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Tuning of magnetoresistance in $(La_{0.67}Ca_{0.33}MnO_3)_{0.97}/(ZnO)_{0.03}$ composite by modification of the sintering temperature

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We report on a detailed study of the electrical resistivity and the magnetoresistance of the $(La_{0.67}Ca_{0.33}MnO_3)_{0.97}/(ZnO)_{0.03}$ (LCMO/ZNO) composite prepared at different sintering temperature by conventional solid state reaction method. The results of scanning electron microscopy indicate that ZnO segregates mostly at the grain boundaries of LCMO. The grain size of the LCMO increases with the sintering temperature. The X-ray diffraction (XRD) result shows that no new phase appeared in the composite except LCMO and ZnO phases. The magnetic and electrical transport was measured over a temperature range of 90-320 K. All samples exhibits characteristic insulator-metal and para-ferromagnetic transition temperature, which decreases with increase in sintering temperature. It is very interesting to note that the MR% is enhanced with the sintering temperature, which is encouraging for potential applications.

Key words: Composites, Sintering temperature, Grain size, Curie temperature, Magnetoresistance.

Introduction

Magnetoresistance (MR), a technologically important physical property, has been reported for a variety of systems, such as metallic multilayers, granular inter metallic alloys and perovskite-type oxides (e.g. manganites) [1]. The origin of the MR effect exhibits substantial differences from system to system and its understanding has remained at the forefront of materials research both because of its industrial applications in magnetic storage and the rich physics that gives rise to the phenomenon. An example of the latter is the colossal MR effect in perovskite manganites $L_{1-x}A_xMO_3$(L = rare earth A = Ca, Sr, Ba) where a mostly intriguing interplay of physical properties such as phase separation, charge ordering and orbital degrees of freedom contribute to it [2-4]. The intrinsic colossal magnetoresistance (CMR) [4] effect which is caused by double exchange (DE) mechanism [5] is usually found during a narrow temperature range near the Curie temperature (T_c) [6] and needs several tesla extra magnetic field. This is not very appealing for practical application. Recently another type of MR has been found in polycrystalline manganites. This kind of MR is mainly dependent on the grain boundary properties and the spin-polarized tunneling of conduction electrons [7], and it usually occurs over a wide temperature range and at a low magnetic field. Hence, it's also called as low-field magnetoresistance (LFMR), which associated with the spin-memory contribution to charge transport across the grain boundary (or interface) by modifying the microstructure of the manganites. There are some other extrinsic magnetoresistance (MR) effects, such as grain boundary MR, spin-polarized transport MR [8, 9]. It could be more useful for practical applications. Several groups of manganite-based inorganic composites have been investigated to enhance the LFMR, such as $La_{0.7}Ca_{0.3}MnO_3$/YSZ, $La_{0.7}Ca_{0.3}MnO_3/CeO_2$, $La_{0.7}Ca_{0.3}MnO_3/ZrO_2$, $La_{0.7}Ca_{0.3}MnO_3/Al_2O_3$ [10-13] and $La_{0.7}Ca_{0.3}MnO_3$/ZnO [14] etc. However, low-field magnetoresistance property is also affected by several factors, sintering temperature, impurity, complicated band structure, electron-electron, electron-magnon scattering, etc. Among these, it is well known that change in the sintering temperature has direct consequence on the electronic and magneto-transport properties of the systems [15].

Although, several works on manganite-ZnO composites [14] have been done, however the effects of sintering temperature on manganite-ZnO composites have not been investigated so far. Therefore, in the present study we report the, structural, magnetic and low field magneto-transport properties in broad temperature range of $La_{0.67}Ca_{0.33}MnO_3)_{0.97}/(ZnO)_{0.03}$ composite as a function of sintering temperature.

Experimental Details

The $La_{0.67}Ca_{0.33}MnO_3)_{0.97}/(ZnO)_{0.03}$ composite is prepared by four steps. Firstly, the pure LCMO was prepared by the conventional solid state reaction method. High

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purity oxide powders made up of La_2O_3, CaO, and Mn_2O_3 were obtained, then ground and reacted in air at 800 °C for 10 h. After that, such mixture was grounded for 2 h and heated in air at 1000 °C for another 10 h. Then this procedure was done again and finally the powders were sintered at 1250 °C for 24 h. So the pure LCSMO was obtained. Secondly, LCMO and ZnO powders by appropriate amounts were mixed according to the desired molar ratio. Thirdly, the mixtures were ground and pressed into pellets. Finally, the pellets were sintered from 1000 to 1300 °C for 24 h, and then furnace-cooled to room temperature.

The structure and the phase purity of the sample was checked at room temperature by means of X-ray powder diffraction (XRD) using a Phillips X'pert (MPD 3040) X-ray diffractometer with Cu $K\alpha$ radiation ($\lambda = 1.5406$ Å) operated at a voltage of 40 kV and a current of 30 mA. The morphology of the grain boundaries and surfaces were investigated by using scanning electron microscopy (SEM, JSM5610). The magnetic measurements of these samples were carried out in the temperature range of 100-390 K at a frequency of 40 Hz by using a quantum design vibrating sample magnetometer (PPMS, 6000 VSM). The electrical properties and magnetoresistance properties were measured at 1T of applied magnetic field.

Results and Discussions

Fig. 1 shows the XRD patterns of as synthesized $(La_{0.67}Ca_{0.33}MnO_3)_{0.97}/(ZnO)_{0.03}$[$(LCMO)_{0.97}/(ZnO)_{0.03}$] composites prepared at different sintering temperatures. The characteristics reflections are indexed to pervoskite crystal structure using POWDER-X software. The LCMO crystallizes in orthorhombic structure having lattice parameter $a = 5.469$ Å, $b = 5.449$ Å and $c = 7.802$ Å. No impurity peaks are observed in the XRD pattern indicating a complete reaction between reactants to form LCMO phase. However, because of very small amount of ZnO, it could not find any ZnO peaks within the sensitivity of the XRD measurement. The zoom of the (121) peak (not shown here) in the diffraction patterns shows the shift in central positions to lower angles with increasing sintering temperature. It is due to change of grain size caused by the sintering temperature [14].

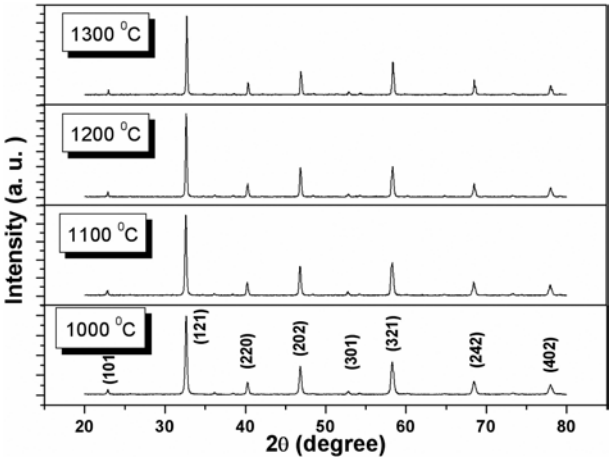

Fig. 1. X-ray diffraction patterns of $(La_{0.67}Ca_{0.33}MnO_3)_{0.97}/(ZnO)_{0.03}$ composites sintered at different temperature.

The surface microstructures employing scanning electron microscope (SEM) for $(LCMO)_{0.97}/(ZnO)_{0.03}$ composites shown in Fig. 2. The SEM micrographs were used to study the coexistence of two phases and the influences of sintering temperature on the morphology of the grain boundaries. The image taken in the back scattering mode of the $(LCMO)_{0.97}/(ZnO)_{0.03}$ composites, clearly shows that all samples have two phases, distinguished by the grey regions of LCMO matrix and the bright regions of ZnO regions. It was also observed that the samples sintered at the different temperature from 1000 to 1300 °C have different average grain size and grain densities. It is clearly seen from Fig. 2 that as the sintering temperature increases from 1000 °C to 1300 °C, the average grain size and the grain

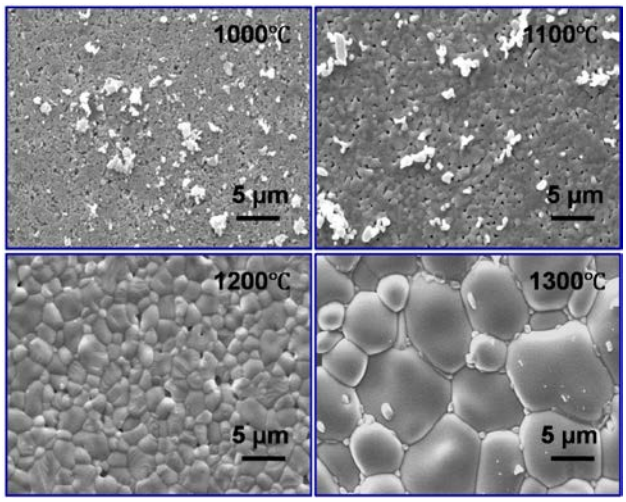

Fig. 2. SEM micrographs of $(La_{0.67}Ca_{0.33}MnO_3)_{0.97}/(ZnO)_{0.03}$ composites sintered at different temperature.

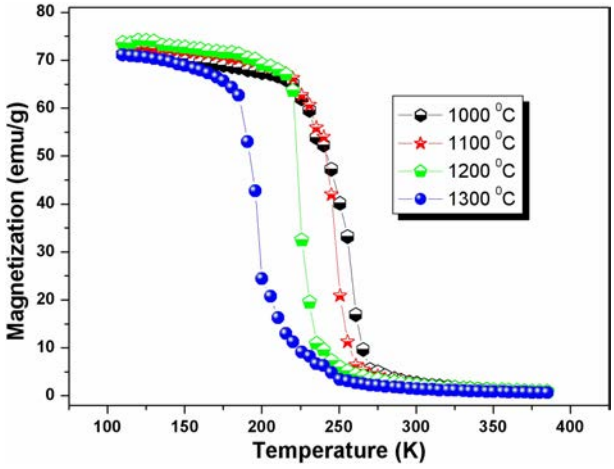

Fig. 3. Temperature dependence of magnetization of $(La_{0.67}Ca_{0.33}MnO_3)_{0.97}/(ZnO)_{0.03}$ composites sintered at different temperature.

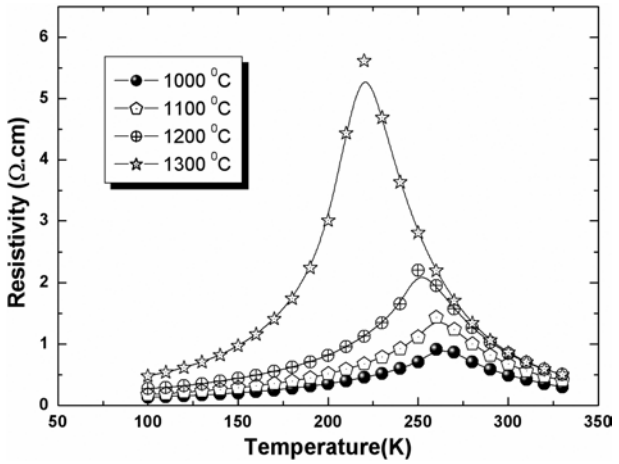

Fig. 4. Temperature dependence of resistivity in zero field of $(La_{0.67}Ca_{0.33}MnO_3)_{0.97}/(ZnO)_{0.03}$ composites sintered at different temperature.

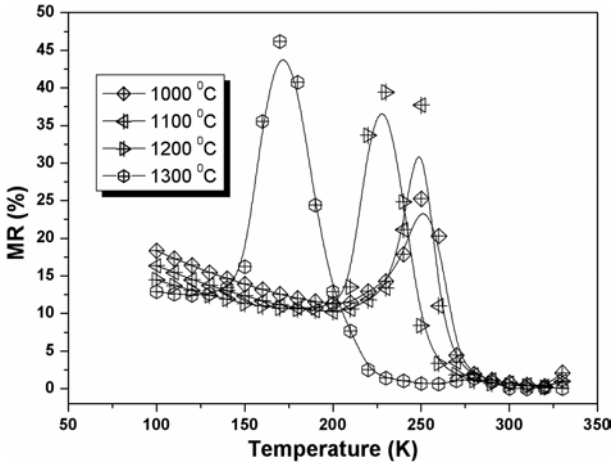

Fig. 5. Temperature dependence of magnetoresistance (MR%) under a magnetic field of H_{dc} = 1T for $(La_{0.67}Ca_{0.33}MnO_3)_{0.97}/(ZnO)_{0.03}$ composites sintered at different temperature.

densities increases.

The field-cooled (FC) temperature dependence of magnetization for $(LCMO)_{0.97}/(ZnO)_{0.03}$ composites taken at 5000 Oe are shown in Fig. 3. In field cooled process, the sample was cooled in the presence of 5000 Oe applied magnetic field from 305 K to 100 K and then magnetization measurement was performed in the presence of the same field during the warming up cycle from 100 K to 380 K. The variation of magnetization vs. temperature (*M-T*) reveals that $(LCMO)_{0.97}/(ZnO)_{0.03}$ composites exhibits a sharp ferromagnetic-paramagnetic (FM-PM) transition occurring at T_c. It was observed that the Curie temperature (T_c) decreases from 260 K (sintered at 1000 °C) to 195 K (sintered at 1300 °C) for $(LCMO)_{0.97}/(ZnO)_{0.03}$ composites as the sintering temperature increased. This behavior may be explained as follows referring to the work of Dutta et al [15]. The magnetic and transport properties are very closely related to the particle or grain size. In this experimental work, the Mn-O-Mn bond angles are varied and the Mn-O-Mn bond lengths of the grains increased. The SEM observation (Fig. 2) shows that the grain size increases with the sintering temperature. Therefore, the Mn-O-Mn bond angles are affected and the Mn-O-Mn bond length in grains increases. This situation would cause the decrease of ferromagnetic properties and therefore T_c also continuously decreases with sintering temperature [15].

The temperature dependence of resistivity (Ω· cm) at zero magnetic field of $(LCMO)_{0.97}/(ZnO)_{0.03}$ composites are shown in Fig. 4. It was found that the composites exhibit an insulating/semiconducting behavior and lower resistivity as the sintering temperature increases. It can be explain according to the change in grain size of the composites. As the grain size decreases, it is more helpful to get the vacancy between the grains and neighbors. Therefore, the existence of vacancy cause more non-magnetic surface layer around the grains. This leads to the increase of the residual resistivity of the material [16]. Fig. 5 reveals the temperature dependence of magnetoresistance (MR) of $(LCMO)_{0.97}/(ZnO)_{0.03}$ composites measured at an applied magnetic field of H_{dc} = 1 Tesla depending on different sintering temperature. The MR value is defined as follows:

$$MR = [\rho_{(0)} - \rho_{(H)}]/\rho_{(0)} \quad (1)$$

Where, $\rho_{(0)}$: zero magnetic field and $\rho_{(H)}$: applied magnetic field resistivity. It was found that, at a magnetic field of 1 Tesla, the maximum MR values of each sample appear in the range from 25 to 47% and tend to increase with the sintering temperature. This phenomenon is attributed to the increased density of the grains at higher sintering temperature. Therefore, it could be helpful for the transport of the magnetic spin and is obviously easier way to improve the MR properties of $(LCMO)_{0.97}/(ZnO)_{0.03}$ composite. However, in order to improve the properties near room temperature for the industrial application, an additional experimental work is needed because the maximum MR value still occurred at a very low temperature (~170), which may be affected by Tc.

Conclusions

We have successfully synthesized and investigated the magnetic as well as the electrical transport behaviors of $LCMO)_{0.97}/(ZnO)_{0.03}$ composite as a function of different sintering temperatures. The Curie temperature (Tc) decreases with increasing the grain size, whereas the metal insulator transitions are shifted towards the position of high sintering temperature side and the resistivity continuously decreased. The MR% increased with the sintering temperature. This phenomenon can be explained on the basis of the density of grains; the high density of grains was observed at higher sintering temperature, which is helpful for the transport of the magnetic spin and therefore favorable for the improvement of the MR properties.

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