Photorefractive Damage in congruent LiNbO₃.
Part II. Magnesium doped Lithium Niobate Crystals

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Abstract. The photorefractive effect in lithium niobate (LN) crystals is one the main drawback for its integration in optoelectronic devices using high light intensity. Doping congruent LN crystals by appropriate dopants like divalent ions such as Mg²⁺ are known, for specific concentrations, to improve their optical damage resistance. We present experimental measurements of the photorefractive damage in a series of magnesium doped congruent lithium niobate, performed with two experimental technique based on the measurement with time of the photoinduced distortion for the first one and based on the direct measurement of the photoinduced birefringence variation with time for the second. The dependences of the photorefractivity and of the photosensitivity on the power and dopant concentration have been investigated and discussed with the consideration of the electro-optic properties dependence with the defect structure of the doped crystals. We conclude that that doping above a second threshold concentration with divalent Mg ions leads to a significant decrease of the photorefractivity with respect to pure congruent crystals. We conclude that doping LN congruent crystals with Mg strongly increase the photorefractive damage resistance and, in association to the interesting electro-optic coefficients, LN:Mg present an interesting alternative for modulating devices to the stoichiometric LN, which is difficult to growth in high quality and in large quantity.

1. Introduction
LiNbO₃ (LN) crystals are of great interest for applications in optics thanks to their large electro-optic (EO) and non linear optical coefficients [1,2]. Nevertheless, the integration of non stoichiometric LN crystal in electro-optic modulators, Q-switches or frequency converters is hampered by a relatively small laser-damage threshold (equal to 0.3 GW/cm² for the congruent composition that we can compare to BaB₂O₄ crystals (BBO) equal to 10 GW/cm²) [3]. In LN crystal, the optical or photorefractive damage is one of the numerous properties that depends on the charge transport properties, which is directly linked to the nature and the concentration of intrinsic defects like antisite NbLi, Li- and Nb-vacancies [4], present in the LN structure. The first origin of the optical damage could be due to thermal effects, such as the thermo-optic effect or pyroelectric effects due to a local heating in the crystal along the light path changing the refractive indices seen by the beam but for relatively high power densities, these effects are negligible compare to the photorefractive effect [5]. So, the main process at the origin of this damage is due to the presence of space charge field induced by the optical beam, which generate mobile charge carriers in the bright region and migrate toward the dark zones. This space charge field induces via the electro-optic effect, modifications of the refractive
indices seen by the beam. The growth of crystals with stoichiometric composition is one of the ways
explored by growers to reduce the optical damage [6,7]. Indeed, the growing of LN crystals with a
ratio R=[Li]/[Nb] closer or equal to one, corresponding to the stoichiometric composition, decrease
the number of intrinsic defects. But, even with ratio R far above one in melt, the growth by conventional
Czochralski technique cannot produce large quantities and constant qualities of stoichiometric crystals
as necessary for applications. These difficulties to obtain large stoichiometric crystals has opened an
alternative way to increase the laser threshold consisting in doping congruent LN crystals with
divalent or trivalent ions such as Mg, Zn, In or Sc ions. [8,9]. Simultaneously some linear and non-
linear optical properties are influenced by these dopant ions [8-10]. Among them, Mg is one of the
most frequently used with Zn. Zhong et al [11] showed that the damage is strongly reduced by the
introduction of 4.6 mol% Mg in a congruent melt while significant reduction of optical damage was
observed at dopant concentrations exceeding 5.5 mol.% MgO by Furukawa et al [7] and Bryan et al
[12].

The purpose of this paper is to investigate the optical damage in four congruent crystals doped with
increasing MgO concentrations. The techniques used for these characterizations were already
described in previous papers [13]. We present the behavior of the photoinduced birefringence change
at saturation and the photoconductivity as a function of the power densities of an Argon pump beam
for this set of crystals. In order to clarify our analysis, the results will be confronted with those
obtained in electro-optical characterizations made on the same crystal samples.

It is to be of note that the optical damage investigations in doped congruent LN are presented in
two publications. The present one is dedicated to the photorefractive behavior of magnesium doped
congruent LN. It follows a first publication, which discussed the photorefractive properties of Zn
doped congruent LN, which were measured within the same experimental processes. Even if both
publications were written to be self-consistent and to be read independently, the present publication
largely summarizes the experimental techniques and proposes a general discussion and comparison of
the photorefractive behavior as a function of the nature and concentration of dopant in these two set of
doped LN families.

2. Crystal presentation
We have performed photorefractive measurements in four congruent magnesium doped crystals with
different concentrations of magnesium. These crystals were grown by K. Polgar [4] using the
Czochralski method with a congruent melt added by Mg in its oxidic form. For the determination of the
dopant concentration in crystals as reported in Table 1, we have considered the segregation coefficient
k_{eff} for Mg doped crystals as proposed by Tan et al. which have reported that k_{eff} for Mg, during growth
changed from 1.3 to 0.95 up to 8 mol% Mg content in the melt [14].

| Table 1. Labels and concentrations of Mg doped Crystals |
|-----------------------------|---------------------|
| Crystal | Mg-oxide in the crystal (mol.%) |
| Mg-1 | 0.12 |
| Mg-2 | 1.04 |
| Mg-3 | 2.77 |
| Mg-4 | 4.61 |

The optical quality of all crystals was checked by an optical transverse mapping, which shown in the
visible range a good optical uniformity without polishing or growth striations, respectively at the
surface or inside crystals. The non-uniformity of the birefringence along the axis does not exceed 10^{-5}
cm$^{-1}$. For a suitable comparison, Y-cut plates with the same thickness equal to 0.68±0.02 mm were especially prepared for the laser-induced birefringence measurements presented in this paper.

3. Experimental methods and results

Photorefractive damage measurements were carried out by means of the two methods presented in details in Ref. [13] and mainly summarize in the previous publication devoted to Zn doped congruent LN, as a part of the present work [15].

The first method, based on the implementation of the pseudo Z-scan method consists of measurements in the far field region and after a pinhole of the dynamic variation of the transmitted intensity, adjusted in our measurements to 475 W/cm$^2$ at the input face of the crystal placed at the focal plane, of an He-Ne spot beam at a wavelength equal to 633 nm. For each crystal, we have recorded as a function of the illuminated time, the two beam intensities $I$ and $I_0$, to determine the characteristic $T(t)$

$$T(t)(\%) = \frac{I}{I_0} = T_{\text{min}} + \Delta T \exp(-t/\tau)$$

where $T_{\text{min}}$ is the minimal transmission at saturation, $\Delta T=100-T_{\text{min}}$, $I_0$ and $I$, the transmitted beam intensities at $t=0$ and at a time corresponding to the saturation of the scattering respectively and $\tau$ is the dielectric relaxation time, which allows the determination of the photoconductivity by the equation:

$$\sigma_{\text{ph}} = \frac{\varepsilon_0 \varepsilon_{33}}{\tau}$$

The experimental results obtained as a function of Mg concentration in crystals are plotted in Fig. 1.

![Figure 1](image-url)  

**Figure 1.** Variations of the transmittance $\Delta T$ (see Eq.1) and photoconductivity $\sigma_{\text{ph}}$ as a function of Mg concentration in LN:Mg crystals for a laser beam intensity equal to 475 W/cm$^2$ at $\lambda = 633$nm.

We see that with the concentration of Mg induces an abrupt increase of the defocusing up to a saturation concentration value around 2 mol.% following by a progressive decrease down to the value obtained for the highly doped. On the other hand, the behaviour of the photoconductivity is opposite among that of $\Delta T$ with a decrease until Mg concentration around 2 mol% and an increase after this threshold.
The second method allows the direct determination of the photoinduced birefringence change $\delta \Delta n$, using the modified FDEOM [16] adapted for photorefractive measurements. [13] Within this method, the optical damage is measured by monitoring the change in the magnitude of the induced birefringence as a function of irradiation time. The characteristic curve representing $\delta \Delta n$ obtained within this method can be fitted with a first order exponential time response function given by

$$
\delta \Delta n(t) = \delta \Delta n_s [1 - \exp(-t/\tau)]
$$

where $\tau$ is the characteristic time of the PR effect and $\delta \Delta n_s$ the saturated value of the birefringence change. We have measured the photoinduced birefringence changes as a function of time, $\delta \Delta n(t)$ with a focused low-intensity He-Ne laser probe beam at a wavelength of 633nm and a focused cw argon laser pump beam oscillating at 514.5nm with a power density of 1.2 kW/cm$^2$. Fig 2 shows the photoinduced birefringence change at saturation and the photoconductivity versus dopant concentration. $\delta \Delta n$ in these samples is predominantly induced by the photorefractive effect $\delta \Delta n_s$ as no significant birefringence changes occurred after illumination when the Ar-laser irradiation is stopped, which allows us to exclude the contributions related to temperature, such as the thermo-optic effect [5]. The relative stability after the end of illumination indicates a weak dark conductivity $\sigma_d$ as observed in pure and doped LN crystals [5]. With a low intensity probe and high intensity pump focus beams, we emphasize that photorefraction is only due to the photovoltaic space charge field generated by the pump beam along the c-axis.

Figure 2. Photoinduced birefringence change at saturation and photoconductivity as a function of Mg concentration for a laser beam intensity equal to 1.2 kW/cm$^2$ at $\lambda = 514.5$ nm.

We see in Fig. 2 that $\delta \Delta n_s$ have the same behaviour versus Mg concentration than the intensity variations, $\Delta T$, reported in Fig. 1. An abrupt increase with the concentration up to a maximum obtained for crystals with intermediary concentration is followed by a progressive decrease down to the value obtained for the highly doped crystal. By else, these measurements done with a different method as those presented above confirm the values and the behaviour of the photoconductivity. The optical damage resistance of crystals labelled Mg-1 and Mg-4 is much higher than that of Mg-2 and Mg-3. We can observe that the concentration threshold is the same for the both properties. These non-monotonous behaviours indicate that the optical damage resistance is lower for both crystals with
intermediary Mg concentration and that, even if pure congruent crystal have a high concentration of intrinsic defects, the defocusing is at a level as low as the highly Mg doped.

4. Discussion
The photorefractive sensitivity, $\delta S$ as defined by Jermann et al. [4] is considered as a figure of merit for the qualification of the photoconduction and the link of the defects in LN crystals. In ferroelectric crystals, $\delta S$ is directly links to the bulk photovoltaic current and it is defined as

$$\delta S = \frac{\Delta n s}{I \tau} = r_{\text{eff}} \left( \frac{j_{\text{ph}}}{\varepsilon_0 \varepsilon_r} \right) ,$$

where $r_{\text{eff}}$ is the effective electro-optic coefficient, $I$ is the light beam intensity and $j_{\text{ph}}$ is the photovoltaic current density. Eq. 4 shows that a large resistance to the photorefractive damage requires low photoinduced birefringence change $\delta \Delta n$ relative to the PV current.

The sensitivity, $\delta S$ versus Mg, is plotted in Fig.3, which points out a complicated dependence on the laser intensity and on the concentration of Mg.

![Figure 3. Photosensitivity for three power densities of the spot beam as a function of Mg concentration in LN:Mg crystals.](image)

We can hence deduce from the curves of $\delta S$ versus Mg dopant concentration, Fig. 3 that the highly doped crystal is the most damage resistant. The behaviour of the sensitivity of Mg doped LN crystals presents the opposite behaviour that the photoconductivity. These data clearly indicate that the main contribution to the variation of photorefraction comes from variations in $1/\sigma_{ph}$ with the concentration.

Various authors [17,18] present the existence of three phases in the substitution and compensation processes involved in LN:Mg doped crystals as a function of the concentration of dopant. We have confirmed [19] by Raman spectroscopy measurements done on the same samples and additional ones with higher Mg concentration above 5 mol%, but unfortunately not convenient for the PR measurements achieved in the present work, the existence of the three phases. In the first phase, when Mg is introduced in the LN lattice up to 3 mol%, it occupy the A sites linked to the natural lithium site and push out the Nb antisites on their “normal” B sites. In the second phase, for Mg doping up to 5 mol%, the site A is strongly affected by Mg ions that incorporate successively instead of Nb antisites, $V_{\text{Li}}$ and Li, without any additional disorder induces in the LN structure. On the contrary, the substitution of Li ions by Mg ions in the third phase induces a large disorder on sites A, while the sites...
B are not directly affected by Mg incorporation, and which shows only a small change of Nb content along the three phases. The concentration of 5 mol% Mg is often referred to as a concentration threshold and manifests itself as a second extremum in the concentration dependence of other optical properties of LN:Mg such as refractive indices, IR absorption, phase matching temperature of SHG, etc… [20]. Therefore, the threshold concentration corresponds to a maximum concentration of Li vacancies. Thus, in the low range, Mg ions replace the niobium on antisites, Nb\_Li and as a consequence, we observe a decrease of the photoconductivity with the increase of Mg concentration up to the first extremum. Above this first extremum, the doping by Mg ions is accompanied by an increase of the lithium vacancies. So that, the photoconductivity increase for higher concentration of Mg in crystal.

The two sets of Zn and Mg lithium niobate crystals, presented in part 1 and 2, respectively in this series of contributions came from growers using various powders and methods for preparation, growing and post growing treatments, which can induce additional effects due to the influence of impurities such as iron present in various valence states. Thus the comparison of absolute experimental values presented in this series of contributions should be considered taking into account this fact.

Nevertheless, it is to be of note that all measurements in a series were done on samples providing from the same powders and growing oven and method performed by the same grower. We can consider that the level of involuntary impurities is the same in all crystals. It was shown that the photoconduction process is mainly dominate by the contribution of Fe\(^{2+}\) ions for low intensities and that Mg ions they do not directly contribute to charge transport processes. However, this study was done using high light intensities (I \(\geq\) 1MW/m\(^2\)) and additional contributions appear in the photoconduction response attributed to Mg ions and to charge compensating vacancies. The non-linear behaviour of the photoconductivity versus Mg concentration, Fig. 2 and the non proportionality of the sensitivity with the power density of the beam, Fig. 3, confirm this proposal. Thus, the bulk photoconductivity is directly and indirectly influence by the doping concentration [12]. The various processes cited herein that contribute to photorefraction, for Mg doped LN crystals are also involved for crystals doped with Zn ions [15]. Nevertheless, due to the higher electronegativity of Zn ions, the threshold in doping concentration observed in some properties takes place at different levels for Zn than for Mg doped crystals [18].

5. Summary
The photorefractive damage of magnesium-doped congruent lithium niobate crystals agrees with the existence of a first extremum for a doping concentration around 2 mol% and a threshold above 5 mol%.

We have shown that the crystal doped with a concentration close to this threshold is the most damage resistant. The photorefractive behaviour of LN crystal was analyzed considering the substitution process that occurs during the growth of Mg doped LN crystals with the doping concentration. We have analyse the obtain results with those obtain for LN:Zn crystals, which present the same behaviour than LN:Mg crystals when considering the difference of the electronegativity of the two dopant ions. LN:Mg and LN:Zn crystals are strongly photorefractive damage resistant when the doping concentration is closer to the respective threshold concentration associated to each dopant. The Mg and Zn doped congruent LN crystals present an interesting alternative for modulating devices to the stoichiometric LN, which is difficult to growth in high quality and in large quantity.

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