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THERMODYNAMIC RESEARCH OF NEW NANODIMENSIONAL LANTHANUM-COBALT(NICKELITE)-CUPRATE-MANGANITES $LaNa_2CoCuMnO_6$, $LaNa_2NiCuMnO_6$

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The thermal capacities of nanodimensional (nanocluster) cobalte (nickelite) - cuprate-manganites of lanthanum and sodium of $LaNa_2CoCuMnO_6$, $LaNa_2NiCuMnO_6$ were investigated with the calorimetry method on the IT-S-400 device in the temperature interval of 298,15 - 673 K. Based on the experimental data the equations of temperature dependence of thermal capacity of the studied compounds were set up. The temperature dependences of thermodynamic functions were estimated with using of measured values of thermal capacity and calculated value of standard entropy.

Key words: thermodynamics, lanthanum, cobalt, nickelite, cuprate, manganite.

INTRODUCTION

Interest in complex oxides of transitional metals is connected with discovery of effects of superconductivity in cuprates and giant and colossal magnetoresistance (CMR) in manganites of the rare-earth elements doped by oxides of alkaline and alkaline-earth metals [1]. It should also be noted that complex oxide compounds consisting of cobalt oxide are perspective thermoelectricians, and the phase based on nickel oxide of $La_{15/8}Sr_{1/8}NiO_4$ has a giant value of dielectric capacitivity [2].

The certain theoretical and practical interest includes the obtaining of new compounds consisting of cuprate and cobaltites, nickelites and manganites of rare-earth, alkaline, alkaline-earth metals, cobalte-cuprate-manganites, nickelite-cuprate-manganites, their nanodimensional particles and a research of their heatphysical properties.

In view of the above the purpose of this paper is the calorimetric research of thermal capacity of our received nanodimensional cobalte (nickelite)-cuprate-manganites of lanthanum, sodium and lithium of $LaNa_2CoCuMnO_6$, $LaNa_2NiCuMnO_6$, calculation of their thermodynamic functions. It should be noted that the literary data on the physical and chemical properties concern generally about the separate manganites, cuprates, cobaltites, nickelites of the rare-earth elements and their derivatives doped with oxides of alkaline and alkaline-earth metals [3-8]. Our researches and literary data in this direction and field are generalized in the paper [9].

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WAYS OF STUDY

$LaNa_2CoCuMnO_6$ and $LaNa_2NiCuMnO_6$ were synthesized with method of the ceramic technology by solid-phase interaction of La_2O_3 (especially pure), CoO (analytically pure), NiO (analytically pure), Mn_2O_3 (analytically pure), Na_2CO_3 (analytically pure), which stoichiometric quantities were burnt off at 800 - 1 200 °C for 20 h, with periodic cooling through 100 °C, milling and stirring. Low-temperature annealing for receiving an equilibrium phase was performed at 400 °C for 10 h. By milling of polycrystalline $LaNa_2CoCuMnO_6$, $LaNa_2NiCuMnO_6$ on Retsch MM301vibration mill (Germany) were received their nanodimensional (nanocluster) particles, which sizes (50 - 100 nm) were determined on the atomic-force microscope (AFM) JSPM-5400 Scanning Probe Microscope "JEOL" (Japan).

The completeness of synthesis and identity of the received compound was controlled with the X-ray phase analysis method performed on DRON-2.0. The indexing of roentgenogram was performed with an analytical method [10]. It was established that compounds crystallized in an isometric system: $LaNa_2CoCuMnO_6$ – a = 14,43 ± 0,02 Å; V^o = 3 005,5 ± 0,07 Å^3; Z = 4; $V^o_{elec.cell}$ = 751,38 ± 0,02 Å^3; $\rho_{roent.}$ = 3,86; ρ_{pick} = 3,72 ± 0,04 g/cm^3. $LaNa_2NiCuMnO_6$ – a = 14,19 ± 0,02 Å; V^o = 2 859,42 ± 0,06 Å^3; Z = 4; $V^o_{elec.cell}$ = 714,86 ± 0,01 Å^3; $\rho_{roent.}$ = 3,38; ρ_{pick} = 3,29 ± 0,02 g/cm^3 [11, 12].

The research of the isobaric thermal capacity of compounds was performed in the interval of 298,15 - 673 K on calorimeter IT-S-400. Calibration of the device was made on the basis of determination of thermal conductivity of the K_T heat meter [13, 14]. Operation of the device was checked with determination of thermal capacity α-Al_2O_3. The received value C^0_p(298,15) α-Al_2O_3 [76,0 ±

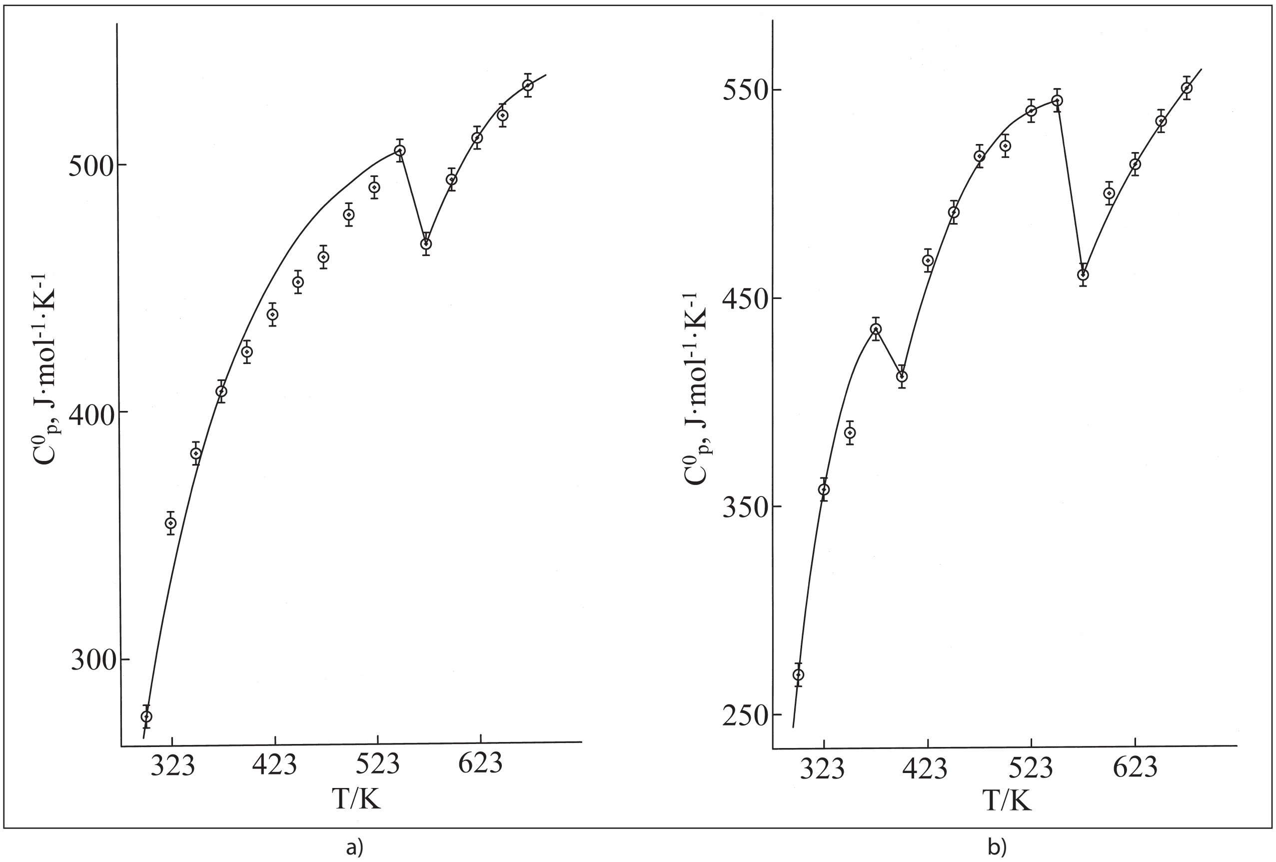

Figure 1 Temperature dependence of thermal capacity of $LaNa_2CoCuMnO_6$ (a), $LaNa_2NiCuMnO_6$ (b)

1,5 J / (mol · K)] will be coordinated with its reference date: [79,0 ± 0,17 J / (mol · K)] [15]. During the calibration and checking the repeated (parallel) measurements in the interval of 298,15 - 548 K with a step 25 K, 5 times were performed, i.e. at each temperature through 25 K it was made per five parallel measurements and results were averaged and processed with methods of mathematical statistics [14]. The mean square deviations ($\bar{\delta}$), and for mole–random components of an error ($\overset{0}{\Delta}$) were measured for values of the specific heat capacities [14].

Results of the calorimetric researches and thermodynamic calculations are demonstrated in Table 1 and Figure 1.

RESULTS AND DISCUSSION

Results of the calorimetric researches in Table 1 and Figure 1 showed that the nanodimensional $LaNa_2CoCuMnO_6$ (548 K) and $LaNa_2NiCuMnO_6$ (373 and 548 K) were subject to II type λ-shaped phase transi-

Table 1 **Experimental values of thermal capacities of $LaNa_2CoCuMnO_6$ and $LaNa_2NiCuMnO_6$**

T / K	$C_{p(specific)} \pm \bar{\delta}$, J / (g · K)	$C^0_{p(m)} \pm \overset{0}{\Delta}$, J / (mol · K)	$C_{p(specific)} \pm \bar{\delta}$, J / (g · K)	$C^0_{p(m)} \pm \overset{0}{\Delta}$, J / (mol · K)
	$LaNa_2CoCuMnO_6$		$LaNa_2NiCuMnO_6$	
298,15	0,6049 ± 0,0109	277 ± 14	0,5869 ± 0,0147	269 ± 19
323	0,7752 ± 0,0144	355 ± 18	0,7810 ± 0,0123	358 ± 16
348	0,8351 ± 0,0091	383 ± 11	0,8408 ± 0,0098	385 ± 13
373	0,8858 ± 0,0164	365 ± 19	0,9498 ± 0,0061	435 ± 8
398	0,9259 ± 0,0080	424 ± 10	0,8989 ± 0,0132	412 ± 17
423	0,9579 ± 0,0069	439 ± 9	1,0220 ± 0,0112	468 ± 14
448	0,9870 ± 0,0095	452 ± 12	1,0715 ± 0,0168	491 ± 21
473	1,0075 ± 0,0135	462 ± 17	1,1318 ± 0,0189	518 ± 24
498	1,0444 ± 0,0166	479 ± 21	1,1429 ± 0,0132	523 ± 17
523	1,0690 ± 0,0083	490 ± 10	1,1787 ± 0,0082	540 ± 10
548	1,1010 ± 0,0184	505 ± 23	1,1894 ± 0,0172	545 ± 22
573	1,0186 ± 0,0160	467 ± 20	1,0061 ± 0,0126	461 ± 16
598	1,0759 ± 0,0098	493 ± 12	1,0924 ± 0,0109	500 ± 14
623	1,1125 ± 0,0134	510 ± 17	1,1216 ± 0,0189	514 ± 24
648	1,1333 ± 0,0177	519 ± 23	1,1670 ± 0,0156	535 ± 20
673	1,1596 ± 0,0214	531 ± 27	1,2034 ± 0,0134	551 ± 17

tions might be connected with Schottky effects, Curie and Neel points, coefficient changes of thermal expansion, conductivity, dielectric capacitivity, etc. Based on temperature of phase transition the equations of temperature dependence of thermal capacity described with some equations [J / (mol · K)] were set up.

$LaNa_2CoCuMnO_6$:

$$C^0_p = (768 \pm 27) - (257{,}9 \pm 9{,}2)\cdot 10^{-3}\ T - (368{,}0 \pm 13{,}10)\cdot 10^5\ T^{-2} \quad (298{,}15 - 548\ K), \tag{1}$$

$$C^0_p = (1\ 333 \pm 47) - (1\ 511{,}4 \pm 53{,}8)\cdot 10^{-3}\ T \quad (548 - 573\ K), \tag{2}$$

$$C^0_p = (1\ 769 \pm 63) - (1\ 139{,}1 \pm 40{,}6)\cdot 10^{-3}\ T - (2\ 131{,}1 \pm 75{,}9)\cdot 10^5\ T^{-2} \quad (573 - 673\ K). \tag{3}$$

$LaNa_2NiCuMnO_6$:

$$C^0_p = (2\ 498 \pm 93) - (3\ 501{,}21 \pm 129{,}9)\cdot 10^{-3}\ T - (1\ 052{,}8 \pm 39{,}1)\cdot 10^5\ T^{-2} \quad (298{,}15 - 548\ K), \tag{4}$$

$$C^0_p = (783 \pm 29) - (932{,}9 \pm 34{,}6)\cdot 10^{-3}\ T \quad (373 - 398\ K), \tag{5}$$

$$C^0_p = (1\ 526 \pm 57) - (1\ 164{,}3 \pm 43{,}2)\cdot 10^{-3}\ T - (1\ 031{,}6 \pm 38{,}3)\cdot 10^5\ T^{-2} \quad (398 - 548\ K), \tag{6}$$

$$C^0_p = (2\ 386 \pm 89) - (3\ 359{,}6 \pm 124{,}6)\cdot 10^{-3}\ T \quad (548 - 573\ K), \tag{7}$$

$$C^0_p = (656 \pm 24) - (143{,}0 \pm 5{,}3)\cdot 10^{-3}\ T - (908{,}1 \pm 33{,}7)\cdot 10^5\ T^{-2} \quad (573 - 673\ K). \tag{8}$$

In order to estimate authenticity of measured values of $C^0_p(298{,}15)$ $LaNa_2CoCuMnO_6$ and $LaNa_2NiCuMnO_6$ they were estimated with an independent Kumok ionic increments method [16] which equal 264,7 and 259,8 J / (mol · K). These estimated values differ from measured values on 5,0 % that confirms the result authenticity of the calorimetric researches within a tolerated error of the device operation.

Considering that the calorimeter technical capabilities are not able to calculate standard entropy of compound directly from the experimental data on thermal capacities, we estimated them with using of the ionic increment system [16] (Table 2). The temperature dependences of $C^0_p(T)$ and the thermodynamic functions $S^0(T)$, $H^0(T) - H^0(298{,}15)$ and $\Phi^{xx}(T)$ (Table 2) were set up with using the known ratios. Errors of functions of $S^0(T)$ and $\Phi^{xx}(T)$ were determined with using of errors of $S^0(298{,}15)$ (± 3,0 %) [16] and the experimental data on $C^0_p(T)$.

The standard enthalpies of formation of $\Delta_f H^0(298{,}15)$ $LaNa_2CoCuMnO_6$, $LaNa_2NiCuMnO_6$ calculated with our developed method [17] were respectively equal – 2 868,1 and 2 869 1 kJ / mol [18].

CONCLUSION

1 Temperature dependences of thermal capacity of nanodimensional (nanocluster) lanthanum cobalte - cuprate-manganite $LaNa_2CoCuMnO_6$ and lanthanum nickelite-cuprate-manganite $LaNa_2NiCuMnO_6$ were investigated with the experimental dynamic calorimetry method of in the interval of 298,15 - 673 K.

2 On curve of dependence of $C_p° \sim f(T)$ for $LaNa_2CoCuMnO_6$ at 548 K and $LaNa_2NiCuMnO_6$ (373 and 548 K) were determined the abnormal rapid changes of the thermal capacity relating to II type phase transition.

3 The equations of temperature dependence of thermal capacity with using of temperatures of phase transition were set up. Referring the experimental data on $C^0_p(T)$ and estimated value $S^0(298.15)$ in the interval of 298,15 - 675 K were determined the temperature dependences of $C^0_p(T)$ and the thermodynamic functions of $S^0(T)$, $H^0(T) - H^0(298.15)$ and $\Phi^{xx}(T)$.

Table 2 **Thermodynamic functions of $LaNa_2CoCuMnO_6$ and $LaNa_2NiCuMnO_6$**

T / K	$C^0_p(T) \pm \mathring{\Delta}$, J / (mol · K)	$S^0(T) \pm \mathring{\Delta}$, J / (mol · K)	$H^0(T) - H^0(298.15) \pm \mathring{\Delta}$, J / mol	$\Phi^{xx}(T) \pm \mathring{\Delta}$, J / (mol · K)
$LaNa_2CoCuMnO_6$				
298,15	277 ± 10	289 ± 9	-	289 ± 19
300	282 ± 10	290 ± 19	560 ± 20	289 ± 19
400	435 ± 15	396 ± 26	37 710 ± 1 340	302 ± 20
500	492 ± 18	501 ± 33	84 550 ± 3 010	331 ± 22
600	493 ± 18	590 ± 39	133 630 ± 4 760	367 ± 24
675	532 ± 19	651 ± 43	172 340 ± 6 140	396 ± 26
$LaNa_2NiCuMnO_6$				
298.15	269 ± 10	280 ± 8	-	280 ± 19
300	278 ± 10	281 ± 19	550 ± 20	280 ± 19
400	410 ± 15	393 ± 26	39 600 ± 1 470	294 ± 20
500	532 ± 20	501 ± 34	88 270 ± 3 270	324 ± 22
600	489 ± 18	595 ± 40	139 580 ± 5 180	362 ± 24
675	553 ± 21	656 ± 44	178 760 ± 6 630	391 ± 26

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