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Calorimetric study of sodium-rich zirconium phosphate

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Abstract

The heat capacity investigation of crystalline pentasodium zirconium tris(phosphate) was carried out in a vacuum adiabatic calorimeter between 7 and 340 K and in a differential scanning calorimeter of the heat bridge type between 330 and 620 K. Between 389 and 424 K, an isostructural solid-to-solid phase transition of $Na_5Zr(PO_4)_3$, has been found, the nature of which is connected with a centering of off-centered zirconium atoms in octahedral sites and an occupation transfer between sodium sites in the structure. The results were used to calculate the characteristics of the phase transition and the thermodynamic functions of $Na_5Zr(PO_4)_3$: the transition temperature T°_{trs}, enthalpy of transition $\Delta_{trs}H^\circ$, entropy of transition $\Delta_{trs}S^\circ$; enthalpy $H^\circ(T) - H^\circ(0)$, entropy $S^\circ(T)$ and Gibbs function $G^\circ(T) - H^\circ(0)$ over the range from 0 to 620 K. From hydrofluoric acid solution microcalorimetry, the enthalpy of solution of $Na_5Zr(PO_4)_3$ at 298.15 K has been determined and the standard enthalpy of formation has been derived. By combining the data obtained by the two techniques, the Gibbs function of formation of $Na_5Zr(PO_4)_3$ at 298.15 K has been calculated.

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Keywords: Pentasodium zirconium tris(phosphate); Heat capacity; Enthalpy of solution; Thermodynamic properties; Calorimetry

1. Introduction

There is a strong need for knowledge on thermodynamic properties for the crystalline phosphates forming structures analogues to the $NaZr_2(PO_4)_3$ (NZP) type family [1] because of the importance of NZP compounds in material science, technology and geochemistry.

NZP materials exhibit high thermal stability, resistance to radiation damage and to the action of aggressive media, low thermal expansion, high ionic conductivity and catalytic activity, and the ability to immobilize radioactive nuclides [2–6].

The basis of NZP structure is a three-dimensional framework of $\{[L_2(TO_4)_3]^{p-}\}_{3\infty}$ type, which consists of discrete L octahedra and isolated T tetrahedra. Two kinds of cavities (1:3 multiplicity), known as M1 and M2 are situated within this framework. In the prototypical structure the M1 site is occupied by sodium ions (Na^+), the M2 site remains vacant, the L site is occupied by Zr^{4+} and T site is occupied by P^{5+}. Four crystallographic sites with different coordination numbers allow the existence of a wide range of iso- and heterovalent ionic substitutions in the framework and its holes. Due to the fact that cations of the same kind can occupy different positions in the structure and various cations are able to enter into positions of the same type, the formation of continuous isomorphous ranges is possible. For example, the concentration range for existence of the

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NZP structure for the system $Na_{9-4x}Zr_x(PO_4)_3$ ($0 \le x \le 2.25$) corresponds to various compounds and solid solutions with $1 \le x \le 2.25$ in the formula. The phosphate series are obtained by partial substitution of tetravalent Zr^{4+} cations by monovalent Na^+ ones. In the sodium-rich phosphate $Na_5Zr(PO_4)_3$ ($x = 1$) sodium cations accommodate within crystallographic sites M1, M2 and L; that means, they are involved in building the framework (together with zirconium) and populate all framework cavities.

Till date there is a gap between the rapid accumulation of structural information for NZP compounds and the much slower rate of their thermochemical investigations. There are only a few references referring to the thermodynamic data of the NZP phosphates family [3,7–11]. The electrochemical ($500\,K < T < 1000\,K$) and calorimetric ($4\,K < T < 800\,K$) studies of the $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$ solid solutions (sodium super ionic conductors) were reported in [7,8]. For $Na_3M_2(PO_4)_3$ (M_2 = Fe_2, Cr_2, ZrMg) solid electrolytes, the temperature dependences of the heat capacity were measured in the range from 10 to 300 K [9,10]. We reported the results of a thermodynamic study on composition $NaZr_2(PO_4)_3$ [11] and on the compounds $MZr_2(PO_4)_3$ with M = K, Rb, or Cs [3].

The present investigation was performed in order to continue the study of thermodynamic properties of sodium containing NZP like structure phosphates. With this aim in view, the temperature dependence of the heat capacity and possible phase transformations on heating and cooling for the crystalline pentasodium zirconium tris(phosphate) were studied in the range from $T \to 0$ to 620 K and the thermodynamic functions $H^\circ(T) - H^\circ(0)$, $S^\circ(T)$, $G^\circ(T) - H^\circ(0)$ calculated. Using a hydrofluoric acid solution calorimetric measurements and using the thermodynamic cycle proposed, enthalpy of reaction $Na_5Zr(PO_4)_3$ synthesis at 298.15 K was calculated. The thermochemical parameters of formation of $Na_5Zr(PO_4)_3$ were estimated at temperature $T = 298.15$ K and pressure $p = 101.325$ kPa.

The phosphate $Na_5Zr(PO_4)_3$ was discovered by investigating of the subsolidus phase diagram of the $NaZr_2P_3O_{12}$–$Na_5ZrP_3O_{12}$ system [12]. It melts with decomposition. The peritectic horizontal line lies at temperature of 1433 ± 5 K. The X-ray structure determination of $Na_5Zr(PO_4)_3$ single crystals was reported in [13].

2. Experimental

2.1. Sample

The compound $Na_5Zr(PO_4)_3$ was prepared by the sol–gel method based upon reactions taking place in aqueous solution. The following reactants were used: $NaNO_3$, $ZrOCl_2 \cdot 8H_2O$, H_3PO_4.

A solution of phosphoric acid, taken in accordance with the stoichiometry of the phosphate, was dropped into the mixture of an aqueous solutions of an sodium nitrate and zirconium oxychloride taken in the stoichiometric ratios under stirring at room temperature. The formed gel was 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 obtained sample is colorless polycrystalline powder. Its phase purity was checked by X-ray diffraction (DRON-2.0 diffractometer, Co Kα radiation), using PDF data. The X-ray pattern contained only reflections of the $Na_5Zr(PO_4)_3$ phosphate. The symmetry of these crystals is rhombohedral (space group $R32$). The unit cell parameters for the synthesized phosphate were derived from least-squares refinement of powder X-ray diffraction data: $a = 9.162(9)$ Å, $c = 22.15(2)$ Å, $V = 1610$ Å^3. The IR spectrum (Specord-75 IR) agrees with data presented elsewhere [14] and shows no evidence of condensed phosphate groups.

The chemical composition and homogeneity of the sample were checked with the aid of a Camebax microprobe analyzer. The results show the homogeneity of the sample and confirmed the stoichiometry of the sample to be $Na_{4.84}Zr_{0.99}P_{3.04}O_{24}$ and is close to the theoretical composition $Na_5Zr(PO_4)_3$. This sample was studied in an adiabatic vacuum calorimeter, in a differential scanning calorimeter, and in a Calvet-type microcalorimeter.

2.2. Calorimetric apparatus and measurement procedure

An automated thermophysical device (BKT-3.07), an adiabatic vacuum calorimeter, was used to measure the heat capacity of the $Na_5Zr(PO_4)_3$ sample in the range from 7 to 340 K. The design of the calorimeter and the procedure of the heat capacity measurements have been described earlier [11,15]. From the calibration and testing results of the calorimeter it was found that the uncertainty of the heat capacity measurements at liquid helium temperatures is within to ±2%. As temperature rises up to 40 K, it decreases to ±0.4% and becomes approximately equal to ±0.2% between 40 and 340 K.

An automated differential scanning calorimeter (ADKTTM) operating by the principle of triple thermal bridge was used to measure the heat capacity, temperature and enthalpy of phase transition in the range from 330 to 620 K. The apparatus design and the measuring procedure were reported in [16,17]. The uncertainty of the measurements of C_p^0 in the above temperature interval was about ±2%, for the transition temperatures ±0.5 K and for the transition enthalpies about ±1.5%.

An automated isothermal differential Calvet-type microcalorimeter (DAK-1-1-A) was employed to measure the enthalpies of solution at 298.15 K. Design and the operation were described earlier [11,18]. 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 reagent-grade KCl in bidistilled water. The value for the standard enthalpy of solution obtained by us $\Delta_{sol}H^\circ = 17.6 \pm 0.4\,\mathrm{kJ\,mol^{-1}}$ (average of 10 experiments) was in agreement with the published value $\Delta_{sol}H^\circ = 17.58 \pm 0.34\,\mathrm{kJ\,mol^{-1}}$ [19]. The 298.15 K enthalpies ($\Delta_r H^\circ$) of the reactions studied are averages of four to six replicates. In conformity with IUPAC recommendations [20], the uncertainty in $\Delta_r H^\circ$ is given as a standard deviation of the average. The net uncertainty in the enthalpy of formation was evaluated as $\sigma = (\sum_i \sigma_i^2)^{1/2}$, where σ_i is the uncertainty in a single measurement.

3. Results and discussion

3.1. Heat capacity

The heat capacity C_p^0 of the $Na_5Zr(PO_4)_3$ was measured in the 7–620 K range. The masses of the samples located in the adiabatic and scanning calorimeters were 1.2407 and 1.5575 g, respectively. One hundred and sixty-three experimental C_p^0 points were taken in two series of measurements over the range of 7–340 K (Table 1). In the range of 330–620 K the C_p^0 values

Table 1
Experimental values of heat capacity (C_p^0 ($\mathrm{J\,mol^{-1}\,K^{-1}}$)) of $Na_5Zr(PO_4)_3$

T (K)	C_p^0
Series 1	
7.12	0.423
7.48	0.499
7.72	0.530
9.10	0.802
10.25	1.247
10.73	1.458
11.43	1.799
12.06	2.123
12.88	2.525
13.74	3.011
14.57	3.510
15.36	4.059
16.15	4.866
16.92	5.607
17.69	6.417
18.46	7.126
19.22	8.088
19.97	9.133
21.73	11.19
24.07	14.72
26.39	18.84
28.73	22.93
31.09	27.72
33.46	32.89
35.84	38.09
38.22	43.57
40.62	49.34
43.02	55.33
45.42	61.57
47.84	67.36
50.27	73.58
52.70	80.10
55.13	86.49
57.57	92.73
60.02	98.71
62.47	105.1
64.91	112.5
67.32	117.9
69.74	123.3
72.18	128.2
74.63	133.9
77.07	139.3
79.50	144.4
81.94	149.1
84.37	154.0
86.81	159.5
89.24	164.2
91.67	168.8
Series 2	
79.79	145.5
81.75	149.9

Table 1 (*Continued*)

T (K)	C_p^0
84.17	154.2
86.60	158.2
89.01	163.9
91.43	168.8
93.84	173.5
96.26	177.8
98.68	182.4
101.09	186.5
103.50	190.9
105.91	195.3
108.32	199.3
110.73	203.4
113.13	207.1
115.54	211.5
117.94	214.8
120.34	218.5
122.74	222.2
125.14	225.4
127.54	229.0
129.93	232.7
132.32	236.0
134.71	239.7
137.10	242.6
139.49	245.9
141.87	248.5
144.25	251.9
146.62	254.9
148.99	258.3
151.36	261.3
153.73	263.7
156.09	266.6
158.46	269.8
160.82	272.5
163.19	275.4
165.55	277.5
167.90	280.4
170.26	283.5
172.62	285.6
174.98	288.6
177.34	290.8
179.69	293.4
182.05	295.4
184.39	298.0
186.74	300.8
189.09	303.0
191.43	305.8
193.77	307.8
196.11	309.4
198.45	312.3
200.78	314.0
203.10	316.3
205.44	317.4
207.77	320.6
210.09	322.7

Table 1 (*Continued*)

T (K)	C_p^0
212.41	325.4
214.74	326.8
217.06	328.2
219.37	330.8
221.68	331.5
223.99	334.1
226.30	336.6
228.59	338.1
230.84	339.8
233.14	342.2
235.43	342.6
237.71	345.4
240.00	346.5
242.29	348.6
244.57	351.1
246.84	353.2
249.12	354.6
251.39	355.6
253.66	357.3
255.91	358.7
258.15	361.1
260.40	362.9
262.66	364.2
264.90	365.8
267.06	366.6
269.29	368.2
271.53	370.0
273.74	372.0
275.97	374.1
278.19	374.9
280.38	376.8
282.59	377.5
284.79	379.7
286.99	380.8
289.16	383.1
291.34	385.4
295.69	387.9
297.86	389.1
300.01	391.2
302.00	391.6
304.14	392.5
306.27	394.6
308.39	395.5
310.50	397.7
312.61	399.1
314.68	400.5
316.74	401.8
318.82	403.5
320.89	404.9
322.95	407.5
325.01	408.4
327.02	410.8
329.02	411.9
331.05	414.0

Table 1 (*Continued*)

T (K)	C_p^0
333.07	415.3
334.83	416.0
336.84	417.6
338.84	420.3
340.83	421.8
Series 3	
330.2	412.2
331.3	414.3
332.5	415.4
333.7	416.1
334.9	417.0
336.1	418.5
337.4	419.6
338.6	421.6
339.9	422.6
341.2	424.1
342.5	425.6
343.8	426.7
345.2	427.5
346.5	428.3
347.8	430.0
349.1	431.2
350.4	433.5
353.1	431.9
354.3	432.1
356.9	434.0
358.1	438.0
359.4	441.5
361.8	443.9
364.2	445.0
365.4	446.3
367.8	447.0
370.1	448.2
372.4	453.0
374.7	454.2
375.9	455.0
378.2	456.9
380.6	457.7
381.8	471.9
383.0	479.3
384.2	480.3
385.4	482.0
387.8	483.4
389.0	485.1
390.2	491.1
391.4	493.1
392.6	494.2
393.9	495.6
395.1	498.0
396.3	511.2
398.7	516.6
400.0	533.3
401.2	536.8

Table 1 (*Continued*)

T (K)	C_p^0
402.4	600.1
403.6	644.3
404.8	776.4
405.9	963.5
406.9	1082
408.0	1039
409.1	929.1
410.3	787.2
411.5	718.5
412.8	608.5
414.1	572.1
415.4	541.2
416.7	527.4
418.0	527.4
419.3	519.1
420.5	514.7
421.8	516.6
424.2	496.0
426.7	497.0
429.1	497.8
431.5	493.6
433.9	491.4
435.1	492.6
437.5	493.1
439.9	491.3
442.4	487.7
444.8	486.6
447.3	491.9
449.8	492.1
452.3	494.0
454.7	493.6
457.2	488.1
459.6	491.9
462.0	492.6
464.4	487.5
466.8	486.2
469.3	490.8
471.7	493.5
474.1	487.2
476.6	486.2
479.1	490.6
481.5	493.1
484.0	493.3
486.4	492.6
488.8	492.9
491.2	491.5
493.6	486.2
496.0	487.3
498.4	493.5
500.8	491.7
503.1	486.2
505.5	486.0
507.9	487.2
510.3	492.5

Table 1 (*Continued*)

T (K)	C_p^0
512.7	489.6
515.2	488.6
517.6	490.8
520.0	484.7
522.4	488.1
524.9	486.2
527.3	493.5
7529.8	494.3
532.2	488.1
534.7	491.5
537.1	487.2
539.5	492.6
541.9	485.7
544.4	489.3
546.8	493.7
549.2	487.8
551.7	491.4
554.0	491.1
556.4	492.6
558.8	489.7
561.1	496.4
563.4	492.1
565.8	490.7
568.2	492.1
570.7	496.7
573.1	499.1
575.5	498.9
577.9	494.0
580.3	490.7
582.8	494.6
585.2	493.5
587.7	499.8
590.1	497.0
592.6	501.4
595.1	502.4
597.6	498.0
600.1	500.9
602.5	503.4
604.9	501.8
607.3	495.5
609.7	499.9
612.2	496.5
616.8	500.8
618.5	497.2
619.9	502.4
Series 4	
347.9	428.2
352.7	434.0
357.4	440.2
362.0	446.9
366.3	443.1
370.5	453.1
374.5	458.5
378.3	462.0
381.9	470.1
385.5	474.0
388.8	490.1
392.1	501.4
395.3	515.6
398.3	514.7
401.4	541.7
404.3	639.4
407.0	851.5
409.6	837.8
412.4	700.8
413.1	654.1
418.4	553.9
421.6	509.7
424.8	483.2
428.2	484.2
431.6	486.9
435.1	484.0
438.6	484.1
442.1	483.5
445.7	482.0
449.4	483.9
453.1	482.5
456.8	483.2
460.6	481.9

of the $Na_5Zr(PO_4)_3$ were measured on continuous heating, typically with two scanning rates, 1 and 3 K min^{-1}. The heat capacity of the sample itself was between 40 and 70% of the total heat capacity (calorimetric ampoule and sample) with changing temperature between 7 and 620 K. A fit of the C_p^0 values was performed by means of power and semilogarithmic polynomials. The root-mean-square deviation of this fit was within ±0.11% in the range 7–40 K, ±0.08% between 40 and 90 K, ±0.05% in the range 90–340 K, ±0.5% in the range 340–620 K. The experimental values of C_p^0 up to 340 K and the fitted curve, at temperatures between 7 and 620 K, are shown in Fig. 1. It is seen that for $Na_5Zr(PO_4)_3$ a solid-to-solid phase transition appears in the temperature interval from 389 to 424 K. As shown in [21], this isostructural transition corresponds to a centering of off-centered zirconium atoms in octahedral sites and Na^+ occupation transfer between sodium sites in the structure.

The phase transition of $Na_5Zr(PO_4)_3$ is reversible. The temperatures of start and end of the transition, named crystal I (crI) and crystal II (crII) are in good

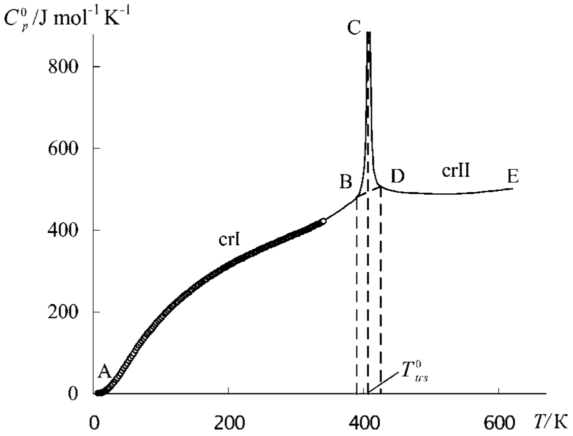

Fig. 1. Temperature dependence of heat capacity C^0_p of $Na_5Zr(PO_4)_3$: AB, crystal I (crI); DE, crystal II (crII).

agreement with the results obtained from X-ray scattering study [21] and high-temperature X-ray diffractometry [5]. The structural and calorimetric data allow characterize the transition from crI to crII, which is accompanied by an abrupt change of the cell parameters [5,21], its volume and absorbtion of a quantity of heat. The transition is of first-order phase.

In other respect, the temperature dependence of the heat capacity (Fig. 1) does not exhibit any peculiarity. Below $T < 389$ K, it gradually increases as the temperature rises (curve AB, crystal I). Above $T > 424$ K, the C^0_p values of the substance are nearly constant (curve DE, crystal II).

3.2. Characteristics of phase transition

The characteristic data of the phase transition, obtained from the results of the measurements in the scanning calorimeter, are summarized in Table 2. The results are shown graphically in Fig. 2.

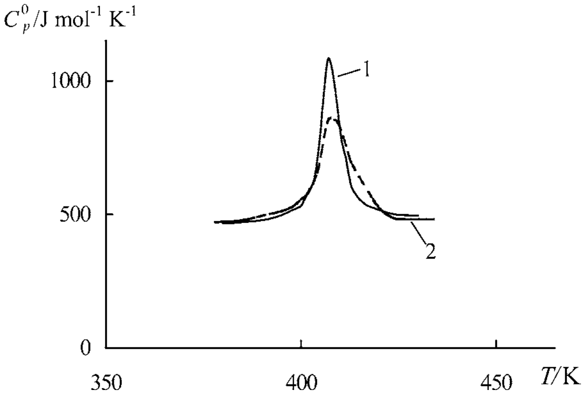

Fig. 2. Temperature dependence of heat capacity C^0_p of $Na_5Zr(PO_4)_3$ at heating rates 1 K min^{-1} (curve 1) and 3 K min^{-1} (curve 2); the endotherms on the curves $C^0_p = f(T)$ are due to phase transition crI → crII.

The temperature corresponding to the maximum value of the apparent heat capacity in the transition range from 389 to 424 K ($C^0_{p,\max}$=1082 J mol^{-1} K^{-1}), is regarded as transition temperature for $Na_5Zr(PO_4)_3$, $T^\circ_{trs} = 406.9$ K. The enthalpy of transition $\Delta_{trs}H^\circ = 4.32 \pm 0.07$ kJ mol^{-1}, was obtained graphically for the enclosed area BCDB (Fig. 1). The entropy of the solid-to-solid phase transition amounts to $\Delta_{trs}S^\circ = \Delta_{trs}H^\circ/T^\circ_{trs} = 10.6 \pm 0.1$ J mol^{-1} K^{-1}.

3.3. Thermodynamic functions

In order to calculate the thermodynamic functions (Table 3) the C^0_p values of $Na_5Zr(PO_4)_3$ were extrapolated from 7 to 0 K with the Debye function for the heat capacity

$$C^0_p = nD\frac{\Theta_D}{T} \tag{1}$$

where D represents the Debye function, n and Θ_D the adjustable parameters. With $n = 3$ and $\Theta_D = 117.8$ K

Table 2
Characteristics of the phase transition crI → crII in $Na_5Zr(PO_4)_3$

Experiment number	β (K min^{-1})	$T_i - T_f$ (K)	$C^0_{p,\max}$ (J mol^{-1} K^{-1})	T°_{trs} (K)	$\Delta_{trs}H^\circ$ (kJ mol^{-1})
1	1	389.0–424.2	1082	406.9	4.34
2	3	388.8–424.8	851.5	406.9	4.27

β is the heating rate of the calorimeter and the substance; T_i and T_f are temperatures of the start (initial) and the end (final) of phase transition crI → crII; $C^0_{p,\max}$ is the maximum heat capacity in the phase transition interval; T°_{trs} is the temperature of the phase transition corresponding to the maximum heat capacity in the phase transition interval; $\Delta_{trs}H^\circ$ is molar enthalpy of phase transition.

Table 3
Thermodynamic functions of $Na_5Zr(PO_4)_3$; $p = 101.325\,kPa$

T (K)	$C_p^0(T)$ ($J\,mol^{-1}\,K^{-1}$)	$H^\circ(T) - H^\circ(0)$ ($kJ\,mol^{-1}$)	$S^\circ(T)$ ($J\,mol^{-1}\,K^{-1}$)	$-[G^\circ(T) - H^\circ(0)]$ ($kJ\,mol^{-1}$)
Crystal I				
0	0	0	0	0
1	0.00120	0	0.00040	0
2	0.00950	0	0.00320	0.000002
3	0.0321	0	0.0107	0.000008
4	0.0760	0.00010	0.0253	0.000025
5	0.148	0.00020	0.049	0.000062
6	0.257	0.00040	0.085	0.000128
7	0.401	0.00070	0.136	0.00024
8	0.605	0.0012	0.202	0.00040
9	0.867	0.0019	0.288	0.00065
10	1.189	0.00300	0.3962	0.00097
15	3.803	0.0149	1.329	0.0050
20	9.012	0.0456	3.049	0.0154
25	16.22	0.1079	5.797	0.0370
30	25.51	0.2110	9.539	0.0751
35	36.25	0.3651	14.26	0.1341
40	47.90	0.5752	19.85	0.2190
45	60.21	0.8451	26.20	0.3339
50	73.00	1.178	33.21	0.4823
60	99.04	2.038	48.82	0.8907
70	123.5	3.153	65.96	1.464
80	145.4	4.500	83.91	2.213
90	166.0	6.058	102.2	3.143
100	184.7	7.812	120.7	4.258
110	202.0	9.746	139.1	5.557
120	218.0	11.85	157.4	7.040
130	232.8	14.10	175.4	8.705
140	246.5	16.50	193.2	10.55
150	259.4	19.03	210.7	12.57
160	271.5	21.69	227.8	14.76
170	282.8	24.46	244.6	17.12
180	293.6	27.34	261.1	19.65
190	303.7	30.33	277.2	22.34
200	313.4	33.41	293.0	25.19
210	322.5	36.59	308.5	28.20
220	331.1	39.86	323.7	31.36
230	339.4	43.21	338.7	34.68
240	347.2	46.65	353.3	38.14
250	354.8	50.16	367.6	41.74
260	362.1	53.74	381.6	45.49
270	369.2	57.40	395.4	49.37
273.15	371.4	58.57	399.7	50.62
280	376.2	61.13	409.0	53.39
290	383.2	64.92	422.3	57.55
298.15	388.9	68.07	433.0	61.04
300	390.2	68.79	435.4	61.84
310	397.4	72.73	448.3	66.26
320	404.8	76.74	461.1	70.81
330	412.6	80.83	473.7	75.48
340	420.8	84.99	486.1	80.28
350	429.7	89.25	498.4	85.20
360	438.3	93.59	510.6	90.25

Table 3 (*Continued*)

T (K)	$C_p^0(T)$ (J mol^{-1} K^{-1})	$H^\circ(T) - H^\circ(0)$ (kJ mol^{-1})	$S^\circ(T)$ (J mol^{-1} K^{-1})	$-[G^\circ(T) - H^\circ(0)]$ (kJ mol^{-1})
370	447.0	98.01	522.8	95.41
380	455.9	102.5	534.8	100.7
390	464.9	107.1	546.8	106.1
400	474.1	111.8	558.7	111.6
406.9	479.8	115.1	566.8	115.5
Crystal II				
406.9	490.1	119.4	577.4	115.5
420	489.9	125.9	593.0	123.0
440	489.7	135.7	615.8	134.9
460	489.5	145.4	637.5	147.2
480	489.3	155.2	658.4	160.0
500	489.0	165.0	678.3	173.1
520	488.5	174.8	697.5	186.7
540	489.0	184.6	715.9	200.6
560	491.2	194.4	733.8	214.9
580	494.2	204.2	751.1	229.5
600	497.8	214.1	767.9	244.5
620	501.7	224.1	784.2	259.8

Eq. (1) reproduces the experimental C_p^0 values in the range 7–11 K with an uncertainty close to ±1%. On calculating the thermodynamic functions, it was assumed that Eq. (1) with the corresponding parameters n and Θ_D reproduces the C_p^0 values at temperature from 0 to 7 K with the same uncertainty. From the $C_p^0(T)$ curve of crystalline $Na_5Zr(PO_4)_3$ the thermodynamic functions were calculated in the temperature range from 0 to 620 K (Table 3). The enthalpy $H^\circ(T) - H^\circ(0)$ and entropy $S^\circ(T)$ were calculated by using the following equations:

$$H^\circ(T) - H^\circ(0) = \int_0^{T^\circ_{\mathrm{trs}}} C_p^0(T)\,\mathrm{d}T + \Delta_{\mathrm{trs}}H^\circ + \int_{T^\circ_{\mathrm{trs}}}^{T} C_p^0(T)\,\mathrm{d}T$$

$$S^\circ(T) = \int_0^{T^\circ_{\mathrm{trs}}} C_p^0(T)\,\mathrm{d}\ln T + \Delta_{\mathrm{trs}}S^\circ + \int_{T^\circ_{\mathrm{trs}}}^{T} C_p^0(T)\,\mathrm{d}\ln T$$

The Gibbs function $G^\circ(T) - H^\circ(0)$ was calculated from the values of $H^\circ(T) - H^\circ(0)$ and $S^\circ(T)$ at corresponding temperatures by using Eq. (2)

$$G^\circ(T) - H^\circ(0) = [H^\circ(T) - H^\circ(0)] - TS^\circ(T) \quad (2)$$

3.4. Standard entropy of formation

Using the standard entropy of the phosphate S°($Na_5Zr(PO_4)_3$, cr, 298.15 K) and reference data on the absolute entropy of the constituent simple substances (Table 4), we calculated the standard entropy of formation of $Na_5Zr(PO_4)_3$. This yields

$$\Delta_f S^\circ(\mathrm{Na_5Zr(PO_4)_3}\ (\mathrm{cr}, 298.15\,\mathrm{K})) = -1161 \pm 1\,\mathrm{J\,mol^{-1}\,K^{-1}}$$

3.5. Standard enthalpy of formation

To derive the standard enthalpy of formation of the investigated phosphate we used the following scheme, considering enthalpy of reaction of $Na_5Zr(PO_4)_3$ with

Table 4
Absolute entropies of the simple substances necessary to calculate the standard entropies of formation of $Na_5Zr(PO_4)_3$; $T = 298.15$ K, $p = 101.325$ kPa

Substance	Physical state[a]	S° (J mol^{-1} K^{-1})	Reference
Na	cr	51.30 ± 0.02	[19]
Zr	cr	39.0 ± 0.2	[22]
P	cr	22.80 ± 0.08	[22]
O_2	g	205.04 ± 0.03	[23]

[a] cr, crystalline; g, gaseous.

Table 5
Experimental scheme for the calculation of enthalpy of reaction of $Na_5Zr(PO_4)_3$ synthesis (298.15 K) obtained from Hess cycle $\Delta_r H_7^\circ = \Delta_r H_1^\circ + \Delta_r H_2^\circ + \Delta_r H_3^\circ - \Delta_r H_4^\circ - \Delta_r H_5^\circ - \Delta_r H_6^\circ$

Reaction number	Steps of cycle	$-\Delta_r H^\circ$ (298.15 K) (kJ mol^{-1})
1	$3H_3PO_4\cdot 8.4H_2O$(sol 1) + $670HF\cdot 2117.2H_2O$(sol 2) → $3H_3PO_4\cdot 670HF\cdot 2125.6H_2O$(sol 3)	2.15 ± 0.05
2	ZrO_2(cr) + sol 3 → $H_2ZrF_6\cdot 3H_3PO_4\cdot 664HF\cdot 2127.6H_2O$(sol 4)	131 ± 2
3	$5NaNO_3$(cr) + sol 4 → $5NaNO_3\cdot H_2ZrF_6\cdot 3H_3PO_4\cdot 664HF\cdot 2127.6H_2O$(sol 5)	4.4 ± 0.5
4	$Na_5Zr(PO_4)_3$(cr) + sol 2 → $Na_2ZrF_6\cdot 3NaH_2PO_4\cdot 664HF\cdot 2117.2H_2O$(sol 6)	319 ± 2
5	$5HNO_3\cdot 8.4H_2O$(sol 7) + sol 6 → $5NaNO_3\cdot H_2ZrF_6\cdot 3H_3PO_4\cdot 664HF\cdot 2125.6H_2O$(sol 8)	−0.29 ± 0.02
6	$2H_2O$(l) + sol 8 → sol 5	0.61 ± 0.03
7	$5NaNO_3$(cr) + ZrO_2(cr) + $3H_3PO_4\cdot 8.4H_2O$(sol 1) → $Na_5Zr(PO_4)_3$(cr) + $5HNO_3\cdot 8.4H_2O$(sol 7) + $2H_2O$(l)	−159 ± 3

Table 6
Calorimetric results for the reaction of $H_3PO_4\cdot 2.8H_2O$ with $HF\cdot 3.16H_2O$[a,b]

Experiment number	$m(H_3PO_4)$ (g)	$\langle\varepsilon(\text{calor})\rangle$ (J g^{-1})	m_1 (g)	$-Q$ (J)	$-\Delta_r H^\circ/m$ (sample) (J g^{-1})	$-\Delta_r H^{\circ c}$ (kJ mol^{-1})
1	0.01699	0.5121	0.7469	0.3825	22.04	2.16
2	0.01652	0.5118	0.7435	0.3805	22.55	2.21
3	0.01725	0.5096	0.7651	0.3899	22.14	2.17
4	0.01711	0.5085	0.7506	0.3817	21.84	2.14
5	0.01687	0.5088	0.7295	0.3712	21.53	2.11
6	0.01770	0.5108	0.7547	0.3855	21.33	2.09
7	0.01816	0.5110	0.8065	0.4121	22.25	2.18
8	0.01665	0.5008	0.7454	0.3733	21.94	2.15
9	0.01788	0.5110	0.7798	0.3985	21.84	2.14
10	0.01704	0.5113	0.7469	0.3819	21.34	2.15

[a] The symbols in table denote the following: $m(H_3PO_4)$, the mass of H_3PO_4 in the experiments; $\langle\varepsilon(\text{calor})\rangle$, mean energy equivalent of the calorimetric system per unit mass of the diagram paper tape used for the registration of the energy released in the experiments; m_1, mass of diagram paper tape with the registration of the given experiment; Q, quantity of energy released from calorimetric system during the process investigated; $\Delta_r H^\circ/m$ (sample), enthalpy of reaction per unit mass of the sample which includes a combined correction of 0.008 J for the enthalpies of the sample forced out into the HF solution, of the reaction of paraffin with the solution and of solvent vaporization; $\Delta_r H^\circ$, molar enthalpy of reaction investigated.

[b] In each experiment 3.00 cm^3 of HF solution was used. The mean temperature of each experiment was 298.15 K.

[c] The molar mass of H_3PO_4 was taken to be 97.9952 g mol^{-1}.

Table 7
Calorimetric results for the reaction of ZrO_2 with $3H_3PO_4\cdot 670HF\cdot 2125.6H_2O$[a,b]

Experiment number	$m(ZrO_2)$ (g)	$\langle\varepsilon(\text{calor})\rangle$ (J g^{-1})	m_1 (g)	$-Q$ (J)	$-\Delta_r H^\circ/m$ (sample) (J g^{-1})	$-\Delta_r H^{\circ c}$ (kJ mol^{-1})
1	0.00666	30.213	0.23419	7.072	1060	130.6
2	0.00706	30.314	0.24847	7.532	1065	131.2
3	0.00717	31.725	0.24113	7.650	1065	131.3
4	0.00708	30.826	0.24645	7.597	1071	132.0
5	0.00715	31.014	0.24328	7.545	1054	129.8
6	0.00689	30.810	0.23671	7.293	1057	130.2
7	0.00719	30.925	0.24440	7.558	1050	129.3
8	0.00991	30.652	0.34895	10.696	1078	132.9

[a] The symbols have the same significance as those in Table 6, with the exception of $\Delta_r H^\circ/m$ (sample) which includes a combined correction of 0.012 J.

[b] In each experiment 3.00 cm^3 of $3H_3PO_4\cdot 670HF\cdot 2125.6H_2O$ solution was used. The mean temperature of each experiment was 298.15 K.

[c] The molar mass of ZrO_2 was taken to be 123.2228 g mol^{-1}.

Table 8
Calorimetric results for the reaction of $NaNO_3$ with $H_2ZrF_6\cdot 3H_3PO_4\cdot 664HF\cdot 2127.6H_2O$[a,b]

Experiment number	$m(NaNO_3)$ (g)	$\langle\varepsilon(\text{calor})\rangle$ ($J\,g^{-1}$)	m_1 (g)	$-Q$ (J)	$-\Delta_r H^\circ/m$ (sample) ($J\,g^{-1}$)	$-\Delta_r H^{\circ c}$ ($kJ\,mol^{-1}$)
1	0.02544	3.7690	0.34890	1.315	51.29	4.36
2	0.02421	3.7851	0.30356	1.149	47.05	4.00
3	0.02499	3.7782	0.31788	1.201	47.66	4.05
4	0.02473	3.7882	0.3719	1.409	56.57	4.81
5	0.02522	3.7751	0.3210	1.212	47.66	4.05
6	0.02680	3.7784	0.4216	1.593	59.07	5.02
7	0.02408	3.7800	0.3407	1.288	53.07	4.51
8	0.02468	3.7788	0.3575	1.351	54.34	4.62
9	0.02477	3.7769	0.3437	1.298	52.00	4.42

[a] The symbols have the same significance as those in Table 6, with the exception of $\Delta_r H^\circ/m$ (sample) which includes a combined correction of 0.01 J.

[b] In each experiment 3.00 cm^3 of $H_2ZrF_6\cdot 3H_3PO_4\cdot 664HF\cdot 2127.6H_2O$ solution was used. The mean temperature of each experiment was 298.15 K.

[c] The molar mass of $NaNO_3$ was taken to be 84.9947 g mol^{-1}.

hydrofluoric acid (Table 5). According to our experimental data, reactions numbers 1–6 in Table 5 yield to true solutions, and have the same stoichiometric coefficients on the left and right side of the reaction. So we can, without analyzing the nature of the products, sum up the reaction numbers 1–6 to obtain the reaction scheme of $Na_5Zr(PO_4)_3$ synthesis (reaction number 7) and to calculate the enthalpy of this reaction. All the enthalpies of determined reactions are collected in Tables 5–9.

Using the relation

$$\begin{aligned}\Delta_r H_7^\circ&(298.15\,K)\\ &= \Delta_f H^\circ(Na_5Zr(PO_4)_3, cr, 298.15\,K)\\ &+5\Delta_f H^\circ(HNO_3, sol, 298.15\,K)\\ &+2\Delta_f H^\circ(H_2O, l, 298.15\,K)\\ &-5\Delta_f H^\circ(NaNO_3, cr, 298.15\,K)\\ &-\Delta_f H^\circ(ZrO_2, cr, 298.15\,K)\\ &-3\Delta_f H^\circ(H_3PO_4, sol, 298.15\,K)\end{aligned}$$

the enthalpy of reaction number 7 and the reported standard enthalpies of formation (Table 10), we calculated the standard enthalpy of formation of $Na_5Zr(PO_4)_3$

$$\begin{aligned}\Delta_f H^\circ&(Na_5Zr(PO_4)_3\,(cr, 298.15\,K))\\ &= -5586 \pm 4\,kJ\,mol^{-1}\end{aligned}$$

Table 9
Calorimetric results for the reaction of $Na_5Zr(PO_4)_3$ with $670HF\cdot 2117.2H_2O$[a,b]

Experiment number	$m(Na_5Zr(PO_4)_3)$ (g)	$\langle\varepsilon(\text{calor})\rangle$ ($J\,g^{-1}$)	m_1 (g)	$-Q$ (J)	$-\Delta_r H^\circ/m$ (sample) ($J\,g^{-1}$)	$-\Delta_r H^{\circ c}$ ($kJ\,mol^{-1}$)
1	0.02806	7.6831	2.3504	18.058	643.01	315.8
2	0.02758	7.6944	2.3637	18.187	658.88	323.6
3	0.02812	7.6894	2.3973	18.434	655.01	321.7
4	0.02946	7.6381	2.4844	18.976	643.62	316.1
5	0.02858	7.6568	2.4347	18.642	651.75	320.1
6	0.02793	7.6685	2.3640	18.128	648.51	318.5
7	0.02841	7.6805	2.4105	18.514	651.15	319.8
8	0.02842	7.6810	2.3946	18.393	646.66	317.6
9	0.03028	7.6819	2.5710	19.750	651.75	320.1

[a] The symbols have the same significance as those in Table 6, with the exception of $\Delta_r H^\circ/m$ (sample) which includes a combined correction of 0.015 J.

[b] In each experiment 3.00 cm^3 of HF solution was used. The mean temperature of each experiment was 298.15 K.

[c] The molar mass of $Na_5Zr(PO_4)_3$ was taken to be 491.1318 g mol^{-1}.

Table 10
Enthalpies of formation substances necessary to calculate the standard enthalpies of formation of $Na_5Zr(PO_4)_3$; $T = 298.15\,K$, $p = 101.325\,kPa$

Substance	Physical state[a]	$-\Delta_f H^\circ$ ($kJ\,mol^{-1}$)	Reference
$NaNO_3$	cr	468.2 ± 0.5	[19]
ZrO_2	cr	1100.6 ± 0.6	[22]
H_3PO_4	sol	1280 ± 1	[22]
HNO_3	sol	193.0 ± 0.5	[22]
H_2O	l	285.83 ± 0.04	[23]

[a] cr, crystalline; sol, solution; l, liquid.

Table 11
Thermochemical parameters of formation of $Na_5Zr(PO_4)_3$

Physical state	$\Delta_f H^\circ$ ($kJ\,mol^{-1}$)	$\Delta_f S^\circ$ ($J\,mol^{-1}\,K^{-1}$)	$\Delta_f G^\circ$ ($kJ\,mol^{-1}$)	$\lg K_f^0$
Crystalline	−5586	−1161	−5240	918

3.6. Thermochemical parameters of formation

Thermochemical parameters of formation are given in Table 11. The Gibbs function of formation $\Delta_f G^\circ$ for $Na_5Zr(PO_4)_3$ at 298.15 K and standard pressure was calculated from the values of $\Delta_f H^\circ$ and $\Delta_f S^\circ$ at corresponding temperature. The logarithmic value of formation reaction constant for $Na_5Zr(PO_4)_3$ was calculated from the value $\Delta_f G^\circ$ by the following equation: $\lg K_f^0 = -\Delta_f G^\circ/[2.303R \times 298.15\,(K)]$. The values of the thermodynamic parameters of formation obtained correspond to the process

$$5Na(cr) + Zr(cr) + 3P(cr, white) + 6O_2(g) = Na_5Zr(PO_4)_3(cr)$$

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