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Thermal behavior of $LaPO_4 \cdot nH_2O$ and $NdPO_4 \cdot nH_2O$ nanopowders

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Abstract Thermal behavior of $LaPO_4 \cdot nH_2O$ and $NdPO_4 \cdot nH_2O$ nanopowders from room temperature to 973 K was investigated by DSC, TA/DTG, ESM, and X-ray study. Mass loss due to the release of adsorbed and hydrate water was found in the range from 323 to 623 K. Phase transitions from hexagonal structure nanopowders to monoclinic one for bulk specimens were found above 873 K.

Keywords Thermal behavior · Nanopowders · Lanthanide orthophosphates

Introduction

A lot of articles on the study of thermal properties and phase transformations for nano-scale substances [1–4] as well as papers devoted to the effect of surface energy on their thermodynamic properties [5, 6] were published recently. The large value of surface energy plays, also, the important role in the shift of phase boundaries [7].

It is known that when the lanthanide orthophosphates crystallize, the hexagonal-structure crystals ($P6_222$ (D_6^4)) are formed containing the residual water up to 0.5 mol per a mole of orthophosphate [8]. At heating up to 1073 K the release of residual water and transformation to the stable modification takes place. Monoclinic monazite structure is stable for lanthanides orthophosphates from La to Tb(Dy) ($P2_1/c$, (C_{2h}^5)) [9], while for compounds containing elements from Tb(Dy) to Lu the stable structure is xenotime-type one ($I4_1/amd$ (D_{4h}^{19})) [10].

The goal of this research was the study of structural transformations of nanomaterials and particles aggregation at heating. Nanocrystalline lanthanide orthophosphates were chosen as the objects of our research from the following considerations: (i) the crystal structures and thermal behavior of these bulk crystalline substances were studied in detail and (ii) these substances are thermally stable up to high temperatures (melting point is in vicinity of 2273 K) [11].

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Experimental section

Synthesis of specimens

Nanopowders of lanthanum and neodymium orthophosphates were prepared by sol–gel technique. At the stoichiometric components ratio (Ln_2O_3, $6HNO_3$, $2NH_4H_2PO_4$) stable colloids form and coagulate at pH ≈ 7 and precipitate as a jelly-like poorly soluble in water deposits ($LnPO_4 \cdot nH_2O$). The precipitates were kept in the mother liquor for 24 h, washed by decantation, filtered off, and dried at the temperature of 385 K in air. X-ray powder diffraction analysis (Cu K_α-radiation) was performed to analyze the obtained products. The average size of the nanoparticles was determined from the broadening of the diffraction peaks according to the Scherrer's formula and with the use of transmission electron microscopy [12, 13]. Samples were the hygroscopic white ($LaPO_4 \cdot nH_2O$) or lilac

($NdPO_4{\cdot}nH_2O$) fine powders. After synthesis they were loaded in sealed containers.

Experimental techniques

NETZSCH thermobalances TG 209 F1 Iris were used to study the mass loss in the temperature range from 298 to 973 K. Measurements were carried out in Ar atmosphere (10 mL/min) with heating rate of 2 K/min.

Electron microscopy was used to determine the shape and size of nanoparticles of $LaPO_4{\cdot}nH_2O$ and $NdPO_4{\cdot}nH_2O$ before and after heating. ESM images were made using the Leo 912 AB Omega scanning electron microscope at accelerating voltage 100 kV.

Variation in lanthanide orthophosphates structure during the heating was studied by X-ray diffraction using the HUBER Diffractometer ($CuK_{\alpha 1}$-radiation, $\lambda = 154.06$ pm, Ge monochromator, transmission geometry).

Thermal behavior of $LaPO_4{\cdot}1.10H_2O$ in the region of samples drying (from 303 to 773 K) was studied in Mettler TA4000 at 10 K/min heating rate in open alumina crucible.

Thermal effects at phase transformations were measured in differential scanning calorimeter DSC 2000 K SETARAM. Fired in air powder of α-Al_2O_3 was used as the reference substance. Reference and measured samples were placed in the alumina 100 μL crucibles. Specimens before and after experiment were weighed using "Analytical microbalance γ-21N4" (accuracy of 0.1 mg). Initial mass of a sample was 27.6 mg. DSC measurements were carried out in dried argon flow and in air.

Results and discussions

Study of the prepared specimens of nano-$LaPO_4{\cdot}nH_2O$ and nano-$NdPO_4{\cdot}nH_2O$ by X-ray analysis allows to determine that initial samples have the hexagonal structure.

The initial samples were studied by DTA/TG analysis to determine the amount of residual water in the specimens. Samples were heated up to 973 K and the mass loss caused by the removing of more then 98% of water from the initial samples was observed in the temperature range from 323 to 623 K. Results of TG measurements are shown in Fig. 1. Based on TG study the following compositions of the orthophosphates were calculated: $LaPO_4{\cdot}1.10H_2O$ and $NdPO_4{\cdot}1.13H_2O$. Reweighing of annealed at 623 K nanopowders showed that after some exposition in air the mass of both samples increased owing to the adsorption of water from humid air. DSC study of $LaPO_4{\cdot}1.10H_2O$ sample revealed the endothermic double-maximum peak (the main peak with the maximum at 135 °C and shoulder one with the maximum at 563 K) in the temperature range from 323 to 598 K (Fig. 1). Heats of the endothermic effects were

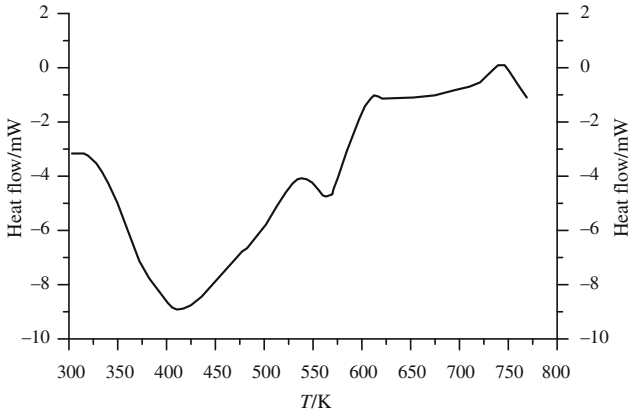

Fig. 1 Curve of heating of sample nano-$LaPO_4{\cdot}1.1H_2O$

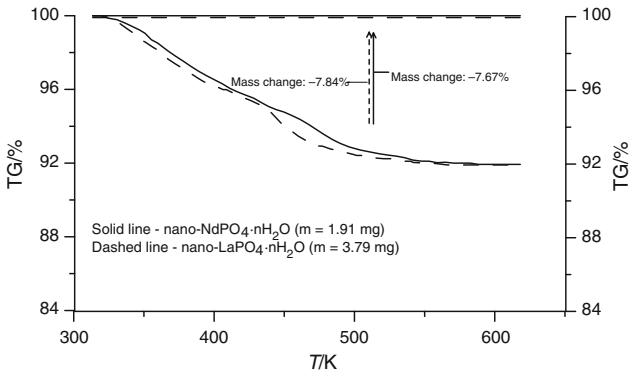

Fig. 2 Mass loss of nano-$LaPO_4{\cdot}nH_2O$ and nano-$NdPO_4{\cdot}nH_2O$ specimens

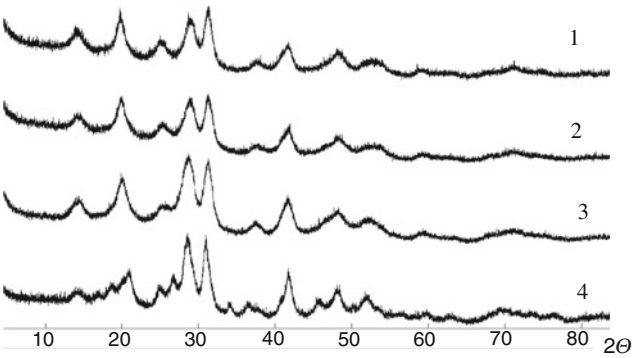

Fig. 3 X-ray study of thermal transformations in nano-$LaPO_4$ ($\cdot nH_2O$): (*1*) initial sample, (*2*) annealed at 573 K in 3 h, (*3*) annealed at 773 K in 2 h, (*4*) annealed at 973 K in 2 h

165 and 15 J/g, respectively. These two peaks can be applied to evaporation of hydrate and adsorbed water of the orthophosphate. It can be noted that two-step mass loss can be observed, also, in Fig. 2.

The search of stability region of nanosized lanthanide orthophosphates is one of the most interesting problems for the substances under investigation. To solve it we carried

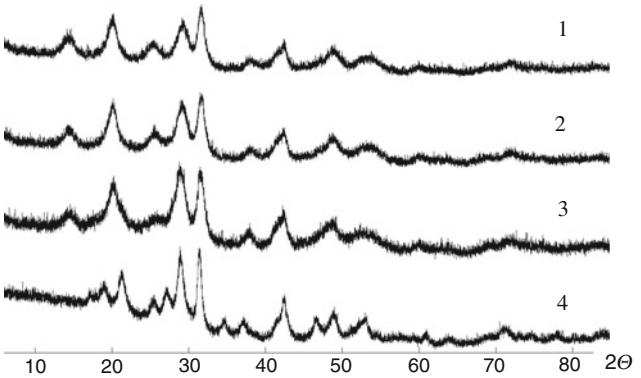

Fig. 4 X-ray study of thermal transformations in nano-$NdPO_4(\cdot nH_2O)$: (*1*) initial sample, (*2*) annealed at 573 K in 3 h, (*3*) annealed at 773 K in 2 h, (*4*) annealed at 973 K in 2 h

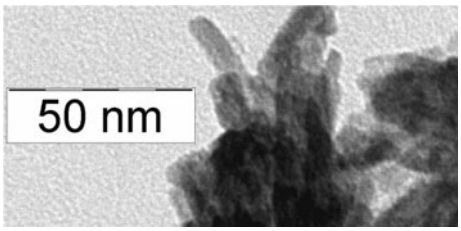

Fig. 5 ESM microphotograph of the initial nano-$LaPO_4 \cdot nH_2O$ specimen

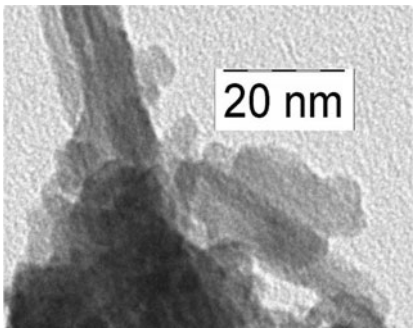

Fig. 6 ESM microphotograph of the nano-$LaPO_4$ specimen after heating up to 623 K

out the X-ray analysis of samples annealed at different temperatures (573 K, 3 h; 773 K, 2 h; 973 K, 2 h). Results of this study are presented in Figs. 3 and 4. Apparently, even after removing the water at 623 K the structure of $LaPO_4$ and $NdPO_4$ nanopowders remains hexagonal and peak widths were the same as at room temperature. It allows concluding that the size of nanoparticles did not change significantly. This conclusion was confirmed by ESM microscopy. The shape and size (from 7 to 25 nm) of nanoparticles after heating up to 323 K, which can be seen in Figs. 5 and 6, are almost invariable.

Only after heating up to 973 K the monazite peaks appeared in X-ray diffraction patterns although quite broadened (Figs. 3, 5 and 4, 5).

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