Crystal Growth Optimization and Characterization of $HgBa_2CuO_{4+\delta}$

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Introduction

Despite decades of research interest, the mystery behind high temperature (T_c) superconductivity has not yet been revealed. The appearance of superconductivity in many unexpected materials indicates our lack of theoretical understanding in this phenomenon [1]. One approach to build up our knowledge is by direct experimental study of the known high T_c superconductors. $HgBa_2CuO_{4+\delta}$ (Hg1201) is one such perfect model which features simple tetragonal lattice structure (as shown in the right figure) that is ideal for research purpose.

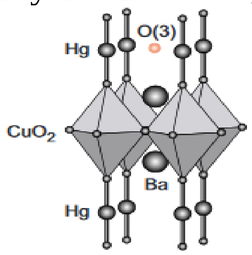


Figure 1. The tetragonal crystal structure of Hg1201 together with the interstitial oxygen dopant O(3). By changing the doping level, the density of the hole in CuO_2 layer can be tuned so that the cuprate can go through a series of phase transitions from antiferromagnetic to fermi liquid regime [2]. Picture reproduced from [3]

Growth Procedure

The progress in the current research, however, is largely impeded by the lack of high purity and sizable samples. A novel synthesis method proposed by Zhao et al [4] has succeeded in synthesizing the record-keeping high purity large Hg1201 samples, and was followed as the general guide line for growth in this study. The growth is summarized as follows:

- Preparation of precursors
  - $Ba(NO_3)_2$ and CuO powder with exact stoichiometric ratio are mixed and grinded thoroughly. The resultant powder is stored in a container for the use of future growths.
  - Before the growth, the precursor is calcined in an oxygen atmosphere which is achieved by employing a specially designed quartz kettle and continuous oxygen flow.
- Reaction and Crystallization to form Hg1201
  - After calcination, precursor is immediately set under vacuum.
  - 2.14g precursor is subsequently put into a zirconium crucible in a N_2 environment
  - The crucible together with 1.5g HgO and a small amount of $MgSO_4$•$7H_2O$ is sealed inside a quartz tube by a welded plug.
  - The quartz tube is then placed inside the furnace with the heating temperature profile shown below.

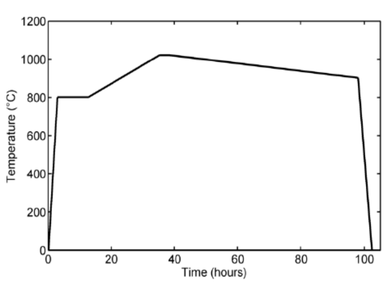


Figure 2. The furnace temperature profile of the growth of Hg1201. The sample is first heated to 800℃. The system then stays at 800℃ for 10h to synthesize Hg1201. The furnace heats up to 1020℃ to melt and mix all the substances in the crucible. The mixture is then slowly cooled down to 900℃ which enables the crystallization of Hg1201. Finally, the furnace cools down to room temperature quickly. Reproduced from [5]

Crystal Characterization

In superconducting state, superconductor tends to expel small external magnetic field by forming a magnetization that opposes the direction of applied field. This is called Meissner effect [6]. However, when the external field strength exceeds some threshold, the superconducting state can break down. For Hg1201 and other type II superconductors, when the external field reaches the first critical field strength H_{c1}, some magnetic flux penetrates the superconductor and form "flux tubes" that allow the passage of magnetic field in some regions while the other regions are still in superconducting state [6].

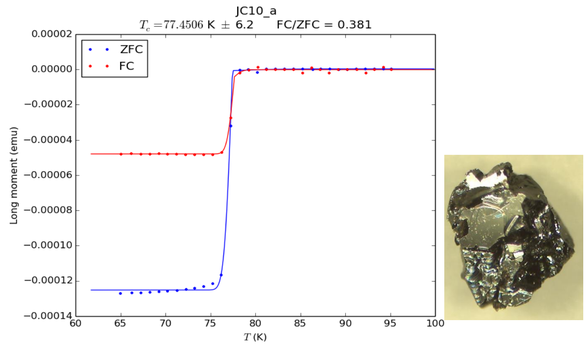
Upon cooling under external magnetic field (Field Cool, FC), as the temperature crosses the critical temperature, the critical field will start at zero and then increase. When H_{c1} is small at the beginning, some magnetic field is allowed to penetrate through the "flux tubes". As temperature further decreases below T_c, H_{c1} increases and eventually exceeds the external field. The internal field will then be expelled out as a result of Meissner effect. However, if non-superconducting defects are present inside the sample, the magnetic field penetrating through them will remain in the defects. This effect is also called magnetic vortex pinning [3]. The trapped magnetic field is in the opposite direction to the magnetization in the Meissner effect. Therefore, the measured magnetization is smaller than that measured under zero field cooling (ZFC). This difference can then be used to infer the purity of the resultant samples.

An ideal high purity superconductor in addition to have small difference between ZFC and FC (high FC/ZFC ratio) should also make sharp transition at T_c. These two effects were used as the standards of estimating the sample quality.

The magnetization was measured by superconducting quantum interference device (SQUID) in a Magnetic Properties Measurement System (MPMS) in this study. The results from the characterization are summarized in the section below.

Results & Conclusion

Several variations from the standard growth procedure were tested including: mass of $MgSO_4$•$7H_2O$, amount of HgO, HgO put inside or outside the crucible, samples' reaction time under 800℃.



a) b)

Figure 3. a) The MPMS curve of one sample from the growth JC10 (mass≈0.3mg) which has sharp transition at its T_c=77.45K and FC/ZFC ratio 38%; b) a photograph of one sample from JC17 (mass=7.2mg). The shiny and flat surface on the top indicates high quality of the sample. It is noteworthy that the first run of JC17 in the furnace was interrupted by the short of the furnace during the crystallization phase. A second run was started three weeks later. The resultant crystal had unexpected good quality. Two possible large samples (0.6315g and 0.2984g) were also picked out and are ready for future study including Neutron Scattering. The surprising result of JC17 was one of the motivation behind trying longer reaction time

The data above were obtained from MPMS. Raw data file was parsed and fitted to a function by a Python program. The ZFC and FC region were split and fitted differently. The fit function was a piecewise defined error function with five parameters, since its shape can approximate the ideal transition quite closely as shown in Figure 3 a). Both the FC/ZFC ratio and T_c were estimated from the fit parameters.

A summary of all growths done by the author has yielded the following observations:

- Less $MgSO_4$•$7H_2O$ in the growth, in general, leads to small crystals with good FC/ZFC ratio; more $MgSO_4$•$7H_2O$ on the other hand, tends to grow large crystals with low FC/ZFC ratio. However, this trend is not deterministic. This conclusion is consistent with the study from a former group member [7].
- The resultant crystal from longer reaction time (20h under 800℃) has slightly higher FC/ZFC ratio than the standard procedure. This small improvement by doubling reaction time also indicates that the reaction time in the standard procedure is already nearly optimal.
- No explicit dependencies on the furnace of the growth or different precursors are observed
- No obvious difference among using 1.5 g HgO, 1.55g HgO and 1.6g HgO is observed. The number of growths done with 1.7g HgO is not sufficient to support any conclusion.
- The effect of putting HgO inside or outside crucible is not clear and requires further exploration. However, according to Michael Veit, a former group member, putting HgO inside the crucible tends to introduce more impurities in the crystals [5].
- The FC/ZFC ratio increases gradually with time as the researcher becomes more experienced but the trend of size of samples is rather inconsistent.

Future Directions

The effect of varying the amount of excess HgO and putting HgO inside or outside the crucible can be explored in the future. In principle, the current growth procedure has already been optimized through years of intensive study in the crystalgrowth of Hg1201. However, the decrease in both quality and size in the crystals compared to some early work in the group [4,5] indicates that some unknown variant is affecting the quality of current growth. The primary goal in the near future will be continuing varying different parameters in the growth to bring the quality back to the previous level achieved in the group.

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