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Upconversion Luminescence from Ho^{3+} and Yb^{3+} Codoped α-$NaYF_4$ Single Crystals

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(Dated: Received on March 16, 2015; Accepted on April 27, 2015)

The Ho^{3+}/Yb^{3+} co-doped α-$NaYF_4$ single crystal was grown successfully for the first time by a modified Bridgman method in which KF was used as assisting flux and a large temperature gradient (70−90 °C/cm) of solid-liquid interface was adopted. Upconversion emissions at green ~544 nm, red ~657 and ~751 nm were obtained under 980 nm laser diode excitation. The intensity at ~544 nm was much stronger than those of ~657 and ~751 nm. The mechanisms of the upconversion emissions were investigated by studying the relationship between the upconversion intensity and pump power. The optimized Yb^{3+} concentration was about 8.08mol% when Ho^{3+} concentration was hold at about 1.0mol%. The results showed that Ho^{3+}/Yb^{3+} doped α-$NaYF_4$ single crystal was a possible candidate upconversion material for the green solid-state laser.

Key words: Ho^{3+}/Yb^{3+}, α-$NaYF_4$ single crystal, Fluorescent intensity, Upconversion

I. INTRODUCTION

Upconversion luminescence, which is a nonlinear process with the absorption of more than one longer wavelength photons and re-emission of a shorter wavelength photon, has attracted much attention since it was firstly reported in 1960s for its special use in potential applications in solid state lasers, biological fluorescence, telecommunications, sensors and volumetric displays [1−3]. In recent decades, much attention has been focused on upconversion luminescence of rare earth (RE) ions such as Er^{3+}/Yb^{3+}, Tb^{3+}/Yb^{3+} and Tm^{3+}/Yb^{3+} for their high upconversion efficiency [4−6]. Among the rare earth ions, the upconversion of Ho^{3+}/Yb^{3+} ions with a strong green emission due to the transition of Ho^{3+}:$(^5F_4+^5S_2)\rightarrow^5I_8$ has been experimentally realized by an energy transfer process from Yb^{3+} to Ho^{3+} ions, in which Yb^{3+} ions as the sensitizer can help to enhance the upconversion intensity of Ho^{3+} ions by its strong absorption of ~980 nm light [7].

The upconversion luminescence of rare-earth ions is also dependent on the host material. Fluorides have become the most investigated efficient upconversion materials for their low phonon energy [7, 8]. So far, $NaYF_4$ has been considered to be one of the most efficient upconversion materials [8]. In the case of Ho^{3+}/Yb^{3+} codoped $NaYF_4$, the studies of the upconversion materials were mainly on nanocrystals and powders [7]. As is well known, single crystals have lower scattering and better chemical durability compared to their powder forms. However, there are scarcely any reports about Ho^{3+}/Yb^{3+} doped upconversion $NaYF_4$ single crystals. There are two crystals of $NaYF_4$, one being cubic α-$NaYF_4$ and the other hexagonal β-$NaYF_4$. $NaYF_4$ single crystal is difficult to grow due to the complexity of NaF-YF_3 system phase equilibrium and the phase transition during the growth [9]. In our previous work, upconversion luminescences in Er^{3+}/Yb^{3+} and Tb^{3+}/Yb^{3+} doped $LiYF_4$ single crystals were studied, and the results showed that the single crystal had the advantage of higher quenching concentration of rare earth ions for upconversion luminescence compared with $LiYF_4$ nano-crystals [5].

In this work, α-$NaYF_4$ single crystals doped with various concentrations of Ho^{3+} and Yb^{3+} were grown by an improved Bridgman method using KF as flux. When KF was added into the starting components of NaF-YF_3, the phase equilibrium between NaF and YF_3 is significantly changed. With this change it becomes possible to crystallize only the composition of α-$NaYF_4$ phase from incongruent melt. The upconversion intensity dependence of pump power was studied to investigate the mechanism of the upconversion emissions.

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DOI:10.1063/1674-0068/28/cjcp1503042 ©2015 Chinese Physical Society

TABLE I Concentration of Ho^{3+} and Yb^{3+} ions in the crystals.

Samples	Er^{3+}/mol%	Yb^{3+}/mol%
1	0.998	0.00
2	0.999	3.02
3	0.998	5.04
4	0.998	8.08
5	0.999	15.15

II. EXPERIMENTS

The raw materials with a purity of 99.99% were prepared to grow fluoride single crystals according to the formula $(30NaF)$-$(18KF)$-$(52-x-yYF_3)$-$(xHoF_3)$-$(yYbF_3)$ (x=0.5, y=0, 1.5, 2.5, 4, 7.5), respectively. The powders were milled in a mortar for about 1 h. All the compounds were sintered in anhydrous HF air at 750 °C for 8 h to remove moisture and oxides in the mixture. The seed oriented along a-axis was put in the bottom of seed well and then the polycrystalline powders were filled into the Pt crucibles with size of ø10 mm×180 mm. Once completely sealed, the crucibles were put into a resistively heated vertical Bridgman furnace. The seeding temperature was about 770−820 °C, and the temperature gradient cross solid-liquid interface was 70−90 °C/cm while the growth speed was about 0.05−0.06 mm/h.

The X-ray diffraction (XRD) was measured using a XD-98X diffract meter (XD-3, Beijing). The emission spectra were obtained with a FLSP 920 type spectrometer (Edinburgh Co., England). The Ho^{3+} and Yb^{3+} concentrations in the α-$NaYF_4$ single crystal were measured by the inductive coupled plasma atomic emission spectroscopy (ICP-AES, PerkinElmer Inc., Optima 3000). All the measurements were performed at room temperature. Table I shows the concentrations of Ho^{3+} and Yb^{3+} in the samples.

III. RESULTS AND DISCUSSION

XRD patterns of the as-grown Ho^{3+}/Yb^{3+} doped α-$NaYF_4$ single crystals are shown in Fig.1. Insert of Fig.1 is the photo of the as-grown single crystal after the white portion at the top of the boule is removed, the white opaque section of the boule is mainly composed of KYF_4. The Ho^{3+} and Yb^{3+} ions substituted for the sites of Y^{3+} ions in α-$NaYF_4$ single crystal because of the identical valence state and similar size between Y^{3+} and doped rare earth ions. The initial and final parts of the crystal are designated A and B, respectively. When compared with JCPD card (No.77-2042), the XRD pattern does not show any significant peak shift or second phase, implying that the crystal of part A and B is purely cubic α-$NaYF_4$ phase. From the above XRD results, it suggests that the introduction of KF, HoF_3

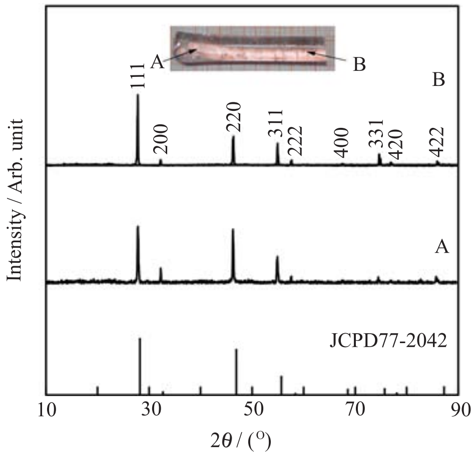

FIG. 1 XRD patterns of Ho^{3+}/Yb^{3+} co-doped α-$NaYF_4$ single crystal of different part. Insert is the photo of α-$NaYF_4$ single crystal.

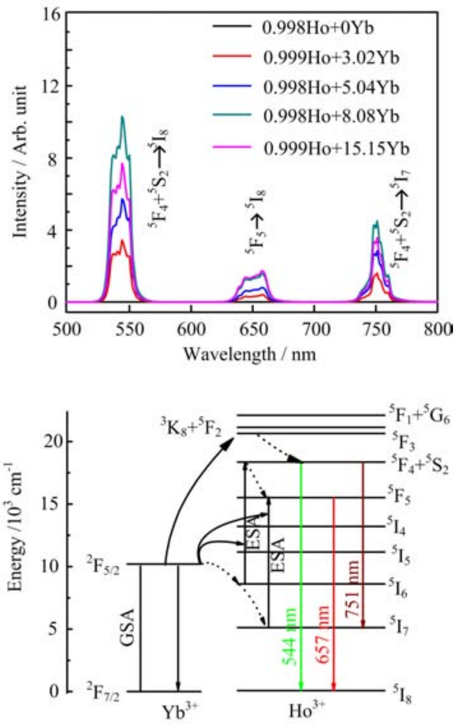

FIG. 2 (a) Comparison of the upconversion luminescence spectra of Ho^{3+}/Yb^{3+} codoped α-$NaYF_4$ single crystals under 980 nm excitation at room temperature. (b) Energy level diagram of Ho^{3+}/Yb^{3+} upconversion and energy transfer process in α-$NaYF_4$ single crystal.

and YbF_3 into NaF-YF_3 system does not change the structure of the grown α-$NaYF_4$ single crystal.

Figure 2 shows the upconversion luminescence spectra of Ho^{3+}/Yb^{3+} doped α-$NaYF_4$ single crystals with a fixed 1mol% Ho^{3+} concentration and 0mol%, 3.02mol%, 5.04mol%, 8.08mol%, 15.15mol% Yb^{3+} concentrations respectively under excitation of 980 nm laser diode.

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Three obvious bands at ∼544, ∼657 and ∼751 nm can be observed in Fig.2. In order to obtain comparable results, upconversion spectra of all samples were tested under the same experimental conditions. The possible upconversion processes of Ho^{3+}/Yb^{3+} co-doped materials have been reported [10, 11]. In order to explain the possible energy transfer process in the Ho^{3+}/Yb^{3+} doped α-$NaYF_4$ single crystal, energy level diagram is shown in Fig.2(b). When pumped by 980 nm laser, the electrons of Yb^{3+} ions at $^2F_{7/2}$ are promoted to Yb^{3+}:$^2F_{5/2}$ state. Then energy transfer process takes place from excited Yb^{3+} ions to the Ho^{3+}:$^5I_6$. The electrons at Ho^{3+}:$^5I_6$ state are promoted to $^5F_4$+$^5S_2$ or dropped to $^5I_7$ through excited state absorption (ESA) or non-radiative relaxation, respectively. Meanwhile, two Yb^{3+}:$^2F_{5/2}$ can transfer energy to one Ho^{3+}:$^5I_8$ and promote it to Ho^{3+}:$^5F_3$, then the Ho^{3+}:$^5F_3$ ion can be promoted to Ho^{3+}:$^5F_4$+$^5S_2$ through nonradiative process. As shown in Fig.2 the $^5F_4+^5S_2\rightarrow^5I_8$ and $^5F_4+^5S_2\rightarrow^5I_7$ radiative transitions lead to 544 nm green emission and 751 nm red emission, respectively. At the same time, the electrons at Ho^{3+}:$^5I_7$ state are promoted to $^5F_5$ through ESA. The 657 nm red emission is the result of $^5F_5\rightarrow^5I_8$ transition. As sensitizer, the presence of Yb^{3+} ions enhances the upconversion emission of Ho^{3+} ion significantly. From Fig.2, the upconversion intensity increases gradually as the concentration of Yb^{3+} increases from 3.02mol% to 8.08mol%, and reaches a maximum when the Ho^{3+} and Yb^{3+} ion concentrations are 0.998mol% and 8.08mol% respectively. When the Yb^{3+} concentration further increases from 8.08mol% to 15.15mol%, the intensity of upconversion emission decreases dramatically due to the concentration quenching of Yb^{3+} ion. Compared with Ho^{3+}/Yb^{3+} doped $NaYF_4$ nano-crystal phosphors [7], Ho^{3+}/Yb^{3+} doped α-$NaYF_4$ single crystal exhibits stronger red upconversion luminescence at ∼751 nm although they both show similar emission at around 544 and 657 nm. This stronger red upconversion luminescence may be due to the stronger effect of the crystal field in the α-$NaYF_4$ single crystal on rare earth ions. It can also be noted from Fig.2 that the intensity of upconversion luminescence increases almost linearly as Yb^{3+} concentration increase from 0 to 8mol%. This suggests that the distribution of rare earths in α-$NaYF_4$ single crystal is homogenous, which is important for improving upconversion luminescence efficiency and preparing relevant optical devices.

In order to explore the upconversion mechanism on green and red emissions of Ho^{3+}/Yb^{3+} codoped α-$NaYF_4$ single crystal, the pump power dependence of green and red emission intensities for 0.998mol% Ho^{3+} and 8.08mol% Yb^{3+} co-doped α-$NaYF_4$ single crystal was measured and shown in Fig.3. It is well known that the upconversion luminescence intensity (I_{UC}) is proportional to certain power n of the excitation power (I_P) as $I_{UC}\propto I_P^n$, where n is the number of absorbed photons required to populate the emission states [12]. Plotted on double logarithmic scales, the emission intensities at ∼544, ∼657, and ∼751 nm due to the transition of $^5F_4+^5S_2\rightarrow^5I_7$, $^5F_5\rightarrow^5I_8$, and $^5F_4+^5S_2\rightarrow^5I_8$, respectively, have fitted slopes of 1.86, 1.61, and 1.58. Due to experimental error and cross-relax progresses, the values of n are not exactly integer. Within the acceptable experimental error, we can calculate the value of n are near to 2. The calculated n values indicate a two-photon upconversion process involved [13]. In this study, probably due to the presence of abundant sensitizer Yb^{3+} ions in the α-$NaYF_4$ single crystals, the slope of upconversion intensity stays linear even when the pump power increases to 600 mW. As a result, the Ho^{3+}/Yb^{3+}-doped α-$NaYF_4$ single crystal can be a promising upconversion laser material for its high efficiency and excellent linearity at high photon flux.

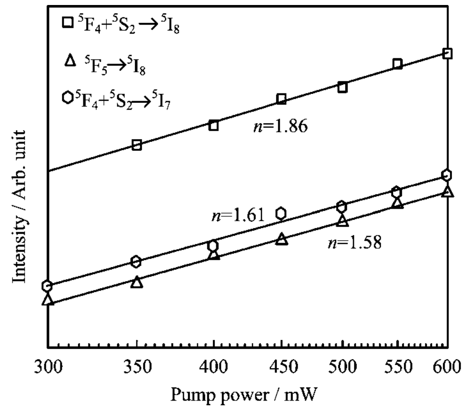

FIG. 3 lg-lg dependences of the upconversion intensities of 0.998mol% Ho^{3+} and 8.08mol% Yb^{3+} co-doped α-$NaYF_4$ single crystal at 544, 657, and 751 nm emissions as a function of the excitation power at 980 nm.

IV. CONCLUSION

Ho^{3+}/Yb^{3+}-doped α-$NaYF_4$ single crystals can be grown by a modified Bridgman method. KF is proven to be an effective flux for the crystal growth from NaY-YF_3 system. The enhanced up-conversion emissions at 544 nm green, 657 and 751 nm NIR can be obtained in the Ho^{3+}/Yb^{3+} co-doped α-$NaYF_4$ single crystal under excitation of a 980 nm diode laser. When the Ho^{3+} concentration is held at ∼1.0mol%, the upconversion emission reaches maximum intensity when the concentration of Yb^{3+} is about 8.08mol%. The present results indicate potential applications of Ho^{3+}/Yb^{3+} doped α-$NaYF_4$ single crystals in optical devices of upconversion luminescence.

V. ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (No.51472125, No.51272109)

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and K. C. Wong Magna Fund in Ningbo University.

[1] N. Bloembergen, Phys. Rev. Lett. **2**, 84 (1959).
[2] S. Heer, M. Wermuth, K. Krämer, D. Ehrentraut, and H. U. Güdel, J. Lumen. **94**, 337 (2001).
[3] H. Guo, Y. M. Qiao, J. F. Zheng, and L. H. Zhao, Chin. J. Chem. Phys. **21**, 233 (2008).
[4] J. S. Kumar, K. Pavani, M. P. F. Graça, and M. J. J. Soares, J. Alloy. Compd. **617**, 108 (2014).
[5] L. Fu, H. Xia, Y. Dong, S. Li, X. Gu, J. Zhang, D. Wang, H. Jiang, and B. J. Cheng, J. Alloy. Compd. **617**, 584 (2014).
[6] S. Fukushima, T. Furukawa, H. Niioka, M. Ichimiya, J. Miyake, M. Ashida, A. Tsutomu, and M. Hashimoto, Micron **67**, 90 (2014).
[7] X. P. Chen, W. J. Zhang, and Q. Y. Zhang, Physica B **406**, 1248 (2011).
[8] F. Vetrone, R. Naccache, A. Zamarron, A. Juarranz de la Fuente, F. Sanz-Rodríguez, L. Martinez Maestro, J. Daniel, G. José, and J. A. Capobianco, Acs Nano **4**, 3254 (2010).
[9] R. E. Thoma, G. M. Hebert, H. Insley, and C. F. Weaver, Inorg. Chem. **2**, 1005 (1963).
[10] P. Du, L. Luo, and J. S. Yu, J. Alloy. Compd. **632**, 73 (2015).
[11] M. Xing, W. Cao, H. Zhong, Y. Zhang, X. Luo, Y. Fu, W. Feng, T. Pang, and X. Yang, J. Alloy. Compd. **509**, 5725 (2011).
[12] F. E. Auzel, P. IEEE **61**, 758 (1973).
[13] M. Pollnau, D. R. Gamelin, S. R. Lüthi, H. U. Güdel, and M. P. Hehlen, Phys. Rev. B **61**, 3337 (2000).

DOI:10.1063/1674-0068/28/cjcp1503042
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