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Calorimetric Research into the Heat Capacity of Novel Nano-Sized Cobalt(Nickelite)-Cuprate-Manganites of $LaBaMe^{II}CuMnO_6$ (Me^{II} = Co, Ni) and their Thermodynamic Properties

B.K. Kassenov[1]*, Sh.B. Kassenova[1], Zh.I. Sagintaeva[1], E.E. Kuanyshbekov[1], M.O. Turtubaeva[2]

[1]Abishev Chemical-Metallurgical Institute, 63 Ermekov Str., 100009 Karaganda, Kazakhstan
[2]Toraigyrov Pavlodar State University, 64 Lomov Str., 140008 Pavlodar, Kazakhstan

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Abstract

The isobaric heat capacities of novel nano-sized cobalt-cuprate-manganite of lanthanum and barium $LaBaCoCuMnO_6$ and nickel-cuprate-manganite of lanthanum and barium $LaBaNiCuMnO_6$ were investigated by dynamic calorimetry over the temperature range of 298.15–673 K. It is found that a λ-shaped effect is observed on the curve of the heat capacity dependence on temperature of $LaBaCoCuMnO_6$ at 523 K, while $LaBaNiCuMnO_6$ also has a similar effect at 473 K. Equations for the temperature dependence of the heat capacity of cobalt(nickelite)-cuprate-manganite of lanthanum and barium are derived with allowance for the temperatures of phase transitions. Based on the experimental data, the fundamental constants – the standard heat capacities of the compounds under study were found. Irrespective of the experimental data, we also calculated the standard heat capacities of the mentioned compounds using the Debye theory using the characteristic temperatures of the elements, their melting points, the Koref and Nernst-Lindemann equations. The obtained calculated data on C_p^0 (298.15) of the compounds were in satisfactory agreement with the experimental data on the standard heat capacity. The standard entropies of $LaBaCoCuMnO_6$ and $LaBaNiCuMnO_6$ were calculated by the ion increment method. We calculated the temperature dependences of the enthalpy $H^o(T)$-$H^o(298.15)$, entropy $\Delta S^o(T)$, and the reduced thermodynamic potential $\Delta\Phi^{**}(T)$.

1. Introduction

Interest in the compounds (manganites, cuprates, nickelites, cobaltites, etc.) being formed from the oxides of transition (3d- and 4f-) and alkaline-earth metals is due to their unique multifunctional properties such as superconductivity, giant (GMR) and colossal magnetoresistance (CMR).

They also possess semiconductor properties and gigantic values of dielectric constant, which is especially important for microelectronics [1–6].

Manganites, having effects of GMR and CMR, can be used in magnetic field sensors, readout heads for high-density magnetic recording, temperature displacement transducers, etc. [7].

It should be noted that GMR has attracted great attention because it has had a significant impact on the development of magnetic storage devices. Since the implementation of GMR-type sensors, the memory capacity has increased by about 100 times [8].

At present, considerable attention is paid to nanocrystalline materials because a substance in a nanocrystalline state manifests special properties (magnetic, optical, etc.) not characteristic for bulk materials [7]. For this reason, producing and researching novel nanocrystalline materials is an important stage in creating materials for a new generation [9].

In view of the above, a certain theoretical and practical interest is in obtaining and researching into the physicochemical properties of novel nano-sized compounds in which manganites, cobaltites, nickelites, and cuprates are represented as single phases like cobalt-cuprate-manganites and nickelite-cuprate-manganites of rare-earth and alkaline earth metals.

*Corresponding author. E-mail: kasenov1946@mail.ru

This paper, based on the above data, presents the results of calorimetric studies of the heat capacity and calculation of the thermodynamic functions of novel nano-sized cobalt-cuprate-manganite and nickelite-cuprate-manganite of lanthanum and barium $LaBaCoCuMnO_6$ and $LaBaNiCuMnO_6$.

2. Experimental part

Using ceramic technology we obtained nano-sized $LaBaCoCuMnO_6$ and $LaBaNiCuMnO_6$ which were subjected to a calorimetric study.

Polycrystalline samples of these compounds were obtained by solid-phase interaction of La_2O_3, NiO, CoO, CuO, Mn_2O_3, and $BaCO_3$ over the range of 800–1200 °C.

By grinding polycrystalline particles in a RETSCH MM301Mixer Mill (Germany), we obtained their nanoparticles. The nanoparticle sizes (50–100 nm) were determined by means of an atomic force microscope (AFM)JSPM-5400 ScanningProbeMicroscope JEOL (Japan).

It was established by X-ray diffraction that the compounds obtained crystallize in a cubic crystal system with the following lattice parameters: $LaBaCoCuMnO_6$ – a = 14.81 ± 2.07 Å, V^0 = 3248.57 ± 6.22 Å^3, Z = 4; V^0_{cell} = 812.14 ± 1.56 Å^3, $\rho_{x\text{-}ray}$ = 4.64 g/cm^3, ρ_{picn} = 4.57 ± 0.01 g/cm^3 and $LaBaNiCuMnO_6$ – a = 14.11±0.02 Å, V^0 = 2808.29 ± 0.06 Å^3, Z = 4, V^0_{cell} = 702.07 ± 0.01 Å^3, $\rho_{x\text{-}ray}$ = 4.66; ρ_{picn} = 4.58 ± 0.01 g/cm^3.
The basic thermal and IR spectroscopic characteristics were determined [10].

Calorimetric study of the heat capacity of the synthesized nano-sized $LaBaCoCuMnO_6$ and $LaBaNiCuMnO_6$ was carried out on an IT-S-400 calorimeter over the range of 298.15–673 K. The device operation principle is based on the comparative method of a dynamic c-calorimeter with a heat meter. The measuring circuit of the device provides the measurement of a temperature level from "minus" 100 to "plus" 400 °C at the fixed points in each 25 °C intervals by means of a built-in DC potentiometer and a switch.

The volume range is minimum of $1\cdot10^6$ J/K·m^3. The time of measuring over the entire temperature range together with the experimental data processing is about 2.5 h. Measurement uncertainties on an IT-S-400 device do not exceed ± 10%. Liquid nitrogen was used as a cooling agent.

The device was calibrated by determining the thermal conductivity of the heat meter K_T [11, 12]. This required several experiments with a copper sample and an empty ampoule. The thermal conductivity of the heat meter was determined by the Eq. 1:

$$K_T = C_{C.S.}(\bar{\tau}_{TM} - \bar{\tau}^0_T) \quad (1)$$

where $C_{c.s.}$ the total specific heat of a copper sample, J/(mol·K); $\bar{t}_{TM}$ is a mean value of the lag time on the heat meter in the experiments with a copper sample, s; $\bar{\tau}^0_T$ is a mean value of the lag time in the experiments with an empty ampoule, s.

The total heat capacity of the copper sample was calculated by the Eq. 2:

$$C_{c.s.} = C_c \cdot m_s, \quad (2)$$

where C_c is a tabulated value of the specific heat capacity of copper, J/(mol·K); m_s is a copper sample mass, kg.

The specific heat value of a substance was calculated by the Eq. 3:

$$C_S = K_T / m_0(\tau_T - \bar{\tau}^0_T), \quad (3)$$

where K_T is heat conductivity of the heat meter; m_0 is the mass of the test substance; τ_T is the temperature lag time on the heat meter, $\bar{\tau}^0_T$ is the temperature lag time on the heat meter in the experiments with an empty ampoule, s.

From the specific heat capacity, we calculated the molar heat capacity taking into account the molar mass. Five parallel experiments were performed for each temperature; the results were averaged and processed by the methods of mathematical statistics.

At each temperature for the specific heat averaged values we calculated the root-mean-square deviation ($\bar{\delta}$) by [13]:

$$\delta = \sqrt{\frac{\sum_{i=1}^{n}(C_i - \bar{C})^2}{n-1}}, \quad (4)$$

where n is the number of experiments, C_i is the measured value of the specific heat, $\bar{C}$ is the arithmetic mean of the measured values of the specific heat.

For the averaged values of the molar heat capacity according to [12, 13], a random error component was calculated:

$$\mathring{\Delta} = \frac{\delta \cdot t_p}{\bar{C}} \cdot 100, \quad (5)$$

where $\mathring{\Delta}$ is a random error component, %, t_p is the Student coefficient (for n = 5, t_p = 2.75 with p = 0.95 of the confidence interval).

A systematic error component was calculated by the formula:

$$\Delta_c = \frac{\overline{C} - C_0}{C_0} \cdot 100, \quad (6)$$

where Δ_c is systematic error component in %, C_0 is the heat capacity value of the standard measure taken at the temperature at which the heat capacity was determined.

The maximum permissible error was calculated by the formula:

$$\Delta = \Delta_C + \overset{\circ}{\Delta} \quad (7)$$

The systematic error and uncertainties in measuring temperature were not considered in our research since they were negligible compared to the random component.

According to the theory of errors, if a random error is significantly greater than the sum of the systematic error of an instrument scale error, then the measurement accuracy of the instrument will be determined by a random error [12, 13], that is, instead of a limiting error, a random error is used.

The reliability of the obtained heat capacity values can be indicated by the fact that the experimental value of the standard heat capacity of sodium arsenate Na_3AsO_4, previously determined on the same IT-C-400 calorimeter [14] and equal to 169.1 J/(mol·K), is in satisfactory agreement with its recommended value (170.3 J/(mol·K)) given in the reference book [15].

The work of the calorimeter was additionally tested in determining the heat capacity of α-Al_2O_3. The obtained value of C_p^0 (298.15) α-Al_2O_3, equal to 76.0 J/(mol·K), is in satisfactory agreement with its recommended value of 79.0 J/(mol·K) [16]. These data also prove the correctness and reliability of the results.

It should be noted, that we carried out studies on the heat capacity of similar compounds on the same calorimeter [17–19].

Table 1 and figure given below present the results of a calorimetric study of the heat capacities of $LaBaCoCuMnO_6$ and $LaBaNiCuMnO_6$.

The measurement results show that the studied compounds on $C_p^0 \sim f(T)$ curves (Fig.) have second-order phase transitions at 523 K ($LaBaCoCuMnO_6$) and at 473 K ($LaBaNiCuMnO_6$) which can be associated with the Schottky effects, the Curie, points and the Néel points, changes in electrical resistance, dielectric constant, etc.

It should be noted that the formation of a ferromagnetic (the Curie point) or an antiferromagnetic (the Néel point) relates to second order magnetic phase transitions. Apart from magnetic transitions, there are electrical ones. When cooling paraelectric, the cases of second-order phase transitions into the ferroelectric state and antiferroelectric state are observed [20]. We observed the same phase

Table 1

Experimental values of the heat capacities of $LaBaNiCuMnO_6$ and $LaBaNiCuMnO_6$ [$C_{p(specific)} \pm \overline{\delta}$, J/(g·K); $C_{p\,(m)}^0 \pm \overset{\circ}{\Delta}$, J/(mol·K)]

T, K	$C_{p(specific)} \pm \overline{\delta}$	$C_{p\,(m)}^0 \pm \overset{\circ}{\Delta}$	$C_{p(specific)} \pm \overline{\delta}$	$C_{op(m)} \pm \overset{\circ}{\Delta}$
	$LaBaCoCuMnO_6$		$LaBaNiCuMnO_6$	
298.15	0.4819 ± 0.0107	265 ± 16	0.4668 ± 0.0138	256 ± 21
323	0.6318 ± 0.0175	347 ± 27	0.6589 ± 0.0172	362 ± 26
348	0.6482 ± 0.0140	356 ± 21	0.7028 ± 0.0072	386 ± 11
373	0.7029 ± 0.0101	386 ± 15	0.7242 ± 0.0090	398 ± 15
398	0.7281 ± 0.0227	400 ± 35	0.7928 ± 0.0117	436 ± 18
423	0.7434 ± 0.0169	409 ± 26	0.8557 ± 0.0130	470 ± 20
448	0.7801 ± 0.0175	429 ± 27	0.8888 ± 0.0101	488 ± 15
473	0.8164 ± 0.0151	449 ± 23	0.9454 ± 0.0242	519 ± 37
498	0.8410 ± 0.0111	462 ± 17	0.8912 ± 0.0156	490 ± 24
523	0.8744 ± 0.0133	481 ± 20	0.8415 ± 0.0157	462 ± 24
548	0.8349 ± 0.0172	459 ± 26	0.7911 ± 0.0207	435 ± 32
573	0.7629 ± 0.0190	419 ± 29	0.8102 ± 0.0147	445 ± 22
598	0.8221 ± 0.0213	452 ± 32	0.8446 ± 0.0111	464 ± 17
623	0.8675 ± 0.0192	477 ± 29	0.8704 ± 0.0131	478 ± 20
648	0.8852 ± 0.0146	487 ± 22	0.9126 ± 0.0163	501 ± 25
673	0.9131 ± 0.0138	502 ± 21	0.9377 ± 0.0118	515 ± 18

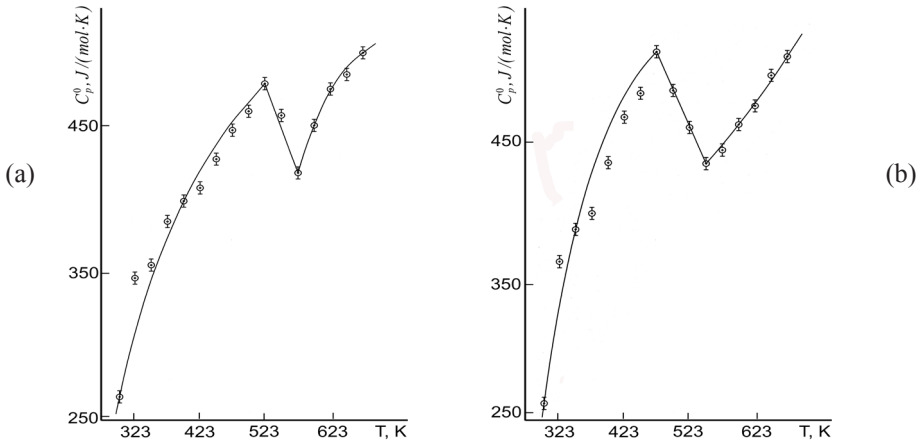

Fig. Dependence of thermal capacities of $LaBaCoCuMnO_6$ (a), $LaBaNiCuMnO_6$ (b) on temperature.

transitions in studying the heat capacity of similar manganites, which were further confirmed by the electrophysical methods, i.e., a second-order phase transition, we revealed in manganites transitions from the semiconductor conductivity to the metallic one and vice versa [21].

Taking into account the temperature of phase transitions, the equations of the temperature dependence of the compounds under study are derived (Table 2).

The standard heat capacities of $LaBaCoCuMnO_6$ and $LaBaNiCuMnO_6$ were also calculated according to Debye [22, 23]. The necessary data for the calculation were the Debye characteristic temperatures (Q_d, K) of the elements constituting a chemical compound and their melting points ($T_{melt.}$, K) [22, 23]. The characteristic temperatures of the elements for the compounds under study were found using the Koref formula [22, 23]:

$$Q_d^{'} = Q_d \sqrt{T_{melt.}^{'} / T_{melt.}} \ , \qquad (8)$$

where $T_{melt.}^{'}$ and $T_{melt.}$ are melting points of a compound and an element. We take the synthesis temperature (1473 K) at which the compound is stable as $T_{melt.}^{'}$ of the compounds under study. Then we find the isochoric heat capacity of the elements using the Debye function and sum them.

The transition from the isochoric heat capacity to the isobaric one is carried out by the Nernst-Lindemann equation:

$$C_p = C_V + 0.0051 \cdot T \cdot C_P^2 / T_{melt.} \qquad (9)$$

The following data were used for the calculation:

La (Q_d = 135 K, $T_{melt.}$ = 1193 K), Ba (Q_d = 116 K, $T_{melt.}$ = 998 K,

Co (Q_d = 386 K, $T_{melt.}$ = 1765 K), Ni (Q_d = 345 K, $T_{melt.}$ = 1726 K),

Cu (Q_d = 310 K, $T_{melt.}$ = 1356 K), Mn (Q_d = 303 K, $T_{melt.}$ = 1517 K,

O_2 (Q_d = 89 K, $T_{melt.}$ = 54.7 K) [22, 23].

Based on the above data, the standard heat capacities of $LaBaNiCuMnO_6$ and $LaBaCoCuMnO_6$ were calculated. They are equal to 252.3 and 252.0 J/(mol K), respectively, and agree with the experimental data within an accuracy of 1.5 and 5.1%.

Table 2

Equations of temperature dependence of the heat capacities of cobalt(nickelite)-cuprate-manganites

Compounds	Equation coefficients $C_p^0 = a + bT + cT^{-2}$, J/(mol·K)			ΔT, K
	a	$b \times 10^{-3}$	$c \times 10^5$	
$LaBaCoCuMnO_6$	516 ± 30	109.6 ± 6.3	251.6 ± 14.6	298.15-523
	1122 ± 65	-(1225.8 ± 71.2)	-	523-573
	2481 ± 144	-(1880.7 ± 109.3)	-(3229.6 ± 187.6)	573-673
$LaBaNiCuMnO_6$	980 ± 49	-(4881.1 ± 24.2)	-(513.0 ± 25.4)	298.15-473
	1054 ± 52	-(1130.1 ± 56.1)	-	473-548
	-(195 ± 10)	-(945.3 ± 46.9)	335.1 ± 16.6	548-673

Table 3
Thermodynamic functions of nano-sized cobalt(nickelite)-cuprate-manganites
[C_p^0 , $S^o(T)$,$\Phi^{xx}(T)$, J/(mol·K); $H^o(T)$-$H^o(298.15)$, J/(mol)]

T, K	C_p^0 (T) ± $\mathring{\Delta}$	$S^o(T)$ ± $\mathring{\Delta}$	$H^o(T)$-$H^o(298.15)$ ± $\mathring{\Delta}$	$\Phi^{xx}(T)$ ± $\mathring{\Delta}$
		$LaBaCoCuMnO_6$		
298	265 ± 15	273 ± 8	-	273 ± 24
300	269 ± 16	275 ± 24	530 ± 30	273 ± 24
325	313 ± 18	298 ± 26	7830 ± 450	274 ± 24
350	348 ± 20	323 ± 28	16110 ± 940	277 ± 24
375	378 ± 22	348 ± 31	25190 ± 1460	280 ± 25
400	402 ± 23	373 ± 33	34950 ± 2030	285 ± 25
425	423 ± 25	398 ± 35	45260 ± 2630	291 ± 26
450	440 ± 26	423 ± 37	56060 ± 3260	298 ± 26
475	456 ± 26	447 ± 39	67270 ± 3910	305 ± 27
500	469 ± 27	470 ± 41	78840 ± 4580	313 ± 28
525	481 ± 28	494 ± 43	90730 ± 5270	321 ± 28
550	447 ± 26	515 ± 45	102300 ± 5940	329 ± 29
575	417 ± 24	534 ± 47	113100 ± 6570	338 ± 30
600	454 ± 26	553 ± 49	124090 ± 7210	346 ± 30
625	478 ± 28	572 ± 50	135780 ± 7890	355 ± 31
650	493 ± 29	591 ± 52	147950 ± 8600	364 ± 32
675	502 ± 29	610 ± 54	160410 ± 9320	372 ± 33
		$LaBaNiCuMnO_6$		
298	256 ± 13	264 ± 8	-	264 ± 21
300	263 ± 13	266 ± 21	520 ± 30	264 ± 21
325	335 ± 17	290 ± 23	8040 ± 400	265 ± 21
350	390 ± 19	317 ± 25	17140 ± 850	268 ± 21
375	432 ± 21	345 ± 27	27430 ± 1360	272 ± 22
400	464 ± 23	374 ± 30	38640 ± 1920	277 ± 22
425	488 ± 24	403 ± 32	50560 ± 2510	284 ± 23
450	507 ± 25	431 ± 34	63000 ± 3130	291 ± 23
475	520 ± 26	459 ± 36	75850 ± 3760	299 ± 24
500	489 ± 24	485 ± 39	88420 ± 4390	308 ± 25
525	461 ± 23	508 ± 40	100290 ± 4970	317 ± 25
550	432 ± 21	529 ± 42	111450 ± 5530	326 ± 26
575	450 ± 22	549 ± 44	122520 ± 6080	335 ± 27
600	465 ± 23	568 ± 45	133960 ± 6640	133960 ± 6640
625	482 ± 24	587 ± 47	145790 ± 7230	354 ± 28
650	499 ± 25	607 ± 48	158050 ± 7840	363 ± 29
675	517 ± 26	626 ± 50	170740 ± 8470	373 ± 30

Due to the technical limitations of an IT-S-400 calorimeter, which do not allow calculating the standard enthalpy of the compounds directly from the experimental data on the heat capacities, we estimated them using the ion increment method [24] according to the scheme:

$$S^o(298.15)LaBaMeCuMnO_6 = S^i(298.15)La^{3+} + S^i(298.15)Ba^{2+} + S^i(298.15)Me^{2+} + + S^i(298.15)Cu^{2+} + S^i(298.15)Mn^{3+} + 6S^i(298.15)O^{2-}, \quad (10)$$

where $S^i(298.15)$ is the entropy increment of ions Me – Co, Ni.

When calculating $S^o(298.15)$ of the compounds according to the scheme (10), the following values of the entropy increments of ions La^{3+} = 40.4; Ba^{2+} = 53.6; Co^{2+} = 37.6; Ni^{2+} = 28.6; Cu^{2+} = 36.5; Mn^{3+} =3 4.7;O^{2-} = 11.7 J/(mol K) [24] were used.

The values of $S^o(298.15)$ of the compounds under study calculated according to the scheme are presented in Table 3.

Further, based on the experimental data on C_p^0 (T) and the estimated values of $S^o(298.15)$, using the known relations [25] with a step of 25 K, we calculated the temperature dependences C_p^0 (T) and the thermodynamic functions $H^o(T)$-$H^o(298.15)$, $\Delta S^o(T)$, $\Delta\Phi^{**}(T)$. They are presented in Table 3.

It should be emphasized that the function of the reduced thermodynamic potential is very convenient for calculating the standard thermal effect of chemical reactions, as well as for calculating chemical equilibria according to the third law of thermodynamics, starting at 298.15 K.

When estimating the errors of the functions $\Delta S^o(T)$ and $\Delta\Phi^{**}(T)$ the estimation errors of $S^o(298.15)$ (~3.0%) were taken into account.

4. Conclusions

1. For the first time, the isobaric heat capacities of nano-sized cobalt-cuprate-manganite $LaBaCoCuMnO_6$ and nickel-cuprate-manganite $LaBaNiCuMnO_6$ were studied by experimental calorimetry over the range of 298.15–673 K.

2. The temperatures of second-order phase transitions were established on the curves of $C_p^0 \sim f(T)$ dependencies of the compounds under study and, taking them into account, the equations of the temperature dependence of the heat capacity were derived.

3. Based on the experimental data on the heat capacities and the estimated value of the standard entropies, the temperature dependences of the thermodynamic functions were calculated.

4. According to Debye, the standard heat capacities of $LaBaCoCuMnO_6$ and $LaBaNiCuMnO_6$ were calculated using the Koref and Nernst-Lindemann equations. Their values agree well with the experimental data.

5. The research results are of interest for the directed synthesis of similar compounds, prediction of promising physical and physicochemical properties of cobalt(nickelite)-cuprate-manganites and similar phases.

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References

[1]. J.G. Bednorz, K.A. Müller, *Z. Physica B* 64 (1986) 189–193. DOI: 10.1007/BF01303701

[2]. S.A. Nikitin, *Soros Educational Journal* [Sorosovskii obrazovatelnyi zhurnal] 2 (2004) 92–98 (in Russian).

[3]. Yu.D. Tretyakov, E.A. Gudilin, *Russ. Chem Rew.* 69 (2000) 3–40. DOI: 10.1070/RC2000v069n01ABEH000526

[4]. Ya.M. Mukovsky, *Mendeleev Chemistry Journal* [Zhurnal Ross.Khim.ob-va im D.I. Mendeleeva] XLV (2001) 32–41. (in Russian).

[5]. Yu. Yerin, Chemistry and chemists [*Himiya i himiki*] 1 (2009) 16–22 (in Russian)

[6]. A. Tarjomannejad, A. Niaei, M. José Illán Gómez, A. Farzi, D. Salari, V. Albaladejo-Fuentes, *J. Therm. Anal. Calorim.* 129 (2017) 671–680. DOI: 10.1007/s10973-017-6264-x

[7]. Yu.D. Tretyakov, O.A. Brylyov, Mendeleev Chemistry Journal [*Zhurnal Ross.Khim.ob-va im D.I. Mendeleeva*] 44 (2000) 10–16 (in Russian).

[8]. P.A. Grünberg, *Phys-Usp.* [Uspekhi Fizicheskikh Nauk] 178 (2008) 1349–1358 (in Russian). DOI: 10.3367/UFNr.0178.200812g.1349

[9]. G.B. Sergeyev. Nanochemistry. Moscow, MSU publ. 2007, 336 p. (in Russian).

[10]. B.K. Kasenov, Sh.B. Kasenova, Zh.I. Sagintayeva, M.O. Turtubayeva, E.E. Kyanyshbekov, *Chemical Journal of Kazakhstan* [Himicheskij zhurnal Kazahstana] 4 (2018) 264–269.

[11]. E.S. Platunov, S.E. Buravoy, V.V. Kurepin, G.S. Petrov. Heatphysical measurements and devices. Leningrad, Mechanical engineering, 1986. 256 p. (in Russian).
[12]. Technical specification and maintenance instructions of IT-S-400. Aktyubinsk, Aktyubinsk plant "Etalon", 1986, 48 p. (in Russian).
[13]. V.P. Spiridonov, L.V. Lopatkin. Mathematical processing of experimental data. Moscow, MSU publ., 1970, 221 p. (in Russian).
[14]. Z.M. Sharipova, B.K. Kassenov, V.O. Bukharitsyn, *Russ. J. Phys. Chem.* [*Zhurnal fizicheskoi himii*] 65 (1991) 1408–1410 (in Russian).
[15]. V.P. Glushko, Thermal constants of substances. Moscow, Science, 1981, 300 p. (in Russian).
[16]. R.A. Robie, B.S. Hemingway, J.R. Fisher, (1978). Thermodynamic properties of minerals and related substances at 298.15 K and 1 bar (10^5 Pa) pressure and at higher temperatures. U.S. Geological Survey Bulletin No. 1452. U.S. Government Printing Office,Washington, DC. 456 p.
[17]. Sh.B. Kassenova, B.K. Kassenov, Zh.I. Sagintayeva, K.T. Ermaganbetov, E.E. Kuanyshbekov, A.A. Seisenova, D.I. Smagulova, *Zhurnal fizicheskoi himii* [Russian Journal of Physical Chemistry] 88 (2014) 836–840 (in Russian). DOI: 10.7868/S0044453714050112
[18]. B.K. Kassenov, M.O. Turtubayeva, Sh.K. Amerkhanova, Sh.B. Kassenova, Zh.I. Sagintayeva, E.E. Kuanyshbekov, A.A. Seisenova, D.I. Smagulova, *Russ. J. Phys. Chem.* 89 (2015) 941–946. DOI: 10.1134/S0036024415050180
[19]. B.K. Kassenov, Sh.B. Kassenova, Zh.I. Sagintayeva, M.O. Turtubayeva, K.S. Kakenov, G.A. Esenbayeva, *Russ. J. Phys. Chem.* 91 (2017) 430–436. DOI: 10.1134/S0036024417030116
[20]. L.A. Reznitskiy. Calorimetry of a solid body. Moscow, MSU publ., 1981, 184 p. (in Russian).
[21]. B.K. Kassenov, Sh.B. Kassenova, Zh.I. Sagintaeva, B.T. Ermagambet, N.S. Bekturganov, I.M. Oskembekov. Double and triple manganites, ferrites and chromites of alkali, alkaline earth and rare earth metals. Moscow, Nauchnyi mir, 2017, 416 p. (in Russian).
[22]. A.S. Morachevsky, I.V. Sladkov. Thermodynamic calculations in metallurgy. Reference. Moscow, Metallurgy, 1985, 137 p. (in Russian).
[23]. A.S. Morachevsky, I.V. Sladkov. Guideline to performance of thermodynamic calculations. Leningrad, LPI named after M.I. Kalinin, 1975, 67 p. (in Russian).
[24]. V.N. Kumok, Problem of coordination of methods of assessment of thermodynamic characteristics. Direct and return problems of chemical thermodynamics. Novosibirsk, 1987, 108–123 (in Russian).
[25]. Ya.I. Gerassimov, A.N. Krestovnikov, S.I. Gorbov. Chemical thermodynamics in nonferrous metallurgy. Moscow, Metallurgizdat, 1973, 296 p. (in Russian).