



Enhanced magnetic properties in low doped $\text{La}_{1-x}\text{Ba}_x\text{MnO}_{3+\delta}$ ($x=0, 0.1$ and 0.2) nanoparticles



Rakesh Dhama¹, Chiranjib Nayek, Ch. Thirimal, P. Murugavel*

Department of Physics, Indian Institute of Technology Madras, Chennai 600036, India

ARTICLE INFO

Article history:

Received 17 July 2013

Received in revised form

22 March 2014

Available online 13 April 2014

Keywords:

Manganite

Nanoparticle

Cationic vacancy

Magnetic property

ABSTRACT

Low doped colossal magnetoresistance $\text{La}_{1-x}\text{Ba}_x\text{MnO}_{3+\delta}$ nanoparticles are synthesized by a sol–gel method along with the parent compound $\text{LaMnO}_{3+\delta}$. The Reitveld refinements on the XRD patterns show that they are crystallized in structure other than their stoichiometric bulk. The crystal structure indicates excess oxygen/cationic vacancies in the compound. The magnetic measurements reveal that the ferromagnetic Curie temperature (T_C) is enhanced after oxygen annealing. The observed T_C is higher than that of their stoichiometric bulk compounds and the values are comparable to the reported tensile strained epitaxial thin films. The estimated $\text{Mn}^{4+}/\text{Mn}^{3+}$ ratio is found to increase in the nanocrystalline samples compared to their bulk samples annealed under the same oxygen atmosphere. The enhancement in Curie temperature could be correlated with the excess oxygen/cationic vacancies.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

The alkaline earth doped rare earth manganites, $\text{R}_{1-x}\text{A}_x\text{MnO}_3$ ($\text{R}=\text{La, Pr, Nd, Sm, etc.}$, and $\text{A}=\text{Ca, Ba, and Sr}$), have immense attraction due to the understanding of fundamentals of physics in these strongly correlated electron systems and their potential technological applications [1–5]. Its large colossal magnetoresistance (CMR) with high spin polarized carriers make them suitable for widespread applications in spintronics. Though the stoichiometric LaMnO_3 is an antiferromagnetic insulator, upon alkaline earth doping (A site ion) it becomes simultaneously ferromagnetic and metal with high magnetoresistance property [5]. However the maximum CMR is observed near the metal–insulator transition temperatures. The change in character of the Curie temperature (T_C) and metal to insulator transition temperature (T_{MI}) have been extensively studied as a function of various parameters such as doping elements, doping concentrations, the synthesis conditions and oxygen stoichiometry, etc. [5–9]. On the other hand, the CMR compounds in nanocrystalline form have reported to show unusual properties such as super-paramagnetism, spin glass behavior, etc. [10–14]. However most of the studies on nanocrystalline $\text{R}_{1-x}\text{A}_x\text{MnO}_3$ compounds are restricted to nominal doping level i.e., $x \geq 0.3$ with very few reports on low doped ($x < 0.3$) compounds. Interestingly, there are reports on increasing transition

temperature well above room temperature and thereby enhancing the CMR values by means of substrate induced strain in low doped $\text{La}_{1-x}\text{Ba}_x\text{MnO}_3$ thin films [15,16]. These effects seem to be pronounced with decrease in film thickness. In this regard, it would be interesting to investigate the structural and magnetic properties of nanocrystalline low doped $\text{La}_{1-x}\text{Ba}_x\text{MnO}_3$ compounds. In the present work, we have prepared $\text{La}_{0.9}\text{Ba}_{0.1}\text{MnO}_3$ and $\text{La}_{0.8}\text{Ba}_{0.2}\text{MnO}_3$ along with the parent LaMnO_3 in nanocrystalline form by a sol–gel technique. We observed enhanced magnetic properties which can be attributed to the oxygen nonstoichiometry in low doped CMR rare earth manganites.

2. Experimental

To synthesize LaMnO_3 , $\text{La}_{0.9}\text{Ba}_{0.1}\text{MnO}_3$ and $\text{La}_{0.8}\text{Ba}_{0.2}\text{MnO}_3$ by the sol–gel method, lanthanum acetate, manganese acetate and the barium carbonates dissolved in nitric acid are chosen as precursor materials. Initially, 0.05 M quantities of the precursors are mixed in a beaker and stirred for 30 min at 60 °C, then 2 M quantity of citric acid dissolved in de-ionized water is added to this mixture. After continuous stirring for 2 h, ethylene glycol is added as a polymerization agent and the mixture is maintained at 90 °C until the formation of brown gel. The gel is preheated at 450 °C for 2 h followed by calcination at 600 °C, 700 °C and 800 °C separately. For comparison, the samples are also made in bulk by a solid state synthesis method and the final calcination is done at 900 °C for 12 h under oxygen flow. The calcined powders are characterized for their structure and morphology by the Pan

* Corresponding author. Tel.: +91 44 22574897.

E-mail addresses: muruga@iitm.ac.in, muruga@physics.iitm.ac.in (P. Murugavel).

¹ Present address: Department of Physics, University of Calabria, Rende 87036, Italy.

Analytical X'Pert PRO diffractometer and Philips CM 20 Transmission Electron Microscope (TEM), respectively. The Mn^{3+} and Mn^{4+} contents are estimated by an iodometric titration method [17]. Magnetization measurements are carried out as a function of temperature from 10 to 300 K in a Lakeshore 7410 Vibrating Sample Magnetometer (VSM) under zero field cooled (ZFC) and field cooled (FC) conditions by applying 200 Oe magnetic field.

3. Results and discussion

The morphology and particle size of the synthesized powders are analyzed by TEM and Fig. 1(a) shows the TEM image of the LaMnO_3 powder annealed at 800 °C. The figure shows that the particles are agglomerated and irregular in shape. The electron diffraction pattern shown in Fig. 1(b) reveals that they are polycrystalline. The histogram in Fig. 1(c) indicates that most of the particles are in nanometer range from 20 to 50 nm. Similar trend is observed for both $\text{La}_{0.9}\text{Ba}_{0.1}\text{MnO}_3$ and $\text{La}_{0.8}\text{Ba}_{0.2}\text{MnO}_3$ samples (not shown in the figure).

The X-ray diffraction patterns for LaMnO_3 (LMO) calcined at 600 °C, 700 °C and 800 °C are shown in Fig. 2(a). The sample calcined at 600 °C shows a signature of amorphous content along with a crystalline phase, whereas the samples calcined at 700 °C and 800 °C show peaks corresponding to crystalline LaMnO_3 compound without any trace of secondary or impurity phases. We have performed the Reitveld refinements on the XRD patterns and confirmed that LaMnO_3 calcined at different temperatures are all crystallized in a rhombohedral phase in $R\bar{3}c$ space group. The lattice parameters for the sample calcined at 600 °C are $a=b=5.4933$ Å and $c=13.3112$ Å and at 800 °C are $a=b=5.5179$ Å and $c=13.3741$ Å. The XRD patterns of $\text{La}_{0.8}\text{Ba}_{0.2}\text{MnO}_3$ calcined at 600 °C, 700 °C and 800 °C are shown in Fig. 2(b). Reitveld refinement on $\text{La}_{0.9}\text{Ba}_{0.1}\text{MnO}_3$ and $\text{La}_{0.8}\text{Ba}_{0.2}\text{MnO}_3$ samples reveals that they crystallized in cubic structure with $\text{Pm}\bar{3}m$ space group.

It is known that the vacancy free stoichiometric LaMnO_3 crystallizes in orthorhombic structure with Mn–O–Mn bond angle at 152° [5]. However it is difficult to synthesize vacancy free LaMnO_3 under normal ambient condition. $\text{LaMnO}_{3+\delta}$ and even $\text{La}_{1-x}\text{R}_x\text{MnO}_{3+\delta}$ can have excess oxygen up to certain doping level if processed under oxygen atmosphere [8]. Since perovskite cannot accommodate excess oxygen in its structure, it can be interpreted in terms of equal distribution of cationic vacancies such as $\text{La}_{1-\gamma}\text{Mn}_{1-\gamma}\text{O}_3$ instead of $\text{LaMnO}_{3+\delta}$ [$\gamma=\delta/(3+\delta)$] [18]. LaMnO_3 undergoes structural change from orthorhombic to rhombohedral structure with increase in

cationic vacancies [5]. As the Mn–O–Mn bond angle approaches 180°, the structure changes to cubic. Thus rhombohedral structure of $\text{LaMnO}_{3+\delta}$ and cubic structure of $\text{La}_{0.9}\text{Ba}_{0.1}\text{MnO}_{3+\delta}$ and $\text{La}_{0.8}\text{Ba}_{0.2}\text{MnO}_{3+\delta}$ nanoparticles confirm the presence of cationic vacancies.

The magnetization measured under zero field cooled (ZFC) and field cooled (FC) conditions as a function of temperature from 10 K to 300 K for $\text{LaMnO}_{3+\delta}$ annealed at 600 °C, 700 °C and 800 °C are shown in Fig. 3. Though stoichiometric $\text{LaMnO}_{3+\delta}$ is an antiferromagnetic insulator, the annealed samples are all ferromagnetic with Curie temperature (T_C) of 95 K, 235 K and 259 K after annealing at 600 °C, 700 °C, and 800 °C, respectively. The difference in ZFC and FC data could be due to superparamagnetic nature of the synthesized nanoparticles. In Fig. 4(a) and (b), we show the magnetization versus temperature plots for $\text{La}_{0.9}\text{Ba}_{0.1}\text{MnO}_{3+\delta}$ and $\text{La}_{0.8}\text{Ba}_{0.2}\text{MnO}_{3+\delta}$ samples. For $\text{La}_{0.9}\text{Ba}_{0.1}\text{MnO}_{3+\delta}$ annealed at 600 °C and 800 °C under ambient conditions, T_C is at 200 K and 230 K, and for $\text{La}_{0.8}\text{Ba}_{0.2}\text{MnO}_{3+\delta}$ annealed at 600 °C and 800 °C under ambient conditions, T_C is at 275 K and ~300 K, respectively. Note that the Curie temperature for stoichiometric $\text{La}_{0.9}\text{Ba}_{0.1}\text{MnO}_3$ and $\text{La}_{0.8}\text{Ba}_{0.2}\text{MnO}_3$ is 165 K and 260 K, respectively [7]. The compounds annealed even under ambient conditions at 600 °C show higher T_C than their bulk compound and T_C is enhanced substantially with increase in annealing temperature. To see the effect of oxygen annealing on T_C , we annealed $\text{La}_{0.9}\text{Ba}_{0.1}\text{MnO}_3$ and $\text{La}_{0.8}\text{Ba}_{0.2}\text{MnO}_3$ samples at 800 °C under oxygen atmosphere for 6 h. The respective magnetization versus temperature plots are shown in Fig. 4(a) and (b). The plots show that after oxygen annealing, T_C for $\text{La}_{0.9}\text{Ba}_{0.1}\text{MnO}_{3+\delta}$ and $\text{La}_{0.8}\text{Ba}_{0.2}\text{MnO}_{3+\delta}$ has increased to 285 K and >300 K, respectively. Overall, annealing the nanoparticles under oxygen atmosphere has resulted in large increase in ferromagnetic transition temperature especially in low doped region (for $x=0.1$).

The enhancement in T_C can be directly correlated with the excess oxygen content (δ)/cationic vacancies (γ) in the compounds. Debrowskii et al. reported that $\text{La}_{0.9}\text{Ba}_{0.1}\text{MnO}_{3+\delta}$ and $\text{La}_{0.8}\text{Ba}_{0.2}\text{MnO}_{3+\delta}$ can have the maximum of 0.13 and 0.05 as δ value after annealing under high oxygen partial pressure [7]. The increase in δ can lead to increase in the $\text{Mn}^{4+}/\text{Mn}^{3+}$ ratio and hence increase in hole doping. Thus the effective hole doping $h=x+2\delta$ in $\text{La}_{1-x}\text{Ba}_x\text{MnO}_3$ can be significantly altered by δ . In $\text{La}_{0.9}\text{Ba}_{0.1}\text{MnO}_{3+\delta}$ and $\text{La}_{0.8}\text{Ba}_{0.2}\text{MnO}_{3+\delta}$, the effective hole doping at maximum δ can be made comparable to the stoichiometric $\text{La}_{0.67}\text{Ba}_{0.33}\text{MnO}_3$ whose T_C is at 340 K [7]. The $\text{Mn}^{4+}/\text{Mn}^{3+}$ ratio estimated by iodometric titration for $\text{LaMnO}_{3+\delta}$, $\text{La}_{0.9}\text{Ba}_{0.1}\text{MnO}_{3+\delta}$ and $\text{La}_{0.8}\text{Ba}_{0.2}\text{MnO}_{3+\delta}$ bulk sample is 0.476, 0.661,

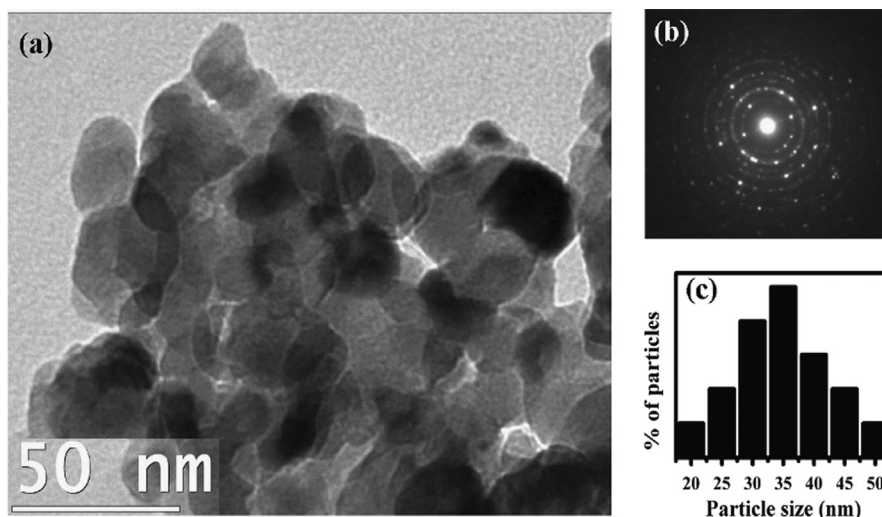


Fig. 1. (a) TEM micrograph and (b) the electron diffraction pattern of LaMnO_3 annealed at 800 °C. (c) The histogram shows the particle size distribution.

Download English Version:

<https://daneshyari.com/en/article/8157003>

Download Persian Version:

<https://daneshyari.com/article/8157003>

[Daneshyari.com](https://daneshyari.com)