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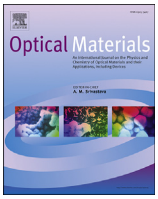

Enhancement of upconversion emission in Er:LiNbO$_3$ by codoping with HfO$_2$ under 1550 nm excitation

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ABSTRACT

An increased red upconversion emission produced under excitation at 1550 nm was observed in hafnium and erbium co-doped lithium niobate (Hf$_{(8\ \mathrm{mol\%})}$/Er:LiNbO$_3$), which can be used to increase the photovoltaic efficiency of solar cells. Three 1550 nm photons were required to arouse the green and red emissions in Hf$_{x\ (x\,=\,2,\,4,\,6\ \mathrm{mol\%})}$/Er:LiNbO$_3$, while the red emitting $^4F_{9/2}$ state was populated by a hybrid two- and three-photon process in Hf$_{(8\ \mathrm{mol\%})}$/Er:LiNbO$_3$. The formation of Er^{3+} cluster sites (Er$^{2+}_{\mathrm{Li}}$-Er$^{2-}_{\mathrm{Nb}}$) lead to an efficient cross relaxation process $^4I_{13/2} + {}^4I_{13/2} \rightarrow {}^4I_{15/2} + {}^4I_{9/2}$ and enhanced red emission in Hf$_{(8\ \mathrm{mol\%})}$/Er:LiNbO$_3$.

1. Introduction

Development of highly efficient photovoltaic solar cells has attracted much research interest for the last years [1]. To reduce a loss of near infrared (NIR) solar radiation, rare earth (RE) ions doped material can be used as a luminescent layer in the solar cells to tune their sensitivity to the solar spectrum [2,3]. Among many RE ions, Er^{3+} ion could be used as a versatile rare earth ion due to its favorable electronic energy level structures, and Er^{3+} ion has two main application fields. The first one is Er^{3+} doped waveguides amplifiers (EDWAs) since the 1.54 μm emission arising from the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition of Er^{3+} ion matches well with the third fiber-optics communication window [4,5]. The second one is photovoltaic, since the $^4I_{15/2} \rightarrow {}^4I_{13/2}$ transition could efficiently upconvert 1550 nm NIR light into visible emissions absorbed by the solar cells. A. Shalav reported [6] that the responsivity of bifacial silicon solar cell is increased in NIR range due to NaYF$_4$:Er phosphors attached. The peak external quantum efficiency is 2.5 ± 0.2% in the silicon solar cell under laser excitation at 1523 nm, and the corresponding internal quantum efficiency is 3.8%. Pursuing the same goal G. Y. Chen demonstrated the intense visible and NIR upconversion (UC) photoluminescence in LiYF$_4$:Er nanocrystals under excitation at 1490 nm [7]. R. M. Rodríguez has converted successfully the infrared (IR) light into UC emission in Er^{3+}-doped Gd$_2$O$_2$S, which could enhance the photovoltaic efficiency of solar cells [8].

Recently, particular attention has been given to LiNbO$_3$ as an excellent host material for RE ion doping. Limitation of highest phonon energy (about 880 cm^{-1}) of LiNbO$_3$ decreases nonradiative relaxation rates according to Miyakawa-Dexter theory [9]. Previous works reported that the anti-photorefractive ions such as Mg^{2+}, Zn^{2+}, In^{3+} and Zr^{4+} not only suppress the optical damage of LiNbO$_3$ but also affect the optical characteristics of the material doped with RE ions [10–13]. L. Sun found that under 980 nm excitation, the heavily doping with MgO enhanced the 1.5 μm emission, while reduced the green UC emission in Er:LiNbO$_3$ [10]. It has been reported by J.W. Shur that UC emission in Zr/Tm:LiNbO$_3$ is about three times higher than that in Zn/Tm:LiNbO$_3$ under 980 nm excitation [13]. For the last years, extensive studies on the holographic properties and the high resistance against ultraviolet photorefraction of hafnium and erbium co-doped lithium niobate (Hf/Er:LiNbO$_3$) crystal have appeared [14]. And it also has been found that Hf/Er-codoped SiO$_2$ planar waveguide is a viable system for 1.5 μm application [15]. However, there are few reports on

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converting 1550 nm light into visible UC emission in Hf/Er:$LiNbO_3$. Therefore, the upconversion emission of Er^{3+} ions induced by excitation at 1550 nm in Hf/Er:$LiNbO_3$ are essential to study to increase the solar cells efficiency.

In this work, the UC luminescence of Hf/Er:$LiNbO_3$ co-doped crystals with different concentration of Hf^{3+} and Er^{3+} ions grown by Czochralski technique is investigated in detail and discussed. The pump dependence analyses and UC mechanisms are proposed under 1550 nm excitation. The ultraviolet (UV)-visible spectra of Hf/Er:$LiNbO_3$ are discussed.

2. Experimental

Congruent (Li/Nb ≈ 48.6/51.4) Er (1 mol%):$LiNbO_3$ crystals codoped with x mol% Hf^{4+} ions ($x = 0, 2, 4, 6$ and 8) are grown along the ferroelectric c axis by Czochralski technique. The purities of raw materials (Li_2CO_3, Nb_2O_5, HfO_2 and Er_2O_3) are 99.99%. The detailed growth process can be described as follows: The raw materials of Li_2CO_3, Nb_2O_5, HfO_2 and Er_2O_3 were mixed for 24 h, and then were heated at 750 °C and 1150 °C, respectively, for 2 h to remove CO_2 and to form polycrystalline powder. The optimum growth conditions were depicted as follows: an 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˜cm2. The boules were cut into Y-cut plates (X × Y × Z = 10 × 2 × 10 mm3) with polished surfaces. The grown five crystals are named as Er-0.0, Hf/Er-2.0/1.0 Hf/Er-4.0/1.0 Hf/Er-6.0/1.0 and Hf/Er-8.0/1.0, respectively. The UC emission spectra excited by the 1550 nm distributed feed back (DFB) laser (ADFB-PU-1550-33-R-FA, Amonics Inc., Hongkong) are recorded by the combined fluorescence lifetime and steady state spectrometer (FLS920, Edinburgh Inc., U.K.). The UV–visible diffuse reflectance spectra of the powders were measured with a UV–vis spectrophotometer (UV9000, Shanghai Metash Instruments Co. LTD, China).

3. Results and discussion

The UC emission spectra of the Hf/Er:$LiNbO_3$ crystals under 1550 nm excitation are shown in Fig. 1. The weak green emissions centered at 525/550 nm and an intense red UC emission at 675 nm are attributed to the transitions of Er^{3+} ion: $^2H_{11/2}$, $^4S_{3/2} \rightarrow {}^4I_{15/2}$ and $^4F_{9/2} \rightarrow {}^4I_{15/2}$, respectively [16,17]. In comparison with Er:$LiNbO_3$ the intensity of the green and red UC emissions is lower in $Hf_{x\ (x = 2,\ 4,\ 6\ \mathrm{mol\%})}$/Er:$LiNbO_3$, while remarkably higher at the Hf^{4+} concentration of 8 mol%. In all of the samples doped with Hf^{4+} ions, the intensity increases with the Hf^{4+} concentration increased. It is well known that the intensity of luminescence is direct related to the local environment, the dopant concentration and the distribution of active ions in a host material. Here, as for the same Er^{3+} content, there should be a constant value for the green and red UC emissions. Therefore, the behavior that the changed intensities of UC emissions are regardless of the Er^{3+} content implies the local environment of Er^{3+} ion is tailored by Hf^{4+} ions under 1550 nm excitation.

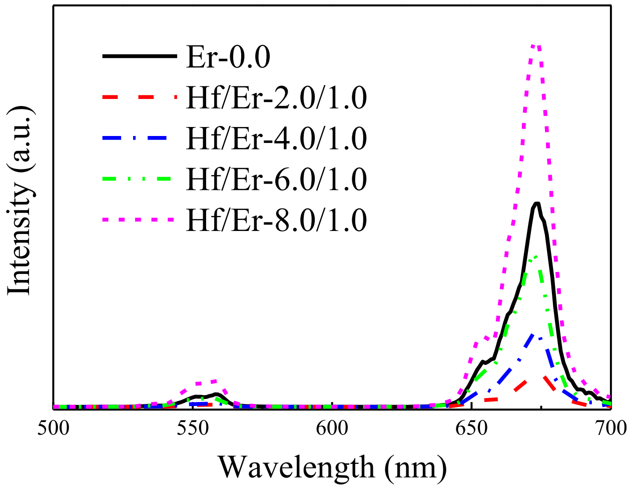

Fig. 1. The UC emission spectra of Hf/Er:$LiNbO_3$ under 1550 nm excitation.

To understand the UC mechanisms, Fig. 2 illustrates a double-logarithmic plot of fluorescence intensity as a function of pump power of 1550 nm excitation. For an unsaturated UC process, the number of photons required to populate the upper emitting state can be obtained by the relation: $I_f \propto P^n$ [18,19], where P is the pump power intensity, I_f is the fluorescence intensity, and n is the number of the 0.8 eV photons (1550 nm laser wavelength) required to induce the green and red UC emissions. As shown in Fig. 2, slopes of the green and red UC emissions are 3.12 and 3.09 for Hf/Er-2.0/1.0, 3.13 and 3.06 for Hf/Er-4.0/1.0, 3.05 and 2.79 for Hf/Er-6.0/1.0, respectively, indicating the three-photon process needed to populate the green and red UC emissions in $Hf_{x\ (x = 2,\ 4,\ 6\ \mathrm{mol\%})}$/Er:$LiNbO_3$ under 1550 nm excitation. The n value of 2.88 suggests the green UC emission is populated by a three-photon process in Hf/Er-8.0/1.0. The fact that the n value of 2.52 for the red UC emission is less than the expected $n = 3$ implies that a two-photon process is involved to induce the red UC emission besides a three-photon process in Hf/Er-8.0/1.0.

Fig. 3 displays the energy levels of Er^{3+} ion as well as the proposed UC mechanisms under 1550 nm excitation. As for the three-photon process to populate the green and red UC emissions, Er^{3+} ions at the ground $^4I_{15/2}$ state absorb three 1550 nm photons and get excited to the upper $^2H_{11/2}$ state through the ground state absorption (GSA: $^4I_{15/2}$ + 0.8 eV (6451 cm^{-1}) photon $\rightarrow {}^4I_{13/2}$) and excited state absorption (ESA1: $^4I_{13/2}$ + 0.8 eV photon $\rightarrow {}^4I_{9/2}$) and ESA3 ($^4I_{9/2}$ + 0.8 eV photon $\rightarrow {}^2H_{11/2}$). The red emitting $^4F_{9/2}$ state is populated via GSA, ESA1 and ESA2 ($^4I_{11/2}$ + 0.8 eV photon $\rightarrow {}^4F_{9/2}$). According to $n = 2.52$, the two-photon process to populate the red UC emission in Hf/Er-8.0/1.0 can be described as follows: after the GSA process, the cross relaxation (CR) process of $^4I_{13/2} + {}^4I_{13/2} \rightarrow {}^4I_{9/2} + {}^4I_{15/2}$, substituting for one-photon process of ESA1,

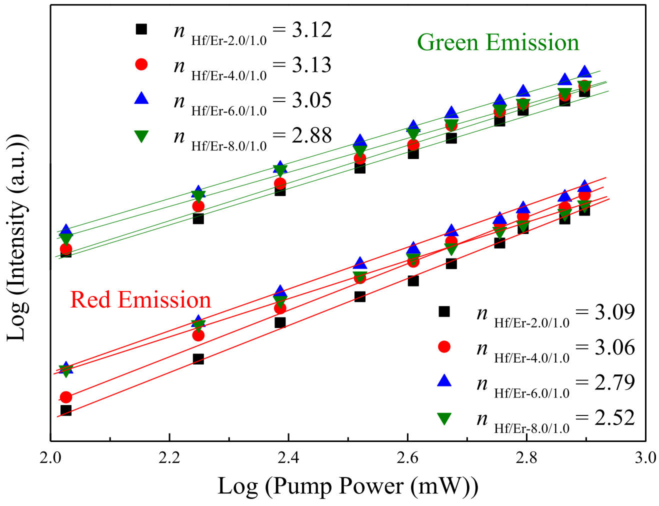

Fig. 2. A double-logarithmic plot of power dependence of green and red UC emission intensities for Hf/Er:$LiNbO_3$ under 1550 nm excitation. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)