

# Comparison of Ultraviolet Upconversion Luminescence Between Thin Film and Bulk of Calcium Fluoride Co-Doped with $\text{Yb}^{3+}/\text{Tm}^{3+}$ Ions

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A calcium fluoride thin film co-doped with  $\text{Yb}^{3+}/\text{Tm}^{3+}$  was deposited on Si substrates by the spin-coating method using trifluoroacetic acid as a fluorine source. The scanning electron microscopy (SEM) image of the sample showed that a thin film with some cracks was formed. After annealing, the cracks disappeared, and the film became thinner. The roughness of the thin film was about 150 nm, which was confirmed by atomic force microscopy (AFM). Moreover, the upconversion luminescence properties of the thin film after annealing were studied. Under infrared light excitation, strong ultraviolet (UV) upconversion luminescence of the thin film was observed. To compare the upconversion properties,  $\text{Yb}^{3+}/\text{Tm}^{3+}$  co-doped calcium fluoride bulk material that has the same components with the thin film was also synthesized. Compared with the bulk material, the UV upconversion emission of thin film was more intense. The mechanism of UV upconversion was determined by analyzing the upconversion spectra. The decrease in the size of the  $\text{CaF}_2$   $\text{Yb}^{3+}/\text{Tm}^{3+}$  particles to the nano-scale in the thin film contributed to the enhancement of the UV UC luminescence.

**Keywords:** Thin Film, Upconversion, Nanoparticles.

## 1. INTRODUCTION

Up-conversion (UC) is one of the physical mechanisms for varying the frequency of light, which means that lower energy light, usually near-infrared or infrared, can be converted to high energy light—ultraviolet (UV) or visible—*via* multiple absorption and energy transfer processes.<sup>1,2</sup> In the field of luminescence, upconversion luminescence has great application prospects, such as use in three-dimensional displays, fiber amplifiers, and anti-counterfeiting technologies.<sup>3,4</sup> In these cases, the research on the UC process in various materials and the impact of the process is very significant. UC luminescence is stronger in fluorides than in other materials due to their low phonon energy and high quantum efficiencies as luminescent hosts<sup>5</sup> therefore, we chose calcium fluoride as the matrix. Calcium fluoride films have been produced by molecular beam epitaxy and the sol-gel method as optical waveguides, anti-reflective coatings, and buffer layers.<sup>6–8</sup>

There were few reports on calcium fluoride films as matrix materials to obtain UC luminescence. Thin film-type UC materials have been studied by some researchers. Previously,  $\text{Zn}_{0.3}\text{Al}_{0.25}\text{Pb}_{0.3}\text{Li}_{0.098}\text{Yb}_{0.1}\text{Tm}_{0.002}\text{F}_{2.354}$  amorphous fluoride film with efficient UV UC emission has been produced by pulsed laser deposition.<sup>9</sup> In that report, the UV UC emissions of the thin film are enhanced greatly compared with the bulk target. To further study the changes of UV UC emission properties in the thin film type materials, rare earth ion-doped calcium fluoride thin film was prepared by the spin-coating method in this work. When the size of particles in the thin film was decreased to nanoscale, strong UV UC luminescence was also observed. The mechanism of UV UC was investigated by analyzing the upconversion spectra. The strong UV UC luminescence of the thin film may contribute to the size of the particles in the thin film decreasing to the nanoscale. This kind of calcium fluoride thin film co-doped with  $\text{Yb}^{3+}/\text{Tm}^{3+}$  has potential applications in planar infrared sensors and flat optical data storage.

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## 2. EXPERIMENTAL DETAILS

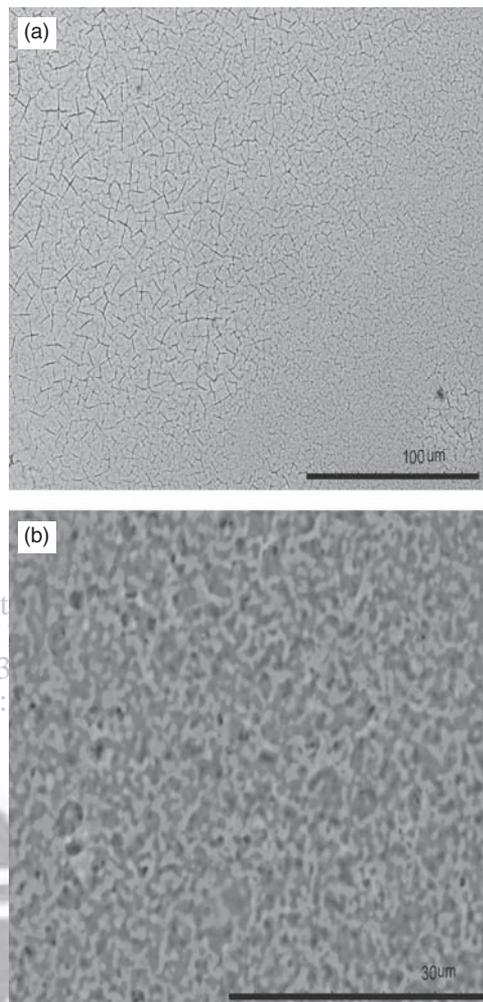
The starting materials were all analytical reagents. The  $\text{CaF}_2:\text{Tm}^{3+}, \text{Yb}^{3+}$  film was fabricated by a simple spin coating method.<sup>10–12</sup> In a typical synthesis, 2.5 mmol  $\text{Ca}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$  was dispersed in 7.5 ml isopropanol under magnetic stirring. Then, 1 ml trifluoroacetic acid (TFA) and 1 ml  $\text{H}_2\text{O}$  were added to the solution. 0.3145 mmol  $\text{Yb}_2\text{O}_3$  (purity  $\geq 99.99\%$ ) was dissolved in hydrochloric acid (37%) at elevated temperature with an electric heater (800 W), and 0.0157 mmol  $\text{TmCl}_3$  (0.005 mol/L) was added to form  $\text{LnCl}_3$  ( $\text{Ln} = \text{Tm}, \text{Yb}$ ) solution. The temperature was increased to evaporate the water and the excess acid. Then, the above  $\text{Ca}^{2+}$  solution was added to this  $\text{LnCl}_3$  mixture while stirring at room temperature to form a colloidal precursor solution. This colloidal solution was used for the film deposition, subsequently. The as-deposited thin film was obtained by spin-coating on silica glass substrates at 2,400 rpm. The film was then heated at 300 °C. While heating, the  $\text{Ca}(\text{CF}_3\text{COO})_2$  decomposed to  $\text{CaF}_2$ , and a dense thin film was formed. In order to increase the thickness of the film, the spin-coating and heating processes were repeated. Then the resulting sample was annealed at 600 °C under the protection of  $\text{NH}_4\text{HF}_2$  and  $\text{N}_2$  gas for 2 h to get the final film. For comparison, a bulk sample was also prepared without the spin-coating process.

The morphology of the thin film before and after annealing was investigated using a scanning electron microscope (SEM, Hitachi TM-1000). The size and roughness of the thin film were measured using atomic force microscopy (AFM, CSPM 5000). The UC luminescence spectra were recorded with a Hitachi F-4500 fluorescence spectrophotometer (2.5 nm for spectral resolution (full width at half maximum) of the spectrophotometer and 400 V for photomultiplier tube voltage) under a 980 nm continuous wave diode laser (CW LD, 2 W) excitation at room temperature.

## 3. RESULTS AND DISCUSSION

The SEM images of the  $\text{Ca}_{0.795}\text{Yb}_{0.2}\text{Tm}_{0.005}\text{F}_2$  thin film before and after annealing at 600 °C are shown in Figures 1(a) and (b), respectively. In the heating procedure, the film was doped with rare earth ions as a result of thermal decomposition of the precursor gel. The  $\text{CO}_2$ , CO, etc. gases leaved the film making it porous while heating at 300 °C. The film before annealing was porous and inhomogeneous. Lots of cracks can be seen in the Figure 1(a). In the annealing procedure, the film was completely fluorinated while the  $\text{NH}_4\text{HF}_2$  existed, and the film became well crystallized. There were still some small cracks in the film after annealing, but the smoothness of the film increased, which can be confirmed by the SEM image in Figure 1(b).

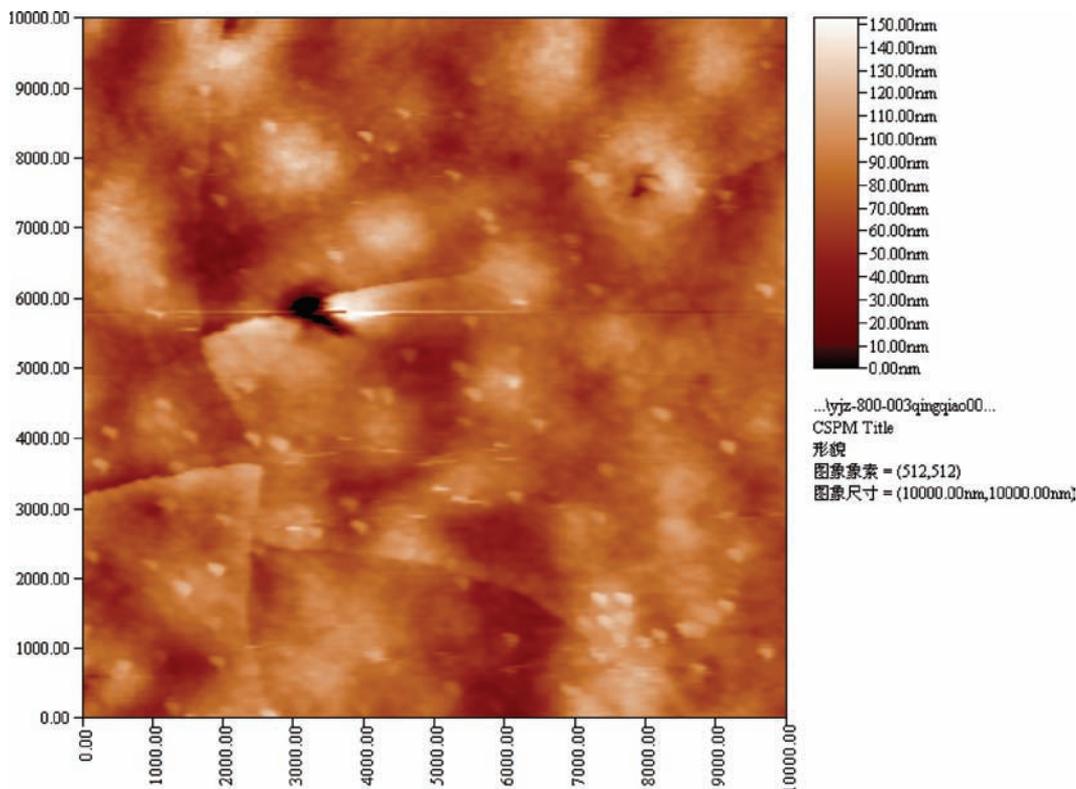
The surface roughness of the annealed  $\text{Ca}_{0.795}\text{Yb}_{0.2}\text{Tm}_{0.005}\text{F}_2$  thin film was studied by AFM, shown in Figure 2.



**Fig. 1.** SEM images of the  $\text{Ca}_{0.795}\text{Yb}_{0.2}\text{Tm}_{0.005}\text{F}_2$  thin films: (a) before annealing and (b) after annealing at 600 °C for 2 h.

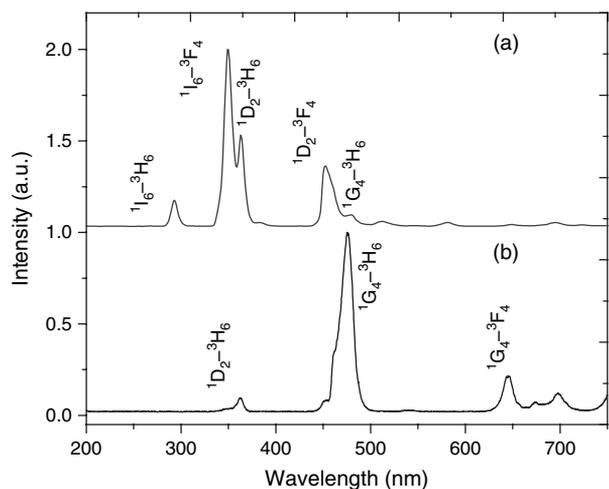
In the AFM image, there are some projecting islands of the small particle aggregations. The AFM image indicates the roughness of the thin film was estimated to be 150 nm. From the image we can see that the particles that composed the thin film are relatively uniform and the size is about 100 nm. This means that the size of the particles is on the nanoscale.

To study the UC luminescence properties of the thin film, the UC emission spectra were detected using a fluorescence spectrophotometer. Figure 3(a) is the UC emission spectrum of the calcium fluoride thin film co-doped with  $\text{Yb}^{3+}/\text{Tm}^{3+}$  in the 200–750 nm wavelength range under 980 nm excitation. Efficient infrared-to-UV UC emissions were obtained. UC emissions centered at  $\sim 291$  nm were produced from the  $^1\text{I}_6 \rightarrow ^3\text{H}_6$  transition,  $\sim 347$  nm from the  $^1\text{I}_6 \rightarrow ^3\text{F}_4$  transition, 362 nm from the  $^1\text{D}_2 \rightarrow ^3\text{H}_6$  transition, 452 nm from  $^1\text{D}_2 \rightarrow ^3\text{F}_4$  transition, 476 nm from  $^1\text{G}_4 \rightarrow ^3\text{H}_6$  transition, and 642 nm from  $^1\text{G}_4 \rightarrow ^3\text{F}_4$  transition, were recorded. In the  $\text{Tm}^{3+}/\text{Yb}^{3+}$  co-doped system,  $\text{Yb}^{3+}$  ions serve as sensitive ions. The energy from  $\text{Yb}^{3+}$



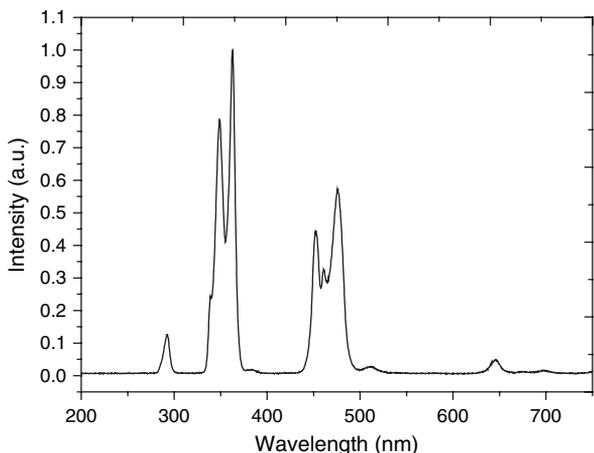
**Fig. 2.** AFM image of  $\text{Ca}_{0.795}\text{Yb}_{0.2}\text{Tm}_{0.005}\text{F}_2$  thin films after annealing at  $600\text{ }^\circ\text{C}$  for 2 h.

ions is transferred to  $\text{Tm}^{3+}$  ions, and through this process the  $^3\text{H}_5$ ,  $^3\text{F}_3(^3\text{F}_2)$ , and  $^1\text{G}_4$  levels are produced. The UV UC mechanism in  $\text{Tm}^{3+}/\text{Yb}^{3+}$  co-doped system has been detailed in other references.<sup>13,14</sup> The UC emission spectrum of the calcium fluoride bulk material co-doped with  $\text{Yb}^{3+}/\text{Tm}^{3+}$  in the 200–750 nm wavelength range under 980 nm excitation is shown in Figure 3(b). The excitation



**Fig. 3.** UC luminescence spectrum of  $\text{Ca}_{0.795}\text{Yb}_{0.2}\text{Tm}_{0.005}\text{F}_2$  thin film (a) and bulk material (b) under 980 nm excitation (the excitation current density is 1.60 mA).

power density was the same with the film material. From the spectra, we can see that the UV UC emission around 291 nm is much stronger in the thin film than in the bulk materials. From the SEM and AFM images of the sample, we confirm that the particle size of the thin film is on the nanoscale. However, the particle size of the bulk materials is on the microscale. In Ref. [9], there are some discussions about the enhancement UV UC with decreasing particle size. With the particle size decreasing, the transition from  $^3\text{F}_2 \rightarrow ^3\text{F}_4(\text{Tm}^{3+})$  will be forbidden. This will enhance the energy transfer (ET) process, and the  $^1\text{D}_2$  level will be populated:  $^3\text{F}_2 \rightarrow ^3\text{H}_6(\text{Tm}^{3+}); ^3\text{H}_4 \rightarrow ^1\text{D}_2(\text{Tm}^{3+})$ . An increase of the amount of the  $^1\text{D}_2$  level will make ET  $^2\text{F}_{5/2} \rightarrow ^2\text{F}_{7/2}(\text{Yb}^{3+}); ^1\text{D}_2 \rightarrow ^1\text{I}_6(\text{Tm}^{3+})$  efficient, and therefore, the UV UC emission ( $^1\text{I}_6 \rightarrow ^3\text{F}_4$ ,  $^3\text{H}_6$ ,  $^1\text{D}_2 \rightarrow ^3\text{H}_6$ ) will be enhanced.<sup>9</sup> In our experiments, the result of UV UC enhancement with decreasing particle size agrees with that conclusion. To test the mechanism further, the bulk material was ground to nanometer powder, and the UV UC emission of the powder in the 200–750 nm wavelength range under 980 nm excitation was obtained (Fig. 4). In this spectrum, the strong UV UC emission around 291 nm is also observed. That is because the particle size of the powder decreased to nanoscale after being ground. This fact confirms the enhancement of UV UC with decreasing particle size in upconversion materials.



**Fig. 4.** UC luminescence spectrum of  $\text{Ca}_{0.795}\text{Yb}_{0.2}\text{Tm}_{0.005}\text{F}_2$  powder material under 980 nm excitation (the excitation current density is 1.60 mA).

#### 4. CONCLUSION

In conclusion,  $\text{Yb}^{3+}/\text{Tm}^{3+}$  co-doped calcium fluoride thin film was synthesized by the spin-coating method using a colloidal solution as the precursor. It was revealed by the SEM image that after annealing, the film became dense and smooth. UV UC emission of the thin film was obtained under 980 nm laser diode excitation. Compared with the bulk material, the UV UC emission of the thin film was more intense. We inferred that the decrease in the size of the  $\text{CaF}_2:\text{Yb}^{3+}/\text{Tm}^{3+}$  particles to the nano-scale in the thin film contributed to the enhancement of the UV UC luminescence. This kind of calcium fluoride thin film

co-doped with  $\text{Yb}^{3+}/\text{Tm}^{3+}$  has potential applications in planar infrared sensors and flat optical data storage.

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