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Ferromagnetic insulating and spin glass properties of $La_{0.7}Sr_{0.3}MnO_3$–TiO_2 composites

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ABSTRACT

In this study, the effect of TiO_2 doping on the electro-magnetic properties of $(1-x)La_{0.7}Sr_{0.3}MnO_3+xTiO_2$ (with $0\% \le x \le 6\%$, in wt%) composites has been investigated. X-ray diffraction observations show the evidence of reaction between the $La_{0.7}Sr_{0.3}MnO_3$ and TiO_2 grains. Also the results show that by increasing TiO_2 doping levels, the metal insulator transition temperatures decrease and the system becomes an insulator. Furthermore, the paramagnetic–ferromagnetic transition temperature also decreases as TiO_2 content increases. The spin glass state exists in the composites with $x=5\%$ and 6%. The dynamic properties of the magnetic properties are investigated by temperature dependence of dc magnetization and frequency dependence of ac susceptibilities. A dynamic scaling analysis of ac susceptibility data using conventional critical slowing down indicates that a finite spin-glass phase-transition temperature (T_g) and a dynamic exponent ($z\nu$) change from 103 K and 9.30 correspondingly for $0.95La_{0.7}Sr_{0.3}MnO_3/0.05TiO_2$ to 133 K and 9.10, for $0.94La_{0.7}Sr_{0.3}MnO_3/0.06TiO_2$. In addition, MR in low temperature of these samples decline simultaneously with occur spin-glass behavior. These results are interpreted as the dilution of Mn^{3+}/Mn^{4+} interactions by the random Ti substitution on the Mn site considerably reduces the ferromagnetic double exchange interaction within the manganese lattice.

1. Introduction

The discovery of colossal magnetoresistance (CMR) in doped manganites and their potential applications in magnetoresistive transducers and sensors triggered increasing attention [1,2]. Moreover, in most of cases the large magnetoresistance (MR) in the perovskite manganites occurs only at high magnetic fields of several tesla, which restrains its use for practical applications. Accordingly, many research groups focused their studies on the extrinsic MR effects found in various magnetic compounds, since they showed a large MR in low magnetic fields. The extrinsic MR in these manganites usually falls into three broad classes, namely grain boundary MR, spin polarized transport in ferromagnetic tunneling junction MR and domain wall MR [3].

In recent years, some attention has been paid to composite systems which are granular manganite/insulator mixtures, such as insulator [4–8], magnetic materials [9–11], or metals [12–15]. In addition to this, manganite–polymer composites have also been studied [16]. Enhancement of the MR, especially near the percolation threshold, in a mixture of metallic ferromagnetic manganite and an insulator has been reported. Kameli et al. [17] have found some interesting phenomena regarding the effect of TiO_2 doping on the structure and magnetic and magneto-transport properties of $(1-x)La_{0.75}Sr_{0.25}MnO_3/xTiO_2$. Their studies show that at low doping level ($x \le 2\%$) TiO_2 mainly goes into the grain-boundary region, but at high doping level ($x \ge 3\%$), some part of the TiO_2 goes into the perovskite lattice substituting Mn in $La_{0.75}Sr_{0.25}MnO_3$ and the remainder segregates as a separate phase at the grain boundaries. In the magnetic field of 8000 Oe and at 77 K MR value of 20% was observed for the composite with a TiO_2 doping level of $x=2\%$. However, so far the researches on the effects of TiO_2 on magnetotransport of manganites composites are quite rare. Moreover, there have been no reports on the spin glass behavior in manganites composites.

In order to better understand the role of TiO_2 on magneto-transport properties of $La_{0.7}Sr_{0.3}MnO_3$, we prepared $(1-x)La_{0.7}Sr_{0.3}MnO_3+xTiO_2$ (LSMO/TiO_2) ($x=0.0$; 0.01; 0.015; 0.02; 0.03; 0.04; 0.05 and 0.06) system by a conventional solid state reaction method combined with high energy milling method. The transport and the magnetic properties of the LSMO/TiO_2 composites are presented here. It has been found that incorporation of the impurity phase (TiO_2) increases the zero-field resistivity of composites and there is a concomitant shift in the value of both

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the paramagnetic–ferromagnetic transition temperature (T_C) and the metal–insulator transition temperature (T_{MI}) to lower values, especially appearance of the spin-glass behavior in samples $x \geq 0.05$. From the relationship between the substitution Mn site by Ti on the magnetic and electrical properties, we will make clear the role of the TiO_2 in spin glass behavior of LSMO–TiO_2 composites.

2. Experiment

Samples of $(1-x)La_{0.7}Sr_{0.3}MnO_3+xTiO_2$ with $0\% \leq x \leq 6\%$, in wt% were prepared through three steps. Firstly, the $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) was prepared by a conventional solid state reaction method combined with high energy milling method. High purity (99.99%) La_2O_3, $SrCO_3$ and MnO powders were mixed in appropriate stoichiometric ratio and ground. The well-mixed powders were preheated at 1250 °C for 15 h and successively heated at 1300 °C for 10 h. Then the LSMO powder was ground by high energy milling machine for 2 h. Secondly, TiO_2 nano powder was grinded by high energy milling machine for 2 h. Finally, appropriate amounts of LSMO and TiO_2 nano powder were mixed and pelletized and sintered at 1200 °C for 5 h.

Room temperature powder X-ray diffraction (XRD) patterns of the samples were recorded with a diffractometer in the 2θ range 20°–75° with a step size of 0.03° using Cu$K\alpha$ radiation. The temperature dependent resistivity, $R(T)$, of the samples was measured by the standard four-probe technique in the temperature range of 30∼300 K using a closed cycle helium refrigerator cryostat with Keithley instruments without or with magnetic fields (0–3 kOe). The magnetization of the samples was measured by a homemade vibrating sample magnetometer (VSM) and a Physical Property Measurement System (PPMS). In addition, AC susceptibility measurements were performed on a homemade system using induction bridge principle at various frequencies.

3. Results and discussion

The room temperature X-ray diffraction (XRD) patterns of LSMO/TiO_2 composite are shown in Fig. 1. It clearly exhibits the lines assignable to rhombohedral LSMO. At lower concentrations of TiO_2, neither TiO_2 nor any other impurities are observed. However, two tiny peaks located at $2\theta \approx 29°$ (see inset of Fig. 1) and 36° are observed for $x=0.06$ sample. The peaks at 29° and 36° related with Mn_3O_4 and TiO_2, respectively, in the composites. This suggests the coexistence of the TiO_2 and LSMO and the formation of Mn_3O_4 from the reaction between TiO_2 and LSMO. Similar results were observed in $La_{0.75}Sr_{0.25}MnO_3/TiO_2$ by Kameli et al. [17]. Moreover,

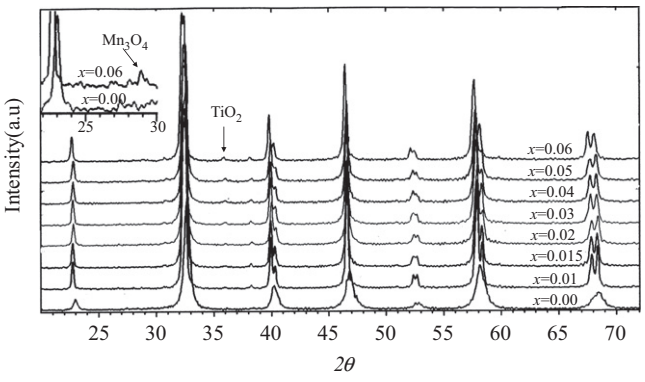

Fig. 1. X-ray diffraction pattern of LSMO/TiO_2, peak of Mn_3O_4 is shown in inset.

one can also observe each peak at 40°, 58° and 68° split into two peaks. These results show that the some portion of Ti goes into the perovskite lattice displacing Mn in LSMO.

Fig. 2 shows typical SEM micrographs as well as the energy dispersive X-ray spectroscopy (EDX) of LSMO/TiO_2 composites with $x=0$ and 0.02, respectively. A clear grain boundary is observed. EDX spectra for $x=0.02$ shows the Ti peak along with La, Sr, Mn and O peaks, which also supports the presence of TiO_2 in the doped composites.

Fig. 3 shows the temperature dependence of magnetization for LSMO/TiO_2 samples measured under field-cooled (FC) and zero field-cooled (ZFC) conditions in a magnetic field of 100 Oe. It clearly shows that all samples exhibit the paramagnetic to ferromagnetic transition. The transition temperature decreases with the increase in the Ti content. T_C of LSMO is close to 365 K, which well agrees with Ref. [18]. However, it drops to 150 K when TiO_2 content is 6%. These results seem to indicate that the double exchange (DE) is depressed due to the changes in bandwidth, which are similar to the results obtained by Kim et al. [19]; and also that the partial substitution of Ti^{4+} ion for the Mn^{4+} ion weakens the double exchange interaction significantly as a result of the dilution of Mn^{3+}–O–Mn^{4+} network [20]. Furthermore, the curves of FC and ZFC are split at lower temperatures when $x \geq 0.05$. This fact implies the formation of ferromagnetic clusters with a spin glass state which has no simple long range ferromagnetic order [21]. The spin-glass (SG) behavior for the $x \geq 0.05$ will be discussed later in detail. In addition, the PM–FM transition broadens with the increase in TiO_2 content. The Ti substitution weakens the DE interaction and breaks the Mn–O–Mn network. This results in the short-range order ferromagnetic clusters with randomly distributed sizes of samples. Furthermore, as more Ti is substituted, more inhomogeneous clusters are formed, which leads to the broadening of the PM–FM transition peak and decreasing the T_C [22].

Fig. 4 represents the resistivity of LSMO/TiO_2 composites in a zero magnetic field as a function of temperature. In the temperature range studied, the resistivity of the samples increases as the TiO_2 content increases. The samples with $x=0$ and 0.01 exhibit metallic behavior in the entire temperature range studied, which was predicted from their metal–insulator transition temperature (T_{MI}), that is, about 365 K for $x=0$ sample [23] and below 350 K for $x=0.01$ sample, respectively. As can be seen in Figs. 3 and 4, the difference between T_C and T_{MI} becomes larger as the TiO_2 content increases and T_{MI} is lower than T_C. This behavior is quite different from that observed in the $La_{0.75}Sr_{0.25}MnO_3/xTiO_2$ composites, which exhibit T_{MI} is close to their T_C. Furthermore, when $x \geq 0.05$, the insulating behavior is observed over the entire temperature range (up to 50 K). We suggest that this is due to SG ordering, which is inconsistent with DE interactions. Increase in resistivity accompanying a decrease in T_{MI} can be explained by the disorder introduced by the Ti doping combined with the replacement of some of the Mn–O–Mn bonds by the Mn–O–Ti bonds [24,25]. Moreover, based on model of Rubinsten [26], we believe that there are two kinds of conduction channels connected parallel in the polycrystalline LSMO/$xTiO_2$. One is related to the LSMO grains, which determines the transport properties of the system. The other one is related to TiO_2 grains, mostly distributed at the grain boundaries of LSMO. Due to the disordered nature of the grain boundaries, grain boundary resistance is larger than that of the grains. In the pure LSMO samples, the electrical transport occurs through a direct contact between the LSMO grains. When TiO_2 insulating is introduced, this direct contact is diluted/disturbed. Since the resistivity of TiO_2 is larger than that of LSMO, the second channel can be regarded as having higher energy barrier that limits the direct conduction between the LSMO grains. Therefore, with the