Influence of Yb$^{3+}$ concentration on upconversion luminescence of Ho$^{3+}$

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Abstract

Upconversion (UC) emissions at 360 nm, 392 nm, 428 nm, 554 nm, and 667 nm were obtained in 0.1 mol% Ho$^{3+}$:Y$_2$O$_3$ (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 Yb$^{3+}$ concentration from 2 to 5 mol% and decreased from 5 to 15 mol%, while the UC luminescence centered at 392 and 428 nm increased with Yb$^{3+}$ concentration from 2 to 11 mol%, then started to reduce with Yb$^{3+}$ concentration until 15 mol%. This comes from the competition between the energy back transfer (EBT) process $\text{I}^5\text{F}_5(\text{Ho}) + 2\text{I}^7\text{F}_5(\text{Yb}) \rightarrow \lambda_5^5(\text{Ho}) + 2\lambda_7^5(\text{Yb})$ as well as $\text{I}^5\text{F}_5(\text{Ho}) + 2\text{I}^5\text{F}_5(\text{Yb}) \rightarrow \lambda_5^5(\text{Ho}) + 2\lambda_5^5(\text{Yb})$ and spontaneous radiation process. The intensity of the UC luminescence centered at 360 nm always increases with Yb$^{3+}$ concentration from 2 to 15 mol%. We believe that it may come from the cooperation of energy transfer process from Yb$^{3+}$ ions in the $\text{I}^5\text{F}_5(\text{Ho})$ 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 to 0.1 mol% Ho$^{3+}$:Y$_2$O$_3$ sample and the standard data for Y$_2$O$_3$. The diffracting peak ratios were completely dissolved in de-ionized water. Subsequently, citric acid was added into the solution with a 1:3 mole ratio of (Y$^3+$+Ho$^3+$+Yb$^{3+}$) 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 Kα (λ = 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 SBR-300) with 3 nm spectral resolution and with an attached photomultiplier tube (Hamamatsu CR1311). All measurements were performed at ambient pressure and room temperature.

1. Introduction

There has been continuous interest in developing rare-earth ion doped upconversion (UC) materials for high-density optical data storage, color display, underwater communications, infrared sensors and doped upconversion (UC) materials for high-density optical data storage, color display, underwater communications, infrared sensors and...
of Y$_2$O$_3$ (JCPDS 43-1036). The spectrum shows that the crystal phase is cubic. No segregation of dopants is observed. There are two $F^i$ sites in cubic Y$_2$O$_3$: 75% of these sites corresponding to point-group symmetry $C_5v$, and the remaining 25% are point-group symmetry $C_3v$. The Ho$^{3+}$ and Yb$^{3+}$ ions may locate on either of these sites in the cubic Ho$^{3+}$/8 mol% Yb$^{3+}$:Y$_2$O$_3$ lattice. However, the selection rules dictate that electric dipole transitions are forbidden for the rare earth dopant ions in the $C_3v$ sites due to its center of inversion. Thus, the observed spectrum has been attributed to ions in sites of $C_5v$ symmetry [22].

Fig. 2 displays the UC emission spectra of 0.1 mol% Ho$^{3+}$/x mol% Yb$^{3+}$:Y$_2$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% Yb$^{3+}$:Y$_2$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 $^5I_8$ → $^5I_{12}$, $^5K_{12}$$^5G_{12}$ → $^5I_{12}$ and $^5G_{12}$ → $^5I_{12}$ transitions of Ho$^{3+}$ ions, respectively. The green, red and NIR UC emissions correspond to the $^5S_2$ → $^5I_{12}$, $^3F_{2}$ → $^3I_{12}$ and $^3S_2$ → $^3I_7$ 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 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 $^5S_2$/F$_{2}$ 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]:

$$I_{up} \propto I_{pump}^n$$  \hspace{1cm} (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 $I_{up}$ versus log $I_{pump}$ 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% Ho$^{3+}$/8 mol% Yb$^{3+}$:Y$_2$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% Yb$^{3+}$:Y$_2$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 $^5S_2$/F$_{2}$ state. Additionally, saturation effects have already occurred at $^5S_2$/F$_{2}$ state in 0.1 mol% Ho$^{3+}$/15 mol% Yb$^{3+}$:Y$_2$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% Yb$^{3+}$:Y$_2$O$_3$ (x = 2, 5, 8, 11, 15) bulk ceramics. This result indicates that intense super saturation effects have occurred in $^3F_2$ 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 $^5S_2$/F$_{2}$ states or the $^3I_{12}$ and $^1I_7$ 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 noted that the $n$ values for
populating the $3K_f^2G_4$ and $5G_5$ states are equal to that of $5F_5$ state absorbing one 976 nm photon-energy transferred by Yb$^{3+}$ ion when doped Yb$^{3+}$ 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 $3F_5$ state absorbing the energy transferred by Yb$^{3+}$ 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 $3S_2/5$ states absorbing the energy transferred by Yb$^{3+}$ ions. Pump power dependence for the UC UC emission at 360 nm in 0.1 mol% Ho$^{3+}$/Y$_2$O$_3$ ($x=2, 5, 8$) bulk ceramics are not displayed because they have a low signal-to-noise ratio. The pump power dependence for the UC emissions centered at 392 and 428 nm come from the electrons in $3S_2/0$ and $3F_5$ states absorbing one 976-nm photon-energy transferred by Yb$^{3+}$ ions.

According to the investigation above, the energy level diagrams of Ho$^{3+}$ and Yb$^{3+}$ ions were presented in Fig. 5 together with the proposed UC mechanism proposed to produce the UV, violet, blue, green, red, and NIR emission bands.

Two ET pathways have been proposed for populating the $3K_f^2G_4$ state. One is due to the ET process: $3S_2/5$F$_4$(Ho) + $2F_{7/2}$(Yb) $\rightarrow$ $3F_5$G$_5$(Ho) + $2F_{7/2}$(Yb), then the electrons on the $(3F, 3F, G_2)_G$ states quickly and nonradiatively decay to the $5K_f^2G_4$ state or the other is due to the ET process: $2F_{7/2}$(Ho) + $2F_{7/2}$(Yb) $\rightarrow$ $5K_f^2G_5$(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 $5K_f^2G_4$ and $5G_5$ states are equal to that of the $3F_5$ state absorbing one 976-nm photon-energy transferred by Yb$^{3+}$ ions when the doped Yb$^{3+}$ ion concentration is in the range of 2–15 mol%. Therefore, the ET process $2F_{7/2}$(Ho) + $2F_{7/2}$(Yb) $\rightarrow$ $5K_f^2G_5$(Ho) + $2F_{7/2}$(Yb) plays an important role to populate the $5K_f^2G_4$ state. Furthermore, the electrons on the $3K_f^2G_4$ state nonradiatively decay to the $5G_5$ state, generating the UC emission at 428 nm.

Two ET processes can excite the Ho$^{3+}$ ions from the $3S_2/0$F$_4$ to $(3F, 3F, G_2)_G$ states, generating the UC radiation at 360 nm. One process is by transferring energy from Yb$^{3+}$ ions in the $2F_{7/2}$ state, and the other is by the cross transfer process $3S_2/5$F$_4$(Ho) + $2F_{7/2}$(Yb) $\rightarrow$ $3F_5$G$_5$(Ho) + $2F_{7/2}$(Yb) + $3F_5$G$_5$(Yb) increases the population of $3F_5$ state, which increases the intensity of the emission from the $5F_5$ state to the $5G_5$ state. As a consequence, the increased emission from $5G_5$ state makes the $5S_2/0$F$_4$ transition more efficient. Therefore, it is evident that the maximum intensity of the UC emission (360 nm) peaked above 15 mol% (Yb$^{3+}$) is a combined effect of ET process by transferring energy from Yb$^{3+}$ ions in the $2F_{7/2}$ state and cross transfer process $3S_2/0$F$_4$ + $5F_5$ $\rightarrow$ $(3F, 3F, G_2)_{G2}$ transition more efficient. Therefore, it is evident that the maximum intensity of the UC emission (360 nm) peaked above 15 mol% (Yb$^{3+}$) is a combined effect of ET process by transferring energy from Yb$^{3+}$ ions in the $2F_{7/2}$ state and cross transfer process $3S_2/0$F$_4$ + $5F_5$ $\rightarrow$ $(3F, 3F, G_2)_{G2}$ transition more efficient.

4. Conclusion

In summary, the Yb$^{3+}$ ion concentration dependence of the intensities of UV, visible and NIR UC emissions of Ho$^{3+}$ ions centered at 360, 392, 428, 554, 667 and 754 nm were investigated under a 976 nm laser diode excitation. The ET processes $3S_2/5$F$_4$(Ho) + $2F_{7/2}$ (Yb) $\rightarrow$ $5F_5$(Ho) + $3F_5$G$_5$(Yb) and $5F_5$(Ho) + $2F_{7/2}$(Yb) + $3F_5$G$_5$(Yb) + $3F_5$G$_5$(Ho) have dominated when doped Yb$^{3+}$ ions are at 5 and 11 mol%, respectively [26].

4.1 Energy level diagrams of Ho$^{3+}$ and Yb$^{3+}$ ions as well as the UC mechanism: $3S_2/5$F$_4$(Ho) + $2F_{7/2}$(Yb) $\rightarrow$ $3F_5$G$_5$(Ho) + $2F_{7/2}$(Yb) + $3F_5$G$_5$(Yb) + $3F_5$G$_5$(Ho) and $5F_5$(Ho) + $2F_{7/2}$(Yb) + $3F_5$G$_5$(Ho) + $3F_5$G$_5$(Yb) work together to populate the $(3F, 3F, G_2)_G$ states. These two processes play a significant role in the UC emission process.

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**Table 1**

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<th>Yb$^{3+}$ concentration</th>
<th>2 mol%</th>
<th>5 mol%</th>
<th>8 mol%</th>
<th>11 mol%</th>
<th>15 mol%</th>
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<td>2.33</td>
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<tr>
<td>n (392 nm)</td>
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<td>2.38</td>
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<tr>
<td>n (754 nm)</td>
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<td>1.93</td>
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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.

References