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THERMODYNAMIC AND ELECTROPHYSICAL INVESTIGATION OF NANOSTRUCTURED COPPER-ZINC MANGANITE OF LANTHANUM AND LITHIUM $LaLi_2CuZnMnO_6$

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The paper demonstrates the results of the experimental investigation of the thermodynamic and electrophysical properties of the new nanostructured copper-zinc manganite of lanthanum and lithium ($LaLi_2CuZnMnO_6$).

Keywords: copper-zinc manganite, lanthanum, lithium, nanostructured particle, thermodynamics, electrophysics properties

INTRODUCTION

Discovery of the effects of superconductivity in cuprates and the giant, colossal magnetic resistance in manganites of the rare-earth elements doped with *s*-element oxides was an impulse in many investigations to obtain materials with the unique physicochemical properties [1-4]. It should also be noted that compounds based on lanthanum oxides and *3d*-elements doped with oxides of the alkaline earth metals are able to have the giant values of the dielectric capacitivity, which are also of interest as materials with the working memory in microelectronics [5].

In addition, semiconductor of ZnO having a band gap (3,37 eV) is a promising material as gas sensors, thin film transistors, microelectric devices, etc. [6]. It should also be stated that manganese-based compounds are of great importance in the ferroalloy metallurgy [7].

In connection with the above-stated, the purpose of this paper is a calorimetric investigation of heat capacity, calculation of the thermodynamic characteristics and the electrophysical study of our new synthesized nanostructured copper-zinc manganite of lanthanum and lithium $LaLi_2CuZnMnO_6$.

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EXPERIMENTAL PART

The polycrystalline $LaLi_2CuZnMnO_6$ was synthesized with the ceramic technology method from La_2O_3, CuO, ZnO, Mn_2O_3 and Li_2CO_3 in the interval of 800 - 1 200 °C.

Their nanostructured particles were obtained by milling on the vibration mill «Retsch», and their sizes (226 - 286 nm) were determined on an electron microscope MJRA3, LMU Tescan.

The radiographic investigations found that $LaLi_2CuZnMnO_6$ crystallizes in the cubic syngony with the following lattice parameters: a = 13,94 ± 0,02 Å, V^o = 2 708,87 ± 0,06 Å^3, Z=4, $V^o_{elec.cell}$ = 677,22 ± 0,02 Å^3, $_{roent.}$ = 4,31; $_{pick.}$ = 4,28 ± 0,02 g/cm^3.

Investigation of the isobaric heat capacity of $LaLi_2CuZnMnO_6$ similarly to [8] was performed in the interval of 298,15 - 673 K on calorimeter IT-S-400. The measuring circuit of the device provides measurement of the temperature level at the fixed points through 25 K. The limit of permissible error of the device according to the passport data is ± 10,0 %. Calibration of the device was made on the basis of the determining of the thermal conductivity of the heat meter K_t [9, 10]. The operation of the device was checked with definition of -Al_2O_3.

The obtained value of C^o_p(298,15) of -Al_2O_3 [76,0 ± 1,5 J / (mol · K)] is satisfactorily consistent with its reference data [79,0 ± 0,17 J / (mol · K)] [11]. During the graduation and verification, the repeated (parallel) measurements were made through 25 K five times and the results were averaged and processed with methods of the mathematical statistics [12]. The mean-square deviation ( ) were calculated for values of the specific heat capacity, and random error components ($\mathring{\Delta}$) were calculated for the molar heat capacity [10].

Table 1 **The experimental values of specific (C_p ± ¯) and molar heat capacities (C^o_p ± ˚) of $LaLi_2CuZnMnO_6$ from temperature**

T / K	C_p ± ¯, J / g · K	C^o_p ± Δ̊, J / (mol · K)
298,15	0,5606 ± 0,0184	242,6 ± 22,1
323	0,6201 ± 0,0066	268,3 ± 7,9
348	0,5195 ± 0,0102	224,8 ± 12,3
373	0,7424 ± 0,0164	321,2 ± 19,7
398	0,7782 ± 0,0093	336,7 ± 11,2
423	0,8542 ± 0,0151	369,6 ± 18,2
448	0,8770 ± 0,0126	379,4 ± 15,2
473	0,9836 ± 0,0135	425,6 ± 16,3
498	1,0847 ± 0,0140	469,3 ± 16,9
523	1,1301 ± 0,0192	488,9 ± 23,1
548	0,6194 ± 0,0134	267,7 ± 16,0
573	0,8175 ± 0,0157	353,7 ± 18,9
598	0,8978 ± 0,0210	388,5 ± 25,3
623	0,9403 ± 0,0138	406,8 ± 16,6
648	1,0378 ± 0,0171	449,0 ± 20,6
673	1,0555 ± 0,0188	456,7 ± 22,6

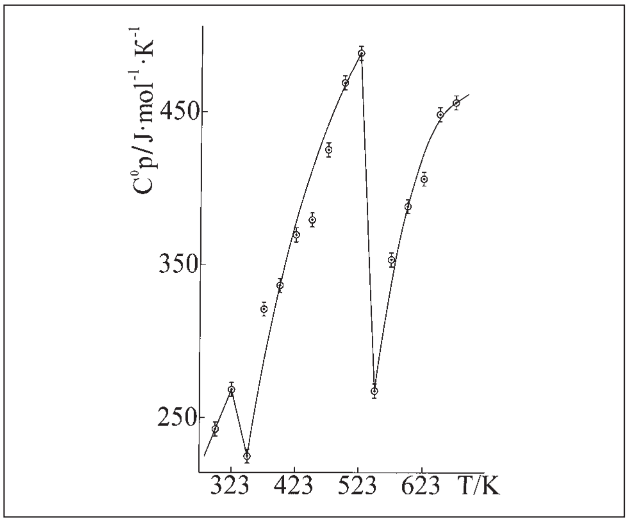

Figure 1 Temperature dependence of heat capacity of $LaLi_2CuZnMnO_6$

The results of the calorimetric investigations are given in Figure 1 and Table 1.

The investigation of the electrophysical properties (the dielectric capacitivity, the electrical resistance) was performed with the measuring of the electrical capacitance of the compound on an LCR device (Taiwan manufacture) at an operating frequency of 1 kilohertz in the interval of 293 - 483 K through 10 K under the procedures of [13, 14]. The results of the electrophysical investigations are illustrated in Figure 2 and Table 2.

DISCUSSION OF RESULTS

As may be inferred from the data of Table 1 and Figure 1 that $LaLi_2CuZnMnO_6$ at 323 - 348 K and 523 - 548 K has changes of the heat capacity relating to II type phase transition, probably due to changes in the dielectric capacitivity, the electrical resistance, detection of Curie and Neel points [15]. Based on the peak temperatures of the II type phase transitions (323 - 523 K), the equations of the temperature dependence of heat capacity of $LaLi_2CuZnMnO_6$ / [J / (mol · K)]:

$$C^o_{p(1)} = -(64{,}0 \pm 3{,}2) + (1\,028{,}6 \pm 51{,}1)\cdot 10^{-3}T,\ (298 - 323\ K), \quad (1)$$

$$C^o_{p(2)} = (830{,}2 \pm 41{,}3) - (1\,739{,}8 \pm 86{,}5)\cdot 10^{-3}T,\ (323 - 348\ K), \quad (2)$$

$$C^o_{p(3)} = (707{,}1 \pm 35{,}1) - (12{,}5 \pm 0{,}6)\cdot 10^{-3}T - (578{,}8 \pm 28{,}8)\times 10^{5}T^{-2},\ (348 - 523\ K), \quad (3)$$

$$C^o_{p(4)} = (5\,110{,}4 \pm 254{,}0) - (8\,837{,}1 \pm 439{,}2)\times 10^{-3}T,\ (523 - 548\ K), \quad (4)$$

$$C^o_{p(5)} = (3\,820{,}3 \pm 189{,}9) - (3\,256{,}3 \pm 161{,}8)\times 10^{-3}T - (5\,308{,}9 \pm 263{,}8)\times 10^{5}T^{-2},\ (548 - 673\ K). \quad (5)$$

It should be noted that the experimentally certain value of the standard thermal capacity C^o_p(298,15) of $LaLi_2CuZnMnO_6$ (242,6 ± 22,1 J / (mol · K)) (Table 1), it will reasonably be agreed with its estimated value calculated with a method of the ionic increments (246,4 J / (mol · K)) according to [16] with an accuracy of 1,57 %.

The standard entropy of $LaLi_2CuZnMnO_6$ was calculated using the method of the ionic increments (S^i) [16] under the scheme:

$$S^o(298{,}15)\ LaLi_2CuZnMnO_6 = S^i(298{,}15)\ La^{3+} + 2S^i(298{,}15)\ Li^{+} + S^i(298{,}15)\ Cu^{2+} + S^i(298{,}15)\ Zn^{2+} + S^i(298{,}15)\ Mn^{3+} + 6S^i(298{,}15)\ O^{2-}. \quad (6)$$

The following values of the ionic entropy increments (S^i, J / (mol · K)) were used to calculate under the scheme (6): La^{3+} = 40,4; Li^{+} = 14,5; Cu^{2+} = 36,5; Zn^{2+} = 34,2; O^{2+} = 11,7 [16]. The estimated value of S°(298,15) of $LaLi_2CuZnMnO_6$ under the scheme (6) was equal to 210,3 ± 6,3 J / (mol · K). Using the equations of the dependences of C^o_p (*T*) $LaLi_2CuZnMnO_6$ (1-5) and its estimated value S°(298,15), the temperature dependences of the thermodynamic functions of the copper-zinc manganite were calculated from the known formula (Table 3).

Further, Table 2 and Figure 2, as mentioned above, demonstrated the results of the temperature dependence of the electrical resistance (R) and the dielectric capacitivity (ε).

As can be seen from the data in Table 2 and Figure 2, $LaLi_2CuZnMnO_6$ has the semiconductor conductivity in the interval of 293 - 343 K, the metallic conductivity at 343 - 383 K, and the semiconductor conductivity again at 383 - 483 K. The band gap in the interval of 293 - 343 K is 1,0 eV, and at 383 - 483 K – 0,90 eV, and $LaLi_2CuZnMnO_6$ can be referred to the narrow-probe semiconductors. It should be noted that the decreasing

Table 2 **The temperature dependences of dielectric capacitivity (ε) and electrical resistance (R) of $LaLi_2CuZnMnO_6$ at a measurement frequency of 1 kHz**

T / K	R / Om	ε	T / K	R / Om	ε
293	190 800	75 987	393	26 160	878 460
303	106 600	97 359	403	22 820	1 622 527
313	49 540	184 641	413	19 340	2 930 886
323	27 280	316 535	423	15 370	6 214 430
333	19 720	432 177	433	12 430	11 827 126
343	17 790	480 058	443	10 080	21 312 606
353	18 150	478 204	453	81 23	38 184 749
363	22 040	433 174	463	6 246	74 756 342
373	25 710	453 709	473	5 116	121 163 050
383	27 340	588 847	483	4 051	203 725 215

Table 3 **Thermodynamic functions of $LaLi_2CuZnMnO_6$, 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
298,15	245 ± 7	-	245 ± 20
300	247 ± 20	487 ± 24	245 ± 20
350	285 ± 23	13 000 ± 646	248 ± 20
400	324 ± 26	27 448 ± 1 364	255 ± 20
450	368 ± 29	46 458 ± 2 308	265 ± 21
500	415 ± 33	68 652 ± 3 412	278 ± 22
550	455 ± 36	89 677 ± 4 457	292 ± 23
600	485 ± 39	106 635 ± 5 300	307 ± 24
650	519 ± 41	127 828 ± 6 353	322 ± 26
675	536 ± 43	139 153 ± 6 916	330 ± 26

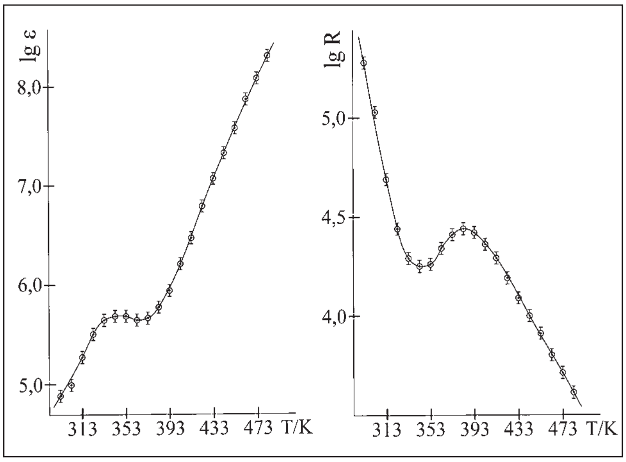

Figure 2 Dependence of dielectric capacitivity (ε) and electrical resistance (R) of $LaLi_2CuZnMnO_6$ on temperature (frequency of 1 kHz)

in heat capacity of $LaLi_2CuZnMnO_6$ on a dependence curve of C^o_p (T) at 323 - 348 K was in line with its transition from the semiconductor to the metallic conductivity at 343 K. Thus it determined the nature of the II type phase transition on a curve of the heat capacity from temperature.

The dielectric capacitivity of $LaLi_2CuZnMnO_6$ at 293 K exceeds the similar characteristic, our measured value of $BaTiO_3$ (ε = 1 296) on this device, which agrees with its recommended value (ε = 1 400 ± 250) [17-19] by 59 times, and at 483 K – 157 195 times. In a small narrow temperature interval from 293 K to 483 K, ε of $LaLi_2CuZnMnO_6$ increases from $7,6 \cdot 10^4$ to $2,0 \cdot 10^8$.

CONCLUSION

The temperature dependence of the heat capacity of the new nanostructured copper-zinc manganite of $LaLi_2CuZnMnO_6$ was first investigated in the interval of 298,15 - 673 K. It was determined that in the studied temperature interval this compound had two abnormal changes in heat capacity related to the II type phase transitions. Its standard entropy was calculated. In the interval of 298,15 - 675 K, the temperature dependences of the thermodynamic functions of S°(T), H°(T) - H°(298,15) $Φ^{xx}$(T) were calculated.

In the interval of 293 - 483 K, the temperature dependence of the dielectric capacitivity and the electrical resistance of $LaLi_2CuZnMnO_6$ were investigated. Regions of the semiconductor and metallic conductivity were identified.

It was determined that this compound had the big values of the dielectric capacitivity, which during the transition from 293 K to 483 K increased from $7,6 \cdot 10^4$ to $2,0 \cdot 10^8$. This material is of interest for the semiconductor and microcapacitor technologies.

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