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Heat Capacity and Standard Thermodynamic Functions of $NaTi_2(PO_4)_3$ and $NaHf_2(PO_4)_3$

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Heat capacity measurements of the crystalline phosphates $NaTi_2(PO_4)_3$ and $NaHf_2(PO_4)_3$ were performed between (6 and 650) K. Their thermodynamic functions, molar heat capacities $C^0_{p,\mathrm{m}}$, enthalpy $[H^o(T) - H^o(0)]$, entropy $S^o(T)$, and Gibbs free energy $G^o(T) - H^o(0)$, over the range from $T \rightarrow 0$ to 650 K, were calculated, and the fractal dimension D_{fr} was evaluated. Standard entropies of formation at $T = 298.15$ K were estimated to be $[(1174 \pm 2)$ and $(1207 \pm 2)]$ $J \cdot K^{-1} \cdot mol^{-1}$ for $NaTi_2(PO_4)_3$ and $NaHf_2(PO_4)_3$, respectively.

Introduction

Crystalline phosphates of the kosnarite structure type are of interest because of their considerable thermal and chemical stability, resistance to radiation damage, and other valuable physical and chemical properties that lead to industrial application possibilities as constructional and functional ceramics.[1,2] The mineral kosnarite, $KZr_2(PO_4)_3$, is isostructural with the large class of solid ionic conductors typified by the material NASICON, $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$,[3] and by NZP, $NaZr_2(PO_4)_3$.[4]

The NZP structure is characterized by the high isomorphic capacity of cations of various sizes and oxidation states. The basis of their structure is a three-dimensional framework $\{[L_2(PO_4)_3]^{p-}\}_{3\infty}$ (L is an octahedrally coordinated cation) built up of corner-shared LO_6 octahedra and PO_4 tetrahedra.[2,4] Two kinds of cavities (1:3 multiplicity) with different oxygen environments, referred to as M1 and M2, are situated within this framework, which is why cations from 0 to 4 per formula unit of the NZP may be included in the structural cavities. In the complex phosphates of sodium and IVB group metals of the general composition $NaL_2(PO_4)_3$ (L = Ti, Zr, Hf), the crystallographic site M1 is occupied by Na^+ ions, and M2 sites remain vacant.[4,5]

Knowledge of the NZP compound thermodynamic functions over a wide temperature range is necessary as they are fundamental characteristics and needed for the different chemical process calculations in which these substances participate. In earlier work[6] the temperature dependence of the $NaZr_2(PO_4)_3$ heat capacity was measured over the range from (7 to 640) K, and the standard ($p^o = 0.1$ MPa) thermochemical parameters of its formation at $T = 298.15$ K were reported.

The purpose of the present investigation is to measure the heat capacities by adiabatic calorimetry and differential scanning calorimetry over the temperature range of $T = (6$ to $650)$ K of the $NaTi_2(PO_4)_3$ and $NaHf_2(PO_4)_3$ compounds, to calculate the standard thermodynamic functions ($C^0_{p,\mathrm{m}}$, $H^o(T) - H^o(0)$, $S^o(T)$, and $G^o(T) - H^o(0)$) of the phosphates over the range from $T \rightarrow 0$ K to $T = 650$ K), to determine the characteristic temperatures and fractal dimensions D_{fr}, to establish the structure topology, to calculate the standard entropies of formation at $T = 298.15$ K of $NaTi_2(PO_4)_3$(cr) and $NaHf_2(PO_4)_3$(cr), and to compare the thermal behavior and thermodynamic characteristics of the series of isostructural compounds $NaL_2(PO_4)_3$ containing IVB group metals where L = Ti, Zr, and Hf.

Experimental Section

Synthesis and Characterization of Samples. The compounds $NaTi_2(PO_4)_3$ and $NaHf_2(PO_4)_3$ were synthesized by solid-state reactions starting from NaCl, TiO_2, $HfO(NO_3)_2 \cdot 2H_2O$, and $NH_4H_2PO_4$. A fine mixture of the stoichiometric amounts of the reactants was dried at 473 K for (10 to 16) h and then thermally processed in unconfirmed air access at (873 and 1073) K for at least 24 h at each stage. Thermal stages were alternated with careful grinding.

All chemicals used were provided by REACHEM,[7] and their purity was not less than 99.5 % (except for $HfO(NO_3)_2 \cdot 2H_2O$, purity > 98 %). The purity of the starting $HfO(NO_3)_2 \cdot 2H_2O$ is

Table 1. Results of Element Analyses (Mass Fraction *w*) on the Calorimetric Samples[a]

sample	Na	Ti or Hf	P	O
$NaTi_2P_3O_{12}$		*w*/%		
		Electron Microprobe Analysis		
1	5.65	23.80	23.06	47.49
2	5.64	23.77	22.98	47.61
3	5.68	23.70	23.10	47.52
4	5.72	23.76	23.05	47.47
5	5.66	23.79	23.00	47.55
average	5.67	23.76	23.04	47.53
		Chemical Analysis		
	5.73	23.80	22.95	47.52
$NaHf_2P_3O_{12}$		*w*/%		
		Electron Microprobe Analysis		
1	3.43	53.81	13.90	28.86
2	3.41	53.70	13.98	29.51
3	3.49	53.73	13.86	28.92
4	3.44	53.76	13.95	28.85
5	3.47	53.79	13.92	28.82
average	3.45	53.66	13.92	28.87
		Chemical Analysis		
	3.49	53.59	14.01	28.91

[a] Actual composition of $NaTi_2P_3O_{12}$: w(Na) = 5.69 %, w(Ti) = 23.73 %, w(P) = 23.02 %, w(O) = 47.56 % and of $NaHf_2P_3O_{12}$: w(Na) = 3.46 %, w(Hf) = 53.69 %, w(P) = 13.98 %, w(O) = 28.88 %.

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Table 2. Experimental Molar Heat Capacities of Crystalline $NaTi_2(PO_4)_3$ (M = 403.704 g·mol^{-1}, p^o = 0.1 MPa)

T/K	$C^0_{p,\mathrm{m}}$/J·K^{-1}·mol^{-1}	T/K	$C^0_{p,\mathrm{m}}$/J·K^{-1}·mol^{-1}	T/K	$C^0_{p,\mathrm{m}}$/J·K^{-1}·mol^{-1}
Series 1					
7.17	0.135	16.61	2.23	45.01	35.31
7.83	0.169	17.33	2.58	48.56	40.52
8.49	0.228	18.03	2.95	52.13	45.97
9.15	0.295	18.73	3.41	55.71	51.23
9.81	0.373	19.43	3.81	59.31	56.47
10.26	0.445	20.10	4.300	62.92	61.82
10.88	0.540	21.67	5.405	66.54	67.41
11.50	0.652	23.96	7.590	70.17	72.93
12.15	0.782	26.98	10.91	74.16	79.24
12.83	0.951	29.46	13.83	77.80	85.01
13.63	1.15	31.81	16.86	81.43	90.18
14.41	1.37	34.18	19.97	85.54	96.45
15.16	1.63	37.80	24.94	88.90	101.4
15.89	1.93	41.49	30.14		
Series 2					
81.75	90.81	113.35	135.4	147.97	176.7
84.30	94.70	115.73	138.8	150.93	179.9
87.01	98.52	118.11	141.7	153.90	183.1
89.06	102.0	120.48	145.1	156.86	185.9
91.43	105.3	122.86	147.8	159.83	188.8
93.81	108.7	125.24	150.4	162.79	192.1
96.18	112.3	127.62	153.4	165.76	195.2
98.56	115.3	129.99	156.4	168.73	198.1
100.93	118.7	133.00	159.9	171.70	200.7
103.42	121.6	136.12	163.7	174.67	204.2
105.81	124.9	139.08	166.6	177.64	206.3
108.32	128.4	142.04	170.1	180.63	209.5
110.84	131.9	145.01	173.3	184.36	213.0
187.43	215.8	244.17	260.9	298.62	293.7
190.39	218.8	247.10	263.4	301.14	294.9
193.37	221.7	250.03	265.2	303.97	296.4
196.34	224.2	252.96	267.3	306.76	297.5
199.32	226.4	255.68	269.0	309.55	299.2
202.30	229.0	258.59	270.7	312.32	300.8
205.27	231.8	261.50	272.9	315.80	302.4
208.36	233.7	264.40	274.5	317.84	303.4
211.41	236.2	267.30	276.0	320.60	305.0
214.37	239.0	270.20	277.4	323.34	306.7
217.34	240.9	273.08	279.1	326.07	308.6
220.31	243.3	275.95	281.0	328.79	310.0
223.26	245.7	278.82	282.5	331.51	311.9
226.95	248.8	281.68	284.1	334.51	313.5
229.39	250.8	284.53	285.8	336.39	313.9
232.40	252.6	287.37	287.4	339.08	315.3
235.35	254.5	290.20	289.2	341.75	316.7
238.29	256.7	293.03	291.0	344.41	318.0
241.23	259.1	295.85	292.4		
Series 3					
331.0	312	356.2	324	374.6	333
333.8	313	357.8	325	376.3	334
336.4	315	359.4	326	378.1	335
339.0	316	361.0	326	379.9	336
341.5	317	362.4	327	381.6	337
344.0	318	363.9	328	383.6	338
346.3	319	365.3	329	385.5	338
348.5	320	367.5	330	387.5	339
350.5	321	369.3	331	389.4	340
352.5	322	371.0	331	391.3	341
354.4	323	372.8	332	393.2	342
395.0	343	423.5	356	480.2	380
396.9	344	425.3	357	482.0	381
398.7	345	427.1	358	483.8	381
400.5	346	429.0	359	485.6	382
402.3	346	430.8	359	487.4	383
404.0	347	432.6	360	489.2	383
405.8	348	434.5	361	491.0	384
407.6	349	436.3	362	492.9	385
409.3	350	438.2	363	494.7	385
411.1	350	440.0	363	496.5	386
412.8	351	441.9	364	498.3	387
414.6	352	443.7	365	500.1	387
416.4	353	445.6	366	501.9	388
418.2	354	447.5	367	503.7	389

Table 2 Continued

T/K	$C^0_{p,\mathrm{m}}$/J·K^{-1}·mol^{-1}	T/K	$C^0_{p,\mathrm{m}}$/J·K^{-1}·mol^{-1}	T/K	$C^0_{p,\mathrm{m}}$/J·K^{-1}·mol^{-1}
419.9	354	450.3	368	505.6	389
395.0	343	451.2	368	507.4	390
396.9	344	453.0	369	509.2	391
398.7	345	454.9	370	511.0	391
400.5	346	456.7	370	512.9	392
402.3	346	458.6	371	514.7	393
404.0	347	460.4	372	516.5	393
405.8	348	462.2	373	518.3	394
407.6	349	464.0	373	520.2	395
409.3	350	465.8	374	522.0	395
411.1	350	467.6	375	523.8	396
412.8	351	469.4	376	525.6	396
414.6	352	471.2	376	527.4	397
416.4	353	473.0	377	529.2	398
418.2	354	474.8	378	531.0	398
419.9	354	476.6	379	532.8	399
421.7	355	478.4	379	534.6	399
536.5	400	574.8	411	610.5	420
538.3	401	576.2	412	612.3	420
540.1	401	578.1	412	614.1	420
541.9	402	579.9	413	615.9	421
543.8	402	581.8	413	617.8	421
545.6	403	583.6	413	619.6	421
547.4	403	585.4	414	621.4	422
549.2	404	587.2	414	623.2	422
551.1	405	589.0	415	625.1	423
552.9	405	590.8	415	626.9	423
554.7	406	592.6	416	628.7	423
556.6	406	594.4	416	630.6	424
558.4	407	596.2	417	632.4	424
560.2	407	598.0	417	634.2	424
562.0	408	599.8	417	636.0	424
563.9	408	601.6	418	637.8	425
565.7	409	603.3	418	639.6	425
567.5	409	605.1	419	641.4	425
569.3	410	606.9	419	643.3	426
571.1	410	608.7	419	645.1	426
572.9	411				

explained by the uncertainty in the H_2O content in this chemical. That is why the hafnium concentration in the solution taken for synthesis was confirmed gravimetrically with cupferron, following a documented procedure.[8]

The samples obtained were colorless polycrystalline powders. Confirmation of the desired compounds was obtained on a Shimadzu XRD-6000 powder X-ray diffractometer over the 2θ range of (10 to 60)°. A Cu anode (30 mA and 30 kV) with filtered monochromatic K_α radiation ($\lambda = 1.54178$ Å) was used in the determination. The X-ray patterns of the samples contained only reflections of $NaTi_2(PO_4)_3$[9] and $NaHf_2(PO_4)_3$[10] phosphates, respectively. The symmetry of these crystals was rhombohedral (space group $R\bar{3}c$). The unit cell parameters for the synthesized phosphates were derived from the least-squares refinement of powder X-ray diffraction data: $a = 8.479(4)$ Å, $c = 21.77(2)$ Å, and $V = 1355$ Å^3 for $NaTi_2(PO_4)_3$, and $a = 8.780(5)$ Å, $c = 22.62(3)$ Å, and $V = 1510$ Å^3 for $NaHf_2(PO_4)_3$. These agreed favorably with those reported elsewhere.[9,10]

The IR spectra of the samples were recorded on an IR Fourier spectrometer FSM-1201 over the range of (1400 to 400) cm^{-1}. They agreed with data presented elsewhere[11] and showed no evidence of condensed phosphate groups.

The homogeneity and chemical composition of the samples were checked 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 (Table 1) confirmed the stoichiometry of the samples to be close to the theoretical composition of $NaTi_2P_3O_{12}$ and $NaHf_2P_3O_{12}$. There were no substantial impurities (within 0.5 %) 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 mass contents were determined by an atomic absorption method on a Perkin-Elmer device. The titanium and hafnium mass contents were determined gravimetrically with cupferron, following a demonstrated procedure.[8] The phosphorus mass contents were determined colorimetrically according to the method employing solutions of ammonium vanadate and ammonium molybdate.[12] Owing to the presence of fluoride, colorimetric determinations were performed with perspex cells on a SF-46 spectrophotometer. Results of analyses (Table 1) proved that the stoichiometries of the obtained samples were close to ideal.

Adiabatic Calorimetry. A precision automatic adiabatic calorimeter (BCT-3) was used to measure heat capacities over the temperature range of $6 \le (T/\mathrm{K}) \le 350$. The calorimeter was established in the Termis joint-stock company at the All-Russian Metrology Research Institute, Moscow region, Russia. The principle and structure of the adiabatic calorimeter are described in detail elsewhere.[13,14] Briefly, all measurements were monitored by a complex-measuring system consisting of a computer, analog-to-digital and digital-to-analog converters, and a switch. The calorimetric ampule is a thin-walled cylindrical vessel made from titanium of $1.5 \cdot 10^{-6}$ m^3. Its mass is 2.0400 g. A miniature iron−rhodium resistance thermometer (a nominal

Table 3. Experimental Molar Heat Capacities of Crystalline $NaHf_2(PO_4)_3$ ($M = 664.884\ \mathrm{g \cdot mol^{-1}}$, $p^o = 0.1$ MPa)

T/K	$C^0_{p,\mathrm{m}}$/$\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$	T/K	$C^0_{p,\mathrm{m}}$/$\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$	T/K	$C^0_{p,\mathrm{m}}$/$\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$
Series 1					
6.03	0.190	25.33	13.01	58.15	58.57
7.27	0.320	27.97	16.78	60.61	61.70
8.51	0.510	30.58	20.66	63.14	65.07
9.75	0.740	33.18	24.40	65.61	68.54
10.99	1.17	35.76	28.09	68.03	71.80
12.23	1.66	38.28	31.91	70.45	75.29
13.48	2.21	40.80	35.37	72.85	78.58
14.72	2.85	43.31	39.15	75.29	81.81
15.96	3.71	45.79	42.57	77.74	85.10
17.16	4.63	48.27	45.88	80.18	88.32
18.43	5.78	50.75	49.04	82.61	91.50
19.71	6.99	53.22	52.27	85.04	94.48
22.56	9.760	55.69	55.41	87.48	97.50
Series 2					
83.57	92.59	119.52	133.7	155.00	168.1
86.77	96.60	122.49	136.6	157.93	170.7
89.82	100.4	125.47	139.5	160.87	173.3
92.85	104.1	128.44	142.4	163.85	176.1
95.88	107.8	131.41	145.4	166.80	178.7
98.89	111.2	134.37	148.5	169.71	181.3
101.90	114.5	137.32	151.7	172.63	183.8
104.89	118.1	140.28	154.7	175.70	186.7
107.89	121.4	143.23	157.5	178.48	189.2
110.89	124.5	146.18	160.3	181.39	192.0
113.87	127.7	149.12	162.8	184.31	194.8
116.85	130.9	152.06	165.7	187.22	197.1
Series 3					
184.11	194.5	244.40	247.4	300.95	294.4
188.28	198.2	248.80	251.0	302.62	295.6
192.33	201.6	252.59	254.5	305.60	298.0
196.37	205.1	256.58	257.9	309.02	300.6
200.40	208.7	260.58	261.2	312.30	303.2
204.42	212.1	264.57	264.5	315.30	305.5
208.45	215.7	268.56	267.7	318.72	308.1
212.47	219.2	272.56	271.3	321.84	310.4
216.49	222.9	276.55	274.9	324.93	313.2
220.52	226.1	280.54	278.3	327.94	314.6
224.30	229.8	284.80	281.6	330.90	317.0
228.56	233.1	288.49	284.6	333.40	318.9
232.58	236.8	292.70	288.0	336.63	321.4
236.30	240.0	295.90	290.5	339.39	323.1
240.59	244.0	298.12	292.2		
Series 4					
322.9	311	351.2	331	378.9	349
324.9	312	353.2	332	380.7	350
326.9	314	355.2	334	382.6	351
328.9	316	357.2	335	384.4	353
331.0	317	359.2	336	386.1	354
333.0	319	361.3	338	387.9	355
335.0	320	363.3	339	389.7	356
337.0	322	365.3	340	391.4	357
339.0	323	367.3	342	393.2	358
341.1	325	369.3	343	394.8	359
343.1	326	371.3	345	396.7	360
345.1	327	373.2	346	398.4	361
347.1	329	375.1	347	399.7	361
349.2	330	377.0	348	401.9	363
403.7	364	459.8	390	516.7	413
405.5	364	461.7	391	518.5	413
407.2	365	463.5	392	520.2	414
409.0	366	465.4	392	522.0	415
410.8	367	467.2	393	523.8	416
412.6	368	469.1	394	525.5	416
414.4	369	470.9	395	527.3	416
416.2	370	472.8	395	529.1	417
418.0	371	474.6	396	530.9	418
419.9	371	476.5	397	532.7	419
421.7	372	478.3	398	534.6	420
423.6	373	480.2	399	536.4	420
425.4	374	482.0	399	538.2	420
427.3	375	483.9	400	540.1	421
429.2	376	485.7	401	541.9	422

Table 3 Continued

$\frac{T}{\mathrm{K}}$	$\frac{C^0_{p,\mathrm{m}}}{\mathrm{J\cdot K^{-1}\cdot mol^{-1}}}$	$\frac{T}{\mathrm{K}}$	$\frac{C^0_{p,\mathrm{m}}}{\mathrm{J\cdot K^{-1}\cdot mol^{-1}}}$	$\frac{T}{\mathrm{K}}$	$\frac{C^0_{p,\mathrm{m}}}{\mathrm{J\cdot K^{-1}\cdot mol^{-1}}}$
431.0	377	487.6	401	543.7	423
432.9	377	489.4	403	545.5	423
434.7	378	491.3	403	547.3	424
436.5	379	493.2	404	549.1	424
438.6	380	495.0	405	550.9	425
440.1	381	496.9	406	552.7	425
441.9	382	498.7	406	554.5	426
443.8	382	500.6	407	556.3	427
445.5	383	502.4	408	558.1	427
447.4	384	504.2	408	559.9	427
449.1	385	506.0	409	561.8	428
450.9	386	507.8	410	563.6	429
452.7	387	509.6	410	565.5	429
454.5	388	511.4	411	567.3	430
456.2	388	513.1	412	569.1	431
458.0	389	514.9	412	571.0	431
572.8	432	599.8	439	624.9	444
574.6	432	601.6	439	626.7	445
576.4	433	603.4	440	628.5	445
578.2	433	605.1	440	630.3	445
580.0	434	606.9	440	632.1	446
581.9	434	608.7	441	633.9	446
583.7	435	610.5	441	635.7	446
585.5	435	612.3	442	637.5	447
587.3	435	614.1	442	639.3	447
589.1	436	615.9	443	641.2	447
590.9	436	617.7	443	643.0	447
592.7	437	619.5	443	644.9	447
594.5	438	621.3	444	646.8	448
596.3	438	623.1	444	648.6	448
598.0	438				

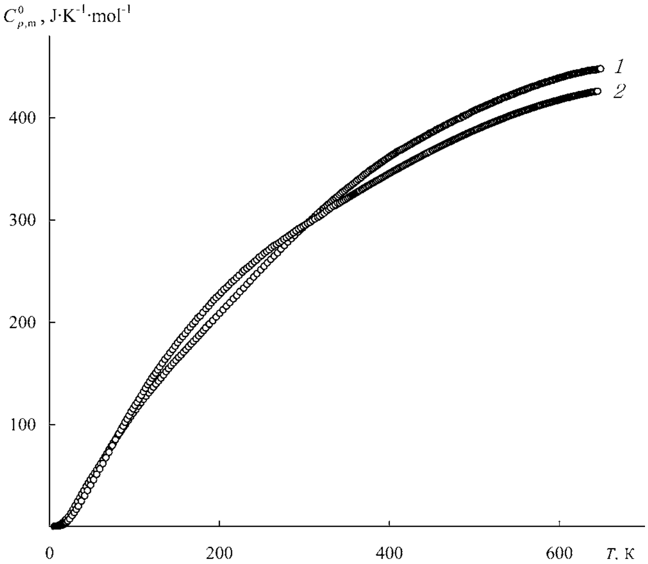

Figure 1. Temperature dependence of the heat capacity of the crystalline substances: $NaHf_2(PO_4)_3$ (1) and $NaTi_2(PO_4)_3$ (2).

resistance of 100 Ω) was applied to measure the temperature of the sample. The thermometer was calibrated on the basis of IST-90 by the Russian Metrology Research Institute, Moscow region, Russia. The difference in temperature between the ampule and an adiabatic shield was controlled by a four-junction copper−iron−chromel thermocouple. The sensitivity of the thermometric circuit was $1 \cdot 10^{-3}$ K and of the analog-to-digital converter 0.1 μV. The energy introduced into the sample cell and the equillibrium temperature of the cell after the energy input were automatically recorded and processed online by a computer. The speed of the computer-measuring system was 10 measurements per second.

To verify the accuracy of the calorimeter, the heat capacities of the standard reference materials (K-2 benzoic acid and α-Al_2O_3)[15,16] prepared at the Institute of Metrology of the State Standard Committee of the Russian Federation were measured over the temperature range of $6 \le (T/\mathrm{K}) \le 350$. The sample masses were (0.7682 and 1.5000) g, respectively. It was established that the apparatus and the measurement technique enable the determination of the heat capacities of substances with an error not exceeding ± 2 % over the temperature range of $6 \le (T/\mathrm{K}) \le 15$, ± 0.5 % between $T =$ (15 and 40) K and ± 0.2 % over the temperature range $40 \le (T/\mathrm{K}) \le 350$ and the measuring of the phase transition temperatures within about ± 0.01 K and the enthalpies of transitions with the error of ± 0.2 %.

Heat capacity measurements were continuously and automatically carried out by means of 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 (0.5 to 2) K. The heating duration was ∼ 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 acquisition of all heat capacity results. Liquid helium and nitrogen were used as coolants. The ampule with the substance was filled with dry helium as a heat exchange gas to the pressure of 4 kPa at room temperature. The sample masses used for calorimetric measurements were (1.013 and 1.250) g for $NaTi_2(PO_4)_3$ and $NaHf_2(PO_4)_3$, respectively. The molar masses of the objects under study were calculated from the IUPAC table of atomic weights.[17] The experimental values of $C^0_{p,\mathrm{m}}$ (136 and 119 points for $NaTi_2(PO_4)_3$ and $NaHf_2(PO_4)_3$, respectively) were obtained in the experiments.

Differential Scanning Calorimetry. An automatic thermoanalytical complex, namely, a differential scanning calorimeter operating on the principle of a triple thermal bridge (ADCTTB),

Table 4. Smoothed Molar Heat Capacities and Thermodynamic Functions of Crystalline $NaTi_2(PO_4)_3$ ($M = 403.704\ g\cdot mol^{-1}$, $p^o = 0.1\ MPa$)

T	$C^0_{p,m}$	$[H^o(T) - H^o(0)]$	$S^o(T)$	$-[G^o(T) - H^o(0)]$
K	$J\cdot K^{-1}\cdot mol^{-1}$	$kJ\cdot mol^{-1}$	$J\cdot K^{-1}\cdot mol^{-1}$	$kJ\cdot mol^{-1}$
5	0.0502	0.000100	0.0167	0.0000210
10	0.400	0.00100	0.133	0.000326
15	1.58	0.00540	0.477	0.00172
20	4.221	0.01920	1.247	0.005749
25	8.649	0.05070	2.630	0.01504
30	14.55	0.1081	4.712	0.03326
35	21.09	0.1971	7.438	0.06328
40	28.02	0.3197	10.70	0.1084
45	35.27	0.4778	14.42	0.1711
50	42.74	0.6727	18.52	0.2534
60	57.51	1.174	27.62	0.4832
70	72.69	1.825	37.62	0.8088
80	88.18	2.629	48.34	1.238
90	103.1	3.587	59.60	1.777
100	117.2	4.689	71.20	2.431
110	130.8	5.929	83.01	3.202
120	144.5	7.305	94.97	4.092
130	156.3	8.809	107.0	5.102
140	167.8	10.43	119.0	6.232
150	178.8	12.16	131.0	7.482
160	189.2	14.00	142.8	8.851
170	199.3	15.95	154.6	10.34
180	209.0	17.99	166.3	11.94
190	218.2	20.13	177.8	13.66
200	227.0	22.35	189.3	15.50
210	235.4	24.66	200.5	17.45
220	243.3	27.06	211.7	19.51
230	250.8	29.53	222.7	21.68
240	258.1	32.07	233.5	23.96
250	265.3	34.69	244.2	26.35
260	271.5	37.37	254.7	28.85
270	277.6	40.12	265.0	31.44
280	283.5	42.93	275.3	34.15
290	289.0	45.79	285.3	36.95
298.15	293.2	48.16	293.4	39.31
300	294.4	48.70	295.2	39.85
310	299.9	51.68	304.9	42.85
320	305.3	54.70	314.5	45.95
330	310.4	57.78	324.0	49.14
340	315.6	60.91	333.4	52.43
350	320.9	64.10	342.6	55.81
360	325.9	67.33	351.7	59.28
370	330.9	70.61	360.7	62.84
380	336	73.9	370	66.5
390	341	77.3	378	70.2
400	345	80.8	387	74.1
420	355	87.8	404	82.0
440	363	94.9	421	90.2
460	372	102	437	98.8
480	380	110	453	108
500	387	117	469	117
520	395	125	484	126
540	401	133	499	136
560	407	141	514	146
580	413	150	528	157
600	417	158	542	168
620	422	166	556	179
640	425	175	570	190
650	427	179	576	196

Table 5. Smoothed Molar Heat Capacities and Thermodynamic Functions of Crystalline $NaHf_2(PO_4)_3$ ($M = 664.884\ g\cdot mol^{-1}$, $p^o = 0.1\ MPa$)

T	$C^0_{p,m}$	$[H^o(T) - H^o(0)]$	$S^o(T)$	$-[G^o(T) - H^o(0)]$
K	$J\cdot K^{-1}\cdot mol^{-1}$	$kJ\cdot mol^{-1}$	$J\cdot K^{-1}\cdot mol^{-1}$	$kJ\cdot mol^{-1}$
5	0.106	0.000100	0.0352	0.0000440
10	0.840	0.00210	0.280	0.000704
15	3.05	0.0109	0.963	0.00354
20	7.250	0.03580	2.371	0.01157
25	12.59	0.08620	4.592	0.02862
30	19.78	0.1670	7.514	0.05841
35	27.03	0.2840	11.11	0.1048
40	34.33	0.4373	15.20	0.1706
45	41.47	0.6270	19.66	0.2575
50	48.16	0.8511	24.37	0.3675
60	60.92	1.397	34.28	0.6604
70	74.59	2.074	44.69	1.055
80	88.04	2.888	55.54	1.556
90	100.6	3.831	66.64	2.167
100	112.6	4.898	77.87	2.889
110	123.6	6.081	89.13	3.724
120	134.2	7.368	100.3	4.672
130	144.0	8.762	111.5	5.731
140	154.4	10.25	122.5	6.902
150	163.8	11.85	133.5	8.181
160	172.7	13.53	144.4	9.572
170	181.5	15.30	155.1	11.07
180	190.8	17.16	165.8	12.67
190	199.7	19.11	176.3	14.38
200	208.4	21.15	186.8	16.20
210	217.2	23.28	197.1	18.12
220	225.9	25.50	207.4	20.14
230	234.6	27.80	217.7	22.27
240	243.5	30.19	227.9	24.50
250	252.2	32.67	238.0	26.82
260	260.7	35.23	248.0	29.25
270	269.1	37.88	258.0	31.78
280	277.8	40.62	268.0	34.41
290	285.9	43.44	277.9	37.14
298.15	292.3	45.79	285.9	39.44
300	293.6	46.33	287.7	39.97
310	301.4	49.31	297.4	42.90
320	309.1	52.36	307.1	45.92
330	316.5	55.49	316.8	49.04
340	323.6	58.69	326.3	52.25
350	330.5	61.96	335.8	55.56
360	337.1	65.30	345.2	58.97
370	343.5	68.70	354.5	62.47
380	350	72.2	364	66.1
390	356	75.7	373	69.7
400	362	79.3	382	73.5
410	367	82.9	391	77.4
420	371	86.6	400	81.3
440	381	94.1	417	89.5
460	390	102	435	98.0
480	398	110	451	107
500	407	118	468	116
520	414	126	484	126
540	421	134	500	135
560	428	143	515	146
580	434	151	530	156
600	439	160	545	167
620	443	169	559	178
640	447	178	574	189
650	448	182	580	195

was used to measure the heat capacities over the temperature range of $330 \le (T/K) \le 650$.[18] The design of the device and the measurement procedure of the heat capacities were demonstrated in detail.[18] 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. As a result of the calibrations, it was found that the calorimeter and the measurement technique make it possible to obtain the heat capacity values with a maximum error of ± 2 % and the transformation temperatures within 0.5 K. Since the heat capacity of the compound examined was also measured over the temperature range of $330 \le (T/K) \le 350$ in the adiabatic calorimeter with an error of ± 0.2 % and the conditions of measurements in the dynamic device were chosen such that within the above temperature interval the $C^0_{p,m}$ values measured with the use of both calorimeters coincided, it was assumed that at $T \ge 350$ K the heat capacities were determined with an error of ± (0.5 to 2.0) %. The results for the heat capacity of the objects under study were obtained over the range of $330 \le (T/K) \le 650$ at the average rate of heating of the calorimeter and the substance of $1.5\ K\cdot s^{-1}$. The sample masses used for the calorimetric measurements were (0.9720 and 0.4704) g for $NaTi_2(PO_4)_3$ and $NaHf_2(PO_4)_3$, respectively.

Table 6. Parameters of the Debye Heat Capacity Functions for $NaTi_2(PO_4)_3$ and $NaHf_2(PO_4)_3$

substance	Θ_D/K	δ/%	temperature interval/K
$NaTi_2(PO_4)_3$	169.1	1.1	7 to 12
$NaHf_2(PO_4)_3$	132.0	1.0	6 to 11

Results and Discussion

All experimental results of the molar heat capacities of $NaTi_2(PO_4)_3$ and $NaHf_2(PO_4)_3$ over the range from $T = (6$ to $650)$ K are shown in Tables 2 and 3 and plotted in Figure 1. The heat capacities of the samples were between (30 and 70) % of the overall heat capacity of the calorimetric ampules with the substances under temperature change from (6 to 650) K.

The heat capacities of the samples rise gradually with increasing temperature, and no phase changes or thermal decompositions occurred.

The experimental points of $C_{p,\mathrm{m}}^0$ in the above temperature interval were fitted by means of the least-squares method using polynomial dependences, and the smoothed heat capacity values are shown in Tables 4 and 5. The root-mean-square deviations of the experimental points from the smoothed $C_{p,\mathrm{m}}^0 = f(T)$ curves were within ± 0.6 % in the range $T = (6$ to $80)$ K, ± 0.3 % from $T = (80$ to $200)$ K, ± 0.05 % between $T = (200$ to $350)$ K, and ± 0.5 % over the range $T = (350$ to $650)$ K, for both samples under study.

As Figure 1 illustrates, the phosphates do not undergo phase transitions in the studied temperature interval. It is seen that the temperature dependences of the molar heat capacities of $NaTi_2(PO_4)_3$ and $NaHf_2(PO_4)_3$ cross: at $100 \leq (T/\mathrm{K}) \leq 300$ the $C_{p,\mathrm{m}}^0(NaTi_2(PO_4)_3) > C_{p,\mathrm{m}}^0(NaHf_2(PO_4)_3)$, and at $T \geq 300$ K the $C_{p,\mathrm{m}}^0(NaTi_2(PO_4)_3) < C_{p,\mathrm{m}}^0(NaHf_2(PO_4)_3)$. It may be explained by the influence of sample's density on its heat capacity. The larger ionic radius and bigger molar mass of the framework-forming cation Hf^{4+} (compared with Ti^{4+}) differently influence the density of the hafnium sample (compared with titanium sample). At high temperatures the heat capacities of both samples are close to the value theoretically predicted from the Dulong and Pti rule: $C_{v,\mathrm{m}}^0(\text{predicted}) = 3RN = 3 \cdot 8.314 \cdot 18 = 449$ $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ (where N is number of atoms in the formula unit).

The values of the fractal dimension D_{fr} for $NaTi_2(PO_4)_3$ and $NaHf_2(PO_4)_3$ were determined from the experimental results of their heat capacities. In the fractal theory of the heat capacity[19−21] of solids, D_{fr} is the exponent at T in the $C_{v,\mathrm{m}}^0 = f(T)$ function. The significance of the D_{fr} value for solids gives information on the topology type of their structure. The relation "heat capacity versus T" is proportional to T^1 in the lower temperature range for chain-structured bodies, T^2 for solids with layer structures, and T^3 in the case of three-dimensional structures.

For sufficient accuracy, it can be taken that isobaric and isochoric heat capacities are equal at temperatures below 50 K. From the ln $C_{p,\mathrm{m}}^0$ versus ln$T$ plot, it is found that at temperatures between (20 and 45) K $D_{\mathrm{fr}} = 3$ for $NaTi_2(PO_4)_3$ and $NaHf_2(PO_4)_3$, within uncertainties of (1.1 and 1.0) %, respectively. This means that crystalline $NaTi_2(PO_4)_3$ and $NaHf_2(PO_4)_3$ have three-dimensional structures.

At lower temperatures, to calculate the thermodynamic functions (Tables 4 and 5), the heat capacities of the studied phosphates were described by the Debye function, $C_{p,\mathrm{m}}^0 \sim T^3$:

$$C_{p,\mathrm{m}}^0 = nD(\Theta_D/T)$$

where D denotes the Debye heat capacity function and n and Θ_D are specially selected parameters. Their values for $NaTi_2(PO_4)_3$ and $NaHf_2(PO_4)_3$ and uncertainties of their determination are presented in Table 6. While calculating the thermodynamic functions, it was assumed that, at $T < (6$ or $7)$ K, this equation reproduces the $C_{p,\mathrm{m}}^0$ values of $NaTi_2(PO_4)_3$ and $NaHf_2(PO_4)_3$ almost with the same accuracies.

Table 7. Absolute Entropies of the Simple Substances Necessary to Calculate the Standard Entropy of Formation of $NaTi_2(PO_4)_3$ and $NaHf_2(PO_4)_3$; $T = 298.15$ K, $p = 0.1$ MPa

substance	physical state[a]	$\Delta_0^{298.15\,\mathrm{K}} S_\mathrm{m}^0/\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$
Na	cr	51.30 ± 0.02
Ti	cr	30.72 ± 0.10
Hf	cr	43.555 ± 0.209
P	cr, white	41.09 ± 0.25
O_2	g	205.152 ± 0.005

[a] cr, crystalline; g, gaseous.

The thermodynamic functions of crystalline $NaTi_2(PO_4)_3$ and $NaHf_2(PO_4)_3$ were calculated from the $C_{p,\mathrm{m}}^0 = f(T)$ curves in the range from (0 to 650) K. The enthalpies $[H^o(T) - H^o(0)]$ and entropies $S^o(T)$ were calculated by numerical integration of the curves with respect to T and ln T, respectively. The Gibbs functions $[G^o(T) - H^o(0)]$ were calculated from $[H^o(T) - H^o(0)]$ and $S^o(T)$ values at respective temperatures.[22] The uncertainties for the function values are ± 2 % at $T < 15$ K, ± 0.5 % from (15 to 40) K, ± 0.3 % from $T = (40$ to $350)$ K, and ± 1.5 % in the temperature range between $T = (350$ and $650)$ K.

Using the value of the absolute entropies (Tables 4 and 5) and the elemental substances[23,24] (Table 7), the standard entropies of $NaTi_2(PO_4)_3$ and $NaHf_2(PO_4)_3$ formation at $T = 298.15$ K were estimated to be [(1174 ± 2) and (1207 ± 2)] $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$, respectively.

The values obtained fit to the following equations:

$$\mathrm{Na(cr) + 2Ti(cr) + 3P(cr, white) + 6O_2(g) = NaTi_2(PO_4)_3(cr)}$$

and

$$\mathrm{Na(cr) + 2Hf(cr) + 3P(cr, white) + 6O_2(g) = NaHf_2(PO_4)_3(cr)}$$

Conclusions

The general aim of these investigations was to report the results of a thermodynamic study of the $NaTi_2(PO_4)_3$ and $NaHf_2(PO_4)_3$ compounds belonging to the kosnarite structure type. The heat capacities of these phosphates were measured by adiabatic calorimetry and differential scanning calorimetry in the temperature range from [(6 or 7) to 650] K. The standard thermodynamic functions for $NaTi_2(PO_4)_3$(cr) and $NaHf_2(PO_4)_3$(cr), $C_{p,\mathrm{m}}^0$, $[H^o(T) - H^o(0)]$, $S^o(T)$, and $[G^o(T) - H^o(0)]$, over the range from $T \to 0$ to $T = 650$ K and the standard entropies of formation at $T = 298.15$ K were derived from these experimental results. The low-temperature ($T \leq 50$ K) dependences of the heat capacity were analyzed on the basis of the heat capacity theory of Debye and the multifractal variant, and as a result, their three-dimensional structure was established. The thermodynamic characteristics of the studied compounds were compared.

Supporting Information Available:

Tables with the experimental molar heat capacities of crystalline $NaHf_2(PO_4)_3$ and $NaTi_2(PO_4)_3$. This material is available free of charge via the Internet at http://pubs.acs.org.

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