

### Effect of Sintering and Annealing Temperatures on the Critical Temperature and Electrical Resistivity of $\text{Bi}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$

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**Abstract:** Samples of the high temperature superconducting system,  $\text{Bi}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$ , were prepared by using the solid state reaction method with different sintering temperatures of 810, 830, 850, 870 and 890 °C. The electrical resistivity measurements exhibited that the sintering and annealing conditions have major effects on the critical temperature of the superconducting compound. The sample prepared at 850 °C has a critical temperature  $T_c \approx 110$  K, meanwhile the sample prepared at 870 °C has a critical temperature  $\approx 80$  K. However, the sample which was prepared at 890 °C showed semiconducting behavior with an activation energy of 6.40 meV. The effect of annealing on the critical temperature has been investigated using the sample prepared at 850 °C. The value of  $T_c$  at the annealing temperature of 400 °C rises from 110 K to 138 K with increasing the annealing time from 24 hrs to 72 hrs. This increase might be due to the increase of oxygen content or to the intergrowth of a large number of Cu-O layers in the cell.

**Keywords:** High temperature superconductors; Semiconductors; Sintering; Annealing; Electrical resistivity.

## Introduction

The discovery of superconductivity between 7 K and 22 K in the Bi-Sr-Cu-O compound has been reported by Michel *et al.* in 1987 [1]. Meada *et al.* [2] and Chu *et al.* [3] reported that adding Ca to the Bi-Sr-Cu-O system produced a material that was superconducting above liquid nitrogen temperature 77 K.

Great attention has been focused on the series compound Bi-Sr-Cu-O which shows superconductivity around 105 K [4]. The properties of these systems show that the superconductors with structure formulae  $\text{Bi}_2\text{Sr}_2\text{CuO}_6$ ,  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$  and  $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$  have  $T_c$  values of 10, 85 and 110 K, respectively [5].

The partial substitution effects on the structure and electrical properties of the high

temperature superconducting compounds  $\text{Bi}_{2-x}\text{Tl}_x\text{Ba}_{2-y}\text{Sr}_y\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$  have been investigated [6]. Makarenko *et al.* studied the annealing effect on critical temperature and resistivity of  $(\text{Bi,Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ , after being irradiated by Co-60 gamma-rays. They found that annealing at 150-200 °C resulted in an increase of resistivity and a drop of critical temperature up to doses of  $2 \times 10^9$  R [7]. The effect of post-annealing on critical current density of (Bi,Pb)-2223/Ag tapes has been reported by Li *et al.* Their results showed that post-annealing at low temperature in reduced oxygen partial pressure can improve the critical current density. They claimed that the effect of post-annealing could be related to the increase of (Bi,Pb)-2223 phase and the formation of  $\text{Pb}_3\text{Sr}_{2.5}\text{Bi}_{0.5}\text{Ca}_2\text{CuO}_y$  (3321 phase) as well as the improvement of grain connectivity [8]. Khalil and Sedky studied the

effect of annealing temperature (750-850 °C), when annealing in air for 50 hrs, on the structural, mechanical and superconducting properties of  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$  system [9]. They found that the critical temperature  $T_c$  increased from 78 up to 100 K with annealing temperature in addition to more sharpening of the transition. This behavior was explained by the improvement of coupling between superconducting grains and by elimination, by annealing, of oxygen disorder and microcracks. Florence *et al.* investigated the effects of rapid thermal annealing on the material and electrical properties of sputter deposited  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  superconducting films [10]. They found that the critical temperature decreased for all annealing times and temperatures above the growth temperature and suggested that this was due to oxygen effusion from thin films.

The aim of this paper is to investigate mainly the electrical properties of the superconductor compound Bi-Ba-Ca-Cu-O using different sintering and annealing temperatures as well as different annealing times.

## Experimental Procedure

High temperature  $\text{Bi}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$  superconductor samples were prepared using the solid state reaction method using appropriate quantities of highly pure  $\text{Bi}_2\text{O}_3$ ,  $\text{CaCO}_3$ ,  $\text{BaCO}_3$  and  $\text{CuO}$ . The mixture was ground with isopropanol by using a gate mortar. The well mixed powder of these oxides was calcimined at 800 °C.

The mixture was pressed into approximately 1 gm pellets, 1.1 cm in diameter and 0.17 cm in thickness. The pressed pellets were initially heated in air from room temperature to different sintering temperatures of 810, 830, 850, 870 and 890 °C for 24 hrs and then slowly cooled to room temperature at a rate of 30 °C/hr. Finally, the sample pellets were annealed at different temperatures of 200, 400, 500, 600 and 700 °C for different annealing times of 24, 48, 72 and 96 hrs.

The X-ray diffraction patterns at room temperature were obtained using Phillips X-ray diffractometer with  $\text{CuK}_\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ).

The electrical resistivity was measured using the standard four-probe method and the electrical contacts to the samples were made using fine copper wires with conductive silver paste. The electrical resistivity measurements have been conducted to determine the critical temperature. The oxygen content in the sample was measured by using the iodometric method [11].

## Results and Discussion

X-ray diffraction measurements on  $\text{Bi}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$  superconductor sintered at 850 °C were reported in a previous article [6]. The structure was found to be single tetragonal phase with lattice parameters  $a = b = 5.43 \text{ \AA}$  and  $c = 34.13 \text{ \AA}$ . The electrical resistivity at various sintering temperatures was obtained and the results are shown in Fig. 1. The critical temperatures and oxygen contents at various sintering temperatures are summarized in Table 1.

As shown in Table 1, the increase of sintering temperature from 810 °C to 870 °C leads to an increase in oxygen content. The critical temperature  $T_c$  has an optimum value with increasing sintering temperature ( $T_c$  has a maximum value when samples are sintered at 850 °C). The superconducting critical transition temperature,  $T_c$  in this work, is defined as the temperature at which the sample resistance drops to zero.

TABLE 1. Critical temperatures for  $\text{Bi}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$  samples with different sintering temperatures.

$T$ (°C)	$T_c$ (K)	$10+\delta$
810	99	10.12
830	95	10.17
850	110	10.22
870	80	10.71
890	Semiconductor: $E_{\text{act}} = 6.35 \text{ meV}$	10.27

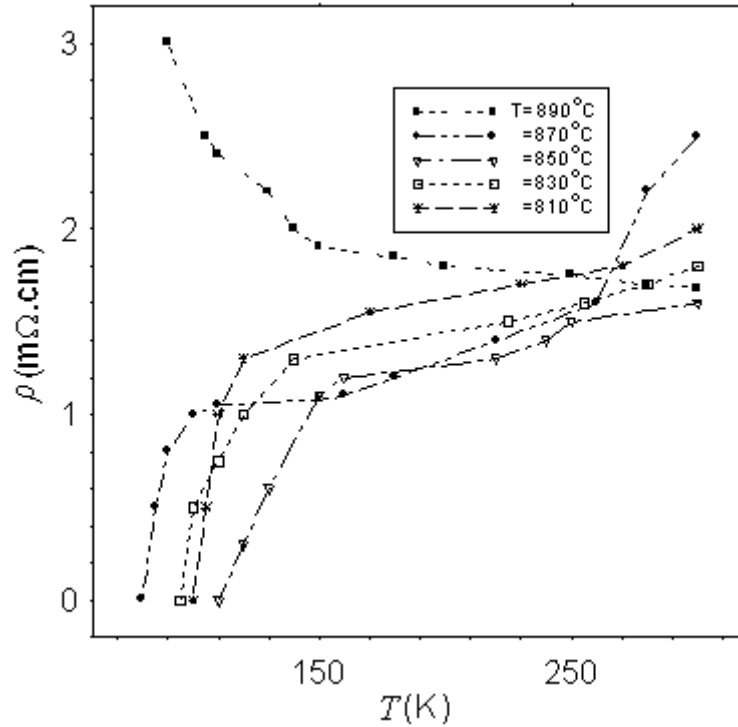


FIG. 1. The resistivity versus temperature for  $\text{Bi}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$  samples prepared at different sintering temperatures.

However, the additional increase in sintering temperature up to 890 °C leads to a drop in the oxygen content and might lead to a structural phase change. Optimal oxygen content is very necessary for the presence of high temperature superconductivity with tetragonal phase, and a shift from this optimal value would result in the formation of a non superconducting phase. The sample sintered at 890 °C showed semiconductor behavior. It is seen from Fig. 1 that the resistivity  $\rho(T)$  of that sample rises exponentially with decreasing temperature. Therefore, the conductivity  $\sigma(T) = 1/\rho(T)$  of the sample, at this sintering temperature, falls exponentially with increasing temperature. In Fig. 2,  $\ln \sigma$  is plotted versus  $1/T$  and the

conductivity is fitted to the expression (Arrhenius Equation):

$$\sigma(T) = \sigma_o \exp(-E_{\text{act}}/kT),$$

where  $\sigma(T)$  is the conductivity at temperature  $T$  in Kelvin,  $\sigma_o = \sigma(1/T = 0)$ ,  $E_{\text{act}}$  is the activation energy and  $k$  is the Boltzmann constant. This fit gave an activation energy of  $\approx 6.35$  meV and  $\sigma_o = 0.764(\text{m}\Omega.\text{cm})^{-1}$ .

The conduction is due to hopping between conduction and valence bands; however electrons in this case are hopping between localized states. The change in the superconducting behavior at different sintering temperatures is probably due to the change in grain connectivity or coupling between the superconducting grains. These results are in good agreement with the results reported in other works [9, 10].

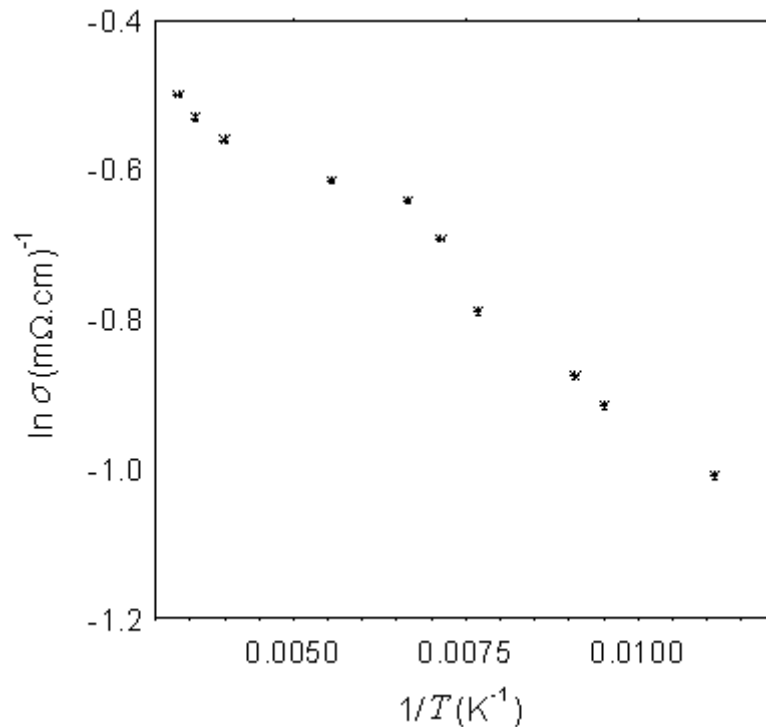


FIG. 2. The natural logarithm of the conductivity,  $\ln \sigma$ , versus temperature for the  $\text{Bi}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$  sample sintered at  $890^\circ\text{C}$ .

The maximum value of  $T_c$  is 110 K for samples prepared at a sintering temperature of  $850^\circ\text{C}$ . These samples, sintered at  $850^\circ\text{C}$ , were then annealed at different annealing temperatures and times. The best value of  $T_c$  was obtained for an annealing temperature of  $400^\circ\text{C}$ . As shown in Fig. 3, it increased from 110 K to 130 K and then decreased with increasing annealing temperature. The

behaviors of the critical temperature,  $T_c$ , and oxygen content with annealing temperature are summarized in Table 2. It is clear from that table that the increase in oxygen content plays a very important role in increasing or decreasing  $T_c$ . This could be caused by decreasing the structure defects and also due to the intergrowth of a large number of Cu-O layers in the unit cell.

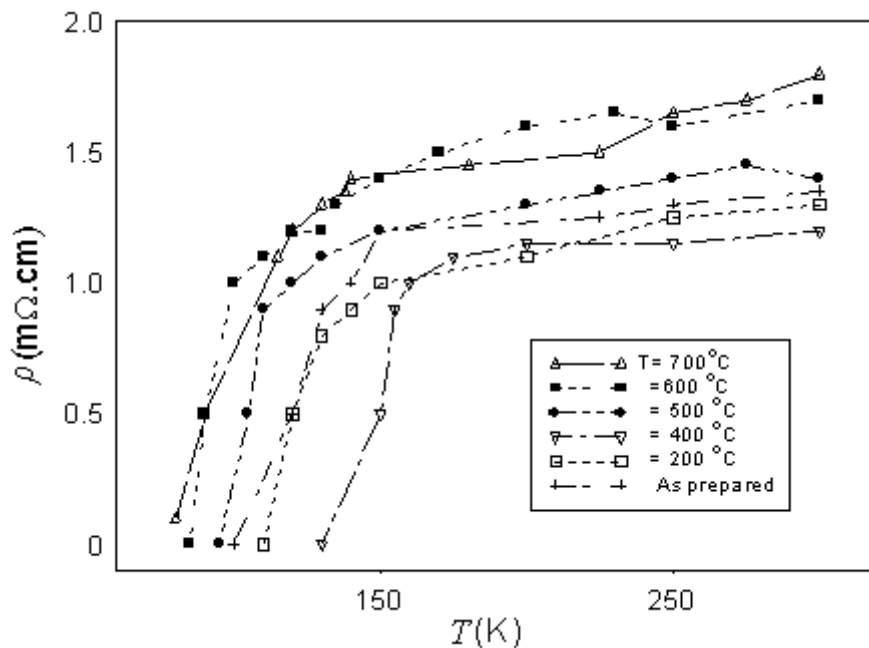


FIG. 3. The resistivity versus temperature for the prepared  $\text{Bi}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$  with different annealing temperatures.

TABLE 2. Critical temperatures for  $\text{Bi}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$  samples sintered at  $850^\circ\text{C}$  with different annealing temperatures.

Annealing Temperature $T$ ( $^\circ\text{C}$ )	Critical Temperature $T_c$ (K)	$10+\delta$
200	110	10.29
400	130	10.38
500	95	9.97
600	86	9.93
700	80	9.90

The behavior of resistivity *versus* temperature for an optimum annealing temperature of  $400^\circ\text{C}$  with time is shown in Fig. 4. It is clear from this figure that

increasing the time of annealing results in an increase in the value of  $T_c$  which saturates at the annealing time of 72 hours with a value of  $T_c \approx 138\text{ K}$ .

TABLE 3. Critical temperatures for annealed  $\text{Bi}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$  superconductors at  $850^\circ\text{C}$  and different annealing times for the annealing temperature of ( $400^\circ\text{C}$ ).

$T_c$ (K)	Annealing time (hr)	$10+\delta$
110	24	10.38
130	48	10.40
138	72	10.42
138	96	10.42

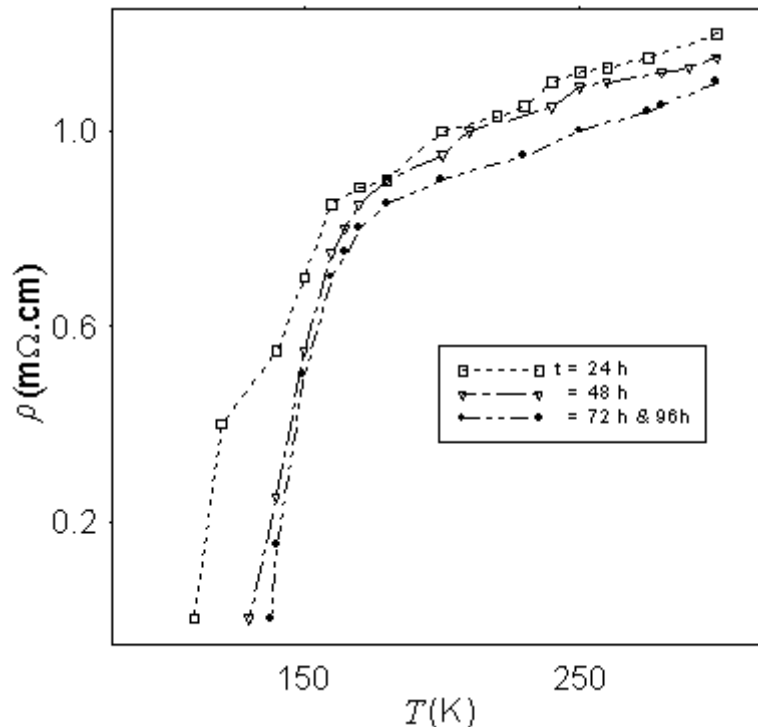


FIG. 4. The resistivity versus temperature for  $\text{Bi}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$  samples annealed at  $400^\circ\text{C}$  for different annealing times.

As shown in Table 3, and from Fig. 4, the increase in  $T_c$  value with increasing of annealing temperature leads to the increase in oxygen content. This might increase the charge carriers, the number of the Cooper pairs, due to more electron-phonon coupling conditions [5].

## Conclusion

Superconductivity is possible in the tetragonal structure and orthorhombic structure, according to sintering temperature.

The optimum value of sintering temperature is  $\approx 850^\circ\text{C}$  which gives the optimum structure and electrical properties. The change in structure and electrical properties might occur at sintering temperatures higher than  $850^\circ\text{C}$  as observed in the samples sintered at  $890^\circ\text{C}$ . This could be due to the creation of oxygen deficiency or change of phase. Annealing temperature and annealing time are very critical to both oxygen content and critical temperature. The highest value of  $T_c$  was obtained at an annealing temperature of  $400^\circ\text{C}$ , and  $T_c$  increased with annealing

time and then saturated beyond the annealing time of 72 hrs. The increase in  $T_c$  by annealing can be caused by more optimum

oxygen content, intergrowth of a large number of Cu-O layers in the cell and a decrease of structural defects.

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