Enhanced $T_c$ of Bi(Pb)2223 Sintered Bulks up to 115 K

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Abstract. Enhancement of $T_c$ was attempted for Bi(Pb)2223 sintered bulks by optimizations of starting cation composition and post-annealing conditions. $T_c$ was enhanced from 110.4 K to 111.4 K after post-annealing at ~700°C in 1%O$_2$. Additional high temperature annealing at ~830°C in air largely improved crystallinity of Bi(Pb)2223 and high $T_c$ up to 114.3 K was achieved. Increases in the c-axis length indicated that the enhancement of $T_c$ is possibly due to changes in cation composition towards the stoichiometric one. An as-synthesized Bi(Pb)2223 bulks starting from Sr-rich compositions showed slightly high $T_c$ of 110.8 K, suggesting suppression of partial substitution of Ca and/or Bi for the Sr-site. In addition, Bi-rich starting composition resulted in decreases of secondary phases without suppression of $T_c$. High temperature post annealing in air performed for these Sr-rich or Bi-rich bulks also improved $T_c$'s up to 114.4 and 114.8 K, respectively.

1. Introduction
The Bi-based cuprates, such as Bi$_2$Sr$_2$CaCu$_2$O$_y$ [Bi2212] and (Bi,Pb)$_2$Sr$_2$Ca$_2$Cu$_3$O$_y$ [Bi(Pb)2223], are most promising materials for practical use among numerous high-$T_c$ superconductors. Bi(Pb)2223 tapes of km-class length have been well developed for various applications, such as power cables, magnets, transformers and motors. Although enhancement of critical current performance of the Bi(Pb)2223 tapes have been done mainly by improvements in its fabrication processes thus far, there are few studies on Bi(Pb)2223 from a view point of materials chemistry in a recent decade.

In our previous study, $J_c$ characteristics of Bi2212 single crystals grown by the floating zone method were found to be improved by control of cation composition towards stoichiometric, Bi: Sr: Ca: Cu = 2:2:1:2, which accompanied a slight enhancement of $T_c$ [1]. This means that nonstoichiometric cation composition in this system suppresses inherent superconductivity due to disordered crystal lattice. Since Bi(Pb)2223 also has nonstoichiometry in cation composition, further improvement in $J_c$ characteristics of Bi(Pb)2223 tapes will be expected by controlling both starting cation compositions and sintering conditions. On the other hand, we have recently succeeded in enhancement of $T_c$ of Bi(Pb)2223 tapes synthesized by the controlled-over-pressure (CT-OP) method up to 116.4 K by annealing at ~700°C in air for a long time [2,3]. More recently, the $T_c$ record was enhanced to 117.8 K. Generation of a non-superconducting Pb3221 phase by such annealing process suggested that the optimal cation composition giving the high $T_c$ is different from the conventional one. Since it requires a long period and great cost to fabricate Bi(Pb)2223 tapes starting from various cation compositions, we have attempted to optimize the cation composition of Bi(Pb)2223 sintered bulk in terms of $T_c$ in the present study.
2. Experimental
The precursor powders of Bi(Pb)2223 with various nominal compositions were prepared from high purity reagents of Bi$_2$O$_3$, PbO, SrCO$_3$, CaCO$_3$ and CuO. Appropriate amounts of these powders were mixed and calcined at 780, 800 and 810°C each for 12 h in air. These precursor powders were filled into Ag tube, pressed uniaxially into tapes by a pressure of ~300 MPa and sealed both ends by pressing. Then these tapes were sintered at ~848°C in air or at 830°C in 5%O$_2$/95%Ar atmosphere for a long time. After removing the Ag sheath, the sintered bulks were annealed in air or in 1%O$_2$/99%Ar. In addition, they were annealed at high temperature around ~830°C in air to improve crystallinity and phase purity of Bi(Pb)2223. The sintered bulks were finally annealed at various temperatures in air and quenched to control oxygen content.

Constituent phases of the samples were analyzed by powder X-ray diffraction (XRD). Superconducting properties were measured by a SUQID magnetometer (Quantum Design MPMS-XL5s). The $T_{c\text{(onset)}}$ of the bulks are defined as the temperature at which the ZFC magnetization measured under $H = 1$ Oe becomes 0.1% of that at 80 K.

3. Results and discussion
3.1. Effect of post-annealing for Bi(Pb)2223 bulks
The Bi(Pb)2223 precursor powder with a nominal composition of Bi$_{1.7}$Pb$_{0.35}$Sr$_2$Ca$_2$Cu$_3$O$_y$ was sintered at 848°C for 160 h in air. Figure 1(a) shows the powder XRD patterns of the Bi(Pb)2223 bulks. After annealing at 700°C for 100 h in air, strong diffraction peaks due to Bi$_{0.5}$Pb$_3$Sr$_2$Ca$_2$CuO$_y$ [Pb3221] were observed in Figure 1(b). Since the lead ion of the Bi(Pb)2223 and Pb3221 phases are divalent and tetravalent, respectively, the generation of Pb3221 phase was found to be suppressed by annealing at 700°C for 100 h in a reducing atmosphere, 1%O$_2$/99%Ar as shown in Figure 1(c). The c-axis lengths of the as-sintered and annealed in 1%O$_2$ bulks estimated by powder XRD patterns are 37.15 Å.

Figure 2 shows the ZFC magnetization curves for the Bi(Pb)2223 bulks annealed at 700°C for 100 h in air and in 1%O$_2$. All the bulks were quenched after annealing at 500°C in air to control the oxygen content. The as-sintered bulk exhibited a typical superconducting transition with a $T_{c\text{(onset)}}$ of 110.4 K, while $T_c$ of the bulk annealed in 1%O$_2$ gas was enhanced up to 111.4 K.

![Figure 1. Powder XRD patterns of Bi(Pb)2223 tapes, (a) as-sintered, (b) annealed in air and (c) annealed in 1%O$_2$.](image1)

![Figure 2. ZFC magnetization curves for Bi(Pb)2223 tapes, as-sintered and annealed in air or in 1%O$_2$.](image2)
3.2. Effect of additional high temperature annealing
As shown in Figure 3, powder XRD analysis revealed that Pb3221 phase was decomposed in the bulks additionally annealed at 800–848°C for 72–360 h in air. The ZFC magnetization curve of the same bulk is shown in Figure 4 together with those of bulks before high temperature annealing. \( T_c \) is enhanced up to 114.3 K after annealing at 830°C for 200 h in air and quenching. This bulk had an apparently long c-axis length, 37.20 Å, indicating that the suppression of partial substitutions of Ca and/or Bi for the Sr-site, which usually occur in the Bi(Pb)2223. Zero resistance was confirmed for this bulk to be achieved at 112.2 K. Slightly low zero resistance temperature is believed to be due to weak grain coupling.

**Figure 3.** Powder XRD patterns of a Bi(Pb)2223 bulk annealed at 830°C in air after annealing at 700°C in 1% \( \text{O}_2 \).

**Figure 4.** ZFC magnetization curves for Bi(Pb)2223 bulks, as-sintered, annealed at 700°C in 1% \( \text{O}_2 \), and annealed at 830°C in air.

3.3. \( T_c \) of Sr-rich and Ca-poor Bi(Pb)2223
Since the Bi(Pb)2212 phase inevitably coexists in Bi(Pb)2223 sintered bulks, the Sr-rich Bi(Pb)2223 bulks with nominal compositions of Bi\(_{1.70}\)Pb\(_{0.35}\)Sr\(_{2+w}\)Ca\(_{2-w}\)Cu\(_3\)O\(_y\) \((w = 0.05, 0.10)\) were synthesized to suppress reduction of Sr content in resulting Bi(Pb)2223 phase by formation of Bi(Pb)2212 phase.

The Sr-rich bulks were synthesized at 830°C for 300 h in 5% \( \text{O}_2 \). Powder XRD analyses revealed that the amount of coexisting Bi(Pb)2212 was slightly increased for a bulk with \( w = 0.10 \). Figure 5 shows the ZFC magnetization curves for the Sr-rich Bi(Pb)2223 bulks. \( T_c \) of the as-sintered Sr-rich bulk with \( w = 0.10 \) was 110.8 K. \( T_c \) of both Sr-rich bulks with \( w = 0.05, 0.10 \) were 114.4 K after post-annealing at 700°C for 100 h in 1% \( \text{O}_2 \), additional annealing at 830°C for 200 h in air and followed by quenching. This indicates that the cation compositions of the Bi(Pb)2223 phase after above annealing process were almost identical independent of the nominal composition.

**Figure 5.** ZFC magnetization curves for Sr-rich Bi(Pb)2223 bulks.
3.4. Effect of Bi-rich composition

The Bi-rich Bi(Pb)2223 bulks with the nominal composition of Bi$_{1.70+b}$Pb$_{0.35}$Sr$_2$Ca$_2$Cu$_3$O$_y$ ($b = 0.05, 0.10$) were synthesized to reduce the secondary phases [4]. Figure 6 shows the powder XRD patterns of the bulks sintered at 848°C in air. The amount of secondary phases, such as Ca$_2$CuO$_3$, in the bulks was clearly decreased by adopting the Bi-rich composition. $T_c$ was enhanced from $\sim$110 K up to $\sim$111 K and 114.5–114.8 K by post-annealing at 700°C and additional high temperature annealing under the same condition described above, respectively. $T_c$ was almost unchanged with nominal Bi content as shown in Figure 7, while the $c$-axis length was slightly decreased with an increase of Bi composition.

![Figure 6. Powder XRD patterns of as-sintered Bi(Pb)2223 bulks with the nominal composition of Bi$_{1.70+b}$Pb$_{0.35}$Sr$_2$Ca$_2$Cu$_3$O$_y$ ($b = 0, 0.10$).](image)

![Figure 7. Variation of $T_c$ for Bi-rich Bi(Pb)2223 bulks.](image)

4. Summary

Enhancement of $T_{(onset)}$ of Bi(Pb)2223 sintered bulks was attempted by controlling of the annealing process and the nominal composition. $T_c$ of Bi(Pb)2223 bulks were enhanced from 110.4 K to 111 K by post-annealing at 700°C in 1%O$_2$. Further enhancement of $T_c$ was achieved by additional high temperature annealing at 830°C in air up to 114.3 K. An increase of $c$-axis after additional high temperature annealing indicated that the observed enhancement of $T_c$ is due to the suppression of partial substitution of Ca and/or Bi for the Sr-site.

$T_{(onset)}$ of the Sr-rich Bi(Pb)2223 bulk was 110.8 K. Amount of secondary phases, such as Ca$_2$CuO$_3$, was found to decrease in the Bi-rich Bi(Pb)2223 bulks. $T_c$ of the Sr-rich and Bi-rich Bi(Pb)2223 bulks were also enhanced up to 114.4–114.8 K after post-annealing and additional high temperature annealing under the same conditions done for bulks with a nominal composition of Bi$_{1.7}$Pb$_{0.35}$Sr$_2$Ca$_2$Cu$_3$O$_y$.

Acknowledgments

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