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Effect of Li/Nb ratio on growth and photorefractive properties of Ce:Fe:$LiNbO_3$ crystals

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Abstract

Ce:Fe:$LiNbO_3$ crystals with different Li/Nb ratios in the melts (Li/Nb = 0.94, 1.0, 1.1, 1.2, 1.44) have been grown for the first time. The absorption spectra, exponential gain coefficient, diffraction efficiency, response time and photoconduction of the crystals were measured. The lattice constants of the crystals were obtained from the measurement of X-ray. With the ratio of Li/Nb increasing, the lattice constants and diffraction efficiency decrease, but the exponential gain coefficient, response time and photoconduction increase.

Keywords: Ce:Fe:$LiNbO_3$; Li/Nb ratio; Crystal growth; Photorefractive; Absorption spectra

1. Introduction

Ce:Fe:$LiNbO_3$ is possessed of the excellent photorefractive properties [1] and is a promising material for applying in holographic storage [2,3]. The crystal is easily grown in large dimension, and has high diffraction efficiency and long information conservation time. However, the long response time and weak photodamage resistance ability restrict its application. We have grown Ce:Fe:$LiNbO_3$ crystals from melts with different Li/Nb ratio [4] and probed into the influences of Li/Nb ratios on lattice constants [5], the absorption spectra and photorefractive properties (exponential gain coefficient, diffraction efficiency, response time and photoconduction).

2. Experimental and results

2.1. Sample preparation

Ce:Fe:$LiNbO_3$ crystals were grown along *c* axis from the melt with the ratio of Li/Nb of 0.94, 1.0, 1.1, 1.2 or 1.44 in a platinum crucible by the Czochralski method. The starting materials were Li_2CO_3, Nb_2O_5, CeO_2 and Fe_2O_3 with a purity of 99.99% or higher. The dopant concentrations of CeO_2 and Fe_2O_3 were 0.10 and 0.03 wt.%, respectively. After mixed fully, the raw materials were filled in a platinum crucible. The axis temperature gradient of the furnace used to grow crystals was 40 °C/cm. The pulling rates to grow Ce:Fe:$LiNbO_3$ were different with Li/Nb ratio, such as 2 mm/h was adopted for the Li/Nb ratio below 1, 1 mm/h for the Li/Nb ratio of 1.1 and 1.2, and the 0.1 mm/h for Li/Nb ratio of 1.44. The

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rotation rates were 10–25 rpm. After experimented by thermal–electric effect, it was found that the as-grown Ce:Fe:$LiNbO_3$ obtained from the melt with the Li/Nb ratio of 1.44 was single domain, but other crystals still were multi-domain. After the crystals with multi-domain were poled, all crystals were cut into wafers for being used in our experiments. Some wafers were oxidized or reduced before used.

2.2. Structure measurement of Ce:Fe:$LiNbO_3$

The phase analyses of sample powders were carried on by a D/max-YB mode X-ray diffractometer. The measurement conditions were the wavelength of 15.405000 nm, copper target and tube voltage/tube current of 40 kV/50 mA. The lattice constants were calculated on a computer by the method of minimum squares for every sample. The results are shown in Table 1. The samples were signed with 1# to 5# instead of Ce:Fe:$LiNbO_3$ grown from the melts with the Li/Nb ratio of 0.94, 1.0, 1.1, 1.2 and 1.44, respectively. It can be seen from the table that the lattice constants decrease with the ratio of Li/Nb increasing for Ce:Fe:$LiNbO_3$.

2.3. Absorption spectra

An UV–Visible-Spectrophotometer of CARY mode was used to measure the absorption spectra of the samples with the thickness of 2 mm. The results of the measurement are shown in Fig. 1. In the spectra diagram, the absorption edges shift to violet more with the ratio of Li/Nb increasing.

2.4. Measurements of photorefractive properties

The exponential gain coefficient is one of the important indicators to evaluate the photorefractive properties of crystals, which represents the ability to transit energy from the pump light with high power to signal light. The exponential gain coefficient Γ can be gained by

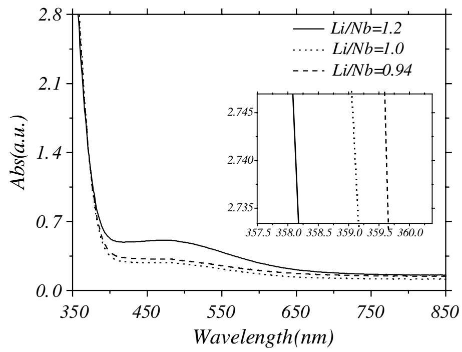

Fig. 1. Absorption spectra of samples.

$$\Gamma = \frac{1}{d}\ln\frac{I_1' I_2}{I_1 I_2'} \tag{1}$$

where d is the thickness of the sample, I_1 and I_2 (I_1' and I_2') is the transmitted light intensity of signal beam and pump beam with (without) coupling, respectively. When the intensity of pump beam is much larger than that of signal beam, i.e. $I_2 \gg I_1$, the exponential gain coefficient Γ is independent of the intensity of pump light ($I_2 \approx I_2'$)

$$\Gamma = \frac{1}{d}\ln\frac{I_1'}{I_1} \tag{2}$$

The diffraction efficiency is one important parameter for crystal used in holographic storage. The diffraction efficiency η is defined as the ratio of the intensity of the diffracted beam I' and the transmitted beam I, i.e.

$$\eta = (I'/I) \times 100\% \tag{3}$$

During erasure of a grating, the photoconduction acts as the main role. At this time, the diffusion field E_{SC} in crystals is

Table 1
Lattice constants of Ce:Fe:$LiNbO_3$ with different Li/Nb ratio

	Sample				
	1#	2#	3#	4#	5#
a (nm)	51.4511	51.4261	51.4257	51.4130	51.3953
b (nm)	51.4511	51.4261	51.4257	51.4130	51.3953
c (nm)	138.4608	138.4429	138.4213	138.2983	138.2983

Table 2
Experimental results of two-wave coupled for $Ce:Fe:LiNbO_3$ doped with different Li/Nb ratio $LiNbO_3$

Sample	Treatment	α (cm^{-1})	d (mm)	Γ (cm^{-1})	2θ (deg)	N_{eff} (cm^{-3})
Li/Nb = 0.94	Reduced	1.64	0.9	30.5	17.2	2.1×10^{15}
Li/Nb = 1.0	Reduced	1.79	0.9	32.0	16.8	2.3×10^{15}
Li/Nb = 1.1	Reduced	1.74	0.9	33.4	20.6	2.5×10^{15}
Li/Nb = 1.2	Reduced	1.82	0.9	34.3	21.7	3.1×10^{15}
Li/Nb = 1.44	Reduced	1.75	0.9	36.2	20.5	3.2×10^{15}
Li/Nb = 0.94	Heavily reduced	2.80	0.8	33.0	28.3	3.1×10^{15}
Li/Nb = 0.94	As-grown	1.34	0.9	16.7	17.2	1.2×10^{15}
Li/Nb = 0.94	Oxidized	1.60	0.9	9.8	16.2	0.8×10^{15}

$Ce:Fe:LiNbO_3$ with different Li/Nb ratio only sign the Li/Nb ratio, λ is the wavelength of the light source, α is the absorption coefficient, d is the thickness of the samples, 2θ is the included angle between the pump light beam and the signal light beam and N_{eff} is the density of the effect carrier.

$$E_{SC}(x,t) = E_{SC}(x)e^{-\sigma_{ph}t/\varepsilon} \tag{4}$$

Because the diffraction efficiency $\sqrt{\eta}$ is nearly the direct proportion to the diffusion field E_{SC}, above equation can be changed to by the logarithmic transformation

$$\ln(\eta/\eta_0) = \frac{2\sigma_{ph}}{\varepsilon}t + \text{constant} \tag{5}$$

where η_0 is the maximum of the diffraction efficiency, σ_{ph} is the photoconduction, and ε is the dielectric constant of the material. It can be seen from Eq. (5) that σ_{ph} is the slope rate of the line $\ln(\eta/\eta_0) \sim 2t/\varepsilon$ [6].

The two-wave coupling light path method was used to measure the photorefractive properties of the samples. An Ar^+ laser operating at 488.0 nm with the polarizing direction in the incident plane was used as the light source. The diameter of pump light beam and signal light beam was 3 and 1 mm, respectively. The intensity of the pump light beam was 2.12 W/cm^2, and the modulation index of 1830 was selected. All the experimental results are shown in Tables 2 and 3.

Table 3
Holographic properties of samples

Sample	η (%)	τ (s)	σ_{ph} (Ω^{-1} cm^{-1})
1#	76.3	138	3.1×10^{-15}
2#	72.2	94	1.2×10^{-15}
3#	70.3	72	3.2×10^{-15}
4#	67.2	34	4.3×10^{-15}
5#	62.4	23	6.0×10^{-15}

3. Discussions

From above mentioned experiments, one can see many regularizing phenomena: with the Li/Nb ratio increasing in $Ce:Fe:LiNbO_3$ crystals, the absorption edge shifts to violet more, the exponential gain coefficient, the density of effect carrier and photoconduction increase, the response time shortens, the diffraction efficiency decreases and so on. All phenomena are relative with the ratios of Li/Nb. In the congruent $LiNbO_3$ crystals, because Li/Nb = 0.94 < 1, there exists an intrinsic defect, Li vacant site. In order to keep the electrical neutrality, a part of Nb occupy Li site to form another intrinsic defect, anti-site Nb (Nb_{Li}^{4+}). Nb_{Li}^{4+} decrease in $LiNbO_3$ crystals with the ratios of Li/Nb ratio increasing. Because the radius of Li^+ is smaller than that of Nb_{Li}^{4+}, the lattice constants decrease with the ratio of Li/Nb increasing. Because the absorption edge shifts to violet with Li/Nb ratio increasing, the photo scattering resistance ability of $Ce:Fe:LiNbO_3$ is improved with Li/Nb ratio increasing. The diffraction efficiency decreases and response time is shortened due to the photoconduction increasing. The exponential gain coefficient increases owing to the intrinsic defects decreasing.

Concludingly, the intrinsic defect decreasing can improve the photorefractive properties, so the doped stoichiometric $LiNbO_3$ is the promising crystal material used in holographic storage. The further work is proceeding.

4. Conclusions

$Ce:Fe:LiNbO_3$ crystals have been grown from the melt with the different ratios of Li/Nb. With the ratios of Li/Nb increasing, the lattice constants decrease, absorption edge shifts to violet, the exponential gain coefficient and photoconduction increase, response time is shortened, but the diffraction efficiency decreases a little. All these are induced by the intrinsic defects decreasing in Ce:Fe:$LiNbO_3$ crystals. Ce:Fe:$LiNbO_3$ crystals grown from high Li/Nb melt with good quality are more promising materials used in the holographic storage than congruent Ce:Fe:$LiNbO_3$ crystals.

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