Study on growth and storage properties of Zn:In:Fe:$LiNbO_3$ Crystals

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ABSTRACT

Zn ions were added into melts with 4.0mol.%, Fe ions were with 0.02mol.%, and In ions were with varying concentration of 0, 1.0, 2.0 and 3.0mol.%. A series of Zn:In:Fe:$LiNbO_3$ Crystals were grown by Czochralski technique. Their absorption spectra and photo-damage resistant ability were measured. The mechanism of the shift of OH^- absorption peak was investigated. Their photorefractive properties were experimentally investigated by using two-beam coupling. The results shown that, the photo-damage resistant ability of Zn(4mol.%):In(3mol.%): Fe(0.02mol.%):$LiNbO_3$ Crystals were two orders than that of magnitude higher than that of Fe:$LiNbO_3$ crystals, and with concentration of Zn and In ions increasing, diffraction efficiency and response time of crystals were shortened. The experiment of associative memory were also carried out with Zn(4mol.%):In(3mol.%):Fe(0.02mol.%):$LiNbO_3$ crystals for the recording device and with Zn(4mol.%):In(2mol.%):Fe(0.02mol.%):$LiNbO_3$ Crystals for phase conjugation.

Keywords: Zn:In:Fe:$LiNbO_3$ Crystals; photo-refractive properties; photo-damage resistant ability; associative memory

1. INTRODUCTION

$LiNbO_3$ crystal has high electro-optic and nonlinear coefficient, which makes it one of the most popular photo-refractive crystals. Doped photorefractive sensitive impurities (Fe) in $LiNbO_3$[1], the photorefractive properties of crystal is enhanced, and doped damage-resistant impurities (Zn or In)[2,3], the photo-damage resistant ability is increased. Fe;$LiNbO_3$ crystal are being widely investigated for applications in holographic data storage. However, Fe:$LiNbO_3$ crystal has two serious disadvantages as follows: (1) the response time is longer; (2) the photo-damage resistant ability is lower. Doped 4.0mol.% Zn ions and different concentration In ions in Fe;$LiNbO_3$, Zn:In:Fe:$LiNbO_3$ crystals are grown in our lab, and have been proved as an excellent photorefractive materials by the experimental results of straightly observing transmission facula distortion, two-beam coupling, and associative memory. When the doped concentration of Zn and In achieves the threshold value, its photo-damage resistance ability is two order of magnitude higher than that of Fe:LiNbO3 crystal. With concentration of Zn and In ions increasing, diffraction efficiency decrease and response time shorten. We use firstly Zn:In:Fe:$LiNbO_3$ crystals for recording element and phase conjugation mirror to carry experiment of holograph associative memory. The results shown that it has the advantages of image processing quality being high and real-time processing.

2. CRYSTAL GROWTH AND SAMPLE PREPARATION

The starting materials used for crystal growth are Li_2CO_3, Nb_2O_5, Fe_2O_3, ZnO and In_2O_3. The purities of them are all 99.99%. The congruent composition of Li:Nb = 0.946 was selected as melt and crystal compositions. The dopant

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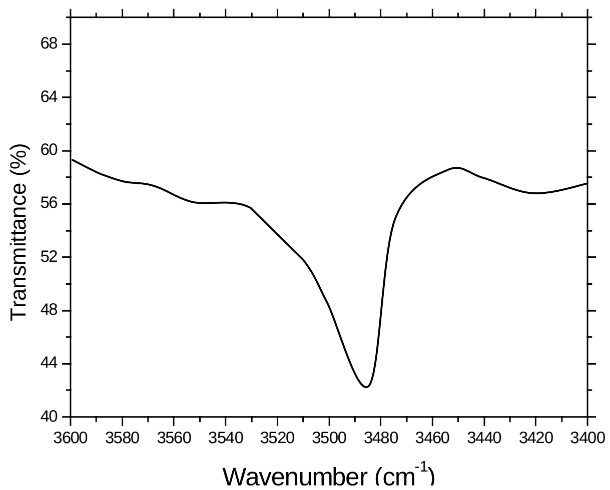
concentration of Fe_2O_3 was 0.01mol.%, that of ZnO was 4mol.%, and that of In_2O_3 was 0.5mol.%, 1mol.%, 1.5mol.% respectively. The appropriately weighed materials were thoroughly mixed and calcined at 700℃ and then sintered at 1150℃ for 2h, respectively.

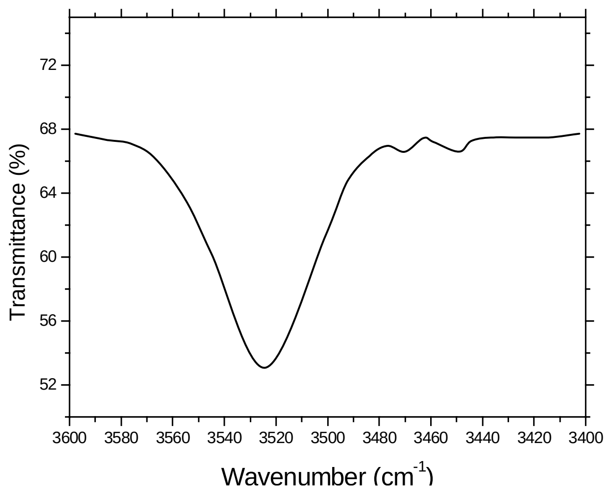
Single crystals of Zn:(4mol.%):In(1mol.%):Fe(0.02mol%):$LiNbO_3$ (1#), Zn:(4mol.%):In(2mol. %):Fe(0.02mol%): $LiNbO_3$ (2#), Zn:(4mol.%):In(3mol.%):Fe(0.02mol.%):$LiNbO_3$ (3#) and Fe(0.02mol%):$LiNbO_3$ (4#) were pulled along c axis from the melt in a platinum crucible by Czochralski technique. The sizes of crystals as grown are 30mm in diameter and 40mm in length. The crystals were grown under the optimum technology conditions: axial temperature of 40-50℃ cm^{-1}, rotating rate of 20 rpm, and pulling rate of 2.0-3.0 mm/h for 1#, 4# and 1.0-2.0 mm/h for 2#, 3#. In such condition, the solid-liquor interface was flat. All as-grown crystals show good symmetry and optical quality. The crystals were polarized with electric field at 5 mA/cm^2 for 6 h at the 1210℃. Then the crystals were cut into samples with size of $10\times10\times3mm^3$ ($a\times b\times c$).

3. INFRARED ABSORPTION SPECTRA OF ZN:IN:FE:$LINBO_3$ CRYSTALS

Because the water content in the atmosphere was brought to $LiNbO_3$ crystal during the growth process, hydrogen in water was integrated with oxygen of the crystal to form the hydrogen bond. The vibration of O-H bond generated an infrared absorption band near 3500cm^{-1}. the position of the doped ions and concentration of threshold value of photo-damage resistant ions in the crystals can be studied by analyzing the change of Infrared absorption spectra[4,5]. Using FTIR– 10300E mode Fourier infrared spectrophotometer, the infrared transmittance spectra of 2# and 3# crystals were measured. The measurement results were shown in Figure 1.



(a) Zn:(4mol.%):In(2mol.%):Fe:$LiNbO_3$



(b) Zn:(4mol.%):In(3mol.%):Fe:$LiNbO_3$

Figure 1. Infrared spectra of Zn:In:Fe:$LiNbO_3$

It could be seen from Figure 1 that OH^- absorption peak was at 3484cm^{-1} for 2# crystal and shifted to 3525cm^{-1} for 3# crystal. There were two kinds of intrinsic defects of Li vacancies(V_{Li}^-) and antisite Nb(Nb_{Li}^{4+}) in $LiNbO_3$ crystals. Li vacancies (V_{Li}^-) showed electronegativity and easily attracted H^+ to make H^+ surround them. Now, the vibration of V_{Li}^---Nb_{Li}^{4+}--OH^- group is around 3484cm^{-1}. When doping 4mol% Zn^{2+} and 2mol% In^{3+} and a little of Fe ions in $LiNbO_3$, they replaced Nb_{Li}^{4+} and were in the form of Zn_{Li}^+, In_{Li}^{2+}, Fe_{Li}^+ and Fe_{Li}^{2+}. They showed electropositive and were repulsive to

H^+ ions. The H^+ ions also concerned around V_{Li}^- and the absorption peak was also around 3484cm^{-1}. When doping 4mol% Zn^{2+} and 3mol% In^{3+} in $LiNbO_3$, the concentration reached the threshold value. Zn^{2+} and In^{3+} would replace Nb_{Nb}^{5+} and they existed in the form of Zn_{Nb}^{3-} and In_{Nb}^{2-}. Zn_{Nb}^{3-} and In_{Nb}^{2-} had stronger attraction, so H^+ gathered around Zn_{Nb}^{3-} and In_{Nb}^{2-}. The vibration of Zn_{Nb}^{3-}--In_{Nb}^{2-}--OH^- group was around 3525cm^{-1}.

4. MEASUREMENT OF PHOTO-DAMAGE RESISTANT PROPERTIES OF ZN:IN:FE:LINBO$_3$ CRYSTAL

4.1. Experimental and results

The photo-damage resistant ability of Zn:In:Fe:$LiNbO_3$ crystal was measured by directly observation transmitted speckle-distortion technique, the experimental set-up is shown by Figure 2.

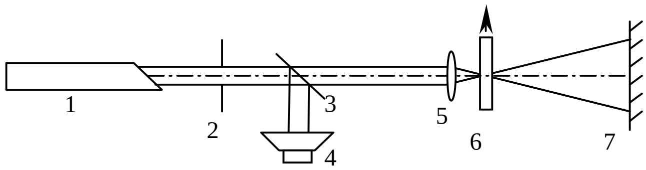


Figure 2. Experimental Set-up for measurement of photo-damage resistant ability.
1: Ar^+ laser, 2: light shed, 3: beam splitter, 4: defector, 5: lens, 6: crystals, 7: screen.

Ar^+ laser with 514.5 nm wavelength was used as the light source. The total intensity that focused on the crystal could be regulated continuously by light shed. The polarized direction was parallel to the c-axis of the crystal. The sample was put on the focus of the lens. When the laser intensity is low, the speckle on the screen is round. When the laser intensity achieves certain value, the speckle begins to distort and is elongated along c-axial of the crystal. The laser intensity just making the speckle elongated is called the light-scattering resistance ability of the crystal. the results are given in Table 1.

Table 1. Photo-damage resistant ability of crystals

Crystals	1#	2#	3#	4#
R(W/cm^2)	3.2×10^2	7.8×10^2	5.3×10^3	6.2×10

The results show that thee photo-damage resistant ability of Zn(4mol%):In(3mol%):Fe:$LiNbO_3$ is two orders of magnitude higher than that of Fe:$LiNbO_3$ and that of Zn(4mol%):In(2mol%):Fe: $LiNbO_3$ is one orders of magnitude higher than that of Fe: $LiNbO_3$.

4.2. Mechanism of the improvement of photo-damage resistant ability of Zn:In:Fe:LiNbO$_3$ crystal

There are two kinds of intrinsic defects (Li vacancy V_{Li}^- and antisite Nb Nb_{Li}^{4+}) and two kinds of impurity defects (Fe^{2+} and Fe^{3+}). And they form the photo-refractive sensitive centers Fe^{2+}/Fe^{3+} and $Nb_{Li}^{4+}/ Nb_{Li}^{5+}$. The photo-refractive effect can occur in $LiNbO_3$ crystal when they participate the charge transport process. As the photo-refractive resistant ions, Zn^{2+} and In^{3+} don't participate the current carrier transport process, so the photo-refractive effect of Zn:In:Fe:$LiNbO_3$ decreased, that is, the photo-refractive resistant effect improved. When the concentration of Zn^{2+} and In^{3+} ions exceeds the threshold, Zn^{2+} and In^{3+} ions replace Nb_{Li}^{4+} completely and replace Nb^{5+} partly. Most of the Fe ions that occupy Li sites leave Li sites and occupy Nb sites. They exist in the form of Fe_{Nb}^{2-}. They are electro- negative and the ability of electron-capture reduces, so the electron-capture plane decreases and the photoconductivity of the crystal enhances. Because of the weakness or the disappearance of the two kinds of photo-refractive sensitive centers, the photo-refractive resistant ability of Zn:In:Fe:$LiNbO_3$ improves.

5. MEASUREMENT OF THE DIFFRACTION EFFICIENCY AND THE RESPONSE TIME OF ZN:IN:FE:LINBO3 CRYSTAL

As holographic storage materials, photo-refractive crystal should possess high diffraction efficiency to make the images recorded in the crystal reappear clearly. The diffraction efficient is defined as the ratio of the diffraction light intensity and the transmission beam intensity before the establishment of the grating. It is $I_2'/I_2 \times 100\%$, in which, I_2 is the transmission beam intensity of I_{20} before the establishment of the grating and I_2' is diffraction light intensity of I_1 in the direction of I_2 after the establishment of the grating. The two-wave coupled path was adopted to measure the diffraction efficiency of the crystal. In the experiment, the light source is He-Ne laser. With λ =514.5nm and the polarization direction in the incident plane (e light). The diameter of the pump light D=1mm and the diameter of the signal light δ =1mm, $I_{10}=I_{20}$=1.8mW. The experimental set-up is shown in figure 3.

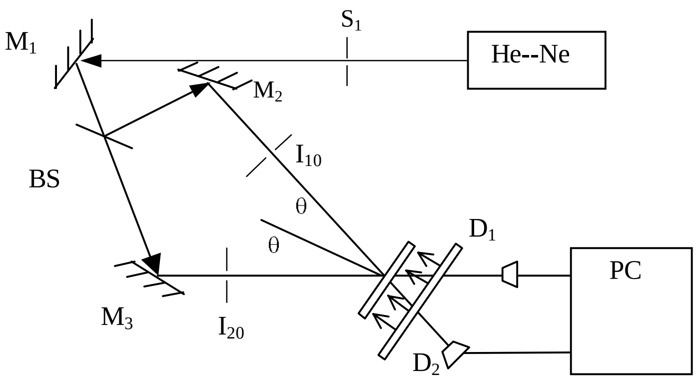


Figure 3. Light path scheme of two-beam coupling

M_1, M_2, M_3,-- reflective mirrors; BS— beam splitter; D_1,D_2—detectors

During the course of measuring, I_{20} was cut off and I_2' was measured in the direction of I_2. The results of the diffraction efficiency are shown in table 2.

The response time τ is that from the incident beam begins to irradiate to the time when the diffraction efficiency achieves $(1-e^{-1})$ of the maximal diffraction efficiency η. The experimental results of the response time are shown in Table 2, too.

Table 2 Holographic recording properties of the Zn:In:Fe:$LiNbO_3$

Crystal	η_0(%)	τ(s)
1#	63	142
2#	58	104
3#	36	48
4#	69	24

6. HOLOGRAPHIC ASSOCIATIVE STOROGE EXPERIMENTAL

The experimental set-up is shown in figure 4.

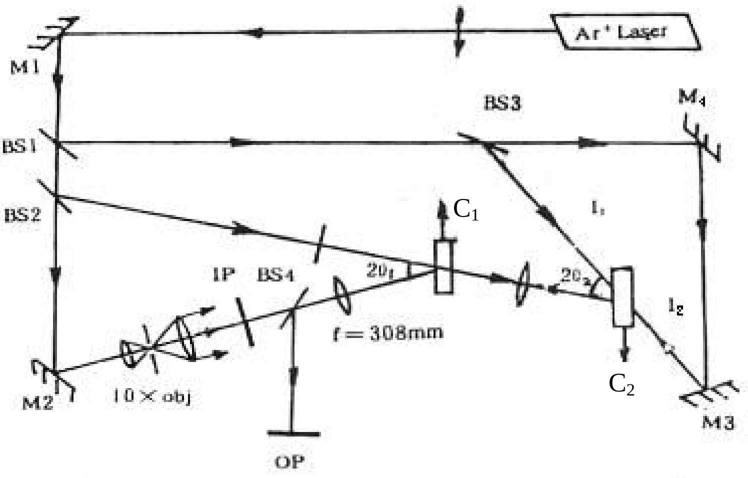


Figure 4. Optical Set-up for holographic associative storoge experiment

IP:Input flat; OP:Output flat; M_1~M_4:Mirror; BS_1~BS_4:Beam splitters;

C_1 :record crystal Zn(4mol%):In(3mol%):Fe:$LiNbO_3$; C2:phase conjugate crystal Zn(4mol%):In(2mol%):Fe:$LiNbO_3$

The light source is Ar^+ laser and the output wavelength is 514.5nm. Zn(4mol%):In(3mol%): Fe:$LiNbO_3$ crystal is adopted as the storage material and Zn(4mol%):In(2mol%):Fe:$LiNbO_3$ crystal acts as phase conjugation lens. The beam splits to reference beam I_3 and object beam I_4 in holographic storage. The angle between them is 13.5^o. The beam ratio is 1:1. Object beam I_4 loads the image information (a in figure 5) and records the image information in Zn(4mol%): In(3mol%):Fe:$LiNbO_3$ crystal. The recording time is 30 seconds. The other two reverse coherent beams I_1 and I_2 split from Ar^+ laser form the pump beams of four-wave mixing phase conjugation lens [Zn(4mol%):In(2mol%):Fe:$LiNbO_3$]. And the angle between I_1 and I_2 is 13^o. The phase conjugation beam returns along the original road and oppositely reads out the holographs in the recording medium. Addressing (b in figure 5) from a part of the storage object, a complete image (c in figure 5) can be received in the output face. The storage images are good in image-forming, clear and complete. The signal-to-noise ratio is high.

(a) (b) (c)

Figure 5 Experimental result of associative memory

(a) input image; (b) input addressing image; (c)read-out image

7. CONCLUSION

Doping ZnO, In_2O_3 and Fe_2O_3 in $LiNbO_3$, Zn:In:Fe:$LiNbO_3$ crystal was grown by Czochralski technique. When the concentrations of Zn^{2+} and In^{3+} increased, the photo-damage resistant ability increased, diffraction efficiency decreased and response time shortened. The photo-damage resistant ability of Zn(4mol%):In(3mol%):Fe:$LiNbO_3$ crystal improved two orders of magnitude higher than that of Fe:$LiNbO_3$. The OH^- absorption peak of shifted to 3525cm^{-1} from 3484cm^{-1} of $LiNbO_3$. the response time increased five times higher than Fe:$LiNbO_3$. The mechanism of the improvement of photo-damage resistant ability and the shift of OH^- absorption peak in Zn:In:Fe: $LiNbO_3$ crystal was investigated. The holographic associative storage were established by using Zn(4mol%):In(3mol%):Fe:$LiNbO_3$ crystal as recording device and Zn(4mol%):In(2mol%):Fe: $LiNbO_3$ crystal as phase conjugation lens. The storage images were clear and complete.

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