



# Influence of chromium doping on the electro-optic properties of lithium niobate

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## Abstract

We present the measurements of the refractive indices and the electro-optic coefficients in lithium niobate crystals doped with a small amount of chromium. It is found that the coefficient  $r_c$  has a significant dependence on the Cr concentration. Electrical moments and deformations, created by  $\text{Cr}^{3+}$  at non-isovalent replacement of host lattice ions, can be responsible for this effect.

**Keywords:** Electro-optics;  $\text{LiNbO}_3$ ; Cr

## 1. Introduction

Lithium niobate (LN) is widely used in many optoelectronic devices due to its rather large electro-optical and non-linear optical properties [1]. It is well known that many physical characteristics of LN depend strongly on the crystal composition and on the presence of specific defects [2,3]. Recently, in contrast to the traditional methods used to obtain congruent crystals, several ways of preparation [4] and growing [5] of crystals with stoichiometric composition were found. The study of the stoichiometric material has shown that many of its properties differ strongly from those in a conventional congruent crystal [6].

Since the understanding of LN properties requires the knowledge of dopant location and its surroundings, many experimental and theoretical investigations were carried

out to determine the models of intrinsic and extrinsic defects [7,8].

Many applications are based on the linear electro-optic effect (EO). Thus, the accurate values of EO coefficients are often required. The goal of the present study is to measure, with high accuracy, the linear EO  $r_c$  coefficient of the chromium-doped LN.

At first look, the EO properties could be affected by both intrinsic and extrinsic defects. Therefore, to study the proper chromium influence on the EO coefficient, we consider crystals with the same composition close to the ideal stoichiometric one.

The measurements were performed around room temperature (25–30°C) at the wavelength  $\lambda = 1.3 \mu\text{m}$ . Since the method used here is based on the measurement of the phase shift induced in the crystal, which is proportional to the value  $n_o^3 r_c$ , a measurement of the refractive indices of the same set of crystals is also required. In addition the measurements of indices can provide a sensitive tool to determine the composition of the samples in the pure crystals [9].

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## 2. Experimental

The crystals used in this study are grown by the Czochralski technique [10] from the melt with the composition  $X_m = [\text{Li}]/[\text{Li} + \text{Nb}] = 54.5\%$  which corresponds to the concentration of Li in the crystal of  $X_c = 49.5\%$ . Such growth from a Li rich melt effectively diminishes the number of intrinsic non-stoichiometric defects as compared to the congruent composition [2,4].

The doping with chromium was realised by the addition of  $\text{Cr}_2\text{O}_3$  to the melt in concentrations of 0, 0.01, 0.05 and 0.275 wt.%.

### 2.1. Refractive index measurements

A Michelson-type interferometer was used to determine the refractive indices of the samples. The parallel plate sample inserted in one arm of the interferometer is rotated around an axis parallel to the  $c$ -axis. The resulting increase in the interferometer order, which can be detected as a rotation angle dependent modulation of the intensity pattern, is then measured by a computer controlled set-up [11]. The extraordinary ( $n_e$ ) and the ordinary ( $n_o$ ) refractive indices are obtained by polarising the light parallel or perpendicular to the rotation axis, respectively.

For the visible and infrared region a helium–neon laser was used, whereas a mercury vapor lamp combined with a 0.2-m monochromator allowed measurements from 400 to 1200 nm.

In Cr-doped LN samples, the measurements were not possible for all the available wavelengths, because of their broad absorption in the visible range [12].

We extrapolate the values of  $n_e$  at the wavelength used in the EO measurements ( $\lambda = 1321$  nm) from the curve  $n(\lambda)$  derived by the fit of the experimental data with the two-terms Sellmeier equation:

$$n_i^2 = 1 + \frac{A_{0,i}}{1 - \lambda_0^2/\lambda^2} + \frac{A_{1,i}}{1 - \lambda_1^2/\lambda^2}, \quad (1)$$

where  $n_i = n_o$  or  $n_e$ ,  $A_0$  and  $A_1$  are the oscillators strengths and  $\lambda_0$  and  $\lambda_1$  the oscillators positions.

The experimental data for some wavelengths are listed in Table 1. Within the accuracy of the present measure-

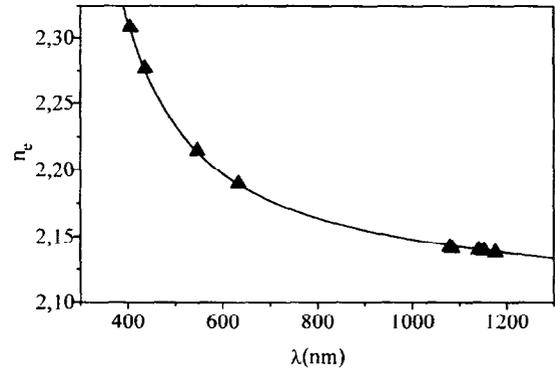


Fig. 1. Extraordinary refractive index ( $n_e$ ) as a function of  $\lambda$  obtained for LN:Cr 0.01 wt%. The continuous line corresponds to the Sellmeier fitting curve. The symbols are the experimental values.

ments ( $10^{-3}$ ) the indices are seemingly independent of the sample for the set of Cr-doped crystals under investigation.

In Fig. 1 we plot the experimental data obtained for  $n_e$  in a 0.01% LN:Cr sample versus the wavelength. The fitting curve obtained with Eq. (1) and the parameters  $\lambda_0 = 177$  nm,  $\lambda_1 = 223$  nm,  $A_0 = 3.416$  and  $A_1 = 0.077$  shows a good agreement between measured and calculated results.

Eq. (1) is then used with the same values of the fitting parameters for all the LN:Cr samples to calculate the extraordinary refractive index  $n_e$  at  $\lambda = 1.3$   $\mu\text{m}$ . For the undoped crystal we use the parameters given in Ref. [13]:  $n_e = 2.137$ .

### 2.2. Electro-optic measurements

The EO  $r_e$  coefficient was determined via the frequency doubling electro-optic modulation method (named FDEOM method) which is a very accurate experimental technique based upon the Sénarmont set-up [14]. The sample was placed between two crossed polarizers. Both modulation  $V_{ac} = V_m \sin(2\pi ft)$  and bias  $V_{dc}$  voltages are applied to the sample, inducing a phase shift  $\Gamma(E)$  between the two principal components of the polarised laser beam entering the crystal. The analyser is adjusted at an

Table 1

Experimental refractive indices measured in three Cr-doped LN crystals. The values at  $\lambda = 1321$  nm are deduced from Eq. (1)

| Crystals<br>$\lambda$ (nm) | LN:Cr 0.01 wt.% |       | LN:Cr 0.05 wt.% |       | LN:Cr 0.275 wt.% |       |
|----------------------------|-----------------|-------|-----------------|-------|------------------|-------|
|                            | $n_o$           | $n_e$ | $n_o$           | $n_e$ | $n_o$            | $n_e$ |
| 1079.8                     | 2.228           | 2.142 | 2.227           | 2.143 | 2.231            | 2.143 |
| 1084.4                     | 2.228           | 2.141 | 2.228           | 2.142 | 2.231            | 2.144 |
| 1140.9                     | 2.226           | 2.140 | 2.225           | 2.141 | 2.227            | 2.143 |
| 1152.3                     | 2.224           | 2.139 | 2.223           | 2.139 | 2.227            | 2.140 |
| 1176.7                     | 2.222           | 2.138 | 2.222           | 2.138 | 2.226            | 2.139 |
| 1321                       |                 | 2.134 |                 | 2.134 |                  | 2.134 |

angle  $\beta = \beta_{2f}$  so that only the optical output signal with the frequency  $2f$  is transmitted throughout the crystal. The corresponding value of  $\beta$  yields the electric field-induced phase shift  $\beta_{2f}(E) = \Gamma(E)/2$ .

With an electric field applied along the  $z$ -axis of the crystal and the light beam propagating along the  $x$ -axis, we access to the effective EO  $r_c$  coefficient ( $r_c = r_{33} - (n_o/n_e)^3 r_{13}$ ). The value of  $r_c$  can be derived from the electric field induced birefringence  $\delta\Delta n(E)$  or the corresponding phase shift  $\Gamma(E)$ :

$$\delta\Delta n(E) = \frac{1}{2} n_e^3 r_c E, \tag{2}$$

$$\Gamma(E) = \frac{2\pi}{\lambda} L \Delta n(E), \tag{3}$$

where  $n_e$  is the extraordinary refractive index,  $\lambda$  is the laser wavelength,  $E$  is the applied electric field,  $L$  is the crystal length along  $x$ .

The direct measurement of the electric field-induced phase shift  $\Gamma(E)$  provides the  $r_c$  coefficient according to

$$n_e^3 r_c = \frac{\lambda d}{\pi L} \frac{\Gamma(E)}{V}, \tag{4}$$

where  $d$  is the crystal thickness along the direction of the applied electric field.

The EO measurements were carried out at 1.3  $\mu\text{m}$  emitted from a 20 mW diode pumped Nd:YLF laser, and 1 kHz ac voltage. To take into account the very large thermo-optical effect present in LN [14], measurements were performed as a function of temperature.

Fig. 2 shows the phase shift  $\Gamma$  obtained as a function of temperature for two different dc voltages in the sample for the LN:Cr 0.275 wt.% crystal. By measuring the difference between the two straight lines for the two dc voltages, we can calculate  $n_e^3 r_c$  according to Eq. (4). Then the  $r_c$  coefficient is deduced since  $n_e$  is known for the same crystal.  $r_c = (13.9 \pm 0.5)$  pm/V at  $T = 26^\circ\text{C}$ . The

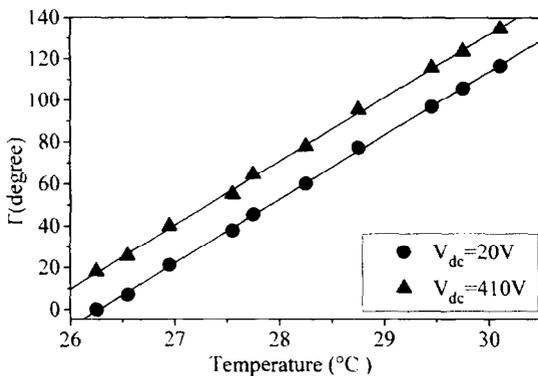


Fig. 2. Temperature dependence of the phase shift in LN:Cr 0.275 wt% LN crystal for two different dc voltages, at  $\lambda = 1321$  nm. The sample has the dimensions  $4 \times 6.47 \times 1.59$  mm<sup>3</sup>.

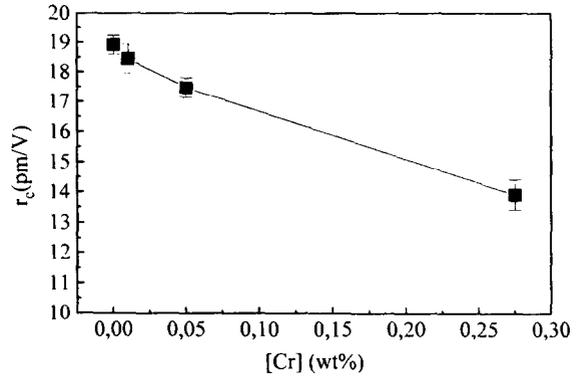


Fig. 3. The electro-optic coefficient  $r_c$  versus Cr concentration in LN:Cr. The line is a guide for the eye.

fact that the lines are strictly parallel reflects the independence of  $r_c$  on the temperature.

According to Eq. (4), the main errors in the determination of  $r_c$  arise from the errors in the phase shift (0.2 degrees for each measurement) and the crystal dimensions  $L$  and  $d$ .

To discard the possibility of a screening which opposes to the external electric field, measurements with dc applied voltage varying from 0 to 500 V have been performed. The obtained phase shift follows a linear behaviour characteristic of the Pockels effect.

The results for the all set of crystals are plotted in Fig. 3 versus the chromium concentration. We note a large dependence of the  $r_c$  coefficient on the concentration of chromium. We have checked that these values of  $r_c$  are independent of frequency from 0 up to 1 MHz.

### 3. Discussion and conclusion

The large variation of the EO coefficient  $r_c$  cannot be attributed to the error in the measurements. Indeed the maximum error of the  $r_c$  coefficient is about  $\Delta r_c = \pm 0.5$  pm/V, whereas the difference between the extreme values of  $r_c$  obtained for the pure and the 0.275% Cr doped crystal is  $\Delta r_c = 5$  pm/V. At first look, the large dependence is surprising since the doping amount is very small. A similarly large dependence of the EO coefficient was reported for BaTiO<sub>3</sub> crystals doped with iron. In this compound the coefficient  $r_{42}$  varies from 1745 pm/V for the undoped to 3450 pm/V for the 0.135% iron doped BaTiO<sub>3</sub> [15,16]. In fact, the presence of oxygen vacancies in barium titanate can lead to a similar behaviour.

Now we attempt to explain this dependence in the case of Cr-doped LiNbO<sub>3</sub>. Since the EO measurements were carried out at relatively low frequency (below 1 MHz), they reflect the variation in the ionic polarisation under the effect of an electric field. The change in  $r_c$  with the

variation of Cr concentration reveals therefore a modification in the lattice structure and thus in the corresponding polarisation. Chromium enters the LN lattice mainly in the  $\text{Cr}^{3+}$  state. Therefore, independently of the possible position in the lattice, i.e.  $\text{Li}^+$ ,  $\text{Nb}^{5+}$  or structural vacancy, it creates complex defects consisting of  $\text{Cr}^{3+}$  ions and charge compensators, because of its non-isovalent replacement of host ions. Several different axial and low-symmetry centers have been really observed in LN at various Cr concentrations [17,18]. These complexes lead to local changes in both the lattice which is slightly deformed and the electric dipole moment. In other terms, the large dependence of the EO coefficient  $r_c$  on the Cr concentration is the signature of a significant change in the structure of defect centers in the LN host lattice.

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### References

- [1] E. Krätzig and O.F. Schirmer, Topics in Applied Physics, ed. P. Günter and J.-P. Huignard (Springer, Berlin, 1988) p. 131.
- [2] Räuber, in: Current Topics in Material Sciences, ed. E. Kaldis (North-Holland, Amsterdam, 1978) p. 481.
- [3] O.F. Schirmer, O. Thiemann and M. Wöhlecke, J. Phys. Chem. Solids 52 (1991) 185.
- [4] P.F. Bordui and R.G. Norwood, J. Appl. Phys. 71 (1992) 875.
- [5] G.I. Malovichko, V.G. Grachev, L.P. Yurchenko, V.Ya. Proshko, E.P. Kokanyan and V.T. Gabrielyan, Phys. Stat. Sol. (a) 133 (1992) K29.
- [6] G.I. Malovichko, V.G. Grachev, E.P. Kokanyan, O.F. Schirmer, K. Betzler, B. Gather, F. Jermann, S. Klauer, U. Schlarb and M. Wöhlecke, Appl. Phys. A 56 (1993) 103.
- [7] N. Iyi, K. Kitamura, F. Izumi, J.K. Yamamoto, T. Hayashi, H. Asano and S. Kimura, J. Sol. State Chem. 101 (1992) 34.
- [8] H. Donnerberg, S.M. Tomlinson, C.R.A. Catlow and O.F. Schirmer, Phys. Rev. B 44 (1991) 4877.
- [9] U. Schlarb, S. Klauer, M. Wesselmann, K. Betzler and M. Wöhlecke, Appl. Phys. A 56 (1993) 311.
- [10] G.I. Malovichko, V.G. Grachev, V.T. Gabrielyan and E.P. Kokanyan, Sov. Phys. Solid State 28 (1986) 1453.
- [11] U. Schlarb and K. Betzler, Ferroelectrics 126 (1992) 39.
- [12] M. Glass, J. Chem. Phys. 50 (1969) 1501.
- [13] U. Schlarb and K. Betzler, J. Appl. Phys. 73 (1993) 3472.
- [14] M. Aillierie, M.D. Fontana, F. Abdi and C. Carabatos-Nedelec, J. Appl. Phys. 65 (1989) 2406.
- [15] F. Abdi, M. Aillierie and M.D. Fontana, Nonlinear Optics 16 (1996) 65.
- [16] G. Godefroy, G. Ormancey, P. Jullien, W. Ousi Benomar and Y. Semanou, Proc. 6th Conf. IEEE 12 (1986).
- [17] G.I. Malovichko, V.G. Grachev and S.N. Lukin, Sov. Phys. Solid. State 28 (1986) 553.
- [18] T.H. Yeom, Y.M. Chang and C. Rudowicz, Solid State Comm. 87 (1993) 245.