

Evidence of electronic phase separation in Er³⁺-doped La_{0.8}Sr_{0.2}MnO₃

V. Ravindranath, M. S. Ramachandra Rao, R. Suryanarayanan, and G. Rangarajan

Citation: *Applied Physics Letters* **82**, 2865 (2003); doi: 10.1063/1.1570001

View online: <http://dx.doi.org/10.1063/1.1570001>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/apl/82/17?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Enhanced ferromagnetism and glassy state in phase separated La_{0.95}Sr_{0.05}MnO₃+ \$\delta\$](#)

J. Appl. Phys. **112**, 103907 (2012); 10.1063/1.4763460

[Conventional and inverse magnetocaloric effects in La_{0.45}Sr_{0.55}MnO₃ nanoparticles](#)

J. Appl. Phys. **110**, 043905 (2011); 10.1063/1.3614586

[Phase separation induced by cation disorder and strain in \(La, Y\)_{2/3}\(Ca, Sr\)_{1/3}MnO₃ films](#)

J. Appl. Phys. **105**, 07D714 (2009); 10.1063/1.3068478

[Lattice-strain-driven ferromagnetic ordering in La_{0.8}Sr_{0.2}MnO₃ thin films](#)

Appl. Phys. Lett. **84**, 777 (2004); 10.1063/1.1645329

[Time dependent effects and transport evidence for phase separation in La_{0.5}Ca_{0.5}MnO₃](#)

J. Appl. Phys. **87**, 5831 (2000); 10.1063/1.372537

An advertisement for COMSOL Multiphysics. On the left, there is a 3D cutaway illustration of a mechanical part, possibly a turbine or engine component, with a color gradient from red to blue indicating a simulation result. The background is dark with a grid pattern. The text 'Over 600 Multiphysics Simulation Projects' is written in large, white, sans-serif font. Below this text is a blue button with the text 'VIEW NOW >>'. In the bottom right corner, the COMSOL logo is displayed, consisting of a small square icon followed by the word 'COMSOL' in white, sans-serif font.

Evidence of electronic phase separation in Er^{3+} -doped $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$

V. Ravindranath and M. S. Ramachandra Rao^{a)}

Materials Science Research Centre and Department of Physics, Indian Institute of Technology Madras, Chennai-600 036, India

R. Suryanarayanan

Laboratoire de Physico-Chimie de l'Etat Solide, Bât 414, Université Paris-Sud, 91405 Orsay, France

G. Rangarajan

Department of Physics, Indian Institute of Technology Madras, Chennai-600 036, India

(Received 25 October 2002; accepted 6 March 2003)

Er^{3+} doping at the La site in $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ showed an unusual increase in Curie/peak resistivity temperature (T_C/T_P) above a certain nominal dopant concentration ($x \geq 0.086$). This increase is attributed to the presence of a cation-deficient ErMnO_3 phase. Further, with increase in T_P the overall resistivity of these compounds also decreases. We explain these results assuming the presence of a nanoscale mixture of charge-ordered antiferromagnetic insulating (CO-AFMI) phase in a ferromagnetic metallic matrix, wherein the increase in T_C/T_P with increase in Er^{3+} content is due to the local destruction of the CO-AFMI phase by the presence of the cation-deficient ErMnO_3 phase. We thus provide an indirect evidence of electronic phase separation in these compounds. © 2003 American Institute of Physics. [DOI: 10.1063/1.1570001]

Magnetotransport properties of colossal magnetoresistive (CMR) manganites are influenced by several factors, such as the chemical strain caused by ionic radii mismatch, grain boundary effects in bulk and polycrystalline thin films, oxygen stoichiometry, etc.¹⁻⁴ Recently, the importance of the role of electronic phase separation in these compounds has been observed by electron microscopy⁵ as well as scanning tunneling microscopy studies.⁶ Several studies⁵⁻¹⁵ reveal unusual electronic and magnetic properties caused by an electronic phase separation into a nanoscale mixture of charge ordered-antiferromagnetic insulating (CO-AFMI) clusters in a ferromagnetic metallic (FMM) matrix or vice versa, and the CMR has been explained as due to a percolative transport through these FMM domains. In this letter, we study the electric and magnetic properties of Er^{3+} -doped $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ (LSMO), and by correlating these results with energy dispersive x-ray analysis (EDX) and scanning electron microscope (SEM) data, we indirectly show evidence for electronic phase separation in these compounds.

Bulk polycrystalline samples of $\text{La}_{0.8-x}\text{Er}_x\text{Sr}_{0.2}\text{MnO}_3$ were prepared by the conventional solid-state-reaction method. Powder x-ray diffraction (XRD) of the samples was carried out using $\text{Cu } K_\alpha$ radiation. Ac magnetic susceptibility measurements were carried out using a commercial ac susceptometer (Sumitomo, Japan) at an operating frequency of 313 Hz and an applied ac magnetic field of 0.1 Oe in the temperature range of 300–12 K. Electrical resistivity measurements were carried out using the four-probe method in the temperature range of 300–40 K.

Figure 1 shows the temperature dependence of ac magnetic susceptibility of the compounds. It is seen that the compounds undergo a paramagnetic to a ferromagnetic transition

with decrease in temperature. However, interesting and intriguing is the fact that while the Curie temperature (T_C) (determined from the peak in the $d\chi'/dT$ curve) decreases with increase in the nominal Er^{3+} content (x) from 0.02 to 0.086, for $x > 0.086$, there is an increase in T_C with increase in the nominal Er^{3+} content.

Figure 2 shows the temperature dependence of electrical resistivity of the compounds. The resistivity data also correlates well with the ac susceptibility data. Interestingly, it is seen that T_P decreases as x increases from 0.02 to 0.086. For $x > 0.086$, there is an increase in T_P to higher temperatures. In addition, in this case there is an overall decrease in the resistivity of the compounds with increase in the nominal Er^{3+} content greater than 0.086.

In order to understand the reason for the unusual prop-

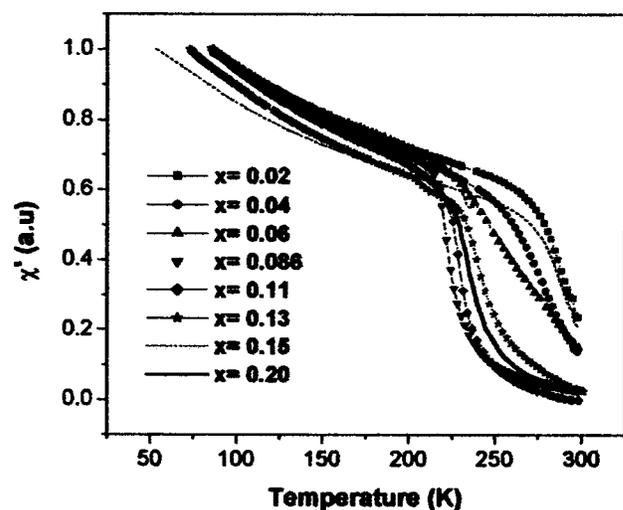


FIG. 1. Temperature dependence of ac susceptibility of Er^{3+} -doped $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ compounds. T_C is found to decrease with increase in Er^{3+} content from $x=0.02$ to 0.086. For $x > 0.086$, T_C increases with increase in Er^{3+} content.

^{a)}Author to whom correspondence should be addressed; electronic mail: msrrao@iitmadras.ac.in

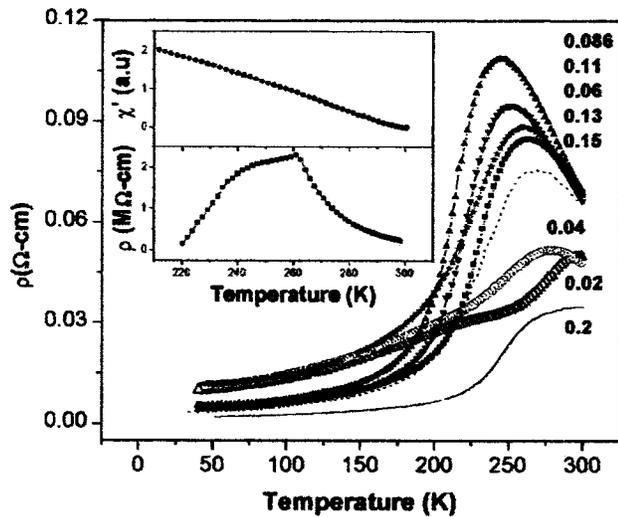


FIG. 2. Temperature dependence of electrical resistivity of the compounds. T_p is seen to decrease as x increases from 0.02 to 0.086. For $x > 0.086$, T_p increases with increase in Er^{3+} content. In addition, the resistivity of the compounds for $x > 0.086$ also decreases over the entire temperature range. Inset shows ferromagnetic insulating nature of the cation-deficient ErMnO_3 phase ($\text{Er}_{0.89}\text{Mn}_{0.78}\text{O}_{3-\delta}$) at room temperature.

erties exhibited by these compounds, a detailed study of the phase purity and microstructure of these compounds was undertaken. XRD data of the compounds did not show the presence of any secondary phase. However, SEM and EDX data provide some interesting information. Figure 3 shows the scanning electron micrographs for two chosen compositions: $x = 0.06$ and 0.15. A comparison of the scanning electron micrographs of the two compounds ($x = 0.06$ and 0.15) shows the presence of precipitates for the $x = 0.15$ composition [seen as white patches in Fig. 3(a)]. In fact, SEM analysis on all the compounds showed presence of precipitates for compounds with a nominal Er^{3+} content (x) > 0.086 , indicating the formation of a secondary phase. The percentage by weight of this secondary phase may be below the detectable limit (< 5 at. %) of XRD. This may be the reason the XRD did not show the presence of any secondary phase. The precipitation of the secondary phase may be due to the large cation size mismatch at the A site with increase in Er^{3+} content, Er^{3+} [ionic radius (i.r.) = 1.01 Å] being small compared to La^{3+} (i.r. = 1.32 Å). However for $x < 0.086$, no such secondary phase formation is seen.

Compositional analysis by EDX reveals that the Er^{3+} content does not increase beyond $x = 0.07$ in the lattice as shown in Table I. This clearly supports the SEM data. Thus, it is clear that the presence of precipitates for $x > 0.086$, seen from the SEM data (Fig. 3) is because of the inability of the

TABLE I. Comparison of the chosen nominal compositions and the compositions obtained from EDX.

Composition	
Nominal	EDX
$\text{La}_{0.76}\text{Er}_{0.04}\text{Sr}_{0.2}\text{MnO}_3$	$\text{La}_{0.76}\text{Er}_{0.03}\text{Sr}_{0.17}\text{MnO}_3$
$\text{La}_{0.69}\text{Er}_{0.11}\text{Sr}_{0.2}\text{MnO}_3$	$\text{La}_{0.73}\text{Er}_{0.07}\text{Sr}_{0.23}\text{MnO}_3$
$\text{La}_{0.67}\text{Er}_{0.13}\text{Sr}_{0.2}\text{MnO}_3$	$\text{La}_{0.74}\text{Er}_{0.06}\text{Sr}_{0.21}\text{MnO}_3$
$\text{La}_{0.65}\text{Er}_{0.15}\text{Sr}_{0.2}\text{MnO}_3$	$\text{La}_{0.71}\text{Er}_{0.07}\text{Sr}_{0.23}\text{MnO}_3$
$\text{La}_{0.6}\text{Er}_{0.2}\text{Sr}_{0.2}\text{MnO}_3$	$\text{La}_{0.68}\text{Er}_{0.07}\text{Sr}_{0.23}\text{MnO}_3$

LSMO lattice in accommodating Er^{3+} content > 0.07 (as seen from the EDX data) leading to the formation of a secondary phase. EDX analysis on the white precipitates seen in the SEM pictures reveals that the secondary phase is predominantly a cation-deficient ErMnO_3 phase (composition of the typical phase is $\text{Er}_{0.89}\text{Mn}_{0.78}\text{O}_3$). This cation-deficient ErMnO_3 phase was prepared by the solid-state-reaction method and was found to be a ferromagnetic insulator at room temperature (inset to Fig. 2). However, it must be noted here that for compounds with $x > 0.15$ sintered at 1300°C (the compounds discussed earlier were, as mentioned before, sintered at 1400°C), XRD showed presence of a secondary phase. The XRD of the cation-deficient phase that was synthesized matches well with the additional lines due to the secondary phase seen in the XRD of 1300°C synthesized compounds with $x > 0.15$. These results will appear elsewhere.

The unusual increase in T_p/T_C and the decrease in resistivity for compounds with $x > 0.086$ (Figs. 1 and 2) may be related to the presence of a cation-deficient ErMnO_3 phase for $x > 0.086$. These results can be explained on the basis of a model that involves the percolative transport of current through ferromagnetic metallic domains, as shown in Fig. 4. It is assumed that there is an electronic phase separation consisting of a nanoscale mixture of CO-AFMI clusters in a FMM matrix in the compounds under study. With increase in the nominal Er^{3+} content, since there is a precipitation of a cation-deficient ErMnO_3 phase which is ferromagnetic for $T < 300$ K, it is believed that the presence of this ferromagnetic secondary phase could cause a local destruction of the CO-AFMI clusters. Since a number of these precipitates are spread in the host LSMO matrix, as shown in Fig. 4, it may be possible that their combined effect would be a decrease in the volume fraction of the CO-AFMI phase. In other words, there may be an increase in the ferromagnetic-metallic volume fraction. This may be the reason for the increase in T_C/T_p for compounds with $x > 0.086$. Such de-

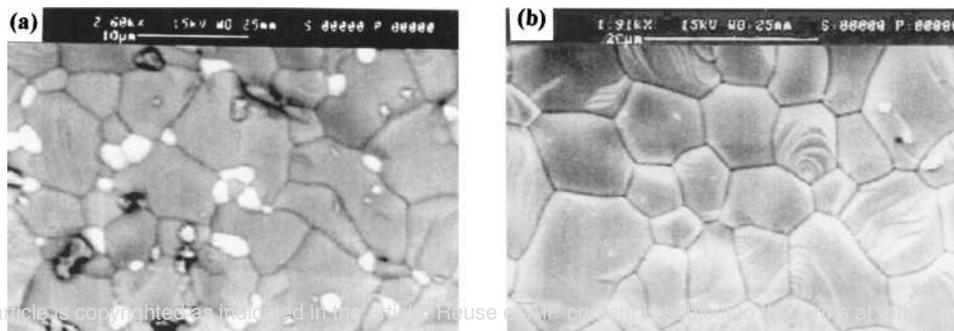


FIG. 3. Typical SEM picture of (a) $\text{La}_{0.65}\text{Er}_{0.15}\text{Sr}_{0.2}\text{MnO}_3$ showing the presence of a secondary phase formation (seen as white patches) and (b) $\text{La}_{0.74}\text{Er}_{0.06}\text{Sr}_{0.2}\text{MnO}_3$ showing no significant secondary phase formation.

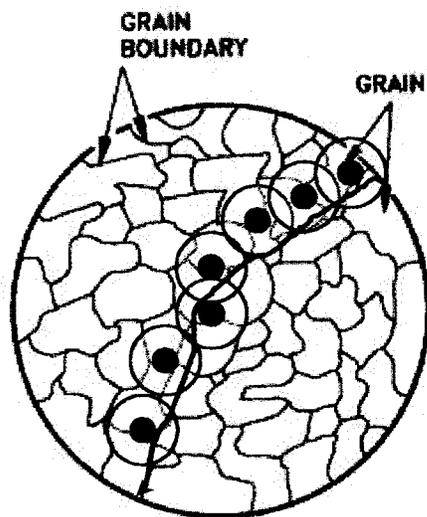


FIG. 4. Percolation of current through FMM regions caused by local destruction of CO-AFMI clusters. The solid black circles represent the cation deficient ErMnO_3 phase, the larger open circles represent the area of influence and the black line through the open circles indicates the conduction path for the current.

struction of the CO-AFMI phases due the presence of a secondary phase has been reported in an earlier study.¹⁵ In this study, it was shown that the addition of 1 mol % of Ho^{3+} to the $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ matrix enhanced the T_p by about 70 K and this was showed to be due to the destruction of the CO-AFMI phase by Ho^{3+} . This study clearly supports the validity of our assumption. Another interesting result is the decrease in the overall resistivity of compounds with $x > 0.086$. It must be noted here that the cation-deficient ErMnO_3 phase has a high resistivity, about 8 orders of magnitude greater than the resistivity of the Er^{3+} -doped compounds. Hence, even though the cation-deficient ErMnO_3 phase becomes metallic below 250 K, the decrease in resistivity of compounds with $x > 0.086$ may not be due to shorting through these metallic regions. Instead, as suggested before, there may be a decrease in the resistivity in regions

where there is a destruction of the CO-AFMI phase causing a decrease in the resistivity for compounds with $x > 0.086$. Hence, these results provide an indirect evidence of electronic phase separation in Er^{3+} -doped $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$.

In conclusion, we find unusual magnetotransport properties exhibited by Er^{3+} -doped $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ compounds. By correlation with ac susceptibility, electrical resistivity, SEM, and EDX data, we show indirect evidence of electronic phase separation in these compounds.

M.S.R.R. would like to thank DST, India for support by way of Project No. MSR/0102/018/DST/MSRA.

- ¹ S. Jin, T. H. Tiefel, M. McCormack, R. A. Fastnacht, R. Ramesh, and L. Chen, *Science* **264**, 413 (1995).
- ² A. Gupta, G. Q. Gong, G. Xiao, P. R. Duncombe, P. Lecoeur, P. Trouilloud, Y. Y. Wang, V. P. Dravid, and J. Z. Sun, *Phys. Rev. B* **54**, R15629 (1996).
- ³ H. L. Ju, J. Gopalakrishnan, J. L. Peng, Qi Li, G. C. Xiong, T. Venkatesan, and R. L. Greene, *Phys. Rev. B* **51**, 6143 (1995).
- ⁴ L. M. Rodriguez-Martinez and J. P. Attfield, *Phys. Rev. B* **54**, R15622 (1996).
- ⁵ M. Uehara, S. Mori, C. H. Chen, and S. W. Cheong, *Nature (London)* **399**, 560 (1999).
- ⁶ M. Fäth, S. Freisem, A. A. Menovsky, Y. Tomoika, J. Aarts, and J. A. Mydosh, *Science* **285**, 1540 (1999).
- ⁷ N. A. Babushkina, L. M. Belova, D. I. Khonski, k. I. Kugel, O. Yu. Gorbenco, and A. R. Kaul, *Phys. Rev. B* **59**, 6994 (1999).
- ⁸ A. M. Balagurov, V. Yu. Pomja Kushin, D. V. Sheptyakov, V. L. Aksenov, N. A. Babushkina, L. M. Belova, A. N. Taldenkov, A. V. Inyushkin, P. Fischer, M. Gutmann, L. Keller, O. Yu. Gorbenco, and A. R. Kaul, *Phys. Rev. B* **60**, 383 (1999).
- ⁹ A. M. Balagurov, P. Fischer, V. Yu. Pomja Kushin, D. V. Sheptyakov, and V. L. Aksenov, *Physica B* **276–278**, 536 (2000).
- ¹⁰ P. Levy, F. Parisi, G. Polla, D. Vega, G. Leyva, H. Lanza, R. S. Freitas, and L. Ghivelder, *Phys. Rev. B* **62**, 6437 (2000).
- ¹¹ E. B. Nyeanchi, I. P. Krylov, X. M. Zhu, and N. Jacobs, *Europhys. Lett.* **48**, 228 (1999).
- ¹² H. Y. Hwang, S.-W. Cheong, P. G. Radealli, M. Marezio, and B. Batlogg, *Phys. Rev. Lett.* **75**, 914 (1995).
- ¹³ M. Jaime, M. B. Salamon, K. Pettit, M. Rubinstein, R. E. Treece, J. S. Horwitz, and D. B. Chrisey, *Appl. Phys. Lett.* **68**, 1576 (1996).
- ¹⁴ E. Dagotto, T. Hotta, and A. Moreo, *Phys. Rep.* **344**, 1 (2001).
- ¹⁵ A. K. Pradhan, B. K. Roul, Y. Feng, Y. Wu, S. Mohanty, D. R. Sahu, and P. Dutta, *Appl. Phys. Lett.* **78**, 1598 (2001).