Study on UV-light-induced absorption in $LiNbO_3$:Fe, Co crystal*

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In this paper, the temporary UV-light-induced absorption in $LiNbO_3$:Fe, Co crystal is investigated for different UV intensities. It is found that the sensitizing process in $LiNbO_3$:Fe, Co can be considered as a combination of two sub-processes with different time constants. Based on the lattice structure and the photochromic mechanism of the material, the two sub-processes are suggested to arise from electron transfer from O^{2-} to Fe^{3+} through two paths with different distances. The two-colour recording experiment in $LiNbO_3$:Fe, Co is also preformed by using UV and green light as gating and writing beams respectively. High sensitivity is obtained in the recording, which is considered as the consequence of direct charge transfer from O^{2-} to Fe^{3+}.

Keywords: lithium niobate, photochromic, charge transfer, photorefractive effect

PACC: 4240E, 4270Q

1. Introduction

Fe-doped lithium niobate ($LiNbO_3$, LN) crystal is one of the most important crystalline materials for optical storage applications.[1] In particular, Buse *et al.* reported that two different photorefractive levels formed in crystals could be utilized for two-colour recording when Mn or Cu was codoped in Fe-doped LN crystals.[2,3] Besides Mn and Cu mentioned above, other transition metal elements were also investigated as codopants. Lee *et al.* investigated the photorefractive properties of near-stoichiometric LN crystals doubly doped with Fe and Tb[4,5] and found that Tb could enhance and stabilize the UV-light-induced absorption (ULIA) in the crystals. They suggested that the ULIA should be due to the electron transfer from O^{2-} ions near lattice defect to Fe^{3+} ions, and it should be very important for the realization of two-colour recording. Recently, we studied the influence of Co codoping on the photorefractive properties of congruent $LiNbO_3$:Fe crystals.[6] Though Co impurity was proved to be an inefficient photorefractive centre in singly-doped LN crystals,[7–9] it was shown in Ref. [6] that Co codoping could result in a strong ULIA in $LiNbO_3$:Fe crystals.

In the present paper, some unusual features of the sensitizing process in $LiNbO_3$:Fe, Co are revealed. These results are compared with conventional doubly-doped LN and are explained from the aspect of charge transfer. In addition, the two-colour recording with high sensitivity is demonstrated in $LiNbO_3$:Fe, Co crystals.

2. Experimental procedure

Samples used in this study were LN crystals codoped with 0.03 mol% Fe_2O_3 and 0.015 mol% Co_2O_3. Doubly-doped LN single crystal was grown along the *c*-axis from congruent melt by using the Czochralski technique. Then it was cut into rectangular-shaped *y*-oriented plates, each with a thickness of 1.2 mm and polished to optical grade.

Figure 1(a) shows the schematic diagram of experimental arrangement for ULIA measurement in the sensitizing process. The spectrum of UV light was

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selected to peak at 365 nm by an appropriate optical filter. ULIA was probed by an unpolarized 780-nm beam emitted from diode laser. The probe light with an intensity of 1 mW/cm^2 incident on the sample along the y-axis. In addition, another reference light was taken out of the probe light just in front of the sample. And the ULIA coefficient is obtained from $\ln[(I_{R1}/I_{R0})/(I_{T1}/I_{T0})]/d$, where I_{T1} (I_{T0}) and I_{R1} (I_{R0}) are the measured intensities of transmission and reference beams with (without) UV irradiation respectively, and d is the sample thickness. Sensitizing experiments were carried out on $LiNbO_3$:Fe:Co crystals. Temporary ULIA data were measured in the sensitizing experiments, where the UV intensities (I_{UV}) were set to be 34, 79, 129, 197, 337, 450 mW/cm^2, separately.

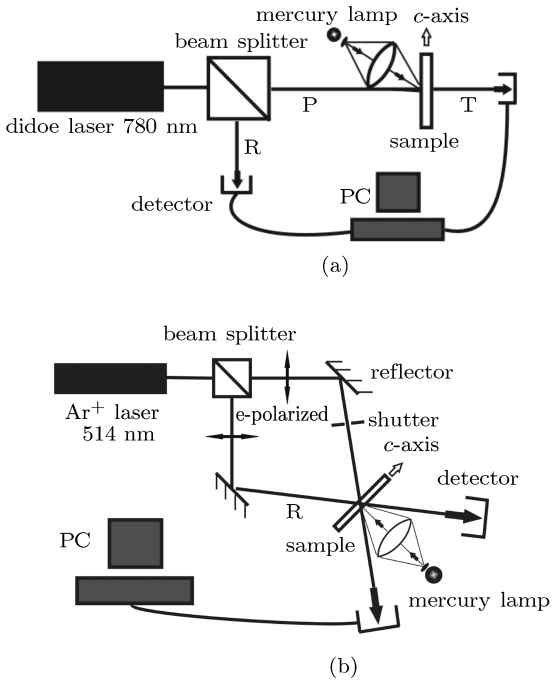


Fig. 1. Schematic diagrams of experimental arrangements for ULIA measurement in sensitizing process (a) and for two-colour recording (b), where probe light is denoted as "P" and reference light is denoted as "R".

The two-colour recording experimental setup is shown in Fig. 1(b): the hologram was written at a crossing angle of 30° on the sample by two extraordinary polarized beams, which were emitted from an Ar$^+$ laser of 514 nm, each with an intensity of 110 mW/cm^2. The UV gating beam with an intensity of 5.4 mW/cm^2 was focused on the sample along the y-axis. In the experiment, the crystal was firstly pre-exposed to the UV light for 1 h. Then the hologram was recorded by the two interference beams, with the UV light simultaneously illuminating the crystal. After the saturation was reached, the hologram was read out with only the uniform reference beam.

3. Results and discussion

The typical temporary data of ULIA in the sensitizing process are plotted in Fig. 2, where the square symbols represent the experimental data obtained in a UV intensity of 129 mW/cm^2. The sensitizing process in photochromic material has been known since the two-centre model was first developed on $LiNbO_3$:Fe, Mn crystals by Adibi *et al.*[1] In their model, the band transfer model proposed by Kukhtarev *et al.*[11] is employed for the charge transport processes. The analysis of the two-colour processes in $LiNbO_3$:Fe, Mn crystals by using this model is quite successful and enables the correct prediction of several dependences.

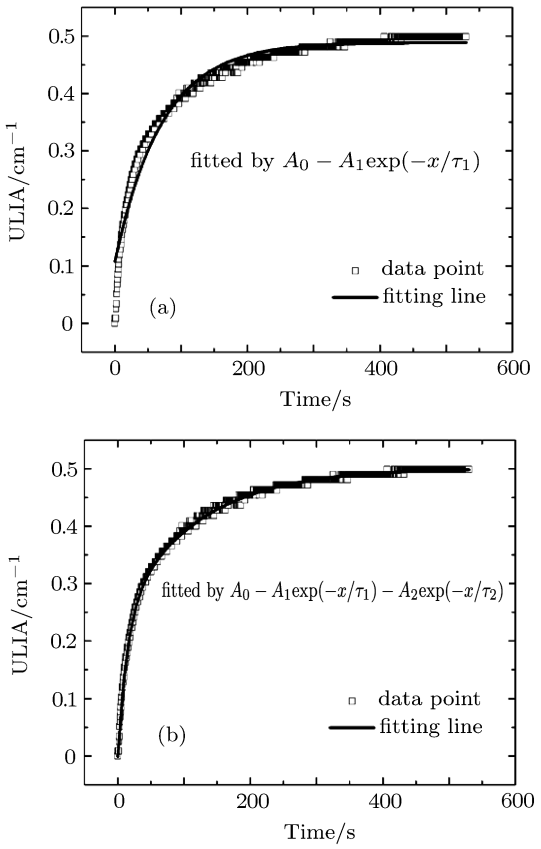


Fig. 2. Typical temporary data of ULIA in the sensitizing process and the fitting results: (a) monoexponential curve and (b) bi-exponential curve. The UV intensity for this set of data is 129 mW/cm^2.

According to this model, the sensitizing curve is expected to obey a monoexponential law. However, our temporary ULIA data cannot be fitted well by

the monoexponential curve, as shown in Fig. 2(a). It means that the monoexponential law based on the band transfer model does not hold true in our case. In Fig. 2(b), the experimental data in the sensitizing process are fitted by a bi-exponential curve: $y = A_0 - A_1 \exp(-x/\tau_1) - A_2 \exp(-x/\tau_2)$. It is surprising that a fairly good result is obtained. The invalidation of the band transfer model indicates that the sensitizing process must include a procedure which involves neither the conduction band nor the valence band.

In Ref. [6], it is shown that the ULIA apparently consists of two different components: one is broad and centred at 500 nm, and the other is relatively narrow and peaked at 750 nm. We also suggested that the electrons should transfer from O^{2-} to Fe^{3+} directly (CT procedure) during UV sensitization, and that the holes left should be thermally excited into the valence band and then partly trapped by Co^{2+} when UV light is absent (see photochromic mechanism in Fig. 3). The evidence of the capture of holes by Co^{2+} is the narrow ULIA component at 750 nm, based on the assignment of absorption bands of Co-doped LN in Ref. [9].

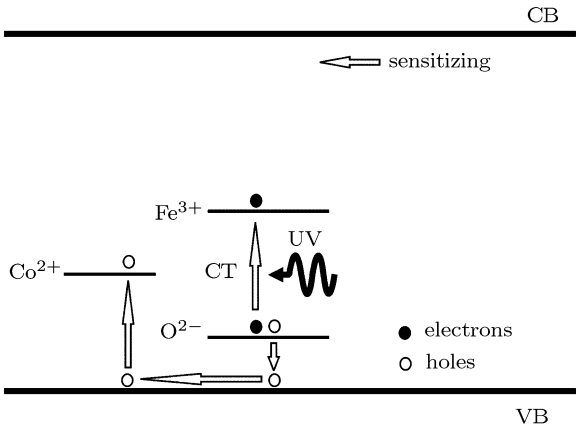


Fig. 3. Schematic diagram of the photochromic mechanism in $LiNbO_3$:Fe, Co crystals.

The direct CT procedure suggested by us is a possible one that can meet this requirement. First, the CT procedure in our case is different from the indirect transfer of electrons via the conduction band suggested by Lee *et al.*[5] In their work, the 313-nm UV laser was used and the electrons could be easily photoexcited into the conduction band. But in our case, the 3.4-eV energy of 365-nm light is just enough for the electron excitation directly to Fe^{3+}. Secondly, the starting level of CT procedure in congruent LN may be slightly higher than the valence band. Based on the Li-vacancy model, the dominate lattice defects in congruent LN should be anti-site niobate ions and Li vacancies. And Li vacancies may distribute around Fe^{3+} for charge compensation, as reported by Zhang *et al.*[12] Thus, it is highly likely that the electrons mainly transfer from O^{2-} ions just near Li vacancies to the adjacent Fe^{3+} ions. Obviously, the Li vacancies will disturb the nearby O^{2-} ions and make the electrons there unstable and more easily photoexcited than those in the valence band. In brief, the sensitizing process should include several procedures but those involving charge transport in the bands just result in the monoexponential behaviour because the charge in the bands is delocalized. Thus, only the direct CT procedure possibly makes the monoexponential law inapplicable to the prediction of the temporary ULIA data.

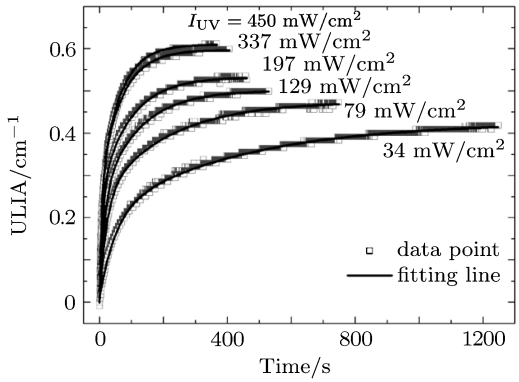


Fig. 4. Fitting results for temporary ULIA data in different UV intensities by using bi-exponential curve. The UV intensities (I_{UV}) were 34, 79, 129, 197, 337, 450 mW/cm^2, separately.

Figure 4 shows the fitting results of temporary ULIA data in different UV intensities by using the bi-exponential curve. The fitting parameters are listed in Table 1. It can be seen from Table 1 that the sensitizing process can be considered as a combination of two sub-processes: one is fast and has a time constant (τ_1) in a range of 6–48 s, the other is relatively slow and has a time constant (τ_2) in a range of 60–420 s. In addition, the fast sub-process is always about 9 times faster than the slow one for any UV intensity, indicating that the origin of the difference between two sub-processes is independent of the UV intensity. Qiao *et al.* have studied the ULIA in a highly Zn-doped $LiNbO_3$ crystal at room temperature.[13] They suggested that Fe ions should have two different locations in crystal lattice: lithium site and niobium

site, which might lead to two sub-processes for electron transfer to Fe^{3+}. However, Fe ions are usually present on niobium site in LN crystals highly doped with damage-resistant impurities (e.g. Mg, In, Zn, etc.) In our sample, no damage-resistant impurities are codoped, and Fe ions are located only on lithium site. Thus, two sub-processes must be related to other factors.

Table 1. Fitting parameters for temporary ULIA data in different UV intensities by using the bi-exponential form.

I_{UV}/mW·cm^{-2}	A_0/cm^{-1}	A_1/cm^{-1}	τ_1/s	A_2/cm^{-1}	τ_2/s
34	0.43	0.19	48.6	0.22	420.4
79	0.47	0.23	22.0	0.23	208.2
129	0.5	0.24	14.1	0.26	117.6
197	0.53	0.25	9.3	0.27	93.7
337	0.59	0.26	7.3	0.32	66.8
450	0.61	0.26	6.3	0.35	60.4

In recent years, a "distance-dependent" model was proposed by many groups to deal with electron (or hole) relaxation, a charge transport process where neither the conduction band nor the valence band was directly involved.[14−19] According to this model, the transfer time for electrons is highly dependent on the transfer distance. Because the CT procedure in $LiNbO_3$:Fe, Co is related to neither the conduction nor the valence band directly, the "distance-dependent" model seems applicable for our case. As discussed above, the electrons mainly transfer from O^{2-} ions just near Li vacancies to the adjacent Fe^{3+} ions.

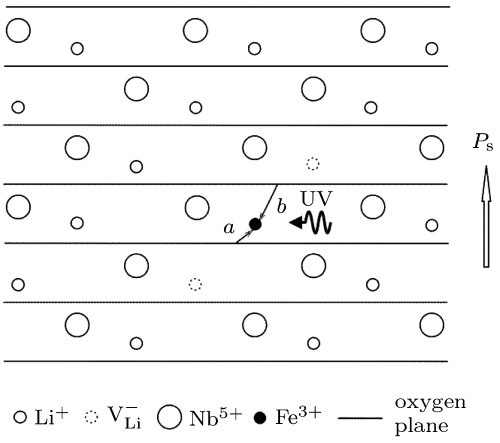


Fig. 5. Lattice structural schematic diagrams of $LiNbO_3$:Fe, Co crystals Fe^{3+} is always located at the Li site and two oxygen planes are adjacent to Fe^{3+}. Li vacancies distribute close to these two oxygen planes for charge compensation. Two transfer paths for electrons are denoted as a and b, respectively.

Figure 5 shows the lattice structural schematics of $LiNbO_3$:Fe, Co crystals. It can be seen from Fig. 5 that Fe^{3+} is always located at the Li site and two oxygen planes are adjacent to Fe^{3+} from up to low. Meanwhile, two nearest Li vacancies distribute close to these two oxygen planes for charge compensation. When UV illumination is present, electrons will transfer from O^{2-} to Fe^{3+}. Undoubtedly, there are two transfer paths for electrons: one is the path a with a short distance; another is the path b with a relatively long distance. Because the transfer time for electrons is distance-dependent, the paths a and b should correspond to the fast and the slow subprocesses of sensitization, respectively. It is obvious that the subprocesses arise from the difference between two transfer paths and this difference is independent of UV intensity. Thus, it is observed that the fast sub-process is always about 9 times faster than the slow one regardless of the UV intensity.

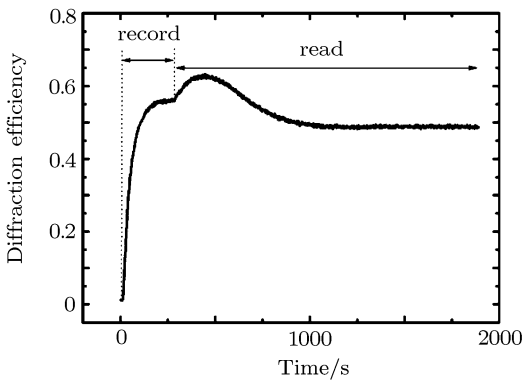


Fig. 6. Typical curve of diffraction efficiency in two-colour recording, where the total writing and UV sensitizing intensities are 220 mW/cm^2 and 5.4 mW/cm^2, respectively.

Another notable result in Ref. [6] is the fast sensitization in $LiNbO_3$:Fe, Co, which can be explained by direct transfer of electrons from O^{2-} to Fe^{3+} through CT procedure. In order to test the effect of fast sensitization on holographic volume storage, the two-colour recording experiments in $LiNbO_3$:Fe, Co was also preformed according to the traditional procedures. The typical curve of diffraction efficiency in two-colour recording is given in Fig. 6. Here, the ratio between the intensities of the total recording and the UV sensitizing light is 40, which is selected based on the sensitization and bleaching experiments in Ref. [6]. From the curve in Fig. 6, we find the grating to be written in a very short time, which yields a recording time constant of 34 s. After a period of readout the grating persists against the homogeneous green beam for the further readout. According to Ref. [20], the sensitivity S' for two-colour recording should be defined as βS, where β is the ratio of $(\eta)^{1/2}$ after sufficient readout to $(\eta)^{1/2}$ at the end of recording. In our case, β=0.93 and $S' = 0.74$. After considering the factor of approximate 3 between electro-optic coefficients for extraordinary and ordinary polarizations, we estimate the recording sensitivity for ordinary polarized beams to be ~ 0.23 cm/J, which is a good result compared with that obtained in $LiNbO_3$:Fe, Mn.[2] The high recording sensitivity is thought to be related to the fast sensitization of the material, which is essentially due to the direct charge transfer from O^{2-} to Fe^{3+} in $LiNbO_3$:Fe, Co. The further work is to investigate the influence of Li composition[21,22] and the Li-deficiency defects[23] on the recording sensitivity in detail.

4. Conclusion

In this paper, the temporary UV-light-induced absorption in $LiNbO_3$:Fe, Co crystals are investigated for different UV intensities. It is found that the sensitizing process can be considered as a combination of two sub-processes: one is fast and has a time constant in a range of 6–48 s, the other is relatively slow and has a time constant in a range of 60–420 s. In addition, the fast sub-process is always about 9 times faster than the slow one for any UV intensity. Based on the lattice structure and the photochromic mechanism of the material, the two sub-processes are suggested to arise from electron transfer from O^{2-} to Fe^{3+} through two paths with different distances. The two-colour recording experiment in $LiNbO_3$:Fe, Co is also preformed by using UV and green light as gating and writing beams respectively. High sensitivity is obtained in the recording. It is thought to be related to the fast sensitization of the material, which is essentially due to the direct charge transfer from O^{2-} to Fe^{3+} in $LiNbO_3$:Fe, Co.

References

[1] Günter P and Huignard J P 1989 *Photorefractive Materials and Their Applications*, Vols. I and II (Heidelberg: Springer-Verlag)

[2] Buse K, Adibi A and Psaltis D 1998 *Nature* **393** 665

[3] Ren L, Liu L, Liu D, Zhou C and Li G 2003 *Opt. Mater.* **23** 261

[4] Lee M, Takekawa S, Furukawa Y, Uchida Y, Kitamura K, Hatano H and Tanaka S 2000 *J. Appl. Phys.* **88** 4476

[5] Lee M, Kim I G, Takekawa S, Furukawa Y, Uchida Y, Kitamura K and Hatano H 2001 *J. Appl. Phys.* **89** 5311

[6] Yan W, Li Y, Shi L, Chen H, Liu S, Zhang L, Huang Z, Chen S and Kong Y 2007 *Opt. Express* **15** 17010

[7] Phillips W, Amodei J J and Staebler D L 1972 *RCA Rev.* **33** 94

[8] McMillen D K, Hudson T D, Wagner J and Singleton J 1998 *Opt. Express* **12** 491

[9] Fujita H, Inoue M and Phillips W 1978 *Jpn. J. Appl. Phys.* **44** 1909

[10] Adibi A, Buse K and Psaltis D J 2001 *Opt. Soc. Am.* B **18** 584

[11] Kukhtarev N V, Markov V B, Odoulov S G, Soskin M S and Vinetskii V L 1979 *Ferroelectrics* **22** 949

[12] Zhang G, Kong Y and Xu J 2001 *Photorefractive Effects, Materials, Devices* ed. G. Salamo and A. Siahmakoun, Vol. 62 *OSA Trends in Optics and Photonics* (Optical Society of America) p. 166.

[13] Qiao H and Tomita Y 2006 *Opt. Express* **14** 5773

[14] Berben D, Buse K, Wevering S, Herth P, Imlau M and Woike Th 2000 *J. Appl. Phys.* **87** 1034

[15] Sturman B, Podivilov E and Gorkunov M 2003 *Phys. Rev. Lett.* **91** 176602

[16] Herth P, Granzow T, Schaniel D, Woike Th, Imlau M and Krätzig E 2005 *Phys. Rev. Lett.* **95** 067404

[17] Merschjann C, Berben D, Imlau M and Wöhlecke M 2006 *Phys. Rev. Lett.* **96** 186404

[18] Carnicero J, Carrascosa M, García G and Agulló-López F 2005 *Phys. Rev.* B **72** 245108

[19] Beyer O, Maxein D, Woike Th and Buse K 2006 *Appl. Phys.* B **83** 527

[20] Adibi A, Buse K and Psaltis D 2000 *Opt. Lett.* **25** 539

[21] Li X C, Kong Y F, Wang L Z and Liu H D 2008 *Chin. Phys.* B **17** 1014

[22] Chen H J, Shi L H, Yan W B, Chen G F, Shen J and Li Y X 2009 *Chin. Phys.* B **18** 2372

[23] Shi L H and Yan W B 2009 *Acta Phys. Sin.* **58** 4987 (in Chinese)