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Concentration-dependent upconversion emission in Er-doped and Er/Yb-codoped $LiTaO_3$ polycrystals

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ABSTRACT

Er-doped and Er/Yb-codoped $LiTaO_3$ polycrystals were synthesized by the solid-state reaction method at 1200 °C. The structural properties of Er/Yb:$LiTaO_3$ polycrystals were confirmed by the X-ray diffraction patterns. The upconversion emission spectra of Er:$LiTaO_3$ polycrystals showed that the intensities of the green and red upconversion emissions enhanced with the increasing concentration of Er^{3+} ions. The increased intensity ratio of the red to green emission was attributed to the two cross relaxation processes $^4S_{3/2}+^4I_{15/2}\rightarrow^4I_{9/2}+^4I_{13/2}$ and $^2H_{11/2}+^4I_{11/2}\rightarrow^4F_{9/2}+^4F_{9/2}$. Upconversion emission tuning from green to red was observed in Er/Yb:$LiTaO_3$ polycrystals under 980 nm excitation. It was proposed that the efficient cross relaxation process ($^4F_{7/2}+^4I_{11/2}\rightarrow^4F_{9/2}+^4F_{9/2}$) and the energy back transfer ($^4S_{3/2}$ Er$+^2F_{7/2}$ Yb$\rightarrow^4I_{13/2}$ Er$+^2F_{5/2}$ Yb) contribute the increased intensity ratio of the red to green emission in Er/Yb:$LiTaO_3$ polycrystals. Studies on the pump power dependence indicated that the green emitting $^4S_{3/2}/^2H_{11/2}$ states and the red emitting $^4F_{9/2}$ state were populated via the energy transfer assisted UC process besides a two-photon process in Er/Yb:$LiTaO_3$ polycrystals.

1. Introduction

There is an interest in rare-earth ion doped materials capable of converting infrared to visible radiation by means of sequential excitation upconversion (UC) [1]. The visible UC emission could be used in the application of the display technologies, optical data storage and biomedical systems [2,3]. To meet the practical application requirements of the multiplexed biological labeling [4–8], many works have been expanded on the UC color output of rare-earth ions. Tuning the UC luminescence not only images and tracks the multiple molecular targets simultaneously, but also allows the scientists to understand, classify and differentiate complex human diseases [9]. It has been reported that adjusting the rate of cross relaxation (CR) process is an efficient route to tune the UC luminescence and govern the optical characteristics of rare-earth ions [10,11]. Chen has found that tuning from the green to red UC emission in Ce/Yb/Ho:$NaYF_4$ nanocrystals could be obtained by adjusting the CR processes of $^5S_2/^5F_4$ (Ho)$+^2F_{5/2}$ (Ce)$\rightarrow^5F_5$ (Ho)$+^2F_{7/2}$ (Ce) and $^5I_6$ (Ho)$+^2F_{5/2}$ (Ce)$\rightarrow^5I_7$ (Ho)$+^2F_{7/2}$ (Ce) [10]. Vetrone reported that the enhancement of red UC emission and the reduction of green one in Er:Y_2O_3 samples under 980 nm excitation are attributed to the increased probability of CR process ($^4F_{7/2}+^4I_{11/2}\rightarrow^4F_{9/2}+^4F_{9/2}$) [11]. Among the lanthanide rare-earth ions, Er^{3+} ion has been the most studied one due to its favorable electronic energy level structures. Kapoor reported that the green emission of 100 mW and the red emission of 270 mW were gained in Er:Y_2O_3 under 975 nm excitation [12]. Zhang found that the color of UC emissions can be tuned from green to red by changing the concentration of Er^{3+} ions in Er:Y_2O_3 [13]. However, the insufficient efficiency of the UC emission limits the practical applications. Yb^{3+} ion is successfully used as a sensitizer to Er^{3+} ion since it has a much large absorption cross-section around 980 nm wavelength and can efficiently transfer its energy to Er^{3+} ion [14–17]. Furtherly, codoping Yb^{3+} ions could tune the UC emission from green to red in Er/Yb:ZrO_2 nanocrystal under 980 nm excitation [18].

Lithium tantalite ($LiTaO_3$) is a prominent multifunctional material, which exhibits the piezoelectric, ferroelectric, acousto-optical, electro-optical and nonlinear optical properties [19–21]. Visible and infrared lasing properties can be obtained by $LiTaO_3$ doped with transition metals or trivalent lanthanides (Ln^{3+}) [22,23]. Er-doped $LiTaO_3$ polycrystal (Er:$LiTaO_3$) has attracted great attention due to its potential applications to integrated devices. This is because Er:$LiTaO_3$ could combine the lasing characteristics of Er^{3+} ion with the nonlinear optical properties presented by $LiTaO_3$ host material. Although the breakthroughs of controllable fluorescence have been achieved in Er/Yb:ZrO_2 nanocrystal, it is unclear that if a similar phenomenon can be also observed in Er/Yb:$LiTaO_3$ polycrystal. Therefore, the effect of Yb^{3+} ions on the optical characteristics of Er^{3+} ion is essential to study in Er:$LiTaO_3$

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polycrystal, driven by the needs for miniaturization and integration of devices.

In this paper, Er-doped and Er/Yb-codoped $LiTaO_3$ polycrystals were synthesized by the solid-state reaction method at 1200 °C. The X-ray diffraction (XRD) was measured to understand the structural properties of $Er:LiTaO_3$ and $Er/Yb:LiTaO_3$ polycrystals. The UC emission spectra and pump power dependences were discussed. The UC mechanisms in $Er:LiTaO_3$ and $Er/Yb:LiTaO_3$ polycrystals under 980 nm excitation were studied.

2. Experimental

$LiTaO_3$ polycrystals doped with 0.5 mol%, 1.0 mol%, 1.5 mol% and 2.0 mol% Er^{3+} ions and Er^{3+} (1 mol%):$LiTaO_3$ polycrystals codoped with 1.0 mol%, 5.0 mol%, 10 mol% and 30 mol% Yb^{3+} ions were prepared by the solid-state reaction method at 1200 °C. The purities of Li_2CO_3, Ta_2O_5, Er_2O_3 and Yb_2O_3 are 99.99%. The powders were fully ground in an agate mortar by hand at least for 4 h. The sufficient fine and fully homogenous powders were pressed into a disk under 20 MPa. The mixture of the chemical precursors was heated at 750 °C for 4 h to resolve the Li_2CO_3 into Li_2O and CO_2. The polycrystals were generated at 1200 °C for 22 h. The raw material compositions (mol%) of the prepared $Er:LiTaO_3$ and $Er/Yb:LiTaO_3$ polycrytals are shown in Table 1.

The X-ray diffraction spectra of $Er:LiTaO_3$ and $Er/Yb:LiTaO_3$ polycrytals were used to identify the crystallization phase, which were measured by the XRD-6000 diffractometer using a copper Ka radiation source. A SPEX1000M spectrometer with a photomultiplier tube was used to measure the UC emission spectra. All these measurements were performed at room temperature.

3. Results and discussion

3.1. Phase and structure analysis

Fig. 1 displays the X-ray diffraction patterns of $LiTaO_3$ polycrystals codoped with Er^{3+} and Yb^{3+} ions (samples 5#, 7# and 8#) and the pure $LiTaO_3$ polycrystal. Since the same properties are obtained in $Er:LiTaO_3$ polycrystals codoped with the different concentration of Yb^{3+} ions, the measured XRD spectra of samples 1#–4# and 6# are not shown in Fig. 1. It can be seen that there are no new peaks observed for the samples 5#, 7# and 8# compared with the pure $LiTaO_3$, suggesting that Er^{3+} and Yb^{3+} ions have no influence on the structures of the samples. The samples are still trigonal system. Consequently, the Er^{3+} and Yb^{3+} ions may occupy the normal Li-site or Ta-site rather than the interstitial sites within the lattice.

3.2. UC luminescence spectra

Fig. 2 shows the UC emission spectra of $LiTaO_3$ polycrystals doped with different concentrations of Er^{3+} ions under 980 nm excitation. The inset is the intensity ratios of the red to green emission $R(r/g)$ in samples 1#, 2#, 3# and 4#. As illustrated in Fig. 2, the green UC emissions have two luminescence peaks at 525 nm and 550 nm, corresponding to the $^2H_{11/2} \rightarrow {}^4I_{15/2}$ and $^4S_{3/2} \rightarrow {}^4I_{15/2}$ transitions of Er^{3+} ion, respectively. The red UC emission centered around 660 nm is attributed to the $^4F_{9/2} \rightarrow {}^4I_{15/2}$ transition [24]. It can be seen that the green and red UC emissions enhance with the increasing concentration of Er^{3+} ions. The inset of Fig. 2 shows that as the concentration of Er^{3+} ions increases, the intensity ratio of the red to green emission $R(r/g)$ is enhanced.

Table 1
Raw material compositions (mol%) of samples.

	Er^{3+} (mol%)	Yb^{3+} (mol%)
1#	0.5	0
2#	1.0	0
3#	1.5	0
4#	2.0	0
5#	1.0	1.0
6#	1.0	5.0
7#	1.0	10.0
8#	1.0	30.0

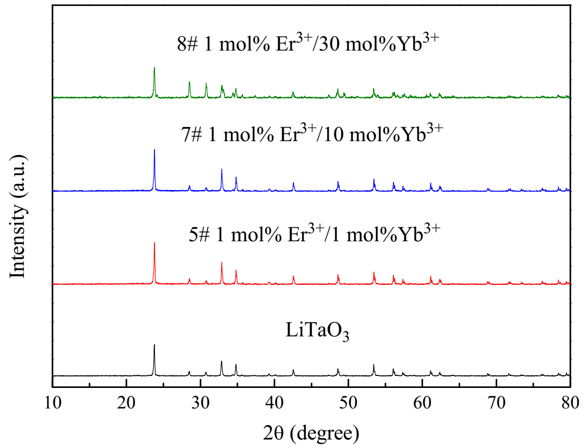

Fig. 1. The X-ray diffraction patterns of $LiTaO_3$ polycrystals codoped without and with Er^{3+} and Yb^{3+} ions.

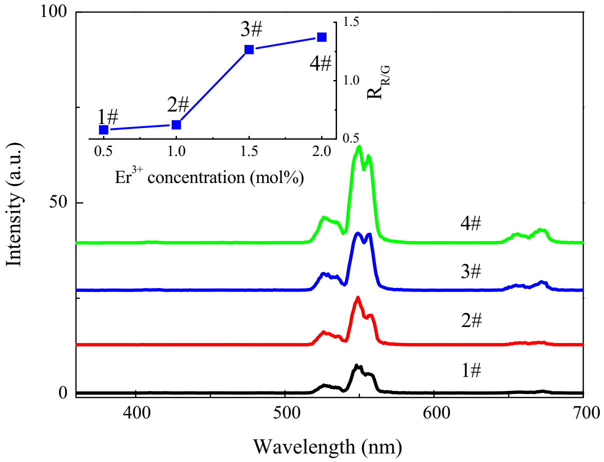

Fig. 2. UC emission spectra of $LiTaO_3$ polycrystals doped with Er^{3+} ions under 980 nm excitation. The inset is the intensity ratios $R(r/g)$ of the red emission to the green emission in $LiTaO_3$ polycrystals doped with different concentrations of Er^{3+} ions.

To analyze the UC mechanism, the dependences of UC emission intensity on excitation power for $Er:LiTaO_3$ polycrystals under 980 nm excitation are displayed in Fig. 3. For an "unsaturated" UC process, the UC emission intensity depends on the excitation power, the required number of photons to produce the fluorescence can be obtained by the relation: $I_f \propto P^n$ [25], where I_f is the intensity of UC emission, P is the excitation power, and n is the required number of photons. As shown in Fig. 3, the slopes of green UC emissions are 2.10 and 2.22 for 3# and 4# samples, respectively. According to the previous work reported by Pollnau [26], the values of 2.10 and 2.22, which are slightly larger than $n=2$, imply that an additional three-photon process is involved to populate the green UC emission besides a two-photon process [27]. As for the red UC emission, the slope values of n are equal to 1.97 and 1.70 for samples 3# and 4#, respectively.