Vol 17 No 3, March 2008
1674-1056/2008/17(03)/1014-06
Chinese Physics B
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The two photorefractive centres in iron doped nearly stoichiometric lithium niobate crystals*

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(Received 14 June 2007; revised manuscript received 3 July 2007)

This paper investigates the photorefractive properties of iron doped lithium niobate with different [Li]/[Nb] ratios. The experimental results show two photorefractive centres for iron doped near-stoichiometric lithium niobate crystal. Besides Fe^{2+} and Fe^{3+} ions, small polarons and bipolarons are considered as another photoactive centre.

Keywords: lithium niobate crystal, photorefractive effect, stoichiometric
PACC: 4270, 7820W

1. Introduction

Lithium niobate ($LiNbO_3$, LN) crystals are extensively studied due to their many applications,[1−5] e.g., holographic volume storage, optical image and signal processing, coherent optical amplification, and phase-conjugation. Iron doped lithium niobate (Fe:$LiNbO_3$, Fe:LN) is one of the most excellent candidate materials for data storage because it has high photorefractive sensitivity and large dynamic range.

However, the congruent $LiNbO_3$ (CLN) crystals usually used contained a considerably large amount of intrinsic defects as a result of non-stoichiometry. According to the Li-site vacancy model,[6] there exist about 4mol% Li vacancies (V_{Li}) and 1mol% antisite Nb ions (Nb_{Li}) defects in CLN crystals. Such a large amount of intrinsic defects greatly degrades the properties of $LiNbO_3$ crystals.[7] Recently, it was reported that nearly stoichiometric Fe:$LiNbO_3$ (Fe:NSLN) crystals have enhanced photorefractive properties.[8−11] It has been proved by theory and experiments that only Fe^{2+}/Fe^{3+} ions are the photoactive centres in Fe:LN crystals at low intensity,[12] while at high light intensity ($10^6 W/m^2$) the two-centre model can describe most results at low and high light intensity.[13] Many nonvolatile storage experiments made with pure NSLN and Fe: NSLN[14−17] have shown the essential relationship between photorefractive properties and intrinsic defects, such as small polarons (Nb_{Li}^{4+}) and bipolarons (Nb_{Li}^{4+}:Nb_{Nb}^{4+}) in the reduced crystals. As far as Fe:NSLN crystals, it is still unclear that with the decrease of intrinsic defects whether the photoactive centre has changed at low light intensity.

In this paper, the recording and erasing process of the photorefractive grating in Fe:LN crystals with different [Li]/[Nb] ratios were investigated, and the electron transition process between small polarons and deep levels was also measured. The experimental results show that there are two photoactive centres in Fe:NSLN crystals.

2. Experiments

Fe:CLN crystal was grown from the congruent melt with 0.025wt% Fe_2O_3 by Czochralski technique at R&D Centre for Photon-Electro Materials of Nankai University. The as-grown crystals were cut to x-oriented plates with the thickness of 1.1mm. In order to obtain $LiNbO_3$ samples with different [Li]/[Nb] ratios, the vapour transport equilibration (VTE) technique was employed.[18] The plates were treated in the powder charges with various [Li_2O]/[Nb_2O_5] ra-

*Project supported by the research funding via Program for Changjiang Scholars of China and Innovative Research Team in University, China and the National Natural Science Foundation of China (Grant No 60578019) and Program for Changjiang Scholars and Innovative Research Team in University.
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tios from 49/51 to 50/50, and they were polished to optical grade. For the doping concentration of Fe is not high, the Li_2O content of all the crystals was characterized by measuring the width of 153cm^{-1} Raman lines[19] and listed in Table 1. Hereafter the Fe:LN crystals with 48.4, 48.9, 49.3, 49.8mol% Li_2O are labelled as Fe:$LN_{48.4}$, Fe:$LN_{48.9}$, Fe:$LN_{49.3}$, Fe:$LN_{49.8}$, respectively. For desired results, all the crystals are reduced in argon atmosphere at 700° for 5 h before experiments.

The absorption spectra of these reduced crystals were measured by a Shimadzu UV-365 spectrophotometer. As shown in Fig.1, an obvious blue shift of absorption edge occurred with increase of Li content. It was reported that the concentrations of Fe^{2+} irons (C_{Fe}^{2+}) can be deduced from absorption spectra at 476nm.[20−22] The distribution coefficient of Fe is near one, therefore the concentration of Fe^{3+} ions (C_{Fe}^{3+}) can be obtained from $C_{Fe} - C_{Fe}^{2+}$, where C_{Fe} is the total iron doping content. The calculated results were also collected in Table 1 of Section 3.

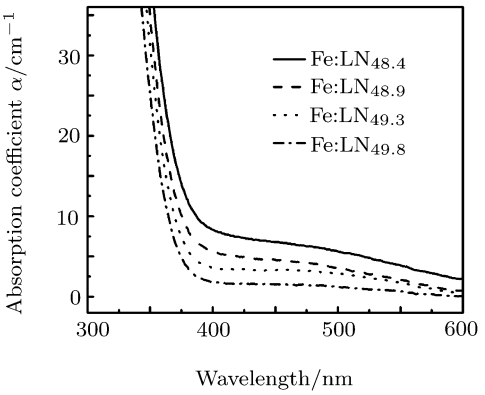


Fig.1. The absorption spectra of Fe:$LiNbO_3$ crystals used in this study.

As shown in Fig.2, a two-beam interference setup was used to measure the photorefractive properties of Fe:LN crystals. A semiconductor laser with the wavelength of 532nm was employed. The output laser beam was split into two beams with the same light intensity (760mW/cm^2). The two extraordinary polarization beams intersected inside the crystal and wrote a photorefractive grating. The photorefractive grating vector $\boldsymbol{K}$ was parallel to the c-axis. The recording process of the photorefractive grating was measured by blocking the signal beam from time to time with a shutter. The erasing process was measured by blocking the signal beam completely, and the reference beam erased the grating. The typical record and erasure process was measured at the grating period Λ of 618nm.

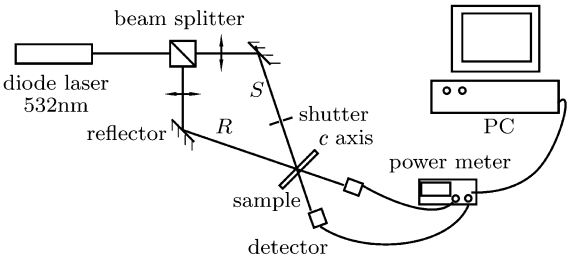


Fig.2. The experimental setup for two-beam interference.

For further investigation into the influence of intrinsic defects on the photorefractive process, we simultaneously probe the transmitted light intensity changes of 780nm and 532nm under 514nm illumination. The experimental setup is shown in Fig.3. The light intensity of 514nm from Ar^+ laser is 1W/cm^2, and that of 780nm and 532nm is 1mW/cm^2.

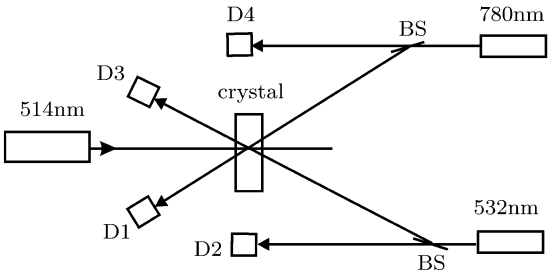


Fig.3. The experimental setup for the light induced absorption changes $\Delta\alpha$ of 532, 780nm light. D1, D2, D3, and D4 are detectors which are all connected to the computer. D1, D3 probe the transmitted light intensity changes of 780 and 532nm through the crystal, respectively; D2, D4 probe the light intensity of 780 and 532nm directly from lasers. BS is the beam splitter.

3. Results and discussion

Figure 4 shows the recording curves of Fe:LN crystals with different [Li]/[Nb] ratios. From this figure we can see that the response time becomes shorter as the content of Li_2O increases. The relationship between response times and C_{Fe}^{2+} of these crystals are drawn in Fig.5, where the response time is defined as the diffraction efficiency reaching to 1/e of the saturation value. We can see from this figure that the response time becomes shorter when C_{Fe}^{2+} gets smaller. As is

well known, the response time should become shorter with increased C_{Fe}^{2+} for Fe:CLN crystals. So, this result indicates that besides $Fe^{2+/3+}$ there should have other photoactive centre in these Fe:NSLN crystals.

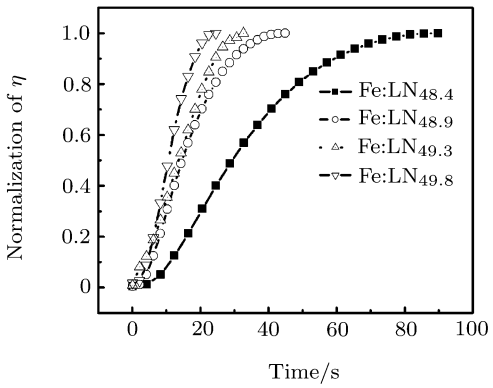


Fig.4. The record curves of Fe:$LiNbO_3$ crystals with different compositions.

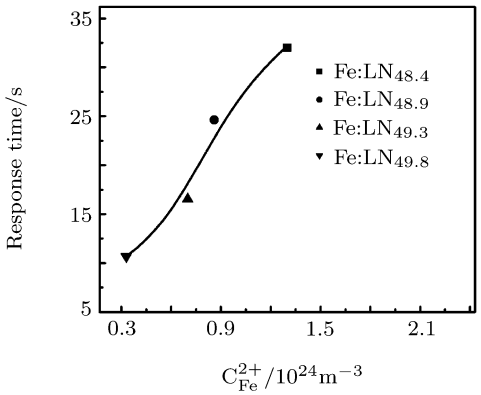


Fig.5. The relationship between response time and concentration of C_{Fe}^{2+}.

The erasing curves of Fe:LN crystals are shown in Fig.6. The photoconductivity can be obtained by measuring the erasure time according to $\sigma_{ph} = \varepsilon\varepsilon_0\tau_e^{-1}$, where ε_0 is the vacuum dielectric constant, ε is the relative dielectric constant, and the erasure time constant τ_e is defined as the time when diffraction efficiency decays to 1/e of its saturation value. The relationship between the photoconductivity and C_{Fe}^{2+}/C_{Fe}^{3+} is shown in Fig.7. From this figure, we can see that the photoconductivity decreases with the increase of C_{Fe}^{2+}/C_{Fe}^{3+}. However, the well-known result deduced from one centre model is $\sigma_{ph} \propto I\ (C_{Fe}^{2+}/C_{Fe}^{3+})$. It is obvious that the Fe^{2+}/Fe^{3+} one centre model is not fit for Fe:NSLN crystals.

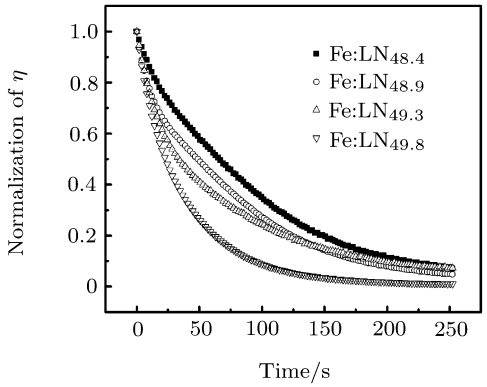


Fig.6. The erasure curves of Fe:$LiNbO_3$ crystals with different compositions.

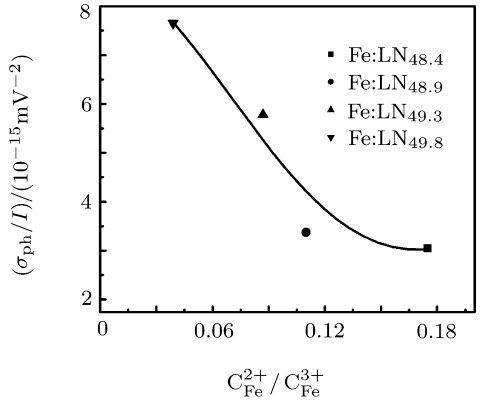


Fig.7. The relationship between $\sigma_{ph}/\ I$ and C_{Fe2+}/C_{Fe3+} of Fe:$LiNbO_3$ crystals.

Because instability of the holographic setup has no influence on the erasure process and no dynamic interaction of the recording waves, the erasure experiment is very useful to determine the kind of the photoactive centres. According to the Fe^{2+}/Fe^{3+} one centre model, the erasing process of Fe doped $LiNbO_3$ crystal should follow a monoexponential function $y = A_1\exp[-x/t_1]$. However, only the erasing curve of $Fe:LN_{48.4}$ crystal (shown in Fig.8) shows an excellent fitting result. We fitted the erasing curves by the biexponential function $y = A_1\exp[-x/t_1] + A_2\exp[-x/t_2]$, where A_1, A_2 denote the proportion of the gratings recorded on the different photorefractive centres, and t_1, t_2 are erasing times. We found that this function describes the erasure process of the other three crystals perfectly. The monoexponentially and biexponentially fitting results of $Fe:LN_{49.3}$, are shown in

Figs.9(a) and 9(b) respectively. The fitting parameters of all the crystals are collected in Table 1. The fitting results of erasure curves indicate that one photorefractive centre is suitable for the congruent crystal, while two centres for the stoichiometric crystals. The two photorefractive centres have also been found in $BaTiO_3$ crystal.[23]

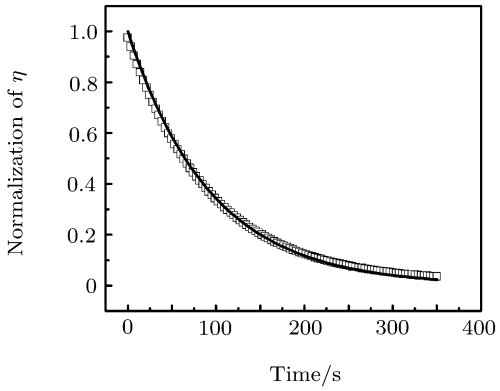


Fig.8. The monoexponential function fitting result of the erasure curve for Fe:$LN_{48.4}$.

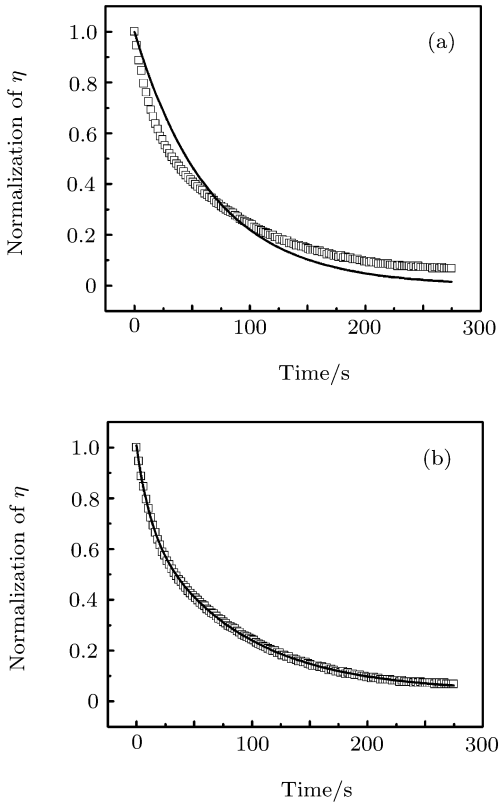


Fig.9. The fitting results of the erasure curve for Fe:$LN_{49.3}$, (a) by monoexponential function, (b) by biexponential function.

As it was known that small polarons (Nb_{Li}^{4+}, an electron was bound to an adjacent Nb_{Li}^{5+}) and bipolarons (Nb_{Li}^{4+}:Nb_{Nb}^{4+}, two electrons were bound in the mean time to adjacent a Nb_{Li}^{5+} and a Nb_{Nb}^{5+}) are responsible for the photorefraction of nominally pure near-stoichiometric crystals. Bipolarons may be dissociated either optically or thermally so that metastable small polarons are formed. Both processes are totally reversible.[24] The highest content of Li_2O in our samples is 49.8mol%, so the concentration of Nb_{Li} ions is much larger than that of doped Fe ions. There should have plenty of bipolarons in our Fe:NSLN crystals.

As we have known that the energy level for bipolaron and small polaron is at about 2.5 eV and 1.6 eV respectively. To further prove that bipolarons/small polarons participate in the photorefractive process for NSLN crystals, the light induced absorption $\Delta\alpha$ of 780nm and 532nm under 514nm light illumination were measured. $\Delta\alpha$ is defined as $\Delta\alpha = -\frac{1}{d}\ln\left(\frac{T_{\text{with}}}{T_{\text{without}}}\right)$, where T_{with} (T_{without}) is the probe transmitted light intensity before and after 514nm light illumination, and d is the thickness of the crystal. Figure 10 shows the experimental result for Fe:$LN_{49.3}$. The maximum of 532nm $\Delta\alpha$ is 0.06cm^{-1}, which is smaller than the fundamental absorption 2.34cm^{-1} at 532nm. The same experimental results occur to Fe:$LN_{48.9}$ and Fe:$LN_{49.8}$. These phenomena indicate that bipolarons were dissociated optically so that metastable small polarons come into being as the pump light was on. When the pump light was off, the excited electrons from metastable small polarons will be trapped by the deep centres again.

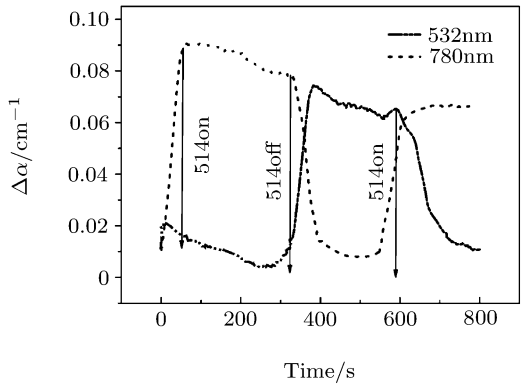


Fig.10. The light induced absorption $\Delta\alpha/cm^{-1}$ of 780 and 532nm under 514nm illumination for Fe:$LN_{49.3}$.

From Table 1 we can see that the longer erasure times of Fe:NSLN crystals are close to the erasing time of Fe:$LN_{48.4}$, so t_1 was regarded as relevant to $Fe^{2+/3+}$ photoactive centre. On the other hand, the shorter erasure times increase with the decrease of Li_2O content, so t_2 should correspond to the other photoactive centre bipolarons/small polarons. With the decrease of the intrinsic defects, the electron conductivity increases. It takes short time to excite electrons from Fe^{2+} to Fe^{3+} during the erasing process. Thus t_1 becomes short with the increase of Li_2O content in crystals. According to the model proposed by Yan *et al*,[25] with the increase of Li_2O content, the intrinsic defects tend to form bipolarons, and the photorefractive grating recorded on them becomes more. Therefore, t_2 becomes long. And the fitting results also indicate that A_1 becomes small and A_2 becomes large with the increase of Li_2O content, which further supports our conclusion.

Table 1. Compositions, concentration of Fe^{2+} and Fe^{3+} ions and fitting parameters of erasing curves for Fe:$LiNbO_3$ crystals used in this study.

sample	composition/mol %	$C_{Fe}^{2+}/10^{24}m^{-3}$	C_{Fe}^{2+}/C_{Fe}^{3+}	fitting parameter			
				A_1	t_1	A_2	t_2
Fe:$LN_{48.4}$	48.4	1.30	0.175	1.000	90	—	—
Fe:$LN_{48.9}$	48.9	0.86	0.110	0.840	83.4	0.191	14.4
Fe:$LN_{49.3}$	49.3	0.70	0.087	0.676	82.7	0.293	11.4
Fe:$LN_{49.8}$	49.8	0.33	0.039	0.670	47.0	0.346	18.4

It seems strange that only C_{Fe}^{2+}/C_{Fe}^{3+} photoactive centre exists in Fe:$LN_{48.4}$ crystal. Akhmadullin *et al*[26] reported that two bipolarons could form a Q polaron. Yan *et al*[25] further proved that Q polarons are predominant in the congruent crystals. For Fe doped $LiNbO_3$ crystal, photovoltaic mechanism was proved to be dominant. However, because the photovoltaic current arises from the local asymmetry of the photorefractive centres in crystal, Q polarons create only very weak photovoltaic effects when one considers their highly symmetric structure (the combination of two equivalent bipolarons). Thus only Fe^{2+}/Fe^{3+} can act as the photoactive centre in the Fe:$LN_{48.4}$ crystal. With the increase of Li_2O content, Q polarons tend to dissociate, and more and more bipolarons form, which act as the other photoactive centre and lead to the enhanced photorefractivity of NSLN crystals.

4. Summary

The photorefractive properties of iron doped $LiNbO_3$ crystals with different Li_2O contents were investigated. The fitting results of erasing curves and light induced absorption further indicate that there are two photoactive centres in Fe:NSLN crystals. Bipolarons and small polarons are indicated as another photoactive centre.

References

[1] Kaldis E and Räube A 1978 *Current Topics in Materials Science* Vol. **1** (Amsterdam: North-Holland)

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

[3] Wang C H, Liu L R, Y Ai M, Zhou Y, Liu D A and Hu Z J 2007 *Chin. Phys.* **16** 100

[4] Zhao H E, Liu S M, Guo R, Wang D Y, Yu X Y, Gao Y M, Huang C F and Xu J J 2003 *Acta Phys. Sin.* **52** 2781 (in Chinese)

[5] Zhou Y, Liu L R, Liu D A, Luan Z and Yan A M 2006 *Chin. Phys.* **15** 2977

[6] Iyi N, Kitammura K, Izumi F, Yamamoto J K, Hayashi T and Kimura S 1992 *J. Solid State Chem.* **101** 340

[7] Kostritskii S M and Sevostyanov O G 1997 *Appl. Phys.* B **65** 527

[8] Zhang T, Wang B, Fang S Q and Ma D C 2005 *J. Phys.* D: *Appl. Phys.* **38** 2013

[9] Kitamura K, Furukawa Y and Ji Y, Zgonik M, Medrano C, Montemezzani G and Günter P 1996 *J. Appl. Phys.* **82** 1006

[10] Furukawa Y，Kitamura K, Ji Y, Montemezzani G, Zgonik M, Medrano C and Günter P 1997 *Opt. Lett.* **22** 501

[11] Liu H D, Xie X, Kong Y F, Yan W B, Li X C, Shi L H, Xu J J and Zhang G Y 2006 *Opt. Mater.* **28** 212

[12] Glass A M, von der Linde D and Negran T J 1974 *Appl. Phys. Lett.* **25** 233

[13] Jermann F and Otten J 1993 *J. Opt. Soc. Am.* B **10** 2085
[14] Bai Y S and Kachru R 1997 *Phys. Rev. Lett.* **78** 2944
[15] Hesselink L, Orlov S, Liu A, Akella A, Lande D and Neurgaonkar R 1998 *Science* **282** 1089
[16] Guenther H, Macfarlane R, Furukawa Y, Kitamura K and Neurgaonkar R 1998 *Appl. Opt.* **37** 7611
[17] Buse K, Jermann F and Krätzig E 1993 *Ferroelectrics* **141** 197
[18] Borbui P F, Norwood R G, Jundt D H and Fejer M M 1992 *J. Appl. Phys.* **71** 875
[19] Wöhlecke M, Corradi G and Betzler K 1996 *Appl. Phys.* B **63** 323
[20] Kurz H, Krätzig E, Keune W, Engelmann H, U Gonser, B Dischler and A Räuber 1977 *Appl. Phys.* **12** 355
[21] Peithmann K, Wiebrock A and Buse K 1999 *Appl. Phys.* B **68** 777
[22] Berben D, Buse K and Wevering S 2000 *J. Appl. Phys.* **87** 1034
[23] Brost G A, Motes R A and Rotge J R 1988 *J. Opt. Soc. Am.* B **5** 1879
[24] Merschjann C, Berben D, Imlau M and Wöhlecke M 2006 *Phys. Rev. Lett.* **96** 186404
[25] Yan W B, Kong Y F, Shi L, Sun L, Liu H, Li X, Zhao D and J Xu 2006 *Appl. Opt.* **45** 2453
[26] Akhmadullin Sh, Golenishchev-Kutuzov V A and Migachev S A 1998 *Phys. Solid State* **40** 1012