Electronic phase separation in (La 1 3 Sm 2 3) 2 3 A 1 3 Mn O 3 (A = Ca , Sr and Ba) compounds

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Citation: Journal of Applied Physics **97**, 10H711 (2005); doi: 10.1063/1.1853277
View online: http://dx.doi.org/10.1063/1.1853277
View Table of Contents: http://scitation.aip.org/content/aip/journal/jap/97/10?ver=pdfcov
Published by the AIP Publishing

Electronic phase separation in $(La_{1/3}Sm_{2/3})_{2/3}A_{1/3}MnO_3$ (A=Ca, Sr and Ba) compounds

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(Presented on 8 November 2004; published online 11 May 2005)

Electrical and magnetotransport properties of $(La_{1/3}Sm_{2/3})_{2/3}A_{1/3}MnO_3$ (A=Ca, Sr, and Ba) compounds, synthesized by the citrate gel route, have been investigated. These compounds crystallize in an orthorhombic structure (space group *Pnma*). Semiconducting-like behavior is observed only in Ca-substituted sample while Ba and Sr-substituted samples show metal-insulator type transition. The high and weakly temperature dependent magnetoresistance at low temperature, thermal irreversibility in field-cooled and zero-field-cooled magnetization, and nonsaturating magnetization behavior are expected in systems with electronic phase separation. The cationic size disorder by varying alkaline earth ions causes the electronic phase separation. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1853277]

INTRODUCTION

Rare earth manganites of the type ABO_3 exhibit many interesting properties such as charge-ordering, colossal magnetoresistance, electronic phase separation, etc.[1,2] The phase separation in manganites has attracted the attention of theoreticians as well as experimentalists. The A-site cation disorder is responsible for the lattice distortion which leads to the localization of e_g electrons, which in turn, leads to electronic phase separation in these materials.[2] Mixing cations of different sizes and charges at the A site is the most straightforward experimental method for systematically tuning the properties of these materials.[3]

In this article we present the results of varying alkaline earth ions (keeping the rare earth ratio fixed) on the magnetic and transport properties of some manganites. The series, $(La_{1/3}Sm_{2/3})_{2/3}A_{1/3}MnO_3$ (A=Ca, Sr, and Ba), was selected for the present study. The A-site ionic radius and its associated cation disorder are the varying parameters in these compounds.

EXPERIMENTAL DETAILS

Polycrystalline samples of $(La_{1/3}Sm_{2/3})_{2/3}A_{1/3}MnO_3$ (A=Ca, Sr, and Ba) were synthesized by the chemical citrate-gel route using high purity La_2O_3, Sm_2O_3, $CaCO_3$, $BaCO_3$, $SrCO_3$, and Mn-acetate. The as prepared powders were calcined at 1000 °C in air for 2 h. The powders were palletized in the form of rectangular bars and sintered at 1200 °C in air. X-ray diffraction patterns of the samples were recorded using Cu K_α radiation (PANalytical, PW 3040/60 Philips). Resistivity measurements at different applied magnetic fields were carried out between 5 and 320 K using the standard four-probe dc method (PPMS) (Quantum Design). Magnetic measurements were made using a vibrating sample magnetometer (Oxford) at different fields and in the temperature range 5–300 K.

RESULTS AND DISCUSSION

All the three samples are found to be single phase crystallizing in the orthorhombic perovskite structure (space group *Pnma*, No. 62). The Ca-substituted sample shows higher orthorhombicity than the other two samples which in turn, is due to smaller ionic size of Ca ion (1.34 Å) in comparison to that of Sr (1.44 Å) and Ba (1.61 Å) ions.[4] The cell parameters were refined by the Rietveld method. The refined lattice parameters are given in Table I.

In $(La_{1/3}Sm_{2/3})_{2/3}A_{1/3}MnO_3$ (A=Ca, Sr, and Ba) series, lattice distortion occurs in the three dimensional MnO_6 octahedra on varying the alkaline earth ions. The A-site average ionic radius, $\langle r_A \rangle$, varies from 1.30 Å for Ca, 1.33 Å for Sr, and 1.39 Å for Ba-substituted samples. The tolerance factor (t) is the ratio of A-O and B-O bond distances in the ABO_3 perovskite which is responsible for the lattice distortion. The tolerance factor increases from Ca- to Ba-substituted samples. The increase of the Mn–O–Mn bond angles enhances the hopping of e_g electron between Mn^{3+} and Mn^{4+} sites via double exchange which favors the ferromagnetic (FM) metallic phase. The ionic radius of O^{2-} is 1.32 Å which is comparable to Sr-substituted sample ($\langle r_A \rangle$=1.33 Å) but somewhat different from $\langle r_A \rangle$ of Ba (1.39 Å)- and Ca 1.30 Å-substituted samples. This mismatch between the sizes may cause lattice distortion and, hence, electronic inhomogeneity at microscopic scale in these samples.[2] The distortion of Mn–O–Mn bond angle caused by lattice distortion, leads to the charge localization effects for Ba- and Ca-substituted samples. Further, it may also cause antiferromagnetic (AFM) interaction due to change in Mn–O–Mn bond angle and distance. Thus the development of AFM regions within the pre-

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TABLE I. Refined lattice parameters, a,b,c using Rietveld method, tolerance factor t, T_{MI}, T_C and percentage of MR in 8 T field for the series, $(La_{1/3}Sm_{2/3})_{2/3}A_{1/3}MnO_3$ (A=Ca, Sr, and Ba).

Systems	a (Å)	b (Å)	c (Å)	t	T_{MI} (K)	T_C (K)	%MR_{max}
$(La_{1/3}Sm_{2/3})_{2/3}Ca_{1/3}MnO_3$	5.4084(3)	7.6394(2)	5.4528(6)	0.9620	⋯	~50	~95
$(La_{1/3}Sm_{2/3})_{2/3}Sr_{1/3}MnO_3$	5.4722(5)	7.7063(7)	5.4599(6)	0.9742	196	200	~80
$(La_{1/3}Sm_{2/3})_{2/3}Ba_{1/3}MnO_3$	5.5056(1)	7.7801(7)	5.5022(8)	0.9950	56	100	~99

dominantly FM regions causes electronically inhomogeneous regions at the microscopic scale.[5] The earlier-mentioned FM and AFM interactions compete with each other and may be responsible for frustration in the system.

The temperature dependence of electrical resistivity, $\rho(T)$, for $(La_{1/3}Sm_{2/3})_{2/3}A_{1/3}MnO_3$ (A=Ca, Sr, and Ba) samples in zero and 8 T fields is shown in Fig. 1. In zero field, semiconducting-like behavior ($d\rho/dT<0$) is observed only in the Ca-substituted sample, down to 70 K below which the resistance of the sample was beyond measurement limit. Typical metal-insulator (MI) type transition is observed in Sr- and Ba-substituted samples at temperature (T_{MI}) of 196 and 56 K, respectively. In the Ba-substituted sample, the semiconducting-like behavior reappears at some temperature below T_{MI}. In the 8 T field, $\rho(T)$ of Ca-substituted sample, becomes nearly temperature independent at low temperatures which indicates the reappearance of FM ordering. High but weakly temperature dependent magnetoresistance (MR) behavior is observed at low temperatures in all the cases as shown in inset of Fig. 1. Table I gives the values of T_{MI} and maximum MR (in 8 T field) values for all the compounds.

The resistivity data of the series $(La_{1/3}Sm_{2/3})_{2/3}A_{1/3}MnO_3$ (A=Ca, Sr, and Ba) are found to be well described by the Mott–VRH model in which $\ln \rho \alpha T^{-1/4}$.[6] This is shown in Fig. 2. The resistivity in the metallic region (in Ba- and Sr-substituted samples) has been fitted to a Zener-double exchange polynomial $\rho=\rho_0+\rho_2T^2+\rho_nT^n$, where ρ_0 is the temperature independent residual resistivity due to scattering by impurities, defects, grain boundaries, and domain walls, ρ_2T^2 is ascribed to the electron-electron and electron-phonon mechanisms,[7] and ρ_nT^n corresponds to the electron-magnon scattering. The value of n for the higher order term has been found to be 4.5 in our systems. The fitted data in metallic region are shown in the inset of Fig. 2.

The plots of magnetization as a function of temperature for $(La_{1/3}Sm_{2/3})_{2/3}A_{1/3}MnO_3$ (A=Ca, Sr, and Ba) compounds are shown in Fig. 3. The FM to paramagnetic transition temperature, T_C in all cases is determined from the minimum in dM/dT (Table I). The T_C is not the same as T_{MI} especially in Ba- and Ca-substituted samples. The discrepancy between T_C and T_{MI} is indicative of destruction of long range FM ordering and the latter leads to charge localization at low temperatures.[8] Thermal irreversibility effect in magnetization, which is due to the competing AFM and FM interactions, is observed below T_C in these compounds. There is strong irreversibility behavior between the zero-field-cooled (ZFC) magnetization and the field cooled (FC) magnetization. The inset in Fig. 3 shows the inverse susceptibility versus temperature plots in 0.01 T for all the samples. It is interesting to note that the susceptibility of Ba- and Ca-substituted samples deviates from the Curie–Weiss (C-W) law while that of Sr-substituted sample does not.

The deviation from C-W law is larger in the case of Ca compound compared to that in Ba compound. This deviation from C-W law indicates the presence of magnetic inhomogenities which is usually taken to be an evidence of electronic phase separation.[9]

Figure 4 shows field dependence of magnetization for $(La_{1/3}Sm_{2/3})_{2/3}A_{1/3}MnO_3$ (A=Ca, Sr, and Ba) samples at 5 K. The magnetization reaches near saturation value in Sr-substituted sample. However, the magnetization of Ba-substituted sample approaches saturation rather slowly (compared to the Sr-substituted sample) while that of Ca-substituted sample is not saturated even in 5 T field. This

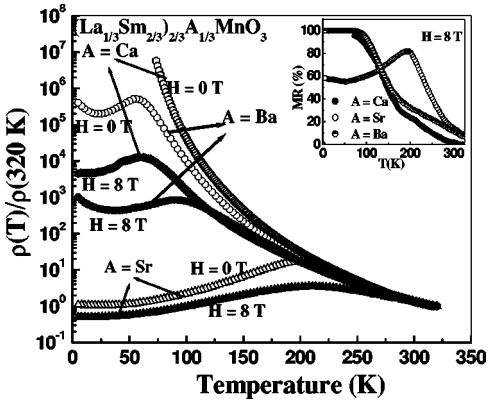

FIG. 1. Variation of normalized electrical resistivity with temperature for the series $(La_{1/3}Sm_{2/3})_{2/3}A_{1/3}MnO_3$ (A=Ca, Sr, and Ba). Inset shows the MR behavior with temperature.

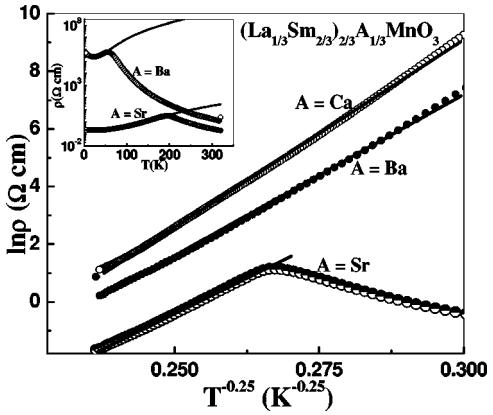

FIG. 2. Theoretical fitting of the experimental resistivity data of $(La_{1/3}Sm_{2/3})_{2/3}A_{1/3}MnO_3$ (A=Ca, Sr, and Ba) compounds.

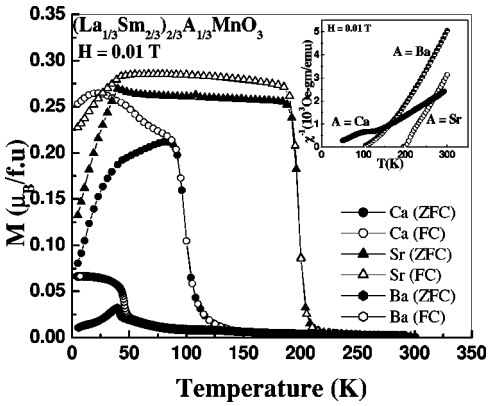

FIG. 3. Temperature dependence of magnetization in a field of 0.01 T in ZFC and FC runs for $(La_{1/3}Sm_{2/3})_{2/3}A_{1/3}MnO_3$ (A=Ca, Sr, and Ba) compounds. Inset shows the plot of inverse of susceptibility vs temperature.

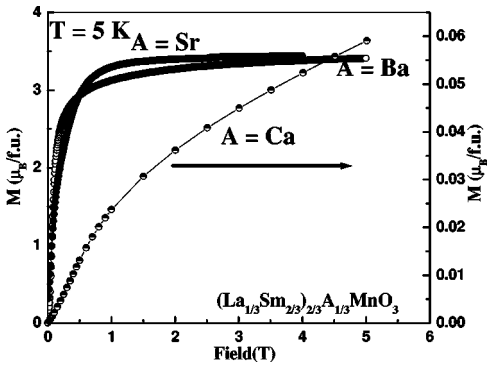

FIG. 4. Isothermal variation of magnetization with field for the series $(La_{1/3}Sm_{2/3})_{2/3}A_{1/3}MnO_3$ (A=Ca, Sr, and Ba) at 5 K.

magnetization behavior of Ca- and Ba-substituted samples support the presence of microscopic inhomogenities due to distortion in MnO_6 octahedra, though this effect is more prominent in Ca containing compound. The maximum magnetization of Sr- and Ba-substituted compounds shows near saturation with values of 3.45 and 3.42 μ_B per formula unit, respectively, which are close to the theoretical value of 3.7 μ_B/f.u. The Ca-substituted sample exhibits a very small magnetic moment of 0.08 μ_B/f.u.. giving a strong evidence of electronic phase separation.[10,11]

CONCLUSIONS

We have investigated the structural and the magnetotransport properties of $(La_{1/3}Sm_{2/3})_{2/3}A_{1/3}MnO_3$ (A=Ca, Sr, and Ba) compounds. The irreversibility in ZFC and FC magnetization behavior in all the samples and strong dependence of resistivity on magnetic field at low temperatures (below 100 K) are suggestive of electronic phase separation in the Ba- and Ca-substituted samples. The electronic inhomogenities at microscopic scale are maximum for Ca containing compound and least for Sr case. This is attributed to size effects which cause distortion of MnO_6 octahedra as confirmed by susceptibility, temperature dependent MR, and M-H behavior. The two competing interactions, namely, the lattice distortion that favors charge localization (insulating phase), and FM ordering which favors metallic phase, presumably lead to electronic phase separation.

ACKNOWLEDGMENT

Two of the authors S.A. and D.B. are thankful to the Department of Science and Technology (DST) India for support of the project.

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