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

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ABSTRACT

Upconversion (UC) emissions at 360 ($(^5F, ^3F, ^5G)_2 \rightarrow {}^5I_8$), 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% Ho^{3+}/x mol% Yb^{3+}:Y_2O_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, 428 and 667 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 [$^5S_2/^5F_4(Ho) + {}^2F_{7/2}(Yb) \rightarrow {}^5I_6(Ho) + {}^2F_{5/2}(Yb)$ as well as $^5F_5(Ho) + {}^2F_{7/2}(Yb) \rightarrow {}^5I_7(Ho) + {}^2F_{5/2}(Yb)$] 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 $^2F_{5/2}$ state and the cross energy transfer process $^5S_2/^5F_4 + {}^5I_6 \rightarrow (^5F, ^3F, ^5G)_2 + {}^5I_8$.

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 Ho^{3+} 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 Ho^{3+} ions [9–17]. Especially, there have been considerable interests in the ultraviolet (UV) UC radiations of Ho^{3+} ions [18–21]. However, most of the studies on the UV UC radiations of Ho^{3+} ions are reported in fluoride and chloride. It is difficult to observe the UV UC emissions of Ho^{3+} ions in oxide. In addition, analyses on detailed mechanism of the UV UC emissions of Ho^{3+} ions are still lacking.

In this work, we report the characteristics of UC emissions of Ho^{3+} ions in 0.1 mol% Ho^{3+}/x mol% Yb^{3+}:Y_2O_3 ($x = 2, 5, 8, 11, 15$) 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 Ho^{3+} ions on Yb^{3+} ion concentrations.

2. Experimental

The Y_2O_3 nanocrystals were prepared with 1 mol% Ho^{3+} and x mol% Yb^{3+} ($x = 2, 5, 8, 11, 15$) 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 $K\alpha$ ($\lambda = 0.1542$ 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% Ho^{3+}/8 mol% Yb^{3+}:Y_2O_3 sample and the standard data for Y_2O_3. The diffracting peak positions correspond well to the standard powder diffraction pattern

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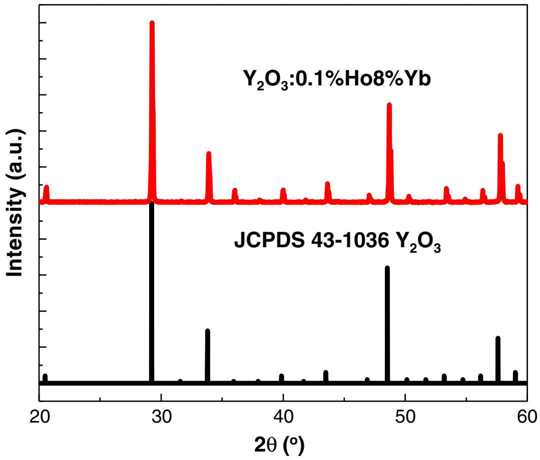

Fig. 1. Measured x-ray-diffraction spectrum of Y_2O_3 ceramic doped with 1 mol% Ho^{3+} ions and 8 mol% Yb^{3+} ions.

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 Ho^{3+}/Yb^{3+}:Y_2O_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% Yb^{3+}:Y_2O_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_2O_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 $(^5F, ^3F, ^5G)_2 \rightarrow {}^5I_8$, $^3K_7/^5G_4 \rightarrow {}^5I_8$ 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 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%.

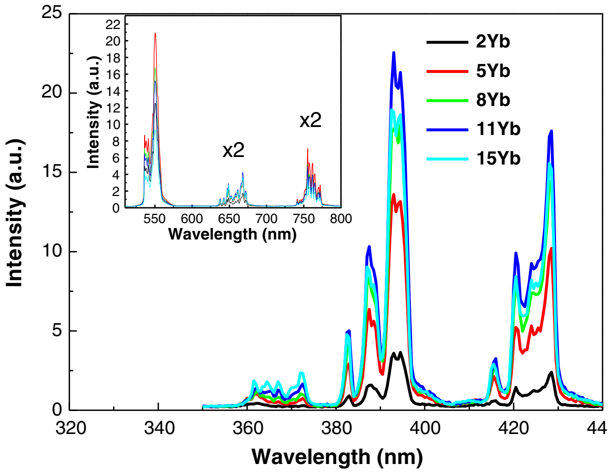

Fig. 2. Measured UV and violet UC emissions in 0.1 mol% Ho^{3+}/x mol% Yb^{3+}:Y_2O_3 ($x=2, 5, 8, 11, 15$) bulk ceramics under 976 nm diode laser excitation. The inset is the visible and NIR UC emissions of 0.1 mol% Ho^{3+}/x mol% Yb^{3+}:Y_2O_3 ($x=2, 5, 8, 11, 15$) bulk ceramics under the same excitation.

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]:

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

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_2O_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_2O_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% Ho^{3+}/15 mol% Yb^{3+}/Y_2O_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_2O_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

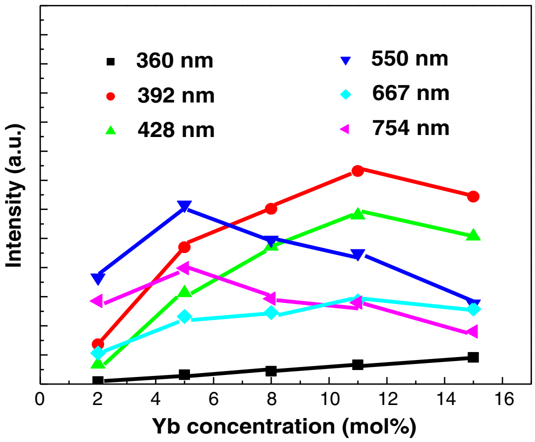

Fig. 3. Intensity of the UC emissions peaked at 362, 392, 428, 550, 667 and 754 nm as a function of Yb^{3+} concentration.