ЕҢБЕК ҚЫЗЫЛ ТУ ОРДЕНДІ
«Ә. Б. БЕКТҰРОВ АТЫНДАҒЫ
ХИМИЯ ҒЫЛЫМДАРЫ ИНСТИТУТЫ»
АКЦИОНЕРЛІК ҚОҒАМЫ

ҚАЗАҚСТАННЫҢ ХИМИЯ ЖУРНАЛЫ

ХИМИЧЕСКИЙ ЖУРНАЛ КАЗАХСТАНА

CHEMICAL JOURNAL of KAZAKHSTAN

АКЦИОНЕРНОЕ ОБЩЕСТВО
ОРДЕНА ТРУДОВОГО КРАСНОГО ЗНАМЕНИ
«ИНСТИТУТ ХИМИЧЕСКИХ НАУК
им. А. Б. БЕКТУРОВА»

4 (68)

ОКТЯБРЬ – ДЕКАБРЬ 2019 г.

ИЗДАЕТСЯ С ОКТЯБРЯ 2003 ГОДА

ВЫХОДИТ 4 РАЗА В ГОД

АЛМАТЫ
2019

UDC 544.032;54.057;546.41;546.43

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SYNTHESIS AND X-RAY STUDY OF CHROMITE – GADOLINI FERRITE COMPOSITION $Gd_{(1-X)}MeCr_{0.5}Fe_{0.5}O_3$(Me = Ca, Mg, x≈0,7)

Abstracts. In the present work the X-ray study of the synthesized sol-gel by the method of new chromite-ferrites phases with the $Gd_{(1-X)}MeCr_{0.5}Fe_{0.5}O_3$ (Me = Ca, Mg, x≈0,7) composition was presented.Chromium oxide, iron oxide, gadolinium oxide, metal carbonates, citric acid and glycerin were used as initial materials. It is shown that the use of citric acid and glycerin as a precipitator has a positive effect on monophase samples. Rainfall was subjected to homogenizing roasting in the temperature range 600-900°C. The reaching the level of sintering of samples was controlled by theX-ray diffraction profiles. The phase composition, crystal characteristics, type of the symmetry, unit cell parameters, radiographic and pycnometric densitieswere investigated by the method of X-ray phase analysis. The correctness of the X-ray diffraction results of the mixed ferrite complex was confirmed by a good agreement between the experimental and calculated values of the inverse values of the squares to the interplanar distances ($10^4/d^2$). Satisfactory consistency of the X-ray values and pycnometric densities proves the correctness of the experimental results.

The article presents results of synthesis and XRF studies of new complex oxide chromite–gadolinium ferrites doped with alkaline earth metals (Ca, Mg). Results revealed the formation of samples with multifaceted structure. Developed oxide of the chromite – ferrite gadolinium has orthorhombic structure.

Keywords: chromium doped ferrite; sol-gel processes; crystal structures; nanostructures; doping; X-ray diffraction.

Introduction. Due to the antiferromagnetic or ferromagnetic properties, the study of the magnetic properties of oxides (ferrites) of rare earth elements has great interest. The importance of chemical homogeneity in the phase states of complex oxides plays big role in their application, especially in terms of magnetic and electrical properties. In recent years, there has been an unprecedented surge of interest in magnetoelectric materials and multiferroics.

The firstoneis characterized by a linear magnetoelectric effect (magnetization encouraged by an electric field and magnetic polarization induced by a magnetic field). Moreover, secondone has spontaneous electrical polarization and magnetization that can be controlled in a "cross" way: cause the magnetization to be switched by an electric field and vice versa by an electric polarization magnetic field. Therefore, magnetoelectric materials provide new opportunities for the conversion of electricity into magnetism and vice versa [1].

EXPERIMENTAL

In this work, we used the sol-gel method using glycerol as a precipitating agent [2].

Samples of chromite – ferrite gadolinium doped with alkaline earth metals (Ca, Mg) were synthesized by sol-gel method, where two different surfactants

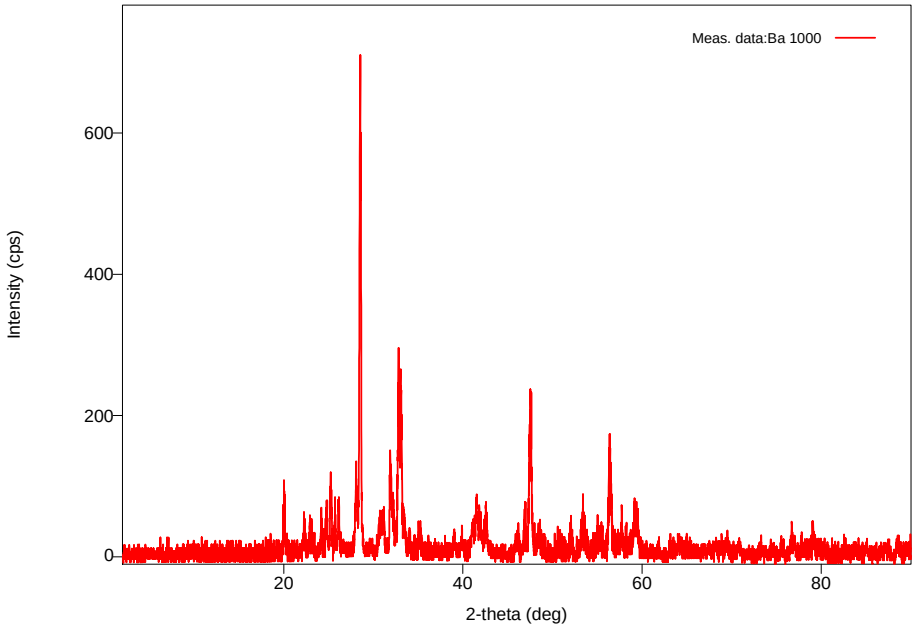

Figure 2.a) – XRD pattern of chromite sample – gadolinium ferrite with the composition of $Gd_{(1-X)}MeCr_{0.5}Fe_{0.5}O_3$ (Me = Ca, Mg, x≈0,7)

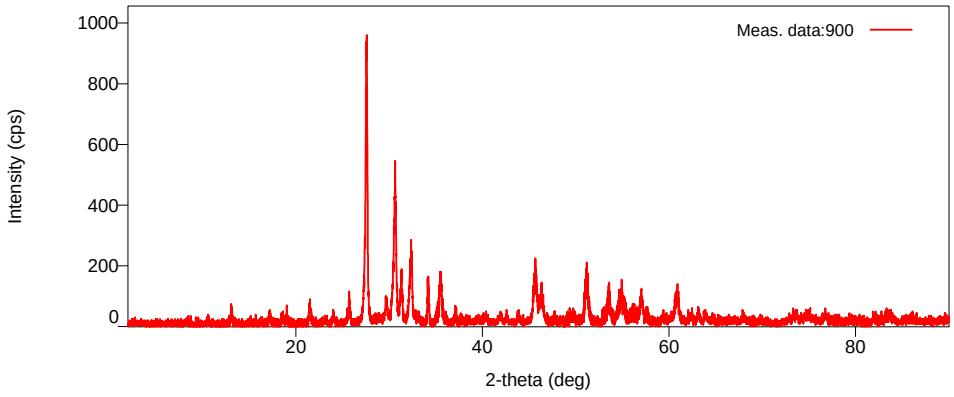

Figure 2.b) – XRD patternof chromite sample – gadolinium ferrite with the composition of $Gd_{(1-X)}MeCr_{0.5}Fe_{0.5}O_3$ (Me = Ca, Mg, x≈0,7)

were used [3]. The use of this method made it possible to get single-phase crystal particles of chromite – gadolinium ferrite.A solid mixture of $Gd_{(1-X)}MeCr_{0.5}Fe_{0.5}O_3$ (Me = Ca, Mg, x≈0,7) was first time synthesized. The parameters of the single cell and X-ray and incometence density were investigated.To obtain chromite - gadolinium ferrite with the formula of $Gd_{(1-X)}MeCr_{0.5}Fe_{0.5}O_3$ (Me = Ca, Mg, x≈0,7), Gd_2O_3, $CaCO_3$, $MgCO_3$, Cr_2O_3, Fe_2O_3 were stoichiometrically calculated and carried out by the sol-gel method. The stoichiometric amount of oxides was mixed and ground in an agate mortar to obtain a homogeneous mixture. To the consequential mixture was added 2 ml of distilled water, 2 ml of glycerin and 3 g of citric acid. To produce the mass of gel,the mixture was put in an electric furnace. After that, they were subjected to repeated annealing in the furnace at a temperature range of 600-900°C with an increase in temperature every 100°C per hour [4]. Annealing was carried out in five stages. At the first stage mixture was hold at 600 °C for 6 hours, at the second stage at 700 °C for 3 hours, at the third stage at 800 °C for 7 hours, the fourth stage at 900 °C for 6 hours, a total duration equals to22 hours [5]. After each stage of synthesis intermediate rubbing was carried out. Upon completion of the synthesis, the furnace was switched off, and the cooling of the resulting compound occurred in the mode of cooling of the muffle furnace. The composition of the final products was controlled by XRF. Radiographic studies were carried out on the miniflex 600 diffractometer (Rigaku, Japan) [6].

RESULTS AND DISCUSSION

The data of the X-ray diffraction of the synthesized chromite-manganites are presented in table1.

Table 1 – Indexing of radiographs of synthesized phases

№	[°2Th.]	d[Å]	Int. [%]	$10^4/d^2$exp.	hkl	$10^4/d^2$theor.
1	2	3	4	5	6	7
$Gd_{(1-x)}CaCr_{0.5}Fe_{0.5}O_3$(x≈0,7)						
1	23.40	3.799	15.0	1.89	(0,0,2)	1.93
2	26.17	3.402	12.0	2.216	(1,1,1)	2.19
3	32.53	2.750	20.0	3.38	(0,2,0)	3.35
4	33.34	2.685	100.0	3.58	(1,1,2)	3.6
5	33.89	2.643	25.0	3.73	(2,0,0)	3.70
6	34.66	2.586	12.0	3.96	(0,2,1)	3.98
7	39.60	2.274	6.0	5.93	(2,1,1)	5.95
8	40.49	2.226	6.0	6.41	(0,2,2)	6.43
9	41.62	2.168	10.0	7.09	(2,0,2)	7.07

Continuation of table 1

1	2	3	4	5	6	7
10	42.95	2.104	8.0	8.00	(1,1,3)	8.02
11	44.10	2.052	2.0	8.91	(1,2,2)	8.93
12	44.90	2.017	1.0	9.62	(2,1,2)	9.60
13	47.65	1.907	25.0	12.58	(2,2,0)	12.60
14	48.05	1.892	18.0	13.10	(0,0,4)	13.8
15	48.93	1.860	10.0	14.32	(0,2,3)	14.34
16	49.21	1.850	15.0	14.74	(2,2,1)	14.76
17	52.78	1.733	2.0	21.47	(2,1,3)	21.45
18	54.16	1.692	25.0	24.95	(1,3,1)	24.93
19	56.07	1.639	3.0	30.83	(3,1,1)	30.85
20	58.48	1.577	10.0	40.58	(1,3,2)	40.60
21	59.18	1.560	12.0	44.02	(0,2,4)	44.04
22	60.15	1.537	30.0	49.34	(2,0,4)	49.30
23	60.85	1.521	6.0	53.58	(2,2,3)	53.55
24	65.19	1.430	10.0	90.38	(1,3,3)	90.36
25	69.35	1.354	5.0	151.9	(0,4,1)	151.7
26	69.94	1.344	12.0	163.8	(2,2,4)	163.10
27	71.15	1.324	5.0	191.3	(4,0,0)	191.0
$Gd_{(1-x)}MgCr_{0.5}Fe_{0.5}O_3(x\approx0,7)$						
1	19.49	4.550	6.0	1.56	(2,0,0)	1.58
2	20.07	4.420	16.0	1.60	(0,1,1)	1.63
3	22.33	3.978	40.0	1.78	(1,1,1)	1.76
4	22.97	3.869	6.0	1.85	(2,0,1)	1.82
5	24.23	3.670	25.0	1.98	(0,0,2)	1.96
6	25.30	3.518	90.0	2.10	(2,1,0)	2.13
7	26.15	3.405	50.0	2.21	(1,0,2)	2.20
8	28.11	3.172	100.0	2.49	(2,1,1)	2.47
9	30.80	2.901	55.0	2.98	(1,1,2)	2.99
10	31.88	2.805	10.0	3.22	(3,0,1)	3.24
11	32.29	2.770	45.0	3.32	(0,2,0)	3.30
12	35.32	2.539	12.0	4.17	(2,1,2)	4.19
13	35.85	2.503	2.0	4.34	(3,1,1)	4.37

End of table 1

1	2	3	4	5	6	7
14	35.97	2.495	6.0	4.39	(1,2,1)	4.36
15	37.98	2.367	10.0	5.17	(2,2,0)	5.15
16	38.07	2.362	8.0	5.21	(1,0,3)	5.24
17	38.49	2.337	6.0	5.39	(3,0,2)	5.40
18	39.99	2.253	16.0	6.13	(2,2,1)	6.14
19	40.74	2.213	6.0	6.55	(0,2,2)	6.53
20	41.50	2.174	60.0	7.01	(1,1,3)	7.04
21	41.91	2.154	40.0	7.27	(3,1,2)	7.25
22	42.01	2.149	50.0	7.34	(1,2,2)	7.36
23	42.93	2.105	10.0	7.99	(4,1,0)	7.96
24	46.01	1.971	8.0	10.7	(3,2,1)	10.5
25	41.90	2.155	35.9	2153.30	(2,0,3)	2153.25
26	42.08	2.145	42.9	2173.42	(1,2,2)	2173.36
27	42.90	2.106	10.7	2254.67	(4,1,0)	2254.59

According to the X-ray study obtained chromite – ferrite gadolinium has orthorhombic structure with a spatial group (table 2).

Table 2 – Type of symmetry and parameters of elementary cells of chromite – ferrite gadolinium composition $Gd_{(1-X)}MeCr_{0.5}Fe_{0.5}O_3$ (Me = Ca, Mg, x≈0,7)

№	Compound	Phase sym-metry	a, Å	b, Å	c, Å	$V_{э.я.}$, Å^3	Z	$P_{X\text{-}ray}$	P_{pyc}
1	$Gd_{(1-x)}CaCr_{0.5}Fe_{0.5}O_3$(x≈0,7)	Ortho-rombic	5.314	5.513	7.592	222.4	4	7.61	7.70
2	$Gd_{(1-x)}MgCr_{0.5}Fe_{0.5}O_3$(x≈0,7)	Ortho-rombic	9.90	8.46	4.861	398.8	4	3.45	3.65

Data indexing of radiographs of synthesized chromite – ferrite of gadolinium show that they have orthorombic structure with the following unit cell parameters:

1. $Gd_{(1-x)}CaCr_{0.5}Fe_{0.5}O_3$ (x≈0,7) - a=5.314, b=5.513, c=7.592, Å, $V_{эл.яч.}$=222.4Å^3, Z=4, $\rho_{рент.}$= 7.61г/см^3, $\rho_{пикн.}$= 7.70 g/cm^3.

2. $Gd_{(1-x)}MgCr_{0.5}Fe_{0.5}O_3$ (x≈0,7) - a=9.90, b=8.46, c=4.86, Å, $V_{эл.яч.}$= 398.8Å^3, Z=4, $\rho_{рент.}$= 3.45 g/cm^3, $\rho_{пикн.}$= 3.65 g/cm^3.

Chromite – ferrite gadolinium doped with alkaline earth metals (Ca, Mg) were synthesized by sol-gel method, where two different surfactants were used

[3].The use of this method made it possible to get single-phase crystal particles of chromite – gadolinium ferrite.A solid mixture of $Gd_{(1-X)}MeCr_{0.5}Fe_{0.5}O_3$ (Me = Ca, Mg, x≈0,7) was first time synthesized.The parameters of the single cell and X-ray and incometence density were investigated.To obtain chromite - gadolinium ferrite with the formula of $Gd_{(1-X)}MeCr_{0.5}Fe_{0.5}O_3$ (Me = Ca, Mg, x≈0,7), Gd_2O_3, $CaCO_3$, $MgCO_3$,Cr_2O_3, Fe_2O_3 were stoichiometrically calculated and carried out by the sol-gel method.

The correctness of the indexing results is confirmed by a satisfactory coincidence of the experimental and calculated values of the inverse squares of the interplanar distances ($10^4/d^2$), as well as the degree of coincidence of the values of the X-ray and pycnometric densities of the studied compounds.

Conclusion. The type of symmetry and the parameters of elementary cells were determined by X-ray method. It is revealed that chromite – ferrite gadolinium obtained by sol-gel method crystallize in orthorhombic structure and correspond to the formulas $Gd_{(1-X)}CaCr_{0.5}Fe_{0.5}O_3$, $Gd_{(1-X)}MgCr_{0.5}Fe_{0.5}O_3$ (where x = 0,5-0,7).

Chromite – ferrite of gadolinium show that they have orthorombic structure with the following unit cell parameters:

1. $Gd_{(1-x)}CaCr_{0.5}Fe_{0.5}O_3$ (x≈0,7) - a=5.314, b=5.513, c=7.592, Å, $V_{эл.яч.}$=222.4Å^3, Z=4, $\rho_{рент.}$= 7.61 g/cm^3, $\rho_{пикн.}$= 7.70 g/cm^3.
2. $Gd_{(1-x)}MgCr_{0.5}Fe_{0.5}O_3$ (x≈0,7) - a=9.90, b=8.46, c=4.86, Å, $V_{эл.яч.}$= 398.8Å^3, Z=4, $\rho_{рент.}$= 3.45 g/cm^3, $\rho_{пикн.}$= 3.65 g/cm^3.

The correctness of the indexing results is confirmed by a satisfactory coincidence of the experimental and calculated values of the inverse squares of the interplanar distances ($10^4/d^2$), as well as the degree of coincidence of the values of the X-ray and pycnometric densities of the studied compounds.

Acknowledgement. This article was prepared by the financial support of the grant of the Ministry of Education and Science of the Republic of Kazakhstan №AP05130165 “Development and physical basis of new crystal systems in the class of multiferroics”.

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Резюме

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$Gd_{(1-X)}CaCr_{0.5}Fe_{0.5}O_3$, $Gd_{(1-X)}MgCr_{0.5}Fe_{0.5}O_3$, (x=0,5-0,7) ҚҰРАМДЫ ХРОМИТ – ФЕРРИТ ГАДОЛИНИЙДІҢ СИНТЕЗІ МЕН РЕНТГЕНОГРАФИЯЛЫҚ ТАЛДАУЫ

Жұмыста $Gd_{(1-X)}MeCr_{0.5}Fe_{0.5}O_3$ (Me = Ca, Mg, x≈0,7) құрамды жаңа хромиттіманганиттер фазасы золь–гель әдісімен синтезделген, рентгендік зерттеу жұмысы жүргізілген. Бастапқы материалдар ретінде хром оксиді, темір оксиді, гадолиний оксиді, металл карбонаттары, лимон қышқылы және глицерин қолданылды. Лимон қышқылы мен глицеринді тұнба ретінде қолдану монофазалық үлгілерге оң әсер етеді. Алынған тұнба 600-1100°С температура диапазонында гомогенизациялық күйдіруге ұшырап, үлгілердің бірігу деңгейіне жетуі рентген дифроктаграммалары негізінде бақыланды. Рентгенофазалық талдау әдісімен кристалдардың фазалық құрамы мен сипаттамалары зерттелді, симметрия түрі, дара ұяшықтардың параметрлері, рентгенографиялық және пикнометриялық тығыздығы анықталды. Күрделі аралас ферриттің рентгендік дифракциясы нәтижелерінің дұрыстығы ($10^4/d^2$) қабықаралық қашықтық квадраттарының кері мәндерінің эксперименталдық және есептік мәндерінің жақсы сәйкес келуімен расталады. Рентгендік және пикнометриялық тығыздықтар мәндерінің қанағаттанарлық келісілуі тәжірибелік нәтижелердің дұрыстығын дәлелдейді.

Түйін сөздер: хроммен допирленген феррит, золь-гельді процестер; кристалды құрылымдар; нанокұрылымдар; допирлеу; рентгендік дифракция.

Резюме

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СИНТЕЗ И РЕНТГЕНОГРАФИЧЕСКОЕ ИССЛЕДОВАНИЕ ХРОМИТА –ФЕРРИТА ГАДОЛИНИЯ СОСТАВА $Gd_{(1-X)}MeCr_{0.5}Fe_{0.5}O_3$(Me = Ca, Mg, x≈0,7)

В настоящей работе представлено рентгенологическое исследование синтезированного золь-геля методом новых хромит-ферритовых фаз состава: $Gd_{(1-X)}MeCr_{0.5}Fe_{0.5}O_3$(Me = Ca, Mg, x≈0,7). В качестве исходных материалов

использовались оксид хрома, оксид железа, оксид гадолиния, карбонаты металлов, лимонная кислота и глицерин. Показано, что применение лимонной кислоты и глицерина в качестве осадителя оказывает положительное влияние на монофазные образцы. Осадки подвергали гомогенизирующему обжигу в интервале температур 600-1100°c, достижение уровня спекания образцов контролировали на основе рентгеновских дифракционных профилей. Методом рентгенофазового анализа исследован фазовый состав и характеристики кристаллов, определен тип симметрии, параметры единичных ячеек, рентгенографические и пикнометрические плотности. Правильность результатов рентгеновской дифракции сложного смешанного феррита подтверждается хорошим совпадением экспериментальных и расчетных значений обратных значений квадратов межплоскостных расстояний ($10^4/d^2$). Удовлетворительная согласованность значений рентгеновской и пикнометрической плотностей доказывает правильность экспериментальных результатов.

Ключевые слова: феррит допированном хромом,золь-гель процессы; кристаллические структуры; наноструктуры; легирование; дифракция рентгеновских лучей.