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SYNTHESIS, CHARACTERIZATION AND THERMODYNAMIC DATA OF COMPOUNDS WITH NZP STRUCTURE

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Data on synthesis, thermal behavior and thermodynamic properties for the NZP phosphates $NaMe_2(PO_4)_3$ and $Na_5Me(PO_4)_3$ (*Me*=Ti, Zr, Hf) are reported. The compounds were synthesized by sol-gel method and solid-state reactions and characterized by X-ray powder diffraction, IR spectroscopy, electron microprobe and chemical analysis. Their thermal behavior was studied by the DTA measurements. The heat capacities of the phosphates were measured between temperatures 7 and 650 K. The fractal dimensions for the phosphates were calculated. The obtained thermodynamic characteristics of these phosphates and also literature data for the compounds of NZP type structure are summarized.

Keywords: *calorimetry, heat capacity, NZP phosphates, synthesis, thermodynamic functions*

Introduction

The crystalline compounds of the sodium zirconium phosphate ($NaZr_2(PO_4)_3$, commonly known as NZP) type structure, have been widely investigated since their discovery and continue to be of great interest as they are proposed in a variety of industrial and scientific applications [1]. The NZP compounds potential to be used in automobile industry, space, telescope technology, etc. Also, they can be used as catalysts and catalytic supports, fast ionic conductors, hosts for immobilizing radioactive waste. Very important feature of many these materials is the high thermal stability and high thermal shock resistance. That's why, knowledge of thermal behavior and thermodynamic properties of the compounds have great fundamental meaning independently of field of their practical application.

These materials exhibit framework crystal structure formed by PO_4 tetrahedra sharing corners with LO_6 octahedra. There are two kinds of cavities, M1 and M2, within this framework. A variety of compositions of this structural family can be achieved based on general crystal-chemical formula $(M1)_{0\to1}(M2)_{0\to3}\{[L_2(TO_4)_3]^{p-}\}_{3\infty}$, where M1, M2 and L are different types of cations positions. This structure allows the high flexibility to cations of various nature and sizes. As a result there is an enormous number of formula types of compounds containing mono- to five-valent cations, belonging to this family. In particular, the concentration ranges for existence of the NZP structure for the systems $Na_xMe_{2.25-0.25x}(PO_4)_3$ (*Me*=Ti, Zr, Hf) correspond to various compounds and solid solutions with x values between 0 to 5 in the formula. The double phosphates of alkali metals and IVB group elements of the composition $NaMe_2(PO_4)_3$ (x=1) are well-known in literature [2–5]. There are data about sodium-rich phosphates $Na_5Ti(PO_4)_3$ [6] and $Na_5Zr(PO_4)_3$ [7] (x=5), in which sodium cations accommodate within crystallographic sites M1, M2 and L; that means they are involved in building the framework (together with titanium or zirconium) and populate all framework cavities. There are no data about the phosphate $Na_5Hf(PO_4)_3$, but the chemical analogy allows to suggest its existence.

As a part of a systematic investigation of the substances of NZP family carried out by our group [8–17], in this work the data on synthesis, thermal behavior and the heat capacity data for the NZP phosphates $NaMe_2(PO_4)_3$ and $Na_5Me(PO_4)_3$ (*Me*=Ti, Zr, Hf) are reported. The obtained thermodynamic characteristics of these phosphates and also literature data for the compounds of NZP type structure are summarized.

Experimental

Synthesis

The crystalline phosphates $NaZr_2(PO_4)_3$ and $Na_5Zr(PO_4)_3$ were synthesized by sol-gel method based upon reactions taking place in aqueous solution. The following reactants were used: $NaNO_3$, $ZrOCl_2\cdot8H_2O$, H_3PO_4. The solutions of phosphoric acid, taken in accordance with the stoichiometry of the phosphates, were dropped into the mixtures of aqueous solutions of sodium nitrate and zirconium oxychloride taken in the

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stoichiometric ratios under stirring at room temperature. The formed gels were dried at 353 K, thermally treated in unconfined air access at 873 and 1073 K with at least 24 h plateau. The thermal treatment stages were alternated with careful grinding.

The samples of crystalline $NaMe_2(PO_4)_3$ and $Na_5Me(PO_4)_3$ (*Me*=Ti, Hf) were synthesized by solid-state reactions starting from NaCl or Na_2CO_3, MeO_2 and $NH_4H_2PO_4$. Fine mixtures of the stoichiometric amounts of the reactants were thermally treated in unconfined air access at 473 K for 12 h to remove water and ammonia. The samples were carefully ground, calcinated at 873 K and then at higher temperatures with at least 24 h plateau at each step. Final temperatures of synthesis were 1073 K for $Na_5Me(PO_4)_3$ and 1473 K for $NaMe_2(PO_4)_3$.

All used chemicals were provided by Reachem, their purity was not less than 99.5% (except $ZrOCl_2{\cdot}8H_2O$, purity>98%). The purity of starting $ZrOCl_2{\cdot}8H_2O$ is explained by the uncertainty in H_2O content in this chemical. That is why the zirconium concentration in the solution taken for the synthesis was confirmed gravimetrically with cupferron, following the procedure [18].

Apparatus and measurement procedure

The phase purity of the synthesized samples was checked by X-ray diffraction on a DRON-3M diffractometer in the range 2θ=10–50°. A Cu anode (12 mA and 28 kV) with filtered monochromatic K_α radiation (λ=0.154178 nm) was used in the determination.

To confirm functional compositions of the phosphates, their IR spectra were recorded on a Specord-75 IR spectrophotometer. Samples were prepared by finely dispersing powder material on a KBr carrier. The vibrations were assigned by using standard characteristic intervals for group vibrations and literature data.

The homogeneity and chemical compositions of the samples were checked by electron microprobe analysis on a CamScan MV-2300 device with a Link INCA ENERGY 200C energy-dispersion detector.

The chemical compositions of the samples were also confirmed by chemical analysis. Known mass of the samples were dissolved in the HF aqueous solutions. The titanium, zirconium and hafnium mass contents were determined gravimetrically with cupferron, following the procedure [18]. The phosphorus mass contents were determined colorimetrically on a SF-46 spectrophotometer (perspex cells) according to the method employing solutions of ammonia vanadate and ammonia molybdate [19]. The alkaline elements contents were measured by atomic absorption spectrometry on a PerkinElmer 603 spectrometer.

DTA measurements were performed on a thermoanalytical complex KARAT [20] in the temperature interval from 298 to 1123 K. The samples were heated under static air, at a heating rate of 20 K min^{-1}.

The heat capacity of the phosphates in the temperature range of 7–350 K was measured with a BCT-3 low-temperature adiabatic vacuum calorimeter with an automatic system to maintain adiabatic conditions during measurements. The design of the calorimeter and the procedure of the heat capacity measurements have been described earlier [21]. From the calibration and testing results it was found that the uncertainty of the heat capacity measurements is within 2% at temperatures from 7 to 10 K, 0.5% between 10 and 40 K and 0.2% in the range 40–350 K.

An automated dynamic calorimeter (ADCTTB) operating by the principle of triple thermal bridge was used to measure the heat capacity, temperatures and enthalpies of phase transitions in the range from 330 to 650 K. The apparatus design and the measurement procedure were reported in [22, 23]. The uncertainty of the measuring of C_p^0 in the above temperature interval was about 1.5%, for the transition temperatures 0.3 K and for the transition enthalpies 0.8%.

Results and discussion

Samples and their characterization

The obtained samples were colorless polycrystalline powders. The X-ray patterns contained only reflections of the synthesized substances [2–7]. The

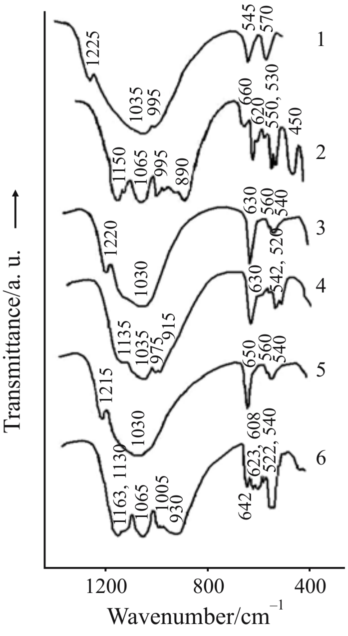

Fig. 1 The IR spectra of the phosphates: 1 – $NaTi_2(PO_4)_3$, 2 – $Na_5Ti(PO_4)_3$, 3 – $NaZr_2(PO_4)_3$, 4 – $Na_5Zr(PO_4)_3$, 5 – $NaHf_2(PO_4)_3$, 6 – $Na_5Hf(PO_4)_3$

new phosphate $Na_5Hf(PO_4)_3$ obtained by us, was the structural analog of the isoformulic titanium and zirconium phosphates. The symmetry of the obtained crystalline compounds is rhombohedral. The unit cell parameters for the synthesized phosphates were derived from least-squares refinement of powder X-ray diffraction data and given in Table 1.

According to the infrared data, the prepared samples (Fig. 1) can be attributed to the orthophosphate class. The characteristic absorption bands of orthophosphate PO_4 tetrahedrons are present in the spectra: broad strong bands in the 1250–1000 cm^{-1} range belonging to the stretching antisymmetric vibrations ν_3 (P–O bond), bands at nearly 995–890 cm^{-1} assigned to the stretching symmetric vibrations ν_1, and bands in the 670–400 cm^{-1} assigned to the bending vibrations ν_4 and ν_2. The IR spectra of the samples agreed with data presented elsewhere [17, 24] and showed no evidence of condensed phosphate groups.

The results of electron microprobe analysis have shown that the samples are homogeneous and consist of crystallites of size 1–50 μm. For example, back-scattered electron image of the sample of $NaTi_2(PO_4)_3$ is shown in Fig. 2. The elemental analysis (electron microprobe and chemical) have shown that their compositions were close to the theoretical values calculated for the formulae $NaMe_2(PO_4)_3$ and $Na_5Me(PO_4)_3$ (Table 2).

Table 1 The unit-cell parameters of the phosphates $NaMe_2(PO_4)_3$ (space group $R\bar{3}c$) and $Na_5Me(PO_4)_3$ (space group $R32$), Z=6

Substance	r^{4+}_{Me}/Å*	The unit-cell parameters		
		a/Å	c/Å	V/Å^3
$NaTi_2(PO_4)_3$	0.61	8.479(4)	21.77(2)	1355
$Na_5Ti(PO_4)_3$	0.61	9.064(4)	21.70(4)	1544
$NaZr_2(PO_4)_3$	0.72	8.802(1)	22.77(1)	1528
$Na_5Zr(PO_4)_3$	0.72	9.162(9)	22.27(2)	1619
$NaHf_2(PO_4)_3$	0.71	8.780(5)	22.62(3)	1510
$Na_5Hf(PO_4)_3$	0.71	9.156(1)	22.25(1)	1615

*effective radius of Me^{4+}

Thermal behavior and heat capacity

DTA curves of the compounds $NaMe_2(PO_4)_3$ showed the absence of any thermal effects in the temperature interval from 298 to 1123 K. The DTA curve of the phosphate $Na_5Ti(PO_4)_3$ showed an endothermic peak at ~1083 K, which probably corresponds to its melting with decomposition. The compounds $Na_5Zr(PO_4)_3$ and $Na_5Hf(PO_4)_3$ underwent reversible phase transitions with maximums at temperatures ~410 and ~520 K respectively. According to literature data [25], $Na_5Zr(PO_4)_3$ melts with decomposition at 1433 K.

The heat capacity of the crystalline phosphates $NaMe_2(PO_4)_3$ and $Na_5Me(PO_4)_3$ (Me=Ti, Zr, Hf) was measured in the temperature range of 7–650 K. From 160 to 180 experimental C^0_p points were taken in the range of 7 to 350 K. In the range of 330–650 K the C^0_p values were measured on continuous heating with scanning rate 1–3 K min^{-1}. Averaging of obtained on the both calorimeters C^0_p points was carried out by

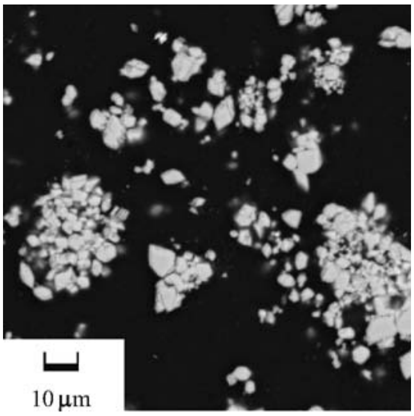

Fig. 2 Back-scattered electron image of the sample of $NaTi_2(PO_4)_3$

Table 2 Compositions of the calorimetric samples $NaMe_2(PO_4)_3$ and $Na_5Me(PO_4)_3$ according to 1 – theoretical values, 2 – electron microprobe data, 3 – chemical analysis

Substance	Mass fraction/%											
	Na			Me			P			O		
	1	2	3	1	2	3	1	2	3	1	2	3
$NaTi_2(PO_4)_3$	5.69	5.66	5.72	23.73	23.77	23.68	23.02	22.95	23.09	47.56	47.62	47.51
$Na_5Ti(PO_4)_3$	25.67	–	25.61	10.69	–	10.74	20.75	–	20.79	42.89	–	42.86
$NaZr_2(PO_4)_3$	4.69	4.67	4.70	37.21	37.19	37.22	18.95	18.96	18.94	39.15	39.18	39.14
$Na_5Zr(PO_4)_3$	23.41	–	23.34	18.58	–	18.63	18.92	–	18.84	39.09	–	39.19
$NaHf_2(PO_4)_3$	3.46	3.42	3.54	53.69	53.65	53.62	13.98	14.02	13.91	28.88	28.91	28.93
$Na_5Hf(PO_4)_3$	19.87	–	19.95	30.86	–	30.77	16.07	–	16.16	33.20	–	33.12

means of power and semilogarithmic polynomials. The root-mean-square deviation of the experimental values from the corresponding smoothed curves $C_p^0=f(T)$ did not exceed the uncertainty of the heat capacity measurements.

For example, the temperature dependence of the molar heat capacity (C_p^0/J mol^{-1} K^{-1}) of $NaHf_2(PO_4)_3$ in the interval 300–400 K is described by the equation:

$$C_p^0=-1.658937{\cdot}10^4+3.173182{\cdot}10^2T-2.489799T^2+\\1.036879{\cdot}10^{-2}T^3-2.411144{\cdot}10^{-5}T^4+\\2.96897{\cdot}10^{-8}T^5-1.5132{\cdot}10^{-11}T^6$$

in the range 400–500 K by the equation:

$$C_p^0=-8.5689{\cdot}10^4+1.1059523{\cdot}10^3T-5.9226797T^2+\\1.68987335{\cdot}10^{-2}T^3-2.7079278{\cdot}10^{-5}T^4+\\2.3105946{\cdot}10^{-8}T^5-8.20213{\cdot}10^{-12}T^6$$

and in the temperature range 500–650 K by the equation:

$$C_p^0=-9.9511{\cdot}10^2+7.4867T-1.27228{\cdot}10^{-2}T^2+\\7.63{\cdot}10^{-7}T^3+1.90183{\cdot}10^{-8}T^4-1.42417{\cdot}10^{-11}T^5$$

The experimental values of the heat capacity of the crystalline phosphates and the smoothed curves $C_p^0=f(T)$ are shown in Fig. 3. It is seen that for $Na_5Zr(PO_4)_3$ and $Na_5Hf(PO_4)_3$ endothermic reversible phase transitions appeared in the temperature intervals from 389–424 and 476–572 K respectively. As shown in [26], the isostructural polymorphic phase transition of $Na_5Zr(PO_4)_3$ corresponds to a centering of off-centered zirconium atoms in octahedral sites and Na^+ occupation transfer between sodium sites in the structure. From the structural and calorimetric data, this order-disorder transition, which is accompanied by an abrupt change of the cell parameters [11, 26], its volume and absorption of a quantity of heat, is characterized as the first-order phase transition. The analogy of the structure of phosphates $Na_5Zr(PO_4)_3$ and $Na_5Hf(PO_4)_3$ let us suppose that the nature of solid-to-solid phase transition of the hafnium containing phosphate is probably also connected to processes of cations ordering-disordering. The curve $C_p^0=f(T)$ for $Na_5Hf(PO_4)_3$ in the transition temperature interval is characteristic for the λ-type phase transition.

The absence of polymorphic transition for the phosphate $Na_5Ti(PO_4)_3$ is provided by the absence of off-centering of titanium atoms [6] and limited occupation transfer between sodium sites in the unit-cell of less volume than in zirconium and hafnium containing substances (Table 1).

The characteristic data of the phase transitions of the investigated phosphates are summarized in Table 3. The temperatures corresponding to the maximum values of the apparent heat capacity in the transition ranges are regarded as transition temperatures. The enthalpies of transitions $\Delta_{trs}H^0$ were obtained graphically from the dependences $C_p^0=f(T)$. The entropies of the phase transitions found by numerical integration of the dependences $C_p^0=f(\ln T)$ and from the formula $\Delta_{trs}S^0=\Delta_{trs}H^0/T_{trs}$ coincided.

The heat capacity of the phosphates $NaMe_2(PO_4)_3$ (*Me*=Ti, Zr, Hf) and $Na_5Ti(PO_4)_3$ has no any special features: it gradually increases with rising temperature and varies a little at temperatures above 500 K.

In view of a development of models describing the temperature dependence of the heat capacity, it

Table 3 Thermodynamic characteristics of phase transitions of $Na_5Zr(PO_4)_3$ and $Na_5Hf(PO_4)_3$

Substance	T_{trs}/ K	$\Delta_{trs}H^0$/ kJ mol^{-1}	$\Delta_{trs}S^0$/ J mol^{-1} K^{-1}
$Na_5Zr(PO_4)_3$	406.9	4.32	10.6
$Na_5Hf(PO_4)_3$	516.5	1.54	3.0

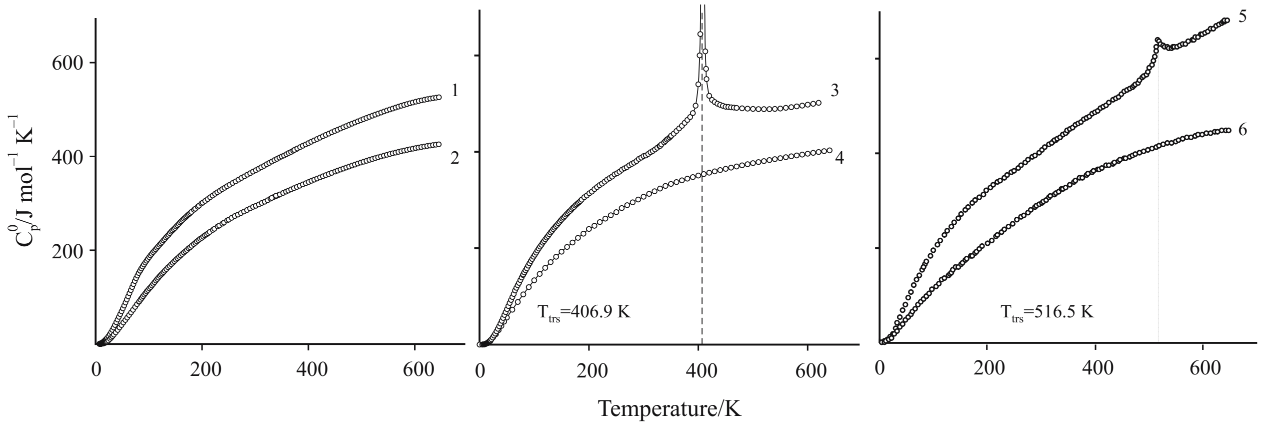

Fig. 3 Temperature dependence of the heat capacity of the crystalline phosphates: 1 – $Na_5Ti(PO_4)_3$, 2 – $NaTi_2(PO_4)_3$, 3 – $Na_5Zr(PO_4)_3$, 4 – $NaZr_2(PO_4)_3$, 5 – $Na_5Hf(PO_4)_3$, 6 – $NaHf_2(PO_4)_3$

was of interest to evaluate the fractal dimension D_{fr} for the investigated phosphates. In the fractal theory of heat capacity [15, 27–29] of solids, D_{fr} is the exponent at T in the heat capacity function. The significance of D_{fr} value for solids gives information on the heterodynamics of their structure. As demonstrated in [27], D_{fr} can be estimated from a $\ln C_v$ *vs.* $\ln T$ plot. It is found that at temperatures between 20 and 50 K $D_{\mathrm{fr}}=3$ for the phosphates $NaMe_2(PO_4)_3$ and $Na_5Me(PO_4)_3$. This means that all the investigated phosphates have spatial (three-dimensional) structure.

At $T<20$ K the heat capacity of the phosphates is described by Debye function for the heat capacity: $C_p^0=nD(\theta_D/T)$, where D denotes the Debye heat capacity function. Characteristic temperatures θ_D for the phosphates were found at the number of degrees of freedom $n=3$. The obtained values are given in Table 4. For the studied phosphates in the rows:

$$NaMe_2(PO_4)_3 \to Na_5Me(PO_4)_3 \ (Me=\mathrm{Ti, Zr, Hf})$$

the decrease of θ_D value is observed. The difference in the θ_D significances, given at the same n value, is connected with different flexibility of the structural frameworks of the substances and allows to make conclusion about lower flexibility of the $NaMe_2(PO_4)_3$ structural frameworks compared with the $Na_5Me(PO_4)_3$. The frameworks of crystalline structure of $Na_5Me(PO_4)_3$ include more flexible sodium (instead of Me) containing polyhedrons. This fact provides earlier (at lower temperatures) activation of atoms oscillations in their structures.

Table 4 Characteristic temperatures θ_D for the phosphates $NaMe_2(PO_4)_3 \to Na_5Me(PO_4)_3$ ($n=3$)

Substance	θ_D/K	ΔT/K	Uncertainty/%
$NaTi_2(PO_4)_3$	169.1	7–12	1.1
$Na_5Ti(PO_4)_3$	104.1	7–11	2.0
$NaZr_2(PO_4)_3$	128.8	9–12	2.2
$Na_5Zr(PO_4)_3$	117.8	7–11	1.0
$NaHf_2(PO_4)_3$	132.0	6–11	1.0
$Na_5Hf(PO_4)_3$	100.6	6–11	1.9

The C_p^0 values of the studied phosphates were extrapolated to 0 K with the Debye function to calculate the thermodynamic functions. The calculations of enthalpies $[H^0(T)–H^0(0)]$ and entropies $S^0(T)$ of phosphates were made by numerical integration of the relations $C_p^0=f(T)$ and $C_p^0=f(\ln T)$, respectively. The Gibbs functions $[G^0(T)–H^0(0)]$ were calculated from the values of $[H^0(T)–H^0(0)]$ and $S^0(T)$ at corresponding temperatures. The absolute entropies of phosphates and literature data [30, 31] allowed us to calculate the standard entropies of phosphates formation at 298.15 K.

The obtained values of thermodynamic functions $[H^0(T)–H^0(0)]$, $S^0(T)$, $[G^0(T)–H^0(0)]$ of phosphates at 298.15 K are given in Table 5, the standard functions of their formation (together with literature data [10, 12, 13]) are presented in Table 6. The known thermodynamic tendencies are observed: the heat capacities, enthalpies $[H^0(T)–H^0(0)]$ and entropies $S^0(T)$ of phosphates $Na_5Me(PO_4)_3$ are higher than for $NaMe_2(PO_4)_3$ (Me=Ti, Zr, Hf). The heat capacity val-

Table 5 The heat capacity and standard thermodynamic functions for phosphates $NaMe_2(PO_4)_3$ and $Na_5Me(PO_4)_3$ at T=298.15 K

Substance	C_p^0/J mol^{-1} K^{-1}	$[H^0(T)–H^0(0)]$/kJ mol^{-1}	$S^0(T)$/J mol^{-1} K^{-1}	$[G^0(T)–H^0(0)]$/kJ mol^{-1}
$NaTi_2(PO_4)_3$	293.2	48.16	293.4	39.31
$Na_5Ti(PO_4)_3$	368.9	65.69	424.0	60.73
$NaZr_2(PO_4)_3$	305.9	51.73	327.1	45.80
$Na_5Zr(PO_4)_3$	388.9	68.07	433.0	61.04
$NaHf_2(PO_4)_3$	292.3	45.79	285.9	39.44
$Na_5Hf(PO_4)_3$	402.4	70.18	452.3	64.67

Table 6 The thermodynamic functions of formation for phosphates $NaMe_2(PO_4)_3$ and $Na_5Me(PO_4)_3$ at T=298.15 K

Substance	$-\Delta_f H^0$/kJ mol^{-1}	$-\Delta_f S^0$/J mol^{-1} K^{-1}	$-\Delta_f G^0$/kJ mol^{-1}	$\lg K_f^0$
$NaTi_2(PO_4)_3$	–	1174(2)	–	–
$Na_5Ti(PO_4)_3$	–	1217(2)	–	–
$NaZr_2(PO_4)_3$	5231(4)	1156(2)	4886(4)	859
$Na_5Zr(PO_4)_3$	5586(4)	1217(2)	5223(4)	915
$NaHf_2(PO_4)_3$	–	1207(2)	–	–
$Na_5Hf(PO_4)_3$	–	1202(2)	–	–

ues of the phosphates (for which there were no phase transitions observed) at high temperatures ($T\to\infty$) were estimated as $C_p^0\to 3Rn_{at}$, where R is gas constant, n_{at} is number of atoms in the formulae unit. The calculated values were 449 J mol^{-1} K^{-1} for $NaMe_2(PO_4)_3$ (Me=Ti, Zr, Hf) and 524 J mol^{-1} K^{-1} for $Na_5Ti(PO_4)_3$. These data are in good agreement with the measured heat capacities of phosphates (taking into account the uncertainty of experiments): C_p^0=427, 403 and 448 J mol^{-1} K^{-1} for $NaTi_2(PO_4)_3$, $NaZr_2(PO_4)_3$ and $NaHf_2(PO_4)_3$, 527 J mol^{-1} K^{-1} for $Na_5Ti(PO_4)_3$ at temperatures 620–650 K.

On the whole the heat capacities of the studied phosphates are in the usual interval for the NZP compounds family [9, 10, 12, 13, 15, 16, 32–36]: 0.5–1.2 J g^{-1} K^{-1} in the temperature range 273–650 K. For different phosphates of the family the C_p^0 depend on the formula and elemental composition of the substance, nature of chemical bonds in it and varies a little for the phosphates with the same formula (for example, $NaMe_2(PO_4)_3$). The big negative values of the Gibbs functions of the NZP phosphates formation (Table 6) indicate their high thermodynamic stability at T=298.15 K and standard pressure.

Conclusions

The general aim of these work was to report the data on synthesis, thermal behavior and thermodynamic properties for the crystalline compounds $NaMe_2(PO_4)_3$ and $Na_5Me(PO_4)_3$ (Me=Ti, Zr, Hf) belonging to the vast family of solids with NZP structure. The heat capacities of the phosphates were measured between temperatures 7 and 650 K. The thermodynamic functions $[H^0(T)-H^0(0)]$, $S^0(T)$, $[G^0(T)-H^0(0)]$ of phosphates and the standard functions of their formation at 298.15 K were calculated. Phase transitions for the phosphates $Na_5Me(PO_4)_3$ (Me=Zr, Hf) were found. Accumulation of the obtained thermodynamic data and analysis of the conditions of the phosphates synthesis will help to obtain materials with required thermal characteristics.

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References

1 V. I. Pet'kov and A. I. Orlova, Inorg. Mater., 39 (2003) 1013.

2 J. L. Rodrigo, P. Carrasco and J. Alamo, Mater. Res. Bull., 24 (1989) 611.

3 M. Šljukić, B. Matković, B. Prodić and S. Scavnicar, Croatica Chem. Acta, 39 (1967) 145.

4 H. Y.-P. Hong, Mater. Res. Bull., 11 (1976) 173.

5 B. E. Taylor, A. D. English and T. Berzins, Mater. Res. Bull., 12 (1977) 171.

6 S. Krimi, I. Mansouri, A. El. Jazouli and J. P. Chaminade, J. Alloys Compd., 188 (1992) 120.

7 J. P. Boilot, G. Collin and R. Comes, J. Solid State Chem., 50 (1983) 91.

8 V. I. Pet'kov, A. I. Orlova and D. A. Kapranov, J. Therm. Anal Cal., 54 (1998) 71.

9 V. I. Pet'kov, K. V. Kir'yanov, A. I. Orlova and D. B. Kitaev, Inorg. Mater., 36 (2000) 387.

10 V. I. Pet'kov, K. V. Kir'yanov, A. I. Orlova and D. B. Kitaev, J. Therm. Anal. Cal., 65 (2001) 381.

11 V. I. Pet'kov, A. I. Orlova, G. N. Kazantsev, S. G. Samoilov and M. L. Spiridonova, J. Therm. Anal. Cal., 66 (2001) 623.

12 V. I. Pet'kov, K. V. Kir'yanov and E. A. Asabina, Russ. J. Phys. Chem., 77 (2003) 707.

13 V. I. Pet'kov, E. A. Asabina, A. V. Markin and K. V. Kir'yanov, Thermochim. Acta, 403 (2003) 185.

14 V. I. Pet'kov, V. N. Loshkarev and E. A. Asabina, Rus. J. Appl. Chem., 77 (2004) 184.

15 V. I. Pet'kov, E. A. Asabina, K. V. Kir'yanov, A. V. Markin, N. N. Smirnova, D. B. Kitaev and A. M. Kovalsky, J. Chem. Thermodyn., 37 (2005) 467.

16 V. I. Pet'kov, E. A. Asabina, A. V. Markin, N. N. Smirnova and D. B. Kitaev, J. Therm. Anal. Cal., 80 (2005) 695.

17 E. A. Asabina, V. I. Pet'kov, A. V. Markin, N. N. Smirnova and A. M. Kovalsky, Russian J. Phys. Chem., 79 (2005) 1936.

18 W. Hillebrand and G. Lundell, Applied inorganic analysis, John Wiley and Sons, Inc., New York, Chapman and Hall, London 1953.

19 F. Umbland, A. Janssen, D. Thierig and G. Wünsch, Theorie und praktische Anwendung von Komplexbildnern, Akademische Verlagsgesellschaft, Frankfurt am Main 1971.

20 V. P. Egunov, Introduction in thermal analysis, SamVen, Samara 1996 (in Russian).

21 R. M. Varuschenko, A. I. Druzhinina and E. L. Sorkin, J. Chem. Thermodyn., 29 (1997) 623.

22 M. Yagfarov, Sh. Zh. Fiz. Khim., 43 (1969) 1620, (in Russian).

23 A. G. Kabo and V. V. Diky, Thermochim. Acta, 347 (2000) 79.

24 V. S. Kurazhkovskaya, A. I. Orlova, V. I. Pet'kov, D. V. Kemenov and L. N. Kuplunnik, J. Struct. Chem., 41 (2000) 61.

25 S. J. Milne and A. R. West, Solid State Ionics, 9/10 (1983) 865.

26 J. P. Boilot, G. Collin and R. Comes, Solid State Commun., 45 (1983) 231.

27 T. S. Yakubov, Docl. Akad. Nauk SSSR, 310 (1990) 145 (in Russian).

28 A. D. Izotov, O. V. Shebershneva and K. S. Gavrichev, In: Proceedings of the all Russian conference on thermal analysis and calorimetry, Kazan, 1996, 200 (in Russian).

29 V. B. Lazarev, A. D. Izotov, K. S. Gavrichev and O. V. Shebersheneva, Thermochim. Acta, 269/270 (1995) 109.
30 J. D. Cox, D. D. Wagman and V. A. Medvedev, Eds, CODATA Key values for thermodynamics, 1989.
31 V. P. Glushko, Ed., Thermal constants of substances, 1–10 (1965–1981) (in Russian).
32 J. Maier, U. Warhus and E. Gmelin, Solid State Ionics, 18/19 (1986) 969.
33 U. Warhus, J. Maier and A. J. Rabenau, Solid State Chem., 72 (1988) 113.
34 M. Barj, K. Chhor, L. Abello, C. Pommier and C. Delmas, Solid State Ionics, 28/30 (1988) 432.
35 L. Abello, K. Chhor, M. Barj, C. Pommier and C. Delmas, J. Mater. Sci., 24 (1989) 3380.
36 M. V. Krishnaiah, J. Joseph, G. Seenivasan and K. V. Govindan Kutty, J. Alloys Compd., 351 (2003) 212.

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