

Effect of Fe concentration on the nonlinear refraction and reverse saturable absorption in ferroelectric X-cut LiNbO₃ crystal

H. L. Saadon*

Laser Applications and Optical Materials Group, Department of Physics, College of Science,
University of Basrah, Basrah 61004, Iraq

*Corresponding author: haithamsaadon@yahoo.com

Received January 12, 2015; accepted April 23, 2015; posted online June 12, 2015

In this Letter, the effects of the iron (Fe) dopant concentration on the nonlinear optical properties of iron-doped ferroelectric X-cut LiNbO₃ crystals plates are studied by using the Z-scan technique with a cw laser at the wavelength of 532 nm. The amount of iron in the compound is varied from 0 to 0.15 mol%. Measurements of nonlinear refractive index n_2 and the nonlinear absorption coefficient β are determined. The sign of the nonlinear refractive index is found to be negative and the magnitude is on the order of 10^{-8} cm²/W. This nonlinear effect increases as the concentration increases from 0 to 0.15 mol%. A good linear relationship is obtained between nonlinear refractive index, nonlinear absorption coefficient, and concentration.

OCIS codes: 190.0190, 160.0160.

doi: 10.3788/COL201513.071901.

Interest in the development of laser technology, nonlinear optical materials with different nonlinear absorption processes like saturable absorption (SA), reverse saturable absorption (RSA), and two-photon absorption (TPA), has attracted significant attention of researchers in view of nonlinear optical device applications. Studies on different optical materials revealed that many materials exhibits more than one nonlinear absorption process simultaneously depending on the wavelength or intensity of the laser beam, doping concentration of the active material, and so on^[1-6]. Li *et al.*^[7] reported the observation of RSA in the pure Z-cut LiNbO₃ crystal with picosecond laser. Wang *et al.*^[8] found the optical nonlinearity in the thin LiNbO₃ film on the picosecond scale is much larger than that of the pure LiNbO₃^[9]. Kostritskii *et al.*^[9] found a transition from SA to RSA with the intensity increase in reduced LiNbO₃ crystal at cw illumination with the red (644 nm) and green (514.5 nm) laser beams. Recently there also has been an increasing interest in the third-order nonlinear susceptibility and the photorefractive effect crystals^[10-13] because the propagation of a strong laser beam in optical nonlinear material is closely related to the nonlinear refraction and absorption^[7,14] and the nonlinear refraction caused by the photorefractive effect in an LiNbO₃ crystal is very large.

Among the experimental methods used for the investigation of nonlinear optical properties of materials, the most comfortable and simplest is Z-scan technique, which allows the determination of both the value and sign of nonlinear refractive index n_2 ^[15].

Using cw Z-scan experiments absorption and nonlinear refraction of the samples under investigation can be determined. It is very important to study the dependence of the optical nonlinearity on the concentration.

This Letter reports the Z-scan studies of pure and Fe-doped ferroelectric X-cut LiNbO₃ crystals at different doping concentrations. The nonlinear refractive index n_2 and nonlinear absorption β were measured with cw laser beam at 532 nm. The optical limiting behavior has been studied.

The experimental setup for cw Z-scan is reported in Refs. [16,17]. Experiments are performed using a cw Nd:Y₃Al₅O₁₂ (YAG) laser operating at 532 nm. A lens was used with the focal length of $f = 50$ mm. The laser beam waist ω_0 at the focus was measured to be 16 μm and the Rayleigh length was found at 1.51 mm to satisfy the basic criteria of the Z-scan experiment. All samples are X-cut 1 mm-thick plates with surfaces polished at an optical grade. Thus, the sample thickness is less than the Rayleigh length for the system. The sample was mounted on a computer-controlled translation stage that moved the sample in the vicinity of the lens focus ($Z = 0$) starting from a position ahead of focus ($-Z$) and moving toward a position behind the focus ($+Z$). The scanning range was about 40 mm in all cases. All measurements were carried out at room temperature for both closed-aperture and open-aperture Z-scan experimental setup.

The experiments are performed for four samples of LiNbO₃ crystals plates, three of them doped with iron (Fe). The crystals were prepared by the Czochralski technique. The specimens were doped by iron at various molar concentrations; 0.0, 0.05, 0.1, and 0.15 mol%.

The UV-visible absorption spectrum of X-cut Fe ferroelectric doped LiNbO₃ crystals is described in Fig. 1. The optical absorption peak is approximately equal to 470 nm. One may choose the excitation wavelength of 532 nm for the nonlinear optical measurements. In comparison, in Ref. [18], Fe-doped LiNbO₃ showed no clear resonance

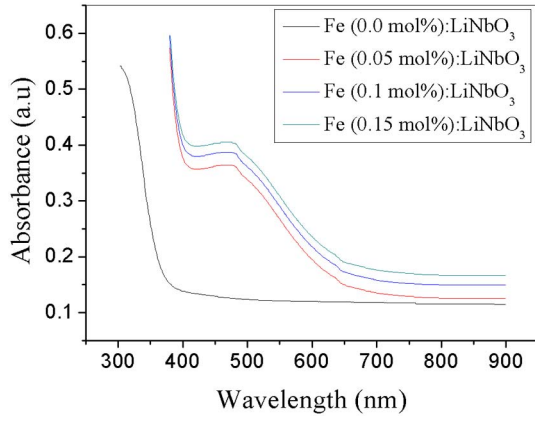


Fig. 1. Optical absorption spectra of ferroelectric X-cut LiNbO₃ crystals at different concentrations of Fe.

absorption peak. One possible explanation is that the Fe impurities were incorporated as aggregates into the host. It shows that the absorption edge of Fe-doped LiNbO₃ successively shift to the violet band in comparison with that of pure LiNbO₃. It is well-known that the position of absorption edge in LiNbO₃ crystal is decided by the forbidden band gap with O²⁻ p state as valence band and Nb⁵⁺ d state as conduction band. In Fe-doped LiNbO₃ crystals when Fe ions enter into lattice of crystal, they substitute Li ions and locate in Li sites^[19]. This will decrease energy gap since the polarization ability of Fe ions is greater than that of the Li ions, so the absorption edge shifted to the red band gap in comparison with that of pure LiNbO₃. This shift in the optical absorption is consistent with behaviors reported in Refs. [18,20,21]. This red shift in optical absorption edge can be attributed to the overall band structure of LiNbO₃ is changing due to Fe-doping^[22].

For the study of nonlinear optical properties, samples are put in a position that nonlinear regime is achieved.

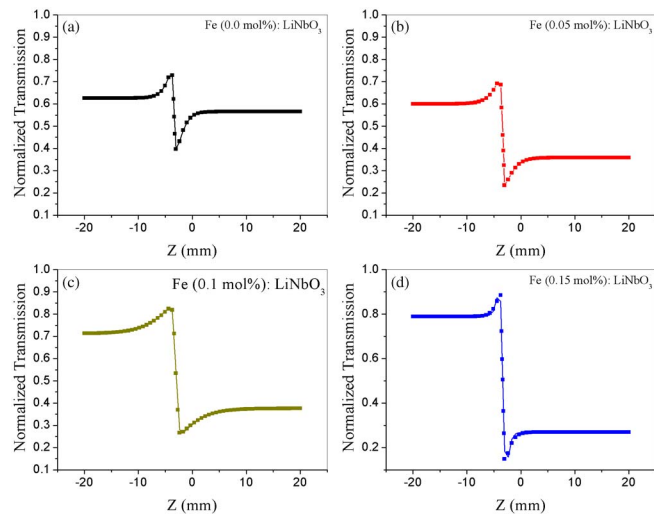


Fig. 2. Closed-aperture Z-scan measurements of the ferroelectric X-cut LiNbO₃ crystals at doping Fe concentration for (a) 0.0, (b) 0.05, (c) 0.1, and (d) 0.15 mol% Fe. Solid line, theoretical fit.

Figure 2 shows the curves for the closed-aperture Z-scan which are obtained at various concentrations of Fe doped LiNbO₃ with a fixed peak intensity of $I_0 = 3 \text{ kW/cm}^2$. It can be seen from the transmittance curve that the signal profile with a peak followed by a valley indicates a negative (self-defocusing) optical nonlinearity. The normalized transmittance for the closed-aperture Z-scan can be written as^[15-17]

$$\Delta T_{p-v} = 0.406(1 - S)^{0.25} \mathbf{k} n_2 I_0 L_{\text{eff}}, \quad (1)$$

where I_0 is the peak intensity at focus, $\mathbf{k} = 2\pi/\lambda$ is the wavevector with λ being the laser wavelength, $L_{\text{eff}} = [1 - \exp(-\alpha_0 L)/\alpha_0]$ is the effective length with α_0 being the linear absorption coefficient and L being the thickness of the sample, and S is the linear transmittance of the aperture given by $S = 1 - \exp\left[-2\left(\frac{r_a}{\omega_a}\right)^2\right]$ where r_a is the radius of the aperture and ω_a is the radius of the laser spot before the aperture.

The origin of nonlinear refraction can be electronic or thermal in nature^[17]. Under cw laser it is expected that the major contribution to the observed optical nonlinearities to the thermal in nature. The energy from the focused laser beam is transferred to sample through linear absorption and is manifested in terms of heating the medium leading to a temperature gradient and, in turn, to the refractive index change across the sample which then acts as a lens. For the Fe-doped LiNbO₃ crystal, the closed-aperture Z-scan shows a peak-valley distance of $\approx 4.4Z_0$. This peak-valley distance is more than 1.7 times the Rayleigh length Z_0 , which is indicated by thermal nonlinearity.

The open-aperture Z-scan measurements are plotted in Fig. 3. The results in Fig. 3 are obtained at different concentrations of Fe-doped LiNbO₃. The open-aperture curves exhibit a normalized valley, indicating the presence of RSA in the samples. The normalized transmittance for the open-aperture Z-scan can be given by^[15-17]

$$\Delta T = \frac{1}{2\sqrt{2}} I_0 L_{\text{eff}} \beta, \quad (2)$$

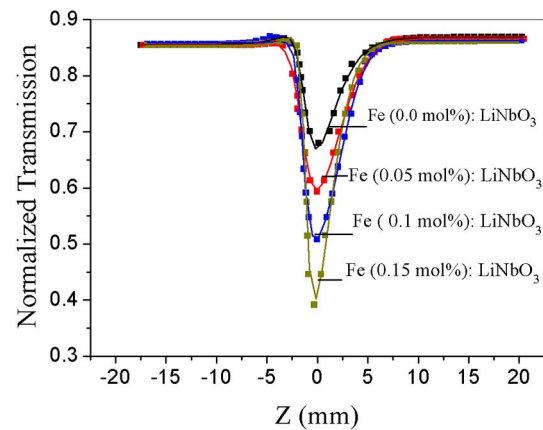


Fig. 3. Open-aperture Z-scan measurements of the ferroelectric X-cut LiNbO₃ crystals at different doping Fe concentrations. Solid line, theoretical fit.

Table 1. Nonlinear Refractive Index n_2 and Nonlinear Absorption Coefficient β at Different Fe Concentrations in Ferroelectric X-Cut LiNbO₃ Crystals

| Sample | n_2 (cm ² /W) | β (cm/kW) |
|------------------------------------|----------------------------|-----------------|
| Fe (0.0 mol%): LiNbO ₃ | -3.12×10^{-8} | 2.36 |
| Fe (0.05 mol%): LiNbO ₃ | -4.75×10^{-8} | 3.73 |
| Fe (0.1 mol%): LiNbO ₃ | -6.11×10^{-8} | 5.15 |
| Fe (0.15 mol%): LiNbO ₃ | -7.84×10^{-8} | 7.05 |

where β is the nonlinear absorption coefficient.

Nonlinear absorption in ferroelectric X-cut LiNbO₃ crystals plates could be due to RSA. RSA is known as positive type of absorption induced by free-carrier absorption (FCA), TPA, or with the combination of the processes^[23]. The origin of TPA requires at least twice incident laser energy E_{photon} less than the direct band gap energy E_g ^[1]. Therefore, the role of TPA in the nonlinear optical effect is not within the range $E_g > 2E_{\text{photon}}$, where $E_{\text{photon}} = 2.3$ eV and $E_g \approx 2.6$ eV. In the present case, the major nonlinear response is due to the RSA.

The measured values of nonlinear refractive index n_2 and nonlinear absorption coefficient β of ferroelectric X-cut Fe-doped LiNbO₃ crystals plates have been determined by means of Eqs. (1) and (2), respectively. The results obtained by such method are listed in Table 1. A peak-valley characteristic of closed experiments is negative and thermal defocusing is the most important mechanism of nonlinearity in these experiments. The sign of the nonlinear refractive index n_2 of a material is thus immediately clear from the sample of graph. The sensitivity to nonlinear refraction is entirely due to aperture, and absence of aperture completely eliminates the effect^[25]. The values of β and n_2 are comparable to the already reported in Ref. [24] for the pure LiNbO₃ crystals. These results are much larger than the previously reported in Ref. [9] at 514.5 nm and pure LiNbO₃ films at 532 nm^[8]. But these results are smaller than that reported previously by A. K. Kole *et al.*^[25] at pulse laser wavelength of 1064 nm for MgO-doped LiNbO₃ crystal.

The effect of doped Fe concentration on nonlinear refractive and nonlinear absorption is shown in Fig. 4. The nonlinear refractive index n_2 and the nonlinear absorption coefficient β increase linearly with the increase of Fe-doping concentration in LiNbO₃ crystals, indicating that the contribution to nonlinear coefficients arises due to the presence of the Fe. This may be attributed to the fact that as the number of particles increases when the concentration increases, more particles get thermally agitated resulting in an enhanced effect.

In conclusion, the nonlinear refractive index n_2 and nonlinear absorption coefficient β of ferroelectric X-cut pure and Fe-doped LiNbO₃ crystals plates at different Fe concentrations (0.0, 0.05, 0.1, and 0.15 mol%) are successfully measured by the cw Z-scan technique. The sign and

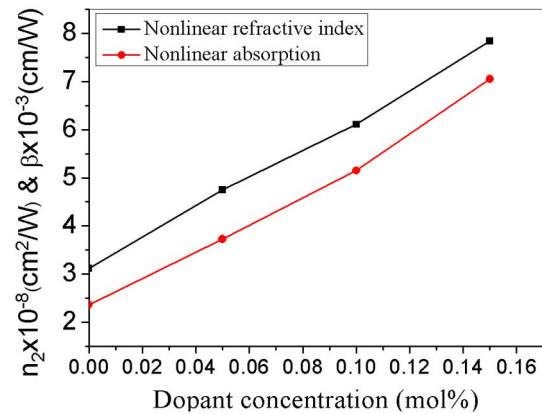


Fig. 4. Nonlinear refractive index n_2 and nonlinear absorption coefficient β as a function of Fe concentration for ferroelectric X-cut LiNbO₃ crystals.

magnitude of nonlinear refractive index are evaluated, and it is found to be on the order of 10^{-8} cm²/W. The X-cut undoped and Fe-doped LiNbO₃ crystals exhibit self-defocusing nonlinear behavior. RSA phenomena is the major nonlinear mechanism observed for the crystals. The crystal samples with different Fe concentrations can be of prime importance to define such parameters needed for the use of these materials in devices and applications.

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