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Structural and optical characterization of Er^{3+}/Yb^{3+}-doped $LiNbO_3$

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ABSTRACT We report the dependence of the unit-cell parameters and the extraordinary and ordinary refractive indices of Er^{3+}/Yb^{3+}-codoped $LiNbO_3$ crystals. Both properties depend in a non-monotonic manner on the Er^{3+}/Yb^{3+} content. A singularity was observed at concentrations of $1.1-1.2$ mol. % in the crystal ($0.6-0.7$ mol. % in the melt). In the same way the Er and Yb concentration influences the periodically poled lithium niobate formation. The observed behavior of refractive indices and unit-cell parameters of Er^{3+}/Yb^{3+}-codoped $LiNbO_3$ crystals could be explained in terms of the RE^{3+}-ion concentration affecting the Li-vacancy concentration and the RE^{3+}-ion positions in the crystal.

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1 Introduction

Lithium niobate combines excellent non-linear, electro-optic and acousto-optic properties with the possibility of rare-earth doping, which has stimulated the interest in this material for photonic applications. When doped with rare-earth ions, the $LiNbO_3$ crystals become luminescent media able to generate and amplify light. This ability, combined with inherent non-linear properties, offers a possibility to design self-Q-switching and self-frequency-doubling laser sources. The progress in the techniques for waveguide fabrication in $LiNbO_3$ have shown the possibility of integrated lasers for lithium niobate doped with rare-earth ions, and a variety of active integrated devices have been demonstrated in recent years. In this way, Er^{3+} and Yb^{3+} are optical ions where a considerable number of useful optical processes take place. Besides the most useful optical properties of the Er ion to produce optical gain and laser oscillation for wavelengths around the 1.55-μm region optical gain and up-conversion lasers in several bands have been demonstrated [1–3]. The bulk-doped crystals appeared interesting for the design of high-gain-switched lasers, as long are they are available up to an Er concentration of 2%, more than five times the mean value for indiffused samples; prerequisite to this goal is fine-gain modeling. This leads to an extensive number of potential applications in different fields, particularly in optical communications and eye-safe laser range finding. In addition, Er^{3+} has absorption bands suitable for laser diode pumping [4]. For instance, efficient diode-pumped all-solid-state lasers and amplifiers at 1.52 μm have been shown already in Er^{3+}-doped bulk $LiNbO_3$ [5]. The incorporation of optical ions in periodically poled lithium niobate (PPLN) structures opens up the additional advantage of the optical processes occurring in the ion. On the other hand, efficient laser action based on Yb^{3+}-active ions has been demonstrated in a variety of crystals [6], with attractive features like high slope efficiency, low thermal loading in resonant pumping, lack of excited-state absorption of laser or pump radiation, etc. Due to the fact that Yb^{3+} has only two states within its $4f$ shell ($^2F_{7/2}$ and $^2F_{5/2}$), it lacks absorption bands in a wide range of wavelengths longer than 1100 nm, which implies an interesting optical window. Furthermore, the emission of the Yb^{3+} ion in $LiNbO_3$ around 1059 nm is strongly π polarized, as required for first-order quasi-phase matching (QPM) in PPLN structures. All these circumstances make Yb^{3+} : PPLN specially attractive for self-pumped intracavity non-linear devices, which bound to result in very efficient low-power devices. Also, the efficiency of Er^{3+}-based devices has been improved in fiber optics and other hosts by codoping with Yb^{3+} ions, which act as sensitizers of the Er^{3+} luminescence. The sensitization operates in such a way that after absorption of the pump light by Yb^{3+} it is efficiently transferred to Er^{3+}, from where it is emitted. The sensitization offers several advantages, which include a stronger absorption cross section in the near-infrared region as well as a broader absorption band (850–1050 nm) providing a wider range of pump wavelengths to be chosen [7]. Therefore Er^{3+}/Yb^{3+} codoping has become an effective method for producing efficient lasers and amplifiers in compact geometry such as fiber or waveguide configurations. Moreover, recently bulk periodically poled lithium niobate crystals doped with Er and Yb have been prepared [8] and second-harmonic generation has been successfully demonstrated by the QPM technique in both Er^{3+} and Yb^{3+} bulk-doped PPLN crystals [9]. Although Er^{3+}/Yb^{3+}-codoped $LiNbO_3$ appears as an obvious candidate in order to tailor the material properties, the details of the Yb^{3+} sensitization cannot be advanced

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a priori because of the complexity of the mechanisms involved, and therefore a systematic experimental characterization is needed. The study of the growth process, optical absorption measurements and spectroscopic analysis of bulk $LiNbO_3 : Er^{3+}/Yb^{3+}$ crystals and waveguides formed by Zn indiffusion were recently presented [10–12]. As a next step in such a systematic study, the aim of the present work was to study the influence of Er^{3+}/Yb^{3+} doping on refractive indices and to correlate these optical data with structural ones such as the unit-cell parameters (a, c and the unit-cell volume V).

2 Experimental

Single crystals of $LiNbO_3 : Er^{3+}/Yb^{3+}$ with different impurity concentrations have been grown by the Czochralski method, in air atmosphere, with automatic diameter control by a crucible-weighing system [10]. The starting materials were congruent $LiNbO_3$ ([Li]/[Nb] = 0.945) and erbium and ytterbium oxides with a purity grade of 99.99%. The initial melts had the same erbium concentration in all cases, 0.5 mol. %, and different ytterbium concentrations 0, 0.1, 0.2, 0.4, 0.5, 1.0, 1.5 and 2.0 mol. %.

The pulling and rotation rates were 0.6 mm/h and 10 rpm, respectively. The growing processes were stopped when 25% of the melt was crystallized, in order to prevent possible variations in the [Li]/[Nb] crystal relation, which would generate changes in the properties of the crystal. The crystals were cooled to room temperature with a rate of 25 °C/h.

The widespread etching procedure in $HF : HNO_3$ (10 min at 110 °C in 1 : 2 by vol.) was followed to reveal the periodic structure. A scanning electron microscope (SEM) was used to check the period and homogeneity of the domain structure.

The refractive indices at 633 nm were calculated by measuring the angle for total reflection in the crystals for light coupled through a high-index prism. For that purpose, an isosceles rutile prism is pressed against the polished phase of an oriented (Z-cut) lithium niobate crystal. The whole assembly is mounted in a rotatory stage driven by a stepping motor, with an angular resolution of 0.001°, which allows a precision of 1×10^{-5} in the refractive-index measurements. The outcoming beam is folded by a mirror attached to the rotary stage and the light intensity measured by a silicon detector. The stepping motor is controlled by a computer and the light intensity is synchronously recorded.

The structural data were obtained as follows. We determined the parameters of the rhombohedral H unit cell by the powder method. The measurements on powders were performed using Cu K_α radiation for angles θ from 54.0 to 78.0. The program DICVOL [13] was used for calculation of lattice parameters using 20 Bragg reflections. For each composition measurements of powders are repeated several times with samples prepared from different parts of the crystal boules. The reproducibility of these data was very high.

3 Results and discussion

The concentration of ytterbium ions in the crystal can be related to the melt concentration with the expression: $[Yb^{3+}{}_{crystal}] \approx K_{eff}[Yb^{3+}{}_{melt}]$, where K_{eff} represents the effective segregation coefficient of these ions in the $LiNbO_3$ crystal and, in this concentration range, it has a value close to 1.5 [12]. The same numerical value for the effective segregation coefficient has been previously found for Er ions ($[Er^{3+}{}_{crystal}]/[Er^{3+}{}_{melt}]$) ≈ 1.5 [12]. This fact indicates that the incorporation of the rare-earth ions into the crystals is well described considering both dopants (erbium and ytterbium) as a single species, with the global melt concentration ($RE^{3+} = Er^{3+} + Yb^{3+}$) governing the effective segregation coefficient [10]. The codoped crystals behave similarly to crystals singly doped with Er^{3+} grown under the same conditions. Rutherford back-scattering/channeling measurements [14] indicate that both rare-earth ions, Er^{3+} and Yb^{3+}, enter into the lithium niobate lattice at the lithium octahedron, located in positions slightly shifted from the Li positions. In the case of these two particular ions the displacement is also very similar (around 0.25 Å).

Following this reasoning, Fig. 1 shows the ordinary and extraordinary indices (a) as well as the values of the a and c crystal lattice parameters (b) as a function of the total rare-earth concentration. Errors in the measurements were estimated at around 0.0002 for refractive indices, and 0.0002 Å for a and $0.0009 - 0.0014$ for c lattice parameters. A singularity at concentrations of $1.1 - 1.2$ mol. % in the crystal ($0.6 - 0.7$ mol. % in the melt) can be observed. Extrema observed in the concentration dependence of the refractive indices at about $1.1 - 1.2$ mol. % (Fig. 1a) correlate with an unusual concentration dependence of the unit-cell parameters a and c (Fig. 1b).

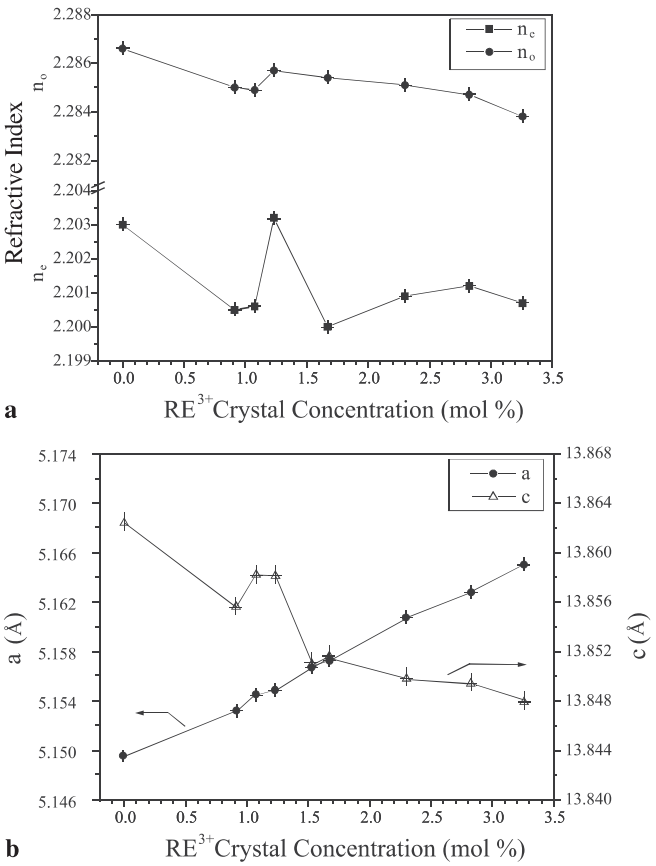

FIGURE 1 Refractive indices (**a**) and lattice parameters (**b**) versus RE^{3+} concentration in the crystals Er^{3+}/Yb^{3+} $LiNbO_3$

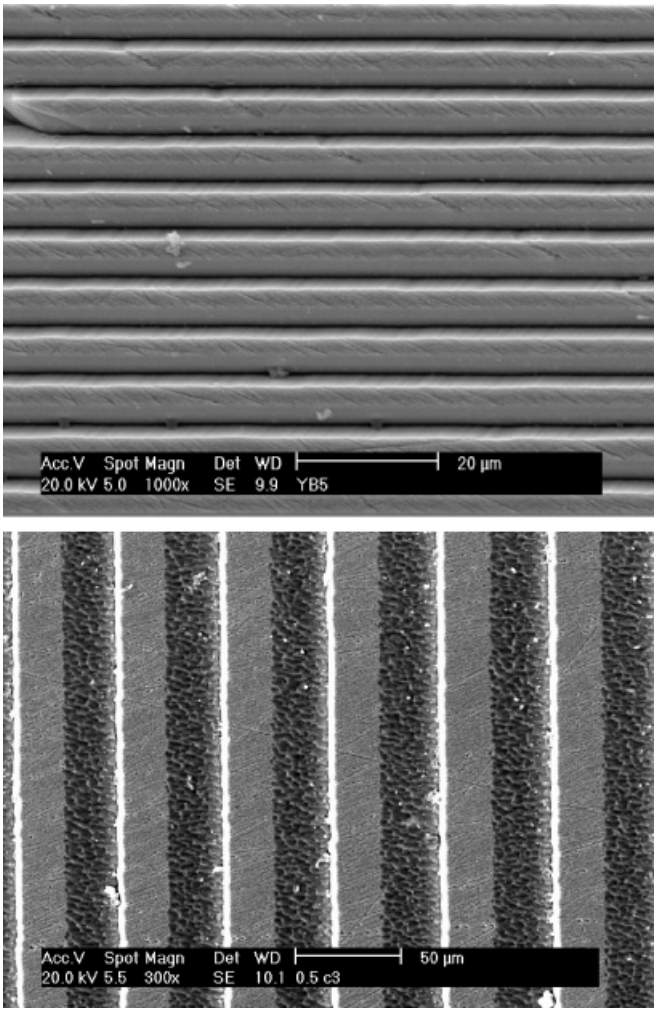

FIGURE 2 SEM micrograph revealing the periodic domain structure for $LiNbO_3$ crystals doped with 0.5% Er, 0.1% Yb (**a**) and 0.5% Er, 0.7% Yb (**b**)

Moreover, the Er and Yb concentration influences in the same way the PPLN formation (Fig. 2). The best PPLN structures, with the highest dopant concentration, have been formed with 0.5 mol. % in both Er and Yb cases as well, as was earlier reported [8]. Below 0.5 mol. % the periodic domain structure was regular (Fig. 2a). When the dopant concentration was higher than 1 mol. % the domain structure becomes disordered and non-periodic.

Similar non-monotonic dependence of the unit-cell parameters and the electro-optical coefficients on Zn doping in optical-damage-resistant $LiNbO_3$: Zn crystals was recently reported [15]. This was accounted for by different types of Zn-ion incorporation into the lattice depending on the Zn concentration in the melt. The low-concentration anomalies were accounted for by a decrease of the Li-vacancy concentration due to the Zn incorporation into Li sites. Anomalies at high concentrations were due to a partial incorporation of Zn ions into Nb sites. Interpreting the dependence of the lattice parameters on c_{Zn} within the model of the intrinsic $LiNbO_3$ defect structure allowed one to give a qualitative explanation of the observed behavior of the electro-optic coefficients. It seems similar reasons could explain the observed behavior of refractive indices and unit-cell parameters of Er^{3+}/Yb^{3+}-codoped $LiNbO_3$ crystals in terms of RE^{3+}-ion concentration affecting the Li-vacancy concentration and the RE^{3+}-ion positions in the crystal.

4 Conclusion

In this work we presented the characterization of the structural properties of $LiNbO_3$ single crystals codoped with Er^{3+} and Yb^{3+}, together with the characterization of the basic optical features of these crystals. Both properties depend in a non-monotonic manner on the Er^{3+}/Yb^{3+} content. A singularity was observed at concentrations of $1.1-1.2$ mol. % in the crystal ($0.6-0.7$ mol. % in the melt). In the same way the Er and Yb concentration influences the PPLN formation. The observed behavior of refractive indices and unit-cell parameters of Er^{3+}/Yb^{3+}-codoped $LiNbO_3$ crystals could be explained in terms of the RE^{3+}-ion concentration affecting the Li-vacancy concentration and the RE^{3+}-ion positions in the crystal.

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