Journal of Solid State Chemistry 182 (2009) 339–347

Contents lists available at ScienceDirect

Journal of Solid State Chemistry

journal homepage: www.elsevier.com/locate/jssc

Facile sonochemical synthesis and photoluminescent properties of lanthanide orthophosphate nanoparticles

Cuicui Yu [a,b], Min Yu [a,b], Chunxia Li [a], Xiaoming Liu [a], Jun Yang [a], Piaoping Yang [a], Jun Lin [a,*]

[a] *State Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, PR China*
[b] *Department of Chemistry, Northeast Normal University, Changchun 130024, PR China*

ARTICLE INFO

Article history:
Received 19 June 2008
Received in revised form
14 October 2008
Accepted 19 October 2008
Available online 5 November 2008

Keywords:
Lanthanide orthophosphate
Ultrasonic irradiation
Nanoparticles
Formation mechanism
Luminescence

ABSTRACT

Uniform lanthanide orthophosphate $LnPO_4$ (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho) nanoparticles have been systematically synthesized via a facile, fast, efficient ultrasonic irradiation of inorganic salt aqueous solution under ambient conditions without any surfactant or template. X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), selected area electron diffraction (SAED), photoluminescence (PL) spectra as well as kinetic decays were employed to characterize the samples. The SEM and the TEM images show that the hexagonal structured lanthanide orthophosphate $LnPO_4$ (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd) products have nanorod bundles morphology, while the tetragonal $LnPO_4$ (Ln = Tb, Dy, Ho) samples prepared under the same experimental conditions are composed of nanoparticles. HRTEM micrographs and SAED results prove that these nanostructures are polycrystalline in nature. The possible formation mechanism for $LnPO_4$ (Ln = La–Gd) nanorod bundles is proposed. Eu^{3+}-doped $LaPO_4$ and Tb^{3+}-doped $CePO_4$ samples were also prepared by using the same synthetic process, which exhibit an orange–red (Eu^{3+}:$^5D_0$–$^7F_{1,2,3,4}$) and green (Tb^{3+}, $^5D_4$–$^7F_{3,4,5,6}$) emission, respectively.

1. Introduction

Nanostructures which have received a well-designed composition and crystal structure can exhibit many interesting novel size- and shape-dependent properties, as well as their unique applications [1–5]. The generation of such small structures is essential to the advance of many areas of modern science and technology, and a number of physical- and chemical-based synthetic methodologies have been developed [6–12]. The synthesis of nanoparticles with well-controlled shapes, sizes, and structures is both scientifically and technically important. So far, much effort has been devoted to the fabrication of nanomaterials with unique shapes, such as ZnO doughnuts [13], CuO flowers [14], NiS with urchin-like nanostructures [15], dendritic micro-pines of magnetic Fe_2O_3 [16], ZnO cup [17], etc. However, they often suffer from the requirements of high temperature, special conditions, tedious procedures, and catalysts or templates. Thus, further explorations of novel morphology of inorganic materials by convenient synthesis methods with low synthesis temperature, cost-effective and less-complicated features are still a big challenge.

Recently, there has been an increased interest and research for lanthanide compounds, including LnF_3, Ln_2O_3, $Ln(OH)_3$, and $LnPO_4$ [18,19]. Among the large number of lanthanide inorganic salts, lanthanide phosphates are widely used as luminescent or laser materials, heat-resistant materials, and hosts for radioactive nuclear waste [20–24]. So far various $LnPO_4$ nanostructures, including redispersible $LnPO_4$ nanoparticles and $LnPO_4$ nanowires/nanorods of some highly polymorphs, have been synthesized [21–26]. Lanthanide orthophosphates have several polymorphic forms. They appear in hexagonal, tetragonal, and monoclinic modifications. The hexagonal structure is the low-temperature phase, and it can transform into the monoclinic structure, while the tetragonal structure is stable after calcinations at 900 °C [27,28]. Very recently, much progress has been made to notably increase the luminescent properties of lanthanide compound nanostructures and lanthanide-doped nanoparticles [29], particularly the pioneering research by Haase and coworkers on the lanthanide-doped $LnPO_4$ ($LnPO_4$:Ln^{3+}) nanoparticles [20,30]. Furthermore, Ce^{3+} and Tb^{3+} coactivated bulk $LaPO_4$ is a highly efficient and commercially applied green ($^5D_4$–$^7F_5$ of Tb^{3+} at 543 nm) phosphor in fluorescent lamps [31,32]. Up to now, most lanthanide phosphate nanomaterials with various 1D structures, such as nanorods, nanowires and nanocables, are prepared by hydrothermal or modified hydrothermal methods such as the hydrothermal microemulsion method and polymer-assisted hydrothermal methods [25,26,33]. However, to monitor

---

* Corresponding author. Fax: +86 431 5698041.
E-mail address: jlin@ciac.jl.cn (J. Lin).

0022-4596/$ - see front matter © 2008 Elsevier Inc. All rights reserved.
doi:10.1016/j.jssc.2008.10.023

the reactions taking place under extreme conditions in an autoclave is practically difficult and inconvenient. Therefore, an easy, efficient and general method needs to be developed for fabricating large number of nanostructured $LnPO_4$ materials.

The sonochemical process, which is simple and operated under ambient conditions, has been proved to be an available technique to obtain novel materials and prepare nanomaterials with unique morphology and unusual properties. During the sonication process, propagation of pressure waves is intense enough to make the formation, growth and implosive collapse of bubbles in liquid medium [34]. These bubbles generate a localized hotspot, which has the extreme high temperatures (>5000 K), pressures (>20 MPa), and cooling rates ($10^{10}\,K\,s^{-1}$) during acoustic cavitation. As a result, the sonication provides an ideal atmosphere for the preparation of nanomaterials. The advantages of this method include a rapid reaction rate, the controllable reaction conditions, and the ability to form materials with uniform shapes, narrow size distributions, and high purities. Here in this paper, we report the preparation of lanthanide orthophosphate $LnPO_4$ (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho) nanoparticles via a facile, fast, efficient ultrasonic irradiation of inorganic salt aqueous solution under ambient conditions without any surfactant or template. The structure, formation mechanism and photoluminescence (PL) properties ($LaPO_4:Eu^{3+}$ and $CePO_4:Tb^{3+}$) for these nanostructures are investigated in detail.

2. Experimental

2.1. Synthesis

All chemicals were of analytical grade, including Ln_2O_3 (Ln = La, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb, Lu), Pr_6O_{11} and Tb_4O_7 (all 99.99%) as well as $Ce(NO_3)_3 \cdot 6H_2O$ were purchased from Science and Technology Parent Company of Changchun Institute of Applied Chemistry. H_3PO_4 (Beijing Chemical Reagent Company). $Ln(NO_3)_3$ precursors were prepared by dissolving the corresponding lanthanide oxides in a diluted nitric acid solution, and the water in the solutions was evaporated by heating. In a typical synthesis, 23 mL of an aqueous solution of $Ln(NO_3)_3$ (2.3 mmol) was added to a diluted H_3PO_4 (30 mL, 11.5 mmol) solution under ultrasonic irradiation for 1 h. The pH value of the mixture was kept at 1–2. Ultrasonic irradiation was accomplished with a high-intensity ultrasonic probe (JCS-206 Jining Co. China, Ti horn, 100 W) immersed directly in the reaction solution. At the end of the sonication, a temperature of about 343 K was reached under ambient air without cooling. The resulting $LnPO_4$ precipitates were then centrifuged, washed with deionized water and absolute ethanol several times, and then dried in a vacuum at 333 K for 12 h for further characterization. $LaPO_4:Eu^{3+}$ and $CePO_4:Tb^{3+}$ samples were prepared in the similar way as that for pure $LnPO_4$. The doping concentration of Eu^{3+} (or Tb^{3+}) is 5 mol% of Ln^{3+} in $LaPO_4$ (or $CePO_4$) host.

2.2. Characterization

The XRD pattern was performed on a Rigaku-Dmax 2500 diffractometer at a scanning rate of 12°/min in the 2θ range from 10° to 70°, with graphite monochromatized Cu$K\alpha$ radiation ($\lambda = 0.15405$ nm). SEM micrographs were obtained using a field emission scanning electron microscope (FE-SEM, XL30, Philips). The morphology, particle size and crystalline phases were studied with the transmission electron microscopy (TEM). The TEM, high-resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) pictures were recorded on a JEOL 2010 transmission electron microscope, using an accelerating voltage of 200 kV. The samples for TEM were prepared by dispersing the diluted suspension of the sample powder onto a carbon coated copper grid and then the grid was put at room temperature for several days. The PL excitation and emission spectra were recorded with a Hitachi F-4500 spectrophotometer equipped with a 150 W Xenon lamp as the excitation source. The luminescence decay curves were obtained from a Lecroy Wave Runner 6100 Digital Oscilloscope (1 GHz) using a 250 nm lasers (pulse width = 4 ns, gate = 50 ns) as the excitation. All the measurements were performed at room temperature.

3. Results and discussion

3.1. Formation, structure and morphology

Under the identical synthetic conditions (ultrasonic irradiation for 1 h), two different types of crystal structure of the $LnPO_4$ products have been identified by XRD analyzes. The XRD patterns of as-obtained hexagonal $LnPO_4$ (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd) and tetragonal $LnPO_4$ (Ln = Tb, Dy, Ho) samples are shown in Fig. 1(a) and (b), respectively. Fig. 1a shows that all the reflection patterns can be readily indexed to a pure hexagonal phase [space group $P6_222$ (180)] for $LnPO_4$ (Ln = La → Gd) samples. The diffraction peaks shown in Fig. 1b are characteristic of a pure tetragonal phase [space group: $I4_1/amd$ (141)] for $LnPO_4$ (Ln = Tb → Ho) samples (JCPDS 32-1292 for $TbPO_4$ as a reference). The cell parameters of all the as-formed lanthanides orthophosphates are listed in Table 1. It can be seen from Fig. 1 that no other impurities can be detected in the synthesized products. Moreover, careful observation reveals that a systematic shift to the smaller d values (or higher 2θ degrees) for the diffraction peaks

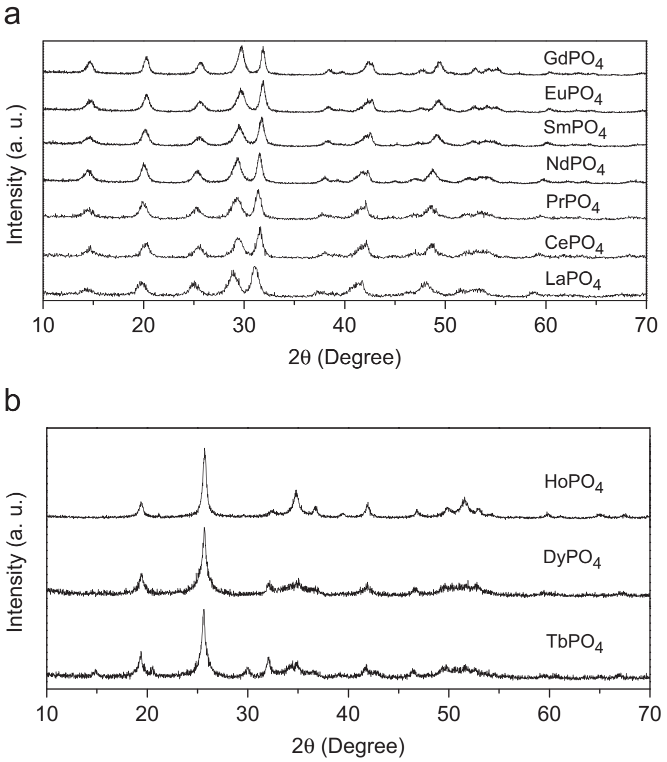

Fig. 1. XRD patterns of the as-prepared lanthanide phosphates (a) hexagonal $(La \rightarrow Gd)PO_4$, (b) tetragonal $(Tb \rightarrow Ho)PO_4$ nanoparticles.