Enhancements of Critical Current Density in the Bi–Pb–Sr–Ca–Cu–O Superconductor by Na Substitution

Duc H. Tran1,*, Tien M. Le1,3, Thu H. Do1, Quynh T. Dinh1, Nhan T. T. Duong1, Do T. K. Anh1, Nguyen K. Man2, Duong Pham3 and Won-Nam Kang3

1Faculty of Physics, VNU University of Science, Hanoi, Vietnam
2International Training Institute for Materials Science (ITIMS), Hanoi University of Science and Technology, Hanoi, Vietnam
3Department of Physics, Sungkyunkwan University, Suwon, Korea

In this paper, we investigated the influences of Na substitution on the enhancements of critical current density (Jc) in the Bi–Pb–Sr–Ca–Cu–O (BPSCCO) superconductors. The Bi1_xPb0.4Sr2Ca2−xNaxCu3O10+δ (where x was ranged from 0 to 0.1) polycrystalline samples were fabricated using solid state reaction technique. The zero electrical critical temperature (Tc) of Na-substituted BPSCCO samples was found to be slightly higher than that of Na-free BPSCCO one. Magnetization Jc data measured at 65 K with field applied parallel to the c-axis of the samples showed that Jc of Na-substituted BPSCCO samples were enhanced. Possible reasons for the Jc enhancements were attributed to the effective flux pinning by crystal defects at Ca layers generated by Na substitution. Improvements of volume pinning force (Fp) in terms of magnitude and position of Fp_max were also obtained. [DOI: 10.2320/matertrans.MD201715]

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1. Introduction

Many efforts have been devoted to study electrical and magnetic properties of the Bi–Sr–Ca–Cu–O (BSCCO) superconductor since it was discovered in 1988.1) It was reported with three phases in BSCCO system expressed as Bi2Sr2CaCu2−xNaxOy (where x was ranged from 0 to 0.1) polycrystalline samples were fabricated by using solid state reaction technique. The zero electrical critical temperature (Tc) of Na-substituted BPSCCO samples was found to be slightly higher than that of Na-free BPSCCO one. Magnetization Jc data measured at 65 K with field applied parallel to the c-axis of the samples showed that Jc of Na-substituted BPSCCO samples were enhanced. Possible reasons for the Jc enhancements were attributed to the effective flux pinning by crystal defects at Ca layers generated by Na substitution. Improvements of volume pinning force (Fp) in terms of magnitude and position of Fp_max were also obtained. [DOI: 10.2320/matertrans.MD201715]

Numerous researches on the Jc enhancement of the BSCCO have been carried out. In addition to accelerating the formation of the Bi-2223 phase, the partial substitution of Pb into Bi site was also observed to improve Jc. Similar results were obtained for the BPSCCO in which alkaline metals and rare-earth elements were substituted.9,11,14,15) In this paper, the enhancements of Jc in Na-substituted Bi1,08Pb0.4Sr2Ca2−xNaxCu3O10+δ superconductor is reported.

2. Experiment

The Bi1.08Pb0.4Sr2Ca2−xNaxCu3O10+δ polycrystalline samples (with x = 0; 0.01; 0.02; 0.04; 0.06; 0.08 and 0.1) were prepared though the conventional solid state reaction technique by using high purity (99.99%) powders of Bi2O3, PbO, SrCO3, CaCO3, CuO and Na2CO3. The mixtures were composed at calculated ratio, mixed and grounded with series of test assertion, before being pressed into pellets and subjected to a four step calcination process in air at 670°C/ 48 hours + 750°C/48 hours + 800°C/48 hours + 820°C/48 hours with intermediate grinding and pressing. The calcined powders were re-pelletized and sintered at 850°C for 160 hours in air. The samples were then freely cooled to the room temperature. According to the Na content (x), the samples were labeled as Na000; Na002; Na004; Na006; Na008; Na010.

The phase formation and the surface morphology of the samples were investigated by using the X-ray powder diffraction method (XRD) (SIEMENS D5005) and scanning electron microscopy (SEM) (JEOL JSM-7600F) measurements. To determine Tc, the temperature dependence of the resistance measured using magnetic property measurement system (Quantum Design MPMS XL-5) with the field applied to the c-axis of samples.
3. Results and Discussions

The structural properties of the samples such as crystallinity, phase purity, crystallite size as well as lattice parameters might be deduced from XRD results. The XRD patterns of the fabricated samples are presented in Fig. 1. It would be noticed that all Na-free and Na-substituted samples consisting of two main superconducting phases: high $T_c$ (Bi-2223) and low $T_c$ (Bi-2212) phases (marked by H and L, respectively). The diffraction intensities of H(00l) plane were relatively stronger than those of other planes, which suggested the $c$-axis oriented growth of Bi-2223 grains. The only secondary phase observed in all samples was identified to be Ca$_2$PbO$_4$ (marked by “+”). The appearance of Ca$_2$PbO$_4$ phase resulted from partial substitutions of Pb into BSCCO accelerated the reaction kinetics and enhanced the formation of the Bi-2223 phase by lowering its sintering temperature. Therefore, the sintering temperature applied for all samples in this report was maintained at 850°C. Interestingly, the peaks of Na-contained phase were absent, which might indicate completed incorporation of sodium in unit cell of BPSCCO samples. The volume fractions of the Bi-2223 ($\%$Bi-2223) and Bi-2212 ($\%$Bi-2212) phases were estimated by following relation:

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

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

where $I_{2223}$ and $I_{2212}$ were the intensity of the XRD peaks corresponding to Bi-2223 and Bi-2212 phases, respectively. The estimated values are given in Table 1. It would be seen that volume fraction of Bi-2223 increased from 72.08% (sample Na000) to 75.86% (sample Na004), then continuously increased to 72.45% (sample Na010). Inversely, volume fraction of Bi-2212 phase decreased from 27.19% (sample Na000) to 24.14% (sample Na004), then continuously increased to 29.35% (sample Na010). Results clearly showed that Na substitutions enhanced the formation of Bi-2223 phase up to $x = 0.04$. The decreases in $\%$Bi-2223 at $x > 0.04$ were possibly attributed to the decomposition phenomenon, in which Bi-2223 was decomposed to Bi-2212. By increasing $x$ (from Na006 sample), the melting temperature of the BPSCCO compounds might reduce, which led to lower temperature required to form Bi-2223 phase. Since sintering temperature of 850°C was kept for our experiments, the decomposition from Bi-2223 to Bi-2212 due to the thermodynamical instability at high temperatures occurred, as previously reported by Chen et al. In order to understand the crystal symmetry of these samples, the lattice parameters were deduced from the XRD results using the orthorhombic symmetry for Bi-2223. Variations of lattice parameters of samples are also given in Table 1.

Values of $a$ and $b$ parameters were found to stay almost the same, while $c$ parameter was found to slightly decrease as Na was partially substituted into Ca site. This could possibly stem from the difference in ionic radii of the elements: the radius of Na$^{+}$ ions (0.97 Å) was smaller than that of Ca$^{2+}$ ions (0.99 Å). The similarity in the lattice parameters might suggest that Na substitutions did not cause a remarkable change in the crystal symmetry of the samples.

The surface morphology of samples were investigated using surface SEM images provided in Fig. 2. It was observed that all samples showed the common features of the plate-like and needle-like grains implying the formations of Bi-2223 and Bi-2212 phases, respectively. The Bi-2223 grains tended to align parallel to the $c$-axis of the samples, those were compared to be in agreement with the H(00l) peaks in the XRD diagrams. The grains, however, were not completely connected, some void formations were observed between them. Moreover, the shape and size of the voids were irregular, explained by the fact that the samples were polycrystalline consisting of randomly oriented grains. The weak links at grain boundaries have been reported to limit the super-current flowing which narrowed the application range of BSCCO superconductor. As Na was partially substituted, the melting temperature of samples decreased. Therefore, the Bi-2223 grains were enlarged, leading to smoother surface with less void. The intergrain connectivity was improved and the effect of weak link at grain boundaries was reduced. For sample Na010, mis-orientation between large grains occurred, leaving some large voids. Besides, the sphere-like grains randomly distributed over the plate-like grains were identified to be Ca$_3$PbO$_4$. The observations were consistent with the appearance of the peaks of Ca$_3$PbO$_4$ in XRD results.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Volume fractions (%)</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>Hole concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na000</td>
<td>72.08</td>
<td>54.724</td>
<td>37.1041</td>
<td>0.131462</td>
<td></td>
</tr>
<tr>
<td>Na002</td>
<td>73.06</td>
<td>54.720</td>
<td>37.0982</td>
<td>0.134005</td>
<td></td>
</tr>
<tr>
<td>Na004</td>
<td>75.86</td>
<td>54.269</td>
<td>37.0912</td>
<td>0.138372</td>
<td></td>
</tr>
<tr>
<td>Na006</td>
<td>74.85</td>
<td>54.273</td>
<td>37.0852</td>
<td>0.136849</td>
<td></td>
</tr>
<tr>
<td>Na008</td>
<td>74.05</td>
<td>54.268</td>
<td>37.0772</td>
<td>0.135397</td>
<td></td>
</tr>
<tr>
<td>Na010</td>
<td>72.45</td>
<td>54.267</td>
<td>37.0712</td>
<td>0.133253</td>
<td></td>
</tr>
</tbody>
</table>

Table 1 Lattice parameters, variations of volume fractions and hole concentrations of Bi$_{1.6}$Pb$_{0.4}$Sr$_2$Ca$_{2-x}$Na$_x$Cu$_3$O$_{10+y}$ samples.
The temperature dependence of the resistance of samples were provided in Fig. 3. It would be seen that all samples showed the metallic behavior at normal state and followed by a superconducting transition to zero resistance at a temperature defined as $T_c$. The values of $T_c$ were found to vary with Na content and reached its maximum at sample Na004, as given in the inset of Fig. 3. Additionally, the normal state resistances of all samples were observed to change with Na content. The highest resistance obtained in sample Na010 was likely to be related to an increase in large voids in sample structure as previously examined by SEM images.

It has been well known that $T_c$ of cuprate superconductors is strongly depended on the hole concentration in the CuO planes. The hole concentration ($p$) was calculated using the empirical relation:\textsuperscript{10)

$$\frac{T_c}{T_c,\text{max}} = 1 - 82.6(p - 0.16)^2$$

in which $T_c,\text{max}$ was taken as 110 K for Bi-2223 superconductor.\textsuperscript{10) Theoretically, the value of $p$ for pure Bi-2223 phase is ranged from 0.116 to 0.160. The calculated results from our experiment data are also listed in Table 1.

The field dependence of $J_c$ for all samples were exhibited in Fig. 4. We deduced $J_c$ from hysteresis loops from modified Bean model $J_c = 20\Delta M/[b(1-b/3a)]$ in which $a$ and $b$ were length and width of the samples, respectively.\textsuperscript{20} $J_c$ of the sample Na000 was recorded to be $\sim 6.1 \times 10^4 \text{A/cm}^2$ at 0 T and started to decrease as field increased. Both self-field and in-field $J_c$ of Na substituted samples were observed to enhance. Similar enhancements of $J_c$ were also obtained in alkaline metal substituted BSCCO samples, however, at lower measurement temperatures of 10 K and 25 K.\textsuperscript{9,11,19} The enhancement of self-field $J_c$ in the Na-substituted samples were probably resulted from the improvement of sample microstructure as evidenced by SEM analyses. The enhancement of in-field $J_c$, however, were attributed to the flux pinning effect. As field and temperature increased, the 3D flux lines transformed to 2D pancake vortices those were mainly located at CuO$_2$ planes.\textsuperscript{13} The co-substitution of Pb into Bi site and Na into Ca site induced crystal defects at Bi.
layer and Ca layer, respectively. Since Ca was situated between two adjacent CuO2 layers, pinning by defects in Ca layers was stronger than by those in distant Bi layers. It resulted in the improved flux pinning properties of samples by substituting Na at the Ca site. As the Na substitution level (x) increased, more point-like defects might be created, leading to stronger Jc enhancements. Among Na-substituted samples, Jc reached the maximum value of \( \sim 8.2 \times 10^4 \text{A/cm}^2 \) at sample Na006. For sample Na008 and Na010, however, enhancements of Jc were slightly lowered due to degraded inter-grain connectivity and increased voids between grains.

To examine the flux pinning properties of samples, the pinning force density \( (F_p) \) was estimated using the relation \( F_p = Jc \times B \). Figure 5 provided the dependence of \( F_p \) on the reduced magnetic field \( b = B/B_{1rr} \). Sample Na000 showed the peak of \( F_p \) (\( F_{pmax} \)) \( \sim 2.7 \times 10^7 \text{N/m}^3 \) and its position was recorded at \( h \sim 0.2 \). As Na was partially substituted, two interesting features were emphasized. First, the absolute value of \( F_p \) was enhanced. Second, the position of \( F_{pmax} \) shifted to higher fields as revealed in the inset of Fig. 5. By using the above Jc enhancement analyses, it would be concluded that the sample Na006 revealed the strongest flux pinning effect, which was evidenced by the highest value of \( F_{pmax} \) of \( \sim 4.3 \times 10^7 \text{N/m}^3 \), and its position was observed at \( h \sim 0.23 \).

4. Conclusions

The enhancement of Jc in the Bi\(_{1.6}\)Pb\(_{0.4}\)Sr\(_2\)Ca\(_{2-x}\)Na\(_x\)Cu\(_3\)O\(_{10+\delta} \) (with x was ranged from 0 to 0.1) polycrystalline superconductors were investigated. It was observed that Na substitution accelerated the formation of high Tc (Bi-2223) phase as confirmed by the XRD and SEM analyses. The volume fraction of the Bi-2223 phase of 75.86%, which was likely to link to the highest enhancement of Tc, was obtained for a Na substitution of x = 0.04. The flux pinning properties of the Na-substituted samples were also found to improve, those were revealed by both the increases in Jc and pinning force density \( F_p \). The maximum enhancement of Jc was generated for a Na substitution of x = 0.06. The improved pinning properties of the Na-substituted samples were attributed to the addition of pinning centers in form of point-like defects as Na was partially substituted into Ca site.

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