Synthesis and Luminescence Properties of $\beta$-NaGdF$_4$:Yb$^{3+}$, Er$^{3+}$ Nanoparticles

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Abstract. Ln (Yb$^{3+}$Er$^{3+}$)-doped NaGdF$_4$ nanoparticles were prepared by a hydrothermal method. The structure and composition of the samples as prepared nanomaterials were characterized by XRD, TEM, and UV-visible absorption-spectrum analysis. Based on further analysis results that are rarely reported, the cyclohexane solution sample shows peaks at 376, 520 and 653nm. The transmitted spectrum indicated that all samples present the pure hexagonal phase with nanorods microstructure. It was found that the Gd ions' doping percentage from 73% to 93% is more beneficial to glow. The synthesis steps of the hydrothermal method are simple and the particles synthesized by this method showed uniform size, table structure and good dispersion. The lanthanide fluoride nanocrystals prepared in this experiment can be used as an excellent optical material. The samples were then irradiated by laser 980 nm at room temperature, and they emitted bright and unusually stable upconvert visible light. Experiments have shown that NaGdF$_4$ (Yb$^{3+}$Er$^{3+}$) can present good up-conversion luminescence. Therefore, it provides us with more possibilities in application fields such as probes, scanning and display.

1. Introduction
The up-conversion luminescence of rare-earth doped materials can be applied in the fields such as compact solid-state laser, information processing, optical storage, color display, temperature measurement and biological fluorescence labeling. On the transformation of rare earth ions doped materials in the field of light has a long and glorious history, Francois Auzel was the first one who observed up-conversion emission from Er$^{3+}$ and Tm$^{3+}$ ions[1-3]. Since the early 20th century, rare earth ion-doped up-conversion materials have attracted people's attention because of their unique properties, such as its stability of the optical performance, longer fluorescence lifetime, larger anti-Stokes shift and sharp luminescence peak. And many industrial products, consumer products, surgical equipment, and medical analysis containing optical components rely on this characteristic of upconverting rare earth ions [4-6], for the reason that up-conversion luminescent materials began to flourish. At the same time, NaGdF$_4$ has also become one of the important choices for up-conversion luminescent substrates. NaGdF$_4$ doped by rare earth ions is one of the most efficient up-conversion phosphors among numerous luminescent materials due to the low phonon energy of host lattice, which reduces the amount of nonradiative transitions [7]. Gd$^{3+}$ ions are characterized by high energy level and long lifetime, narrow

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emission bands, stable optical properties, and low toxicity. As one of efficient major materials, the NaGdF₄ matrix has received extensive attention in the field of rare earth optics for its low phonon energy, high up-conversion efficiency, and wide ultraviolet-infrared optical transparency. In recent years, there have been a large number of related researches on the chemical synthesis, luminescence regulation and mechanism analysis of rare earth-doped NaGdF₄ materials. However, there are still deficiencies in nanocrystal size control, up-conversion luminescence efficiency improvement, radiation reabsorption, energy transfer etc, and some of the key scientific issues still face challenges.

In this work, the co-doping of Gd³⁺ and Yb³⁺ would improve the luminescence properties of rare earth-based materials and the monodispersity. In addition, information about nanoparticles can be accurately obtained.

2. Materials and Methods

Laboratory balances were used for sample weighing powders purity NaOH(96%), NaF(98%), the Ln(NO₃)₃ (Ln=Gd³⁺, Yb³⁺, Er³⁺) Gd(NO₃)₃: 0.5mol/L, Yb(NO₃)₃: 0.5mol/L, Er(NO₃)₃: 0.1mol/L) Oleic-acid (analytically pure) and deionized water. Ln(Yb³⁺, Er³⁺) doped NaGdF₄ nanoparticles were prepared by a hydrothermal method. The oleic acid was used as a surfactant to stabilize the UCNPs[8]. During the experiment, 1mmol lanthanide ions were added. The doping ratio in each kind of ions is shown in table 1 below. The samples obtained are labeled as S1, S2, S3, S4 and S5.

| Sample number | Gd(NO₃)₃ (ml) | Yb(NO₃)₃ (ml) | Er(NO₃)₃ (ml) |
|---------------|--------------|--------------|--------------|
| 1             | 1.46         | 0.5          | 0.2          |
| 2             | 1.56         | 0.4          | 0.2          |
| 3             | 1.66         | 0.3          | 0.2          |
| 4             | 1.76         | 0.2          | 0.2          |
| 5             | 1.86         | 0.1          | 0.2          |

Take a clean beaker, and add 1.2 g NaOH, 2 ml deionized water, 8 ml ethanol, 20 ml oleic acid and 8 ml NaF solution with a concentration of 1 mol/l. Add 1mmol rare earth ions into the mixed solution, where the ions are Gd³⁺, Yb³⁺, Er³⁺, and put the beaker and the reactants on a magnetic stirrer to stir for 30 minutes. Finally, the stirred solution is placed in the reaction kettle, the reaction temperature is 190 degrees, and the duration is 24 hours.

After the reaction, open the reaction cooled down to room temperature. Then the products were collected and separated by centrifugation, washed with ethanol for several times final deionized water wash was performed, and then dried in air at 60 °C for 20 hours. The precipitates (NaGdF₄:Yb³⁺ Er³⁺) 0.02g were dispersed in 3 mL of cyclohexane to do the further experiment.

X-ray diffractometer (Rigaku 2500 PC, Japan) Cu-Kα target radiation (λ=0.154nm), the operating voltage is 40kV, the current is 30mA, the test angle (2θ) is 20~80°. The transmittance of the transparent ceramics was measured by a dual-beam UV-visible spectrophotometer (SHIMADZU, UV-1902). The SEM images of samples were obtained by Using a SPI3800N scanning electron microscope (SEM, JEOL, JSM-7610F) operated at 10 kV. Fluorescence spectra and decay curves were measured on a spectrometer (Hitachi Instruments F-4600) with an980-Laser (Opolette laser by Opotek) as the excitation source.

3. Results & Discussion

NaGdF₄: Ln³⁺ nanocrystalline with cubic and hexagonal phase two phase, high temperature stability of the six-nation phase with higher fluorescence intensity, especially for this conversion luminescence more favorable, the cell structure is shown in Fig 1. The NaGdF₄ nanocrystals prepared by hydrothermal method can be completely dissolved in cyclohexane to form a clarification solution, and the sample
obtained is excited at 980nm. The optical photograph of samples are shown in the inset of Fig. 2. From the optical photograph taken, we can see the green light gradually increasing and red light decreasing from left to right in the photograph visible from left to right, showed increasing green light and decreasing red light. Figure 3 is the XRD diagram of the samples prepared under different doping conditions when NaF was used as fluoride source, all the diffraction peaks can be attributed to the pure hexagonal structure of NaGdF₄ (JCPDS No. 27-0699) [10-11]. No other impurity phases were observed in the XRD image, indicating that all the samples crystallized well.

![Figure 1. Structure of β-NaGdF₄ crystal phase](image1.png)

![Figure 2. Optical image of the sample solution under a 980 laser at room temperature](image2.png)

![Figure 3. (a) XRD pattern of nanoparticles samples with different doped(Ln= Gd, Yb, Er), (b) S3 sample solution absorption spectra](image3.png)
Figure 4. (a) UC emission spectra of different matrices doped with Ln (Gd, Yb, Er) at a pump of 980 nm, (b) The possible UC luminescence mechanism of Er$^{3+}$.

Figure 4(a) scattered from the S3 samples in cyclohexane solution absorption spectra of the observed sample Er$^{3+}$ at the UV spectrum is dominated by the host lattice strong and narrow absorption bands, peak appears at 376 nm, 520nm and 653nm. From emission spectra Figure 4(b) made up of $^4\text{H}_{11/2}$, $^4\text{S}_{3/2}$ and $^4\text{F}_{9/2}$ transition to $^4\text{I}_{15/2}$ due to their higher absorption cross-section at 980 nm through the ETU process.

From microstructure and morphology of samples by TEM and HRTEM observation, all samples outer wall of the rod of the sample form, form uniform, high quality. Figure 5 (A) shown that the morphology of sample S1 as figure scale in 100nm, from picture is still at long stick sample morphology length to diameter is higher, for multiple low resolution TEM images of hundreds of particles of statistical analysis it is concluded that the average grain size of 10nm in diameter, long-stemmed than 10:1. Figure 5(B) is the high-resolution HRTEM image of S1 sample with a graphic scale of 5nm, in which the two-dimensional lattice diffraction image can be clearly seen, indicating that the sample has high crystallinity, few defects and improved monodispersion characteristics.
Figure 5. (A) Scanning electron microscopy of S1, (B) HRTEM image of S1, (C) SEM image of S3, (D) SEM image of S5

Fig 5(C) is the morphology of S3 samples. From the figure, it can be seen that the appearance of the sample is not unique, and most of the particles are spherical instead of strip or bar, from which clear lattice stripe phases can be seen, indicating that the sample has good crystallization. Fig 5(D) is the morphology of S5 samples. It is still a long rod-like sample, but the aspect ratio becomes lower and the average diameter is less than 20 nm. With the increase of Gd ions, the diameter of the sample gradually decreases, making it easier to grow into other shapes. Gd$^{3+}$ ions play a very good role in adjusting the size and morphology of particles.

4. Conclusions
To sum up, a series of crystalline nanomaterials with good monodispersity were successfully synthesized by the hydrothermal synthesis with oleic acid as the surfactant in this experiment. The whole reaction adopts aqueous solution as the reaction medium, which is non-toxic to the environment and can be used for synthesizing other rare earth fluorides. The NaGdF$_4$:Yb, Er nanocrystals obtained from this reaction have a diameter of 10-20 nm and a narrow particle size distribution, which provides an analytical method for measuring cyclohexane solution samples by ultraviolet-visible absorption spectroscopy. By changing the ratio of Yb$^{3+}$ and Gd$^{3+}$ in the NaGdF$_4$ sample, it is found that the sample size gradually decreases with the increase of the Gd$^{3+}$ content. The size of the sample can be reduced to the nanometer level, and the monodisperse doping ratio has been studied in detail.

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