

# Photochromic effect in LiNbO<sub>3</sub>: Fe :Co

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**Abstract:** In this paper, Co<sub>2</sub>O<sub>3</sub> was codoped in LiNbO<sub>3</sub>: Fe crystals. It was found that Co codoping can give rise to the strong photochromic effect in LiNbO<sub>3</sub>: Fe. Based on the UV-VIS-NIR absorption spectra, photorefractive sensitivities, and EPR results for both virgin and sensitized states of the crystal, the photochromic mechanism in this material was suggested as follows. During sensitization, electrons transfer from O<sup>2-</sup> to Fe<sup>3+</sup> directly while holes are thermally excited from O<sup>-</sup> into the valence band and then partly trapped by Co<sup>2+</sup>, which leads to the darkening of the crystal. In bleaching process, the electrons are excited from Fe<sup>2+</sup> to the conduction band by green light and recombine with the holes on the Co<sup>2+</sup> level. Sensitizing/bleaching experiments were also carried out in LiNbO<sub>3</sub>: Fe: Co crystals. Fast sensitization found for this material is beneficial to two-color recording.

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OCIS codes: (130.3730) Lithium niobate; (300.1030) Absorption; (190.5330) Photorefractive.

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## 1. Introduction

In the past several decades, Fe-doped lithium niobate (LiNbO<sub>3</sub>: Fe, LN: Fe) crystals have been extensively studied as a material for volume holographic memory applications because of their excellent photorefractive properties [1]. In this material, electrons can be excited from Fe<sup>2+</sup> by light and, upon migration, are retrapped by Fe<sup>3+</sup>, giving rise to the photorefractive effect. Element Mn and Cu can also be doped as photorefractive impurities, and Mn<sup>2+</sup>/Mn<sup>3+</sup> and Cu<sup>+</sup>/Cu<sup>2+</sup> act as photorefractive levels in singly-doped crystals [2]. Crystals doped with two types of impurities can be obtained through codoping. Recently, Mn or Cu was codoped with Fe in LN to form two different photorefractive levels in crystal for two-color recording [3,4]. Besides Fe, Mn and Cu mentioned above, other transition metal elements, such as Co, have also been investigated as dopants. Unfortunately, it was proved by many experiments that Co is not an efficient photorefractive center in singly-doped crystals [5,6], because the visible absorption produced in LN doped with Co arises from localized electronic states and cannot be utilized for photoexciting electrons [5,7]. However, impurities without absorption suitable for photoexciting electrons sometimes also influence the photorefractive properties of the material. Recently, Lee et al. found out that the photorefractive properties of Fe-doped (or nominally pure) near-stoichiometric LN crystals can be affected significantly by Tb impurity [8,9]. In their work, Tb neither induces any obvious absorption in spectrum nor acts as a photorefractive center, but it can enhance and stabilize the UV-light-induced absorption (e.g. photochromic effect) in the crystals. The above discussion raises a question of whether Co can affect the photorefractive properties of material indirectly when it is codoped with Fe in LN.

In this paper, Co<sub>2</sub>O<sub>3</sub> was codoped in LiNbO<sub>3</sub>: Fe crystals. It was revealed that Co codoping can give rise to the strong photochromic effect in LiNbO<sub>3</sub>: Fe and affect the photorefractive properties of the material significantly. Further investigations on UV-VIS-NIR absorption and EPR spectra showed that Fe and Co ions are all involved in the photochromic process. We also discussed the photochromic mechanism in LiNbO<sub>3</sub>: Fe: Co, which is slightly different from that in LiNbO<sub>3</sub>: Fe: Mn [10]. Sensitizing/bleaching experiments were carried out on LiNbO<sub>3</sub>: Fe: Co crystals. The results indicate the potential of this material for two-color recording. Though the material focused by our work is still limited in the series of LN crystals doped with Fe, this work is of value in the search both for new phenomena in doubly-doped photorefractive crystals and for feasible applications in the optical-memory devices based on two-color recording.

## 2. Experimental setup

Samples used in this study were LN crystals codoped with 0.03 mol% Fe<sub>2</sub>O<sub>3</sub> and 0.015 mol% Co<sub>2</sub>O<sub>3</sub>. Doubly-doped LN single crystal was grown along the c-axis from congruent melt by using the Czochralski technique. Then it was cut to rectangular-shaped y-oriented plates with thickness of 1.2 mm and polished to optical grade.

A 20-W mercury lamp was used as the incoherent UV light source. The spectrum of UV light was selected to peak at 365 nm by an appropriate optical filter. The UV light was loosely focused by a lens to irradiate the sample. In order to investigate the UV-light-induced absorption (ULIA) at different wavelengths, the unpolarized light absorption spectra along the

y-axis from the sample were measured by shimadzu UV-365 spectrometer. EPR study was also performed to characterize the photochromic centers. For this study, the sample was prepared in rectangular rod and mounted on fused-silica glass tube with c-axis perpendicular to the magnetic field. EPR measurements were carried out at a radio frequency of 9.85 GHz with the modulation frequency of 100 kHz by using a Bruker EMX-6/1 X-band spectrometer at room temperature.

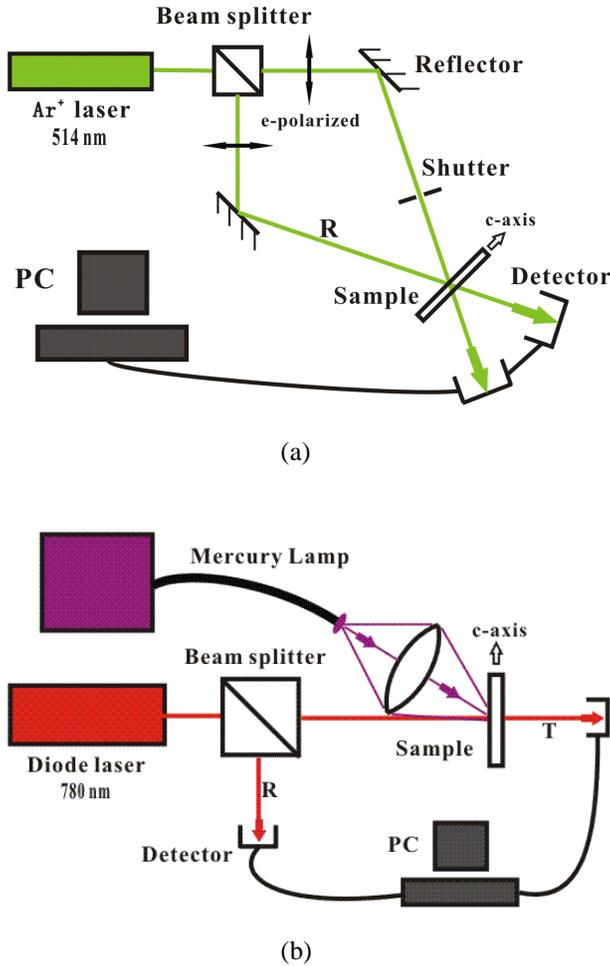


Fig. 1. (a). Schematic of the experimental arrangement for one-color recording. Two e-polarized beams with equal intensities of  $110 \text{ mW/cm}^2$  were used for the recording. The readout beam is denoted as “R”. (b). Schematic of the experimental arrangement for sensitizing and bleaching. UV light emitted from mercury lamp was used for sensitizing. The intensity of the NIR probe beam is  $1 \text{ mW/cm}^2$ . The expanded green beam for bleaching is omitted in the figure. The transmission and reference beams are denoted as “T” and “R”, respectively.

One-color recording was performed to characterize the photorefractive properties. As shown in Fig. 1(a), the grating was written at a crossing angle of  $30^\circ$  on the sample by two extraordinary polarized beams, which were emitted from an  $\text{Ar}^+$  laser of 514 nm and with equal intensities of  $110 \text{ mW/cm}^2$ . The grating wave vector was aligned along the c-axis of the sample. Sensitivity can be obtained through  $S = (d(\eta)^{1/2}/dt|_{t=0}) / (I_{\text{Rec}}L) = (A_0/\tau_r) / (I_{\text{Rec}}L)$ , where  $A_0$  is the saturation hologram strength,  $\eta$  is diffraction efficiency,  $\tau_r$  is recording time constant,  $I_{\text{Rec}}$  is the total recording intensity, and  $L$  is the thickness of the recording medium [11]. Note that  $(\eta)^{1/2} = A$ , where  $A$  is the hologram strength. Diffraction efficiency is defined as  $I_D / (I_D + I_T)$ ,

where  $I_D$  and  $I_T$  are the diffracted and transmitted intensities of the readout beam, respectively. Recording time constant is defined as the period of time from commence to  $(1-1/e)$  of the saturation hologram strength.

Figure 1(b) shows the schematic of the experimental arrangement for sensitizing and bleaching. ULIA was probed by an unpolarized 780 nm beam emitted from diode laser. The probe light with the intensity of  $1\text{mW}/\text{cm}^2$  impinged on the sample along the y-axis. The transmitted light was detected by a photo-detector with a filter placed in front to block scattered 365-nm pump UV light. A 514 nm beam was expanded for bleaching. In addition, another reference light was taken out from the probe light just before the sample. And the ULIA coefficient was obtained from  $\ln[(I_{R1}/I_{R0})/(I_{T1}/I_{T0})]/d$ , where  $I_{T1}$  ( $I_{T0}$ ) and  $I_{R1}$  ( $I_{R0}$ ) are measured intensities of transmission and reference beams with (without) UV irradiation respectively, and  $d$  is the sample's thickness. By this way, we can reduce as much as possible the drifts caused by power fluctuation of diode laser.

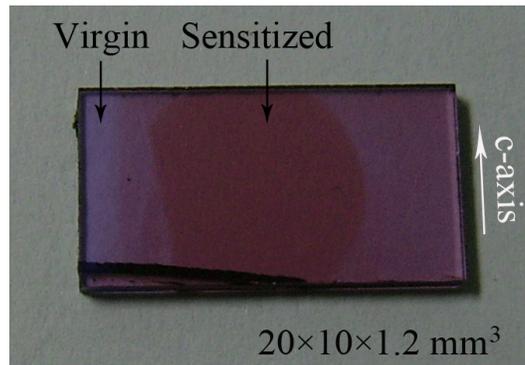


Fig. 2. Photograph of the sample with both virgin and sensitized states. The virgin state presents a purple color while the sensitized state exhibits the dark reddishness.

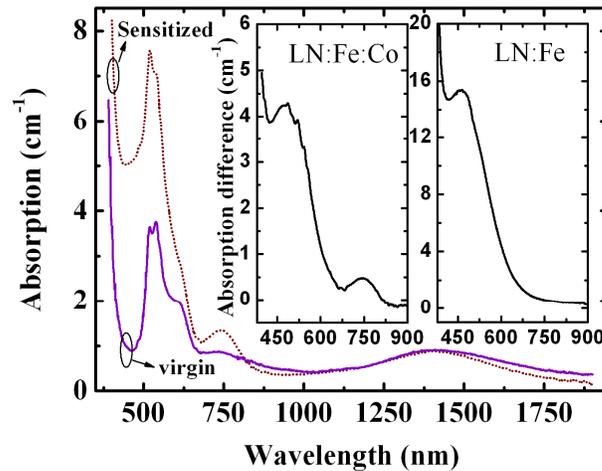


Fig. 3. Unpolarized light absorption spectra for both virgin and sensitized states. The left inset shows the UV-light-induced absorption, e.g. the absorption difference between the virgin and sensitized states. For comparison, the right inset shows the absorption difference between LN singly-doped with Fe and pure LN.

### 3. Results

The virgin sample presents a purple color and looks very like LN crystals singly-doped with Co [6]. However, under UV irradiation, the sample color changes rapidly to the dark reddishness that is often exhibited by LN crystals singly-doped with Fe [6]. This dark reddish sample can be recovered to its virgin state by irradiating with visible light. In other words, the sample can be sensitized by UV light and bleached by visible light. Figure 2 shows the photograph of the sample with both virgin and sensitized states.

Figure 3 illustrates the unpolarized light absorption spectra of the two different states. From the spectrum of the virgin state, we can see a series of bands overlap in the range from 500 to 1500 nm. These bands are consistent with the results obtained in LN crystals singly-doped with Co [6]. Fujita et al. [7] suggested that they are all due to d-d transition of Co ions. Among them, the band at 1450 nm and those near 550 nm correspond to  $\text{Co}^{2+}$ , and that centered at 750 nm is assigned to  $\text{Co}^{3+}$ . After UV sensitization, it is interesting to find an increase of absorption below 820 nm. This ULIA, which is showed in the left inset of Fig. 3, apparently consists of two different components: the broad one centered at 500 nm and the relatively narrow one peaked at 750 nm. For comparison, the right inset shows the absorption difference between LN singly-doped with Fe and pure LN. One can see that the broad component of the ULIA is very similar in shape to the band induced by  $\text{Fe}^{2+}$ - $\text{Nb}^{5+}$  intervalence transfer in the right inset.

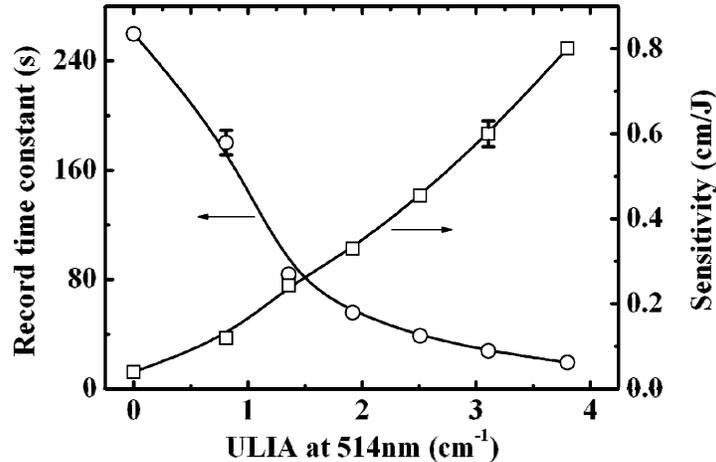


Fig. 4. Recording time constant and sensitivity plotted with the ULIA at 514 nm, where the variable ULIA was controlled by the UV exposure fluence.

One-color recording was performed on the sample with different UV exposure fluence. For the virgin state, the sensitivity of holographic recording is very small, but it boosts up tens of times after UV irradiation. In Fig. 4, the recording time constant and sensitivity are plotted with the ULIA at 514 nm, where the variable ULIA was controlled by the UV exposure fluence. The above results show that the ULIA markedly improves the performance of the sample in one-color recording.

The EPR spectra of the virgin  $\text{LiNbO}_3$ : Fe: Co crystals are shown in Fig. 5. The EPR signals found there should not be assigned to  $\text{Fe}^{2+}$  and  $\text{Co}^{2+}$  ions because homogeneous broadening, due to rapid spin-lattice relaxations, prevents the observation of EPR signals from them at room temperature [12,13]. Thus, these signals must arise from  $\text{Fe}^{3+}$ , which can also be confirmed by the previous  $\text{Fe}^{3+}$  EPR spectra [14]. The insets of Fig. 5 show the EPR signals for the virgin and sensitized states, respectively. The reduction of  $\text{Fe}^{3+}$  signal intensity after UV sensitization is clearly seen.

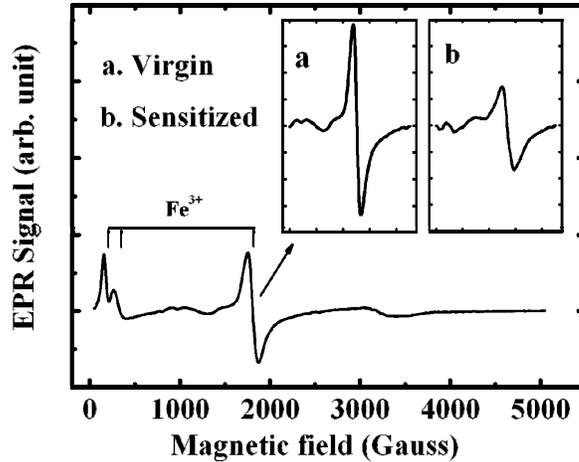


Fig. 5. EPR spectra of LiNbO<sub>3</sub>: Fe: Co crystals. The left and right insets show the EPR signals near 2000 Gauss for the virgin and sensitized states, respectively.

Sensitizing/bleaching experiments were carried out on LiNbO<sub>3</sub>: Fe: Co crystals. Figure 6(a) shows the sensitizing curves of the ULIA in different UV intensities ( $I_{UV}$ ). The inset of Fig. 6(a) gives the dependence of sensitizing time constant (labeled as Time Cons. in the figure) on UV intensity, where sensitizing time constant is defined as the period of time from commence to  $(1-1/e)$  of the saturated absorption. Our results show that the sensitization of LiNbO<sub>3</sub>: Fe: Co is very fast. Even for the lowest UV intensity of 34 mW/cm<sup>2</sup>, we can obtain a short sensitizing time constant of 166 s in LiNbO<sub>3</sub>: Fe: Co. Note that in LiNbO<sub>3</sub>: Fe: Mn, tens of minutes is usually required for sensitization process [10]. In addition, it is evident in the inset of Fig. 6(a) that, the sensitization time constant initially decreases rapidly with the increase of UV intensity, followed by a gradual saturation near 100 mW/cm<sup>2</sup>, indicating UV intensity of 100 mW/cm<sup>2</sup> is suitable for highly efficient sensitization. Figure 6(b) shows the bleaching curves of the ULIA in different bleaching intensities ( $I_B$ ). The inset of Fig. 6(b) gives the dependence of bleaching time constant on bleaching intensity, where bleaching time constant is defined as the period of time from commence to  $(1/e)$  of the initial absorption.

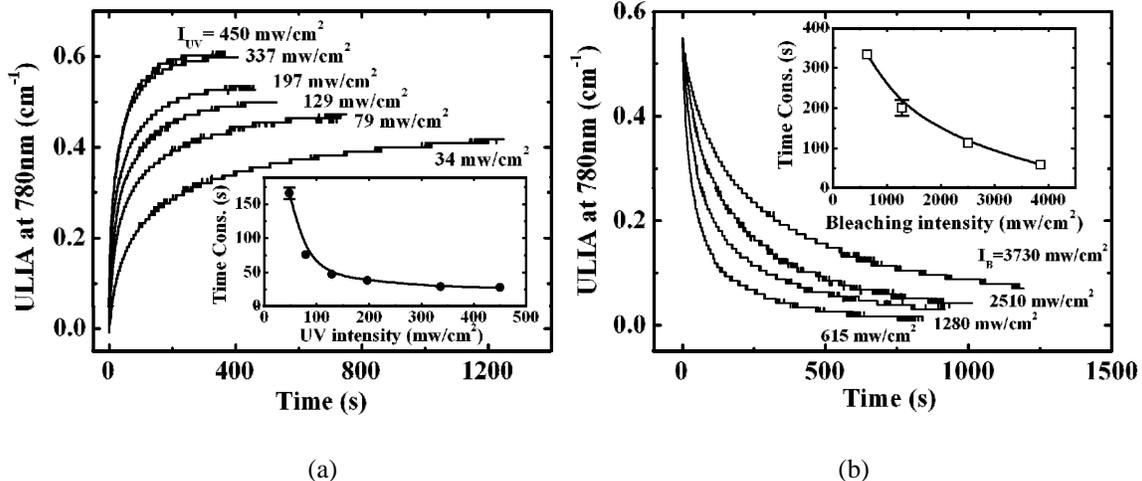


Fig. 6. (a). Sensitizing curves of the ULIA in different UV intensities. The inset shows the dependence of sensitizing time constant on UV intensity. (b). Bleaching curves of the ULIA in different bleaching intensities. The inset shows the dependence of bleaching time constant on bleaching intensity.

#### 4. Discussion

For LN crystals containing Fe impurity, the broad band centered at 500 nm usually appears owing to  $\text{Fe}^{2+}\text{-Nb}^{5+}$  intervalence transfer [12]. However, it is nearly absent in the absorption spectrum of virgin  $\text{LiNbO}_3\text{:Fe:Co}$  crystals, which indicates that few electrons are trapped by  $\text{Fe}^{3+}$  in the virgin state. After UV sensitization, a broad component centered at 500 nm is found in the ULIA and this component is very similar in shape to the band induced by  $\text{Fe}^{2+}\text{-Nb}^{5+}$  intervalence transfer. Thus the ULIA at 500 nm is likely to be induced by the appearance of a large number of  $\text{Fe}^{2+}$ . However,  $\text{Co}^{2+}$  can also give rise to the absorption near 500 nm, so further justifications are needed. In one-color recording with green light, sensitivity is found to increase with the ULIA, which gives another support to our above suggestion that the ULIA near 500 nm is caused by  $\text{Fe}^{2+}$ , because sensitivity is generally in proportion to the amount of  $\text{Fe}^{2+}$  in crystal [15]. The most decisive proof of our suggestion comes from the comparison of EPR signals between the virgin and sensitized states. The  $\text{Fe}^{3+}$  signal intensity decreases obviously after UV sensitization, which reveals that the ULIA near 500 nm is due to the valence change from  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$ .

The above discussion shows that electrons will transfer to  $\text{Fe}^{3+}$  ions after UV sensitization. But, where are the electrons from? We know that LN crystals, even nominally pure ones, maybe contain undesigned Mn impurity with low concentration of several ppm. But, in our case, electrons should not come from the deep traps formed by Mn impurity because no  $\text{Mn}^{2+}$  signals, consisting of several six-hyperline sets [8], have been found in the EPR spectra of the virgin state. There is little likelihood of electrons photoexcited from  $\text{Co}^{2+}$  because the absorption of  $\text{Co}^{2+}$  arises from localized electronic states. One possible way is charge transfer (CT) from  $\text{O}^{2-}$  to  $\text{Fe}^{3+}$  induced by UV irradiation. This CT process has been justified by many researchers from both experimental and theoretical aspects [2,12]. However,  $\text{Fe}^{3+}$  also exists in LN singly-doped with Fe, yet no obvious photochromic effect can be found even in the oxidized crystals. How can we explain this discrepancy and what is the role of Co in the photochromic process of  $\text{LiNbO}_3\text{:Fe:Co}$ ? Since the holes self-trapped at  $\text{O}^{2-}$  ions (in the form of  $\text{O}^-$  ions) are unstable at room temperature [16], they are thermally excited into the valence band after the CT process. In LN singly-doped with Fe, all the holes will be retrapped by  $\text{Fe}^{2+}$  when UV light is absent. Thus we cannot observe the photochromic effect there. In the case of  $\text{LiNbO}_3\text{:Fe:Co}$ , we tentatively give a hypothesis that holes have an opportunity to be trapped by  $\text{Co}^{2+}$ . This hypothesis seems reasonable if we notice that holes can be captured by  $\text{Co}^{2+}$  in some cobalt-doped  $\text{ABO}_3$  compounds such as  $\text{BaTiO}_3\text{:Co}$  [17,18]. As shown in Fig. 7, part of holes are trapped by  $\text{Co}^{2+}$  and cannot return to  $\text{Fe}^{2+}$  when UV light is absent, which leads to the dark reddishness of the sensitized state. Evidence for the above suggestions is the narrow ULIA component peaked at 750 nm, which should be assigned to  $\text{Co}^{3+}$  ( $\text{Co}^{2+}$  with trapped holes) according to the suggestion of Fujita et al [7]. Based on our discussion, the amount of  $\text{Co}^{2+}$  will reduce after UV irradiation, which seems conflicting with the nearly unchanged absorption at 1450 nm in the sensitized state. However, the absorption at 1450 nm is also influenced by other factors. Kurz et al. studied detailedly the photorefractive properties of  $\text{LiNbO}_3\text{:Fe}$  crystals in combination with optical absorption-, Mössbauer- and EPR-measurements and drew a very important conclusion about the association of the optical band around 500 nm with  $\text{Fe}^{2+}$ . Besides this result, they also suggested that  $\text{Fe}^{2+}$  can cause another broad band at 1200 nm due to the crystal-field splitting of  $\text{Fe}^{2+}$  level at 500 nm [12]. Thus, we believe that both  $\text{Fe}^{2+}$  and  $\text{Co}^{2+}$  contribute to the absorption at 1450 nm. Though the amount of  $\text{Co}^{2+}$  reduces after UV irradiation, the  $\text{Fe}^{2+}$  formed by UV irradiation may keep the absorption at 1450 nm unchanged. Figure 7 also shows the mechanism of bleaching: electrons are excited from  $\text{Fe}^{2+}$  to the conduction band by green light and then recombine with holes on  $\text{Co}^{2+}$  level.

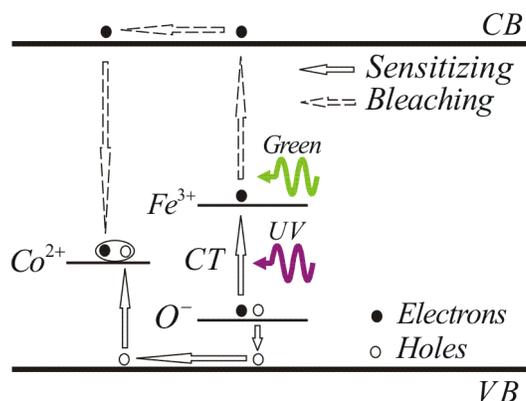


Fig. 7. Sketch of the photochromic process in LiNbO<sub>3</sub>: Fe: Co. The solid and dash arrows denote the sensitizing and bleaching processes, respectively.

In LiNbO<sub>3</sub>: Fe: Co, two levels (Fe<sup>3+</sup> and Co<sup>2+</sup>) are involved in the photochromic process, which is similar to the case of LiNbO<sub>3</sub>: Fe: Mn (Fe<sup>3+</sup> and Mn<sup>2+</sup>) [10]. However, in LiNbO<sub>3</sub>: Fe: Co, electrons transfer from O<sup>2-</sup> to Fe<sup>3+</sup> level directly through CT process under UV irradiation, which is different from the indirect transfer of electrons from Mn<sup>2+</sup> to Fe<sup>3+</sup> level via the conduction band in LiNbO<sub>3</sub>: Fe: Mn. Faster sensitization is found in LiNbO<sub>3</sub>: Fe: Co, as compared with the previous result obtained in LiNbO<sub>3</sub>: Fe: Mn. This is probably because the direct transfer of electrons in LiNbO<sub>3</sub>: Fe: Co is more efficient than the indirect transfer of electrons in LiNbO<sub>3</sub>: Fe: Mn. Additionally, the Co<sup>2+</sup> level in LiNbO<sub>3</sub>: Fe: Co cannot be photoexcited and only exists as the recombination center for holes and electrons, which is also different from the photorefractive levels in LiNbO<sub>3</sub>: Fe: Mn. In the work of Lee et al., Tb codoping can also induce significant ULIA in Fe-doped LN crystals, and the ULIA is attributed to the valence change from Fe<sup>3+</sup> to Fe<sup>2+</sup> as well. However, this phenomenon only exists in near-stoichiometric crystals and is not found in congruent ones [8].

From the bleaching and sensitizing time constants, we can estimate the optimum ratio of recording and sensitizing intensities for two-color recording with green and UV light [10]. Comparing the insets of Fig. 6(a) and (b), we find the optimum intensity ratio approximately ranging from 35 to 40. For example, if we choose 100 mW/cm<sup>2</sup> as the UV intensity, we find the sensitizing time constant for this intensity is around 65s and the corresponding bleaching intensity with the same time constant is about 3700 mW/cm<sup>2</sup>, which yields a ratio of 37. The ratio range in our case is slightly higher than that (25~30) for LiNbO<sub>3</sub>: Fe: Mn [10], which may be due to the fast sensitization in LiNbO<sub>3</sub>: Fe: Co. The higher ratio is advantageous to producing strong gratings in two-color recording.

The storage time of the photoinduced index is another important issue concerning two-color recording. Generally, the storage time is connected with the stability of the level on which the photoinduced index is recorded. For example, LiNbO<sub>3</sub>: Mn is proved to have a longer storage time than LiNbO<sub>3</sub>: Fe because the deeper Mn level is more stable than Fe level [19]. In LiNbO<sub>3</sub>: Fe: Co, the photoinduced index should be recorded finally in Co level. Thus, the energy and stability of the Co level may govern the storage time. As mentioned above, Co impurity has no absorption suitable for photoexciting electrons with visible light, which indicates that Co level should be relatively deep and stable as compared with Fe and Mn levels. Therefore, LiNbO<sub>3</sub>: Fe: Co is expected to have relatively long storage time. Further experiments are underway to prove this suggestion.

## 5. Conclusion

In this paper, the strong photochromic effect was found in LiNbO<sub>3</sub>: Fe: Co crystals. The crystal can be darkened by UV light and bleached by visible light. For both the virgin and sensitized states, UV-VIS-NIR absorption and EPR spectra were measured, and the one-color recording sensitivities were also studied. The results showed that a large number of Fe<sup>2+</sup> and

$\text{Co}^{3+}$  ions appear in the sensitized state. Based on these results, we explained the photochromic mechanism in  $\text{LiNbO}_3:\text{Fe}:\text{Co}$  as follows. During sensitization, electrons transfer from  $\text{O}^{2-}$  to  $\text{Fe}^{3+}$  directly while holes are thermally excited from  $\text{O}^{\cdot}$  into the valence band and then partly trapped by  $\text{Co}^{2+}$ , which leads to the darkening of the crystal. In bleaching process, electrons are excited from  $\text{Fe}^{2+}$  to the conduction band by green light and recombine with holes on the  $\text{Co}^{2+}$  level. Sensitizing/bleaching experiments were also carried out in  $\text{LiNbO}_3:\text{Fe}:\text{Co}$  crystals. Fast sensitization process found for this material was attributed to the direct transfer of electrons from  $\text{O}^{2-}$  to  $\text{Fe}^{3+}$  level through CT process. In addition, we also got the optimum ratio of the recording and sensitizing intensities for two-color recording. The relatively high ratio was attributed to the fast sensitization in  $\text{LiNbO}_3:\text{Fe}:\text{Co}$  crystals.

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