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Effect of compositional homogeneity on the magnetic properties of $La_{0.7}Ca_{0.3}MnO_3$

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Dc magnetization and ac magnetic susceptibility have been measured in the temperature range 80–300 K for $La_{0.7}Ca_{0.3}MnO_3$, synthesized by the conventional ceramic and the low temperature combustion methods and annealed at different temperatures. Temperature dependence of the dc magnetization and the ac susceptibility is strongly dependent on the processing conditions resulting in compositional inhomogeneity in the samples. A sharp ferromagnetic transition is observed only for a compositionally homogeneous sample.

The discovery of unusually high magnetoresistance (known as giant magnetoresistance, GMR) in the ferromagnetic perovskite manganites, $Ln_{1-x}Ca_xMnO_3$ (Ln = La, Pr, Nd, *etc.*) has stimulated the need for a detailed study of their electrical transport and magnetic properties.[1] Jonker and Van Santen[2] first reported the onset of ferromagnetism in the system $La_{1-x}Ca_xMnO_3$. Wollan and Koehler[3] made a detailed investigation of the magnetic structure of this system from neutron diffraction studies. The double-exchange (DE) magnetic interaction between Mn^{3+} and Mn^{4+}, as proposed by Zener, explained the origin of ferromagnetism in these compounds.[4] Recently it has been shown that small magnetic polarons are responsible for the pronounced magnetoresistance of these compounds at the Curie temperature.[5] The GMR effect in this system has been studied extensively using single crystals, thin films, and polycrystalline samples derived from different processing routes. Large variations in the Curie temperature are reported for a single composition processed by different methods. Various types of anomalies in their structural, electrical, and magnetic properties are also reported.[6–11] The Curie temperature[12] and magnetic entropy change[13] of low temperature synthesized compounds (by the combustion of a urea–nitrate mixture or by the sol–gel method) are shown to depend on particle size; maximum T_c and entropy changes are observed for bigger particles obtained by heating the sample at higher temperatures. Since the GMR effect can be controlled by manipulating the grains and grain boundaries,[14] the low temperature synthesized compounds, which always give finer particles, offer control over grain/grain-boundary related electronic properties. As these properties depend on the extent of compositional, magnetic, and structural homogeneities, compositional homogeneity at a microscopic level is the most desired factor as it leads to a uniform distribution of Mn^{3+}/Mn^{4+} in the compound. The extent of the DE interaction between Mn^{3+} and Mn^{4+} which determines the T_c as well as the sharpness of the ferromagnetic transition, and the degree of resistivity anomaly at T_c, thus, may depend purely on the compositional homogeneity.

In order to understand the origin of the different types of anomalies reported for the magnetic properties of the manganites, we have studied the magnetic behavior of $La_{0.7}Ca_{0.3}MnO_3$ synthesized by two different methods; (i) by the conventional ceramic method and (ii) by combustion synthesis or the urea–nitrate method, and annealed at different temperatures. The magnetic properties were evaluated using low field ac susceptibility (ACS), high field dc magnetization, and field cooled (FC) and zero field cooled (ZFC) magnetization measurements. The ACS measurements were pursued as this technique can provide more information about magnetic ordering and the presence of other magnetic impurities in a sample.[15]

Experimental

$La_{0.7}Ca_{0.3}MnO_3$ was prepared by the combustion synthesis method (hereafter referred to as the combustion sample) following the literature method,[12] and was annealed in air at different temperatures (600–1300 °C). In the ceramic synthesis method (referred in the text as the ceramic sample), the corresponding oxides were mixed in the required molar ratio and heated initially at 1000 °C for 72 h with six intermediate grindings, and subsequently annealed in air at higher temperatures (1000–1300 °C). The samples were characterized by powder X-ray diffraction (XRD) method using a Philips PW1730 powder X-ray diffractometer. The powder XRD patterns of all the samples revealed their single phase nature without any secondary or impurity phases. The microstructural features were obtained using a Leica-Cambridge 440 scanning electron microscope. The Mn^{4+} content of the samples was estimated by redox titrations using potassium permanganate and iron(II) ammonium sulfate solutions. The low field (at 10 Oe and 27 Hz) ac susceptibility (ACS) studies were performed using the mutual inductance technique in an APD cryogenics closed-cycle helium cryostat (50–300 K). The dc magnetization measurements were carried out on a EG&G PAR vibrating sample magnetometer (VSM) model 4500 attached to a Janis liquid nitrogen cryostat (80–300 K).

Results and Discussion

In Fig. 1 the temperature dependence of the dc magnetization (measured at 5000 Oe) is shown for the samples prepared by the ceramic and combustion methods and annealed at different temperatures. The samples annealed below 1300 °C show an initial increase in the magnetization at *ca.* 270 K and show a broad magnetic transition with no well defined transition temperature. The ceramic sample annealed at 1000 °C and the combustion sample annealed at 1200 °C show a second broad transition below *ca.* 240 K. After annealing at 1300 °C for 48 hours, the first magnetic transition becomes sharp and is shifted to *ca.* 245 K for the combustion sample with a small step in the magnetization at *ca.* 230 K. On the other hand, a

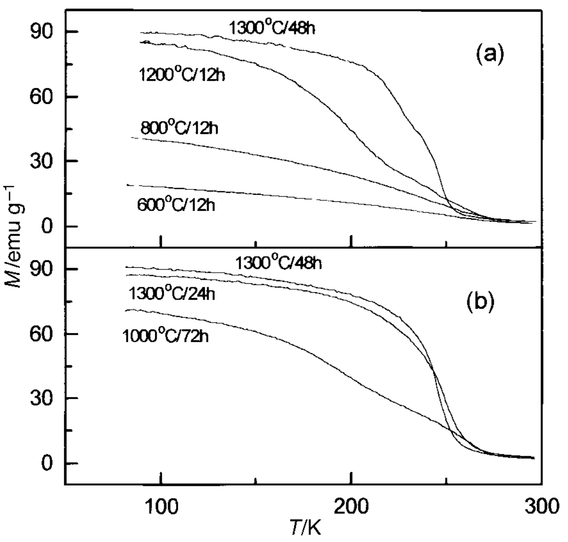

Fig. 1 Temperature dependence of the magnetization ($H_A = 5000$ Oe) of $La_{0.7}Ca_{0.3}MnO_3$ annealed at various temperatures: (a) prepared by the combustion method, and (b) prepared by the ceramic method

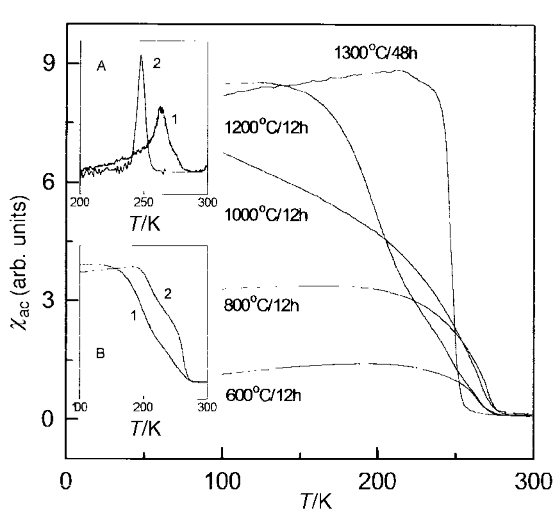

Fig. 2 Temperature dependence of the ac susceptibility of $La_{0.7}Ca_{0.3}MnO_3$ synthesized by the combustion method and annealed at various temperatures. Inset A: the $d\chi_{ac}/dT$ curves of (1) 1000 °C and (2) 1300 °C annealed samples; inset B: ACS curves of the samples annealed at 1200 °C, prepared by (1) combustion and (2) ceramic methods.

well defined $T_c \approx 245$ K is obtained for the ceramic sample annealed at 1300 °C for 48 hours.

Fig. 2 shows the temperature variation of the ac susceptibility measured on the combustion samples. The samples annealed up to 1200 °C show an initial increase in the susceptibility above 260 K. After annealing at 1200 °C, the susceptibility curve shows multiple steps at lower temperatures, as well as the initial increase at *ca.* 265 K. Even the sample annealed at 1300 °C for 48 h shows a small step at *ca.* 230 K apart from the sharp transition at $T_c = 246$ K. The magnetic transition temperature (T_c), which corresponds to the maximum in the $d\chi_{ac}/dT$ curve of each sample, is indicated in Table 1. Inset A Fig. 2 shows the derivative of the susceptibility, $d\chi_{ac}/dT$, of the samples annealed at 1000 °C (curve 1) and 1300 °C (curve 2). Curve 1 is very broad with a maximum at 266 K and shoulders at *ca.* 270 K and *ca.* 245 K, whereas curve 2 shows only a sharp maximum at 246 K. The ac susceptibility behavior of the ceramic (curve 2) and combustion (curve 1) samples annealed at 1200 °C is compared in inset B. Both curves show almost identical behavior.

The ACS curves of the ceramic samples are shown in Fig. 3. The natures of the ac susceptibility curves of the samples annealed up to 1200 °C are identical. As observed in Fig. 2, an initial increase in the susceptibility is observed below *ca.* 270 K and a second rise at low temperature is observed at 185 K for the 1000 °C annealed sample. The temperature at which this second transition occurs is shifted to higher temperatures (see Table 1) as the annealing temperature is increased to 1200 °C (193 K for curve b and 208 K for curve c) with an increase in the magnitude of the transition below 270 K, and finally both the transitions are merged together to form a single broad

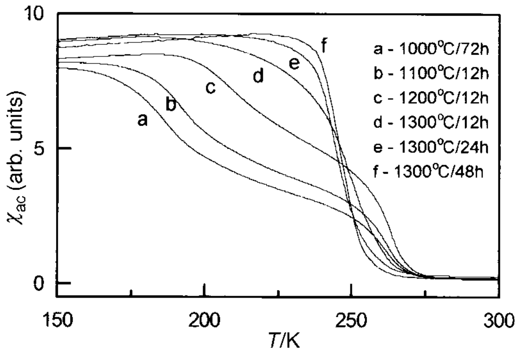

Fig. 3 Temperature dependence of the ac susceptibility of $La_{0.7}Ca_{0.3}MnO_3$ synthesized by the ceramic method and annealed at various temperatures

Table 1 Mn^{4+} content and the Curie temperature(s) of the samples annealed at various temperatures (T_c corresponds to the tempreature at which the $d\chi_{ac}/dT$ shows a maximum value)

sample	annealing temperature/°C; duration/h[a]	Mn^{4+} content (%)	T_c/K
$La_{0.7}Ca_{0.3}MnO_3$ (ceramic)	1000; 72	34	262, 185
	1100; 12	32	263, 193
	1200; 12	32	263, 208
	1300; 12	30	249
	1300; 24	30	245
	1300; 48	30	245
$La_{0.7}Ca_{0.3}MnO_3$ (combustion)	600; 12	62	264
	800; 12	42	270
	1000; 12	34	266
	1200; 12	32	265, 246, 195
	1300; 48	30	246
$La_{0.9}Ca_{0.1}MnO_3$ (ceramic)	1000; 72	14	265, 216
	1100; 12	14	263, 164
	1200; 12	12	150
	1300; 12	10	155
	1300; 48	10	155

[a] The ceramic samples initially annealed at 1000 °C; 72 h are subsequently annealed at higher temperatures.

transition for the sample annealed at 1300 °C for 12 hours. This magnetic transition becomes sharp for the sample annealed at 1300 °C for longer duration ($T_c \approx 245$ K).

Fig. 4 shows the FC and ZFC curves of the ceramic sample annealed at two different temperatures. The FC and ZFC curves deviate at a temperature slightly below $T_c \approx 245$ K for the high temperature annealed sample, whereas for the low temperature annealed sample this deviation starts at *ca.* 265 K, close to the first magnetic transition observed in the ac susceptibility curve (Table 1). Both the FC and ZFC curves show a second magnetic transition at *ca.* 185 K. For the combustion samples also similar FC and ZFC curves were obtained.

In $La_{1-x}Ca_xMnO_3$, maximum T_c (*ca.* 270 K) is observed for $x=0.33$, and T_c decreases as x is decreased or increased from this value.[16] The temperature at which the dc magnetization and the ac susceptibility of the low-temperature-annealed samples show an initial increase is close to the T_c of $La_{0.67}Ca_{0.33}MnO_3$, indicating the presence of small amounts of the $x=0.33$ phase in the samples. The onset of a first magnetic transition below *ca.* 270 K with a second broad magnetic transition at a lower temperature, and the absence of a well defined magnetic ordering temperature for the samples annealed below 1300 °C, indicate that the samples prepared by the ceramic method and the combustion method, annealed at low temperatures, may contain different compositions (different x values) in the series $La_{1-x}Ca_xMnO_3$. It is possible that on initial heating of the mixture of oxides (ceramic method) and in the decomposed urea–nitrate mixture (combustion method), phases with different compositions in the entire range $0 \leqslant x \leqslant 1$ are formed. On further heating of this mixture at higher temperatures, the compositional range is narrowed, and finally after heating at a higher temperature for sufficient duration, the required composition is obtained. That is, the samples annealed at low temperatures are compositionally inhomogeneous. The increasing FC magnetization (Fig. 4) at low temperatures for the low-temperature-annealed sample indicates the presence of a paramagnetic phase along with the ferromagnetic phase(s) in the sample.

The Curie temperatures of the manganites containing excess oxygen are reported to be higher than those of the stoichiometric samples, and this effect is more pronounced for $LaMnO_3$ and low Ca doped samples.[2,17] The higher T_c of the oxygen-excess compositions is due to the presence of an excess of Mn^{4+} in the compounds and a maximum T_c of *ca.* 270 K is observed for 33% Mn^{4+} containing compositions. This Mn^{4+} content is equivalent to that present in $La_{0.67}Ca_{0.33}MnO_3$, which shows a magnetic transition at *ca.* 270 K.[16]

In the present results, however, the origin of the first magnetic transition at *ca.* 270 K is due to compositional inhomogeneity only and not due to the excess of Mn^{4+} in $La_{0.7}Ca_{0.3}MnO_3$. This can be justified with the following reasons. (1) The Curie temperature for the first magnetic transition at *ca.* 263 K remains unchanged for the ceramic samples annealed up to 1200 °C, though the Mn^{4+} content is decreased slightly (see Table 1). (2) If the magnetic transition at *ca.* 263 K is due to excess Mn^{4+}, there is no reason for a second magnetic transition at a lower temperature (Fig. 3). The Curie temperature for this second transition increases with increasing annealing temperature and this transition must be due to the presence of another phase with a different composition. (3) There is not much variation in the T_c of the combustion sample with annealing temperature up to 1200 °C, though the estimated Mn^{4+} content is continuously decreased. With decreasing Mn^{4+} content, the transition temperature is expected to be decreased. (4) The combustion sample, when annealed below 1200 °C and containing excess Mn^{4+}, showed a single (broad) magnetic transition above 260 K; the same sample when annealed at 1200 °C showed three magnetic transitions as evidenced from three maxima in the $d\chi_{ac}/dT$ curve, though this sample contained less Mn^{4+} compared to the low-temperature-annealed samples.

The above facts indicate that the observed anomalous magnetic behavior of those samples processed below 1300 °C is due to the presence of phases with varying compositions in the $La_{1-x}Ca_xMnO_3$ system. Validity for the above arguments comes from the results of Baythoun and Sales who had earlier shown by careful EDAX analysis that the samples prepared by a low temperature sol–gel process and annealed at a temperature as high as 1400 °C were not compositionally homogeneous.[18] The ideal composition $La_{0.5}Sr_{0.5}MnO_3$ synthesized by them at low temperatures and annealed at 1200 °C had only 50% of the total sample within a compositional band of x between 0.4 and 0.6, with the rest of the sample having other compositions in the range $0 \leqslant x \leqslant 1$ in $La_{1-x}Sr_xMnO_3$. Similarly, after annealing at 1400 °C, 64% of the sample had the ideal composition but the rest of the phases were between $x=0.3$ and $x=0.6$. A similar distribution of the various compositions in $La_{1-x}Ca_xMnO_3$ is responsible for the observed magnetic behavior in our experiments. The magnetic transition (at 245 K) of the combustion sample annealed at 1300 °C is sharper (Fig. 2) than that of the sample prepared by the ceramic method and annealed under similar conditions (Fig. 3). This implies that the ceramic sample annealed at 1300 °C for 48 h is still inhomogeneous but with the additional phases having compositions above and below, but very close to, $x=0.3$. The combustion sample, on the other hand, has two, almost fixed, compositions, one with $x=0.3$ and another with $x \approx 0.25$.

In order to show that the $x=0.33$ phase is formed initially, for low Ca doped samples also, the ACS curves of the composition $La_{0.9}Ca_{0.1}MnO_3$ prepared by the ceramic method are shown in Fig. 5. For the sample annealed at 1000 °C for 72 h, a small increase in the susceptibility is observed at *ca.*

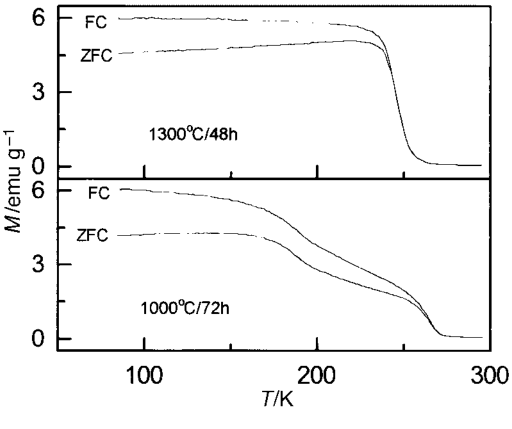

Fig. 4 Temperature dependence of FC and ZFC magnetization (H_A= 100 Oe) of $La_{0.7}Ca_{0.3}MnO_3$ prepared by the ceramic method and annealed at two different temperatures

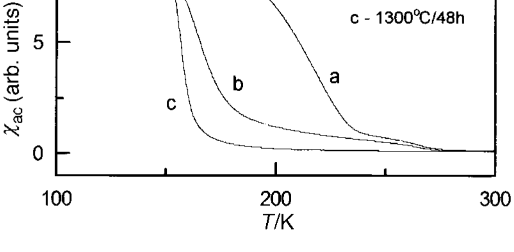

Fig. 5 Temperature dependence of the ac susceptibility of $La_{0.9}Ca_{0.1}MnO_3$ synthesized by the ceramic method and annealed at various temperatures

270 K with a broad transition at $T_c \approx 216$ K. As the annealing temperature is increased, the contribution at *ca.* 270 K is decreased and the broad magnetic transition is shifted to lower temperatures and a well defined magnetic transition at 155 K is observed for the sample annealed at 1300 °C for 36 hours. T_c values and the Mn^{4+} content of this composition annealed at different temperatures are compared, in Table 1, with that of the $La_{0.7}Ca_{0.3}MnO_3$ ceramic sample synthesized and annealed under identical conditions.

The broad nature of the magnetic transition as well as the apparent low-T_c of the combustion samples[12] annealed at low temperatures [Fig. 1(a)] can be explained on the basis of compositional inhomogeneity. As both the ceramic and combustion samples processed below 1300 °C show an initial rise in the susceptibility at *ca.* 270 K, it can be attributed to the presence of the phase $La_{0.67}Ca_{0.33}MnO_3$ in the samples. The sample will have different compositions in $La_{1-x}Ca_xMnO_3$, whose T_c is a maximum for $x = 0.33$ and continuously decreased as x is increased or decreased from this value. The sum of the high field magnetization curves of all those phases with differing transition temperatures will appear as a continuously increasing curve as if the magnetic transition is very broad, with no well defined Curie temperature. The temperature at which maximum slope is obtained from the $\mathrm{d}M/\mathrm{d}T$ curve (as reported in ref. 12) then corresponds to the T_c of the major phase present in the sample. For the 800 °C annealed sample, the $\mathrm{d}M/\mathrm{d}T$ curve showed a broad maximum at *ca.* 235 K whereas the $\mathrm{d}\chi_{ac}/\mathrm{d}T$ curve gave a maximum at 270 K. The $\mathrm{d}\chi_{ac}/\mathrm{d}T$ curves of the combustion synthesized sample annealed at 1000 °C and 1300 °C shown in Fig. 2 (inset A) indicate that the T_c of the low temperature annealed sample is higher than that of the high temperature annealed sample. The derivative curve of the 1000 °C annealed sample is very broad with a shoulder at *ca.* 270 K and a broad feature below 250 K apart from the peak at 266 K, showing contribution from different phases. These derivative curves are similar to the magnetic entropy change curves obtained by Guo *et al.*[13] (magnetic entropy, S_M, is related to $\mathrm{d}M/\mathrm{d}T$) and the higher entropy change for the high temperature annealed sample is then a reflection of the increased homogeneity of that sample, rather than the change in the particle size as reported. Though a sharp increase in the magnetization at *ca.* 270 K for $x = 0.33$ is reported,[13] the magnetization increases continuously as the temperature is lowered to 78 K, and the total magnetization at this temperature is much less than that obtained for the $x = 0.3$ sample in the present study. The continuous increase in the magnetization below T_c as the temperature is decreased is due to the presence of ferromagnetic phase(s) which orders at a higher temperature, and paramagnetic contributions from those phases order at a relatively lower temperature (or from phases with very low Ca concentrations which are not ferromagnetic).

The present results give evidence for the fact that compositional inhomogeneity is responsible for the dependence of T_c on the processing conditions. The different values of T_c for the same composition, and almost identical values of T_c for different compositions, in $La_{1-x}Ca_xMnO_3$, reported in the literature,[6–11] thus arise due to non-homogeneity of the sample and also point to the fact that whatever the desired composition may be, the compound obtained upon processing below 1300 °C will be a mixture of different phases. The effect of compositional inhomogeneity may not be evident in the high field magnetization curves of the low temperature processed $La_{0.67}Ca_{0.33}MnO_3$ (and those samples with substitution in the lanthanum site of this composition) because maximum T_c in the system $La_{1-x}Ca_xMnO_3$ is observed for $x = 0.33$. However, if the T_c observed for this composition is less than that expected, then the observed T_c will be an indication of the major phase present in the sample. This may be the reason for the large differences in T_c of the composition $La_{0.67}Ca_{0.33}MnO_3$ reported by different groups[7,9,10,13] and identical T_c values for those samples processed at temperatures $\geqslant 1300$ °C.[6,7]

The above arguments appear to be equally applicable to all the perovskite type compounds in the system $La_{1-x}A_xMO_3$ (A = Ca, Sr, Ba, *etc.*; M = Mn, Co). For example, the compound $La_{0.875}Sr_{0.125}MnO_3$ prepared at 1000 °C is reported[19] to show true paramagnetic behavior only above 360 K, the T_c of the composition with $x = 0.33$ observed in the $La_{1-x}Sr_xMnO_3$ system.[20] Our studies on the $La_{1-x}Sr_xCoO_3$ system also showed similar compositional inhomogeneity effects for samples processed at low temperatures.

As the low-temperature-annealed samples show the presence of phases with varying compositions between $LaMnO_3$ and $CaMnO_3$ which will have slightly varying lattice parameters, each peak in the powder X-ray diffraction pattern will be the sum of the individual peaks corresponding to the individual phases. Therefore the overall XRD peak will be broader than that expected due to particle size broadening alone, for the low temperature synthesized compounds. One of the peaks in the powder XRD patterns of ceramic and combustion samples of $La_{0.7}Ca_{0.3}MnO_3$ annealed at different temperatures are shown in Fig. 6. The ceramic sample annealed at 1000 °C for 36 h shows a broad and asymmetric peak whereas after annealing at the same temperature for 72 h the shoulder at the higher angle side has disappeared. Similarly for the combustion sample annealed at 600 °C, a broad and asymmetric peak is observed, and the width and asymmetry of this peak are decreased after annealing at higher temperatures. Interestingly, the grain size observed (from an SEM photograph) for the ceramic sample annealed at 1000 °C for 36 h is > 1 μm which is almost double that of the average grain size of the combustion sample (*ca.* 500 nm) annealed at 1000 °C for 12 h, though the width of the XRD peak is much higher for the ceramic sample. The asymmetry in the reflection of the low temperature annealed samples indicates the presence of additional phases. Evaluation of the size of the particles from such broad and asymmetric XRD peaks will be in error as it may not provide the actual size of the particles. The general conclusion that 'absence of any extra reflections in the powder XRD pattern is an indication of single phase nature of the compound' is also not valid based on these arguments.

From the present results it is concluded that for the calcium substituted lanthanum manganites, the anomalies reported in the magnetic behavior of low-temperature processed samples

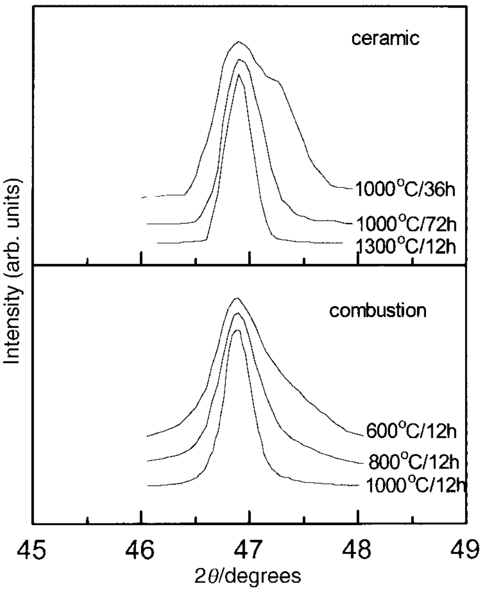

Fig. 6 Powder XRD pattern from the (200) plane of $La_{0.7}Ca_{0.3}MnO_3$, prepared by the ceramic and combustion methods, and annealed at different temperatures

are due to compositional inhomogeneity which leads to magnetic as well as structural inhomogeneity.

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References

1 A. P. Ramirez, *J. Phys.: Condens. Matter*, 1997, **9**, 8171.
2 G. H. Jonker and J. H. Van Santen, *Physica*, 1950, **16**, 337.
3 E. O. Wollan and W. C. Koehler, *Phys. Rev.*, 1955, **100**, 545.
4 C. Zener, *Phys. Rev.*, 1951, **82**, 403.
5 J. M. De Teresa, M. R. Ibarra, P. A. Algarabel, C. Ritter, C. Marquina, J. Blasco, J. Garcia, A. del Moral and Z. Arnold, *Nature*, 1997, **386**, 256.
6 S. J. L. Billinge, R. G. DiFrancesco, G. H. Kwei, J. J. Neumeier and J. D. Thompson, *Phys. Rev. Lett.*, 1996, **77**, 715.
7 R. H. Heffner, L. P. Lee, M. F. Hundley, J. J. Neumeier, G. M. Luke, K. Kojima, B. Nachumi, Y. J. Uemura, D. E. MacLaughlin and S.-W. Cheong, *Phys. Rev. Lett.*, 1996, **77**, 1869.
8 J. W. Lynn, R. W. Erwin, J. A. Borchers, Q. Huang, A. Santoro, J-L. Peng and Z. Y. Li, *Phys. Rev. Lett.*, 1996, **76**, 4046.
9 G. H. Rao, J. R. Sun, J. K. Liang and W. Y. Zhou, *Phys. Rev. B*, 1997, **55**, 3742.
10 J. M. D. Coey, M. Viret, L. Ranno and K. Ounadjela, *Phys. Rev. Lett.*, 1995, **75**, 3910.
11 R. Mahendiran, S. K. Tiwary, A. K. Raychaudhuri, T. V. Ramakrishnan, R. Mahesh, N. Rangavittal and C. N. R. Rao, *Phys. Rev. B*, 1996, **53**, 3348.
12 R. D. Sanchez, J. Rivas, C. V. Vazquez, A. L. Quintela, M. T. Causa, M. Tovar and S. Oseroff, *Appl. Phys. Lett.*, 1996, **68**, 134.
13 Z. B. Guo, Y. W. Du, J. S. Zhu, W. P. Ding and D. Feng, *Phys. Rev. Lett.*, 1997, **78**, 1142; Z. B. Guo, J. R. Zhang, H. Huang, W. P. Ding and Y. W. Du, *Appl. Phys. Lett.*, 1997, **70**, 904.
14 N. D. Mathur, G. Burnell, S. P. Isaac, T. J. Jackson, B.-S. Teo, J. L. MacManus-Driscoll, L. F. Cohen, J. E. Evetts and M. G. Blamire, *Nature*, 1997, **387**, 266.
15 P. A. Joy, S. K. Date and P. S. Anil Kumar, *Phys. Rev. B*, 1997, **56**, 2324.
16 P. Schiffer, A. P. Ramirez, W. Bao and S.-W. Cheong, *Phys. Rev. Lett.*, 1995, **75**, 3336.
17 A. Tiwari and K. P. Rajeev, *J. Mater. Sci. Lett.*, 1997, **16**, 521.
18 M. S. G. Baythoun and F. R. Sale, *J. Mater. Sci.*, 1982, **17**, 2757.
19 D. N. Argyriou, J. M. Mitchell, C. D. Potter, D. G. Hinks, J. D. Jorgensen and S. D. Bader, *Phys. Rev. Lett.*, 1996, **76**, 3826.
20 H. Y. Hwang, S.-W. Cheong, N. P. Ong and B. Batlogg, *Phys. Rev. Lett.*, 1996, **77**, 2041.

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