



Magnetoresistive and magnetocaloric response of manganite/insulator system



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ABSTRACT

In this work, we have studied structural, electro-magnetic and magnetocaloric properties of $\text{La}_{0.7}\text{Ba}_{0.3}\text{MnO}_3/x\text{TiO}_2$ manganite/insulator system with $0 \leq x \leq 0.08$. X-ray diffraction (XRD) shows the coexistence of TiO_2 and $\text{La}_{0.7}\text{Ba}_{0.3}\text{MnO}_3$ phases in doped composites through their characteristic peaks. This reveals their interaction lack preserving the R-3c rhombohedral structure for all composites. Due to interaction lack, TiO_2 is suggested to segregate at grain boundaries weakening grains connectivity and decreasing metal-semiconductor transition temperature (T_{ms}). The segregated TiO_2 hinders conduction between grains leading to carriers tunneling that increases the low field magnetoresistance (LFMR) of $\text{La}_{0.7}\text{Ba}_{0.3}\text{MnO}_3$ from -3% to -3.3 , -3.5 and -3.7% for $x = 0.02$, 0.04 and 0.06 for doped composites. The dc magnetization measurements reveal the constant value of Curie temperature (T_c) and its non impact by doping level referring to the TiO_2 – $\text{La}_{0.7}\text{Ba}_{0.3}\text{MnO}_3$ interaction lack. Also, the magnetocaloric properties of $\text{La}_{0.7}\text{Ba}_{0.3}\text{MnO}_3$ are enhanced with TiO_2 doping, where, the relative cooling power (RCP) of $\text{La}_{0.7}\text{Ba}_{0.3}\text{MnO}_3$ has been enhanced from 35 J/kg to 51 , 47 , 49 and 50 J/kg for $x = 0.02$, 0.04 , 0.06 and 0.08 composites at 1.5 T magnetic field.

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1. Introduction

Magnetoresistive doped manganites interest with several outstanding phenomena associated with their structural, electrical and magnetic properties, as the colossal magnetoresistance (CMR) phenomenon for magnetic recording applications [1] and magnetocaloric effect (MCE) for magnetic refrigeration technology [2]. The electro-magnetic response of these oxides relies on the mixed valence state $\text{Mn}^{3+}/\text{Mn}^{4+}$ that plays a vital role in the double exchange mechanism (DE), the change in Mn-O-Mn angle and in the e_g electron mobility. So, any disturbance in this ratio may change the electro-magnetic properties. In fact, potential magnetic applications favor the high values of CMR that can be achieved at high magnetic fields, what retard their technological implementation. However, high values of MR have been observed in polycrystalline granular

materials and multilayered manganites [3] at low applied magnetic fields (LFMR), pointing to the relevant role of grain boundaries. This discovery has increased the interest in grain boundaries synthesis and their modification either by annealing process [4], preparation methods [5] or artificial defects [6]. The LFMR has been studied carefully and attributed to spin polarized tunneling and scattering mechanisms across grain boundaries according to the polarization ability [7].

Another important property of manganites is the MCE that used in magnetic cooling technology as an alternative to gas compression mode [8]. In magnetic materials, the MCE arises from the change in lattice magnetic entropy (ΔS) as a result of magnetic field application. The applied magnetic field orients the unpaired spins lowering their entropy, this is compensated by an increase in lattice entropy (ΔS) that leads to heat releasing. As spin orientation reaches maximum at T_c under an applied magnetic field, so, ΔS is expected to show a maximum at the same temperature too. With this property, manganites have been explored for magnetic refrigeration applications and found to be good candidates as $\text{La}_{0.67}\text{Ba}_{0.22}\text{Sr}_{0.11}\text{Mn}_{1-x}\text{Ti}_x\text{O}_3$ [9] and $\text{Pr}_{0.5}\text{Eu}_{0.1}\text{Sr}_{0.4}\text{MnO}_3$ [10]. This is because of the high

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magnetization, the high T_C , the chemical stability, the simple preparation methods, the low cost and the negligible magnetic hysteresis advantages that have put manganites in comparison with the high MCE Gd [11] and Gd based alloys [12]. For example, $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ shows a MCE response of 5.27 J/kg.K at 1.5T magnetic field, nearly twice larger than Gd based alloys at low magnetic fields [13].

Manganite/insulator system is an inhomogeneous system consists of manganite and insulator materials. This system is characterized by the interaction lack between compounds that keeps the intrinsic properties of the manganite material. Therefore with this system, we can make use of the spin polarized properties and the heterogeneous granular advantages, where, the secondary insulating phase works as an energy barrier at grain boundaries and hinders conduction between grains leading to the spin tunneling and the LFMR. This work has two important aims, first one is the attempt to enhance the LFMR of $\text{La}_{0.7}\text{Ba}_{0.3}\text{MnO}_3$ (LBMO) by the artificial boundaries, this is by introducing TiO_2 insulator as a secondary phase forming LBMO/ $x\text{TiO}_2$ system. The second aim is to explore the magnetocaloric properties of this system, which are expected to be promising because we talking about a change in the MCE properties at the same temperature range (T_C).

2. Experimental method

LBMO/ $x\text{TiO}_2$ ceramic samples with $x = 0, 0.02, 0.04, 0.06$ and 0.08 were prepared in several steps. LBMO was prepared by the sol–gel method using $\text{LaN}_3\text{O}_9 \cdot 6\text{H}_2\text{O}$, $\text{Ba}(\text{OOCCH}_3)_2$ and $\text{Mn}(\text{OOCCH}_3)_2 \cdot 4\text{H}_2\text{O}$ starting raw compounds. Stoichiometric solutions of these salts were mixed and stirred together, then 1:1 volume ratio of citric acid was added during the stirring process and resulted in a white colloid. After drying, the brown xerogel was ground and calcined at 600°C for 8 h. The obtained black powder was pressed and sintered at 1200°C for 24 h. TiO_2 nanotubes (NTs) were prepared by the electrochemical anodization method as reported in [14], where Ti foils with high purity (99.6%) were cleaned ultrasonically in acetone, isopropanol, ethanol and de-ionized water, respectively. The anodization process was carried out at room temperature for 24 h in electrochemical cell with platinum grid cathode at constant dc voltage (60 V). The electrolyte solution was a mixture of ammonium fluoride (0.3%), ethylene glycol and de-ionized water (1.8%). The resultant TiO_2 NTs were calcined at 400°C for 2 h to increase their crystallinity obtaining the anatase phase [15]. Finally, stoichiometric amounts of LBMO and TiO_2 NTs were mixed, pelletized and sintered at 800°C for 24 h.

The crystal structure was examined by XRD at room temperature and the structural information was obtained by Rietveld refinement using FULLPROF program. The surface morphology was carried out using scanning electron microscope (SEM). Electrical resistivity measurements in zero and 0.5T magnetic field were measured by the standard four-point Van der Pauw technique, and the magnetic measurements were performed using SQUID magnetometer.

3. Results and discussion

3.1. Structure

XRD patterns in Fig. 1a show the single phase of LBMO with additional peaks of TiO_2 in doped composites at $2\theta = 25.32^\circ$ and 48.25° . The coexistence of TiO_2 with the LBMO phase in all doped composites suggests their interaction lack that preserves the R-3c rhombohedral structure of LBMO with doping level as

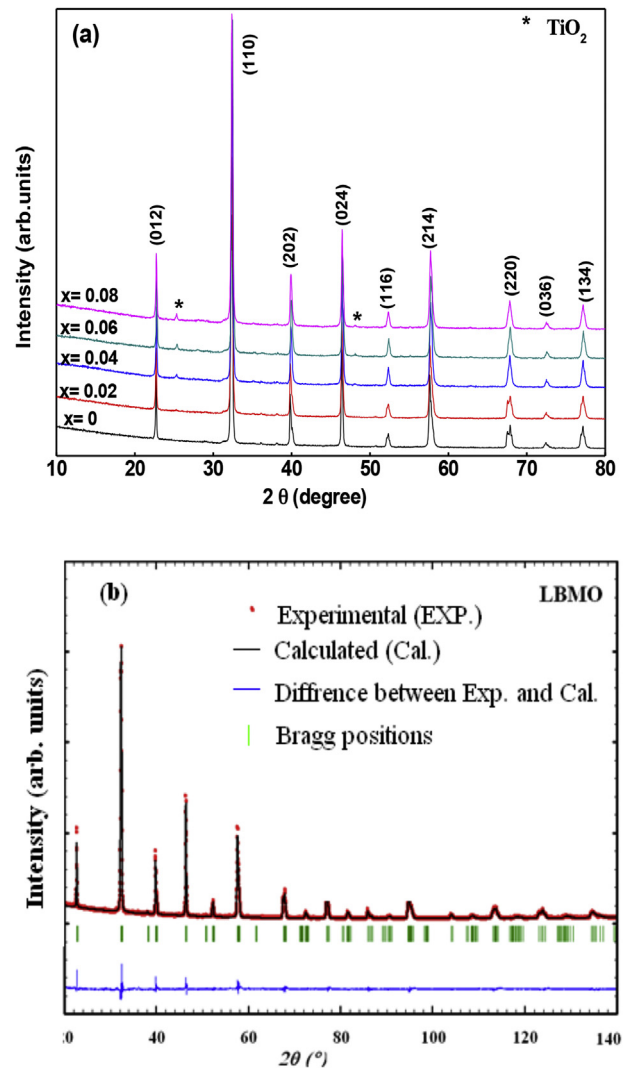


Fig. 1. (a) XRD patterns of LBMO/ $x\text{TiO}_2$ composites, $0 \leq x \leq 0.08$ and (b) Rietveld based calculated profile of the undoped compound LBMO.

proved by Reitveld refinement. Where, Fig. 1b shows Reitveld profile for LBMO compound as an example with refinement factors listed in Table 1 as the goodness of fitting (χ^2), the crystallographic factor (R_f) and the Bragg factor (R_B). TiO_2 –LBMO interaction lack may be supported by SEM micrographs, where, Fig. 2 shows TiO_2 NTs destruction, during preparation process, and their precipitation at the boundaries and on the surfaces of LBMO as segregated grains. This explains the insignificant change in cell volume, lattice constants (a, c), SEM grain size and structure stability with increasing doping level as seen in Table 1. Moreover, the presence of La, Ba, Mn and Ti elements were confirmed for the nominal composition by the energy dispersive

Table 1

Lattice constants, cell volume (V), SEM grain size and Rietveld agreement factors for LBMO/ $x\text{TiO}_2$.

Composition	a(Å)	c(Å)	V(Å) ³	Grain size (μm)	χ^2	R_f	R_B
x = 0	5.54368	13.483	358.86	0.748	3.12	5.44	5.30
x = 0.02	5.54093	13.483	358.52	0.659	2.65	3.12	3.02
x = 0.04	5.5349	13.503	358.25	0.659	3.39	4.04	3.35
x = 0.06	5.5347	13.503	358.20	0.684	5.39	4.59	4.13
x = 0.08	5.5360	13.497	358.22	0.635	2.85	4.60	3.98

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