Phase II Final Report

Homogenous BSCCO-2212 Round Wires for Very High Field Magnets

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a. Identification and Significance of the Problem or Opportunity

The performance demands on modern particle accelerators generate a relentless push towards higher field magnets. In turn, advanced high field magnet development places increased demands on superconducting materials. Nb_3Sn conductors have been used to achieve 16 T in a prototype dipole magnet and are thought to have the capability for ~18 T for accelerator magnets (primarily dipoles but also higher order multipole magnets). However there have been suggestions and proposals for such magnets higher than 20 T [1]. The High Energy Physics Community (HEP) has identified important new physics opportunities that are enabled by extremely high field magnets:

- 20 to 50 T solenoids for muon cooling in a muon collider (impact: understanding of neutrinos and dark matter)
- 20+ T dipoles and quadrupoles for high energy hadron colliders (impact: discovery reach far beyond present)

This proposal addresses the latest SBIR solicitation that calls for grant applications that seek to develop new or improved superconducting wire technologies for magnets that operate at a minimum of 12 Tesla (T) field, with increases up to 15 to 20 T sought in the near future (three to five years). The long-term development of accelerator magnets with fields greater than 20 T will require superconducting wires having significantly better high-field properties than those possessed by current Nb_3Sn or other A15 based wires. Given the existing materials science base for Bi-2212 wire processing, we believe that

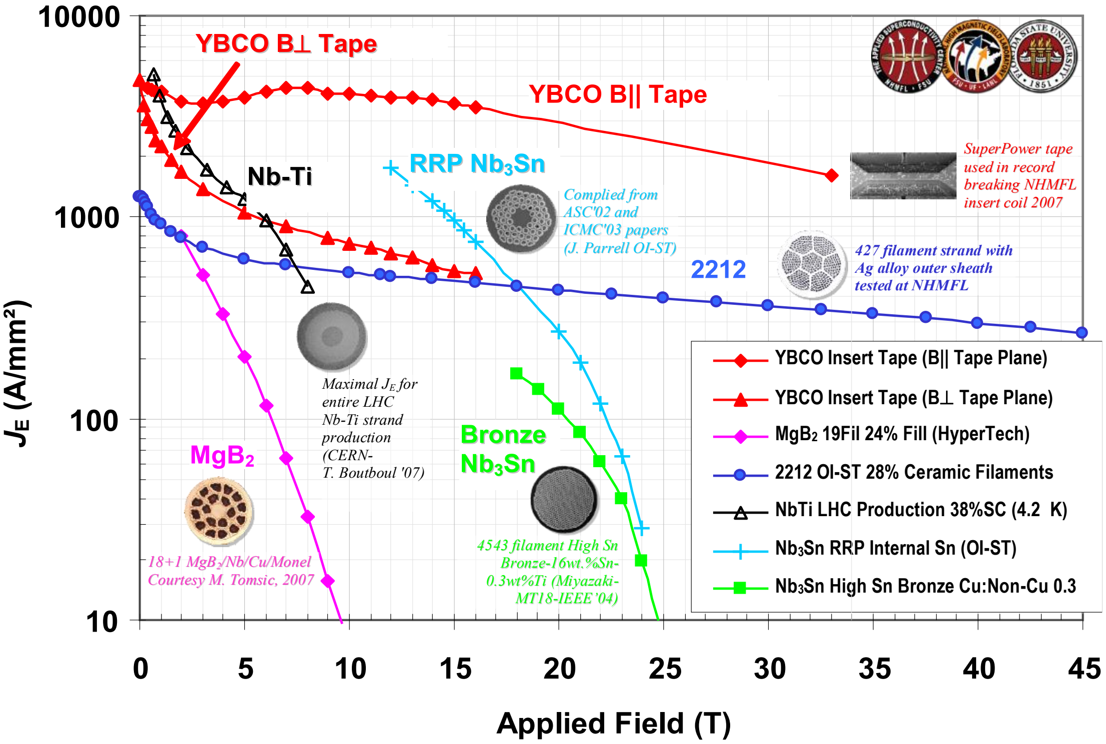


Figure 1. Engineering critical current density J_E at 4.2K for representative high J_c superconducting conductors of YBCO, MgB_2, Bi-2212, Nb-Ti and Nb_3Sn. Courtesy Peter Lee with data sourced as indicated.

$Bi_2Sr_2CaCu_2O_y$ (Bi-2212) round wires can be produced in km-long piece lengths with properties suitable to meet both the near term and long term needs of the HEP community. The key advance will be the translation of this materials science base into a robust, high-yield wire technology.

While the processing and application of A15 materials have advanced to a much higher level than those of the copper oxide-based, high T_c (HTS) counterparts, the HTS materials have the very significant advantage of an extremely high H_{c2}. For this reason, $Bi_2Sr_2CaCu_2O_y$ (Bi-2212, or 2212) in the form of a multifilamentary Ag alloy matrix composite is beginning to attract the interest of the magnet community for future extremely high-field magnets or magnet-insert coils for 4.2K operation. Fig. 1 shows an example of excellent J_E (engineering current density) in Bi-2212 round wire at fields up to 45 T, demonstrating the potential for high field applications of this material. For comparison, the Nb_3Sn wires used in magnets in the 16 – 18 T range typically perform with J_E in the range 200 – 500 A/mm^2; the Bi-2212 wire retains this level of performance to fields at least as high as 45 T, and probably significantly higher. Bi-2212 conductors have in fact been used to generate a 25 T field in a superconducting insert magnet [2]. These two factors- the very high field critical current performance of Bi-2212, and the already demonstrated capability of this material for high field magnets up to 25 T, strongly suggest this material as a leading contender for the next generation high field superconducting (HFS) wire. This potential was recognized by the US Academy of Science's Committee on Opportunities in High Magnetic Field Science. Their report of the same name specifically calls out the high field potential for this material, and suggests that 30 T magnets appear feasible based on the performance of 2212 [3].

There are several requirements for HFS conductors. The most obvious is J_E (B, T), the engineering current density at the field and temperature of operation. As shown in Fig. 1, Bi-2212 excels in this regard. Stability requirements for magnets dictate that the effective filament diameter should be less than 30 micrometers, something that Bi-2212 multifilamentary wire can uniquely satisfy among the HFS superconducting wire technologies. Additional requirements include mechanical properties that prevent stress limitation of J_E at the operating conditions, resistive transition index (n-value) sufficiently high to meet the field decay requirements (in persistent magnets), piece lengths long enough to wind coils, and acceptably low costs. HEP has traditionally used very high current magnets made from Rutherford cables, and the ability to be cabled is another key advantage.

Very high on the list of materials able to fulfill the requirements above is Bi-2212 round wire. Both cables and high field coils on a small scale have been demonstrated using this material. By contrast, YBCO is a single-filament tape that is not easy to cable. As shown in Figure 1 these tapes are highly anisotropic in their current density. In the good orientation the performance is considerably better than Bi-2212, however at the highest fields measured, the isotropic current behavior of 2212 exceeds the bad orientation of YBCO. The isotropic behavior of Bi2212 round wire simplifies the engineering of high field magnets. Isotropy, high J_E at high fields, the ability to be cabled, and significantly longer piece lengths than those currently available in YBCO coated conductors are compelling reasons to continue the development of Bi-2212 round wire for HEP.

Nationwide Status of BSCCO-2212 Round Wire Efforts

During the time since this Phase 1 effort was originally conceived and proposed in autumn 2007, there have been three significant developments in the Bi-2212 situation in the United States. First, there is a critical issue for the two U.S. wire manufacturers regarding the problem of the wire leaking 2212 liquid when partial-melt heat treated after winding into either coils or cables. Second, a national consortium of laboratories (Very High Field Superconducting Magnet Collaboration, or VHFSMC) has written a proposal, apparently on the verge of funding from HEP, to advance the technology of Bi-2212 round wire along with coils and cable made from this material [4]. The third development: we are told that the primary source of precursor powder for U.S. manufacturers (Nexans in Germany) is now available only in very large quantity orders which cannot be supported by the present U.S. program [5].

This pushback on U.S. wire manufacturers concerning melt leakage has prompted substantial changes in the wire processing. These changes have significantly reduced the Jc performance now reported, in some cases by as much as 50%. These changes have in turn caused pushback on the powder manufacturer to provide precursor that both helps restore this lost Jc and that helps reduce leaking. SCI Engineered Materials is being told by our SBIR wire partner OST that the two urgent priorities today are a precursor composition that is optimized for their wires including the novel leak-proof process and new configuration; and a change in powder particle size that reduces surface area and thus the potential for adsorbed carbon, which can evolve CO_2 during melt processing, causing internal pressure in the wire and potentially contributing to leaking.

Regarding the new VHFSMC, we are told that the expected program will either require or strongly prefer a U.S. precursor powder supply. Also, funding for this program is expected to support R&D in the labs of the consortia members (as well as purchase of wire from the U.S. manufacturers). Regarding an industrial R&D effort, the proposal recommends that small businesses related to the program seek funding from the SBIR program. One challenge with this approach is that the time required from Phase I proposal to results from a Phase II program is typically four years (7 months from proposal submission to Phase 1 funding, 11 months for Phase 1 performance + final reporting + Phase II proposal, 3 months to Phase II funding, and 24 months for Phase II performance). However the VHFSMC is presently a two year plan, so new Phase I SBIR proposed work is unlikely to benefit the program.

Regarding the present U.S. precursor source, most U.S. wires have been manufactured using foreign powders [see for example Ref 6, 7]. Substantial R&D work was done by OST to optimize the composition of the precursor made in Germany for their wires [6]. This work showed that different heat treatments were required for each composition in order to maximize Jc, and even with the particular optimized heat treatment, maximum Jc differed by as much as a factor of four for different precursor compositions. However the OST results to date on SCI precursor suggest that the best composition is different for this powder made by a very different method, as will be shown in the Phase II plan below. A number of factors likely contribute to this difference, such as powder phase composition, particle size distribution, melting and recrystallizing features, etc., which will be discussed in detail in the technical proposal below.

These factors taken together are prompting a strong push for SCI to shift this Phase II proposal away from the Phase I doping and calcination studies to respond to the urgent need for precursor that :

a) helps restore Jc performance lost through wire process changes while minimizing leaking;
b) accelerates progress on suitable precursor available for the new VHFSMC program;
c) establishes a viable U.S. supply of 2212 precursor with good reproducibility.

b. Anticipated Public Benefits

The proposed SBIR brings together a unique team of high T_c powder manufacturer, world-class wire/magnet manufacturer, and the world class HTS materials expertise of a national lab in order to facilitate the development and commercialization of high T_c conductors. Currently, the price of the BSCCO-2212/Ag composite multifilament round wire is about \$10-\$15/m for piece lengths of about 300 meters. With successful completion of this SBIR program, piece lengths of the order of 1-2 kilometers will be demonstrated with performance characteristics in excess of the current DOE HEP specifications for round BSCCO-2212/Ag wire. This new development is expected to reduce the price of BSCCO-2212/Ag to \$5-7/m or \$10-\$14/kAm. The proposed approach takes advantage of all of the lessons learned from the last several years of processing activities, and provides a real opportunity to leap-frog past the existing conventional processing options to finally deliver on the promise of High T_c conductors in the near term.

With the conductors NbTi and Nb_3Sn approaching their performance limits, the enhanced BSCCO-2212/Ag wires will be instrumental in extending magnetic fields at operating temperatures near 4.2K. The significant critical field performance of the HTS material promises insert coils which can yield fields well in excess of the currently available 20 T produced using Nb_3Sn. If reliable, cost effective wires can be produced from BSCCO-2212, additional higher temperature applications, specifically above 10 K but below 20 K, where closed-cycle refrigeration can be utilized, will be enabled.

The development of cost effective, high performance, multi-filamentary BSCCO-2212/Ag wires will enable the production of next generation of insert magnets, which may operate at fields in excess of 20 T. The availability of these high field magnets will benefit the pursuit of high-energy physics, advanced MRI (or NMR) analysis, and energy storage devices (SMES and micro SMES). The High-Energy Physics community, Chemical and Medical industry, and Electric Utility industry are potential customers for this product.

The market for superconducting wire has historically been driven by the medical industry through its application of NMR technology. It is conceivable that a high performance, low cost BSCCO-2212 wire could replace NbTi wires in this application. Further, the use of superconducting magnets in research, such as high-energy physics, continues to increase. The opportunity to reach magnetic fields in excess of 20T will be very attractive to researchers and create a significant market for BSCCO-2212 wires.

Medical NMR may benefit from the higher fields achievable with BSCCO-2212 wires through increased resolution. Currently, NbTi and Nb_3Sn wires are used in the construction of these magnets. At present, ultra high magnetic fields can only be achieved using large and inefficient Bitter style magnets. The development of the proposed BSCCO-2212 wire could obsolete the Bitter designs by enabling superconductive magnet systems, which are both energy efficient and compact.

BSCCO 2212 wire today provides the only viable superconductor for making Rutherford cable that can operate at fields higher than the 18-20 T range accessible using Nb_3Sn. Using OST wire made under the previous Phase II SBIR referred to above, Lawrence Berkeley National Lab has made experimental 14-strand cables that demonstrate the feasibility of cabling this wire. This material thus provides the potential for extending high current Rutherford cable applications into the 20 to 30 T range.

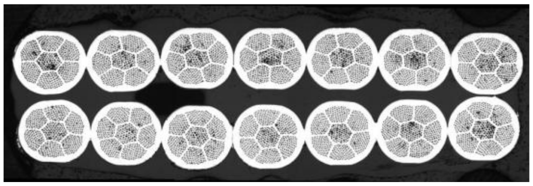


Fig. 2: Trial Rutherford Cable Made at Lawrence Berkeley Lab in fall 2005 from OST 2212 wire.

It is critical to US competitiveness in HTS technology that a US led team meet or beat the performance of its next nearest international competitor. The proposed technology leverages DOE HTS powder technology developed at Sandia National Lab, Argonne National Lab, Los Alamos National Lab and the publicly held SCI. To the best of our knowledge, this proposed government backed research is unique in that it represents the only significant and sustained US industrial effort in BSCCO 2212 wires. Without the support requested in the proposed Phase II effort, it is possible that the US will concede the market for high field, BSCCO based, HTS conductor to its international rivals.

SCI is the only choice for the new VHFSMC as the Bi-2212 powder supplier. Steady improvement in powder fabrication and progress toward acceptable wire performance under DOE's SBIR funding have provided a baseline to speed up precursor production capability being available for the new VHFSMC program.

c. Phase I Results:

The original goal of Phase 1 was to determine the calcination conditions at a fixed dopant type and amount that would yield Bi-2212/Ag composite wires having improved short sample J_c values in excess of 2100 A/mm^2 and J_E values in excess of 600 A/mm^2 at

12T and 4.2K with a variability of these properties of less than -10% from the optimum value.

Task II: Preparation and Evaluation of BSCCO-2212 Powders

A chemical precipitation method is currently used at SCI to produce BSCCO - 2212 powders. The standard solid state reaction method used to prepare bulk superconducting powders involves calcination (elevated temperature reaction) of a mixture of ball-milled oxides and carbonates in desired molar ratio. However, ball milling the oxides and/or carbonates may lead to inadequate mixing of powders leading to compositional inhomogeneities, inadequate stoichiometry control, the formation of secondary phases, and may introduce additional powder grinding steps which can further influence the quality and reproducibility of the final product.

In general, chemical precipitation of powders from solutions provides a method for eliminating the problems associated with the solid state mixing process. Through the chemical precipitation method one can produce intimately mixed precursor powders prior to calcination, promoting the solid state reactions required to produce desired superconducting phases. Stoichiometry and purity of chemically prepared powders can be higher than those prepared using the standard solid state mixing method. In a typical co-precipitation process, an aqueous solution containing highly soluble metal salts, such as nitrates, of the cations are mixed with a solution containing highly soluble salts of the precipitating anions such as hydroxides and carbonates. When the solutions are mixed, an insoluble precipitate is formed. The precipitate is calcined to form the desired superconducting phases. In the case of the SCI process for producing BSCCO-2212 powders, a precursor containing carbonates and hydroxides of bismuth, strontium, calcium, and copper in the desired molar ratios is produced using the ultrasonically assisted precipitation process to insure full and homogenous precipitation of all cations in solution.

The calcination process is performed in a low-pressure furnace at an O_2 pressure of 3-5 torr to produce single phase BSCCO-2212 powders with low carbon content. In the process to produce multifilament BSCCO-2212/Ag composite round wires, the carbon content of the BSCCO-2212 powder must be kept at or below 100 ppm to avoid blistering of the Ag sheath during thermal processing. During thermal processing carbon dioxide gas evolves from the BSCCO-2212 powder due the presence of carbonates. After calcination in ambient atmospheres, small amounts of residual carbonates can be present in the BSCCO-2212 powder in amounts well over 100 ppm. By calcining the powder in a reduced pressure atmosphere, the thermodynamic driving force for the decomposition of carbonates is much higher and carbon contents of 100 ppm or less can be obtained. At present, SCI is routinely producing Bi-2212 powders with carbon content less than 100 ppm.

In addition, when exposed to ambient atmospheres, BSCCO-2212 can absorb carbon dioxide and water from the air. With exposure to air, the carbon content can increase to amounts between 300 and 350 ppm. In order to prevent the absorption of carbon from air, SCI packages BSCCO-2212 powders in a dry nitrogen atmosphere in a glove box immediately after removing the powder from the vacuum calcination furnace. After packaging, the powder containers are stored in a vacuum desiccator until used. The quality control measurements used the characterize the finished product are tap density, x-ray diffraction analysis (XRD), and Leco Carbon Analysis.

SCI prepared 3 powder lots using the processes described above utilizing calcining temperatures of 830, 820, and 790°C with a hold time of 8 hours in order to determine the window of calcining temperatures that yield the highest J_c and J_E values as well as the most consistent properties in BSCCO-2212/Ag composite multifilamentary round wires. The dopant type and amount added to the powders after calcination were determined by the results of a previous Phase I effort (DE-FG02-07ER84831) designed to determine the optimum type and amount of dopant.

After the powders were prepared, they were used to fabricate BSCCO-2212/Ag tapes using a dip coating and partial melt process developed by OST. Data obtained from dip coated tape samples has been shown in previous work by the team to be a consistent indicator of how well a specific Bi-2212 powder will perform in round wire configuration. This process can be performed much faster and at significantly lower cost than the preparation of short round wire samples and is best suited for screening evaluations in a Phase I program. To prepare tape samples, Bi-2212 powder is dispersed in a organic solvent/organic binder mixture to form a viscous slurry. 20 to 30 meter lengths of silver tape substrate are coated using the OST dip coating machine, which controls thickness to within ~2%. When dry, the sample is then ready for partial melt processing. In typical partial melt processing, the tape is first heated above the melting point of 2212 to a set temperature T_m, and is held at this temperature for short period of time. Bi-2212 powder melts incongruently at about 870 °C into a liquid and $(Sr,Ca)CuO_2$, normally referred to as 1:1 alkaline earth cuprate phase (1: 1) AEC, and Cu free phase of nominal composition $Bi_2(Sr,Ca)_4O_x$.. By processing at temperatures between 870°C and 900°C in oxygen atmospheres most of these phases react with the liquid to form BSCCO-2212 [2], however, as described above, without additives, some low temperature superconducting phase BSCCO-2201 forms and the larger grains of AEC and copper free phases remain. All of these phases negatively affect the superconducting properties of the composite wires. In previous Phase I work, $SrCa_2Zr_2O_7$ was shown to significantly reduce the size, amount, and distribution of these phases during the partial melt step and the reduction of BSCCO-2201 phase during the re-crystallization step to form primarily aligned BSCCO-2212 phase that lead to improved superconducting properties of dip coated tapes and Bi-2212/Ag composite round wires. In addition, the microstructure of the samples exhibited the presence of very small particles of the dopant which may provide flux pinning in addition to controlling the formation of second phases. The tapes prepared under Task II were evaluated for J_C as a function of magnetic field at 4.2K self field to determine the effects of the calcining conditions on the superconducting properties of the BSCCO-2212 layer. The OST portion of Task II was to prepare dip-coated tape samples, and measure self field I_c, for the purpose of determining a $J_c(T_m)$ curve for each calcining condition.

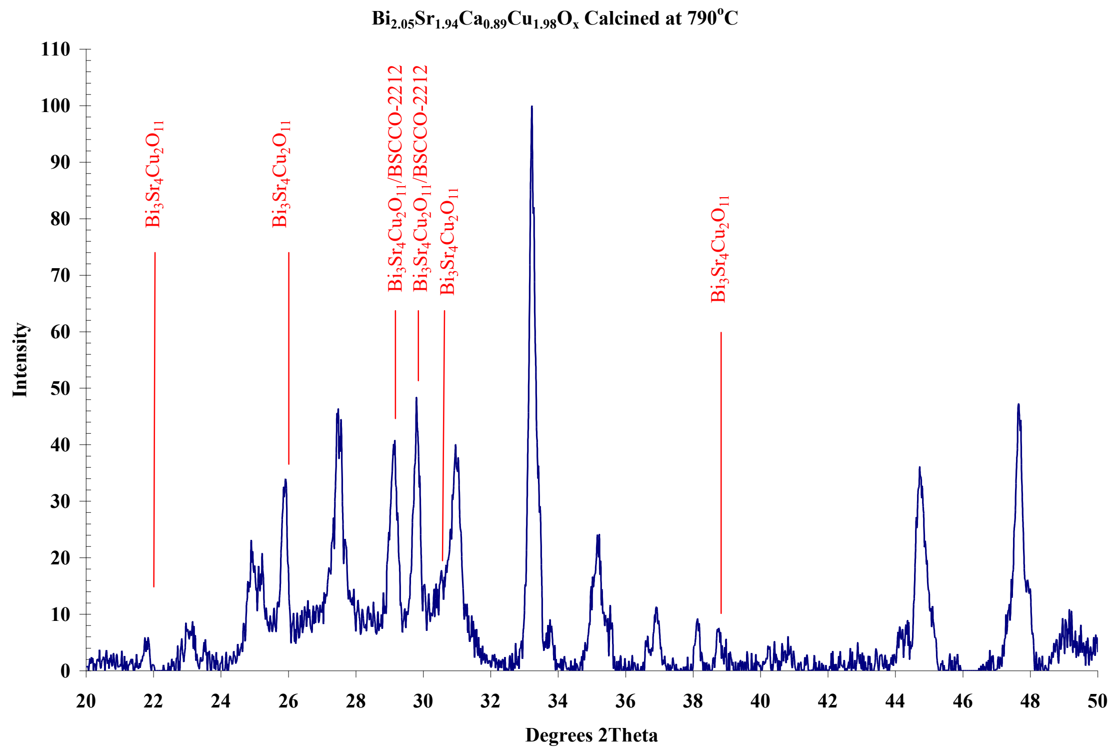
SCI prepared two base lots of BSCCO-2212 precursor powder. The two lots were formulated to produce compositions of $Bi_{2.05}Sr_{1.94}Ca_{0.89}Cu_{1.98}O_x$ and $Bi_{2.17}Sr_{1.94}Ca_{0.89}Cu_{1.98}O_x$, each with 0.1 mole percent Ag added to aid in melt processing during wire and tape fabrication. The $Bi_{2.05}$ composition was chosen because previous work with SCI precursor demonstrated best Jc performance with this composition. The $Bi_{2.17}$ composition was chosen because previous work at OST with Nexans precursor demonstrated best Jc performance with this composition. ICP spectroscopy was performed on the starting solutions prior to the precipitation process to insure the proper stoichiometry was achieved. The precursor powders were divided into 3 sublots; each sublot calcined at either 790°C, 820°C, or 830°C. After calcination, each sublot was further divided into two lots; one of these lots processed with 0.125% $Sr_2Zr_2O_7$ dopant.

After the powders were prepared, they were evaluated for stoichiometry (ICP), phase purity (XRD), tap density, and melting characteristics (DTA) before they were sent to OST and used to fabricate Bi-2212/Ag tapes using a dip coating and partial melt process.

After the precipitation step mentioned above, the Bi-2212 precursor precipitate was heat treated at 500°C for 6 hours in air to "burn-off" residual organic base material that remains after rinsing the precipitate. Without this step, residual base material may not pyrolyze completely during vacuum calcination resulting in a high residual carbon content in the calcined powder. Phase analysis of the resultant precursor powder indicates that the precursor is composed primarily of Bi_2CuO_4 with a minor amount of Bi-2212.

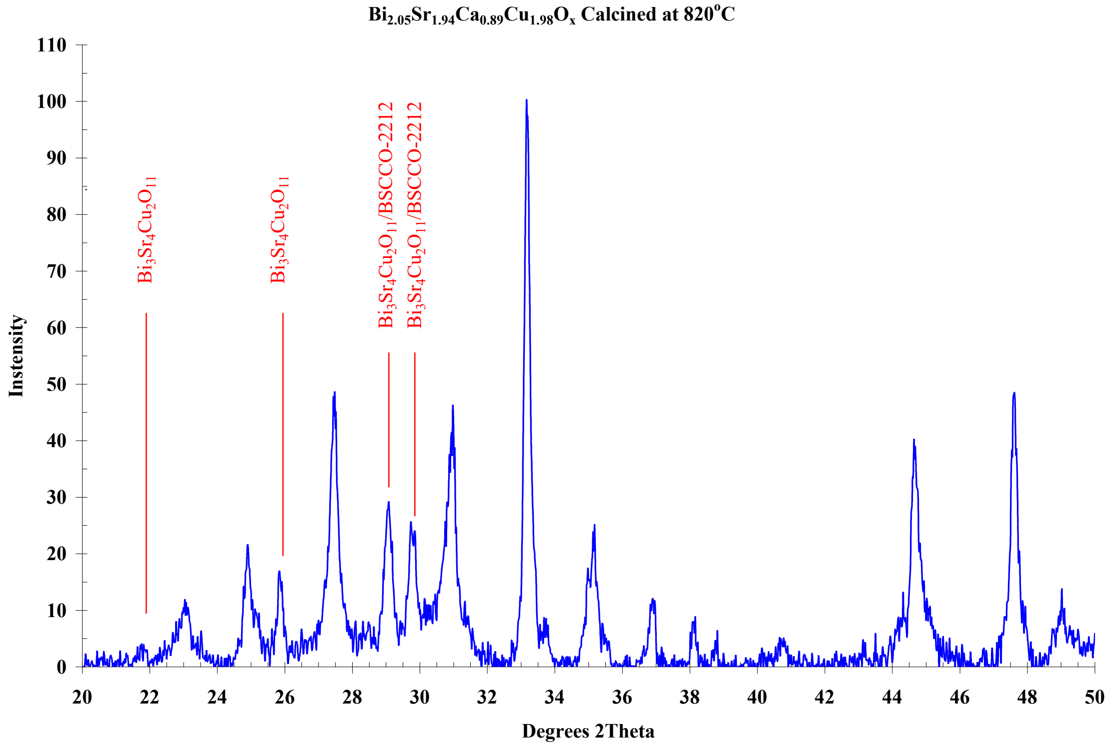
XRD analysis of powders calcined at 790°, 820°, and 830°, and 845°C (just below the melting point for the precursor) for 8 hours indicates that the phase assemblage after calcining does not vary with bismuth stoichiometry. As shown in Fig. 3, $Bi_{2.05}Sr_{1.94}Ca_{0.89}Cu_{1.98}O_x$ ($Bi_{2.05}SCCO$) precursor calcined at 790°C resulted in a material containing predominately Bi-2212 phase with approximately 20-30% $Bi_3Sr_4Cu_2O_{11}$ phase present.

At 820°C the amount of $Bi_3Sr_4Cu_2O_{11}$ was significantly reduced to less than 20% as shown in Fig. 4. After calcining at 830°C, the amount of $Bi_3Sr_4Cu_2O_{11}$ phase was further reduced to slightly over 10% as shown in Fig. 5. The $Bi_3Sr_4Cu_2O_{11}$ content was insignificant and the material was predominately Bi-2212 phase after calcining at 845°C, as can be seen in Fig. 6.



$Bi_{2.05}Sr_{1.94}Ca_{0.89}Cu_{1.98}O_x$ Calcined at 790°C

Fig. 3: XRD Pattern of $Bi_{2.05}$SCCO Precursor Calcined at 790°C



$Bi_{2.05}Sr_{1.94}Ca_{0.89}Cu_{1.98}O_x$ Calcined at 820°C

Fig. 4: XRD Pattern of $Bi_{2.05}$SCCO Precursor Calcined at 820°C

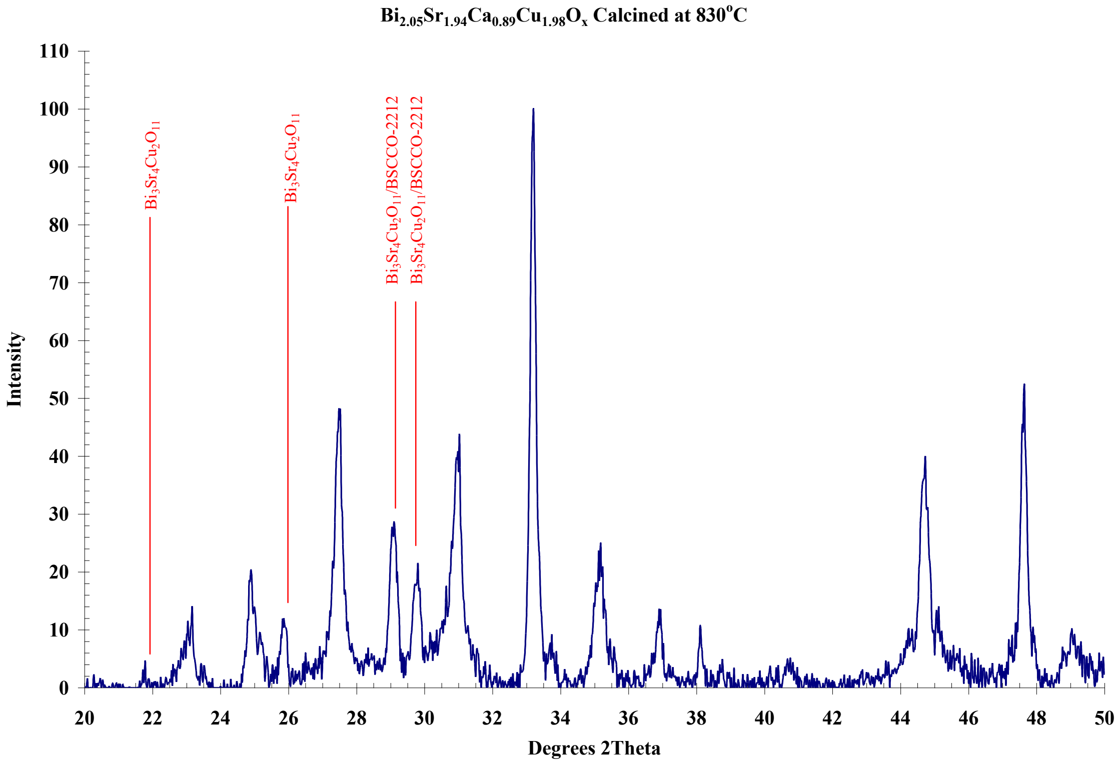


Fig. 5: XRD Pattern of Bi2.05SCCO Precursor Calcined at 830ºC

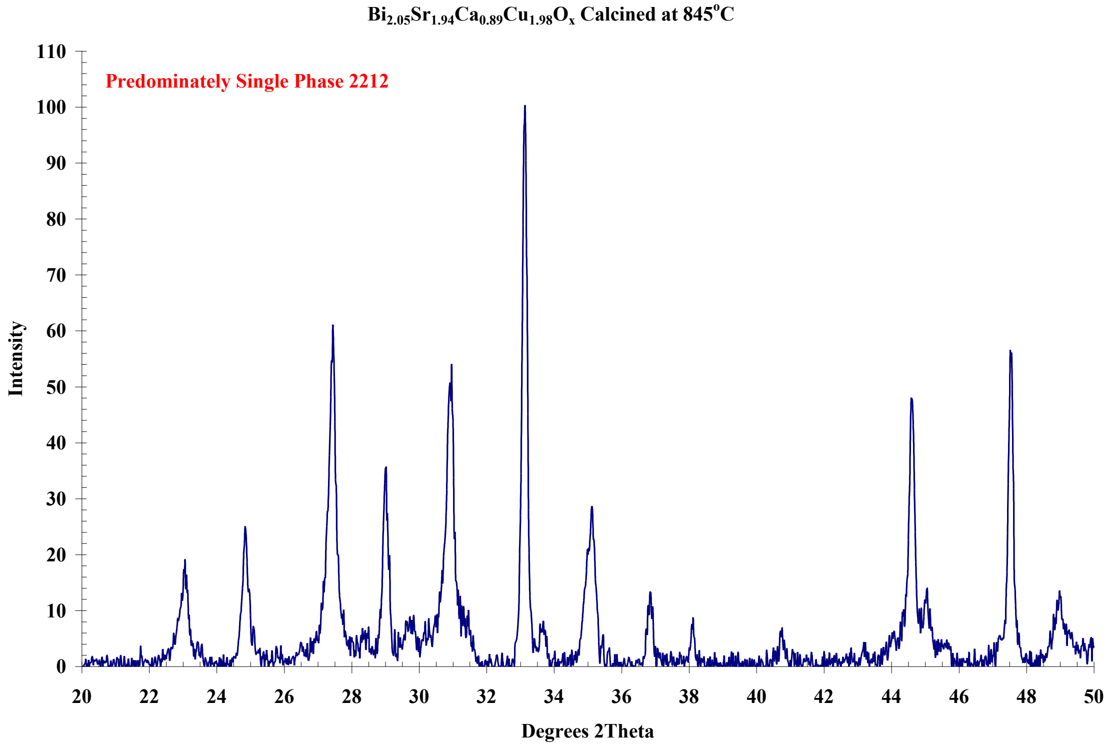


Fig. 6: XRD Pattern of Bi2.05SCCO Precursor Calcined at 845ºC

The phase content of the powders with the $Bi_{2.17}Sr_{1.94}Ca_{0.89}Cu_{1.98}O_x$ ($Bi_{2.17}$SCCO) stoichiometry were significantly different than the phase content of the powders with $Bi_{2.05}$SCCO stoichiometry. As shown in Figs 7-9 the amount of $Bi_3Sr_4Cu_2O_{11}$ phase in the powders with $Bi_{2.17}$SCCO stoichiometry is much higher at each calcining temperature evaluated.

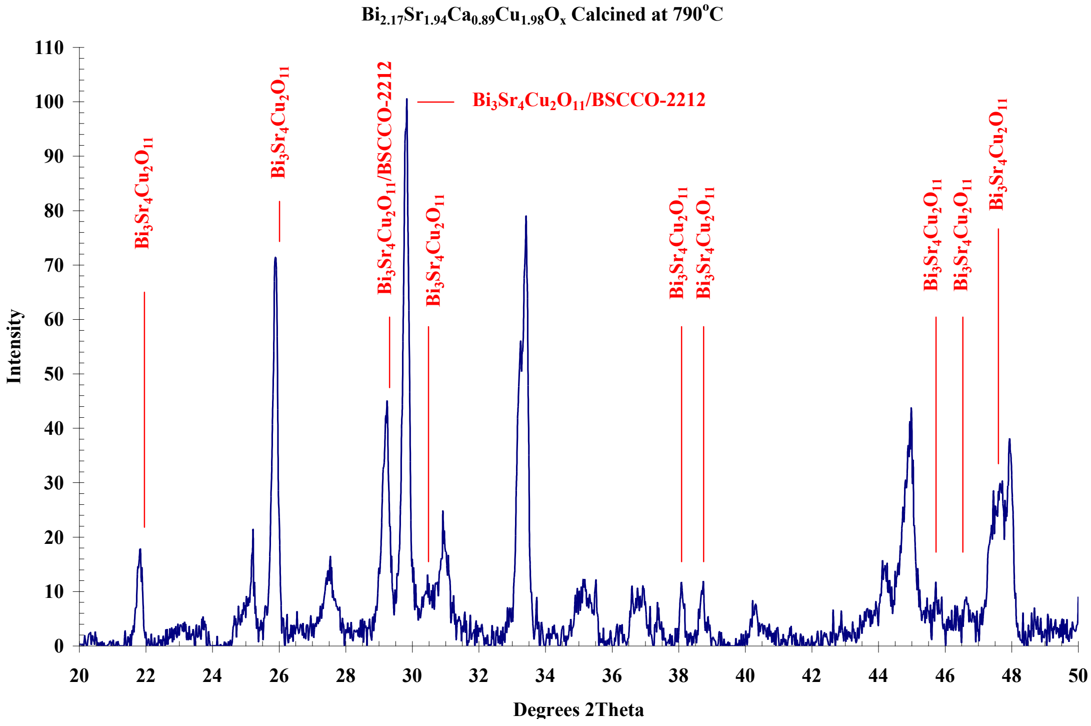


Fig. 7: XRD Pattern of $Bi_{2.17}$SCCO Precursor Calcined at 790°C

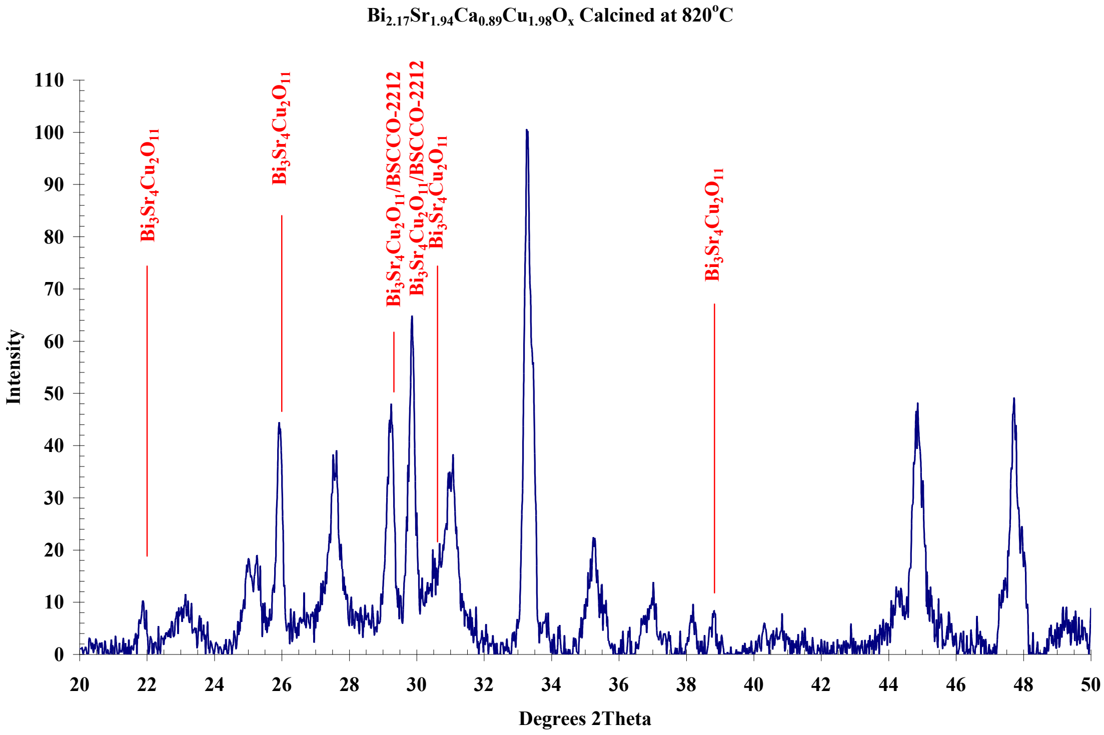


Fig. 8: XRD Pattern of $Bi_{2.17}$SCCO Calcined at 820°C

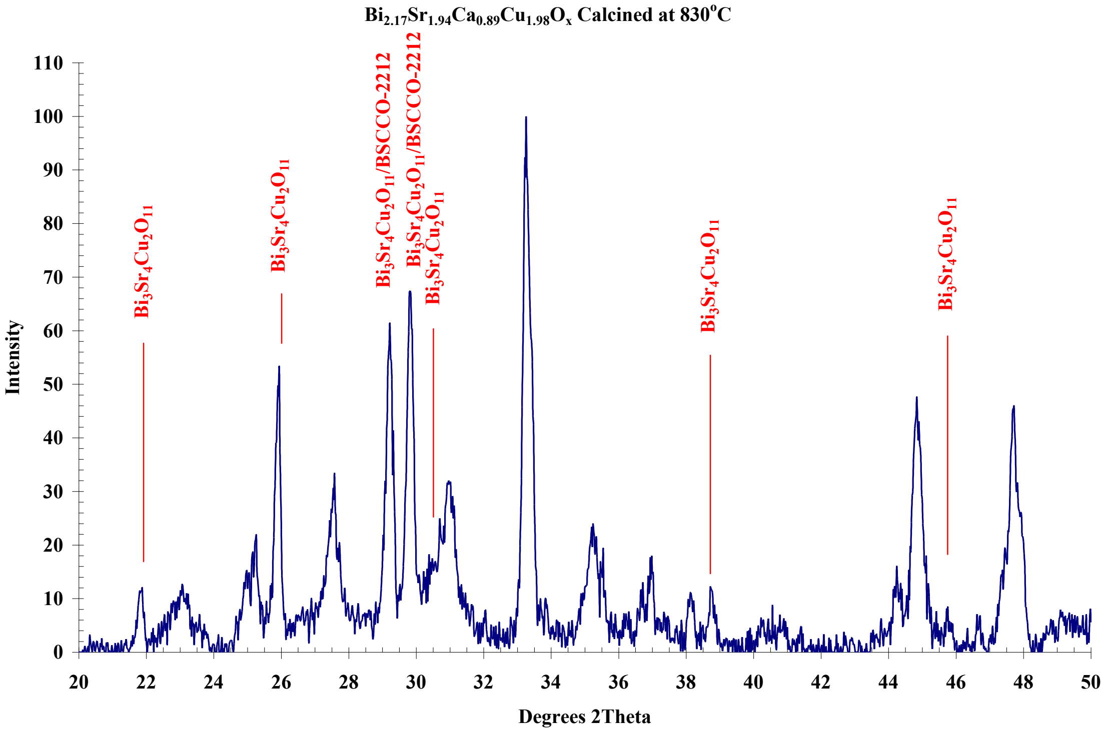


Fig. 9: XRD Pattern of $Bi_{2.17}$SCCO Calcined at 830°C

The tap density and of the powders was also measured and the results are summarized in Table 1.

Table 1: Tap Density Results of $Bi_{2.15}SCCO$ Powders After Calcining

Calcining Temp (°C)	Tap Density (g/cc)
790	1.370
820	1.205
830	1.136
845	1.030

The tap density results appear to be counterintuitive as in most cases the tap density of ceramic powders increases with increasing calcining temperature where in the case of Bi-2212 prepared with the sonically assisted precipitation process and vacuum calcination the tap density results indicate the opposite trend.

Carbon content measurements performed by SCI using the Leco method also show a similar counterintuitive trend. The data shown in Table 2 shows that residual carbon content also increases with increasing calcining temperature. The results also indicate that the particle size of the powder decreases with increasing calcining temperature as residual carbon is more difficult to remove from the powder particles as their size decreases.

Table 2: Carbon Content of $Bi_{2.15}SCCO$ Powders After Calcining

Calcining Temp (°C)	Carbon Content (ppm)
820	110
830	164
845	242

DTA measurements of pure powder provided a problem as the signal from the sample during melting and freezing was not much larger than the noise of SCI's DTA system. However, the signal was greatly enhanced when small pieces of BSCCO-2212/Ag composite wire were used as the sample. The thermal conductivity of the silver provided enhanced heat transfer from the sample to the measurement thermocouple thus enhancing the signal. The addition of silver powder to BSCCO-2212 powder samples in the same ceramic to silver ratio found in the wires was evaluated, but the silver powder appeared to react with the ceramic powder resulting in melting temperature significantly lower than experienced in wire and tape fabrication. At the time, small pieces of unprocessed tape samples were not available but testing on such samples is proposed in Phase II of this project. The DTA results for wire are presented in the section reporting on Task III results.

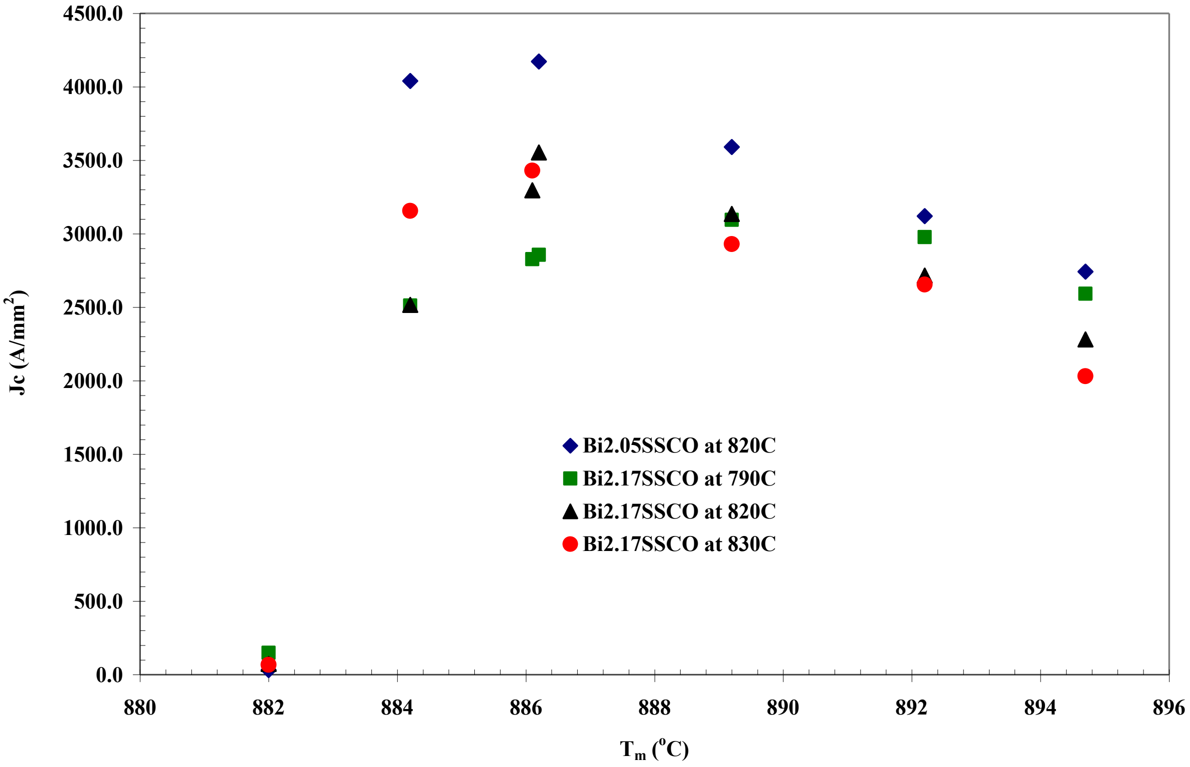
After characterization at SCI, the powders were sent to OST for dip-tape evaluation as described above. The results of the dip-tape analysis are provided in Table 3 and Fig. 10.

Table 3: Summary of Dip-tape Sample Results
Properties Measured at 4.2K Self Field

Material	Peak T (°C)	Peak I_c (A)	Peak J_c (A/mm^2)
Bi$_{2.05}$SCCO Calcined at 820°C	886.2	1040.3	4173
Bi$_{2.17}$SCCO Calcined at 790°C	889.2	940.5	3096
Bi$_{2.17}$SCCO Calcined at 820°C	886.1	1037.7	3553
Bi$_{2.17}$SCCO Calcined at 830°C	886.1	872.5	3430

The doped samples were not run due to contamination that occurred during the mixing process. The source of contamination was identified and the process has been modified to prevent it in the future, however there was not enough time to prepare and evaluate samples under this Phase I project. The doped samples will be evaluated during the proposed Phase II of the present project.

Fig 10 J_c Vs Melt Temperature Measured at 4.2K Self Field



As can be seen by examining Table 3, the calcining temperature does have a slight effect on the J_c of tapes prepared with Bi-2212 powders. The calcining temperature also has an effect on the melt processing range of the tapes with the lower calcining temperature providing the widest window of processing as shown by the data collected for the $Bi_{2.17}SCCO$ sample prepared with powder calcined at 790ºC. The powders produce at higher temperature exhibited a much smaller processing window which is defined at the temperature range where the difference between the J_c of a particular melt temperature is greater than 90% of the peak J_c.

A much more significant effect on Jc was the Bi content of the powders. The peak J_c for the $Bi_{2.05}SCCO$ powder was 17% greater than the peak J_c for the $Bi_{2.17}SCCO$ powder. Due to previous experience at OST, the $Bi_{2.17}SCCO$ composition was chosen for wire fabrication. This composition was shown in reference X to produce the best Jc values using Nexans precursor, and due to the urgency of the new VHFSMC program OST aimed to compare results using SCI precursor with the foreign sourced material. Since the powder calcined at 820ºC exhibited the highest J_c in dip coated tape, it was selected for use in Task III for preparation of Bi-2212/Ag composite multifilamentary round wires.

Task III: Preparation and Evaluation of Composite Multifilamentary Round Wires

The powders produced in Task II were used to fabricate two multifilament Bi-2212/Ag composite round wires using the OST thermomechanical process. A schematic of the process is shown in Fig. 11.

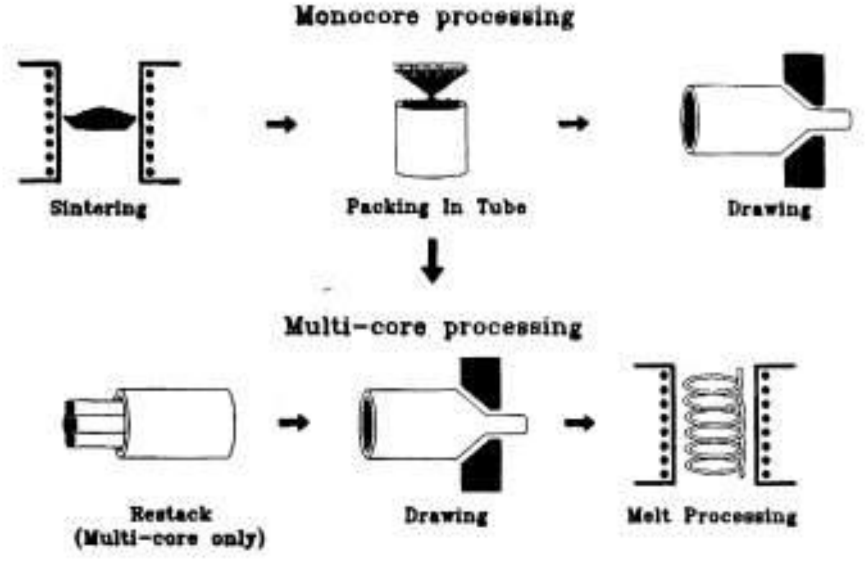


Figure 11: Schematic of the OST Thermomechanical Process for Fabricating Multifilament BSCCO-2212/Ag Composite Wires

Powder prepared by SCI was introduced into Ag billets at OST to form Bi-2212/Ag composite monofilaments. The processing schedule developed at OST takes into account the strength ratios of the silver and BSCCO as well as the percent reduction and the inner to outer radii of the silver tube. Careful consideration and optimization of these parameters allows fabrication of composites with uniform cross-section. After drawing through a series of round dies, the Bi-2212 monofilaments were cut and stacked into another silver tube. The multifilament billets after assembly were processed through a similar series of reduction schedules to final wire diameters of 1.3-1.5 mm. Both billets were drawn 100 meter lengths without any breaks. Both billets used the same powder lot, the Bi-2.17 composition, since OST desired to compare results with those for the best Nexans precursor. The billets were designated PMM081029 and PMM081210. Figure 12 compares cross-sections of the two wires at final size.

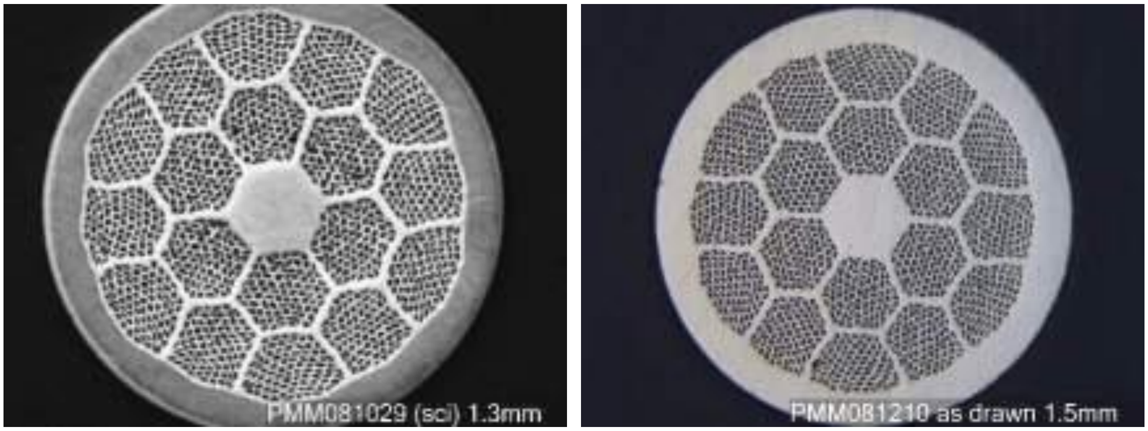


Fig. 12 Cross-section view of both wires in final size.

The multifilamentary wires were cut into shorter lengths and used to fabricate 1 meter barrel shaped coils. The coils were used to perform the partial melt process optimization trials.

A sample of wire PMM081210 was sent to SCI for DTA analysis along with a sample of wire produced with a $B_{2.17}$SCCO powder supplied by Nexans for comparison. The heating and cooling behaviors of both samples are summarized in Fig. 13 and 44 below:

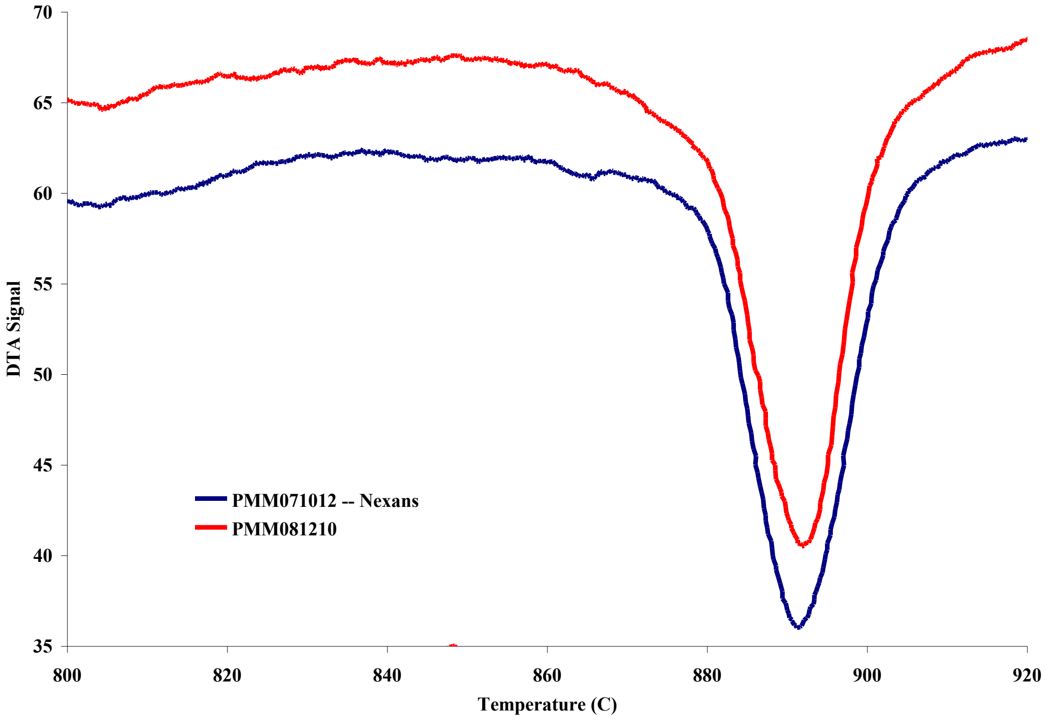


Fig. 13: DTA Heating Curve for $Bi_{2.17}SCCO/Ag$ Composite Wire

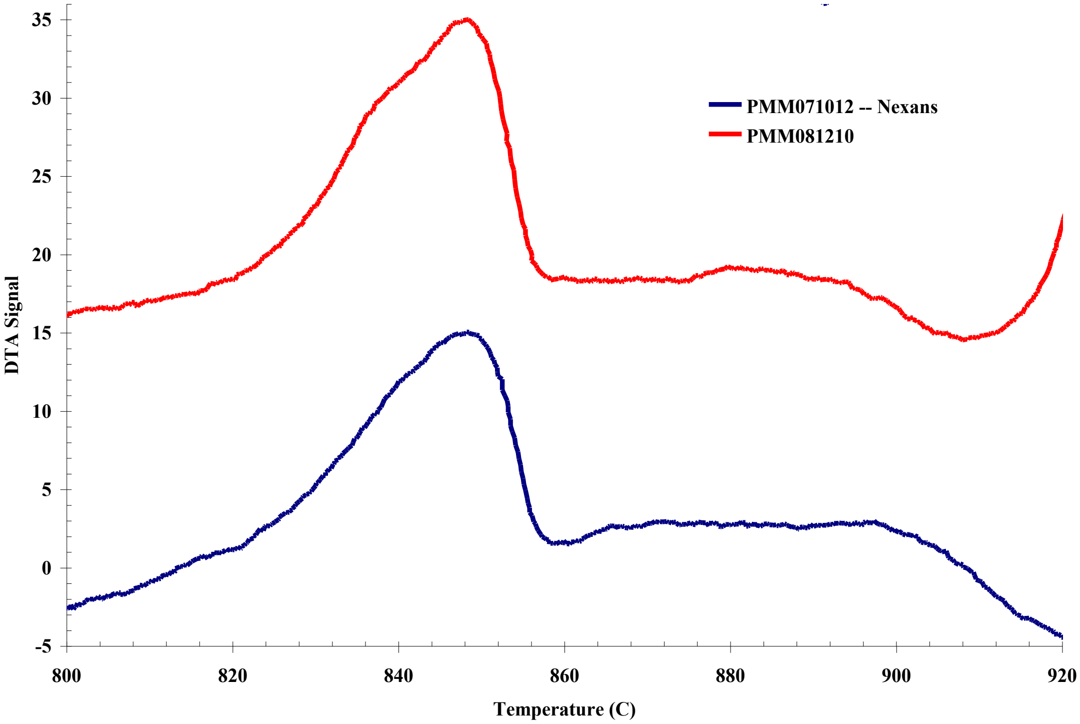


Fig. 14: DTA Cooling Curve for $Bi_{2.17}SCCO/Ag$ Composite Wire

As can be seen in the figures, there is not much difference between the melting and cooling characteristics of both wire samples and the melting points are around the optimum processing temperature for the wires (data shown below).

After fabrication, the coils were evaluated for J_c, I_c, and J_E at 4.2K in a magnetic field of 12T. The results of the coil evaluation are presented below in Table 4 and Fig. 15:

Table 4: Results comparison for the two wires fabricated and characterized at OST

Billet No.	**PMM081029**	**PMM081210**
Powder Lot Nominal composition	P08-0082, calcined @820°C 2.17:1.94:0.89:2.00	P08-0082, calcined @820°C 2.17:1.94:0.89:2.00
Fill factor		
Packed density (%)	34.8	36.0
85x18 wire at final size (%)	27.5	28.0
Cross-section		
Final wire size (mm)	**1.30**	**1.50**
Characterization		
Peak Avg. Ic (A, 4.2K & 12T)	**247**	**335**
Peak J_E (A/mm^2, 4.2K&12T)	186	190
Peak Jc (A/mm^2, 4.2K&12T)	676	679

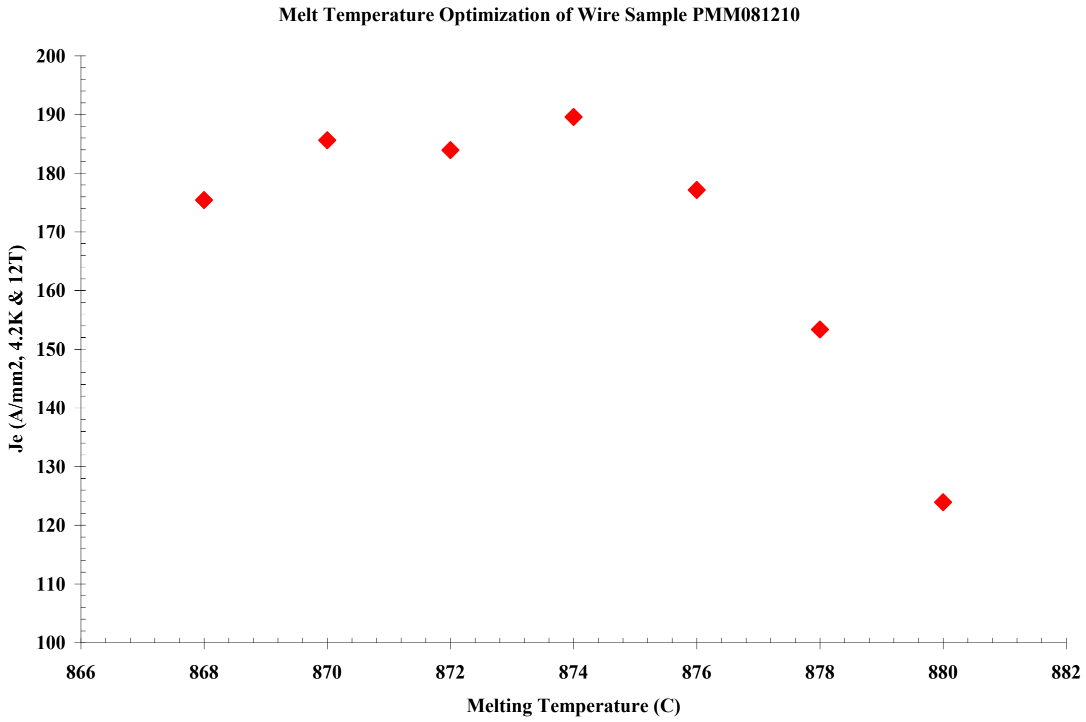


Fig. 15: Summary of Melt Temperature Optimization of Coil Sample PMM081210

Fig 16: Barrel coil samples illustrating the elimination of leakage during processing

As shown in the data, the peak J_E of the coil was 190 A/mm^2 at 4.2K and 12T in contrast to a previous result which was 500 A/mm^2. The reason for the reduced J_E was the wire fabrication process modification at OST that was implemented to eliminate sheath leakage during the partial melt process. Fig. 16 shows two coils, one that was processed using the older OST process and one prepared with the new process. As can be seen in the figure, the leakage problem has been remarkably reduced using the new process, but at the expense of the reduced Jc and J_E values.

The microstructure of the wire samples was characterized using SEM and EDS at LANL. Fig. 17 compares the filament structures formed in the two wires after reaction. Table 5 compares the average cation ratios for the Bi-2212 filaments in the two reacted wires, as determined by quantitative EDS analysis in the SEM, using a stoichiometric Bi-2212 glass standard. The composition after reaction tracks fairly closely the precursor composition.

Table 5: Average cation ratios determined for the Bi-2212 filaments in the two wire

Billet No.	Sr	Bi	Ca	Cu
PMM081029	1.91	2.17	0.94	1.96
PMM081210	1.93	2.20	0.93	1.93

a)

b)

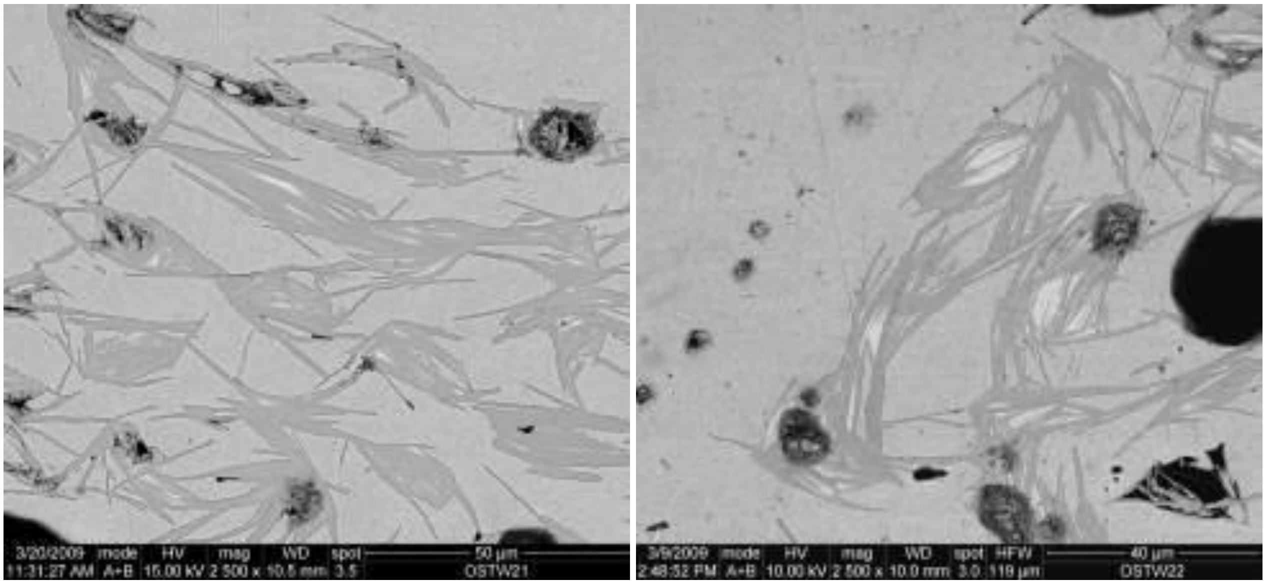


Fig 17: Reacted filament structures for the two billets: a) PMM081029 and b) PMM081210

Phase I Conclusions

- J_E values at 4.2K & 12T for billets PMM081210 and PMM081029, processed in a leak-free process, are approximately 200 A/mm^2, which is acceptable for cable and coil applications.
- The calcining temperature has a direct impact on precursor powder tap density and carbon content.
- The starting powder compositions and characteristics have some impact on tape process condition and J_E performance.
- These J_E values are below those previously reported due to changes in the wire architecture and processing that have significantly reduced melt leakage.
- A comparison made in this study shows that the Ic/Je values of the wires made of Nexans and SCI precursor powders by same process have <15% in difference.
- There is good reason to believe, based on previous studies with Nexans precursor, that optimization of the starting composition in SCI precursor may lead to improvements in Jc.

d. Proposed Phase II Effort

Technical Objectives

As described in the background information, recent efforts at OST have focused on responding to urgent pushback from their HEP partners that are making cables and coils using the Bi-2212 round wire. The primary focus over the last year was on reducing or eliminating leakage of the melt by changing the wire production process. A secondary focus was on comparing the U.S. manufactured SCI precursor with the more intensively studied Nexans precursor from Germany. These efforts did necessitate revising the initial plan of this Phase I effort. It must be said that dramatic success was demonstrated at reducing leakage, however, these changes reduced Jc performance significantly. Given the new HEP sponsored VHFSMC program needs of substantial quantities of leak-free wire that uses precursor manufactured in the U.S., we are proposing a Phase II powder development effort that directly addresses these urgent needs of the HEP community.

There are two urgent priorities today that will serve as the technical objectives of the proposed Phase II program. The first is the identification of a precursor composition made by SCI's chemical method that is optimized for OST wire in the new configuration and modified leak-free process. The goal is to achieve J_c performance in leak free, practical conductor that is closer to the very high performance achieved in past strand, where J_c was the only performance criteria. To restore J_c performance lost through wire processing is very critical for the VHFSMC program. A systematic study of precursor composition on J_c has never been made for SCI powder in wire; however based on literature reports and coincidental data gleaned from other studies and reported below, starting composition is likely to have the largest effect on J_c of any presently controllable factors.

The second priority is a change in powder phase purity and particle size that reduces surface area and thus the potential for adsorbed carbon. Secondary phase and C contamination (in the form of CO_2) are detrimental to J_c improvement. Moreover, the carbonate can evolve CO_2 during melt processing, causing internal pressure in the wire and potentially contributing to leaking. We have shown in this Phase I work that the calcining temperature can be used to increase powder phase purity.

These objectives will be achieved through the completion of the following tasks:

Task I: Powder Synthesis

Task I of the proposed Phase II project will be to synthesize a number of precursor powder compositions. Holesinger previously examined a wide range of Bi-2212 precursor compositions (Physica C, 217, 85, 1993). His work demonstrated several key concepts: there is a wide range of precursor compositions that resulted in single phase 2212; the solid solution 2212 region depends on both oxygen partial pressure and temperature; the stability of the solid solution region depends strongly on the Sr/Ca ration, with the Sr-rich end of the solid solution the most stable region. These concepts were previously used to select a range of starting compositions in Nexans precursor for comparison in OST wire; a study which resulted in substantial increases in round wire Jc (Miao et al, *Adv. Cryog. Eng*. V52, 673, 2006). Based on the success of OST work, we propose using a range of starting compositions for comparison in OST wire. Moreover, OST wire results using SCI powders with different compositions presented in table 8 indicate that the powder composition has also strong impact on wire performance. We also note that the optimum composition may be different from that which is successful for the Nexans precursor, a difference likely due to the very different powder production methods. Selection of actual compositions would be preceded by an updated literature study to confirm most likely cation ratios for high Jc in wire. Additional work since the Holesinger and Miao studies has been done by Showa Electric and Nexans. Task I will be performed by SCI and will be completed during the first quarter of the proposed project.

Task II: Optimization of Precursor Phase Purity and Tap Density

After a range of compositions has been selected and the precursor synthesized by SCI in Task I, BSCCO-2212 powder phase purity and tap density will be optimized at SCI through appropriate calcination. These precursors will be characterized by DTA for onset of melting and crystallization, by ICP for stoichiometry, and by XRD for phase purity. The powders will be supplied to OST for wire fabrication. Task II will be performed by SCI and will be completed during the first quarter of the proposed project.

Task III: Wire Manufacture

Using powder supplied by SCI from Task II, Bi-2212/Ag round wires will be manufactured by OST using a powder-in-tube process. In brief, a silver tube will be filled with Bi-2212 precursor powder, drawn to a specified size and cut into pre-determined lengths. 85 monocore elements with such lengths will be bundled and stacked into another silver tube, drawn to a specified size and cut once again into predetermined lengths. Seven such lengths will be bundled and restacked into AgMg alloy tube and drawn to final size.

Table 6. J_c results in wires made from various SCI powder compositions

Nominal composition	Bi	Sr	Ca	Cu	Sr/Ca	Bi/Ca	Je (A/mm2)	Jc (A/mm2)
Bi2.20Sr2.00Ca1.00Cu2.00Ag0.1Ox	2.2	2.0	1.0	2.0	2.00	2.20	810	3682
Bi2.05Sr1.74Ca1.22Cu1.95Ox	2.05	1.74	1.22	1.95	1.43	1.68	472	1851
Bi2.18Sr1.90Ca0.84Cu2.08Ox	2.18	1.9	0.84	2.08	2.26	2.60	902	3341
Bi2.10Sr2.08Ca1.08Cu1.98Ox	2.1	2.08	1.08	1.98	1.93	1.94	736	3286
Bi2.15Sr1.97Ca1.01Cu1.98Ox	2.15	1.97	1.01	1.98	1.95	2.13	1141	5117
Bi2.16Sr1.96Ca1.05Cu1.99Ox	2.16	1.96	1.05	1.99	1.87	2.06	900	3689
Bi2.06Sr2.04Ca0.87Cu2.03Ox	2.06	2.04	0.87	2.03	2.34	2.37	979	4184
Bi2.05Sr1.91Ca0.91Cu1.99Ag0.1Ox	2.05	1.91	0.91	1.99	2.10	2.25	1314	5113
Modified process								
Bi2.02Sr1.98Ca0.90Cu1.95Ag0.1Ox	2.02	1.98	0.9	1.95	2.20	2.24	1019	3919

Table 6 is a summary of Bi-2212 performance in OST wires made from SCI powders over the past several years, showing several nominal precursor compositions tried. From the table, it is clearly observed that variations in the cation ratios in the starting precursors (including cation stoichiometry, impurity levels, and starting phase assemblage) have greatly affected the performance of the Bi-2212/Ag wires made from SCI powder. Note that these compiled results do not represent a systematic study of composition, but are results gleaned from a range of wires intended to study other factors.

Although not well understood, the microstructure corresponding to Bi-2212 wires' Jc/J_E values, when each composition wire is given its Jc/J_E-optimization heat treatment, is evidently controlled to a great extent by the starting powder composition. As shown in Figure 18, significant differences (including porosity, grain alignment, and non-superconducting phases) are observed in transverse cross-section filament structures in between wires with different compositions. Similar differences were observed with Nexans precursor starting compositions [6].

After many years of work on Bi-2212 wires from SCI powders, as shown in the Figures 19 and 20, the trends in Jc vs. starting powder composition in Bi-2212 round wire suggests that the optimum area of the cation ratios in the starting precursors for round wires is Bi/Ca ratio of 2.1 to 2.3 and Sr/Ca ration of 1.8 to 2.4.

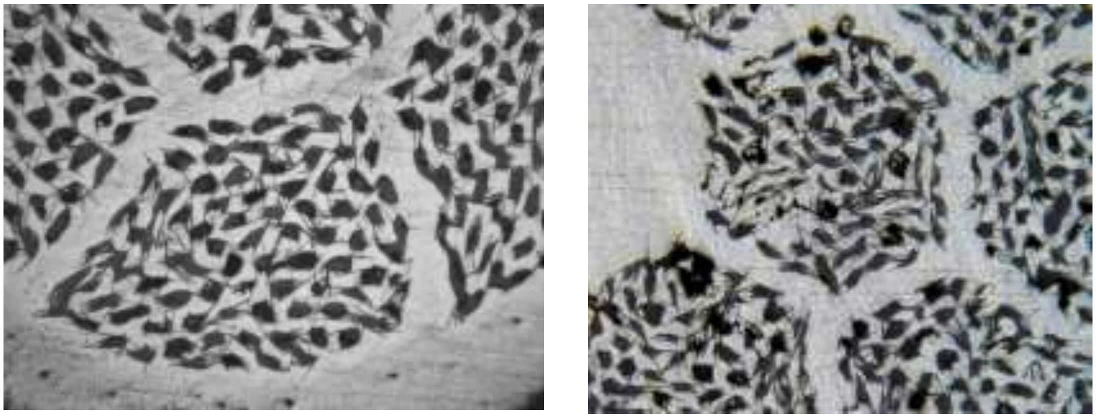


Fig. 18: Transverse cross-sections of reacted filament structure in Bi-2212 wires with two compositions: Bi2.05Sr1.91Ca0.91Cu1.99Ag0.1Ox (L) and Bi2.10Sr2.08Ca1.08Cu1.98Ox (R).

The overall objective of the proposed Phase II project is to determine the most suitable precursor composition for fabricating fine filament wires. To this end, we propose a preliminary plan for three different cation stoichiometries (see Table 7) with different Sr/Ca ratios, e.g. nominal composition Bi:Sr:Ca:Cu = 2.10:x:3-(x+Ca):1.99. This preliminary selection is based on previous experiments and experience with SCI precursor in OST wire. Figures 19 and 20 present a summary of J_c data gleaned from these wires as a function of precursor Sr/Ca ratio (Fig. 19) and Bi/Ca ratio (Fig. 20).

Table 7: Three precursor compositions with varying Sr/Ca

Bi	Sr	Ca	Cu	Sr/Ca
2.10	2.05	0.90	1.99	2.31
2.10	1.95	0.95	1.99	2.12
2.10	1.85	1.00	1.99	1.98

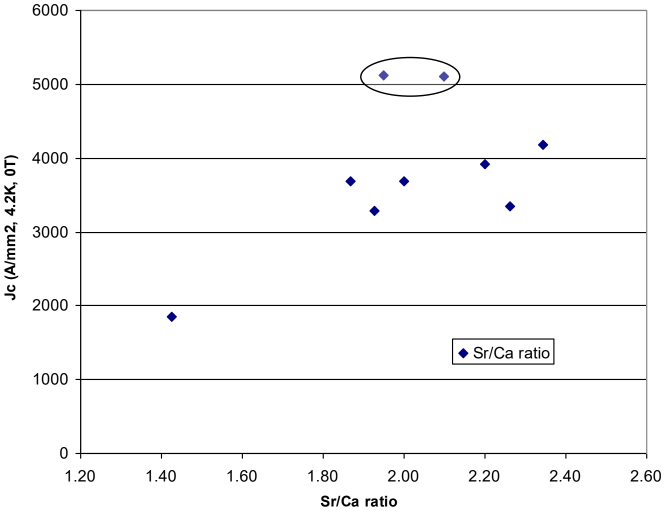


Figure 19 J_c vs. Sr/Ca ratio in OST Bi-2212 wires made from SCI powders.

Task III will be performed by OST and will be completed during the fourth quarter of the proposed Phase II project.

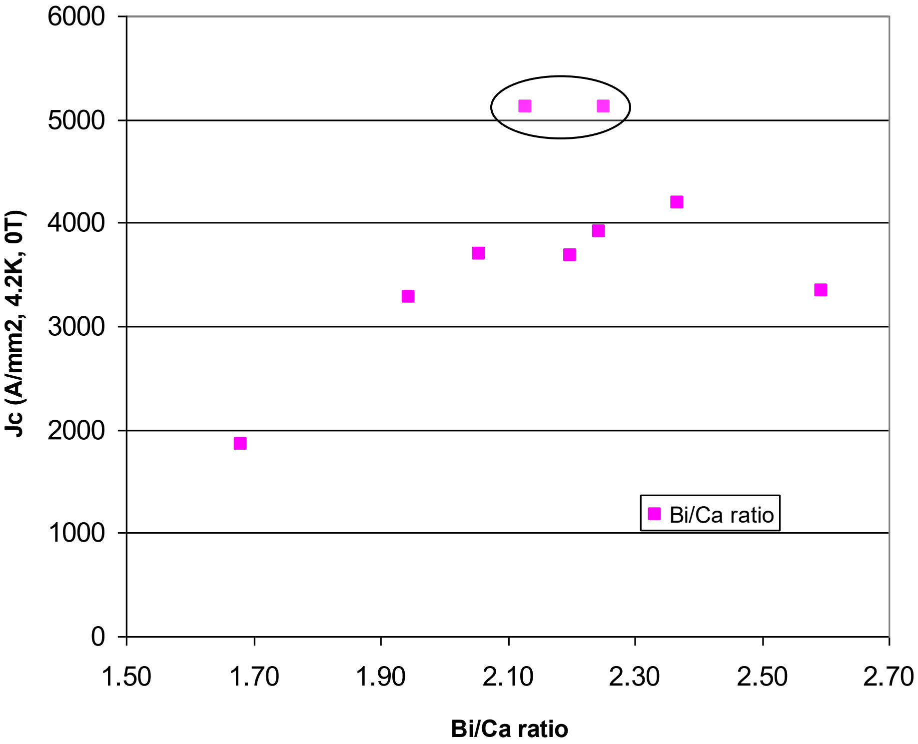


Figure 20 J_c vs. Bi/Ca ratio in OST Bi-2212 wires made from SCI powders.

Task IV: Statistically Designed Heat Treatment Matrix

A key to successful optimization of composition will be a determination of the appropriate heat treatment for each composition. Bi-2212/Ag wires are heat treated in a flowing oxygen atmosphere using a partial melt-solidification process, with the general profile shown in Figure 21, where T_m and T_a are melting and annealing temperatures, R_c are the various cooling rates, and T_{cr} is the temperature at which the cooling rate is changed. Previous procedure for optimizing J_c and J_E in a billet was to choose a schedule (heating and cooling rates, melting and annealing temperatures and dwell times), then run a series of samples with this schedule with varying T_m, which has the most substantial influence on microstructure and hence current density. However, R_c, T_a and anneal time (t_a) can also affect J_c. For this study we will use a statistically designed experiment (SDE) with these 4 factors and several levels of each in an effort to further optimize the heat treatment profile for best current density. Table 8 shows the SDE, which is a low resolution Taguchi L8 matrix modified to include one four-level factor (T_m). T_{sm} and T_{ss} are the melting and solidification onset temperatures as determined by DTA. Since each precursor composition has different T_{sm} and T_{ss}, the wire billets made from the four precursors in Table 7 each will have a unique SDE (a total minimum 32 heat treatments), and each will have a different optimum heat treatment profile which gives maximum J_c for that precursor composition.

This task will include making the SDE HT matrix specific for each precursor composition based on the DTA data acquired in Task 1, which will give T_{sm} and T_{ss}; heat treatment at OST of

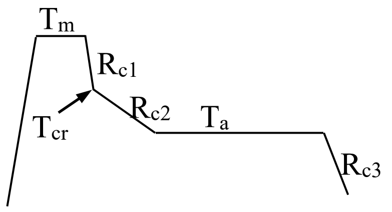


Figure 21 Schematic heat treatment profile.

Table 8 SDE heat treatment matrix.

Factors:	T_m (°C)	R_{c2} (°C/m)	T_a (°C)	t_a (hr.)
Trial 1	T_{sm}	2.5	T_{ss}-30	20
Trial 2	T_{sm}	6	T_{ss}-5	80
Trial 3	T_{sm}+2	2.5	T_{ss}-30	80
Trial 4	T_{sm}+2	6	T_{ss}-5	20
Trial 5	T_{sm}+4	2.5	T_{ss}-5	20
Trial 6	T_{sm}+4	6	T_{ss}-30	80
Trial 7	T_{sm}+7	2.5	T_{ss}-5	80
Trial 8	T_{sm}+7	6	T_{ss}-30	20

multiple short straight samples of wire from each billet according to the matrix; analysis by OST in collaboration with LANL of the Taguchi metric (J_c) results which will identify the relative importance of each of the SDE factors in determining J_c; and repeating at OST the most successful heat treatments in 1 meter long barrel samples for a higher sensitivity determination of I_c, J_c and J_E in wires from each starting composition. Task IV will be performed by OST and will be completed during the second quarter of year 2 of the proposed project.

Task V: I_c, J_c and J_E Measurements

OST will measure I_c in multiple (4 to 6) short samples from each of the 32 SDE trials described above and obtain an average I_c result for each trial. Despite efforts to keep nominally the same wire architecture, there may be differences in the final diameter and ceramic fraction in each final wire due to possible variations in dies, particle size distribution and tap density. So in order to make the most consistent comparisons between billets and precursor compositions, OST will measure final wire diameters and ceramic fractions for each wire in order to accurately determine Jc and J_E. These short sample measurements will provide the data for analysis of the Taguchi matrix described in Task IV.

After the best trials (heat treatment parameters) are determined, these heat treatments will be repeated with 1 meter long wire samples wound on heat treatment barrels and a more sensitive determination of I_c, J_c and J_E will be made. Task VI will be completed during the third quarter of year two of the proposed Phase II project.

Task VI: Microstructure, Microchemistry, and Structure-Property Correlations

The best wires from each starting composition will be selected for microstructural study at LANL. SEM will be used to examine reacted filament size and morphology. EDS analysis will measure the average 2212 composition in the reacted filaments and the range and distribution of final composition. SEM plus EDS will also be used to characterize second phase regions in the final reacted wire cross sections. TEM will be used for a higher resolution study of reacted filament morphology and composition.

The aim of this task is to understand the relationship between J_c and the filament structure and chemistry. Understanding of these correlations is expected to provide a basis for continued improvements in J_c. Task VII will be completed during the third quarter of year two of the proposed Phase II project.

Task VII: Wire Deliveries

The ultimate goal of this proposed effort is to provide high performance, homogenous lengths of wire to the U.S. collaborative VHFSCM program. If we succeed in achieving useful lengths of wire in these trials, the intention is to deliver the wire to this program for use in coil and cable development. Task VII will be completed during the fourth quarter of year 2 of the proposed Phase II project.

Performance Schedule

The schedule for the completion of the proposed Phase II project is summarized in the Gantt Chart below:

Tasks	**1Q1**	**1Q2**	**1Q3**	**1Q4**	**2Q1**	**2Q2**	**2Q3**	**2Q4**
Task I: Powder Synthesis	X							
Task II: Precursor Optimization		X						
Task III: Wire Manufacture				X				
Task IV: Heat Treatment SDE						X		
Task V: I_c, J_c, J_E, Measurement							X	
Task VI: Microstructure							X	
Task VII: Wire Deliveries								X

d. Phase II Final Report

The final report for this Phase II effort will be presented in a task by task format.

Task I: Powder Synthesis

Under Task I of the project, a series of BSCCO powders were prepared with varying Sr/Ca ratios to determine the effect of the Sr/Ca ratio on the superconducting properties of BSCCO materials. A summary of the chemical analysis (ICP) of the five powders prepared for this study are provide in Table 9 below:

Powder Lot No.	**Composition (Analytical data)**				
	Bi	**Sr**	**Ca**	**Cu**	**Sr/Ca Ratio**
P10-0008	2.16	1.82	1.12	1.90	1.62
P10-0009	2.17	1.94	0.97	1.92	2.00
P10-0010	2.18	1.92	1.00	1.90	1.92
P10-0011	2.17	1.98	0.92	1.93	2.15
P10-0012	2.18	2.04	0.88	1.90	2.32

Table 9: Summary of the ICP Analysis of Compositions with Varying Sr/Ca Ratios

The powders were sent to OST for dip-tape evaluation of superconducting properties. OST's report is provided below:

Summary of tape evaluation for SCI BSCCO powders with varying Sr/Ca Ratios

The overall objective of the dip-tape evaluation is to determine the most suitable precursor composition for fabricating Bi-2212 tapes/wires.

Experimental detail

1) SCI provided 5 precursor powders with varying Sr/Ca ratio and fixing Bi~2.17 and Cu ~1.90 (see Table 1 for detail).
2) Each >20m dip-coated tape was made from 5 powders, following a well-established procedure at OST.
3) Multiple samples were heat treated at 8 different melting temperatures and a peak Jc was determined.
4) The tape samples exhibiting the best superconducting properties from each powder sent to LANL for SEM studies.

Results and discussion

Table 10, shown below, summarizes all the data collected during the evaluation of the tapes produced with powder compositions of varying Sr/Ca ratio. Figure 1 shows a comparison of all Jc results on dip coated tapes heat treated in a range of melting process temperatures.

Powder Lot No.	Composition (Analytical data)					Peak T_m (°C)	Avg. Peak
	Bi	Sr	Ca	Cu	Sr/Ca ratio	Dip-coating tape	J_c (A/mm^2)
P10-0008	2.16	1.82	1.12	1.90	1.62	890.8	1895
P10-0009	2.17	1.94	0.97	1.92	2.00	886.7	3854
P10-0010	2.18	1.92	1.00	1.90	1.92	886.7	3358
P10-0011	2.17	1.98	0.92	1.93	2.15	886.7	3950
P10-0012	2.18	2.04	0.88	1.90	2.32	884.9	3591

Table : 10 Summary of powder lots, composition and peak Tm and J_c in dip-coated tapes

The results indicate that the highest Jc value of (~3900A/mm^2) is obtained in the powder compositions with the Sr/Ca ratio of 2.00~2.15. The Jc value in powder P10-0011 is 15~20% higher than that of Nexans powder (#521), both having the similar composition. It is also observed that the Sr/Ca ratio >2.15 leads to lower melting process temperature. Fig. 2 is clearly showing the peak Jc vs Sr/Ca ratio in this work.

Fig. 3 summarizes that peak Jc values and delta Tm windows for 10% off peak Jc value for all powders. The powder P10-0011 with best Jc performance has a reasonable melt processing window of ~6°C.

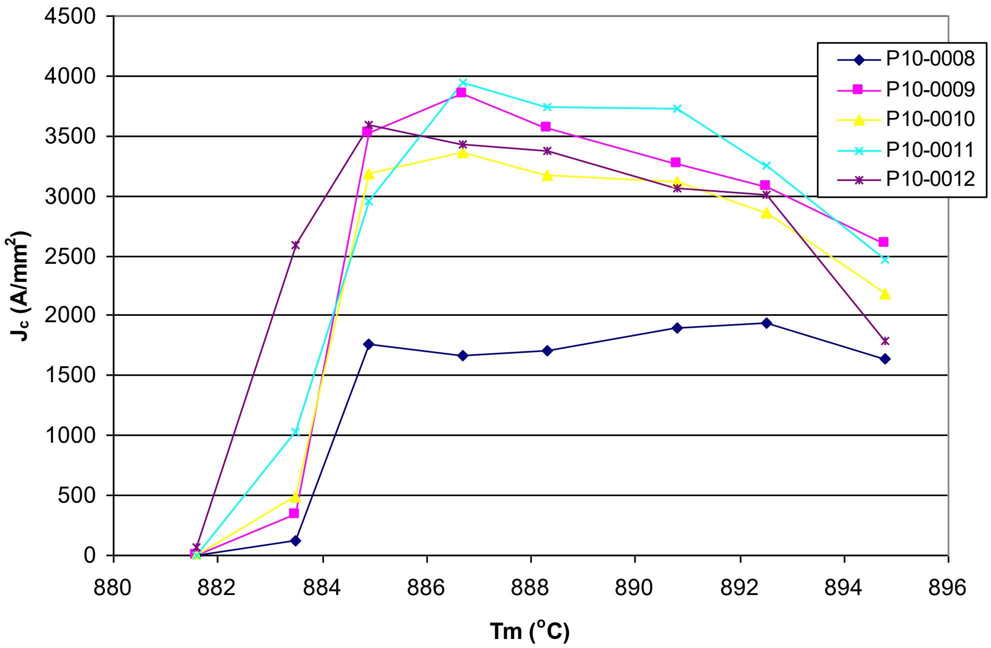


Fig. 22: J_c-T_m optimization curves for 5 powder lots with the composition listed at Table 1

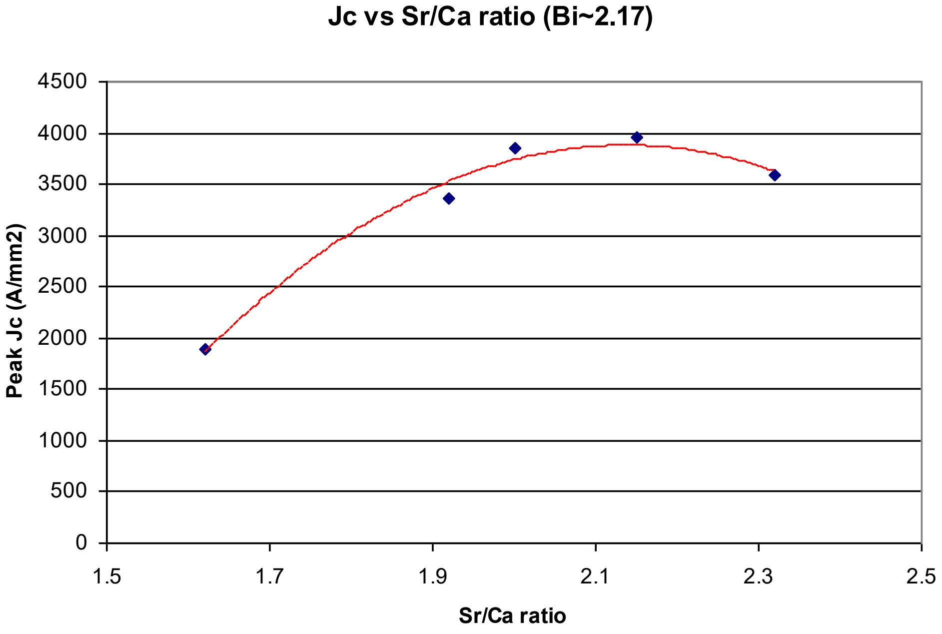


Fig. 23: J_c vs Sr/Ca ratio of different powder lots

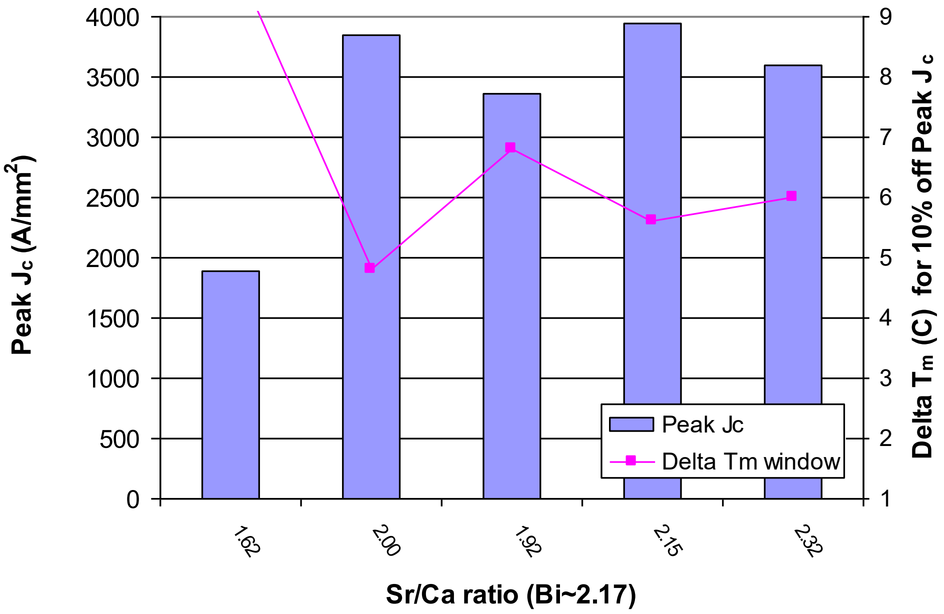


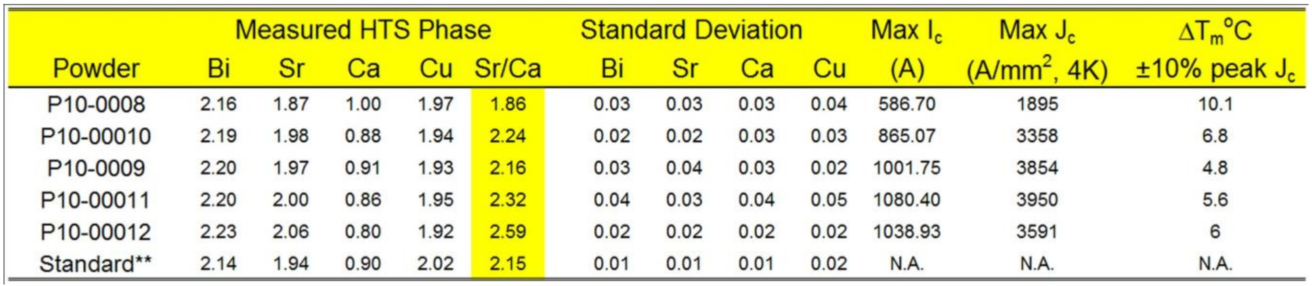
Fig. 24: Peak J_c-and delta Tm window for 10%off peak Jc for dip-coated tapes

Conclusions

- Precursor powder composition has a significant effect on tape J_c performance.
- The highest Jc value of (~3900A/mm^2) is obtained in the powder composition $Bi_{2.17}Sr_{1.98}Ca_{0.92}Cu_{1.93}O_x$ with the Sr/Ca ratio of ~2.15.
- The Jc value in powder P10-0011 is 15~20% higher than that of Nexans powder (#521) in the same heat treatment condition, both having the similar composition.
- The higher Sr/Ca ratio (>2.15) may lead to lower melting process temperature.
- The powder P10-0011 with best Jc performance has a reasonable melt processing window of ~6°C.

LANL performed SEM characterization of the dip-coated tapes and provided the following results.

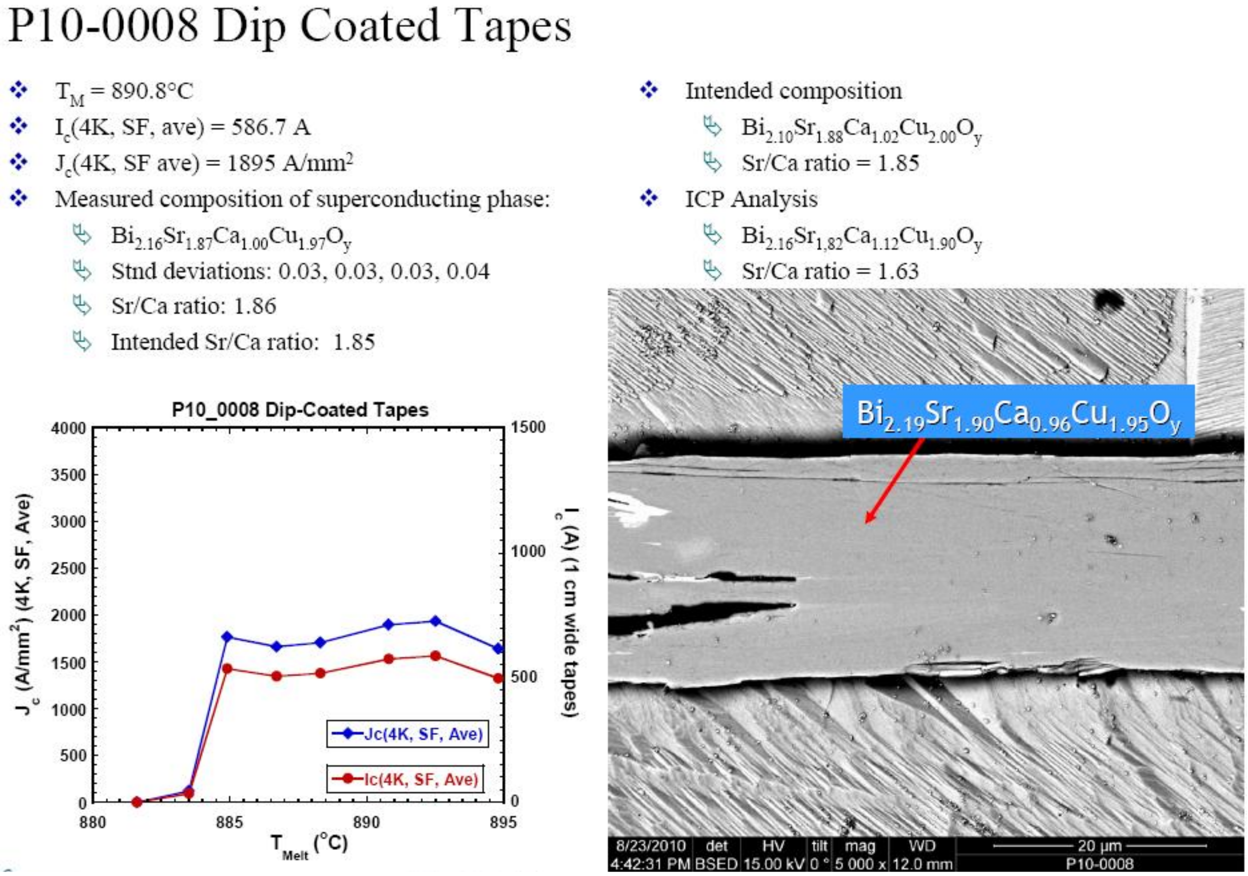
Table 11 below provides a summary of the EDS measurements on the high temperature superconducting phase found in the dip coated tapes for each BSCCO powder composition prepared in Task I.



	Measured HTS Phase					Standard Deviation				Max I_c	Max J_c	ΔT_m°C
Powder	Bi	Sr	Ca	Cu	Sr/Ca	Bi	Sr	Ca	Cu	(A)	(A/mm^2, 4K)	±10% peak J_c
P10-0008	2.16	1.87	1.00	1.97	1.86	0.03	0.03	0.03	0.04	586.70	1895	10.1
P10-00010	2.19	1.98	0.88	1.94	2.24	0.02	0.02	0.03	0.03	865.07	3358	6.8
P10-0009	2.20	1.97	0.91	1.93	2.16	0.03	0.04	0.03	0.02	1001.75	3854	4.8
P10-00011	2.20	2.00	0.86	1.95	2.32	0.04	0.03	0.04	0.05	1080.40	3950	5.6
P10-00012	2.23	2.06	0.80	1.92	2.59	0.02	0.02	0.02	0.02	1038.93	3591	6
Standard**	2.14	1.94	0.90	2.02	2.15	0.01	0.01	0.01	0.02	N.A.	N.A.	N.A.

Table 11: Composition of HTS Phases Found in BSCCO Dip-Coated Tapes

A summary of the SEM analysis for each composition is provided below:

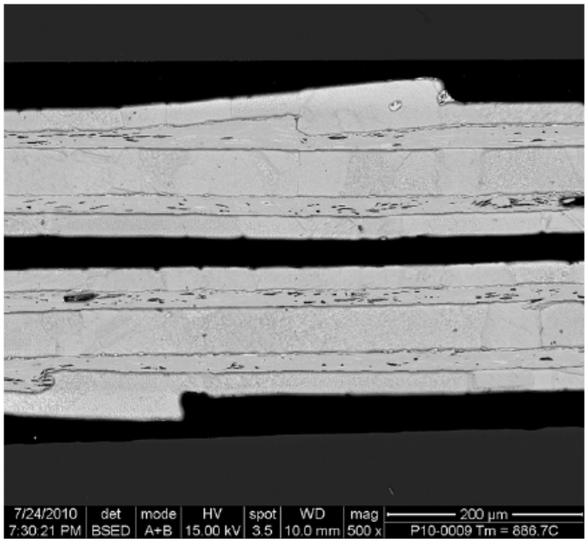


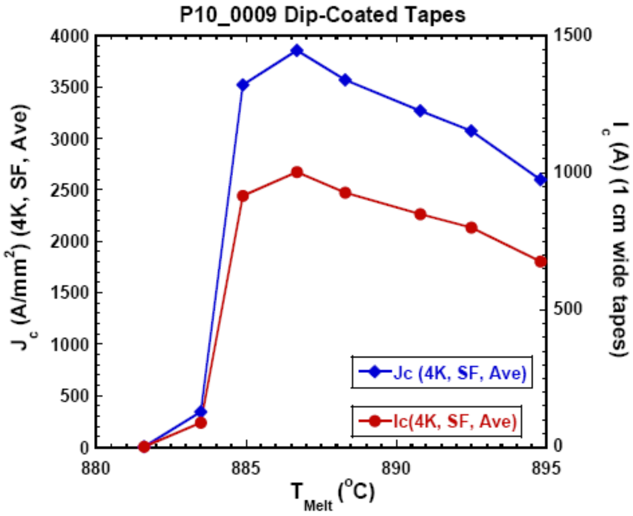
P10-0008 Dip Coated Tapes

- T_M = 890.8°C
- I_c(4K, SF, ave) = 586.7 A
- J_c(4K, SF ave) = 1895 A/mm^2
- Measured composition of superconducting phase:
  - $Bi_{2.16}Sr_{1.87}Ca_{1.00}Cu_{1.97}O_y$
  - Stnd deviations: 0.03, 0.03, 0.03, 0.04
  - Sr/Ca ratio: 1.86
  - Intended Sr/Ca ratio: 1.85
- Intended composition
  - $Bi_{2.10}Sr_{1.88}Ca_{1.02}Cu_{2.00}O_y$
  - Sr/Ca ratio = 1.85
- ICP Analysis
  - $Bi_{2.16}Sr_{1.82}Ca_{1.12}Cu_{1.90}O_y$
  - Sr/Ca ratio = 1.63

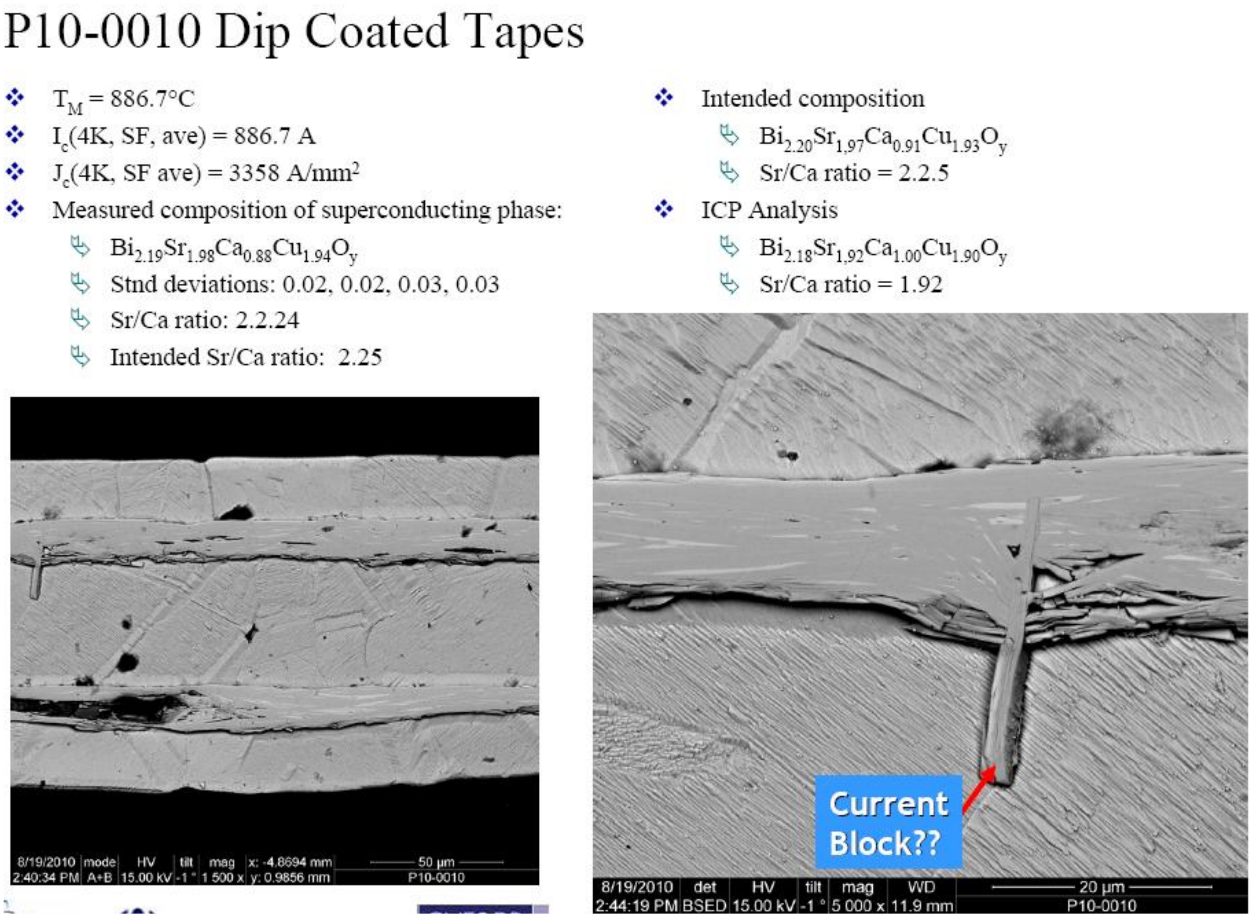
P10-0009 Dip-Coated Tape

- $T_M = 886.7°C$
- I_c(4K, SF, ave) = 1001.8 A
- J_c(4K, SF ave) = 3854.3 A/mm^2
- Measured composition of superconducting phase:
    - $Bi_{2.20}Sr_{1,97}Ca_{0.91}Cu_{1.93}O_y$
    - Stnd deviations: 0.03, 0.04, 0.03, 0.02
    - Sr/Ca ratio: 2.16
    - Intended Sr/Ca ratio: 2.0





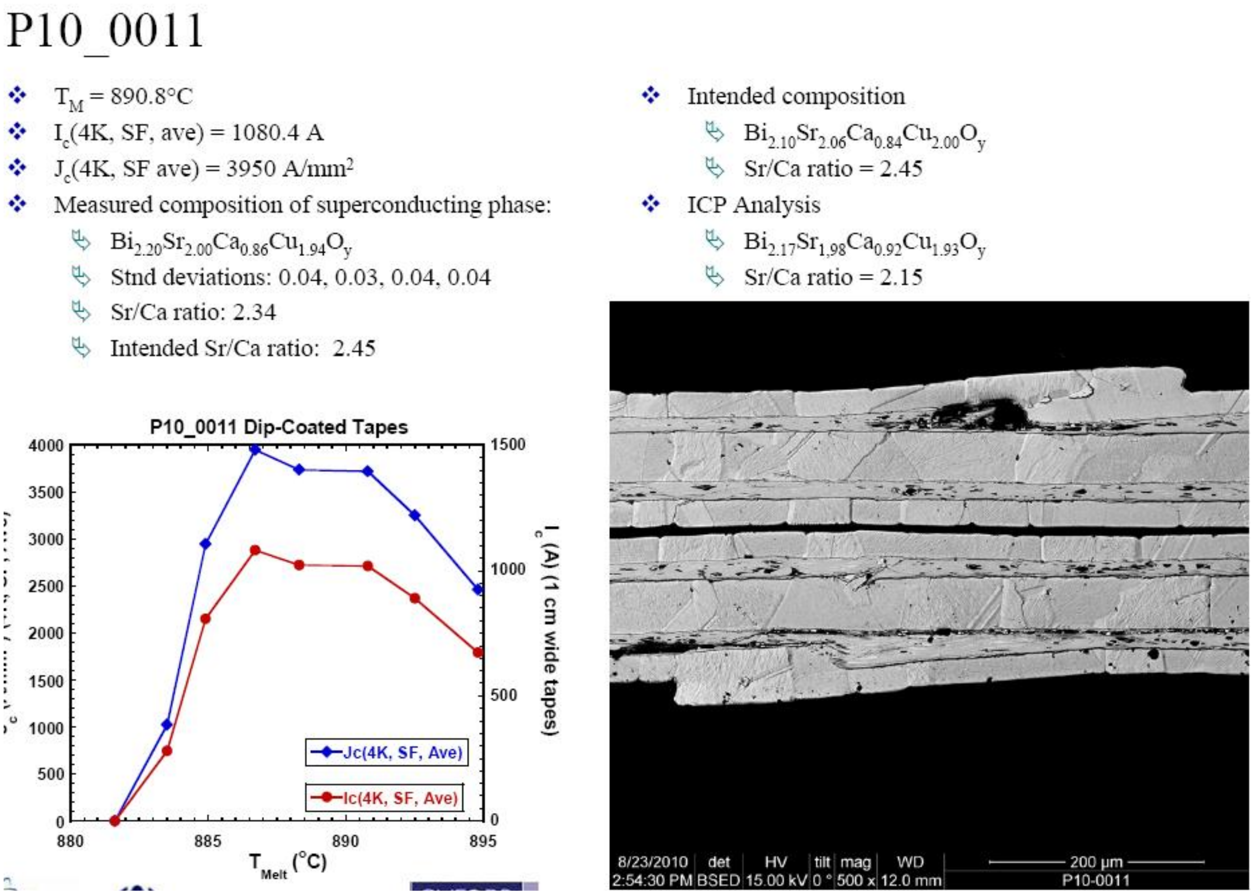
- Intergrowths of Bi-2210
- Cu-free and AEC secondary phases.
- Some of the dark spots are pores caused by the etching process that removes silver from within the BSCCO layers.



P10-0010 Dip Coated Tapes

- T_M = 886.7°C
- I_c(4K, SF, ave) = 886.7 A
- J_c(4K, SF ave) = 3358 A/mm^2
- Measured composition of superconducting phase:
  - $Bi_{2.19}Sr_{1.98}Ca_{0.88}Cu_{1.94}O_y$
  - Stnd deviations: 0.02, 0.02, 0.03, 0.03
  - Sr/Ca ratio: 2.2.24
  - Intended Sr/Ca ratio: 2.25
- Intended composition
  - $Bi_{2.20}Sr_{1,97}Ca_{0.91}Cu_{1.93}O_y$
  - Sr/Ca ratio = 2.2.5
- ICP Analysis
  - $Bi_{2.18}Sr_{1,92}Ca_{1.00}Cu_{1.90}O_y$
  - Sr/Ca ratio = 1.92

Current Block??

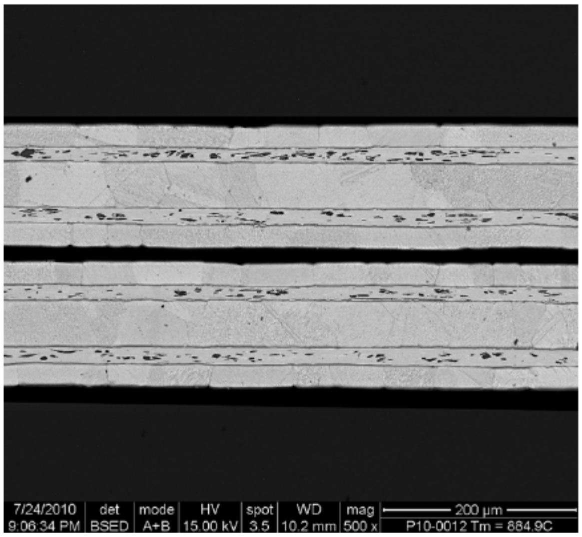


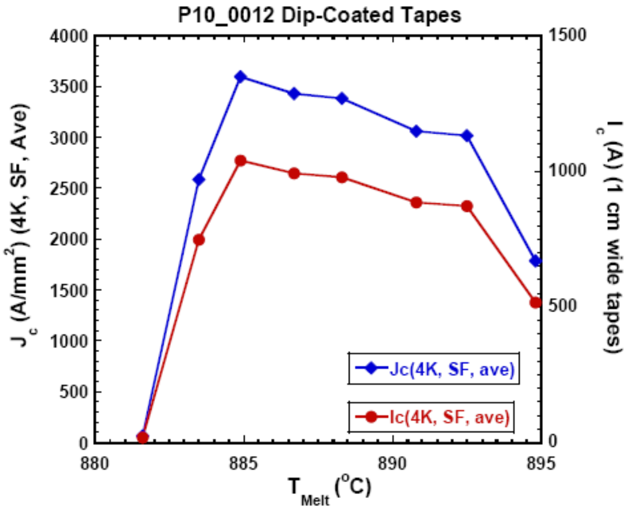
P10_0011

- T_M = 890.8°C
- I_c(4K, SF, ave) = 1080.4 A
- J_c(4K, SF ave) = 3950 A/mm^2
- Measured composition of superconducting phase:
  - $Bi_{2.20}Sr_{2.00}Ca_{0.86}Cu_{1.94}O_y$
  - Stnd deviations: 0.04, 0.03, 0.04, 0.04
  - Sr/Ca ratio: 2.34
  - Intended Sr/Ca ratio: 2.45
- Intended composition
  - $Bi_{2.10}Sr_{2.06}Ca_{0.84}Cu_{2.00}O_y$
  - Sr/Ca ratio = 2.45
- ICP Analysis
  - $Bi_{2.17}Sr_{1.98}Ca_{0.92}Cu_{1.93}O_y$
  - Sr/Ca ratio = 2.15

P10_0012 Dip-Coated Tape

- $T_M = 884.9°C$
- I_c(4K, SF, ave) = 1038.9 A
- J_c(4K, SF ave) = 3591.4 A/mm^2
- Measured composition of superconducting phase:
  - $Bi_{2.23}Sr_{2.06}Ca_{0.80}Cu_{1.92}O_y$
  - Stnd dev: all 0.02
  - Sr/Ca ratio: 2.59
  - Intended Sr/Ca ratio: 2.32





- High densities of Bi-2201 intergrowths.
- Cu-free and AEC phases.
- Some of the dark spots are pores caused by the etching process that removes silver from within the BSCCO layers.

Based on the results of the dip-coated tape testing and the SEM evaluations, the target composition $Bi_{2.10}Sr_{2.06}Ca_{0.84}Cu_{2.00}O_x$ will be used for all subsequent tasks.

Task II: Optimization of Precursor Phase Purity and Tap Density

A study was performed earlier during a concurrent SBIR Phase II project where the optimum calcining conditions and tap density for BSCCO powders produced by SCI were determined. The results of this work is contained in the Final Report for Award # DE-FG02-07ER84831 submitted in April of 2012. This study indicated that a calcining temperature of 820°C and a tap density between 1.8 and 2.0 g/cm^3 were the optimum. BSCCO powders produced for the subsequent tasks of this project were prepared using these parameters.

Tasks III – V Wire Fabrication, Heat Treatment, and Wire Performance

The results for these three tasks will be presented in one section as they were all performed by OST. Based on the results of the previous tasks, two 5 kg lots of BSCCO powder were prepared by SCI and sent to OST. The results are summarize in the OST report presented below:

Summary of Tasks III – V for Award # DE-FF02-08ER89484

The overall objective of tasks III - V was to determine the most suitable processing conditions for fabricating Bi-2212 wires using the SCI developed in the previous tasks. Two long length Bi-2212/Ag Composite round wires were fabricated using the standard OST powder-in-tube (PIT) technique. Samples of both wires were processed by the melting- recrystallization heat treatment with parameters selected through a statistical design of experiments (DOE) to determine the effect of heat treatment variables on wire Ic values measured under applied field. Following is a summary of the experimental procedures and testing results.

I. Experimental detail

1) Two 85x18 multifilamentary wires (Billet No. PMM110915-1 & -2) were been fabricated by the powder-in-tube processes, packed with SCI powders in two compositions: SCI powder P11-0082 ($Bi2.159Sr1.942Ca0.963Cu2Ag0.1Ox$) and P11-0083 ($Bi2.166Sr1.929Ca0.923Cu2.1Ag0.1Ox$),.
2) Commercial pure Ag and AgMg alloy tubes were used.
3) By using OST standard reduction schedule, the wires were drawn down to the final size of 1.2 mm in ~130 meter length.
4) Cross-sections of all wires were analyzed and fill factor was measured.
5) The wires were heat-treated by applying the partial-melt and solidification process in the flowing oxygen atmosphere.
6) The heat treatment conditions were systematically tested using different process temperatures.
7) The I_c/J_E values were measured on 1 meter barrel samples at 4.2 K under applied field from 5-15 T, using 0.1μV/cm criterion.
8) The best samples for each wire were sent to Terry/LANL for microstructure analysis.

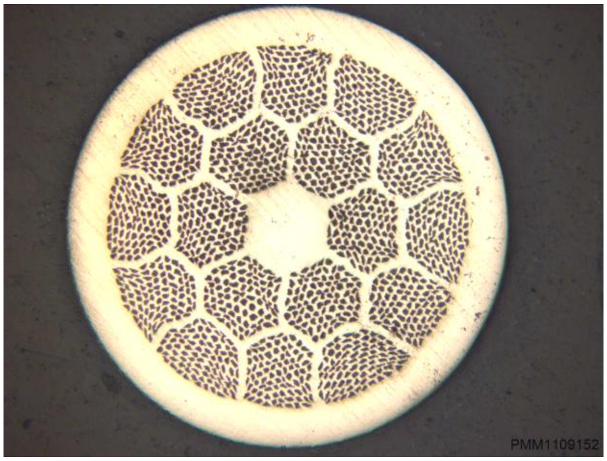
II. Results and discussion

1. Wire characteristics

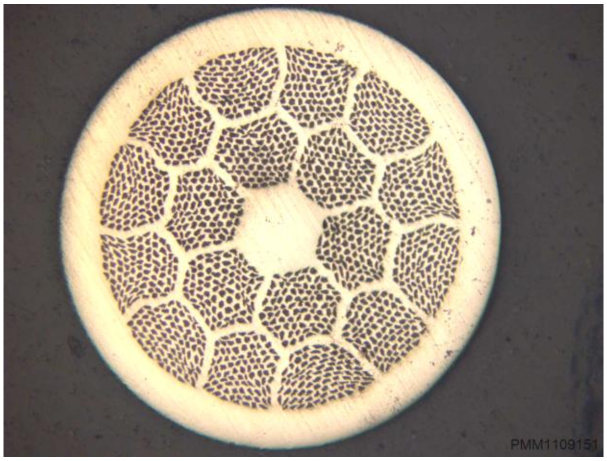
Table 12 presents both wires process information and characterization detail. The wires are made in 85 x 18 filament configuration and their cross-section view by optical microscope is shown in figure 25. It can be seen that the average filament diameter is around 16 micron and both wires have uniform microstructure, indicating good powder homogeneity.

Table 12 Characterization of the wires prepared with SCI powders prepared in Tasks I and II

Billet No.	**PMM110915-1**	**PMM110915-2**
Powder Lot	P11-0082, calcined @820°C	P11-0083, calcined @820°C
Nominal composition	Bi2.159Sr1.942Ca0.963Cu2Ag0.1Ox	Bi2.166Sr1.929Ca0.923Cu2.1Ag0.1Ox
Fill factor		
Packed density (%)	37	38
Wire at final size (%)	24.6	25.0
Cross-section		
Final wire size (mm)	**1.2**	**1.2**
Characterization (1m barrel sample)		
Peak Avg. Ic (A, 4.2K & 12T)	**247**	**277**
Peak J_E (A/mm^2, 4.2K&12T)	218	245
Peak Jc (A/mm^2, 4.2K&12T)	886	980



PMM110915-2



PMM110915-1

Fig. 25 Cross-section view of both wires in final size (1.2mm).

2. Heat treatment study and performance evaluation

Fig. 26 shows the typical OST heat treatment profile with at least 10 variable parameters. Based on earlier heat treatment optimization results, 7 variables were fixed and 3 of them were used as factors in this DOE study, as shown in table 13 and 14.

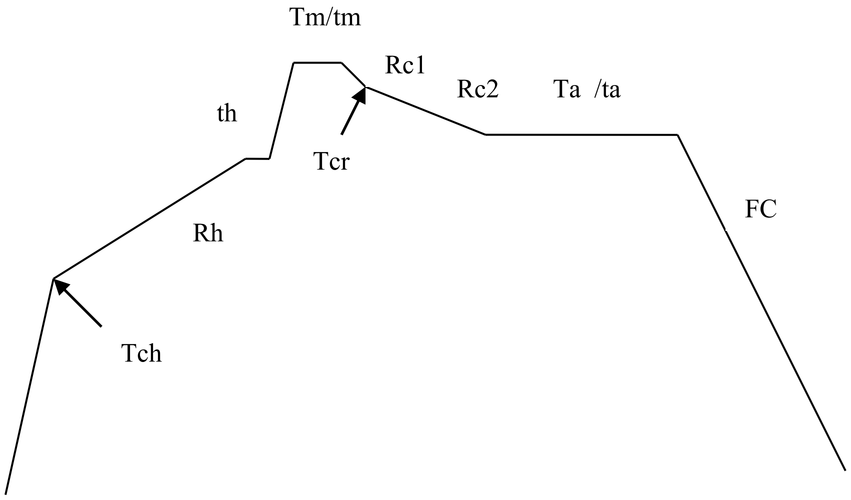


Fig. 26 Schematic drawing of the typical heat treatment profile with most of variable parameters indicated.

Table 13: **HeatTreatment ParametersVaried in the DOE Study**

Control Factors		**Level 1**	**Level 2**
Factor 1	Tm	Tmelt	Tmlt+2°C
Factor 2	**Tch x th**	**620°C x 2 h**	**720°C x 24 h**
Factor 3	Tcr	874°C	Tmlt-10°C

Table 14: **Fixed Heat Treatment Parameters**

Fixed parameters		
tm	0.1	h
Rh	2	°C/h
Th	850	°C
Rc1	10	°C/h
Rc2	2.5	°C/h
Ta	840	°C/h
ta	60	h

The Ic/J_E values versus different conditions from this heat treatment study are shown in Figure 27 and 28. All the J_E value obtained from this study are in the range of 200-250 A/cm^2 (4.2K and 12T), which is still more than 20% lower than that of wires made of Nexans commercial powders (300 A/cm^2 in average), using same wire configuration and thermo-mechanical process conditions.

It can be seen from Figure 27 that the treatment temperature higher than the standard Tm (optimized melting temperature based on Nexans regular commercial powder using "521" composition) will leads to lower performance for both billets, indicating the change in powder composition within this study range does not have a significant impact on wire melting behavior, i.e. the melting character of both billets is still similar to that made of "521" composition. The pre-treatment temperature and duration do not really affect the performance either, as shown in Figure 3.

For both billets heat treated at Tm, using Tm- 10C as recrystallization temperature can reduce J_E variation (see Figure 28), while treated at Tm+ 2C will make the impact of recrystallization temperature on performance less significant. The J_E dependence on applied magnetic field for both wires, heat treated in 1 m barrel and under optimized conditions is presented in Figure 5. The J_E value of >230 A/mm^2 at 4.2K & 12T were achieved in both wires. The wires are not sensitive to the applied field as the wires made of Nexans powder.

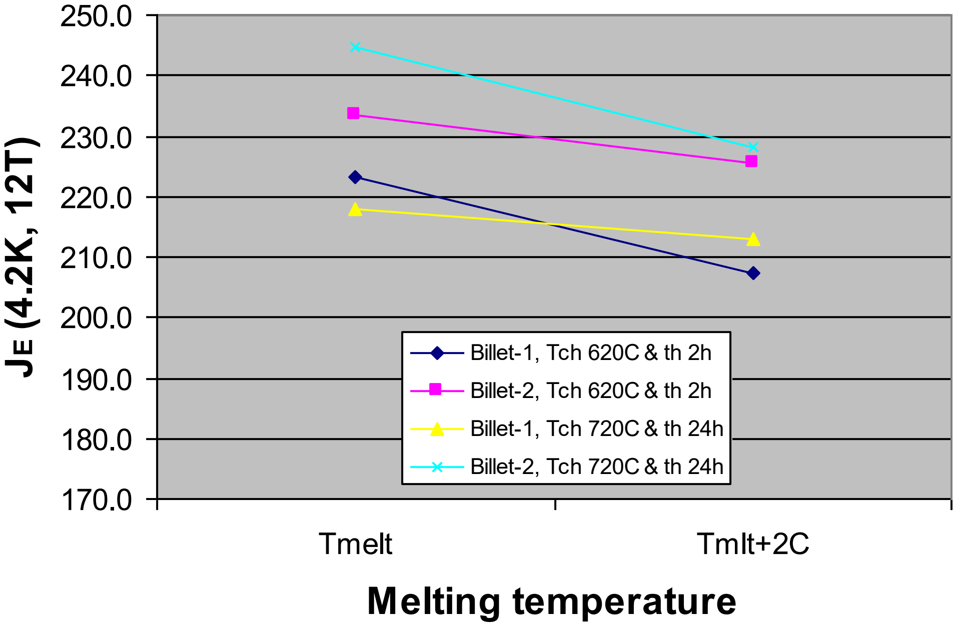


Fig. 27: J_E (4.2K and 12T) value as a function of melting temperature for both wire PMM110915-1 &-2 with variation of pre-heat treatment condition on 1 meter barrel samples

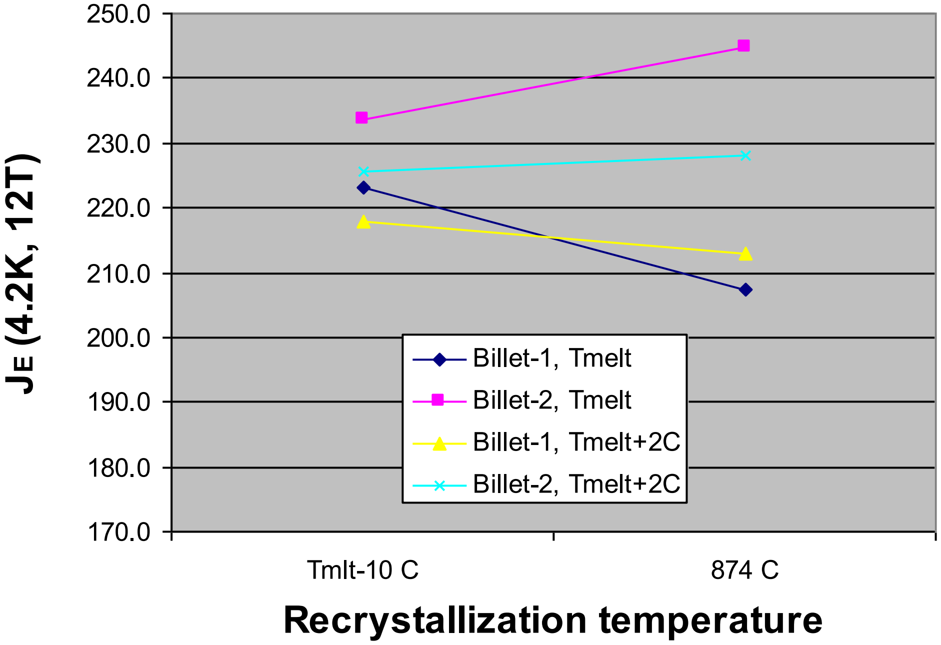


Fig. 28: J_E (4.2K and 12T) value as a function of recrystallization temperature for both wire PMM110915-1 &-2 with variation of melting treatment temperature on 1 meter barrel samples

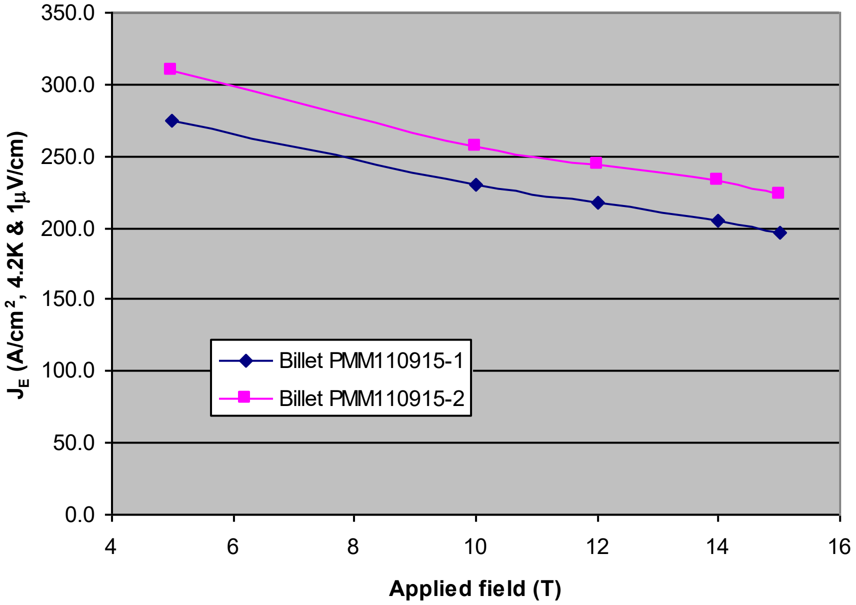


Fig. 5 J_E (4.2K) value as a function of applied field for both wire PMM110915-1 &-2 processed in optimized conditions on 1 meter barrel samples and with criterion of 0.1μV/cm.

Actually, the J_E value change by different heat treatment parameters of this test is relative small (< 5%), which is within our measurement variation. The results indicate that the new powders made of slightly modified "521" composition have similar melting and recrystallization behaviors as Nexans powder. Our standard heat treatment conditions, optimized based on Nexans "521" commercial powder are still suitable for the new powders.

3. Conclusions

- The J_E value of >230 A/mm^2 at 4.2K, 12T were obtained in both wires, about 20% lower than that of wire made of Nexans powder.
- The slightly modified "521" composition keeps similar melting and recrystallization behaviors as Nexans powder.
- Our standard heat treatment conditions are still suitable for the new powders.
- These results indicate that the objectives of the Phase II project were not going to be met by determining the optimum Sr/Ca ratio, optimum calcining temperature, and optimized wire heat treatment process as the Phase I results promised. As a result of this finding, no additional work was performed on this project.

Task VI: Microstructural Evaluations

The results of the microstructural evaluations of the wire samples are summarized below:

Technical Objectives

Recent efforts at OST have focused on responding to needs from their HEP partners for leak-free wire (leakage occurring from the heat treatment process) for the purpose of making cables and coils using the Bi-2212 round wire. While this focus has reduced or eliminated leakage of the melt by changing the wire production process, it has come with some degradation in the overall properties of the wires. The goal of this work is to achieve J_c performance in leak free, practical conductor that is closer to the very high performance achieved in past strand, where J_c was the only performance criteria. The technical objectives developed to achieve the goal of the proposed Phase II program are the following:

1. Identification of a precursor composition made by SCI's chemical method that is optimized for OST wire in the new configuration and modified leak-free process.
2. Produce changes in the powder phase purity and particle size that reduces surface area and thus the potential for adsorbed carbon, which can be a cause for leakage during processing.

These objectives were addressed in the following work plan consisting of six tasks.

Task 1: Powder Synthesis
Task 2: Optimization of Precursor Phase Purity and Tap Density
Task 3: Wire Manufacture
Task 4: Statistically Designed Heat Treatment Matrix
Task 5: I_c, J_c and J_E Measurement
Task 6: Microstructure, Microchemistry, and Structure-Property Correlations
Task 7: Task VII: Wire Deliveries

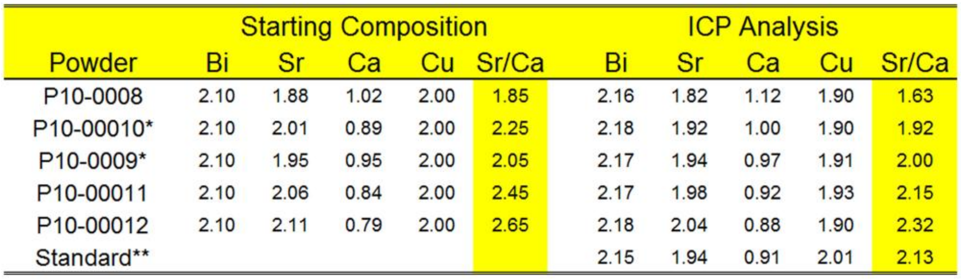
Synopsis

LANL's primary role was in Task 6 to provide the microstructural characterization of the fully-processed conductors produced with each powder composition used this Phase II project. Compositional analysis of dip-coated tapes showed a relationship between J_c and powder composition. Characterization work was not carried out for the corresponding wires as the decision was made to stop work after measurements of the wire J_c's produced results that were lower than wire performance of current standard OST wire. Based on the Microstructural analysis of the dip-coated tapes, the poor performance could have been due to the noted Cu deficiency in the as-produced powders and the resulting excess of Cu-free phases produced in fully-processed tapes.

Compositional Analysis of Dip Coated Tapes

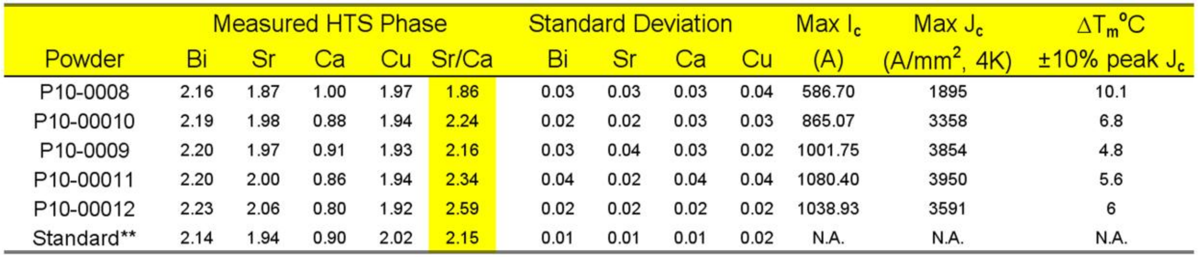
Shown in Table I are the compositions of the powders used in the production of dip-coated tapes. Compared against a standard, the powders appeared to be Cu-deficient and off-target relative to the intended Sr/Ca ratios. The data also suggests that samples P10-0010 and P10-0009 were switched, which is supported by the measured EDS data of the Bi-2212 grain compositions in Table II taken from fully processed tapes. In general, there was a broad plateau above a Sr/Ca ratio of approximately 2.1 for which J_c was maximized. This is shown in Figure 1 where the J_c values are plotted against the measured Sr/Ca ratios. Within the errors of the measurements and the narrow range of measured I_c values in this range, no optimal value for the Sr/Ca ratio could be readily identified. The highest J_c was recorded for a Sr /Ca ratio of 2.34 as shown in Table II. The data marked as Standard come from the analysis of the glassy Bi2212 standard used as the reference for quantitative analysis. Table II shows the results of performing point-to-point analysis on the standard and comparing it to itself.

Table I: Summary of the intended starting powder compositions and the corresponding ICP measurements of their compositions.



	Starting Composition					ICP Analysis				
Powder	Bi	Sr	Ca	Cu	Sr/Ca	Bi	Sr	Ca	Cu	Sr/Ca
P10-0008	2.10	1.88	1.02	2.00	1.85	2.16	1.82	1.12	1.90	1.63
P10-00010*	2.10	2.01	0.89	2.00	2.25	2.18	1.92	1.00	1.90	1.92
P10-0009*	2.10	1.95	0.95	2.00	2.05	2.17	1.94	0.97	1.91	2.00
P10-00011	2.10	2.06	0.84	2.00	2.45	2.17	1.98	0.92	1.93	2.15
P10-00012	2.10	2.11	0.79	2.00	2.65	2.18	2.04	0.88	1.90	2.32
Standard**						2.15	1.94	0.91	2.01	2.13

Table II: Energy dispersive spectroscopy measurements of the Bi2212 phase composition in fully processed, dip-coated tapes taken in the scanning electron microscope.



	Measured HTS Phase					Standard Deviation				Max I_c	Max J_c	ΔT_m°C
Powder	Bi	Sr	Ca	Cu	Sr/Ca	Bi	Sr	Ca	Cu	(A)	(A/mm^2, 4K)	±10% peak J_c
P10-0008	2.16	1.87	1.00	1.97	1.86	0.03	0.03	0.03	0.04	586.70	1895	10.1
P10-00010	2.19	1.98	0.88	1.94	2.24	0.02	0.02	0.03	0.03	865.07	3358	6.8
P10-0009	2.20	1.97	0.91	1.93	2.16	0.03	0.04	0.03	0.02	1001.75	3854	4.8
P10-00011	2.20	2.00	0.86	1.94	2.34	0.04	0.02	0.04	0.04	1080.40	3950	5.6
P10-00012	2.23	2.06	0.80	1.92	2.59	0.02	0.02	0.02	0.02	1038.93	3591	6
Standard**	2.14	1.94	0.90	2.02	2.15	0.01	0.01	0.01	0.02	N.A.	N.A.	N.A.

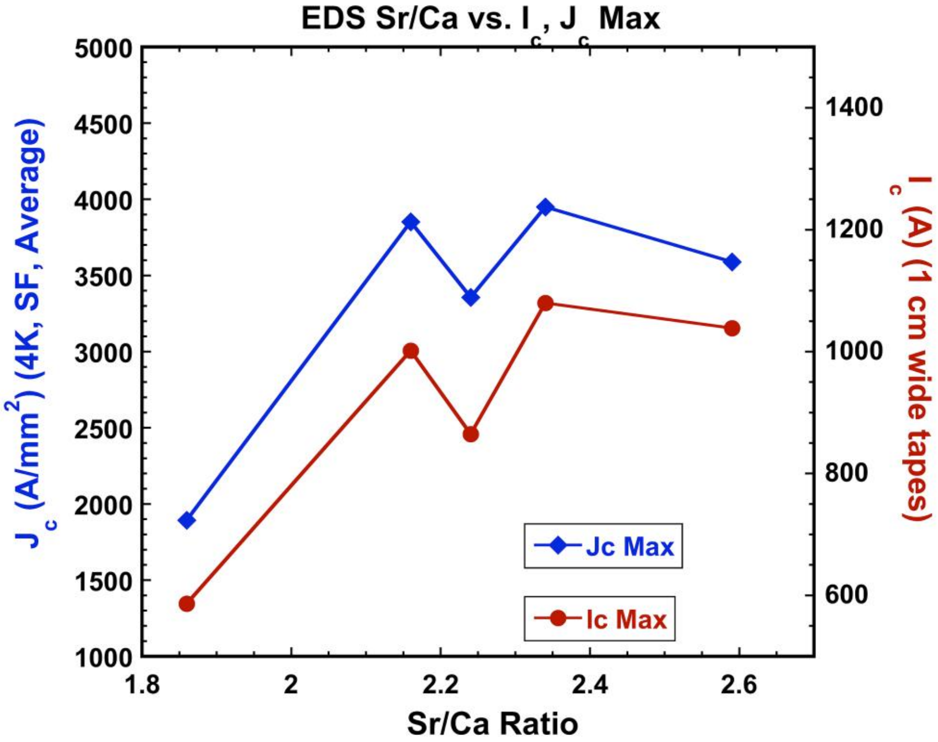


Figure 1: Plot of the measured Jc (Oxford) versus the measured Sr/Ca ratio of the Bi-2212 grains in dip-coated tapes made with the P10 series of powders.

Dip Coated Tape Microstructure

The Cu-deficiencies noted in the ICP and EDS data of Tables I and II appear to have affected the dip-coated tapes in at least two ways. First, as shown in Figures 2 and 3, the presence of the large, blocky Cu-free phases disrupts the alignment of the Bi2212 film. It also appears that the Cu-free phase coincides with additional porosity in the films. Secondly, as shown in Figure 4 and summarized in Table II, the composition of the Bi-2212 phase itself in fully processed tapes is Cu-deficient, Bi-rich due to the high density of Bi-2201 intergrowths. Both of these processes likely lead to performance degradation in the dip-coated tapes and likely the wires as well.

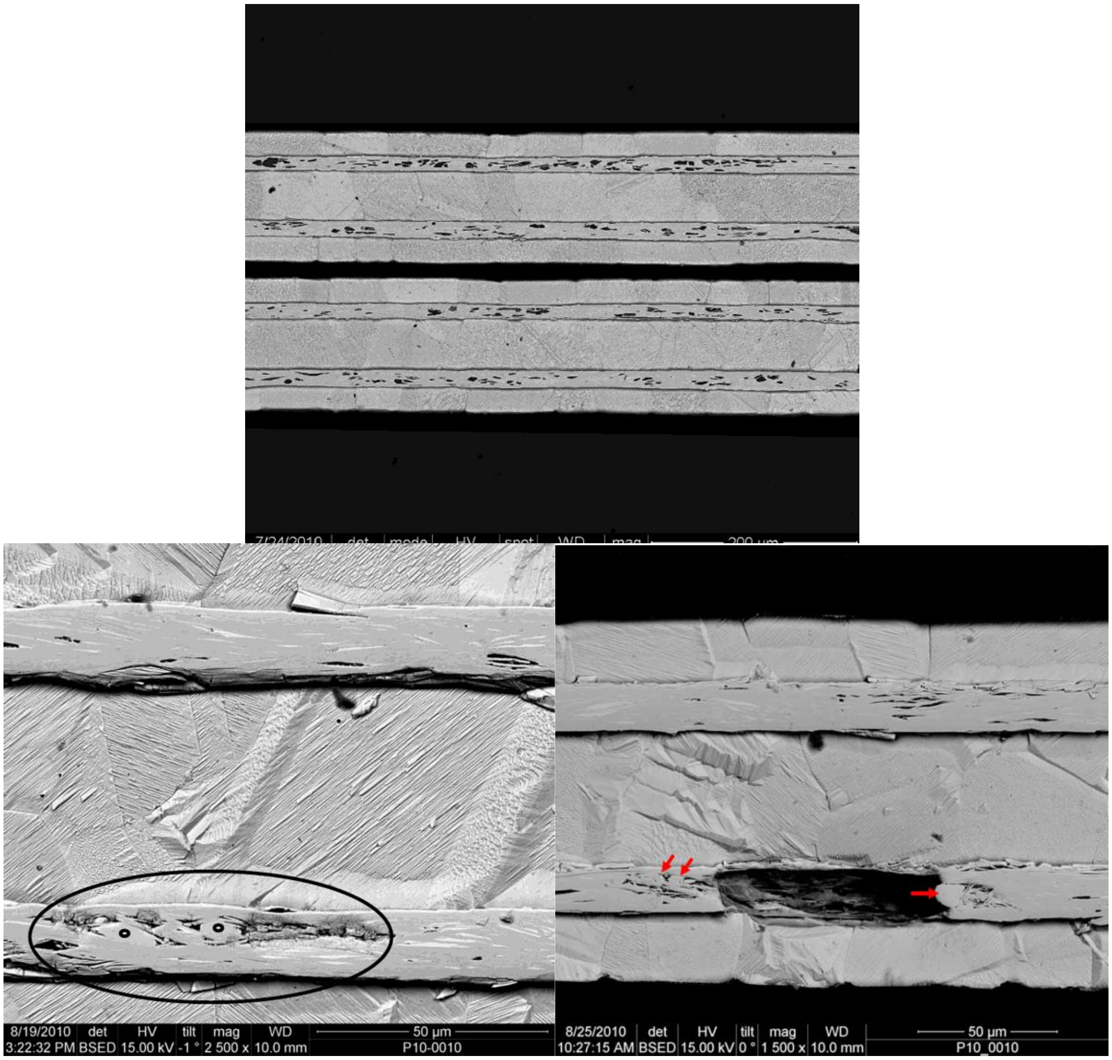


Figure 3: SEM images of disruptions in the Bi-2212 film morphology and the corresponding presence of Cu-free phases. Cu-free phases are marked by the dots within the circle on the left and the arrows on the right.

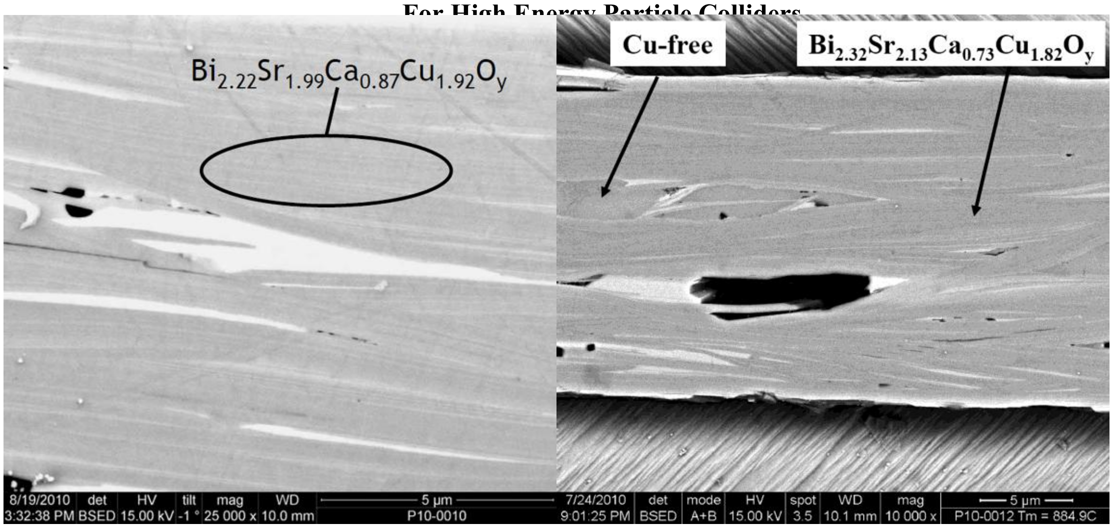


Figure 4: SEM images of the Bi-2201 intergrowths and grains in the Bi-2212 superconducting phases and the corresponding measurements of the composition.

Task VII: Wire Deliveries

As mentioned in the conclusions drawn from Task V, the promise of optimizing calcining conditions, composition, and wire melt processing conditions did not yield the desired results of producing Bi-2212/Ag composite wires that met or exceeded the performance of wire produced using Nexans commercially supplied powders. Due to this result it was determined to cease work on this project and not to supply wire to the U.S. collaborative VHFSCM program under this project since no improvements over currently available technology were obtained.

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