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Upconversion for enlarging solar spectrum response in near-stoichiometric and congruent Er:LiNbO$_3$ crystals

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To increase the photovoltaic efficiency of solar cell, the visible luminescence produced at the excitation of the near infrared laser light in near-stoichiometric and congruent LiNbO$_3$ crystals heavily doped with Er^{3+} ions (Er:NSLN and Er:CLN, respectively) were investigated. An enhancement of the green upconversion emission observed in Er:NSLN crystal was attributed to the inefficient cross relaxation processes of $^2H_{11/2} + {}^4I_{13/2} \rightarrow {}^4I_{11/2} + {}^4F_{9/2}$ and $^4F_{7/2} + {}^4I_{11/2} \rightarrow {}^4F_{9/2} + {}^4F_{9/2}$. The Er content in the crystal was measured by an inductively coupled plasma mass spectrometry (ICP-MS). The OH$^-$ absorption and UV–vis-near infrared absorption spectra indicated that the Er^{3+} cluster sites ($\mathrm{Er}_{\mathrm{Li}}^{2+}$—$\mathrm{Er}_{\mathrm{Nb}}^{2-}$) were dissociated in Er:NSLN crystal. The strong green upconversion emission produced by Er:NSLN crystal will be beneficial for improving the practical performance of solar cells.

1. Introduction

Driven by the needs for enlarging the solar spectrum response in solar cells, trivalent rare-earth ions doped host materials, which could up-convert easily the absorbed near-infrared (NIR) sunlight into visible luminescence, have regained much attention [1–3]. For examples, the photovoltaic efficiency of dye-sensitized solar cell is suppressed since it only has a high absorption in the visible range of 400–700 nm [4]. Due to the wide bandgap (1.7–1.8 eV) of the dye-sensitized solar cell, the NIR (>700 nm) sunlight would be lost in dye-sensitized solar cell. Therefore, the erbium (Er^{3+}) ion has become an excellent candidate for application in the solar cell since its intermediate levels $^4I_{9/2}$ and $^4I_{11/2}$ have the long lifetimes and can efficiently convert the 800 and 980 nm wavelength sunlight into the visible luminescence [5–7]. It is believed that converting the near infrared sunlight into the visible UC luminescence is an effective way to reduce the spectral mismatch losses of dye-sensitized solar cell.

Researches on upconversion (UC) luminescence of rare-earth ions based on crystals, nanomaterials, glass and polymers have been widely demonstrated [8–10]. Among these host materials, versatile LiNbO$_3$ crystal, which exhibits the electro-optic, piezoelectric and nonlinear optical physical properties [11–14], may compensate for the single-function of these host materials and provide more probabilities for the miniaturization devices. Compared with the congruent ([Li]/[Nb] = 0.946) LiNbO$_3$ (CLN) crystal [15], near-stoichiometric LiNbO$_3$ (NSLN) crystal presents more excellent properties, such as the low coercive field strength required for ferroelectric domain reversal, large electro-optic, nonlinear effects and the photorefractive effect suppressed at a low concentration of anti-photorefractive ions [16,17].

The optical characteristics of rare-earth ion can be related to the structure of host materials. In general, there are two types of the Er^{3+} ion distribution in LiNbO$_3$ crystal lattice. One is the Er^{3+} isolated site which is $\mathrm{Er}_{\mathrm{Li}}^{2+}$ (the Er^{3+} ion locates in Li site) or $\mathrm{Er}_{\mathrm{Nb}}^{2-}$ (the Er^{3+} ion locates in Nb site) [18]. The other one is the Er^{3+} cluster site ($\mathrm{Er}_{\mathrm{Li}}^{2+}$—$\mathrm{Er}_{\mathrm{Nb}}^{2-}$) [19] which consists of one $\mathrm{Er}_{\mathrm{Li}}^{2+}$ site and one $\mathrm{Er}_{\mathrm{Li}}^{2+}$ site. According to the Li defect model [20,21], as Er^{3+} ions enter into the CLN crystal lattice, Er^{3+} ions substitute firstly for the antisites $\mathrm{Nb}_{\mathrm{Li}}^{4+}$ (the Nb^{5+} ions locate in Li sites) and occupy Li sites. And then Er^{3+} ions occupy the normal Li sites, and $\mathrm{Er}_{\mathrm{Li}}^{2+}$ isolated sites are formed. Based on the bond valence model, the Er^{3+} ions begin to enter into the normal Nb sites when the concentration of Er^{3+} ions is higher than 1.9 mol% [31]. Accordingly, it is possible that the Er^{3+} cluster sites maybe formed in CLN crystal heavily doped with Er^{3+} ions (>1.9 mol%). However, since the decreased intrinsic defect $\mathrm{Nb}_{\mathrm{Li}}^{4+}$ caused by the increased [Li]/[Nb] ratio in NSLN crystal, it is unclear if a similar phenomenon can also be observed in Er:NSLN crystal. On the other hand, the optical characteristics of Er^{3+} ion are strongly dependent on the distribution of Er^{3+} ion in the LiNbO$_3$ host material [22,23]. The intensity ratio of the green to red UC emission could be adjusted by tuning the rate of cross relaxation (CR) process. Therefore, it is imperative to know the effect of the increased [Li]/[Nb] ratio on the distribution and the optical characteristics of

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Er^{3+} ion in Er:NSLN crystal. A more systematic and deeper investigation on Er:NSLN is essential to carry out.

In this paper, near-stoichiometric and congruent $LiNbO_3$ crystals heavily doped with Er^{3+} ions were grown by the Czochralski technique. The concentration of Er^{3+} ions in the crystal was determined by the inductively coupled plasma mass spectrometry (ICP-MS). The visible green and red UC emissions were studied under 800 nm excitation. The OH^- absorption and UV–vis near infrared spectra were measured to understand the structural characteristics of Er:NSLN crystal.

2. Experimental methods

Near-stoichiometric ([Li]/[Nb] = 1 in the melt) and congruent (([Li]/[Nb] = 0.946 in the melt) $LiNbO_3$ crystals doped with 3 mol% Er^{3+} ions were grown along ferroelectric *c* axis by Czochralski technique. The detailed process of crystal growth has been shown in the previous works [24,25]. These grown crystals are named as Er:NSLN and Er:CLN, respectively.

The Er^{3+} content in the crystal was determined by use of the inductively coupled plasma mass spectrometry (ICP-MS, Optima 7500 Series, Agilent Technologies Inc., BeiJing). Fourier-Transform spectrophotometer (Niconet-710, Nicolet, USA) was used to obtain the OH^- absorption spectra at room temperature. Perkin–Elmer Lambda 900 spectrophotometer was used to measure the UV–vis near infrared absorption spectra which were performed with unpolarized light and with a sample oriented in such a manner that the light propagated along the *y* axis of the crystal. The scanning wavelength range was 310–1650 nm, and the scanning step and scanning speed were fixed at 1 nm and 600 nm/min, respectively. The UC emission spectra were excited by the 800 nm diode laser, and the pump power dependences were obtained with the various output power.

3. Results and discussion

Fig. 1 shows the UC emission spectra of Er:CLN and Er:NSLN crystals under 800 nm excitation. As illustrated in Fig. 1, the green UC emissions centered at 525/550 nm correspond to the $^2H_{11/2}/^4S_{3/2} \rightarrow {}^4I_{15/2}$ transitions of Er^{3+} ion, respectively. The weak red UC emission at 660 nm arises from the $^4F_{9/2} \rightarrow {}^4I_{15/2}$ transition [26,27]. It is obvious that the increased green UC emissions are observed for Er:NSLN crystal, and the red UC emission remains almost constant. By use of ICP-MS measurement, the content of Er^{3+} ions in the crystal are obtained to be 4.22 ± 0.02 mol% and 4.41 ± 0.01 mol%, respectively, for Er:NSLN and Er:CLN crystals. The value of segregation coefficient (R_{seg}) can be calculated by the relation $R_{seg} = C_{cry}/C_{mel}$, where C_{cry} means the concentration of Er^{3+} ion measured from the grown crystal by ICP-MS, and C_{mel} is the concentration of Er^{3+} ion in the melt. Consequently, the segregation coefficients of Er^{3+} ions are calculated to be 1.407 ($R_{seg} = C_{cry}/C_{mel}$ = 4.22 mol%/3 mol%) and 1.470 (R_{seg} = - C_{cry}/C_{mel} = 4.41 mol%/3 mol%), for Er:NSLN and Er:CLN, respectively. The concentrations of Er^{3+} ions in the crystal are found to be 7.96×10^{20} cm^{-3} and 8.33×10^{20} cm^{-3} for Er:NSLN and Er:CLN, respectively. It is well known that the fluorescent intensity depends on the dopant concentration and the distribution of active ions in a host material. Since the concentration of Er^{3+} ions in the Er:NSLN is smaller than that in Er:CLN crystal, the stronger green and red UC emissions are expected to observe in Er:CLN crystal. However, the intensities of green and red UC emissions in Er:NSLN crystal are higher than those in Er:CLN crystal. This is an indication that the fluorescence intensity is regardless of the Er^{3+} content. Therefore, it is proposed that the distribution of Er^{3+} ions plays an important role in the optical characteristics of Er^{3+} ions in Er:$LiNbO_3$ crystal. As illustrated in Fig. 1, the intense green UC emissions suggest that Er:NSLN crystal exhibits potential applications in the fields of dye-sensitized solar cells.

To better understand the UC mechanisms, log–log plots of the green UC emission intensity as a function of pump power are displayed in Fig. 2. The relation $I \propto P^n$ [28,29] is used to obtain the required number of photons, where *P* is the pump intensity, *I* is the intensity of the green UC emission and *n* is the required number of photons to populate the green emitting state. It can be seen from Fig. 2 that the slope value is 1.80 for Er:NSLN crystal, implying that the green UC emissions are populated via a two-photon process.

Fig. 3 shows the energy level diagram of Er^{3+} ions. The well known two-photon process induced by 800 nm excitation can be described as follows. Under 800 nm excitation, two 800 nm photons excite the Er^{3+} ions from the ground state $^4I_{15/2}$ to the upper state $^2H_{9/2}$ via ground state absorption process (GSA:$^4I_{15/2}$ + a 800 nm photon → $^4I_{9/2}$ and excite state absorption (ESA1: $^4I_{9/2}$ + a 800 nm photon → $^2H_{9/2}$). The nonradiative transition of the $^2H_{9/2}$ state populates the green emitting $^2H_{11/2}/^4S_{3/2}$ states. The population of the green emitting $^2H_{11/2}$ state also arises from ESA2 process ($^4I_{13/2}$ + a 800 nm photon → $^2H_{11/2}$). The $^4I_{13/2}$ state is populated via the nonradiative relaxation process of the $^4I_{9/2}$ state. The two cross relaxation processes of CR1: $^2H_{11/2} + {}^4I_{13/2} \rightarrow {}^4I_{11/2} + {}^4F_{9/2}$ and CR2:

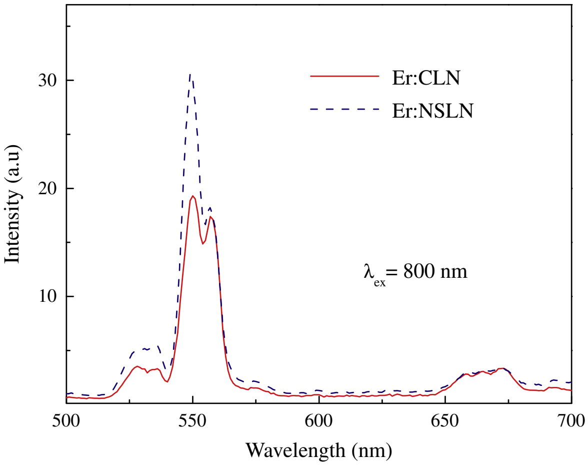

Fig. 1. The UC emission spectra of Er:CLN and Er:NSLN crystals under 800 nm excitation.

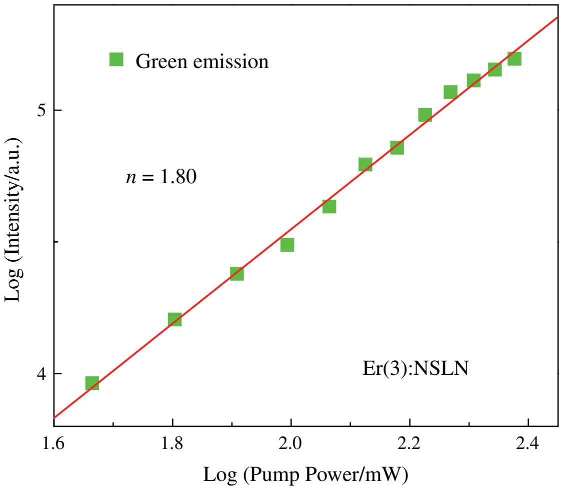

Fig. 2. The pump power dependence of green UC emission in Er:NSLN crystal under 800 nm excitation. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)