

Preparation and Luminescence Properties of Rare Earth Doped Upconversion Phosphors

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Abstract: Upconversion luminescence GdF₃: Er³⁺, Yb³⁺ phosphors were prepared under different reaction conditions by a hydrothermal method. X-ray diffraction (XRD), field emission scanning electron microscope (SEM) and upconversion (UC) emission spectra were used to characterize the samples. The results of XRD indicate that the formation of cubic phase GdF₃ depends on the hydrothermal reaction time and reaction temperature. The results of SEM show that morphology of the sample changes with changing different reaction temperatures. The results of the upconversion emission spectra show: under 980nm infrared excitation, that green emission is from ²H_{11/2}→⁴I_{15/2} and ⁴S_{3/2}→⁴I_{15/2} transitions of Er³⁺ ions and red emission comes from ⁴F_{9/2}→⁴I_{15/2} transitions of Er³⁺ ions. A: Red emission intensity is significantly stronger than the green emission intensity, B: Green emission intensity is significantly stronger than the red emission intensity for two samples.

1. Introduction

Upconversion luminescent materials refer to new materials that absorb low-energy light through multi-photon combinations and emit high-energy single photon^[1]. The Er³⁺, Tm³⁺, Ho³⁺ and Pr³⁺ in upconversion luminescence ions have abundant energy levels and long lifetimes of sub-stable energy levels, providing the prerequisites for efficient output of upconversion luminescence, and they have good absorption in the infrared or near-infrared wavelengths and high energy transfer efficiency between them and the commonly used sensitizer ion Yb³⁺, making it easy to achieve efficient upconversion luminescence. In this way, upconversion luminescent materials have promising applications in upconversion lasers, optical communications, anti-counterfeit identification, infrared imaging and bio-detection^[2-5].

Gadolinium fluoride (GdF₃) has a low refractive index, chemically stable, insoluble with good infrared transmission properties, and its single crystals can be used as optical coatings, fiber doping, laser crystals, laser amplifiers, etc. Gd³⁺, fluorescently inert with a dense shell layer, has no four-electron, and features a suitable substrate material for studying the spectroscopic properties of rare earth ions. Gadolinium fluoride is widely used as a luminescent material in a variety of applications because of its ability to emit monochromatic, quantum-efficient red fluorescence.

Rare earth fluoride based upconversion luminescent materials have excellent optical properties, and their preparation methods mainly include the following broad categories: high temperature solid phase method, sol-gel method, hydrothermal method and co-precipitation method and other methods. This experiment adopted a hydrothermal synthesis method with a low reaction

temperature, a process that can be easily controlled, which is conducive to the production of perfect crystals, and due to its small and uniform grain size, material properties can also be improved^[6].

2. Experiment

2.1 Sample Preparation

Raw materials included: $\text{Gd}(\text{NO}_3)_2$ (99.99%); $\text{Er}(\text{NO}_3)_2$ (99.99%); $\text{Yb}(\text{NO}_3)_2$ (99.99%); NaBF_4 (analytically pure), HNO_3 (analytically pure), $\text{NH}_3 \cdot \text{H}_2\text{O}$.

The $\text{Gd}(\text{NO}_3)_2$, $\text{Er}(\text{NO}_3)_2$ and $\text{Yb}(\text{NO}_3)_2$ were dissolved in deionised water to form nitrate solutions at concentrations of 0.1 mol L^{-1} , 0.05 mol L^{-1} and 0.1 mol L^{-1} respectively.

NaBF_4 is added in the stirring state, and the molar ratio of NaBF_4 to rare earth ions is 1:1; adjusted the solutions to different pHs with 1:1 (V/V) ammonia, mixed them for 30 min before transferring the mixture to the 50 mL teflon vessel, filled them to 4/5 of the lining and covered up, then put them into the stainless steel reactors and tightened, placing them in the oven for thermal insulation: (a) held them at heat preservation at $180 \text{ }^\circ\text{C}$ for 24 h with pH values of 3,5,7; (b) adjusted the pH=5 and held them at heat preservation under the following two conditions: (1) $160 \text{ }^\circ\text{C}$, $170 \text{ }^\circ\text{C}$ and $180 \text{ }^\circ\text{C}$ for 24 h and (2) $180 \text{ }^\circ\text{C}$ for 5 h, 15 h and 24 h. Then the precipitates were naturally cooled to room temperature and sample powders were finally obtained after the precipitates were centrifuged and washed 2-3 times with distilled water and ethanol and dried in an oven at $60 \text{ }^\circ\text{C}$.

2.2 Experimental Measurement

Instruments used to analyse the structure, morphology and luminescence properties of the samples included: Dandong Tongda TD-3500 X-ray diffractometer with the $\text{CuK}\alpha$ line ($\lambda = 0.15406 \text{ nm}$) as the radiation source; Hitachi SU8010 field emission scanning electron microscope; a 980 nm semiconductor laser as the excitation light source with an excitation power density range of $28\text{-}63 \text{ W}\cdot\text{cm}^{-2}$, and an Acton2758 monochromator was used to collect with LN/CCD-1100PB as the detector.

3. Result and Discussion

3.1 Structural Analysis of Samples

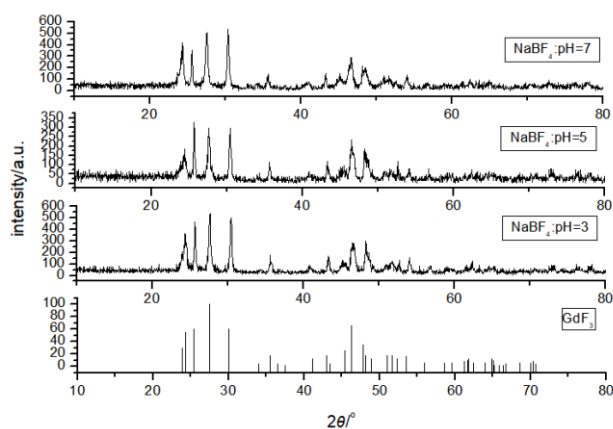


Figure 1 XRD patterns of $\text{GdF}_3:\text{Er}^{3+}, \text{Yb}^{3+}$ at different pHs

Figure 1 shows the XRD patterns of the phosphors prepared by hydrothermal method with a 1:1

molar ratio of rare earth ions to NaBF_4 , a reaction time of 24h, a reaction temperature of 180 °C and pHs of 3,5,7 respectively. As can be seen from the figure, diffraction peaks of the samples all match the GdF_3 standard card (JCPDS12-0788), indicating that the samples obtained are cubic GdF_3 . Although the pH of the reaction process is different, the position of the 2θ value of the sample diffraction peak remains the same. Different pHs affect the growth of different crystalline surfaces of the crystals.

Fig.2 shows the XRD patterns of the phosphors prepared by hydrothermal method with a molar ratio of 1:1 of rare earth ions to NaBF_4 , a reaction temperature of 180 °C, a pH value of 5 and reaction times of 5h, 15h and 24h respectively. As can be seen from the figure, diffraction peaks of the samples all match the GdF_3 standard card (JCPDS12-0788), indicating that the samples obtained are cubic GdF_3 . Although the reaction times were different, GdF_3 phase was all produced at the same time. However, as the reaction time increases, the half-height width of the diffraction peak of the sample becomes smaller and its average grain size becomes larger. To that extent, the longer reaction time can facilitate the growth of the sample grains.

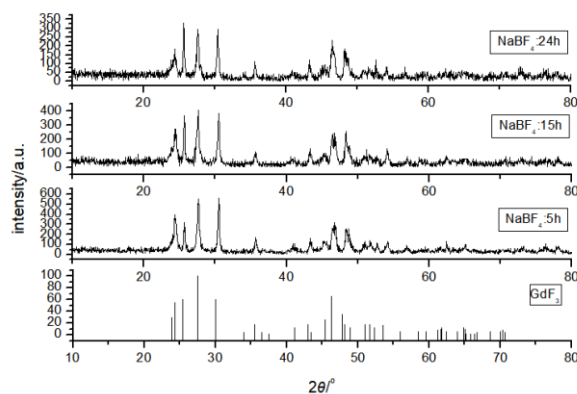


Figure 2 XRD patterns of $\text{GdF}_3:\text{Er}^{3+}, \text{Yb}^{3+}$ at different reaction times

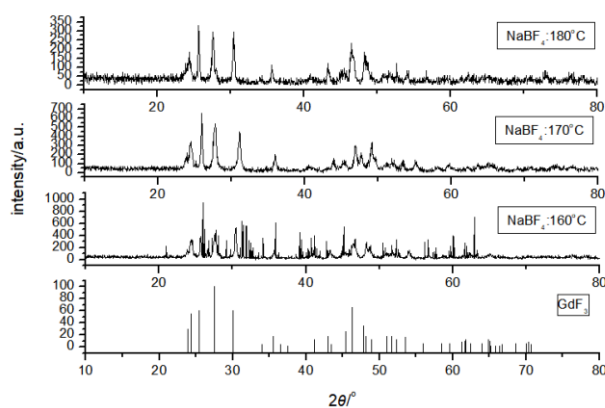


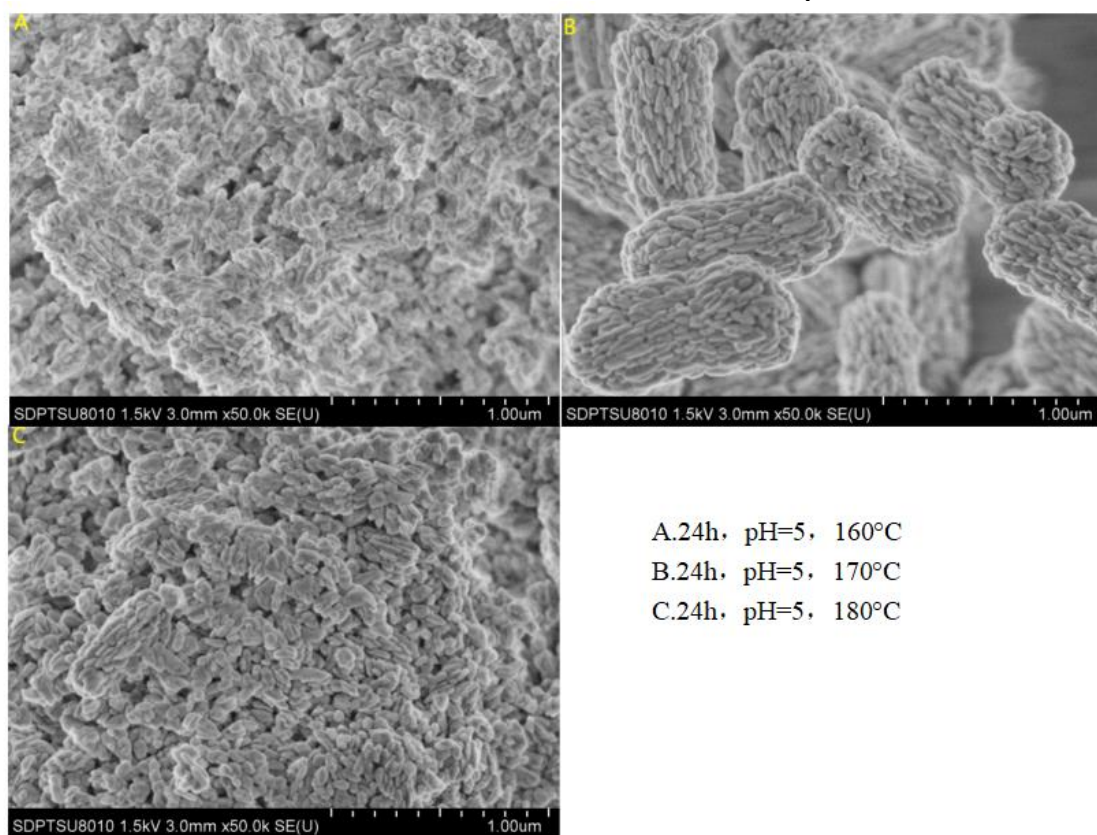
Figure 3 XRD patterns of $\text{GdF}_3:\text{Er}^{3+}, \text{Yb}^{3+}$ at different reaction temperatures

Figure 3 shows the XRD patterns of the phosphors prepared by hydrothermal method with a molar ratio of 1:1 of rare earth ions to NaBF_4 , the pH=5, a reaction time of 24h, a pH value of 5 and reaction temperatures of 160 °C, 170 °C and 180 °C respectively. As can be seen from the figure, diffraction peaks of the samples match the GdF_3 standard card (JCPDS12-0788) except at 160 °C, indicating that the samples obtained are cubic GdF_3 . As the reaction temperature increases, the half-height width of the sample diffraction peak gradually decreases, indicating that the average grain size gradually increases. This is due to the increase in reaction temperature and the decrease in crystal surface energy, allowing the grains to continue to grow^[7]. Therefore, the increase in

temperature favours the increase in grain size. Although the reaction temperatures were different, the GdF_3 phase was all produced at the same time.

3.2 Morphological Analysis of Samples

Fig.4 shows $GdF_3:0.5\%Er,15\%Yb$ upconversion phosphors prepared at reaction temperatures of 160 °C, 170 °C and 180 °C, with a reaction time of 24h and pH=5. At a reaction temperature of 160 °C, the sample has a blurred boundary and is poorly dispersed. At 170 °C, the sample is a "peanut" of clustered particles with clear boundaries and good dispersion. At 180 °C, the sample is composed of granules of uniform length, with good dispersion and clear boundaries. This shows that as the reaction temperature increases, the grain size of the sample increases and the clustering phenomenon decreases, which facilitates the luminescence of the sample.



A.24h, pH=5, 160°C
 B.24h, pH=5, 170°C
 C.24h, pH=5, 180°C

Figure 4 SEM graph of $GdF_3:Er^{3+}, Yb^{3+}$ phosphors

3.3 Luminous Properties of Samples

Fig.5 shows the upconversion emission spectrogram of samples double doped with $GdF_3:0.5\%Er,15\%Yb$ under 980nm laser excitation with a 1:1 molar ratio of rare earth ions to $NaBF_4$ and pH=5. Green light emission at 514-535 nm all comes from the transition of the electrons from Er^{3+} at the $^2H_{11/2}$ and $^4S_{3/2}$ energy levels to the $^4I_{15/2}$ energy level. Red light emission at 636-688 nm is from by the transition of the electrons from Er^{3+} at the $^4F_{9/2}$ energy level to the $^4I_{15/2}$ energy level, and red light is stronger than green light.

Fig.6 shows the upconversion emission spectrogram of the $GdF_3:1\%Er,15\%Yb$ double doped sample under the same conditions. Green light emission at 513-537nm, 537-565nm in the spectrogram all comes from the transition of the electrons from Er^{3+} at the $^2H_{11/2}$ and $^4S_{3/2}$ energy

levels to the $^4I_{15/2}$ energy level. Red light emission at 640-675 nm is from the transition of the electrons from Er^{3+} at the $^4F_{9/2}$ energy level to the $^4I_{15/2}$ energy level, and green light is stronger than red light.

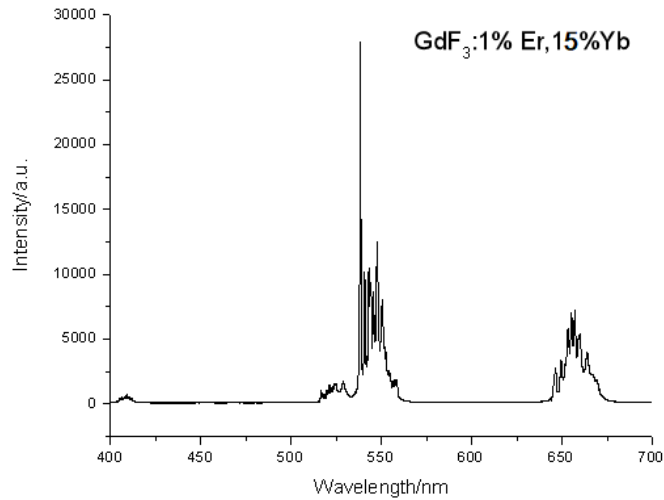


Figure 5 Spectrogram of GdF₃:0.5% Er, 15% Yb phosphors

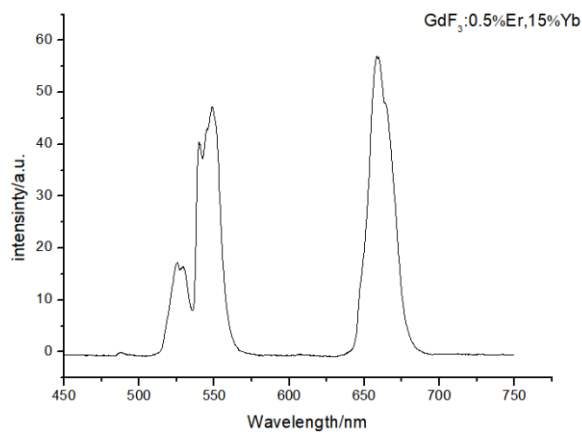


Figure 6 Spectrogram of GdF₃:1% Er, 15% Yb phosphors

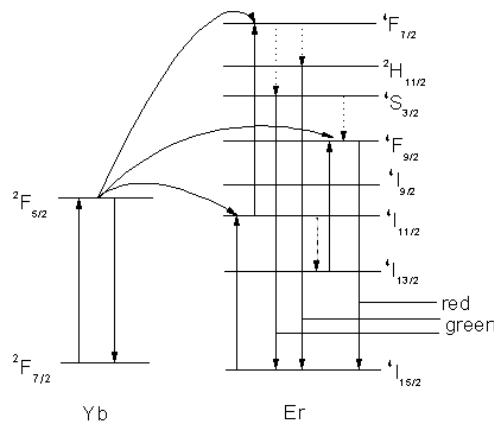


Figure 7 Energy level diagram of Er^{3+} and Yb^{3+}

Fig.7 Energy transfer process in the upconversion luminescence system of GdF₃:Er³⁺,Yb³⁺ can be described as follows^[8], with the energy transfer (ET) process dominating due to the greater

absorption of 980 nm pumping light by Yb^{3+} . After absorbing 980nm photons, Yb^{3+} is excited from the ground state to the $^2\text{F}_{5/2}$ level, which is close in energy to the $^4\text{I}_{11/2}$ energy level of Er^{3+} , and energy transfer occurs between the two. Electrons at the $^4\text{I}_{11/2}$ energy level of Er^{3+} may undergo two processes, one is the absorption of energy transferred from the $^2\text{F}_{5/2}$ energy level of Yb^{3+} to be excited to the $^4\text{F}_{7/2}$ energy level, and the other is the relaxation of electrons at the $^4\text{I}_{11/2}$ energy level to the $^4\text{I}_{13/2}$ energy level, and the transition of $^4\text{F}_{9/2}$ and $^2\text{H}_{11/2}$, $^4\text{S}_{3/2}$ to the $^4\text{I}_{15/2}$ energy level to emit red and green light. Due to the relatively small phonon energy of GdF_3 , $^4\text{I}_{11/2}(\text{Er})$ to $^4\text{I}_{13/2}(\text{Er})$ and $^4\text{F}_{7/2}(\text{Er})$ to $^2\text{H}_{11/2}$ relaxations occurs, resulting in enhanced red light emission energy. In fig.6, energy difference between the $^4\text{S}_{3/2}$ to $^4\text{F}_{9/2}$ energy levels and the $^2\text{H}_{11/2}$ to $^4\text{I}_{13/2}$ energy levels is also small, meaning that the relaxation probability between them is small, so that the green light emission is stronger than the red light.

In order to visualise the luminescence of the synthetic samples, the colour coordinates have been calculated below, in which the colour coordinate value for $\text{GdF}_3:0.5\%\text{Er},15\%\text{Yb}$ is A (0.4176,0.5633) and the colour coordinate value for $\text{GdF}_3:1\%\text{Er},15\%\text{Yb}$ is B (0.3141,0.6679), just as shown Fig.8. Upconversion luminescence colour of sample A is at the yellow-green light junction, biased towards yellow light, while the upconversion luminescence colour of sample B is within the green light spectrum.

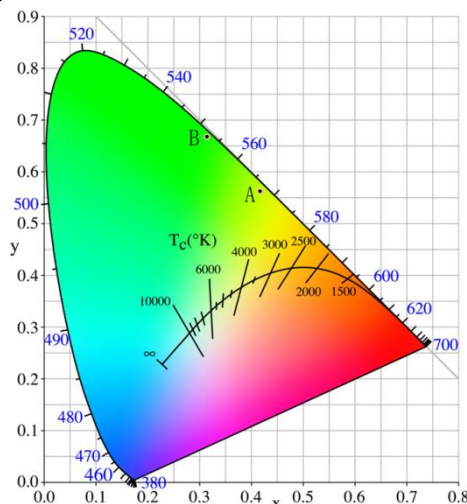


Figure 8 Coordinate graph of $\text{GdF}_3:\text{Er}^{3+}, \text{Yb}^{3+}$ phosphors

4. Conclusion

$\text{GdF}_3:0.5\%\text{Er}, 15\%\text{Yb}$ upconversion phosphors were synthesized by hydrothermal method under different conditions. Results of the XRD study show that the conditions for the formation of cubic GdF_3 are: (1) Molar ratio of rare earth ions to NaBF_4 is 1:1 (2) Reaction times are 5h, 15h and 24h. (3) Reaction temperatures are 170 °C and 180 °C. Results of the SEM study show that different reaction temperatures have certain different effects on the morphology of the samples, which are granular or clustered "peanut" in composition. Results of the upconversion emission spectrum study show that under 980 nm laser excitation, the upconversion green emission is from $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$ and $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ transitions of Er^{3+} ions and red emission comes from $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$ transitions of Er^{3+} ions. Colour coordinate results show that the upconversion luminous colours of the two samples are respectively located at the junction of coordinate A: yellow-green light, biased towards yellow light, and coordinate B: within green light spectrum.

Acknowledgments

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