



# Sonochemical preparation of pure *t*-LaVO<sub>4</sub> nanoparticles with the aid of tris(acetylacetonato)lanthanum hydrate as a novel precursor



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## ABSTRACT

Herein a simple and fast method is introduced for the synthesis of lanthanum orthovanadate (LaVO<sub>4</sub>) nanoparticles under ultrasound irradiation. The effect of tris(acetylacetonato)lanthanum hydrate ([La(acac)<sub>3</sub>·3H<sub>2</sub>O]) and La(OAc)<sub>3</sub> as two different precursors on the morphology and phase purity of LaVO<sub>4</sub> was investigated. To optimum the particle size of the products, sonication time and the kind of surfactants have been changed. The as-synthesized products were characterized by XRD, FT-IR, SEM, TEM, and EDS. Based on the obtained results, it was found that the size and shape of the sonochemically formed LaVO<sub>4</sub> nanoparticles were dramatically dependent on the sonication time, type of surfactant and lanthanum precursor. According to the XRD results, it was observed that pure tetragonal phase lanthanum orthovanadate (*t*-LaVO<sub>4</sub>) could be obtained only by using [La(acac)<sub>3</sub>·3H<sub>2</sub>O] as precursor under ultrasound irradiation for 30 min. On the other hand, monoclinic phase lanthanum orthovanadate (*m*-LaVO<sub>4</sub>) with poor crystallinity has been produced by vigorous stirring at room temperature without sonication.

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## 1. Introduction

Lanthanide orthovanadates as important rare earth compounds have been widely applied as polarizers, laser host materials, phosphors, and catalysts because of their unique electronic structure and the numerous transition modes involving the 4f shell of rare earth ions [1–4]. LaVO<sub>4</sub> as a member of this family crystallizes in two polymorphs, that is, monoclinic (*m*-) monazite type and tetragonal (*t*-) zircon type. It was reported that by increasing ionic radius, lanthanide ions show a strong tendency toward monazite-structured orthovanadate due to its higher oxygen coordination number of 9 as compared with 8 of the zircon one. Based on this reason, LaVO<sub>4</sub> chooses the monazite type as the thermodynamically stable state, while the other lanthanide orthovanadates normally exist in the zircon type [5,6]. LaVO<sub>4</sub> nanocrystals are known as suitable host for luminescent activators [7], active catalyst [4], and promising phosphor candidate [8,9].

The production of the zircon type LaVO<sub>4</sub> (*t*-LaVO<sub>4</sub>) is the main challenge since it is metastable and cannot be obtained by conventional methods. Xie et al. synthesized tetragonal phase LaVO<sub>4</sub> with La(NO<sub>3</sub>)<sub>3</sub> and NaVO<sub>4</sub> as starting materials at 180 °C by controlling the reaction pH via hydrothermal treatment [10]. Although Jia

and his co-workers prepared monoclinic and tetragonal phased LaVO<sub>4</sub> nanocrystals, they found that the use of chelating ligands such as EDTA was favorable for the formation of pure tetragonal phase LaVO<sub>4</sub> [9]. Fan et al. introduced a microemulsion-mediated hydrothermal method at 170 °C as a new approach for the synthesis of *t*-LaVO<sub>4</sub> nanowires by using La(NO<sub>3</sub>)<sub>3</sub> and NaVO<sub>3</sub> as La and V precursors [11]. A sonochemical method has been established for the synthesis of spindle-like *t*-LaVO<sub>4</sub> nanoparticles after sonication of the solution involving La<sub>2</sub>O<sub>3</sub> and NH<sub>4</sub>VO<sub>3</sub> for 1 h [12].

So far, the use of the coordination compounds as precursor has been widely developed to prepare nano-sized materials [13–18]. In this work, by using [La(acac)<sub>3</sub>·3H<sub>2</sub>O] as a coordination compound of lanthanum, pure tetragonal phased LaVO<sub>4</sub> nanoparticles were obtained. On the other hand, monoclinic and tetragonal phased LaVO<sub>4</sub> nanoparticles were synthesized with La(OAc)<sub>3</sub> and NH<sub>4</sub>VO<sub>3</sub> as starting reagents after sonication of the reaction solution for 30 min at the same conditions. In addition, the effect of sonication time and type of surfactant on the particle size of the products was studied. LaVO<sub>4</sub> nanoparticles were characterized by SEM, TEM, FT-IR, XRD, and EDS.

## 2. Experimental

### 2.1. Materials and physical measurements

All the chemical reagents including La(OAc)<sub>3</sub>, NH<sub>4</sub>VO<sub>3</sub>, [La(acac)<sub>3</sub>·3H<sub>2</sub>O], sodium dodecyl sulfate (SDS), polyvinylpyrrolidone

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**Table 1**  
The preparation conditions of nanostructures.

Sample No.	Precursor	Surfactant	Sonication time (min)	Products	Particle size (nm)	Figure of SEM images
1	La(OAc) <sub>3</sub>	No	10	<i>m</i> -LaVO <sub>4</sub> plus <i>t</i> -LaVO <sub>4</sub>	63–219	1a and b
2	La(OAc) <sub>3</sub>	No	30	<i>m</i> -LaVO <sub>4</sub> plus <i>t</i> -LaVO <sub>4</sub>	56–134	1c
3	La(OAc) <sub>3</sub>	No	50	<i>m</i> -LaVO <sub>4</sub> plus <i>t</i> -LaVO <sub>4</sub>	56–260	1d and e
4	La(OAc) <sub>3</sub>	PVP	30	<i>m</i> -LaVO <sub>4</sub> plus <i>t</i> -LaVO <sub>4</sub>	70–113	3a
5	La(OAc) <sub>3</sub>	PEG	30	<i>m</i> -LaVO <sub>4</sub> plus <i>t</i> -LaVO <sub>4</sub>	66–114	3b
6	La(OAc) <sub>3</sub>	CTAB	30	<i>m</i> -LaVO <sub>4</sub> plus <i>t</i> -LaVO <sub>4</sub>	70–133	3c
7	La(OAc) <sub>3</sub>	SDS	30	<i>m</i> -LaVO <sub>4</sub> plus <i>t</i> -LaVO <sub>4</sub>	56–80	3d
8	[La(acac) <sub>3</sub> ·3H <sub>2</sub> O]	No	10	<i>t</i> -LaVO <sub>4</sub>	78–173	4a
9	[La(acac) <sub>3</sub> ·3H <sub>2</sub> O]	No	30	<i>t</i> -LaVO <sub>4</sub>	63–125	4b
10	[La(acac) <sub>3</sub> ·3H <sub>2</sub> O]	No	50	<i>t</i> -LaVO <sub>4</sub>	78–94	4c
11	[La(acac) <sub>3</sub> ·3H <sub>2</sub> O]	PVP	30	<i>t</i> -LaVO <sub>4</sub>	35–50	5a
12	[La(acac) <sub>3</sub> ·3H <sub>2</sub> O]	PEG	30	<i>t</i> -LaVO <sub>4</sub>	70–100	5b
13	[La(acac) <sub>3</sub> ·3H <sub>2</sub> O]	CTAB	30	<i>t</i> -LaVO <sub>4</sub>	30–45	5c
14	[La(acac) <sub>3</sub> ·3H <sub>2</sub> O]	SDS	30	<i>t</i> -LaVO <sub>4</sub>	10–12	5d
15	La(OAc) <sub>3</sub>	No	No	<i>m</i> -LaVO <sub>4</sub>	20–25	10a and b

(PVP-8000), polyethylene glycol (PEG-4000), and cetyltrimethylammonium bromide (CTAB) were purchased from the commercial market and used without further purification. A multiwave ultrasonic generator (Sonicator 3000; Bandeline, MS 72, Germany), equipped with a converter/transducer and titanium oscillator (horn), 12.5 mm in diameter, operating at 20 kHz and 60 W/cm<sup>2</sup>, was used for the ultrasonic irradiation. All the ultrasonication experiments were carried out at ultrasonic power between 100 and 110 mW measured by calorimetry. The Fourier transform infrared (FT-IR) spectra were recorded on Magna-IR, spectrometer 550 Nicolet in KBr pellets in the range of 400–4000 cm<sup>-1</sup>. The XRD patterns were collected from a diffractometer of Philips Company with X'PertPro monochromatized Cu K $\alpha$  radiation ( $\lambda = 1.54 \text{ \AA}$ ). A Cam Scan MV2300 scanning electron microscope (SEM) was used to investigate the morphology of the products. Transmission electron microscope (TEM) images were obtained on a LEO912-AB transmission electron microscope with an accelerating voltage of 100 kV. The energy dispersive spectrometry (EDS) analysis was studied by XL30, Philips microscope.

## 2.2. Synthesis of LaVO<sub>4</sub> nanoparticles

LaVO<sub>4</sub> nanoparticles were prepared by reaction between lanthanum precursors and ammonium metavanadate (NH<sub>4</sub>VO<sub>3</sub>) with molar ratio of 1:1 under ultrasound irradiation. In a typical experiment, 2 mmol of lanthanum source (La(OAc)<sub>3</sub> or [La(acac)<sub>3</sub>·3H<sub>2</sub>O]) was dissolved in 50 mL of ethanol and then, added into a solution of NH<sub>4</sub>VO<sub>3</sub> (2 mmol of NH<sub>4</sub>VO<sub>3</sub> dissolved in 50 mL of distilled water) dropwise. The mixture of starting reagents was exposed to ultrasound irradiation for 10, 30, and 50 min. The yellow resulting precipitates obtained under various conditions (Table 1) were collected and washed repeatedly with distilled water and ethanol several times and finally dried at 50 °C in vacuum. To investigate the surfactant effect, further experiments were carried out with the aid of 0.5 g of SDS, PVP, PEG, and CTAB at the same preparation conditions. When the surfactants were applied, the sonication time was 30 min. The dried products were analyzed by SEM, XRD, TEM, FT-IR, and EDS.

## 3. Results and discussion

Fig. 1 depicts SEM images of the LaVO<sub>4</sub> nanoparticles synthesized by La(OAc)<sub>3</sub> at different sonication times. Fig. 1, parts a and b, shows the SEM images of the LaVO<sub>4</sub> nanoparticles obtained after sonication for 10 min (sample 1). The formation of very uniform plate-like microstructures composed of nanoparticles is observed in Fig. 1a and b. The particle sizes of the sample 1 are in the range

of 63–219 nm. Although the morphology of the products after sonication for 30 min (sample 2) was plate-like microstructures, particle sizes of the sample 2 were in the range of 56–134 nm (Fig. 1c). By further increasing sonication time from 30 to 50 min, morphology of the products was still plate-like microstructures composed of nanoparticles with particle sizes between 56–260 nm (Fig. 1d and e). Based on these results, it was found that the optimum sonication time for the preparation of LaVO<sub>4</sub> nanoparticles with smaller particle size was 30 min. The phase identification of the sample 2 was performed by powder X-ray diffraction (XRD). Most of the reflection peaks in Fig. 2 can be indexed to the tetragonal phase LaVO<sub>4</sub> (*t*-LaVO<sub>4</sub>) with space group of *I41/amd* and cell constants  $a = 7.4900 \text{ \AA}$ ,  $b = 7.4900 \text{ \AA}$ , and  $c = 6.5900 \text{ \AA}$  (JCPDS 32-0504). The reflections marked as “•” can be ascribed to the monoclinic phase LaVO<sub>4</sub> (*m*-LaVO<sub>4</sub>) with space group of *P21/n* (JCPDS 50-0367).

The influence of surfactants on the morphology of the final products was investigated in the sonochemical synthesis process. It is well-known that the presence of surfactants due to their high steric hindrance effects during the formation of nanostructures has a great effect on the shape and size of the final products. For example, sodium dodecyl sulfate (SDS) [19], cetyltrimethylammonium bromide (CTAB) [20], polyvinylpyrrolidone (PVP) [15], and polyethylene glycol (PEG) [21] have been widely investigated and applied to control the morphology of nanostructures. In this work, we used these surfactants to control the particle size and morphology of LaVO<sub>4</sub>. SEM images of the products generated by La(OAc)<sub>3</sub> as lanthanum precursor after sonication for 30 min in the presence of PVP (sample 4), PEG (sample 5), CTAB (sample 6), and SDS (sample 7) are shown in Fig. 3a–d, respectively. The particle sizes of the samples 4–7 are in the range of 70–113, 66–114, 70–133, and 56–80 nm, respectively. As shown in Fig. 3, very homogeneous nanoparticles with smaller grain sizes have been produced by SDS due to the presence of negative charges on the surface of this anionic molecule. The negative charges of SDS molecule are related to the SO<sub>4</sub><sup>2-</sup> group. In fact, the interaction of the La<sup>3+</sup> cations with SDS molecules is higher than that of the La<sup>3+</sup> cations with other surfactants. Because of this reason, the La<sup>3+</sup> cations were capped by SDS molecules for the in situ formation of the La–SDS compound. When the NH<sub>4</sub>VO<sub>3</sub> solution was added into the solution, the La–SDS compound could release the La<sup>3+</sup> ions to generate the LaVO<sub>4</sub> nuclei. The strong interaction of the La<sup>3+</sup> cations and SDS molecules could prevent the crystal growth and agglomeration of the products. On the other hand, it was found that the effect of PVP and PEG as polymeric surfactants on the morphology and particle size of the products was the same (Fig. 3a and b). As shown in the SEM image of the product synthesized by CTAB (Fig. 3c), the LaVO<sub>4</sub> nanoparticles are highly agglomerated. As we are aware, CTAB is known as a cationic surfactant, which cannot efficiently

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