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Forming of Nanoscale Structure in Manganite Ceramics with Superstoichiometric Manganese

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The new method for obtaining of the nanoscale structure by means of superstoichiometric manganese in lanthanum manganite $(La_{0.65}Sr_{0.35})_{1-x}Mn_{1+x}O_{3\pm\Delta}$ (x = 0, 0.1, 0.2) ceramics sintered at 1500 °C is developed. The increasing of x content from 0.1 to 0.2 leads to forming internal nanosize multilayer structure of ceramic grains with layer size of 190 and 280 nm, respectively. The correlation between such nanostructure and magnetoresistive properties is revealed.

Keywords: Colossal magnetoresistance, Lanthanum manganite, Nanostructure, Magnetic multilayers.

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1. INTRODUCTION

Recently the magnetic multilayered nanosystems are investigated intensively as objects already found an application in microelectronics including non-volatile memory devices, sensors, and semiconductor circuits. These applications are related primarily to their magnetic and transport properties in nanoscale multilayer systems which significantly differ from the properties of homogeneous macrosize systems. Thus, in addition to applied interest the magnetic multilayer systems are of a great interest from the point of view of analysis of the conduction mechanisms and the interlayer exchange mechanisms in magnetic nanostructures. By "nanostructure" is understood both a multilayer system which the layer thickness may range from several angstroms to several nanometers, and a system whose transverse dimensions are kept within these borders (for example, nanocomposites). In magnetic nanocomposites [1] a high magnetoresistance was discovered (to 10 %), and depending on the concentration of magnetic nanoparticles in dielectric matrix in the nanocomposite either tunneling or metallic conductance will prevail. It is necessary noted that, no matter the large magnetoresistance and the simple manufacture technology, the reversal magnetization processes in nanocomposites occur in relatively high magnetic fields (up to several tens of kOe) that to hinder their broad applied application.

An important problem encountered in the practical application of nanomaterials in electronic devices is the problem of the stability of their physical characteristics. Relaxation processes and interactions with the environment in nanosystems, containing a large number of interfaces, pores and vacancies can have a significant effect on the properties of their important applications both positive and negative ways.

In this work new method of obtaining of nanosize structure in $(La_{0.65}Sr_{0.35})_{1-x}Mn_{1+x}O_{3\pm\Delta}$ (x = 0, 0.1, 0.2) manganite ceramics by means of superstoichiometric manganese, and results of study of its magnetoresistive properties are presented.

2. EXPERIMENTS

The ceramic samples were prepared from nanocrystalline manganite powder with different superstoichiometric manganese contents produced by the unique method [2]. X-ray diffraction measurements showed that the final powders have a single phase perovskite-like structure. To obtain ceramics, the powders compacted in pellets were sintered in two stages at 1000 °C for 5 hours, and at 1500 °C for 2 hours in air in slow heating / cooling mode (100 °C/h). To restore the oxygen stoichiometry all samples were annealed in air at 300 °C for 5-6 h. The microstructure, grain size and

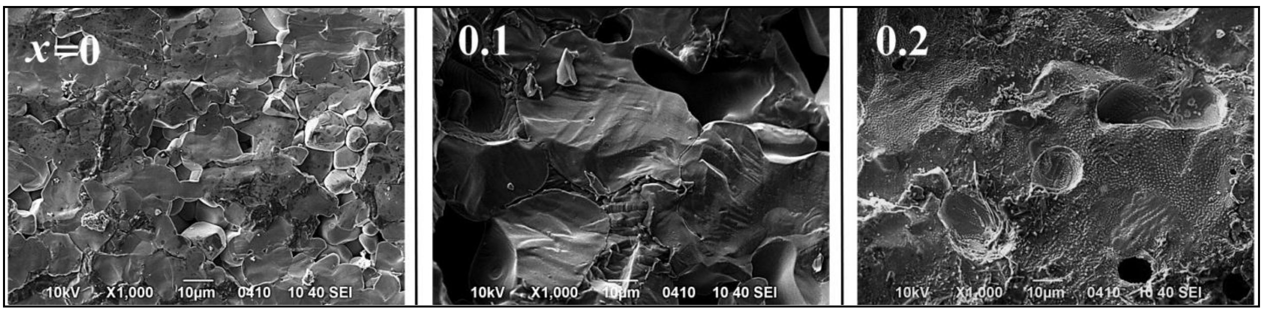

Fig. 1 – SEM images of cleaved surfaces of $(La_{0,65}Sr_{0,35})_{1-x}Mn_{1+x}O_{3\pm\Delta}$ ceramic samples with different contents of x sintered at 1500 °C.

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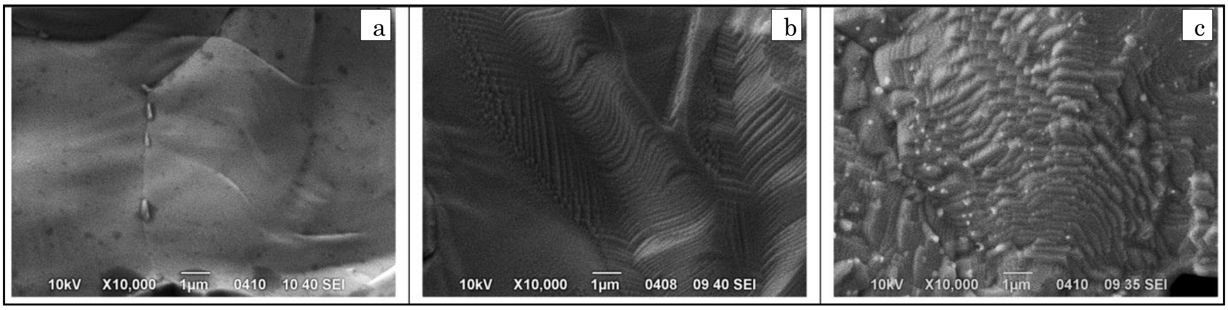
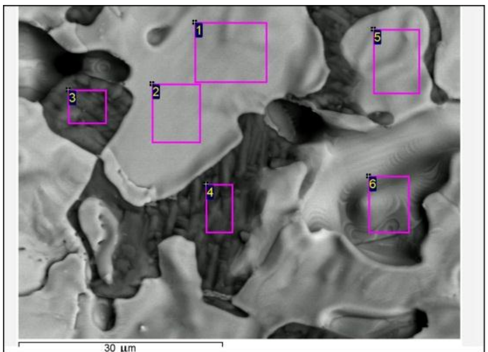


Fig. 2 – SEM images of thermally etched cleaved surfaces of $(La_{0.65}Sr_{0.35})_{1-x}Mn_{1+x}O_{3\pm\Delta}$ ceramic samples $x = 0$ (a), 0.1 (b), and 0.2 (c).

elemental analysis of ceramic samples were investigated by a scanning electron microscope (SEM) JEOL JSM-6490LV with energy-dispersive spectroscope (EDS) INCA Penta FETx3. The samples were split, the cleaved surfaces were thermally etched at 1000 ° C for 3 hours for revealing of internal grain microstructure. The imaginary part of magnetic susceptibility was measured by a modulation method [3] for inductive frequency plant (operating frequency of 5 MHz), the amplitude of modulation field was $H_{\text{mod}} = 4$ Oe. Magnetoresistance was measured by using standard four probe method in applied magnetic fields $H = 0$ and 5 kOe in the temperature range of 80-400 K.

3. RESULTS AND DISCUSSIONS

The experimental results of SEM investigations of the ceramic samples with different superstoichiometric manganese contents shown in Fig. 1. It seems the increasing x from 0 to 0.2 leads to a rise in the grain size on the order of magnitude and densification of material. However, after thermal etching of cleaved surface in samples with x = 0.1 and 0.2 (see Fig. 2 (b) and (c)) a complex nanosize multilayered structure of grains was found with average layer thicknesses of 190 and 290 nm, respectively. Moreover, the layers have not only



Spectrum	O	Mn	Sr	La
	atom.%	atom.%	atom.%	atom.%
1	60.81	19.29	5.67	14.23
2	56.78	21.90	5.43	15.88
3	50.95	48.40	0.13	0.53
4	63.93	34.74	0.23	1.09
5	61.96	18.95	5.46	13.63
6	67.81	15.60	5.39	11.20
Average	60.38	26.48	3.72	9.43
Standard deviation	5.87	12.62	2.74	6.84
Max	67.81	48.40	5.67	15.88
Min	50.95	15.60	0.13	0.53

Fig. 3 – EDS quantitate analysis of etched cleaved surface of $(La_{0.65}Sr_{0.35})_{0.9}Mn_{1.1}O_{3\pm\Delta}$ ceramic sample ($x = 0.1$)

different thicknesses, but also a different orientation. The sample with $x = 0$ is no layers (Fig. 2a). Such sharp grain growth and the emergence of layered grain structure are clearly associated with the presence of superstoichiometric manganese and its participation in the formation of the microstructure during sintering. According to [4] at sintering of multicomponent materials the melting of some component (in this case, the excess manganese) is possible, and appearance of a liquid phase substantially influences the process of sintering and forming the microstructure. In witness of this supposition the EDS microanalysis results are adduced in Fig. 3. As seems the release of excess manganese on the grain boundary is observed which is accompanied by decrease in its percentage in the grain. In addition, the appearance of layered structure within the grain is most likely due to the mechanism of sectorial-zoning growth [5, 6] which is implemented during the crystal growth in impurities presence. In this case, such layered growth can be carried out in the dissolution-precipitation process during sintering in the liquid phase presence [7] which is melted excess manganese. This evolution of ceramics microstructure affected its properties as well. Fig. 4 shows the temperature dependence of the imaginary part of magnetic susceptibility in manganite samples with different content superstoichiometric Mn. It seems the sample with $x = 0$ has a single phase with a Curie temperature (T_C) of 351 K corresponding to a given composition. However, in the samples with $x = 0.1$ and 0.2 there are several magnetic phases with different T_C. Fig. 4 shows that the sample with $x = 0.1$ has two ferromagnetic phases with $T_C = 351$ and 335 K while sample with $x = 0.2$ has three phases with $T_C = 336$, 332, and 309 K, respectively. This fact indicates that such magnetic inhomogeneity is most likely due to the appearance of the nanostructure within the grain which is different in chemical composition (with different contents of excess Mn and Sr) [8]. The validly of the above assumptions also is confirmed by the experimental results of CMR effect measuring (Fig. 5). As can be seen, with increasing x the CMR peak rises in almost 2.5 times, moreover, its temperature decreases by 50 K and the under-peak area broadens along the temperature axis. However, all transition areas don't shift along temperature axis and are part of each other indicating the presence of several magnetic phases in the ceramics with different contents of excess Mn and Sr with increasing x. It should be noted that the low-temperature curves are significantly different from each other. Despite the increase in grain size and decrease the number of boundaries and, consequently, decrease the

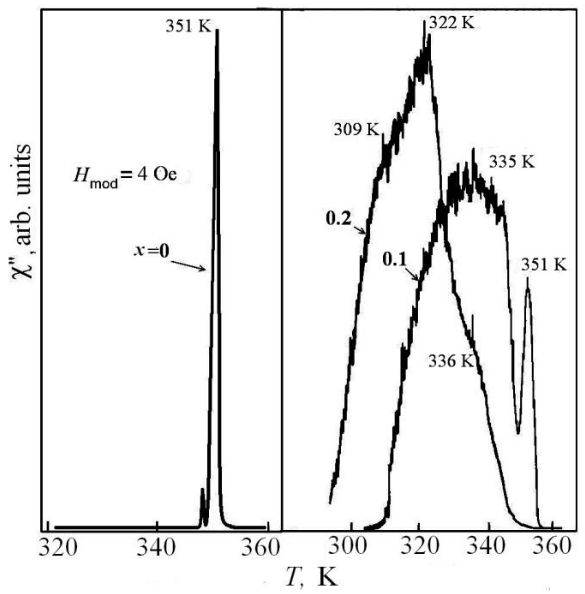


Fig. 4 – The imaginary part of magnetic susceptibility for determination of T_C in ceramic samples with different content of x

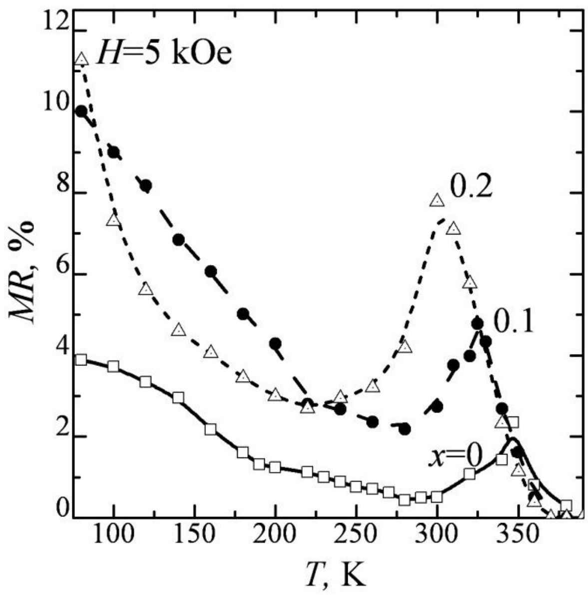


Fig. 5 – Temperature dependence of negative magnetoresistance of ceramic samples with different content of x

tunneling type magnetoresistance [8], but its value rises in with increasing x. Such behavior is probably related to nanosized layered grain structure, as well as different thicknesses of these layers.

4. CONCLUSION

In summary, for the first time it is found that the presence of superstoichiometric manganese leads to a forming internal nanosize grain structure of ceramics. The increase in x from 0.1 to 0.2 promotes changing the nanostructure and the layer thickness from 190 to 290 nm which are different in strontium and excess manganese contents. These changes of the microstructure lead to the magnetic inhomogeneity of ceramics, reduction of T_C and CMR peak temperature, and an increase in peak values of 2.5 and higher tunnel magnetoresistance at low temperatures.

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