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Optical characteristics of Er^{3+} ion in Er/Yb:$LiNbO_3$ crystal: Comparison with the dissimilar effect of anti-photorefractive ions Zn^{2+}, In^{3+} and Zr^{4+}

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ABSTRACT

The different influences of Zn^{2+}, In^{3+} and Zr^{4+} ions on the optical characteristics of Er^{3+} ion in Er/Yb:$LiNbO_3$ crystals were discussed. An enhanced 1.54 μm emission was observed for Zr/Er/Yb:$LiNbO_3$ crystal, but the Zn^{2+} tri-doping resulted in a decreased one, and the intensity of 1.54 μm emission remained about same in In/Er/Yb:$LiNbO_3$ crystal. The populations of the green emitting $^4S_{3/2}/^2H_{11/2}$ states were achieved through the three-, two- and two-phonon processes in Zn/Er/Yb:$LiNbO_3$, In/Er/Yb:$LiNbO_3$ and Zr/Er/Yb:$LiNbO_3$ crystals, respectively. Zn^{2+} and In^{3+} ions affected the optical characteristics of Er^{3+} ion via modifying the Er^{3+} ion occupancy in Er/Yb:$LiNbO_3$ crystal. The formation of Er_{Li}^{2+}–Er_{Nb}^{2-} ion pairs caused by the Zn^{2+} and In^{3+} ions could increase the rate of cross relaxation process. The OH^- absorption spectra showed that the incorporation of Zr^{4+} ions increased OH^- content, which increased the probability of the nonradiative relaxation process of $^4I_{11/2}\rightarrow{}^4I_{13/2}$ (Er) in Zr/Er/Yb:$LiNbO_3$ crystal. The J–O intensity parameters Ω_t ($t=2$, 4 and 6), the radiative lifetime (τ_{rad}) and fluorescence branching ratio (β) in Zr/Er/Yb:$LiNbO_3$ crystal were predicted by Judd–Ofelt theory. Füchtbauer–Ladenburg and McCumber methods were carried out to calculate the emission cross-sections at 1.54 μm emission. The gain cross-section, estimated as a function of the population inversion ratio, allowed us to evaluate a potential laser performance of Zr/Er/Yb:$LiNbO_3$ crystal.

1. Introduction

Erbium doped lithium niobate (Er:$LiNbO_3$) crystal, emitting Stokes or anti-Stokes luminescence, plays an important role in the applications of lasers, biological imaging, infrared detection, and solar cells [1–3]. In particular, the standard telecommunication wavelength at 1.54 μm, arising from the $^4I_{13/2}\rightarrow{}^4I_{15/2}$ transition of Er^{3+} ion, matches well the "windows of transparency" [4]. Er:$LiNbO_3$ crystal has been used as one of most promising host materials to meet the requirement of integration and miniaturization, since it could combine the lasing characteristics of Er^{3+} ion with the electro-optic and nonlinear optical properties of $LiNbO_3$ crystal [5,6].

The photorefractive effect, inducing the birefringence changes at high laser intensities, limits the performance of Er:$LiNbO_3$ crystal. Until now, comprehensive studies on the suppression of the photorefractive effect in Er:$LiNbO_3$ crystal have been investigated. It has been found that codoping with anti-photorefractive ions, such as Mg^{2+}, Zn^{2+} and In^{3+}, not only improves the photorefractive effect

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but also tunes the intensity of Stokes or anti-Stokes luminescence in Er:$LiNbO_3$ crystal. Sun and Zhang reported that MgO, ZnO and In_2O_3 codoping could enhance the 1.54 μm emission and simultaneously suppress the green upconversion (UC) emission in Er:$LiNbO_3$ crystal [7–10]. The J–O intensity parameters Ω_t ($t=2$, 4 and 6), the radiative lifetime (τ_{rad}) and fluorescence branching ratios (β) of Er:$LiNbO_3$ crystals codoped with Zn^{2+}, Mg^{2+}, In^{3+}, Sc^{3+} and Hf^{4+} ions have been calculated and discussed by Judd–Ofelt (J–O) theory [10–14]. Although breakthroughs in the optical characteristics of Er^{3+} ion in Er:$LiNbO_3$ crystals codoped with these conventional anti-photorefractive ions have been gained, their high threshold concentrations constitute still the main limitation for the crystal of good optical quality [15–18]. Therefore, Zr^{4+} ion, which has a low doping threshold (2.0 mol%) and a distribution coefficient close to 1 [19], will become the most promising anti-photorefractive ion. It is generally accepted that Yb^{3+} ion is used as a sensitizer to generate highly efficient Stokes or anti-Stokes luminescence in Er^{3+}-doped host materials under 980 nm excitation. This is because Yb^{3+} ion has a large absorption cross-section around 980 nm wavelength and can transfer efficiently its energy to Er^{3+} ion [20,21]. Recently, spectroscopic characteristics of Er^{3+} ion in Er/Yb:$LiNbO_3$ crystals tri-doped with Zn^{2+} and In^{3+} ions have been discussed based on J–O theory [22,23]. However, to our knowledge, there are no detailed works on the spectroscopic analysis of Zr/Er/Yb:$LiNbO_3$ crystal. Moreover, it is unclear that if the different effect of Zn^{2+}, In^{3+} and Zr^{4+} ions on the optical characteristics of Er^{3+} ion would be observed in Er/Yb:$LiNbO_3$ crystal.

In this paper, Er^{3+} (1 mol%)/Yb^{3+} (1 mol%):$LiNbO_3$ crystals tri-doped without and with Zr^{4+} ions were grown by the Czochralski technique. For a comparison, the upconversion and near infrared emission spectra of Zn/Er/Yb:$LiNbO_3$ and In/Er/Yb:$LiNbO_3$ crystals grown by the Czochralski technique have been investigated. The OH^- absorption spectra of Er/Yb:$LiNbO_3$ and Zr/Er/Yb:$LiNbO_3$ crystals were studied. The intensity parameters Ω_t ($t=2$, 4 and 6), the radiative lifetime (τ_{rad}) and fluorescence branching ratio (β) in Zr/Er/Yb:$LiNbO_3$ crystal were calculated by J–O theory. McCumber and Füchtbauer–Ladenburg methods were used to discuss the emission cross-section spectra of 1.54 μm emission, as well as the gain cross-section spectrum for the $^4I_{13/2}\rightarrow{}^4I_{15/2}$ transition was also analyzed.

2. Experimental

Congruent ([Li]/[Nb]=0.946) Er/Yb:$LiNbO_3$ crystals tri-doped with ZnO, In_2O_3 and ZrO_2 were grown by the Czochralski technique. The purities of the raw materials Li_2CO_3, Nb_2O_5, Er_2O_3, Yb_2O_3, ZnO, In_2O_3 and ZrO_2 were 99.99%. The mixtures, which were mixed for 24 h, were heated at 750 °C for 2 h to remove CO_2 and then formed polycrystalline powder via heating up to 1150 °C for 2 h. The optimum technology conditions of crystal growth were the axial temperature gradient of 40–50 K/cm, the rotating rate of 10–25 rpm and the pulling rate of 0.5–2 mm/h. The grown crystals were polarized at 1200 °C with a current density of 5 mA/cm^2. The polarized crystals were cut into Y-plates ($X\times Y\times Z\approx 10\times 2\times 10$ mm^3) with optically polished surfaces. The compositions of these grown crystals are listed in Table 1.

Table 1
Compositions of the crystals in the melt.

Sample no.	Er^{3+}	Yb^{3+}	Zn^{2+}	In^{3+}	Zr^{4+}
	(X mol%)				
Er/Yb-0.5	0.5	0.5	0	0	0
Er/Yb-1	1.0	1.0	0	0	0
Zn/Er/Yb:LN	0.5	0.5	5.0	0	0
In/Er/Yb:LN	0.5	0.5	0	2.0	0
Zr/Er/Yb:LN	1.0	1.0	0	0	2.0

The inductively coupled plasma mass spectrometry (ICP-MS, Optima 7500 Series, Agilent Technologies Inc, Beijing) was used to determined the Er^{3+} ion content ([Er^{3+}]/[Nb^{5+}] ratio) in the crystal, and the obtained concentrations of Er^{3+} ion in Zr/Er/Yb:LN, Er/Yb-1 and Zn/Er/Yb:LN crystals were 2.719×10^{20} cm^{-3}, 2.832×10^{20} cm^{-3} and 1.416×10^{20} cm^{-3}, respectively. The power-controllable diode laser, operating at 980 nm wavelength, was used to measure the near infrared and upconversion emission spectra. All fluorescence emission spectra were recorded at the same geometry by using the spectrometer (Bruker optics 500IS/SM) equipped with a semiconductor cooled charge coupled device detector (DV440, Andor). The Fourier-Transform spectrophotometer (Niconet-710, Nicolet, USA) was used to measure the OH^- absorption spectra. The UV–vis-near infrared absorption spectra in the range from 300 to 1650 nm were measured by the CARY spectrophotometer.

3. Results

3.1. Optical characteristics of Er^{3+} ion

Fig. 1 shows the near infrared emission spectra of Er/Yb-0.5, Er/Yb-1, Zn/Er/Yb:LN, In/Er/Yb:LN and Zr/Er/Yb:LN crystals under 980 nm excitation. The near infrared emission centered at 1540 nm corresponds to the $^4I_{13/2}\rightarrow{}^4I_{15/2}$ transition of Er^{3+} ion. It is can be seen from Fig. 1A that Zr/Er/Yb:LN presents the 1.54 μm emission about 3 times stronger than Er/Yb-1 crystal, which favors to meet the requirement of broadband amplification and lasing around 1.54 μm wavelength. As illustrated in Fig. 1B and C, the intensity of 1.54 μm emission remains about the same in In/Er/Yb:LN, while the introduction of Zn^{2+} ions leads to a drastically decreased 1.54 μm emission in Zn/Er/Yb:LN crystal.

The UC emission spectra of Er/Yb:$LiNbO_3$ crystals tri-doped with Zn^{2+}, In^{3+} and Zr^{4+} ions under 980 nm excitation are displayed in Fig. 2. The strong emission peaks at 525/550 nm are assigned to the $^2H_{11/2}/^4S_{3/2}\rightarrow{}^4I_{15/2}$ transitions of Er^{3+} ion, respectively, and a weak red emission peak at 660 nm corresponds to the $^4F_{9/2}\rightarrow{}^4I_{15/2}$ transition [24]. As shown in Fig. 2A and B, the intensity of green UC emission increases with the incorporation of Zn^{2+} ions, whereas decreases with the tri-doping with In^{3+} ions. As for