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EFFECT OF TEMPERATURE ANNEALING ON PERIODICALLY POLED RARE-EARTH DOPED LITHIUM NIOBATE CRYSTAL

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Rare earth doped Periodic Poled Lithium Niobate crystals prepared by the off-centered Czochralski growth technique have been submitted to several annealing proceses either at $T>T_c$ as $T<T_c$. It is shown that an annealing process at $T>T_c$ eliminates the periodic domain structure in the surface but not in the bulk crystal, where the periodic structure is not damaged for a low cooling rate, while it is strongly damaged for a quenching process. When the annealing process is performed at temperatures very close to the Curie temperature but below, the periodic domain structures do not disappear even from the surface, but they are strongly damaged when temperature is cooled down following a quenching procedure. When temperature is reduced following a low cooling rate process the surface domain structure is not affected.

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1. Introduction

Periodically Poled Lithium Niobate (PPLN), which provides large second-order nonlinearity and high transparency, has led to the development of optical devices that are based on high-yields frequency mixing. Typical examples are blue light sources using second-harmonic-generation and communication-band-wavelength converters using difference-frequency-generation. Devices integrating non-linear optical elements for Quasi Phase Matched (QPM) frequency conversion will provide more varieties in waveguide devices. A key issue for implementation of such devices is to improve the fabrication method of ferroelectric domain inverted gratings in rare earth doped LN. In particular, Wëbjorn et al [1] show that thermal diffusion treatments at high temperature for rare-earth doped $LiNbO_3$ (LN) create a domain-inverted layer on the initial +z face and this layer prevented fabrication of the domain-inverted grating. Suppression of the formation or removal of this layer is required for grating fabrication. Recently it has been demonstrated [2] an Er-diffused LN self-frequency-doubling waveguide laser with a grating of 17 μm fabricated after domain-inverted layer by polishing. A grating with period of about 7 μm, required for Nd: LN self-frequency doubling waveguide lasers has also been demonstrated [3]. Problem is that all these fabrication processes are quite complicated and time consuming.

Bulk Periodic Poled LN (PPLN) structures are very important due to the fact that they allow for introduction of optically active ions in the LN matrix, and thus to the combination of the laser properties of these ions with the excellent nonlinear optical properties of LN. In this way using bulk PPLN substrates will allow us to prepare waveguide devices with several rare-earth ions in the LN matrix and to have accessibility to the desired self-frequency-converted waveguide laser by selecting the appropriate ion and period. The only problem arrives from thermal processes needed for most of the waveguide fabrication techniques. Annealed Proton Exchange waveguides require low process temperatures but they have the intrinsic drawback that supports only extraordinary guided modes,

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posing thus limitations in implementation of polarization-independent nonlinear optical wavelength converters and integration of several devices. Other techniques such as Ti-in diffusion [4-6], available commercially from long time to prepare waveguide devices, allow to obtain samples guiding the light through the periodic structure, allowing blue and green light through QPM-Second Harmonic Generation in PPLN. These techniques involve high temperature process, between 700 ºC- 900 ºC. But they have a problem, the so-called optical damage, especially at short wavelengths [7], which makes these techniques not the most recommendable into the field of nonlinear optics applications or optical communications. Destruction of the PPLN structures is related with the required high temperature thermal processes. In particular it has been shown that an annealing process at temperatures close Tc, for a monodomain crystal, will destroy the monodomain nature of the crystal converting it in a polydomain structure if no external force is applied to keep the monodomain structure (for instance an external electric field).

In this work, and based on the necessary application of temperature processes during waveguide fabrication, we have studied the effect of the annealing processes in air atmosphere for rare-earth bulk doped PPLN structures at temperatures below and above T_c. Selected dopants were Er, Yb, and Nd due to their very interesting laser properties when introduced in a LN matrix and the potential use of these properties for their application in waveguide devices.

2. Experimental

PPLN structures were fabricated using the off-centered Czochralski crystal growth technique by inducing fluctuations in the growth temperature when growing out of the symmetry axis of the temperature field. Details of the growth process are given in ref [8]. Er, Yb and Nd were used as dopants with a concentration 0.5 mol% added to the melt in the form of oxides. Seeds were oriented along the x- direction. Pulling and rotation rates were 2mm/h and 10rpm, respectively, and thus the ferroelectric domain structure has a period of 6.7μm. Crystals were cooled to RT following a quenching procedure. Samples were cut along y- and z- axis, polished and etched in a $HF:HNO_3$ mixture at RT to reveal the ferroelectric domain structure. After that, samples were re-polished and submitted to four annealing processes.

1. Annealing at 1130 ºC during 24 h with a cooling rate of 20 ºC/h.
2. Annealing at 1130 ºC during 24 h where a quenching procedure was used to cool the crystal to RT.
3. Annealing at 1170 ºC during 24 h followed by a cooling rate of 20 ºC/h.
4. Annealing process was at 1170 ºC during 24h followed of a quenching procedure.

For the annealing processes the PPLN samples were hold by a Pt grating contained in a Pt crucible of 5 cm in diameter and 4 cm in length. System is closed with a Pt sheet to homogenize Li atmosphere during the procedure.

After annealing, samples were etched and observed with a Scanning Electron Microscope (SEM) and the variations in the Li/Nb ratio and dopant concentration were studied by Wavelength Dispersion X-ray (WDX) analyses. In this way the periodical domain structure is characterized either compositionally or structurally.

3. Results and discussion

The results described below have been divided in two groups as a function of the value of the annealing temperature:

A.- For annealing temperatures T higher than T_c (annealing processes 3 and 4). In theses cases the crystal face facing to the bottom of the crucible is strongly damaged. The upper face is highly brilliant independently of the cooling rate used after the annealing process. We can observe a large amount of Pt inclusions with the typical hexagonal forms even if samples were not in contact with the Pt crucible or sheets.

Taking into account the strong relevance of the cooling rate after off-centered Cz crystal growth [9], the effect of the cooling rate after the annealing processes has been analyzed. In particular it has been observed that the PPLN structure in the surface of the samples is destroyed appearing a completely rough surface after annealing processes for both quenching rates. However the PPLN structure in the bulk crystals is not destroyed and it is enough to remove about one micron to observe the PPLN structures. Figure 1 shows the PPLN of the bulk crystal after removing about 1 micron of the surface for an annealing process at T>Tc followed by a slow cooling rate (a) and a quenching process (b). It can be observed that the periodic domain structure is maintained in both cases after the annealing process even if we have used temperatures which are higher than the Curie temperature, and thus the PPLN structures were in the paraelectric phase during 24h. This fact is quite important because even if the PPLN structures go through the phase transition, the ferroelectric domain structure obtained during off-centered Cz growth technique remains unaltered. The main reason to which we attribute this behavior will be given later.

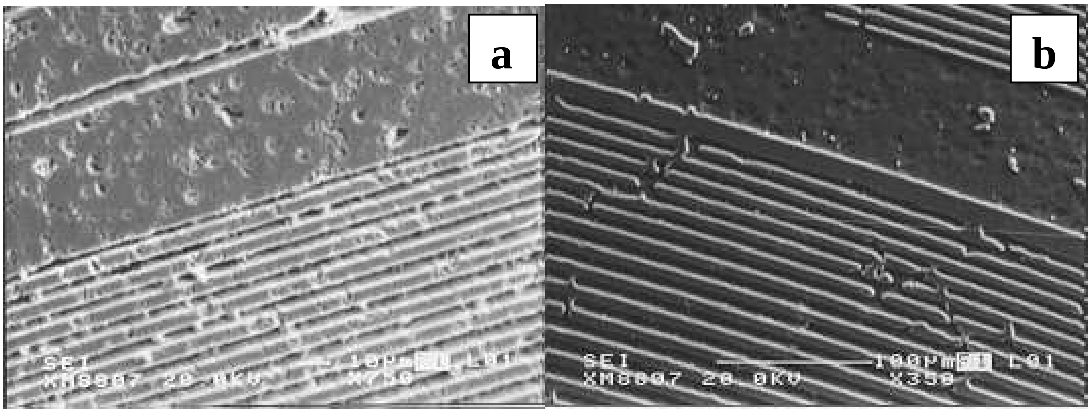

Fig. 1. Periodic structure of the tailored LN domain samples after removing about 1μm of the surface after an annealing process at $T>T_c$ followed by a slow cooling rate (a) and a quenching process (b).

B.- For annealing temperatures below the Curie temperature ($T<T_c$), which correspond to annealing processes 1 and 2, the crystal face facing to the bottom of the crucible is also damaged. The upper face appears very rough when a quenching process is used to cool the crystals, but the domain structure does not disappear at all even at the surface of the sample. Fig. 2 shows the surface of a Yb:PPLN sample after an annealing process at $T<T_c$ followed by a quenching to RT where it can be observed that the periodic domain structure is damaged but not destroyed. This effect takes place in Nd:PPLN samples where the surface domain structure does not disappear although is strongly damaged.

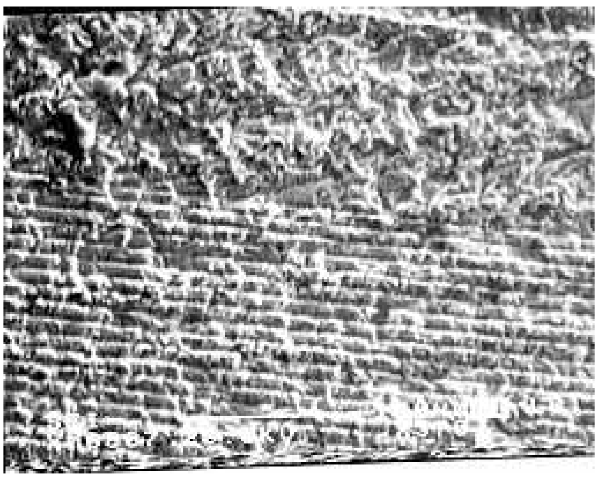

Fig. 2. Surface of a Yb:PPLN sample after an annealing process at $T<T_c$ followed by a quenching process.

It is very worth to note that rare earth doped singledomain samples were submitted to the same annealing-quenching processes and that the ferroelectric domain structure of these crystals turned to a polydomain structure typical of as-grown Cz LN crystals [10]. This fact seems to indicate that PPLN structures obtained during off-centered Cz growth is more stable than the single-domain one.

To study the stability of the PPLN structures obtained during an off-centered Cz growth technique do not disappear an external electric field of 1.5 V/cm was applied during both annealing processes. The procedure to bulk electric field repolarization has been described in ref. [11]. It has been observed that the domain structure is not re-polarized even after 12 h of applied electric field at high temperature (temperatures close and above the transition temperature).

This fact seems clearly related with the formation of a Li/Nb gradient along the PPLN structures measured in off-centered Cz PPLN crystals. As it has been previously published the origin of these ferroelectric structures lays in the formation of a Li gradient along the ferroelectric domains caused by thermal gradients during the off centered growth [12] due to temperature fluctuations leading to rotational striations. Thus, it is clear that it is not possible to change Li composition along the ferroelectric domains, neither with the application of an electric field at high temperature nor with an annealing process. This fact indicates that off-centered growth structures are more stable than those prepared by other techniques due to the origin of the structure does not lye in a electrical space charge field but in a compositional one. Thus, the only possible change in the Li/Nb ratio occurs due to Li diffusion in the first layer of the sample.

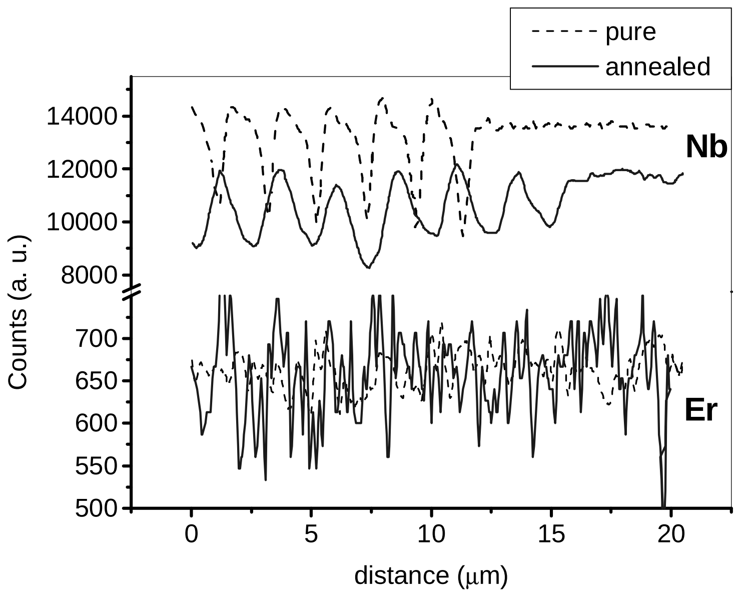

Fig. 3. WDX profiles measured along an Er:PPLN sample before (a) and after (b) an annealing process.

In this way the Li/Nb ratio has been characterized through the variation of the Nb composition along the PPLN structure. Fig. 3 shows the typical WDX profiles measured along an Er:PPLN sample before and after an annealing process. It can be observed that in both cases Nb composition varies along the periodic structure, while the Er dopant concentration is constant within experimental error. The maximum Nb level concentration corresponds with negative domains [12] and thus with Nb_{Li} sites in the vacancy model defects [13]. Positive domains can be considered as Nb poor regions. It is important to note that amplitude of the Nb modulation decreases after the annealing process. Decreasing in the amplitude modulation can be regarded as a migration of the Nb ions to the surface of the sample, during the Li out-diffusion process taking place when the annealing takes place in air atmosphere, occupying thus the created Li vacancies. Due to this migration process the total Nb concentration in the surface is lower in annealed crystals than in virgin ones.

4. Conclusions

The effect of the annealing process for rare-earth doped PPLN structures, during waveguide fabrication has been studied.

The PPLN structures obtained during off-centred Czochralski growth are more stable than the single domain ones.

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