ABSTRACT

Of dissertation for the doctor of philosophy degree (PhD)
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Hydrothermal synthesis and properties of oxide crystal matrix for the immobilization of radioactive waste

The dissertation is devoted to the production of phosphate materials in the form of powders by the hydrothermal method and the preparation of ceramics based on them. In this work, we studied the processes of the formation of nanocrystalline lanthanum orthophosphate powders (hereinafter referred to as lanthanum phosphate or LaPO4) with crystal structures of rhabdophan and monazite having crystallite sizes of ~ 10 nm. Technological modes of obtaining nanopowders of anhydrous lanthanum orthophosphate and their sintering with obtaining dense ceramics with porosity at the level of 5-7% and not containing open pores were determined with the aim of using the obtained materials as a matrix for the immobilization of radioactive waste. The influence of technological parameters of the synthesis of lanthanum phosphate on its structure and properties is determined.

Relevance of the research topic. The scope of materials based on lanthanum orthophosphate, including nanomaterials, has been constantly expanding recently. Due to the high melting point, chemical resistance, thermophysical and thermomechanical properties, $LaPO_4$-based materials are promising for use as refractories. The high level of mechanical properties and compatibility with many oxides allows us to consider the possibility of using lanthanum orthophosphate as a component of a composite material for structural purposes. Such an application is especially promising when using nanoparticles with quasi-one-dimensional morphology (nanorods). The large isomorphic capacity of the LaPO4-based phase with respect to alkaline-earth ions, lanthanide and actinide ions, as well as the chemical and radiation stability of materials based on rare-earth phosphates (REEs) make them promising for use as matrices for immobilization of radioactive waste. Of particular interest in this regard is manifest in materials based on REE orthophosphates with a monazite structure. Such materials can also be used as carriers of radioisotopes for biomedical applications.

In recent years, the use of $LaPO_4$ doped with alkaline-earth ions, primarily calcium and strontium ions, has been actively considered in order to obtain materials with high proton conductivity. In addition, they can be used as luminescent materials due to the excellent optical characteristics for the manufacture of such products as optical display panels, cathode ray tubes and plasma panels. These compounds can be used as matrices by doping with Ce^{3+}, Pr^{3+}, Nd^{3+}, Eu^{3+}, Tb^{3+}, Ho^{3+}, Er^{3+}, Tm^{3+}, Yb^{3+} ions.

The **aim** of the thesis is to obtain lanthanum phosphate by hydrothermal treatment and study the dependence of the physicochemical properties of materials

based on lanthanum phosphate on the conditions of receipt; obtaining crystalline ceramics based on the obtained compound.

To achieve the goal, the following tasks were set:

1) Synthesize lanthanum phosphate by various methods, including the deposition method followed by heat treatment and hydrothermal synthesis with direct and indirect heating, and determine the conditions for the production of nanomaterial with a monazite crystal structure.

2) Determine the optimal conditions for the technological mode of sintering of crystalline ceramics from the obtained powders of $LaPO_4$ lanthanum phosphate with a monazite structure.

3) Determine the thermal and physico-mechanical properties of the obtained ceramic materials based on $LaPO_4$ lanthanum phosphate.

4) Issue recommendations on obtaining nanocrystalline materials based on LaPO4 lanthanum phosphate by hydrothermal treatment.

5) Investigate the phase formation in the $LaPO_4$ - YPO_4 system.

Objects of research: lanthanum phosphate ($LaPO_4$), $La_{1-x}Y_xPO_4$.

Subject of research: hydrothermal synthesis of $LaPO_4$ lanthanum phosphate, physicochemical, thermal properties of ceramic materials based on $LaPO_4$, phase formation in the $LaPO_4$ - YPO_4 system.

Subject of scientific research: hydrothermal synthesis of lanthanum orthophosphate with the structure of monazite; physico-mechanical properties of ceramic materials based on lanthanum monazite phosphate.

Research methods. When performing research on the topic of the dissertation, the following synthesis methods and modern methods of physical and chemical research were used: hydrothermal synthesis with direct and indirect heating; X-ray powder analysis (XRD); high temperature X-ray diffraction analysis; scanning electron microscopy and X-ray microanalysis; thermogravimetry (TG); differential thermal analysis (DTA); IR spectroscopy dilatometry; helium pycnometry; research of microhardness, porosity, thermal diffusivity.

Source database and research materials are 183 sources of literature on methods of hydrothermal synthesis of lanthanum orthophosphate, phase transformation, production of ceramic materials, as well as other areas of natural science related to the topic of this study.

Scientific novelty:

- Technological conditions have been determined that make it possible to obtain nanocrystalline lanthanum orthophosphate powders with a monazite structure, as well as to sinter ceramic materials with porosity of 5-7%;

- The influence of pH, temperature and duration of hydrothermal treatment on the morphology and structure of monostructured lanthanum phosphate was determined.

- It was shown that a sharp decrease in porosity to ~ 5% with a slight increase in grain size (200-400 nm) leads to the thermal treatment of lanthanum phosphate in the form of a nanopowder at a temperature of 1100 ° C. For the obtained material, the limiting values of thermal conductivity (λ (25°C) = 3.2 W/m · K), microhardness

(H_v (25°C) = 4.6 ± 0.4 GPa), Young's modulus (E (25°C) = 132 ± 9 GPa), fracture toughness (K_{1c} (25 ° C) = 1.6 ± 0.1 MPa · $m^{1/2}$);

- It was shown that the presence of an impurity phase of lanthanum metaphosphate does not significantly affect the possibility of using this material as a structural or heat-insulating material up to 1500 ° C as an alternative to a single-phase material based on LaPO4. At the same time, the presence of inclusions of lanthanum metaphosphate has a stabilizing effect on the dependence of the coefficient of linear thermal expansion of the material on the technological parameters of its synthesis;

- The effect of doping lanthanum phosphate with yttrium under hydrothermal conditions under microwave heating on the structural state of the obtained nanocrystalline materials was determined.

The theoretical significance of the research. The revealed features of the hydrothermal synthesis of lanthanum phosphate and yttrium-doped compounds based on it (phase changes, changes in the size of nanoparticles and their shapes) make a theoretical contribution to the chemistry of lanthanum, while certain technological sintering modes of ceramics are of theoretical interest in the chemical technology of lanthanum and its compounds.

The practical value. The obtained results on the synthesis of lanthanum phosphate by the hydrothermal method and sintering of nanocrystalline ceramic materials are of practical engineering value, since materials based on them can be used as materials for immobilization and storage of radioactive waste. Due to the high effective cross-section of lanthanum, together with excellent mechanical and physicochemical properties, the materials obtained have a high prospect of using them in nuclear energy and the uranium industry for immobilization of radioactive waste and protection against ionizing radiation.

The main points for the defense of the thesis:

– Phase transition of lanthanum phosphate from the structure of rhabdophan to the structure of monazite, observed at 520-540 ° C and not accompanied by a significant change in the size of nanoparticles (10 nm). Up to a temperature of 600 ° C, the formation of LaPO4 nanocrystals with both the structure of rhabdophan and monazite proceeds according to the nucleation mechanism, and only after 700 ° C the crystal growth process is activated.

– Decrease in porosity (up to ~ 5%) of $LaPO_4$-based ceramic material mixed with LaP_3O_9 phase with a slight grain growth (200-400 nm) as a result of heat treatment of ceramics at 1100 ° C with measured thermal conductivity (λ (25 ° C) = 3.2 V t / m · K), microhardness (H_v (25 ° C) = 4.6 ± 0.4 GPa), Young's modulus (E (25°C) = 132 ± 9 GPa), fracture toughness (K_{1c} (25°C) = 1.6 ± 0.1MPa · $m^{1/2}$). The coefficient of linear thermal expansion of the material weakly depends on the heat treatment of the material and is (8.2 ± 0.2) · 10-6 K-1.

– The presence of LaP3O9 (~ 7.5 vol.%) In LaPO4 does not significantly affect its thermophysical, mechanical and thermomechanical characteristics, which suggests the possibility of using this material as a structural or heat-insulating (up to 1500 ° C) as alternatives to single phase LaPO4 based material.

– With increasing pH, the morphology of the nanoparticles of the formed lanthanum phosphate and the crystallite sizes change. The minimum time for the phase transition of the hexogonal crystal structure to monoclinic during hydrothermal treatment at 210 ° C is observed when using microwave heating.

Main results of the research are published in 12 scientific papers, including:

− in two articles published in international scientific journals that have a non-zero impact factor according to the information database of Thomson Reuters (ISI Web of Knowledge, Thomson Reuters);

− in two articles published in journals recommended by the Committee for Control in the Sphere of Education and Science of the Ministry of Education and Science of the Republic of Kazakhstan;

− in 8 theses of reports at foreign and republican international conferences and symposia.

The structure and scope of the thesis.

The thesis consists of an introduction, four sections, an opinion, as well as a list references of 184 titles. The work is presented in 123 pages, contains 64 figures and 10 tables.

The following conclusions can be made from **the results of this thesis:**

1) Obtained nanocrystalline particles of lanthanum orthophosphate by hydrothermal conditions with different morphological characteristics, crystallite sizes and crystal structure depending on pH, temperature, time and hydrothermal treatment method. Hydrothermal treatment at a temperature of 190 ° C and pH = 1 leads to the growth of highly anisotropic quasi-one-dimensional nanostructures. Lanthanum orthophosphate nanorods with a monazite structure are formed by the mechanism of oriented intergrowth and recrystallization of crystallites.

2) It was shown that to ensure the transformation of the hexagonal LaPO4 monoclinic phase under hydrothermal conditions, it is necessary to carry out processing at a temperature of at least 190 ° C. This effect can be associated with inhibition of the dehydration process, which leads to stabilization of the hexagonal phase. The formation of m-$LaPO_4$ nanocrystals with minimum sizes of about 7-8 nm does not depend on the hydrothermal treatment method, and these sizes are the minimum possible for the monazite structure under these conditions.

3) It was shown that hydrothermal treatment by microwave heating of the hydrothermal fluid provides nanocrystalline m-LaPO4 with the highest rate, smallest crystallite and particle sizes compared to hydrothermal treatment with an external method of heating the autoclave.

4) It was shown that at temperatures up to 500 ° C, lanthanum nanocrystalline orthophosphate with a rhabdophan structure loses crystalline hydrate water and at 520-540 ° C transforms into a nanocrystalline phase with a monazite structure. The transition is not associated with a change in crystallite size, i.e. nanocrystals of the anhydrous phase of lanthanum orthophosphate with a monazite structure both at the time of structural transformation and to temperatures of 600-700 ° C remain about 10 nm in size. Up to a temperature of 600 ° C, the process of formation of LaPO4 nanocrystals with both the structure of rhabdophan and monocyte proceeds

according to the nucleation mechanism, and only after 700 ° C the crystal growth process is activated.

5) It was shown that when doping lanthanum orthophosphate with yttrium, the unit cell parameters of the rhabdophan and monazite phases monotonically decrease with increasing yttrium content in the samples, which indicates the formation of solid solutions and the replacement of lanthanum atoms with relatively small atoms in the crystal structure of rhabdophan and monazite. The parameters of the xenotime cell are practically unchanged, which may indicate that lanthanum atoms are not included in the structure of xenotime YPO_4.

6) It was shown that upon the preparation of ceramics based on lanthanum orthophosphate mixed with LaP_3O_9 phase by sintering nanocrystalline powders at 1100 ° C, the porosity sharply decreases in the material to ~ 5% with a slight grain growth (200-400 nm). Material has extreme values of thermal conductivity (λ (25 ° C) = 3.2 W / mK), microhardness (H_v (25 ° C) = 4.6 ± 0.4 GPa), Young's modulus (E (25 ° C) = 132 ± 9 GPa), fracture toughness (K_{1c} (25 ° C) = 1.6 ± 0.1MPa · $m^{1/2}$). The coefficient of thermal expansion of the material weakly depends on the heat treatment mode of the material and is (8.2 ± 0.2) · 10^{-6} K^{-1}.

7) Comparison of data on the thermophysical, mechanical, and thermomechanical characteristics of the obtained materials based on the $LaPO_4$ composition with the inclusion of ~ 7.5 vol % of the LaP_3O_9 phase with similar properties of single-phase materials based on lanthanum orthophosphate. That showed the presence of an impurity phase of lanthanum metaphosphate does not significantly affect the possibility of using this material as a structural or heat-insulating material in the temperature range of at least 1500 ° C as an alternative to a single-phase material based on $LaPO_4$.

Evaluation of completeness of the solutions for the given tasks. All the objectives set for solving the purpose of this dissertation are solved in full. The hydrothermal method was used to synthesize lanthanum orthophosphate with the structure of monazite, the structure was deciphered by powder X-ray powder diffraction (using Rietveld refinement) and IR spectroscopy. The technological conditions for obtaining ceramics based on the obtained lanthanum orthophosphate are determined. The physicochemical methods determined the characteristics of the synthesized powders of the studied phosphates. The basic schemes for producing ceramics based on LaPO4 with a monazite structure obtained by the hydrothermal method were developed.

Thus, the objectives of the dissertation research have been achieved - lanthanum orthophosphate with a monazite structure was obtained by the hydrothermal treatment method, ceramic materials were obtained, and their physical and mechanical properties were studied.

Evaluation of technical and economic efficiency of the proposed solutions in the thesis. The solutions proposed in the framework of this dissertation can form the basis for obtaining crystalline matrices for immobilization of radioactive waste. The hydrothermal treatment method is less energy consuming in producing lanthanum orthophosphate with a monocytic structure.