EFFECT OF NANO-SIZE SnO₂ ADDITION ON (Bi,Pb)-Sr-Ca-Cu-O SUPERCONDUCTOR

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ABSTRACT

In this study the influence of nano-SnO₂ particles addition on the critical current density \( J_C \) in Bi₁₆Pb₀.₄Sr₂Ca₂Cu₃SnₓO₁₀ superconductor ceramic with \( x \) ranging from 0 to 0.05 was investigated. The samples were prepared using the co-precipitation technique with sintering time of 48 h at 850°C. The characterizations were carried out using DC resistivity measurement, X-ray diffraction (XRD) and scanning electron microscopy (SEM). The critical current density, \( J_C \) and the transition temperature, \( T_{C-onset} \) for sample with 0.02 wt% were found to be the highest with a maximum \( J_C \) 1212 mA/cm² and a maximum \( T_{C-onset} \) 112 K. XRD and SEM analysis indicated that nano-SnO up to 0.02% wt enhance the formation of low-\( T_C \) (Bi-2212) phase fraction.

Keywords: Nano-SnO; Bi₁₆Pb₀.₄Sr₂Ca₂Cu₃SnₓO₁₀

INTRODUCTION

Since the discovery of (Bi,Pb)-Sr-Ca-Cu-O (BSCCO) high-\( T_C \) superconductors [1,2], great progress has been achieved in enhancing transport properties of (Bi,Pb)Sr₂Ca₂Cu₃O₁₀₋δ (Bi2223) superconductor. The transition temperature (\( T_C \)) and critical current density (\( J_C \)) are the most important superconducting properties that would be taken into account in technological applications [3]. The major limitations of Bi-system superconductor applications are the intergrain weak links and weak flux pinning capability. Many efforts have been made in order to improve phase purity, grain alignment in turn reduce weak link in Bi2223 superconductor [4, 5]. Chemical doping and introduction of nano-sized particles in bulk high-\( T_C \) superconductors have generated great interest because they represent an easily controlled and efficient tool for improving the superconducting properties [6]. Chemical dopants and preparation methods influence the microstructure and electrical properties of superconducting material. Regarding nanoparticle addition, only a few are reported to react with the high-\( T_C \) superconductor materials during processing to become therefore second-phase defects [7-10]. There are several report results of improved \( J_C \) values through introducing nanometer particles such as MgO [11, 12], ZrO₂ [13], \( \gamma-Fe_2O_3 \) [14], Al₂O₃ [15] into high \( T_C \) superconductors. These results prove that particle addition may be a potential way to improve flux pinning considerably. However, the influence of these particles on the intergrain weak links in terms of intergranular critical current is
unknown [12]. The objective of this work is to study the effect of nano-size (~50 nm) SnO₂ addition in (Bi₁.₆Pb₀.₄)Sr₂Ca₂Cu₃O₁₀ bulk superconductor with respect to critical temperature, critical current density, structure and microstructure are reported.

**METHOD**

The ultra fine (Bi₁.₆Pb₀.₄)Sr₂Ca₂Cu₃O₁₀ superconductor powders were developed from the co-precipitation method. The material was prepared using metal acetates of bismuth, lead, strontium, calcium and copper (purity ≥ 99.99%), oxalic acid, de-ionized water and isopropanol. The dried-up powders were heated for first calcinations at 730 °C for 12 hours. The calcined powder was reground and heated again at 845 °C for 24 h. 0.01 wt% to 0.05 wt% of nano SnO₂ was added to the powders. The grains size of nano SnO₂ is in average of 50 nm (Figure). The powders were ground thoroughly and then pressed into pellet with diameter of 13 mm and thickness of 2 mm. The pellets were sintered at 850 °C for 48 hours. The electrical resistance–temperature measurements were carried out by the four-point probe technique in conjunction with a CTI cryogenics closed-cycle refrigerator (Model 22). The XRD patterns of the bulks were recorded using a Siemens D 5000 diffractometer with CuKα radiation. The microstructure was examined by Philips Scanning Electron Microscope (Model XL-30).

![Figure 1: TEM micrograph of nano SnO₂](image)

**RESULTS AND DISCUSSION**

Measurements of resistivity dependence on the temperature ρ(T) for different samples with various amount of SnO₂ addition (x=0.0wt% to x=0.05wt %) are shown in Figure
2. All samples exhibit a normal metallic behaviour followed by decrease in critical temperature $T_{c-zero}$ as the SnO$_2$ concentration was increased. That was due to the decrease in the high-$T_C$ phase and increase in the formation of low-$T_C$ phase. However the resistance dropped with single-step features in all samples implying that these samples consisting mainly of 2223 phase. The zero resistance temperature, $T_{c-zero}$ and onset temperature $T_{c-onset}$ for the non-doped sample were at 98K and 108K, respectively. The sample with 0.02 wt% SnO$_2$ showed improvement in $T_{c-zero}$ and $T_{c-onset}$ by 4K and 2K, respectively as compared to the undoped sample. Hence 0.02wt% nano SnO$_2$ can be the appropriate amount of addition that exhibits the highest $T_c$. The decreasing of $T_c$ value for all samples with SnO$_2$ adding up to 0.02 wt% indicates that the strength of coupling between the grains of mixed phases has been decreased resulting in a weaker-link[16].

Figure 2: Resistance versus temperature of Bi$_{1.6}$Pb$_{0.4}$Sr$_2$Ca$_2$Cu$_3$O$_{10}$ (SnO$_2$)$_x$

Table 1 shows the critical temperature, $T_c$ and critical current density $J_c$ at 30 K and 77 K. The highest value of critical current density, $J_c$ (1212 mA cm$^{-2}$) was recorded in sample 0.02 wt%. It is clear that the addition of small amount of SnO$_2$ (0.02wt %) enhanced the current-carrying capacity of Bi-2223 ceramics. Beyond 0.02 wt% the $J_c$ decreased.
Table 1: $T_{c-onset}$, $T_{c-zero}$, $J_c$, volume fraction of phase 2223 and 2212

<table>
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<tr>
<th>SnO$_2$ Concentration</th>
<th>$T_{c-onset}$ (K)</th>
<th>$T_{c-zero}$ (K)</th>
<th>$J_c$(mA cm$^{-2}$) at 30K</th>
<th>$J_c$(mA cm$^{-2}$) at 77K</th>
<th>Volume Fraction</th>
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</tbody>
</table>

Figure 3 shows the XRD patterns of the non-added and nano SnO$_2$ added Bi-2223 bulk samples. All samples with nano SnO$_2$ addition contain low-$T_c$ peaks which correspond to the 2212 phase. Several peaks have been shifted toward either higher or lower value of 2$\theta$ angle as the concentration of SnO$_2$ increase. The peaks belonging to 2223 high-$T_c$ phase (0012H), (119H), (220H), (039) and (1111H) existed in all samples. The peaks (111H) and (013H) exist only in all SnO$_2$ adding samples. Meanwhile, the peaks corresponding (200H) and (115H) diminished as the concentration of SnO$_2$ increased was found to be disappeared at x=0.05wt%. Unknown peak (*) existed in all SnO$_2$ adding samples at 2$\theta$= 31.06$^\circ$. It was observed that the lattice parameter c was found to decrease and volume fraction of Bi-2223 phase decrease with increasing of SnO$_2$ up to 0.02wt% as shown in table 1. This caused a decrease in the volume of the unit cell and a decrease in the intensity of the 2223 phase. However the crystallographic structure remains in the tetragonal form.

![X-ray diffraction patterns](image.png)

Figure 3: X-ray diffraction patterns for Bi$_{1.6}$Pb$_{0.4}$Sr$_2$Ca$_2$Cu$_3$O$_{10-x}$ (SnO$_2$)$_x$
Figure 4 (a, b, c, d, e and f) shows scanning electron micrograph taken on fractured surface of samples x=0.0 to 0.05 wt%. All samples exhibit common features of plate-like layered grains, which are randomly distributed and connected to each other. Samples with low concentration of SnO$_2$ showed bigger grain size than the high SnO$_2$ concentration one. The un-doped sample shows bigger grain size than the sample with high nano SnO$_2$ adding. XRD and SEM analysis indicated that all samples with SnO$_2$ adding showed 2212 peaks which correspond to the low-superconductor phase. An improvement in superconducting properties was obvious for 0.02 wt% sample where the sample still dominated by high-superconductor phase. Above that concentration, the grain size decreased and become shorter and thicker as compared to the undoped sample.

Figure 4: SEM micrographs for Bi$_{1.6}$Pb$_{0.4}$Sr$_2$Ca$_2$Cu$_3$O$_{10}$(SnO)$_x$ samples with (a)x=0 wt%, (b)x=0.01 wt%, (c)x=0.02 wt%, (d)x=0.03 wt%, (e)x=0.04 wt% and (f)x=0.05 wt%
CONCLUSION

In conclusion the addition of Nano-SnO$_2$ tends to suppress the superconductivity. However, this work shows experimentally that the addition of nanoparticles SnO$_2$ can significantly enhance the critical current density, $J_c$ of bulk $(\text{Bi}_{1.6}\text{Pb}_{0.4})\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$, 0.02 wt% can be the appropriate amount of addition as it exhibits the highest $T_c$ and $J_c$.

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REFERENCES