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Sergey M. Kostritskii, Michel Aillerie. Z-scan study of nonlinear absorption in reduced LiNbO₃ crystals. *Journal of Applied Physics*, 2012, 111, pp.103504. 10.1063/1.4716470 . hal-00699510

HAL Id: hal-00699510

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Citation: *J. Appl. Phys.* **111**, 103504 (2012); doi: 10.1063/1.4716470

View online: <http://dx.doi.org/10.1063/1.4716470>

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Z-scan study of nonlinear absorption in reduced LiNbO₃ crystals

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(Received 5 January 2012; accepted 12 April 2012; published online 17 May 2012)

The nonlinear absorption (NLA) was studied by open-aperture Z-scan experiments in the chemically reduced nominally pure LiNbO₃ crystals at cw-illumination with the red (644 nm) and green (514.5 nm) laser beams. The magnitude of the measured NLA is considerably different from the reported Z-scan results obtained in as-grown LiNbO₃. The positive sign of NLA obtained with the red light has been related to the generation of the small bound polarons absorbing in red and near-IR ranges. Application of green light results in the light-induced transparency, i.e., the Z-scan traces show negative sign of NLA. Intensity dependence of Z-scan traces allows for conclusion that the photo-induced dissociation of small Nb_{Li}⁴⁺:Nb_{Nb}⁴⁺ bipolarons and sequent generation of small polarons gives the dominating contribution to the nonlinear optical absorption in reduced crystals with a large bipolarons concentration. © 2012 American Institute of Physics.

[<http://dx.doi.org/10.1063/1.4716470>]

I. INTRODUCTION

Recently, a new interest to lithium niobate (LiNbO₃) crystals was stimulated by the study of small polarons and bipolarons.^{1,2} Besides of fundamental aspects, polarons are very perspective entities for practical purposes, e.g., the polarons can be used in the holography as intrinsic photorefractive centers in undoped and doped LiNbO₃ crystals, including chemically reduced nominally pure ones.^{2,3} There are many hints that short-living small polarons strongly influence the photorefractive sensitivity. Furthermore, it has been shown that small bound polarons may act as intermediate shallow traps in a multi-step recording scheme for phase holograms featuring non-destructive read-out.^{3,4} To optimize the crystal properties for photorefractive holography, it is necessary to study the efficiency of single polarons excitation. We propose to use the open-aperture Z-scan method, as it has been established³ that the photorefractive sensitivity is proportional to the light-induced absorption. Indeed, both effects have the same microscopic origin related to the photo-generation of small single Nb_{Li}^{3•} polarons caused by light-induced dissociation of small Nb_{Li}⁴⁺:Nb_{Nb}⁴⁺ bipolarons. Note that the Z-scan technique is a well-established method for quantitative measurement of the nonlinear absorption (NLA) and nonlinear refraction (NLR).⁵

II. SAMPLES CHARACTERISTICS AND EXPERIMENTAL TECHNIQUES

A LiNbO₃ crystal grown from a melt of 48.5 mol. % Li₂O has been used for preparation of the reduced samples studied, which are listed in Table I. These six samples were annealed in pure hydrogen atmosphere (partial pressure of 0.1 atm) at different temperatures ranged from 500 to 700 °C for various times in range from 0.5 to 11 h. One additional sample of the as-grown (unreduced) crystal was used as a

reference specimen for the comparative study of the chemical reduction effect on NLA. All the samples were Z-cut 2-mm-thick plates with the front and back Z-surfaces polished at an optical-grade.

The typical optical absorption spectra are shown in Fig. 1. As can be seen from our data, the strength of the bipolaron absorption band depends on the reduction temperature in a strongly nonlinear way. This fact makes it difficult to control the reduction process and may lead to arbitrarily different results for slightly altered experimental conditions.⁶⁻⁹ Since the dependence of bipolaron concentration on the reduction conditions in nominally pure LiNbO₃ is not generally known, the most convenient characterization is given by the properties of the bipolaron band itself. According to Ref. 6, we will refer to the linear absorption coefficient α_0 at $\lambda = 500$ nm, i.e., at a maximum of the bipolaron absorption band, as the degree of reduction.

Experimental information on NLA was obtained from open aperture Z-scan measurements.⁵ The beam of argon-ion laser operating at 514.5 nm was focused by a lens with focal length $f = 200$ mm into the z-cut LiNbO₃ sample. This argon-ion laser generates a Gaussian light beam with an adjustable output power, corresponding to a light intensity I_0 in the 0.05 to 3.5 kW/cm² range at the focal point (i.e., at $z = 0$). The samples were scanned in the vicinity of the lens focus ($z = 0$) starting from a position ahead of focus ($-z$) and moving toward a position behind the focus ($+z$). The scanning range was about ± 25 mm in all the experiments. The data were collected at every 0.2 mm along the lens axis, by translating the sample under test through its focal point using a computer controlled stepper motor. Besides, we use a laser diode at $\lambda = 644$ nm in a second series of NLA measurements with the same open-aperture Z-scan set-up. Calibrated neutral density filters were used to vary I_0 from 0.04 to 1.2 kW/cm². The thickness of a sample (2 mm) was chosen in such a way that it was smaller than the Rayleigh range z_R of the focusing lens. The Rayleigh range was evaluated by

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TABLE I. Samples notation, linear optical absorption coefficient α_0 at $\lambda = 514.5$ nm, maximum light-induced change of absorption coefficient $\Delta\alpha$ observed at saturation of NLA (see Fig. 6), i.e., $\Delta\alpha$ is equal to $\Delta\alpha^{\max}$ defined by Eq. (6), and NLA coefficient β' for the reduced LiNbO₃ samples. β' was evaluated from the Z-scan data on $\Delta\alpha$ values measured with 514.5-nm laser beam at $I_0 = 59.5$ W/cm², as $\Delta\alpha = \beta' \sqrt{I_0}$. The signs of $\Delta\alpha$ and β' were defined in accordance with the expression for the total absorption coefficient $\alpha = \alpha_0 + \Delta\alpha$.

Sample #	1	2	3	4	5	6
α_0, cm^{-1}	4.6	10.6	19.1	25.3	27.6	37.4
$\Delta\alpha, \text{cm}^{-1}$	-2.25	-6.8	-12.5	-16.8	-18.3	-24.3
$\beta', \text{W}^{-0.5}$	-0.09	-0.23	-0.44	-0.56	-0.61	-0.88

$z_R = \pi\omega_0^2/\lambda$; as the beam waist $\omega_0 = 42f/\pi d$ at the focal point ($z = 0$), where d is the beam diameter at the aperture, i.e., $z_R = 5.9$ and 4.8 mm at $\lambda = 644$ and 514.5 nm, respectively.

Note that the Z-scan response with a fully open aperture is insensitive to the nonlinear refraction and is only a function of the nonlinear absorption.^{5,10} Such Z-scan traces with no aperture are expected to be symmetric with respect to the focus ($z = 0$) and the coefficient of nonlinear absorption can be easily calculated from a transmittance curve, when the low-intensity Z-scan background is subtracted to reduce the effects of linear sample inhomogeneities.¹¹

III. EXPERIMENTAL RESULTS

In Fig. 2, the normalized transmission is shown for an open aperture Z-scan as a function of the distance along the lens axis for 514.5-nm and 644-nm laser beams in the deeply reduced crystal having high values for the linear absorption coefficient α_0 at the both wavelengths. The transmission without an aperture was measured in the far field as the sample was moved through the focal point. The curve (1) of Figure 2 depicts the open aperture response, which accounts for a decrease in the transmittance T due to nonlinear absorption of the 644-nm laser beam. Such a shape of the optical response is typical for open-aperture Z-scan measurements in the as-grown nominally pure and doped LiNbO₃

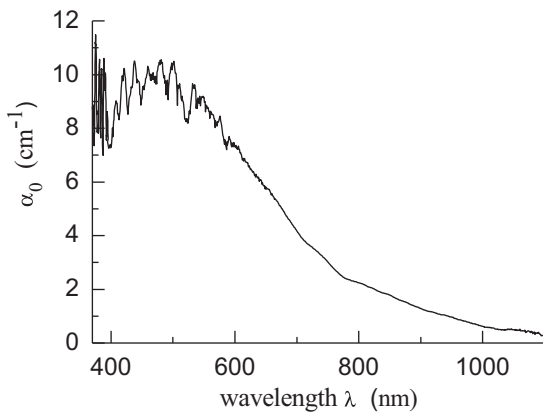


FIG. 1. Spectral dependence of the linear absorption coefficient α_0 for the moderately reduced nominally pure LiNbO₃ crystal (sample #2). Sample notation is given in accordance with Table I.

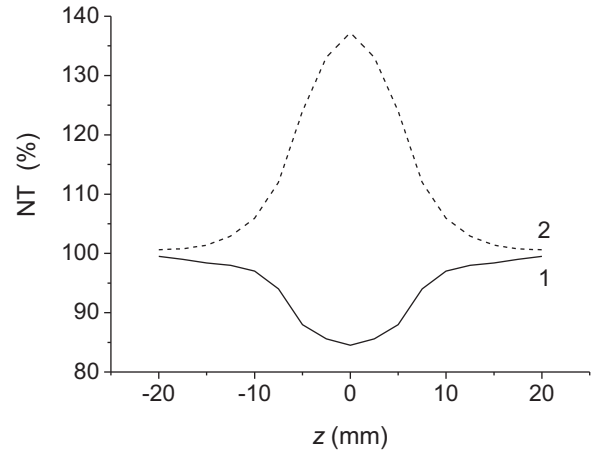


FIG. 2. Open-aperture Z-scan traces measured in the deeply reduced crystal, sample #6, with 644-nm (1) and 514.5-nm (2) laser beams, respectively. The light intensities of 1.2 and 1.9 kW/cm² were used for Z-traces (1) and (2), respectively. Both transmittances $T(z)$ are normalized to the corresponding transmittance T_L in the linear regions (i.e., regions of large $|z|$). Thus, the normalized transmittance given in this plot is $NT = (T(z)/T_L) \times 100\%$.

crystals.^{12–15} In this case called reverse saturable absorption (RSA),¹⁶ the sample experiences the strongest I at focus ($I = I_0$ at $z = 0$); therefore, it absorbs the most energy and allows least transmittance. Away from the focus in the directions of both increasing and decreasing z , transmittance increases evenly because the irradiance decreases symmetrically about the focus. However, the magnitude of this decrease of T has much larger values in the reduced crystals in comparison with an as-grown nominally pure Z-cut sample of same thickness, when the light intensity I_0 is fixed to any constant level within the range available with the 644-nm laser used. The open-aperture response, curve (2) in Fig. 2, obtained for the deeply reduced crystals ($\alpha_0 > 20 \text{ cm}^{-1}$, i.e., in the samples #4–6, Table I) with the 514.5-nm laser beam demonstrates the increase of T with I , i.e., $T(z)$ has a maximum value at $z = 0$, which is typical for SA,^{10,16} when the nonlinear absorption has negative sign. It can be related to the bleaching of the defect centers absorbing at this laser wavelength in the deeply reduced crystals. In contrast to the reduced LiNbO₃, no alteration of NLA sign has been observed in as-grown LiNbO₃ crystals at the change of light wavelength from 644 to 514.5 nm.

As reported in Fig. 3, a more complicated situation is observed in the moderately reduced crystals (i.e., in the samples #1, 2, and 3, Table I), where the transmittance peak broken into two peaks at $\pm z_p$, separated by a transmittance valley T_v at focus for Z-scan tracing with moderate- and high-intensity 514.5-nm laser beams. According to the Z-scan theory,^{10,16} it means that T increases with I to some point and then decreases with I , reaching a valley value T_v at $z = 0$. This feature suggests the transition from SA to RSA with the intensity increase. Note that the total absorption remains saturable in the region far outside ($-z_p, +z_p$). At around $\pm z_p$ and inside ($-z_p, +z_p$), nonlinear absorption turns to be reverse saturable. The pronounced asymmetry of the Z-scan curve can be related to I dissipation with the sample depth, as the measured ratios T_p^+/T_p^- and T^+/T^- (in the

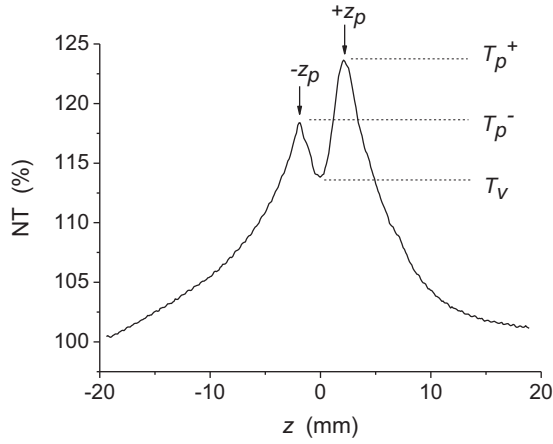


FIG. 3. Open-aperture Z-scan trace measured in the reduced crystal, sample #2, with 514.5-nm laser beam having $I_0 = 1.7 \text{ kW/cm}^2$.

region far outside ($-z_p, +z_p$) are sharply decreasing to 1 with the decrease of α_0 within the range ($1.5 \leq \alpha_0 \leq 20 \text{ cm}^{-1}$) specific for the moderately reduced lithium niobate. At the same time, such a decrease of α_0 results in a marked reduction of T_p^+ and T_p^- , while $(T_p^{+(-)} - T_v)$ keeps a nearly constant value if I_0 is fixed at comparative study of the different samples. However, if the intensity I_0 has a low value (below some specific threshold level), then the Z-scan curves in the moderately reduced crystals have the shape observed typically in the deeply reduced samples, as shown in Fig. 2(2).

A contrast shape of Z-scan curves is observed in the slightly reduced crystals (at $\alpha_0 < 1 \text{ cm}^{-1}$), where $T_v < 1$ has been observed at any I_0 , Fig. 4. The similar behavior was observed¹⁴ in the as-grown undoped LiNbO₃ with a rather high optical absorption ($\alpha_0 = 0.665 \text{ cm}^{-1}$, i.e., crystal was inherently slightly reduced because of insufficient post-growth oxidation treatment). Moreover, our findings allow for assumption that the two unexplained small peaks observed at the both sides of the deep transmission valley¹⁴ can be related to the defects induced by the chemical reduction of LiNbO₃ crystals.

NLA can be determined directly from a $T(z)$ curve measured by the open aperture Z-scan. For a small nonlinear

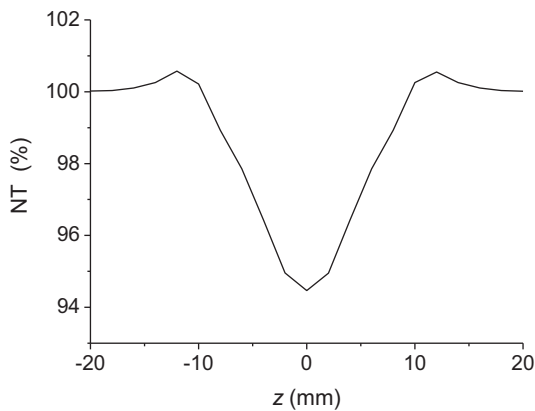


FIG. 4. Open-aperture Z-scan trace measured in the as-grown crystals (linear absorption coefficient is 0.14 cm^{-1} at 514.5 nm, thus, it can be regarded as a slightly reduced crystal because of nonsufficient post-growth oxidation) with 514.5-nm laser beam having $I_0 = 1.9 \text{ kW/cm}^2$.

absorption, the normalized change in transmittance ($\Delta T = T(z) - 1$) becomes¹⁰:

$$\Delta T(z) = -q_0/2\sqrt{2}, \quad (1)$$

where

$$q_0 = \Delta\alpha L_{\text{eff}} / (1 + z^2/z_R^2), \quad (2)$$

where $L_{\text{eff}} = [1 - \exp(-\alpha_0 L)]/\alpha_0$ is the effective length, α_0 is the linear absorption coefficient, L is the thickness of the sample, $\Delta\alpha$ is the light-induced change in absorption (i.e., in the total absorption coefficient, which is equal to $\alpha = \alpha_0 + \Delta\alpha$), z is the actual sample position relative to the focus, and z_R is the Rayleigh range. The change in optical absorption coefficient $\Delta\alpha$ refers to the ordinary polarization, since the optical axis of the crystal under test was always set parallel to the propagation direction of the laser beam.

However, it has been established^{17,18} that the depth of the transmission valley in a Z-scan trace at $z = 0$ (or equivalently the largest change in transmittance, $\Delta T(0)$) is not directly proportional to q_0 at significant NLA, when $q_0 \geq 0.2$. As a consequence, for transmittance changes $\Delta T(0) \geq 0.07$, the data analysis of experimental Z-scan traces to evaluate the NLA values needs to be based on the more general equation¹⁸

$$\Delta T(z) = 1 - \ln(1 + q_0)/q_0. \quad (3)$$

Comparative study of Z-scan traces obtained at different laser powers demonstrates that $\Delta\alpha$ has pronounced sublinear intensity dependence in the reduced crystals (see Fig. 3) that is in contrast to the quasi-linear intensity dependence in the as-grown crystals. The latter dependence observed by us is in accordance with the previous data¹²⁻¹⁵ on NLA in the unreduced crystals.

In as-grown (unreduced) crystals, the change in absorption $\Delta\alpha$ is related to the nonlinear absorption through

$$\Delta\alpha = \beta I_0, \quad (4)$$

where β is the nonlinear absorption coefficient (in cm/kW) and I_0 is the intensity of the laser beam at the focus ($z = 0$).

By applying the open-aperture Z-scan theory,⁵ we numerically calculated the normalized transmittance as a function of the Z position using β as a free parameter. From the best fit of Eq. (2) to the experimental data, β was calculated for all the samples studied.

The open aperture Z-scan data was used to evaluate the nonlinear absorption coefficient β for the as-grown LiNbO₃ crystals at excitation with both the laser wavelengths (514.5 and 644 nm) used in our experimental study. The experimental data on $T(z)$ yields the following values for nonlinear absorption: $\beta = 0.45 \text{ cm/kW}$ at 514.5 nm and $\beta = 0.08 \text{ cm/kW}$ at 644 nm. Note that such a spectral dependence is general feature of NLA.¹⁹ These β values are much smaller than the previously reported values ($\beta = 2.7 \text{ cm/kW}$ was evaluated¹³ at $\lambda = 532 \text{ nm}$ and $\beta = 5 \text{ cm/kW}$ was evaluated¹⁴ at $\lambda = 514.5 \text{ nm}$) obtained with continuous wave (cw)-laser beams for the undoped as-grown lithium niobate crystals. At

the same time, our data are in quite satisfactory agreement with NLA magnitude observed in undoped LiNbO₃ films¹⁵ ($\beta = 0.39 \text{ cm/kW}$ at $\lambda = 532 \text{ nm}$). This difference can be attributed to the significant influence of the photorefractive effect on NLA measurements, as the photorefractive effect depends strongly on many uncontrollable crystal parameters and specific excitation conditions.^{20,21} Such an influence is the inherent factor for undoped as-grown crystals.^{12–14,20} Besides, photorefraction can be controlled (strongly suppressed) by introducing certain dopants (like Mg, Zn, or In),^{7,12} or by periodic poling.¹³ For example, in the as-grown Mg-doped congruent LiNbO₃, with a Mg concentration $\geq 5 \text{ mol. \%}$, and in periodically poled undoped crystals, the β values are lower by three orders of magnitude at similar experimental conditions (sample thickness and laser power)^{12,13,22} that indeed confirms our conclusion on origin of the marked variation of data on β values in as-grown LiNbO₃ crystals at cw-illumination.

The photorefractive effect in the crystal is largely suppressed under picosecond laser radiation and the third-order nonlinearity contribution to the NLA coefficient becomes to be dominating. The picosecond laser pulses are too short for the marked photorefractive process to be observed, if the interval between the pulses is far greater than the photorefractive relaxation time. According to the data on the dynamics of photorefractive effect¹¹ in LiNbO₃ crystals, in the laser irradiance range of a typical Z-scan experiment with ns-pulses, the photorefractive effect takes at least $1 \mu\text{s}$ to manifest itself and takes 10 ms to relax. Thus, the magnitude of β for NLA induced by ns-pulses (it is about²³ $2.5 \times 10^{-7} \text{ cm/kW}$) at practically the same wavelength (532 nm) as in our experiments is about seven orders of magnitude lower than that caused by the photorefractive effect at cw-illumination. This β value is in agreement with the coefficient of $9 \times 10^{-7} \text{ cm/kW}$ that has been theoretically derived for the two-photon absorption process.²³

In the reduced crystals, the light-induced absorption changes $\Delta\alpha$ have been found to be a much more significant and proportional to the square root of I_0 within the quite low-intensity range, Tables I and II. These $\Delta\alpha(I_0)$ dependences, for the both 644-nm- and 514.5-nm-excitations plotted in Figs. 5 and 6, respectively, demonstrate the tendency to saturation even at the moderate intensities. It is important to note that there is a spectral dependence of the NLA coefficient β' (obtained by fitting the experimental dependences by $\Delta\alpha(I_0) = \beta' \sqrt{I_0}$) as well as a maximum value of NLA, i.e., $\Delta\alpha$ value observed at maximum I_0 .

IV. DISCUSSION

To explain the anomalous dependence of $\Delta\alpha$ on I_0 , we took into account that the dominating mechanism of nonlinear absorption in reduced crystals at low and moderate intensities I_0 is the photo-dissociation of bipolarons B into single polarons P , which can be described by a second-order reaction $B \leftrightarrow P + P$ as proposed in Ref. 24. Note that this finding is in contrast to the other mechanisms of NLA in LiNbO₃ reported in Refs. 12–15 and 22, as all these mechanisms can be described by a first-order reaction. The latter term is used in accordance with the definition given previously.²⁴

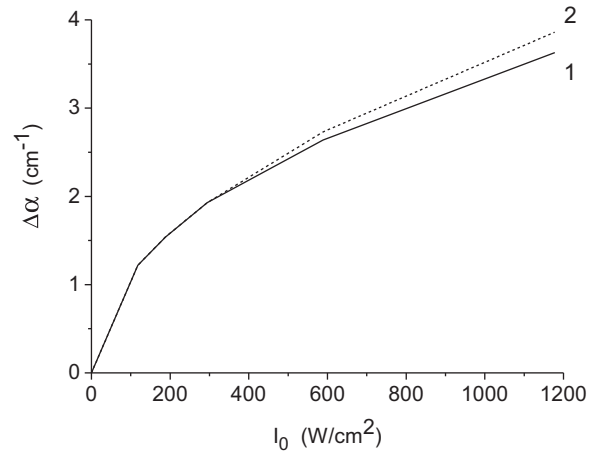


FIG. 5. Curve (1)—maximum light-induced change $\Delta\alpha$ of optical absorption coefficient evaluated from T value versus the light intensity I_0 at the focus of a 644-nm laser beam in the deeply reduced crystal, sample #6; curve (2)—theoretical dependence $\Delta\alpha \sim \sqrt{I_0}$ normalized to experimental values of $\Delta\alpha$ evaluated at low I_0 (40 W/cm^2).

At room temperature, almost all of these polarons are paired forming the bipolarons in equilibrium. Bipolarons can be broken into single polarons again by illumination within visible range. At room temperature, single polarons are short-living ($\leq \text{ms}$) because of their small activation energy (0.3 eV) for annihilation.^{6,7} Such a photo-dissociation of bipolarons changes the optical absorption spectrum of the crystals. The broad absorption band near 500 nm has been attributed to the presence of bipolarons and a narrower band at 760 nm (a short-wavelength tail is extended down to 600 nm) has been assigned to the formation of single polarons under illumination with proper wavelength.^{3,7,24} Therefore, the existence of such a dissociation-annihilation process in cw illuminated crystals is expected to manifest itself in the optical absorption change dependent on the wavelength of pump laser beam.

Thus, the photon-induced dissociation of small Nb_{Li}⁴⁺: Nb_{Nb}⁴⁺ bipolarons, absorbing in the green spectral range, results in a light-induced transparency, i.e., SA effect, when

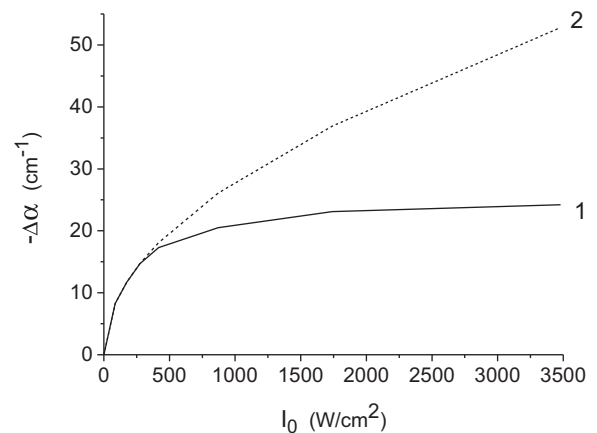


FIG. 6. Curve (1)—maximum light-induced change $\Delta\alpha$ of optical absorption coefficient evaluated from T value versus the light intensity I_0 at the focus of a 514.5-nm laser beam in the deeply reduced crystal, sample #6, curve (2)—theoretical dependence $\Delta\alpha \sim \sqrt{I_0}$ normalized to experimental values of $\Delta\alpha$ evaluated at low I_0 (60 W/cm^2).

$\Delta\alpha$ has negative sign (Eq. (3)), at excitation with 514.5-nm laser beam. The generation of the small bound $\text{Nb}_{\text{Li}}^{4+}$ polarons, absorbing significantly in the red and near IR ranges, yields a positive light-induced absorption $\Delta\alpha$ related to the RSA at excitation with the 644-nm laser beam. According to the data on spectral shape of the bipolaron absorption band,⁷ the red light is still sufficient for one-photon dissociation of bipolarons due to a high light intensity within focused laser beam despite of a small linear absorption α_0 at this wavelength.

Combined solution of equations, describing the dissociation-annihilation process and optical absorption, gives the following dependence²⁴ of the light-induced absorption changes $|\Delta\alpha|$ on I_0

$$|\Delta\alpha| = N \times s(gI_0/r)^{1/2} = \beta' \sqrt{I_0}, \quad (5)$$

with $s = s_P - 0.5s_B$, where s_P denotes the absorption cross section of polarons and s_B that of bipolaron, g and r are generation and recombination rates, respectively, of small bound polarons in the photo-induced dissociation process of bipolarons.

Using the maximum transmission change ΔT measured at $z=0$ in the various reduced crystals as input data for Eqs. (1)–(3) and (5), the values of nonlinear absorption coefficient β' specific for the polaron generation/dissociation process are evaluated, Tables I and II. These β' values evaluated with the aid of the Z-scan technique have the same order of magnitude that its value reported previously²⁴ ($\beta' = 0.27 \text{ W}^{-0.5}$). At the same time, there is an alteration of the β' sign and a significant increase (almost in eight times) of the $|\beta'|$ magnitude, when the pump wavelength changes from 644 to 514.5 nm for any deeply reduced crystal studied, as shown by the values reported in Table II. Such a drastic spectral dependence of β' is in accordance with the data²⁴ on the light-induced changes of the polaron/bipolaron absorption in the reduced LiNbO_3 crystals.

It is important to note that with the increase of I_0 the absorption changes tend to saturate and the intensity dependence of $|\Delta\alpha|$ can be well described by

$$|\Delta\alpha| = |\Delta\alpha^{\text{max}}| \{1 - \exp(-I_0/I_0^s)\}, \quad (6)$$

where I_0^s is a characteristic quantity, which decreases with the increase of the linear absorption coefficient α_0 in accordance with the saturation behavior²⁴ of the bipolaron photo-dissociation.

The maximum values $|\Delta\alpha^{\text{max}}|$ of the light-induced absorption change measured with the high-intensity 514.5-nm

TABLE II. Samples notation, linear optical absorption coefficient α_0 at $\lambda = 644$ nm, maximum light-induced change of absorption coefficient $\Delta\alpha$ observed at $I_0 = 1200 \text{ W/cm}^2$, and NLA coefficient β' [Eq. (5)] for the reduced LiNbO_3 samples. β' was evaluated from $\Delta\alpha$ values measured with 644-nm laser beam at $I_0 = 38 \text{ W/cm}^2$.

Sample #	1	2	3	4	5	6
α_0, cm^{-1}	2.6	5.9	10.7	14.1	15.4	20.8
$\Delta\alpha, \text{cm}^{-1}$	0.43	1.15	2.01	2.56	2.85	3.63
$\beta', \text{W}^{-0.5}$	0.013	0.031	0.056	0.077	0.084	0.112

laser beam are proportional to α_0 in the deeply reduced crystals, i.e., in the samples with $\alpha_0 \geq 20 \text{ cm}^{-1}$, Table I. The light-induced absorption changes observed with the 644-nm laser beam is far from saturation, i.e., $\Delta\alpha \ll \Delta\alpha^{\text{max}}$ (see Fig. 5 and Table II), even at maximum intensity available with focused radiation of the 644-nm laser diode used in our study. However, the maximum light-induced absorption change $\Delta\alpha$ is also proportional to the linear absorption coefficient α_0 , Table II.

Recently, the highly efficient ns-pulse-recording volume holographic gratings in the reduced lithium niobate have been achieved by the optical generation of a spatially modulated small polaron density.³ The absorption change is related to the variation of the population density of small polarons and causally affects the index of refraction via the Kramers-Kronig relation. Thus, the data on open-aperture Z-scan may be used for preliminary estimation of the holographic efficiency in the differently reduced nominally pure crystals. Optimization of the chemical reduction conditions might enable further improvements to be achieved.

V. SUMMARY

Chemically reduced nominally pure LiNbO_3 crystals were prepared and characterized for NLA using the open-aperture Z-scan technique at the wavelength of 514.5 and 644 nm. Z-scan spectra reveal the sign alteration of NLA across this wavelength range with a positive sign of NLA at 644 nm accompanied by a negative one for NLA at 514.5 nm. These anomalous nonlinearities in reduced LiNbO_3 induced by low- and moderate-intensity illumination are established to be mainly due to a two-photon absorption process associated with the photodissociation of bipolarons, which are generated in large quantity by the chemical reduction annealing. It has been found that the NLA of the deeply reduced crystals is much larger than that of the as-grown (unreduced) lithium niobate.

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