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Up-conversion white light of $Tm^{3+}/Er^{3+}/Yb^{3+}$ tri-doped CaF_2 phosphors

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Abstract

$Tm^{3+}/Er^{3+}/Yb^{3+}$ tri-doped CaF_2 phosphors were synthesized using a hydrothermal method. The phosphors were characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), and up-conversion (UC) emission spectra. After annealing, the phosphors emitted white light under a 980 nm continuous wave diode laser (CW LD 2 W) excitation. As the excitation power density changed in the range of 20–260 W/cm^2, the chromaticity coordinates of the UC light of the phosphor $Ca_{0.885}Tm_{0.005}Er_{0.01}Yb_{0.1}F_2$ fell well in the white region of the 1931 CIE diagram. For the proportion of red, green and blue (RGB) in white light is strict, key factors for achieving UC white light, such as host materials, rare earth ions doping concentrations, annealing temperatures, as well as the excitation power densities, were investigated and discussed.

Keywords: Up-conversion; White light; $Tm^{3+}/Er^{3+}/Yb^{3+}$ tri-doped CaF_2

1. Introduction

For a variety of purposes, such as displays, backlight, and alternatives to general lighting (incandescent light bulb), there is a large interest in cheap, efficient generation of (white) light sources [1,2]. Up-conversion (UC) is one of physical mechanisms for varying the frequency of light, where lower energy light, usually near-infrared (NIR) or infrared (IR), is converted to high energies, ultraviolet (UV) or visible, via multiple absorption and energy transfer processes. More attention has been paid to UC white light in recent years, for the excitation source is infrared laser, which is compact, power-rich, inexpensive, and also can be obtained easily in commerce. Exploring UC white light sources is challenging for scientists today, because blue and white light emitters are not as efficient as green and red ones, and bias dependent color variation, and so in [3,4]. Generally, two ways can be employed in obtaining UC white light: (1) mixing red, green, and blue (RGB) UC phosphors in an appropriate proportion, and (2) synthesizing one single UC phosphor to convert infrared light into a combination of RGB or yellow and blue. Using the first way, Milliez et al. obtained white light with chromaticity coordinates (0.3127, 0.3297) through mixing different UC phosphors [5]. However, more researchers are interested in using single material to get UC white light, which is in lower manufacturing costs than those in the mixing strategy. da Silva et al. obtained white light in lanthanide-doped fluoride-based glasses using double and single excitation sources, respectively [6,7]. In 2005, Sivakumar et al. demonstrated UC white light with sol–gel-derived thin film

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[8]. In this article, using a hydrothermal method, we synthesized novel UC white light phosphors based on a $Tm^{3+}/Er^{3+}/Yb^{3+}$ tri-doped system. The conditions for achieving white light were explored for RGB proportion in white light is strict. The experimental results indicate that the $Tm^{3+}/Er^{3+}/Yb^{3+}$ tri-doped CaF_2 phosphor should be a promising candidate for white light sources and three dimensional displays.

2. Experimental

Here we adopt a hydrothermal method to synthesize $Tm^{3+}/Er^{3+}/Yb^{3+}$ tri-doped CaF_2 phosphors [9]. The phosphors were prepared from analytical reagents: $CaCO_3$, Tm_2O_3 (99.99%), Er_2O_3 (99.99%) and Yb_2O_3 (99.99%). In a typical procedure for preparation of $Ca_{0.885}Tm_{0.005}Er_{0.01}Yb_{0.1}F_2$, 44.25 mmol $CaCO_3$, 5 mmol Yb_2O_3, 0.5 mmol Er_2O_3, and 0.25 mmol Tm_2O_3 were dissolved in hydrochloric acid (37%) at elevated temperature with an electric cooker (800 W) to form clear solution. Then hydrofluoric acid (40%) was added dropwise into the clear solution to form colloidal solution while stirring with a magnetic stirrer. After vigorously stirred for more than 0.5 h, the colloidal solution was transferred into two 50 mL stainless Teflon-lined autoclaves and treated at 130 °C for 12 h. After cooling to room temperature naturally, the upper clear solution was discarded and the remainder was isolated via centrifugation. Then the resultant materials were dried in vacuum at 55 °C for 6 h. However, the resultant powder had hardly luminescence under 980 nm excitation. After annealed at 600 °C for 0.5 h in an argon atmosphere, the phosphors were obtained and bright UC fluorescence was observed under a 980 nm continuous wave diode laser (CW LD 2 W) excitation. For comparison, samples $Ca_{0.89-x}Tm_xEr_{0.01}Yb_{0.1}F_2$ ($x = 0.003, 0.01$), $Ca_{0.895-y}Tm_{0.05}Er_yYb_{0.1}F_2$ ($y = 0.005, 0.015$), and $Ca_{0.985-z}Tm_{0.05}Er_{0.01}Yb_zF_2$ ($z = 0.025, 0.05$) were also prepared with the same procedure as the above one. Furthermore, the phosphors $Ca_{0.885}Tm_{0.005}Er_{0.01}Yb_{0.1}F_2$ were annealed at 500 °C and 700 °C for 0.5 h, for the study of annealing temperature dependence of UC emission spectra. To identify the crystallization phase, X-ray diffraction (XRD) analysis was carried out with a powder diffractometer (Model Rigaku RU-200b), using nickel-filtered Cu Kα radiation ($\lambda = 1.5406$ Å). The size and the morphology were characterized by field emission scanning electron microscopy (FE-SEM) (Hitachi S-4800). Under 980 nm excitation, UC emission spectra were recorded with a fluorescence spectrophotometer (Hitachi F-4500). All measurements were performed at room temperature.

3. Results and discussion

Fig. 1a and b are XRD patterns of the sample $Ca_{0.885}Tm_{0.005}Er_{0.01}Yb_{0.1}F_2$ before and after annealed at 600 °C, respectively. All diffraction peaks can be easily indexed to those of the cubic phase CaF_2 with space group $Fm\bar{3}m$ (225), which are in good agreement with the standard values for the bulk cubic CaF_2 (JCPDS 77–2245). Due to the preferential growth effect caused by different synthesis routes, the relative intensities of (111) and (220) planes in the sample are different from those in JCPDS 77–2245. From the patterns, we inferred that the unannealed sample was nanometer-sized and grew up after annealing. Fig. 1c and d are FE-SEM images of $Ca_{0.885}Tm_{0.005}Er_{0.01}Yb_{0.1}F_2$ before and after annealed at 600 °C, respectively, which confirm that the unannealed samples were nanoparticles with an average size about 50 nm and grew up to ~200 nm after annealing.

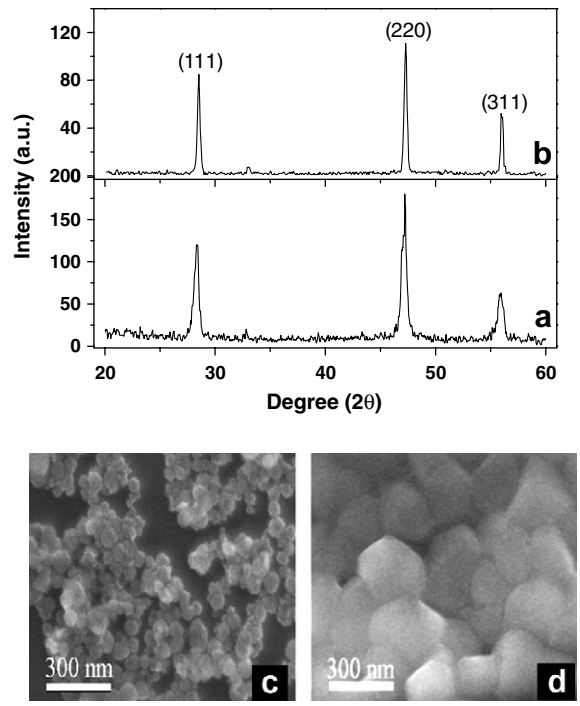

Fig. 1. XRD patterns and FE-SEM images of $Ca_{0.885}Tm_{0.005}Er_{0.01}Yb_{0.1}F_2$, (a, c) unannealed, (b, d) annealed at 600 °C.

Fig. 2 is a schematic energy-level diagram of Tm^{3+}, Er^{3+}, and Yb^{3+} ions, as well as energy transfer and cross relaxation (CR) processes. Under 980 nm excitation, Yb^{3+} ions successively transfer energy to Tm^{3+} and Er^{3+}

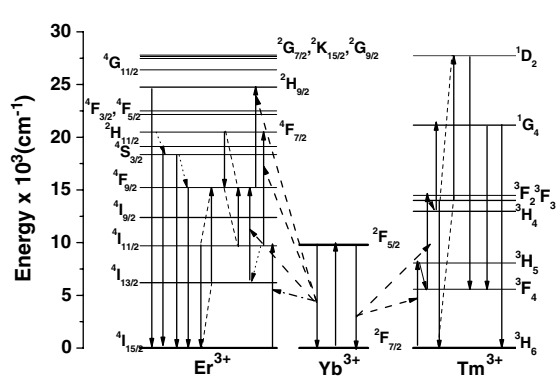

Fig. 2. Schematic energy-level diagram of Tm^{3+}, Er^{3+} and Yb^{3+}.

ions, while Er^{3+} ions absorb 980 nm photons, too. For a Yb^{3+} and Tm^{3+} codoped system, Yb^{3+} ions transfer energy to Tm^{3+} ions to populate the $^3H_5$, $^3F_2$ ($^3F_3$), and $^1G_4$ levels [10]. And the $^1D_2$ level was populated through the CR process: $^3F_3 \rightarrow {}^3H_6$, $^3F_3 \rightarrow {}^1D_2$ (Tm^{3+}) [11]. For a Yb^{3+} and Er^{3+} codoped system, green ($^2H_{11/2}$, $^4S_{3/2} \rightarrow {}^4I_{15/2}$) and red ($^4F_{9/2} \rightarrow {}^4I_{15/2}$) emissions have been widely investigated [12,13]. As has been proposed, the red UC emission of Er^{3+} is more dependent on concentration than the green one. With the concentration of Er^{3+} increasing, indicating the short distance between Er^{3+} ions, there will be a relative increase of the red emission intensity to the green one [14,15]. Based on the energy matching conditions, two CR processes: $^4I_{11/2} \rightarrow {}^4I_{15/2}$, $^4I_{13/2} \rightarrow {}^4F_{9/2}$, and $^4F_{7/2} \rightarrow {}^4F_{9/2}$, $^4I_{11/2} \rightarrow {}^4F_{9/2}$ may be the main up-conversion processes in populating the $^4F_{9/2}$ level [16]. And the $^2H_9$ level was populated through the energy transfer process: $^4F_{9/2} \rightarrow {}^2H_9$ (Er^{3+}), $^2F_{5/2} \rightarrow {}^2F_{7/2}$ (Tm^{3+}) [17]. In the $Tm^{3+}/Er^{3+}/Yb^{3+}$ tri-doped system, Tm^{3+} and Er^{3+} interaction should not be ignored. However, we are interested in the UC emissions in this communication, the interaction between Tm^{3+} and Er^{3+} and the luminescence dynamics are under intensively studied.

Fig. 3 shows an UC emission spectrum of the sample $Ca_{0.885}Tm_{0.005}Er_{0.01}Yb_{0.1}F_2$, which was obtained under excitation with pumping power density of 32 W/cm^2. Violet ~408 nm emission originates from the transition $^2H_{9/2} \rightarrow {}^4I_{15/2}$ of Er^{3+} ions, blue emissions ~452 nm and ~475 nm from transitions $^1D_2 \rightarrow {}^3F_4$ and $^1G_4 \rightarrow {}^3H_6$ of Tm^{3+} ions, green emissions ~521 nm and ~537 nm from transitions $^2H_{11/2} \rightarrow {}^4I_{15/2}$ and $^4S_{3/2} \rightarrow {}^4I_{15/2}$ of Er^{3+} ions, and red emissions ~654 nm from the transition $^4F_{9/2} \rightarrow {}^4I_{15/2}$ of Er^{3+} ions and ~646 nm from the transition $^1G_4 \rightarrow {}^3F_4$ of Tm^{3+} ions, respectively. White light was observed for RGB emissions occurred simultaneously, and chromaticity coordinates confirmed that further. The calculated chromaticity coordinates were 0.310 and 0.340 [18], which fell well in the white region of the 1931 Commission International I'Eclairage (CIE) diagram [19]. The white light can be obtained even when the excitation power density was lowered to 20 W/cm^2. When the excitation power density changed in the range of 20–260 W/cm^2, the chromaticity coordinates fell within the white region of the CIE diagram. As the excitation power density increases further, the chromaticity coordinates ran out of the white light range of the CIE diagram. The dependence of chromaticity coordinates on excitation power density was shown in Table 1. For clarity, the chromaticity coordinates were drawn in the CIE diagram in Fig. 4. From the experimental results, we concluded that the $Tm^{3+}/Er^{3+}/Yb^{3+}$ tri-doped CaF_2 phosphors have enormously potential application values in cheap white light sources.

Emission and control of the relative intensities of the RGB is required, for white light is compound. Affecting RGB emission factors, such as host material, doping concentration of rare earth ions, excitation power densities, as well as annealing temperatures, are investigated in this communication. We used YF_3 as host matrices, yet the red light is lacking, and the LaF_3 matrices have the same problem. We studied alkaline earth fluorides, and chose CaF_2 as host material. Fig. 5 are UC emission spectra as functions of rare earth ions doping concentrations and

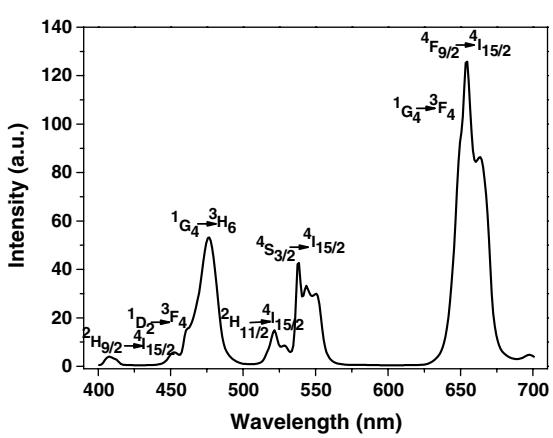

Fig. 3. Typical UC emission spectrum of $Ca_{0.885}Tm_{0.005}Er_{0.01}Yb_{0.1}F_2$ annealed at 600 °C under a 980 nm diode laser excitation (power density = 32 W/cm^2).

Table 1
Chromaticity coordinates (x, y) dependences on excitation power density P (W/cm^2)

P (W/cm^2)	(x, y)	P (W/cm^2)	(x, y)
20	(0.337, 0.352)	100	(0.272, 0.334)
32	(0.310, 0.340)	120	(0.275, 0.340)
44	(0.297, 0.337)	140	(0.276, 0.334)
56	(0.290, 0.336)	180	(0.278, 0.349)
68	(0.283, 0.333)	260	(0.281, 0.365)
80	(0.275, 0.333)	–	–

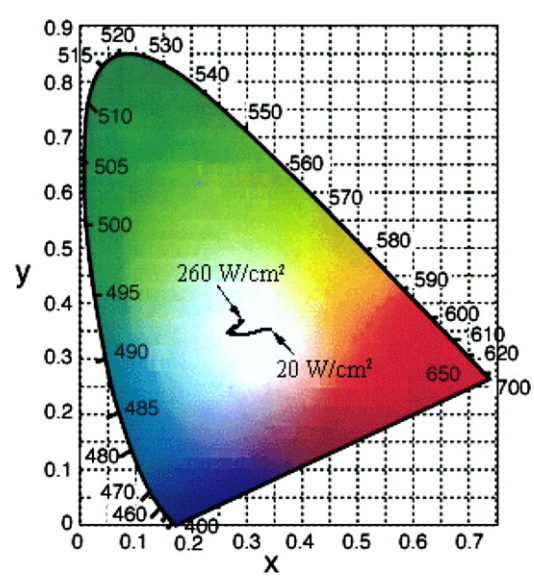

Fig. 4. Chromaticity coordinates dependence on excitation power density on the 1931 CIE diagram.

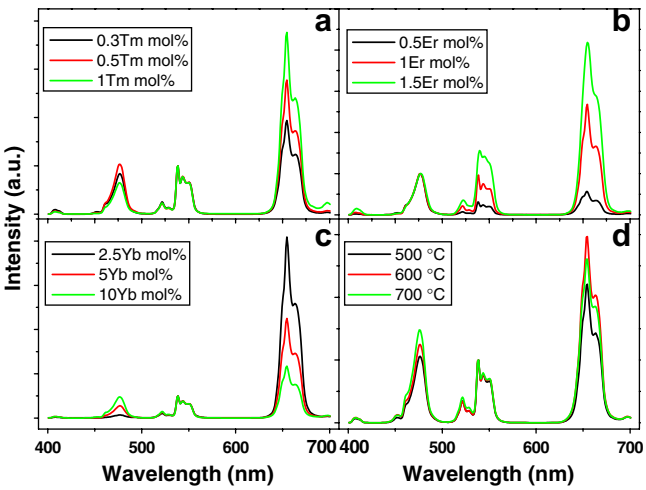

Fig. 5. UC emission spectra as functions of (a) Tm^{3+} concentrations ($Ca_{0.89-x}Tm_xEr_{0.01}Yb_{0.1}F_2$), (b) Er^{3+} concentrations ($Ca_{0.895-y}Tm_{0.05}Er_yYb_{0.1}F_2$), (c) Yb^{3+} concentrations ($Ca_{0.985-z}Tm_{0.05}Er_{0.01}Yb_zF_2$), and (d) annealing temperatures ($Ca_{0.885}Tm_{0.005}Er_{0.01}Yb_{0.1}F_2$), all under 980 nm excitation (power density ≈32 W/cm^2).

annealing temperatures, which were all obtained under the same excitation power density (≈32 W/cm^2) and normalized for comparison. Fig. 5a is UC emission spectra of phosphors $Ca_{0.89-x}Tm_xEr_{0.01}Yb_{0.1}F_2$. With the concentration of Tm^{3+} ions increasing, blue emissions first increased then decreased, while red emissions increased always, and violet emission ($^2H_{9/2} \rightarrow {}^4I_{15/2}$) of Er^{3+} ions decreased. The concentration quenching phenomena of Tm^{3+}ions were observed, while the interaction between Tm^{3+} and Er^{3+} ions became stronger. UC emission spectra dependence on Er^{3+} concentrations is shown in Fig. 5b. Analyzing the spectra carefully, we found that the green and red emissions were first lacking then surplus with Er^{3+} concentration increasing, which meant that an appropriate concentration of activators was important in achieving UC white light. Yb^{3+} ions acting as sensitizer concentrations had great effect on the UC emission spectra, too. The UC emission spectra of phosphors $Ca_{0.985-z}Tm_{0.05}Er_{0.01}Yb_zF_2$ are shown in Fig. 5c. With the increase of Yb^{3+} concentration, blue emissions increased while red emissions decreased. Clearly, the activators (Tm^{3+} and Er^{3+} ions) had different abilities accepting energies from the sensitizer (Yb^{3+}). It is well known that the annealing process affects the luminescence of phosphors greatly. The UC emission spectra of the phosphor $Ca_{0.885}Tm_{0.005}Er_{0.01}Yb_{0.1}F_2$ dependence on annealing temperatures are shown in Fig. 5d. Blue emissions of Tm^{3+} ions became stronger with increasing annealing temperatures, while red emission of Er^{3+} ions first became stronger then weaker. The spectra in Fig. 5d suggest that the annealing process affected the UC luminescence of the Tm^{3+} and Er^{3+} ions differently. From the experimental result, we learnt that the interaction between the rare earth ions, the energy transfer processes, and the luminescence dynamics are very complex and confusing in the $Tm^{3+}/Er^{3+}/Yb^{3+}$ tri-doped system. In a word, the host material, the rare earth ions doping concentration, and the annealing temperatures, including excitation power densities, are very crucial in generating UC white light.

4. Conclusions

In conclusion, $Tm^{3+}/Er^{3+}/Yb^{3+}$ tri-doped CaF_2 phosphors were synthesized using a hydrothermal method. In the range of 20–260 W/cm^2 of the pumping power density of a 980 nm diode laser, the chromaticity coordinates of the UC light of the phosphor $Ca_{0.885}Tm_{0.005}Er_{0.01}Yb_{0.1}F_2$ annealed at 600 °C fell in the white region of the CIE diagram. The conditions for achieving white light were explored and investigated. The control of RGB emissions, the interactions between doping ions, and the luminescence dynamics are being intensively studied. The experimental results show that the phosphor should be a promising material for white light sources and three dimensional displays.

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