Journal of Thermal Analysis and Calorimetry, Vol. 65 (2001) 381–389

THERMODYNAMIC PROPERTIES OF THE $MZr_2(PO_4)_3$ (M=Na, K, Rb OR Cs) COMPOUNDS

V. I. Pet'kov, K. V. Kir'yanov, A. I. Orlova and D. B. Kitaev

Department of Chemistry, Nizhni Novgorod State University, Gagarin av. 23,
603950 Nizhni Novgorod, Russia

Abstract

The enthalpies of the solution of $MZr_2(PO_4)_3$ (M=Na, K, Rb or Cs) compounds have been measured by the help of a differential automatic isothermal Calvet calorimeter and the standard enthalpies of formation have been derived. The temperature dependencies of the standard heat capacity of the samples of crystalline $NaZr_2(PO_4)_3$ and $CsZr_2(PO_4)_3$ were studied between 7 and 340 K in an automatic adiabatic vacuum calorimeter. The main thermodynamic functions $H^0(T)–H^0(0)$, $S^0(T)$ and $G^0(T)–H^0(0)$ have been determined. The Gibbs energies of formation of the $NaZr_2(PO_4)_3$ and $CsZr_2(PO_4)_3$ at 298.15 K were calculated on the basis of these experimental data and the enthalpy of formation data. Qualitative explanations for the results observed were presented.

Keywords: alkali-zirconium phosphates, enthalpies of solution, heat capacity, NZP structure, thermodynamic functions

Introduction

The crystalline phosphates forming structures analogues of $NaZr_2(PO_4)_3$ (NZP) type family are subjects of many research works. The reason for such an interest consists in the complexity of their properties.

NZP phosphates are stable under the action of high temperature (up to 2000 K), high pressure, γ-radiation (up to $5\cdot10^8$ Gy) and for α-particles (up to $9\cdot10^{13}$ particles and the same quantity of recoil atoms per 1 mg), under the action of aggressive media, under the combined action of high temperature (up to 673 K), pressure (up to $6\cdot10^7$ Pa), and water action [1–3]. Some phosphates with such a structure and having special compositions are characterized by ultralow thermal expansion (a near-zero value), high ionic conductivity (Na^+ conductivity of Nasicon solid solution systems to 0.2 Ω^{-1} cm^{-1} at 600 K) and catalytic activity [4–6].

The basis of this structure is a mixed anionic framework of $\{[Zr_2(PO_4)_3]^-\}_{3\infty}$ type, which consists of discrete Zr octahedra and isolated P tetrahedra. Sodium cations are situated in some of the cavities of the anionic framework that are open for occupation, and play the role of compensators of negative charge.

A wide range of the structural analogues contains phosphates of many kinds of elements of different sizes and oxidation states. Among them are alkali, alkaline

1418–2874/2001/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

earths, transitional elements. These elements substitute sodium and zirconium in the NZP structure and also enter the vacant crystallographic positions. NZP family has widened because of the possibility of the substitution of phosphorus with 4-, 5-, or 6-valent elements such as silicon, arsenic, vanadium or sulfur.

NZP structure predetermines many important properties of substances useful for modern and future technology. That is why knowledge of the thermal and thermodynamic properties, such as heat capacity, enthalpy, entropy and Gibbs functions of formation, formation reaction constant, etc., must be fundamental to every application in NZP materials technology.

Although there are a lot of literature cites that deal with NZP phosphates family, there are only few reference concerning the standard thermodynamic data [7–10].

The electrochemical ($500\ \mathrm{K}<T<1000\ \mathrm{K}$) and calorimetric ($4\ \mathrm{K}<T<800\ \mathrm{K}$) studies of the $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$ ($0\leq x\leq 3$) solid solutions were reported elsewhere [7, 8]. For $NaZr_2(PO_4)_3$ (x=0), heat capacity was measured above room temperature. The thermodynamic functions of crystalline $NaZr_2(PO_4)_3$ for T=0 to 340 K and p=101.325 kPa and its standard enthalpy, entropy and Gibbs energy for T=298.15 K were already published [10].

The present investigation was performed in order to determine the standard enthalpies of formation of NZP like structure orthophosphates of $MZr_2(PO_4)_3$ (M=Na, K, Rb or Cs) composition. With this aim in view, calorimetric measurements of the solution enthalpies of $MZr_2(PO_4)_3$ compounds with hydrofluoric acid at 298.15 K were carried out. Table 1 shows experimental scheme for the calculation of enthalpies of reaction of $MZr_2(PO_4)_3$ synthesis. From these results and the enthalpies of different auxiliary processes, the standard enthalpies of formation values of the compounds investigated were calculated.

Table 1 Experimental scheme for the calculation of enthalpies of reaction of $MZr_2(PO_4)_3$ synthesis (298.15 K) obtained from Hess cycle: $\Delta_r H_7^0=\Delta_r H_1^0+\Delta_r H_2^0+\Delta_r H_3^0-\Delta_r H_4^0-\Delta_r H_5^0-\Delta_r H_6^0$

Reaction No.	Steps of cycle	$\Delta_r H^0$
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)	$\Delta_r H_1^0$
2	$2ZrO_2$(cr)+sol 3→ $2H_2ZrF_6\cdot 3H_3PO_4\cdot 658HF\cdot 2129.6H_2O$(sol 4)	$\Delta_r H_2^0$
3	MX(cr)*+sol 4→ $MX\cdot 2H_2ZrF_6\cdot 3H_3PO_4\cdot 658HF\cdot 2129.6H_2O$(sol 5)	$\Delta_r H_3^0$
4	$MZr_2(PO_4)_3$(cr)+sol 2→ $MF\cdot 2H_2ZrF_6\cdot 3H_3PO_4\cdot 657HF\cdot 2117.2H_2O$(sol 6)	$\Delta_r H_4^0$
5	$HX\cdot 8.4H_2O$(sol 7)+sol 6→ $MX\cdot 2H_2ZrF_6\cdot 3H_3PO_4\cdot 658HF\cdot 2125.6H_2O$(sol 8)	$\Delta_r H_5^0$
6	$4H_2O$(1)+sol 8→sol 5	$\Delta_r H_6^0$
7	MX(cr)+$2ZrO_2$(cr)+$3H_3PO_4\cdot 8.4H_2O$(sol 1)→ $MZr_2(PO_4)_3$(cr)+$HX\cdot 8.4H_2O$(sol 7)+$4H_2O$(1)	$\Delta_r H_7^0$

$^*X$ – Cl^- or NO_3^-

We also present our results on the precise measurements of the temperature dependence of the heat capacity, C_p^0 of the crystalline $NaZr_2(PO_4)_3$ and $CsZr_2(PO_4)_3$ phosphates in the range from 7 to 340 K.

By combining the data obtained by the two techniques, the standard Gibbs functions of formation of $NaZr_2(PO_4)_3$ and $CsZr_2(PO_4)_3$ were determined.

Experimental

A set of samples with the composition, described by the general formula $MZr_2(PO_4)_3$ (M=Na, K, Rb or Cs) was prepared by the sol–gel method based upon reactions taking place in aqueous solutions. The following reagent grade reactants were used: $NaNO_3$, KNO_3, RbCl, CsCl, $ZrOCl_2\cdot 8H_2O$, H_3PO_4.

A solution of phosphoric acid, taken in accordance with the stoichiometry of the phosphate, was dropped into the mixture of the aqueous solutions of an alkali metal salt and zirconium oxychloride taken in the stoichiometric ratios under stirring at room temperature. The gel formed was dried at 353 K and then thermally treated at 873 and 1073 K with at least 24 h plateau at each step. The thermal treatment stages were alternated with careful grinding.

The obtained samples are colorless polycrystalline powders. Their phase purity was checked by X-ray diffraction (DRON-3.0 diffractometer, CuK_α radiation), using PDF data. The X-ray patterns contained only reflections of $MZr_2(PO_4)_3$ where M is Na, K, Rb or Cs. The unit cell parameters for the synthesized phosphates are given in a previous paper [11]. The IR spectra (Specord-75IR) agree with data presented elsewhere [12] and show no evidence of condensed phosphate groups. The chemical compositions and homogeneity of the samples were checked with the aid of a Camebax microprobe analyzer. The results showed the homogeneity of the samples and confirmed that their compositions were close to the theoretical values calculated for the general formula $MZr_2(PO_4)_3$.

Heat capacity was measured in the range of 7 to 340 K using an automatic adiabatic vacuum calorimeter. The calorimeter design and the operational procedure were described in detail elsewhere [13, 10]. The reliability of the calorimeter operation was tested by measuring C_p^0 of standard benzoic acid and corundum. It was established that the apparatus and the measurement procedure allowed us to obtain C_p^0 of the substances in the condensed state with an error of not more than 2 per cent at T=5 to 10 K, 0.4 per cent in the range 10 to 40 K and within 0.2 per cent between 40 and 340 K.

The enthalpies of solution at 298.15 K were determined by help of a DAK-1-1-A automatic isothermal differential Calvet-type microcalorimeter. Its design and the operation were described earlier [10, 14]. 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 $\Delta_{sol}H^0$=17.6±0.4 kJ mol^{-1} (average of 10 experiments) was in agreement with the published value $\Delta_{sol}H^0$=17.58±0.34 kJ mol^{-1} [15].

The 298.15 K enthalpies ($\Delta_r H^0$) of the reactions studied are averages of four to six replicates. In conformity with IUPAC recommendations [16], the uncertainty in $\Delta_r H^0$ 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.

Results and discussion

The heat capacities of crystalline $NaZr_2(PO_4)_3$ and $CsZr_2(PO_4)_3$ were measured at temperatures between 7 and 340 K. The sample titanium cell with 1.5 cm^3 internal volume was filled with 1.1633 g $NaZr_2(PO_4)_3$ or 1.2915 g $CsZr_2(PO_4)_3$ powder. For $NaZr_2(PO_4)_3$ 153 experimental points of C_p^0 were obtained and for $CsZr_2(PO_4)_3$ 184 experimental points were obtained. The results (Fig. 1) demonstrate that the temperature dependency of heat capacity has no any special features: it smoothly increases with rising temperature.

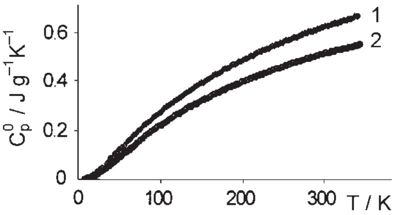

Fig. 1 Temperature dependence of heat capacity (C_p^0) of $NaZr_2(PO_4)_3$ (curve 1) and $CsZr_2(PO_4)_3$ (curve 2)

To calculate thermodynamic functions, the heat capacities of the substances were extrapolated from T=7 K to $T\to 0$ with the Debye functions for the capacity:

$$C_p^0 = nD\frac{\theta_D}{T} \tag{1}$$

where D is a symbol of the Debye function, n and θ_D are adjustable parameters which indicate the number of atomic vibrations in the crystal lattice and the characteristic temperature, respectively; for $NaZr_2(PO_4)_3$ n=2 and θ_D=96.53 K and for $CsZr_2(PO_4)_3$ n=6 and θ_D=126.59 K. With these parameters, Eq. (1) describes the experimental points of C_p^0 in the range T=9 to 14 K with an error of 1.1% for $NaZr_2(PO_4)_3$ and with an error of 1.8% for $CsZr_2(PO_4)_3$. On calculating the thermodynamic functions it was assumed that Eq. (1) reproduced the C_p^0 values at temperature below 9 K with the same precision. The calculations of $\Delta_0^T H^0$ and $\Delta_0^T S^0$ were made by numerical integration of the relations $C_p^0=f(T)$ and $C_p^0=f(\ln T)$, respectively, and $\Delta_0^T G^0$ was evaluated from the corresponding values of $\Delta_0^T H^0$ and $\Delta_0^T S^0$ and by the relations:

$$\Delta_0^T G^0 = \Delta_0^T H^0 - T\Delta_0^T S^0$$

Table 2 Thermodynamic functions of $CsZr_2(PO_4)_3$; p=101.325 kPa

T/K	C_p^0/ J mol^{-1} K^{-1}	$H^0(T)$–$H^0(0)$/ kJ mol^{-1}	$S^0(T)$/ J mol^{-1} K^{-1}	–[$G^0(T)$–$H^0(0)$]/ kJ mol^{-1}
		Crystal		
0	0.0000	0.0000	0.0000	0.000000
1	0.0019	0.0000	0.0006	0.000000
2	0.0153	0.0000	0.0051	0.000003
3	0.0517	0.0000	0.0172	0.000013
4	0.1227	0.0001	0.0409	0.000041
5	0.2396	0.0003	0.0799	0.000100
6	0.4139	0.0006	0.1380	0.000207
7	0.6573	0.0012	0.2191	0.000383
8	0.9808	0.0020	0.3270	0.000654
9	1.365	0.0031	0.4655	0.001048
10	1.909	0.0049	0.6444	0.001516
15	5.894	0.0236	2.108	0.008037
20	11.38	0.0665	4.539	0.02425
25	17.53	0.1381	7.709	0.05464
30	24.93	0.2441	11.55	0.1025
35	32.50	0.3875	15.96	0.1711
40	40.64	0.5702	20.83	0.2629
45	48.63	0.7936	26.08	0.3800
50	56.52	1.056	31.61	0.5241
60	72.31	1.701	43.31	0.8976
70	88.19	2.503	55.65	1.392
80	106.1	3.473	68.56	2.012
90	120.1	4.606	81.91	2.765
100	133.6	5.876	95.28	3.652
110	147.1	7.281	108.7	4.671
120	159.5	8.814	122.0	5.825
130	171.4	10.47	135.2	7.111
140	182.8	12.24	148.4	8.529
150	193.6	14.12	161.3	10.08
160	203.9	16.11	174.2	11.76
170	213.6	18.20	186.8	13.56
180	222.8	20.38	199.3	15.49
190	231.5	22.65	211.6	17.55
200	239.9	25.01	223.7	19.72

Table 2 Continued

T/K	C_p^0/ J mol^{-1} K^{-1}	$H^0(T)$–$H^0(0)$/ kJ mol^{-1}	$S^0(T)$/ J mol^{-1} K^{-1}	–[$G^0(T)$–$H^0(0)$]/ kJ mol^{-1}
210	248.0	27.45	235.6	22.02
220	255.7	29.97	247.3	24.43
230	263.2	32.56	258.8	26.96
240	270.3	35.23	270.2	29.61
250	277.2	37.97	281.3	32.37
260	283.8	40.78	292.4	35.24
270	290.3	43.65	303.2	38.21
273.15	292.2	44.56	306.6	39.17
280	296.6	46.58	313.9	41.30
290	302.7	49.58	324.4	44.49
298.15	307.4	52.06	332.8	47.17
300	308.5	52.63	334.7	47.79
310	313.9	55.75	344.9	51.18
320	318.7	58.91	355.0	54.68
330	323.4	62.12	364.9	58.28
340	329.1	65.38	374.6	61.98

The smoothed values of the heat capacities and thermodynamic functions of the phosphates are presented elsewhere [10] (for $NaZr_2(PO_4)_3$) and Table 2 (for $CsZr_2(PO_4)_3$).

Using the standard entropies of the phosphates, S^0($NaZr_2(PO_4)_3$, cr, 298.15 K) and S^0($CsZr_2(PO_4)_3$, cr, 298.15 K) and reference data on the absolute entropy of the constituent simple substances (Table 3), we calculated the standard entropies of formation of $NaZr_2(PO_4)_3$ and $CsZr_2(PO_4)_3$: $\Delta_f S^0$($NaZr_2(PO_4)_3$, cr, 298.15 K)=–1101±1 J mol^{-1} K^{-1}, $\Delta_f S^0$($CsZr_2(PO_4)_3$, cr, 298.15 K)=–1129±1 J mol^{-1} K^{-1}.

Table 3 Absolute entropies of the simple substances necessary to calculate the standard entropies of formation of $NaZr_2(PO_4)_3$ and $CsZr_2(PO_4)_3$; T=298.15 K, p=101.325 kPa

Substance	Physical state*	S^0/J mol^{-1} K^{-1}	Reference
Na	cr	51.30±0.02	[15]
Cs	cr	85.2±0.2	[15]
Zr	cr	39.0±0.2	[17]
P	cr	22.80±0.08	[17]
O_2	g	205.04±0.03	[18]

*cr – crystalline; g – gaseous

To derive the standard enthalpies of formation of phosphates investigated we have used the scheme, considering enthalpies of reaction of $MZr_2(PO_4)_3$ with hydrofluoric acid (Table 1). According to our experimental data, reactions (1)–(6) in Table 1 yield to true solutions, and have the same stoichiometric coefficients on the left and right, so we can, without analyzing the nature of the products, sum up the reactions (1)–(6) to obtain the reaction scheme of $MZr_2(PO_4)_3$ synthesis (reaction 7) and to calculate the enthalpy of this reaction. All the enthalpies of reactions determined are collected in Table 4.

From the data derived, it may be seen that enthalpies of reaction of $MZr_2(PO_4)_3$ with hydrofluoric acid (Table 4, Reaction No. 4) are exothermic with enthalpy (absolute value) decreasing from the sodium derivative to the caesium one. Probably these differences in the enthalpies are caused, first of all, by high crystalline lattice energies of phosphates having smaller alkali cations.

Table 4 Experimental results for enthalpies of reactions studied (298.15 K) necessary for calculation of the standard enthalpies of formation of $MZr_2(PO_4)_3$

Reaction No.	$-\Delta_r H^0$(298.15 K)/kJ mol^{-1}			
	sodium	potassium	rubidium	caesium
1	2.15±0.05	2.15±0.05	2.15±0.05	2.15±0.05
2	131±2	131±2	131±2	131±2
3	4.4±0.5	–14.0±0.6	–0.5±0.2	–0.8±0.3
4	200±2	154±1	136±3	144±7
5	–0.29±0.02	–0.29±0.02	–0.10±0.01	–0.10±0.01
6	0.61±0.03	0.061±0.03	0.60±0.03	0.60±0.03
7	71±4	98±4	130±5	121±8

Table 5 Enthalpies of formation substances necessary to calculate the standard enthalpies of formation of $MZr_2(PO_4)_3$ (M=Na, K, Rb or Cs); T=298.15 K, p=101.325 kPa

Substance	Physical state*	$-\Delta_f H^0$/kJ mol^{-1}	Reference
$NaNO_3$	cr	468.2±0.5	[15]
KNO_3	cr	494.5±0.5	[15]
RbCl	cr	435.2±0.3	[15]
CsCl	cr	442.4±0.3	[15]
ZrO_2	cr	1100.6±0.6	[17]
H_3PO_4	sol	1280±1	[17]
HNO_3	sol	206.0.±0.5	[17]
HCl	sol	159.9±0.3	[17]
H_2O	l	285.83±0.04	[18]

*cr – crystalline, sol – solution, l – liquid

Since participants of reaction (4) distinguish chemical nature of alkali cation in phosphate ($MZr_2(PO_4)_3$) and alkali ion in solution (MF), the mentioned process is bound up with destroy of $MZr_2(PO_4)_3$ crystalline lattice and hydration of M^+ ion in aqueous solution. The first item always has positive value (process is endothermic). The hydration process of alkali metal ions in aqueous solution is, on the contrary, exothermic [15]. Consequently, the values of the enthalpies of reaction (4) are negative, because the item related with the hydration of ions in aqueous solution exceeds the crystal lattice energies of $MZr_2(PO_4)_3$. Decrease of the absolute values of hydration enthalpies of alkali metal ions in the series Na^+–K^+–Rb^+–Cs^+ is the main factor in decreasing of absolute values of total enthalpies of reaction (4) in indicated series.

Using the relation

$$\Delta_r H_7^0\ (298.15\ \mathrm{K})=$$
$$\Delta_f H^0(\mathrm{MZr_2(PO_4)_3,\ cr,\ 298.15\ K})+\Delta_f H^0(\mathrm{HX,\ sol,\ 298.15\ K})+$$
$$4\Delta_f H^0(\mathrm{H_2O,\ 1,\ 298.15\ K})-\Delta_f H^0(\mathrm{MX,\ cr,\ 298.15\ K})-$$
$$2\Delta_f H^0(\mathrm{ZrO_2,\ cr,\ 298.15\ K})-3\Delta_f H^0(\mathrm{H_3PO_4,\ sol,\ 298.15\ K}),$$

the enthalpy of reaction (7), and reported standard enthalpies of formation (Table 5), we calculated the standard enthalpies of formation of $MZr_2(PO_4)_3$ (M=Na, K, Rb, Cs). Thermochemical parameters of formation are given in Table 6.

Table 6 Standard molar thermodynamic quantities for the formation of $MZr_2(PO_4)_3$ (M=Na, K, Rb, Cs) at T=298.15 K and p=101.325 kPa; $\Delta_f H^0$,$\Delta_f S^0$, $\Delta_f G^0$, enthalpy, entropy, and Gibbs function of formation; K_f, formation reaction constant

Substance	Physical state*	$-\Delta_f H^0$/ kJ mol^{-1}	$-\Delta_f S^0$/ J mol^{-1} K^{-1}	$-\Delta_f G^0$/ kJ mol^{-1}	K_f
$NaZr_2(PO_4)_3$	cr	5231±5	1101±1	4903±5	7±1
$KZr_2(PO_4)_3$	cr	5284±5	–	–	–
$RbZr_2(PO_4)_3$	cr	5303±6	–	–	–
$CsZr_2(PO_4)_3$	cr	5301±9	1129±1	4964±9	7±1

*cr – crystalline

Conclusions

We reported the results of thermodynamic study on the compounds of the $MZr_2(PO_4)_3$ composition (M=Na, K, Rb or Cs) belonging to the vast family of solids with NZP structure.

Heat capacity measurements carried on $NaZr_2(PO_4)_3$ and $CsZr_2(PO_4)_3$ between 7 and 340 K at constant pressure were used to calculate their thermodynamic functions $C_p^0, \Delta_0^T H^0, \Delta_0^T S^0$ and $\Delta_0^T G^0$ and to find the standard entropies $\Delta_f S^0$.

Calorimetric measurements of the solution enthalpies of $MZr_2(PO_4)_3$ compounds with hydrofluoric acid at 298.15 K were used to determine the standard enthalpies of formation $\Delta_f H^0$ of the orthophosphates.

By combining the data obtained, Gibbs energies of formation $\Delta_f G^\circ$ and the thermodynamic constants of the formation reaction K_f of alkaline zirconium phosphates from the corresponding elements in their standard states at 298.15 K have been calculated.

The data given in this paper represent one of the first attempts of utilization of precise calorimetry in the study of NZP compounds. Accumulation of such thermodynamic data will help to solve the problem of the phosphates controlled synthesis and to determine the possibilities of reaction involving them.

* * *

The authors are grateful to N. N. Smirnova for the participation in the measurements of the heat capacity of $CsZr_2(PO_4)_3$. We also would like to thanks Prof. B. V. Lebedev for assistance without which the study could not have been performed.

This research was supported by the Russian Foundation for Basic Research, Projects No. 98-03-32571 and 00-03-40136, and by the Ministry of Education of the Russian Federation, Grant No. 97-12-3.3-9.

References

1 V. I. Pet'kov and A. I. Orlova, J. Therm. Anal. Cal., 54 (1998) 71.
2 A. I. Kryukova, I. A. Kulikov, G. Yu. Artemeva, V. T. Demarin, O. V. Pechenevskaya and V. A. Alferov, Radiokhimiya, 34 (1992) 82.
3 A. I. Orlova, V. N. Ziryanov, A. R. Kotelnikov, V. T. Demarin and Ye. V. Rakitina, Radiokhimiya, 35 (1993) 120.
4 E. Breval and D. K. Agraval, Brit. Ceram. Trans. J., 94 (1995) 27.
5 L. B. Goodenough, H. Y.-P. Hong and J. A. Kafalas, Mat. Res. Bull., 11 (1976) 203.
6 A. I. Orlova, V. I. Pet'kov, S. G. Gul'yanova, M. M. Ermilova, S. N. Yenealem, O. K. Samuilova, T. K. Chehlova and V. M. Gryaznov, Russian J. Phys. Chem., 73 (1999) 1767.
7 J. Maier, U. Warhus and E. Gmelin, Solid State Ionics, 18–19 (1986) 969.
8 U. Warhus, J. Maier and A. Rabenau, J. Solid State Chem., 72 (1988) 113.
9 L. Abello, K. Chhor, M. Barj, C. Pommier and C. Delmas, J. Mater. Sci., 24 (1989) 3380.
10 V. I. Pet'kov, K. V. Kir'yanov, A. I. Orlova and D. B. Kitaev, Inorg. Mater., 36 (2000) 387.
11 V. I. Pet'kov, A. I. Orlova and O. V. Egorkova, J. Struct. Chem., 37 (1996) 933.
12 V. S. Kurazhkovskaya, A. I. Orlova, V. I. Pet'kov, D. V. Kemenov and L. N. Kaplunnik, J. Struct. Chem., 41 (2000) 61.
13 R. M. Varushchenko, A. I. Druzhinina and E. L. Sorkin, J. Chem. Thermodyn., 29 (1997) 623.
14 E. Calvet and H. Prat, Microcalorimetrie: Applications physico-chimiques et biologiques, Masson, Paris 1956.
15 Thermal Constants of Substances, V. P. Glushko (Ed.), VINITI, Moscow 1981, issue 10.
16 IUPAC Recommendations, J. Chem. Thermodyn., 13 (1981) 603.
17 Thermal Constants of Substances, V. P. Glushko (Ed.), Nauka, Moscow 1965–1981, issues 1–9.
18 J. D. Cox, D. D. Wagman and V. A. Medvedev, CODATA Key Values for Thermodynamics, Hemisphere Publ. Co., New York, Washington 1989.