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## Cesium containing $\beta$ -tridymite and maricite type phosphate ceramics: synthesis, structure and thermophysical properties

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The family of phosphates with a general formula  $A(I)B(II)PO_4$  ( $A(I)$  – monovalent metal;  $B(II)$  – divalent metal with a tetrahedral coordination) includes the groups of compounds with different structure types:  $\beta$ -tridymite, arcanite, glaserite, maricite, olivine. The compounds of this family have been studied because of their ferroelectric, electrochemical and luminescent properties, catalytic activity. Interest in  $\beta$ -tridymite structure phosphates, containing cesium in a high concentration and possessing thermal, chemical and radiation stability, are conditioned by an opportunity to use them as ceramic for  $^{137}\text{Cs}$   $\gamma$ -radiation sources for commercial and medical applications. Data on thermodynamic properties of  $\beta$ -tridymite type phosphates are limited by compounds  $\text{CsZnPO}_4$ ,  $\text{CsMgPO}_4$ . It is known, that some species of liquid radioactive wastes contain high concentrations of stable isotopes (sodium, nickel, iron, chromium) and radionuclide cesium  $^{137}\text{Cs}$ . Investigations of hydrolytic stability of single-phase  $\text{CsMgPO}_4$  ceramic, which was obtained by “hot” and “cold” pressure and spark plasma sintering method, were shown that these objects can be used as matrix for storage of cesium containing radioactive nuclear wastes.

In this work we have studied phase formation regularities and thermophysical properties of phosphates system  $\text{CsMPO}_4$  ( $M = \text{Co, Mn}$ ),  $\text{Cs}_{1-x}\text{Na}_x\text{NiPO}_4$  ( $0 \leq x \leq 1$ ).

The samples were synthesized by the co-precipitation method. The aqueous solution of phosphoric acid taken in accordance with the stoichiometry sample was added to stoichiometric mixture of metal nitrate or chloride solutions. The reaction mixture was dried at 353 K and thermally treated at 873 and 973 K. All the thermal treatment stages were alternated with grinding.

X-ray powder diffraction measurements indicated that limited solid solutions in  $\text{Cs}_{1-x}\text{Na}_x\text{NiPO}_4$  system of the tridymite and maricite structural types were obtained. The samples of  $\text{CsMnPO}_4$  and  $\text{CsCoPO}_4$  were crystallized at ambient temperature in tridymite structural type.

The samples were investigated by DTA method over the temperature range 298–1273 K. Thermal decomposition of  $\text{NaNiPO}_4$  ( $x = 1$ ) was researched.

Crystal structure of  $\text{CsNiPO}_4$  and  $\text{NaNiPO}_4$  were refined by Rietveld method at 298 K.  $\text{CsNiPO}_4$  crystal structure is characterized by three-dimensional framework, which is formed six-membered rings of tetrahedra  $\text{NiO}_4$  and  $\text{PO}_4$ , linked by common vertices, and by large cavities that are occupied by Cs cations.  $\text{NaNiPO}_4$  crystal structure consists of edge-sharing chains of  $\text{NiO}_6$  octahedra running parallel to the b axis, which are crossconnected by the  $\text{PO}_4$  tetrahedra, giving rise to large ten-coordinate cavities in which the Na ions are located.

The heat capacity measurements of  $\text{CsMnPO}_4$  and  $\text{CsCoPO}_4$  crystalline phosphates were performed over the temperature range 5–650 K. The temperature dependence of the heat capacity of crystalline  $\text{CsMnPO}_4$  showed that for the phosphate two phase transitions were found at 6.86 K and 126.99 K. The temperature dependence of the heat capacity of crystalline  $\text{CsCoPO}_4$  showed that for the phosphate three phase transitions were found at 311, 481 and 512 K. For the studied compounds the characteristics of phase transitions and the thermodynamic functions over the temperature range from T (0 to 650) K and standard entropy of formation at 298.15 K were calculated.

The thermal expansion behavior of  $\text{CsMPO}_4$  ( $M = \text{Ni, Co, Mn}$ ) and  $\text{NaNiPO}_4$  was studied by high-temperature X-ray powder diffraction at the temperature range 298–973 K. The samples expand anisotropically and belong

to high-thermal expansion materials. The prepared ceramics showed a volume thermal expansion coefficient of  $(3\div 7) \cdot 10^{-5} \text{ K}^{-1}$ .

The high specific content of the cesium in  $\beta$ -tridymite structure some phosphates in combination with thermal and hydrolytic stability account for the prospects for their using as safe ceramic materials for cesium  $\gamma$ -radiation sources.

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