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Suppression of optical damage at 532 nm in Holmium doped congruent lithium niobate

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Abstract: Optical damage experiments were carried out in a series of Holmium doped congruent lithium niobate (Ho:cLN) crystals as a function of dopant concentration and laser intensity. The light induced beam distortion was recorded with a camera and a detector under the pseudo-Z-scan configuration. At 532 nm, strong suppression of the optical damage was observed for the 0.94 mol. % doped crystal. Increased resistance to optical damage was also observed at 488 nm. The suppression of the optical damage is predominantly attributed to the reduction of the Nb antisites due to the holmium doping.

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References and links
1. R. L. Sutherland, *Handbook of Nonlinear Optics* (Marcel Dekker, 2003).
2. L. Arizmendi, “Photonic applications of lithium niobate crystals,” Phys. Status Solidi 201(2), 253–283 (2004).
3. T. Volk and M. Wohlecke, *Lithium Niobate: Defects, Photorefraction and Ferroelectric Switching* (Springer, 2008).
4. A. Ashkin, C. D. Boyd, J. M. Dziedzic, R. G. Smith, A. A. Ballman, J. J. Levinstein, and K. Nassau, “Optically-induced refractive index inhomogeneities in LiNbO3 and LiTaO3,” Appl. Phys. Lett. 9(1), 72–74 (1966).
5. G. Nava, P. Minzioni, I. Cristiani, N. Argiolas, M. Bazzan, M. V. Ciampolillo, G. Pozza, C. Sada, and V. Degiorgio, “Photorefraction effect at 775 nm in doped lithium niobate crystals,” Appl. Phys. Lett. 103(3), 031904 (2013).
6. L. Razzari, P. Minzioni, I. Cristiani, V. Degiorgio, and E. P. Kokanyan, “Photorefractivity of Hafnium-doped congruent lithium–niobate crystals,” Appl. Phys. Lett. 86(13), 131914 (2005).
7. M. O. Ramirez, D. Jaque, J. A. Sanz Garcia, L. E. Bausa, and J. E. Munoz Santiago, “74% slope efficiency from a diode-pumped Yb3+:LiNbO3: MgO laser crystal,” Appl. Phys. B 77, 621–623 (2003).
8. A. Wnuk, M. Kaczkan, Z. Frukacz, I. Pracka, G. Chadeyron, M.-F. Joubert, and M. Malinowski, “Infra-red to visible up-conversion in holmium-doped materials,” J. Alloy. Comp. 341(1-2), 353–357 (2002).
9. A. Lorenzo, L. E. Bausa, J. A. Sanz Garcia, and J. Garcia Solé, “Optical absorption intensities and fluorescence dynamics of Ho3+ in LiNbO3,” J. Phys. Condens. Matter 8(31), S581–S591 (1996).
10. A. Lorenzo, L. E. Bausa, and J. Garcia Solé, “Optical characterization of Ho3+ ions in LiNbO3 and LiNbO3: MgO crystals,” J. Phys. Condens. Matter 6(5), 1065–1078 (1994).
11. R. N. Balasanyan, V. T. Gabrielyan, E. P. Kokanyan, and I. Feldvari, “Composition and homogeneity of LiNbO3 crystals as related to growth-conditions. 1. The influence of electric-field,” Crystallography 35, 1540–1544 (1990).
12. V. Bermudez, M. D. Serrano, J. Tornero, and E. Dieguez, “Er incorporation into congruent LiNbO3 crystals,” Solid State Chem. 112, 699–703 (1999).
13. L. Rebouta, M. F. Da Silva, J. C. Soares, D. Serrano, E. Dieguez, F. Agullo-Lopez, and J. Tornero, “Non-axial sites for Er in LiNbO3,” Appl. Phys. Lett. 70(9), 1070–1072 (1997).
14. F. Qin, Y. Zheng, Y. Yu, Z. Cheng, P. S. Tayebi, W. Cao, and Z. Zhang, “Ultraviolet and violet upconversion luminescence in Ho3+-doped Y2O3 ceramic induced by 532-nm CW laser,” J. Alloy. Comp. 509(4), 1115–1118 (2011).
15. H. Qiao, Y. Tomita, J. Xu, Q. Wu, G. Zhang, and Z. Zhang, “Observation of strong stimulated photorefractive scattering and self-pumped phase conjugation in LiNbO3: Mg in the ultraviolet,” Opt. Express 13(19), 7666–7671 (2005).
16. S. M. Kostritskii, M. Aillerie, and O. G. Sevostyanov, “Self-compensation of optical damage in reduced nominally pure LiNbO3 crystals,” J. Appl. Phys. 107(12), 123526 (2010).
1. Introduction

Lithium niobate (LN) is one of the most technologically important optical ferroelectrics used in a wide variety of applications including highly efficient periodically poled nonlinear waveguides, optical modulators, Q-switches, and beam deflectors [1–3]. With a wide transparency range, LN seems like an excellent candidate for a laser gain medium either as a host for rare earth ions or by frequency mixing of infrared light. However LN suffers from optical damage, caused by the modulation of the refractive index by high intensity laser beams, leading to beam distortions and limiting its use in high power applications [4].

According to the one center model, the photorefractive (PR) effect in stoichiometric LN is caused by trace amounts of transition metal impurities which trap photoexcited electrons and create of photovoltaic fields inside the crystal [3]. Coupling between the linear electro-optic coefficient and the photovoltaic fields modulates the local refractive index. For congruent compositions ([Li]/[Nb] = 0.94), the PR effect is primarily caused by Nb antisites (Nb5+) cations occupying Li1+ sites [3,5] and can be suppressed by the introduction of certain “optical damage resistant” impurities which reduce the number of Nb antisites [4–6]. For example, laser experiments with Yb doped Mg:LN yielded an impressive 74% slope efficiency with an M2 beam profile of ~1.2 indicating significant suppression of the PR distortion [7].
In this work we investigate the 532 nm and 488 nm continuous wave (cw) optical damage in a series of Ho₂O₃ doped congruent lithium niobate crystals (denoted as Ho:cLN). Holmium (Ho³⁺) is typically used as a dopant in infrared laser crystals which are pumped by Thulium lasers at 1.9 μm and emit at ~2.1 μm [8]. However, studying the optical damage dynamics of Ho:cLN in visible wavelengths is essential because Ho³⁺ doped or co-doped crystals are considered strong candidates for green/blue lasers due to the strong Ho³⁺ visible upconversion [8–10].

2. Materials and optical measurements

A series of Ho:cLN crystals were grown with the Czochralski technique with Ho₂O₃ concentration ranging from 0.0047 to 0.94 mol. % (0.0094-1.88 mol. % Ho³⁺) in the melt. Here we define the Ho₂O₃ mol. % as the ratio of [Ho₂O₃]/([Ho₂O₃] + [cLiNbO₃]). Further details on the crystal growth can be found in [11]. The samples were cut in rectangular pieces aligned with the X, Y, and Z principal axes of LN and were polished to optical quality. Measurements were carried out with the Y axis parallel to the propagation direction of the light because under this configuration all the samples had the same interacting thickness. From this point forward, the 0.0047, 0.047, 0.47 and 0.94 mol. % Ho:cLN crystals will be referred to as Samples 1, 2, 3 and 4, respectively.

Room temperature optical absorption spectra were collected with a UV-VIS spectrophotometer and the π polarized (polarization∥ Z) spectra from 300 to 700 nm are shown in Fig. 1(a). As the Ho³⁺ concentration increases, characteristic absorption bands appear and become stronger with increasing Ho³⁺ content. For instance, the absorption band around 550 nm is assigned to the Ho³⁺ 5I₈ → (5S₂, 5F₄) transitions whereas the absorption peak around 650 nm is assigned to the 5I₈ → 5F₅ transition [9,10]. Room temperature π polarized emission spectra from 500 to 800 nm were also recorded with a monochromator under 180 mW of 532 nm cw excitation provided by a diode pumped, frequency doubled Nd:YVO₄ laser. The excitation light was focused onto the sample with an f = 75 mm lens, and fluorescence was collected perpendicular to the laser propagation direction in order prevent excitation light from reaching the detector. The emission spectra of the Ho:cLN samples are shown in Fig. 1(b). A strong green, a weak red, and an infrared band around 760 nm were observed. For Samples 1-3, as the Ho³⁺ concentration increases, the fluorescence intensity also increases; however the fluorescence intensity for Sample 4 is slightly lower than that of Sample 3, indicating the onset of fluorescence quenching above 0.47 mol. %. In comparison, fluorescence quenching in Er doped LiNbO₃ occurs at 1-1.5 mol. % Er₂O₃ [12,13].

A simplified energy level diagram of the Ho³⁺ ions in LN and the proposed downconversion mechanisms under 532 nm excitation are shown in Fig. 1(c). The 5S₂ and 5F₄ levels are populated via strong ground state absorption (GSA) of the nearly resonant 532 nm photons. Radiative decay to the ground state (5S₂, 5F₄ → 5I₈) is responsible for the strong emission at ~550 nm, whereas the weak red emission can be attributed to the 5F₅ → 5I₈ transition [9]. Finally, the infrared band observed around 760 nm can be assigned to the 5S₂, 5F₄ → 5I₇ transition [14].

3. 532 nm cw optical damage experiments

The effect of the Ho³⁺ concentration on the cw optical damage at 532 nm was systematically investigated using the direct observation technique. A schematic of the experimental setup is shown in Fig. 2(a). The laser light was focused onto the sample with an f = 75 mm focal length lens and collimated with another lens (f = 50 mm). The samples were placed slightly behind the focal plane with the Z axis parallel to the polarization direction of the light. The 1/e² radius of the beam at the input face of the samples was measured to be ~79 μm with the knife edge technique. The peak intensity is calculated from 2P_{inc}/πw₀², where P_{inc} is the incident laser power, w₀ is the focused 1/e² radius of the Gaussian beam.
Fig. 1. Optical characterization of Ho:LN crystals under $\pi$ configuration. Room temperature: (a) absorption spectra, and (b) fluorescence intensity under 532 nm excitation. (c) Partial energy level diagram of Ho$^{3+}$ ions in LN and proposed downconversion mechanisms. Solid arrows: radiative transitions, dashed arrows: non-radiative transitions.

The CCD images in Fig. 2(a) show the transmitted beam profile at 1.52 kW/cm$^2$ without any sample and with Samples 1 and 4 after 5 minutes of continuous laser irradiation. The beam propagating through Sample 1 distorts along the Z axis and preferentially smears toward the $-Z$ direction [4]. This type of unidirectional photorefractive distortion is consistent with a diffusion dominant mechanism such as the bulk photovoltaic effect [15]. Interestingly, the smearing of the beam is not uniform: part of the energy which was initially confined in the Gaussian mode is transferred to the $-Z$ direction leaving low intensity patches in the center of the mode. On the other hand, the portion of the distorted beam outside the original Gaussian boundary is actually a speckle pattern. The speckle pattern was observed even when a longer focal length lens ($f = 250$ mm) was used, indicating that it is likely originating due to the thickness of the samples (4 mm) which allows for constructive and destructive interference between the incident and scattered light caused by the light-induced refractive index modulation. In contrast, the CCD image for Sample 4 shows the beam profile retaining its Gaussian shape albeit somewhat more focused. The variation in the spatial uniformity of the beam profile is due to the existence of optically inhomogeneous areas inside Sample 4.

Analysis of the CCD images is similar to the procedure described in [5]. The beam distortion is quantified in terms of the ratio $R = d_s/d_o$, where $d_s$ ($d_o$) is the distance between 10% and 90% of the integrated intensity with (without) the sample in the beam path. $R$ is shown in Fig. 2(b) as a function of the peak intensity and mol. %. Two distinct intensity regimes can be identified: for intensities lower than 0.5 kW/cm$^2$ all samples exhibit similar self-focusing behavior. For intensities greater than 0.5 kW/cm$^2$, Samples 1-3 show significant beam smearing whereas the beam propagating through Sample 4 experiences very little distortion. In fact for intensities greater than 3 kW/cm$^2$ we could not obtain reliable data for Samples 1-3 because the smeared beam clipped on the active area of the CCD.

Since the CCD measurements provide only a snapshot of the beam distortion, continuous time-dependent experiments were also carried out under the pseudo-Z-scan configuration. The experimental set-up is essentially identical to the one used for the CCD observations, with the exception that the collimating lens is removed and the CCD is replaced with a photomultiplier tube placed in the far field (~1.15 m from the front surface of the samples). A 2 mm aperture in front of the detector allows sampling of a small fraction of the central portion of the diverging beam.
As shown in Figs. 3(a) and 3(b), at 0.027 kW/cm² both samples show small changes in the amplitude of the transient transmission indicating insignificant beam distortions, consistent with the CCD observations. At 2.55 kW/cm² Sample 1 shows a significant intensity decrease between 0 and 13 seconds due to PR beam defocusing which is then accompanied by slower transient oscillations as shown in Fig. 3(d). For Sample 4, a small drop in the intensity initially occurs, with the signal reaching a minimum at ~3 seconds, and then gradually increasing. As shown in Fig. 3(e), the signal at t = 300 sec is higher than that recorded immediately after unblocking the beam. For comparison, we have included the time dependence of the transmitted laser beam without any sample in the beam path at both intensity levels in Figs. 3(c) and 3(f). Even though the signals are noisy, their temporal variation is smaller than that observed in Fig. 3(e). The temporal behavior observed in Sample 4 in Fig. 3(e) could be indicative of a small transient reversal of the initial PR defocusing.

The maximum change in the extraordinary refractive index $|\Delta n_{e, \text{max}}|$ due to optical damage can be approximated as:

$$\left|\Delta n_{e, \text{max}}\right| \sim A \left(\frac{I_{\text{max}}^{\text{trans}}}{I_{\text{min}}^{\text{trans}}}\right)^{1/2} - 1$$

where A is a scaling factor which takes into account the projection of the light’s solid angle onto the detector, and $I_{\text{max}}^{\text{trans}} / I_{\text{min}}^{\text{trans}}$ is the light induced change in the transmission of the crystals [16]. Starting from (1) the ratio $|\Delta n_{e, \text{max}}^{\text{Sample 1}}| / |\Delta n_{e, \text{max}}^{\text{Sample 4}}|$ is evaluated to be 0.404 and 33.28 at 0.027 and 2.55 kW/cm².
4. 488 nm cw optical damage experiments

Optical damage experiments were also carried out at 488 nm with a cw Argon ion laser, although they were not as extensive as those carried out at 532 nm. Since iron contamination is the most common culprit of PR damage, the beam distortion at 488 nm is expected to be more severe when compared to that at 532 nm under the same irradiation conditions [17]. Figure 4 shows the transmitted beam profiles after propagation through Samples 1-4 at 0.5 kW/cm². The top row shows that Samples 1-3 induce significant unidirectional elongation of the beam profile along the Z direction. In Sample 4 the beam profile appears larger than the beam profile without a sample in the beam path, but the distortion is much smaller than those observed in Samples 1-3. Overall, when compared to Samples 1-3, Sample 4 exhibits increased resistance to optical damage at 488 nm.

5. Infrared absorption spectra

FTIR absorption measurements were also carried out because the spectroscopic properties of OH⁻ inside the LiNbO₃ lattice are strongly influenced by their surroundings, making them sensitive to the stoichiometry of the crystal [3], which in turn is influenced by the dopant concentration. Figure 5 shows the FTIR transmission spectrum from 3400 to 3560 cm⁻¹. For clarity the spectra were shifted in the vertical direction. The absorption peaks between 3440 cm⁻¹ and 3520 cm⁻¹ can be attributed to the OH⁻ stretch mode in the LiNbO₃ lattice [18]. All samples exhibit broad bands with some additional structure at low wavenumbers, characteristic of congruent composition [3]. The shape of the bands for Samples 1 and 2 are
identical with the main peak located at 3484.74 cm$^{-1}$ for both. As the concentration increases, the IR peaks shift to higher wavenumbers and the strength of the absorption band decreases when compared to those of Samples 1 and 2, whereas Sample 4 has slightly stronger absorption than Sample 3. The peak of the IR band is 3487.63 cm$^{-1}$ for Sample 3 and 3492.25 cm$^{-1}$ for Sample 4. Finally, the peak separation between the lowest and highest doped samples is 7.5 cm$^{-1}$.

6. Discussion

The incorporation of Ho$^{3+}$ in cLN at 0.94 mol. % is beneficial in suppressing optical damage for incident intensities up to at least 15 kW/cm$^2$ at 532 nm. Increased optical damage resistance was also observed at 488 nm. Since optical damage is closely related to the defect structure of a material, the observed suppression must be related to the modification of the cLN defect structure by the incorporation of the Ho$^{3+}$ cations, and by extension their influence on the physical properties of the crystals. The effect of rare earth dopants on the linear electro-optic coefficient $r_{ij}$, the photovoltaic field $E_{pvs}$, and therefore $\Delta n_e$ has been investigated.
Beam elongation was observed at intensities as low as 14.7 W/cm$^2$, reaching steady state at ~0.3 seconds for 0.3 mol. % Er$^{3+}$ doping. In contrast, self-focusing was observed in all of our samples for intensities smaller than 0.5 kW/cm$^2$ at 532 nm. As the intensity increases beyond 1 kW/cm$^2$, beam smearing occurs in Samples 1-3, whereas for Sample 4 the beam retains its Gaussian profile even though some smearing initially occurs due to PR defocusing.

Among the known optical damage resistant impurities of LiNbO$_3$, only scandium (Sc$^{3+}$) and indium (In$^{3+}$) are trivalent [3, 20–26]. Similar, to almost all impurity ions, these cations prefer the Li octahedra, and they reduce optical damage by removing the Nb antisite. It is believed that at low concentrations, impurities replace the Nb antisites, and upon reaching a threshold concentration most, if not all, of the antisites are removed. Above this critical concentration, impurities can replace regular Li or Nb sites. The change in the crystal stoichiometry above and below the threshold concentration has spectroscopic signatures which can be detected with infrared or Raman spectroscopy [3]. The dependence of the OH$^-$ IR band on the doping concentration can be summarized as follows: below the threshold, the position and shape of the IR band is virtually unchanged, above the threshold it is shifted to higher frequencies, whereas in the intermediate range the spectra contains a mixture of the bands characteristic of the low and highly doped compositions. Also, the separation of the OH$^-$ band peak above and below the concentration threshold depends strongly on the type of the incorporated impurity. For Sc$^{3+}$ and In$^{3+}$ the reported peak separation is in the order of 20 cm$^{-1}$ [23,24], but increased optical damage resistance was reported even when the peak separation of a Sc$^{3+}$ doped sample was by less than 10 cm$^{-1}$ from that of undoped congruent LiNbO$_3$ [20].

Trivalent impurities are also predicted to suppress optical damage at lower threshold concentration than divalent impurities, thus making them more desirable for practical crystal growth [27]. The lower doping threshold concentration can be explained from the most favorable solution reaction for trivalent cations which is given by:

$$5(\text{In,Sc})_2O_3 + 24V_{Li} + 6\text{Nb}^{4+}_i + '\text{LiNbO}_3' \rightarrow 10(\text{In,Sc})^{2+}_i + 20V_{Li} + 3\text{Nb}_2O_3,$$

(2)

as compared to the one for MgO:

$$5\text{MgO} + 8V_{Li} + 2\text{Nb}^{4+}_i + '\text{LiNbO}_3' \rightarrow 5\text{Mg}^{2+}_i + 5V_{Li} + \text{Nb}_2O_3.$$  

(3)

Here, we use the standard Kroger-Vink notation where “•” represents a single positive charge, “••” is a single negative charge, $V_{Li}$ is a Li vacancy, $\text{Nb}^{4+}_i$ represents the Nb antisite and ‘$\text{LiNbO}_3$’ represents the bulk of perfectly grown LiNbO$_3$. By comparing (2) and (3), the replacement ratio of $\text{Nb}^{4+}_i$ by a given impurity increases from 2:5 for MgO to 3:5 for In$^{3+}$ and Sc$^{3+}$. This trend has been verified experimentally. For example, optical damage resistance at 488 nm was observed in a 1 mol. % Sc$_2$O$_3$ doped congruent LiNbO$_3$ [20], whereas complete suppression of the PR distortion was achieved at 1.5 mol. % doped or co doped crystals [21, 22]. It has also been proposed that complete replacement of all Nb antisites could be achieved with less than 1 mol. % of Sc$_2$O$_3$ given that the ratio [Li]/[Nb] is maintained as 0.94 [23]. On the other hand, for In$_2$O$_3$ the reported threshold concentration varies significantly ranging from 3 mol. % in the crystal as determined by the direct observation technique [24] to 1.85 mol. % in the melt as deduced by an increase in the photoconductivity of the doped sample by two orders of magnitude when compared to that of undoped LiNbO$_3$ [26].

Rare earth cations also primarily substitute into the Li$^+$ sites (ionic radius 0.68 Å) although somewhat shifted for the nominal Li position [28]. Er$^{3+}$ (ionic radius 0.96 Å) diffuses into the Nb antisites, causing readjustment in the number of Li vacancies in order to maintain charge neutrality [29, 30]. Ho$^{3+}$ (ionic radius 0.97 Å) also diffuses into the Nb antisites and with high enough concentration (threshold concentration) suppression of the PR effect should be achieved. To the best of our knowledge, suppression of optical damage in LiNbO$_3$ with rare

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earth ion dopants alone has not been reported. This is likely due to the fact that for rare earths dopants high doping concentrations are usually avoided because of reduced fluorescent output as well as the difficulty associated with growing high quality highly doped crystals. Since rare earth cations are trivalent, it is reasonable to assume that suppression of the optical damage will occur at a doping concentration range similar to the one observed in Sc\(^{3+}\) and In\(^{3+}\). Unfortunately, this range is quite wide with the lowest reported threshold concentrations being 1.5 mol. % for Sc\(_2\)O\(_3\) [21] and 1.85 mol. % for In\(_2\)O\(_3\) [26], both of which are higher than the 0.94 mol. % for Sample 4. Based on our observations at 532 and 488 nm, as well as the behavior of the characteristic IR absorption bands, we can conclude that Sample 4 has the lowest concentration of Nb antisites leading to significant suppression of optical damage. Since the PR effect is typically the strongest at 488 nm, complete suppression of the optical damage at 488 nm is the key for identifying the critical threshold concentration. Since the 488 nm beam propagating through Sample 4 was somewhat distorted we suspect that the doping concentration in Sample 4 is near but likely below the critical threshold concentration required to fully suppress optical damage at 488nm; however it is high enough to suppress optical damage at 532 nm. In order to accurately determine the threshold concentration we would need more samples to study such as a sample with concentration between 0.47 and 0.94 mol. % as well as samples with concentration higher than 0.94%.

Finally, the time dependent behavior of the transmitted intensity of Sample 4 suggests the possibility of secondary optical damage recovery mechanisms assisting in the optical damage suppression. These mechanisms are found in recent reports of pyroelectric spatial solitons [31, 32], suppression of PR damage with a steady state temperature gradient [33], and observation of self-compensation of optical damage in chemically reduced LN [16]. At low intensity regimes, where laser-induced heating is negligible, optical damage was assumed to originate primarily due to the bulk photovoltaic effect. However, as the laser intensity increases, pyroelectric and thermo-optic effects can become more prominent and lead to spatial modulation of the refractive index [34]. The total change in the extraordinary refractive index is then given by \(\Delta n_e = \sum_i \Delta n_{ei}\), where \(i\) denotes contributions from the photovoltaic, pyroelectric and thermo-optic effect. Taking into account the absorption coefficients of Samples 1, 3 and 4 at 532 nm, the temperature gradient \(\nabla T\) at the surface of the samples was estimated from the analytical model of the Kirchoff transform of the heat equation [35]:

\[
\nabla^2 T = -\frac{w^2 S}{\chi}.
\]

Here \(w\) is the 1/e\(^2\) radius of the incident beam, \(S\) describes the heating source, and \(\chi\) is the thermal conductivity which was approximated as that of cLN for all samples [3]. For 2.7-1500 mW incident power (corresponding to 0.0027 and 15.38 kW/cm\(^2\) respectively), the maximum temperature increase in Sample 1 was calculated to be 0.003-1.709 K, 0.013-7.52 K in Sample 3, and 0.021-11.927 K in Sample 4. In addition, the maximum temperature gradient along the XZ (XY) direction was calculated to be 1.72 (0.03), 15.4 (0.84), and 25.9 (2.36) K/cm for Samples 1, 3 and 4 at 1500 mW at the input face of the crystal. According to [33] the XZ temperature gradient in Sample 4 is well within the range for suppression of photorefractive damage observed in nominally pure LiNbO\(_3\) crystals. On the other hand, the calculated temperature gradient of Sample 3 (15.4 K/cm) is closer to the lower limit of the reported temperature gradient (12.5 K/cm), but interestingly no recovery of the optical damage was observed. This indicates that compensation of optical damage due to a laser induced temperature gradient transverse to the propagation direction is not observed in these samples. Higher order longitudinal pyroelectric effects, described in [11] could be partly responsible for the slow intensity recovery observed in Sample 4.

In conclusion, 0.94 mol. % Ho:cLN is a nonlinear material with increased functionality owing to its fluorescent properties, and improved resistance to optical damage, both of which
are achieved with only one type of dopant. Since the concentration requirements for optical
damage suppression and maximum fluorescence yield seem to be incompatible, the optimum
doping concentration must be a compromise allowing for optical damage suppression and a
reasonable fluorescence yield is achieved. Refinement of crystal growth techniques ensuring a
higher Li⁺ content in the LiNbO₃ and reduction of the clustering and precipitation of rare
earth cations inside the host material would be beneficial for this optical damage resistance
scheme.

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