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THERMODYNAMIC DATA OF THE NZP COMPOUNDS FAMILY

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The thermodynamic data for NZP compounds $MZr_2(PO_4)_3$ (*M*=Na, K, Rb, Cs, $Zr_{0.25}$) and $Na_5D(PO_4)_3$ (*D*=Ti, Zr) are reported. The heat capacities of the phosphates were measured between *T*=7 and *T*=640 K. The standard enthalpies entropies, and Gibbs functions of formation at *T*=298.15 K were derived. The obtained thermodynamic characteristics of phosphates of the NZP type structure and literature data are summarized. Thermodynamic functions of reactions of solid-state synthesis were calculated and the usability of ceramic technology for obtaining NZP compounds was proved.

Keywords: *calorimetry, enthalpy of solution, heat capacity, phosphates, thermodynamic functions*

Introduction

The crystalline compounds and solid solutions of the $NaZr_2(PO_4)_3$ (NZP) type structure form a large family of inorganic substances attracting wide research interest due to their stability to the extreme environmental conditions (high temperature and pressure, aggressive media, radiation), high thermophysical properties (thermal shock resistance, near-zero thermal expansion, low thermal conductivity), ionic conductivity, catalytic activity.

The family of NZP compounds is already known not only for its useful physico-chemical properties, but also for flexibility with regard to ionic substitution. Extremely wide variations of cation composition with the conservation of crystallographic characteristics close to those of NZP permit to create new materials with desired properties [1]. The general crystal chemical formula for NZP is described as $(M1)(M2)_3\{[L_2(TO_4)_3]^{p-}\}_{3\infty}$ with the structure containing a three-dimensional framework of strongly bonded $L_2(TO_4)_3$ units made up of corner-sharing LO_6 octahedra and TO_4 tetrahedra. Two kinds of cavities (M1 and M2) within the framework are formed.

Though plenty of information on the synthesis, crystal structure and many important properties of NZP substances is available, thermodynamic information on these compounds is scanty [2–6]. Nevertheless, knowledge of thermal behaviour and thermodynamic properties of NZP materials is needed for solving the problem of their controlled synthesis and for a further discussion of their possible applications in different fields and probable optimizations.

As a part of a systematic investigation of the substances of NZP family carried out by our group [7–13], the thermodynamic data for NZP compounds $MZr_2(PO_4)_3$ (*M*=Na, K, Rb, Cs, $Zr_{0.25}$) and $Na_5D(PO_4)_3$ (*D*=Ti, Zr) are reported. The obtained thermodynamic characteristics of phosphates of the NZP type structure and also literature data for other NZP compounds are summarized. Thermodynamic aspects of the synthesis of some NZP substances are analyzed.

Experimental

The crystalline NZP compounds $MZr_2(PO_4)_3$ (*M*=Na, K, Rb, Cs, $Zr_{0.25}$) and $Na_5Zr(PO_4)_3$ were synthesized by sol–gel procedure, as described in detail elsewhere [7]. The following reagent grade reactants were used: $NaNO_3$, KNO_3, RbCl, CsCl, $ZrOCl_2 \cdot 8H_2O$, H_3PO_4. The sample of crystalline $Na_5Ti(PO_4)_3$ was synthesized by solid-state reactions [14] starting from Na_2CO_3, TiO_2 and $NH_4H_2PO_4$. 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 the 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 [15].

The obtained samples are colorless polycrystalline powders. Their phase purity was checked by X-ray diffraction (DRON-3M diffractometer, CuK_α radiation), using PDF data. The X-ray patterns contained only reflections of the synthesized phosphates. The unit cell parameters were given earlier [16].

The IR spectra (Specord-75 IR) agree with data presented elsewhere [17, 18] and show no evidence of condensed phosphate groups.

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The homogeneity and chemical composition of the samples were checked by electron microprobe analysis (Camebax and CamScan MV-2300 devices). The results have shown the homogeneity of the samples, their compositions were close to the theoretical values calculated for the formulae $MZr_2(PO_4)_3$ and $Na_5D(PO_4)_3$ and given in Table 1.

The chemical composition of the samples was also confirmed by chemical analysis. Known masses of the samples were dissolved in the HF aqueous solutions. The zirconium and titanium contents were determined gravimetrically with cupferron, following the procedure [15]. The phosphorus contents were determined colorimetrically (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 (Perkin-Elmer 603 spectrometer). Results of analyses prove that the stoichiometry of every sample is close to ideal (Table 1).

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

The heat capacity of the samples of 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 calorimeter design and the operational procedure have been described earlier [21]. From the calibration and testing results of the calorimeter it was found that the relative 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 of 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 of 330–640 K. The apparatus design and the operational procedure were reported elsewhere [22, 23]. The relative uncertainty of the measurements 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%.

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 already been described [24]. For calibration, a known current was passed through the cell-assembly heater over a certain time. The reliability of the calorimeter operation was tested in experiments on the solution of especially chemical high-purity KCl in bidistilled water. The value for the standard enthalpy of solution obtained by us $\Delta_{sol}H^0(298.15)$= 17.6±0.4 kJ mol^{-1} (average of ten experiments) was in agreement with the published value $\Delta_{sol}H^0(298.15)$= 17.58±0.34 kJ mol^{-1} [25]. The 298.15 K enthalpies (Δ_rH^0) of the reactions studied are averages of four to eleven replicates. The uncertainty intervals quoted are twice standard deviations of the mean [26].

Results and discussion

DTA curves of the compounds $MZr_2(PO_4)_3$ (M=Na, K, Rb, Cs, $Zr_{0.25}$) showed the absence of any thermal effects in the temperature interval from 298 to 1073 K. A reversible phase transition of the phosphate $Na_5Zr(PO_4)_3$ has been observed at T~407 K (Fig. 1). According to the literature data [27], it melts with decomposition at 1433±5 K. The DTA curve of $Na_5Ti(PO_4)_3$ shows an endothermal peak observed about 1083 K (Fig. 1), which probably corresponds to its melting. By using X-ray diffraction after each isothermal stage it was established that the compound $Zr_{2.25}(PO_4)_3$ ($\equiv Zr_3(PO_4)_4$) decomposes at 1173 K.

Table 1 Composition of the calorimetric samples $MZr_2(PO_4)_3$ and $Na_5D(PO_4)_3$ according to 1 – theoretical values, 2 – electron microprobe data, 3 – chemical analysis

Substance	Mass fraction/%											
	*M**			*D**			P			O		
	1	2	3	1	2	3	1	2	3	1	2	3
$NaZr_2(PO_4)_3$	4.69	4.67	4.70	37.21	37.19	37.22	18.95	18.96	18.94	39.15	39.18	39.14
$KZr_2(PO_4)_3$	7.72	7.69	7.73	36.02	36.01	36.06	18.35	18.33	18.31	37.91	37.97	37.90
$RbZr_2(PO_4)_3$	15.46	15.42	15.47	33.00	32.97	33.03	16.81	16.85	16.80	34.73	34.76	34.70
$CsZr_2(PO_4)_3$	22.14	22.16	22.15	30.39	30.36	30.38	15.48	15.50	15.45	31.99	31.98	32.02
$Zr_3(PO_4)_4$		–		41.87	41.89	41.92	18.96	18.92	18.93	39.17	39.15	39.15
$Na_5Zr(PO_4)_3$	23.41	22.81	–	18.58	18.51	–	18.92	19.31	–	39.09	42.89	–
$Na_5Ti(PO_4)_3$	25.67	–	25.61	10.69	–	10.74	20.75	–	20.79	42.89	–	42.86

*The symbols in the table denote the following: *M*=Na, K, Rb, Cs; *D*=Ti, Zr

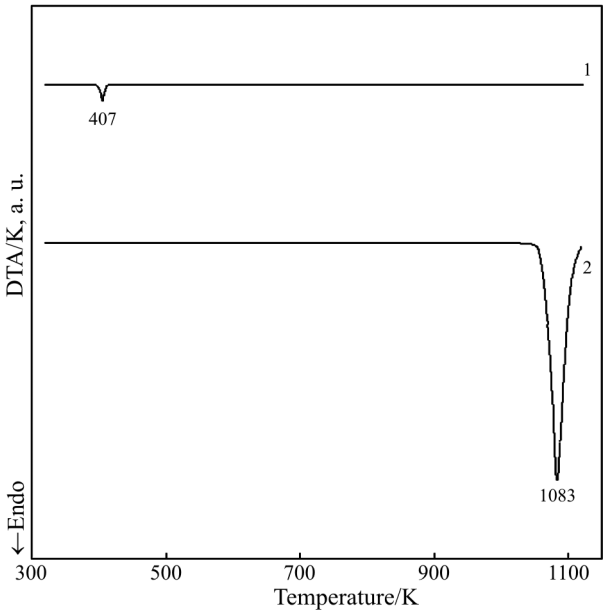

Fig. 1 DTA curves of $Na_5D(PO_4)_3$ samples: D=1 – Zr, 2 – Ti. Heating rate: 20 K min^{-1}

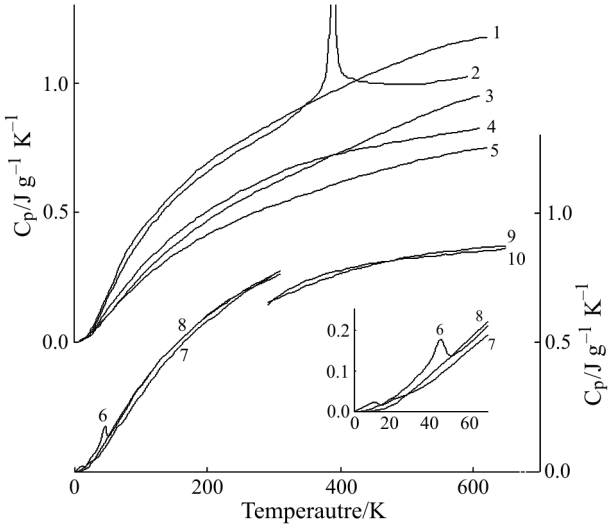

Fig. 2 Temperature dependences of heat capacity of NZP-type compounds: 1 – $Na_5Ti(PO_4)_3$, 2 – $Na_5Zr(PO_4)_3$, 3 – $Zr_3(PO_4)_4$, 4 – $NaZr_2(PO_4)_3$, 5 – $CsZr_2(PO_4)_3$, 6 – $Na_3Fe_2(PO_4)_3$, 7 – $Na_3Cr_2(PO_4)_3$, 8 – $Na_3MgZr(PO_4)_3$, 9 – $Na_4Zr_2Si_3O_{12}$, 10 – $Na_3Zr_2Si_2PO_{12}$

The heat capacity of the compounds $MZr_2(PO_4)_3$ (M=Na, Cs, $Zr_{0.25}$) and $Na_5D(PO_4)_3$ (D=Ti, Zr) was measured in the range from T=7 to T=640 K. Averaging of the experimental C_p^0 points was carried out by means of power and semilogarithmic polynomials on a computer. The root-mean-square deviations of the experimental values from the corresponding smoothed curves for all substances did not exceed 0.14% in the range of 7–40 K, 0.08% between 40 and 90 K, 0.05% from 90 to 350 K, and 0.5% at temperatures from 330 to 640 K.

The heat capacity of the investigated phosphates (except $Na_5Zr(PO_4)_3$) increases monotonically over the entire temperature range studied. The phosphate $Na_5Zr(PO_4)_3$ in the range of 389–424 K undergoes an isostructural phase transition, the nature of which is connected with the centering of off-centered zirconium atoms in octahedral sites and Na^+ occupation transfer between sodium sites in the structure [28]. The thermodynamic characteristics of the phase transition of $Na_5Zr(PO_4)_3$ have been determined: T_{trs}^0 =406.9 K, $\Delta_{trs}H^0$=4.32±0.07 kJ mol^{-1}, $\Delta_{tr}S^0$=10.6±0.1 J mol^{-1} K^{-1}.

According to our own and literature data [2–6] for the known compounds of NZP type family, the heat capacity varies a little above 500–600 K (Fig. 2). The phase transitions observed in [5] for $Na_3Fe_2(PO_4)_3$ (T_{trs}^0 =47 K) and $Na_3Cr_2(PO_4)_3$ (T_{trs}^0 =12 K) are associated with antiferromagnetic ordering processes.

To calculate the thermodynamic functions $H^0(T)$–$H^0(0)$, $S^0(T)$, $G^0(T)$–$H^0(0)$ in the temperature range 0–640 K for the $MZr_2(PO_4)_3$ and $Na_5D(PO_4)_3$, the heat capacities were extrapolated to $T\rightarrow 0$ K with the Debye functions for the heat capacity. The standard enthalpies, entropies and Gibbs functions and the parameters of Debye functions (n and Θ_D) have been reported by us earlier [9, 11, 12]. Using their standard entropies and reference data [25, 29, 30] on the absolute entropies of the constituent simple substances, the standard entropies of formation of the investigated phosphates at T=298.15 K were calculated.

To derive the standard enthalpies of formation at T=298.15 K of the $MZr_2(PO_4)_3$ (M=Na, K, Rb, Cs, $Zr_{2.25}$) and $Na_5Zr(PO_4)_3$ we used the thermodynamic cycles, considering enthalpies of their reactions with hydrofluoric acid. The cycles are reported by us in the works [8, 9, 11, 12] and are similar to that for $Zr_3(PO_4)_4$ given in Table 2, enthalpies of reactions determined are collected in Table 3. When our results for enthalpy of reactions of phosphates synthesis are combined with other data from [25, 29, 30], the standard enthalpies of phosphates formation were obtained.

From the values of the standard enthalpies and entropies of phosphates formation, the standard Gibbs functions of their formation and the logarithmic values of formation reaction constants $\lg K_f^0 = -\Delta_f G^0/[2.303R\cdot 298.15\ \text{K}]$ were found. Details can be found elsewhere [8, 9, 11, 12]. The heat capacities of the investigated substances at T=298.15 K and thermochemical parameters of their formation and also literature data for other NZP compounds are listed in Table 4.

In the light of the beginning of manufacture of NZP ceramics [31] and the variety of their important applications, it was of interest to study thermodynamic aspects of NZP materials synthesis.

Table 2 Experimental scheme for the calculation of enthalpy of reaction of $Zr_3(PO_4)_4$ synthesis (298.15 K) obtained from Hess cycle: $\Delta_r H_5^0 = \Delta_r H_1^0 + \Delta_r H_2^0 - \Delta_r H_3^0 - \Delta_r H_4^0$

Reaction No.	Steps of cycle	$-\Delta_r H^0$(298.15 K)/kJ mol^{-1}
1	$4H_3PO_4 \cdot 11.2H_2O$(sln 1)+893.3HF·2822.9H_2O(sln 2)= =$4H_3PO_4 \cdot 893.3HF \cdot 2834.1H_2O$(sln 3)	4(2.15±0.02)
2	$3ZrO_2(cr)$+sln 3=$3H_2ZrF_6 \cdot 4H_3PO_4 \cdot 875.3HF \cdot 2840.1H_2O$(sln 4)	3(130.9±0.8)
3	$Zr_3(PO_4)_4(cr)$+sln 2=$3H_2ZrF_6 \cdot 4H_3PO_4 \cdot 875.3HF \cdot 2822.9H_2O$(sln 5)	301±2
4	$17.2H_2O(l)$+sln 5=sln 4	17.2(0.56±0.01)
5	$3ZrO_2(cr)+4H_3PO_4 \cdot 11.2H_2O$(sln 1)=$Zr_3(PO_4)_4(cr)+17.2H_2O(l)$	91±2

Table 3 Individual values of the molar enthalpy of reactions 1–4

$-\Delta_r H^0$/kJ mol^{-1}, reaction No.							
1		2		3		4	
2.16		130.6		304.7		0.52	
2.21		131.2		305.4		0.58	
2.17		131.3		301.0		0.59	
2.14		132.0		299.5		0.56	
2.11		129.8		304.2		0.55	
2.09		130.2		302.9		0.57	
2.18		129.3		295.5			
2.15		132.9		304.5			
2.14				301.0			
2.15				297.1			
				298.7			
mean value and twice standard deviation of the mean							
2.15	0.02	130.9	0.8	301	2	0.56	0.01

Usually in solid-state method of NZP ceramics synthesis, the salts of alkali metals, zirconia and ammonia dihydrogen phosphate are used:

$$NaCl(cr)+2ZrO_2(cr)+3NH_4H_2PO_4(cr) \rightarrow \rightarrow NaZr_2(PO_4)_3(cr)+3NH_3(g)+4H_2O(g)+HCl(g) \quad (1)$$

$$CsCl(cr)+2ZrO_2(cr)+3NH_4H_2PO_4(cr) \rightarrow \rightarrow CsZr_2(PO_4)_3(cr)+3NH_3(g)+4H_2O(g)+HCl(g) \quad (2)$$

$$5NaCl(cr)+ZrO_2(cr)+3NH_4H_2PO_4(cr) \rightarrow \rightarrow Na_5Zr(PO_4)_3(cr)+3NH_3(g)+2H_2O(g)+5HCl(g) \quad (3)$$

To analyze the conditions for the formation of NZP substances we calculated the standard thermodynamic functions for the reactions of their synthesis (1)–(3). Standard enthalpies and entropies of the reactions at temperatures above 298.15 K were calculated in assumption that the sum of heat capacities of reagents taken in accordance with the stoichiometric coefficients $\Delta(nC_p^0)$ at 298.15 K is constant in the temperature interval from 298.15 K to T [32]:

$$\Delta_r H^0(T) = \Delta_r H^0(298.15) + \Delta(nC_p^0)(T - 298.15)$$

$$\Delta_r S^0(T) = \Delta_r S^0(298.15) + \Delta(nC_p^0)\ln(T/298.15)$$

Table 4 Heat capacities of the crystalline NZP substances and thermochemical parameters of their formation at T=298.15 K

Substance	C_p^0(298.15 K)/ J g^{-1} K^{-1}	C_p^0(298.15 K)/ J mol^{-1} K^{-1}	$-\Delta_f H^0$(298.15 K)/ kJ mol^{-1}	$-\Delta_f S^0$(298.15 K)/ J mol^{-1} K^{-1}	$-\Delta_f G^0$(298.15 K)/ kJ mol^{-1}	$\lg K_f^0$
$NaZr_2(PO_4)_3$	0.6238	305.9	5231	1156	4886	856
$KZr_2(PO_4)_3$	–	–	5284	–	–	–
$RbZr_2(PO_4)_3$	–	–	5303	–	–	–
$CsZr_2(PO_4)_3$	0.5122	307.4	5301	1185	4948	867
$Zr_3(PO_4)_4$	0.5915	387.0	3597	1535	3139	550
$Na_5Zr(PO_4)_3$	0.7919	388.9	5586	1217	5223	915
$Na_5Ti(PO_4)_3$	0.8239	368.9	–	1217	–	–
$Na_3Fe_2(PO_4)_3$*	0.7586	353.2	–	1169	–	–
$Na_3Cr_2(PO_4)_3$*	0.7570	346.6	–	1198	–	–
$Na_3MgZr(PO_4)_3$*	0.7473	350.8	–	1197	–	–
$Na_3Zr_2Si_2PO_{12}$*	0.6623	351.4	5830	1128	5494	962
$Na_4Zr_2Si_3O_{12}$*	0.6632	365.2	6278	1146	5936	1040

*data of other authors [2–6].

The $\Delta(nC_p^0)$ values are –13.621, –14.088 and –27.05 J mol^{-1} K^{-1} for $NaZr_2(PO_4)_3$, $CsZr_2(PO_4)_3$ and $Na_5Zr(PO_4)_3$, respectively (Table 5).

Standard Gibbs functions of reactions at every temperature were calculated from the equation: $\Delta_r G^0(T)=\Delta_r H^0(T)-T\Delta_r S^0(T)$.

It is seen (Table 6) that the used reactions of solid-state synthesis are endothermic. Gibbs functions at T=298.15 K are positive; i.e. the formation of the starting reactants mixture at the temperature is favored over the formation of double phosphates. Derived temperatures of synthesis at standard pressure are not high: T~430 K for $NaZr_2(PO_4)_3$, T~410 K for $CsZr_2(PO_4)_3$ and T~570 K for $Na_5Zr(PO_4)_3$. For this reason, ceramic technology is one of the commonly used methods for obtaining such compounds.

Table 5 Heat capacities of the reagents used for the synthesis of NZP compounds at T=298.15 K

Substance	Physical state	C_p^0/J mol^{-1} K^{-1}	Ref.
NaCl	*cr*	50.50	25
CsCl	*cr*	52.47	25
ZrO_2	*cr*	56.19	29
$NH_4H_2PO_4$	*cr*	142.3	29
NH_3	*g*	35.56	29
H_2O	*g*	33.58	29
HCl	*g*	29.13	30

Table 6 Standard thermodynamic functions of reactions 1–3

Temperature/K	$\Delta_r H^0$/kJ mol^{-1} for reaction		
	1	2	3
298.15	520.1	481.1	824.6
400	518.7	479.7	821.9
450	518.0	479.0	820.5
500	517.4	478.3	819.1
550	516.7	477.6	817.8
600	516.0	476.9	816.5
	$\Delta_r S^0$/J mol^{-1} K^{-1} for reaction		
	1	2	3
298.15	1218	1195	1455
400	1214	1190	1447
450	1212	1189	1444
500	1211	1187	1441
550	1210	1186	1438
600	1208	1185	1437
	$\Delta_r G^0$/kJ mol^{-1} for reaction		
	1	2	3
298.15	157.0	125.0	390.7
400	33.2	3.5	242.9
450	–27.5	–56.0	170.6
500	–88.1	–115.4	98.5
550	–148.6	–174.7	26.5
600	–209.0	–234.0	–45.4

Conclusions

The general aim of the investigations was to present the thermodynamic data obtained in the course of the undertaken systematic study of the structural peculiarities and properties of NZP compounds coupled with the variety of their possible important applications. For the first time consistent thermodynamic data for the substances of the NZP type structure are summarized in this work. Accumulation of such thermodynamic data and analysis of the conditions of the phosphate synthesis will help to obtain new ceramics with the required thermal characteristics. It was found that the calculated temperatures of synthesis at standard pressure for the crystalline double alkaline zirconium orthophosphates are 430–570 K. As a result, such compounds are often synthesized using ceramic technology as a traditional method.

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