Intergrain Magnetoresistance in Electron-Doped Sr_2FeMoO_6

M. Venkatesan, C. B. Fitzgerald, U. V. Varadaraju, and J. M. D. Coey, *Member, IEEE*

***Abstract*—Electron-doped double perovskite compounds ($Sr_{2-x}La_x$)$FeMoO_6$ ($x = 0.0, 0.5, 0.7$) were synthesized by combustion synthesis using Oxalic acid dihydrazide as fuel. There is an increase in Curie temperature (T_C) with La substitution up to a value of 172 °C for ($Sr_{1.3}La_{0.7}$)$FeMoO_6$. The compound ($Sr_{1.5}La_{0.5}$)$FeMoO_6$ with increased T_C compared to the undoped sample, exhibits a intergrain magnetoresistance of about 3% in a field of 0.1 T. The presence of magnetoresistance in La-doped samples prepared by combustion synthesis is due to the increased number of intergrain tunnel barriers.**

***Index Terms*—Curie temperature, magnetoresistance, resistivity, X-ray diffraction.**

I. Introduction

THE half-metallic double perovskite Sr_2FeMoO_6 has attracted interest compared to the optimally doped mixed valent manganites due to its potential for use in sensors and magnetoelectronic devices [1]–[4]. Recent studies showed that La substitution at the Sr site (electron doping) increases the Curie temperature significantly [5] but the samples prepared by solid state reaction fail to show any appreciable magnetoresistance at room temperature. Since the low field magnetoresistance is dominated in these materials by intergrain transport, we have synthesized ceramic material with nanometer-size crystallites by a novel combustion synthesis method in an effort to improve the magnetoresistive response. Combustion synthesis is a novel technique for producing ceramics with ultrafine crystallites which offers fine tuning of composition and high chemical homogeneity in multicomponent ceramics. To achieve higher Curie temperature together with low field magnetoresistance, we have synthesized electron-doped compounds *viz.*, ($Sr_{2-x}La_x$)$FeMoO_6$ ($x = 0.0, 0.5, 0.7$) by combustion synthesis using Oxalic acid dihydrazide (ODH) as fuel. Here, we report the observation of intergrain magnetoresistance in electron doped Sr_2FeMoO_6, which is otherwise absent in the samples prepared by the conventional solid state reaction. In addition, the behavior of high field magnetoresistance of Sr_2FeMoO_6, prepared by solid state reaction and combustion reaction is compared with that of pressed powder.

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M. Venkatesan, C. B. Fitzgerald, and J. M. D. Coey are with the Physics Department, Trinity College, Dublin 2, Ireland (e-mail: venkatem@tcd.ie; jcoey@tcd.ie; perri@maths.tcd.ie).

U. V. Varadaraju is with the Materials Science Research Center and Department of Chemistry, Indian Institute of Technology, Madras, India (e-mail: uvr@msrc.iitm.ernet.in).

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II. Experimental Methods

Combustion synthesis was carried out to develop fine grained crystallites and to increase the number of grain boundaries. The synthesis conditions were optimized as reported elsewhere [6]. Single-phase ($Sr_{2-x}La_x$)$FeMoO_6$ was prepared using a mixture of metal nitrates as "oxidizers" [$Sr(NO_3)_2$, $La(NO_3)_3.3H_2O$, $Fe(NO_3)_3.9H_2O$ and $(NH_4)_6Mo_7O_{24}.4H_2O$ (dissolved in nitric acid)] in the presence of a fuel to induce highly exothermic redox reactions. ODH was used as fuel. The oxidizer : fuel ratio was calculated based on the valencies of the oxidizers (O) and fuel (F) as defined in propellant chemistry, keeping O/F = 1 in order to release the maximum energy in the reaction. Strontium, lanthanum and iron nitrates are dissolved in water separately, while ammonium molybdate is dissolved in nitric acid and the three solutions are mixed in decreasing order of solubility. ODH solution is added finally to the saturated solution. The light green gel is then introduced into a preheated furnace at 300 °C for 5 min for the combustion reaction. The as-combusted powder is heat treated at 400 °C to decompose the unreacted nitrates and at 700 °C to remove any organic traces. The powders are then pressed into pellets and sintered at 1200 °C in 5% H_2/Ar atmosphere to obtain single-phase ($Sr_{2-x}La_x$)$FeMoO_6$. Since the initial reaction time is very short, the resulting crystalline phases nucleate but do not grow, thus yielding crystallites of about 100–200 nm. Phase analysis was carried out using powder X-ray diffraction. Resistivity measurements were performed using a linear four probe method with a MULTIMAG variable flux source in a magnetic field of up to 1 T. High field magnetoresistance measurements (up to 25 T) were carried out using a pulse-field magnetometer.

III. Results

The single phase nature of all the compounds was confirmed by powder X-ray diffraction patterns as shown in Fig. 1. All the compounds were indexed on the basis of tetragonal unit cell. The grain size, determined through scanning electron microscopy, is about 100–200 nm.

Fig. 2 shows the magneto-thermogravimetry plot of Sr_2FeMoO_6, ($Sr_{1.5}La_{0.5}$)$FeMoO_6$ and ($Sr_{1.3}La_{0.7}$)$FeMoO_6$. The Curie temperature increases upon La substitution from 410 K (137 °C) for $x = 0$, to 425 K (152 °C) for $x = 0.5$ and reaching a value of 445 K (172 °C) for $x = 0.7$.

The room temperature resistivity of ($Sr_{1.3}La_{0.7}$)$FeMoO_6$ is 30 mΩcm compared to that of 20 mΩcm for undoped sample. The transport property in these materials is determined by electron tunneling between grains. The presence of a large numbers of tunneling barriers, developed due to fine grain

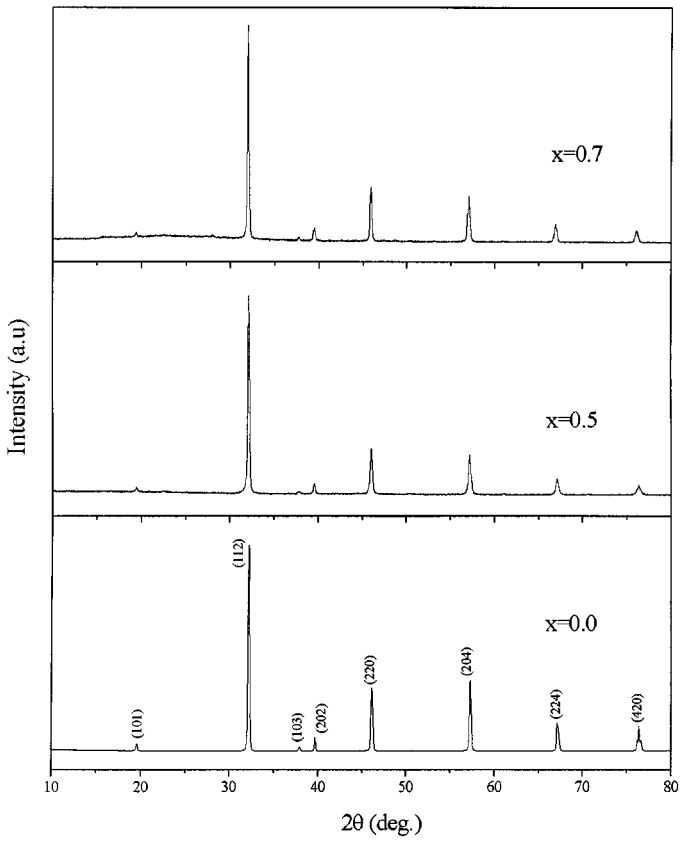

Fig. 1. X-ray diffraction patterns of $(Sr_{2-x}La_x)FeMoO_6$.

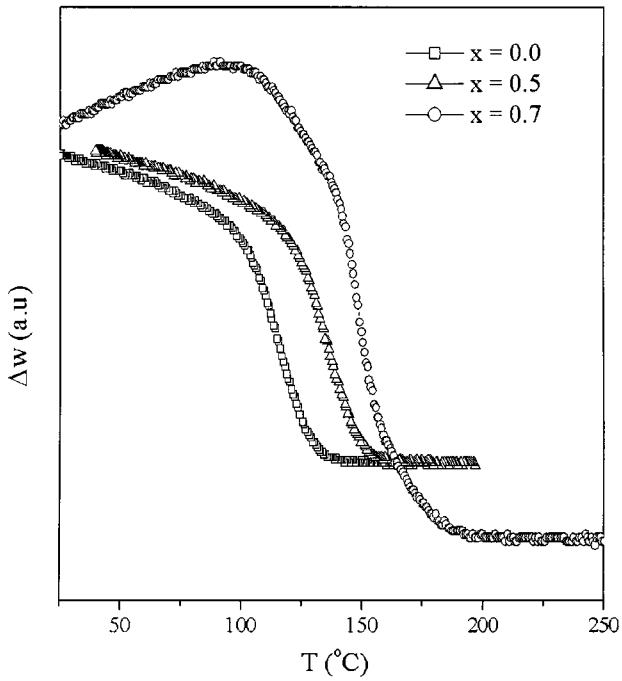

Fig. 2. Increase in T_C with x in $(Sr_{2-x}La_x)FeMoO_6$.

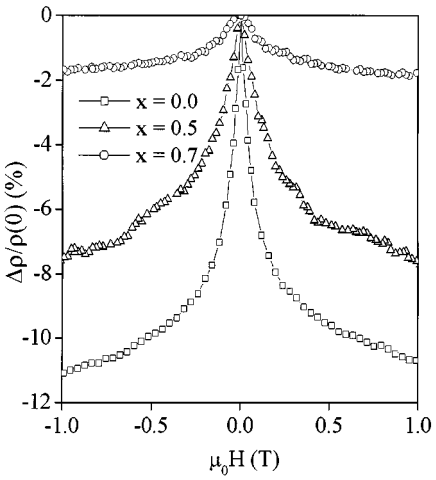

Fig. 3. Room temperature magnetoresistance in $(Sr_{2-x}La_x)FeMoO_6$.

microstructure, increases the magnitude of resistivity for combustion synthesized sample. Fig. 3 shows the room temperature magnetoresistance of Sr_2FeMoO_6, $(Sr_{1.5}La_{0.5})FeMoO_6$ and $(Sr_{1.3}La_{0.7})FeMoO_6$. The undoped sample shows a remarkably sharp decrease in resistance at low fields, a change of about 6.5% in 0.1 T.

Magnetoresistance is maintained even in La-doped samples. The compound $(Sr_{1.5}La_{0.5})FeMoO_6$ with a T_C of 425 K (152 °C) exhibits a MR of about 3.0% at 0.1 T. On the other hand, the compound $(Sr_{1.3}La_{0.7})FeMoO_6$ having a T_C of 445 K (172 °C) shows a MR of 0.8% at 0.1 T. It should be noted that there is no appreciable room temperature magnetoresistance in La-doped samples prepared by conventional solid state reaction. This indicates that the presence of magnetoresistance in these electron doped materials correlates well with the large intergrain tunnel barriers due to the decrease of the grain size.

Turning now to the high field magnetoresistance, the field dependence for ceramic (prepared by solid state reaction and combustion synthesis) and pressed power compacts (solid state reaction) are compared in Fig. 4. The high field magnetoresistance at 77 K is practically identical for solid state and combustion-synthesized ceramic materials compared to the results on pressed powder compacts. All samples exhibit concave variation beginning as $|H|$, but the ceramic samples approach saturation in higher fields. On the other hand, it appears that the high field powder magnetoresistance is unsaturated even at 25 T.

The powder magnetoresistance measurements confirm the high degree of spin polarization (80% at 77 K) in Sr_2FeMoO_6. An estimate of the degree of spin polarization in Sr_2FeMoO_6 is best made from the powder magnetoresistance data, because there the coupling between the grains is minimal and the magnetization directions in the unmagnetized state can be taken to be random. Extrapolating the magnetoresistance to $1/H = 0$ gives a value of 39% for the magnetoresistance, defined as $\Delta\rho/\rho(0) = (\sigma_{||} - \sigma_r)/\sigma_{||}$, where $\sigma_{||}$ is the conductivity in the fully-aligned state and σ_r is the conductivity in the zero field state, where the particle moments are supposed to be randomly aligned. The transmission across a tunnel barrier between two misaligned half-metallic nanoparticles whose magnetic axes are at an angle θ_{ij} varies as $\cos^2(\theta_{ij}/2) = (1 + \cos\theta_{ij})/2$. In the random state $\langle\cos\theta_{ij}\rangle = 0$, whereas in the fully-aligned state $\langle\cos\theta_{ij}\rangle = 1$. The maximum possible powder magnetoresistance is therefore 50%. For imperfect spin polarization, the transmission varies as $P^2\cos^2(\theta_{ij}/2)$, giving a saturated magnetoresistance $\Delta\rho/\rho = P^2/(1 + P^2)$. Hence we deduce

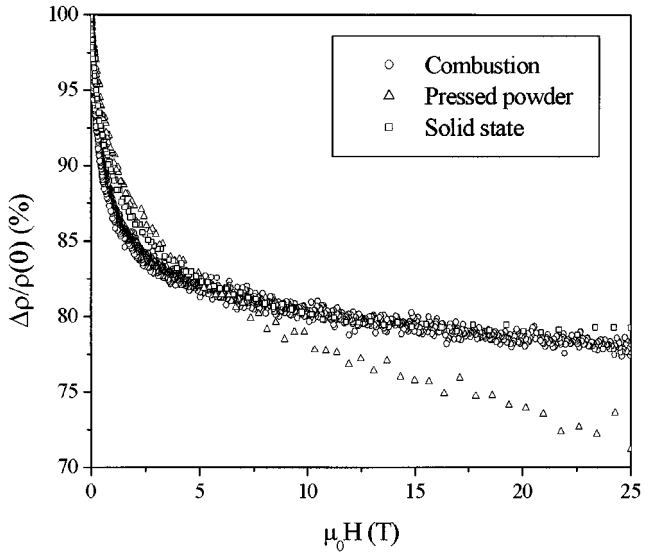

Fig. 4. High field magnetoresistance of ceramic and pressed powder compacts measured at 77 K.

$P = 80\%$ as the spin polarization at 77 K. The large fields needed to saturate the powder magnetoresistance suggest that the spins at the particle surfaces are misaligned from the ferromagnetic axis due to antiferromagnetic exchange coupling. This is associated with antisite defects [7], which will have greatest influence at the surface where the $t_{2g}^{\downarrow}$ (Mo/Fe) band electrons, mainly responsible for the ferromagnetic coupling of the $Fe^{3+\uparrow}$ cores, will tend to be localized.

IV. Conclusion

Structural and magnetotransport properties of La-doped Sr_2FeMoO_6 were investigated. The Curie temperature is increased by about 40 °C compared to the undoped sample while maintaining the room temperature low field magnetoresistance. The existence of useful magnetoresistance together with the enhanced Curie temperature makes these materials promising for possible magnetoresistive sensor applications.

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