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ХИМИЯ ҒЫЛЫМДАРЫ ИНСТИТУТЫ»
АКЦИОНЕРЛІК ҚОҒАМЫ

# ҚАЗАҚСТАННЫҢ ХИМИЯ ЖУРНАЛЫ

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«ИНСТИТУТ ХИМИЧЕСКИХ НАУК
им. А. Б. БЕКТУРОВА»

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# SYNTHESIS OF NEW NANOSIZED (NANOCLUSTER) COBALT (NICKELITE)-CUPRATE-MANGANITES

**Abstract.** Synthesis of cobalt (nickelite)-cuprate-manganites of the composition $LaMgCoCuMnO_6$ and $LaMgNiCuMnO_6$ were carried out by solid-phase interaction of stoichiometric amounts of $La_2O_3$ ( extra-pure grade), NiO, CoO, CuO, $Mn_2O_3$ and $MgCO_3$ (*analytical grade*) in the interval 800-1200 °C for 20 hours. To obtain equilibrium phases at low temperatures, low-temperature annealing was carried out at 400 ° C for 10 hours. On a vibrating mill of “Retsch” company (Germany) of the "MM301" brand, polycrystalline samples of new compounds were ground to nanoscale (nanoclusters) particles. The dimensions of the nanoclusters are determined using the “JSPM-5400” Scanning Probe Microscope "JEOL" electron microscope. X-ray phase analysis of new nanosamples were carried out on a DRON-2.0 unit. The analytical method of X-ray indications is established that the synthesized compounds are crystallize in cubic syngony with the following lattice parameters: $LaMgCoCuMnO_6$ − a=14,12±0,02Å; $V^o$=2814,87±0,06Å$^3$; Z=4; $V^o_{el.cell}$=703,72±0,02Å$^3$; $\rho_{X\text{-}ray}$=4,19g/cm$^3$; $LaMgNiCuMnO_6$ − a=14,38±0,02Å; $V^o$=2973,56±0,06Å$^3$; Z=4; $V^o_{el.cell}$ =743,39±0,02Å$^3$; $\rho_{X\text{-}ray}$=4,22g/cm$^3$.

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

The end of the XX century and the beginning of the XXI century were marked by outstanding discoveries in the field of inorganic materials science: the discovery of superconductivity in cuprates, giant (colossal) magnetoresistance in manganites of rare-earth elements partially replaced by alkaline-earth metal oxides [1, 2]. Along with these discoveries, the effect of a giant value of the dielectric constant in nickelite $La_{15/8}Sr_{1/8}NiO_4$, has recently been revealed, which opens up good prospects for technological solutions in electronics [3].

In connection with the above, in order to obtain new promising compounds, the results of synthesis of nanoscale (nanocluster) cobalt-cuprate-manganite and nickelite-cuprate-manganite of lanthanum and magnesium $LaMgCoCuMnO_6$ and $LaMgNiCuMnO_6$ are given in this paper. Earlier, we studied cobalt-manganites, nickelite-manganites and cuprate-manganites of rare-earth, alkaline and alkaline-earth metals [4-10].

The synthesis of the above $LaMgCoCuMnO_6$ and $LaMgNiCuMnO_6$ was carried out by solid-phase interaction of the reagents in the range of 800-1200 ° C according to the reactions:

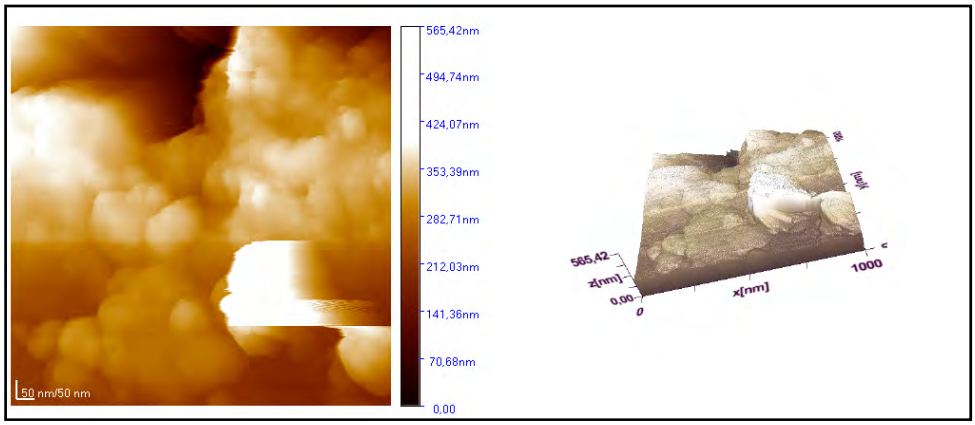
$$0{,}5La_2O_3+CoO+CuO+0{,}5Mn_2O_3+MgCO_3 = LaMgCoCuMnO_6+CO_2, \quad (1)$$

$$0{,}5La_2O_3+NiO+CuO+0{,}5Mn_2O_3+MgCO_3 = LaMgNiCuMnO_6+CO_2. \quad (2)$$

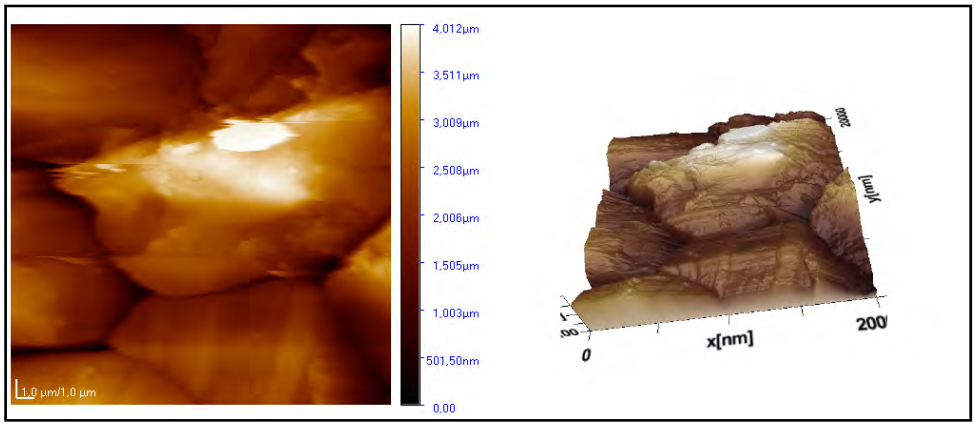
The purity of the starting materials: $La_2O_3$ – “extra-pure grade” and the rest-qualification “analytical grade”. The annealing time at 800-1200 ° C is 20 hours. Before each increase through 200 ºC (800 ºC, 1000 ºC, 1200 ºC) the mixtures were cooled and thoroughly mixed. For stable at low temperature modifications annealing was carried out at 400 ° C for 10 hours.

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 1).




a)




b)

Figure 1 − Electron microscopy of $LaMgCoCuMnO_6$ (a) and $LaMgNiCuMnO_6$ (b)

Table 1 − Indication of X-ray patterns of powders of nanoscale (nanocluster) cobalt-cuprate-manganite and nickelite-cuprate-manganite

| $I/I_0$ | $d$, Å | $10^4/d^2_{exp.}$ | $hkl$ | $10^4/d^2_{calc.}$ |
|---|---|---|---|---|
| $LaMgCoCuMnO_6$ | | | | |
| 18 | 3,920 | 650,8 | 422 | 651,0 |
| 6 | 2,944 | 1154 | 599 | 1166 |
| 100 | 2,763 | 1310 | 444 | 1302 |
| 19 | 2,503 | 1596 | 731 | 1600 |
| 13 | 2,464 | 1647 | 650 | 1654 |
| 4 | 2,340 | 1826 | 733 | 1817 |
| 22 | 2,251 | 1973 | 830 | 1980 |
| 14 | 2,120 | 2225 | 910 | 2223 |
| 29 | 1,952 | 2624 | 940 | 2630 |
| 5 | 1,745 | 3284 | 11.0.0 | 3281 |
| 4 | 1,695 | 3481 | 880 | 3471 |
| 34 | 1,592 | 3946 | 11.5.0 | 3959 |
| 9 | 1,494 | 4480 | 10.8.1 | 4474 |
| 6 | 1,462 | 4678 | 13.2.0 | 4691 |
| 12 | 1,377 | 5274 | 13.5.1 | 5288 |
| 6 | 1,300 | 5917 | 13.7.0 | 5911 |
| 13 | 1,232 | 6588 | 15.3.3 | 6589 |
| 7 | 1,224 | 6675 | 14.5.5 | 6671 |
| $LaMgNiCuMnO_6$ | | | | |
| 3 | 4,82 | 430,4 | 410 | 431,0 |
| 16 | 3,89 | 660,8 | 510 | 658,3 |
| 3 | 2,952 | 1147 | 630 | 1139 |
| 100 | 2,756 | 1317 | 640 | 1317 |
| 12 | 2,426 | 1699 | 733 | 1696 |
| 8 | 2,314 | 1868 | 750 | 1874 |
| 19 | 2,249 | 1977 | 752 | 1974 |
| 26 | 2,098 | 2272 | 930 | 2279 |
| 29 | 1,945 | 2643 | 10.2.2 | 2633 |
| 5 | 1,867 | 2869 | 10.3.2 | 2861 |
| 8 | 1,743 | 3292 | 11.3.0 | 3291 |
| 3 | 1,700 | 3460 | 11.4.0 | 3469 |
| 13 | 1,484 | 4541 | 11.7.3 | 4532 |
| 15 | 1,374 | 5297 | 10.10.3 | 5291 |
| 4 | 1,296 | 5954 | 15.3.1 | 5950 |
| 7 | 1,263 | 6269 | 14.6.4 | 6279 |
| 13 | 1,230 | 6610 | 16.2.1 | 6608 |
| 7 | 1,212 | 6808 | 16.3.2 | 6811 |

X-ray diffraction study of nanophases was carried out on a DRON 2.0. 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 analytically method [11]. Below in table 1 shows the results of the X-ray diffraction.

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: $LaMgCoCuMnO_6$ – $a$=14,12±0,02*Å*; $V^o$=2814,87±0,06$Å^3$; $Z$=4; $V^o_{el.cell}$=703,72±0,02 $Å^3$; $\rho_{X\text{-}ray}$=4,19 g/cm$^3$; $LaMgNiCuMnO_6$ – $a$=14,38±0,02*Å*; $V^o$=2973,56±0,06$Å^3$; $Z$=4; $V^o_{el.cell}$=743,39±0,02 $Å^3$; $\rho_{X\text{-}ray}$=4,22 g/cm$^3$. Satisfactory agreement of $10^4/d^2_{exp}$. and $10^4/d^2_{calc}$. shows the correction of the results of the indication.

Thus, nanoscale (nanocluster) cobalt-cuprate-manganite $LaMgCoCuMnO_6$ and nickelite-cuprate-manganite $LaMgNiCuMnO_6$ were synthesized for the first time. The type of their syngony and parameters of the lattices were determined.

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**Резюме**

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ЖАҢА НАНОӨЛШЕМДІ (НАНОКЛСТЕРЛІК)
КОБАЛЬТ (НИКЕЛИТ)-КУПРАТ-МАНГАНИТТЕРДІҢ СИНТЕЗІ

Соңғы формуласы $LaMgCoCuMnO_6$ және $LaMgNiCuMnO_6$ болатын кобальт (никелит)-купрат-манганиттердің ситезі $La_2O_3$ (маркасы «аса таза»), NiO, CoO, CuO, $Mn_2O_3$ және $MgCO_3$ (квалификациясы «талдау үшін таза») стехиометриялық өлшемдерін 20 сағат бойы 800-1200 ºС қатты фазалы әрекеттесу жолымен жүргізілді.

Төмен температурада тепе-тең фазалар алу үшін төмен температуралық қыздыруды 10 сағат бойы 400 ºС жүргізілді.

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 аналитикалық әдіспен индицирлеу барысында синтезделініп алынған қосылыстар тор көрсеткіштері келесідей кубтық сингонияда кристалданатыны анықталды:

$LaMgCoCuMnO_6$ – $a=14,12\pm0,02$Å; $V^{o}=2814,87\pm0,06$Å$^3$; $Z=4$; $V^{o}_{эл.ұя.}=703,72\pm0,02$Å$^3$; $\rho_{рент.}=4,19$г/см$^3$; $LaMgNiCuMnO_6$ – $a=14,38\pm0,02$Å; $V^{o}=2973,56\pm0,06$Å$^3$; $Z=4$; $V^{o}_{эл.ұя.}=743,39\pm0,02$Å$^3$; $\rho_{рент.}=4,22$г/см$^3$.

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

**Резюме**

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СИНТЕЗ НОВЫХ НАНОРАЗМЕРНЫХ (НАНОКЛАСТЕРНЫХ)
КОБАЛЬТО(НИКЕЛИТО)-КУПРАТО-МАНГАНИТОВ

Синтез кобальто(никелито)-купрато-манганитов в пересчете на конечные формулы $LaMgCoCuMnO_6$ и $LaMgNiCuMnO_6$ проводили путем твердофазного взаимодействия стехиометрических количеств $La_2O_3$ (марки «ос.ч.»), NiO, CoO, CuO, $Mn_2O_3$ и $MgCO_3$ (квалификации «ч.д.а.») при температурах 800-1200 ºС в течение

20 ч. Для получения равновесных фаз при низких температурах проводили низкотемпературный отжиг при 400 ºС в течение 10 ч. 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 нанообразцов проводили на дифрактометре ДРОН-2,0. Индицированием рентгенограмм соединений аналитическим методом установлено, что синтезированные соединения кристаллизуются в кубической сингонии со следующими параметрами решетки: $LaMgCoCuMnO_6$ – a=14,12±0,02Å; $V^o$=2814,87±0,06Å$^3$; Z=4; $V^o_{эл.яч.}$=703,72±0,02Å$^3$; $\rho_{рент.}$=4,19г/см$^3$; $LaMgNiCuMnO_6$ – a=14,38±0,02Å; $V^o$=2973,56±0,06Å$^3$; Z=4; $V^o_{эл.яч.}$=743,39±0,02Å$^3$; $\rho_{рент.}$=4,22 г/см$^3$.

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