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Highly efficient cooperative up-conversion of Yb^{3+} in $NaYF_4$

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Abstract Strong blue cooperative up-conversion emission around 475 nm has been observed in Yb^{3+}-doped hexagonal $NaYF_4$. The influence of concentration of the Yb^{3+} ion on the luminescence intensity is investigated. It is found that the sample shows the strongest cooperative luminescence when the Yb^{3+} ion concentration is 75%. The investigation shows that hexagonal $NaYbF_4$ is an efficient blue up-converted phosphor, which might be potentially applicable in three-dimensional solid-state fluorescence display.

Introduction

Rare-earth (RE) activated materials are widely applied to phosphor, fiber amplifiers, solid-state laser, etc. [1, 2]. Among the RE ions used as luminescence centers, Yb^{3+} ion is especially attractive because high-power InGaAs diode lasers are available to directly pump the Yb^{3+} absorption band around 980 nm. Yb^{3+} ion consists of only two levels, and has only one electronic excited state that is located in the near infrared region [3–5]. The strong electron–phonon coupling of Yb^{3+} ion in glasses or crystals results in the broadband character of the optical transition [6, 7]. Due to these unique features, high-efficiency, high-power, tunability and mode locking have been reported for InGaAs diode laser pumped Yb^{3+} lasers [4, 5]. On the other hand, the Yb^{3+}–Yb^{3+} cooperative up-conversion in crystals as well as in glasses has also attracted much attention since it was first observed by Nakazawa and Shionoya in $YbPO_4$ [8–11]. This special up-conversion is interesting, for it locate at the blue region, which has potential application in three-dimensional solid-state fluorescence display [12, 13].

Hexagonal $NaYF_4$ is one of the most suitable hosts for rare earth to realize green, blue and red up-conversion [14–16]. Up-converted emissions of $Er^{3+}$and Tm^{3+} ions sensitized by Yb^{3+} ions in $NaYF_4$ are widely reported [17–20]. However, the Yb^{3+} cooperative up-conversion process in the hexagonal $NaYF_4$ has not been reported as yet. In this work, we investigate the blue Yb^{3+}–Yb^{3+} cooperative up-conversion in the Yb^{3+}-doped hexagonal $NaYF_4$ under excitation of 980 nm diode laser.

Experimental

The samples used in this work were prepared by using high-temperature solid reaction process. The high-purity starting materials were NaF, YF_3 and YbF_3. The samples were synthesized in molar composition of $NaY_{1-x}Yb_xF_4$, where x was varied from 0.05 to 1. Accurately weighed 5-g batches of raw materials were thoroughly mixed and moved into corundum crucible. The batches were heated at 700 °C for 6 h in an electric furnace under a hydrogen fluoride gas atmosphere. After the heating treatment the samples were naturally cooled to the room temperature.

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Up-conversion emission spectra were measured from 450 to 500 nm by exciting the samples with a 980 nm diode laser at room temperature. The dependence of the up-converted emission intensity on pumping powers for different samples was obtained by changing the excitation powers. All the measurements were performed at the same condition, so as to ensure the relative luminescence intensity comparable.

Results and discussion

Structures of the samples were investigated by X-ray diffraction, indicating that all the samples have crystallized into hexagonal $NaYF_4$ [21]. The cell parameters a and c of some samples have been calculated in terms of the X-ray diffraction data. As is shown in Fig. 1, the unit cell parameters a (Å) and c (Å) decrease linearly with the increasing of Yb^{3+} concentration, obeying the Vegard's rule [22]. The result reveals that that the Yb^{3+} ions can be easily doped into $NaYF_4$ lattice through the high-temperature solid reaction route.

Figure 2 shows the up-conversion emission spectra of the $NaY_{1-x}Yb_xF_4$ ($x = 5\%$) under 980 nm excitation. The sensitized up-conversion emission bands centered on 475 nm was observed under 980 nm excitation. The blue emission band is strong enough so that it can be clearly seen by the naked eye as the excitation power is low as 50 mw/mm^2.

Figure 3 shows the dependence of emission intensity upon the YbF_3 concentration under 980 nm excitation. One may find that the intensity of the 475 nm emission band increase with the increase of Yb^{3+} concentration, exhibits a maximum value when the Yb^{3+} concentration is approximately 75 mol%, and then decrease quickly with the further enhancement of the Yb^{3+} concentration.

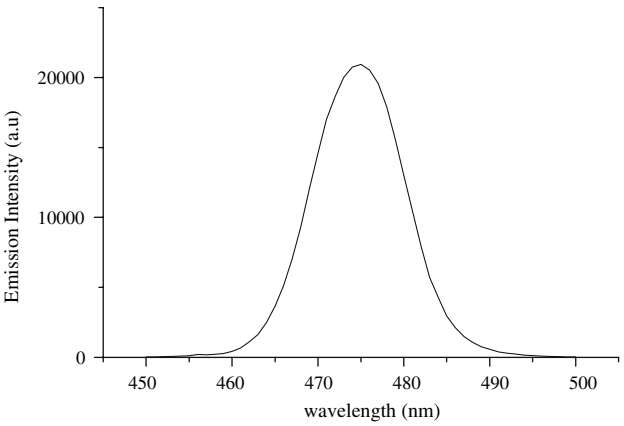

Fig. 2 Up-conversion luminescence spectrum in the $NaY_{1-x}Yb_xF_4$ ($x = 5\%$) under 980 nm excitation

It is well known, the visible up-conversion emission intensity I_{UC} is proportional to the Nth power of the IR excitation intensity (pumping power) I_p:

$$I_{UC} \propto I_p^N$$

where $N = 1, 2, 3\ldots$, representing the order of multiphoton transitions being a number of IR quanta absorbed per one visible photon emission [23–26]. The excitation power dependence of the blue (475 nm) cooperative up-conversion luminescence in the $NaY_{1-x}Yb_xF_4$ ($x = 5\%$) was shown in Fig. 4. The output slope for 475 nm emission band is 1.81. The emission band exhibits approximately quadratic power law behaviors against excitation power, indicating that the emission is a two-photon process.

The blue emission luminescence is ascribed to the simultaneous de-excitation of pairs of Yb^{3+} ions [27]. After the Yb^{3+} ions are excited from the $^2F_{7/2}$ level to the $^2F_{5/2}$ level under 980 nm pumping. The excited Yb^{3+}–Yb^{3+} ion

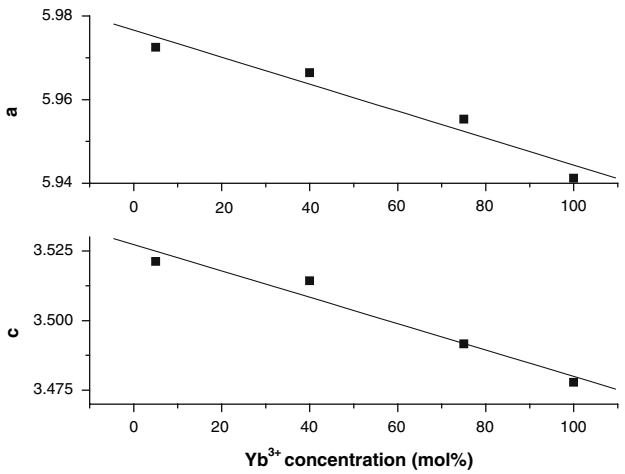

Fig. 1 Unit cell parameters a (Å) and c (Å) vs. Yb^{3+} concentration in hexagonal $NaY_{1-x}Yb_xF_4$ (x = 0.05, 0.4, 0.75, 1.00)

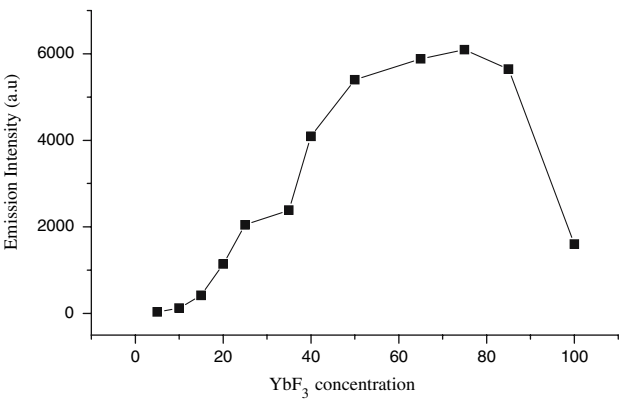

Fig. 3 Dependence of emission intensity upon the YbF_3 concentration in the $NaY_{1-x}Yb_xF_4$ ($x = 5\%$) under 980 nm excitation

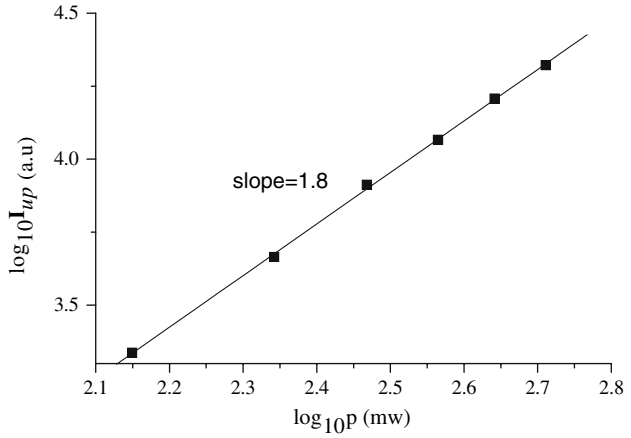

Fig. 4 Double-logarithmic plot of excitation power dependence of up-conversion luminescence intensity in the $NaY_{1-x}Yb_xF_4$ ($x = 5\%$)

pairs can radiate visible a 475 nm blue luminescence by following process:

$$^2F_{5/2}(Yb^{3+}) + ^2F_{5/2}(Yb^{3+}) \rightarrow ^2F_{7/2}(Yb^{3+}) + ^2F_{7/2}(Yb^{3+}) + hv$$

This phenomenon is called cooperative up-conversion [28, 29]. The cooperative phenomenon occurs when the distance between two excited Yb^{3+} ions is short enough.

As can be seen from Fig. 3, the intensity of the 475 nm blue cooperative up-conversion luminescence decreases when the concentration of Yb^{3+} ion is more than 75%. When the doping concentration is enough high, the following energy transfer between the Yb^{3+} ions may efficiently occur:

$$^2F_{5/2}(Yb^{3+}) + ^2F_{7/2}(Yb^{3+}) \rightarrow ^2F_{7/2}(Yb^{3+}) + ^2F_{5/2}(Yb^{3+})$$

Obviously, this energy transfer might reduce the excited Yb^{3+}–Yb^{3+} ion pairs, decreasing the probability of cooperative up-conversion. As a result, the cooperative up-conversion luminescence decreases when the concentration of Yb^{3+} ion is too high.

Conclusion

Blue cooperative up-conversion emission centered at 475 nm was observed in the Yb^{3+}-doped hexagonal $NaYF_4$. The power and concentration dependent on up-conversion behaviors have been investigated. The blue emission exhibits approximately quadratic power law behaviors against excitation power, showing that a two-photon process is responsible for the emission. The sample shows the strongest emission when the concentration of Yb^{3+} ions is 75%. A luminescence quenching takes place when the concentration of Yb^{3+} ions is above 75%. It is believed that the energy transfer of $^2F_{5/2}(Yb^{3+}) + ^2F_{7/2}(Yb^{3+}) \rightarrow ^2F_{7/2}(Yb^{3+}) + ^2F_{5/2}(Yb^{3+})$ can reduce the excited Yb^{3+}–Yb^{3+} ion pairs, resulting in the decrease the probability of cooperative up-conversion at higher doping concentration.

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