Effect of Co$_3$O$_4$ Nanoparticles Addition on (Bi,Pb)-2223 Superconductor

A. N. Jannah, R. Abd-Shukor, and H. Abdullah

**Abstract**—The effect of nano Co$_3$O$_4$ addition on the superconducting properties of (Bi, Pb)-2223 system was studied. The samples were prepared by the acetate coprecipitation method. The Co$_3$O$_4$ with different sizes (10-30 nm and 30-50 nm) from $x=0.00$ to $0.05$ was added to Bi$_{1-x}$Pb$_x$Sr$_2$Ca$_2$Cu$_3$O$_{y_0}$(Co$_3$O$_4$)$_x$. Phase analysis by XRD method, microstructural examination by SEM and dc electrical resistivity by four point probe method were done to characterize the samples. The X-ray diffraction patterns of all the samples indicated the majority Bi-2223 phase along with minor Bi-2212 and Bi-2201 phases. The volume fraction was estimated from the intensities of Bi-2223, Bi-2212 and Bi-2201 phase. The sample with $x=0.01$ wt% of the added Co$_3$O$_4$ (10-30 nm size) showed the highest volume fraction of Bi-2223 phase (72%) and the highest superconducting transition temperature, $T_c$ (~102 K). The non-added sample showed the highest $T_c$ (~103 K) compared to added samples with nano Co$_3$O$_4$ (30-50 nm size) added samples. Both the onset critical temperature $T_{c(onset)}$ and zero electrical resistivity temperature $T_c(R=0)$ were in the range of 103-115 ±1K and 91-103 ±1K respectively for samples with added Co$_3$O$_4$ (10-30 nm and 30-50 nm).

**Keywords**—Bi(Pb)-Sr-Ca-Cu-O superconductor, coprecipitation, nano Co$_3$O$_4$, transition temperature $T_c$.

I. INTRODUCTION

Bi-Sr-Ca-Cu-O-based high temperature superconductors, either in bulk form such as wires and tapes or as components of more complex composites, have shown some potentials for commercialization. There have been many studies to improve the superconducting properties, in particular the critical current density ($J_c$). Many research groups have investigated the effects of adding different elements or nano-particles in order to improve $J_c$ and $T_c$ [1]-[10]. These studies helped in the understanding of the mechanism of superconductivity in high $T_c$ cuprates. The investigation of the influence of nano particles on superconductors is very important from the viewpoint of practical application. In this work, Co$_3$O$_4$ nano-particles was added to Bi(Pb)-Sr-Ca-Cu-O as magnetic impurities in the superconductor system. In this work, the structure, phase formation and electrical properties of Bi(Pb)-Sr-Ca-Cu-O with nano Co$_3$O$_4$ addition were investigated. The samples were characterized by SEM, XRD and electrical resistance measurement.

II. EXPERIMENTAL DETAILS

Samples of Bi$_{1-x}$Pb$_x$Sr$_2$Ca$_2$Cu$_3$O$_{y_0}$(Co$_3$O$_4$)$_x$ with 0.01 wt%, 0.02wt%, 0.03wt%, 0.04wt% and 0.05 wt% were prepared by the acetate coprecipitation method. Two sets of precursor powder were prepared; one set was added with nano Co$_3$O$_4$ (10-30 nm size) and the other set was added with nano Co$_3$O$_4$ (30-50 nm size). The non-added sample was used as a reference. The mixture were thoroughly mixed and ground and calcined at 845°C, with the heating rate of 2°C/min and cooling rate of 2°C/min for 24 h. Then, the samples were reground and pressed into pellets and heated at 850°C in an air for 48 h. Morphological and structural analyses of the samples were performed by an SEM and X-ray diffractometer, respectively. The transport properties were measured by the standard four point probe method.

III. RESULTS AND DISCUSSION

Fig. 1(a) and (b) present the electrical resistance versus temperature in zero magnetic field of the superconducting samples with pure Bi(Pb)-Sr-Ca-Cu-O and nano Co$_3$O$_4$ addition with different sizes (10-30 nm and 30-50 nm) at $x=0.01$wt%, 0.02wt%, 0.03wt%, 0.04wt% and 0.05wt%. The dc electrical resistivity measurements show a well defined metallic behavior and superconducting transitions for all the compositions. All the samples show the zero electrical resistivity $T_c(R=0)$ within the range 70-103 ±1K, while onset temperatures $T_{c(onset)}$ are 83-115 ±1K (Table I). The highest superconducting transition temperature, $T_c$ is shown by the sample with nano Co$_3$O$_4$ (10-30 nm size) addition at $x=0.01$wt%, with $T_c$~102 K and the normal-state resistivity lower than the pure sample. The high $T_c$ for the $x=0.01$ wt% sample may be due to homogeneity in the sample. Excessive Co$_3$O$_4$ degraded the superconductivity of Bi2223, which can affect the transport properties in this type of material [1].

A. N. Jannah is with the Faculty of Applied Sciences, University Technology MARA, 72000, Kuala Pilah, Negeri Sembilan, Malaysia (e-mail: nurjannah@ns.uitm.edu.my).

R. Abd-Shukor is with School of Applied Physics, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia (e-mail: ras@ukm.my).

H. Abdullah is with the Department of Electrical, Electronic and Systems Engineering, Faculty of Engineering and the Built Environment, University Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia (e-mail: huda@vlsi.eng.ukm.my).
The lower zero resistance transition temperature with increasing Co3O4 content could be interpreted as a result of the suppression of superconductivity by the Co3O4. It was observed that Co3O4 added samples showed a broader transition, which indicates weak links between superconducting grains and lower percentage of Bi2223 phase transition, which indicates weak links between grains. Therefore, the increase in \( T_c \) with the addition of nano Co3O4 addition in the sample is associated with the enhancement in 2223 phase formation and the improved links between grains.

Several peaks were shifted toward either higher or lower value of 2\( \theta \) angle as the concentration of Co3O4 increased. Some of the added samples have peaks belonging to the 2201 phase. However the crystallographic structure remains in the tetragonal form.

Tables I and II show the \( T_{onset}, T_{zero} \), and volume fraction for non-added Bi(Pb)-Sr-Ca-Cu-O and nano Co3O4 addition at \( x=0.01 \text{wt\%} \) and 0.05wt\%. From the table, sample with nano Co3O4 addition that exhibited the highest \( T_c \) showed a slight decrease of the Bi 2212 phases and an enhancement of the 2223 phase volume fraction. It can be seen from Table I that the Bi-(2223) phase in sample with \( x=0.01 \text{wt\%} \) addition of Co3O4 (10-30 nm size) has the highest percentage of Bi-2223 phase and reaches maximum value of 72%. With further increase in Co3O4 the percentage of the 2223 phase decreased and the percentage of 2212 phase increased. A decrease of 2223 phase volume fraction with an increase of 2212 phase was clearly seen for both Co3O4, addition (10-30 nm and 30-50 nm sizes). This indicates that a small amount of nano Co3O4 addition plays a certain role in the phase formation of the BSCCO system and may enhance the critical temperature and the phase formation of 2223 phase. The size of the nano Co3O4 also played a significant role in decreasing the \( T_c \) in addition to the effect of secondary phase particles.

The SEM micrographs of the cross sectional view of the samples for Bi(Pb)-Sr-Ca-Cu-O and Co3O4 added samples are shown in Fig 3. Superconducting grains are seen to be connected with each other strongly and the surface morphology of the sample comprises of platelets and layered grains with uniform and homogenous microstructure. The platelet-type features are also found in nano Co3O4 added samples but the size of the grains was larger than the pure one. For sample with \( x=0.01 \text{wt\%} \), a compact platelets were observed and this may be able to establish connectivity between grains. Therefore, for nano addition of Co3O4 the appropriate amount of magnetic impurities can be the appropriate amount of magnetic impurities and Co3O4 can be the appropriate amount of magnetic impurities and Co3O4 added samples. In this work, all the peaks of Bi-2223, Bi-(2212) and Bi-(2201) phases have been used for the estimation of the volume fraction of the phases. The volume fraction of the Bi-(2223) phase relative to the Bi-(2212) phase and Bi-(2201) phase could be estimated from the intensities according to

\[
\text{Bi}(2223) = \frac{\sum I(2223)}{\sum I(2223) + \sum I(2212) + \sum I(2201)} \times 100
\]

\[
\text{Bi}(2212) = \frac{\sum I(2212)}{\sum I(2223) + \sum I(2212) + \sum I(2201)} \times 100
\]

\[
\text{Bi}(2201) = \frac{\sum I(2201)}{\sum I(2223) + \sum I(2212) + \sum I(2201)} \times 100
\]

where I is the intensity of the number of peaks corresponding to the respective phase present.
LATTICE AND RESISTIVITY MEASUREMENTS OF SAMPLES ADDED WITH CO3O4

The results of XRD and lattice and resistivity measurements of samples added with CO3O4 can improve the superconducting properties of the samples. The sample with 0.01 wt% CO3O4 (10-30 nm size) addition had the highest Tc of 102 K as against 100 K for the non-added samples. The same sample also exhibited the highest volume fraction of the 2223 phase. As the amount of Co content increased the amount of secondary phases also increased which obstructed the flow of supercurrent in the system. The size of the nano CO3O4 also played a significant role in decreasing the Tc in addition to the affected of secondary phase. Even though magnetic impurities suppress superconductivity, these results showed that an appropriate amount of nano CO3O4 can improve the superconducting properties of the Bi-based samples, while excessive CO3O4 addition led to the degradation of the superconductivity of Bi2223.

IV. CONCLUSION

In conclusion, nano CO3O4 addition to Bi(Pb)-Sr-Ca-Cu-O can improve the superconducting properties of the samples. The sample with 0.01 wt% CO3O4 (10-30 nm size) addition had the highest Tc of 102 K as against 100 K for the non-added samples. The same sample also exhibited the highest volume fraction of the 2223 phase. As the amount of Co content increased the amount of secondary phases also increased which obstructed the flow of supercurrent in the system. The size of the nano CO3O4 also played a significant role in decreasing the Tc in addition to the affected of secondary phase. Even though magnetic impurities suppress superconductivity, these results showed that an appropriate amount of nano CO3O4 can improve the superconducting properties of the Bi-based samples, while excessive CO3O4 addition led to the degradation of the superconductivity of Bi2223.

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