-erasure-pause cycles of different durations at \( E = 0 \) or \( E = 10 \) kV cm⁻¹ applied external electric fields, respectively. The geometry and the beam intensity were unchanged during the measurement.

After the series of photorefractive measurement with total writing-erasure exposure doses up to \( d = 3.2 \times 10^4 \) J cm⁻², the samples were first inspected by optical microscopy (OM). Then the input and output surfaces of the samples were studied in detail by using a Jeol JSM 6300 scanning electron microscope (SEM) equipped with a Noran-Explorer energy dispersive X-ray spectrometer (EDS) system at acceleration voltages between 5 and 25 kV. To avoid electric charging the investigated \( XZ \) surfaces of samples were covered with carbon films. Different imaging and electron beam microanalytical working modes of the SEM were used to investigate and compare the surface morphology of unexposed and exposed areas of samples.

3. Results and discussion

After completing the FWM diffraction efficiency measurements, definite traces of structural damages could be observed on the exposed spot area of both the input and output \( XZ \) surfaces of the samples by OM and SEM if the total illumination dose was 'high enough'. On the laser-exposed places of the samples round, slightly opaque spots could already be seen by visual observation. In these exposed spots, a peripheric ring-like region which seems to be the mostly deteriorated area can be recognized by OM and SEM at low magnification. A section of such a damage ring and its surroundings are shown in Fig. 1a. In the damage ring (region B in Fig. 1a) characteristic surface damage traces, such as full or truncated triangle features of oriented sharp contours of about 100 \( \mu \)m sizes can be observed which do not occur in the unexposed sample areas (region A in Fig. 1a). Their sizes radically decrease towards the center of the exposed spot (region C in Fig. 1a).

At higher magnification it is well recognizable that the rough triangle features are cracked pits showing shelly cleavage step structures (e.g. at arrow 1 in Fig. 1b). Besides these rough features, a net of dark, mainly parallel straight lines can also be observed (e.g. at arrow 2 in Fig. 1b). Their orientations are parallel to the contour lines of the rough features which approximately correspond to the intersection lines between the \( XZ \) surface plane and the cleavage planes of \{102\} types. They are surface cracks. The intersections of these lines often show saw-tooth-like figures (e.g. at arrow 3 in Fig. 1b). The contrasts appearing at their contours both in the secondary electron and topographic contrast imaging modes of
dark straight lines can also be seen (e.g. at arrow 4 in Fig. 1b and in detail in Fig. 1c) which are parallel to the X or Z directions and which may be near-surface polygonized line defects, e.g. dislocations. This can be cleared only by further investigations. Densely and randomly distributed dark dots of submicron sizes (Fig. 1c) appear also in the background of the fine network. They seem to be small, single or coagulated surface bubbles or inclusions in the topographic contrast imaging mode of the SEM at higher magnification. According to EDS analysis of the samples, detectable presence of some enriched foreign elements, such as Na, Mg, Al and V could be found only in these dot-like damage traces. Whereas at the fine net lines and the cracks some relative enrichment in Nb could be established from the measured Nb/O concentration ratios. These facts indicate that the structural damage processes are accompanied by some displacement of the matrix and impurity components in the crystal lattice. Certain impurity ions seem to move and accumulate during the PR processes, forming small inclusion particles and bubbles. They can cause locally excess light absorption, initiating further damage processes due to thermal stresses etc., likely as it happens in the damaging at high laser intensities [2]. Similar bubble-like surface features were earlier found in pulse-laser damaged areas of V2O5 crystals which seemed to initiate the damage processes [15].

Parallel, diffuse, fine straight lines of poor contrasts with about 2.3 \( \mu m \) periodicity distance can also be recognized at high magnification in certain SEM indicate that they are cracked surface crusts bending out more or less from the sample surface.

A fine, approximately orthogonal network of thin
exposed microregions of the samples (see the arrows in Fig. 2) which, according to the precalculation, can be the remains of the gratings written several months before the microscopic investigations. It should be noted that in the structurally damaged samples such rests of gratings could be observed one and a half years later after writing-in.

The defect densities were investigated by optical microscopy. The detectable defects were the different triangular type rough defects marked with the arrows 1 and 3 in Fig. 1b. The densities of these defects both on the input and the output surfaces of the illuminated crystal regions show an increase with the increasing doses. The defect density within the exposed spots shows a typical radial distribution. It is the highest at the peripheric region of the illuminated spot and decreases by a factor of 0.1 at the central region. The defect density ratio of output/input surfaces was also found approximately to be 0.1:1. This ratio approximately corresponds to the calculated intensity decrease of the illuminating beam passing through the 1 mm thick absorbing sample. The highest OM detected defect density was found to be \(1.7 \times 10^5\) cm\(^{-2}\) at the peripheric region of the spot exposed with a dose of \(3.2 \times 10^4\) J cm\(^{-2}\). On the base of the tendency of defect densities at increasing doses, a critical dose for appearance of structural damages could be estimated, \(d_c = 1.5 \times 10^4\) J cm\(^{-2}\). Thus the expression 'high enough' used before, means doses \(d > d_c\).

We tried to find the indications for these cumulative type, structural damages in the previously recorded time-dependence of the photorefractive diffraction efficiencies. The typical temporal development of the PR diffraction efficiencies (\(\eta\)) registered on LiNbO\(_3\):Fe crystals is illustrated in Fig. 3. The curve measured at external electric field \(E = 0\) shows a smooth increase up to approximately 100 s and then a transient saturation maximum will be arrived. After that a fluctuating decrease occurs which is well-known in the literature [8,16,17]. Switching over to an erasure process at a given time (see 'OFF' in Fig. 3), a fast decrease occurs with a 'local' secondary maximum at an average time of 100 s after the switching. If the total exposition doses were below \(d_c\), the secondary maximum decreased in the pause-free successive measurement cycles. Whereas they were approximately equal if an irradiation-free pause of several hours was between the successive cycles. Over the critical doses the secondary maximum almost disappeared. Similar behavior was found at curves measured at an external electric field \(E = 10\) kV cm\(^{-1}\).

According to the well-known theory for the temporal development of the PR diffraction efficiency (\(\eta\)), the grating (writing) process can be described by the relation [5,8]

\[
\eta = \exp\left(-\frac{\alpha d}{\cos \theta}\right) \times \sin^2 \left[\frac{\pi d}{2A \cos \theta} \Delta n_s \left(1 - \exp\left(- \frac{t}{\tau_g}\right)\right)\right]
\]

and the bleaching (erasure, dark decay) by the relation

\[
\eta = \exp\left(-\frac{\alpha d}{\cos \theta}\right) \times \sin^2 \left[\frac{\pi d}{2A \cos \theta} \Delta n_s \exp\left(- \frac{t}{\tau_b}\right)\right],
\]

where \(\alpha\) is the absorption coefficient of the crystal sample, \(d\) is the crystal thickness, \(\theta\) is the beam crossing angle, \(A\) is the wavelength of the writing beam, \(\Delta n_s\) is the saturation value of the refractive index change, and \(\tau_g\) and \(\tau_b\) are characteristic time constants for writing and erasure, respectively.

Since the fluctuations in \(\eta(t)\) at times higher than about 100 s make difficult the quantitative evalua-
tions, the attention was firstly directed for the smooth early beginning \((t \leq 30\ s)\) writing and erasure courses of the \(\eta(t)\). In these cases the \(\eta\) values were below a few percents allowing the use of the known approximations \(\sin(x) \approx x\) and \(\exp(-x) \approx 1 - x\).

Thus, instead of Eq. (1) one can obtain for writing a simplified parabolic relation:

\[
\eta \approx \frac{\eta_{\text{max}}}{\tau_g},
\]

(3)

where

\[
\eta_{\text{max}} \equiv K_1 K_2^2 \quad \text{and} \quad K_1 \equiv \exp\left(-\frac{\alpha d}{\cos \theta}\right),
\]

(4)

\[
K_2 \equiv \frac{\pi d}{2\lambda \cos \theta} \Delta n_x
\]

marks were used.

If \(\sin(x) \approx x\) is only fulfilled, then

\[
\eta \approx \frac{\eta_{\text{max}}}{\tau_g} \left(1 - \exp\left\{-\frac{t}{\tau_g}\right\}\right)^2.
\]

(5)

For the bleaching instead of Eq. (2), the

\[
\eta \approx \eta_{\text{max}} \exp\left\{-\frac{2t}{\tau_b}\right\}
\]

(6)

approximate relation can be obtained assuming only the fulfilling of \(\sin(x) \approx x\).

As demonstrated in Fig. 4 the measurement points fall into straight lines of slopes between 1.6 and 2.0 in a double logarithmic representation. That means, that in the early beginning sections the measured \(\eta(t)\) are parabolic according to Eq. (3). The measurement points belonging to different relative doses \(d_1/d_0\) are separated into two approximately parallel branches both at \(E = 0\) and \(E = 10\ \text{kV cm}^{-1}\) external electric fields, as marked by F and P in Fig. 4. The marks F and P mean the following: F ‘fresh’, measured in virgo or after a long relaxation pause and P ‘preloaded’, measured without a previous relaxation pause or after previous doses over the critical one. This separation into two branches of the beginning course of \(\eta(t)\) suggests that the PR processes in the preloaded, unrelaxed state of crystals and in the relaxed ones differ. After exceeding the critical dose no relaxation recovery was found.

The characteristic time constants \(\tau_g\) can be calculated by using either the Eqs. (3) or (5). \(\tau_g\) was found to vary between 11 and 77 s showing an increasing tendency with the increasing total doses. The average value is about 30 s. From the measured...
values of $\eta_{\text{max}}$ and experimental parameters in Eqs. (4) the saturation values of the refractive index changes $\Delta n_s$ could be calculated. They have shown a decreasing tendency from $3.4 \times 10^{-4}$ down to $0.79 \times 10^{-4}$ at increasing doses below the critical one.

The erasure (bleaching) branches of $\eta(t)$ curves also show some systematic changes with increasing doses. This is demonstrated in Fig. 5 in a semilogarithmic representation according to Eq. (6). The inset in Fig. 5a sketches the erasure courses of $\eta(t)$ after switching ‘OFF’ which consist of, at least, two exponential sections. The first fast sections, as illustrated in Fig. 5a seem to be independent from the previous total doses with and without the presence of an external electric field. Here the average characteristic time $\tau_{\text{bi}} \approx 30 \text{ s}$ is practically equal to the average $\tau_{\text{g}}$ found and mentioned before according to certain previous assumptions [18]. The second (Fig. 5b) and third (unillustrated) sections seem to be very sensitive with respect to the external fields and the prehistory of samples. Their characteristic times show wide variations, such as $\tau_{\text{h2}} \approx 87$–650 s, $\tau_{\text{h3}} \approx 200$–4200 s, and suggest a decreasing tendency with increasing doses. For comparison the characteristic time of the dark decay was found to be 4000 s. It is to note that some remains of grating written into the samples stored in the dark could still visually be observed by the aid of optical phase contrast microscopy one and a half years after writing. On the base of phase contrast theory [19,20] from a visually well detectable minimum contrast of $0.1$–$0.01$, a refraction index change $\Delta n \approx 10^{-5}$–$10^{-6}$ remaining in the samples could be estimated. This $\Delta n$ value would then indicate the existence of a prolonged characteristic time for dark decay: $\tau_{\text{bo}} \approx 10^7 \text{ s}$.

The typical changes of the characteristics, both in the beginning write-in and erasure periods of the $\eta(t)$ courses, may be indications of cumulative structural damages occurring in the PR processes at increasing total laser doses and then definitely be detected.

4. Summary

To the best of our knowledge, this is the first systematic study on cumulative structural laser dam-

ages occurred in photorefractive measurements at very low laser intensities. Systematic changes in the time dependence of the diffraction efficiency at increasing laser doses were shown. These changes may be indications of latent structural damage processes manifesting only above a critical dose. A critical dose of about $1.5 \times 10^4 \text{ J cm}^{-2}$ was estimated for the detectable initiation of cumulative structural damages. This or a similar threshold value can be a lifetime limitation at the practical application of LiNbO$_3$:Fe crystal and of other optical materials. Further study is needed to explain the details of the formation of damage traces and their initial micro-processes.

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