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# Up-conversion luminescence in $Er^{3+}/Yb^{3+}$ co-doped $LiYF_4$ single crystals

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The absorption spectra and up-conversion (UC) luminescence of $Er^{3+}/Yb^{3+}$ ions co-doped $LiYF_4$ single crystals synthesized by vertical Bridgman method were investigated. Up-conversion emissions at 519, 522, 529 nm, and 541, 550 nm, and 649, 655, 669 nm were observed. The yellowish green light can be achieved from 2.14 mol% $Er^{3+}$ and 4.04 mol% $Yb^{3+}$ co-doped $LiYF_4$ crystal. The mechanisms of UC emissions are proposed based on the pump power dependent UC spectra. A cooperative energy transfer process from excited $Yb^{3+}$ to $Er^{3+}$ in the form of two-photons has been presented in $LiYF_4$ at room temperature.

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*Keywords:* Up-conversion, Crystal growth, $LiYF_4$ single crystals, $Er^{3+}$, $Yb^{3+}$

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## 1. Introduction

Up-conversion (UC) luminescence also meaning an anti-stokes luminescence, which the emission of a higher energy photon follows the absorption of two or more low energy photons, has attracted wide attention in some areas, such as biosensors, infrared pumped visible eye-safe lasers, optical telecommunication, photovoltaics and display technology during the past decades[1-4]. A lot of materials doped with rare earth ions, which can be used for up-conversion luminescence, have been reported in glasses [5], nanocrystals [6] and ceramics [7], etc.

Among the trivalent rare earth ions, the up-conversion process of $Er^{3+}$ ions sensitized by $Yb^{3+}$ ions from infrared to visible light has been widely studied because of a larger absorption cross section at near infrared (NIR) of $Yb^{3+}$ and the high-efficiency energy transfer from $Yb^{3+}$ to $Er^{3+}$ ions[8]. Some kinds of studies have been reported on the UC emission of $Er^{3+}/Yb^{3+}$ co-doped materials [4-9]. In order to obtain higher UC efficiency, available host materials play another key role for UC light. Actually, owing to the low phonon energy, fluorides are the mostly investigated materials [10]. Among those materials, the $Er^{3+}/Yb^{3+}$ co-doped $NaYF_4$ powder has a high UC emission efficiency due to its lower phonon energy, relatively high optical damage threshold, and low non-linear refractive indices [9]. Because of the similar ordered structure and rigid crystal lattice in the $RYF_4$ (R=Li, Na, K, etc.) family crystals, it is proposed that the $LiYF_4$ single crystals also possess advantages of excellent UC emission for $Er^{3+}/Yb^{3+}$, and have high efficiency of UC emission like that of $NaYF_4$.

Generally speaking, powders have strong scattering and low transmission while glasses or ceramics have low optimum mechanical, chemical properties, and low luminescent efficiency [11], they are deficient to be applied effectively in optical devices. Some recent works focus on the performance of rare earth doped $LiYF_4$ single crystals on near and mid-infrared luminescence and LED emission [11-15]. Unfortunately, there are scarcely reports on UC emission of $Er^{3+}/Yb^{3+}$ co-doped $RYF_4$ (R=Li, Na, K, etc.) single crystals due to the difficult growth of the crystals. Since the $RYF_4$ (R=Li, Na, K, etc.) single crystals surpass their powders in transmission which is induced from the scattering of the nanoparticles and is of excellent thermal and mechanical properties and high luminescent efficiency, they become possible to extend the limitations of their powders, and have benefit in practical applications.

In a previous work, we reported spectral properties and energy transfer progress in $Er^{3+}/Yb^{3+}$ codoped $LiYF_4$ crystal[16]. In this work, the enhanced up-conversion at visible wavelength of $Er^{3+}/Yb^{3+}$ co-doped $LiYF_4$ single crystal was exhibited under excitation of 966 nm light, and the UC mechanisms were investigated through the pump power dependent UC emission.

## 2. Experimental

The raw materials (LiF, $YF_3$, $ErF_3$, and $YbF_3$) with a purity of 99.99% were chosen to grow the fluoride single crystals. We prepared the single crystals with a molar ratio of LiF: $YF_3$: $ErF_3$=51.5:47.5:1.0 (A) and LiF: $YF_3$: $ErF_3$: $YbF_3$= 51.5:45.5:1.0:2.0 (B), in which the rare earths of $ErF_3$ and $YbF_3$ were doped into the materials to displace the location of $YF_3$. Temperature gradient of the solid-liquid interface is about 50-60 °C, and the growth speed is about 0.1-0.15mm/h. The specific details and processes for crystal growth were described in Ref. [15]. The as grown single crystals were cut into small pieces and well-polished to about 2.2 mm thickness as inserted in Fig. 1 for optical measurements.

The structures of $LiYF_4$ single crystals was tested by a XD-98X diffract meter (XD-3, Beijing), with CuKα radiation at 0.15403 nm, and the scanning $2\theta$ was from 10° to 90° with 0.02° increments and 6 s swept time. The absorption spectra from 350 nm to 1100 nm were recorded with a Cary 500 UV/VIS/NIR spectrophotometer (Agilent Co., America). The fluorescence was measured using a FLSP 920 type spectrometer (Edinburgh Co., England). The concentrations of $Er^{3+}$ and $Yb^{3+}$ were measured through ICP（Inductive Coupled Plasma Emission Spectrometer）. In (A), the concentration of $Er^{3+}$ is 2.12 mol%; in (B), $Er^{3+}$ and $Yb^{3+}$ are 2.14 mol% and 4.04 mol%, respectively. All the measurements were carried out at room temperature.

## 3. Results and discussion

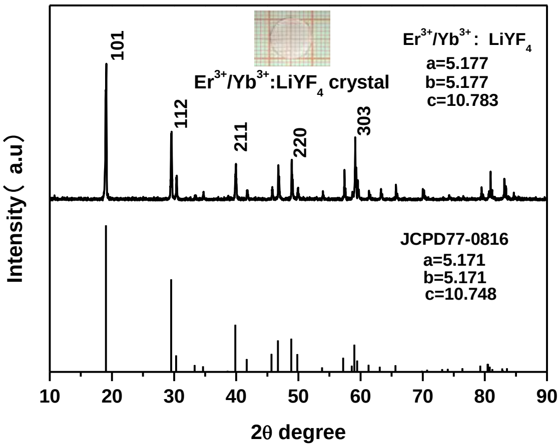

*Fig. 1. X-ray diffraction patterns of $Er^{3+}/Yb^{3+}$ co-doped $LiYF_4$ single crystal. Insert is the photo of polished $Er^{3+}/Yb^{3+}$ co-doped $LiYF_4$ single crystal.*

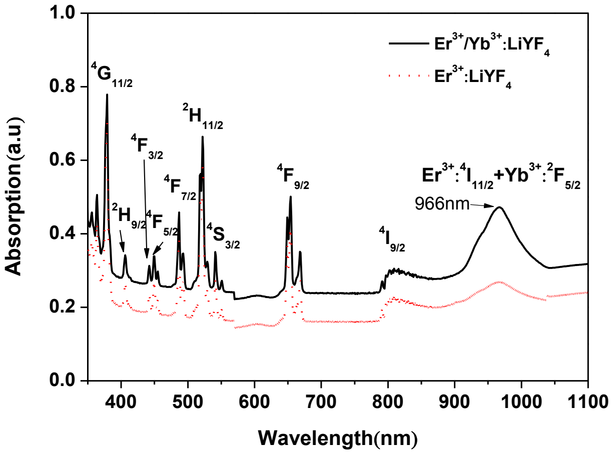

*Fig. 2. The absorption spectra of $Er^{3+}$ single doped and $Er^{3+}/Yb^{3+}$ co-doped $LiYF_4$ single crystals.*

Fig. 1 shows the XRD pattern of the grown single crystal. The diffraction peak positions of the crystal match perfectly with those of $LiYF_4$ in the JCPD card (77-0816), one can deduce that the grown crystal is a single orthorhombic phase, which is the scheelite ($CaWO_4$) structure, and the lattice constants can be calculated from XRD to be a = b = 5.177 Å, c = 10.783 Å.

Fig. 2 shows the absorption spectra of $Er^{3+}$ singly doped and $Er^{+3}/Yb^{+3}$ co-doped $LiYF_4$ single crystals at room temperature. Through the absorption spectra, we can find that there are some absorption peaks among the visible lights and a wide absorption peak from 940 nm to 1000 nm peaked at 966 nm. The corresponding energy levels were also labeled in Fig. 2. The wide band is attributed to the overlap of the $^2F_{5/2}$ energy level of $Yb^{3+}$ ions and $^4I_{11/2}$ of $Er^{3+}$ ions. It is very beneficial to the output of up-conversion luminescence under 966 nm excitation.

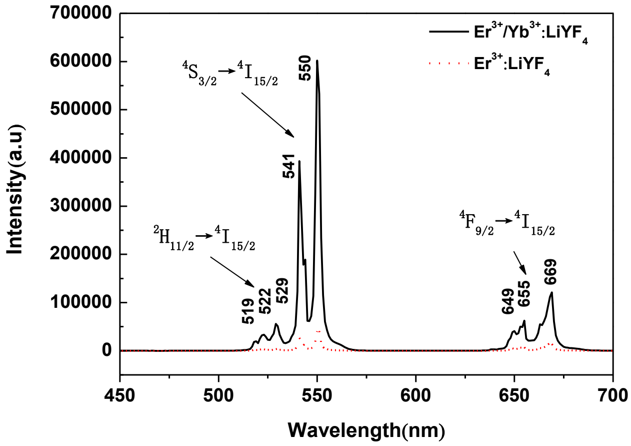

*Fig. 3. Up-conversion luminescence spectra of $Er^{3+}$ and $Er^{3+}/Yb^{3+}$ co-doped $LiYF_4$ single crystals under 966 nm excitation.*

Fig. 3 shows the comparison of up-conversion luminescence spectra of $Er^{3+}$ singly doped and $Er^{3+}/Yb^{3+}$ co-doped $LiYF_4$ single crystals in the range of 450-700 nm under 966 nm laser irradiation. It can be observed 519, 522, 529, 541, 550, 649, 655, and 669 nm emissions for both singly and double doped samples. The 519, 522, and 529 nm green emissions are attributed to the $^2H_{11/2} \rightarrow {}^4I_{15/2}$ of $Er^{3+}$ ions; 541 and 550 nm green emissions are to $^4S_{3/2} \rightarrow {}^4I_{15/2}$; 649, 655, and 669 nm red emissions are to $^4F_{9/2} \rightarrow {}^4I_{15/2}$. By comparison, the up-conversion emissions intensity of singly and double doped samples, the $Er^{3+}/Yb^{3+}$ co-doped $LiYF_4$ crystal appears much stronger than that of $Er^{3+}$ singly doped $LiYF_4$, one can deduce that the introduction of $Yb^{3+}$ can enhance the up conversion emission effectively. Due to the good energy match between $^4I_{11/2}$ and $^4F_{7/2}$ of $Er^{3+}$ ions and $^2F_{5/2}$ of $Yb^{3+}$ ions, when the $Er^{3+}/Yb^{3+}$ co-doped $LiYF_4$ single crystal is excited by 966 nm light, the energy of $Yb^{3+}$ ions absorbed from 966 nm light can transfer to $Er^{3+}$ ions efficiently. The CIE chromaticity coordinates of the $Er^{3+}/Yb^{3+}$ co-doped

$LiYF_4$ single crystal is shown in Fig.4. The CIE coordinates (x, y) of the crystal is (0.269, 0.6909) and its color temperature Tc = 6128 K, which is yellowish green color. As we all know that the yellowish green color is sensitive to human eyes, this performance gives possibility for electro-optical devices.

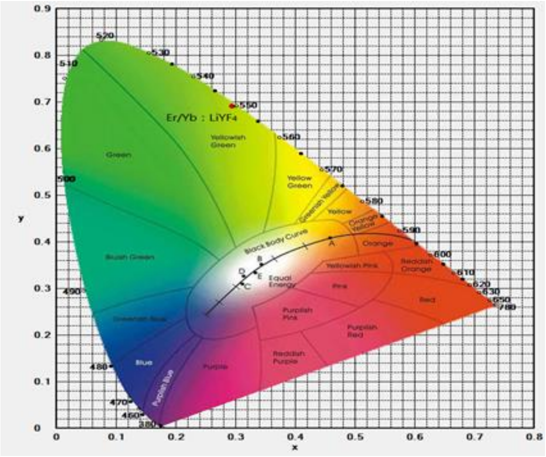

*Fig. 4. CIE chromaticity coordinates of 2.14mol% $Er^{3+}$ and 4.04mol% $Yb^{3+}$ co-doped LiYF4 crystal.*

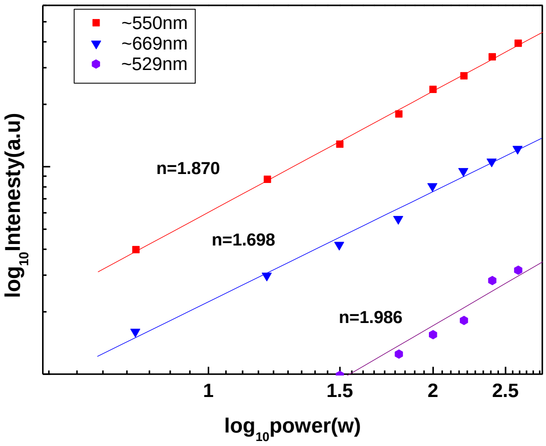

*Fig. 5. Log–log plot of the up-conversion intensities of $Er^{3+}$ /$Yb^{3+}$ co-doped LiYF4 single crystal on around 529,550, 669 nm emission at the excitation power of 966 nm.*

In order to know the UC dynamics of $Er^{3+}/Yb^{3+}$ ions co-doped LiYF4 single crystals, the log–log plot of the up-conversion intensities of $Er^{3+}$ /$Yb^{3+}$ co-doped $LiYF_4$ single crystal on green and red emission at the excitation power of 966 nm had also been measured and shown in Fig. 5. It has been confirmed that the relation between the emission intensity $I_{em}$ and the infrared power of excitation intensity P is $I_{em} \propto p^n$ in the simplest UC processes, where the n is the number of pump photons required exciting the emitting state, which is indicated by the slope of the luminescence intensity versus pump power in double-logarithmic coordinate [16]. Generally, a realistic UC system that produces detectable UC luminescence will exhibit an intensity-versus-power dependence, which is less than $P^n$ [17]. It can be seen from Fig. 5 the slopes of the luminescence intensity versus pump power in double-logarithmic coordinate for around 529, 550 and 669 nm emissions are 1.986, 1.870, and 1.698, respectively. The nearly square dependences indicate that the up-conversion process to arrive the ${}^2H_{11/2}$ and ${}^4S_{3/2}$ or ${}^4F_{9/2}$ levels need two-photon, and it tally with theory very well.

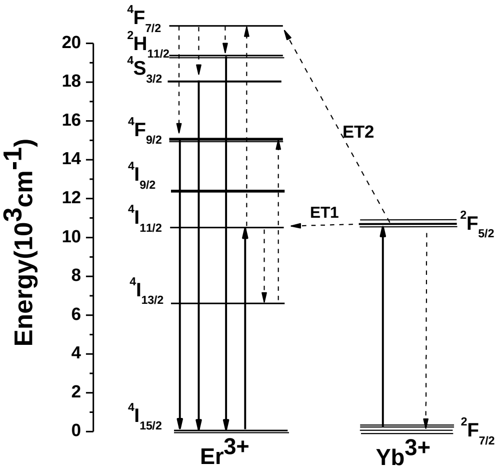

*Fig. 6. Energy level diagram of $Er^{3+}/Yb^{3+}$ co-doped $LiYF_4$ single crystal.*

The possible up-conversion luminescence mechanisms of $Er^{3+}/Yb^{3+}$ co-doped materials have been reported elsewhere [19] [20]. Here we try to quantitatively investigate the energy transfer between $Yb^{3+}$ and $Er^{3+}$ under excitation by 966 nm light. Based on the analysis above, UC luminescence mechanisms of $Er^{3+}/Yb^{3+}$ co-doped $LiYF_4$ are proposed and shown in Fig. 6. Pumping at 966 nm, the energy of pumping light is mainly absorbed by $Yb^{3+}$ ions via ${}^2F_{7/2}$ to ${}^2F_{5/2}$. Due to the good energy match, it is easily taken place that energy transfers from excited $Yb^{3+}$ ions to their nearby $Er^{3+}$ ions. One excited $Yb^{3+}$ ion can transfer their energy to an $Er^{3+}$ ion and excites the ground-state ${}^4I_{15/2}$ to excited ${}^4I_{11/2}$ (ET1), or two excited $Yb^{3+}$ ions can transfer their energy to an $Er^{3+}$ ion and excite the ground-state ${}^4I_{15/2}$ to excited ${}^4F_{7/2}$ (ET2). Meanwhile, the $Er^{3+}$ ions at the excited ${}^4I_{11/2}$ state can absorb a photo of 966 nm pump light or energy transfer from $Yb^{3+}$ ions and populate to ${}^4F_{7/2}$ state. Then, the $Er^{3+}$ ions at ${}^4F_{7/2}$ state can relax nanradiatively to the ${}^2H_{11/2}$ and ${}^4S_{3/2}$ state, leading to the green ${}^2H_{11/2}\rightarrow{}^4I_{15/2}$ and ${}^4S_{3/2}\rightarrow{}^4I_{15/2}$ emissions. The excited $Er^{3+}$ ions can farther relax nanradiatively to ${}^4I_{9/2}$ state; also, the $Er^{3+}$ ions in the ${}^4I_{11/2}$ state can relax nanradiatively to the ${}^4I_{13/2}$ state and then populate to ${}^4F_{9/2}$ state via absorb a phonon of 966 nm pumping light or energy transfer from $Yb^{3+}$ ions, and leading to the red ${}^4F_{9/2}\rightarrow{}^4I_{15/2}$ emissions.

## 4 Conclusions

The enhanced up-conversion green and red lights can be obtained in the $Er^{3+}/Yb^{3+}$ co-doped $LiYF_4$ single crystal grown by a modified Bridgman method under excitation by a 966 nm diode laser. The UC emissions of the green and red lights arise from two-photon process from excited $Yb^{3+}$ to $Er^{3+}$ energy transfer through the investigation of the pump power dependent UC spectra . The UC green and red lights can be combined to a yellowish green light which is very sensitive to eyes. Such $Er^{3+}/Yb^{3+}$ co-doped $LiYF_4$ single crystals may have potential application in the fields of biosensors, infrared pumped visible eye-safe lasers, optical telecommunication and displaying devices.

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