Thermodynamic properties of crystalline phosphate Ba$_{0.5}$Zr$_2$(PO$_4$)$_3$ over the temperature range from $T \rightarrow 0$ to 610 K

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Abstract The temperature dependence of the heat capacity of crystalline barium zirconium phosphate $C_p^o = f(T)$ was measured over the temperature range 6–612 K. The experimental data obtained were used to calculate the standard thermodynamic functions $C_p^o(T)$, $H^o(T) - H^o(0)$, $S^o(T)$, $G^o(T) - H^o(0)$ over the temperature range from $T \rightarrow 0$ to 610 K and standard entropy of formation at 298.15 K. The data on the low-temperature ($6 \leq T/K \leq 50$) heat capacity were used to determine the fractal dimension of Ba$_{0.5}$Zr$_2$(PO$_4$)$_3$. Conclusions concerning the topology of the structure of phosphate were drawn. Thermodynamic properties of M$_{0.5}$Zr$_2$(PO$_4$)$_3$ (M = Ca, Sr, Ba) were compared.

Keywords Calorimetry · Heat capacity · Phosphate · Thermodynamic functions

Introduction

Phosphate Ba$_{0.5}$Zr$_2$(PO$_4$)$_3$ belongs to structural family of the mineral kosnarite KZr$_2$(PO$_4$)$_3$ [1, 2]. These phosphates possess high chemical, thermal and radiation stability, low thermal expansion, ability to include cations a different charge, and the size in crystal structure that allows designing hi-tech materials on their basis with demanded properties [3].

Ba$_{0.5}$Zr$_2$(PO$_4$)$_3$ keeps stability at action of high and low temperatures, has low thermal expansion, forms wide regions of solid state solutions with other substances of kosnarite family—it makes it perspective for use as a basis ceramics which properties can be purposefully regulated at the expense of composition change [3].

Earlier we and other authors studied the phase formation and thermodynamic properties of phosphates ML$_2$(PO$_4$)$_3$ (M = Li, Na, K, Rb, Cs, L = Ti, Zr, Hf) and M$_{0.5}$L$_2$(PO$_4$)$_3$ (M = Ca, Sr; L = Ti, Zr, Hf) phosphates with kosnarite structure [4–8]. In this study results of experimental studying of temperature dependence of a heat capacity of crystal compound Ba$_{0.5}$Zr$_2$(PO$_4$)$_3$ over the temperature range 6–612 K are presented, the standard thermodynamic functions $C_p^o(T)$, $H^o(T) - H^o(0)$, $S^o(T)$, $G^o(T) - H^o(0)$ over the temperature range from $T \rightarrow 0$ to 610 K and standard entropy of formation at 298.15 K are calculated. Thermodynamic properties of M$_{0.5}$Zr$_2$(PO$_4$)$_3$ (M = Ca, Sr, Ba) are compared.

Experimental

Sample characteristics

Phosphate Ba$_{0.5}$Zr$_2$(PO$_4$)$_3$ was prepared by the sol–gel method. The starting materials for its synthesis were BaCl$_2 \cdot$2H$_2$O, ZrOCl$_2 \cdot$8H$_2$O, and H$_3$PO$_4$ of kh. ch. (chemically pure) grade. Stoichiometric amounts of aqueous solutions of barium chloride and zirconium oxychloride (to prevent hydrolysis, zirconium oxychloride was dissolved in distilled water acidified with hydrochloric acid) were mixed under continuous stirring at room temperature. A solution of orthophosphoric acid, also taken in the amount corresponding to the stoichiometry of the product, was then slowly added under stirring. The gel formed was dried at 363 K and subjected to thermal treatment under the

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conditions of free access of air at 873, 1073, and 1373 K for no less than 24 h at each stage. Heating stages alternated with grinding.

The sample synthesized was a white polycrystalline powder. Its composition and structure were substantiated by X-ray diffraction, electron-probe analysis, and IR spectroscopy.

The X-ray powder pattern of the sample was recorded on a Shimadzu XRD-6000 diffractometer using filtered CuK_α radiation. The set of interplanar distances was compared with the data reported in [2]. The X-ray pattern only contained reflections characteristic of $Ba_{0.5}Zr_2(PO_4)_3$. The cell parameters (space group $R\overline{3}$, $a = 8.6468(6)$ Å, $c = 23.9436(2)$ Å, $V = 1550.35(1)$ Å^3, $Z = 6$) were determined from the indexed diffractogram over the 2θ angle range $12°$–$140°$ and refined by the method of least squares.

The chemical composition and homogeneity of the sample were controlled by X-ray spectral microanalysis using a CamScan MV-2300 scanning electron microscope equipped with a Link INCA ENERGY 200C energy dispersion detector. The compositions were calculated by the PAP correction method. Considering measurement errors (± 2 at.%), its composition corresponded to the $Ba_{0.52(3)}Zr_{2.01(4)}Hf_{0.02(0)}P_{2.96(5)}O_{12}$ formula.

The absorption spectrum of the sample prepared by the fine-dispersity film method on a KBr substrate was recorded on a Specord 75 IR spectrophotometer over the frequency range 1400–400 cm^{-1}. The positions and shapes of absorption bands were similar to those reported in [9] and typical of orthophosphates.

Apparatus and procedures for calorimetric measurements

The temperature dependence of the heat capacity C_p^o of the sample was measured over the temperature range 6–320 K on a BKT-3.07 thermophysical unit, which was a fully automated adiabatic vacuum calorimeter with discrete heating. The design of the calorimeter and the procedure for measurements were similar to those described in [10]. The reliability of calorimeter operation was checked by measuring the heat capacity of special-purity copper (OSCh-11-4 brand) and standard synthetic corundum and benzoic acid (K-2 brand). Calibration and test experiment results showed that the error in heat capacity measurements was no more than ± 2% at temperatures from 6 to 15 K. The errors decreased to ± 0.5% as the temperature increased to 40 K and were ± 0.2% over the temperature range 40–340 K. The absolute error in temperature measurements was 5×10^{-3} K according to ITS-90. The calorimetric ampoule contained 0.7842 g of the investigated substance.

Measurement of a heat capacity of the sample of phosphate $Ba_{0.5}Zr_2(PO_4)_3$ over the temperature range 300–612 K carried out with use of differential scanning calorimeter DSC204F1 of manufacture of firm Netzsch Geratebau, Germany. The design of calorimeter DSC204F1 and a work technique are similar described in work [11]. Checking of reliability of work of a calorimeter carried out by means of standard calibration experiments on measurement of thermodynamic characteristics of fusion n-geptan, mercury, indium, tin, lead, bismuth, and zinc. As a result of calibrations, it was found that the equipment and a measurement technique allow to measure temperatures of phase transformations with a margin error ± 0.2 K, enthalpy of transitions—± 1%. A heat capacity defined by standard technique Netzsch Software, the error of definition C_p^o, did not exceed ± 2.5%. Measurements spent at average speed of heating of an ampoule with substance of 5 K/min in argon atmosphere. The calorimetric ampoule contained 0.045 g of the investigated substance.

Results and discussion

Heat capacity

The heat capacity of crystalline $Ba_{0.5}Zr_2(PO_4)_3$ was studied over the temperature range 6–612 K (Table 1). Measurements on the adiabatic calorimeter gave 145 experimental values of C_p^o. The experimental values were averaged using power and semilogarithmic polynomials, which gave deviations of measurement results from the averaged $C_p^o = f(T)$ curve that did not exceed measurement errors.

All the experimental values and the averaging curve over the temperature range 6.2–610 K are shown in Fig. 1. We see that the heat capacity of $Ba_{0.5}Zr_2(PO_4)_3$ has no singularities and smoothly increases as the temperature grows. The curve kind $C_p^o = f(T)$ is typical of compounds with structure of kosnarite. Similar dependences $C_p^o = f(T)$ have been received by us earlier [7, 8] for $Ca_{0.5}Zr_2(PO_4)_3$ and $Sr_{0.5}Zr_2(PO_4)_3$ (Fig. 2). Absence of any polymorphic transformations on curves $C_p^o = f(T)$ in the studied area of temperatures is caused by stability of crystal phosphates.

We deemed it interesting to process low-temperature ($25 \leq T/K \leq 50$) heat capacity data taking into account the multifractal character of the vibrational states of atoms and determine the fractal dimension, D, of the structure [12, 13] and receive value of fractal dimensions, D, proceeding from the equation:

$$\ln C_v = \ln A + D\ln(T/\theta_{max}) \qquad (1)$$

where A is a constant for a particular solid, θ_{max} is the characteristic temperature, and D is the fractal dimension.

Table 1 Experimental data of molar heat capacity of Ba$_{0.5}$Zr$_2$(PO$_4$)$_3$, in J mol^{-1} K^{-1}; $M = 604.69$ g mol^{-1}, $p° = 0.1$ MPa

T/K	$C_p°$
Series 1	
6.26	0.361
6.50	0.402
6.64	0.429
6.75	0.449
6.85	0.470
6.92	0.483
6.98	0.495
7.04	0.508
7.08	0.517
7.09	0.520
7.25	0.554
7.46	0.606
7.73	0.673
8.10	0.773
8.41	0.867
8.72	0.968
9.04	1.08
9.69	1.32
10.37	1.63
11.06	2.00
11.63	2.33
12.47	2.77
13.56	3.54
14.62	4.35
15.66	5.049
16.68	5.852
17.69	6.548
18.75	7.314
19.68	7.995
21.43	9.39
23.79	11.47
26.14	14.12
28.50	17.40
30.87	20.98
33.26	24.57
35.67	28.07
38.08	31.42
40.32	34.49
42.56	37.55
44.99	41.20
47.43	44.88
49.87	48.77
52.31	52.56
54.76	56.64
57.21	60.43
59.66	64.29
62.11	67.91

Table 1 continued

T/K	$C_p°$
64.57	71.60
67.02	75.30
69.47	78.84
71.93	82.52
74.39	86.50
76.84	90.55
79.15	94.54
81.70	98.90
84.22	103.1
86.68	107.0
89.14	110.4
91.59	114.1
Series 2	
84.17	103.1
86.91	107.2
89.87	111.7
92.82	115.7
95.30	119.0
97.90	122.3
100.64	125.6
103.59	129.1
106.07	131.8
108.80	135.1
109.51	135.9
112.47	139.4
115.43	143.1
118.39	146.3
121.36	149.6
124.32	152.9
127.28	156.3
130.25	159.9
133.21	163.5
136.18	166.8
139.15	170.2
142.12	173.6
145.11	176.8
148.08	179.8
151.06	182.9
154.03	186.0
156.93	188.7
159.78	191.4
162.40	194.0
165.20	196.2
167.92	198.8
170.90	201.6
173.88	204.3
176.86	207.0
179.84	209.5

Table 1 continued

T/K	C_p^o
182.82	211.5
185.80	214.1
188.78	216.4
191.77	219.0
194.76	221.6
197.74	223.8
200.52	225.9
203.26	228.0
206.26	230.2
209.02	232.4
210.27	233.4
212.50	234.9
215.22	237.3
217.97	239.4
220.95	241.8
223.92	244.3
226.89	246.8
229.66	249.1
232.34	251.2
235.29	253.4
238.24	255.4
241.18	257.3
244.11	259.3
247.04	261.0
249.95	263.1
252.85	265.5
254.91	266.7
257.51	268.4
260.38	270.4
263.25	272.3
266.09	274.6
268.92	276.5
271.73	278.7
274.52	280.6
275.66	281.3
278.16	282.8
280.93	284.3
283.69	286.5
286.42	288.2
289.14	289.9
291.85	291.9
294.69	294.0
297.42	295.9
300.13	297.9
302.83	299.6
305.51	301.5
308.19	303.1
310.85	305.3

Table 1 continued

T/K	C_p^o
314.36	307.5
316.74	309.0
319.39	310.9
Series 3	
301.9	299
304.4	301
306.9	303
309.4	304
311.9	306
314.4	307
316.9	309
319.4	311
321.9	312
324.4	313
326.9	315
329.4	316
331.9	317
334.4	319
336.9	320
339.4	321
341.9	323
344.4	324
346.9	325
349.4	327
351.9	328
354.4	329
356.9	330
359.4	331
361.4	332
364.4	333
366.9	333
369.4	334
371.9	335
374.4	335
376.9	336
379.4	337
381.9	338
384.4	339
386.9	340
389.4	340
391.9	341
394.4	342
396.9	343
399.4	344
401.9	344
404.4	345
406.9	346
409.4	347

Table 1 continued

T/K	C_p^o
411.9	347
414.4	348
416.9	349
419.4	349
421.9	350
424.4	350
426.6	351
429.4	352
431.9	353
434.4	353
436.9	355
439.4	355
441.9	356
444.4	357
446.9	358
449.4	359
451.9	359
454.4	360
456.9	360
459.4	361
461.9	362
464.4	363
466.9	363
469.4	364
471.9	365
474.4	365
476.9	366
479.4	367
481.9	367
484.4	368
486.9	368
489.4	369
491.9	369
494.4	370
496.9	371
499.4	371
501.9	372
504.4	372
506.9	373
509.4	373
511.9	374
514.4	374
516.9	375
519.4	375
521.9	376
524.4	376
526.9	377
529.4	377

Table 1 continued

T/K	C_p^o
531.9	378
534.4	378
536.9	379
539.4	379
541.9	380
544.4	381
546.9	381
549.4	382
551.9	382
554.4	383
556.9	383
559.4	383
561.9	384
564.4	384
566.9	385
569.4	385
571.9	385
574.4	386
576.9	386
579.4	386
581.9	387
584.4	387
586.9	387
589.4	387
591.9	388
594.4	388
596.9	388
599.4	389
601.9	389
604.4	389
606.9	390
609.4	390
611.9	390

The D value is an indirect characteristic of the topology of the structure and can be used to draw conclusions about the geometric characteristics of the structure of solids. For chain, layered, and three-dimensional structures, $D = 1, 2$, and 3, respectively.

We can, without the introduction of substantial errors, assume that, at $T < 50$ K, C_p^o equals C_V. This assumption and the corresponding experimental heat capacity data over the temperature range 25–50 K give $D = 3$ (with an uncertainty of $\pm 0.5\%$) for Ba$_{0.5}$Zr$_2$(PO$_4$)$_3$, which corresponds to its framework structure. Note that this conclusion is in agreement with the structural data on Ba$_{0.5}$Zr$_2$(PO$_4$)$_3$ [2].
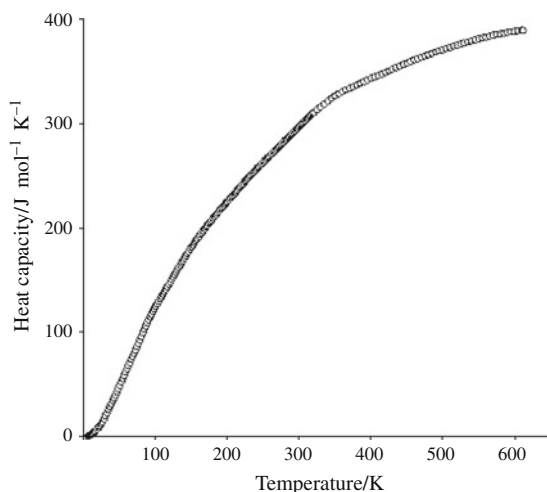
Fig. 1 Heat capacity of crystalline phosphate $Ba_{0.5}Zr_2(PO_4)_3$
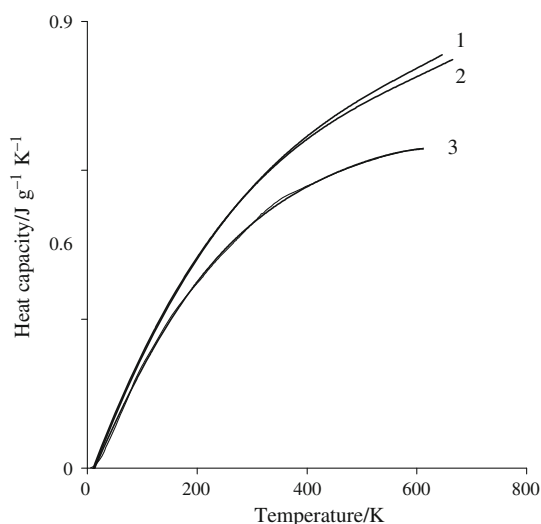
Fig. 2 Heat capacity of phosphates $Ca_{0.5}Zr_2(PO_4)_3$ (*1*), $Sr_{0.5}Zr_2(PO_4)_3$ (*2*), $Ba_{0.5}Zr_2(PO_4)_3$ (*3*)

At $T < 20$ K and lower (to the temperature of the beginning of measurements), the heat capacity of $Ba_{0.5}Zr_2(PO_4)_3$ is described by the Debye heat capacity function:

$$C_p^o = n\mathbf{D}(\theta_{\mathbf{D}}/T) \tag{2}$$

where **D**—a symbol of function of a heat capacity of Debye.

The characteristic Debye temperature $\theta_{\mathbf{D}} = 138.5$ K was found from the experimental values C_p^o over the temperature range 6–12 K at the number of degrees of freedom $n = 6$. The $\theta_{\mathbf{D}}$ value was calculated by (2) with an error of 0.6%, which did not exceed the error in measurements C_p^o over the temperature range specified.

Table 2 Fractal dimensions, D, and characteristic temperatures θ_{max}

Compound	Temperature range/K	D	θ_{max}/K	δ^a/%
$Ca_{0.5}Zr_2(PO_4)_3^b$	7–12	3	112.8	1
	30–50	3	218.6	0.5
$Sr_{0.5}Zr_2(PO_4)_3^c$	7–12	3	113.5	0.5
	30–50	3	193.9	1.7
$Ba_{0.5}Zr_2(PO_4)_3$	6–12	3	138.5	0.6
	25–50	3	207.7	0.9

Number of degrees of freedom $n = 6$

[a] Error in the fitting

[b] Values of D and θ_{max} have been calculated using data from [8]

[c] Values of D and θ_{max} have been taken from [7]

In Table 2 for comparison are resulted fractal dimensions and characteristic temperatures of Debye $Ba_{0.5}Zr_2(PO_4)_3$ and studied by us earlier $Ca_{0.5}Zr_2(PO_4)_3$ and $Sr_{0.5}Zr_2(PO_4)_3$ [7, 8]. All compounds, judging by values of D and the data of structural analysis, have framework structure. The numerical values θ_{max} calculated for an identical interval of temperatures allow to do some conclusions about relative rigidity of frameworks of compared phosphates. Judging by values of characteristic temperatures of Debye, rigidities of their frameworks are close.

Thermodynamic functions

The standard thermodynamic functions of crystalline $Ba_{0.5}Zr_2(PO_4)_3$ (Table 3) were calculated after the extrapolation of the temperature dependence of its heat capacity from 6 to 0 K using the Debye heat capacity function for solids (Eq. 2) with the parameters given above. It was assumed that Eq. 2 reproduced the C_p^o values at $T < 6$ K with the error specified above.

The $H°(T) - H°(0)$ enthalpy and $S°(T)$ entropy of the compound were calculated by the numerical integration of the $C_p^o = f(T)$ and $C_p^o = f(\ln T)$ dependences, respectively, and the $[G°(T) - H°(0)]$ Gibbs function, using the enthalpies and entropies of the compound at the corresponding temperatures. It was assumed that function calculation errors made no noticeable contribution to the accuracy of function determination, that is, did not exceed the heat capacity measurement errors specified above.

The absolute entropies of the compound under study $S°$ ($Ba_{0.5}Zr_2(PO_4)_3$, к, 298.15) = 307.1 ± 1.0 J/(mol K) (Table 3) and the corresponding simple substances $S°$ (Ba, cr, 298.15) = 62.48, $S°$ (Zr, cr, 298.15) = 38.994 ± 0.167, $S°$ (P, cr, 298.15) = 41.09 ± 0.25, $S°$ (O_2, g, 298.15) = 205.152 ± 0.005 J/(mol K) taken from [14, 15] were used to calculate the standard entropy of formation

**Table 3** Standard thermodynamic functions of Ba$_{0.5}$Zr$_2$(PO$_4$)$_3$; $M = 604.69$ g mol^{-1}

T/K	C_p^o/ J mol^{-1} K^{-1}	$H^o(T) - H^o(0)$/ kJ mol^{-1}	$S^o(T)$/ J mol^{-1} K^{-1}	$-[G^o(T) - H^o(0)]$/ kJ mol^{-1}
5	0.183	0.000200	0.0611	0.0000760
10	1.46	0.00360	0.486	0.00122
15	4.578	0.01830	1.618	0.005987
20	8.246	0.05030	3.443	0.01859
25	12.78	0.1022	5.738	0.04121
30	19.63	0.1824	8.637	0.07672
40	34.05	0.4523	16.31	0.2001
50	48.93	0.8651	25.46	0.4077
60	64.78	1.435	35.80	0.7132
70	79.63	2.157	46.90	1.126
80	95.96	3.033	58.57	1.653
90	111.9	4.075	70.83	2.300
100	124.8	5.260	83.30	3.070
110	136.5	6.567	95.75	3.966
120	148.1	7.990	108.1	4.985
130	159.7	9.529	120.4	6.128
140	171.1	11.18	132.7	7.393
150	181.8	12.95	144.9	8.781
160	191.7	14.82	156.9	10.29
170	200.8	16.78	168.8	11.92
180	209.3	18.83	180.5	13.67
190	217.6	20.97	192.1	15.53
200	225.4	23.18	203.4	17.51
210	233.1	25.47	214.6	19.60
220	241.3	27.84	225.7	21.80
230	249.1	30.30	236.6	24.11
240	256.5	32.83	247.3	26.53
250	263.4	35.42	257.9	29.06
260	270.3	38.09	268.4	31.69
270	277.1	40.83	278.7	34.42
280	284.0	43.64	288.9	37.26
290	290.8	46.51	299.0	40.20
298.15	296.4	48.90	307.1	42.67
300	297.6	49.45	309.0	43.24
310	304.5	52.46	318.8	46.38
320	310.6	55.54	328.6	49.62
330	316	58.7	338	53.0
340	322	61.9	348	56.4
350	327	65.1	357	59.9
360	331	68.4	366	63.5
370	334	71.7	376	67.2
380	337	75.1	385	71.0
390	340	78.5	393	74.9
400	344	81.9	402	78.9
410	346	85.3	411	83.0
420	349	88.8	419	87.1

Table 3 continued

T/K	C_p^o/ J mol^{-1} K^{-1}	$H^o(T) - H^o(0)$/ kJ mol^{-1}	$S^o(T)$/ J mol^{-1} K^{-1}	$-[G^o(T) - H^o(0)]$/ kJ mol^{-1}
430	353	92.3	427	91.3
440	356	95.9	435	95.7
450	359	99.4	443	100
460	361	103	451	105
470	364	107	459	109
480	367	110	467	114
490	369	114	474	118
500	371	118	482	123
510	373	121	489	128
520	376	125	496	133
530	378	129	504	138
540	380	133	511	143
550	382	137	518	148
560	383	140	525	153
570	385	144	531	159
580	386	148	538	164
590	388	152	545	169
600	389	156	551	175
610	390	160	558	180

of Ba$_{0.5}$Zr$_2$(PO$_4$)$_3$, $\Delta_f S^o$ (Ba$_{0.5}$Zr$_2$(PO$_4$)$_3$, к, 298.15) = -1156 ± 2 J/(mol K). This value corresponds to the reaction:

$$0.5\text{Ba(cr)} + 2\text{Zr(cr)} + 3\text{P(cr, white)} + 6\text{O}_2\text{(g)}$$
$$= \text{Ba}_{0.5}\text{Zr}_2\text{(PO}_4)_3\text{(cr)}$$
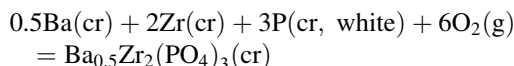
To summarize, we for the first time studied the isobaric heat capacity of crystalline phosphate Ba$_{0.5}$Zr$_2$(PO$_4$)$_3$ over the temperature range 6–612 K, calculated its thermodynamic functions $C_p^o(T)$, $H^o(T) - H^o(0)$, $S^o(T)$, and $G^o(T) - H^o(0)$ over the temperature range 0–610 K, and determined the standard entropy of its formation from simple substances at 298.15 K. By data of low-temperature heat capacities, fractal dimension D is calculated and the type of topology of structure Ba$_{0.5}$Zr$_2$(PO$_4$)$_3$ is defined.

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