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Nonvolatile two-color holographic recording in Tm-doped near-stoichiometric $LiNbO_3$

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Abstract

We have observed ultraviolet-induced visible absorption and performed two-color holographic recording at green, red, and near-infrared light in thulium doped near-stoichiometric $LiNbO_3$ crystal. The diffraction efficiency and sensitivity of the recording process at all wavelengths are increased by ultraviolet gating light. Characteristics of recording in the visible are explained by a two-center model. Two-color recording in the near-infrared exhibits significant improvements of the fixed diffraction efficiency and the role of small polarons is discussed in the visible and near-infrared recording with ultraviolet sensitizing light.

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1. Introduction

Photorefractive lithium niobate has been investigated intensively in the past three decades because it has been considered as a promising recording medium for holographic data storage. However, the volatility of the stored information during readout has been an obstacle for many applications. Two-color or photon-gated holography that employs an independent gating beam has been proposed to solve this problem. Significant progress in this subject has been made in recent years. Bai et al. [1] and Hesselink et al. [2] demonstrated high photorefractive sensitivity and

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nonvolatile two-color holographic storage in undoped or doped $LiNbO_3$ via a long-lived intermediate state. Recently, near-stoichiometric crystals doped with rare-earth ions, such as Tb or Pr ions have been reported to show more enhanced sensitivity and nondestructive readout of information stored by two-color holographic technique than previously reported results [3,4]. Subsequently, it was realized that the intermediate state in $LiNbO_3$ is attributed to the small polaron formed at the anti-site defect Nb_{Li} and the sensitizing centers are the bi-polarons or dopant-induced deep centers. In this two-color recording technique, charge carriers are generated by photon ionization from deep centers and holograms are recorded in prolonged small polarons by near-infrared light. Hologram erasure during readout can be avoided by using one of the writing beams as a readout beam, because electrons will move from small polarons to deep traps, such as unintentionally doped iron ions, where stable holograms are formed. The long lifetime of the small polaron in stoichiometric $LiNbO_3$ is crucial for the performance of two-color holography since it is directly related to the recording sensitivity. The lifetime of small polarons varies from milliseconds to seconds depending on the crystal stoichiometry, the degree of reduction, and doped ions to reduce neighboring defects [5,6]. The storage process in this recording needs three types of centers which are ultraviolet absorption centers, small polarons and deep traps [3–5]. However, small polarons in congruent crystals make little contribution to two-color holographic storage because of their short lifetimes. Since a nonvolatile recording scheme relies on the existence of deep and shallow centers with different energy levels in the band gap, extrinsic dopants may act as two types of centers. To achieve nonvolatile holographic storage without using small polarons, Buse et al. [7] performed the two-color recording in Mn and Fe doped congruent $LiNbO_3$ and interpreted with a two-center model. Mn and Fe ions are deep sensitizing and shallow recording centers, respectively, in the double-doped system. Because of the energy levels of Fe ions, they used the red instead of the near-infrared light for recording. Final nonvolatile holograms are stored in Mn centers during readout.

In this work, we try to link two different models by using different recording wavelengths under ultraviolet illumination. We present characteristics of two-color holographic recording with 514, 633, and 830 nm in a 500 ppm Tm doped stoichiometric $LiNbO_3$ crystal. Tm ions have not been previously doped in near-stoichiometric $LiNbO_3$ for holographic recording. When we use ultraviolet gating light of 355 nm and recording light of 514 or 633 nm, the two-center model with the ultraviolet absorption centers and deep traps can explain the holographic storage process. The role of small polarons is not important in the recording process in the visible because the peak of its absorption is in the near-infrared. We report the optimum gating-recording intensity ratio for maximum diffraction efficiency which is one of characteristics in two-center model [7]. When we use ultraviolet gating light of 355 nm and recording light of 830 nm, the model with an intermediate level of the small polaron can explain the holographic storage process. We discuss persistent holographic storage at 514 and 830 nm within the scope of two kinds of two-color holographic recording models.

2. Experimental

The stoichiometric $LiNbO_3$ crystals doped with 0.05 mol% of Tm_20_3 used for this investigation were grown by the high temperature top seeded solution method [8] in a diameter controlled growth apparatus from K_2O–Li_2O–Nb_2O fluxes. The crystal was grown well below the melting point and the Curie temperature of congruent $LiNbO_3$. After growth it was cooled in air at a 100 °C/h rate. It received no special heat treatment. It was cut and polished into $4.35 \times 4.75 \times 6$ mm ($a \times b \times c$). The ultraviolet- induced visible and infrared absorption spectra were measured by two spectrophotometers (Flowspek, UVIKON XL and Hitachi, U-3501) separately. Two mutually coherent and extra-ordinarily polarized beams at a wavelength of 514, 633 or 830 nm with equal intensity were used as writing beams at a crossing angle of 40° on the incident crystal surface of *b*-axis. A grating vector of a written hologram was set along the crystal *c*-axis to utilize the largest electro-optic coefficient r_{33}. The

gating beam from a mercury lamp (365 nm) or from the third harmonic (355 nm) of a Q-switched Nd:YAG laser also served to increase the population of recording centers. The gating beam was parallel to the bisector of the two writing beams and overlapped with the two writing beams in the crystal. It also served as an erasing beam. We did not use ultraviolet pre-exposure during recording, because pre-exposure has no influence on the saturation and the fixed diffraction efficiencies [9]. The on and off status of each beam was controlled by electronic shutters via a computer. During the recording phase, one of the writing beams was blocked from time to time and the other beam was diffracted from the written grating to measure the diffraction efficiency. During the reading, only the diffracted beam was continuously detected by a photodiode. To prevent a direct photodiode response to the gating light, we placed an interference filter and a small aperture in front of the photodiode. All the measurements were performed at room temperature.

3. Results and discussion

Absorption measurements were performed before and after 365 nm ultraviolet-illumination for 90 min with 45 mW/cm^2, as illustrated in Fig. 1. The unexposed sample shows no apparent absorption structures in the visible and infrared wavelength ranges due to unintended impurities such as Fe that may have been incorporated during crystal growth. This indicates that concentrations of these impurities in our crystal are negligibly low. Absorption spectrum of the exposed sample was measured 15 min after ultraviolet exposure. The band-gap energy of the crystal is larger than that in congruent crystals indicating that the crystal is highly stoichiometric. The spectrum exhibits several sharp peaks due to absorption by Tm^{3+} ions in a $LiNbO_3$ crystal field. This spectrum structure is slightly different from that of Tm ions in YAG [10] in terms of peak positions and intensities, indicating the effect of a different crystal field. Noticeable absorption peaks can be assigned to the $^3H_4$, $^3F_{2,3}$, $^1G_4$, and $^1D_2$ 4f states of the Tm^{3+} ions. It is also evident that the ultraviolet treatment results in an increase in the absorption but does not change the spectral structure of Tm ions in the visible as compared with that before ultraviolet illumination, which excludes the possibility of charge state change of Tm ions. Since the absorption coefficient at the band edge was measured as 15 cm^{-1} at 304 nm, we estimate the 49.9% composition of Li_2O [11]. Fig. 2 shows the line shape of the OH^- bond's stretching vibration absorption in the infrared. The structure associated with the IR peaks is due to five different proton sites in the oxygen planes of $LiNbO_3$ each having different

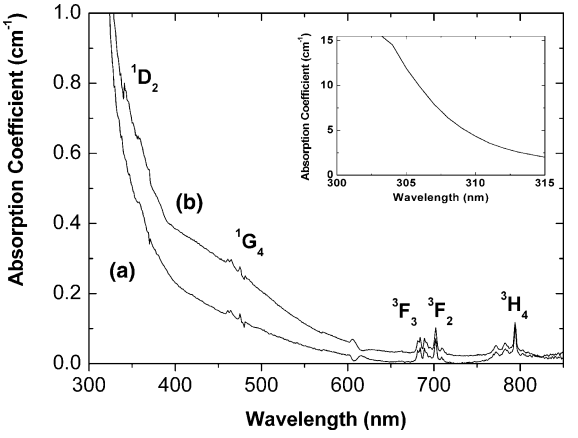

Fig. 1. Absorption spectra of Tm:$LiNbO_3$ (a) before and (b) after a 90 min exposure of 365 nm light at 45 mW/cm^2. The inset shows the absorption edge before UV exposure.

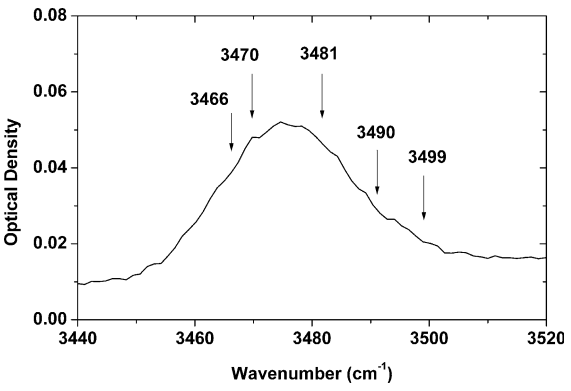

Fig. 2. OH^- stretching vibration absorption spectra of lithium niobate crystals of different compositions. Arrows indicates five different proton sites [2].

cationic environments. The intensity of the two energy transitions (3499 and 3490 cm^{-1}) which indicates Li deficiency is much weaker than that of the two others (3481 and 3470 cm^{-1}). The lowest energy component (3466 cm^{-1}) is too weak to be observed. Comparing with the previous report [2], we estimate that the composition of Li_2O in the crystal is larger than 49.6 mol%.

Temporal evolution of 355 nm-induced absorption in Fig. 3 was measured by a weak probe beam at 633 nm. The rise time and magnitude of the induced absorption showed strong dependence on pump intensity and were 2.6 s and 0.3 cm^{-1} for 250 mW/cm^2, respectively. A possible explanation for the ultraviolet-induced absorption is that the incident light photo-excites one electron from an ultraviolet-sensitive center related to lattice defect and the excited electron is trapped by shallow traps and eventually by deep traps [12]. Fast dark decay of shallow traps is due to thermal ionization to the conduction band or directly trapping in the deep traps. The induced absorption shows a near-exponential dark decay. The decay time of 12 s is three times longer than the lifetime found in Tb doped crystals [3] which is 4 s. However, it is much longer than that in undoped stoichiometric crystals [5]. Thus, doping of rare-earth ions enhances the lifetime of shallow traps. The shallow traps are assumed to be small polarons, which may be

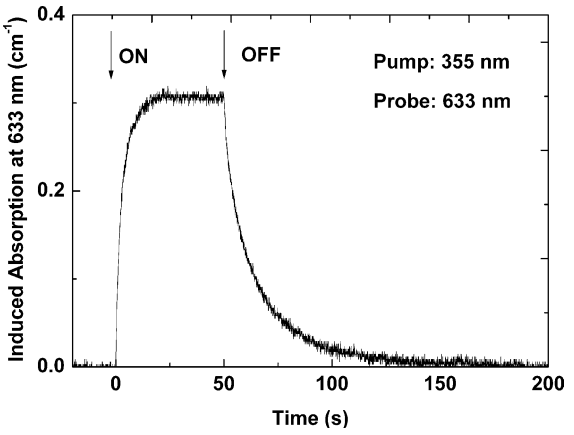

Fig. 3. Time evolution of ultraviolet-induced absorption measured by a weak beam at 633 nm with pump intensity of 250 mW/cm^2 at 355 nm. Two arrows indicate the shutter control.

stabilized by doped Tm ions filling the Li sites, located close to Nb_{Li}^{4+}, resulting in prolonged lifetime. The lifetime of small polarons also depends on the concentration of deep traps. In case of the less available deep traps in rare-earth ion doped crystals than in undoped ones, small polarons may have the longer lifetime, because probability of electron transfer to deep traps depend on physical distance of the deep and shallow traps [6]. Small polarons have an absorption peak at 780 nm with broad band at room temperature [2]. Thus, they have little absorption at 633 nm. It indicates that long time ultraviolet exposure enhances population of deep traps by being filled by electrons in conduction band and shallow traps eventually. We estimate about a ppm concentration of deep traps by using the induced absorption spectrum in Fig. 1 and the reported absorption characteristics of irons in lithium niobate [13]. Although, both the sensitizing ultraviolet absorption centers and deep recording centers have their absorptions at ultraviolet wavelengths, the dominant effect of ultraviolet exposure during hologram recording is to transfer electrons from the ultraviolet absorption centers to the recording centers. The fact that the recording wavelength of 633 or 514 nm is slightly detuned from the absorption peaks of Tm^{3+} ions excludes the possibility of electron ionization from Tm ions in holographic recording. The measured diffraction efficiency in percentage (%) is defined as $I_d/(I_d + I_t) \times 100$, where I_t and I_d are the transmitted and the diffracted beam intensities of the readout beam, respectively. The two-color recording sensitivity S is defined as a displayed equation,

$$S = \frac{1}{I_w d} \left. \frac{\partial \sqrt{\eta}}{\partial t} \right|_{t=0}, \quad (1)$$

where η, I_w and d are diffraction efficiency, total recording intensity and grating thickness, respectively. Saturation diffraction efficiency and sensitivity as a function of gating ultraviolet intensity with a constant recording intensity of 11 W/cm^2 at 633 nm are depicted in Fig. 4. The gating intensities larger than the optimum value lead to a decrease of diffraction efficiency because the strong gating light erases the grating and depopulate electrons from the recording centers. With the smaller

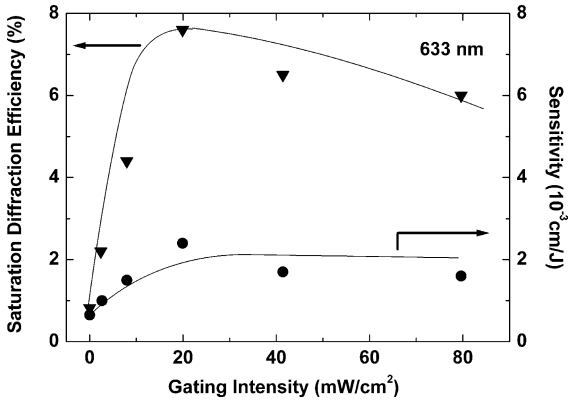

Fig. 4. Dependence of saturated diffraction efficiency and sensitivity on gating intensity at 355 nm with recording intensity of 11 W/cm^2 at 633 nm.

gating intensity, diffraction efficiency will be also reduced because the weaker ultraviolet light produces the less population of recording centers. The sensitivity increases with low gating intensity due to the increased population of recording centers but saturates in high intensity. The non-zero saturation diffraction efficiency and sensitivity without gating beam are assumed to be non-zero density of the filled deep traps. The dependence of saturation diffraction efficiency on the recording intensity with a constant gating intensity of 16 mW/cm^2 is shown in Fig. 5. The ratio of the recording to the gating intensity corresponding to the maximum saturation diffraction efficiency in Fig. 4 is about the same as that in Fig. 5. It is consistent with the two-center model that the saturation diffraction efficiency only depends on the ratio between the intensities of the recording and gating beams and a suitable intensity ratio leads to the maximum saturation diffraction efficiency [9,13,14]. The optimum condition for high diffraction efficiency in the experiment is the gating intensity of 20 mW/cm^2 and recording intensity of 11 W/cm^2 at 633 nm, corresponding to a gating-to-recording intensity ratio of 0.002. When we used 514 nm instead of 633 nm for recording, saturation diffraction efficiency showed dependence on gating and recording intensities as illustrated in Figs. 5 and 6. Two sets of data show dependence on intensity ratio and maximum diffraction efficiency of 17% at gate-to-recording intensity ratio

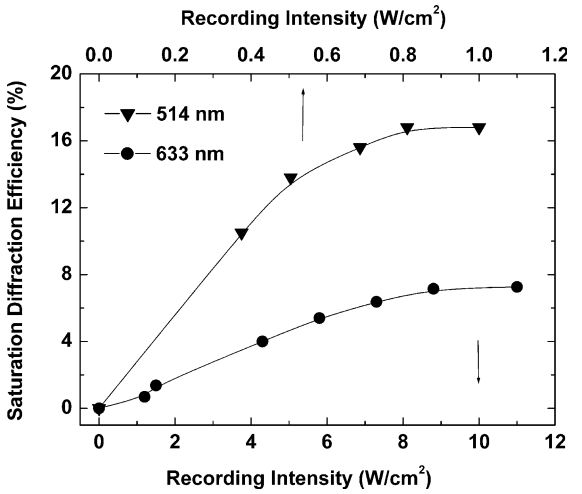

Fig. 5. Dependence of saturated diffraction efficiency on writing intensity at 633 nm with gating intensity of 16 mW/cm^2 and at 514 nm with gating intensity of 3 mW/cm^2.

of 0.0025 which is close to the value in the case of recording at 633 nm. The sensitivity increased to 0.04 cm/J without saturation as gating intensity increased up to 4 mW/cm^2 as shown in Fig. 6. The larger saturation diffraction efficiency and sensitivity compared with those at 633 nm can be explained by the larger absorption at 514 nm from the filled deep traps. The sensitivity is much improved compared with those of other rare-earth ion doped near-stoichiometric $LiNbO_3$ crystals under three-center, two-color holographic recording.

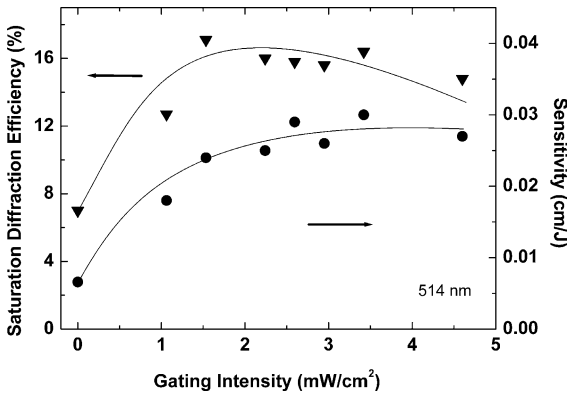

Fig. 6. Dependence of saturated diffraction efficiency and sensitivity on gating intensity at 355 nm with total recording intensity of 0.75 W/cm^2 at 514 nm.

The maximum sensitivities for 0.01%Tb, 0.2%Pr, and 0.05%Er doped near-stoichiometric crystals have been reported as 1.1×10^{-2},5×10^{-3}, and 9×10^{-4} cm/J, respectively, [3,4,15]. Considering these results of other near-stoichiometric $LiNbO_3$ crystals which use small polarons for recording, we believe that the underlying mechanism of the observed sensitivity improvements in Tm:$LiNbO_3$ may be related to the involvement of deep traps as recording centers, because of its large absorption at 514 nm. Meta-stable small polarons may also contribute to the sensitivity as a reservoir to feed electrons to deep traps. Non-zero sensitivity without gating light in Fig. 6 is assumed to be due to the non-zero density of the filled recording centers.

To compare nonvolatile two-color recording processes of the two-center and three-center models, we used green and near-infrared recording lights separately. We found four times enhanced sensitivity and persistent diffraction efficiency of 0.03% with recording intensity of 140 mW/cm^2 at 514 nm and ultraviolet gating intensity of 3 mW/cm^2 at 355 nm as shown in Fig. 7. It can be explained by the two-center model. When we read the hologram, it shows the fast initial decay which is due to mainly erasing of holograms formed in deep traps. The weak but nonvolatile diffraction efficiency is due to the residual holograms stored in the ultraviolet absorption centers. It exists for several days. The weakness of nonvolatile diffraction efficiency can be explained by the two-center model if the ultraviolet absorption centers outnumber the deep traps [9,15]. When we erased the weak nonvolatile hologram with ultraviolet light, it decreased slowly with 3 mW/cm^2 and much faster with 80 mW/cm^2. For three-center, two-color recording, we used recording intensity of 1.4 W/cm^2 at 830 nm and weak gating light of 3 mW/cm^2 at 355 nm and obtained much enhanced persistent diffraction efficiency of 0.3% as shown in Fig. 8, and is much larger than the value in Er or In doped lithium niobate crystals [15,16]. At the initial stage of readout process, the diffraction efficiency decreases a little and then remains constant. This is because some gratings recorded in small polarons decay during the initial reading process. Most of electrons in the small polarons

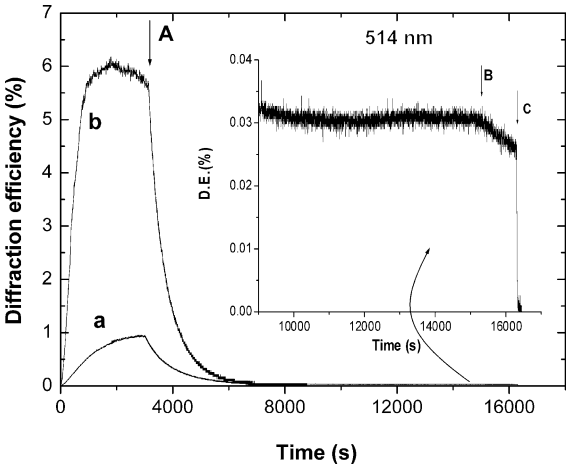

Fig. 7. Nonvolatile holographic recording at 514 nm (a) without gating and (b) with gating at 355 nm. In the recording stage, gating and total recording intensities are 3 and 140 mW/cm^2, respectively. The gating and one recording light are off at A in reading stage. The inset illustrates a nonvolatile readout in case of two-color recording until the ultraviolet light is on at B with 3 mW/cm^2. The faster erasing with ultraviolet light starts at C with 80 mW/cm^2.

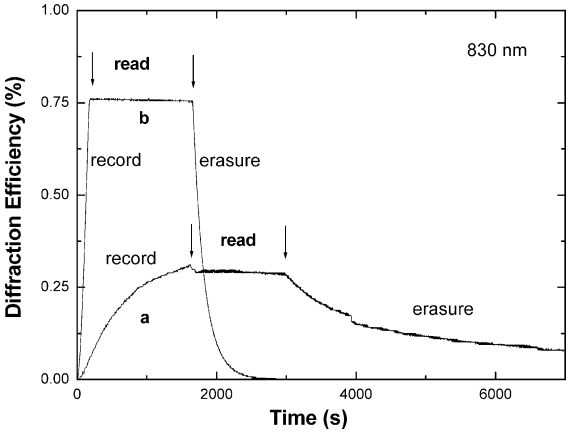

Fig. 8. Nonvolatile holographic recording at 830 nm with gating at 355 nm. In the recording stage, gating and total recording intensities are (a) 3 mW/cm^2, 1.4 W/cm^2, and (b) 10 mW/cm^2, 6.2 W/cm^2, respectively. The gating and one recording light are off in reading stage. The ultraviolet light is on for erasing.

are thermally excited to the conduction band and ultimately captured by deep traps or other defects, which decreases diffraction efficiency. The near-

infrared reading beam cannot erase existing main holograms in deep traps effectively because the traps have little absorption at 830 nm as shown in Fig. 1. The decay time of recorded hologram during readout was estimated 30 h. Nonvolatile readout of 0.75% was obtained with recording intensity of 6 W/cm^2 at 830 nm and ultraviolet gating light of 10 mW/cm^2 and the estimated decay time was about 20 h. However, weaker reading intensity of 1 mW/cm^2, which is still high in the practical point of view, continuous readout over a year is expected. The sensitivity is estimated as about 10^{-3} cm/J and can be increased by strong ultraviolet light intensity as in the case of other stoichiometric lithium niobate crystals [5]. During recording at 830 nm, the small polarons are preexisting intermediate recording centers to produce final holograms in deep traps. Thus, the concentration and lifetime of small polarons are very important to get a high and stable nonvolatile diffraction efficiency. In addition, the concentration of deep traps has to be increased to get more electrons in the conduction band to make strong grating. For nonvolatile holographic recording in this material with visible recording under ultraviolet illumination, the concentration of extrinsic deep traps such as Fe ions has to be much higher than ultraviolet absorption centers. However, the role of Tm ions in producing ultraviolet absorption centers has not been completely understood and will require further analyses. In the case of two-color recording in the near-infrared with ultraviolet light, the concentration of deep traps has to be also increased to improve persistent diffraction efficiency as in Tb, Er:$LiNbO_3$ [12]. Thus, in both two-color recordings, we expect that proper gating and recording intensities and more concentration of deep traps can improve the performance of Tm:$LiNbO_3$ for nonvolatile two-color holography further.

4. Conclusion

Light-induced absorption revealed the existence of shallow and deep traps in Tm doped $LiNbO_3$. We assumed that they are small polarons and unintended Fe ions, which are hardly avoidable. Two-color holographic recording at 514 and 633 nm showed that maximum saturation diffraction efficiency could be obtained with optimum ratio of gating and recording intensities, and sensitivity was much enhanced with ultraviolet gating at 355 nm. We applied the two-center model to explain the two-color holographic recording process for ultraviolet gate recording in the visible. Nonvolatile hologram readout observed at 514 nm was explained by the grating formed in the ultraviolet absorption centers. Nonvolatile readout by a single 830 nm beam with 3 W/cm^2 was demonstrated and explained by a three-center, two-color holographic recording process with the role of prolonged lifetime of small polarons. Performance of Tm doped stoichiometric $LiNbO_3$ may be improved if it contains more Fe ions as in the case of Tb, Fe doped stoichiometric $LiNbO_3$ [12].

Acknowledgments

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