HIGH Tc (>110K) Bi, Tl, AND Y-BASED SUPERCONDUCTING CIRCUIT

ANNUAL REPORT

to

Aeronautics and Space Administration
Langley Research Center
Hampton, VA 23665-5225

March 7, 1990 - February ...

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Investigators:
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NAG-1-1108

DEVELOPMENT OF HIGH Tc (>110K) Bi, Tl and Y-BASED MATERIALS AS SUPERCONDUCTING CIRCUIT ELEMENTS

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I. Introduction

This report details work that was carried out over the period from March 7, 1990 to February 21, 1991, in the Ceramic Engineering Department of Clemson University under NASA contract No. NAG-1-1108. The work is the initial phase of a program involving the development of high Tc superconducting circuit elements primarily in the Bi-Sr-Ca-Cu-O and Tl-Ba-Ca-Cu-O compositional systems, although it was also proposed to investigate any Yttria-based compositions which might exhibit exceptional characteristics as conductors, coils and other circuit elements. This effort is intended to build on the results of the previous contract (NAG-1-820) which involved the development of the $YBa_2Cu_3O_{7-x}$ (123) material in circuit elements; and more specifically, a superconducting grounding link for the SAFIRE (Spectroscopy of the Atmosphere using Far Infra-Red Emission) program.

The technology developed for the SAFIRE grounding link involves a rigid-structure approach to superconducting elements rather than the flexible-wire idea promoted by most other institutions. In principle, the rigid-structure concept is quite simple and is tailor-made to take advantage of the inherent desirable properties of the superconducting ceramics while at the same time recognizing the low strength and basic brittleness of these materials. This is accomplished by pre-forming, sintering and testing the ceramic superconductor prior to bonding it to a rigid supporting substrate which is then totally encapsulated for further support and environmental protection. This approach has the advantages of (1) pre-testing of the superconducting material separate from the substrate, (2) optimization of the development of superconductivity in the ceramic without temperature limitations imposed by the substrate, (3) wider selection of substrate materials since the high temperature processing step precedes mounting of the superconductor to the printed circuit board, (4) freedom from firing shrinkage and other material compatibility problems and (5) high anticipated reliability because of its simplicity, rigid design and total encapsulation from the environment.

Although the yttria-based material seems to be well suited to the SAFIRE application because of its particular Tc of 92K, there are other applications where high Tc's are desirable, and indeed, are necessary. Of the higher Tc materials known to date, the Bi-Sr-Ca-Cu-O and Tl-Ba-Ca-Cu-O systems are the only proven ones with Tc's up to 125K. Consequently, it was proposed in the first year of this project to select specific compositions within those systems and to develop processes for the fabrication of these materials. Development work involving specific applications and devices are to follow in the second year.

(1)

The investigative effort covered in this report involved work associated with the Bi, Tl and Y-based superconductors. Specifically, it includes the compositions $Bi_2Sr_2Ca_2Cu_3O_m$, $(Bi,Pb)Sr_xCa_yCu_zO_m$ and $Y_5Ba_6Cu_{11}O_m$, all of which have been reported to possess a Tc in excess of 110K. Advantages of the new materials would include (1) higher Tc of 110-125K, (2) less oxygen stoichiometry sensitivity and (3) less moisture sensitivity. Possible disadvantages include (1) more difficult processing (i.e., longer times and more critical temperatures) to achieve single phase material and (2) special handling of the toxic thallium raw materials.

This report is presented in two parts; i.e., Part I dealing primarily with the Bi-based materials and a small amount of work on a Y-based composition and Part II covering work on the Tl-based materials.

Annual Report

Development of High T_c (> 90 K) Bi, Tl and Y-Based

Materials as Superconducting Circuit Elements

Part I : Bi and Y-Based Materials

Submitted to

National Aeronautics and Space Administration

Langley Research Center

Submitted by

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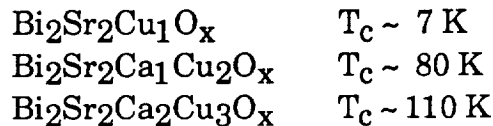
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I. Introduction

1. Bismuth-Based Materials

Maeda and his coworkers announced the existence of a superconducting phase in the Bi-Sr-Ca-Cu-O (BSCCO) system with a critical temperature (T_c) of 105 K in January 1988[1]. Shortly thereafter many other investigators confirmed the existence of three superconducting phases and presented structural data on them[2-6]. The new compound consisted of an oxygen deficient perovskite layer containing copper oxide planes sandwiched between bismuth oxide layers. The number of copper oxide planes corresponds to the n in the chemical formula $Bi_2Sr_2Ca_{n-1}Cu_nO_x$ where n = 1, 2, or 3. As the number of copper oxide planes increases, so does the critical temperature. The three main compounds are,

$$Bi_2Sr_2Cu_1O_x \qquad T_c \sim 7\ K$$
$$Bi_2Sr_2Ca_1Cu_2O_x \qquad T_c \sim 80\ K$$
$$Bi_2Sr_2Ca_2Cu_3O_x \qquad T_c \sim 110\ K$$

and are shown in Figure 1. The highest T_c material is very difficult to synthesize in phase-pure form because separation of the 110 K (2223) phase from the 80 K (2212) phase is near impossible in bulk form. The 110 K phase has a very small sintering temperature range and long sintering times are required to obtain bulk material which is almost phase-pure. Many investigators, because of work done by Sleight and his coworkers on $BaPb_{1-x}Bi_xO_3$ [7], worked on doping the BSCCO material with lead. They showed that the lead increased the percentage of the 110 K phase and decreased the sintering temperature and time[8-13]. The lead has also been shown to act as a flux and promote crystallization. Another reason for lead doping is to increase the apparent valence of copper. As with the lanthanum-based system, the copper valence should be greater than 2+. By replacing some of the Bi^{3+} with Pb^{2+}, the apparent valence of copper is increased. Other phases that were present in other investigators work

were Ca_2PbO_4, Ca_2CuO_3, a semiconducting phase, $(Sr, Ca)_xCu_yO_z$ and excess CuO. Some of these investigators believe that the Ca_2PbO_4 phase, the CuO and the 80 K phase interact with one another in some way to form the 110 K phase. The way in which these mechanisms work is still unclear at this time.

The amount of strontium in these superconductors has also been investigated. It was shown that as the amount of strontium in the superconductor was increased, the 80 K phase tends to form instead of the 110 K phase[14-16]. The reason for this is that the 80 K phase is strontium-rich and leaves the leftover calcium in the Ca_2PbO_4 form. The optimum amount of strontium was found to be somewhere between 1.6 and 1.95 moles. Because of these ideas the composition decided upon for this work was $Bi_{1.6}Pb_{0.4}Sr_{1.9}Ca_{2.05}Cu_{3.05}O_x$.

Besides having a Tc approximately 15 K higher than that of Y-Ba-Cu-O, which possibly makes it less sensitive to magnetic fields and increases the Jc, the biggest advantage of the bismuth-based superconductors are their resistance to moisture degradation and chemical attack. In the Y-Ba-Cu-O material, unreacted barium in a moist environment results in the rapid formation of alkaline conditions on the sample surface and accelerated degradation. This is basically due to the formation of $BaCO_3$. The bismuth-based superconductors do not contain barium and therefore do not have the problem with moisture degradation. Another advantage of the bismuth-based materials is they are less oxygen sensitive than the Y-Ba-Cu-O material. This could explain why the bismuth-based materials do not have to be annealed and can be produced by hot pressing. The biggest disadvantages of the bismuth-based superconductors are the amount of sintering time required to produce an almost pure 110 K phase and the small temperature range in which the 110 K phase can be produced.

2. Yttrium-Based Materials

In October 1989, a team of scientists from Wayne State University and

Ford Motor Company reported the existence of a near room temperature superconductor in the YBCO system. The compound, $Y_5Ba_6Cu_{11}O_y$, was reported to have critical temperatures in the 235 K to 265 K range, although there was a problem with reproducibility. The investigators believed that oxidation at low temperatures, 150 °C to 70 °C, helped to stabilize this high-T_c phase, so the samples were annealed in oxygen for 96 hours at 150 °C. They also used high pressures on the order of 130 atmospheres of oxygen to synthesize this material. The investigators used an acetone bath with dry ice, rather than liquid nitrogen, to confirm the T_c's because of the ease of temperature control. This material did not show a "full" Meissner effect but the investigators speculated that this was either due to the microstructure or to the fact that the superconducting path could be more filamentary which would imply that "the observed phenomena is not bulk-like."[17]

II. Objectives

The objectives of this work were to (1) develop a reliable and reproducible process for producing bismuth-based superconductors, (2) adapt previously developed techniques for superconducting grounding straps to the bismuth-based materials (this included tapecasting, tape cutting, sintering, electroding, mounting tapes on PC boards and encapsulating), (3) evaluate new compositions in the YBCO system that were reported to have T_c's in the 235 K to 265 K range and (4) characterize and evaluate the superconducting devices.

III. Experimental Procedure

In the work in the bismuth-based system, the superconductors were synthesized in bulk and tapecast form. In both cases, the starting materials were Bi_2O_3, PbO, $SrCO_3$, $CaCO_3$ and CuO. The powders were measured out and ball milled with distilled water for one hour and dried at 100 °C for 18 hours. The dried powder was then pressed into pellets and

calcined at 810 °C for 12 hours and at 830 °C for 12 hours. For the bulk material, the calcined powder was ground, pressed into one square inch pellets and sintered at 845 °C for 20 to 200 hours. For the tapecast material, the calcined powder was ground and ball milled with trichloroethylene for one hour and dried at 100 °C for 18 hours. The dried powder was then mixed with a commercial binder, B73305 from Metoramic Sciences, Inc., in the ratio of 150 grams of powder to 80 grams of binder and ball milled for one hour. The mixture was deaired for ten minutes and tapecast by a conventional tapecasting process[18]. The tape was cut into strips with the dimensions 25.4 mm x 2.0 mm x 0.5 mm. The strips were sintered at 845 °C for 20 to 200 hours. Both processes also had an optional annealing stage at 300 °C to 500 °C for fifteen hours. A flow chart for both processes can be seen in Figure 2, and the furnace schedule and operation can be seen in Figure 3. Some preliminary work in fast heating and quenching has been done in the bulk system. In fast heating, the square inch pellets were put into the furnace at 845 °C rather than being ramp heated at 100 °C/hour. In quenching, the pellets were removed from the furnace at 845 °C and cooled by the atmosphere to room temperature in a few minutes. The electrodes were applied using a commercial silver paste, C8710 from Heraeus Inc., Cermalloy Division, and fired at 845 °C for 18 minutes.

In the work in the YBCO system, the "superconductors" were synthesized in both bulk and tapecast form. The starting materials were Y_2O_3, $BaCO_3$ and CuO. The procedure used to synthesize the bulk and tapecast materials was the same as that of the bismuth-based superconductors except the dried powder was calcined three times at 925 °C for 12 hours and annealed at 450 °C for 12 hours. The calcined powder was sintered at 910 °C for 12 hours and annealed at 150 °C for 24 hours in both air and oxygen. The electrodes were applied using the same silver paste and firing method as was used in the bismuth-based superconductors except the firing temperature was 910 °C. A flow chart for the process can be seen in Figure 4, and the furnace schedule and operation can be seen in Figure 5.

All of the materials were first tested for the Meissner effect. The

critical temperature for both the bulk and the tapecast materials was evaluated using a standard four point method. The resistance was measured with a Keithley 580 micro-ohmmeter with a sensitivity of 10^{-6} Ω. In addition to critical temperature measurements, the structures of the samples were examined by powder X-ray diffraction (XRD) using Cu K_α radiation, and scanning electron microscopy (SEM) was used to observe the homogeneity and surface morphology of the materials.

IV. Results and Discussion

1. BSCCO Bulk Material

Figure 6 shows the resistance versus temperature curves for compacts which were prepared at 845 °C for 20 and 200 hours in air. The curve of the 200 hour compact showed that the material had a sharp transition to the superconducting state at 108.1 K, where as the curve of the 20 hour compact had a wide transition from 120 K (onset) to 98.9 K (zero). This wide transition is due to a second phase of $(Bi,Pb)_2Sr_2Ca_1Cu_2O_x$ or 2212. All of the compacts had a certain percentage of the 2212 phase, but this phase decreased and the $(Bi,Pb)_2Sr_2Ca_2Cu_3O_x$ or 2223 phase increased as the sintering time increased. This can be seen from the X-ray diffraction data shown in Figure 7. The four patterns are from compacts which were prepared at 845 °C for 20, 28, 33 and 100 hours. Observing the double peak at approximately 35 degrees, one can see that as the sintering time increased the amount of the 2212 phase decreased and the 2223 phase increased. The room temperature resistivities, between 10 and 15 mΩ, and the onset of superconductivity, 120 K, was about the same for both compacts. The only measured difference was the transition width which was influenced by the amount of each phase present. The amount of each phase present, which is due to the sintering time, also influenced the critical temperature of the compacts. The sintering time versus critical temperature curve shown in Figure 8 shows that as the sintering time increased the critical

temperature increased. From 20 to 50 hours the critical temperature increased linearly by 6 K, but only by 3 K over the next 150 hours. This is basically due to the conversion of the 2212 phase to the 2223 phase. At first, the material is almost all 2212 phase, so it is easier to convert it to the 2223 phase, but as more and more 2223 phase is formed, the driving force for conversion of the 2212 phase to the 2223 phase is decreased dramatically. As the material was converted to the 2223 phase the grain size increased and the grains exhibited a more flaky appearance as shown in the SEM micrographs in Figure 9. The grain size ranged from five to ten microns in the 20 hour compact to 20 to 30 microns in the 200 hour compact.

The amount of pressure applied when pressing the pellets also influenced the critical temperature. Figure 10 shows the resistance versus temperature curves for two compacts sintered at 845 °C for 125 hours. The compact pressed at 3,200 psi. had a T_c of 106.8 K, while the compact pressed at 20,120 psi. had a T_c of 107.3 K. This was due to the increase in densification and reactivity of the higher pressed compact. The 20,120 psi. compact's room temperature resistivity is about one half that of the 3,200 psi compact, which is also due to increased densification, but the transition widths are about equal. From the SEM micrographs, shown in Figure 11, one can see that the compact pressed at 20,120 psi is much more dense and oriented than the compact pressed at 3,200 psi.

The preliminary results on the fast heating and quenching showed that the heating and cooling rates were important factors in the processing of the BSCCO materials. Four pellets were sintered at 845 °C for 54 hours. The slow heat/slow cool compact had the highest T_c of 104.7 K. The slow heat/quench compact's T_c dropped to 102.9 K. The two compacts that were fast heated had T_c's in the 101.2 to 101.4 range. The resistance versus temperature curves for these materials can be seen in Figure 12. This study showed that while the cooling rate was important to the T_c of the compact, it was not as influential as the heating rate. More work needs to be done in this area to get a better idea as to the influence of these rates.

2. BSCCO Tapecast Material

The tapecast material required a longer processing time than the bulk material to achieve superconductivity above 77 K. Figure 13 shows a resistance versus temperature curve for a tape sintered at 845 °C for 20 hours. The tape still had 0.94 mΩ resistance at 77.3 K but just like the bulk material, the lower sintering time specimens had a higher percentage of 2212 phase. This is clearly shown by the extremely large transition width of the T_c curve. The onset was still 120 K but the transition width was in excess of 43 K. The smallest sintering time required to achieve superconductivity was 28 hours and the T_c was 98.2 K. The resistance versus temperature curves for the 28 hour tapecast and bulk materials can be seen in Figure 14. Again, both curves had an onset of 120 K, but the transition width of the tape was wider that that of the compact. Hence, the T_c of the bulk material, 99.7 K, was higher than that of the tape, 98.2 K. Also, the room temperature resistivities of the tapecast materials were four times higher than that of the bulk materials. From the X-ray diffraction data, shown in Figure 15, one can see that the tape has several overlapping and low intensity peaks which are undefined unlike the bulk compact. Again, observing the double peak at thirty-five degrees, the tape was primarily 2212 while the bulk was half 2212 and half 2223. Observing the surface morphology of a tape and a compact that were prepared at 845 °C for 33 hours, shown in the SEM micrographs in Figure 16, the tapecast material has a much smaller grain size than the bulk material. Referring to the 20 hour compact in Figure 9 and comparing it to the 33 hour tape, one can immediately see the similarities. The grain size and density are about the same but the tape appears to have better orientation than the 20 hour compact.

There is, however, a problem with the tapecast material. After 30 hours sintering a percentage of the tapes started to curl and fracture. As the sintering time increased so did the percentage of unacceptable tapes. A sintering time versus critical temperature curve in the 28 to 48 hour sintering time range is shown in Figure 17. The curve appears linear in

this range just like the curve for the bulk material in this range except the increase in T_c is only 1.5 K.

3. YBCO Material

The synthesis of the reported near room temperature superconductor, $Y_5Ba_6Cu_{11}O_y$, was not successful. None of the materials prepared ever showed even a small hint of the Meissner effect. The resistance versus temperature curves for the tapecast samples annealed in air and oxygen are shown in Figure 18. Both curves showed semiconducting behavior although the tape annealed in oxygen does show a drop in resistance around the 123 onset temperature. The resistivities however are very different; i. e., the oxygen annealed tape's resistivities are three orders of magnitude lower than that of the air annealed tape's. The tapes were not subjected to the extreme pressures that the previous investigators used.[17]

V. Conclusions

In conclusion, a reliable and reproducible process for producing the bulk bismuth-based superconductors has been developed, however, the tapecast material needs more work. The BSCCO material has been characterized by critical temperature data, X-ray diffraction data and surface morphology. In the case of T_c, it is not critical to anneal the material, but as the critical current density or bulk density is investigated, an annealing step may be required. At this time, it appears that the BSCCO material has the possibility of producing a better grounding strap than that of the 123 material. We were unable to reproduce the near room temperature superconductors in the YBCO system.

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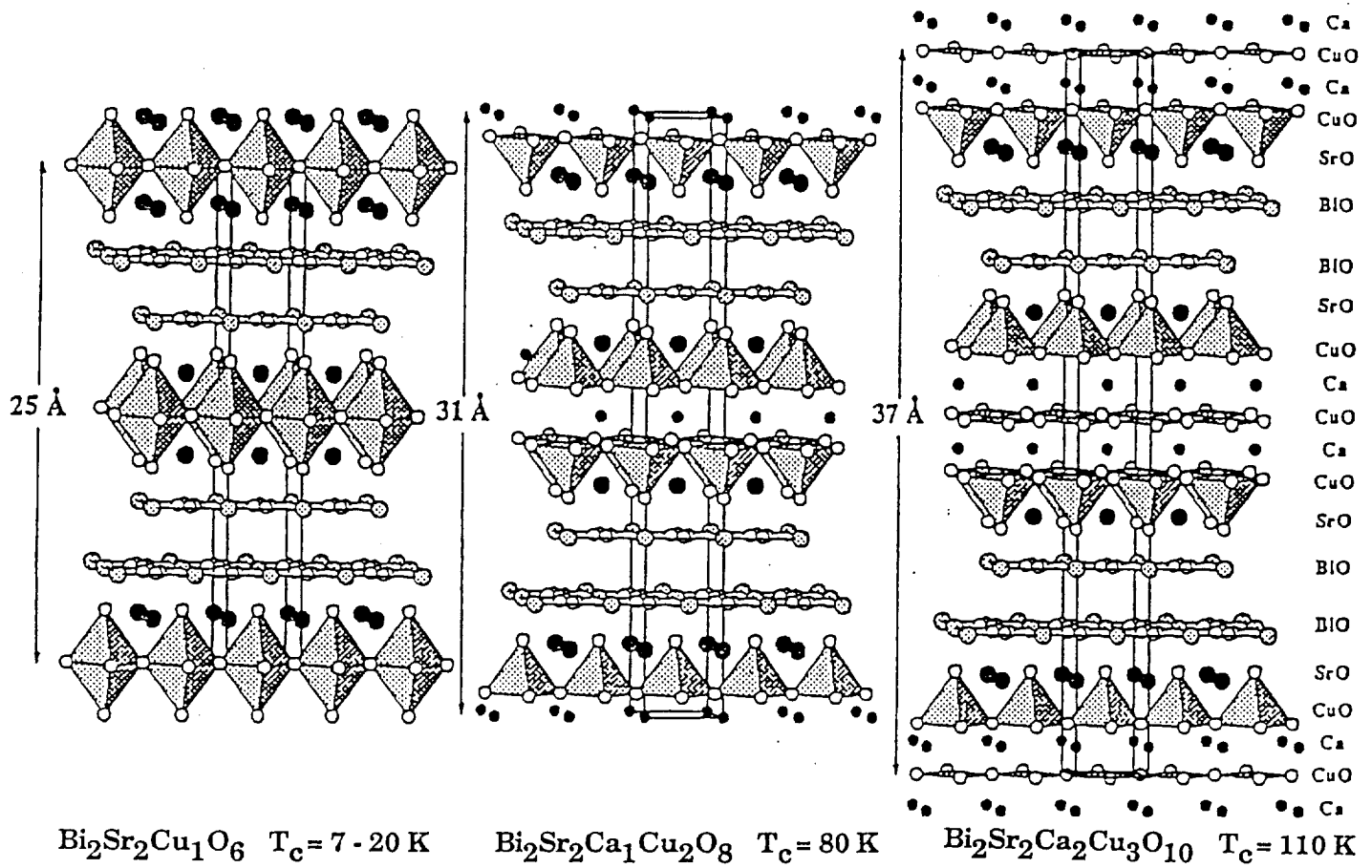
25 Å   31 Å   37 Å

Labels (right side): Ca, CuO, Ca, CuO, SrO, BIO, BIO, SrO, CuO, Ca, CuO, Ca, CuO, SrO, BIO, BIO, SrO, CuO, Ca, CuO, Ca

$Bi_2Sr_2Cu_1O_6$ $T_c = 7 - 20$ K $Bi_2Sr_2Ca_1Cu_2O_8$ $T_c = 80$ K $Bi_2Sr_2Ca_2Cu_3O_{10}$ $T_c = 110$ K

Figure 1 The structures of the three bismuth-based superconductors $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}$, where n equals 1, 2, or 3 and is the number of CuO planes sandwiched between double layers of BiO.

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                    ┌──────────────────────────────────┐
                    │            Weigh out              │
                    │  Bi2O3, PbO, SrCO3, CaCO3 and CuO │
                    │   according to the batch information│
                    │        sheet seen in Table 1      │
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                              │
                    ┌──────────────────────────────────┐
                    │     Mix with 150 ml of H2O        │
                    │     per 100 grams of batch and    │
                    │        ball mill for one hour     │
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                    │  Dry at 100 °C for eighteen hours │
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                    │      Pelletize and calcine for    │
                    │          twelve hours at          │
                    │            1.  810 °C             │
                    │            2.  830 °C             │
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                    │       Grind calcined material     │
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        │    Bulk Material     │          │   Tapecast Material   │
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        ┌─────────────────────┐          ┌──────────────────────┐
        │   Press material into│          │ Mix with trichloroethylene│
        │   a square inch pellet│         │  and ball mill for one hour│
        └─────────────────────┘          └──────────────────────┘
                │                                   │
        ┌─────────────────────┐          ┌──────────────────────┐
        │  Sinter pellet at 845 °C│       │    Dry at 100 °C for  │
        │    for 20 to 200 hours │        │      eighteen hours   │
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        │ Anneal pellet at 300 °C to│     │ Mix with binder in the ratio│
        │  500 °C for fifteen hours │     │  of 150 grams of powder to│
        └─ ─ ─ ─ ─ ─ ─ ─ ─ ─ ─┘          │ 80 grams of binder and ball│
                                          │     mill for one hour │
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                                          │   Tapecast and let each│
                                          │   side dry for one hour│
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                                          │  Cut tape into strips and│
                                          │  sinter strips at 845 °C│
                                          │    for 20 to 200 hours │
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                                          │  Anneal tape at 300 °C to│
                                          │  500 °C for fifteen hours │
                                          └─ ─ ─ ─ ─ ─ ─ ─ ─ ─ ─┘
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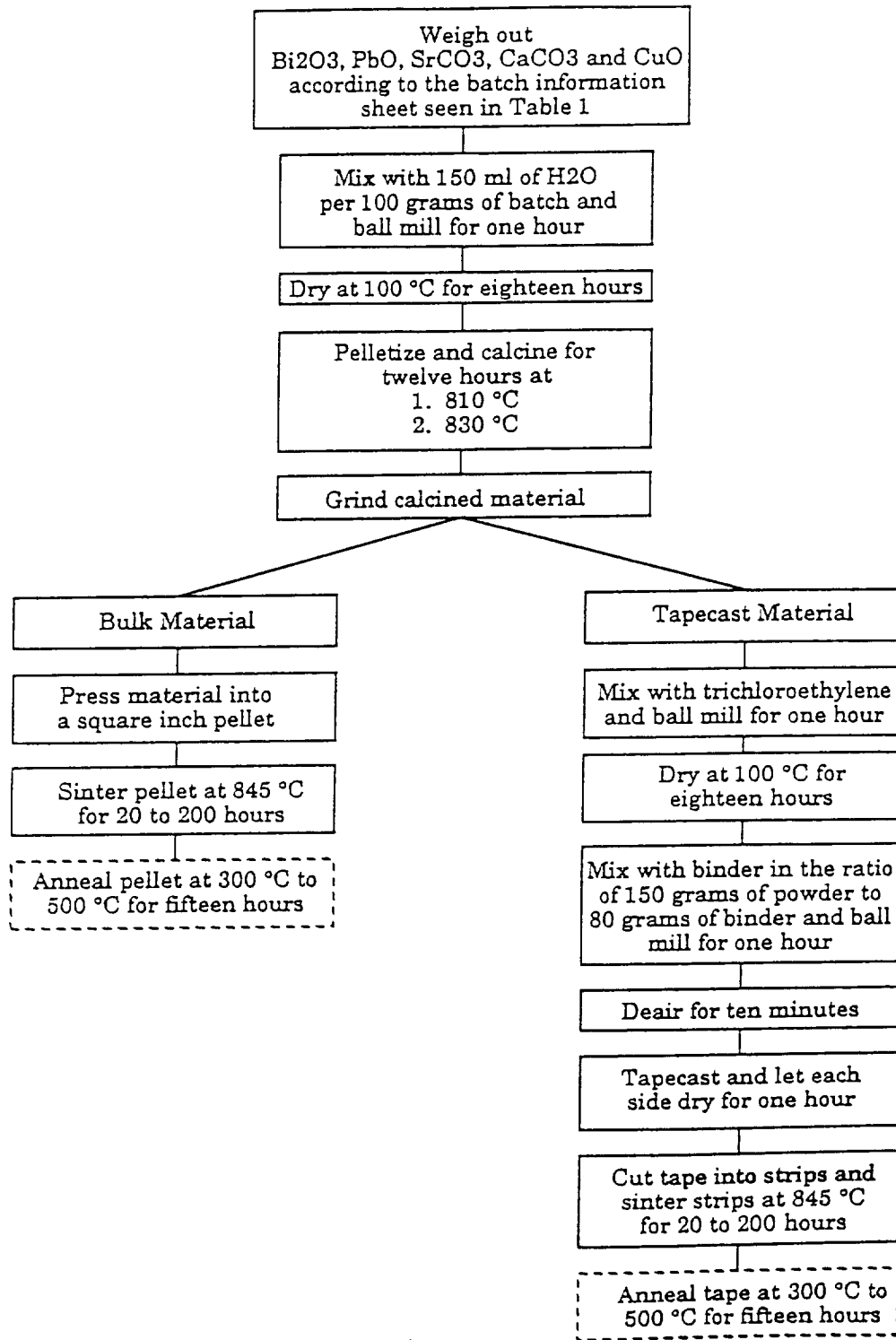
Figure 2 Flow chart for the bulk and tapecast bismuth-based materials showing the procedures used to synthesize these materials. The calcining step is a two part process and the annealing step is optional.

Batch Information Sheet

Composition # 1   **Batch # 1**

Formula $Bi_{1.6}Pb_{0.4}Sr_{1.9}Ca_{2.05}Cu_{3.05}O_x$

Batch Size 400 gms.   **Date** October 29, 1990

Raw Materials and Source

Bi2O3 Fisher   **CaCO3** Malinckrodt   **CaO** N/A

CuO Fisher   **SrCO3** Malinckrodt   **PbO** Fisher

Batching

Oxide	Mole Wt	Moles	Formula Wt	Wt %	% Oxide	Batch Wt
Bi2O3	465.96	0.80	372.768	36.672	100.000	146.689
SrO	103.62	1.90	196.878	19.369	70.189	110.379
CaO	56.08	2.05	114.964	11.310	56.030	80.743
CuO	79.54	3.05	242.597	23.866	100.000	95.465
PbO	223.19	0.40	·89.276	8.783	100.000	35.131
			1016.483	100		468.408

Table 1 The batch information sheet for the bismuth-based materials showing the raw materials used, their source, and the amount of each needed to achieve the required batch size.
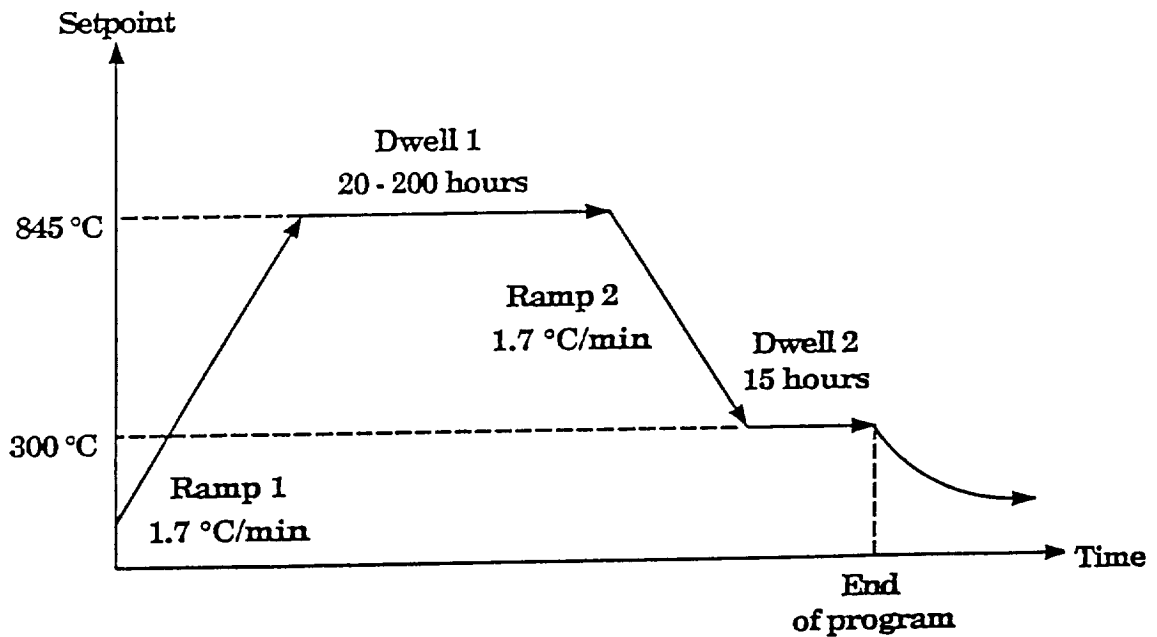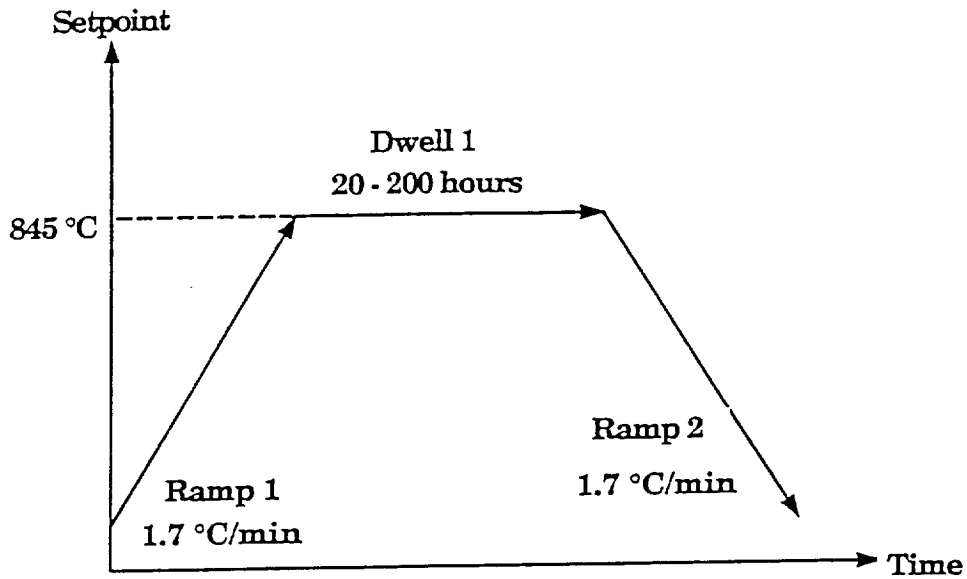
Figure 3 The furnace schedule and operation for the bulk and tapecast bismuth-based materials. The top schedule is for the furnace where only a sintering step is required. The bottom schedule is for the furnace where the optional annealing step is added.

```
                    ┌─────────────────────────────┐
                    │         Weigh out           │
                    │  Y2O3, BaCO3 and CuO according │
                    │ to the batch information sheet seen │
                    │          in Table 2         │
                    └─────────────────────────────┘
                             │
                    ┌─────────────────────────────┐
                    │   Mix with 150 ml of H2O    │
                    │  per 100 grams of batch and │
                    │    ball mill for one hour   │
                    └─────────────────────────────┘
                             │
                    ┌─────────────────────────────┐
                    │ Dry at 100 °C for eighteen hours │
                    └─────────────────────────────┘
                             │
                    ┌─────────────────────────────┐
                    │  Pelletize and calcine three │
                    │ times for twelve hours at 925 °C │
                    │     and anneal at 450 °C for │
                    │        twelve hours         │
                    └─────────────────────────────┘
                             │
                    ┌─────────────────────────────┐
                    │   Grind calcined material   │
                    └─────────────────────────────┘
```

Bulk Material

- Press material into a square inch pellet
- Sinter pellet at 910 °C for twelve hours
- Anneal Pellet at 150 °C for Twenty four hours in air or oxygen

Tapecast Material

- Mix with trichloroethylene and ball mill for one hour
- Dry at 100 °C for eighteen hours
- Mix with binder in the ratio of 150 grams of powder to 80 grams of binder and ball mill for one hour
- Deair for ten minutes
- Tapecast and let each side dry for one hour
- Cut tape into strips and sinter strips at 910 °C for twelve hours
- Anneal tape at 150 °C for twenty four hours in air or oxygen

Figure 4 Flow chart for the bulk and tapecast materials in the YBCO system showing the procedures used to synthesize these materials.

Batch Information Sheet

Composition # 1   **Batch # 1**

Formula $Y_5Ba_6Cu_{11}O_x$

Batch Size 400 gms.   **Date** August 12, 1990

Raw Materials and Source

Y2O3 Molycorp   **BaCO3** Fisher   **BaO** N/A

CuO Fisher

Batching

Oxide	Mole Wt	Moles	Formula Wt	Wt %	% Oxide	Batch Wt
Y2O3	225.81	2.50	564.525	23.926	100.000	95.702
BaO	153.34	6.00	920.04	38.993	77.700	200.737
CuO	79.54	11.00	874.94	37.082	100.000	148.326
			2359.505	100		444.765

Table 2   The batch information sheet for the materials in the YBCO
system showing the raw materials used, their source, and the
amount of each needed to achieve the required batch size.
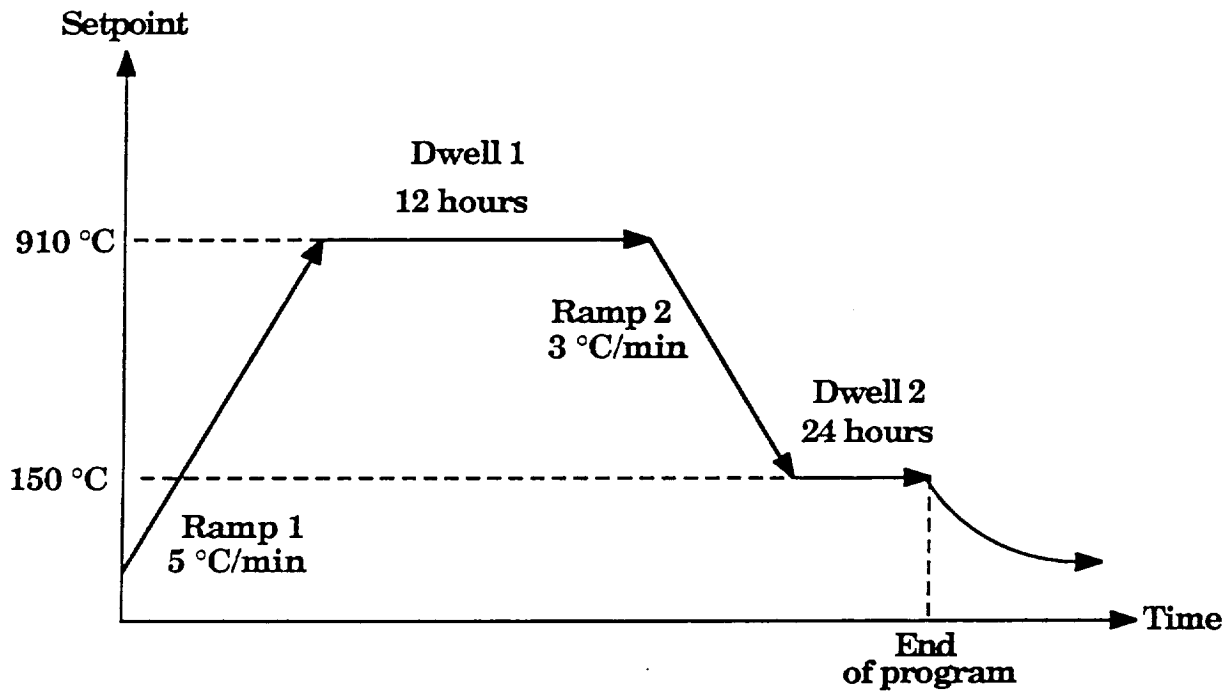
Figure 5 The furnace schedule and operation for the bulk and tapecast materials in the YBCO system.
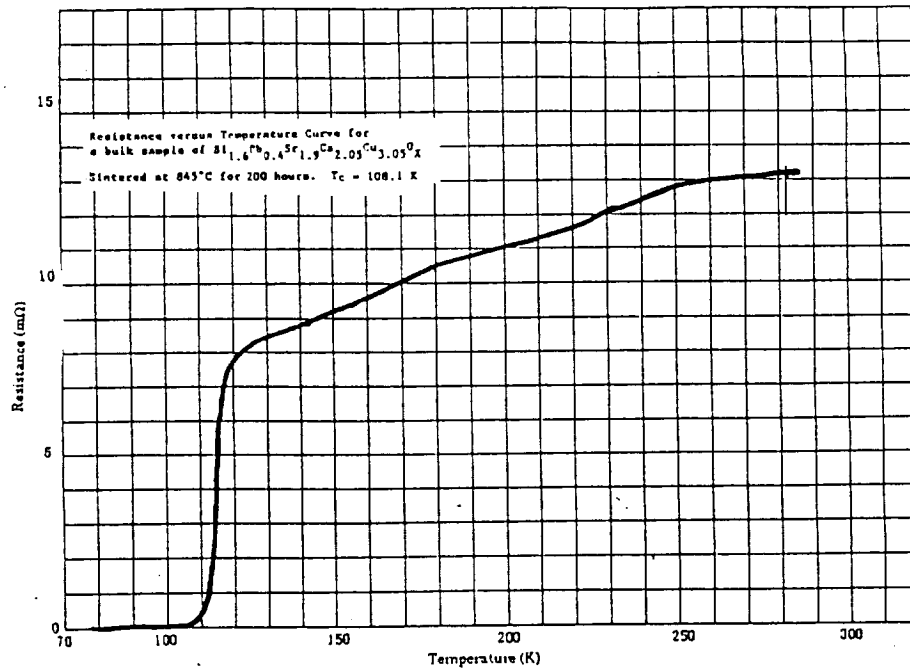
a) BSCCO sintered for two hundred hours. The Tc was 108.1 K.
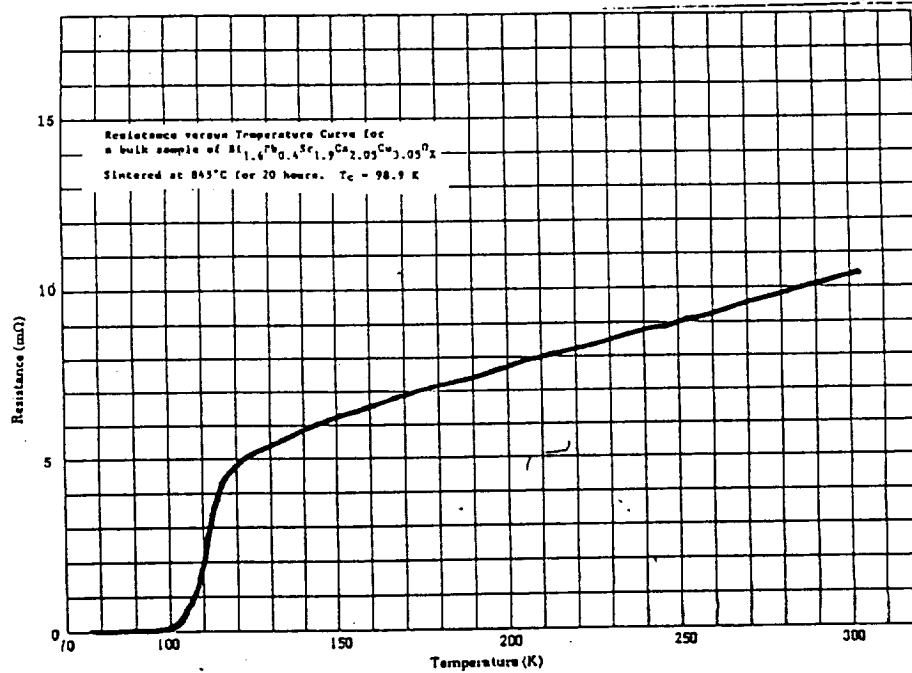
b) BSCCO sintered for twenty hours. The Tc was 98.9 K.

Figure 6 Resistance versus Temperature curves for bulk samples of $Bi_{1.6}Pb_{0.4}Sr_{1.9}Ca_{2.05}Cu_{3.05}O_x$ sintered at 845 °C for different times in air.
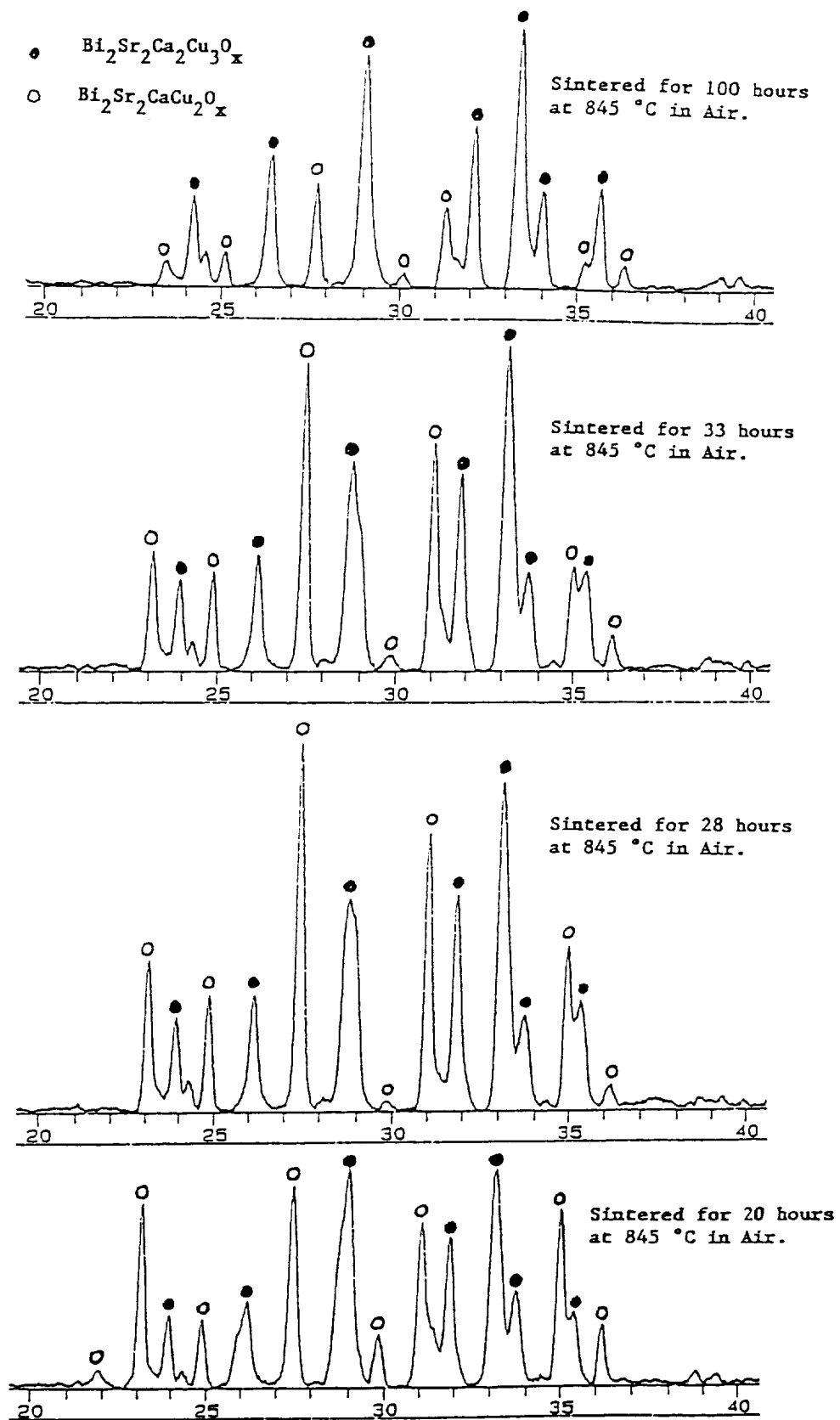
Figure 7 X-ray Diffraction data for four bulk compacts sintered at 845 °C for times ranging from 20 to one hundred hours in air.
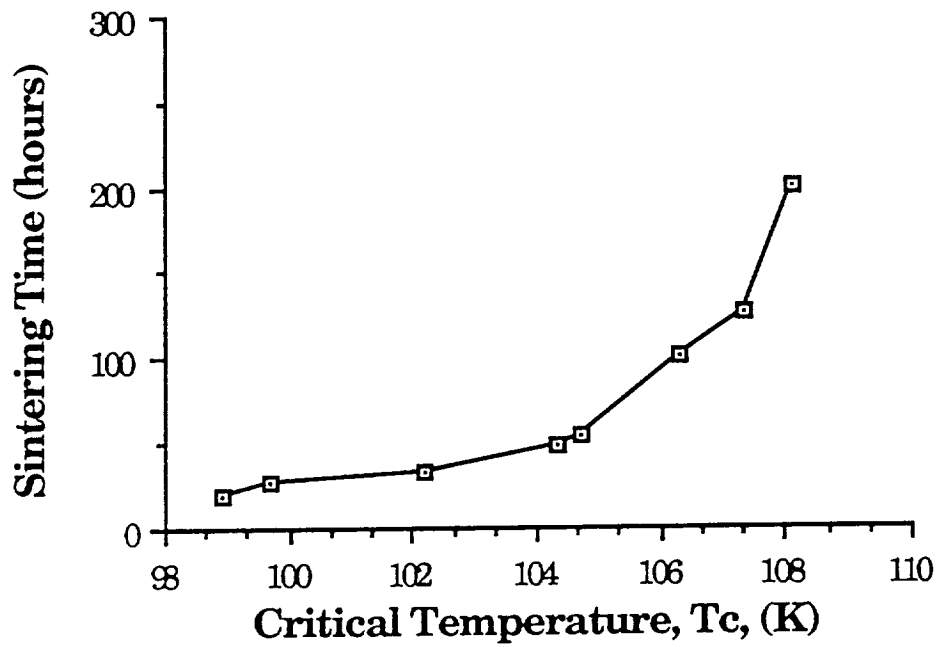
Figure 8 Sintering Time versus Critical Temperature curve for bulk $Bi_{1.6}Pb_{0.4}Sr_{1.9}Ca_{2.05}Cu_{3.05}O_x$ showing an increase in T_c as sintering time increases.
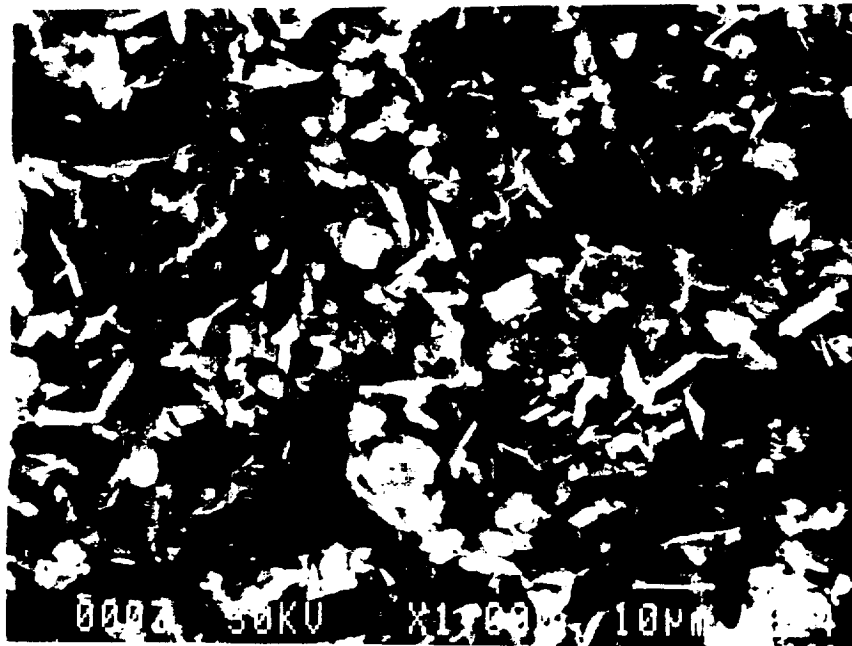
a) Pellet sintered for twenty hours.
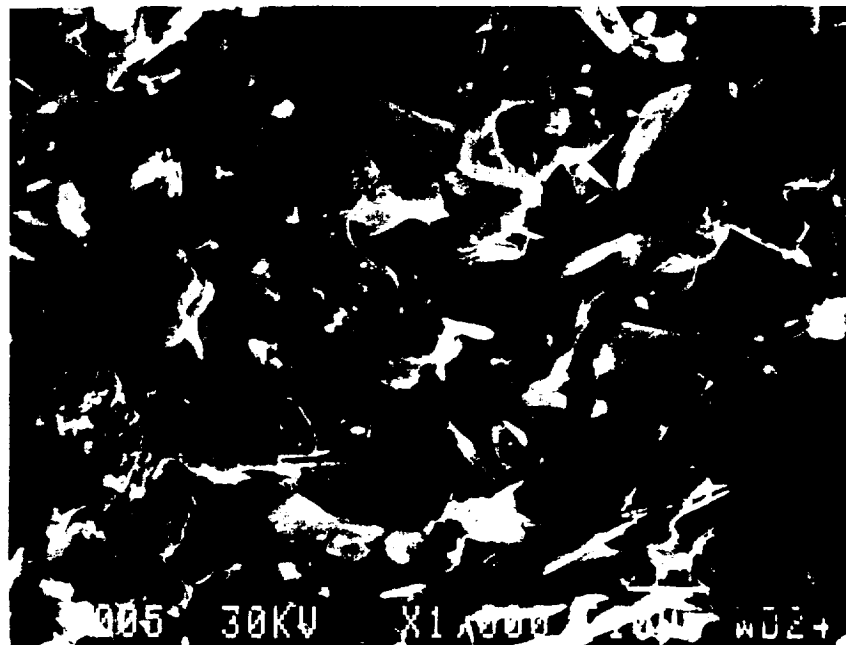
b) Pellet sintered for 33 hours.

Figure 9 SEM micrographs for $Bi_{1.6}Pb_{0.4}Sr_{1.9}Ca_{2.05}Cu_{3.05}O_x$ pellets sintered at 845 °C for different amounts of time in air.
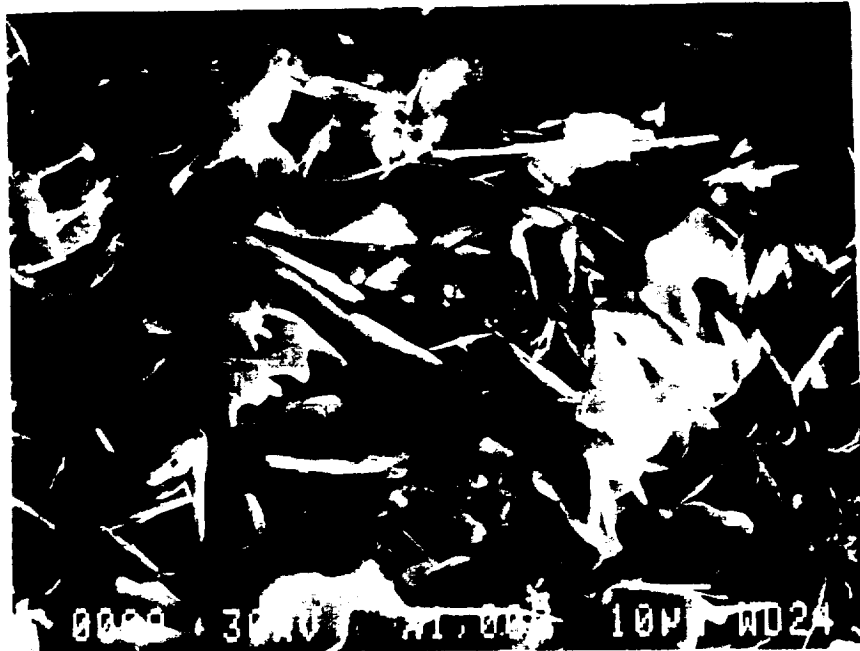
c) Pellet sintered for 125 hours.

d) Pellet sintered for 200 hours.

Figure 9 (Continued)
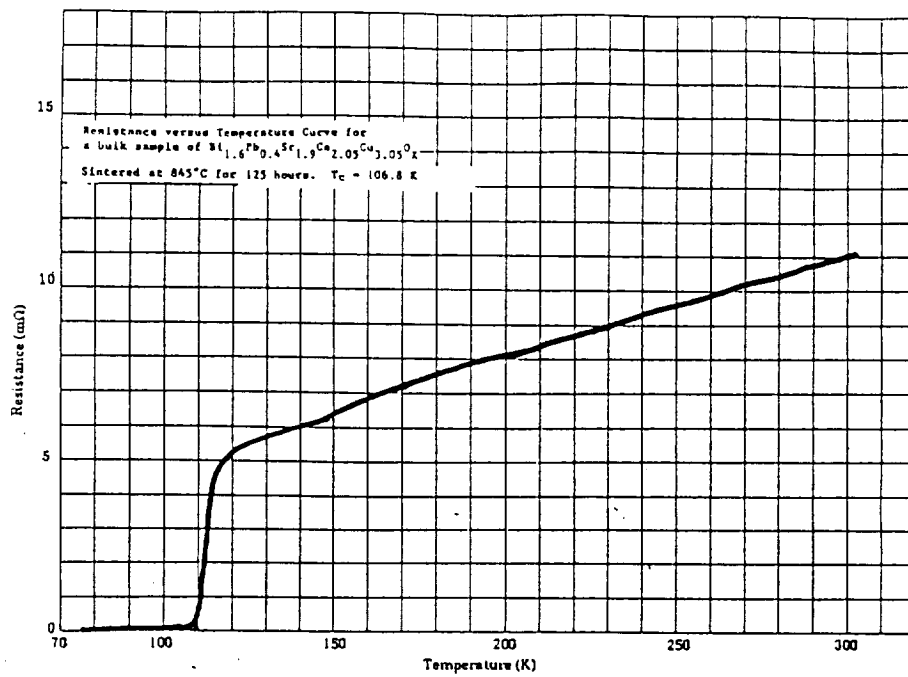
a) Pellet pressed at 3200 psi. The T_c was 106.8 K.
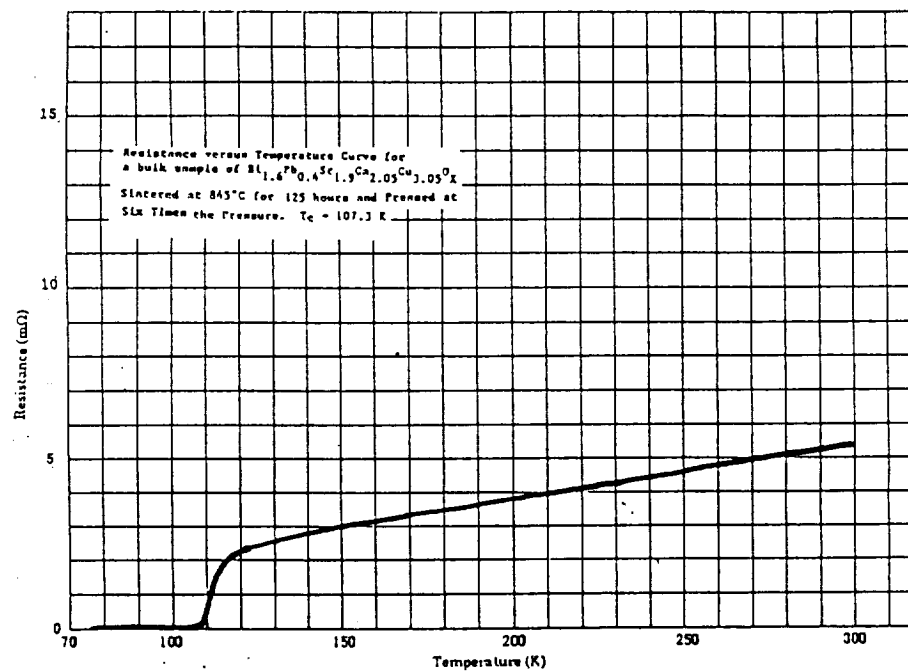
b) Pellet pressed at 20120 psi. The T_c was 107.3 K.

Figure 10 Resistance versus Temperature curves for bulk samples of $Bi_{1.6}Pb_{0.4}Sr_{1.9}Ca_{2.05}Cu_{3.05}O_x$ pellets pressed at different pressures and sintered at 845 °C for 125 hours in air.
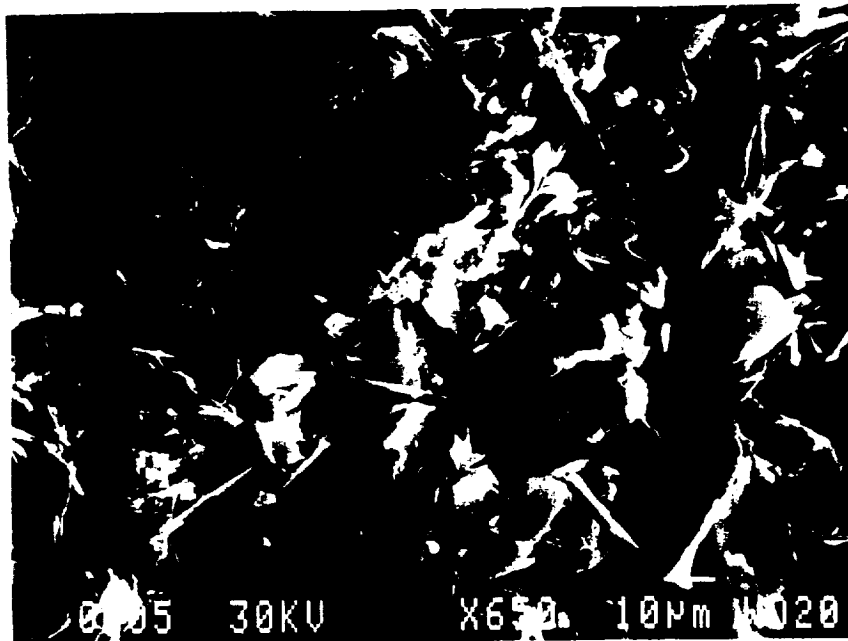
a) Pellet pressed at 3200 psi.

b) Pellet pressed at 20120 psi.

Figure 11 SEM micrographs for $Bi_{1.6}Pb_{0.4}Sr_{1.9}Ca_{2.05}Cu_{3.05}O_x$ pellets pressed at different pressures and sintered at 845 °C for 125 hours in air.
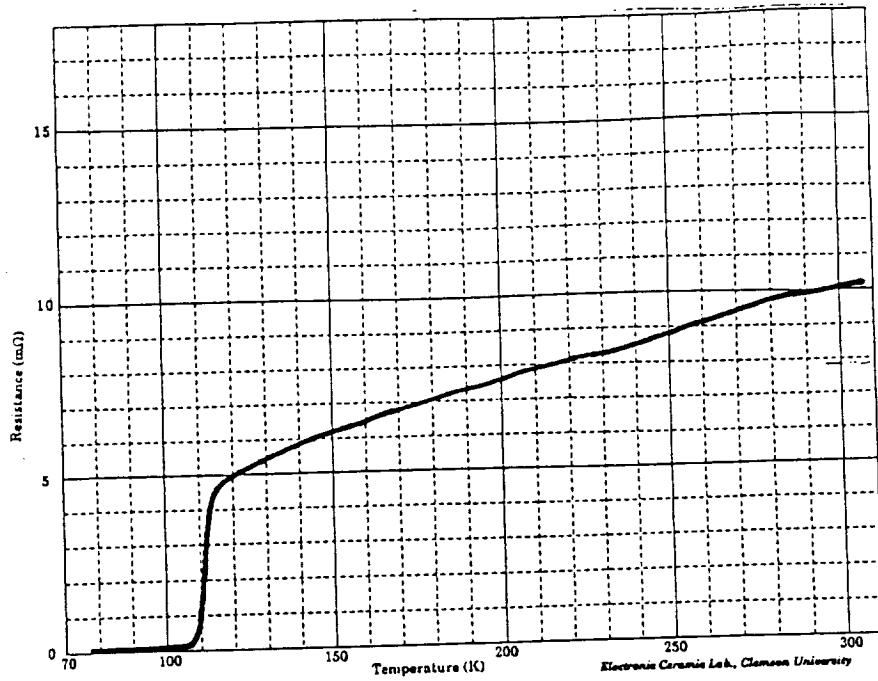
a) Pellet with a slow heating and cooling rate. The T_c was 104.7 K.
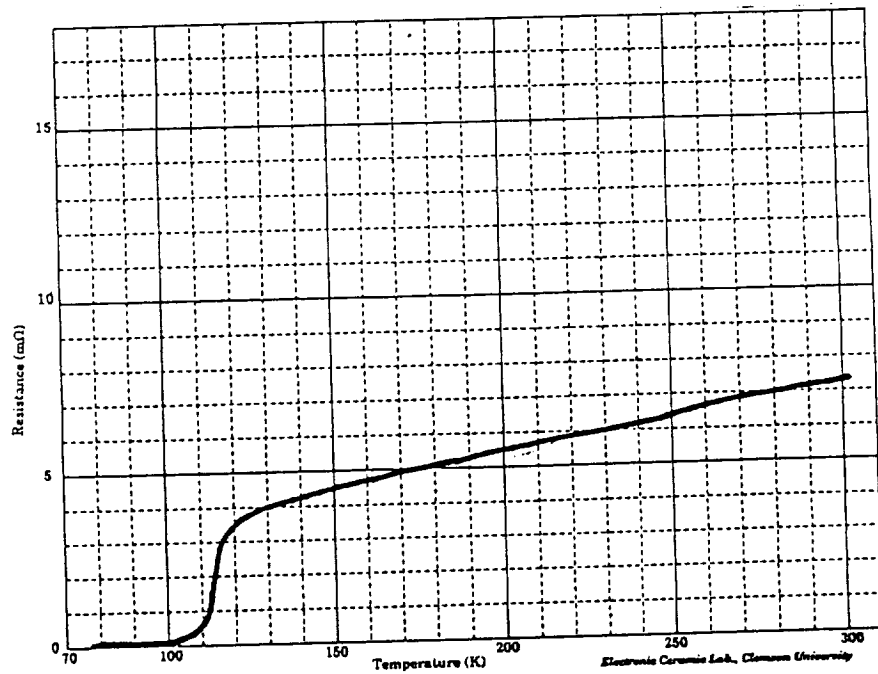
b) Pellet with a slow heating rate and quenched. The T_c was 102.9 K.

Figure 12 Resistance versus Temperature curves for bulk samples of $Bi_{1.6}Pb_{0.4}Sr_{1.9}Ca_{2.05}Cu_{3.05}O_x$ sintered at 845 °C for fifty-four hours in air. Determining influence of heating/cooling rate.

c) Pellet with a fast heating rate and slow cooling rate. The T_c was 101.4 K.
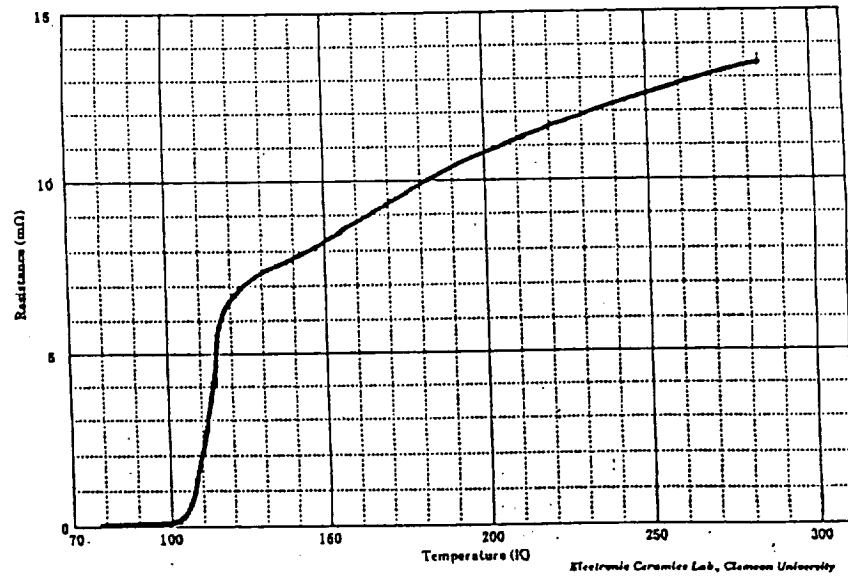
d) Pellet with a fast heating rate and quenched. The T_c was 101.2 K.

Figure 12 (Continued)
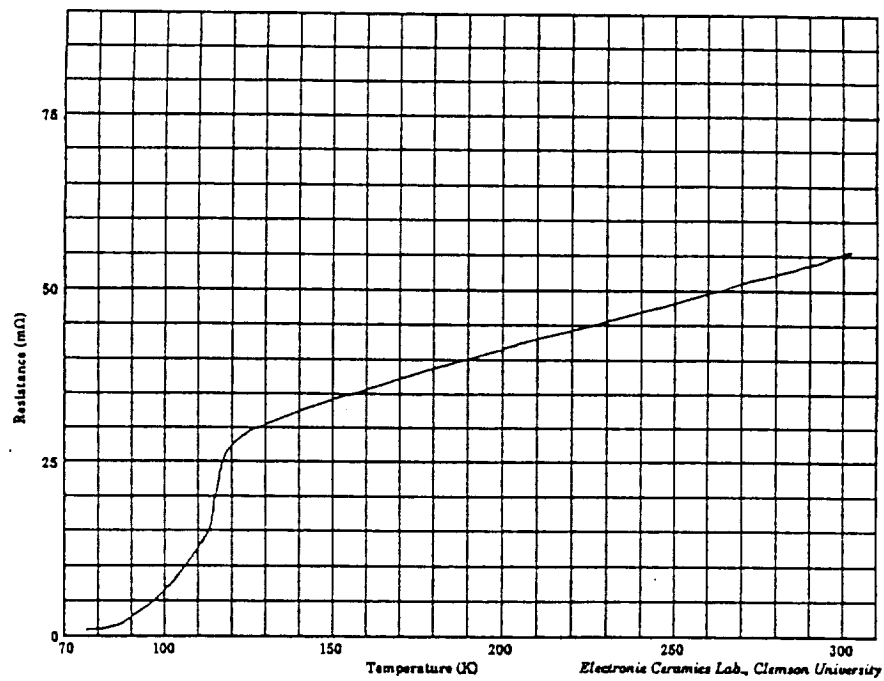
Figure 13 Resistance versus Temperature curve for a tapecast sample of $Bi_{1.6}Pb_{0.4}Sr_{1.9}Ca_{2.05}Cu_{3.05}O_x$ sintered at 845 °C for 20 hours in air. The tape did not superconduct and had a resistance of 0.94 mΩ at 77.3K.

Resistance versus Temperature Curve for
a bulk sample of $Bi_{1.6}Pb_{0.4}Sr_{1.9}Ca_{2.05}Cu_{3.05}O_x$
Sintered at 845°C for 28 hours. $T_c = 99.7$ K
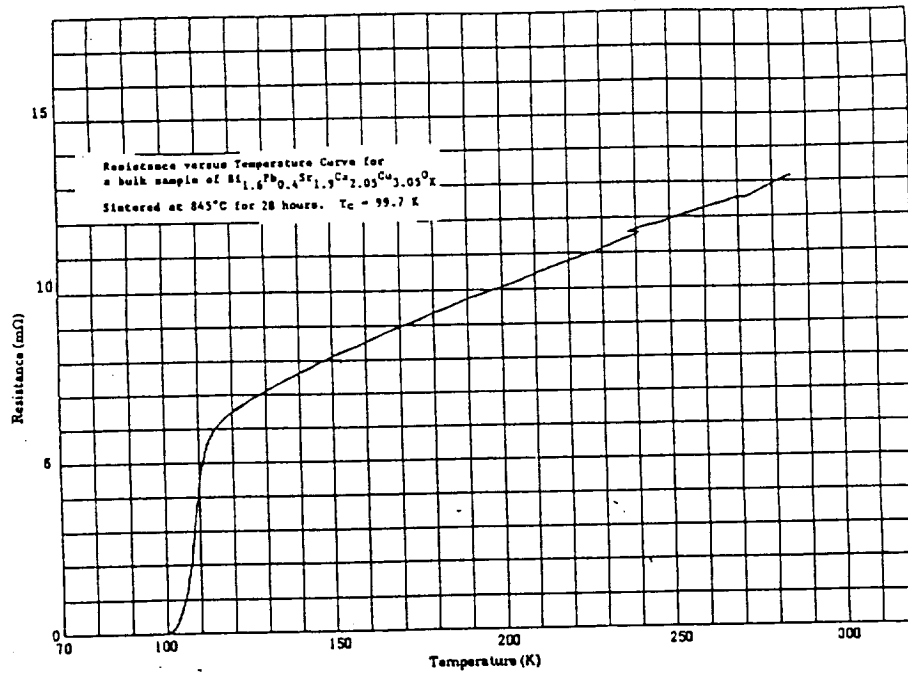
a) BSCCO bulk material. The T_c was 99.7 K.

Electronic Ceramics Lab., Clemson University
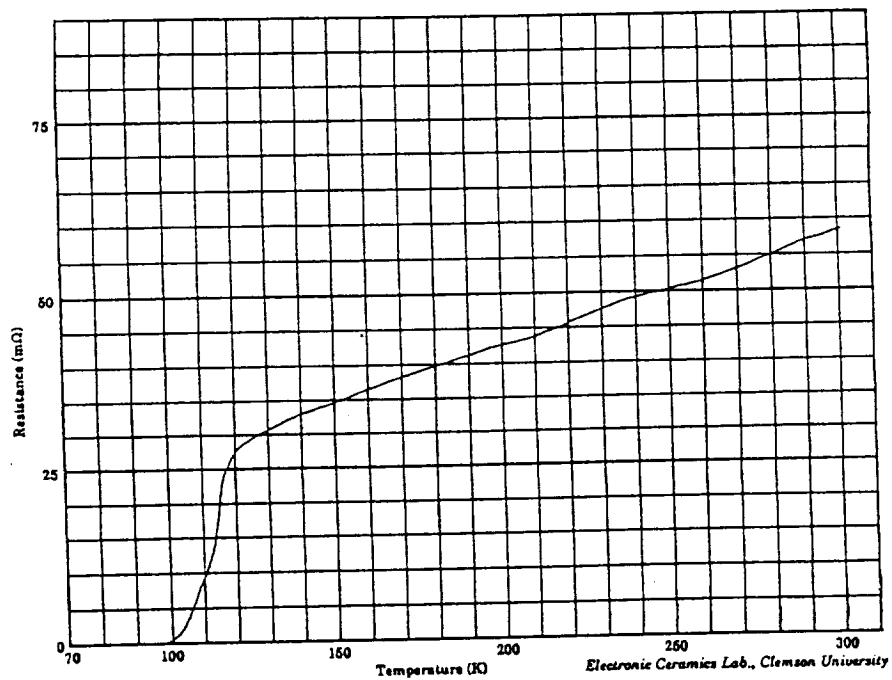
b)   BSCCO tapecast material. The Tc was 98.2 K.

Figure 14 Resistance versus Temperature curves for a bulk and a tapecast sample of $Bi_{1.6}Pb_{0.4}Sr_{1.9}Ca_{2.05}Cu_{3.05}O_x$ sintered at 845 °C for twenty-eight hours in air.
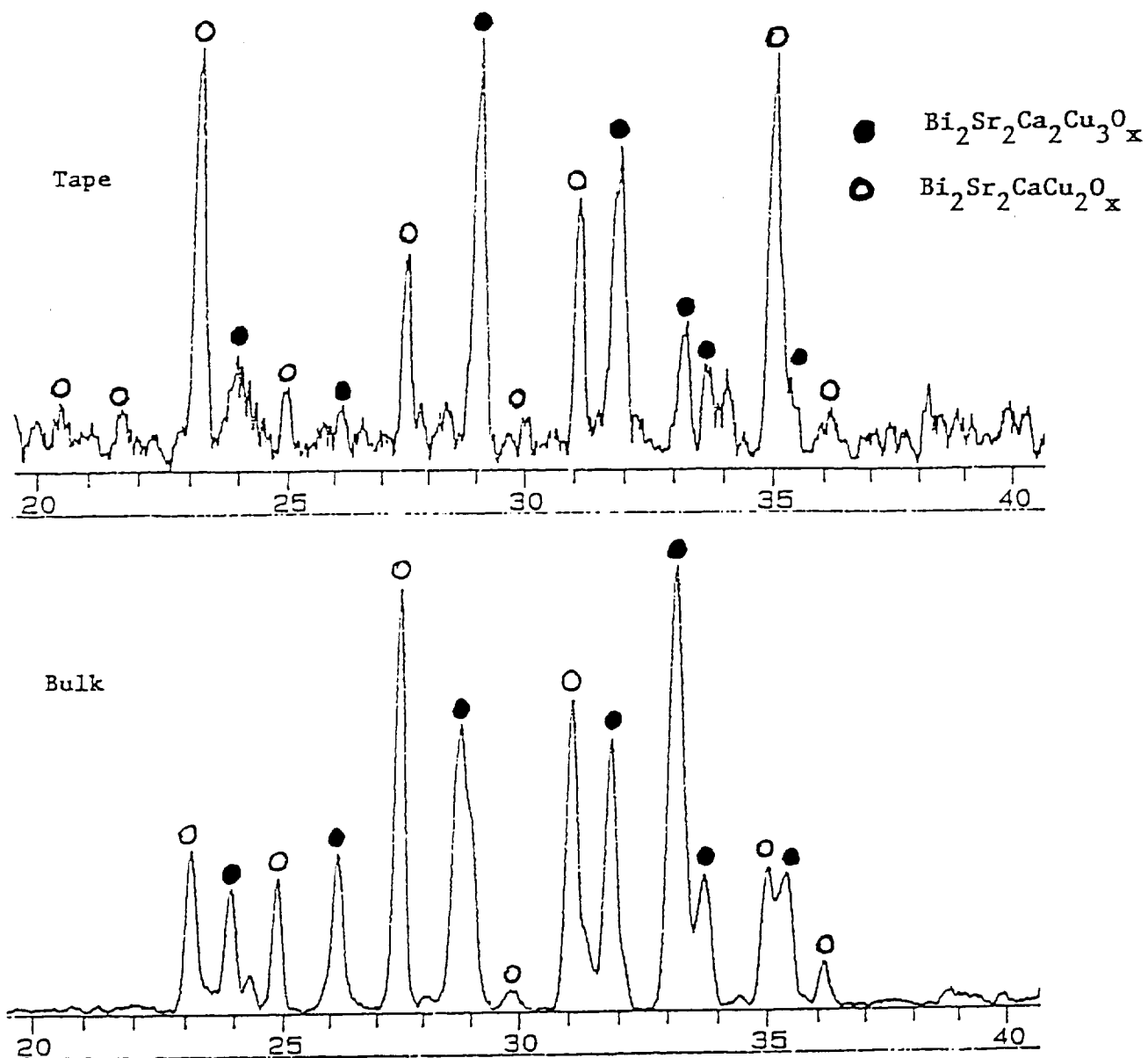
Figure 15 X-ray Diffraction data for a bulk compact and a tape sintered at 845 °C for twenty-eight hours in air.
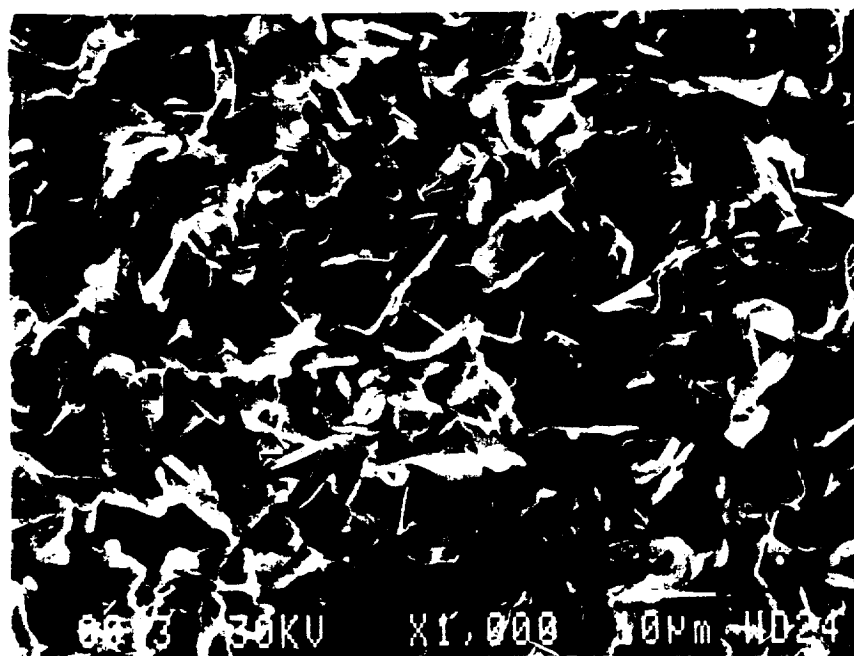
Figure 16 SEM micrograph for a $Bi_{1.6}Pb_{0.4}Sr_{1.9}Ca_{2.05}Cu_{3.05}O_x$ tape sintered at 845 °C for thirty-three hours in air.
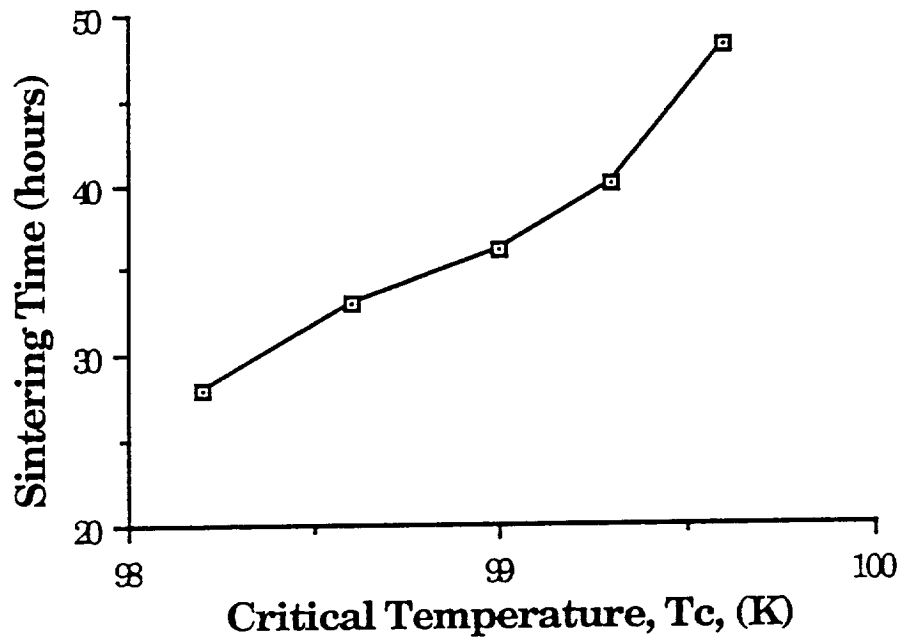
Figure 17 Sintering Time versus Critical Temperature curve for the $Bi_{1.6}Pb_{0.4}Sr_{1.9}Ca_{2.05}Cu_{3.05}O_x$ tapecast material, showing a linear increase in T_c as sintering time increases.
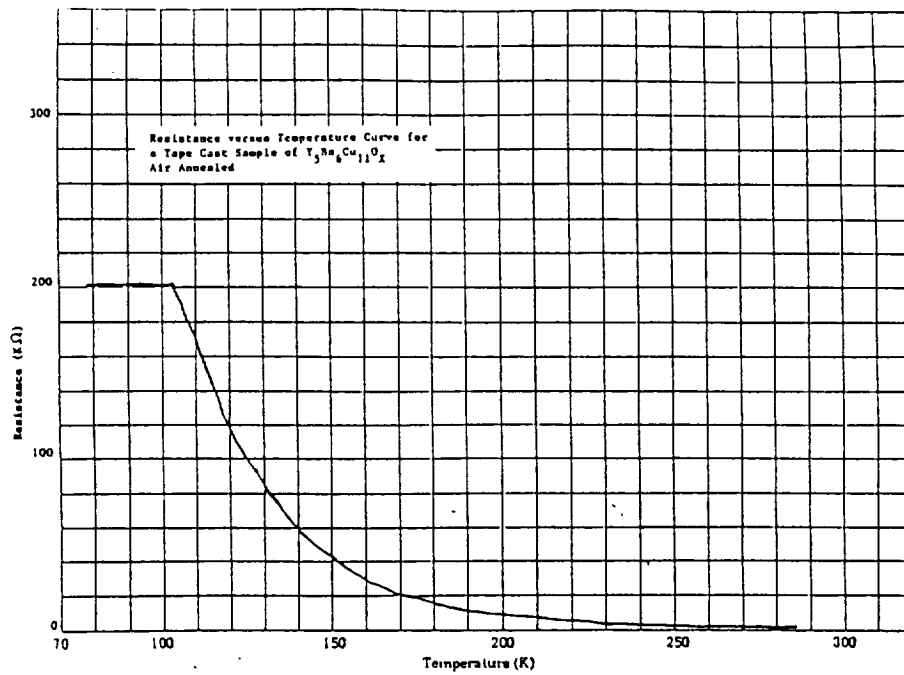
a) YBCO annealed in air.
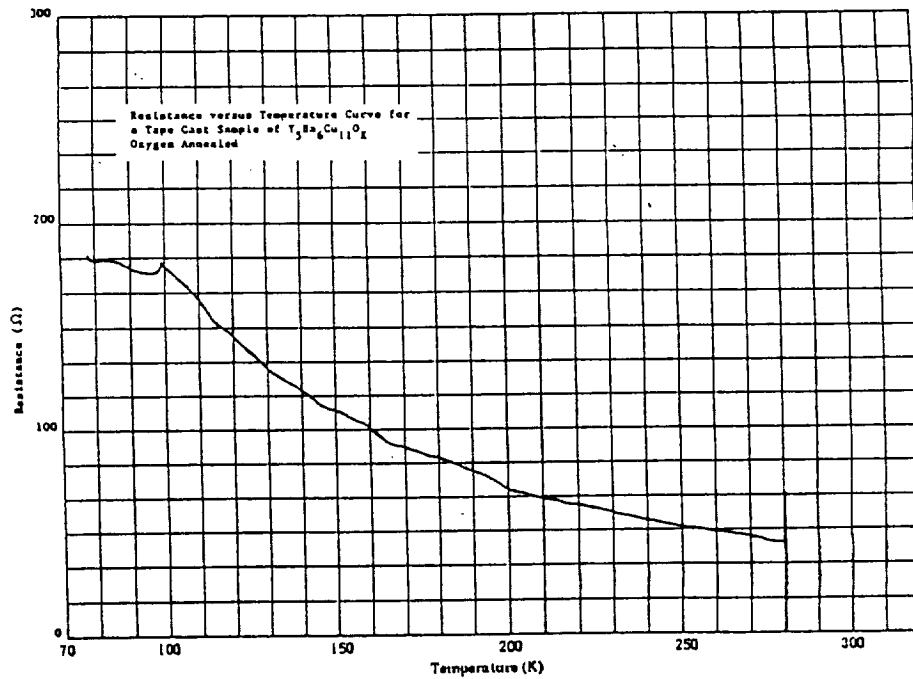
b)   YBCO annealed in oxygen.

Figure 18 Resistance versus Temperature curves for tapecast samples of
$Y_5Ba_6Cu_{11}O_x$ annealed for twenty-four hours in air or oxygen.

Annual Report

Part II

Development of Tl-Based Materials

submitted to

National Aeronautics and Space Administration
Langley Research Center

submitted by
Phillip Gilmour

Principal Investigator
Gene H. Haertling

Department of Ceramic Engineering
Clemson University
Contract No. NAG-1-1108
June 1991

Abstract

Several methods of processing the high temperature superconductor $Tl_2Ba_2Ca_2Cu_3O_{10}$ were investigated; i.e. different precursor compositions were sintered at various sintering times and temperatures. The highest superconducting temperature was found to be 117.8K when fired at 900°C for three hours. Higher sintering temperatures produced a melted sample which was nonsuperconducting at liquid nitrogen temperature. Also, a preliminary study found Li_2O substitutions for copper appeared to increase the transition temperature and create a fluxing action upon sintering. It was suggested lower sintering temperatures might be obtained with lithium additions to produce reliable $Tl_2Ba_2Ca_2Cu_3O_{10}$ processing methods.

I. Introduction

Thallium-based superconductors are layered materials often described as intergrowths of perovskite and rocksalt layers. Three of the most commonly occurring thallium superconductors are shown in Figure 1. With increasing layering there is a concomitant increase in transition temperature. The $Tl_2Ba_2Ca_2Cu_3O_{10}$ structure [the so called Tl-2223 phase] exhibits the highest reproducible superconducting transition temperatures to date, 120-125K.

There are several potential advantages of Tl-2223 compared to other high-temperature superconductors. Unlike $YBa_2Cu_3O_{7-\delta}$ [the 123 structure] there is no phase transition down to 1K,[2] therefore no microcracking can occur for this reason, although differential thermal expansion of different lattice directions could present a problem.[3] Complete phase formation of Tl-2223 is much more easily attained than the bismuth analogue, $Bi_2Ca_2Cu_3O_{10}$. Also, the intrinsic critical current density, greater than $1x10^8$ A/cm^2, is believed to be at least an order of magnitude higher than the 123 system.[4]

However there are disadvantages of thallium superconductors; probably foremost among these are thallium toxicity and volatility. The highly volatile nature of thallium arises from the transition

$$Tl_2O_3 \rightarrow Tl_2O + O_2 \quad 875°C.$$
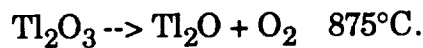
The reduction of Tl_2O_3 close to the sintering temperature creates a low melting point compound. Thallous oxide also exhibits a low boiling point which creates significant thallium loss. To ameliorate this problem, oxygen sintering is often used to shift the above reaction to the left. Thallium loss is further reduced by complete encapsulation or wrapping the material in an inert metal foil. Yet, these steps usually do not yield consistent results. Loss of thallium presents a major problem for reliable fabrication of thallium superconductors.

If one were to peruse the literature on thallium superconductor processing, a confusing and contradictory picture of how to attain the highest transition temperature and optimize the critical current density would arise. As an example, some studies use stoichiometric mixtures of thallium, barium, calcium, and copper oxides to maximize the superconducting transition temperature.[5,6] Another study suggests reduced amounts of calcium will stabilize the highest transition temperatures;[7] while yet another investigation shows increased calcium at the expense of thallium will yield high transition

temperatures.[8] Part of the confusing state of thallium superconductor processing stems from the similar free energies of layered structures; however, a large contribution to thallium superconductor fabrication variability arises from the volatility of thallium and attaining correct oxygen stoichiometry and distribution.[9,10,11] The initial phase of the research to develop high transition temperature, high critical current density thallium superconductor tapes for the SAFIRE project will investigate reliable processing of these materials. This part of the investigation may yield information not only of value for production of high quality thallium superconductor tapes, but may be applicable to improvement of alternative processing modes of thallium, bismuth, and other high-temperature superconductors.

II. Powder Synthesis Methods

Three routes were used to prepare precursor materials for sintering ceramic $Tl_2Ba_2Ca_2Cu_3O_{10}$. The first method consists of mixing the oxide compounds Tl_2O_3, BaO_2, CaO, and CuO and firing without prior calcination. (Barium peroxide was used since oxygen is evolved upon reduction of BaO_2 to BaO at 800K; it was hoped generation of oxygen within the material close to the sintering temperature would reduce thallium volatility.) Some investigations, such as Ginley et. al.,[5] used this simple procedure to form Tl superconductors with transition temperatures up to 120K.

A second method of oxide precursor formation was calcination of BaO_2, CaO, and CuO at 925°C for 24 hours to form the low melting point compound $Ba_2Ca_2Cu_3O_7$. Sheng and Hermann[6] developed this method to aid densification by liquid phase sintering. Stoichiometric amounts of thallic oxide were mixed with the precurosor material prior to sintering.

The third preparation was performed by batching CaO and CuO and firing for 925°C for 24 hours. Barium peroxide was added with Tl_2O_3 prior to sintering. This method is a modification of Sheng and Hermann's procedure. This process was done in order to examine the effects of oxygen generation within the material, by barium peroxide reduction, with a calcined material, $Ca_2Cu_3O_5$, and Tl_2O_3.

The general ceramic processing scheme is shown in Figure 2. Stoichiometric amounts of the initial oxides† were thoroughly mixed in a porcelain mortar and pestle. If the precursors were calcined, the powders were placed on an alumina setter and heated with the furnace to 925°C. After

calcining for 8 hours, the material was allowed to cool with the furnace. The calcined material was ground and passed through a 100 mesh sieve. This process was performed three times for a total calcination time of 24 hours.

After the calcination step, Tl_2O_3 and the remaining oxide constituents were added to the calcined material in stoichiometric proportions. (To reduce thallium loss, thallic oxide is usually added prior to sintering and not in the calcination step.) Green pellets, 13mm diameter by 3 mm thick, were formed by pressing 1.5g of material at a pressure of $2.7\times10^3 Kg/cm^2$ [3.9×10^4 psi].

The green pellets were wrapped in silver foil and fast-fired in flowing oxygen. Oxygen was fed into the furnace to reduce thallium volatility. After the specified soak time, pellets were taken out of the furnace and air-quenched to room temperature.

Pellets were electroded by firing with silver paste[‡] at 600°C for 20 minutes and cooled with the furnace. Due to the low temperature (and consequently low thallium volatility), pellets were not wrapped in silver foil.

III. Sintering Studies of $Tl_2Ba_2Ca_2Cu_3O_{10}$

Tables 1, 2, and 3 show the results of sintering the three different batches for precursor powders. Sintering temperatures of 870°C, 880°C, 890°C, 900°C and 910°C were studied with soak times ranging between 30 and 180 minutes. As seen in the tables, there appears to be a gradual increase in the superconducting critical transition temperature with increasing sintering temperature and soak times for all types of preparations studied. Apparently, the superconducting ceramics produced without prior calcination (Table 1) form a superconducting phase more readily compared to batches which were calcined. The trend is clearly illustrated in Table 3; sintering the batch which contained $Ba_2Ca_2Cu_3O_7$ as a precursor for 30 minutes, did not yield a superconducting material at the lower sintering temperatures studied. Whereas the higher temperature superconducting phases seemed to gradually develop for batches which were

---

[†]The raw powders were: Tl_2O_3/Malinckrodt, Lot 3800KCAM; BaO_2/ Eastman Kodak Co. Lot A16A; CaO/Fisher Scientific, Lot 864342; CuO/Fisher Scientific, Lot 901219; and LiO_2/Johnson Matthey Electronics, Lot K26A20.

[‡]The silver paste was formulated to fire at 600°C: Dupont conductor composition #7095, Lot 77D114.

calcined, sintering with the original metal oxides did not appreciably increase the transition temperature with time or temperature.

Figure 3 shows SEM photomicrographs of as-fired surfaces of the ceramic pellets (batched with Tl_2O_3, BaO_2, CaO, and CuO as the precursors) which were sintered for three hours at 870°C and 890°C. The surface of the 870°C fired sample shows appreciable cracking. Cracking can also be seen in the 890°C sintered sample. The microcracking appears to be a problem for all pellets sintered from the separate constituent oxides. Large scale cracking was also obvious when examined without the aid of a microscope, yet cracking was not observed for pellets which had calcined material as a sintering precursor. This created a deleterious effect when the samples were cooled to liquid nitrogen temperature. Figure 4 illustrates the resistance as a function of temperature for a pellet sintered from the original oxide powders. The discontinuites on the curve were accompanied by an audible "snap" and indicated sample cracking. Cracking of the ceramic occurred in most samples prepared this way; however, few samples containing $Ca_2Cu_3O_5$ or $Ba_2Ca_2Cu_3O_7$ as a precursor showed the phenomenon when cooled.

Figure 3 also shows considerable melting of the pellet surface fired at 890°C. The relatively high transition temperature of the sample, 112.3K, seems to agree with the generally acknowledged observation that slight melting must occur to create the high transition temperature phase Tl-2223.

A fracture surface of both samples is shown in Figure 5. The sample fired at 890°C shows plate-like morphology similar to the Tl-2223 phase identified by Sheng and Hermann.[6] The ceramic fired at lower temperature showed similar areas but were not as prevalent.

The powder x-ray diffraction patterns shown in Figure 6 show higher temperature superconducting phases appear to be formed at increased sintering temperatures and extended soak times. When Tl_2O_3, BaO_2, and $Ca_2Cu_3O_5$ were sintered for thirty minutes at 900°C, a mixture of superconducting phases is present: $Tl_2Ba_2CuO_6$ (T_c=85K), $Tl_2Ba_2CaCuO_8$ (T_c=110K) and $Tl_2Ba_2Ca_2Cu_3O_{10}$ (T_c=120K). However when sintered for 180 minutes, the transition temperature of the ceramic jumped to 117.8K as seen in Figure 7, and the material is almost entirely Tl-2223. If this batch is sintered for 180 minutes but the temperature is decreased to 880°C, complete conversion to the Tl-2223 phase does not occur as evident in Figure 6. Instead a mixture of Tl-2212 and Tl-2223 phases suggests one

should sinter close to the melting point of the material to optimize the transition temperature.

It was mentioned that pellets were fired at 910°C in this study. All samples fired at this temperature, resulted in melting the sample and silver foil. Consequently, the material was exposed to the furnace atmosphere and thallium loss resulted. The samples exhibited no superconductivity down to liquid nitrogen temperature.

IV. Additions of Li_2O to $Tl_2Ba_2Ca_2Cu_3O_{10}$

As previously mentioned, optimization of the superconducting properties is accomplished by complete encapsulation or wrapping in an inert metal foil and sintering in an oxygen atmosphere. Because of this added processing constraint, lithium oxide additions to the superconductor were investigated. Lithium has been used in ceramic processing to induce liquid phase sintering, lower sintering temperatures, and increase the fired density of the ceramic.[12,13,14] The mechanism by which lithium reduces sintering temperature is generally ascribed to creating oxygen vacancies which increase anion diffusion upon sintering.[15] Since the correct oxygen distribution is critical to create a high temperature superconductor, it was thought that small concentrations of lithium could reduce sintering temperatures, thereby reducing thallium volatility at sintering temperature, while possibly improving the electrical properties of the superconductor.

A literature review of alkali metal and lithium additions to superconductors shows a series of papers by Kawai, et. al. [16,17,18] in which lithium added $Bi_2Sr_2CaCu_2O_8$ acts as a sintering aid. It was found that up to 40% of the copper could be replaced by lithium to dramatically reduce the sintering temperature to 710°C while improving phase purity and increasing the transition temperature from 80K to 91K. The increased transition temperature is particularly remarkable since gross substitutions of lithium for copper yielded a transition temperature comparable to the highest values reported for this compound.

In our investigation, 1.0, 3.3, and 6.7 mole percent substitutions of lithium for copper were added by calcining BaO_2, CaO, CuO, and LiO_2 for 24 hours at 920°C with three intermediate grindings. Thallic oxide was added to the calcined powder and mixed in a mortar and pestle. Formation of the green pellets was

carried out in the same manner as described previously. The pellets were wrapped in silver foil and sintered in flowing oxygen at 900°C for 30, 60, and 90 minutes.

As evident in Figure 8, increasing amounts of lithium increases the critical transition temperature. Sintering for only one-half hour resulted in a transition temperature of 108.8K for the highest lithium concentration. When sintered for one hour, the samples with the two greatest lithium concentrations melted. However, Figure 9 shows the lowest lithium concentration did not melt at this soak time and exhibits a transition at 115.7K. This suggests that not only sintering temperature but also soak time is critical to optimize the superconducting properties with or without lithium additions. Also, soak times of one and one-half hour resulted in melted, nonsuperconducting samples for all lithium concentrations.

This preliminary study suggests superconducting properties can be improved with lithium additions. Furthermore, sample melting containing higher lithium concentrations and longer sintering times suggest lithium produces a strong fluxing action as expected. This initial study appears quite promising. Since the previous studies by Kawai et. al. indicate large substitutions of lithium for copper steadily improve the superconducting properties and reduce sintering temperature (these are much greater lithium concentrations than the amounts used in this study), it is possible improved superconductors and more reliable processing (due to lower thallium volatility at lower temperature) can be developed.

V. Summary of Results

High-temperature thallium superconductors were obtained by flash-firing silver wrapped green pellets under flowing oxygen.

1. Sintering Tl_2O_3, BaO_2, and $Ca_2Cu_3O_5$ appear to yield the most desirable results. The highest transition, 117.8K, occurred when sintered at 900°C for 3 hours.

2. Sintering the oxides Tl_2O_3, BaO_2, CaO, and CuO resulted in cracked samples. Further cracking appeared when the ceramics were cooled to liquid nitrogen temperature.

3. To obtain nearly pure phase $Tl_2Ba_2Ca_2Cu_3O_{10}$, temperatures near, but not exceeding, the melting point of the material must be reached.

4. Sintering less than three hours did not result in appreciable formation of $Tl_2Ba_2Ca_2Cu_3O_{10}$. Shorter times yielded a mixture of superconducting phases.

5. Lithium oxide additions increase the superconducting transition temperature and possibly create a fluxing effect upon sintering.

VI. References

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Compounds Used for Sintering: Tl_2O_3, BaO_2, CaO, and CuO

Sintering Temperature		870°C	880°C	890°C	900°C
Soak Time	30 min	97.5K	98.2K	98.3K	104.4K
	60 min	103.7K	103.1K	102.6K	102.9K
	120 min	104.4K	104.3K	104.9K	107.1K
	180 min	104.6K	103.4K	112.3K	104.3K

Table 1

Critical superconducting temperature of the nominal compostion $Tl_2Ba_2Ca_2Cu_3O_{10}$ as a function of sintering time and temperature. Powders used for sintering: Tl_2O_3, BaO_2, CaO, CuO.

Compounds Used for Sintering: Tl_2O_3, BaO_2, $Ca_2Cu_3O_5$

Sintering Temperature		870°C	880°C	890°C	900°C
Soak Time	30 min	96.8K	99.9K	99.2K	104.0K
	60 min	103.7K	106.8K	102.0K	106.2K
	120 min	102.0K	103.6K	103.5K	110.9K
	180 min	107.4K	102.9K	109.8K	117.8K

Table 2

Critical superconducting temperature of the nominal compostion $Tl_2Ba_2Ca_2Cu_3O_{10}$ as a function of sintering time and temperature. Powders used for sintering: Tl_2O_3, BaO_2, $Ca_2Cu_3O_5$.

Compounds Used for Sintering: Tl_2O_3, $Ba_2Ca_2Cu_3O_7$

Sintering Temperature		870°C	880°C	890°C	900°C
Soak Time	30 min	X	X	X	105.9K
	60 min	96.7K	96.4K	96.5K	105.2K
	120 min	96.0K	104.0K	114.8K	107.3K
	180 min	102.6K	105.2K	-------	-------

Table 3

Critical superconducting temperature of the nominal compostion $Tl_2Ba_2Ca_2Cu_3O_{10}$ as a function of sintering time and temperature. Powders used for sintering: Tl_2O_3, $Ba_2Ca_2Cu_3O_7$. X denotes nonsuperconducting at liquid nitrogen temperature.

Tl$_2$Ba$_2$CuO$_6$ Tl$_2$Ba$_2$CaCu$_2$O$_8$ Tl$_2$Ba$_2$Ca$_2$Cu$_3$O$_{10}$

a   b   c
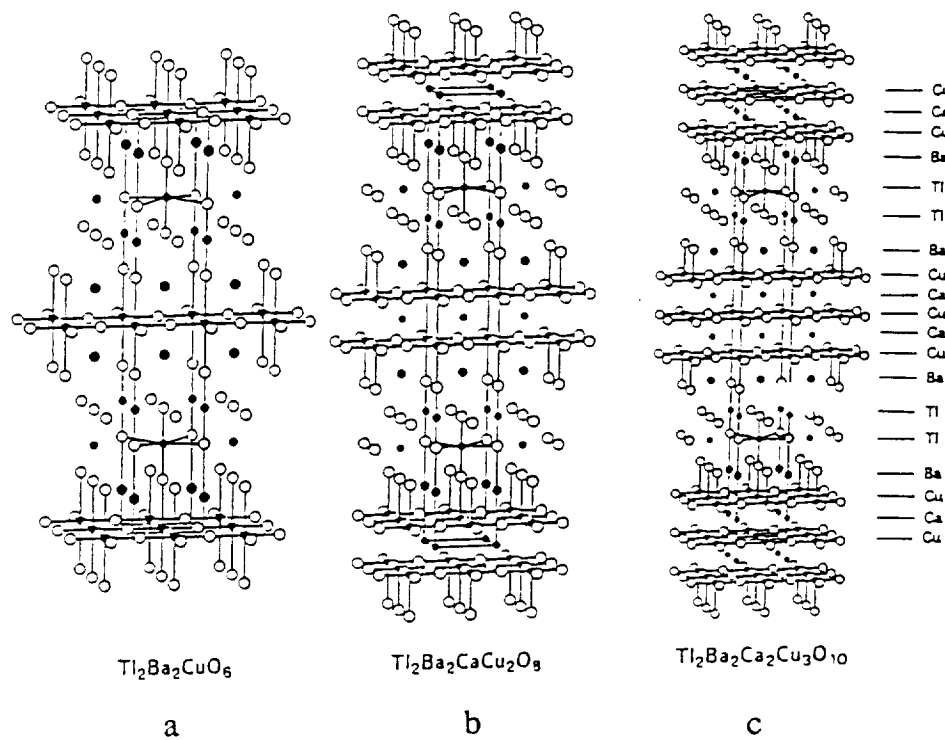
Figure 1

Commonly Appearing Superconducting Phases. Torardi, et. al.[1]

a) Tl$_2$Ba$_2$CuO$_6$ [T$_c$=85K]

b) Tl$_2$Ba$_2$CaCu$_2$O$_8$ [T$_c$=110K]

c) Tl$_2$Ba$_2$Ca$_2$Cu$_3$O$_{10}$ [T$_c$=120K]

Batch I   **Batch II**   **Batch III**

Mix Stoichiometric Amounts of Tl2O3, BaO2, CaO, and CuO in a Mortar and Pestle.

Mix Stoichiometric Amounts of CaO and CuO in a Mortar and Pestle

Mix Stoichiometric Amounts of BaO2, CaO, and CuO in a Mortar and Pestle

Calcine at 925°C for 24 hours with Two Intermediate Grindings

Mix Stoichiometric Amounts of Tl2O3 and BaO2 with Calcined Ca2Cu3O5 in a Mortar and Pestle

Mix Stoichiometric Amounts of Tl2O3 with Calcined Ba2Ca2Cu3O7

Flash-Fire Silver Wrapped Foil in Flowing Oxygen 870-910°C for 30-180 Minutes

Electrode with Silver Paste 600°C, 20 Minutes Cool with Furnace

Figure 2

Flow Sheet of Three Methods of Forming a Superconductor Ceramic with the Nominal Composition $Tl_2Ba_2Ca_2Cu_3O_{10}$

a

b
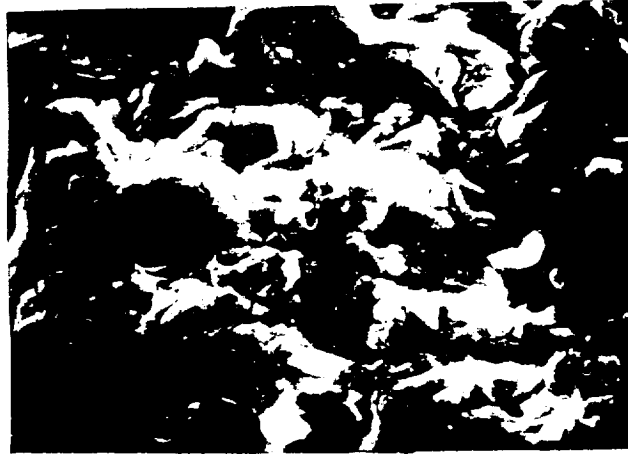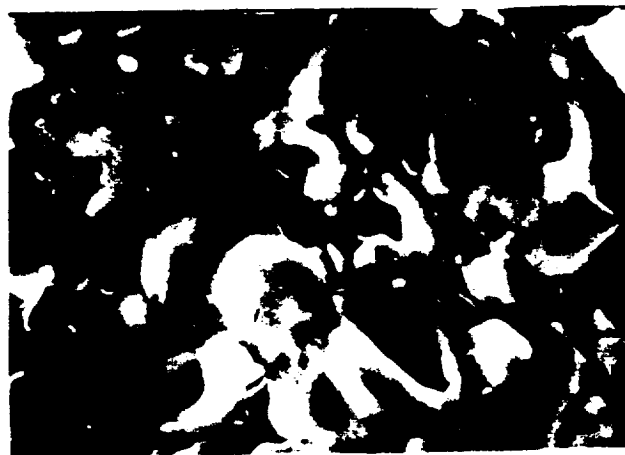
1500 MAGNIFICATION

Figure 3

SEM Photomicrographs of As-Fired
Surface Pellet Batched with Tl_2O_3, BaO_2, CaO, CuO
a) fired at 870°C for three hours
b) fired at 890°C for three hours
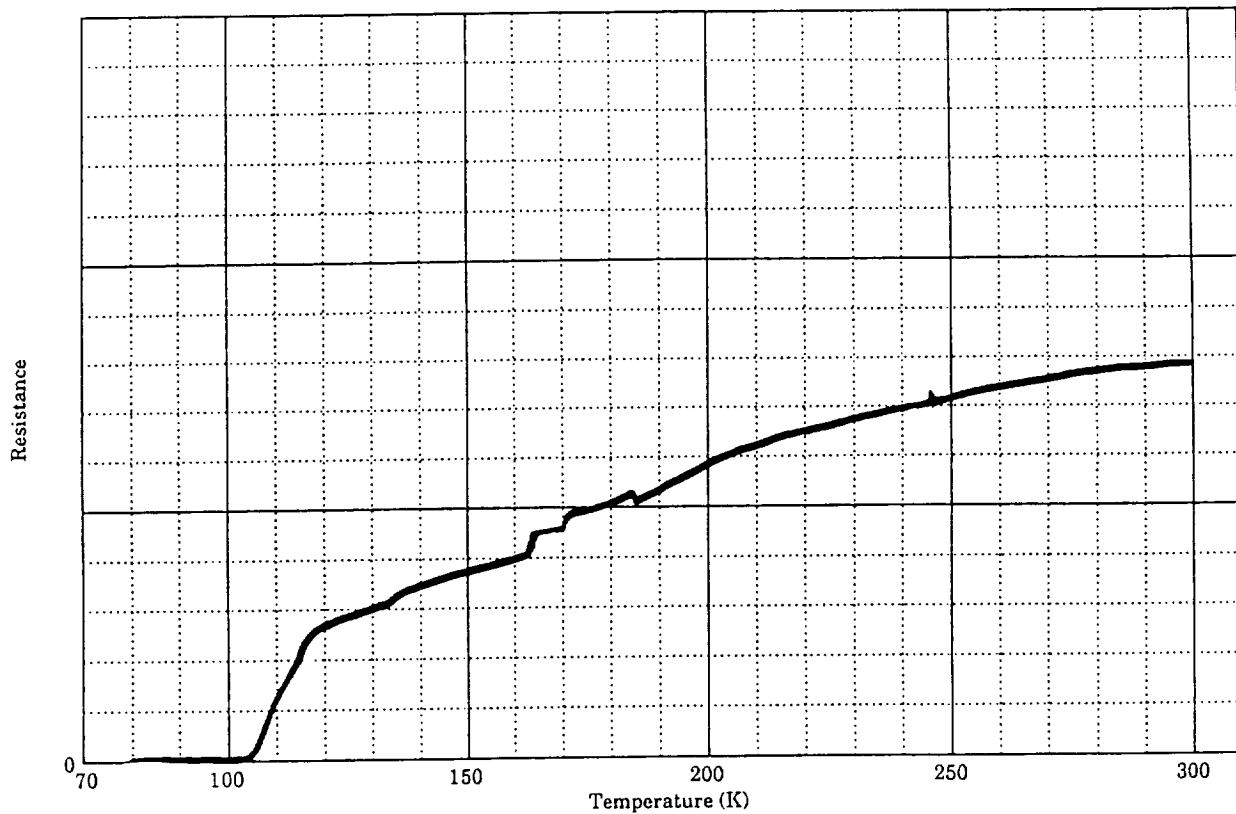
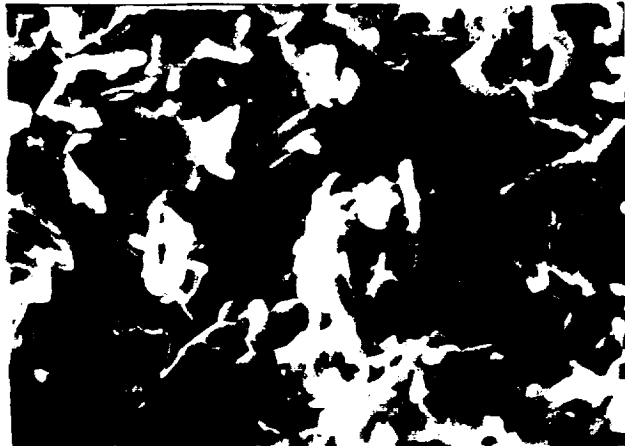**Figure 4**

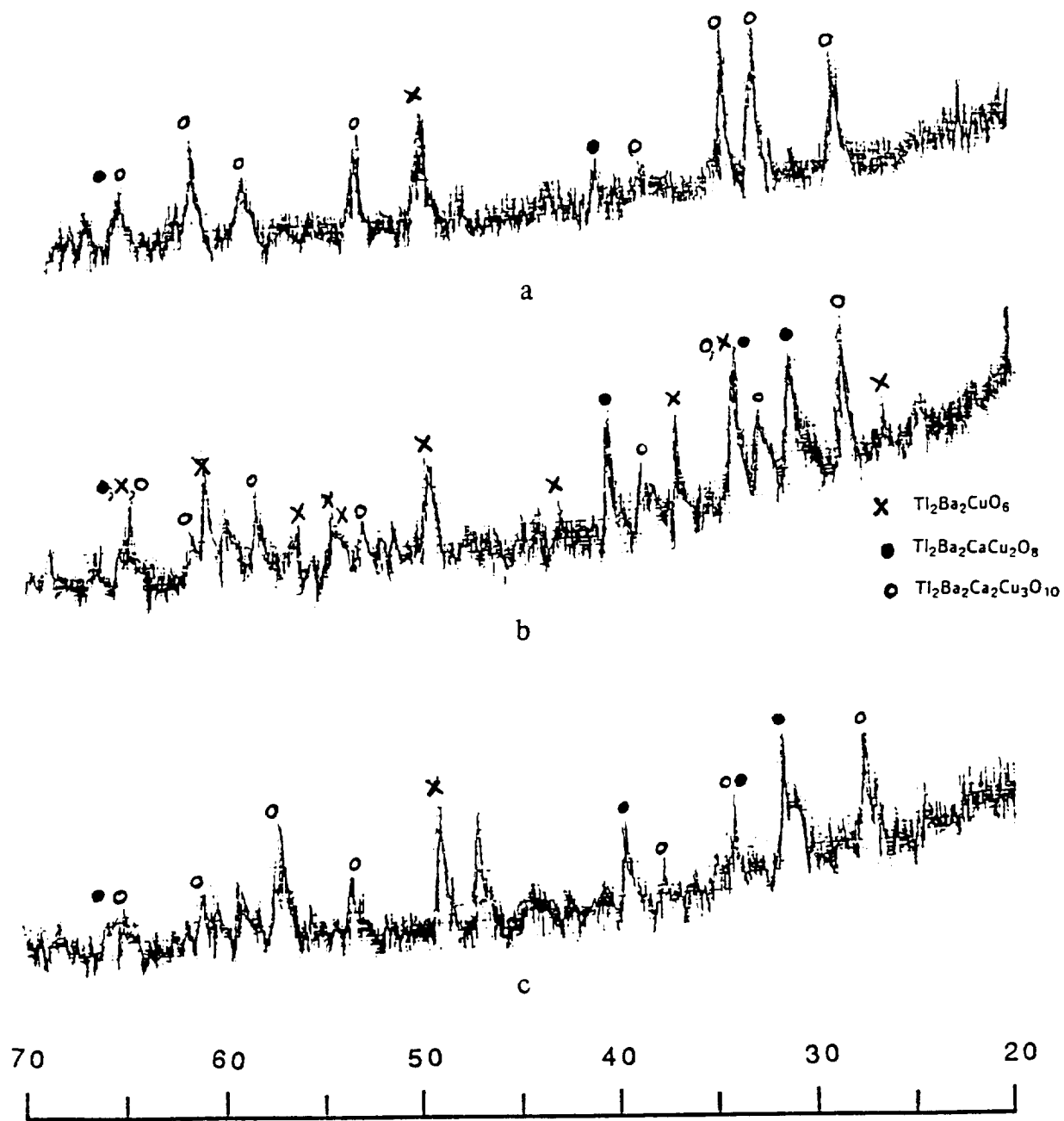Resistance as a Function of Temperature for a Pellet
Batched by Tl_2O_3, BaO_2, CaO, CuO. Fired for One Hour at 880°C.
Discontinuities indicate cracking. [T_c=104.4K]

a

b
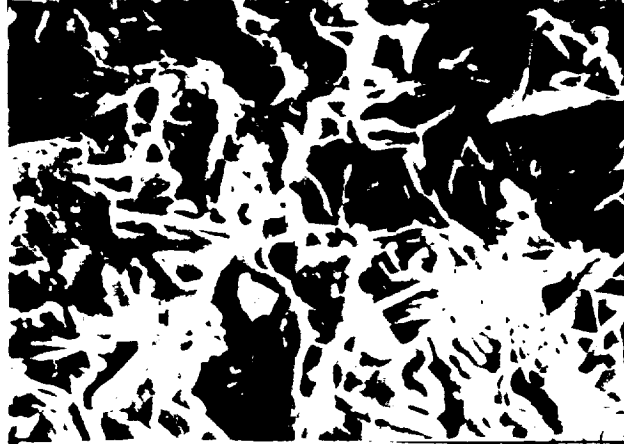
1500 MAGNIFICATION

Figure 5

SEM Photomicrographs of Fractured Surface
Ceramic Pellets Batched with Tl_2O_3, BaO_2, CaO, CuO
a) fired at 870°C for three hours
b) fired at 890°C for three hours

Figure 6

X-Ray Diffraction Profiles of Ceramic
Samples Batched with Tl_2O_3, BaO_2, and $Ca_2Cu_3O_5$
a) fired at 900°C for 180 minutes
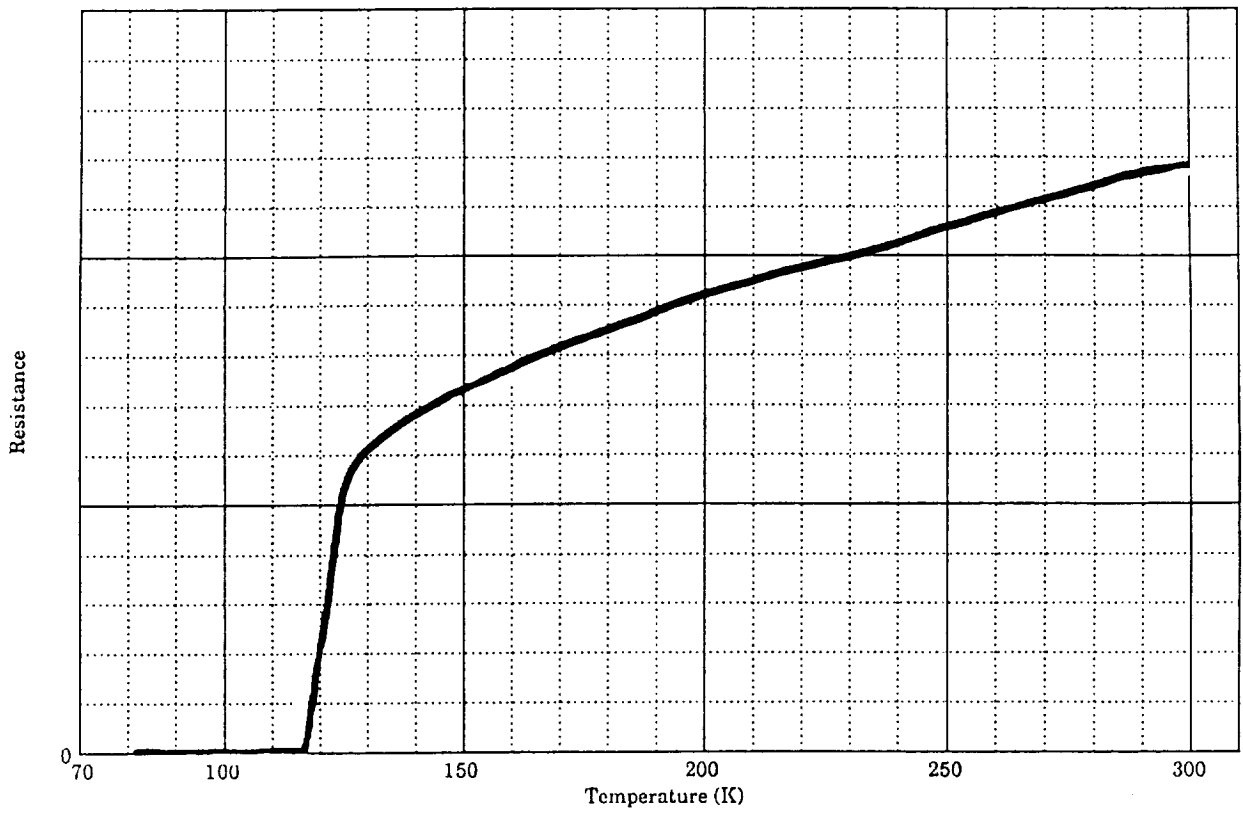b) fired at 900°C for 30 minutes
c) fired at 880°C for 180 minutes

Figure 7

Resistance as a Function of Temperature for a
Ceramic Sample Batched with Tl_2O_3, BaO_2, and
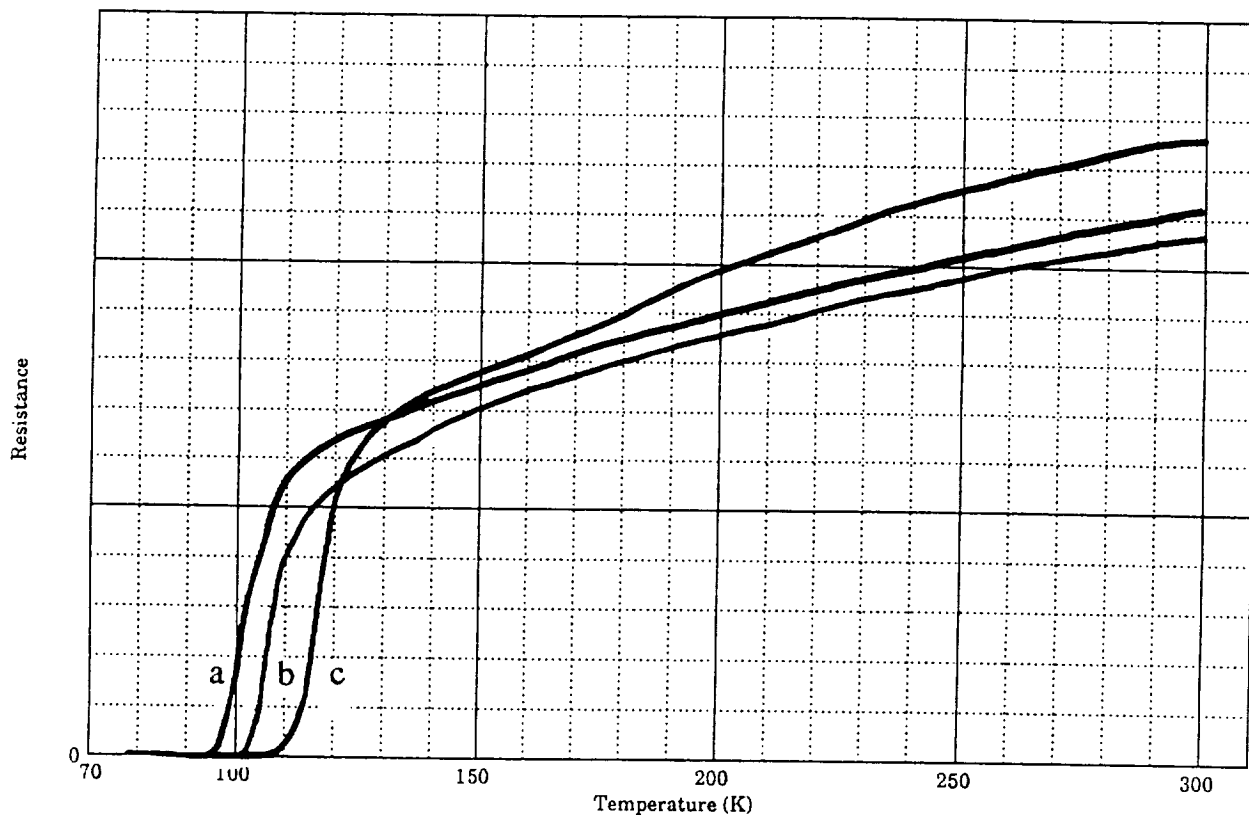$Ca_2Cu_3O_5$ and Sintered at 900°C for Three Hours [T_c=117.8K]

Figure 8

Resistance as a Function of Temperature for Ceramics Batched
with Tl_2O_3 and $Ba_2Ca_2Cu_{3-x}O_7/Li_x$ Fired at 900°C for 30 Minutes
a) x=0.06 [T_c=93.3K]
b) x=0.10 [T_c=101.2K]
c) x=0.20 [T_c=108.0K]

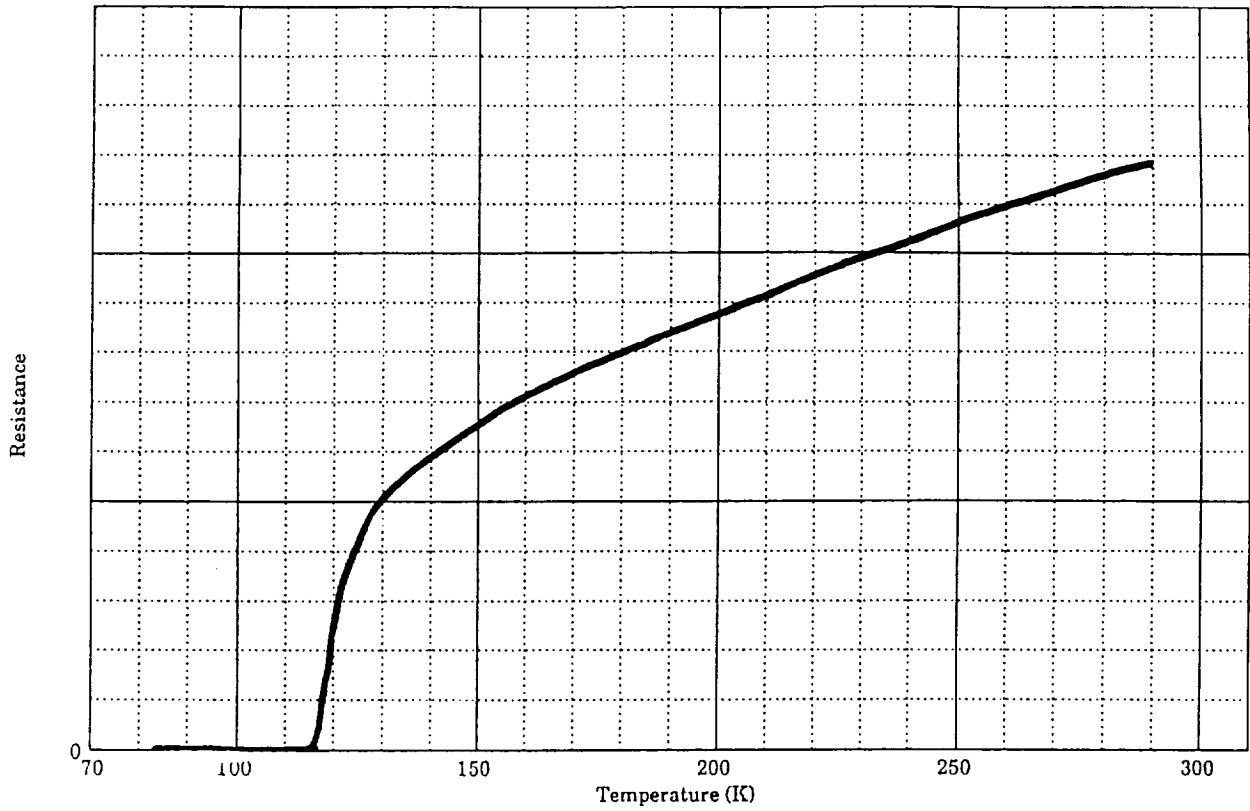**Figure 9**

Resistance as a Function of Temperature for Ceramics
Batched with Tl_2O_3 and $Ba_2Ca_2Cu_{2.94}Li_{0.06}O_7$ Fired at 900°C for 60 Minutes.
[T_c=115.7K]