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SYNTHESIS AND X-RAY STUDY OF NANOSIZED LaCaCoCuMnO₆ AND LaCaNiCuMnO₆ SYSTEM

Abstract. From oxides of lanthanum, copper (II), cobalt (II), nickel (II), manganese (III) and calcium carbonate at temperatures 800-1200 °C for 20 hours by the method of ceramic technology synthesized cobalt-cuprate-manganite lanthanum and calcium LaCaCoCuMnO₆ and nickelite-cuprate-manganite lanthanum and calcium LaCaNiCuMnO₆.

On a vibrating mill of "Retsch" company (Germany) of the "MM301" brand, polycrystalline samples of new compounds were ground to nanosized (nanoclusters) particles.

The X-ray diffraction of the obtained nanosized (nanoclusters) phases indicates that they crystallize in cubic syngony with the following lattice parameters: LaCaCoCuMnO₆ – $a=14,01\pm 0,02\text{\AA}$; $V^{\circ}=2746,77\pm 0,06\text{\AA}^3$; $Z=4$; $V^{\circ}_{\text{el.cell}}=686,69\pm 0,02\text{\AA}^3$; $\rho_{\text{X-ray}}=4,13\text{g/cm}^3$; $\rho_{\text{pycn.}}=4,08\pm 0,01\text{g/cm}^3$; LaCaNiCuMnO₆ – $a=14,74\pm 0,02\text{\AA}$; $V^{\circ}=3204,74\pm 0,06\text{\AA}^3$; $Z=4$; $V^{\circ}_{\text{el.cell}}=801,19\pm 0,02\text{\AA}^3$; $\rho_{\text{X-ray}}=4,15\text{g/cm}^3$; $\rho_{\text{pycn.}}=4,13\pm 0,01\text{g/cm}^3$.

Keywords: synthesis, cobalt-cuprate-manganite, nickelite-cuprate-manganite, lanthanum, alkaline earth metals, X-ray, nanoscale, nanoclusters.

Cuprates, manganites, cobaltites and nickelites of rare-earth elements doped with alkaline-earth oxides have unique physicochemical properties [1-4]. It is of interest to obtain new nanosized compounds that include manganites, cuprates, cobaltites and nickelites of rare earth and alkaline earth metals. It should be noted that in [5-9] we first obtained polycrystalline and nanosized samples of manganite-ferrites, chromite-manganites, cuprate-manganites of rare-earth, alkaline and alkaline-earth metals.

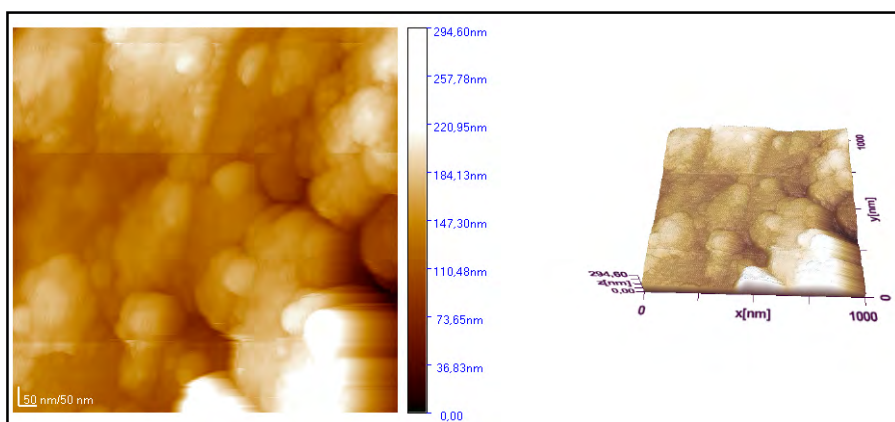
In connection with the foregoing, we report here the results of the synthesis and X-ray diffraction studies of the nanosize (nanocluster) cobalt-cuprate-manganite lanthanum and calcium LaCaCoCuMnO₆ and nickelite-cuprate-manganite lanthanum and calcium LaCaNiCuMnO₆.

Synthesis of cobalt (nickelite)-cuprate-manganites was carried out by high-temperature interaction of stoichiometric quantities of La₂O₃ (e.c), CoO, NiO, CuO, Mn₂O₃ and CaCO₃ (p.f.a). Mixtures of these substances were thoroughly mixed, ground in an agate foot, which were then transferred to alundum crucibles and annealed in a "SNOL" oven at 800-1200 °C for 20 hours. Before each temperature increase (up to 800, 1000 and 1200 °C), the mixtures were cooled, carefully rubbed. An annealing at 400 °C for 10 hours was carried out to obtain stable at low temperature phases.

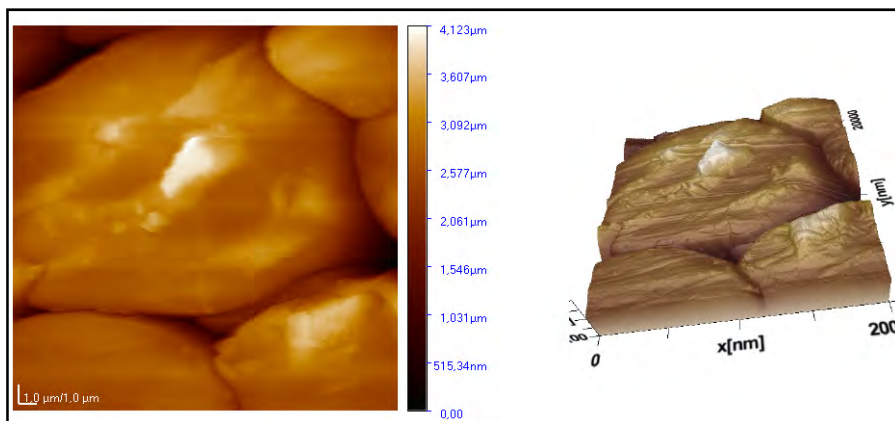
Nano-sized particles of synthesized new compounds were obtained by grinding them on a vibratory mill of the company "Retsch" (Germany) of the brand "MM301". Speed from 3 to 30 Hz (180-1800 vibrations per minute). The grinding time is 40-60 minutes. The sizes of the crushed particles were established on an electronic microscope JSPM-5400 Scanning Probe Microscope "JEOL" (Japan). The electron microscopies of the investigated compounds are shown below (Figure).

It should be noted that there are various methods for producing nanoparticles. In our case, the machining of the composite by exposure to powerful mechanical pulses is used, similarly to [10]. Not individual oxides are crushed to the nano level, like lanthanum, calcium, etc., but new compounds formed by solid-phase interaction: polycrystalline cobalt (nickelite)-cuprate-manganites of lanthanum and calcium.

X-ray diffraction study of nanophases was carried out on a DRON 2.0.



a)



b)

Electron microscopy of LaCaCoCuMnO_6 (a) and LaCaNiCuMnO_6 (b)

Shooting conditions: CuK α radiation, Ni filter, U = 30 kV, J = 10 mA, counter rotation speed 2 tur/min, scale range 1000 pulses/s, $\tau = 5$ s, $2\theta = 10-90^\circ$.

The intensity of the diffraction maxima was estimated from a one-hundred-point scale. The X-ray diffraction patterns of the compounds were determined by the analytical method [11]. The pycnometric density was determined by the method of [12]. Toluene was used as an indifferent fluid. IR spectroscopic study of the obtained compounds was studied on a FTIM-1201 Fourier spectrometer. The powder was mixed with KBr to form a 2 mm thick tablet. The measurements were carried out in the transmission coefficient measurement mode.

The results of the X-ray diffraction of the new compounds obtained are shown in the table below.

Indication of X-ray patterns of powders of nanoscale (nanocluster) cobalt-cuprate-manganite and nickelite-cuprate-manganite

I/I_0	$d, \text{\AA}$	$10^4/d_{\text{exp}}^2$	hkl	$10^4/d_{\text{calc}}^2$
LaCaCoCuMnO ₆				
7	3.834	680,3	511	680,0
100	2.722	1350	721	1361
8	2.529	1563	651	1562
7	2.320	1858	831	1865
7	2.300	1890	751	1890
15	2.218	2033	900	2041
7	2.005	2487	755	2494
36	1.919	2715	10.4.4	2721
31	1.565	4083	990	4082
14	1.355	5446	10.10.4	5442
10	1.212	6808	13.10.1	6803
LaCaNiCuMnO ₆				
5	4.560	480.9	421	481.0
10	3.834	680	521	687.0
100	2.719	1353	731	1351
7	2.518	1577	742	1580
10	2.429	1695	750	1695
5	2.319	1860	900	1855
15	2.218	2033	762	2038
5	2.127	2210	665	2221
11	2.098	2272	755	2267
34	1.921	2710	10.3.3	2702
5	1.723	3368	11.5.1	3366
28	1.572	4047	887	4053
7	1.487	4522	996	4534
5	1.367	5351	13.8.1	5359
11	1.358	5422	14.5.4	5427
11	1.215	6774	14.10.0	6778

Based on the indication of the X-ray patterns of the new nanoscale (nanocluster) compounds established that they crystallize in a cubic system with the following lattice parameters: LaCaCoCuMnO_6 – $a=14,01\pm 0,02\text{\AA}$; $V^{\circ}=2746,77\pm 0,06\text{\AA}^3$; $Z=4$; $V^{\circ}_{\text{el.cell}}=686,69\pm 0,02\text{\AA}^3$; $\rho_{\text{X-ray}}=4,13\text{g/cm}^3$; $\rho_{\text{pycn.}}=4,08\pm 0,01\text{g/cm}^3$; LaCaNiCuMnO_6 – $a=14,74\pm 0,02\text{\AA}$; $V^{\circ}=3204,74\pm 0,06\text{\AA}^3$; $Z=4$; $V^{\circ}_{\text{el.cell}}=801,19\pm 0,02\text{\AA}^3$; $\rho_{\text{X-ray}}=4,15\text{g/cm}^3$; $\rho_{\text{pycn.}}=4,13\pm 0,01\text{g/cm}^3$. The satisfactory agreement of the experimental and calculated values of $10^4/d^2$ as well as the x-ray and pycnometric densities, shows the correctness of the results of the indication.

IR spectroscopy of compounds is characterized by the following absorption bands.

LaCaCoCuMnO_6 . The absorption band at 609.6 cm^{-1} can be attributed to a vibration of ν_i (MnO_6), a harmonic frequency of WcCoO , 1057.1 cm^{-1} to a change in the symmetry of the CoO_3 group, 1454.5 and 1639.7 cm^{-1} to changes in symmetry group MnO_3 .

LaCaNiCuMnO_6 . The absorption bands at 609.6 and 659.7 cm^{-1} can be attributed to the ν_i (MnO_6) vibration, the harmonic frequency WcNiO , 1458.4 and 1635.8 cm^{-1} to the symmetry changes of the MnO_3 group.

When decoding of IR spectra was guided by a monograph [13].

Thus, nanoscale (nanocluster) cobalt-cuprate-manganite lanthanum and calcium LaCaCoCuMnO_6 and nickelite-cuprate-manganite lanthanum and calcium LaCaNiCuMnO_6 were obtained for the first time, the types of their syngony and parameters of the lattices and IR spectroscopic characteristics were determined.

The work was carried out in accordance with the agreement concluded between the Ministry of Education and Science of the Republic of Kazakhstan and Zh .Abishev Chemical-Metallurgical Institute under the grant of (IRN: AP05131317, AP05131333).

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Резюме

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НАНОӨЛШЕМДІ LaCaCoCuMnO_6 ЖӘНЕ LaCaNiCuMnO_6 ҚҰРАМДЫ СИНТЕЗІ ЖӘНЕ ОЛАРДЫ РЕНТГЕНОГРАФИЯЛЫҚ ТҮРҒЫДАН ЗЕРТТЕУ

Лантан, мыс(II), кобальт (II), никель (II), марганец (III) тотықтары мен кальций карбонатынан керамикалық технология әдісімен 20 сағат бойы 800-1200 °C температураларда лантан және кальций кобальт (никелит)-купрат-манганиттері LaCaCoCuMnO_6 және LaCaNiCuMnO_6 ситезделді Retsch (Германия) компаниясының «ММ301» маркалы вибрациялық диірменінде үгіту жолымен поликристалдық үлгілер наноөлшемді (нанокластерлік) бөлшекке дейін үгітілді, «JSPM-5400» Scanning Probe Microscope «JEOL» (Япония) электрондық микроскопының көмегімен олардың өлшемдері анықталды. ДРОН-2,0 дифрактометрінде алынған жаңа наноүлгілерге рентгенофазалық талдау жүргізілді. Рентгенограммаларын индицирлеу барысында синтезделініп алынған наноөлшемді (нанокластерлік) фазалардың тор көрсеткіштері келесідей кубтық сингонияда кристалданатыны анықталды: LaCaCoCuMnO_6 – $a=14,01\pm 0,02\text{Å}$; $V^0=2746,77\pm 0,06\text{Å}^3$; $Z=4$; $V^0_{\text{эл.үя.}}=686,69\pm 0,02\text{Å}^3$; $\rho_{\text{рент.}}=4,13$; $\rho_{\text{пикн.}}=4,08\pm 0,01$ г/см³; LaCaNiCuMnO_6 – $a=14,74\pm 0,02\text{Å}$; $V^0=3204,74\pm 0,06\text{Å}^3$; $Z=4$; $V^0_{\text{эл.үя.}}=801,19\pm 0,02\text{Å}^3$; $\rho_{\text{рент.}}=4,15$; $\rho_{\text{пикн.}}=4,13\pm 0,01$ г/см³.

Түйін сөздер: синтез, кобальт-купрат-манганит, никелит-купрат-манганит, лантан, сілтілі-жер металдары, рентгенография, наноөлшемдер, нанокластерлер.

Резюме

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СИНТЕЗ И РЕНТГЕНОГРАФИЧЕСКОЕ ИССЛЕДОВАНИЕ
НАНОРАЗМЕРНЫХ LaCaCoCuMnO_6 И LaCaNiCuMnO_6

Из оксидов лантана, меди (II), кобальта (II), никеля (II), марганца (III) и карбоната кальция методом керамической технологии при температурах 800-1200 °С в течение 20 ч синтезированы кобальто-купрато-манганит лантана и кальция LaCaCoCuMnO_6 и никелито-купрато-манганит лантана и кальция LaCaNiCuMnO_6 . На вибрационной мельнице компании Retsch (Германия) марки «ММ301» поликристаллические образцы новых соединений измельчены до наноразмерных (нанокластерных) частиц, размеры которых определены с использованием электронного микроскопа JSPM-5400 Scanning Probe Microscope «JEOL». Рентгенофазовый анализ полученных новых нанобразцов проводили на дифрактометре ДРОН-2.0. Индексированием рентгенограмм, полученных наноразмерных (нанокластерных) фаз, установлено, что они кристаллизуются в кубической сингонии со следующими параметрами решетки: LaCaCoCuMnO_6 – $a=14,01\pm 0,02\text{Å}$; $V^0=2746,77\pm 0,06\text{Å}^3$; $Z=4$; $V^0_{\text{эл.яч.}}=686,69\pm 0,02\text{Å}^3$; $\rho_{\text{рент.}}=4,13$; $\rho_{\text{пикн.}}=4,08\pm 0,01$ г/см³; LaCaNiCuMnO_6 – $a=14,74\pm 0,02\text{Å}$; $V^0=3204,74\pm 0,06\text{Å}^3$; $Z=4$; $V^0_{\text{эл.яч.}}=801,19\pm 0,02\text{Å}^3$; $\rho_{\text{рент.}}=4,15$; $\rho_{\text{пикн.}}=4,13\pm 0,01$ г/см³.

Ключевые слова: синтез, кобальто-купрато-манганит, никелито-купрато-манганит, лантан, щелочноземельные металлы, рентгенография, наноразмеры, нанокластеры.