Superconductivity and Cryogenics
Vol.11, No.2, (2009), pp.7~10

Effects of $BaCO_3$ purity on the superconducting properties of top seeded melt growth processed $Y_{1+x}Ba_2Cu_3O_y$ superconductors

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Received 26 March 2009; accepted 23 April 2009

***Abstract*-- Effects of $BaCO_3$ purity on the superconducting properties of top seeded melt growth (TSMG) processed $Y_{1+x}Ba_2Cu_3O_{7-y}$ (Y1+x, x=0.1 and 0.2) superconductors were investigated. $YBa_2Cu_3O_{7-y}$ (Y123) powder prepared using $BaCO_3$ with 99.75% purity and commercially available Y123 powder of 99.9% were used for the fabrication of single Y123 grain superconductors. T_c values of the Y1+x samples prepared using low purity Y123 powder were slightly lower than those of the samples prepared using a high purity powder. In addition to the lower T_c, an anomalous peak effect in the intermediate magnetic fields was observed in Y1+x samples prepared using the low purity $BaCO_3$ powder. The slight decrease in T_c and the anomalous peak effect are ascribed to the possible incorporation of a Y123 phase with impurity elements such as strontium and calcium included in the $BaCO_3$ powder of 99.7%. The result suggests that the low purity $BaCO_3$ powder of a low price can be used as a raw power for the fabrication of single grain YBCO bulk superconductors.**

1. INTRODUCTION

Critical current density (J_c) of high-temperature ceramic superconductors can be dependent on a processing method. The J_c of oxide bulk superconductors prepared by the classical ceramic process using powders is known to be lower than those of the films and single crystal [1]. Due to the weak link nature of grain boundaries, the J_c of the oxide superconductors rapidly decays in the presence of a small magnetic field [2].

Compared with the poly-grain superconductors, a melt-textured YBCO superconductor showed a relatively high J_c even at high magnetic fields [3-5]. The high J_c value is ascribed to the unique microstructure including the textured Y123 grains, Y_2BaCuO_5 (Y211) particles and many other fine size defects such as stacking faults, dislocation, transformation twins developed inside the Y123 grains [6]. The impurity problem in the melt processed YBCO superconductors appears to be less severe than in the poly-grain superconductor. Not clearly clarified in detail, the YBCO grains growing in a melt are considered not to incorporate with the impurity elements.

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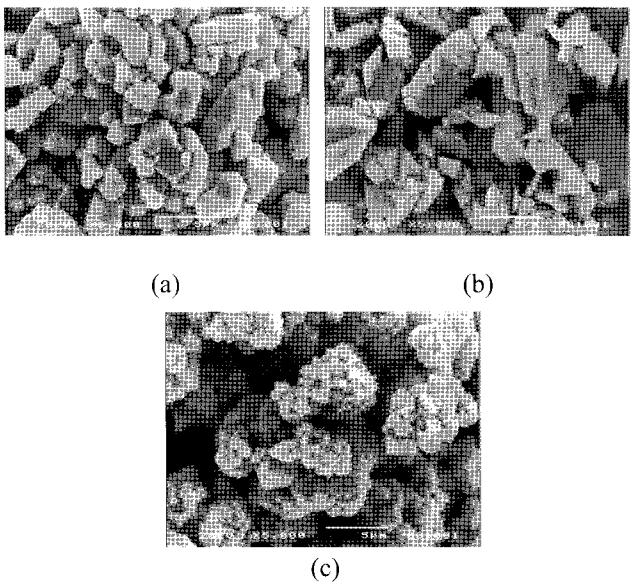
If the impurity problem in oxide superconductors can be solved, low purity precursor powders of low prices can be used as raw materials and the cost-effective method can thus be developed. The aim of this study is to understand the possibility of a use of a low purity $BaCO_3$ powder as a raw powder of melt processed YBCO superconductors. A Y123 powder prepared using a low purity $BaCO_3$ was used as a precursor for TSMG processed YBCO superconductors. The effect of the phase purity on the superconducting properties of the TSMG-processed YBCO bulk superconductors is reported.

2. POWDER SYNTHESIS

Powders used in this study were Y_2O_3, $BaCO_3$ and CuO and a main variable was purity of $BaCO_3$ powder. $BaCO_3$ (purity 99.75%) and Y_2O_3(99.9%) and CuO(99.9%) were used for synthesis of a Y123 powder. 0.05% Sr and 0.02% Ca are impurity of 99.75% $BaCO_3$ powder. Fe, S, Cl and H_2O are also involved, but their amounts are negligible.



(a) (b)

(c)

Fig. 1. SEM micrographs of (a) $BaCO_3$, (b) Y_2O_3 and (c) CuO powders used for synthesis of a Y123 powder.

Fig. 1 shows the scanning electron micrographs (SEM) of (a) $BaCO_3$, (b) Y_2O_3 and (c) CuO powders. $BaCO_3$ powder is 3-5㎛ in size and granular in shape, Y_2O_3 powder is about 5㎛ in size and plate-like in shape and CuO powder is present in a form of agglomerates of powders smaller than 1㎛.

To synthesize a Y123 powder, $BaCO_3$ and Y_2O_3 and CuO powders were weighed to Y:Ba:Cu=1:2:3 and mixed by ball milling using ZrO_2 balls and ethanol. The milled powder was dried in a vacuum oven to remove the solvent. For calcination, the dried powders were put in an alumina crucible, placed at the center of a muffle furnace and heat treated at 800 ℃ -900 ℃ . The calcined powder was repeatedly crushed and heat treated again until the powder mixture is completely converted to a Y123 phase. The details of the synthesis process were well described in our previous report [7].

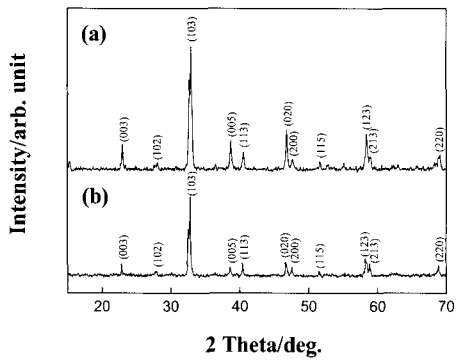
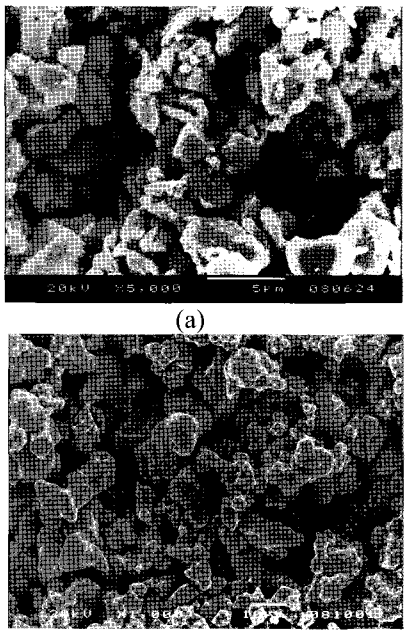


Fig. 2. XRD patterns of (a) commercially available Y123 powder of 99.9% and (b) Y123 powder synthesized using a $BaCO_3$ powder of 99.75%.



(a)

(b)

Fig. 3. SEM micrographs of (a) commercially available Y123 powder of 99.9% and (b) Y123 powder synthesized using a $BaCO_3$ powder of 99.75%.

Fig. 2 shows powder X-ray diffraction (XRD) patterns of (a) commercially available Y123 powder (Solvay Germany, 99.9% purity) and (b) Y123 powder synthesized using a $BaCO_3$ powder of 99.75%. The XRD patterns of both powders are exactly the same as a single Y123 phase. No other second phase peak is observed in the scanned two theta angle range. The formation reaction of a Y123 phase seems to be well done in the powder mixture using a $BaCO_3$ powder of a low purity.

Fig. 3 shows SEM micrographs of (a) Solvay Y123 powder and (b) as-synthesis Y123 powder. The Solvay Y123 powder looks like fractured particles and the average size is about 2-3㎛, which is attributed to the particle granulation by crushing. The as-synthesized Y123 powder is also granular in shape and the size distribution is 5-10㎛, but the particle surface is softer than that of sample (a).

3. TSMG PROCESS

Using Solvay (high purity) and as-synthesized Y123 (low purity) powders, single grain YBCO bulk superconductors were fabricated by a TSMG process. To make an Y211 excessive composition, Y_2O_3 and Y123 powders were weighed to $Y_{1.1}Ba_2Cu_3O_x$ (Y1.1) and $Y_{1.3}Ba_2Cu_3O_x$ (Y1.3) compositions and mixed by ball milling. 1 wt.% CeO_2 was added to the powder mixture with an aim of Y_2BaCuO_5 (Y211) refinement [8]. The powder mixtures were uniaxially pressed in a steel mould into pellets. The uniaxially pressed pellets were isostatically pressed again in a water chamber. A single grain $Sm_{1.8}Ba_{2.4}Cu_{3.4}O_y$ (Sm1.8) bulk crystal, whose melting point is slightly higher than Y123, was used as a seed for the growth of single grain $Y_{1+x}Ba_2Cu_3O_x$ (Y1+x) samples. A Sm1.8 seed was placed on the center of top surface of Y1+x pellets, the seeded pellets were located in a muffle furnace and the melt growth heating cycles was applied to the pellets. The applied heating cycles for the growth of a single Y123 grain and for oxygenation were the same as that described in our previous work [9].

Fig. 4 shows photos of top surfaces of Y1+x samples prepared by a seeded melt growth process. All top surfaces show a successful growth of Y123 grains at the seeds except small subsidiary Y123 grains grown at the sample edges of some samples. The Y123 grains appear to start to grow at the seeds in a limited nucleation condition irrespective to the type of Y123 powders used in this study.

4. SUPERCONDUCTING PROPERTIES

Magnetic measurements were carried out using a Quantum Design's Magnetic Property Measurement System (MPMS). The superconducting transition temperature (T_c) was defined as the onset temperature at which diamagnetic properties were observed. The magnetic J_c was calculated from the magnitude of the magnetization loop using Bean model [10]. To measure T_c and J_c of samples, the rectangular bar type samples were cut from the top surfaces of the TSMG-processed Y1+x samples.

Because the seeded region (normally centers of samples) can be contaminated by Sm diffusion from a seed during melting, the samples for the T_c/J_c measurements were taken the regions far from the seeds.

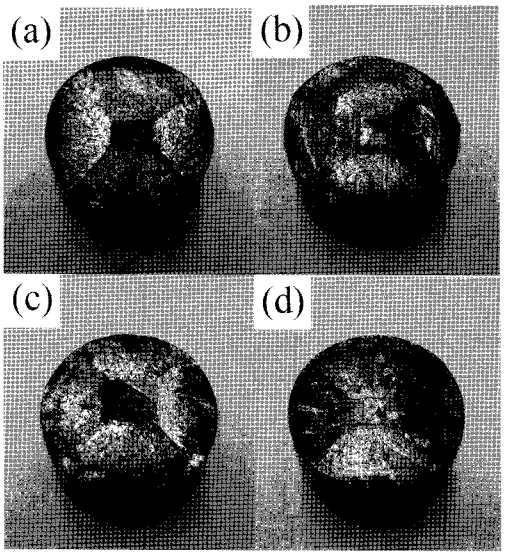


Fig. 4. Photos of top surfaces of seeded melt growth processed $Y_{1.1}Ba_2Cu_3O_x$ ((a), (c)), $Y_{1.3}Ba_2Cu_3O_x$ ((b), (d)) samples prepared using (a), (b) commercially available Y123 powder and (c), (d) Y123 powder synthesized using a low $BaCO_3$ powder of 99.75%.

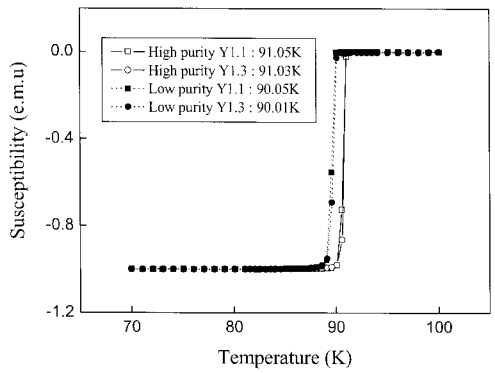


Fig. 5. Magnetic susceptibility curves of seeded melt growth processed $Y_{1+x}Ba_2Cu_3O_x$ bulk samples prepared using commercially available Y123 powder and Y123 powder synthesized using a $BaCO_3$ powder of 99.75%.

Fig. 5 shows magnetic moment-temperature curves of Y1+x samples. All samples show sharp superconducting transitions near 90K. The T_c values of high purity Y1.1 and Y1.3 samples are 91.5K and 91. 3K, while the T_c values of low purity Y1.1 and Y1.3 samples are 90.5K and 90K, respectively. The T_c values of Y1+x sample prepared using a low purity $BaCO_3$ powder are slightly lower than those of high purity Y1+x samples, which are supposed to be caused by impurity incorporation to an Y123 superconducting phase. The very small T_c difference about 1K indicates that the amount of the incorporated impurities was quite small. The T_c values about 90K are high enough for the practical applications of YBCO bulk superconductors. No noticeable effect of Y-excessive composition on a T_c value is found.

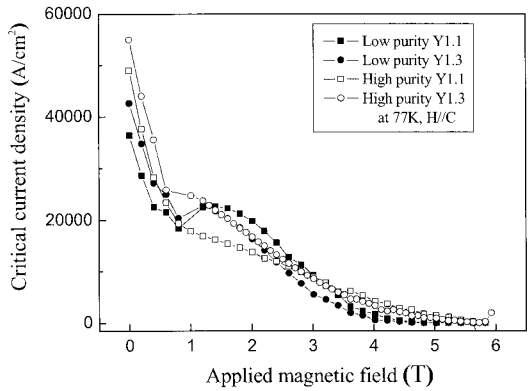


Fig. 6. J_c-B curves of seeded melt growth processed $Y_{1+x}Ba_2Cu_3O_x$ bulk samples using commercially available Y123 powder and Y123 powder synthesized using a low purity $BaCO_3$ powder.

Fig. 6 shows J_c-B curves of Y1+x samples at 77K. The magnetic J_c of both high and low purity Y1+x samples are affected by added amount of Y_2O_3 (actually Y211 content): the J_c values of the higher Y_2O_3 composition sample was relatively higher due to the positive effect of Y211 on J_c, which was generally reported in elsewhere [11]. The J_c-B curves of the low purities Y1+x samples are different from those of the high purity samples. The J_c values of the high purity Y1+x samples decrease as B field increases, but the J_c-B curves of the low purity Y1+x samples show a strong anomalous peak effect at the intermediate magnetic fields of 1T-3T, which might be caused by chemical flux pinning. The peak effect is also observed in the high purity Y1+x samples, but the effect is clearer in sample prepared using low purity powder. Because of the peak effect in low purity Y1+x samples, the J_c values (20,000 A/cm^2) at 2 T of low purity Y1.3 samples is higher than that (16,700 A/cm^2) high purity Y1.3 samples. The anomalous peak effect at the intermediate magnetic fields might be attributed to the incorporation of the impurity elements such as strontium and calcium included in the low purity $BaCO_3$ powder. When considering the fact that the price of the technical grade $BaCO_3$ powder is much lower than that of the high purity power, it is expected that a cost effect process will be developed using the $BaCO_3$ powder used in this study.

5. CONCLUSION

In this work, the possibility of a use of a low purity $BaCO_3$ powder as a raw material for the fabrication of TSMG-processed Y123 bulk superconductors was investigated. The single grain Y123 bulk superconductors was fabricated using a commercially available Y123 powder of 99.9% and the Y123 powder prepared using $BaCO_3$ powder of 99.75%. The T_c values of the TSMG-processed Y1+x samples (low purity) were slightly

lower than those of the samples prepared using high purity Y123 powder due to the possible incorporation with a Y123 phase of impurity elements such as strontium and calcium. The possible flux pinning associated with the impurity incorporation was observed as a peak effect in the intermediated magnetic fields of 1T-3T in the Y1+x samples prepared using a low purity $BaCO_3$ powder. This result suggests that the low purity $BaCO_3$ powder of a low price can be used as a raw power for the development of a cost-effect process of single grain YBCO bulk superconductors.

ACKNOWLEDGMENT

This research was supported by a grant (R-2006-1-248) from Electric Power Industry Technology Evaluation & Planning, Republic of Korea. A part of this work was also supported by the National Nuclear R & D Program of the Ministry of Education, Science and Technology (MEST), Republic of Korea.

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