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Electro-optic properties in undoped and Cr-doped $LiNbO_3$ crystals

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Abstract. We have investigated the electro-optic and dielectric properties of $LiNbO_3$ along the ferroelectric c axis in pure and chromium-doped crystals. We have studied four series of samples with various crystal compositions and doping concentrations to separate the influence of the intrinsic defects related to the non-stoichiometry and the effect of the introduction of chromium. In pure and slightly doped crystals, the electro-optic coefficient r_c shows a non-monotonous dependence on the controlled crystal composition, which reflects a similar behaviour of the corresponding dielectric permittivity. In the highly Cr-doped crystals r_c displays a large decrease with increasing Cr concentration whatever the crystal composition. The results have been discussed by means of the $LiNbO_3$ structure and the substitution site dynamics.

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$LiNbO_3$ (LN) is considered as a standard material for many acousto-optic, electro-optic and optoelectronic applications [1, 2].

Generally, a serious limitation of a material used for technological application occurs if properties are not reproducible from one sample to another or if they are sensitive to defects.

In principle $LiNbO_3$ crystals can be obtained from a Li_2O–Nb_2O_5 solid solution extending from 45 to 50 mole% Li_2O. Single crystals with large dimensions and a good homogeneity and optical quality can be achieved from the congruently melting composition (at about 48.5 mole%) using the Czochralski technique [3].

Most investigations of the physical properties and applications of LN have been made on congruent crystals. However, these Li-poor crystals present different kinds of intrinsic defects to maintain the charge neutrality and therefore, can be also easily doped by extrinsic defects.

Intrinsic and extrinsic defects can both affect the properties so that a non-defect material is in principle more desirable especially for optical applications. Thus an increase in the optical damage threshold is expected in approaching the stoichiometric composition (50 mole% Li_2O) [4]. Consequently, some efforts have been made to find procedures for obtaining crystals with the stoichiometric composition, or close to it. Several methods have been successful in producing such crystals [5–7].

In using crystals with, now available, varying compositions it was clearly established that the linear optical properties, for instance the refractive index, strongly depend on the nature and the concentration of extrinsic defects [8]. They can be also affected by the nonstoichiometry intrinsic defects [9]. Nevertheless, the combined influence of these two kinds of defects had not so far been investigated. Furthermore, just a few studies were made into the electro-optic (EO) and nonlinear optical (NLO) properties [10, 11]. The role of defects on these properties is however necessary to control or to optimise the characteristics of the material for some applications. Moreover the study of the influence of defects can also provide information on the processes at the origin of the EO and NLO properties of LN, which had not previously been elucidated.

We have recently reported a large variation of the EO properties with the chromium concentration in Cr-doped crystals of a composition close to the stoichiometry [12]. In the present study we have extended our investigations to several series of pure and Cr-doped crystals with varying compositions and doping concentrations, so that we can analyse the specific roles of intrinsic and extrinsic defects on the EO properties of LN.

1 Characterization of the crystals

The deviation from the stoichiometric composition is usually described by the parameter x as the ratio between the Li concentration and the total amount of cations. We denote by x_m and x_c this ratio in the melt and crystal respectively ($x_m = x_c$ only for the congruent composition). The relationship be-

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tween both quantities is not linear so the determination of the composition x_c generally requires specific investigations.

Using the Czochralski technique four kinds of crystals were prepared with different controlled compositions and various chromium concentrations.

In the first series, pure crystals were grown by the Czochralski method from the congruent melt $x_m = 48.46\,\%$ with an addition of 0, 2, 4, or 6 wt% K_2O to the melt. It was shown [13] that this method is able to give crystals with a composition x_c close to the stoichiometry. Moreover potassium ion is nearly absent in the crystal. The second series corresponds to Cr-doped crystals of various compositions but with a fixed low Cr concentration (0.06 at.%).

The third and the fourth series relate to Cr-doped crystals of various concentrations prepared from Li-rich melt $x_m = 54.54\,\%$ and congruent composition ($x_m = 48.4\,\%$), respectively.

The first and second series were used to study the effect of the composition variation in pure and Cr-doped crystals, whereas the third and fourth series were devoted more to giving an insight into the proper influence of the Cr doping which can vary according to the concentration of intrinsic defects.

It is particularly important to define with accuracy the composition of the pure crystals. Generally it is possible to use the relationship between the Li_2O mole fraction in the melt and the Li concentration obtained from analysis of the crystal. However the relationship depends on the results obtained by the authors [5, 7, 14]. In the case of crystals grown with K_2O added to the melt, this calibration cannot be used. Consequently, it is always more correct to determine the composition by means of indirect analyses based on the determination of the physical properties of the material, which depend strongly on the composition.

Several techniques can be used to determine the composition. A survey of the most usual techniques was recently published [15]. They differ in accuracy and resolution. In particular the extraordinary refractive index is affected by the deviation from the stoichiometric composition. Thus n_e varies from 2.200 down to 2.187 at $\lambda = 632.8$ nm between the extreme compositions of the pure series I. But the accuracy in the determination of x_c that is achieved by using this technique was not sufficient to distinguish all crystals used in our investigations. We have used two other methods more suitable for determining the composition in all series, EPR and Raman scattering. We derive the composition from the Fe^{3+} EPR linewidth and the lowest-frequency phonon Raman linewidth respectively. In accordance with [16–19], the calibration of these techniques was done on standard crystals.

The compositions obtained by these methods for all crystals of series I are summarised in Table 1. We can note that the results are in remarkable agreement for both techniques. The methods are sufficiently accurate ($\Delta x_c < 0.1\,\%$) to be able to discriminate between the various crystals which have different compositions except for the samples I-3 and I-4. This simply means that sample I-3 prepared with 4% K_2O added to the melt has the same composition as the crystal obtained from Li-rich melt ($x_m = 54.54$ mole%) without K_2O.

This shows indirectly the efficiency of the method of LN crystal growth with an addition of K_2O to the melt to obtain crystals close to the stoichiometric composition [6, 7].

In Cr-doped crystals, we cannot assume that all crystals have the same composition as the pure crystal obtained from the same composition of the melt. Indeed, the introduction of chromium or other doping, can lead to a change in the concentration of intrinsic defects in the crystals [20]. The effect of doping is therefore expected to be a composition different from the initial composition of the melt.

The indirect change in crystal composition due to Cr doping is usually difficult to detect because of the complicated dependence of a physical property on the direct effect of doping and the effect of the change in the composition, indirectly caused by impurity.

In highly Cr-doped crystals, these two effects cannot be separated, so we will study further the whole influence of Cr doping on the EO properties in crystals of series III and IV.

In contrast, we can consider that for crystals with a small amount of doping, the direct effect can be neglected and we attempt to determine the apparent crystal composition with the same techniques which were used in the case of undoped crystals. We can therefore derive from the Raman linewidth the crystal composition for samples of the series II grown from various concentrations of Li_2O in the melt. Results are reported in Table 2.

We note that the composition in doped crystals is slightly larger than that in pure crystals. First we note that the value of x_c is significantly different from that of x_m, except for sample II-2 which corresponds to the congruent composition.

2 Electro-optic results

Here we are especially interested in the EO coefficient r_c which can be measured when the electric field E applied to the crystal is along the ferroelectric c axis and the laser beam is propagating along the x axis. r_c is an effective EO coefficient given by

$$r_c = r_{33} - \left(\frac{n_o}{n_e}\right)^3 r_{13}\,, \tag{1}$$

where n_o and n_e are the ordinary and the extraordinary refractive indices when n_o electric field is applied to the crystal. The

Table 1. Compositions in the pure crystals (series I) as deduced from Raman scattering (RS) linewidth Γ of the lowest frequency phonon and EPR spectroscopy. All crystals were grown from 48.46 mole% Li_2O in the melt with addition of K_2O except I-4 which was prepared from a Li-rich melt ($x_m = 54.54$ mole% Li_2O)

Samples	x_m/(mole%)	K_2O/(%)	Γ/cm^{-1}	x_c (RS)/ mole% Li_2O	x_c (EPR)/ mole% Li_2O
I-1	48.46	0	10.75	48.38 ± 0.05	48.40 ± 0.02
I-2	48.46	2	9.15	49.00 ± 0.05	49.07 ± 0.02
I-3	48.46	4	7.935	49.46 ± 0.04	49.53 ± 0.02
I-4	54.54	0	7.755	49.53 ± 0.04	49.50 ± 0.01
I-5	48.46	6	6.48	50.01 ± 0.03	50.00 ± 0.01

Table 2. The composition in crystals doped with 0.06 at.% Cr as deduced from the Raman mode linewidth Γ. It is compared with the composition of corresponding pure crystals grown from the same melt, as obtained from EPR Fe^{3+} linewidth. When x_m increases, the behaviour of Γ is similar to that in pure crystals reported in Table 1

Samples	x_m/mole%	x_c/mole% pure	Γ/cm^{-1}	x_c/mole% doped
II-1	42.86	46.69	14.15	47.07 ± 0.06
II-2	48.46	48.38	10.00	48.67 ± 0.05
II-3	53.49	49.30	8.47	49.26 ± 0.04
II-4	60.00	49.85	6.63	49.96 ± 0.03

EO coefficient is deduced from the measurement of the phase shift as a function of E. The phase shift can be expressed as

$$\Gamma = \frac{2\pi}{\lambda} L \Delta n \tag{2}$$

corresponding to the birefringence

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

where $n_e - n_o$ is the spontaneous birefringence and the second term is the electric field-induced birefringence which is related to the EO coefficient. The corresponding phase shift $\Gamma(E)$ is determined with a high accuracy using a Sénarmont setup [21] by the difference between the values when a dc voltage V is successively applied or not applied on the sample. By this way we obtain the dc (continuous) EO coefficient as

$$r_c = \left| \frac{2e}{n_e^3} \frac{\Delta n(E)}{V} \right| = \left| \frac{\lambda e}{\pi n_e^3 L} \frac{d\Gamma}{dV} \right| \,, \tag{4}$$

where λ is the laser wavelength, L the crystal length along the x axis, and e is its thickness along the z axis.

In fact, in the variation of the phase shift with E, we have to consider the contribution associated with a change in L due to the inverse piezoelectric effect. This phase retardation here is very small compared to that caused by the EO effect and therefore can be neglected.

An additional source of the phase shift dependence can arise from a change of the spontaneous birefringence due to a temperature shift during measurements [21]. To discard the influence of this thermo-optic effect, we have recorded the dependence of the retardation Γ on the temperature in a small range around room temperature and the EO phase shift is thus yielded by the difference between two plots obtained with and without the field. Typical results obtained in two different crystals are shown in Fig. 1. We have determined the (dc) EO coefficient r_c in pure and Cr-doped crystals at 1321 nm by means of a 20-mW diode-pumped Nd:YLF laser.

We have also performed some EO measurements as a function of the frequency of an ac modulating field. In this case, only an ac electric field is applied on the crystal and we measure the modulation depth, from which the value of r_c is derived for different frequencies [22].

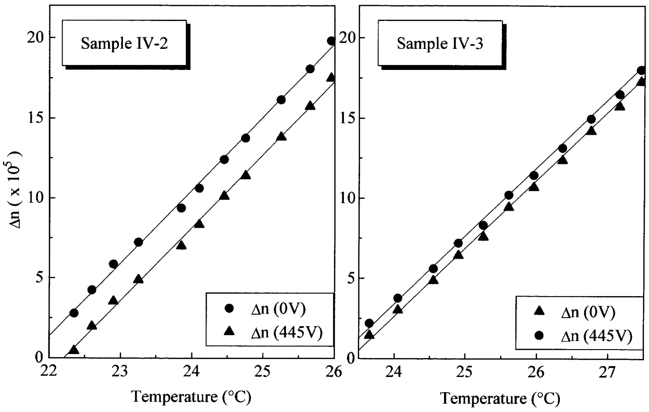

Fig. 1. Relative variation of the birefringence which is induced by a temperature change as measured for two different dc voltages, at $\lambda = 1321$ nm, in two Cr-doped crystals. The sample IV-2 with $L = 3.72$ mm and $e = 1.8$ mm is doped with 0.06 at.% Cr and the sample IV-3 with $L = 4.5$ mm and $d = 2.245$ mm is doped with 0.7 at.% Cr. The slope of the curves provides the thermo-optic coefficient whereas the shift between data recorded at the same temperature for two different dc voltages is related to the EO coefficient (cf (3))

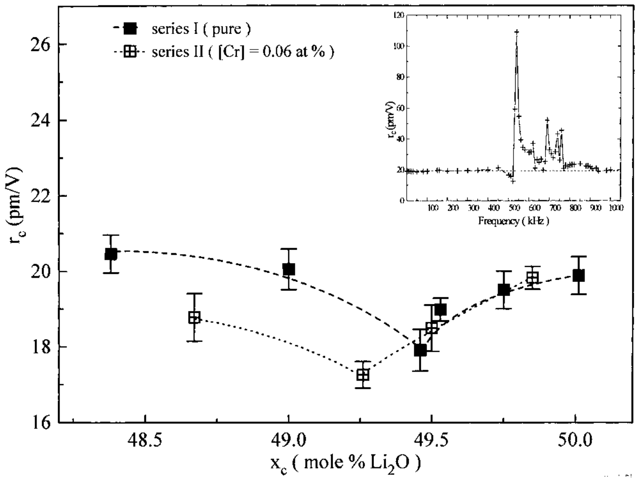

Fig. 2. Electro-optic r_c coefficient versus crystal composition in the pure samples of series I and in the 0.06 at.% Cr-doped crystals of series II. Inset: the frequency dependence of r_c is shown in the congruent pure crystal

In Fig. 2 we summarise the values of the EO coefficient r_c obtained in pure crystals with various compositions. The variation of r_c with x_c is significant, compared with the good accuracy of the measurements. Indeed r_c equal to 20.4 pm V^{-1} in the congruent crystal diminishes to 17.9 pm V^{-1} in I-3 ($x_c = 49.5$ mole%) then increases again when x_c approaches the stoichiometric composition and finally attains 19.9 pm V^{-1} in the stoichiometric crystal. We also report in Fig. 2 the values in 0.06 at.% Cr-doped crystals (series II). This series also shows large variations between four samples. This result confirms the dependence of the coefficient on the composition. The shift between values in pure and doped crystals for $x_c < 49.4$ % is significant despite the small amount (0.06 at.%) of Cr doping. However, this self effect of Cr seems to depend on the composition since this shift vanishes for the stoichiometric composition

$r_c = 19.8\,\mathrm{pm\,V^{-1}}$ in the doped crystal compared with $r_c = 19.9\,\mathrm{pm\,V^{-1}}$ in the pure material.

The inset in Fig. 2 shows the frequency dependence of r_c for the crystal I-1. The EO coefficient is nearly independent of frequency in the whole frequency range available in our measurements, 0 up to 1 MHz. Only a small increase is detected between the values below and above piezo-electic resonances.

Figure 3 displays the dependence of r_c on the Cr concentration as derived from the measurements in the two series of Cr-doped crystals. The variation of r_c, which is large for the series III ($x_m = 54.54$ mole%), is even stronger for the congruent series IV ($x_m = 48.4$ mole%). We can note that for low concentration (< 0.08 at.%) congruent samples display larger EO coefficients than the nearly stoichiometric crystals, as in pure materials.

The dependence of r_c on the chromium doping is much larger than its dependence on the composition. Thus the maximum of the shift caused by a variation of x_c is $2.5\,\mathrm{pm\,V^{-1}}$ in pure materials whereas the shift due to Cr doping is around $5\,\mathrm{pm\,V^{-1}}$ in Li-rich crystals, and $12.5\,\mathrm{pm\,V^{-1}}$ in congruent crystals.

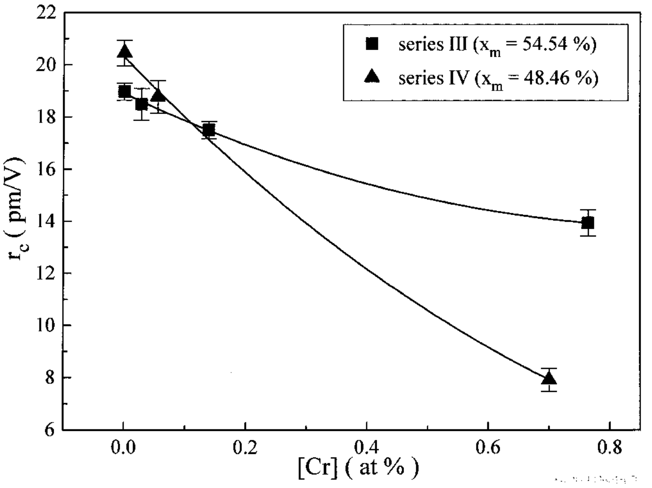

Fig. 3. Electro-optic r_c coefficient versus Cr concentration for crystals of series III and IV. The lines are a guide for the eye

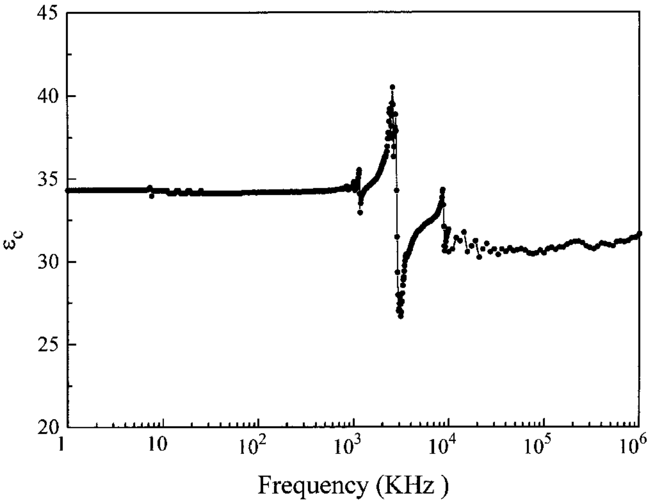

Fig. 4. Dielectric permittivity ε_c versus the frequency in the congruent pure LN crystal

Results in pure crystals of series I clearly indicate that r_c is sensitive to the crystal composition. The introduction of Cr into the LN crystal can cause a change in the composition and thus lead to a variation of r_c. This effect, however, even if it exists, is negligible with respect to the direct influence of Cr on the EO properties, which is likely to be the main cause of the dependences of r_c shown in Fig. 3. Therefore it can be reasonable to assume in the analysis of the results that for each series (III and IV) the crystal composition is nearly constant ($x_c = 49.5$ mole% and 48.4 mole% respectively) and the doping concentration only is varying.

3 Dielectric measurements

Generally the behaviour of the EO coefficient is closely linked to the corresponding behaviour of linear dielectric permittivity. The relationship between r and the ε quantities was thus used to describe the temperature dependence of the EO coefficient [23] or its frequency dependence [24].

We have therefore undertaken measurements of the permittivity ε_c in the same crystals used in the EO investigations.

To establish the possible link of the EO coefficient r_c with the corresponding dielectric permittivity, we studied successively the dependence of ε_c on frequency in pure and doped crystals, on the crystal composition and on the Cr concentration. Then we compared these dependences with the respective behaviours of the coefficient r_c. We have thus measured the real and imaginary parts of the dielectric permittivity in a large frequency range up to 1 GHz by means of the impedance analysers HP 4051 and HP 4191A.

The permittivity ε_c recorded in the congruent pure crystal is plotted in Fig. 4. Piezoelectric resonances are lying between 500 and 1200 kHz. If we except this frequency range, the value of ε_c exhibits only a small variation between both sides of piezoelectric resonances. This shift (about 2) corresponds to the electromechanical contribution to ε_c. Furthermore, we have shown in a recent paper devoted to the Raman measurements in LN [25] that the permittivity remains constant between 1 GHz and several THz since the Lyddane–Sachs–Teller relationship gives a value of 29 from optical phonon frequencies. This means that ε_c does not present a large dispersion versus frequency and that its main contribution of ε_c has an ionic origin. If we subtract from the total value of ε_c the purely electronic contribution given by the refractive index squared (n_e^2) and the electromechanical part, we find indeed an ionic contribution of about 23.5.

The dielectric behaviour of ε_c is very similar in all pure and Cr-doped crystals. Only the low frequency level (at 1 kHz) varies slightly with the composition. Since the refractive index changes slightly and the electromechanical contribution is constant between the congruent and the stoichiometric crystals, this means that only the variation of the ionic contribution with the composition x_c explains the change of ε_c at 1 kHz in pure materials. In the whole frequency range, the permittivity ε_c does not exhibit any significant change with concentration in Cr-doped crystals in contrast to the small dependence on the composition in the pure crystals. In doped crystals, the dielectric permittivity measured at low frequency

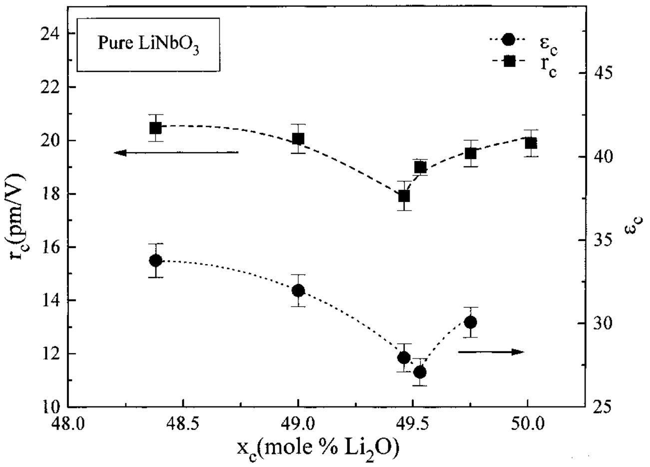

Fig. 5. Comparison of the crystal composition dependence x_c between the electro-optic coefficient r_c and the dielectric permittivity ε_c as measured at 1 kHz in the pure samples of series I

is nearly unaffected by the Cr content and the electronic permittivity.

Since both the EO coefficient r_c and the permittivity ε_c measured at 1 kHz are dependent on the composition in pure crystals (series I), they are compared and plotted in Fig. 5. We note that their behaviours are remarkably similar.

4 Interpretation

4.1 *Origin of the variations of* r_c *in pure and* Cr-*doped crystals*

Now we attempt to interpret the dependences of the EO properties in LN on both the crystal composition x_c and the Cr concentration. First, we discuss the various contributions to the EO coefficient.

In an inorganic crystal, the various contributions to the EO coefficient can be generally separated [23, 24, 26] as

$$r^{\mathrm{T}} = r^{\mathrm{d}} + r^{\mathrm{I}} + r^{\mathrm{E}} , \qquad (5)$$

where r^{d} is the mechanical contribution (piezo-optic effect) due to the crystal deformation caused by the inverse piezoelectric effect, r^{I} is the ionic contribution and r^{E} is the direct electronic contribution. These contributions occur in separate frequency ranges. If r^{T} corresponds to the coefficient of the free sample (unclamped), i.e. to the sum of all contributions at zero frequency, $r^{\mathrm{S}} = r^{\mathrm{I}} + r^{\mathrm{E}}$ is the coefficient in the clamped conditions which impede the mechanical deformation of the crystal.

The contributions r^{d} which appears at acoustic frequencies can be determined by the difference in the plot $r(\omega)$ between the values of the coefficient below and above the piezoresonances. It can be also related to the components of the elasto-optic p and the piezoelectric d tensors by

$$r^{\mathrm{d}}_{i,j} = p_{i,k} d_{k,j} \qquad (6)$$

The term r^{E} can be calculated from the knowledge of the SHG coefficient $d^*_{j,i}$ by

$$r^{\mathrm{E}}_{i,j} = -\frac{4}{n_i^2 n_j^2} d^*_{j,i} . \qquad (7)$$

In the congruent LN crystal we calculate $r^{\mathrm{d}}_{\mathrm{c}} = -0.7\,\mathrm{pm\,V^{-1}}$ and $r^{\mathrm{E}}_{\mathrm{c}} \approx 5\,\mathrm{pm\,V^{-1}}$ from the values of elasto-optic, piezoelectric [27], and SHG coefficients [11].

We note that $r^{\mathrm{d}}_{\mathrm{c}}$ agrees with the increase difference between values measured above and below the piezoresonances. The piezo-optic contribution to the total coefficient r^{T} is very low especially if compared with other ferroelectric oxides (It is half of the total value of the coefficient in r_{42} in $\mathrm{BaTiO_3}$ [22]). On the other hand the purely electronic contribution is not negligible compared with the whole value r^{T} measured at low frequency ($r^{\mathrm{T}}_{\mathrm{c}} = 20.4\,\mathrm{pm\,V^{-1}}$). However, neither a change in $r^{\mathrm{d}}_{\mathrm{c}}$ nor in $r^{\mathrm{E}}_{\mathrm{c}}$ can be likely to be invoked to explain the large dependences in the EO coefficients r_c on the composition and on Cr doping.

Indeed, $r^{\mathrm{d}}_{\mathrm{c}}$ was checked to be very small and nearly constant between various pure and doped samples. Even if the SHG coefficients and the refractive indices n_o and n_e which are associated with $r^{\mathrm{E}}_{\mathrm{c}}$ in (7) are known to vary slightly with the composition in pure crystals, the induced change in r^{E} is too weak to explain the variations of $r^{\mathrm{T}}_{\mathrm{c}}$ reported in Fig. 2. In doped crystals the SHG coefficients d_{31} and d_{32} are unknown but the refractive indices are nearly insensitive to Cr doping so that the change in r^{E} with doping is not likely to be larger than $1\,\mathrm{pm\,V^{-1}}$.

Consequently the large dependences of r_c on the concentration of both the intrinsic and extrinsic defects have to originate from some changes in the ionic contribution r^{I}. This term derives from the change of the reciprocal optical susceptibility under the applied electric field which is indirectly caused by the ionic polarisation.

The coefficient r_c can be thus connected to the corresponding permittivity ε_c via the polarization-optic coefficient f_c as

$$r_c = \varepsilon_0(\varepsilon_c - 1) f_c . \qquad (8)$$

The coefficient f_c is defined as the derivative of the reciprocal susceptibility resulting from the ionic polarization.

The polarization optic coefficient f_c is derived from (8) and the values of ε_c and r_c. We find, in pure crystals, a value of f_c which is remarkably constant with the composition x_c, $(0.075 \pm 0.005)\,\mathrm{m^2\,C^{-1}}$. The behaviour of r_c, reported in Fig. 5, consequently reflects the dependence of ε_c on the composition and mainly originates from a change in ionic polarizability.

The coefficient f_c is also determined for doped crystals. Its value varies between 0.07 and $0.08\,\mathrm{m^2\,C^{-1}}$ in all crystals with low Cr concentration (< 0.7 at.%). It decreases strongly for larger concentrations in congruent and in nearly stoichiometric crystals.

4.2 *Structure of defects and variations of the EO properties*

Among several models proposed to explain the structure of non-stoichiometric LN crystal, we retain the description suggested by Lerner et al. [28] In this model, the relative excess of Nb ions is substituted for the vacant Li sites, in the so-called Nb antisites, whereas the charge compensation is insured by 4 Li vacancies for each Nb ion. Within this framework, the concentration of Nb antisites and the number of Li ions can be calculated.

The number of Nb antisites and therefore Li vacancies is large in Li-poor crystals and decreases on approaching the stoichiometric composition. The relative contents of Nb antisites and Li ions can likely affect the electro-optic properties as well as the optical properties.

Two processes can be invoked to contribute to the electro-optic effect in $LiNbO_3$, the ionic and electronic polarizabilities of the Nb ion (process 1) and the deformability of the oxygen octahedron around Li (process 2). Each process can change with the number of Nb antisites and the Li ions in the crystal. In congruent or Nb-rich crystals, the number of Nb ions substituting for Li is relatively large, favouring the process 1 and a large ionic polarization. This gives rises to a large dielectric permittivity ε and therefore, as shown above (see (8)), to a large r_c.

When x_c approaches the stoichiometric composition, the number of antisites diminishes whereas the Li concentration increases, so process 2 becomes more important, which leads to large values of ε_c and r_c.

Now we turn to the behaviour of r_c in the Cr-doped crystals. First, we consider the series II of crystals doped with 0.06 at.% Cr. This concentration of extrinsic defects can be considered small compared with the concentration of intrinsic defects (Nb_{Li}) related to the non-stoichiometry. We have shown above that the apparent composition of the crystal is only slightly shifted by a small chromium doping (see Table 2). Accordingly, a change in r_c due to a small Cr doping is expected to be comparable to the variation due to a small change of the composition x_c in the pure crystals, if we neglect the self influence of chromium ions on the EO properties. In fact, our results reported above (see Fig. 2) show that r_c is significantly lower in 0.06 at.% Cr-doped crystals than in pure Li-poor crystals with the same composition, whereas the values are nearly the same for doped and pure samples in Li-rich crystals.

This comes from the fact that the introduction of a small amount of Cr, even if it affects only slightly the crystal composition x_c, can lead to a significant change in the substitution site. Luminescence of Cr in LN indeed reveals that for low concentration (smaller than 0.1 at.%) the Cr ions are substituted mainly for the Li sites [29, 30]. Consequently the number of niobium antisites Nb_{Li} is smaller in Cr-doped crystals than in pure crystals. Since the number of antisites was shown to be correlated to the EO properties in pure crystals, a smaller number leads to a decrease in the value r_c in the Cr-doped crystals. In doped crystals with the composition close to the stoichiometry the EO properties are governed by process 2 related to the number of Li ions, which is nearly unaffected by a small Cr doping. Consequently the EO coefficient has nearly the same value in pure and doped Li-rich crystals.

This interpretation explains the composition dependence of r_c in crystals doped with a small Cr amount, as reported in Fig. 2. It confirms the origin of the mechanisms responsible for the large EO properties in pure LN. These properties are closely related to the number of Nb antisites. The EO coefficient r_c is large in crystals with composition close to the stoichiometry, even if the number of antisites is small because of a large amount of Li sites surrounded by deformable oxygen octahedra. In other words the EO properties of LN can be favoured by two competitive mechanisms, the non-stoichiometry intrinsic defects and the ordering of the lattice structure, which mainly act on the congruent composition side and the stoichiometry side, respectively. This interpretation also holds for Cr-doped crystals with a small concentration.

In the highly doped LN crystal, as the Nb_{Li} antisites are rapidly filled, the dynamics of site substitution by chromium ions is more complicated as revealed by new recent luminescence experiments [30]. In particular they can occupy neighbouring Li and Nb sites leading to the formation of Cr^{3+}–Cr^{3+} dimers [18]. This disorder in the Cr-doped LN lattice obviously increases with the deviation from the stoichiometry and with increasing doping concentration. This explains the large decrease of the EO coefficient r_c with Cr concentration which is still enhanced in the congruent crystal compared to the nearly stoichiometric crystal (see Fig. 2).

5 Conclusions

We have reported a significant variation of the EO coefficient r_c in the pure crystals with the content of intrinsic defects related to the deviation from the stoichiometric composition. This behaviour is closely linked to a similar dependence of the dielectric permittivity along the ferroelectric c axis and can be attributed to the partial occupation by Nb ions of Li sites. In the Cr-doped crystals the EO coefficient r_c decreases abruptly with increasing Cr concentration. This decrease is larger in the congruent samples than in the nearly stoichiometric samples. As the dielectric constant is nearly unaffected, this large dependence of r_c with Cr doping is attributed to a change of the polarization-optic coefficient due to a disordering in the lattice caused by the doping.

Results in pure and doped crystals show that the EO properties in LN originate from the Nb polarizabilities and the deformability of the oxygen octahedron aound a Li ion. The efficiency of these processes is closely linked to the structure of the lattice and site dynamics by Nb and Li ions, which are affected by both the crystal composition and the doping. At the variation of intrinsic and extrinsic defect concentrations, the structure of both kinds of defect centres can be changed and this can lead indirectly to a change in the local electric field and EO properties of the whole material.

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