



Influence of Yb³⁺ concentration on upconversion luminescence of Ho³⁺

Ying Yu^{a,*}, Yangdong Zheng^a, Feng Qin^a, Lixin Liu^a, Changbin Zheng^a, Guanying Chen^a, Zhiguo Zhang^{a,*}, Wenwu Cao^{a,b,*}

^a Department of physics, Harbin Institute of Technology, 150001, Harbin, PR China

^b Materials Research Institute, The Pennsylvania State University, University Park, PA 16802, USA

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ABSTRACT

Upconversion (UC) emissions at 360 ($(^5F_3, ^3F_4, ^5G_2 \rightarrow ^5I_8)$), 392 ($(^3K_7, ^5G_4 \rightarrow ^5I_8)$), 428 ($(^5G_5 \rightarrow ^5I_8)$), 554 ($(^5S_2, ^5F_4 \rightarrow ^5I_8)$), 667 ($(^5F_5 \rightarrow ^5I_8)$) and 754 ($(^5S_2, ^5F_4 \rightarrow ^5I_7)$) nm were obtained in 0.1 mol% Ho³⁺/x mol% Yb³⁺:Y₂O₃ (x=2, 5, 8, 11, 15) bulk ceramics under infrared (IR) excitation at 976 nm. The intensity of the UC luminescence centered at 554 and 754 nm increased with Yb³⁺ concentration from 2 to 5 mol% and decreased from 5 to 15 mol%, while the UC luminescence centered at 392, 428 and 667 nm increased with Yb³⁺ concentration from 2 to 11 mol%, then started to reduce with Yb³⁺ concentration until 15 mol%. This comes from the competition between the energy back transfer (EBT) process [$(^5S_2, ^5F_4(\text{Ho}) + ^2F_{7/2}(\text{Yb}) \rightarrow ^5I_6(\text{Ho}) + ^2F_{5/2}(\text{Yb}))$] as well as $(^5F_5(\text{Ho}) + ^2F_{7/2}(\text{Yb}) \rightarrow ^5I_7(\text{Ho}) + ^2F_{5/2}(\text{Yb}))$] and spontaneous radiation process. The intensity of the UC luminescence centered at 360 nm always increases with Yb³⁺ concentration from 2 to 15 mol%. We believe that it may come from the cooperation of energy transfer process from Yb³⁺ ions in the $^2F_{5/2}$ state and the cross energy transfer process $(^5S_2, ^5F_4 + ^5I_6 \rightarrow (^5F_3, ^3F_4, ^5G_2) + ^5I_8)$.

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1. Introduction

There has been continuous interest in developing rare-earth ion doped upconversion (UC) materials for high-density optical data storage, color display, undersea communications, infrared sensors and biomedicine [1–3], utilizing the powerful capability of transforming infrared light into visible and ultraviolet (UV) radiations. Trivalent Ho³⁺ ions constitutes an intriguing active ion for UC emissions, since it has a broad fluorescent spectrum ranging from vacuum ultraviolet (VUV) to IR [4–8]. Therefore, many researchers have focused their attention on the UC emissions of Ho³⁺ ions [9–17]. Especially, there have been considerable interests in the ultraviolet (UV) UC radiations of Ho³⁺ ions [18–21]. However, most of the studies on the UV UC radiations of Ho³⁺ ions are reported in fluoride and chloride. It is difficult to observe the UV UC emissions of Ho³⁺ ions in oxide. In addition, analyses on detailed mechanism of the UV UC emissions of Ho³⁺ ions are still lacking.

In this work, we report the characteristics of UC emissions of Ho³⁺ ions in 0.1 mol% Ho³⁺/x mol% Yb³⁺:Y₂O₃ (x=2, 5, 8, 11, 15) bulk ceramics. We have measured the dependence of luminescence intensity on pump power in order to understand the mechanism of the UC emissions. We have also characterized the dependence of the max intensity of different UC emissions of Ho³⁺ ions on Yb³⁺ ion concentrations.

2. Experimental

The Y₂O₃ nanocrystals were prepared with 1 mol% Ho³⁺ and x mol% Yb³⁺ (x=2, 5, 8, 11, 15) ion doping using the sol-gel method. Yttrium, holmium and ytterbium nitrates in corresponding molar ratios were completely dissolved in de-ionized water. Subsequently, citric acid was added into the solution with a 1:3 mole ratio of (Y+Ho+Yb) to citric acid. After complete dissolution, the pH of the solution was adjusted to 6.0 by addition of ammonium hydroxide. The resulting solution was dried at 120 °C for 24 h until it was transformed into a black bulk, which was calcined at 800 °C for 2 h. The calcined powders were pressed into flat 13 mm diameter disks of 1 mm in thickness, which were then sintered at 1300 °C for 24 h to form ceramic samples. The crystal structures were identified by x-ray diffraction (XRD) with Cu K α ($\lambda = 0.1542$ nm) radiation. The UC fluorescence spectra were obtained by irradiation of a 976 nm diode laser with the maximum power output of 500 mW. The UV, visible and NIR UC emissions from the samples were collected by a lens-coupled monochromator (Zolix SBP-300) with 3 nm spectral resolution and with an attached photomultiplier tube (Hamamatsu CR131). All measurements were performed at ambient pressure and room temperature.

3. Results and discussions

Fig.1 presents the XRD patterns of 0.1 mol% Ho³⁺/8 mol% Yb³⁺:Y₂O₃ sample and the standard data for Y₂O₃. The diffracting peak positions correspond well to the standard powder diffraction pattern

* Corresponding authors.

E-mail addresses: yubarbara1981@163.com (Y. Yu), zhangzhiguo@hit.edu.cn (Z. Zhang), dzk@psu.edu (W. Cao).

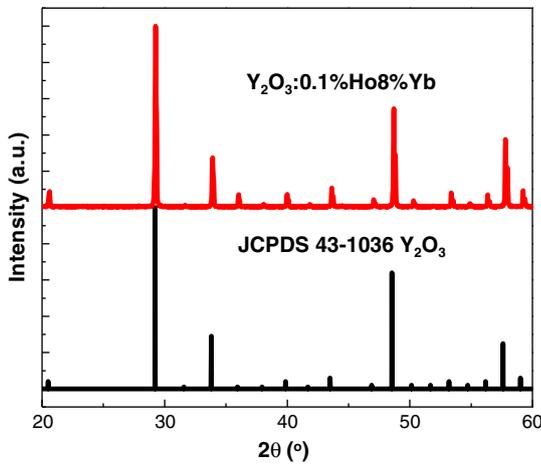


Fig. 1. Measured x-ray-diffraction spectrum of Y_2O_3 ceramic doped with 1 mol% Ho^{3+} ions and 8 mol% Yb^{3+} ions.

of Y_2O_3 (JCPDS 43-1036). The spectrum shows that the crystal phase is cubic. No segregation of dopants is observed. There are two Y^{3+} sites in cubic Y_2O_3 : 75% of these sites corresponding to point-group symmetry C_2 , and the remaining 25% are point-group symmetry C_{3i} . The Ho^{3+} and Yb^{3+} ions may locate on either of these sites in the cubic $\text{Ho}^{3+}/\text{Yb}^{3+}:\text{Y}_2\text{O}_3$ lattice. However, the selection rules dictate that electric dipole transitions are forbidden for the rare earth dopant ions in the C_{3i} sites due to its center of inversion. Thus, the observed spectrum has been attributed to ions in sites of C_2 symmetry [22].

Fig. 2 displays the UC emission spectra of 0.1 mol% Ho^{3+}/x mol% $\text{Yb}^{3+}:\text{Y}_2\text{O}_3$ ($x = 2, 5, 8, 11, 15$) bulk ceramics in the wavelength range of 370–450 nm under 976 nm diode laser excitation. The inset presents the visible and near infrared (NIR) UC emissions of 0.1 mol% Ho^{3+}/x mol% $\text{Yb}^{3+}:\text{Y}_2\text{O}_3$ ($x = 2, 5, 8, 11, 15$) bulk ceramics. The intensities of red and NIR UC emissions are very weak compared to green emissions. In order to make them visible on the same figure, their signals have been magnified 2 times. The observed UC emissions centered at 360, 392 and 428 nm are assigned to the ($^5F_7, ^3F_4, ^5G_2 \rightarrow ^5I_8$, $^3K_7, ^5G_4 \rightarrow ^5I_8$ and $^5G_5 \rightarrow ^5I_8$ transitions of Ho^{3+} ions, respectively. The green, red and NIR UC emissions correspond to the $^5S_2/^5F_4 \rightarrow ^5I_8$, $^5F_5 \rightarrow ^5I_8$, and $^5S_2/^5F_4 \rightarrow ^5I_7$ transitions of Ho^{3+} ions, respectively.

In order to show a clear picture of the UC emission intensities of Ho^{3+} ions with increasing Yb^{3+} ion concentrations, we illustrate the intensity of UC emissions peaked at 360, 392, 428, 554, 667 and

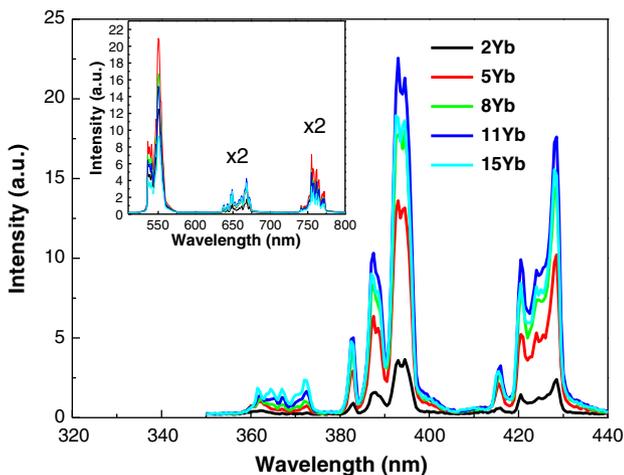


Fig. 2. Measured UV and violet UC emissions in 0.1 mol% Ho^{3+}/x mol% $\text{Yb}^{3+}:\text{Y}_2\text{O}_3$ ($x = 2, 5, 8, 11, 15$) bulk ceramics under 976 nm diode laser excitation. The inset is the visible and NIR UC emissions of 0.1 mol% Ho^{3+}/x mol% $\text{Yb}^{3+}:\text{Y}_2\text{O}_3$ ($x = 2, 5, 8, 11, 15$) bulk ceramics under the same excitation.

754 nm with the increase of Yb^{3+} ion concentrations in Fig. 3. As shown in Fig. 3, both the green and NIR UC emissions increase dramatically with Yb^{3+} ion concentrations from 2 to 5 mol% then decrease with Yb^{3+} ion concentrations from 5 to 15 mol%. The same trend of the green and NIR UC emissions with Yb^{3+} ion concentrations arises from the fact that both emissions are emitted from the same upper $^5S_2/^5F_4$ state. On the other hand, the UC emissions centered at 392, 428 and 667 nm also increase with Yb^{3+} ion concentration but peaked at 11 mol%. There is no maximum intensity of the UV UC emission centered at 360 nm with increasing Yb^{3+} ion concentrations up to 15 mol%, i.e., the UV UC emission peaked at 360 nm continuously increases with the Yb^{3+} ion concentrations from 2 to 15 mol%.

To identify the detailed UC mechanism, the dependence of the UC emission intensity (I_{up}) on pump power (I_{pump}) was investigated. It is found that the number of photons that are required to populate the upper emitting state can be obtained by the following relation [23]:

$$I_{\text{up}} \propto I_{\text{pump}}^n \quad (1)$$

where n is the number of the pumping photons required to excite the emitting state, I_{up} is the fluorescent intensity and I_{pump} is the pump laser power. A plot of $\log I_{\text{up}}$ versus $\log I_{\text{pump}}$ yields a straight line with slope n . Fig. 4 illustrates the pump power dependence of 360, 392, 428, 554, 667 and 754 nm UC emissions of a typical sample (0.1 mol% $\text{Ho}^{3+}/8$ mol% $\text{Yb}^{3+}:\text{Y}_2\text{O}_3$). For comparison, the pump power dependence of 360, 392, 428, 554, 667 and 754 nm UC emissions of 0.1 mol% Ho^{3+}/x mol% $\text{Yb}^{3+}:\text{Y}_2\text{O}_3$ ($x = 2, 5, 8, 11, 15$) bulk ceramics are compiled in Table 1. The n values for the green and NIR UC emissions of all samples agree well with each other from Table 1. This also arises from the fact that both emissions are from the same upper $^5S_2/^5F_4$ state. Additionally, saturation effects have already occurred at $^5S_2/^5F_4$ state in 0.1 mol% $\text{Ho}^{3+}/15$ mol% $\text{Yb}^{3+}:\text{Y}_2\text{O}_3$ bulk ceramic at power density range of 0.26–37.9 W/cm^2 . The well known two-photon UC emissions centered at 667 nm have experimental slope n values < 1.50 at power density range of 0.26–37.9 W/cm^2 for 0.1 mol% Ho^{3+}/x mol% $\text{Yb}^{3+}:\text{Y}_2\text{O}_3$ ($x = 2, 5, 8, 11, 15$) bulk ceramics. This result indicates that intense super saturation effects have occurred in 5F_5 state at the power density range of 0.26–37.9 W/cm^2 . The one-photon mechanisms of green and red UC emissions mean that the UC rates at the $^5S_2/^5F_4$ and 5F_5 states or the 5I_6 and 5I_7 state are much higher than the radiation decay rates [24]. Combined with high UC rates at higher energy levels, the saturation effect at green and red UC emissions might lead to successive saturation effect for the upper levels. The n values of the UV (392 nm) and violet (428 nm) UC emissions of all samples are also shown in Table 1. It is note that the n values for

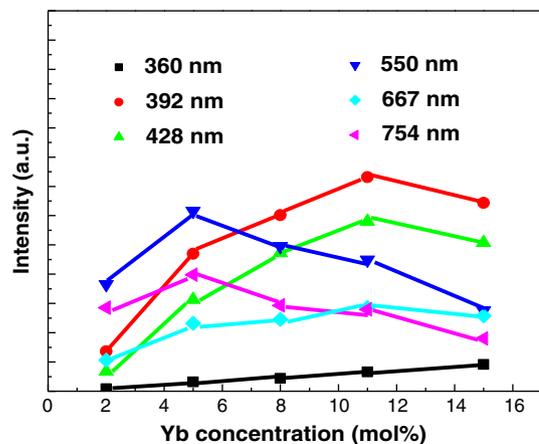


Fig. 3. Intensity of the UC emissions peaked at 362, 392, 428, 550, 667 and 754 nm as a function of Yb^{3+} concentration.

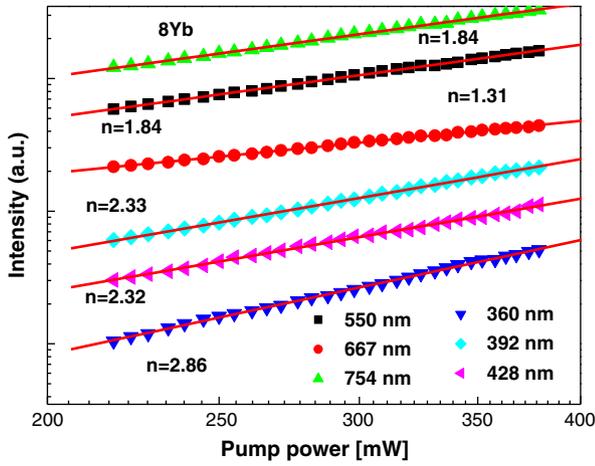


Fig. 4. The excitation power dependence curves of the UC emissions of 0.1 mol% Ho³⁺/8 mol% Yb³⁺/Y₂O₃ ceramic.

populating the ³K₇/⁵G₄ and ⁵G₅ states are equal to that of ⁵F₅ state absorbing one 976 nm photon-energy transferred by Yb³⁺ ion when doped Yb³⁺ ion concentration is between 2 and 15 mol%. This gives convincing evidence that the mechanism of the UC emissions centered at 392 and 428 nm come from the electrons in ⁵F₅ state absorbing the energy transferred by Yb³⁺ ions. The conclusion is different from previous reports [20,21], which showed that the population of the UC emissions centered at 392 and 428 nm come from electrons in ⁵S₂/⁵F₄ states absorbing the energy transferred by Yb³⁺ ions. Pump power dependence for the UV UC emission at 360 nm in 0.1 mol% Ho³⁺/x mol% Yb³⁺:Y₂O₃ (x = 2, 5) bulk ceramics are not displayed because they have a low signal-to-noise ratio. The pump power dependence for the UV UC emission at 360 nm in 0.1 mol% Ho³⁺/x mol% Yb³⁺:Y₂O₃ (x = 8, 11, 15) bulk ceramics are displayed in Table 1. It is noted that the pump power dependence for UV UC emission at 360 nm is equal to that of ⁵S₂/⁵F₄ state absorbing one 976-nm photon-energy transferred by Yb³⁺ ions.

According to the investigation above, the energy level diagrams of Ho³⁺ and Yb³⁺ ions were presented in Fig. 5 together with the proposed mechanism to produce the UV, visible and NIR UC emissions. The pump photons of 976 nm laser only excite Yb³⁺ ion, because Ho³⁺ ion have no matched excited level above its ground state. It has been demonstrated that two-photon energy transfer (ET) process from excited Yb³⁺ ions is the dominant pathway to promote the Ho³⁺ ions to the ⁵S₂/⁵F₄ state, which generates the green (554 nm) UC emission [25]. The ⁵I₇ state is populated either by nonradiative relaxation from the ⁵I₆ state or by radiative decay from the ⁵S₂/⁵F₄ state. The ⁵S₂/⁵F₄ → ⁵I₇ transition produces UC emission at 754 nm. Then saturation energy transfer (ET) process from excited Yb³⁺ ions promotes the Ho³⁺ ions from the ⁵I₇ to ⁵F₅ states, which generates the red (667 nm) UC emission. The maximum intensity of the UC emissions centered at (554, 754) nm and 667 nm occur at 5 and 11 mol%, respectively (shown in Fig. 3). It comes from the fact that energy back transfers (EBT) from Ho³⁺ to Yb³⁺ [⁵S₂/⁵F₄ (Ho) + ²F_{7/2}(Yb) → ⁵I₆(Ho) + ²F_{5/2}(Yb) and ⁵F₅(Ho) + ²F_{7/2}(Yb) → ⁵I₇

Table 1
Measured the numbers of the laser photons required for ultraviolet, visible and NIR UC emissions of 0.1 mol% Ho³⁺/x mol% Yb³⁺:Y₂O₃ (x = 2, 5, 8, 11, 15) bulk ceramics.

Yb ³⁺ concentration	2 mol%	5 mol%	8 mol%	11 mol%	15 mol%
n (360 nm)			2.86	2.50	2.31
n (392 nm)	2.45	2.38	2.33	2.30	2.13
n (428 nm)	2.45	2.38	2.32	2.22	2.21
n (550 nm)	1.95	1.90	1.84	1.59	1.44
n (667 nm)	1.42	1.37	1.31	1.28	1.21
n (754 nm)	1.97	1.93	1.84	1.63	1.43

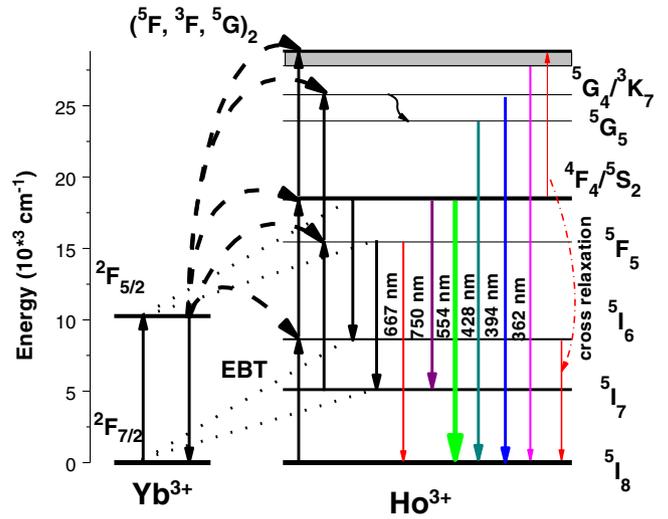


Fig. 5. Energy level diagrams of Ho³⁺ and Yb³⁺ ions as well as the UC mechanism proposed to produce the UV, violet, blue, green, red, and NIR emission bands.

(Ho) + ²F_{5/2}(Yb)] have dominated when doped Yb³⁺ ions are at 5 and 11 mol%, respectively [26].

Two ET pathways have been proposed for populating the ³K₇/⁵G₄ state. One is due to the ET process: ⁵S₂/⁵F₄(Ho) + ²F_{5/2}(Yb) → (⁵F, ³F, ⁵G)₂(Ho) + ²F_{7/2}(Yb), then the electrons on the (⁵F, ³F, ⁵G)₂ states quickly and nonradiatively decay to the ³K₇/⁵G₄ state; the other is due to the ET process: ⁵F₅(Ho) + ²F_{5/2}(Yb) → ³K₇/⁵G₄(Ho) + ²F_{7/2}(Yb). The question is which one is the dominate mechanism. According to the analysis in Fig. 3 and Table 1, the n values for populating the ³K₇/⁵G₄ and ³G₅ states are equal to that of the ⁵F₅ state absorbing one 976 nm photon-energy transferred by Yb³⁺ ions when the doped Yb³⁺ ion concentration is in the range of 2–15 mol%. Therefore, the ET process ⁵F₅(Ho) + ²F_{5/2}(Yb) → ³K₇/⁵G₄(Ho) + ²F_{7/2}(Yb) plays an important role to populate the ³K₇/⁵G₄ state. Furthermore, the electrons on the ³K₇/⁵G₄ state nonradiatively decay to the ⁵G₅ state, generating the UC radiation at 428 nm.

Two ET processes can excite the Ho³⁺ ions from the ⁵S₂/⁵F₄ to (⁵F, ³F, ⁵G)₂ states, generating the UC radiation at 360 nm. One process is by transferring energy from Yb³⁺ ions in the ²F_{5/2} state, and the other is a cross transfer process ⁵S₂/⁵F₄ + ⁵I₆ → (⁵F, ³F, ⁵G)₂ + ⁵I₈. The EBT process ⁵S₂/⁵F₄(Ho) + ²F_{7/2}(Yb) → ⁵I₆(Ho) + ²F_{5/2}(Yb) increases the population of ⁵I₆ level, which increases the intensity of the emission from the ⁵I₆ state to the ⁵I₈ state. As a consequence, the increased emission from ⁵I₆ to ⁵I₈ state makes the ⁵S₂/⁵F₄ → (⁵F, ³F, ⁵G)₂ transition more efficient. Therefore, it is evident that the maximum intensity of the UV UC emission (360 nm) peaked above 15 mol% (Yb³⁺) is a combined effect of ET process by transferring energy from Yb³⁺ ions in the ²F_{5/2} state and cross transfer process ⁵S₂/⁵F₄ + ⁵I₆ → (⁵F, ³F, ⁵G)₂ + ⁵I₈.

4. Conclusion

In summary, the Yb³⁺ ion concentration dependence of the intensities of UV, visible and NIR UC emissions of Ho³⁺ ions centered at 360, 392, 428, 554, 667 and 754 nm were investigated under a 976 nm laser diode excitation. The EBT processes ⁵S₂/⁵F₄(Ho) + ²F_{7/2}(Yb) → ⁵I₆(Ho) + ²F_{5/2}(Yb) and ⁵F₅(Ho) + ²F_{7/2}(Yb) → ⁵I₇(Ho) + ²F_{5/2}(Yb) dominate when the Yb³⁺ ion concentrations are 5 and 11 mol%, respectively, which makes the intensity of UC emissions centered at (554, 754) and (392, 428, 667) nm decrease. In addition, the ET process by transferring energy from Yb³⁺ ions in the ²F_{5/2} state ⁵I₈ → ⁵I₆ → ⁵S₂/⁵F₄ → (⁵F, ³F, ⁵G)₂ and the cross transfer process ⁵S₂/⁵F₄ + ⁵I₆ → (⁵F, ³F, ⁵G)₂ + ⁵I₈ work together to populate the (⁵F, ³F, ⁵G)₂ states. These two

mechanisms make the UC luminescence at 360 nm quench at a level >15 mol% (Yb^{3+}). This means that we can further increase the Yb^{3+} ion concentration to increase the intensity of the UV UC emission at 360 nm, and at the same time, decrease the intensity of other UC emissions.

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