# MELT PROCESSING OF Bi-Ca-Sr-Cu-O SUPERCONDUCTORS

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## ABSTRACT

Several Bi-Ca-Sr-Cu-O compositions were melted in $Al_2O_3$ or Pt crucibles at temperatures between 1050C and 1200C. As-quenched specimens crystallized from the upper surfaces, while the bottom layers were glassy. Glass formation was improved for higher $Bi_2O_3$ concentrations. The crystalline portions were highly conductive, while the glassy layers were insulating. Both did not show superconductivity down to 10K. Thermal treatment in air caused a dramatic effect on the electronic properties; and annealing at 865C for long periods converted the two types of specimens (previously glassy or crystalline) to superconductors, at least for one composition. Aluminum impurity (up to 8.6 atom. pct.) had no detectable effect on the transition temperatures, i.e., $T_C \simeq 85K$ for all superconducting samples. The flake-like ($Bi_2Ca_1Sr_2Cu_2$) phase, reported by other authors, was responsible for superconductivity.

## INTRODUCTION

The discovery of high temperature superconducting materials (1-4) (HTSC) was a major breakthrough in modern science and technology. At present, a large number of processing techniques are being explored, the main goals being the development of HTSC with diverse geometries having improved properties, especially high critical temperatures ($T_C$), high critical current densities ($j_C$), mechanical strength, etc. While it is recognized that the overall chemical composition has the strongest influence on both electrical resistance and critical temperature, the processing technique was demonstrated to have a strong effect on the microstructure and on the critical current density.

Melt processing techniques are potentially very interesting because, in principle, they can be used to fabricate complex geometries, such as wires, films and odd-shaped articles. They also can provide great flexibility for microstructural control, as well as for enhancing properties through chemical homogeneity.

In this paper we describe the melt processing, heat treatment and resulting properties of a new family of HTSC, Bi-Ca-Sr-Cu-O, recently discovered by Maeda, et al. (3). The main objective of the present paper is to explore the possibility of obtaining single-phase materials through controlled crystallization of the 2223 phase. A second objective is to verify the glass formation ability of the new system.

PREVIOUS WORKS ON MELT PROCESSING OF HTSC Y-Ba-Cu-O

A few papers have been published on the melt processing of Y-Ba-Cu-O high temperature superconductors (HTSC). McKittrick, et al. (5) have melted three compositions along the $YBa_2Cu_3O_{9-x}$ - $BaCuO_2$ tie-line and solidified them with different cooling rates. Rapid solidification resulted in new, previously unreported phases. Slower solidification rates yielded multiphase materials. Annealing in $O_2$ transformed them to the $YBa_2Cu_3O_{9-x}$ orthorhombic phase plus varying amounts of $BaCuO_2$. All materials showed superconductivity at 88K. Komatsu, et al. (6) reported on $YBa_2Cu_3O_7$ which was melted in a Pt crucible at 1400C for 2 hours. The melt was subjected to three different quenching histories; and all showed $Y_2O_3$ and $BaCuO_2$ as crystalline phases. An interesting observation was made that after annealing at 900C for 48 hours the three specimens had zero resistance at similar temperatures, $T_c \simeq 90K$. Jin, et al. (7) described the crystallization of slowly cooled $YBa_2Cu_3O_{7-x}$, which resulted in needlelike, somewhat aligned grains. An additional heat treatment was given to ensure the proper oxygen stoichiometry. Critical current densities of 7400 $A/cm^2$ in zero field and 1000 $A/cm^2$ in 1.0T at 77K resulted. More recently, the same authors reported that with further improvements in processing, the critical currents were increased to 1.7 x $10^4$ $A/cm^2$ in zero field and 4 x $10^3$ in 1.0T, the highest ever reported for bulk samples.

Kim, et al. (8) splat-cooled a $YBa_2Cu_3O_{7-x}$ melt between twin rollers. No evidence of superconductivity was found for the "as-quenched" material which was 10-20 μm thick and had some microcrystals ($Y_2O_3$) in an amorphous matrix. Superconductivity only developed after heat treatment at high temperatures (~900C) with a further treatment at 430C for 6 hours in flowing oxygen. $T_c$ was 90K.

Takahashi, et al. (9) melted $YBa_2Cu_3O_{7-x}$ in a Pt crucible at 1300C for 1 minute and roller-quenched the liquid. Partially amorphous films, 10-500 m in thickness, were heat-treated at 950C for 8 hours in air and slowly cooled. $T_c$ was 87K and $j_c$ = 1.3 $A/cm^2$.

An interesting observation in these studies is the (expected) difficulty of glass formation for the $YBa_2Cu_3O_{7-x}$ composition. In no case was a pure glass obtained.

Bi-Ca-Sr-Cu-O

Two announcements appeared in recent issues of High $T_c$ Update. The first was by Hinks, et al. (10) and the second by Komatsu, et al. (11). The latter authors describe (in abstract form) the melting and crystallization of Bi-Ca-Sr-Cu-O compositions with the highest $T_c$ (R=0) at 92K.

Th-Ca-Ba-Cu-O

There have been announcements that HTSC Th-Ca-Ba-Cu-O materials have been melt-processed and show transition temperatures as high as 125K.

EXPERIMENTAL METHODS

Three different compositions in the Bi-Ca-Sr-Cu-O system, with compositions 2223, 4334 and 4223, were melted in $Al_2O_3$ or Pt crucibles at temperatures varying from 1050C to 1200C for 15 minutes.* The batch materials were reagent grade $Bi_2O_3$, $CaCO_3$, $SrCO_3$, $Sr(NO_3)_2$ and CuO. The first three compositions were chosen based on recent reports (12,13) that identify two superconducting phases in the new system: the $T_c$ = 110K phase (2223) and the $T_c$ = 85K phase (2122). Both of these phases could not be obtained in isolation by sintering powders having the exact stoichiometric compositions, the recommended starting composition being 4334. In the present work, we attempted to make glasses and subsequently to crystallize single phase HTSC materials. The third composition, 4223, was made in order to test the effect of Bi on glass formation in this system.

The melts were very fluid and highly corrosive and, hence, a substantial amount of Al is expected to be dissolved in the liquid when melting is carried out in $Al_2O_3$ crucibles. Composition 2223P was melted in a Pt crucible and no sign of chemical attack was observed. In this case, $Sr(NO_3)$ was used instead of $SrCO_3$ to prevent reduction of Bi and consequent alloying with Pt. Some spillage of liquid occurred during melting.

The liquids were cast on graphite molds or quenched between two steel plates. Table I summarizes the compositions investigated. The glass yield is defined here as the thickness of the bottom layer (which first touched the mold on casting) and appeared glassy (shiny) to the eye. It should be noted, however, that SEM observations and X-ray diffraction analysis have shown a modest degree of crystallinity in both the 2223 and 4334 "glassy" layers. The glassy layers in the 4223 samples were X-ray amorphous.

The heat treatments were carried out in a muffle furnace. The specimens were inserted into the cool furnace which was then slowly heated to the desired temperature, between 845C and 885C, and held at that temperature for periods up to 40 hours. After the holding periods, the specimens were allowed to cool inside the furnace.

The resulting microstructures were analyzed by optical and scanning electron microscopy. Four probe d.c. electrical measurements were performed by the linear 4-point and the Van de Paun configurations. A current of 1 mA was used during the measurement. Silver paste was used to attach Indium leads to the samples.

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*The numbers indicate the atomic compositions of Bi, Ca, Sr and Cu. Further designations A and P refer to samples melted in $Al_2O_3$ and Pt crucibles respectively.

Table I

(Relative Atom. % Metal)

| | 2223A | 2223P | 4334 | 4223 | |
|---|---|---|---|---|---|
| Bi | 22.2 | 22.2 | 28.6 | 36.4 | |
| Ca | 22.2 | 22.2 | 21.4 | 18.2 | |
| Sr | 22.2 | 22.2 | 21.4 | 18.2 | |
| Cu | 33.3 | 33.3 | 28.6 | 27.3 | |
| Thicknesses of Glassy Layer | 3mm | zero | 1mm | 6mm | Cast Samples |
| | | Ø.2mm | | | Pressed Cooled Samples |

Dry helium gas (dried by flowing through a liquid $N_2$ trap) flowed through the cryostat at all times during the measurement to improve heat transfer. Wide angle X-ray diffraction was used to characterize the crystallinity of the samples and to identify the crystalline phases. An optical microscope with hot stage was used to observe the processes of crystallization and melting.

RESULTS

A.  Scanning Electron Microscopy

Figure 1a shows a typical SEM micrograph of cast 2223 material which had been melted in $Al_2O_3$.  Figure 1b shows a corresponding micrograph of 2223 material which had been melted in Pt and rapidly quenched between steel plates.  The greater thickness of the "glassy" layer in the sample melted in the $Al_2O_3$ crucible is evident - despite the more rapid cooling used with the sample melted in Pt.  The "glassy" regions are seen to contain some small crystals, which appear to be associated with bubbles (seed) in the material. These crystals were identified by x-ray diffraction as consisting entirely of the 2122 phase. The crystalline regions in these as-cooled specimens consist of plate-shaped crystals as well as a matte-appearing second phase. X-ray diffraction confirmed the presence of two phases.

Figure 1c shows the 2223 material after subsequent heat treatment of the "glassy" material to produce crystallization.  The presence of micaceous (plate-like) crystals is clearly seen, as are crystals of a second, matte appearing phase. Figure 1d shows a cast sample of 4334 material which had been melted in $Al_2O_3$.  The thickness of the "glassy" layer is seen to be larger than that in the 2223 material. As with the 2223A samples, some small crystals are seen in the "glassy" regions; and these crystals are the 2122

phase. The crystalline regions again consist of two phases, one of which is the plate-like in appearance and which was identified by diffraction as the 2122 phase.

## B. Optical Microscopy Observations

When heated in an oxygen atmosphere while viewed in an optical microscope, crystallization of the "glassy" 2223A material was observed to occur rapidly at temperatures in the range of 850C (growth rates were in the range of mm/sec). on further heating, partial melting was observed in the range of 925C. At higher temperatures, none of the plate-like crystals were seen; but the matte-appearing fine-grained crystals persisted until temperatures approaching 1200C.

By comparison, the 2223P material was observed to crystallize in periods as short as 10 sec. at temperatures in the range of 860-870C. On further increasing of the temperature, melting was observed to begin at about 890C; and by about 1050C, the sample was molten save for a small volume fraction of the matte appearing phase. This phase persisted to temperatures above 1220C.

## C. Resistivity vs. Temperature Behavior

### 2223

Figure 2 shows the relative resistances of composition 2223A (initially "glassy") which had been heat treated respectively at 845C for 4 hours, 865C for 40 hours and at 860C for 28 hours. The absolute values of the resistance at 273K (for similar geometries) were typically 0.02 , 0.004 and 0.12 (arbitrary units), respectively. The as-cast "glassy" specimen had a resistance of 24. Hence, there is a difference of 4 orders of magnitude between the least and the most resistive specimens. The resistivity at 300K of sample 2223A heated at 840C is 5700 $\Omega$-cm.

Figure 2 also shows the dramatic changes in behavior caused by different heat treatments. For treatment at 845C, a metallic behavior is observed, with a superconductive onset at $T_{on}$ = 110K, although zero-resistance behavior was not detected at temperatures above 85K. With a long treatment (40 hours) at 865C, the specimen warped slightly and was dark black. The resistance drops continuously with decreasing temperature and undergoes a clear transition with $T_C$ = 85K. The "anomaly" reported by several authors between 110K and 120K is clearly seen and indicates the presence of another superconducting phase. When the "glassy" specimen is heated at 885C, it partially melts, a shiny surface is obtained, and it fails to exhibit superconducting behavior, at least at temperatures down to 85K.

Figure 3 shows the relative resistance plots for three different compositions (2223A, 2223Pt and 2223B)** heated to 865C for several hours.

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**Sample 2223A was melted in a rather porous $Al_2O_3$ crucible, while sample 2223B was melted in an impervious $Al_2O_3$ crucible. The amount of attack on the crucible by the melt was much greater for 2223A than for 2223B.

In spite of the differences in chemical compositions (different $Al_2O_3$ contents), they all show metallic behavior and have zero resistance at approximately 85K.

## 4334

Figure 4 shows the relative resistances of composition 4334 as-quenched (crystalline side) and heated to 845C for 4 hours and to 875C for 2 hours. A similar trend as that shown by the 2223 composition is observed. Both as-quenched sides ("glassy" and crystalline) do not superconduct down to 10K. The glassy layer has a much higher resistance and is not shown in the graph. The "glassy" specimen heated to 845C has a much lower resistance which does not vary significantly down to 85K. The "glassy" specimen heated to 875C shows a superconducting onset at about 110K, but did not superconduct at temperatures above 85K.

## As-quenched Specimens

The only composition for which relatively thick specimens (6mm) could be made totally glassy, as confirmed by X-ray diffraction, is the 4223 material. The resistance of both the glassy and as-quenched crystalline layers did not drop to zero at any temperature above 10K. The 4334 composition exhibited similar behavior, although both "glassy" and crystalline layers showed inflections at 85K and onset at about 40K, implying the existence of some fractions of two superconducting phases.

Overall, it can be safely stated that none of the as-quenched samples (glassy, "glassy" or crystalline) superconduct at temperatures above 10K.

## DISCUSSION

The present work has demonstrated that melting, quenching and subsequent crystallization plus annealing provides a useful alternative route to powder or vapor-phase processing for forming superconducting Bi-Ca-Sr-Cu-O materials. When combined with previous data on melt-processed Y-Ba-Cu-O materials, the present results provide support for such processing as an attractive route to forming high-$T_c$ superconductors in useful shapes. This route offers the attractive features which accompany liquid state processing.

A significant aspect of the present study is the ability to quench the liquid into the glassy state. In this regard, it was found that the incorporation of $Al_2O_3$ in the 2223 melt has a clearly beneficial effect in promoting glass formation without deleteriously affecting the critical temperature for superconducting behavior. Similar beneficial effects of $Al_2O_3$ on glass formability are expected for the other Bi-Ca-Sr-Cu-O compositions as well. In the work reported here, the $Al_2O_3$ was obtained by partial dissolution of the crucible in the melt; but in on-going work, it is provided by additions to the batch.

Considering the high fluidity of these melts at temperatures near the liquidus (they pour rather like water), it is remarkable that they can be formed as substantially amorphous materials by simple casting - at least for the samples containing $Al_2O_3$. This likely reflects a sizable barrier to crystal nucleation and/or a large temperature dependance of the viscosity - or alternatively a relatively small interval between the upper temperature limit of stability of the 2122 phase ($T_{L'}$) and the glass transition temperature ($T_g$). Based on observations of the cast/quenched specimens, it appears that the matte-appearing phase on the liquidus is not the first to nucleate on cooling. Rather, it is the 2122 phase, which presumably reflects its smaller crystal-melt interfacial energy. On this basis, the relative factor in considering glass formation is not $T_{liquidus} - T_g$, but rather $T_{L'} - T_g$.

The addition of $Al_2O_3$ has only a modest effect on the viscosity at a given temperature (judging from the pouring behavior). The effect of $Al_2O_3$ on glass formability must then be related to its role in reducing $T_{L'}$ and/or the crystal-melt interfacial energy, or in decreasing the crystal growth rate via its effect on the interdiffusion coefficient in the melt.

The observation of small crystals associated with pores in the "glassy" cast material very likely reflects nucleation on second-phase impurities, rather than simply on the liquid-vapor interfaces of the pore surfaces. The nature of the suggested second-phase impurities remains to be identified. The subsequent crystallization of such "glassy" material is presently being investigated to elucidate the role of the observed crystallites and thermal history of the glass.

It is noteworthy that x-ray diffraction of the "glassy" material in both the 2223 and 4334 samples indicates the presence of a small amount of only the 2122 phase (the phase suggested as responsible for high temperature superconducting behavior). After complete crystallization, however, both samples show the presence of two crystalline phases with distinctive morphologies. The crystallization process as observed in the optical microscope took place too rapidly to permit detailed observation of the sequence of phase development; but presumably growth of the small 2122 crystals present in the "glassy" material was accompanied/followed by nucleation and growth of the matte phase.

Based on the present observations, it appears that the preferred heat treatment schedules in the literature for preparing superconducting samples of the 2223 and 4334 compositions involve partial melting of the 2122 phase. In particular, it appears that these heat treatments involve a reorganization via dissolution/re-precipitation, which may involve some increase in the volume fraction of the 2223 phase at the expense of the 2122 phase, but almost certainly involves the development of more favorable interconnected morphologies of the preferred phase(s).

The times required for complete crystallization of the samples at 865C are much shorter than the heat treatment times used to prepare the superconducting samples (less than a minute vs. several hours). Experiments presently underway should clarify whether the long-time heat treatments are required for superconducting behavior.

At the present writing, it appears that superconducting material of the 2223 composition can only be prepared by crystallization in a narrow range of temperature (845C < T < 885C). The origin of this behavior is not satisfactorily understood at the present time, but must involve the development of different phase assemblages/microstructures at the different temperatures. X-ray diffraction indicates a similar distribution of diffraction peaks in material crystallized at 865C. Also of note is the marked difference in conductivity behavior over the temperature range 275K-125K among glasses crystallized at 845C, 865C, and 885C.

Regardless of the details of the crystallization process, it appears that extended heat treatments - much longer than those required to develop a substantial degree of crystallinity - are required to obtain superconducting samples.  Whether these extended heat treatments are required for reasons of oxygen stoichiometry, or for the development of appropriate crystalline-phase assemblages, remains unclear at the present writing.

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Figure 1a: SEM micrograph of composition 2223 melted in $Al_2O_3$ and cast in a graphite mold.
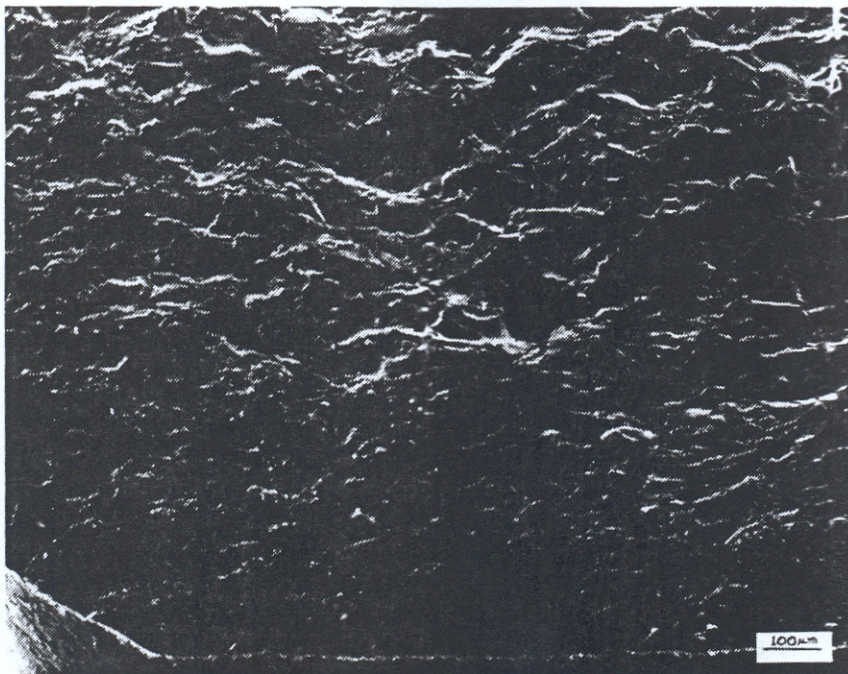


Figure 1b: SEM micrograph of composition 2223 melted in Pt and cast in a graphite mold.
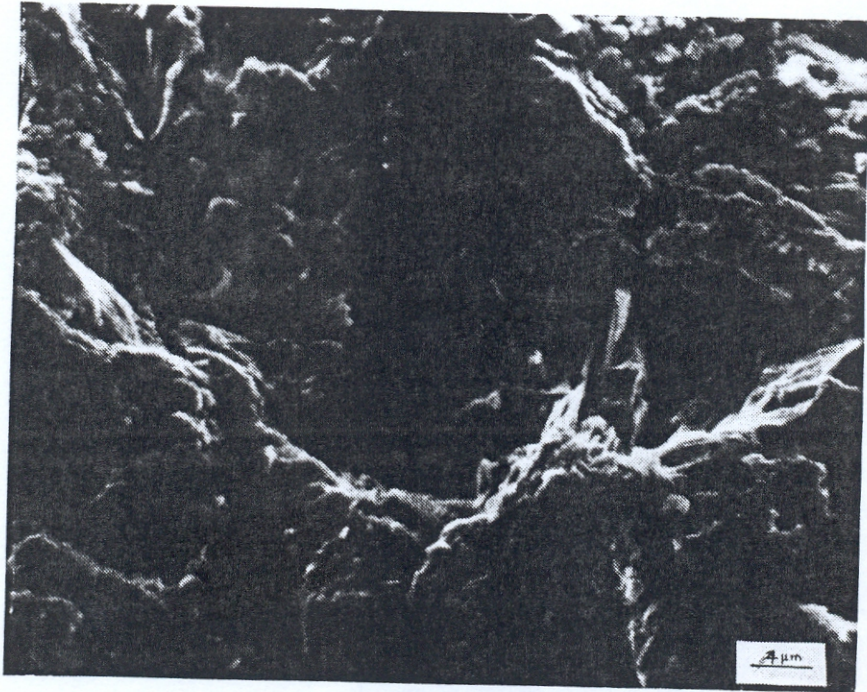
Figure 1c: SEM micrograph of the "glassy" region of sample 2223A crystallized at 865C.
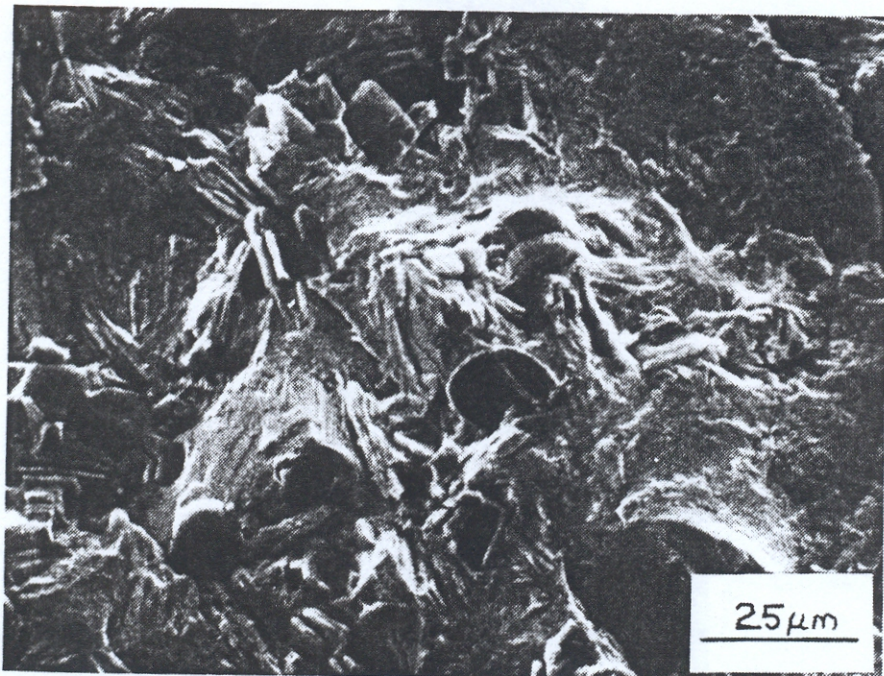


Figure 1d: SEM micrograph of composition 4334 melted in $Al_2O_3$ and cast in a graphite mold.
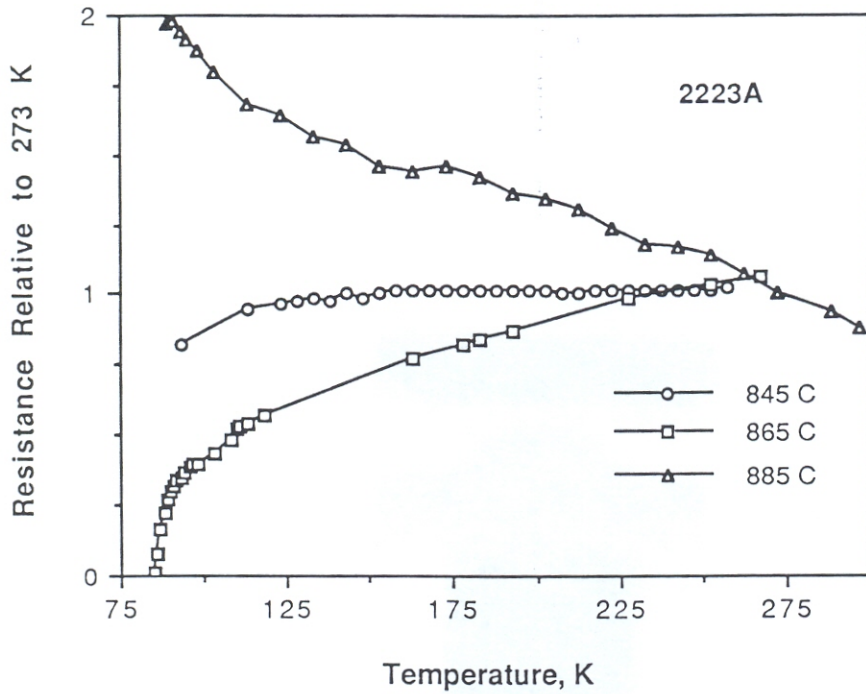
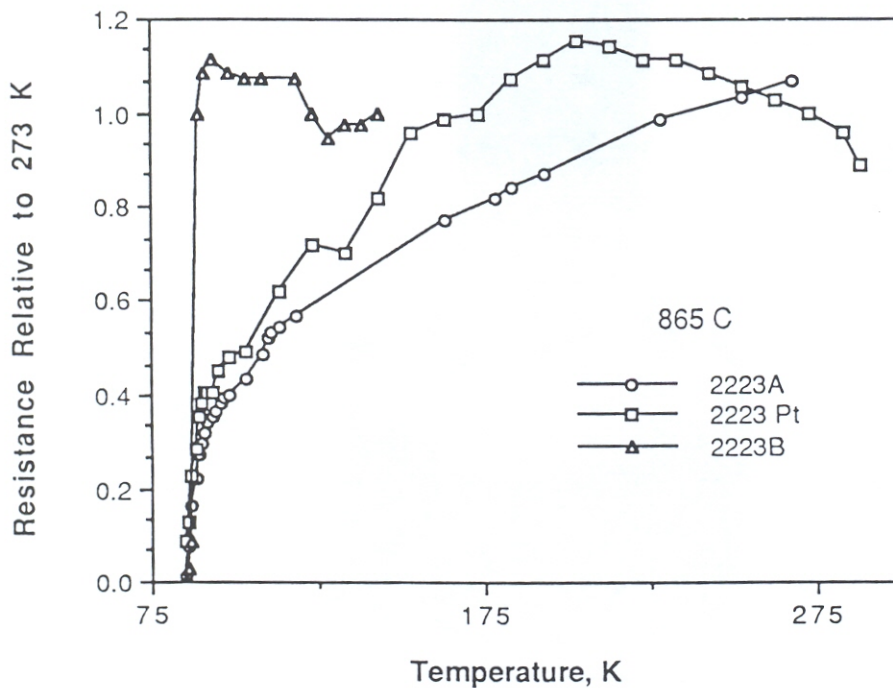Figure 2: Resistance vs. Temperature relations for composition 2223A crystallized at 845, 865, and 885C



Figure 3: Resistance vs. Temperature relations for samples 2223A, 2223P, and 2223B crystallized at 865C.
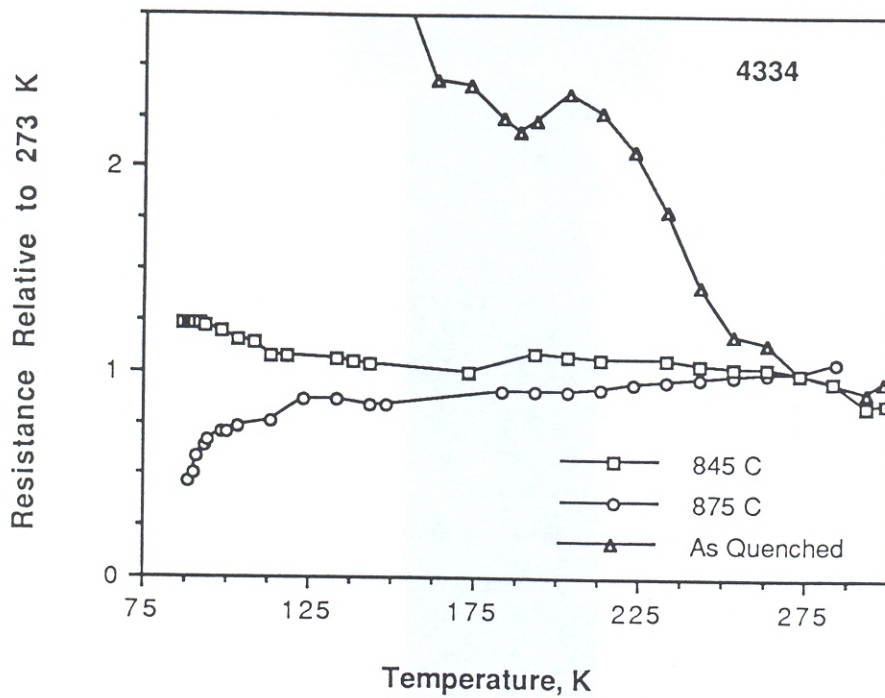
Figure 4: Resistance vs. Temperature relations for composition 4334 as cast and after crystallization at 845C and 875C.