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Enhancements of Critical Temperature in Bi-Pb-Sr-Ca-Cu-O Superconductors

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Abstract: In this work, the effects of sintering temperature and Na subtitution on zero critical temperature ($T_{c,0}$) in Bi-Pb-Sr-Ca-Cu-O superconductors were investigated. The $Bi_{1.6}Pb_{0.4}Sr_2Ca_{2-x}Na_xCu_3O_{10+\delta}$ bulk samples with x = 0.00 and 0.05 (BPSCCO) were prepared by using the solid state reaction technique at elevated sintering temperatures of 840 and 850^{o}C. To examine the improvements of structural and superconducting properties of the BPSCCO samples, the X-ray diffraction (XRD), scanning electronic microscope (SEM) and DC resistance versus temperature (R-T) measurements were carried out. The experimental findings exhibit a co-existence of the high T_c (Bi-2223) and low T_c (Bi-2212) phases in all samples. The estimated volume fraction of the Bi-2223 phase was increased from 71.4 to 75.7%, and the average size of the Bi-2223 grains was enlarged from 4.5 to 9.8 μm as changing the sample preparation conditions. The improved connectivities between the Bi-2223 grains were also obtained by quantitively analyzing the relation between $T_{c,0}$ and residual resistance ratio (RRR). These improvements were likely to be reasons for the enhancements of $T_{c,0}$ in the BPSCCO samples.

Keywords: BPSCCO, Bi-2223, Bi-2212, $T_{c,0}$, RRR.

1. Introduction

Since the discovery of high temperature superconductors, a lot of intensive studies have been made to enhance the superconducting properties of the system [1, 2]. There are a number of studies focusing on improvements of critical temperature (T_c) due to the large potential of this material for use in superconducting devices operated at liquid nitrogen temperatures. $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4+\delta}$ (BSCCO) is one of the most widely studied superconducting systems, with T_c varying between 20 K and 110 K and directly related to the three superconducting phases in the system [3, 4]. Those phases were found to

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be different basing on a number of the Cu-O_2 consecutively layers in its crystal structure, namely, Bi-2201 phase (n = 1 and T_c ~ 20 K), Bi-2212 phase (n = 2 and T_c ~ 80 K) and Bi-2223 phase (n = 3 and T_c ~ 110 K) [5, 6]. The Bi-2223 phase, hence, is really important for technological applications. However, it is practically difficult to obtain them in an isolated form due to due to the high complexity reaction and the numerous phase being available during Bi-2223 phase formation [7]. Besides varying the sintering temperature, many researches on substituting and doping effects have also been performed to enhance the formation and stability of Bi-2223 [7]. The partial substitution of Bi with Pb has been found to be the most effective way to stabilize the Bi-2223 phase [8, 9]. It was also reported that optimal concentration of Pb is 0.4 [10, 11]. Pb atoms acted as efficient nucleation and growth sites for the formation of the Bi-2223 phase and improve the diffusion of the Ca and Cu atoms [12]. Motivated by these studies, alkaline metals (Li, Na, K, Rb, Cs) could be potentially substituted elements as their ionic radii (73–181 pm) overlap those of Bi, Pb, Sr, Ca, and Cu [7]. Furthermore, alkaline metals have a^{+1} valence state; hence, their addition is attractive from the point of changing hole carrier concentrations [13]. To compare the effects of sintering temperature and substitution on the zero critical temperature ($T_{c,0}$) of the Bi-Pb-Sr-Ca-Cu-O compounds, structural and superconducting properties of $Bi_{1.6}Pb_{0.4}Sr_2Ca_{2-x}Na_xCu_3O_{10+\delta}$ bulk samples (with x = 0.00 and 0.05) sintered at different temperatures were investigated. The results showed that both increasing the sintering temperature and substituting Na enhanced $T_{c,0}$ of the BPSCCO samples, and the higher enhancement of $T_{c,0}$ was obtained by the latter technique.

2. Experiment

Two sets of the BPSCCO samples (two pure and one Na substituted) were fabricated in the stoichiometric ratios:

$Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_{10+\delta}$ (pure)

$Bi_{1.6}Pb_{0.4}Sr_2Ca_{1.95}Na_{0.05}Cu_3O_{10+\delta}$ (Na substituted)

The BPSCCO samples were prepared by using solid state reaction technique from purity chemicals Bi_2O_3, PbO, $SrCO_3$, $CaCO_3$ CuO, and $NaCO_3$ (Aldrich, > 99.9%). Stoichiometric amounts of the ingredients were weighed, completely mixed and ground. The final powders were then pressed into pellets and subjected to a four stage calcination process in air at elevated temperatures of 670, 750, 800, 820 ^oC (48 hours for each stage). Two sintering processes were applied for the pure BPSCCO samples in air at 840 and 850 ^oC for 168 hours; these samples were named as 840 (0.00) and 850 (0.00). To investigate the effect of substitution, the sintering process was applied for the pure and Na substituted samples in air at 840 ^oC for 168 hours; these samples were named as 840 (0.00) and 840 (0.05).

Microstructural examinations of the BPSCCO samples were performed by using the Xray diffraction (XRD) and scanning electron microscopy (SEM). Superconducting properties of the BPSCCO samples were characterized by using the four probe measurement.

3. Results and discussions

The XRD patterns of the fabricated samples demonstrating changes in the phase formation and intensity with different fabrication conditions were presented in Figure 1. All samples - Na-free BPSCCO sintered at 840 and 850^oC and Na-substituted BPSCCO sintered at 840^oC – show the peaks of both high-T_c (Bi-2223) (marked by H) and low-T_c (Bi-2212) (marked by L) phases. Traces of

Ca_2PbO_4 (marked by +) impurity phase is also found in all samples. The absence of Na-contained impurity might indicate that Na has completely entered into the BPSCCO structure. The volume fraction of each superconducting phase were calculated by using the equation [7]:

$$\%\mathrm{Bi}-2223=\frac{\sum \mathrm{I}_{2223}}{\sum \mathrm{I}_{2223}+\sum \mathrm{I}_{2212}}\times 100\% \tag{1}$$

$$\%\mathrm{Bi}-2212=\frac{\sum \mathrm{I}_{2212}}{\sum \mathrm{I}_{2223}+\sum \mathrm{I}_{2212}}\times 100\% \tag{2}$$

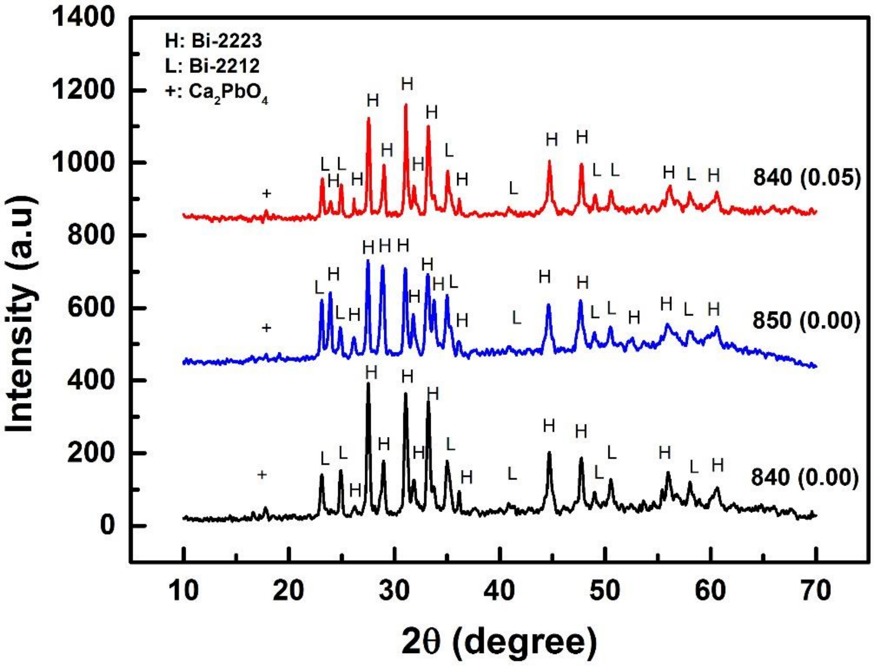

Figure 1. Xray diffraction patterns of the BPSCCO samples fabricated at different conditions. Formations of the Bi-2212 (L) and Bi-2223 (H) superconducting phases are clearly observed.

Table 1. The volume fraction of the superconducting phase and the average size or the Bi-2223 grains.

Samples	Volume fraction (~ %)		Average size (μm)
	Bi-2212	Bi-2223	
840 (0.00)	28.6	71.4	4.6
850 (0.00)	27.0	73.0	9.6
840 (0.05)	24.3	75.7	9.8

The calculated results were provided in Table 1. It would be clearly seen that the Bi-2212 phase fraction decreased from 28.6 % to 27.0 % and 24.3 %, and that of the Bi-2223 phase increased from

71.4 % to 73.0 % and 75.7 %. The increases in the Bi-2223 phase fraction as both increasing the sintering temperature from 840 to 850°C and substituting Na to Ca site might suggest that the two experiment techniques enhance the formation of the Bi-2223 phase. The average size of the Bi-2223 grains was deduced from the corresponding peak by using the Scherrer equation [14]: $t = 0.9\lambda/(\Delta\theta\cos\theta_B)$, where t is the size needed to be calculated, λ is the wavelength of the X-ray Cu-Kα radiation, and $\Delta\theta$ is the full width at half maximum of the Bi-2223 peak at the angle θ_B (half of the 2θ value shown in Figure. 1). The calculated results are listed in Table 1, those strongly support the positive effects of sintering temperature and substitution on microstructure of the BPSCCO samples [15].

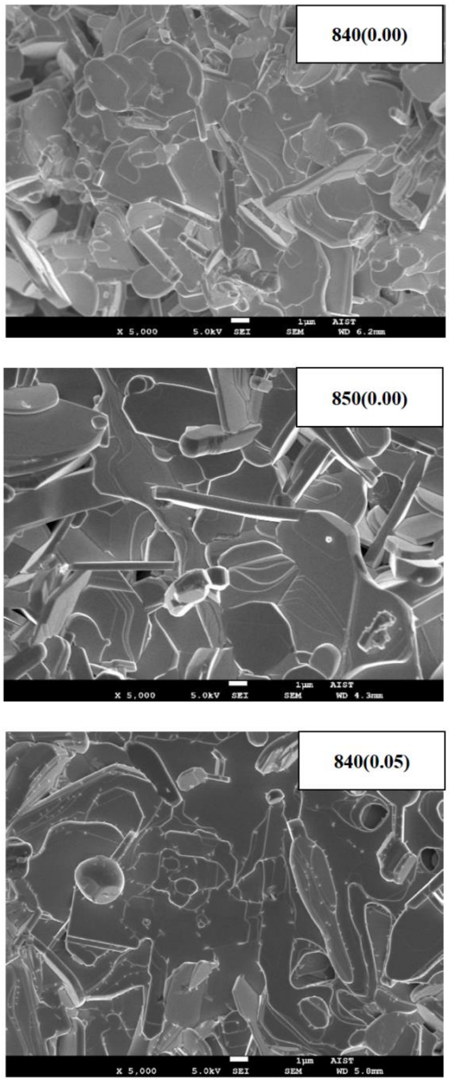

Figure 2. Surface SEM images of the BPSCCO samples. The Bi-2223 (plate-like) grains shows the enlarged size and improved connectivity as changing the fabrication conditions.

Another examination of the phase formation was performed by using the SEM analyses. Figure 2 displays the surface SEM images of the BPSCCO samples. It is obviously observed that there were the formations of plate-like and needle-like grains in all samples, those might imply the presence of the Bi-2223 and Bi-2212 phases, respectively [16]. While all samples show the randomly distributed plate-like morphology, the average size of the Bi-2223 grains were found to be increased from ~ 4.5 to ~9.5 and ~9.8 μm, which was comparable to the calculations obtained from the XRD analyses. It would be pointed out that larger sized grains generally induce less grain boundaries. As a results, the enhanced connectivities between these grains were obtained, which was evidenced by less porosity in the 850 (0.00) and 840 (0.05) BPSCCO samples. Additionally, the Ca_2PbO_4 impurity phase was detected in forms of the sphere-like grains discretely located in all BPSCCO samples [17].

Table 2. Detailed dc resistance results such as onset and zero resistance critical temperatures, transition width (ΔT_c), residual resistance ratio, and hole concentration belongs to the BPSCCO samples

Samples	$T_{c,onset}$ (K)	$T_{c,0}$ (K)	ΔT_c	RRR	Hole concentration, p
840 (0.00)	113.0	89.1	23.9	2.28	0.109
850 (0.00)	118.0	101.5	16.5	2.78	0.118
840 (0.05)	118.0	105.1	13.0	2.96	0.123

Figure 3 provides normalized resistance versus temperature of the BPSCCO samples. All of the BPSCCO samples exhibit a metallic behavior at high temperature region with a metal-superconductor transition as decreasing temperature. The metal – superconductor transitions were determined by $T_{c,onset}$ and $T_{c,0}$, those were associated with the transition of isolated grains and that of inter-granular component. Both $T_{c,onset}$ and $T_{c,0}$ were found to be increased from 113.0 K to 118.0 K and from 89.1 K to 105.1 K, respectively, as increasing the sintering temperature from 840 to 850°C and substituting Na to Ca site. The corresponding transition width ($\Delta T_c = T_{c,onset} - T_{c,0}$) was obtained to be decreased, which implied that higher sintering temperature and substitution effect induced small traces of low T_c phase, hence the dominant phase in the 850 (0.00) and 840 (0.05) samples is high T_c.

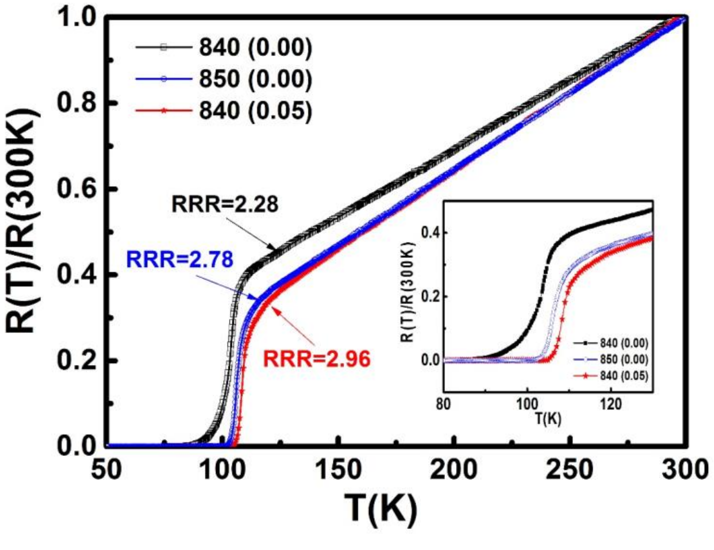

Figure 3. The temperature dependence of the normalized resistance of BPSCCO samples fabricated at different conditions. An enlarged view in a vicinity of the superconducting transition are is given in the inset.

The qualitative improvement in the grain connectivity was supported by the residual resistance ratio (RRR) defined as R(300 K)/R(120 K) [18]. The RRR values of the BPSCCO samples are also presented in Table 2. It was obtained that the RRR values were increased through increasing the sintering temperature from 840 to 850 ^{o}C as well as substituting Na to Ca site. The larger RRR is, the higher quality sample is. Particularly, a decrease in R(120 K) was believed to be due to a decrease in impurity or disorder scattering in the lattice [19]. As a result, an decrease in the lattice strain was induced, leading to the enhancements of $T_{c,0}$. To confirm that idea, a relation between the resistance and $T_{c,0}$ was exhibited in Figure 4. The dependence of $T_{c,0}$ on the RRR was found which was properly fitted by using a simple linear function [19-20].

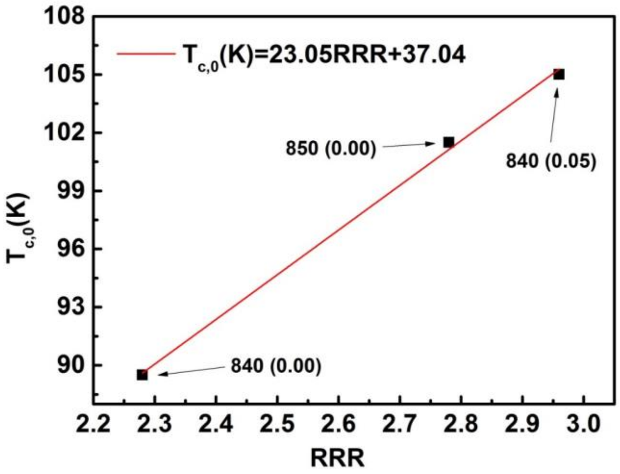

Figure 4. A correlation between the zero critical temperature ($T_{c,0}$) and the residual resistance ratio (RRR) of the BPSCCO samples.

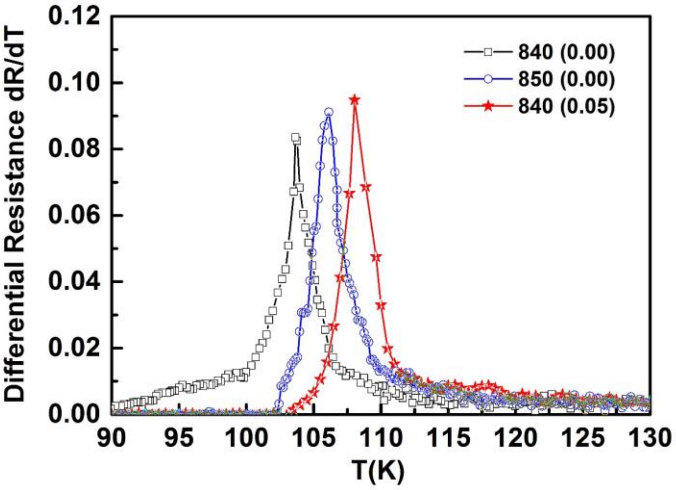

Figure 5. The first derivative of resistance dR/dT versus temperature of the BPSCCO samples. The dR/dT peaks are found to shift towards higher temperature as varying fabrication conditions.

The first derivatives resistance versus temperature of the BPSCCO samples were provided in Figure 5. The dominant Bi-2223 phase was thought to be a possible reason for the appearances of single dR/dT peaks with a width at half maximum decreased from 2.63 to 2.53 and 2.36. Moreover, the position of dR/dT peaks was observed to shift toward higher temperature from 103.7 K to 106.1 K and 108 K. The reduced width at half maximum and shifting were likely to be correlated to the increases in the volume fraction and average size of the Bi-2223 grains as examined by XRD and SEM analyses.

A relationship between the zero critical temperature ($T_{c,0}$) and the hole concentration p in the CuO_2 layers is presented in Figure 6. The value of p was calculated by using the equation [7, 14, 15, 16, 19]:

$$p = 0,16 - \left[\left(1 - \frac{T_{C0}}{T_{C,onset}} \right) / 82,6 \right]^{1/2} \qquad (3)$$

From literatures, the values of p for unsubstituted Bi-2223 were ranged from 0.116 to 0.160 [7, 21]. The calculated values of p in our BPSCCO samples were listed in Table 2, those were belong to the underdoped region. It would be said that $T_{c,0}$ was parabolically dependent on the hole concentration, which was compared to be in agreement with other reports [7, 22]. Hence, the larger hole concentrations in the CuO_2 layers were, the higher $T_{c,0}$ was.

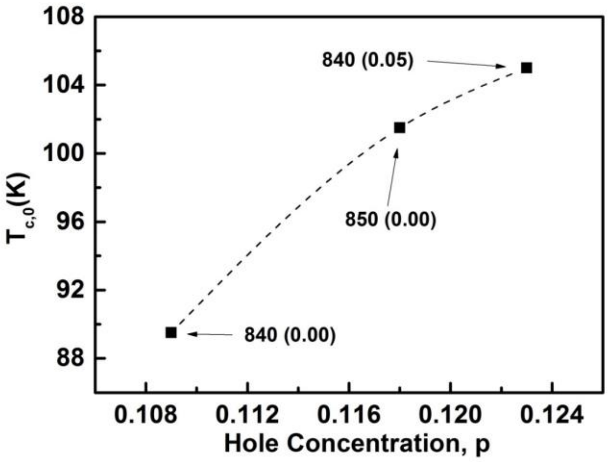

Figure 6. Hole carrier concentration in $Cu–O_2$ layers at different $T_{c,0}$ of the BPSCCO samples.

4. Conclusions

The effects of sintering temperature and substitution on structural and superconducting properties of the BPSCCO samples were investigated. By increasing sintering temperature from 840 to 850 ^{o}C and substituting Na to Ca site, $T_{c.0}$ of the BPSCCO sample were found to enhanced. The enhancements were attributed to the formations of the Bi-2223 phase. The volume fraction and grain size of the Bi-2223 estimated from XRD and SEM results were shown to be increased. The connectivities between the Bi-2223 grains were also improved as revealed by the temperature dependence of the RRR. In comparison, the Na-substitution was believed to be more beneficial to the enhancement of $T_{c,0}$ in BPSCCO.

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