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Growth and optical damage properties of In:Zn:$LiNbO_3$ waveguide substrate

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In:Zn:$LiNbO_3$ crystals doped with different indium concentrations were grown by Czochralski technique. The optical damage threshold value and ultraviolet-visible absorption spectra of the In:Zn:$LiNbO_3$ crystals were measured. The In:Zn:$LiNbO_3$ crystals were made into optical waveguide substrates using hexanedioic acid as proton exchange agent. The optical damage resistant ability of those optical waveguide substrates was investigated by the m-line method. The optical damage threshold values of In(2mol.%):Zn(3mol.%):$LiNbO_3$ crystal and optical waveguide substrate are two orders of magnitude higher than those of pure $LiNbO_3$.

1 Introduction

Lithium niobate ($LiNbO_3$) single crystal is of great interest for several decades due to its excellent nonlinear optical, piezoelectric and optic-electric properties [1]. It has various applications such as optical switch, frequency conversion, optical modulators and so on [2]. Proton exchange (PE) waveguide in $LiNbO_3$ substrate is widely used in integrated optics for its strong optical nonlinearity, large beam confinement and simply fabrication process [3,4]. But pure $LiNbO_3$ crystal shows a serious drawback of optical damage when it is irradiated with the high-power laser beam [5,6], which is limiting its usability. Various $LiNbO_3$ crystals doped with different optical damage resistant impurities have been prepared by the Czochralski technique. The optical damage problem of pure $LiNbO_3$ crystal can be greatly reduced by doping with MgO [7], ZnO [8], In_2O_3 [9], or Sc_2O_3 [10], etc. In the present work, we propose to dope In_2O_3 and ZnO into $LiNbO_3$ to grow In:Zn:$LiNbO_3$ crystals. The concentration of Zn^{2+} or In^{3+} in $LiNbO_3$ is respectively lower than its single-doped threshold concentration and the concentration of In^{3+} is changeable. In this paper, the shift mechanism of the absorption edges and enhance mechanism of the optical damage resistant ability on the In^{3+} concentration are discussed.

2 Experimental

Preparation of crystal samples In(1mol.%):Zn:$LiNbO_3$, In(1.5mol.%):Zn:$LiNbO_3$, In(2mol.%):Zn:$LiNbO_3$ crystals were grown by the Czochralski method. The intermediate frequency furnace was used as the heater. The starting materials were Li_2CO_3, Nb_2O_5, In_2O_3, ZnO with the purity of 99.99%. The Li/Nb ratio of the melts to grow the congruent $LiNbO_3$ is 0.946. The concentration of Zn is 3mol.%. The concentrations of In^{3+} are

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1mol.%, 1.5mol.% and 2mol.%, respectively. The compositions of the samples were listed in table 1. To prepare polycrystalline materials, the raw materials were mixed thoroughly, calcinated at 850°C for 4h, and sintered at 1150°C for 4h. The pulling rate was 2mm/h, the rotation rate was 20rpm and the temperature gradient was 30-40K/cm. The diameters and heights of these crystals were about 30mm and 50mm, respectively. The as-grown crystals were polarized in another furnace where the temperature was hold at about 1200°C for 4h with a direct current of 5 mA/cm^2. Then the crystals were cut into wafers of 15×10×2mm^3. Then all the samples were polished to optical grade. Using hexanedioic acid as the proton exchange resource, PE In:Zn:LiNbO$_3$ waveguide substrates were prepared.

Table 1 The compositions of the samples.

Crystal	$1^{\#}$	$2^{\#}$	$3^{\#}$	LiNbO$_3$	PE $1^{\#}$	PE $2^{\#}$	PE $3^{\#}$	PE LiNbO$_3$
In^{3+} (mol.%)	1.0	1.5	2.0	0	1.0	1.5	2.0	0
Zn^{2+} (mol.%)	3.0	3.0	3.0	0	3.0	3.0	3.0	0

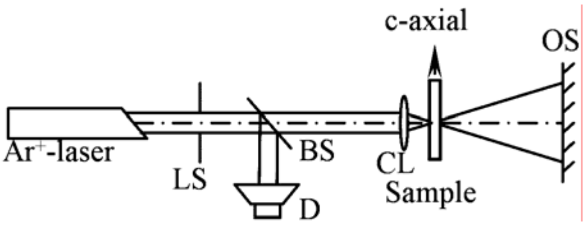

Fig. 1 Setup for testing photo damage resistant ability of In:Zn:LiNbO$_3$ crystals. LS: light shed; S: beam splitter; CL: lens; D: power detector; OS: observation screen.

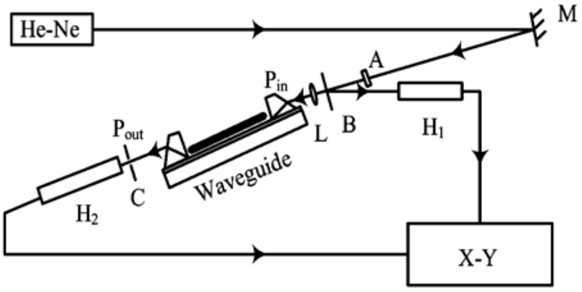

Fig. 2 Experimental arrangement of m-line method. A: light attenuator; B: a piece of glass; C: crack; L: Fourier lens; H_1 and H_2: photoelectric multipliers; P_{in} and P_{out}: input prism and output prism; X-Y: X-Y recorder with double pens.

Ultraviolet-visible absorption spectra and optical damage measurements The ultraviolet-visible absorption spectra of In:Zn:LiNbO$_3$ crystals were measured with a CARYIE style ultraviolet- visible spectrometer. The range was from 300nm to 1000nm. The facula-distortion observing method was applied to measure the optical damage resistant ability of the In:Zn:LiNbO$_3$ crystals. The experimental setup was shown in figure 1. The Ar^+ laser (λ=488.0nm) was employed as the light source, and the output intensity of the beam could be regulated. The beam transited the light shed and convex lens and then focused on the sample. The focula could be observed on the screen. The polarization direction of the beam was along the c-axis of the crystal. When the power intensity was low, there was no optical damage and the facula was round. When the power intensity achieved a certain value, the facula began to elongate along the c-axis of the crystal. The optical damage occurred. When the facula shape distorted, the power density of the output beam could be recorded by the power detector. This value is defined as the optical damage threshold (R), which is an important parameter to evaluate the optical damage resistant ability of the crystal.

The optical damage resistant ability of the In:Zn:LiNbO$_3$ waveguide substrates were measured by the m-line technique. The optical path was shown in figure 2. The He-Ne laser operated at 632.8nm was adopted as the light source. The waveguide and the input part of the rutile prism system were placed at the focus of the Fourier lens (f=250mm). The light transit through the waveguide and then went through the output part. The central facula of the m-line was accepted by the photoelectric multiplier through the crack C. The intensity of the input and the output could be obtained by the X-Y recorder with double pens. The intensity of the incident light could be regulated by the light attenuator. At the same time, we could observe the change of the center facula of the m-line.

It could be seen from the experiments that the brightness of the center facula of the m-line increased followed with the increasing of the incident intensity. The output value increased simultaneously. When the incident intensity achieved a certain value, the output value decreased suddenly and the center facula elongated. Finally, the center facula changed to a bright line. The optical damage occurred. The process of the optical damage was shown in figure 3. The optical damage threshold value of the waveguide substrate (E_0) was defined as the incident laser intensity irradiating on the waveguide when the center facula suddenly elongated.

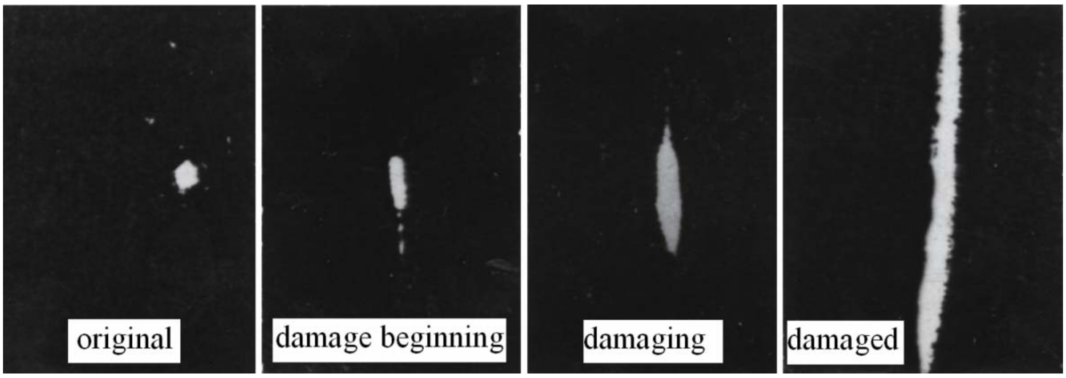

Fig. 3 M-line pictures of PE In:Zn:$LiNbO_3$ waveguide substrate during optical damage.

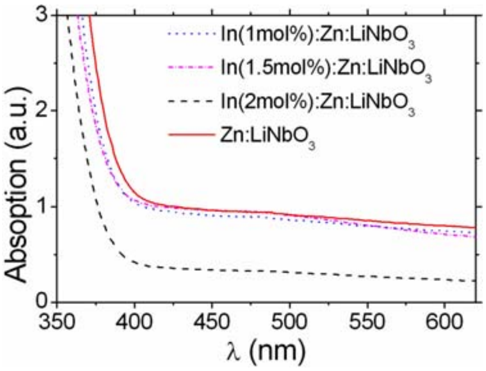

Fig. 4 Ultraviolet-visible absorption spectra of In:Zn:$LiNbO_3$ crystals.

3 Results and discussion

Figure 4 shows the ultraviolet-visible absorption spectra of the In:Zn:$LiNbO_3$ crystals. It can be seen that the absorption edges of the In:Zn:$LiNbO_3$ crystal shift to ultraviolet compared with Zn:$LiNbO_3$ and the shift extent increases with the increasing of the In^{3+} concentration.

The principal structure of $LiNbO_3$ crystal is formed by oxygen octahedron. The optical absorption edge is decided by the valence-electron energy from the 2p-orbits of O^{2-} to the 4d-orbits of Nb^{5+}. So the valence-electronic state of O^{2-} directly affects the site of the absorption edge. If the doping ions make the O^{2-} polarization ability increase, the energy for the electron transition decreases and the absorption edge shifts to infrared. On the contrary, the absorption edge shifts to ultraviolet. The polarization ability can be expressed by Z^{*2}/r, where Z^* is the effective nuclear charge number and r is the radius of the ion. $Z^*=Z-\sum s$, where Z is the nuclear charge number and $\sum s$ is the shield factor. The polarization abilities of Nb^{5+}, In^{3+} and Li^+ are 44.8, 22.8 and 2.5, respectively. From the viewpoint of Li-vacancy model, there are Li^+ vacancies in congruent pure $LiNbO_3$ crystal and the Li^+ vacancies are filled by Nb^{5+} to form antisite defects $(Nb_{Li})^{4+}$ [11,12]. In the case of In:Zn:$LiNbO_3$ crystals, when In^{3+} concentration is low, In^{3+} ions occupy $(Nb_{Li})^{4+}$. When In^{3+} concentration achieves a certain value, the additional In^{3+} ions begin to occupy Nb-site. This leads to the polarization ability of O^{2-} decreasing and the electron transition energy increasing. So the absorption edges of In:Zn:$LiNbO_3$ crystals shift to ultraviolet with the increasing of the In^{3+} concentration.

The results of the optical damage resistant ability of In:Zn:$LiNbO_3$ crystals and substrates are shown in table 2 and table 3, respectively. As can be seen, no matter among the crystals or among the waveguide substrates, the optical damage resistant ability of In(2mol.%):Zn:$LiNbO_3$ is about two orders of magnitude higher than that of pure $LiNbO_3$. Principal role for the parameters of the photo-damage plays electron-phonon anharmonicity, which is determined by the antisite Nb $(Nb_{Li})^{4+}$ and oxygen vacancies of $LiNbO_3$ crystal [13,14]. From the viewpoint of Li-vacancy model, when In^{3+} and Zn^{2+} concentration is low, In^{3+} and Zn^{2+} ions occupy antisite Nb $(Nb_{Li})^{4+}$ and exist in the forms of $(In_{Li})^{2+}$ and $(Zn_{Li})^{+}$. When their concentration is above a certain value, In^{3+} and Zn^{2+} ions begin to occupy Nb-site and exit in the forms of $(In_{Nb})^{2-}$ and $(Zn_{Nb})^{3-}$. Their ability to capture electrons decrease and the photoconductivity of In(2mol.%):Zn:$LiNbO_3$ crystal increase rapidly. According to the Scalar expression [15], the photorefractive ability of the $LiNbO_3$ crystal increases with the decrease of the photoconductivity. So with the increasing of the photoconductivity, the optical damage resistant ability of In(2mol.%):Zn:$LiNbO_3$ increase obviously.

Table 2 Optical damage resistant ability (*R*) of In:Zn:$LiNbO_3$ crystals.

Sample	1#	2#	3#	$LiNbO_3$
R (W/cm²)	$1.3\times10^3\pm5$	$2.8\times10^3\pm5$	$1.8\times10^4\pm10$	$1.9\times10^2\pm1$

Table 3 Optical damage threshold value (E_0) of In:Zn:$LiNbO_3$ waveguide substrates.

Sample	PE 1#	PE 2#	PE 3#	PE $LiNbO_3$
E_0 (J/cm²)	8.9×10^4	1.5×10^5	5.7×10^6	3.1×10^4

4 Conclusion

To solve the low optical damage resistant ability of $LiNbO_3$ crystal, In:Zn:$LiNbO_3$ crystals have been grown by doping In_2O_3 and ZnO in $LiNbO_3$ crystal. The In:Zn:$LiNbO_3$ waveguide substrates have been prepared by proton exchange. In the In:Zn:$LiNbO_3$ crystals and waveguide substrates, the optical damage resistant abilities of In(2mol.%):Zn:$LiNbO_3$ increase two orders of magnitude higher than those of pure $LiNbO_3$.

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