

Growth and optical properties of Zn:Ce:Cu:LiNbO₃ single crystals

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Abstract

A series of congruent crystals Zn:Ce:Cu:LiNbO₃ crystals doped with Zn(0,3,5,7 mol%) were grown by using Czochralski method. OH[−] vibrational band and fundamental absorption edge were used to deduce the defect structure. Photorefractive properties were measured by two-wave coupling and light induced scattering experiments. It was found that the response and erasure time shorten with the increase of Zn doping concentration, whereas threshold intensity to optical damage of Zn(7 mol%):Ce:Cu:LiNbO₃ was two orders of magnitude higher than that of Ce:Cu:LiNbO₃. In this paper, site occupation mechanism of impurities were also discussed to explain the high resistance ability to optical damage and fast response speed in the Zn:Ce:Cu:LiNbO₃ crystal.

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1. Introduction

Lithium niobium (LiNbO₃) crystals, with excellent non-linear optical and photorefractive properties, have been extensively applied to volume holographic storage, piezoelectric, electro-optic, waveguide and non-linear optical devices [1–4]. Doping with photorefractive sensitivity elements (Fe [5], Ce [6], Mn [7], Cu [8], etc.) can effectively improve photorefractive effect in LiNbO₃, but long response time and strong light-induced scattering are also induced [9]. When these crystals are used as holographic storage media, the lower quality of the storage information limited its application. To solve this question, suppress the generation of noise, reduce the bit error rate, and improve

resistance ability to light-induced scattering, Zn can be doped into LiNbO₃ [10].

When LiNbO₃ crystal is applied to holographic storage, the other key problem is that the phase grating can be erased by the readout light of symmetrical intensity [11]. To achieve the non-volatile recording in LiNbO₃, Liu et al. [12] found it can be realized two-center reading in Ce:Cu:LiNbO₃. However, the response time and resistance ability to optical damage of Ce:Cu:LiNbO₃ cannot meet the challenges. In this paper, Zn²⁺ ions doped into Ce:Cu:LiNbO₃ crystals can significantly improve the resistance ability to optical damage and shorten the response time.

2. Experimental

2.1. Crystal growth and sample preparation

Zn:Ce:Cu:LiNbO₃ crystals were grown from congruent melts by the conventional Czochralski (CZ) method. The

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Table 1
Ratio and composition of raw materials

Crystals	Ce:Cu:LiNbO ₃	Zn:Ce:Cu:LiNbO ₃	Zn:Ce:Cu:LiNbO ₃	Zn:Ce:Cu:LiNbO ₃
Zn ₂ O ₃ (mol%)	0	3	5	7
Ce ₂ O ₃ (wt%)	0.1	0.1	0.1	0.1
CuO (wt%)	0.02	0.02	0.02	0.02
[Li]/[Nb] (mol ratio)	0.946	0.946	0.946	0.946
Growth atmosphere	Air	Air	Air	Air

starting materials were all ultrapure. Compositions of the raw materials were shown in Table 1.

The crystals were pulled along [001] direction at a rate of 1–2 mm/h and rotating rate of 10–20 rpm, and the axial temperature gradient of the IF furnace was 30–35 °C/cm. After growth, the crystals were cooled down to room temperature at a rate of 60 °C/h. Then, the crystals were polarized in another resistive furnace in which the temperature gradient was almost close to zero using an applied DC electric density of 5 mA/cm² for 30 min at 1200 °C. All as-grown crystals appeared to be transparent, crack-free, and inclusion-free. Lastly, from the middle of the crystals, some slices were cut into the size of 10 × 2 × 10 mm³ ($x \times y \times z$). The (010) faces were ground using SiC powder and then polished to optical grade using a 0.25 μm diamond solution for experimental characterization.

2.2. Measurement

The infrared transmittance spectra of the crystals were measured by Fourier conversion infrared spectrophotometer with a wave number range of 3000–4000 cm^{−1} at room temperature. The ultraviolet–visible absorption spectra of the Zn:Ce:Cu:LiNbO₃ were recorded by using CARYIE style UV–visible spectrophotometer with a wavelength range of 300–900 nm.

The photorefractive properties were measured by two-wave coupling method including dependence of photoconductivity on light intensity, diffraction efficiency, erasure time and so on. The experimental setup was shown in Fig. 1 and a He–Ne laser with wavelength of 632.8 nm was used.

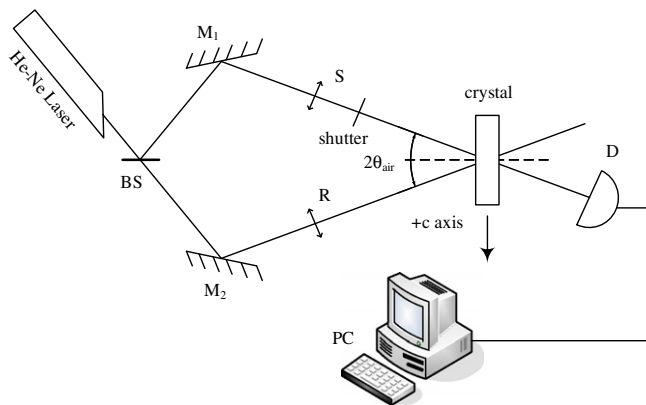


Fig. 1. Light path scheme of two-beam coupling experiment: BS: beam splitter; M₁, M₂: mirrors; D: detector; S: signal beam; R: reference beam; PC: personal computer.

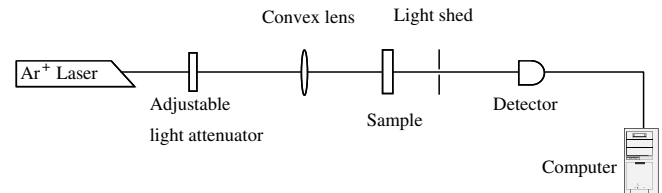


Fig. 2. Experimental setup of the light-scattering resistance ability.

Light-induced scattering experiment was used to measure the optical damage resistance ability for the Zn:Ce:Cu:LiNbO₃ crystals. The experimental setup was shown in Fig. 2. A He–Ne laser beam (wavelength $\lambda = 632.8$ nm), whose intensity can be controlled by an adjustable light attenuator and its polarizing direction was parallel to the c -axis, irradiated to the samples after convergence through the convex lens. The crystals were deposited on the focal plane of the lens.

3. Spectroscopy

3.1. Infrared transmittance spectra

Infrared transmittance spectra of the crystals are shown in Fig. 3. The OH[−] absorption peaks of Ce:Cu:LiNbO₃, Zn(3 mol%):Ce:Cu:LiNbO₃ and Zn(5 mol%):Ce:Cu:LiNbO₃ are located at about 3484 cm^{−1}. However, the OH[−] absorption peak of Zn(7 mol%):Ce:Cu:LiNbO₃ is at 3529 cm^{−1}.

The infrared transmittance spectra of the crystals mainly reflect the vibrational absorption peak change of OH[−] combined with the defect group and can be considered as a probe of crystal defect structure [13]. Many intrinsic defects, such as anti-site niobium Nb_{Li}⁴⁺ and lithium vacancy V_{Li}[−], existed in the congruent LiNbO₃ crystals. The H⁺ ions segregated at lithium vacancy V_{Li}[−] due to their electronegativity and formed V_{Li}[−]–OH[−] complexes. When the concentration of Zn ions is under threshold in the Zn:Ce:Cu:LiNbO₃, Zn²⁺ replace Nb_{Li}⁴⁺ to form Nb_{Li}⁺. The H⁺ do not segregate at Zn_{Li}⁺, because of being repelled. So the vibration absorption peak still kept at about 3484 cm^{−1}. When the concentration of Zn ions exceeds its threshold value, all Nb_{Li}⁴⁺ were replaced completely and a part of Zn²⁺ ions occupying Nb_{Li}⁵⁺ and Li⁺ site formed Zn_{Nb}^{3−} and Nb_{Li}⁺ defects, respectively. The H⁺ ions drifted to Zn_{Nb}^{3−} defects because they have a much stronger attraction to H⁺ than V_{Li}[−]. It is mainly responsible for OH[−]

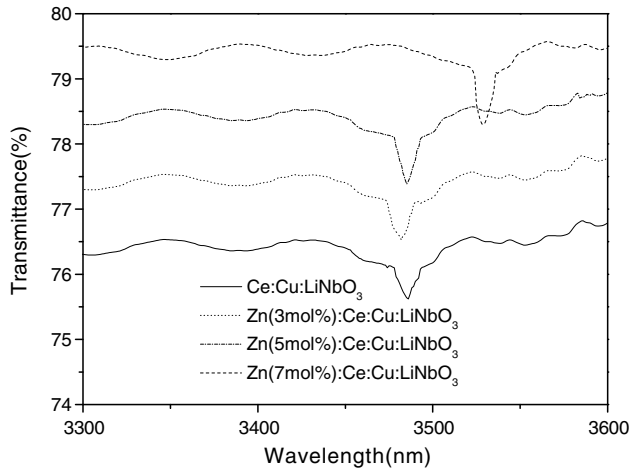


Fig. 3. The infrared absorption spectra of Zn(0, 3, 5, and 7 mol%):Ce:Cu:LiNbO₃ crystals.

absorption peak of 3529 cm⁻¹ that the Zn³⁺-OH⁻ complexes were formed.

3.2. Ultraviolet–visible absorption spectra

The non-polarized light ultraviolet–visible absorption spectra of the crystals were shown in Fig. 4. When the concentration of Zn ions is under threshold in Zn:Ce:Cu:LiNbO₃ crystals, the absorption edges shifted to the violet band compared with that of the Ce:Cu:LiNbO₃. The absorption edges of Zn(7 mol%):Ce:Cu:LiNbO₃ shifted to longer wavelength compared with that of Zn(5 mol%) crystals.

It was well known that the absorption edge in LiNbO₃ corresponds to energy of the electron transition from the valence band(p state of the oxygen ion) to the conduction band(d state of the transition-metal niobate ions). Therefore, the intensity of the Nb–O bond will affect the energy gap between the valence band and the conduction band, i.e. forbidden band gap [14]. When Both Ce ions and Cu ions were incorporated into the lattice of crystal, two valences

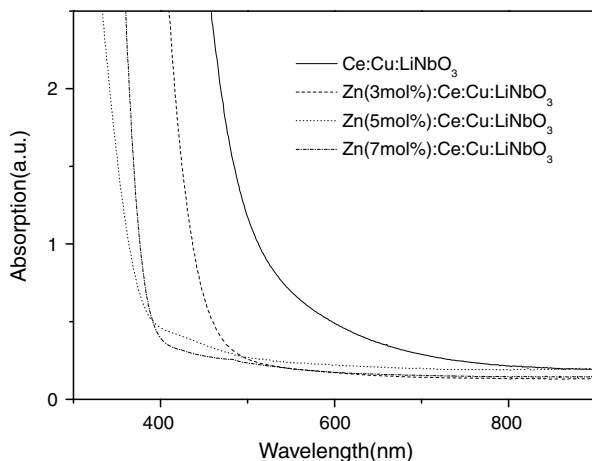


Fig. 4. Absorption spectra of Zn(0, 3, 5, and 7 mol%):Ce:Cu:LiNbO₃ crystal.

of Ce and Cu substituted Li ions and occupied Li sites. Some defects formed including Cu_{Li}²⁺, Ce_{Li}³⁺, Cu_{Li}⁺, Cu_{Li}²⁺, and so on. The concentration of V_{Li}⁻ increased for the charge balance. This increased the deformation level of the electron clouds of oxygen ions and resulted in a decrease in the energy gap since the polarization ability of Ce and Cu ions was greater than that of the Li ions. Therefore, The absorption edge of Ce:Cu:LiNbO₃ shifted to longer wavelength compared with the undoped LiNbO₃. When Zn ions were doped into Ce:Cu:LiNbO₃ below the threshold concentration, Zn ions preferentially replaced anti-site Nb ions and located at Nb_{Li}⁴⁺ sites. The width of forbidden band gap increase because of the decrease of Nb_{Li}⁴⁺ concentration and the presence of Nb_{Li}⁴⁺ defects, which resulted in the absorption edge of Zn(3, 5 mol%):Ce:Cu:LiNbO₃ shifted to shorter wavelength. When the Zn-doped concentration was increased over the threshold, after all the Nb_{Li}⁴⁺ were replaced completely, the additional Zn ions occupied Li and Nb sites, and most of Ce and Cu ions were pushed to Nb sites. The absorption edge shifted to longer wavelength because the arisen Zn_{Nb}³⁺-3Zn_{Li}⁺ defects increase the width of forbidden band gap.

4. Photorefractive properties

4.1. Dependence of photoconductivity on light intensity

The photoconduction can be describing as [15]

$$\tau_c = \frac{\epsilon\epsilon_0}{\delta_d + \delta_{ph}} \quad (1)$$

where τ_c is the dielectric relaxation time, $\epsilon\epsilon_0$ is the dielectric constant of LiNbO₃, δ_d and δ_{ph} are dark conductivity and photoconductivity, respectively. Because δ_d can be neglected for $\delta_d \ll \delta_{ph}$ in our measurement, the $1/\tau_c$ is proportional to δ_{ph} . So the light intensity dependence of the photoconductivity can be determined by measuring the erasure time at different light intensities. The results were shown in Fig. 5. From the Fig. 5, the photoconductivity were proportional to the light intensity though there were two photorefractive center in Zn:Ce:Cu:LiNbO₃ crystals [16]. It implied that there is only one level of participating in the photorefractive process under the experimental condition. The results show that the photoconduction increased with the increase of the Zn doped concentration under the identical light intensity, and the fast response speed can be obtained with the higher Zn doped concentration in Zn:Ce:Cu:LiNbO₃ crystals.

4.2. Diffraction efficiency

Diffraction efficiency η was defined as the ratio between the diffractive and transmitting intensities, i.e.,

$$\eta = \frac{I_d}{I_d + I_t} \quad (2)$$

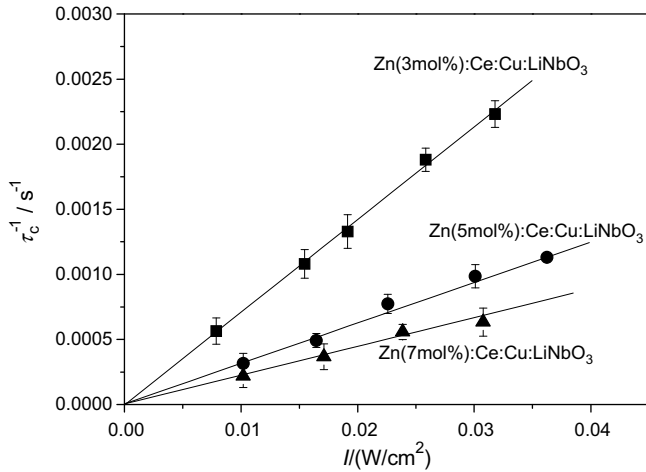


Fig. 5. Dependence of light intensity on erasure time in Zn:Ce:Cu:LiNbO₃.

where I_t is the transmitting intensity of signal beam before the grating was built and I_d is the diffractive intensity of signal beam after the grating was built. Using Kogelnik's formula [17]

$$\eta_{\max} = \sin^2 \left(\frac{\pi d \Delta \eta_{\text{sat}}}{\lambda \cos \theta_{\text{cry}}} \right) \quad (3)$$

where $\eta_{\max}$ is the maximum of diffraction efficiency, d is the thickness of the sample, λ is the signal light wavelength, θ_{cry} is an angle of incident light, the saturated photorefractive index change $\Delta \eta_{\text{sat}}$ can be calculated. After diffraction efficiency of holographic gratings had reached its maximum value in the experiment, the signal beam was blocked and the reference beam was saved to erase the gratings. Erasure time τ_e was defined as time interval from $\eta_{\max}$ to that diffraction efficiency reached $\eta_{\max}/e$, where $\eta_{\max}$ was the maximum of diffraction efficiency. The results of the diffraction efficiency and erasure time were listed in Table 2. From Table 2, it can be observed that the diffraction efficiency, erasure time and photorefractive index change decreased with the increase of Zn doping concentration.

4.3. Light-induced scattering

To estimate the ability of these crystals to resist photorefractive, resistance ability R to optical damage was defined as the ratio of the light scattered intensity I' to the incident light intensity I , $R = I'/I$ in the crystals as a function of I . Fig. 6 shows the results of the ratio R depend

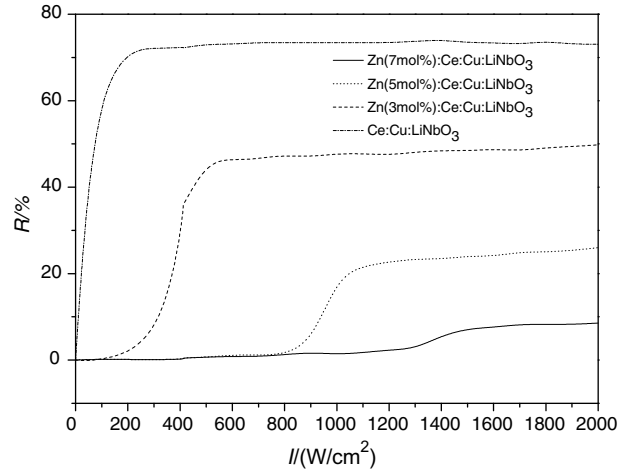


Fig. 6. Dependence of the ratio R of the light-scattered intensity to the incident light intensity vs. the incident light intensity.

on the incident light intensity. Threshold intensity induced by the transmitted beam scattering increases with an increase of Zn doping concentration. When the Zn doping concentration reached 7 mol% in the Zn:Ce:Cu:LiNbO₃ crystals, the threshold intensity was two orders of magnitude higher than that of Ce:Cu:LiNbO₃. Furthermore, the light scattered intensity to the high Zn doping was also much weaker than that of the Ce:Cu:LiNbO₃ even if the incident intensity were over the threshold intensity.

5. Results and discussion

According to a expression $\Delta \eta \approx AK\alpha I / (\delta_d + \delta_{ph})$ ($\delta_d \ll \delta_{ph}$), where A is the generalized electro-optical coefficient, k is the Glass constant, α is the optical absorption coefficient, I is the light intensity, and δ_d and δ_{ph} are dark conductivity and photoconductivity, respectively, the photorefraction $\Delta \eta$ can be obtained to explain the experimental results of photorefractive properties [18,19], because it is possible to reduce optical damage by increasing only photoconductivity in our experiment. The photorefraction decreases with an increase of cationic vacancy photoconductivity, whereas the photovoltaic current is almost unvaried. In Ce and Cu co-doped LiNbO₃ crystals, Ce⁴⁺ and Cu²⁺ are the dominant electron acceptor. A reduced capture section of Ce⁴⁺ and Cu²⁺ are responsible for the observed increase in photoconductivity. If the concentration of Ce⁴⁺ and Cu²⁺ acceptor were negligible, Nb⁴⁺ would be the most probable electron acceptor in the congruent LiNbO₃. From the above discussion in Sections 3.1 and 3.2, when the concentration of Zn in Zn:Ce:Cu:LiNbO₃ crystals was below the Zn²⁺ threshold concentration, Ce⁴⁺ and Cu²⁺ ions still occupied Li sites, thus the Ce⁴⁺ and Cu²⁺ ions did not lose their electron acceptor properties. The increase of photoconductivity was aroused by the concentration of Nb⁴⁺ decreasing since the Zn²⁺ ions replaced. Nb⁴⁺ However, the resistance ability to optical damage of Zn(3 mol%, 5 mol%):Ce:Cu:LiNbO₃ did not noticeably improve despite

Table 2
Experimental results of diffraction efficiency and erasure time

Sample	$\eta_{\max}$ (%)	t_e (S)	$\Delta \eta_{\text{sat}}$ (10^{-5})
Ce:Cu:LiNbO ₃	68.2	981	6.43
Zn(3 mol%):Ce:Cu:LiNbO ₃	56.4	847	5.62
Zn(5 mol%):Ce:Cu:LiNbO ₃	43.5	468	4.76
Zn(7 mol%):Ce:Cu:LiNbO ₃	36.7	313	4.30

the increase in photoconductivity [see Table 2 and Fig. 6]. As the Zn doping level were up to 7 mol%, after all $\text{Nb}_{\text{Li}}^{4+}$ were replaced completely, both Ce^{4+} and Cu^{2+} were pushed to Nb sites and lose their electron acceptor properties since $\text{Ce}_{\text{Nb}}^{2-}$ and $\text{Cu}_{\text{Nb}}^{3-}$ were electronegative. So the capture section of Ce^{4+} and Cu^{2+} decreases significantly, which drastically increased in photoconductivity. Therefore, the resistance ability to optical damage of the $\text{Zn}(7 \text{ mol}\%):\text{Ce}:\text{Cu}:\text{LiNbO}_3$ crystal was much higher than that of the other crystals [see Fig. 6]. Because increased photoconductivity indicated that motion of photo-induced charge carriers would become fast and the space charge field form faster, photorefractive response speed become fast.

6. Conclusion

In this paper, crack-free and inclusion-free $\text{Zn}:\text{Ce}:\text{Cu}:\text{LiNbO}_3$ single crystals were grown by using Czochralski method. From the experimental results of the OH^- vibrational band and fundamental absorption edge, we can deduce that Zn^{2+} ions initially occupied $\text{Nb}_{\text{Li}}^{4+}$ sites and then replaced Li and Nb sites when Zn doping was up to the threshold concentration (7 mol%). Simultaneously, Ce^{4+} and Cu^{2+} were repelled to Nb sites from Li sites and lost their electron acceptor properties. This aroused an increase in photoconductivity. Therefore, in $\text{Zn}(7 \text{ mol}\%):\text{Ce}:\text{Cu}:\text{LiNbO}_3$, response time and erasure time shorten, and the threshold intensity to optical damage was two orders of magnitude higher, in comparison with the $\text{Ce}:\text{Cu}:\text{LiNbO}_3$.

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