Effects of TiO$_2$ addition on the superconducting properties of Bi-Sr-Ca-Cu-O system

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The effects of TiO$_2$ addition in Bi$_2$Sr$_2$CaCu$_2$O$_8$-Ti$_y$ (Bi-2212) with $y = 0$, 0.05, 0.10 and 0.15 and (Bi$_{1.6}$Pb$_{0.4}$)Sr$_{1.6}$Ca$_2$Cu$_{2.8}$O$_{10}$-Ti$_y$ (Bi-2223) with $y = 0$, 0.10, 0.20 and 0.40 are studied and compared. The samples have been investigated by powder X-ray diffraction (XRD), dc electrical resistance, critical current density (J_c) and scanning electron microscopy (SEM). The XRD patterns of the Bi$_2$Sr$_2$CaCu$_2$O$_8$-Ti$_y$ materials showed the Bi-2212 as the dominant phase. In the TiO$_2$ added samples (with $y = 0.05$ and 0.1), the c lattice parameter decreased slightly from the non-added sample showing the possibility of Ti incorporating into the crystal structure of the Bi-2212 phase. In the undoped (Bi$_{1.6}$Pb$_{0.4}$)Sr$_{1.6}$Ca$_2$Cu$_{2.8}$O$_{10}$ material, the XRD pattern showed the existence of mixed phases of Bi-2223 and Bi-2212. The TiO$_2$ added Bi-2223 samples do not show any systematic variation in the c lattice parameter, indicating that Ti may not be incorporated into the Bi-2223 crystal structure. The T_c values in both systems decreased with the addition of TiO$_2$. The critical current densities, J_c at 40 K in the Bi$_2$Sr$_2$CaCu$_2$O$_8$ system and at 77 K in the (Bi$_{1.6}$Pb$_{0.4}$)Sr$_{1.6}$Ca$_2$Cu$_{2.8}$O$_{10}$ system also decreased with the addition of TiO$_2$. SEM micrographs of both systems showed a slight decrease in average grain size when TiO$_2$ was added. © *2000 Kluwer Academic Publishers*

1. Introduction

The Bi-Sr-Ca-Cu-O system consists of a series of superconducting phases having structural formulae Bi$_2$Sr$_2$Ca$_{n-1}$Cu$_n$O$_x$ with $n = 1$ (Bi-2201 phase, $T_c \approx 20$ K), 2 (Bi-2212 phase, $T_c \approx 85$ K) and 3 (Bi-2223 phase, $T_c \approx 110$ K) [1–3]. Since their discovery, the effect of additions or substitutions in the Bi-Sr-Ca-Cu-O system with different elements having different ionic radii and bonding character have been studied by various investigators [for example, 4–20]. The superconducting properties are either enhanced or destroyed, depending on the characteristics of the added or substituted elements. For example, the addition of Li helps to induce an increase in the transition temperature, T_c, for the Bi-2201 and Bi-2223 phases. It also enhanced the superconducting volume in Bi-2212 phase and increase the transport critical current density (J_c) of the Bi-2212 and Bi-2223 phases [4, 6, 10]. On the other hand, Fe and Co doped Bi-2212 showed a decrease in T_c with increasing doping concentration [5]. In Ti-doped Bi-2212 single crystals, TEM studies have shown the evidence of defects which can enhance flux pinning [19, 20]. The addition of a small amount of Ti is reported to enhance the Bi-2223 formation [12]. But the volume fraction of Bi-2223 phase in In doped material, decreases with In concentration [14]. In Mo substituted Bi-2223 samples, the volume fraction of Bi-2223 phase increases with in-creasing Mo concentration but depresses the T_c of this system slightly [16].

Among the copper-oxide family of high temperature superconductors, the Bi-based one is the most promising material for tapes and wires fabrication. One of the most common methods of making superconductor wires and tapes is the powder in tube method where Ag tubes are normally employed. For better mechanical properties, Ag-Ti alloy tube has been suggested in place of Ag because it is expected have a microhardness twice as high as that of pure Ag when used as the sheath materials for tapes and wires [13].

The aim of this work is to study the effect of addition of TiO$_2$ on the superconducting properties of polycrystalline Bi-2212 and Bi-2223 in view of the possibility of using Ag-Ti alloy for tapes fabrication. We studied both Bi-2212 and Bi-2223 in order to compare directly the effect of the addition on both systems especially on phase formation and critical current density. Starting compositions, heating temperatures and sintering time are as discussed in the next section. Only small concentrations are considered since large concentrations are detrimental to their superconducting property [12]. For preparation of the Bi-2223 phase, we have chosen a nominal composition with lower concentration of Sr because a deficient environment is necessary to supply the appropriate holes concentration, thus enhancing

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the superconducting properties of the compound [21].

2. Experimental procedure

Polycrystalline samples of Bi-2212 and Bi-2223 superconductors were prepared by solid state reactions using high purity (99.999%) Bi_2O_3, $SrCO_3$, $CaCO_3$, CuO and PbO powders with nominal compositions of $Bi_2Sr_2CaCu_2O_8$ and $(Bi_{1.6}Pb_{0.4})Sr_{1.6}Ca_2Cu_{2.8}O_{10}$. The powders were weighed and mixed thoroughly to obtained the required stoichiometric ratios. In preparing the $Bi_2Sr_2CaCu_2O_8$ series, the mixed powders were heated at $800\,°C$ for 48 hours with several intermittent grindings. The resultant powders were then mixed thoroughly with TiO_2 powder (purity 99.999%) with nominal composition of $Bi_2Sr_2CaCu_2O_8$-Ti_y ($y = 0, 0.05, 0.10$ and 0.15) and pressed into pellets of 13 mm diameter and 2 mm thickness. The pellets were sintered at $855\,°C$ in air for 48 hours and then quenched in air.

In preparing the $(Bi_{1.6}Pb_{0.4})Sr_{1.6}Ca_2Cu_{2.8}O_{10}$-$Ti_y$ series, the mixed powders were heated at $800\,°C$ for 40 hours with several intermittent grindings. The powders were then mixed with TiO_2 powder (purity 99.999%) with nominal composition of $(Bi_{1.6}Pb_{0.4})Sr_{1.6}Ca_2Cu_{2.8}O_{10}$-$Ti_y$ with $y = 0, 0.10, 0.20$ and 0.40. The resultant powders were pressed into pellets and heated in air at $840\,°C$ for 240 hours followed by furnace cooling to room temperature.

X-ray diffraction (XRD) patterns were recorded on a Siemens D5000 diffractometer using Cu K_α radiation. Electrical resistance measurements were carried out using the standard four point-probe dc method with silver paste contacts. The experimental set-up consisted of a closed cycle refrigerator from CTI Cryogenics (model 22), a temperature controller from LakeShore (model 330), and a constant current source (Keithley 220). The critical current density (J_c) was measured on bar-type samples with cross sectional dimensions of approximately 1.5 mm by 2.5 mm. $T_{c\,zero}$ is defined as the temperature at which the electrical resistance dropped to zero. The onset of superconductivity, $T_{c\,onset}$ was taken as the temperature at which the tangent of the resistance versus temperature curve intersects with the tangent of the part where resistance dropped precipitously. The critical current densities were determined using the 1 μV/cm criterion at 40 K for the $Bi_2Sr_2CaCu_2O_8$-Ti_y series and at 77 K for the $(Bi_{1.6}Pb_{0.4})Sr_{1.6}Ca_2Cu_{2.8}O_{10}$-$Ti_y$ series. The microstructures of the samples were also analyzed by a Philips XL 30 scanning electron microscope (SEM).

3. Results and discussion

Fig. 1 shows the XRD patterns of $Bi_2Sr_2CaCu_2O_8$-Ti_y with $y = 0$ and 0.15. The XRD patterns of the non-doped and TiO_2 doped samples show peaks that can be indexed on the basis of a Bi-2212 structure. The (002) peak, which is characteristic of the Bi-2212 phase, can be observed clearly in both the undoped and Ti doped samples. The c lattice parameters decreased with in-
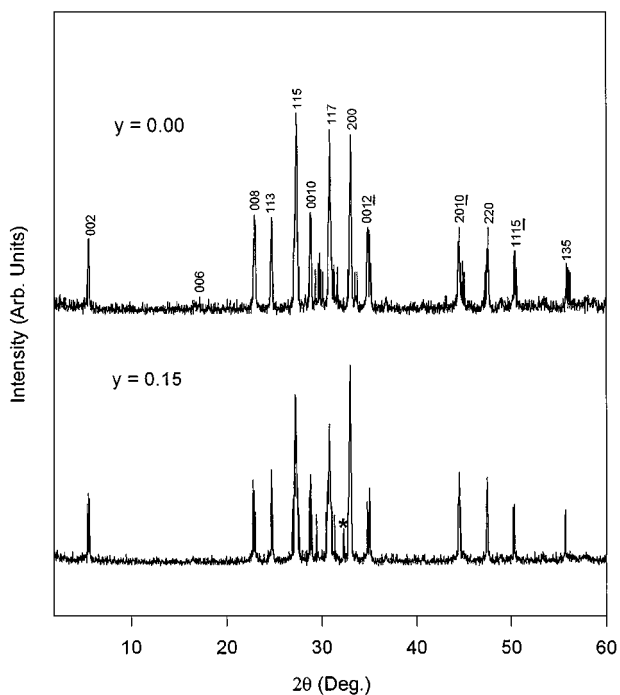

Figure 1 XRD patterns for $Bi_2Sr_2CaCu_2O_8$-Ti_y with $y = 0$ and 0.15. Peak due to $SrTiO_3$ is indicated by (*).

creasing Ti content, i.e. $c = 30.823$ Å, 30.731 Å and 30.723 Å for $y = 0, 0.05$ and 0.1, respectively. No systematic variation in a and b lattice parameters is observed.

When metals are added into a superconductor compound, they will either substitute themselves onto suitable atomic sites or segregate as impurity phases and not become part of the structure. There are also cases in which both situations occurred. For the Ti added samples, the XRD patterns show similar patterns as for the undoped sample except for a few unaccountable peaks. Since Ti exists in the oxidation state, Ti^{4+} and considering its ionic radius (0.68 Å) is close to that of Cu^{2+} (0.72 Å), it is quite possible that Ti goes to the Cu site. This explains the decrease in the c lattice parameter for the Ti added samples. Thus, there is a possibility for the Ti atoms to be incorporated into the crystal structure of the Bi-2212 phase.

Fig. 2 shows the XRD patterns for powdered $(Bi_{1.6}Pb_{0.4})Sr_{1.6}Ca_2Cu_{2.8}O_{10}$-$Ti_y$ with $y = 0$ and 0.10. The patterns showed the coexistence of Bi-2212 and Bi-2223 phases. The volume fraction of the Bi-2223 phase (V_{2223}) versus the Bi-2212 phase (V_{2212}) is determined using the relation

$$V_{2223} = \frac{I_{2223}(00\underline{10})}{I_{2223}(00\underline{10}) + I_{2212}(008)}$$

where $I_{2223}(00\underline{10})$ is the XRD peak intensity of $(00\underline{10})$ in Bi-2223 and $I_{2212}(008)$ is the peak intensity of the neighbouring peak (008) in Bi-2212 [14]. It is observed that V_{2223} decreased with increasing Ti concentration. $V_{2223} = 47\%$, 38% and 33% for $y = 0, 0.10$ and 0.20, respectively. Even though the samples are not predominantly Bi-2223, the volume fraction is sufficient to form a continuous network of Bi-2223 phase grains. This is reflected by the above 100 K $T_{c\,zero}$, for

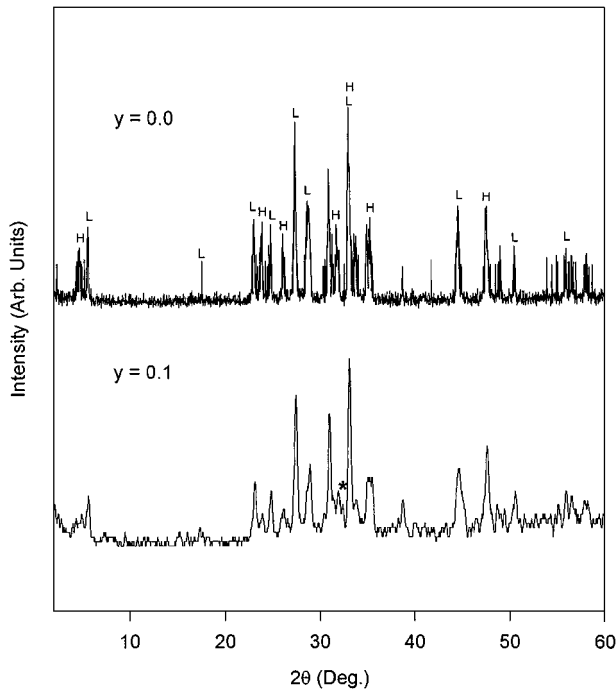*Figure 2* XRD patterns for $(Bi_{1.6}Pb_{0.4})Sr_{1.6}Ca_2Cu_{2.8}O_{10}$-$Ti_y$ with $y = 0$ and 0.10. Peaks belonging to the Bi-2223 phase are indicated by (H) and those belonging to the Bi-2212 phase by (L). Peak due to $SrTiO_3$ is indicated by (*).

Figure 4 The critical temperature, $T_{c\,zero}$ and $T_{c\,onset}$ and the critical current density, J_c at 40 K for $Bi_2Sr_2CaCu_2O_8$-Ti_y with $y = 0, 0.05, 0.10$ and 0.15.

the $y = 0$ and 0.10 samples. As reported by Grivel *et al.* [13], as more Ti enters the structure, it gives rise to a new structural phase with secondary phases formed such as Bi-2201 phase, Ca_2CuO_3 and $SrTiO_3$. The slight decrease in $T_{c\,onset}$ may be due to the presence of minute amounts of Ti in the structure of the Bi-2223 phase [13]. The dramatic decrease in $T_{c\,zero}$ in the Ti added samples as V_{2223} is further decreased may be due to the presence of the secondary phases which reduces the effective percolative paths. Lu *et al.* [12] reported that there was no evidence of Bi-2223 in
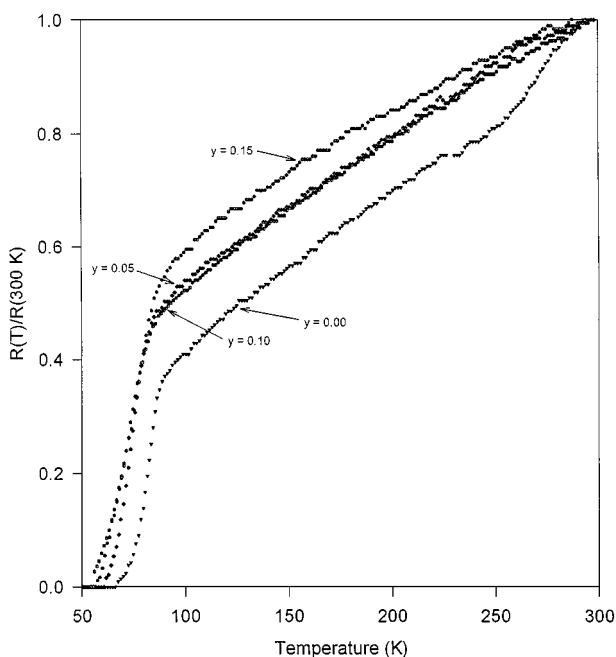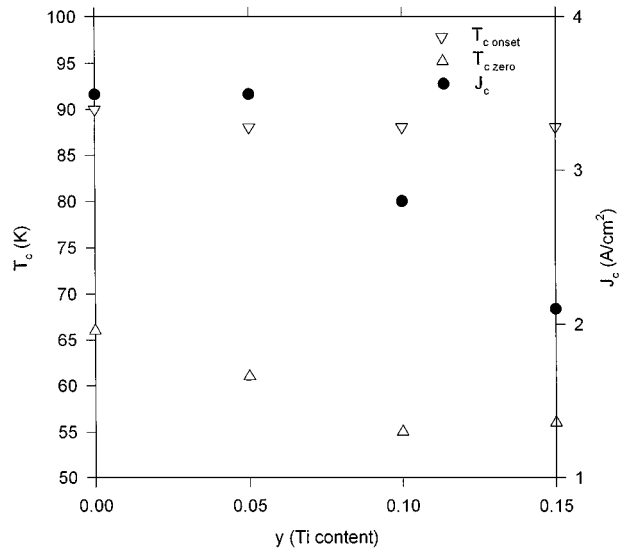
Ti-substituted $(Bi_{1.6}Pb_{0.4})Sr_2Ca_2Cu_{3-x}Ti_xO_{10+y}$ compounds with $x \geq 0.3$. This is in close agreement with our XRD pattern which revealed no Bi-2223 phase for sample with $y = 0.4$.

The c lattice parameter of the Ti added $(Bi_{1.6}Pb_{0.4})Sr_{1.6}Ca_2Cu_{2.8}O_{10}$-$Ti_y$ samples do not show any systematic variation with % Ti added and the structure remains tetragonal. This indicates that the solubility of Ti in the structure of Bi-2223 phase is small (i.e. $y < 0.1$), if any.

Fig. 3 shows the temperature dependence of the electrical resistance for $Bi_2Sr_2CaCu_2O_8$-Ti_y with $y = 0, 0.05, 0.10$ and 0.15. All samples showed a metallic normal state behaviour. The values of $T_{c\,onset}$ and $T_{c\,zero}$ are as shown in Fig. 4. $T_{c\,onset}$ for the Ti added sample show a slight decrease from 90 K to 88 K but $T_{c\,zero}$ for

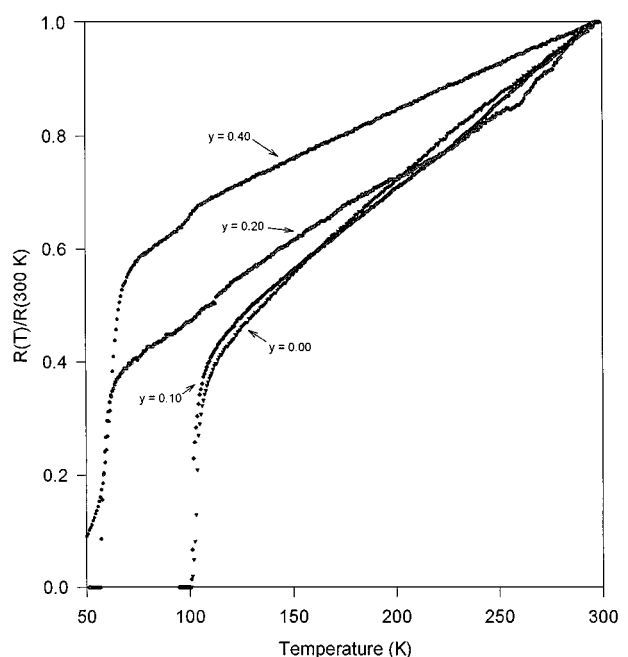*Figure 3* The normalized electrical resistance versus temperature of $Bi_2Sr_2CaCu_2O_8$-Ti_y with $y = 0, 0.05, 0.10$ and 0.15.

Figure 5 The normalized electrical resistance versus temperature of $(Bi_{1.6}Pb_{0.4})Sr_{1.6}Ca_2Cu_{2.8}O_{10}$-$Ti_y$ with $y = 0, 0.10, 0.20$ and 0.40.
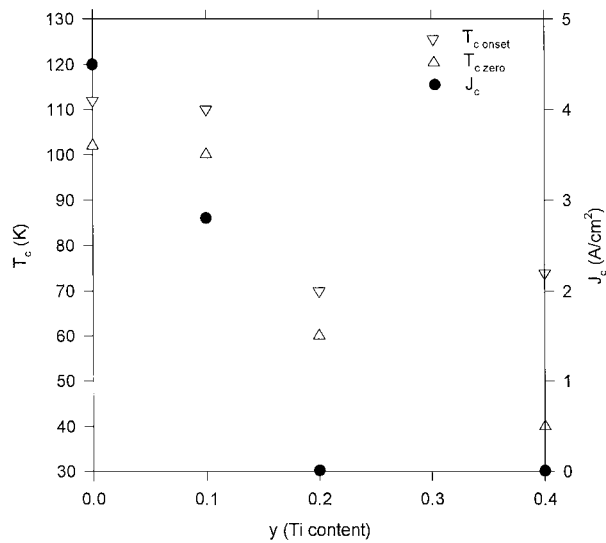
Figure 6 The critical temperature, $T_{c\,zero}$ and $T_{c\,onset}$ and the critical current density, J_c at 77 K for $(Bi_{1.6}Pb_{0.4})Sr_{1.6}Ca_2Cu_{2.8}O_{10}$-$Ti_y$ with $y = 0, 0.10, 0.20$ and 0.40.

the Ti added samples decreased by 5–10 K from the un-doped sample. This is expected since the formation of impurities such as $SrTiO_3$ will reduce the content of Sr in the structure. Sr is one of the necessary elements to provide a lattice framework conducive to superconductivity [11]. Fig. 3 also shows the appearance of a *tail* at $T_{c\,zero}$ in each sample and this phenomenon is linked to the presence of the Bi-2201 phase as an impurity phase [22].

Fig. 4 shows the critical current density, J_c at 40 K of $Bi_2Sr_2CaCu_2O_8$-Ti_y. The J_c values decreased in the Ti added samples. The existence of secondary phases and impurities such as Bi-2201 phase, Ca_2CuO_3, CuO and $SrTiO_3$ may suppress the current carrying capacity of these samples since they exacerbate the weak-link problems [23]. As reported by Konstantinov *et al.* [24], one of the factors that influences J_c is the presence of impurities that are not acting as flux pinning centers. Thus Ti in our samples does not seem to act as a flux pinning centers for the Bi-2212 phase.
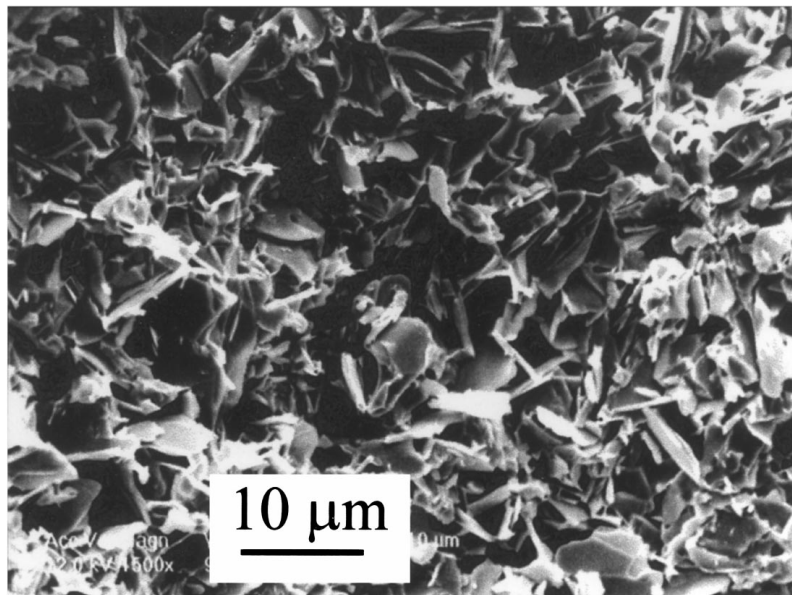
(a)
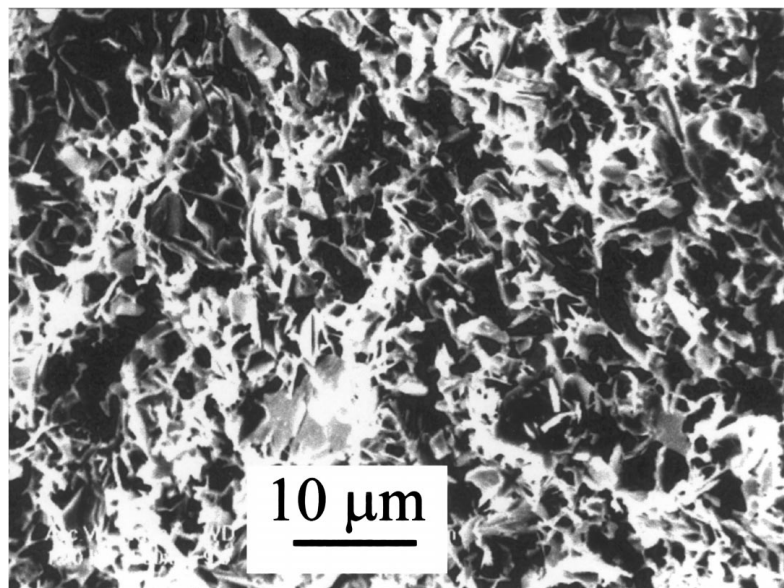
(b)

Figure 7 SEM micrographs of $Bi_2Sr_2Ca_1Cu_2O_8$-Ti_y with (a) $y = 0$ and (b) $y = 0.15$.

Fig. 5 shows the temperature dependence of electrical resistance for $(Bi_{1.6}Pb_{0.4})Sr_{1.6}Ca_2Cu_{2.8}O_{10}$-$Ti_y$ with $y = 0, 0.10, 0.20$ and 0.40. It shows the absence of a *tail* in the samples. The absence of a *tail* is a contributing factor in the attainment of higher T_c values. This indicates that prolonged heat treatment (for about 240 hours), can promote the formation of the Bi-2223 phase. Impurity phases can lead to a *tail* in the resistance versus temperature curves as shown by the Bi-2212 samples which were heated for only 48 hours in the final heating stage. The $y = 0.4$ sample showed a $T_{c\,zero}$ of < 50 K and this is attributed to the presence of impurities and non-superconducting phases as discussed above. $T_{c\,onset}$ and $T_{c\,zero}$ are as shown in Fig. 6. $T_{c\,zeros}$ of 100 K or more are achieved in the undoped sample as well as the $y = 0.10$ sample.

Fig. 6 shows the J_c at 77 K for $(Bi_{1.6}Pb_{0.4})Sr_{1.6}Ca_2Cu_{2.8}O_{10}$-$Ti_y$. It indicates a distinct degradation in J_c values in the Ti added samples. J_c for the $y = 0.20$ and 0.40 sample decreased by three orders of magnitude (1×10^{-3} and 5×10^{-3} A/cm^2, respectively) compared to the undoped sample indicating the severity of the effect of Ti overdoping in the system. This is probably due to the disruption of the connectivity among Bi-2223 grains by Ti bearing compounds such as $SrTiO_3$ (detected from X-ray diffraction pattern) which may reside near the boundaries. The connectivity among Bi-2223 grains is reflected by the volume fraction of Bi-2223 phase. The lowering of the volume fraction of Bi-2223 phase with increasing Ti (determined semi-quantitatively) resulted in lower J_c values.

Fig. 7a and b show the SEM micrographs for $Bi_2Sr_2CaCu_2O_8$-Ti_y with $y = 0$ and 0.15, respectively. Fig. 7a shows grains with an average size of less than 5 μm. Fig. 7b shows that the average size decreases for $y = 0.15$. The same result is also obtained for the Bi-2223 series. Hence, TiO_2 controls the grain size of the Bi-2212 and Bi-2223 systems.

4. Conclusion

Our results show that the addition of TiO_2 to both $Bi_2Sr_2CaCu_2O_8$ and $(Bi_{1.6}Pb_{0.4})Sr_{1.6}Ca_2Cu_{2.8}O_{10}$ is detrimental to superconducting properties. The addition of TiO_2 in $Bi_2Sr_2CaCu_2O_8$ results in the Ti atoms incorporating into the crystal structure of the Bi-2212 phase. In $(Bi_{1.6}Pb_{0.4})Sr_{1.6}Ca_2Cu_{2.8}O_{10}$, the addition of TiO_2 does not change the crystal structure of the Bi-2223 phase. In both systems, a reduction in T_c and J_c is observed with TiO_2 addition. One possible application related to this finding is the used of Ag-Ti alloys as sheath materials for the fabrication of Bi-Sr-Ca-Cu-O superconducting wires and tapes. This may be possible only if a small quantity of Ti is added into the systems, $y < 0.15$ in the $Bi_2Sr_2CaCu_2O_8$-Ti_y system and $y \leq 0.1$ in the $(Bi_{1.6}Pb_{0.4})Sr_{1.6}Ca_2Cu_{2.8}O_{10}$-$Ti_y$ system.

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