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INFLUENCE OF POST-TREATMENT ON OPTICAL PROPERTIES OF $Sc:Ce:Cu:LiNbO_3$ CRYSTALS

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The congruent Sc(3 mol%):$Ce:Cu:LiNbO_3$ single crystals were grown by the Czochralski method and three kinds of different samples were prepared by proper reduction or oxidation post-treatment processes. The extrinsic defect structures of samples were determined by infrared transmittance spectra. Two-wave coupling and light induced scattering experiments were used to measure the photorefractive properties. It is found that the reduction treatment made erasure time and diffraction efficiency decrease, but light-induced scattering resistance increase; the inverse case occurred with oxidation treatment. Analysis indicated that photoconductivity change was responsible for photorefractive properties.

Keywords: $Sc:Ce:Cu:LiNbO_3$; post-treatment; photorefractive properties.

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1. Introduction

Doped lithium niobium ($LiNbO_3$) crystals, with excellent nonlinear optical and photorefractive properties, have been extensively applied to volume holographic storage, piezoelectric, electro-optic, waveguide and nonlinear optical devices.[1–4] Doping with photorefractive sensitivity elements (Fe,[5] Ce,[6] Mn,[7] Cu,[8] etc.) would increase the photorefractive effect of $LiNbO_3$, but cause long response times and strong light-induced scattering, which confined its application in practice. To solve this problem, optical damage resistant impurities, such as MgO,[9,10] ZnO,[11] In_2O_3,[12] and Sc_2O_3,[13] were introduced into the crystals. In addition, post-treatment processes (oxidation or reduction) are also alternative methods to change the photorefractive properties. For example, the exponential gain coefficient of Ce:Fe:$LiNbO_3$ and the sensitivity of Mg:Mn:Fe:$LiNbO_3$ can be enhanced by the reduction treatment.[14,15]

Liu *et al.*[16] found that nonvolatile holographic recording can be realized in Ce:Cu:$LiNbO_3$ crystals. However, the response time of the Ce:Cu:$LiNbO_3$ crystals are long. Because of Sc^{3+} ions can significantly improve the light-induce scattering resistance and decrease the response time, we doped Sc^{3+} (3 mol%) ions into Ce:Cu:$LiNbO_3$ crystals and studied their photorefractive properties after different post-treatment processes. In addition, the influence of post-treatment processes on the properties is also discussed.

2. Experimental Details

2.1. *Crystal growth and sample preparation*

Sc(3 mol%):Ce(0.1 wt%):Cu(0.02 wt%):$LiNbO_3$ single crystals were grown from congruent melt by the conventional Czochralski (CZ) method using an intermediate frequency (IF) furnace. The starting materials used to grow the crystal were CeO_2, CuO, Sc_2O_3, Li_2CO_3 and Nb_2O_5 with the purity of 99.99%. The ratio of $Li/Nb = 0.946$ (molar ratio) was selected as melt composition.

The crystals were pulled along the [001] direction at a rate of 2 mm/h and a rotating rate of 15–25 rpm. 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. The crystals were then polarized in another resistive furnace in which the temperature gradient was almost close to zero applying DC electric density of 5 mA/cm^2 for 30 min at 1200°C. The as-grown crystal was transparent, crack-free, and inclusion-free. Finally, the crystals were sliced along the y-side with the size of $10 \times 2 \times 10$ mm^3 ($a \times b \times c$). Some of samples were buried into Li_2CO_3 powder to be reduced at 550°C for 30 h, and some were buried into Nb_2O_5 powder to be oxidized at 1150°C for 24 h. The samples were ground using SiC powder and then polished to optical grade using a 0.25 m diamond solution.

2.2. *Measurement*

The infrared transmittance spectra of the samples were measured by Fourier conversion infrared spectrophotometer with a wave number range of 3000–4000 cm^{-1}

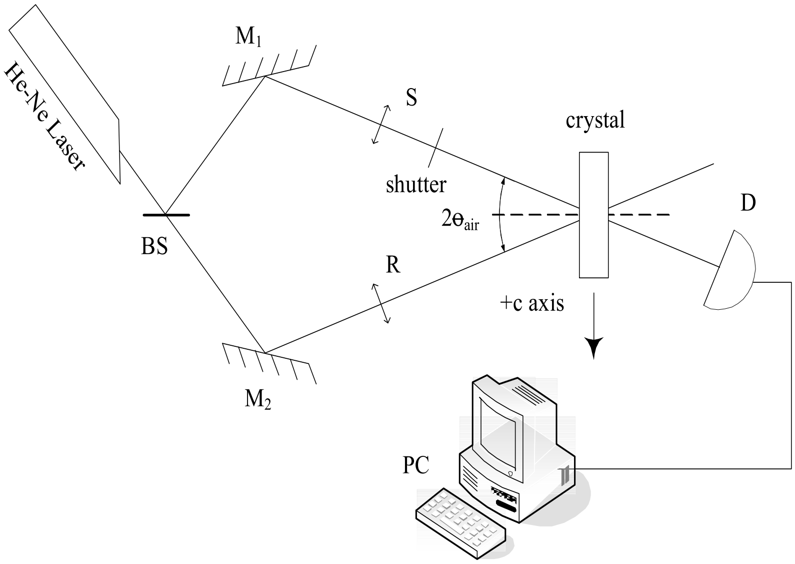

Fig. 1. Light path scheme of two-beam coupling experiment: BS: beam splitter; M1, M2: mirrors; D: detector; S: signal beam; R: reference beam; PC: personal computer.

at room temperature. The photorefractive properties, such as diffraction efficiency and erasure time, were measured by two-wave coupling method. The experimental setup is shown in Fig. 1 and a He–Ne laser with wavelength of 632.8 nm was used.

Light-induced scattering was used to characterize the resistance ability to the optical damage for the Sc:Ce:Cu:$LiNbO_3$ crystals. The experimental setup is shown in Fig. 2. A He–Ne laser beam with wavelength 632.8 nm was used to irradiate the samples after convergence through the convex lens. The He–Ne laser beam intensity can be controlled by an adjustable light attenuator and its polarizing direction was parallel to the *c*-axis. The crystal was placed on the focal plane of the lens.

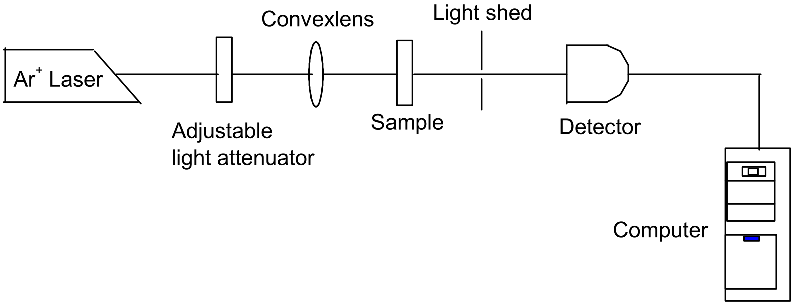

Fig. 2. Experimental setup of the light-scattering resistance ability.

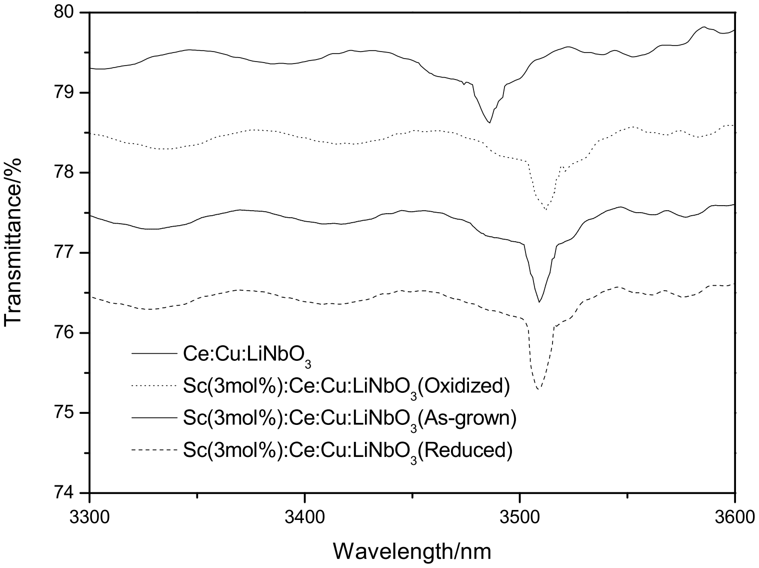

Fig. 3. Infrared transmittance spectra of Sc(3 mol):Ce:Cu:$LiNbO_3$ under different treatments.

3. Results and Discussion

3.1. *Infrared transmittance spectra*

The infrared transmittance spectra of crystals are shown in Fig. 3. The OH^- absorption peak of Ce:Cu:$LiNbO_3$ is located at 3484 cm^{-1}. After post-treatment, the OH^- absorption peaks of Sc(3 mol%):Ce:Cu:$LiNbO_3$ are at about 3510 cm^{-1} as well as as-grown sample. This indicates that the Sc concentration in samples is over the threshold and the post-grown treatments do not influence the defect structure. When Sc ions exceed its threshold concentration, it took priority of replacing anti-site Nb. Subsequently, the additional ions begin to replace Nb sites forming Sc_{Nb}^{2-} defects and Ce and Cu ions at Li sites were repelled to Nb sites. The H^+ in the OH^-–V_{Li}^- complexes are attracted by Sc_{Nb}^{2-} defects forming OH^-–Sc_{Nb}^{2-} complexes because Sc_{Nb}^{2-} defects have a stronger attraction to H^+ than V_{Li}^-, which is responsible for the absorption peak at about 3510 cm^{-1}.

3.2. *Dependence of photoconductivity on light intensity*

The photoconduction can be described as[17]

$$\tau_c = \frac{\epsilon\epsilon_0}{\sigma_d + \sigma_{ph}} \tag{1}$$

where τ_c is the dielectric relaxation time, $\epsilon\epsilon_0$ is the DC dielectric constant along the direction of the grating wave vector K, σ_d and σ_{ph} are dark conductivity and photoconductivity, respectively. σ_{ph} can be neglected for $\sigma_d \ll \sigma_{ph}$ in our measurement, i.e. $1/\tau_c$. The results of light intensity dependence on the photoconduction are shown

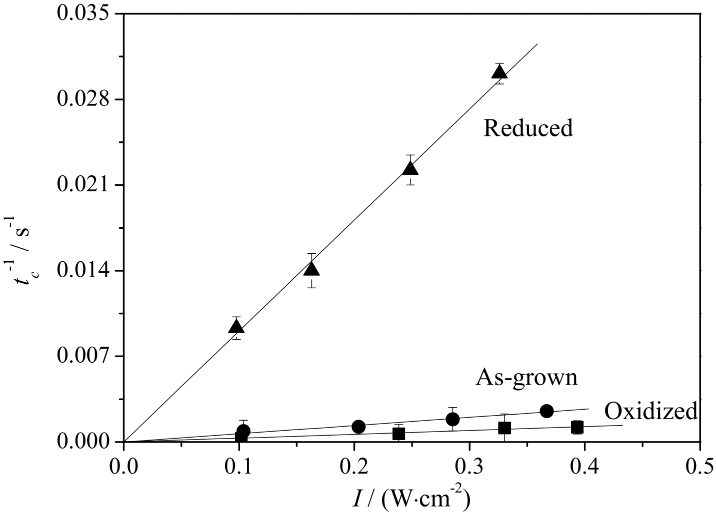

Fig. 4. Dependence of light intensity on erasure time in Sc(3 mol%):Ce:Cu:LiNbO$_3$ crystal with oxidation or reduction.

in Fig. 4. It is observed that the photoconductivity was proportional to the light intensity though there were two photorefractive centers in the Sc:Ce:Cu:LiNbO$_3$ crystals. It implied that there is only one energy level taking part in the photorefractive process under the experimental condition.[18] The results indicated that the photoconduction of reduced Sc:Ce:Cu:LiNbO$_3$ crystal is the highest, that of oxidized smallest under the identical light intensity. Higher photoconductivity implied that the carrier moved faster and the response time decreased.

The Ce^{3+} and Cu^{+} are the most probable electron donors in the Sc:Ce:Cu:LiNbO$_3$, whereas the Ce^{4+} and Cu^{2+} are electron acceptors. The free electron concentration of the reduced sample is the highest compared with that of the oxidized and the as-grown samples because concentration of the donors (Ce^{3+} and Cu^{+}) is the highest. According to the formula $\sigma_{\mathrm{ph}} = e\mu_e N_e$,[19] where e is the electronic charge, μ_e is electron mobility, N_e is average (DC) electron concentration in the conduction band, it can be inferred that the photoconductivity of the reduced sample is the highest, which is responsible for the shortest response time. Therefore, it is necessary for shortening response time to perform the reduction treatment.

3.3. *Diffraction efficiency*

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

$$\eta = \frac{I_{\mathrm{d}}}{I_{\mathrm{d}} + I_{\mathrm{t}}} \tag{2}$$

Table 1. Experimental results of the diffraction efficiency and erasure time.

State	$\eta_{\max}/(\%)$	$T_e/(s)$	$\Delta_{\text{sat}}/(10^{-5})$
Reduction	17.3	30	2.84
As-grown	31.2	313	3.92
Oxidation	35.4	548	4.22

where I_{t} is the transmitting intensity of the signal beam before the grating was built and I_{d} is the diffractive intensity of the signal beam after the grating was built. Using Kogelnik's formula[20]

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

where η is the maximum of diffraction efficiency, d is the sample thickness, λ is the signal light wavelength, θ_{cry} is half of the included angle between incident lights, the saturated photorefractive index change Δn can be calculated. After diffraction efficiency of holographic gratings reached maximum value in the experiment, the signal beam was blocked and the reference beam was kept to erase the gratings. The erasure time τ_e can be obtained by fitting the erasing curve. The results of the diffraction efficiency, erasure time, and the saturated photofractive index change are listed in Table 1.

The experimental results show that for the reduction sample, the erasure time is much shorter in comparison with that of the as-grown and the oxidized, whereas the oxidized crystal presented the highest diffraction efficiency. Because the donor concentration decreased after oxidization, the photoconductivity of Sc:Ce:Cu:LiNbO$_3$ is much smaller and the saturated photorefractive index change is much higher compared with that of the as-grown and the reduced states. The decreasing photoconductivity is responsible for the long erasure time, and the increasing saturated photorefractive index change resulted in the maximal diffractive efficiency increasing.

3.4. *Light-induced scattering*

The light-induced scattering ability resistance R is defined as the ratio between the scattered light intensity I' and the incident light intensity I, i.e., $R = I'/I$, as a function of I. Figure 5 gives the results of R depend on the incident light intensity. The experimental results showed that the light-induced scattering resistance ability increased significantly by doping Sc in comparison with that of the Ce:Cu:LiNbO$_3$ sample, and that the light-induced scattering did not occur until the incident light intensity reached a certain value. The reduction treatment made the light-induced scattering resistance ability increase; inversely, the oxidation treatment made it decrease. According to the expression $\delta\Delta n = (n_e^3)[Kj_{\text{ph}}/(\sigma_{\text{d}} + \sigma_{\text{ph}})](\sigma_{\text{d}} \ll \sigma_{\text{ph}})$, where n_e is the extraordinary light refractive index, K is the electro-optical

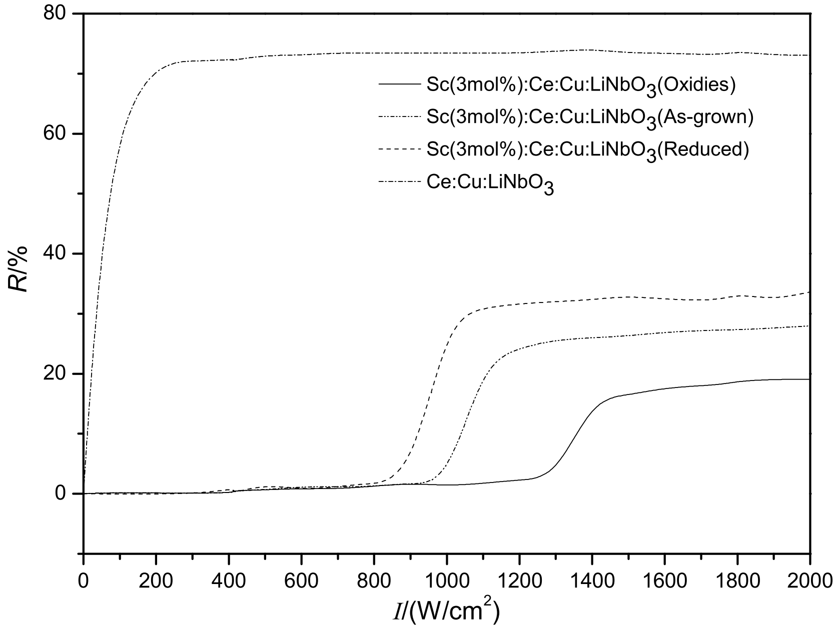

Fig. 5. Dependence of light intensity on erasure time in Sc(3 mol%):Ce:Cu:LiNbO3 crystal with oxidation or reduction.

coefficient, j_{ph} is the photogalvanic current, and σ_{d} and σ_{ph} are dark conductivity and photoconductivity, respectively, the photorefractive index change Δn is proportional to the ratio of the photogalvanic current to the photoconductivity.[21] The reduction treatment increased the photoconductivity because of larger carrier mobility and less electron traps of Ce^{4+} and Cu^{2+}. So the increasing photoconductivity is primarily responsible for the increasing light scattering resistance and the decreasing diffraction efficiency. However, the oxidation treatment caused the inverse effect.

4. Conclusion

In this paper, crack-free and inclusion-free Sc:Ce:Cu:LiNbO3 single crystals were grown by using the Czochralski method. The crystals have higher light-induced scattering resistance ability and shorter response time compared with that of Ce:Cu:LiNbO3. The infrared transmittance spectra indicated that the defect structures are not influenced by the post-treatment. However, the reduction treatment makes the photoconductivity increase, which results in shorter erasure time and lower diffraction efficiency, but higher light-induced scattering resistance ability. The oxidized treatment makes the diffraction efficiency and erasure time increase, but reduced the light-induced scattering resistance ability. It is clear that proper post-treatment is of key importance for improving the photorefractive properties of Sc(3 mol%):Ce:Cu:$\mathrm{LiNbO_3}$.

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