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# Preparation and Properties of High- $T_c$ Bi-Pb-Sr-Ca-Cu-O Thick Film Superconductors on YSZ Substrates

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# Preparation and Properties of High- $T_c$ Bi-Pb-Sr-Ca-Cu-O Thick Film Superconductors on YSZ Substrates

## Abstract

An evaluation of four firing profiles was performed to determine the optimum processing conditions for producing high- $T_c$   $\text{Bi}_{1.8}\text{Pb}_{0.33}\text{Sr}_{1.87}\text{Ca}_2\text{Cu}_3\text{O}_x$  thick films on yttria-stabilized zirconia substrates. Using these four profiles, the effects of sintering temperatures of 830-850°C and soak times of 0.5 to 12 hours were examined. In this study,  $T_{c,\text{zero}}$  values of 100K were obtained using a firing profile in which the films were sintered for 1.5 to 2 hours at 840 to 845°C and then quenched to room temperature. X-ray diffraction analyses of these specimens confirmed the presence of the high- $T_c$  phase. Films which were similarly fired and furnace cooled from the peak processing temperature exhibited a two-step superconductive transition to zero resistance, with  $T_{c,\text{zero}}$  values ranging from 85 to 92K. The other firing profiles evaluated in this investigation yielded specimens which either exhibited critical transition temperatures below 90K or did not exhibit a superconductive transition above 77K.

## Introduction

Shortly after the first report of superconductivity above 77K in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  ceramics [1], the Bi-Sr-Ca-Cu-O family of ceramic superconductors was discovered [2]. This new class of materials is unique among high temperature superconductors because it does not contain a rare-earth cation, and several compositions within this material system exhibit superconductivity. The superconductors within this family have the general formula  $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4}$ , where  $n=1$  to 3 and indicates the number of Cu-O layers in the crystal structure. The highest  $T_c$  phase has three Cu-O layers (i.e.,  $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ , or 2223) and exhibits a superconductive transition at 110K. Similarly, the 2212 phase has two Cu-O layers and the 2201 phase has a single copper oxide plane. These latter two compositions exhibit superconductive transition temperatures of 60-85K and 20K respectively [3].

Since the initial discovery of superconductivity in Bi-Sr-Ca-Cu-O ceramics, the preparation of single phase 2223 materials has proven difficult because the 2212 phase is thermodynamically more favorable at elevated temperatures than the 2223 phase [4-5]. The partial substitution of PbO for  $\text{Bi}_2\text{O}_3$  has since been found to help stabilize the high- $T_c$  composition, thereby increasing the volume fraction of this phase [6-7]. By stabilizing the high- $T_c$  phase in Bi-Sr-Ca-Cu-O ceramics, higher process yields have become possible for products utilizing these compositions.

Some of the proposed applications of these unique materials require the preparation of thick film lead assemblies [8] and hybrid circuits [9]. Thick film manufacturing [10] is a cost-effective process for producing multilayer hybrid circuits containing both superconductive and conventional electronics technologies. In this report, the preparation and properties of screen-printed Bi-Pb-Sr-Ca-Cu-O thick films on polycrystalline yttria-stabilized zirconia (YSZ) substrates is described.

## Experimental Procedure

The superconductive material employed in this work has the nominal chemical composition  $\text{Bi}_{1.8}\text{Pb}_{0.33}\text{Sr}_{1.87}\text{Ca}_2\text{Cu}_3\text{O}_x$  (i.e., Pb-substituted 2223). The powder possessed an average particle size of 12  $\mu\text{m}$ , and ninety percent of the powder possessed an equivalent spherical diameter below 20  $\mu\text{m}$ . To produce thick films, the superconductive powder was blended with an organic vehicle system and deposited onto yttria-stabilized zirconia substrates using a 200 mesh stainless steel screen patterned by photolithography. The dimensions of the printed films were 19.0 mm x 6.4 mm x 25  $\mu\text{m}$ .

After deposition, the thick film specimens were fired in air using one of the four firing profiles described in Table 1. In this report, the four furnace cycles will be referred to as firing profiles 1 through 4. In each case, the specimens were heated to the sintering temperature at a rate of 5°C/min where they were allowed to soak at the peak processing temperature for 0.5 to 12 hours. After the allotted sintering time had expired, the specimens were either furnace cooled at a rate of -5°C/min or quenched to room temperature.

Table 1. Firing profiles used to densify Bi-Pb-Sr-Ca-Cu-O thick films.

Firing profile	Temperature profile
1	Heat to max temp / hold / furnace cool
2	Heat to max temp / hold / quench
3	Heat to max temp / hold / cool to 800°C / hold / furnace cool
4	Heat to max temp / hold / cool to 800°C / hold / quench

Firing profiles 1 and 2 use the standard heating rate of 5°C/min to heat the specimens to the peak temperature where they were maintained for the prescribed time. After soaking at the peak temperature, the specimens were either furnace cooled at a rate of -5°C/min or quenched to room temperature depending on the firing profile employed. Profiles 3 and 4 differ from 1 and 2 in that an annealing step at 800°C was introduced into

the firing cycle after the specimens were exposed to the peak sintering temperature. During this annealing process, the specimens were maintained at 800°C for 8 hours prior to cooling or quenching to room temperature. In this study, thick film specimens were fired at temperatures of 830, 835, 840, 845, and 850°C using each of the four firing profiles.

After firing, the critical transition temperature and critical current density of each specimen were measured using a d.c. four probe resistance technique. An applied current of 10 $\mu$ A was used in the resistance versus temperature measurements, and the cross-sectional areas of the films were measured using a profilometer. In addition to measuring the electrical properties of the films, Cu-k x-ray diffraction (XRD) and scanning electron microscopy (SEM) analyses were also performed on selected specimens.

## Experimental Results

The thick film specimens exhibiting the highest superconductive transition temperatures were prepared using firing profile 2. These results were obtained by firing the films for either 2 hours at 840°C or for 1.5 hours at 845°C and quenching the specimens to room temperature. The films prepared in this manner exhibited  $T_{c,onset}$  temperatures of approximately 110K, and reached  $T_{c,zero}$  at 100K as shown in Figure 1. Although these films exhibited the highest  $T_{c,zero}$  values obtained in this study, the resistance versus temperature data showed that a small “tail” did exist between the  $T_{c,onset}$  and  $T_{c,zero}$  temperatures. In these cases, the difference between these two values, or  $T_c$ , is 10K as seen in Figure 1.

X-ray diffraction analyses of the 100K films confirmed the existence of the high- $T_c$  phase. The data from the diffraction scan shows a strong diffraction peak at  $2\theta = 4.8^\circ$ . The presence of an intense peak at this angle is indicative of the high- $T_c$  phase in Bi-Sr-Ca-Cu-O ceramics as described by Mizuno et al. [7]. Furthermore, the diffraction pattern shown in Figure 2 is in good agreement with the data presented for the 2223 phase in that report.

The thick films fired for longer than 2 hours at 840°C (or longer than 1.5 hours at 845°C) using profile 2 exhibited superconductive transitions with more pronounced “tails”. The presence of these “tails” is indicative of the coexistence of two superconductive phases in the fired component. In this study, several specimens were produced which possess  $T_{c,onset}$  temperatures of 110K but reach zero resistance below 92K. A typical example of this behavior is shown in Figure 3. In this case the  $T_{c,onset}$  temperature was approximately 110K and the  $T_{c,zero}$  temperature was 88K. The data shown in this figure is from a specimen fired at 840°C for 4 hours and quenched to room temperature.

Films fired for extended periods beyond the optimal sintering time failed to exhibit zero resistance above 77K. In most of these instances, however, a superconductive onset was observed above 100K. Figure 4 shows an example of this behavior in which the  $T_{c, \text{onset}}$  temperature is 110K, but the sample fails to reach zero resistance above 77K. In this example, the specimen exhibits a strong  $T_{c, \text{onset}}$  behavior initially followed by a sharp decrease in resistance. However, at the point where  $R(T)/R(298) = 0.25$ , the slope of the resistance versus temperature plot changes, indicating the presence of a second superconductive phase. The data shown in Figure 4 was obtained from a specimen which was fired at 840°C for 6 hours and quenched to room temperature.

Similar two-step superconductive transitions were also obtained for all of the specimens produced in experiments utilizing either furnace cooling or an 800°C annealing treatment after sintering at the peak processing temperature (i.e., profiles 1, 3, and 4). To illustrate this trend, Figure 5 compares the  $T_{c, \text{zero}}$  values for specimens fired at 840°C for 0.5 to 4 hours using firing profiles 1 and 2. This plot shows that the  $T_{c, \text{zero}}$  values of the specimens prepared using the quenching process were consistently higher than those prepared using a firing profile in which the films were slowly cooled to room temperature.

Comparing Figures 6 and 1 further illustrates the effects of furnace cooling and quenching on the  $\text{Bi}_{1.8}\text{Pb}_{0.33}\text{Sr}_{1.87}\text{Ca}_2\text{Cu}_3\text{O}_x$  films. These two graphs show the resistance versus temperature data for thick film specimens which were fired at 840°C for 2 hours but cooled differently. The data in Figure 6 was obtained from a slowly cooled (i.e., -5°C/min) specimen whereas the data in Figure 1 was obtained from a specimen that was quenched to room temperature. The superconductive transitions observed in these two figures are typical of the differences between furnace cooled and quenched materials produced throughout this investigation.

X-ray diffraction analyses of the furnace cooled films revealed the presence of the lower- $T_c$  2212 phase. As shown in Figure 7, a small diffraction peak at  $2\theta = 5.7^\circ$  ( $d = 15.50$ ) accompanies the larger peak at  $2\theta = 4.8^\circ$  ( $d = 18.67$ ). The peak at  $2\theta = 5.7^\circ$  is attributable to the 2212 phase [7]. Although this peak is relatively small compared to the adjacent peak at  $2\theta = 4.8^\circ$ , the presence of this peak confirms the coexistence of the 2223 and 2212 phases. The only prior indication of the presence of a second superconductive phase was the two-step superconductive transitions observed in Figures 3, 4, and 6.

Throughout this work, critical current density values on the order of 1 to 10 A/cm<sup>2</sup> were obtained for all specimens exhibiting superconductivity above 77K. SEM analyses of these thick film microstructures revealed the presence of a plate-like grain morphology typical of Bi-Sr-Ca-Cu-O ceramics [11]. These evaluations also revealed the presence of pores between the superconductive grains. The relatively low  $J_c$  values observed in this

study are attributable to the porosity present in the fired films. SEM micrographs showing both the plate-like grain structure and the porosity present in the high- $T_c$  thick films are shown in Figures 8 and 9.

## Discussion

Each of the superconductive thick films produced in this study exhibited a  $T_c$  value of at least 10K. The larger  $T_c$  values, such as the one shown in Figure 3, indicate the coexistence of the lower  $T_c$  2212 phase. As shown by both the resistance versus temperature and XRD data, the films produced in this study are predominately comprised of the high- $T_c$  phase. However, extended exposure to the peak sintering temperature resulted in the partial decomposition of the 2223 phase and the formation of the thermodynamically favored 2212 phase and a calcium cuprate liquid. This transformation occurs at high temperatures according to the reaction [12]:



Additionally, because the 2212 phase is thermodynamically favored, the high- $T_c$  phase is also partially transformed to the lower- $T_c$  phase during the cooling process. Thus, all of the specimens produced in this study which were slowly cooled to room temperature possessed lower  $T_{c,zero}$  values than similarly fired and quenched specimens. Quenching the specimens from the peak processing temperature to room temperature minimizes the time available for this phase transformation to occur, thereby yielding a higher concentration of the 2223 phase.

During this work, a firing profile which resulted in the production of  $\text{Bi}_{1.8}\text{Pb}_{0.33}\text{Sr}_{1.87}\text{Ca}_2\text{Cu}_3\text{O}_x$  thick films with critical transition temperatures of 100K was successfully identified. However, these films possessed relatively low critical current density values (i.e., 1-10 A/cm<sup>2</sup>) as compared to published results for  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  thick films (i.e., 100-200 A/cm<sup>2</sup>) [13-14]. It has been found that the current carrying capacity of superconductive ceramics is governed by the degree of intergranular connectivity present in the microstructure [15]. In the case of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  ceramics, intergranular connectivity can be optimized by sintering near the melting temperature followed by an annealing treatment in an oxygen rich atmosphere at 600°C [16].

The relatively low critical current density values obtained for the 2223 films produced in this study are attributable to the different sintering behaviors of these two compositions. Whereas dense  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  superconductors may be produced by sintering near the melting point of the compound, the 2223 compound thermally decomposes into the lower- $T_c$  2212 phase near the melting point. Therefore, as the 2212 composition is formed, the volume fraction of the 2223 phase present in the fired film is diminished.

Thus, although films with high superconductive transition temperatures were successfully produced, these materials possess relatively low critical current densities as compared to  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  thick films.

## Conclusions

The effects of four firing profiles on the properties of  $\text{Bi}_{1.8}\text{Pb}_{0.33}\text{Sr}_{1.87}\text{Ca}_2\text{Cu}_3\text{O}_x$  thick films were evaluated. In this study, specimens fired for either 2 hours at 840°C or for 1.5 hours at 845°C and quenched to room temperature exhibited  $T_{c,\text{zero}}$  values of 100K. Similarly fired specimens which were slowly cooled were found to possess a lower- $T_c$  secondary phase (i.e., 2212). In these instances, the specimens exhibited  $T_{c,\text{onset}}$  and  $T_{c,\text{zero}}$  temperatures of 110 and 85-92K respectively. The coexistence of the 2212 phase along with the 2223 phase was verified by Cu-k x-ray diffraction. The presence of the lower- $T_c$  secondary phase is attributable to the thermodynamic stability of the 2212 phase which forms during cooling. In this study, specimens which were quenched from the peak processing temperature to room temperature consistently exhibited higher  $T_{c,\text{zero}}$  values than those which were slowly cooled to room temperature. Quenching the specimens to room temperature increased the fraction of the 2223 phase present by minimizing the time available for the phase transformation to the 2212 phase to occur.

All of the thick films produced in this study exhibited relatively low critical current densities as compared to reported values for  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  thick films. Typically, these films exhibited  $J_c$  values ranging from 1 to 10 A/cm<sup>2</sup>. SEM analyses of these films revealed porous microstructures which limit the current carrying capacity of the films. The porosity observed in the fired films is a result of the short firing cycles employed to produce films with large concentrations of the 2223 phase.

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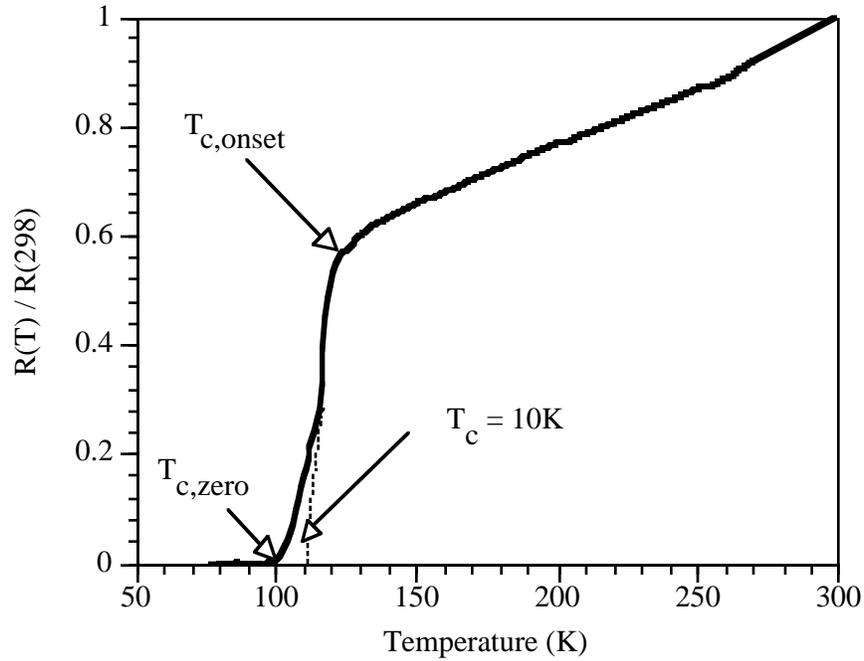


Figure 1. Normalized resistance versus temperature data for a thick film specimen fired at 840°C for 2 hours and quenched to room temperature according to firing profile 2. The film exhibits  $T_{c,onset}$  and  $T_{c,zero}$  values of 110 and 100K respectively.

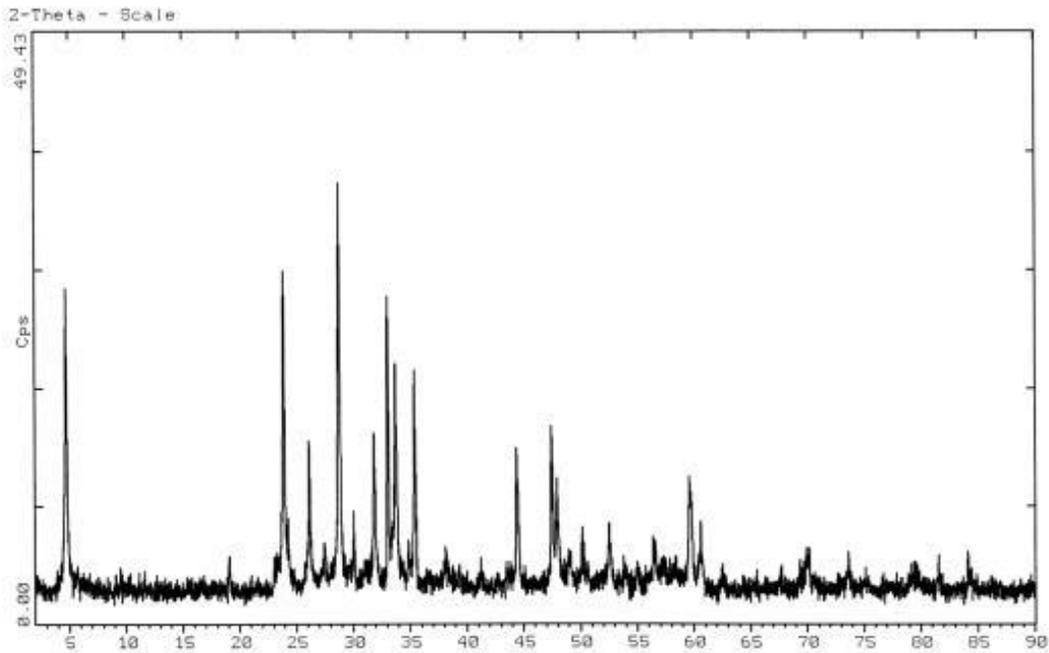


Figure 2. X-ray diffraction data showing the presence of the 2223 phase. The specimen possessed a  $T_{c,zero}$  value 100K.

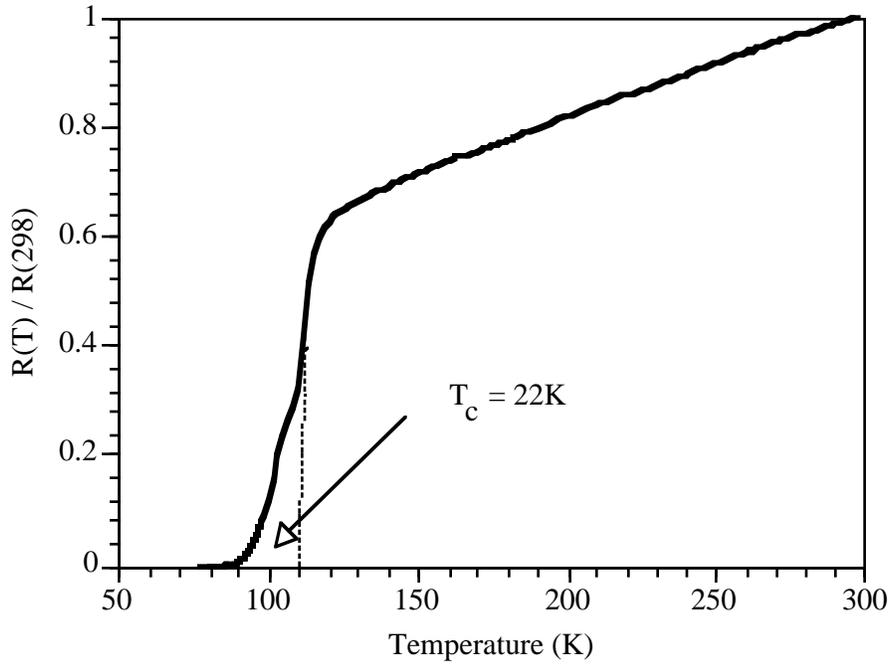


Figure 3. Normalized resistance versus temperature data for a thick film specimen fired at 840°C for 4 hours and quenched to room temperature according to firing profile 2. The film possesses a  $T_{c,zero}$  value of 88K.

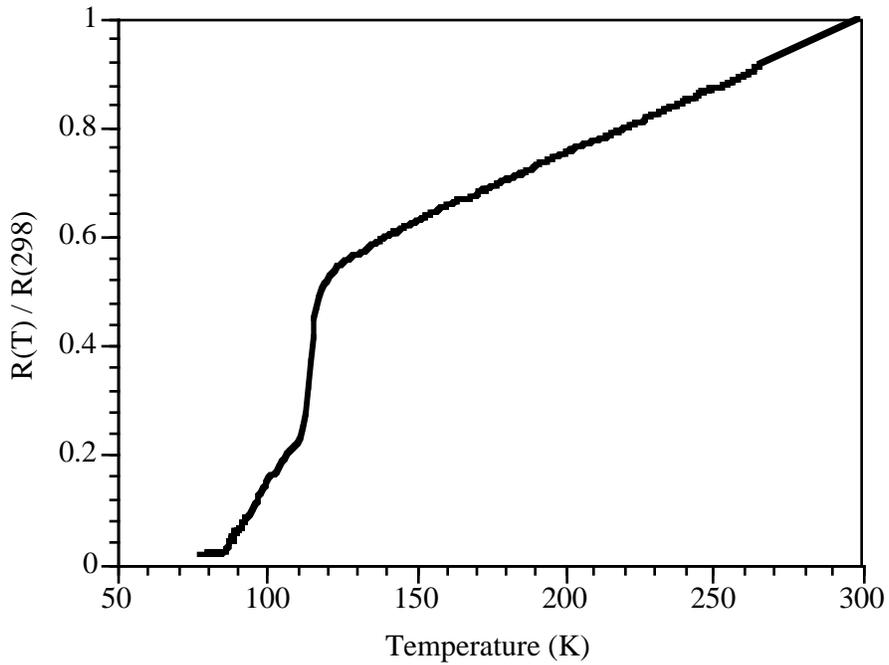


Figure 4. Normalized resistance versus temperature data for a thick film specimen fired at 840°C for 6 hours and quenched to room temperature according to firing profile 2. Films prepared using these firing conditions did not exhibit zero resistance above 77K.

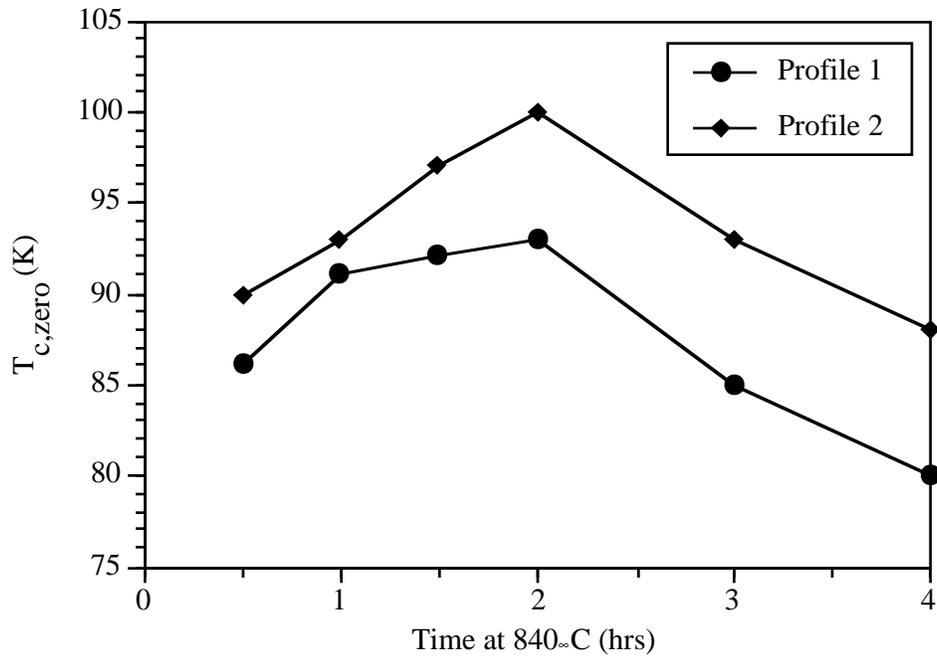


Figure 5. Comparison of  $T_{c,zero}$  values for thick films fired for 0.5 to 4 hours at 840°C using firing profiles 1 (furnace cooling to room temperature) and 2 (quenching to room temperature).

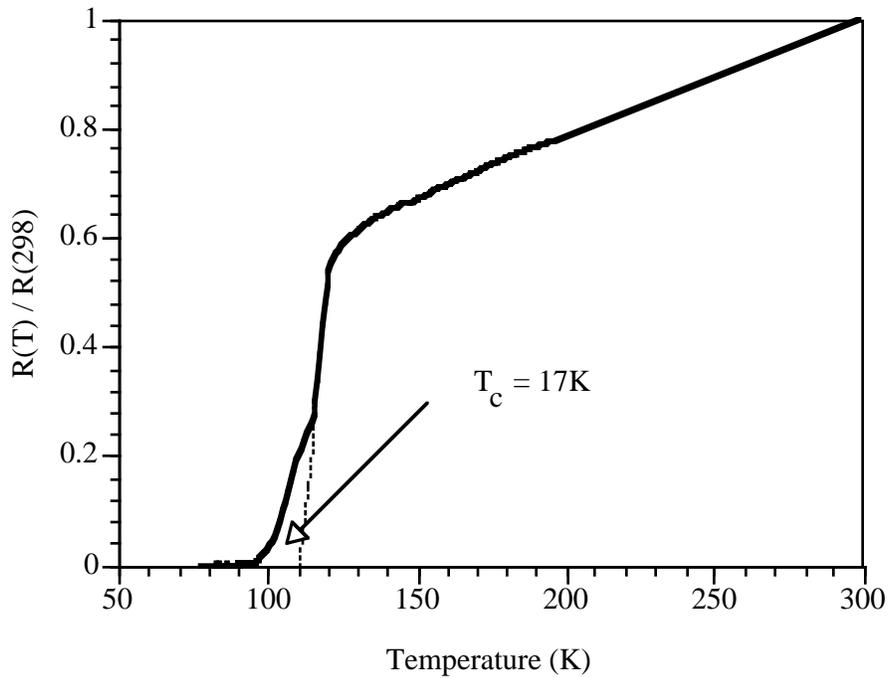


Figure 6. Normalized resistance versus temperature data for a thick film specimen fired at 840°C for 2 hours and furnace cooled according to firing profile 1. The  $T_{c,zero}$  and  $T_c$  values of this specimen are 93 and 17K respectively.

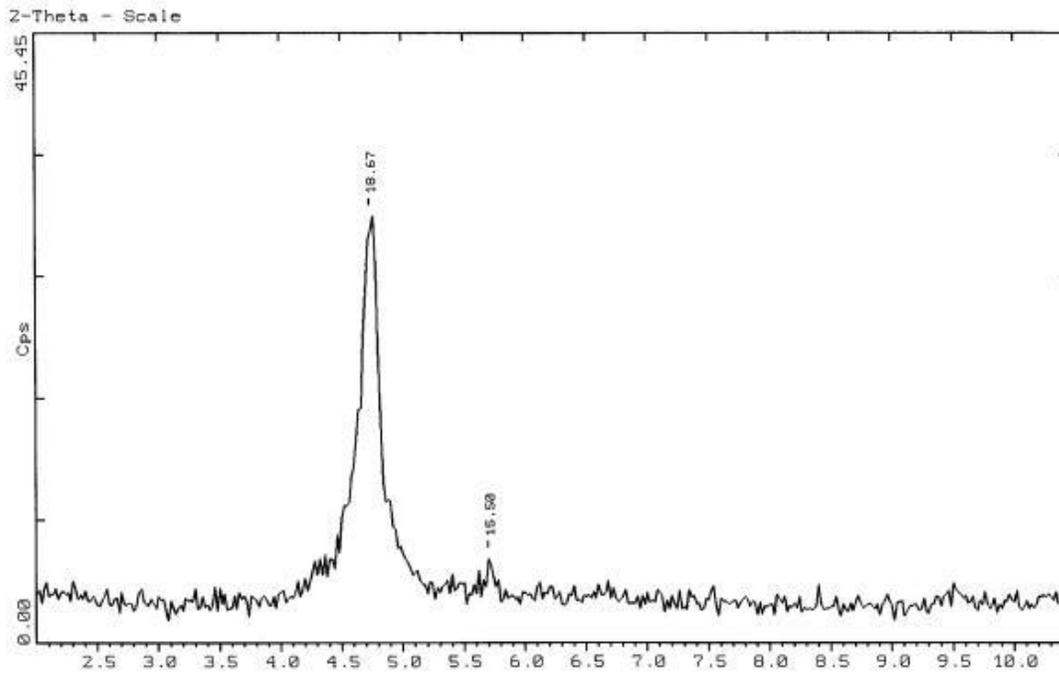


Figure 7. X-ray diffraction data showing the presence of a small 2212 peak at  $2\theta = 5.7^\circ$  ( $d = 15.50$ ). The specimen possessed a  $T_{c,zero}$  value of 93K.

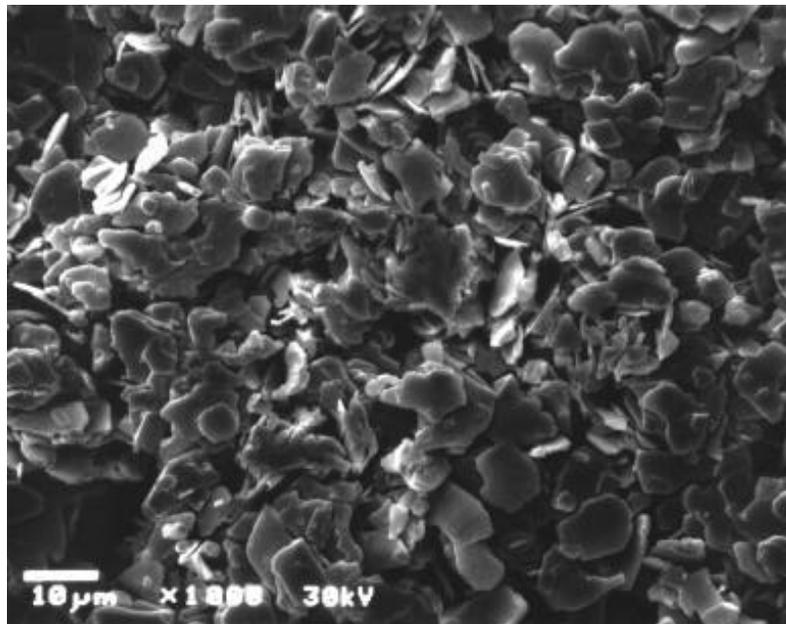


Figure 8. SEM micrograph showing the plate-like grain structure indicative of Bi-Sr-Ca-Cu-O ceramics (magnification = 1000x).

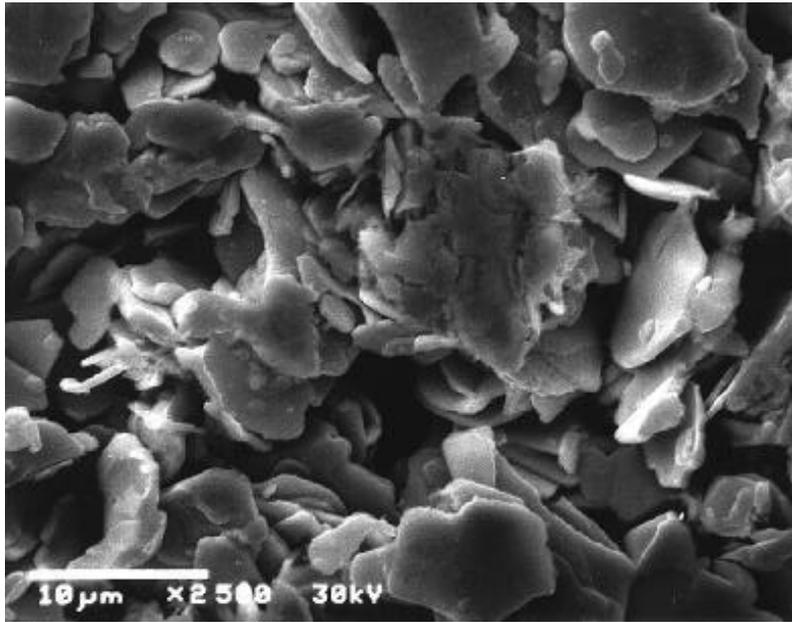


Figure 9. SEM micrograph showing the presence of pores between the superconductive grains in a 2223 thick film (magnification = 2500x).