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Synthesis and magnetic properties of $Y_{0,5}Ca_{0,5}Cr_{0,5}Mn_{0,5}O_3$ compounds

Abstract. *In this work,a solid solution of chromite-manganite of the composition $Y_{0,5}Ca_{0,5}Cr_{0,5}Mn_{0,5}O_3$ was synthesized using the sol-gel method. Based on the results of experimental studies of the magnetostatic properties of the polycrystalline system$Y_{0,5}Ca_{0,5}Cr_{0,5}Mn_{0,5}O_3$. It is found that the predominant is the intracrystalline ferromagnetic interaction, while the intercrystalline interaction is antiferromagnetic in nature.In the field of 2000 Oe and 5000 Oe at a temperature of 5 K, the magnetic moment is not even positive. These dependencies were obtained after the sample was in a large negative field. This initial moment is approximately equal to the residual moment on the hysteresis loop for a temperature of 5 K. When the external field is increased gradually, for example, in increments of 250 Oe, this moment increases to 1.2 emu/g at 2000 Oe. Based on the results of magnetostatic measurements, it was found that hysteresis loops of magnetization are observed at low temperatures.*

Keywords: *Sol-gel method, X-ray diffraction, yttrium-calcium chromite-manganite, the antiferromagnetic interaction.*

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Introduction. The rare earth manganese oxide $RMnO_3$ (R is a rare earth element such as La, Pr, etc.) has a natural perovskite crystal structure and antiferromagnetism. When the rare earth element R is partially replaced by the divalent alkaline earth metal elements, perovskite oxides of the general formula $R_{1-x}A_xMnO_3$ (A is a divalent elements such as Ca, Sr, Ba, etc.) is formed [1, 2]. In recent decades, there are a lot of interest in these materials which have unique physical properties such as metal–insulator transition behavior near the Curie temperature Tc, colossal magneto-resistance, phase coexistence, charge ordering and so on [3–6]. These characteristics make manganese oxides have good application prospect in magnetic recording devices, magnetic sensors and bolometric devices, etc. [7, 8]. In recent years, a large number of experiments on the effect of Mn-doping on the properties of $La_{1-x}Ca_xMn_{1-y}B_yO_3$ (B = Cr, Co, Ti, etc.) polycrystalline materials have show that the Curie temperature and the MI transition temperature are decrease. However, temperature coefficient of resistance (TCR) increases to a certain value first and then decreases [10, 11]. Kumar et al. found double peaks in Cr doping at Mn-site, which was attributed the additional peak to antiferromagnetic (AFM) interaction due to the super exchange (SE) mechanism between Cr^{3+} /Cr^{3+} and/or Cr^{3+}/Mn^{4+} ions, except for the intrinsic peak by DE interaction in ϱ–T curves [12]. Mollah et al. reported that the Cr doping at Mn site exhibited ferromagnetic (FM) insulating state at low temperature [13]. In addition, it is found that Cr doping has rather slow decreasing effect on T_C and T_{MI} of the parent compound [9]. The effect of Cr doping on $La_{0.71}Ca_{0.29}MnO_3$ polycrystalline ceramics was studied in this experiment. The $La_{0.71}Ca_{0.29}Mn_{1-x}Cr_xO_3$ powder was prepared by sol–gel method, and then high-density, low-resistivity polycrystalline ceramics were obtained by optimizing the sintering conditions. Compared with other methods for preparing perovskite manganese oxides, such as conventional solid-state reaction and co-precipitation, the powder prepared by the sol–gel method has the advantages of small particle size, good uniformity, and more accurate chemical measurement. In the paper, $La_{0.71}Ca_{0.29}Mn_{1-x}Cr_xO_3$ polycrystalline ceramics were synthesized by sol–gel method with methanol as solvent. Compared with aqueous solution, this

method not only can shorten the experiment time, but also can retain the advantage of aqueous solvent sol–gel [14-15].

In the literature, there is almost no data on the properties of yttrium-based manganites, and the introduction of chromium ions instead of manganese ions expands the variety of possible exchange interactions. Therefore, we decided to investigate the magnetic properties of polycrystalline yttrium-calcium chromite-manganites.

Experimental. For the first time,a solid mixture of $Y_{0,5}Ca_{0,5}Cr_{0,5}Mn_{0,5}O_3$ was synthesized by the sol-gel method. The raw materials used were chromium oxide, manganese oxide, yttrium oxide, strontium carbonate, citric acid and glycerine (chemical clean). It is shown that the use of citric acid and glycerol as a precipitator has a positive effect on the monophasicity of samples. The stoichiometric amount of oxides is mixed and ground in an agate mortar until a homogeneous mixture is obtained. To the resulting mixture, add 2 ml of distilled water, 2 ml of glycerol and 3 g of citric acid. To get the gel, the mass is heated in an electric oven. After that, they were subjected to repeated annealing in a muffle furnace in the temperature range of 600-1100° C with an increase in temperature every 100° C per hour. Annealing was performed in six stages. The first stage is 600º C, the second stage is 700º C, the third stage is 800º C, the fourth stage is 900º C, the fifth stage is 1000º C, the sixth stage is 1100º C with a total duration of 39 hours. Intermediate grinding was performed after each stage of synthesis.

The formation of new phases was controlled by X-ray phase analysis, which was carried out on the X-ray diffractometer Miniflex 600 (Rigaku). XRF data can be used to identify the phase and relative percentages of the different phases of the prepared materials. Magnetic characteristics were studied on the MPMS-XL SQUID magnetometer in fields up to 50 kOe.

Results and discussion. The formation of a new phase was studied by x-ray phase analysis, which was performed on an x-ray diffractometer Miniflex 600 (Rigaku). For Figure 1 presents an x-ray diffraction image of the sample. The absence of any additional reflections indicates the phase purity of the sample. The use of Sol-gel synthesis method gives the best result. On the basis of x-ray indexing of synthesized chromite-manganite, it was found that chromite – manganite crystallizes in the orthorhombic syngony with the following parameters of elementary cells:$Y_{0,5}Ca_{0,5}Cr_{0,5}Mn_{0,5}O_3$ – a = 5.42Å , b = 7.51Å, c = 5.26Å, Z=4, $V^{un.cell.}$= 214.74Å^3, $p_{x\text{-}ray}$ = 6.03g/cm^3; $p_{pyc.}$ = 6.02 g/cm^3.

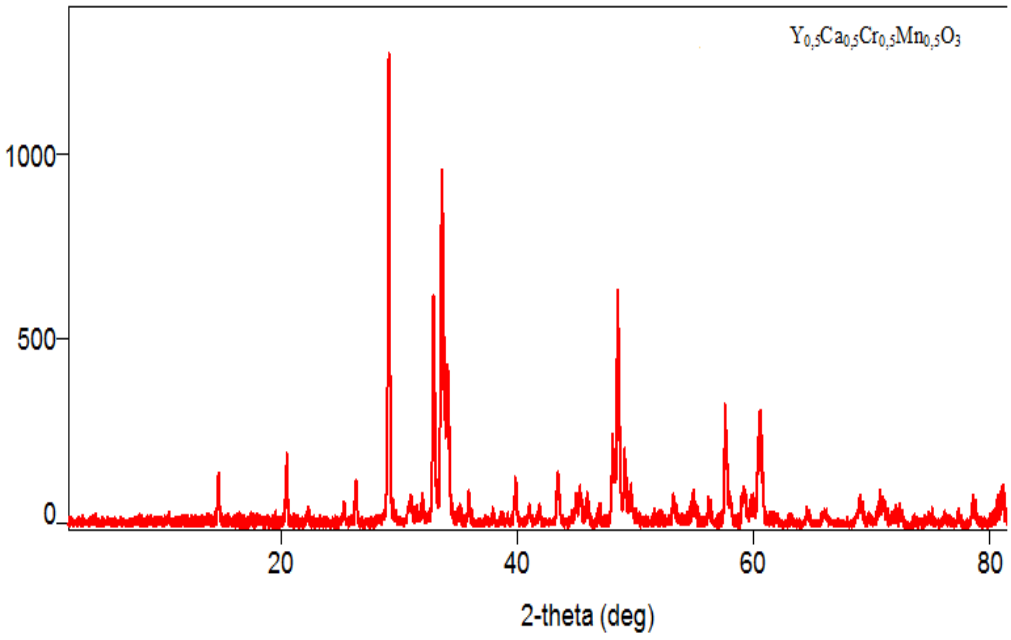

Figure1. X-ray powder of $Y_{0,5}Ca_{0,5}Cr_{0,5}Mn_{0,5}O_3$

The temperature and field behavior of the magnetic moment depends on the prehistory below the temperature of 130 K. With the same initial temperature and the same applied field, the temperature dependencies might look different. Moreover, the initial moment could be either positive or negative.

First, it was found that the sample does not always respond to a sharp change in the field. If the sample was cooled without a field from a temperature of 200 K to 5 K and then a field of 2000 Oe was set, the magnetic moment remained small (about 0.038 emu/g). In addition, a slight relaxation was observed over time (Fig. 2, left). If the external field is increased gradually, for example, in increments of 250 Oe, this moment increases to 1.2 emu/g at 2000 Oe (Fig. 2, on the right).

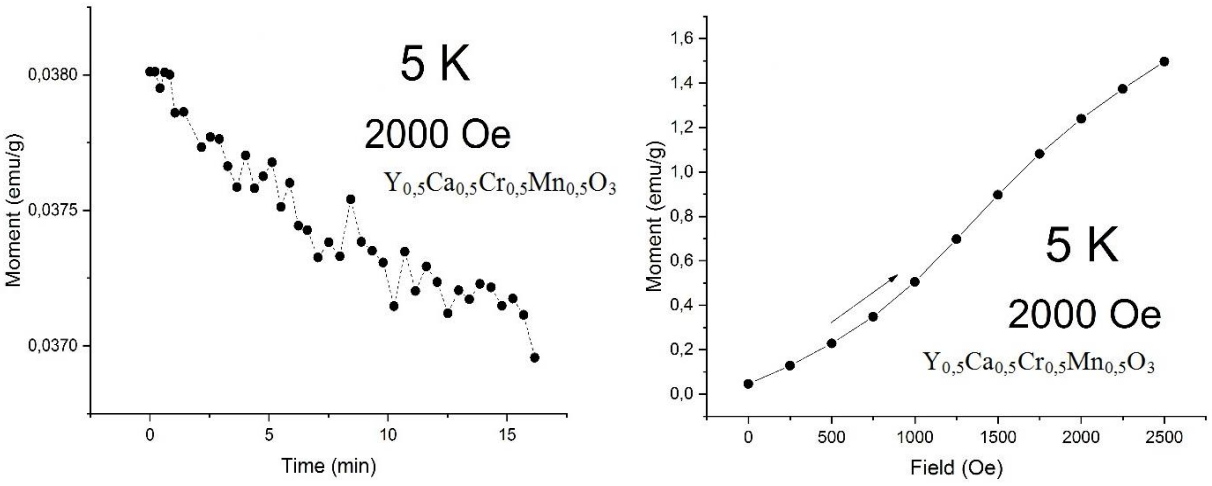

Figure 2. Left: the magnetic moment of the sample is 3 after applying the 2000 Oe field. On the right: the same magnetic moment, but depending on the external field when changing in increments of 250 Oe

Second, the initial moment depends on the magnetic background. As you can see in Figure 3, in the field of 2000 Oe and 5000 Oe at a temperature of 5 K, the magnetic moment is not even positive. These dependencies were obtained after the sample was in a large negative field. This initial moment is approximately equal to the residual moment on the hysteresis loop for a temperature of 5 K.

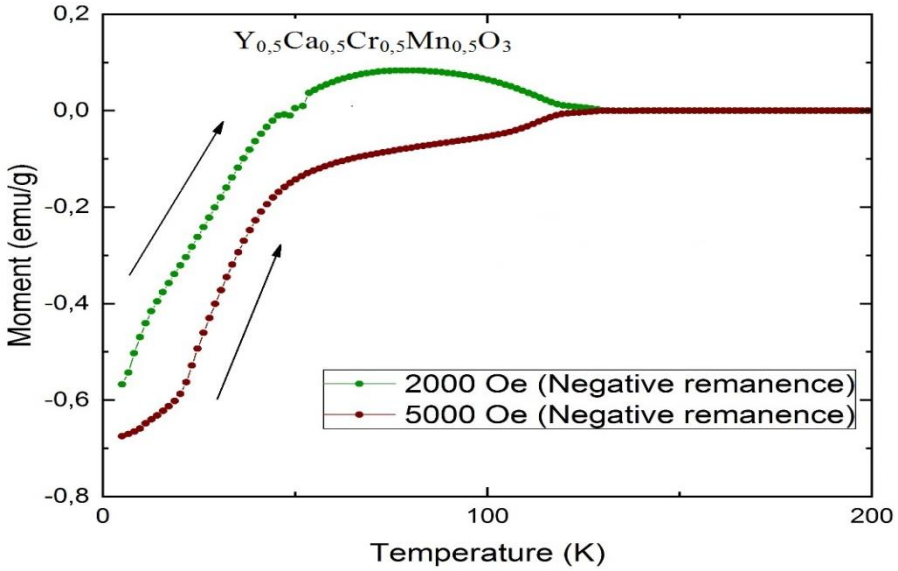

Figure 3. Temperature dependences of thawing in the field after the sample stays in a large negative field

Partial hysteresis loops with different histories were also obtained. A shift in the center of the loop was detected. For example, at a temperature of 55 K, after staying in the negative field -50000 Oe, the loop is located below the origin (Fig. 4).

The center of the loop is lowered by approximately the value of the residual moment after removing the field -50000 Oe. After staying in the positive field of 50000 Oe, the loop shifts to the top (Fig. 5). The magnetization process does not coincide with what was observed after cooling in the zero field from a temperature of 200 K (the black line in Fig. 5).

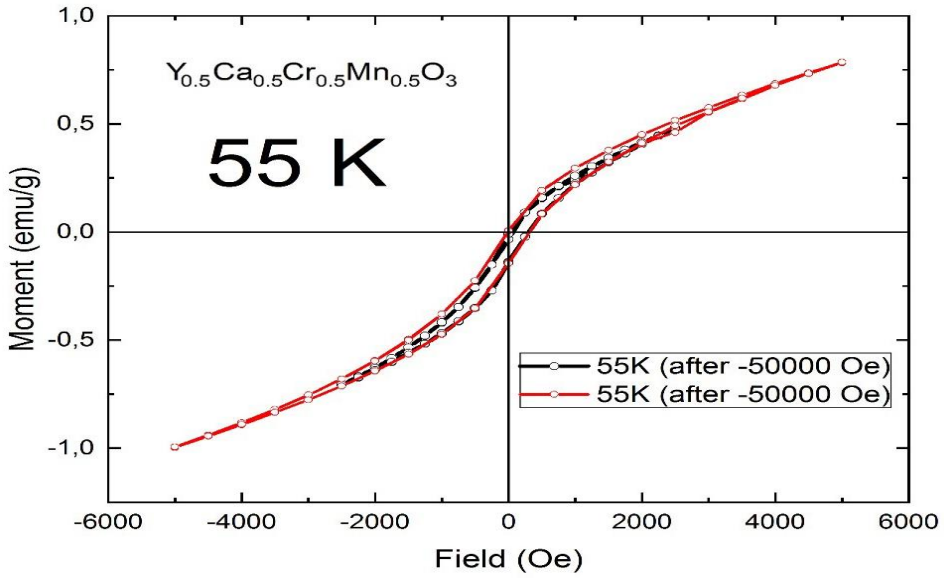

Figure 4. Private hysteresis loops at a temperature of 55 K

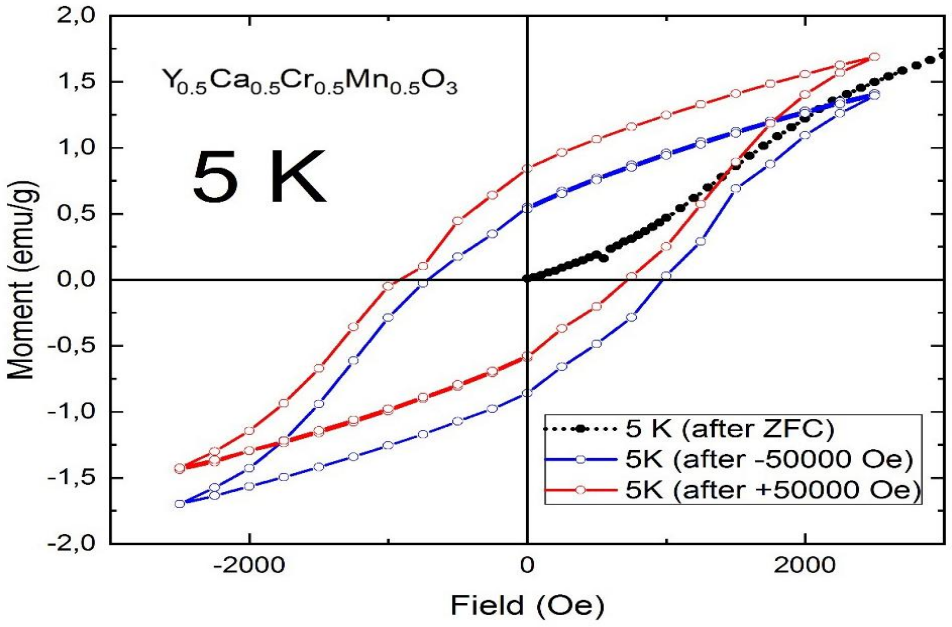

Figure 5. Partial hysteresis loops at a temperature of 5 K. The black color is the magnetization curve after cooling in the zero field

Private loops at a temperature of 72 K are shown in Figure 6.

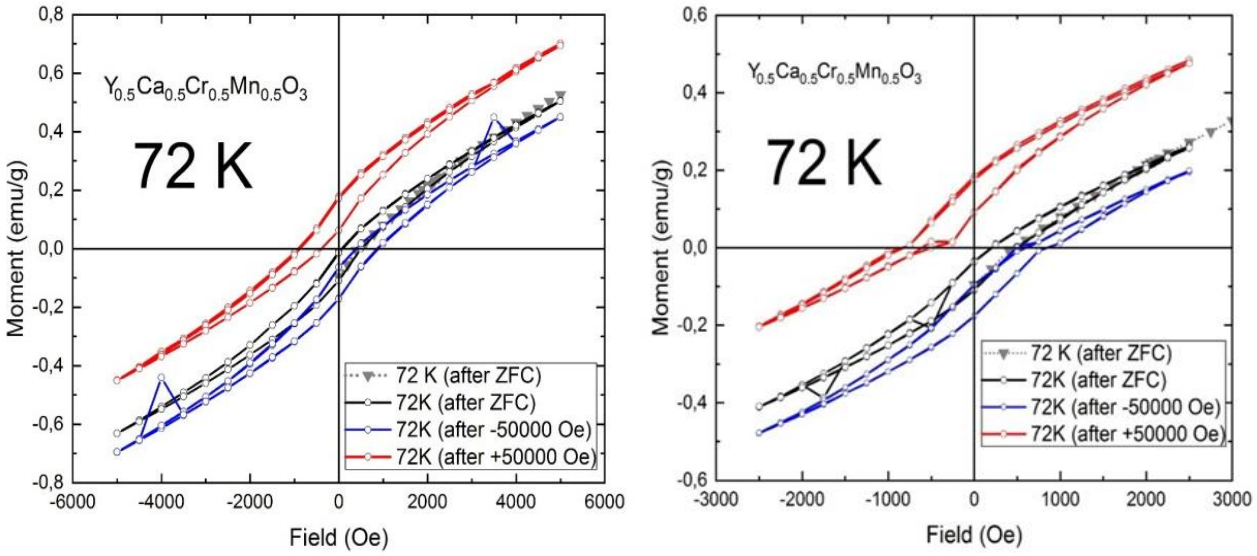

Figure 6. Partial hysteresis loops at a temperature of 72 K. Gray color – the magnetization curve after cooling in the zero field

In addition to the offset, there is a strong asymmetry of the loop at a small range of the external field (Fig. 7).

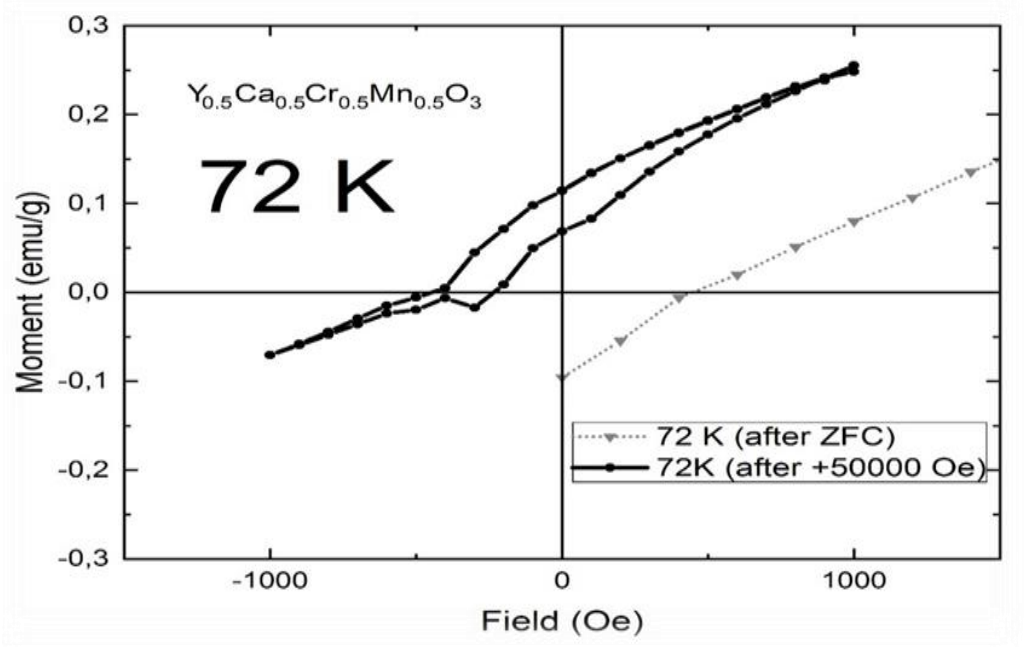

Figure 7. Private loop at 72 K in a small field

This suggests that the granules are ferromagnetic, randomly oriented in space, and there is an antiferromagnetic interaction between the granules. In this case, the intercrystalline exchange interactions should be less than the intracrystalline one. It is clear that in such a system there is a competition of intercrystalline interactions. Then the magnetization in small magnetic fields H ≤ HEX, (where HEX is the exchange field of the intercrystalline interaction) is determined by the rotation of the magnetic moments of ferromagnetic crystallites, and here the magnetization behavior is similar to spin-glass. Behavior in higher magnetic fields (H > HEX) is determined by overcoming intergranular antiferromagnetic interactions and reversal of the magnetic moments of crystallites along the direction of the external magnetic field. In strong magnetic fields, magnetization is associated with overcoming the strongest interparticle interactions and within partial magnetic anisotropies.

Summary. In this paper, the problems of synthesis, structural analysis and morphology of crystals of synthesized powders are considered for the first time. The symmetry type and parameters of the elementary cells were determined by x-ray method. It was found that chromite-manganites obtained by Sol-gel crystallization have an orthorhombic structure and correspond to the formula $Y_{0,5}Ca_{0,5}Cr_{0,5}Mn_{0,5}O_3$. Based on the results of magnetostatic measurements, it was found that hysteresis loops of magnetization are observed at low temperatures.

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$Y_{0,5}Ca_{0,5}Cr_{0,5}Mn_{0,5}O_3$ қосылысының синтезі және магниттік қасиеттері

Аңдатпа. Бұл жұмыста $Y_{0,5}Ca_{0,5}Cr_{0,5}Mn_{0,5}O_3$ құрамды жаңа хромитті-маганиттің қатты ерітіндісі золь–гель әдісімен синтезделген. Жаңа хромитті-маганиттің сингония түрі, элементарлық ұяшық параметрлері, рентгенографиялық және пикнометрлік тығыздығы анықталды. Рентген фазалық талдау нәтижесі бойынша хромитті-манганиттер орторомбтық перовскит құрылымы бойынша индицирленеді. $Y_{0,5}Ca_{0,5}Cr_{0,5}Mn_{0,5}O_3$ поликристалды жүйенің магнитостатикалық қасиеттері эксперименттік зерттеу нәтижелері бойынша алынды. Кристалды ферромагнитті өзара әрекеттесу басым болатыны анықталды, ал кристалды өзара әрекеттесу антиферромагнитті сипатқа ие. 2000 Ое және 5000 Ое өрісінде 5 К температурада магниттік момент оң болып табылмайды. Бұл тәуелділіктер үлгі үлкен, теріс өрісте болған соң алынды. Сыртқы өріс біртіндеп ұлғайған кезде, мысалы, 250 Ое қадамымен, бұл сәт 2000 Ое кезінде 1,2 emu/g дейін артады. Магнитостатикалық өлшеулердің нәтижелері негізінде магниттіліктің гистерезистік тұзақтары төменгі температураларда байқалатыны анықталды.

Түйін сөздер: Золь-гель әдісі, рентгендік дифракция, иттрий-кальцийлі хромитті-манганит, антиферромагниттік өзара әрекеттесу.

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Синтез и магнитные свойства соединений $Y_{0,5}Ca_{0,5}Cr_{0,5}Mn_{0,5}O_3$

Аннотация. В настоящей работе золь-гель методом был синтезирован твердый раствор хромито - манганита состава $Y_{0,5}Ca_{0,5}Cr_{0,5}Mn_{0,5}O_3$. Определены тип сингонии, параметры элементарной ячейки, рентгенографические и пикнометрические плотности нового хромита-манганита. Установлено, что синтезированный хромито-манганит кристаллизуется в орторомбической сингонии и имеет перовскитподобную структуру. Магнитостатистические и магниторезонансные свойства поликристаллической системы $Y_{0,5}Ca_{0,5}Cr_{0,5}Mn_{0,5}O_3$ установлены по результатам экспериментальных исследований. Получено, что преобладающим является внутрикристаллическое ферромагнитное взаимодействие, при этом межкристаллическое взаимодействие носит антиферромагнитный характер. Установлено, что преобладающим является внутрикристаллическое ферромагнитное взаимодействие, в то время как межкристаллическое взаимодействие носит антиферромагнитный характер. В поле 2000 Oe и 5000 Oe при температуре 5 K магнитный момент даже не является положительным. Эти зависимости были получены после того, как образец находился в большом отрицательном поле. Магнитный момент примерно равен остаточному моменту на петле гистерезиса при температуре 5 K при постепенном увеличении внешнего поля, например, с шагом 250 Oe, этот момент увеличивается до 1,2 emu/g при 2000 Oe. На основании результатов магнитостатических измерений было установлено, что гистерезисные петли намагниченности наблюдаются при низких температурах.

Ключевые слова: золь-гель метод, рентгеновская дифракция, иттрий-кальциевый хромито-манганит, антиферромагнитное взаимодействие.

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