Complex phosphates, containing elements with oxidation degrees +1 and +4

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Abstract

Crystal-chemical approach provided the scientific basis for the design of new compounds with a desirable structure and properties. In the present investigation we generalized and systematized our and literature data on synthesis, structures, thermal and physical characteristics of double and more complex anhydrous phosphates containing M+ and M4+ cations (M+ – H, NH4, Li, Na, K, Rb, Cs, Cu, Ag, Ti; M4+ – Ti, Zr, Hf, U, Th, Np, Pu). In order to study the influence of M+ and M4+ cationic radii on the stability regions of different structural types, we investigated the phase formation in the M+1–xM'+xM4+2(PO4)3 systems (M+, M'+ – Li, Na, K, Rb, Cs; M4+ – Ti, Zr, Hf) with smoothly varying compositions. The compounds and solid solutions were studied using an X-ray diffraction technique (using Rietveld method of structure refinement), electron microprobe analysis, IR-spectroscopy, adiabatic calorimetry (in the range 6–320 K) and differential scanning calorimetry (in the range 300–650 K).

Keywords: complex phosphates, structural type, synthesis, NZP, scandium tungstate, langbeinite, thermophysical properties

1. Introduction

Progress in the solid state chemistry is largely associated with creating multicomponent chemical substances, developing new processes (including synthesis) and conditions of materials processing. Crystal-chemical data are the keynote for the design of new compounds with a desirable structure and properties.

Double and triple phosphates of alkali (or other monovalent) and d(f)-elements are of interest for the
purpose of creating new practically useful materials. Some of these substances are characterized by framework structures with \([\{L_2(PO_4)_3\}]^{3p}\) frameworks \((L\) is an octahedrally coordinated cation). Such compounds are considered as hi-tech ceramics basis due to their stability in the extreme environmental conditions (high temperature and pressure, aggressive media, radiation), near-zero thermal expansion parameters, high ionic conductivity, catalytic activity [1].

The structural frameworks of the considered complex phosphates are formed by \(L_2(PO_4)_3\) fragments from corner-shared two \(LO_6\)-octahedra and three \(PO_4\)-tetrahedra. Different linking variants of \(L_2(PO_4)_3\) fragments lead to several structural types of the phosphates (Fig. 1). The structural types of \(NaZr_2(PO_4)_3\) (NZP/NASICON, mineral analog is kosnarite \(KZr_2(PO_4)_3\), sp. gr. \(R 3\bar{c}\)), \(Sc_2(WO_4)_3\) (SW, sp. gr. \(P 2_1/n\)), \(K_2Mg_2(SO_4)_3\) (langbeinite, sp. gr. \(P 2_1/3\)) are well-known [2-4].

The NZP structure has two types of framework cavity sites: \(M1\), surrounded by six nearest \(O\) atoms, and \(M2\), surrounded by eight nearest \(O\) atoms (Fig. 1a). Structure-forming \(L\) cations with mainly covalent metal–oxygen bonds usually have medium ionic radii (about 0.6…0.8 Å) and high oxidation degrees (+5…+3), and \(M\) sites are preferably occupied by cations with larger sizes and oxidation degrees +1 and +2, but on the whole all structural sites may be occupied by a wide variety of different cations.

The SW structure has several (depending on structure deformation) \(M\)-sites, surrounded by four-five nearest \(O\) atoms, in the framework cavities. The sizes of the cavity cations are usually smaller than those in the case of NZP structure and just slightly larger than the framework cation sizes.

The langbeinite structure contains two types of \(M\) interstitial positions surrounded by nine \(O\) atoms. So this structure is typical of the phosphates containing large cations (more than 1.5 Å) with low oxidation degrees (+1 and +2) in the cavity sites.

Thus, the realization of the given structural type depends on the nature (electron arrangement, radii, charges) of cations which form a substance, their ratio and occupation of structural positions. The unique NZP network structure enables a variety of chemical iso- and heterovalent substitutions in the framework as well as at the interstitial sites enclosed by the framework.

Fig. 1. Linking of \(L_2(PO_4)_3\) fragments in different structural types: (a) NZP (\(M1\) and \(M2\) – cavity sites); (b) scandium tungstate; (c) langbeinite

Within systematic investigation of complex phosphates, in the present work we generalized our and literature data on synthesis, structures and physicochemical characteristics of double and more complex
phosphates containing M⁺ and M⁴⁺ cations (M⁺ – H, NH₄, Li, Na, K, Rb, Cs, Cu, Ag, Ti; M⁴⁺ – Ti, Zr, Hf, U, Th, Pu, Np). In order to study the influence of M⁺ and M⁴⁺ cationic radii on the stability regions of different structural types, we investigated the phase formation in the M⁺₁₋ₓM⁺ₓM⁴⁺₂(PO₄)₃ systems (M⁺, M⁺ – Li, Na, K, Rb, Cs; M⁴⁺ – Ti, Zr, Hf). The phosphates were studied using an X-ray diffraction technique (using Rietveld method of structure refinement), electron microprobe analysis, IR-spectroscopy, adiabatic vacuum and differential scanning calorimetry.

2. Experimental

Theoretical generalization of literature data on complex phosphates was performed according to crystal chemical approach.

The crystalline phosphates M⁺₁₋ₓM⁺ₓM⁴⁺₂(PO₄)₃ (M⁺, M⁺ – Li, Na, K, Rb, Cs) with pairs of different alkali metals M and M' were synthesized by precipitating method (M⁴⁺ – Ti, Zr) and solid-state reactions (M⁴⁺ – Hf). The starting materials for their synthesis were Li₂CO₃, MCl (M = Na, K, Rb, Cs), TiOCl₂, ZrOCl₂, HfO₂ and NH₄H₂PO₄ of chemically pure grade.

In accordance with precipitating method the aqueous solutions of the starting reactants were mixed under continuous stirring, then the reaction mixture was dried at 363 K and thermally processed in unconfined air access at 873, 1073 and 1173 K for at least 24 h at each stage. Thermal stages were alternated with careful grinding. According to solid-state method, a fine mixture of the stoichiometric amounts of the reactants was dried at 473 K for 10–16 h, then thermally processed in unconfined air access at 873 K and 1073–1473 K with a step interval of 100 K for at least 24 h at each stage.

The obtained samples were white polycrystalline powders. Their chemical composition and homogeneity were checked with the aid of a CamScan MV-2300 microprobe with a Link INCA ENERGY 200C energy-dispersion detector. The uncertainty of the chemical composition determination was within 2.5 % mass.

Phase purity was established by powder X-ray diffraction (XRD) at Shimadzu XRD-6000 diffractometer (CuKα radiation). Unit cell parameters of the compounds were determined at room temperature from the corresponding diffraction patterns indexed within 2θ range 10–60°. The data for the structure refinement were collected between 2θ 5–110° with a step interval of 0.02°. Structure refinements were performed by the Rietveld method with Rietan-97 [5] and JANA2000 program [6].

The functional composition of the samples was confirmed by IR spectroscopy on a Shimadzu FTIR 8400S spectrometer within the range of 1400–400 cm⁻¹.

Heat capacity of some phosphates was studied in the range 6-320 K (BCT-3 calorimeter [7]) and 300-650 K (ADCTTB calorimeter) [8]. Thermal conductivity of some ceramic samples was measured in the range 298-673 K (IT-λ-400 device) [9].

3. Phase formation of complex phosphates containing M⁺ and M⁴⁺ cations (M⁺ – H, NH₄, Li, Na, K, Rb, Cs, Cu, Ag, Ti; M⁴⁺ – Ti, Zr, Hf, U, Th, Pu, Np) with different molar ratio M⁴⁺ : PO₄⁻³

The structure of known double and triple phosphates containing M⁺ and M⁴⁺ cations depends on a combination of factors. Crystal-chemical analysis showed that the main structure-forming factors for complex phosphates are the geometrical proportionality of M⁺ and M⁴⁺ ionic sizes and cation molar ratios.
3.1. Phosphates with molar ratio $M^{4+} : PO_4^{3-} = 1:1.5$ and $1:3$

The main approaches to the synthesis of single crystals and powders of the phosphates with the molar ratio $M^{4+} : PO_4^{3-} = 1:1.5$ and $1:3$ ($M'M^{4+}_2(PO_4)_3$ and $M''M^{4+}(PO_4)_3$) are based on the reactions taking place in: (a) solid phases, (b) aqueous or organic solutions (precipitating and hydrothermal methods), (c) in melts (in alkali chlorids, boron oxide).

The solid state method of $M'M^{4+}_2(PO_4)_3$ and $M''M^{4+}(PO_4)_3$ synthesis allows us to obtain high-purity substances for structural and other investigations. But this method requires a long time of thermal treatment stages, using high temperatures of synthesis and the careful grinding of reaction mixture.

Synthesis by precipitating method may be performed in aqueous solutions or organic media (Pechini method). Its advantages are synthesis procedure simplicity, high composition control and powder particle size, a short time and low temperature of thermal treatment. The method of crystallization in aqueous solutions becomes more universal if high pressures are used (hydrothermal method), but this procedure requires the determination of optimal synthesis conditions (reagents ratio, temperature, pressure).

Synthesis in melts of alkali chlorids or boron oxide allows us to obtain single crystals of the samples, but it requires a long drying and the cleaning of the obtained phosphates and using of high temperatures.

Structural data analysis showed that the main structural feature of $M'M^{4+}_2(PO_4)_3$ and $M''M^{4+}(PO_4)_3$ phosphates is belonging to the types with $\{[L_2(PO_4)_3]\}^\infty_3$ frameworks (NZP, scandium tungstate or langbeinite). Symmetry relationships [1] between the structures of such substances are shown in Fig. 2. The most symmetric space group $R\bar{3}c$ is in the center of the diagram. The NaZr$_2$(PO$_4$)$_3$ and KZr$_2$(PO$_4$)$_3$ representatives of the NZP family crystallize in this space group. The subgroups of $R\bar{3}c$ are situated higher. Lower symmetry of the structure is connected with insignificant distortion of framework as a result of including different atoms in framework and cavity sites. The space groups of the phosphates, which frameworks are built from the fragments of two L-octahedra and three P-tetrahedra, connected by another way than in NZP, are situated lower in the diagram.

![Fig. 2. Symmetry relationships between the structures of $\{[L_2(PO_4)_3]\}^\infty_3$ framework phosphates [1].](image)

The compounds described by the formula $M'M^{4+}_2(PO_4)_3$ are most widely distributed among double phosphates of $M^+$ and $M^{4+}$ cations (Table 1). Many representatives of the phosphates belong to NZP structure with trigonal symmetry. The comparison of X-ray diffraction results show the correlation between metal cations radio and unit cell parameters $a$ and $c$. The occupation of M1 sites by large ions leads an increase in $c$ parameter (Fig. 1). The process is connected with the deformation of PO$_4$ tetrahedra (an increase in O–P–O angle and decrease in distance between parallel columns), so $a$ parameter reduces.
The structure of lithium containing phosphates LiM^{4+}_3(PO_4)_{3} depends on synthesis method, treatment temperature and etc. LiTi_2(PO_4)_{3} and LiGe_2(PO_4)_{3} have NZP type structure, and lithium containing phosphates of zirconium, hafnium and tin crystallize in NZP structure and other polymorphic modifications (Table 1). The phosphates of d-transition metals with M^{+} – Na, K, Rb, NH_4, Cu, Ag crystallize in NZP structure (space groups R\bar{3}c, R\bar{3}). For KTi_2(PO_4)_{3} and NH_4M^{4+}_2(PO_4)_{3} (M^{4+} – Ti, Zr) langbeinite modifications are also known. The compounds CsM^{4+}_2(PO_4)_{3} (M^{4+} – Ti, Zr, Hf) crystallize in different structural types. The geometric factor, connected with the disposition of large cesium ions in cavities and small titanium ions in framework sites, leads to the crystallization of CsTi_2(PO_4)_{3} with cubic structure, differing from NZP and langbeinite structures.

Table 1. Literature data on the structures of M^{+}M^{4+}_2(PO_4)_{3} compounds

<table>
<thead>
<tr>
<th>Substance</th>
<th>Space group (crystal system)</th>
<th>Literature</th>
<th>Substance</th>
<th>Space group (crystal system)</th>
<th>Literature</th>
</tr>
</thead>
<tbody>
<tr>
<td>M^{+}Ti_2(PO_4)_{3}</td>
<td>R\bar{3}c</td>
<td>1</td>
<td>LiSn_2(PO_4)_{3}</td>
<td>R\bar{3}c (450 K), P\bar{1} (250 K)</td>
<td>13</td>
</tr>
<tr>
<td>(M^{+} – Li, Na, K, Rb, NH_4, Cu, Ag)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CsTi_2(PO_4)_{3}</td>
<td>I\bar{a}\bar{3}d</td>
<td>10</td>
<td>NaSn_2(PO_4)_{3}</td>
<td>R\bar{3}c (1073 K), R\bar{3} (673 K)</td>
<td>18</td>
</tr>
<tr>
<td>LiZr_2(PO_4)_{3}</td>
<td>R\bar{3}c (423 K), C\bar{1}, P2/n, Pbna (623 K)</td>
<td>11, 12</td>
<td>M^{+}Sn_2(PO_4)_{3}</td>
<td>R\bar{3}c</td>
<td>14</td>
</tr>
<tr>
<td>M^{+}Zr_2(PO_4)_{3}</td>
<td>R\bar{3}c</td>
<td>1</td>
<td>M^{+}Th_2(PO_4)_{3}</td>
<td>Cc</td>
<td>19</td>
</tr>
<tr>
<td>(M^{+} – Li, Na, K, Rb, Cs, H, NH_4, Cu, Ag)</td>
<td></td>
<td></td>
<td>NaTh_2(PO_4)_{3}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LiHF_2(PO_4)_{3}</td>
<td>R\bar{3}c (320 K), P\bar{1} (175 K)</td>
<td>13</td>
<td>KU_2(PO_4)_{3}</td>
<td>R\bar{3}c, C2/c</td>
<td>21</td>
</tr>
<tr>
<td>M^{+}HF_2(PO_4)_{3}</td>
<td>R\bar{3}c</td>
<td>1, 14</td>
<td>RbU_2(PO_4)_{3}</td>
<td>R\bar{3}c</td>
<td>21</td>
</tr>
<tr>
<td>(M^{+} – Na, K, Rb, Cs, H, NH_4, Cu, Ag)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LiGe_2(PO_4)_{3}</td>
<td>R\bar{3}c</td>
<td>15</td>
<td>NaNP_2(PO_4)_{3}</td>
<td>Trigonal, Cc</td>
<td>21</td>
</tr>
<tr>
<td>M^{+}Ge_2(PO_4)_{3}</td>
<td>R\bar{3}</td>
<td>16</td>
<td>KNP_2(PO_4)_{3}</td>
<td>Trigonal, Cc</td>
<td>21</td>
</tr>
<tr>
<td>(M^{+} – Na, K, Rb, Cs, H, NH_4, Cu, Ag)</td>
<td></td>
<td></td>
<td>NaNP_2(PO_4)_{3}</td>
<td>Trigonal, Cc</td>
<td>21</td>
</tr>
<tr>
<td>NaGeTi(PO_4)_{3}</td>
<td>R\bar{3}</td>
<td>17</td>
<td>RbNP_2(PO_4)_{3}</td>
<td>R\bar{3}c</td>
<td>21</td>
</tr>
</tbody>
</table>

The M^{+}M^{4+}_2(PO_4)_{3} compounds are characterized by high thermal stability. The melting (decomposition) temperatures of M^{+}Zr_2(PO_4)_{3} with M^{+} – Li, Na, K are 1963, 1923 and 1883 K, correspondingly. CsZr_2(PO_4)_{3} is stable up to 1500 K, it is a perspective material for radiocesium immobilization from nuclear wastes.

The Na_5M^{4+}_3(PO_4)_{3} (M^{4+} – Ti, Zr, Hf) phosphates crystallize in NZP structure [22]. Sodium cations (together with titanium, zirconium and hafnium) form structural framework \{[NaM^{4+}_3(PO_4)_3]^{3+}\}_{3n} and also completely occupy cationic sites in the framework cavities (M1 and M2). The compounds with the expected composition M_3Zr(PO_4)_2 with M – Li, K, Rb and Cs don’t exist, M_2Zr(PO_4)_2 and simple phosphate mixtures are identified in these systems.

So, in spite of structural distortions in NZP type compounds, the basic structural motive stays
invariable. This fact allows wide variations possibilities for cations in all structural sites without destruction of initial structural motive and formation of continuous solid solutions series.

Basing on crystal chemical approach, we predicted, synthesized and investigated the phases of variable compositions $M^{+1-x}M'^{+x}(PO_4)_3$ (M', M'' – Li, Na, K, Rb, Cs) of NZP type structure. The possibility of the solid solution formation in these systems is caused by crystallization of double phosphates in NZP type and relatively small difference between M' and M'' cationic radii.

The results of investigation showed that crystallographic parameters of solid solutions smoothly change within the regions of solid solution formation (Fig. 3, a). IR spectra gradually change with the smooth change of phosphates compositions (Fig. 3, b). Structural investigation by the Rietveld method revealed that alkali metals cations in the Na$_{0.5}$K$_{0.5}$M$^{4+}_2$(PO$_4$)$_3$ (M$^{4+}$ – Ti, Hf), K$_{0.5}$Rb$_{0.5}$Ti$_2$(PO$_4$)$_3$ and Li$_{0.5}$K$_{0.5}$Hf$_2$(PO$_4$)$_3$ were statistically distributed in completely occupied M1 sites [23].

Concentration limits of solid solution existence in the systems of titanium, zirconium and hafnium phosphates depend on relative difference in bond lengths of alkali metal–oxygen $\Delta d/d_1$ in double phosphates $M'M^{4+}_2$(PO$_4$)$_3$ and $M''M^{4+}_2$(PO$_4$)$_3$ (Table 2). Continuous solid solutions may exist at room temperature if $\Delta d/d_1$ does not exceed 11% (except Li$_{1-x}$K$_x$Hf$_2$(PO$_4$)$_3$ system). There are no noticeable solid solutions in the systems with $\Delta d/d_1 > 21\%$. As ionic radii of Hf$^{4+}$ (0.71 Å) and Zr$^{4+}$ (0.72 Å) are almost identical, there are almost the same phase formation regularities in the systems of zirconium and hafnium containing phosphates. The forming of continuous solid solutions in the Li$_{1-x}$K$_x$Hf$_2$(PO$_4$)$_3$ system is probably connected with hafnium atom electronic structure, leading to the stability of LiHf$_2$(PO$_4$)$_3$ rhombohedral modification (compared with LiZr$_2$(PO$_4$)$_3$).

Lower concentration limits of NZP structure in titanium phosphates may be explained by the small ionic radius of the framework forming cation Ti$^{4+}$ ($r_{Ti^{4+}} = 0.61$ Å) and the difficulty of the incorporation of large cations Cs$^+$ in the cavities of NZP [Ti$_2$(PO$_4$)$_3$]$^+$ framework. As it was shown earlier, CsTi$_2$(PO$_4$)$_3$
phosphate crystallizes in the structure with another spatial connection of framework-forming polyhedra. So the radius of the cavity cations has influence on the stability of the given framework type.

For the MM$^{4+}_2$(PO$_4$)$_3$ with large M$^{4+}$ f-element cations (Th, U, Np, Pu), obtained at temperatures from 773–873 to 1373–1573 K, crystal modifications related to KTh$_2$(PO$_4$)$_3$ are formed (Table 1). An increase in temperature up to 1773–1873 K leads to their polymorphic transitions with NZP structure formation. U, Np and Pu-containing compounds with M$^+$ – Rb crystallize in NZP structure. Compounds LiPu$_2$(PO$_4$)$_3$ and NaU$_2$(PO$_4$)$_3$ are not described in NZP modifications.

Table 2. Concentration regions of NZP solid solutions in the M$^+_{1-x}$M$^{4+}$$_x$(PO$_4$)$_3$ (M$^{4+}$ – Ti, Zr, Hf) systems

<table>
<thead>
<tr>
<th>M</th>
<th>M’</th>
<th>Ti</th>
<th>M</th>
<th>M’</th>
<th>Zr</th>
<th>M</th>
<th>M’</th>
<th>Hf</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li Na</td>
<td>0–1</td>
<td>9</td>
<td>K</td>
<td>Phase mixture</td>
<td>21</td>
<td>Phase mixture</td>
<td>24</td>
<td>0–1</td>
</tr>
<tr>
<td>Na K</td>
<td>0–1</td>
<td>11</td>
<td>Rb</td>
<td>0–0.3, 0.7–1</td>
<td>15</td>
<td>0–1</td>
<td>11</td>
<td>0–1</td>
</tr>
<tr>
<td>Cs</td>
<td>0–0.2</td>
<td>–</td>
<td>0–0.3, 0.7–1</td>
<td>13</td>
<td>0–1</td>
<td>0–0.3, 0.7–1</td>
<td>0–1</td>
<td></td>
</tr>
<tr>
<td>K Rb</td>
<td>0–1</td>
<td>4</td>
<td>Cs</td>
<td>0–0.3</td>
<td>–</td>
<td>0–1</td>
<td>3</td>
<td>0–1</td>
</tr>
<tr>
<td>Rb Cs</td>
<td>Phase mixture</td>
<td>–</td>
<td>0–1</td>
<td>2</td>
<td>0–1</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\[\Delta d/d_1 = (d_{M'-O} - d_{M-O})/d_{M-O}\]

3.2. Phosphates with molar ratio M$^{4+}$ : PO$_4$ = 1:2

Phosphates with molar ratio M$^{4+}$ : PO$_4$ = 1:2 (M$^+$_2M$^{4+}$(PO$_4$)$_3$, M$^+$(HPO$_4$)$_2$(PO$_4$)$_2$) crystallize in layered structures with low (monoclinic or triclinic) symmetry (Table 3). Such substances may have different polymorphic modifications depending on synthesis conditions.

Table 3. Crystallographic characteristics of M$^+$_2M$^{4+}$(HPO$_4$)$_2$(PO$_4$)$_2$ polymorphs

<table>
<thead>
<tr>
<th>Compound</th>
<th>Space group</th>
<th>Z</th>
<th>a, Å</th>
<th>b, Å</th>
<th>c, Å</th>
<th>(\beta (\alpha, \beta, \gamma)), °</th>
<th>Literature</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaZr(HPO$_4$)(PO$_4$)</td>
<td>P2/c</td>
<td>4</td>
<td>8.8666</td>
<td>5.3583</td>
<td>16.1284</td>
<td>115.96</td>
<td>24</td>
</tr>
<tr>
<td>KZr(HPO$_4$)(PO$_4$)</td>
<td>P2/c</td>
<td>4</td>
<td>9.2208</td>
<td>5.3280</td>
<td>16.6336</td>
<td>114.351</td>
<td>25</td>
</tr>
<tr>
<td>NH$_4$Zr(HPO$_4$)(PO$_4$)</td>
<td>P2/m</td>
<td>2</td>
<td>5.3284</td>
<td>6.6217</td>
<td>11.326</td>
<td>96.63</td>
<td>26</td>
</tr>
<tr>
<td>β-NaHf(HPO$_4$)(PO$_4$)</td>
<td>–</td>
<td>4</td>
<td>8.730</td>
<td>5.160</td>
<td>18.12</td>
<td>123.75</td>
<td>27</td>
</tr>
<tr>
<td>α-Na$_2$Zr(PO$_4$)$_2$</td>
<td>–</td>
<td>–</td>
<td>8.74</td>
<td>5.38</td>
<td>20.9</td>
<td>124.5</td>
<td>28</td>
</tr>
<tr>
<td>Na$_2$Zr(PO$_4$)$_2$</td>
<td>R$\bar{3}$c</td>
<td>6</td>
<td>8.792</td>
<td>–</td>
<td>22.723</td>
<td>–</td>
<td>2</td>
</tr>
<tr>
<td>K$_2$Zr(PO$_4$)$_2$</td>
<td>P$\bar{3}$</td>
<td>1</td>
<td>5.176</td>
<td>–</td>
<td>9.011</td>
<td>–</td>
<td>29</td>
</tr>
<tr>
<td>α-Na$_2$Hf(PO$_4$)$_2$</td>
<td>–</td>
<td>4</td>
<td>8.747</td>
<td>5.380</td>
<td>20.936</td>
<td>124.42</td>
<td>27</td>
</tr>
<tr>
<td>β-Na$_2$Hf(PO$_4$)$_2$</td>
<td>–</td>
<td>4</td>
<td>8.779</td>
<td>5.308</td>
<td>19.025</td>
<td>126.52</td>
<td>27</td>
</tr>
<tr>
<td>γ-Na$_2$Hf(PO$_4$)$_2$</td>
<td>–</td>
<td>–</td>
<td>8.794</td>
<td>–</td>
<td>22.698</td>
<td>–</td>
<td>27</td>
</tr>
<tr>
<td>Li$_2$Sn(PO$_4$)$_2$</td>
<td>R3</td>
<td>1</td>
<td>4.980</td>
<td>–</td>
<td>9.124</td>
<td>–</td>
<td>29</td>
</tr>
</tbody>
</table>
The $\text{M}^+\text{2M}^{4+}$(PO$_4$)$_2$ and $\text{M}^+\text{HM}^{4+}$(PO$_4$)$_2$ are obtained by thermal dehydration of corresponding aqueous phosphates. The dehydration and thermal decomposition of the compounds with $\text{M}^{4+}:\text{PO}_4^{3-} = 1:2$ lead to the formation of thermally stable framework phosphates.

At present, layered phosphates have no industrial applications, that may be connected with the absence of convenient methods of their obtaining.

4. Properties of complex phosphates with framework structures

Many complex phosphates may be used as high-technological ceramics with ultra-low thermal expansion, thermally stable and thermo-insulating materials and etc [1]. As the knowledge of thermophysical properties is necessary regardless of the field of substances practical using, we have studied heat capacity and heat conductivity of the representatives of NZP phosphates [31, 32].

Heat capacity of the NaM$^{4+}$(PO$_4$)$_3$ and Na$_5$M$^{4+}$(PO$_4$)$_3$ (M$^{4+}$ = Ti, Zr, Hf) compounds was measured in the temperature range 6–650 K. Heat capacity of the phosphates increases over the entire temperature range studied (Fig. 4). On the whole, for NZP phosphates of different compositions it amounts to 0.5–1.2 J/(g K) at 273–650 K and varies a little at $T > 500$ K. Heat capacity increases in the rows NaM$^{4+}$(PO$_4$)$_3 \rightarrow$ Na$_5$M$^{4+}$(PO$_4$)$_3$ as the number of atoms in the unit cell increases. Phase transitions on the heat capacity curves for Na$_5$Zr(PO$_4$)$_3$ and Na$_5$Hf(PO$_4$)$_3$ are connected with the disordering of Na$^+$ and Zr$^{4+}$ (Hf$^{4+}$) ions.

Fig. 4. Temperature dependences of heat capacity of NZP compounds: (1) Na$_5$Ti(PO$_4$)$_3$, (2) NaTi$_2$(PO$_4$)$_3$, (3) Na$_5$Zr(PO$_4$)$_3$, (4) NaZr$_2$(PO$_4$)$_3$, (5) Na$_5$Hf(PO$_4$)$_3$, (6) NaHf$_2$(PO$_4$)$_3$. 

$$C_p^0, \text{J/(mol K)}$$

$$C_p^0, \text{J/(mol K)}$$

$$C_p^0, \text{J/(mol K)}$$

$$T_c = 406.9 \text{ K}$$

$$T_c = 516.5 \text{ K}$$
Thermal conductivity of NaM\(^{4+}\)(PO\(_4\))\(_3\) and Na\(_2\)M\(^{4+}\)(PO\(_4\))\(_3\) (M\(^{4+}\) – Ti, Zr, Hf) ceramic samples (relative density 70–80%) was studied in the temperatures 298–673 K.

The approximated thermal conductivity values of the near-zero porosity of NZP ceramics samples at above temperature interval are (0.6–1.4 W/(m·K). It is important that on the whole NZP ceramics have lower heat conductivity than industrial stabilized zirconia, which is the main ceramic-forming component of widely applied thermal-resistant materials.

**Conclusion**

The presented investigation reflects the extension of the range of objects and crystal structures of complex phosphates containing M\(^+\) and M\(^{4+}\) cations. The comparison of these compounds shows the similarity of formal features (composition, simple structural polyhedra) and allows us to identify some structural regularities depending on the size factor (cation ionic radii), cation nature, water molecule presence and etc.

The phosphates with molar ratio M\(^{4+}\) : PO\(_4^3-\) = 1:2 crystallize in layered structures with monoclinic or triclinic symmetry, and phosphates with the molar ratio M\(^{4+}\) : PO\(_4^3-\) = 1:1.5 and 1:3 mainly crystallize in framework structures. All investigated structures are built from MO\(_6\), MO\(_9\), PO\(_4\) or HPO\(_4\) polyhedra. Among these compounds, crystalline phosphates of the framework NZP structure type are of interest because of their considerable thermal and chemical stability, resistance to radiation damage and other valuable physical and chemical properties that lead to industrial application possibilities as constructional and functional ceramics.

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References


