



Well-defined sodium lanthanum tungstate hierarchical microcrystals: Controllable synthesis and luminescence properties



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ABSTRACT

Well-defined sodium lanthanum tungstate $[\text{NaLa}(\text{WO}_4)_2]$ microcrystals with a variety of morphologies have been synthesized via a controllable solvothelmal route. The as-synthesized $\text{NaLa}(\text{WO}_4)_2$ particles are well-dispersed with a narrow size distribution. The morphology and particle size of the $\text{NaLa}(\text{WO}_4)_2$ samples can be easily tuned in a controlled manner by changing the reaction conditions, including reaction temperature, component of solvent, and organic additives. The as-obtained $\text{NaLa}(\text{WO}_4)_2 \cdot \text{Ln}^{3+}$ ($\text{Ln} = \text{Dy}, \text{Sm}, \text{Tb}, \text{and Eu}$) samples exhibit intense characteristic green-yellow, orange-red, green, and red emissions under ultraviolet excitation, which might find potential applications in the fields of advanced flat panel displays, optoelectronic devices, and light emitting diodes (LEDs). This facile synthesis strategy may be of much significance for the fabrication of other well-defined rare earth tungstate functional materials.

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1. Introduction

In recent years, constructing materials with fascinating hierarchical three-dimensional architectures is of great importance not only due to the fundamental scientific interest but also for the potential applications [1,2]. Such materials may offer opportunities to explore their novel optical, magnetic, electronic, or mechanical properties [3]. To date, many synthesis routes have been developed to fabricate the inorganic functional materials. Among them, the solvothelmal method has been proven to be an effective and convenient process for the synthesis of various inorganic functional materials due to its mild reaction conditions, tunable reaction parameters, ease of operation, and large-scale production capability [4,5]. During the solvothelmal process, the morphology and particle size of the product can be tuned by the choice of solvent, surfactants, or reaction parameters such as reaction time and temperature and pH value of the initial precursor solution [6]. Therefore, it remains a challenge to select appropriate solvent, surfactants, and reaction parameters for the controllable synthesis of inorganic hierarchical architectures with well-defined morphology, uniform particle size, as well as promising novel properties.

Great efforts have been focused on the tungstate materials which have been found various promising applications in fields of catalysis, quantum electronics, and lasers [7]. Kaczmarek et al. reported the controllable synthesis and luminescence properties of Eu^{3+} and Dy^{3+} doped $\text{Y}(\text{WO}_3)_2(\text{OH})_3$ microspheres and flower-like $\text{La}_2(\text{WO}_4)_3$ [8]. Among various tungstate materials, the double alkaline rare earth tungstates in general formula of $\text{ARE}(\text{WO}_4)_2$ (A represents alkali metal ions; RE represents rare earth ions) have attracted great interest, which are mainly concentrated on obtaining single crystals [9]. In recent years, it has been demonstrated that $\text{ARE}(\text{WO}_4)_2$ is a promising host candidate for lanthanide ions (Ln^{3+}) activated luminescent materials due to its broad charge transfer band centered at near-UV wavelength and good thermal and chemical stability [7,10–12]. Other double tungstates (e.g. $\text{Aln}(\text{WO}_4)_2$) as host for the luminescence of lanthanide ions were also investigated [13,14]. In particular, the Ln^{3+} doped $\text{NaRE}(\text{WO}_4)_2$ materials generally exhibit better luminescence properties than the traditional alkaline earth metal tungstates MWO_4 ($\text{M} = \text{Ca}, \text{Sr}, \text{and Ba}$), which may be applied as promising phosphors for visual display and solid-state lighting. However, to our knowledge, the previous studies for Ln^{3+} doped $\text{NaRE}(\text{WO}_4)_2$ luminescent materials were focused on $\text{NaY}(\text{WO}_4)_2$, and the investigations for other $\text{NaRE}(\text{WO}_4)_2$ type luminescent materials are limited [15,16]. As we know, the 4f shell of La^{3+} is vacant and thus f–f transitions are unavailable, which are necessary for luminescent host materials. The corresponding lanthanum compounds are the most

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inexpensive among all rare-earth tungstates [10]. Therefore, the $\text{NaLa}(\text{WO}_4)_2$ material could be served as ideal host candidate for the matrix of lanthanide activator ions. To date, it is still a challenge to fabricate well-defined Ln^{3+} doped $\text{NaLa}(\text{WO}_4)_2$ luminescent materials with diverse morphologies by suitably tuning the synthesis conditions. Moreover, to our knowledge, great research attention was concentrated on the luminescence of Eu^{3+} , Tb^{3+} , Er^{3+} , $\text{Yb}^{3+}/\text{Er}^{3+}$, $\text{Yb}^{3+}/\text{Tm}^{3+}$, $\text{Yb}^{3+}/\text{Ho}^{3+}$ doped $\text{NaLa}(\text{WO}_4)_2$ phosphors [7,10,11,16], but the Dy^{3+} and Sm^{3+} doped $\text{NaLa}(\text{WO}_4)_2$ luminescent materials were seldom reported.

In this paper, uniform and well-dispersed $\text{NaLa}(\text{WO}_4)_2$ microcrystals with diverse morphologies have been synthesized via a controllable solvothermal method. The crystal phase, shape, and particle size can be easily tuned in a controlled manner by changing the reaction conditions.

2. Experimental section

$\text{Ln}(\text{NO}_3)_3$ ($\text{Ln} = \text{La}, \text{Dy}, \text{Sm}, \text{and Eu}$) and $\text{Tb}(\text{NO}_3)_3$ aqueous solutions were prepared by dissolving Ln_2O_3 (99.99%) and Tb_4O_7 (99.99%) in HNO_3 solution at elevated temperature with agitation. All other chemicals were of analytical grade and used directly without further purification.

In a typical synthesis, 1 mmol $\text{La}(\text{NO}_3)_3$ solution was first added in ethylene glycol (EG, 20 mL). Then, 0.66 g of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (2 mmol) was dissolved in deionized water (15 mL). Subsequently, the two solutions were mixed together, and the mixture became turbid immediately. After vigorous stirring for 30 min, the as-obtained mixing solution was transferred into a 50 mL Teflon bottle held in a stainless steel autoclave, sealed, and maintained at 180 °C for 12 h. Finally, the precipitates were separated by centrifugation, washed with deionized water and ethanol in sequence, and dried in air. The as-prepared sample was denoted as S1. Other samples (S2–S6) were prepared by the similar procedure except for different reaction temperature (160, 200 °C), solvent, or additives (sodium dodecyl benzenesulfonate, SDBS). The detailed experimental conditions as well as the morphologies of the products are summarized in Table 1. We take sample S1 as a representative example to illustrate the luminescence properties of the lanthanide activator ions Ln^{3+} doped $\text{NaLa}(\text{WO}_4)_2$ samples. A similar process were employed to prepare Ln^{3+} ($\text{Ln} = \text{Dy}, \text{Sm}, \text{Eu}, \text{and Tb}$) doped samples except for adding a stoichiometric amount (5 mol%) of $\text{Ln}(\text{NO}_3)_3$ aqueous solutions instead of $\text{La}(\text{NO}_3)_3$.

The samples were characterized by powder X-ray diffraction (XRD) performed on a D8 Advance diffractometer (Bruker). Fourier transform infrared spectroscopy (FT-IR) spectra were measured with a Perkin–Elmer 580B infrared spectrophotometer. The morphology and composition of the samples were inspected using JSM-7500F cold field scanning electron microscope JEOL equipped with an energy-dispersive X-ray (EDX) spectrum. Photoluminescence (PL) excitation and emission spectra were recorded with a Hitachi F-7000 spectrophotometer equipped with a 150 W xenon lamp as the excitation source. All measurements were performed at room temperature.

3. Results and discussion

3.1. Phase identification, structure, and morphology

Fig. 1a shows the XRD pattern of the sample S1. One can see that the diffraction peaks agree well with the reported data of $\text{NaLa}(\text{WO}_4)_2$ with tetragonal phase [JCPDS Card No. 79-1118, Space group: $I41/a$ (88)]. No other additional peak can be detected, revealing the formation of pure tetragonal phase of $\text{NaLa}(\text{WO}_4)_2$. Moreover, it can be seen that the diffraction peaks of the $\text{NaLa}(\text{WO}_4)_2$ sample are very strong and sharp, so we can say this

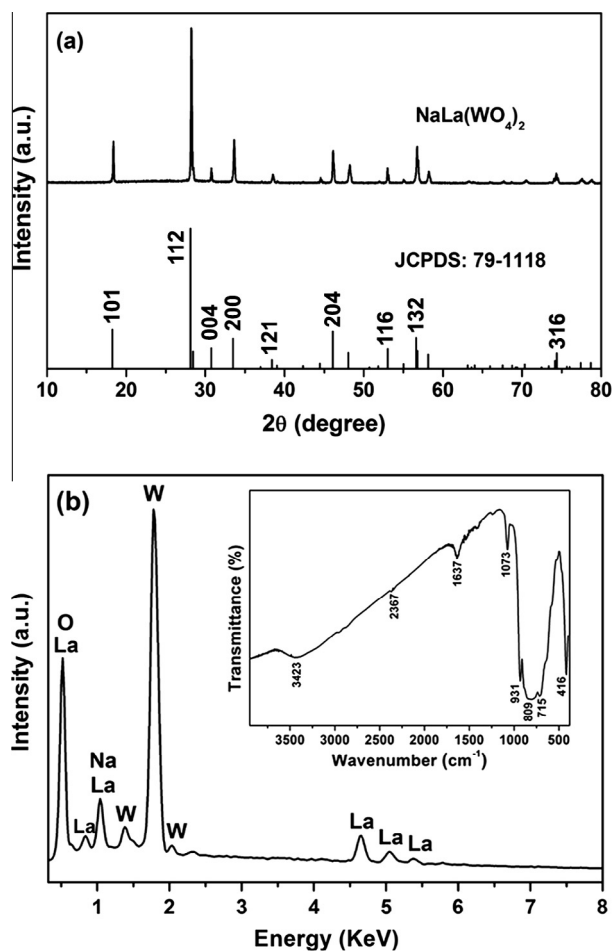


Fig. 1. (a) XRD pattern and (b) EDX spectrum of sample S1. Inset in (b) is the FT-IR spectrum of sample S1. The standard data of tetragonal $\text{NaLa}(\text{WO}_4)_2$ (JCPDS No. 79-1118) is presented as a reference.

product has high crystallinity. This is important for phosphors, because high crystallinity generally means less traps and stronger luminescence. The unit cell parameter and particle size were also investigated from the XRD result. The lattice constants of sample S1 are calculated to be $a = b = 0.5349$ nm and $c = 1.1628$ nm, which are well compatible with the literature value of $a = b = 0.5346$ nm and $c = 1.1626$ nm (JCPDS Card No. 79-1118). The crystallite size of the samples can be estimated from the Scherrer's equation: $D = 0.89\lambda/\beta \cos\theta$, where D is the average grain size, the factor 0.89 is characteristic of spherical objects, λ is the X-ray wavelength (0.15405 nm), β and θ are the full-width at half-maximum and diffraction angle of an observed peak, respectively. The estimated average crystallite size of sample S1 is calculated to be 53 nm. The EDX spectrum of the sample S1 confirms the presence of sodium (Na), lanthanum (La), tungstate (W), and oxygen (O) elements

Table 1

Summary of the experiment conditions and the corresponding morphologies and dimensions of the samples^a.

Sample	Solvent	Additives	Temperature/°C	Morphology
S1	EG (20 mL) + H ₂ O (15 mL)	–	180	Microspindles with pointed end
S2	EG (20 mL) + H ₂ O (15 mL)	–	160	Microspindles with arc-shaped end
S3	EG (20 mL) + H ₂ O (15 mL)	–	200	Microspindles with pointed end
S4	H ₂ O (35 mL)	–	180	Irregular microcrystals
S5	H ₂ O (35 mL)	SDBS (0.348 g)	180	Microplates
S6	EG (10 mL) + H ₂ O (25 mL)	–	180	Microspindles and branched architectures

^a Solvothermal time: 12 h.

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