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Magnetoresistance of composites based on manganite $La_{0.7}Sr_{0.3}MnO_3$ and oxides NiO, TiO_2

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Magnetoresistive properties of ceramic composites based on ferromagnet $La_{0.7}Sr_{0.3}MnO_3$ and oxides of nickel and titanium with different ratios of components were studied. Two methods were used to prepare the composites: calcination of $La_{0.7}Sr_{0.3}MnO_3$ compositions mixed with dispersed titanium and nickel powders, and $La_{0.7}Sr_{0.3}MnO_3$ mixed with oxides of these metals at a temperature of 1150 °C. For the compositions 98% $La_{0.7}Sr_{0.3}MnO_3$ /2% TiO_2 and 88% $La_{0.7}Sr_{0.3}MnO_3$ /12% NiO (mass%) the negative magnetoresistivity reaches 7.5

Keywords: ferromagnet, oxides, manganite, composite, spin-dependent tunneling, negative magnetoresistance.

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The effects of spin-dependent tunneling of electrons in weak constant magnetic fields have been studied for a long time and have practical applications in superlattices of ferromagnetic metals [1,2]. It is of interest to examine the magnetoresistive capabilities of ceramic ferromagnet–non-ferromagnet compositions, where spin-dependent tunneling normally manifests itself near the so-called percolation threshold [3]. The Slonczewski model [4] is used to characterize the conductance in this case. Such conditions are optimum for the formation of multiple tunneling barriers (in other words, magnetic tunneling contacts) [5]. Both ferromagnetic *d*-metals and manganites may be used as ferromagnetic components [3.5–10]. The methods of vacuum sputtering of *d*-metals or ferromagnetic manganite $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) in the form of thin layers have been used most often in the preparation of magnetoresistive composites [3,5].

In contrast to [3,5], the research reported in [6,7] was focused on the procedure of fabrication and magnetoresistive properties of LSMO-based composites where the second component was germanium oxide or copper oxide. In the former case, LSMO was synthesized directly in a mixture with germanium oxide in atmosphere at a temperature of approximately 1100 °C. In [7], the initial compositions before heat treatment at a temperature of ~ 1000 °C were mixtures of pre-synthesized LSMO and dispersed copper. With this fabrication procedure, LSMO crystallites were „wrapped“ in copper oxides, and the resulting ceramics demonstrated a negative magnetoresistance (MR) of approximately 7 % at room temperature in a constant magnetic field of 15 kOe.

The aim of the present study is to establish the relation between the magnetoresistance magnitude of composites based on ferromagnetic LSMO and TiO_2 and NiO oxides and their composition and method of fabrication.

The study is the first to use dispersed titanium (GOST TU 14-22-57–92) and nickel (GOST 9722–97) powders with a particle size up to 100 μm and synthesized manganite LSMO in fabrication of composites with different ratios of components. Compositions based on LSMO and titanium oxide TiO_2 (GOST TU 6-09-3811–79) in the rutile phase and nickel oxide NiO (GOST TU 6-09-4125–80) were also synthesized for comparison. The percentage of the ferromagnetic LSMO phase ranged from 1 to 99 mass% depending on the ratio of components. Following homogenization and pressing under a pressure of 300 MPa, the samples underwent heat treatment in atmosphere at a temperature of 1150 °C for 3 h. The composites were then subjected to full-profile X-ray diffraction analysis (CuK_α radiation, $\lambda = 1.5406$ Å) in order to determine the phase composition. The microstructure of composites was examined using an EVO 40 (Carl Zeiss, Germany) scanning electron microscope. Electrodes were deposited in the reaction of silver reduction from silver nitrate at a temperature of 550 °C. The electrical resistance was measured using the two-electrode method in a constant magnetic field with a strength up to 15 kOe at room temperature with the current directed along and across the field. The measurements in zero field were performed at temperatures ranging from room temperature to 180 °C.

The magnetoresistance was calculated as

$$\mathrm{MR} = [(R(H) - R(0))/R(0)] \cdot 100\,\%, \qquad (1)$$

where $R(0)$ is the sample resistance in zero external field and $R(H)$ is its resistance in a magnetic field.

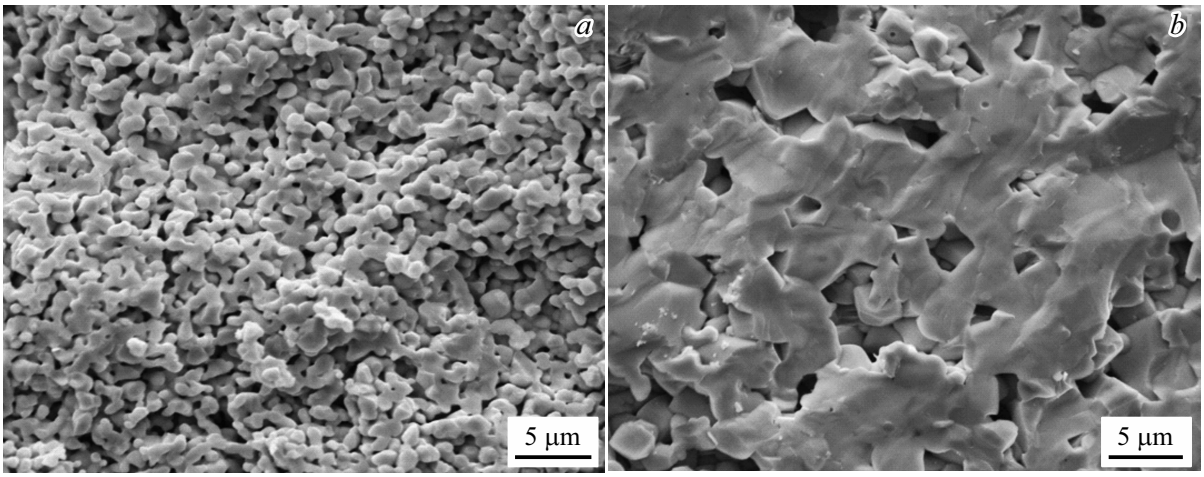


Figure 1. *a* — microstructure of the composite with an initial composition of 90 % LSMO/10 % Ni after heat treatment; *b* — microstructure of the composite with an initial composition of 90 % LSMO/10 % NiO after heat treatment.

The influence of titanium oxide in the rutile phase added to LSMO on the magnetoresistive properties of LSMO/TiO_2 composites was characterized in [8,9]. The MR values achieved for 98 % LSMO/2 % TiO_2 (mass%) compositions were 20 % in magnetic fields of approximately 10 kOe at a temperature of 77 K [8,9]. At room temperature, the reported MR was at the level of a fraction of a percent. According to the data on resistivity of LSMO/TiO_2 compositions from [8,9], the resistance increases sharply when the titanium oxide content exceeds 2 mass%. This could be indicative of crossing of the percolation threshold, but the authors made no mention of this. In the present study, the crossing of the percolation threshold in the region of titanium oxide content of 2 mass% was established.

Figure 1 presents the characteristic microstructure of the two studied composites differing in the procedure of their fabrication. It is evident that the 90 % LSMO/10 % Ni composition has a porous structure consisting largely of individual grains with rounded edges. The pattern for the initial composition of 90 % LSMO/10 % NiO differs significantly from that observed for 90 % LSMO/10 % Ni, with cleavage proceeding mostly along the grains with a seemingly homogeneous internal structure. The average size of LSMO agglomerates surrounded by nickel oxide is close to 1 μm in the former case and 10 μm in the latter case. Note that a similar pattern of differences in microstructure is observed for the LSMO/Ni, LSMO/NiO, LSMO/Ti, and LSMO/TiO_2 initial compositions within a wide range of titanium and nickel oxide concentrations.

According to X-ray diffraction data, no changes in the LSMO cell parameters potentially indicative of the introduction of titanium or nickel atoms into the LSMO structure are seen in the LSMOTiO_2, NiO composites within the entire studied range of titanium and nickel oxide concentrations. The estimate of the relative change in average sizes of coherent scattering regions (CSRs) calculated using the Scherrer formula reveals the influence of the initial composition (prior to heat treatment) on them. The CSR size in composites with the LSMO/Ti initial composition decreases by ~ 20 % (from 267 to 218 Å) with an increase in titanium content from 1 to 4 mass%. In composites with the LSMO/Ni initial composition, the CSR size decreases approximately by 30 % (from 320 to 213 Å) with an increase in initial nickel content from 2 to 15 mass%. As the oxide content increases from 1 to 15 mass% in composites with the LSMO/(NiO or TiO_2) initial composition, the CSR size varies only slightly: from 283 to 267 Å (by 9 %). This CSR fragmentation is likely to affect the microstructure, which, in turn, affects the nature of dependence of magnetoresistance on the concentration of titanium or nickel oxides in two methods of preparation of composites.

According to the obtained results, compositions with a low titanium oxide ($\leqslant 2$ mass%) and nickel oxide ($\leqslant 12$ mass%) content are far from the transition in terms of the ratio of metal–dielectric components at room temperature.

To illustrate the ferromagnetic metal–paramagnetic dielectric temperature phase transition, Fig. 2 presents an example temperature dependence of resistivity for the 98 % LSMO/2 % TiO_2 composition. This experimental dependence makes it clear that the metallic conductivity of the composite changes to the semiconductor one with an activation energy from 0.20 to 0.75 eV as the TiO_2 oxide content exceeds 2 mass%. In the case of nickel oxide, a similar dependence is seen above 12 mass%. These data suggest that compositions with component ratios of 98 % LSMO/2 % TiO_2 and 88 % LSMO/12 % NiO are near the percolation threshold.

The room-temperature dependences of resistivity on the magnetic field strength for compositions near the percolation threshold are shown in Fig. 3.

It should be noted that no saturation of magnetoresistance was observed in our experiments up to a magnetic field

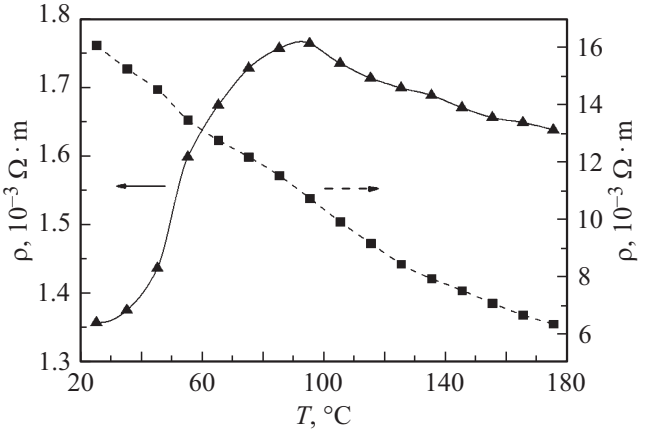


Figure 2. Temperature dependences of resistivity of the 98 % LSMO/2 % TiO_2 (triangles) and 97 % LSMO/3 % TiO_2 (squares) composites recorded without the influence of an external magnetic field.

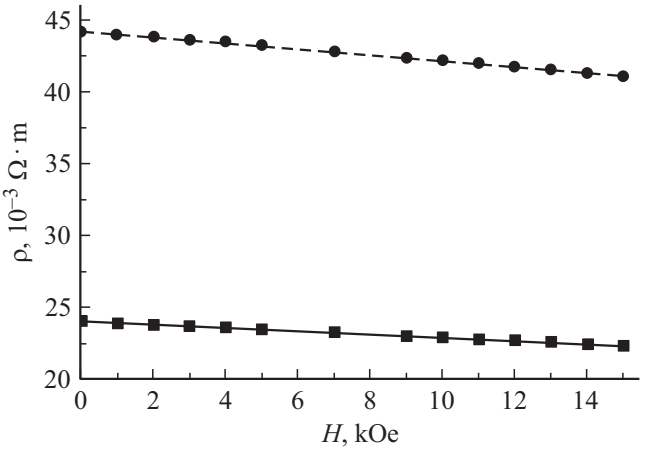


Figure 3. Dependences of resistivity of the 98 % LSMO/2 % TiO_2 (circles) and 88 % LSMO/12 % NiO (squares) composites on the strength of a constant magnetic field at room temperature.

strength of 15 kOe, and the dependence of magnetoresistance on the magnetic field strength is linear, which is convenient for application in constant magnetic field sensors. The specific features of magnetoresistance of compositions prepared in two different ways with different concentrations of metals and their oxides are presented in Fig. 4.

It is worthy of note that, compared to the dependences for compositions with dispersed metals being the initial components, the dependence of magnetoresistance on the oxide content for composites initially containing oxides of nickel and titanium metals changes more sharply.

Thus, the resistance reduction in a constant magnetic field in the 98 % LSMO/2 % TiO_2 and 88 % LSMO/12 % NiO compositions prepared using an original fabrication procedure is an extrinsic effect of magnetoresistance associated with spin-dependent intergranular tunneling of carriers in a constant magnetic field. Ceramics with the 98 % LSMO/2 % TiO_2 and 88 % LSMO/12 % NiO compositions, which are suitable for practical application, have an isotropic magnetoresistance of up to 7.5 % at room temperature and a somewhat extended region of high magnetoresistance values near the component concentrations in the percolation region. Note that, in contrast to the present study, the authors of [9] did not detect the magnetoresistance of LSMO/TiO_2 composites at room temperature.

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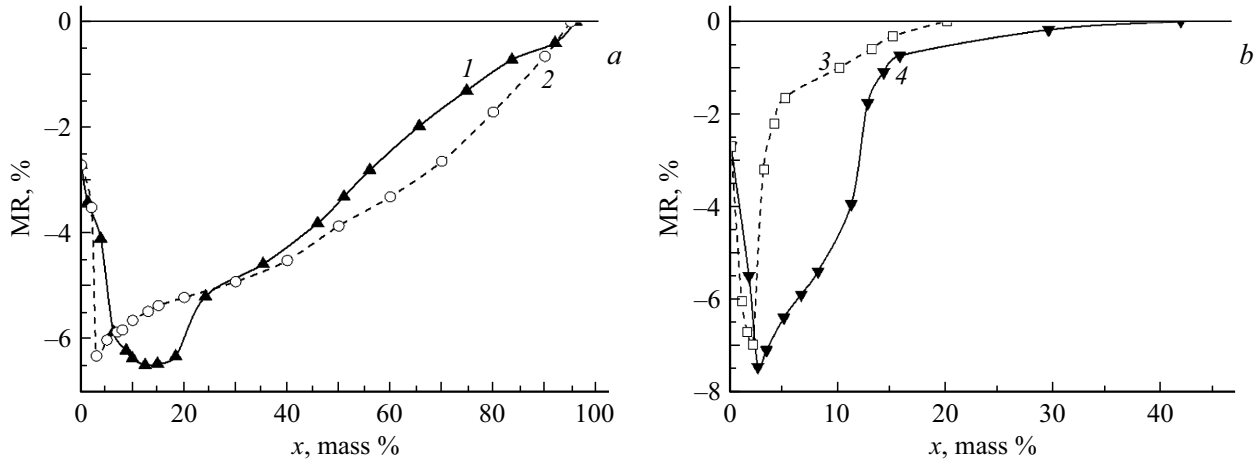


Figure 4. Dependences of magnetoresistance of different compositions after synthesis on percentage x of metals and their oxides. *a*) *1* — initial composition LSMO/Ni, *2* — LSMO/NiO; *b*) *3* — initial composition LSMO/Ti, *4* — LSMO/TiO_2.

Conflict of interest

The authors declare that they have no conflict of interest.

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