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Mechanism of enhancement in magnetoresistance properties of manganite perovskite ceramics by current annealing

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ABSTRACT

Studies on spintronics have provided solid evidence that the grain boundaries (GBs) in polycrystalline manganite can produce a strong extrinsic magnetoresistance (MR). This type of MR, called Low-field MR (LFMR), is larger than the intrinsic MR and can be triggered over a wide range of temperature. However, the existence of more GBs would bring about the weakening of magnetism and decrease the magnitude of MR simultaneously. Here we show that during annealing the application of electric-current to a representative ferromagnetic manganite perovskite, polycrystalline $La_{2/3}Sr_{1/3}MnO_3$ (LSMO), can produce more GBs and improve low-field magnetization, which leads to enhanced MR effect and field-response sensitivity as compared to the traditional-annealed sample. By using static micromagnetic models combined with the theories of spin-polarized intergrain tunneling and charge carrier hopping across domain wall, the observed enhancement of magnetoresistive response in current-annealed LSMO can be well explained.

1. Introduction

In the past decades, considerable interests have been drawn towards the ferromagnetic manganite perovskite due to their unique physical properties such as half-metallicity, colossal magnetoresistance (CMR), optical properties, magnetocaloric effect and so on [1–4]. Among them, the optimally doped $La_{2/3}Sr_{1/3}MnO_3$ (LSMO) is a well-known ferromagnetic metal with nearly total spin polarization, environmental stability, and the highest Curie temperature, which make it a promising candidate for room-temperature spintronic applications [5]. The intrinsic CMR effect of LSMO is dominated by double exchange mechanism which can be applied to explain its inherent coupling between transport property and magnetic state [6,7]. The transport probability of e_g electrons arises when the angle between the adjacent t_{2g} core spins of Mn ions decreases with increasing external magnetic field (H), leading to a negative CMR effect [7]. However, the intrinsic CMR effect needs high driving magnetic field and it is triggered only near the Curie temperature. Hence, the performance of low-field and room-temperature magnetoresistance (MR) in LSMO is fundamentally limited, which restricts its practical application to some extends.

It is well known that natural and artificial grain boundaries (GBs) can provide intergrain barriers for spin-polarized electron tunneling, which results in the extrinsic MR effect, i.e. low-field MR (LFMR), in polycrystalline LSMO [8–10]. The LFMR effect needs low driving magnetic field on the order of several kOe and can be observed over a wide range of temperature, which seems to be more appropriate for applications in device [10]. Usually, the larger the number of GBs in polycrystalline LSMO is, the stronger the LFMR effect appears [11]. However, the existence of more GBs with small grain sizes would bring about the weakening of magnetism in LSMO [11]. It is reported that the transport property of LSMO is strongly coupled with magnetic state and MR values for both intrinsic and extrinsic effects are directly proportional to m^2 at low-field region, here the normalized magnetization m is defined as the ratio of low-field magnetization M to the saturation value M_S [10,12]. Therefore, owing to the existence of more GBs in LSMO, the weakened magnetization is likely to decrease the magnitude of MR enhancement. In this sense, it is of great value to explore an experimental technique which could not only bring more GBs, but also maintain or even increase the magnetization of the sample. Previous studies demonstrated that annealing sample with an electric-current

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passing through it can improve various physical properties such as mass sensitivity [13], near-ballistic transport [14], giant magnetoimpedance response [15–17], domain-wall velocity [18], and luminescence efficiency [19]. It is worth mentioning that electric-annealing can produce reduction of grain size in many systems, such as α-Fe [20], cold rolled nickel [21], zirconia [22], and $Cu_{50}Ti_{50}$ [23], which is a promising method to generate more GBs in the current-annealed materials as compared to the traditional-annealed ones. On the other hand, the current annealing method can increase the saturation magnetization and decrease the anisotropy constants in many magnetic materials [15–17,24].

In this work, the effects of current annealing on magnetic and transport properties of polycrystalline LSMO are investigated. It is founded that the current-annealed LSMO exhibits an enhanced MR effect, which is logically ascribed to the combined effects of more GBs and improved low-field magnetization caused by electric current annealing method. In order to deeply understand structure–property relationship and MR enhancement mechanism, we calculate the anlytical MR formula based on static micromagnetic theory. The calculations are consistent with the experimental results of MR enhancement in current-annealed LSMO, which can provide the theory basis for materials design strategy.

2. Experiment

The polycrystalline sample of LSMO was synthesized via the sol–gel method. First, 1x mol La_2O_3 was dissolved in a dilute nitric acid solution. Then 1x mol $Sr(NO_3)_2$, 3x mol $Mn(CH_3COO_2)_2 \cdot 6H_2O$ and certain amount of ethanol were added to the solution. 7x mol $C_6H_8O_7 \cdot H_2O$ were used as the complexing agent and certain dilute nitric acid was used to control the value of pH = 2. After a moment, a certain amount of polyethylene glycol (4 g/100 ml) were added to the solution. The mixed solution was heated at 85 °C under constant stirring to become sol and heated at 85 °C to allow the formation of gel. Then the gel was dried at 120 °C in an oven to form gelatinous precursor. After removing organic substances (at 500 °C), the powder was pelletized and then calcined at 1300 °C in air. The obtained ceramics were divided into two chips of L10 × W5 × T2.5 mm^3, which were polished before current annealing to ensure a good electrical contact. One was post-annealed in air with a dc current of I = 1000 mA passing through its L axis direction. The annealing temperature increased to 400 °C in about 80 min and kept for 0.5 h. After that, the samples were cooled to room temperature. The current-annealed sample is referred as LSMO-I. The other one was post-annealed under the same conditions but with I = 0 during the thermal process. For comparison, the latter sample with I = 0 is referred as LSMO-A.

The structural characterizations were carried out by X-ray diffraction (XRD) at room temperature. The magnetic hysteresis loops (*M-H* loops) were measured using a vibrating sample magnetometer (VSM, Lakeshore 7400). A standard dc four-probe method was used to measure the MR and the temperature-dependent transport properties.

3. Results and discussions

The XRD patterns in Fig. 1 exhibit single phase of perovskite structure with rhombohedral symmetry and $R\bar{3}c$ space group for both LSMO-A and LSMO-I. The XRD full width at half maximum (FWHM) values of the (110) peak for LSMO-A and LSMO-I are 0.266° and 0.294°, respectively. The current-annealed sample has larger value of the FWHM, indicating smaller average grain size and larger number of GBs in LSMO-I. The relative small grain sizes can be also observed in the electric-annealed crystalline α-Fe [20], polycrystalline zirconia [22], and $Cu_{50}Ti_{50}$ [23]. It is known that the driving force of grain growth F can be written as $F = 2\sigma/R$, here R is the curvature radius of GB and σ is interfacial energy which is generally given as a sum of distortion energy, electrostatic energy, etc. The electrostatic energy is born out of

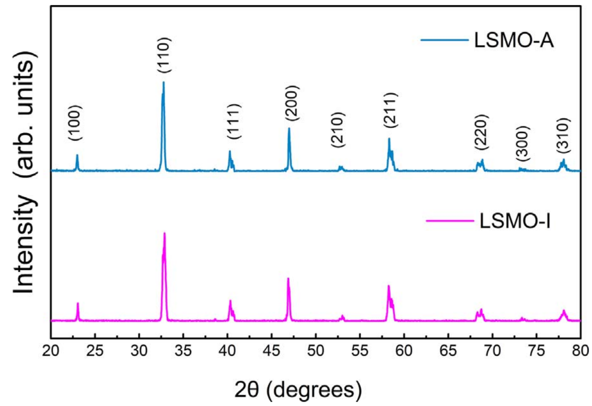

Fig. 1. Room temperature XRD patterns for LSMO-A and LSMO-I.

the interaction between charged defects in GB and opposite charges [25]. With the passage of current in LSMO-I during heating treatment, the electric field would weaken the electrostatic interactions between dissimilar charges, leading to reduced interfacial energies and weaker driving forces. Thus the growth of grain is restrained and smaller grains are retained without being swallowed up. As a result, LSMO-I possesses smaller average grain size and more GBs.

Fig. 2(a) illustrates the magnetic hysteresis loops of LSMO-A and LSMO-I at room temperature. The values of saturation magnetization (M_S) are 65.5 emu/g and 68.6 emu/g for LSMO-A and LSMO-I, respectively. We also calculate the normalized magnetization $m = M/M_S$ and plot m^2vs.H curves which are exhibited in Fig. 2(b) for both LSMO-A and LSMO-I, respectively. It is shown that both M and m^2 of LSMO-I are larger than those of LSMO-A at a certain value of low-field, implying

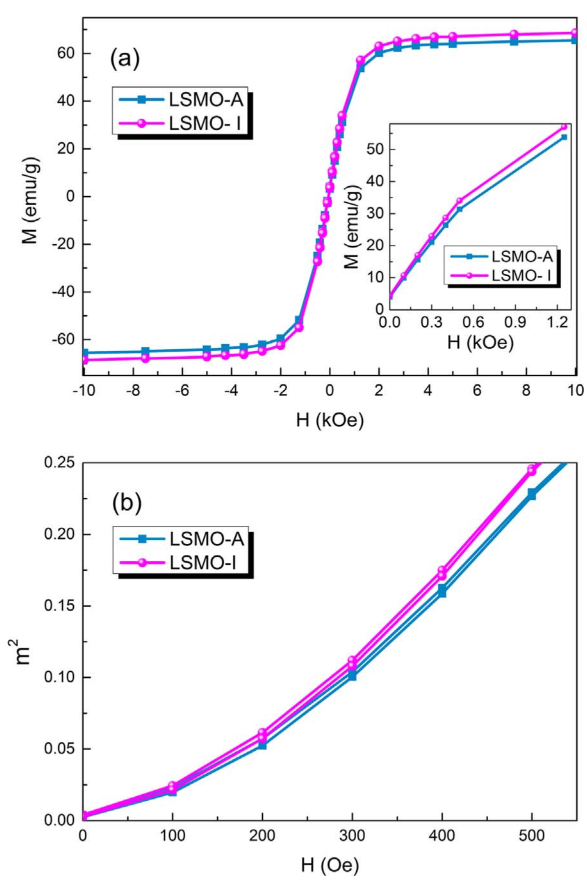

Fig. 2. (a) Magnetization hysteresis loops of LSMO-A and LSMO-I. The inset is Low-field magnetization as a function of magnetic field. (b) m^2-H curves for LSMO-A and LSMO-I.