Two-color recording performance in Mn-doped near-stoichiometric LiNbO$_3$ crystals

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Two-color holographic recording was performed in near-stoichiometric LiNbO$_3$ crystals doped with 50-ppm Mn, where the crystals were thermally annealed in different oxidation/reduction atmospheres. Two-color recording properties including sensitivity, dynamic range, activity energy, and dark decay time were measured and compared, and the results were explained reasonably by measuring some characteristic material parameters.

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Two-color holography is a practical solution to destructive readout existing inherently in conventional one-color holographic recording in photorefractive materials. Though two-color sensitivity and refractive index change are enhanced in near-stoichiometric lithium niobate (SLN) by post-growth reduction treatment, the obtained sensitivities still remain low in the range of 10^{-3}–10^{-2} cm/J[1,2]. Recently, we reported the sensitivity was improved up to 0.21 cm/J in as-grown SLN doped with 8 ppm of Mn, where the gating beam of 350 nm is from a krypton ion laser[3]. For practical write/read memory system, low-cost compact diode lasers are needed. Now the violet GaN diode laser of around 405 nm with continuous-wave (CW) operation for several thousand hours is available.

In this paper, we grew SLN crystals doped with 50-ppm Mn that are suitable to use violet light of 405 nm as gating light, and measured their holographic storage properties.

SLN crystals doped with 50-ppm Mn were grown by the top-seeded solution method using Li-rich melt of 55 mol% Li$_2$O and 45 mol % Nb$_2$O$_5$. Samples were cut and polished to be X-plates of 1.95-mm thickness. The samples were annealed in three different atmospheres, i.e., dry oxygen at 1000 °C for 10 h, vacuum at 950 °C for 4 h, and dry nitrogen at 950 °C for 4 h. The ultraviolet (UV) visible absorption spectra of the samples were measured by using a JASCO V-570 spectrometer. UV-visible absorption spectra of the four samples are shown in Fig. 1.

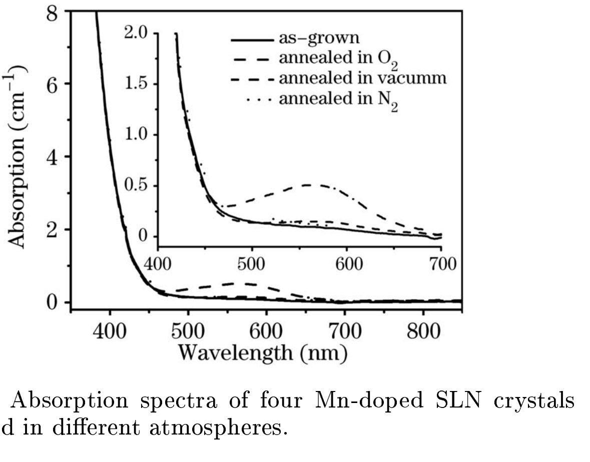

Fig. 1. Absorption spectra of four Mn-doped SLN crystals annealed in different atmospheres.

It is shown that annealing does not induce obvious absorption change at the wavelengths shorter than 420 nm. It is also found that absorption coefficients of the four samples at 405 nm are the nearly same moderate value of 3.2 cm^{-1}. Violet light of 405 nm is suitable to be used as gating light for these crystals, because it can both pass through the sample and efficiently gate for two-color holographic recording. Oxidization annealing in oxygen causes the material to become dark and an absorption band of Mn^{3+} centered near 577 nm, which is not responsible for photorefractive effect. Reduction annealing in nitrogen induces a weak bipolaron absorption band. Annealing in vacuum causes the sample to be oxidized weakly because a weak absorption band centered at 577 nm appears. Generally, annealing in vacuum induces reduction of crystals. The reason may be due to low vacuum degree.

During the two-color recording experiment, the extraordinarily polarized beam from a Ti:sapphire laser of 778 nm for writing was split into two beams of the equal intensity, and the grating period is 1.67 μm. The ordinarily polarized beam from a krypton ion laser of 407 nm is used for gating. The experimental method was the same as before[3]. All the experiments were carried out under the same conditions.

The write-read-erase process of two-color holography in as-grown sample is nearly the same as that in SLN doped with 8-ppm Mn in Ref. [3]. The recording process can be understood easily with a two-center charge transport model, in which Mn$^{2+/3+}$ and bipolaron $\mathrm{Nb}_{\mathrm{Li}}^{4+/5+}\mathrm{Nb}_{\mathrm{Nb}}^{4+/5+}$ as well as small polaron $\mathrm{Nb}_{\mathrm{Li}}^{4+/5+}$ act as deep traps and shallow traps, respectively. Important parameters in characterizing holographic data storage materials are two-color recording sensitivity, dynamic range, and hologram lifetime. The two-color recording sensitivity $S_{\eta 2}$ is defined as $S_{\eta 2} = 1/(I_{\mathrm{w}} d)\partial\sqrt{\eta}/\partial t|_{t=0}$, where d is the crystal thickness, I_{w} is the total writing intensity, and the dynamic range is expressed by a useful metric $M/\#$, which can be written as a product of erasure time τ_{e} and the writing slope $\partial\sqrt{\eta}/\partial t|_{t=0}$. The dark decay time of holograms in the dark determines hologram lifetime. The temperature dependence of the dark decay time yields the activation energy E_{a} for the dark decay, and extrapolation to room temperature yields hologram lifetime τ.

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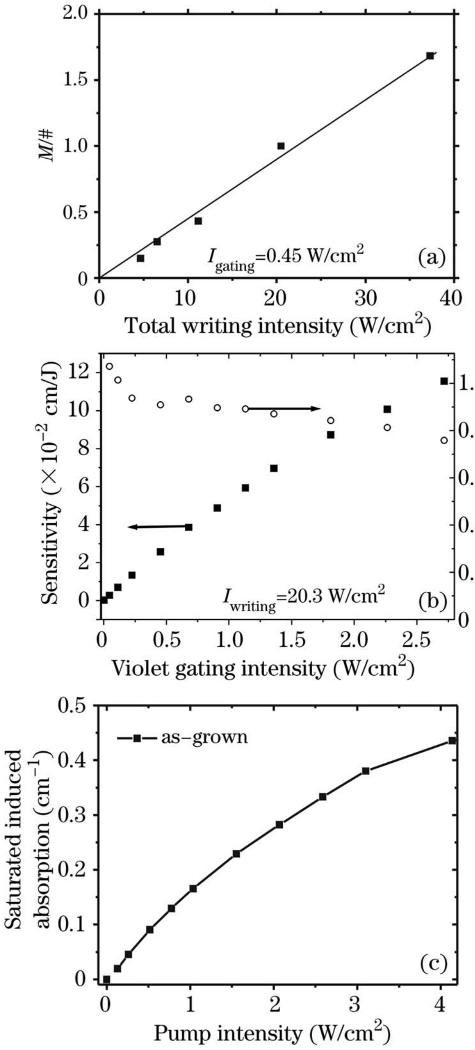

Fig. 2. (a) $M/\#$ versus the total writing intensities; (b) the sensitivity S and $M/\#$ versus the gating intensities; (c) saturated light-induced absorption at 852 nm versus pumping intensities in the as-grown sample.

We measured the dependence of the total writing intensity and the gating intensity on the sensitivity and the $M/\#$ in the as-grown sample, as shown in Fig. 2. In two-color recording, the writing slope is proportional to the total writing intensity for two equal-intensity writing beams, and erasure is caused by the gating light, which result in an $M/\#$ proportional to the total writing intensity. As expected, the $M/\#$ increases linearly with increasing total writing intensity under a constant gating intensity of 0.45 W/cm^2, as shown in Fig. 2(a). The obtained $M/\#$ is nearly same as that in SLN doped with 8 ppm of Mn[3]. The sensitivity increases with increasing gating intensity, and a saturation behavior is expected for large intensities, as shown in Fig. 2(b). We get a high sensitivity of 0.12 cm/J with gating light intensity of 2.6 W/cm^2, which is much larger than the reported value of reduced SLN[1,2], but is lower than that of SLN doped with 8 ppm of Mn where UV of 350 nm was used for gating and small polaron lifetime is relatively longer[3]. There exists a trade-off between the sensitivity and the $M/\#$, as shown in Fig. 2(b). The gating light with too high intensity will erase partly the hologram and restrain the strength of written hologram during the gating process, that is, the writing process.

The two-color recording sensitivity depends on population of small polarons, that is, light-induced absorption change at near infrared (IR) wavelength. We measured light-induced absorption change at 852 nm by use of light of 407 nm for pumping. Figure 2(c) illustrates the measured dependence of saturated induced absorption on pump intensity in the as-grown sample, and the measured lifetime of small polarons is about 0.2 s. Compared with 0.3-s lifetime in as-grown SLN crystal doped with 8 ppm of Mn[3], it does not decrease so much. So the induced absorption is also high, which leads to a high sensitivity.

The dark decay time of holograms determines the lifetime of the stored information. The temperature dependence of the dark decay times, measured in the range of 70–120 °C, obeyed an Arrhenius law on the absolute temperature. The results were extrapolated to room temperature and gave a value of 0.56 year in the as-grown sample, which is longer than that of reduced SLN crystals. The proton compensation mechanism dominates the dark decay process for congruent $LiNbO_3$ crystals doped with Mn contents lower than 0.2 at.-% Mn[4]. The concentrations of protons were estimated by measuring the IR absorption of OH^- stretching vibration at room temperature by a Fourier transform-IR spectrometer, thus, the influence of the proton concentrations on the dark decay of the written hologram was investigated.

Two-color holograms were recorded in other three crystals and there were similar dependences of sensitivity, $M/\#$, and induced absorption change on intensities of writing and gating beams with Fig. 2. We summarize these characteristic parameters sensitivity S, dynamic range $M/\#$, dark decay time at room temperature τ, induced absorption change $\Delta\alpha$ at 852 nm, lifetime of small polaron τ_s of these crystals and OH^- absorption coefficient in Table 1.

Table 1. Comparison of Characteristic Parameters of Four Mn-Doped SLN Crystals

Sample	Annealing	α_{OH^-} (cm^{-1})	$\Delta\alpha$ (cm^{-1})^a	τ_s (ms)	Nonvolatility	S (cm/J)^a	$M/\#^b$	E_a (eV)	τ (year)
1	As-Grown	0.22	0.33	∼ 200	Medium	0.1	0.28	0.98	0.56
2	O_2	0.28	0.05	< 40	Highest	0.005	0.09	1.08	0.65
3	Vacuum	0.10	0.16	∼ 80	High	0.023	0.15	1.09	1.76
4	N_2	0.06	0.45	∼ 300	Low	0.28	0.46	0.96	1.56

^{a}Gating intensity: 2.2 W/cm^2; ^{b}writing intensity: 7 W/cm^2.

The OH^- absorption peaks do not shift before and after the annealing treatment in these four crystals, except for change of values of absorption peaks because of different annealing atmospheres. Annealing in dry N_2 and vacuum may decrease the proton concentration effectively. It is seen that the dark decay time is mainly dependent on the proton concentration, i.e., the IR absorption of OH^- stretching vibration, though the activity energies have small difference for crystals annealed under different atmospheres. The dark decay mechanism may be identified as proton compensation, and the activity is around 1.0 eV.

The annealing treatment will change the degree of oxidation/reduction, i.e., the ratio of Mn^{3+}/Mn^{2+}, and reduction annealing treatment will induce bipolarons absorption. Oxidation annealing treatment in O_2 will shorten greatly the lifetime of the small polarons, while reduction treatment will prolong the lifetime, as shown in Table 1. The shortness of small polaron lifetime in oxidation crystal induces the decrease of small polaron population, i.e., light-induced absorption change, then the decrease of two-color sensitivity, as shown in Table 1. It is also found that the dynamic range $M/\#$ increases with the reduction degree of crystals. Because reduction-annealing treatment in N_2 increase the concentration of donors Mn^{2+} and bipolarons, the IR readout will give rise to erasure of the written holograms and the crystal annealed in N_2 has the lowest resistance to IR readout. These results show that reduction-annealing treatment will increase the sensitivity and the dynamic range simultaneously, but decrease nonvolatility, and there exists a trade-off between sensitivity and nonvolatile readout. One solution to this problem is the use of light with wavelength shorter than 778 nm, in that case, we may get good overall two-color holographic recording characteristics, high sensitivity, high dynamics, and long dark decay time for reduction crystals.

To utilize low-cost compact diode lasers as gating light source, SLN crystals doped with 50-ppm Mn were grown and annealed in different oxidation/reduction atmospheres. Two-color nonvolatile holographic characteristics of these crystals were measured and compared. These results can be reasonably explained by measuring UV-visible absorption spectra, IR absorption of OH^- stretching vibration, induced absorption change by gating light, and lifetime of small polaron τ_s of these crystals.

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