Synthesis and Characterization of High-$T_c$ Superconductors

Introduction

A superconductor below its superconducting transition temperature can conduct electricity with essentially zero resistive losses. While numerous applications can be imagined for such a material, the most common practical application is in the production of very high field electromagnets. In the electromagnets, large currents are introduced into a coil of superconductor. Because the current travels with no resistive loss, the current (and the accompanying field) can persist virtually indefinitely, as long as the material of the coil remains in the superconducting state. Such electromagnets are commonly used in NMR spectrometers and in MRI medical imaging. The problem with more widespread application of these superconducting electromagnets is that most materials only behave as superconductors at very low temperature. As a result, the coil in a typical NMR or MRI needs to be cooled to temperatures around 10 K. This can be done in a localized space using liquid He. The high cost of He, however, makes many other possible applications of superconducting magnets—like magnetically levitated trains—impractical.

In the 1980s, a new class of superconductors was discovered that had much higher superconducting critical transition temperatures ($T_c$). Unlike most classic superconductors, which are based on pure metals, these new superconductors are metal oxides with a layered perovskite structure. The remarkable thing about this new class of materials is that for the first time, $T_c$ moved above 77 K, which means that the superconductors could be cooled with liquid nitrogen, rather than liquid He. Unfortunately, despite the high $T_c$, these materials have not found widespread applications to date, in large part because of their brittleness and thus the difficulty of producing wires that can truly act as zero resistance conductors when cooled.

In the powder form the synthesis of these materials, which usually contain at least three different metals, involves a straightforward high-temperature reaction often called “shake and bake” chemistry after the 80s-style spice mix. In the reaction, simple inorganic salts of each element are ground together (shake) and then alloyed at very high temperatures so that each grain can react with its neighbors (bake). Because solid state diffusion is very slow, multiple heating and grinding cycles are usually needed to produce a homogeneous material. Ceramic solids can then be produced by pressing the powder under very high pressure, often with a small amount of a polymer binder.

The most common high temperature superconductor has a chemical formula YBa$_2$Cu$_3$O$_{7-x}$. These materials are often called 1-2-3 superconductors, referring to the stoichiometry. In this lab, you will produce a YBa$_2$Cu$_3$O$_{7-x}$ superconductor using shake and bake methods. You will do this by simply grinding a stoichiometric mixture of Y, Ba, and Cu salts and then repeatedly heating and regrinding the sample. The method is fairly easy, but you need a lot of patience in grinding to get a well-mixed sample, and multiple heating and grinding cycles are needed to produce a high quality sample in the end. One big reason for this is that an impurity (non-superconducting phase) with a different stoichiometry can
form, which prevents current from flowing between superconducting grains. Heating at \( \sim 500^\circ C \) in oxygen converts this non-superconducting phase to a liquid state so that it can flow away from the true superconductor and produce a much lower resistance sample.

Characterization of the superconducting transition temperature will be done in three ways. In the first case, you will simply test if your material is a superconductor by placing your pellet in a pool of liquid nitrogen and seeing if the superconductor can levitate a magnet. This is known as the Meissnner effect. In the second part, you will attach a resistance temperature detector (RTD) to your pellet and then actually measure resistance as a function of temperature as your sample warms from 77 K toward room temperature. Finally, you will use a magnetometer to measure the temperature where magnetic fields are excluded from the superconducting phase.

**Procedure**

**Overview**

Day 1 Grind your stoichiometric mixture of metal salts and start heating the sample.

Day 2 Regrind your sample and reheat the powder. (This is a very short day! If at all possible, do this on a non-lab day.)

Day 3 Regrind the powder yet again and press pellets. Start the pellets heating. (This is another short day.)

Day 4 Measure Meissner effect and measure 4-point conductivity versus temperature on your pellet. At a time you arrange with Ignacio, measure magnetization versus applied magnetic field using the SQUID magnetometer.

**Synthesis of 1-2-3 Superconductors**

To make superconductors via the “shake and bake” method, grind together about 25 grams (total mass) of a stoichiometric mixture of barium carbonate (BaCO\(_3\)), yttrium oxide (Y\(_2\)O\(_3\)), and copper oxide (CuO). Do this calculation carefully as you will not get a functional superconductor if you do not use reagents in the correct proportion. Remember to include any water of hydration in your calculations. To make a good quality material in the end, you need to grind your starting material a lot. This means grinding constantly with a mortar and pestle for over an hour! Take turns with your lab partner and have a nice conversation while you do it.

Heat the powder in two or three ceramic boats using the temperature program described below. This should generate a black powder. If your powder is green, your stoichiometry is likely incorrect. If you generate a mixture of green and black, that is fine; simply use the black parts. Regrind (again well) and
reheat the black powders a second time (the color should not change). If time permits, take some of this powder and mix it with 2-3 wt% polyvinyl alcohol. Press this mixture into a pellet using the pellet press and heat the pellet along with your powder. After the second heat treatment, regrind the rest of the powders one final time and again mix with 1–2 wt% polyvinyl alcohol. Press this mixture into several pellets and heat a final time according to the temperature program described below. These final pellets should be suitable for magnetic measurements. For measuring the Meissner effect, you may also be able to use the pellet that you made on day 2.

**Measurement of the Meissner Effect**

Place your pellet in a Petri dish and fill the dish with liquid nitrogen. Place a small but very strong magnet over the pellet. If your pellet is a superconductor, the magnet will levitate above the pellet (provided it is not too large). Take a picture of your floating magnet so you have something to put in your lab report. If you can not levitate a magnet, your stoichiometry may be incorrect. If you do not see good levitation with your samples, try using the commercial YBCO pellet which should show a very strong Meissner effect. Use the Meissner effect to find your best pellets and use these for conductivity measurements.
Measurement of Conductivity vs. Temperature

To measure conductivity versus temperature you will need the setup illustrated in figure 1. Gather all the supplies indicated, including thermally conductive grease, a Keithley 2000 and 2400, the glass dewar flask (located in the big cupboard next to the back sink), the 4-wire resistance leads/clip, a small binder clip bent to ∼2 mm air gap, the RTD, and (not shown) silver paste.

Add a thin layer of thermal grease to the black side of your RTD and silver paste your pellet so to contact the outer probes of the test clip (see figure 1b). Now clamp the sample and ensure that the probes are hitting the silver paste. Next stick the RTD to the sample and clip down as in figure 1c. Once you have all the leads attached to your pellet as shown in figure 1c, you are ready for four-point probe electrical measurements as a function of temperature. Wrap the pellet and probe in kim wipes to ensure thermal equilibrium during the cooling process upon removal from liquid N₂. Use the labview program New Superconductor Measure.vi located in the Labview Programs folder found on the desktop to source 0.5 A of current (across leads 1,4) while measuring the voltage (across leads 2,3). This program can speak to two Keithleys at the same time in order to simultaneously measure the 4-wire resistance of the sample and the resistance (i.e. temperature) of the RTD. At room temperature, you should read a voltage drop on the Keithley 2400 of only ∼1 mV while measuring a resistance of just mΩ on the program when 0.5 A is sourced. Once you confirm that the room temperature values are reasonable (including the temperature), dunk the entire device in a beaker of liquid nitrogen and let it equilibrate at 77 K for a few minutes (see Figure 2). After the big bubbles go away along with a minute or two, run the program. Your RTD temperature reading on the program should now read 77–78 K, and the 4-wire resistance should be small and maybe even slightly negative.

Collect data using LabView for ∼20 s in the liquid N₂ bath and then pull it from the liquid N₂ and let it warm up slowly. Have one lab member concentrate on holding the pellet/clip/RTD assembly just barely above the liquid N₂—having the binder clip just slightly in the liquid N₂ is good. Collect data up to ∼200 K. You can recool your pellet and repeat the process, but be aware that thermal cycling often causes the pellets to crack, so if the resistance goes up when you cool it the second time, you are unlikely to get good data on the second run. If you cannot see the onset of superconductivity in any of your pellets, try repeating the experiment with the commercial YBCO pellet. Use this data to determine the superconducting transition temperature, $T_c$, for your material.
If all GPIB computers/cables are in use, you can always use the serial port to connect the Keithley to a computer—just make sure that the correct VISA Resource Name is selected in the .vi program.

Figure 2: Dunk your sample in liquid N$_2$. After the big bubbles go away and a minute goes by, run the program.

Magnetization Measurements

These measurements make use of a SQUID (Superconducting QUantum Interference Device) magnetometer. If you have not used this equipment previously in your own research, you will need to work with an experienced user. Luckily, once you get things started, the data mostly collects itself. To make the sample, mount a small piece of your pressed pellet in a gel capsule and secure the capsule so that the YBCO cannot move in the magnetic field (either pack the capsule with cotton, or put the smaller half of the capsule in upside-down to press it against the pellet. Tape the capsule together with Kapton tape and put it in a straw. Insert the sample into the magnetometer using standard procedures. Measure magnetization as a function of temperature from 200 K down to about 20 K at a low field of around 100 Oe. Use this data as a second measurement of $T_c$. To learn about critical fields in this superconductor, measure magnetization as a function of field from 0 field up to 5 tesla. Can you identify the lower and upper critical fields? Refer to the SQUID manual for more details on these measurements.

Some Thought Questions

1. What limits the diffusion of atoms in the solid state? How could you fix this?
2. Why are the heating and cooling ramp rates important?
3. How is a four-point probe measurement used to determine resistivity? Why is it better than a simple two-connection measurement?

4. How does the Meissner effect work? Why don’t people levitate trains using this effect?

5. How do the two $T_c$ values that you measured compare, and how do these compare to values in the literature for similar materials? What are the sources of error in the value you measured?

6. The value of $x$ in $YBa_2Cu_3O_{7-x}$ affects the $T_c$ of the material. Can you estimate a value of $x$ by comparing your measured $T_c$ values to those presented in the literature?

7. What are the values of the upper and lower critical field in your material? What do these values tell you about the nature of flux lines in this superconductor?