Third column electro-optical coefficients of zirconium-doped congruent lithium niobate crystals

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ABSTRACT

All coefficients of the third-column of the unclamped and clamped electro-optic tensor of zirconium-doped congruent $LiNbO_3$ single crystals, in the concentration range up to 2.5 mol%, are determined as function of the dopant concentration by direct techniques based on interferometric and Sénarmont optical arrangements at the wavelength of 633 nm and at room temperature. It is found that all the unclamped and clamped electro-optic coefficients are relatively constant, except for the sample doped with 2 mol% of zirconium. From the obtained experimental values, the acoustic contribution is then deduced and found constant over all the studied samples. Finally, the electro-optic behavior of LN:Zr as function of the dopant concentration was confirmed by dielectric characterizations.

1. Introduction

Lithium niobate (LN) crystals have good optical quality and uniformity, an excellent electro-optic, piezoelectric, acoustic and nonlinear optical properties [1,2]. Generally LN crystals of congruent composition, with the molar ratio R = [Li]/[Nb] = 0.946, are generally used in a lot of optical and acoustic devices due to their physical properties but also because of their high optical quality and growth facilities. Nevertheless, for successful applications in devices, the main drawback of congruent LN is its relatively low optical damage resistance compared to other competing oxide crystals such as $LiTaO_3$ (LT) or BaB_2O_4 (BBO) [2,3]. This photorefractivity of LN is mainly linked to the presence in congruent LN crystals of intrinsic defects due to the presence of Nb ions on antisites, i.e. on Li sites [4,5]. Different approaches have been developed to reduce the photorefractive damage in LN. One of them consists of decreasing the number of intrinsic defects by growing LN crystals with the ratio R closer to the one corresponding to the stoichiometric composition [6,7]. The second approach consists in doping congruent LN crystals by appropriate ions, removing the native defects by introducing the dopant ions at lithium site. Significant

reduction of optical damage was observed in doped samples by divalent ions such as Mg^{2+} [8,9] and Zn^{2+} [10,11] with a threshold of about 5.5 mol%MgO [12,13], 7 mol%ZnO [14,15], respectively. Same observations were also established for LN doped by trivalent ions such as Sc^{3+} and In^{3+}, with the threshold about 1.5 mol% for both ions [16,17]. Some years ago, the optical damage dependence with dopant concentration has been also established for crystals doped with tetravalent ions [18,19]. It was shown that a reduction of photorefractivity could be achieved with lower dopant concentration than in the case of divalent ions, especially with hafnium ions with a threshold around 3 mol% [20,21]. Starting with these physical crystal properties and growth considerations, some crystal grower groups as the one of Kokanyan et al. [22] have grown crystals with other tetravalent dopant ions, as zirconium. They shown that zirconium presents a distribution coefficient closer to one at the threshold concentration around 2 mol%ZrO_2 [23,24].

Among other optical and physical properties and closely linked in crystals of the LN family to the optical damage effect, the electro-optic properties are also mainly influenced by photorefractive-resistant impurities or dopants [15]. As examples, it was found that electro-optic properties of LN crystals doped with Zn or Mg ions present a huge oscillation with the concentration [9,14]. By opposition, no significant dependence of the electro-optic properties on the doping concentration was observed in hafnium doped LN crystals [21]. Similarly, the constant-stress combined

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electro-optic coefficient r_c of zirconium doped LN crystals appears only to be slightly influence on Zr [23]. Nevertheless, the behavior with the Zr concentration of the direct coefficients r_{113} and r_{133} of the third column of the electro-optic tensor was not until yet determined.

In the present work we focalized on the electro-optic properties of zirconium-doped congruent LN crystals, hereafter noted LN:Zr. We provide a direct determination of the values for the unclamped (noted r^T) and clamped (noted r^S) electro-optic coefficients r_{113}, r_{133} and r_c of a series of congruent LN:Zr crystals, with concentration from 0 up to 2.5 mol%ZrO$_2$. Samples were grown from the same charge, thus we emphasize that they have the same amount of unintended impurity trace. Our experiments lead to conclude that an effective and relatively abrupt kink in the electro-optical properties exists for crystals around 2 mol%Zr that is in full accordance with the threshold observed in optical damage. This behavior exists for all the unclamped and clamped coefficients of the third column of the electro-optic tensor, while the acoustic contribution remains constant in the studied concentration range.

2. Experimental methods

The measurements are performed using both a Mach–Zehnder type interferometric and the one-beam Sénarmont-type ellipsometric techniques, both for an applied field parallel to the z-axis of the crystal and for light propagation along the x-axis. With the first technique, we have investigated the electro-optic coefficients r_{113} and r_{133}, while with the second technique, we have investigated the combined coefficient r_c. All measurements were performed at room temperature and using a He–Ne laser (633 nm).

For the determination of the unclamped electro-optic coefficients r_{eff}^T, we used a method called the "Modulation Depth Method" (MDM) [25]. This method consists in the measurement of the amplitude of the modulated beam induced by an ac-voltage applied on the sample under test. In the present study, we performed measurements with an ac-voltage of up to peak-to-peak amplitude equal to 250 V at 1 kHz. For the determination of the clamped (i.e. constant strain) electro-optic coefficients r_{eff}^S, we used a method called the "Time Response Method" (TRM), which consists in the measurement of the time response of the EO crystal to a fast step voltage [26]. This method also alloys the determination of the unclamped EO coefficients when the long time range contribution is considered in the EO response. We performed measurements with a pulse voltage of amplitude 300 V having a rise time equal to 5 ns and a repetition rate equal to 10 μs. It is to be of note that the unclamped coefficients can be determined by both methods MDM and TRM allowing the validation of the experimental results. In the same manner, we can note that the combined EO coefficients can be directly measured by the Sénarmont arrangement, offering a high accuracy and verified by its determination from the direct EO coefficients as measured by the interferometric setup.

Under the above-mentioned conditions, within both MDM and TRM methods, the absolute value of the effective EO coefficient r_{eff} can be determined within an equation having the form [25,26]:

$$r_{eff} = A \frac{1}{I_{Max} - I_{min}} \frac{\lambda}{\pi n^3} \frac{d}{L} \frac{\Delta I_E(v,t)}{\Delta V(v,t)}, \tag{1}$$

where $A = 2$ or 1 for interferometric or Sénarmont measurements, respectively. In this equation, d is the inter-electrode distance, L the length of the crystal along the beam-propagation direction, λ is the vacuum wavelength, n the refractive index seen by the eigen-wave propagating in the crystal, I_{Max} and I_{min} the maximum and minimum of the transmitted intensity and ΔI_E is the peak-to-peak amplitude of the sinusoidal (in MDM method) or step voltage (in TRM method) modulated-detected signal, ΔV is the cor-

responding amplitude of the modulated voltage applied to the crystal.

We are interested in the coefficients of the third column in LiNbO$_3$ crystals (trigonal structure C_{3v} = 3 m), thus, all measurements were done with an apply electric field $E = (0,0,E_3)$ along the z-direction. Considering that in the trigonal structure, $r_{113} = r_{223}$, it results that only two direct and one combined EO coefficients have to be determined. In interferometric measurements, with a light propagation along the x axis (y axis), the field-induced effective change in the refractive index for each polarization component is [27]:

$$\delta n_0(E) = -(1/2)n_0^3 \delta(1/n_0^2) = -(1/2)n_0^3 r_{113}E_3, \tag{2a}$$

and

$$\delta n_e(E) = -(1/2)n_e^3 \delta(1/n_e^2) = -(1/2)n_0^3 r_{333}E_3. \tag{2b}$$

In non-interferometric or ellipsometric measurements using the Sénarmont configuration with a light propagation along the x axis (y axis), for a polarization of the input beam at 45° of the z axis, the field-induced effective change in the birefringence is:

$$\delta \Delta n(E) = (1/2)n_e^3 r_c E_3, \tag{3}$$

with the combined coefficient defined as:

$$r_c = r_{333} - (n_0/n_e)^3 r_{113}. \tag{4}$$

Finally, the acousto-optic contributions, defined by $r_{eff}^a = r_{eff}^T - r_{eff}^S$, applied to the determination of the EO coefficients of the third column, can be deduced from the elasto-optic p_{ijkl}^E at constant electric field and piezoelectric d_{kij} tensors for the trigonal structure [28] and are found, for the direct EO coefficients, r_{113} and r_{333} equal to:

$$r_{113}^a = (p_{1111}^E + p_{1122}^E)d_{311} + p_{1133}^E d_{333} \text{ and}$$
$$r_{333}^a = 2p_{3311}^E d_{311} + p_{3333}^E d_{333}, \tag{5}$$

and for the combined EO coefficient r_c, this contribution is equal to:

$$r_c^a = \left\{ p_{3333}^E - (n_0/n_e)^3 p_{1133}^E \right\} d_{333}$$
$$+ \left\{ 2p_{3311}^E - (n_0/n_e)^3 (p_{1111}^E + p_{1122}^E) \right\} d_{311}. \tag{6}$$

3. Experimental results and discussion

We present in Fig. 1 an illustration of the experimental optical signal $\Delta i(t)$ recorded at the output of the interferometric setup when the voltage $\Delta V(t)$ is applied on the LN:1.5 mol%Zr sample set in both r_{113} and r_{333} configurations. In this figure, $\Delta i(t)$ is represented for two different time scales corresponding, in the long time range to the unclamped contribution to the electro-optic effect and in the short time range to the clamped one. We observed in the long-time range, some oscillations of the optical signal with periods related to the main piezoelectric frequency resonances. By else, no difference in the level of the signal in the two time ranges is observed pointing out the negligible amplitude of the acoustic contribution in these two opto-geometrical configurations.

After the Z-transform of the two time dependent signals, $\Delta i(t)$ and $\Delta V(t)$, the frequency dispersion of the EO coefficients is calculated from the ratio of $\Delta i(v)$ and $\Delta V(v)$ according to Eq. (1) [26]. We report in Fig. 2 the frequency dependence of the EO coefficients of the LN:1.5 mol%Zr crystal and we can observed that the answer is flat and quite at the same level on both sides of the piezoelectric resonances. Remarks: we also report in Fig. 2, the frequency behavior of the dielectric permittivity of the LN:1.5 mol%Zr crystal, results that will be discussed further.