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Synthesis and Magnetic Properties of Polycrystalline $La_{0.7}Sr_{0.3}MnO_3$ Manganite Films

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The magnetic properties of manganite films obtained by extraction pyrolysis have been investigated. The effect of solution concentration and annealing conditions on the magnetic properties of the materials under study has been established. It has been found that thermomagnetic effects in the materials depend on annealing temperature and external magnetic field.

Keywords: magnetic properties, thin films, synthesis, pyrolysis; manganites.

Introduction

Manganites with the perovskite structure have been the subject of intensive study due to the presence of colossal magnetoresistance (CMR) [1]. The properties of these compounds depend on their composition, preparation conditions, and dimensionality of a system [2]. Current concepts [1 and 3] attribute the CMR effect to the phenomenon of electronic phase separation. The transition

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of a system to the granular or quasi-two-dimensional state may substantially change the energy structure of a substance, which adds new properties to the system. Granular or polycrystalline manganite films can be obtained by different methods [4–8]. It was found that the magnetic and transport properties of the film structures strongly depend on grain size. For example, a decrease in particle size from 60 to 10 nm at $T < 300\,K$ yields an increase in magnetoresistance by a factor of about 5 and changes conductivity from metallic to semiconductor [9]. It was shown [10] that with the change in grain size from 14 to 27 nm, the Curie temperature grows from 220 to 234 K.

In this study, we synthesized $La_{0.7}Sr_{0.3}MnO_3$ manganite films using the extraction pyrolytic method and investigated their magnetic properties.

1. Synthesis

It is known that the use of a solution technology results in the formation of nanostructured magnetic samples. The extraction pyrolytic method provides stoichiometric accuracy and purity of complex oxides. Sometimes, upon extraction of various metals, heteronuclear compounds are formed. The formation of the heteronuclear co-extractable compounds allows one to obtain materials with the uniform distribution of components during pyrolytic synthesis, which is indirectly confirmed by the thermogravimetric study of the extracts and their mixtures.

The thermogravimetric analysis showed that Sr, Mn, and Ca carboxylates decompose in the narrow temperature range 620–780 K with the formation of highly reactive oxides, which is confirmed by the calculated weight loss curves. Thermal decomposition of a mixture of the carboxylates goes in two stages with the exo effects at 470 and 700 K. Within the temperature range 470–560 K, organic acids are evaporated, which is superimposed on thermal decomposition of the carboxylates.

Successive annealing of a homogeneous amorphous oxide leads to significant reduction of the temperature at which the complex oxide phase is formed. Study of the phase formation showed that, unlike the solid-state synthesis at which $LaSrMnO_3$ is formed at the temperature of 1570 K, the phase formation of the pyrolysis products starts at 920 K and finishes at 1000 K; as a result, a single-phase lanthanum manganite is obtained.

In order to study the magnetic properties of the polycrystalline $La_{0.7}Sr_{0.3}MnO_3$ manganite films, we synthesized the samples by the extraction pyrolytic method. The method consists in extraction of components from water solutions, mixing the components in a specified ratio, deposition of the solution onto a substrate, and subsequent pyrolysis. A film was deposited onto a fused quartz substrate by centrifuging with a rotational speed of 3000 rpm.

The formation of an oxide film is significantly affected by the concentration of the deposited solution. To obtain manganite films, the solutions with concentrations of 2 and 4 % were used. After deposition of a moistening film, the samples were dried over a heater at the temperatures 390–410 K. Then, the films were placed into a vertical furnace. After pyrolysis at a temperature of 770 K for 5–10 min, the films were cooled for 2 min beyond the furnace and the next layer was deposited. During pyrolysis, an amorphous or fine-crystalline layer was formed. Ten layers were deposited in total. The obtained films were annealed in air at different temperatures.

2. The Effect of Synthesis Conditions on the Structure and Magnetic Properties of the Manganite Films

The physical properties of the polycrystalline $La_{0.7}Sr_{0.3}MnO_3$ films were investigated on the samples obtained at solution concentrations of 2 and 4 %.

The X-ray fluorescent analysis confirmed that film composition corresponds to the chemical formula $La_{0.7}Sr_{0.3}MnO_3$.

The results of X-ray diffraction showed that the films obtained at the pyrolysis stage and not subjected to successive annealing were amorphous. Successive annealing led to the formation of a polycrystalline single-phase perovskite. Typical diffraction patterns of the films after annealing are shown in Fig. 1. The grain size calculated by a half-width of the main peak o f the diffraction patterns is 28 nm.

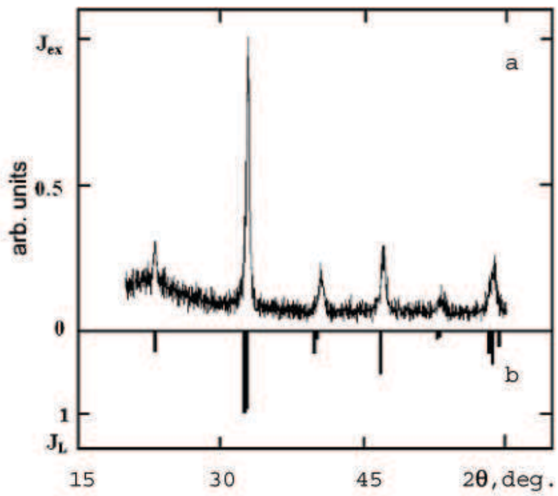

Fig. 1. Diffraction patterns of the annealed $La_{0.7}Sr_{0.3}MnO_3$ film (a) and the manganite of the same composition from [3] (b)

The results obtained with an atomic force microscope showed that the manganite films after pyrolysis are amorphous, while the films annealed in air contain grains whose sizes depend on annealing temperature and time (Fig. 2 and Fig. 3). In particular, the increase in annealing time from 10 minutes to 1 hour results in the grain growth from 30 to 180 nm.

Investigations of the magnetic properties of the manganite films showed that at the same annealing temperature (Ta = 1000 K) the magnetic properties are determined by solution concentration. Fig. 4 depicts the magnetic moment of a unit area for films 1 (part 1) and 2 (part 2) versus magnetic field (part a) and temperature (part b). The curves were taken in weak magnetic fields with a SQUID magnetometer. One can see that when solution concentration is 4 % (film 1), the field dependence of the magnetic moment is extended and not saturated.

The observed difference between the films is also revealed in the temperature behavior of the magnetic moment. For film 1, the thermomagnetic effects are observed and the temperature dependence is typical of spin glasses. Similar dependencies were reported in the study of the

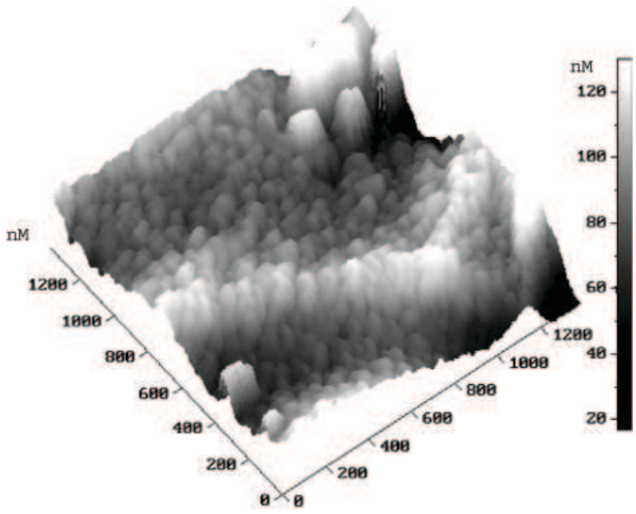

Fig. 2. Micrographs of the $La_{0.7}Sr_{0.3}MnO_3$ film surface after annealing at 1000 K for 10 minutes (solution concentration is 4 % and grain size is 30 nm)

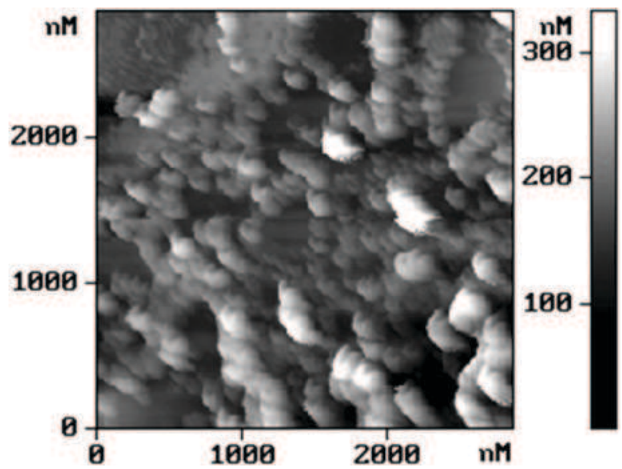

Fig. 3. Micrographs of the $La_{0.7}Sr_{0.3}MnO_3$ film surface after annealing at 1000 K for 1 hour Grain size is 180 nm

magnetic properties of diluted lanthanum manganites [5]. For film 2, the temperature behavior of the magnetic moment is typical for ferromagnets.

One can see that inhomogeneity of the magnetic structure is determined by solution concentration. This correlation may be attributed to separation of the magnetic phases due to chemical heterogeneity at high solution concentrations.

We investigated the magnetic properties of the films synthesized using 2 % solution as a function of annealing conditions. All the samples were deposited in a single cycle and had the thickness $t = 270$ nm. It was established that magnetization of the films obtained at the same pyrolysis temperature depends on both temperature and time of annealing. Film sample

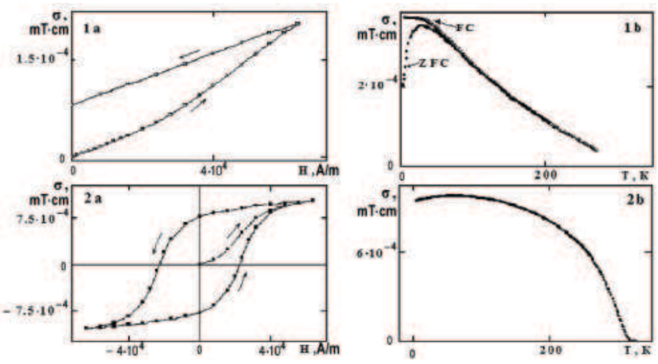

Fig. 4. The dependencies of the magnetic moment of a unit area for films 1 and 2 on (a) magnetic field ($T = 4.2\,\mathrm{K}$) and (b) temperature ($H = 40\,\mathrm{kA/m}$). Film thicknesses are 350 and 270 nm

F1 was first annealed at 870 K and studied; then, the second annealing 1000 K was performed. Film sample F2 was annealed only at 1000 K. Each annealing was two hours long. The field dependencies of magnetization taken from films F1 and F2 showed the following. Sample F1 does not exhibit saturation in fields $H < 80\,\mathrm{kA/m}$ after the first annealing and the hysteresis loop represents a superposition of two loops. After the second annealing, magnetization increases, saturation is reached, and the hysteresis loop is characteristic of a ferromagnet. However, the final parameters of the magnetization curve of this film differ from the analogous parameters of film F2 whose loop is wider and saturation magnetization is lower.

As is seen in Fig. 5, the temperature dependencies of magnetization for films F1 and F2 strongly differ.

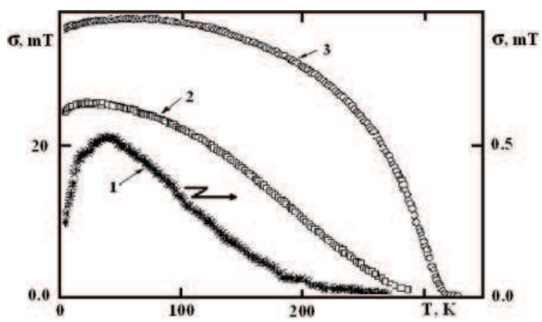

Fig. 5. Temperature dependencies of magnetization for the manganite films prepared from 2 % solution: (1) F1, $Ta = 870\,\mathrm{K}$; (2) F1, $Ta = 1000$ K; (3) F2, $Ta = 1000\,\mathrm{K}$ (all the measurements were made in $H = 64\,\mathrm{kA/m}$)

After the first annealing, sample F1 reveals the strong thermomagnetic effects (curve 1) and the temperature dependence of magnetization is similar to that typical of spin glasses. After the second annealing, the situation noticeably changes; however, the $\sigma(T)$ curve still has a cusp (curve 2). For film F2, the thermomagnetic effects are much weaker and the magnetization behavior is close to that typical of ferromagnets. Note also a significant difference in the Curie temperatures (T_c) and the magnetization behavior in the vicinity of T_c between samples F1 and

F2. After annealing, the Curie temperature grows and the transition becomes brighter.

3. Conclusions

In this study, the following results have been obtained:
• For the first time, the $La_{0.7}Sr_{0.3}MnO_3$ manganite films were synthesized by extraction pyrolysis.
• Using the X-ray diffraction analysis, the formation of a polycrystalline single-phase perovskite on a fused quartz substrate upon isothermal annealing in air at temperatures of 1000 K and higher has been established.
• The effect of the synthesis conditions on the magnetic properties of the films has been demonstrated; in particular spin-glass-like behavior of magnetic moment temperature dependence of films obtained at solution concentration of 4 % and also at annealing temperature of 870 K has been found.

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Синтез и магнитные свойства поликристаллических пленок манганита $La_{0.7}Sr_{0.3}MnO_3$

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В статье представлены результаты исследования магнитных свойств пленок манганита, полученных экстракционно-пиролитическим методом. Показано влияние концентрации раствора на магнитные свойства. Установлено существование термомагнитных эффектов, зависящих от температуры отжига и магнитного поля.

Ключевые слова: магнитные свойства, тонкие пленки, синтез, пиролиз, манганиты.