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Communications

Green Lighting Upconversion in Yb^{3+}, Er^{3+} Co-doped $PbWO_4$

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Over the several decades, lanthanide doped upconversion (UC) luminescence has received considerable attention because of their potential applications such as novel displays technologies like three-dimensional displays,[1] solar cells[2] and bio-technologies.[3] Many lanthanide ions have been researched for luminescent centers for UC materials. Among them, Er^{3+} ions doped UC phosphors are most popular one due to their abundant energy level for UC luminescence and high luminescent quenching concentration compared with other lanthanide ions.[4] In addition, for enhancement of UC emission efficiency, Yb^{3+} ion is generally used as co-dopant ions because that has large absorption cross section around 980 nm and can possible effective energy transfer to the activator ions through the multi photon process.[5]

In this article, we investigate the influence of Er^{3+} concentrations on UC luminescence of Er^{3+}/Yb^{3+} co-doped $PbWO_4$ matrix. $PbWO_4$ is selected as a good host material because $PbWO_4$ has high irradiation damage resistance and it is very stable chemically, mechanically and thermally.[6] Moreover, the W^{6+} ions in scheelite matrices have strong polarization induced by large electric charge and small radius, which leads to decrease of symmetry and enhance stark energy splitting in the crystal field.[7] Therefore, we consider that $PbWO_4$ can be suitable matrix for UC materials. The structural and UC luminescent properties are investigated and related mechanism of Er^{3+}/Yb^{3+} co-doped $PbWO_4$ ($PbWO_4:Er^{3+}/Yb^{3+}$) system are studied in detail.

Figure 1 shows room-temperature UC luminescent spectra of the $PbWO_4:Er^{3+}/Yb^{3+}$ with the variation of Er^{3+} concentrations from 0.1 to 5 mol % excited at 980 nm. Figure 1(a) present the UC luminescent spectra in a range from 490 to 710 nm and Figure 1(b) show the relative UC intensity of green and red emission with variation of Er^{3+} concentration. The UC emission is dominated by strong green emission, while red emission is so weaker than green emission. The $PbWO_4:Er^{3+}/Yb^{3+}$ (2/8 mol %) specimen exhibited strongest green emission visible to the naked eyes excited by 980 nm laser diode (100 mW), as shown in inset of Figure 1(a). The UC luminescent spectra of The $PbWO_4:Er^{3+}/Yb^{3+}$ consisted of three regions:[8] (1) green emissions near 530 nm assigned to $^2H_{11/2} \rightarrow {}^4I_{15/2}$ transition, (2) the intense green emission near 550 nm will be attributed to $^4S_{3/2} \rightarrow {}^4I_{15/2}$ transition and (3) the relatively weak red emission around 656 and 670 nm attributed to $^4F_{9/2} \rightarrow {}^4I_{15/2}$ transition, which are contributed to intra 4f transitions of Er^{3+}. As seen from the Figure 1(b), as

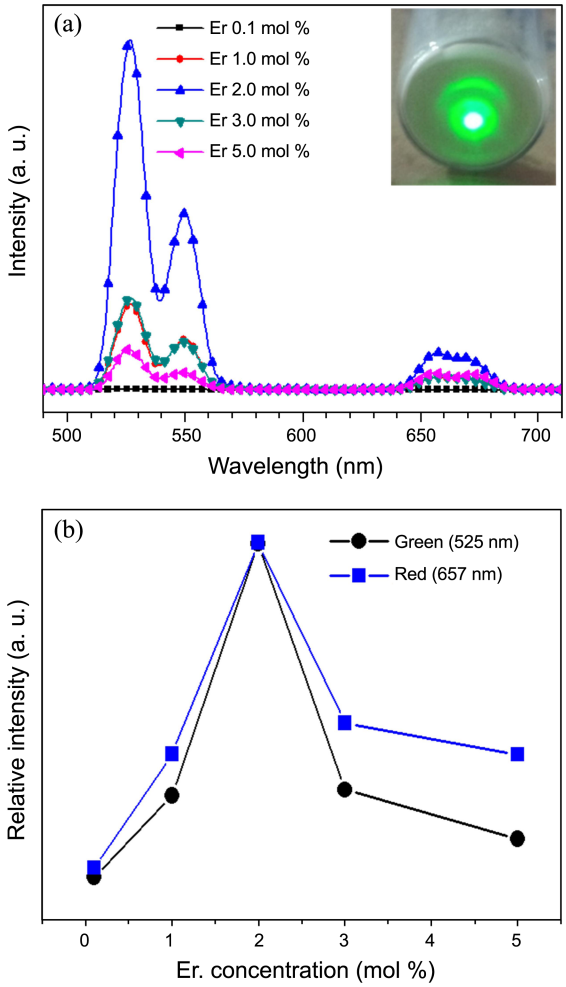

Figure 1. Photoluminescence spectra (PL) of $PbWO_4:Er^{3+}/Yb^{3+}$ with the variation of (a) Er^{3+} concentrations at fixed Yb^{3+} to 8 mol. The inset photograph shows strong green emission for the $PbWO_4:Er^{3+}/Yb^{3+}$ (2/8 mol %) observed by the naked eyes excited at 980 nm laser diode. (b) UC emission intensities of green and red emission with variation of Er^{3+} concentrations.

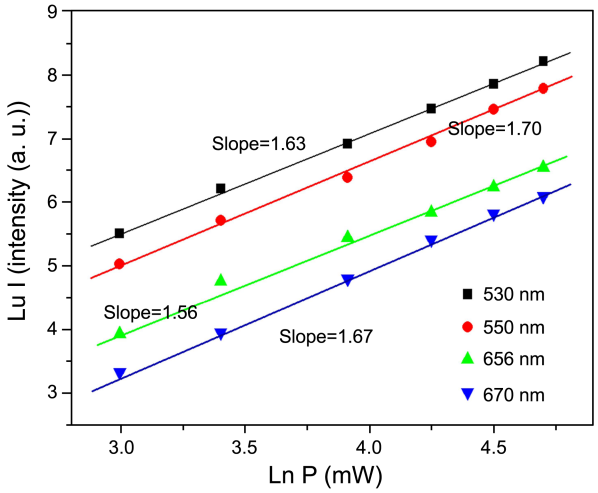

Figure 2. Dependence of UC emission intensities on the pumping power at 530, 550, 656 and 670 nm for the $PbWO_4:Er^{3+}/Yb^{3+}$ (2/8 mol %).

increasing Er^{3+} concentrations, the intensities of green and red emissions regions increase up to 2 mol %, while intensities of emission decrease over 2 mol % due to concentration quenching effect.[9]

Figure 2 presents that the green and red UC emission intensities of $PbWO_4:Er^{3+}/Yb^{3+}$ (2/8 mol %). are plotted in a double-logarithmic diagram. In UC process, I (emission intensity) is proportional to the n value power of P, that is:[10]

(1) $I \propto P^n$

Where n value is the number of the pumping photons, I is the emission intensity and P is the pumping power. The results above indicate that slopes of n value are 1.63, 1.70, 1.56 and 1.67 for green emissions at 530, 550 nm and red emissions at 656, 670 nm, respectively. The n value for green emission at 530, 550 nm is close to 2, while red emission at 656, 670 nm is slightly less than that of green emissions. These results mean that the UC mechanism corresponding to green and red emissions can be considered via a two-photon process.

The UC emission mechanism and population processes for the green ($^4H_{11/2}$, $^4S_{3/2} \rightarrow {}^4I_{15/2}$) and red ($^4F_{9/2} \rightarrow {}^4I_{15/2}$) UC luminescence in $PbWO_4:Er^{3+}/Yb^{3+}$ system are illustrated in Figure 3. At the excitation of 980 nm, Er^{3+} and Yb^{3+} ions are initially excited from the ground state to the excited state through the ground state absorptions (GSA) process (Er^{3+}: $^4I_{15/2} \rightarrow {}^4I_{11/2}$, Yb^{3+}:$^2F_{7/2} \rightarrow {}^2F_{5/2}$) and the energy transfer (ET) process of $^2F_{5/2}(Yb^{3+}) + {}^4I_{15/2}(Er^{3+}) \rightarrow {}^2F_{7/2}(Yb^{3+}) + {}^4I_{11/2}(Er^{3+})$ are responsible for the population at $^4I_{11/2}$ level in Er^{3+}, respectively. For the green emissions, the energy transition from $^4I_{11/2}$ level to $^4F_{7/2}$ level of Er^{3+} is involved into three possible processes as follows: [11,12]

(2) ESA: $^4I_{11/2}$ + a photon (980 nm) $\rightarrow {}^4F_{7/2}$

(3) ET: $^2F_{5/2}(Yb^{3+}) + {}^4I_{11/2}(Er^{3+}) \rightarrow {}^2F_{7/2}(Yb^{3+}) + {}^4F_{7/2}(Er^{3+})$

(4) CR (cross relaxation): $^4I_{11/2}(Er^{3+}) + {}^4I_{11/2}(Er^{3+}) \rightarrow {}^4F_{7/2}(Er^{3+}) + {}^4I_{15/2}(Er^{3+})$

These three possible processes can populate to the $^4F_{7/2}$ level from the $^4I_{11/2}$ level in Er^{3+}, and then $^4F_{7/2}$ level relaxes rapidly and non-radiatively to the next lower levels at $^2H_{11/2}$ and $^4S_{3/2}$ in Er^{3+}. As a result, above mentioned processes can produce the green emissions in the spectral lines near 530 and 550 nm. The UC emission is dominated by strong green emission at 530 nm ($^4I_{11/2} \rightarrow {}^4I_{15/2}$) and 550 nm ($^4S_{3/2} \rightarrow {}^4I_{15/2}$). For the red emission, on the other hand, $^4F_{9/2}$ level is generated by non-radiatively relaxation from $^4S_{3/2}$ to $^4F_{9/2}$ level and cross relaxation $^4F_{7/2} + {}^4I_{11/2} \rightarrow {}^4F_{9/2} + {}^4F_{9/2}$ transition. Finally, $^4F_{9/2}$ level relaxes radiatively to the ground state at $^4I_{15/2}$ level and release red emission at 656 and 670 nm.

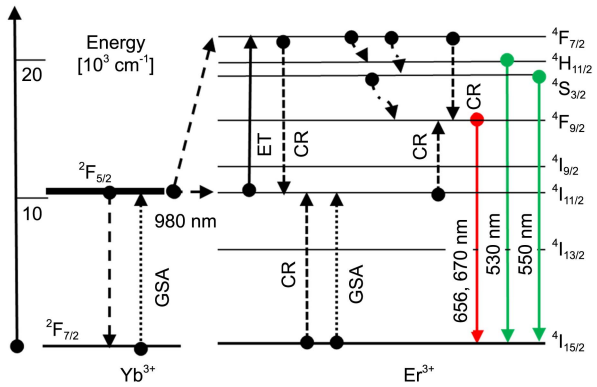

Figure 3 A simplified energy level diagram of Er^{3+} with Yb^{3+} ions and the dominant upconverting mechanisms in $PbWO_4:Er^{3+}/Yb^{3+}$ under 980 nm excitation.

In this article, we have synthesized $PbWO_4:Er^{3+}/Yb^{3+}$ UC phosphors with the variation of Er^{3+} concentrations. Under NIR excitation, $PbWO_4:Er^{3+}/Yb^{3+}$ phosphors showed bright green UC luminescence that are visible to naked eyes at 530 and 550 nm with weak red emission at 656 and 670 nm. The optimum doping concentration of Er^{3+} for highest green UC luminescence was 2 mol %. Moreover, it was found that a two photon process is responsible for both UC luminescence of green and red emission in $PbWO_4:Er^{3+}/Yb^{3+}$ UC system.

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