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Magnetization Study of the Magnetocaloric Properties in $La_{0.7}Ca_{0.23}Sr_{0.07}MnO_3$ Manganite by *In Situ* Electron Holography

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The negative environmental impact of conventional cooling appliances is extensive as this equipment employs refrigerants such as hydrofluorocarbons (HFC), which are potent greenhouse gases with thousands of times the global warming potential of carbon dioxide [1]. Therefore, as global warming is a growing concern, alternative techniques to conventional gas compression (CGC) must be realized to avoid a climate catastrophe. Recently, magnetic refrigeration technology has emerged as an innovative and potential low carbon technology due to its superior cooling efficiency, solid-state compact design, and promising substitution of CGC techniques to eliminate HFC gases in the atmosphere [2]. In essence, magnetic refrigeration relies on the entropy change of magnetic materials when exposed to an external magnetic field. Such entropy change forms the basis for the magnetocaloric effect (MCE) as the temperature of the material rises or decreases as the magnetic field is applied or removed, respectively. When estimating the MCE, the isothermal entropy change and the adiabatic temperature gradient must be considered as the maximum value of magnetic entropy change occurs at the Curie temperature (T_C) in relation to a ferromagnetic to paramagnetic phase transition. Therefore, a T_C near room temperature is vital for applications in magnetic refrigeration [3]. Among magnetocaloric materials, manganites possess higher chemical stability, tunable T_C, and are cost-effective making them promising candidates for future magnetic refrigeration technology [4]. In this work, we present the analysis of the magnetocaloric properties of a $La_{0.7}Ca_{0.23}Sr_{0.07}MnO_3$ manganite ceramic pellet studied by vibrating sample magnetometry (VSM) and *in situ* off-axis electron holography (EH).

The fabrication method for $La_{0.7}Ca_{0.23}Sr_{0.07}MnO_3$ follows the procedure described by Botello-Zubiate et al. [5] where the nominal compositions were prepared from high-purity oxide and carbonate powders: La_2O_3 (99.99%), Mn_2O_3 (99.99%), $SrCO_3$ (99.99%), and $CaCO_3$ (99.99%). Magnetic measurements were performed using the VSM option of a VersaLab Quantum Design physical properties measurement system. The magnetization (M) vs. temperature (T) was measured with a constant magnetic field of 500 Oe in the range of 50-290 K with a heating rate of 10K/min. The isothermal magnetization (M) vs. applied magnetic field curves were measured in the temperature range of 100-390 K with magnetic fields up to 20 kOe. Structural analysis was employed using high-resolution transmission electron microscopy (HRTEM) and EH was performed using a specialized cryoholder in a JEOL ARM 200F TEM operated at 200 kV.

Figure 1a displays the M vs. T curve where a sharp phase transition can be observed around T_C = 294 K, which is calculated from the minimum of the dM/dT vs. T curve (inset of Fig. 1a). As temperatures lie below the T_C, the magnetization increases sharply for fields below 2 kOe and saturates for fields above 5.3 kOe, which is typical for a ferromagnetic material as shown in Figure 1b. Also, by observing the area between the curves we can estimate that the greatest magnetic entropy change occurs between 290 and 300 K. Additionally, by measuring the magnetization in small intervals of field and temperature

changes, the standard Maxwell relation can be approximated [6] to calculate the magnetic entropy change ($-\Delta S_M(T, H)$) using the isothermal magnetization curves as shown in Figure 1c. The maximum $-\Delta S_M$ value increases with respect to the applied magnetic field resulting in values of 0.90, 1.51, 1.90, and 2.18 J/kg·K at 0.5, 1, 1.5, and 2 T, respectively. Notably, these values are comparable to magnetocaloric parameters of (La-Ca-Sr)MnO_3 materials [4], with a T_C closer to ambient temperature. For TEM analysis, a fine powder was prepared from the pellet using a mortar and pestle. The powder was placed in a vial with ethanol, sonicated, and subsequently drop casted in a TEM holey carbon grid. A high crystalline sample can be observed in Figure 2a, as confirmed by the inset representing the FFT of that region. Furthermore, EH was employed to map the magnetic configuration of a $La_{0.7}Ca_{0.23}Sr_{0.07}MnO_3$ grain (Figure 2b) and observe the local ferromagnetic to paramagnetic phase transition. Holograms were acquired in magnetic field-free conditions at temperatures of 200, 298, and 360 K after the application/removal of an external magnetic field produced by the objective lens. To remove the electrostatic contribution, we used HoloWorks 5.0.7 [7] in Digital Micrograph. The phase reconstruction consisted of subtracting the complex phases captured at 200 and 298 K from the complex phase captured at 360 K. The resulting magnetic phase contour maps demonstrate the remanent state of the grain where a paramagnetic behavior is evident as seen in Figure 2c, as no surrounding stray magnetic field lines are observed. On the contrary, subsequent *in situ* cooling to 200 K displays a small net magnetization (Figure 2d) emanating from the outer edges where magnetic field lines curl around the sample due to a ferromagnetic phase transition below T_C. It is important to note that within the grain no particular alignment of the in-plane magnetization is sustained denoted by the random colors in the map. This behavior is consistent with the isothermal curve at 200 K where the bulk $La_{0.7}Ca_{0.23}Sr_{0.07}MnO_3$ sample exhibits a low remanent magnetization (Mr/Ms) of 0.023. Therefore, the stray magnetic field lines around the grain originate from the remanent magnetic domains represented by 2.3% of the magnetic saturation (Ms). As can be seen, EH coupled with VSM analysis provides a thorough and powerful investigation of the local magnetization and the magnetocaloric properties in $La_{0.7}Ca_{0.23}Sr_{0.07}MnO_3$.

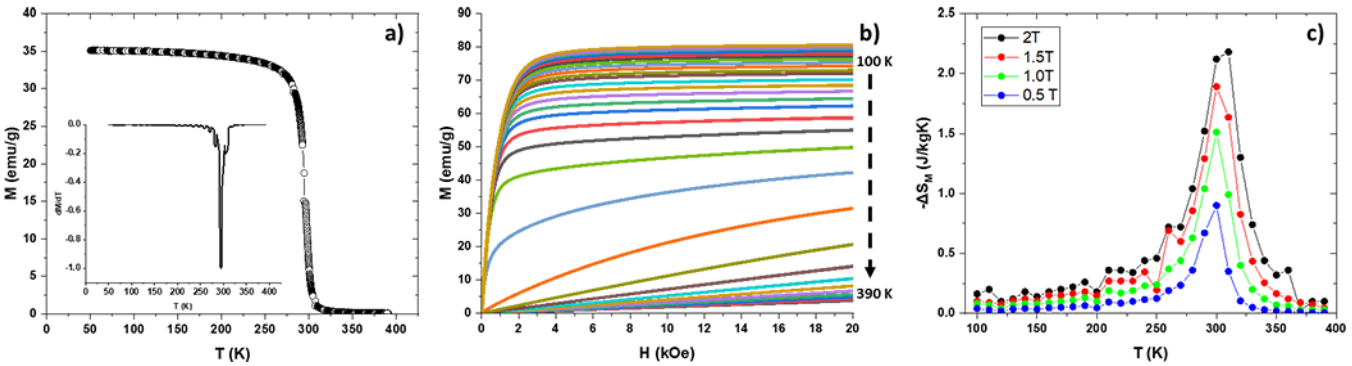

Figure 1. VSM analysis of $La_{0.7}Ca_{0.23}Sr_{0.07}MnO_3$: a) M vs. T curve measured with a field of 500 Oe. Inset shows dM/dT vs. T to calculate a T_C of 294 K. b) Isothermal magnetization curves from 100-300 K. c) $-\Delta S_M(T)$ curves with an applied magnetic field of 0.5-2 T.

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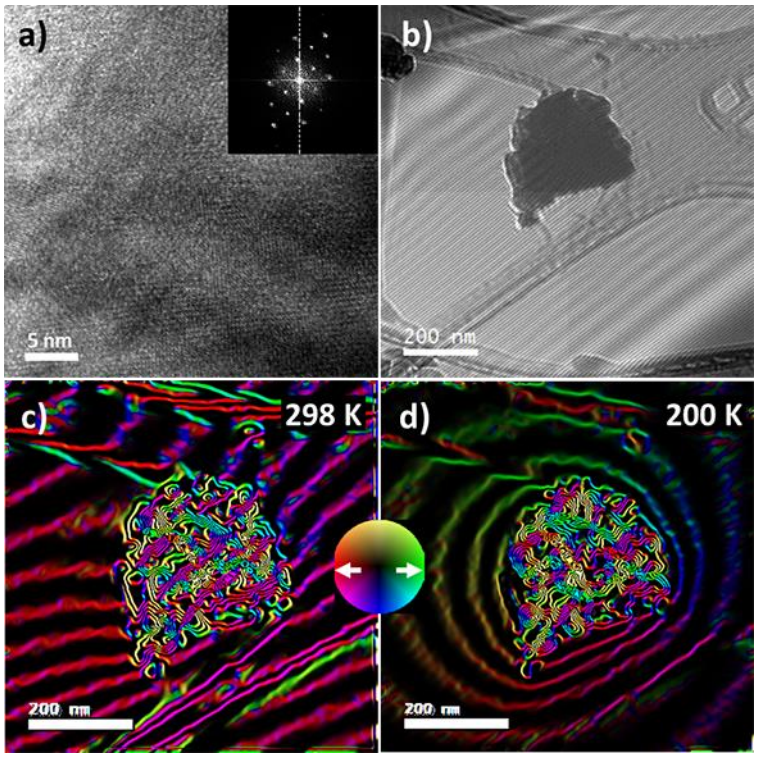

Figure 2. a) HRTEM of $La_{0.7}Ca_{0.23}Sr_{0.07}MnO_3$ showing high crystallinity. Inset represents the fast fourier transform (FFT). b) Hologram of sample. c)-d) Magnetic contour images taken at 298 and 200 K, respectively. The color wheel indicates the magnetization direction.

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