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Preparation of bismuth cuprate superconductor single crystal and iodine intercalated compound

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**PREPARATION OF BISMUTH CUPRATE SUPERCONDUCTOR
SINGLE CRYSTAL
AND
IODINE INTERCALATED COMPOUND**

A Thesis

Presented To

The Faculty of the Department of Chemistry

San Jose State University

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

by

Angelica Alvarado

December 1997

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ABSTRACT

Preparation of Bismuth Cuprate Semiconductor Single Crystal and Iodine Intercalated Compound

By

Angelica Alvarado

The work describes the growth of a $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ single crystal with an area of up to $4 \times 12 \text{ mm}^2$. The experiments revealed that a large-area crystal was obtained from a starting composition of bismuth (Bi), strontium (Sr), calcium (Ca) and copper (Cu) in proportions 2:2:1:2 respectively using a new method. Based on the investigation of the temperature dependence of formed phases in the system, the growth mechanism for a pure crystal depends on the cooling time. The superconducting critical temperature of the 2:2:1:2-phase single crystal was determined.

The effect of iodine intercalation on the structure the 2:2:1:2 phase was determined. The X - Ray data indicate that the intercalation with iodine changed the crystal structure. The superconducting transition temperature decreased for the intercalated phase.

A model for the distribution of iodine and bismuth atoms in the average structure of the intercalated phase 2:2:1:2 ($\text{IBi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$) is presented.

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CHAPTER 1

INTRODUCTION

1.1 Superconductivity: History and Recent Work

Superconductivity is the ability of some substances to conduct electricity without resistance and without energy loss while at very low temperatures. Since the discovery of superconductors by Dutch Physicist Heike Kamerlingh Onnes in 1911,¹ many materials have been examined to determine whether they are superconductors² (See Figure 1.1, Page 32). Kamerlingh Onnes was devoted to quantitative research in physics - quantitative analysis being the measurement of the proportion of known components in a mixture. Kamerlingh Onnes studied conformity in the behavior of gases and set out to obtain precise measurements of gas properties. To better understand how gases actually behave, Kamerlingh Onnes found it necessary to slow the movement of gas molecules to near immobility. He accomplished this by operating at very low temperatures nearing absolute zero.

Kamerlingh Onnes discovered the remarkable disappearance of electrical resistance from a thin rod of mercury while submersed in liquid helium at 4K. He realized that the mercury had passed into a different electrical phase, later called the superconducting phase. This phase was created by cooling the mercury below a certain temperature known as the critical temperature, T_c . Above this specified temperature the material no longer displays superconducting properties and is considered to be in the normal state (See Figure 1.2, Page 33)

1.2 The Meissner Effect

In 1933, Walter Meissner and R. Ochsenfeld² discovered another important property of materials in the superconducting phase called the Meissner Effect. The Meissner Effect is the ability of a material to expel an applied external magnetic field. This has been the key test in finding materials possessing the ability to be superconductors.

The magnetic properties of superconductors are as remarkable as their electronic properties. In addition, an explanation of superconductivity involves both magnetic and electronic phenomena in an inseparable way. The relation between these phenomena is apparent in the Meissner Effect. If a material is a perfect conductor and exhibits no electrical resistance it will not be penetrated by magnetic flux when it is brought into a magnetic field (See Figure 1.3, Page 34). The reason for the exclusion is that as the flux begins to enter the sample, electric currents are induced on the surface of the superconductor, and an opposing magnetic field is produced. Since the electric current remains undiminished in a superconductor, the reverse field persists and the applied magnetic field does not penetrate the sample (See Figure 1.4, Page 35).

The main goal of superconductor research is to find materials with inexpensive composition that increase the temperature at which they possess superconducting properties. In 1941, scientists reported superconductivity properties in niobium nitride at 16K. In 1953, vanadium-3 silicon was found to superconduct at 17K. In 1962, Westinghouse scientists developed the first commercial niobium-titanium superconducting wire. In 1972, John Bardeen, Leon Cooper, and John Schrieffer won the Nobel Prize in

superconducting wire. In 1972, John Bardeen, Leon Cooper, and John Schrieffer won the Nobel Prize in Physics for the first successful theory of how superconductive materials work. In 1986, at IBM Research, Alex Muller and Georg Bednorz made a ceramic compound at 35K. In 1987, Paul Ching - Wu Chu of the University of Houston and Maw - Kuen Wu of the University of Alabama substituted yttrium for lanthanum and made a ceramic that superconducts at 98K. IBM and AT&T Bell Labs scientists produced a ceramic superconductor at 125K².

Bednorz and Muller's discovery of superconductivity in copper oxides initiated further research on the physical properties of new and more complex materials (See Figure 1.5, Page 36). Thus, increased research in Solid State Chemistry could prove very useful even absolutely necessary, since it would not only affect academic results, but could influence the industrial world.

Bismuth (Bi) was introduced in May 1987³ as a potential cation for generating superconductivity in the presence of copper (Cu). The structural studies of the superconducting phases of a bismuth strontium calcium copper oxygen compound with a transition temperature at $T_c = 80\text{K}$ was identified as $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$. Structural models were developed (See Figure 1.6, Page 37).

Table I, Page 27, lists the interatomic distances in bismuth cuprates. These models are referred to in the literature by $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$ (See Figure 1.7, Page 38).

1.3 Phase Diagram of $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$ ⁴

All materials exist in gaseous, liquid, or solid form. The form depends on the conditions or state variables such as composition, temperature, pressure, magnetic field and electrostatic field. The term “phase”⁵ refers to the region of composition space occupied by a physically homogeneous material. Any change in condition of state, no matter how small, will result in a different phase.

The temperature region where the 2:2:1:2 phase occurs (See Figure 1.8, Page 39) was examined to find how to grow large crystals. The raw material showed a partial melting above 885°C⁵ and almost complete melting above 950°C. With a decrease in temperature, the 2:2:0:1 phase is first formed in the temperature range 900 to 1000°C in the melt, and the 2:2:1:2 phase appears at 885°C when cooled to room temperature (See Figure 1.9, Page 40).

This result suggests that the 2:2:1:2 phase is not primarily crystallized from the 2:2:1:2 composition and that it is formed through a reaction, in which a 2:2:1:2 phase is formed, below 885°C⁵. Therefore, a lower cooling rate of 1°C per hour was expected to be effective for growing a larger crystal. The growth experiments demonstrated that the size of a 2:2:1:2 phase crystal increases with a decrease in cooling rate during growth. The largest crystal was obtained from 2:2:1:2 composition at a cooling rate of 1°C per hour.

1.4 Intercalation with Iodine

Intercalation is the insertion of adducts or guest species (in this case iodine) ions or molecules in between the layers or galleries of the host lattice (See Figure 1.9, Page 40). Intercalation is most common in layered structures which are highly anisotropic, intra-planar binding forces being much greater than the inter-planar ones. Intercalation compounds are important for chemists, physicists, engineers, and material scientists in the areas of structural phase transitions, sub-micron structures, two dimensional physics, band theory, synthesis of materials with specific structures and properties, electrical and thermal transparent structures, and magnetic and superconducting properties.

1.5 Objective

The purpose of this thesis was to develop a procedure to grow a single, large, high quality superconductor crystal of $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$. The thesis investigated the crystal growth conditions for the 2:2:1:2 phase, the starting composition, the cooling method used to develop of a pure crystal, and iodine intercalation into $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$ to form a $\text{IBi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$ crystal. The characterization of the compounds determined by X-ray fluorescence and diffraction.

1.6 Thesis Overview

Chapter 2 presents the experimental method for the preparation of pure $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$ crystals and the intercalation of the crystals with iodine. The Meissner Effect test, identification of components through X-ray fluorescence and X-ray diffraction, SEM and ESR results are described in chapter 3. The discussion is in chapter 4. The conclusions from the experimental data are given in chapter 5.

CHAPTER 2

EXPERIMENT

2.1 Experimental Setup

2.1.1 Starting Materials

The starting materials, bismuth oxide (Bi_2O_3), calcium carbonate (CaCO_3), strontium carbonate (SrCO_3) and copper oxide (CuO), used in the experiment were powder-type reagents from Aldrich Chemical Company⁶. The percent purity of each the starting materials were as follows: Bi_2O_3 (99.999%), CaCO_3 (99.995%), SrCO_3 (99.999%), and CuO (99.999%). These were dried in an oven at 41°C for three days.

2.1.2 Weighing Procedure

Starting materials were chosen in the weight proportion 2:2:1:2 respectively for Bi_2O_3 , CaCO_3 , SrCO_3 and CuO .

Table II. Starting material weight, purity and ratio of $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_x$ ⁷ for single crystal preparation.

Element	Ratio	Molecular Weight	Grams	% Purity
Bi_2O_3 ,	2.0	465.96	8.9927	99.9998
SrCO_3	2.0	147.63	5.6982	99.999
CaCO_3	1.0	100.087	1.9316	99.995
CuO	2.02	79.55	3.3775	99.999

Each 20 gram sample of powder was put on a piece of paper and weighed on an analytical balance. This process was repeated three times to insure accuracy of the readings.

2.1.3 Grinding Materials

All weighed materials were placed in a agate mortar ground with a pestle for 30 minutes until no noticeable inhomogenities were found and the compound looked like a very fine powder. Then the powder was passed through a 125 micrometer sieve to assure proper mixing.

Several samples, each containing approximately 20 grams of powdery starting material, were placed in glass beakers, covered with perforated aluminum foil and placed in a box oven. The oven was set at 100°C and the samples were left in the oven for 24 hours.

2.1.4 Preparing Pellets

Pellets of the powder material were prepared by a pelletizing process. This involved placing the fine powder poured into a space under a steel rod. Pressure was applied to sandwich powder in the space into a desired pellet thickness. The powder was pressurized at 15 pounds per square inch for a period of one minute. Several pellets were produced by this process. The pellets were removed from the pelletizer and placed into a crucible and covered with an alumina cover to prevent bismuth evaporation or

contamination. The crucible was placed into a box oven at 890°C until pellets were sintered.

2.2 Crystal Preparation

2.2.1 Single Crystal Preparation

The pellets were placed in both alumina and ceramic crucibles. Each crucible was placed in a refractory material to be analyzed separately with the purpose of finding the appropriate crucible for developing a superconductor crystal of $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$. It was necessary to cover the crucibles so that none of the constituents would evaporate from the melt and also to prevent contamination from the oven during the crystal growth process. The alumina cover also helped to reduce bismuth evaporation. The crucibles were first placed in a box oven for 24 hours at 100°C. Approximately 20 grams of starting materials were placed in each crucible. The pellets were placed in a vertical oven.

2.2.2 Furnace Ramp Parameters

A Marshall vertical oven was used for crystal growing procedure (See Figure 2.1, Page 41). The alumina crucible was placed into the oven in zone 2 at ambient temperature (See Figure 2.2, Page 42). The oven was programmed with appropriate ramp parameters (See Table III, Page 28).

2.3 Crystal Growth

2.3.1 Process Description

The crystals used in this study were grown using a directional solidification approach⁸ employing a stationary crucible in a strong temperature gradient (approximately 10°C per cm). As the average oven temperature decreased from above the melting point of the $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$,⁹ one point or side of the crucible reached the crystallization temperature first. A crystallization zone proceeds across the crucible as the average temperature is further reduced. The volume of the melt in this zone, at any one time, was controlled by the size of the temperature gradient across the crucible. The growth rate of the crystals across the crucible was determined by the temperature ramp rate.

The following chart represents the temperature ramp parameters used in the experiment:

Table VII Temperature ramp parameters

Details of the heating schedule are as follows: after rapid heating, the temperature was held at 980°C for 10 hours, cooled at 1°C per hour to 830°C and then cooled to 800°C over 5 hours¹⁰. The furnace was then switched off and the crucible was cooled in air to room temperature over a three hour period. Preparation of a single sample took a total of 175.9 hours. Once ambient temperature was reached, the sample was removed.

2.3.2 Harvesting Crystals

After completion of the ramp parameters,¹¹ the alumina crucible was carefully broken. The portion of the sample removed from the crucible, referred to as the house, contained a cavity in which the scales of crystals were formed (See Figure 2.3, Page 43). The crystals were dislodged from the soft matrix of flux using a surgical scalpel. The platelets were removed and cleaved using a needle and tweezers.

2.4 Iodine Intercalation

2.4.1 Iodine Sample Preparation

The intercalation of single crystals of $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$ is the insertion of adducts or guest species such as ions or molecules between the layers of the host lattice.¹² The pure $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$ crystals were prepared as described above in section 2.1 to 2.3. The samples were prepared in a glass tube. The tube was placed in the beaker that contained iodine crystals.

2.4.2 Intercalation with Iodine

Elemental iodine crystals were placed in the bottom of a Pyrex tube. The tube with pure $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$ crystals was placed into the Pyrex tube with iodine crystals. Iodine was intercalated by sealing the entire Pyrex tube and annealing at 120°C for a period of 48 hours. During this process the iodine was absorbed into the $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$ crystals.

In High Resolution Electron Microscope (HREM) images¹², the image on the left shows a $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$ film without iodine. The image on the right shows that in the iodine intercalation, iodine atoms appeared between the Bi-O planes as pictured:

Figure 2.4

HREM image depicts iodine atom placement in pure crystal during iodine intercalation

Images indicate that iodine intercalation alters the symmetry of the pure material.

2.5 Sample Characterization:

2.5.1 The Meissner Effect

A test to check for the Meissner Effect was set up in the lab. One of the resulting $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$ crystals was laid in a petry dish in an atmosphere of liquid nitrogen for supercooling.¹³ The sample was placed over a magnet for a few minutes. The sample began to float magically in the chilled air repelled by the opposing magnetic force. This phenomenon was proof that the material was showing the behavior of a superconductor with absence of resistance.

2.5.2 XRF (X-ray Fluorescence)

A single crystal of $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$ was analyzed by XRF using a small amount of sample powder. The powder was placed on a glass slide and laid in the XRF instrument. Reference data was entered which gave expected α and β angle locations¹⁴ of each element in the sample (SeeTable IV, Page 29). The instrument was used to precisely show the angle location and concentration of all the elements in the sample. The data obtained showed all the elements present in the $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$ single crystal. X-ray fluorescence studies were carried out using an SP6 4 - X Ray Spectrogoniometer system at the proper settings (See Figure 2.5, Page 44).

2.5.3 XRD (X-ray Diffraction)

A single crystal of $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$ was analyzed by XRD using a small amount of powder and crystalline samples. This mix was placed on a glass slide and laid in the XRD instrument. The instrument was used to see what phases were present in the compound. The analysis showed the presence of the 2:2:1:2 phase. Observing this phase indicated that the conditions used for development of the single crystal were appropriate ones used (See Figure 2.6, Page 45). The sample analysis took approximately three hours per sample.

2.5.4 ESR (Electron Spin Resonance)

A single crystal of $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$ was analyzed by ESR using a sample mounted on top of a wooden stick. The crystal was placed in an ESR instrument to see if the crystal obtained from the experiment has superconducting characteristics. The ESR analysis began at room temperature until the field indicated the onset of superconductivity.

2.5.5 SEM (Scanning Electron Microscope)

A single crystal of $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$ was analyzed by SEM. The crystal was placed on the SEM instrument with the purpose of magnifying the surface of a pure crystal and analyzing the elements present in the sample. Samples of crystals with iodine intercalated were also examined.

2.6 Problems

The procedures described were the successful ones. It is important to note that each heating experiment should be done at the suggested temperature and for the given length of time. Otherwise, the product of each heating could be a very light green mixture if the starting materials were not heated enough. The product could also be a black metallic ceramic phase grown on the crucible and hard to isolate. The latter was due to excessive heat or prolonged heating. The sample should be pelletized before placing in the furnace. The pellet sample has a better energy transfer, and this helps the formation of the single crystal. Otherwise, it is impossible to develop a superconductive crystal. The $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$ compound is characterized by its high transition temperatures and high critical magnetic field. The preparation method of Bi-Sr-Ca-Cu-O was not obtained by trial and error, but by deduction from the phase diagram as described in chapter 3.

CHAPTER 3

RESULTS

3.1 Temperature

3.1.1 Ramp Parameters for Growing a Single Crystal

The multi-solidified materials contained mainly the 2:2:1:2 phase of $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$. In the 2:2:1:2 composition, the temperature region where 2:2:1:2 phase occurred was examined to grow a larger crystal. The raw material showed partial melting above 830°C and almost complete melting above 980°C. With a decrease in temperature, the 2:2:1:2 phase was first formed in the range of 900°C to 1000°C in the melt and then appeared at 830°C and after being cooled to room temperature.

3.1.2 Cooling Rate

The results suggest that the 2:2:1:2 phase is formed through a lower cooling rate and effective for growing a larger crystal. The growth experiments demonstrated that the size of a 2:2:1:2 phase crystal increased by decreasing the cooling rate during growth. The largest crystal was obtained from the 2:2:1:2 composition at the cooling rate of 1°C per hour.

A lower cooling rate was expected to be effective for growing a larger crystal. The largest crystal had an area of $4 \times 12 \text{ mm}^2$. Overall, the crystals had average dimensions of approximately 2 cm^2 (See Figure 3.1, Page 46).

3.2 ESR Results

The temperature was lowered until a zero field energy loss appeared. This temperature revealed where the superconducting behavior of the crystal was found. The crystal exhibited superconductive properties at 85.7°K using ESR analysis (See Figure 3.2, Page 47).

3.3 XRF Results

XRF analysis showed the 2θ angle of each element present in the samples (See Figure 3.3, Page 48). The amount of sample lost during the experiment was determined to be insignificant.

3.4 XRD Results

The sample was analyzed for nearly 3 hours. A print out of the analysis gave XRD information such as 2θ angle, D-spacing and the relative intensity from the samples (See Table V, Page 30). The XRD data was represented graphically to distinguish the different phases found in the pure $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$ crystal (See Figure 3.4, Page 49). XRD results obtained from the single crystal showed the 2:2:1:2 phase was present in the sample.

3.5 SEM Results

Under SEM analysis, all the elements in the samples were found in the spectrum data produced (See Figure 3.5, Page 50). The physical properties of the crystal surface were observed through the SEM analysis.

The surface of the crystal appeared even, smooth and glossy (See Figure 3.6, Page 51). The very thin layers and flexible texture of the crystals gave the appearance of fish scales (See Figure 3.7, Page 52). There was virtually no porosity and no cracks observed in the samples.

The presence of aluminum was found in the SEM spectrum data (See Figure 3.8, Page 53). This was due to the aluminum from the alumina crucible being partially absorbed into the sample during the heating process. The aluminum absorption was only observed in one of the many samples prepared and analyzed.

3.6 Iodine Intercalation

3.6.1 SEM Results With Iodine

SEM analysis showed the surface of the crystal changed tremendously with intercalation. When the contents of the crucibles were removed, the intercalated $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$ crystals had become porous, dry and dull (See Figure 3.9(a), Page 54) instead of a black, glossy, and flexible material. The superconducting samples had irregular borders and some samples surfaces contained spots believed to be impurities.

These properties were a direct consequence of adding iodine to the pure crystal (See Figure 3.9(b), Page 55). The spectral data produced during SEM analysis detected iodine in the compound sample, as was expected (See Figure 3.10, Page 56).

3.6.2 XRF Results With Iodine

The Intercalation of iodine was confirmed by x-ray diffraction. During the heating process iodine was absorbed into the bismuth oxide sample. This was determined by weighing samples before and after the intercalation, heating processes. Samples that were examined absorbed nearly the same amount of iodine in each case.

Table VI. Amount of iodine absorbed by pure crystal samples 48 hours after heating process.

Sample Number	Pure Crystal Weight (grams)	Weight after 48 Hours @ 120°C with Iodine (grams)	% of Iodine absorbed into crystal (grams)
1	0.0273	0.0389	29.82
2	0.0301	0.0421	28.50
3	0.0224	0.0346	35.26

With SEM and XRF analysis conclusive that iodine intercalation had altered the crystal properties to those less desirable in good superconductor material, no further analysis was done on these samples.

3.7 Problems

The data reported were obtained during successful experiments. In a few samples in which ceramic crucibles were used, a region of greenish-yellow polycrystalline material was noticed around the top rim of the melt. This was a result of a reaction with the ceramic crucibles (See Figure 3.11, Page 57). The crystals observed in these samples were dark nodules coated with yellow particles (See Figure 3.12, Page 58). The mix traveled up the side of the crucible about 3 cm. Also black material on the bottom of the crucible was found. Small cavities with black crystals were present in the side of the crucibles (See Figure 3.13, Page 59). These were mostly cupric oxide.

CHAPTER 4

DISCUSSION

Many samples were prepared in this work using different ramp parameters, crucible materials, and cooling time temperatures. In comparing the experiments, the best results were obtained when alumina crucibles were used. The use of ceramic crucibles affected the growing and the quality of the $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_x$ crystal compounds. It was noted that the formation of a dark green material was the consequence of using the ceramic crucibles instead of the alumina crucibles. The porosity and texture of the ceramic crucibles affected the formation of the crystal. More than 50 percent of the sample was absorbed by the ceramic crucible during the process at high temperature parameters.

A small amount of sample was absorbed on the surface of the crystal using the alumina crucibles, but no loss was observed by absorption after the ramp parameters. The properties of the crystal were found to depend strongly on the specific annealing condition.

During the crystal growing process, it was found that the ramp temperature parameters, cooling time and amount of sample used in the preparation of the compound were also responsible for the quality of the $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_x$ crystals. The results obtained for the growing process of a single crystal were dependent on the conditions of temperature, crucible material and cooling ramp parameters.

The XRD results confirmed the presence of the 2:2:1:2 phase in the $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$ crystal. XRF analysis showed the location of each component in the mixture of $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$. The XRD and XRF results were as expected from the beginning of the experiment.

The pure single crystal of $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_x$ was intercalated with iodine an $\text{IBi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_x$ crystal. Results obtained by x-ray diffraction indicated that comparing the pure crystal (See Figure 4.1[a], Page 60) to the iodine intercalated crystal (See Figure 4.1[b], Page 60), different 2θ angles occurred under the same conditions. Therefore, the structure of the crystal was changed by iodine intercalation.

Iodine intercalation also altered the crystal texture, color and flexibility. Spots were observed on the surface of the crystal, inflexible, dry and dull surface in the intercalated crystals were some of the properties observed in the intercalation with iodine. All the properties beneficial to good superconductivity were lost after the iodine intercalation.

The SEM results showed that the pure crystal surface was smooth compared with the surface of iodine intercalated crystal. The porosity of the surface, its dryness and irregularities were easy to detect.

CHAPTER 5

CONCLUSIONS

The slow-cooling technique (1°C/h from 835°C to room temperature) and 2:2:1:2 proved to be the proper combination for obtaining good results in the growth of a single crystalline $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_x$ superconductor.

Procedures for mixing components and forming pellets were the most important steps in proper growth of the $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_x$ single crystal. The starting materials, bismuth oxide (Bi_2O_3), calcium carbonate (CaCO_3), strontium carbonate (SrCO_3) and copper oxide (CuO), were mixed until no inhomogenities were observed. The mixture was pressurized into pellets to insure good heat transfer properties. The sintered pellets were placed in a crucible made of aluminum, which produced the best quality and largest crystals during the growing process.

In the phase diagram study, the appropriate 2:2:1:2 ratio was used in order to produce large, high-quality, single crystals. The critical temperature for superconductivity was found at 85K. The necessary temperature range of the crystal growth was from 830°C to 845°C along with a proper cooling time of approximately 1°C per hour. Thermal equilibrium stability in the solution was found at this temperature and composition.

It is also important to note that each heating experiment should be done at the suggested temperature and length of time. Otherwise, the product of each heating could be a very light green mixture if the starting materials were not heated enough. A greenish-

yellow material present around the top rim of the crucible could be an excess of Bi_2O_3 , but the excess of Bi_2O_3 is not crucial to the formation of large, high-quality single crystals in the 2:2:1:2 system.

Various analyses were performed to identify the properties of the crystal. By x-ray diffraction, the 2:2:1:2 phase was found in the sample and in the correct proportion. X-ray fluorescence was used to locate the 2θ angle from each element present. The SEM analysis of the pure crystal indicated that the surface appeared smooth, black and glossy. These are typical properties of superconductors. Use of the Meissner Effect confirmed that the compound was, indeed, superconducting.

Intercalating iodine between the two Bi-O planes of the pure crystal altered the physical properties of the superconductor. After the intercalation, changes on the surface of the crystals were observed. The surface appeared porous and yellow - green in color. The crystal also showed a lost flexibility. These properties were observed by SEM analysis.

The proportion of compound used, cooling time, mixing procedure, pellet preparation, and ramp temperature are all integral components for obtaining good results in the process of crystal growth.

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TABLE I

Interatomic distances in bismuth cuprates $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$.

Bond		Sample 1	Sample 2	Sample3
Bi-O(3)	X 1	2.159	2.439	2.466
Bi-O(2)	X 2	2.251	2.191	2.123
Bi-O(2)	X 2	2.404	2.378	2.442
Bi-O(2)	X 2	3.073	3.097	3.131
Bi-O(2)	X 2	3.260	3.299	3.266
Bi-O(2)	X 2	3.451	3.462	3.33
Sr-O(3)	X 1	2.165	2.298	2.321
Sr-O(1,1)	X 2	2.236	2.661	2.92
Sr-O(1,2)	X 2	2.719	2.319	2.246
Sr-O(3)	X 2	2.791	2.954	3.052
Sr-O(3)	X 2	2.865	2.712	2.694
Sr-O(1,1)a	X 1	3.387	3.07	3.082
Sr-O(1,1)a	X 2	-	-	2.398 (X 0.19)
Sr-O(3)	X 2	-	-	2.642 (X 0.19)
Ca-O(1,2)	X 4	2.296	2.315	2.248
Ca-O(1,1)	X 4	2.873	2.700	2.513
Ca-O(1,1)a	X 4	-	-	2.872 (X 0.19)
Ca-O(1,1)a	X 4	-	-	3.079 (X 0.19)
Cu-O(1,2)	X 2	1.936	1.873	1.902
Cu-O(1,1)	X 2	1.988	1.987	1.956
Cu-O(3)	X 1	2.481	1.988	2.094
Cu-O(1,1) a	X 2	-	-	1.933 (X 0.19)
Cu-O(1,1) a	X 2	-	-	2.229 (X 0.19)

TABLE III

Marshall oven ramp parameters including oven setting, temperature variations and setting duration.

Program Setting		Temperature	Duration in hours
Pr1		300 C/h	3.20
PL1		980 C	-
Pd1		10 h	10.00
Pr2		1 C/h	150.00
PL2		830 C	-
Pd2		0 h	0.00
Pr3		6 C/h	5.00
PL3		800 C	-
Pd3		0 h	0.00
Pr4		100 C/h	7.80
PL4		25 C	-
Pd4		0 h	-

TABLE IV

Referenced alpha and beta angles of starting material elements.

Element	Z	Alpha	Beta
Ca	20 K	113.08	100.22
Cr	24K	69.35	62.36
Cu	29 K	45.03	40.45
Sr	38 K	25.15	22.42
Ba	56 K	87.13	79.22
W	74 K	43.02	37.12
Tl	81 K	34.90	29.21
Bi	83 K	33.01	27.35

TABLE V

XRD analysis of pure $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$ crystal sample.

Entry	2 Theta	D-Spacing	Relative Intensity
1	28.96996	3.082045	100
2	34.92298	2.569113	94.7
3	23.06863	3.855371	81.5
4	59.94852	1.543001	45.1
5	47.13631	1.928023	38.8
6	17.28883	5.129015	10.4
7	31.5365	2.83683	10
8	26.08202	3.416377	8.6
9	20.80247	4.29959	8.5
10	66.66864	1.402852	7.8
11	22.43359	3.96305	7
12	11.52862	7.675493	6.8
13	21.79062	4.078511	6.7
14	17.91942	4.949921	6.6
15	15.745	5.628277	6.5
16	20.11015	4.413631	6.5
17	21.23968	4.183044	6.4
18	24.0886	3.694387	6.4
19	11.16758	7.922811	6.3
20	12.54901	7.05358	6.3
21	14.71282	6.020721	6.2
22	11.96045	7.399324	6.2
23	12.82526	6.902262	6.2
24	14.26333	6.209429	6.2
25	13.37034	6.622073	6.1
26	13.85425	6.391845	6.1
27	10.45943	8.457573	6.1
28	88.69098	1.102888	5.7
29	28.15194	3.169712	5.5
30	80.99061	1.187122	5.3
31	27.73244	3.216699	5.3

32	97.03551	1.029018	4.9
33	31.13486	2.872503	4.8
34	53.66553	1.707844	4.3
35	34.14669	2.62572	4.2
36	32.72174	2.65783	4.2
37	42.33199	2.135036	3.9
38	36.36229	2.470657	3.8
39	44.31545	2.043974	3.8
40	38.14	2.3594991	3.7
41	38.14947	2.358927	3.6
42	37.21404	2.416044	3.5
43	39.21079	2.297489	3.4
44	40.99855	2.201342	3.3
45	56.8908	1.618446	3.3
46	39.99239	2.254372	3.1
47	43.84232	2.064927	3
48	40.25523	2.240258	3
49	43.06289	2.100478	2.9
50	46.41	1.956489	2.7
51	44.90453	2.018519	2.7
52	45.57145	1.990519	2.6
53	48.70011	1.869708	2.5
54	49.30545	1.848161	2.4
55	50.44978	1.808893	2.4
56	70.37831	1.337723	2.3
57	49.91134	1.827137	2.3
58	59.26349	1.55919	2.3
59	59.04078	1.564538	2.2
60	52.09191	1.755669	2.2
61	51.41571	1.777158	2.2
62	77.42274	1.232656	2.2
63	58.625711	1.574621	2.1
64	57.98875	1.59036	2.1
65	63.40425	1.466975	2.1
66	58.37773	1.580717	2
67	55.71546	1.649769	2
68	66.37597	1.408325	2
69	55.732	1.649318	2
70	65.46174	1.425761	1.7
71	85.17234	1.139208	1.7
72	71.80669	1.314587	1.7
73	78.41334	1.219548	1.6
74	84.94719	1.141651	1.6
75	73.07865	1.294816	1.5
76	78.907	1.213153	1.5
77	75.81277	1.254775	1.5
78	76.71243	1.242288	1.5
79	80.33298	1.195174	1.5
80	75.55667	1.25839	1.4
81	79.811226	1.201668	1.4

FIGURE 1.1

Discovery timeline of increasing temperatures in superconductor compounds¹⁴

FIGURE 1.2

Behavior of superconductor material: normal state vs. superconductive state

FIGURE 1.3

Magnetic behavior of superconductor material: normal state (field penetrated) vs. superconductive state (field does not penetrate sample)

FIGURE 1.4

Meissner Effect¹⁵

FIGURE 1.5

Discovery timeline of increasing number of components combined to locate more superconductive materials

SUPERCONDUCTING MATERIALS

FIGURE 1.6

Crystal structure¹⁶ of $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$

FIGURE 1.8

Diagram of 2:2:1:2 phase ratio of chemical variables and temperature range in which crystal is formed

- Only represents the composition
- 4 Variables
- The phase 2:2:1:2 - grow to 840°C
- Tetrahedron

FIGURE 1.9

Post-annealing temperature with phase distribution¹⁸

FIGURE 2.1

Vertical oven: $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$ crystal prepared in zone II

FIGURE 2.2

Vertical oven zone distribution (zone 2 temperature at equilibrium, zone 1 temperature low, zone 3 temperature high)

FIGURE 2.3

Entire crystal housing recovered from crucible

FIGURE 2.5

SP6 4-X-ray Spectrogoniometer settings used in experiment

XRF 2-theta scan

GE SPG 2 SpectroGoniometer Model 11GN1 S.N. 7097621

GE X-Ray Tube Model EA75 W/Cr 2800W/2000W Max.

5 December 1991

45kV/40mA

4 degree 2-theta per min.

0.5 sec. time constant

100k cps range full scale

LiF (200) crystal $2d=4.0267$

Beam Tunnel

Soller Slit 0.010°

7-SPG Proportional Flow Counter Tube @ 1401V

FIGURE 2.6

SPG 3 Spectrogoniometer settings used in experiment

XRD 2-theta scan

GE SPG 3 Spectrogoniometer with Omega motion model 11GN6A1 S.N. 682340
 GE X-Ray Tube CA-8-S/Cu (Small Focal Spot) 50kV Max.
 Anode Grounded, beryllium window, Coolidge X-ray tube of the hot cathode
 5 December 1991

45kV/15mA

0.03 step

0.5 sec. time constant

100k cps range full scale

Cu K-alpha = 1.5405981

beam slit 3 degree

soller slit medium resolution

detector slit 0.2 degree

filter Ni foil absorber 0.0007"

6-SPG Xe counter tube @2580V

FIGURE 3.1

Glossy black areas depict pure $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$ crystals

FIGURE 3.2

ESR analysis of pure $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$ crystal determined what temperature superconduction occurs

FIGURE 3.3

X-ray fluorescence located angle elements used in preparation of $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$ crystal

FIGURE 3.5

SEM spectrum analysis of pure $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$ crystal

FIGURE 3.6

SEM analysis of $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$ crystal shows smooth surface

FIGURE 3.7

Magnified surface shows scales formed during SEM analysis of $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$ crystal

FIGURE 3.8

SEM spectrum analysis shows presence of aluminum in samples where aluminum crucibles were used

FIGURE 3.9 [a]

3.9[a] SEM analysis of iodine intercalated crystal show porosity on the surface of $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$ crystal

FIGURE 3.9 [b]

SEM analysis of iodine intercalated crystal shows yellowish-brown discoloration on the surface.

FIGURE 3.10

SEM spectrum analysis of pure $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$ crystal intercalated with iodine

FIGURE 3.11

Yellow polycrystalline material forms from sample reaction with ceramic crucible

FIGURE 3.12

Dark nodule crystals coated with yellow particles

FIGURE 3.13

Black crystals formed on sides of ceramic crucible

FIGURE 4.1

[a] X-ray diffraction patterns of $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$ pure crystal

[b] X-ray diffraction patterns of iodine intercalated crystal