

Facile, alternative synthesis of lanthanum phosphate nanocrystals by ultrasonication

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Abstract

Highly luminescent, rhabdophane ($\text{Ce}_{0.33}\text{La}_{0.66}\text{PO}_4 \cdot n\text{H}_2\text{O}$) nanorods and nanoparticles were prepared in aqueous solutions by ultrasonication, at pH 1 and pH 12, respectively. Both nanorods (5 to 9 nm wide and several tens to several hundreds nm long) and nanoparticles (elongated, connected 5 nm particles) were as small and as uniform as products obtained from methods that utilize complexing agents or surfactants, only with no complexing agent. This method of synthesis by ultrasonication is a fast and simple method and it is expected to be applicable for the synthesis of other nanocrystalline lanthanide phosphates.

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1. Introduction

Lanthanide-doped nanocrystals have recently been intensively studied [1–6] due to their diverse applications, e.g., in telecommunication components, solid-state lasers, displays, LEDs [7], luminescent markers, imaging [8], phosphors, and scintillators [9]. Among various hosts for lanthanide dopants, lanthanum phosphate (LaPO_4) has proven to be an appropriate host due to its high melting temperature [10], chemical stability, and high light yields of the doped materials [11]. Although several methods, including wet chemical precipitation [12,13], sol–gel [14,15], and hydrothermal [16], were reported for the synthesis of bulk lanthanum phosphate in aqueous solutions, only hydrothermal method was commonly used for the preparation of corresponding nanocrystals [17–22]. The hydrothermal method, however, yielded phase-pure rhabdophane or monazite LaPO_4 (depending on growth temperatures) in high yields, their particle sizes and size distributions were normally large [18, 21,22] and complexing agents were required to form more

uniform nanocrystals [17,23]. Although excess amounts of these complexing agents could be removed, and surface-bound agents might not interfere in most applications, an alternative method for the preparation of LaPO_4 and lanthanide phosphate nanocrystals in general should still be explored with the aim of eliminating the use of any external complexing agent.

In the search for an alternative method for the synthesis of lanthanum phosphate nanocrystals in an aqueous environment, sonochemistry is the method of choice because it consistently produces nanometer-sized inorganic materials [24]. Sonochemistry arises from acoustic cavitation, that is, the formation, growth, and implosive collapse of bubbles within a liquid [25]. The collapsing bubbles generate localized hot spots. The extreme conditions formed in these hot spots have been experimentally determined to feature transient temperatures of ~ 5000 K, pressures of ~ 1800 atm, and cooling rates in excess of 10^{10} K/s [26,27]. The high cooling rate, however, hinders the organization and crystallization of the products. For this reason, in all cases involving volatile precursors where gas phase reactions are predominant, amorphous nanoparticles are obtained [24]. On the other hand, if the precursor is a nonvolatile compound, the reaction occurs in a 200 nm ring surrounding the collapsing

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bubble [28]. In this case, the sonochemical reaction occurs in the liquid phase and the products can be either amorphous or crystalline, depending on the temperature in the ring region where the reaction takes place. The temperature in this ring is lower than that inside the collapsing bubble, but higher than the temperature of the bulk. Suslick and co-workers estimated the temperature in the ring region at 1900 °C [28]. By ultrasonication of appropriate reactants with low vapor pressures in liquid media, several nanocrystalline materials, including transition metal oxides [29,30], zinc sulfide [31], bismuth sulfide [32], bismuth selenide [33], and indium phosphide [34], were obtained. In this study, cerium-doped lanthanum phosphate, $(\text{Ce}_{0.33}\text{La}_{0.66})\text{PO}_4 \cdot n\text{H}_2\text{O}$, nanocrystals were prepared by ultrasonication under both acidic and basic conditions. To our knowledge, this is the first report on the synthesis of a lanthanide phosphate by sonochemistry.

2. Materials and methods

Lanthanum chloride heptahydrate (99.9%, Aldrich), cerium(III) chloride heptahydrate (99.999%, Aldrich), phosphoric acid (85.8%, J.T. Baker), sodium hydroxide (97%, Aldrich), and ammonium phosphate, dibasic $((\text{NH}_4)_2\text{HPO}_4$, Reagent Grade 98.4%, J.T. Baker) were used without further purification. Freshly deionized water was used to prepare all solutions. All reactions were done in jacketed sonochemical reaction vessels under nitrogen atmosphere to prevent the oxidation of Ce^{3+} by oxygen in the air. All solutions were purged under a strong nitrogen flow for at least 30 min prior to their use. The temperature of reactions was controlled not to exceed 80 °C by a strong air flow through the jacket of the reaction vessel.

In a typical synthesis of $(\text{Ce}_{0.33}\text{La}_{0.66})\text{PO}_4 \cdot n\text{H}_2\text{O}$ under an acidic condition (pH 1), 0.1 M phosphoric acid (10.0 mL) was added dropwise to a mixture of 0.1 M lanthanum chloride solution (6.7 mL, 0.67 mmol) and 0.1 M cerium(III) chloride solution (3.3 mL, 0.33 mmol) irradiated by a high-intensity ultrasound (Sonics and Materials VCX 750 sonifier, 20 kHz, 30 W/cm²). The obtained cloudy solution was sonicated at 30 W/cm² for another 1 h and the colloidal solution became more transparent. The temperature at the end of reaction was consistently around 80 °C. The stable, translucent colloidal solution (pH 1) was characterized and used without further separation. The overall concentration of lanthanides in the reaction mixture was 0.05 M.

In a typical synthesis of $(\text{Ce}_{0.33}\text{La}_{0.66})\text{PO}_4 \cdot n\text{H}_2\text{O}$ under a basic condition (pH 12), an aqueous solution (5.0 mL) containing lanthanum chloride heptahydrate (0.75 g, 2.0 mmol) and cerium(III) chloride heptahydrate (0.37 g, 1.0 mmol) was added dropwise to the 1.0 M sodium hydroxide solution (10.0 mL) irradiated by a high-intensity ultrasound (Sonics and Materials VCX 750 sonifier, 20 kHz, 30 W/cm²). A solution of ammonium phosphate, dibasic (0.40 g, 3.0 mmol) in deionized water (10.0 mL) was then added dropwise to the sonicated (30 W/cm²) reaction mixture (pH $\approx$ 10). The

pH of the reaction was adjusted to pH 12 by adding 4.0 M sodium hydroxide solution. The white, opaque solution was sonicated at 30 W/cm² for another 1 h. The temperature at the end of reaction was also consistently around 80 °C. The $(\text{Ce}_{0.33}\text{La}_{0.66})\text{PO}_4 \cdot n\text{H}_2\text{O}$ product was separated by centrifuge at 6300g for 10 min and washed twice in a copious amount of deionized water. Upon washing, the product, dispersed in deionized water, became translucent colloidal solution (i.e., peptization). The overall concentration of lanthanides in the reaction mixture was 0.10 M.

The reaction mixture of $(\text{Ce}_{0.33}\text{La}_{0.66})\text{PO}_4 \cdot n\text{H}_2\text{O}$ prepared at pH 1 and the separated $(\text{Ce}_{0.33}\text{La}_{0.66})\text{PO}_4 \cdot n\text{H}_2\text{O}$ product prepared at pH 12 were examined on an HD-2000 scanning transmission electron microscope (STEM, probe size $\sim$ 0.3 nm) operating at 200 kV. A Thermo Electron NORAN System SIX (Version 1.3) was used to determine the elements present in samples by energy-dispersive X-ray analysis (EDX). High resolution TEM images were taken on a Hitachi HF-2000, 200 kV scanning transmission electron microscope (STEM). The electron diffraction pattern was obtained by a Fourier transform operation. Prior to the powder X-ray diffraction (XRD) analysis, water was removed, under vacuum, from the $(\text{Ce}_{0.33}\text{La}_{0.66})\text{PO}_4 \cdot n\text{H}_2\text{O}$ sample prepared at pH 1. XRD patterns of samples obtained from reactions were recorded using a Siemens D5005 X-ray diffractometer, with a Cu anode target (K_α -ray, $\lambda = 0.154$ nm) and operating at 40 kV and 40 mA. Emission and excitation spectra of colloidal solutions were recorded on a SPEX Fluorolog spectrofluorometer, Model FL3-22, equipped with double-grating monochromators, and with a 450 W xenon lamp as the excitation source. Emission spectra were corrected for the sensitivity of the photomultiplier tube, and excitation spectra were corrected for the intensity of the xenon lamp.

3. Results and discussion

Particle sizes and morphology of the as-synthesized cerium-doped lanthanum phosphate, $(\text{Ce}_{0.33}\text{La}_{0.66})\text{PO}_4 \cdot n\text{H}_2\text{O}$, were analyzed by transmission electron microscopy (TEM). The particle morphology was highly pH dependent. From an acidic reaction condition (pH 1), thin nanorods of 5 to 9 nm diameter and several tens to several hundreds of nanometer length were observed (Fig. 1). As a control experiment, $(\text{Ce}_{0.33}\text{La}_{0.66})\text{PO}_4 \cdot n\text{H}_2\text{O}$ was also prepared under conditions (Section 2, pH 1) identical except that the reaction mixture was heated at 90 °C, instead of being sonicated at 30 W/cm². Figs. 2a and 2b are low-magnification, dark-field TEM images of the reaction mixture from the control experiment after 1 and 3 h reaction times, respectively. Mixtures of nanorods and nanoparticles were observed at both time intervals. This provided an evidence of the superior control of particle growth and morphology by ultrasonication, especially within a short reaction time, than that of the regular heating method. It is also important to clarify that each of the

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