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Photo-refractive properties of Mg:In:Fe:$LiNbO_3$ crystal

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Abstract

Mg:In:Fe:$LiNbO_3$ crystals were grown using the Czochralski technique by doping $LiNbO_3$ with MgO, In_2O_3 and Fe_2O_3. Infrared absorption spectra of the crystals were measured and the mechanisms underlying the OH^- absorption peak shift to shorter wavelengths were studied. The photo-refractive threshold of Mg:In:Fe:$LiNbO_3$ crystals was measured by direct observation of the transmission facula distortion. The photo-refractive properties of Mg:In:Fe:$LiNbO_3$ crystal were initially studied for the case when the concentration of co-doping with Mg^{2+} and In^{3+} ions was below their threshold level. It was found that the photo-damage threshold of Mg(3 mol%):In(2 mol%):Fe(0.06 wt%):$LiNbO_3$ crystals was two orders of magnitude higher than that of Fe:$LiNbO_3$.

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1. Introduction

$LiNbO_3$ is a potentially useful material for nonlinear-optical, electro-optical and piezoelectric applications due to its high mechanical and thermal stability and large electro-optical coefficients [1]. The $LiNbO_3$ devices are severely limited by the photo-damage effect when they are used at higher laser intensities, which induces the birefringence change and deforms the laser beams [2]. Some damage-resistant impurities have been discovered, such as Mg, Zn, In and Sc, which lead to an obvious decrease of the photo-damage effect in $LiNbO_3$ and they receive much attention [3]. On the other hand, the photo-refractive effect of pure $LiNbO_3$ crystals is weaker, which limits their application in the field of light amplification, holographic storage and phase conjugation. Yet impurities, such as Fe, Cu, Mn and Ce, in the crystal can increase its photo-refractive effect. Optimizing $LiNbO_3$ crystals for high resistance to photo-damage and strong photo-refractive effect by doping with damage-resistant impurities and sensitive impurities is very attractive for the device development [4]. In this work, Mg:In:Fe:$LiNbO_3$ crystals have been grown for the first time and their photo-refractive properties have been studied.

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2. Experimental

2.1. Preparation of Mg:In:Fe:$LiNbO_3$ crystals

Mg:In:Fe:$LiNbO_3$ crystals were grown by the Czochraski method from high-purity materials. The atomic ratio of Li to Nb was 0.946. The concentrations of MgO and Fe_2O_3 were 3 mol% and 0.03 wt%, respectively. The concentrations of In_2O_3 were 1, 2 and 3 mol%. The pulling rate was 1 mm/h along the c direction with a rotation rate of 20 rpm, and the position of the crucible was optimized to keep that axial interface temperature gradient of 30°C/cm. The crucible dimensions were ϕ 80 mm × 60 mm. The typical as-grown crystal size was 30 mm in diameter and 60 mm in height. The crystals were poled in another furnace where the temperature was held at about 1210°C with an applied DC electric current of 5 mA/cm^2. The single-domain crystals were cut into samples with a thickness of 2 mm along the c-axis.

2.2. Infrared absorption of Mg:In:Fe:$LiNbO_3$ crystals

The infrared transmission spectra of Mg:In:Fe:$LiNbO_3$ crystals were measured in the range of 3000–4000 cm^{-1} by a Fourier infrared spectrophotometer (Figs. 1 and 2).

The position of the OH^- absorption peak for a pure $LiNbO_3$ crystal is at 3482 cm^{-1} [5]. Our experimental results show that for Mg:In (1 mol%):Fe:$LiNbO_3$ crystals it peaks at 3483 cm^{-1}, while for the Mg:In(2 mol%):Fe:$LiNbO_3$ crystals the peak shifts to 3530 cm^{-1}. There exist intrinsic lattice defects, such as antisite Nb_{Li}^{4+} defects and Li^+ vacancies, in $LiNbO_3$ crystals. Li^+ vacancies attract H^+ ions due to their effective negative charge, which results in the H^+ accumulation around Li vacancies. Therefore, the absorption peak of OH^- of pure $LiNbO_3$ presumably mainly reflects the OH^- vibration around Li^+ vacancies. Mg^{2+} and In^{3+} dopants substitute for Nb_{Li}^{4+} defects and exist in the form of $(Mg_{Li})^+$ and $(In_{Li})^{2+}$ in $LiNbO_3$, while H^+ do not assemble being repelled by these defects. The referred absorption peak still reflects the OH^- vibration around Li^+ vacancies, but the position of the absorption peak of OH^- shifts slightly as explained below. The Mg^{2+} and In^{3+} dopants also replace Nb^{5+} and exist in the form of $(Mg_{Nb})^{3-}$ and $(In_{Nb})^{2-}$ centers in the crystal after completing the replacement of Nb_{Li}^{4+} defects. The concentration of Mg^{2+} and In^{3+} ions corresponds then to the concentration threshold value. $(Mg_{Nb})^{3-}$ and $(In_{Nb})^{2-}$ centers have a stronger attractive force for H^+ than Li^+ vacancies , which results in the H^+ drift to the $(Mg_{Nb})^{3-}$ and $(In_{Nb})^{2-}$ defects, and the shifted absorption peak reflects now the OH^- vibration around $(Mg_{Nb})^{3-}$ and $(In_{Nb})^{2-}$. In summary, the infrared absorption peak of $LiNbO_3$ doped with high concentrations of Mg^{2+} and In^{3+} shifts to shorter wavelengths.

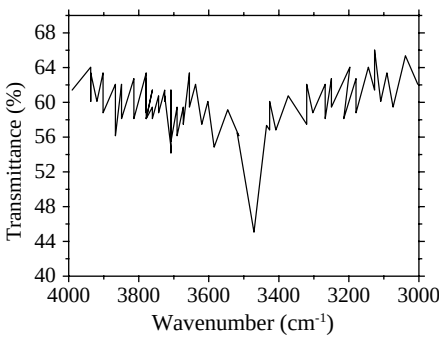

Fig. 1. IR optical transmission of Mg(3 mol%):In(1 mol) Fe(0.03 wt%):$LiNbO_3$.

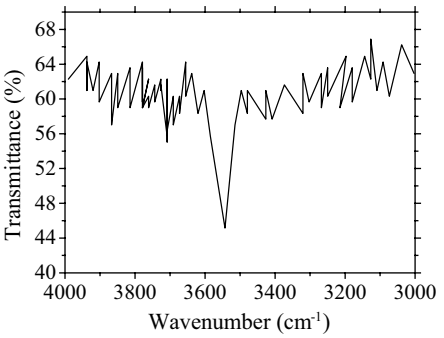

Fig. 2. IR optical transmission of Mg(3 mol%):In(2 mol) Fe(0.03 wt%):$LiNbO_3$.

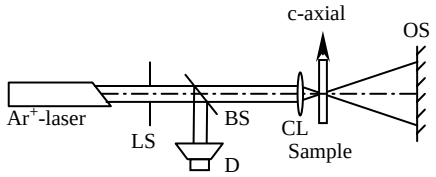

Fig. 3. Experimental setup of the photo-damage resistance ability (LS = light shed; BS = beam splitter; D = detector; CL = convex lens; OS = observation screen).

Table 1
Photo-damage threshold values of crystals

Crystal	R (W/cm^2)
Mg:In(1 mol%):Fe:LiNbO$_3$	7.70×10^3
Mg:In(2 mol%):Fe:LiNbO$_3$	4.15×10^4
Mg:In(3 mol%):Fe:LiNbO$_3$	4.25×10^4
Fe:LiNbO$_3$	1.10×10^2
LiNbO$_3$	2.71×10^2

2.3. Measurement of the photo-damage threshold value of crystals

The directly observed transmitted speckle method was used for the photo-damage evaluation (Fig. 3). An Ar^+ laser at the 514.5 nm wavelength was used as the light source, and its intensity could be controlled by the attenuator. The beam passed through the diaphragm of the lens and was then focused on the crystal.

When the laser intensity was low, the photo-damage phenomenon did not happen, i.e. the speckle was round. The photo-damage effect happened and the speckle was elongated along the c-axis of the crystal when the laser intensity increased to a certain value. The light intensity that made the speckle elongated was defined as the photo-damage threshold value R of the crystal. The experimental results are given in Table 1. Apparently, the photo-damage threshold value of Mg:In(2 mol%):Fe:LiNbO$_3$ and Mg:In (3 mol%):Fe:LiNbO$_3$ crystals are more than two orders of magnitude higher than that of Fe: LiNbO$_3$ crystals.

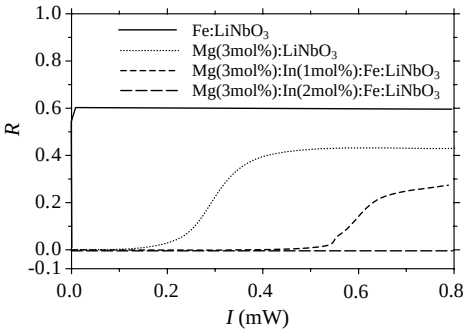

Fig. 4. Dependence of the ratio of the total power of photo-scattered noise I' on the intensity of illumination laser I.

3. Photo-refractive properties of Mg:In:Fe:LiNbO$_3$ crystals

The results obtained above show that the photo-damage resistance ability of Mg:In:Fe:LiNbO$_3$ is two orders of magnitude higher than that of Fe:LiNbO$_3$ crystals when all concentrations of Mg^{2+} and In^{3+} dopants in LiNbO$_3$ are higher than the concentration threshold value. However, the photo-scattered intensity I' depends strongly on the input light intensity I for the given Mg:In:Fe:LiNbO$_3$ crystal if all concentrations of Mg^{2+} and In^{3+} dopants in LiNbO$_3$ are below the concentration threshold value. Photo-scattered noise, which can be defined as the optical intensity that limits or distorts the hologram, was produced only when the input light intensity was higher than a certain value. Fig. 4 shows the intensity ratio, $R = I'/I$, in the crystals as a function of I.

The photo-scattered noise reflects the effect of the threshold value for the transmitted intensity which is called the threshold value effect of photo-scattered intensity, or the threshold value intensity. The threshold value intensity of doped Mg:In:Fe: LiNbO$_3$ crystals increases with increasing the ion concentration of damage-resistant impurities. Table 2 shows the threshold value intensities, diffractive efficiencies of gratings and refractive response times of the crystals with the Ar^+ laser operating at the 488 nm wavelength. The diffractive efficiency is defined by the ratio I'_s/I_s, where I' and I_s are the intensities of the diffracted and signal light, and the refractive response time describes the speed of grating formation and

Table 2
Photorefractive properties of Mg:In:Fe:$LiNbO_3$ crystals

Crystal	Threshold value intensity (mW)	Diffractive efficiency (%)	Response time (s)
Fe:$LiNbO_3$	0.1	75	120
Mg(3 mol%):$LiNbO_3$	20	65	55
Mg:In(1 mol%):Fe:$LiNbO_3$	50	55	45
Mg:In(2 mol%):Fe:$LiNbO_3$	200	20	18
Mg:In(3 mol%):Fe:$LiNbO_3$	220	18	17

erasure. The experimental setup for measuring these quantities is shown in Fig. 3.

The threshold intensity of Mg:In:Fe:$LiNbO_3$ crystals increases with the increasing concentration of In^{3+} and changes abruptly when the concentration of In^{3+} reaches its threshold value. The diffractive efficiency and response time decrease with the increasing concentration of In^{3+} when the concentration of In^{3+} is beyond its threshold value. The diffractive efficiency is only one fourth of Fe:$LiNbO_3$.

4. Conclusions

Mg:In:Fe:$LiNbO_3$ crystals have been grown for the first time by doping $LiNbO_3$ with damage-resistant impurities, Mg^{2+} and In^{3+}, and Fe. It is found that the photo-damage resistance ability, diffractive efficiency and response time of Mg:In:Fe:$LiNbO_3$ crystals is improved by adjusting the concentrations of In^{3+} and Mg^{2+} ions. The infrared transmission spectra of Mg:In:Fe:$LiNbO_3$ crystals have been also measured. It has been found that the position of the OH^- absorption peak of Mg:In(1 mol%):Fe:$LiNbO_3$ crystals is 3483 cm^{-1} (the same as $LiNbO_3$), but that of Mg:In(2 mol%):Fe:$LiNbO_3$ has shifted to 3530 cm^{-1}. The photo-damage threshold value of the crystals has been measured by direct observation of transmitted speckle patterns, and the photo-damage threshold value of Mg:In(2 mol%):Fe:$LiNbO_3$ crystals is two orders of magnitude higher than that of Fe:$LiNbO_3$ crystals, which shows that the concentration of In^{3+} and Mg^{2+} in crystal have reached their threshold value concentration. The photo-scattered noise shows the threshold value effect for the transmitted intensity when the concentrations of In^{3+} and Mg^{2+} in the crystal are below their threshold values.

Acknowledgements

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