

## Magnetoresistance of the Ferromagnetic Combined System

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For the ferromagnetic combined samples, results of x-ray diffraction patterns showed no evidence of reaction between the  $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ ,  $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$  and  $\text{CoFe}_2\text{O}_4$ . For the amount of  $\text{CoFe}_2\text{O}_4$  increased, the Curie temperature of combined samples showed no appreciable change, whereas a metal-semiconductor transition temperature rapidly decreased. For the  $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$  and 20 wt %  $\text{CoFe}_2\text{O}_4$  combined sample, the metal-semiconductor transition temperature was decreased to 160 K compared with the  $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$  with 192 K.

**Key words :** Mössbauer spectroscopy, Magnetoresistance, Combined sample, Grain boundary

### 1. Introduction

The magnetotransport properties of the perovskite  $\text{La}_{0.67}\text{A}_{0.33}\text{MnO}_{3+\delta}$  (A=Ca, Sr etc.) system have received attention recently after the discovery of the colossal magnetoresistance (CMR) effect in the ferromagnetic phase of the system [1, 2]. A prominent feature of these materials is a metal-insulator transition near the ferromagnetic transition temperature [3]. Recent extensive studies have revealed that the doped manganites showed a variety of phenomena besides the large MR effect, such as magnetostructural phase transition [4], magnetovolume effect [5], change-ordering transition [6], magnetic-field-induced insulator to metal transition [7, 8] and grain boundary effect [9, 10]. The grain boundaries and interfaces can be an important factor of low field magnetoresistance in polycrystalline samples [11, 12].

In the present work, we have studied the magnetoresistance properties in combined materials by introducing insulating magnetic  $\text{CoFe}_2\text{O}_4$  powders into polycrystalline  $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$  and  $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ . An amount of  $\text{CoFe}_2\text{O}_4$  powder for the combined materials has a weight percentage (wt %) 10, 15 and 20.

### 2. Experiment

The  $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ (LCMO),  $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ (LSMO), and  $\text{CoFe}_2\text{O}_4$ (CF) combined samples were prepared

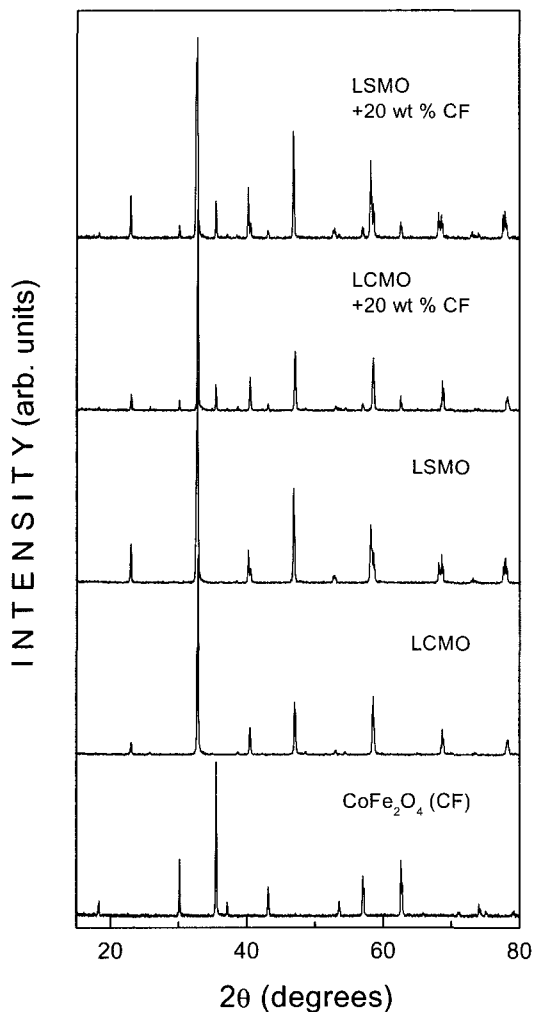
process by two steps. At first, the  $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ ,  $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ , and  $\text{CoFe}_2\text{O}_4$  powders were prepared by a sol-gel process [13]. Second, the LCMO, LSMO, and CF powders were mixed and 1000 °C for 30 min to obtain the  $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$  and  $\text{CoFe}_2\text{O}_4$ , and  $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$  and  $\text{CoFe}_2\text{O}_4$  combined samples. In the first step, stoichiometric amounts of  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{Ca}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$  or  $\text{Sr}(\text{CH}_3\text{CO}_2)_2$  and  $\text{Mn}(\text{CH}_3\text{CO}_2)_2 \cdot 4\text{H}_2\text{O}$  were dissolved into 2-methoxyethanol. The stock solutions were refluxed for 24 hours at 80 °C, than distilled  $\text{H}_2\text{O}$  was added for hydrolysis. Dried sol-gel was prepared through vacuum distillation of the solution and was dried in a hot oven at about 100 °C. The  $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$  and  $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$  powders can be obtained after a heat treatment at 1300 °C in  $\text{O}_2$  for 12 h. The  $\text{CoFe}_2\text{O}_4$  powder were also prepared by a similar citrate-gel route and obtained by annealing at 1000 °C for 12 h.

The x-ray diffraction patterns of the samples were obtained with  $\text{Cu } K_\alpha$  radiation. Mössbauer spectra were measured with a  $^{57}\text{Co}(\text{Rh})$  source moving at room temperature while absorbers were kept fixed at room temperature. The temperature dependence of magnetization and magnetoresistance were measured as a function of external field at temperature ranging from 77 to 320 K.

### 3. Results and Discussion

The x-ray diffraction patterns of LCMO, LSMO, CF and the combined samples with 20 wt % CF at room temperature are shown in Fig. 1. The x-ray spectra of LCMO, LSMO and CF indicate that the perovskite and

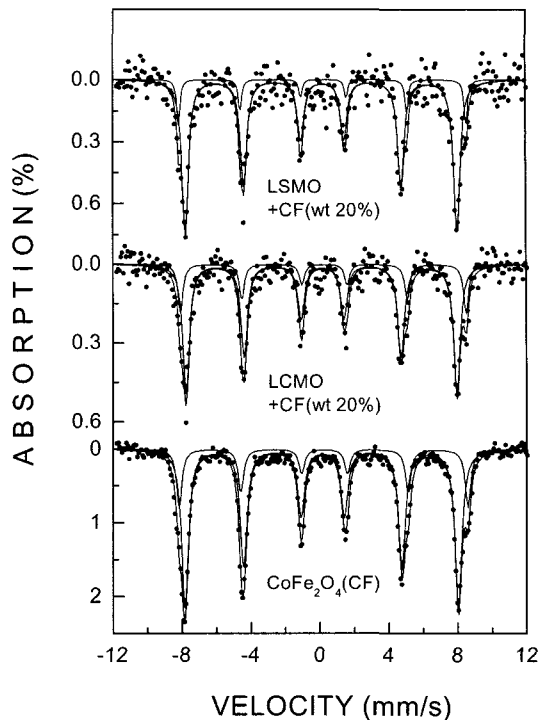
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**Fig. 1.** X-ray diffraction patterns of LCMO, LSMO, CF and CF 20 wt % combined samples.

spinel single phases have formed. The combined samples with 20 wt % CF show two different patterns of x-ray diffraction peaks, which correspond to a cubic spinel and a orthorhombic or rhombohedral perovskite structure. No other diffraction peaks is observed that the reaction between the LCMO, LSMO and CF.

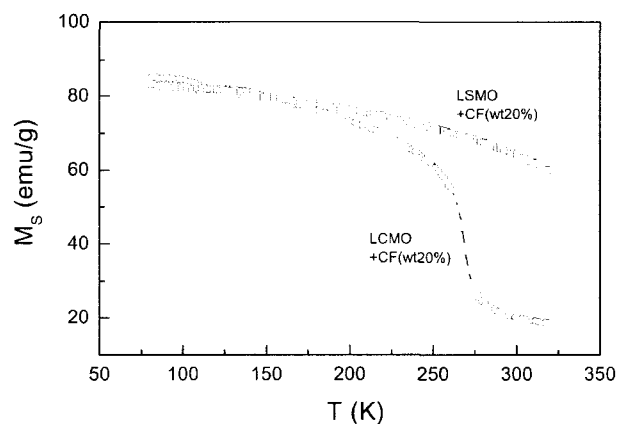
Figure 2 shows Mössbauer spectra of the combined samples with 20 wt % CF and the cobalt ferrite at room temperature. These spectra are composed of two six-line hyperfine patterns of the A and the B sites for the spinel cobalt ferrite. Using a least-squares computer program, two sets of six Lorentzians lines were fitted to the Mössbauer spectra under the usual constraints [14], which are valid when the quadrupole interaction is much weaker than the magnetic hyperfine interaction. The isomer shift value at room temperature for A and B site are consistent with those of the high spin  $Fe^{3+}$  charge state. The results of the computer analysis are presented in Table 1. For the



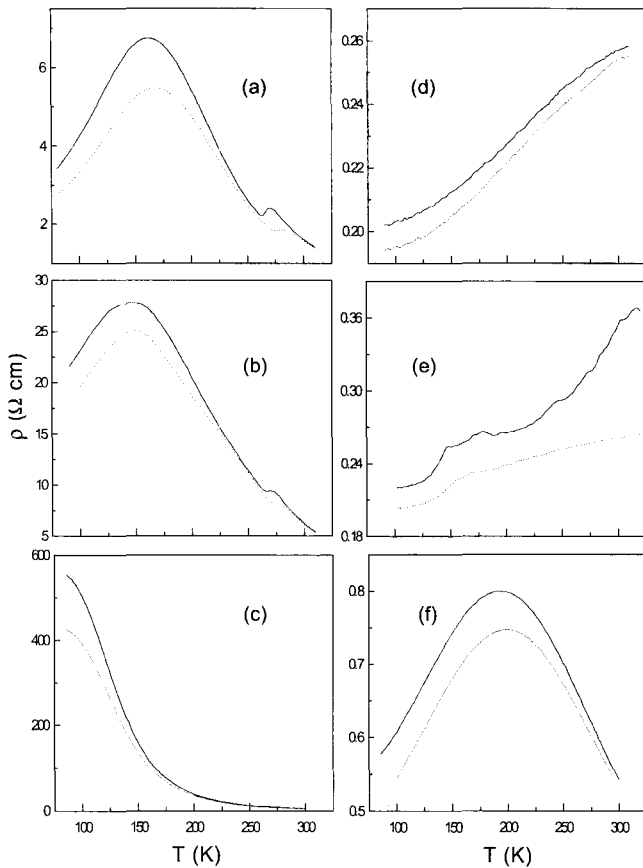
**Fig. 2.** Mössbauer spectra for CF and CF 20 wt % combined samples at room temperature.

combined samples with 20 wt % CF, no appreciable difference in the Mössbauer spectrum have been observed on the paramagnetic LCMO and ferromagnetic LSMO powders. It was indicated that the magnetic interaction between the LCMO, LSMO, and CF was little existed.

Figure 3 shows the temperature dependence of magnetization for the combined samples with 20 wt % CF, which was measured using a vibrating sample magnetometer in an applied field of 5 kOe. For the LCMO and 20 wt % CF combined sample, the Curie temperature and the



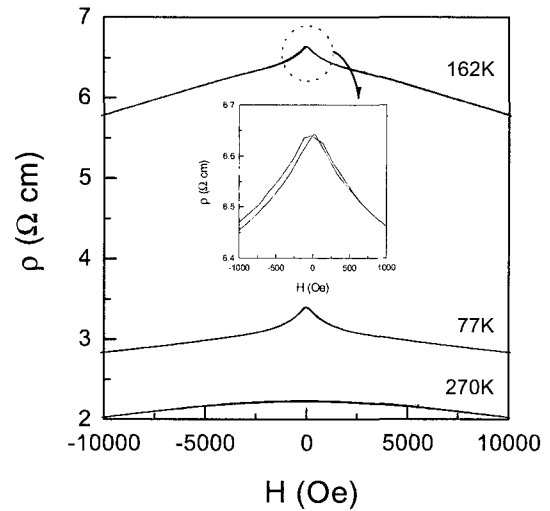
**Fig. 3.** The temperature dependence of magnetization under applied field 5 kOe of CF 20 wt % combined samples.



**Fig. 4.** The temperature dependence of resistivity under applied field 0 (solid lines) and 15 kOe (dot lines) for Combined samples with CF: (a) LCMO+10 wt% CF, (b) LCMO+15 wt% CF, (c) LCMO+20 wt% CF, (d) LSMO+10 wt% CF, (e) LSMO+15 wt% CF, (f) LSMO+20 wt% CF.

magnetization at 77 K have 270 K and 85 emu/g which are similar values as the pure LCMO. The shape of magnetization curve for combined samples did not change compared to the curve of pure LCMO and LSMO samples. It was indicated that combined samples had a mixed state of LCMO or LSMO and CF powders.

The temperature dependence of resistivity for the combined samples (10, 15 and 20 wt % CF) measured under the zero and 15 kOe applied field are shown in Fig. 4. Defining the MR at a given temperature as  $\delta\rho/\rho(0)=$



**Fig. 5.** The field dependence of resistivity at various temperatures for the LCMO and CF 10 wt % combined sample.

$-\frac{[\rho(H)-\rho(0)]}{\rho(0)}$ , we find that the Curie temperature of combined samples show no appreciable change, in all the combined samples, with increasing the amount of CF, whereas a metal-semiconductor transition temperature rapidly decreased. For the LSMO sample with 20 wt %  $\text{CoFe}_2\text{O}_4$ , the metal-semiconductor transition temperature ( $T_{\text{SC-M}} = 192 \text{ K}$ ), was decreased about 160 K compared with the LSMO sample. Under an applied field of 15 kOe, the magnetoresistance ratio of combined sample with 20 wt %  $\text{CoFe}_2\text{O}_4$  is 7.3% at 192 K.

Figure 5 shows the external field dependence of resistivity for the LCMO and 10 wt % CF combined sample at 77, 162 and 270 K. At the interfaces of grain between the combined materials, the magnetic scattering of polarized charge carriers may be responsible for the enhanced low field magnetoresistance of the combined samples. For the curve at 77 K and 162 K, the curve shape of low field area shows grain boundary effects and the temperature dependence of resistivity has larger value than the pure LCMO sample. But the curve at 270 K of Fig. 5 is shown that the curve shape has no grain boundary effects. The metal-semiconductor transition temperature of pure LCMO sample was 270 K.

**Table 1.** The magnetic hyperfine field  $H_{\text{hf}}$ , isomer shift  $\delta$ , magnetization  $M_S$  at 77 K measured at  $H_{\text{Appl}} = 5 \text{ kOe}$ , metal-semiconductor transition temperature  $T_{\text{SC-M}}$ , and magnetoresistance ratio with external field 15 kOe for LCMO and LSMO and CF 20 wt % combined samples

Sample	$H_{\text{hf}}$ (kOe)		$\delta$ (mm/s)		$M_S$ (emu/g)	$T_{\text{SC-M}}$ (K)	MR (%)
	A-site	B-site	A-site	B-site			
LCMO + CF 20 wt %	489	515	0.14	0.25	85	Lower 77	-
LSMO + CF 20 wt %	490	519	0.15	0.22	82	192	7.3

In conclusion, we have studied the grain boundary effects on electrical resistivity and metal-semiconductor transition temperature of the combined mixture samples. The grain boundary effect could be understood of the magnetic scattering between grains induced by the combined  $\text{CoFe}_2\text{O}_4$  powders.

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### References

- [1] S. Jin, H. M. OBryan, T. H. Tiefel, M. McCormack, and W. W. Phodes, *Appl. Phys. Lett.* **66**, 382 (1995).
- [2] Y. Tomioka, A. Asamitsu, Y. Moritomo, H. Kuwahara, and Y. Tokura, *Phys. Rev. Lett.* **74**, 5108 (1995).
- [3] R. von Helmont, J. Wecker, K. Samwer, L. Hamwer, L. Haupt, and K. Bärner, *Appl. Phys. Lett.* **76**, 6925 (1994).
- [4] A. Asamitsu, Y. Moritomo, Y. Tomioka, T. Arima, and Y. Tokura, *Nature* **373**, 407 (1995).
- [5] M. R. Ibarra, P. A. Algarable, C. Marquina, J. Blasco, and J. Garcia, *Phys. Rev. Lett.* **75**, 3541 (1995).
- [6] A. P. Ramirez, P. Schiffer, S-W. Cheong, C. H. Chen, W. Bao, T. T. M. Palstra, P. L. Gammel, D. J. Bishop, and B. Zegarski, *Phys. Rev. Lett.* **76**, 3188 (1996).
- [7] H. Y. Hwang, S-W. Cheong, P. G. Radaeli, M. Marezio, and Batlogg, *Phys. Rev. Lett.* **75**, 914 (1995).
- [8] M. R. Lees, J. Barratt, G. Balakrishana, D. McK. Paul, and M. Yethiray, *Phys. Rev. B* **52**, 14 303 (1995).
- [9] J. M. D. Coey, *J. Appl. Phys.* **85**, 5576 (1999).
- [10] Yonglai Fu, *Appl. Phys. Lett.* **77**, 118 (2000).
- [11] H. Y. Hwang, S. W. Cheong, N. P. Ong, and B. Batlogg, *Phys. Rev. Lett.* **77**, 2041 (1996).
- [12] X. L. Wang, S. X. Dou, H. K. Liu, M. Ionescu, and B. Zeimetz, *Appl. Phys. Lett.* **73**, 396 (1998).
- [13] C. S. Kim, S.-I. Park, and Y. J. Oh, *J. Magn. Soc. Japan* **23**, 105 (1999).
- [14] H. N. Ok and J. G. Mullen, *Phys. Rev.* **168**, 563 (1968).