

# Nonvolatile photorefractive holographic recording in Sc:Ce:Cu:LiNbO<sub>3</sub>

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## Abstract

In this paper experimental studies of nonvolatile photorefractive holographic recording in Ce:Cu:LiNbO<sub>3</sub> crystals doped with Sc(0,1,2,3 mol%) were carried out. The Sc:Ce:Cu:LiNbO<sub>3</sub> crystals were grown by the Czochralski method and oxidized in Nb<sub>2</sub>O<sub>5</sub> powders. The nonvolatile holographic recording in Sc:Ce:Cu:LiNbO<sub>3</sub> crystals was realized by the two-photon fixed method. We found that the recording time of Sc:Ce:Cu:LiNbO<sub>3</sub> crystal became shorter with the increase of Sc doping concentration, especially doping with Sc(3 mol%), which exceeds the so-called threshold, and there was little loss of nonvolatile diffraction efficiencies between Sc(3 mol%):Ce:Cu:LiNbO<sub>3</sub> and Ce:Cu:LiNbO<sub>3</sub> crystals.

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**Keywords:** Sc:Ce:Cu:LiNbO<sub>3</sub> crystal; Two-photon fixed method; Holographic recording

## 1. Introduction

Holographic storage in photorefractive crystal [1–3] has high storage density owing to three-dimensional storage and a high readout rate owing to parallel retrieval. The maximal storage and treatment capacity of the volume photo-refractive recording are 10<sup>12</sup> bit/cm<sup>2</sup>, which are four orders of magnitude higher than that of the two-dimensional recording [4]. Now, a key problem is that the phase grating is erased by the readout light of symmetrical intensity and thus the recorded hologram is erased [5]. Using Ce:Cu:LiNbO<sub>3</sub> crystal, Liu et al. [6] had achieved the non-volatile recording by means of two-photon fixed method and they found that the oxidized Ce:Cu:LiNbO<sub>3</sub> crystal has both the capacities of nonvolatile holographic recording and high signal-to-noise ratio reconstruction. But the recording time of the Ce:Cu:LiNbO<sub>3</sub> crystal was still long. We doped Sc in Ce:Cu:LiNbO<sub>3</sub> to grow Sc:Ce:Cu:LiNbO<sub>3</sub> for improving these properties. The two-wave coupling diffraction efficiency of the crystals was measured and we found that the recording time of Sc:Ce:Cu:LiNbO<sub>3</sub> crystals became shorter with the increase of Sc doping concentration, especially in Sc(3 mol%), which exceeds the so-called threshold

concentration and there was little loss of nonvolatile diffraction efficiencies between Sc(3 mol%):Ce:Cu:LiNbO<sub>3</sub> and Ce:Cu:LiNbO<sub>3</sub> crystals.

## 2. Crystals growth

The Sc(0,1,2,3 mol%):Ce:Cu:LiNbO<sub>3</sub> crystals were grown by Czochralski technique, containing 0.02 wt% of Cu and 0.1 wt% of Ce. The ratio of Li to Nb was 0.946. The crystals were placed in a furnace for polarizing at electric current intensity 5 mA/cm<sup>2</sup> for 30 min at 1200°C and annealing for 8 h to room temperature. The crystals were poled at 1200°C and were cut into wafers with a dimension of 10 × 10 × 3.4 mm<sup>3</sup>. All wafers were oxidized in Nb<sub>2</sub>O<sub>5</sub> powders to be oxidized at 1100°C for 24 h, as listed in Table 1.

## 3. Spectra of Sc:Ce:Cu:LiNbO<sub>3</sub> crystals

### 3.1. Infrared absorption spectra of Sc:Ce:Cu:LiNbO<sub>3</sub> crystals

The water in the raw material and air makes the H<sup>+</sup> ions enter the crystal and form O–H–O during the course of crystal growing. The infrared absorption band of OH<sup>−</sup> is near 3500 cm<sup>−1</sup> [7]. The infrared absorption spectra

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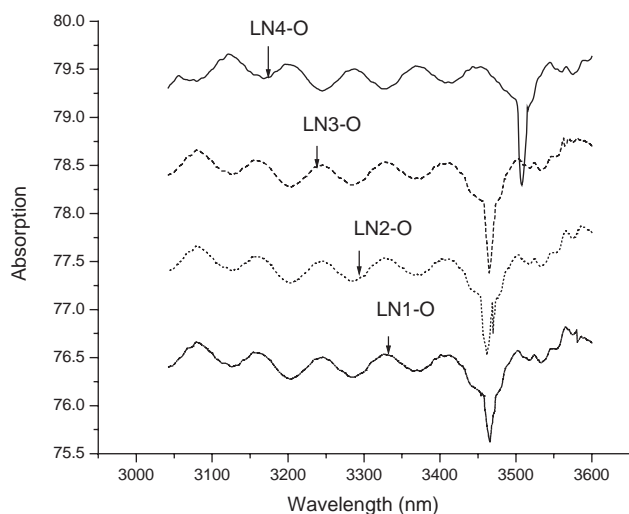
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Table 1

The doped Sc:Ce:Cu:LiNbO<sub>3</sub> crystal samples in experiment

Crystals	Composition	Dopant in starting melt
LN1-O	LiNbO <sub>3</sub> :Ce:Cu	0.02 wt%CuO, 0.1 wt%Ce <sub>2</sub> O <sub>3</sub>
LN2-O	LiNbO <sub>3</sub> :Sc:Ce:Cu	0.02 wt%CuO, 0.1 wt%Ce <sub>2</sub> O <sub>3</sub> , 1 mol%Sc <sub>2</sub> O <sub>3</sub>
LN3-O	LiNbO <sub>3</sub> :Sc:Ce:Cu	0.02 wt%CuO, 0.1 wt%Ce <sub>2</sub> O <sub>3</sub> , 2 mol%Sc <sub>2</sub> O <sub>3</sub>
LN4-O	LiNbO <sub>3</sub> :Sc:Ce:Cu	0.02 wt%CuO, 0.1 wt%Ce <sub>2</sub> O <sub>3</sub> , 3 mol%Sc <sub>2</sub> O <sub>3</sub>

Fig. 1. The infrared absorption spectra of Sc(0,1,2,3 mol%):Ce:Cu:LiNbO<sub>3</sub> crystals.

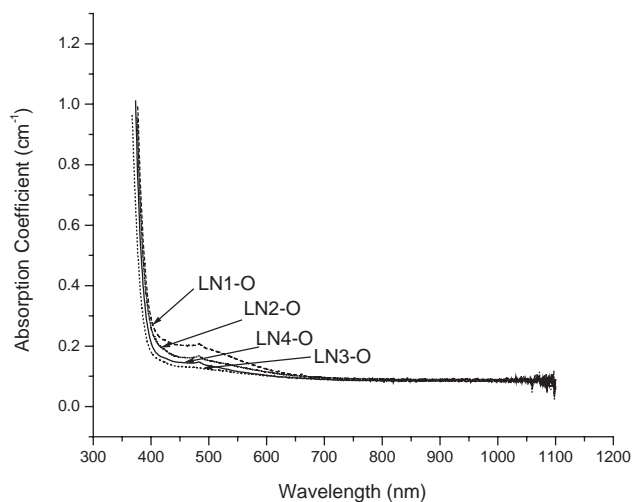
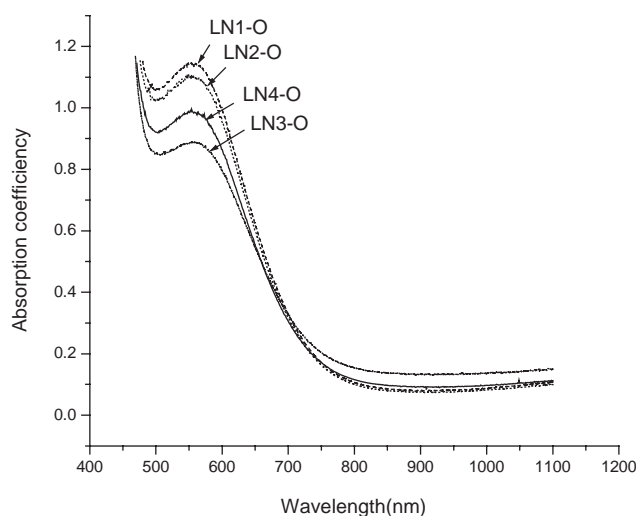
of crystals were measured by Fourier spectrophotometer from the range of 3000–3600 cm<sup>-1</sup>. The results are shown in Fig. 1. The OH<sup>-</sup> absorption bands of Sc(0,1,2 mol%):Ce:Cu:LiNbO<sub>3</sub> crystals are at 3484, 3486, 3488 cm<sup>-1</sup>, respectively. However, the OH<sup>-</sup> absorption band of Sc(3 mol%):Ce:Cu:LiNbO<sub>3</sub> is at 3510 cm<sup>-1</sup>.

### 3.2. Absorption spectra of Sc:Ce:Cu:LiNbO<sub>3</sub> crystals

Figs. 2 and 3 show absorption spectra of Sc(0,1,2,3 mol%):Ce:Cu:LiNbO<sub>3</sub> crystals with and without UV light with non-polarized light in wavelength 300–1000 nm. The UV light at  $\lambda = 313$  nm was obtained by filtering an Hg–Xe lamp which has several characteristic peaks in the range of 300–500 nm.

As shown in Fig. 2, the absorption edges of Sc(1,2,3 mol%):Ce:Cu:LiNbO<sub>3</sub> crystals shift to the violet with the increase of Sc doping concentration comparing with Ce:Cu:LiNbO<sub>3</sub> crystals. However, comparing with Sc(2 mol%):Ce:Cu:LiNbO<sub>3</sub>, the absorption edge of Sc(3 mol%):Ce:Cu:LiNbO<sub>3</sub> shifts to the red.

In Fig. 3, we found that when illuminated with UV light, visible absorption bands centered near 550 nm were observed. The observed photo-induced absorption band might be due to the valence charge of Ce<sup>3+</sup> ions. The photochromic

Fig. 2. Absorption spectra of Sc(0,1,2,3 mol%):Ce:Cu:LiNbO<sub>3</sub> crystal.Fig. 3. Absorption spectra of Sc(0,1,2,3 mol%):Ce:Cu:LiNbO<sub>3</sub> crystal with UV light.

process in Sc:Ce:Cu:LiNbO<sub>3</sub> can be understood in terms of the photo-induced charge transfer of an electron from Ce<sup>3+</sup> shallow traps in the crystal to Cu<sup>2+</sup> deep traps via the conduction band. Fig. 4 illustrates a possible charge transfer mechanism of Sc:Ce:Cu:LiNbO<sub>3</sub>. The photo-excited electrons will be first captured on the Ce<sup>3+</sup> shallow traps, fol-

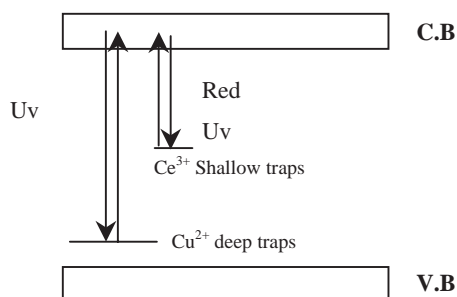


Fig. 4. Charge transfer mechanism of Sc:Ce:Cu:LiNbO<sub>3</sub>. CB, conduction band; VB, valence band.

lowed by a series of de-trapping and trapping before they are ultimately trapped on the Cu<sup>2+</sup> deep traps.

#### 4. Nonvolatile two-color holographic recording

In this experiment, these crystals were pre-exposed to the UV light (intensity, 0.03 W/cm<sup>2</sup>) for 1 h. Then two-color recordings were carried out in Sc(0,1,2,3 mol%):Ce:Cu:LiNbO<sub>3</sub> crystals at  $\lambda = 633$  nm together with the UV light. A He–Ne laser ( $\lambda = 633$  nm) was split into two beams of equal intensity, with each being 20 mW/cm<sup>2</sup>. These two beams of extraordinary polarization were made to intersect symmetrically inside the crystal of 3.4 mm thickness so that the grating vector is parallel to the crystal *c*-axis. In the process of recording, one of the recording beams was blocked by a shutter from time to time, so that we could use the other recording beam to monitor the grating buildup process and to measure the diffraction efficiency  $\eta$ . Here  $\eta$  was defined as  $I_d/(I_d + I_t)$ , where  $I_d$  and  $I_t$  were the diffracted and transmitted intensities of the readout beam, respectively. A few percent of diffraction efficient could be achieved. The experimental setup is shown in Fig. 5.

Fig. 6 illustrates the evolution of diffraction efficiency during recording and readout. The grating could be erased by illumination with the readout beam plus gating beam, or the gating beam only.

As shown in Fig. 6, the diffraction efficiencies suffer a substantial decrease at the initial stage of readout process and then remain constant. This is because in the oxidation state, many of the Cu<sup>2+</sup> deep traps have enough empty traps to store a hologram and thus after recording, the UV light is switched off; the red light initially removes the electrons from the Ce<sup>3+</sup> shallow traps until all of them are trapped in Cu<sup>2+</sup> deep traps and readout becomes nonvolatile. In Table 2, some characteristic parameters of holographic storage in the oxidation state of Sc(0,1,2,3 mol%):Ce:Cu:LiNbO<sub>3</sub> crystals were compared. We found that the recording speed became faster with the increase of Sc doping concentration in the crystal, especially in Sc(3 mol%), which exceeds the so-called threshold concentration. And the gaps of saturation and nonvolatile diffraction efficiencies are different. The reason for the difference may be that the effect of Sc on the

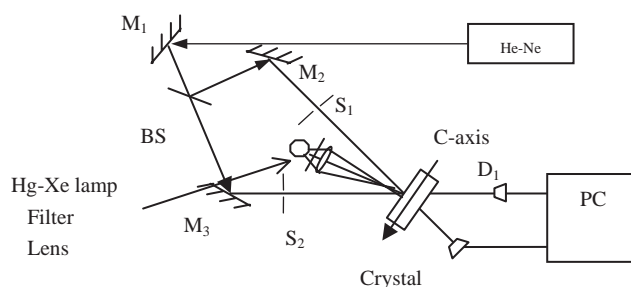


Fig. 5. Experimental light path of two-photon holographic storage diffraction efficiency. M<sub>1</sub>, M<sub>2</sub>, M<sub>3</sub>: mirrors; BS: beam splitter; D<sub>1</sub>, D<sub>2</sub>: detector; S<sub>1</sub>, S<sub>2</sub>, S<sub>3</sub>: diaphragm; PC: computer.

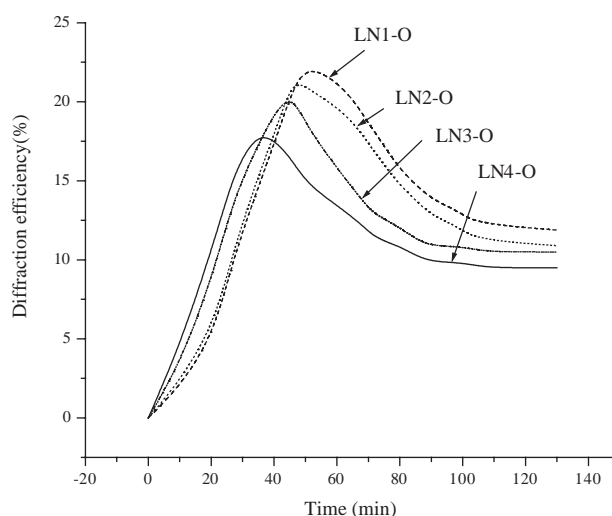


Fig. 6. Recording and readout characteristic measured after UV exposure.

absorption cross-sections and the electron-recombination coefficients of the Cu<sup>2+</sup> deep traps and the Ce<sup>3+</sup> shallow traps is different.

#### 5. Conclusion

In this paper, we have demonstrated nonvolatile recording in Sc(0,1,2,3 mol%):Ce:Cu:LiNbO<sub>3</sub> crystals. We showed the effect of Sc on the oxidation state of the crystal on recording and readout responses. The experimental results showed that the recording speed was faster with the increase of Sc doping concentration in the crystal, especially in Sc(3 mol%), which exceeds the so-called threshold concentration, and that its recording time became shorter, and at the same time little loss of nonvolatile diffraction efficiencies could be achieved.

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Table 2

Characteristic parameters of non-volatile holographic storage in the four oxidized Sc:Ce:Cu:LiNbO<sub>3</sub> crystals

Crystals	Writing times (min)	Saturation diffraction efficiency (%)	Non-volatile diffraction efficiency (%)
LN1-O	51	22.46	11.89
LN2-O	47	21.44	10.91
LN3-O	45	20.39	10.5
LN4-O	34	18.09	9.51

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