Improvement of photorefractive properties and holographic applications of lithium niobate crystal

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Abstract: Based on analyzing and synthesizing the effects of In doping, Fe doping and oxidation state, we propose an efficient way to improve photorefractive properties of LiNbO₃ crystal. According to the proposed way, a sample of In:Fe:LiNbO₃ crystal is grown and achieves larger dynamic range, higher sensitivity and better signal-to-noise ratio than Fe:LiNbO₃ crystal (Fe:0.03wt.%) that is generally considered as a preferable storage medium for high-density holographic data storage. In a coherent volume 0.074cm³ of this crystal, 2030 holograms have been successfully multiplexed and exactly identified in a compact volume holographic data storage and correlation recognition system.

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OCIS codes: (160.3730) Lithium niobate; (210.2860) Holographic and volume memories.

References and Links

1. Introduction

Volume holographic memories have attracted intense interest because of their potential in high capacity storage, fast parallel process and content addressability [1]. To a large extent, the system performances depend on the properties of storage media. For holographic storage materials, two of the most important parameters are dynamic range ($M/\#$) and sensitivity ($S$). In addition, low scattering will result in high signal-to-noise ratio (SNR) [1–3].

Photorefractive lithium niobate (LiNbO$_3$) crystal has been widely investigated for applications in holographic data storage. Usually transition-metal dopants, such as Fe, Cu, Ce and Mn, are added to the melt to improve the photorefractive effect. And Fe is most effective in producing large improvements in both dynamic range and sensitivity. Many successful demonstrations of holographic storage systems have been achieved in Fe:LiNbO$_3$ crystals [1, 4]. One approach to boosting the $M/\#$ and sensitivity for Fe-doped LiNbO$_3$ crystal is to increase the Fe doping level. However, the higher the concentration of Fe, the larger the photorefraction effect will be. The characteristic will cause strong scattering noise harmful for holographic storage. Thus a trade-off between $M/\#$, $S$ and SNR has to be considered when we design Fe:LiNbO$_3$ crystals for holographic applications, and 0.03wt.% Fe has been generally considered as a preferable doping concentration for high-capacity holographic data storage.

It is well known that damage-resistant dopants (e.g., Mg, Zn, In, etc.) have been doped in LiNbO$_3$ crystal to reduce optical damage [5, 6]. Among them, In impurity is the most "efficient" due to the lowest threshold concentration which was reported about 1.5–2.0mol.%. Volk et al. [5] detailedly analyzed the properties of In-doped LiNbO$_3$ crystals. Qiao et al. [7] got a high sensitivity of photorefractive effect in In:LiNbO$_3$ crystal, and the significant suppression of the photorefractive light-induced scattering has been observed in In:Fe:LiNbO$_3$ crystal [6]. All these experiments show that doping In is a very efficient way to increase the photorefractive sensitivity and the damage-resistance ability of LiNbO$_3$ crystal. However, the photorefraction is inversely proportional to the photoconductivity [5], so it is difficult to get high $S$ and SNR simultaneously with large $M/\#$ in singly doped In:LiNbO$_3$ crystal.

Therefore, it is expected that In:Fe:LiNbO$_3$ crystal combining with the advantages of In doping and Fe doping is a promising photorefractive material for holographic applications. Some papers have investigated the characteristics of In:Fe:LiNbO$_3$ crystals [6, 8], but little research has been addressed to tailor the material parameters in order to achieve large dynamic range and high sensitivity that holographic storage systems require. Since the effect of Fe doping on photorefractive properties of LiNbO$_3$ crystal has been extensively studied [9–12], in this paper we will firstly investigate the properties of In:Fe:LiNbO$_3$ crystals with various In concentrations. Next, based on analyzing and synthesizing the effects of In doping, Fe doping and oxidation state, we propose an efficient way to improve photorefractive properties of LiNbO$_3$ crystal. Moreover, according to the proposed way, a sample of In:Fe:LiNbO$_3$ crystal is grown and compared with Fe:LiNbO$_3$ crystal (Fe:0.03wt.%) under the same experimental conditions. Finally, we applied this crystal to a compact volume holographic data storage and correlation recognition system, and got excellent performances.

2. Experiments on the effect of Indium doping

In the experiments, we used four congruently melting In:Fe:LiNbO$_3$ samples whose concentrations of In were 0.5, 1, 2 and 3mol% in the melt, which we referred to as InFe1, InFe2, InFe3 and InFe4. For comparison, a sample of single doped Fe:LiNbO$_3$ crystal (referred as Fe1) was also investigated. All samples have the same Fe concentration of 0.03wt%, the grown state and the dimensions of 10×10 (thickness)×10mm$^2$. Additionally, these samples are 45°-cut and polished to optical quality.

The experimental setup is a typical 90°-geometry system. A He-Ne laser beam at the wavelength of 632.8nm was used to record and erase holograms. To get the maximum dynamic range and sensitivity, the crystals were immersed in a sodium chloride solution which was used to minimize the influence of the photovoltaic field [10], and then placed on a rotation stage. The light beam with a diameter of 4mm was split by the PBS into two equal-
intensity beams as a reference beam and an object beam. The grating vector was always aligned along the c axis. During recording, the object beam was blocked from time to time to measure the holographic diffraction efficiency as the ratio of diffracted and incident light intensities. After the grating reached the saturation, we used Bragg-mismatched erasure [2].

Figure 1 shows a typical recording and erasing behavior of the single grating in In:Fe:LiNbO₃ crystal. The temporal trace of $\eta$ during recording and erasing could be well described by functions given by $\eta(t) = \sin^2\left\{\left(\pi\Delta n_{\text{sat}}L/\lambda\cos\theta\right)\left[1-\exp\left(-t/\tau_r\right)\right]\right\}$ and $\eta(t) = \sin^2\left\{\left(\pi\Delta n_{\text{sat}}L/\lambda\cos\theta\right)\exp\left(-t/\tau_e\right)\right\}$, respectively. Here $\theta$ is the incident angle inside the crystal, $\tau_r$, $\tau_e$ are the recording and erasing time constants, $\lambda$ is the wavelength outside the crystal, $\Delta n$ is the amplitude of refractive-index change, and $L$ is the effective interaction length. In addition, $M/\#$, $S$ can be defined as $M/\# = (A_0/\tau_r)$ and $S = (A_0/\tau_e)/(IL)$, where $A_0 = \pi\Delta n_{\text{sat}}L/\lambda\cos\theta$, and $I$ is the total incident recording intensity [3]. Therefore, a good fit between experimental data and functions of the diffraction efficiency indicates that the values of $M/\#$, $S$ can be well obtained by the experimental curves.

![Fig. 1. Experimentally measured and fitting curves of In:Fe:LiNbO₃(In:2mol%,Fe:0.03wt.%).
Fig. 2. Dynamic range M/\# and sensitivity S of In:Fe:LiNbO₃ crystals versus In concentrations.](image)

Figure 2 illustrates the dependences of measured $M/\#$ and $S$ of In:Fe:LiNbO₃ crystals on In doping concentrations. Different In concentrations correspond to different samples. The asterisk signs describe the sensitivity and show that $S$ increases similarly linearly with the increase of In concentration under 2mol% i.e., the threshold concentration of In-doped LiNbO₃ crystal. However, when In concentration increases to 3mol%, the sensitivity sharply improves with the increasing ratio twice as large as that of the threshold concentration below. In addition, the dot signs represent dynamic range, and $M/\#$ decreases with In concentration increasing, but it is surprising that InFe1 has an identical value of $M/\#$ with Fe1. And $M/\#$ changes sharply when In concentration is improved from 0.5mol% to 1mol% and from 2mol% to 3mol%. Comparing the properties of InFe1 with InFe4, we can find that $S$ has a sharp increase by a factor of 2.3, but $M/\#$ strongly decreases by a factor of 3.5.

Holographic properties of LiNbO₃ crystal mainly depend on photorefractive centers. In doubly doped In:Fe:LiNbO₃ crystal, In ions do not participate in the charge transport and simply affect concentrations and incorporation of other ions which contribute to the photoconductivity [5]. When In concentration is below the threshold, In ions incorporate onto Li-sites, removes NbLi and also substitute both for Fe²⁺ and Fe³⁺. Therefore the photoconductivity $\sigma_{\text{ph}}$ increases due to a reduction of NbLi and a variation of the ratio Fe²⁺/Fe³⁺. The increase of $\sigma_{\text{ph}}$ will cause time constants $\tau_r$, $\tau_e$ to reduce. Though $A_0$ reduces too, $A_0/\tau_r$ is still improved due to the sharp increase of $\sigma_{\text{ph}}$. So the sensitivity increases with In concentrations under 2mol% shown as Fig. 2. Generally $\tau_r$, $\tau_e$ change at the same magnitude for Fe:LiNbO₃ crystal [9]. However, the asymmetry in the reduction of time constants exists for In:Fe:LiNbO₃ crystal, which can be explained in terms of a multiple-defect-center model.
When In concentration is above 0.5mol%, a complete disappearance of Nb from In:Fe:LiNbO₃ crystal perhaps happens [5], and the asymmetry disappears. With a decrease of \( A_0 \), \( M/# \) will decrease dramatically. When In concentration is beyond the threshold, In ions incorporate both onto Li (InLi) and Nb (InNb) sites, and Fe³⁺ incorporates mainly onto the Nb-sites, loosing its acceptor properties [5]. It will result in a sharp increase of photoconductivity, and \( M/# \), \( S \) change greatly.

Therefore, slightly In doping (such as 0.5mol%) under the threshold concentration in In:Fe:LiNbO₃ crystal could be a good way to improve the sensitivity with small \( M/# \) changing.

### 3. Improvement of photorefractive properties

Due to the trade-off between \( M/# \), \( S \) and SNR, Fe:LiNbO₃ crystal with 0.03wt.% Fe has been generally considered as a preferable storage medium for volume holographic data storage. Nevertheless, for practical holographic memories, larger dynamic range and higher sensitivity are required, and it is always attracting to dope the highest possible Fe concentration in LiNbO₃ crystal. Since there is a limit on the highest practical doping concentration (0.06wt.%) of Fe:LiNbO₃ for electron tunneling effect [11], and any further increase of the doping concentration beyond the limit cannot result in larger \( M/# \) and sensitivity, 0.06wt% Fe is an ideal doping concentration for the improvement of the photorefractive properties of LiNbO₃ crystal [9, 11].

Obviously, if Fe concentration directly increases to 0.06wt.%, the scattering noise will increase and can not be suitable for holographic applications. As discussed in Section 2, slightly In doping (0.5mol% In) in Fe:LiNbO₃ crystal is an efficient way to solve the problem. On one hand, In doping can greatly reduce the scattering noise caused by the increase of Fe doping, that is to say, In doping makes it possible to dope high Fe concentration in LiNbO₃ crystal with the assurance of a suitable SNR. On the other hand, In doping also improves the sensitivity of LiNbO₃ crystal. Simultaneously, the value \( M/# \) is perhaps reduced by slightly In doping at a certain degree compared with Fe:LiNbO₃ crystal (Fe:0.06wt.%), but it still increases compared with Fe:LiNbO₃ crystal (Fe:0.03wt.%). Therefore, the whole photorefractive properties of LiNbO₃ crystal will be improved.

In addition, \( M/# \) and \( S \) in Fe-doped LiNbO₃ crystals are strong functions of the oxidation state [9, 12]. Typically, the more the crystal is reduced, the larger the sensitivity will be. However, too large absorption coefficient \( \alpha \) which is related to the oxidation state [9], will greatly shorten the storage time. Moreover, there exists an optimal value \( \alpha \) for maximum \( M/# \). A theoretical model has been developed and shown that the optimum \( \alpha \) for the crystal with thickness \( d \) is \( \alpha d = 1 \) [12]. So a suitable oxidation state is needed to get excellent photorefractive properties.

Taking into account of the effects of In doping, Fe doping and oxidation state, we find that it may be an efficient way for improving photorefractive properties in In:Fe:LiNbO₃ crystal by doping Fe concentration as high as possible that promises to get large dynamic range and high sensitivity, slight In concentration that is used to reduce the scattering noise caused by high Fe concentration and improve sensitivity simultaneously with small \( M/# \) changing, and suitable thermal annealing that makes excellent photorefractive properties. The desired \( M/# \), \( S \) and SNR for practical applications can be achieved by appropriately designing these parameters.

According to the proposed way, In:Fe:LiNbO₃ crystal with 0.5mol% In, 0.06wt.% Fe is grown (referred as InFe5). The dimension is 20×20×30mm³. After thermal annealing it is slightly oxidized with \( \alpha = 0.25cm^{-1} \) at \( \lambda = 632.8nm \) and \( \alpha = 0.5cm^{-1} \) at \( \lambda = 532nm \). The holographic properties of InFe5 are measured under the same experimental conditions as section 2. From the single-hologram measured and fitting curves, we can calculate \( \tau_r \), \( \tau_e \), \( \Delta n_{sat} \) and \( M/# \), \( S \). Table 1 describes these photorefractive properties of InFe5 crystals. For comparison, those of Fe1 crystal are also listed.
Table 1. Photorefractive properties of Fe1&InFe5 crystals

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\eta_m$ (%)</th>
<th>$\tau_r$ (min)</th>
<th>$\tau_e$ (min)</th>
<th>$M/#$</th>
<th>$S$ (cm J)</th>
<th>$\Delta n_{sat}$ ($10^{-5}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe1</td>
<td>36</td>
<td>59</td>
<td>320</td>
<td>3.83</td>
<td>0.01</td>
<td>2.50</td>
</tr>
<tr>
<td>InFe5</td>
<td>61</td>
<td>51</td>
<td>380</td>
<td>7.47</td>
<td>0.02</td>
<td>3.59</td>
</tr>
</tbody>
</table>

Note that $M/\#$ is proportional to the effective interaction length $L$ [1, 3]. The values of $L$ for Fe1 and InFe5 are both 4mm, so the value $M/\#$ can be directly comparable. The results show that InFe5 has larger diffraction efficiency, smaller $\tau_r$ and bigger $\tau_e$ than Fe1. A larger $\Delta n_{sat}$ results from the increase of Fe doping, and slightly In doping causes that the increase of $\Delta n_{sat}$ is less than twice. All that makes InFe5 crystal achieve the values $M/\# = 7.47$ and $S = 0.02cm/J$, twice as large as those of Fe1.

Furthermore, we performed a holographic image storage experiment to evaluate the scattering characteristics of InFe5 crystal and Fe1 crystal. An argon-ion laser beam with the wavelength of 514nm was used to store and retrieve holograms in a 90° geometry system. The reconstructed holograms are shown in Fig. 3, from which we can see that the reconstructed hologram from InFe5 has a quite high SNR and even a bit better than that from Fe1. Undoubtedly, doping 0.5mol% In efficiently suppressed the scattering noise caused by high Fe doping concentration and improved the SNR of the crystal.

![Fig. 3. The reconstructed hologram from: (a) Fe:LiNbO3 crystal (Fe1); (b) In:Fe:LiNbO3 crystal (InFe5).](image)

In summary, according to the way suggested above, we have grown a sample of In:Fe:LiNbO3 crystal with 0.5mol%In, 0.06wt.%Fe and slightly oxidized state, and achieved larger $M/\#$, higher $S$ and better SNR than Fe:LiNbO3 crystal with 0.03wt.%Fe under the same experimental conditions.

4. Applications in holographic memories

To verify that such good photorefractive properties of In:Fe:LiNbO3 (In: 0.5mol%, Fe: 0.06wt.% , slightly oxidized state) are achievable for practical holographic memories, we applied this crystal to a compact volume holographic data storage and correlation recognition system. This system is a typical 90°-geometry recording setup. A diode-pumped solid-state laser ($\lambda = 532nm$) is used as the light source, and all of the holograms are angular-fractal multiplexed in a coherent volume of the crystal which is immersed in a sodium chloride solution to minimize the influence of the photovoltaic field on the multiplexed holograms. Inputting an original image to illuminate the coherent volume, we can get the correlation results of the image with all stored holograms with a charge coupled device (CCD). A holographic diffuser is put just before the spatial light modulation (SLM, 1024×768 pixels) to suppress the sidelobes of correlation patterns and the cross-talk noise caused by them [13].

Recently we have achieved good experimental results in Fe:LiNbO3 crystal (Fe:0.03wt%, grown state, 17×17×25mm³, referred as Fe2) in this system [14]. The single hologram recording experiments show that InFe5 crystal has a maximum tolerable exposure time of 15s larger than 10s in Fe2, and a minimum tolerable exposure time of 0.8s smaller than 1.3s in Fe2, which is due to its larger dynamic range and higher sensitivity than Fe2 crystal. It is expected that better performances will be achieved in InFe5 crystal.
In order to realize high capacity holographic storage in InFe5 crystal, an appropriate exposure time schedule must be designed according to the characteristics of the crystal and the system. The often adopted original time schedule put forth by Psaltis et al. [15], is based on the invariability of writing- and erasure-time constants. In our system, the holographic diffuser is very effective to improve the recognition accuracy, but it brings a serious problem that the object beam becomes quite weak after passing through the diffuser, which causes that recording a hologram will need longer exposure time, and the whole recording time will greatly increase. What’s worse, long exposure time will cause the dynamic increase of photoconductivity. It results from the effect of running holograms [9] and the gradual increase of the photovoltaic electric current. The change of the photoconductivity will cause the dynamic reduction of time constants. And the previously stored holograms will be badly erased under the original time schedule. Derived from the original time schedule model, the exposure time of each hologram in the same horizontal direction (called a row) varies approximately according to the exponential function with a decay constant. We amended the time schedule by multiplying the decay constant of each row with a restraint factor that changes referencing to the recorded result of the last row. The adaptable restraint factor compensates for the dynamic change of time constants, and the new exposure time schedule promises to equalize the diffraction efficiency of all stored holograms.

In a coherent volume 0.074cm³ of InFe5 crystal, with the new exposure time schedule, we have successfully multiplexed 2030 images using 70 angles in the horizontal direction and 29 lines in the vertical direction. The longest exposure time is 10s, while the shortest is 0.9s, and the whole recording time is 91min, 13.3% shorter than that in Fe2 crystal which has achieved the same storage capacity. Figure 4 shows the correlation spots array of the 2030 holograms read by a white blank. There is an approximately uniform diffraction efficiency except a few images which are not well recorded because of the inaccuracy of the shutters. Inputting the original image one by one, we can get the correlation recognition results of all 2030 holograms. The correlation accuracy is about 98.4%, which also indicates that almost all of the 2030 holograms have been recorded well and the storage density of 21Gbits/cm³ has been achieved in In:Fe:LiNbO3 crystal.

5. Conclusion

An efficient way has been proposed to improve the photorefractive properties of LiNbO3 crystals. In:Fe:LiNbO3 crystal grown according to this way has got larger dynamic range, higher sensitivity and better signal-to-noise ratio than Fe:LiNbO3 crystal, and achieved a high-density holographic data storage. The experimental results prove that the way proposed is effective and feasible.

Acknowledgments

This work was supported by National Natural Science Foundation of China (No. 60277011) and National Research Fund for Fundamental Key Projects NO.973 (G19990330).