Photo-Induced Carriers in Near-Stoichiometric $LiNbO_3$:Fe Crystal *

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We detect the photo-induced carriers in near-stoichiometric iron doped $LiNbO_3$ crystal by the holographic technique. The results show that the dominant carriers are electrons in the sample with Li/Nb ratio of 0.9988. By analysis of the OH^- absorption spectra of the crystal, we contribute the electron domination in near-stoichiometric Fe-doped $LiNbO_3$ crystal to the existence of Nb_{Li} which provides the anti-site defect to Fe^{2+}.

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For many years lithium niobate (LN) has been of great interest in areas of both fundamental science and applications because of its ferro-, pyro-, and piezoelectric properties as well as large electro-optic, acousto-optic and photoelastic coefficients along with strong photorefractive and photovoltaic effects.[1,2] Soon after the discovery of photorefraction in 1966, transitional metal ions such as Fe were used to improve the photorefractive properties of LN crystals.[3] Normal LN crystals are congruent, not stoichiometric. The number ratio of lithium ions to niobium ions is generally to be 48.6/51.4. The congruent LN crystals contain a considerably large number of intrinsic defects that would affect the properties of the crystals including the photorefraction. Thus many attempts have been performed to increase the Li/Nb ratio to obtain stoichiometric samples. It is expected that the stoichiometric crystals can show great performance improvement, such as higher photorefractive gain, faster response time and so on.[3,4] In the last several years, stoichiometric LN attracted a great deal of attention.[5−7]

In order to describe the photorefraction in stoichiometric LN crystal, we should clarify the photo-induced carriers in the crystal. It is well known that in reduced and as-grown congruent LN crystals, the dominant carriers are electrons.[8] Although the photorefractive properties of near-stoichiometric LN crystals have been widely studied, no experiment until now has been performed to determine the sign of carriers in near-stoichiometric samples. In the present work, the sign of carriers in a near-stoichiometric LN:Fe crystal is investigated by the holographic technique developed by Staebler and Amodei.[9] The results show that the carriers of domination are electrons. Combined with the results of other researchers on carriers in LN crystals, we also analysed the source of electron-dominations with the help of OH^- absorption spectra.

In our experiments, we used a near-stoichiometric Fe-doped (250 ppm) LN crystal with a Li_2O content of 49.97 mol% (corresponding to the Li/Nb ratio of 0.9988) grown by the VTE method[10] from a congruent sample. The sample was a y-plate in dimensions of $a \times b \times c = 8.0 \times 1.0 \times 10.0\,\mathrm{mm}^3$, and reduced at 500°C for half an hour in Ar gas. The Li_2O content was determined by the measurement of the Raman line width. The Raman scattering method allows the determination of the composition within an absolute accuracy of 0.05 mol% that was sufficient to discriminate clearly the various crystals under investigation.[11] For the quite strong piezoelectric effect in $LiNbO_3$ crystals, the $+c$ axis orientation of our sample was confirmed by the method of piezoelectricity.[1]

Since the fanning scattering in near-stoichiometric Fe-dope LN is symmetric, the sign of the carriers cannot be confirmed by observation of the relative direction of the fanning scattering to the $+c$ axis of the crystals.[12] Thus we used the holographic technique described in detail as follows. According to Staebler and Amodei's theory,[9] when the grating in an LN crystal is read out, the readout beam and its diffracted beam would write a "new" grating into the crystal with the same or opposite phase related to the previously grating. The new grating would therefore enhance or diminish the overall diffraction efficiency depending on the sign of the carriers and the relative orientation of the readout beam to the $+c$ direction of the crystal. For example, let us consider the geometry shown in Fig. 1. The $-c$ direction is close to the R beam. If the dominant carriers are electrons

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in the crystals, when we read out the phase grating by the R beam, the new grating has the same phase with the original grating, and it slows down the erasure process of the grating. If the dominant carriers are holes, the new grating has a phase shift of π to the original grating. Therefore, the erasure process needs a shorter time. By comparing the erasure time of different cases, we can determine the dominant carriers.

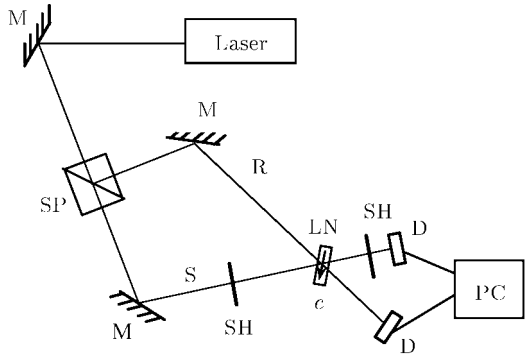


Fig. 1. Schematic drawing of our experimental setup: M, mirrors; SP, splitter; R/S: reference and signal beams; SH: shutters; PC: personal computer; D: detectors; LN: $LiNbO_3$ crystal.

With the experimental setup shown in Fig. 1, we recorded the phase gratings in our near-stoichiometric crystal. The phase grating was written by two ordinarily polarized plane waves from a solid-state laser of $\lambda = 532\,\mathrm{nm}$ with the bisector of the two beams normal to the sample. The crossing angle between the two writing beams was 18° in air. The intensity of each beam was $180\,\mathrm{mW/cm^2}$. In order to monitor the temporal behaviour of the writing process, we blocked the S beam from time to time and measured the intensity of the diffracted beam. The diffraction efficiency was defined as $\eta = I_D/(I_D+I_T)$, where I_D and I_T were the intensities of diffracted and transmitted beams respectively. In our LN crystal, the phase grating recorded by two extraordinary polarized beams has the diffraction efficiency much higher than the grating recorded by two ordinarily polarized beams. However, the extraordinarily polarized beam would also cause strong fanning scattering and add errors to the measurement of the erasure process of the phase grating. Choosing the ordinary writing beams can avoid the quick appearance of strong fanning and can make the measurement more precise.

The erasure results are shown in Fig. 2. The squares and triangles present the normalized erasure process when R was closed to the $-c$ and $+c$ axes, respectively. For both the erasure processes, the gratings can be written to the same diffraction efficiency of 10%, and then the diffraction efficiency is normalized. The erasing intensity was kept to be $180\,\mathrm{mW/cm^2}$. Here, τ_+ and τ_- represent the exponential decay time constant of η with the $-c$ axis close and away from the R beam, respectively. From the curves, we can obtain $\tau_- = 67.8\,\mathrm{s}$ and $\tau_+ = 102.2\,\mathrm{s}$, which could obviously work out a negative $\delta\tau = \tau_- - \tau_+$. Therefore, we could conclude that the electrons can be dominant in our near-stoichiometric LN: Fe crystal.

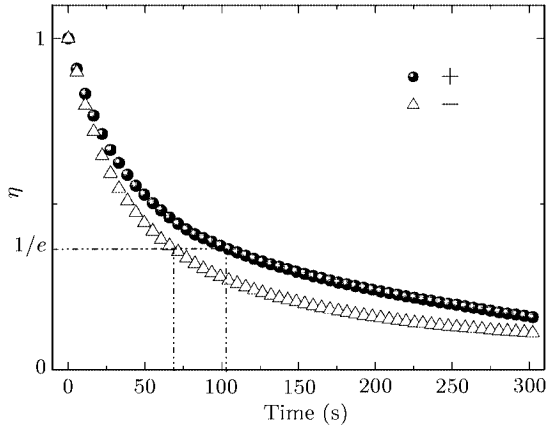


Fig. 2. Exponential decay of normalized diffraction efficiency. Circles and triangles represent the sample aligned in the opposite direction.

It is quite interesting to make clear why the dominant carriers are still electrons in near-stoichiometric LN, i.e. ascertaining the occupancy of Fe^{2+} in the crystal which would provide the photo-induced charge for photorefraction. Thus we should make clear what changes in LN from a congruent sample to a stoichiometric one. OH^- absorption spectra can be taken as a means by which we could probe the defect structure of the crystals.[13] The OH^- absorption spectra of our near-stoichiometric LN:Fe crystal as well as a congruent sample with the same dopants and nearly the same oxidization/reduction state were measured by a Nicolet-701 FT-IR spectrometer with the incident light along the y-axis, as shown in Fig. 3. It is obvious from Fig. 3 that the OH^- absorption band consists of a strong $3466\,\mathrm{cm^{-1}}$ absorption peak, a medium $3481\,\mathrm{cm^{-1}}$ peak and a weak $3489\,\mathrm{cm^{-1}}$ peak. According to the results of Kong *et al.*[14] and Grone and Kapphan,[15] the $3466\,\mathrm{cm^{-1}}$ peak can be thought to be related to H^+ at the Li site while $3481\,\mathrm{cm^{-1}}$ and $3489\,\mathrm{cm^{-1}}$ peaks are related to Nb_{Li}^{5+} with two different ion environments around V_{Li}^-. That is to say, in our sample the quantity of intrinsic anti-site defects Nb_{Li} still exists although the amount is greatly reduced by promoting the Li/Nb ratio. Thus we could say that the source of photo-induced electrons in LN must be concerned with cations at Li vacancies.

Another interesting question is that whether it is possible that holes become dominant in the LN crystals. According to the results of Orlowski and Kratzig,[8] holes in Fe-doped LN with strong oxidization are the dominant charges. Wang *et al.*[16] and Deng *et al.*[17] also found that in Mg-doped and Zn-

doped LN crystals with high dopant concentration, the dominant photo-induced carriers change from electrons to holes. In strong oxidized and Mg- or Zn-doped LN crystals, the diffraction efficient is quite low, which means the density of holes is low. We are performing the research to find LN crystals with high density of holes as the dominated charges. For LN crystals with high density of holes, we can realize more extensive applications.

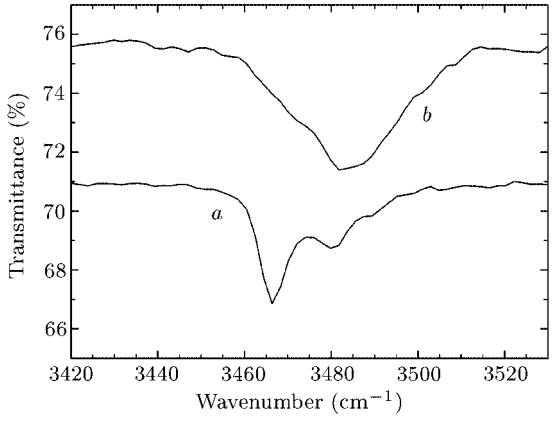


Fig. 3. OH absorption spectra of $LiNbO_3$:Fe crystals. (a) Near stoichiometric sample, (b) congruent sample.

In summary, we have studied the sign of photo-induced free carriers of near-stoichiometric $LiNbO_3$:Fe by the holographic technique. The results show that the dominant carriers are still electrons when the Li/Nb ratio reaches 0.9988. The OH^- spectrum analyses show that the Fe^{2+} ions at the location of Li-ion vacancy provide the dominant electrons for photorefraction in our near-stoichiometric Fe-doped $LiNbO_3$ crystals.

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