



# Defect structure and nonvolatile hologram storage properties in Hf:Fe:Mn:LiNbO<sub>3</sub> crystals

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## ABSTRACT

A series of Hf:Fe:Mn:LiNbO<sub>3</sub> crystals with various levels of HfO<sub>2</sub> doping were grown by Czochralski technique. The infrared spectra and ultraviolet spectra were measured and discussed to investigate their structure and defects. The optical damage resistance was characterized by the transmitted beam pattern distortion method. The nonvolatile two-color holographic recording experimental results showed that the recording speed was faster with the increase of HfO<sub>2</sub> doping concentration and at the same time little loss of nonvolatile diffraction efficiencies could be achieved.

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## 1. Introduction

Lithium niobate (LiNbO<sub>3</sub>) crystal is one of the most widely used photorefractive materials in the holographic volume storage [1,2]. A key problem in holographic storage using photorefractive LiNbO<sub>3</sub> crystals is the volatility. The phase grating is easily erased by the readout light of symmetrical intensity. An effective technique was developed to realize nonvolatile recording in LiNbO<sub>3</sub> crystals doped with shallower iron centers (Fe<sup>2+/3+</sup>) and deeper manganese centers (Mn<sup>2+/3+</sup>) [3,4]. But its applications in holographic memory devices are severely limited by optical damage [5]. Doping with damage-resistant additives is found to be an effective method to increase the optical damage resistance [6]. Some damage-resistant elements, such as Zn [7], Mg [8], In [9], Sc [10] and Hf [11], have been used to decrease the optical damage of LiNbO<sub>3</sub>. Especially, the effects Hf<sup>4+</sup> ions in Fe:LiNbO<sub>3</sub> crystals were dissimilar to Mg<sup>2+</sup> or Zn<sup>2+</sup>. The HfO<sub>2</sub> doping concentration above its threshold value, the response rate and sensitivity are greatly improved. Meanwhile, the saturation diffraction efficiency remains at a high value.

In this paper, HfO<sub>2</sub> was the first time doped into Fe:Mn:LiNbO<sub>3</sub> crystals. Our purposes are to study the ions location in the host lattice and the nonvolatile holographic storage properties of Hf:Fe:Mn:LiNbO<sub>3</sub>.

## 2. Experimental

### 2.1. Crystals growth and sample preparation

Hf:Fe:Mn:LiNbO<sub>3</sub> crystals were grown by Czochralski method in an air atmosphere. Various factors affecting the control of crystal growth and the relationship among these factors were analyzed, and an auto monitoring and adjusting diameter-constant control system was built up. Using this control system, various levels of HfO<sub>2</sub> doping crystals were successfully grown. These crystals show smooth surface from shoulder, body to tail. One of the crystals was shown in Fig. 1.

The crystals were placed in a furnace for polarizing at electric current intensity 5 mA/cm<sup>2</sup> for 30 min at 1200 °C and annealing for 8 h to room temperature. The crystals were cut into wafers with a dimension of 8 mm × 8 mm × 2.5 mm. All wafers were oxidized in Nb<sub>2</sub>O<sub>5</sub> powders to be oxidized at 1100 °C for 18 h, as listed in Table 1.

### 2.2. Measurements

The OH<sup>-</sup> infrared absorption peaks of the samples were measured by Fourier infrared spectrophotometer in the wavelength range of 3000–4000 cm<sup>-1</sup> at room temperature.

The ultraviolet–visible optical absorption spectra of Hf:Fe:Mn:LiNbO<sub>3</sub> crystals were measured by a CARY1E UV–vis spectrophotometer. The measurement range was from 300 to 900 nm.

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**Table 1**  
The doped Hf:Fe:Mn:LiNbO<sub>3</sub> crystal samples in experiment.

| Crystals | Composition                 | Dopant in starting melt                                                                      |
|----------|-----------------------------|----------------------------------------------------------------------------------------------|
| LN1      | Fe:Mn:LiNbO <sub>3</sub>    | 0.03 wt% Fe <sub>2</sub> O <sub>3</sub> , 0.1 wt% MnO <sub>2</sub>                           |
| LN2      | Hf:Fe:Mn:LiNbO <sub>3</sub> | 3 mol% HfO <sub>2</sub> , 0.03 wt% Fe <sub>2</sub> O <sub>3</sub> , 0.1 wt% MnO <sub>2</sub> |
| LN3      | Hf:Fe:Mn:LiNbO <sub>3</sub> | 4 mol% HfO <sub>2</sub> , 0.03 wt% Fe <sub>2</sub> O <sub>3</sub> , 0.1 wt% MnO <sub>2</sub> |
| LN4      | Hf:Fe:Mn:LiNbO <sub>3</sub> | 5 mol% HfO <sub>2</sub> , 0.03 wt% Fe <sub>2</sub> O <sub>3</sub> , 0.1 wt% MnO <sub>2</sub> |



Fig. 1. The as-grown boule.

The optical damage resistance ability of the crystals was observed by straightly observing transmission facula distortion method. Fig. 2 shows the experimental setup. An argon-ion laser was used as light source, and the incident beam power level could be adjusted by an attenuator. The crystal *c*-axis was set parallel to the polarization direction of the laser beam and placed on the back focal plane of the convex lens. The power density of the beam spot passing through a pinhole on a light shield was measured by a photodiode connected with a computer. When the laser's power intensity achieves certain value, light scattering appears inside the crystal and the facula is elongated along *c*-axial of the crystal. The laser power intensity, which brings the distortion of the facula transited the crystal, is called the light-scattering ability resistance of the crystal.

The holographic properties were investigated by two waves mixing in transmission geometry at a fixed grating spacing (as shown in Fig. 3) at room temperature. In this experiment, these crystals were pre-exposed to the UV light (intensity, 40 mW/cm<sup>2</sup>) for 1 h. Then two-color recordings were carried out in Hf:Fe:Mn:LiNbO<sub>3</sub> crystals at  $\lambda$  532 nm together with the UV light. A Nd:YAG laser was split into two beams of equal intensity, with each being  $\sim$ 30 mW/cm<sup>2</sup>. These two beams of extraordinary polarization were made to intersect symmetrically inside the crystal of 2.5 mm thickness so that the grating vector was parallel to the crystal *c*-axis. In the process of recording, one of the recording beams was blocked by a shutter from time to time, so that we could use the other recording beam to monitor the grating build-up process and to measure the diffraction efficiency  $\eta$ . Here  $\eta$  was defined as

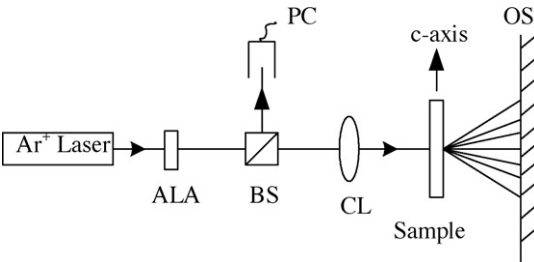


Fig. 2. Experimental setup of the light-scattering resistance ability. ALA: adjustable light attenuator, BS: beam splitter, PC: photodiode, CL: convex lens, OS: observation screen.

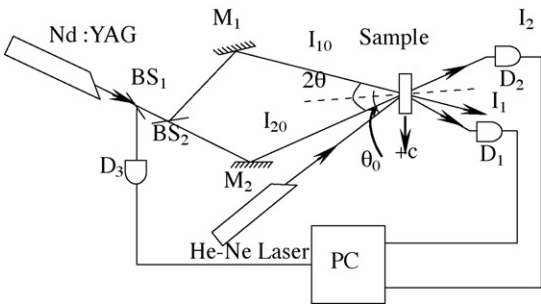


Fig. 3. Experimental setup of holographic storage. M<sub>1</sub>, M<sub>2</sub>: mirrors; BS<sub>1</sub>, BS<sub>2</sub>: beam splitters; D<sub>1</sub>–D<sub>3</sub>: detectors.

$I_d/(I_d + I_t)$ , where  $I_d$  and  $I_t$  were the diffracted and transmitted intensities of the readout beam, respectively. A few percent of diffraction efficient could be achieved.

3. Results and discussion

3.1. Spectra analysis

The results are shown in Fig. 4. The OH<sup>−</sup> absorption peak of LN1 is located at 3482 cm<sup>−1</sup>, and the OH<sup>−</sup> absorption peak of LN2 is at 3483 cm<sup>−1</sup>. However, the OH<sup>−</sup> absorption peaks of LN3 and LN4 crystals shift to 3489 cm<sup>−1</sup>. The FWHM of absorption peaks of LN1 and LN2 is wider than that of LN3 and LN4.

In congruent LiNbO<sub>3</sub>, the ratio of Li to Nb is less than 1. The crystal is under the state of Nb-rich and Li-poor, so there are anti-site Nb defects Nb<sub>Li</sub><sup>4+</sup> and Li vacancy V<sub>Li</sub><sup>−</sup> defects in congruent LiNbO<sub>3</sub>. In the case of the Fe:Mn:LiNbO<sub>3</sub>, the doped Mn and Fe ions were located at Li<sup>+</sup> site in the formation of Mn<sub>Li</sub><sup>+2+</sup> and Fe<sub>Li</sub><sup>+2+</sup>. When the doped concentration of Hf<sup>4+</sup> ions in Fe:Mn:LiNbO<sub>3</sub> crystal was lower, Hf<sup>4+</sup> replaced Nb<sub>Li</sub><sup>4+</sup>. The OH<sup>−</sup> absorption peaks will not change obviously. When the concentration of Hf<sup>4+</sup> exceeded the threshold, a part of Hf<sup>4+</sup> ions began to occupy Nb sites and existed in the form of Hf<sub>Nb</sub><sup>−</sup>. Because Hf<sub>Nb</sub><sup>−</sup> has higher ability to attract H<sup>+</sup> than that of V<sub>Li</sub><sup>−</sup>, which make the H<sup>+</sup> ions gather near the Hf<sub>Nb</sub><sup>−</sup>. The mainly OH<sup>−</sup> absorption peaks located at 3489 cm<sup>−1</sup> described the vibration absorption situation of OH<sup>−</sup> around Hf<sub>Nb</sub><sup>−</sup>. High concentration of Hf<sup>4+</sup> formed more Hf<sub>Nb</sub><sup>−</sup> defects, so the OH<sup>−</sup> absorption peak becomes sharper.

We know that in Zn:Fe:LiNbO<sub>3</sub> crystals with its ZnO doping concentrations above threshold, besides 3529 cm<sup>−1</sup> absorption peak related with Zn<sub>Nb</sub><sup>3−</sup>–(V<sub>Li</sub><sup>−</sup>–OH<sup>−</sup>) complex, another peak corresponding to the vibration of Fe<sub>Nb</sub><sup>2−</sup>–(V<sub>Li</sub><sup>−</sup>–OH<sup>−</sup>) appears at 3504 cm<sup>−1</sup> [7]. It should be noted that 3504 cm<sup>−1</sup> absorption peak is not present in LN3 and LN4, which suggests that most of Fe and Mn ions are unaltered their position and still located at Li sites.

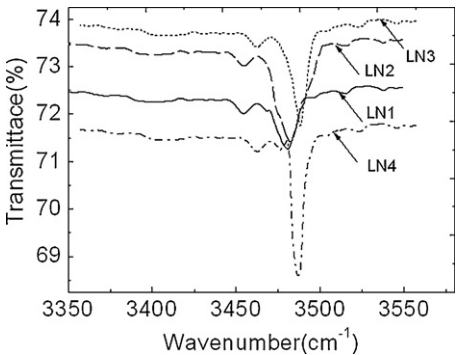


Fig. 4. The infrared absorption spectra of Hf:Fe:Mn:LiNbO<sub>3</sub> crystals.

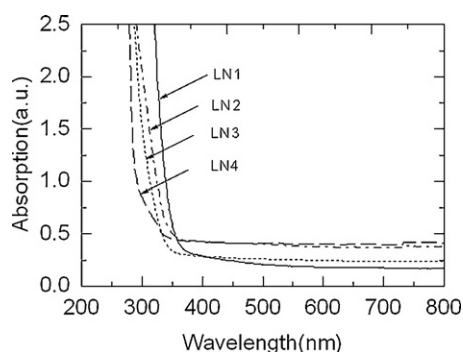


Fig. 5. UV absorption spectrum of Hf:Fe:Mn:LiNbO<sub>3</sub>.

Fig. 5 shows the ultraviolet–visible absorption spectra of the Hf:Fe:Mn:LiNbO<sub>3</sub> crystals. It can be clearly seen that the absorption edges of LN2, LN3 and LN4 crystals successively shifted to the violet band, in comparison with that of the LN1.

The fundamental optical absorption edge is decided by valence electron transition energy from  $2p$  orbits of  $O^{2-}$  to  $4d$  orbits of  $Nb^{5+}$ . So the valence electronic state of  $O^{2-}$  directly affects the site of the absorption edge. In this paper, the phenomenon of the absorption-edge shift is explained by  $Z^*/r$ , where  $Z^* = Z - \Sigma s$ ;  $Z$ ,  $\Sigma s$ , and  $r$  are the effective nuclear charge number, the atomic ordinal number of the ion, the shield factor, and the radius of the ion, respectively. The polarization ability of the ions was calculated by  $Z^* = Z - \Sigma s$ , where the value for  $Nb^{5+}$ ,  $Fe^{3+}$ ,  $Fe^{2+}$ ,  $Mn^{3+}$ ,  $Mn^{2+}$ ,  $Hf^{4+}$ , and  $Li^+$  are 52.5, 55.3, 42.2, 48.3, 33.6, 44.6, and 2.5, respectively.

The interaction of positive and negative ions results in the change of the polarization ability of  $O^{2-}$ . If the polarization ability of the doping ion is lower than that of the replaced ion, which makes the polarization ability of  $O^{2-}$  decrease, the energy required by the electron transition increases. In this way the absorption-edge shifts to the violet band. We know that in the Fe:Mn:LiNbO<sub>3</sub> crystal, the Fe and Mn ions occupy the normal Li sites. When the HfO<sub>2</sub> doping concentration is below the threshold concentration, most of the  $Hf^{4+}$  ions replace the  $Nb_{Li}^{4+}$  ions and form  $Hf_{Li}^{3+}$ . As the polarization ability of  $Hf^{4+}$  is lower than that of  $Nb^{5+}$ , the absorption edges of the LN2 shift to shorter wavelength compared with that of the LN1. When the doping concentration of HfO<sub>2</sub> is above the threshold concentration, all of the  $Nb_{Li}^{4+}$  ions are replaced by a portion of the  $Hf^{4+}$  ions and the remaining  $Hf^{4+}$  begin to occupy normal Nb sites. As the polarization ability of  $Hf^{4+}$  is lower than that of  $Nb^{5+}$ , so the absorption-edge positions of the LN3 and LN4 successively shifted to the violet band.

### 3.2. The optical damage resistance ability

The results of the photo-damage-resistant ability of Hf:Fe:Mn:LiNbO<sub>3</sub> crystals are shown in Table 2. The results indicated that the photo-damage-resistant ability of LN3 and LN4 is about one order of magnitude higher than LN1.

According to the following well-known simplified Scalar expression,  $\delta\Delta n \approx B\kappa\alpha I/\sigma$ , where  $B$  is the generalized electro-optical coefficient,  $\kappa$  is the glass constant,  $\alpha$  is the optical absorption coefficient,  $I$  is the intensity of the light and  $\sigma$  is the conductivity ( $\sigma = \sigma_d + \sigma_p$ ,  $\sigma_d$  is the dark conductivity and  $\sigma_p$  is the photoconductivity,  $\sigma_d \ll \sigma_p$ , so  $\sigma \approx \sigma_p$ ), the photorefractive ability of the

Table 2

The results of optical damage resistance ability ( $R$ ) of the Hf:Fe:Mn:LiNbO<sub>3</sub> crystals.

| Crystal                  | LN1               | LN2               | LN3               | LN4               |
|--------------------------|-------------------|-------------------|-------------------|-------------------|
| $R$ (W/cm <sup>2</sup> ) | $1.8 \times 10^2$ | $3.3 \times 10^2$ | $7.9 \times 10^3$ | $8.1 \times 10^3$ |

Table 3

Characteristic parameters of nonvolatile holographic storage in the oxidized Hf:Fe:Mn:LiNbO<sub>3</sub> crystals.

| Crystals | Writing times (min) | Saturation diffraction efficiency (%) | Nonvolatile diffraction efficiency (%) |
|----------|---------------------|---------------------------------------|----------------------------------------|
| LN1      | 47                  | 29.5                                  | 19.2                                   |
| LN2      | 34                  | 25.1                                  | 14.7                                   |
| LN3      | 25                  | 20.8                                  | 12.4                                   |
| LN4      | 26                  | 20.1                                  | 12.5                                   |

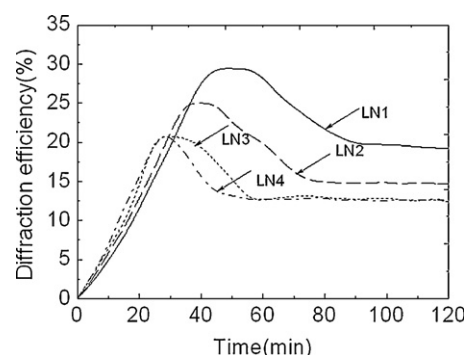


Fig. 6. The dependence of the diffraction efficiency on the time.

LiNbO<sub>3</sub> crystal increases with the decrease of the photoconductivity. From the analysis above, we know that when the HfO<sub>2</sub> doping concentration is below the threshold concentration, most of the  $Hf^{4+}$  replaces the  $Nb_{Li}^{4+}$ . The increasing photoconductivity, which is mainly attributed to the decrease of anti-site  $Nb_{Li}$ , induces the increase in photo-damage resistance ability. When the HfO<sub>2</sub> doping concentration is over the threshold concentration, most of the  $Nb_{Li}^{4+}$  ions disappeared, so the photo-damage resistance ability will never increase.

### 3.3. Nonvolatile hologram storage properties

The results of holographic storage properties of Hf:Fe:Mn:LiNbO<sub>3</sub> are shown in Table 3. In Table 3, the response time of LN3 and LN4 is shorter than that of LN1 and LN2, though the diffraction efficiency has a little decrease. As it has been commented above,  $Fe^{3+}$  and  $Mn^{3+}$  ions also remain at Li sites in LN3 and LN4 acting as electron acceptors, therefore, the nonvolatile saturation diffraction efficiency of LN3 and LN4 crystal do not greatly decrease with respect to that of LN2 (Fig. 6).

## 4. Conclusion

In this paper, a series of Hf:Fe:Mn:LiNbO<sub>3</sub> crystals were prepared by Czochralski method. We studied the behavior of OH<sup>-</sup> absorption peak, fundamental absorption edge, and optical damage as a function of HfO<sub>2</sub> doping concentration.  $Hf^{4+}$  takes priority in replacing anti-site Nb in Hf:Fe:Mn:LiNbO<sub>3</sub> crystals, when the concentration of HfO<sub>2</sub> exceeds its threshold value, and  $Hf^{4+}$  replaces  $Nb^{5+}$ , forming  $Hf_{Nb}^{4-}$ . Few of Fe and Mn ions are repelled to  $Nb^{5+}$  sites by  $Hf^{4+}$ . The optical damage resistance of Hf:Fe:Mn:LiNbO<sub>3</sub> increases rapidly when the concentration of HfO<sub>2</sub> exceeds the threshold value. The nonvolatile two-color holographic recording experimental results showed that the recording speed was faster with the increase of HfO<sub>2</sub> doping concentration, especially in LN3 and LN4, which exceeded the so-called threshold concentration, and at the same time little loss of nonvolatile diffraction efficiencies could be achieved.

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