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Superconducting Phases in Bulk and Thin Film LA_2CuO_4

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Brandon is a junior majoring in Physics. He conducted this research under the mentorship of Dr. Hashini Mohotalla with the funding of an Adrian Tinsley program grant.

Abstract

La_2CuO_4 is considered as the parent material of all high temperature superconductors. The magnetic nature of the material is antiferromagnetic and it is an insulator. During this research we produced a superconductor by doping ceramic La_2CuO_4 with excess oxygen. There are different methods to intercalate excess oxygen into a sample, but in this project we used an electrochemical method. After oxidation, the superconducting properties were measured using a Quantum Design MPMS SQUID magnetometer. The superconducting transition temperature (T_C) was observed near 40 K with a superconducting volume fraction of 16%. Further oxidation increased the superconducting volume fraction to 48.3% with the same observed T_C. According to previous work, super-oxygenated La_2CuO_{4+y} material phase separates into an oxygen rich superconducting phase with a T_C near 40 K and an oxygen poor magnetic phase that also orders near 40 K. In order to study the magnetic phase closely, we grew a thin film with thickness near 200nm of La_2CuO_4 on a $LaAl_2O_3$ substrate using a Pulse Laser Deposition (PLD) chamber. We checked the epitaxial growth of the film using an X-ray diffraction technique and verified that the thin film was grown correctly. We found that the electrochemical technique is not suitable to dope excess oxygen into the thin film because it ruins the surface. Therefore, as a part of this project we designed an ozone generation system to attach to the PLD. This will help us to grow thin films in an oxygen rich environment and produce superconducting films with better surface qualities.

I. Introduction

High temperature superconductors are considered to be an essential part of condensed matter Physics. The phenomenon of superconductivity is characterized by conduction of electricity without resistance when cooled below its critical temperature (T_C), as well as by the repulsion of magnetic field known as the Meissner effect [2]. Based on this theory, current can flow continuously in a closed loop of superconducting material with 100% efficiency.

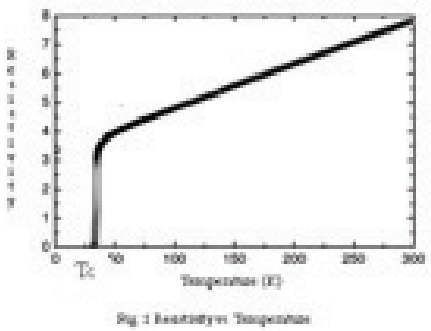


Fig.1 shows that when a material is cooled below Tc, resistance drops to zero. When this happens, the material becomes superconducting. As you can see, these temperatures can be extremely low. The critical temperature in this graph is below 50K.

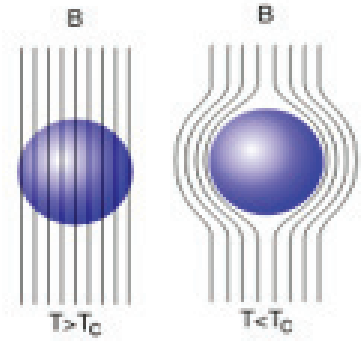


Fig. 2 displays the Meissner effect. On the left, magnetic field lines are going through the material because temperature is less than Tc. On the right we see repulsion of magnetic field lines because the temperature is less than Tc.

There are two types of superconductors, namely Type I and Type II. Type I superconductors are composed of metals and metalloids that show some conductive properties at room temperature. They require incredibly low temperatures to slow down molecular vibrations sufficiently enough to facilitate unimpeded electron flow. Electrons with opposite spin can become paired, forming Cooper pairs, which allow this unrestricted current. Type II superconductors are usually comprised of metallic compounds and alloys. They are mechanically harder than Type I and exhibit substantially higher magnetic fields. The first High T_C superconductor, $La_{2-x}Ba_xCuO_4$, was discovered in 1986 by Bednorz and Muller; they later won Nobel Prize in Physics in 1987 [5]. Based on the observed properties in type II superconductors, we can assume that this might play an important role in searching for a solution to the current energy crisis.

II. Why La_2CuO_4?

Since the material was readily available to us at the University of Connecticut, and La_2CuO_4 has a simple structure compared to other high T_C superconductors (Fig. 4, 5), it is an ideal system to study. La_2CuO_4 is an antiferromagnetic insulator at room temperature unless oxidized or a divalent cation is introduced into the system (Fig. 3) [4].

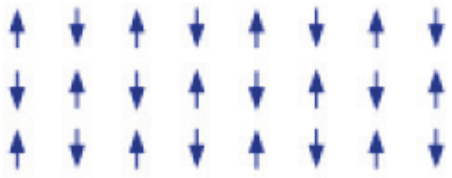


Fig. 3 is a depiction of antiferromagnetism. The spins of electrons align in a pattern which point in opposite directions. In general, antiferromagnetic materials exhibit this pattern at lower temperatures.

When a Lanthanum (La) ions are replaced by a divalent cation (e.g. Strontium – Sr, or Barium -Ba), or when the material is oxidized, the system shows superconducting properties at temperatures below 40K. When excess oxygen is added to the system, instead of it occupying chains in the structure, it goes into interstitial sites.

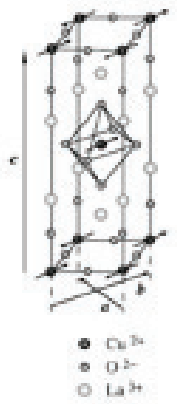
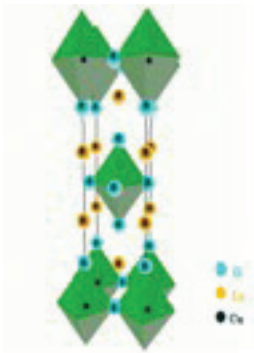


Fig. 4 this is the structure of La2CuO4, it has the simplest structure among all high temperature superconductors. The structure is orthorhombic at room temperature.

Fig. 5 is another diagram of the orthorhombic structure of La2CuO4.



We report on the experiments conducted and their results below. In Section III we discuss the oxidation of our sample and the method used. Section IV explores the experiments done with the SQUID magnetometer and the results obtained. Using the Pulsed Laser Deposition chamber as well as thin film growth is explained in Section V. Characterization of the film with the X-ray Diffractometer is analyzed in section VI, and future work with ozone is discussed in section VII including research, design, and benefits of using an ozone generation system.

III. La_2CuO_4 Bulk Sample Oxidation via Electrochemistry

Oxidation of our sample was essential in our research because it changes the properties of the sample from insulating to a superconducting. After making a 0.4 M solution of NaOH, we made an electrochemical cell as shown in Fig. 6. In order to setup the cell, we cleaned three platinum wires and used them as our three electrodes; working electrode (WE), Counter electrode (CE) and the reference electrode (RE). The sample was wrapped using a Pt mesh and attached to the WE. Since platinum is a good conductor, tightly wrapping the sample with it promotes electrical flow across the RE and WE so the circuit is complete and Oxygen atoms enter the system. We applied .78 V through the cell to start the oxidation process and waited five days.

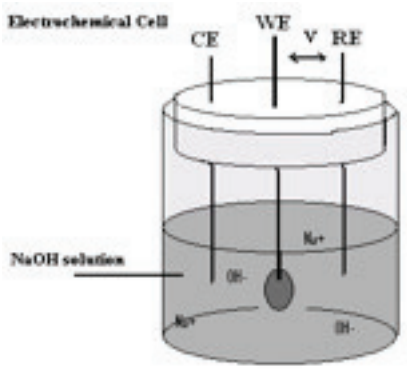


Fig. 6 is a diagram of the electrochemical cell. Electrodes are labeled from left to right as Counter Electrode, Working Electrode, and Reference Electrode.

During oxidation, we checked the voltage frequently to make sure it was near .78 V. It was important to monitor the voltage to make sure it did not go above .90 V as it reverses the desired reaction in the solution.

The oxidation reaction inside the cell is as follows:

$$La_2CuO_4 + 2yOH^- \rightarrow La_2CuO_{4+y} + yH_2O$$

As seen in the reaction above, changing the solution is essential because the oxygen gradually gets used up over time as the oxidation reaction occurs.

IV. SQUID Experiments

The Superconducting Quantum Interference Device (SQUID) is a very sensitive magnetometer used to measure extremely small magnetic fields. This probe was used on La_2CuO_{4+y} bulk material to figure out how much of our material was superconducting and to determine the T_C. We also used the SQUID on the as grown sample as well as the oxidized bulk sample to measure the magnetic ordering temperature. The temperature dependence of the magnetization scans are shown in Fig. 7.

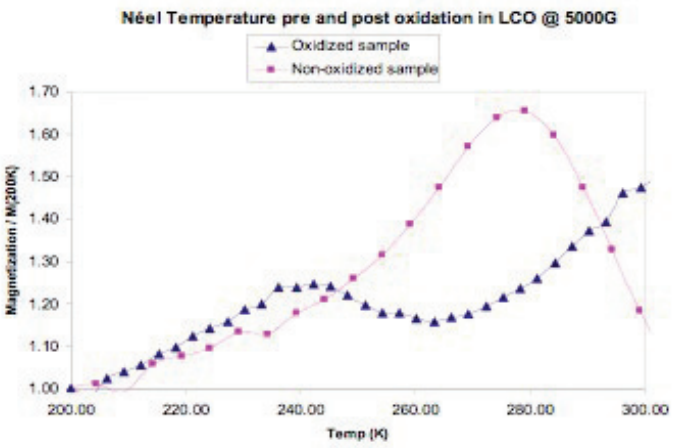


Fig.7 is a normalized graph of Magnetization vs. Temperature. This graph indicated the Neel Temperatures of both as grown and oxidized samples.

The measured temperature was slightly lower than expected (~279K). Since the ordering temperature of the as grown sample should be between 280K and 320K [1], we think this could be due to the fact that the sample was aged and had been sitting at standard atmospheric conditions. If a sample is aged, this means that oxygen can work its way into the system over time. If this happens, the ordering temperature will be slightly lower than expected.

Another SQUID experiment shown in Fig. 8 (scan done at 20 G), measured the diamagnetic response of our oxidized sample. Diamagnetism is the weak repulsion from a magnetic field, and can properly be observed in certain substances in the presence of an external magnetic field using the SQUID magnetometer. When we measure the diamagnetic response of a sample, we can use the data to calculate the superconducting volume fraction (V_{SC}).

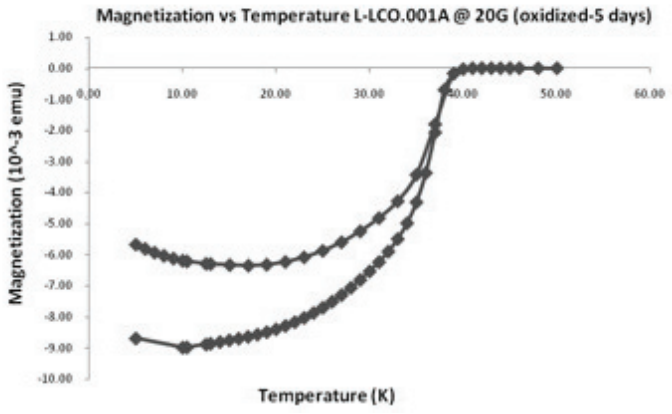


Fig. 8 is a graph of magnetization vs. temperature. This is the diamagnetic response seen for La2CuO4+y. These are the values received after oxidizing the sample for five days.

The Meissner effect shows that a superconductor behaves as if B=0 inside the sample. We can obtain a useful equation from this assumption to calculate $V_{SC.}$ The equations are as follows (EQ. 1, 2)

$$B = H + 4\pi M = 0$$

$$\frac{M}{H} = -\frac{1}{4\pi}$$

Where M is the magnetization and H is the applied field. Using Eq. 2, we can calculate V_{SC}. Since we can rewrite M = $\mu\mu$/V, $M = \frac{Ba}{V}$ Eq. 2 can be expressed as follows:

$$4\pi \frac{Ba/V}{H} = -1$$

Where $\mu\mu$ is the magnetic moment measured, V is volume, and H is the field applied. Since we know that density is $\rho = \text{mass}/V$ $\rho = \text{mass}/V$ we can make a substitution for V and obtain:

$$\frac{Ba\rho}{mH} = X$$

Eq. 4 is called the volume susceptibility, and we can therefore express an equation to figure out how much of our material is superconducting.

$$Vsc = 4\pi X = -1 \quad 100\% \ superconducting$$

As you can see by Eq. 5, we have expressed the superconducting volume fraction, and can now calculate how much of our sample is superconducting after the five day oxidation process.

$$4\pi \frac{(-6.33x10^{-3})(7)}{(.1749)(20)} = -.159178$$

$$= 16\%$$

We can see from our calculations that our sample is 16% superconducting. We decided to put the sample back into oxidation for a few more weeks. The sample was taken out and followed the same procedure to get the temperature scans of magnetization using the SQUID magnetometer.

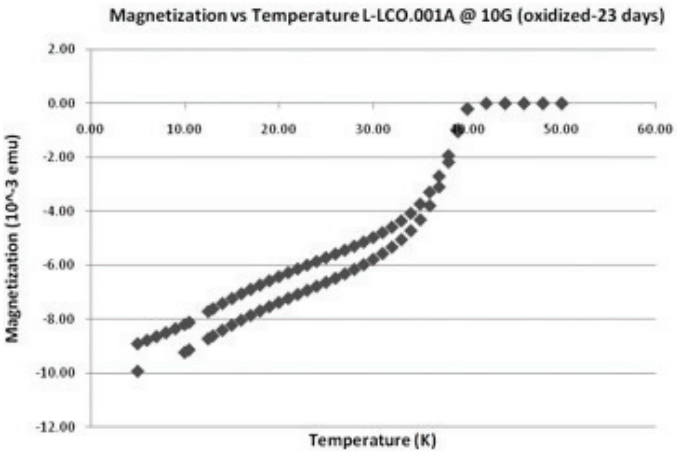


Fig. 9 is another graph of magnetization vs. temperature. This is the second scan done on the sample after the 23 day oxidation process.

As shown in Fig 9, the diamagnetic fraction is larger than before. This scan was done with a 10 G applied magnetic field.. The response is not as clear as the first scan; this is believed to be caused by impurities as well as the non-homogeneous distribution of oxygen in the system. We baked the sample at 100° C to correct this problem. We used Eq. 5 again to calculate the superconducting volume fraction:

$$4\pi \frac{(-6.73x10^{-3})(7)}{(.1749)(10)} = -.483543$$

$$= 48.3\%$$

From this calculation, we see the sample is 48.3% superconducting. Clearly, from the experimental results, V_{SC} increased as a function of time.

V. Pulsed Laser Deposition (PLD)

The PLD, shown in Fig. 10, is used to grow thin films of the materials that we are interested in. The reason why we study thin films is because it allows us to characterize the local structure of a material. With bulk material, there are complications in studying the local structure due to the atomic interactions inside the solid.

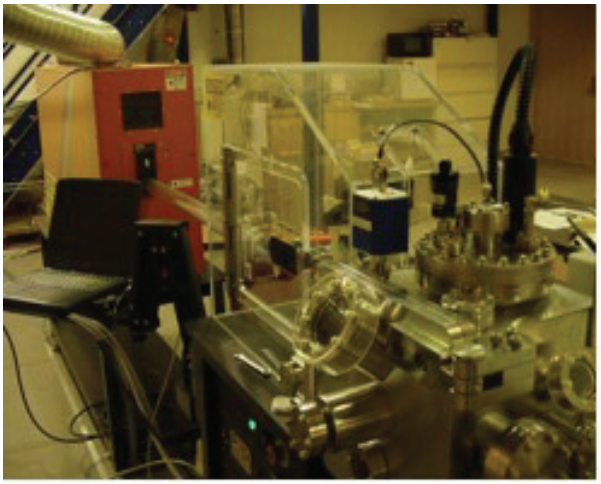


Fig. 10 is a picture of the PLD used at The University of Connecticut. A Class IV laser travels into the optics chamber which gets reflected into the sample chamber. The sample target is mounted inside and is blasted by the laser which produces a plume of plasma that deposits onto the substrate. This is all done over a course of a day.

The Class IV laser pulses a beam which travels into the optics chamber where it is reflected and goes into the metal growth chamber seen on the far right. Inside the chamber we mounted a sample target of La_2CuO_4 (LCO) that was ablated and the result was a plume consisting of the target material. Inside the plume are stoichiometric proportions of lanthanum, copper, and oxygen. The plume then deposited onto a 1 cm^2 piece of $LaAl_2O_3$ (LAO) substrate which was mounted directly above the target. The reason for choosing LAO as the substrate was because it is oriented in the (001) direction and has a similar a-b lattice parameters to the La_2CuO_4 material. This is essential to thin film growth, because it will not grow properly if the structures are not aligned correctly. For growth conditions during this experiment, we had a substrate temperature of 800° C, a chamber pressure of $2.9x10^{-6}$ Torr, laser energy 0.2523J (frequency ~4Hz), and a growth time of 10 minutes. The thin film is about 200 nm thick, and the LAO substrate is about 2mm thick. Although the growth time seems short, the entire process can take up to a day because of the precision of keeping the chamber under vacuum (pressure goes up while heating). After the film is grown, we took it out of the chamber and prepared it for X-Ray Diffraction experiments to check if the film was grown correctly.

VI. X-Ray Diffraction Experiment

This experiment can be used on both powders as well as thin films. With thin films, this experiment is very helpful because it verifies that the thin film has grown with the proper orientation. The X-Ray Diffractometer was used on the LCO thin film (Fig.11, 12). Since the substrate used was LAO (001), any peaks we see on the results of the X-Ray Diffraction experiment must show the film was epitaxially grown (along the (00*l*) plane). We verify this using Bragg's Law:

Using lattice parameters a, b, c, and Miller Indices (*hkl*), a relationship can be expressed as follows:

$$n\lambda = 2d\sin\theta$$

Because the film is epitaxially grown along c axis, only (00*l*) peaks will appear. (h = k = 0)
We can then rewrite Eq. 2 as follows:

$$d = \frac{1}{\sqrt{\left(\frac{h}{a}\right)^2 + \left(\frac{k}{b}\right)^2 + \left(\frac{l}{c}\right)^2}}$$

With Eq. 3, we can substitute our solution for d into Eq. 1. Assuming n = 1, we obtain:

$$d = \frac{1}{\sqrt{\left(\frac{0}{a}\right)^2 + \left(\frac{0}{b}\right)^2 + \left(\frac{l}{c}\right)^2}} = \frac{1}{\sqrt{\left(\frac{l}{c}\right)^2}} = \frac{c}{l} \qquad (3)$$

Based off of this equation, we can generate a set of 2Θ values specific to our material. We know c, λ is wavelength of the X-Rays emitted by the Diffractometer, and l is any integer. These 2Θ values can be compared with the results given by the experiment and any epitaxial peaks not shown on the X-Ray Diffraction results is may indicate a poorly grown film. If the results of the experiment however show all peaks generated, then we can conclude that the film is grown properly.

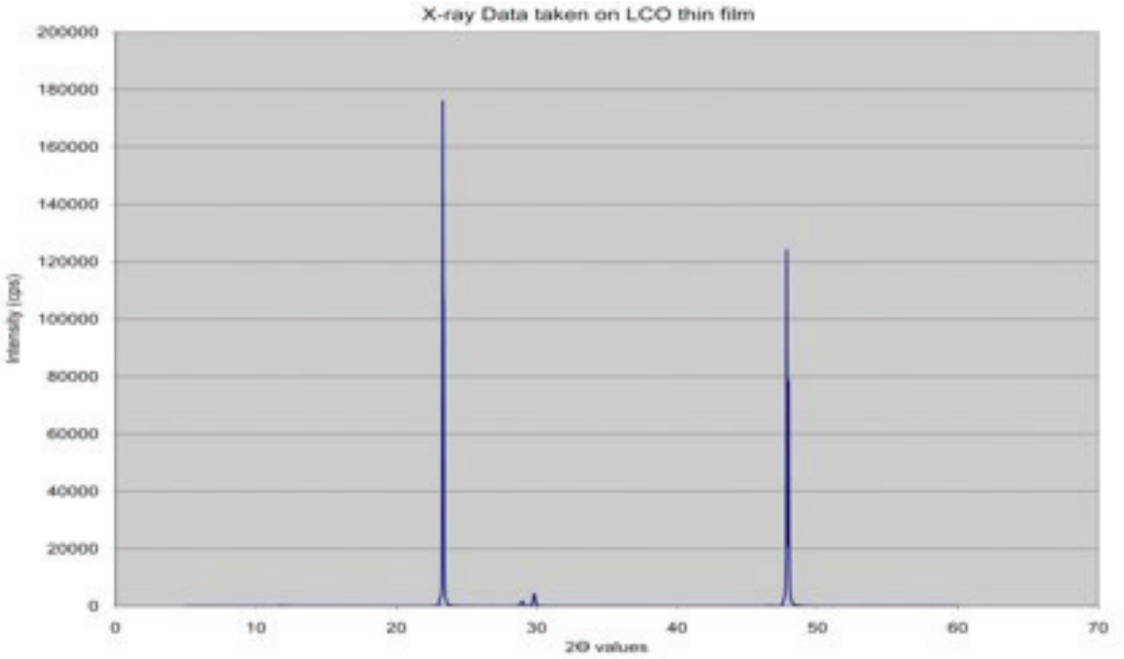


Fig.11 is Intensity vs. 2Θlinear scaled graph of the X-Ray Diffraction experiment. Only LAO substrate peaks are visible on this scale.

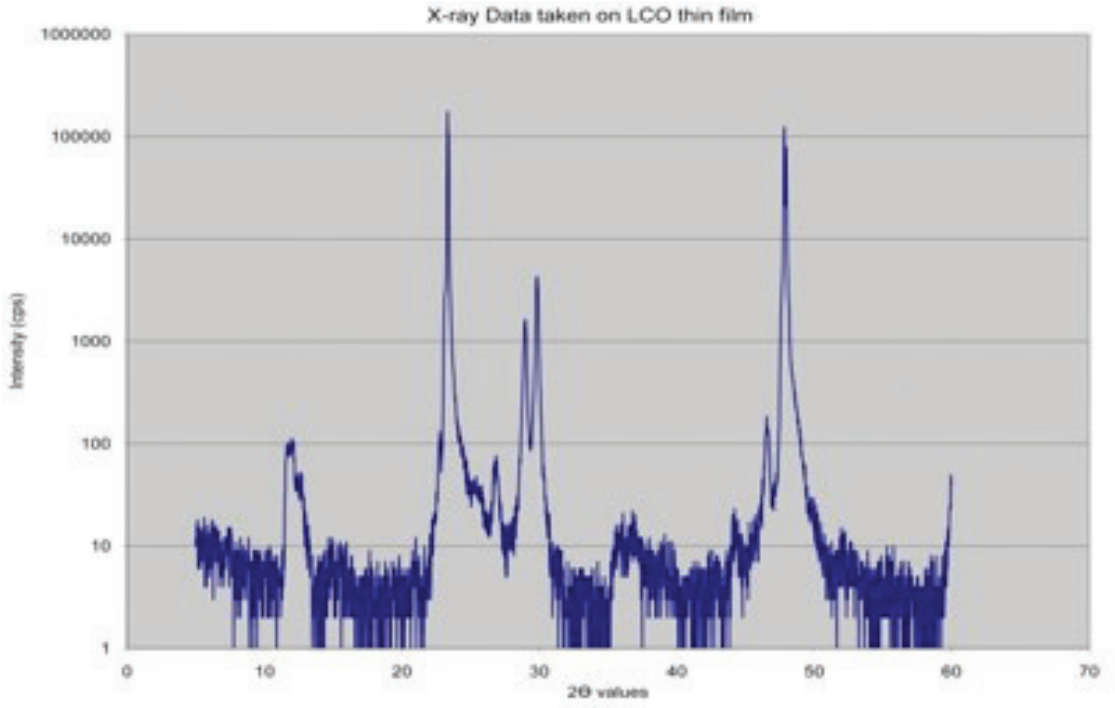


Fig.12 is Intensity vs. 2Θlogarithmic scaled graph of the X-Ray Diffraction experiment. Thin films as well as LAO substrate peaks are visible on this scale.

As shown in Fig. 11, from the X-Ray, substrate peaks are substantially larger than the films from the LCO thin film. Since the substrate is much thicker than the thin film, it gives a larger signal than the thin film. If we change the axis to a logarithmic scale (Fig. 12), we can see the LCO thin film peaks along with the LAO substrate peaks.

VII. Ozone Generation

The electrochemical oxidation method is harmful to the thin film surface. As a result, ozone has been researched as an oxidizing agent for our thin films. Ozone is a powerful oxidizer. An ozone generator (Fig. 13) has been designed, built, and awaits testing. It will eventually be used in the PLD system to grow thin films in an ozone rich environment. This method is beneficial because it does not damage the thin film surface, and the samples are expected to be superconducting after growth in the PLD.

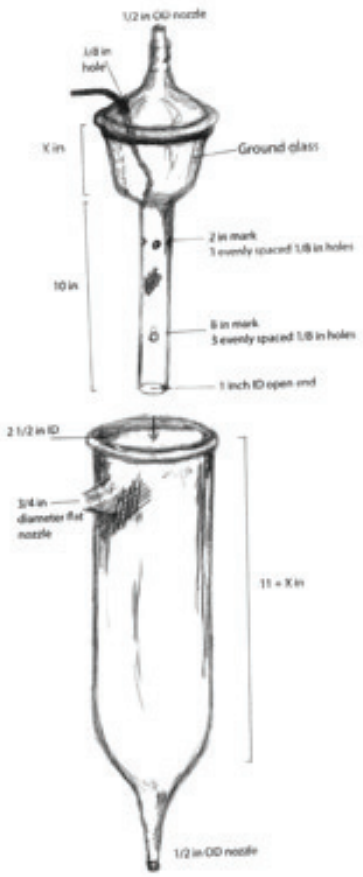


Fig. 13 is a schematic drawing of the Ozone Generator. Design done by Brandon Green.

Our primary focus for ozone generation is based off of the idea of a corona discharge created between two conducting plates. The amount of ozone produced is inversely proportional to the gap between the plates. The other contributing factors to the amount of ozone produced are the amount of voltage applied across the cell, as well as the flow rate of oxygen into it [3]. The two glass tubes are lined with an aluminum mesh to act as the two conducting plates. Oxygen is flowed through the top and goes into the cell. As it flows in, the bottom of the inner tube is corked, forcing flow out of the holes drilled in the inner tube. This causes the gas to travel through the gap between the two conducting plates which drive the reaction to produce ozone. A voltage of ~10kV and a frequency of 18 – 21 kHz are essential to drive the reaction [1]. If successful, this ozone generator will allow The University of Connecticut's Condensed Matter Physics group to add this system to their Pulsed Laser Deposition chamber. The benefit of adding this generator to the PLD is that it will allow thin films to be grown in an ozone rich environment, which will produce films that are already oxidized with a smooth surface. Unfortunately, we have not had the chance to test the generator yet because of the lack of essential supplies that allow the running of this experiment safely.

Conclusion

The electrochemical method of oxidation was successful in producing a superconductor from the ceramic bulk La_2CuO_4 material, T_C was near 40K. The La_2CuO_4 thin film was successfully grown in the PLD. The X-ray Diffractometer gave data showing that the thin film was successfully grown in the (00*1*) direction. This film has been oxidized via electrochemistry and still awaits SQUID results. The ozone generator has been built and it is hoped that it will eventually be added to the Pulsed Laser Deposition chamber to grow thin films in an ozone rich environment. The two oxidation methods will be compared, and it is hoped the ozone generator will produce superconducting films with undamaged surfaces.

Parts of this research project still remain unfinished, but the experiments conducted showed strong success. We hope to continue my work with researching an ozone generation system, and test my design. If we can produce an oxidized thin film out of the chamber, it could mean better experimental results.

Acknowledgements

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