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White upconversion luminescence in CaF_2: Yb^{3+}/Eu^{3+} powders via incorporating Y^{3+} ions

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White upconversion luminescence (UCL) was achieved under 980 nm excitation in CaF_2: Yb^{3+}/Eu^{3+} material using Y^{3+} to adjust the luminescence performance. In this luminescence system, Yb^{3+} not only plays the role of sensitizer of Eu^{3+}, but also generates green fluorescence from Yb^{3+} dimers (2-Yb^{3+}) by cooperative transitions in CaF_2 matrix. One of the primary color of green corresponds to the 2-Yb^{3+} cooperative emission exactly. Eu^{3+} acts as an activator for emitting red and blue fluorescence simultaneously. Interestingly, the color of the UCL can be controlled by adjusting the doping concentration of Y^{3+} ions, and white UCL was realized when the concentration of Y^{3+} was 1%.

In the past decades, many scientists have devoted themselves to the research on upconversion of lanthanide-doped materials. Ln^{3+} ions are suitable for optical upconversion processes since they can be easily populated by near-infrared radiation (NIR) with abundant energy levels.[1-5] Especially, the development of white UCL materials is still a hotspot because of its unique application potential, driven by the needs for lighting sources in optical devices, backlight sources, solid-state three-dimensional displays, etc.[6-8] The spectral range of Ln^{3+} ions covers the entire visible region, so the white fluorescence can be obtained by doping the appropriate Ln^{3+} ions to corresponding matrixes. For decades, there have many reports on upconversion multicolor and white fluorescence in different Ln^{3+}-doped materials.[9-13] For example, Downing et al. achieved white UCL by compositing addition of individual sharp emission bands of red, green, and blue fluorescence in two-frequency pumped $Pr^{3+}/Er^{3+}/Tm^{3+}$ co-doped HMFGs.[9] Wang et al. reported the white light upconversion that was produced by broad-band emission from a single compound in vacuum.[13] Here, we propose a different approach by which the special properties of Ln^{3+} were utilized for getting white UCL in the Yb^{3+}, Eu^{3+}, Y^{3+} co-doped CaF_2 materials. To be specific, 2-Yb^{3+} cooperative emission provides the green light for a primary color, and Eu^{3+} plays the role of acceptors offers blue and red light simultaneously. In addition, the effect of Y^{3+} is to regulate the spectral structure by destroying 2-Yb^{3+} cooperative luminescence.

UCL of the samples was investigated under a 980 nm excitation. It is to be highlighted that Yb^{3+} ions in CaF_2 host not only play the role of sensitizing Eu^{3+} ions but also emit and green fluorescence by cooperative transitions of Yb^{3+}-dimers in the range of 480~540 nm.[14] Such a special spectral characteristics means that we can obtain white UCL by introducing single Ln^{3+} ion to emit upconversion blue and red fluorescence, where Eu^{3+} is precisely a good candidate for blue and red upconversion luminescence.[15, 16]

We demonstrate a novel strategy that a suitable concentration of Y^{3+} was doped into the precursor material of CaF_2: Yb^{3+}/Eu^{3+} to balance the proportion of three primary colors for white UCL. In this process, the Y^{3+} was used to destroy Yb^{3+}-dimers that it could adjust the luminescence performance of the samples.

Under 980 nm excitation, strong green emission can be observed from CaF_2:Yb^{3+} sample, which is from Yb^{3+}-dimers in CaF_2 host by cooperative transitions, as shown in Fig. 1(a). The fluorescence color can be tuned just by introducing the Eu^{3+} in CaF_2:Yb^{3+} system since Eu^{3+} has rich energy levels and can emit blue and red light as a frequently-used activator. Furthermore, the incorporation of Y^{3+} was exploited to adjust the proportion of the three primary colors and obtain white light emission. Fig. 1(b) is the upconversion luminescence spectra of the $Yb^{3+}/Eu^{3+}/Y^{3+}$ co-doped CaF_2. As presented in these spectra, the emission intensity of Yb^{3+}-dimers is far stronger than that of Eu^{3+} in the sample without Y^{3+} ions. Therefore, trivalent Y^{3+} was introduced to balance the proportion of the primary colors. The luminous intensity of Yb^{3+}-dimers and Eu^{3+} ions both decreases significantly with increasing the amount of Y^{3+}, then approaches a minimum at a certain amount of 2%. The relationship between overall emission intensity and Y^{3+} concentrations was shown in Fig. S1. In this mechanism, Y^{3+}

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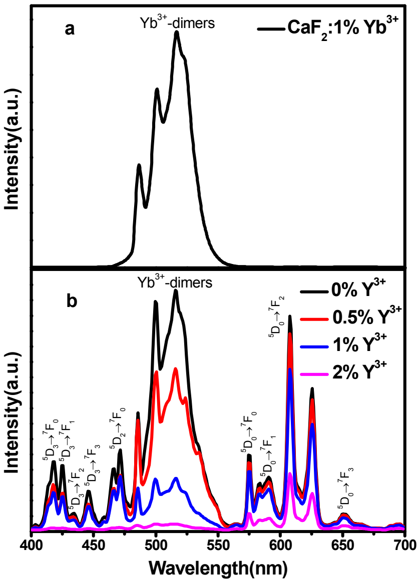

Fig. 1 Upconversion emission spectra of Yb^{3+} single doped CaF$_2$ (a) and different concentrations of Y^{3+} co-doped CaF$_2$: Yb^{3+}/Eu^{3+} powders under 980 nm excitation in the region of 400~700 nm (b).

ions replace Yb^{3+} or Ca^{2+} ions and occupy their lattice sites to form a longer distance between two single Yb^{3+} ions. Therefore, the decrease of Yb^{3+}-dimers is due to a small probability of Yb^{3+} ions to be pairs after Y^{3+} was introduced into the materials. The blue emission has a series of luminescence peaks at 417 nm, 424 nm, 434 nm, 446 nm, and 470 nm that corresponds to the $^5D_3\rightarrow{}^7F_j$ (j=0, 1, 2, 3) and $^5D_2\rightarrow{}^7F_0$ transitions of Eu^{3+} ions, the green emission, and the red emission peaks at 608 nm and 625 nm originated the $^5D_0\rightarrow{}^7F_2$ transitions of Eu^{3+} ions.

For convenience of spectra analysis, the color coordinates were calculated with the CIE 1931, and the chromaticity diagram of the samples is shown in Fig. 2. It can be seen that the chromaticity of upconversion emissions change gradually as Y^{3+} doping concentration increasing. Illustrations in the top of the figure represent the series of luminescence photos of the samples. As the concentration of Y^{3+} was changed from 0% to 2%, the emitting light colors of samples vary from blue green to orange red. It is worth noting that when Y^{3+} concentration is 1.0%, the optimum proportion of three primary colors of blue, green and red can be attained, the color coordinate is (0.308, 0.338), which is very closed to the standard white-light coordinate of (0.33, 0.33).[17]Therefore, in CaF$_2$:Yb^{3+}/Eu^{3+} system, the upconversion white light can be achieved by adjusting the concentrations of Y^{3+}.

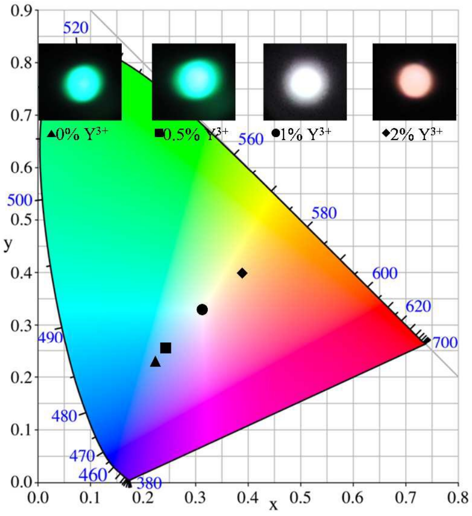

Fig. 2 Chromaticity diagram for different concentrations of Y^{3+} co-doped CaF$_2$:Yb^{3+}/Eu^{3+} powders upon 980 nm excitation.

Fig. 3(a) shows the log-log plot of upconversion emission intensities of CaF$_2$ co-doped with Yb^{3+}/Eu^{3+}/Y^{3+} (1 mol%) excited by a 980 nm laser. The upconversion emission intensities increase gradually with increasing pumping power from 53 mW to 245 mW. It was well known that the relationship between upconversion emission intensity (I_{UC}) and the excitation power (P) follows the law of $I_{UC} \propto P^n$, where n is the number of sequential photons required to excite the upconversion emitting level.[18] As given in Fig. 3(a), the value of n for the blue $^5D_2\rightarrow{}^7F_0$ transition of Eu^{3+} ions is 2.35, which shows that the blue UC emissions originate from a three-photon process. For the red $^5D_0\rightarrow{}^7F_2$ transition of Eu^{3+} ions,

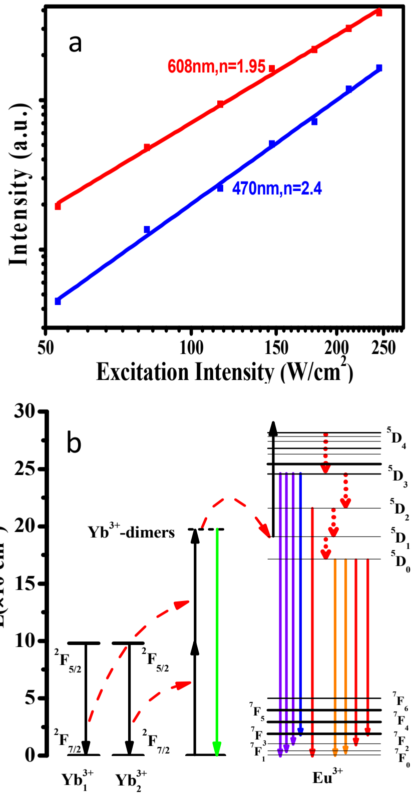

Fig. 3 (a) Log–log plots of upconversion emission intensity as a function of pump power of the 980 nm laser. (b) Energy level diagram of Yb^{3+} and Eu^{3+}, as well as the proposed upconversion mechanisms under 980 nm excitation.

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the value of n is 1.95, indicating that the red upconversion emissions originate from a two-photon process.

According to the above results, the possible upconversion populating mechanisms in $Yb^{3+}/Eu^{3+}/Y^{3+}$ co-doped CaF_2 are schematically presented in Fig. 3(b). Yb^{3+}-dimers can be formed in $CaF_2:Yb^{3+}$ polycrystalline, and emit strong green UC emission when exposed to a 980 nm laser excitation. For red emission from Eu^{3+}, energy transfer (ET) occurs from an excited Yb^{3+}-dimer to a Eu^{3+} ion to populate its $^5D_1$ level. Subsequent $^5D_1 \rightarrow {}^5D_0$ transition can be generated by phonon-assisted non-radiative relaxation. Then, the $^5D_0 \rightarrow {}^7F_2$ transition generates the red emission at around 608 nm and 625 nm. Moreover, the excited states of $^5D_0$ and $^5D_1$ absorb a 980 nm photon and transit to an upper level of $^5D_4$, then relax to the lower levels of $^5D_{3,\ 2,\ 1,\ 0}$ through a series of nonradiative relaxations. Therefore, the emission peaks are observed at 417 nm, 424 nm, 434 nm, 446 nm, and 470 nm could be attributed to the transitions $^5D_3 \rightarrow {}^7F_j$ (j=0, 1, 2, 3) and $^5D_2 \rightarrow {}^7F_0$, of Eu^{3+} ion respectively. As a result, these transitions play leading roles in blue emissions.

Another evidence for the energy transfer between Yb^{3+} and Eu^{3+} can be found from dynamical analysis. The decay curves of cooperative luminescence at 500 nm were measured under chopped 978 nm excitation. As shown in Fig. 4, we can see that the lifetime curve in $CaF_2:Yb^{3+}$ shows a nearly single exponential function, and the decay lifetime becomes short dramatically because of a portion of energy can pass from Yb^{3+}-dimers to Eu^{3+} ions in $CaF_2:Yb^{3+}/Eu^{3+}$. As is known, there are no energy transfer processes from Y^{3+} to Yb^{3+}, therefore, when Yb^{3+}-dimers are destroyed by Y^{3+}, its decay lifetime will increases in general. However, it is interesting to observe that the lifetimes of Yb^{3+}-dimers gradually decreases with increasing concentration of Y^{3+} when Eu^{3+} ions are present. This result indicates that an efficient energy transfer exists between the Yb^{3+}-dimers and Eu^{3+} ions.

In this letter, white light upconversion materials were successfully synthesized from Yb^{3+}/Eu^{3+} co-doped CaF_2 via incorporation of Y^{3+} ions. Eu^{3+} plays an important role in this system to provide both blue and red emissions as an activator. Meanwhile, the function of Yb^{3+} has strategic significance, because it provides green emission of the primary colors. A novel way of white light generation was obtained by modulating Y^{3+} concentrations to adjust the materials luminous performance under near infrared excitation. The significance of our work is to explore a new approach to obtain upconversion white light, and to broaden the range of optional materials.

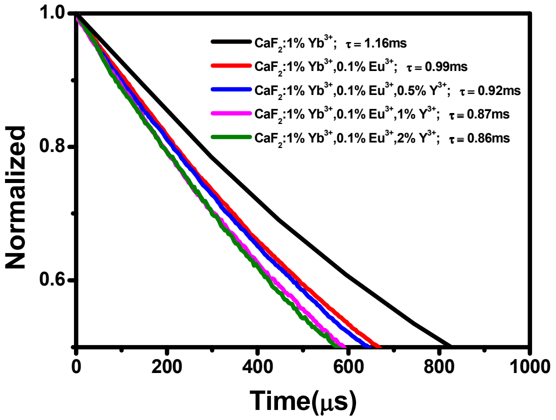

Fig. 4 Fluorescence decay curves of 500 nm emission from Yb^{3+}-dimers for different samples.

Experimental section

The bulk materials of CaF_2 co-doped with Eu^{3+}, Yb^{3+}, and Y^{3+} was synthesized by a modified high temperature solid phase method. Firstly, 5 mmol CaF_2 (99.99%), 0.05 mmol YbF_3 (99.99%), and 0.005 mmol Eu_2O_3 (99.99%) powders were mixed together and grinded fully in a agate mortar, then heated in a platinum crucible under nitrogen atmosphere at 1400 °C for 2 h. Secondly, the sintered sample was grinded again when it was cooled to room temperature, and different concentrations of Y_2O_3 were added into it. Finally, the mixture was calcined again at 1400 °C for 2 h. Power adjustable and continuous wave (CW) laser diodes (980 nm, 3 W) and a Hitachi F-4500 fluorescence spectrophotometer (PMT voltage is 400 V) were employed for upconversion spectral analysis. The spectral scan range was from 400 to 700 nm with a resolution of 1 nm. All the fluorescence spectra were performed in the same conditions. Photoluminescence decay measurements were performed with a chopped 978 nm laser as the excitation source, and the collected signal was fed into a 1 GHz digital oscilloscope (DPO4104B, sampling rate 5GS s^{-1}). On the basis of the CIE 1931 standard, the color coordinates of upconversion spectra were calculated. The pictures of samples' luminescence were photographed with a Nikon camera (D300s).

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