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SYNTHESIS AND X-RAY INVESTIGATION OF NOVEL NANOSTRUCTURED COPPER-ZINC MANGANITES OF LANTHANUM AND ALKALI METALS

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The aim of this work is to synthesize new nanostructured copper-zinc lanthanum and alkaline metal manganites. Polycrystalline copper-zinc manganites of lanthanum and alkali metals were synthesized by the method of ceramic technology from lanthanum (III), copper (II), zinc (II), manganese (III) oxides, and lithium, sodium, and potassium carbonates in the range of 800-1200 °C. Nanostructured particles were obtained by grinding the synthesized polycrystalline compounds at the «MM301» vibration mill of «Retsch» (Germany). By indexing X-ray images of nanostructured copper-zinc lanthanum and alkaline metal manganites, it was found that they crystallize in cubic syngony. Their lattice parameters are determined. There is a pattern in the change of the lattice parameters from the ionic radii of alkaline metals.

Keywords: copper-zinc manganite, lanthanum, alkali metals, synthesis, nanostructured particles of X-ray phase analysis.

Introduction

The development of modern branches of science and technology is impossible without directed synthesis and research of materials with a set of necessary physical and chemical properties. Currently, the object of close attention of researchers is oxide materials with semiconducting, ferroelectric, piezoelectric and pyroelectric and superconducting properties and high mixed (electronic and ionic or metallic) conductivity. These materials include rare-earth manganites of the composition $R_{1-x}M_xMnO_{3-\delta}$ (R – rare-earth elements, M – is a divalent cation). The discovery of a giant negative resistance in manganites (1993-1994) of the La (Ca, Ba) MnO3 type with a perovskite structure was the beginning of work in the field of synthesis and research of new, previously unknown compounds formed in systems consisting of oxides of rare-earth elements, alkaline earth metals. and manganese (III).

Materials with colossal reluctance can be used as magnetic field sensors, high-density magnetic recording heads, displacement and temperature sensors. Compounds based on oxides of the transition 3*d*- and 4*f*-elements with a perovskite structure or close to it (manganites, zincates, cuprates, nickelates, cobaltites of rare-earth metals) and their solid solutions with oxides of the alkali and alkaline earth metals were widely used due to their interesting properties such as a high value of an electrical conductivity in a significant temperature range, the electronic conductivity character (semiconductor *n*- or *p*-type or metal), the magnetic and superconducting properties, etc. [1-7].

In addition, many publications of scientists from near and far abroadand also our papers on synthesis and investigation of the physicochemical properties of compounds of the above mentioned classes were summarized in our monographs [8-12]. It should also be noted that manganese-based compounds are widely applied in the ferroalloy industry [13, 14].

1. Experimental technique

In order to accumulate various unique properties of the individual compounds in a single complex, i.e. combining of cuprates, zincates and manganites as the copper-zinc manganites, the phases of composition of $LaMe^I_2CuZnMnO_6$ (Me^I – Li, Na, K) were synthesized. A similar work on the synthesis of lanthanum and sodium cobalt-copper manganite was published by us in [15]. To synthesize $LaMe^I_2CuZnMnO_6$ compounds

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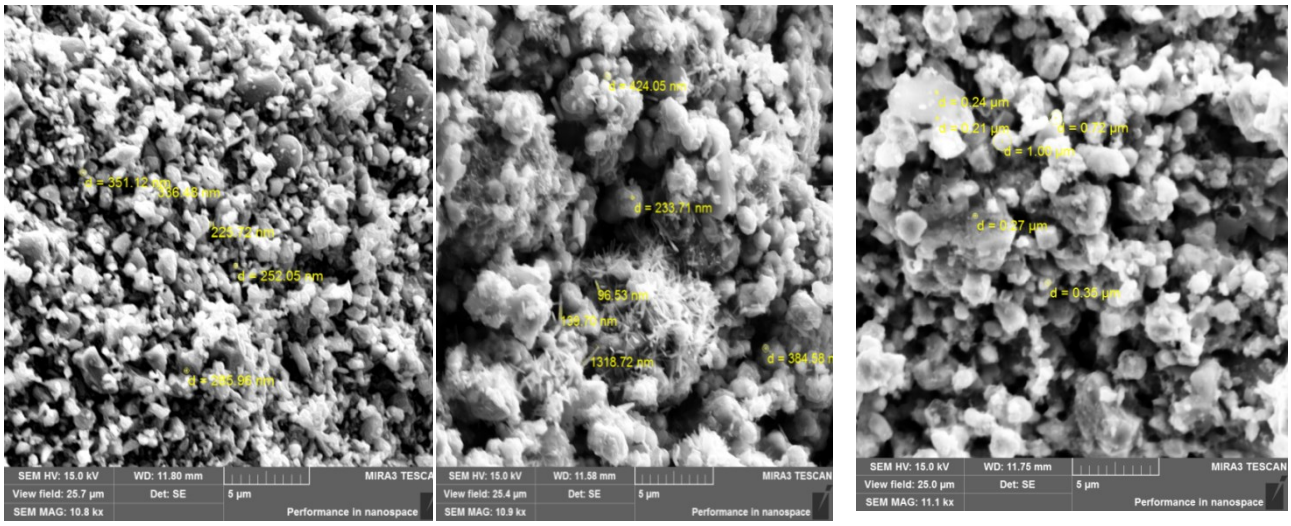
the source materials were oxides of lanthanum La_2O_3 ("puriss. spec."), copper CuO, zinc ZnO, manganese Mn_2O_3, carbonates of Li_2CO_3,Na_2CO_3 and K_2CO_3 ("p.a."), their stoichiometric quantities were milled well and mixed up in an agate mortar, then mixtures in the alundumcrucibles were annealed in SNOL furnace at a temperature of 800 °C for 10 h in the air. Then they were cooled to a room temperature, mixed and milled. Further they were heat-treated at 1200 °Cfor 20 h. The mixtures were cooled again to a room temperature, milled and mixed. To obtain the stable equilibrium phases at low temperatures, the mixtures were annealed at 400 °Cfor 10 h.

Further, to obtain the nanostructured particles of the copper-zinc manganites, their polycrystalline samples were mixed to the nanostructured particles on Retsch MM301 vibration mill (Germany) at the Karaganda Technical University. The particle sizes were determined on an electron microscope Mira 3 LMU, Tescan (Fig. 1) and an atomic-force microscope JSPM-5400 Scanning Probe Microscope "JEOL" (Japan) at the E.A. Buketov Karaganda University (Fig. 2).



$LaLi_2CuZnMnO_6$ $LaNa_2CuZnMnO_6$ $LaK_2CuZnMnO_6$

Fig. 1. SEM images

The data of Figure 1 demonstrates that $LaLi_2CuZnMnO_6$ is characterized with the particle sizes in the range of 226-285 nm, $LaNa_2CuZnMnO_6$ - 97-384 nm and $LaK_2CuZnMnO_6$ - 210-650 nm.

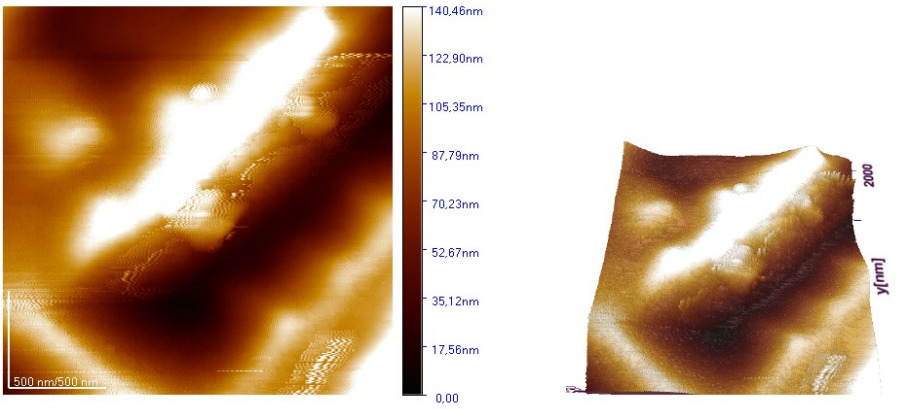
The X-ray analysis of the obtained nanostructured particles was performed on DRON-2.0. The conditions of exposure: CuK_α– radiation, U = 30 kV, I = 10 mA, a rotation speed - 100 pulses per second, time constant τ = 5 sec, an angle interval -2 θ from 10 to 90°. Intensity of the diffraction maxima was estimated on 100-point scale. The X-ray patterns were indicated by an analytical method [16]. Density of each compound was measured 4-5 times and the results were averaged. The procedure and calculating formula were taken from [17]. The table below shows results on assignment of indices of X-ray patterns of the nanostructured copper-zinc manganites.

2. Results and discussion

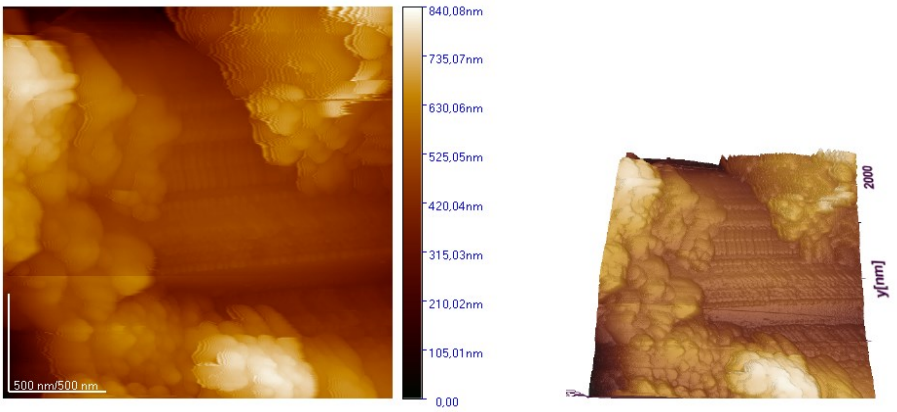
The obtained nanoscale particles of the copper-zinc manganites can be classified as the nanostructured. Referring to recommendations of the 7th International conference on nanotechnologies (Germany, Wiesbaden, 2004), the following types of nanomaterials were distinguished: the nanoporous structures, nanoparticles, nanotubes and nanofibers, nanodispersions (colloids), nanostructured surfaces and films, nanocrystals and nanoclusters. According to [18], 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 are generally referred to as the nanostructured particles, and their linear sizes can be significantly larger than 100 nm.

Based on the assignment of indices of X-ray patterns of the nanostructured copper-zinc manganites, it was defined that they crystallize in the cubic syngony with the following parameters of lattice: $LaLi_2CuZnMnO_6$ – a = 13.94±0.02 Å, V^o= 2708.87±0.06 $Å^3$, Z = 4, $V^o_{elec.cell}$ = 677.22±0.02 $Å^3$, $\rho_{roent.}$= 4.31

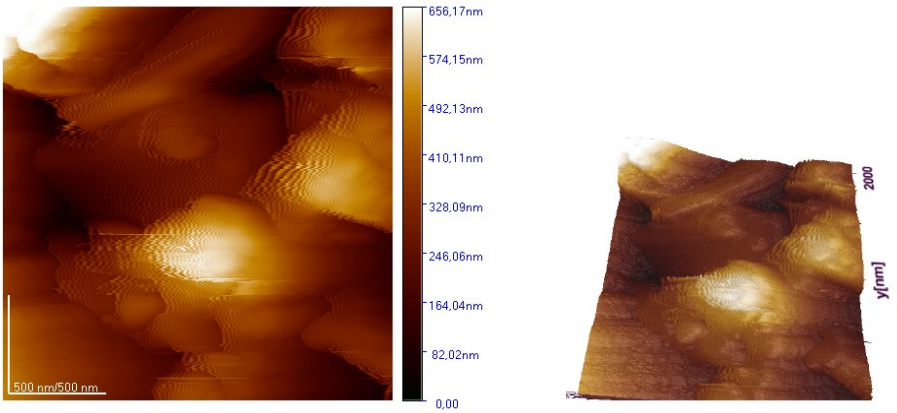
g/cm^3; $\rho_{pick.}$= 4.28±0.02 g/cm^3; $LaNa_2CuZnMnO_6$ – a = 14.82±0.02 Å, V^o = 3254.95±0.06 Å^3, Z = 4, V$^o_{elec.cell}$ = 813.74±0.02 Å^3, $\rho_{roent.}$= 4.13 g/cm^3; ρ_{pick}= 4.09±0.05 g/cm^3; $LaK_2CuZnMnO_6$ – a = 15.30±0.02 Å, V^o = 3581.58±0.07 Å^3, Z = 4, V$^o_{elec.cell}$ = 895.39±0.02 Å^3, $\rho_{roent.}$ = 3.91; $\rho_{pick.}$= 3.88±0.01 g/cm^3.The errors of the parameters " a " are determined by averaging all the diffraction lines (d, Å) established on the X-ray images of the studied compounds, for $LaLi_2CuZnMnO_6$ out of 17 maxima of the diffraction lines, for $LaNa_2CuZnMnO_6$ out of 13, for $LaK_2CuZnMnO_6$ out of 15 d, Å.



$LaLi_2CuZnMnO_6$



$LaNa_2CuZnMnO_6$



$LaK_2CuZnMnO_6$

Fig. 2. Atomic-force microscopic image and 3D surfaces

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Table 1. Assignment of indices of X-ray patterns of the nanostructured of $LaLi_2CuZnMnO_6$ (I), $LaNa_2CuZnMnO_6$ (II) and $LaK_2CuZnMnO_6$ (III)

I/I^0	d, Å	$10^4/d^2$ (experimental)	hkl	$10^4/d^2$ (calculated)
$LaLi_2CuZnMnO_6$				
38	3.882	663.6	511	664.0
18	2.865	1218	710	1229
100	2.749	1323	721	1327
14	2.509	1588	810	1598
23	2.449	1667	420	1671
12	2.367	1785	830	1794
22	2.245	1984	900	1991
78	1.939	2660	10.2.2	2655
6	1.864	2878	10.4.1	2875
8	1.725	3361	10.6.1	3368
6	1.697	3472	11.4.2	3466
37	1.586	3975	12.3.3	3982
12	1.433	4870	14.1.1	4867
16	1.375	5289	14.3.1	5295
14	1.361	5399	13.5.5	5383
12	1.229	6620	16.3.3	6612
14	1.222	6697	16.4.0	6686
$LaNa_2CuZnMnO_6$				
14	3.902	656.8	520	657.0
100	2.757	1316	730	1314
11	2.604	1475	740	1472
10	2.525	1568	743	1562
13	2.475	1632	822	1631
11	2.321	1856	910	1857
16	2.247	1980	664	1993
35	1.945	2643	10.4.1	2650
7	1.737	3314	981	3307
34	1.572	4046	13.3.1	4054
9	1.475	4596	11.9.1	4598
17	1.374	5297	15.3.0	5300
15	1.229	6620	16.6.0	6613
$LaK_2CuZnMnO_6$				
17	3.890	660.8	440	661.0
100	2.756	1316	800	1322
15	2.600	1479	822	1487
13	2.526	1567	662	1569
16	2.364	1789	655	1776
14	2.249	1977	844	1982
50	1.945	2643	880	2643
7	1.740	3303	12.4.0	3304
8	1.624	3792	12.6.2	3800
30	1.588	3965	888	3965
7	1.459	4698	15.1.1	4688
5	1.410	5630	12.10.0	5039
17	1.375	5289	16.0.0	5286
4	1.295	5963	16.4.4	5947
13	1.229	6620	17.4.4	6629

A good fit of the experimental and calculated values of $10^4/d^2$ (Table 1), the X-ray and picnometric densities points out the correctness and assurance of results of assignment of indices. Based on [16], the experimentally determined density refers to a real crystal and it should be slightly below than ideal. This statement also confirms that the pycnometric (experimental) densities of our obtained copper zinc manganites are relatively lower than the X-ray (ideal).

By analogy of [8, 19], the synthesized copper-zinc manganitescan be assigned to the space group *Pm3m* of perovskite. In connection with raising the sizes of the ionic radiuses in a row of$Li^+ \rightarrow Na^+ \rightarrow K^+$, the values of «*a*» parameter is increased, and the values of volumes of the crystalline lattices and the elementary cells are increased in a row of$LaLi_2CuZnMnO_6 \rightarrow LaNa_2CuZnMnO_6 \rightarrow LaK_2CuZnMnO_6$.

Conclusion

The polycrystalline copper-zinc manganites of the composition of $LaLiMe^I_2CuZnMnO_6$ (Me^I – Li, Na, K) were first synthesized by a method of the ceramic technology. By milling them on a vibration mill, their nanostructured particles were obtained. It was found that all obtained nanostructured copper-zinc manganites crystallize in the cubic syngony. Their lattice parameters, X-ray and pycnometric densities were determined.

It was found that with an increase in the ionic radii in the series Li and K, the lattice parameters of the studied manganites increase. The research results work make a certain contribution to the inorganic materials science, nanotechnology, radiography and crystal chemistry of nanostructured inorganic compounds and serve as the basis for further research in order to identify valuable and promising physicochemical properties of these new obtained nanomaterials.

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