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Tunable visible upconversion emission in Er^{3+}/Yb^{3+}-codoped $KCaBO_3$ phosphors by introducing Ho^{3+} ions

Subrata Das [a,*,1], A. Amarnath Reddy [a,2], S. Surendra Babu [b], G. Vijaya Prakash [a]

[a] Nanophotonics Laboratory, Department of Physics, Indian Institute of Technology Delhi, New Delhi 110016, India
[b] Directorate of Laser Systems, Research Centre Imarat, Hyderabad 500069, India

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ABSTRACT

Herein, the tunable upconversion (UC) emission from $KCaBO_3$ phosphors, codoped with fixed Er^{3+}, Yb^{3+} and various Ho^{3+}-concentrations, has been demonstrated. Under 980 nm laser excitation, strong tunability from green to red color emission was successfully achieved via controlling the Ho^{3+}-codoping in $KCaBO_3$:Er^{3+},Yb^{3+},$x$$Ho^{3+}$ phosphor due to efficient two-photon excitations and inter-ion energy transfer (from Yb^{3+} to Er^{3+}/Ho^{3+}) mechanisms. Substantial decrease in the green–red intensity ratio from 3.94 to 0.21 and systematic enhancement in energy transfer efficiency (η), with the increment of Ho^{3+}-content, supported the above mechanisms.

1. Introductions

Recently, considerable efforts have been dedicated to the exploration of materials capable of emitting multicolor tunable luminescence under shorter wavelength excitation for their important applications in lighting, displays, bio-labels and other optoelectronic devices. However, multicolor upconversion (UC) emission can also be achieved from an optimized combination of multiple rare-earth (Re) ions, which can be efficiently excited with near infrared (NIR) light [1–5]. Codoping of Yb^{3+} sensitizer with Er^{3+} or Ho^{3+} activators remarkably enhances the UC efficiency due to the large absorption cross-section of Yb^{3+} in the NIR region and efficient energy-transfer (ET) to adjacent Re^{3+} activators. Essentially, due to similarity in the energy levels between Er^{3+} and Ho^{3+}, the combined system containing Er^{3+}, Ho^{3+}, and Yb^{3+} ions could be ideal for precise selection of wide range of multicolor visible emission via controlled energy transfer mechanisms [1,6]. Indeed, the UC emission tunability is strongly dependent on host–activator interactions, structure of host matrix, excited state absorption (ESA) and energy-transfer (ET) between the f–f transitions of sensitizer to the activator, solubility of dopants and fabrication methods [5–9]. In low-phonon energy hosts, such as fluorides, the color tunable UC properties are strongly enhanced due to the relatively high multi-photon relaxation rates [2,6], despite major limitations, such as moisture sensitivity and chemical/mechanical instability [7,10–12]. Inorganic orthoborates can be a special choice for UC phosphor due to their wide range of transparency over a broad spectral range, designer-flexible lattice structure and durable for chemical/mechanical and high-laser usages. Alkali/alkaline-earth mixed borates have already demonstrated their importance as red/green down converted (DC) and UC phosphors for many optical applications [8,9,13]. Recently, we have reported the ability of Er^{3+}/Yb^{3+}-codoped $KCaBO_3$ as a potential UC green phosphor [8]. In another report, we have presented a new class of single-phased Dy^{3+}/Eu^{3+}-codoped $KCaBO_3$ phosphors, which showed excellent white-light emission upon UV-excitations [13]. According to structural geometry, $KCaBO_3$ material has strong capability to adopt high concentration of trivalent rare-earth ions [8,13]. In this work, green emitting $KCaBO_3$:Er^{3+},Yb^{3+} phosphor has been codoped with Ho^{3+} ions and the multicolor UC emissions have been achieved via the proper adjustment of Ho^{3+} ions in $KCaBO_3$:2 wt%Er^{3+},16 wt% Yb^{3+}. The scope of the present work is to offer an influential and easily implemented method to achieve a multicolor emitting single system via upconversion.

2. Experimental details

Various Ho^{3+} ions (x=0–4 wt%) codoped $KCaBO_3$:2 wt%Er^{3+}, 16 wt%Yb^{3+} phosphors were synthesized via a solid-state reaction method as described in our previous reports [8,13]. The upconverted (UC) and downconverted (DC) emission measurements were carried out using home built setups with respective laser

* Corresponding author. Tel.: +91 11 2659 1326; fax: +91 11 2658 1114.
E-mail addresses: phy_subrata@yahoo.co.in (S. Das), prakash@physics.iitd.ac.in (G. Vijaya Prakash).
[1] Current address: Department of Chemical Engineering, National Taiwan University, Taipei, Taiwan, R.O.C.
[2] Current address: Department of Materials and Ceramics Engineering, University of Aveiro, CICECO, 3810-193 Aveiro, Portugal.

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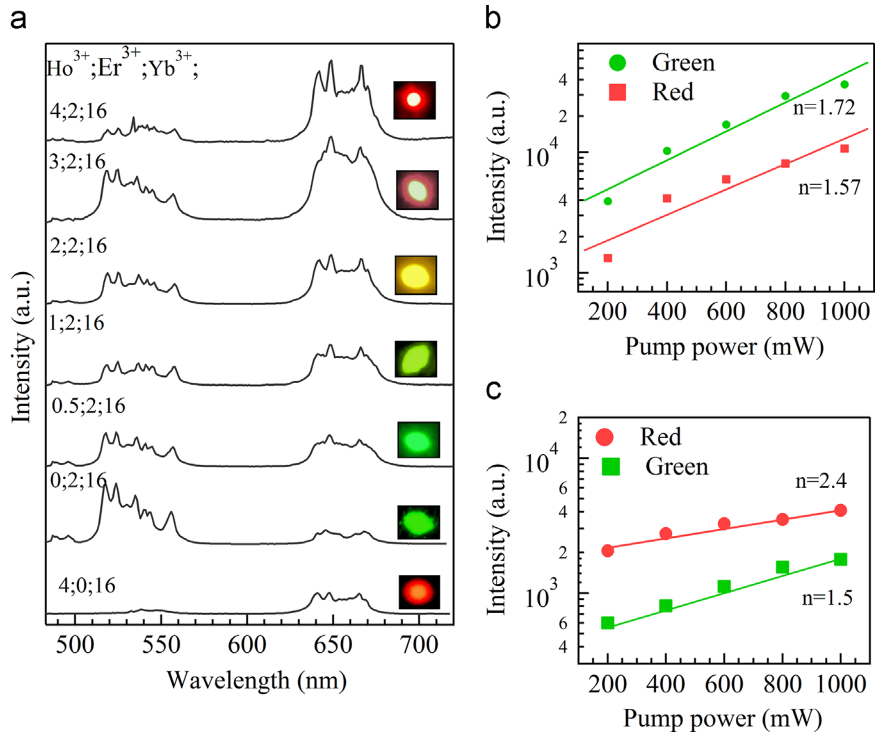

Fig. 1. (a) Upconversion (UC) emission spectra of x%Ho^{3+}-codoped (x=0–4) $KCaBO_3$:Er^{3+},Yb^{3+} phosphors (λ_{exc}=980 nm). The images shown for each plot represent the true colors of phosphors, as seen visible to a naked eye. The log–log plot of UC emission intensity versus pumping power for green (524 nm) and red (660 nm) emissions of (b) $KCaBO_3$:Er^{3+},Yb^{3+} and (c) $KCaBO_3$:Er^{3+},Yb^{3+},4%Ho^{3+} phosphors.

sources of 980 and 532 nm. The emitted light was dispersed into a monochromator (Acton-SP2300) coupled to a photo multiplier tube (PMT) through an appropriate lens system. For time resolved emission, mechanical chopper (12 Hz), lock-in amplifier, and digital storage oscilloscope were employed.

3. Results and discussion

The upconversion (UC) emission from $KCaBO_3$:Er^{3+},Yb^{3+} phosphors, codoped with x%Ho^{3+} ions, is depicted in Fig. 1(a). Strong emission bands centered at 524, 548 and 660 nm attribute to Er^{3+}:$^2H_{11/2}\rightarrow{}^4I_{15/2}$, Er^{3+}:$^4S_{3/2}\rightarrow{}^4I_{15/2}$+$Ho^{3+}$:$^5S_2$, $^5F_4\rightarrow{}^5I_8$, and Er^{3+}:$^4F_{9/2}\rightarrow{}^4I_{15/2}$+$Ho^{3+}$:$^5F_5\rightarrow{}^5I_8$ transitions, respectively. Weak blue emission (487 nm) has also been observed due to Er^{3+}:$^4F_{7/2}\rightarrow{}^4I_{15/2}$ transitions. Importantly, Er^{3+}:$^4S_{3/2}\rightarrow{}^4I_{15/2}$ and Er^{3+}:$^4F_{9/2}\rightarrow{}^4I_{15/2}$ transitions (547 and 656 nm, respectively) are overlapped with that of Ho^{3+}:$^5S_2$,$^5F_4\rightarrow{}^5I_8$ and Ho^{3+}:$^5F_5\rightarrow{}^5I_8$ transitions (547 and 660 nm, respectively) significantly. Due to such large overlap, enhancement in the respective emission with the Ho^{3+}-concentration has been observed.

In order to understand ET and populating mechanisms, the UC emission intensity (I) has been plotted against infrared pump-power (P) according to equation $I\propto P^n$, where n represents the number of photons absorbed in the process. The linear fits of log(I) versus log(P) and the as estimated slope values for green and red bands of $KCaBO_3$:Er^{3+},Yb^{3+},x%Ho^{3+} (x=0,4) are represented in insets of Fig. 1(b) and (c), respectively. The estimated slopes are more than one, indicating a two-photon UC process [(Er^{3+}: ($^4I_{11/2}$+photon$\rightarrow{}^4F_{7/2}$), Ho^{3+}:($^5I_6$+photon$\rightarrow{}^5S_2$,$^5F_4$)] without any avalanche mechanism. However, considerable decrease in Green-to-Red integrated emission intensity ratio (GRR) with increasing Ho^{3+}-content indicates the strong ET from Er^{3+} to Ho^{3+} ions and thus leads to the possibilities of the color tunability in the present phosphor materials. For comparison, the downconversion emission for all samples has been recorded under 532 nm laser excitation and illustrated in Fig. 2(a). Unlike the UC, the DC spectra contain a broad green emission in the range 538–650 nm, corresponding to the transitions Er^{3+}:$^4S_{3/2}\rightarrow{}^4I_{15/2}$+$Ho^{3+}$:$^5S_2$,$^5F_4\rightarrow{}^5I_8$. The intensity of this overlapping peak increased monotonically with the increase of Ho^{3+}-content. Such an enhancement is expected due to increase of depopulation of Ho^{3+}:$^5S_2$,$^5F_4$ states caused by direct radiation (see Supporting information). Fig. 2(b) represents the schematic energy levels of the Er^{3+}, Ho^{3+} and Yb^{3+} ions and sequential quadratic dependence of UC and the DC emission processes. As illustrated in the energy diagram, UC initiates through Yb^{3+}-sensitizer excitation and ET to Er^{3+} and Ho^{3+} ions and consequently favors the simultaneous inter-ion ET between Er^{3+} and Ho^{3+} ions. Moreover, excited state absorption (ESA) and cross-relaxation (CR) processes in both Er^{3+} and Ho^{3+} ions significantly improve the UC efficiency. The excitation processes based on the long-lived $^4I_{11/2}$ level of Er^{3+} ion and the $^5I_6$ level of Ho^{3+} ion are as follows:

Excited state absorption (*ESA*): Er^{3+}: ($^4I_{11/2}$+photon$\rightarrow{}^4F_{7/2}$), Ho^{3+}: ($^5I_6$+photon$\rightarrow{}^5S_2$,$^5F_4$).

Cross-relaxation (*CR*): Er^{3+}:[($^4I_{11/2}$+$^4I_{11/2}$)$\rightarrow$($^4F_{7/2}$+$^4I_{15/2}$)] and Ho^{3+}:[($^5S_2$,$^5F_4$+$^5I_7$)$\rightarrow$($^5F_5$+$^5I_6$)].

Energy transfer (*ET*): Er^{3+}:$^2H_{11/2}$+$^4S_{3/2}\rightarrow$$Ho^{3+}$:$^5S_2$+$^5F_5$ levels and Er^{3+}:$^4F_{9/2}\rightarrow$$Ho^{3+}$:$^5F_5$.

As a consequence of ET from Er^{3+} to Ho^{3+} and cross relaxation in Er^{3+} and Ho^{3+} ions, the relative green intensity decreases and the red emission increases since the average distance between the dopant ions decrease. This is evident by the presence of a very strong red emission in 4%Ho^{3+} codoped sample with a relatively smaller GRR value (Table 1). It is interesting to note that the GRR values sharply decrease with respect to the increase of Ho^{3+}-concentration (Fig. 3(a)), which is a supportive evidence for efficient inter-ionic ET Er^{3+}:$^2H_{11/2}$+$^4S_{3/2}\rightarrow$$Ho^{3+}$:$^5S_2$+$^5F_5$.

The ET efficiency (η) between Er^{3+}:$^2H_{11/2}$ and Ho^{3+}:$^5S_2$ levels can be further estimated [3] from the experimental radiative