

An experimental design approach for hydrothermal synthesis of NaYF₄: Yb³⁺, Tm³⁺ upconversion microcrystal: UV emission optimization



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ABSTRACT

Ultraviolet (UV) emissions of hydrothermally synthesized NaYF₄: Yb³⁺, Tm³⁺ upconversion crystals were optimized using the response surface methodology experimental design. In these experimental designs, 9 runs, two factors namely (1) Tm³⁺ ion concentration, and (2) pH value were investigated using 3 different ligands. Introducing UV upconversion emissions as responses, their intensity were separately maximized. Analytical methods such as XRD, SEM, and FTIR could be used to study crystal structure, morphology, and fluorescent spectroscopy in order to obtain luminescence properties. From the photo-luminescence spectra, emissions centered at 347, 364, 452, 478, 648 and 803 nm were observed. Some results show that increasing each DOE factor up to an optimum value resulted in an increase in emission intensity, followed by reduction. To optimize UV emission, as a final result to the UV emission optimization, each design had a suggestion.

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1. Introduction

The synthesis of materials capable of converting photons from low to high energy has attracted much attention. This non-linear process is known as upconversion. The upconversion process gives the ability to display visible or ultraviolet emissions using low-cost, non-destructive near-infrared light as excitation source, which is invisible to the human eye, abundant in nature to explicit materials called upconversion particles [1,2]. Researchers have reported various applications of these particles including color displays, upconversion lasers [3], security and QR printing inks [4,5], absorbent for dye removal in solutions [6], solar cells, sensors [7], etc. Rare earth doped fluoride materials revive these applications due to fluoride's low phonon and vibrational energy, high refractive index, good optical transparency, thermal and environmental stability, high quantum efficiency as host and specific characteristics of lanthanide ions as dopants [8–13]. Lanthanides offer narrow emission lines, large Stokes shift, no photo-bleaching, as well as long luminescence lifetimes [14,15]. Thulium ion as a result of its metastable energy levels and wide emission spectra from ultraviolet to near-infrared under the excitation of 980 nm. Laser,

is one of the most popular lanthanide ions acting as activator [9]. Due to local symmetry restrictions around Tm³⁺ ions, the use of a sensitizer such as Ytterbium is essential to have a strong upconversion emission [2].

Hydrothermal synthesis is an efficient solution approach for synthesizing upconversion crystals, and produces monodispersed particles with high crystallinity. Upconversion emission's intensity depends on several factors such as host lattice, dopants type and concentration, reaction time and temperature, annealing temperature, and synthesis parameters [10]. Cao et al. [11], reported the tunability of red emission in NaYF₄: Yb³⁺, Tm³⁺ nanoparticles as a function of Yb³⁺ doping concentrations. Xiaoge et al. [7], optimized reaction time, dopant concentration and annealing temperature for NaYF₄: Yb³⁺, Tm³⁺ nanoparticles at 60% Yb³⁺ concentration, reacting at 180 °C for 24 h. Jang et al. [12], synthesized various shapes of nanoparticles by changing surfactant, additives and lanthanide doping.

In this study, three response surface methodology (RSM) was introduced in the hydrothermal synthesis of NaYF₄: Yb³⁺, Tm³⁺ upconversion particles in order to identify the optimized condition (Tm ion concentration and pH value) using three different ligands. The synergistic effects of these factors on crystalline structure and phase, morphology of particles and upconversion emission were evaluated. Finally, an optimization for UV upconversion emissions were done.

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Table 1
9 runs of central composite design of experiment in detail.

Run	CA		BA		SDSS	
	Tm concentration (%)	pH	Tm concentration (%)	pH	Tm concentration (%)	pH
1	2.2	4.5	1.2	3	0.2	6
2	1.2	6	2.2	6	1.2	6
3	2.2	3	1.2	6	2.2	6
4	1.2	3	1.2	4.5	0.2	4.5
5	0.2	3	0.2	6	1.2	4.5
6	1.2	4.5	0.2	3	1.2	3
7	2.2	6	0.2	4.5	2.2	4.5
8	0.2	6	2.2	4.5	0.2	3
9	0.2	4.5	2.2	3	2.2	3

Table 2
FWHM driven of Scherrer equation for samples containing different ligands.

Particles containing ligand	Average crystallite size (Å)	FWHM ($^{\circ}2\theta$)
Butanoic acid	454	0.1476
Citric acid	408	0.2214
Sodium dioctyl Sulfosuccinate	469	0.1771

2. Materials and methods

Yttrium, ytterbium and thulium oxide were purchased from Y.S. Z China. Sodium fluoride purchased from Rikhem Co. Russia. Nitric acid, citric acid, butanoic acid, sodium hydroxide and ethanol were from Merck. Sodium dioctyl Sulfosuccinate was ordered from Sigma–Aldrich. All chemicals used in this research were used as received with no further purification.

2.1. Hydrothermal synthesis of $\text{NaY}_{(80-x)}\text{F}_4: \text{Yb}_{(20)}\text{Tm}_{(x)}$ upconversion micro-particles

The $\text{NaY}_{(80-x)}\text{F}_4: \text{Yb}_{(20)}\text{Tm}_{(x)}$, ($x = 0.2, 1.2$ and 2.2) micro-crystals were hydrothermally prepared using butanoic acid (BA), citric acid (CA) and Sodium dioctyl Sulfosuccinate (SDSS) as ligands. Typically [16], rare earth nitrates and 15 ml of ligand solution were mixed and vigorously stirred for 1 h. A solution of NaF was added dropwise to the mixture and a colloidal mixture

was formed. After 30 min of stirring and tuning of pH value, the white complex was transferred into Teflon autoclave and heated for 18 h at 200 °C. After naturally cooling down to room temperature, the white precipitate was washed in ethanol and deionized water by centrifuging three (3) times and dried in vacuum oven at 80 °C for 3 h.

Three central composite design (CCD) were employed for the hydrothermal synthesis of $\text{NaYF}_4: \text{Yb}^{3+}, \text{Tm}^{3+}$ upconversion particles. The CCDs were used to evaluate the combined effects of two independent variables: Tm^{3+} concentration (0.2%, 1.2% and 2.2%), ligand type (BA, CA and SDSS) and pH value (3, 4.5 and 6) for particles containing three ligands, (BA, CA and SDSS) on the upconversion emission's intensity of the resulting crystals. The results of the experimental conditions by CCDs are presented in Table 1. Each experiment consisted of 9 runs. Design expert software was used for the analysis of experimental data [18–21].

2.2. Upconversion powder characterizations

To validate the design, a series of analysis including SEM, XRD, EDS, and PL spectroscopy were performed.

Powder X-ray diffraction (XRD) patterns were obtained with a STADI P X-ray diffractometer (Germany) equipped with an Imaging Plate Position Sensitive Detector. Scanning electron microscopy (SEM) images of the powder samples were taken using LEO 1455VP. In order to determine the elemental compositions of micro-particles, Energy-dispersive X-ray (EDS) spectroscopy by Mira 3-XMU FESEM, was used.

To measure the emitted upconversion luminescence (Fig. 1), the synthesized powders were placed in a sample holder to form a smooth, flat disk and was irradiated with a 980 nm CW laser diode, coupled to an Ocean Optics fluorescent spectrophotometer. All measurements were carried out at room temperature.

3. Results and discussion

The role of variation of the Tm^{3+} ion concentration and pH value on crystal phase of upconversion particles were probed. Fig. 2 shows the XRD profiles of hydrothermally synthesized crystals. The peaks of samples are characteristic of hexagonal phase NaYF_4 , according to JCPDs file number 16-0334, while relative intensities are different as a result of preferential orientation growth of

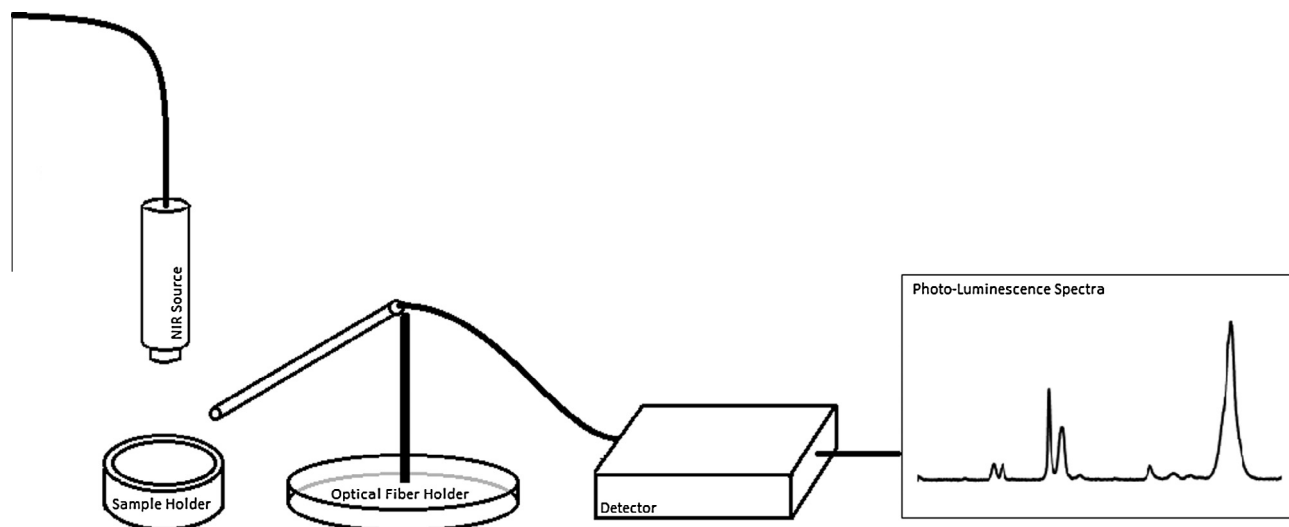


Fig. 1. Upconversion emission measurement setup used in this research.

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