

Thermodynamics and Electrophysics of New LaCaCuZnMnO₆ Copper–Zinc Manganite of Lanthanum and Calcium

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Abstract—Copper–zinc lanthanum and calcium manganite LaCaCuZnMnO₆ was synthesized from oxides of lanthanum(III), copper(II), zinc(II), manganese(III), and calcium carbonate in the temperature range of 1073–1473 K. Nanostructured particles were obtained by grinding the material in a vibratory mill. The heat capacity of the compound was studied in the range of 298.15–673 K on an IT-S-400 calorimeter. On dependence curve $C_p^o \sim f(T)$ at 598 K, an anomalous jump in heat capacity was detected. The temperature dependences of the electrical resistance and relative permittivity were studied on an LCR-781 setup (Taiwan) at 293–483 K and at frequencies of 1, 5, and 10 kHz. That the conductivity has a semiconductor character has been established. At 483 K, an anomalously high value of the permittivity was revealed at all studied frequencies.

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INTRODUCTION

The synthesis and study of the physicochemical properties of cuprates and manganites of rare earth elements doped with oxides of alkaline-earth metals and possessing the effects of superconductivity, colossal magnetoresistance, dielectric permittivity, semiconductor, and other properties are of great interest to researchers [1–5].

In view of the foregoing, the purpose of this work is to study the physicochemical properties not of cuprate, manganite, or zincate or rare-earth and alkaline-earth metals separately, but of them in a united complex, i.e., as copper–zinc manganite. Based on this, the purpose of this article is the synthesis of copper–zinc lanthanum and calcium manganite and the study of its thermodynamic and electrophysical properties.

EXPERIMENT

Synthesis of LaCaCuZnMnO₆ was carried out in the course of the solid-phase interaction of La₂O₃ (“special purity” brand), CuO, ZnO, Mn₂O₃, and CaCO₃ (“analytical analysis” qualification) in the temperature range of 1073–1473 K for a total of 30 h. Nanostructured particles of LaCaCuZnMnO₆ with sizes within 100–200 nm were obtained by grinding under certain conditions from a polycrystalline sample in a Retsch vibrating mill (Germany). The dimensions were determined on a Mira 3LMU electron microscope (Tescan) (Fig. 1).

X-ray phase analysis of nanostructured LaCaCuZnMnO₆ was carried out on a DRON-2.0 diffrac-

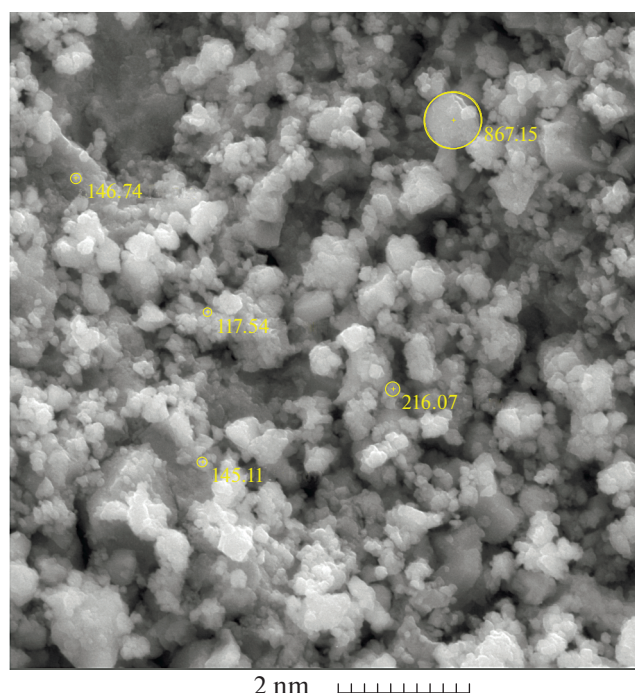


Fig. 1. Image of LaCaCuZnMnO₆ on a Mira 3LMU electron microscope (Tescan); numbers are particle diameters, nm.

Table 1. Comparison of the heat-capacity values of Al_2O_3 used to check the operation of the calorimeter

T, K	$C_p^\circ(T), \text{J}/(\text{mol K})$	
	[11]	[10]
180	44.50	43.83
230	64.86	61.18
250	70.37	67.08
280	77.07	74.82
300	76.31	79.41
350	86.49	88.86
400	94.12	95.21
450	100.26	101.8
500	105.47	106.1
550	110.09	109.7
600	114.29	112.5
650	118.20	114.9

tometer. The shooting conditions were $U = 30 \text{ kV}$, $J = 10 \text{ mA}$, counter-rotation speed of 20 rpm, scale range of 1000 pulses/s, time constant $\tau = 5 \text{ s}$, and angle interval 2θ from 10° up to 90° . The intensity of diffraction peaks was determined on a 100-point scale. Data acquisition for the radiograph was carried out by an analytical method [6]. The pycnometric density was determined according to [7]. On the basis of radiographs, it was found that nanostructured LaCaCuZnMnO_6 crystallizes in the cubic system with the following lattice parameters: $a = 13.69 \pm 1.78 \text{ \AA}$, $V^\circ = 2564.6 \pm 5.35 \text{ \AA}^3$, $Z = 4$, $V_{\text{эл.яч}}^\circ = 641.15 \pm 1.34 \text{ \AA}^3$, $\rho_{\text{rent}} = 4.43 \text{ g/cm}^3$, and $\rho_{\text{picnic}} = 4.41 \pm 0.03 \text{ g/cm}^3$.

The isobaric heat capacity of nanostructured LaCaCuZnMnO_6 was measured at 298.15–673 K on an IT-S-400 calorimeter. The principle and method of operation of the calorimeter are described in detail in [8, 9]. The measuring circuit of the device provides temperature measurement at points with a step of 25 K. The calorimeter was calibrated on the basis of determining the thermal conductivity of the heat meter by conducting five parallel experiments with a copper sample and an empty ampoule. The operation of the calorimeter was checked by measuring the heat capacity of $\alpha\text{-Al}_2\text{O}_3$ in the range of 180–650 K using liquid nitrogen as a coolant and comparing the obtained results with new literature data on the heat capacities of $\alpha\text{-Al}_2\text{O}_3$ [10]. Table 1 shows comparisons of the heat capacity of $\alpha\text{-Al}_2\text{O}_3$ (“analytical analysis” qualification, TU 6.09-426-75), measured on a calorimeter [11] with data from [10]. The results show good agreement between the data—within 3–4% (Table 1). For each average value of the specific heat from five parallel experiments, standard deviation δ was determined, as were the random components of

the error for the averaged values of the molar-heat capacities [9]. The marginal error in determining the heat capacity, according to the passport data, is $\pm 10.0\%$. Coefficient errors in dependence equations $C_p^\circ \sim f(T)$ were determined by averaging the average random errors of the experimental values of the heat capacities.

The study of electrical properties was carried out according to the procedure of [12], i.e., measuring the electrical capacitance of copper–zinc manganite on an LCR-781 commercial device (Taiwan) at operating frequencies of 1, 5, and 10 kHz every 10 K in the range of 293–483 K. The accuracy of measuring the electrical capacitance, relative permittivity, and electrical resistance, according to the passport data of the device, is equal to $\pm 0.05\%$ [13]. A plane-parallel sample was prefabricated in the form of a disk 10 mm in diameter and 5–6 mm thick with a binder additive. Pressing was carried out under a pressure of 20 kg/cm^3 . The resulting disc was fired in a silite furnace at a temperature of 673 K for 6 h. The disc was then carefully polished on both sides.

The permittivity was determined from the electrical capacitance of the sample. To obtain the relationship between electric induction and electric-field strength, the Sawyer–Tower scheme was used. The band gap was calculated using the formula

$$\Delta E = \frac{2kT_1T_2}{0.43(T_2 - T_1)} \lg \frac{R_1}{R_2},$$

where k is the Boltzmann constant, $8.6173303 \times 10^{-5} \text{ eV K}^{-1}$, and R_1 and R_2 are resistance at T_1 and T_2 .

To confirm the reliability of the data obtained, the dielectric constant of a standard substance, barium titanate BaTiO_3 , was measured at frequencies of 1 and 5 kHz. The values obtained for the permittivity of BaTiO_3 at 293 K are 1296 (at 1 kHz) and 1220 (at 5 kHz), which are in satisfactory agreement with the recommended value of 1400 ± 250 [14–16].

RESULTS AND DISCUSSION

Table 2 and Fig. 2 show the results of calorimetric studies, from which it follows that, at 598 K, a λ -shaped anomalous heat capacity jump is observed on dependence curve $C_p^\circ(T)$ for LaCaCuZnMnO_6 , which is probably associated with a second-order phase transition due to changes in magnetic, electrical, and other characteristics. The graph in Fig. 2 was constructed on the basis of experimental data using the KOMPAS-3D LT program. Taking into account the phase-transition temperature, equations for the temperature dependence of the heat capacity of copper–zinc manganite are derived, which are described by the following polynomials, $\text{J}/(\text{mol K})$:

Table 2. Experimental heat capacities of LaCaCuZnMnO₆

T, K	$C_p^\circ(T) \pm \bar{\delta}, \text{J}/(\text{g K})$	$C_p^\circ(T) \pm \bar{\Delta}, \text{J}/(\text{mol K})$
298.15	0.4841 ± 0.0139	222 ± 18
323	0.4873 ± 0.0084	224 ± 11
348	0.5638 ± 0.0068	259 ± 9
373	0.5830 ± 0.0171	267 ± 22
398	0.6181 ± 0.0144	284 ± 18
423	0.6589 ± 0.0150	302 ± 19
448	0.7040 ± 0.0134	323 ± 17
473	0.7633 ± 0.0124	350 ± 16
498	0.7998 ± 0.0096	367 ± 12
523	0.8063 ± 0.0159	370 ± 20
548	0.8205 ± 0.0163	376 ± 21
573	0.8300 ± 0.0163	381 ± 21
598	0.8617 ± 0.0140	395 ± 18
623	0.8058 ± 0.0110	370 ± 14
648	0.8301 ± 0.0151	381 ± 19
673	0.8652 ± 0.0125	397 ± 16

$$C_{p(1)}^\circ = (337 \pm 17) + (166.0 \pm 8.6) \times 10^{-3} T - (145.9 \pm 7.6) \times 10^5 T^{-2} \quad (298.15-598 \text{ K}),$$

$$C_{p(2)}^\circ = (1009 \pm 52) + (1026.4 \pm 53.3) \times 10^{-3} T \quad (598-623 \text{ K}),$$

$$C_{p(3)}^\circ = (30 \pm 2) + (544.6 \pm 28.3) \times 10^{-3} T \quad (623-673 \text{ K}).$$

The standard heat capacity of LaCaCuZnMnO₆ was also calculated using the ion-increment method [17] and the Kopp–Neumann rule [18], and the obtained values were 232.3 and 230.1 J/(mol K), respectively, which agrees with the experimental value of 222 J/(mol K) with an accuracy of 4.4 and 3.5%.

Due to the fact that the technical characteristics of the calorimeter do not allow calculating the standard entropy of LaCaCuZnMnO₆ directly from the experimental data on heat capacity, its value was calculated using the system of ionic entropy increments [17] according to the following scheme:

$$\begin{aligned} S^\circ(298.15, \text{LaCaCuZnMnO}_6) &= S^i(\text{La}^{3+}) \\ &+ S^i(\text{Ca}^{2+}) + S^i(\text{Cu}^{2+}) + S^i(\text{Zn}^{2+}) \\ &+ S^i(\text{Mn}^{3+}) + 6S^i(\text{O}^{2-}), \end{aligned}$$

where S^i are ionic entropy increments. When calculating according to this scheme, the entropy increments of the following ions, J/(mol K), are used: $S^i(\text{La}^{3+}) =$

40.4, $S^i(\text{Ca}^{2+}) = 32.0$, $S^i(\text{Cu}^{2+}) = 36.5$, $S^i(\text{Zn}^{2+}) = 34.2$, $S^i(\text{Mn}^{3+}) = 34.7$, and $S^i(\text{O}^{2-}) = 11.7$ [17]. The value thus calculated is $S^\circ(298.15, \text{LaCaCuZnMnO}_6) = 248 \pm 7.0 \text{ J}/(\text{mol K})$.

Based on the experimental data on heat capacities and the calculated value of the standard entropy, temperature dependences $C_p^\circ(T)$ and thermodynamic

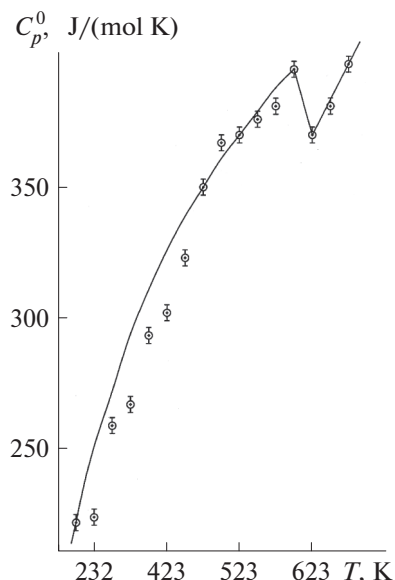
**Fig. 2.** Temperature dependence of the heat capacity of LaCaCuZnMnO₆.

Table 3. Values of thermodynamic functions of LaCaCuZnMnO₆

T, K	$S^\circ(T) \pm \Delta, J/(\text{mol K})$	$H^\circ(T) - H^\circ(298.15) \pm \Delta, J/\text{mol}$	$F^{\text{xx}}(T) \pm \Delta, J/(\text{mol K})$
298.15	248 ± 7	–	248 ± 20
300	249 ± 21	447 ± 20	248 ± 20
350	288 ± 24	13040 ± 690	251 ± 21
400	327 ± 27	27790 ± 1460	258 ± 21
450	366 ± 30	44120 ± 2320	268 ± 22
500	403 ± 33	61660 ± 3240	280 ± 23
550	438 ± 36	80220 ± 4220	292 ± 24
600	472 ± 39	99630 ± 5240	306 ± 25
650	502 ± 41	118580 ± 6240	320 ± 26
675	517 ± 43	128360 ± 6750	327 ± 27

functions $S^\circ(T)$, $H^\circ(T) - H^\circ(298.15)$, and $F^{\text{xx}}(T)$ LaCaCuZnMnO₆ are calculated (Table 3).

The study of the temperature and frequency dependences of dielectric permittivity ϵ of nanostructured LaCaCuZnMnO₆ shows very large values. Thus, at 483 K, the values of ϵ for LaCaCuZnMnO₆, which are equal to $5.53 \times 10^8 \pm 2.76 \times 10^5$ (at 1 kHz), $4.1 \times 10^7 \pm 2.05 \times 10^4$ (at 5 kHz), and $1.29 \times 10^7 \pm 6.45 \times 10^3$ (at 10 kHz), exceed those of the reference BaTiO₃ at 483 K by 256 339 times (at 1 kHz), 19 522 times (at 5 kHz), and 6145 times (at 10 kHz) (Table 4). Figure 4

shows the temperature dependences of the electrical resistance and permittivity at a frequency of 1 kHz. Large values of the permittivity of LaCaCuZnMnO₆ at 483 K can be caused, according to [19], by high dielectric losses. In [4], giant values of the permittivity ($\epsilon = 10^5 - 10^6$) for La_{15/8}Sr_{1/8}NiO₄ ceramics. The authors also explain the nature of this phenomenon within the framework of the theory of the Maxwell–Wagner effect, according to which dielectric losses are large in the region of intermediate frequencies, since the period of oscillations of the electric-field strength is

Table 4. Electrophysical characteristics of LaCaCuZnMnO₆

T, TO	C, nF	R, Ω	E	loge	log R, Ω
293	7.804	337500	67399	4.83	5.53
303	8.2832	320200	71538	4.85	5.51
313	9.0174	293900	77879	4.89	5.47
323	10.634	257000	91841	4.96	5.41
333	12.788	220900	110444	5.04	5.34
343	18.859	176100	162876	5.21	5.25
353	30.879	138300	266687	5.43	5.14
363	46.445	110900	401123	5.60	5.04
373	90.926	79060	785283	5.90	4.90
383	174.08	56930	1503444	6.18	4.76
393	349.36	39130	3017251	6.48	4.59
403	572.22	28530	4941984	6.69	4.46
413	1195.7	19240	10326676	7.01	4.28
423	2237.1	13410	19320738	7.29	4.13
433	4152.9	9478	35866566	7.55	3.98
443	7630.2	6861	65898305	7.82	3.84
453	12390	5161	107006369	8.03	3.71
463	22183	3734	191583720	8.28	3.57
473	35339	2832	305205657	8.48	3.45
483	64081	2012	553436252	8.74	3.30

comparable to the relaxation time of the surface polarization. In the case under consideration, the region under study is in the range of 1–10 kHz, which can be attributed to intermediate frequencies.

It should be noted that the correctness and reliability of the obtained results are confirmed by the accuracy of the LCR-781 instrument ($\pm 0.05\%$) and satisfactory agreement of the value of ε for the standard substance BaTiO₃ obtained on this installation with its recommended value.

The temperature dependence of the electrical resistance shows the semiconductor nature of the conductivity in the studied temperature range. The band gap is 0.49 eV, and LaCaCuZnMnO₆ can be classified as a narrow-probe semiconductor.

CONCLUSIONS

For the first time, nanostructured particles of copper–zinc lanthanum and calcium manganite with the composition of LaCaCuZnMnO₆ have been obtained. In the temperature range of 298.15–673 K, the temperature dependences of the heat capacity were studied, where a second-order phase transition was found at 598 K. At 298.15–675 K, the temperature dependences of the thermodynamic functions are calculated.

At 293–483 K and frequencies of 1, 5, and 10 kHz, the permittivity and electrical resistance were studied. The results show that the obtained material is of interest for microelectronics and microcapacitor technology.

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