ELSEVIER

Journal of Alloys and Compounds 239 (1996) 142–146

Journal of ALLOYS AND COMPOUNDS

Magnetic field dependence of samples of nominal composition $Bi_{1.6}Pb_{0.4}Sr_2Ca_3Cu_4O_y$ (2234) prepared by various techniques

E. Yanmaz, I.H. Mutlu[1], S. Nezir, M. Altunbas

Karadeniz Technical University, Faculty of Arts and Sciences, Department of Physics, 61080 Trabzon, Turkey

Received 13 October 1995; in final form 4 January 1996

Abstract

The effect of magnetic field was investigated by measuring the resistivity as a function of temperature in different magnetic fields on $Bi_{1.6}Pb_{0.4}Sr_2Ca_3Cu_4O_y$ (2234) samples prepared by solid state reaction, ammonium nitrate and melt quench methods. It was found that the transition temperatures T_c of samples changed with changing magnetic fields. The amount of change was found to be dependent on the sample preparation technique. The samples prepared by solid state reaction and ammonium nitrate methods were affected by magnetic field more than melt quench-annealed samples. Additionally, the critical current density J_c of samples decreased with increased magnetic field.

Keywords: BSCCO system; Magnetic field dependence; Preparation methods; Transition temperature

1. Introduction

After the discovery of La–Ba–Cu oxide superconductors [1], many works have been reported, finding new superconducting oxides and researching their physical properties. The physical properties common to all high-T_c superconductors were summarized by Tanaka [2], for example low carrier concentration, controllability of carrier concentrations, existence of semiconductor phase, appearance of antiferromagnetism in semiconductor phase and two-dimensionality, etc.

All high-T_c superconducting materials have two-dimensional (2D) CuO_2 planes in their crystal structure. The electrical conduction is mostly in the CuO planes, and it is expected that the high-T_c superconductivity will appear in the CuO plane. It is well known that the high-T_c superconductors are very sensitive to material defects [3]. For instance, a small amount of oxygen deficiency and some disorder in the crystal structure affect the critical temperature of the superconductor.

The purpose of this work is to investigate systematically the magnetic field dependence of $Bi_{1.6}Pb_{0.4}Sr_2Ca_3Cu_4O_y$ (2234) samples produced using different preparation methods [4]. Our analysis makes it possible to obtain fairly reliable information on some physical properties of these materials. It was found that the transition temperature T_c and the critical current density J_c of samples changed with increasing magnetic field.

2. Experimental procedure

Commercial powders of 3N purity, Bi_2O_3, PbO, $SrCO_3$, CaO and CuO in the stoichiometric ratios of $Bi_{1.6}Pb_{0.4}S_2Ca_3Cu_4O_y$ (2234), were well mixed by milling. To achieve superconductivity, this starting composition was treated in three different methods, as follows.

2.1. Solid state reaction method

The above composition was calcined at 840°C for 10 h and slowly cooled to room temperature. The calcined powders were pressed into pellets and then annealed at 845°C for 100 h in air.

---

[1] Permanent address: University of Harran, Faculty of Arts and Sciences, Dept. of Physics, Sanliurfa Turkey.

PII S0925-8388(96)02231-1

2.2. Ammonium nitrate method

The appropriate amounts of powders Bi_2O_3, PbO, $SrCO_3$, CaO and CuO in the ratio of $Bi_{1.6}Pb_{0.4}Sr_2Ca_3Cu_4O_{12}$ (2234) were dissolved in liquid ammonium nitrate at 180°C and a chemically homogeneous mixture was obtained. Ammonium nitrate was evaporated at higher temperatures (210–750°C) in the form of H_2O and N_2O. This mixture was held at 750°C for 4 h. The resulting powders containing binary and ternary metal oxides were pressed into pellets and annealed at 845°C in air for 100 h.

2.3. Melt quench method

The appropriate amounts of powders Bi_2O_3, PbO, $SrCO_3$, CaO, CuO and Ag_2O in the stoichiometric ratios of $Bi_{1.6}Pb_{0.4}Sr_2Ca_3Cu_{4-x}Ag_xO_{12}$ (2234) for $x = 0$ and $x = 0.5$ were well mixed by milling and calcined at 840°C for 10 h in air. The two calcined powders were held in separate alumina crucibles at 1150°C until the samples were completely melted. The melts were poured onto a precooled copper plate and pressed quickly by another copper plate to obtain approximately 1.5 to 2 mm thickness of plate-like amorphous material. Finally, the precursor materials produced by melt quenching were annealed at 845°C for 100 h in air to achieve superconductivity.

The superconducting transition temperatures and critical current densities at 77 K were carried out by a four-probe continuous d.c. method. Measurements were performed in different magnetic fields produced with an electromagnet made by Walker Scientific Inc. (model HV7W; input 100 V, 50 A). Indium was used as contact material. The critical current of samples was determined when a voltage of 5 mV was detected between the inner contacts. X-ray powder diffraction analyses at room temperature using Cu Kα radiation were performed to examine the phases present in the samples.

3. Results and discussion

The X-ray diffraction patterns of samples annealed at 845°C for 100 h are shown in Fig. 1. The peaks indicate that all samples contain the high-T_c (2223) and low-T_c (2212) phases. The dominant phase in samples is the high-T_c phase which corresponds to a transition temperature of 110 K. It was found that the addition of Ag into a BSCCO sample (Fig. 1(d)) caused the slightly increased amount of low-T_c phase compared with the undoped melt quenched sample (Fig. 1(c)). This may be due to the decrease in melting temperature of the sample. It was seen that the density and connection of the superconducting phases of the Ag-added sample were better than in other samples, causing the increase in critical current density J_c of the sample.

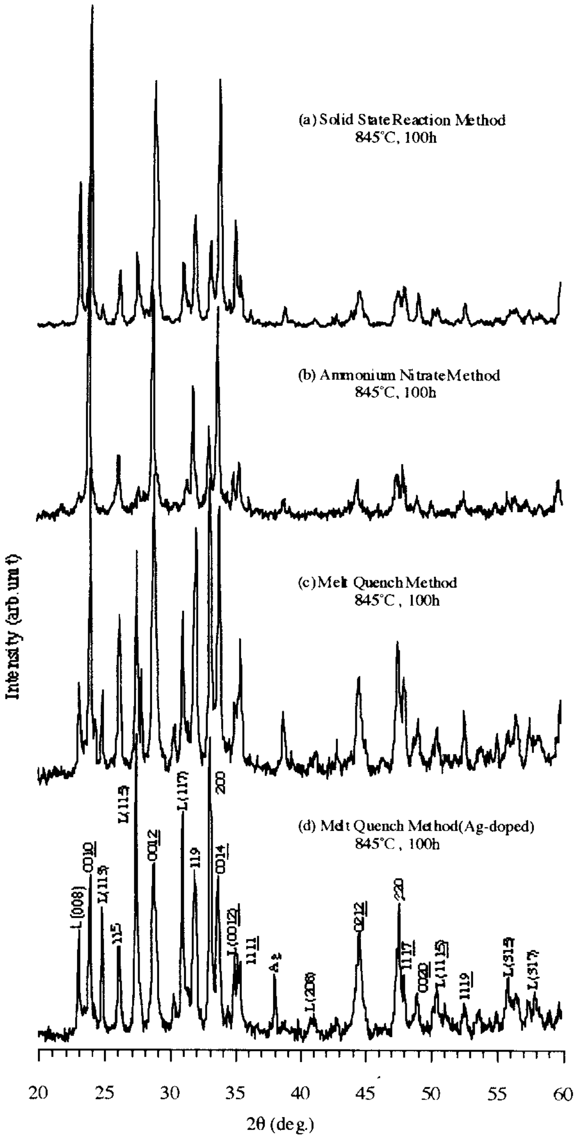

Fig. 1. X-ray (Cu Kα) powder diffraction patterns of annealed (845°C, 100 h) samples prepared by (a) solid state method, (b) ammonium nitrate method and (c), (d) melt quench method.

The resistivities of samples prepared by different preparation methods as a function of temperature in different applied magnetic fields are shown in Figs. 2 to 5. The superconducting transition temperature of all types of sample after 100 h annealing at 845°C was found to be around 110 K in zero magnetic field. These curves also indicate the amount of high-T_c phase formed in the samples during annealing. It can clearly be seen that the dominant superconducting phase is the high-T_c phase (2223). But, the annealed 2234 sample prepared by the method of liquid ammonium nitrate (Fig. 3) shows a step transition which is an indication of the presence of the low-T_c (2212,

$T_c = 90$ K) and high-T_c (2223, $T_c = 110$ K) phases together in zero magnetic field. This result is confirmed by X-ray diffraction analysis.

Fig. 2 shows the resistivity curves of a solid state reacted 2234 sample measured in different magnetic fields. The figure indicates that when an external field is applied to the sample, the transition temperature of the sample can be lowered. It is expected that further increasing the magnetic field will cause a further decrease in transition temperature. However, it was found that when the applied field was increased from 9×10^3 Gauss to 12×10^3 Gauss, the transition curve remained almost the same. It was thought that this sample contained weak links between superconducting grains. This weak-link behaviour could be due to the presence of non-superconductive phases, one of the low-T_c phases or porosity between grains in the sample. All of these can be expected from samples prepared by different methods [5–7]. It can be assumed that the field will penetrate into the sample from the grain boundaries containing the weak link. Then, the superconductivity in the grain boundary will diminish and cause the decrease in zero resistive transition temperature. One can suggest why the superconducting transition temperature is not decreased further for fields of over 9×10^3 Gauss: it is well known that superconductors have two kinds of critical current density, *inter*grain critical current density J_{cm} and *intra*grain critical current density J_{cg}) [8]. Generally, the intragrain critical current density is much higher than the intergrain critical current density ($J_{cg} \gg J_{cm}$). It is also known that the current density of superconductors may depend on the applied field [8]. Therefore, when the current density induced by the field approaches the intergrain critical current density, the superconductivity between grains breaks down and causes the decrease in transition temperature. However, when the applied field is between H_{c1} and H_{c2} (for type II) the vortices are nucleated and the superconductivity within the grain continues. If the applied field reaches H_{c2} then the superconductivity within the grain will again diminish and the resistance will appear [8–10]. Therefore, this result indicates that the applied field used in this work is not enough to break the superconductivity in the grain.

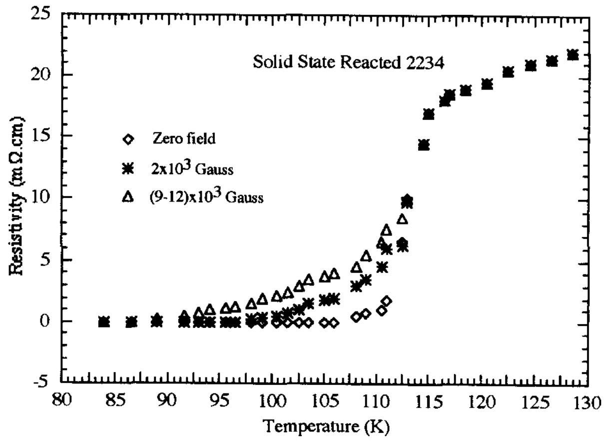

Fig. 2. Variation of resistivity as a function of temperature in different magnetic fields indicated for a sample prepared by the solid state reaction method.

Another important aspect in understanding the mechanism of high-T_c superconductors is the fluctuation near T_c. The pronounced rounding of $\rho(T)$ curves above T_c indicates that critical fluctuations near T_c play an essential role in the BSCCO system, and similar behaviour has been observed for other copper oxide superconductors [11,12].

According to Abrikosov's flux theory [13] on type II superconductors in a magnetic field, there exist vortices or flux lattices which disperse in the superconducting regions in a regular array, each vortex containing one quantum of flux ($\phi_0 = h/2e$). The formation of a rigid flux lattice is important for the dissipation process, because a relatively small number of pinning centres is enough to pin all of the flux lines. Therefore, the flux lattice melting, which is more important in the 2D systems, can be responsible for the dissipation process near the critical temperature. In most previous works, the effects of thermal motion of the vortices have been neglected when discussing the motion of the vortices under a magnetic field [14]. In this work, in the presence of an external magnetic field, there is a significant broadening of the zero resistive transition regions in the BSCCO system. It is considered that the effect of finite temperature fluctuations on the properties of the flux lattices or vortex structure is changed by magnetic field. When a current flows in a type II superconductor, which is free of lattice defects, there is an energy loss because each vortex generates electric fields in the superconductor which cause a dissipative superconducting structure [15]. In order to transport larger resistanceless currents in type II superconductors, the motion of the vortices must be impeded by pinning centres, which could be inhomogeneities, dislocations, impurities, etc. [16,17].

Fig. 3 shows the variation of resistivity as a function of temperature for a 2234 sample prepared in liquid ammonium nitrate measured in different magnetic fields. Details of this preparation technique have been given previously [18]. As can be seen from the figure, the transition temperature changes systematically with magnetic field. It is thought that even in zero magnetic field the sample shows the low-T_c and high-T_c phases together. Therefore, the magnetic field easily penetrates into the sample and results in an increase of the normal region showing the resistance. It was also reported [18] that, using this method, the relative

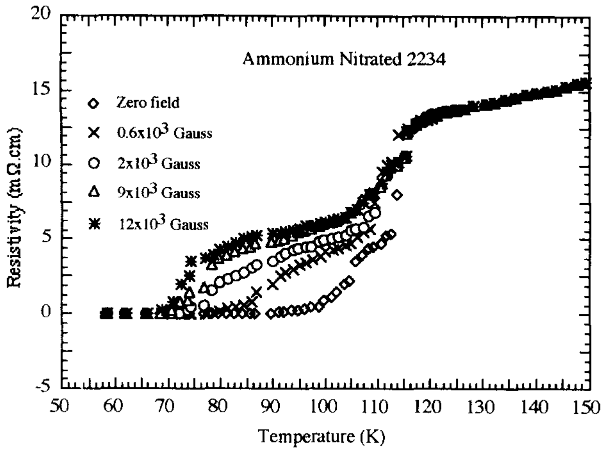

Fig. 3. Variation of resistivity as a function of temperature in different magnetic fields indicated for a sample prepared by the ammonium nitrate method.

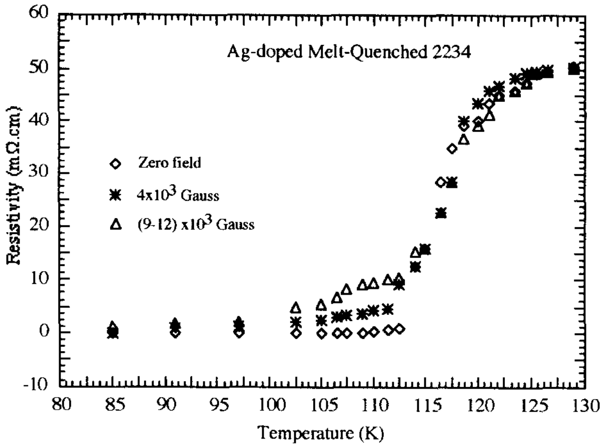

Fig. 5. Variation of resistivity as a function of temperature in different magnetic fields indicated for an Ag-doped ($x = 0.5$) sample prepared by the melt quench method.

density of the sample decreased sharply (by around 50%). This result indicates that the connectivity between superconducting grains is also very weak. Therefore, this type of sample is more susceptible to external effects, for example magnetic field [18].

Fig. 4 shows the variation in resistivity as a function of temperature for the sample prepared by the melt quench method. It was found that the melt quench-annealed sample was affected less by the magnetic field than the sample prepared by the liquid ammonium nitrate method. This could be due to microstructural differences. The density of the sample, in comparison with samples prepared by other methods, is high (around 95% of theoretical density) and shows a more homogeneous structure [4,19]. So, the weak-link effect is very small in this sample. At the same time, the non-superconducting phases were dispersed into the superconducting grain, and therefore the grain boundaries are much cleaner than those of the samples prepared by other methods [17].

By adding Ag into a BSCCO system (Fig. 5), the physical properties of the superconductors were improved. This may be due to the increase in pinning centres, which cause the increase in critical current density J_{cm}. This idea was supported by the measurement of the critical current densities at 77 K in a magnetic field, as shown in Fig. 6. As can be seen, melt quench-annealed samples (with or without Ag) show higher critical current density than the sample prepared by solid state reaction. The critical current density of the sample prepared by the liquid ammonium nitrate method was found to be around 5 A cm^{-2} in zero field (not included in the figure). In a magnetic field, it fell sharply to zero due to the presence of a high amount of low-T_c and non-superconducting phases.

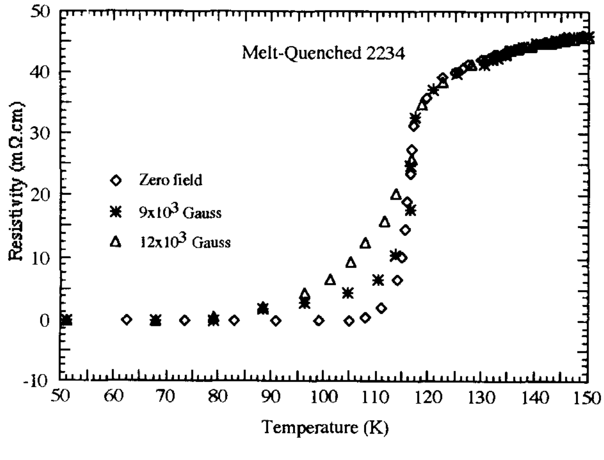

Fig. 4. Variation of resistivity as a function of temperature in different magnetic fields indicated for a sample prepared by the melt quench method.

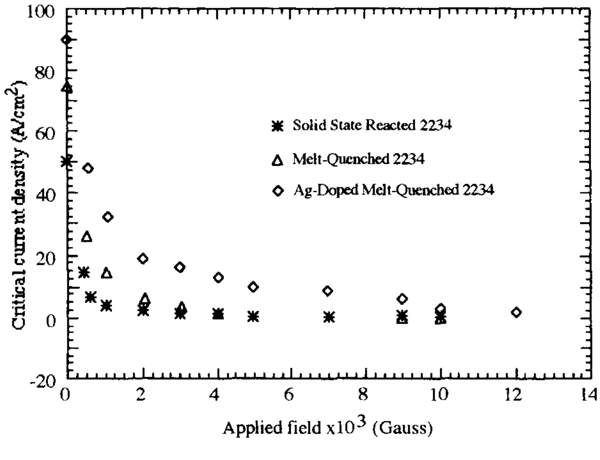

Fig. 6. Magnetic field dependence of the critical current densities for samples prepared by the solid state reaction and melt quench methods.

In summary, the starting composition of 2234 BSCCO samples was obtained by solid state reaction, ammonium nitrate and melt quench methods. In the presence of an external magnetic field, there is a significant broadening of the zero resistive transition regions in the BSCCO system. It is considered that the effect of finite temperature fluctuations on the properties of flux lattices or vortex structure is changed by magnetic field. It was found that the melt quench-annealed sample was affected less by the magnetic field than the sample prepared by the liquid ammonium nitrate method. By adding Ag into the BSCCO system, the physical properties of the superconductors were improved. This may be due to the increase in number of pinning centres, which causes the increase in critical current density J_{cm}.

Acknowledgements

This work was supported by the Research Fund of Karadeniz Technical University, Trabzon, Turkey.

References

[1] J.G. Bednorz and K.A. Muller, *Z. Phys. B, 64* (1986) 189.
[2] S. Tanaka, *IEEE Trans. Magn., 27* (1991) 2.
[3] A. Maeda, M. Hase, I. Tsukada, K. Noda, S. Takebayashi and K. Uchinokura, *Phys. Rev. B, 41* (10) (1990) 6418.
[4] E. Yanmaz, *Turk. J. Phys., 18* (1994) 631.
[5] J. Wosik, L.M. Xie, R. Chau, A. Samaan and J.C. Wolfe, *Phys. Rev. B, 47* (14) (1993) 8968.
[6] S.M. Cassidy, L.F. Cohen, M.N. Cuthbert, J.R. Laverty, G.K. Perkins, A.D. Caplin, S.X. Dou, Y.C. Guo, H.K. Liu, F. Liu and E.L. Wolf, *J. Alloys Comp., 195* (1993) 503.
[7] S.A. Sergeenkow, *Physica C, 205* (1993) 1.
[8] S. Çelebi and M.A.R. LeBlanc, *Phys. Rev. B, 49* (1994).
[9] S. Samarappuli, A. Schilling, M.A. Chernikov and H.R. Ott, *Physica C, 201* (1992) 159.
[10] H. Hojaji, S. Hu, A. Barkatt, D.D. Davis and A.N. Thorpe, *Physica C, 195* (1992) 135.
[11] H. Küffer, I. Apflestedt, W. Schauer, R. Flükiger, R. Meier-Hirmer and H. Wühl, *Z. Phys. B: Condens. Matter, 69* (1987) 159.
[12] A. Schilling, O. Jeandupeux, J.D. Guo and H.R. Ott, *Physica C, 216* (1993) 6.
[13] A.A. Abrikosov, *Sov. Phys. JETP, 5* (1957) 1174.
[14] M. Tinkham, *Phys. Rev. Lett., 61* (1988) 1658.
[15] I.H. Mutlu, S. Bending and S. Stoddart, *Turk. J. Phys., 17* (9) (1993) 648.
[16] S.A. Zhou, *Electrodynamic Theory of Superconductors*, Peter Peregrinus, 1990, p. 188.
[17] S. Gotoh, M. Murakami, N. Koshizuka and S. Tanaka, *Physica B, 165–166* (1990) 1379.
[18] M. Altunbas, E. Yanmaz, S. Nezir, H. Karal and Yu.A. Vidadi, *J. Alloys Comp., 215* (1994) 263.
[19] S. Elschner, J. Bock and H. Bestgen, *Supercond. Sci. Technol., 6* (1993) 413.