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Investigation on photorefractive properties of In:Mn:Fe:$LiNbO_3$

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Abstract

In:Mn:Fe:$LiNbO_3$ crystal was grown by the Czochralski method and oxidized for the first time. The OH^- absorption band of In(3 mol%):Mn:Fe:$LiNbO_3$ crystal was found to be at 3507 cm^{-1}. The nonvolatile holographic recording in In(3 mol%):Mn:Fe:$LiNbO_3$ crystal was realized by the two-photon fixed method. The recording time of In:Mn:Fe:$LiNbO_3$ crystal is only a half of that of Mn:Fe:$LiNbO_3$ crystal, and the ratio of signal to noise is improved, too. At last, the mechanism of OH^- absorption band shifting and two-photon fixed was discussed.

Keywords: In:Mn:Fe:$LiNbO_3$ crystal; Two-photon fixed method; Holographic recording

1. Introduction

Holographic recording devices have the merits that the storage capability is large, the data transmission speed is fast and the addressing time is very short [1,2]. The maximal storage and treatment capacity of the volume photo-refractive recording is 10^{12} bit/cm^2, which is four orders of magnitude higher than that of the two-dimension recording [3]. Now, a key problem is that the phase grating is easily erased by the readout light of symmetrical intensity and the recorded hologram can be erased, too [4]. Using Mn:Fe:$LiNbO_3$ crystal, the nonvolatile recording can be achieved by means of the two-photon fixed method [5,6]. But the recording time of Mn:Fe:$LiNbO_3$ crystal is long and the ratio of signal to noise is low. When doping In^{3+} in Mn:Fe:$LiNbO_3$ crystal, it was found that its recording time became shorter and the signal-to-noise ratio was increased.

2. Experimental

2.1. Growth of In:Mn:Fe:$LiNbO_3$ crystals

In:Mn:Fe:$LiNbO_3$ crystals were grown by Czochralski technique. The ratio of Li to Nb was 0.946. The doped concentration of $MnCO_3$ and Fe_2O_3 was 0.02 and 0.1 wt%, respectively, and In(1 mol%):Mn:Fe:$LiNbO_3$, In(3 mol%):Mn:Fe:$LiNbO_3$ crystals were grown by doping 0.5 or 1.5 mol% In_2O_3 in Mn:Fe:$LiNbO_3$ crystal. The crystals were poled at 1200 °C and were cut into wafers with the dimension of $10 \times 10 \times 2$ mm^3. Some wafers were oxidized in Nb_2O_5 powders.

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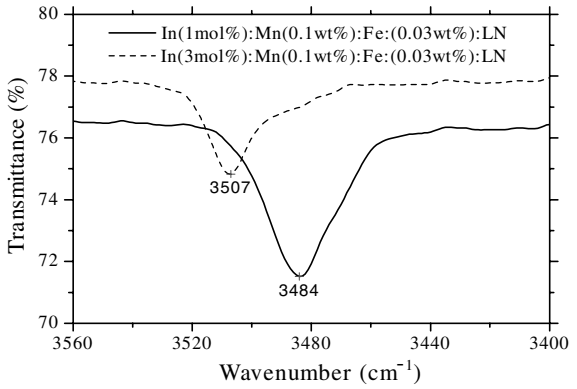

Fig. 1. The infrared absorption spectra of crystals.

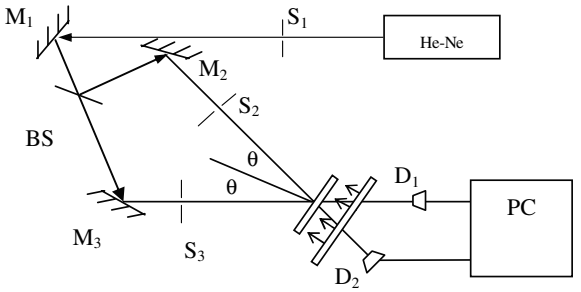

Fig. 2. Experimental light path of two-photon holographic storage diffraction efficiency—M_1, M_2, M_3: mirrors; BS: beam splitter; D_1, D_2: detector; S_1, S_2, S_3: diaphragm; PC: computer.

2.2. Infrared absorption spectra of In:Mn:Fe:$LiNbO_3$ crystals

The water and air in the raw material and make the H^+ ions enter the crystal and form O–H–O during the course of crystals growing. The infrared absorption band of OH^- is near 3500 cm^{-1} [7]. The infrared absorption spectra of crystals were measured by Fourier spectrophotometer from the range of 3200–4000 cm^{-1}. The results are shown in Fig. 1. The OH^- absorption band of In(1 mol%):Mn:Fe:$LiNbO_3$ crystal is at 3484 cm^{-1} and that of In(3 mol%):Mn:Fe:$LiNbO_3$ is at 3507 cm^{-1}. The location of the OH^- absorption band of In(1 mol%):Mn:Fe:$LiNbO_3$ crystal is the same as that of the pure $LiNbO_3$ crystal [8,9].

2.3. Two-photon fixed method in doping $LiNbO_3$ crystals

If the crystal doped with two or more dopants with different transition level of electrons was used in holographic storage and the recording and gating lights with corresponding energy were chosen, the two-photon holographic storage could be realized. We used $Mn^{2+/3+}$ and $Fe^{2+/3+}$ as the dopants to grow Mn:Fe:$LiNbO_3$ crystals. The nonvolatile storage was achieved by means of double-photon fixed method. But the recording time of the Mn:Fe:$LiNbO_3$ crystal was long and the ratio of signal to noise was low. So we doped In element in Mg:Fe:$LiNbO_3$ to grow In:Mn:Fe:$LiNbO_3$ for improving these properties. The two-photon two-wave coupling diffraction efficiency of the crystals was measured for the first time. The experimental setup is shown in Fig. 2.

The included angle 2θ between signal light and pump light was fixed at 21°. As the first step, the samples were radiated under ultraviolet light for 1 h. Then, He–Ne laser was turned on to record the information in the crystal. Finally, when the diffraction efficiency reached its maximum value, the ultraviolet light was turned off and only one incident light beam was used to erase. The dependence of the diffraction efficiency on the time was shown in Fig. 3. The results show that the recording time of the (3 mol%):Mn:Fe:$LiNbO_3$ crystal is only a half of that of the Mn:Fe:$LiNbO_3$ crystal. The exact values of the recording time for the In(3 mol%):Mn:Fe:$LiNbO_3$ and Mn:Fe:$LiNbO_3$ crystal are 19 and 38 min, respectively.

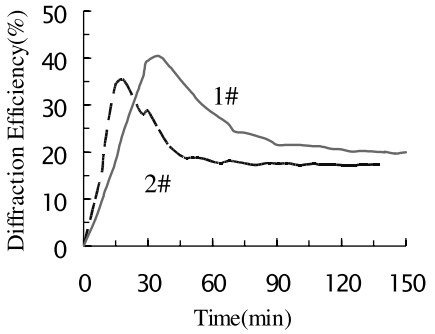

Fig. 3. The dependence of the diffraction efficiency on the time: 1#—Mn:Fe:$LiNbO_3$ crystal; 2#—In:Mn:Fe:$LiNbO_3$ crystal.

3. Discussion and some preliminary concluding remarks

3.1. Shifting of OH^- absorption band

In congruent $LiNbO_3$, the ratio of Li to Nb is less than 1, i.e. the crystal is under the state of Nb-rich and Li-poor, so there exist antisite Nb defects (Nb_{Li}^{4+}) and Li vacancy defects in congruent $LiNbO_3$ [10–12]. The electronegative of the Li vacancies easily attracts the H^+ ions to get together around the Li vacancies. The OH^- absorption bands mainly reflected the vibration situation of OH^- near Li vacancies. In $LiNbO_3$, the doped Mn and Fe ions were located at Li^+ site in the formation of Mn_{Li}^{+} and $Fe_{Li}^{+/2+}$, which excluded H^+. So H^+ still congregates around the Li vacancies, and the OH^- absorption band of $LiNbO_3$ and Mn:Fe:$LiNbO_3$ crystal are both near 3484 cm^{-1}. When the doped concentration of In^{3+} ions in Mn:Fe:$LiNbO_3$ crystal was lower, In^{3+} replaced Nb_{Li}^{4+} and existed in the formation of In_{Li}^{2+}. So the H^+ ions cannot congregate around it and the OH^- absorption band will not change obviously. When the concentration of In^{3+} exceeded the threshold, a part of In^{3+} ions began to occupy Nb sites and existed in the form of In_{Nb}^{2-}. Because In_{Nb}^{2-} has higher ability to attract H^+ than that of Li vacancy, which make the H^+ ions gather near the In_{Nb}^{2-}, in such way the more energy was needed to excite OH^- vibration. The infrared spectra mainly described the vibration absorption situation of OH^- around In_{Nb}^{2-}. In comparison with Mn:Fe:$LiNbO_3$ crystal, the OH^- absorption band of In(3 mol%):Mn:Fe:$LiNbO_3$ crystal shifts from 3484 to 3507 cm^{-1}. The decrease of the photorefractive centers improved the photorefractive resistance ability of crystal and increased the ratio of signal to noise.

3.2. Mechanism of two-photon holographic storage

Two-photon fixed method is to use one gating lights to radiate crystals for exciting the electron in deeper level before grating was recorded and during the course of recording. The crystal is sensitive to the recording light only when the gating light exists and the holographic storage can be realized.

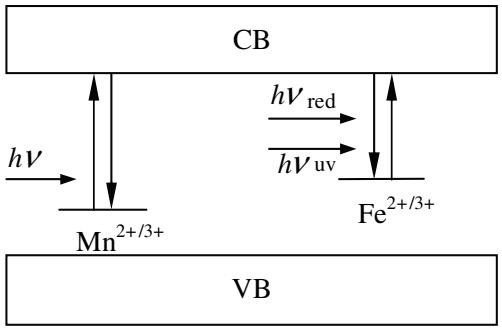

Fig. 4. Charge-transport of two-photon holographic storage.

When the gating light is turned off, the crystal is not sensitive to the recording light and the readout light cannot erase the hologram recorded. In our experiments, the ultraviolet light was adopted as the gating light, the He–Ne laser was the recording light and the electron was considered as the only charge-carrier. The process of charge-transport of two-photon holographic storage in the crystal is shown in Fig. 4.

The ultraviolet light can excite the electrons in Mn and Fe cavities to the conduction band, while the output beam of He–Ne laser can only excite the electrons in Fe cavities to the conduction band. At the same time, the electrons in the conduction band transfer and be captured by the Mn cavities and Fe cavities. During the course of radiation, the ultraviolet light excites a part of electrons in the deeper cavities into the shallower ones. So the donor density increases in the shallower cavities and decreases in the deeper cavities. If the ultraviolet light radiates the crystal during the recording course, it can continuously excite the electrons in the deeper cavities into the shallower cavities, which increase the donor density in shallower cavities and acceptor density in the deeper cavities. Meanwhile, the recording light can excite the electrons in the shallower cavities into the conduction band, the electrons in the conduction band transfer and are captured by the deeper and shallower cavities. As a result, the donor density increases in the shallower cavities and decreases in the deeper cavities. Just due to such a dynamic progress, the space-charge field can be built up simultaneously in the deeper and shallower cavities,

which is main effect of the ultraviolet light in the two-photon holographic storage. Because the center of Fe cavities is located at 1.3 eV (shallower cavities) and Mn cavities is located at 1.4 eV (deeper cavities), the He–Ne laser operating at 632.8 nm with the power of 12 mW is chosen as the recording light and the ultraviolet light with the wavelength of 351 nm and the power of 20 mW is adopted as the gating light. The two-photon holographic storage is realized in the Mn:Fe:$LiNbO_3$ and In:Mn:Fe:$LiNbO_3$ crystals. Because the concentration of In^{3+} in the In:Mn:Fe:$LiNbO_3$ crystals is exceed its threshold, the photo-scattering resistance ability and the signal to noise of crystal increases and the recording time decrease due to the increase of photo-conduction induced by the In dopant.

Acknowledgements

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