DOI 10.31489/2022No2/42-47

UDC 621.386.8:385.592+537.226+537.226.1

ELECTROPHYSICAL PROPERTIES OF NEW NANOSTRUCTURED COPPER-ZINC MANGANITE OF LANTHANUM AND MAGNESIUM

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The polycrystalline copper-zinc manganite was synthesized by the solid-phase interaction in the range of 800-1200 °C of oxides of lanthanum (III), copper (II), zinc (II), manganese (III) and magnesium carbonate, thus its nanostructured particles were first obtained by grinding on the vibrating mill "Retsch" (Germany). The X-ray investigations determined that the nanostructured manganite is crystallized in the cubic syngony. On the LCR-7817/827 device (Company «Good Will Instrument Co., Ltd., Taiwan») in the range of 293-483 K at frequencies equal to 1.5 and 10 kHz, the dielectric constant and electrical resistance were investigated and it was found that this compound at 293-353 K has the semiconductor conductivity, at 353-373 K - metal and at 373-483 K - semiconductor conductivity again. The band gap widths were calculated. The permittivity at 483 K reaches gigantic values at all frequencies. Referring to the above, the objective of this paper is to study the temperature dependence of the dielectric constant and the electrical resistance of a new nanostructured copper-zinc manganite of lanthanum and magnesium.

Keywords: copper-zinc manganite, lanthanum, magnesium, nanostructured particles, electron microscopy, X-ray, electrophysics, semiconductor.

Introduction

Manganites of the rare-earth elements doped with oxides of alkaline-earth metals with effects of the giant and colossal magnetic resistance can be used in the magnetic field sensors, reading heads for the magnetic recording of high density and sensors of the moved temperature [1]. In addition, manganites can have the semiconductor, ferroelectric, radioluminescent and other properties [2-4]. It should also be noted that recently similar new compounds, based on nickelates of lanthanum and strontium, were obtained. They have the giant values of the dielectric constant, which are of interest as materials with the high values of working memory [5]. It should also be noted that these materials are not only promising, but in some cases used as electrodes for high-temperature fuel cells, catalysts for afterburning exhaust gases, oxygen membranes, thermistors, sensors [6]. Perovskites, which include oxides of manganese, rare earth and alkaline earth metals, are also of interest as an anode material for a solid oxide fuel cell [7]. Based on the foregoing, the study of the physicochemical properties of new analogous compounds has a certain scientific and practical interest.

1 Experimental technique

The starting materials to synthesize this compound were La_2O_3 ("puriss. spec."), ZnO, Mn_2O_3, $MgCO_3$ (qualification ("p.a.")), their stoichiometric amounts were thoroughly mixed, milled and annealed in the range of 800-1200 °C for 30 h. The mixture was cooled at 800 °C, 1000 °C and 1200 °C with the repeated mixing and milling. The low-temperature annealing was made at 400 °C for 10 h [8]. Then, on the vibration mill "Retsch" (Germany), the polycrystals of the formed alloy were ground to nanostructured particles, their sizes were determined on MJRA electron microscope, 3LMU Tescan (Fig.1). The X-ray phase analysis of nanostructured $LaMgCuZnMnO_6$ was performed on a diffractometer DRON-2,0 under conditions: CuK_α - radiation, U = 30 kV, J = 10 mA, rotation speed - 1000 pulses per second, time constant t = 5 sec, angle interval - 2θ from 10 to 90°.

The intensity of diffraction maxima was estimated on 100-point scale. The X-ray patterns were indicated by the analytical method [9]. The pycnometric density was determined according to [10]. Toluene was used as the indifferent liquid. Figure 2 shows the diffractogram of the nanostructured $LaMgCuZnMnO_6$. Similarly, we synthesized copper-zinc manganites of lanthanum and alkali metals [11].

The study of the electrophysical properties (dielectric constant, electric resistance) was performed by the measuring of the electric capacity of a sample on LCR-7817/827 device with a basic error of 0.05% (Company «Good Will Instrument Co., Ltd., Taiwan ») at frequencies of 1, 5 and 10 kHz. The plan-parallel samples were previous made as discs (diameter - 10 mm, thickness - 1.3 mm) with a binder.

Pressing was performed at pressure of 20 kg/cm^3. The resulting discs were baked at temperature of 400 °C in SNOL furnace for 6 h. Further, their thorough double-sided grinding was made. The two-electrode system was used. The dielectric constant was determined from the electric capacitance. Sawyer-Tower circuit was used to obtain the dependence between the electric induction and electric field intensity [12].

The value of the dielectric constant (ε) was determined by the formula:

$$C = \varepsilon_0 \cdot \varepsilon \cdot S/h, \qquad (1)$$

where ε_0 – is the electrical constant, S – is the area, h – is the thickness of the sample, C – is the electric capacitance. In its turn $\varepsilon = C \cdot h/\varepsilon_0 \cdot \varepsilon$; $\varepsilon_0 = 8.85 \cdot 10^{-12}$ Ф/м; $S = \pi \cdot d^2/4$.

The electrophysical investigations were tested by measuring of the dielectric constant (ε) of the standard $BaTiO_3$ at frequencies of 1 and 5 kHz and 293 K, equal to 1296 and 1220 and which were satisfactorily with its recommended value of 1400 ± 250 [12-15].

2 Results and discussion

As can be seen from Fig. 1 the nanostructured $LaMgCuZnMnO_6$ is characterized by the following particle sizes of 122.65, 138.43, 159.34, 162.02 and 214.90 nm. Referring to [16], if a nanoparticle has a complex shape and structure, then a linear size of a particle as a whole are not studied, but a size of its structural element is exanimated as characteristic. Such particles, as a rule, are called nanostructured, and their linear sizes can significantly exceed 100 nm [16].

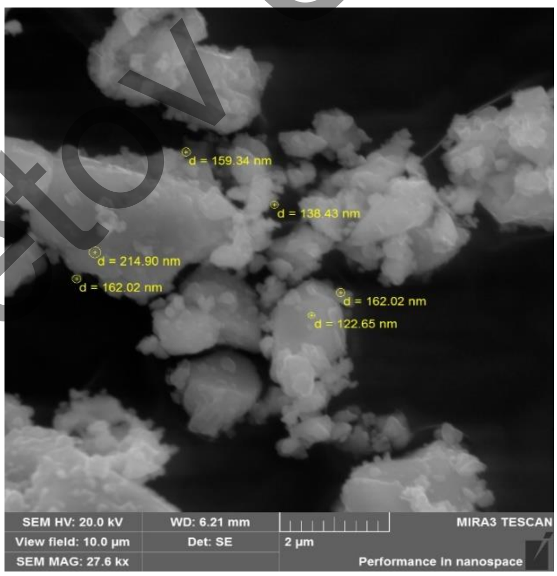

Fig. 1. The electron microscopy of the nanostructured $LaMgCuZnMnO_6$

Based on the results of the X-ray investigations, it was determined that the nanostructured $LaMgCuZnMnO_6$ crystallizes in the cubic syngony with the following lattice parameters: a = 13.53 ± 0.02 Å, V^o = 2476.81 ± 0.06 Å^3, Z = 4, $V^o_{elec.cell}$ = 619.20 ± 0.02 Å^3, $\rho_{roent.}$= 4.52; ρ_{pick} = 4.50 ± 0.01 g/cm^3 [8]. The correctness and reliability of the obtained results were confirmed by the satisfactory agreement of the experimental and calculated values of $10^4/d^2$, as well as a good coincidence of the X-ray and picnometer densities.

The investigation of the electrophysical properties of $LaMgCuZnMnO_6$ in the range of 293-483 K showed that its electrical resistance at transition from 293 K to 483 K decreases by 58.5 times (at 1 kHz), by 48 times (at 5 kHz) and by 39.6 times (at 10 kHz). This compound in the range of 293-353 K has the semiconductor conductivity, at 353-373 K - metallic and at 373-483 K - semiconductor conductivity again. Calculations of the gap width showed that they in the range of 293-353 K are 0.83 eV, and at 373-483 K - 0.80 eV, and this material can be attributed to the narrow-probe semiconductors. There is also a decrease in the electrical resistance with an increase in frequency from 1 to 10 kHz. Table and Figure 2 show the results of measurement of the dielectric constant and electrical resistance of nanostructured $LaMgCuZnMnO_6$.

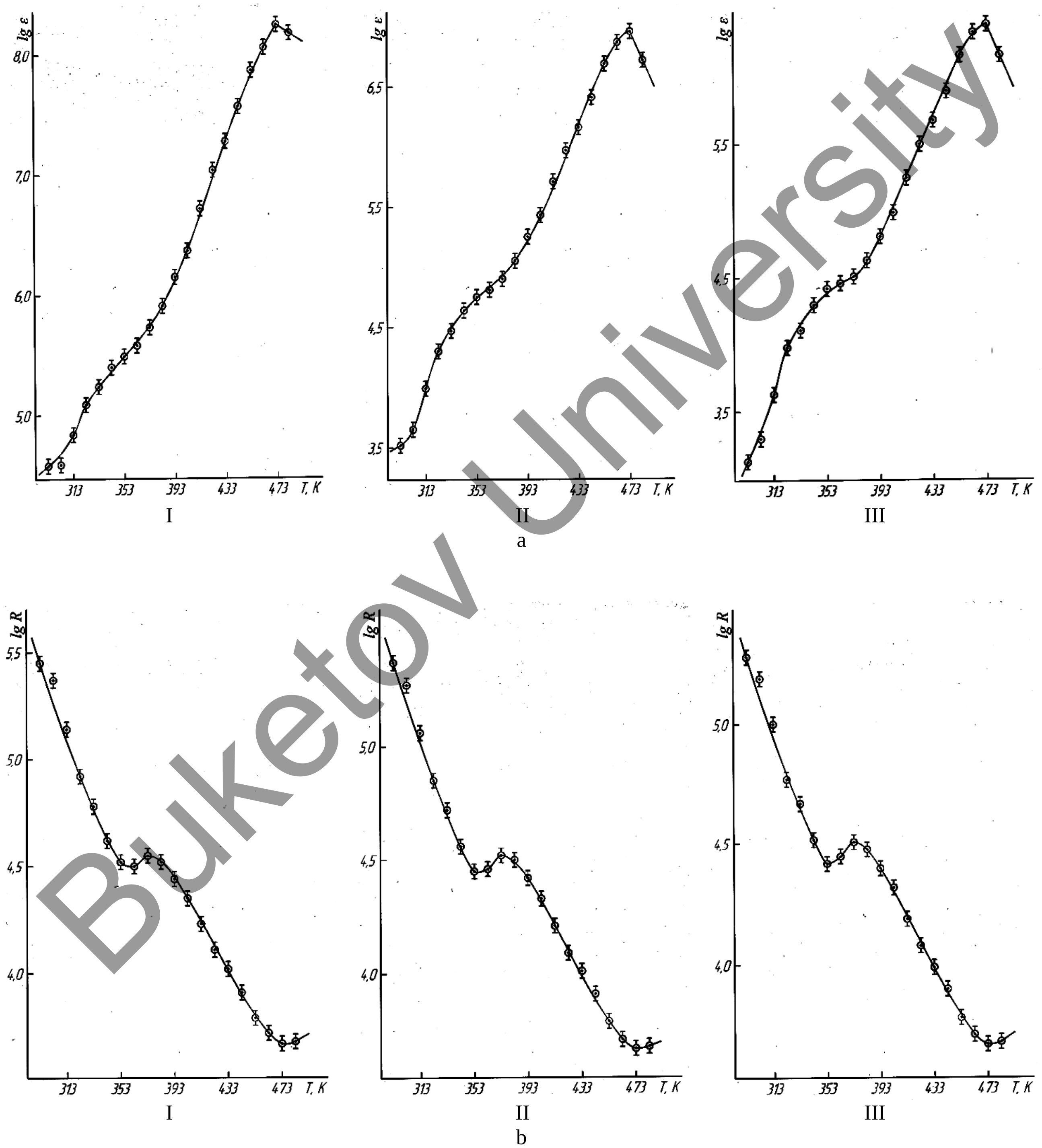

Fig. 2. Dependence of dielectric constant (a) and electric resistance (b) of $LaMgCuZnMnO_6$ on temperature and frequencies equal to 1 kHz (I), 5 kHz (II) and 10 kHz (III)

Table 1. The electrical resistance (R) and dielectric constant (ε) of $LaMgCuZnMnO_6$ in the range of 293-483 K and at frequencies equal to 1 kHz (I), 5 kHz (II) and 10 kHz (III)

T, K	**ε**	**lg ε**	**R, Ohm**	**lg R,**
1	2	3	4	5
		I		
293	38373	4.58	281200	5.45
303	38907	4.59	235600	5.37
313	69267	4.84	137600	5.14
323	123013	5.09	83160	4.92
333	172773	5.24	60410	4.78
343	249329	5.40	41380	4.62
353	310274	5.49	32830	4.52
363	376458	5.58	31690	4.50
373	543143	5.73	35290	4.55
383	811040	5.91	33360	4.52
393	1418691	6.15	27330	4.44
403	2361222	6.37	22560	4.35
413	5188888	6.72	16940	4.23
423	10868329	7.04	12870	4.11
433	18885890	7.28	10580	4.02
443	36933319	7.57	8201	3.91
453	73942927	7.87	6222	3.79
463	115858793	8.06	5206	3.72
473	178977293	8.25	4701	3.67
483	149764295	8.18	4804	3.68
		II		
293	3331	3.52	232600	5.37
303	4475	3.65	187400	5.27
313	9882	3.99	114500	5.06
323	19861	4.30	70110	4.85
333	29214	4.47	51900	4.72
343	43594	4.64	35920	4.56
353	56719	4.75	28460	4.45
363	64649	4.81	28960	4.46
373	80017	4.90	33270	4.52
383	111505	5.05	31390	4.50
393	175883	5.25	26230	4.42
403	270971	5.43	21600	4.33
413	510893	5.71	10330	4.01
423	933391	5.97	12410	4.09
433	1436252	6.16	10340	4.01
443	2563820	6.41	8047	3.91
453	4882148	6.69	6130	3.79
463	7374141	6.87	5151	3.71
473	9155421	6.96	4684	3.67
483	5263953	6.72	4804	3.68
		III		
293	1370	3.14	191800	5.28
303	1991	3.30	153700	5.19
313	4288	3.63	99010	5.00
323	9538	3.98	59400	4.77
333	13006	4.11	47140	4.67
343	20013	4.30	32950	4.52
353	26317	4.42	26410	4.42
363	28552	4.46	27940	4.45
373	32123	4.51	32260	4.51
383	42851	4.63	30270	4.48

Table continuation

1	2	3	4	5
393	65084	4.81	25080	4.40
403	97125	4.99	20930	4.32
413	178668	5.25	15640	4.19
423	314822	5.50	12020	4.08
433	482378	5.68	9841	3.99
443	801036	5.90	7855	3.90
453	1464248	6.17	6052	3.78
463	2183670	6.34	5095	3.71
473	2500774	6.40	4676	3.67
483	1474252	6.17	4837	3.68

The dependence of the electrical resistance on the reciprocal temperature in the range of 293-343 K is described by the equation:

$$lgR = -0{,}05 + 1573 / T, \quad (2)$$

and in the range 373-483 K:

$$lgR = 0{,}35 + 1575 / T, \quad (3)$$

by the solution of which the activation energies of conduction were calculated, equal to 30.12 kJ/mol (ΔT = 293-343 K) and 30.16 kJ/mol (ΔT = 373-483 K), respectively.

The dielectric constant in a small narrow temperature range of 293 K to 483 K increases very rapidly from $3.8 \cdot 10^4$ to $1.5 \cdot 10^8$ (1 kHz), $3.3 \cdot 10^3$ to $5.3 \cdot 10^6$ (5 kHz) and $1.4 \cdot 10^3$ to $1.5 \cdot 10^6$. Large values of the permittivity at 293-483 K can be caused, according to [17], by high dielectric losses. Giant values of permittivity ($\varepsilon = 10^5$-10^6) for $La_{15/8}Sr_{1/8}NiO_4$ ceramics were established in [5] and they also explain the nature of this phenomenon in terms of the theory of the Maxwell-Wagner effect, according to which dielectric losses are large in the region of intermediate frequencies, t .to. the period of oscillations of the electric field strength was compared with the relaxation time of the surface polarization. In our case, the investigated area of the object is in the range of 1-10 kHz, which can also be attributed to intermediate frequencies. It should also be noted that a decrease in values of dielectric constant was observed with the increasing frequency. These results show that in the indicated narrow temperature range this compound is, in our view, of interest for microcondensator technology.

Conclusions

The nanostructured copper-zinc manganite of lanthanum and magnesium of $LaMgCuZnMnO_6$ was first obtained. In the range of 293-483 K and at frequencies equal to 1, 5 and 10 kHz, the electrical resistance and dielectric constant of the copper-zinc manganite were investigated. It was determined that this compound in the range of 293-353 K has the semiconductor conductivity, metal conductivity in the range of 353-373 K, and semiconductor conductivity in the range of 373-483 K. The widths of band gap equal to 0.83 eV (293-353 K) and 0.80 eV (373-483 K) were calculated. The activation energies of conduction were calculated in the intervals 293-343 K and 373-483 K, equal to 30.12 and 30.16 kJ/mol, respectively. The dielectric constant of $LaMgCuZnMnO_6$ at a relatively low temperature of 483 K reaches up to $1{,}5 \cdot 10^8$ (1 kHz), $5{,}3 \cdot 10^6$ (5 kHz) and $1{,}5 \cdot 10^6$ (10 kHz). The research results presented in this paper show that the nanostructured $LaMgCuZnMnO_6$ is of interest for the semiconductor and microcondensator technology.

Acknowledgments

This research was funded by the Science Committee of the Ministry of Education and Science of the Republic of Kazakhstan (Grant No. AP08855601).

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Article accepted for publication 05.05.2022

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