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Microwave-assisted hydrothermal synthesis of $CePO_4$ nanostructures: Correlation between the structural and optical properties

D. Palma-Ramírez [a], M.A. Domínguez-Crespo [a,*], A.M. Torres-Huerta [a], H. Dorantes-Rosales [b], E. Ramírez-Meneses [c], E. Rodríguez [a]

[a] Instituto Politécnico Nacional, CICATA-Unidad Altamira, Km 14.5, Carretera Tampico-Puerto Industrial Altamira, C.P. 89600 Altamira, Tamps, Mexico
[b] Instituto Politécnico Nacional, ESIQIE, Departamento de Metalurgia, C.P. 07300 México D.F., Mexico
[c] Universidad Iberoamericana, Departamento de Ingeniería y Ciencias Químicas, Prolongación Paseo de la Reforma 880, Lomas de Santa Fe, C.P. 01219 México D.F., Mexico

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ABSTRACT

In this work, the microwave-assisted hydrothermal method is proposed as an alternative to the synthesis of cerium phosphate ($CePO_4$) nanostructures to evaluate the influence of different synthesis parameters on both the structural and optical properties. In order to reach this goal, two different sets of experiments were designed, varying the reaction temperature (130 and 180 °C), synthesis time (15 and 30 min) and sintering temperature (400 and 600 °C), maintaining a constant pH = 3. Thereafter, two experimental conditions were selected to assess changes in the properties of $CePO_4$ nanopowders with pH (1, 5, 9 and 11). The crystal structure and morphology of the nanostructures were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM) and scanning electron microscopy (SEM), respectively. Diffuse reflectance properties of $CePO_4$ with different microstructures were studied. The results demonstrated that by using the microwave-assisted hydrothermal method, the shape, size and structural phase of $CePO_4$ can be modulated by using relatively low synthesis temperatures and short reaction times, and depending on pH, a sintering process is not needed to obtain either a desired phase or size. Under the selected experimental conditions, the materials underwent an evolution from nanorods to semispherical nanoparticles, accompanied by a phase transition from hexagonal to monoclinic.

1. Introduction

In recent years, $CePO_4$ nanostructures have become increasingly important in a variety of applications such as fluorescence, ion exchange, catalytic materials and ceramic composite materials with high mechanical properties [1] as a result of their low dimensionality and the quantum confinement effect. The technological application of these nanostructured materials is strongly dependent on their morphology, crystalline phase and particle size. $CePO_4$ presents two phases: monoclinic and hexagonal [2,3]. Few studies on the production of $CePO_4$ nanostructured materials have been found in the literature. The hexagonal phase can be easily obtained at low temperatures, while the monoclinic phase could be prepared via the solid state reaction and hydrothermal method at high temperatures [2]. Among these methods, the hydrothermal synthesis seems to be potentially useful to obtain $CePO_4$ nanostructures; the preparation of inorganic nano or micromaterials by this technique features advantages such as the use of simple equipment, low cost, high-uniform area production, low process temperatures, catalyst-free growth, environmental friendliness and very-easy-to-control particle sizes; however, it usually requires long reaction times (about 24 h) to reach the nanoscale [3,4]. As an enhancement of the typical hydrothermal method, the microwave-assisted route has the advantage of producing nanostructures with shorter synthesis times as a consequence of the efficient and fast heating during the reaction process [5]. Particularly for $CePO_4$, Ekthammathat et al. [6] have reported that monoclinic nanorods can be synthesized from $Ce(NO_3)_3{\cdot}6H_2O$ and $Na_3PO_4{\cdot}12H_2O$ at pH 1 by a simple microwave radiation for 60 min, while Patra and coworkers [7] obtained rhabdophane-type hexagonal nanorods by the microwave-assisted solvothermal synthesis, using a domestic microwave oven.

To the best of our knowledge, there have been few published studies related to the synthesis of $CePO_4$ nanostructures using microwave energy. The aim of this work is to determine the effects of the synthesis parameters on the structural, morphological and optical properties of $CePO_4$ nanostructures produced by the

* Corresponding author.
E-mail address: mdominguezc@ipn.mx (M.A. Domínguez-Crespo).

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Table 1
Experimental design used to obtain $CePO_4$ nanoparticles using a pH ~3.

Experiment at pH ~3	Reaction temperature (T_r, °C)	Synthesis time (t, min)	Sintering temperature (T_s, °C)
1	130	15	400
2	180	15	400
3	130	30	400
4	180	30	400
5	130	15	600
6	180	15	600
7	130	30	600
8	180	30	600

microwave-assisted hydrothermal method. For this purpose, variables such as reaction time, synthesis and sintering temperature as well as pH of the media have been evaluated.

2. Experimental details

2.1. Preparation of $CePO_4$ nanostructures

Tripolyphosphoric acid solution (0.035 mol^{-1}, $H_5P_3O_{10}$) was obtained by using a cation exchange resin (Dowex 50W X4 100-200 mesh) for conversion of sodium tripolyphosphate, $Na_5P_3O_{10}{\cdot}5H_2O$ (purum p.a., ⩾98.0% (T), Sigma–Aldrich).

$CePO_4$ nanostructures were synthesized by mixing $Ce(NO_3)_3{\cdot}6H_2O$ (0.10 mol) (Sigma–Aldrich, 99% trace metals basis) and $H_5P_3O_{10}$ (0.10 mol). The microwave reaction was performed in a microwave oven (CEM-MARS, frequency 2.45 GHz, power of 200 W). The synthesis process was as follows: 50 ml of $Ce(NO_3)_3{\cdot}6H_2O$ were added dropwise to 25 ml of $H_5P_3O_{10}$ under stirring; then, deionized water was added to adjust a final volume of 100 ml at pH ~3. Thereafter, solutions were transferred into a Teflon container (autoclave). The autoclave was sealed and heated for each experiment by varying both the synthesis temperature (130 and 180 °C) and time (15 and 30 min). Subsequently, the precipitate was separated by filtration and dried for 24 h at 90 °C and sintered at two different temperatures (see Table 1).

From these initial experiments, the synthesis conditions of the samples labeled as 7 and 8 were chosen to evaluate changes in the morphology and particle size of $CePO_4$ nanopowders at different pH values. These effects were analyzed at pH = 1, 5, 9, and 11. HNO_3 (37%) and NH_4OH (30%) were used to adjust the pH values either in alkaline or acid medium.

2.2. Characterization of nanopowders

The structure of the $CePO_4$ nanoparticles was determined by X-ray powder diffraction (XRD) with a Bruker D8 Advance diffractometer equipped with a Lynxeye detector and Cu K_α radiation (λ = 1.5405 Å) at 35 kV and 25 mA. Data were collected at room temperature in the 2θ range of 15–70°, step size of 0.016 and step time of 0.5 s. To evaluate the effects of the reaction parameters and sintering temperature on the structural and vibrational properties of $CePO_4$, Fourier transform infrared spectroscopy (FTIR) was carried out. The spectra were recorded on a Perkin Elmer spectrometer using KBr pellets, 4 cm^{-1} of resolution setting and range of 1300–450 cm^{-1}. The samples were scanned 40 times. Scanning electron microscopy was used to evaluate morphological changes in the $CePO_4$ nanopowders using a JEOL JSM-6300 apparatus (20 kV), whereas transmission electron microscopy was used to corroborate the structure and phase composition of the samples by using a JEOL-2000 FX-II working at an accelerating voltage of 100 kV. The analysis of the average particle size and size distribution were determined by dynamic light scattering, using deionized water as dispersant medium in a Malver Zetasizer Nano ZSP, model ZEN5600. The particle size of the dispersions was described by the cumulants mean diameter, and the size distribution was described by the polydispersity index and the size distribution plot. The optical properties of the samples were followed by ultraviolet–visible diffuse reflectance spectroscopy (UV–Vis DR) using a 110-mm-diameter-integrating-sphere accessory mounted on a Cary 5000

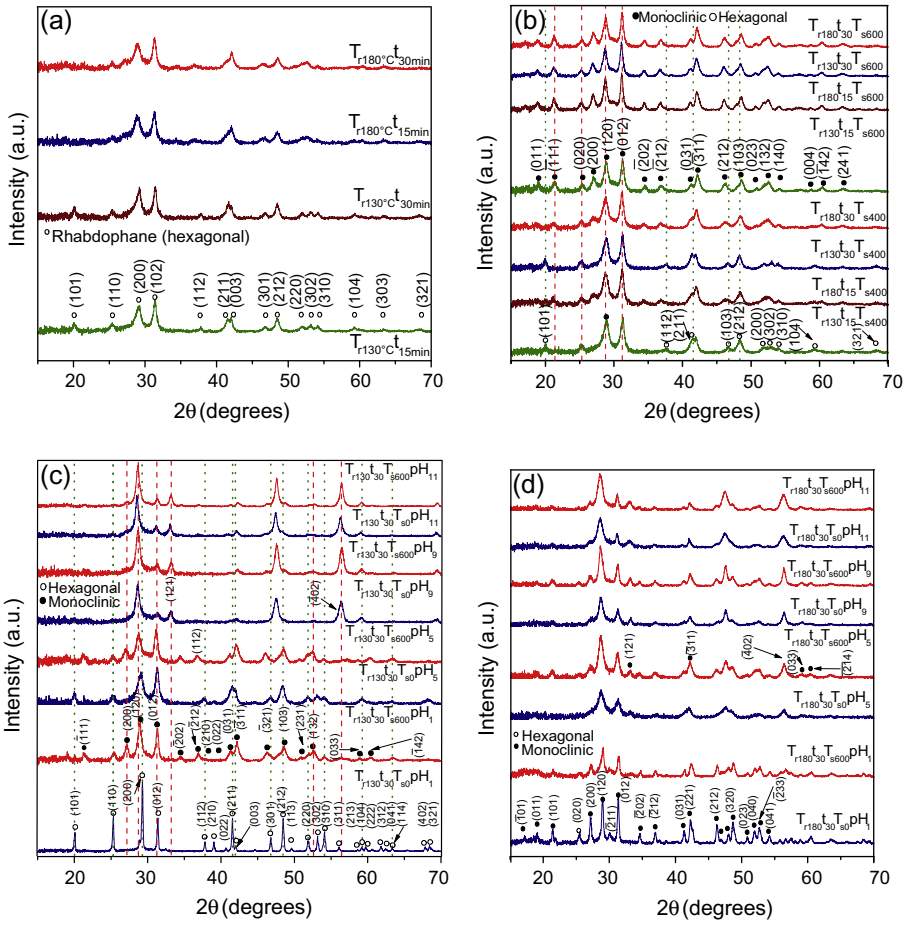

Fig. 1. X-ray diffraction patterns of (a) non-sintered $CePO_4$ powders obtained under the stated conditions, (b) $CePO_4$ nanoparticles sintered at two different temperatures (400 and 600 °C), (c) samples synthesized under experiment 7 conditions at different solution pH values and (d) samples synthesized under experiment 8 conditions at different solution pH values.