Single-band near-infrared quantum cutting of Ho^{3+} - Yb^{3+} codoped KLu_2F_7 phosphors by energy clustering

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Abstract: A single-band near-infrared (NIR) quantum cutting (QC) is efficiently achieved for 1190 nm fluorescence by structuring Ho^{3+} - Yb^{3+} couple as energy clustering in KLu_2F_7 host under excitation of ultraviolet-to-green photons. In comparison with Ho^{3+} singly doping, the intensity of NIR emission was enhanced by at least 5 times as 75% Yb^{3+} is codoped into $\text{KLu}_2\text{F}_7\text{:Ho}^{3+}$. On the basis of experimental data and theoretical analysis, the formation of Yb^{3+} (fractional Ho^{3+}) energy clustering at sub-lattice level is demonstrated to account for resonant energy transfer (ET) of $\text{Ho}^{3+} \rightarrow \text{Yb}^{3+}$, back ET of $\text{Yb}^{3+}: {}^2\text{F}_{5/2} \rightarrow \text{Ho}^{3+}: {}^5\text{I}_6$, and the crucial energy preserving by confining Yb^{3+} energy migration. By mean of steady and dynamic spectroscopies, an internal quantum yield for the single-band 1190 nm emission is appropriately evaluated to be more than 190% for $\text{K}(\text{Lu}_{0.24}\text{Ho}_{0.01}\text{Yb}_{0.75})_2\text{F}_7$ without any obvious concentration quenching. This nanostructured design of single-band NIR QC will open up novel available way to get efficient NIR emitters, which can boost the promising applications of solar cells, optical communication, short-wavelength infrared (SWIR) bio-imaging *in vivo*, etc.

Keywords: Near-infrared quantum cutting; Ho^{3+} - Yb^{3+} ; Single band; Energy clustering.

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1. Introduction

Efficient near-infrared (NIR) luminescent materials were widely developed to promote their applications in photovoltaics, laser, optical communication, infrared photon counter, short-wavelength infrared (SWIR) bio-imaging *in vivo*, etc [1-5]. Within all kinds of rare earth dopants, Ho^{3+} , because of its abundant intra-4f energy level structure, was investigated for colorful NIR emissions in 800-2200 nm that facilitates enlarging transmission capacity of optical networks, and improving photoresponse of narrow bandgap solar cells [6-9]. To achieve strong NIR emission like $\text{Ho}^{3+}: {}^5\text{I}_6 \rightarrow {}^5\text{I}_8$ at about 1190 nm, one typical approach is to codope Yb^{3+} as sensitizer that is efficiently pumped by a commercial 980 nm laser diode (LD) [10]. Whereas inevitable visible upconversion of Ho^{3+} will predominate the whole energy conversion, to be large energy losses relative to $\text{Ho}^{3+} \sim 1190$ nm emission [11]. Alternatively, another approach is quantum cutting (QC), i.e., downconversion of an ultraviolet (UV)-to-green photon to two or three ~ 1190 nm photons in Ho^{3+} singly and/or $\text{Ho}^{3+}\text{-Yb}^{3+}$ co-doped materials [12-16]. However, multiplexing emissions like Ho^{3+} at about 675 and 2000 nm and Yb^{3+} at 1000 nm are still non-ignorable energy losses relative to $\text{Ho}^{3+} \sim 1190$ nm emission [17].

In practice, QC-related energy dynamics were utilized to design efficient NIR emitter (most are $\text{RE}^{3+}\text{-Yb}^{3+}$ codoped systems) through doubly or triply cutting a UV-to-blue photon into NIR photons [18-30]. To enhance luminescence efficiency, explorations have been done through developing new efficient phosphors [19-22], utilizing spin-allowed transitions of ions and/or ion groups [23,24], introducing other metal ions (e.g. Ag) [25,26], controlling the propagation of electromagnetic radiation [27,28], and adjusting excitation conditions [29,30].

For a series of $\text{RE}^{3+}\text{-Yb}^{3+}$ ($\text{RE} = \text{Tb, Tm, Pr, Nd, Ho}$) codoping systems, maximum quantum yield (QY) was evaluated to be greater than 190% on the basis of cooperative and resonant QC dynamics [31,32]. However, disregarding the specific application as downconverting layer to improve the photoresponse of *c*-Si solar cells [33], the prevailing $\text{Yb}^{3+} \sim 1000 \text{ nm}$ QC systems exhibit shortcomings as follows: i) Yb^{3+} concentration is rather low before reaching fluorescence quenching threshold, which is commonly lower than 10%, in all the known NIR QC systems [31,32]. It means that major energy losses inevitably happen in either case of incomplete spectra conversion at optimal Yb^{3+} NIR emission or that of detrimental CQ at high Yb^{3+} concentration; ii) $\text{Yb}^{3+} \sim 1000 \text{ nm}$ fluorescence is just overlapped with absorption band of water, which cannot be extensively developed in the applications of optical communication, SWIR bioimaging *in vivo*, etc [2-5]. Besides, single-band NIR QC phenomena are never reported till now, and its ET mechanism is not demonstrated yet, especially at extremely high Yb^{3+} -doping concentration.

Here we focus on the nanostructure-manipulated NIR QC system with capacities of two-step resonant ET processes to drastically enhance $\text{Ho}^{3+} \sim 1190 \text{ nm}$ emission that can be feasibly utilized in optical communication, and SWIR bioimaging *in vivo*, as well as narrow bandgap solar cells like GaSb and Ge cells. By structuring Yb^{3+} energy clusters at a sub-lattice level in KLu_2F_7 host, the optimal single-band $\text{Ho}^{3+} \sim 1190 \text{ nm}$ emission is successfully achieved through a first resonant ET of $\text{Ho}^{3+}: {}^5\text{F}_4, {}^5\text{S}_2 \rightarrow \text{Yb}^{3+}: {}^2\text{F}_{5/2}$, and a sequential nearly resonant ET of $\text{Yb}^{3+}: {}^2\text{F}_{5/2} \rightarrow \text{Ho}^{3+}: {}^5\text{I}_6$ at an amazingly high 75% Yb^{3+} concentration under excitation of green photons around 536 nm. It can be believed that our results will open up one available way to design and develop novel single-band NIR QC

systems with emission beyond $\text{Yb}^{3+} \sim 1000$ nm.

2. Experimental

Polycrystalline phosphors of $\text{K}(\text{Lu}_{0.99-x}\text{Ho}_{0.01}\text{Yb}_x)_2\text{F}_7$ ($x = 0, 0.05, 0.1, 0.3, 0.5, 0.75, 0.99$) were prepared through traditional solid state reaction. Starting materials of anhydrous KF (99.95%, 3% molar excess), LuF_3 (99.99%), HoF_3 (99.99%), and YbF_3 (99.99%) were homogeneously mixed, then preheated at 200 °C using argon gas protection for 2 h, and finally sintered at 620 °C for 8 h. Phase identification of the obtained products was performed with X-ray powder diffraction (Philips PW1830) with a Cu K_α radiation source operated at 40 kV and 40 mA. Diffuse reflectance spectra were measured on a Cary 5000 UV-VIS-NIR spectrophotometer with a double out-of-plane Littrow monochromator using BaSO_4 as a standard reference. Photoluminescence (PL) spectra were recorded on an Edinburgh FLS920 spectrofluorometer with a continuous wave 450 W xenon lamp as the excitation source. Moreover, luminescence decay curves were recorded through the FLS920 system equipped with a microsecond μF900 xenon lamp. Within the steady and dynamic PL measurements, a Hamamatsu R928 photomultiplier tubes (PMT) and a liquid-nitrogen cooled R5509-72 NIR PMT were employed for photon detection in wavelength ranges of 600-800 nm and 900-1300 nm, respectively. Besides, NIR emission spectra of Yb^{3+} were measured under excitation of 940 nm by means of a computer controlled *iHR 320* spectrometer fitted with a 450 W xenon lamp and an InGaAs photodetector for photoresponse in 960-1300 nm (Horiba Jobin-Yvon corp.). Fluorescent decay curves of $\text{Yb}^{3+}: {}^2\text{F}_{5/2}$ level were acquired using a Digital Phosphor Oscilloscope (TDS3012C, Tektronix) equipped on the *iHR 320* spectrometer with a 980 nm

pulsed LD. Appropriate optical filters were employed to avoid any possible interference in all spectral measurements.

3. Results and discussion

KYb₂F₇ has an orthorhombic structure with space group *Pnam* with the unit cell dimensions of $a = 11.71 \text{ \AA}$, $b = 13.24 \text{ \AA}$, $c = 7.73 \text{ \AA}$ ($Z = 8$), which is isotypic to the structure type of β -KEr₂F₇ [34]. In this crystal structure, four species of ytterbium atoms are surrounded by eight fluorine atoms. These fluorine anions form, respectively, three quadratic antiprisms and one dodecahedron, derived from a distorted cube. Two antiprisms and the dodecahedron share two of their faces to form (Yb₃F₁₇)⁸⁻ groups. These groups are bidimensionally linked and the planes they form are joined together by the third antiprism, as shown in **Figs. 1(a-b)**. The short distance between two neighboring ytterbium atoms within the four polyhedra is from 3.41 to 3.55 $\text{\AA}$, where the ytterbium atoms form an array of discrete tetrahedral (typically regarded as the Yb cluster). To make it clear, **Figs. 1(c) and 1(d)** exhibit the schematic view of the lattice arrangement of Yb atoms in orthorhombic-phase KYb₂F₇ along the *a*- and *b*- axis direction, respectively. The crystalline structure of KYb₂F₇ orthorhombic-phase where Yb³⁺ ions are distributed in arrays of tetrad clusters has been treated by Wang *et al.* in detail [35]. Based on the short distance between two nearby Yb³⁺ ions within tetrad cluster (3.41-3.55 $\text{\AA}$) and the relatively long distance (3.75-3.83 $\text{\AA}$) between Yb clusters, Wang *et al.* concluded that the ET probability within the Yb³⁺ cluster (P_{intra}) is an order of magnitude higher than the probability of inter-cluster ET (P_{inter}) [35]. Furthermore, ET to defects or impurities within the cluster will be confined but replaced by energy

migration to preserve excitation energy over Yb sub-lattice.

In practice, Aléonard reported the structure including a series of KRE_2F_7 ($\text{RE} = \text{Y}, \text{Er}, \text{Tm}, \text{Yb}, \text{Lu}$) compounds [34]. For Yb- and Lu-based isotypic compounds, a stable solid solution $\text{K}(\text{Yb}_x\text{Lu}_{1-x})_2\text{F}_7$ can be obtained with an orthorhombic structure because of their similar ionic radii ($r_{\text{Yb}^{3+}} = 0.985 \text{ \AA}$; $r_{\text{Lu}^{3+}} = 0.977 \text{ \AA}$) and comparable chemical properties. Herein, we usually choose the standard data of KYb_2F_7 orthorhombic-phase as a reference. No evidence for the presence of a second crystalline phase was found in the XRD patterns (**Fig. 2**), where all the narrow sharp diffraction peaks are well indexed to those of pure KYb_2F_7 orthorhombic-phase (JCPDS No. 27-0459). These results indicate we successfully prepared the well-crystalized pure $\text{K}(\text{Lu}_{0.99-x}\text{Ho}_{0.01}\text{Yb}_x)_2\text{F}_7$ phosphors.

To reveal the effect of Yb^{3+} cluster on Ho^{3+} : $^5\text{I}_6 \rightarrow ^5\text{I}_8$ emission, we measured the visible and NIR emission spectra of $\text{K}(\text{Lu}_{0.99-x}\text{Ho}_{0.01}\text{Yb}_x)_2\text{F}_7$ under excitation of 536 nm [**Fig. 3(a)**]. As anticipated, the PL band around 1190 nm is observed strongly due to Ho^{3+} : $^5\text{I}_6 \rightarrow ^5\text{I}_8$ transition, and fast enhances in PL intensity as Yb^{3+} concentration increase even up to $x = 0.99$. In contrast, PL intensity of 657 nm ($^5\text{F}_5 \rightarrow ^5\text{I}_8$) and that of 748 nm ($^5\text{F}_4, ^5\text{S}_2 \rightarrow ^5\text{I}_7$) of Ho^{3+} rapidly decrease and nearly become integral ‘zero’ following Yb^{3+} concentration continuously increases to $x = 0.99$. These results indicate that ET from Ho^{3+} to Yb^{3+} takes place efficiently. Here it is of great interest that PL intensity of Yb^{3+} : $^2\text{F}_{5/2} \rightarrow ^2\text{F}_{7/2} \sim 1000 \text{ nm}$ does not clearly increase as normal cases reported extensively, but keeps nearly constant before $x = 0.30$ and declines slightly till $x = 0.99$, as comparatively shown in the inset of **Fig. 3(a)**. Moreover, $\text{Yb}^{3+} \sim 1000 \text{ nm}$ emission features rather feeble intensity relative to $\text{Ho}^{3+} \sim 1190 \text{ nm}$ at any case of $x \sim 0.05\text{-}0.99$. These phenomena reveal that in $\text{K}(\text{Lu}_{0.99-x}\text{Ho}_{0.01}\text{Yb}_x)_2\text{F}_7$

hosts, the excited energy in $\text{Yb}^{3+}: {}^2\text{F}_{5/2}$ state does not radiate as NIR photons around 1000 nm but is efficiently back-transferred to the nearby Ho^{3+} ions, finally enabling single-band 1190 nm emission. On the other hand, decay curves of 657 and 748 nm emissions of Ho^{3+} were recorded as a function of Yb^{3+} concentration upon 536 nm pulsed excitation [Figs. 3(b-c)]. Once Yb^{3+} ions co-doped into $\text{K}(\text{Lu}_{0.99}\text{Ho}_{0.01})_2\text{F}_7$, the decay time of ${}^5\text{F}_4, {}^5\text{S}_2$ excited state [Fig. 3(b)] and that of ${}^5\text{F}_5$ excited state [Fig. 3(c)] declines fast, especially at $x > 0.1$, relative to that of Ho^{3+} -single doping. An initial lifetime $\sim 204.61 \mu\text{s}$ of ${}^5\text{F}_4, {}^5\text{S}_2$ state in $\text{K}(\text{Lu}_{0.99}\text{Ho}_{0.01})_2\text{F}_7$ monotonously decrease to $18.54 \mu\text{s}$ as $x \sim 0.75$ Yb^{3+} introduced into $\text{K}(\text{Lu}_{0.24}\text{Ho}_{0.01}\text{Yb}_{0.75})_2\text{F}_7$, and that of ${}^5\text{F}_5$ state $\sim 102.73 \mu\text{s}$ in $\text{K}(\text{Lu}_{0.99}\text{Ho}_{0.01})_2\text{F}_7$ gradually reduce to $7.61 \mu\text{s}$ in $\text{K}(\text{Lu}_{0.24}\text{Ho}_{0.01}\text{Yb}_{0.75})_2\text{F}_7$. It should point out that we could not acquire the corresponding decay curves at $x = 0.99$ just because the emissions at 657 and 748 nm are both too feeble to be nearly zero [Fig. 3(a)]. These results additionally validate that the efficient ET from ${}^5\text{F}_4, {}^5\text{S}_2$ and ${}^5\text{F}_5$ excited states of Ho^{3+} to the ${}^2\text{F}_{5/2}$ state of Yb^{3+} does take place in $\text{K}(\text{Lu}_{0.99-x}\text{Ho}_{0.01}\text{Yb}_x)_2\text{F}_7$ phosphors.

Schematic energy level diagram in Fig. 4 illustrates the possible ET mechanism between Ho^{3+} and Yb^{3+} ions: once $\text{Ho}^{3+}: {}^5\text{F}_4, {}^5\text{S}_2$ state is excited by green photons around 536 nm, cross-relaxation ET of $\text{Ho}^{3+}: {}^5\text{F}_4, {}^5\text{S}_2 + \text{Yb}^{3+}: {}^2\text{F}_{7/2} \rightarrow \text{Ho}^{3+}: {}^5\text{I}_6 + \text{Yb}^{3+}: {}^2\text{F}_{5/2}$ will resonantly take place (ET1, i.e., first-step of NIR-QC), causing the appearance of $\text{Yb}^{3+} \sim 1000$ nm emission, and obvious decrease of PL intensity of $\text{Ho}^{3+} \sim 748$ nm especially at elevated Yb^{3+} concentration. Following energy decay accelerated by ET1 to $\text{Ho}^{3+}: {}^5\text{I}_6$ state, PL intensity of $\text{Ho}^{3+}: {}^5\text{I}_6 \rightarrow {}^5\text{I}_8$ at ~ 1190 nm monotonically increases (corresponding to the second-step of NIR-QC). Besides, the energy in populated $\text{Yb}^{3+}: {}^2\text{F}_{5/2}$ state will be sequentially transferred to

the 5I_6 state of neighboring Ho^{3+} by means of a called BET process [16,17], which is especially efficient in the energy clustering of KYb_2F_7 host lattice with minimum Ho^{3+} -to- Yb^{3+} distance ~ 3.41 - 3.55 Å. Here the energy mismatch of about 1300 cm^{-1} between $Yb^{3+}: ^2F_{5/2}$ and $Ho^{3+}: ^5I_6$ states can be easily compensated by emitting three phonons [36]. As a result, even Yb^{3+} concentration exceeds quenching threshold of $x \sim 0.30$, PL intensity of $Yb^{3+} \sim 1000\text{ nm}$ does not obviously improve at all [Fig. 3(a)]. On the other hand, following energy populates $Ho^{3+}: ^5F_5$ state via multi-phonon relaxation (MPR) process from the excited $^5F_4, ^5S_2$ state (Fig. 4), another cross-relaxation ET of $Ho^{3+}: ^5F_5 \rightarrow ^5I_7 + Yb^{3+}: ^2F_{7/2} \rightarrow ^2F_{5/2}$ (ET2) efficiently occur, significantly reducing PL intensity of $Ho^{3+}: ^5F_5 \rightarrow ^5I_7$ at about 657 nm , but enhancing the population of $Yb^{3+}: ^2F_{5/2}$ intermediate energy reservoir to finally feed $Ho^{3+}: ^5I_6$ state for $\sim 1190\text{ nm}$ emission.

To give an insight into BET process of $Yb^{3+}: ^2F_{5/2} \rightarrow Ho^{3+}: ^5I_6$, NIR emission spectra of $K(Lu_{0.99-x}Ho_{0.01}Yb_x)_2F_7$ were recorded under excitation of 940 nm using a 960 nm long-pass filter before the detector. In the measurement, NIR 940 nm excitation light from a 450 W xenon lamp would be weak enough to uncreate any upconversion (no emission detected practically). Under this situation, the $Ho^{3+}: ^5I_6 \rightarrow ^5I_8$ at $\sim 1190\text{ nm}$ is only caused by the BET process once the Yb^{3+} energy clustering absorbs NIR photons around 940 nm . As expected, PL intensity of $Ho^{3+} \sim 1190\text{ nm}$ features monotonic enhancement by increasing Yb^{3+} concentration (Fig. 5), while that of $Yb^{3+} \sim 1000\text{ nm}$ increase to a maximum at $x \sim 0.5$ and then decrease obviously due to concentration quenching and/or efficient BET process at $x > 0.5$. The inset of Fig. 5 shows the dependence of overall integrated NIR PL intensity on Yb^{3+} concentration under excitation of 940 nm . It is of great interest that the overall integrated

emission intensity first increases and then retains nearly constant with the increase of Yb^{3+} concentration. These results prove that: i) Yb^{3+} energy clustering indeed completely preserves excitation energy without efficient long-distance migration to impurities and defects in the sub-lattice level of KYb_2F_7 host; ii) as $\text{Yb}^{3+}: {}^2\text{F}_{5/2}$ excited, BET process of $\text{Yb}^{3+}: {}^2\text{F}_{5/2} \rightarrow \text{Ho}^{3+}: {}^5\text{I}_6$ does occur efficiently for much stronger $\text{Ho}^{3+} \sim 1190$ nm luminescence.

The role of Yb^{3+} energy clustering in preserving excitation energy can be further verified by decay curves of Yb^{3+} emission upon pulsed light directly exciting Yb^{3+} into the ${}^2\text{F}_{5/2}$ state [Fig. 6(a)]. As Yb^{3+} concentration increases, the decay of Yb^{3+} fluorescence keeps nearly unchanged till $x \sim 0.5$, and then behave a relatively obvious change tendency. Practically the lifetime of $\text{Yb}^{3+}: {}^2\text{F}_{5/2}$ state just slightly decreases from 1200 to 780 μs in comparison with some typical Yb^{3+} -doped hosts, such as lifetime ~ 891 μs at 1% Yb^{3+} and 220 μs at 20% Yb^{3+} in YAG, ~ 700 μs at 1% Yb^{3+} and 50 μs at 25% Yb^{3+} in Y_2O_3 , ~ 157 μs at 5% Yb^{3+} and 42 μs at 20% Yb^{3+} in KY_3F_{10} [37-39]. These results confirm that the energy migration to quenching centers (nearby impurities and defects) is well confined by the formation of Yb^{3+} clusters in $\text{K}(\text{Lu}_{0.99-x}\text{Ho}_{0.01}\text{Yb}_x)_2\text{F}_7$, even for the concentrated sample doped with 99% Yb^{3+} . Additionally, efficient BET of $\text{Yb}^{3+}: {}^2\text{F}_{5/2} \rightarrow \text{Ho}^{3+}: {}^5\text{I}_6$ can be evidenced by the luminescent decay behaviors of ${}^5\text{I}_6$ state versus Yb^{3+} concentration. As shown in Fig. 6(b), the pulsed light of 644 nm was used to excite $\text{Ho}^{3+}: {}^5\text{F}_5$ state, which completely avoids any other interference like ET1 process. By increasing Yb^{3+} concentration, the lifetime of $\text{Ho}^{3+} \sim 1190$ nm fast increases to 3.02 ms at $x \sim 0.1$ relative to that of 2.70 ms in Ho^{3+} singly doping, and almost keep stable till $x \sim 0.75$ (specific values listed in Table 1). It is of significant interest that, once Yb^{3+} ions are introduced into $\text{K}(\text{Lu}_{0.99}\text{Ho}_{0.01})_2\text{F}_7$ host, the build-up of decay curves of $\text{Ho}^{3+} \sim 1190$ nm all

prolong remarkably relative to that of Ho^{3+} singly doping, as comparatively shown in the inset of **Fig. 6(b)**. Experimentally, the build-up time of Ho^{3+} singly doping, about 165 μs , is extended to 210, 245, 345, 315, 275, and 225 μs for the sample co-activated by $x \sim 0.05, 0.1, 0.3, 0.5, 0.75,$ and 0.99 Yb^{3+} (**Table 1**), respectively. These results demonstrated that following Yb^{3+} is excited via ET2 process from $\text{Ho}^{3+}: ^5\text{F}_5$ excited state, the confined ‘excitation energy’ in Yb^{3+} energy clustering efficiently enable a Stokes BET process to populate $\text{Ho}^{3+}: ^5\text{I}_6$ state, which resultantly prolongs the energy dynamics of $\text{Ho}^{3+}: ^5\text{I}_6 \rightarrow ^5\text{I}_8$ at $\sim 1190 \text{ nm}$. Moreover, as Yb^{3+} concentration x increases to 0.5, the build-up time of $\text{Ho}^{3+} \sim 1190 \text{ nm}$ slightly reduces from a maximum $\sim 345 \mu\text{s}$ to 315 μs , which also suggests that, besides BET of $\text{Yb}^{3+}: ^2\text{F}_{5/2} \rightarrow \text{Ho}^{3+}: ^5\text{I}_6$, energy quenching of $\text{Yb}^{3+}: ^2\text{F}_{5/2}$ excited state might take place some way at higher Yb^{3+} concentration because of introduction of impurities and/or defects.

For NIR QC material, the QY of spectral downconversion is a critical factor to judge its availability as combined with electronic devices. However, due to the limitation of semiconducting detectors, it is not feasible for us to practically measure the external QY for NIR QC systems with UV/visible photo-excitation but with NIR/IR photo-emission [40]. On the basis of experimental data and theoretical analysis, the two-photon NIR QC mainly involving 1190 nm emission comprises of a first-step ET1 of $\text{Ho}^{3+}: ^5\text{F}_4, ^5\text{S}_2 \rightarrow \text{Yb}^{3+}: ^2\text{F}_{5/2} \rightarrow \text{Ho}^{3+}: ^5\text{I}_6$, and a sequential $\text{Ho}^{3+}: ^5\text{I}_6 \rightarrow ^5\text{I}_8$ (**Fig. 4**). Therefore, the internal QY can be rationally evaluated as

$$\eta_{QC} = \eta_{^5\text{S}_2, ^5\text{F}_4} (1 - \eta_{\text{ET1}}) + \eta_{^2\text{F}_{5/2}} \eta_{\text{ET1}} + \eta_{^5\text{I}_6} \eta_{\text{ET1}} \quad (1)$$

where the radiative efficiency of $^5\text{F}_4, ^5\text{S}_2$ and $^5\text{I}_6$ states of Ho^{3+} , $\eta_{^5\text{S}_2, ^5\text{F}_4}$ and $\eta_{^5\text{I}_6}$, and that of

Yb^{3+} : $^2\text{F}_{5/2}$ state, $\eta_{^2\text{F}_{5/2}}$, can be appropriately set to unit by considering the spectroscopies and the corresponding decay behaviors of $\text{K}(\text{Lu}_{0.99-x}\text{Ho}_{0.01}\text{Yb}_x)_2\text{F}_7$ samples. Here the ET1 efficiency, η_{ET1} , can be calculated by ratio of $\tau_{x\text{Yb}^{3+}}^{^5\text{S}_2}$ to $\tau_{0\text{Yb}^{3+}}^{^5\text{S}_2}$, which, lifetime of Ho^{3+} : $^5\text{F}_4$, $^5\text{S}_2$, refer to the case of $x\text{Yb}^{3+}$ codoping and that of Ho^{3+} singly doping. As a result, the upper limit of internal QY is obtained to be about 191% in $\text{K}(\text{Lu}_{0.24}\text{Ho}_{0.01}\text{Yb}_{0.75})_2\text{F}_7$ sample.

To further examine the NIR QC of 1190 nm single band emission and its efficiency, excitation spectrum by monitoring 1190 nm ($^5\text{I}_6 \rightarrow ^5\text{I}_8$) of $\text{K}(\text{Lu}_{0.24}\text{Ho}_{0.01}\text{Yb}_{0.75})_2\text{F}_7$ was compared with the diffuse reflection spectrum of $\text{K}(\text{Lu}_{0.24}\text{Ho}_{0.01}\text{Yb}_{0.75})_2\text{F}_7$ by normalizing band at 644 nm (corresponding to $^5\text{F}_5$ excited state), as shown in **Fig. 7**. It is known that only one photon around 1190 nm can be yielded from the excited $^5\text{F}_5$ state by normal decay or BET following ET2 process, but more than one 1190 nm photon would be generated from the excited $^5\text{F}_4$, $^5\text{S}_2$ state by the two-photon NIR- QC if it happens some way. We can see that the integrated intensity of the $^5\text{I}_8 \rightarrow ^5\text{F}_4$, $^5\text{S}_2$ excitation band is determined to be about 1.93-fold more than that of the $^5\text{I}_8 \rightarrow ^5\text{F}_5$ absorption band. This result additionally validates that the two-photon NIR QC for 1190 nm emission does efficiently occur in by structuring Ho^{3+} - Yb^{3+} couple in KLu_2F_7 (**Fig. 1**). Especially, at elevated Yb^{3+} concentration like $x \sim 0.75$, nearly all the visible excitation energy is expectedly doubly-split into NIR emission energy for the 1190 nm single band fluorescence without obvious concentration quenching [**Fig. 3(a)**].

4. Conclusions

In summary, we successfully synthesized the orthorhombic $\text{K}(\text{Lu}_{0.99-x}\text{Ho}_{0.01}\text{Yb}_x)_2\text{F}_7$ polycrystalline phosphors. Under excitation of green photons around 536 nm, single-band

1190 nm emission of Ho^{3+} : $^5\text{I}_6 \rightarrow ^5\text{I}_8$ was manipulated with 5-fold stronger intensity in $\text{K}(\text{Lu}_{0.24}\text{Ho}_{0.01}\text{Yb}_{0.75})_2\text{F}_7$ in comparison with that in $\text{K}(\text{Lu}_{0.99}\text{Ho}_{0.01})_2\text{F}_7$. The intrinsic clues to efficiently preserving energy intra- Yb^{3+} clustering and BET of Yb^{3+} : $^2\text{F}_{5/2} \rightarrow \text{Ho}^{3+}$: $^5\text{I}_6$ was dug systematically by steady and dynamic spectroscopies. Based on NIR QC mechanisms, the total internal QY for NIR QC fluorescence in $\text{K}(\text{Lu}_{0.24}\text{Ho}_{0.01}\text{Yb}_{0.75})_2\text{F}_7$ was calculated to be $\sim 191\%$ by means of ET1 efficiency. Moreover, through a rigorous comparison between the integrated intensity of excitation bands (corresponding to $^5\text{F}_4$, $^5\text{S}_2$ and $^5\text{F}_5$ states) by monitoring 1190 nm emission and that of absorption bands (attributed to $^5\text{F}_4$, $^5\text{S}_2$ and $^5\text{F}_5$), the internal QY of single-band 1190 nm emission is evaluated to be about 90% in $\text{K}(\text{Lu}_{0.24}\text{Ho}_{0.01}\text{Yb}_{0.75})_2\text{F}_7$ phosphor sample. All these results emphasize the unique properties of two-photon NIR QC for single-band 1190 nm emission achieved by nano-structured design. The further development of single-band NIR QC will significantly promote the application of solar cells, laser, infrared photon counter, optical communication, SWIR bio-imaging *in vivo*, etc.

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References

- [1] L. Wondraczek, E. Tyystjärvi, J. Méndez-Ramos, F. A. Müller, Q. Y. Zhang, Shifting the sun: solar spectral conversion and extrinsic sensitization in natural and artificial photosynthesis, *Adv. Sci.* 2 (2015) 1500218.
- [2] M. J. F. Digonnet, *Rare-Earth-Doped Fiber Lasers and Amplifiers, Revised and Expanded*, Marcel Dekker Inc, New York, 2001.
- [3] D. J. Naczynski, M. C. Tan, M. Zevon, B. Wall, J. Kohl, A. Kulesa, S. Chen, C. M. Roth, R. E. Riman and P. V. Moghe, Rare-earth-doped biological composites as in vivo shortwave infrared reporters, *Nat. Commun.* 4 (2013) 3199.
- [4] S. V. Eliseeva and J. C. Bünzli, Lanthanide luminescence for functional materials and bio-sciences, *Chem. Soc. Rev.* 39 (2010) 189-227.
- [5] D. C. Yu, R. Martín-Rodríguez, Q. Y. Zhang, A. Meijerink and F. T. Rabouw, Multi-photon quantum cutting in $\text{Gd}_2\text{O}_2\text{S:Tm}^{3+}$ to enhance the photo-response of solar cells, *Light: Sci. Appl.* 4 (2015) e344.
- [6] J. Y. Allain, M. Le Flohic, M. Monerie and H. Poignant, Halide glasses holmium in ZBLAN: interplay of lasing, co-lasing and excited-state absorption, *J. Non-Cryst. Solids* 161 (1993) 270-273.
- [7] E. Rukmini and C. K. Jayasankar, Spectroscopic properties of Ho^{3+} ions in zinc borosulphate glasses and comparative energy level analyses of Ho^{3+} ions in various glasses, *Opt. Mater.* 4 (1995) 529-546.
- [8] K. Driesen, V. K. Tikhomirov, C. Görller-Walrand, V. D. Rodriguez and A. B. Seddon, Transparent Ho^{3+} -doped nano-glass-ceramics for efficient infrared emission, *Appl. Phys. Lett.* 88 (2006) 073111.
- [9] D. C. Yu, X. Y. Huang, S. Ye, M. Y. Peng and Q. Y. Zhang, Efficient near-infrared quantum splitting in $\text{YVO}_4:\text{Ho}^{3+}$ for photovoltaics, *Sol. Energy Mater. Sol. Cells* 101 (2012) 303-307.
- [10] A. Brenier, L. C. Courrol, C. Pédrini, C. Madej and G. Boulon, Yb^{3+} and Tm^{3+} ions as sensitizers for the Ho^{3+} infrared emission in $\text{Gd}_3\text{Ga}_5\text{O}_{12}$ garnet and up-conversion energy losses, *Phys. Rev. B* 49 (1994) 881-887.
- [11] B. Zhou, E. Y.-B. Pun, H. Lin, D. L. Yang and L. H. Huang, Judd–Ofelt analysis, frequency upconversion, and infrared photoluminescence of Ho^{3+} -doped and $\text{Ho}^{3+}/\text{Yb}^{3+}$ -codoped lead bismuth gallate oxide glasses, *J. Appl. Phys.* 106 (2009) 103105.
- [12] K. M. Deng, T. Gong, L. X. Hu, X. T. Wei, Y. H. Chen and M. Yin, Efficient near-infrared quantum cutting in $\text{NaYF}_4:\text{Ho}^{3+}, \text{Yb}^{3+}$ for solar photovoltaics, *Opt. Express* 19 (2011) 1749-1754.
- [13] H. Lin, D. Q. Chen, Y. L. Yu, A. P. Yang and Y. S. Wang, Near-infrared quantum cutting in $\text{Ho}^{3+}/\text{Yb}^{3+}$ codoped nanostructured glass ceramic, *Opt. Lett.* 36 (2011) 876-878.
- [14] D. C. Yu, X. Y. Huang, S. Ye, M. Y. Peng, Q. Y. Zhang and L. Wondraczek, Three-photon near-infrared quantum splitting in $\beta\text{-NaYF}_4:\text{Ho}^{3+}$, *Appl. Phys. Lett.* 99 (2011) 161904.
- [15] D. C. Yu, S. Ye, X. Y. Huang and Q. Y. Zhang, Enhanced three-photon near-infrared quantum splitting in $\beta\text{-NaYF}_4:\text{Ho}^{3+}$ by codoping Yb^{3+} , *AIP Adv.* 2 (2012) 022124.
- [16] X. J. Zhou, Y. J. Wang, X. Q. Zhao, L. Li, Z. Q. Wang and Q. X. Li, Near-infrared quantum cutting via downconversion energy transfers in $\text{Ho}^{3+}/\text{Yb}^{3+}$ codoped tellurite glass ceramics, *J. Am. Ceram. Soc.* 97 (2014) 179-184.

- [17] T. J. Chen, X. L. Yang, W. B. Xia, X. J. Gao, W. Li and S. G. Xiao, Near-infrared quantum cutting in $\text{Ho}^{3+}/\text{Yb}^{3+}$ co-doped $\text{BaZr}_{0.8}\text{Y}_{0.2}\text{O}_{3-\delta}$, *Mater. Sci. Eng. B* 211 (2016) 20-25.
- [18] P. Vergeer, T. J. H. Vlugt, M. H. F. Kox, M. I. den Hertog, J. P. J. M. van der Eerden and A. Meijerink, Quantum cutting by cooperative energy transfer in $\text{Yb}_x\text{Y}_{1-x}\text{PO}_4:\text{Tb}^{3+}$, *Phys. Rev. B* 71 (2005) 014119.
- [19] J. Li, L. Chen, Z. Hao, X. Zhang, L. Zhang, Y. Luo and J. Zhang, Efficient near-infrared downconversion and energy transfer mechanism of $\text{Ce}^{3+}/\text{Yb}^{3+}$ codoped calcium scandate phosphor, *Inorg. Chem.* 54 (2015) 4806-4810.
- [20] Z. H. Luo, Y. F. Liu, C. H. Zhang, J. X. Zhang, H. M. Qin, H. C. Jiang and J. Jiang, Effect of Yb^{3+} on the crystal structural modification and photoluminescence properties of $\text{GGAG}:\text{Ce}^{3+}$, *Inorg. Chem.* 55 (2016) 3040-3046.
- [21] L. Lin, H. Lin, Z. Wang, J. Chen, R. Huang, X. Rao, Z. Feng and Z. Zheng, Quantum-cutting of $\text{KYF}_4:\text{Tb}^{3+}$, Yb^{3+} under multiple excitations with high Tb^{3+} concentration, *Opt. Mater.* 36 (2014) 1065-1069.
- [22] T. Grzyb, K. Kubasiewicz, A. Szczeszak and S. Lis, Energy migration in $\text{YBO}_3:\text{Yb}^{3+},\text{Tb}^{3+}$ materials: Down- and upconversion luminescence studies, *J. Alloys Compd.* 686 (2016) 951-961.
- [23] J. Zhao, C. Guo, T. Li, D. Song and X. Su, Near-infrared down-conversion and energy transfer mechanism in Yb^{3+} -doped $\text{Ba}_2\text{LaV}_3\text{O}_{11}$ phosphors, *Phys. Chem. Chem. Phys.* 17 (2015) 26330-26337.
- [24] L. T. Lin, X. M. Wu, T. Wang, D. J. Chen, C. Deng, J. X. Meng and L. W. Cao, Designing a dual-mode broadband solar spectral converter: The example of Bi^{3+} , Cr^{3+} , Yb^{3+} -tridoped perovskite, *J. Alloys Compd.* 673 (2016) 411-419.
- [25] B. Zheng, S. Xu, L. Lin, Z. Wang, Z. Feng and Z. Zheng, Plasmon enhanced near-infrared quantum cutting of $\text{KYF}_4:\text{Tb}^{3+}$, Yb^{3+} doped with Ag nanoparticles, *Opt. Lett.* 40 (2016) 2630-2633.
- [26] H. Wang, S. Ye, T. Liu, S. Li and D. Wang, Molecular-like Ag clusters and Eu^{3+} co-sensitized efficient broadband spectral modification with enhanced Yb^{3+} emission, *J. Am. Ceram. Soc.* 99 (2016) 2376-2381.
- [27] Q. Wang, J. Qiu, Z. Song, Z. Yang, Z. Yin, D. Zhou and S. Wang, NIR enhancement based on energy transfer process of $\text{Ce}^{3+}-\text{Yb}^{3+}$ in inverse opal photonic crystals, *J. Am. Ceram. Soc.* 99 (2016) 911-916.
- [28] Q. Wang, J. Qiu, Z. Song, Z. Yang, Z. Yin, D. Zhou and S. Wang, Enhancement of Tb-Yb quantum cutting emission by inverse opal photonic crystals, *Opt. Mater.* 54 (2016) 229-233.
- [29] D. Gao, D. Tian, G. Xiao, B. Chong, G. Yu and Q. Pang, Up/down conversion switching by adjusting the pulse width of red laser beams in $\text{LaF}_3:\text{Tm}^{3+}$ nanocrystals, *Opt. Lett.* 40 (2015) 3580-3583.
- [30] K. Grzeszkiewicz, L. Marciniak, W. Strek and D. Hreniak, Downconversion in $\text{Y}_2\text{Si}_2\text{O}_7:\text{Pr}^{3+}$, Yb^{3+} polymorphs for its possible application as luminescent concentrators in photovoltaic solar-cells, *J. Lumin.* 177 (2016) 172-177.
- [31] B. M. van der Ende, L. Aarts and A. Meijerink, Lanthanide ions as spectral converters for solar cells, *Phys. Chem. Chem. Phys.* 11 (2009) 11081-11095.
- [32] Q. Y. Zhang and X. Y. Huang, Recent progress in quantum cutting phosphors, *Prog. Mater. Sci.* 55 (2010) 353-427.

- [33] B. S. Richards, Luminescent layers for enhanced silicon solar cell performance: Down-conversion, *Sol. Energy Mater. Sol. Cells* 90 (2006) 1189-1207.
- [34] S. Aleonard, Y. Le Fur, M. F. Gorius and M. T. Roux, Structure cristalline de la phase β -K Er_2F_7 . Composés isotopes, *J. Solid State Chem.* 34 (1980) 79-89.
- [35] J. Wang, R. R. Deng, M. A. MacDonald, B. L. Chen, J. K. Yuan, F. Wang, D. Z. Chi, T. S. Andy Hor, P. Zhang, G. Liu, Y. Han and X. G. Liu, Enhancing multiphoton upconversion through energy clustering at sublattice level, *Nat. Mater.* 13 (2014) 157-162.
- [36] D. C. Yu, J. Ballato and R. E. Riman, Temperature-dependence of multiphonon relaxation of rare-earth ions in solid-state hosts, *J. Phys. Chem. C* 120 (2016) 9958-9964.
- [37] D. C. Yu, F. T. Rabouw, W. Q. Boon, T. Kieboom, S. Ye, Q. Y. Zhang and A. Meijerink, Insights into the energy transfer mechanism in Ce^{3+} - Yb^{3+} codoped YAG phosphors, *Phys. Rev. B* 90 (2014) 165126.
- [38] F. Auzel, G. Baldacchini, L. Laversenne and G. Boulon, Radiation trapping and self-quenching analysis in Yb^{3+} , Er^{3+} , and Ho^{3+} doped Y_2O_3 , *Opt. Mater.* 24 (2003) 103-109.
- [39] D. Serrano, A. Braud, J. L. Doualan, W. Bolaños, R. Moncorgé and P. Camy, Two-step quantum cutting efficiency in Pr^{3+} - Yb^{3+} codoped KY_3F_{10} , *Phys. Rev. B* 88 (2013) 205144.
- [40] S. Möller, A. Hoffmann, D. Knaut, J. Flottmann and T. Jüstel, Determination of vis and NIR quantum yields of Nd^{3+} -activated garnets sensitized by Ce^{3+} , *J. Lumin.* 158 (2015) 365-370.

Figure captions:

Fig. 1 Crystal structure diagram of orthorhombic-phase KYb_2F_7 on the (a) (100) and (b) (010) direction (the K atom is emitted). Schematic illustrations for the lattice arrangement of Yb atoms in viewed from the (c) [100] and (d) [010] planes, respectively.

Fig. 2 XRD patterns of $\text{K}(\text{Lu}_{0.99-x}\text{Ho}_{0.01}\text{Yb}_x)_2\text{F}_7$ ($x = 0, 0.05, 0.10, 0.30, 0.50, 0.75, 0.99$) phosphors, corresponding to curves (a-g), respectively, and the standard data for KYb_2F_7 (JCPDS Card No. 27-0459) as a reference.

Fig. 3 Dependence of visible-NIR emission spectra (a) and decay curves of $^5\text{F}_4, ^5\text{S}_2$ (b) and $^5\text{F}_5$ (c) excited states of Ho^{3+} on Yb^{3+} concentration (x) in $\text{K}(\text{Lu}_{0.99-x}\text{Ho}_{0.01}\text{Yb}_x)_2\text{F}_7$ under excitation of 536 nm. Inset of Fig. 2(a) shows the integrated intensity of $\text{Yb}^{3+}: ^2\text{F}_{5/2} \rightarrow ^2\text{F}_{7/2}$ and $\text{Ho}^{3+}: ^5\text{I}_6 \rightarrow ^5\text{I}_8$ emissions as a function of Yb^{3+} concentration.

Fig. 4 Energy-level diagram schematically illustrating the proposed ET mechanisms of two-photon NIR QC in $\text{K}(\text{Lu}_{0.99-x}\text{Ho}_{0.01}\text{Yb}_x)_2\text{F}_7$, mainly involving ET and BET processes and energy preserving intra- Yb^{3+} energy cluster.

Fig. 5 NIR PL spectra of $\text{K}(\text{Lu}_{0.99-x}\text{Ho}_{0.01}\text{Yb}_x)_2\text{F}_7$ under excitation of 940 nm. Inset shows the total integrated intensity of the whole NIR region versus Yb^{3+} concentration.

Fig. 6 Decay curves of $\text{Yb}^{3+}: ^2\text{F}_{5/2} \rightarrow ^2\text{F}_{7/2}$ at 1010 nm (a) and that of $\text{Ho}^{3+}: ^5\text{I}_6 \rightarrow ^5\text{I}_8$ at 1190 nm (b) of $\text{K}(\text{Lu}_{0.99-x}\text{Ho}_{0.01}\text{Yb}_x)_2\text{F}_7$ upon pulsed light excitation of 980 and 644 nm, respectively.

The inset of Fig. 5(b) shows the build-up in the first 1.05 ms of decay curves for clarity.

Fig. 7 Comparison of diffuse reflectance spectrum (dashed red curve) with excitation spectrum (solid blue line) by normalizing the integrated intensity of $^5I_8 \rightarrow ^5F_5$ transition for $K(Lu_{0.24}Ho_{0.01}Yb_{0.75})_2F_7$ phosphor. The excitation spectrum monitored at 1190 nm was corrected for wavelength-dependent instrument response.

Table captions:

Table 1. Lifetime and rise time of Ho^{3+} : $^5\text{I}_6 \rightarrow ^5\text{I}_8 \sim 1190 \text{ nm}$ in $\text{K}(\text{Lu}_{0.99-x}\text{Ho}_{0.01}\text{Yb}_x)_2\text{F}_7$ samples under pulsed light excitation of 644 nm.

Figures:

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Table 1

Yb^{3+} content (x)	τ_{decay} (ms)	τ_{rise} (μs)
0	2.70	165
0.05	2.81	210
0.10	3.02	245
0.30	2.93	345
0.50	2.73	315
0.75	2.45	275
0.99	2.19	225