Low-field magnetoresistance of $(1 - x)\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3 + x\text{La}_{1.5}\text{Sr}_{0.5}\text{NiO}_4$ nanocomposite

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Abstract
In this report we present low-field magnetoresistance (LFMR) of $(1 - x)\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3 + x\text{La}_{1.5}\text{Sr}_{0.5}\text{NiO}_4$ $(x = 0–0.3)$ nanocomposites at temperatures ranging from 30 to 300 K. These materials were synthesized by reactive mechanical ball milling combined with the heat treatment. Experimental results have revealed that the Curie temperature is almost independent of $x$, while the metal–insulator transition temperature shifts from 254 K for $x = 0.0$ to 65 K for $x = 0.2$. Particularly, the samples with $x \geq 0.25$ exhibit insulating properties. Magnetoresistance (MR) of all the samples is observed at an applied magnetic field of 3 kOe. In order to explore their MR nature at changing temperature, we analyzed carefully the obtained data basing on the phenomenological model related to the spin polarized transport (SPT) of conduction electrons at grain boundaries.

Keywords: manganite composites, grain boundary, electrical transport

Classification numbers: 5.02, 5.11

1. Introduction
In recent years, colossal magnetoresistance (CMR) in perovskite manganites of $\text{R}_{1-x}\text{A}_x\text{MnO}_3$ ($\text{R} = \text{rare-earth elements, and } \text{A} = \text{Ca, Sr, Ba, etc}$) has been studied extensively. Basically, two intrinsic and extrinsic CMR effects have been found in the manganite compounds. The intrinsic CMR effect has the maximum near the metal–insulator transition temperature ($T_{\text{MI}}$) accompanied by a simultaneously paramagnetic-to-ferromagnetic (PM–FM) transition at the Curie temperature ($T_{\text{C}}$). This effect is caused by the double exchange (DE) mechanism proposed by Zener [1]. However, the intrinsic CMR effect in perovskite manganites can only be triggered at high-magnetic fields of several Teslas, disqualifying them from practical applications. The extrinsic CMR effect is absent in a single crystal, and related to natural and artificial grain boundaries. This effect happens at low temperatures and low magnetic fields. At low temperatures, moreover, the low-field magnetoresistance (LFMR) in polycrystalline manganites is very much pronounced, but its value drops sharply with increasing temperature and magnetic field. These manganite materials can be thus applied in sensors at low temperatures. Nowadays, researchers are focusing on obtaining a large value of the magnetoresistance (MR) at a low field. Many attempts have been made to enhance the LFMR effect in perovskite manganites by mixing CMR materials with a secondary phase, which could be an insulator [2–5], a magnetic material [6, 7], or a metal [8, 9]. Although these behaviours of the manganite composites have been extensively studied, their physical origins remain unknown. Andres et al [10] have proposed a phenomenological model as considering two parallel...
conduction channels for explaining the magneto-transport properties of polycrystalline manganites. After that, Li et al [11] have suggested the phenomenologic percolation model based on phase segregation to explain magnetotransport properties of polycrystalline manganites.

Though there are many reports on CMR composites, the studies related to a colossal dielectric material, such as La$_{1-x}$Sr$_x$TiO$_3$ (LSTO) [12], in the secondary phase of CMR composites have not been carried out. In this work we study the effects of LSNO on the electrical transport and LFMR properties of the (1 − x)La$_{0.7}$Ca$_{0.3}$MnO$_3$ + xLa$_{1.5}$Sr$_0.5$NiO$_4$ (LCMO/LSNO, with x = 0, 0.05, 0.10, 0.15, 0.20, 0.25 and 0.30 in mole) nanocomposites.

2. Experimental

(1 − x)La$_{0.7}$Ca$_{0.3}$MnO$_3$ + xLa$_{1.5}$Sr$_0.5$NiO$_4$ (0.0 ≤ x ≤ 0.3) nanocomposites were prepared by the reactive mechanical ball milling combined with the heat treatment. The reactive mechanical milling method was done on a D8000-Spex machine as follows:

In the first step, two material types in nanopowder of La$_{0.7}$Ca$_{0.3}$MnO$_3$ and La$_{1.5}$Sr$_0.5$NiO$_4$ were prepared:

- La$_2$O$_3$, CaO and Mn$_3$O$_4$ (99.9%) were chosen as starting materials to prepare La$_{0.7}$Ca$_{0.3}$MnO$_3$. The starting materials were thoroughly mixed and milled for 8 h. The powdered products obtained from the milling were then annealed in air for 3 h at 900° C [13].
- La$_2$O$_3$, SrO and NiO (99.9%) were chosen as starting materials to prepare La$_{1.5}$Sr$_0.5$NiO$_4$. The starting materials were thoroughly mixed and milled for 6 h. The powdered products obtained from the milling were annealed in air for 1 h at 700° C [13].

In the second step, both LCMO and LSNO powders were mixed with ratio of (1 − x)LCMO : xLSNO (0.0 ≤ x ≤ 0.3) and then were pressed into pellets. Finally, all the samples were sintered in air at 1000° C for 3 h. Phase structures of all the samples were checked by x-ray diffraction (XRD), using a SIEMENS D5000 diffractometer equipped with Cu-Kα radiation (λ = 1.5406 Å). Grain size and surface morphology of all the samples were observed by using the field emission scanning electron microscopy (FE-SEM). The magnetic properties of the samples were investigated by using a vibrating sample magnetometer (VSM) located at grain boundaries and on the surfaces of LCMO grains. The coexistence of two phases (LCMO and LSNO) was also confirmed on FE-SEM images (see figure 2). The representative FE-SEM images of LCMO/LSNO composites with x = 0 and 0.25 are shown in figures 2(a) and (b), respectively. The interface between LSNO and LCMO can be distinguished clearly. It can be seen that the grain size of pure LCMO is around 150 nm, and remains unchanged in the composite sample. Each LCMO grain is surrounded by LSNO grains without forming clusters, meaning that the LCMO and LSNO phases exist dependently for the x = 0.25 composite.

Magnetization measurements from 100 to 300 K were performed under the field cooling (FC) mode, with an applied magnetic field of 100 Oe. Temperature dependences of magnetization curves for LCMO/LSNO nanocomposites are shown in figure 3(a). The ferromagnetic (FM) to paramagnetic (PM) phase transition temperature (Tc) determined as the peak of dM(T)/dT (see figure 3(b)) is about 252 K and almost independent of LSNO content in the samples. A similar result has also been reported earlier on LCMO nanoparticles [4, 14, 15]. The magnetic transition temperature was practically the same for all the samples. This is the reason to confirm that the FM–PM phase transition is an intrinsic and intra-grain property of the LCMO phase. It can be inferred that no chemical reaction took place between the LCMO and LSNO in the viewpoint of magnetism. The magnetization value of the composites decreases with increasing x because of reducing the volume fraction of the LCMO phase and extra magnetic disorders due to LSNO dielectric content. This demonstrates that the ferromagnetic order is weakened, and magnetic disorders are increased with increasing LSNO content. It means that dielectric LSNO material diluted the magnetizatic properties of the composites. Magnetization values of all the samples were determined at T = 100 K and H = 10 kOe, see figure 3(c). The decrease in magnetization is only due to the increase of the dielectric material concentration in the samples.

The temperature dependence of resistivity was measured by the four-probe method between 30 and 300 K. As plotted in

![Figure 1. XRD patterns of LCMO/LSNO composites recorded at room temperature.](image-url)
Figure 2. FE-SEM images of LCMO/LSNO composites with \( x = 0 \) (a) and 0.25 (b).

Figure 3. Temperature dependences of magnetization under an applied field of 100 Oe for LCMO/LSNO composites (a), \( dM/dT \) (b), and \( x \) (LSNO) dependence of magnetization at 100 K under an applied field of 10 kOe (c).

Figure 4, the resistivity \( (\rho) \) (in the log scale) of the composites exhibits a strong dependence on the LSNO content. For all the samples, the resistivity increases very quickly as the LSNO content increases. Moreover, pure LCMO exhibits a transition of low temperature metallic to high temperature insulating with a sharp transition peak at \( T_{MI} = 251 \) K, which is also close to the Curie temperature. When the LSNO content is increased, the electric resistivity increases. The temperature \( T_{MI} \) is shifted successively towards lower temperatures, and the transition peak becomes broader. The values of the transition temperature are 251, 197, 145, 130 and 65 K for the samples with \( x = 0.0, 0.05, 0.10, 0.15 \) and 0.20, respectively. A similar increase of \( \rho \) values as well as the decrease of \( T_{MI} \) in the composites have been reported for LCMO : Al\(_2\)O\(_3\) [4], and LCMO : CuO [2]. The metal–insulator transition is completely suppressed in our experimental measurement range for doping levels higher than 20% \( (x > 0.2) \). The increase of electric resistivity and strong decrease of \( T_{MI} \) is caused by the LSNO induced disorders, and by increasing the paramagnetic insulating LSNO phase fraction in composites. This could result from an increase in electron scattering at LCMO grain boundaries, as a result of disorders due to LSNO doping in the LCMO grain boundary region. Moreover, in pure LCMO polycrystals, the electrical transport is achieved through a direct contact between LCMO grains. However, in doped composites, there are two kinds of conduction channels connected in parallel to each other [10, 16]. One is related to LCMO grains and the other is LSNO. Since the LSNO was mainly distributed at the grain boundaries and on the surfaces of LCMO grains producing energy barriers to the electrical transport process, an obvious higher resistivity was observed for the doped composites.

The magnetic-field dependences of MR for all the samples studied at 30 K are shown in figure 5. The MR ratio
A steady increase of MR as approaching \( T_c \), resulting from the intrinsic contribution \( \text{MR}_{\text{int}} \) was observed in a high magnetic field as reported by other authors \cite{17,18}.

In order to explain the magnetic-field dependence of magnetoresistance in LCMO granulars, we used a phenomenological model which takes into account the spin-polarized tunneling at the grain boundaries \cite{4,16}. The intrinsic contribution to the magnetoresistance is separated from the contribution coming from intergranular spin-polarized transport, paying attention to the domain wall motion across the grain boundaries in an applied magnetic field. According to this model we get the following expression:

\[
\text{MR} = -A' \int_0^H f(k) \, dk - JH - KH^2. 
\] (1)

Within the approximation of the model, in the zero field, domain walls are pinned at the grain boundaries as pinning centers with pinning strengths \( k \). The grain boundaries have a distribution of pinning strengths (defined as the minimum field needed to overcome a particular pinning barrier) given by \( f(k) \), expressed as follows:

\[
f(k) = A \exp(-Bk^2) + Ck^2 \exp(-Dk^2).
\] (2)

All the adjustable fitting parameters, \( A, B, C, D, J, K \) with \( A' \) absorbed in \( A \) and \( C \), determined from a nonlinear least square fitting to calculate the MR arising from spin-polarized transport (\( \text{MR}_{\text{spt}} \)), which is defined as follows:

\[
\text{MR}_{\text{spt}} = - \int_0^H f(k) \, dk.
\] (3)

The experimental MR(\( H \)) curves at 30 K for all the samples were fitted to equation (1) (solid lines in figure 5), and the values of \( \text{MR}_{\text{spt}} \) were also found. Under an applied field of 3 kOe, the values of the MR and \( \text{MR}_{\text{spt}} \) at 30 K are almost unchanged when \( x \leq 0.15 \), but they increase rapidly and reach maximum values with \( \text{MR} \sim 37\% \) and \( \text{MR}_{\text{spt}} \sim 36\% \) for \( x = 0.25 \) (see inset in figure 5). At this point, we must adduce percolation as the underlying effect most likely to explain the transport property and MR results presented before. It is necessary to justify the percolation threshold value obtained, which is around 25\% (\( x = 0.25 \)) for our composites. The MR upturn around the percolation value in composites could be related to the formation of an infinite cluster that will enormously increase spin tunneling between ferromagnetic regions.

4. Conclusion

Manganite/dielectric composite systems have been produced, and carefully characterized by several experimental techniques. We have observed that no reaction between LCMO and LSNO took place, and most LSNO was distributed at the grain boundaries. The electrical transport is progressively destroyed as LSNO concentration increases and the extent can be qualitatively predicted by a two channel model presented in the text. We have analyzed our experimental MR data following a phenomenological
model to separate out the MR arising from the spin-polarized transport and from the intrinsic contribution in our nanosized LCMO/LSNO composite samples. We also have been able to observe the percolation threshold in this system for 25% of the dielectric component and around this critical point a great increase of MR and MR\textsubscript{sp} has been detected.

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