Thermochimica Acta 474 (2008) 47–51

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Refined heat capacity of $LaPO_4$ in the temperature range 0–1600 K

K.S. Gavrichev[a,*], M.A. Ryumin[a], A.V. Tyurin[a], V.M. Gurevich[b], L.N. Komissarova[c]

[a] Kurnakov Institute of General and Inorganic Chemistry, RAS, Leninsky Prospect, 31, Moscow 119991, Russia
[b] Vernadsky Institute of Geochemistry and Analytical Chemistry, RAS, Kosygin Street 19, Moscow 119991, Russia
[c] Chemical Department, Moscow State University, Vorob'evy Gory, Moscow 119889, Russia

ARTICLE INFO

Article history:
Received 2 January 2008
Received in revised form 10 March 2008
Accepted 9 May 2008
Available online 24 May 2008

Keywords:
Lanthanum orthophosphate
Heat capacity
Thermodynamic properties

ABSTRACT

The critical analysis of literature heat capacity data in the temperature range 0–1600 K was carried out. It was shown that joining of $C_p(T)$ curves obtained by the different methods was performed improperly. Experimental heat capacity of $LaPO_4$ was measured in the region 16–324 K by the adiabatic calorimetry. The obtained data allows to consist the results of different works and to fit the lanthanum orthophosphate heat capacity in the wide temperature range. Standard thermodynamic properties were calculated on the basis of the refined heat capacity data: $C_p^0(298.15\,K) = 102.5 \pm 0.2\,J\,K^{-1}\,mol^{-1}$, $S^0(298.15\,K) = 108.7 \pm 0.2\,J\,K^{-1}\,mol^{-1}$, $H^0(298.15\,K) - H^0(0\,K) = 17.44 \pm 0.03\,kJ\,mol^{-1}$, $\Phi^0(298.15\,K) = 50.21 \pm 0.20\,J\,K^{-1}\,mol^{-1}$.

1. Introduction

High thermal stability of the lanthanid orthophosphates makes it possible to use them in the elaboration of the new advanced materials. In part, the ability to incorporate actinides in quite large quantities with the formation of solid solutions as well as good resistance to α-decay is very attractive.

Lanthanum orthophosphate belongs to $Ln^{III}PO_4$ (Ln^{III} = La–Dy) group with the monazite ($CePO_4$) structure. The parameters of unit cell (space group $P2_1/n$, $Z = 4$) are: $a = 6.831$ Å, $b = 7.070$ Å, $c = 6.503$ Å, $\beta = 103.27$ [1]. The main structure fragments are LnO_9 polyhedron each linked with six neighboring polyhedron by the edge. Linkage is taking place by the connection of six polyhedron in oval-like circle inside of which PO_4 polyhedron is located. Such structure is the characteristic for orthophosphates, arsenates and vanadates of 3^+-charged cations with large ionic radia (La–Gd and Bi). This group of orthophosphates has the high thermal stability ($T_m > 2270$ K). They are almost insoluble in water, non-hygroscopic and have high chemical stability.

Low temperature heat capacity of the lanthanum orthophosphate (sample mass 38.8 mg) was measured in [2] by hybrid adiabatic relaxation method in the temperature range from 2 to 380 K. The uncertainty of measurements reported in this work is estimated by the authors from 1 to 3% depending on the temperature (higher precision generally above 100 K). Heat capacity was fitted in the temperature range from 10 to 380 K by the equation (in $J\,K^{-1}\,mol^{-1}$):

$$C^0_{p,m} = -1.0111 - 0.0955T + 0.0144T^2 - 1.3306 \times 10^{-4}T^3 + 5.54156 \times 10^{-7}T^4 - 1.10366 \times 10^{-9}T^5 + 0.848485 \times 10^{-12}T^6. \quad (1)$$

Critical assessment of the experimental heat capacity and fitted curve showed that starting from 250 K smoothed $C_p(T)$ values, estimated by Eq. (1) using coefficients given in [2, Table 6], is located below experimental ones. For example, at 300 K smoothed $C_p = 99.03\,J\,K^{-1}\,mol^{-1}$ and authors presented for $LaPO_4$ value $C_p = 101.28$ at 298.15 K. In addition, calculation of C_p value using Eq. (1) at 12 K gives the negative value. By the way, the coefficients of Eq. (1), given in [2], were corrected in [3] (number of the decimals has been increased) to accurately reproduce the published experimental values.

The high temperature enthalpy $H^0(T) - H^0(298.15\,K)$ of $LaPO_4$ was measured in [4] in the region 373.0–1595.7 K using the drop calorimeter with massive isothermal shield. Coefficients of equations describing the temperature dependences of $LaPO_4$ heat capacity and enthalpy increment in the range 298–1600 K were calculated on the basis of the experimental data:

$$C^0_p(T) = 119.37 + 9.20 \times 10^{-3}T - 15.63 \times 10^5 T^{-2}, \quad (2)$$

$$H^0(T) - H^0(298.15\ K) = 119.37T + 4.60 \times 10^{-3}T^2 + 15.63 \times 10^5 T^{-1} - 40832. \quad (3)$$

---

[*] Corresponding author. Tel.: +7 495 9542911; fax: +7 495 9541279.
E-mail address: gavrich@igic.ras.ru (K.S. Gavrichev).

0040-6031/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2008.05.004

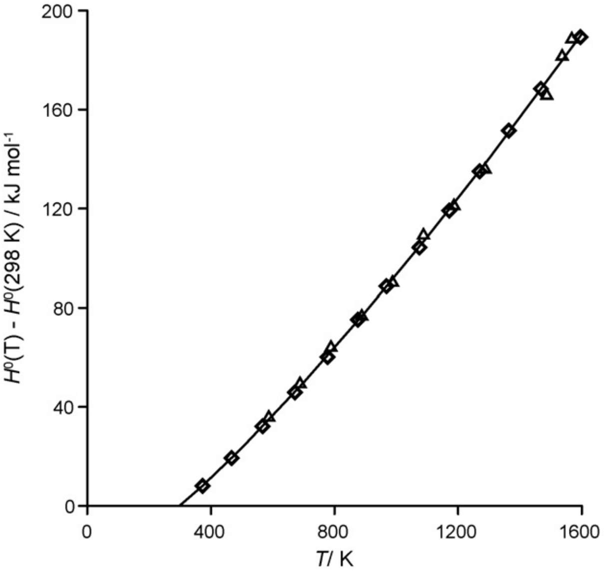

Fig. 1. Enthalpy increment of $LaPO_4$ from [3] (rhombus) and [4] (triangles), solid line—Eq. (3).

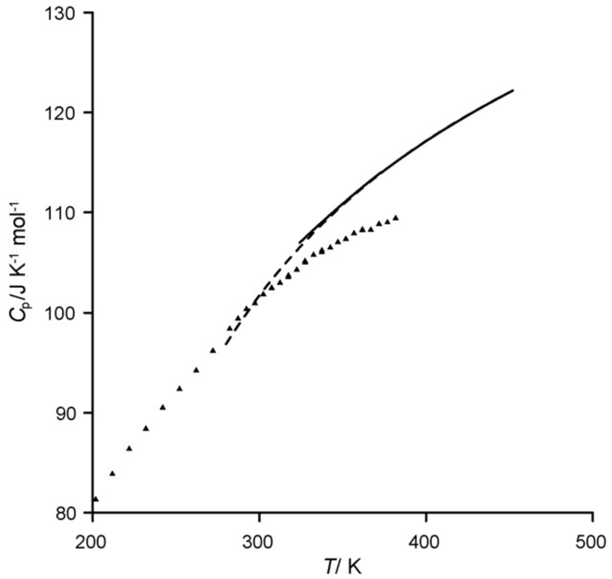

Fig. 2. Intersection of low and high temperature heat capacity curves: filled triangle, [2]; solid line, [3]; dashed line, [4].

Uncertainties of the heat capacity vary from 1.6% at 298 K to 0.5% at 800 K and 1.8% at 1600 K.

Popa et al. [3] carried out the high temperature measurements of enthalpy increment using Setaram Multi-detector High Temperature Calorimeter (MHTC-96) equipped by the drop mode. Their results are in good agreement with drop-calorimetric enthalpy data by Tsagareishvili et al. [4], although the heat capacity data by Popa et al. [3] have the larger point deviation (Fig. 1). Fitting of enthalpy data was performed together with data [3] and $C_p^0(298.15\ K) = 101.28\ J\ K^{-1}\ mol^{-1}$ from [2]:

$$C_p^0(T) = 121.1275 + 30.1156 \times 10^{-3}T - 25.625 \times 10^5 T^{-2} \quad (4)$$

with the uncertainty of 3%. Detail consideration of the region of joining of low and high temperature $C_p(T)$ curves showed that they do not coincide but intersect (Fig. 2).

The refinement of low temperature heat capacity was based on experimental study, joining of low and high temperature data and calculation of the thermodynamic properties of $LaPO_4$ in the wide temperature range were the goals of this research.

2. Experimental

Precipitation from the solution was used to synthesized the lanthanum orthophosphate. The lanthanum sesquioxide ("pure for analysis" grade, 99.9 mol.%) was dissolved in concentrated HNO_3 at moderate (~323 K) heating. Ammonia solution was added to the formed solution of lanthanum nitrate to the point of pH 7–8. Obtained $La(OH)_3$ was repeatedly washed by the bidistilled water to remove soluble nitrates. The separation of liquid and solid phases was made by the repeated decantation. Pre-calculated amount of the phosphoric acid was added to the sediment at the intensive mixing and was kept during 12 h. Obtained precipitate of the orthophosphate was carefully washed by water. Obtained $LaPO_4 \cdot nH_2O$ was dried initially at 333 K and fired at 773 and 1173 K. Purity of the obtained lanthanum orthophosphate was verified by X-ray diffraction at the room temperatures using by DRON-3M setup. Unit cell parameters of the obtained $LaPO_4$ ($a = 6.841(3)$ Å, $b = 7.065(3)$ Å, $c = 6.503(2)$ Å, $\beta = 103.27(3)$) are in good agreement with literature data [1].

The prepared sample of $LaPO_4$ was white-colored powder with grain size from 10 to 100 μm. Heat capacity measurements were carried out in the adiabatic calorimeter TERMIS BKT-3. Heat capacity measurements were carried out in the automatic regime using the operating system with PC and unit of analogous control and data acquisition. Samples were loaded in the thin-wall cylindrical titanium containers (inner volume 1 cm^3) sealed by indium. The 100-Ω iron–rhodium thermometer (ITS-90 scale) was used for the temperature measurement. Setup design and operating procedures were reported elsewhere [5]. The reliability of the measuring procedure was verified by measurements of standard substance K-1 benzoic acid. The uncertainties of heat capacity measurements was ±2% at the temperatures below 20 K, ±0.4% in the range 20–50 K and 0.2% in the range 40–350 K. Sample weight was 1.42707 g; the molecular mass calculated from [6] was 233.877 g mol^{-1}.

Experimental $C_p(T)$ points (Table 1) were smoothed using the ADEK equation [7]:

$$C_p^0(T) = a_0 T (C_v)^2 + n\left[\left(\frac{1}{3}\right)\sum_{j=1}^{3} a_j D_j\left(\frac{\theta_j}{T}\right) + a_4 E\left(\frac{\theta_E}{T}\right) + a_5 K\left(\frac{\theta_L}{T}, \frac{\theta_U}{T}\right)\right], \quad (5)$$

where n is the number of atoms in molecule (for $LaPO_4$ $n = 6$); D and E are Debye and Einstein functions, K is Kieffer K-function [8]; θ_1, θ_2, θ_3, θ_E, θ_L, θ_U are the characteristic temperatures; a_0, a_1, a_2, a_3, a_4, a_5 the linear coefficients. The *a and θ* values were calculated by LSM [9]. The Eq. (5) was used for calculation of entropy, enthalpy change and derived Gibbs energy.

3. Results and discussions

Measurements of $LaPO_4$ heat capacity was carried out in the region 25–324 K. In the range 25–200 K data [2] and our results are in good agreement, whereas above 200 K experimental curves are separate (Fig. 3). Smoothing of the experimental curve accordingly with Eq. (5) allows to calculate the thermodynamic properties and coefficients (Table S1, Supplementary materials), and to extrapolate

Table 1
Experimental heat capacity of $LaPO_4$

T (K)	C_p^0 (J K^{-1} mol^{-1})	T (K)	C_p^0 (J K^{-1} mol^{-1})	T (K)	C_p^0 (J K^{-1} mol^{-1})	T (K)	C_p^0 (J K^{-1} mol^{-1})
25.03	3.418	58.89	22.97	111.60	51.16	208.46	82.89
25.80	3.691	59.72	23.49	112.25	51.55	211.61	83.64
26.57	3.997	60.54	24.01	114.04	52.08	214.75	84.46
27.34	4.269	61.37	24.55	114.70	52.52	217.89	85.24
28.12	4.620	62.20	25.10	116.47	53.12	220.27	86.55
28.89	4.940	63.03	25.60	117.16	53.55	223.51	87.38
29.68	5.294	63.86	26.14	119.61	54.49	226.73	88.15
30.46	5.695	64.69	26.66	122.06	55.51	229.94	88.77
31.24	6.098	65.52	27.24	124.51	56.30	233.13	89.33
32.03	6.511	66.35	27.76	126.96	57.27	236.34	89.95
32.86	6.925	67.19	28.22	129.40	58.21	239.53	90.87
33.65	7.346	68.02	28.62	131.85	59.09	242.69	91.56
34.44	7.659	68.86	29.07	134.29	59.99	245.83	92.05
35.24	8.049	69.70	29.48	136.73	60.84	248.99	92.61
36.04	8.576	70.93	30.26	139.17	61.67	252.14	93.33
36.84	9.023	72.58	31.21	141.61	62.60	255.28	94.20
37.64	9.523	73.58	31.56	144.05	63.49	258.37	94.93
38.44	9.994	74.82	32.17	146.46	64.31	261.31	95.40
39.25	10.48	76.07	33.31	148.90	65.12	264.37	95.93
40.05	10.95	77.32	33.78	151.33	65.92	267.41	96.50
40.86	11.44	78.55	34.74	153.76	66.80	270.48	97.19
41.67	11.92	80.58	36.06	156.18	67.59	273.52	97.78
42.48	12.40	82.23	36.90	158.61	68.21	276.54	98.45
43.29	12.88	83.88	37.58	161.03	69.15	279.55	99.00
44.10	13.34	85.53	38.39	163.45	69.96	282.53	99.55
44.92	13.87	87.18	39.57	165.87	70.75	285.49	100.2
45.76	14.39	88.83	40.58	168.29	71.39	288.42	100.6
48.20	16.03	90.48	41.33	170.70	72.25	291.33	101.2
49.02	16.52	92.13	42.17	173.11	73.03	294.21	101.7
49.84	17.11	93.78	42.97	175.52	73.72	297.05	102.3
50.65	17.64	95.43	43.79	177.92	74.42	299.79	102.8
51.47	18.19	97.08	44.53	180.31	75.07	302.76	103.4
52.29	18.72	101.86	46.91	182.70	75.83	306.59	104.1
53.11	19.27	102.42	47.17	185.04	76.53	310.93	105.0
53.93	19.79	104.27	47.95	187.44	77.24	315.50	105.8
54.75	20.27	104.88	48.25	189.83	77.90	320.00	106.5
55.57	20.78	106.71	49.05	192.21	78.51	324.45	106.9
56.40	21.36	107.34	49.42	199.36	80.46		
57.22	21.86	109.16	50.14	202.14	81.27		
58.04	22.41	109.80	50.46	205.30	82.08		

curves from 324 to 373 K (starting point of [4]). Our extrapolation curve coincides rather well with Eq. (2) of [4] in the range 373–450 K and differ from [3]. Critical assessment of the data obtained in this work and the literature ones allows us to recommend the heat capacity from the following works as most reliable for different temperature ranges:

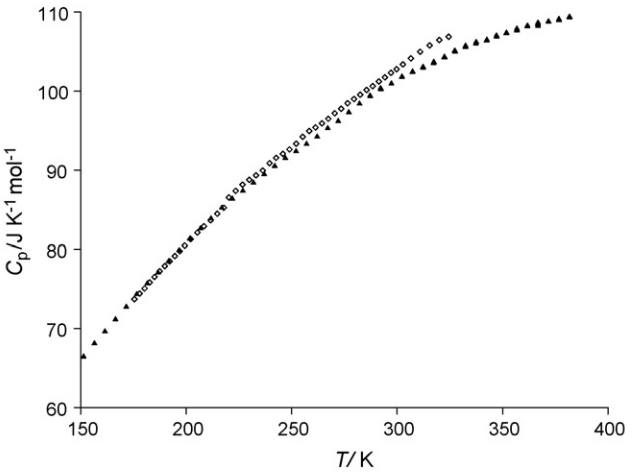

Fig. 3. Comparison of heat capacity from [2] (filled triangle) and this work (rhombus).

(1) 2–25 K—[2] (experimental);
(2) 25–324 K—this work (experimental);
(3) 324–373 K—this work (extrapolation);
(4) 373–1600 K—[4] (experimental).

As well as heat capacity curve in the wide temperature range cannot be described by one equation, we gradually smoothed the experimental data with the overlapping of the smoothing regions and presented the results in Table 1. Smoothing of $LaPO_4$ heat capacity data from [2] in the range from 2 to 25 K was carried out using the polynomial, described in [10]:

$$C_p^0(T) = \sum_{j=0}^{m} A_j(1 - \exp(-0.001T)^j. \qquad (6)$$

The deviation of experimental points for the ranges 2–25 K and 25–324 K is given in Figs. S1a and S1b (Supplementary materials), relatively. Smoothed values of the heat capacity, entropy, enthalpy change and derived Gibbs energy are presented in Table 2. At the temperature 25 K $C_p^0(T)$ quantities were calculated by the Eqs. (5) and (6) differ by 0.001 J K^{-1} mol^{-1} (3.202 and 3.201 J K^{-1} mol^{-1}, relatively).

The refined standard thermodynamic functions at 298.15 K are: $C_p^0(298.15\,K) = 102.5 \pm 0.2$ J K^{-1} mol^{-1}, $S^0(298.15\,K) = 108.7 \pm 0.2$ J K^{-1} mol^{-1}, $H^0(298.15\,K) - H^0(0\,K) = 17.44 \pm 0.02$ kJ mol^{-1}, $\Phi^0(298.15\,K) = 50.21 \pm 0.20$ J K^{-1} mol^{-1}.

Table 2
Smoothed thermodynamic properties of $LaPO_4$

T (K)	$C_p^0(T)$ (J K^{-1} mol^{-1})	$S^0(T)$ (J K^{-1} mol^{-1})	$H^0(T) - H^0(0)$ (J mol^{-1})	$\Phi^0(T)$ (J K^{-1} mol^{-1})
2	.00122	.00041	.00061	.00011
4	.01153	.00372	.01169	.00080
6	.03674	.01262	.05778	.00299
8	.08437	.02910	.1754	.00718
10	.1669	.05610	.4214	.01396
12	.2994	.09746	.8805	.02408
14	.4971	.1576	1.668	.03848
16	.7738	.2412	2.928	.05820
18	1.141	.3527	4.831	.08431
20	1.605	.4961	7.565	.1179
25	3.201	1.015	19.34	.2411
30	5.306	1.776	40.39	.4298
35	7.890	2.783	73.21	.6909
40	10.82	4.024	119.9	1.027
45	13.97	5.479	181.8	1.439
50	17.23	7.119	259.8	1.924
60	23.73	10.84	464.7	3.092
70	29.93	14.97	733.3	4.490
80	35.68	19.34	1062	6.071
90	40.96	23.86	1445	7.795
100	45.82	28.43	1880	9.629
110	50.30	33.01	2361	11.55
120	54.48	37.56	2885	13.53
130	58.40	42.08	3449	15.55
140	62.10	46.55	4052	17.60
150	65.60	50.59	4691	19.68
160	68.93	55.29	5363	21.77
170	72.09	59.57	6069	23.87
180	75.12	63.77	6805	25.97
190	78.01	67.91	7570	28.07
200	80.78	71.98	8365	30.16
210	83.44	75.99	9186	32.25
220	85.98	79.93	10,030	34.33
230	88.41	83.81	10,900	36.39
240	90.75	87.62	11,800	38.45
250	92.99	91.37	12,720	40.49
260	95.13	95.06	13,660	42.52
270	97.19	98.69	14,620	44.53
280	99.17	102.3	15,600	46.53
290	101.1	105.8	16,600	48.51
300	102.9	109.2	17,620	50.48
320	106.3	116.0	19,720	54.36
340	*109.4*	*122.5*	*21,870*	*58.18*
360	*112.3*	*128.8*	*24,090*	*61.93*
373	113.9	132.9	25,560	64.41
400	117.1	141.0	28,680	69.31
450	122.0	155.1	34,670	78.07
500	126.0	168.2	40,870	86.43
550	129.4	180.3	47,260	94.42
600	132.4	191.7	53,810	102.1
650	135.2	202.4	60,500	109.4
700	137.7	212.6	67,320	116.4
750	140.1	222.1	74,270	123.1
800	142.4	231.3	81,330	129.6
850	144.6	240.0	88,500	135.8
900	146.7	248.3	95,780	141.8
950	148.7	256.3	103,170	147.7
1000	150.8	263.9	110,660	153.3
1050	152.8	271.3	118,250	158.7
1100	154.7	278.5	125,930	164.0
1150	156.6	285.4	133,720	169.1
1200	158.5	292.1	141,600	174.1
1250	160.4	298.6	149,570	179.0
1300	162.3	305.0	157,640	183.7
1350	164.2	311.1	165,800	188.3
1400	166.0	317.1	174,060	192.8
1450	167.9	323.0	182,410	197.2
1500	169.7	328.7	190,850	201.5
1550	171.5	334.3	199,380	205.7
1600	173.4	339.8	208,000	209.8

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tca.2008.05.004.

References

[1] G. Lohmueller, Acta Crystallogr. B 29 (1973) 141.

[2] C. Thiriet, R.J.M. Konings, P. Javorsky, N. Magnani, F. Wastin, J. Chem. Thermodyn. 37 (2005) 131.

[3] K. Popa, D. Sedmidubsky, O. Beneš, C. Thiriet, R.J.M. Konings, J. Chem. Thermodyn. 38 (2006) 825.

[4] D.Sh. Tsagareishvili, G.G. Gvelesiani, V.P. Orlovskii, T.V. Belyaevskaya, V.P. Repko, Inorg. Mater. 8 (1972) 1790.

[5] R.M. Varushchenko, A.I. Druzhinina, E.L. Sorkin, J. Chem. Thermodyn. 29 (1997) 623.

[6] http://physics.nist.gov/PhysRefData/Compositions/.

[7] K.S. Gavrichev, N.N. Smirnova, V.M. Gurevich, V.P. Danilov, A.V. Tyurin, M.A. Ryumin, L.N. Komissarova, Thermochim. Acta 448 (2006) 63.

[8] S.W. Kieffer, Rev. Geophys. Space Phys. 17 (1979) 35.

[9] V.M. Gurevich, V.E. Gorbunov, K.S. Gavrichev, I.L. Khodakovskii, Geochem. Int. 4 (1999) 367–377.

[10] V.M. Gurevich, V.G. Khlyustov, Geokhimiya 6 (1979) 829.