The Synthesis and Atomic Spacing of $La_{.5}(Ca_{.5-x}Sr_x)MnO_3$ for x = 0.3 and 0.4, and the effect of UV radiation on the resistance of these materials

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Abstract

In a previous study, the structural data for samples of $La_{.5}(Ca_{.5-x}Sr_x)MnO_3$ was examined at x = 0, 0.1, 0.2, 0.3, and 0.5 compositions. For x = 0 to 0.2 the samples exhibited a linear increase in the atomic spacing. However, at x = 0.3, the atomic spacing was greatly increased relative to that for x = 0 to x = 0.2. For x = 0.5, the atomic spacing is once again consistent with that for x = 0 to 0.2. To examine if this deviation in the atomic spacing at x = 0.3 is a real feature of the compound, it was proposed to reexamine synthesis of that composition and X-ray examination of it to see if that deviation from the trend of the atomic spacing that is exhibited by the other compositions (x = 0, 0.1, 0.2 and 0.5) is repeated. It may also be important to examine if the composition at x = 0.4 shed any light on the question. Consequently samples in which x = 0.4 was also synthesized and examined using x-ray diffraction to deduce the atomic spacing information.

In order to resolve the question raised above, it will be necessary to synthesize samples having composition $La_{.5}(Ca_{0.2}Sr_{0.3})MnO_3$ and $La_{.5}(Ca_{0.1}Sr_{0.4})MnO_3$. After fabrication of these samples, x-ray diffraction (XRD) will be performed to analyze the atomic spacing of the material using Scherer's equation

$$S=k\frac{\lambda}{\beta cos\Theta},$$

where k is a constant (~1), λ is the x-ray wavelength, β is the width of the x-ray intensity peak (radians), and Θ is the angle of the diffraction peak. Note that the constant 0.9 is also a value for k that has been used by other researchers and could be used here. However, the previous study

used k = 1 so that value is used in this study. Also, to ensure the results at x = 0.3 are repeatable, it is important to fabricate an additional sample of $La_{.5}(Ca_{.2}Sr_{.3})MnO_3$ using the process from the previous experiment. Hence, one component of our experiment is to prepare samples having the composition of x = 0.3 and x = 0.4. The second component of our study involves measuring the resistance of these two samples when they are exposed to ultraviolet (UV) radiation. This is important because the exposure to UV radiation on some materials have been known to cause a change in their physical properties. This component is described in more detail in "*Ultraviolet Radiation effects on the Electrical Resistivity of Some La(Ca/Sr)MnO_3 Materials*."

Introduction

$LaMnO_3$ has a perovskite crystal structure of the form ABO_3. It has been recently discovered, to have the capacity to transition from insulating to metallic. Through this discovery, a range of applications have become possible. Some basic applications of this material is the ability to be used as solar cells, in devices used to store energy, and to be used as electrical output devices.

Our hypothesis is the atomic spacing at x = 0.3 reported in the previous study is due to a stoichiometric error when the sample was originally synthesized. This would explain why the data for this sample does not follow the trend of the other compositions. However, if the stoichiometry is correct, the deviation in atomic spacing suggests other internal processes are occurring in the materials. We believe that the x = 0.3 and x = 0.4 should show similar characteristics. Therefore, if the stoichiometry in the previous study was correct then these two compositions should exhibit similar behaviors and they should both deviate from the linear trend in the atomic spacing exhibited by the other four compositions.

Methodology

Using solid-state reaction techniques, we fabricated samples of $La_{.5}(Ca_{.5-x}Sr_x)MnO_3$, for x = 0.3 and 0.4. In order to characterize the crystal structure, we will use x-ray diffraction (XRD). To determine the atomic spacing, we will perform calculations using Scherer's equation. If possible, we will do compositional analysis using scanning tunneling microscopy. We will obtain an average composition value at x=.3 and x=.4. Using a furnace, the material will be heated at 1200 ^oC to decarbonize the material then grinded, pressed into pellets, and sintered at 1500 ^oC.

In order to carry out this research, the following will be needed:

A sample of $La_{.5}(Ca_{.5-x}Sr_x)MnO_3$, where x=.3 and .4, an x-ray diffraction (XRD) of the samples, the values for β and Θ for the specific diffraction peaks, a precision constant current source, a sensitive voltmeter, a mortar and pestle, hydraulic pressing machine, and a furnace with the ability to maintain 1500 ^oC.

Procedure

In order to fabricate the samples, we first needed to balance a chemical equation which would allow 4 grams of the material to be produced. The compounds used were La_2O_3, $SrCO_3$, $CaCO_3$, and MnO_3. They were then grinded for 30 minutes using a mortar and pestle. Once this was done, the material was weighed and placed into an Al_2O_3 container (boat). The boat was placed into the furnace that gradually heated up to 1200 ^oC. The purpose of this step is to remove the carbon (decarbonize) from the bulk material. After the decarbonizing process, the material was grinded again for 15 minutes and pressed into pellets. Next, they were placed back into the furnace. Once placed into the furnace the second time, it is decarbonized at 1250 ^oC for and hour

then ramped up to 1500 ^{o}C where it is sintered for 12 hours. This is to cause the materials to bond and mesh. The pellets are taken out of the furnace and measured for dimensions and mass. Once analyzed, they were cut into rectangular shaped bars, re-examined for mass and dimensions and placed onto flash cards. Conductive paint was placed on both ends of the material. Copper wire was also attached to the material to perform a 4-probe analysis with voltage going across it and current running through it. The x=.3 and x=.4 were fabricated and analyzed using the same procedures.

Data Analysis and Results

Samples were fabricated using the procedures previously mentioned. Upon the fabrication each sample was analyzed for physical properties. Both (x=0.3, 0.4) samples displayed ferromagnetic metallic behaviors. Where x=0.3, the sample is referred to as 270614; and 010714 for x=0.4. The samples were cut into a rectangular shape to produce several bars (bars are indicated by letters [A,B,C] at the end of the sample identification number) to be tested for its resistivity, V-I characteristics, and the effects of UV radiation. Resistivity is given by

$$\rho=\frac{RA}{l},$$

where R is the resistance of the material, A is the cross-sectional area (width*height) and l is the length between the conductive silver paint.

The mass of 270614 before it was pressed was 1.831 grams. After it was pressed and sintered, its mass reduced to 1.752 grams. Its diameter is 11.25mm and its thickness is 1.25mm. The fabrication of 010714 produced two pellets. After the decarbonizing process, there was 2.677 grams of material (powder form). The synthesis of the pellets produced a 1.208 gram pellet and a 1.287 gram pellet. The diameter was 12.9mm with a thickness of 2.1mm and 11.9mm with a thickness of 2.9mm, respectively. Further measurements of the samples are listed in the charts following.

Table I. Dimensions of 270614A

Length (mm)	Width(mm)	Height(mm)
4.9	3.1	2.1
4.5	3.5	2.1
4.7	3.5	2.1
4.6	3.5	2.1
4.2	3.6	2.1
4.1	3.1	2.1
4.1	3.1	2.1
4.3	3.3	2.2

Table II. Dimensions of 270614B

Length(mm)	Width(mm)	Height(mm)

7.0	4.1	2.1
7.1	3.5	2.0
7.1	2.8	1.9
7.1	3.1	1.4
6.8	4.0	2.1
7.1	4.0	2.2
7.2	3.9	1.8
7.1	4.1	1.1

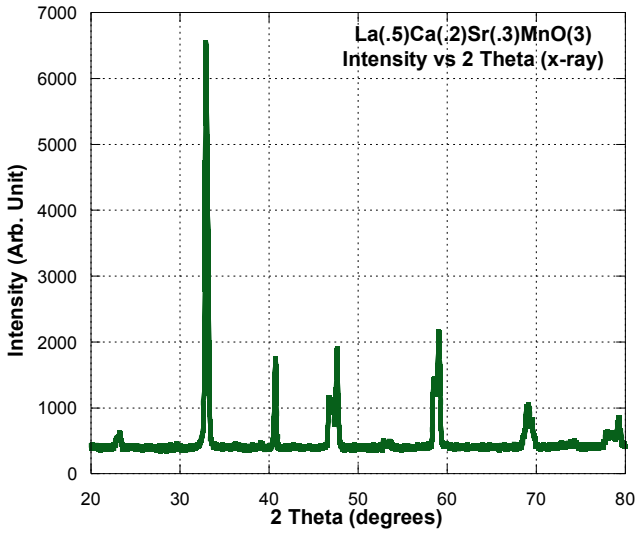
Table III. Dimensions of 270614C

Length(mm)	Width(mm)	Height(mm)
3.9	1.0	2.2
3.1	1.8	2.2
3.9	2.0	2.2
4.0	2.0	2.3
3.89	2.0	2.2
3.9	1.1	2.2
3.9	2.0	2.5
4.1	1.5	2.7

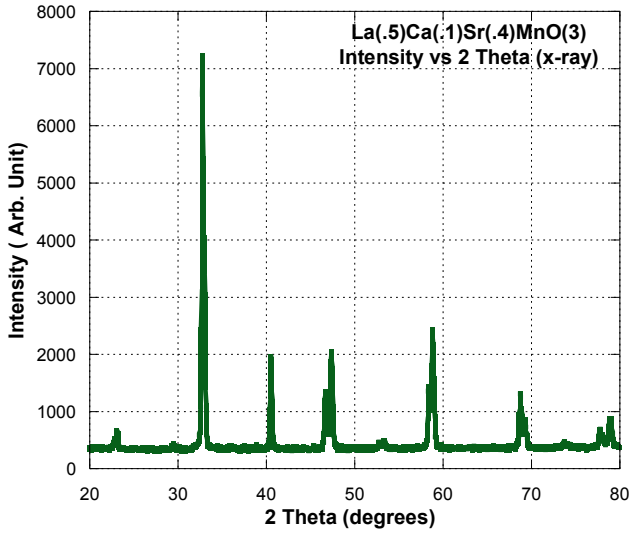
Table IV. Dimensions of 010714A

Length(mm)	Width(mm)	Height(mm)
5.1	4.0	1.8
5.22	4.0	1.8
5.2	3.1	1.8
5.1	3.6	1.7
5.5	4.0	1.8
5.4	4.0	1.8
5.9	4.1	1.8
5.8	4.1	1.8

Graph I. Intensity vs Angle (2Ɵ) for x=.3



Graph II. Intensity vs Angle (2Θ) at x=.4



Sample Identity ↓	Properties Found →	h (height)	w (width)	l (length)	R (electrical resistance)	ρ (electrical resistivity)	A (Atomic spacing)
270614A (x=.3)		2.11 mm	3.34 mm	4.425mm	5.6375×10^{-2} Ω	8.978×10^{-2} Ωm	33.0 nm
010714A (x=.4)		1.788 mm	3.86 mm	4.89 mm	7.8675×10^{-3} Ω	1.1101×10^{-3} Ωm	38.5 nm

The calculations used to determine the resistivity and atomic spacing were based off the average values from the previous tables.

Conclusion

The results suggests there is an internal process occurring at x = 0.3 that doesn't occur in the other variables. The trend for the atomic spacing at x = 0.4 exhibits similar traits to the other values (excluding x=.3). Resistance at room temperature was fairly low. Also, the exposure to UV radiation had no effect on the material[Ref]. Further research may want to focus on where the deviation in x=.3 begins. For example, studies of x=2.95 or 2.98 and x=3.02 and 3.05 may expose where the atomic spacing begins to deviate out of the range of 3.82-3.85 nm.

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