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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
January 1, 1993 through December 31, 1993

Submitted to
Division of Advanced Energy Projects
Office of Basic Energy Sciences
ER-16, GTN
Department of Energy
Washington, DC 20545
CMR-93-1

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December 1993

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REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
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1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE Dec. 31, 1993	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-FG03-89ER-13987		
6. AUTHOR(S) Robert S. Feigelson 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-92-1 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) This report covers the research done on "Growth of High T_c Superconducting Fibers using a Miniaturized Laser-Heated Float Zone Process" during the 12 months from Jan. 1, 1993 until Dec. 31, 1993. The effort during this period were directed into two areas; the influence of growth conditions on the properties of the superconducting fibers and the construction of the advanced fiber growth station. In the first area of emphasis, studies were done on constitutional super cooling effect, the influence of processing parameters on T_c , the correlation between T_c and growth parameters and the mechanical properties of 2212 fibers. These studies showed that there are two types of interfacial breakdowns; one type that involves low temperature inclusions caused by excessive solute buildup and another involving high temperature inclusions which require two conditions to be met. These conditions are: 1) significant compositional gradients in the melt and 2) an interface melt temperature near the peritectic decomposition temperature. Analysis of the experimental data lead to the hypothesis that fibers with the highest crystallinity are grown from SrO-rich 2212 melts. Evaluation of the constitutional supercooling responsible for the high temperature inclusions suggested that growth under these conditions was most vulnerable to disruption by HT inclusions. T_c increased with growth temperature for as-grown fibers. The concentration of SrO in the fibers had a parabolic relationship with temperature. The same parabolic relationship was observed between composition and T_c . The thermal history of 2212 crystals has been shown to influence their oxygen content which played a significant role in determining their T_c 's. Fiber heat treatment and the ambient gaseous atmosphere were found to dominate the T_c variations measured in this study. Super conducting fibers of less than 100 μ m in diameter are quite flexible. A 90 μ m 2212 fiber was bent to a 5cm radius. Delaminations parallel to the c-plane are found in fractured single crystal fibers. The construction of the Advanced Fiber Growth Station continued during this year. Both the laser and its associated support equipment arrived in the latter part of the year and some initial testing of the laser system was accomplished. A control panel has been designed to operate the feed and positioning motors which control the fiber growth. The microscope for fiber viewing has been acquired.				
14. SUBJECT TERMS High T_c Superconductors, BSCCO, BiSrCaCuO, Superconducting Fibers/Ceramics, LHPG High T_c . Phase Equilibria			15. NUMBER OF PAGES 27	
			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	

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

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

I. INTRODUCTION

This program, initially planned for three years and extended through this fifth year, has been devoted to establishing the viability of the laser-heated pedestal growth (LHPG) method for the preparation of wire of the high T_c superconductor $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$. This material not only exhibits a high superconducting transition temperature and high critical current densities, but also has better thermodynamic properties (low volatility in particular) than other high T_c superconducting materials. In particular this material has become one of the most attractive materials for superconducting wire applications.

This program had as its main goals 1) finding the most appropriate starting compositions capable of producing long lengths of wire with uniform structure and composition, high superconducting transition temperatures, and critical current densities, 2) maximizing the growth velocity to enhance the economic viability of the growth method and 3) determining the maximum length of fiber which can be produced. To address these issues, we have made 1) an in-depth study of the thermodynamic and kinetic factors which affect growth rates and the properties of the fibers produced, 2) designed and started construction of an advanced fiber growth system which will permit better control of system parameters, and 3) developed techniques to enhance fiber throughput via increased growth velocity. Almost 75 percent of this program was successfully completed by the end of the initial three year period. No-cost extensions extending the program through this reporting period were necessary due to delays in obtaining the CO_2 laser necessary for our advanced fiber growth system. This delayed the completion of the growth system and the final crystal growth experiments.

During the prior year we located a company promising a laser with better specifications, and deliverable during this current year. Results during the period January 15, 1989 to December 31, 1992 are summarized in Progress Reports CMR 89-3 dated April 1989, CMR 90-8 dated November 1990, and CMR 91-1 dated December 1991, and CMR 92-1 dated December 1992.

II. PROGRESS TO DATE

This report covers the fifth year of this program. Almost all of the materials research work had been completed during the previous four year period with the bulk of the work remaining focussed on the fiber growth equipment. During this last 12 month period, as covered in this fifth year report, the emphasis has been on 1) finishing up some superconducting property measurements on Bi-Sr-Ca-Cu-O fibers with different compositions, and 2) completing construction and testing of the advanced fiber growth system.

A. 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.

1. Constitutional Supercooling Effects

Several studies [1-3] 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 liquidus. 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:

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

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_{Li}^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:

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

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_{Li}^i has the lower slope of the majority phase liquidus and $(C_{L0}^i - C_S^i)$ 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}^i has a higher slope (than that of the primary phase liquidus) and $(C_{L0}^i - C_S^i)$ 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 1 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:

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

The fastest crystal growth should then be possible when $G_L \cdot D_L^{\text{Bi}}$ is relatively high and when $m_L^{\text{Bi}} \cdot (C_{L0}^{\text{Bi}} - C_S^{\text{Bi}})$ 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 $(C_{L0}^{\text{Bi}} - C_S^{\text{Bi}})$ 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.

Table 1. 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

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 1. As predicted, the observed Bi_2O_3 segregation at the growth interface was relatively low when starting materials A and B were used.

Figure 1 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 $\sim 20^\circ\text{C}$ 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 our previous work, 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 1: Variation in Bi_2O_3 segregation coefficient with measured growth temperature.

Figure 2: SrO content of 2212 crystals and their melts as a function of observed growth temperature.

2. Influence of Processing Parameters on T_c

a. Background

Considerable variation in the T_c of 2212 phase superconductors has been observed in samples of varied composition. [4,5] 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 [4,6-8], 2) defects in the atomic stacking sequence within the crystal structure [5-11], and 3) variation in the oxygen content through atomic vacancies on the oxygen sites. [5,12-14] These are discussed below.

b. Cation inter-substitutions

The existence of substitutional defects in the 2212 crystal structure was established by the neutron diffraction study of Lee et al. [7]. 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 [4,15-16] as well as the results of the present work (see Table 1). 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 [4] 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 3 as a function of their relative compositions.

Figure 3: Variation of superconducting T_c with crystal bismuth content and Ca:Sr ratio, from Ono [4].

c. Atomic layer stacking defects

Previous authors [5-11] 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 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, 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.

d. 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. [5,12-14] 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 4 and 5 document some of the results of these studies.

Figure 4 is reproduced from Buckley et al. [5]. 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 4: R vs. T curves of polycrystalline "2212" samples quenched from different annealing temperatures, from Buckley et al. [5]

Figure 5 is reproduced from Mitzi et al. [12]. 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 5 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 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. [14] 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.

Figure 5: Magnetic susceptibility as a function of temperature for crystals of differing oxygen content, from Mitzi et al. [26]

3. Correlation Between T_c and Growth Parameters

Table 2 lists the crystal compositions, melt compositions, growth temperatures (M_{ps}) and superconducting T_c 's of six internally homogeneous 2212 rods crystallized in the present study. Examination of the data in Table 2 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. [17] study. This may be seen in Figure 6, 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 7, 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 1).

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

Table 2: T_c with other Data from LHPG Samples

Trial #	Source Mat'l	Crystal Composition				M_p (°C)	T_c (K)
		Bi	Sr	Ca	Cu		
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. 6: Sample T_c (for both LHPG and thin film [15] samples) plotted vs. crystal growth temperature.

Figure 7: SrO content of 2212 crystals and their melts as a function of observed sample T_c .

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 8 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 9 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 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. [15] 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 [4,5,12-14], 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.

Figure 8: 90 micron diameter 2212 fiber bent into a 5 cm radius.

Figure 9: SEM micrograph of the fracture surface of a 90 micron single crystal fiber that was bent until fracture occurred.

B. ADVANCED FIBER GROWTH STATION

1. History and Background

One of the program goals was to prepare long lengths (> 100 mm) of small diameter (< 100 μm) 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 $20\text{ }\mu\text{m}$ 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 $10\text{-}50\text{ }\mu\text{m}$ 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 world at the time, and 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 and third years a CO_2 laser was ordered but due to numerous production problems, as mentioned earlier, the initial order had to be cancelled and a new laser company identified. 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, in a pre-production phase but an order was placed early in 1992.

Through the end of 1992, the manufacturer had not yet delivered the laser, and we were forced to request several no-cost extensions to continue facility construction at a reduced level of effort because most of the components had to be interfaced with the laser power supply or the associated LHPG control electronics. Table 3 identifies the major LHPG system components that had been planned for the LHPG system and which were either worked on during the 1993 time frame or were held off on pending delivery of the laser. Figure 10 illustrates the system's major components.

Table 3: 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

Figure 10: Schematic illustration of advanced LHPG system's major components

2. Current Year's Progress

a. Laser Support Equipment

During the current reporting interval (cal. 1993), equipment required to operate the laser was acquired and installed. Operation of the UTOS laser required a stable, 50A, 26 Vdc power supply to be user supplied. A 50A Lambda supply, acquired in 1992, was installed in the control panel while we were awaiting delivery of the laser. Likewise, a user supplied water chiller needed to cool the laser head, a $\pm 1^{\circ}\text{C}$ Remcor chiller, was acquired early in the year anticipating delivery of the laser.

b. United Technologies Optical Systems (UTOS) CO₂ Laser

During the first eight months of the year, manufacturing problems with the laser continued. Most were caused by the fact that the commercialized version had been re-engineered to reduce its cost, and considerable difficulties were encountered with its internal rf-generator that excites the plasma tube. By August, these problems had been resolved and manufacturer's testing for power stability was underway. Since the need for long-term power stability to better than $\pm 0.5\%$ was essential for fiber diameter uniformity and growth interface stability, it was essential that laser stability be verified. In early September, the laser was finally shipped to Stanford, and the balance of the year was devoted to setting it up in a configuration where we could control its output power and measure power stability. We have had only limited experience with the laser during the last months of the year, and cannot verify its long term reliability. However, its short term stability appears to be better than its $\pm 0.25\%$ specifications and according to tests performed by the vendor during its construction, its power output is closer to 50 W than the 40 W specified. Table 4 summarizes the UTOS laser specifications.

Late in the year, United Technologies requested that the unit be returned for a warranty replacement of its internal rf generator assembly because in the intervening timeframe, they had identified a problem of overheating that needed to be corrected. We deferred this interruption in order to continue system integration and testing.

Table 4: United Technologies LC-40 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.

c. Optical train

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 had been planned using the standard three piece diamond-turned copper reflexicon system (OFC Corporation) originally designed at Stanford. This unit, also delivered early in the program, is designed to produce a near-diffraction-limited line focus around the perimeter of the molten zone, as described in the research sections of these yearly reports. When we began testing the laser late in the year, we discovered that the gold coating on the surface of all three reflexicon components had developed numerous sub-millimeter diameter "blisters" in the gold coating during the several year period we had to wait for the laser to be delivered. During this time the optic was stored on the top of the optical table in its kinematic mount. This metallurgical failure mechanism had not been seen in either of the two earlier versions of this optical component both of which had been at Stanford for much longer lengths of time. Its cause could not be determined, but was assumed to be a metallurgical defect introduced during the manufacturers final electro-plating step. It unfortunately required that the final focusing stage be remachined and recoated prior to use. (The unit was well out of the manufacturer's warranty period by the time the defect was discovered.) Resurfacing and recoating of the mirror have been deferred into the following year of the program when additional resources were hoped for to help cover the costs of refinishing.

d. Mechanical systems

Optically encoded miniature dc servo-motors (Micro Mo, Inc.) for feeding and pulling to minimize fluctuations in instantaneous growth rate had been built into the LHPG apparatus. (High ratio MicroMo 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.) During this reporting interval we began designing and constructing the motor control panel used by the operator to control all mechanical aspects of the growth process. Although we hope to have a computer-controlled growth process by the end of the program, we began with a manual control system that required the operator to monitor the growth process using the Wild M-8 microscope. All of the motor controls will be

mounted on a miniature control console that can be positioned in front of the microscope, in keeping with our desire to have an ergonomic growth station. This task has proved to be quite complex because it requires that a single two-axis joy stick control more than one optically phase-locked motor set, and simple multi-pole, multi-throw mechanical switching is not readily compatible with the feedback motor controllers. The control panel has been designed, but construction and testing are not yet finished. This task will be continued in the next program interval.

e. Optical monitoring and fiber diameter measurement

The final components of the long working distance, high resolution optical microscope (Wild Heerbrug, M-8), relied on for process monitoring and for fiber diameter measurement using a high resolution CCD camera mounted on a beam-splitting side arm, have been acquired. An orthogonal view is planned by using an existing short working distance telescope and a second CCD camera. The system is designed to employ a frame grabber and a video analyzer card for quantitatively determining fiber diameters. However, these components have still not yet been acquired since frame grabber technology has been improving each year, its cost continues to decline, and we are not yet completed the system in a much simpler manual control mode. A generic 386 PC was acquired this year and installed in the control panel anticipating the need to process fiber diameter data from the frame grabber when it finally is added to the system.

III. REFERENCES

- [1] M. J. Cima, X. P. Jiang, H. M. Chow, J. S. Haggerty, M. C. Fleming, R. A. Laudise, and D. W. Johnson, *J. Mater. Res.* 5, 1834(1990).
- [2] Z. Lu, L. V. Moulton, R. S. Feigelson, R. J. Raymakers, and P. N. Peszkin, *J. Crystal Growth* 106, 732 (1990).
- [3] D. Gazit, P. N. Peszkin, L. V. Moulton, J. M. Brenner, and R. S. Feigelson, Proc. of 118th TSM AIME High T_c Supercond. Symp., Las Vegas, NV (February 28, 1989); Edited by S. H. Whang and A. DesGupta, *The Minerals, Metals and Mater. Soc.* (1989).
- [4] A. Ono, *Jpn. J. Appl. Phys.* 28, L1372 (1989).

- [5] R. G. Buckley, J. L. Tallon, I. W. M. Brown, M. R. Presland, N. E. Flower, P. W. Gilberd, M. Bowden, and N. B. Milestone, *Physica C* **629**, 156(1988).
- [6] B. Chalmers, *Principles of Solidification*, John Wiley & Sons, NY (1964), pp. 126-185.
- [7] P. Z. Lee, Y. Gao, H. S. Shwu, V. Pericek, R. Restori, P. Coppens, A. Darvskikh, J. C. Phillips, A. W. Sleight, and M.A. Subramanian, *Science* **244**, 62(1989).
- [8] Z. Xu, P. D. Han, L. Chang, A. Asthana, and D. A. Payne, *J. Mater. Res.* **5**, 39(1990).
- [9] R. Ramesh, C. J. D. Hetherington, G. Thomas, S. M. Greene, C. Jiang, M. L. Rudee, and H. L. Luo, *Appl. Phys. Lett.* **53**, 615(1988).
- [10] J. M. Tarascon, W. R. McKinnon, P. Barboux, D. M. Hwang, B. G. Bagley, L. H. Greene, G. W. Hull, Y. LePage, N. Stoffel, and M. Giroud, *Phys. Rev. B* **38**, 8885(1988).
- [11] R. Ramesh, S. M. Greene, Y. Mei, A. E. Manzi, and H. L. Luo, *J. Appl. Phys* **66**, 1265(1989).
- [12] D. B. Mitzi, L. W. Lombardo, A. Kapitulnik, S. S. Laderman, and R. D. Jacowitz, "Growth and properties of oxygen- and ion-doped $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+d}$ single crystals," *Phys. Rev. B* **41**, 6564 (1990).
- [13] D. E. Morris, C. T. Hultegren, A. M. Markelz, J. Y. T. Wei, N. G. Asmar, and J. H. Nickel, *Phys. Rev. B* **39**, 6612(1989).
- [14] G. Triscone, J. Y. Genoud, T. Graf, A. Junod, and J. Muller, *Physica C* **176**, 247(1991).
- [15] S. J. Golden, T. E. Bloomer, F. F. Lange, A. M. Segadaes, K. J. Vaidya, and A. K. Cheetham, "Processing and characterization of thin films of the two-layer superconducting phase in the Bi-Sr-Ca-Cu-O system: evidence for solid solution," *J. Amer. Ceram. Soc.* **74**, 123 (1991).
- [16] B. Hong and T. O. Mason, *J. Am. Ceram. Soc.* **74**, 1045 (1991).
- [17] J. Luo, X. P. Jiang, H. M. Chow, M. J. Cima, J. M. Graybeal, T. P. Orlando, and D. A. Rudman, *IEEE Trans. Mag.* **27**, 1499 (1991).