The influence of postannealing on structural and superconducting properties of Bi-2212 ceramics

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Abstract

The effect of postannealing on the structural and superconducting properties of Bi-2212 sintered ceramic samples prepared by solid state reaction method has been investigated. Postannealing times were varied from 0 h to 192 h at 700 °C. Electrical resistivity studies showed that postannealed samples at 96 h have the lowest room temperature values while critical transition temperature does not change significantly. XRD data have shown that Bi-2212 phase content does not change, independently of the posannealing length. In addition, J_c values, calculated from the hysteresis loops using the Bean's model, increased with increasing postannealing time until 48 h and decrease for longer ones.

Keyword: Bi-2212; XRD; Electrical resistivity; hysteresis loops

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1. Introduction

Among the high-temperature superconducting materials, the Bi-2212 phase is considered as the most attractive because it has high chemical stability and is relatively easy to synthesize for many technological and industrial applications [1-7].

Although Bi-2223 phase has the highest superconducting transition temperature, in the Bi-based family, the production of pure phase materials is a difficult task and requires long processing times [8,9]. Moreover, small stoichiometric variations can modify the final superconducting properties [10], particularly when taking into account that the quaternary $\text{Bi}_2\text{O}_3\text{-SrO-CaO-CuO}$ system shows more than 20 stable phases [11]. On the other hand, ceramic superconductors possess some disadvantages such as intergrain weak links and weak flux pinning capability [12], together with their poor mechanic properties, imposed by their ceramic nature [13]. As a consequence, many strategies have been used in order to improve the properties of BSCCO materials. Some of them are related with the preparation of high homogeneous precursors with small particle sizes using different synthetic methods [14-17] while other ones have been centered on the grain orientation [18-20]. Moreover, the effect of cationic substitution on the superconducting properties of these materials has been studied in previous works, as for example Pb^{2+} by Bi^{3+} [21-23], or metallic additions, typically metallic Ag [24-27].

On the other hand, it is well known that pinning centers in Bi-2212 superconducting materials play an important role on the electrical properties of this kind of superconductors. In fact, many works are dealing with the formation of pinning centers by addition of different compounds, as MgO [28], transition

metal oxide-based materials [29,30], rare earth oxides [31,32], etc, or by the introduction of intrinsic structural defects promoted, for example, by neutron irradiation [33] or by controlled decomposition of the superconducting phase [34,35].

The aim of this work is the improvement of the superconducting properties of Bi-2212 ceramic materials by developing a simple procedure to produce effective pinning centers. It will be studied the Bi-2212 phase controlled decomposition, using postannealing treatments at temperatures out of the Bi-2212 stability region, and its effect on the superconducting properties.

2. Experimental

Samples composition has been chosen from the phase diagram equilibrium for the pseudo-binary $\text{Bi}_{2.18}\text{Sr}_{3-y}\text{Ca}_y\text{Cu}_2\text{O}_{8+\delta}$ system [11], taking $y=0.8$. This value has been selected in order to get the samples out of the Bi-2212 stability region with relatively small changes in temperature. The polycrystalline

$\text{Bi}_{2.1}\text{Sr}_{2.2}\text{Ca}_{0.8}\text{Cu}_2\text{O}_y$ samples were prepared using the classical solid state method from Bi_2O_3 (Aldrich, 99%), SrCO_3 (Aldrich, 99.9%), CaCO_3 (Aldrich, 99.9%), and CuO (Aldrich, 99.99%) commercial powders. They were weighed in the appropriate proportions, mixed using an agate mortar and ball milled at 300 rpm for 30 minutes. After milling, the powders were subjected to a thermal treatment consisting in two different steps: 750 °C for 12 h and at 820 °C for 24 h, with an intermediate milling in a ball mill for 2 hours at 300 rpm, in order to produce the total carbonates decomposition before the sintering process. The obtained homogeneous mixture was then pressed into 13 mm diameter pellets under 375 MPa applied pressure, followed by a sintering process at 860 °C for

120 h, under air, to produce nearly pure Bi-2212 phase with the adequate oxygen content, which maximizes the measured T_c values [36].

The sintered specimens, except one which has been kept as reference, were then subjected to a postannealing process for different times to slowly decompose the Bi-2212 phase. The decomposition temperature has been determined from the phase diagram equilibrium [11] to be around 700 °C and, as a consequence, the thermal process has been carried out using different times (0, 48, 96, 144, and 192 h) at 700 °C to produce the following reaction:

where the last two species are non-superconducting phases and they can be considered as good candidates to be effective pinning centers when possessing the adequate sizes. Taking into account the postannealing times, the samples will be herein after denoted as B1, B2, B3, B4, and B5, respectively.

The produced phases have been determined using X-ray powder diffraction analyses and were performed in a Rigaku Ultima IV X-Ray Diffractometer between $2\theta = 3-60^\circ$ with Cu $K\alpha$ radiation. The surface morphologies were studied in a Zeiss/Supra 55 Scanning Electron Microscopy (SEM).

Resistivity and magnetic measurements were carried out using Cryogenic Limited PPMS (from 5 to 300 K) which can reach temperatures about to 2 K in a closed-loop He system.

3. Results and discussion

The powder XRD patterns performed on all samples are displayed in Figure 1. From these graphs, it is clear that all the patterns are very similar and show no evident difference with postannealing time, compared with the reference one

(with no postannealing treatment). In this figure, major peaks correspond to the Bi-2212 phase, indicating that the sintering conditions have been adequate in order to produce a high amount of the superconducting phase. On the other hand, some minor peaks can be identified in all samples, corresponding to the typical nonsuperconducting secondary phase Bi_2CuO_4 (marked with a + in Figure 1). When considering the effect of postannealing processes, XRD patterns do not change significantly, indicating that the decomposition reaction is relatively slow.

Figure 2 shows the micrographs performed on fractured surfaces of all the samples. At first sight, it can be seen that all the samples are mainly composed by randomly oriented plate-like grains with different sizes, as it is the typical feature of solid state synthesis. When the micrographs are observed in more detail, it can be seen that sintered samples present randomly dispersed small grains (smaller than $2\text{ }\mu\text{m}$) together with bigger ones (see figure 2a).

Postannealing processes slightly change the microstructure found in the sintered materials, increasing the size of these small grains and reducing their number, as can be seen in Figure 2b, after 48 h postannealing treatment.

Further postannealing time leads to the disappearance of these grains. This effect is a typical behaviour towards the reduction of the system energy even if in this particular case it is a slow process, due to the relatively low postannealing temperature. Moreover, the decomposition products of Bi-2212 phase following eq. 1 cannot be observed in these images, which is an interesting feature as the effective pinning centers should have a very small particle size.

The electrical resistivity versus temperature curves for all the samples, from 5 to 300 K are displayed in Fig. 3. The determined T_c (onset) values for the B1, B2, B3, B4 and B5 samples have been found to be about 88.5, 84.94, 83.64, 79.4, and 79.2 K, respectively. These values indicate that T_c value of samples decreases with increasing annealing time which is an indication of the Bi-2212 phase decomposition with the postannealing treatment. In spite of the decrease of T_c with annealing time, room temperature resistivity of samples slightly decreases with changing annealing time from 0 to 192 h. This effect can be associated to the modification in the holes content. Moreover, in the plot it can also be observed that all the samples show metallic behavior above T_c (onset) value, indicating that Bi-2212 phase is still the major one, in agreement with the XRD data.

The magnetic hysteresis cycles, performed at applied fields of ± 2 T for all the samples, at 10 and 20 K, are presented in Figures 4 and 5, respectively. In these figures, it can be seen that all samples possess approximately the same area enclosed by the magnetization curves, which is a consequence of the similar amount of Bi-2212 phase in the bulk samples. On the other hand, B2 sample shows the highest magnitude of magnetization which can be due to the Bi-2212 slow decomposition. This process leads to the formation of non-superconducting phases ($\text{Sr}_3\text{Bi}_2\text{O}_6$ and $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41-x}$) from the Bi-2212 one, in agreement with eq. 1. These phases are growing with the postannealing time and can only act as effective pinning centers when they are very small. In this case, the optimal size is reached after 48 h postannealing time, leading to higher magnetization values. Further time increases the secondary phases

sizes, reducing the number of effective pinning centers and, as a consequence, decreasing the magnetization values.

Critical current density (J_c) values of the samples were calculated from the hysteresis loops at 10 K and 20 K using the Bean's model [37]:

$$J_c = 30 \frac{\Delta M}{d}$$

where J_c is the magnetization current density in ampères per square centimeter.

$\Delta M = M_+ - M_-$ is measured in electromagnetic units per cubic centimeter, and d is the thickness of sample.

Figure 6 and 7 show the calculated critical current densities for all the samples, as a function of the applied field, at 10 K and 20 K, respectively. As can be seen from the figures, J_c values gradually decrease with the magnetic field and increasing annealing time. B1 and B2 samples show the highest J_c values due to their larger magnetization curves. The highest J_c values are in agreement with reported experimental results for BSCCO system in the literature [38-40].

Taking into account the M-H data displayed in Figures 4 and 5, and the J_c values in Figures 6 and 7, it can be easily deduced that long postannealing time affects negatively the superconducting properties of samples due to the decomposition of Bi-2212 ceramics and the growth of the produced non-superconducting particles. On the other hand, adequate postannealing time leads to samples with enhanced pinning properties, as it has been found for sample B2 which possesses the highest remnant magnetization [41].

4. Conclusion

In summary, the effect of postannealing process on the superconducting properties of Bi-2212 ceramics has been investigated. T_c values slightly

decrease when the treatment time increases, indicating the Bi-2212 phase decomposition. The best conditions for producing effective pinning centers in the samples have been found to be 48 h treatment, which is reflected in its highest remnant magnetization, compared with the other samples.

Acknowledgements

All samples have been prepared in the MEİTAM Central Laboratory in Mersin University in Turkey. SEM measurements have been made in the MEİTAM Central Laboratory in Mersin University, other measurements in this study have been made in the METU Central Laboratory in Middle East Technical University in Ankara in Turkey.

References

1. Yildirim, G., Yücel, E., Bal, S., Dogruer, M., Varilci, A., Akdoğan, M., Terzioğlu, C., Zalaoglu, Y.: J. Supercond. Nov. Magn. doi: 10.1007/s10948-011-1284-4 (2011)
2. Okada, M.: Supercond. Sci. Technol. 13, 29 (2000)
3. Runde, M.: IEEE Trans. Appl. Supercond. 5, 813 (1995)
4. Godeke, A., Cheng, D., Dietderich, D.R., English, C.D., Felice, H., Hannaford, C.R., Prestemon, S.O., Sabbi, G., Scanlan, R.M., Nishioka, Y., Hasegawa, J.T.: IEEE Trans. Appl. Supercond. 18, 516 (2008)
5. Miao, H., Meinesz, M., Czabai, B., Parrell, J., Hong, S., AIP Conference Proceedings 986, 423 (2008)
6. Biju, A., Aloysius, R.P., Syamaprasad, U.: Supercond. Sci. Technol. 18, 1454 (2005)

7. Zhao, B., Wan, X., Song, W., Sun, Y., Du, J.: *Physica C* 337, 138 (2000)
8. Sotelo, A., Majewski, P., Park, H.S., Aldinger, F.: *Physica C* 272, 115 (1996)
9. Sotelo, A., de la Fuente, G.F., Lera, F., Beltran, D., Sapina, F., Ibañez, R., Beltran, A., Bermejo, M. R.: *Chem. Mater.* 5, 851 (1993)
10. Sotelo, A., Angurel, L.A., Ruiz, M.T., Larrea, A., Lera, F., de la Fuente, G.F.: *Solid State Ionics* 63, 883 (1993)
11. Majewski, P.: *Supercond. Sci. Technol.* 10, 453 (1997)
12. Jia, Z.Y., Tang, H., Yang, Z.Q., Xing, Y.T., Wang, Y.Z., Qiao, G.W.: *Physica C* 337, 130 (2000)
13. Sotelo, A., Mora, M., Madre, M. A., Diez, J. C., Angurel, L. A., de la Fuente, G. F.: *J. Eur. Ceram. Soc.* 25, 2947 (2005)
14. de la Fuente, G.F., Sotelo, A., Huang, Y., Ruiz, M.T., Badia, A., Angurel, L. A., Lera, F., Navarro, R., Rillo, C., Ibañez, R., Beltran, D., Sapiña, F., Beltran, A.: *Physica C* 185, 509 (1991)
15. Ruiz, M. T., de la Fuente, G. F., Badia, A., Blasco, J., Castro, M., Sotelo, A., Larrea, A., Lera, F., Rillo, C., Navarro, R.: *J. Mater. Res.* 8, 1268 (1993)
16. Sotelo, A., Szillat, H., Majewski, P., Aldinger, F.: *Supercond. Sci. Technol.* 10, 717 (1997)
17. Sotelo, A., Rasekh, Sh., Madre, M. A., Diez, J. C.: *J. Supercond. Nov. Magn.* 24, 19 (2011)
18. Huang, Y., de la Fuente, G. F., Sotelo, A., Badia, A., Lera, F., Navarro, R., Rillo, C., Ibanez, R., Beltran, D., Sapina, F., Beltran, A.: *Physica C* 185, 2401 (1991)
19. Marinel, S., Bourgault, D., Belmont, O., Sotelo, A., Desgardin, G.: *Physica C* 315, 205 (1999)

20. de la Fuente, G. F., Ruiz, M. T., Sotelo, A., Larrea, A., Navarro, R.: Mater. Sci. Eng. A 173, 201 (1993)
21. Sotelo, A., Mora, M., Madre, M.A., Amaveda, H., Diez, J.C., Angurel, L.A., Mayoral, M.C.: Bol. Soc. Esp. Ceram. V. 45, 228 (2006)
22. Shi, L., Dong, Q., Zhang, Y.: Physica C 341, 649 (2000)
23. Mora, M., Sotelo, A., Amaveda, H., Madre, M. A., Diez, J. C., Capel, F., Lopez-Cepero, J. M.: J. Eur. Ceram. Soc. 27, 3959 (2007)
24. Dou, S.X., Song, K.H., Liu, H.K., Sorrell, C.C.: Physica C 160, 533 (1989)
25. Madre, M.A., Amaveda, H., Mora, M., Sotelo, A., Angurel, L.A., Diez, J.C.: Bol. Soc. Esp. Ceram. V. 47, 148 (2008)
26. Sotelo, A., Madre, M. A., Diez, J. C., Rasekh, Sh., Angurel, L. A., Martinez, E.: Supercond. Sci. Technol. 22, 034012 (2009)
27. Özkurt, B., Madre, M. A., Sotelo, A., Yakinci, M. E., Özçelik, B.: J. Supercond. Nov. Magn. 25, 799 (2012)
28. Zhao, B., Song, W.H., Wu, X.C., Du, J.J., Sun, Y.P., Wen, H.H., Zhao, Z.X.: Physica C 361, 283 (2001)
29. Makarova, M.V., Kazin, P.E., Tretyakov, Yu.D., Jansen, M., Reissner, M., Steiner, W.: Physica C 419, 61 (2005)
30. Özkurt, B., Madre, M. A., Sotelo, A., Diez, J. C.: J. Mater. Sci.: Mater. Electr. DOI: 10.1007/s10854-012-0899-y (2012)
31. Vinu, S., Sarun, P.M., Biju, A., Shabna, R., Guruswamy, P., Syamaprasad, U.: Supercond. Sci. Technol. 21, 04501 (2008)
32. Kaya, C., Özçelik, B., Özkurt, B., Sotelo, A., Madre, M. A.: J. Mater. Sci: Mater. Electron. 2012 DOI: 10.1007/s10854-012-0979-z (2012)

33. Weigand, M., Eisterer, M., Giannini, E., Weber, H.W.: Phys. Rev. B 81, 014516 (2010)
34. Majewski, P., Elschner, S., Aldinger, F.: Physica C 249, 234 (1995)
35. Sotelo, A., Constantinescu, G., Rasekh, Sh., Torres, M. A., Diez, J. C., Madre, M. A.: J. Supercond. Nov. Magn. DOI: 10.1007/s10948-012-1922-5 (2012)
36. Sotelo, A., Peña, J.I., Angurel, L.A., Diez, J.C., Ruiz, M.T., de la Fuente, G.F., Navarro, F.R.: J. Mater. Sci. 32, 5679 (1997)
37. Bean, C.P.: Phys.Rev.Lett. 8, 250 (1962)
38. Özkurt, B., Ekicibil, A., Aksan, M.A., Özçelik, B., Yakıncı, M.E., Kıymaç, K.: J. Low. Temp. Phys. 149, 105 (2007)
39. Özkurt, B.: J. Supercond. Nov. Magn. 25, 1775 (2012)
40. Özkurt, B., Madre, M.A., Sotelo, A., Diez, J.C.: J. Mater. Sci.: Mater. Electron. DOI: 10.1007/s10854-012-0899-y (2012)
41. Albiss, B.A., Obaidat, I.M., Gharaibeh, M., Ghamlouche, H., Obeidat, S.M.: Solid State Commun. 150, 1542 (2010)

Figure captions

Figure 1. Powder XRD patterns of the B1, B2, B3, B4 and B5 samples. Bi-2212 diffraction peaks are identified by a * while those corresponding to the Bi_2CuO_4 secondary phase are shown by a +.

Figure 2. SEM micrographs obtained on fractured surfaces of a) B1; b) B2; c) B3; d) B4 and e) B5 samples.

Figure 3. Resistivity as a function of temperature curves for the different postannealed samples.

Figure 4. Magnetization hysteresis curves measured at 10K for all samples.

Figure 5. Magnetization hysteresis curves measured at 20K for all samples.

Figure 6. Calculated critical current densities for all the samples at 10K, as a function of the external applied field.

Figure 7. Calculated critical current densities for all the samples at 20K, as a function of the external applied field.

Figure 1

2 μ m

EHT = 20.00 kV
WD = 11.1 mm

Signal A = SE2
Mag = 7.00 K X

Date :6 Aug 2012
Time :13:53:20

1 μ m

EHT = 20.00 kV
WD = 11.0 mm

Signal A = SE2
Mag = 7.00 K X

Date :6 Aug 2012
Time :14:07:00

1 μ m

EHT = 20.00 kV
WD = 11.3 mm

Signal A = SE2
Mag = 7.00 K X

Date :6 Aug 2012
Time :14:24:18

1 μ m

EHT = 20.00 kV
WD = 11.2 mm

Signal A = SE2
Mag = 7.00 K X

Date :6 Aug 2012
Time :14:36:50

1 μ m

EHT = 20.00 kV
WD = 11.2 mm

Signal A = SE2
Mag = 7.00 K X

Date :6 Aug 2012
Time :14:50:06

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7