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Original Research Paper

$NaLuF_4$:Yb,Tm up-conversion materials: Investigation of UV emission intensity by experimental design

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ABSTRACT

$NaLuF_4$ doped Yb/Tm upconversion phosphor was synthesized by a facile hydrothermal method, using EDTA as a chelating agent. The influence of synthesis parameters was investigated on UV emission intensity through face-centered central composite design (CCD). Four parameters including F:RE ratio, pH value, reaction time and ethanol percent were considered as independent variables. It was found that pH value and F:RE ratio have the highest effect on emission intensity and the ethanol percent and the reaction time have mild and low influence on it. Furthermore, at pH 4, nano spherical particles with cubic phase were formed and change of other parameters had low influence on phase transformation. However, the hexagonal micro prisms with the hexagonal phase were predominant at pH $\geq$ 6. The role of EDTA was indicated on phase transformation and aggregation of particles at the various value of pH. It was shown that the crystal phase, the surface smoothness and the particle size are influential factors on UV emission intensity.

1. Introduction

In recent years, lanthanide (Ln) doped up-conversion (UC) materials have attracted great interest due to their various potential applications in many fields such as photovoltaic, 3D display, drug delivery, laser, security and 3D printing [1–10]. Until now, numerous hosts have been demonstrated for studying UC phenomenon. $NaYF_4$ has attracted particular attention owing to lower phonon energy and higher refractive index. It has been reported as excellent host for UC phosphorous. $NaYF_4$ possess cubic (α) and hexagonal (β) phases in which β-phase has more efficiency due to low symmetry and intrinsic crystalline anisotropy. Compared to previously used hosts, $NaYF_4$ exhibits more intensive UC emission. In this regard, studied have been focused on this host, while other hosts receive relatively low attention [11–13]. Recent investigations showed that $NaLuF_4$ is more efficient than $NaYF_4$, specifically for the UV wavelengths. This is due to greater atomic mass of Lu and its smaller atomic radius compared to Tm and Yb atoms. This leads to lower phonon energy and crystal defects. Moreover, Lu^{3+} is more suitable for increasing the 4f-4f transition probability and population life time as well as decreasing the conversion efficiency [14–17].

UVUC emission intensity depends significantly on the material's physical properties including: crystal phase, particle size, surface smoothness, morphology and crystallinity. These physical properties can be manipulated by tuning synthesis reaction condition [18,19]. Hydrothermal synthesis functions as a facile, mild, environmentally-friendly and controllable route for preparation of phosphorous materials. The effects of reaction temperature and time, pH, pressure, fluoride concentration, fluoride source, chelating agents, surfactants and inorganic salts have been studied. These studies are focused especially on the physical and optical properties of $NaYF_4$:Yb, (Er, Tm, Ho) by one-factor-at-a-time method [20–25]. To the best of our knowledge, a few research have been conducted on the effects of hydrothermal variables on the physical and optical properties of $NaLuF_4$:Yb, Tm [26–28].

The present study aimed at investigating the influence of synthesis parameters including F:RE, pH, the ethanol percent and the reaction time on both emission intensities at UV wavelengths of 345 and 362 nm. Thereafter, the impacts of these variables on crystal phase, morphology and particle size, hydrothermal reaction

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yield and elemental composition and surface chemistry of phosphors is put into discussion. The number of experiments was designed, using the face-centered, central composite design (CCD) of experiments. Thanks to design-expert software, version 7.0.0, we managed to design four factors at three levels. Emission Intensity at wavelengths of 345 and 362 nm considered as a response. Upon the analysis of variance (ANOVA), the significance level was considered as 5%. The design summery and experiments design with results are shown in Tables 1 and 2.

2. Experimental

2.1. Materials

The rare earth oxides (99.99%) were purchased from Joysine Tech. Co. Ltd. (China). NH_4F, NaF, NaOH, ethylenediaminetetraacetic acid disodium salt (Na_2EDTA), cetyltrimethylammonium bromide (CTAB) were purchased from Merck Millipore (Germany). Deionized water was used in all of experiments. The chemicals were of analytical grade and were used as received without further purification.

2.2. Sample preparation

The rare earth nitrates were prepared by dissolving the corresponding oxide in dilute nitric acid at an elevated temperature and then evaporating in vacuum oven. 10 ml aqueous solution, containing 1.2 mmol EDTA (Y^{n-}), was gently mixed with 10 ml aqueous solution of rare earth at the temperature of 50 °C and intensively stirred for 30 min. 0.24 mmol CTAB and adequate amount of ethanol was further added to solution. Afterwards, appropriate amount of solution of NaF (0.5 M) and NH_4F (2 M) were mixed and the result was added to solution drop by drop under vigorous stirring for another 1 h. The pH value was tuned by dilute HNO_3 and ammonia solution. By means of deionized water, all samples came to an identical amount of 70 ml. The obtained suspension was transferred to a 87 ml Teflon-lined autoclave, sealed and maintained at 200 °C for several times. The autoclave rested to naturally cool down to room temperature, the precipitates were hence collected and washed with ethanol and deionized water in sequence for 3 times and then dried at 80 °C for 12 h. EDTA: RE and Na: RE molar ratio were considered at constant value of 1 and 8 respectively. The molar concentration of rare earth cations were 0.795, 0.20 and 0.005 for Lu, Yb and Tm, respectively.

Table 1
Design summery.

Factor	Name	Unit	Low	High
A	F:RE	–	8	16
B	EtOH	%	0	20
C	pH	–	4	8
D	t	h	12	18

Table 2
Experiments design and results.

Sample	A:F:RE	B:EtOH%	C:pH	D:t h	Intensity 345 (a. u.)	Intensity 362 (a. u.)
S1	16	20	8	12	4260	5306
S2	16	20	4	12	2512	2756
S3	16	0	8	18	3766	4760
S4	8	20	4	18	2170	2314
S5	16	0	4	18	2521	2640
S6	8	0	8	12	2300	2606
S7	8	20	8	18	2395	2686
S8	8	0	4	12	2150	2315
S9	8	10	6	15	2636	3223
S10	16	10	6	15	4413	5861
S11	12	0	6	15	3514	4771
S12	12	20	6	15	4516	5960
S13	12	10	4	15	2766	3070
S14	12	10	8	15	3911	5055
S15	12	10	6	12	3449	4592
S16	12	10	6	18	3841	5161
S17	12	10	6	15	4587	6159
S18	12	10	6	15	4501	6099

2.3. Characterization

Phase analysis and composition of samples were determined by a PW 1800 Philips X-ray diffractometer with Cu Kα radiation (λ = 1.54187 A). Morphology and particle size of materials were studied, using LEO 1455VP Scanning electron microscopy (SEM). Elemental analysis of samples was performed on a Vista-Pro Inductively coupled plasma optical emission spectroscopy (ICP-OES). upconversion emission spectra of phosphors were depicted by a Perkin-Elmer LS 55 Luminescence Spectrometer equipped with external adjustable IR diode laser 980 nm as excitation source. Energy dispersive X-ray (EDX) patterns were recorded by a Mira-Tescan field emission scanning electron microscopy (FE-SEM).

3. Results and discussion

The crystal structures and phase purity of the samples were studied by XRD measurements. Fig. 1a shows the XRD patterns of selected as-prepared samples at pH 4. The samples were the mixture of α and β phase of $NaLuF_4$ according to standard cards of JCPDS No. 27-0725 and 27-0726, respectively. Fig. 1b demonstrates XRD patterns of special samples prepared at pH 6 and 8. As shown, the dominant crystal phase in sample of S6 is α, sample S3 has a little α phase and other samples possess pure β phase. The difference in relative intensity of XRD patterns results from preferential orientation crystal growth [26].

As seen in Fig. 1a, predominant phase in pH 4 is α phase. It is noticeable that with adjusting pH at 4, hydrolysis of fluoride ion would be accelerated. Consequently conversion to HF occurs. This conversion leads to reduced concentration of fluoride ions in solution according to Eqs. (1) and (2):

$$NaF \rightleftharpoons Na^+ + F^- \quad (1)$$

$$F^- + H_2O \rightleftharpoons HF + OH^- \text{ with adding acid}$$

$$F^- + H_2O \overset{H^+}{\rightleftharpoons} HF + OH^- \quad (2)$$

With decreasing F^- concentration, its competitive ability with EDTA is weakened. This decreases the release of RE ions from EDTA-RE complexes and formation of beta phase. Furthermore, the pH values have a significant influence on both existing forms and the chelating ability of Y^{n-}. EDTA is present in the form of mostly Y^{2-} at mild acidic medium that makes its chelating power is weakened. Therefore, it is high probable that at pH 4, EDTA enhances nucleation rate and prevents particle aggregation and growth [27,28].

In contrast, at pH 6 and 8, EDTA forms stable complexes with RE cations. This differently delays nucleation and growth rate based on LaMer model [29,30]. Also fluoride concentration is limitedly affected from basic pH values. Consequently, fluoride ion induces more beta phase formation.

SEM images of the samples that are prepared at the pH 4 are shown in Fig. 2. The $NaLuF_4$:Yb, Tm turned out to be nearly spherical particles with particle size from 130 to 200 nm.

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