Observing the Dynamics of Phase Changes in

$(La_{1-y}Pr_y)_{1-x}Ca_xMnO_3$ Thin Films

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Abstract

Thin films of the manganite $(La_{1-y}Pry)_{1-x}Ca_xMnO_3$ grown on a (NGO) substrate at low temperatures show a coexistence of antiferromagnetic charge order insulator (AFM-COI) and ferromagnetic metal (FMM) phases. Resistance as a function of temperature allows us to see when and where the phases changes occur and when compared with time, the property changes such as the thermal equilibrium is visible. The gold wire applied to the sample, helps apply a non-uniform electric field which contributes to dielectrophoresis at the low temperature. Percolation helps the sample become FM and expand regions at low temperature to make it the dominating phase. However, various dopings of the sample have different properties that can be changed with the increase in voltage or by applying a magnetic field. We observed the dynamics of these phase changes to determine what is needed to completely understand the sample.

Introduction

Perovskite Manganese Oxides also known as Manganites, were discovered in the 1950's and has a host of performance attributes. What makes each sample unique is that these attributes can evolve and happen at different moments. In Figure 1, the green represents La^{3+}, Pr^{3+} or Ca^{2+}, the blue represents the oxygen in the sample and the pink is for Mn^{3+} or Mn^{4+}.They exhibit properties such as Colossal Magnetoresistance (CMR) and Colossal Electro-Resistance (CER). Previous research has shown that manganites have a variety of responses to external agents related to temperature, electric and magnetic fields and changes in chemical doping.[1] These properties vary with the mixed valence of Mn in the sample which allows the sample to have multiple phases concomitantly, the ferromagnetic magnetic phase (FMM) and the anti ferromagnetic charge-ordered insulating phase (AFM-COI) and the paramagnetic insulating phase. The material $(La_{1-y}Pr_y)_{1-x}Ca_xMnO_3$ (LPCMO) has three major phase changes at different temperature values. At low temperatures the FMM and AFM-COI compete and coexist. Due to percolation FMM regions can connect to each other at low temperatures. The changes in the y-v-value indicate the varying amount of praseodymium in the sample. Praseodymium has the effect of making the sample more insulating. Studies show that at low temperatures the sample is in a more glassy mixed phase of FMM and AFM-COI. One sample of the LPCMO that is being tested is the $(La_{1-y}Pr_y)_{1-x}Ca_xMnO_3$ with (x = .33 and y =.6 (LP6)). For the LP6 sample, the AFM-COI to FMM transition occurs at a lower temperature leading to a freezing of the phase boundaries and a glassy phase separated state. Which means at

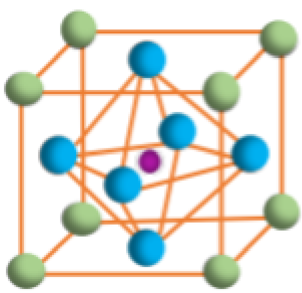
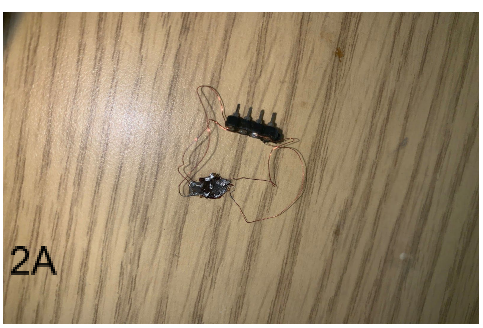
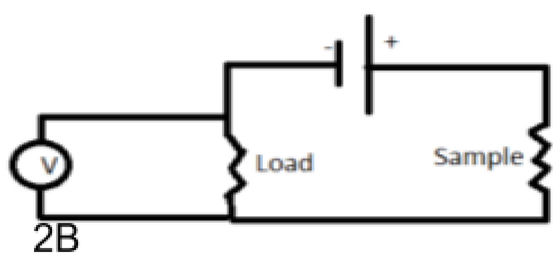


Fig. 1 is the Perovskite Structure of Manganite.

low temperatures the phases are more glassy and less dynamic.[2] The dynamic behavior of the phases is quantified by measuring the resistance as a function of time to the time at different temperature marks. It allows you to see where exactly is the LP6 more susceptible to changing from FM to AFM-COI. The question is, what exactly are the dynamics of the samples? At low temperatures, LPCMO is predominantly ferromagnetic which results in a low resistance. As the temperature of the sample starts to rise, it changes into an insulator with a high resistance. This ferromagnetic to insulating first order transition and hence, allows phase coexistence. The coexisting phases and properties of manganites have been studied profusely. However, manganites have the ability to abruptly change phases at different temperatures which can create a hysteresis. have completed temperature sweeps to observe the magnetic memory of thin films. As the sample is cycled, there seems to be a change in its magnetic and electric properties at low temperature after each thermal cycle.[3] This can be related to the amount of time the sample spent at each temperature.





Methods

The LPCMO films were previously grown using via pulsed laser deposition and was grown on (NGO) substrates. In order to prepare the sample, it had to be attached to the electrical contacts using indium solder to connect a gold wire from the sample to the sapphire, and using a copper wire to attach it to the four pin connector (Figure 2A). After attaching, the sample was placed on the probe using the adhesive GE-Varnish and then placed in the dewar. The temperature of the sample was set to twenty Kelvins and the temperature of the needle valve had to be set to half the temperature of the sample. To acquire a complete set of data, the sample must go through a heating and cooling run. The temperature range is set from twenty to three hundred kelvins at zero magnetic field and it is programmed to take data every 2 Kelvin. To acquire data for the cooling run with respect to time, the sample had to go through a run from 20-150-20 Kelvins at 10 V and then data was taken at 20k for 900-1000 seconds. After this measurement, the sample was heated to 150 and cooled to 30k and the same steps were repeated for 40 & 50k. The heating run was acquired similarly. The data for the 20k run was exactly the same. For the rest of the temperature values, the sample was cooled to the previous value you and then heated to the value that is being tested. For the LP5, data was obtained through running resistance vs. temperature from 20-150-20 at different step sizes. The step sizes changes how fast or slow the run is by choosing how often you want data to be taken. Data was gained using the two probe method (figure 2b) and measurements were acquired using LabVIEW and it was analyzed using Origin 2015.

Results

Figure 3 shows resistance vs. temperature measurements for the LP6 on a log scale resistance at 10 volts. The warming and cooling run is highlighted to differentiate between the two parts of the run. In the run, markers were placed to note each temperature point in the graph that is being observed, these markers were particularly placed at low temperature values to study the dynamics of the phase separation.

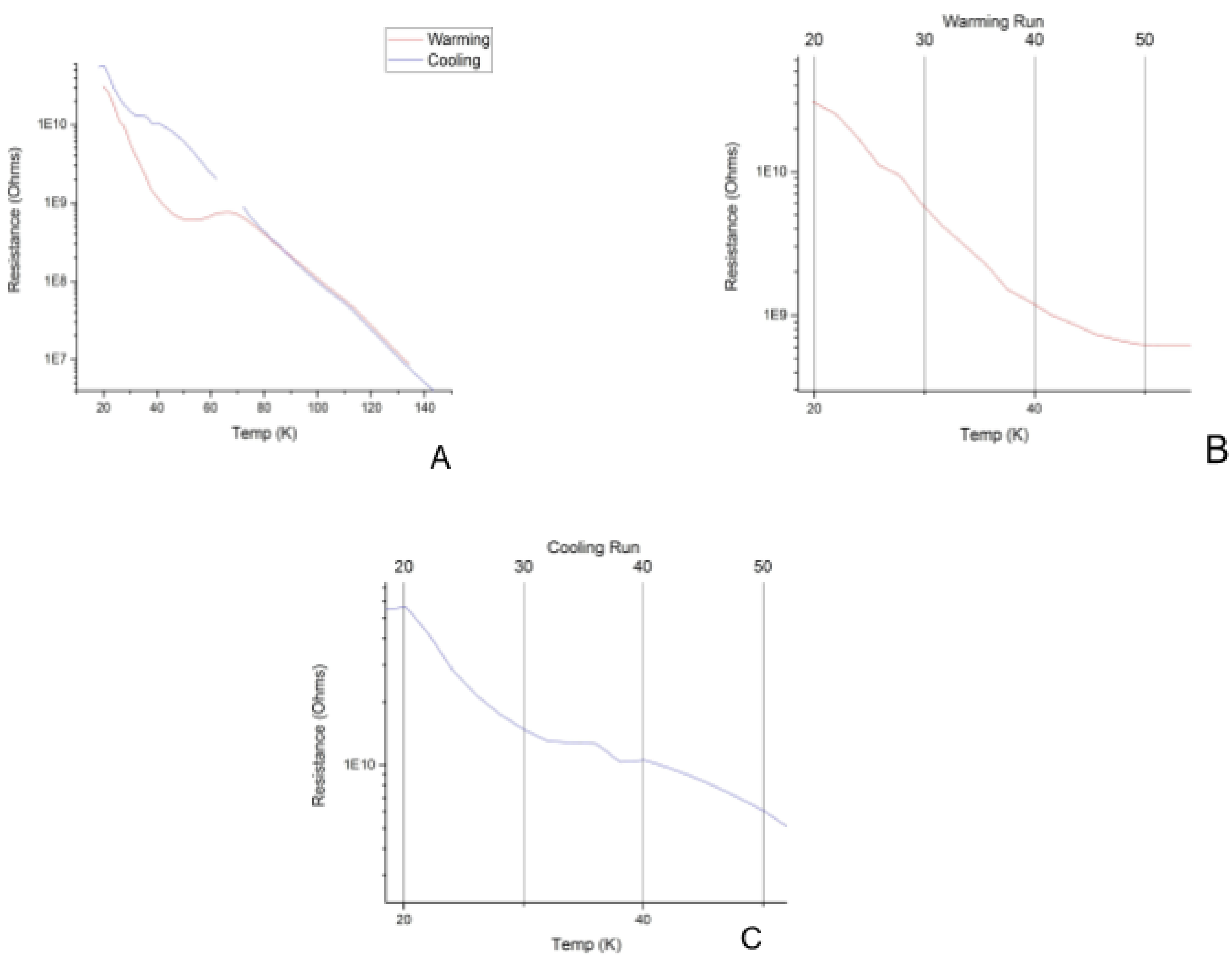


Figure 3a is a graph showing the Resistance vs. Temperature at 10 volts. The graph starts at 20k then it warms up to 200k, then cooled back to 20k. At low temperatures the sample is metallic. As the temperature rises, it goes *through a phase transition into an insulator. B) is a close up of the range that is being studied from 20-50k with marks at each point. C) is a close up of the warming run from 20-50k with also marks at each point being observed.*

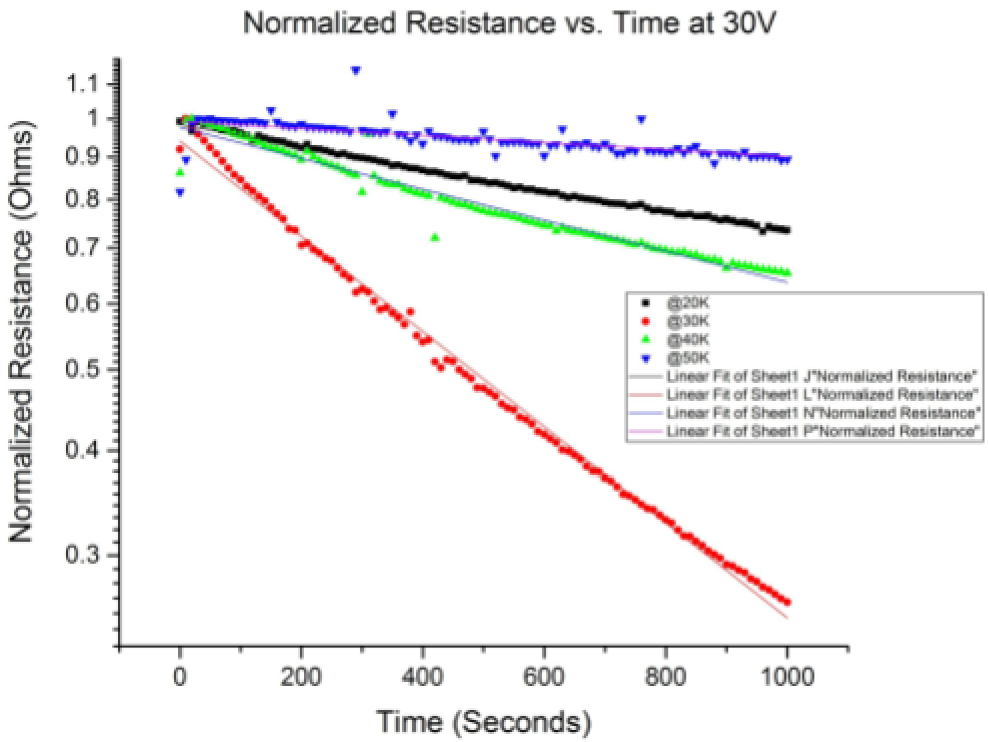
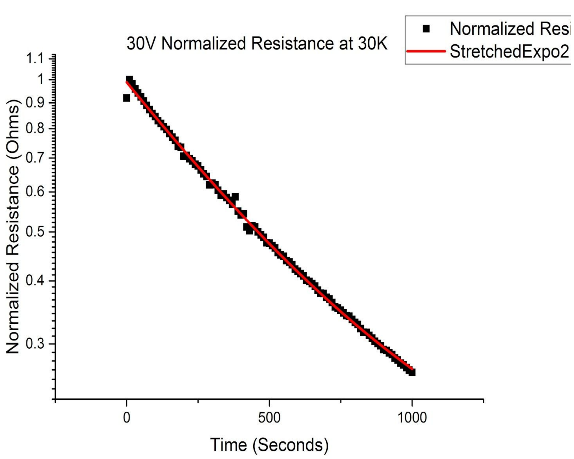


Figure 4 is a graph showing the resistance vs time's warming run at 30V. The resistance vs time measurements were taken at 20,30,40,50 Kelvin from a range of 900-1000 seconds at each temperature. C) Is the cooling run of the resistance vs. time at 30V

In order to observe the dynamics of the phase changes, measurements had to be taken at each temperature with respect to time. At each temperature (20,30,40, & 50K) the sample was observed for 900-1000 seconds (fig. 4). At 20K, the resistance over time seemed to decrease. When the sample begins to reach 30K it changed drastically and the resistance of the LP6 dropped and after it



passes 30k it slows back down and due to the completion of the phase change that occurred. In figure 5, the line of best fit did not suit the run at 30k, so it was found that a stretched

Fig. 5 Is a stretched exponential of the data taken at 30k to give the line of best fit.

exponential would best fit the trend. The stretched exponential is due to the fluctuation of phases which have similar energies at low temperature values and is vitrified. At higher values like 40 & 50K the phases are “devitrified”again and regain their dynamic behavior and is back to insulating. In the cooling run changes seem to be more evident due to the reconnecting of FM regions (percolation). It was decided to do a warming run increasing the voltage to 40 V in order to observe what changes may occur. Dielectrophoresis happens faster when you increase the voltage. The higher the voltage the more the transitions become apparent. In figure 7, the trends at 20,40, and 50K behave in a manner similar to the previous measurements at 30 V. At 30K, there is a change in the curve , this could be due to the state the sample is in at that temperature and it is presumed to be more glassy. At this point, the sample is mostly in the ferromagnetic stage and as it the trend reaches higher temperature values the phase change is concluded. The LP5 was used to test a similar material and measure where the transition is complete (Fig. 8). In the LP6 the phase transition isn’t complete unless it has a magnetic field applied to it. At low temperatures the LP5 is completely metallic and in this sample the dynamics of the phase changes are gone because the

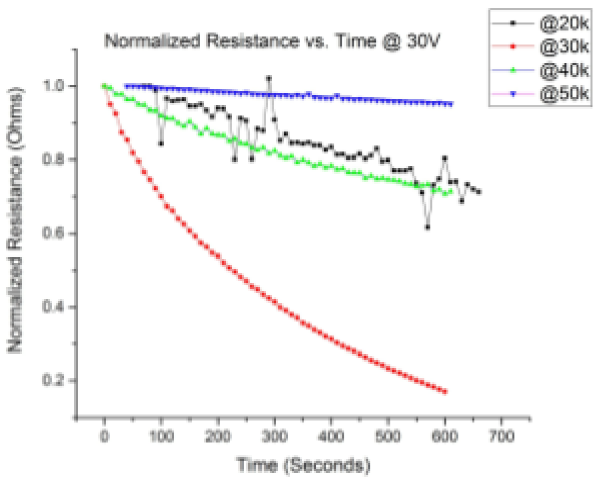


Figure 6 is the Warming run of the resistance vs. time at 30V

FM is dominating. When measurements for resistance vs. time were taken for the LP5, the trend at the temperatures were unchanging due to the domination of the FM. The slower you go, the longer you can stay in the supercooled state. Defects in the material play a role in the ability to observe this phenomenon. Similar to the super cooling of water, the cleaner the water the more effective it is to study. In our thin films, we didn't see much difference in the LP5 and we are not to see the effects clearer. To truly look at the effects, it is necessary that a cleaner thin film is created.

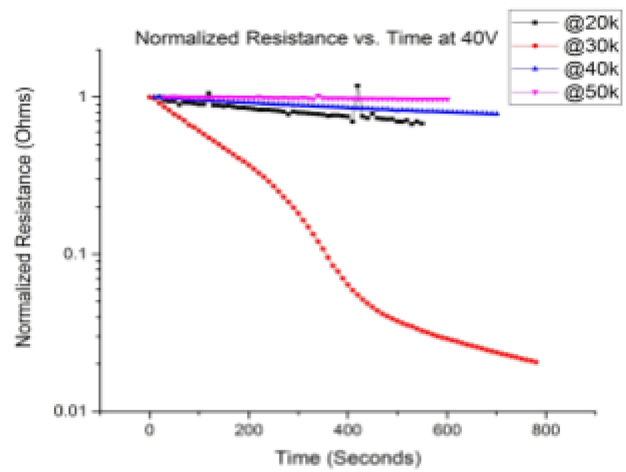


Figure 7 is a graph of resistance vs. time at 40V to show how the increase of voltage has an effect on the transition

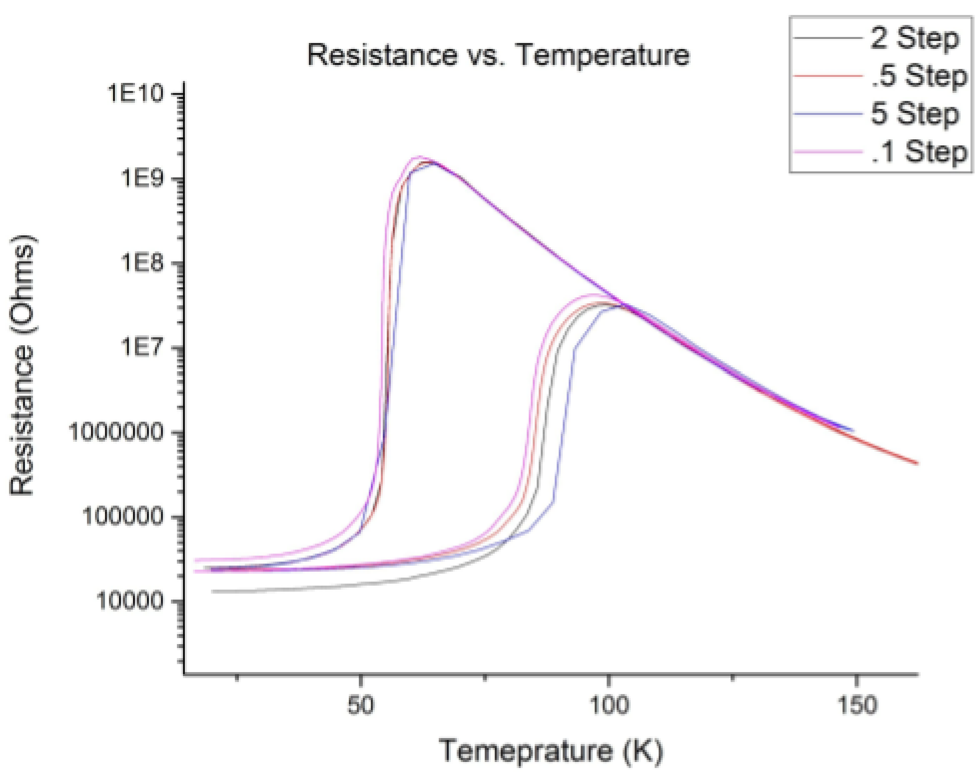


Figure 8 is a graph of resistance vs.time from 20-150-20k of the LP5. The step sizes are the temperature rates at which the program takes data. The .1 step line was shifted 3.5k to the left to better observe the hysteresis and to compare them to the other trends.

Conclusion

In conclusion, we observed the dynamics of phase changes in LPCMO thin films. The LP5 film with lower Pr concentration shows a stable ferromagnetic metallic phase at low temperature while the LP6 film with higher Pr concentration shows a vitrified mixed phase state at low temperatures. Warming the LP6 sample to 30 K devitrified the mixed phase state leading to voltage driven percolation at 40 V. The properties of the hysteresis in the resistance vs. temperature curves for the LP5 sample show that in order to obtain results clear evidence of supercooling(warming) results a “cleaner” thin film will need to be developed via pulsed laser deposition. Also, the properties of the hysteresis can be further studied by stopping and starting at different temperature values within the loop. The LP5 .1 step data in figure 8 required a shift of 3.5 because it was further right then the rest of the trend, that we don’t necessarily have an answer for. Further studying of the LP6 more with respect to time along with the resistance vs. temperature.

Acknowledgments

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