Nonvolatile holographic storage in triply doped $LiNbO_3$:Hf, Fe, Mn crystals*

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It has been suggested to use $LiNbO_3$:Fe, Mn crystal for solving the problem of information volatility during the read-out process with all-optical facilities, but the minute order response time is far from the requirements for the real-time information processing. We present the nonvolatile holographic storage properties of $LiNbO_3$:Hf, Fe, Mn. The response time is shortened to 5.0 s, and the sensitivity S' is enhanced to 0.22 cm/J in this triply doped crystal. The experimental results show that the HfO_2 doping threshold is 5.0 mol.%. Thus it seems that we have found a useful tetravalent dopant for $LiNbO_3$:Fe, Mn that can obviously improve the nonvolatile holographic recording sensitivity.

Keywords: holography, nonvolatile, photorefractive material, lithium niobate, sensitivity

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1. Introduction

With the rapid development of photo-electronics information technology, large-capacity holographic storage has become one of the promising next generation storage technologies following the magnetic and compact disk storage. Due to the advantages of small size, large storage capacity, fast transfer rate, and parallel computing, photorefractive crystals have attracted great attention. Since the photorefractive effect[1] in $LiNbO_3$ crystal was first discovered in 1966, it has become the backbone of holographic storage. $LiNbO_3$:Fe crystal is one of the most frequently used singly-doped crystals in holographic storage, but the long response time, low recording sensitivity and volatility of the recorded information impede its application to holographic volume storage. The recording time can be shortened by increasing the Li_2O content in $LiNbO_3$:Fe crystal[2–5] or doping damage-resistant elements into $LiNbO_3$:Fe, such as Mg, Zn, In, and Sc.[6–9] However, due to the substantial decrease of diffraction efficiency, the recoding sensitivity cannot be improved by these two methods, and the problem of information volatility still exists. $LiNbO_3$ doubly doped with iron and manganese ($LiNbO_3$:Fe, Mn)[10] is well known for the first realization of nonvolatile holographic storage using two-center holographic technique. The information volatility in the reading process has been successfully solved, but the major drawbacks, i.e., low sensitivity and long response time remain to be overcome. It is the burning question, how to improve both the volatility and low recording sensitivity synchronously.

Newly discovered single-doped tetravalent ion hafnium (Hf^{4+})[11] and zirconium (Zr^{4+})[12] lithium niobate crystals each have an excellent anti-photorefractive property, and it is noted that when Hf^{4+} and Zr^{4+} are co-doped into $LiNbO_3$:Fe, the short response time and high diffraction efficiency can be achieved simultaneously,[13–15] which leads to a substantial increase in recording sensitivity. Because only the traditional one-color holography can be realized using $LiNbO_3$:Hf, Fe and $LiNbO_3$:Zr, Fe, the information volatility is still the fatal issue. However, the research results imply that it is a very useful method to improve the two-center holographic sensitivity by doping Hf or Zr into the $LiNbO_3$:Fe, Mn. Kong *et al.*[16] and Liu *et al.*[17] recently have reported on the improvement of the sensitivity value S of the well-known nonvolatile holographic materials $LiNbO_3$:Fe, Mn and $LiNbO_3$:Cu, Ce by co-doping Zr into these crystals. As far as we know, the nonvolatile holographic property of $LiNbO_3$:Hf, Fe, Mn has not been investigated. Here in this paper, the two-center nonvolatile holographic experimental results of $LiNbO_3$:Hf, Fe, Mn are reported.

2. Experiments

$LiNbO_3$:Hf, Fe, Mn crystals were grown along the c axis from congruent melt (Li_2O 48.38 mol%, Nb_2O_5 51.62 mol%) by the Czochralski technique at the School of Physics, Nankai University. The values of HfO_2 content were selected to be 2, 3, and 5 mol % respectively, and Fe_2O_3 and MnO were, respectively, 0.075 wt% and 0.01 wt% for all three crystals. These crystals were labeled as $LiNbO_3$:Hf_2, Fe, Mn, $LiNbO_3$:Hf_3, Fe, Mn and $LiNbO_3$:Hf_5, Fe, Mn. After being annealed and polarized, the crystal was cut into a 3-mm plate along the y axis, and then was polished to optical grade. Re-

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cent theoretical and experimental results[18–20] showed that the oxidized crystal has a high fixed diffraction efficiency. Therefore, all the crystals are oxidized in the air at 700 °C for 8 h.

The OH^- absorption spectra and UV-visible absorption spectra of crystals were measured by a Magna-560 Fourier transform infrared spectrophotometer and a Beckman DU-8B spectrophotometer, respectively, with the incident light transmitting along the *y* axis at room temperature.

The nonvolatile holographic storage experimental setup is illustrated schematically in Fig. 1. An extra-ordinarily polarized beam from a laser-diode-pumped frequency-doubled Nd:YAG 532-nm laser was split into two beams of equal light intensity 300 mW/cm^2. The two beams illuminated the crystal symmetrically. The spatial period of the grating was 700 nm, and the grating wave vector was parallel to the *c* axis of the crystal to utilize the largest electro–optic coefficient γ_{33}. A filtered Hg lamp was used as the UV gating light with the central wavelength 365 nm (light intensity 10 mW/cm^2), and the propagation direction of the gating beam was set to be parallel to the bisector of the two writing beams. The $LiNbO_3$:Hf, Fe, Mn crystals were pre-exposed by the UV light for 1 h. Then the hologram was recorded by the two coherent writing beams and UV light, until the saturated diffraction efficiency was reached. During fixing of the hologram, only the reference beam was on, and the hologram can be erased quickly using the UV light.

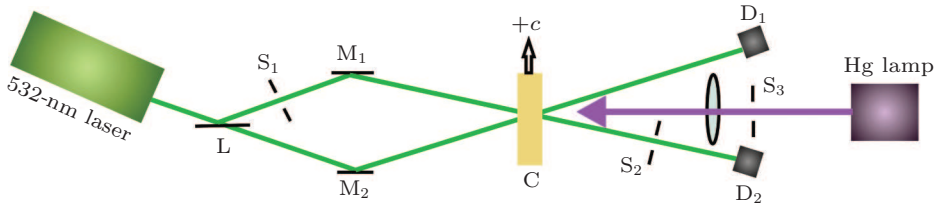


Fig. 1. (color online) Experimental setup for the two-center nonvolatile holographic storage: BS: beam splitter; M_1–M_2: mirror; S_1–S_3: electronic shutter; D_1–D_2: detector; L: lens; C: crystal.

3. Results and discussion

The UV-visible absorption spectra of the crystals are shown in Fig. 2, and from it we can see that for $LiNbO_3$:Fe, Mn doped with 2, 3, 5 mol% of HfO_2, the absorption edges ($\alpha = 15$ cm^{-1}) are at 380.1, 378.4, 374.9 nm, respectively, and it is noted that the absorption edge blue-shift reaches the maximum with the HfO_2 doping concentration 5 mol%. Our former research[21] concerning the absorption edge of $LiNbO_3$ demonstrates that the origin of such an absorption edge is attributed to the intrinsic defects of Li vacancies (V_{Li}) and the absorption edge blue-shift occurs due to the decrease of Li vacancies, which means that the stronger absorption edge blue-shift occurs, the more Li vacancies are eliminated. The experimental result indicates that the amount of V_{Li} in the $LiNbO_3$:Hf_5, Fe, Mn is the smallest in the three crystals, predicting that the remarkably improved recording sensitivity *S* should be obtained in it during the two-center nonvolatile holography.

Figure 3 shows the OH^- absorption spectra of $LiNbO_3$:Hf, Fe, Mn crystals, in which the absorption band is located about 3484 cm^{-1} for $LiNbO_3$:Hf_2, Fe, Mn and near 3487 cm^{-1} for $LiNbO_3$:Hf_5, Fe, Mn. Just as reported in mono-doped $LiNbO_3$:Hf[11] and doubly doped $LiNbO_3$:Hf, Fe crystals,[13] the presence of 3487-cm^{-1} absorption band

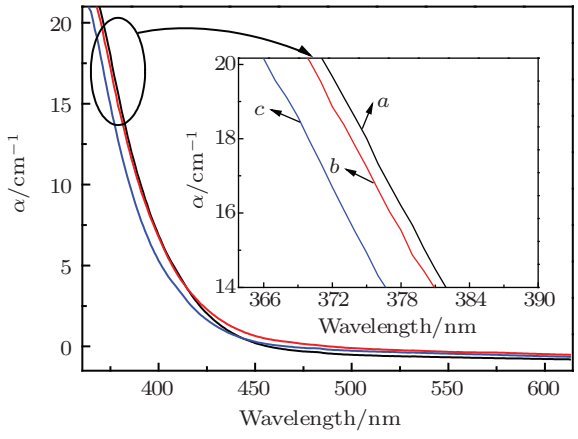


Fig. 2. (color online) UV absorption edges of $LiNbO_3$:Hf, Fe, Mn crystals, *a*: $LiNbO_3$:Hf_2, Fe, Mn; *b*: $LiNbO_3$:Hf_3, Fe, Mn; *c*: $LiNbO_3$:Hf_5, Fe, Mn.

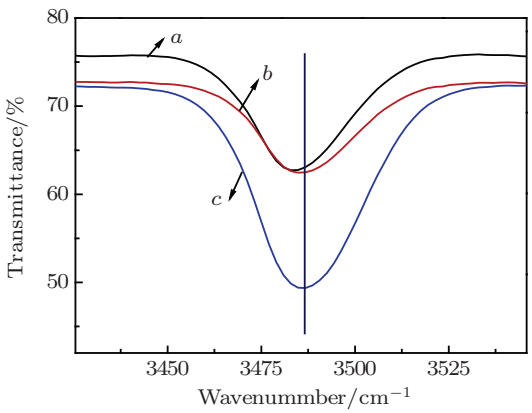


Fig. 3. (color online) OH^- absorption spectra of $LiNbO_3$:Hf, Fe, Mn crystals. *a*: $LiNbO_3$:Hf_2, Fe, Mn; *b*: $LiNbO_3$:Hf_3, Fe, Mn; *c*: $LiNbO_3$:Hf_5, Fe, Mn.

indicates that the doping concentration of Hf has reached the threshold value in triply doped $LiNbO_3$:Hf_5, Fe, Mn. As is well known, when the doping concentration of Mg in $LiNbO_3$:Mg, Fe goes above the threshold value, a peak at 3507 cm^{-1} will appear in its OH^- absorption spectrum, which indicates that Fe^{3+} ions change their location from Li-sites to Nb-sites.[22] But in Fig. 3, no 3507-cm^{-1} absorption peak can be observed, which suggests that Fe^{3+} ions are still located at Li-sites in $LiNbO_3$:Hf_5, Fe, Mn crystal though the doping concentration of Hf is above its threshold.

The nonvolatile holographic storage is achieved in all the $LiNbO_3$:Hf, Fe, Mn crystals. Figure 4 shows the two-center holography experimental results of $LiNbO_3$:Hf_5, Fe, Mn. The diffraction efficiency η is defined as I_d/I_{rec}, where I_d and I_{rec} are the diffracted and the total recording intensity, respectively. η_s and η_f represent the saturation value and fixed value of the diffraction efficiency, respectively, and the response time τ is defined as the time when η reaches $1/e$ times of the saturation value η_s. As shown in Fig. 4, the saturation and fixed diffraction efficiency are 49.8% and 17.5%, respectively, and the response time reduces to 5.0 s; when fixing the hologram, the diffraction efficiency does not monotonically decease, but increases first and then decreases, resulting from the self-enhancement. The self-enhancement nonvolatile holographic storage was first observed in $LiNbO_3$:Fe, Mn crystal,[23] which is very effective in obtaining a higher fixed diffraction efficiency value compared with the general nonvolatile holographic storage.

Experimental results on the saturation and fixed diffraction efficiency, response time, and sensitivity of all the crystals are listed in Table 1. The photorefractive sensitivity S is a vital index describing how fast the hologram can be recorded with a fixed light intensity and crystal thickness. The value of S is generally calculated as $S = (1/I_{rec}L)(\partial\sqrt{\eta}/\partial t)|_{t=0}$, where η, t, I_{rec}, and L represent the diffraction efficiency, time, total recording intensity, and crystal thickness, respectively. Considering the partial erasure in the fixing process in a two-center holography, the equation has been modified into $S' = \beta * (1/I_{rec}L)(\partial\sqrt{\eta}/\partial t)|_{t=0}$, where β is the ratio of $\sqrt{\eta}$ after fixing to that before fixing.[24] From Table 1, we can see that with the increase of the HfO_2 concentration, the values of sensitivities S and S' increase significantly, and when the HfO_2 concentration reaches 5 mol%, the values of sensitivities S and S' are improved to 0.38 cm/J and 0.22 cm/J, respectively. Until now, the best experimental values for S and S' obtained in $LiNbO_3$:Fe, Mn are 0.15 cm/J and 0.08 cm/J.[25] As mentioned before, $LiNbO_3$:Zr, Fe, Mn crystal shows excellent nonvolatile holographic properties, and the values of S and S' are improved to 3.47 cm/J and 1.31 cm/J, respectively;[16] Zr ions are also helpful for improving the values of recording sensitivity of $LiNbO_3$:Cu, Ce, for which the S and S' increase to 0.312 cm/J and 0.099 cm/J, respectively.[17]

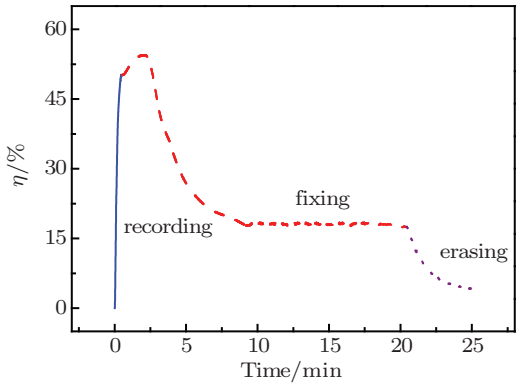


Fig. 4. (color online) Nonvolatile holographic recording, fixing, and erasing curve of $LiNbO_3$:Hf_5, Fe, Mn. The recording time is 5.0 s and the fixing time is about 25 min.

Table 1. Two-center nonvolatile holographic storage properties for different HfO_2-doping concentrations.

Sample	$LiNbO_3$:Hf_2, Fe, Mn	$LiNbO_3$:Hf_3, Fe, Mn	$LiNbO_3$:Hf_5, Fe, Mn
η_s/%	40.5	43.5	49.8
η_f/%	14.2	9.8	17.5
S/(cm/J)	0.12	0.22	0.38
S'/(cm/J)	0.07	0.10	0.22
τ_r/s	30.4	10.1	5.0

The low recording sensitivity S of the commercial congruent $LiNbO_3$ results mainly from the large number of intrinsic defects: Li site vacancies (V_{Li}^-) and charge compensated antisite Nb (Nb_{Li}^{5+}) ions. Some of Nb_{Li}^{5+} ions trapping electrons form small polarons (Nb_{Li}^{4+}) with 1.6-eV binding energy,[26] and some of Nb_{Li}^{5+} ions together with the neighboring normal site Nb_{Nb}^{5+} by trapping a pair of electrons become the bipolarons ($Nb_{Li}^{4+}Nb_{Nb}^{4+}$) with 2.5-eV[27] binding energy. The small polarons and the bipolarons can transform reciprocally by illumination with suitable wavelength light or by heat treatment. Hesselink *et al.*[28] successfully achieved the nonvolatile holography in stoichiometric pure $LiNbO_3$ crystal, with these two kinds of polarons used as the shallow and deep photorefractive centers. However, it should be necessarily pointed out that only when the coherent recording wavelength is near 780 nm and the Li_2O content reaches 49.6 or more, can bipolarons/small polarons act as the effective photorefractive centers. The holographic properties of $LiNbO_3$ crystal mainly depends on the photorefractive centers. To record a strong hologram in $LiNbO_3$ crystal, the excitation, motion, and trapping of electrons must repeat many times due to the very low electron mobility. For $LiNbO_3$:Hf, Fe, Mn crystal, because Hf ions do not participate in the charge-transport process, Fe and Mn ions still present the shallow and photorefractive centers, respectively. During two-center holographic recording in $LiNbO_3$:Hf, Fe, Mn, the recording light excites electrons mainly from the Fe centers to the conduction band, and these electrons are trapped in either Fe or Mn centers after having moved a short distance in the conduction band. The electrons

trapped in Fe centers can be used in the next cycle of excitation, motion, and trapping, whereas those trapped in Mn centers need to be transferred back to the Fe center (through the conduction band) by UV light before participating in another cycle. When Hf ions are doped into $LiNbO_3$:Fe, Mn crystal with concentration above threshold, these Hf ions will substitute antisite Nb ions completely, therefore small polarons and bipolarons mostly disappear. Consequently the moving distances as well as lifetimes of electrons excited from dopants become longer. Most electrons are trapped by $Fe^{2+/3+}$ ions directly. The average time of each cycle will be reduced greatly as compared with that in $LiNbO_3$:Fe, Mn. So the response speed and the sensitivity of two-center holographic storage in $LiNbO_3$:Hf, Fe, Mn is improved.

To enhance the recording sensitivity of $LiNbO_3$:Fe, Mn, there are two necessary requirements that must be met simultaneously: one is reducing the response time, and the other is retaining high diffractive efficiency. To date, two different methods have accomplished the above-mentioned tasks: increasing the Li_2O content[29] and co-doping tetravalent optical damage resistant elements[16,17] in the doubly doped $LiNbO_3$:Fe, Mn and $LiNbO_3$:Cu, Ce crystals. In fact, because of the complex growth process and poor optical quality, the stoichiometric $LiNbO_3$:Fe, Mn encounters great difficulty in becoming a practically nonvolatile storage material. The tetravalent optical-damage-resistant elements Hf and Zr rely on the same principle for improving the $LiNbO_3$:Fe, Mn photorefractive property, that is to say, both the ions only push Nb_{Li}^{5+} ions to the normal Nb site, but do not affect the occupation of $Fe^{2+/3+}$.[16] Since the Mn^{2+} ion and Mn^{3+} ion have the same valence state as that of the $Fe^{2+/3+}$ ion, lower than 4+ of Hf valence, we can reasonably assume that the tetravalent ions have negligible influence on the occupations of the Mn^{2+} ion and Mn^{3+} ion. Therefore, the two-color holographic recording sensitivity S of $LiNbO_3$:Hf, Fe, Mn is greatly improved by doping Hf with the threshold value of 5 mol%. Shi in her Ph.D. dissertation[30] also reported that the difference between two-center holographic properties of $LiNbO_3$:Hf, Fe, Mn, and the experimental results comes mainly from the different reduction–oxidation states of the crystals.

It should be noted that the response time obtained in our experiment is 5.0 s, which is much shorter than that of widely used congruent $LiNbO_3$:Fe, Mn, while it is still longer than the shortest response time of $LiNbO_3$:Zr, Fe, Mn reported by Kong *et al*.[16] This is due to the very low power of UV light employed herein, and the experimental result also indicates that high UV light intensity is needed to gain a large sensitivity value.[31] We can reasonably predict that the response time will be further reduced by utilizing higher power UV light, and thus the sensitivity value can also be substantially enhanced.

4. Conclusions

In this paper, a triply doped crystal $LiNbO_3$ Hf, Fe, Mn is designed and grown, and the high sensitivity S' 0.22 cm/J, short response time 5.0 s, are obtained by doping 5 mol% Hf into $LiNbO_3$:Fe, Mn crystal. Therefore, it is an outstanding candidate for the nonvolatile holographic storage.

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