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Final Technical Report
on
**GROWTH OF HIGH T_c SUPERCONDUCTING FIBERS USING
A MINIATURIZED LASER-HEATED FLOAT ZONE PROCESS**
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ABSTRACT

The primary objective of this program (funded initially from January 15, 1989 through January 14, 1992) was to explore the potential of the laser-heated pedestal growth (LHPG) process, a minaturized float zone method, for the preparation of long, flexible fibers of the high T_c copper-oxide ceramic superconductors having wire-like morphology. Most of the research was focused on the growth and characterization of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ (2212), one of the then-recently discovered phases found to be capable of carrying high currents at temperatures above 77°K . The LHPG method involves growing fibers with specific phase content and structure directly from a melt of carefully controlled composition. This makes it quite different from wire-drawing methods which simply stretch a billet of controlled average composition, usually at relatively high rates and elevated temperatures. Our major concern was whether the LHPG method could be used to produce high T_c fibers in lengths long enough for use and evaluation as superconducting wires. Promising preliminary work had been carried out under a six month DOE start-up program through the Los Alamos National Laboratories (Contract No. 9-XF8-7082W-1; July 15, 1988 - January 15, 1989), and that work provided an important foundation for the current program.

Critical issues studied here included determinations of 1) the most suitable fiber compositions for growth, 2) the maximum allowable growth velocities which could be achieved before fiber structural properties deteriorated, and 3) the maximum lengths of fiber which could be produced within a reasonable time frame. To address these issues, this program involved an in-depth study of 1) the thermodynamic and kinetic factors which affected growth rate and fiber properties, 2) techniques to enhance fiber throughput by combining, for example, increased growth velocity with post-growth heat-treatment processing, and 3) the design and construction of an advanced fiber growth system to permit better control of system parameters. The program has worked out very successfully and has resulted in a number of significant accomplishments.

When this program began, very little was known about the extent of solid solubility in the Bi-2212 system or how to produce dense homogeneous ceramic feedstock for the fiber growth process. The preparation of compositionally uniform starting material for the growth of small ($<50\text{ }\mu\text{m}$) diameter fibers became a major challenge because inhomogeneities in source material composition can cause growth instabilities which, in turn, cause structural, property, and diameter changes along the fiber. Three approaches to the problem of preparing uniform feedstock were investigated: cold-pressing and sintering, hot-pressing, and melt quenching to form a dense, homogeneous glass phase followed by

recrystallization. Materials from outside vendors were also evaluated, but were found to be of poor compositional homogeneity and density. We were forced to carry out a thorough investigation of the phase equilibria near the single phase existence range which contained the Bi-2212 phase in order to prepare single phase feedstock. Based on these studies we were able to develop a cold-pressing and sintering procedure for preparing dense ceramic samples with uniform single phase composition that allowed faster growth rates, higher quality and longer lengths..

Regarding fiber growth of high T_c superconducting fibers, we found initially that 2212 fibers solidified from Bi_2O_3 -rich and SrO -poor melts at temperatures between 840 and 900° C and that growth temperatures increased with increasing melt concentrations of Bi_2O_3 and CuO . Based on these observations, along with our improved understanding of the phase equilibria in the system, we were able to increase the maximum growth rates for single phase fiber growth from 5 mm/hr to over 20 mm/hr. We also found that smaller diameter fibers could be grown at faster rates due to the increased axial temperature gradients at the melt/solid interface which reduced problems related to constitutional supercooling. At higher growth velocities, multiphase fibers displaying poor or no superconductivity were produced. The composition and morphology of these non-superconducting phases were carefully analyzed and a heat-treatment process developed for converting them into the superconducting phase via a solid-state reaction at 800° C.

By rapidly freezing entire fiber-melt-feedstock systems during growth and analyzing for composition along their lengths, we were able to reveal important details about the 2212 peritectic reaction and the local phase equilibria in the Bi-Sr-Ca-Cu-O system. The nature of the phase relationships and the solid solubility issues involved in the growth of Bi-2212 crystals which solidify incongruently were thus revealed. Using the model $\text{CaO-Al}_2\text{O}_3$ system, we were also able to show how the minaturized float zone (LHPG) technique could be used to determine relevant phase equilibria data in more complex material systems like the superconductor materials being studied here. We elucidated for the first time, the relationship between thermal gradients, interface shape and the phases produced by the LHPG process during incongruent solidification.

The effect of oxygen concentration in the growth atmosphere was evaluated in terms of fiber phase content, average composition, and morphology. Air proved to be the most suitable ambient for the growth of 2212 fibers. We were surprised to find that seed composition and orientation also had a strong effect on a fiber's growth stability, composition and morphology, particularly in the initial transient region. The possibility of using electric fields during crystallization to improve growth rate was explored, but preliminary results were inconclusive.

As all of these findings were incorporated into our growth process, the quality of the fibers improved. The highest critical current densities ever measured in bulk samples of Bi-2212 material, $60,000 \text{ A/cm}^2$ at 68K, were achieved in single crystal and/or highly grain-oriented fibers grown during this study. We achieved the first ever flexible specimens of bulk ceramic superconductors, which are normally very brittle, by preparing multi-cm fibers $\leq 100 \text{ }\mu\text{m}$ in diameter. Ultimately, we were able to reduce fibers diameters to $25 \text{ }\mu\text{m}$ (1 cm in length), and we were able to grow them up to 14 cm in length ($100 \text{ }\mu\text{m}$ diameter). Because of their small diameters, these fibers could be bent in radii less than 5 cm. In addition, superconducting Bi-2212 grain-aligned ribbons were grown for the first time by the LHPG method using platinum guide wires.

A detailed understanding of the relationship between fiber growth rate and diameter, and the effect of growth rate on fiber structure and quality was developed. Measurement of as-grown 2212 fiber T_c s showed that T_c increased with growth temperature. While the relationship between fiber composition and growth temperature was found to be complex, it was concluded that T_c s might be maximized further if growth temperatures can be increased.

Due to a long series of difficulties in procuring a CO_2 laser with suitable power stability, the construction of our advanced fiber growth station was delayed well beyond the original ending date of the program, and multiple no-cost extensions were sought to extend the program through the end of 1994. The new growth station had been designed to incorporate greater mechanical and laser power stability than the LHPG system existing at the time, which should have resulted in fiber growth under conditions of improved diameter control and interface stability. As of this writing, the laser has been back and forth to the vendor, and it has only just achieved what we think is reliable operation. It now needs to be integrated into the growth station, a task which was long-delayed because of the procurement problem. The growth station will require one additional major component (a vacuum chamber) to be engineered and fabricated. Otherwise, the growth station has been completed to the point where engineering evaluation is now being carried out. Final completion and use will, however, require additional funding from other sources.

I. INTRODUCTION

The primary objective of this program was to establish the viability of the laser-heated pedestal growth (LHPG) method, a miniaturized float zone process, for the economical preparation of superconducting wires from the new class of high T_c superconducting copper oxide ceramics. These new materials excited the imagination and interest of scientists worldwide, and important applications were envisaged. It is not surprising, however, that many important questions arose concerning their suitability for certain applications. These included not only whether they would have suitable physical and electrical properties, but also whether economical, effective processing techniques could be developed. Extensive efforts to produce both thin films and wires were underway when this program began, thin films for electronic devices and wires for motor, magnet and power transmission applications. Most of the early work to develop wires of the new high T_c superconductors was concentrated on fabricating them in the form of polycrystalline ceramics. These materials typically had grains with random crystallographic orientations and intergranular barriers between the grains which limited critical current densities to much less than the highest values which could be obtained from single crystals. Of the numerous ceramic processing techniques that researchers have studied for making long lengths of polycrystalline superconducting wires, the extrusion of powders in Ag tubes currently seems to be yielding the most economically viable wire with reasonably good properties. The grains are continuously aligned so that the appropriate current carrying planes are directed along the wire axis. Single crystal wires would further enhance current carrying capacity by eliminating these "weak links" (grain boundaries).

For superconducting motor, magnet or transmission line applications, long lengths (kms) of small diameter fibers capable of carrying large critical currents at temperatures above 77° K are needed. While high T_c fibers grown by the LHPG method were shown to possess excellent superconducting properties in our preliminary work (LLNL Contract. No. 9-XF8-7082W-1), an important concern was whether these fibers could be made in long enough lengths and with diameters small enough for prototype superconducting devices.

Critical issues considered during the course of this program included: 1) the most appropriate compositions which can yield long lengths of uniform structure and composition with high superconducting transition temperature, T_c , and high critical current densities, J_c , 2) the maximum allowable growth velocity which can be used before degradation of the fiber properties, and 3) the maximum length of fiber which can be produced. To address these issues, this program involves an in-depth study of 1) the

thermodynamic and kinetic factors which affect growth rates and the properties of the fibers produced, 2) the development of a dedicated advanced fiber growth system which will permit better control of system parameters, and 3) the development of techniques to enhance fiber throughput via increased growth velocity under stable growth conditions and post growth annealing of multiphase fibers grown in excess of this stable growth rate.

Specific program tasks included the following : 1) making high quality dense and homogeneous starting materials of various superconducting compositions, 2) fiber growth, 3) fiber characterization (composition, structure, and properties), and 4) design of a new, advanced fiber growth station. A summary of the work carried out during the early stages of this program can be found in the relevant DOE progress reports, CMR 89-8 and CMR 90-8. These reports describe our research on:

1. New methods for preparing starting (feedstock) material.
2. Thermodynamic and kinetic studies, including preliminary phase equilibrium studies, and the influence of feedstock composition on melting behavior and superconducting properties.
3. Early attempts to optimize the starting material so as to achieve increased growth rates and improved microstructures.
4. The influence of growth rate on microstructure, composition and superconducting properties, and a determination of whether fiber growth velocities can be increased by changing growth parameters such as temperature gradient, atmosphere (pressure and composition), etc. without sacrificing growth stability, or by post-growth annealing.
5. Annealing high growth rate fibers containing aligned non-superconducting phases to determine if aligned superconducting phases could be formed.
6. Developing techniques using existing LHPG facilities for growing small diameter 20-50 μm fibers of various ceramic superconducting phases, particularly Bi-Cr-Ca-Cu-O and/or newer compositions as they develop, and evaluating their composition, structure and superconducting properties.
7. Growth of fibers for evaluation.
8. Detailed property measurements.
9. Design of an advanced fiber growth system capable of producing long lengths of single crystal or grain-oriented 20-50 μm diameter fibers of the ceramic superconductors.

This Final Technical Report summarizes the balance of the research carried out, most of which as a logical extension of the issues identified above.

II. BACKGROUND

A. High- T_c Superconductors

Historically, the development of new high- T_c superconductors started in 1986, with the paper of Bednorz and Muller [1]. They reported a new $(La,Ba)_2CuO_4$ superconductor which became superconducting at 35K. At this time, transition temperatures (T_c) above 30K had never been observed and, indeed, were predicted by some to be impossible. This discovery thus generated a great deal of scientific excitement. Interest in the new oxide superconductors increased still further in the next year when Wu et al. [2] reported the discovery of the superconductor $YBa_2Cu_3O_7$. This compound can be superconducting at temperatures as high as 95K. This was the first superconductor found to superconduct at temperatures above 77K, the boiling temperature of liquid nitrogen at a pressure of one atmosphere. The discovery of this material thus made possible superconducting devices which require only liquid nitrogen cooling. It also fuelled the development of other oxide superconductors with the hope that room temperature superconductors could be developed.

Several other superconducting systems were also identified in 1987 and 1988. Michel et al. [3] identified a 20K superconductor in the Bi-Sr-Cu-O system. This was an important discovery, since this system contained none of the relatively expensive rare-earth oxides. A short time later, Maeda [4] reported superconductivity at 85K in the closely-related Bi-Sr-Ca-Cu-O system, as well as a possible transition at an even higher temperature, which turned out to be a 110K superconductor. The superconducting T_c s rose still further when Sheng and Hermann [5] reported a transition at ~ 120 K in the Tl-Ba-Ca-Cu-O system. Another unique superconductor was reported in the K-Ba-Bi-O system by Matheiss et al. [6]. While this material had a T_c of only 30K, it was the first high- T_c superconductor reported which did not contain copper oxide. Following these initial successes, the development of new superconductors is still continuing.

A separate, but equally important, challenge is the development of commercial devices from these newly-identified materials. Economically, superconductors with transition temperatures above 77K are preferred. This rules out a number of the simpler and more easily processed high- T_c materials. In addition, the most useful superconductors for many applications must be simultaneously flexible and capable of carrying substantial currents. This is difficult given the brittle nature of the superconducting oxides.

The fabrication of oxide-bearing material with these characteristics is only possible in microstructures containing elongated grains and/or additional ductile phases. Such

crystallization is difficult to achieve because of the complex melting behaviors of these materials. Most of the high- T_c superconductors melt at relatively high temperatures ($>800^\circ\text{C}$); melting is therefore often accompanied by both vaporization from the melt and contamination of the melt by many container materials. Identification of successful melt-processing techniques is thus a major challenge for many of these superconductors.

The $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ (2212) superconductor is a member of a larger family of superconductors with oxide layer structures which have the formula: $(\text{AO})_m\text{M}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2}$ [7], where m ($= 1$ or 2) indicates the number of AO sheets which are stacked consecutively. A in this case may be either thallium, bismuth, lead or mixtures of two of the three. The subscript n indicates the number of parallel copper oxide planes in the unit cell. This is usually 1, 2 or 3, although other values have been reported. M indicates the metals, strontium or barium. A number of the superconducting compounds in this family are listed in Table 1 which is reproduced from reference [7].

Of these compounds, the 2212 superconductor is the most easily melt-processed among those with T_c s above 77K. It has been observed to crystallize from melts of similar composition at temperatures in the vicinity of 850°C [8]. The $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ (2223) superconductor (like the $\text{YBa}_2\text{Cu}_3\text{O}_7$ superconductor) crystallizes only within a narrow ($<20^\circ\text{C}$) range of temperatures from melts of significantly different composition. Compounds which contain lead oxide and/or thallium oxide have greater stability ranges, but they also have greater volatility over their melts and greater toxicity of the components released.

The $(\text{AO})_m\text{M}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2}$ compounds are all closely related structurally and have been extensively studied. Figure 1 shows the unit cells of the $n = 1, 2$ and 3 superconductors in the specific case of the Bi-Sr-Ca-Cu-O system (the 2212 compound is the $n=2$ member of this group). These structures are pseudo-tetragonal (actually orthorhombic, but very similar in the a and b directions). They consist of oxide a - b planes which have a regular stacking sequence along the c -axis and have highly anisotropic electrical properties, carrying current much more easily along the a - b planes than in the c -direction. They also often crystallize with interlayer stacking faults, creating a blend of two or more superconducting phases within an otherwise homogeneous samples. In real samples, significant inter-substitution between the chemically similar strontium and calcium ions also occurs.

Ono's study [1] was one of the first (of several) to show that the 2212 superconductor exists over a range of compositions. Surprisingly, Ono's solid solubility range did not include the stoichiometric composition $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$. The single phase compositions found can be described by the formula: $\text{Bi}_{2+x}(\text{Sr,Ca})_{3-x}\text{Cu}_2\text{O}_{8+d}$, where x

Table 1: $(AO)_m M_2 Ca_{n-1} Cu_n O_{2n+2}$ Superconductors

Compound	a(Å)	c(Å)	T _c (K)
TlBa ₂ CuO ₅	3.83	9.55	•
TlBa ₂ CaCu ₂ O ₇	3.833	12.68	90
TlBa ₂ Ca ₂ Cu ₃ O ₉	3.853	15.91	110
TlBa ₂ Ca ₃ Cu ₄ O ₁₁	3.850	19.01	122
(Tl,Bi)Sr ₂ CuO ₅	3.745	9.00	50
(Tl,Bi)Sr ₂ CaCu ₂ O ₇	3.800	12.07	90
(Tl,Pb)Sr ₂ CaCu ₂ O ₇	3.800	12.15	90
(Tl,Pb)Sr ₂ Ca ₂ Cu ₃ O ₉	3.808	15.23	122
Tl ₂ Ba ₂ CuO ₆	3.866	23.24	90
Tl ₂ Ba ₂ CaCu ₂ O ₈	3.855	29.42	110
Tl ₂ Ba ₂ Ca ₂ Cu ₃ O ₁₀	3.849	35.66	122
Bi ₂ Sr ₂ CuO ₆	3.796	24.62	12
Bi ₂ Sr ₂ CaCu ₂ O ₈ [†]	3.823	30.90	90
Bi ₂ Sr ₂ Ca ₂ Cu ₃ O ₁₀ [†]	3.818	37.88	110

*Not superconducting.

[†]Cell dimensions are for an idealized subcell.

varies from 0.05 to 0.20, the Ca:Sr ratio from 0.33 to 2.05, and d from near 0.0 to 0.3. Ono's study also showed that the oxygen content in these materials varied with both the Bi₂O₃-content and heat-treatment procedure used to improve their superconducting properties.

B. Float-Zone 2212 Growth

The copper oxide superconductors in general, and the 2212 Bi-Sr-Ca-Cu-O superconductor in particular, are interesting because they have been found to exhibit superconducting transition temperatures (T_cs) which are high enough to make a variety of devices possible. The design of such devices is greatly aided if one can quantify the anisotropy in the material's superconducting properties by testing single crystal samples. The development of techniques for growing single crystal samples of newly discovered phases thus plays an important role in their development.

Figure 1: Atomic arrangements in the: (a) 2201 ($n=1$), (b) 2212 ($n=2$), and (c) 2223 ($n=3$) superconductors.

The potential importance of using the laser-heated pedestal growth (LHPG) technique to do this for the 2212 superconductor was first demonstrated by Feigelson et al. [9]. They reported that a single crystal of the 2212 phase had a T_c of 82K and a relatively high J_c of 5×10^4 A/cm². They also reported that crystals grown by the LHPG technique had a preferred growth direction lying within the a-b plane. Compared to standard high temperature solution growth methods which produce very thin a-b platelets, this technique produced rod shaped samples comparatively thick in the c direction which lay perpendicular to the rod lengths. The a-b planes lying along the lengths of the rods so that the rods exhibited minimum resistivity in their long direction, made them excellent candidates for applications which required long, thin, superconducting current-carrying elements.

Unfortunately, these results (particularly the high J_c s) proved difficult to reproduce reliably. Subsequent work, including that presented here, has shown that the electronic properties of 2212 crystals are sensitive both to their growth conditions and any subsequent heat-treatment steps. For example, it was shown that the exact 2212 stoichiometry is not contained within the 2212 solid-solubility range [10]. Extended LHPG crystallization of homogeneous single phase samples thus required starting material with a non-stoichiometric composition [11]. This could be accomplished either through repeated float-zone processing of the source rod (as was done in Feigelson et al. [9]) or by the direct fabrication of homogeneous source rods of an appropriate composition (as described in detail by Peszkin et al. [12]).

Controlled growth conditions were also found to be important. Gazit et al. [13] and Cima et al. [14] have both demonstrated the importance of combining the high thermal gradient at the growth interface, which characterizes LHPG processing, with relatively slow (<10 mm/hr) growth rates to produce single phase materials. The production of single crystal samples provided additional challenges. Luo et al. [15] had demonstrated that such samples are required for high sample J_c s, while Lu et al. [16] discussed the conditions under which single crystal LHPG samples are produced.

As with other 2212 sample preparation techniques, it was also demonstrated that post-growth heat-treatment can significantly alter the electronic properties of the final samples. Brenner et al. [17] demonstrated that post-growth heat-treatments of samples crystallized at a variety of growth rates changed both their T_c s and J_c s. Such samples were also subjected to thermal processing in the LHPG growth chamber following crystallization. Brody et al. [18] and Gazit et al. [19] have demonstrated that variations in the oxygen content of the growth atmosphere produced substantial variations in sample crystallization temperature, phase content, and as-grown sample T_c .

III. EXPERIMENTAL METHODS

This section discusses the various experimental techniques used to 1) make the starting materials for the LHPG crystallization studies, 2) carry out the growth experiments, and 3) analyze the phases produced. Also reviewed are the basic techniques for determining the phase diagrams which were used in this research.

The critical importance of starting material quality in the high T_c superconductors was made amply clear during the early phase of this program. Ideally, a theoretically dense homogeneous, completely reacted polycrystalline ceramic of uniform diameter is desired for source rods. Fluctuations in melt composition or volume caused by flaws in the feedstock material lead to changes in fiber diameter and properties, and make control of the growth process difficult. Porosity or incompletely reacted material introduce gas bubbles into the melt which sporadically burst, perturbing melt volume and heat flow in the molten zone. Multi-phase source rods containing unreacted grains of a size comparable to the source rod diameter lead to changes in melt composition during growth. Source rods of variable diameter create changes in melt volume and, therefore, in the microscopic growth velocity. Finally, source rods which change their shape by swelling when in contact with the melt make growth difficult. Knowledge of phase equilibria relationships and kinetic factors is vital if these problems are to be solved and controlled growth processes developed.

A. Phase Diagram Studies

The determination of solid/solid and solid/melt equilibria plays an important role in the fields of metallurgy, mineralogy, ceramics, composites, and material science. A number of techniques are available for determining phase diagrams; the three most prevalent being: 1) solid-state reaction, 2) differential thermal analysis (DTA), and 3) the direct analysis of unidirectional solidification experiments. Each of these techniques, and their advantages and disadvantages, are discussed below.

1. Solid-state reactions

The various compounds which make up a new materials system are often identified using solid-state reaction methods. [20] In these techniques, powdered starting materials are combined in the desired stoichiometry, reacted at elevated temperature, then equilibrated in the temperature range of interest. The phases present can then be evaluated

by a number of analytical techniques, including x-ray diffraction, electron dispersive spectroscopy (EDS), wavelength dispersive spectroscopy (WDS) and/or other chemical micro-analytical methods. Using this approach, the structure and composition of the solid phases which form within a given system at a given temperature can be determined. While this technique is relatively straightforward, extended periods of heat-treatment may be required, and repeated grinding and mixing steps may be necessary before complete reaction is accomplished.

Unfortunately, the solid-state reaction technique usually requires major modifications before it can be used to determine solid/melt equilibria. Both the inhomogeneity and reactivity of the samples can be increased when they are partially melted. Sample inhomogeneity may increase when melt migration leads to segregation of lower-melting temperature components to either the bottom of the sample or other parts of the sample container. Subsequent reaction between the sample components is then prevented by their physical separation.

A sample's reactivity with its surroundings may be greater when it is molten than when it is solid. In such cases, the container material and the ambient atmosphere have a strong influence on the final phase content of the samples. This is a particular problem in the BSCCO system since its molten constituents react vigorously with most container materials, and they are sensitive to the partial pressure of oxygen in the ambient environment.

2. Differential thermal analysis

Differential thermal analysis (DTA) is often used to identify the principle features of the solid/melt equilibria. [21] For this technique, a sample of small mass is heated within an inert container, while the increase in its temperature, with respect to a reference, is recorded. DTA identifies both first and second order phase transitions by noting variations in the rate at which the sample absorbs heat from its surroundings as its temperature changes. Segregation, on melting, is minimized by two factors: 1) using the smallest practical sample size, and 2) using a relatively rapid (relative to the sample deformation rate) heating or cooling rate. Solidus temperatures are determined from the observed onset of the melting reaction, during sample heating. Liquidus temperatures are determined from the temperature at which the melting reaction is observed to cease. Solidus and liquidus temperatures may thus be determined over the entire phase diagram.

The DTA technique is most useful for simple, two-phase, solid/melt reactions. Once the analyzed reaction involves several phases or more than one solid, the influence of reaction kinetics on sample heat flow must be considered. In such cases, the more complex

chemical reactions may not keep pace with the moderate rates of temperature change used in this technique. The DTA results will then describe metastable (rather than equilibrium) reactions. In the complex $\text{Bi}_2\text{O}_3\text{-SrO-CaO-CuO}$ system, this was often a problem.

3. Unidirectional solidification

The controlled growth of high quality crystals requires precise phase equilibria information. To acquire the most accurate data, it is often useful to modify crystal growth experiments as a way to extract more useful crystal/melt coexistence conditions, even though modified experiments may deviate from true equilibrium. If the temperature at the growth interface can be measured during the growth process and the crystal and its melt quenched as rapidly as possible, the composition and distribution of the phases within the quenched melt and solid, particularly at the solidification interface, can be identified. [22,23] This procedure was applied in this study, and it provided us with a convenient method of systematically acquiring information on the crystal/melt equilibrium for the materials under investigation.

B. Sample Preparation

1. $\text{Ca}_3\text{Al}_2\text{O}_6$

As part of this research, a study of the LHPG crystallization of $\text{Ca}_3\text{Al}_2\text{O}_6$, an incongruently melting compound in the $\text{CaO-Al}_2\text{O}_3$ system was also undertaken. This relatively well-characterized material was used to verify that the float zone technique could be used to determine phase relationships in a relatively complex system having some similarity to the oxide superconductor. By identifying the solid composition produced from a particular melt composition, the crystallization path, as predicted from the phase diagram, could be traced. Variations in growth conditions were induced by changing the growth rate and source material composition. The results obtained in this study were consistent with what was expected from the published $\text{CaO-Al}_2\text{O}_3$ phase equilibria. Because of the relative simplicity of this technique, and the well-understood phase relations in the $\text{CaO-Al}_2\text{O}_3$ system, we were able to characterize the LHPG process for an incongruently-melting compound. These experiments provided us with a better understanding of the phenomena likely to influence LHPG processing of the more complex BSCCO system.

a. Starting material

Calcium aluminate source material was synthesized from powders of CaCO_3 (Cerac 99.98%) and Al_2O_3 (Baker 99.7%) mixed in the desired stoichiometries. The thoroughly mixed powders were calcined in a three-step process. They were held in a platinum crucible at 1000° , 1200° and 1300°C for 10 hours each. Between heat-treatment steps, the powders were mixed, ground in a Diamondite (alumina) mortar and pestle, and passed through a 200 mesh sieve. This heat-treatment process yielded a fine $\text{Ca}_3\text{Al}_2\text{O}_6$ powder.

Two $\text{Ca}_3\text{Al}_2\text{O}_6$ compositions were studied: the first was ~5% CaO-rich, while the second was ~5% Al_2O_3 -rich. Preparation of starting material with the exact $\text{Ca}_3\text{Al}_2\text{O}_6$ composition was also attempted, but not achieved, due to differential loss of small quantities of material during the preliminary processing steps. All of the important features sought were, however, successfully revealed by examining the LHPG-crystallized samples from these two off-stoichiometric compositions. Further tests with the exact $\text{Ca}_3\text{Al}_2\text{O}_6$ composition were therefore unnecessary.

After reaction, the powders were hot-pressed to form ceramic disks from which source rods of each composition were obtained. Hot-pressing was accomplished using a graphite die under an argon atmosphere at 1200°C and 5000 psi for 2 hours. Cylindrical $\text{Ca}_3\text{Al}_2\text{O}_6$ pellets with a measured density of approximately 85% resulted. Polished cross-sections of the ceramic pellets were inspected by scanning electron microscopy. These revealed the pellets to have a small grain size ($<50\text{ nm}$) and to be predominantly single-phase and homogeneous in density.

Long square rods were then cut from disks of each composition, using a diamond saw with oil lubricant. The resulting rods were 1-2 cm long and 1 x 1 mm square in cross-section. They were stored in a desiccator to avoid reaction between atmospheric moisture and any residual unreacted CaO in the samples.

b. Source (feed) rods

The as-prepared square rods were next rapidly recrystallized by the LHPG technique to produce round nonporous polycrystalline source rods. In this procedure, the rods were mounted in the LHPG apparatus and a molten calcium aluminate droplet was formed on their upper end using the focused laser-beam. A fine (0.1 mm diameter) platinum wire was dipped into the top of the melt to initiate (seed) the crystallization process. Platinum was used because it remains solid and chemically inert when exposed to molten calcium aluminate. The initial steps in this process are illustrated in Figure 2.

Figure 2: Early stages in sample crystallization by the LHPG technique: (a) creation of molten zone on top of the source rod, (b) early stage of sample crystallization, and (c) later stage of sample growth.

Recrystallization was performed in air, at a rate of 24 mm/hr, with a small diameter ($\sqrt{2}:1$) reduction ratio. This solidification rate far exceeded the constitutional supercooling criteria and, therefore, multiple phases formed in the recrystallized rods. The recrystallized rods were also rotated as they solidified to increase their homogeneity and straightness. The source rod solidified in this manner was composed of a fine-grained, multi-phase material of uniform net cross-sectional composition.

c. Fiber growth

Relatively slow growth rates were used during the subsequent growth of $\text{Ca}_3\text{Al}_2\text{O}_6$ fibers from these source rods. After an initial transient growth stage, $\text{Ca}_3\text{Al}_2\text{O}_6$ samples with 300-500 μm diameter were produced. The initial portions of these samples were subsequently discarded. Both CaO- and Al_2O_3 -rich source materials were used in producing these samples. Four growth rates (2.4, 4.8, 9.6 and 19.2 mm/hr) were used to test the variation in melt composition with growth rate.

Previous work on the CaO- Al_2O_3 system has shown that the phases coexisting in this system are sensitive to the presence of moisture. [24] During the present study, the Al_2O_3 -rich samples were solidified in room air and dry argon, while the CaO-rich samples were crystallized in dry oxygen and dry argon. The argon atmosphere produced more transparent melts and permitted a clearer view of the crystal/melt interface. Experiments carried out in room air were performed to compare the results with that predicted by the wet environment phase diagram; the remaining experiments were performed in dry oxygen and could be compared with the dry air atmosphere phase diagram. [24] The three different types of atmospheres used in the growth chamber were created by flowing various gases at 5 cfh (1 ft^3 total volume) through the chamber during growth. Prior to growth, the chamber was purged for one hour with the desired gas, either ambient air (uncontrolled humidity), dry oxygen, or dry argon (purified over hot titanium sponge).

Approximate melt temperature measurements were performed in room air by microfocus optical pyrometry. These indicated that the crystallization of all samples occurred within the approximate temperature range of 1350 to 1550°C as predicted by the relevant phase diagrams. [23] It was not obvious why the samples solidified in argon should have clearer melts than those solidified in dry oxygen or room air. This would make an interesting topic for future study and one which should be resolved before attempting to employ optical pyrometry for precise temperature measurement in calcium aluminate melts.

After at least 5 mm of crystal had been grown under conditions of constant melt volume and surface morphology, the runs were halted. The crystallization

was terminated very abruptly by interrupting the laser-beam with a block of graphite. The resulting samples contained of the last 5 mm of crystallized $\text{Ca}_3\text{Al}_2\text{O}_6$, the quenched melt, and the source rod. These samples were mounted in epoxy and polished to expose their lengthwise cross-sections. This procedure allowed for a careful microscopic examination of the morphology and compositional profiles in the molten zone and at the growth and dissolution interfaces during steady-state growth.

2. $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$

BSCCO samples were prepared for LHPG processing using techniques similar to those discussed above. The techniques used with this system, however, had to overcome two additional complications. In the first place, a larger number of components were involved and it was more difficult to form a solid charge which melted homogeneously. Secondly, variations in the oxygen content during processing led to different reaction products, necessitating careful control of the ambient atmosphere during starting material preparation and growth.

a. Starting material

Figure 3(a) shows a schematic representation of the desired geometry of the LHPG molten zone. This geometry and how it was formed has been discussed previously. Figures 3(b-d) illustrate how undesirable molten-zone geometries can form when unsuitable starting materials are used. For optimal results, the starting materials used in LHPG processing need to have uniform composition and melting characteristics. A source rod of such starting material provides a constant flow of material to the melt as it is pushed upwards. This is the case illustrated in Figure 3(a). Figure 3(b) shows the case when an inhomogeneous source materials is used. These materials produce abrupt changes in the molten zone composition, as grains of differing composition are incorporated into the melt. Such starting materials may also cause perceptible changes in the molten zone geometry. In the two most extreme cases, this can lead to the termination of growth which occurs when the molten zone shrinks until the growing sample and the source rod to freeze together. Inhomogeneities may also interrupt growth by increasing the length of the molten zone until it cannot be held together by surface tension.

The source rods initially used in the LHPG apparatus were square, ceramic rods with a 1 x 1 mm (1000 x 1000 μm) cross-section. For this source rod size, starting materials with inhomogeneities of <50 μm diameter were found to support relatively stable zones. Starting material which contained inhomogeneities >250 μm diameter, on the other hand, were found to sporadically disrupt the growth process. Substantial care was

Figure 3: Schematic representations of: (a) the desired geometry of the molten zone during LHPG (float-zone) crystallization, (b) growth from inhomogeneous starting material, (c) growth from porous starting material, and (d) growth from source material which is not in phase equilibrium with the melt, and "rims" or swells with time.

required, therefore, to form relatively dense 2212 ceramic specimens which did not contain inhomogeneities greater than 100 μm in diameter.

Porosity in the starting material can have a disruptive influence on the growth process, as illustrated in Figure 3(c). The presence of gas bubbles in the molten zone was observed to disrupt heat and mass flow at the interfaces and, as mentioned previously, produce significant changes in the molten zone geometry. Under these conditions, it is difficult to maintain stable growth conditions for extended periods of time.

An additional and unexpected problem was also found during the growth of BSSCO samples when using several of the prepared source materials. This was termed "rimming" and is illustrated in Figure 3(d). During "rimming," dendritic crystals were observed to grow rapidly upward and outward from the source rod/melt interface. As it progresses, the source material appears to swell, the remaining melt is consumed, and the melt volume becomes unstable. Float-zone crystal growth using these source materials was therefore not possible.

The starting material preparative techniques which produced "rimming" are described later in this section. Most of these were found to produce unstable intermediate compounds in the starting material. Rimming may thus have resulted when these

metastable phases reacted to form stable phases upon heating or when they came into contact with the melt.

The starting material for 2212 growths was most easily produced by a solid-state reaction of powdered oxides and carbonates. This technique was first described by Maeda et al. [4] when they reported their discovery of a high temperature superconductor in the BSSCO system. The most successful technique explored in the present study was a refinement of the cold-pressing procedures of Ono. [10]

Twelve different compositions were prepared for the 2212 crystallization study using Bi_2O_3 , SrCO_3 , CaCO_3 , and CuO powders. The powders were all at least 99.5 % pure and were obtained from Johnson Matthey or Cerac. The twelve starting material compositions were designated U, V, W, X, Y, Z, R, P, E, Q, A, and B. These are listed in Table 2. Following the convention of Ono, [10] the coefficient for copper was fixed at 2.0, while the bismuth, strontium and calcium coefficients totaled 5.0.

The powders were ground and mixed in an agate mortar and pestle in the first processing step. They were then calcined several times for eight hours at temperatures between 760 and 800°C in air, in an alumina crucible. The samples were reground between each calcining step and care was taken not to melt the charges. Problems associated with phase separation of the melt on cooling and reaction with the alumina crucible were thus prevented. This technique produced a homogeneous, fine-grained black powder of each composition.

Ceramic disks were formed from the reacted powders by cold-pressing at 20,000 psi gauge pressure. The mechanical integrity of the pressed pellets was improved by a two-step sintering process. The as-pressed disks were sintered in air, first at 840°C for 5 hours, then at 866°C for 40 hours.

Polished sections of the final ceramic disks were examined by scanning electron microscopy (SEM). Those which did not appear completely reacted were crushed and refired. The resulting fine-grained, polycrystalline samples had densities of approximately 80% of theoretical. This processing technique was described by Moulton et al. [11] while further optimization of this technique is described by Peszkin et al. [12]

Figures 4(a-c) illustrate the solid/melt interface first formed when the ceramic source rod is melted. These are SEM micrographs of the internal cross-sections of rapidly-quenched droplets. The three samples consist of the melted tops of ceramic rods of differing compositions. Since all three compositions are incongruently-melting, they form multiphase molten (mushy) zones just above the peritectic decomposition. They were all found to form a Bi_2O_3 -rich liquid which contained grains of various refractory oxides in the mixed phase region.

Table 2: Compositions of Starting Materials

<u>Starting Material</u>	<u>Composition (Bi: Sr: Ca: Cu)</u>				<u>(Ca:Sr)</u>
V	2.00:	1.60:	1.40:	2.00	0.875
P	2.20:	1.50:	1.30:	2.00	0.867
E	2.05:	1.60:	1.35:	2.00	0.844
Z	2.10:	1.60:	1.30:	2.00	0.813
Q	2.40:	1.50:	1.10:	2.00	0.733
Y	2.10:	1.80:	1.10:	2.00	0.611
X	2.15:	1.80:	1.05:	2.00	0.583
W	2.20:	1.80:	1.00:	2.00	0.556
R	2.05:	1.95:	1.00:	2.00	0.513
U	2.00:	2.00:	1.00:	2.00	0.500
A	2.15	2.10	0.75	2.00	0.357
B	2.17	2.13	0.70	2.00	0.329

a)

b)

c)

Figure 4: Scanning electron micrographs of quenched molten oxide droplets on ceramic source rods. Source rods have compositions (a) W, (b) Y, and (c) V. The source rod in (b) contains a large CuO grain which would interfere with stable sample growth.

The solid/melt interface formed from composition V, as seen in Figure 4(c), is shown at greater magnification in Figure 5. This micrograph reveals several regions containing multiple phases at this boundary. It thus confirms that the melting reactions in the BSCCO system can be quite complex.

b. Source rods

Source rods for the final growth process had dimensions of 20 x 1 x 1 mm. These were cut from the original ceramic pellets using a diamond saw and oil lubricant. Acetone was used to remove the oil and mounting wax for the ceramic rods after slicing.

Once mounted in the LHPG apparatus, they were melted and recrystallized in air, at a rate of 24 mm/hr. A 2:1 pull to feed rate was used, resulting in the reduction of the source rod diameter to approximately 850 μ m (0.85 mm). During growth, the crystallizing rod was slowly rotated (at $\sim$ 4 rpm) to increase the symmetry of the source rods generated.

The initial stages of recrystallization produced material of inhomogeneous composition and phase content which were discarded. After approximately 1 cm of growth, the composition and phase content of the recrystallized material became uniform. The microstructure of the recrystallized material varied with the composition of the source rod used. It was, however, always relatively fine-grained (maximum grain size <50 μ m) and contained three or more different phases.

Two other methods for preparing source rods were also employed in this study. In one technique, single-phase source rods were slowly crystallized from two known solidus compositions. In the second technique, unusually large source rods were fabricated from starting material of a known liquidus composition.

In the first technique, single phase source rods were obtained from compositions Y and Z (Table 2). They were made by first recrystallizing rapidly (at 24 mm/hr), but with a smaller difference between the feed and pull rates (1.5 : 1 instead of 2 : 1). They were then crystallized at a slower rate (4.8 mm/hr), once again using the lower diameter reduction ratio. These rods had the same approximate diameter as the standard source rods.

In the second technique, large (20 x 2 x 2 mm) ceramic rods of composition Q were cut and rapidly recrystallized (24 mm/hr) by LHPG melting into large diameter ($\sim$ 1.8 mm) source rods. In this case, the crystallizing samples were also rotated. The major difference between the processing of these source rods and those of normal size was that significantly higher laser-power was required for melting.

Single phase, $\sim$ 500 μ m diameter samples were then grown from these large diameter source rods at the standard 4.8 mm/hr pull rate, using a large (4:1) diameter

Figure 5: Higher magnification micrograph of complex solid/melt interface in Figure 4(c).

reduction. These samples contained substantial lengths (5 to 7 mm) of single-phase material with only a gradual compositional variation along the length of the sample.

This set of experiments was performed in order to verify that the initial transient stages of multiphase growth can be avoided, if the initial melt composition is pre-adjusted to an appropriate liquidus composition. This technique produced sample rods which were initially single phase. It was also successful in prolonging single-phase crystallization for 5-7 mm before extended multiphase growth took over.

c. Fiber growth

All of the 2212 compositions described above (Table 2) were crystallized in air. The final growth step was always carried out using a 4.8 mm/hr pull rate. This procedure yielded ~600 micron diameter, rod-shaped samples. These often contained long lengths of 2212 material with and without minority phase inclusions.

The compositions labelled A and B in Table 2 were measured by Lu. [16] Use of these compositions allowed for an examination of the segregation behavior in more strontium-rich 2212 compositions. The influence of starting material composition on growth will be presented later with the other results of these experiments.

Several initial stages of multiphase growth were observed to precede the stable (extended) growth stage. Growth was judged to be stable if at least one hour (~5 mm) of unchanging surface morphology and constant melt volume was achieved. This criterion was met in the first seven hours of growth for all compositions tested.

As mentioned previously, the various stages of growth could be preserved for later study by abruptly quenching the melt. The initial melt quench rates were on the order of 500°C/sec. The quenched samples contained 1) the as-grown 2212 crystals, 2) a glassy frozen melt, and 3) the source rod. After removing from the growth apparatus, the entire "composite" sample was mounted in epoxy and polished lengthwise to reveal its interior structure; the as-grown crystal growth interface, quenched melt, source rod/melt interface, and the source rod.

d. Molten zone temperatures

The first analytical measurements and optical evaluations were carried out while growth was in progress. The molten zone could be easily observed by self-illumination. The 2212 compositions studied in these experiments had melting temperatures in the 800 to 950°C range. BSCCO melts and solids have emissivities close to that of a black body (~0.95). [25] The axial temperatures in the molten zones ranged from ~800 to ~1200°C (the maximum temperature being at the point where the laser beam

impacts the melt surface). A focused microscope illuminator was also used when examining the cooler parts of the crystallized sample. A microfocus optical pyrometer (20-50mm spot size) was used to measure the temperatures at various places on the melt surface. These temperature measurements were reproducible to $\pm 10^{\circ}\text{C}$ and were not corrected for emissivity. The temperature gradient in the melt near the growth interface was determined by measuring the temperatures at several locations in the top quarter of the melt. Near the growth interface, it was on the order of $500\text{-}1000^{\circ}\text{C}/\text{mm}$.

e. Alternate preparation methods

While previous sections describe successful techniques for preparing 2212 starting material, this section describes several less successful techniques which were also attempted. These techniques did not produce material which supported stable float-zone growth in the LHPG apparatus. Their failure, however, provides excellent examples of the peculiarities of working in the BSCCO system.

(1) Hot Pressing

Pellets of the 2212 composition were hot-pressed from prereacted oxide powders and ground 2212 composition glasses. Powders were hot-pressed in an argon atmosphere, inside a copper liner within a graphite die. A pressure of 2300 kilograms was applied, while the powders were heat-treated at a temperature of 650°C . The hot-pressing sequence (including approximately 8 hours of heating and 8 hours of cooling) lasted 24 hours. The resulting pellets were 2.54 cm (1 inch) in diameter. In all cases, hot-pressing produced ceramic pellets of higher density than those produced by cold-pressing ($>80\%$ theoretical density).

The hot-pressed pellets, however, contained an outer layer of red Cu_2O . The identity of this material was determined by electron dispersive analysis (EDS). Close inspection of several runs also revealed red grains within the interior of the pellet. Again, elemental analysis showed these grains to be Cu_2O .

In these experiments, the use of starting powders dried in methyl alcohol were least successful. In this case, the oxygen content of the charge was reduced and the sample melted as it was heated to 650°C . This resulted in structural damage to the graphite die.

Hot-pressing of incompletely-reacted starting materials was also a problem, in that the ceramic remained incompletely reacted after hot-pressing. The resulting ceramics still contained several phases and did not melt homogeneously. In several cases, these starting materials rimmed dramatically when melted in the LHPG apparatus. The details of the rimming process are discussed later.

Hot-pressing of homogeneous 2212 glasses was also attempted. The resulting ceramics appeared promising, because microscopic examination showed them to be dense and homogeneous. Unfortunately, they also rimmed catastrophically when melted in the LHPG apparatus.

(2) Glasses

Attempts were also made to fabricate starting material from quenched 2212 glasses. In early experiments, glasses were created from prereacted 2212 powders melted in Coors high-alumina crucibles. Melting was accomplished by heating the charge to approximately 1000°C inside a resistance furnace for 30 minutes. This technique was successfully employed by Mitzi et al. [26] to create melts for the growth of 2212 crystals at similar temperatures. In the present study, the hot melt was poured onto a copper die at room temperature and pressed with a copper plunger. The rapidly quenched melt formed a somewhat fractured, glassy plate, approximately 1.5 mm thick. Relatively large (at least 1.5 cm x 2 cm) flat pieces were selected from the resulting fractured material. These were annealed at temperatures between 400 and 600°C which transformed them into fine-grained, crystalline material which could be sliced with a diamond saw.

Three difficulties were initially encountered during recrystallization of the BSCCO glasses. First, the quenched glasses were found to melt at temperatures (~700°C) well beneath the melting temperatures of 2212 crystal (840-900°C). They were also observed to contain aluminum oxide, leached from their alumina containers. Finally, the annealed glasses when used in the LHPG apparatus were observed to rim catastrophically on contact with the melt and, therefore, could not be used for float-zone growth.

The first difficulty was encountered during recrystallization of the glasses. The 2212 crystalline phase does not form directly from the glass at temperatures below 800°C. The glass plates, however, deformed significantly due to partial melting when heated above 500°C. A single step heat-treatment above 800°C produced either metastable phases and/or samples which were warped due to partial melting.

Differential thermal analysis (DTA) of the quenched glass was carried out to determine the source of this problem. Samples heated at a rate of 10°C/min revealed an exothermic glass transition at ~450°C, preceded and followed by several smaller exothermic reactions. These were followed by a prominent (endothermic) melting reaction which began at ~840°C. These DTA curves are typical of those found in other glass systems.

Controlled recrystallization was accomplished by using a multi-step, programmable, PID controller which could provide a more controlled heat-treatment procedure. Using this equipment, the glass was annealed at progressively higher

temperatures (520°, 620°, 720°, 780°, and 825°C) in four to eight hour increments without the sample undergoing melting.

The second problem mentioned above, the presence of aluminum oxide contamination in the recrystallized glass, was confirmed by electron dispersive analysis (EDS). Significant fractions of alumina were discovered in some of the minority oxides phases present in these samples. It was therefore concluded that contamination of the BSCCO glass occurred during melting in the alumina crucibles.

A preliminary survey of likely crucible materials was then undertaken. This was carried out by mixing prereacted powders with powders of the candidate crucible materials, then heating them in the DTA apparatus. The materials tested included boron nitride (BN), magnesia (MgO), zirconia (ZrO_2), tin oxide (SnO_2), gold, and alumina (Al_2O_3).

DTA scans of the melting and cooling curves of each powder combination were obtained. To prevent damage to the platinum DTA cups, the powders were contained in an alumina sample holder lined with platinum or gold foil. The combined powders were first heated to 1000°C, then cooled at rates of 20°C/min. After cooling, the phase content of a sample cross-section was examined by EDS analysis.

Several of the materials studied could be ruled out by the striking changes they brought about in the DTA cooling curve. The least promising crucible materials were found to be zirconia (ZrO_2), tin oxide (SnO_2) and alumina (Al_2O_3). Later EDS analysis of these charges confirmed that the changes in the DTA cooling curves were caused by solidification of intermediate phases containing the offending contaminants.

Most of the remaining materials were ruled out through microscopic examination of the melt/solid interface between a piece of the solid crucible material and the BSCCO melt. BSCCO melts were observed to attack platinum foil and produce oxides doped with platinum on cooling. Boron nitride (BN) crucibles are not very stable in air at 1000°C [27] and the decomposition by-products of BN reduced the bismuth and copper oxide components of the melt. The melt was thus separated into two, immiscible liquids and metallic bismuth-copper components.

Pure gold has a melting point of 1065°C. [27] It cannot reliably be used to hold a BSCCO melt at 1050°C without mechanical deformation. In addition, after prolonged contact with the BSCCO melt at temperatures from 800 to 900°C, the gold was observed alloy with metallic copper from the melt. The resulting gold-copper alloys start to melt at lower temperatures than pure gold.

Of the materials tested, only magnesia (MgO) proved promising. It did not combine with the melt, even in powdered form. Further experiments confirmed the suitability of MgO as an inert container material for BSCCO melts. Microscopic

examination of quenched melt/MgO interfaces showed no intermediate $\text{Bi}_2\text{O}_3\text{-SrO-CaO-CuO-MgO}$ compounds. It also revealed no detectable MgO contamination of the melt, and only minor intergranular attack of the polycrystalline MgO solid. Subsequent to this work, the published studies of Golden et al. [28] and Lombardo et al. [29] have confirmed that MgO is indeed inert to prolonged exposure to BSCCO melts.

The quenched melt experiments were therefore resumed using dense, high purity, MgO crucibles (manufactured by UBE in Japan). Melts prepared in these containers consistently produced glasses with minimal contamination. As before, these were quenched between a copper plate and plunger to form homogeneous, glassy plates. By annealing the glass at progressively higher temperatures (as discussed earlier), it was possible to perform eight hour anneals at $\sim 825^\circ\text{C}$ without partial melting of the charges.

The last problem encountered in the production of float-zone source rod from recrystallized glasses was the rimming of these recrystallized glasses on contact with the laser-heated melt. When glass source rod was left in contact with the melt for more than a minute, a dramatic reaction resulted. Rapid recrystallization, accompanied by significant source rod swelling, was observed at the source rod/melt interface in each case. The rimming phenomenon eventually consumed all remaining melt and effectively stopped the float-zone growth process.

Prolonged heat-treatment at 825°C did appear to lessen the rimming problem. The geometries of the float-zone melt still changed with time, however. At this point in the study, the heat-treatment steps required to anneal quenched 2212 glasses at 825° were far more complex than that used to produce cold-pressed material, while still producing material which melted less uniformly. Since there no advantage had been found in working with annealed glasses, the development of this process was abandoned.

C. Post-Growth Sample Analysis

The geometry and compositional profiles of the "composite" samples produced were analyzed using the techniques described in this section.

1. Microprobe analysis of BSCCO samples

The samples prepared by the methods discussed above were examined using wavelength dispersive spectroscopy (WDS). WDS analysis, using a JEOL 733 Scanning Electron Microscope, was used to evaluate phase content and the compositional profiles in the composite (crystallized 2212, quenched melt and source rod) samples. The chemical compositions of various 10 micron diameter regions were obtained using

electrons accelerated with 15 kV. Standardization was performed using metallic bismuth and copper, wollastonite (CaSiO_3), and strontium titanate (SrTiO_3) standards. Consecutive measurements were reproducible to approximately 2 atomic % of the total content of each element (for example, a bismuth stoichiometry of 2.00 would be reproducible to approximately ± 0.04).

2. Microprobe analysis of $\text{CaO-Al}_2\text{O}_3$ samples

Similar, calcium aluminate "composite" samples were also examined using WDS analysis. The WDS standards used for these samples were wollastonite (CaSiO_3) and kyanite (Al_2SiO_5). Once again reproducibility of ± 2 atomic % was assumed.

An added complication in this study was the increased difficulty of forming glasses from $\text{CaO-Al}_2\text{O}_3$ melts. These melts tended to separate, on quenching, into fine grained (size < 20 μm) dendritic structures, rather than a homogeneous glass. It was thus more difficult to obtain reproducible melt composition measurements and it was occasionally difficult to obtain meaningful composition profiles within the boundary layer at the growth interface.

Several melts were found to contain both phase-separated regions and homogeneously-quenched regions in the interior of the melt. These were used to check the validity of compositional measurements in the phase-separated melts. Microprobe measurements on 10 mm diameter spots were obtained for both cases. No shift in melt composition between the homogeneous and phase-separated regions was observed. It was therefore concluded that compositional information on the two-phase, quenched melts could accurately be determined using a 10 mm spot size. This was accomplished, however, at the expense of spatial resolution in these measurements.

Automated microprobe scans were also performed across the growth interfaces of samples containing homogeneously-quenched melts. These measurements produced composition versus position data, which allowed the solute buildup in the melt near the solidification front to be determined.

3. Superconducting transition temperature measurements

Electrical resistance versus temperature (R vs. T) curves were obtained from polished cross-sections of homogeneous 2212 crystals. This was accomplished without subjecting the samples to post-growth treatments at elevated temperatures. The microprobe samples were lightly polished to remove their conducting graphite coating (applied to prevent sample charging in the scanning electron microscope). They were then cut to expose 0.6 mm wide and 5.0 mm long sections of crystal. Electrical contact was made

with four evaporated gold stripes and silver epoxy contact pads. R vs. T measurements were then obtained using the four-probe method, as shown in Figure 6. The resulting R vs. T curves displayed a single sharp superconducting transition. A T_c value for each sample was determined from the temperature at which resistance was observed to drop to zero.

(b)

Figure 6: (a) Illustration and (b) micrograph of sample geometry for T_c measurement.

IV. RESULTS AND DISCUSSION

A. Crystallization Studies

1. $\text{Ca}_3\text{Al}_2\text{O}_6$

The $\text{Ca}_3\text{Al}_2\text{O}_6$ study was initiated to examine the crystal growth of a relatively simple, incongruently-melting solid by the float-zone technique. The results of this study were used to analyze the more complex Bi-Sr-Ca-Cu-O system which was the main subject of this program.

The liquidus curve defining the $\text{Ca}_3\text{Al}_2\text{O}_6 + \text{L}$ phase fields lies between 1363 and 1544°C. [24] The illumination from the molten zone was very bright during growth. Consequently, the shape of the growth interface could be easily observed through the transparent $\text{Ca}_3\text{Al}_2\text{O}_6$ fiber crystal. Grain boundaries or inclusions within the crystal were also visible.

At the end of each growth run, the laser-heating of the molten zones was abruptly blocked, resulting in a rapid quench of the hot zone to room temperature. The "composite" samples (consisting of the $\text{Ca}_3\text{Al}_2\text{O}_6$ crystal, growth interfaces, and the frozen melt) were then analyzed using the SEM method. The various calcium aluminate phases could be clearly differentiated by atomic number contrast. The compositional profiles along the surface of the quenched sample cross-sections were obtained by microprobe analysis. Automated microprobe scans were used to examine the solute-enriched layers at the $\text{Ca}_3\text{Al}_2\text{O}_6$ growth interfaces, as well as the bulk compositions of the melt.

This study explored mass transport in the melt during the float-zone growth of an incongruently melting material by: 1) examining the compositional profiles in the quenched melts, and 2) examining the variation in melt composition as the growth rate varies. Heat and mass transport effects were also inferred from interface shapes and visual observation of second phase transport within the zone.

a. Phase equilibria

The CaO- Al_2O_3 binary system has been the subject of previous research by several groups. Their findings have been summarized by Hallstedt. [24] The phase equilibria pertinent to the melt growth of $\text{Ca}_3\text{Al}_2\text{O}_6$ is summarized in Figures 7 and 8. These phase diagrams show that there are differences in the way $\text{Ca}_3\text{Al}_2\text{O}_6$ crystallizes depending upon whether a dry or wet environment is present. Note that the phase fields in Figure 8 have been slightly shifted to accommodate the compound $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$

Dry Atmosphere Phase Diagram:

Figure 7: Portion of CaO-Al₂O₃ binary phase diagram which describes the crystallization of Ca₃Al₂O₆ in a dry environment. Constructed from information in [24].

Wet Atmosphere Phase Diagram:

Figure 8: Portion of CaO-Al₂O₃ binary phase diagram which describes the crystallization of Ca₃Al₂O₆ in an environment which contains water vapor. Constructed from information in [24].

(or $12 \text{ CaO} \cdot 7 \text{ Al}_2\text{O}_3$), which is only stable in the presence of water vapor. [24] This data indicates that $\text{Ca}_3\text{Al}_2\text{O}_6$ can be crystallized from Al_2O_3 -rich melts at temperatures between 1363 and 1544°C. It also shows that, on heating, $\text{Ca}_3\text{Al}_2\text{O}_6$ solid will decompose to form CaO and an Al_2O_3 -rich oxide melt in both environments.

The major difference between these phase diagrams, however, is their eutectic compositions and the range of temperatures at which $\text{Ca}_3\text{Al}_2\text{O}_6$ crystallization can occur. Under dry conditions (Figure 7), the eutectic composition is 35.8 mole % Al_2O_3 and $\text{Ca}_3\text{Al}_2\text{O}_6$ can solidify at temperatures between 1363 and 1544°C. Under wet conditions (Figure 8), the eutectic composition is 34.3 mole % Al_2O_3 and $\text{Ca}_3\text{Al}_2\text{O}_6$ solidifies only at temperatures between 1435 and 1535°C.

During the float-zone growth of $\text{Ca}_3\text{Al}_2\text{O}_6$ from either stoichiometric or Al_2O_3 -rich melts, Al_2O_3 is the component rejected by the solid at the growth interface. For growth above the peritectic decomposition temperature, CaO will also crystallize with solute (Al_2O_3) enrichment of the melt. Once the melt composition reaches approximately 29 mole% Al_2O_3 , the $\text{Ca}_2\text{Al}_2\text{O}_6$ crystallizes instead.

The inclusions within portions of float-zone samples can be characterized as containing either higher temperature (HT) or lower temperature (LT) phases. CaO inclusions (from the above peritectic decomposition process) are more likely to form from CaO-rich (higher liquidus temperature) starting materials. Crystals containing inclusions of eutectic material are more likely for Al_2O_3 -rich (lower liquidus temperature) starting materials. The eutectic is composed of either combined $\text{Ca}_3\text{Al}_2\text{O}_6$ and CaAl_2O_4 solids in a dry environment or combined $\text{Ca}_3\text{Al}_2\text{O}_6$ and $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ under a wet gaseous atmosphere.

b. Results

(1.) Visual observation of the molten zone

The growth process, melting reaction, and circulation of particles and gas bubbles in the molten zone could be studied easily by visual observation of the floating zone during growth. This technique was used to examine the CaO grain incorporation during growth of $\text{Ca}_3\text{Al}_2\text{O}_6$ from CaO-rich source rods. During melting of these multiphase source rods, CaO nodules gradually appeared and protruded into the melt while the source rod dissolved. After a while, these nodules disappeared suddenly, only to reappear at the $\text{Ca}_3\text{Al}_2\text{O}_6$ growth interface. Once present, these were slowly incorporated into the $\text{Ca}_3\text{Al}_2\text{O}_6$ crystal as growth front advanced.

Because of the steep liquidus defining the "CaO + liquid" phase field, as seen in Figure 7, it is likely that the CaO grains originated during the dissolution of the source

material and then were transported, without dissolving, from the melting interface to the growth interface by the vigorous convective currents in the zone. These interfaces were only <500 mm apart and, therefore, particles could travel across the zone in less time than it would take for them to dissolve. This mechanism was supported by the observation of similar-sized particles circulating rapidly in the Marangoni driven melt convection.

Originally, it had been assumed that the CaO grains (along with other refractory oxide inclusions) were completely dissolved by the melt and then nucleated and grew at the growth interface. Quenched molten zones, however, showed that these inclusions extended into the melt beyond the rest of the solids and probably break off and travel to the growth interface on the convective current. This type of convective transport is clearly not the type of conventional mass transport discussed earlier.

In samples of $\text{Ca}_3\text{Al}_2\text{O}_6$ grown from Al_2O_3 -rich source rod in an argon environment, grains were observed to grow with sharp facets and deep grooves between them. Relatively opaque inclusions solidified at the tips of the grain boundary grooves. The inclusions, therefore, became opaque a short distance ($\sim 100\ \mu\text{m}$) behind the main growth front. A similar effect was also observed at the melting interface of Al_2O_3 -rich samples. In this case, the multiphase source rods became clearer a short distance away from the melt, as the Al_2O_3 -rich inclusions within them melted. Thus we could also observe the formation of the LT phase as it occurred.

(2.) Phase distribution in quenched samples

Microprobe measurements confirmed that all the crystals contained >95% (by volume) $\text{Ca}_3\text{Al}_2\text{O}_6$. No stoichiometric variations in the composition of the $\text{Ca}_3\text{Al}_2\text{O}_6$ phase was observed.

Float-zone growth of $\text{Ca}_3\text{Al}_2\text{O}_6$ from the two source rod compositions (Al_2O_3 - or CaO-rich) produced concrete examples of the presence of both HT and LT phases. Growth from CaO-rich source rod consistently produced crystals containing included arrays of nodular CaO grains. These appeared at regular intervals along the length of the sample and were generally found near the outer surfaces of these rod-shaped crystals. Microprobe analysis indicated that these grains were virtually pure CaO and contained no detectable aluminum.

Growth from Al_2O_3 -rich source rods produced continuous, narrow Al_2O_3 -rich inclusions at the grain boundaries of the $\text{Ca}_3\text{Al}_2\text{O}_6$ phase. They were also observed at the outer surface of the samples. Microprobe measurements of these "thin" inclusions showed considerable variation in composition, but they were always Al_2O_3 -rich relative to the compositions of the quenched melts.

Figures 9 and 10 are SEM micrographs of a CaO-rich and an Al₂O₃-rich sample, respectively. In Figure 9, the light-colored CaO inclusions (nodules) extended into the melt, beyond both solid/melt interfaces (melting and freezing).

Figure 10 shows the faceting of Ca₃Al₂O₆ grains during their growth from a Al₂O₃-rich melt. This micrograph also illustrates the separation of the Ca₃Al₂O₆ grains by Al₂O₃-rich inclusions once solidification was complete. In quenched samples, the Al₂O₃-rich inclusions solidify at the tips of v-shaped grooves. These grooves were formed in the region where the crystal facets meet the Ca₃Al₂O₆ grain boundaries.

(3.) Compositional profiles of quenched samples

Most Al₂O₃-rich melts did not phase-separate during cooling, unlike the CaO-rich melts. They could therefore be used to measure the compositional variations within the melt with a higher spatial resolution, as discussed in the previous chapter. In addition, the grooves in the growth front were unusually broad (see Figure 10). Consequently, the compositional gradients in the quenched melt could easily be observed directly from variations in the gray levels in the photomicrographs.

A perceptible darkening of the melt adjacent to the Ca₃Al₂O₆ grains, and particularly at the mouth of the grooves, is apparent. In general, such darkening in the back-scattered electron image indicates Al₂O₃-enrichment. Microprobe measurements have confirmed that the darker regions of the quenched melts, were also richer in Al₂O₃.

Figures 11 and 12 show plots of the quenched melt composition with distance from the growth front, for several samples. These graphs show that the bulk of the melt was homogeneous, while solute-enrichment existed in the boundary layer at the growth interface.

Figure 11 demonstrates that nonplanar growth results in lateral segregation of Al₂O₃ in the melt. This result is shown for two different growth rates. Lateral solute segregation could be deduced from the greater solute buildup within the v-shaped grooves compared with the faces of the facets. In these plots, position has been measured along the growth direction. Because these interfaces are not flat, the growth front position ($z=0$) was somewhat ambiguous.

The compositional data in Figure 12 were obtained from the crystallized phases, where they extended furthest into the melt from the growth interface. The four profiles give compositional variations in the melts formed from Al₂O₃-rich samples which were solidified at four different growth rates (2.4, 4.8, 9.6, and 19.2 mm/hr). The solute-enriched layers of the melt during crystallization can be seen to be <20 microns thick. Also, the bulk melt compositions were found to vary with growth rate. The well-known BPS (Burton, Prim and Slichter) relation predicts solute enrichment in the bulk of the melt

Figure 9: SEM micrograph of internal sample cross section, revealing the morphological features of a molten zone quenched during the crystallization of CaO-rich $\text{Ca}_3\text{Al}_2\text{O}_6$ samples.

Figure 10: SEM micrograph of internal sample cross section, revealing the morphological features of a molten zone quenched during the crystallization of Al_2O_3 -rich $\text{Ca}_3\text{Al}_2\text{O}_6$ samples.

Figure 11: Compositional profile (along growth direction) at the solidification interfaces of two Al_2O_3 -rich samples. These demonstrate the enhanced solute-buildup which occurs in the melt within the v-grooves for two different growth rates.

which increases with decreased growth rate. This can be seen from the data in Table 3, which gives the averaged bulk melt compositions (C_{LB} values) for each growth rate and starting material composition tested.

Table 3 also gives calculated values for the effective segregation coefficient $k_{\text{eff}} = C_S/C_{LB}$ for each growth rate and composition. These values express the degree of solute segregation which occurs at the growth front, in terms of the composition of the solidifying sample (C_S) divided by the bulk melt composition (C_{LB}).

The microprobe measurements have limited spatial resolution because of the size and penetration of the electron beam. Far more reliable measurements could, therefore, be made on the bulk melt than the melt very close to the growth interface. Unfortunately, it was the interfacial melt composition which was of greater interest, as this is the composition which corresponds to the liquidus during near-equilibrium growth.

Table 3: Variation on Solute Segregation with Growth Rate

Growth Rate (mm/hr)	Bulk Melt Composition (mole % Al_2O_3)		$k_{\text{eff}} = C_S/C_{LB}$	
	CaO-rich	Al_2O_3 -rich	CaO-rich	Al_2O_3 -rich
2.4	28.1	34.3	0.89	0.71
4.8	26.9	32.5	0.93	0.82
9.6	26.9	32.0	0.93	0.83
19.2	-	30.3	-	0.88

Figure 12: Compositional profiles (along the growth direction) near the flat facets protruding furthest into the quenched melt. These are shown for similar samples grown at different rates (2.4, 4.8, 9.6, and 19.8 mm/hr).

This difficulty can be resolved by using either of two methods. In the first method, compositional measurements are taken at several growth rates. The BPS relation can then be used to identify the melt composition as the growth rate approaches zero velocity. This value should correspond to the equilibrium liquidus composition. In the second method, a close approximation of the equilibrium liquidus value in the bulk of the melt can be obtained by growing very slowly. The bulk melt composition then approaches that at the interface.

The first method was used in the $\text{Ca}_3\text{Al}_2\text{O}_6$ growth study to check the appropriateness of the BPS theory for the float-zone growth of an incongruently melting material. The second method was used in the 2212 crystallization studies to avoid the increased complexity of four component segregation.

c. Discussion

(1.) Influence of growth parameters on phase relationships

The microstructure of the crystallized samples did not vary greatly with growth rate. This was true for both CaO- and Al_2O_3 -rich compositions. The CaO-rich samples showed no discernable variation at all. Each sample predominantly contained $\text{Ca}_3\text{Al}_2\text{O}_6$, along with periodic arrays of small CaO grains. The periodic incorporation of CaO grains reflects the stability of three phases at the peritectic temperature. This did not change for the range of growth rates examined.

Since the CaO-rich samples were solidified in a dry oxygen atmosphere, Figure 7 contains the appropriate phase diagram for comparison with these samples. In this figure, the only liquid composition shown to coexist with both CaO and $\text{Ca}_3\text{Al}_2\text{O}_6$ is that at the junction of the CaO and $\text{Ca}_3\text{Al}_2\text{O}_6$ liquidus curves. This composition is approximately 28.2 mole % Al_2O_3 . This melt composition was, therefore, expected at the growth interface for all growth rates.

The visual observations discussed earlier suggested that the CaO grains were transported through the melt without dissolving. Their transport through the molten zone was thus not limited by normal diffusion or convection mechanisms. There was, therefore, no reason to expect variations in their spacing with growth rate and none was observed.

The Al_2O_3 -rich samples were solidified with humidity-bearing room air flowing through the chamber. The phase diagram in Figure 8 is, therefore, pertinent to this case. $\text{Ca}_3\text{Al}_2\text{O}_6$ grains, separated by inclusions of the $\text{Ca}_3\text{Al}_2\text{O}_6/\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ eutectic, would be expected during growth from Al_2O_3 -rich source rod due to enhanced Al_2O_3 -enrichment. This was indeed the situation found for all growth rates. The $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ solidified in a

thin layer, separated by layers of $\text{Ca}_3\text{Al}_2\text{O}_6$ which had solidified on the $\text{Ca}_3\text{Al}_2\text{O}_6$ grains (thus forming a divorced eutectic). Some variation in the inclusion spacing was observed.

At higher growth rates, the eutectic inclusions became more closely spaced. This was possible, due to the occasional incorporation of inclusions within $\text{Ca}_3\text{Al}_2\text{O}_6$ grains. These additional inclusions result from the increased rate of solute rejection, relative to the rate of mass transport in the melt, at higher growth rates. This effect is similar to the change in cell spacing at the crystal growth interface, due to constitutionally supercooling.

This effect has been modelled by balancing the rate of lateral solute segregation with the rate at which solute is generated by the advancing crystallization front. [28] The cell spacing is then proportional to $(G_L R)^{-1}$, where G_L is the temperature gradient at the interface and R is the growth rate. [30] The inclusions in our samples were not closely-spaced enough to test this relation.

(2.) Variation Of Melt Composition With Growth Rate

The variation in solute segregation with growth rate was examined using the treatment developed by Burton, Prim and Slichter (BPS). The BPS relation can be expressed in the form:

$$\ln(C_{LB} - C_S) = \ln(C_{L0} - C_S) - \left(\frac{d}{D_L}\right)R. \quad (1)$$

C_{LB} , C_S and C_{L0} are the compositions in the bulk of the melt, in the crystallizing solid, and in melt at the $\text{Ca}_3\text{Al}_2\text{O}_6$ interface, respectively, R is the growth rate, D_L is the diffusivity of the solute in the melt, and d is the effective thickness of the solute boundary layer.

In this study, values for C_{LB} and C_S at several growth rates were determined. Equation (1) was used to determine values for C_{L0} and d/D_L from a linear fit to the experimental data plotted in the form: $\ln(C_{LB} - C_S)$ versus R . This is shown in Figure 13. Experimental values for C_{L0} were derived by extrapolating to zero growth rate ($R=0$). These values of C_{L0} were compared with the relevant equilibrium liquidus compositions in Table 4. The agreement was found to be excellent, when compared to the experimental error in the composition measurements.

d. Conclusions

The data obtained in this study was generally in excellent agreement with well-known solidification theory. The microstructures found for the float-zone growth of $\text{Ca}_3\text{Al}_2\text{O}_6$ from CaO- and Al_2O_3 -rich compositions of source rod could be predicted from the CaO- Al_2O_3 phase diagrams. CaO-rich samples contained CaO nodules within the $\text{Ca}_3\text{Al}_2\text{O}_6$ grains. Samples crystallized from Al_2O_3 -rich source rod contained continuous inclusions (of a divorced eutectic nature), located between the $\text{Ca}_3\text{Al}_2\text{O}_6$ grains.

Table 4: Comparison with Published Phase Diagrams

Case	Calculated C_L	Phase Diagram C_{L0}	Calculated k_0	k_{eff}
CaO-rich	28.5	28.2	0.89	0.93
Al ₂ O ₃ -rich	34.3	34.0	0.77	0.82

Figure 13: BPS plot of experimental composition values from both CaO-rich and Al₂O₃-rich samples.

Melt compositions, measured by microprobe analysis, were also found to follow theoretical predications. The predicted solute-rich boundary layers were observed for several compositional profiles, taken perpendicular to the growth interface. Automated microprobe scans also showed that the bulk of the melt was compositionally homogeneous.

The only unexpected effect during the $\text{Ca}_3\text{Al}_2\text{O}_6$ float-zone growth experiments involved the transport of CaO grains from the source rod-melt (melting) interface to the growth (freezing) interface. These grains travelled on strong convective currents within the molten zone created by the Marangoni effect. This was observed only during float-zone growth using CaO-rich source material and indicates that the growth experiments were not under equilibrium conditions.

The variation in melt temperature with growth rate also supports prior analyses of mass transport processes in molten zones. Bulk melt compositions for the Al_2O_3 -rich samples fell on the $\text{Ca}_3\text{Al}_2\text{O}_6$ liquidus. These varied with growth rate, in agreement with the BPS relation. Less variations were observed in the bulk melt compositions of CaO-rich samples. These were essentially all within experimental error of the liquidus composition at the peritectic point.

The data obtained from this study was in good agreement with the established CaO- Al_2O_3 phase diagrams and solidification theory. Conversely, this shows that useful phase equilibrium information on incongruently melting materials can be extracted from these miniaturized float-zone growth experiments.

2. $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$

In this section, the relationship between crystal and melt composition during the float-zone growth of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+d}$ is discussed. It begins with a summary of the limited phase equilibrium information available in the literature. It covers the 2212 solid solubility ranges, as determined by Ono, [10] Golden et al., [28] and Hong et al., [30] as well as the limited crystal and melt composition data which may be determined from other crystal growth studies. The results of the current study are compared with these results and with those of Lombardo's recent bulk crystallization study. [31] Finally, the variation in segregation coefficient of the various components in the superconductor with crystal composition are discussed. The trends found did not generally depend on the experimental method employed, thus all available data was considered.

a. Phase equilibria

(1.) Solid solubility and solid/solid equilibria

As mentioned previously, $\text{Bi}_2(\text{Sr,Ca})_3\text{Cu}_2\text{O}_{8+d}$ (2212) is one of three distinct superconducting phases in the $\text{Bi}_2\text{O}_3\text{-SrO-CaO-CuO}$ (BSCCO) system. [4,32,33] This phase is much easier to crystallize from the melt than the higher- T_c (~110 K) 2223 superconductor, which exists in equilibrium with its melt only over a very narrow temperature range. The third superconducting phase, the 2201 superconductor ($T_c < 20$ K) can also be solidified from the melt but its low T_c makes it of less practical importance.

The solubility range of the 2212 phase, has been explored in many studies, among them references. [10,28,30,34-37] There are some significant discrepancies in the interpretation of their x-ray diffraction results, for example, differences in the identities of the crystal structures of some of the solid phases formed. This is not surprising since many of the BSCCO phases have complex x-ray patterns with strong similarities and which exist over unexplored composition regions. In part, these differences may be explained by the type of experimental techniques used. In the current studies, the only concern was the composition of minority-phase inclusions and not their crystal structures.

The complex quaternary BSCCO system contains a number of phase fields which contain the 2212 compound. Schweizer et al., [34] for instance, reported equilibrium between the 2212 phase and three other solid phases in four different phase fields. This is illustrated in Figure 14, which summarizes the results of Schweizer et al. as they apply to 2212 phase stability. Their detailed results, unfortunately, do not include the melt-solid phase equilibria regions of most relevance to crystal growth processors. On the other hand, the solid-state reaction techniques used were useful in identifying regions of the phase fields which were either partially or completely molten at a particular temperature. However, the segregation of various components during solidification make this data unreliable for identifying specific "melt-solid" relationships.

The solid-state reaction experiments performed by Ono [10] produced the most detailed description of the 2212 solid solubility range available in the early stages of our study. In Ono's study single-phase, polycrystalline samples of a variety of compositions were made. The compositions which produced single phase (within the limits of his analytical techniques) samples were of the form: $\text{Bi}_2(\text{Bi,Sr,Ca})_3\text{Cu}_2\text{O}_{8+d}$, which implied that to stabilize the 2212 structure, excess Bi is required on the Sr and Ca sites.

Ono's samples were prepared by reacting CuO , Bi_2O_3 , SrCO_3 , and CaCO_3 powders at elevated temperatures. The final reaction steps occurred in air at temperatures between 865 and 885°C. This is quite close to the temperatures at which the various 2212 compositions are known to melt.

Figure 15 illustrates 2212 solid solubility ranges reported by Ono, [10] and others. Note that the compositions are all significantly Bi_2O_3 -rich compared to the stoichiometric "2212" composition. Using a standard normalization (the sum of the metal ion coefficients equals 7.0), the total bismuth content of Ono's single-phase samples varied from 2.05 to 2.20. In addition, the calcium-to-strontium ratio in these same samples varied between 0.3 and 1.2.

This figure (15) shows a planar cut through the Bi_2O_3 -SrO-CaO-CuO compositional tetrahedron. The relative orientation of this plane within the tetrahedron is shown, along with that of the plane examined by Schweizer et al. [34] in Figure 16(a).

The Ono solid solubility range is also shown in the pseudo-ternary representation of $\text{Bi}_x(\text{Sr,Ca})_y\text{Cu}_z\text{O}_n$ in Figure 17. This figure reduces the BSCCO compositional tetrahedron to a ternary representation by viewing the alkaline earth oxides (SrO and CaO) as indistinguishable. This is often a useful representation because these oxides are chemically similar and the compounds in the BSCCO system often display extensive (Sr,Ca)O intersolubility.

In Figure 17, the Ono solubility range is confined to the $\text{Cu}=2$ line. This was a result of Ono's experimental design. He presumed that compositions of the form $\text{Bi}_2(\text{Bi,Sr,Ca})_3\text{Cu}_2\text{O}_8$ would completely describe the solubility range of the 2212 solid. His experiments were thus not designed to test the copper oxide solubility.

Lee et al. [37] used x-ray diffraction to examine samples which had been first equilibrated at 850 and 900°C, then quenched in liquid nitrogen. They only considered samples with a Sr:Ca ratio of 2:1. At 850°C they found that the 2212 phase can be in equilibrium with a variety of other compounds.

Golden et al. [28] also examined the solubility range of 2212, but by an unusual technique. Rather than producing samples by the solid-state reaction of powders, they formed superconducting thin films of various compositions on MgO substrates. This was accomplished by melting organic precursors. The coated substrates were then subjected to extended heat-treatment at sub-solidus temperatures. Figures 15 and 17 illustrate the compositional range of the single-phase thin films produced by this technique. This range of compositions is treated here as their "solid solubility" range, and they are noticeably more Bi_2O_3 -rich and SrO-poor than the other solubility regions discussed.

The data given by Schweizer et al. [34] on the compositional ranges for the 2201 and 2212 superconductors (Figure 14) was obtained at a temperature of 830°C. This study provided limited data on the compositional range of the melt in this isothermal section.

Most recently, Hong et al. [30] identified these phases present at 860°C along the binary joins between 2212 and the other compounds that they believed were present in the

Figure 15: Ternary representation of compositions $\text{Bi}_x\text{Sr}_y\text{Ca}_z\text{Cu}_2\text{O}_{8+d}$. This shows the solid solubility ranges determined by Ono [10] and Golden et al.[28] and Hong et al. [30]

Figure 16: Plane sections of the BSCCO tetrahedron showing the relative orientations of: (a) the Cu=2, iso-copper plane and (b) the planar section analyzed by Schweizer et al. [34] The 2212 phase is located roughly at the intersection of these two planes. The Schweizer plane contains all three superconducting compounds in the BSCCO system.

Figure 17: Ternary $\text{Bi}_x(\text{Sr,Ca})_y\text{Cu}_z\text{O}_n$ representation which shows the solid solubility ranges determined by Ono [10] and Golden et al. [28] and Hong et al. [30]

Table 5: Melt and Crystal Compositions from Literature

Reference	Crystal Composition	Melt Composition	Crystallization Temperature
[28]	2.10: 1.94: 0.88: 2.07		
[32]	-2.0: 1.5: 1.5: 2.0		885°C
[36]	2.2: 1.8 1.0: 2.0 2.2: 2.1: 0.7: 2.0 2.3: 1.2: 0.5: 2.0		
[37]	2.2: 1.8: 1.0: 2.0	2.4: 1.5: 1.0: 1.8 (2.5: 1.55: 1.05: 1.9)	
[38]	2.11: 2.11: 0.89: 2.00 (2.05: 2.05: 0.86: 1.94)		
[39]	2.18: 1.87: 0.99: 1.97	2.6: 1.9: 1.0: 2.6 (2.25: 1.65: 0.85: 2.25)	
[26]	2.5: 2.0: 1.0: 2.2 (2.3: 1.8: 0.9: 2.0)	2.80: 1.61: 0.91: 1.68	850°C (in 1 atm O ₂)
[41]	2.13: 1.95: 0.75: 2.0 (2.18: 2.00: 1.01: 2.05)		
	2.1: 1.9: 0.9: 2.0 (2.13: 1.93: 1.02: 2.03)	2.2: 1.6: 0.85: 1.8 (2.4: 1.75: 0.92: 1.95)	

BSCCO system at elevated temperatures. They identified the limits of the 2212 solid solubility range by measuring the compositions of the Bi₂(Sr,Ca)₃Cu₂O_{8+d} grains in their multi-phase samples. This solid solubility range is shown in Figures 15 and 17.

The technique Hong et al. [30] used in their study provided accurate information on only a few key data points, but these points were carefully chosen. Unfortunately, they did not include information on the solid (2212)-melt equilibria. As one can observe from Figure 14, the data of Schweizer et al. shows that the applicable melt compositions do not lie along the binary joins investigated in Hong et al.'s study. Consequently, they missed a large portion of the CaO-rich 2212 phase found by Ono.

(2.) Melt/solid equilibria

Many studies have been concerned with the growth of 2212 crystals from oxide melts, [8,9,26,32,33,37-41] including several [9,14,26,40,41] which employed the float-zone technique. Their results confirmed the existence of a "2212 + liquid" phase field. The resulting melt and crystal compositions reported in these studies are summarized in Table 5. The compositions listed in parentheses have been normalized to Bi+Sr+Ca+Cu=7.0. Typically, crystals of the nominal composition Bi_{2.1}Sr_{1.9}Ca_{1.0}Cu₂O_y can be grown in the 850 to 890°C temperature range. The melt compositions reported were Bi₂O₃-rich and SrO-poor when compared with the crystal compositions growing from them.

Table 6: Experimental Compositions and Melting Temperatures

Crystal Composition		Melting Temperature
2.10: 1.71: 0.85: 2	(2.21: 1.80: 0.89: 2.10)	835°C
2.16: 1.53: 0.95: 2	(2.28: 1.61: 1.00: 2.11)	830
2.38: 1.57: 0.92: 2	(2.43: 1.66: 0.97: 2.11)	830
2.25: 1.45: 0.96: 2	(2.36: 1.52: 1.01: 2.10)	835
2.38: 1.33: 0.94: 2	(2.51: 1.40: 1.00: 2.11)	810
2.35: 1.40: 0.96: 2	(2.45: 1.46: 1.04: 2.09)	810
2.45: 1.38: 0.94: 2	(2.53: 1.43: 0.97: 2.07)	800
2.20: 1.92: 0.66: 2	(2.27: 1.98: 0.68: 2.06)	840
2.19: 1.68: 0.67: 2	(2.34: 1.80: 0.72: 2.14)	840
2.18: 1.89: 0.73: 2	(2.24: 1.95: 0.75: 2.06)	845
2.10: 1.81: 0.83: 2	(2.18: 1.87: 0.86: 2.08)	845
2.24: 1.32: 1.12: 2	(2.35: 1.38: 1.17: 2.10)	820
2.34: 1.15: 1.20: 2	(2.45: 1.20: 1.26: 2.09)	785

Golden et al. [28] provided additional information on the "2212 + liquid" phase field. They determined the melting temperatures of their thin films by optical and differential thermal analysis. Their compositions and the associated melting temperatures are listed in Table 6. The melting temperatures in this study were significantly lower than those reported in other studies and were consistent with their unusually Bi₂O₃ and CuO-rich crystal compositions.

As yet, no one has found a unique composition which is congruently-melting. It is more difficult to prepare large high quality crystals of incongruently-melting compounds due to segregation phenomena at the growth interface. To avoid this problem, they must be crystallized from melt compositions which differ from the solidifying solid and, therefore, at relatively slow growth rates. By examining the segregation coefficients for each of the major components in these 2212 float-zone growth studies, compositions were found which crystallize with minimum segregation. These results are discussed in later sections.

b. Results

(1.) Mass transport in BSCCO melts

Figure 18 shows a schematic drawing for the float-zone growth of an incongruently-melting solid, along with the temperature (Figure 18(a)) and compositional (Figure 18(b)) profiles which would result. The degree of solute buildup and depletion at the solid/liquid interfaces depend on growth rate .

The compositional variations within the boundary layer can be determined by the relative rates of reaction at the interfaces and solute transport across the molten zone. Unless the growth rate is infinitely slow, one would not expect the complete elimination of compositional variation. Any molten zone from which crystallization is occurring at a finite rate thus contains nonsymmetric compositional profiles which drive any diffusive transport which occurs in the melt.

Figures 19 (a-c) show SEM micrographs of the cross sections of three 2212 samples quenched during the stable growth period. Each sample exhibits a different type of structure and phase content: (a) contains the higher temperature (HT) phase, (b) is a single-phase sample and (c) contains the lower temperature (LT) phase.

The major goal of this study was to produce inclusion-free 2212 crystals, i.e. the case shown in Figure 19(b). The sample shown in Figure 19(a) contains not only 2212 grains (grey) but also dark refractory oxide inclusions which had a low Bi_2O_3 content. Figure 19(c) also contains Bi_2O_3 -rich fine-grained inclusions running parallel to the growth direction. In all cases, however, the solid formed from a Bi_2O_3 -rich molten zone.

Since Bi_2O_3 acts as a flux for many refractory oxides, [42] it was not surprising to find the Bi_2O_3 acting as a solvent during the growth of 2212 crystals. It was also consistent with the results of prior 2212 crystallization studies which are listed in Table 5. It was also not surprising to see the formation of Sr-Ca-Cu oxides, as these are much higher melting temperature phases.

It can be seen from Figures 19 (a) and (c) and Figure 20 that a mushy (melt+solid) zone exists at the melting interfaces. The appearance of these zones showed that a solute-depleted regions existed in the melt at these interface regardless of whether multiphase or single phase source rods were used.

(2.) Influence of starting material composition

An important goal of this study was to determine a suitable starting material composition to use for the growth of long 2212 single crystals. This was

Figure 18: Representative (a) temperature and (b) composition profiles in the melt and solids near the molten zone. These are shown along the growth direction, which has been rotated 90° from its experimental orientation.

Figure 19: Composite electron micrographs of quenched sample cross-sections (diameters $\sim 600 \mu\text{m}$) grown with feedstock compositions (a) W, (b) Y, and (c) V. These images were obtained during microprobe analysis and show how the bulk of the data was collected; the handwritten numbers indicate analysis points.

Figure 20: Internal cross section of quenched $\text{Bi}_2(\text{Sr,Ca})_3\text{Cu}_2\text{O}_{8+\delta}$ growth front. This sample was crystallized from a single-phase source rod of composition Y and is approximately 500 μm diameter.

Table 7: Effects of Starting Material Composition

Starting Material	Composition (Bi: Sr: Ca: Cu)				Comments
Y	2.10:	1.80:	1.10:	2.00	Best composition for stable, single phase growth.
P	2.20:	1.50:	1.30:	2.00	Produced stable, single phase (SP) growth.
Z	2.10:	1.60:	1.30:	2.00	Produced stable, SP growth.
E	2.05:	1.60:	1.35:	2.00	Produced stable, SP growth.
A	2.15	2.10	0.75	2.00	Produced stable, SP growth.
B	2.17	2.13	0.70	2.00	Produced stable, SP growth.
X	2.15:	1.80:	1.05:	2.00	Produced substantial lengths of SP growth.
R	2.05:	1.95:	1.00:	2.00	Produced substantial lengths of SP growth.
U	2.00:	2.00:	1.00:	2.00	Nominal composition. Produced some SP growth.
V	2.00:	1.60:	1.40:	2.00	Variant of nominal composition. Did not produce SP growth.
W	2.20:	1.80:	1.00:	2.00	Produced short lengths of SP growth.
Q	2.40:	1.50:	1.10:	2.00	Produced SP growth from the initial melt, but did not support extended, SP growth.

accomplished using 850 mm diameter multiphase source rods prepared as described in a previous section.

Table 7 gives the different starting material compositions investigated in this study and the resulting microstructures produced after steady-state growth had been achieved. These compositions are plotted along with the Ono's [10] solubility data in Figure 21.

Stable, single phase 2212 material was successfully produced using the starting compositions designated Y, Z, E, P, A, and B. Of these, composition Y was identified as particularly dependable. It allowed a relatively easy transition from the early, multi-phase growth stage to steady-state growth with relatively little component segregation. Samples grown with this starting material composition also had relatively high T_{cs} .

On the other hand, it was found that compositions E and P exhibited a more complex transient behavior before single-phase growth could be achieved and the samples grown from starting material Z had lower T_c s. Compositions A and B were not extensively studied. They did, however, produce stable, single-phase material, which was SrO- and CuO-rich. These compositions exhibited relatively low Bi_2O_3 segregation and are, therefore, promising candidates for future work.

When starting materials of compositions U or R were used, multi-phase growth persisted for 2-3 hours before single-phase growth was observed. Attempts to grow more than 3-5 mm single-phase material were, however, not successful due to a periodic disruption of the growth process leading to the incorporation of refractory oxide inclusions. Thus, while several millimeter lengths of single-phase sample were often generated using U or R composition starting material, their growth was prone to catastrophic breakdown. Note that compositions R and U both contain insufficient Bi_2O_3 to lie within the Ono solubility region in Figure 21.

Composition V is also Bi_2O_3 -poor compared to the compositions in the Ono solubility region. Single-phase growth was never achieved with starting material of composition V. Instead, samples were consistently multiphase. The refractory oxide inclusions do not have a high electrical conductivity and can form insulating barriers between the 2212 grains. These samples did not conduct well along their lengths, unless the electrical contacts were connected to a single 2212 grain.

Starting materials of compositions X, W, and Q produced single phase growth very soon after the growth process began, but this was followed by multiphase growth with LT inclusions. Typically, these inclusions were first observed as trapped melt at the 2212 grain boundaries. In later stages, they were also observed to form within the 2212 grains. Thus, at the lower growth temperatures, it appears that constitutional supercooling is still a problem even for growth at 4.8 mm/hr in a steep ($\sim 1000^\circ/\text{cm}$) temperature gradient.

The duration of the single-phase steady-state growth regime varied for compositions X, W, and Q. Inclusions were not apparent in samples produced using X until after 5-8 mm of single-phase material had been grown. This composition was initially thought to be suitable for stable, single-phase growth, but the growth of long samples, however, showed that it was not. Compositions W and Q, on the other hand, provided more extreme examples of transient, single-phase growth. These compositions produced <2.5 mm of single phase material.

Figure 21: Ternary representation of starting material compositions $\text{Bi}_x\text{Sr}_y\text{Ca}_z\text{Cu}_2\text{O}_{8+d}$ (where $x+y+z=5.0$) and their position relative to Ono's $\text{Bi}_2(\text{Sr,Ca})_3\text{Cu}_2\text{O}_{8+d}$ solid solubility [10] region.

(3.) Crystal/melt equilibria at the growth front

The compositions of a variety of crystals grown in this study are listed in Table 8. They are accompanied by 1) the letter designating of the starting material composition, 2) the composition of the molten zone, 3) their growth temperatures, and 4) the solid phases found at the growth interface.

Many of these samples were quenched during an early stages of growth and, therefore, the composition of the growing crystal differed from that of the starting material because the melt composition had not yet reached its steady-state value. For this reason, growth was terminated only after the molten zone geometry and surface appearance remained unchanged for at least 15 minutes. Using this procedure assured that the phases present in the quenched molten zones were representative of true steady-state equilibrium. The composition values given in Table 8, therefore, give a good picture of the ("2212" + melt) phase field.

c. Analysis

(1.) Solid solubility ranges

The compositional data given in Table 8 are plotted in Figures 22 and 23, alongside the Ono [10], Golden et al.[28] and Hong et al.[30] solubility data. In Figure 22, the crystal compositions is represented as triangles and the melt compositions as circles. Both sets of symbols are projected on the $\text{Bi}_x\text{Sr}_y\text{Ca}_z\text{Cu}_2\text{O}_{8+d}$ plane. Figure 23 shows the same information, but using the form $\text{Bi}_x(\text{Sr,Ca})_y\text{Cu}_2\text{O}_n$. The gray-level in these symbols indicates the type of solid phases present at the growth interface. Single-phase regions are indicated by the white symbols. HT and LT phases are represented by black and gray symbols, respectively. Related compositions at each interface are connected by tie-lines in Figures 22 and 23. These are represented by a solid line when an approximately planar growth interface was observed, otherwise they are represented as a dashed line.

Several observations can be made concerning the compositional data plotted in Figure 22. First, the observed crystal compositions correspond closely to those in the Ono solubility range. The melt compositions are all Bi-rich and Sr-poor with respect to both the Ono solid solubility values. These can be expressed by the segregation coefficients ($k=C_S/C_L$). The segregation coefficient measured for Bi_2O_3 was <1.0 and >1.0 for SrO. The CaO segregation coefficient varied about both sides of 1.0.

The melts compositions found in this study corresponded closely to the Golden solubility values. The Golden solubility range thus corresponds more to the liquidus,

TABLE 8: Data Obtained from Composite Samples

Trial	Source	Crystal Comp (Bi: Sr: Ca: Cu)				Melt Comp (Bi: Sr: Ca: Cu)				Temp	Inclusions
#1	(B)	2.16	2.05	0.77	2.02	2.40	1.81	0.68	2.11*	-	None
2	(Y)	2.16	1.77	1.10	1.97	2.44	1.47	1.09	2.00	>875°C	None
3	(X)	2.23	1.76	1.06	1.95	2.36	1.58	1.02	2.04	890	None
4	(E)	2.17	1.61	1.20	2.01	2.40	1.40	1.22	1.98	890	None
5	(Z)	2.17	1.56	1.24	2.02	2.40	1.26	1.16	2.18*	880	None
6	(P)	2.17	1.56	1.27	2.01	2.35	1.21	1.20	2.25*	880	None
7	(A)	2.15	2.00	0.80	2.05	2.22	1.63	0.69	2.46*	-	None
8	(Y)	2.22	1.77	0.99	2.02	2.39	1.52	1.02	2.06*	>875	None
9	(E)	2.11	1.55	1.31	2.02	2.37	1.38	1.29	1.95*	>875	None
10	(Z)	2.19	1.59	1.23	1.97	2.52	1.28	1.19	2.02	875	None
11	(YY)	2.21	1.70	1.11	1.97	2.52	1.41	1.10	1.97	870	None
12	(YY)	2.13	1.76	1.10	2.01	2.47	1.47	1.03	2.03	865	None
13	(V)	2.17	1.60	1.20	2.03	2.49	1.18	1.25	2.08*	>875	Ca ₂ CuO ₃
14	(U)	2.17	1.92	0.89	2.01	2.54	1.73	0.90	1.83*	900	CaO
15	(R)	2.14	1.92	0.96	1.98	2.20	1.67	0.95	2.18*	890	Sr ₂ CuO ₃ ?
16	(ZZ)	2.26	1.41	1.31	2.02	2.72	1.16	1.28	1.83*	865	Nonplanar
17	(QQQ)	2.21	1.59	1.20	2.01	2.76	1.26	1.06	1.93*	845	Nonplanar
18	(X)	2.19	1.77	1.04	2.00	2.63	1.45	1.04	1.88*	840	Bi ₂ O ₃ -rich
19	(W)	2.21	1.76	1.02	2.01	2.63	1.40	1.03	1.94*	840	Bi ₂ O ₃ -rich
20	(QQQ)	2.28	1.58	1.18	1.96	2.91	1.09	1.24	1.76*	<850	Bi ₂ O ₃ -rich

Figure 22: Ternary projection of crystal and melt compositions on the $\text{Bi}_x\text{Sr}_y\text{Ca}_z\text{Cu}_2\text{O}_{8+d}$ planar section. Crystal compositions are shown as triangles, while melt compositions are shown as circles. Symbols which are white indicate ~planar, single-phase crystallization fronts, while grey symbols represent cases of non-planar solidification fronts. Lines connect the various crystal compositions to their respective melt compositions.

Figure 23: Ternary $\text{Bi}_x(\text{Sr,Ca})_y\text{Cu}_z\text{O}_n$ representation of crystal and melt compositions. The various symbols have the same meaning as in Figure 24.

rather than the solidus values of the 2212 phase. This contradicts the conclusion of Golden et al., [28] but is not unreasonable considering the nature of the experiments performed.

Golden et al.'s thin films were crystallized by first rapidly melting the mixed components, then allowing them to crystallize. They were also homogenized at elevated temperatures for extended (> 2 hours) times. The 2212 thin films may thus have started as the first solid to crystallize from the melt. They may then have been transformed to single phase films of the original melt composition through later subsolidus annealing processes. The results of our study and that of Golden et al. can thus be viewed as complimentary.

Figure 23 allows one to consider the case of CuO segregation on a ternary section by treating (Sr,Ca)O as a single component. Since SrO and CaO have similar chemistry, this is the most valid technique for describing the BSCCO system as pseudo-ternary. The CuO segregation coefficient is shown to vary about unity in this figure. One may also observe that the CuO content of the 2212 crystals deviates significantly from Ono's assumption that the copper coefficient will always be exactly 2.0. [10]

Both figures show that the more careful composition measurements of Hong et al. [30] resulted in the closest fit between their solubility range and the compositions of inclusion-free 2212 crystals.

(2.) Comparison with bulk crystallization data

The solid and melt compositions measured in the present study may be compared with the earlier crystal growth data listed in Table 5. The present study has produced significantly more data than was previously available. All studies were consistent in finding that 2212 crystals form from melts which are Bi₂O₃-rich and SrO-poor, at temperatures between 820 and 900°C.

Additional crystal growth data was also available from an as-yet unpublished, flux flow study by Lombardo. [31] In this study, 2212 crystals were quenched during growth from melts in MgO crucibles. Microprobe measurements of the as-grown crystals and their melts were then made. This data is compared, in Figures 24 and 25, with the crystal and melt compositions in single-phase LHPG samples.

The Bi_xSr_yCa_zCu₂O_{8+d} representation in Figure 24 shows that Lombardo's crystal and melt compositions are fairly consistent with the float-zone data. The crystals prepared in these experiments had compositions corresponding closely to those of Hong et al. [30] Once again, these crystals were observed to solidify from Bi₂O₃-rich and SrO-poor melts.

The Bi_x(Sr,Ca)_yCu₂O_{8+d} representation in Figure 25 shows the close agreement between the Hong solubility data and Lombardo's crystal compositions. This figure shows graphically that the copper content in the latter's crystals was greater than that observed in

Figure 24: Ternary projection of crystal and melt compositions on the $\text{Bi}_x\text{Sr}_y\text{Ca}_z\text{Cu}_2\text{O}_{8+d}$ planar section, from LHPG and bulk crystallization [31] studies. White symbols illustrate data from the LHPG experiments, while grey symbols represent compositions from the bulk crystallization study. Otherwise the symbols have the same meaning as before.

this study. The melts were also lower. Thus, it is possible that different experimental setups can affect the copper oxide segregation coefficient.

(3.) Component Segregation

The segregation behavior of Bi, Ca, Sr and Cu during the float-zone growth of 2212 is compared with that found for the flux growth experiment of Lombardo. [31] Figures 26 through 31 plot the variations in segregation coefficient for the various elements as a function of first, growth temperature, then composition for both sets of experiments. The dark symbols indicate the LHPG data, while open symbols represent the bulk crystallization data.

Figure 26 gives the variation of the bismuth and copper oxide segregation coefficients with observed growth temperature. It shows that, as growth temperature increased, the segregation coefficient of bismuth oxide increased toward unity. The segregation coefficient of copper oxide, meanwhile, decreased with increasing growth temperature. In this case, the segregation coefficient passed through unity (indicating that there was no copper oxide segregation) around 865° C; the middle of the temperature range explored. Combined, these two results clearly show that congruent crystallization of 2212 is not likely in room air because the segregation of both bismuth and copper cannot be simultaneously eliminated.

Similar plots show that the strontium oxide, calcium oxide and (Sr,Ca)O component segregation coefficients did not vary monotonically with observed growth temperature. They also did not vary monotonically with the copper or bismuth oxide contents in the crystals or melts. There was, however, a strong relationship between both the SrO:CaO ratio and the net SrO+CaO content in the melt, and that in the corresponding crystals. This interdependence of the SrO and CaO content is shown in Figures 27 and 28.

The behavior of the copper and bismuth oxide segregation coefficients also showed a striking interdependence. These coefficients are plotted versus bismuth and copper oxide melt composition in Figures 29 and 30. Once again, the bismuth and copper oxide segregation coefficients do not simultaneously approach 1.0 in these plots. It was also apparent that the influence of the bismuth oxide content of the melt on copper oxide segregation differed between the LHPG and flux growth studies. This was the only significant difference observed.

The interrelationship between the Bi, (Sr,Ca), and Cu segregation coefficients for both data sets are summarized in Figure 31. Despite a significant spread in the data, it is still apparent that increased bismuth oxide segregation was accompanied by a decrease in copper oxide segregation in both studies. As before, the (Sr,Ca)O segregation coefficient appeared to be independent of the other system variables.

Figure 26: Segregation coefficients, k_{Bi} , $k_{\text{(Sr,Ca)}}$, and k_{Cu} , plotted vs. growth temperature.

Figure 27: Variation in Ca:Sr ratio in crystal composition, as the Ca:Sr ratio in the melt varies. Results shown for both LHPG and bulk crystallization [31] data.

Figure 28: Variation in (Sr,Ca) segregation coefficients as the (Sr,Ca) content of the melt varies. Results shown for both LHPG and bulk crystallization [31] data.

Figure 29: Variation in Bi and Cu segregation coefficients as the Bi content of the melt varies. Results shown for both LHPG and bulk crystallization [31] data.

Figure 30: Variation in Bi and Cu segregation coefficients as the Cu content of the melt varies. Results shown for both LHPG and bulk crystallization [31] data.

Figure 31: Variation in (Sr,Ca) and Cu segregation coefficients as the Bi segregation coefficient varies. Results shown for both LHPG and bulk crystallization [31] data.

d. Conclusions

While the phase relations in the BSCCO system have been studied by many groups, the temperatures and compositions of the 2212 liquidus and solidus surfaces has not been available. This data is of great importance in designing controlled experiments for the reproducible melt growth of high quality crystals of the 2212 superconductor. The present study produced new data concerning these phase relations by analyzing the crystal and melt compositions, and the growth temperature of miniaturized float-zone samples. These samples were prepared from starting materials having a number of possible 2212 phase compositions.

Comparison between our results and those of other studies shows that our 2212 phase sample compositions formed a subset of the solid solubility ranges reported by Ono [10] and Hong et al. [30]. A moderate degree of agreement was also found between our melt (liquidus) compositions and the "2212 solubility range" reported by Golden et al. [28]. In addition, the crystal composition, melt composition and crystallization temperature data gathered in this study was observed to be typical of the data available from the flux growth experiments.

As a result of these experiments, a successful technique for the growth of long, single-phase 2212 samples was developed. These experiments showed that such growth was more easily obtained for some starting material compositions, while it was impossible for others. Composition Y ($\text{Bi}_{2.1}\text{Sr}_{1.8}\text{Ca}_{1.1}\text{Cu}_2\text{O}_y$) was found to produce single-phase material most easily of all the compositions studied.

The growth temperature, crystal composition, and melt composition were identified for a number of single-phase 2212 growth interfaces. These measurements were used to characterize the relevant 2212 crystal/melt equilibrium conditions. It was found that 2212 crystals typically solidify from Bi_2O_3 -rich and SrO-poor melts.

The growth temperatures were found to increase with increasing melt concentrations of bismuth and copper oxide. The combined bismuth and copper oxide content of the crystals, however, was found to be relatively invariant. It was thus concluded that component segregation of the bismuth and copper oxide components during 2212 crystallization is interdependent. The copper oxide segregation coefficient was observed to increase above 1.0 as the bismuth oxide coefficient increased toward 1.0 from below. Based on this analysis, congruent 2212 solidification (in air) does not appear to be possible.

V. INFLUENCE OF GROWTH CONDITIONS ON PROPERTIES

The 2212 growth experiments produced crystal samples with varied composition within the 2212 solubility range and which crystallized at temperatures between 840 and 900°C from a relatively wide range of melt compositions. Data from twenty 2212 crystal samples were used for property analysis. The first part of this section deals with strategies for avoiding constitutional supercooling, and hence inclusion incorporation, during growth. This was accomplished by examining the trends in component segregation during crystallization and its influence on the stability of solidification front curvature. We show that there are two separate trends in inclusion incorporation (corresponding to the two types of inclusions possible within incongruently-melting crystals) and that obtaining single-phase samples at maximum growth rates requires minimizing the adverse effects of both.

The second part of this section is concerned, with the influence of the growth conditions on the onset of superconductivity. Following a literature survey, observed sample transition temperatures were compared with corresponding cation compositions and growth conditions. Analysis was performed on data from six long homogeneous 2212 crystals (0.6 mm diameter rods > 5 mm in length) grown under stable growth conditions. The compositional uniformity of these samples (relative to sintered polycrystalline material) provided us with an unusual opportunity to separate interface and grain boundary effects from the 2212 bulk superconducting transition. This section will show that of all the growth conditions studied, growth temperature was the factor which most influenced the T_c s of our 2212 samples.

A. Constitutional Supercooling Effects

Several studies [14,16,19] have shown that planar, single-phase 2212 growth interfaces are not stable at higher growth rates (>4.8 mm/hr in the case of our apparatus). This is due to the effects of constitutional supercooling. We can divide constitutional supercooling problems for incongruently-melting compounds into two classes. The first can also be seen with congruently-melting compounds with impurities. Both congruently and incongruently-melting solids can thus crystallize with low temperature (LT) inclusions. These LT inclusions solidify from solute-enriched melt trapped within channels in the growing crystal.

The LT inclusions also occurred at lower growth rates when the samples were polycrystalline. The formation of these inclusions is expedited when grain boundary

grooves in the growth front cause localized solute buildup. Despite differing growth geometries, the factors which lead to both forms of LT inclusion are the same. This case can thus be modelled in the same way as traditional constitutional supercooling, but using decreased effective diffusivities.

The second form of constitutional supercooling is possible only for incongruently-melting materials, when the crystal solidifies from a melt described by the high-temperature end of the liquidus curve. This case results from the discontinuity of effective liquidus slope at the junction of two liquidi. Generally, the liquidus which corresponds to the crystallization of one or more high temperature (HT) phases is much steeper in slope. Interface instability is thus possible at higher G/R (interface temperature gradient/ growth rate) values. Consequently, single phase growth from such melts may be interrupted by the nucleation of higher-melting temperature compounds ahead of the interface. The HT phases become inclusions if the original phase crystallizes around them.

All versions of constitutional supercooling (in a quaternary system) can be examined using a set (of four) constitutional supercooling relations:

$$G_L/R \geq (m_L^i (C_{L0}^i - C_S^i)/D_L^i, \quad (1)$$

where i = indicates which of the system components is being considered. Here, G_L is the thermal gradient in the melt at the growth front and D_L^i is the diffusivity of the i^{th} component in the melt. R is the growth rate, C_S^i and C_{L0}^i are the solid and melt compositions, and $m_L^i = dT/dC^i$ is the slope of the liquidus in the phase diagram, all with respect to the i^{th} component.

These relations can be rearranged to yield the approximate maximum crystal growth rates (R_i) determined by the segregation of each component. These then have the form:

$$R_i \leq G_L D_L^i / m_L^i (C_{L0}^i - C_S^i). \quad (2)$$

Growth for a particular case will, therefore, be dominated by the component with the lowest growth rate. Equation 2 shows that the dominant component may be either that with the lowest melt diffusivity, the greatest liquidus slope or the highest degree of component segregation. For the two cases of constitutional supercooling described above, equation 2 applies to the minimum of two crystallization reactions. For the case of constitutional supercooling which results in LT inclusions, equation 2 relates to the crystallization from the liquidus of the majority phase. Thus, m_{L1} has the lower slope of the majority phase

liquidus and $(C_{L0}^{Bi} - C_S^{Bi})$ is the difference in composition between the melt and the crystallizing solid at low temperatures.

When HT phase inclusions are produced, however, equation 2 refers to the crystallization reaction of the HT phase(s). In this case, m_{Li} has a higher slope (than that of the primary phase liquidus) and $(C_{L0}^{Bi} - C_S^{Bi})$ is the greater difference in composition between the melt and the crystallizing HT solids. Thus, once the melt composition is within the range which allows HT phase crystallization, constitutional supercooling may proceed in spite of G/R values which would otherwise result in stable growth.

The data listed in Table 8 will be used to identify the primary causes of inclusion incorporation during 2212 crystal growth. Eight of the samples in this table had markedly nonplanar interfaces. Of these, those with the LT inclusions (samples 16-20) show the greatest segregation behavior of all samples. Those with HT inclusions (samples 13-15), solidified from melt compositions on the 2212 liquidus nearer the peritectic decomposition temperature ($890 \pm 20^\circ\text{C}$). Samples containing LT inclusions also grew from melts with unusually high Bi_2O_3 contents. Limited transport of Bi_2O_3 across the melt thus also appears to play a major role in causing the LT inclusions. The samples which contained HT inclusions (Bi_2O_3 -free, Sr-Ca-Cu-O compounds) were also observed to crystallize consistently from Bi_2O_3 -rich melts, but less Bi_2O_3 segregation was observed. It is thus probable that Bi_2O_3 segregation is still often a significant factor in the formation of HT inclusions, despite their different inclusion formation mechanism. The fact that all of the HT inclusions observed in this study were Bi_2O_3 -free also supports this hypothesis.

The best choice for the component which governs the onset of constitutional supercooling (based on our data) is thus Bi_2O_3 segregation. The form of Equation 2) which applies to Bi_2O_3 -segregation may be expressed as:

$$R \leq G_L \cdot D_L^{Bi}/m_L^{Bi} (C_{L0}^{Bi} - C_S^{Bi}). \quad (3)$$

The fastest crystal growth should then be possible when $G_L \cdot D_L^{Bi}$ is relatively high and when $m_L^{Bi} \cdot (C_{L0}^{Bi} - C_S^{Bi})$ is minimized. The first condition may be met through an optimal experimental design, one which maintains a steep thermal gradient at the growth interface in a well-stirred melt. The second condition should be met, instead, through the appropriate choice of melt or crystal composition.

Our experimental results suggested that LT inclusions were formed due to large values of $(C_{L0}^{Bi} - C_S^{Bi})$ in equation 3, while HT inclusions resulted from the high value of m_L^{Bi} on the HT phase liquidus. Desirable growth compositions are therefore those which minimize Bi_2O_3 segregation, while avoiding growth from compositions which have a

peritectic reaction. To predict the optimal crystal and melt composition one must identify 1) the growth conditions near the top of the 2212 liquidus surface and thus likely to produce HT inclusions and 2) the trends in Bi_2O_3 segregation during 2212 growth.

The above analysis showed that a first order approach for avoiding inclusion-incorporation is to minimize Bi_2O_3 segregation. This minimizes LT phase incorporation and should also identify the conditions which produce crystals of the highest perfection. This was accomplished by identifying the factors which could be correlated with low Bi_2O_3 segregation. The strongest correlation was with high SrO content in both the crystal and its melt. Starting materials with higher SrO content (compositions A: $\text{Bi}_{2.15}\text{Sr}_{2.10}\text{Ca}_{0.75}\text{Cu}_2\text{O}_y$ and B: $\text{Bi}_{2.17}\text{Sr}_{2.13}\text{Ca}_{0.70}\text{Cu}_{2.00}\text{O}_y$) were therefore prepared and tested. Using source rods of these compositions, stable, single-phase 2212 crystals were indeed obtained, with minimal Bi_2O_3 segregation. The results of two such experiments are included in Table 8. As predicted, the observed Bi_2O_3 segregation at the growth interface was relatively low when starting materials A and B were used.

Figure 32 summarizes the degree of Bi_2O_3 -segregation observed, for all samples, as a function of growth temperature. For approximately planar single-phase 2212 growth, segregation decreased (approached a segregation coefficient of unity) with increasing growth temperatures. Inclusions of both types led to substantial increases in Bi_2O_3 -segregation.

Once the Bi_2O_3 segregation is minimized, proximity to the solid and melt compositions involved in peritectic decomposition also decreases the practical growth rates which can be achieved. Figure 6.2 shows that both the crystal and its melt show a sharp increase in SrO contents at growth temperatures above 880 °C (within ~20°C of the peritectic decomposition reaction). Furthermore, the samples which contain HT inclusions, also showed the highest SrO contents. It thus appears that increased SrO content both increases the growth temperature and the likelihood for HT inclusions.

This conclusion is contrary to that of the previous section, in that it suggests starting material with lower SrO content may provide the most stable growth at higher growth rates (by discouraging HT inclusion formation). It is, however, in agreement with the unexpected experimental observation that source rod of composition P ($\text{Bi}_{2.20}\text{Sr}_{1.50}\text{Ca}_{1.30}\text{Cu}_{2.00}\text{O}_y$) produced unusually stable, single-phase growth (once several transient stages of growth had passed). This composition has the lowest SrO content among the starting materials tested.

Figure 32: Variation in Bi_2O_3 segregation coefficient with measured growth temperature.

Figure 33: SrO content of 2212 crystals and their melts as a function of observed growth temperature.

B. Influence of Processing Parameters on T_c

1. Background

Considerable variation in the T_c of 2212 phase superconductors has been observed in samples of varied composition. [10,43] The relationship between the composition of a 2212 crystal and its T_c is difficult to isolate, partly because compositional variations in a quaternary-oxide solid solution are complex. In addition, the electronic properties in such an oxide may be profoundly influenced by relatively subtle compositional variations; for instance, the electrical resistivity in semiconductors is determined by dopant concentrations in the ppm range.

Previous studies have shown that three interdependent mechanisms give rise to compositional variations in the 2212 phase: 1) the incorporation of substitutional point defects at the cation sites [10,23,44,48], 2) defects in the atomic stacking sequence within the crystal structure [45-48], and 3) variation in the oxygen content through atomic vacancies on the oxygen sites. [26,43,49,50] These are discussed below.

2. Cation inter-substitutions

The existence of substitutional defects in the 2212 crystal structure was established by the neutron diffraction study of Lee et al. [44]. They observed: 1) bismuth substitution onto strontium and calcium sites, and 2) the exchange of strontium and calcium atoms on their respective sites. The substitution of Bi onto Sr and Ca sites produces a Bi:(Sr,Ca) ratio greater than 2:3 in 2212 crystals. Bi:(Sr,Ca) ratios $>2:3$ were confirmed in several other studies [10,28,30] as well as the results of the present work (see Table 8). The exchange of Sr and Ca atoms on their respective sites is consistent with the results from the many compositional studies of the 2212 phase, including the present study. Similar inter-substitution has also been observed in the other BSCCO system compounds.

Ono [10] has demonstrated that such cationic inter-substitution influences the T_c s of 2212 samples of differing compositions, but with similar thermal histories. The observed values for samples (quenched from a 800°C anneal) are given in Figure 34 as a function of their relative compositions.

3. Atomic layer stacking defects

Previous authors [45-48] have studied the influence of atomic layer stacking sequences on the resistivity of the 2212 superconductor using transmission electron microscopy (TEM) and electron diffraction analysis. They found that stacking faults in

Figure 34: Variation of superconducting T_c with crystal bismuth content and Ca:Sr ratio, from Ono [10].

2212 crystals can lead to multiple-step superconducting transitions (usually of the higher temperature 2223 phase) in samples which, on macroscopic examination, appear single-phase. Since each stable stacking sequence in the BSCCO system may be characterized by its differing copper content (illustrated in Figure 1), such defects should lead to compositional variations in the 2212 phase. Compositional analysis of faulted crystals, however have not revealed significant deviations from the ideal 2212 copper concentration. Similar to semiconductors, even small defect densities and hence subtle compositional variations may have a significant influence on the electrical properties associated with this type of defect.

Multiple step (85 and 110 K) transitions were frequently observed in the R vs. T curves obtained from our float-zone grown 2212 samples. These, however, were not examined extensively and are not included among the samples analyzed here. The T_c s reported here were obtained from samples with single-step transitions and thus should not be greatly affected by stacking fault defects.

4. Variations in oxygen content

The influence of oxygen content on the T_c of 2212 phase superconductors has been determined from annealing experiments on mostly polycrystalline samples. [26,43,49,50] These studies verified that when the oxygen content of the 2212 crystals is changed, there is not a corresponding change in cation content. They also showed that the oxygen content of 2212 crystals can be significantly altered during heat-treatment by either controlling the oxygen partial pressure or varying the heat-treatment temperature. Figures 35 and 36 document some of the results of these studies.

Figure 35 is reproduced from Buckley et al. [43]. In this study, polycrystalline 2212 samples were annealed in air, then quenched into liquid nitrogen. The T_c s were observed to increase with increasing annealing temperature. This study also correlated the measured variation in T_c with a decrease in the c -axis lattice parameter. Since the c -axis parameter decreases with increasing oxygen content, they concluded that the 2212 sample T_c s increased as their oxygen content decreased.

Figure 36 is reproduced from Mitzi et al. [26]. In this study, the superconducting properties of $\text{Bi}_{2.10}\text{Sr}_{1.94}\text{Ca}_{0.88}\text{Cu}_{2.07}\text{O}_{8+d}$ crystals annealed in atmospheres with differing oxygen partial pressures were examined. Figure 36 shows the resulting magnetic susceptibility curves of their samples. They also quantified changes in the oxygen content with thermal gravimetric analysis (TGA). They thus verified that the T_c and c -axis lattice parameter decreased with increasing crystal oxygen content. They also correlated the

Figure 35: ρ vs. T curves of polycrystalline "2212" samples quenched from different annealing temperatures, from Buckley et al. [43]

Figure 36: Magnetic susceptibility as a function of temperature for crystals of differing oxygen content, from Mitzi et al. [26]

decrease in T_c with an increase in the charge carrier density using Hall effect measurements.

The most extensive characterization of T_c variations with oxygen content was the work of Triscone et al. [50] on the "ideal" 2212 composition. They found maximum sample T_c s for varied atmospheric oxygen pressure and heat-treatment temperature combinations. From their results, they also identified an optimal hole concentration (caused by oxygen vacancies) in the electronic structure of 2212 crystals.

The oxygen contents of the samples grown in the present study were not measured directly. The growth temperature (at the crystallization interface) was, however, measured by optical pyrometry. This provided a rough indication of the complete thermal history of each sample during crystallization, which would in turn significantly influence the oxygen content of the as-grown samples. This was our principle means of studying the oxygen content of our crystals.

C. Correlation Between T_c and Growth Parameters

Table 9 lists the crystal compositions, melt compositions, growth temperatures (M_p s) and superconducting T_c s of six internally homogeneous 2212 rods crystallized in the present study. Examination of the data in Table 9 reveals that no simple relationship exists between composition and T_c . This Table does, however, reveal a straight-forward correlation between T_c and growth interface temperature: T_c increases in an approximately linear fashion with increasing growth temperature. This correlation holds at the lower growth temperatures observed in the Golden et al. [28] study. This may be seen in Figure 37, which plots the T_c s measured in both the present study and that of Golden et al. versus growth (solidus) temperature.

This trend is also supported by the variation of sample T_c with the measured strontium contents of the 2212 crystals and their melts. This is illustrated in Figure 38, which shows that the variation in T_c with Sr content is similar to the variation in growth temperature with Sr content in single phase samples (shown in Figure 32).

Given that: 1) there is no monotonic increase in T_c with cationic composition and 2) sample heat-treatment has been observed to change both the oxygen content and T_c s of 2212 samples, it is likely that the observed variation in the T_c s of our samples results from their variable oxygen content. This was not measured directly in our study. It is possible to conclude, however, based on our results, that the 2212 sample crystallization conditions mainly influence the T_c s of the as-crystallized materials by changing their

Table 9: T_c with other Data from LHPG Samples

<u>Trial #</u>	<u>Source Mat'l</u>	<u>Crystal Composition</u>				<u>Mp (°C)</u>	<u>T_c (K)</u>
		<u>Bi</u>	<u>Sr</u>	<u>Ca</u>	<u>Cu</u>		
1	E	2.12	1.59	1.28	2.01	890	82
2	Y	2.21	1.74	1.01	2.03	890	83
3	U	2.16	1.95	0.86	2.03	900	85
4	E	2.17	1.62	1.19	2.01	890	81
5	X	2.17	1.78	1.05	2.01	840	76
6	Z	2.20	1.61	1.24	1.98	875	79

Figure. 37: Sample T_c (for both LHPG and thin film [28] samples) plotted vs. crystal growth temperature.

Figure 38: SrO content of 2212 crystals and their melts as a function of observed sample T_c .

heat-treatment history. Maximization of sample T_c thus results from the maximization of sample growth temperature.

D. Mechanical Properties of 2212 Fibers

For motor and magnet winding applications it is important that the superconductor wire can be bent around a relatively small radius of curvature. The bulk high T_c superconductors are brittle ceramics with poor mechanical properties. It is well known, however, that flexibility can be induced in brittle materials as the sample thickness is decreased below some critical value. We purposely grew some 2212 fibers with smaller diameters to determine the minimum size necessary to achieve a practical bending radius. Figure 39 shows a 90 micron diameter 2212 fiber bent into a 5 cm radius. This is the first demonstration of the flexibility of a bulk ceramic superconductor. Smaller diameter fibers should be capable of much smaller bending radii. Figure 40 shows the fracture surface of a 90 micron single crystal fiber bent until broken. One can clearly see the mica-like delaminated structure of this material which also demonstrates the single crystal nature of this fiber. The cleavage planes are [001].

E. Conclusions

The above results showed that there are two types of interfacial breakdowns possible, and that both can lead to the formation of multiple phases during the float-zone growth of the 2212 as the growth rate is increased. The first type involved low temperature inclusions (LT) caused by excessive solute buildup during the crystallization from lower temperature melt compositions. The second type involved high temperature inclusions (HT). For this case to occur, two conditions must be met: there must be both (1) significant compositional gradients in the melt and (2) an interfacial melt composition located near peritectic decomposition temperature (the junction of two liquidus surfaces).

Preliminary analysis of the experimental data suggests that Bi_2O_3 segregation played a major role in triggering interface breakdown. Further analysis indicated that SrO-rich 2212 compositions solidify with lower Bi_2O_3 segregation. The high temperature growth of SrO-rich 2212 compositions are thus hypothesized to result in samples with the highest crystalline perfection.

Evaluation of constitutional supercooling of the second type (which results in HT inclusions) suggested, however, that 2212 growth under the above conditions is the most vulnerable to disruption by HT inclusions, and that mid-liquidus range growth will be the

Figure 39: 90 micron diameter 2212 fiber bent into a 5 cm radius.

Figure 40: SEM micrograph of the fracture surface of a 90 micron single crystal fiber that was bent until fracture occurred.

most stable at higher growth rates. Among those starting material compositions tested, the sample containing the least SrO was observed to produce the best example of such growth.

For as-grown 2212 samples, the T_c increased with growth temperature. This trend was also found by Golden et al. [28] at growth temperatures lower than those used in this study. The relationship between crystal composition and growth temperature was found to be complex, since the strontium oxide concentrations of the 2212 crystals and their melts had a parabolic relationship with growth temperature. The same parabolic relationship was also observed between composition and sample T_c .

Since the thermal history of 2212 crystals has been shown to significantly influence their oxygen content [10,26,43,49,50], it was concluded that the oxygen contents of the crystals (which were not measured) had played the most significant role in determining their T_c s. Therefore, in agreement with previous studies, sample heat-treatment and their ambient gaseous atmosphere were found to dominate the sample T_c variations measured in this study.

Superconducting fibers less than about 100 microns in diameter are quite flexible. A 90 micron diameter 2212 fiber was bent to a 5 cm radius and smaller fibers should be more flexible yet. After fracturing, delaminations parallel to the c-plane are formed in single crystal fibers.

VI. ADVANCED FIBER GROWTH STATION

A. History and Background

Stanford's fiber growth equipment in use at the time this program was conceived (in 1988) was already almost 10 years old. Originally designed as a versatile system for exploring a wide variety of materials ranging from 20 μm to 2 mm in diameter, it had been highly successful in achieving those goals, producing over 60 different compounds in single crystal fiber form. Along the way, we had made numerous minor modifications and improvements to its optical and mechanical components in order to meet the varying requirements of each individual material. However, because this high T_c superconducting materials program had very specialized requirements, we felt it would ultimately be necessary to build a more advanced system from the ground up. One of our program goals was to prepare long lengths (> 100 mm) of small diameter (< 100 μm) superconducting fibers under very stable (controlled) growth conditions, and our existing LHPG system was not ideally suited for this application. A major objective of this program, therefore, became the design and construction of a dedicated fiber growth system capable of routine preparation of 10-50 μm diameter fibers of uniform diameter and in long lengths.

Improvements in laser stability and focusing optics, diameter control, fiber and source rod mounting and guiding, mechanical stability, and the incorporation of motor drive systems with greater precision were identified as essential. Several different approaches were possible in each area, and the design phase involved a thorough evaluation of each alternative to identify those that best met the goals of the program. Since there were only a handful of LHPG systems in the entire world at the time, each built by a different group, a proven design did not yet exist. Therefore, we were faced with prioritizing system requirements; modifying existing components, or designing from scratch when our specialized needs could not be met; and integrating the individual components into a complete system. Table 10 identifies the major LHPG system components that are found in typical LHPG systems.

B. System Design Issues

The first year of this program began with a study to clarify design concepts by surveying existing LHPG facilities in the U.S. Following that, a preliminary design was

Table 10: LHPG System Components

1. Laminar Flow Clean Area
2. Fiber Preparation/Evaluation
 - a. Microscope
 - b. Gauging and mounting
3. Operating Console
 - a. Microprocessor interfacing
 - b. Power monitoring and control
 - c. Process monitoring and control
 - d. Growth chamber ambient control
4. Fiber Monitoring
 - a. Optical monitoring
 - b. Video monitoring and recording
 - c. Video analysis
5. Vibration Isolation Optical Table
 - a. Optical train
 - b. Growth chamber
 - c. Loading and unloading chamber access
 - d. Microscopic viewing reference
6. Vacuum, Purge Gas, and Laser Cooling Support

generated and thorough evaluations of the two most critical system components, the stability of the CO₂ heating laser and the precision translation stages, were initiated. Early on, it was decided to focus on ergonometics since all the LHPG designs surveyed required the operators to maintain uncomfortable seated or standing positions, and were judged too difficult to operate for the prolonged periods required to grow high T_c superconducting fibers. Our system design proceeded from the process-monitoring microscope eyepoint position of a comfortably seated operator. As far as we know, no other LHPG system has yet been designed in this manner. Table 11 summarizes the major system components and their sources. Figure 41 illustrates the system's major components.

TABLE II

MAJOR HIGH T_c LHPG SUBSYSTEMS

Item	Description	State-of-Art	Source	Purchase	Use
CO ₂ Laser	cw, ultrastable in pointing stability, wavelength and power. 25 Watts req'd. Dither stabilized.	yes	California Laser, Inc. (Model CL-250 waveguide, sealed CO ₂ Laser)	1989	Immediate
Optical Focusing	Diffraction-limited focus in a 20 mm high band around a 30 mm dia fiber. Circular symmetry highly desirable.	yes	Pneumo-Precision, Inc. (Custom diamond-tuned copper optics)	1989 Pending	Immediate
Mechanical Translation	Ultrastable feed and pull stages for moving material into and out of molten zone.	yes	Micro-Mo, Inc. (Miniature dc phase locked gearhead motor with computerized control)	1989 Pending	Immediate
Optical Monitoring	Diffraction limited monitoring of 20 mm x 30 mm molten zone from 200 mm distance. Large numerical aperture may be necessary.	yes	Wild Heerbrugg, Ltd. (Stereo-zoom, long working distance microscope) or Questar, Inc. (Short working distance telescope)	1989 Pending	Early 1990
Optical Table	Vibration isolation and mounting of optical train and growth chamber. 8"-10" through port required.	No	Oriel (Custom 30" x 48" table)	1989 Pending	Late 1989

MAJOR HIGH T_c LHPG SUBSYSTEMS, continued

Item	Description	State-of-Art	Source	Purchase	Use
Optical Beam Handling	Direct CO ₂ beam, attenuate, and merge with alignment laser beam.	No	Newport	1989	Late 1989
Mechanical Positioning	Intermittent X,Y,Z positioning	No	Oriel	1989 Pending	Late 1989
Environ- mental and Ambient Control	Vacuum-capable growth chamber with controlled atmosphere purge and slight, ≤ 1 atm, overpressure capable.	No	Huntington Vacuum	1990	Mid 1990

Figure 41: Schematic illustration of advanced LHPG system's major components.

1. CO₂ laser and laser stability

The experimental portion of this program quickly revealed an absolute need for laser stability in the growth of high T_c compounds. The ± 2 -5% stability of our already-existing (Coherent, Model 42) cw laser proved to be the source of most of the detrimental growth rate fluctuations that caused multiple phases to occur in the fibers. RF pulse-modulated lasers were found to have acceptable short term output power stabilities but were eliminated because most produced multi-mode rather than single TEM₀₀ mode outputs. (TEM₀₀ mode output is necessary to achieve the diffraction limited focusing necessary to the growth of fibers under 50 μ m diameter, which was one of our primary objectives.) Of all the commercial CO₂ lasers in production at the time, only one model, a dc-excited 25 watt cw CO₂ grating-stabilized sealed waveguide laser from Laser Photonics, Inc., seemed to offer the output power level and long term power stability we felt was necessary for the project. In autumn of 1989, the vendor was able to supply acceptable output recordings from engineering prototypes and a purchase order was placed. The first unit arrived in late 1989, but it did not meet specifications and was returned to the vendor. Production difficulties were then encountered, and several versions of this particular laser were obtained over the following 2-year interval for evaluation. In the end, none were acceptable and the order was canceled in late 1991.

A new search was initiated in late 1991. By this time, laser technology had advanced and a laser with superior specifications had become available from United Technologies Optical Systems (UTOS). This newer laser, a commercial version of a military rf-excited single-mode, single-frequency power-stabilized laser, offered twice the power output of the Laser Photonics unit. It was, however, also in a pre-production phase. A purchase order was placed in summer of 1992. Again, production difficulties were encountered by the manufacturer and a working version was not delivered until 8/30/93. The vendor soon afterward notified us that potential problems could arise due to excessive heating of the internal rf power supply, and the unit was returned in early May, 1994 for warranty repairs. With the rf power supply problem resolved, the laser was returned to Stanford on 5/17/94, two and one half years beyond the program's original ending date. Numerous no-cost program extensions had to be requested during that interval, since completion of much of the optical train and the vacuum system hinged on having the laser in hand and functioning. Little time and very few remaining funds were available, therefore, for completion and testing of the system. Furthermore, the bulk of our growth studies on BSCCO fibers ended in 1991 and the improved growth stability offered by this new laser could not be fully exploited for the growth of high T_c compounds.

Table 12 summarizes the UTOS laser specifications. We have had only limited experience with the laser and cannot verify its long term reliability. However, its short term stability appears to be better than its $\pm 0.25\%$ specifications and its power output is closer to 50 W than the 40 W specified according to tests performed by the vendor during its construction.

2. Optical train

As the UTOS laser output power is fixed at its maximum value, the variable IR waveplate/analyzer stage is used to control the power level delivered to the molten zone. Focusing onto the target is accomplished using the standard three piece diamond-turned copper reflexicon system (OFC Corporation) originally designed at Stanford. This unit produces a near-diffraction-limited line focus around the perimeter of the molten zone, as described in the research section of this report.

3. Mechanical systems

Optically encoded miniature dc servo-motors (Micro Mo, Inc.) are used for feeding and pulling to minimize fluctuations in instantaneous growth rate. High ratio gearheads are used to achieve the very slow feed and pull rates (on the order of 5 mm/hr) needed to grow single phase BSCCO fibers.

4. Optical monitoring and fiber diameter measurement

A long working distance, high resolution optical microscope (Wild Heerbrug) is relied on for process monitoring and for fiber diameter measurement using a high resolution CCD camera mounted on a beam-splitting side arm. An orthogonal view will be obtained by using an existing short working distance telescope and a second CCD camera. The system was originally designed to employ a frame grabber and a video analyzer card for quantitatively determining fiber diameters. These components were purposely not acquired early in the program since frame grabber technology was improving each year and its cost continues to decline. These components will be added later if follow-on funding can be obtained.

5. System configuration

The entire system is mounted on a pneumatically sprung vibration isolation table. Figures 42-49 illustrate various parts of the system in its current configuration. The only major component not yet completed (besides the video fiber diameter measuring system) is a vacuum/pressure chamber for controlling the atmosphere during growth. We

Table 12: United Technologies Optical Systems Model 40 CO₂ Laser

<u>SPECIFICATIONS/MODEL</u>	<u>LC40 - 37Z-CW</u>
Output power (Watts) at 10.6 Microns	40
Wavelength (Microns)	9.2-10.8*
Beam Diameter (mm) (1/e ²)	1.6
Beam Divergence (full angle) (mrad)	9.0
Polarization	Fixed Linear
Free Space Mode	TEM ₀₀
Gain Linewidth (FWHM) (MHz)	450
Cavity Length (cm)	112.9 Folded
Free Spectral Range (MHz)	132.7 MHz
Amplitude Stability (%)	.5 **
Input Power	28 vdc/1400 w
Excitation (Internal to pkg.)	R. F.
Cooling	Water 1.5 gal/min.
Beam Height (in.)	3.84
Dimensions (in.) Height	5.72
Width	5.75
Length	21.38
Weight (lbs.)	29
Fixed Grating (10.6 μ m line)	Yes
Automated Cavity Length Stabilizer	Yes
D. C. Power Supply	Lambda
Pulse Modulation	No

* The nominal operating wavelength is ten microns. Fixed rotational line operation requires a grating configuration.

** Required autonomous cavity length stabilizer. $\pm$ 4% for open loop power stability w/o grating.

Figure 42: Overall system configuration showing the optical table, control panel and operator station.

Figure 43: Operating station with process monitoring microscope and the local control panel which integrates all necessary control functions at the operator's fingertips.

(a)

(b)

Figure 44: Kinematically mounted modular focusing optics: a) heat-from-above configuration in which the fiber is pulled upward; and b) inverted heat-from-below configuration in which the fiber is pulled downward.

Figure 45: Beam steering optics breadboard which permits the laser to be removed from the system without loss of optical alignment.

Figure 46: Kinematically mounted periscope (foreground) raises the laser beam to the elevation of the reflexicon input port and adjusts depending on the orientation of the modular focusing optic package.

Figure 47: Feed / pull stages mounted on independent motor-driven x-y adjustable support posts. (Modular focusing optics removed for visibility.)

Figure 48: Feed / pull stage with capillary that supports feed stock / growing fibers.

Figure 49: Process monitoring microscope (Wild M-8) with beam splitter and CCD camera attached. This allows the operator to monitor the growth process on one of two video monitors. The other shows an orthogonal view which will be obtained by an existing close working-distance telescope / CCD camera (not shown).

decided to hold off on this component until we had grown a variety of compounds in fiber form and identified any unforeseen problems.

C. Current Status

Following the arrival of the laser, the second half of 1994 was devoted to completing the optical beam line and completing the motor and power control system. This task entailed only brief testing of the laser to ensure that it was operating and to verify the position of the beam relative to the optical table height. Once the optical train was completed, we began testing the variable waveplate/analyzer which was designed to attenuate the output beam to precisely controllable levels using a motor-driven rotary stage. Difficulties were encountered in obtaining stable laser output power, however, and during testing, the surface of one of the laser's internal cavity mirrors burned due to a manufacturing flaw. This required the laser to be sent back for repairs again. (Field repair of this laser is not possible because of its sealed waveguide design.) The manufacturer, UTOS, has in the meantime gone out of the laser business and we are now relying for service on DiMaria Electro-Optic Systems, Inc. (DEOS) which bought the manufacturing rights to the laser and is knowledgeable about its construction and service. As of the writing of this final technical report, the laser mirror has been replaced at DEOS and the unit is undergoing an extended full power test prior to being returned to Stanford. (Since this program's remaining funds have long since been expended, we have had to rely on another source of funds to cover the repair costs.)

The status of the LHPG system is that all of the mechanical components and control electronics have been completed to the point where we can grow test fibers. The vacuum chamber and the frame grabber/diameter control system components will have to be purchased using other resources. Our short term plans are to verify laser performance by growing test fibers when the unit is returned to Stanford. Completion of the advanced LHPG system will have to be postponed, however, until additional program support becomes available.

VII. OVERALL CONCLUSIONS

The major goal of this program was to explore the potential of the laser-heated pedestal (float zone) growth method for the preparation of flexible wires (fibers) of the new Bi-Sr-Ca-Cu oxide ceramic superconductors. This method, which involves drawing wires directly from a melt, allows precise control of the growth process through the control of melt composition, has led to the preparation of the first high quality single crystal samples of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ and the first demonstration of flexibility in a bulk oxide superconductor. During the course of this program a large number of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ superconducting fibers were grown under a variety of conditions. Optimal fibers had transition temperature onsets of 105 K, zero resistance at 85 K, and critical current densities of 40,000 amps/cm² at 68 K.

The critical issues which were studied included: 1) optimizing source and fiber composition to yield high quality crystals (homogeneous, single phase material) with improved superconducting properties, 2) understanding the relationships between processing parameters and material properties, 3) developing techniques for maximizing fiber throughput, 4) improve control of fiber diameter and length..

At the outset of this program, little was known about the phase relationships in this quaternary system except that the oxide superconductor appeared to be a peritectic compound. One of the features of the float zone method is that it allows the extraction of useful phase equilibria information by analyzing the segregation behavior occurring during the solidification experiments. We tested this hypothesis in our laser heated-pedestal growth system by crystallizing a similar (model) peritectic compound in the $\text{CaO-Al}_2\text{O}_3$ system for which the phase equilibria are well known. The results were compared with the Bi superconductor solidification data and from this we were able to reveal important features of the phase equilibria in our system, including the high and low temperature phases which appear under non-ideal conditions, the solid solubility range, the segregation behavior of the various components, and the maximum melting point composition. In addition to helping with the growth of high quality superconductor materials, this part of the program showed that the LHPG method can be an important tool for revealing useful thermodynamic information on complex systems.

The quality of the source material used for growth is vital if high quality fibers are to be grown. High density, completely reacted, homogeneous material is required. Much effort went into developing the appropriate starting powder particle size, particle size distribution, calcining temperature, pressing regimes, and sintering conditions. As a

result, we were able to prepare the highest quality polycrystalline $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ ceramic achieved to that time. Retrograde densification (density decreasing with temperature and time) was found to occur in this material due to changes in grain morphology.

Various starting material compositions were investigated and the resulting fiber compositions were compared with the limited literature data on ceramic samples and films. We were able to find a composition having the maximum melting temperature consistent with the growth of this compound. This was very important because it influenced compositional control (the preparation of single phase starting material) and permitted maximum growth rates.

Due to the peritectic nature of the Bi superconductor, growth takes place from solution. Crystallization velocities from solution are normally much slower than from pure melts due to the rejection of the solvent phase at the growth interface. One of our main goals was to find the maximum possible growth rate so as to increase fiber throughput. At the maximum melting composition, segregation is minimized and growth rates of high quality material can be higher. We also studied the relationship between growth rate, temperature gradient, and diameter. It was found that growth rates can be significantly increased by reducing fiber diameter. Nevertheless, the rates achievable under the best of conditions were only in the mm/hr range and, therefore, the growth of fibers even a few meters long (suitable for a small prototype motor winding, for example) would take many days.

Another strategy we explored for increasing fiber throughput was to grow at very high growth rates under unstable conditions. This led to aligned multiple nonsuperconducting phases. We found that with post-growth heat-treatment, we could re-form the superconducting phase by solid state reaction, and that the grain alignment was such as to optimize the critical current along the fiber axis. It is not known if fibers prepared in this manner will have superconducting properties as good as optimally grown material of the superconducting phase, and further studies may be justified in this area..

We designed and built an advanced fiber growth system to provide much enhanced stability during fiber growth of complex materials such as the oxide superconductors. The heart of this system is a state-of-the-art stable CO_2 laser heat source. One of the main problems with controlling the stability of the molten zones during fiber growth has been laser power fluctuations. These can lead to diameter variations, inclusions etc. Unfortunately, we experienced many delays in procuring the type of laser required, and we only just now are expecting a working system in house. So, the fiber growth station will not be tested until after this program has ended.

Nevertheless, this advanced system should allow us to make significant improvements in the quality of single crystal fibers of complex compounds, which will benefit materials research and future technologies.

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IX-A PUBLICATIONS

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IX-B. PARTICIPATING PERSONNEL

A. FACULTY AND STAFF

Position

R. S. Feigelson	Director, Advanced Materials Processing Lab Center for Materials Research Professor (Research), Materials Science & Engineering Department
R. K. Route	Senior Research Associate
R. C. DeMattei	Senior Research Associate
P. N. Peszkin	Scientific & Engineering Associate
M. Wolf	Scientific & Engineering Associate
R. J. Raymakers	Research Technician

B. GRADUATE STUDENTS

Department / Degrees Earned

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Z. Lu	MS&E / Ph.D. (1995)
L. V. Moulton	MS&E / Ph.D (1993)

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Institution

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