



## La<sub>0.7</sub>Ca<sub>0.3</sub>MnO<sub>3</sub> / Mn<sub>3</sub>O<sub>4</sub> composites: Does an insulating secondary phase always enhance the low field magnetoresistance of manganites?

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## La<sub>0.7</sub>Ca<sub>0.3</sub>MnO<sub>3</sub> / Mn<sub>3</sub>O<sub>4</sub> composites: Does an insulating secondary phase always enhance the low field magnetoresistance of manganites?

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Composites of magnetoresistive La<sub>0.7</sub>Ca<sub>0.3</sub>MnO<sub>3</sub> (LCMO) with insulating Mn<sub>3</sub>O<sub>4</sub> are useful as a model system because no foreign cation is introduced in the LCMO phase by interdiffusion during the heat treatment. Here we report the magnetotransport properties as a function of sintering temperature  $T_{\text{sinter}}$  for a fixed LCMO/Mn<sub>3</sub>O<sub>4</sub> ratio. Decreasing  $T_{\text{sinter}}$  from 1250 °C to 800 °C causes an increase in low field magnetoresistance (LFMR) that correlates with the decrease in crystallite size (CS) of the LCMO phase. When plotting LFMR at (77 K, 0.5 T) versus 1/CS, we find that the data for the LCMO/Mn<sub>3</sub>O<sub>4</sub> composites sintered between 800 °C and 1250 °C follow the same trend line as data from the literature for pure LCMO samples with crystallite size  $> \sim 25$  nm. This differs from the LFMR enhancement observed by many authors in the “usual” manganite composites, i.e., composites where the insulating phase contains cations other than La, Ca or Mn. This difference suggests that diffusion of foreign cations into the grain boundary region is a necessary ingredient for the enhanced LFMR. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.3694664>]

### I. INTRODUCTION

Polycrystalline manganites are known<sup>1</sup> to exhibit grain-boundary-related magnetoresistance (usually called low field magnetoresistance, LFMR) in addition to intrinsic colossal magnetoresistance. Many authors have shown that LFMR may be enhanced by mixing the magnetoresistive manganite with an insulating secondary phase (see Ref. 1, pp. 26–27 for an overview up to 2006 and Refs. 2–6 for a few recent examples). However, most studies have focused on investigating the dependence of the magnetoresistance as a function of the percentage of insulating phase without considering the influence of the heat treatment. In most composite systems, the analysis of such data would indeed be difficult because high temperature sintering promotes ionic diffusion and usually results in a pronounced shift of the manganite composition. On the contrary, we found<sup>7–9</sup> that La<sub>0.7</sub>Ca<sub>0.3</sub>MnO<sub>3</sub> (LCMO)/Mn<sub>3</sub>O<sub>4</sub> suits very well as a model composite system: by using Mn<sub>3</sub>O<sub>4</sub> as an insulating phase, we ensure that no foreign cation is introduced in the LCMO phase. Recently, two other groups have chosen the similar La<sub>0.7</sub>Sr<sub>0.3</sub>MnO<sub>3</sub>/Mn<sub>3</sub>O<sub>4</sub> system for the same reason, when investigating room temperature magnetoresistance at very low field<sup>2</sup> or strain effects in nanocomposite epitaxial thin films grown by pulsed laser deposition.<sup>6</sup>

In the present work our purpose was to study how the grain-boundary-related magnetotransport properties of the LCMO/Mn<sub>3</sub>O<sub>4</sub> composite are affected by other parameters than the amount of Mn<sub>3</sub>O<sub>4</sub>. Therefore, we kept a constant LCMO/Mn<sub>3</sub>O<sub>4</sub> ratio and varied the sintering temperature  $T_{\text{sinter}}$  in order to modify parameters such as crystallite size, grain size, and porosity. The LCMO/Mn<sub>3</sub>O<sub>4</sub> ratio was

selected so that even the most porous composite (i.e., sintered at the lowest temperature) would still be on the “conducting side” of the percolation threshold. We assumed a percolation threshold of 20 vol % LCMO, corresponding to the value found in the case of LCMO/Mn<sub>3</sub>O<sub>4</sub> samples sintered at 1300 °C.<sup>7</sup>

### II. EXPERIMENTAL

La<sub>0.7</sub>Ca<sub>0.3</sub>MnO<sub>3</sub>/Mn<sub>3</sub>O<sub>4</sub> composites were prepared by spray drying<sup>10</sup> of an aqueous solution of metallic acetates containing La, Ca, and Mn in molar ratio 7/3/42. After heating for 2 h at 600 °C and 800 °C to decompose the precursors, pellets were pressed and sintered for 2 h at temperatures ranging from 800 °C to 1200 °C. Another sample was sintered at 1250 °C for 12 h. Samples were characterized by X-ray diffraction (Siemens D5000, Cu K<sub>alpha</sub> radiation), electron microscopy (Philips XL-30 ESEM with EDAX), density measurement (Archimedes’ method in 1-butanol), and chemical titration of Mn average oxidation state.<sup>11</sup> Crystallite sizes were determined by X-ray diffraction (XRD) pattern fitting with Topas software<sup>12</sup> using the fundamental parameters approach to model the instrumental contribution. Magnetic and magnetoresistance properties were measured with a Physical Property Measurement System from Quantum Design.

### III. RESULTS AND DISCUSSION

X-ray diffraction patterns (Fig. 1) confirm that composites of LCMO perovskite and Mn<sub>3</sub>O<sub>4</sub> are obtained at all temperatures. At 800 °C and 900 °C, a small amount of Mn<sub>2</sub>O<sub>3</sub> is detected in addition to the main phases. The crystallite size (not to be confused with the grain/particle size) was determined from the width of the XRD reflections, taking into account a correction for instrumental broadening. Crystallite

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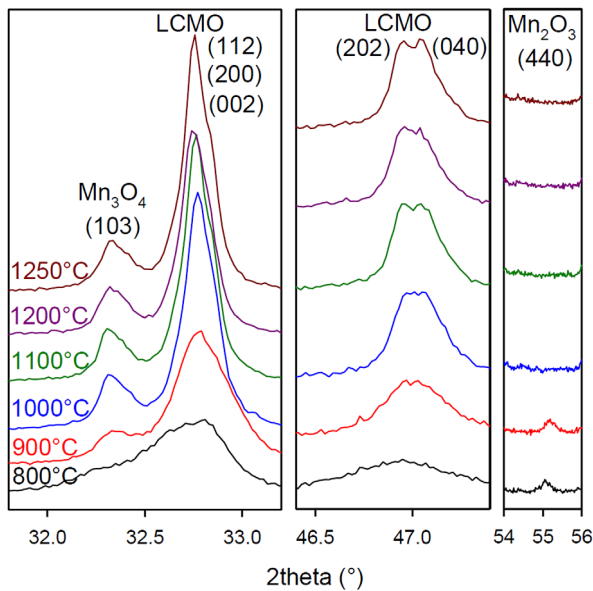


FIG. 1. (Color online) X-ray diffraction data: Zooms in several 2θ ranges show representative reflections of the LCMO, Mn<sub>3</sub>O<sub>4</sub> and Mn<sub>2</sub>O<sub>3</sub> phases as a function of sintering temperature. Reflection indices are given for Pnma (LCMO), I4<sub>1</sub>/amd (Mn<sub>3</sub>O<sub>4</sub>), and Ia-3 (Mn<sub>2</sub>O<sub>3</sub>) space groups.

size was found to increase from  $\sim 35$  nm to  $\sim 110$  nm when  $T_{\text{sinter}}$  increases from 800 °C to 1250 °C (Fig. 2(a)).

The average Mn oxidation state decreases from 2.90 to 2.83 when  $T_{\text{sinter}}$  increases. This is consistent with the transformation of Mn<sub>2</sub>O<sub>3</sub> into Mn<sub>3</sub>O<sub>4</sub> and the reported trend for manganites.<sup>13</sup> The average Mn oxidation states for the highest  $T_{\text{sinter}}$  agree well with the calculated value (2.82) for a nominal “La<sub>0.7</sub>Ca<sub>0.3</sub>MnO<sub>3</sub> + 3.2 Mn<sub>3</sub>O<sub>4</sub>” composite.

Increasing  $T_{\text{sinter}}$  from 800 °C to 1250 °C increases the bulk density from 60% to 95% of the theoretical density. Since the LCMO / Mn<sub>3</sub>O<sub>4</sub> ratio is constant, there is a direct correspondence with the LCMO volume fraction in the composite and both scales are used to present the data in Fig. 2(b). The electron micrographs shown in Figs. 2(c) and 2(d) for the samples sintered at 800 °C and 1250 °C confirm the increase in density and reveal the growth of the grains from

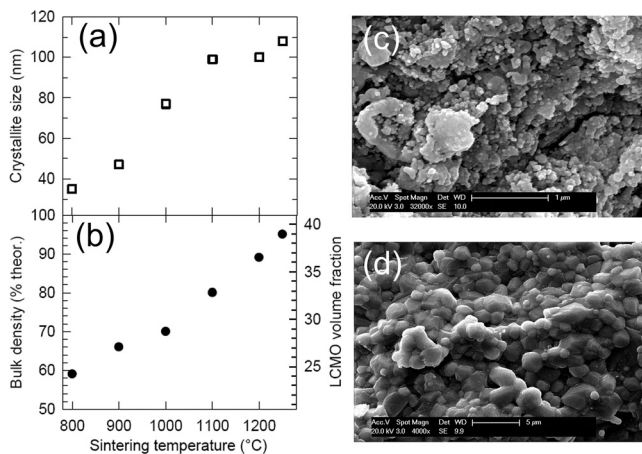


FIG. 2. (a, b) Crystallite size, bulk density, and LCMO volume fraction vs sintering temperature. (c, d) Secondary electron micrographs of unpolished cross-sections of LCMO/Mn<sub>3</sub>O<sub>4</sub> composites sintered at 800 °C (c) and 1250 °C (d) - scale bars 1 and 5 μm, respectively.

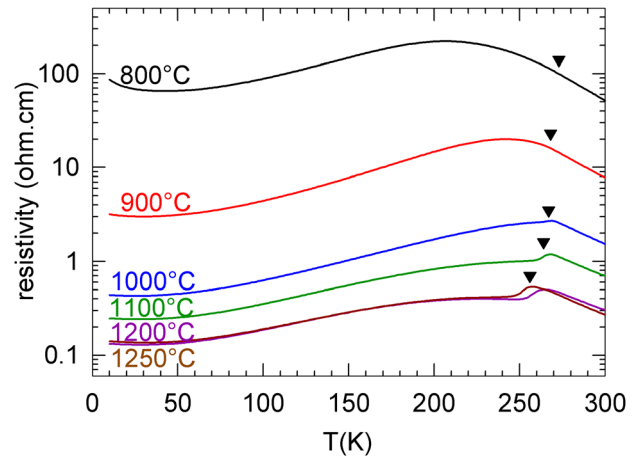


FIG. 3. (Color online) Temperature dependence of the electrical resistivity of the LCMO/Mn<sub>3</sub>O<sub>4</sub> composites sintered at various temperatures. Arrow heads correspond to Curie temperatures.

agglomerated primary particles to well-connected prismatic particles of a few microns.

The temperature dependence of the electrical resistivity  $\rho(T)$  of all samples is shown in Fig. 3. At all temperatures,  $\rho$  tends to decrease when  $T_{\text{sinter}}$  increases. The Curie temperature ( $T_C$ ) of each sample (obtained from magnetic susceptibility measurements) is marked by an arrow and decreases slightly from 273 K to 257 K when  $T_{\text{sinter}}$  decreases from 1250 °C to 800 °C. The  $\rho(T)$  curves of the composites sintered at 800 °C or 900 °C display a broad maximum at temperatures significantly below  $T_C$ , as frequently observed in samples sintered at low temperature, where the small grain size enhances the contribution from the grain boundaries.<sup>14</sup>

The magnetoresistance (MR) at 77 K is plotted as a function of applied magnetic field in Fig. 4. As expected, MR at low field is larger for the lowest  $T_{\text{sinter}}$ . However the enhancement is not very strong, e.g., MR at 0.5 T increases only from 12% to 16% when  $T_{\text{sinter}}$  decreases from 1250 °C to 800 °C. By comparison, similar or even higher MR values are obtained for pure LCMO samples<sup>10</sup> sintered at the same temperatures but with slightly smaller crystallite size due to

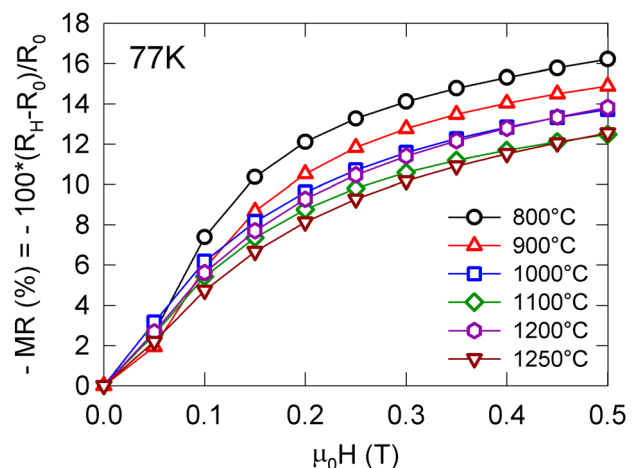


FIG. 4. (Color online) Magnetoresistance at 77 K as a function of applied magnetic field for LCMO/Mn<sub>3</sub>O<sub>4</sub> composites sintered at various temperatures.

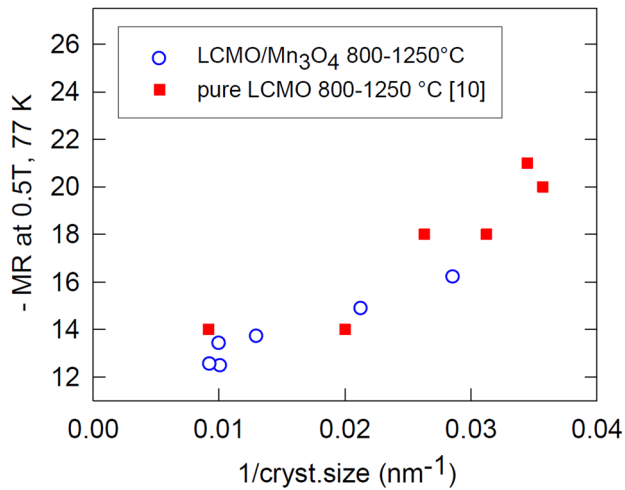


FIG. 5. (Color online) Magnetoresistance at 77 K, 0.5 T as a function of inverse crystallite size, for composites (empty symbols) or pure LCMO (full symbols) from our work.

a different pre-calcination treatment. Figure 5 shows MR (77 K, 0.5 T) versus the inverse of crystallite size  $1/CS$  for the two sets of data. It turns out that the data points follow the same trend, although one set is for composites (blue empty circles) and the other one for pure manganite samples (red squares). This observation differs from the LFMR enhancement observed by many authors in other manganite composites.<sup>1</sup> By comparison with the LCMO/Mn<sub>3</sub>O<sub>4</sub> system investigated here, the “usual” composite systems (i.e., where an LFMR enhancement is observed) contain cations other than La, Ca or Mn in the insulating phase. This difference suggests that diffusion of foreign cations into the grain boundary region is a necessary ingredient for the enhanced LFMR.

Figure 5 presents only a few data points, corresponding to two series of samples prepared by the same synthesis method (spray drying) and sintered at similar temperatures. In Fig. 6, additional data points are presented for bulk polycrystalline samples prepared by other synthesis methods and/or at other temperatures. These data were collected from our previous work<sup>7</sup> and from the literature.<sup>15–22</sup> The only selection criteria were (i) data availability, (ii) La<sub>0.7</sub>Ca<sub>0.3</sub>MnO<sub>3</sub> or La<sub>0.67</sub>Ca<sub>0.33</sub>MnO<sub>3</sub> composition of the manganite phase, and (iii) insulating phase containing no foreign cation able to diffuse into the manganite phase (in the case of composites). Actually, data availability is quite a severe filter because only a few authors report crystallite size (not to be confused with grain/particle size observed by microscopy). Besides, MR data are presented at various temperatures and magnetic fields. In Figs. 5 and 6, we chose 77 K because it is the temperature for which most data are available. When selecting a value of applied field  $\mu_0H$ , we had to consider the fact that the slope of the LFMR is influenced by the geometry of the sample;<sup>10</sup> below the saturation magnetic field, the difference between the *applied* magnetic field and the *internal* magnetic field (which is the relevant parameter) depends on the demagnetization factor. This is the reason why we decided to report MR for  $\mu_0H = 0.5$  T instead of a lower value.

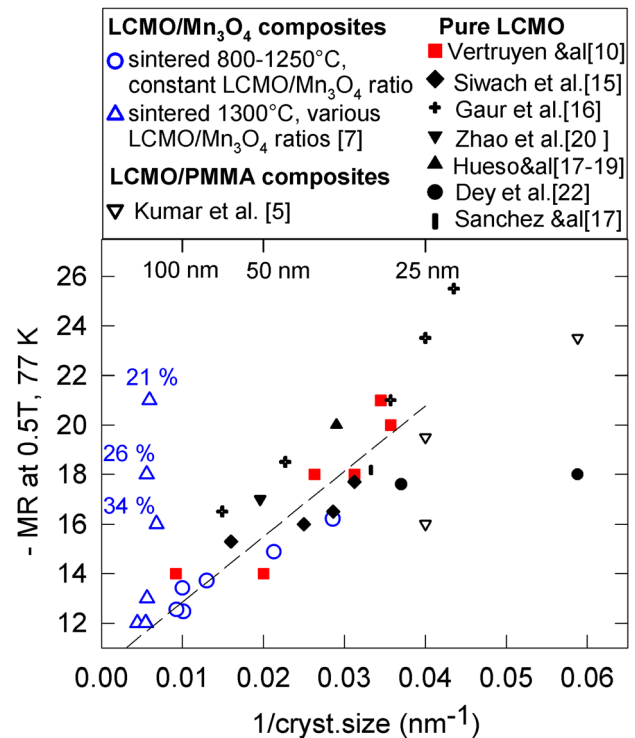


FIG. 6. (Color online) Magnetoresistance at 77 K, 0.5 T as a function of inverse crystallite size, for composites (empty symbols) or pure LCMO (full symbols) from our work or from other groups (see legend). LCMO volume fraction (in %) is given for some composites. The dashed line is a guide for the eye.

In Fig. 6, full symbols correspond to pure LCMO samples (La<sub>0.7</sub>Ca<sub>0.3</sub>MnO<sub>3</sub> or La<sub>0.67</sub>Ca<sub>0.33</sub>MnO<sub>3</sub>) whereas empty symbols correspond to composites (LCMO/Mn<sub>3</sub>O<sub>4</sub> and LCMO/polymethylmethacrylate). Data for crystallite size below 25 nm are scarce and seem very much scattered, probably due to the overwhelming influence of the surface effects, as discussed for example by Dey and Nath.<sup>22</sup> In the case of crystallite sizes above  $\sim 25$  nm, data agree rather well with the trend line already observed in Fig. 5, except for a few composite samples sintered at high temperature (see discussion below). There is a significant scattering of the data points but the dispersion is actually much smaller than expected: considering that the data points correspond to samples with different porosities, grain sizes, grain connectivities,... (due to different synthesis conditions), the agreement is actually amazingly good. It is interesting to note that a similar trend was reported in a study of Manh *et al.*,<sup>23</sup> who found a linear increase of  $MR_{spt}$  versus  $1/CS$  for La<sub>0.7</sub>Ca<sub>0.3</sub>MnO<sub>3</sub> samples at 30 K, where  $MR_{spt}$  is the contribution of intergranular spin-polarized transport.

To complete the analysis of Fig. 6, it is necessary to discuss the data (blue empty triangles) corresponding to composites with various LCMO/Mn<sub>3</sub>O<sub>4</sub> ratios, sintered at 1300 °C for 40 h, whose properties were described in our previous papers.<sup>7–9</sup> Due to the long heat treatment at high temperature, the crystallite size is too large to introduce a significant broadening of the XRD reflections and the CS values of 150–200 nm should be best read as “ $\geq 150$ –200 nm,” or  $1/CS < 0.005$  nm<sup>-1</sup>. The MR(77 K, 0.5 T) of these

composites follows the general trend as long as the LCMO volume fraction is  $\geq 40\%$ . For LCMO volume fraction between 40% and the percolation threshold ( $\sim 20\%$ ), MR increases with decreasing LCMO content. It is *a priori* unexpected to find enhanced magnetoresistance only in composites sintered at high temperature, but this may be related to the recent results of Kang *et al.*<sup>2</sup> on LSMO/Mn<sub>3</sub>O<sub>4</sub> composites, where improved LFMR is attributed to the formation of sharp and clean interfaces acting as effective spin-dependent scattering centers.

#### IV. CONCLUSIONS

In conclusion, we found that LFMR at (77 K, 0.5 T) for LCMO/Mn<sub>3</sub>O<sub>4</sub> composites sintered between 800 °C and 1250 °C is not higher than for pure LCMO samples prepared by the same method at similar temperatures. This suggests that the presence of an insulating phase is not in itself sufficient to obtain an enhancement of LFMR. On the other hand, LFMR enhancement is commonly reported in the literature for composites whose insulating phase contains cations other than La, Ca or Mn, i.e., “foreign” cations able to diffuse into the manganite phase. This suggests that diffusion of foreign cations into the grain boundary region is a necessary ingredient for the enhanced LFMR in composites prepared in the usual range of temperatures and dwelling times.

Because of a small difference of crystallite sizes between the two series of samples, it was necessary to investigate the dependence of LFMR at (77 K, 0.5 T) as a function of the inverse of crystallite size. The limited number of data points suggested the existence of a trend line. Unexpectedly, data for samples prepared by other techniques and at other temperatures agree rather well with the observed trend, as long as crystallite size is  $> \sim 25$  nm. In the present paper we compared only magnetoresistance data at 77 K, 0.5 T. More generally, our results suggest that valuable information about the role of crystallite size, porosity, grain size, connectivity,... could be gained from investigation of large sets of samples prepared by various techniques. Despite the extended literature devoted to magnetoresistive manganites, this approach would probably require an extensive work of synthesis of new samples because only a few of the numerous literature papers on magnetoresistive manganites report simultaneously data such as porosity, crystallite size or sample shape. In particular, it would be interesting to investigate

La<sub>0.7</sub>Sr<sub>0.3</sub>MnO<sub>3</sub>-based systems, as a prototype of broad-bandwidth manganite compounds.

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