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The influence of the sintering temperature on the structural and the magnetic properties of doped manganites: $La_{0.95}Ag_{0.05}MnO_3$ and $La_{0.75}Ag_{0.25}MnO_3$

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ABSTRACT

$La_{1-x}Ag_xMnO_3$ samples were synthesized by standard sol–gel method with Ag concentrations of x=0.05 and 0.25. The samples from each concentration were pressed and sintered at 1000, 1200 and 1400 °C for 24 h in air for a systematic study. They were examined structurally by Atomic Force Microscopy (AFM), Scanning Electron Microscopy (SEM) with Energy Dispersive Spectroscopy (EDS) and X-ray Diffraction (XRD) and magnetically by Magnetic Properties Measurements System (MPMS). AFM and SEM analyses show that surface morphology changes with Ag concentration and sintering temperature (T_S). It was observed that high temperature sintering leads Ag to leave material as determined from EDS analyses. XRD spectra exhibited that the crystal structure changes with Ag concentration while showing pronounced change with the sintering temperature. From the magnetic measurements, the Curie temperatures (T_C) and the isothermal magnetic entropy changes ($-\Delta SM$) were calculated. It was observed that T_C increases with Ag concentration and decreases with T_S. The maximum $-\Delta SM$ was calculated to be 7.2 J/kg K under the field change of 5 T for the sample sintered at 1000 °C with x=0.25.

1. Introduction

Recent investigations have shown high enough Magnetocaloric Effect (MCE) in less costly manganite compounds such as $A_{1-x}B_xMnO_3$, promising their potential applications in magnetic refrigeration systems operating around room temperature [1–3]. This has accelerated the studies on manganite based materials. Among these, $La_{1-x}A_xMnO_3$ (A is a divalent or a monovalent atom such as Ca, Sr, Ba, Pb, Ag, K, Na, etc.) compounds have been investigated extensively [4–11]. $LaMnO_3$ itself is an antiferromagnetic and an insulator material with perovskite structure [12]. However, an alkali or an alkaline earth cation substitution for La in $La_{1-x}A_xMnO_3$ system gives rise to intriguing magnetic and electrical properties, i.e. large MCE that is comparable to that of Gd based alloys, near room temperature [3]. It is known that in $La_{1-x}A_xMnO_3$, magnetic properties are favored by A site dopant [7,13,14]. A monovalent or a divalent atom substitution for La improves the magnetic properties, i.e. higher T_C [14] and MCE, according to the double-exchange mechanism [15]. Recent investigations with Ag substitution in $La_{1-x}A_xMnO_3$ system have exhibited good magnetic properties since each Ag^{1+} oxidizes two Mn^{3+} ions to Mn^{4+} ions that is favored by double exchange mechanism.

The present study aims to explore the effects of Ag concentration (x=0.05, 0.25) and T_S at elevated temperatures (1000, 1200 and 1400 °C) in $La_{1-x}Ag_xMnO_3$ system. Our results show that in these compounds maximum solubility of Ag^{1+} in $LaMnO_3$ decreases with increasing T_S.

2. Experimental procedure

In this study, $La_{1-x}Ag_xMnO_3$ samples with x=0.05 and 0.25 have been prepared by sol–gel method. Appropriate amounts of La_2O_3, $Ag(NO_3)_2$ and $Mn(NO_3)_2$ with desired stoichiometries were dissolved in dilute HNO_3 solution at 150 °C. Then citric acid and ethylene glycol were added to the mixture. Viscous residual was formed by slowly boiling this solution at 200 °C. The obtained residual was dried slowly at 300 °C until dry-gel was formed. Finally, the residual precursor was burned in air at 600 °C in order to remove organic materials produced during chemical reactions. The material obtained from this process was ground by using an

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agate mortar to have fine powder. Three sets of pellets were produced from each composition by pressing into 13 mm radii and 2 mm thicknesses under 3 tons. Each pellet set was then separately sintered at 1000, 1200 and 1400 °C for 24 h in air and cooled down to room temperature in the furnace.

AFM study was carried out using Solver-PRO AFM with a maximum scan area of $62 \times 62\ \mu m^2$. Measurements were made in contact mode. The AFM cantilever used in the measurements is CSG10 series with a typical length of 250 μm, thickness of 35 μm, and spring constant of 0.1 N/m. SEM investigations were performed using a JEOL SEM 7700F, equipped with an EDS system. XRD was performed ($10^\circ \leq 2\theta \leq 70^\circ$) using a Bruker D8 Advance X-ray Diffractometer with a $CuK\alpha_1$ radiation.

The magnetic properties were measured using a Quantum Design MPMS with a closed cycle helium cryostat operating from 10 to 340 K with magnetic fields up to 5 T. From the temperature dependence of magnetization ($M(T)$), T_C values were determined at an applied field of 100 Oe. In the measurement sequences, the samples were first cooled down to 10 K under zero field (ZFC), and magnetization was measured up to 340 K in the absence of a magnetic field. Later, a field of 100 Oe was turned on for field cooled magnetization down to 10 K (FC). In order to determine magnetic characteristics, $M(H)$ measurements were made around T_C from H=0 to 5 T at constant temperatures and at each set of measurements the temperature was changed with steps of 3 K for both increasing and decreasing values.

3. Results and discussions

3.1. AFM analyses

AFM images for $La_{0.95}Ag_{0.05}MnO_3$ and $La_{0.75}Ag_{0.25}MnO_3$ are shown in Figs. 1 and 2. Firstly, for confirmation that sol–gel prepared samples have formed nanometer sized particles, an AFM image of as-prepared palletized samples before sintering has been taken as presented in Fig. 1. As it is clearly seen, 100–200 nm sized particles gather as groups in the structure. The effects of Ag concentration and T_S on the surface morphology of the samples were also investigated by AFM. Only AFM images of 0.25 Ag doped samples sintered at 1200 and 1400 °C are given in Fig. 2 for brevity. An increase in T_S results in growth of grain sizes for both Ag concentrations. Nearly 3–5 times increase in grain size is observed as a result of rising T_S from 1200 to 1400 °C.

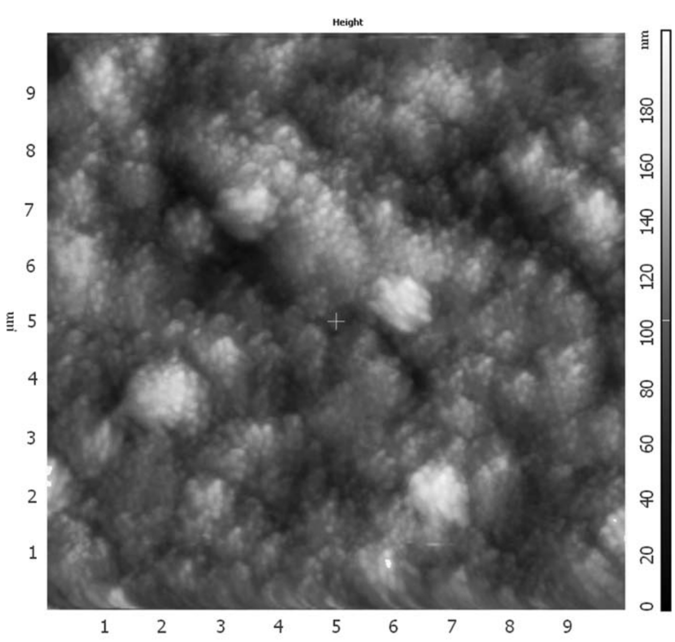

Fig. 1. AFM images of $La_{0.95}Ag_{0.05}MnO_3$ before sintering,

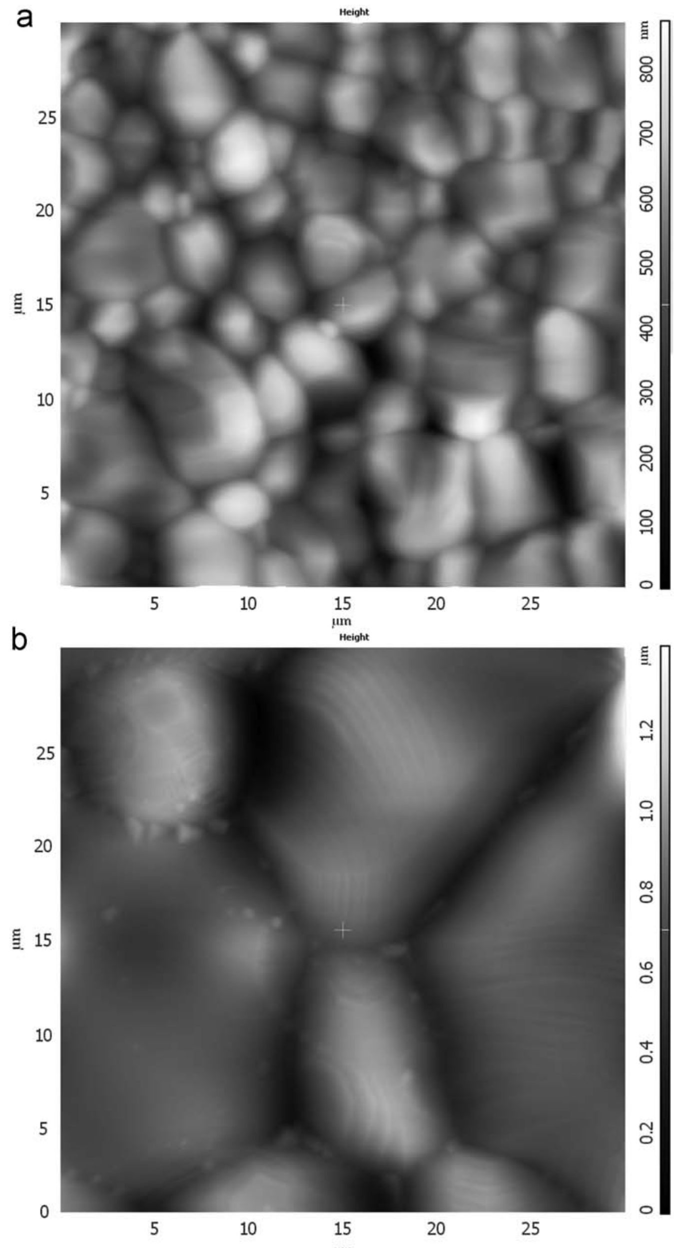

Fig. 2. AFM images of the samples with (a) x=0.25 T_S=1200 °C, and (b) x=0.25 T_S=1400 °C.

An increase in Ag concentration leaves the average grain sizes almost unchanged. In addition, very fine particles were observed at grain boundaries as seen in Fig. 2b. It is very likely that these particles are metallic Ag particles [16] since there is a trace of metallic Ag in the XRD pattern of the same sample. It is also well known that the grain boundaries of polycrystalline materials are the places where the surface energy is minimum. For this reason, these places are most likely locations for excess Ag that leave the perovskite structure under high T_S.