

Collapse of charge order and enhancement of magnetocaloric effect in nanostructured (La,Pr,Ca)MnO₃

M. H. Phan¹, M. B. Morales¹, S. Chandra¹, N. S. Bingham¹, C. L. Zhang², S. W. Cheong²,
T. H. Hoang³, H. D. Chinh³, and H. Srikanth¹

¹Department of Physics, University of South Florida, Tampa, FL 33620, USA

²Rutgers Center for Emergent Materials and Department of Physics & Astronomy, Rutgers University,
Piscataway, New Jersey 08854, USA

³Department of Inorganic Chemistry, University of Technology, Dai Co Viet Street, Hanoi, Viet Nam

The independent discoveries of colossal magnetoresistive (CMR) effect for magnetic sensor technology [1] and large magnetocaloric (LMC) effect for magnetic refrigeration technology [2] in manganites with the general formula of $R_{1-x}M_x\text{MnO}_3$ ($R = \text{La, Pr, Nd, Sm}$, and $M = \text{Sr, Ca, Ba, and Pb}$) have stimulated intense research into their properties. These materials exhibit rich variety in terms of coexisting and competing magnetic and electronic phases [1]. Of particular interest is the charge-ordered (CO) insulating phase that is unstable under various perturbations such as carrier doping, magnetic field, electric field and current. From a magnetic cooling perspective, the CO manganites such as $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ and $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ are of great interest as they show LMC effects around a temperature where the field-induced magnetic, electron and structural phase transitions concurrently occur (from the antiferromagnetic (AFM) charge-ordered state to ferromagnetic (FM) charge-disordered state) [2]. A recent trend of research in the field of manganites is to study the effect of the reduction in particle size on the physical properties of the materials [3-5]. It has been reported that there is a collapse of charge ordering and an appearance of ferromagnetic order in $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ and $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ when the particle size falls below few tens of nanometers [3]. The destabilization of CO into FM is attributed to the subtle change that occurs in the structure on size reduction. This is consistent with a recent theoretical prediction that the ferromagnetic correlation arises from the surface effect [4]. It is believed that at the surface of CO nanoparticles, the charge distribution is inhomogeneous thus inducing a weak FM correlation. A strong modification of the charge ordering state, magneto-transport and magnetocaloric properties have recently been reported in nanocrystalline $\text{Pr}_{0.65}(\text{Ca}_{0.6}\text{Sr}_{0.4})_{0.35}\text{MnO}_3$ [5]. However, a clear understanding of the correlation between the structure and magnetism has remained elusive primarily due to the complexity of the system.

We present here the first study of the magnetic property and magnetocaloric effect in single crystalline and nanocrystalline $\text{La}_{5/8}\text{Pr}_{3/8-x}\text{Ca}_x\text{MnO}_3$ (LPCMO) with $x = 0.275$, which is well known as a mixed-valent manganite system [6]. We reveal that there is a strong collapse of charge ordering and a large enhancement of MCE in the nanocrystalline sample. The single crystalline sample was synthesized in an optical floating-zone furnace, while the nanocrystalline sample was prepared by sol-gel method. The X-ray diffraction (XRD) confirmed the quality of the samples without any impurity. The particle size of the nanocrystalline sample was determined to be about 40 nm by transmission electron microscopy (TEM) and XRD. Magnetic and magnetocaloric measurements were conducted using a commercial Physical Property Measurement System (PPMS) from Quantum Design with a temperature range of 5 – 300K and applied fields up to 7T. To evaluate the MCE, the isothermal magnetization curves were collected at different fixed temperatures ranging from 5 K to 300K. The magnetic entropy change ΔS_M is calculated from a family of the isotherms using the Maxwell relation, $\Delta S_M = \int (\partial M / \partial T)_H dH$, where M is the magnetization, H is the magnetic field and T is the temperature.

The DC magnetization data reveal that the LPCMO single crystal (the bulk sample) undergoes multiple magnetic transitions. A peak at $T_{CO} \sim 210\text{K}$ is due to the CO transition, and a shoulder at a lower temperature, $T_N \sim 175\text{K}$, arises from AFM order. As T is further decreased, the magnetization sharply increases and an FM transition is observed at $T_C \sim 90\text{K}$. At $T < T_{CO}$, the metamagnetic transitions are seen

in the M-H isotherms, and the large variations of the magnetization are observed around T_{CO} and T_C . As a result, the large magnetic entropy changes are achieved around T_{CO} and T_C . However, the case is very different for the nanocrystalline sample. The nanocrystalline sample undergoes a paramagnetic to ferromagnetic transition at $T_C \sim 210K$, and the metamagnetic state is only observed around T_C . As compared with the single crystal, the metamagnetic transitions occur at much lower fields in the nanocrystalline sample. These results underscore the important fact that the charge-ordering state is largely suppressed and the ferromagnetic order is established in the nanocrystalline sample. From the magnetic cooling perspective, it is very interesting that as compared with the single crystal, a larger magnetic entropy change is observed over a wider temperature range thus leading to a larger magnetic refrigerant capacity in the nanocrystalline sample. This important finding opens up a new opportunity for developing novel nanostructured materials for active magnetic refrigerators.

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