CHARACTERIZATION OF IRON DOPED LITHIUM NIOBATE
FOR HOLOGRAPHIC STORAGE APPLICATIONS

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ABSTRACT

A detailed study of eight systematically chosen Fe:LiNbO₃ crystals is presented. Correlation between the photorefractive sensitivity and various chemical properties of Fe:LiNbO₃ is investigated in order to ascertain optimum performance of Fe:LiNbO₃ crystals in holographic storage and display applications. Concentrations of Fe²⁺ and Fe³⁺ ions have been determined from optical and EPR spectra while impurities have been detected from x-ray emission and infrared spectra. Particular emphasis is placed on investigating the dependence on Fe²⁺ and Fe³⁺ ion concentrations of the photorefractive sensitivity. The photorefractive sensitivity is shown to depend primarily on the concentration of Fe²⁺ ions in Fe:LiNbO₃. This fact seems to suggest that Fe²⁺ ions are the impurity centers responsible for the photorefractive effect in Fe:LiNbO₃. Spectral dependence of the photorefractive sensitivity and its modification due to oxygen annealing are also reported. Our results indicate that an unannealed Fe:LiNbO₃ crystal containing 0.05 mole % Fe with 20-25% of the ions in the Fe²⁺ state and the remainder in the Fe³⁺ state possesses the most favorable photorefractive sensitivity.

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I. Introduction

In recent years considerable interest has evolved in certain electro-optic crystals as potential real-time optical storage media capable of efficient, reversible, high density and fast recording and display of images or holographic information¹. The physical mechanism responsible for the formation of phase holograms in such crystals is the photorefractive effect. This process consists of the optical excitation and subsequent transport and retrapping of electrons which originate from localized centers in such crystals^{2,3}. Early theories described the transport of charge carriers in terms of diffusion or drift in a constant electric field^{2,3}. More recently, Glass et al.⁴ have suggested a new approach, namely the charge carriers are photogenerated and displaced in a spatially preferred direction. Photo-excited space charge patterns, resembling the intensity profile of the generating holographic intensity pattern in turn set up electric fields that distort the index of refraction of the crystal through the electrooptic effect. In this manner the refractive index modulation, which generates a volume phase hologram, can be used as a mechanism for information storage. Although this effect has been observed in several ferroelectric crystals, including LiNbO_3 ^{2,3,5}, LiTaO_3 ^{2,5,6}, BaTiO_3 ⁷ and SBN ⁸, their relatively low

recording and erasure sensitivities compared to other direct optical recording media⁹ has been a practical drawback. At this time, the most promising of these crystals is LiNbO_3 which has a large electrooptic coefficient and whose sensitivity can be increased several orders of magnitudes by optimizing the charge transport mechanism. Free electrons are provided by Fe ions present in significant concentrations even in undoped LiNbO_3 , and substantial improvements in sensitivity have been made by doping LiNbO_3 with transition metals, in particular with Fe. Apart from the dependence on total iron concentration, the photorefractive sensitivity of $\text{Fe}:\text{LiNbO}_3$ is believed to depend also on the concentrations of the two valence states of Fe viz. Fe^{2+} and Fe^{3+} 10^{-14} . The relative concentrations of Fe^{2+} and Fe^{3+} ions in a given crystal of $\text{Fe}:\text{LiNbO}_3$ can be altered by subjecting the crystal to oxidizing or reducing heat treatments^{10,11,13}. To a lesser extent, the sensitivity can also be improved by applying a large electric field or by writing with short optical pulses¹⁵.

In view of the importance of improving the photorefractive sensitivity of $\text{Fe}:\text{LiNbO}_3$ for potential use in holographic storage applications, we report in this paper a detailed characterization of chemical and holographic properties of $\text{Fe}:\text{LiNbO}_3$. In order to determine optimum crystal properties we have chosen crystals with a systematic variation of concentrations and crystal treatments. The nature and abundance of impurities present in LiNbO_3 affect the photorefractive sensitivity. Impurities have, therefore, been identified and their concentrations determined by various measurements. These measurements include proton beam induced x-ray emission spectra, IR absorption spectra, optical absorption spectra and EPR. The absolute concentrations of

Fe^{2+} and Fe^{3+} ions for both annealed and unannealed crystals with the same Fe dopant concentrations have been deduced by using optical and EPR spectra. Changes in the Fe^{2+} and Fe^{3+} concentrations produced by oxygen annealing are examined. Correlation of the photorefractive sensitivity with concentrations of Fe, Fe^{2+} and Fe^{3+} has been quantitatively investigated and the effects of inadvertent impurities in $\text{Fe}:\text{LiNbO}_3$ are discussed qualitatively. Spectral dependence of photorefractive sensitivity and its modification due to oxygen annealing, and hence also due to reduction, have been studied.

Changes in optical absorption spectra have been ascribed to changes in Fe^{2+} concentrations^{13,14,16} which in turn have been associated with changes in photorefractive sensitivity¹⁷⁻¹⁹. Fe^{3+} ions in $\text{Fe}:\text{LiNbO}_3$ have been identified by both EPR spectra²⁰⁻²² and by magnetic susceptibility measurements¹⁶. Recently, a direct confirmation of the existence of a Fe^{2+} state in LiNbO_3 has been made by investigating the Mössbauer spectra of $\text{Fe}:\text{LiNbO}_3$ ²³. In this paper we present comprehensive correlation of these chemical properties with the photorefractive sensitivity of $\text{Fe}:\text{LiNbO}_3$. Our experimental results and analysis indicate that the Fe ion responsible for the increase of absorption in the optical spectrum of $\text{Fe}:\text{LiNbO}_3$, viz - Fe^{2+} , is also mainly responsible for increasing the photorefractive sensitivity. The photorefractive sensitivity increases almost linearly with increasing Fe^{2+} concentration but then saturates; this seems to suggest that in addition to the absolute Fe^{2+} concentration the relative concentrations of Fe^{2+} and Fe^{3+} ions are also important in determining the photorefractive sensitivity. This interpretation is substantiated by the fact that the decrease in photorefractive sensitivity upon oxygen annealing follows a pattern very

similar to that of the decrease in Fe^{2+} concentrations (or increase in Fe^{3+} concentrations). As a result, there exist optimum values of Fe, Fe^{2+} and Fe^{3+} concentrations for which the sensitivity is most favorable: 0.05 mole % Fe doped LiNbO_3 with 20-25% Fe^{2+} (and 75-80% Fe^{3+}). It should be noted that in general any further increase in the net CW photorefractive sensitivity of $\text{Fe}:\text{LiNbO}_3$ will be limited by the accompanying increase in optical absorption without a corresponding increase in the sensitivity.

Furthermore, the diffraction efficiency curves for different crystals are in good agreement with an analytical expression for diffraction efficiency based upon a non-linear dynamic theory for photorefractive phase hologram formation proposed by the authors^{24,25}. This is especially true for the time scales of the oscillatory diffraction efficiency curves.

The detailed characterization of $\text{Fe}:\text{LiNbO}_3$ reported herein is useful not only from a practical standpoint but also because it assists in examining the nature of the physical processes and impurity centers involved in photorefractive volume phase holography, which is so far only partially understood. These studies lead us to the relation between hologram forming dynamics and the nature and concentration of the impurity center responsible for the photorefractive effect. In fact, this would be the essential first step towards tailoring ferroelectric crystals or predicting their properties for holographic storage applications. In Sec. II are presented spectroscopic measurements of the physical properties of LiNbO_3 . In Sec. III are reported the measurements of the photorefractive properties. The analysis and conclusions are presented in Secs. IV and V, respectively.

II. Spectroscopic Measurements of Physical Properties

In order to investigate the dependence of photorefractive sensitivity on iron concentration and on the valence states of iron, $\text{Fe}:\text{LiNbO}_3$ crystals were chosen with wide ranging and systematically varying Fe concentrations. Eight crystals were studied; two each with the following Fe dopant concentrations: 0.005%, 0.02%, 0.05% and 0.1% per mole. A wide range of Fe^{2+} and Fe^{3+} concentrations was obtained by selecting these eight crystals such that four of them were annealed in an oxygen atmosphere while the other four (one of each iron concentration) were not subjected to any heat treatment. The annealing process was done in an oxygen atmosphere at 100°C/hour. The physical dimensions of the cut and polished crystals were chosen for convenience to be: 1 cm (a-axis) by 0.1 cm (b-axis) by 1 cm (c-axis).²⁶ The following measurements were made on all eight LiNbO_3 crystals.

(A) X-ray emission spectra

The presence of impurities in $\text{Fe}:\text{LiNbO}_3$ other than the main dopant, Fe, can affect the photorefractive sensitivity of $\text{Fe}:\text{LiNbO}_3$ either adversely or favorably. Therefore, to make any meaningful correlation of the photorefractive sensitivity with the iron concentration, one needs to detect the presence of other impurities and measure their concentrations. The elemental analysis of the crystals was done using two techniques. The first of these techniques employs proton beam induced x-ray emission spectroscopy²⁷ to detect and determine the concentrations of all elements with $Z > 20$ present in the LiNbO_3 crystals. Samples analyzed by this technique included the 0.005%, 0.02% and 0.1% per mole Fe doped annealed

and unannealed LiNbO_3 crystals. Powdered crystals in the form of a thin layer were used as targets for the proton beam.

The measured spectra for all samples show peaks corresponding to Fe and Nb as expected, but they also reveal the unexpected presence of Ni in substantial quantities in all six samples. In Table I we list the measured concentrations of Ni. Comparison of the concentrations for the annealed and unannealed samples shows that Ni is not introduced by the annealing process, but must enter during growth in the melt or poling. Substantial quantities of Ni in otherwise Fe doped LiNbO_3 crystal can modify the holographic properties of the crystals²⁸.

(B) I-R spectra

Since x-ray emission analysis is limited to elements with $Z > 20$, IR absorption spectroscopy is used to identify impurities with $Z < 20$. In particular hydrogen is an impurity that has been known to enter LiNbO_3 crystals and to reduce its photorefractive sensitivity²⁹⁻³². Mechanisms by which hydrogen reduces the susceptibility of LiNbO_3 to refractive index change are not known; but for a proper evaluation of crystal sensitivities and comparison of their performance, one must include the relative concentrations of hydrogen in these crystals. Hydrogen diffuses into the crystals during the poling process and combines with the oxygen in LiNbO_3 to form OH ions. The presence of hydrogen in LiNbO_3 is manifested by an OH^- , 0-1 stretching vibrational band in the near infra-red at approximately $2.86 \mu\text{m}$. All eight Fe: LiNbO_3 crystals investigated exhibit this band and one of the crystals, the 0.05% Fe doped annealed crystal, more so than the

others (approximately twice - see Fig. 1). The data presented here was taken with a Beckman Type 8 IR spectrophotometer at room temperature. The spectra are unpolarized; however the c-axis of the crystal in each case was oriented parallel to the slits and the direction of the beam was perpendicular to the c-axis. The peak absorptions and hence the relative concentrations of the OH^- ions are shown in Table II. A peak absorption of about 1 to 2.5 cm^{-1} corresponds to an H ion concentration of the order of $10^{16} - 10^{17} / \text{cm}^3$.³⁰ The effect of the substantially higher absorption in one of the crystals as compared to the others is discussed in connection with Fig. 11.

(C) Optical spectra

Absorption of $\text{Fe}:\text{LiNbO}_3$ in the visible region of the spectrum is mainly due to the Fe^{2+} state of the iron dopant. The band at 484.5 nm has been attributed to $\text{Fe}^{2+} \rightarrow \text{Nb}^{5+}$ intervalence charge transfer¹⁶ and its intensity is proportional to the Fe^{2+} concentration. We have therefore used this band together with the EPR spectra of $\text{Fe}:\text{LiNbO}_3$ to determine the absolute concentrations of Fe^{2+} and Fe^{3+} ions.

Optical absorption spectra were recorded with a Cary 17 spectrophotometer at room temperature. Spectra for all eight crystals, taken with the beam perpendicular to the c-axis for $E_{\perp}c$ (σ -spectrum) and $E//c$ (π -spectrum) for each of these crystals are shown in Figs. 2a, 2b. In Fig. 3 the absorption spectral data is replotted to show the change upon oxygen annealing in the intensity of the band at 484.5 nm , and also in the absorption at longer wavelengths in the visible. The intensity of the band at 484.5 nm is linear with the Fe concentration for both the annealed and

unannealed crystals. Hence the ratios of intensities of this band yield the relative concentrations of Fe^{2+} ions present in each crystal (Fig. 4, Table III.)

From 2a and 2b a marked shift of the absorption edge towards shorter wavelengths upon oxygen annealing is evident. Pure LiNbO_3 has an oxygen $2p\pi$ valence band and Nb $d\sigma$ conduction band with a bandgap of 3.72 eV^{16} . The absorption edge of pure LiNbO_3 is therefore at approximately 350 nm. The shift in the absorption edge of LiNbO_3 towards longer wavelengths upon doping with Fe is due to the excitation of electrons from the oxygen valence band to the shallow Fe impurity states in the bandgap¹⁶. This shift towards longer wavelengths is greater with increasing Fe concentration and for σ polarization as compared to the π polarization and for unannealed crystals as compared to annealed crystals, suggesting a modification of the band structure of LiNbO_3 by the Fe^{2+} impurities.

(D) EPR measurements

Fe^{3+} ions are responsible for the EPR spectrum of $\text{Fe}:\text{LiNbO}_3$. EPR spectra can therefore be used to calculate the relative concentrations of Fe^{3+} ions in a $\text{Fe}:\text{LiNbO}_3$ crystal. Hence it is possible to obtain for any pair of annealed and unannealed crystals with the same iron concentration, the ratio of their Fe^{2+} and Fe^{3+} contents, obtained independently from optical absorption and EPR data respectively. In this manner, it is possible to determine the absolute concentrations of Fe^{2+} and Fe^{3+} ions for each of the eight $\text{Fe}:\text{LiNbO}_3$ crystals under investigation.

For the trigonal C_{3v}^6 structure of LiNbO_3 and for the Fe substituting for Nb or Li with octahedral coordination with O, the crystal field is

approximately axially symmetric. With the inclusion of Zeeman and second order interactions only, the spin Hamiltonian for Fe^{3+} in LiNbO_3 ^{11,16,20-22} is given by

$$H = g\beta\vec{H}\cdot\vec{S} + D[S_z^2 - \frac{1}{3}S(S+1)]$$

The EPR spectrum of single crystal $\text{Fe}^{3+}:\text{LiNbO}_3$ exhibits a large orientational dependence and hence is not useful for a comparative study. The EPR analysis was therefore carried out using powdered samples of annealed and unannealed crystals with 0.005, 0.02 and 0.1 mole % Fe.

EPR spectra for each of the six $\text{Fe}:\text{LiNbO}_3$ crystals mentioned above, were taken on a Varian E-line EPR spectrometer at a frequency of 9.3 GHz at 70°K from 0 to 4000 Gauss (Fig. 5). The absorption peak at approximately 300 Gauss was sufficiently strong to allow a room temperature measurement in all six samples. This absorption peak corresponds to the transition

$|-1/2\rangle \rightleftharpoons |-3/2\rangle$ that does not exhibit any angular dependence as described in Ref. 22. A scan was made for each powdered sample over the absorption signal at 300 Gauss. The variation of signal height with change of orientation of the powdered samples with respect to the magnetic field was found to be negligible. However, for each sample an average value of the EPR signal at 300 Gauss was obtained from measurements for four different orientations.

The relative magnitudes of the average signal heights for the various samples normalized with respect to sample weight and receiver gain give the relative concentrations of the Fe^{3+} ion in the six $\text{Fe}:\text{LiNbO}_3$ crystals investigated. Samples of annealed and unannealed 0.05 mole percent Fe were not available. However, the concentrations of Fe^{3+} in these two crystals can be estimated

from the extrapolation of the graphical representation of this data. The results of the EPR analyses are summarized in Table IV and Fig. 6. We have used these results, together with those obtained by optical absorption measurement, to obtain for any pair of annealed and unannealed Fe:LiNbO_3 crystals with a given Fe concentration, the absolute concentrations of Fe^{2+} and Fe^{3+} ions. These results are listed in Table V.

III. Measurement of Photorefractive Properties

For holographic storage applications the quantity of prime interest is the photorefractive sensitivity. The dependence of photorefractive sensitivity on the physical properties of the crystals and the experimental parameters such as writing and reading wavelengths, are important to attain the most favorable storage characteristics and to shed some light upon the physical mechanisms responsible for the process. In this section we discuss the correlation of the diffraction efficiency and photorefractive sensitivity of Fe:LiNbO_3 crystals with the experimental data described in Section II, such as iron dopant concentration, crystal treatment and recording wavelength.

(A) Experimental arrangement and techniques

Plane wave holograms were recorded in Fe:LiNbO_3 crystals using the experimental arrangement shown in Fig. 7. The coherent radiation source used was an argon ion laser operating in the TEM_{00} transverse mode and a single longitudinal mode with a linewidth of about 50 MHz and a frequency jitter of ± 100 MHz, as monitored by an optical spectrum analyzer. Intensity fluctuations were less than two percent. The optical recording beam was split into a reference beam and an object beam and their intensities were equalized to within 2 percent using neutral density filters. The two beams, each with a 3 mm diameter, intersected in the crystal at an angle of 12° to form interference fringes in the direction perpendicular to the writing plane. The c-axis of the crystal was oriented to lie in the writing plane and perpendicular to the bisector of the writing angle. The thickness of the crystals perpendicular to the c-axis is 1 mm. The incident, reflected, transmitted and diffracted beams were measured using an EG&G

model 580 radiometer.

Holograms were read at the same wavelengths as those used for recording them. This was accomplished by briefly interrupting the recording process at regular intervals of time, blocking one of the recording beams and measuring the diffracted beam without disturbing the system. Six different argon laser lines were used for writing and reading holograms (4574, 4727, 4765, 4880, 4965 and 5145 Å), with the polarization perpendicular to the writing plane. For all crystals and wavelengths, the experimental conditions and the technique for measurement were identical.

(B) Definitions of experimental parameters

We now define the quantities in terms of which the experimental results have been measured and interpreted. The diffraction efficiency (η) of a hologram for any crystal and for any wavelength at a given time t , has been defined as the percentage of the initially ($t = 0$) transmitted read beam that is diffracted by the hologram at time t . Values of η are obtained at regular intervals of time, and plotted as a function of time to give the holographic writing curve.

Photorefractive sensitivity may be defined as the net energy density (i.e., corrected for reflected component) required to produce a hologram of one percent diffraction efficiency. Such a quantity is difficult to determine experimentally, especially when writing with a pulsed radiation source. An alternative definition would be given by the net energy density required to produce a hologram with a specified diffraction efficiency. Such a definition would not always provide a unique basis for the comparison of

sensitivities for different crystals, since η , in general, is not a linear function of exposure. We therefore define a new sensitivity. In view of the diversity of existing methods of interpreting experimental results and the ensuing ambiguity in comparing results reported in the literature, we specify our procedure in detail.

The slope of the diffraction efficiency with respect to the writing time is taken at any specific value of diffraction efficiency η ; this given value of η is common for all crystals and wavelengths. We define the sensitivity in terms of the product of the net power density and the reciprocal of this slope. If the aforementioned slope is taken at a low value of η , say 10%, where η grows almost linearly in time, the intercept on the time axis equals very closely the time required to attain that η value and our definition reduces to the energy density required to produce a hologram with a given diffraction efficiency.

According to the coupled wave theory by Kogelnik³³ for diffraction from a transmission hologram, any particular value of the diffraction efficiency corresponds to a certain value of the coupling constant of the holographic grating, or equivalently the corresponding refractive index modulation. This modulation is related directly to the energy density required to produce it. In so doing, however, the effect of beam attenuation inside the crystal has to be explicitly taken into account. This is especially true when the increase in crystal absorption that accompanies high dopant concentration levels outweighs the increase in photorefractive sensitivity. We have incorporated the beam attenuation effect by introducing

a parameter

$$\Gamma = (1 - e^{-\alpha L})/\alpha L \quad (1)$$

(α = absorption coefficient of the crystal, L = crystal thickness). The quantity, Γ represents the ratio of the average beam intensity inside the crystal to the incident intensity, viz. $I_{\text{avg}}/I_0 \equiv \Gamma$. For the ideal case where the crystal has no absorption $\Gamma = 1$ and $I_{\text{avg}} = I_0$. Consequently, this value of I_{avg} will be achieved for a crystal with Γ different from 1 if the incident beam I_0 is inversely scaled w.r.t. Γ i.e., (I_0/Γ) . We have therefore defined the effective photorefractive sensitivity as

$$S = (\Delta n/\Delta E)\Gamma \quad (2)$$

where Δn is the refractive index change associated with a fixed value of η and ΔE is the incident energy density required to produce it.

(C) Experimental results

The experimentally measured diffraction efficiency curves for all eight Fe:LiNbO₃ crystals are depicted in Fig 8. Due to the differences in intensities used for recording holograms in these crystals, the abscissa has been taken to be the writing energy density or exposure instead of time. The η -curves shown in Fig. 8 were obtained for recording and reading wavelengths of 4579 Å. For all cases the polarization of the recording and reading beams was perpendicular to the c-axis and measurements were made at room temperature.

Increase in the initial slope of the η -curves with increasing Fe

concentration is evident from Fig. 8. Also it is clear that the slope of the η -curves is substantially higher for the unannealed crystals as compared to that of the annealed crystals of the same Fe concentration. Note also that the slope of the η -curves in the initial linear regime can provide a good measure of the photorefractive sensitivity. Furthermore, it is interesting to note that for crystals with low Fe concentration, η -curves are linear in the exposure range investigated, whereas within the same exposure range crystals with high Fe concentration show a remarkable oscillatory behavior, i.e., the time scales for these curves are substantially different indicating a great difference in the rates at which the space charge field or the refractive index modulation builds up in these crystals. This will be discussed in greater detail in Section IV.

The dependence of photorefractive sensitivity on iron concentration and crystal treatment is shown in Fig. 9. For all crystals except X-1, the photorefractive sensitivities were obtained for a diffraction efficiency of 10 percent, which, as is evident from Fig. 8, is well within the initial linear regime of η . For X-1 the photorefractive sensitivity was calculated at an η value of 2 percent, due to the long time that would be needed to write a hologram in that crystal to 10 percent diffraction efficiency. However, due to the linear nature of the η -curve in this region, the calculated value of sensitivity is the same as what it would be at $\eta = 10$ percent.

To emphasize the effect of absorption in the crystal, photorefractive sensitivities without the attenuation parameter Γ are also plotted in Fig. 9. It is interesting to observe the great difference in the sensitivities of the unannealed and annealed crystals. Furthermore, for the unannealed

crystals a saturation is seen in the photorefractive sensitivity as a function of Fe concentration without the inclusion of attenuation effects. With the inclusion of Γ the photorefractive sensitivity for the unannealed crystals increases with increasing Fe concentration, reaches a maximum value and then decreases again, thus indicating the predominance of absorption in crystals with high Fe concentration. The effect of absorption in the crystal can thus be judged from the difference in the sensitivity curves with and without the factor Γ . The annealed crystals, which have a much lower sensitivity, show only a slight modification when taking into account the absorption parameter Γ . In Fig. 10 are plotted the ratios of the photorefractive sensitivities (with and without the attenuation parameter Γ) of the unannealed to the annealed crystals of the same Fe concentration and the ratios of their corresponding Γ 's. First, since the ratios of sensitivities are greater than unity for all crystals, all unannealed crystals have higher sensitivities than their annealed counterparts. This is to be expected from the results of Fig. 9. For crystals with low Fe concentration, attenuation effects are negligible and the curves of the ratios of photorefractive sensitivities with and without the attenuation factor Γ almost coincide. For crystals with high Fe concentration the effective sensitivity is not enhanced because of the counteracting influence, namely the beam attenuation factor. For example, for the 0.1% per mole Fe doped crystal $\Gamma_{UA}/\Gamma_A \simeq 0.44$ and $(\Delta n/\Delta E)_{UA}/(\Delta n/\Delta E)_A \simeq 5$. On the other hand, for the 0.05% per mole Fe doped crystal, $\Gamma_{UA}/\Gamma_A \simeq 0.66$ and $(\Delta n/\Delta E)_{UA}/(\Delta n/\Delta E)_A \simeq 46$ i.e., gain in photorefractive sensitivity is far greater than the increase in absorption of the unannealed crystal. This

shows explicitly that the optimal region for recording phase holograms in unannealed $\text{Fe}:\text{LiNbO}_3$, with high photorefractive sensitivity and low absorption is 0.04 to 0.07 percent per mole Fe.

The spectral dependence of the photorefractive sensitivity for all eight $\text{Fe}:\text{LiNbO}_3$ crystals is shown in Fig. 11. Six different wavelengths were used: 4579, 4727, 4765, 4880, 4965 and $5145 \text{ \AA}$. The values of photorefractive sensitivities plotted in Fig. 11 and the corresponding attenuation parameters Γ are listed in Tables VI and VII. It is evident from Fig. 11 that photorefractive sensitivities of all crystals except X-1 and X-7 within the limits of experimental error, increase linearly with decreasing wavelength. It is interesting to compare the spectral dependence of the photorefractive sensitivity with that of optical absorption (see Figs. 2 and 3): while the optical absorption shows a distinct peak and decreases with decreasing wavelength near $4845 \text{ \AA}$, no such dependence is observed in the sensitivity curve. This difference may perhaps be significant in considering the bulk photovoltaic effect⁴.

For two crystals, X-1 and X-7 the spectral dependence of sensitivity departs from the general linear behavior (Fig. 11). From the data given in Tables I and II, it can be seen that crystal X-1 has a high Ni concentration while crystal X-7 has a high OH^- concentration as compared to the other crystals. We may qualitatively explain the general shapes of the sensitivity curves for X-1 and X-7 as follows. OH^- ions decrease the conductivity of the crystals for short wavelengths so as to reduce the sensitivity whereas for longer wavelengths they enhance the sensitivity²⁹⁻³². For X-1, the higher concentration of Ni, which has a high absorption in the

shorter wavelengths plotted in Fig. 11 (Reference [34]), increases the sensitivity, while for λ close to $5000 \text{ \AA}$ Ni does not have a high absorption and hence does not enhance the sensitivity. As a result the shape of the photorefractive sensitivity curve for λ close to $5000 \text{ \AA}$ does not depart from the general linear behavior exhibited by the other crystals. Crystal X-7 was subjected to γ -radiation from a 7 mCi source for about seven days in the course of Mössbauer measurements. This resulted in a slightly increased sensitivity (curve X-7 $_{\gamma}$ in Fig. 11), possibly due to the creation of defect centers, but there is no change in the general shape of the sensitivity curve.

IV. Analysis

Based on the data given in the two preceeding sections, we now consider the role played by the two valence states of iron, i.e., Fe^{2+} and Fe^{3+} in the photorefractive effect. In particular, we examine the effect of oxygen annealing and establish the correlation between photorefractive sensitivity and Fe^{2+} concentration. In addition, with the aid of our theory^{24,25} we relate crystal parameters to the diffraction efficiency and the photorefractive sensitivity.

Fig. 12 shows the increase in the absolute concentration of Fe^{3+} ions upon oxygen annealing of $\text{Fe}:\text{LiNbO}_3$. On a logarithmic scale, the Fe^{3+} concentration increases linearly with the Fe concentration in the crystal up to about 0.04% per mole Fe, but then begins to saturate. Another way of stating this saturation is that with increasing Fe concentration the fractional occupancy of the Fe^{3+} state (Fe^{3+}/Fe) in the unannealed crystal decreases (see Table V).

We examine the dependence of photorefractive sensitivity on the concentrations of the two valence states of iron. In the previous section we have investigated photorefractive sensitivity as a function of Fe concentration separately for the annealed and unannealed crystals (see Fig. 9). We now consider the dependence of photorefractive sensitivity on the Fe^{2+} ion concentrations. The differences in (a) sensitivities of the annealed and unannealed crystals and (b) the corresponding percentages of Fe^{2+} ions are plotted in Fig. 13 as a function of Fe concentration. The remarkable similarity in the two curves shows explicitly a direct relation between photorefractive sensitivity and Fe^{2+} ion concentration.

We plot in Fig. 14 photorefractive sensitivity directly as a function of the absolute Fe^{2+} concentration in these crystals (Table V). (As in Table V, crystals X-1 and X-2 have not been included in Fig. 14 since the very small optical absorption observed at $4845 \text{ \AA}$ does not allow estimation of Fe^{2+} and Fe^{3+} concentrations.) Note that unlike Fig. 9 where the photorefractive sensitivities for the annealed and unannealed crystals lie on two separate curves, we have in Fig. 15 a single curve for photorefractive sensitivity regardless of whether the crystal is annealed or not annealed, depending only on their Fe^{2+} concentrations. No such dependence is seen on Fe^{3+} concentrations, for which we once again have separate plots for the annealed and unannealed crystals, as in Fig. 9. From Fig. 14 it can be seen that the photorefractive sensitivity increases initially as a linear function of the Fe^{2+} concentration, just as in the case of optical absorption (Fig. 4), but then begins to decrease. We will discuss this point further in the following paragraphs.

First we analyze the dependence of the time scale of the oscillatory diffraction efficiency curves on the concentrations of Fe ions in Fe:LiNbO_3 (see Fig. 8). In Ref. [25] we showed that the diffraction efficiency of a Fe:LiNbO_3 crystal is a function of exposure with writing beam intensity as a variable parameter. There a systematic dependence between the writing beam intensity and the time required for η to reach a maximum value was observed, in agreement with the nonlinear dynamic theory for space charge field²⁴. In this work the diffraction efficiency is plotted

as a function of exposure with the concentration of Fe ions in the Fe:LiNbO_3 crystals as a variable parameter. As in the previous case²⁵ the time scale involved in the η curves can be described with the aid of the same formulation.²⁴ The space charge field or the diffraction efficiency η evolves in time scaled with the crystal parameters and intensity as

$$t/\tau_g = (e\mu\tau/\epsilon) (\alpha I t / \hbar\omega) \quad (3)$$

Here, e, μ, τ, ϵ denote respectively the electronic charge, mobility, trapping time and the permittivity of the crystal. The effect of the beam attenuation inside the crystal is taken into account by expressing the intensity $I = I_0 \Gamma$, as in Sec. III. Hence

$$t/\tau_g = (\Delta E)/T(\lambda) \quad (4)$$

$$\Delta E \equiv I_0 t, \quad T(\lambda) = \hbar\omega \epsilon / e\mu\tau\alpha\Gamma \quad (5)$$

with ΔE denoting incident exposure and $T(\lambda)$ the corresponding scaling factor. Thus, if T_6 and T_8 correspond to the times required by crystals X-6 and X-8 to reach maximum η values on an exposure scale in Fig. 8, we have from Eq. (5)

$$\frac{T_6}{T_8} = \frac{\alpha_8 \Gamma_8}{\alpha_6 \Gamma_6} \quad (6)$$

Upon inserting the values of α 's and Γ 's in Eq. (6) from Table 7, we obtain

$$\frac{T_6}{T_8} = 0.79$$

whereas, measuring this ratio directly from the experimental curves of Fig. 8 we also get

$$\frac{T_6}{T_8} = 0.8$$

This good agreement between theory and experiment is a further confirmation of our previous studies^{24,25}. As pointed out previously, the values of sensitivity were obtained in the regime of η linear in exposure. In this linear regime,^{24,35} the refractive index modulation is proportional to the exposure as well as the equivalent electron drift field which contains components due to drift, diffusion and the bulk photovoltaic effect⁴. Hence the sensitivity reads as

$$S = \left[\left(\frac{1}{2} n_e^3 r_{33} e \mu \tau \right) / (e \hbar \omega) \right] \propto \frac{1}{L} \int_0^L dz e^{-\alpha z} E(z) \quad (7)$$

where n_e , r_{33} are the extraordinary index of refraction and the electro-optic coefficient of the crystal. Eq. (7) gives the sensitivity in terms of crystal parameters, beam attenuation and the equivalent electron drift field, $E(z)$. We now use Eq. (7) to discuss Fig. 14. If $E(z)$ is a constant independent of the attenuation coefficient, α or the intensity and hence of the crystal depth (z), Eq. (7) reduces to

$$S \propto (1 - e^{-\alpha L}) \quad (7a)$$

In this case, the sensitivity increases with increasing α or Fe^{2+} concentration and then saturates. This saturation is obviously due to the fact that with increasing α the depth of the refractive index modulation is degraded rapidly.

Note, however, that the effect of beam attenuation on S does not entirely explain our experimentally observed curve (Fig. 14), which in fact begins to decrease after reaching a maximum value. This suggests that the equivalent electron drift field, $E(z)$ depends on α as well as intensity, hence on z . This interpretation is consistent with the results of our previous work²⁵ and those of Ref. [36]. Hence a quantitative description of the curve in Fig. 14 is only possible if the various contributions to $E(z)$ are known independently.

V. Conclusions

We have carried out a detailed and methodical study of eight systematically chosen Fe:LiNbO₃ crystals. As a result, we have

- (1) determined the concentration of Fe²⁺ and Fe³⁺ ions in Fe:LiNbO₃ from optical absorption and EPR measurements
- (2) established the relation between the photorefractive sensitivity and Fe²⁺, Fe³⁺ and Fe concentrations
- (3) investigated the spectral dependence, the effect of oxygen annealing and of other impurities on the photorefractive sensitivity
- (4) analyzed the diffraction efficiency curves for different crystals and corresponding sensitivities with the dynamic theory of hologram formation
- (5) qualitatively discussed the role of the bulk photovoltaic effect in hologram writing sensitivity.

We have shown in the course of this work that for the crystals examined by us, there exists an optimal set of crystal characteristics for which the photorefractive sensitivity is most favorable. The optimal parameters are: (a) 0.05% per mole Fe concentration, (b) Fe²⁺/Fe ~ 20-25%, (c) $\alpha \sim 13.5 \text{ cm}^{-1}$ and (d) crystal thickness 0.1 cm. For these parameters, the sensitivity has been observed to be $6 \times 10^{-4} \text{ cm}^2/\text{J}$ at 4579 Å. We compare this sensitivity with the highest sensitivities reported in the literature and have summarized it in Table VIII.

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Figure Captions

- Figure 1: OH⁻, O-1 stretching vibrational band in the near infrared absorption spectrum. Spectra for other Fe:LiNbO₃ crystals are similar to that of X-8.
- Figure 2: (a) Optical absorption spectra of all eight Fe:LiNbO₃ crystals; polarization E_{1c}, (b) polarization dependence of the optical absorption spectrum for 0.05 and 0.1 mole % Fe doped unannealed LiNbO₃ crystals.
- Figure 3: Effect of oxygen annealing on the optical absorption spectrum for a 0.1 mole % Fe doped LiNbO₃ crystal.
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- Figure 7: Experimental arrangement used for measuring photorefractive sensitivity.
- Figure 8: Dependence of holographic diffraction efficiency curves upon exposure for eight Fe:LiNbO₃ crystals at a fixed writing wavelength.
- Figure 9: Dependence of the photorefractive sensitivity on Fe concentration for a set of eight Fe:LiNbO₃ crystals, corrected and uncorrected for absorption.

Figure 10: Comparison of ratios of photorefractive sensitivities and attenuation factors of unannealed and annealed $\text{Fe}:\text{LiNbO}_3$ crystals of the same Fe concentration.

Figure 11: Spectral dependence of photorefractive sensitivity for a set of eight $\text{Fe}:\text{LiNbO}_3$ crystals.

Figure 12: Effect of oxygen annealing on Fe^{2+} and Fe^{3+} concentrations.

Figure 13: Comparison of change in photorefractive sensitivity and change in percentage of Fe^{2+} concentrations for a set of eight $\text{Fe}:\text{LiNbO}_3$ crystals.

Figure 14: Dependence of photorefractive sensitivity of a set of eight $\text{Fe}:\text{LiNbO}_3$ crystals on Fe^{2+} concentrations.

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Fe:LiNbO ₃ crystal	Fe conc. mole %	treat- ment	(Ni/Nb) ppm by wt.	($\frac{\text{Ni}}{\text{Fe}+\text{Ni}}$)%
X-1	0.005	A	223	47
X-2	0.005	UA	81	29
X-3	0.02	A	108	25
X-4	0.02	UA	83	17
X-5	0.1	A	709	28
X-6	0.1	UA	704	28

TABLE I

Fe:LiNbO ₃ crystal	Fe conc. mole %	treat- ment	OH ⁻ ratios
X-1	0.005	A	1.4
X-2	0.005	UA	1.5
X-3	0.02	A	1.4
X-4	0.02	UA	1.2
X-5	0.1	A	1.0
X-6	0.1	UA	1.0
X-7	0.05	A	3.2
X-8	0.05	UA	1.3

TABLE II

Fe:LiNbO ₃ crystal	Fe conc. mole %	treat- ment	Fe ²⁺ ratios
X-1	0.005	A	1.0
X-2	0.005	UA	1.0
X-3	0.02	A	1.0
X-4	0.02	UA	4.0
X-5	0.1	A	4.5
X-6	0.1	UA	57
X-7	0.05	A	2.5
X-8	0.05	UA	25

TABLE III

Fe:LiNbO ₃ crystal	Fe conc. mole %	treat- ment	Fe ³⁺ ratios
X-1	0.005	A	1.0
X-2	0.005	UA	1.0
X-3	0.02	A	3.8
X-4	0.02	UA	3.6
X-5	0.1	A	17
X-6	0.1	UA	13
X-7	0.05	A	8.8
X-8	0.05	UA	7.0

TABLE IV

Fe:LiNbO ₃ crystal	Fe conc. mole %	treat- ment	Fe ²⁺ conc. mole %	Fe ³⁺ conc. mole %	$\frac{\text{Fe}^{2+}}{\text{Fe}^{3+}}$	$\frac{\text{Fe}^{2+}}{(\frac{\text{Fe}^{2+}}{\text{Fe}^{3+}})}\%$	$\frac{\text{Fe}^{3+}}{(\frac{\text{Fe}^{2+}}{\text{Fe}^{3+}})}\%$
X-1	0.005	A	~	$\lesssim 5 \times 10^{-3}$	~	~	~
X-2	0.005	UA	~	$\lesssim 5 \times 10^{-3}$	~	~	~
X-3	0.02	A	3.0×10^{-3}	19.7×10^{-3}	0.015	2.0	98
X-4	0.02	UA	1.2×10^{-3}	18.8×10^{-3}	0.064	6.0	94
X-5	0.1	A	0.20×10^{-2}	9.80×10^{-2}	0.019	2.0	98
X-6	0.1	UA	2.40×10^{-2}	7.60×10^{-2}	0.320	24	76
X-7	0.05	A	0.10×10^{-2}	4.90×10^{-2}	0.022	2.0	98
X-8	0.05	UA	1.10×10^{-2}	3.90×10^{-2}	0.280	22	78

TABLE V

Fe:LiNbO ₃ crystal		X-1	X-2	X-3	X-4	X-5	X-6	X-7	X-8
Fe conc. mole %		0.005	0.005	0.02	0.02	0.1	0.1	0.05	0.05
treatment		A	UA	A	UA	A	UA	A	UA
recording wavelength, Å	sensi- tivity (cm ² /J)								
		x10 ⁻⁷	x10 ⁻⁵	x10 ⁻⁵	x10 ⁻⁴	x10 ⁻⁴	x10 ⁻³	x10 ⁻⁵	x10 ⁻³
4579	$\frac{(\Delta n/\Delta E)}{(\Delta n/\Delta E)} \Gamma$	43.1	1.50	1.77	1.43	2.27	1.20	4.05	1.10
		36.4	1.23	1.40	1.11	1.75	0.41	3.35	0.60
4727	$\frac{(\Delta n/\Delta E)}{(\Delta n/\Delta E)} \Gamma$	9.95	1.05	1.67	1.87	1.81	0.90	1.99	0.94
		8.42	0.86	1.32	1.44	1.39	0.29	1.65	0.51
4765	$\frac{(\Delta n/\Delta E)}{(\Delta n/\Delta E)} \Gamma$	20.7	1.22	1.35	1.05	2.27	1.31	5.06	1.06
		17.5	1.00	1.07	0.80	1.72	0.42	4.16	0.57
4880	$\frac{(\Delta n/\Delta E)}{(\Delta n/\Delta E)} \Gamma$	6.35	1.29	0.81	0.89	1.88	1.26	3.45	0.97
		5.37	1.05	0.64	0.68	1.45	0.41	2.84	0.52
4965	$\frac{(\Delta n/\Delta E)}{(\Delta n/\Delta E)} \Gamma$	8.07	1.65	1.08	0.85	1.63	1.17	2.32	1.01
		6.86	1.35	0.86	0.66	1.26	0.38	1.93	0.55
5145	$\frac{(\Delta n/\Delta E)}{(\Delta n/\Delta E)} \Gamma$	4.57	1.34	0.80	0.85	1.28	0.85	0.99	0.73
		3.89	1.10	0.63	0.66	1.00	0.29	0.83	0.41

TABLE VI

Fe:LiNbO ₃ crystal	X-1	X-2	X-3	X-4	X-5	X-6	X-7	X-8
Fe conc. mole %	0.005	0.005	0.02	0.02	0.1	0.1	0.05	0.05
treatment	A	UA	A	UA	A	UA	A	UA
recording wavelength, Å								
attenuation								
4579	$\alpha_1 \text{ cm}^{-1}$ Γ	3.45 0.846	4.14 0.819	4.95 0.789	5.41 0.772	5.53 0.768	28.1 0.335	3.91 0.828
4727	$\alpha_1 \text{ cm}^{-1}$ Γ	3.45 0.846	4.14 0.819	4.95 0.789	5.53 0.768	5.53 0.768	29.1 0.325	3.91 0.828
4765	$\alpha_1 \text{ cm}^{-1}$ Γ	3.45 0.846	4.14 0.819	4.95 0.789	5.53 0.768	5.76 0.760	29.4 0.323	4.03 0.823
4880	$\alpha_1 \text{ cm}^{-1}$ Γ	3.45 0.846	4.14 0.819	4.95 0.789	5.41 0.772	5.53 0.768	29.4 0.323	4.03 0.823
4965	$\alpha_1 \text{ cm}^{-1}$ Γ	3.34 0.850	4.14 0.819	4.84 0.793	5.30 0.776	5.41 0.772	28.8 0.328	3.80 0.832
5145	$\alpha_1 \text{ cm}^{-1}$ Γ	3.34 0.850	4.03 0.823	4.95 0.789	5.30 0.776	5.18 0.781	27.4 0.341	3.68 0.837

TABLE VII

crystal	writing technique	$\left(\frac{\Delta n}{\Delta E}\right) \frac{\text{cm}^2}{\text{J}}$	α^{-1}_{cm}	Γ	$\left(\frac{\Delta n}{\Delta E}\right) \cdot \Gamma \frac{\text{cm}^2}{\text{J}}$
<u>BELL LABS</u> 0.05% Cu ²⁺ :LiNbO ₃	CW at 5145Å	3.6×10^{-6}	0.72	0.93	3.4×10^{-6}
	50 MW/cm ² 10 ps pulses at 5300Å	4.1×10^{-5}	0.25	0.98	4.0×10^{-5}
	500 MW/cm ² 10 ps pulses at 5300Å	3.1×10^{-4}	2.5	0.79	2.4×10^{-4}
<u>RICE CRYSTAL</u> 0.05% Fe:LiNbO ₃ , unannealed	CW at 5145Å	7.3×10^{-4}	12.9	0.56	4.1×10^{-4}
	CW at 4579Å	11×10^{-4}	13.5	0.55	6.0×10^{-4}
	CW at 5145Å	$\sim 10^{-9}$	$<10^{-2}$	1	$\sim 10^{-9}$
undoped LiNbO ₃					

TABLE VIII