Growth and Annealing Study of High-Temperature Superconductor $HgBa_2CaCu_2O_{6+\delta}$

Sanjeev Mishra

Greven Lab

Supervisor: Martin Greven

Abstract

Monocrystalline samples of the high-temperature superconductor $HgBa_2CaCu_2O_{6+\delta}$ (Hg1212) were grown and characterized by their critical temperature (T_c). As-grown samples removed from growth tubes were found to have inhomogeneous hole-dopant concentration and were treated through an annealing process. Annealing improved the quality of the samples and prepared them for future measurement.

Introduction

Since its discovery in elemental Mercury in 1911 [1], superconductivity has remained one of the most active areas of research in condensed matter and low-temperature physics. The superconducting state is characterized by two unique properties: zero electrical resistance within the material and the expulsion of all internal magnetic fields within the superconducting material. The latter is known as the Meissner effect [2]. Both of these effects are only observed when the material is cooled below a critical temperature, denoted T_c. The main difficulty with superconductivity is that the critical temperatures of many superconducting substances are well below room temperature; observed critical temperatures seemed to plateau around the early 1980's at about 20-30 Kelvin.

In 1986, superconductivity was discovered in a class of complex copper-oxide compounds called the cuprates [3]. The critical temperatures of these compounds are far greater than those of traditional superconductors—reaching a maximum of 140 K. The superconducting state of the cuprates is controlled by a process called doping, in which oxygen interstitials are carefully introduced to add or remove electrons from the material. By plotting the electron (or hole) doping concentration versus temperature, one can construct a phase diagram. A schematic of such a phase diagram is given in Figure 1.

A problem with high-temperature superconductivity is that the theoretical model that successfully explains traditional superconductivity fails to explain high-temperature superconductivity. Electron-phonon interactions, the traditional mechanism of the superconductivity, have been measured to be too small to account for superconductivity in the cuprates and other high-temperature superconductors (HTSCs) [4]. Therefore, a careful study of these HTSCs—specifically, the cuprates—is necessary in order to uncover the true source of the high-temperature superconducting state.

The cuprate family of superconductors contains well over 100 compounds. The cuprates' basic structure is a copper-oxygen layer. The compounds differ in the way their copper-oxygen layers are stacked, and in the nature of the intervening layers. Of all the cuprates, the Hg-based compounds feature the highest T_c values. Our group has performed extensive studies of the simplest of the Hg-based materials, the single-copper oxygen layer compound $HgBa_2CuO_{4+\delta}$

(Hg1201). The goal of my work was to grow and anneal samples of the double-layer compound $HgBa_2CaCu_2O_{6+\delta}$ (Hg1212), in which the copper-oxygen layers are stacked in pairs. The purpose of this effort is to gain insight into the cuprates' physical properties by comparing experimental results with those for the Hg1201and another double-layer cuprate $YBa_2Cu_3O_{6+y}$ (YBCO), which is another well-studied compound.

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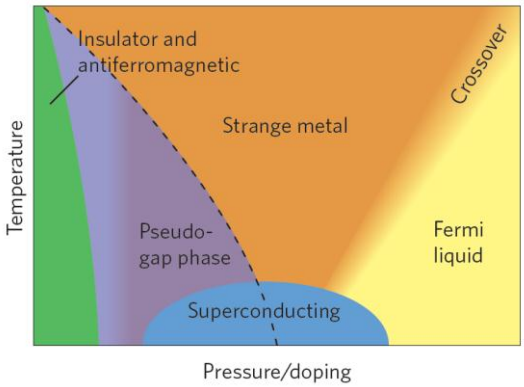

Figure 1 – Schematic phase diagram of the cuprates with dependency on hole doping level and temperature. Note the superconducting "dome" (blue) [5].

Crystal Synthesis

The growth of Hg1212 involves a solid-gas state chemical reaction at elevated temperature and pressure:

$$2CuO + 2BaO + CaO + HgO \rightarrow HgBa_2CaCu_2O_6$$

A precursor of Ba_2CuO_3 is sintered in a crucible under a constant oxygen flow at a temperature of 250ºC. Next, the precursor is removed from the crucible and ground to a very fine powder in a nitrogen-rich environment using a mortar and pestle. Then, powdered Mercury (II) oxide, Calcium (II) oxide, and the precursor are deposited into the interior of a zirconia growth crucible. Magnesium (II) sulfate hydrate is then added to the bottom of a quartz tube, along with the growth crucible containing the powders. The quartz tube is then sealed under a high vacuum

(approximately 500 mTorr) and put into a furnace. A rendering of a sealed quartz tube in a growth furnace is given in Figure 2.

The furnace heats the quartz tube and powders according to the temperature profile given in Figure 3. During the first part of the heating process, where the temperature is increased to, and then held at 780°C, the reactants decompose, which produce vaporous mercury and oxygen gas. Mercury and oxygen gas then react with the mixture of calcium (II) oxide and precursor to produce Hg1212. During this period, pressure typically maximizes but then soon decreases as mercury gas is produced and then used up during the synthesis of Hg1212. Next, the temperature is ramped up once more to 1020°C to allow the Hg1212 to melt and homogenize. After the Hg1212 is sufficiently homogenous, the temperature is lowered to allow Hg1212 crystals to form around nucleation sites. Once the temperature profile is completed, the quartz tube is removed from the furnace. The tube and crucible are then broken using a hammer to expose a small cone at the bottom of the growth crucible that contains the Hg1212 crystals.

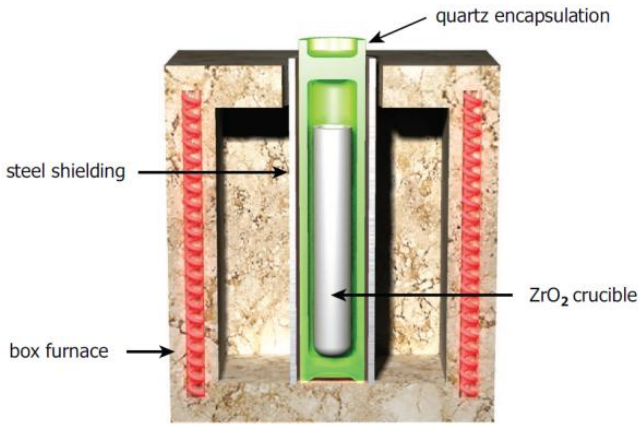

Figure 2 – Schematic of growth crucible inside growth furnace. The precursor, CaO, and HgO are placed inside the crucible, while the $MgSO_4$ hydrate is placed outside of the crucible but inside the quartz tube [6].

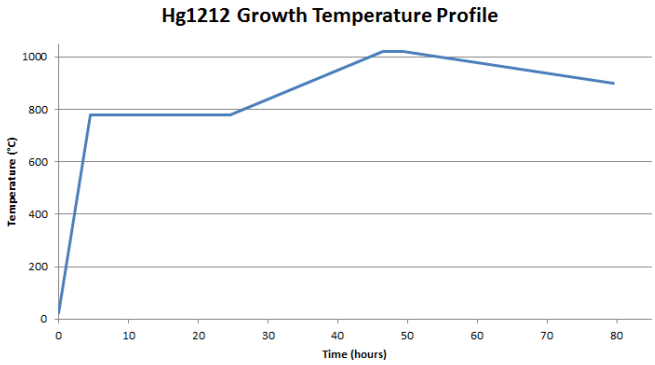

Figure 3 – Growth profile for Hg1212, which is formed at 780ºC. The sample then melts and then cools [7].

Measurement of Critical Temperature

Measurements of samples are performed in a Quantum Design, Inc. Magnetic Properties Measurements System (MPMS) that utilizes superconducting quantum interference device (SQUID) magnetometry. This instrument cools samples to below their critical temperatures and measures small changes in their magnetic moments. Above the critical temperature, the diamagnetic component of the magnetic moment is very small (close to zero.) However, when the temperature of the sample reaches the critical temperature, the magnetic moment becomes extremely large and negative due to the aforementioned Meissner effect. By measuring the magnetic moment across a wide range of temperatures, the critical temperature of the sample can be determined.

There exist some deviations from ideal superconducting behavior in as grown Hg1212 samples that are investigated in the measurement process. First, due to inhomogeneity and impurities within an Hg1212 crystal, the superconducting transition does not occur instantaneously at the critical temperature; rather, there is a small range of temperatures over which the superconducting transition occurs—the sharper the transition, the higher the sample quality. (The specific T_c is taken as the temperature at which the magnetic moment is at the half of its maximum.) Second, the Meissner effect is not fully realized in as grown samples. This is because magnetic flux vortices are pinned at impurities within the sample when it is cooled below T_c in an applied magnetic field. This effect can be quantified by taking the ratio of the magnetic moment of the sample with an applied magnetic field (field-cooled, or FC) to the magnetic moment of the sample in the absence of the magnetic field (zero-field-cooled, or ZFC) below the T_c. For better quality, annealed samples, this ratio approaches unity. Third, samples are not usually completely uniformly doped to the same extent. Consequently, some parts of the sample superconduct at higher temperature than others. This leads to a gradual sloping in the SQUID data before the primary component of the superconducting transition. However, this can be remedied by annealing.

An Hg1212 growth was completed according to the procedure outlined earlier. The magnetic moment of this sample versus its temperature is given in Figure 4. Note that these data are only zero-field cooled. The critical temperature of this sample was measured to be about 92 K, while its critical temperature transition width was found to be 40 K. The gradual

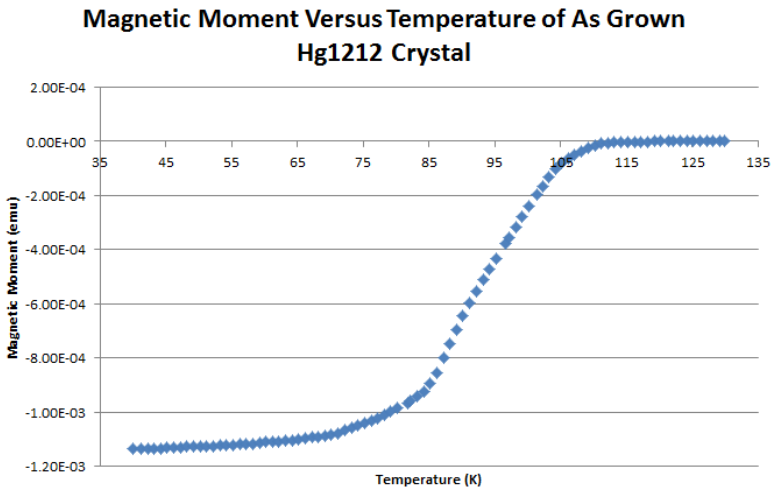

Figure 4 – Magnetic moment versus temperature of an as-grown Hg1212 crystal labeled 119_5. Its critical temperature is 92 K, while its transition width is 40 K. This data is zero-field cooled (ZFC).

sloping of the data, along with the broad transition, are caused by impurities in the sample and non-uniform doping. The impurities arise from poor reaction between the precursor and calcium (II) oxide, as well as from the presence of magnesium (II) hydrate sulfate during the synthesis of the Hg1212 crystals. The doping of the sample can be made more uniform through a process known as annealing, which is discussed next.

Annealing of Samples

The hole concentration of samples can be altered after they are grown by a process known as annealing [8]. This is accomplished by placing the sample in a furnace under some elevated temperature and gas condition. For example, to increase the hole concentration, samples are annealed under a constant flow of oxygen gas; to lower the hole concentration, samples are annealed with nitrogen or kept inside a vacuum. Samples are typically annealed for several weeks to several months at a time to insure that the sample is uniformly treated.

A sample labeled AN2 was annealed at 550°C under a constant flow of oxygen gas. SQUID data for this sample is given in Figure 5. The sample's critical temperature was measured to be 107 K, while its transition width was measured to be 25 K. Additionally, there is less of the gradual sloping behavior in the annealed data of Figure 4 than the as-grown data of Figure 3. This is because annealing the sample homogenized its doping concentration so that most of the sample went through the superconducting transition at roughly the same temperature. This all indicates that the sample is successfully annealed and ready for future measurement.

Conclusion

The above data demonstrate that the method that has been developed to produce monocrystalline Hg1212 successfully at produces medium-quality, smaller crystals. To improve the quality of these samples, one could attempt to make small variations on the growth

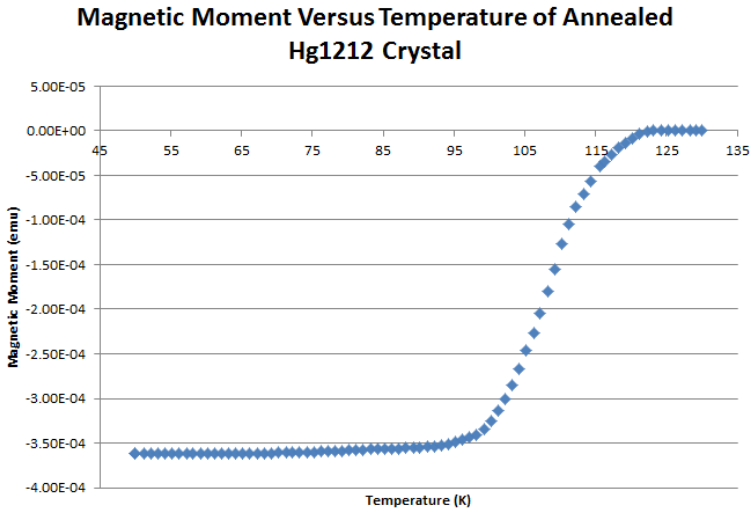

Figure 4 – SQUID (ZFC) data for a sample labeled AN2. The critical temperature of this sample after annealing was measured to be 107 K, while its transition width was 25 K. Less gradual sloping behavior in the data is associated with uniform doping.

conditions presented here and see how these changes affect the samples critical temperature transition width. Additionally, field-cooled data could be taken for Hg1212 crystals to better assess the extent to which impurities are present in as-grown samples.

To produce larger crystals, one could add more HgO to the growth crucible to drive the chemical reaction towards greater production of Hg1212. However, because of the vaporization of HgO inside the furnace, one would have to use quartz tubes that are able to withstand higher partial pressures. Once larger, high-quality monocrystalline samples of Hg1212 are produced, measurements such as the Hall effect, thermoelectric power, and magnetoresistance can be performed on the samples to better assess the nature of superconductivity in Hg1212.

Acknowledgements

I thank Professor Martin Greven for welcoming me into his lab and giving me the opportunity to learn about these exotic compounds. I would also like to thank Yang Tang for his invaluable assistance during the completion of this study. I would like to thank Vikram Nagarajan and Jacob Freyermuth, and the rest of my peers whose help allowed me to complete this study and whose knowledge helped give me a deeper understanding of the principles behind my work.

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