Thermodynamic properties of compounds with kosnarite-type structure

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Synthesis and thermodynamic properties of the crystalline kosnarite-type structure compounds, viz., AMe\(_{2.25-0.25}\)(PO\(_4\))\(_3\) (A = Na, Cs; Me = Ti, Zr, Hf; x = 0, 1 and 5) are reported. The heat capacities of the phosphates have been measured between 6 and 650 K. Investigations on the isostructural solid-to-solid phase transitions of Na\(_2\)Zr(PO\(_4\))\(_3\) and Na\(_2\)Hf(PO\(_4\))\(_3\) show centering of the off-centered Me atoms in octahedral sites and Na\(^+\) occupation transfer between sodium sites. The transition temperatures (\(T^\text{tr}_{\text{on}}\)), enthalpy of transition (\(\Delta\text{H}^\text{tr}\)), entropy of transition (\(\Delta\text{S}^\text{tr}\)), molar heat capacities (\(C^\text{p,m}\)), enthalpy (\(\Delta\text{H}(T) - \Delta\text{H}(0)\)), entropy (\(\Delta\text{S}(T)\)) and Gibbs) energy (\(\Delta\text{G}(T)\)) are calculated from the experimental data. Standard enthalpies of formation at \(T = 298.15\) K for the phosphates Zr\(_3\)(PO\(_4\))\(_3\), NaZr\(_2\)(PO\(_4\))\(_3\), CsZr\(_2\)(PO\(_4\))\(_3\) and Na\(_2\)Zr(PO\(_4\))\(_3\) are estimated by solution reaction calorimetry. By combining the data obtained by the two techniques, their Gibbs energies of formation at 298.15 K have been obtained. Thermodynamic functions of the reactions for solid-state synthesis of the compounds of kosnarite-type structure are calculated.

**Keywords:** Thermodynamic properties, Phase transitions, Solid-to-solid phase transitions, Calorimetry, Heat capacity, Phosphates, Kosnarite-type structures

The compounds of kosnarite \(K\text{Zr}_2(PO_4)_3\) type structure (also known as Na\(_2\)Zr(PO\(_4\))\(_3\), NZP, NASICON) have been widely investigated, in particular for practical applications as low thermal expansion materials, solid electrolytes for batteries and sensors, ceramic forms for nuclear waste immobilization, catalysts, luminescent materials, etc. The kosnarite type phosphates are easily synthesized, thermally very stable and can accommodate a large fraction of cation substitutions. Kosnarite-like phosphates are also used as model systems for studying broad and diverse isomorphism of cations and anions. A variety of compositions can be achieved based on the general crystal-chemical formula \([M1][M2]_3[[L_2(PO_4)_2]]_3\), where M1 and M2 are the cavity cations and L the framework-forming cations. All the types of crystallographical positions are available for cation substitutions in the kosnarite structure.

The standard thermodynamic functions of such substances are necessary for the optimization of their synthesis, formulating thermal balances, construction of phase diagrams and physiochemical analysis of model systems of these substances. The compounds Zr\(_{2.25}(PO_4)_3\) (\(\equiv\) Zr\(_3\)(PO\(_4\))\(_3\))\(_{3-4}\), CsZr\(_{2}(PO_4)_3\)\(_{5-7}\), NaMe\(_3\)(PO\(_4\))\(_3\)\(_{5-8,11}\) and Na\(_2\)Me(PO\(_4\))\(_3\)\(_{10,12-15}\) are known in literature and information about their structure and some thermodynamic properties are available. In the present study, kosnarite-type phosphates of the A\(_x\)Me\(_{2.25-0.25}\)(PO\(_4\))\(_3\) (A = Na, Cs; Me = Ti, Zr, Hf; x = 0, 1 and 5) systems are studied. The thermodynamic characteristics of A\(_x\)Me\(_{2.25-0.25}\)(PO\(_4\))\(_3\) phosphates are summarized. The study shows the applicability of ceramic synthesis for the compounds with kosnarite-type structure.

**Materials and Methods**

The compounds, Zr\(_{2.25}(PO_4)_3\), NaZr\(_2\)(PO\(_4\))\(_3\), CsZr\(_2\)(PO\(_4\))\(_3\) and Na\(_2\)Zr(PO\(_4\))\(_3\), were synthesized by precipitating method. The following reactants were used: NaNO\(_3\), CsCl, ZrOCl\(_2\)-8H\(_2\)O, H\(_2\)PO\(_4\). The phosphates, NaMe\(_2\)(PO\(_4\))\(_3\) and Na\(_2\)Me(PO\(_4\))\(_3\) (with Me = Ti and Hf), were synthesized by solid state reactions starting from NaCl, TiO\(_2\), HfO(NO\(_3\))\(_2\)-2H\(_2\)O and NH\(_4\)H\(_2\)PO\(_4\). The final temperatures of synthesis were in the range of 1023–1173 K. The thermal treatment stages were alternated with careful grinding.

All the chemicals were provided by REACHEM\(_{16}\) and their purity was not less than 99.5% (except ZrOCl\(_2\)-8H\(_2\)O and HfO(NO\(_3\))\(_2\)-2H\(_2\)O, purity > 98% due to uncertainty in the H\(_2\)O content). Hence, zirconium and hafnium concentrations in the solutions
taken for synthesis were confirmed gravimetrically with cupferron, following a documented procedure. The samples obtained were colorless polycrystalline powders. The confirmation of the desired compounds were obtained on a Shimadzu XRD-6000 powder X-ray diffractometer over the 2θ range of 10–60°. A Cu anode (30 mA and 30 kV) with filtered monochromatic Kα radiation (λ = 1.54178 Å) was used in the determination. The X-ray patterns of the samples contained only reflections of the synthesized phosphates. The unit cell parameters for the synthesized phosphates were derived from least squares refinement of powder reflections of the synthesized phosphates. The unit cell parameters for the synthesized phosphates were derived from least squares refinement of powder X-ray diffraction data (Table 1) and agreed favorably with those reported elsewhere. The homogeneity and chemical composition of the calorimetric samples were checked by electron microprobe analysis on a CamScan MV-2300 device with a Link Inca Energy 200C energy-dispersion detector.

Table 1 – The unit cell parameters of the studied phosphates

<table>
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<th>Comp.</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>V (Å³)</th>
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<tr>
<td>Zr₃(PO₄)₄</td>
<td>8.802(3)</td>
<td>23.06(4)</td>
<td>1547</td>
</tr>
<tr>
<td>NaTi₂(PO₄)₃</td>
<td>8.479(4)</td>
<td>21.77(2)</td>
<td>1355</td>
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<tr>
<td>Na₂Ti(PO₄)₃</td>
<td>9.063(4)</td>
<td>21.70(4)</td>
<td>1544</td>
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<tr>
<td>Na₂Zr(PO₄)₃</td>
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<td>22.77(1)</td>
<td>1528</td>
</tr>
<tr>
<td>CsZr(PO₄)₃</td>
<td>8.576(1)</td>
<td>24.91(1)</td>
<td>1586</td>
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<tr>
<td>Na₂Zr(PO₄)₃</td>
<td>9.162(9)</td>
<td>22.27(2)</td>
<td>1619</td>
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<tr>
<td>NaHf₂(PO₄)₃</td>
<td>8.780(5)</td>
<td>22.62(3)</td>
<td>1510</td>
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<tr>
<td>Na₂Hf(PO₄)₃</td>
<td>9.156(1)</td>
<td>22.25(1)</td>
<td>1615</td>
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</table>

The IR spectra of the samples recorded on an IR Fourier spectrometer (FSM-1201, Eurolab) over the range of 1400–400 cm⁻¹ agreed with literature data and showed no evidence of condensed phosphate groups.

The homogeneity and chemical composition of the samples were confirmed by electron microprobe analysis on a CamScan MV-2300 device with a Link Inca Energy 200C energy-dispersion detector operated at 20.0 kV. The results showed the homogeneity of the calorimetric samples. Microprobe analysis confirmed the stoichiometry of the samples to be close to the theoretical compositions. There were no substantial impurities (within w ≤ 0.005) of other elements in the samples.

The chemical compositions of the samples were also confirmed by chemical analysis. Known masses of the samples were dissolved in the HF aqueous solutions. The sodium and cesium mass contents were determined by an atomic absorption method on a Perkin-Elmer device. The titanium, zirconium and hafnium mass contents were determined gravimetrically with cupferron. The phosphorus mass content was determined colorimetrically using solutions of ammonium vanadate and ammonium molybdate. Due to the presence of fluoride, colorimetric determinations were performed with Perspex cells on a SF-46 spectrophotometer. Results of analyses proved that the stoichiometries of the obtained samples were close to ideal (Table 2).

### Adiabatic calorimetry

A precision automatic adiabatic calorimeter (BCT-3) was used to measure heat capacities over the temperature range 6–350 K. The calorimeter was constructed at the All Russian Metrology Research Institute, Moscow Region, Russia. The principle and structure of the adiabatic calorimeter are described in detail elsewhere.

To verify the accuracy of the calorimeter, the heat capacities of standard reference materials (K-3 benzoic acid and α-Al₂O₃) prepared at the Institute of Metrology of the State Standard Committee of the Russian Federation (Moscow, Russian Federation) were measured over the temperature range of 6–350 K. Results showed that the apparatus and the measurement technique enable the determination of the heat capacities with a relative

<table>
<thead>
<tr>
<th>Comp.</th>
<th>A (1)</th>
<th>A (2)</th>
<th>A (3)</th>
<th>Me (1)</th>
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<tr>
<td>CsZr(PO₄)₃</td>
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<td>33.20</td>
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uncertainty $\leq \pm 0.02$ (<0.1 J K\(^{-1}\) mol\(^{-1}\)) over the 6–15 K temperature range, $\pm 0.005$ (<0.3 J K\(^{-1}\) mol\(^{-1}\)) between 15 and 40 K, and $\pm 0.002$ (<0.9 J K\(^{-1}\) mol\(^{-1}\)) from 40–350 K. The phase transition temperatures were measured within about $\pm 0.01$ K and the enthalpies of transitions with a relative uncertainty of $\pm 0.002$ (<0.01 kJ mol\(^{-1}\)).

Heat capacity measurements were continuously and automatically carried out by the standard method of intermittently heating the sample and alternately measuring the temperature. The heating rate and temperature increments were controlled at 0.01 K s\(^{-1}\) and at 0.5–2 K. The heating duration was $\approx$10 min, and the temperature drift rates of the sample cell measured in an equilibrium period were always kept within 0.01 K s\(^{-1}\) during the experiments. Liquid helium and nitrogen were used as coolants. The titanium ampoule with the studied substance was filled with dry helium as a heat exchange gas to the pressure of 4 kPa at room temperature.

Differential scanning calorimetry

A differential scanning calorimeter operating on the principle of a triple thermal bridge (ADCTTB) was used to measure the heat capacities over the temperature range of 330–650 K. The design of the device and the measurement procedure of the heat capacities are given elsewhere\(^{20}\). The reliability of the calorimeter operation was checked by measuring the heat capacity of a standard sample of synthetic corundum and the thermodynamic characteristics of fusion of indium, tin and lead. It was found that with this calorimeter and the measurement technique it was possible to obtain heat capacity values with a maximum relative uncertainty of $\pm 0.02$ and transformation temperatures within 0.5 K. Since heat capacity of the compound was also measured over the temperature range 330–350 K in an adiabatic calorimeter (with a relative uncertainty of $\pm 0.002$) and the conditions of measurements in the dynamic device were chosen such that within this temperature interval the $C\text{\textprime}_{p,m}$ values measured with both the calorimeters coincided, it was assumed that at $T \geq 350$ K heat capacities were determined with relative uncertainty of $\pm 0.005–0.02$; 2–10 J K\(^{-1}\) mol\(^{-1}\). The heat capacities were obtained over the range of 330–650 K at the average rate of heating of 1–3 K s\(^{-1}\).

Solution calorimetry

An automated isothermal differential Calvet-type microcalorimeter (DAC-1-1-A) was employed to measure the enthalpies of solution at $T = 298.15$ K. Its design and operation have been described\(^{21}\). For calibration, a known current was passed through the cell assembly heater over a certain time. The reliability of the calorimeter operation was tested with a solution of chemically high-purity KCl in doubly distilled water. The value for the standard enthalpy of solution obtained by us $\Delta_{\text{sol}}H_{\text{m}}^\circ$ (298.15) = 17.6 ± 0.4 kJ mol\(^{-1}\) (average of ten experiments) was in agreement with the published value\(^{22}\) $\Delta_{\text{sol}}H_{\text{m}}^\circ$(298.15) = 17.58 ± 0.34 kJ mol\(^{-1}\). The enthalpies at 298.15 K ($\Delta H^\circ$) of the reactions studied are averages of 3–7 replicates. In conformity with IUPAC recommendations\(^{23}\), the uncertainty in $\Delta H^\circ$ is given as a standard deviation of the average. The net uncertainty in the enthalpy of formation was evaluated as $\sigma = (\Sigma \sigma_i^2)^{1/2}$, where $\sigma_i$ is the uncertainty in a single measurement.

Results and Discussion

The experimental values of the molar heat capacity of the studied phosphates $A_{\text{Me}}\text{Me}_2\text{Zr}_{2-x}\text{(PO}_4\text{)_3}$ between 7–650 K and the smoothed curves $C\text{\textprime}_{p} = f(T)$ are shown in Fig. 1. The heat capacities of the phosphates $\text{Zr}_x(\text{PO}_4)_3$ ($x = 0$), $\text{NaMe}_x(\text{PO}_4)_3$ ($x = 1$; $\text{Me} = \text{Ti, Zr, Hf}$), $\text{CsZr}_x(\text{PO}_4)_3$, $\text{Na}_5\text{Ti}(\text{PO}_4)_3$ ($x = 5$) increase gradually with increasing temperature with no phase change or thermal decomposition. Endothermic reversible phase transitions for $\text{Na}_2\text{Zr}(\text{PO}_4)_3$ and $\text{Na}_2\text{Hf}(\text{PO}_4)_3$ appear in the temperature intervals of 389–424 K and 476–572 K respectively. The phase transformations correspond to the centering of the off-centered zirconium and hafnium atoms in the octahedral sites and Na\(^+\) occupation transfer between sodium sites in the structure\(^{24}\). The transition on the $\text{Na}_2\text{Zr}(\text{PO}_4)_3$ curve is the first-order phase transition ($T^\circ_{\text{trs}} = 406.9$ K, $\Delta_{\text{trs}}H^\circ = 4.32 \pm 0.07$ kJ mol\(^{-1}\), $\Delta_{\text{trs}}S^\circ = 10.6 \pm 0.1$ J K\(^{-1}\) mol\(^{-1}\)), and the curve $C\text{\textprime}_{p,m} = f(T)$ for $\text{Na}_2\text{Hf}(\text{PO}_4)_3$ in the transformation temperature interval is characteristic of the $\lambda$-type phase transition ($T^\circ_{\text{trs}} = 516.5$ K, $\Delta_{\text{trs}}H^\circ = 1.54 \pm 0.01$ kJ mol\(^{-1}\), $\Delta_{\text{trs}}S^\circ = 3.00 \pm 0.03$ J K\(^{-1}\) mol\(^{-1}\)). Unfortunately, there is no data on $\text{Na}_2\text{Hf}(\text{PO}_4)_3$ structure at temperatures higher than the transition temperature. It is only known that there is off-centering of hafnium atoms in $\text{Na}_2\text{Hf}(\text{PO}_4)_3$ at room temperature. Hence, it is reasonable to assume that the phase transition is connected with the centering of hafnium atoms in its structure, although we cannot come to a conclusion about the difference
in nature of the $C_{p,m}^{0}$ versus $T$ curves for NaHf(PO$_4$)$_3$ and Na$_2$Zr(PO$_4$)$_4$. Na$_2$Ti(PO$_4$)$_3$ possessing no polymorphism contains a non-split titanium site and is characterized by lower mobility of Na$^{+}$ cations in relatively small framework cavities as compared to the zirconium and hafnium phosphates of the same general formula.

At 6–12 K, the heat capacity of the phosphates is described by the Debye function for the heat capacity: $C_{p,m}^{0} = nD(\theta_D/T)$, where $D$ denotes the Debye heat capacity function; the characteristic temperatures $\theta_D$ for phosphates were found at degrees of freedom $n = 3$ (refs 4, 7, 10, 11, 15). The $C_{p,m}^{0}$ values of the studied phosphates were extrapolated to 0 K with the same function. The experimental points of $C_{p,m}^{0}$ at temperatures $T > 12$ K were fitted by means of the least squares method using power and semilogarithmic polynomial dependencies. The root mean square deviations of the experimental points from the corresponding smoothed $C_{p,m}^{0} = f(T)$ curves were within ±0.006 in the range of 11–80 K, within ±0.003 in the range 80–200 K, within ±0.0005 in the range 200–350 K, and within ±0.005 over the range of 350–650 K, for all the samples under study.

The temperature dependence of the molar heat capacity $C_{p,m}^{0}$ (J mol$^{-1}$ K$^{-1}$) of NaHf$_2$(PO$_4$)$_3$ is described by Eq. (1) in the interval of 300–400 K,

$$C_{p,m}^{0} = -1.658937 \cdot 10^{4} + 3.173182 \cdot 10^{2} T - 2.489799 T^2$$
$$+ 1.036879 \cdot 10^{2} T^3 - 2.411144 \cdot 10^{5} T^4$$
$$+ 2.96897 \cdot 10^{5} T^5 - 1.5132 \cdot 10^{11} T^6,$$  

(1)

by Eq. (2), in the range 400–500 K,

$$C_{p,m}^{0} = -8.5689 \cdot 10^{4} + 1.1059523 \cdot 10^{3} T - 5.9226797 T^2$$
$$+ 1.6898735 \cdot 10^{2} T^3 - 2.7079278 \cdot 10^{5} T^4$$
$$+ 2.3105946 \cdot 10^{5} T^5 - 8.20213 \cdot 10^{12} T^6,$$  

(2)

and, in the temperature range from 500–650 K by Eq. (3),

$$C_{p,m}^{0} = -9.951 \cdot 10^{3} + 7.4867 T - 1.27228 \cdot 10^{2} T^2$$
$$+ 7.63 \cdot 10^{7} T^3 + 1.90183 \cdot 10^{8} T^4$$
$$- 1.42417 \cdot 10^{11} T^5,$$  

(3)

The smoothed heat capacity values at 298.15 K are shown in Table 3.

The heat capacities of the phosphates (for which no phase transitions were observed) at high temperatures were estimated as $C_{p,m}^{0} \to 3Rm$, where $R$ is the gas constant, $m$ is the number of atoms in the formulae unit. The calculated values were 574 J mol$^{-1}$ K$^{-1}$ for Zr$_3$(PO$_4$)$_4$, 449 J mol$^{-1}$ K$^{-1}$ for NaMe$_2$(PO$_4$)$_3$ (Me = Ti, Zr, Hf) and CsZr$_2$(PO$_4$)$_3$, 524 K for Na$_2$Ti(PO$_4$)$_3$. Experimental $C_{p,m}^{0}$ points for the studied phosphates at high temperatures were close to the above values. On shifting from NaMe$_2$(PO$_4$)$_3$ phosphates to Na$_3$Me(PO$_4$)$_3$ $C_{p,m}^{0}$ increases (Fig. 1), i.e. the general rule is observed according to which the growth of atomic quantity in a unit cell results in increase in heat capacity.

The thermodynamic functions of crystalline phosphates were calculated from the $C_{p,m}^{0}(T)$ curve in the range of 0–650 K. The enthalpies [$H(T) - H(0)$] and entropies $S(T)$ were calculated by using Eqs (4) and (5) respectively.

Fig. 1 – Temperature dependence of the heat capacity of the crystalline phosphates. [1, NaHf$_2$(PO$_4$)$_3$; 2, NaTi$_2$(PO$_4$)$_3$; 3, NaZr$_2$(PO$_4$)$_3$; 4, Na$_3$Hf(PO$_4$)$_3$; 5, Na$_2$Ti(PO$_4$)$_3$; 6, Na$_2$Zr(PO$_4$)$_3$; 7, Zr$_3$(PO$_4$)$_3$; 8, CsZr$_2$(PO$_4$)$_3$].
The free energy functions \[ G^0(T) - H^0(0) \] were obtained as follows:

\[ G^0(T) - H^0(0) = H^0(T) - H^0(0) - T S^0(T) \]

The obtained values of heat capacities and derived thermodynamic functions of the investigated phosphates at 298.15 K are given in Table 3.

As a part of the thermodynamic description of the studied phosphates, we estimated their standard thermochemical parameters of formation at \( T = 298.15 \) K. Using their standard entropies and reference data on the absolute entropy of the constituent compounds (Table 4),22,25 the standard molar entropies of formation were calculated (Table 5).

To derive the standard enthalpy of the formation of the investigated phosphates we used the thermodynamic cycles, considering enthalpies of the reaction of the phosphates with hydrofluoric acid.4, 26, 27.

In an earlier report, inaccurate value of the standard enthalpy of \( \text{Zr}_4(\text{PO}_4)_4 \) formation was given due to error in calculations using the corresponding thermodynamic cycle. The correct cycle is presented in Table 6.

When the present results for enthalpy of reaction of \( \text{Zr}_4(\text{PO}_4)_4 \) synthesis are combined with other data from the literature22, 25, the standard molar enthalpy of formation of \( \text{Zr}_4(\text{PO}_4)_4 \) was obtained as follows:

\[ \Delta H^0(\text{Zr}_4(\text{PO}_4)_4, \text{cr}, 298.15K) = H^0(298.15K) - 6 \times \Delta H^0(\text{H}_2\text{O}, \text{l}, 298.15K) + 6 \times \Delta H^0(\text{Zr}_2, \text{cr}, 298.15K) \]

The summary equations for the experimental schemes for the enthalpy calculations of other phosphate synthesis reactions are:

\[
\begin{align*}
\text{NaNO}_3(\text{cr}) + 2\text{ZrO}_2(\text{cr}) + 3\text{H}_2\text{PO}_4(\text{sln}, 2.8\text{H}_2\text{O}) &= \text{Na}_2\text{Zr}_2(\text{PO}_4)_3(\text{cr}) + \text{HNO}_3(\text{sln}, 8.4\text{H}_2\text{O}) + 4\text{H}_2\text{O}(\text{l}) \\
\text{CsCl(cr)} + 2\text{ZrO}_2(\text{cr}) + 3\text{H}_2\text{PO}_4(\text{sln}, 2.8\text{H}_2\text{O}) &= \text{Na}_2\text{Zr}_2(\text{PO}_4)_3(\text{cr}) + \text{HCl}(\text{sln}, 8.4\text{H}_2\text{O}) + 4\text{H}_2\text{O}(\text{l}) \\
5\text{NaNO}_3(\text{cr}) + \text{Zr}_2\text{O}_3(\text{cr}) + 3\text{H}_2\text{PO}_4(\text{sln}, 2.8\text{H}_2\text{O}) &= \text{Na}_2\text{Zr}_2(\text{PO}_4)_3(\text{cr}) + 5\text{HNO}_3(\text{sln}, 1.6\text{H}_2\text{O}) + 2\text{H}_2\text{O}(\text{l})
\end{align*}
\]

All the determined enthalpies of the phosphate formations are collected in Table 5.

The combination of the enthalpies of phosphate formation with their entropies of formation allowed us to calculate their standard molar Gibbs functions of formation (Table 5).
The analysis of conditions for the formation of the phosphates is important for their industrial production. Such compounds are usually synthesized by the ceramic technology:

\[ 3\text{ZrO}_2(\text{cr}) + 4\text{NH}_4\text{H}_2\text{PO}_4(\text{cr}) \rightarrow \text{Zr}_3(\text{PO}_4)_3(\text{cr}) + 4\text{NH}_3(\text{g}) + 6\text{H}_2\text{O}(\text{g}) \]

\[ \text{NaCl}(\text{cr}) + 2\text{ZrO}_2(\text{cr}) + 3\text{NH}_4\text{H}_2\text{PO}_4(\text{cr}) \rightarrow \text{NaZr}_2(\text{PO}_4)_3(\text{cr}) + 3\text{NH}_3(\text{g}) + 4\text{H}_2\text{O}(\text{g}) + \text{HCl}(\text{g}) \]

\[ \text{CsCl}(\text{cr}) + 2\text{ZrO}_2(\text{cr}) + 3\text{NH}_4\text{H}_2\text{PO}_4(\text{cr}) \rightarrow \text{CsZr}_2(\text{PO}_4)_3(\text{cr}) + 3\text{NH}_3(\text{g}) + 4\text{H}_2\text{O}(\text{g}) + \text{HCl}(\text{g}) \]

\[ 5\text{NaCl}(\text{cr}) + \text{ZrO}_2(\text{cr}) + 3\text{NH}_4\text{H}_2\text{PO}_4(\text{cr}) \rightarrow 5\text{Na}_2\text{Zr}(\text{PO}_4)_3(\text{cr}) + 3\text{NH}_3(\text{g}) + 2\text{H}_2\text{O}(\text{g}) + 5\text{HCl}(\text{g}) \]

The calculation of standard thermodynamic functions of phosphate synthesis at temperatures above 298.15 K was undertaken using Eqs (7) and (8).

\[ \Delta H_f^0(T) = \Delta H_f^0(298.15) + \Delta(nC_p,m)(T-298.15) \ldots(7) \]

\[ \Delta S_f^0(T) = \Delta S_f^0(298.15) + \Delta(nC_p,m)ln(T/298.15) \ldots(8) \]

assuming that the algebraic sum of the heat capacities of the reactants taking into account their stoichiometric coefficients \( \Delta(nC_p,m) \) at 298.15 K is constant in the temperature interval of 298.15 K to \( T \). The calculated Gibbs energies of reactions are positive at 298.15 K and become negative at \( T > 405 \) K for \( \text{Zr}_3(\text{PO}_4)_3 \), \( T > 430 \) K for \( \text{NaZr}_2(\text{PO}_4)_3 \), \( T > 410 \) K for \( \text{CsZr}_2(\text{PO}_4)_3 \) and at \( T > 570 \) K for \( \text{Na}_2\text{Zr}(\text{PO}_4)_3 \). Hence, derived temperatures of synthesis at standard pressure are not high and the kosnarite-like phosphates may be obtained by solid state reactions.

**Conclusions**

In the present study, the thermodynamic properties of the crystalline compounds \( \text{A}_x\text{Me}_{2.25-0.25}\text{(PO}_4)_3 \) \( (\text{A} = \text{Na}, \text{Cs}; \text{Me} = \text{Ti}, \text{Zr}, \text{Hf}; \ x = 0, 1 \ and \ 5) \) belonging to the vast family of solids with kosnarite-type structure have been analysed. The obtained values for \( C_{p,n}^0, [H_f^0(T) - H_f^0(0)], S_f^0(T), G_f^0(T) - H_f^0(0), \Delta H_f^0(298.15 \text{ K}), \Delta S_f^0(298.15 \text{ K}), \Delta G_f^0(298.15 \text{ K}) \) are crucial for thermochemistry of the studied substances family and allow accurate thermodynamic calculations in these systems. It is known that such phosphates may be suitable for applications requiring high thermal shock resistance (refractory lining, fixtures for high-tolerance brazing, semiconductor substrates, catalytic supports and optical benches), in electronics (solid electrolytes and substrates), in mechanical engineering and transportation systems (parts of motors) and in power engineering (thermal barrier coating materials, radiation resistant insulating materials and host structures for nuclear waste immobilization). The obtained thermodynamic data and analysis of the conditions of the phosphate synthesis will help to obtain materials with required thermophysical properties.

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**References**


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**Table 6 – Experimental scheme for the calculation of enthalpy of reaction of \( \text{Zr}_3(\text{PO}_4)_3 \) synthesis \( \Delta H_f^0(298.15 \text{ K}) \)** obtained from Hess cycle: \( \Delta H_f^0 = \Delta H_f^0(0) + \Delta H_f^0(0) - \Delta H_f^0(0) - \Delta H_f^0(0) \)

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction ( ^a )</th>
<th>( -\Delta H_f^0 ) (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>( 4\text{H}_3\text{PO}_4(\text{sol}, 2.8\text{H}_2\text{O}) + 893.3\text{HF(sol, 3.16\text{H}_2\text{O})} + 2834.1\text{H}_2\text{O(l)} ) = ( 4\text{H}_3\text{PO}_4\cdot 893.3\text{HF:2834.1H}_2\text{O(l) (sol 1)} )</td>
<td>4( (2.15 \pm 0.02) )</td>
</tr>
<tr>
<td>2.</td>
<td>( 3\text{ZrO}_2(\text{cr}) + \text{sol 1} = 3\text{H}_2\text{ZrF}_4\cdot 4\text{H}_3\text{PO}_4\cdot 875.3\text{HF:2840.1H}_2\text{O (sol 2)} )</td>
<td>3( (130.9 \pm 0.8) )</td>
</tr>
<tr>
<td>3.</td>
<td>( \text{Zr}_3(\text{PO}_4)_3(\text{cr}) + 893.3\text{HF(sol, 3.16\text{H}_2\text{O})} + 2822.9\text{H}_2\text{O} ) = ( 3\text{H}_2\text{ZrF}_4\cdot 4\text{H}_3\text{PO}_4\cdot 875.3\text{HF:2822.9H}_2\text{O (sol 3)} )</td>
<td>301\pm2</td>
</tr>
<tr>
<td>4.</td>
<td>17.2\text{H}_2\text{O(l)} + \text{sol 3} = \text{sol 2}</td>
<td>17.2( (0.56 \pm 0.01) )</td>
</tr>
<tr>
<td>5.</td>
<td>( 3\text{ZrO}_2(\text{cr}) + 4\text{H}_3\text{PO}_4(\text{sol, 2.8H}_2\text{O}) = \text{Zr}_3(\text{PO}_4)_3(\text{cr}) + 6\text{H}_2\text{O(l)} )</td>
<td>91 \pm 2</td>
</tr>
</tbody>
</table>

\( ^a \) (sol, 2.8H\(_2\)O): H\(_3\)PO\(_4\), dissolved in the ratio 1H\(_3\)PO\(_4\):2.8H\(_2\)O; (l): liquid.
16 *Chemical Reagents and High-pure Chemicals (Catalog)*, (REACHEM, Khimia, Moscow) 1990.