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Progress Report
on
**GROWTH OF HIGH T_c SUPERCONDUCTING FIBERS USING
A MINIATURIZED LASER-HEATED FLOAT ZONE PROCESS**
for the period
Contract No. DE-FG03-89ER-13987
November 6, 1990 through December 31, 1991

Submitted to
Division of Advanced Energy Projects
Office of Basic Energy Sciences
ER-16, GTN
Department of Energy
Washington, DC 20545
CMR-91-?

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December 1991

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.				
1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE 12/31/91	3. REPORT TYPE AND DATES COVERED Progress Report		
4. TITLE AND SUBTITLE Growth of High T_c Superconducting Fibers Using a Miniaturized Laser-Heated Float Zone Process		5. FUNDING NUMBERS DE-FG03-89ER13987		
6. AUTHOR(S) Robert S. Feigelson (Principal Investigator) Roger K. Route Robert C. DeMattei				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Center for Materials Research Stanford University Stanford, CA 94305-4045		8. PERFORMING ORGANIZATION REPORT NUMBER CMR-91-1 SPO 6462		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Basic Energy Sciences, ER-16 Department of Energy Germantown, MD 20545		10. SPONSORING/MONITORING AGENCY REPORT NUMBER FTR		
11. SUPPLEMENTARY NOTES The view, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of position, policy, or decision, unless so designated by other documentation.				
12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited.		12b. DISTRIBUTION CODE		
13. ABSTRACT (Maximum 200 words) <p>This report summarizes the progress made on the project "Growth of High T_c Superconducting Fibers Using a Miniaturized Laser-Heated Float Zone Process" during the 14 month period from Nov. 6, 1990 to Dec. 31, 1991. The studies during this period focused primarily on phase diagram studies, phase relations in the calcium aluminate system and on $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ (BSCCO). Some work was also done on the Advanced Fiber Growing Station.</p> <p>Because of the complicated phase relationships found in the incongruently melting BSCCO system, the incongruently melting $\text{Ca}_3\text{Al}_2\text{O}_6$ phase of the calcium oxide-aluminum oxide system was studied as a model material. The data obtained was in agreement with well known solidification theory. Fibers grown from calcium oxide rich sources contained calcium oxide nodules which transported from the melting source interface to the growth interface, while those grown from aluminum oxide rich sources contained continuous inclusions of a divorced eutectic. The melt compositions were also found to follow theoretical predictions. The agreement of this data with the phase diagram and solidification theory demonstrates that phase equilibrium information can be extracted from fiber growth experiments.</p> <p>BSCCO feed rods were made from 12 different compositions. Fibers were grown from these rods and the melts were abruptly quenched which preserves the as-grown 2212 fiber, a glassy frozen melt and the source. A future study of these sections will reveal the phase relationships that exist in the BSCCO system. Melt temperature gradients of 500-1000°C/cm were measured near the interface in these experiments.</p> <p>During this reporting period, work continued on the mechanical components of the Advanced Fiber Growth Station.</p>				
14. SUBJECT TERMS High T_c Superconductors, BSCCO, BiSrCaCuO , Superconducting Fibers/Ceramics, LHPG High T_c . Phase Equilibria		15. NUMBER OF PAGES 48		
		16. PRICE CODE		
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT UL	

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GROWTH OF HIGH T_c SUPERCONDUCTING FIBERS USING A MINIATURIZED LASER-HEATED FLOAT ZONE PROCESS

I. INTRODUCTION

The primary objective of this three-year 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 have, since their recent discovery, excited the imagination and interest of scientists world-wide, and important applications have been envisaged. It is not surprising, however, that many important questions have arisen concerning their suitability for certain applications. These include not only whether they have the properties required, but also whether economical, effective processing techniques can be developed. Extensive efforts to produce both thin films and wires are underway in many laboratories, the former for electronic devices and the latter for motor, magnet and power transmission applications.

This program has concentrated on one of the new types of high T_c copper oxide based superconductors $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$. It exhibits high transition temperatures and high critical currents and also has better thermodynamic properties (low volatility in particular) compared with other superconducting materials. This superconductor has become one of the most attractive materials for superconducting wire applications.

Most of the current activities to develop wires of the new high T_c superconductors have concentrated on polycrystalline ceramic samples. Most of these efforts have yielded grains with random crystallographic orientations and intergranular barriers between the grains which have limited critical current densities to much less than the highest values which can be obtained with single crystal samples. While numerous, relatively inexpensive ceramic processing techniques are currently under study for making long lengths of polycrystalline superconducting wires which can carry high currents, the ability to overcome the above problem has not yet been totally successful. Grains which can be continuously aligned so that the appropriate current carrying planes are directed along the wire axis (c-axis normal), or single crystal wires will eliminate these "weak links" (grain boundaries) mentioned above and one of the newest ceramic techniques, the extrusion of powder in silver tubes, seem very promising.

II. BACKGROUND ON LHPG GROWTH

Preliminary experiments (1,2) carried out during the last few years on the growth of the Bi containing superconductors using the LHPG method have yielded very encouraging results, including fibers with transition temperature onsets of 105° K, zero resistance at 85° K, minimum critical current densities of 40,000 amps/cm² at 68° K and flexibility in fibers 100 mm in diameter or smaller. These fibers, having the nominal composition Bi₂Sr₂CaCu₂O₈ (2212), have an oriented grain structure with the current carrying planes parallel to the fiber axis and superior properties compared to wires produced by ceramic processing techniques. At slower growth rates single crystal fibers can be produced which do not exhibit intergranular barriers that can impede current flow.

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 the fibers grown by the laser-heated float-zone growth method have been shown to possess excellent superconducting properties, an important concern is whether these fibers can be made in long lengths and small diameters (to 25 mm). To date we have grown them up to 14 cm in length (100 mm diameter). The prospects look very good for dramatically increasing the lengths of even the smallest diameter fibers with appropriate modifications to the LHPG equipment and growth technique.

Critical issues which are being considered during the course of this program include, 1) the most appropriate compositions which can yield long lengths of uniform structure and composition with high superconducting transition temperature, T_c , and 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 and the growth of many fibers simultaneously.

Results during the period January 15, 1989 to November 5, 1990 are summarized in Progress Reports CMR 89-3 dated April 1989, and CMR 90-8 dated November 1990

III. PROGRESS TO DATE

During the 12 month period covered by this report the emphasis has been focused on developing strategies for increasing the growth velocity of single phase fibers while maintaining the excellent superconducting properties already demonstrated. This has necessitated our 1) Obtaining more information concerning the phase relationships in the Bi-Sr-Ca-Cu-O system, 2) improving the quality of the ceramic starting materials used for fiber growth, 3) reducing fiber diameter and 4) the set-up of the new advanced fiber growth system.

A. Phase Diagram Studies

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. To facilitate our knowledge of the LHPG solidification of incongruently melting materials such as the BSCCO superconductor, we chose to study the relevance of kinetic effects on the phase equilibria using a simpler model system. The well-known $\text{CaO-Al}_2\text{O}_3$ system chosen.

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 are being used in this study.

1. Solid-state reactions

The various compounds which make up a new materials system are often identified using solid-state reaction methods. [3] 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. [4] 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. [5,6] 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. Phase Relations in the $\text{CaO-Al}_2\text{O}_3$ System

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 as a model system 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 CaO-Al₂O₃ phase equilibria. Because of the relative simplicity of this technique, and the well-understood phase relations in the CaO-Al₂O₃ 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.

1. Sample Preparation

Calcium aluminate source material was synthesized from powders of CaCO₃ (Cerac 99.98%) and Al₂O₃ (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 Ca₃Al₂O₆ powder.

Two Ca₃Al₂O₆ compositions were studied: the first was ~5% CaO-rich, while the second was ~5% Al₂O₃-rich. Preparation of starting material with the exact Ca₃Al₂O₆ 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 Ca₃Al₂O₆ 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 Ca₃Al₂O₆ 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 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.

2. 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 1.

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.

3. 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 mm 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. [7] 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. [7] The three different types of atmospheres used in the growth chamber were created by

Figure 1. Early stages in sample crystallization by the LHPG technique: a) creation of the molten zone on top of the source rod, b) early stage of sample crystallization and c) later stage of sample growth.

flowing various gases at 5 cfh (1 ft³ 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. [6] 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 Ca₃Al₂O₆, 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.

4. Post-Growth Sample Analysis

The geometry and compositional profiles of the samples produced were analyzed using wavelength dispersive spectroscopy (WDS). WDS analysis, using a JEOL 733 Scanning Electron Microscope, was used to evaluate both the phase content and the compositional profiles in the Ca aluminate samples as well as the 2212 crystalline material, quenched melts, source rods. The chemical compositions of various 10 micron diameter regions were obtained using electrons accelerated with 15 kV. Standardization was performed using, wollastonite (CaSiO₃), kyanite (Al₂SiO₅) metallic bismuth and copper, and strontium titanate (SrTiO₃) 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). A complication in the study of the Ca aluminates was the increased difficulty of forming glasses from CaO-Al₂O₃ 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 μm 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 μm 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.

5. Crystallization Studies

The liquidus curve defining the $\text{Ca}_3\text{Al}_2\text{O}_6 + \text{L}$ phase fields lies between 1363 and 1544°C. [7] 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 resulting "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 $\text{CaO-Al}_2\text{O}_3$ binary system has been the subject of previous research by several groups. Their findings have been summarized by Hallstedt. [7] The phase equilibria pertinent to the melt growth of $\text{Ca}_3\text{Al}_2\text{O}_6$ are summarized in Figures 2 and 3. 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 3 have been slightly shifted to accommodate the compound $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ (or $12 \text{ CaO} \cdot 7 \text{ Al}_2\text{O}_3$), which is only stable in the presence of water vapor. [7] 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 2), 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 3), 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

Dry Atmosphere Phase Diagram:

Figure 2: Portion of CaO-Al₂O₃ binary phase diagram which describes the crystallization of Ca₃Al₂O₆ in a dry environment. Constructed from information in [7].

Wet Atmosphere Phase Diagram:

Figure 3: Portion of CaO-Al₂O₃ binary phase diagram which describes the crystallization of Ca₃Al₂O₆ in an environment which contains water vapor. Constructed from information in [7].

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 2, 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 $<500\text{ }\mu\text{m}$ 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 ($\sim 100\text{ mm}$) 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 4 and 5 are SEM micrographs of a CaO-rich and an Al_2O_3 -rich sample, respectively. In Figure 4, the light-colored CaO inclusions (nodules) extended into the melt, beyond both solid/melt interfaces (melting and freezing).

Figure 5 shows the faceting of $\text{Ca}_3\text{Al}_2\text{O}_6$ grains during their growth from a Al_2O_3 -rich melt. This micrograph also illustrates the separation of the $\text{Ca}_3\text{Al}_2\text{O}_6$ grains by Al_2O_3 -rich inclusions once solidification was complete. In quenched samples, the Al_2O_3 -rich inclusions solidify at the tips of v-shaped grooves. These grooves were formed in the region where the crystal facets meet the $\text{Ca}_3\text{Al}_2\text{O}_6$ grain boundaries.

(3.) Compositional profiles of quenched samples

Most Al_2O_3 -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 5). Consequently, the compositional gradients in the quenched melt could easily be observed directly from variations in the gray levels in the photomicrographs.

Figure 4: SEM micrograph of internal sample cross section, revealing the morphological features of a molten zone quenched during the crystallization of CaO-rich $\text{Ca}_3\text{Al}_2\text{O}_6$ sample.

Figure 5 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.

A perceptible darkening of the melt adjacent to the $\text{Ca}_3\text{Al}_2\text{O}_6$ grains, and particularly at the mouth of the grooves, is apparent. In general, such darkening in the back-scattered electron image indicates Al_2O_3 -enrichment. Microprobe measurements have confirmed that the darker regions of the quenched melts, were also richer in Al_2O_3 .

Figures 6 and 7 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 6 demonstrates that nonplanar growth results in lateral segregation of Al_2O_3 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 7 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 Al_2O_3 -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 which increases with decreased growth rate. This can be seen from the data in Table 1, which gives the averaged bulk melt compositions (C_{LB} values) for each growth rate and starting material composition tested.

Table 1 also gives calculated values for the effective segregation coefficient $k_{\text{eff}} = C_{\text{S}}/C_{\text{LB}}$ 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

Figure 6: 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.

greater interest, as this is the composition which corresponds to the liquidus during near-equilibrium growth.

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

Table 1: Variation on Solute Segregation with Growth Rate

Growth Rate (mm/hr)	Bulk Melt Composition (mole % Al_2O_3)		$k_{eff} = C_S/C_{LB}$	
	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 7: 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).

melting material. The second method was used in the 2212 crystallization studies to avoid the increased complexity of four component segregation.

(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 discernible 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 2 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 3 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 modeled by balancing the rate of lateral solute segregation with the rate at which solute is generated by the advancing crystallization front. [8] 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. [9] 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:

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

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 8. 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 2. The agreement was found to be excellent, when compared to the experimental error in the composition measurements.

c. 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.

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

Table 2: 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 8: BPS plot of experimental composition values from both CaO-rich and Al₂O₃-rich samples.

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 traveled on strong convective currents created by the Marangoni effect within the molten zone. 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.

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

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.

1. Starting material

The source rods initially used in the LHPG apparatus were square, ceramic rods with a 1 x 1 mm (1000 x 1000 mm) cross-section. For this source rod

size, starting materials with inhomogeneities of <50 mm diameter were found to support relatively stable zones. Starting material which contained inhomogeneities >250 mm diameter, on the other hand, were found to sporadically disrupt the growth process. Substantial care was required, therefore, to form relatively dense 2212 ceramic specimens which did not contain inhomogeneities greater than 100 mm in diameter.

The starting material for 2212 growths was most easily produced by a solid-state reaction of powdered oxides and carbonates. 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 3. 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].

Table 3: Compositions of Starting Materials

Starting Material	Composition (Bi: Sr: Ca: Cu)				(Ca:Sr)
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

The solid/melt interface formed from composition V, as seen in Figure 9(c), is shown at greater magnification in Figure 10. 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.

2 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 ~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

a)

b)

c)

Figure 9. Scanning electron micrographs of quenched molten oxide droplets on ceramic 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 the sample growth.

Figure 10. Higher magnification of the complex solid/melt interface in Figure 9c).

the composition of the source rod used. It was, however, always relatively fine-grained (maximum grain size $<50\text{ }\mu\text{m}$) 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 ($20 \times 2 \times 2\text{ mm}$) ceramic rods of composition Q were cut and rapidly recrystallized (24 mm/hr) by LHPG melting into large diameter ($\sim 1.8\text{ mm}$) 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, $\sim 500\text{ mm}$ 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 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 $5\text{--}7\text{ mm}$ before extended multiphase growth took over.

3. Fiber growth

All of the 2212 compositions described above (Table 3) 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 labeled A and B in Table 3 were measured by Lu. [13] 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.

4. 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). [14] 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 500-1000°C/mm.

5. Phase Relationships in the $\text{Bi}_2\text{O}_3\text{-SrO-CaO-CuO}$ System

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 currently being studied by comparison with the Ca aluminate results discussed above. We have begun by making a study and 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 variation in segregation coefficient of the various components in the superconductor with crystal composition will be evaluated.

IV. ADVANCED FIBER GROWTH STATION

A. History and Background

One of our program goals was to prepare long lengths (> 100 mm) of small diameter (< 100 μ m) superconducting fibers under very stable (controlled) growth conditions. Our existing LHPG system was not ideally suited for this application. This fiber growth equipment was originally conceived as a versatile system for exploring a wide variety of materials ranging from 20 mm to 2 mm in diameter. Numerous minor modifications and improvements to its optical and mechanical components were made 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 thought it was important to build a entirely new, more advanced system. One of the major objectives of this program became, therefore, the design and construction of a dedicated fiber growth system capable of routine preparation of 10-50 mm 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.

During the first year of this program studies were undertaken to clarify design concepts and draft a preliminary design. During the second year the final design was generated and a thorough evaluation of the two most critical system components, the cw CO₂ heating laser and the precision translation stages, were carried out. During this period a number of components were ordered.

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. 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 late this year.

B. Current Progress

A search for a new laser source was initiated during this reporting period. We found that the laser technology had advanced since we began this activity and a laser with superior specifications has 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. Table 4 summarizes the UTOS laser specifications. It is, however, also in a pre-production phase but we plan to place an order early in 1992. Since this phase of the program work will not be completed by the original end date of this program, Jan 14, 1992, we have requested a no-cost extension for an additional year.

As the UTOS laser output power is fixed at its maximum value, a variable IR waveplate/analyzer stage will be used to control the power level delivered to the molten zone. Focusing onto the target will be 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.

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

A long working distance, high resolution optical microscope (Wild Heerbrug) will be relied on for process monitoring and for fiber diameter

Table 4: 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 μm 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. ± 4% for open loop power stability w/o grating.

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 entire system will be mounted on a pneumatically sprung vibration isolation table. Figures 11-12 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.

Figure 11. Feed/pull stage with capillary that supports feed stock/growing fibers.

a)

b)

Figure 12. 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.

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VI. APPENDIX

1991 Publications

Processing of $\text{Bi}_{2.1}\text{Sr}_{1.8}\text{Ca}_{1.1}\text{Cu}_2\text{O}_8$ source material for float-zone fiber growth

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(Received 19 February 1991; accepted 24 June 1991)

$\text{Bi}_{2.1}\text{Sr}_{1.8}\text{Ca}_{1.1}\text{Cu}_2\text{O}_8$ fibers having excellent superconducting properties can be grown by a laser-heated float zone process. In order to maintain stable growth conditions and thereby obtain fibers free of diameter fluctuations and voids, dense ceramic starting material containing only the 2212 phase is required. In this study various processing parameters, including calcining and sintering temperatures and times, grain size of the powders used, and pressing pressures were optimized to yield dense, chemically homogeneous starting material. It was found that under most conditions there was no increase in the density on sintering. Retrograde densification was the usual situation except at higher pressures and was found to depend on pressing pressure, calcination history, and sintering temperature. Cold-pressing at higher pressures (100 000 psi) yielded denser but chemically inhomogeneous material. Ceramic samples sintered for long times (>48 h) yielded source rods that produced instabilities during fiber growth, presumably due to preferential loss of mass during sintering.

I. INTRODUCTION

A laser-heated miniaturized float zone technique has been shown to be a useful technique for growing superconducting Bi-Sr-Ca-Cu-O fibers.^{1,2} This technique produces grains aligned along the fiber axis and with the c-axis oriented normal to the growth direction. The Cu-O planes therefore are ideally oriented for electrical conduction along the fiber. One of our primary goals has been the growth of long lengths of small, constant diameter ($\sim 30\text{ }\mu\text{m}$) fibers of $\text{Bi}_{2.1}\text{Sr}_{1.8}\text{Ca}_{1.1}\text{Cu}_2\text{O}_8$, at high growth rates. In order to prepare such fibers, starting material with compositional and dimensional uniformity is needed.

Recent work by Ono³ suggested that single phase 2212 ceramic samples can be prepared only from compositions containing bismuth in excess of the stoichiometric amount. This extra Bi presumably goes onto the alkaline earth sites replacing strontium or calcium [$\text{Bi}_2(\text{Bi}, \text{Sr}, \text{Ca})_2\text{Cu}_2\text{O}_8$]. The single phase region is also affected by the Ca/Sr ratio. Based on Ono's work, Moulton *et al.*⁴ were able to produce more uniform source material and thereby fibers with more uniform diameter and composition than those grown from the stoichiometric 2212 starting composition. When using small diameter source rods, as required for the growth of small diameter fibers, major growth instabilities can occur due to the presence of a nonuniform distribution of second phase particles and gaseous inclusions (porosity).⁴

This paper discusses the effect of various processing parameters on the composition, density, and micro-

structure of $\text{Bi}_{2.1}\text{Sr}_{1.8}\text{Ca}_{1.1}\text{Cu}_2\text{O}_8$ starting material to be used for float-zone fiber growth. The goal was to determine the optimum processing conditions (including calcining and sintering temperatures and times, grain size, and pressing pressures) necessary to achieve dense and chemically homogeneous starting material.

II. EXPERIMENTAL

Figure 1 depicts a flow chart of the best (though laborious) processing steps and conditions found in this study. Attempts to shorten the procedure were not successful. Control of the particle size at each step of the process was achieved by sieving the powders through a 325 mesh ($44\text{ }\mu\text{m}$) screen. Ceramic samples with nominal composition $\text{Bi}_{2.1}\text{Sr}_{1.8}\text{Ca}_{1.1}\text{Cu}_2\text{O}_8$ were made using Bi_2O_3 , SrCO_3 , CaCO_3 , and CuO powders. All raw materials were supplied by the Johnson-Matthey Company and were 99.999% pure. The individual oxides were ground in an agate mortar and pestle and sieved. These oxides were weighed out, carefully mixed together, and then subjected to a three-step calcining procedure in air (using alumina crucibles), first at $760\text{ }^\circ\text{C}$ for 48 h, then $800\text{ }^\circ\text{C}$ for 48 h, and finally $840\text{ }^\circ\text{C}$ for 48 h. The samples were reground and sieved before and after each step. After calcining, the samples were ground, sieved, and uniaxially cold-pressed into round pellets at gauge pressures in the range of 5000 to 100 000 psi. Time at maximum pressure was approximately 3 min. The pressing was accomplished using a Carver press and two steel dies, one of 31.7 mm I.D. (5000 psi to

FIG. 1. Flow chart for standard processing procedure.

approximately 15 g for the larger die and 5 g for the smaller one. In order to minimize powder flow and die sticking, the dies were carefully lubricated with a very thin layer of WD-40 oil. After pressing, the green (presintered) densities of the resultant pellets were determined by measuring the diameter, thickness, and weight. These pellets were then sintered for two days at 860 °C in an air atmosphere. The sintered samples were reground, sieved, repressed, and sintered once more under the same conditions. The pellets were sintered on zirconia disks in a horizontal tube furnace.

Polished samples were examined by scanning electron microscopy (SEM) and energy dispersive analysis (EDS) to determine microstructure and phase composition. X-ray diffraction and thermogravimetric analyses (TGA) were also performed on selected samples. The ultimate test, however, was how well these samples performed as source rods during fiber growth. After sintering, the pellets were mounted onto graphite plates with wax and cut, using kerosene as a lubricant, into square cross section rods $1 \times 1 \text{ mm}^2$ and approximately 30 mm long. Acetone was used to dissolve the wax after completion of the cutting. The source rods were then baked at 150 °C for 24 h. Finally, starting material for fiber growth was prepared from these source rods using the float-zone technique⁴ with a growth rate of 30 mm/h. and a source rod to fiber diameter ratio of 2:1.

III. RESULTS

A. Calcining

Calcining conditions were optimized, as described in Fig. 1, to yield nearly completely reacted powders. This in turn gave us less gas entrapment in the final starting material.

Partial powder melting during the calcining step had a significant effect on the quality of the final product. First, it made powders difficult to remove from the alumina crucibles, leading to contamination and the formation of Al-rich phases. Second, unwanted phases crystallize from the melt because of the incongruent melting behavior of this compound, and the presence of these phases complicates the sintering process. Grinding and sieving operations were also adversely affected. The inhomogeneous nature of the powders caused mass-loss during handling, thereby changing the initial composition. In order to avoid partial melting, the firing temperature was lowered from 770 °C to 760 °C, and the calcining time was increased to 48 h.

Maric *et al.*³ reported that by first decomposing CaCO_3 and SrCO_3 to SrO and CaO , respectively, at 1250 °C, carbon impurities would be eliminated and the formation of Bi-rich liquid phase minimized. Using this procedure as a first step (followed by the usual fabrication routine) led to samples that showed

24 000 psi range), and the other 13 mm I.D. (24 000 psi to 100 000 psi range). The amount of powder used was

the presence of CuO inclusions (particle size greater than $100\text{ }\mu\text{m}$).

The particle size of the calcined powder greatly affected the final grain structure in the ceramic samples. This variable will be discussed later.

B. Influence of pressing pressure

Figure 2 shows the green density and densities after the first and second sintering as a function of pressing pressure. As can be seen, the densities after the first sintering were always smaller than their respective green densities for all pressures studied. The densities after the second sintering (particularly at lower pressing pressures) were also smaller than the green densities. At higher pressing pressures, however, the final densities were the same as the green densities. The best density achieved in this study was $\sim 5.5\text{ g/cm}^3$ for a multiphase sample and 4.5 g/cm^3 for single phase material. The calculated theoretical value is 6.62 g/cm^3 .⁵ Under most conditions there was no increase in the density on sintering, contrary to the usual situation in ceramic processing. In fact, retrograde densification was the usual situation for this material except at higher pressing pressures. This was also observed by Johnson and Rhodes⁶ for the stoichiometric 2212 composition. They attributed this phenomenon to the formation of thin plate-like crystallites that grow in a randomly oriented fashion and push the structure apart. Figure 3 shows the typical morphology of a sample that had undergone retrograde densification. Plate-like crystals are clearly

FIG. 2. Green density, density after 1st sintering, and density after 2nd sintering versus pressing pressure.

FIG. 3. Typical SEM microstructure of sample that experienced retrograde densification.

present, in accordance with Johnson's⁶ results. In Fig. 4, the microstructures found for samples sintered after being pressed at different pressures are shown. The structures are open and plate-like at lower pressures with only one phase present (the 2212 superconducting phase).

At 100 000 psi, a small amount of $\text{Sr}_{0.15}\text{Ca}_{0.85}\text{CuO}_2$ was found in the sample. This phase was not detectable by powder x-ray diffractometry. Schultze *et al.*⁷ have studied phase equilibria in the system $\text{Bi}_2\text{O}_3\text{--SrO--CaO--CuO}$ at $850\text{ }^\circ\text{C}$. They found that $\text{Sr}_{0.15}\text{Ca}_{0.85}\text{CuO}_2$ is in equilibrium with the 2212 superconducting phase at that temperature (which is close to our sintering temperature of $860\text{ }^\circ\text{C}$). It is not clear whether pressure has an influence on second-phase formation, or whether porosity obscures the second phases in samples pressed at lower pressures. Fiber growth from this multiphase source material was unstable, whereas stable growth conditions prevailed with source material pressed in the 20 000–24 000 psi range (single phase, according to EDS).

The particle size of the powders used during the calcining process was found to have a significant effect on the final microstructure of sintered specimens. As indicated earlier, the normal calcining procedure involved grinding and sieving the powders to a particle size of $\sim 44\text{ }\mu\text{m}$ (325 mesh). One calcining experiment was performed using powders with a particle size as large as $50\text{ }\mu\text{m}$ (passed through a 200 mesh screen), with the hope of reducing the processing time. After the three-step calcining procedure, the powders were sieved through a 325 mesh screen for cold-pressing and sintering according to the procedure described in Fig. 1. This resulted in a lower density and an unusual open grain structure after the first sintering step compared with source material prepared following the standard

FIG. 4. Microstructures achieved at the end of ceramic processing as shown by SEM, for different cold-pressing pressures: (a) 10 000 psi ($\rho = 3.65 \text{ g/cm}^3$), (b) 15 000 psi ($\rho = 3.87 \text{ g/cm}^3$), (c) 24 000 psi ($\rho = 4.3 \text{ g/cm}^3$), and (d) 100 000 psi ($\rho = 5.62 \text{ g/cm}^3$).

procedure. Densities achieved after the second sintering were similar to those obtained by the standard procedure, although the grain structure was quite different.

Figure 5 shows the microstructure found after the first and second sintering of samples prepared: (1) following the standard procedure (see Fig. 1), and (2) using a larger particle size during the calcining step (both samples were pressed at 24 000 psi). The sample prepared following the standard procedure was single phase, while that with larger particle size contained $\text{Sr}_{0.15}\text{Ca}_{0.85}\text{CuO}_2$. As expected, fiber growth from this multiphase source material did not produce good results.

C. Sintering temperature

The influence of sintering temperature on densification was investigated (see Table I). When the sintering temperature was reduced from 860 °C to 840 °C, retro-

grade densification was drastically reduced. Figure 6 shows the microstructure obtained after the first sintering. It can be seen that the sample has a dense microstructure with some $\text{Sr}_{0.15}\text{Ca}_{0.85}\text{CuO}_2$ inclusions—not the open plate-like structure formed at the higher sintering temperature. Retrograde densification found after sintering at 860 °C might be due to $\text{Sr}_{0.15}\text{Ca}_{0.85}\text{CuO}_2$ particles reacting with the matrix phase to enhance grain growth. This seems plausible since materials prepared by the standard fabrication procedure (as shown in Fig. 1) experience most of the density reduction during the first sintering step (at 860 °C), presumably due to the reaction between the second phase (formed at 840 °C during calcining) and the matrix. Once the material was reground, repressed, and sintered for the second time (at 860 °C) the retrograde densification phenomenon was drastically reduced.

FIG. 5. Microstructures after the first and second sintering of samples prepared (1) following standard procedure and (2) using bigger particle size during calcination: (a) first sintering ($\rho = 4.24 \text{ g/cm}^3$), (b) second sintering ($\rho = 4.3 \text{ g/cm}^3$), (c) first sintering ($\rho = 3.2 \text{ g/cm}^3$), and (d) second sintering ($\rho = 4.1 \text{ g/cm}^3$).

D. Sintering time

Samples were processed at 840°C and 860°C and annealed for up to 168 h to study the relationship between

density and sintering time. Figure 7 shows density versus sintering time (after the second sintering step). It can clearly be seen from this figure that the material does not densify with increasing sintering time. In fact, there is a slight trend for the density to decrease with longer annealing times. This is consistent with the grain growth postulate of Johnson and Rhodes.⁹

Long-term sintered materials (>48 h) yielded source rods that led to instabilities during fiber growth, even though x-ray and SEM results showed little compositional or structural differences when compared to short-term sintered samples (except for a larger grain size in the long-term annealed samples). Preliminary thermogravimetric studies revealed that short-term sintered samples behaved differently than the long-term annealed samples, losing weight incongruently. Maric *et al.*⁸ also

TABLE I. Influence of sintering temperature on densification of calcined powders.

Sample	Sintering step	Sintering temp. ($^\circ\text{C}$)	Green density (g/cm^3)	Sintered density (g/cm^3)	Δ (%)
#1	1	840°	4.58	4.30	6
	2	840°	4.40	4.30	2
#2 ^a	1	860°	4.59	3.89	15
	2	860°	4.46	4.39	1.5

^aRepresentative result for the standard procedure (Fig. 1).

FIG. 6. Microstructures achieved after first sintering of sample sintered at 840 °C.

found that 2212 ceramic samples subjected to long-term annealing at 870 °C experienced a phase separation and deterioration of the superconducting properties at 77 K.

IV. DISCUSSION

As stated earlier, the ultimate measure of starting material quality is how it performs during fiber growth. Bubble formation in the melt during growth is the most obvious manifestation of poor quality source material (Fig. 8). These bubbles can easily be seen to originate at the melting interface and then travel through the zone to the growth interface where they cause the molten zone to become inflated. These bubbles often are incorporated into the fiber, causing large diameter fluctuations (about

FIG. 7. Density after second sintering versus sintering time.

FIG. 8. Bubble formation in the melt during growth from a "poor" quality source material.

50%). Better source rod material produced fewer, smaller bubbles which disappear before reaching the freezing interface. Figure 9 depicts the typical morphology of a

FIG. 9. Fiber grown from (a) "poor" source materials and (b) "good" source material.

fiber grown from (a) a "poor" quality source material and (b) a "good" source material. It can clearly be seen that the better source material provides stable growth conditions, and fibers grown from them had excellent diameter uniformity without automatic diameter control.

Two parameters were used to characterize the quality of the starting materials. One was the relative diameter fluctuation $\delta d/d_0$, where

$$\delta d = \frac{1}{N} \sqrt{\sum_{i=1}^N (d_i - d_0)^2}$$

$$d_0 = d_s \sqrt{\frac{V_s}{V_f}} \sqrt{\frac{D_s}{D_f} \left(1 - \frac{m_e}{M}\right)}$$

and d_i is the measured fiber diameter at the i th position, N the number of measuring points, d_s the diameter of the source rod, V_s , V_f , D_s , and D_f the feeding and pulling rates and the densities of the source rod and fiber respectively, M the mass fed into the molten zone per unit time, and m_e the mass evaporating from the molten zone per unit time. The term d_0 can be obtained from mass conservation equations and can also be measured experimentally by measuring the diameter at the beginning of the growth when there are few bubbles which do not disturb the fiber diameter. The value $\delta d/d_0$ is a property of the material being studied. For instance, for fibers that exhibit good diameter uniformity such as sapphire, $\delta d/d_0 < 5\%$. This value is significantly lower than those so far obtained in 2212 superconductor fiber-growth experiments. Values of $\delta d/d_0$ for these experiments were between 9% for very good samples and 16% for very bad ones. Larger $\delta d/d_0$ values mean more bubbles accumulated in one accumulating event.

Another parameter which can be used to give some measure of quality of the starting materials is the frequency of the diameter fluctuations expressed as $1/\lambda$, where

$$\lambda = \frac{\sum_{i=1}^N \lambda_i}{N}$$

and λ_i is the length between maxima in the fiber diameter. For the same $\delta d/d_0$, larger $1/\lambda$ indicates that bubble accumulation must be occurring more frequently. Values for $1/\lambda$ were between 0.18 and 0.48 mm^{-1} .

V. CONCLUSIONS

The specific processing parameters necessary for fabricating relatively dense and chemically homogeneous $\text{Bi}_{2.1}\text{Sr}_{1.8}\text{Ca}_{1.1}\text{Cu}_2\text{O}_8$ starting material for laser-heated float zone fiber growth were determined. Careful control of purity, powder particle size, pressing conditions, and both sintering and calcining procedures

is vital. Partial melting during the calcining process should be avoided in order to prevent preferential loss of components during handling and the formation of unwanted phases in the final product.

It was found that under most conditions there was no increase in the density on sintering. Retrograde densification is the usual situation except at higher pressures. Excessive reduction in density during the first sintering step should be avoided since it can lead to the formation of second-phase particles ($\text{Sr}_{0.15}\text{Ca}_{0.85}\text{CuO}_2$ or CuO) in the final product. The retrograde densification phenomenon was found to depend on pressing pressure, calcining history (i.e., particle size and the way carbonates were reacted), and sintering temperature. Plate-like structures were observed as a result of this phenomenon, in accordance with previous results reported in the literature.⁶ Materials sintered for a relatively long time (>48 h) produced source rods that led to instabilities during fiber growth.

The best fabrication conditions for preparing relatively dense (i.e., 4.5 g/cm^3 density value) single-phase starting material for fiber growth included the following: (1) use of a three-step calcining procedure at increasing temperatures of (a) 760 °C, (b) 800 °C, and (c) 840 °C, respectively; a soak time for each step of 48 h with intermediate grinding and sieving through a 325 mesh screen; (2) cold-pressing this calcined powder at 24 000 psi and sintering at 860 °C for two days. The latter step is repeated with intermediate grinding and sieving.

ACKNOWLEDGMENTS

The authors thank Dr. Roger K. Route, Stanford University, for helpful discussions. This work was supported by the Department of Energy, Contract No. DE-FG03-89ER13987, and the NSF-MRL Program through the Center for Materials Research at Stanford University.

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