

SURFACE MODIFICATION AND ELECTRON TRANSPORT OF (LaSr)MnO NANOPARTICLES

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Strontium-doped lanthanum manganite $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ (LSM) is the most used cathode material for solid oxide fuel cells (SOFCs). Although strontium-doping increases the electronic conductivity, the ionic conductivity of the material remains poor. In order to improve the efficiency of SOFCs, the ionic conductivity properties of the cathode must be improved without a significant decrease in its catalytic and electrical properties. The ionic conductivity of LSM can be increased by creating oxygen vacancies. However, as LaMnO_3 is doped with strontium, the favored mechanism of the charge compensation is cation oxidation.

As is well known, many complex oxides including lanthanum manganites easily form variation in stoichiometry or defects, including oxygen vacancies, at surface boundaries. So, by increasing the cathode material surface we increase the number and decrease the distance the oxygen vacancies must travel to the points where the electrolyte, air, and the cathode come together, and thus increase the effective ionic conductivity. As the grain-boundary transport processes in manganites depend sensitively on Mn-O-Mn bond state, which, in its turn, determines the magnetic properties of the compound [1], any structural disorder near the grain boundary of the nanoparticle can be easily detected through its surface magnetic disorder. That is why, in this report, oxide/oxide and oxide/metal (Ag) resistance, magnetoresistance (MR), and nuclear magnetic resonance (NMR) measurements have been performed to study the surface modification and electron transport of $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ nanoparticles.

For this study, $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ nanoparticles were synthesized by co-precipitation method using MW heating and ultrasound treatment [2]. In the first step stoichiometric amounts $\text{La}(\text{NO}_3)_3$, $\text{SrCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{CO}_3$ were dissolved in a liquid solution. All chemicals used in the synthesis procedure were reagent grade. Nanometer scaled $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ samples were then prepared directly by annealing at 1000°C for 60 min. The phase of the samples has been determined by x-ray diffraction. The $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ patterns of pure rhombic perovskite structure have been formed. However, using transmission electron microscopy (TEM), we find that the samples have been characterized by two morphology types (see Fig. 1.): by the particles of a relatively large size (100-200 nm) and shapes close to rectangular, and by fine scale (~ 50 nm) particles with isometric shape. Both types of particles have the same TEM image which corresponds to x-ray diffraction data. We suppose that two types of the particle morphology are due to the presence of two oxide phases on early stages of $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ syntheses processes.

The temperature dependencies of resistance and MR for $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ compact, as well as oxide/oxide junctions and $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3/\text{Ag}$ metallic contacts have been investigated. We observe normal MR (a smaller resistance in higher magnetic field) for $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3/\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ interface. For metallic $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3/\text{Ag}$ interface it has been found that the minimum resistance is observed at the coercive field and increases at higher fields (see Fig. 2.). We discuss the MR results in a model of an extrinsic surface effect on oxide grain contacted

with silver. It is reasonable to consider that, in case of LSM/Ag metallic contact, the Ag exists in the form of metal around grain boundary and helps to increase the local Mn spin disorder. So, for at least several monolayers below the surface boundary the Mn-O-Mn bond state is considerably different from the bulk one.

For ^{55}Mn NMR spectrum of $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ nanoparticles at $T = 77$ K the dominant line is the one at $f = 377$ MHz, that is typical for mixed-valent metallic like manganites and it corresponds to fast hopping of electron holes ($f_{\text{hop}} \gg f_{\text{NMR}}$) among the Mn sites. Closer inspection reveals an additional relatively small contribution at $f = 321$ MHz, corresponding to quasilocated ($f_{\text{hop}} < f_{\text{NMR}}$) Mn^{4+} ions. This line may be attributed to the surface of the nanoparticles, where the double exchange interactions should be reduced because of an existence of the broken bonds. In accordance with such attribution, the Mn^{4+} line disappears after firing the sample, which results in the strong increase of the average grain size of the particles.

In conclusion, we have performed the oxide/oxide and oxide/Ag resistance, MR, and NMR measurements to study the surface modification and electron transport of $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ nanoparticles. We discuss the results in a model of the structural disorder near the grain boundary that we have detected through the surface magnetic disorder. We report the observation of an inverse MR (a lower resistance in lower magnetic field) for $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3/\text{Ag}$ metallic interface and a normal MR (a smaller resistance in higher magnetic field) for $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3/\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ interface.

1. M. Ziese, Rep. Prog. Phys. 65, 143 (2002).

2. I. Danilenko, *et. al.*, Pros. 9-th CIMTEC World Ceramics Congress, Techna, Faenza- Part A, 305 (1999).

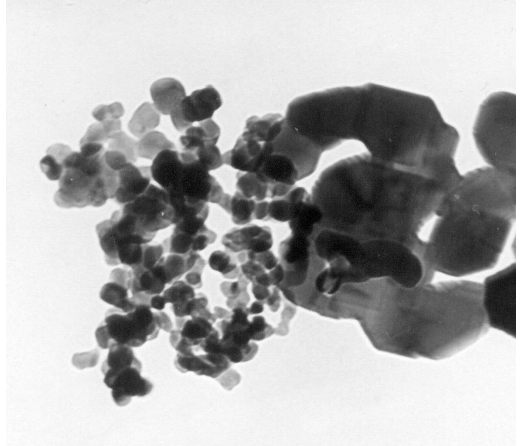


Fig. 1. TEM image of $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ representative sample.

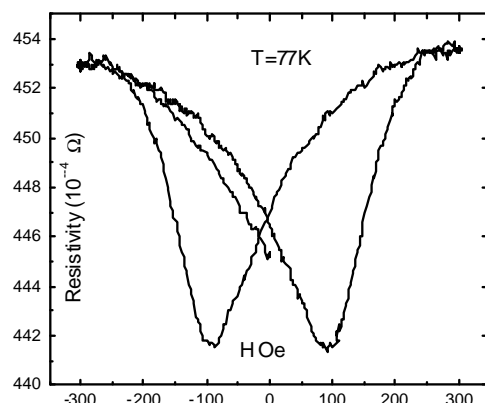


Fig. 2. MR of $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3/\text{Ag}$ metallic interface.