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Effect of [Li]/[Nb] ratios on the photorefraction and scattering properties in In: Fe: Cu: $LiNbO_3$ crystals at 488 nm wavelength

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ABSTRACT

The high sensitivity, fast response and the high quality reconstructions are observed in various [Li]/[Nb] ratios In:Fe:Cu:$LiNbO_3$ crystals at 488 nm wavelength based on the two-beam coupling experiment. The strong blue photorefraction is contributed by the two-center effect and the remarkable characteristic of being in phase between the two gratings recorded in shallow and deep trap centers. The blue photorefraction is enhanced significantly with the increasing of [Li]/[Nb] ratios under the same experimental conditions. The sensitivity *S*" is reduced to 0.46 J/cm, simultaneously the response time is as fast as 4.4 s and the erase phenomenon is not obvious in In:Fe:Cu:$LiNbO_3$ crystals which [Li]/[Nb] ratio is 0.986 in crystal. Increasing [Li]/[Nb] ratios improve the damage-resistant ability of the crystals, but lead to a more serious beam fanning. Experimental results definitely show that the near-stoichiometric In: Fe: Cu: $LiNbO_3$ crystal becomes a promising candidate for blue photorefractive holographic recording.

1. Introduction

Lithium niobate ($LiNbO_3$, LN) crystal is one of the most important widely used photorefractive materials in holographic volume storage. Fe:$LiNbO_3$ is one of the most excellent candidate materials for optical data storage due to its high diffraction efficiency, high data storage density and long storage lifetime. However, several problems, such as long response time, low sensitivity and strong light-induced scattering, impede the application of Fe:$LiNbO_3$ crystal in holographic storage [1–3].

Doping different kinds of chemical elements is a direct and effective method to improve the photorefractive properties of $LiNbO_3$ crystals. Recently, the control of the [Li]/[Nb] ratio in $LiNbO_3$ crystals has been demonstrated to be another of key importance in the improvement of the photorefractive properties [4,5]. The near-stoichiometric $LiNbO_3$ (SLN) crystals have been attracted much attention in both scientific and application fields. Increasing the [Li]/[Nb] ratio in $LiNbO_3$ can greatly reduce the intrinsic defect concentration, and thus the response time can be shortened to the order of seconds in stoichiometric crystals. The response time is 100 ms in Chen XJ's work [6], and it hits 0.6 s in Kitamura's report [7]. Optical damage resistance is improved remarkably by 1.8 mol.% MgO doped $LiNbO_3$ crystal in near-stoichiometric composition [8]. The near-stoichiometric Mg-doped $LiNbO_3$ crystals have been widely studied, but there are few reports about photorefractive properties in In-doped near-stoichiometric $LiNbO_3$ crystals although In^{3+} ions play a special role in blue photorefraction [9]. In addition, to improve further the blue photorefraction of the doped $LiNbO_3$ crystals, the tri-doped In:Fe:Cu:$LiNbO_3$ crystals were act as the investigated samples, whose photorefractive properties can be enhanced contributed to the two-center effect of Cu and Fe traps [10].

In our previous published article of reference [11,12], the defect structure, the light-induced birefringence as well as the reduction/oxidation treatment on the blue photorefraction in the congruent In:Fe:Cu:$LiNbO_3$ crystals with different In^{3+} ions were investigated detailedly. And in [13], there are only two [Li]/[Nb] ratios samples were investigated and the beam fanning as well as the like-lens effect of the samples are not considered. To further optimize the photorefractive properties, in this paper, two-center doped In:Fe:Cu:$LiNbO_3$ crystal with various [Li]/[Nb] ratios of 0.946, 1.050, 1.200, and 1.380 was grown by the Czochralski method. The infrared OH^- absorption spectra was measured to investigate the defect structure of In:Fe:Cu:$LiNbO_3$ crystals. The diffraction efficiency, the recording sensitivity as well as the two-wave coupling gain were also investigated by using the two-wave coupling experiment. Meanwhile, the beam fanning and the like-lens effect as well as the reconstructed images of the crystals are investigated systematically. The experimental results show that the near-stoichiometric In:Fe:Cu:$LiNbO_3$ crystal is a promising recording materials in blue photorefraction.

2. Materials and Experiments

To obtain the two sensitive centers crystals in our experiments, $LiNbO_3$ crystals were grown in air by the Czochralski method and

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doped with 0.075 wt.% Fe_2O_3, 0.01 wt.% CuO and 0.5 mol.% In_2O_3 (1.0 mol.% In^{3+}), respectively. The raw material purity of the dopants is 99.999. The ratios of [Li]/[Nb] are 0.946, 1.050, 1.200 and 1.380 from the melts, respectively. The Li and Nb contents were analyzed by ICP-AES (inductively coupled plasma atomic emission spectrometry), and the results are shown in Table 1. In order to grow good quality crystals, the following optimum growth conditions were selected: the temperature gradient above the melt was 2.5 °C/mm, the pulling speed was 0.2 mm/h, and the seed rotation speed was 15 rpm, respectively. After growth, the crystal was cooled down to room temperature at a speed of 80 °C/h. All samples were poled in another furnace where the temperature gradient was almost equal to zero with a DC electric current density of 5 mA/cm^2 for 30 min. The crystals were cut to $20\times10\times1.8$ mm^3 and all sides were optically polished. The *c*-axis is along the longer edge. The positive direction of the c-axis was determined by the pyroelectric effect. No post-treatment was applied to the samples.

Because OH^- stretching vibration is sensitive to the change of the environment around the ion, the OH^- absorption spectra can be used as a probe for impurities. To investigate the defect structure of the doped $LiNbO_3$ crystals, the infrared transmission spectra of the crystals were measured in the spectra range 3000–4000 cm^{-1} by a Fourier spectrophotometer at room temperature. At the same time, the UV-Visible absorption spectra of the crystals in the range of 300-800 nm at room temperature has been introduced.

The photorefractive properties of the samples were investigated by using the typical two-wave coupling experimental setup. An extraordinarily polarized beam from Ar^+ ion laser (488 nm) is split into two recording beams with equal intensities, and both diameters are 1.0 mm. The two writing beams illuminate the crystal symmetrically so that the grating-vector of the interference pattern is aligned to the *c* axis of the crystal. The grating spacing is 0.53μm. Considering the surface reflection loss of the crystals, the effective intensity of the total recording beams in front of the crystal is 0.51 W/cm^2. The on and off status of each beam is controlled by electronic shutters. All the experimental procedures are performed at room temperature.

3. Results and discussion

3.1. OH^- absorption spectra and UV-Visible absorption spectra

Fig. 1 shows the OH^- absorption spectra of In:Fe:Cu:$LiNbO_3$ crystals with various [Li]/[Nb] ratios. The spectra of the crystals with [Li]/[Nb] ratios in crystal 0.917 and 0.932, present a broad non-symmetrical absorption band at approximately 3483 cm^{-1}. While for the crystals with [Li]/[Nb] ratios 0.974 and 0.986, the absorption bands are shifted directly to 3506 cm^{-1} with a narrow band. When the [Li]/[Nb] ratios change from 0.932 to 0.974, the absorption peak shifts to 3506 cm^{-1} directly, which indicates that the concentration of In ions reaches its threshold concentration and it will mostly probably occupy the Nb sites [14]. The threshold concentration of In^{3+} in In:Fe:Cu:$LiNbO_3$ crystal decreases with the increasing of the [Li]/[Nb] ratio. Although there is no 3466 cm^{-1} peak appears which indicates the crystal is close to the stoichiometric [15,16], the results show that the samples with 0.974 and 0.986 [Li]/[Nb] ratios are the near-stoichiometric crystals in 1.0 mol.% In^{3+}-doped Fe:Cu:$LiNbO_3$ crystals which the concentration of In^{3+} is below its threshold concentration (~3.0 mol.%) in congruent crystals.

Table 1
The blue photorefractive characteristics of the samples.

Crystals	[Li]/[Nb] in the melt	[Li]/[Nb] in crystal	η (%)	Δn ($\times10^{-5}$)	τ_w (s)	τ_e	S'' (J/cm)
In:Fe:Cu:	0.946	0.917	46.51	5.77	12.2	148.3 s	1.49
$LiNbO_3$	1.050	0.932	49.56	6.01	9.6	305.1 s	1.12
	1.200	0.974	56.85	6.57	7.9	209 days	0.85
	1.380	0.986	58.98	6.74	4.4	545 days	0.46

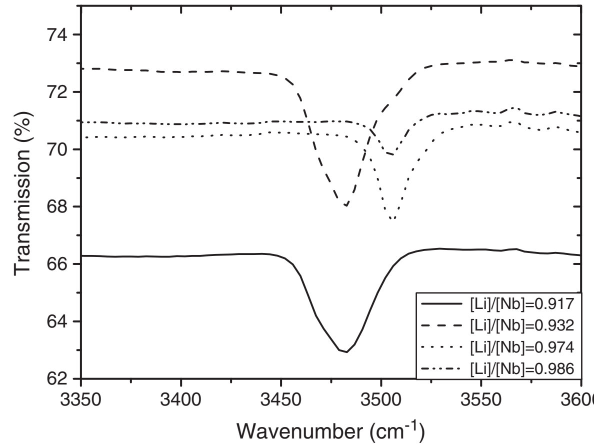

Fig. 1. OH^- absorption spectra of the crystals.

The UV-Visible absorption spectra of In:Fe:Cu:$LiNbO_3$ crystals with various [Li]/[Nb] ratios are presented in Fig. 2. From Fig. 2, it can be seen that the absorption coefficient of the doped crystals increases with the increasing ratios of [Li]/[Nb] except the crystal with [Li]/[Nb] = 0.917 which has the biggest absorption coefficient at 488 nm wavelength.

3.2. Blue photorefractive properties

The photorefractive properties are also investigated based on the two-beam coupling setup. During recording, one of the writing beams is blocked from time to time while the other writing beam is served as a readout beam to measure the diffraction efficiency of the written grating. The diffraction efficiency η of the grating is defined as $I_d/(I_d+I_t)$, in which I_d and I_t are the diffracted and transmitted light intensity, respectively. The typical recording and erasing curves are shown in Fig. 3. The temporal behavior of η during recording and erasing could be well described by the functions of $\sqrt{\eta(t)} = \sqrt{\eta_{sat}}\,[1-exp(-t/\tau_w)]$ and $\sqrt{\eta(t)} = \sqrt{\eta_{sat}}\,exp(-t/\tau_e)$, where η_{sat} is the saturation diffraction efficiency during recording, τ_w and τ_e are the recording (response time) time constant and erase time constant, respectively.

The experimental results are summarized in Table 1, in which the amplitude of refractive index change Δn is calculated from diffraction efficiency η according to $\eta = \sin^2[\pi\Delta n d/(\lambda\cos\theta)]$ [17], where α is the absorption coefficient, λ is the free-space wavelength, d is the effective interaction length, and θ is the Bragg angle of the readout

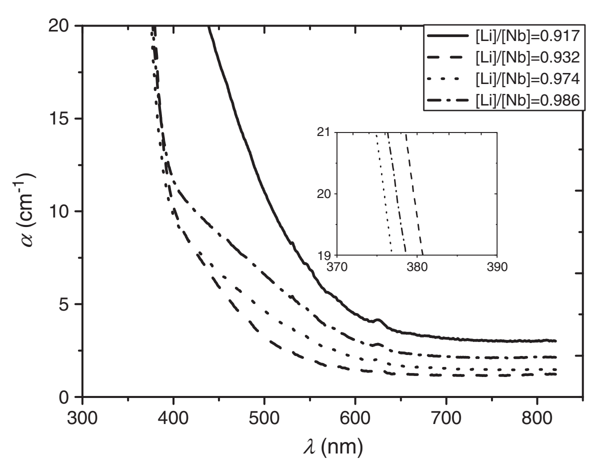

Fig. 2. Optical absorption spectra of the crystals.