PROCESSING AND OPTIMIZATION OF BULK La₁₋ₓCaₓMnO₃±δ

A Senior Thesis
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Group: Engineering I
Processing and Optimization of Bulk $\text{La}_{1-x}\text{Ca}_x\text{MnO}_{3+\delta}$

by

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Abstract

Processing and Optimization of Bulk La$_{1-x}$Ca$_x$MnO$_{3\pm\delta}$

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The following explores the first systematic research conducted at Texas A&M University studying preparation techniques of the bulk La$_{1-x}$Ca$_x$MnO$_{3\pm\delta}$ colossal magnetoresistance (CMR) family. Three sample sets of bulk La$_{1-x}$Ca$_x$MnO$_{3\pm\delta}$ were fabricated using different preparation techniques. Details of each technique and the subsequent sample characterization are presented. Focus of the study was directed to compositions in the range 0.25<x<0.55 because these compositions exhibit a insulator-to-metal transition associated with the paramagnetic-to-ferromagnetic (FM) transition upon cooling. Resistance, susceptibility, wavelength dispersion (WDS), x-ray diffraction and BSE photograph data is presented and compared for compositions of different sample sets. In all three sets, unexpected trends and inconsistencies in resistance and susceptibility were observed. BSE photographs confirm sample inhomogeneity, although WDS and x-ray diffraction data suggests that the bulk of the samples are the correct composition. Future changes in preparation techniques are explored. In conclusion, more research is needed to optimize reaction/annealing temperatures and duration parameters to fabricate more homogeneous bulk La$_{1-x}$Ca$_x$MnO$_{3\pm\delta}$ magnetoresistance materials.
Processing and Optimization of Bulk La$_{1-x}$Ca$_x$MnO$_{3\pm\delta}$

Introduction

Though the paramagnetic-to-ferromagnetic transition accompanied by a sharp drop in resistivity has been known to exist in some perovskite materials since 1950, interest in these materials has recently been renewed. This revival has been sparked by the realization that the magnetoresistance (MR), due to the correlation between the magnetization and resistivity, can be very large. [1] Since the discovery of giant magnetoresistivity (GMR) in 1988 and colossal magnetoresistivity (CMR) in 1994, researchers are continuously optimizing MR materials.

The majority of current research in MR materials is in thin films because of the immediate commercial applications of the results. However, limited research involves bulk MR materials. This systematic research was needed to optimize the properties and processing conditions of bulk MR materials, more specifically the La$_{1-x}$Ca$_x$MnO$_{3\pm\delta}$ family, to better understand the origins of the MR effect. The principal objective of the research was to study the magnetoresistive properties of the bulk La$_{1-x}$Ca$_x$MnO$_{3\pm\delta}$ family varying $x$ from 0.25 to 0.85.

Proper processing of the bulk material must be understood and optimized, since magnetoresistive thin films are grown using bulk MR targets. Texas A&M University has just begun to research MR thin films; therefore, this research will provide a foundation for current and future Texas A&M University researchers to fabricate quality bulk and MR thin films.
Experimental

Three different sample sets of bulk La-Ca-Mn-O were prepared to compare different reaction techniques of the starting powders. The samples were fabricated by mixing the proper stoichiometric proportions of the starting powders. Table 1 details the procedures used for each sample set. As shown in Table 1, there were several preparation procedures that were varied among the three sample sets. Most of the variations were implemented due to unexpected resistance versus temperature trends seen with sample set #1, which will be presented later. Some of the most notable changes and explanations of preparation procedures are explored.

The starting powders used in sample set #1 were lanthanum oxide (La$_2$O$_3$, 99.99% pure), calcium oxide (CaO, 99.95% pure) and manganese (II) carbonate (MnCO$_3$, 99.9% pure). The most drastic preparation change was the use of calcium carbonate (CaCO$_3$, 99.5% pure) in sample sets #2 and #3 as a starting powder instead of calcium oxide used in set #1. The calcium oxide was suspected in absorbing water from the atmosphere during the reaction phase causing strange characterization behavior in sample set #1. All powders were thoroughly mixed individually and then together using a mortar and pestle before the furnace reaction in an alumina crucible.

The ball milling in sample set #1 was included to ensure proper mixing, but was taken out of the procedures for sample sets #2 and #3 to eliminate the possible introduction of contaminants. Substituting the ball milling was a very thorough grinding procedure using a mortar and pestle to ensure proper mixing.
<table>
<thead>
<tr>
<th>Preparation Step</th>
<th>Sample Set #1</th>
<th>Sample Set #2</th>
<th>Sample Set #3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial Powders</td>
<td>La$_2$O$_3$, CaO, MnCO$_3$</td>
<td>La$_2$O$_3$, CaCO$_3$, MnCO$_3$</td>
<td>La$_2$O$_3$, CaCO$_3$, MnCO$_3$</td>
</tr>
<tr>
<td>Ball Milled?</td>
<td>√</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reaction #1</td>
<td>24 hrs. @ 1100°C</td>
<td>5 hrs. @ 1250°C</td>
<td>5 hrs. @ 1250°C</td>
</tr>
<tr>
<td>Grinded?</td>
<td></td>
<td>√</td>
<td></td>
</tr>
<tr>
<td>Pressed?</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reaction #2</td>
<td>24 hrs. @ 1100°C</td>
<td>12 hrs @ 1380°C</td>
<td>12 hrs @ 1380°C</td>
</tr>
<tr>
<td>Grinded?</td>
<td></td>
<td>√</td>
<td></td>
</tr>
<tr>
<td>Pressed?</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reaction #3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Grinded?</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pressed?</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 1: Powder Sample Set Preparation Procedures

All reactions were carried out in either a Carbolite or Lindberg box furnace in air or oxygen. Table 2 shows an example of the standard program parameters used during the powder reaction phase. A different furnace reaction program was used to prepare sample sets #2 and #3 to match a reaction procedure (refer to Table 1 for details) found in literature. [2] This new reaction procedure was adopted because the furnace program used in sample set #1 was suspected to be too short in duration and low in temperature to ensure proper crystal formation.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Setting</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ramp Rate 1:</td>
<td>3.0°C per minute</td>
</tr>
<tr>
<td>Dwell Temperature 1:</td>
<td>1100°C</td>
</tr>
<tr>
<td>Dwell Time 1:</td>
<td>1440 minutes (24 hours)</td>
</tr>
<tr>
<td>Ramp Rate 2:</td>
<td>3.0°C per minute</td>
</tr>
<tr>
<td>Dwell Temperature 2:</td>
<td>30°C</td>
</tr>
<tr>
<td>Dwell Time 2:</td>
<td>0 minutes</td>
</tr>
</tbody>
</table>

Table 2: Standard Box Furnace Program Parameters for Powder Reaction
In sample set #3, the powders were pressed using a cold uniaxial press (Carver Autopellet Laboratory Press). Table 3 gives the standard press program used throughout the sample preparations. The pressing procedure was included to reduce the amount of space between adjacent molecules, making diffusion of La, Ca, Mn and O atoms easier and producing more uniform crystals during the reaction process. These were the main differences between the different preparation procedures. Other minor changes will be discussed.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Setting</th>
</tr>
</thead>
<tbody>
<tr>
<td>Force:</td>
<td>30,000 lbs.</td>
</tr>
<tr>
<td>Dwell Time:</td>
<td>120 seconds</td>
</tr>
<tr>
<td>Decompression Time:</td>
<td>Slow</td>
</tr>
</tbody>
</table>

Table 3: Standard Press Program

After the lengthy reaction of the powders, a small portion of the powder charge was mixed with a few drops of acrylic binder (Duramax B-1020) to improve the strength and durability of the final pellet. The powder was then pressed using the Carver Press to get ceramic pellets (using the standard press program) with a diameter of 31mm and a thickness that varied from 3-4mm. The pellet was then sintered in a box furnace at 1100°C for 12 hours using a ramp rate of 3.0°C per minute. The sintering process serves two purposes:

- burn off the acrylic binder, and
- increase the strength of the pellets. [3]
After sintering, the pellets were cut using a diamond-coated wire saw. During this procedure, the pellet was mounted using wax and cooled using distilled water. The sliced pellet was then placed in a box furnace at 300°C for 3-4 hours using a ramp rate of 3.0°C per minute to remove the water introduced in the cutting process. After cooling, the individual slices were polished to approximately 10mm x 3mm x 2mm dimensions using polishing paper (wet/dry Buehler). Silver wire contacts were then placed onto the samples using a two-part silver epoxy (Epo-Tek H20E) that was allowed to dry for >30 minutes in a 180°C furnace. The samples were then mounted onto a Lakeshore four-lead resistance probe for resistance measurements.

Resistance was measured using the standard four-point technique over a temperature range of 300K to 20K. A cryostat (APD Cryogenics) with a closed cycle helium compressor was used to take the measurements. Data acquisition was automated using LabVIEW software, a Lakeshore controller (DRC-91C) to control the temperature in the cryostat and Keithley instruments to measure currents and voltages.

Selected samples were analyzed by wavelength dispersion spectometry (WDS) using a Cameca SX-50 microprobe in the Texas A&M University Geology Department. The WDS measurements verified the samples’ composition. Selected powder charges were analyzed by x-ray diffraction to confirm their crystal structure. Lastly, susceptibility was measured for selected samples to document their magnetic characterization.
Results and Discussion

In sample set ¹I, seven different pellet compositions were prepared, \( x = 0.15, 0.25, 0.33, 0.45, 0.55, 0.70, \) and \( 0.85 \). The focus of sample sets ²² and ³³ were in the \( x = 0.25-0.55 \) range for several reasons:

- mid-range compositions exhibit a insulator-to-metal transition associated with the paramagnetic-to-ferromagnetic (FM) transition upon cooling,
- outer boundary compositions of this range exhibit FM insulator characteristics, and
- compositions above \( x = 0.5 \) have a ground state which is anti-ferromagnetic (AFM) and insulating. [2]

In sample set #1, pellets for all seven compositions were prepared. During the preparation, some “special” procedures were required to produce a more durable pellet to withstand polishing:

- acrylic binder quantity had to be modified for each composition,
- powders were pressed two or three times in the Carver press to produce a tightly compact pellet, and
- ramp rate of the box furnace during sintering was lowered to \( 1^\circ C \) per minute to reduce stress fractures within the pellet due to quick temperature changes.

Qualitatively, as the value of \( x \) decreased, it became more difficult to fabricate a pellet that would not disintegrate during polishing even after implementing the above procedures.
Figure 1 shows the resistance versus temperature (resistance) measurement taken for the $x=0.15$ composition. As expected the sample exhibited characteristics of an insulator. [2]

Figure 2 compares the resistance curves before and after annealing for the $x=0.25$ composition. This composition was expected to exhibit ferromagnetic and metallic characteristics [2]; however, a paramagnetic-to-ferromagnetic transition was not observed upon cooling.

The following numbering/lettering system is used in all figures to label the appropriate progression in annealing. The measurement of the initial sample before annealing is labeled 1 and each subsequent measurement after annealing is labeled 2, then 3 and so on... A letter following the number will differentiate annealing progressions for different samples.
Figures 3 and 4 are the most curious from sample set #1. Although both compositions clearly showed a paramagnetic-to-ferromagnetic transition with metallic characteristics at low temperatures, there were many unpredicted anomalies.

Figure 3 shows the resistance curve comparisons for $x=0.33$ before and after annealing (note the resistance axis in LOG scale). The curve transition from 1 to 2 was the most surprising, since previous research concluded that $T_c$ was to increase and the resistance was to decrease with annealing. [3] This sample exhibited the exact opposite trend. However, after the second annealing, it appeared that the material crystals ordered better and the expected trend was observed for the remaining annealing periods. Other unexpected characteristics of the resistance curves are the low $T_c$ temperatures ($< 188K$) and broad tail during transition into the FM metallic phase. In previous research, $T_c$ was shown to be $\sim 260K$ [2] with a very steep drop in resistance when cooled below $T_c$ and transitioning into the metallic phase [2,4,5].
Figure 3: $x=0.33$ Sample Set #1 – Resistance vs. Temperature Annealing Comparison

Figure 4: $x=0.45$ Sample Set #1 – Resistance vs. Temperature Annealing Comparison
Figure 4 shows the resistance annealing curves for $x=0.45$. This graph is more disturbing since previous research has shown that annealing La-Ca-Mn-O in an oxygen atmosphere should produce a better MR material, meaning that the transition temperature should increase and the resistance of the sample should decrease, more than a sample that is annealed in an air atmosphere. However, when two separate samples were annealed, one in an oxygen ($O_2$) atmosphere and the other in air, the sample annealed in $O_2$ (transition from curve 1 to 2a) exhibited a stronger opposite trend than the sample annealed in air (transition from curve 1 to 2b). As the case with the $x=0.33$ sample, the expected trend was observed after the second annealing period. Also resembling the $x=0.33$ composition, the $x=0.45$ transition into the metallic phase was broader than expected. In addition, the $T_c$ of ~228K was much lower than the expected value of ~250K found in literature. [2]

Figure 5 combines the resistance curves for $x=0.55$, 0.70 and 0.85 since all three compositions exhibited no transition temperature and behaved as AFM insulators as observed in previous research. [2]

Once all sample set #1 data was gathered and the inconsistencies reviewed, it was decided to verify the composition of La, Ca, Mn and O for $x=0.25$, 0.33 and 0.45. The O percentage was computed by stoichiometry and not by actual measurement. Results showed that all three samples were within 5-10% of the nominal composition. The higher percentage error is caused by the surface roughness of the samples.
Figure 5: $x=0.55$, 0.70 and 0.85 Sample Set #1 – Resistance vs. Temperature Curve

Figure 6 shows a BSE photograph taken of the $x=0.33$ sample surface at 100x magnification (note that the brighter areas denote elements with higher atomic numbers and the darker areas are those with lower atomic numbers). The large bright areas in Figure 6 were discovered to be high concentrations of La and the darker areas were high concentrations of Ca. Note that the large, pure black areas are surface pores and not high concentrations of Ca. This was also found in the $x=0.45$ sample, shown in Figure 7 at 100x magnification. All of the sample surfaces were rough and porous in appearance. Furthermore, the grain sizes and ordering were non-uniform without any apparent organization. This suggests a non-homogeneous crystal structure.
Figure 6: $x=0.33$ Sample Set #1 — BSE Surface Photograph @ 100x

Figure 7: $x=0.45$ Sample Set #1 — BSE Surface Photograph @ 100x
After completion of the resistance and WDS measurements for sample set \#1, focus was directed to compositions \(x=0.25, 0.33, 0.45\) and 0.55 for sample sets \#2 and \#3 to solve the annealing trend issues exhibited in samples \(x=0.33\) and 0.45. Also, this range contains compositions with insulator-to-metal transitions with \(x=0.33\) being the optimal composition. It was immediately theorized the preparation procedure was flawed. The focus of the remaining research was to investigate and solve this fabrication issue.

In sample set \#2, it was decided to only produce pellets for the \(x=0.33\) and 0.45 since the abnormal trend in the resistance curve was observed in these compositions. The same “special” procedures used during the preparation of sample set \#1 were used in sample set \#2 to obtain durable pellets. A new box furnace program was used in preparing set \#2, which made a noticeable texture difference between the reacted powders from set \#1 and \#2. Sample set \#2 powders were much harder and more tightly bound after reacting. This can be attributed to the longer reaction program that allowed the powders to fully react and produce stronger crystal bonds.

Figures 8 and 9 show the resistance curves before and after annealing for \(x=0.33\) and 0.45, respectively. In both compositions, the expected resistance curve trends were observed after the first annealing. The longer the samples were annealed the better the crystal structure of the bulk grains, which produced a better MR material with higher transition temperatures and lower resistance. However, both samples still had lower \(T_c\) values compared to those reported in the literature [2] and broad transitions into the metallic phase below \(T_c\).
Figure 8: $x=0.33$ Sample Set #2 – Resistance vs. Temperature Annealing Comparison

Figure 9: $x=0.45$ Sample Set #2 – Resistance vs. Temperature Annealing Comparison
Shortly after the $x=0.33$ and 0.45 samples were completed in sample set #2, it was decided to add an intermediate grinding steps between furnace reactions. This ensured proper uniformity and crystal growth in the powder. This change was the basis for sample set #3 which encompassed the four compositions in the range of $x=0.25$ to 0.55. Figures 10 through 13 show the resistance curves for $x=0.25$, 0.33, 0.45 and 0.55, respectively. Sample set #3 exhibited the same unexpected characteristics seen in set #2. For $x=0.33$ and 0.45 the $T_c$ values were extremely low and the transitions into the metallic phase were very broad.

Figure 10: $x=0.25$ Sample Set #3 – Resistance vs. Temperature Curve
Figure 11: $x=0.33$ Sample Set #3 – Resistance vs. Temperature Annealing Comparison

Figure 12: $x=0.45$ Sample Set #3 – Resistance vs. Temperature Annealing Comparison
Figures 14 and 15 compare the starting resistance curves for the standard sample from each set for \( x = 0.33 \) and 0.45. If taken separately, two completely different conclusions could be made. Looking at Figure 14 for \( x = 0.33 \), the changes in preparation procedures through the sample sets (from \#1-\#2-\#3) helped fabricate a better MR material since \( T_C \) increased and the resistance decreased. However, looking at Figure 15 for \( x = 0.45 \), both \( T_C \) and resistance decreased through the sample sets.
Figure 14: $x=0.33$ – Comparison of Standard Resistance vs. Temperature Curve After Reaction Process Between Sample Sets

Figure 15: $x=0.45$ – Comparison of Standard Resistance vs. Temperature Curve After Reaction Process Between Sample Sets
WDS measurements were then taken for \( x = 0.25 \) and 0.55. Different from the first WDS samples, these samples were placed into a clear epoxy, some of which was absorbed by the sample. After hardening, the epoxy helped keep the sample grains from dislodging during an intimate three-step polishing procedure. This preparation produced a much smoother sample surface than before, which allowed more accurate WDS measurements. The overall compositions of the samples were again within 5-10% of the nominal value; however, visual abnormalities were found.

Figures 16 and 17 are BSE photographs of the \( x = 0.25 \) sample surface at 100x and 500x, respectively. In Figure 17, you can see the noticeable bright La rich streak. The darker grains were found to be slightly rich in Ca. Again, note that the dark, pure black areas are surface pores.

Figures 18 through 21 are BSE photographs for the \( x = 0.55 \) sample at 100x, 500x, 1000x, and 3000x respectively. In Figure 21 you can clearly see dark gray, elongated grains approximately 5\( \mu \)m in length. Through WDS measurements, these grains were found to have a much higher percentage of Ca than the nominal value. This suggests that the sample may contain different structural phases. A logical explanation for the different phases is that the \( x = 0.55 \) composition is on the border between having a FM or AFM ground state (with \( x = 0.5 \) being the border) [2]. Therefore, the sample may have a non-homogeneous crystal structure, with part of the sample having a structure similar to compositions with \( x < 0.50 \) and the remaining structure resembling compositions with \( x > 0.50 \).
Figure 16: $x=0.25$ Sample Set #3 – BSE Surface Photograph @ 100x

Figure 17: $x=0.25$ Sample Set #3 – BSE Surface Photograph @ 500x
Figure 18: $x=0.55$ Sample Set #3 – BSE Surface Photograph @ 100x

Figure 19: $x=0.55$ Sample Set #3 – BSE Surface Photograph @ 500x
Figure 20: x=0.55 Sample Set #3 – BSE Surface Photograph @ 1000x

Figure 21: x=0.55 Sample Set #3 – BSE Surface Photograph @ 3000x
After all resistance and WDS measurements were complete, x-ray diffraction measurements were taken. Figures 22 and 23 show x-ray data for $x=0.33$ and 0.45 (not annealed) taken from sample set #1. Figures 24/25, 26/27, 28/29 and 30/31 show x-ray data for $x=0.25, 0.33, 0.45$ and 0.55 from sample set #3 before/after annealing. The appropriate d-spacing is labeled for each peak on all of the x-ray figures.

With close inspection, it can be seen that as the value of $x$ increases the x-ray diffraction peaks shift slightly ($< 1^\circ$) to the right (slightly greater $2\theta$) and the d-spacing for each corresponding peak decreases. In the $x=0.33$ and 0.45 samples, there is a decrease in d-spacing before and after annealing which confirms that a more compact crystal structure has been formed. This trend was expected since annealing should produce a better ordered crystal structure. Surprisingly, there was not a significant difference in the x-ray data between sample sets #1 and #3 for $x=0.33$ and 0.45. If sample set #1 had not fully developed the proper crystal structure, the x-ray data would have shown the discrepancies. When compared to previous documented research, all of the x-ray data looks consistent with the La-Ca-Mn-O crystal structure. [7] The following are the crystal plane coordinates corresponding to the different peaks:

\[
\begin{align*}
2\theta &\approx 23^\circ & (200) \\
2\theta &\approx 33^\circ & (202) \\
2\theta &\approx 40.5^\circ & (222) \\
2\theta &\approx 47^\circ & (400), (004) \\
2\theta &\approx 53^\circ & (402), (204) \quad \text{not significant in } x=0.45 \text{ and } 0.55 \\
2\theta &\approx 54.5^\circ & (421) \quad \text{not significant in } x=0.45 \text{ and } 0.55 \\
2\theta &\approx 59^\circ & (620), (026)
\end{align*}
\]
Figure 22: $x=0.33$ Sample Set #1 - X-Ray Diffraction Data

Figure 23: $x=0.45$ Sample Set #1 - X-Ray Diffraction Data
Figure 24: \( x=0.25 \) Sample Set #3 - X-Ray Diffraction Data Before Annealing

Figure 25: \( x=0.25 \) Sample Set #3 - X-Ray Diffraction Data After Annealing
Figure 26: $x=0.33$ Sample Set #3 - X-Ray Diffraction Data Before Annealing

Figure 27: $x=0.33$ Sample Set #3 - X-Ray Diffraction Data After Annealing
Figure 28: $x=0.45$ Sample Set #3 - X-Ray Diffraction Data Before Annealing

Figure 29: $x=0.45$ Sample Set #3 - X-Ray Diffraction Data AfterAnnealing
Figure 30: $x=0.55$ Sample Set #3 - X-Ray Diffraction Data Before Annealing

Figure 31: $x=0.55$ Sample Set #3 - X-Ray Diffraction Data After Annealing
Since three sets of samples were fabricated and none of them produced the ideal resistance curves, it was decided to take magnetic measurements of sample set #3 for selected compositions. Figures 32 through 35 plot $\chi'$ and $\chi''$ versus temperature for $x=0.25, 0.33, 0.45$ and 0.55 before and after annealing.

Since the resistance characterization was non-ideal, the magnetization characteristics were also anticipated to be non-ideal. In Figure 33, the transition slope of $\chi'$ for $x=0.33$ is expected to be very sharp like that seen for $x=0.45$ in Figure 34. However, the magnetic transition temperatures for both $x=0.33$ and 0.45 are similar to values reported in literature [2] and much higher than the resistance transition temperatures.

Figures 36 and 37 plot the normalized resistance ($R/R_{\text{max}}$) and normalized susceptibility ($\chi'/\chi'_{\text{max}}$) vs. temperature for annealed $x=0.33$ and 0.45 from sample set #3 to compare the electrical and magnetic transition temperatures. It has been documented through previous research that the electrical and magnetic $T_C$ values should be very close (within 5-10K). [2] However, Figures 36 and 37 clearly show $T_C$ differences greater than 50K.
Figure 32: $x=0.25$ Sample Set #3 - $\chi'$ and $\chi''$ vs. Temperature

Figure 33: $x=0.33$ Sample Set #3 - $\chi'$ and $\chi''$ vs. Temperature
Figure 34: $x=0.45$ Sample Set #3 - $\chi'$ and $\chi''$ vs. Temperature

Figure 35: $x=0.55$ Sample Set #3 - $\chi'$ and $\chi''$ vs. Temperature
Figure 36: $x=0.33$ Sample Set #1 Annealed – Normalized $R (R/R_{\text{max}})$ and Normalized $\chi'$ ($\chi'/\chi'_{\text{max}}$) vs. Temperature

Figure 37: $x=0.45$ Sample Set #1 Annealed – Normalized $R (R/R_{\text{max}})$ and Normalized $\chi'$ ($\chi'/\chi'_{\text{max}}$) vs. Temperature
Conclusion

The BSE photographs confirm inhomogeneity, although the WDS and x-ray diffraction data suggests that the bulk of the samples are the correct composition. However, the inhomogeneous distribution may affect resistance more than magnetization, which explains the lower resistance transition temperatures compared to the magnetic transition temperatures.

Exploring the possibility of fabrication procedure faults, these changes could be implemented for future sample sets.

- use purer forms (≥99.99%) of the starting powders,
- react the powders in an oxygen atmosphere,
- exclude the use of distilled water when slicing the pellet to eliminate the possibility of unwanted reactions, and
- exclude the use of wax when slicing the pellet to eliminate the possibility of contamination.

In conclusion, more research is needed to optimize reaction/annealing temperatures and duration parameters to fabricate better bulk \( \text{La}_{1-x}\text{Ca}_x\text{MnO}_3 \) magnetoresistance materials. The fabrication of quality bulk \( \text{La}_{1-x}\text{Ca}_x\text{MnO}_3 \) pellets is very important to the success of future research in this CMR family. Without proper pellets, La-Ca-Mn-O thin films can not be produced since the chemical composition of the films depend highly on the target stoichiometry and quality (e.g. density, uniformity, or surface condition). [8]
References


