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The effect of In^{3+} doping on the optical characteristics of Ho:$LiNbO_3$ crystals ☆

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HIGHLIGHTS

- In:Ho:$LiNbO_3$ crystals were grown at different In_2O_3 doping concentrations.
- The blue, green, violet and red upconversion emission can be obtained from In:Ho:LiNbO3 crystals.
- Light-induced scattering of In(5 mol%):Ho:$LiNbO_3$ can be improved considerably.

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ABSTRACT

A series of Ho:$LiNbO_3$ crystals doped with x mol% In^{3+} ions (x = 0, 1, 3 and 5 mol%) were grown by the conventional Czochralski technique. Up-conversion emission spectra was observed under 808 nm femtosecond laser excitation in the In^{3+} doped Ho:$LiNbO_3$ crystals at room temperature. The experimental results indicate that blue, green, violet and red up-conversion emission can be obtained from In^{3+} doped Ho:$LiNbO_3$ crystals. From the pump energy dependence investigation, it is known that the up-conversion mechanism is the two-photon process. The light-induced scattering was investigated as a function of exposure energy. The effect of In^{3+} on the optical characteristics of Ho^{3+} in $LiNbO_3$ crystal was investigated and concluded, and is reported here. The surface the as-prepared In^{3+} doped Ho:$LiNbO_3$ is very smooth and practically free of droplets as highlighted by atomic force microscopy (AFM). The root-mean-square (rms) surface roughness of the sample was determined to be 11.573 nm.

1. Introduction

Rare earth ion doped lithium niobate (RE^{3+}:$LiNbO_3$) is one of the most relevant systems in the integrated optics since it combines the fantastic spectroscopic properties of RE^{3+} and the outstanding nonlinear, acousto-optical and electro-optical properties of the $LiNbO_3$ host material [1]. In the RE^{3+} ions, Ho^{3+} is one of the most important active ions, which could be fired by visible light and infrared lasers. The optical characteristics of Ho:$LiNbO_3$ crystal depend, to some extent, on the concentration of the intrinsic defects (Nb occupied Li sites and Li vacancies). The photorefractive damage effect, which limits the performance of Ho:$LiNbO_3$ crystal, can be suppressed by co-doping with the anti-photorefractive ions such as of Mg, Zn, In, Hf, Zr and Sc [2–7]. Among the anti-photorefractive ions, In^{3+} is considered to be the most effective due to the lower threshold concentration which was reported to be about 1.5–2.0 mol% [8].

In this work, congruent $LiNbO_3$ crystals co-doped with fixed Ho^{3+} and different In^{3+} concentrations were grown along the ferroelectric c axis by the conventional Czochralski technique with congruent melt composition ([Li]/[Nb] = 0.946) [9]. The up-conversion emission spectra, power pump dependence and the up-conversion mechanism were measured and investigated to understand the optical characteristics of In^{3+} doped Ho:$LiNbO_3$ crystals. The light-induced scattering in these crystals was studied as a function of exposure energy.

2. Experiments details

Concentration of Ho^{3+} was fixed at 0.5 mol% in the melt, while In^{3+} concentrations were varied to be 0, 1, 3 and 5 mol%. The samples were labeled as In-0, In-1, In-3 and In-5, respectively. The

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growth conditions were as follows: axial temperature gradient 40–50 °C/cm, rotating rate 10–25 rpm, and pulling rate 0.5–2 mm/h. After growth, the crystals were cooled down to room temperature at a speed of 80 °C/h. All the samples were polarized at 1200 °C with a current density of 5 mA/cm^2. The polarized crystals were cut to *Y*-plates ($X \times Y \times Z = 10 \times 2 \times 10$ mm^3) with carefully polished surfaces.

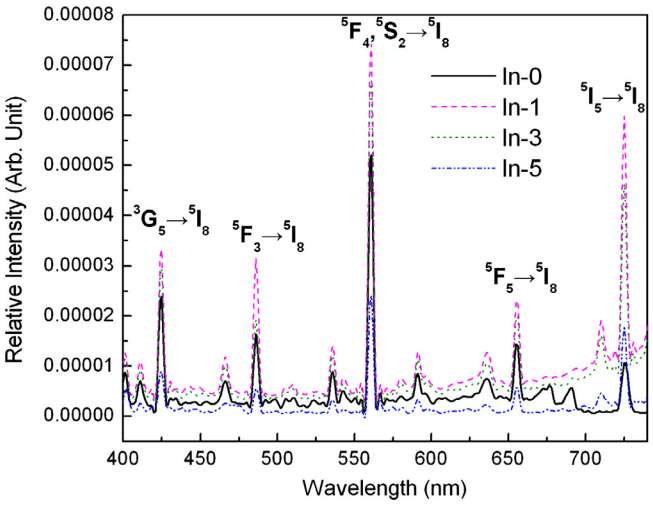
Ti: sapphire laser operating at 808 nm was used as the excitation source to measure the up-conversion emission spectra of the samples. Incident exposure energy was employed to evaluate the light-induced scattering resistance ability [10,11]. An extraordinary polarized beam (e-polarized, wavelength 532 nm, beam diameter 2 mm) was incident onto the samples to be analyzed. A neutral density filter (NF) was utilized in varying incident intensity. The scattered light was blocked by an adjustable aperture and only the transmitted light was detected by a photo-detector. Atomic force microscopy was performed to examine the surface morphology and surface roughness. The surfaces were scanned in contact mode and the images were subsequently analyzed with the Software package of Digital Instruments. All the measurements were conducted at room temperature in air.

3. Results and discussion

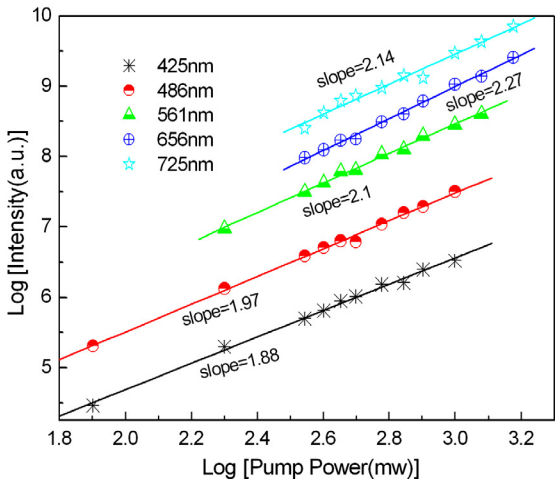
Fig. 1a gives the up-conversion emission spectra of samples excited by focused femtosecond laser. The main emission peaks in this work are assigned to the respective electronic transitions according to the energy level data measured by Reddy et al. [12]. For an unsaturated up-conversion process, the number of photons which is responsible for the conversion mechanism can be calculated by [13]:

$$I_f \propto P^n \tag{1}$$

where I_f is the fluorescent intensity, P is the pump power, and n is the number of the laser photons required. Double logarithmic plot of the relationship between pump energy and up-conversion emission integral intensities of the samples is shown in Fig. 1b, where n equals the slope of the graph of ln (I_f) versus ln (P). The slopes close to 2 imply that the up-conversion emission is a two photons process.



(a) The up-conversion emission spectra.



(b) Double logarithmic plot of the relationship between pump energy and up-conversion emission integral intensities

Fig. 1. Testing result of up-conversion emission spectra of In:Ho:$LiNbO_3$ under excitation at 808 nm.

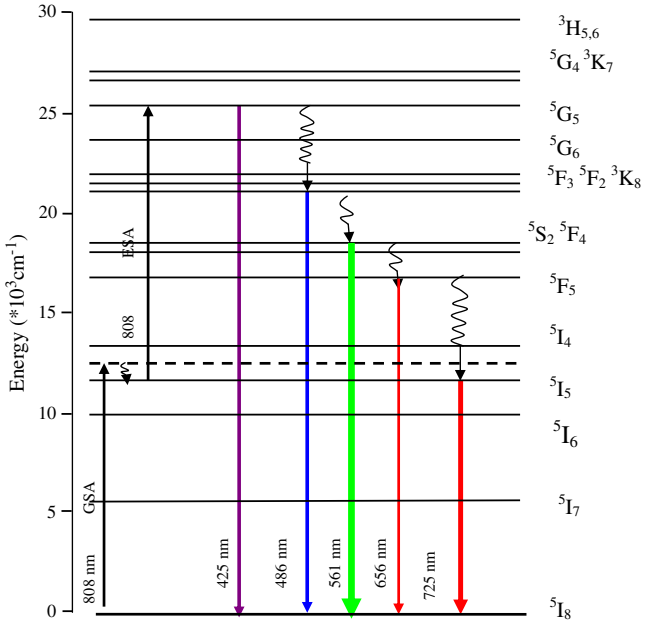


Fig. 2. Energy levels of Ho^{3+} ion as well as the proposed up-conversion mechanism.

Based on the above results, up-conversion excitation and luminescence processes are proposed, as shown in Fig. 2. The following up-conversion mechanism is proposed for explaining the blue, green, violet and red emission under excitation at 808 nm. Ho^{3+} simultaneously absorbs two 808 nm photons to $^5G_5$ level, followed by nonradiative relaxation to $^5F_3$, $^5F_2$ and $^3K_8$ levels in turn via multi phonon relaxation. The $^5F_2$ state relaxes to the $^5F_3$ and $^5S_2$ states in cascade, which emit the blue 486 nm ($^5F_3 \rightarrow ^5I_8$) and green 561 nm ($^5F_4$, $^5S_2 \rightarrow ^5I_8$) radiations. The partial populations at $^5G_5$ level directly relax to $^5I_8$ states in cascade, which emit the violet 425 nm ($^5G_5 \rightarrow ^5I_8$) radiation. The populations at $^5F_4$, $^5S_2$ levels are followed by nonradiative relaxation to $^5F_5$ states, partial populations at $^5F_5$ level are followed by nonradiative relaxation to $^5I_5$ states in cascade, which emit the red 656 nm ($^5F_5 \rightarrow ^5I_8$) and 725 nm ($^5I_5 \rightarrow ^5I_8$) radiations.

Fig. 3 shows the dependence of up-converted intensity of samples on In^{3+} concentration under excitation at 808 nm. We can see