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Abstract
Periodically poled lithium niobate bulk crystals doped with hafnium have been grown by the off-centred Czochralski technique. The role of Hf ions in the formation of periodic poled structures has been characterized by structural and compositional techniques. A periodical modulation in Nb and in Hf concentration, as a function of the initial Hf concentration in the melt, has been observed. The periodic modulation observed in Hf and/or Nb concentration along the periodic structure has been attributed to the special feature in the incorporation of Hf ions into the $LiNbO_3$ lattice. The shape of the solid–liquid interface influences the formation of the periodical structure and the character of the compositional modulation.

1. Introduction

Interest in periodic poled lithium niobate (PPLN) crystals increases continuously due to the exceptional possibilities for PPLN to generate light in the low wavelength region through quasi-phase-matched second harmonic generation (QPM-SHG) [1]. To obtain SHG there are two possibilities, (i) the very well known and restricted birefringent phase matching, and (ii) the QPM technique, which uses the periodic modulation of the nonlinear coefficient [1]. The QPM technique allows for longer interaction length and a higher efficiency due to the higher value of the nonlinear coefficient involved in the process. The availability for SHG combined with the well known properties of lithium niobate (LN) to host laser ions [2] and the possibility to tailor the PPLN structures in an aperiodical way during growth allows for self-frequency doubled lasers [3], simultaneous multi-self-frequency processes [4] and many other possibilities. Furthermore it has been published that PPLN structures reduce the photorefractive damage taking place in bulk LN [5], which is a very interesting property for cw laser applications working at high power levels.

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Impurity ions in LN play an important role in the formation of the internal space charge field and thus, in the formation of the ferroelectric domain structure [6] through a built-in internal electric field, which is determined by the lattice site and nature of the impurities. In particular rare-earth ions, which are incorporated into the Li octahedra, are forced to move down towards the nearest oxygen triangle [7] due to their large size, influencing in this way the LN domain structure. Moreover, one can note that changes in the Li/Nb ratio modify the LN domain structure probably due to changes in the lattice parameter value [8].

The preparation of PPLN structures by the off-centred Czochralski (Cz) growth technique needs the addition of a given impurity to the melt. In fact pure PPLN cannot be obtained during growth [9]. This experimental result has generated some controversy in the origin of the compositional gradients leading to the built-in electric field necessary to form the periodic structure during growth. Naumova *et al* [10] have pointed out a Li/Nb constant ratio with a Nd gradient concentration in the PPLN structure, while Bermúdez *et al* [9] have shown a Li/Nb ratio gradient along the periodic domain structure with a constant dopant concentration for impurities such as Er, Yb, Y and Nd.

Due to the above discrepancies, Hafnium (Hf) ions have been selected in this work to study the compositional gradients along the PPLN structures. In our opinion, Hf ions fit due to their special characteristics related to their incorporation in the LN lattice as a function of the Li/Nb ratio [11]. In this way, combining ion beam and hyperfine interaction measurement in bulk congruent and stoichiometric Hf doped LN crystals, it has been demonstrated that in congruent LN crystals Hf ions fully replace Li positions, while in near stoichiometric LN crystals Hf ions replace both Li and Nb positions in a relative fraction which depends on the Hf amount in the melt [12]. In particular, for 0.2 mol% Hf in the melt 90% of the Hf ions are in Li sites and the rest in Nb sites, while for 1 mol% Hf in the melt only 40% of the Hf ions are in Li sites [12]. These properties offer us an important tool to improve the knowledge of the PPLN formation from the compositional point of view, using the modulation of the Li/Nb ratio in the PPLN structure previously published [9]. In summary the addition of Hf ions to a PPLN structure during growth could solve the previous mentioned discrepancies in the literature about the origin of the built-in internal electric field.

The objective of this work was to prepare Hf doped PPLN structures by the off-centred Cz technique with different Hf concentrations. The behaviour of the Hf composition and the changes in the Li/Nb ratio along the periodic domain structure will allow us to improve the knowledge of the origin of the PPLN formation during growth.

2. Experiment

Hafnium doped PPLN crystals were grown by the off-centred Cz growth technique [13] from a congruent LN melt containing a variable Hf concentration ranging from 0.1 mol% to 1 mol%, which was added to the melt as HfO_2. In the off-centred Cz technique the crystal grows 5 mm out of the symmetry axis of the temperature field, allowing for a radial thermal gradient during growth. The pulling and the rotation rate were 2 mm h^{-1} and 10 rpm respectively. Seeds are oriented along the x-direction. The growth process finishes by quenching the crystal to room temperature in order to freeze the periodic structure along the whole crystal volume [14]. After growth, samples were cut along the c-direction and optically polished. A chemical etching with HF:HNO$_3$ mixture at the boiling point allows us to reveal the periodic domain structure.

The periodic domain structures were observed with a scanning electronic microscope (SEM) and the variations in the Li/Nb ratio and Hf concentration have been studied by wavelength dispersion x-ray (WDX) analyses.
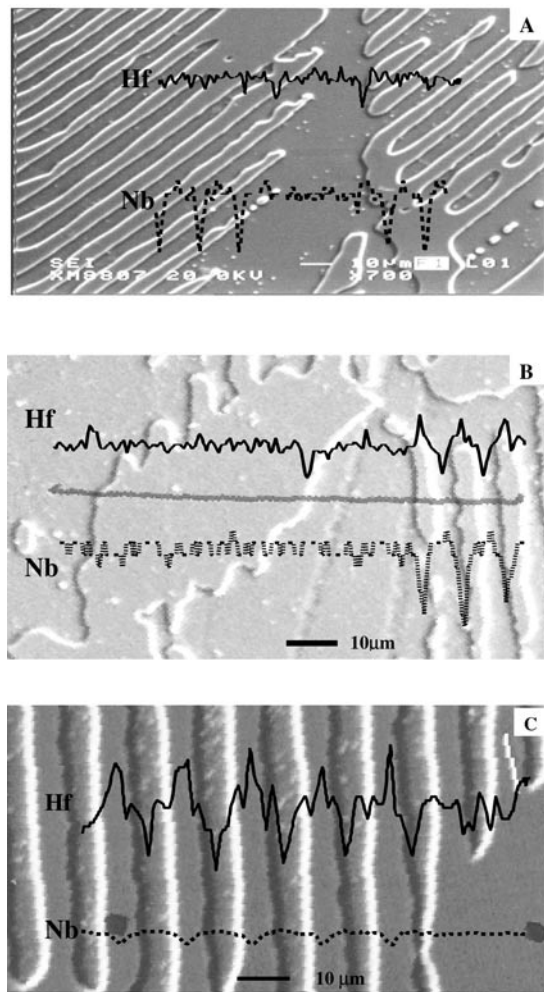
Figure 1. Modulation of the Nb and Hf concentration along the periodic domain structure for a strong convex (a), almost convex (b) and flat (c) solid–liquid interface (see text).

3. Results and discussion

The experimental results obtained during this work show that PPLN structures doped with Hf are strongly dependent on the Hf concentration in the melt, following the same behaviour as described for congruent bulk single domain LN crystals [11, 12]. For a Hf concentration in the melt lower than 0.25 mol%, the PPLN structures are totally inhomogeneous along the crystal radius and length, while the radial periodic domain structure follows the solid–liquid interface shape. For a 0.5 mol% Hf concentration, the periodic domain structure is continuous along the crystal radius as shown in the literature for other dopants [9, 10, 13, 14, 17]. For Hf concentrations higher than 0.5 mol% the domain structure is completely polydomain. These experimental results indicate that the formation of Hf doped PPLN structures is strongly dependent on the intrinsic and/or extrinsic defect density, as recently published for bulk LN domain structures [14–16].
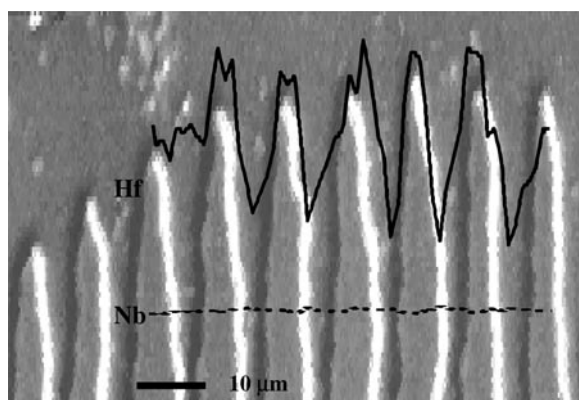
Figure 2. Hf and Nb concentration modulation along the PPLN structures finishing in a macrodomain.

Taking into account the results described above, PPLN structures doped with 0.5 mol% Hf have been analysed for different solid–liquid interface shapes. Figure 1 shows the variation of the Hf and Nb concentration for a strongly convex (a), almost convex (b) and completely flat (c) interface where the radius/height ratio of the interface is 150/3, 150/1 and 150/0.15 respectively. In the case of a strongly convex interface shape (radius/height ratio 150/3) as shown in figure 1(a), where the concentrations are normalized and in arbitrary units (au), it can observed that the fashioned structure is related to a periodic modulation in the Nb concentration while the Hf concentration is almost constant along the periodic structure. It is worth noting that the signal corresponding to the Nb concentration in the negative and positive domains in the periodic structure, lies respectively up and down the Nb concentration of the macroscopic non-periodic bulk domains. In the case of an almost convex interface shape (radius/height 150/1 ratio) shown in figure 1(b), it can be observed that there exists a periodic modulation in both Nb and Hf concentration along the periodic structure, while the Nb concentration in the bulk non-periodically poled areas is constant, independent of the positive and negative character of the macrodomains. It is important to note that the concentration modulation observed for both Nb and Hf ions cannot be attributed to the topographic relief observed in figure 1(b). The topographical height difference due to the different etch rate between both domains is around 1 μm, as measured by atomic force microscopy [17]. In the case of a completely flat interface (radius/height 150/0.15) which is shown in figure 1(c), both Hf and Nb concentrations vary periodically, although the Nb variation is rather small. The maximum and minimum of the Hf and Nb concentrations are opposite in phase, a fact previously published by Naumova *et al* [10] for PPLN structures co-doped with Nd and Mg.

Taking into account the key importance of the Li/Nb ratio in the formation of PPLN structures, and considering the results shown in figure 1(c), where a small variation in the Nb concentration is presented, a detailed study at the frontier of the PPLN structures with the macroscopic domains was carried out in order to understand the origin of the destruction of the PPLN structure in this region. Figure 2 shows the Hf and Nb concentration modulation along the edge of a PPLN structure ending in a macrodomain, where the signal is always normalized and in au. It can be observed that the measured Hf concentration modulation is higher than the one previously observed in figure 1 for the centre of a 0.5 mol% Hf doped structure. The strong modulation in the Hf concentration would be directly related to the charge gradient able

to avoid the PPLN formation during growth, probably due to the locally microscopic Hf excess leading to a polydomain structure as previously discussed in figure 1. The modulation in the Nb concentration is negligible and has practically disappeared.

Differences in the PPLN formation related with the Hf concentration can be directly associated with the difference in the Hf lattice site as a function of the Li/Nb ratio [11]. At this point, one must consider that previously published data show that (i) for a congruent LN crystal with low Hf concentration, the Hf ions are in Li sites, while for increasing dopant concentration and/or with a Li/Nb ratio approaching to the stoichiometric value, the Hf ion increases the occupancy at Nb positions sites [11, 12], and (ii) for crystals grown in an asymmetric temperature field a Li/Nb modulation has been observed along the periodic domain structure [9]. Thus taking into account these two facts the Hf lattice positions could differ from one domain to another along the PPLN structure. Consequently, in positive periodic domains, where the Li/Nb value measured by the SIMS technique is higher than one [9], Hf ions must be placed preferentially in the Nb sites. In negative domains, where the Li/Nb ratio is lower than one, Hf ions must occupy preferentially the Li position. Thus the behaviour in the PPLN formation with the Hf concentration seems to be directly related to the difference in the Hf lattice site as a function of the Li/Nb ratio [11]. The Hf occupancy of the positive and negative bulk macrodomains will be the same due to the fact that the Li/Nb ratio is constant in either positive or negative domains. More work is under way to study the effect of the Hf concentration modulation along the periodic structure in the optical properties of the PPLN crystals.

The appearance of a polydomain structure for Hf concentrations above 0.5 mol% in the melt seems to be related with the increase in the occupancy of the Nb lattice positions due to changes in the Li/Nb ratio, and thus with the built-in internal electric field created by the spatial charge gradient necessary to compensate the charge excess induced by the Hf ion in both Li and Nb positions. This internal field must be different at both positions due to the modification of the introduced defect density either $(Hf_{Li})^{2+}$ or $(Hf_{Nb})^{2-}$, and differences in the compensating mechanisms.

Another important feature is the one related with the modulation of the Hf concentration as a function of the solid–liquid interface. In the literature there are two proposals to understand the PPLN formation by inducing a compositional gradient during growth: (i) the first one assumes that the dopant concentration varies with the domain structure while the Nb concentration is constant [10] and (ii) the second one establishes that the dopant concentration keeps constant while the Li/Nb ratio is modulated along the periodical domain structures [11]. To understand these differences it has been pointed out that the appearance of either a dopant or a Li/Nb modulation would be governed by (i) the solid–liquid interface, (ii) the value of the segregation coefficient of the impurity and (iii) the cooling process after growth [14]. Results obtained by Hf doping in this work point out that the modulation in the Li/Nb ratio along the periodic structures is the most acceptable explanation, but further studies with microRBS techniques should be carried out to determine the Hf lattice position in both positive and negative domains of the periodic structure.

4. Conclusions

The role of the Hf ion in the PPLN formation by the off-centred Cz technique is completely different from that previously studied for rare-earth ions [9]. The incorporation of the Hf ions in the Li or Nb site as a function of the value in the Li/Nb ratio controls the formation of the PPLN structures by controlling the dopant amount in Li or Nb positions.

Acknowledgments

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