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Magneto-transport and magnetic properties of $(1-x)La_{0.7}Ca_{0.3}MnO_3+xAl_2O_3$ composites

T.D. Thanh [a], P.T. Phong [a,b,*], N.V. Dai [a], D.H. Manh [a], N.V. Khiem [c], L.V. Hong [a], N.X. Phuc [a]

[a] Institute of Material Science, Viet Nam Academy of Science and Technology, Hanoi City, Viet Nam
[b] Nhatrang Pedagogic College, 1- Nguyen Chanh Str., Nhatrang City, Khanhhoa Province, Viet Nam
[c] Department of Natural Sciences, Hongduc University, 307 -Le Lai Str. Thanhhoa City, Viet Nam

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ABSTRACT

We report magneto-transport and magnetic properties of $(1-x)La_{0.7}Ca_{0.3}MnO_3+xAl_2O_3$ composites synthesized through a solid-state reaction method combined with a high energy milling method. Most interestingly, the effective magnetic anisotropy is found to decrease with increase in the non-magnetic insulating Al_2O_3 phase fraction in the composites. In addition, we observed that the magnitude of low-field magnetoresistance arising from spin-polarized tunneling of conduction electrons, as well as that of high-field magnetoresistance, displays a Curie–Weiss law-like behavior. Finally, we found that the temperature dependence of low and high-field magnetoresistance is controlled predominantly by the nature of temperature response of surface magnetization of the particles.

1. Introduction

Magneto-transport and magnetic properties in manganites have been one of the most frequently studied topics in solid state physics since the discovery of colossal magnetoresistance (CMR) up to 1300% in LCMO thin film at $T=200$ K [1]. CMR is restricted to a narrow range of temperature around the ferromagnetic–paramagnetic phase transition, and this makes it difficult to apply for electronic devices. Recently, another type of MR, extrinsic CMR in manganites, has been discovered. The extrinsic CMR, which is related to the grain boundaries, can be explained by spin-polarized tunneling [2]. The tunneling process takes place across the interfaces or grains separated by an energy barrier related to the magnetic disorder. Hence diluting with an insulating material in the manganites can adjust the barrier layer and thus influence the tunneling process. Since these extrinsic effects acted as pinning centers in demagnetization by domain wall displacement, a small field can align the neighboring ferromagnetic (FM) grains and as a result, enhanced MR response is achieved at low magnetic fields and low temperatures. The effect has been named as low field magnetoresistance (LFMR).

Several groups have attempted to enhance LFMR by making a composite of these CMR oxides with a secondary phase like an insulating oxide, as well as with a hard FM material or also with a polymer [3–14]. However, these studies focus only on enhancing LFMR values, paying less attention to the relationships between magnetic state of grain surface and magnetoresistance of composites, whereas spin misorientation at the magnetically virgin state of the system is crucial to obtain enhanced MR. In addition, the surface dislocations and the presence of extra phases in contact with the grain boundary change locally the anisotropy, thus providing pinning centers for the surface spin. When an external magnetic field is applied, the spin disorder is suppressed and Mn spins within the disordered region realign along the field direction. As a consequence, MR improvement is obtained.

In a previous work [9], we have investigated the crystalline structures and LFMR properties of $(1-x)La_{0.7}Ca_{0.3}MnO_3+xAl_2O_3$ ($LCMO/Al_2O_3$). However, the magneto-transport and magnetic properties of $LCMO/Al_2O_3$ have not clearly been shown. In this paper, we present a detailed study of magneto-transport and magnetic properties of $LCMO/Al_2O_3$ composites synthesized through a solid-state reaction method combined with a high energy milling method, especially its temperature and magnetic field dependence. Most interestingly, we observed that the effective magnetic anisotropy (K_{an}) decreases with increase in Al_2O_3 content, which is attributed to the increase in the non-magnetic insulating Al_2O_3 phase fraction in composites. Further, we also observed that the magnitude of LFMR, arising from spin-polarized tunneling of conduction electrons, as well as that of high-field magnetoresistance (HFMR), displays a Curie–Weiss law-like behavior. In order to explore the basic physics behind the temperature dependence of LFMR, our data have been analyzed using a phenomenological model [15] based on the spin-polarized

* Corresponding author at: Nhatrang Pedagogic College, 1-Nguyen Chanh Str., Nhatrang City, Khanhhoa Province, Viet Nam.
E-mail address: ptphong.nh@khanhhoa.edu.vn (P.T. Phong).

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tunneling of conduction electrons at the grain boundaries. Further, by analyzing the data in the following theoretical perspective proposed by Lee et al. [16], we found that the temperature dependence of MR is governed predominantly by the nature of temperature response on the surface magnetization (M_S) of manganite composite particles.

2. Experiment

The LCMO/Al_2O_3 (x=0, 0.01, 0.02, 0.03, 0.04 and 0.05) composites were prepared in three steps. First, LCMO powder was synthesized by a conventional solid-state reaction method combined with a high energy milling method. High purity (99.99%) La_2O_3, $CaCO_3$ and MnO powders were mixed in the appropriate stoichiometric ratio and ground. The well-mixed powders were preheated at a temperature of 1250 °C for 15 h. Subsequently, it was heated at 1300 °C for 10 h. Next the LCMO and Al_2O_3 powders were ground by the energy milling machine for 2 h. Finally the appropriate amounts of LCMO nanopowder and Al_2O_3 powder were mixed and the homogenous powder was pressed into pellets at a pressure of 10 MPa/cm^2 and sintered at 900 °C for 3 h.

Structural characterization was carried out by employing the X-ray diffraction (XRD) technique at room temperature in the 2θ range of 20–75° with a step size of 0.03° using CuK$_\alpha$ (λ=1.5406 Å) radiation and surface morphology was observed by scanning electron microscopy (SEM). Magnetic measurements were performed by utilizing a vibrating sample magnetometer (VSM) in the temperature range 80–300 K. Resistivity and magnetoresistance (MR–H) of all the composites were examined by Physical Property Measurement Systems (PPMS) in a magnetic field from 0 to 30 kOe at a temperature range from 5 to 300 K.

3. Results and discussion

The XRD patterns of the composites clearly showed that the correlative peaks of LCMO do not shift. The perovskites phase of LCMO is preserved for all x weight fractions of Al_2O_3 considered, which would be indicative of the coexistence of two phases in the composite. The direct evidence of two phases also comes from SEM micrographs. Representative SEM micrographs of LCMO/Al_2O_3 composites with x=0 and 0.03 are shown in Fig. 1. The Al_2O_3 regions present a different contrast, and exhibit dispersion of particles in LCMO. Moreover, energy dispersive X-ray (EDX) spectra of the doped composite for x=0.03 showed the aluminum peak along with La, Ca, Mn and O peaks, which also prove the presence of Al_2O_3 in the doped composites.

The paramagnetic (PM) to ferromagnetic (FM) phase transition temperature (T_C) determined from the peak of dM/dT is almost independent of Al_2O_3 content and is about 250 K for all the samples. This is attributed to the fact that the PM–FM phase transition is an intrinsic and intragrain property. The general behavior of magnetization vs. temperature indicates long-range ferromagnetism . The observed constancy of T_C also indicates that stoichiometry of LCMO phase within the grains remains essentially unchanged as Al_2O_3 is not accommodated within the perovskite structure and it occupies only the boundaries of the LCMO grains.

The magnetic hysteresis loops recorded at 5 K for all samples are shown in Fig. 2. Magnetization of the samples increases rapidly at low field and then tends to saturate at higher field. The value of magnetization of composites again decreases with x because of reduced volume fraction of the LCMO phase. This demonstrates that ferromagnetic order is weakened and magnetic disorder increases with Al_2O_3 content.

In order to understand the nature of field dependence of magnetization in the ferromagnetic regime, the magnetization curves were analyzed by using the "*law of approach to the saturation*" (LAS) of an assembly of particles with uniaxial anisotropy [17]:

$$M(H) = M_s[1-a/H-b/H^2]+\chi_d H \quad (1)$$

where M_s is the saturation magnetization, and a and b are suitable constants and χ_d is the high-field differential susceptibility. The best fits of the magnetization curves using Eq. (1) are shown in Fig. 3 for samples with x=0, 0.03 and 0.05 by considering a, b, M_s and χ_d as free parameters. We define K_{an} as the magnetic

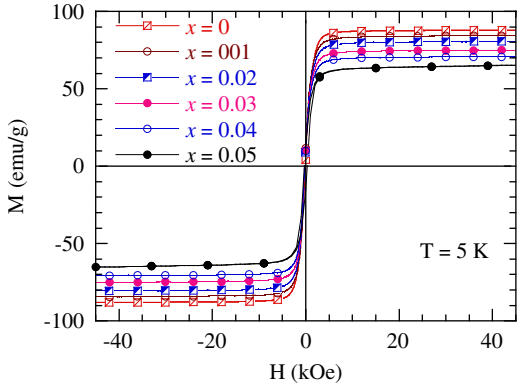

Fig. 2. Magnetic hysteresis loops at 5 K for all samples with various Al_2O_3 contents.

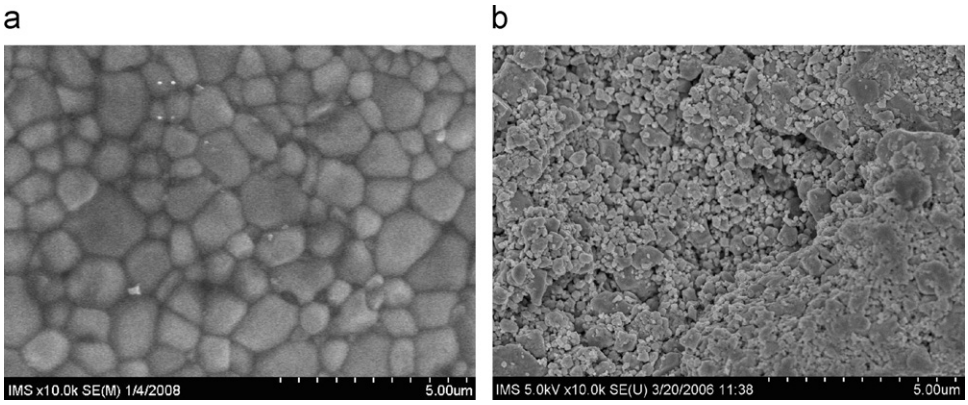

Fig. 1. SEM photograph of LCMO/Al_2O_3 samples with x=0 (a) and x=0.03 (b).