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Modified Pechini synthesis of La, Ce, and Pr orthophosphates and characterization of obtained powders

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Abstract In this study, lanthanum, cerium, and praseodymium orthophosphates were synthesized by the modified Pechini method. The compounds were analyzed using XRD, TG/DSC, FTIR methods, and the isothermal nitrogen adsorption technique. The results showed that mesoporous and nanocrystalline powders can be synthesized by this method. Moreover, due to the limited formation of lanthanide polyphosphates on the surface of the powders the modified Pechini method allows better control of the compound stoichiometry in comparison with the commonly used method of phosphates precipitation from solutions rich in H_3PO_4.

Keywords Rare-earth phosphate · Modified Pechini synthesis · TG/DSC · X-ray diffraction

Introduction

In recent years many papers on obtaining light rare-earth element orthophosphates (of both monazite and rhabdophane types) have been published. Monazite is a thermodynamically stable form of $LnPO_4$, forming in the Ln_2O_3–P_2O_5 system (where *Ln* is La–Gd) at 1:1 mole ratio [1, 2]. It is also possible to obtain the monazite structure of Tb and Dy orthophosphates; however, it is assumed to be thermodynamically metastable [3]. Rhabdophane has a hexagonal structure and is obtained through precipitation from aqueous lanthanide salt solutions in the presence of PO_4^{3-} anions. Rhabdophane is a hydrated form of $LnPO_4$, which according to literature reports contains 0.5–1.5 of water molecule per 1 mol of the compound [1–4]. As rhabdophane is heated first the water is lost (at a temperature of about 600 °C) and then a polymorphic change takes place and an orthophosphate with a monoclinic structure, i.e., monazite, forms.

The great interest in lanthanide orthophosphates is due to its special physicochemical properties. Research on monoclinic $CePO_4$ shows that it is characterized by very slight chemical reactivity toward both dilute and concentrated oxoacids, hydracids, bases, by low thermal conductivity and a very high melting point (2045–2072 °C) [5, 6]. Owing to their properties monazites can be used as high temperature barrier coatings or components of special purpose ceramics [7–12]. Its very slight chemical reactivity, water-insolubility, and the possibility of substituting a radioactive element (Th, U) for the lanthanide make monazite a promising matrix material for immobilizing radioactive waste [13–16]. The large number of publications on methods of obtaining lanthanide orthophosphates is also due to the latter's optical properties, such as luminescence in different spectral ranges and selective radiation absorption in the visible, ultraviolet, and infrared light (lasers safe to the human eye and UV screens). The Ce and La orthophosphates doped with Sr show protonic conductivity whereby they can be used as an electrolyte in sensor technologies or fuel cells [17, 18].

The development of the existing and new technologies in catalysis, power industry, optical, and sensor systems spurs a search for materials with specific physicochemical properties. Such properties are obtained by designing new compounds with a specific crystal structure and an atypical chemical composition, by modifying the useful properties of the known phases by introducing specific dopes or by

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synthesizing nanomaterials. However, the phases produced by the different methods do not show the intended properties even though the specified chemical composition, structure, and crystallite size have been obtained. A major factor here is the methods of synthesis used and more precisely, the degree of phase purity and homogeneity of the samples, its morphology, the type, and amount of the impurities [19–21].

In the production of nanocrystallites, it is a common practice to lower the temperature of the synthesis whereby their excessive growth is prevented. Also care is taken to maintain a high degree of powder homogeneity, especially when doped multicomponent phases are to be obtained. Such possibilities are offered by methods employing solutions from which sparingly soluble phases are precipitated. In order to increase the rate of powders synthesis and at the same time to improve their chemical homogeneity and morphology the initial solutions are heated up under elevated pressure (hydrothermal methods) or subjected to ultrasounds. It should be noted that despite the initially good intermixing (at the atomic level) of metal ions in the solution, the forming precipitates may undergo segregation due to even the slightest differences in the solubility of the individual compounds. As a result, it may be difficult to obtain multicomponent and doped compounds. The methods of synthesizing rare-earth orthophosphates through precipitation from solutions are very commonly used [4, 22, 23].

Nanocrystallites can also be produced by the sol–gel method using organic compounds (mainly alcoholates) or inorganic compounds (usually hydroxides). Through proper choice of reactants one can produce homogenous (in their whole volume) sols and by gelating them one can fix the high degree of preparation homogenization. The secondary reaction products (water, organic residue, ammonia, or nitrogen oxides) are removed at a temperature below 400–500 °C, which usually suffices for the phases to crystallize. Because of the high costs of the other metals alcoholates, this type of sol–gel method is usually limited to obtaining preparations rich in SiO_2, Al_2O_3, or TiO_2. For this reason it is not popular for LnPO$_4$ producing.

A derivative of the sol–gel methods is the synthesis route and patented by Pechini [24]. In this method carboxylic acids (e.g., citric acid) are used as the reagents chelating metal ions in the solution, glycols are used to gelate the preparation and prevent undesirable products from precipitating. Initially this synthesis process was used to obtain mono- and multicomponent oxide materials and was limited to solutions in which sparingly soluble salts (e.g., sulfates or phosphates) do not undergo precipitation. Owing to its good control of the stoichiometry of obtained compounds, the method is used to produce multicomponent, doped phases. Its other advantages, such as the availability of the reagents, their low toxicity, the considerable easier formation of phases at a lowered synthesis temperature, and a reduction in crystallite size, were quickly perceived, which resulted in a large number of investigations into the effect of the type of used substrates, their concentration and thermal treatment on the quality of the preparations. Nevertheless, also in the case of this method one needs to be careful when producing complex phases since the carboxylic acid salts forming in this process may easily undergo selective precipitation or decomposition, disturbing the homogeneity of the final product [25].

Here we present the research results of the low-temperature synthesis of La, Ce, and Pr orthophosphates, focusing on the effect of the method used on the quality of the obtained powders, especially the phase purity of the preparations and their morphology and microstructure. The characteristics of the polycrystalline powders produced by the Pechini method and through precipitation from solutions containing PO_4^{3-} ions are described. The quality of the obtained samples was evaluated using XRD, TG/DSC, BET, and FTIR methods. The results facilitate the choice of a proper method of synthesizing rare-earth element orthophosphates depending on the desired parameters of the powders and their intended use.

Experimental

Synthesis of LnPO$_4$

Some methods of synthesis are usually applied to obtain lanthanide phosphates with general formula LnPO$_4$. In our research the LnPO$_4$ powders, where Ln = La, Ce, Pr, were prepared by modified Pechini method. Additionally, the sample of $CePO_4$ composition was obtained by precipitation from phosphoric acid solution.

Aqueous solutions of lanthanum and cerium nitrates—$Ce(NO_3)_3 \cdot 6H_2O$ (POCh Gliwice, analytically pure), $La(NO_3)_3 \cdot 6H_2O$ (Fluka, ≥99.0%)—were chosen as the sources of lanthanide ions. The solution of praseodymium ions was prepared by dissolution of $PrCO_3OH$ (Aldrich, 99.99%) in small amount of nitric acid.

In the Pechini process adopted for synthesis of orthophosphates, the citric acid and ethylene glycol were mixed with solutions of lanthanides nitrates in the following molar ratios: citric acid: Ln^{3+}—2:1, citric acid: ethylene glycol—1:1. The obtained solutions have been heated at 80 °C under mixing until a viscous liquid obtained. Then $NH_4H_2PO_4$ in the appropriate molar ratio was added under stirring. The heating has been continued until a foam obtained, then the samples were put in electric drier for 20 h at 120 °C. Further calcination of dried gels was performed in a furnace preheated at 500 °C.

The $CePO_4$ powder was obtained by precipitation from H_3PO_4 solution (15 wt% of P_2O_5) too. After the solution has been refluxed for several hours, the obtained precipitate was filtered, several times washed by boiling deionized water and dried at 80 °C.

The final products obtained in both methods were subjected to further characterization.

Experimental conditions

Powder XRD patterns of the synthesized samples were obtained on a Siemens D5000 diffractometer using Cu Kα radiation ($\lambda = 0.154$ nm). Measurements were performed in an angle range of 2θ: 5–60° with the scanning rate of 3–6° min^{-1} (total measurement time: 3–6 h).

The phase composition of powders was also analyzed by Fourier transform infrared spectroscopy on Perkin–Elmer System 2000 (KBr pellets).

Thermal analyses were carried out using TG/DSC Setsys^{TM} 1500 (Setaram) calorimeter under flowing argon (scanning rate 10 K min^{-1}, platinum crucibles, sample weight 0.001–0.020 g) up to 1200 °C.

The surface area value and pore size distribution were determined by multipoint BET method by nitrogen adsorption using Autosorb 1, Quantachrome Autosorb Automated Gas Sorption System (Quantachrome Instruments).

Results and discussion

The XRD patterns of the samples showed only one well-crystallized phase, i.e., $LnPO_4{\cdot}nH_2O$ with a hexagonal structure, to be present. Figure 1 shows diffraction patterns of the obtained samples. As the ionic radius of lanthanide decreases, the angle of the reflections becomes larger. This is connected with the decrease in size of the elementary cell of rhabdophane, due to the difference in the size of the rare-earth elements' ionic radii, amounting to 114, 107, and 106 pm for, respectively, La^{3+}, Ce^{3+}, and Pr^{3+}. Only crystalline monazite (a monoclinic structural form of orthophosphate) was found to be present in the diffraction spectra of the samples sintered at a temperature of 900 °C for 1 h.

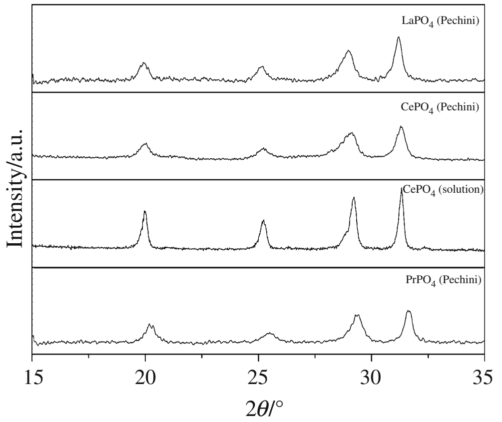

Fig. 1 The XRD patterns of $LaPO_4$, $CePO_4$, $PrPO_4$ samples prepared by Pechini route (preheated at 500 °C, 20 h) and $CePO_4$ precipitated from solution at 80 °C

In order to estimate the average size of crystallites in the prepared samples the Scherrer equation was used: $D = \frac{K\lambda}{B\cos\theta}$, where D/nm is the average crystallite size in the direction perpendicular to the (hkl) plane of a given reflection. $K = 0.9$ is the Scherrer constant [26], $\lambda = 0.154$ nm—the wavelength of radiation Cu Kα and B—the full-width at half-maximum (FWHM) of the diffraction peak at angle θ. The calculated average size of crystallites in the phases having a rhabdophane structure depend on the method of obtaining them and amount to 16 and 29 nm for, respectively, the modified Pechini method and the method of precipitating from H_3PO_4 solutions. Regardless of the rare-earth element forming the orthophosphate, the powders obtained by the modified Pechini method had the same crystallite size (15–16 nm).

An analysis of the diffraction spectra of samples sintered at 900 °C showed that the thermal treatment of the preparations results not only in a change in the structure of the orthophosphates, but also in the growth of crystallites, which reach the average size of 27 and 47 nm for, respectively, the Pechini method and the precipitation method. Thus, the crystal size increases nearly twofold in the temperature range of up to 900 °C, but it seems that the rate of crystal growth does not depend on the type of synthesis. The type of lanthanide (La, Ce, Pr) has not been found to influence the size of the obtained crystallites.

A thermal analysis of the obtained samples showed them to be hydrated to a considerable degree. Figure 2 shows typical heating TG and DSC curves for $CePO_4$ samples

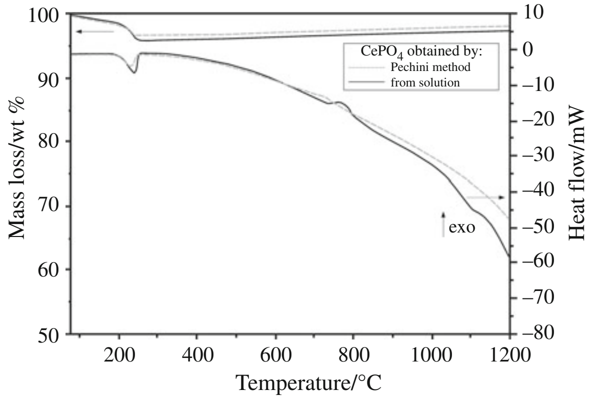

Fig. 2 The DSC/TG curves of the hydrated $CePO_4$ obtained by Pechini route (*gray*) and precipitated from H_3PO_4 solution (*black*)

obtained by the two different synthesis methods. As a result of the heating to 300 °C the mass of the samples decreases by 3.2–4.2% (the TG curve). Two endothermic effects on the DSC curve correspond to this mass loss, the first effect at a temperature of about 120 °C and the second at T ≈ 240 °C. Both the temperature range of the process and its two-stage course have already been observed by different authors and interpreted as the evaporation of moisture present on the material's surface (the former of the processes), followed by the release of zeolitically bound water (at the higher temperature) [1, 4]. This water contributes to the stabilization of the hexagonal structure since it gets incorporated into the open spaces which form tunnels along the crystalline axis in the hexagonal structure. The measured preparation mass decrement corresponds to the liberation of 0.4–0.5 mol H_2O per 1 mol $Ln\text{PO}_4$. It is quite interesting that the samples produced by the Pechini method were obtained through sintering at a temperature of 500 °C whereby the compounds were dehydrated without any change to the crystalline structure of the orthophosphate. When the preparations are stored in atmospheric conditions, the phosphates immediately undergo rehydration, which can be observed during thermal analyses of the samples.

Weak exothermic effects in the DSC curves were observed at a temperature of about 700 °C. The effects were stronger for the samples synthesized by precipitation from the H_3PO_4 solution than for the samples obtained by the Pechini method, but no changes in the TG profiles were denoted. In this temperature range $Ln\text{PO}_4$ undergoes phase transition from the hexagonal to monoclinic (monazite) structure, which is confirmed by the XRD examinations carried out by the present and by other authors [4]. This process takes place at a slightly lower temperature ($\Delta t \approx 50$ °C) in the sample produced by the Pechini method. The phase transition temperature reduction effect in the nanocrystalline preparations may be due to the higher surface energy of the smaller grains. The greater specific surface area development and the facilitated diffusion through grain boundaries (faster than volumetric diffusion) accelerate the growth of the new phase.

Another slight endothermic effect appeared in the heating DSC curve for the sample synthesized through precipitation from the H_3PO_4 solution. Since $Ln\text{PO}_4$ orthophosphates with the monazite structure do not show any phase changes in this temperature range and the X-ray patterns of the samples did not show any other phases than $Ln\text{PO}_4$ to be present, the registered thermal effect can be ascribed to the impurities present in the samples, in the amount undetectable by XRD. In [4, 27] bands characteristic of $P_2O_7^{4-}$ ions were found (by FTIR) in the samples obtained by precipitation from acid solutions rich in PO_4^{3-}. Since anhydrous diphosphates of lanthanides (Ln^{3+}) are unknown and the absorption bands at wavenumbers 1200–1330 cm^{-1} are characteristic of stretching modes $\nu_{as}(\text{PO}_2)$, the impurities observed by the authors of [4, 27] are probably metaphosphates. They may form at a temperature of about 950 °C as a result of the reaction of $Ln\text{PO}_4$ with the excess H_3PO_4 adsorbed on its surface [28]:

$$Ln\text{PO}_4 + 2\text{H}_3\text{PO}_4 \rightarrow Ln(\text{PO}_3)_3 + 3\text{H}_2\text{O},$$

and the amount of the forming secondary phase depends on the surface development of the obtained orthophosphates. Lucas et al. [28] proved that impurities in the form of $Ln(\text{PO}_3)_3$ undergo thermal decomposition at temperatures higher than 1050–1350 °C. The decomposition is an endothermic process and it is accompanied by a slight mass decrement connected with the removal of the excess diphosphate pentaoxide (evaporating in the form of a dimer) in accordance with the reaction:

$$2Ln(\text{PO}_3)_3 \rightarrow 2Ln\text{PO}_4 + \text{P}_4\text{O}_{10}(\text{g}).$$

Therefore, the endothermic effect observed in the DSC curve in this study was ascribed to the decomposition of lanthanide metaphosphates and since the amount of impurities was small (undetectable by XRD), the decrement in the preparation mass during heating was not registered in the TG curve. This interpretation of the effect is consisted with the FTIR results.

The FTIR spectra of the preparations obtained by the Pechini method and, for comparison, of the powders obtained through precipitation from solutions showed that all the powders obtained at a temperature up to 500 °C display the characteristic bands of rare-earth orthophosphates with rhabdophane structure [29] (Fig. 3). The two distinct absorption bands located at 540 and 620 cm^{-1} correspond to the vibrations ν_4 of the PO_4^{3-} groups while the intensive bands in the 950–1070 cm^{-1} range can be ascribed to the vibrations ν_1 of the PO_4^{3-} groups and

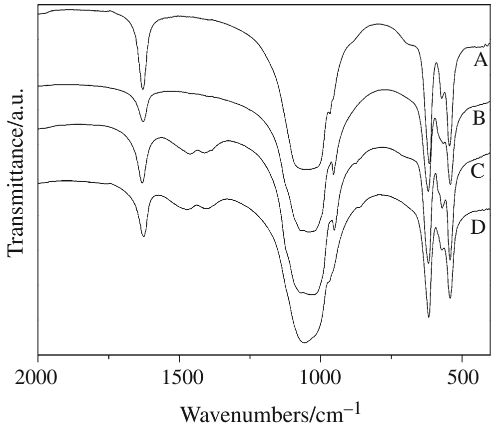

Fig. 3 The FTIR spectra of CePO_4 precipitated from solution at 80 °C (**a**), CePO_4 (**b**), LaPO_4 (**c**), and PrPO_4 (**d**) obtained by Pechini method at 500 °C

asymmetrical vibrations v_3 of the P–O bands. The spectra include strong bands at about 1630 cm^{-1}, characteristic of the deformation vibrations of water molecules (Fig. 3). The presence of the bands in the spectra is justified by the incorporation of zeolitic water molecules into the rhabdophane structure.

In the case of the $LaPO_4$ and $PrPO_4$ samples produced by the Pechini method, additional bands were found in the 1460–1410 cm^{-1} range, indicating the presence of C=O and C–H bonds originating from organic residua (citric acid and ethylene glycol molecules) uncombusted during the synthesis (Fig. 3). Incompletely combusted products of citric acid and ethylene glycol were also observed by the naked eye, since the synthesized powders turned darker and greyish.

According to the author's knowledge, the higher efficiency of organic residual combustion follows spontaneous ignition, which is sometimes observed also in the Pechini process. Citric acid and its decomposition products may ignite in the presence of nitrate ions and a metal with a few oxidation states. This is often used to facilitate the synthesis and reduce the energy expenditures on the thermal treatment of the samples. The authors know from experience that such spontaneous ignition may occur during the synthesis of phosphates produced by the modified Pechini method [30]. In atmospheric conditions cerium occurs in oxidation state +3 or +4, which makes this element very active during spontaneous ignition processes. Also the known catalytic properties of cerium compounds may play some role in the efficiency of combustion of the samples.

Moreover, in the FTIR spectra for $LaPO_4$ and $PrPO_4$ one can distinguish two weak bands at a frequency of 710 and 880 cm^{-1} (Fig. 3). In this wavenumber range, absorption for the P–O–P bond, present in both di- and metaphosphates, is registered [31]. The bands disappeared in the powdres subjected to further treatment (grinding and calcination at 900 °C). Considering the good control of sample stoichiometry in the Pechini method and the absence of such bands in the samples with cerium, the fact that small amounts of seconadry phases (di- or metaphosphates) form may be due to the poorer homogeneity of the $PrPO_4$ and $LaPO_4$ powders, resulting from the non-proper combustion of the samples.

The FTIR spectra of the *Ln*PO_4 samples heat-treated at 900 °C (Fig. 4) show that the temperature increase to 900 °C results in the formation of monazite and in poorer symmetry of the compound, which is reflected in the splitting of the bands in the range of 990–1090 cm^{-1} and 540–580 cm^{-1} and in increased absorption at about 955 cm^{-1} [32]. Additional, wide, and weak band is visible at about 1270 cm^{-1} in the FTIR spectrum of the $LaPO_4$ sample obtained by precipitation and calcined at 900 °C. The band appears in the range of vibrations $v_{as}(PO_2)$ characteristic of metaphosphates [31, 33–35]. The presence of this band validates the interpretation of the TG/DSC results, presented earlier.

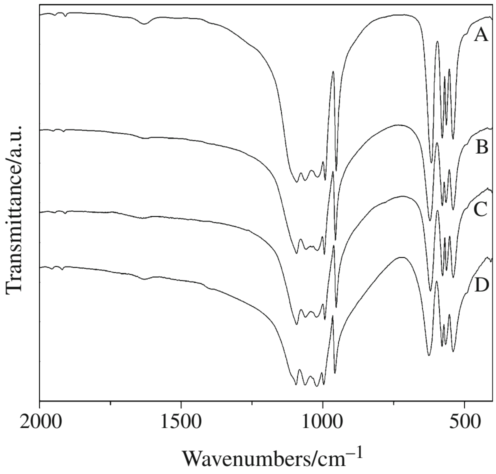

Fig. 4 The FTIR spectra of $LnPO_4$ samples sintered at 900 °C: $CePO_4$ precipitated from solution (**a**), $CePO_4$ (**b**), $LaPO_4$ (**c**), and $PrPO_4$ (**d**) obtained by Pechini method

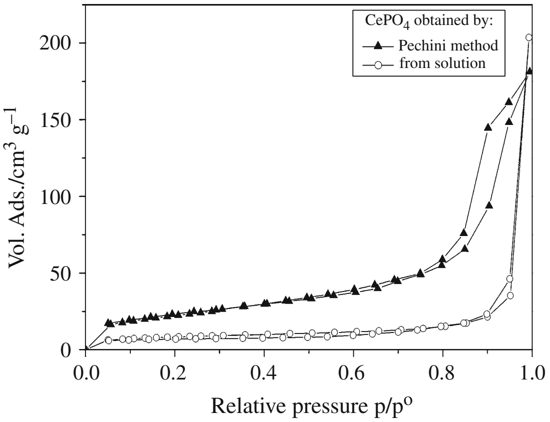

Fig. 5 The N_2 adsorption–desorption isotherms for $CePO_4$ powders obtained by Pechini route at 500 °C (*filled triangle*) and precipitated from H_3PO_4 solution at 80 °C (*open circle*)

Figure 5 shows nitrogen adsorption isotherms for the $CePO_4$ samples produced through precipitation from solutions and by the Pechini method. The gas adsorption results for the samples obtained by the two methods indicate considerable difference in the morphology of the powders. In the case of the sample obtained through precipitation from the H_3PO_4 solution, curve of type II (according to IUPAC [36]) was registered, which suggests that the obtained powder is non-porous. The second isotherm corresponds to type IV, and it has a characteristic hysteresis loop indicating the presence of mesopores, which lead to the capillary condensation of the adsorbate inside the pores.

The BET specific surface area determined from the nitrogen adsorption measurements amounted to 81, 70, and 58 $m^2 g^{-1}$ for, respectively, $CePO_4$, $LaPO_4$, and $PrPO_4$ produced by the Pechini method, while the $CePO_4$ sample synthesized from the aqueous solution of phosphoric acid had an S^{BET} value of 28 $m^2 g^{-1}$. In the series of samples produced by the Pechini method the smallest specific surface development was observed in the praseodymium orthophosphate sample.

The gas adsorption results were also used to determine the pore size distribution in the powders. Figure 6 shows a comparison of pore diameter distribution for the $CePO_4$ samples obtained by the two methods, whereas Fig. 7 compares the results for the samples with different chemical composition, synthesized by the Pechini method. The diameter of mesopores in the $CePO_4$ and $LaPO_4$ is the same (ca. 20 nm), but the one for the $PrPO_4$ sample is twice larger. The increase in the pore diameter and the lower surface development of the $PrPO_4$ powder are most probably due to the slightly different combustion process of polyester resin under the influence of the additional portion of nitric acid (and the higher mole ratio NO_3^-/Ln^{3+}) used to dissolve the praseodymium hydroxycarbonate for the synthesis (see "Experimental" section). Since in the Pechini method NO_3^- ions are the main oxidizer in the combustion of citric acid (CA) and ethylene glycol (EG), an even slight increase in their concentration may result in major changes in the combustion mechanism of the samples. The main cause of powder porosity in combustion methods (to which the Pechini method belongs) is the liberation of synthesis by-products in the form of gases (e.g., nitrogen[II, IV, V] oxides or CA and EG derivatives). Not only the type of combustion fuel, but also its mole ratio to the oxidizer significantly affects the mechanism of the synthesis and the quality of the product, including the amount and size of pores. Therefore, if the amount of HNO_3 used in the synthesis is increased, this may result in a larger size of pores in the $PrPO_4$ sample.

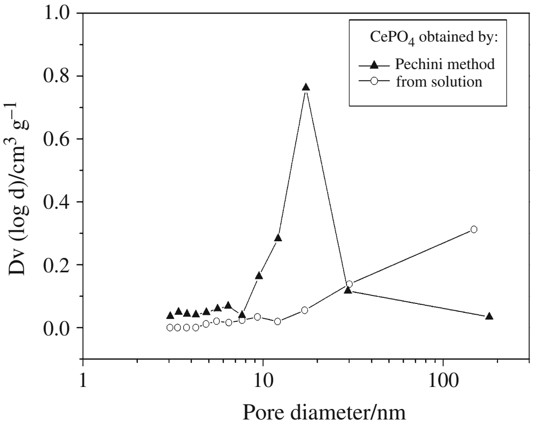

Fig. 6 The pore size distribution in $CePO_4$ powders obtained by Pechini route at 500 °C (*filled triangle*) and precipitated from H_3PO_4 solution at 80 °C (*open circle*)

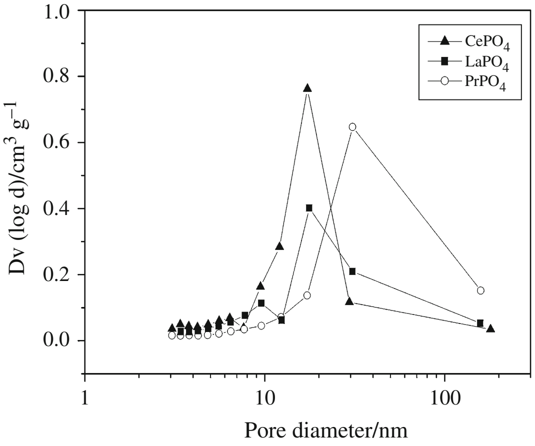

Fig. 7 The pore size distribution in $CePO_4$ (*filled triangle*), $LaPO_4$ (*filled square*), and $PrPO_4$ (*open circle*) powders obtained by Pechini route at 500 °C

Conclusions

Despite the higher synthesis temperature applied during Pechini method, obtained lanthanum, cerium, and praseodymium orthophosphates are characterized by a nearly twice smaller average crystallite size (about 16 nm) in comparison with that of the orthophosphates produced through precipitation from a phosphoric acid solution at a temperature of 80 °C. The smaller crystal size is accompanied by increased value of the specific surface area of the samples and the occurrence of mesopores. Such characteristics are essential for materials used in technologies based on reactions proceeding on active surfaces, i.e., catalysis and thermal barrier coatings. The application of Pechini method to $LnPO_4$ production allows better control of the stoichiometry of the compound and prevents excessive phosphate ions from adsorbing on the surface of the powders as is the case in the precipitation method. Thanks to the limitation of the formation of intermediate phases, which are impurities difficult to remove, and the fact that the initial reactants in the Pechini method are metal ion solutions (i.e., homogenous mixtures at the atomic level); the method can be used to synthesize doped phases, which are in particular desirable for optical technologies.

The analytical results also show that the course of polyester resin combustion has a qualitative effect on the obtained powders. The type of lanthanide ion forming the orthophosphate and the amount of the nitric acid used in the synthesis have an influence on the value of specific surface area of the powders, the pore size distribution, and on any residual from the combustion of the resins.

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