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## The Effect of Cd Doping on Bi-Based Superconductor

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**Abstract:** In this study, the Cd substitution effects on Bi-based superconductors have been investigated. Samples of  $\text{Bi}_{1.6}\text{Pb}_x\text{Cd}_z\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ , where  $(z, x) = (0.01, 0.39), (0.02, 0.38), (0.03, 0.37), (0.04, 0.36), (0.05, 0.35), (0.06, 0.34), (0.07, 0.33), (0.08, 0.32), (0.09, 0.31)$  and  $(0.1, 0.3)$  were fabricated by the solid state reaction method, using the powders of  $\text{Bi}_2\text{O}_3$ ,  $\text{PbO}$ ,  $\text{CuO}$ ,  $\text{CaCO}_3$ ,  $\text{SrCO}_3$  and  $\text{CdO}$  as starting materials. The structural analysis was carried out by XRD, SEM and EDX measurements. The XRD results show that the unwanted phases in the samples were reduced by increasing the amount of Cd and annealing time. The maximum fraction of Bi (2223) phase obtained in the sample with  $z = 0.04$  and annealing time of 270 h. The critical temperature ( $T_c$ ) and critical current density ( $J_c$ ) were measured at 77 K. The maximum critical current density and the critical temperature were obtained in a sample with  $z = 0.04$  for annealing time of 270 h. In order to study the effect of Cd on the room temperature resistivity of the samples, the V-I curves of the samples were measured at room temperature. The resistance of Cd-doped samples at room temperature increase when the amount of Cd is increased. It decreases by increasing the annealing time.

**Key words:**  $\text{Bi}_{1.6}\text{Pb}_x\text{Cd}_z\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ , superconductivity, critical temperature, critical current density, microstructure, XRD, SEM, EDX, susceptibility

### INTRODUCTION

Since the discovery of high temperature superconductor in 1986 (Bednorz and Muller, 1986; Rao *et al.*, 1993), a great effort has been made to search for systems with higher transition temperatures than that of nitrogen. With Pb doping in the Bi-Sr-Ca-Cu-O system, superconductivity with transition temperatures of about 110 K were found by Green *et al.* (1988) and Zargar Shoushtari *et al.* (2002). Superconductors with high critical temperatures, especially Bi (2223) phase, because of their high capacities for applications which need to high critical current density are highly considered (Mead *et al.*, 1990). Although superconductors with high critical temperatures have higher critical current densities than those with lower critical temperatures, however ceramic superconductors with high critical temperature usually have small critical current densities because of granular nature and the weak links of the grains (Rose-Innese and Rhoderick, 1988; Sokolovsky *et al.*, 2003). Magnetic and electric properties of ceramic superconductors depend on the grains and the links between them. A tremendous effort has been done to improve the links between the grains and the properties of the Bi-based superconductor for example by doping them with Pb (Dou *et al.*, 1989; Pissas *et al.*, 1990), Sm (Yilmazlar *et al.*, 2006), Y (Landau and Keller, 2007), Sn

(Seyoum *et al.*, 1990), Ag (Zargar Shoushtari *et al.*, 2006) and MgO (Zhao *et al.*, 2001). The substitution effects of Cd for Bi in the Bi-La-Ca-Cu-O system (Sasakura *et al.*, 2001) and for Ca in  $\text{La}_3\text{CaBa}_3\text{Cu}_7\text{O}_y$  (La-3137) (Kandyel and Elsabay, 2006) have been investigated. The results show that the substitution of Cd for Bi and for Ca decreases the superconducting transition temperature, through the reduction of the oxygen content. In this study, by doping of Cadmium in  $\text{Bi}_{1.6}\text{Pb}_x\text{Cd}_z\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$  superconductor, in which  $x+z = 0.4$ , we have studied the critical current density, the critical temperature and the microstructure.

### MATERIALS AND METHODS

To make the samples of  $\text{Bi}_{1.6}\text{Pb}_x\text{Cd}_z\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$  with  $x+z = 0.4$ , given amounts of certain powders of  $\text{Bi}_2\text{O}_3$ ,  $\text{PbO}$ ,  $\text{CdO}$ ,  $\text{SrCO}_3$ ,  $\text{CaCO}_3$  and  $\text{CuO}$  with high pure degree in suitable stoichiometric proportions were weighed. After mixing, the powders were grained for an hour. In order to prevent creating additional phases during the process, the mixture of powders was calcined for 15 h at  $820^\circ\text{C}$ . Calcinated powders were grained for an hour. Some bars and pellets with 20 mm in diameter and 3 mm thick were prepared. Then they put in an Alumina crucible and placed in the furnace and the procedure of sintering was done in air. After ending the annealing stage, the experiment of Meissner effect was done on samples at the

liquid nitrogen temperature. For  $z > 0.5$ , the synthesized samples show no superconductivity above 77 K. Samples were prepared with  $(z, x) = (0.01, 0.39), (0.02, 0.38), (0.03, 0.37), (0.04, 0.36), (0.05, 0.35), (0.06, 0.34), (0.07, 0.33), (0.08, 0.32), (0.09, 0.31)$  and  $(0.1, 0.3)$ . They were put in an Alumina crucible and placed in electrical furnace. Then the experiment of Meissner effect was done on these ten samples in the liquid nitrogen and most of the samples had shown this effect well. The critical current density and critical temperature of the samples were measured by the standard four-probe method. The AC susceptibility measurements were performed using a Lake Shore AC susceptometer, Model 7000.

X-ray diffraction (XRD) patterns of samples were taken on a Philips X-ray diffractometer Model PW1840. The microstructure characterization was performed using SEM and EDX and the images obtained by a scanning electron microscope Model 1455VP of the LEO Company.

**RESULTS AND DISCUSSION**

Figure 1 shows the results of XRD measurement patterns of the samples. Based on our XRD measurements (Fig. 1), we observed that by substitution of Cd for Bi up to 0.04 the Bi (2223) phase increases in the sample and Cd acts as a phase stabilizer. As can be seen, the samples consisted of a mixture of Bi (2223), Bi (2212) and Bi (2201) phases as the major constituents. From the XRD results one can notice that the volume of Bi (2223) phase decreases with increasing the amount of Cadmium (sample c). The results of XRD show that the optimum amount of Cadmium is about  $z = 0.04$  (sample b), which has the highest volume fraction of Bi (2223) phase. The volume fraction of the phases can be estimated using various methods (Yurchenko *et al.*, 2003). We have used all the peaks of the Bi (2223), Bi (2212), Bi (2201) and CdO phases for the estimation of the volume fractions of the phases and ignored the voids.

The percentage of each phase in the samples were calculated as follows:

$$\text{Bi(2223)(\%)} \approx \frac{\sum I[\text{Bi(2223)}]}{q} \times 100$$

$$\text{Bi(2212)(\%)} \approx \frac{\sum I[\text{Bi(2212)}]}{q} \times 100$$

$$\text{Bi(2201)(\%)} \approx \frac{\sum I[\text{Bi(2201)}]}{q} \times 100$$

$$\text{CdO(\%)} \approx \frac{\sum I(\text{CdO})}{q} \times 100$$

Table 1: Relative volume fractions of Bi (2223), Bi (2212), Bi (2201) and CdO

Sample	Amount of Cd	Bi (2223) (%)	Bi (2212) (%)	Bi (2201) (%)	Cd (%)
a	0.02	47.74	40.28	17.98	-
b	0.04	74.32	25.76	-	-
c	0.06	18.43	56.81	20.52	1.08

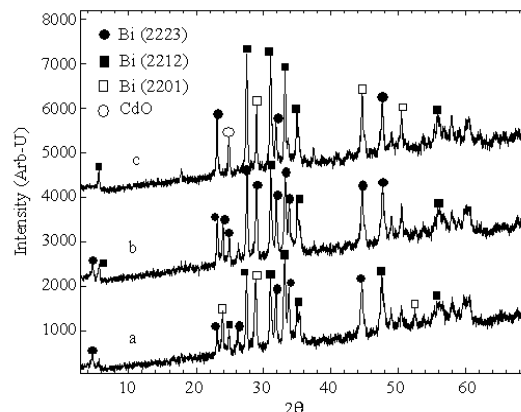


Fig. 1: XRD patterns of samples with different Cadmium amounts: 0.02 (a), 0.04 (b) and 0.06 (c) with annealing time of 270 h

Where:

$$q \approx \sum I[\text{Bi(2223)}] + \sum I[\text{Bi(2212)}] + \sum I[\text{Bi(2201)}] + \sum I(\text{CdO})$$

where, I is the intensity of the present phases. The volume fractions of the phases for all the samples are given in the Table 1. As it shows, the maximum volume fraction of Bi (2223) phase obtained for sample with  $z = 0.04$  (sample b). By increasing the amount of  $z > 0.04$ , the volume fraction of Bi (2223) phase decreases from 74.32% (sample b) to 18.43% (sample c). Also by decreasing  $z$  to the amounts less than 0.04, the volume fraction Bi (2223) phase decreases from 74.32% (sample b) to 47.74% (sample a).

Figure 2 shows the  $T_c$  versus the Cd content for different sintering times. One can see that the critical temperatures of samples increase by increasing the amount of Cd up to  $z = 0.04$  and then decreases for  $z > 0.04$ . Also by increasing sintering time up to 270 h, the critical temperature of the sample increases. We attribute the increase in the  $T_c$  to enhancement of Bi (2223) phase in the sample. Also, the XRD data show that if we increase Cd content above 0.04, the other phases of Bi-Sr-Ca-Cu-O system with lower  $T_c$  are grown, which causes a decrease in  $T_c$ . So the maximum  $T_c$  was observed for the sample with Cd content of 0.04 and sintering time of 270 h. Figure 2 also show that by increasing of

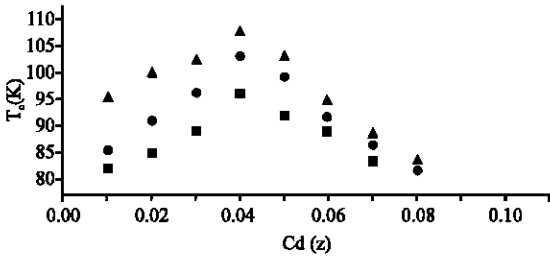


Fig. 2: The critical temperature of doped sample versus the amount of cadmium for annealing times (■) 90, (●) 180 and (▲) 270 h

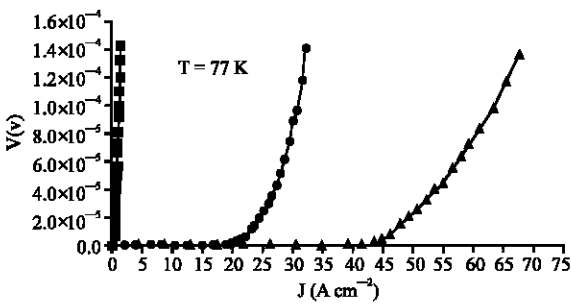


Fig. 3: The V-J curves for different annealing times of (■) 90, (●) 180 and (▲) 270 h for the sample with Cd content of 0.04

sintering time up to 270 h, the  $T_c$  of all samples increases. The results of this investigation are well compatible with the results of XRD patterns (Fig. 1).

Figure 3 shows the V-J curves of the sample with  $z = 0.04$  annealed at different times which are taken at liquid nitrogen. One can observe that by increasing the annealing time, the critical current densities of the samples increase. This result suggests that the intergranular coupling increases by increasing the annealing temperature.

Figure 4 shows the measured  $J_c$  versus the amount of Cd doped in the samples for different annealing times. Our observations suggest that not only Cd acts as a Bi (2223) phase stabilizer but also either causes some improvement between the grains or increases the flux pinning centers. Figure 4 show that if we increase the Cd content,  $J_c$  increases too. Also by increasing the annealing time up to 270 h, the  $J_c$  increases as well. So the maximum  $J_c$  was found for  $\text{Bi}_{1.6}\text{Pb}_{0.36}\text{Cd}_{0.04}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ , annealed for 270 h. When, the amount of cadmium gets more than 0.04, the unwanted phases such as Bi (2212) and Bi (2201) will increase in the sample. These unwanted phases play the role of the weak links and decrease the critical current density. It is shown that the Bi (2201) phase locates mainly between the superconducting grains, preventing

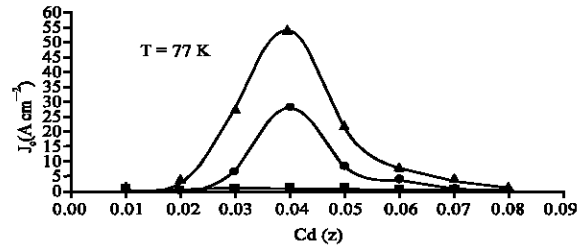


Fig. 4: The critical current density of doped samples as a function of the cadmium amounts for annealing times of (■) 90, (●) 180 and (▲) 270 h

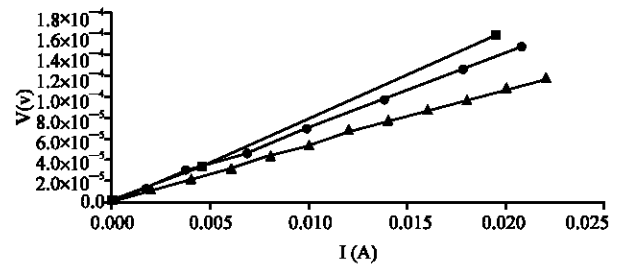


Fig. 5: The V-I curves for different annealing time (■) 90, (●) 180 and (▲) 270 h for the sample with 0.04 cadmium at room temperature

the super current flow (Guo *et al.*, 1998). It was also shown that  $J_c$  was raised as the Bi (2201) phase decreased in Bi (2223) tapes (Guilmeau *et al.*, 2002). Deng *et al.* (2000) using scanning electron microscopy have observed that the residual Bi (2212) phase is situated at grain boundaries of Bi (2223) phase.

Figure 5 shows the room temperature V-I curves of the sample with  $z = 0.04$  annealed at different times. One can see that the normal state resistance of the samples will decrease by increasing the annealing time. This means that the junctions between the grains have been improved in the sample by increasing the annealing time.

In Fig. 6 we have plotted the resistance of doped samples as a function of the cadmium amounts for different annealing times at the room temperature. It shows that increasing the period of annealing time up to 270 h the resistance decreases. So the minimum R was found for  $\text{Bi}_{1.6}\text{Pb}_{0.36}\text{Cd}_{0.04}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ , annealed for 270 h. When the amount of cadmium gets more than 0.04, the resistance of normal state of the samples will increase. The reason is that entering higher amounts of cadmium oxide in the samples, the other unwanted phases will be grown. These phases will weaken the junctions between the grains; therefore the electric resistance of normal state will increase.

Figure 7 shows the results of susceptibility measurements for samples with  $z = 0.03, 0.04$  and  $0.05$  for

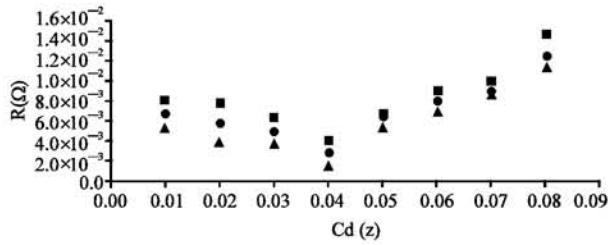


Fig. 6: The resistance of doped samples as a function of the Cadmium amounts for annealing times of (■) 90, (●) 180 and (▲) 270 h at the room temperature

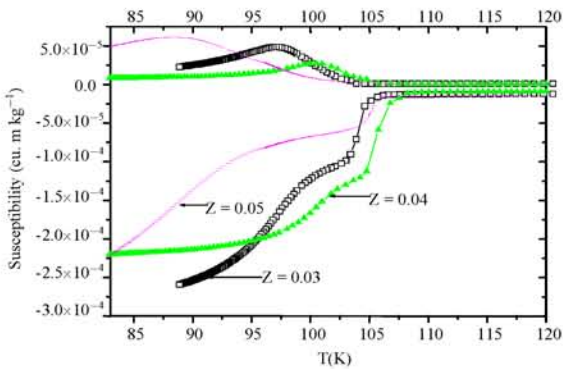


Fig. 7: Temperature dependence of the susceptibility for samples with cadmium content of 0.03, 0.04 and 0.05

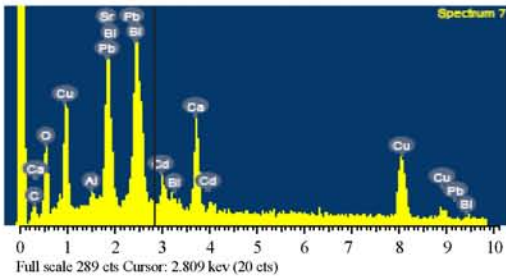


Fig. 8: The EDX images of the sample with the amount of cadmium 0.04 with annealing time of 270 h

cadmium. The temperature dependencies of the real  $\chi'$  and imaginary  $\chi''$  parts of AC susceptibility for all of the samples were measured in ac field of 50 A/m with a frequency of 333 Hz, which was applied parallel to the long dimension of the samples. In particular the imaginary component of the AC susceptibility has been widely used to probe the nature of weak links in polycrystalline superconductors. It is also employed to estimate some of the important physical properties like critical current density (Gencer *et al.*, 1996; Sedky and Youssif, 2001). The real part ( $\chi'$ ) of AC susceptibility in polycrystalline

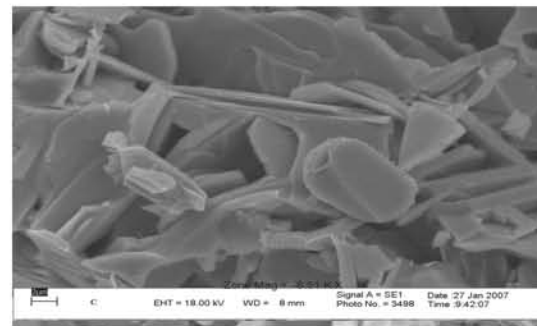
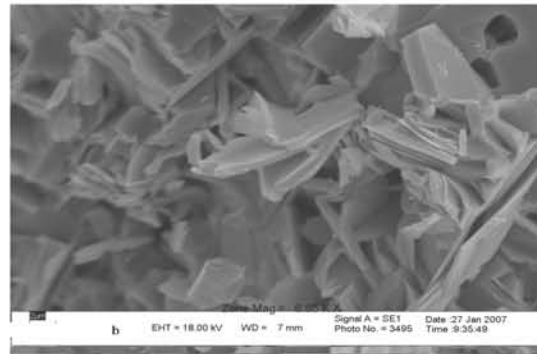
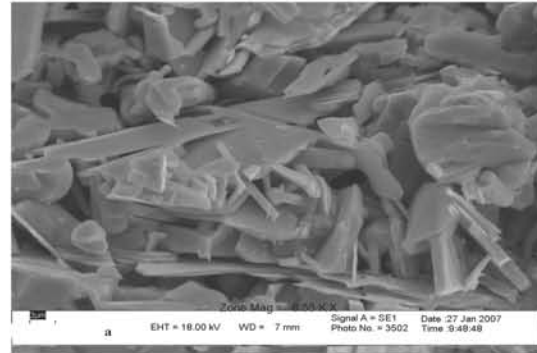


Fig. 9: The SEM micrographs of samples with different amounts of cadmium (a) 0.04, (b) 0.06 and (c) 0.02 with annealing time of 270 h

samples shows two drops as the temperature is lowered below the onset of diamagnetic transition and correspondingly the derivative of the  $\chi'(T)$  displays two peaks. The first sharp drop at critical temperature is due to transition within the grains and the second gradual change is due to the occurrence of the superconducting coupling between the grains. The imaginary part  $\chi''$  shows a peak which is a measure of the dissipation in the sample. It can be seen from the curves that the maximum value of the critical temperature for the sample with  $z = 0.04$  is obtained.

The results of EDX images show that there is not unwanted element in the samples except Aluminium which is due to the substrate (Fig. 8). This implies that the

samples are not contaminated during the synthesis process.

Figure 9 shows the SEM micrographs for samples with amounts of cadmium 0.02, 0.04 and 0.06 with annealing time for 270 h. It seems that the increase in the amount of cadmium more than  $z = 0.04$  leads to the formation of pores. As one can see the gradual decrease of superconducting properties is observed with decreasing amount of cadmium. It seems that decreasing the amount of cadmium the values of  $z$  less than 0.04 leads to the formation of large grains. These pores and large grains act as weak links between the grains, destroying grain connectivity and disrupting current flow. These results are in agreement with the results of x-ray diffraction patterns and the critical current densities.

### CONCLUSION

We have studied the role of Cd in the synthesis of  $\text{Bi}_{1.6}\text{Pb}_x\text{Cd}_z\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$  with  $(z, x) = (0.01, 0.39), (0.02, 0.38), (0.03, 0.37), (0.04, 0.36), (0.05, 0.35), (0.06, 0.34), (0.07, 0.33), (0.08, 0.32), (0.09, 0.31)$  and  $(0.1, 0.3)$ . Samples were prepared by solid state reaction using different annealing times. The results of susceptibility measurements for the samples show that the critical temperature of the sample with  $z = 0.04$  is more than the others. We can conclude that the sample doped with cadmium having  $z = 0.04$  with annealing time of 270 h, can increase the percentage of Bi (2223) phase. The results of these investigations are well compatible with the results of XRD patterns. Present results also show the maximum value of the critical current density and the critical temperature were obtained for the sample with annealing time 270 h and Cd content of 0.04.

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