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Double-frequency properties of In:LiNbO$_3$ crystals

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1 mol%, 2 mol%, 3 mol%, 4 mol% and 5 mol% In^{3+} doped LiNbO$_3$ crystals were grown by the Czochralski method, respectively. Oxidized treatment of some crystals was carried out. The infrared transmission spectra and photo-damage resistance of the samples were measured. The results showed that the OH$^-$ absorption peaks of In(3mol%):LiNbO$_3$, In(4mol%):LiNbO$_3$ and In(5mol%):LiNbO$_3$ crystals were located at about 3508 cm^{-1}, while those of In(1mol%):LiNbO$_3$ and In(2mol%):LiNbO$_3$ crystals were located at about 3484cm^{-1}. When the doped In^{3+} concentration reached its threshold in LiNbO$_3$ crystal, photo-damage resistance of In:LiNbO$_3$ crystals was two orders of magnitude higher than that of pure LiNbO$_3$ crystal. The experimental results of the second harmonic generation (SHG) showed that the phase matching temperatures of In:LiNbO$_3$ crystals were lower than those of Zn:LiNbO$_3$ and Mg:LiNbO$_3$ crystals and the SHG efficiency reached 38%. Oxidization treatment was also found to make the dark trace resistance of crystals increase.

1 Introduction

Lithium Niobate (LiNbO$_3$) single crystal has excellent nonlinear optical properties, but its optical damage resistance is low [1, 2]. To improve the properties, different photo-damage-resistant impurities, i.e. Mg^{2+}, Zn^{2+} or In^{3+} ions, were doped in LiNbO$_3$ crystals. A small quantity of In^{3+} can significantly improve the photo-damage resistance of Lithium Niobate, whereas by doping Zn^{2+} or Mg^{2+} to improve its photo-damage resistance, much larger quantity of Zn^{2+} or Mg^{2+} was needed. When the doped In^{3+} reaches its threshold concentration, the photo-damage resistance of In:LiNbO$_3$ crystal is two orders of magnitude higher than that of undoped LiNbO$_3$ crystal, meanwhile the absorption peak of the infrared spectra shifts to 3484 cm^{-1} , for undoped LiNbO$_3$ crystals, it is at 3508 cm^{-1} [3,4]. And the phase matching temperature is also lower than those of Zn:LiNbO$_3$ and Mg:LiNbO$_3$ crystals [5, 6]. In this paper, we present the experimental results on LiNbO$_3$ crystals with different concentrations of In ions. Their photo-damage resistance and SHG were measured, and the creating mechanism of dark trace was discussed.

2 Experiments

2.1 Crystals growth and sample preparation

In (1mol%):LiNbO$_3$ (1#), In (2mol%):LiNbO$_3$(2#), In: (3mol%):LiNbO$_3$(3#), In (4mol%):LiNbO$_3$(4#) and In (5mol%):LiNbO$_3$(5#) crystals were grown along the c-axis by the Czochralski technique using an intermediate-frequency heating furnace. The melt composition was Li/Nb=48.6/51.4. The concentration of In$_2$O$_3$ was 0.5, 1, 1.5, 2 and 2.5 mol% in the melts, respectively. The pulling rate of crystals was 1-2 mm/h and the rotation rate was about 20 rpm. The grown crystals were all about φ30mm×30mm. After growth, the crystals were annealed

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to room temperature at a rate of 80K/h. The crystals were poled at 1200°C, and the poling current was 5 mA/cm^2. Then the crystals were cut into plates with $8\times8\times3(a\times c\times b)$ mm^3 perpendicular to y-axis of the crystals and polished on both sides using SiC powders and diamond paste. Some plates were oxidized at 1100°C for 10 h.

2.2 Infrared transmission spectra

The infrared transmission spectra of 1#, 3#, 5# in the range of 3400- 3600 cm^{-1} were obtained with a Fourier IR Spectrometer. Infrared transmission spectra of the samples are shown in Figure 1.

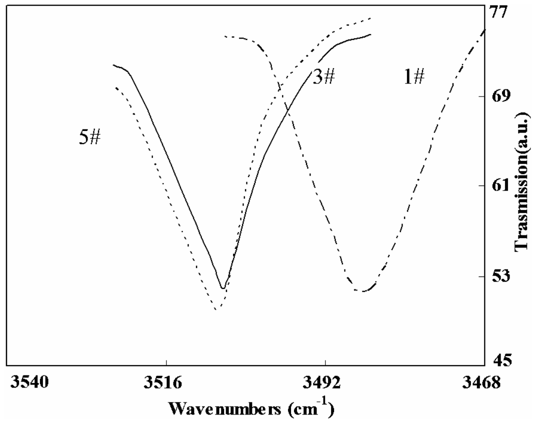

Fig. 1 Infrared transmission spectra of samples doped with different In ion concentrations.

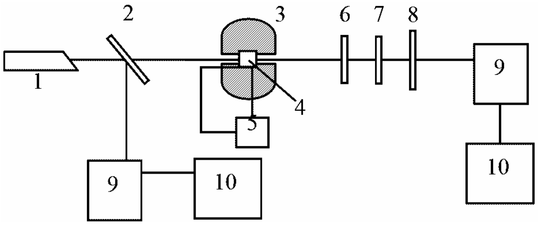

Fig. 2 Experimental setup for SHG measurement. 1: Laser, 2: Beam splitter, 3: Heater, 4: Sample, 5: Temperature controller, 6: 1.06μm reflective mirror, 7: Green glass, 8: 0.53μm interference light filter, 9: Energy detector, 10: Galvanometer.

2.3 Photo-damage resistance

The photo-damage resistance of In:LiNbO$_3$ crystals was measured by the transmission facular distortion method. That is, using focused laser beams irradiate the crystal, then cast the transmission laser beam to an observing screen, compare with the facular shape of the laser beam after the laser passes through and before it passes through the crystal and determine the photo-damage resistance. Taking the laser with the wavelength 488 nm as the light source, the laser power intensity which induces the distortion of the facular passing through the crystal is defined as the photo-damage resistance (R) of the crystal. The results were shown in table 1.

Table 1 Photo-damage resistance of crystals.

Crystal	R(w/cm^2)	T_{pm}(°C)	η(%)
1#	7.2×10^2	24	23
2#	3.3×10^3	37	31
3#	7.8×10^4	49	38
4#	4.6×10^4	53	34
5#	4.2×10^4	68	31

2.4 Second harmonic generation (SHG)

The experimental set-up [9] for the second harmonic generation measurement is shown in figure 2. A Nd:YAG laser with an output wavelength of 1.06μm and a nominal pulse width of 11.5 ns was employed. The front and back faces of samples were plated with reflection reducing coatings with wavelength of 1.06 μm and 0.53μm, respectively. The 2 mm long sample was placed in a small furnace with a precise temperature controller. The phase matching temperature T_{pm} was achieved by adjusting the temperature to make the SHG energy reach its maximum value. The SHG efficiency (η) was defined as the energy ratio of the SHG beam peak value to that of the fundamental beam. The measuring results of T_{pm} and η were also shown in Table 1.

When the crystal was illuminated by a laser with single pulse, the dependence of the SHG efficiency (η) on power intensity of the incident light is shown in Fig. 3.

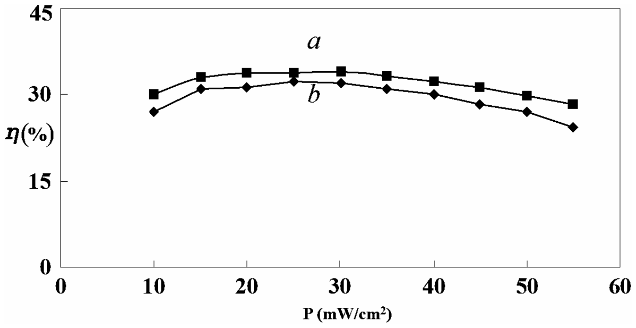

Fig. 3 Dependence of SHG efficiency (***η***) on power intensity of (a) Oxidized 3 # , and (b) As-grown 3 #.

2.5 Occurrence of dark trace

In the process of SHG, if the LiNbO$_3$ crystal was illuminated by a strong laser beam, there was a broad absorption band covering all visible light ranges, which is called the dark trace in the crystal. The dark trace will result in increase of the absorption of the double-frequency light and decrease of the SHG efficiency (η). In order to find the relationship of the dark trace between the ground-frequency light and double-frequency light, we used the Nd:YAG pulse laser with 1064nm wavelength to illuminate the crystal for a long time, but the dark trace was not observed. When the Nd:YAG pulse laser with 532nm wavelength was used to illuminate the crystal, the dark trace appeared in the crystal. But after stopping illuminating a few hours, the dark trace diminished.

3 Results and discussion

From Figure 1, it can be seen that the OH$^-$ vibration absorption peak of 1# sample is located at 3484cm^{-1}, while those of 3# and 5# are located at 3508 cm^{-1}. It is due to that the concentration of In^{3+} in 1# is below its threshold concentration, the In^{3+} ions occupy the antisite Nb (Nb$_{Li}$)$^{4+}$ sites or the Li$^+$ vacancies sites. The vibration of OH$^-$ is still the same as in a pure LiNbO$_3$ crystal. While In^{3+} ions in 3# and 5# are above the threshold concentration, the additional In^{3+} ions begin to occupy the Nb-sites, so the OH$^-$ vibration absorption peaks of 3# and 5# shift to 3508cm^{-1}.

The photo-damage resistance of 3# is two orders of magnitude higher than that of 1#. When In^{3+} in the LiNbO$_3$ exceeds its threshold concentration, In^{3+} ions replace all (Nb$_{Li}$)$^{4+}$ and some of In ions enter the Nb-sites and form (In$_{Nb}$)$^{-1}$. The electron-capturing ability of (In$_{Nb}$)$^{-1}$ is greatly decreased, so the photo-refractive effect of crystal decreases and the photo-damage resistance increases.

The measured phase match temperature T_{pm} of SHG is 49°C, which is lower than those of Mg:LiNbO$_3$ and Zn:LiNbO$_3$ crystals. Figure 3 shows the dependency of SHG efficiency (η) on the input laser power intensity. When the power intensity is lower, the SHG efficiency increases with the power intensity increasing. When power intensity reaches 30 mW/cm^2, the SHG efficiencies (η) reach the maximum values. For 3# (oxidization treatment), the maximum SHG efficiency is 35.5%, while the maximum SHG efficiency of 3# (as-grown) is 32%. And the efficiencies begin to decrease with power intensity increasing, dark traces occur in the crystals. The dark trace resistance of oxidized In (3mol%): LiNbO$_3$ is higher than that of as-grown In (3mol%): LiNbO$_3$ crystal. This is because that there are Li$^+$ vacancies and O vacancies (V$_o$, V$_o^-$) in LiNbO$_3$ [8-10]. Li$^+$ vacancies release cavities, which are captured by O vacancies. The absorption peaks of V$_o$ and V$_o^-$ capturing cavities are at 400nm and 520nm, respectively. The number of V$_o$ and V$_o^-$ in oxidized LiNbO$_3$ crystal is less than that in as-grow LiNbO$_3$ crystals. When 532 *nm* laser illuminates the crystal, only a small number of cavities are captured by the O vacancies. So the dark trace in the oxidized In (3mol%): LiNbO$_3$ crystal is weaker and the SHG efficiency is higher.

4 Conclusions

In this paper, different In:LiNbO$_3$ crystals were grown using the Czochralski method. Through the measurements, it was found that the OH$^-$ vibration absorption peaks of In(3mol%):LiNbO$_3$ and In

(5mol%):$LiNbO_3$ crystals are all located at 3508cm^{-1}, and the threshold concentration of In^{3+} in $LiNbO_3$ crystal was found below 3 mol%. The photo-damage resistance of the crystals is two orders magnitude higher than that of In (1mol%):$LiNbO_3$ crystal, whose quantity of In^{3+} is below the threshold. The SHG efficiency (η) of oxidized In (3mol%): $LiNbO_3$ crystal is higher than that of as-grown In(3mol%):$LiNbO_3$ crystals. And we also found that the occurrence of dark trace is a cooperative result of Li^+ vacancies and O vacancies.

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