Journal of Alloys and Compounds 665 (2016) 394–403

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Annealing temperature effect on magnetic and magnetocaloric properties of manganites

Abd El-Moez A. Mohamed [a, b, *], V. Vega [b, c], M. Ipatov [d], A.M. Ahmed [a], B. Hernando [b]

[a] Physics Department, Faculty of Science, Sohag University, Sohag 82524, Egypt
[b] Physics Department, Faculty of Science, Oviedo University, Oviedo 33007, Spain
[c] Laboratory of Nanoporous Membranes, Oviedo University, Oviedo 33006, Spain
[d] Materials Physics Department, Faculty of Chemistry, Basque Country University, San Sebastian 20018, Spain

ARTICLE INFO

Article history:
Received 4 December 2015
Received in revised form
7 January 2016
Accepted 8 January 2016
Available online 11 January 2016

Keywords:
Composite materials
Rare earth alloys and compounds
Grain boundaries
Magnetization
Magnetocaloric effect

ABSTRACT

In this work, we investigate the effect of annealing process at different temperatures (600 and 800 °C) on structural, magnetic and magnetocaloric properties of $La_{0.7}Ba_{0.3}MnO_3/xTiO_2$ system with x = 0.04 and 0.06. Crystal structure analysis shows the R-3c rhombohedral symmetry for composites in both annealing temperatures indicating structure stability. Magnetization and coercive field of doped composites increase with increasing annealing temperature, while there is no effect on their Curie temperature (T_c) that remains constant at 348 K due to the TiO_2-$La_{0.7}Ba_{0.3}MnO_3$ interaction lack. Increasing annealing temperature is found to be an effective process that can positively affect the magnetocaloric properties. Where, the relative cooling power of doped composites increases from 50 to 62 J/kg for x = 0.04 composite and from 54 to 66 J/kg for x = 0.06 composite with increasing annealing temperature from 600 to 800 °C. Moreover, the experimental results of magnetic entropy change have been modulated using Landau theory and the calculations have indicated the negligible contribution of elastic, magnetoelastic and magnetoelectronic coupling in the magnetocaloric properties of $La_{0.7}Ba_{0.3}MnO_3/xTiO_2$ system in both annealing temperatures.

1. Introduction

Magnetic refrigeration technique is one of the most promising techniques in cooling technology because of the efficient and the environmental safe cooling applications, which have encouraged the experimental and the theoretical studies in this direction. Obtaining low cost and high performance magnetocaloric materials is not an easy target because of the associated demerits. For example, Gd shows a large magnetocaloric effect (MCE) in room temperature range [1], but it is an expensive element and tends to oxidation. Current researches seek to balance the needs of technical applications by obtaining high MCE performance with fewer disadvantages by investigating various kinds of magnetic materials treated in different conditions.

Recently, manganites oxides have been paid attention for MCE applications because of the outstanding physico-chemical properties that enable them to work with chemical stability and high magnetization. The *magnetoresistive/insulator* system is an inhomogeneous system consisting of non-reacted manganite and insulator materials such as $La_{0.7}Sr_{0.3}MnO_3/ZrO_2$ [2]. The main idea behind this system depends on the interaction lack between manganite and insulator materials that keeps on the intrinsic properties of the manganite material. This enables us to tune the T_c related phenomena as the MCE at the same temperature range [3]. In fact, the insulator distribution at the grain boundaries and on the surface of the manganite grains is the key role of this system properties. For instance, the insulator distribution changes the boundaries resistance that increases magnetization disconnection leading to the spin tunneling between grains and hence to the low field magnetoresistance [4]. The insulator distribution may be affected by annealing temperature modifying magnetic properties

* Corresponding author. Physics Department, Faculty of Science, Oviedo University, Oviedo 33007, Spain.
E-mail address: abdmoez_hussien@science.sohag.edu.eg (A.A. Mohamed).

http://dx.doi.org/10.1016/j.jallcom.2016.01.057
0925-8388/

and related phenomena. Accordingly, after we have studied the effect of insulator doping level in $La_{0.7}Ba_{0.3}MnO_3/xTiO_2$ system ($0 \leq x \leq 0.08$) in a previous study [3] and managed to enhance the MCE of $La_{0.7}Ba_{0.3}MnO_3$ at the same temperature range, it is a fruitful to study the influence of insulator distribution by annealing temperature and its effect on magnetic and magnetocaloric properties of $La_{0.7}Ba_{0.3}MnO_3/xTiO_2$ system that has not been knocked before in these systems.

2. Experimental method

Polycrystalline $La_{0.7}Ba_{0.3}MnO_3/xTiO_2$ ceramic samples with x = 0.04 and 0.06 composites were prepared in several steps. $La_{0.7}Ba_{0.3}MnO_3$ (LBMO) was prepared by the sol-gel method using $LaN_3O_9.6H_2O$, Ba $(OOCCH_3)_2$ and Mn $(OOCCH3)_2.4H_2O$ raw as reported in Ref. [5] and sintered at 1200 °C for 24 h. TiO_2 nanotubes (NTs) were prepared by the electrochemical anodization method of titanium foils (99.6%) as reported in Ref. [6]. Then, the resultant TiO_2 NTs were annealed for 2 h at 400 °C. Stoichiometric amounts of LBMO and TiO_2 were mixed and pressed, then annealed at different temperatures of 600 °C and 800 °C for 24 h. Crystal structure was examined by x-ray diffraction (XRD) at room temperature, and the patterns were analyzed using Rietveld refinement method with FULLPROF program. Surface morphology was carried out using scanning electron microscope (SEM), while, magnetic and magnetocaloric characterizations were performed using SQUID magnetometer.

Table 1
Symmetry, cell volume (V), SEM grain size (G) and XRD crystallite size (P) of LBMO/*x*TiO2 composites annealed at 600 and 800 °C.

Composition	Condition	Symmetry	V (Å)^3	G (μm)	P (nm)
x = 0	as-prepared	R-3c	358.86	0.74	32
x = 0.04	600 °C	R-3c	358.17	0.63	34
	800 °C	R-3c	358.25	0.65	33
x = 0.06	600 °C	R-3c	358.23	0.67	33
	800 °C	R-3c	358.20	0.68	34

3. Results and discussion

3.1. Structure

XRD patterns of LBMO/$xTiO_2$ composites annealed at 600 and 800 °C are shown in Fig. 1. The single phase of the undoped LBMO compound indicates the high homogeneity and the complete reaction between elements. The patterns of doped composites are characterized by an additional peak of TiO_2 at $2\theta = 25.32°$ revealing its coexistence with LBMO phase. This suggests TiO_2-LBMO interaction lack in doped composites that seems to be preserved with increasing annealing temperature due to the quite similar peak intensity of TiO_2 in both annealing temperatures. The interaction lack leads to several consequences as structure stability at the R-3c rhombohedral symmetry, cell volume (V) insignificant change and constant value of XRD crystallite size (P) for composites in both

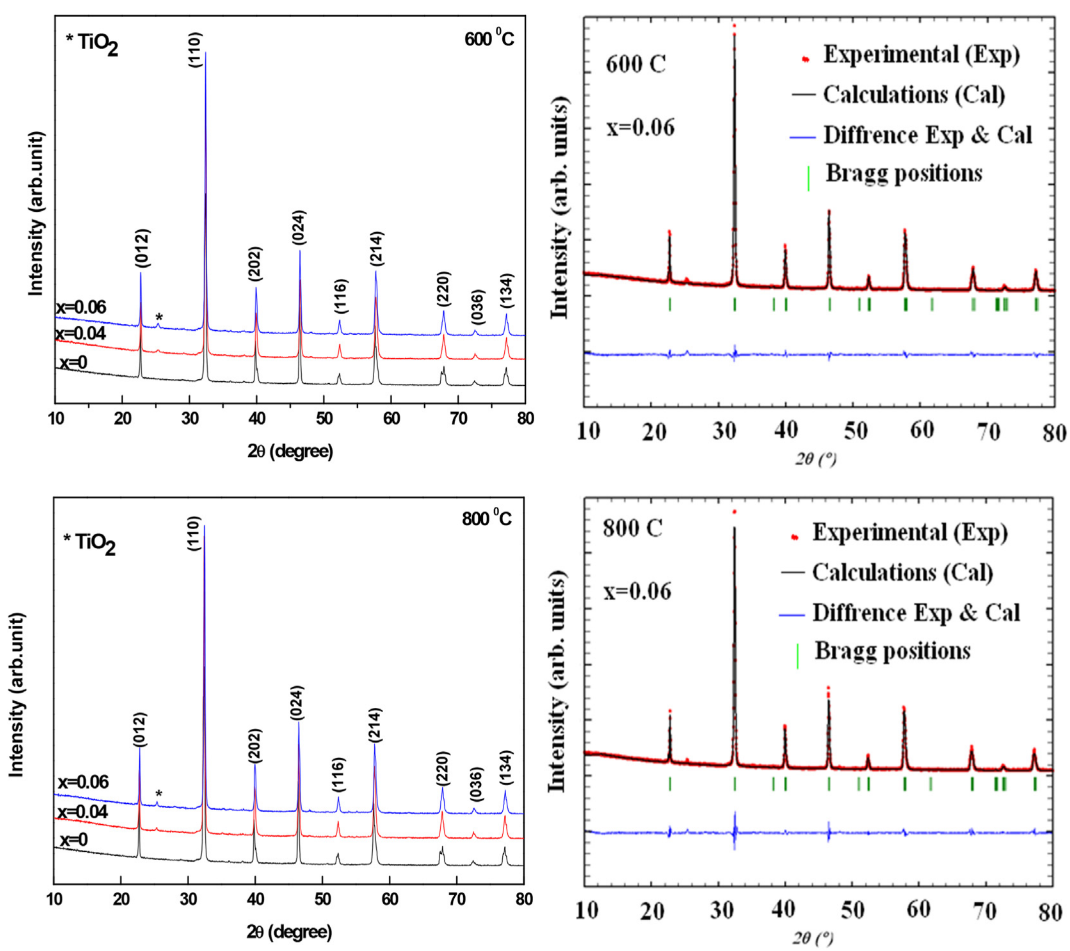

Fig. 1. XRD patterns of LBMO/$xTiO_2$ composites and Rietveld refinement profile for x = 0.06 composite annealed at 600 and 800 °C.