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Low Sm Doping Effects on the Low-Field Magnetoresistive Properties in $(La_{1-x}Sm_x)_{0.67}Sr_{0.33}MnO_3$ Perovskite

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ABSTRACT

A series of polycrystalline samples $(La_{1-x}Sm_x)_{0.67}Sr_{0.33}MnO_3$ (X=0.00, 0.05 and 0.10) were prepared using the conventional solid-state reaction method. The XRD analysis indicated that all the samples were fully crystalline and in a single phase with a rhombohedral structure after a sintering at 1200ºC for 24 hours in air. Meanwhile, the Atomic Force Microscopy measurements showed that a small amount of Sm doping in La sites affected the grain growth and this might affect the grain boundary layer, thus resulting in the reduction of the Curie temperature, T_C. Extrinsic magnetoresistance (MR) was observed for all the samples with a large negative MR at low field (0-0.1 or 0.2T) region, followed by a slower varying MR at high field (0.1 or 0.2-1T). The highest low-field MR value of -4.6% (at 0.1T) and -6.1% (at 0.2T) were observed for sample X=0.10 and X=0.05, respectively. Hence, these indicated that the extrinsic MR was grain size dependent and was therefore enhanced with a small amount of Sm substitution in La sites.

Keywords: **Low-field magnetoresistance, polycrystalline manganites**

ABBREVIATIONS

Magnetoresistance (MR),
Low Field Magnetoresistance (LFMR),
X-ray Diffraction (XRD),
Atomic Force Microscope (AFM)
Vibrating Sample Magnetometer (VSM)

INTRODUCTION

Doped manganite oxides of the ferromagnetic compounds, $A_{1-x}B_xMnO_3$ (where A=La, Pr, Nd etc. and B=Ba, Sr, Ag, etc.) (Ibarra *et al*., 1998; Im *et al*., 2007; Urushibara *et al*., 1995; Cheng *et al*., 2004) which show Colossal Magnetoresistance (CMR) effect have received huge attraction due to their potential in the application as a magnetic sensing element. Manganites usually exhibit metal-insulator transition (T_{MI}) accompanied by a simultaneous magnetic phase transition or Curie temperature (T_C). The double exchange mechanism, proposed by Zener (1951) and the Jahn-Teller (JT) effect (Millis *et al*., 1995) are commonly used to explain the above phenomena. When a significant high magnetic field is applied, the temperature of T_{MI} changes and the resistivity decreases correspondingly. These changes show a maximum near T_C or T_{MI} for single crystal compounds or epitaxial thin films commonly recognized as an intrinsic magnetoresistance (MR) effect (Mukovskii

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et al., 1999). Therefore, a number of works have been carried out to tailor the material with higher magnetoresistance in lower field and proper temperature range (room temperature). By tuning the composition of these compounds (e.g. doping A or B site with other ions of different sizes or charges), one can actually control or modify its transport or magnetic properties. The recent reports confirm that polycrystalline compounds do not only show an intrinsic MR effect but also an extrinsic MR effect in a relatively lower filed (i.e. the effect which is commonly known as the Low-Field Magnetoresistance, LFMR) (Nam *et al*., 2001). This effect is believed to be due to the spin-polarized tunnelling or spin-dependent scattering across the disordered grain boundaries layers (Miller *et al*., 2000; Xia *et al*., 2007; Zhang *et al*., 2007) and is mostly affected by the grain size, grain size distribution and the preparation conditions. Many works have been carried out to enhance the LFMR effect by introducing weak links at the grain boundaries (Zhang *et al*., 2007; Lu *et al*., 2006) or by introducing doping at the A or B site (Cheng *et al*., 2004; Zhang *et al*., 2006). In this paper, the effects of Samarium (Sm) substitution in the La site, concluded from an investigation on the structure, electrical properties and magnetic properties of the samples, are reported.

MATERIALS AND METHODS

Polycrystalline samples of $(La_{1-x}Sm_x)_{0.67}Sr_{0.33}MnO_3$ with X=0.00, 0.05 and 0.10 were prepared using the conventional solid-state reaction method. Appropriate amounts of high-purity La_2O_3, Sm_2O_3, $SrCO_3$ and MnO_2 powders (purity >99.5%) were mixed and pre-sintered at 900ºC for 12 hours in air. After the pre-sintered powder was ground, it was pressed into a pellet and then sintered at 1200ºC for 24 hours in air. X-ray diffraction (XRD) with the Cu K_α radiation and the Atomic Force Microscope (Quesant AFM: Q-Scope 350) were respectively used to characterize the structure and microstructure of the samples. The temperature dependence of the magnetization of the sample was measured at 313K to 393K by a Vibrating Sample Magnetometer (VSM, LakeShore 7400) and the magnetoresistance effect was measured using a DC four-point probe technique with an applied filed of 1 Tesla from 100K to 300K.

RESULTS AND DISCUSSION

Fig. 1 shows the XRD spectra of the samples, before and after the sintering process. In all cases the samples were shown to have more peaks before the sintering than after it. By comparing the XRD patterns, before and after the sintering process, one can deduce that the partially reacted starting powder during the calcination process (at 900ºC for 12 hours) has indeed reacted well and formed the end product of the bulk sample after the sintering process (at 1200ºC for 24 hours). Those missing peaks (marked with *) observed might be the ones of the starting precursor powder (La_2O_3, Sm_2O_3, $SrCO_3$ and MnO_2) which had not fully been reacted to form the single phase $(La_{1-x}Sm_x)_{0.67}Sr_{0.33}MnO_3$ powder which was only obtained after the sintering process. All the XRD patterns for the sintered samples, which were measured at room temperature, matched with the ICDD standard (reference code 00-050-0308), where all the samples are in the single phase rhombohedral structure with no detectable secondary phases which agrees with an earlier report (Im *et al*., 2007; Urushibara *et al*., 1995). Hence, crystallization was completed after sintering at 1200ºC for 24 hours in air. Sm has a smaller ionic radius (0.964Å) as compared to Lanthanum (La) (1.06Å). When smaller atom (Sm) is replaced with a bigger atom (La), one would expect some reduction in the lattice parameter, which is indicated by the increase of the 2 Theta angle shown in *Fig. 1*.

The distribution of the grains was characterized using the Atomic Force Microscope (AFM). *Fig. 2* shows the AFM images obtained at the room temperature for all the samples. The pure sample (X=0.00) has a relatively bigger grain size distribution, ranging from 2.5±0.1μm to 3.7±0.1μm.

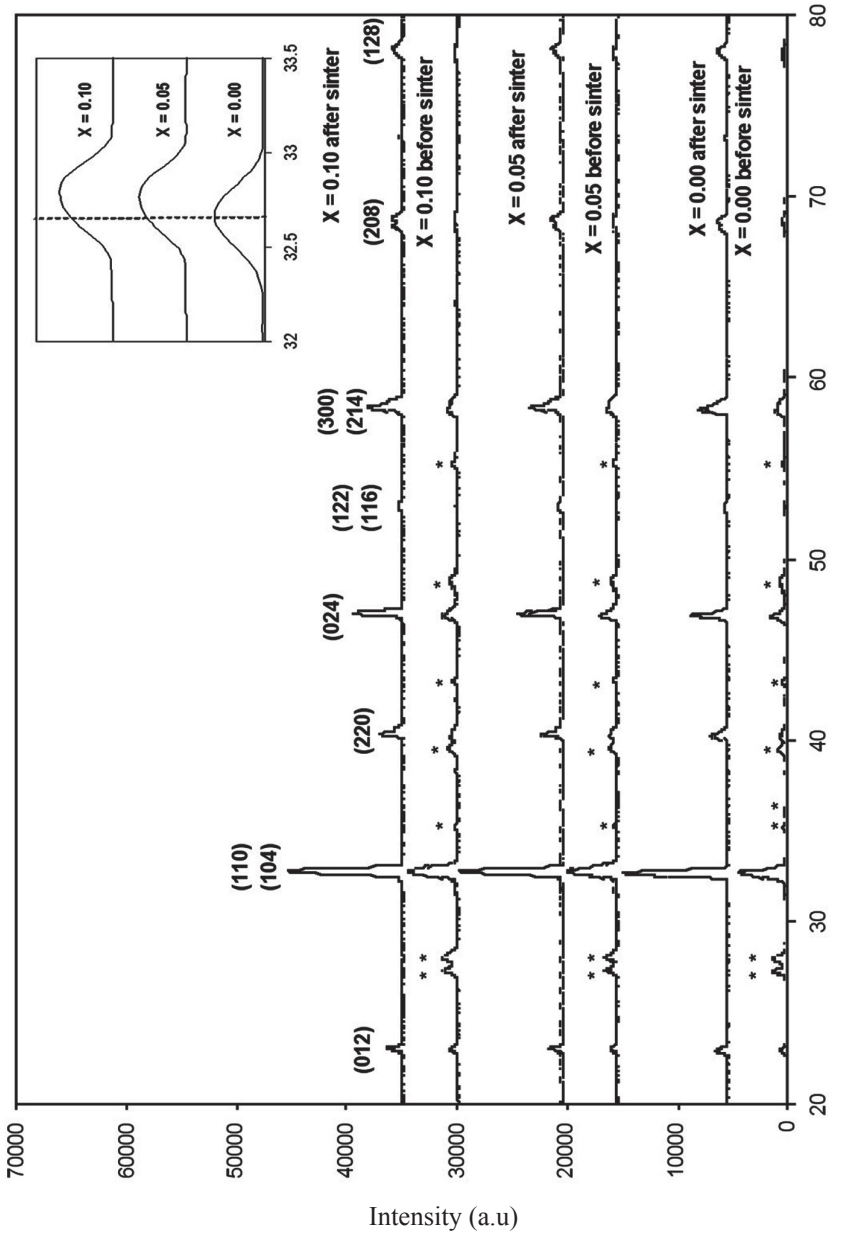

*Fig. 1: XRD pattern of $(La_{1-x}Sm_x)_{0.67}Sr_{0.33}MnO_3$ before and after sintering at open air. Peak marked with * represents the peak for the starting powder (La_2O_3, Sm_2O_3, $SrCO_3$ and MnO_2). The inset shows the shift of the main peak (32.6°) position due to the substitution of Sm*

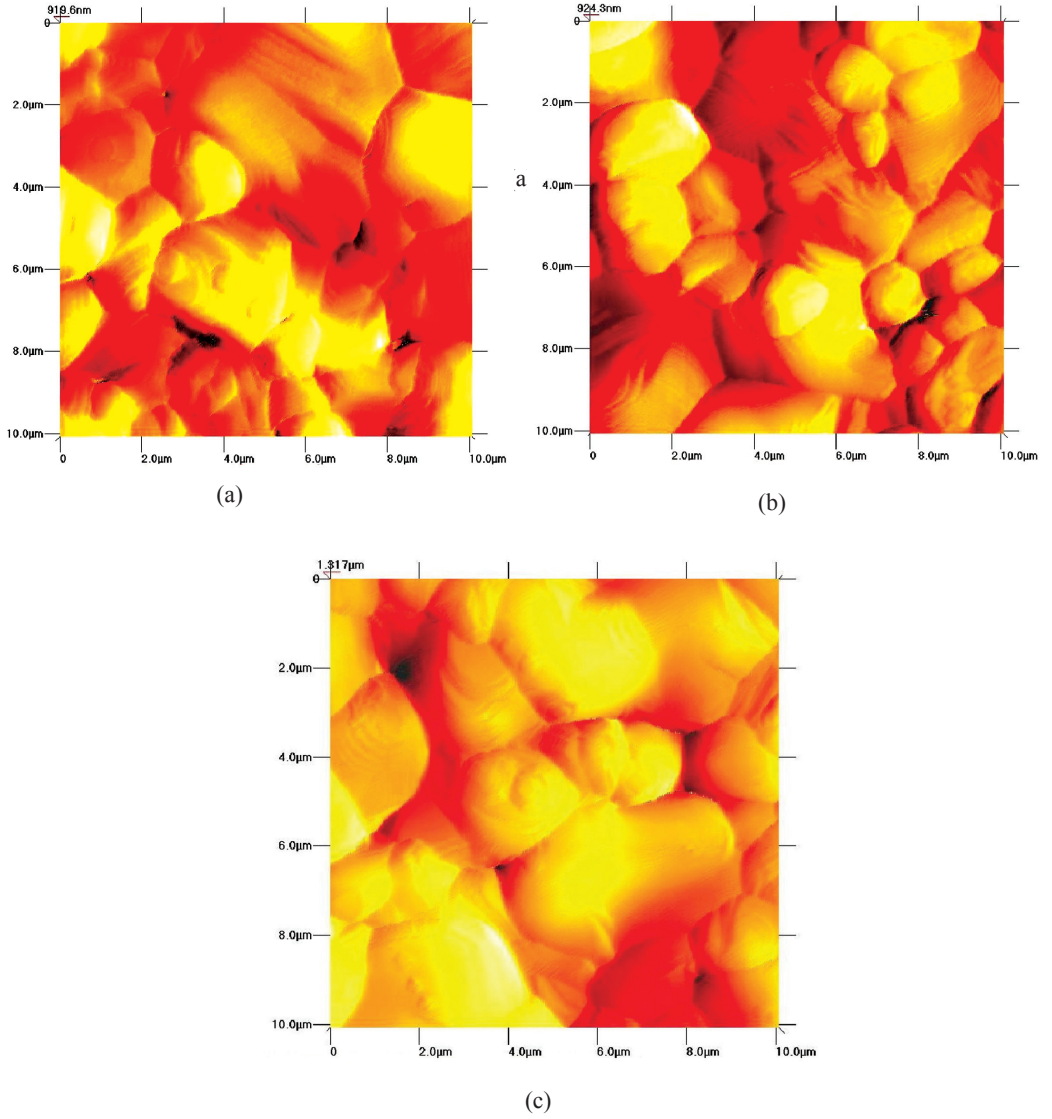

Fig. 2: AFM micrograph of $(La_{1-x}Smx)_{0.67}Sr_{0.33}MnO_3$ samples (a) X=0.00, (b) X=0.05 and (c) X=0.10

Furthermore, the distribution of the grain sizes is reduced to 1.8±0.1μm to 2±0.1μm when X=0.05 of Sm is substituted. When more Sm is introduced (X=0.10), the distribution of the grain sizes is once againd increased to 2.2±0.1μm to 2.7±0.1μm, indicating that substituting a small amount of Sm in the La site will affect the growth of grain.

The temperature dependences of magnetization in all the samples are shown in *Fig. 3(a)*. All the samples show a significant transition of paramagnetic to ferromagnetic phase which occurs at the temperature called the Curie temperature, T_C [defined as the temperature where dm/dt is minimum as shown in *Fig. 3(b)*]. The Curie temperature for the pure sample is 370K. This value

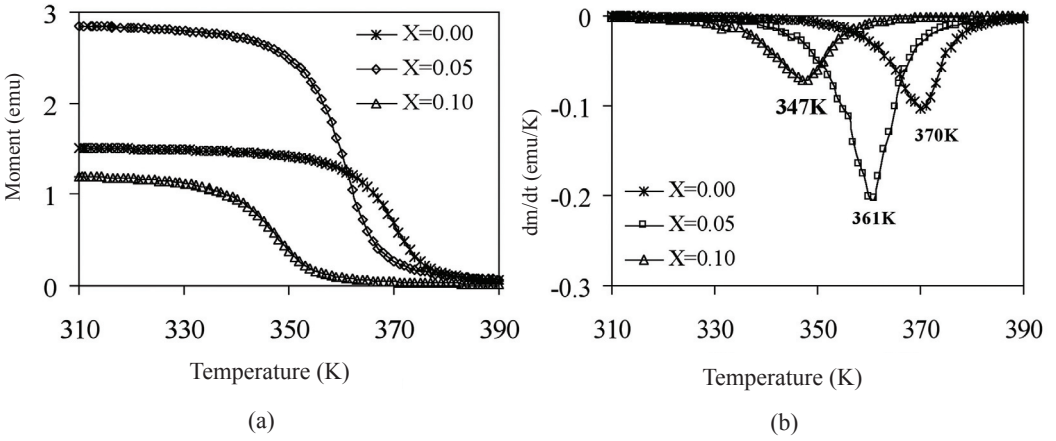

Fig. 3: (a) Moment vs. temperature, and (b) dm/dt vs temperature for $(La_{1-x}Sm_x)_{0.67}Sr_{0.33}MnO_3$ sample

is in agreement with the report by Cheng *et al*. (2004). When La is substituted with Sm (X=0.05), the Curie temperature drops to 361K and continues to decrease to 347K for X=0.10. This might be due to the change in the structure dimension (lattice spacing), as indicated in the XRD results. The La substitution by Sm changes the Mn-O-Mn chains, which then forces the magnetic ordering to occur at lower temperature.

Figs. 4(a), (b), and *(c)* show the MR ratio versus the external magnetic field H curves for all the samples at several temperatures. The MR ratio is calculated as $MR=(R_H - R_O)/R_O$. All the curves exhibit the behaviour similar to the samples with grain boundaries structure. A large negative MR at low field (0-0.1 or 0.2T) region, followed by a slower varying MR at a high field (0.1 or 0.2-1T) region is therefore observed. This behaviour, known as the Low-Field Magnetoresistance (LFMR) is commonly observed in polycrystals and believed to be influenced by the grain boundaries (Nam *et al*., 2001; Miller *et al*. 2000; Xia *et al*. 2002; Zhang *et al*., 2007). The MR is almost linear with H and it continuously decreases without any sign of saturation up to the highest measuring field. Samples X=0.00 (*Fig. 4(a)*) and X=0.10 (*Fig. 4(b)*) show a similar behaviour in the two regions of MR (0 to 0.1T and 0.1 to 1T) but the MR value is found to be larger for X=0.10. However, for X=0.05 [*Fig. 4(c)*], the MR pattern is slightly different from that of the other samples, where the small field region is 0 to 0.2T. These might be related to the size of the grain, in which smaller grain size in sample X=0.05 might have larger or thicker grain boundaries that require higher field to align the magnetic spin in the grain or at the grain boundary. Therefore, the results reveal that extrinsic MR is enhanced with small Sm substitution and grain size dependent. Overall, the highest low-field MR value of -4.6% (at 0.1T) and -6.1% (at 0.2T) are observed for samples X=0.10 and X=0.05, respectively. However, the room temperature high-field MR (at 1T) of -10.5% is given by sample X=0.05. The temperature dependence of the MR for all the samples is shown in *Fig. 4(d)*. The MR ratio drops monotonically with the decreases of the temperature. As for samples X=0.00 and X=0.10, they gave similar slopes, being higher compared to that of sample X=0.05. This might be related to the difference in the grain distribution shown by the AFM results, whereby smaller grains need higher field to fully align the magnetic spin.

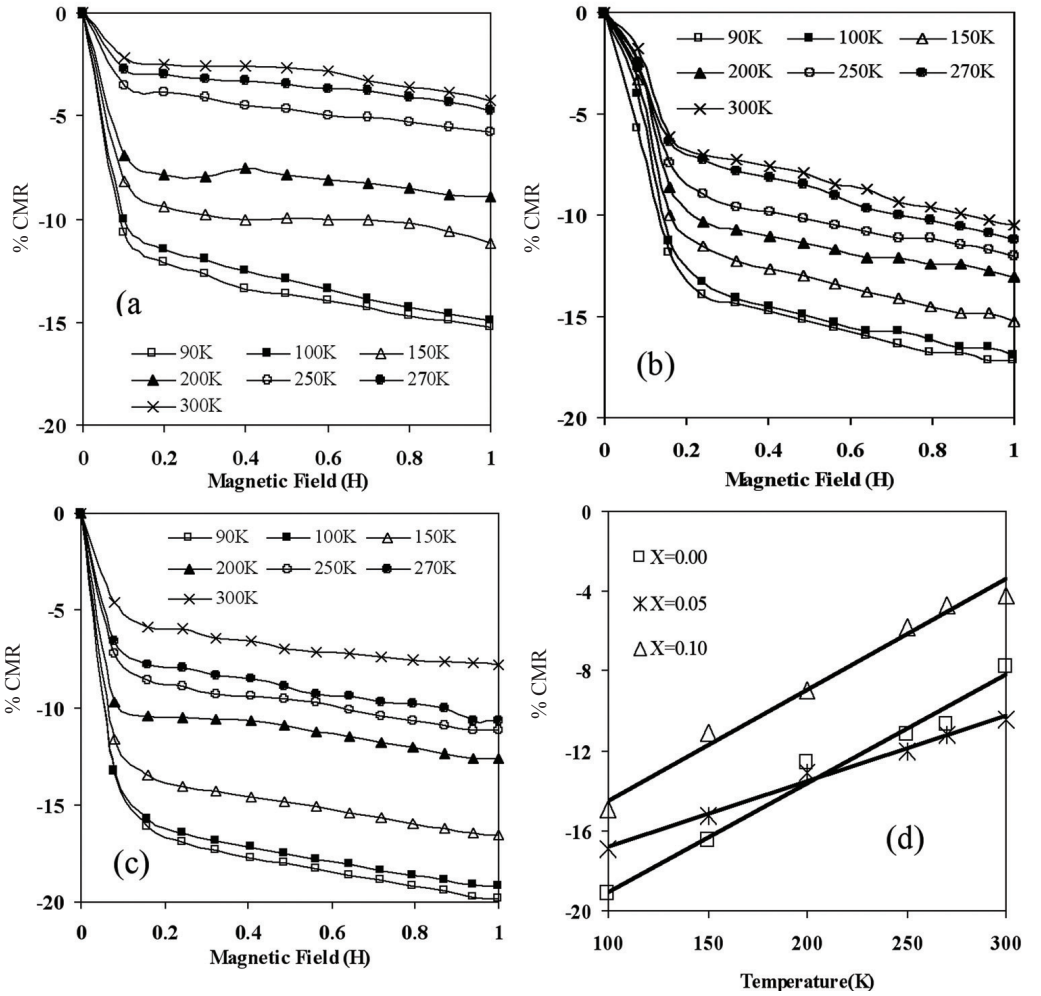

Fig. 4: Field dependence of the MR curve at different temperatures for (a) X=0.00, (b) X=0.05, (c) X=0.10, (d) temperature dependence of the MR ratio in 1 Tesla field

CONCLUSIONS

In this study, the structure, the magnetic and the MR effect in bulk polycrystalline $(La_{1-x}Sm_x)_{0.67}Sr_{0.33}MnO_3$ (X=0.00, 0.05 and 0.10) samples were investigated. The replacement of La by a small amount of Sm has been shown to change its properties. It affects the grain growth and reduces the magnetic phase transition, T_C. However, the extrinsic MR behaviour or known as the Low-Field Magnetoresistance is enhanced. The highest low-field MR value of -4.6% (at 0.1T) and -6.1% (at 0.2T) are observed for samples X=0.10 and X=0.05, respectively.

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