The \( r_{33} \) electro-optic coefficient of Er:LiNbO\(_3\)

A. Petris\(^1\), S. Heidari Bateni\(^2\), V.I. Vlad\(^1\), M. Alonzo\(^2\), F. Pettazzi\(^2\),
N. Argiolas\(^3\), M. Bazzan\(^3\), C. Sada\(^3\), D. Wolfersberger\(^4\) and E. Fazio\(^2,\*)

\(^1\) Dept. Lasers, Nat. Inst. Laser Plasma Radiation Phys., Bucharest, Romania
\(^2\) Energetics Department, La Sapienza University, Rome, Italy
\(^3\) Department of Physics G.Galilei, University of Padova, Italy
\(^4\) LMOPS Laboratory, SUPELEC & University Paul Verlaine, Metz, France

**Abstract**

By exploiting a Mach-Zehnder interferometer, the \( r_{33} \) electro-optic coefficient of erbium bulk-doped lithium niobate crystals grown by Czochralski technique was measured depending on the erbium content. The \( r_{33} \) coefficient decreases with the erbium concentration. Such trend has been connected with both the reduction of the lattice parameter, measured by high resolution X-ray diffraction, and the increasing of the lattice defects.

\* corresponding author: eugenio.fazio@uniroma1.it
Introduction

Erbium doped lithium niobate (LiNbO₃) crystals plays a key role as active material for the realization of integrated laser sources thanks to the optical, opto-mechanical and electro-optical properties that this material possesses and on which many devices can be based. In the past, erbium incorporation in lithium niobate was obtained mainly by local doping technique such as ion implantation¹², thermal diffusion from thin film¹³⁻¹⁴⁻¹⁵⁻¹⁶⁻¹⁷⁻¹⁸, ion exchange¹¹⁻¹²⁻¹³⁻¹⁴⁻¹⁵ and the bulk doping¹⁶⁻¹⁷⁻¹⁸. The local doping has many drawbacks, as it can be realized only in regions close to the surface, the maximum achievable erbium content is limited and it is not compatible with buried waveguides geometries which, instead, demonstrated to enhance the optical coupling with the fibres.

Bulk doping by means of the Czochralski growth would allow instead the achievement of quite high doping levels keeping very high crystalline quality. Consequently this technique looks promising for the realization of 3D integrated active devices.

Recently 3D waveguides by means of soliton waveguides¹⁹ have been generated in lithium niobate, opening the road for realising 3D integrated structures and circuits, guaranteeing a higher degree of compactness and integration.

Bright soliton formation in erbium doped lithium niobate was recently demonstrated²⁰, showing specific behaviours as function of the doping level. Thus, we considered that erbium doping might change the nonlinear optical properties of the bulk material. For this reason we analyse in the present paper the influence of erbium doping on the r₃₃ electro-optic coefficient, the one responsible for soliton formation¹⁹. To our knowledge in the past only P. Nekvindova et al ii²¹ measured the r₃₃ coefficient of erbium doped lithium niobate. In this unique case the measurement was performed on annealed proton exchange waveguides doped in bulk with erbium at the only concentration of 500 ppm. Consequently in such work an average value of r₃₃ inside the waveguides was measured.

In the present work a characterisation of the bulk r₃₃ coefficient for 5 different concentrations of erbium doping will be performed on lithium niobate samples.

Samples

The experiments were performed using lithium niobate crystals doped in volume by erbium at nominal concentrations in the starting melt composition ranging within 0.0 mol% and 0.7 mol%. Samples were grown by Czochralski method, at a pulling rate of 3 mm/h along the ĉ crystallographic axis and at a rotation rate close to 30 rpm²². The obtained boules were poled after growth by applying a constant current density of about 3 mA/cm² while they
were cooled from the paraelectric to the ferroelectric phase, in order to achieve a single
domain state through the whole sample volume. By exploiting the x-ray diffraction technique,
they were oriented and then cut in slices with the major surface perpendicular to the \( \hat{c} \)
direction. Finally the slices were annealed in air for 6 hours at 950 °C and optically polished
using a Logitech PM5 lapping machine with standard techniques. The final used crystals
were 8 mm along \( \hat{a} \), 6 mm along \( \hat{b} \), and 1 mm along \( \hat{c} \) (such dimension will be called \( h \) latter
on). Such dimensions have been chosen in order to ensure over the whole sample a uniform
electric field, externally applied along \( \hat{c} \) as bias and consequently reduce the boundary
dispersion. Silver contacts were finally deposed over the two 8x6 faces.

**Interferometric measurement of \( r_{33} \)**

The electro-optic coefficient \( r_{33} \) was therefore measured exploiting the Mach-Zehnder
interferometric set-up shown in Fig. 1.

![Mach-Zehnder interferometer](image)

A He-Ne laser was used as laser source in the interferometer, due to its good transversal
mode quality (TEM\(_{00}\)) and long coherence length (tens of centimeters). A very low input
intensity (about 150 nW/cm\(^2\) on the crystal) was used to avoid both photorefractive and
photovoltaic effects in the material during the measurement (the typical measurement lasts
several minutes): in fact, according to T. Fujiwara et alii\(^{23}\), an optical power as low as 5 nW,
like the one used here, would ensure accurate and photorefractive-photovoltaic-free
measurements of the electro-optic effect. The beam was cleaned and enlarged by a telescopic-
asymmetric spatial filtering and then controlled in power and polarization by two polarizers,
ensuring the extraordinary polarization state impinging on the sample. The two interferometer
arms were balanced in intensity by using neutral filters, in order to increase the interference
fringe visibility up to 95%, and then recombined on a CCD camera which was computer
interfaced. The angle between the interfering beams was adjusted in order to ensure a good
fringe spacing (~ 65 µm) on a CCD (with squared pixels as large as 4.65x4.65 µm\(^2\)).
Moreover, the interference fringes were also oriented parallel to the crystallographic \( \hat{c} \)-axis to
increase stability and to neglect charge transport mechanisms responsible for the photorefractive-photovoltaic effects. Samples were positioned in one arm of the interferometer and electrically polarized by applying a DC voltage $V_{2\pi}$ along $\hat{\epsilon}$: the voltage for $2\pi$ shift of the interference pattern was recorded as function of the doping concentration.

The nonlinear electro-optic phase-shift $\Delta\phi_{NL}(E)$ between the interferometer arms linearly depending on the applied electric field:

$$\Delta\phi_{NL}(E) = 2\pi = \frac{\pi}{\lambda} n_e^3 r_{33} \frac{V_{2\pi}}{h} L,$$  \hspace{0.5cm} (1)

where $n_e$ represents the extraordinary index of refraction at the operational wavelength $\lambda$, $L$ is the electrode length. Reversing such equation, the electro-optic coefficient $r_{33}$ can be calculated:

$$r_{33} = \frac{2h\lambda}{L n_e^3 V_{2\pi}}.$$  \hspace{0.5cm} (2)

At fixed doping concentrations, the estimation of the electro-optic coefficient was performed by averaging over 20 measurements of $V_{2\pi}$. The data dispersion was in the range of 0.1-1 %. A systematic analysis of the result reproducibility was performed by checking the electro-optic response of each sample in four-five different points across it. The $r_{33}$ values therefore obtained present a semi-dispersion close to 1%. A final estimation of the $r_{33}$ coefficient given by the average over all the $r_{33}$ measurements is reported in Fig.2.

![Figure 2](https://example.com/fig2.png)

**Figure 2** – Dependence of the $r_{33}$ coefficient on the erbium concentration.

We have to point out here that the variation of the linear extraordinary refractive index $n_e$ with the erbium content was very low, and consequently we believe this will not affect the present estimation. The electro-optic results in fig.2 on erbium bulk-doped samples were compared with the coefficient of one undoped sample grown by Crystal Technology (congruent crystal, 1 mm thick). The obtained $r_{33}$ value for such undoped sample was 29.6
pm/V, compatible with the literature\textsuperscript{25} ($r_{33} = 30-33$ pm/V) for congruent undoped commercially available lithium niobate samples.

**Measurement of crystallographic elementary cell**

The influence of erbium on the material lattice was monitored by exploiting high resolution X-ray diffraction on the measured samples. The structural investigation showed clearly that the grown crystals were homogeneous, with an non-constant elementary cell along $\hat{c}$. By measuring the (0 0 12) X-ray diffraction, the lattice parameter was found to linearly decrease as a function of erbium content $\rho$, as shown in fig. 3. Such result is in agreement with the Vegard’s law\textsuperscript{26,27,28}.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure3.png}
\caption{Dependence of the lattice parameter on the erbium concentration.}
\end{figure}

Erbium incorporation induces a cell parameter contraction with respect to the pure crystal ($C_{\text{pure}} = (13,86655 \pm 0.00014)$ Å, where as pure sample a Crystal Tech. crystal was measured as reference). The linear fit gives a value of $(13,86621 \pm 0.00008)$ Å for the undoped cell, and a slope of $(-0.0077 \pm 0.0001)$ Å/mol\% (R=0.998) for the erbium-induced modification. Since the lattice parameter contraction is linear with erbium content, we can infer that the erbium ion incorporates always in the same site in agreement with previously published data\textsuperscript{29-30-31-32}.

**Discussion**

A modification of the lithium niobate properties with doping was indeed expected. F. Abdi et alii\textsuperscript{33}, measuring the electro-optical properties of lithium niobate doped in volume with zinc, found a trend similar to fig.2, connected with the doping-induced disorder in the lattice.

We would expect a similar behaviour when erbium is introduced as dopant. Already from stoichiometric to congruent lithium niobate, a disorder is introduced in the lattice which affects the electro-optic properties as well. Congruent undoped lithium niobate crystals differ
from the stoichiometric ones for the presence of local defects. The type and quantity of defects can be summarised by the chemical formula\textsuperscript{34,35}:

\[
[\text{Li}_{1-5d}\text{Nb}^*_5][\text{Nb}_{1-4d\text{V}}\text{Nb}_{4d}]\text{O}_3
\]  

where “d” represents the defect concentration, \(\text{Nb}^*\) a niobium ion occupying a lithium site (niobium antisite), and \(\text{V}\text{Nb}\) represents a vacancy of niobium atoms on their proper sites. Such situation corresponds to the coexistence of stoichiometric elementary cells with defects where lithium is substituted by niobium. In order to keep the electric neutrality of the whole crystal, such defects extend over 5 cells, as summarised in tab.1.

<table>
<thead>
<tr>
<th>Electric charge/cell</th>
<th>Li</th>
<th>Nb</th>
<th>O\textsubscript{3}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
<td>+4</td>
<td>-1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Nb</td>
<td>Nb\textsuperscript{*}</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Nb</td>
<td>Nb (\emptyset)</td>
</tr>
<tr>
<td>N\textsuperscript{o} of cells</td>
<td>1</td>
<td>1</td>
<td>4</td>
</tr>
</tbody>
</table>

\textbf{Tab.1 – Crystalline structure of undoped congruent lithium niobate\textsuperscript{30}.} Here \(\text{Nb}^*\) represents niobium antisite, and \(\emptyset\) a vacancy.

According to eq. (3) the overall estimation of defect concentration in intrinsic lithium niobate gives a value between 0.5 and 0.7\%, much smaller than the electro-optic variation from stoichiometric to congruent lithium niobate crystals, which instead is of the order of 10-20\% (with respects to stoichiometric values).

Thus, defects should extend their influence over the whole crystalline lattice, strongly modifying the whole electro-optic polarisability at once, and should happen for doping cases as well. In fact the lattice parameter measurement in fig. 3 varies linearly for every erbium concentration. The introduction of doping keeps the homogeneity of the whole lattice even if new defects are generated.

From literature\textsuperscript{36} it is known that trivalent impurities are likely to occupy sites in the cation sublattices, and in particular Er ions will occupy Li positions, for concentrations lower than 0.8 mol.\%. In spite of the different ionic radii between Li\textsuperscript{+} and Er\textsuperscript{3+} ions, the erbium doped lithium niobate lattice is normally well ordered, with high coherent fractions of Er and Nb occupying their relative lattice positions. Thus, we expect that for concentrations lower than 0.2 mol\%, erbium will generate new defects with similar structure, just replacing one niobium antisite, according to the formula:

\[
[\text{Li}_{1-5d-3x}\text{Nb}^*_5\text{Er}_{3x}][\text{Nb}_{1-4d-2x}\text{V}\text{Nb}_{4d+2x}]\text{O}_3
\]  

6
where $x$ is the concentration of erbium atoms. Such condition is represented in tab.2.

<table>
<thead>
<tr>
<th>Electric charge/cell</th>
<th>Li</th>
<th>Nb$^+$</th>
<th>Nb$^+$</th>
<th>Nb$^+$</th>
<th>Er</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^0$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N° of cells</td>
<td>1</td>
<td>4</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Tab.2** – Crystalline structure of slightly Er doped lithium niobate. Er$^{3+}$ will replace Nb$^{+5+}$, generating consequently one more stoichiometric cell.

It should be noted here that for every niobium antisite filled up by erbium, the electric charge neutrality ensures a defect ranging over 3 elementary cells.

Speaking about electro-optic polari sability, the total electric charge per cell does not change strongly. Consequently we expect here a quadratic decreasing of the electro-optic coefficient (see the dotted line in fig.2), consequence of the linear reduction of the lattice parameter and of the linear increase of the number of defects.

For larger doping levels, erbium will enter inside the already present defects of the congruent state. The whole lattice becomes slightly more ordered (or just the disorder does not grow up much), passing through the transient regime:

\[
\begin{align*}
[Li_{1-5x-3z-y}Nb_{5d+2x}^+Er_{x+y}^+VLi_{2y}][Nb_{1-4z-2x+3y}^+VNB_{4d+2x}]O_3
\end{align*}
\]

(5)

(where now $x+y$ corresponds to the erbium concentration) towards a more stable defect structure:

\[
\begin{align*}
[Li_{1-4z}Nb_{4z}^+Er_{4z}][Nb_{1-2z}^+VNB_{2z}]O_3
\end{align*}
\]

(6)

sketched in tab.3.

<table>
<thead>
<tr>
<th>Electric charge/cell</th>
<th>+4</th>
<th>+2</th>
<th>-3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb$^+$ Er Er</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nb Nb O3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N° of cells</td>
<td>1</td>
<td>1</td>
<td>2</td>
</tr>
</tbody>
</table>

**Tab.3** – Defect structure for Er$^{3+}$ concentrations larger than 0.4 mol%.

In such regime the overall number of defects does not increase, while the lattice constant still decreases linearly. As a consequence, the electro-optic coefficient decreases with a saturating trend while the erbium concentration approaches the value 1 mol %.
Such model well describes the experimental results obtained on photorefractive soliton formation. However, a Raman characterization of samples is now in progress to investigate the structural modification induced by erbium incorporation and consequently to validate the proposed model. In fact Raman analysis can supply information on structural disorder which cannot be evidenced by measuring functional properties like the electro-optic coefficients. However, a Raman characterization of samples is now in progress to investigate the structural modification induced by erbium incorporation through and to correlate Raman spectra for validate the whole proposed model.

Conclusions

We have presented a systematic study of the electro-optic coefficient $r_{33}$ in erbium doped lithium niobate crystals as function of the erbium concentration: the experimental results showed a decrease of the $r_{33}$ value. In order to clarify the role of dopant, a structural characterization was performed, measuring crystal uniformity and cell dimension. It emerged that the cell parameter along the $\hat{c}$ axis linearly decreases with the erbium content following the Vegard law. These results suggests that the Er ion incorporates always in the same site reducing the $\text{Nb}_{\text{Li}}$ and the $\text{V}_{\text{Li}}$ defects concentrations, which is similar to the effect obtained by increasing the Li/Nb ratio. A model for erbium-induced defects was then introduced. For concentration lower than 0.2 %mol erbium will generate new defects, forcing the electro-optic coefficient to decrease quadratically. For larger concentration erbium affects intrinsic defects too, originating a linear decreasing of the electro-optic coefficient. Such measurements well describe the experimental results obtained during photorefractive spatial soliton formation.

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AMDG.
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