Local doping of Lithium Niobate crystals by Fe diffusion: a depth-resolved study of photorefractive properties

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Outline

introduction

Fe:LiNbO$_3$ doping and characterization

Photorefractive properties and optical set-up

depth-resolved holographic measurements

conclusion
The material

Lithium Niobate (LiNbO$_3$)

Uniaxis Ferroelectric material with electro-optic effect

\[ n_o = \frac{1}{2} n_o r_{13} E_z \]
\[ n_e = \frac{1}{2} n_e r_{33} E_z \]

- \( r_{13} \approx 9.6 \text{ pm/V} \)
- \( r_{33} \approx 31 \text{ pm/V} \)

1. Optical modulators
2. Integrated waveguides

New goals: optical memories by holographic recording thanks to photorefractivity
The photorefractive effect

1. presence of donor/acceptor centers
2. photoexcitation process at suitable wavelength in the bright region
3. trapping of charges in the dark region

Fe is one of the most exploited donor/center dopant
Photorefractive properties in LiNbO$_3$

Variation of the refractive index $n$ induced by inhomogeneous illumination

The refractive index pattern (i.e. grating) is correlated to the light pattern.
Photorefractive properties: physics

Charge migration is due to drift, diffusion and bulk photovoltaic effect

\[ j_{tot} = j_{drift} + j_{diffusion} + j_{photovoltaic} \]

Electric space charge field \( E_{sc} \) depends on the exposition time \( t \)

\[ E_{sc} = E_{sc,sat} \left( 1 + e^{t/\tau_c} \right) \]

Once center model and inhomogeneous illumination in Fe:LiNbO₃

\[ E_{sc,sat} \mu Fe^{3+} \]

\[ \frac{1}{\tau_{sc}} \mu_{ph} \mu I \frac{Fe^{2+}}{Fe^{3+}} \]
Photorefractive properties

Inhomogeneous illumination

\[ I(z) = I_0 \left[ 1 + m \sin(K \times z) \right] \]

\[ m = \frac{I_{\text{max}} - I_{\text{min}}}{I_{\text{max}} + I_{\text{min}}} \]

The refractive index pattern (grating) is correlated to the light pattern
Final goal: integrated optical sensor

Grating efficiency \[ \eta = \frac{I_d}{I_d + I_t} \]

**Writing**
- Waveguides
- Reference
- Waveguide
- Hologram
- Signal

**Reading**
- Reference
- Output
- Unknown input
Applications

Selective identification of chemical substances by optical methods

Integrated optical memories
Few works on Fe-diffused LiNbO$_3$ samples (waveguide configuration) limited to estimate the photorefractive properties.

Need to measure the real photorefractive parameters and correlation of all the physical properties.
Iron deposition

- Sample cutting: polished LiNbO$_3$ x-cut slabs

- **Fe film deposition:** RF magnetron sputtering
deposition rate: $(4.15 \pm 0.02) \times 10^{14}$ at/s·cm$^2$

- Fe film quality: **X-Ray Reflectivity** (film thickness)

  Film thickness 5-20 nm
  Density $5 \times 10^{22}$ at/cm$^3$

  *Atomic Force Microscope*
Iron in-diffusion

1. Diffusion process:
   - wet O₂ atmosphere
   - 1100°C
   - duration: 20h

2. Reducing treatments:
   - wet Ar (96%) + H₂ (4%)
   - 500°C
   - duration: 20 min-6h

Longer reducing treatments increasing reduction degree [Fe²⁺]/[Fe³⁺]
Compositional characterization

Secondary Ion Mass Spectrometry: determination of the total Fe content

Fe semi-gaussian concentration profile

\[ c_{Fe}(x) = \frac{N_{Fe}}{\sqrt{D_{Fe} t}} e^{\frac{x^2}{4D_{Fe}t}} \]

\[ \omega^2 = D_{Fe} \cdot 2t \]

\[ C_{\text{sup}} = (18.0 \pm 0.4) \times 10^{24} \text{ at/m}^3 \]

\[ \omega_{Fe} = (21.3 \pm 0.5) \mu\text{m} \]

Reduction treatment does not affect Fe distribution
Iron in-diffusion

Activation energy

\[ E_A = (2.8 \pm 0.1) \text{eV} \]

Compositional characterization

Reducing treatment does not increase significantly the hydrogen content

Reduction degree = $\frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]}$

\[
\begin{align*}
\text{Fe}^3+ + O^2^- + \frac{1}{2} H_2 & \leftrightarrow \text{Fe}^2+ + OH^- \\
\text{Nb}^5+ + O^2^- + \frac{1}{2} H_2 & \leftrightarrow \text{Nb}^4+ + OH^- 
\end{align*}
\]
Optical characterization

Fe\(^{2+}/Fe^{3+}\)

C band 3.1 eV

D band 2.6 eV

A band 1.1 eV

VB

532 nm \(\rightarrow\) Fe\(^{2+}\)

342 nm \(\rightarrow\) Fe\(_{\text{tot}}\)

Reduction degree

\[
\frac{[Fe^{2+}]}{[Fe^{3+}]}
\]

Optical characterization

Compositional characterization by measuring the optical transmission $T$

D band intensity is proportional only to $\text{Fe}^{2+}$

$$OD = \log \frac{T_{\text{FeLN}}}{T_{\text{pureLN}}}$$

as-diffused: $\frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} \approx 0.18 \%$

reduced: $\frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} \approx 4.6 \%$

$$\text{Fe}^{2+}_{fluence} = \frac{OD}{\text{Fe}^{2+}}$$
Optical characterization

<table>
<thead>
<tr>
<th>Peak</th>
<th>Transition</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1 eV (1128 nm)</td>
<td>$^5\text{A} - ^5\text{E (Fe}^{2+}\text{)}$</td>
</tr>
<tr>
<td>2.6 eV (477 nm)</td>
<td>$\text{Fe}^{2+} - \text{Nb}^{5+}$</td>
</tr>
<tr>
<td>3.1 eV (400 nm)</td>
<td>$\text{O}^{2-} - \text{Fe}^{3+}$</td>
</tr>
<tr>
<td>2.57 eV– 2.91 eV (483 nm – 426 nm)</td>
<td>d- d ($\text{Fe}^{3+}$)</td>
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Optical Absorption: involving the total amount of $\text{Fe}^{2+}$

Estimation of absorption coefficient $\alpha_{\text{sup}}$ at the surface

$$\alpha_{\text{sup}} = \frac{\text{Optical Density}}{\text{Fluence}} \cdot c_{\text{sup}}^{\text{Fe}^{3+}}$$

$$\text{OD} = -\log \left( \frac{T_{\text{LN}}}{T_{\text{FeLN}}} \right)$$

Fluence ($\text{Fe}^{2+}$) = $\text{OD}/\sigma_{532}$
Structural characterization: H-XRD

Rocking curve $\omega-2\theta$ to determine the lattice mismatch $\xi$

\[
\Delta \omega = d - d_{\text{substrate}}
\]

Lattice mismatch

$\Delta \omega$ (degrees)

Reciprocal space map (220)

Interplanar distance in the substrate $d_{\text{sub}}$
Structural characterization

The maximum lattice deformation $\xi$ induced at the surface of iron doped lithium niobate crystal by thermal diffusion depends on:

1. Fe concentration
2. reduction degree

$$\text{surface} = m_1C_{\text{Fe surface}} + m_2$$

$$\text{surface} = OD \frac{C_{\text{Fe surface}}}{[\text{Fe}]_{\text{fluence}}}$$

*Ciampolillo, Sada et al. J. Appl. Phys. 107, 084108 (2010)*
Photorefractive properties

Holographic technique \rightarrow \text{Refractive index grating as} \text{ diffraction grating}

One center model
Kogelnik’s theory

\[ \eta \equiv \frac{I_d}{I_d + I_t} = \sin^2 \left( \frac{\pi \Delta n L}{\lambda \cos(\theta)} \right) \]

\( \theta \) Angle between the incident beam and fringes plane
Photorefractive properties

Local study of photorefractive properties by light-induced formation of $\mu$-holograms

Scans along x axis
Fe concentration $C_{Fe}(x)$

In-depth profiles of photorefractive properties
Holographic set-up

μ - holograms  ➔  Confined interference area  ➔  Focused beams

Holographic parameters

Interference area: probe size

5-10 μm

50.6 μm

$2\theta_{in}$

$d_1 = 50.6 \mu m$

$d_2 = 983.6 \mu m$
Holographic parameters

Angle between interference beams

\[ 2\theta_{in} = (5.89 \pm 0.01)° \]

Grating parameters

\[ \begin{align*}
K &= K_z = (1.22 \pm 0.07) \times 10^6 \text{ m}^{-1} \\
\Lambda &= (5.15 \pm 0.30) \text{ µm}
\end{align*} \]

Maximum intensity

\[ I_{\text{max}} = (35 \pm 4) \times 10^4 \text{ W/m}^2 \]
Holographic measurements

Hologram recording: space charge field build-up

Monitoring time evolution of $I_d \rightarrow \eta(t) \rightarrow E_{sc}(t)$

One center model

$$E_{sc} = \frac{2n}{n^3 r_{eff}}$$

$$n = \arcsin \left( \sqrt{\frac{\cos(q)}{L}} \right)$$

$$r_{eff} = r_{33} \cos^2(q) - r_{13} \sin^2(q) + \frac{n_e}{n_o} (r_{33} - r_{13}) \sin^2(q)$$
Diffused Fe:LN: recording curves

Scans along the diffusion direction (x axis)

- $E_{sc,sat}$ decreases
- $\tau_{sc}$ increases
E_{sc} in-depth profile of diffused FeLN

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diffused Fe:LN sample

- experimental space-charge field
- gaussian fit

Undoped sample

- experimental space-charge field

Fe^{2+}/Fe^{3+}=0.18 %
$E_{sc}$ in-depth profile of diffused FeLN

$\text{Fe}^{2+}/\text{Fe}^{3+} = 0.18\%$

$\tau_{sc} \approx 120s$
Holographic erasing time

Erasing time depends on the dark conductivity of the doped material.
$E_{sc}$ in-depth profile of diffused FeLN

$E_{sc}$ in-depth profile similar to $c_{Fe}$:

\[
E_{sc} \propto [Fe^{3+}]
\]

$\omega_C = (23.5 \pm 1.3) \, \mu m$

$\omega_{Fe} = (21.3 \pm 0.5) \, \mu m$

Enhanced photorefractive effect in Fe-doped samples

\[
\begin{align*}
LiNbO_3 & \quad E_{sc, sat} = (3.5 \pm 0.1) \times 10^5 \, V/m \quad |\Delta n| = (5.7 \pm 0.1) \times 10^{-5} \\
Fe:LiNbO_3 & \quad E_{sc, sat} = (4.3 \pm 0.4) \times 10^6 \, V/m \quad |\Delta n|_{0\,\mu m} = (7.3 \pm 0.9) \times 10^{-4}
\end{align*}
\]
Photoconductivity in as-diffused Fe:LN

\[ \frac{1}{\mu_{ph}} \]

\[ \mu_{sc} \]

\[ \frac{[Fe^{2+}]}{[Fe^{3+}]} \]

Fe\textsuperscript{2+} confined near the surface of the sample

\[[Fe^{2+}]/[Fe^{3+}]\] is not constant in the doped layer

New results!

\( \omega_{\sigma} = (3.2 \pm 0.9) \mu m \)

\[ \text{photoconductivity (x } 10^{-12} \text{ } \Omega^{-1} \text{ } m^{-1}) \]

\[ \text{depth (} \mu m \) \]

experimental data

fit
Optical absorption $\rightarrow$ total Fe$^{2+}$ amount $[\text{Fe}^{2+}] = 2.4 \cdot 10^{19}$ at/m$^2$

Space charge field proportional to Fe$^{3+}$

Photovoltaic current in-depth profile proportional to Fe$^{2+}$
Conclusions

Study of photorefractive mechanisms in Fe-diffused samples

- new optical set-up based on $\mu$-hologram recording
- in-depth profiles of photorefractive properties
- new insights on iron reduction mechanism

Iron doping allows great enhancement of photorefractivity

- high reproducibility
- for permanent grating, need of thermal fixing process
Work in progress

Detailed investigation of reduction process

influence of $T$, $c_{Fe}$, intrinsic defects on photorefractive response of Fe-diffused crystals

Development of integrated devices based on Fe-diffused LiNbO$_3$

- waveguide integration,
- exploitation of holographic stage in all-optical devices
- study of thermal fixing process for permanent refractive index grating
Lithium niobate

Compound system $\text{Li}_2\text{O} – \text{Nb}_2\text{O}_5$

$n_e = 2.23$ and $n_o = 2.31$

Li – Nb - vacancy

Electro-optic effect

$\Delta \left( \frac{1}{n^2} \right)_{ij} = \sum_k r_{ijk} E_k + \sum_{k,l} s_{ijkl} E_k E_l + ..$
Data analysis conditions

holograms thickness
L = (199 ± 8) µm

**thick hologram**

Kogelnik’ equation

$$\eta \equiv \frac{I_d}{I_d + I_t} = \sin^2 \left( \frac{\pi \Delta n L}{\lambda \cos(\theta)} \right)$$

Simplified solutions

$$E_{sc,sat} \sim E_{phv}$$

Samples with

[Fe$^{3+}$] ~ 18 · 10$^{25}$ m$^{-3}$

[Fe$^{2+}$]/[Fe$^{3+}$] ~ 4%

$$E_D \approx 3 \cdot 10^5 \text{ V/m}$$

$$E_{phv} \approx 8 \cdot 10^6 \text{ V/m}$$

$$E_q \approx 4 \cdot 10^8 \text{ V/m}$$

$$E_q' \approx 9 \cdot 10^9 \text{ V/m}$$

holograms thickness
L = (199 ± 8) µm

**thick hologram**

Kogelnik’ equation

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Samples with

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Undoped LiNbO$_3$ samples

**Repeatability**

Measurements relative error $\sim 13\%$

**In-depth measures**

$E_{sc}$ increases when interference area is inside the sample

$E_{sc}$ and $\tau_{sc}$ constant inside the crystal

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A. Zaltron - Ph.D. Thesis
Undoped LiNbO$_3$ samples

$E_{sc, sat} = |E_{phv}| = (35.1 \pm 0.9) \times 10^4 \ \text{V/m}$

$|\Delta n| = (5.7 \pm 0.1) \times 10^{-5}$  

*(Althoff et al.)*

$\sigma_{ph} = (13.4 \pm 0.4) \times 10^{-12} \ \Omega^{-1}\text{m}^{-1}$

*(Buse et al.)*
Reduced Fe:LiNbO_3 samples
Validity of the one-center model in Fe:LN

**One-center model**

\[ I < 10^4 \text{ W/m}^2 \]

\[ \mu I \]

**This work**

\[ I_{\text{max}} = 3.5 \cdot 10^5 \text{ W/m}^2 \]

**Two-centers model**

\[ I > 10^6 - 10^7 \text{ W/m}^2 \]

\[ \sigma_{ph} \propto aI + bI^2 \]

\[ c_{Fe} = 1.8 \times 10^{25} \text{ at/m}^3 \]

A. Zaltron - Ph.D. Thesis
Photoconductivity in as-diffused Fe:LN

Photoconductivity in depth profile

Nominally pure LiNbO$_3$

$\sigma_{ph} = (13.4 \pm 0.4) \times 10^{-12} \ \Omega^{-1}m^{-1}$

Undoped area (at 90 $\mu$m) of Fe:LiNbO$_3$

$\sigma_{ph} = (0.06 \pm 0.01) \times 10^{-12} \ \Omega^{-1}m^{-1}$

During diffusion process electrons move toward the higher concentration of empty traps?
Photoconductivity in reduced Fe:LN

$\sigma_{ph} \mu I Fe^{2+} / Fe^{3+}$

[Fe$^{2+}$]/[Fe$^{3+}$] not constant

- at 0 μm [Fe$^{2+}$]/[Fe$^{3+}$] ~ 12%
- at 50 μm [Fe$^{2+}$]/[Fe$^{3+}$] ~ 1%

$\sigma_{ph}$ in-depth profile

- as-diffused: $\omega_\sigma = (3.2 \pm 0.9)$ μm
- reduced: $\omega_\sigma = (15.5 \pm 3.0)$ μm
The reducting treatments:

1. increase the amount of Fe\(^{2+}\) in the material;

2. promote the diffusion of the reducing electrons (first captured by the Fe\(^{3+}\) near the surface and then migrate inside the material).
$E_{sc}$ in-depth profile of reduced FeLN

Agreement with iron concentration profile

\[ \omega_E = (22.1 \pm 1.3) \, \mu m \quad \text{and} \quad \omega_{Fe} = (21.3 \pm 0.5) \, \mu m \]

\[ E_{sc, sat} = (3.9 \pm 0.2) \times 10^6 \, V/m \quad |\Delta n| = (6.6 \pm 0.9) \times 10^{-4} \]

$E_{sc}$ does not depend on light intensity

$\frac{Fe^{2+}}{Fe^{3+}} = 4.6\%$
Δn in-depth profile of reduced FeLN

Agreement with iron concentration profile?
Dark conductivity

Negligible with light: $I > 1 \text{ W/cm}^2$ at room temperature

Without light: erasing of refractive index grating

Protonic conductivity

- above 70°- 80°C
- at room temperature for [Fe] < 0.1% mol

Electrons tunneling between Fe atoms

- at room temperature for [Fe] > 0.5% mol
- depends on reduction degree
Dark conductivity

![Graph showing the dark conductivity over time with exponential and linear fit equations.]

- **Experimental data**
- **Exponential fit:** \( \tau = (3.68 \pm 0.65) \times 10^5 \text{s} \)
- **Linear fit:** \( \tau = (4.06 \pm 0.44) \times 10^5 \text{s} \)

\[
\frac{\mathcal{E}}{\varepsilon_0} = \sigma_{\text{tot}} = \sigma_{\text{ph}} + \sigma_{\text{dark}} \approx \sigma_{\text{ph}}
\]

- \( \sigma_{\text{dark}} = (6.4 \pm 1.3) \times 10^{-16} \Omega^{-1} \text{m}^{-1} \)
- \( \sigma_{\text{tot}} \approx 10^{-12} \Omega^{-1} \text{m}^{-1} \)
Photovoltaic current in reduced Fe:LN

\[ j_{phv} \propto I [Fe^{2+}] \]

[Fe\textsuperscript{2+}] profile differs from [Fe\textsuperscript{3+}] one

\[ \omega_j = (10.8 \pm 1.6) \text{ \mu m} \]

Electrons concentrated at the surface of the sample

Surface reduction degree \ ~ 10\%: agreement with photoconductivity values