Tuning of colossal magnetoresistance via grain size change in $La_{0.67}Ca_{0.33}MnO_3$

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In this article, we show how colossal magnetoresistance effect (CMR) can be tuned in polycrystalline mixed valence manganite $La_{0.67}Ca_{0.33}MnO_3$ via changing grain size by means of a sol-gel method. Below a critical diameter (150 nm), CMR disappears, but large intergrain MR remains even well above T_c ($1.2T_c$ for ≈95 nm particles). Possible explanation for this effect involves single magnetic domain behavior in samples annealed at low temperature. © *1999 American Institute of Physics.* [S0021-8979(99)05819-3]

I. INTRODUCTION

The rediscovery of colossal magnetoresistance (CMR) in mixed valence manganites of the type $A_{1-x}B_xMnO_3$ (A=La, Nd, Pr, etc., a trivalent rare earth and B=Ca, Sr, Ba, etc., a divalent element)[1,2] has led to great experimental and theoretical efforts in this area.[3] Early studies of single crystals showed that a great change in resistivity under the effect of a magnetic field was only present at or near the magnetic phase transition temperature (T_c).[4–6] This effect was explained as a consequence of a strong spin-phonon coupling,[7] and more recently in an experimental way, via the presence of magnetic polarons.[8,9] In polycrystalline samples, intergrain magnetoresistance is also present superimposed on the CMR effect.[6,10–13] Spin-polarized tunneling or spin-dependent scattering between neighboring grains seems to be responsible for this kind of magnetoresistance.[6,14] Although CMR is an intrinsic property of mixed valence manganites, extrinsic influences (such as grain size in polycrystalline samples) dramatically modify this response. This could lead to a complex behavior in which both effects (intrinsic CMR and extrinsic intergrain MR) are present at the same time.

In this article, we show how CMR response can be tuned changing grain size in polycrystalline $La_{0.67}Ca_{0.33}MnO_3$. Below a certain critical diameter, CMR is no longer present but an important low-field intergrain magnetoresistance appears, even at temperatures well over T_c.

II. EXPERIMENT

In order to obtain a polycrystalline reference pattern, ceramic samples of $La_{0.67}Ca_{0.33}MnO_3$ were prepared from high purity oxides (CaO, La_2O_3, MnO, and MnO_2) by conventional solid state reaction, with a final sintering treatment of 100 h at 1300 °C in a static air atmosphere. Nanometric particles were prepared by the sol-gel technique. We have employed an aqueous solution of $La(NO_3)_3 \cdot 6H_2O$, $Mn(NO_3)_2 \cdot 6H_2O$, $Ca(NO_3)_2 \cdot 4H_2O$ of stoichiometric proportions and urea as a gelificant agent in a fixed concentration ($[\text{urea}]/([La^{3+}]+[Ca^{2+}]+[Mn^{2+}]=10$). The geling agent and the molar relationship [urea]/[salts] was optimized to obtain homogeneous samples at lower temperatures, as it was described in detail by Vázquez–Vázquez *et al.*[15] That solution is slowly evaporated at temperatures ranging from 75 to 137 °C (melting point of urea). When cooling, a gel is formed, and later, it is decomposed heating it at 250 °C for 3 h, yielding the precursor to prepare the final samples. This precursor is annealed at different temperatures up to 1100 °C for 6 h. Complete crystallization was observed at 600 °C (3 h). Particle sizes (D) were measured by means of scanning electron microscopy (SEM) (see Fig. 1 and Table I). A deviation from the mean diameter ⩽15% was observed for all the samples. Moreover, transition electron microscopy (TEM) analysis revealed elongated rather than spherical particles. Oxygen content was found to be close to the stoichiometric value by yodometric analysis, in the range $3 \pm \delta = 3.01(2)$ for all the samples. Through x-ray diffraction we detected a high crystallinity and absence of spurious phases for samples annealed at $T > 700$ °C.

Magnetization hysteresis loops were measured using a vibrating sample magnetometer from 77 to 300 K in fields up to 10 kOe. Resistivity measurements were made by the standard four probe method at a constant current. Magnetoresistance is defined as $\%MR = 100 \times [\rho(H=0) - \rho(H=5\ \text{kOe})/\rho(H=0)]$.

III. RESULTS AND DISCUSSION

In Table I, we show the change in particle size as a function of the annealing temperature (see also Fig. 1). We have varied the grain size from 95 nm (sol-gel sample, 800 °C) to around 20 μm in the ceramic sample. This provides us a very wide range to explore the whole range of MR behavior. Instead of deviation around mean size, we can ensure that no size distribution effects are present in our systems, since the diameters of different sets of particles are different enough to prevent this effect.

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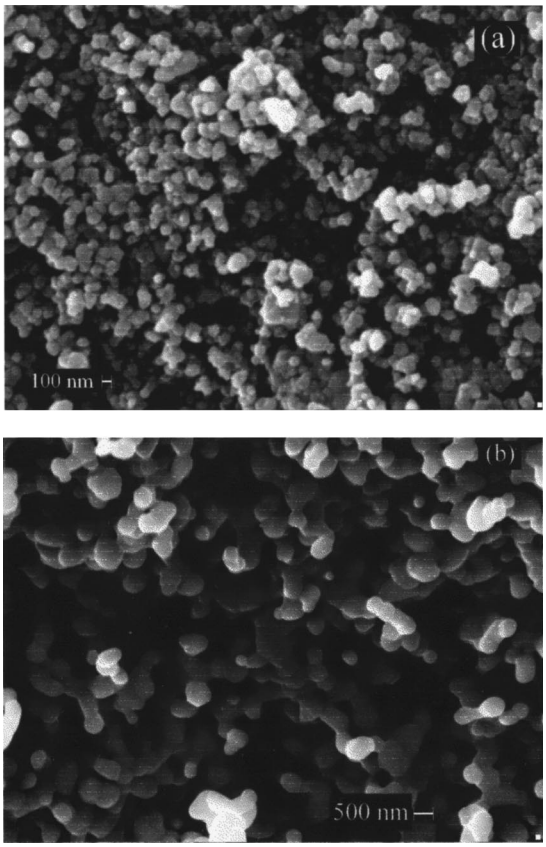

FIG. 1. SEM photograph of $La_{0.67}Ca_{0.33}MnO_3$ particles with very different size. (a) Sample sintered at 800 °C with grain size around 95 nm. (b) Sample sintered at 1100 °C with grain size around 500 nm.

In Fig. 2, we plot coercive field (H_c) and squareness (SQ), defined as remanence (M_R) over saturation magnetization (M_S), ($SQ=M_R/M_S$), at $T=100\,K$ versus sintering temperature for samples with different grain size. The tendency of H_C and SQ to decrease seems to indicate a gradual change from single domain to multidomain magnetic behavior as grain size increases.[16,17] On the other hand, T_C remains constant for all the samples (see Fig. 3). The decrease in low temperature magnetization in small grain size samples is attributable to the presence of a nonmagnetic surface layer created by noncrystalline material that is more important as the particle size decreases.[18] The change in magnetization near phase transition indicates good magnetic homogeneity in all the cases, independent of grain size distribution. The lost of long range ferromagnetic order in smaller grain size samples causes the more gradual decrease in magnetization curve, as shown in Fig. 3.

TABLE I. Particle size dependence of the annealing temperature. As we can see, a wide range of particle sizes was studied.

Method	Sintering treatment	Particle size
Sol-gel	800 °C (6 h)	95±14 nm
Sol-gel	900 °C (6 h)	150±21 nm
Sol-gel	1000 °C (6 h)	250±38 nm
Sol-gel	1100 °C (6 h)	0.5±0.1 μm
Ceramic	1300 °C (more than 100 h)	≈20 μm

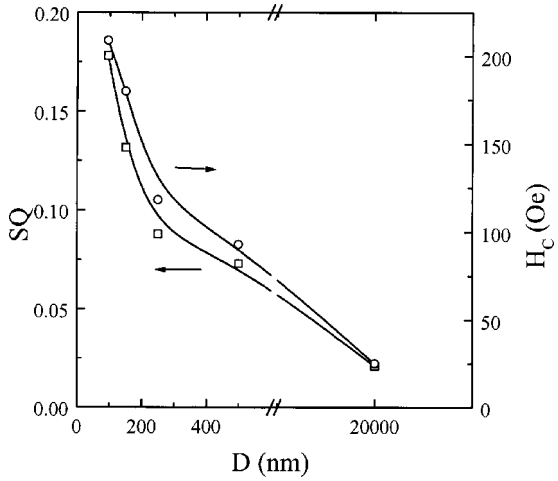

FIG. 2. Grain size dependence of coercive field (H_C) and squareness ($SQ=M_R/M_S$). We can observe how both values decrease as grain size increases. Lines are guides to the eye.

The key point of this article is presented in Fig. 4, where magnetoresistance versus reduced temperature is plotted for the series of samples studied. The characteristic CMR peak observed around metal–insulator transition T_{M-I} decreases continuously as grain size does, and for sol-gel samples sintered at 900 °C ($D\approx150$ nm), intrinsic colossal magnetoresistance completely disappears. Below the transition temperature, an increasing intergrain magnetoresistance response appears in every case, but it is largest for smaller grain size samples. Intergrain MR remains measurable until $1.2T_C$ for the smallest grain sample. This significantly increases the interval of MR response of the material, which could have an evident role in the development of MR sensors, since provides a measurable response in a wide range of temperature.

Magnetoresistance behavior versus reduced temperature allows us to distinguish two separate groups of samples: samples treated at temperatures lower than 1000 °C show the

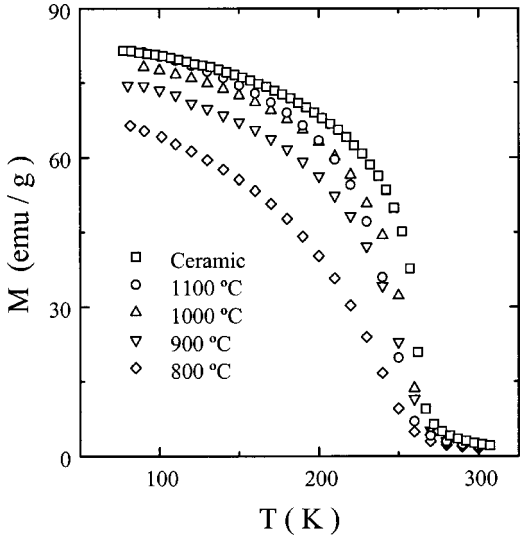

FIG. 3. Grain size dependence of magnetization. It is clear from the figure that T_C is nearly the same for all the samples studied, independent of grain size.

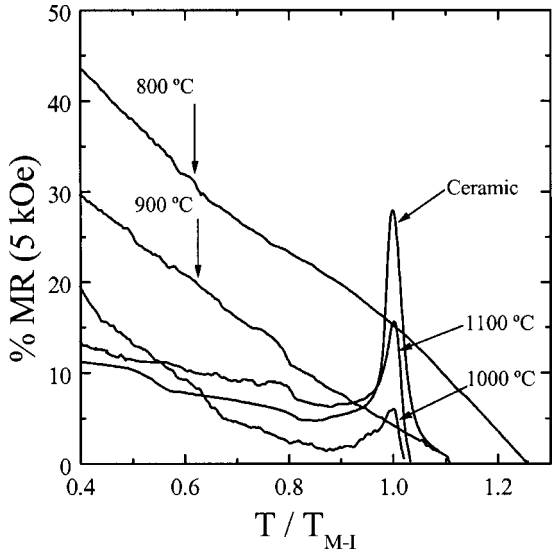

FIG. 4. Magnetoresistance percentage at a constant field of 5 kOe (%MR) vs reduced temperature (T/T_{M-I}) for several particle size samples. The appearance of CMR peak around $T_C \approx T_{M-I}$ is clearly observed.

same steep slope in the evolution of MR versus T, that leads to a high magnetoresistance value at low temperature. By contrast, high temperature treated samples present the intrinsic CMR associated with metal–insulator transition and a small intergrain MR, with a less pronounced slope in the MR versus temperature curve (Fig. 4). Strong differences in low field magnetoresistance at 77 K are shown in Fig. 5. We can observe how intergrain effect produces a magnetoresistance loop in the case of small particles. This consequence, strongly related to magnetization hysteresis loop,[13] is negligible in the biggest particle size process.

It is clear from these results that a reduction in sintering temperature leads to the progressive destruction of intrinsic colossal magnetoresistance. This effect could be related with a transition from single domain to multidomain regime, which promotes the presence of domain walls in the bigger particles. These walls could act themselves as scattering centers altered by the presence of a magnetic field or, in a more suitable way, as a significant circumstance in the appearance of the intrinsic mechanism that produces CMR. The data presented here can be related to the theory developed by Zhang *et al.*[19] This author relates the CMR peak in manganese perovskites to the presence of thermally activated magnetic domains. Although this kind of domains are different from static ones, the absence of domain walls could be related with the progressive destroy of the intrinsic mechanism that cause CMR.

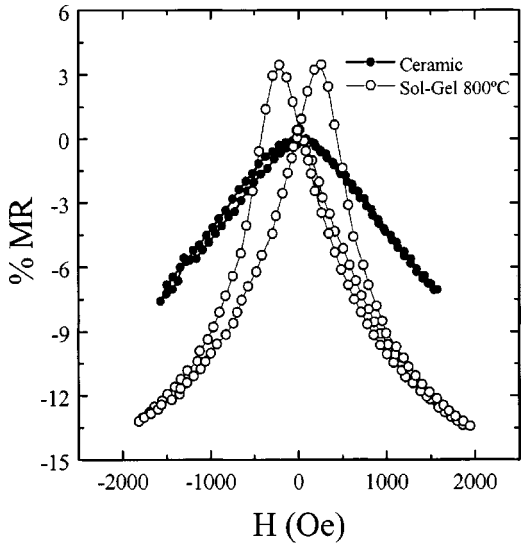

FIG. 5. Low field magnetoresistance at 77 K for two samples with very different grain size; 95 nm (sol-gel 800 °C) and ≈20 μm (ceramic 1300 °C). The presence of hysteresis in MR is successfully explained in a tunneling model for conduction between grains.

On the other hand, the increase in the influence of boundaries reducing grain size promotes a rise in tunneling magnetoresistance (see Fig. 4), that inhibits the intrinsic response of the material, that is, the CMR peak around the phase transition. Extrinsic magnetoresistance becomes so important that intrinsic counterpart influence is negligible.

Even taking into account these explanations, we should not forget the intrinsic chemical inhomogeneity reported in similar compounds sintered at low firing temperature.[20–22] These inhomogeneities presented in other samples, could be related to the absence of a colossal magnetoresistance peak. The mixture of several different magnetic phases may be responsible for the destruction of intrinsic CMR behavior in similar situations. In any case, this subject should have a complete theoretical study just to clarify the additional results presented here.

IV. CONCLUSIONS

In summary, we have shown how colossal magnetoresistance can be tuned in $La_{0.67}Ca_{0.33}MnO_3$ by changing grain size. Below a certain particle size CMR response disappears, but intergrain magnetoresistance remains measurable until $1.2T_C$. This result could be important from the academic and technological point of view. High temperature MR observed at low fields could be useful in the development of practical magnetoresistive devices.

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[1] R. von Helmolt, J. Wecker, B. Holzapfel, L. Schultz, and K. Samwer, Phys. Rev. Lett. **71**, 2331 (1993).
[2] K. Chahara, T. Ohno, M. Kasai, and Y. Kozono, Appl. Phys. Lett. **63**, 1990 (1993).
[3] See, for a review, A. P. Ramirez, J. Phys.: Condens. Matter **9**, 8171 (1997).
[4] A. Urushibara, Y. Moritomo, T. Arima, A. Asamitsu, G. Kido, and Y. Tokura, Phys. Rev. B **51**, 14103 (1995).
[5] J. Z. Liu, I. C. Chang, S. Irons, P. Klavins, R. N. Shelton, K. Song, and S. R. Wasserman, Appl. Phys. Lett. **66**, 3218 (1995).
[6] H. Y. Hwang, S-W. Cheong, N. P. Ong, and B. Batlogg, Phys. Rev. Lett. **77**, 2041 (1996).
[7] A. J. Millis, P. B. Littlewood, and B. I. Shraiman, Phys. Rev. Lett. **74**, 5144 (1995).

[8] S. J. L. Billinge, R. G. DiFrancesco, G. H. Kwei, J. J. Neumeier, and J. D. Thomsom, Phys. Rev. Lett. **77**, 715 (1996).
[9] J. M. De Teresa, M. R. Ibarra, P. A. Algarabel, C. Ritter, C. Marquina, J. Blasco, J. García, A. del Moral, and Z. Arnold, Nature (London) **386**, 256 (1997).
[10] A. Gupta, G. Q. Gong, Gang Xiao, P. R. Duncombe, P. Lecoeur, P. Trouilloud, Y. Y. Wang, V. P. Dravid, and J. Z. Sun, Phys. Rev. B **54**, 15629 (1996).
[11] R. D. Sánchez, J. Rivas, C. Vázquez-Vázquez, M. A. López-Quintela, M. T. Causa, M. Tovar, and S. B. Oseroff, Appl. Phys. Lett. **68**, 134 (1996).
[12] R. Mahesh, R. Mahendiran, A. K. Raychaudhuri, and C. N. R. Rao, Appl. Phys. Lett. **68**, 2291 (1996).
[13] L. E. Hueso, F. Rivadulla, R. D. Sánchez, D. Caeiro, C. Jardón, C. Vázquez-Vázquez, J. Rivas, and M. A. López-Quintela, J. Magn. Magn. Mater. **189**, 321 (1998).
[14] X. W. Li, A. Gupta, Gang Xiao, and G. Q. Gong, Appl. Phys. Lett. **71**, 1124 (1997).
[15] C. Vázquez-Vázquez, M. C. Blanco, M. A. López-Quintela, R. D. Sánchez, J. Rivas, and S. B. Oseroff, J. Mater. Chem. **8**, 991 (1998).
[16] H. Kronmüller, in *Supermagnets, Hard Magnetic Materials*, edited by G. J. Long and F. Grandjean (Kluwer, Amsterdam, 1991), p. 461.
[17] A. H. Morrish, *The Physical Principles of Magnetism* (Wiley, New York, 1965).
[18] J.-H. Park, E. Vescovo, H.-J. Kim, C. Kwon, R. Ramesh, and T. Venkatesan, Phys. Rev. Lett. **81**, 1953 (1998).
[19] S. Zhang and Z. Yang, J. Appl. Phys. **79**, 7398 (1996).
[20] M. S. G. Baythoun and F. R. Sale, J. Mater. Sci. **17**, 2757 (1982).
[21] J. R. Sun, G. H. Rao, and Y. Z. Zhang, Appl. Phys. Lett. **72**, 3208 (1998).
[22] K. P. S. Anil, J. P. Alias, and S. K. Date, J. Mater. Chem. **8**, 1219 (1998).