Upconversion and downconversion luminescence performance of Nd^{3+}/Yb^{3+} co-doped $YNbO_4$ under 808 nm/980 nm excitation

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Luminescence performance of $YNbO_4$ powder material co-doped with Nd^{3+} and Yb^{3+} ions excited under 808 nm/980 nm laser diode (LD) is reported. Upconversion emission spectra of $YNbO_4$: Nd^{3+} / Yb^{3+} excited under 808 nm and 980 nm LD are recorded, and the results indicate that the strongest emission peak under 980nm excitation is located at 540 nm with green color, but located at 420 nm and 475 nm under 808 nm LD excitation. The upconversion fitting results indicate that all of upconversion luminescence belong to two-photon absorption process. Moreover, downconversion emission spectra in the scope from 900 nm to 1700 nm excited under 808 nm and 980 nm LD are also measured and luminescence process are analyzed.

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1. Introduction

Nowadays rare-earth (RE) co-doped materials with excellent luminescence properties have been intensely investigated due to its huge potential application in these fields such as photoelectric devices, flat plate display and laser technologies [1-3]. In trivalent rare earths (RE^{3+}), Nd^{3+} is one of the most frequently used luminescence ions because that the transitions at $^4F_{3/2}\rightarrow{}^4I_{13/2}$ (915 nm), $^4F_{3/2}\rightarrow{}^4I_{11/2}$ (1064 nm) and $^4F_{3/2}\rightarrow{}^4I_{9/2}$ (1340 nm) in the NIR-range are the most suitable for the commented applications [4]. Especially, Nd^{3+} doped YAG crystal is the most excellent laser crystal with high combination properties and is widely used in military field, industrial field and medical field. Moreover, Nd^{3+}-doped upconversion luminescence materials, which can convert NIR light into UV/visible light, offer the excellent prospects for the next generation of photodynamic therapy on deeper tissues, and is also investigated by many researchers [5,6].

The luminescent properties of the Nd^{3+} ions are considerably influenced by their located network and circumambient cations. Many Nd^{3+}-doped laser crystals have been discovered and studied deeply, including Nd^{3+}:YAG, Nd^{3+}: vanadates, and Nd^{3+}:tantalates. Among these crystals, the compounds of ABO_4 composition (A=Y, La, and Lu; B=P and V) are suggested to be used as excellent hosts [7-11].

$YNbO_4$ belongs to this family of compounds. $YNbO_4$ is one kind of excellent luminescence host material. When the pure $YNbO_4$ is excited at 260 nm it emits a broad emission band at 405 nm [12]. Two crystalline forms are recognized for $YNbO_4$, the high temperature tetragonal phase corresponding to the scheelite structure and the low temperature monoclinic ally distorted monoclinic phase (M-fergusonite) [13]. The reversible phase transition between the two phases has been observed in the temperature range 500–800°C depending on the rare earth (RE) ions [14, 15]. $YNbO_4$ doped with RE ions (Eu^{3+}, Sm^{3+}, Dy^{3+}, Er^{3+} and Nd^{3+}) have also outstanding photoluminescence properties [15-22].

When excited under different light wavelength, different luminescence phenomenon will be observed in RE ions. Yb^{3+} ions are always used as sensitization ions due to its large absorption cross at around 980 nm, and Nd^{3+} ions have a stronger absorption band centered at around 808 nm. Luminescence properties of Nd^{3+}/Yb^{3+} co-doped luminescence materials under excited through common commercial 980 nm LD and 808 nm LD will reveals different energy level transition procedure of Nd^{3+}/Yb^{3+} ions affected by host materials.

In this article, luminescence performance of $YNbO_4$ co-doped with Nd^{3+} and Yb^{3+} ions excited under 808 nm/980 nm LD is reported. Firstly, Nd^{3+} /Yb^{3+} co-doped $YNbO_4$ powder material is prepared through solid-state reaction, X-ray diffraction (XRD) pattern is investigated to analyze phase composition of the prepared sample. Secondly, Upconversion emission spectra of prepared sample excited under 808 nm and 980 nm LD are collected and corresponding energy level transition procedure of

Nd^{3+} and Yb^{3+} ions are analyzed. Then, relationships between upconversion luminescence intensity and exciting current of 808 nm and 980 nm LD are fitted, and upconversion luminescence procedure is derived. In the end, emission spectra in the scope from 900 nm to 1700 nm excited under 808 nm and 980 nm LD are also measured and downconversion luminescence properties have been studied.

2. Experiment

2.1. Material preparation

Weighing a share of raw material with mass of 10 grams according to mole ratio as Nb_2O_5: Y_2O_3: Nd_2O_3: Yb_2O_3 = 50: 40: 2: 8. In raw material, Nd_2O_5, Y_2O_3 and Yb_2O_3 are spectroscopic reagent and Nb_2O_5 is analytical reagent. Weighed raw material is grinded and mixed thoroughly by using agate mortar, then placed into a ceramic crucible. The ceramic crucible filled with raw material are put into a muffle furnace and calcined at 1300 ℃ for two hours, respectively, then are taken out and cooled to room temperature naturally. Cooled sample is grinded again in agate mortar and encased in a sample bag for next measurement.

2.2. Material performance measurement

A Hitachi DMAX-3A X-ray diffraction (XRD) equipment with scanning scope from 10°to 80°is used to record XRD pattern and analyze phase composition of the prepared sample.

Upconversion emission spectrum is measured by adopting Zolix Omi-λ150 monochromator and PMTH-S1-CR131 photomultiplier. Emission spectrum in scope from 900 nm to 1700 nm is measured by using AvoSpec-NIR256-1.7 fiber spectrum and AVASPHERE-50-LS-HAL integrating sphere.

3. Results and discussion

3.1. Phase composition

The measured XRD pattern of prepared sample is shown in the upper part of Fig. 1, and the lower part of Fig. 1 shows the characteristic peaks distribution of $YNbO_4$ crystal according to the 23-1486th PDF card. It can be seen from Fig. 1 that main X-ray diffraction peaks of the prepared sample match well with characteristic peaks of monoclinic fergusonite-type $YNbO_4$ crystal structure, which illustrates that Nb_2O_5 completely reacts with Y_2O_3 and generates single-phase $YNbO_4$. The prepared Ho^{3+}/Yb^{3+} co-doped $YNbO_4$ sample belongs to I2/a space group and the unit cell parameters are $a = 0.519nm, b = 1.054nm, c = 0.601nm, \alpha = \gamma = 90°$ and $\beta = 95.435°$.

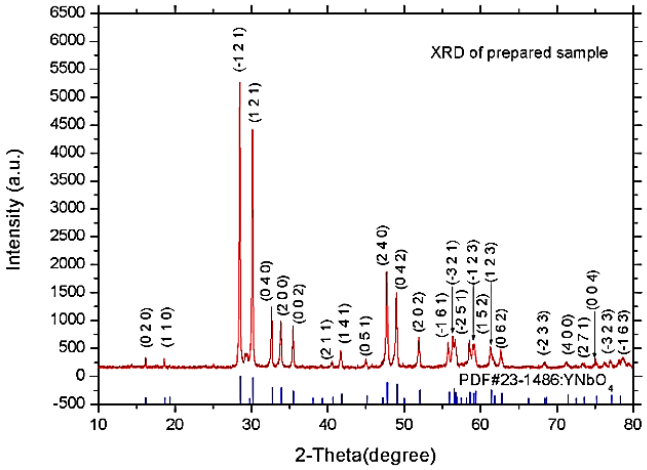
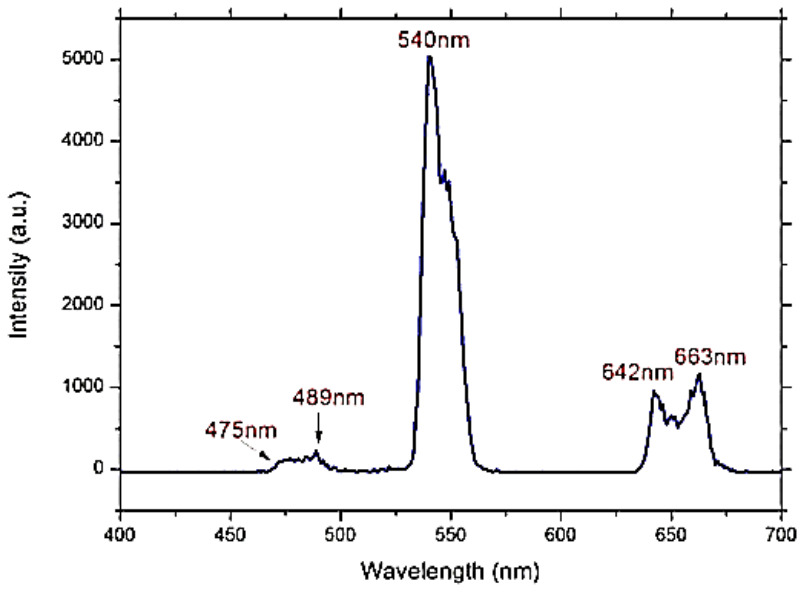


Fig. 1. XRD pattern of Nd^{3+}/Yb^{3+} co-doped $YNbO_4$ powder

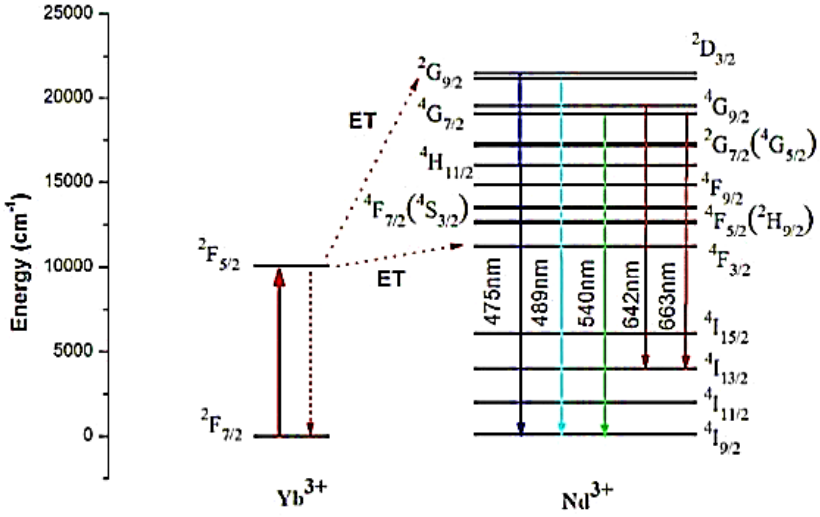
3.2. Upconversion luminescence

Fig. 2 shows upconversion emission spectrum of the prepared sample and corresponding energy level transitions of Nd^{3+} and Yb^{3+} ions excited under 980 nm LD. In Fig. 2, 'ET' represents energy transfer from Yb^{3+} ions to Nd^{3+} ions. It can be seen from Fig. 2 (a) that in the scope from 400 nm to 700 nm, there are mainly three stronger emission peaks: 475 nm and 489 nm, 540 nm, 642 nm and 663 nm, belonging to blue light, green light and red light, respectively. It is obvious that green light is stronger than red light and blue light.

The three groups of emission peaks can be explained through energy level transitions of Nd^{3+} and Yb^{3+} ions shown in Fig. 2(b). When an Yb^{3+} ion populated at energy level $^2F_{5/2}$ transit back to ground state $^2F_{7/2}$ then transfer energy to an Nd^{3+} ion, the Nd^{3+} ion will transit from ground state $^4I_{9/2}$ to energy level $^4F_{3/2}$. Another Yb^{3+} ion at $^2F_{5/2}$ state can transfer energy to the Nd^{3+} ion and make it transit from $^4F_{3/2}$ to $^2D_{3/2}$. Electron populated at energy level $^2D_{3/2}$ can transit back to ground state $^4I_{9/2}$ directly, and release a photon with wavelength 475 nm, and can also go to energy level $^2G_{9/2}$ through non-radiative transition, then transits back to ground state $^4I_{9/2}$ and release a 489 nm photon. Moreover, electron at $^2D_{3/2}$ can also transit to $^4G_{9/2}$ and $^4G_{7/2}$ without radiation, then transitions of $^4G_{7/2}$ to $^4I_{9/2}$, $^4G_{9/2}$ to $^4I_{13/2}$ and $^4G_{7/2}$ to $^4I_{13/2}$ take place, and release photons with wavelength 540 nm, 642 nm and 663 nm, respectively.



(a) Upconversion emission spectrum

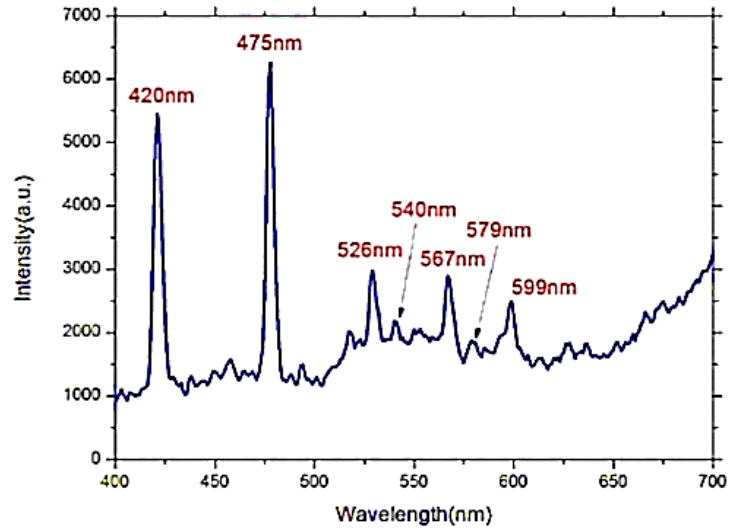


(b) Energy level transitions of Nd^{3+} and Yb^{3+} ions

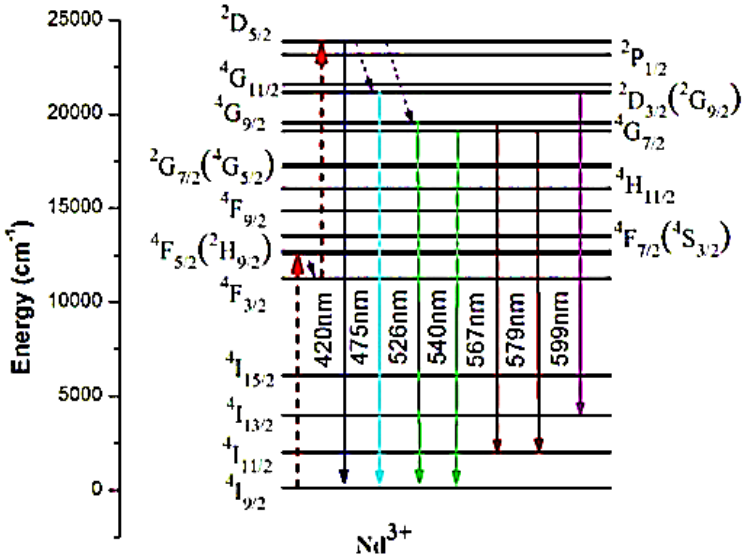
Fig. 2. Upconversion emission spectrum and energy level transitions excited under 980 nm LD

Upconversion emission spectrum of prepared sample and corresponding energy transitions of Nd^{3+} ions excited under 808 nm LD is shown in Fig. 3. It is very different with upconversion spectrum in Fig. 2(a) that 420 nm emission peak appears and the blue luminescence peaks of 420 nm and 475 nm are stronger than green emission peaks at 526 nm, 540 nm, 567 nm and 579 nm and red emission peak at 599 nm. This phenomenon is attributed to that 808 nm photon has higher energy than 980 nm photon and is easier to make transition of Nd^{3+} ions to higher energy level through two-photon absorption process.

Energy level transitions of Nd^{3+} ion excited under 808 nm LD is shown in Fig. 3(b). It can be seen that an Nd^{3+} ion can absorb an 808 nm photon and transits from ground state $^4I_{9/2}$ to energy level $^4F_{5/2}$, then transits back to $^4F_{3/2}$ without radiation, due to longer lifetime of energy level $^4F_{3/2}$. The Nd^{3+} ion can absorb an 808nm photon again and transits to energy level $^2D_{5/2}$. The Nd^{3+} ion populated at $^2D_{5/2}$ can go back to ground state $^4I_{9/2}$ and release a photon with wavelength 420 nm. An Nd^{3+} ion at energy level $^2D_{5/2}$ can also relax to energy level $^2D_{3/2}$ through non-radiative transition, then transits back to ground state $^4I_{9/2}$ and release a 475 nm photon, or transits to energy $^4I_{13/2}$ and release a 599 nm photon. Moreover, an Nd^{3+} ion at energy level $^2D_{5/2}$ can transit to energy levels $^4G_{9/2}$ or $^4G_{7/2}$ without radiation, then release photons with wavelength 526 nm, 567 nm, 540 nm and 579 nm through transitions of $^4G_{9/2}$ to $^4I_{9/2}$, $^4G_{9/2}$ to $^4I_{11/2}$, $^4G_{7/2}$ to $^4I_{9/2}$ and $^4G_{7/2}$ to $^4I_{11/2}$, respectively.



(a) Upconversion emission spectrum



(b) Energy level transitions of Nd^{3+} ions

Fig. 3. Upconversion emission spectrum and energy level transitions excited under 808 nm LD

Theoretically, Up-conversion luminescence intensity I_{lumin} has relationship with working current of excitation LD as follows [23]:

$$I_{lumin} = k^n \cdot (i - i_0)^n \ , \tag{1}$$

where, k is proportional coefficient with relation to performance of LD, i_0 represents LD's threshold current and i is LD's working current. Here, n depicts absorbed photon number.

Take the logarithm of two sides in Eq. (1), then

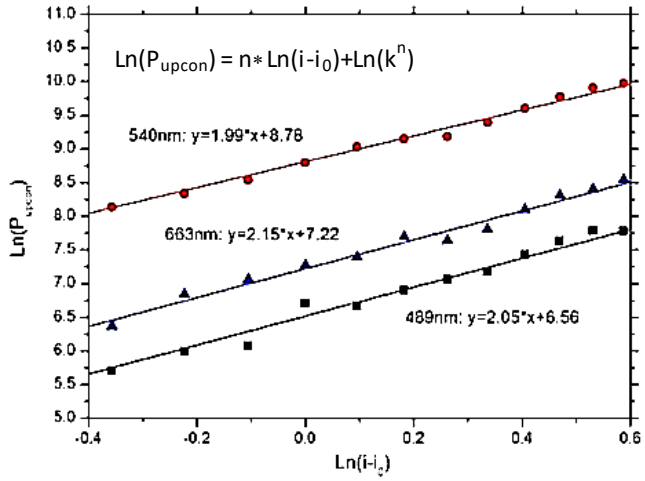
$$\mathrm{Ln}(I_{lumin}) = n \cdot Ln(i - i_0) + Ln(k^n), \tag{2}$$

here, $\mathrm{Ln}(f)$ means natural logarithm of function f.

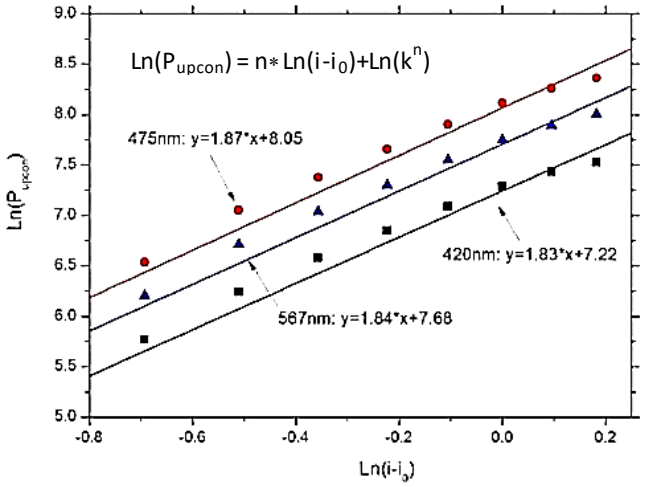
Eq. (2) is a linear equation, and slope is equal to the absorption photon number n.

According to Eq. (2), relationship curves between up-conversion luminescence intensity and LD's working current are fitted linearly, and the fitting results are shown in Fig. 4. In Fig. 4, horizontal coordinate represents the logarithm of LD's working current and vertical coordinate represents the logarithm of upconversion luminescence intensity. Moreover, dots represent experimental data and solid lines are fitting results.

It can be seen from Fig. 4(a) that under 980 nm LD excitation, the linear slope of three up-conversion peaks corresponding to wavelength 540 nm, 663 nm and 489 nm are 1.99, 2.15 and 2.05, respectively. The fitted results mean that the three up-conversion luminescence procedure all belong to two-photon absorption, which is agreement with energy level transitions in Fig. 2(b).



(a) 980 nm LD excitation



(b) 808 nm LD excitation

Fig. 4. Linear fitting of upconversion intensity to working current of 980 nm and 808 nm LD

Linear fitted results under 808 nm LD excitation are shown in Fig. 4(b). Here, the threshold current of 808 nm LD is $i_0 = 0.4A$. It can be seen from Fig. 4(b) that the linear slope of three up-conversion peaks corresponding to wavelength 475 nm, 567 nm and 420 nm are 1.87, 1.84 and 1.83, respectively, which mean that the three upconversion luminescence procedure all belong to two-photon absorption, matching well with analysis in Fig. 3(b).

Therefore, both of upconversion luminescence of Nd^{3+}/Yb^{3+} co-doped $YNbO_4$ under 980 nm and 808 nm excitation belong to two-photon absorbing process, but due to different photon energy of 980 nm and 808 nm laser, upconversion emission peaks under 808 nm excitation are mainly located at blue light range and those peaks under 980 nm excitation lie at green light range.

3.3. Down-conversion luminescence

In order to know luminescence characteristic of Nd^{3+}/Yb^{3+} co-doped $YNbO_4$ powder comprehensively, emission spectra of the prepared sample within scope from 900 nm to 1700 nm are also recorded.

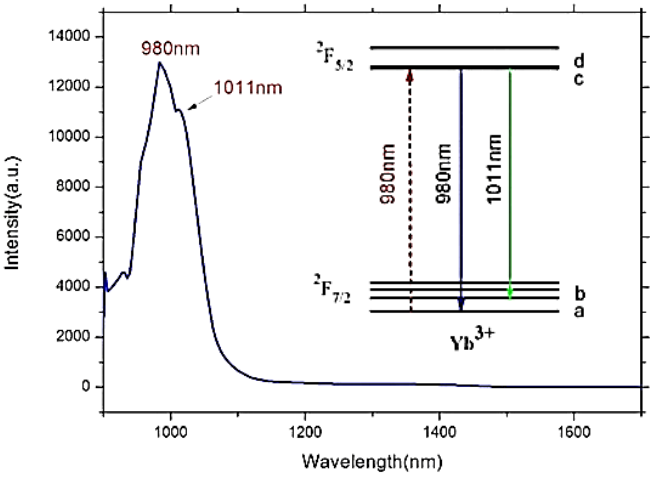


Fig. 5. Down-conversion emission spectrum excited under 980 nm LD

Emission spectrum excited under 980 nm LD is shown in Fig. 5. It can be seen that there are a strong emission peak at 980 nm and a weaker emission peak at 1011 nm. Energy level diagram of an Yb^{3+} ion is illustrated in top-right inlet picture of Fig. 5. Due to electric field effect, energy level of Yb^{3+} ion generate Stark split in crystal field of $YNbO_4$. Energy level $^2F_{5/2}$ splits to three sub energy levels and ground state $^2F_{7/2}$ splits to four sub energy levels. Under 980 nm LD excitation, an Yb^{3+} ion populated at sub-level a of $^2F_{7/2}$ transits up to sub-level *c* of $^2F_{5/2}$. When the Yb^{3+} ion transits back to the sub-level *a*, a photon with wavelength 980 nm will be released. A transition from sub-level *c* to sub-level *b* can generate a photon with wavelength 1011 nm. It should be noticed that three sub-levels of *a*, *b* and *c* can be taken as the ground state, the lower energy level and the upper energy level respectively and make up a four-energy-level systemfor realizing Yb^{3+} ion laser.

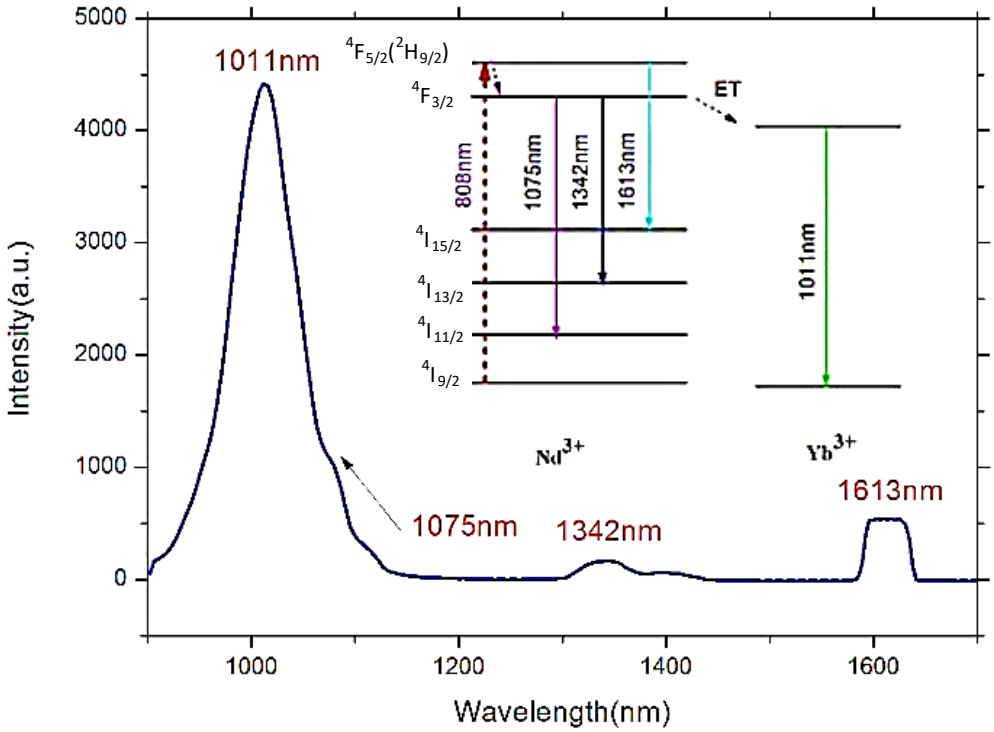


Fig. 6. Down-conversion emission spectrum excited under 808 nm LD

Down-conversion emission spectrum of the prepared sample excited under 808 nm LD is shown in Fig. 6. In Fig. 6, 'ET' represents energy transfer from Nd^{3+} ions to Yb^{3+} ions. It can be seen in Fig. 6 that there exist four emission peaks at 1011 nm, 1075 nm, 1342 nm and 1613 nm, respectively. Transitions between energy levels of Nd^{3+} and Yb^{3+} ions are shown in the top-right inlet of Fig. 6. Under excitation of 808 nm LD, an Nd^{3+} ion populated at ground state $^4I_{9/2}$ transits up to energy level $^4F_{5/2}$. Transition from $^4F_{5/2}$ to $^4I_{15/2}$ will generate a photon with wavelength 1613 nm. Moreover, the Nd^{3+} ion at energy level $^4F_{5/2}$ can also go to energy level $^4F_{3/2}$ through non-radiative transition, then transits down to energy level $^4I_{13/2}$ or $^4I_{11/2}$ and releases a photon with wavelength 1342 nm or 1075 nm. Furthermore, a Nd^{3+} ion at $^4F_{3/2}$ can also transfer energy to a Yb^{3+} ion and cause a transition of the Yb^{3+} ion from $^2F_{7/2}$ to $^2F_{5/2}$, then the Yb^{3+} ion release a photon with wavelength 1011 nm through the same transition as that shown in Fig. 5.

It is obvious that downconversion luminescence of prepared sample excited under 980 nm LD are mainly generated through energy level transitions of Yb^{3+} ions, but downconversion luminescence under 808 nm excitation belong to transitions in both of Nd^{3+} ions and Yb^{3+} ions.

4. Conclusion

In conclusion, upconversion and downconversion luminescence characteristic of Nd^{3+}/Yb^{3+} co-doped $YNbO_4$ is reported. Firstly, a powder sample of Nd^{3+}/Yb^{3+} co-doped $YNbO_4$ is prepared by using solid-state reaction, and measured results of XRD indicate that main composition of prepared sample is $YNbO_4$. Secondly, up-conversion emission spectrum of prepared sample excited under 980 nm and 808 nm are measured, respectively. Under 980 nm LD excitation, the highest emission peak is located at 540 nm green light, and the highest emission peak is at 420 nm blue light. Through curve fitting to relationship between up-conversion luminescence intensity and LD's working current, it can be concluded that all main up-conversion emission peaks under 980 nm and 808 nm excitation correspond to two-photon absorption process. At last, emission spectrum of the prepared sample within scope from 900 nm to 1700 nm under 808 nm LD and 980 nm LD excitation are measured. The results indicated that luminescence under 980 nm LD excitation is mainly caused by transition between energy levels of Yb^{3+} ions, and both Yb^{3+} ions and Nd^{3+} ions take part in the luminescence process under 808 nm LD excitation.

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