

GROWTH OF $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ WITH ENHANCED FLUX-PINNING PROPERTIES

by

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DEPARTMENT APPROVAL

of a senior thesis submitted by

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This thesis has been reviewed by the research advisor, senior thesis instructor,
and department chair and has been found to be satisfactory.

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ABSTRACT

GROWTH OF $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ WITH ENHANCED FLUX-PINNING PROPERTIES

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Superconductivity was discovered in 1911, and high-temperature, type-II superconductivity was discovered in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ in 1986. $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ has one of the highest recorded T_c s among superconductors. This makes $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ one of the most interesting and easiest superconductors to study, because liquid nitrogen can be used to cool the superconductor below the transition temperature (T_c). I present a method for making $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ bulk superconductors that demonstrate flux pinning properties using the Melt-Textured growth process. Various problems with growth were identified throughout the fabrication process. Precursor powders, granularity, crucible materials, impurities, temperature control, and furnace calibration were identified as possible problems that impeded the growth of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ crystals. Ultimately, I succeeded in growing both a 1.5" diameter $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ puck that could levitate and maintain superconductivity for up to 45 seconds (uninsulated), as

well as a smaller puck that could demonstrate both levitation and enhanced flux-pinning properties.

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Chapter 1

Introduction

1.1 Historical Context

In 1822, Michael Faraday liquefied Chlorine gas, igniting one of the fiercest competitions amongst scientists to date. After liquefying a number of other gases, Faraday found a small set of gases that would not liquefy despite his best efforts using the technology available to him at the time. Hydrogen, oxygen, nitrogen, carbon monoxide, nitric oxide and the yet to be discovered gas Helium, were thought to be permanent gases, gases that could not be liquefied. Two laboratories became the effective front lines in the war to see who could first liquefy these permanent gases. The first lab was headed by the famous experimentalist, James Dewar, and the second by Dutch physicist, Heike Kamerlingh-Onnes. These two personalities would dominate the field of low temperature physics for nearly twenty years. Each raced to liquefy hydrogen, which at the time, was thought to have the lowest temperature in liquid form of any of the permanent gasses. However, in 1895 helium became available on the earth for the first time. Helium was predicted to have an even lower boiling point. At this time, Heike Kamerlingh-Onnes decided that he should forgo the liquefaction of hydrogen

and instead focus on liquefying helium. The Dutch physicist succeeded in liquefying helium in 1908. Physicists and chemists now had a new medium in which to perform experiments at the extremely low temperature of 4.22K [1]. And, with the use of machine pumps, the temperature can be lowered to as little as 1.5K.

It was with this new low temperature liquid that Kamerlingh-Onnes sought to answer one of the most puzzling questions of the day: how does the resistance of an object behave at low temperatures? The experimental data showed that as the temperature of a material decreased, its resistance also decreased. The ability to examine the behavior of materials at low temperatures had reached a relative standstill until the development of readily available liquid helium.

There were a number of theories about the nature of resistance at low temperatures. One theory suggested that the resistance would level off somewhere above zero, while still another theory predicted the resistance to increase. To settle the debate, Kamerlingh-Onnes conducted an experiment using an extremely pure sample of mercury. This experiment consisted of dropping the temperature of the mercury to the temperature of liquid helium and recording the resistance as the temperature decreased. At 4.2K the resistance of the sample of mercury suddenly vanished. The Dutch physicist had serendipitously discovered superconductivity.

As new superconductors were discovered a pattern began to emerge. All of the single element superconductors enter the superconducting state at low temperatures, from 1K-10K. The diatomic superconductors transition into the superconducting state in the range of 5K-30K. As superconductors of increasing complexity were discovered, 3 element, 4 element, and more recently 5 element superconductors had an increasing range of transition temperatures (Table 1). The highest recorded transition temperature, at atmospheric pressure, belongs to mercury barium calcium copper

Table 1. Transition temperatures increase with molecular complexity

Superconductor	# of Elements	# of Atoms	T_c
Al	1	1	1.2K
Hg	1	1	4.2K
NbN	2	2	15.7K
V ₃ Si	2	4	16.9K
Nb ₃ Sn	2	4	17.9K
Nb ₃ (AlGe)	3	5	20.7K
YBa ₂ Cu ₃ O _{7-δ}	4	≤ 13	93K

oxide, with a transition temperature (T_c) of 138K.

Superconductors became a popular subject of research among scientists. In 1933 Walther Meissner and Robert Ochsenfeld cooled lead down to its superconducting transition temperature of 7.2K. Once in the superconducting state, an external magnetic field was applied to the lead. The defining property of a superconductor is the complete absence of resistance below the critical temperature. As a result, electric currents can be formed within the superconductor at no energetic cost to the superconductor. Electric currents give rise to magnetic fields, thus when the lead was exposed to an external magnetic field the superconductor formed its own magnetic field that opposed the applied field. This creation of a magnetic field to oppose an applied field is referred to as *diamagnetism*, and in superconductors, which expel the entirety of the applied field, is referred to as *perfect diamagnetism*. The perfect diamagnetism exhibited by superconductors is called the *Meissner effect* in honor of its discoverer(Fig.1.1).

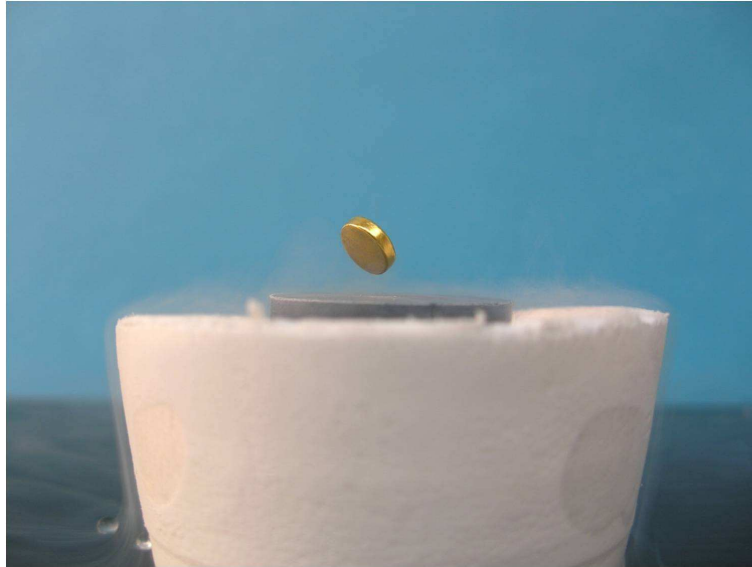


Figure 1.1 The Meissner effect demonstrated by a YBCO superconductor sitting in a styrofoam cup filled with liquid nitrogen and a small, gold colored neodymium magnet.

1.2 Theory

Superconductivity is a physical phenomenon that could not be explained in classical terms, because superconductivity is an inherently quantum phenomenon. A conductor consists of two main components: the atomic nuclei that form the lattice and the valence electrons that are free to conduct electricity. The lattice is free to vibrate. Certain lattice vibrations are quantized and these quantized vibrations are known as phonons. These quantized vibrations in the superconducting state can be used to “communicate” between electrons.

Classically, as an electron travels through the lattice, the coulomb force attracts the atomic nuclei that form the lattice. These nuclei pull in and free up the path for another electron moving in the opposite direction. The second electron can now move more freely. The interaction between these two electrons, the Cooper pair (Fig. 1.2), is mediated by the motion of the lattice i.e. phonons. This was first proposed by John

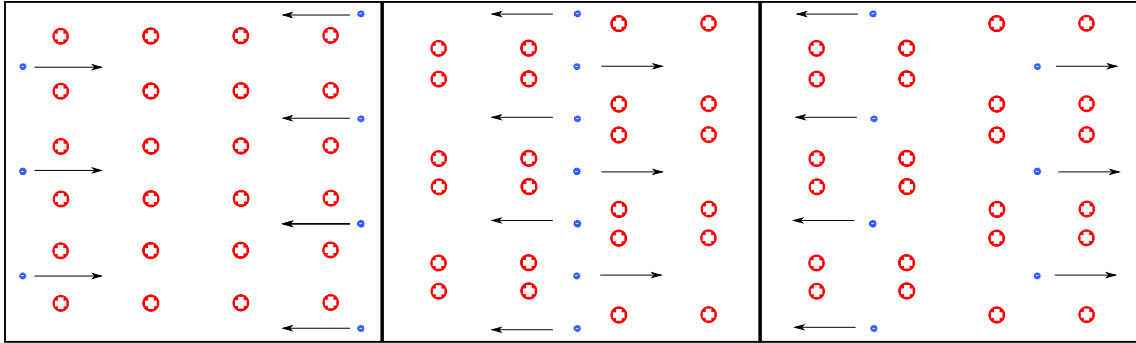


Figure 1.2 This sequence shows the procession of electrons through the lattice when the solid is in the superconducting state. The red circles represent the nuclei that make up the lattice, and the blue circles represent the electrons moving through the lattice. Electrons passing through the lattice attract the nuclei and deform the lattice. This deformation of the lattice enables an electron with different spin to move through the space more freely than through the unperturbed lattice. The electrons of opposite spin are coupled through the lattice vibrations, and are called Cooper pairs.

Bardeen, Leon Cooper, and John Robert Schrieffer. Their theory would come to be known as BCS theory and would completely explain conventional superconductivity.

As the investigation into superconductivity continued, a number of superconductors were found to exhibit a different set of properties than those superconductors previously studied. These would come to be called Type-II superconductors. Type-II properties arise from a “mixed state”, where there are inclusions of non-superconducting regions inside a superconductor (Fig.1.3). This is different from Type-I superconductors are either in the superconducting state, or not. Non-superconducting regions allow an applied magnetic field to pass through the mass of the superconductor. The non-superconducting regions are bounded by loops of electric current, or vortices, which occur randomly in a pure single-crystal type-II superconductors.

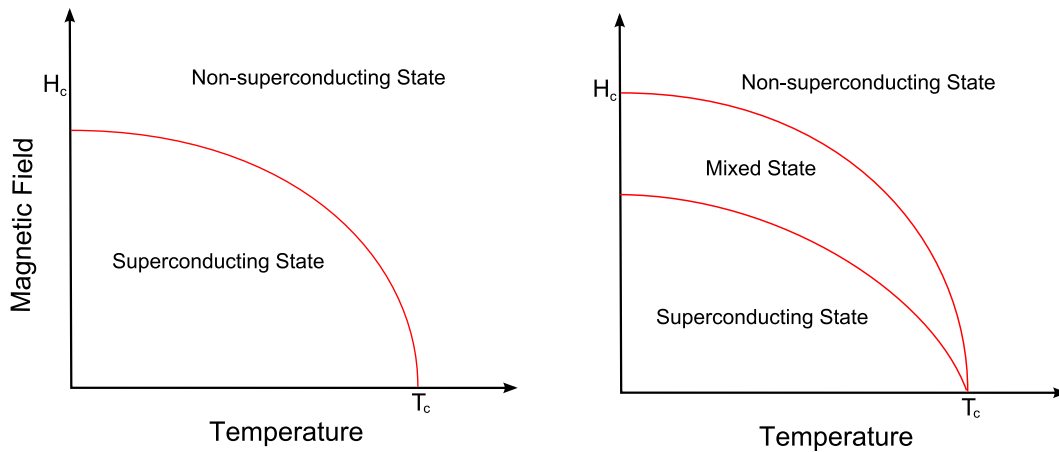


Figure 1.3 A characteristic graph of the boundaries of the transition from non-superconducting to a mixed state to normally superconducting.

Vortices tend to occur at places that are already prone to low levels of superconductivity, such as crystal grain boundaries and impurities. As a result, vortices remain at fixed physical locations in polycrystalline and impure superconductors. The magnetic field that passes through these vortices is given a preferred path through the superconductor. A Type-II superconductor has a preferred orientation in a magnetic field. The flux lines are pinned to their locations within the bulk of the superconductor and are often referred to as “flux-pinned vortices”. Thus a Type-II superconductor exhibits the type I property of canceling magnetic fields throughout its bulk (diamagnetism), but also has flux-pinned vortices the superconductor can levitate, and maintain its position and orientation in an applied magnetic field (Fig.1.4).

Bardeen, Cooper, and Schrieffer could only explain superconductivity up to a maximum temperature of 30K. However, in 1986, a superconductor was recorded as having a T_c of 35K. The following year, $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (YBCO, or Y-123) was discovered, with a T_c of 93K. This was a revolution in the field of superconductivity for two main reasons. First, that superconductors can now be studied using liquid

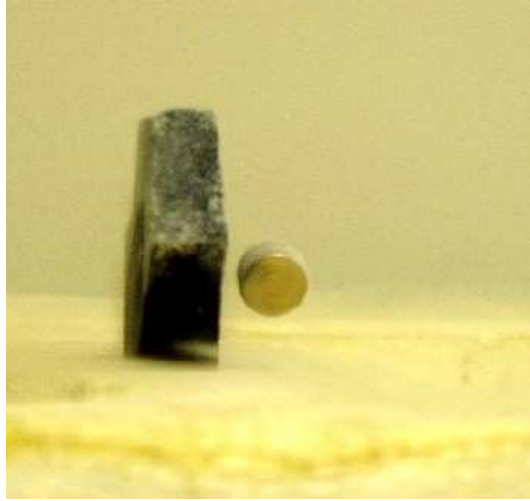
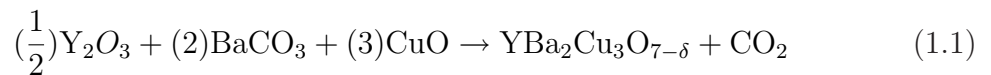


Figure 1.4 A black superconductor sitting on its edge with a small magnet pinned above the surface of the superconductor (In this picture the top edge of the image is up) [2].

nitrogen, which is much cheaper than liquid helium which normally is required for the study of conventional, low temperature superconductors. The second reason is that it provided the scientific community with a new, unexplained phenomenon to study. As yet, there are still a number of competing models that seek to explain this physical effect, but no consensus has been reached about the cause of superconductivity at high temperatures, within the scientific community.

Despite the physical complexity associated with explaining superconductivity, superconductors remain relatively simple to make. All that is necessary to make $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ is to carefully adhere to a specific recipe. Begin by mixing together the chemical compounds that contained the desired elements according to a this formula:



where (Y_2O_3) is yttrium oxide, (BaCO_3) is barium carbonate, and (CuO) is cop-

per(III) oxide. These “precursor powders” must be mixed thoroughly and ground to a uniform particle size. To make a bulk superconductor the precursors must be pressed in a pellet. This pellet must then be fired according to a specified heating profile.

The final product should be a puck-shaped superconductor of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. This stoichiometric equation contains a term that reads: $\text{O}_{7-\delta}$. This is because the amount of oxygen varies and can even be adjusted by further annealing of the puck. The purpose of annealing is to increase the amount of oxygen to an optimal level. If there is too much oxygen ($\delta = 0$), the T_c will drop from 93K to as low as 87K. However, if there is too little oxygen, then the T_c can drop to well below 77K. The minimum oxygen required to achieve superconductivity in YBCO above 77K is $\delta = 0.2$.

A discussion of the fabrication of superconducting pucks would not be complete without a discussion of impurities. As mentioned earlier impurities determine the placement of the flux pinning vortices as well as the quality of the superconductivity of the puck. Therefore, a careful balance must be struck when dealing with impurities. Too few impurities, and there won't be enough places for flux-pinned vortices to form readily, while too many impurities would completely destroy superconductivity altogether. By carefully preparing an extremely pure sample of YBCO and including an equally regulated amount of impurities, it is possible to augment the physical properties of the superconductor. Determining the level of impurities required to meet minimum for prominent flux-pinning while simultaneously maintaining the proper crystal structure to support strong magnetic levitation is a complicated process and will be discussed further on.

1.2.1 Melt-Textured Growth

Melt-textured growth is a process by which superconductors can be imbued with enhanced flux pinning properties. Melt-textured growth (MTG) works by utilizing

the properties of materials at differing temperatures. By examining the phase diagram for a particular mixture of elements, and looking at what compounds form and at what temperature, MTG can control the formation of impurities and affect the changes in the internal structure by directly controlling the environment the superconductor is grown in. To form crystals, I added unit cells to lattice causing the appearance of growth.

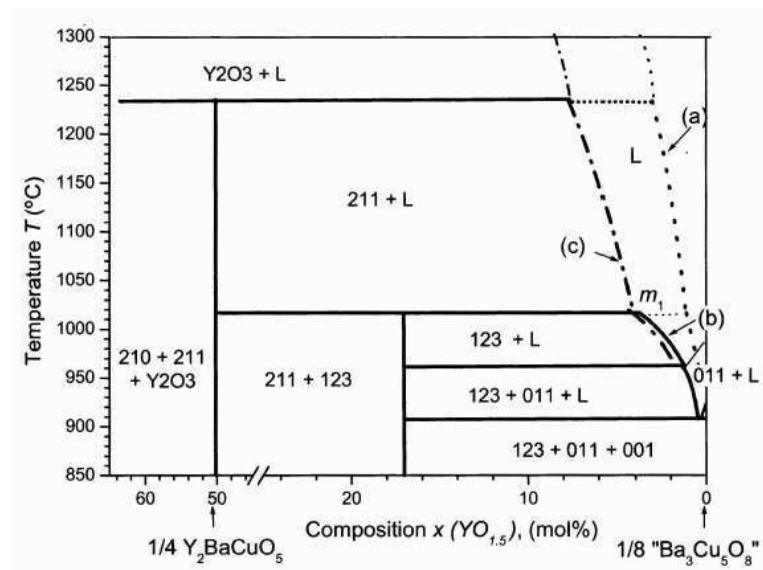


Figure 1.5 This is the temperature phase diagram for YBCO. This shows which phases of YBCO are formed and at what temperature. It is by examining this diagram that firing profiles for making enhanced flux pinning superconductors can be determined. [?]

Y-211 is the naturally occurring, non-superconducting phase of YBCO, which I use as the impurity. Introduction of Y-211 requires the MTG firing profile to go into the temperature regime that forms Y-211 ($>1000^\circ\text{C}$). To ensure that these impurities remain small, and evenly dispersed, the time spent in this regime must be short, and then the puck must be cooled to below the peritectic temperature (1005°C). The peritectic temperature is the temperature below which which are liquid, formed above

this temperature, begins to solidify to form Y-123. As a result of the short period of time spent above the peritectic temperature, the Y-211 inclusions are very small. These inclusions serve as nucleation sites for the Y-123. The Y-123 must form large crystal domains for the Meissner Effect to be as strong as possible. To promote crystal growth, the liquid Y-123 must be slowly cooled at first. To halt the formation of other phases of YBCO, once the superconductor has reached a suitable low temperature, it must be quickly cooled down to room temperature [5].

1.3 Goals

My goal is to create a large (1.5" dia.) puck of YBCO that displays flux-pinning properties. The inherent complexity associated with fabricating a superconductor with enhanced flux-pinning requires a multistage approach. The first stage was to simply make a polycrystalline puck of YBCO of a small size. The purpose of starting with a small size (0.25" dia.) was ensure that I could follow the basic recipe for making a puck and develop the skills necessary to accurately scale up into larger pucks. The next stage was to scale the puck up into a larger (1.5" dia.)puck. Then I tried to create a small(1/2" dia.) puck that demonstrated visible flux pinning properties. This process was also divided to include the development of very pure impurities which would be necessary to control the flux-pinning properties of the superconductor. Finally, using the skills I acquired through the earlier trials to make a large, single crystal of YBCO that could demonstrate flux-pinning properties. Since it would be likely that during this process there would be a number of failed trials, the last goal was to use x-ray diffraction to examine the contents and quality of the pucks at various stages throughout this process. X-ray diffraction can potentially tell me what impurities are in my pucks and what the crystalline quality of my pucks

are. This information is crucial to the iterative process that is single crystal growth of YBCO with enhanced flux-pinning properties.

Chapter 2

Experiment

The fabrication of a superconductor consists of a number of steps where each step is a variation on one of five techniques. In the most reduced possible procedure, all that is really necessary is to weigh out the precursor powders, mix them together thoroughly, grind them to a uniform particle size, press the powder into the desired shape, and then fire the pressed pellet according to a prescribed firing profile. To fully understand the procedures used to make the puck at the center of each successive stage, it is necessary to elaborate on the details of the techniques used.

2.1 Fabrication Techniques

Before beginning any of the procedures I used, it is was absolutely necessary to establish an immaculate working area. In my preparations I used a plastic lunch tray covered with aluminum foil that I changed after each use. I also wore a lab coat, gloves, and eye protection. Generally, lab safety guidelines as well as the chemical hygiene plan were implemented. This is almost goes without saying, but for reasons other than safety, it was beneficial to observe these rules.

2.1.1 Weighing

The scale I used during all of my measurements was a Denver Instruments APX-200. This model is outfitted with a small glass enclosure to prevent air currents in the room from disturbing the scale, and is sensitive to ± 0.0001 gram. Before weighing, the scale must first be balanced, and calibrated. To balance the scale, I simply placed the scale on a stable, flat surface and adjusted the knobs on the back and sides of the scale until the bubble level showed that the scale was level. To calibrate the scale, I placed a weighing boat on the scale stage and close the glass enclosure. The scale indicated when the measurement was stable. Once the scale indicated that the measurement was stable, I pressed and held the zero key to complete calibration.

To weigh out the precursor powders for YBCO, I began with barium peroxide, barium carbonate, or yttrium oxide. Barium peroxide/barium carbonate as well as yttrium oxide are hydrophilic and as a result, stick to the weighing boat and any other surface that has been exposed to air for any length of time. Copper (III) Oxide however, is not. This makes this compound quite useful in collecting any residue that has accumulated on the weighing boat after weighing. By using copper(III) oxide last and “cleaning” the weighing boat out with it, I increased the accuracy of my measurements.

2.1.2 Mixing

Mixing the precursors is done in either one of two ways. The first way is to gradually add the weighed precursors to an agate mortar and grind them together. The second method is to carefully fill a medium glass phial, close the phial, and then shake the phial by hand for ten minutes.

2.1.3 Grinding

I ground the powders by placing the mixed powders into an agate mortar, and using the pestle, I pressed the powders together into the bottom of the mortar. By moving the pestle back and forth, and by turning the mortar I ensured that the mixture was as homogenous as possible. Grinding superconducting pucks that have already been fired required a different technique. Already formed superconductors are much harder, and therefore much more difficult to grind. To grind such a puck, I first broke the puck into manageable pieces by placing the puck at the bottom of the agate mortar, and tapping the center of the puck with the pestle to crack it in half. I took out one of the halves, and broke the remaining half. I repeated this process until the pieces were small enough to grind ($\approx 10\mu m$). When cracking the pucks into more manageable pieces, the pucks had a tendency to explode upon breaking, sending YBCO shrapnel everywhere, to minimize losses, I performed this whole process underneath a dome of aluminum foil.

2.1.4 Pressing

Pressing the powder was done using a pellet press. Pellet presses vary greatly in size and design. I primarily used two main pellet presses, a small 1/2" dia. and a 1.5" dia. Regardless of the design, every pellet press consists of two main parts, the pressing chamber, and the mandrel (the part that does the pressing). Every pellet press procedure consists of the same 3 steps: filling the press with the materials, pressing the materials, and then finally extracting the puck shaped pellet.

One of the main goals of my research was to make a large superconductor. Large in this case means a superconducting puck with a diameter of 1.5". To accomplish this, I fabricated a pellet press from stainless steel. The details of this

press and its use can be found in the appendix(Fig. A.1).

2.1.5 Heating Profiles

The heating profile is the step in the process to which the the final outcome is most sensitive. Slight variations in this step can destroy superconductivity altogether. It is for this reason that great care has been taken to ensure that the profiles used to fire the superconductors were accurate.

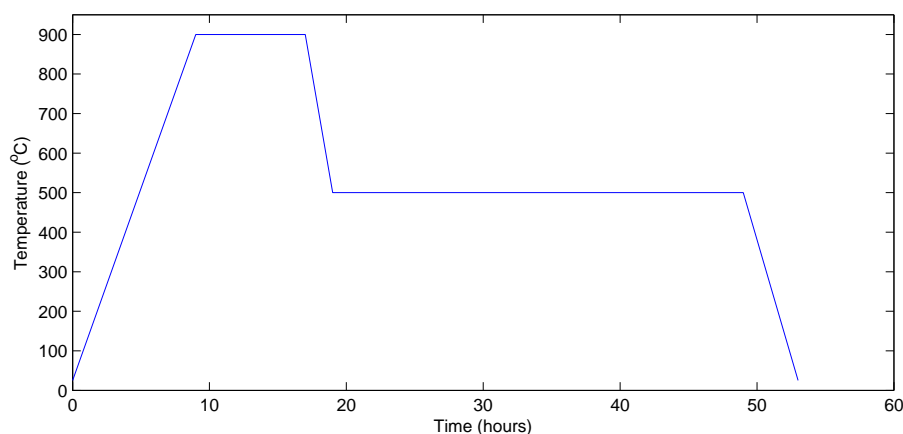


Figure 2.1 This heating profile is the tried and tested profile used by Professor Janet Hunting. This profile regularly produced polycrystalline superconductors that exhibited good levitation.

The first profile I used was a profile that was given to me by Professor Janet Hunting, and was a profile she used for a laboratory experiment for one of her upper level chemistry classes(Fig.2.1). This profile resulted in polycrystalline superconductors that could levitate strongly in a magnetic field, but did not demonstrate any visible flux pinning properties.

The second profile I used was a slightly modified version of the first. This profile was obtained by contacting an engineer at Colorado Superconductor Inc(Fig.2.2),

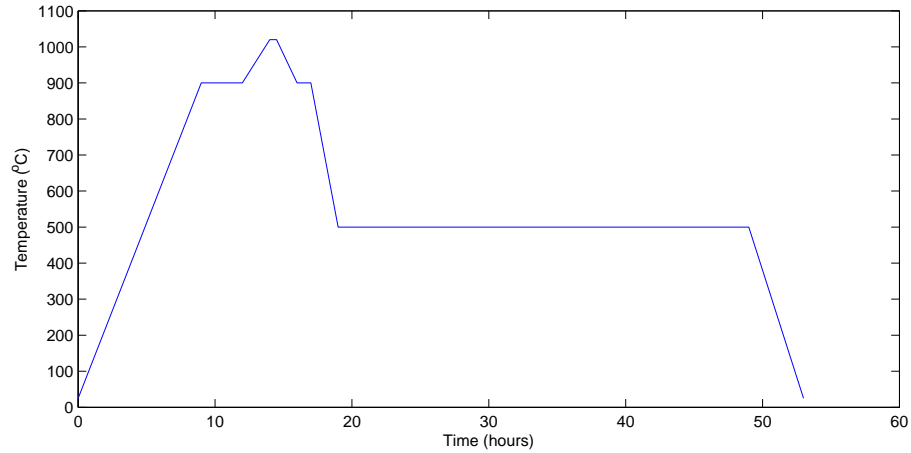


Figure 2.2 This heating profile is a profile that is similar to the profile used by Colorado Superconductors Inc. This profile yielded a polycrystalline superconductor which exhibited moderate flux pinning.

who suggested we modify our current profile by increasing the peak temperature from 900°C to 1020°C. This produced a polycrystalline superconductor that demonstrated good levitating properties as well as some flux pinning.

The third profile I used marks the departure from my old methodology for producing superconductors(Fig.2.3). This profile was obtained by correspondence with Dr. Kazumasa Iida from Dresden, Germany. This profile does not seek to make a flux pinning superconductor. Rather, the purpose of this profile is to produce as pure YBCO as possible and is part of a multi stage firing process for producing a flux pinning, polycrystalline superconductor. This process is known as Melt-Textured Growth(MTG).

The next profile is the heart of the MTG process, as it is this process that will ultimately lead to a flux pinning superconductor [6]. This heating profile forms a non-superconducting phase of YBCO (Y-211) at the temperature of 1040°C and allows these impurities to be dispersed, then rapidly cools the puck to a temperature of

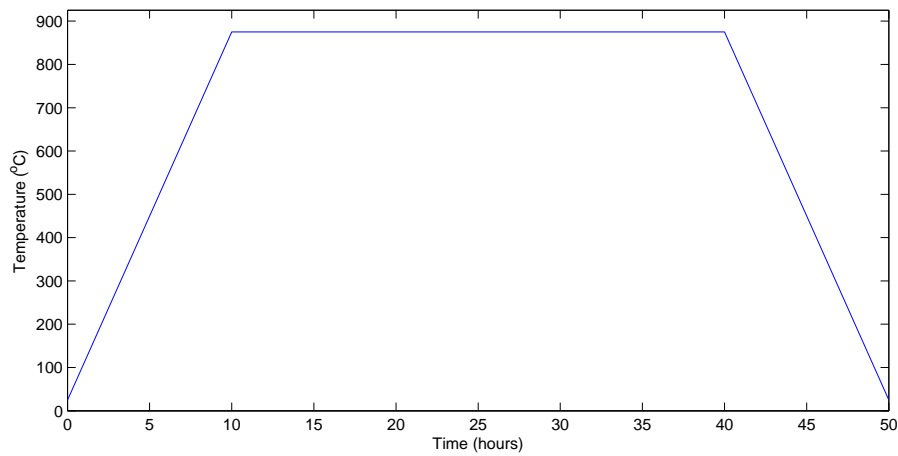


Figure 2.3 This heating profile is the profile used in refining YBCO, and is referred to as the calcinating profile.

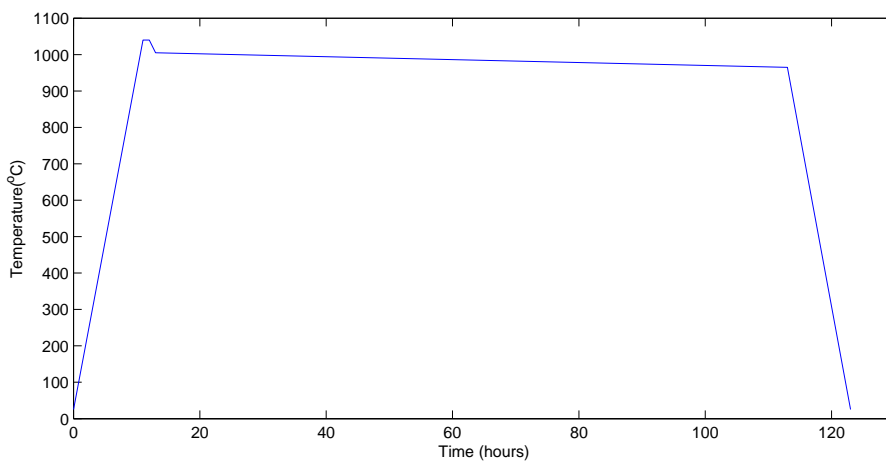


Figure 2.4 This heating profile is melt-textured growth firing profile. This firing profile seeks to form all of the impurities necessary for flux pinning, as well as dispersing them throughout the bulk of the puck.

1005°C and then slowly cools to 965°C where the superconducting phase of YBCO (Y-123) can crystalize around the impurities (Fig.2.4).

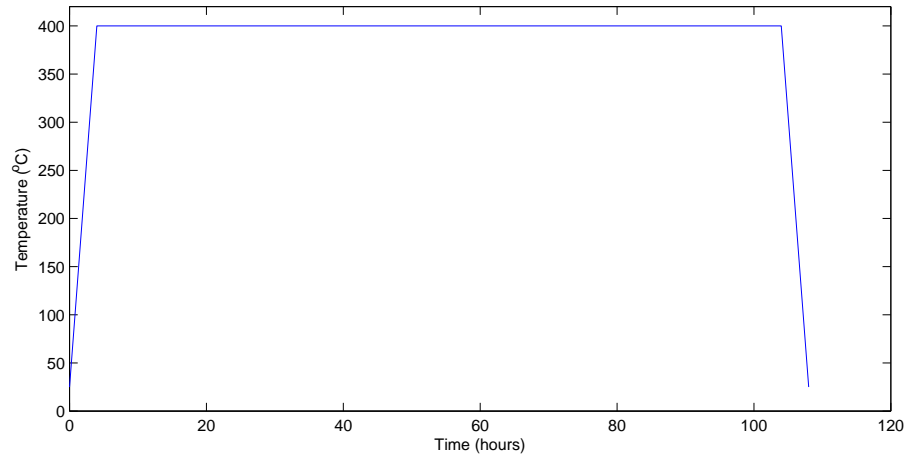


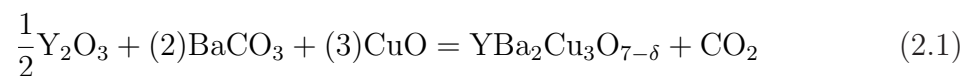
Figure 2.5 A puck was annealed using this profile under flowing oxygen. This was done to increase the oxygen content to the optimal doping.

Once the MTG profile was completed, the puck will not have the optimal doping. To remedy this, the puck must be additionally fired in flowing oxygen at 400°C for 100 hours.

After re-evaluating Dr.Iida's profile and determining that the puck was being heated at too high a temperature, a new profile was made, with one small modification: the peak temperature was lowered to 1020°C. All other aspects of the melt-textured growth process were left unaltered.

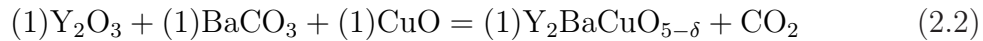
2.2 Puck Fabrication Procedures

The first step on the way to making enhanced flux-pinning pucks was to make a polycrystalline superconductor. To do this I used the methods detailed above. I began with the equation for making Y-123:

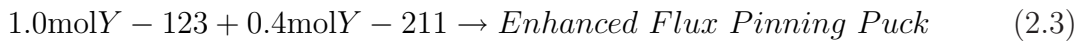


Since 1 mole of Y-123 weighs 666.2008g, which was far too much material to process at one time, it was desirable to scale down the size of the final puck to something more manageable. To do this, I selected the final weight of the puck to be 3 grams. Then I simply divided this mass by the final mass of Y-123 to find the scaling constant (in this case = 0.0045). By multiplying the masses of each precursor powder by the scaling constant, I got the proportional masses of the precursors that would be required to make the smaller puck. By weighing out these amounts and using the grinding procedure to mix and homogenize the powders, the mixture is ready for pressing and firing. The firing profile I used was the profile detailed in (Fig.2.1).

To produce a puck of Y-211, I used the same procedure used to make a 3g puck of Y-123 but instead of being guided by the equation above, I used the stoichiometric formula for making Y-211:



Upon further investigation, it became clear that I would need to create extremely pure samples of Y-123 and Y-211. To create such samples, I had to rely on the tried and tested process known as calcination. Calcination consists of all of the procedures above done with a specific firing profile, and then iterated. The iteration means that a puck that is produced from one round of calcination must then be crushed, ground into a fine powder, pressed, and then re-fired. The firing profile I used was detailed in (Fig.2.3).



To make an enhanced flux-pinning superconductor using the Melt-Textured Growth procedure, I used the purified precursor materials, and then mixed them according

to the prescribed recipe (eq.2.3). The mixed, purified precursors, were then ground to homogeneity, then pressed, and finally fired according to (Fig.2.4). The resultant pucks do not contain the appropriate oxygen content required to have the desired critical temperature. In other words, they do not have the right doping. To remedy this, the pucks must be further fired under flowing oxygen, or annealed to improve the doping. The annealing profile is detailed in (Fig.2.5).

2.3 X-Ray Powder Diffraction

In order to make conclusions about the internal nature of one of the superconductors, it was necessary to perform x-ray powder diffraction. X-ray diffraction is the process by which x-rays are passed into a prepared sample of the powder you wish to analyze, the rays reflect off of different layers in the lattice, and thus constructively or destructively interfere. Since the powder is made up of randomly arranged crystals, the overwhelming majority of crystals re-emit destructively with one another. However, a small minority of the crystals are aligned in such a way that they constructively interfere. The x-rays are directed at the sample from different angles. The constructive interference is detected at an angle specific to lattice spacing of the crystal being scanned. A chemical compound can be identified by the peaks and their associated angles. I used a Shimadzu XDS-6000 Powder Diffraction machine to perform my measurements. This particular machine is setup to be able to compare the scanned data card to a card database and determine based on similarity which elements or compounds are contained in the sample. It was by this method that I determined the composition of the pucks.

Chapter 3

Problems With Growth

In the course of my research, I ran into a number of problems that interfered with the growth of superconductors that demonstrate enhanced flux pinning properties. The source of the problems was never immediately apparent, and different trials were affected by different problems. Each step in the procedure was a new opportunity to introduce error, and indeed at each step I found some new problem that needed to be understood and mitigated.

3.1 Precursor Powders

The precursor powders are the starting point for any puck and largely determine the final quality of the properties the puck demonstrates. The precursor powders used during my research were originally Barium Peroxide (BaO_2 , 98%), Copper (III) Oxide (CuO_3 , 99.9%) and Yttrium Oxide (Y_2O_3 , 99.99%), but then I replaced the Barium Peroxide with Barium Carbonate (BaCO_3 , 99.9%). This was done because Barium Carbonate can be obtained at a higher purity. Precursor purity is important because the impurities associated with barium oxides are typically other heavy met-

als, and other metals would not only create grain boundaries between YBCO crystals, which would impede superconductivity, but also react with the other chemicals to destroy the stoichiometric accuracy of the final powder.

3.1.1 Granularity

Granularity was another issue I considered when selecting the Barium Carbonate. The Barium Carbonate is available at slightly smaller grain sizes than the Barium Peroxide. The grain sizes of precursors need to be similar and very small to improve the homogeneity of the final mix of powder and ultimately the grain sizes of the YBCO. Small grain size contributes to the ease of the diffusion of the various chemicals used. Diffusion is the process by which the constituent elements "move" through the bulk of the puck during firing. Better diffusion increases the chances that the elements will come into contact with other elements and form the right compounds. In other words, smaller grain sizes yields more accurate stoichiometry.

I performed an experiment comparing the effect differences in grain size has on the final outcome of the puck. I did this by preparing two pucks with identical amounts of impurity, as well as size, and crucible material. The only difference between the pucks preparation was the source of precursor powders. One puck was made using the calcined powders, while the other was made using unpurified precursor powders. The calcined powders were ground by hand and as a result have an irregular grain size, whereas the unpurified powders were ground by ball mill from the factory, and are much more consistent in grain size. The results of the experiment showed that the puck made with the unpurified powders superconducted and pinned flux at a sufficiently high temperature demonstrated by cooling to 77K. This experiment showed that the regularity and size of the grains can dramatically affect the final behavior of the pucks.

3.2 Crucible

The crucible is the material on which the puck is fired. This material must meet a few basic requirements to be considered usable in this procedure. The first is that the crucible must be able to withstand the maximum temperature that it will be fired at for the duration of the firing. Second, this material must not be reactive with what is being fired. Traditionally, Alumina, or Aluminum Oxide (Al_2O_3), is used as the basic crucible material because of its availability and relatively low cost. However, it became clear from successive iterations of calcination early on that the purity of the pucks was not improving, and in fact, was worsening. The Alumina crucible seemed to be the issue. As it turned out, Alumina is not rated to be stable the higher operating temperatures and was contaminating the pucks with aluminum.

Magnesium Oxide (MgO) was chosen to replace Alumina because Magnesium Oxide is rated to temperatures near 2000°C . Magnesium Oxide is also considerably cheaper than Alumina and available in a variety of shapes and sizes. Since the goal is to make large pucks, it is necessary to use a large crucible. Unfortunately, MgO turned out to be extremely reactive with the puck materials made evident by the extreme flow of liquid material out of the puck and onto the crucible. The flow was so severe that the liquid actually managed to flow around the edges and bond to the underside of the crucible. As a result, MgO was removed from the list of possible crucible materials.

The crucible material that was mentioned a few times in the literature, and was suggested to me by Dr. Iida was Zirconia, or Zirconium Oxide (Zr_2O_3). This material has been proven in other settings to be the ideal crucible material for this reaction. Zirconia is stable at the higher temperatures as well as being non-reactive with the material being fired. The ideal crucible configuration is for the pucks to be fired on

two very small rods made from Zirconia. This is done to minimize the area of contact and thereby reduce the possibility for contamination. Experiments to date show that this material works, but is prone to wetting by liquid phase formed at the higher temperatures. This causes the Zirconia rods to adhere to the bottom of the pucks which is undesirable for aesthetic reasons.

3.3 Amount of Impurities

As mentioned earlier, control of the impurities is crucial to the success of any superconductor, especially so in superconductors that should demonstrate enhanced flux-pinning properties. As a result of a string of failed trials at making such a puck, I came to the conclusion that the amount of impurity prescribed by the recipe detailed in Eq. 2.3 was too much. It comes out that if this recipe is followed the total weight that the impurity contributes is approximately 25% of the total weight. This weight does not contribute to levitation whatsoever. I then set out to perform an experiment to see how much impurity is best with an upper limit of 0.4mol of Y-211. I mixed four pucks, the first had 0.0mols of Y-211, this was done to establish a lower bound for the experiment, by firing this puck with the other using the MTG profile I should at least get one puck that superconducts. The second puck had 0.1mol of Y-211, and the third has 0.2mol of Y-211. The results can be seen in Fig.3.1

The pucks were arranged in increasing impurity from left to right. After a cursory evaluation, I determined that these pucks were not going to work. Each puck appeared to be extremely melted, and on the surface, large green areas of impurity. Testing these pucks in liquid nitrogen verified my initial suspicion that the pucks would not pin flux, but what was surprising was that none of the pucks superconducted either. This experiment was a failure in terms of the stated goal of comparing varied levels



Figure 3.1 This figure shows the results of the control experiment to determine the appropriate amount of impurity for a superconductor to demonstrate enhanced flux-pinning properties. The pucks are arranged in increasing impurity. The puck on the bottom left has no impurity, while the puck on the upper right has 0.4 mol of impurity.

of impurities and determining which pucks was closest to flux-pinning. However, I did notice an indirect correlation between how much impurity the pucks contained and the degree to which the pucks were melted. The more impurity contained in the puck, the less the puck was melted. This confirms that the Y-123 does go into the liquid phase during firing, and that without Y-211, the pucks cannot retain enough superconducting material to levitate. Still, the ideal amount of impurity has not yet been determined.

3.4 Temperature Control

When making a superconductor, the control of the temperature during firing is the most important step. Small deviations from the prescribed firing profile have significant effects on the properties of the resultant puck. A number of different heating profiles were used, and each heating profile yielded pucks that displayed varying levels of superconductivity and flux pinning. However, once Dr. Iida's profile was implemented, all progress was reversed. Not one puck fired this way pinned flux, and in

fact, none of them superconducted.

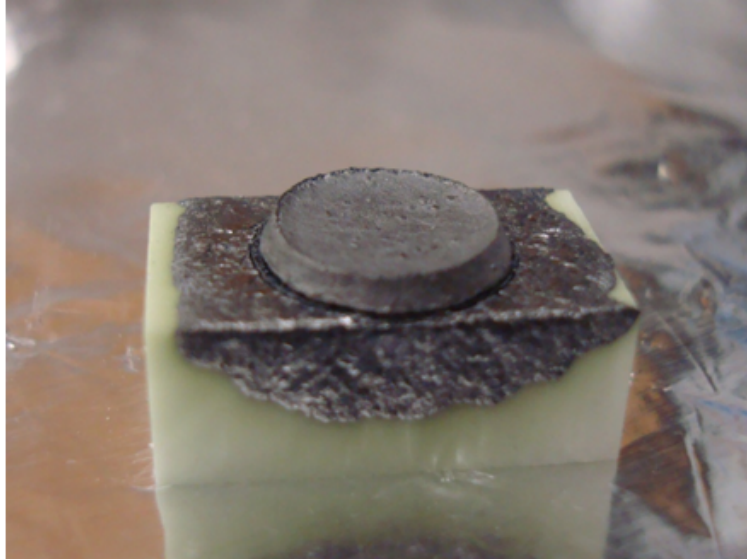


Figure 3.2 This is a picture of one of the MTG pucks after initial firing and annealing. It is clear from this image that the superconductor has melted and that a large amount of material flowed out of the puck and onto the crucible.

This led me to believe that there was something wrong with the temperature profile. A small revision to the the profile in figure 2.4, the peak temperature was lowered to 1020°C. This profile, too, did not yield any working pucks. In fact there was not a noticeable difference between the pucks produced by either profile, the pucks looked as melted and silvery as pucks fired using Dr.Iida's profile. This led me to believe that the firing profile was not necessarily the source of the melting.

3.4.1 Oven Calibration

I proceeded under the assumption that the firing profile was not causing the melting. Since the profile was no longer being considered, this left one other possibility: The oven itself was not properly calibrated. The oven setup consists of a 3" diameter

tube furnace and a controller. If the furnace's internal thermocouple is not properly calibrated, the firing profile will be inaccurate. To calibrate the oven, Andrew Hope took the temperature of the oven at specific intervals using an external thermometer and noted the difference between the two. By carefully mapping the deviations, Andrew Hope created calibration relation between the desired temperature and the displayed temperature.

3.5 Best Results to Date

My target was to make a large superconducting puck that demonstrates enhanced flux pinning properties, and in this regard I did not succeed. However, I did succeed in making two pucks that separately achieve aspects of my final objective. One puck is a large (1.5" diameter, 0.25" thick) which demonstrates superconductivity well by levitating relatively far above the track, and maintains superconductivity for up to 40 seconds (uninsulated).

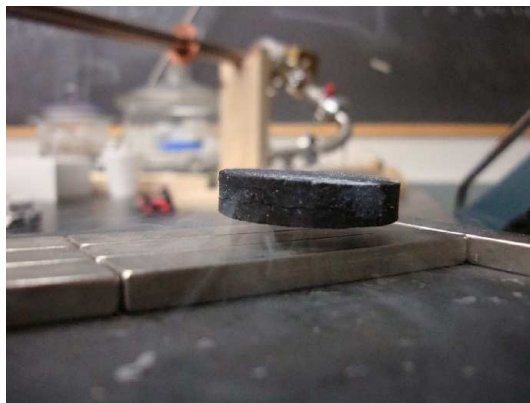


Figure 3.3 The Meissner effect demonstrated by one of my 1.5" diameter YBCO superconductors. This superconductor was made using the Calcination process (Fig.2.3).

A large puck is desirable because its size directly affects the strength of the levi-

tation and the pinning force, as well as the time it takes for the puck to warm up to above T_c . This superconductor was made using the calcination process which yields a nearly pure puck of Y-123. The pellet press used to make this puck was designed and machined by me.

The other puck achieved the enhanced flux pinning properties that eluded me for three years. This puck was the result of the most recent attempt to achieve enhanced flux-pinning properties, after the oven was calibrated. Although both pucks showed similar levels of melting, the puck with the smaller grains maintained a more structured, cylindrical shape, whereas the purified puck looked far more rounded and squat.

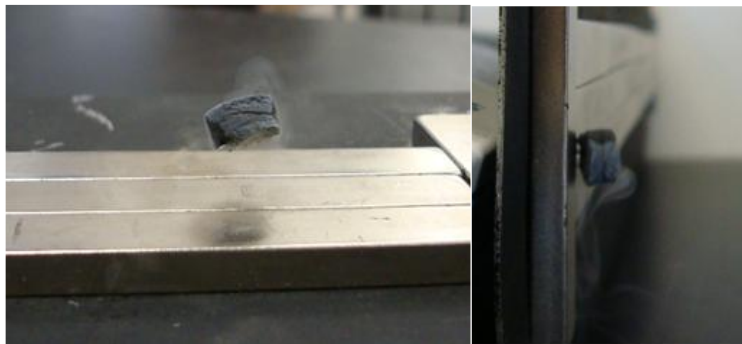


Figure 3.4 Pictured on the left is a superconducting puck levitating above a magnetic track. Pictured left is the same puck held in place by the pinning force.

The puck that demonstrated flux-pinning is quite small however, and does not maintain superconductivity for very long (approx. ≈ 5 sec). Since the puck is small the short levitation period is not very surprising. Still, the puck should be able to maintain superconductivity a little while longer which leads me to believe that this puck does not have optimal doping. The other puck fired alongside the obviously successful puck, showed large crystals at or near the surface of the puck and did demonstrate minor amounts of levitation and flux pinning, this too, suggests below

optimal doping.

3.5.1 Successful Procedures

To make the large superconducting pucks begin by weighing out the precursor powders for a 15 gram sample of Y-123 according to equation 2.1. These powders should then be thoroughly mixed and crushed. Next, pour the powders into the assembled large pellet press (Blue Prints: A.1), press the pucks to 7,000 pounds. Remove the pressed puck, place it on a zirconia crucible and fire it using the profile detailed in figure 2.3. The resultant puck should be pulverized, re-pressed and fired again. Typically, three iterations is sufficient to form a nearly pure puck of Y-123.

For the superconducting puck that demonstrates enhanced flux-pinning properties, measure out the precursor powders for a 2.5 gram puck of Y-123 and a 0.344 gram puck of Y-211 using equations 2.1 and 2.2 respectively. After these powders are mixed together and ground thoroughly, they should be pressed at 5,000 pounds in a small pellet press. This puck should then be placed on two zirconia rods in an alumina crucible and then fired using the profile detailed in figure 2.4. Once the puck is out of the furnace, it should be annealed at 400°C for 100 hours.

Chapter 4

Conclusion

The purpose of my research was to create large superconducting pucks, 1.5" in diameter, which could levitate in a magnetic field, as well as generate a sufficiently strong pinning force that would allow the puck to suspend in the magnetic field. In a sense, I did not succeed in my goal. I did, however, manage to bring this goal to within the reach of any future students who wish to continue this project. I succeeded in making a small superconducting puck that levitates and pins flux. Not only does it pin flux, it maintains complete suspension until the superconductor warms up to above T_c . Unfortunately, it is clear from the short duration the puck remains levitating, that the T_c is much lower than ideal (93K).

4.1 Future Work

What was made clear by the success of my most recent superconductors, is that a lot of work remains to be done. The most recent pucks need to be evaluated by x-ray diffraction to determine composition. Control experiments need to be performed to determine best crucible material, as well as if machine grinding would improve the

results. The puck made from refined precursors should have worked better, than the unrefined puck. I hypothesize that by annealing the puck at a higher temperature, this might improve the doping, and thereby increase the T_c .

Appendix A

Pellet Press Design Specifications

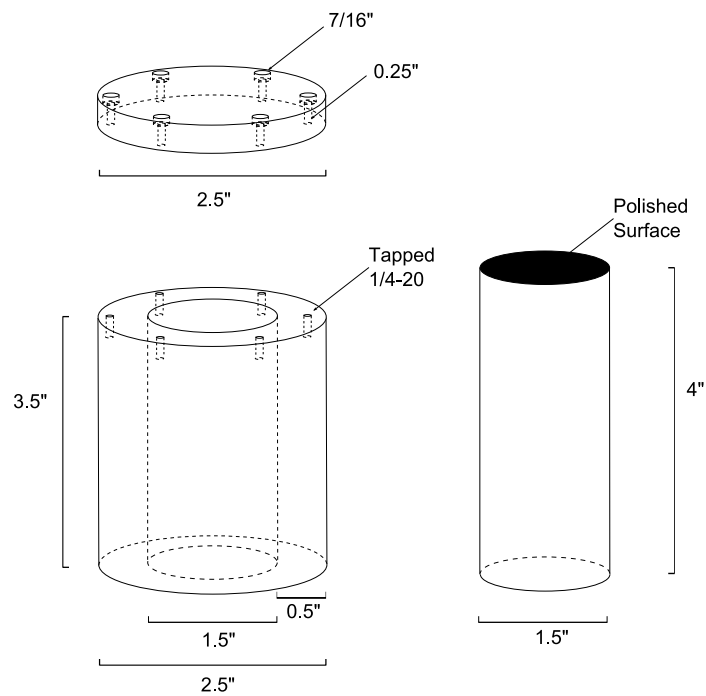


Figure A.1 This pellet press was machined out of stainless steel to limit maintenance and limit the amount of rust impurities added to the pucks during pressing. The top of the press is intended to be held in place by 6 1/4-20 hex-nut machine screws.

Appendix B

Table of Pucks Made

Table B.1 This is the preparation data for all of the pucks made.

Puck #	Phase	Precursor Powders	Mixing	Impurities	Press
1	Y-123	Y ₂ O ₃ , BaO ₂ , CuO	Hand mixed	Naturally occurring	1/2"
2	Y-123	Y ₂ O ₃ , BaO ₂ , CuO	Hand mixed	Naturally occurring	1.5
3	Y-123	Puck 2	Hand mixed	Naturally occurring	1.5
4	Y-123	Y ₂ O ₃ , BaO ₂ , CuO	Hand mixed	Naturally occurring	1.5
5	Y-123	Puck 4	Hand mixed	Naturally occurring	1.5
6	Y-123	Y ₂ O ₃ , BaO ₂ , CuO	Hand mixed	Naturally occurring	1.5
7	Y-123	Puck 6	Hand mixed	Naturally occurring	1.5
8	Y-123	Y ₂ O ₃ , BaO ₂ , CuO	Hand mixed	Naturally occurring	1.5
9	Y-123	Y ₂ O ₃ , Ba ₂ CO ₃ , CuO	Hand mixed	Naturally occurring	1/2"
10	Y-211	Y ₂ O ₃ , Ba ₂ CO ₃ , CuO	Hand mixed	Naturally occurring	1/2"
11	Y-123	Puck 9	Hand mixed	Naturally occurring	1/2"
12	Y-211	Puck 10	Hand mixed	Naturally occurring	1/2"
13	Y-123, Y-211	Pucks 11 \& 12	Hand mixed	Y-211 (0.4 molar ratio)	1/2"
14	Y-123	Y ₂ O ₃ , Ba ₂ CO ₃ , CuO	Hand mixed	Naturally occurring	1.5"

Continued on next page

Table B.1 – continued from previous page

Puck #	Phase	Precursor Powders	Mixing	Impurities	Press
15	Y-211	Y ₂ O ₃ , Ba ₂ CO ₃ , CuO	Hand mixed	Naturally occurring	1.5"
16	Y-123	Puck 14	Hand mixed	Naturally occurring	1.5"
17	Y-211	Puck 15	Hand mixed	Naturally occurring	1.5"
18	Y-123, Y-211	Pucks 16 \& 17	Hand mixed	Y-211(0.4 molar ratio)	1/2"
19	Y-123	Y ₂ O ₃ , Ba ₂ CO ₃ , CuO	Hand mixed	Naturally occurring	1.5"
20	Y-211	Y ₂ O ₃ , Ba ₂ CO ₃ , CuO	Hand mixed	Naturally occurring	1.5"
21	Y-123	Puck 19	Hand mixed	Naturally occurring	1.5"
22	Y-211	Puck 20	Hand mixed	Naturally occurring	1.5"
23	Y-123, Y-211	Pucks 21 \& 22	Hand mixed	Y-211(0.4 molar ratio)	1/2"
24	Y-123	Puck 19	Hand mixed	Naturally occurring	1.5"
25	Y-211	Puck 20	Hand mixed	Naturally occurring	1.5"
26	Y-123, Y-211	Pucks 21 \& 22	Hand mixed	Y-211 (0.4 molar ratio)	1/2"
27	Y-123, Y-212	Pucks 21 \& 23	Hand mixed	Y-211 (0.0 molar ratio)	1/2"
28	Y-123, Y-213	Pucks 21 \& 24	Hand mixed	Y-211 (0.1 molar ratio)	1/2"
29	Y-123, Y-214	Pucks 21 \& 25	Hand mixed	Y-211 (0.2 molar ratio)	1/2"

Continued on next page

Table B.1 – continued from previous page

Puck #	Phase	Precursor Powders	Mixing	Impurities	Press
30	Y-123, Y-215	Pucks 21 \& 26	Hand mixed	Y-211 (0.4 molar ratio)	1/2"
31	Y-123, Y-216	Pucks 21 \& 27	Hand mixed	Y-211 (0.2 molar ratio)	1/2"
32	Y-123, Y-217	Y ₂ O ₃ , Ba ₂ CO ₃ , CuO	Hand mixed	Y-211 (0.2 molar ratio)	1/2"
33	Y-123, Y-218	Puck 31	N/A	Y-211 (0.2 molar ratio)	1/2"

Table B.2 This shows the conditions for firing and annealing the pucks as well as their final properties.

Puck #	Crucible	Firing Profile	Annealing	Superconductivity	Flux-Pinning
1	Alumina	1	N/A	Yes. Low levitation height	None
2	Alumina	1	N/A	Yes. Low	None
3	Alumina	1	N/A	Yes. Slightly higher levitation height than puck 2	barely noticeable
4	Alumina	2	N/A	Yes. Low levitation height	yes, not strong
5	Alumina	2	N/A	Yes. Lower than puck 4	None
6	Alumina	1	N/A	Yes. Low levitation height	None
7	Alumina	1	N/A	Yes. Low levitation height, no improvement	None

Continued on next page

Table B.2 – continued from previous page

Puck #	Crucible	Firing Profile	Annealing	Superconductivity	Flux-Pinning
8	Magnesium Oxide	1	N/A	None. Significant melting	None
9	Alumina	3	N/A	Yes	None
10	Alumina	3	N/A	N/A	None
11	Alumina	3	N/A	Yes	None
12	Alumina	3	N/A	N/A	None
13	Alumina	4	Yes. Profile 5	None. Significant melting /wetting to crucible.	None
14	Alumina	3	N/A	Yes	None
15	Alumina	3	N/A	N/A	None
16	Alumina	3	N/A	Yes	None
17	Alumina	3	N/A	N/A	None
18	Alumina	4	Yes. Profile 5	None. Significant melting /wetting to crucible.	None
19	Alumina	3	N/A	Yes	None

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Table B.2 – continued from previous page

Puck #	Crucible	Firing Profile	Annealing	Superconductivity	Flux-Pinning
20	Alumina	3	N/A	N/A	None
21	Alumina	3	N/A	Yes	None
22	Alumina	3	N/A	N/A	None
23	Zirconia	4	Yes. Profile 5	None. Significant melting. Puck adhered to crucible.	None
24	Alumina	3	N/A	Yes	None
25	Alumina	3	N/A	N/A	None
26	Zirconia rods	4	Yes. Profile 5	None. Significant melting. Puck adhered to crucible.	None
27	Zirconia rods	4	Yes. Profile 5	None. Significant melting. Puck adhered to crucible.	None
28	Zirconia rods	4	Yes. Profile 5	None. Significant	None

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Table B.2 – continued from previous page

Puck #	Crucible	Firing Profile	Annealing	Superconductivity	Flux-Pinning
29	Zirconia rods	4	Yes. Profile 5	melting. Puck adhered to crucible. None. Significant	None
30	Zirconia rods	4	Yes. Profile 5	melting. Puck adhered to crucible. None. Significant	None
31	Zirconia rods	4	Yes. Profile 5	melting. Puck adhered to crucible. Yes. Low levitation height	not noticeable
32	Zirconia rods	4	Yes. Profile 5	Yes, Strong superconductivity	Strong flux-pinning
33	Alumina	N/A	Re-annealed. Profile5	Yes, Strong superconductivity	Strong flux-pinning

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