Improvement of photorefractive properties in Hf:Fe:$LiNbO_3$ crystals with various [Li]/[Nb] ratios*

Sun Xiu-Dong(孙秀冬)†, Shi Hong-Xin(石宏新), Luo Su-Hua(骆素华), Meng Qing-Xin(孟庆鑫), and Jiang Yong-Yuan(姜永远)

Department of Physics, Harbin Institute of Technology, Harbin 150001, *China*

(Received 5 January 2010; revised manuscript received 12 March 2010)

Photorefractive properties of Hf:Fe:$LiNbO_3$ crystals with various [Li]/[Nb] ratios have been investigated at 488 nm wavelength based on the two-wave coupling experiment. High diffraction efficiency and large recording sensitivity are observed and explained. The decrease in Li vacancies is suggested to be the main contributor to the increase in the photoconductivity and subsequently to the induction of the improvement of recording sensitivity. The saturation diffraction efficiency is measured up to 80.2%, and simultaneously the recording sensitivity of 0.91 cm/J is achieved to in the Hf:Fe:$LiNbO_3$ crystal grown from the melt with the [Li]/[Nb] ratio of 1.20, which is significantly enhanced as compared with those of the Hf:Fe:$LiNbO_3$ crystal with the [Li]/[Nb] ratio of 0.94 in melt under the same experimental conditions. Experimental results definitely show that increasing the [Li]/[Nb] ratio in crystal is an effective method for Hf:Fe:$LiNbO_3$ crystal to improve its photorefractive properties.

Keywords: diffraction efficiency, recording sensitivity, Hf:Fe:$LiNbO_3$ crystals
PACC: 4265, 4270, 4280T, 8140T

1. Introduction

Photorefractive lithium niobate ($LiNbO_3$, LN) crystal has been extensively investigated as one of the most promising holographic recording materials due to its excellent photorefractive properties. Transition-metal elements, such as Fe, Cu and Mn are usually added into $LiNbO_3$ to improve its photorefractive characteristics.[1] Among them, Fe:$LiNbO_3$ is one of the most important holographic storage materials because of its high diffraction efficiency and long storage lifetime. However, several problems, such as low response speed and strong light-induced scattering, seriously limit the application of Fe:$LiNbO_3$ crystal in holographic volume storage. Doping with damage resistant dopants, such as Mg, Zn, In and Sc, has been found to be an effective method to solve these problems.[2−5] As a result, response speed and signal-to-noise ratio are remarkably improved, nevertheless diffraction efficiency apparently decreases.

Recently, Kokanyan *et al.*[6,7] and Li *et al.*[8] reported that Hf is a novel effective damage-resistant element for $LiNbO_3$ crystal, and its threshold concentration is about 4 mol% in melt for the congruent one. Hf^{4+} is a tetravalent ion and its valence is higher than that of other damage-resistant dopants, therefore the optical properties of Fe:$LiNbO_3$ crystals co-doped with HfO_2 may be different from those co-doped with other damage-resistant elements.[9,10]

As is well known, $LiNbO_3$ crystal is not grown stoichiometric, and generally the number of Li^+ is less than that of Nb^{5+} in the crystal. Therefore, congruent $LiNbO_3$ crystal contains many Li vacancies and antisite Nb intrinsic defects. Many optical properties of $LiNbO_3$ are sensitive to the [Li]/[Nb] ratio in the crystal. With the increase of the [Li]/[Nb] ratio, the structures and properties of the crystal change significantly.[11,12]

In this paper, the photorefractive properties of Hf:Fe:$LiNbO_3$ crystals with various [Li]/[Nb] ratios are investigated at 488 nm wavelength by means of two-wave coupling experiments. The experimental results show that the photorefractive properties of Hf:Fe:$LiNbO_3$ crystals are greatly improved by increasing the [Li]/[Nb] ratio. The Hf:Fe:$LiNbO_3$ crystal grown from the melt with the [Li]/[Nb] ratio of 1.20 exhibits excellent holographic recording properties, a high diffraction efficiency, a fast response speed, and a large recording sensitivity.

*Project supported by the Fundamental Research Foundation of Commission of Science Technology, Industry for National Defense of China (Grant No. 2320060089), and National Basic Research and Development Program of China (Grant No. 2007CB3070001) and Program of Excellent Team in Harbin Institute of Technology, China.
†Corresponding author. E-mail: xdsun@hit.edu.cn
© 2010 Chinese Physical Society and IOP Publishing Ltd

2. Experiments

2.1. Sample preparation

Three as-grown $LiNbO_3$ crystals co-doped with 0.03 wt% of Fe_2O_3 and 4 mol% of HfO_2 were prepared in air by the Czochralski technique along the c-axis direction. The staring materials used for crystal growth were Li_2CO_3, Nb_2O_5, Fe_2O_3 and HfO_2, and the purity of these materials was 99.99%. The composition in melt was selected to be [Li]/[Nb]=0.94, 1.05, and 1.20, and were labeled as Hf:Fe:$LN_{0.94}$, Hf:Fe:$LN_{1.05}$, and Hf:Fe:$LN_{1.20}$, respectively. After growth, the crystals were cut into 2 mm plates along the y-faces and were polished to optical quality.

2.2. Measurements

To investigate the crystal composition and defect structure, the inductively coupled plasma atomic emission spectrometry (ICP-AES) of the samples was measured by means of an Optima 5300DV optical emission spectrometer. The crushed samples were dissolved in HNO_3–HF solution in a closed Teflon vessel and heated for 20 min on the heating plate. Then they were placed in an automatic microwave digestion furnace to microwave digestion. The solution with dissolved samples was cooled down to room temperature, and then prepared as the standard concentration solutions for testing. The contents of Li, Nb, Fe, and Hf in the crystal were analysed by the ICP-AES.

The photorefractive properties of the crystals were investigated by using the two-wave coupling experiment. An extraordinary polarised beam from an Ar^+ laser operating at 488 nm was split into two beams with equal light intensity of 125 mW/cm^2. The two beams were coherently interfered in the crystal. The grating vector was aligned along the c-axis to utilise the largest electro-optic coefficient γ_{33}. The crossing angle of the two beams on the incident crystal surface was 30°. The grating spacing was 0.94 μm. During 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 buildup process and to measure the diffraction efficiency η. Here η was defined as $I_d/(I_d + I_t)$, where I_d and I_t were the diffracted and transmitted light intensities of the readout beam, respectively.

3. Results and discussion

3.1. ICP-AES analysis

In the ICP-AES experiment, we can obtain the weight ratio of elements in the crystal. On the basis of these data, the chemical formulas of the samples can be obtained. The calculation method of chemical formulas is given in the following. First, we transform the weight ratio of elements in the crystal into the molar ratio of elements in crystal. Then, the number of oxygen per unit formula is fixed to 3.00, and the precondition of charge neutrality is common. Here, the valence of Fe ions is taken to be 3, because the concentration of Fe^{3+} ions is one or two orders of magnitude larger than that of Fe^{2+} ions. Finally, the number of Li vacancies is calculated by subtracting the amounts of Li, Nb, Fe, and Hf from the total amount of cation sites (=2.00). The results of compositional analysis by means of the ICP-AES method and the obtained chemical formulas for Hf:Fe:$LiNbO_3$ crystals are summarised in Table 1. It can be found that as the [Li]/[Nb] ratio in melt increases, the crystal exhibits an increase of [Li]/[Nb] ratio, which is close to unit. For the Hf:Fe:$LiNbO_3$ crystals with [Li]/[Nb]=0.94, 1.05 and 1.20 in melt, the ratios of [Li]/[Nb] in the crystal are 0.909, 0.941 and 0.986, respectively. In our samples, the HfO_2 concentration reaches its threshold concentration, so Nb_{Li}^{4+} defects are completely disappeared in the samples. Moreover, the concentration of Li vacancies decreases with the increase of the [Li]/[Nb] ratio in the crystal.

Table 1. The results of compositional analysis by means of the ICP-AES method and the obtained chemical formulas for Hf:Fe:$LiNbO_3$ crystals. □:Li vacancy.

sample	[Li]:[Nb]:[Fe]:[Hf] weight ratio in crystal	[Li]/[Nb] molar ratio in crystal	chemical formula
Hf:Fe:$LN_{0.94}$	4.983:73.40:0.04123:4.812	0.909	$Li_{0.9015}$ $Fe_{0.0009}$ $Hf_{0.0339}$ $\square_{0.0716}$ $Nb_{0.9921}$ O_3
Hf:Fe:$LN_{1.05}$	5.629:80.11:0.03743:5.603	0.941	$Li_{0.9269}$ $Fe_{0.0008}$ $Hf_{0.0359}$ $\square_{0.0509}$ $Nb_{0.9855}$ O_3
Hf:Fe:$LN_{1.20}$	5.890:79.97:0.03925:5.587	0.986	$Li_{0.9644}$ $Fe_{0.0008}$ $Hf_{0.0356}$ $\square_{0.0210}$ $Nb_{0.9782}O_3$

3.2. Photorefractive properties

Figure 1 shows the typical grating recording curves. The temporal behaviour of diffraction efficiency η during grating recording can be well described by the function

$$\sqrt{\eta(t)} = \sqrt{\eta_{\rm sat}}(1 - \exp(-t/\tau_{\rm r})), \tag{1}$$

where $\eta_{\rm sat}$ is the saturation diffraction efficiency during recording, and $\tau_{\rm r}$ is the response time constant. The amplitude of refractive index change $\Delta n_{\rm sat}$ can be calculated from the saturation diffraction efficiency $\eta_{\rm sat}$ according to Kogelnik formula[13]

$$\eta_{\rm sat} = \sin^2\left(\frac{\pi \Delta n_{\rm sat} d}{\lambda \cos\theta_{\rm r}}\right), \tag{2}$$

where d is the thickness of the crystal, λ is the free-space wavelength, and $\theta_{\rm r}$ is the Bragg angle of the readout beam inside the crystal.

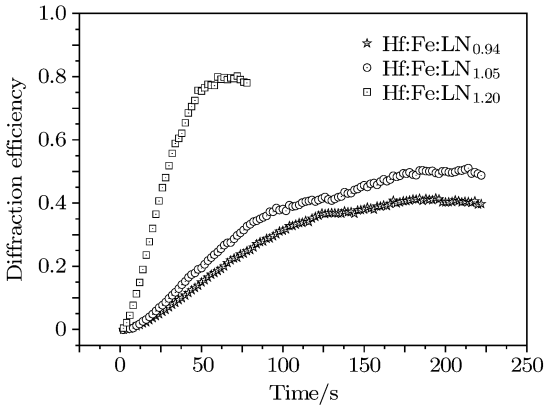


Fig. 1. Dependence of diffraction efficiency on time.

Recording sensitivity S is an important parameter in a holographic data storage system. The higher the sensitivity is, the faster the response speed is. Recording sensitivity S can be measured by single hologram recording experiment.[14] From the single hologram recording curve, we can calculate the S value from

$$S = \frac{1}{Id}\left.\frac{{\rm d}\sqrt{\eta}}{{\rm d}t}\right|_{t=0}, \tag{3}$$

where I is the total recording light intensity, ${\rm d}\sqrt{\eta}/{\rm d}t$ is the recording slope defined as the initial time derivative of the square root of diffraction efficiency.

The photorefractive properties of Hf:Fe:$LiNbO_3$ crystals are shown in Table 2, from which we can see that with the increase of the [Li]/[Nb] ratio in the crystal, the photorefractive properties of Hf:Fe:$LiNbO_3$ crystals are greatly improved. When the ratio of [Li]/[Nb] in the melt is 0.94, the saturation diffraction efficiency is 41.6%, and the response time is 53.6 s. When the ratio of [Li]/[Nb] in the melt increases to 1.20, the saturation diffraction efficiency of 80.2% is obtained, and simultaneously the response time is reduced to 19.7 s. Compared with the Hf:Fe:$LN_{0.94}$ crystal, the response time shortens 2.72 times, the refractive index change improves by a factor of 1.57, and the recording sensitivity has a sharp increase by a factor of 3.79 in Hf:Fe:$LN_{1.20}$ crystal.

Table 2. Photorefractive properties of Hf:Fe:$LiNbO_3$ crystals.

sample	$\eta_{\rm sat}$/%	$\Delta n_{\rm sat}/10^{-5}$	$\tau_{\rm r}$/s	S/cm·J^{-1}
Hf:Fe:$LN_{0.94}$	41.6	5.01	53.6	0.24
Hf:Fe:$LN_{1.05}$	51.0	5.58	49.0	0.28
Hf:Fe:$LN_{1.20}$	80.2	7.86	19.7	0.91

Photorefractive properties of $LiNbO_3$ crystal mainly depend on its photorefractive centre. In Hf:Fe:$LiNbO_3$ crystals, $Fe^{2+/3+}$ ions are the photorefractive sensitive ions and Hf^{4+} ions are the optical damage-resistant ions. In the photorefractive process, $Fe^{2+/3+}$ ions are the dominating photorefractive centres and Hf^{4+} ions do not participate in charge transport process. It is well known that the response time $\tau_{\rm r}$ is inversely proportional to the photoconductivity $\sigma_{\rm ph}$ according to the equation of $\tau_{\rm r} \propto \varepsilon\varepsilon_0/\sigma_{\rm ph}$, where ε is the dielectric constant, and ε_0 is the permittivity of free-space. At low concentration of optical damage-resistant impurities, the increase of $\sigma_{\rm ph}$ is related to the removal of electron traps, $\sigma_{\rm ph} \sim 1/[{\rm Nb_{Li}}]$. When the concentration of optical damage resistant impurities is above the threshold, the increase of $\sigma_{\rm ph}$ may be related to the increase of the hole component, $\sigma_{\rm ph} \sim 1/[V_{\rm Li}]$.[15–17] In our samples, the HfO_2 concentration exceeds its threshold concentration, so Nb_{Li}^{4+} defects are completely replaced by Hf^{4+} ions to form Hf_{Li}^{3+} defects, and the photoconductivity is inversely proportional to the concentration of Li vacancies. From the results of the ICP-AES experiment, it can be obtained that the concentration of Li vacancies decreases with the increase of the [Li]/[Nb] ratio in the crystal. Thus, with the increase of the [Li]/[Nb] ratio in the crystal, the photoconductivity increases, the response time shortens, and the recording sensitivity improves. In addition, the value of the saturation diffraction efficiency is related to the concentration of $Fe^{2+/3+}$ ions, especially to the concentration of Fe^{2+} ions. While the concentration of Fe^{2+} ions can be obtained from the UV–visible absorption spectra.[18]

Figure 2 shows the UV–visible absorption spectra of Hf:Fe:$LiNbO_3$ crystals with various [Li]/[Nb] ratios, from which it can be seen that the concentration of Fe^{2+} ions increases as the [Li]/[Nb] ratio increases. So,

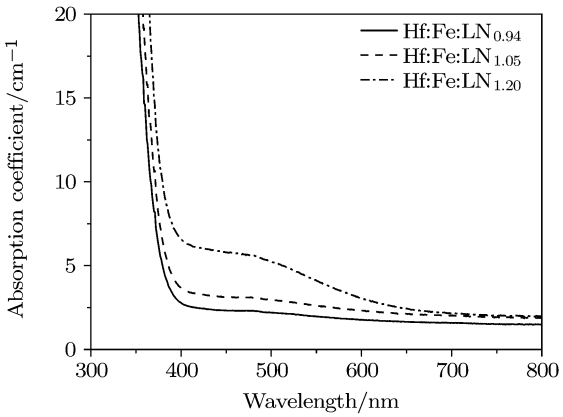


Fig. 2. UV–visible absorption spectra of Hf:Fe:$LiNbO_3$ crystals.

the saturation diffraction efficiency of Hf:Fe:$LiNbO_3$ crystals improves with the increase of the [Li]/[Nb] ratio in the crystal.

4. Conclusion

In summary, the photorefractive properties of Hf:Fe:$LiNbO_3$ crystals with various [Li]/[Nb] ratios have been investigated by means of the two-wave coupling experiment. The results show that the photorefractive properties are significantly improved with the increase of the [Li]/[Nb] ratio in the crystal. Among all samples, the Hf:Fe:$LiNbO_3$ crystal with the [Li]/[Nb] ratio of 0.986 shows the best holographic recording properties, whose refractive index change, response time, and recording sensitivity are 7.86×10^{-5}, 19.7 s and 0.91 cm/J, respectively. Therefore, increasing the [Li]/[Nb] ratio in the crystal is an effective method for Hf:Fe:$LiNbO_3$ crystal to improve its photorefractive properties.

References

[1] Phillips W, Amodei J J and Staebler D L 1972 *RCA Rev.* **33** 94

[2] Zhang G Y, Xu J J, Liu S M, Sun Q, Zhang G Q, Fang Q Y and Ma C L 1995 *Proc. SPIE* **2529** 14

[3] Volk T R, Razumovski N V, Mamaev A V and Rubinina N M 1996 *J. Opt. Soc. Am.* B **13** 1457

[4] Guo Y B, Liao Y, Cao L C, Liu G D, He Q S and Jin G F 2004 *Opt. Express* **12** 5556

[5] Zheng W, Liu B, Bi J C and Xu Y H 2005 *Opt. Commun.* **246** 297

[6] Kokanyan E P, Razzari L, Cristiani I, Degiorgio V and Gruber J B 2004 *Appl. Phys. Lett.* **84** 1880

[7] Razzari L, Minzioni P, Cristiani I, Degiorgio V and Kokanyan E P 2005 *Appl. Phys. Lett.* **86** 131914

[8] Li S Q, Liu S G, Kong Y F, Deng D L, Gao G Y, Li Y B, Gao H C, Zhang L, Hang Z H Chen S L and Xu J J 2006 *J. Phys.: Condens. Matter* **18** 3527

[9] Li S Q, Liu S G, Kong Y F, Xu J J and Zhang G Q 2006 *Appl. Phys. Lett.*. **89** 101126

[10] Yan W B, Chen H J, Shi L H, Liu S G and Kong Y F 2007 *Appl. Phys. Lett.* **90** 211108

[11] Furukawa Y, Sato M, Kitamura K, Yajima Y and Minakata M 1992 *J. Appl. Phys.* **72** 3250

[12] Li X C, Kong Y F, Wang L Z and Liu H D 2008 *Chin. Phys.* B **17** 1014

[13] Kogelnik H 1969 *Bell Syst. Tech. J.* **48** 2909

[14] Mok F, Burr G and Psaltis D 1996 *Opt. Lett.* **21** 896

[15] Volk T, Maximov B, Sulyanov S, Rubinina N and Wöhlecke M 2003 *Opt. Mater.* **23** 229

[16] Xu Z P, Xu S W, Zhang J, Liu X R and Xu Y H 2005 *J. Cryst. Growth* **280** 227

[17] Fan Y X, Li H T and Zhao L C 2007 *Opt. Mater.* **30** 492

[18] Kurz H, Krätzig E, Keune W, Engelman H, Gonser U, Dischler B and Räuber A 1977 *Appl. Phys.* **12** 355