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THERMODYNAMIC AND ELECTROPHYSICAL PROPERTIES OF NANOSIZED COBALT-CUPRATE-MANGANITE AND NICKELITE-CUPRATE-MANGANITE OXIDES

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Cobalt-cuprate-manganite $LaCaCoCuMnO_6$ and nickelite-cuprate-manganite $LaCaNiCuMnO_6$ oxides, were synthesized with ceramic processing technology from calcium carbonate and oxides of La(III), Co(II), Ni(II), Cu(II) and Mn(III). The nanodimensional particles were received with the milling at Retsch (Germany). The experimental and calculation methods determined their thermodynamic and electrophysical characteristics.

Key words: $LaCaCoCuMnO_6$, $LaCaNiCuMnO_6$, thermodynamic, electrophysics, property.

INTRODUCTION

Manganites, cuprates, nickelites, cobaltites of the rare-earth elements doped with alkaline-earth metal oxides possess the unique properties such as superconductivity, giant and colossal magnetoresistance. And they are of interest as materials with high values of the working memory [1-3]. The receiving and studying of the physicochemical properties of compounds containing oxides of the above mentioned elements, forming the phases as cobalt-cuprate-manganites and nickelite-cuprate-manganites of the rare-earth and alkaline-earth metals, have a certain scientific and practical importance.

WAYS OF STUDY

In connection with the above-stated, $LaCaCoCuMnO_6$ and $LaCaNiCuMnO_6$ were synthesized from lanthanum oxide (especially pure), calcium carbonate, cobalt oxides (II), nickel (II), copper (II) and manganese (III) (analytically pure) by the ceramic technology method similar to [4]. Their high-temperature synthesis was performed in interval of 800 – 1 200 ºC for 30 h with the periodic cooling at 800 ºC, 1 000 ºC, 1 100 ºC, and with stirring and milling of mixtures in an agate mortar.

Low temperature annealing was performed at 400 °C for 10 h. By milling of polycrystalline samples on Retsch MM301vibration mill were received their nanodimensional particles, which sizes were determined on the atomic-force microscope JSPM-5400 Scanning Probe Microscope "JEOL" [5].

By indication of X-ray diffraction (XRD) patterns of compounds [6] recorded on DRON-2.0 diffractogram (CuK_α – radiation, U = 30 kV, I = 10 mA, scale range of 1 000 pulses per second, time constant τ = 5 sec, angle interval 2θ from 10º to 90º degrees), the types of their syngony and the parameters of grid were determined. The pycnometric density of compounds was defined with the procedure using toluene as an indifferent fluid ("analytically pure") [7].

Based on the aforesaid researches, it was established that the received new nanodimensional compounds crystallize in the cubic syngony with the following parameters of grid: $LaCaCoCuMnO_6$ – a = 14,01 ± 0,02 Å; V^o = 2 746,77 ± 0,06 Å^3; Z = 4; $V^o_{elec.cell}$ = 686,69 ± 0,02 Å^3; $\rho_{roent.}$ = 4,13; ρ_{pick} = 4,08 ± 0,01 g/cm^3; $LaCaNiCuMnO_6$ – a = 14,74 ± 0,02 Å; V^o = 3 204,74 ± 0,06 Å^3; Z = 4; $V^o_{elec.cell}$ = 801,19 ± 0,02 Å^3; $\rho_{roent.}$ = 4,15; ρ_{pick} = 4,13 ± 0,01 g/cm^3 [5].

The temperature dependence of the heat capacity of compounds was investigated in the interval of 298,15 - 673 K on IT-S-400 calorimeter. The device operation principle is based on the comparative method of the dynamic *c*- calorimeter with the heat meter. The measuring circuit of the device provides measurement of the temperature level from - 100 to 400 °C in the fixed points through 25 K. A limit of error of this device according to the technical specification is ± 10 %. The standard for calibration was a copper sample. A detailed experimental procedure is described in papers [8, 9]. Five parallel experiments were performed at each temperature, and their results were averaged to determine the mean square deviation ($\overline{\delta}$) for a specific heat capacity and random components of error ($\mathring{\Delta}$) for a molar heat capacity. A calorimeter operation was checked with determining of the standard heat capacity of α-Al_2O_3 and its experimental value (76,0 J / mol · K) conform to the reference data (79,0 J / mol · K) [10].

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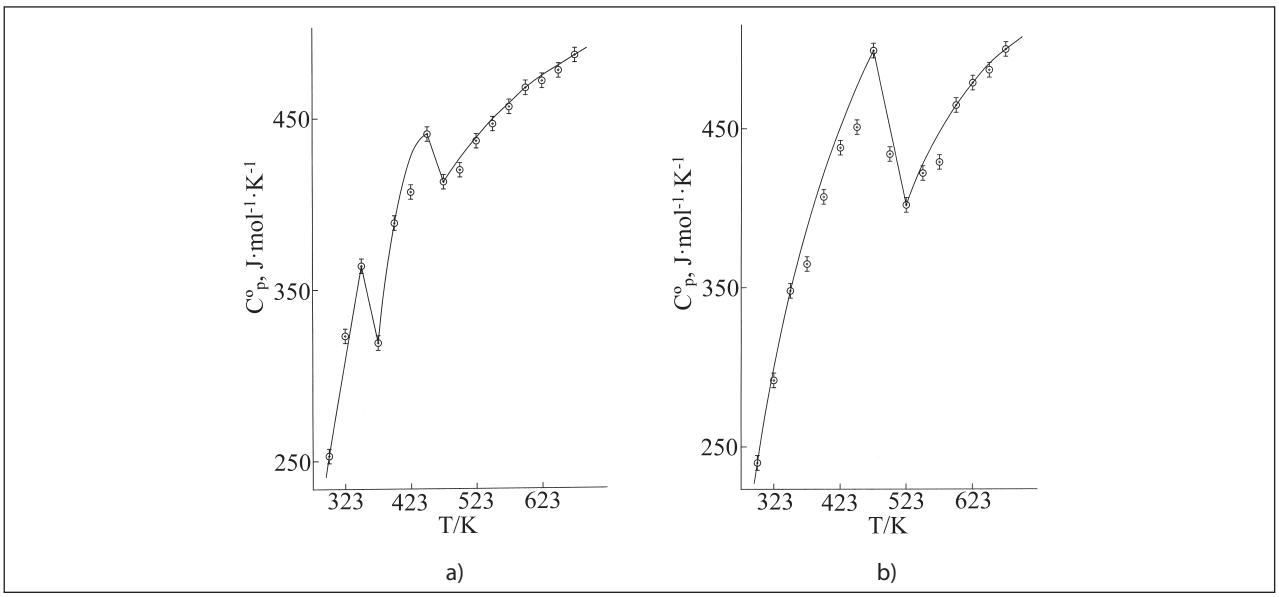

Figure 1 Temperature dependence of heat capacity of $LaCaCoCuMnO_6$ (a) and $LaCaNiCuMnO_6$ (b)

The results in Figure 1 and Table 1 demonstrate that some abnormal λ-shaped peaks relating to II type phase transitions were observed on the dependence curve of $C^0_p \sim f(T)$ for $LaCaCoCuMnO_6$ at 348 K and 448 K, and $LaCaNiCuMnO_6$ at 473 K. These phase transitions are associated to the Schottky effects, with Curie and Neel points et al. [11].

Table 1 **Experimental values of molar heat capacities of $LaCaCoCuMnO_6$ (I) and $LaCaNiCuMnO_6$ (II), $C^0_p \pm \mathring{\Delta}$, J / mol · K**

T / K	$C^0_p \pm \mathring{\Delta}$	
	I	II
298,15	253 ± 12	240 ± 10
323	323 ± 21	292 ± 15
348	364 ± 19	348 ± 17
373	319 ± 20	365 ± 18
398	389 ± 26	407 ± 22
423	407 ± 22	438 ± 19
448	441 ± 21	451 ± 18
473	413 ± 23	499 ± 25
498	420 ± 25	434 ± 16
523	437 ± 16	402 ± 11
548	447 ± 11	422 ± 18
573	457 ± 17	429 ± 15
598	468 ± 21	465 ± 15
623	472 ± 19	479 ± 10
648	478 ± 22	487 ± 20
673	487 ± 21	500 ± 14

RESULTS AND DISCUSSION

On the basis of the set temperatures of phase transitions on the dependence curve of $C^0_p \sim f(T)$, the equations of the temperature dependence of the heat capacity of the compounds were calculated in Table. 2.

As the technical capabilities of calorimeter do not permit to calculate the standard entropies of compounds directly from experimental data on heat capacities, they were calculated with using a system of ionic entropy increments [12]. Thus, the temperature dependences of the thermodynamic functions presented in Table 3 were calculated from the experimental data on heat capacities and the calculated values for standard entropies and also the known ratios. In order to determine an error, the accuracy of the calculating standard entropy of compounds (± 3,0 %) was taken [12].

The standard heat capacities of $LaCaCoCuMnO_6$ and $LaCaNiCuMnO_6$ were also calculated under Debye [13, 14]. The necessary data to calculate were the Debye characteristic temperatures (Q_d, K) of the elements making a chemical compound and their melting points ($T_{m.p.}$, K) of elements of compounds [13, 14]. The characteristic temperatures of the elements for the

Table 2 **Equation coefficients of temperature dependence of manganites of $C^0_p = a + b \cdot T + c \cdot T^{-2}$, J / mol · K**

Compound	a	$b \times 10^{-3}$	$c \times 10^5$	ΔT / K
$LaCaCoCuMnO_6$	– (410 ± 20)	2 226 ± 110	–	298,15 - 348
	990 ± 49	– (1 800 ± 89)	–	348 - 373
	3 556 ± 175	– (4 602 ± 226)	– (2 118,0 ± 104,2)	373 - 448
	947 ± 47	– (1 128 ± 56)	–	448 - 473
	539 ± 27	24 ± 1	– (307,3 ± 15,1)	473 - 673
$LaCaNiCuMnO_6$	513 ± 21	267 ± 11	– (312,4 ± 12,6)	298,15 - 473
	1 417 ± 57	– (1 941 ± 78)	–	473 - 523
	984 ± 40	– (372 ± 15)	– (1 059,2 ± 42,6)	523 - 673

Table 3 **Thermodynamic functions of cobalt (nickelite) – cuprate - manganites, S° / T, Φ^{xx} / T, J / mol · K, H° / T - H°(298,15), J / mol**

T / K	S° / T	H° / T - H°(298,15)	Φ^{xx} / T
LaCaCoCuMnO$_6$			
298,15	251 ± 7	–	251 ± 20
300	253 ± 20	510 ± 20	251 ± 20
400	346 ± 27	33 020 ± 1 620	263 ± 21
500	440 ± 35	75 450 ± 3 710	290 ± 23
600	522 ± 41	120 410 ± 5 920	321 ± 25
675	579 ± 46	156 280 ± 7 690	347 ± 27
LaCaNiCuMnO$_6$			
298,15	242 ± 7	–	242 ± 17
300	244 ± 17	486 ± 20	242 ± 17
400	342 ± 24	35 070 ± 1 410	255 ± 18
500	446 ± 31	81 730 ± 3 280	283 ± 20
600	525 ± 37	125 190 ± 5 030	317 ± 22
675	582 ± 41	161 600 ± 6 500	343 ± 24

studied compounds were determined by Koref formula, and transition from the isochoric to isobaric heat capacity of compounds was performed with using the Nernst – Lindeman equation [13, 14]. Under the above-mentioned, the standard heat capacities of $LaCaCoCuMnO_6$ and $LaCaNiCuMnO_6$ (250,7 and 251,4 J / mol · K, respectively) were calculated, which correspond to the experimental data with accuracy of 0,9 and 4,5 %.

The standard enthalpies of $LaCaCoCuMnO_6$ and $LaCaNiCuMnO_6$, determined by our procedure, are 3 156,3 and – 3 157,3 kJ / mol, respectively.

In addition, the electrophysical characteristics of the nanodimensional compounds obtained on LCR device (Taiwan) were studied.

Determination of the electrical characteristics (dielectric permittivity ε, an electrical resistance R) was made with measuring of the electrical capacitance C of samples on LCR-800 (meter of L, C, R), where there were an operating frequency -1 kHz, an interval of 293 - 483 K continuously, dry air in thermostatic mode , hold-up time at each fixed temperature. The procedure to determine the electrophysical characteristics was described in detail in paper [4].

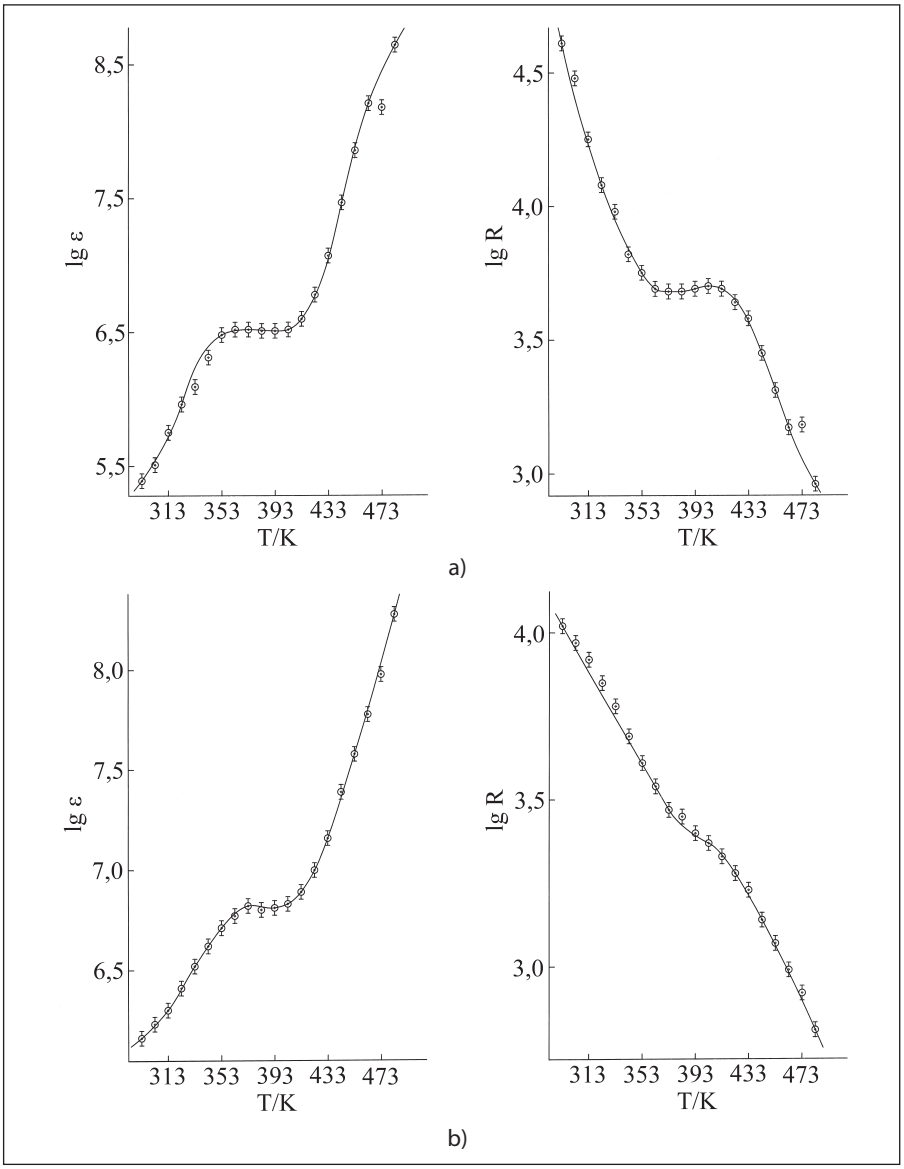

Figure 2 Temperature dependences of dielectric permittivity (ε) and electrical resistance (R) of $LaCaCoCuMnO_6$ (a) and $LaCaNiCuMnO_6$ (b) on temperature

The Figure 2 demonstrates the temperature dependences of the dielectric permittivity and electrical resistance of $LaCaCoCuMnO_6$ and $LaCaNiCuMnO_6$.

Analysis of the data showed that $LaCaCoCuMnO_6$ in the interval of 293 - 363 K demonstrated some semiconductor properties and can be observed band gap equal to 0,76 eV. The electrical resistance was approximately constant in the interval of 363 - 413 K. The interval of 413 - 483 K of semiconductor conductivity and band gap (1,42 eV) were again found (Figure 2, a). $LaCaNiCuMnO_6$ in all studied temperature interval (293 - 483 K) demonstrated the semiconductor conductivity with band gap of 0,43 eV. The dependence curve of the dielectric constant from temperature showed a small deviation at 383 K (Figure 2, b). Both compounds can be referred to narrow-probe semiconductors. It should be stated that compounds had the high dielectric permittivity (ε). The values for $LaCaNiCuMnO_6$ increased from $1{,}46 \cdot 10^6$ at 293 K to $1{,}89 \cdot 10^8$ at 483 K and for $LaCaCoCuMnO_6$ - from $2{,}45 \cdot 10^5$ at 293 K to $4{,}46 \cdot 10^8$ at 483 K.

The received results demonstrated that nanodimensional $LaCaCoCuMnO_6$ and $LaCaNiCuMnO_6$ are perspective for semiconductor and microcapacitor technology.

CONCLUSION

By the method of the dynamic calorimetry in an interval of 298,15 - 673 K, the heat capacities of the studied manganites were first investigated, the temperatures of II type phase transitions were determined, and equations for the temperature dependence of the heat capacity were calculated. Referring to the experimental and calculated data, their temperature dependences of thermodynamic functions were determined.

Under the independent procedure of Debye method with using of the Koref and Nernst-Lindemann equations, the standard heat capacities of the studied compounds were calculated, and their values corresponded to the experimental data, within their error determination.

The electrophysical researches demonstrated that both compounds had the semiconductor properties, high electrical capacity characteristics, and are also of interest as materials with the working memory.

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Note: The responsible translator for English language is Issakova Yelena Pavlovna, Karaganda, Kazakhstan.