

Synthesis and structure of polycrystals $\text{MnCo}_2\text{O}_4\text{-GdCrO}_4$

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ABSTRACT

The article discusses the synthesis and structure of polycrystalline nanocomposite $\text{MnCo}_2\text{O}_4\text{-GdCrO}_4$ material. The sol-gel method was used as a synthesis of the study. Using X-ray phase analysis (XPA), the structure of the synthesized nanomaterial composition was determined: spinel – cobalt manganate and perovskite – gadolinium chromite. Based on the results of the analysis, it was established that the polycrystalline two-phase composite is a system of spinel-cubic and perovskite-tetragonal types. Morphological analysis of the nanocomposite was carried out using a scanning electron microscope (SEM). According to the data obtained as a result of SEM, the elemental composition was confirmed and the average nanosize of the nanomaterial was obtained, and the content of the compound increased to x2000 was determined, the particle size of MnCo_2O_4 is 383-281 nm, GdCrO_4 – 1.63-1.34 μm ; increased to x4000, particle size – MnCo_2O_4 277-219 nm, GdCrO_4 – 1.48-1.27 μm ; increased to x6000, particle size – MnCo_2O_4 239-209 nm, GdCrO_4 – 1.21-1.07 μm .

Keywords: spinel, perovskite, supercapacitor, battery, electrocatalyst, refrigerator, ferromagnetic, research, magnetocaloric, effect, parameters

1. Introduction

Research in multifunctional materials for advanced energy technologies aimed at overcoming major challenges in energy conversion and storage. Material development transition metal oxides have attracted attention due to their high electronegativity, rich redox reactions and high density of active sites, low cost, environmental friendliness and excellent electrochemical performance [1].

Materials with the typical chemical formula AB_2O_4 spinel have gained widespread acceptance and application in the field of energy storage and storage [2], and also as electrocatalysts. Particular attention is paid to spinel materials with a bimetallic oxide structure, since they can lead to the creation of materials with higher electrochemical activity, electrical conductivity and more abundant redox reactions compared to monometallic oxides A and B [3]. Some studies report recent progress in the use of NiCo_2O_4 spinels in batteries [4], supercapacitors [5], and sensors [6]. Very recently

[2] summarized the major achievements of MCo_2O_4 (M=Co, Ni, Zn, Cu, Fe and Mn) based 2D spinel materials as an integrated electrode, detailing various other nanomaterials and Co based 2D spinel materials for this applications. Current applications of MnCo_2O_4 spinel are especially in energy conversion and storage. In fact, this compound has gained wide recognition as a promising, versatile and cost-effective bifunctional non-noble metal electrocatalyst due to its high redox stability, complementarity and synergy of both transition metals (manganese and cobalt), as well as efficient alternating valence states [7-10] In addition In addition, it is important that the supercapacitor has a suitable pore size distribution and a large specific surface area, which will reduce electrolyte consumption by regulating the porous structure and morphology of the electrode, which determines ion diffusion and conductivity, thereby affecting the capacity of the supercapacitor [11]. Various morphologies of MnCo_2O_4 can be prepared and tested for suitability as a supercapacitor electrode,

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such as spheres [12], granular [13], nanorods [14, 15], nanosheets [16-18], cuboid microcrystals [19], nanoneedles [20], tunable porous [21], nanocages [22], network-like porous [23, 24], cubes [25, 26] and hollow spheres [27]. The use of spinel materials based on MnCo_2O_4 materials for energy storage and conversion are promising components of a new concept of energy technologies. It is also important to emphasize that other applications are possible, for example, the use of MnCo_2O_4 -based catalysts to convert greenhouse gases (CO_2) and toxic gases (CO) into chemical fuels. From this perspective, MnCo_2O_4 -based materials play a key role towards a more sustainable society and industrial applications.

In recent years, research into magnetocaloric materials has attracted worldwide interest due to the high potential of their use in magnetic cooling processes [28, 29]. The zircon-type ferromagnetic phase GdCrO_4 is characterized by high values of magnetocaloric (MC) parameters. The effect of high MC is enhanced by polarization of Gd^{3+} ions by Cr^{5+} ions through the weaker Gd-Cr interaction. The effect should be considered when searching for new compounds with high MC effect in the range of liquid hydrogen or natural gas, concerning the liquefaction of gases by magnetization-demagnetization cycles [30]. The metal gadolinium exhibits magnetocaloric effect (MCE) through a second-order phase transition from paramagnetic to ferromagnetic (FM) at room temperature ($T_C = 293$ K) and has been used as a cooling material in prototype magnetic refrigerators since the 1970s, starting with Brown's refrigerator [31]. However, 1997 discovered the so-called «giant FEM» in $\text{Gd}_5\text{Si}_2\text{Ge}_2$ [32], many studies have been conducted mainly in intermetallic compounds containing rare earth elements [33]. In oxides, such examples are numerous, especially for rare earth transition metal oxides. $\text{Gd}_3\text{Ga}_5\text{O}_{12}$ [34], RMnO_3 [35], EuR_2O_4 [36] and RMn_2O_5 [37], where R = rare earths, have high thermal and chemical stability and exhibit large FEMs in the low-temperature region. In addition, the ferromagnetic in zircon phase GdCrO_4 can be used for magnetic cooling. New families without rare earths in the composition have also been investigated as materials for cooling near room temperature [38]. Previously, Mataev et al. synthesized chromite-manganite phases by sol-gel method, the composition of which was studied by X-ray diffraction [38]. Previously, Mataev et al. synthesized chromite-manganite phases by sol-gel method, the composition of which was studied by XPA diffraction method, a single-phase composite nanomaterial was obtained [39].

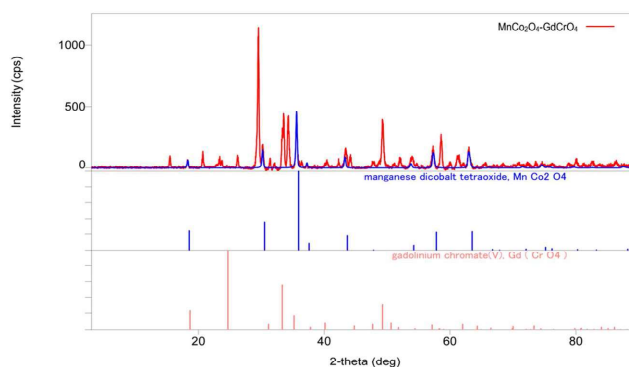


Fig. 1. Diffraction pattern of a polycrystalline MnCo_2O_4 - GdCrO_4 composite.

2. Experimental part

2.1. Materials and research methods

The following starting reagents were used as materials: gadolinium (III) oxide (Gd_2O_3), 99.99% TU 48-4-200-72, Russia); manganese (III) oxide (Mn_2O_3), 99.99% GOST/TU 6-09-3364-78, Russia); chromium (III) oxide (Cr_2O_3), 99% GOST TU 6-09-4272-84, Russia); cobalt (II) carbonate (CoCO_3), 99.99% GOST 5407-78, Russia). The following equipment and measurement methods were used: an alumina crucible (diameter 50 mm (5 cm)); a Brazilian agate mortar (diameter 140 mm (14 cm)). XPA was used to determine the phase composition – using Miniflex 600 RIGAKU diffractometer ($U=30$ kV, $J=10$ mA, rotation speed 1000 pulses per second, time constant $t = 5$ s, angular interval 2θ from 5 to 90° , Japan) and SEM JSM-6510LV JEOL (magnification $\times 5 - \times 300,000$ (equivalent to a photo plate size of 120 mm x 90 mm); acceleration voltage: 500 V – 30 kV; resolution in high vacuum mode: 3.0 nm using

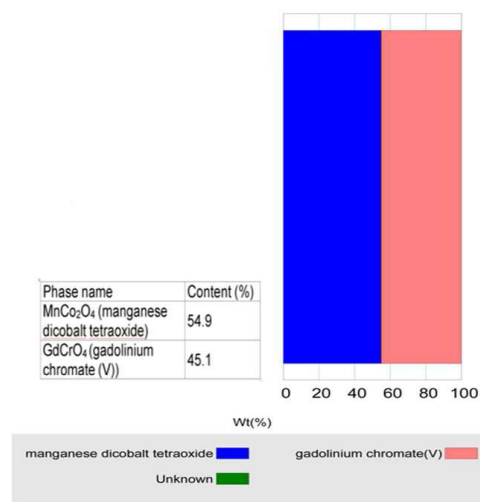


Fig. 2. Results of quantitative analysis of the composite.

Table 1. Result of quantitative analysis of the crystal lattice

№	Phase formula	a, Å	b, Å	c, Å	V, Å ³	Space group	Z	Theor. Density(g/cm ³)
1.	MnCo ₂ O ₄	8.336(8)	8.336(8)	8.336(8)	579.2(10)	Fd $\bar{3}$ m	8	5.418
	GdCrO ₄	7.587(14)	7.587(14)	6.138(14)	353.3(12)	I41	4	5.288

a tungsten cathode (at 30 kV), 8 nm (at 3 kV), 15 nm (at 1 kV); resolution in low vacuum mode: 4.0 nm (at 30 kV) Japan). Calculation and processing of 3D reconstruction surface data were performed using SEM (JEOL).

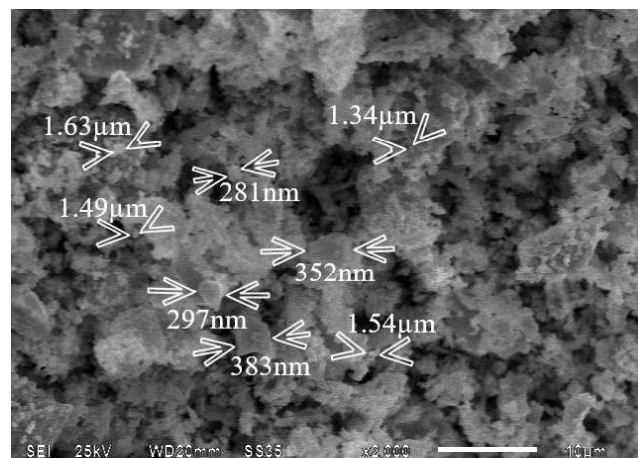
2.2. Synthesis – obtaining a composite nanomaterial by the sol-gel method

Two-phase MnCo₂O₄-GdCrO₄ nanomaterial synthesis was carried out by the sol-gel method. The metal oxides were doped with cobalt carbonate. The metal oxides were split in stoichiometric ratios. Citric acid and glycerin were used in the reaction as the precipitating agent, which favorably affected the formation of a homogeneous phase in the samples. Stoichiometric amounts of oxides were ground in an alumina crucible and mixed in an agate mortar until a homogeneous mixture was obtained. Distilled water, glycerin, and citric acid were added to the mixture. The mass was heated in an electric oven to obtain a gel. The resulting gel was treated in a muffle furnace at a temperature of 600 °C for 25-35 minutes. After transforming into powder, the composition was repeatedly fired, increasing the temperature in the range of 600-1100 °C. The firing was divided into six stages, with a total duration of 35 hours. After each synthesis stage, intermediate grinding and loading into the X-ray apparatus were performed. As a result of the work, a multifunctional two-phase spinel-perovskite nanocomposite was synthesized. The crystal structure of the complex oxide compound was obtained by SEM and XPA diffraction methods.

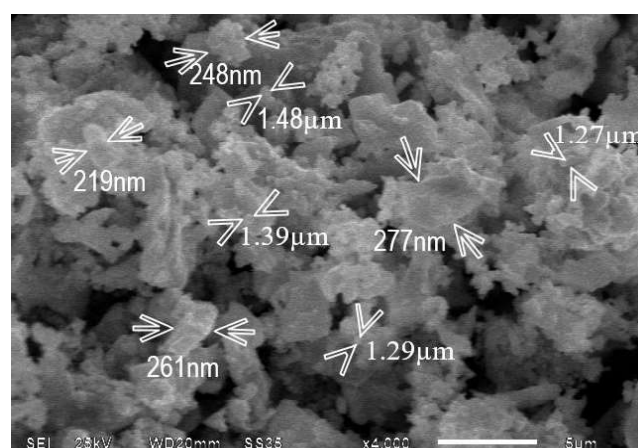
3. Results and discussion

The analyzed structures of the obtained spinel-perovskite nanomanganite determined its phase composition by the XPA method. The results of the XPA of the powdered polycrystalline samples showed two composites: cobalt manganate (MnCo₂O₄) and gadolinium chromite (GdCrO₄), the ferromagnetic phase of the zircon type (Fig. 1).

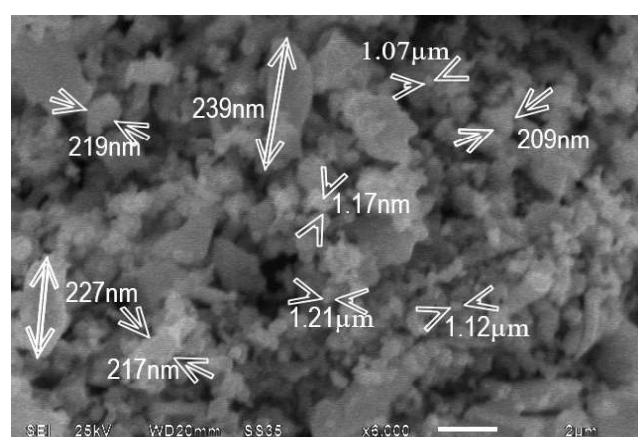
In the inset of Fig. 2, a quantitative analysis of the composite is presented. The results of the quantitative analysis (internal standard method) and calibration data allowed determining that their percentage ratios



(a)



(b)



(c)

Fig. 3. Scanning electron microscopy increased particle size up to: (a) x2,000 MnCo₂O₄ 383-281 nm, GdCrO₄ 1.63-1.34 μm; (b) x4000 MnCo₂O₄ 277-219 nm, GdCrO₄ 1.48-1.27 μm; (c) x6000 MnCo₂O₄ 239-209 nm, GdCrO₄ 1.21-1.07 μm.

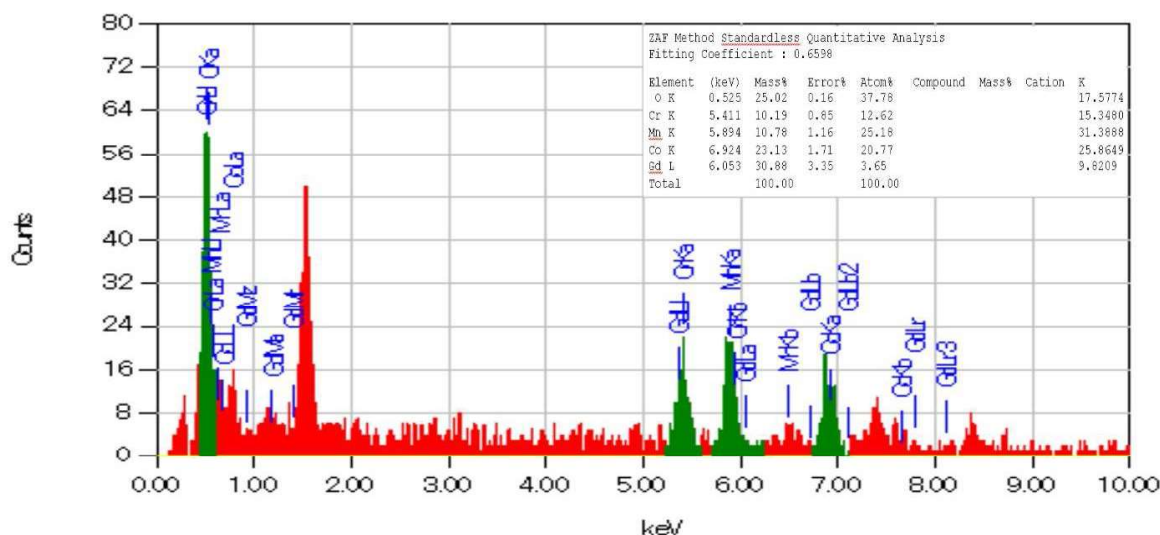


Fig. 4. Elemental composition of two-phase nanomaterial MnCo_2O_4 - GdCrO_4 .

are 54.9% for cobalt manganate (MnCo_2O_4) and 45.1% for gadolinium chromite (GdCrO_4).

The result of refining the structural parameters shows that the binary phase with cubic and tetragonal crystal lattice structures is presented in Table 1.

The phase MnCo_2O_4 with a formula unit number $Z=8$ crystallizes in a cubic lattice with the space group $\text{Fd}\bar{3}\text{m}$. The phase GdCrO_4 , respectively, with $Z=4$ crystallizes in a tetragonal lattice with the space group I41 (Table 1).

Scanning electron microscopy (JSM-6510LV JEOL) showed availability conglomerates (Fig. 3 a, b, c): increased up to $\times 2,000$ spatial resolution $10\ \mu\text{m}$ particle size MnCo_2O_4 383-281 nm, GdCrO_4 1.63-1.34 μm ; spatial resolution increased up to $\times 4000$ $5\ \mu\text{m}$ particle size MnCo_2O_4 277-219 nm, GdCrO_4 1.48-1.27 μm ; spatial resolution increased

to $\times 6000$ $2\ \mu\text{m}$ particle size MnCo_2O_4 239-209 nm, GdCrO_4 1.21-1.07 μm . Such dimensions particles emphasizes efficiency sol-gel synthesis in obtaining homogeneous microstructures.

Measurements of the mass of elements in a two-phase nanomaterial using scanning electron microscope data confirm that the initial composition coincides with the elemental analysis data (Fig. 4).

The 3D model generated by the SEM (JEOL) provides solutions for analytics and visualization, constructing 3D color intensity maps, anaglyphic images, profiles, and measurements of nanomaterial growth (Fig. 5). Studying the microstructure on the 3D model revealed four layers of color: the highest being red, followed by yellow, green, and blue. The images, essentially, represent a two-dimensional representation of the sample surface. SEM enables an improved understanding of complex microstructures. The metrological surface of the layers is as follows: red + 12 μm – 24 μm ; yellow + 10 μm – 18.5 μm ; green + 6.5 μm – 24.5 μm ; blue – 24 μm – 28 μm .

This 3D image is intuitive understandable and possible calculate characteristics surfaces. The most high from the surface (red layers) +12 μm , the most deep (blue layers) – 28 μm . The results of the structural analysis expand the database of nanocomposite materials with promising electrophysical properties.

4. Conclusion

The phase structure and morphological analysis were carried out using SEM of the resulting two-phase nanomaterial. According to the results of the study, the crystallographic results confirmed that the types of two-phase polycrystals are cubic and tetragonal

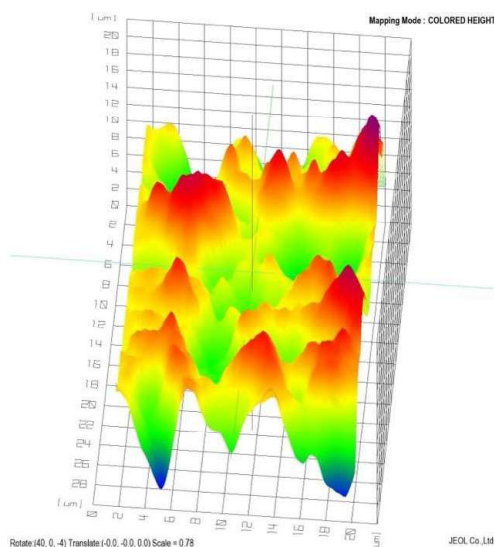


Fig. 5. P E M - 3D surface reconstruction.

lattice system. With formula units of the amount of cobalt manganate $Z=8$, it is determined that the shape parameter of the cubic unit cell is $a,b,c=8.336 \text{ \AA}$, and the tetragonal gadolinium chromite compound $Z=4$, the unit cell parameter is $a=7.587 \text{ \AA}$, $b=7.587 \text{ \AA}$, $c=6.138 \text{ \AA}$. Also, by determining the cell volumes of $\text{MnCo}_2\text{O}_4=579.2 \text{ \AA}^3$, $\text{GdCrO}_4=353.3 \text{ \AA}^3$, the formation of nanoscale product and its elemental composition were proved.

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MnCo₂O₄-GdCrO₄ поликристалдарының синтезі және құрылымы

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АНДАТПА

Мақалада поликристалды нанокөпозиттік MnCo₂O₄-GdCrO₄ материалының синтезі мен құрылымы қарастырылады. Зерттеудің синтезі ретінде золь-гель әдісі қолданылды. Рентгендік фазалық талдау (РФА) көмегімен синтезделген наноматериал құрамы анықталды: шпинель - кобальт манганаты және перовскит - гадолиний хромит. Талдау нәтижелері бойынша поликристалды екі фазалы көпозиттің шпинельді-кубтық және перовскит-тетрагональды типті жүйе екендігі анықталды. Нанокөпозиттің морфологиялық талдауы сканерлеуші электронды микроскоптың (СЭМ) көмегімен жүргізілді. СЭМ нәтижесінде алынған мәліметтер бойынша элементтік құрамы расталды және наноматериалдың орташа наноөлшемі алынды, қосылыстың мөлшері анықталып бөлшектердің өлшемі x2000 дейін ұлғайғанда MnCo₂O₄ 383-281 нм (nm), GdCrO₄ 1.63-1.34 мкм

(μm); бөлшектердің өлшемі $\times 4000$ ұлғайғанда MnCo_2O_4 277-219 нм (nm), GdCrO_4 1.48-1.27 мкм (μm); бөлшектердің өлшемі $\times 6000$ ұлғайғанда MnCo_2O_4 239-209 нм (nm), GdCrO_4 1.21-1.07 мкм (μm) дейін өсті.

Түйін сөздер: Шпинель, перовскит, суперконденсатор, аккумулятор, электрокатализатор, тоңазытқыш, ферромагниттік, зерттеу, магнитокалориялық, эффект, параметрлер

Синтез и структура поликристаллов MnCo_2O_4 - GdCrO_4

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АННОТАЦИЯ

В статье рассмотрены синтез и структура поликристаллического нанокompозитного MnCo_2O_4 - GdCrO_4 материала, полученного методом золь-гель. Методом рентгенофазового анализа (РФА) определена структура синтезированной

композиции наноматериала: шпинель – манганат кобальта и перовскит – хромит гадолиния. По результатам анализа установлено, что поликристаллический двухфазный композит представляет собой сингонию шпинель-кубического и перовскит-тетрагонального типов. Морфологический анализ нанокompозита проводился с помощью сканирующего электронного микроскопа (СЭМ). По данным, полученным в результате СЭМ, подтвержден элементный состав и определены средний наноразмер наноматериала, а также содержание соединения, увеличенного до $\times 2000$, размер частиц MnCo_2O_4 – 383-281 нм, GdCrO_4 – 1.63-1.34 мкм; увеличенного до $\times 4000$, размер частиц – MnCo_2O_4 277-219 нм, GdCrO_4 – 1.48-1.27 мкм; увеличенного до $\times 6000$, размер частиц – MnCo_2O_4 239-209 нм, GdCrO_4 – 1.21-1.07 мкм.

Ключевые слова: шпинель, перовскит, суперконденсатор, батарея, электрокатализатор, холодильник, ферромагнитная, исследования, магнитокалорических, эффект, параметры