Tb^{3+}/Yb^{3+} 共掺 α-NaYF$_4$ 单晶近红外到可见光的合作上转换发光

张加忠^1，夏海平^1，姜永章^1，杨 硕^1，谷雪梅^1，章践立^1，江浩川^2，陈宝玖^3

(1. 宁波大学光电子功能材料重点实验室，宁波 浙江 315211；
2. 中国科学院宁波材料与技术工程研究所，宁波 浙江 315211；
3. 大连海事大学物理系，大连 辽宁 116026)

摘 要：用 980 nm 的近红外激光泵浦 Bridgman 方法生长的 Tb^{3+}/Yb^{3+}共掺的 α-NaYF$_4$ 单晶，研究了其上转换荧光以及荧光强度与泵浦功率的关系。结果表明：2 个或者 3 个激发态的 Yb^{3+}离子传递能量给 1 个 Tb^{3}离子并引发了双光子或三光子上转换。高效的三光子上转换的 381、414、435 和 462 nm 光和双光子上转换的 481、541、587、651、659 和 668 nm 光分别产生于 Tb^{3+}离子的 $^5D_3{\rightarrow}^7F_J$ (J = 6, 5, 4, 3)和 $^5D_4{\rightarrow}^7F_J$ (J = 6, 5, 4, 3, 2,1)辐射跃迁。现有实验下，当 Tb^{3+}的掺杂量为 0.52%(摩尔分数)时，Yb^{3+}的最佳掺杂量为 7.98%，并可以进一步增加。以上结果表明了 Tb^{3+}/Yb^{3+}共掺的 α-NaYF$_4$ 单晶在上转换绿光固体激光材料方面的潜在应用。

关键词：氟化钇钠单晶；铽/镱共掺；上转换发光；稀土发光

Cooperative Near-Infrared to Visible Up-conversion Luminescence of Tb^{3+}/Yb^{3+} Co-doped α-NaYF$_4$ Single Crystal

ZHANG Jiazhong^1, XIA Haiping^1, JIANG Yongzhang^1, YANG Shuo^1, GU Xuemei^1, ZHANG Jianli^1,
JIANG Haochuan^2, CHEN Baojiu^3

(1. Key Laboratory of Photoelectronic Materials, Ningbo University, Ningbo 315211, Zhejiang, China;
2. Ningbo Institute of Materials Technology and Engineering, the Chinese Academy of Sciences, Ningbo 315211, Zhejiang, China;
3. Department of Physics, Dalian Maritime University, Dalian 116026, Liaoning, China)

Abstract: The up-conversion (UC) luminescence and the pump power dependence on the UC emissions of the Tb^{3+}/Yb^{3+} co-doped α-NaYF$_4$ single crystals grown by the Bridgman method under the excitation of near-infrared light at 980 nm were investigated. The results show that three or two excited Yb^{3+} ions transferring the energy to a Tb^{3+} ion can lead to the three- or two-photon UC process. The efficient three- photon UC emission at 381, 414, 435 and 462 nm and the two-photon UC emissions at 481, 541, 587, 651, 659 and 668 nm occur due to the transitions $^5D_3{\rightarrow}^7F_J$ (J = 6, 5, 4 and 3) and $^5D_4{\rightarrow}^7F_J$ (J = 6, 5, 4, 3, 2 and 1) of Tb^{3+}, respectively. The optimized Yb^{3+} concentration is 7.98% (mole fraction) at Tb^{3+} concentration of 0.52%. It is indicated that Tb^{3+}/Yb^{3+} doped α-NaYF$_4$ single crystal is a promising candidate of the UC material applied for the green solid-state laser.

Keywords: sodium yttrium fluoride single crystal; terbium/ytterbium co-doped; up-conversion luminescence; rare-earth luminescence

1 Introduction

The up-conversion (UC) luminescence is a process, which emits higher-energy visible photons after absorbing lower-energy infrared photons. This is widely used in sensing, volumetric displays, biological fluorescence and photo dynamic therapy due to its unique features in sharper emission lines, superior photostability

and near absence of background light [1–4].

Some rare earth elements doped oxide, fluoride, sulfide, and fluoride-oxide compounds for the UC luminescence were investigated [3–4]. It is known that the multi-phonon nonradiative decay rate is mainly responsible for the reduction of the luminescence intensity, and it can be given as [5]:

$$W_n = W_0[1-\exp(\hbar\nu/kT)]^{-n} \qquad (1)$$

where W_n is the decay rate at temperature T, W_0 is the decay rate at 0 K, ν is the relevant phonon's frequency, $n = \Delta E/\hbar\nu$, ΔE is the energy gap between the levels involved. When ΔE is equal to or less than 4–5 times of the phonon energy, the multi-phonon nonradiative relaxation with the emission of a few high energy phonons becomes competitive with radiative processes [6]. In order to reduce the multi-phonon nonradiative relaxation and realize the high efficient UC luminescence, low maximum phonon energy hosts are required. Fluoride NaYF$_4$ is considered as one of the most efficient UC materials due to its low phonon energy [7–9]. NaYF$_4$ in form of single crystal is easier to realize their applications due to the high transmission for lights, good physical and mechanical performance, as well as good chemical durability. However, little work on the UC emission in NaYF$_4$ single crystals has been reported due to the difficult growth of NaYF$_4$ single crystal.

Tb^{3+} ions have attracted great attentions in recent years due to its unique properties, which can emit bright green light, and be used in photonics system [10–12]. In the absence of intermediate levels, Tb^{3+} ions cannot absorb the near-infrared (NIR) excitation photons to generate the UC. Yb^{3+} ions have a great absorption cross section around 980 nm. By co-doping with Yb^{3+} ions, we could realize the UC of Tb^{3+}. In this case, Tb^{3+} ions can emit its characteristic luminescence by absorbing energy from pairs of excited Yb^{3+} ions.

The efficient UC emission from a pair of Tb^{3+}/Yb^{3+} was realized in tellurite glasses [13]. In this paper, Tb^{3+}/Yb^{3+} was co-doped in α-NaYF$_4$ single crystals grown by the flux Bridgman method. The effect of ionic ratio between Tb^{3+} and Yb^{3+} on the UC emissions was investigated. The high efficient UC luminescence of Tb^{3+}/Yb^{3+} co-doped α-NaYF$_4$ single crystal under 980 nm excitation was analyzed, and the UC mechanism was discussed.

2　Experimental

Samples with a purity of 99.99% NaF, KF, YF$_3$, TbF$_3$, and YbF$_3$ were prepared according to the formula 30NaF–18KF–(52−χ−γ)YF$_3$–χTbF$_3$–γYbF$_3$ (χ=0.5, γ=0, 1.0, 2.5, 4.0), respectively. The mixture of those materials was ground in a mortar for 1 h. In a high-temperature hydrofluorination method, the powders were sintered with anhydrous HF at 750 ℃ for 8 h. The moisture and oxygen impurities in the fluoride powders were removed

after sinterring. The growth orientation was directed along a-axis by using an oriented seed crystal. The seed was firstly put in the bottom of seed well and then the sintered polycrystalline powders were filled in Pt crucibles of ϕ10 mm×150 mm size. The crucibles were completely sealed and put into the vertical Bridgman growing furnace. The growing process was carried out by lowering the crucible at a rate of 0.05–0.06 mm/h. The seeding temperature was 770–820 ℃ and the temperature gradient across the solid-liquid interface was 70–90 ℃/cm.

The X-ray diffraction (XRD) pattern of the sample was measured using a model XD-98X X-ray diffractometer (Purkinje General, Beijing, China). The emission spectra were obtained with a model FLSP 920 spectrometer (Edinburgh Co., UK). The Tb^{3+} and Yb^{3+} concentrations in α-NaYF$_4$ single crystal were measured by an inductive coupled plasma atomic emission spectroscopy (ICP-AES, PerkinElmer Inc., Optima 3000, USA). Concentration of Tb^{3+} and Yb^{3+} ions in the α-NaYF$_4$ single crystals as shown in Table 1. All the measurements were performed at room temperature.

Table 1　Concentration of Tb^{3+} and Yb^{3+} ions in the α-NaYF$_4$ single crystals

Sample No.	Mole fraction of Tb^{3+}/%	Mole fraction of Yb^{3+}/%
S1	0.51	0
S2	0.52	1.98
S3	0.51	4.97
S4	0.52	7.98

3　Results and discussion

Figure 1(a) is the photograph of polished Tb^{3+}/Yb^{3+} co-doped α-NaYF$_4$ (α-NaYF$_4$:Tb/Yb) single crystal. Clearly, the α-NaYF$_4$:Tb/Yb single crystal is transparent and appears slightly yellow color. Figure 1(b) shows the XRD patterns of the grown single crystal. The diffraction peak positions of the crystal match perfectly with those of cubic α-NaYF$_4$ in the JCPDS card (77–2042). The lattice constants of α-NaYF$_4$:Tb/Yb single crystal were calculated from the XRD pattern data as the following lattice parameters: $a=b=c=0.546$ nm, which are close to the standard parameters ($a=b=c=0.547$ nm). Also, it is indicated that all the samples can be crystallized into a pure cubic phase, and Y^{3+} sites of α-NaYF$_4$ single crystals are substituted by Tb^{3+} and Yb^{3+} ions.

Figure 2 shows the UC emission spectra of all the samples in the wavelength range 450–700 nm. Clearly, there are the UC emissions at ~381, ~414, ~435, ~462, ~481, ~541, 587, 651, ~659 and 668 nm, and the corresponding radiative energy transfer processes occur. Compared to the relative intensity of all the

samples, the intensity at ~462, ~481, ~541, 587, 651, ~659 and 668 nm increases rapidly as the Yb^{3+} content increases from 0 to 7.98% in mole.

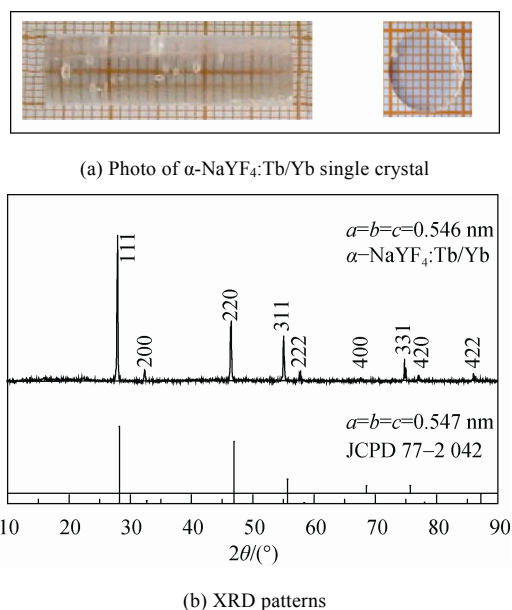(a) Photo of α-NaYF₄:Tb/Yb single crystal

(b) XRD patterns

Fig. 1　Photo of polished α-NaYF₄:Tb/Yb single crystal and XRD patterns of α-NaYF₄:Tb/Yb single crystal

There is no concentration quenching although the Yb^{3+} is 7.98%. In order to know the exact UC emission color, the CIE chromaticity coordinates of Tb^{3+}/ Yb^{3+} co-doped α-NaYF₄ single crystals are calculated. The CIE coordinates (x, y) are (0.265 2, 0.686 7), (0.2606, 0.668 2) and (0.255 7, 0.566 3), for 0.52%Tb/1.98%Yb, 0.51%Tb/4.97%Yb and 0.52%Tb/7.98%Yb α-NaYF₄ single crystals, respectively. All the samples appear a yellow-green color, which can be applied for sensing, volumetric displays, biological fluorescence and photo dynamic therapy.
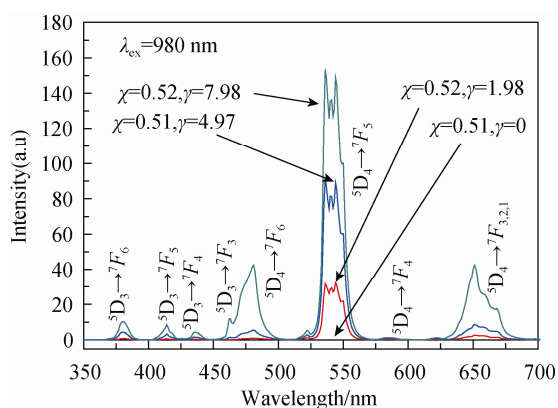

Fig. 2　Comparison of the up-conversion luminescence spectra of α-NaYF₄:χTb/γYb single crystals under 980 nm excitation at room temperature

Figure 3 shows the UC intensity of 0.52%Ho³⁺ and 7.98%Yb³⁺ co-doped α-NaYF₄ single crystals as a function of the excitation power at 980 nm. It is well

known that the UC luminescence intensity (I_{UC}) is proportional to some power n of the excitation power (I_P), i.e., $I_{UC} \propto I_P^m$, where m is the number of absorbed photons required to populate the emission states [14]. The up-conversion intensity at different wavelengths was calculated from its luminsecence spectra of different pump powers at 980 nm. The emission intensities at ~381, ~414, ~435, ~462, ~481, ~541, 587, 651, ~659 and 668 nm are fitted to the slopes of 2.94, 2.83, 2.86, 2.92, 1.89, 1.94, 1.90, 1.87, 1.92 and 1.86, respectively, indicating that the emissions at ~381, ~414, ~435 and ~462 nm are the three-photon UC process, while the emissions at ~481, ~541, 587, 651, ~659 and 668 nm are the two-photon UC process. Since Tb^{3+} ions do not absorb the incident 980 nm radiation, its excitation is dependent on the energy transfer from the excited Yb^{3+} ions.
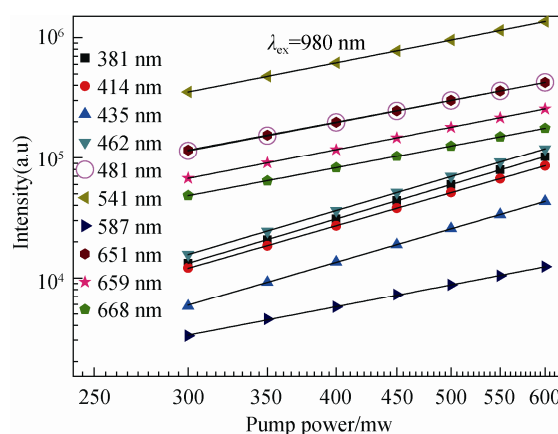

Fig. 3　Up-conversion intensity of 0.52%Tb³⁺ and 7.98%Yb³⁺ co-doped α-NaYF₄ single crystals as a function of the excitation power at 980 nm

Figure 4 shows the energy level diagram of Tb^{3+} and Yb^{3+}. Clearly, no transfer of excitation energy from an Yb^{3+} in $^2F_{5/2}$ level to Tb^{3+} occurs. It is reasonable to consider the energy transfer simultaneously from a pair of Yb^{3+} ions both excited to the $^5F_{5/2}$ level to a Tb^{3+} ions. When pumped by 980 nm laser, Yb^{3+} ions are firstly excited from $^2F_{7/2}$ to $^2F_{5/2}$ level, and then a couple of excited Yb^{3+} ions can transfer the energy to a Tb^{3+} ion and excite Tb^{3+} ion to $^5D_4$. In Fig. 2, the main intense green emission at ~541 nm is assigned to the $^5D_4 \rightarrow {}^7F_5$ transition. Other blue emission at ~481 nm and red emission at ~651, ~659 and 668 nm are corresponding to $^5D_4 \rightarrow {}^7F_6$ and $^5D_4 \rightarrow {}^7F_J$ (J=3, 2, 1), respectively, and Figure 3 shows all the energy transfer processes [15]. There is also a weak peak at ~583 nm due to the transition of $^5D_4 \rightarrow {}^7F_4$. Also, three Yb^{3+} ions can transfer the energy to a Tb^{3+} ion and excite Tb^{3+} ion from $^7F_6$ to $^5D_3$, the excited Tb^{3+} ion at $^5D_4$ can absorb one 980 nm photon and excite to $^5D_1$ and then relax to $^5D_3$ nonradiatively (see Fig. 4). In Fig. 2, the emissions at 381, 414, 435 and 461 nm are emitted due to transition of

$^5D_3\rightarrow{}^7F_J$ (J=6,　5, 4, 3), respectively. Some of the emission peaks show energy stark splitting of Tb^{3+} under the action of α-NaYF$_4$ single crystals. Almost all the possible UV, blue, green and red luminescences appear in the Tb^{3+}/Yb^{3+} doped α-NaYF$_4$ single crystals possiblily due to the well cubic phase and low phonon energy of the single crystals. When Tb^{3+} concentration is 0.52%, the total UC intensity reaches its maximum value at Yb^{3+} concentration of 7.98%. It is expected that the UC emission could be further improved by further increasing the Yb^{3+} concentration.
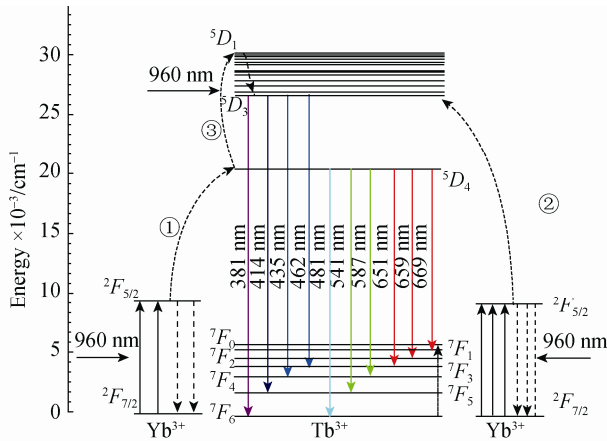

Fig. 4　Simplified Energy level diagram and possible upconversion luminescence mechanisms of Tb^{3+} and Yb^{3+} ions codoped α-NaYF$_4$ single crystals.

4　Conclusions

α-NaYF$_4$ single crystals co-doped Tb^{3+} ion at 0.51% and in the range of Yb^{3+} ion from 0% to 7.98% were grown by the improved Bridgman method. The UC emissions in the range of UV and VIS rapidly increased as the Yb^{3+} content increased from 0 to 7.98% under a 980 nm diode laser excitation. The three-photon process was due to the UC emissions at 381, 414, 435 and 462 nm, and the two-photon process was due to the emissions at 481, 541, 587, 651, 659 and 668 nm. The green emission at ~541 nm due to $^5D_4\rightarrow{}^7F_6$ was the most intense in all the UC emissions. A yellow-green color could be generated by a simultaneous mixture of all the UC emissions. The results proposed that the Tb^{3+}/Yb^{3+} codoped α-NaYF$_4$ single crystals could have potential applications in the optoelectronic fields such as sensing, volumetric displays, biological fluorescence and photo dynamic therapy.

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