Effects of nanosized Bi$_2$O$_3$ addition on the superconducting properties of Bi$_{1.6}$Pb$_{0.4}$Sr$_2$Ca$_2$Cu$_3$O$_{10}$

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Received: 2 July 2019 / Accepted: 29 August 2019 / Published: 29 October 2019

The effects of nanosized Bi$_2$O$_3$ (150 nm) addition on Bi$_{1.6}$Pb$_{0.4}$Sr$_2$Ca$_2$Cu$_3$O$_{10}$ ((Bi,Pb)-2223) superconductor have been investigated. Samples with nominal starting composition (Bi,Pb)-2223(Bi$_2$O$_3$)$_x$, with $x = 0$–0.15 wt.% were prepared using the co-precipitation method. The structure and microstructure were examined by using powder X-ray diffraction (XRD) method and scanning electron microscopy (SEM), respectively. The onset-temperature ($T_{c\text{-onset}}$), zero-resistance-temperature ($T_{c\text{-zero}}$), and transport critical current density ($J_c$) were determined by using the four-probe technique. The XRD patterns confirmed the presence of Bi,Pb-2223 phase. $J_c$ of all Bi$_2$O$_3$ added samples were higher than the non-added sample. The highest $J_c$, $T_{c\text{-zero}}$ and hole concentration ($p$) was observed in the $x = 0.01$ sample. At 77 K, $J_c$ of $x = 0.01$ wt. % was about 42 times higher than the non-added sample. This could be due to the enhanced flux pinning as the size of Bi$_2$O$_3$ was between the coherence length and penetration depth of (Bi,Pb)-2223.

**Keywords**: nanosized Bi$_2$O$_3$; flux pinning centers; transport critical current density

1. INTRODUCTION

The Bi$_{1.6}$Pb$_{0.4}$Sr$_2$Ca$_2$Cu$_3$O$_{10}$ ((Bi,Pb)-2223) high-$T_c$ superconductor is one of the most promising materials for applications as tapes or wires. However, the transport critical current density ($J_c$) is strongly suppressed by weak links and weak pinning of magnetic flux lines [1-3]. The coherence length ($\xi$), penetration depth ($\lambda$) and magnetic flux size in a superconductor is in the nanometer range. The weak pinning of magnetic flux lines decreases $J_c$ with increasing temperature and magnetic field, due to the motion of the vortices.

The penetration depth, $\lambda$ of (Bi,Pb)-2223 superconductor is about 1000 nm and the coherence length $\xi$ is 2.9 nm. It is expected that the interaction between the pinning center (e.g. nanoparticles) and magnetic flux lines will be strong for a particle with size $d$ where $\xi < d < \lambda$ [4]. The introduction of
nanosized particles as defects into (Bi,Pb)-2223 can be an effective method to improve flux pinning without destroying the superconductivity and thus enhance \( J_c \) [e.g. 5,6]. The size and type of nanoparticles as the magnetic flux pinning center in YBa\(_2\)Cu\(_3\)O\(_7\) and (Bi,Pb)-2223 are important parameters [7-13]. In a previous study, we have investigated the effect of nanosized PbO (10 – 30 nm) on \( J_c \) of Bi\(_{1.6}\)Pb\(_{0.4}\)Sr\(_2\)Ca\(_2\)Cu\(_3\)O\(_{10}\) tapes [5].

Bismuth oxide has been useful in enhancing the superconducting properties of the cuprates such as the bismuth- and thallium-based high temperature superconductors. When Bi\(_2\)O\(_3\) (50-80 nm) was added to (Bi,Pb)-2223, the samples with composition (Bi,Pb)-2223(Bi\(_2\)O\(_3\))\(_{0.06}\) showed the highest \( J_c \) [14]. It would be interesting to investigate the effects of Bi\(_2\)O\(_3\) with other size on the (Bi,Pb)-2223 phase. In this work, Bi\(_2\)O\(_3\) with size 150 nm was added into (Bi,Pb)-2223. This size was chosen because it is between \( \xi \) and \( \lambda \). The onset temperature \( T_c-\)onset, zero resistance temperature \( T_c-\)zero and \( J_c \) of (Bi,Pb)-2223(Bi\(_2\)O\(_3\))\(_x\) for \( x = 0 \) to 0.15 wt. % were measured. The structural and microstructural properties of (Bi, Pb)-2223 were also investigated.

2. EXPERIMENTAL DETAILS

The pellets were prepared from high purity powders (> 99%) of Bi(CH\(_3\)CO\(_2\))\(_3\), Pb(CH\(_3\)CO\(_2\)).3H\(_2\)O, Sr(CH\(_3\)CO\(_2\)).1/2H\(_2\)O, Ca(CH\(_3\)CO\(_2\)).H\(_2\)O, and Cu(CH\(_3\)CO\(_2\)).H\(_2\)O with nominal starting composition Bi\(_{1.6}\)Pb\(_{0.4}\)Sr\(_2\)Ca\(_2\)Cu\(_3\)O\(_{10}\). The powders were prepared by the acetate co-precipitation technique, where the filtered precipitate was calcined in a tube furnace for 12 h at 730 °C to remove the volatile materials. An additional calcination was performed for 24 h at 845 °C to start the formation of (Bi,Pb)-2223 superconducting phase. The size of the precursor powder was a few micrometers. Bi\(_2\)O\(_3\) with size 150 nm (US-nano, 99+% purity) was added into (Bi,Pb)-2223 with different concentrations (\( x = 0, 0.01, 0.05, 0.01 \) and 0.15 wt.%). The mixed powders were ground and then pressed into pellets of ~ 12 mm diameter and ~ 2 mm thickness and sintered for 48 h at 845 °C. The heating and cooling rate was 2 °C/min.

The phase and structure of the samples were examined by a D8 Advance X-ray diffractometer (XRD) from Bruker AXS with a CuK\(_\alpha\) source (\( \lambda = 0.15406 \) nm). The volume fraction of Bi-2223 (high-\( T_c \) phase) and Bi-2212 (low-\( T_c \) phase) was estimated from the total intensities of these phases using the following equations [15,16]:

\[
\text{Bi-2223 \%} = \frac{\sum I_{2223}}{\sum I_{2223} + \sum I_{2212}} \times 100% \\
\text{Bi-2212 \%} = \frac{\sum I_{2212}}{\sum I_{2223} + \sum I_{2212}} \times 100% 
\]

The microstructure of the samples was recorded using a Zeis VPSEM (Leo 1450). The size of Bi\(_2\)O\(_3\) was determined by transmission electron microscope (HRTEM, JEOL JEM-2100F). The four-probe technique was used to determine \( T_c-\)onset and \( T_c-\)zero of the pellets. The effect of nanosized Bi\(_2\)O\(_3\)
on $J_c$ was determined by using four-probe technique from 30 to 77 K in self-fields. The 1-$\mu$V/cm criterion was used to determine $J_c$.

3. RESULTS AND DISCUSSION

![XRD patterns](image)

**Figure 1.** XRD patterns of (Bi,Pb)-2223(Bi$_2$O$_3$)$_x$ for $x = 0, 0.01, 0.05, 0.10, \text{ and } 0.15$ wt. %. ($H$) indicates the high-$T_c$ phase and ($L$) indicates the low-$T_c$ phase
Figure 2. SEM micrographs of (Bi,Pb)-2223(Bi$_2$O$_3$)$_x$; (a) $x = 0$ wt. %, (b) $x = 0.01$ wt. %, (c) $x = 0.05$ wt. %, (d) $x = 0.10$ wt. %, and (e) $x = 0.15$ wt. %

Figure 1 shows the XRD patterns of (Bi,Pb)-2223(Bi$_2$O$_3$)$_x$ for $x = 0$, 0.01, 0.05, 0.01, and 0.15 wt.%. The XRD patterns showed that a small amount of nanosized Bi$_2$O$_3$ did not hinder the formation of (Bi, Pb)-2223 phase. Most of the peaks corresponded mainly to the Bi-2223 (high-$T_c$ phase). Minor peaks due to the Bi-2212 (low-$T_c$) phase was also present in the samples. In addition, a small peak signifying the Ca$_2$PbO$_4$ phase was observed at $2\theta \approx 17.6^\circ$ in all samples. The lattice parameters $a$, $b$, and $c$ of the non-added sample are 5.415, 5.407, and 37.12 Å, respectively. The lattice parameters in Bi$_2$O$_3$ added samples were almost the same as those of the non-added sample. It is therefore likely that a small amount of nanosized Bi$_2$O$_3$ did not affect the (Bi,Pb)-2223 crystal structure. SEM micrographs for (Bi, Pb)-2223(Bi$_2$O$_3$)$_x$, ($x = 0$, 0.01, 0.05, 0.01, and 0.15 wt.%) are shown in Figures 2(a-e). SEM of all the samples showed plate-like grain structure of the high-$T_c$ phase (Bi-2223).
The temperature dependence of electrical resistance for all samples exhibited metallic normal state behavior (Figure 3). $T_{c\text{-onset}}$ and $T_{c\text{-zero}}$ for the non-added sample is 110 K and 98 K, respectively. The sample with $x = 0.01$ wt. % showed the highest $T_{c\text{-zero}}$ (99 K) among the samples and the same $T_{c\text{-onset}}$ compared with non-added sample (Table 1). It is probable that very small addition of nanosized Bi$_2$O$_3$ ($x = 0.01$ wt. %) slightly improved the intergranular links[17].

![Figure 3. Temperature dependence of electrical resistance of (Bi, Pb)-2223(Bi$_2$O$_3$)$_x$ for $x = 0$, 0.01, 0.05, 0.10, and 0.15 wt. %](image)

Table 1. Lattice parameters, volume fraction, $T_{c\text{-onset}}$, $T_{c\text{-zero}}$ $J_c$, (at 30 and 77 K) and hole concentration ($p$) of (Bi,Pb)-2223(Bi$_2$O$_3$)$_x$ for $x = 0$ - 0.15 wt. %

<table>
<thead>
<tr>
<th>$x$</th>
<th>$a$ /Å</th>
<th>$b$ /Å</th>
<th>$c$ /Å</th>
<th>BiPb-2223 / %</th>
<th>BiPb-2212 / %</th>
<th>$T_{c\text{-onset}}$ / K</th>
<th>$T_{c\text{-zero}}$ / K</th>
<th>$p$ hole conc. /mA cm$^{-2}$</th>
<th>$J_c$ (30 K) /mA cm$^{-2}$</th>
<th>$J_c$ (77 K) /mA cm$^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>5.415</td>
<td>5.407</td>
<td>37.12</td>
<td>74</td>
<td>26</td>
<td>110</td>
<td>98</td>
<td>0.15934</td>
<td>344±10</td>
<td>59±2</td>
</tr>
<tr>
<td>0.01</td>
<td>5.403</td>
<td>5.417</td>
<td>37.11</td>
<td>72</td>
<td>28</td>
<td>110</td>
<td>99</td>
<td>0.15939</td>
<td>4620±90</td>
<td>2500±50</td>
</tr>
<tr>
<td>0.05</td>
<td>5.416</td>
<td>5.409</td>
<td>37.11</td>
<td>71</td>
<td>29</td>
<td>109</td>
<td>98</td>
<td>0.15934</td>
<td>2310±70</td>
<td>1640±50</td>
</tr>
<tr>
<td>0.10</td>
<td>5.414</td>
<td>5.409</td>
<td>37.12</td>
<td>74</td>
<td>26</td>
<td>108</td>
<td>97</td>
<td>0.15928</td>
<td>2250±40</td>
<td>1020±20</td>
</tr>
<tr>
<td>0.15</td>
<td>5.413</td>
<td>5.411</td>
<td>37.10</td>
<td>71</td>
<td>29</td>
<td>108</td>
<td>97</td>
<td>0.15928</td>
<td>1840±60</td>
<td>690±20</td>
</tr>
</tbody>
</table>
The charge carriers, $p$ (hole concentration) in the samples can be calculated according to the following equation [16, 18]:

$$p = 0.16 \left( \frac{1}{82.6} \frac{T_c}{T_c^{\text{max}}} \right)^{1/2}$$

where $T_c^{\text{max}}$ for (Bi, Pb)-2223 superconductor was taken at 110 K.

The $\text{Bi}_2\text{O}_3$ content dependence of hole concentration, $p$, $T_{\text{c-onset}}$ and $T_{\text{c-zero}}$ are shown in Figure 4. The hole concentration, $p$ for $x = 0.01$ wt. % sample showed the highest value. The $x = 0.05$ wt. % sample showed similar hole concentration, $p$ compared to the non-added sample. The hole concentration, $T_{\text{c-onset}}$ and $T_{\text{c-zero}}$ for $x > 0.05$ wt. % samples were slightly lower than those of the non-added sample. It is clear that $T_{\text{c-onset}}$ and $T_{\text{c-zero}}$ with $x > 0.05$ wt. % decreased slightly due to the decrease of the hole concentration, $p$.

![Figure 4](image-url). Nanosized $\text{Bi}_2\text{O}_3$ content dependence of hole concentration ($p$), $T_{\text{c-onset}}$ and $T_{\text{c-zero}}$ for $x = 0$, 0.01, 0.05, 0.10, and 0.15 wt. %
Figure 5. $J_c$ of (Bi,Pb)$_x$-2223(Bi$_2$O$_3$)$_{1-x}$ as a function of temperature for $x = 0$, 0.01, 0.05, 0.10, and 0.15 wt. %

Figure 6. $J_c$ of (Bi,Pb)$_x$-2223(Bi$_2$O$_3$)$_{1-x}$ as a function of different adding concentrations for $x = 0$, 0.01, 0.05, 0.10, and 0.15 wt. %
$J_c$ for all samples as a function of temperature is shown in Figure 5. In general, $J_c$ decreased with the increased of temperature from 30 to 77 K due to the thermally activated flux creep. All of the Bi$_2$O$_3$ added samples showed much higher $J_c$ compared with the non-added sample. For the non-added sample, $J_c$ at 30 and 77 K was 344 mA/cm$^2$ and 59 mA/cm$^2$, respectively. The $x = 0.01$ wt. % sample showed the highest $J_c$, which was 4615 mA/cm$^2$ and 2500 mA/cm$^2$ at 30 and 77 K, respectively. The improved $J_c$ may be due to the enhancement of flux pinning strength as a result of nanosized Bi$_2$O$_3$ at the grain boundaries.

$J_c$ showed a sudden decrease when the amount of Bi$_2$O$_3$ was increased to more than $x = 0.01$ wt. % (Figure 6). The lattice parameters, hole concentration, $p$, $T_{c\text{-onset}}$, $T_{c\text{-zero}}$, and $J_c$ at 30 and 77 K of the samples are summarized in Table 1. It is interesting to note that nano PbO addition also increased $J_c$ of the BiPb-2223 superconductor [5]. Hence, although these two elements are already in the parent compound, addition of nanosized Bi$_2$O$_3$ and PbO led to the enhancement of $J_c$ without suppressing the transition temperature. The enhancement of $J_c$ is possibly due to enhanced grain connectivity as a result of nanosized Bi$_2$O$_3$ at the grain boundaries. Smaller Bi$_2$O$_3$ (50-80 nm) addition showed $x = 0.06$ wt. % as the highest $J_c$ value [14]. In this work, 150 nm Bi$_2$O$_3$ was used and a smaller amount ($x = 0.01$ wt. %) was sufficient to optimize $J_c$.

In conclusion, the effects of nanosized Bi$_2$O$_3$ addition on the superconducting properties of bulk Bi$_{1.6}$Pb$_{0.4}$Sr$_2$Ca$_2$Cu$_3$O$_{10}$ (Bi$_2$O$_3$)$_x$ samples were investigated. The optimal amount which showed the highest $J_c$, $T_{c\text{-zero}}$, and hole concentration, $p$ was $x = 0.01$ wt. %. $J_c$ of $x = 0.01$ wt. % was about 13 and 42 times larger than the non-added sample at 30 and 77 K, respectively. The enhancement of $J_c$ may be due to the fact that the particles size of Bi$_2$O$_3$ is larger than $\xi$ and smaller than $\lambda$ of (Bi, Pb)-2223, which can increase the flux pinning ability in the samples.

ACKNOWLEDGMENTS
This research was supported by the Ministry of Education, Malaysia under grant no. FRGS/1/2017/SG02/UKM and Thamar University, Thamar, Yemen.

References