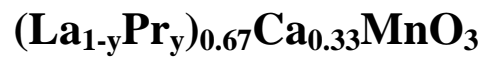


Colossal Electroresistance in



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Abstract

At low temperatures, LaPrCaMnO_3 (LPCMO), a perovskite manganite, exhibits a coexistence of ferromagnetic metallic and charge ordered insulating phase. It has been observed that applying an electric field to this material affects the resistance of LPCMO thin films. The purpose of this project was to test whether it was possible that the resistance and electric field coupling was due to a spatial shift in its phases via dielectrophoresis. During the course of this project I improved the methodology of testing the electroresistance effect by designing microstructures of the LPCMO thin film that focused the electric field.

I. Introduction

Perovskite manganites have the structure shown in Figure 1. The double-exchange mechanism that occurs in this cubic structure causes a ferromagnetic metallic phase (FMM) to occur at low temperatures. Another property of the perovskite structure is the Jahn-Teller effect^[1]; this distortion of the cubic structure causes a charge-ordered insulating phase (COI) to compete with the FMM phase. These two phases coexist below the Curie temperature and are separated by a first order transition. The coexistence of FMM, COI, and paramagnetic insulating (PMI) phases in manganites is extremely sensitive to the temperature, magnetic field, and strain on the film. These properties have been studied in $(\text{La}_{1-y}\text{Pr}_y)_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ (LPCMO).

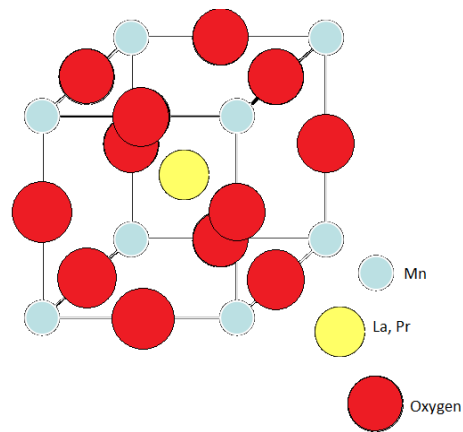


Figure 1: Perovskite structure of LPCMO.

However, a coupling between resistance and applied electric field has also been observed in LPCMO^[2], a property that is less understood. When a voltage is applied to LPCMO, the resistance suddenly drops above a certain electric field. The aim during this experiment was to study the underlying reason for the electric field effect.

One explanation for the breakdown of the resistance caused by electric field is that the FMM domains stretch parallel to the electric field due to dielectrophoresis. This is a possibility because phase-separation itself provides the nonuniform electric field within the sample that is required for dielectrophoresis^[3]. Furthermore, the fluid phase separation of LaPrCaMnO₃ below its Curie temperature makes dielectrophoresis a possibility.

A lengthening of the FMM domains would increase the FMM occurrence in the direction parallel to the electric field, causing the resistivity to drop along one axis of the sample. The only way to conclude that a drop in resistance is not simply due to a breakdown of COI regions to FMM is if the magnetic properties of the material would remain the same. Thus, if dielectrophoresis causes the electroresistance effect, then the saturation magnetization should remain the same after application of a field.

Testing this model for the electric field effect has previously been impractical. The average film size is normally 5 x 5 mm. This size requires a very high voltage to get a sufficient electric field to observe the resistance breakdown. A smaller sample on the order of microns would require a more reasonable voltage. However since a micron scale sample has a very low volume, the signal produced by its magnetization is too small to be detected by the superconducting quantum interference device (SQUID).

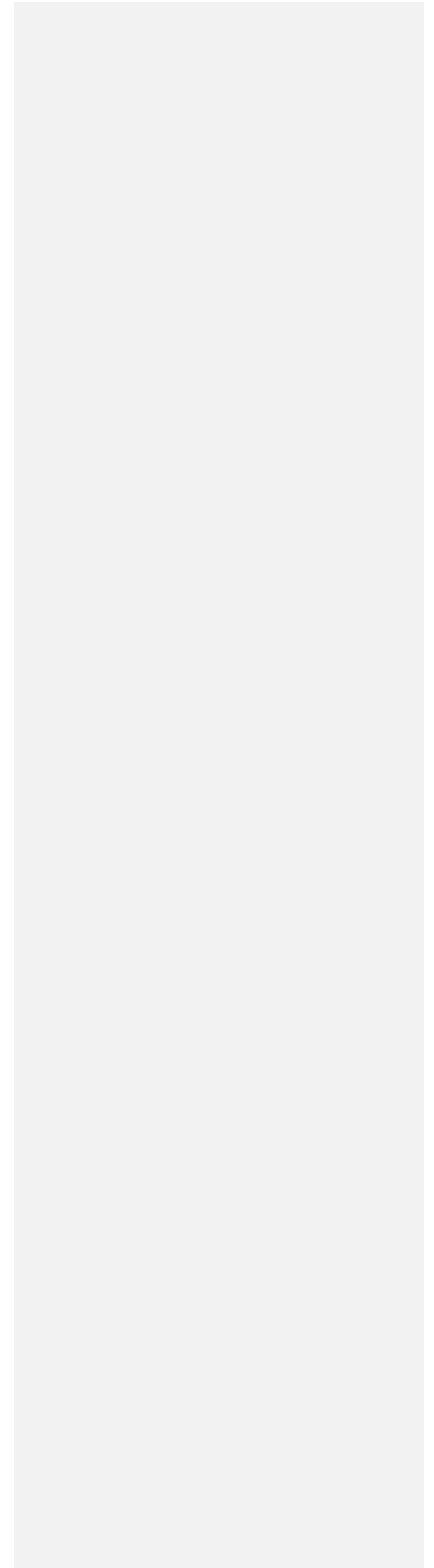
One method of solving the problem of applying a large electric field to a large sample was to use an array of micron-scale squares, as shown in Figure 3. Such a microstructure allows us to localize the electric field to a region where the sample is small enough to cause resistance breakdown. Yet, at the same time, the overall volume of film is large enough to be measured. For this experiment, I designed several microstructure patterns for film growth. After a film was

grown on rectangular substrate, I etched it via photolithography to get a film that was shaped into these patterns.

2. Sample Preparation

2.1 Film Growth

The LPCMO film was grown using pulsed laser deposition. It was deposited on a 10mm by 10 mm NdGaO₃ (NGO) substrate in an oxygen atmosphere. Deposition was for 12 minutes and the resulting film thickness was in the range of 30 nm. Although growth conditions of the film were optimized, some surface roughness could result from the surface miscut of NGO. Due to the extremely small size of the structure, this could affect the electric behavior of the film. To prevent this, I annealed the substrate before growth to promote step flow growth and a smoother film ^[4]. This was expected to result in a singly terminated surface and minimize island formation. Before growth, the substrates were first annealed in a Thermolyne furnace for 30 minutes at 950 C. The difference in the substrate surface can be seen in Figure 2.



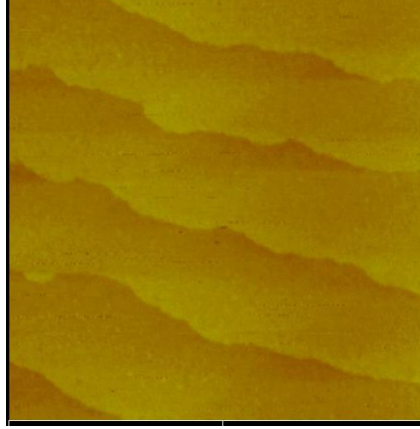
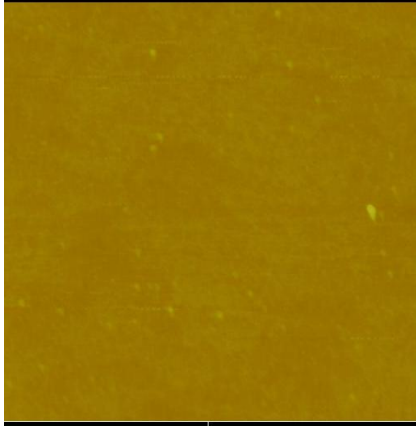


Figure 2: a) NGO before annealing.

b) NGO after annealing.

2.2 Photolithography

I designed the microstructure patterns using AutoCAD. The design was converted to a photomask consisting of chromium patterns on a glass plate, by Photo-sciences Inc. The main pattern used for this film is shown in Figure 3. Figure 3 a) shows the pattern of manganite film, where b) shows the pattern to be used for gold electrodes used for the electric field measurements.

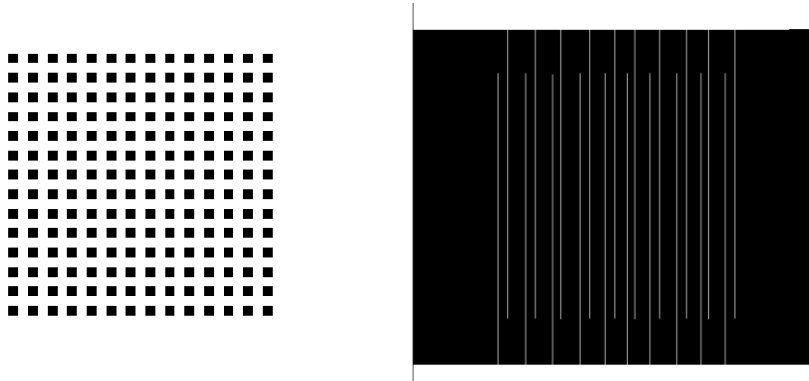


Figure 3 : a) Photomask film pattern. b) Electrode pattern.

HyoungJeen Jeen and I performed photolithography using equipment at the Nanoscale Research Facility. The photolithography process consists of spin-coating a light-sensitive photoresist onto a surface and exposing a pattern of it to UV light. The UV exposed part is chemically removed using a developer (for positive photoresist) and the underlying material can then be etched out while the area still covered with photoresist is protected from the etchant. In this case, photoresist M1813 was first spin-coated onto the 5x5 LaPrCaMnO₃ sample. Then the sample was baked at 105 C for 60 seconds. After this, it was aligned with the needed portion of the photomask using the Karl Suss Ma6 mask aligner. The sample was then exposed to UV light and developed in MIF300 developer. The resulting pattern of photoresist only covered the regions indicated by Figure 3.

The sample was etched using a solution of concentrated KI and about 3% HCl. The etching time for submerging the sample was determined to be 40 seconds.

2.3 Measurements

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The magnetization measurements were taken by SQUID magnetometer. The sample magnetization was taken along both the $(1\bar{1}0)$ and (001) axis of NGO substrate. The (10) axis was expected to give a clearer signal from LPCMO, because it is the easy magnetization axis of LPCMO on NGO. The M vs H measurement of the sample magnetization was taken at 10 K with the field varied from -2000 to 2000 Oe.

Electric field versus resistance will later be measured in a 9T magnetic field to measure the resistance with a varying external voltage. Gold contacts will be deposited to align with the array structure. This deposition will be performed by lift-off photolithography. Gold electrodes will be deposited by sputtering in the pattern shown in Figure 3 b).

3. Results

The first microstructure we made is shown in Figure 4. In Figure 4 a), the light microscope view shows unetched manganite residue on the right side of the etched sample. I corrected this manually using a small amount of etching solution with a syringe. Figure 4 b) shows an Atomic Force Microscope (AFM) image of the first array at the boundary between one of the 100 μm squares and the underlying NGO substrate. The step height estimated by this AFM scan was approximately 28 nm. This step height was about the same as the thickness of the film grown, indicating that etching was deep enough to expose NGO.

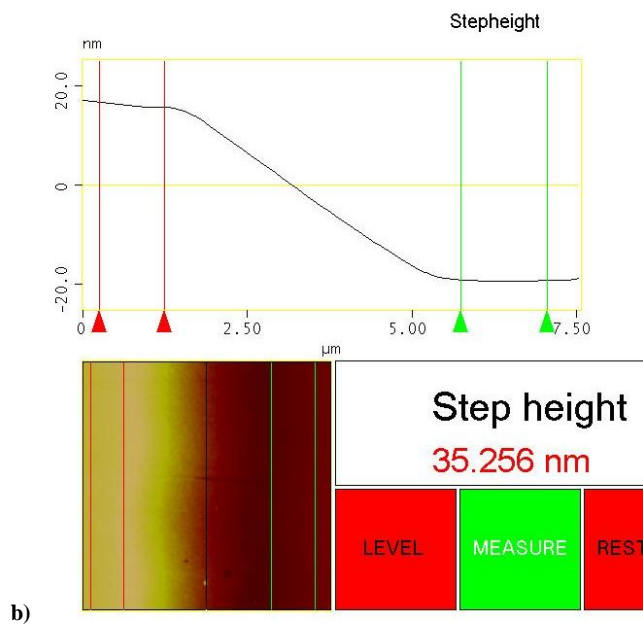
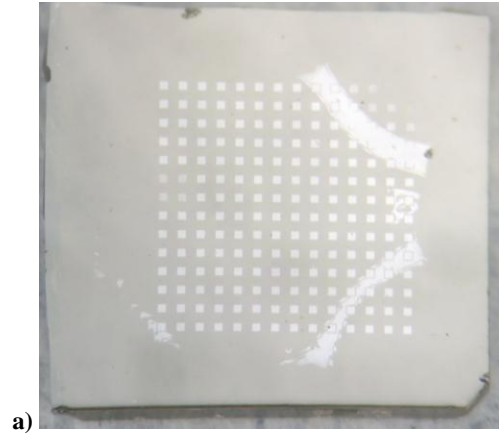


Figure 4: a) Square array film b) AFM view of step between NGO (right) and LPCMO (left)

The SQUID was then used to gather magnetization data of the sample along its easy $(1\bar{1}0)$ axis. The resulting magnetization curve also included the signal from the NGO substrate. I subtracted this signal by averaging the linear fit of the upper and lower part of the curve ^[2]. The resulting plot of M vs. H with NGO's approximate signal subtracted is shown in Figure 5.

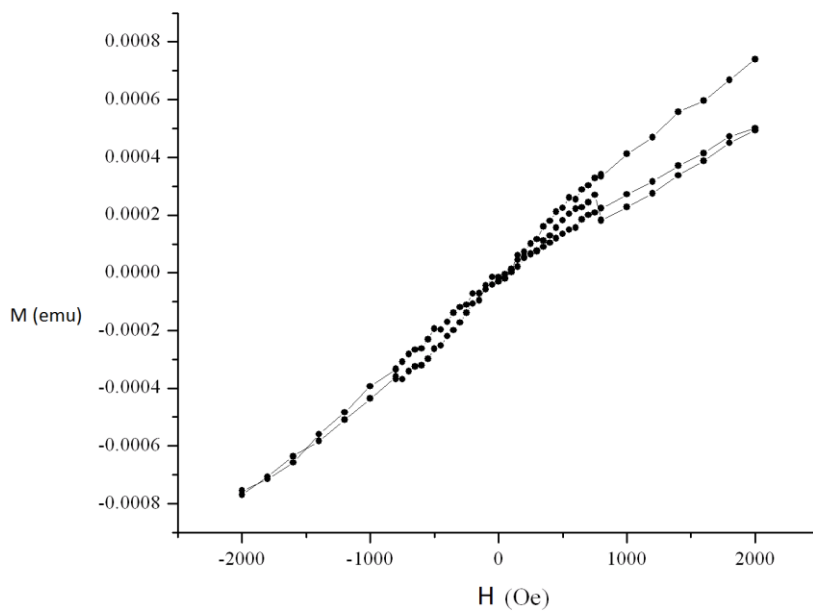


Figure 5: Magnetization vs. applied field in $(1\bar{1}0)$ direction.

The lack of a hysteresis loop indicates that the signal of LPCMO was too weak to be measured by the SQUID. The magnetization in these figures is likely background noise and unsubtracted signal from the paramagnetic substrate. The magnetization measurement was repeated along the (001) axis (thought to be the hard axis), shown in Figure 6. This measurement

also lacked a hysteresis, and thus lacked any FMM signal. From this result I concluded that the sample volume of this particular microstructure was too small to be detected by the SQUID.

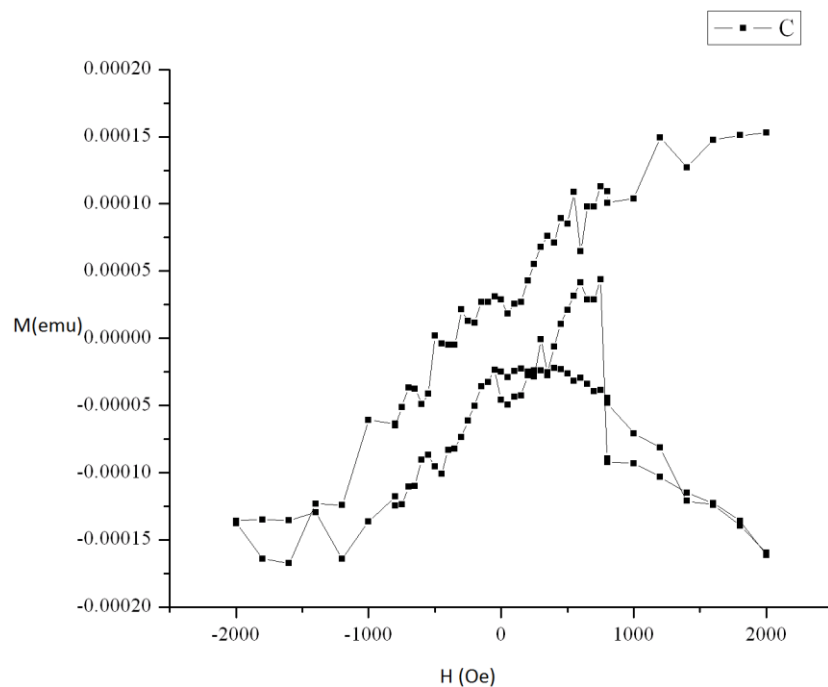


Figure 6: M vs H in 011 direction.

In order to compensate for this low magnetization signal, the next array I etched was the fine 27 x 27 array of squares. Though the scale of the squares is still the same size (100 um by 100um), the array is denser; in this case the total volume of LPCMO is much greater and is expected to give a stronger signal.

During the course of this experiment, I successfully made microstructures of LPCMO thin film. However the electroresistance effect has not yet been tested on these microstructures, and I have yet to obtain an accurate magnetization value. In the near future I plan to continue to improve this process and eventually test the electric field effect on LPCMO resistance. If electric field can truly modify the magnetic properties of manganite thin films, many applications in computer memory would become possible.

Acknowledgements

1. S.Dong, S.Dai, X.Y. Yaho, K.F. Wang, C. Zhu and J. –M.Liu, *Phys. Rev. B*, **74**, **104404** (2006).
2. Jeen, H. 2009, “Electric field induced anisotropic transport properties of phase separated La(1-y)PrCaMnO₃ thin films”, *American Physical Society*
3. S. Dong, H. Zhu and J. Liu, *Phys. Rev. B*, **76**, 132409 (2007).
4. J. Mannhart and D.G. Schlom, *Science* **327**, 1607 (2010).