Synthesis and up-conversion luminescence of Yb^{3+} – Ho^{3+} co-doped $\text{Na}(\text{Y}_{1.5}\text{Na}_{0.5})\text{F}_6$ nanorods

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Abstract. We present the optical up-conversion (UC) study for Yb^{3+} – Ho^{3+} co-doped $\text{Na}(\text{Y}_{1.5}\text{Na}_{0.5})\text{F}_6$ nanorods synthesized by employing a facile hydrothermal method. Numbers of Ho^{3+} ion up-conversion emissions have been observed under 980 nm infrared diode laser excitation. Three UC emissions of interest, ultraviolet, violet and blue, are specially identified at 359, 387, 418 and 483 nm, corresponding to $^5G_5'/^3H_6 \rightarrow ^5I_8$, $^5G_4/^3K_7 \rightarrow ^5I_8$, $^5G_5 \rightarrow ^5I_8$ and $^5F_3/^5F_2/^3K_8 \rightarrow ^5I_8$ transitions, respectively. It is also found that the centre wavelength of blue UC emission shifts to 475 nm gradually as Ho^{3+} concentration decreases. Lastly, a brief analysis about UC mechanism is demonstrated according to the experimental results.

Keywords. $\text{Na}(\text{Y}_{1.5}\text{Na}_{0.5})\text{F}_6$; nanorods; up-conversion.

1. Introduction

In recent years, rare-earth (RE) doped nanoscale materials have attracted tremendous interest due to their potential for applications in nanoscale optics and optoelectronics such as optical sensor, compact solid-state lasers and especially biological luminescent labels (Luo and Cao 2007; Wang *et al* 2009, 2010; Ji *et al* 2010; Zheng *et al* 2010). So far, UC emission properties of various RE^{3+} (Er^{3+} , Tm^{3+} , Yb^{3+} , Ho^{3+} and Gd^{3+}) ions doped fluoride materials at their strong frequency UC emissions have been well studied (Boyer *et al* 2007; Kumar *et al* 2009; Kim *et al* 2009; Cao *et al* 2010a, b). Among these trivalent RE ions, Ho^{3+} is of great interest as a result of its abundant energy levels, which are corresponding to the wide emissions spanning from ultraviolet to infrared. However, most of the researches are mainly focused on visible UC emissions (Martín *et al* 1998) and few investigations with attention paid onto short-wavelength UC emissions of Ho^{3+} ions have been reported. Recently, violet UC emission have been observed in nanoglass-ceramics comprising of $\text{Yb}^{3+}/\text{Ho}^{3+}$ co-doped NaYF_4 nanocrystals under 980 nm laser excitation (Santana-Alonso *et al* 2010). Chen *et al* (2010) reported the shortest wavelength (247 and 290 nm) of UC emissions in $\text{Yb}^{3+}/\text{Ho}^{3+}$ co-doped hexagonal NaYF_4 powders under diode laser excitation of 970 nm (Chen *et al* 2010).

Among all the UC host materials, fluoride hosts are strong and efficient up-converters owing to low phonon energies, adequate thermal and environmental stability (Wang *et al* 2008a, b). NaYF_4 (Boyer *et al* 2006; Cao *et al* 2010a, b), as a kind of fluoride host, is regarded as one of the most excellent host lattices for UC luminescence. It is known that NaYF_4

mainly exhibits two polymorphic forms, which are cubic and hexagonal phases. Previous studies showed that the hexagonal phase of NaYF_4 is much better than cubic phase NaYF_4 in UC luminescence (Liu *et al* 2006). Recently reported that NaYF_4 with different phase, shape and size have been synthesized by tuning the hydrothermal temperature, time and amount of NaOH (Zhang *et al* 2009).

In this work, we report highly uniform Yb^{3+} – Ho^{3+} co-doped hexagonal $\text{Na}(\text{Y}_{1.5}\text{Na}_{0.5})\text{F}_6$ one-dimensional nanorods synthesized using a simple hydrothermal approach. Under 980 nm excitation, as-prepared nanorods emit ultraviolet-to-visible UC fluorescence. The corresponding UC mechanisms have been proposed and discussed.

2. Experimental

Rare-earth nitrates $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Ho}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Yb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were of high purity (>99.99%) and other chemicals like NaF, NaOH, ethanol and oleic acid were of analytical grade. The samples used in this work were prepared by facile hydrothermal method, which can be referred to in Wang and Li (2007) and Zhang *et al* (2007) with some subtle modifications. First, accurately weighed 0.35 g (8.75 mmol) of NaOH, 8 ml oleic acid (90 wt%) and 12 ml ethanol were mixed well to get a white viscous solution. Then, 8 ml of NaF (0.5 M) solution and 1.5 ml (1.2 mmol) of rare-earth nitrate were added into the solution with vigorous stirring. After 30 min aging, the resulting solution was transferred into 25 ml teflon bottle held in a stainless steel autoclave, sealed and hatched at 170 °C for 24 h. When the system was naturally cooled down to room temperature, the obtained products were washed with ethanol and deionized

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water in sequence for several times to remove oleic acid and other remnants and then dried at 60 °C for another 24 h.

The crystal structures and phase purity of the sample were examined by X-ray diffraction (XRD) with Cu K α radiation ($\lambda = 1.5406$ Å) in the range of $10^\circ \leq 2\theta \leq 85^\circ$. Morphology and size of the samples were characterized by scanning electron microscopy (SEM). UC spectra were picked by spectrophotometer under 980 nm laser excitation with variable power. All measurements were performed at room temperature.

3. Results and discussion

Figure 1(a) shows SEM image of the as-prepared nanorods. These nanorods display uniform morphology with about 1260 nm in length and 280 nm in diameter. XRD pattern of the as-prepared NaY_{0.8-x}Yb_{0.2}Ho_xF₆ ($x = 0.25\%$) in figure 1(b) exhibits that sample crystallized in the hexagonal β -Na(Y_{1.5}Na_{0.5})F₆ structure with space group $P6_3/m$,

Figure 1. (a) SEM image of Na(Y_{1.5}Na_{0.5})F₆: Yb³⁺, Ho³⁺ nanorods and (b) XRD pattern of as-prepared Na(Y_{1.5}Na_{0.5})F₆ nanorods co-doped with 20 mol% Yb³⁺ and 0.25 mol% Ho³⁺ ions.

is consistent with the standard X-ray diffraction (JCPDS 16-0334). No second phase is detected in XRD pattern, revealing that the high pure hexagonal phase of Na(Y_{1.5}Na_{0.5})F₆ has been fabricated. The lattice constants were calculated in terms of XRD data and the lattice is of size $a = b = 6.00$ and $c = 3.49$ Å.

Figure 2 shows UC emission spectrum of Yb³⁺/Ho³⁺ (20/0.25 mol%) co-doped Na(Y_{1.5}Na_{0.5})F₆ nanorods, excited by 980 nm diode laser (power ≈ 238 mW). An intense green emission centred at about 539 nm is observed, which is ascribed to the $^5S_2/^5F_4 \rightarrow ^5I_8$ transition of Ho³⁺. The red and blue emissions approximately centred at 750, 645 and 483 nm are assigned to $^5S_2/^5F_4 \rightarrow ^5I_7$, $^5F_5 \rightarrow ^5I_8$ and $^5F_3/^5F_2/^3K_8 \rightarrow ^5I_8$ transitions, respectively. Besides red, green and blue emissions, violet and ultraviolet UC emissions at 418, 387, 359 nm corresponding to $^5G_5 \rightarrow ^5I_8$, $^5G_4/^3K_7 \rightarrow ^5I_8$ and $^5G_5/^3H_6 \rightarrow ^5I_8$ transitions of Ho³⁺ ions are also detected. The inset of figure 2 shows a digital photograph of UC luminescence in ethanol solutions (1 wt%) of Na(Y_{1.5}Na_{0.5})F₆: 20% Yb³⁺, 0.25% Ho³⁺.

To understand UC emission mechanisms, we studied the pump power dependence of luminescence intensity. Generally, for an unsaturated UC luminescence, the number of photons that needs to populate the upper emitting state can be estimated by the following relation: $I_{UC} \propto I_p^n$, where I_{UC} is the UC luminescence intensity, I_p the pumping power and n the number of pumping photons required (Cao *et al* 2010a, b). Figure 3 shows double-logarithmic plots of I_{UC} vs I_p . The slopes of the linear fittings are 1.63, 1.81, 1.66 and 2.58, respectively for 750, 645, 539 and 483 nm. The 483 nm band exhibits approximately cubic power law behaviours vs pumping power, indicating this emission is obtained through a three-photon process. The other three emission bands approximately exhibit quadratic power law behaviours vs

Figure 2. Room temperature UC emission spectrum of Na(Y_{1.5}Na_{0.5})F₆ co-doped with 20 mol% Yb³⁺ and 0.25 mol% Ho³⁺ under 980 nm excitation at 238 mW. Inset shows photograph of nanorods dissolved in ethanol and excited with 980 nm laser.

Figure 3. Double-logarithmic plot of excitation power dependent luminescence intensity in 20 mol% Yb^{3+} and 0.25 mol% Ho^{3+} co-doped $\text{Na}(\text{Y}_{1.5}\text{Na}_{0.5})\text{F}_6$ nanorods.

pumping power, indicating these processes are caused by two-photon absorption.

UC mechanisms in $\text{Yb}-\text{Ho}$ system have been studied in many host materials (Gouveia-Neto *et al* 2008; Naccache *et al* 2009). Figures 4 and 5 shows partial energy level diagrams of Yb^{3+} and Ho^{3+} ions as well as possible proposed UC mechanism. First, Yb^{3+} ions are excited to $^2F_{5/2}$ level through ground state absorption process when 980 nm photon is absorbed. After that, via subsequent non-resonant excited state absorption (ESA) and energy transfer (ET) processes, Ho^{3+} ions are excited to 5S_2 , 5F_4 levels. Radiation emissions from 5S_2 , 5F_4 levels to ground state 5I_8 with green emission at 540 nm or to 5I_7 level with red emission at 750 nm. On the other side, from 5S_2 , 5F_4 levels, a third pump photon is absorbed to populate 5G_3 level and then decays to ($^5G'_5$, 3H_6), (5G_4 , 3K_7), 5G_5 and (5F_3 , 5F_2 , 3K_8) levels by non-radiative multi-phonon relaxation (Santana-Alonso *et al* 2010), with corresponding violet, blue emissions at 359, 387, 418 and 484 nm when ions de-excite to the ground state 5I_8 . In addition, there are two ways that may be responsible for the population of 5F_5 level. One is by non-radiative multi-phonon relaxation process from 5F_4 , 5S_2 levels. The other is that Ho^{3+} in 5I_6 excited state relaxes non-radiatively to the intermediate level 5I_7 . Ho^{3+} in 5I_7 level absorbs a second pumping photon through ESA/ET process and reaches 5F_5 level.

UC spectra of as-prepared $\text{Na}(\text{Y}_{1.5}\text{Na}_{0.5})\text{F}_6$ nanorods with fixed Yb^{3+} concentration and variable Ho^{3+} content were also investigated. From figure 4(a), the intensity of all emission bands were observed to increase as Ho^{3+} concentration increases. Moreover, for blue emission, the peak of wavelength shifts to 475 nm, when Ho^{3+} ions concentration decreases to 0.05 mol%. Blue co-operative UC emission around 475 nm has been reported in Yb^{3+} doped hexagonal NaYF_4 crystals (Wang *et al* 2008a, b). We also observed blue emission centred at 475 nm in $\text{Na}(\text{Y}_{1.5}\text{Na}_{0.5})\text{F}_6:\text{Yb}^{3+}$ (20 mol%) under 980 nm excitation. It is explained that the blue emission luminescence is

Figure 4. (a) Room temperature UC emission spectra of $\text{Na}(\text{Y}_{1.5}\text{Na}_{0.5})\text{F}_6:\text{Yb}^{3+}/\text{Ho}^{3+}$ (20/0.05–1 mol%). Samples were excited at 980 nm with 73 mW laser and (b) UC emission peak intensity ratios, $I_{750\text{nm}}/I_{645\text{nm}}$ and $I_{539\text{nm}}/I_{645\text{nm}}$ as a function of Ho^{3+} concentration.

Figure 5. Energy-level diagram of $\text{Yb}^{3+}-\text{Ho}^{3+}$ ions system and possible mechanism for UC luminescence.

caused by the simultaneous radioactive relaxation of a pair of excited Yb^{3+} ions accompanied by a photon in the following process (Nakazawa and Shionoya 1970): $^2F_{5/2}(\text{Yb}^{3+}) + ^2F_{5/2}(\text{Yb}^{3+}) \rightarrow ^2F_{7/2}(\text{Yb}^{3+}) + ^2F_{7/2}(\text{Yb}^{3+}) + h\nu$. So in

$\text{Yb}^{3+}/\text{Ho}^{3+}$ co-doped $\text{Na}(\text{Y}_{1.5}\text{Na}_{0.5})\text{F}_6$ nanorods, with Ho^{3+} ions decreasing, the densities of $\text{Yb}^{3+}-\text{Yb}^{3+}$ ion pairs would be correspondingly increased, so that they could lead the centre wavelength of blue emission shifts to 475 nm gradually. In addition, the peak intensity ratios, $I_{539\text{nm}}/I_{645\text{nm}}$ and $I_{750\text{nm}}/I_{645\text{nm}}$ were depicted in figure 4(b). With the increase of Ho^{3+} concentration, these ratios increase gradually. ET probability (S) can be written as $S = N_{\text{D}}N_{\text{A}}W_{\text{ET}}$, where N_{D} and N_{A} are the densities of donor and acceptor states and W_{ET} represents ET rate (Xiao *et al* 2004). It is obvious that as donor Ho^{3+} ions increase, the probability of ET would be increased correspondingly. Additionally, $^5\text{F}_5$ state via non-radiative decaying from $^5\text{F}_4$, $^5\text{S}_2$ levels requires several phonons to bridge the gap between these energy levels and does not contribute significantly to the enhancement of $^5\text{F}_5$ red emission (Naccache *et al* 2009). As a result, 539 and 750 nm emissions increase rather than 650 nm.

4. Conclusions

In conclusion, $\text{Yb}^{3+}/\text{Ho}^{3+}$ co-doped $\text{Na}(\text{Y}_{1.5}\text{Na}_{0.5})\text{F}_6$ nanorods were synthesized by simple hydrothermal method. Under 980 nm excitation, ultraviolet-to-red UC emissions were observed. In addition, UC mechanism was discussed. For the $\text{Yb}^{3+}/\text{Ho}^{3+}$ co-doped $\text{Na}(\text{Y}_{1.5}\text{Na}_{0.5})\text{F}_6$ nanorods, ultraviolet, violet, blue, green and red UC fluorescence can be attributed to the transitions $^5\text{G}'_5/{}^3\text{H}_6 \rightarrow ^5\text{I}_8$, $^5\text{G}_4/{}^3\text{K}_7 \rightarrow ^5\text{I}_8$, $^5\text{G}_5 \rightarrow ^5\text{I}_8$, $^5\text{F}_3/{}^5\text{F}_2/{}^3\text{K}_8 \rightarrow ^5\text{I}_8$, $^5\text{S}_2/{}^5\text{F}_4 \rightarrow ^5\text{I}_8$, $^5\text{F}_5 \rightarrow ^5\text{I}_8$ and $^5\text{S}_2/{}^5\text{F}_4 \rightarrow ^5\text{I}_7$ of Ho^{3+} , respectively. Due to co-operative UC, the peak of blue emission shifts to lower frequency with decreasing Ho^{3+} concentration. Our results indicate that this kind of rare-earth doped hexagonal $\text{Na}(\text{Y}_{1.5}\text{Na}_{0.5})\text{F}_6$ nanorods have promising applications in nanoscale optical sensors, displays and solid-state lasers.

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