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Grain size modification in the magnetocaloric and non-magnetocaloric transitions in La$_{0.5}$Ca$_{0.5}$MnO$_3$ probed by direct and indirect methods

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The influence of grain size in the magnetic properties of phase separated manganites is an important issue evidenced more than a decade ago. The formation of long range ordered phases is suppressed as the grain size decreases giving place to a metastable state instead of the ground state. In this work, we present a study of the magnetocaloric effect in the prototypical manganite La$_{0.5}$Ca$_{0.5}$MnO$_3$ as a function of the grain size. The differences obtained using direct and indirect methods are discussed in the framework of domain walls in the ferromagnetic phase of the system. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4898129]

The discovery in 1997 of giant magnetocaloric effect (MCE) near room temperature in Gd based compounds[1] triggered a constant growth in the number of scientific publications dedicated to the study of the mentioned effect. The main motivation is the high cost of production of Gd which difficult the production of magnetic refrigeration systems in commercial scale. A large number of compounds has been proposed to replace Gd such as As based compounds,[2] heusler alloys,[3] and manganites.[4]

The MCE in solid materials is produced by the magnetic entropy change induced when an external magnetic field is applied. In standard ferromagnetic systems, an increase in the magnetic field reduces the magnetic entropy and if the field is applied adiabatically, the lattice thermal entropy increases, giving rise in the sample temperature change.

In more complex systems, the above simplified scenario may not be enough to describe the behavior of the entropy change. A strong coupling between different degrees of freedom (magnetic, electronic, etc.) is usually responsible for such a mixed change of the state of the system by the application of a magnetic field. Depending on the characteristics of the different degrees of freedom the corresponding terms in the first law of thermodynamic may increase the heat change. But it can also be compensated, leading in a reduction, the suppression, or even the inversion of the temperature change (the so called inverse magnetocaloric effect (IMCE) (Ref. 5)). Because of this reason, a large number of scientific works has been devoted to the understanding of the MCE in cases beyond the standard ferromagnetic systems.[6]

The most commonly used methods to study MCE can be divided in two well distinguished groups, according to the physical quantity that is measured to take account the effect.

The direct methods are those where the temperature change or the heat exchanged with the environment is directly measured. Once determined any of these magnitudes, the total entropy change can be estimated in non adiabatic conditions.

In the indirect methods, MCE is obtained through thermodynamic relations between the entropy and other measured magnitude such as magnetization or resistivity.[7] The most accepted way to obtain the entropy change is using a Maxwell's relation (MR)

$$\frac{\partial S}{\partial H} = \frac{\partial M}{\partial T}.$$

Then, the entropy change can be estimated performing a numerical integration of a set of magnetization loops at different temperatures as

$$\Delta S(T,H) = \frac{1}{\Delta T}\int_0^H [M(T + \Delta T, H') - M(T, H')]dH'.$$

The main advantage of this approach is the use of a standard experimental technique to reach the entropy values, instead of a specific setup designed to measure the sample temperature change.[8]

During early years a lot of work was devoted to demostrate that, under certain circumstances, the results obtained by MR were in good agree with those extracted from direct methods.[8] But the use of the MR in cases where the system is out of equilibrium can lead to an overestimation of MCE.[6,9] In the last few years, due to the increase of the complexity of the studied compounds, the validity of the MR approach has been revised by a growing part of the scientific community.[6,10–12]

The continuous search for materials with large MCE stimulated further research in complex magnetic oxides,[4,13] including mixed valence manganese based compounds, commonly named as *manganites*. One of the most interesting properties of manganites is the spatial coexistence of regions with different magnetic ordering, the so called phase separation phenomena.[14] In systems with phase separation (PS), it is possible to tune the magnetic and structural properties by a variety of parameters such as electric and magnetic field, strain, doping, confinement, and grain size.[15–17]

In most of the cases of phase separation coexists an insulating antiferromagnetic (AFM) charge ordered phase

(CO) and a metallic ferromagnetic one (FM).[18] One of the most studied systems with phase separation is $La_{0.5}Ca_{0.5}MnO_3$.[19,20] In this system, the coexistence between the different magnetic phases can be controlled by external stimuli (radiation, electric field) or by the modification of synthesis parameters, particularly modifying the grains size (GS) in ceramic samples.[17] The increase in the GS favor the long range ordering of the CO state over the FM. The low temperature CO ground state of the system is strongly suppressed for small GS, and when it is increased the system can reach the CO state. The influence of GS in the MCE was recently studied in phase separated systems revealing a complex scenario, where the validity of the methods used to estimate the magnitude of the effect must be carefully revised.[21,22]

In this work, we present a study of MCE in the manganite $La_{0.5}Ca_{0.5}MnO_3$ which presents phase separation. The study will be performed as a function of GS. We will compare the results obtained from differential thermal analysis (DTA) and from indirect measurements with particular focus on the use of the MR relation. The hysteresis of the magnetization loops will be also analyzed and described in the framework of domain walls displacement and related with the differences observed between direct and indirect methods.

It has to be noted that the understanding of the phase separation in the $La_{0.5}Ca_{0.5}MnO_3$ system escapes to the aim of this work. We will assume the phase separated scenario accepted and widely discussed in previous works,[17,23] and we will not deal neither with the origin of the phase separation nor with the possibilities of any alternative description.

Polycrystalline samples of $La_{0.5}Ca_{0.5}MnO_3$ were synthesized following a citrate/nitrate decomposition method using 99.9% purity reactants. To increase grain size, sub sequential thermal treatments have been performed to the samples as is decrypted in Levy *et al.*[16] The grain size of the samples was estimated from SEM microphotographs.

Magnetization measurements were made in a Quantum Design VersaLab with the VSM and the heat capacity accessories. For the DTA measurements, we used a home made system formed by two Cernox CX-1080-SD thermometers (manufactured by Lake Shore Cryotronics) on a Teflon piece to ensure thermal insulation between the sample and the reference thermometers. The reference used was a piece of alumina.

The whole system was mounted in a VersaLab's transport puck, allowing us to perform magnetization, Cp and DTA measurements in the same range of magnetic field and temperature.

As it was previously reported, the change of the GS of the samples induces important changes in the magnetic behavior. We can see those changes in Figure 1, where we show magnetization measurements of the entire set of samples with an applied field of 1 T on cooling. The grain size of the samples goes from 180 nm in sample A to 1300 nm in sample E (see table in Figure 1 for details).

All the samples present an FM ordering at around the same temperature Tc = 250 K but, while the sample with smallest GS (A) remains FM in all the temperature range below Tc, a clear FM to anti ferromagnetic transition is observed in the rest of the samples at T = 150 K.
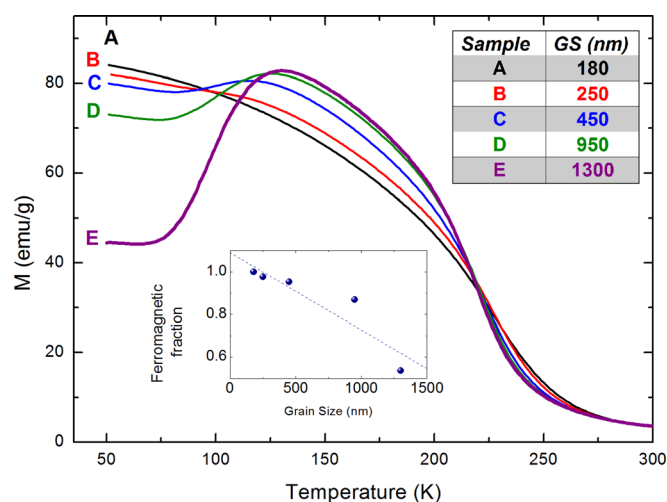

FIG. 1. Magnetization as a function of temperature with an applied magnetic field of 1 T for samples with different grain size. Inset: ferromagnetic fraction at 50 K as a function of grain size. Table: grain size for each sample.

Sample	GS (nm)
A	180
B	250
C	450
D	950
E	1300

Measurements are performed with H = 1, which is enough to saturate the FM phase but not strong enough to induce a ferromagnetic fraction enlargement.[24]

Because of that the FM fraction at low temperature can be estimated as the ratio between the magnetization at 50 K of the sample and the same value on the sample A (fully FM).

In the inset of Figure 1, we show the FM fraction at low temperature as a function of the GS, being close to 20% in the sample with the largest GS. This change in the magnetic behavior can be interpreted as an evidence of the frustration of the CO state (associated with the AFM ordering) due to small GS. The localization of the charges implies the presence of a long range Jahn-Teller distortion that is suppressed by the disruptive change in the lattice due to the grain boundary.[17] Similar behavior has been reported in other compounds,[23,25,26] indicating that the GS is an extra ingredient to take into account when the magnetic properties are studied.

To analyze how GS affects the MCE, we used two independent methods to estimate the magnitude of ΔS and ΔT.

In the first method, we used isothermal magnetization curves and the above mentioned Maxwell's relation to obtain the adiabatic entropy change due to the application of the magnetic field. In Figure 2, we present the temperature dependence of the entropy change for the different samples with an applied magnetic field of 3 T.

In all the samples, we observe a negative peak close to Tc that can be associated to the paramagnetic (PM) to FM transition. The maximum entropy change remains almost constant at 2–3 J/kg-K for the entire series of samples.

An additional (positive) peak is observed at a lower temperature, around 150 K. The maximum entropy change in this peak increases as the grain size became larger. According with the magnetization data, this peak can be associated with the FM to CO transition.

The obtained value of ΔS for the sample E (largest GS) for H = 3 T is 10 J/kg-K, similar to the obtained for pure Gd around room temperature[27] and in other half doped manganites such as $Pr_{0.5}Sr_{0.5}MnO_3$ (Ref. [28]) and $Nd_{0.5}Sr_{0.5}MnO_3$ (Ref. [29]) measured using the same method.
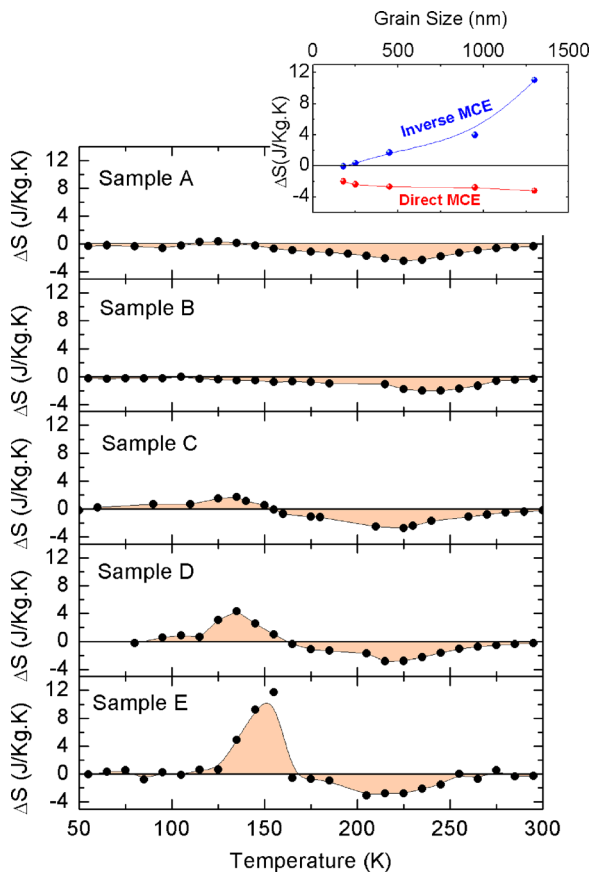
FIG. 2. Entropy change as a function of temperature for all the samples with a magnetic field of 3 T. Inset: Intensity of both peaks in the entropy change as a function of GS.

FIG. 3. Adiabatic temperature change (ΔT_{AD}) for samples A, C, and E as a function of temperature when the magnetic filed is increased from 0 to 3 T. The values of ΔT_{AD} where extracted from DTA measurements taking into account the heat exchange between the sample and the sample holder.

According with the presented data, we can conclude that the MCE has been enhanced increasing the grain size, since an additional peak in the entropy change is observed and its magnitude is controlled by the GS.

To complete the picture we performed differential thermal analysis measurements, allowing us to determine the sample temperature change during the application of the magnetic field. In all the cases, the sample was zero field cooled to the target temperature and then the field was applied with a constant rate of 200 Oe/s and the heat exchanged with the environment has been taken into account.[30]

In Figure 3, we present the adiabatic temperature change (ΔT_{AD}) extracted from DTA measurements for samples A, C, and E. A positive peak can be observed around 225 K. This is consistent with the expected behavior from the entropy change associated with the PM to FM transition. Surprisingly, we do not observe any peak related with the FM to CO transition. It has to be noted that according to the entropy change values obtained from magnetization, the expected temperature change should be three times larger than the observed from the PM/FM transition.

Another important aspect to consider is the presence of hysteresis in the magnetization as a function of magnetic field curves. To examine these feature in depth, we calculated the magnetic work (W) defined as the area enclosed between the curves obtained increasing and decreasing the magnetic field (between 0 and 3 T). In Figure 4, we present W as a function of temperature for all the measured samples.
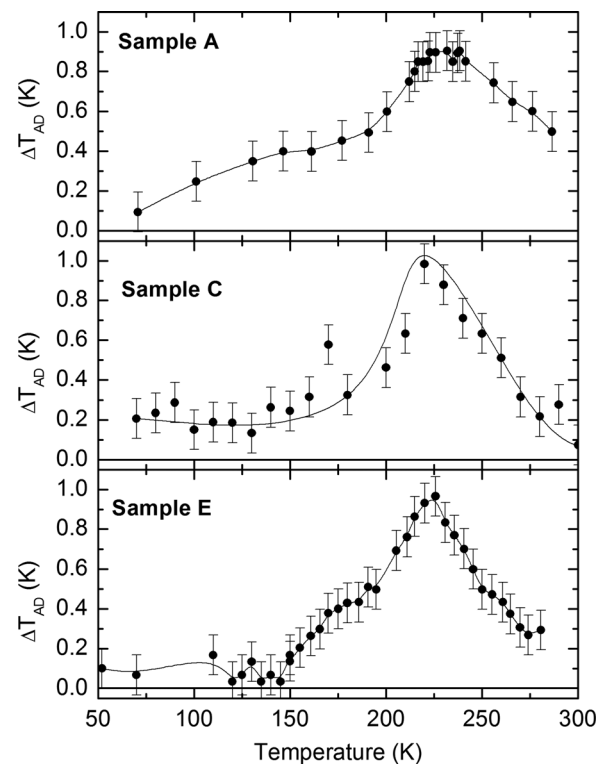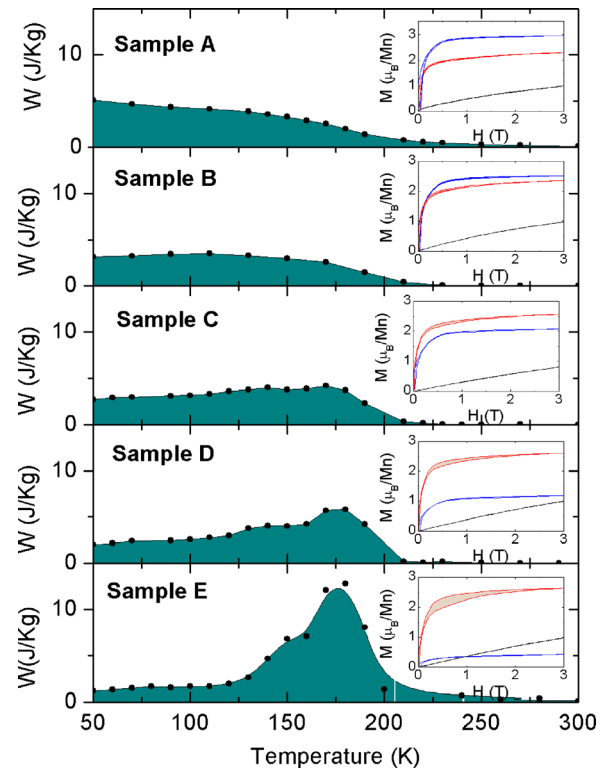

FIG. 4. Magnetic work defined as the area enclosed by the increasing and decreasing magnetic field curves as a function of temperature for different samples. In the insets we show magnetization loops at 250 K (black), 170 K (red), and 60 K (blue).

In all the samples, W is almost zero above the Curie temperature, indicating the absence of hysteresis in the paramagnetic phase. But when the FM phase is present we observe a strong relation between the temperature dependence of W and grain size.

For smaller grain size (samples A, B, and C), the magnetic work presents an increase on cooling giving rise to a constant value below 175 K. Samples D and E present a maximum at 175 K, decreasing its value and keeping constant below 75 K. It is interesting to note that in the temperature range in which W peak occurs coincides with the range where the CO phase appears.

The temperature behavior of W can be explained considering the Jiles-Atherton model[31] to describe the magnetization curves. In this model, the hysteresis is produced by impedances to domain wall motion caused by pinning sites encountered by the domain walls as the move. Because of that the system at a given field H cannot reach the global minimum energy state, giving place to a hysteretic magnetization loop.

The pinning sites could be grain boundary or any kind of inhomogeneities within a grain, for example, tangles of dislocation and precipitates or nonmagnetic inclusions.

The model consider that the domain walls are flexible so that they not only can move but also can bend. When the domain walls bend while being held by a pinning site, it results initially in a *reversible* change in the magnetization.

In our case, the formation of the CO phase increase the amount of pinning centers in the sample, enhancing the reversible change in the magnetization.

On cooling, at 200 K, the CO phase start a nucleation process, increasing the density of pinning sites in the material which is reflected in the increase of W. Once the CO phase is nucleated, the nuclei start to grow in size, decreasing the amount of FM phase present. As a consequence, W is reduced as the magnetic signal decreases.

The origin of the peak in the ΔS is the presence of a reversible component to the magnetization in this temperature region.

The energy associated with the magnetization difference is not exchanged with the environment because is used internally to bend the wall domain and recovered when the magnetic field is turned off. Because of that we did not observe a temperature change in the sample in this temperature region. The reversible nature of the bending of domain walls makes the entropy change calculated by Maxwell's relation convertible in magnetic work and not in heat exchanged with the environment.

In summary, we presented a study about the influence of grain size in the magnetic and magnetocaloric properties of $La_{0.5}Ca_{0.5}MnO_3$. The system is characterized by two well distinguished magnetic transitions, a PM to FM one at 225 K and a FM to a phase separated CO + FM at 150 K. The MCE associated with the first transition do not present a significant dependence with grain size, and results extracted from magnetization measurements are in good agreement with those obtained from DTA measurements.

The second transition, related with the formation of the CO phase, presents a strong dependence with grain size. The entropy change obtained from magnetization measurements

is not consistent with the temperature change extracted from DTA measurements.

The hysteretic behavior in the magnetization loops which was explained using a Jiles and Atherton model of domain walls in the FM phase. In this framework, the formation of the CO phase modifies the density of pinning sites increasing the hysteresis in the magnetization loops. This additional pinning site increases the magnetic entropy calculated by Maxwell relation, but this entropy cannot be used for applications since it is not converted in heat and is related with the reversible bending of the domain walls.

It is just an example of how the inadequate use of the Maxwell's relation can lead to a fake conclusion. Even when the entropy change observed was larger than the observed in Gd based compound it is not possible to use this change in applications. The presence of hysteresis in the magnetization vs magnetic field curves is indicative of the presence of an additional term in the first law of thermodynamics that must be considered before any conclusion. In the studied case, this feature was observed in the FM to PS transition; meanwhile, it is not present in the FM transition, where the entropy change is converted in a temperature change as expected.

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