Improved nonvolatile holographic storage sensitivity of near-stoichiometric LiNbO$_3$:Fe:Mn crystals

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Received May 12, 2012; accepted July 10, 2012; posted online November 30, 2012

We investigate the nonvolatile holographic storage characteristics of near-stoichiometric LiNbO$_3$:Fe:Mn crystals with different Li$_2$O contents. Experimental results indicate that the optimal value of Li$_2$O content is about 49.6 mol%. Nonvolatile sensitivity $S'$ considerably improved to 0.15 cm/J because of the use of near-stoichiometric LiNbO$_3$:Fe:Mn with 49.6 mol% Li$_2$O.

**OCIS codes:** 210.2860, 190.5330, 090.7330, 160.5320, 160.3730.

doi: 10.3788/COL201210.122101.

Holographic data storage is a promising next-generation optical data storage technology because of its huge data capacity and fast data transfer rates; it is poised to change the way data written and retrieved]^{[4]}. Among various holographic storage materials, lithium niobate (LiNbO$_3$, LN) single crystals have been touted as potential storage materials for next-generation volume holographic memory because they are easily grown, low cost, and excellent photoelectric performance]^{[2,3]}. Two major issues, namely, volatility and low recording sensitivity, currently impede the development of volume holographic memory. Several techniques, including thermal and electrical fixing]^{[4-6]}, were developed to overcome volatility, but such techniques present practical disadvantages. Rapid optical refreshment of memory is also impossible. To solve this problem, Buse et al. demonstrated a two-center holographic recording technique, in which a LiNbO$_3$:Fe:Mn crystal was used in an all-optical experimental setup; however, low recording sensitivity was the main disadvantage of the technique]^{[6]}. Many factors that influence the recording sensitivity $S$ of congruent LiNbO$_3$:Fe:Mn were theoretically and experimentally investigated]^{[7-11]}. Another all-optical solution is the one-color quasi-nonvolatile holographic recording technique]^{[12]}, which realizes high asymmetry in grating buildup and readout erase rates in reduced LiNbO$_3$:In:Fe crystal.

Near-stoichiometric LiNbO$_3$ crystals exhibit significantly improved photorefractive properties]^{[13-16]}. Two-color nonvolatile holography was achieved in singly Fe-doped and pure near-stoichiometric LiNbO$_3$ crystals]^{[17-21]}, and the enhanced recording sensitivity $S$ of stoichiometric LiNbO$_3$:Cu:Ce was reported]^{[22]}. These experimental results indicate that intrinsic defects are instrumental in improving the photorefractive properties of LiNbO$_3$. The nonvolatile holographic performance of LiNbO$_3$:Fe:Mn crystal has been extensively studied]^{[7-11]}, but to the best of our knowledge, the influence of Li$_2$O content on the nonvolatile holographic properties of the doubly doped crystal remains unclear.

In the current work, we investigated the nonvolatile holographic properties of LiNbO$_3$:Fe:Mn crystals that have different Li$_2$O contents. An improved recording sensitivity $S'$ of 0.15 cm/J was achieved with near-stoichiometric LiNbO$_3$:Fe:Mn. LiNbO$_3$:Fe:Mn crystals with different Li$_2$O contents were prepared. LiNbO$_3$:Fe:Mn single crystal was grown along the $z$ axis from a congruent melt (48.38-mol% Li$_2$O, 51.62-mol% Nb$_2$O$_5$: 0.075-wt.-% Fe$_2$O$_3$, 0.01-wt.-% MnO) by the Czochralski process. The as-grown crystals were then cut into $x$-oriented plates. The vapor transport equilibration technique was employed to obtain LiNbO$_3$:Fe:Mn crystals with different Li$_2$O contents]^{[23]}. The plates were treated in powder charges with Li$_2$O/Nb$_2$O$_5$ ratios that ranged from 48.4/51.6 to 49.8/50.2, and then polished to optical grade with a thickness of 0.85 mm. The composition of each crystal was characterized by measuring the width of 153-cm$^{-1}$ Raman lines]^{[24]}. The Li$_2$O content of each crystal is listed in Table 1. Theoretical and experimental results]^{[7-8]} show that the oxidation–reduction state of the crystals strongly affects the nonvolatile holographic properties of LiNbO$_3$:Fe:Mn. The nonvolatile holographic properties of all the crystals in their original states were measured firstly. After the experiments, all the original-state crystals were reduced in argon gas at 700 °C for 4 h. Reduction in argon gas was repeated at 700 °C for 2 h.

The nonvolatile experimental setup is schematically illustrated in Fig. 1. An A4000 Hg lamp was used as the UV sensitizing light (365-nm central wavelength; 60-mW/cm$^2$ light intensity). An extraordinarily polarized beam from the Nd:YAG 532 nm laser was split into two beams with a light intensity of 600 mW/cm$^2$. The two recording beams were made to intersect symmetrically with respect to the $x$ axis inside the crystal to ensure that the grating vector of the interference pattern was aligned parallel to the $c$ axis of the crystal. The external intersected angle between the two beams was 30°. The signal light was occasionally blocked a computer-controlled electronic shutter S2 during recording to enable the reference beam to read out the written hologram and trace the temporal development of the hologram. The diffracted beam located after the hologram and the transmitted reference light were detected using D1 and D2, respectively. The propagation direc-

**Table 1**

<table>
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<th>Li$_2$O (%mol)</th>
<th>Reduction State</th>
<th>Li$_2$O</th>
<th>Nb$_2$O$_5$</th>
<th>Fe$_2$O$_3$</th>
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<td>48.4</td>
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<td>51.62</td>
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<td>Oxidation</td>
<td>50.2</td>
<td>0.075</td>
<td>0.01</td>
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tion of the grating beam was set parallel to the bisector of the two writing beams. The “on” and “off” states of the sensitizing and signal beams were controlled by shutters S1, S2, and S3. Electronic shutter S3 was placed in front of the detector. The “on” and “off” states of S1 and S2 were set out of phase with each other to prevent direct exposure of the detector to the transmitted signal beam.

Nonvolatile holographic storage was achieved in all the crystals. Figure 2 shows the experimental results for LN_{48.36}:Fe:Mn. Diffraction efficiency $\eta$ is defined as $I_d/(I_d+I_t)$, where $I_d$ and $I_t$ are the diffracted and transmitted intensities of the reference beam, respectively. The figure also shows that during fixing, diffraction efficiency $\eta$ initially decreased to almost 50% in a short period before stabilizing. As a result, all gratings that were recorded on the shallow centers were totally erased and only those that were recorded on the deep centers remained.

Photorefractive sensitivity $S$ is the key index that describes how fast a hologram can be recorded at a fixed light intensity and material thickness. For two-color holography, given the partial erasure during the fixing process, the expression of $S$ was modified to $S' = \beta * (1/\eta) |(\partial/\partial t)_{\eta=0}$, where $\beta$ is the ratio of $\sqrt{\eta}$ after fixing and before fixing [9]. The $S'$ of all the crystals in different states are shown in Fig. 3. Sensitivity was highest after the first reduction, with sensitivity $S'$ reaching its maximum when $N_A \approx (0.8–0.9)N_{Mn}$ ($N_{A,S}$ the initial electron concentration in the Mn traps) [10]. For the original-state crystals, most of the traps were empty; thus, only a very weak hologram could be recorded. After the first reduction process, $N_A$ reached its optimum value and about 80% to 90% of the Mn traps were initially filled by electrons. After the second reduction process, more than 90% of the Mn traps were initially filled by electrons. Even though a very strong hologram could be recorded in this case, the majority of the hologram was destructive (i.e., $\beta$ with a very small value). The experimental results show that the reduction of the original-state crystal during the first 4 h improved sensitivity, but further reduction visibly decreased sensitivity.

The experimental results for the two-color nonvolatile holography of saturation diffraction efficiency $\eta_s$, fixing diffraction efficiency $\eta_f$, photorefractive sensitivity $S$, and the $S'$ of all the crystals after the first reduction are listed in Table 1.

The relationship among $\eta_s$, $S'$, and Li$_2$O content is depicted in Fig. 4. Two key indexes were improved by increasing Li$_2$O content, and the maximum values of $\eta_s$, $S'$, that is, 35.42% and 0.15 cm/J, were simultaneously achieved in LN$_{49.6}$:Fe:Mn. However, the further increase in Li$_2$O content decreased photorefractive sensitivity $S'$. The improved nonvolatile holography properties of near-stoichiometric LN$_{49.6}$:Cu:Ce were reported in Ref. [22], and the optimal Li$_2$O content in LiNbO$_3$:Cu:Ce coincides with that derived in the current work.

For two-center nonvolatile holographic recording in LiNbO$_3$:Fe:Mn crystal, saturation diffraction efficiency $\eta_s$ is determined according to the amount of electrons on the shallow centers, and recording sensitivity $S'$ depends

![Fig. 1. Experimental setup for two-color nonvolatile holographic storage. BS: beam splitter; M1-M2: mirrors; S1-S3: electronic shutters; D1-D2: detectors; L: lens; C: crystal.](Image 318x701 to 544x751)

![Fig. 2. Nonvolatile holographic performance of LN$_{48.4}$:Fe:Mn.](Image 378x537 to 505x636)

![Fig. 3. Relationship between $S'$ and Li$_2$O contents in LiNbO$_3$:Fe:Mn of different oxidization-reduction states.](Image 482x138)

<table>
<thead>
<tr>
<th>Sample</th>
<th>LN$_{48.1}$:Fe:Mn</th>
<th>LN$_{48.4}$:Fe:Mn</th>
<th>LN$_{48.8}$:Fe:Mn</th>
<th>LN$_{49.6}$:Fe:Mn</th>
<th>LN$_{49.7}$:Fe:Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition (Li$_2$O mol%)</td>
<td>48.1</td>
<td>48.4</td>
<td>48.8</td>
<td>49.6</td>
<td>49.7</td>
</tr>
<tr>
<td>Recording $S'$ (cm/J)</td>
<td>0.10</td>
<td>0.13</td>
<td>0.19</td>
<td>0.23</td>
<td>0.18</td>
</tr>
<tr>
<td>$S'$ (cm/J)</td>
<td>0.05</td>
<td>0.09</td>
<td>0.11</td>
<td>0.15</td>
<td>0.12</td>
</tr>
<tr>
<td>$\eta_s$ (%)</td>
<td>17.42</td>
<td>21.38</td>
<td>25.27</td>
<td>35.42</td>
<td>30.46</td>
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<tr>
<td>$\eta_f$ (%)</td>
<td>4.34</td>
<td>10.96</td>
<td>11.47</td>
<td>15.05</td>
<td>13.54</td>
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</table>
clearly characterize the charge transport process induced absorption (ULIA) and bleaching experiment primarily on the speed of electrons that are excited from ultraviolet (UV) light-induced absorption; these two sets of results imply that for nonvolatile holographic storage, a bipolaron/small polaron is another photorefractive center that is crucial in improving nonvolatile holographic properties. At an appropriate Li$_2$O content in the crystal, the amount and lifetime of bipolarons increase.

In conclusion, nonvolatile holographic storage is realized in near-stoichiometric LiNbO$_3$:Fe:Mn crystals. The influence of Li$_2$O content on nonvolatile holographic properties of LiNbO$_3$:Fe:Mn is investigated in detail. Increasing Li$_2$O content in LiNbO$_3$:Fe:Mn is favorable for improving recording sensitivity and diffraction efficiency. The optimum Li$_2$O content is about 49.6 mol%.

This work was supported by the Shanxi Province Technology Project for Higher Education under Grant No. 20091105.

References

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