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ScienceDirect
Materials Research Bulletin 43 (2008) 631–638
Materials Research Bulletin
www.elsevier.com/locate/matresbu

Giant magnetoresistance in $La_{0.67}Ca_{0.33}MnO_3$ granular system with CuO addition

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Received 16 March 2006; received in revised form 31 August 2006; accepted 6 April 2007
Available online 10 April 2007

Abstract

We report on a heterogeneous precipitation method to modify the surfaces of $La_{0.67}Ca_{0.33}MnO_3$ (LCMO) grains with CuO. It is shown that such a modification causes transport and magnetoresistance (MR) properties of the composites largely different from that observed in pure LCMO granular system. Especially, a significant enhancement in MR is observed near the insulator–metal transition temperature (T_{IM}). The maximum MR reaches as high as ~88 and ~90% at a low magnetic field of 0.3 T for the modified samples of LCMO/xCuO with $x = 4$ and 15 mol%, respectively. Compared to pure LCMO, the CuO-modified samples have a substantial decrease in resistivity (ρ) at the temperature regions apart T_{IM}. Furthermore, for the $x = 4\%$ sample, a considerable thermal hysteresis is observed at the same temperature region where abnormal MR effect appears. On the basis of magnetization measurement and structural analysis, a possible interpretation for the experimental observations is presented.

PACS : 75.30.Vn; 71.30.+ h; 75.30.Kz

Keywords: A. Ceramics; B. Chemical synthesis; C. X-ray diffraction; D. Electrical properties; D. Magnetic properties

1. Introduction

In the past decades, perovskite manganites have attracted much attention for the discovery of colossal magnetoresistance (CMR) in the vicinity of their Curie temperature T_C [1,2]. A noteworthy feature of perovskite manganites is their nearly 100% spin polarization [3,4] caused by the half metallic nature. However, the potential application of these materials has been limited by large fields of several tesla for the observation of CMR effect. The magnetic domains in the polycrystalline samples are defined by the grains and they mostly switch independently in a field [5]. Using grain boundary to manipulate magnetic behavior may thus prove to be a useful method for significantly improving the low-field sensitivity of these materials.

Recently, enhanced low-field magnetoresistance (LFMR) response has been observed in some ferromagnetic-insulator (FM-I) type composites, such as $La_{2/3}Sr_{1/3}MnO_3$-CeO_2, $La_{0.67}Ca_{0.33}MnO_3$-$SrTiO_3$, $La_{2/3}Ca_{1/3}MnO_3$-polymer, $La_{0.7}Ca_{0.3}MnO_3$-ZrO_2, etc. [6–9]. This enhancement can be explained in the model of spin-polarized tunneling with

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0025-5408/$ – see front matter © 2007 Published by Elsevier Ltd.
doi:10.1016/j.materresbull.2007.04.006

insulator layers as barriers. Similar observations have been shown earlier in polycrystalline manganites with the natural grain boundaries as tunneling junctions thereby enhancing the LFMR [10,11]. Moreover, if a conducting metal is introduced into the manganites matrices to form ferromagnetic-metal-type composites [12,13], enhanced MR has also been obtained due to the modification of grain boundaries and/or magnetic scattering.

Ghosh et al. [14] studied the effects of transition elements (Fe, Co, Cr, Cu, Zn) substitution of Mn ions in $La_{0.7}Ca_{0.3}MnO_3$ and found Cu substituted sample showed an unusual electrical transport behavior. It exhibited ρ–T behavior similar with that of ceramic LCMO with T_{IM} ~240 K while the resistivity reduced overall. It was interpreted that Cu had substantially large ionic radii as compared to the average Mn radius, so Cu^{2+} ions in the proximity of the grain boundary may be attracted towards the boundary in order to release the local strain, which improved the grain boundary conductivity. Recently, it was reported that a substantial enhancement of LFMR can be realized in the composites of $La_{0.67}Ca_{0.33}Mn_{1-x}Cu_xO_3$ [15]. It was supposed that a Cu-dependent material was formed surrounding the LCMO grains, which induced local spin disorder. This can be realized either through the segregation of Cu^{2+} towards the grain surface in order to release the increased local strain due to doping at Mn sites with larger Cu [15] or by directly introducing CuO to modify the surfaces of LCMO grains in a chemical method.

In the present work, we report on a heterogeneous precipitation method to directly introduce CuO (Cu^{2+}) to the grain boundaries or surfaces of LCMO grains. Experimental results show that through such a way the MR near the insulator–metal (I–M) transition temperature can be substantially enhanced even upon the application of rather small magnetic fields.

2. Experiments

A heterogeneous precipitation method was employed to prepare nominal LCMO/xCuO composites (x = 0, 4, and 15 mol%). $Cu(NO_3)_2$ was used as a source of CuO. Firstly, we used a sol–gel method followed by a sintering treatment at 1100 °C for 3 h to prepare LCMO powders of small grain size according to the nominal composition of $La_{0.67}Ca_{0.33}MnO_3$. The basic structure of perovskite feature could be formed which was confirmed by X-ray diffraction analysis. Secondly, the pre-prepared LCMO powders were mixed with $Cu(NO_3)_2$ aqueous solution. The mixture solution was stirred strongly while proper amount of NaOH aqueous solution pouring into it. During this process, the following chemical reaction occurred, namely, $Cu^{2+} + 2OH^- \rightarrow Cu(OH)_2\downarrow$, which led to generation of $Cu(OH)_2$ precipitates. After filtration, the LCMO/$Cu(OH)_2$ precipitates were washed with distilled water in order to remove the other residual ions such as Na^+, NO_3^-, etc., and dried to obtain LCMO/CuO composite powders. Lastly, the obtained powders were ground carefully for homogeneous mixing and pressed into pellets of 10 mm in diameter. The pellets were finally sintered at 1000 °C for 2 h to get the target composites.

Transport and magnetic properties were measured with a standard four-probe method in a commercial Physical Property Measurement System (Quantum Design PPMS).

3. Results and discussion

The X-ray diffraction (XRD) spectrum of LCMO/xCuO with x = 0, 4 and 15% is shown in Fig. 1. It is found that the stoichiometry of the LCMO phase is preserved in all specimens as is indicated by XRD line positions which almost remain unchanged. The second phase can be detected only for samples with larger x-value (=15%) and is assigned to be insulating CuO (labeled by asterisks).

Indicated by solid circles in Fig. 2 is temperature dependence of resistivity (ρ) measured in zero magnetic field for pure LCMO. It has a much lower T_{IM} (~174 K) and larger ρ comparing to ceramic $La_{2/3}Ca_{1/3}MnO_3$ (~256 K) prepared in a standard solid-state reaction route at high sintering temperature. This can be qualitatively attributed to the magnified grain boundary effect due to smaller grain size caused by lower sintering temperature (1000 °C). As shown in Fig. 2 (open up triangles and circles), the CuO-modified samples display an observable downshift of T_{IM} and a substantial reduction of ρ at the temperature regions apart T_{IM}, which forms a sharp contrast with that observed in the case of $La_{0.67}Ca_{0.33}Mn_{1-x}Cu_xO_3$ [13].

In the inset of Fig. 2 we plot the low-T data in an extended scale for all the three samples. Two striking phenomena can be found in this plot. One is a substantial reduction in low-T resistivity for the samples with CuO addition. For instance, the ρ at 10 K has only a value of ~0.25 and ~0.52 Ω cm for the x = 4 and 15% samples, respectively. While the corresponding value for pure LCMO is as high as ~15 Ωcm. The other is that a resistivity minimum is significantly