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Hydrothermal synthesis and up-conversion luminescence properties of $NaYF_4$:Yb^{3+},Tm^{3+} phosphors

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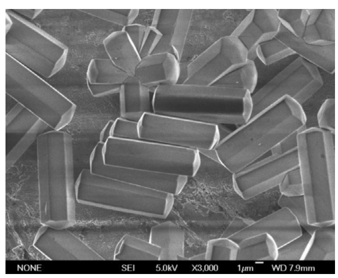
HIGHLIGHTS

- $NaYF_4$:Yb^{3+},Tm^{3+} up-conversion luminescence phosphors have been fabricated.
- The preparation conditions were optimized by single factor and orthogonal experiment design.
- The influence of the complexing agent types on $NaYF_4$:Yb^{3+},Tm^{3+} products was discussed.
- The crystal form of the target products was hexagonal prisms.
- The target products exhibited the bright blue up-conversion luminescence emission.

GRAPHICAL ABSTRACT



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ABSTRACT

An up-conversion luminescent material, $NaYF_4$ doped with rare-earth (RE), possessed a high luminescence efficiency and excellent stability. As described herein, a series of hexagonal nano-prismatic $NaYF_4$:Yb^{3+},Tm^{3+} up-conversion phosphors had successfully been synthesized through mild hydrothermal method. The influence of hydrothermal time, the content of sodium tartrate, activator, sensitizer and ammonium fluoride on the luminescence properties of the target product were systematically investigated by means of single factor experiments. Based on the single factor experiments, the orthogonal method was used to obtain the optimal preparation conditions of the sodium tartrate/RE mole ratio, the sensitizer Yb^{3+} ions content, the NH_4F/RE mole ratio, and the hydrothermal time which were 0.5, 23%, 11, 13 h, respectively. The fluorescent emission spectra analysis results showed that the strongest blue up-conversion luminescence emission peaks ($^1G_4 \rightarrow {}^3H_6$ transition of Tm^{3+} ion) of the $NaYF_4$:Yb^{3+},Tm^{3+} phosphors using sodium tartrate as complexing agent was located at 477 nm under 980 nm near infrared (NIR) laser diode excitation. Finally the target products using different complexing agent were prepared at optimum preparation condition, and characterized by X-ray diffraction, scanning electron microscope. The crystal structure of products using tartaric acid and citric acid as complexing agent was hexagonal, consisting of spheres with 100 nm diameter.

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1. Introduction

Up-conversion phosphors comprising proper host–dopant combinations can convert a near-infrared excitation into a visible emission through lanthanide doping [1]. These unique anti-Stokes emitters have evolved as a rapidly growing field due to creation of new applications in diverse fields such as displays, biological assays, and solar cells [2–11]. Up to now, the $NaYF_4$ fluorides have been known to be the most efficient host for up-conversion, especially for co-doped Yb^{3+}, Tm^{3+} up-conversion systems due to the optimal low lattice phonon energy, high thermal stability and the presence of $NaYF_4:Yb^{3+},Tm^{3+}$ crystals which were found to exhibit distinct up-conversion fluorescence for green and blue up-conversion phosphors [12–19]. At ambient temperature and pressure, the $NaYF_4$ exists in two polymorphs: cubic (α-$NaYF_4$) and hexagonal (β-$NaYF_4$), depending on the synthesis method. The β-$NaYF_4$ has been reported as the most efficient host material. Moreover, in the rare-earth luminescent ions, Tm^{3+} ions also has a wealth of multi-level energy and multitudinous metastable levels [20], due to its $^1D_2 \rightarrow {}^3F_4$, $^1I_6 \rightarrow {}^3H_4$ and $^1G_4 \rightarrow {}^3H_6$ transitions of Tm^{3+} ions which are located in the vicinity of 450 nm wavelength and 480 nm. Besides, it has intense fluorescence emission intensity in the blue range. Herein, with exceptional up-conversion properties, Yb^{3+}, Tm^{3+} co-doped $NaYF_4$ crystals have received great research interest for their unique properties different from their bulk counterparts at home and abroad. The electrons of Yb^{3+} ions on the ground state are excited to a higher energy level, and subsequently energy is transferred to Tm^{3+} ions due to the energy overlap of the transition dipoles [21]. Finally the energy is released by Tm^{3+} ions in the form of light emission and partial heat.

However, few studies have explored the application of orthogonal experimental design (OED) to optimize synthesis conditions. Practical work usually requires multi-factor analysis, and multi-factor experiments include full factorial design and fractional factorial design. Full factorial design tests all possible combinations of factors and the number of full factorial experiment is too large to implement. The OED is a multi-factor experiment design method based on the orthogonal array. It will select representative point from full factorial experiment in a way that the points are distributed uniformly within the test range and thus can represent the overall situation, and is highly efficient for the arrangement of multi-factor experiment with optimal combination levels. The orthogonal design has several advantages: (1) the data points are distributed evenly; (2) the number of trials needed to complete the experiment is relatively small; (3) the test results could be analyzed through range analysis and variance analysis. The OED has the following characteristics: (1) use fractional factorial experiment instead of full factorial experiment; and (2) understand the full experiment through the analysis of fractional experiment [22].

Because Tm^{3+} ions coverage was mainly reported with visible light emitting, in order to get high property up-conversion nanocrystals, the preparation and characterization of $NaYF_4:Yb^{3+},Tm^{3+}$ up-conversion crystals were reported in this work. These rare-earth co-doped crystals were synthesized by a facile hydrothermal approach, of which the blue up-conversion emission was observed under the 980 nm NIR laser diode excitation. The influence of hydrothermal time, the content of sodium tartrate, activator, sensitizer and ammonium fluoride on the luminescence properties of the target product were investigated by means of single factor experiments. Based on the single factor experiments, the preparation condition was optimized by orthogonal experiment. The target products using different complexing agent were prepared on the optimized preparation condition, and characterized by X-ray diffraction, scanning electron microscope, and fluorescence spectra analysis.

2. Experimental

2.1. Materials and methods

2.1.1. Hydrothermal synthesis

All of the chemicals are of analytical grade reagents and used without further purification. RE hydrochloride standard solutions were fabricated by dissolving the corresponding metal oxide (99.99%) in small amount of hydrochloric acid and then diluting it with distilled water at elevated temperature under vigorous stirring and excess hydrochloric acid was removed by evaporation. Sodium tartrate, EDTA, trisodium citrate, citric acid, tartaric acid, NaCl, NH_4F solution were weighed and dissolved into the appropriate amount of distilled water with an agitator in 200 mL breaker, stirred until completely dissolved, then transferred to the 250 mL volumetric flask and shaken well, respectively. $NaYF_4:Yb^{3+},Tm^{3+}$ up-conversion luminescence phosphors using sodium tartrate as a complexing agent was first prepared by facile hydrothermal method. In a typical procedure for preparation of $NaYF_4:Yb^{3+},Tm^{3+}$ up-conversion luminescence phosphors, the reagents were weighed appropriately according to the nominal composition of $(1-x-y)\ YCl_3 + xTmCl_3 + yYbCl_3 + zNH_4F + 0.75zNaCl$. (z represents the value of NH_4F and NaCl concentration, while x and y represent that of Tm^{3+} and Yb^{3+} ions, respectively). 0.2 mol/L of the prepared YCl_3 solution, mixed with 0.2 mol/L $YbCl_3$ solution, 0.01 mol/L $TmCl_3$ solutions were stirred with an agitator to form homogeneous hydrochloride solution. After that, the sodium tartrate (0.2 mol/L) was added to the mixed hydrochloride solution to form a white suspension. Subsequently, the aqueous solution mixture of sodium chloride (2 mol/L) and ammonium fluoride was poured slowly into the above solution. After being stirred for 1 h, the resultant complex precursor solution was transferred to a Teflon bottle placed in a stainless steel autoclave, which was sealed and maintained for hydrothermal treatment at 180 °C for a period of time. As the autoclave was cooled to room temperature naturally, the precipitates were separated by centrifugation, washed with deionized water and absolute ethanol for three times in sequence, and then vacuum drying at 80 °C for 12 h to get rid of the solvent. Finally, the obtained powders were ground using an agate mortar and pestle and were then subjected to various characterization.

2.1.2. Characterization

The structures of the products were examined by X-ray diffraction (XRD) patterns obtained from a German Bruker D8-Advance X-ray powder diffractometer (Cu target, working voltage 40 kV, working current 40 mA, $\lambda = 1.54187$ Å, 2θ angle ranges from 10 to 80° with a step of 0.02 and counting time of 0.5 s). The size and morphology of the powders were observed by a Field Emission Scanning Electron Microscope (FESEM, Model Tecnai G^2 F20 S-TWIN, America FEI Corp.). Samples were prepared by placing a drop of an absolute ethyl alcohol dispersion of nanocrystals on the surface of a copper grid. Photoluminescence (PL) excitation and emission spectra were recorded with a Hitachi F-2700 spectrophotometer. The operation voltage was 400 V, with a slit width of 2.5 and 2.5 for excitation and emission, respectively. The up-conversion emission spectra were measured by using 980 nm optical fiber coupled laser as the excitation source. All the measurements were performed under room temperature.

3. $NaYF_4:Yb^{3+},Tm^{3+}$ preparation conditions of single factor optimization

The total amount of rare earth ions was 2 mmol, and hydrothermal temperature was 180 °C in a single factor experiment. Product number was represented by T. The up-conversion

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