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NEW NANO-SIZED (NANOCLUSTER) COBALT- CUPRATE - MANGANITES OF LANTHANE AND ALKALINE METALS AND THEIR X-RAY DIFFRACTION STUDY

Abstract. The search for new combined manganese, copper and cobalt-containing nanomaterials and the study of their properties *is quite interesting* for inorganic materials science, especially for microelectronics. Interest in such compounds is due to the polyfunctionality of the demonstrated properties and the flexibility of the composition, allowing many elements of the periodic system to be adopted.

Cobalt-cuprate-manganites of the composition $LaMe^{I}_2CoCuMnO_6$ (Me^{I} – Li, Na, K) were synthesized by ceramic technology of lanthanum oxide (III), cobalt oxide(II), copper oxide (II), carbonates of manganese (III), lithium, sodium and potassium in the interval 800-1200 °C. After every 100 ° C, the formulations were cooled, rubbed and reheated. To obtain equilibrium phases at low temperatures, low-temperature annealing was carried out at 400 ° C for 10 hours. Their nanoscale (nanoclusters) particles were obtained by grinding on a vibrational mill from Retsch (Germany) of the brand "MM301". The dimensions were determined on an electronic microscope JSPM-5400 Scanning Probe Microscope "JEOL" (Japan). Prepared nanoparticles (nanoclusters) compounds of the size of 40-90 nm. X-ray phase analysis of new compounds was carried out on a DRON-2.0 unit. The analytical method of X-ray indications is established that the synthesized nanoscale new phases crystallize in cubic syngony with the following lattice parameters: $LaLi_2CoCuMnO_6$ – a=11,33±0,02 Å; V^0=2563,20±0,06Å^3; Z=4; $V^0_{el.cell}$=640,80±0,02Å^3; $\rho_{X\text{-}ray.}$ = 4,0 g/cm^3; $LaNa_2CoCuMnO_6$ – a=14,43±0,02 Å; V^0=3005,5±0,07Å^3; Z=4; $V^0_{el.cell}$ =751,38±0,02Å^3; $\rho_{X\text{-}ray.}$ = 3,86 g/ cm^3; $LaK_2CoCuMnO_6$ – a=14,90±0,02 Å; V^0=3306,90±0,06 Å^3; Z=4; $V^0_{el.cell}$ =826,52±0,02Å^3; $\rho_{X\text{-}ray.}$ = 3,68 g/ cm^3. Based on X-ray phase analysis, it can be assumed that the nanoscale cobalt-cuprate-manganites obtained are related to the space group *Pm3m.*

Key words: cobalt, cuprate, manganite, lanthanum, alkali metals, synthesis, nanoparticles, radiography.

Introduction. Cuprates, manganites, cobaltites, nickelites of rare-earth elements doped with light oxides of alkali and alkaline-earth metals have unique physical and physicochemical properties, both superconducting and semiconductor, and are also of interest as materials having giant (colossal) magnetoresistance, dielectric permittivity values. It is very important for microelectronics as substances with high operative memory [1-16].

In Zh. Abishev Chemical-Metallurgical Institute for a number of years conducted purposeful research on the synthesis and study of the physicochemical properties of double and triple manganites, chromites, ferrites, zincate-manganites, the results of which are generalized in monographs [17, 18].

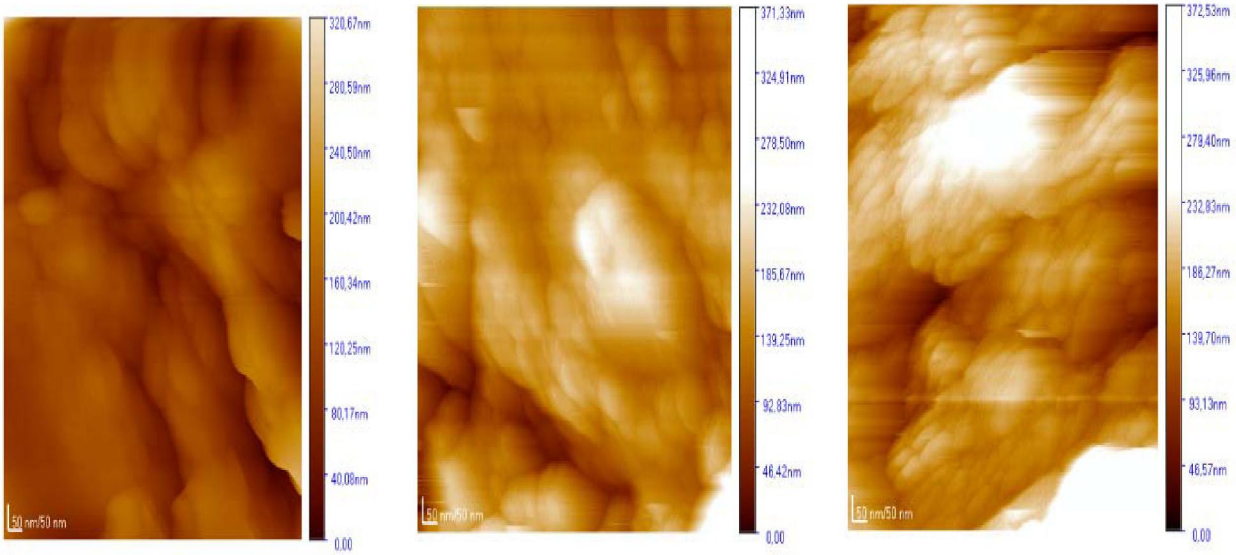
Of definite scientific and practical interest is the preparation of perovskite-like compounds, where cobaltites, cuprates and manganites are represented as a single phase, like cobalt-cuprate-manganites.

For this purpose, in this work presents the results of the synthesis and study of new radiographic nanoscale (nanocluster) cobalt-cuprate-manganite composition $LaMe^{I}_2CoCuMnO_6$, where Me^{I} - Li, Na, K.

Methods. Ceramic processing technology, X-ray phase analysis, electron microscopy.

Results of the research. The initial reagents for the synthesis were La_2O_3 (extra-pure grade), Li_2CO_3, Na_2CO_3, K_2CO_3, CoO, CuO, Mn_2O_3 of qualifications ″ Analytical grade ″. Solid-phase synthesis was carried out by reacting the above substances at 800-1200° C for 20 hours with intermittent cooling and grinding of the mixtures through 100 ° C. Low-temperature annealing of the mixtures was carried out at 400° C for 10 hours.

Nanosized particles of synthesized cobalt-cuprate-manganites were obtained by grinding on the vibratory mill of Retsch (Germany), brand MM301. The sizes of the crushed particles were established on an electronic microscope JSPM-5400 Scanning Probe Microscope "JEOL" (Japan). Nanoparticles (nanoclusters) from 40 to 90 nm were obtained. Below at the figure, their electron microscopic images are shown.



a b c

Figure – Electron microscopy $LaLi_2CoCuMnO_6$ (a), $LaNa_2CoCuMnO_6$ (b), $LaK_2CoCuMnO_6$ (c)

X-ray diffraction study of nanophases was carried out on a DRON 2.0. Conditions of shooting: CuK-radiation., Ni filter, U = 30 kV, I = 10 mA, counter rotation speed 2 rpm, scale range 1000 pulses per second, time constant, =5 seconds, angular interval 2□ from 10 up to 90 degrees. 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 [19].

Below in Table shows the of the results of the X-ray diffraction of synthesized compounds.

Satisfactory agreement of $10^4 / d^2_{exp.}$ and $10^4 / d^2_{calc.}$ shows the correction of the results of the indication. The imposition of X-ray radiographs indications shows that all synthesized nanoscale (nanocluster) cobalt-cuprate-manganites crystallize in a cubic system with the following lattice parameters: $LaLi_2CoCuMnO_6$ – a=11,33±0,02 Å; V^0=2563,20±0,06Å^3; Z=4; $V^0_{el.cell}$=640,80±0,02Å^3; $\rho_{X-ray.}$ = 4,0 g/cm^3; $LaNa_2CoCuMnO_6$ – a=14,43±0,02 Å; V^0=3005,5±0,07Å^3; Z=4; $V^0_{el.cell}$ =751,38±0,02Å^3; $\rho_{X-ray.}$ = 3,86 g/ cm^3; $LaK_2CoCuMnO_6$ – a=14,90±0,02 Å; V^0=3306,90±0,06 Å^3; Z=4; $V^0_{el.cell}$ =826,52±0,02Å^3; $\rho_{X-ray.}$ = 3,68 g/ cm^3. Based on X-ray phase analysis, it can be assumed that the compounds belong to the space group *Pm3m*.

By analogy [20, 21] it can be assumed that the ions La +, Li +, Na +, K + are in the centers of the unit cells and have coordination numbers (c.n.) in oxygen equal to 12, and at the nodes of the unit cells there are ions Co^{2+}, Cu^{2+} and Mn^{3+}, which c.n. is 6 in oxygen.

In connection with the increase in ionic radii in $Li^+ \rightarrow Na^+ \rightarrow K^+$, an increase in the "a" parameter, the volume of crystal lattices, and elementary cells is also observed.

Table - Indication of X-ray patterns of cobalt-cuprate-manganites

J/J^0	d, Å	$10^4/d^2$ exp.	hkl	$10^4/d^2$ calc.
$LaLi_2CoCuMnO_6$				
9	4,691	454,4	410	454,4
26	3,891	660,5	500	668,2
5	2,866	1217	631	1230
100	2,742	1330	550	1337
11	2,521	1573	553	1577
18	2,442	1677	651	1657
12	2,320	1858	653	1871
22	2,245	1984	831	1978
7	2,209	2049	832	2058
4	2,024	2441	931	2432
42	1,939	2660	10.0.0	2673
8	1,741	3299	775	3288
8	1,728	3349	10.5.0	3341
32	1,584	3985	10.7.0	3983
16	1,568	4067	12.2.2	4063
9	1,427	4911	12.6.2	4918
11	1,374	5297	14.1.1	5292
11	1,364	5375	14.2.1	5373
12	1,224	6675	10.10.7	6656
$LaNa_2CoCuMnO_6$				
24	5,569	322,4	320	322,4
7	4,490	496,0	420	496,0
19	3,862	670,5	511	669,6
100	2,736	1335	552	1339
14	2,315	1866	751	1860
17	2,236	2000	900	2009
51	1,932	2679	10.2.2	2678
8	1,876	2841	953	2852
5	1,846	2934	10.3.3	2916
5	1,715	3400	11.4.0	3398
36	1,581	4000	12.4.1	3993
14	1,565	4083	10.8.1	4092
3	1,501	4438	13.3.1	4439
15	1,373	5305	14.3.3	5307
11	1,360	5406	13.7.0	5406
12	1,264	6675	16.3.2	6671
12	1,217	6752	16.4.0	6746
$LaK_2CoCuMnO_6$				
21	3,868	668,4	520	668,4
7	3,097	1042	630	1037
6	2,867	1216	641	1222
100	2,736	1336	730	1337
16	2,527	1566	644	1567
9	2,442	1677	830	1683
14	2,320	1858	900	1867
16	2,240	1993	921	1982
5	2,130	2204	844	2213
36	1,932	2679	10.4.0	2674
6	1,873	2850	11.1.1	2835
8	1,728	3349	980	3342
27	1,580	4006	13.2.1	4010
11	1,569	4062	12.4.4	4057
11	1,373	5305	15.2.1	5301
7	1,358	5422	15.3.1	5416
8	1,229	6620	16.4.4	6638
12	1,222	6697	17.1.1	6707

Conclusion. Thus, cobalt-cuprate-manganites of the composition $LaMe^{I}_{2}CoCuMnO_{6}$ (Me^{I} – Li, Na, K) were synthesized for the first time. Their nanoscale (nanocluster) particles were obtained. The type of their syngony and the parameters of the lattices were determined by X-ray diffraction.

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REFERENCES

[1] Tretyakov YD, Brylev OA (**2000**) Journal of the Russian Chemical Society DI Mendeleev [Zhurnal Rossijskogo Himicheskogo Obshhestva im DI Mendeleeva] 65, 4: 10-16. (In Russian)

[2] Portnoy KI, Timofeev NI (**1986**) Oxygen compounds of rare earth elements [Kislorodnye soedinenija redkozemel'nyh jelementov]. Metallurgy, Moskow. ISBN: П2605000000-138/040(01)-86

[3] Suzdalev IP, Suzdalev PI (**2001**) Success of chemistry [Uspehi himii] 70, 3: 203-240. (In Russian)

[4] Tretyakov YD, Goodilin EA (**2000**) Success of chemistry [Uspehi himii] 69, 1: 3-39. (In Russian)

[5] Yerin Yu (**2009**) Chemistry and Chemists [Himija i himiki] 1:16-22 http://chemistry-chemists.com/N1_2009/16-22.pdf (In Russian)

[6] Kellerman DG (**2001**) Success of chemistry [Uspehi himii] 70, 9: 874-889. (In Russian)

[7] Khoronenkova SV, Eremin EA (**2002**) Bulletin of the Moscow State University. Chemical series [Vestnik MGU. Serija himicheskaja] 43, 5: 304-306 (In Russian)

[8] Ivanova NB, Ovchinnikov SG, Korshunov MM, Eremin IM, Kazak NV (**2009**) Successes of physical sciences [Uspehi fizicheskih nauk] 179, 8: 837-860. (In Russian)

[9] Shevelkov AV (**2008**) Success of chemistry [Uspehi himii] 77, 1: 3-22. (In Russian)

[10] Robert R, Aguirre MH, Hug P, Reller A, Weidenkaff A (**2007**) High-temperature thermoelectric properties of Ln(Co, Ni)O_3 (Ln=La, Pr, Nd, Sm, Gd and Dy) compounds, Acta Materialia, 55, 15: 4965-4972. https://doi.org/10.1016/j.actamat.2007.05.020

[11] Klyndyuk AI, Matsukevich IV (**2012**) Sviridov's reading [Sviridovskie chtenija] 8:44-50. (In Russian)

[12] Makshina EV, Borovskikh LV, Kustov AL, Mazo GN, Romanovsky (**2005**) Journal of Physical Chemistry [Zhurnal fizicheskoj himii] 70, 1: 253-257. (In Russian)

[13] Balakirev VF, Barkhatov VP, Golikov YuG, Mayzel OG (**2000**) Manganites: equilibrium and unstable states. URO RAS, Ekaterinburg. ISBN: 5-7691-0968-8

[14] Melkomerova MA, Bazuev GV (**2006**) Journal of Inorganic Chemistry [Zhurnal neorganicheskoj himii] 51, 3: 400-415. (In Russian)

[15] Medvedev DA, Zhuravleva TA, Murashkina AA, Sergeeva VS, Antonov BD (**2010**) Journal of Physical Chemistry [Zhurnal fizicheskoj himii] 84, 9: 1777-1781. (In Russian)

[16] Rykova AI, Cherny AS, Khatsko EN, Buchanko FN (**2009**) Nanomaterials [Nanomaterialy] 7, 3: 859-866. (In Russian)

[17] Kasenov BK, Kasenova ShB, Sagintayeva ZhI, Yermagambet BT, Bekturganov NS, Oskembekov IM (**2017**) Double and triple manganites, ferrites and chromites of alkaline, alkaline-earth and rare-earth metals. Scientific world, Mockow. ISBN: 978-5-91522-448-2

[18] Kasenov BK, Bekturganov NS, Yermagambet BT, Kasenova ShB, Sagintayeva ZhI, Isabaeva MA (**2016**) Manganites, chromites, ferrites of alkali, alkaline-earth and rare-earth metals. Litera LLP, Karaganda. ISBN: 978-601-210-194-2

[19] Kovba LM, Trunov VK (**1969**) X-ray phase analysis. Publishing house of Moscow University, Moscow. ISBN: К20502-147/077(02)-76141-75

[20] West A (**1988**) Solid State Chemistry. World, Moscow. Part 1. ISBN: 5-03-000056-9

[21] Kasenov BK, Oralova AT, Mustafin ES, Zhumadilov EK (**1998**) Journal of Inorganic Chemistry [Zhurnal neorganicheskoj himii] 43, 2: 196-197. (In Russian)

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ЛАНТАН ЖӘНЕ СІЛТІЛІ МЕТАЛДАРДЫҢ ЖАҢА НАНОӨЛШЕМДІ (НАНОКЛАСТЕРЛІК) КОБАЛЬТ-КУПРАТ-МАНГАНИТТЕРІ ЖӘНЕ ОЛАРДЫ РЕНТГЕНОГРАФИЯЛЫҚ ТҰРҒЫДАН ЗЕРТТЕУ

Аннотация. Жаңа қосарласқан марганец, мыс және қобальтқұрамды наноматериалдарға ізденіс және олардың қасиеттеріне зерттеулер жүргізу бейорганикалық материалдануда, әсіресе микроэлектроника үшін елеулі қызығушылық тудырады.

Осындай қосылыстарға қызығушылық олардың берілген қасиеттерінің полифункционалдылығымен және құрамдарының периодтық жүйенің көптеген элементерін қабылдау икемділігімен байланысты.

Керамикалық технологиямен лантан (III), кобальт(II), мыс (II), марганец (III) тотықтары мен литий, натрий және калий карбонаттарынан 800-1200 °С аралықта $LaMe^{I}_{2}CoCuMnO_{6}$ (Me^{I} – Li, Na, K) құрамды кобальт-купрат-манганиттері синтезделіп алынды.

Әрбір 100 °С сайын құрамдар суытылып, араластырылып және қайта қыздырылды. Төмен температурада тепе-тең фазалар алу үшін 10 сағат бойы 400 °С-та төмен температуралық қыздыру жүргізілді.

Retsch (Германия) компаниясының «MM301» маркалы вибрациялық диірменінде үгіту жолымен олардың наноөлшемді (нанокластерлік) бөлшектері алынды, «JSPM-5400» Scanning Probe Microscope «JEOL» (Япония) электрондық микроскопында олардың өлшемдері анықталды.

Қосылыстардың өлшемі 40-90 нм болатын нанобөлшектері (нанокластері) алынды.

Жаңа қосылыстарға рентгенофазалық талдау ДРОН-2,0 дифрактометрінде жасалды. Рентгенограммаларын аналитикалық әдіспен индицирлеу барысында синтезделіп алынған наноөлшемді жаңа фазалардың тор көрсеткіштері келесідей кубтық сингонияда кристалданатыны анықталды: $LaLi_2CoCuMnO_6$ – a=11,33±0,02 Å; V^0=2563,20±0,06Å^3; Z=4; $V^0_{эл.ұя.}$=640,80±0,02Å^3; $\rho_{рент.}$ = 4,0 г/см^3; $LaNa_2CoCuMnO_6$ – a=14,43±0,02 Å; V^0=3005,5±0,07Å^3; Z=4; $V^0_{эл.ұя.}$=751,38±0,02Å^3; $\rho_{рент.}$ = 3,86 г/см^3; $LaK_2CoCuMnO_6$ – a=14,90±0,02 Å; V^0=3306,90±0,06Å^3; Z=4; $V^0_{эл.ұя.}$=826,52±0,02Å^3; $\rho_{рент.}$ = 3,68 г/см^3. Рентгенофазалық талдау негізінде алынған наноөлшемді кобальт-курат-манганиттердің *Pm3m* кеңістіктік топқа жататынын болжауға болады.

Түйін сөздер: кобальт, купрат, манганит, лантан, сілтілі металл, синтез, нанобөлшектер, рентгенография.

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НОВЫЕ НАНОРАЗМЕРНЫЕ (НАНОКЛАСТЕРНЫЕ) КОБАЛЬТО-КУПРАТО-МАНГАНИТЫ ЛАНТАНА И ЩЕЛОЧНЫХ МЕТАЛЛОВ И ИХ РЕНТГЕНОГРАФИЧЕСКОЕ ИССЛЕДОВАНИЕ

Аннотация. Поиск новых совмещенных марганец, медь и кобальтсодержащих наноматериалов и изучение их свойств представляет определенный интерес для неорганического материаловедения, особенно для микроэлектроники. Интерес к подобным соединениям обусловлен полифункциональностью демонстрируемых свойств и гибкостью состава, позволяющий принимать многие элементы периодической системы. По керамической технологии из оксидов лантана (III), кобальта (II), меди (II), марганца (III) и карбонатов лития, натрия и калия в интервале 800-1200 °С синтезированы кобальто-купрато-манганиты состава $|LaMe^I_2CoCuMnO_6$ (Me^I – Li, Na, K). Через каждые 100 °С составы охлаждались, перетирались и заново нагревались. Для получения равновесных фаз при низких температурах проводили низкотемпературный отжиг при 400 °С в течение 10 часов. Измельчением их на вибрацилонной мельнице компании Retsch (Германия) марки «MM301» получили их наноразмерные (нанокластерные) частицы, размеры которых определены на электронном микроскопе JSPM-5400 Scanning Probe Microscope «JEOL» (Япония). Получены наночастицы (нанокластеры) соединений размером 40-90 нм. Рентгенофазовый анализ новых соединений проводили на установке ДРОН-2,0. Аналитическим методом индицирования рентгенограмм установлено, что синтезированные наноразмерные новые фазы кристаллизуются в кубической сингонии со следующими параметрами решетки: $LaLi_2CoCuMnO_6$ – a=11,33±0,02 Å; V^0=2563,20±0,06Å^3; Z=4; $V^0_{эл.яч.}$=640,80±0,02Å^3; $\rho_{рент.}$ = 4,0 г/см^3; $LaNa_2CoCuMnO_6$ – a=14,43±0,02 Å; V^0=3005,5±0,07Å^3; Z=4; $V^0_{эл.яч.}$=751,38±0,02Å^3; $\rho_{рент.}$ = 3,86 г/см^3; $LaK_2CoCuMnO_6$ – a=14,90±0,02 Å; V^0=3306,90±0,06Å^3; Z=4; $V^0_{эл.яч.}$=826,52±0,02Å^3; $\rho_{рент.}$ = 3,68 г/см^3. На основании рентгенофазового анализа можно предположить, что полученные наноразмерные кобальто-купрато-манганиты относятся к пространственной группе *Pm3m*.

Ключевые слова: кобальт, купрат, манганит, лантан, щелочные металлы, синтез, наночастицы, рентгенография.

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