



# Cerous phosphate gels: Synthesis, thermal decomposition and hydrothermal crystallization paths



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## ABSTRACT

Since their discovery in the late 19th century, cerium (IV) phosphates have been a very poorly studied class of rare earth compounds. In this paper, a facile method of amorphous cerous phosphate gels preparation is proposed, starting from nanocrystalline ceria and allowing for large-scale synthesis of these compounds. The use of this method provides deeper insight into the chemical composition and structure of cerous phosphate gels, and enables the peculiarities of their crystallization under hydrothermal conditions in H<sub>2</sub>O and H<sub>3</sub>PO<sub>4</sub> aqueous solutions to be traced. Only Ce<sup>+3</sup> compounds crystallize in a neutral medium if they are present in the composition of the cerous phosphate gels. For Ce<sup>+4</sup> compounds to crystallize, a significant amount of orthophosphoric acid should exist in a reaction mixture. These features are likely to be related to the fact that crystalline Ce<sup>+4</sup> orthophosphates can only exist in the form of acid salts.

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## 1. Introduction

Rare earth elements (REE) compounds are widely used in various high-tech applications, such as the production of lasers, catalysts and permanent magnets [1]. Trivalent REE orthophosphates are among the most extensively studied REE compounds [2–7]. They are of interest as X-ray and gamma-ray scintillators, thermophosphors for remote temperature measurements, biomaterial hosts, and so on [8–11]. Orthophosphates of REEs having another oxidation state (+4) are only known for cerium, and even these compounds are still poorly studied, despite the fact that cerium is one of the most widespread REEs. Tetravalent cerium is thought not to form individual neutral orthophosphates [12], and Ce<sup>+4</sup> hydroorthophosphates are typically amorphous substances of variable composition. Nevertheless, the formation of crystalline Ce<sup>+4</sup> hydroorthophosphates was recently reported by Nazaryal et al. [13,14]. Possible practical applications of such compounds were discussed earlier. For instance, Alberti et al. [15] have reported high ion exchangeability of cerous phosphates, Barboux et al. [16] have described their noticeable proton conductivity. Nazaryal et al. [13,14] have indicated the possible use of cerous phosphates as sorbents and heterogeneous catalysts.

Ce<sup>+4</sup> hydroorthophosphates were first synthesized as yellow, gel-like substances by Hartley [17] as early as 1882. The synthetic procedure

comprised the interaction of cerium (III) nitrate with sodium phosphate taken in various molar ratios. In 1968, Larsen and Cilley [18] synthesized the same compounds by the interaction of (NH<sub>4</sub>)<sub>2</sub>[Ce(NO<sub>3</sub>)<sub>6</sub>] with orthophosphoric acid. Larsen and Cilley also found that Ce<sup>+4</sup> phosphates are cation-exchange materials that can exchange hydroxonium ions for alkali metal ions (Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>). The systematic studies of PO<sub>4</sub><sup>3-</sup>/Ce<sup>+4</sup> system [15] allowed the following four different Ce<sup>+4</sup> orthophosphates to be separated: amorphous cerium orthophosphate with the molar ratio P:Ce ~ 1.7, cerium orthophosphate with P:Ce ~ 1.15 containing up to ~7% of sulfate ions, cerium orthophosphate with P:Ce = 1.5, and fibrous cerium orthophosphate (suggested composition is Ce(HPO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O). The last compound was then investigated thoroughly by Barboux et al. [16]. Starting from cerium (+4) orthophosphate solutions, Herman and Clearfield [19] also prepared several gel-like fibrous substances with the following compositions: Ce(OH)<sub>x</sub>(PO<sub>4</sub>)<sub>x</sub>(HPO<sub>4</sub>)<sub>2-2x</sub>·yH<sub>2</sub>O, Ce(HPO<sub>4</sub>)<sub>2</sub>·xH<sub>2</sub>O, and Ce(OH)<sub>0.7</sub>(PO<sub>4</sub>)<sub>1.1</sub>. In turn, Rajesh et al. [20] synthesized cerium phosphate gel by the interaction of cerium (III) nitrate and orthophosphoric acid in an ammonia atmosphere. Using thermal analysis data only, they wrote the overall gel composition as CePO<sub>4</sub>·H<sub>2</sub>O. Based on the data presented, we can conclude that the composition and the structure of amorphous Ce<sup>+4</sup> hydroorthophosphates are still poorly understood.

Hydrothermal treatment of Ce<sup>+4</sup> hydroorthophosphate gels can result in their crystallization. For example, Nazaryal et al. [13,14] were the first to succeed in the preparation of crystalline Ce<sup>+4</sup> hydroorthophosphate, Ce(PO<sub>4</sub>)(HPO<sub>4</sub>)<sub>0.5</sub>(H<sub>2</sub>O)<sub>0.5</sub>, by hydrothermal

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treatment of a cerium dioxide solution in orthophosphoric acid. They also solved the structure of this compound: it has a monoclinic system and possesses a layered structure (space group C2/c; unit cell parameters  $a = 21.0142(3) \text{ \AA}$ ,  $b = 6.55082(7) \text{ \AA}$ ,  $c = 6.94382(6) \text{ \AA}$ ,  $\beta = 91.983(1)^\circ$ ,  $V = 955.32(2) \text{ \AA}^3$ ). Note that a substance of the same composition was also synthesized by Brandel et al. [21]. In turn, Yang et al. [22] hydrothermally synthesized a crystalline  $\text{Ce}^{+4}$  hydroorthophosphate of the  $\text{Ce}(\text{H}_2\text{O})(\text{PO}_4)_{3/2}(\text{H}_3\text{O})_{1/2}(\text{H}_2\text{O})_{1/2}$  composition (monoclinic system also, unit cell parameters  $a = 15.706(2) \text{ \AA}$ ,  $b = 9.6261(9) \text{ \AA}$ ,  $c = 10.1632(4) \text{ \AA}$ ,  $\beta = 121.623(7)^\circ$ ). With the hydrothermal treatment duration increased, this compound transformed into rhabdophane ( $\text{CePO}_4 \cdot x\text{H}_2\text{O}$ ). Yang et al. [22] attributed this unexpected change in the valence state of cerium ( $\text{Ce}^{+4} \rightarrow \text{Ce}^{+3}$ ) to the presence of organic admixtures, which can act as reducing agents under hydrothermal conditions.

This short review contains almost all experimental data on amorphous and crystalline  $\text{Ce}^{+4}$  orthophosphates published in more than a century. In this paper, we propose a facile and versatile method of cerous phosphate gels synthesis, starting from nanocrystalline ceria and allowing for large-scale synthesis of these compounds. The use of this method has enabled us to gain a deeper insight into the chemical composition and the structure of cerous phosphate gels, and to trace the peculiarities of their crystallization under hydrothermal conditions.

## 2. Experimental

### 2.1. Starting materials

The following substances were used as received without further purification:  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (99%, Aldrich #238538), orthophosphoric acid (85 wt.% aq., analytical grade, Khimmed Russia),  $\text{Ce}_2(\text{CO}_3)_3 \cdot x\text{H}_2\text{O}$  (Aldrich #325503), nitric acid (65 wt.% aq., extra-pure grade, Khimmed Russia), aqueous ammonia (25 wt.%, extra-pure grade, Khimmed Russia), isopropanol (extra-pure grade, Khimmed Russia), distilled or deionized (18 M $\Omega$ ) water.

### 2.2. Materials synthesis

To synthesize amorphous cerous phosphate gels, we developed a new method, based on the dissolution of nanocrystalline ceria (particle size of 5 nm, synthesized by precipitation from 0.08 M cerium(III) nitrate, according to Ivanov et al. [23]) in excess of hot (100 °C), concentrated orthophosphoric acid. In preliminary experiments, we also used coarser  $\text{CeO}_2$  samples (7 nm, synthesized as described by Baranchikov et al. [24]; 15 nm, prepared *via* thermolysis of  $\text{Ce}_2(\text{CO}_3)_3 \cdot x\text{H}_2\text{O}$  at 700 °C for 1 h). In a typical dissolution experiment, 0.10 g (on anhydrous basis) of  $\text{CeO}_2$  powder was added to the 5 ml of 85 wt.%  $\text{H}_3\text{PO}_4$  solution preheated to 100 °C. Then the system was mixed for 20 min at 100 °C until the complete dissolution of  $\text{CeO}_2$  and then cooled to ambient temperature (the cerium concentration in the resulting solution was 0.12 M). Then deionized water was added to the solution dropwise under stirring. Upon the addition of water, gradual formation of gel-like precipitates was observed. Thus to obtain gels water was added to the solutions up to 1:27  $\text{H}_3\text{PO}_4$ : $\text{H}_2\text{O}$  molar ratio. To purify the gels from orthophosphoric acid, they were dialyzed against deionized water for 1–2 weeks, with periodic changes of water. Dialysis was performed using Pur-A-Lyzer™ Mega Dialysis Kit (3.5 kDa). The final electrical conductivity of the mother liquor was less than 0.01 mS. After the dialysis the gels were dried in air at 50 °C overnight.

Hydrothermal treatment of the initial gels (containing residual orthophosphoric acid) and the dialyzed gels redispersed in deionized water or in a 1 wt.%  $\text{H}_3\text{PO}_4$  aqueous solution was performed using a Berghof Speedwave MWS 4 microwave system. We used microwave heating to minimize the duration of the non-isothermal heating stage and to provide the most homogeneous heating of reaction mixtures. The initial or redispersed gels were placed in Berghof DAP-100 100 ml

Teflon autoclaves (filling coefficient of 40%) and treated hydrothermally at 120 °C, 140 °C, 155 °C, 170 °C, 180 °C or 220 °C for 1 h. In each case, the heating rate was 30 °C/min, relative microwave power 60%. After hydrothermal-microwave treatment autoclaves were cooled in air, the precipitates were decanted, washed with distilled water until neutral pH and dried in air at 50 °C overnight.

### 2.3. Methods of analysis

To determine the valence state of cerium in cerous phosphate solutions, differential spectrophotometry was used [25]. This direct method has a high sensitivity in determining  $\text{Ce}^{+3}$  and  $\text{Ce}^{+4}$  in aqueous media, and allows detecting  $\geq 2 \mu\text{g/l}$   $\text{Ce}^{+3}$  in the presence of 8-fold excess of  $\text{Ce}^{+4}$  [26]. UV-vis spectra were registered using a Cary 5000 UV-Vis-NIR spectrometer. All measurements were performed at ambient temperature. The recorded spectra were treated as proposed by Stoyanov et al. [26].

X-ray powder diffraction patterns were recorded with a Bruker D8 Advance or Rigaku D/MAX 2500 diffractometers using  $\text{CuK}\alpha$  radiation in the  $2\theta$  range 3–120° at a  $2\theta$  step of 0.01–0.02° and a counting time of 0.3–0.5 s per step. An analysis of the initial wet gels containing orthophosphoric acid was performed using a Bruker D8 Advance diffractometer with a horizontal goniometer axis. The gels were placed into the deepening of a plastic sample holder and their surfaces were levelled using a glass slide. The excess liquid was carefully removed with filtering paper. Full-profile analysis of the X-ray diffraction patterns of crystalline substances was performed using JANA2006 [27] and TOPAS 4.2 software. Fourth-order Chebyshev polynomials were used to fit the background. The overall fitting was performed using the fundamental parameter approach. The weighted profile residuals ( $R_{wp}$ ) were from 3 to 6.

The structure (scanning electron microscopy, SEM) and the chemical composition (energy dispersive X-ray analysis, EDX) of the samples were analyzed on a Carl Zeiss NVision 40 high-resolution scanning electron microscope equipped with an Oxford Instruments X-MAX (80 mm<sup>2</sup>) detector, and operating at an accelerating voltage of 1–20 kV. SEM images were taken with an Everhart-Thornley detector (SE2).

The structure of the samples was additionally studied by means of transmission electron microscopy (TEM) with a Carl Zeiss Libra 200MC analytical transmission electron microscope with a field emission gun and a corrected Omega energy filter. TEM images were taken at an accelerating voltage of 200 kV in the bright-field mode.

Thermal analysis was performed on a simultaneous TGA/DSC/DTA SDT Q-600 analyzer (TA Instruments) upon linear heating to 1200 °C (heating rate of 10 °C/min) or 1400 °C (20 °C/min) in a 100 ml/min air-flow. Mass-spectroscopic analysis of the gases evolved during thermolysis was performed using a Netzsch TG 209 F1 thermal analyzer equipped with a Netzsch 403 C Aeolos quadrupole mass spectrometer upon linear heating to 950 °C in argon at a heating rate of 10 °C/min.

## 3. Results and discussion

To obtain initial cerous phosphate solutions, nanodispersed cerium dioxide was dissolved in hot 85% orthophosphoric acid. It is known that, when orthophosphoric acid is heated, oligophosphoric acids can form [28]. To find out whether this actually takes place we have performed gravimetric analysis [29] (precipitation of orthophosphate with ammonium molybdate in the presence of nitric acid) of two solutions, solution 1 and solution 2 (both without adding  $\text{CeO}_2$ ). Solution 1 containing only 85%  $\text{H}_3\text{PO}_4$  was heated at 100 °C for 1 h. Solution 2 was prepared by mixing 85%  $\text{H}_3\text{PO}_4$  and 65%  $\text{HNO}_3$  (the  $\text{H}_3\text{PO}_4$ : $\text{HNO}_3$  molar ratio was chosen to be equal to described in [29]) followed by heating at 100 °C for 1 h. Nitric acid was added to solution 2 to initiate the transformation of oligophosphoric acids, which could exist in the solution, into orthophosphoric acid. A comparative analysis of the orthophosphate

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