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Spectroscopic properties of near-stoichiometric In:Er:$LiNbO_3$ crystals

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ABSTRACT

The congruent and near-stoichiometric In(2 mol%):Er(1 mol%):$LiNbO_3$ crystals have been grown by the Czochralski method from melts having compositions of 48.6 and 58 mol% Li_2O, respectively. The OH^- absorption spectra were characterized to investigate the structure defects of the crystals. The appearance of the 3508 cm^{-1} absorption peak manifests that the threshold concentration of In^{3+} is below or near 2 mol% in In:Er:$LiNbO_3$ crystal with melt [Li]/[Nb] ratio of 1.38. The [Li]/[Nb] ratios in the crystals are estimated from the shift of ultraviolet absorption edge. In addition, the influence of [Li]/[Nb] ratio on the Judd–Ofelt intensity parameter Ω_λ is analyzed using the Judd–Ofelt theory. The upconversion fluorescence spectra excited by an 800 nm femtosecond laser were measured at room temperature. The results show that three emission peaks centered at 535, 551 and 673 nm exist in both crystals but an additional 400 nm peak appears in the In:Er:$LiNbO_3$ crystal with [Li]/[Nb] ratio of 1.38 in melt. The 400 nm emission peak is verified experimentally to be the second harmonic generation (SHG) of 800 nm light.

1. Introduction

The combination of the excellent electro-optic and nonlinear optical properties of lithium niobate ($LiNbO_3$, LN) together with the possibility of rare-earth (RE) doping has stimulated the interest in this material for integrated photonic applications [1]. Among RE ions, trivalent erbium has been considered as a suitable ion for both visible and infrared emissions due to its unique energy level structure. Excellent luminescence properties have been found in the Er^{3+} doped LN systems [2–4]. Though Er:LN crystal is beneficial for upconversion waveguide lasers and white light luminescence for its intense green and red emissions in visible wavelength region, its applications are severely limited by the optical damage that induces change in birefringence at high laser intensities [5].

Some photo-damage-resistant dopants have been discovered, such as divalent (Mg^{2+} [6], Zn^{2+} [7]), trivalent (Sc^{3+} [8], In^{3+} [9]) and tetravalent (Hf^{4+} [10], Zr^{4+} [11]) ions, which can lead to a strong decrease in the optical damage to $LiNbO_3$. Among all these dopants, In^{3+} ion has a low photo-damage-resistant threshold concentration which is 3 mol% and has a good photo-damage-resistance property [12]. But there is less research in In-doped Er:LN crystal compared to other dopants. Zhen et al. [12] reported the defect structures and the ability of photorefractive damage resistance of congruent In:Er:LN crystals with different In-doped concentration. Sun et al. [13] measured the 1.5 μm emission and green UC emission properties of Er(1 mol%) doped and In(3 mol%)/Er(1 mol%)-codoped congruent LN crystals. Zhang et al. [14] analyzed the In and Er concentrations in congruent In:Er:LN crystals using neutron activation analysis and measured some spectroscopic properties of them. All these three researches improve the properties of Er:LN crystals by changing the In_2O_3 doping concentration. As we know, the increase of [Li]/[Nb] ratio in LN crystal can also improve optical damage resistance at lower dopant's concentration, such as 0.78 mol% MgO doping in near-stoichiometric LN (SLN) crystal which is grown from a melt of [Li]/[Nb]=1.38, has no measurable photorefractive damage at 532 nm up to the input intensity of 2 MW/cm^2 [15]. Moreover, many optical properties of LN are sensitive to the [Li]/[Nb] ratio in the crystal. With the increase of [Li]/[Nb] ratio in the LN crystal, many properties of the crystal change distinctly [16].

In this paper, the In:Er:SLN crystal is grown from a Li-rich melt by the Czochralski method. The unpolarized ultraviolet (UV)–visible (vis) absorption spectra, the near-infrared (NIR) absorption spectra and the infrared (IR) transmission spectra are investigated and compared with congruent In:Er:LN crystal. The spectroscopic properties of the samples are studied based on the Judd–Ofelt (J–O) theory [17,18]. The upconversion (UC) luminescence properties under 800 nm femtosecond laser excitation is discussed in this work.

2. Experimental

2.1. Crystal growth

LN crystals used in our experiments were grown in a diameter-controlled Czochralski apparatus using a SiC heater at atmosphere

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Table 1
Composition of the raw materials and growth parameters of IELN and IESLN crystals.

Crystal	[Li/Nb] (molar ratio)	[Er_2O_3] in melt (mol%)	[In_2O_3] in melt (mol%)	Temperature gradient (°C cm^{-1})	Rotating rate (rpm)	Pulling rate (mm h^{-1})	Dimension (mm)
IELN	0.946	0.5	1	30–40	30–35	2.0	$\Phi 35 \times 40$
IESLN	1.38	0.5	1	15–20	10–20	0.5	$\Phi 30 \times 35$

and doped with 2 mol% In and 1 mol% Er. The ratios of [Li]/[Nb] ratios in melts are 0.94 and 1.38. These two samples were denoted as IELN and IESLN. The raw materials used for the crystal growth were Li_2CO_3 (4 N purity), Nb_2O_5 (4 N purity), In_2O_3 (spectral purity), and Er_2O_3 (spectral purity). To prepare the doped LN polycrystalline materials, the thoroughly mixed raw materials were put into a platinum (Pt) crucible, and calcined at 700 °C and 1150 °C for 2 h. Due to the existence of segregation effects, temperature gradients at the solid–liquid boundary and thermal stresses in the body of crystals during the growth process, different crystal samples corresponded to different growth conditions. The raw material compositions and the optimum growth conditions for different samples are shown in Table 1.

After growth, the crystals were cooled to room temperature at a rate of 60 °C/h. All crystals exhibited good morphology and optical quality. Through measurements of the pyroelectric effect, a single-domain structure was found in IESLN crystals obtained from the melt with the [Li]/[Nb] ratio of 1.38, while multi-domain structures were revealed in IELN crystals. The crystals with multi-domain structures required a poling treatment prior to optical measurement and were placed in a furnace where the temperature gradient was below 5 °C/cm for polarization. After being held at a temperature of 1200 °C for 8 h, the crystals were polarized with a current density of 5 mA/cm^2. During the cool down process, the temperature was decreased rapidly from 1000 to 800 °C to avoid the "dissolve-off". All the grown crystals were y-cut into 8 mm(X) × 2.4 mm(Y) × 10 mm(Z) slices from the middle parts of the crystals. At last, the (0 1 0) faces were ground and then polished to optical grade.

2.2. Measurements

The OH^- IR transmittance spectra of the samples were measured at room temperature using a Nicolet Avatar-360 FT-IR spectrometer in the energy range from 3400 to 3550 cm^{-1}. The UV–vis absorption spectra of the crystals were tested at room temperature by an Avantes AvaSpec-2048 Fiber Optic Spectrometer in the wavelength range of 200–1100 nm. The near-infrared spectroscopy was performed at room temperature (25 °C) using a Bruker MPA FT-NIR system with the OPUS software. UC fluorescence spectra were measured using an 800 nm Ti:sapphire mode-locked femtosecond laser, with 76 MHz repetition rate and 200 fs pulse duration, as an excitation source. The beam passed through a convex lens, and then was focused on the crystal. The sample was excited at a very edge position and side fluorescence was collected from the same edge in a direction normal to the excitation beam by a Fiber Optic Spectrometer (AvaSpec-2048).

3. Results and discussion

3.1. Infrared transmission spectra and OH^- absorption peak shift

Because OH^- stretching vibration is sensitive to the change of the environment around the ion, the OH^- can be used as a probe for the locations of impurities in the crystal lattice [19]. The IR transmittance spectra of the OH^- stretching mode at room temperature for the two crystals with the same thicknesses are shown in Fig. 1.

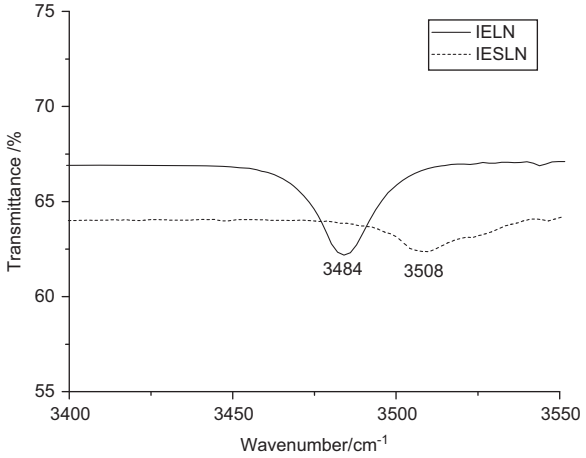

Fig. 1. IR transmittance spectra of IELN and IESLN.

As can be seen from Fig. 1, IELN presents a broad non-symmetrical absorption band at approximately 3484 cm^{-1}, while the OH^- absorption peak of IESLN shifts to 3508 cm^{-1}.

The mechanism of the absorption-peak shift is described as follows: in the pure congruent LN crystal, the ratio of [Li]/[Nb] is 0.946. The number of Li^+ is less than that of Nb^{5+}. Some of the Nb^{5+} occupy the Li sites, so the anti-site Nb (Nb_{Li}^{4+}) and Li vacancy appear. H^+ ions are easily attracted by Li vacancies due to their effective negative charge and forms $(V_{Li})^-$–OH^- complexes, whose absorption peak is at 3482 cm^{-1} [12]. In the In:Er:LN crystal, In^{3+} and Er^{3+} replace Nb_{Li}^{4+} and Li^+, respectively, to form In_{Li}^{2+} and Er_{Li}^{2+} when the concentration of In^{3+} is lower than its threshold value. H^+ stays far away from In_{Li}^{2+} and Er_{Li}^{2+} because they repulse each other. So the OH^- absorption peaks of the In:Er:LN crystal do not show an obvious change compared with that of the pure LN crystal. However, in the IESLN crystal, as the [Li]/[Nb] ratios increase, the concentration of Li^+ ions increase, and Nb_{Li}^{+4} ions significantly reduce. Li^+ ions repel all the Nb_{Li}^{4+} back to Nb sites. They also repel In_{Li}^{2+} to Nb sites which form In_{Nb}^{2-}. The negatively charged In_{Nb}^{2-} attract H^+ and form In_{Nb}^{2-}–OH^- complexes, so more energy is required for O–H vibration, which results in the blue-shift of absorption peak to 3508 cm^{-1}. The appearance of the 3508 cm^{-1} absorption band indicates that the 1 mol% In_2O_3-doped in Er:SLN crystal is just near or above the threshold concentration [12]. It is worth noting that the In_2O_3 doping threshold concentration of IESLN crystal is less than that of IELN which is 1.5 mol% [14]. This conclusion is the same as reported in Ref. [20] that the In_2O_3 doping threshold concentration decreases as the ratio of [Li]/[Nb] increases.

3.2. Optical absorption characteristics and J–O analysis

Fig. 2 shows the unpolarized UV–vis–NIR absorption spectra of the samples. From Fig. 2, we know that the two samples exhibit