

Comparison of the crystallisation and solid state reaction methods for the preparation of rare-earth orthophosphates

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Abstract Two easy laboratory methods for preparation of rare-earth orthophosphates (crystallisation from phosphoric acid solution and solid-state reaction with $(\text{NH}_4)_2\text{HPO}_4$) were compared on the basis of the products' properties with a focus on their application as new inorganic pigments. The preparation method has a significant influence on optical properties. The samples prepared by crystallisation have lighter and less rich colour and also change colour more under sunlight irradiation. The surface properties analysed by SEM and presence of a greater amount of phosphoric acid in the crystallisation procedure influence the pH and resistivity of aqueous extract of products and thus their corrosion-inhibition properties. The optical properties of rare-earth orthophosphates and their preliminary corrosion tests show their potential application as highly efficient corrosion-inhibition pigments.

Keywords Rare-earth phosphate · Inorganic pigments · Optical properties · Corrosion · Lightfastness · Thermal analysis

Introduction

The synthetic forms of lanthanide orthophosphates find applications in various areas such as environmentally-friendly inorganic pigments [1, 2], solid-state protonic conductors [3], phosphors [4, 5], materials for radioactive waste storage [6], interlayers in oxide/oxide composites [7]

and so forth. They are usually obtained by crystallisation from phosphoric acid solution [8], the wet chemical precipitation method [9, 10], high temperature solid-state reactions [11–13], or the sol–gel and hydrothermal method. The physical–chemical properties (chemical composition, crystalline structure, colour, morphology) which influence the thermal behaviour and pigment-application properties of the prepared powders depend on the synthesis route.

This paper focuses on the synthesis of LnPO_4 ($\text{Ln} = \text{La}, \text{Nd}$) with the aim of obtaining compounds with corrosion-inhibition properties. In this case, chlorides, nitrates, or sulphates are problematic impurities [14, 15] and therefore solid-state reactions and crystallisation from phosphoric acid solution were chosen for the preparation in our laboratory. The present work deals with the synthesis of doped lanthanide orthophosphate powders using two methods and with the characterisation of the products. The influence of the synthesis method on the colour properties, lightfastness, morphology, pH of aqueous extract, and preliminary corrosion-inhibition properties of the different products are reported.

Experimental

The powders were prepared by crystallisation from phosphoric acid solution [8, 16] and by solid-state reaction using $(\text{NH}_4)_2\text{HPO}_4$ as the phosphorus resource [11, 17–19].

An appropriate amount of Ln_2O_3 (La_2O_3 , Nd_2O_3 , Bochemie, CZ) was mixed with distilled water for the crystallisation process (100 cm^3 of 0.04 M suspension) and then 27 cm^3 of H_3PO_4 (85%, Lachema, CZ) was added at ambient temperature. The mixture was left to stand overnight or for a longer period of time and then transferred to a flask covered with reflux condenser, heated, and kept

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boiling for 2 h with continuous stirring. The solid obtained was filtered off, washed with distilled water until a neutral pH was obtained, and dried at 85 °C. The parts of hydrated products were also heated at 1150 °C for 120 min in an electric furnace.

The lanthanide oxides were mixed with phosphate precursor $(\text{NH}_4)_2\text{HPO}_4$ (Lachema, CZ) for the high temperature solid-state synthesis. The starting mixture was carefully mixed in the agate mortar. The mixture was heated in an air atmosphere in an alumina crucible in an electric furnace, with a heating rate of 10 °C min^{-1} , and then heated at 450 °C for 60 min and finally at 1,150 °C for 180 min. In the present work compounds were prepared with the formula $\text{La}_{(1-x)}\text{Nd}_x\text{PO}_4$ ($x = 0; 0.25; 0.5; 0.75;$ and 1).

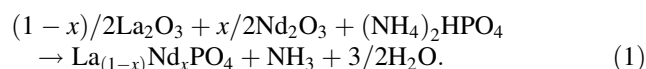
The investigation of the thermal behaviour of the reaction mixtures or products of crystallisation was performed by simultaneous thermal analysis using TG-DTA (Jupiter STA, Netzsch, Germany) in ceramic crucibles, the heating rate was 10 °C min^{-1} , and $\alpha\text{-Al}_2\text{O}_3$ was used as a reference material. X-ray diffraction patterns were obtained (D8 Advance, Bruker AXS, UK) using monochromated CuK_α radiation and a scintillation detector. The colour properties of prepared compounds were examined by measuring the spectral reflectance in the visible region of light (spectrophotometer ColourQuest XE, HunterLab, USA). The measuring system used the colour space CIE $L^*a^*b^*$. The measurement conditions were as follows: Illuminant D65 (6,500 K), 10° complementary observer, and measurement geometry $d/8^\circ$. Determination of changes in colour properties was carried out after exposure of the particle samples under glass to daylight. The samples in a glass cuvette were exposed to a xenon light source (Q-panel test chamber, Lab Products, USA) for 360 h at an irradiance setting at 340 nm and 0.51 W m^{-2} [20]. An electron microscope (JOEL JSM 5500LV, Joel Inc., USA) was used for characterisation of the prepared powders with respect to their particle size and overall appearance.

We tested corrosive decreases of steel plate in aqueous extract with the aim of evaluating rare-earth orthophosphates as corrosion-inhibition pigments. Determination of the decrease in corrosiveness in aqueous extract followed the pH and resistivity measurements. The pH values and resistivity were measured for 28 days in 10% water suspension of pigments. The specific conductivity was determined by a conductometer and the pH value by a glass electrode (InoLab, WTW, Germany). Weighted steel plates with nominal dimensions were put into aqueous suspension of prepared pigment and measured for 28 days. The following indicators of the area and even corrosion can be determined from the obtained values: K_m (corrosive decrease on the unit of area), U_R (decrease in size), v_k (corrosive speed with respect to the mass loss of a steel

plate), and v_u (corrosive speed with respect to the decrease in the size of the steel plate) [21].

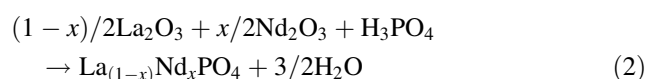
Results and discussion

The synthesis of monazite $\text{La}_{(1-x)}\text{Nd}_x\text{PO}_4$ from $(\text{NH}_4)_2\text{HPO}_4$ and rare-earth oxides can be described by the following reaction:



The reaction mixture for the preparation of $\text{La}_{0.5}\text{Nd}_{0.5}\text{PO}_4$ by the solid state method was analysed by TG and DTA (Fig. 1) and the calcination product was analysed by X-ray diffraction (Fig. 2). Several thermal effects and important mass loss are observed on thermoanalytical curves from room temperature to 900 °C, all assigned as the thermal decomposition of $(\text{NH}_4)_2\text{HPO}_4$ with evolution of NH_3 and H_2O [22]. The observed mass loss is higher than that calculated for $(\text{NH}_4)_2\text{HPO}_4$ because the La_2O_3 also participates in the total mass loss [23]. The purity of Ln_2O_3 was analysed before synthesis and the amount of reactants was arranged. The exothermic peak with a maximum at 1,027 °C is connected with the final formation of pure $\text{La}_{0.5}\text{Nd}_{0.5}\text{PO}_4$. Actually, only the monazite phase was identified by X-ray analysis for the sample fired at 1,150 °C [11].

The synthesis of $\text{La}_{(1-x)}\text{Nd}_x\text{PO}_4$ by the crystallisation method can be described by the following reaction:



The crystallisation product $\text{La}_{0.5}\text{Nd}_{0.5}\text{PO}_4$ was analysed by TG and DTA (Fig. 3) and by X-ray diffraction (Fig. 4). The double endothermic effect (minimums at 161 and 310 °C) corresponds to the loss of water [24]. The exothermic peak with a maximum at 759 °C without any

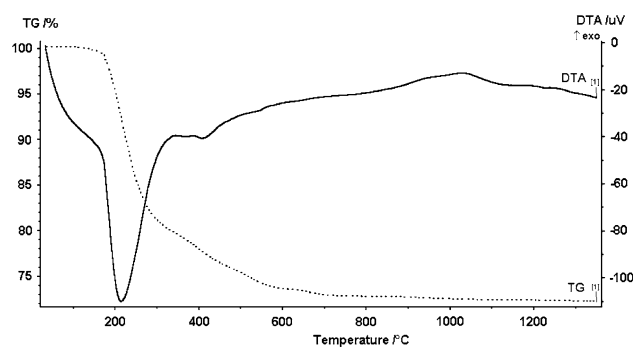


Fig. 1 TG and DTA curves of reaction mixture for the $\text{La}_{0.5}\text{Nd}_{0.5}\text{PO}_4$ sample obtained by solid-state synthesis (mass: 355 mg)

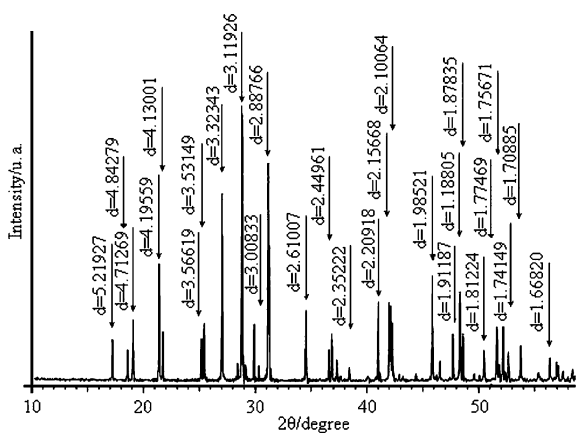


Fig. 2 X-ray diffraction pattern of the sample $\text{La}_{0.5}\text{Nd}_{0.5}\text{PO}_4$ (1,150 °C) obtained by solid-state synthesis

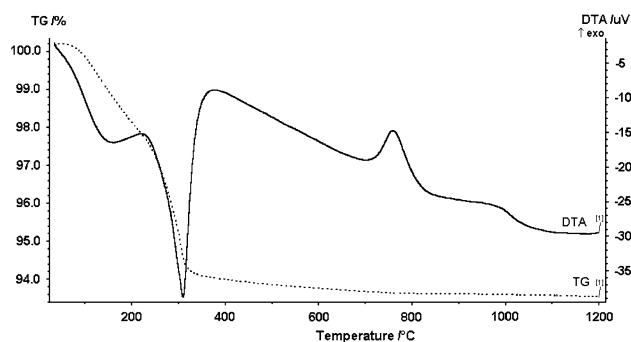


Fig. 3 TG and DTA curves of the $\text{La}_{0.5}\text{Nd}_{0.5}\text{PO}_4 \cdot x\text{H}_2\text{O}$ sample obtained by crystallization (mass: 353 mg)

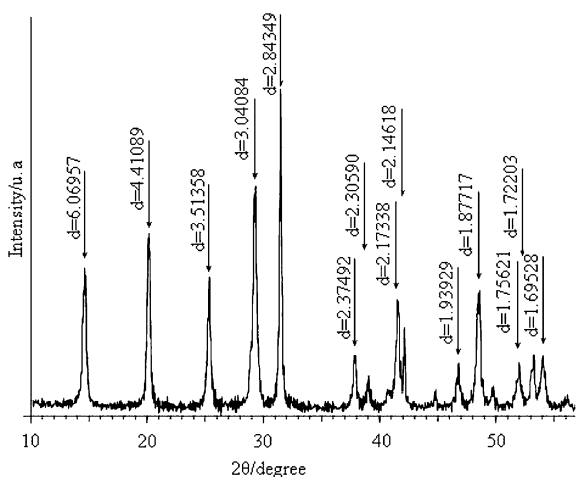


Fig. 4 X-ray diffraction pattern of the sample $\text{La}_{0.5}\text{Nd}_{0.5}\text{PO}_4 \cdot x\text{H}_2\text{O}$ obtained by crystallization

mass change on the TG curve is associated with polymorphic transformation (the change from hexagonal to monoclinic crystal structure) [25, 26]. The one-phase

system created by the hydrated form of $\text{La}_{0.5}\text{Nd}_{0.5}\text{PO}_4$ was proved by X-ray analysis.

Table 1 shows the colour properties of the samples prepared by different methods. The samples are deeper (decreasing L^*) in every case with increasing amounts of Nd and contain greater amounts of red hue (increasing a^*) and blue hue (decreasing b^*), and this characteristic makes them more interesting as pigments. The total colour difference was calculated according to the formula $\Delta E_{CIE}^* = (\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2})^{1/2}$ (3) to evaluate the influence of the preparation method. This value expresses the colour difference between samples prepared by solid-state reaction and by crystallisation and those prepared by solid-state reaction and by crystallisation with subsequent calcination. The ΔE_{CIE}^* values are in both cases between 2 and 4.5, which means that the colour difference is mostly perceptible (boundary value) to the human eye and also that the preparation method has a significant influence on the colour properties of products. The samples prepared by crystallisation have lighter and less colour. The pure LaPO_4 is white; the samples with Nd are light purple.

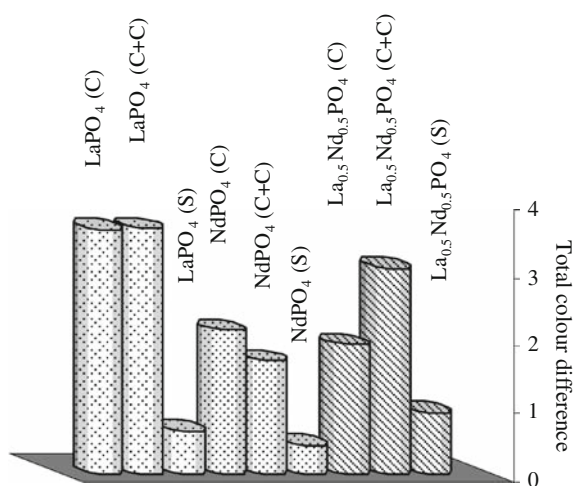
The lightfastness of powders, expressed as the total colour difference between the non-irradiated samples and the irradiated samples, is given in Fig. 5. The samples were exposed to a radiation load of 661 kJ m². The most stable compounds were prepared by solid-state reaction. They have ΔE_{CIE}^* of about 1, making them almost imperceptible to the human eye. The total colour difference was determined as the difference between the non-irradiated and the irradiated samples under the previously mentioned conditions. The other preparation methods show values of ΔE_{CIE}^* between 2 and 4. With regard to lightfastness, solid-state reaction is the most suitable method of synthesis. Generally, all the prepared samples have good resistance to sunlight.

Electron microscopy was also used to characterise the rare-earth orthophosphates with respect to their overall appearance. Figure 6 demonstrates the similar, compact particles for compounds prepared at elevated temperatures. The sample $\text{La}_{0.5}\text{Nd}_{0.5}\text{PO}_4$ prepared by crystallisation has an open crumbled structure created by the agglomeration of small particles. The surface properties are important for pigment application, mainly due to their effect on corrosion-inhibition properties [15].

The values for pH and resistivity (ρ) of 10% pigment water suspension are given in Table 2. The preparation methods have a significant influence on product behaviour, with a focus on pH value and resistivity measurements. The pH values of solid-state synthesis products and products calcinated at 1,150 °C are within the range of 6–7 and increase during the period of the measurement. The pH values also increase with the amount of Nd. Generally, the

Table 1 The colour properties of prepared compounds by different methods

Sample	Solid-state synthesis			Crystallization				Crystallization with calcination			
	L^*	a^*	b^*	L^*	a^*	b^*	ΔE_{CIE}^*	L^*	a^*	b^*	ΔE_{CIE}^*
LaPO ₄	95.45	0.09	0.84	92.38	-0.27	2.32	3.43	94.31	-0.51	1.69	1.54
La _{0.75} Nd _{0.25} PO ₄	90.65	3.92	-1.89	90.34	2.21	-2.50	1.99	88.07	5.24	-1.65	2.91
La _{0.5} Nd _{0.5} PO ₄	87.32	5.63	-2.26	88.97	4.59	-3.73	2.44	85.22	7.86	-2.46	3.07
La _{0.25} Nd _{0.75} PO ₄	86.89	7.73	-4.14	87.73	5.09	-3.90	2.78	82.93	8.91	-2.54	4.43
NdPO ₄	83.70	9.13	-4.29	85.39	6.61	-5.35	3.21	82.15	9.42	-3.35	1.84

**Fig. 5** The total colour difference of pigments after sunlight irradiation (C = crystallization, C + C = crystallization with following calcination, S = solid-state reaction)

alkalinity of rare-earth decreases with their ion radius. The same values for crystallisation products are between 4 and 6, because their surface (Fig. 6) can bond strongly with phosphoric acid, which can be released afterwards into the water extract. The slightly acidic pH range is suitable for the high corrosion-inhibition efficiency of the phosphate pigments [27, 28]. The crystallisation products show the biggest difference between the 1st and 28th day of resistivity measurements, indicating a greater solubility of hydrated products. On the other hand, the principle of the effectiveness of phosphate corrosion-inhibition pigments is

based on their partial solubility and on the creation of new compounds with background material, possibly with elements of the coatings in which they are applied.

Table 3 presents the decreases in the parameters of the corrosive steel plate in aqueous suspension with synthesised rare-earth orthophosphates. These values show that samples prepared by crystallisation with calcination at 1,150 °C in comparison to other methods of preparation present the worst corrosion-inhibition properties, but generally the results indicate good efficiency according to preliminary corrosion tests. The corrosion-inhibition properties of newly synthesised compounds are usually described only in terms of the difference between the efficiency of commercially used pigments and that of the new one. Zinc phosphate dihydrate and zinc phosphomolybdate are two corrosion-inhibition pigments that are widely used today. For comparison, the parameters of zinc phosphate dihydrate are $K_m = 10.71 \text{ g m}^{-2}$, $U_r = 0.0013 \cdot 10^{-3} \text{ mm}$, $v_k = 0.3508 \text{ g m}^{-2} \text{ day}^{-1}$, and $v_u = 0.0166 \text{ mm year}^{-1}$, while those of zinc phosphomolybdate are $K_m = 8.26 \text{ g m}^{-2}$, $U_r = 0.0011 \cdot 10^{-3} \text{ mm}$, $v_k = 0.2360 \text{ g m}^{-2} \text{ day}^{-1}$, and $v_u = 0.0112 \text{ mm year}^{-1}$. The parameters were obtained under the same conditions. The presence of free phosphoric acid significantly influences the behaviour of the products of the crystallisation method, which is described by fluctuating values in this case. The absolute order of corrosion-inhibition efficiency of methods can be expressed as follows (from the most efficient): crystallisation > solid-state synthesis > crystallisation with calcination. The pure NdPO₄ shows the lowest K_m and v_u values for all preparation methods. The presence of Nd in compounds has a positive effect. The results and conclusions are given only

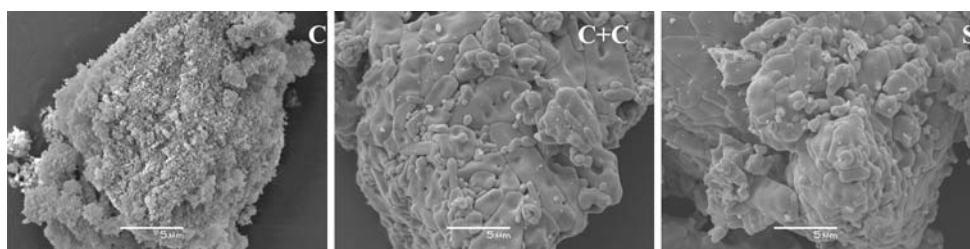
Fig. 6 SEM characterization of the sample La_{0.5}Nd_{0.5}PO₄ (C = crystallization, C + C = crystallization with following calcination, S = solid-state reaction)

Table 2 pH and resistivity measurement

Sample	Solid-state synthesis				Crystallization				Crystallization with calcination			
	1 day		28 day		1 day		28 day		1 day		28 day	
	pH	ρ ($\mu\Omega$ cm)	pH	ρ ($\mu\Omega$ cm)	pH	ρ ($\mu\Omega$ cm)	pH	ρ ($\mu\Omega$ cm)	pH	ρ ($\mu\Omega$ cm)	pH	ρ ($\mu\Omega$ cm)
LaPO ₄	5.3	0.123	6.2	0.182	4.3	0.032	5.4	0.133	5.7	0.114	6.8	0.135
La _{0.75} Nd _{0.25} PO ₄	6.1	0.112	6.6	0.120	4.2	0.051	5.5	0.238	6.1	0.068	6.9	0.087
La _{0.5} Nd _{0.5} PO ₄	6.1	0.072	6.6	0.082	4.2	0.050	5.2	0.370	6.2	0.119	6.7	0.118
La _{0.25} Nd _{0.75} PO ₄	6.2	0.043	6.9	0.046	4.4	0.030	5.8	0.154	6.2	0.053	7.1	0.060
NdPO ₄	6.5	0.025	7.3	0.024	4.4	0.041	5.9	0.385	6.7	0.075	7.0	0.076

Table 3 Corrosive decreases of steel plates in aqueous extract of lanthanum orthophosphates

Sample	K_m (g m ⁻²)	$U_r \times 10^{-3}$ (mm)	v_k (g m ⁻² day ⁻¹)	v_u (mm year ⁻¹)
<i>Solid-state synthesis</i>				
LaPO ₄	12.36	1.61	0.4414	0.0209
La _{0.75} Nd _{0.25} PO ₄	13.04	1.69	0.4657	0.0221
La _{0.5} Nd _{0.5} PO ₄	12.73	1.65	0.4548	0.0217
La _{0.25} Nd _{0.75} PO ₄	10.70	1.39	0.3822	0.0181
NdPO ₄	7.69	1.00	0.2748	0.0130
<i>Crystallization</i>				
LaPO ₄	9.77	1.27	0.3488	0.0267
La _{0.75} Nd _{0.25} PO ₄	11.07	1.44	0.3954	0.0285
La _{0.5} Nd _{0.5} PO ₄	7.51	0.97	0.2681	0.0271
La _{0.25} Nd _{0.75} PO ₄	10.94	1.42	0.3907	0.0242
NdPO ₄	6.79	0.88	0.2425	0.0221
<i>Crystallization with calcination</i>				
LaPO ₄	15.78	2.05	0.5636	0.0267
La _{0.75} Nd _{0.25} PO ₄	16.85	2.19	0.6013	0.0285
La _{0.5} Nd _{0.5} PO ₄	15.98	2.08	0.5706	0.0271
La _{0.25} Nd _{0.75} PO ₄	14.31	1.86	0.5112	0.0242
NdPO ₄	13.70	1.70	0.4668	0.0221
Water	19.19	3.49	0.7855	0.0394

on the basis of steel corrosion products that were presented in the aqueous extract. The reactions of the pigment with the binder were not considered.

Conclusions

The products of both the examined methods are comparable. The crystallisation method as well as solid-state synthesis give pure orthophosphate products. This was proved by DTA and X-ray analysis. The white and light purple anhydrous samples have more dark and rich hues. Total colour differences (ΔE_{CIE}^*) between samples prepared by different methods can be described as boundary values between perceptibility and imperceptibility to the human eye. The colour stability under sunlight irradiation is best

for the samples prepared by solid-state reaction ($\Delta E_{CIE}^* = \pm 1$), but neither do the other samples show large instability. The preliminary corrosion tests (degradation of steel plates in water extract of orthophosphate powders) show good inhibition properties of rare-earth orthophosphates. The parameters of the tested rare-earth orthophosphates are comparable with the parameters of commercially used products. The surface properties and presence of a greater amount of phosphoric acid in the crystallisation procedure have an influence on the pH and resistivity of aqueous extract of products and finally on the corrosion-inhibition properties of products, too.

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