An-Najah J. Res., Vol. 4 , No. 10 (1996)

The Effects of Substrate Material , Quenching And Annealing on the Properties of High Temperature Superconductor BSCCO (Bi-2212) Thick Tapes

تأثير نوعية المفترش (الطبقة التحتية) والمعاملة الحرارية على خصائص شرائح BSCCO الفائقة الموصلية

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ABSTRACT

The effects of substrate material and heat treatment conditions on the electrical and thermal properties for partially melt-solidified superconducting tapes BSCOO (2212), grown on single crystal MgO and Ag / MgO substrates m were investigated. Results show that the resistivity of the normal state varies with the size and orientation of the grains. It is found that larger grains lower both the concentration of second phases and the grain boundaries, hence decreasing the resistivity of the normal state and enhancing the critical current density of the superconducting state. also , the material of the substrate has no effect on either the resistivity or the critical current density of the Bi-2212 phase. Heat treatment conditions and the annealing atmosphere play an important role in determining the critical current density and the transition temperature. Slow cooling from 840°C lowers both the critical current and the transition temperature; while quenching the sample from 840°C to room temperature and annealing it in a nitrogen atmosphere increase both the critical current density and the transition temperature.

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ملخـــــص

تمـت دراسـة تـأثير نوعيـة المفـترش (الطبقـة التحتيـة) والمعاملـة الحراريـة لشـرائح مادة BSCCO الفائقة الموصلية والتي عملت على مفترش من الفضة ، او على بلورة من MgO ، فوجد أن المقاومة النوعية لهذه المادة تعتمد على حجم البلـورات الصغيرة المكونـة للمـادة وميلانها ، كما أن البلورات الكبيرة تقلل تركيز الشوائب والحدود المشتركة مع البلـورات الاخـرى .وهـذا بـدوره يؤدى الى تقليل المقاومية للمادة في الحالـة العاديـة ، وزيـادة مقـدار التيـار الحـرج فـي الحالـة الفائقة الموصلية. كذلك فقد وجد أن نوعية المفترش (الطبقة التحتية) ليس لها تأثير على كل مـن المقاومية او التيار الحرج لمادة BSCCO (2212) عندما تكون في الحالة الفائقة الموصلية . أيضا فقد وجد للمعاملة الحرارية والغاز المستعمل لهذا الغرض تأثيرا كبيرا على مقدار التيار الحرج ومقدار درجـة حرارة الانتقال من الحالة العادية الى الحالة الفائقة الموصلية, وان خفض درجة الحرارة من ٨٤٠ °س الى درجة حرارة الغرفة ببطيء فأنه يقلل من التيار الحرج ودرجة حرارة الانتقال الـى الحالة الفائقة الموصلية. اما التبريد السريع لدرجة حرارة الغرفة والمعاملة في جو من النتيروجين فأنه يزيد من مقدار التيار الحرج وزيادة درجة حرارة الانتقال الى الحالة الفائقة الموصلية .

Introduction

It was found that several factors affect the critical current density of BSCCO (2212) high temperature superconductor thick film tapes. These factors include grain boundaries, second phases, microcracks and the texture of the tape (Yang et al. 1993, Tagano et al. 1991, Tomomtsu et al. 1991). Also, the size, shape and alignment of the grains were found to play an important role in determining the Jc of the polycrystalline superconductor BSCCO (Yang et al. 1993, Tagano et al. 1991, Tomomtsu et al. 1991, Hensel et al. 1993). The texture of the $B_2Sr_2CaCu_2O_x$ could be improved by growing a tape sample using partial melting of the superconductor (Kase et al. 1991, Zhang et al. 1992, Noji et al. 1993). The thickness of the tape was found to be important in aligning the grains and increasing the critical current density (Kase et al.1991, Zhang et al. 1992). A highly aligned textured was observed for tapes of thickness less than 20 μm, while the alignment of the grains was less pronounced for tapes of thickness greater than 30 μm. The critical current density was found to increase as the superconductor thickness was decreased. This suggests that thinner films have fewer and smaller second phases as well as better alignment of the grains.

The heat treatment conditions of the sample growth play an important role in determining the microstructure of the superconductor and, hence, its electrical and magnetic properties. Noji et al. (1993) showed that the growth of second phases on the tape surfaces is dependent on the cooling rate from the sintering temperature to room temperature. The superconductor properties of BSCCO tape were found to be dependent on annealing and sintering temperatures, time period of heat treatments, and the furnace atmosphere (Dimesso et al. 1992). The effect of the cooling rate and applied magnetic field on critical current density of the Bi-2212 superconductor tape was studied by Shimoyama et al. (1992a) who found that a fast cooling rate suppresses the decomposition of the Bi-2212 phase and therefore, improves the grain coupling of the superconductor.

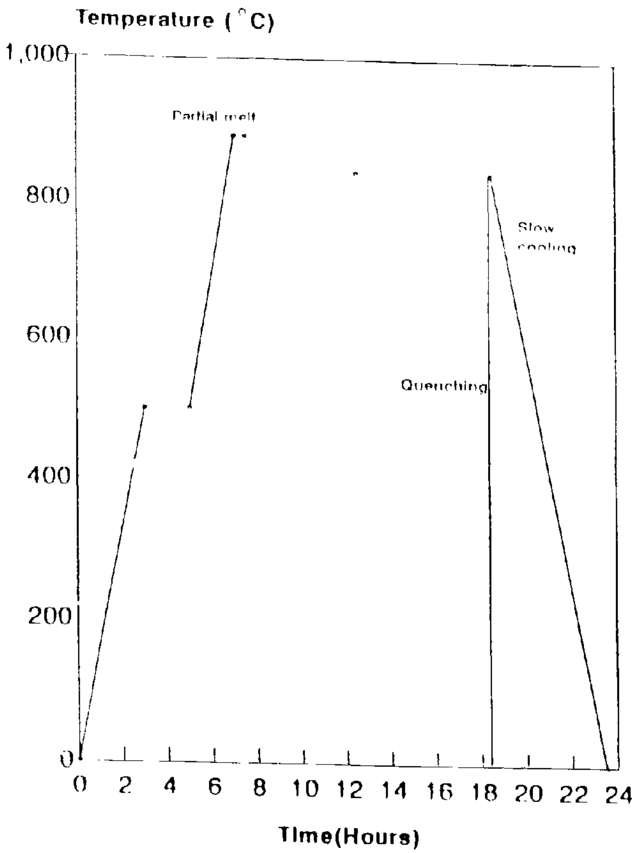
Grain sizes and grain boundaries significantly affect the electrical properties and the critical transition temperature of the specimen. The resistivity of the grains and grainboundaries (Tanaka et al. 1991) was found to depend on intra-grain orientation, and a large anisotropy of the resistivity in **a** and **b** directions was observed for a single grain. A sample of large grains grown from melt showed higher Tc and critical current density than another sample of small grains (Lee et al. 1991). The differences in superconducting properties between these samples were attributed to the crystal growth conditions and weak-link behavior at grain boundaries. The oxygen nonstoichiometry in BSCCO superconductor was found to have an important effect in determining Tc, Jc and thermodynamic quantities of the specimen (Shimoyama et al 1992b, Morimoto et al 1992). A possible existence of two phases of the Bi-2212 compound, differing in their oxygen content, was suggested by Morimoto et al. (1992).

In this study, we investigate the dependence of the electrical and structural properties of thick films of the high temperature superconductor BSCCO (Bi-2212) on substrate material and growth conditions. The films were grown on various substrates of different types by partial melting of the solid at temperature between 890 to 900 °C depending on thesubstrate. Various growth conditions were used in order to study their effect on the electrical, thermal, and structural properties of the BSCCO (Bi-2212) superconductor.

Experimental Method

In the present study, a high quality commercial fine powder of $Bi_2Sr_2CaCu_2O_x$ was used to cast tapes of the superconductor. The powder was mixed with an organic formula consisting of a solvent (trichloroethylene), a binder (poly-vinal butyral), and a dispersant (sorbitan-trioleate). The mixture was mixed well to ensure a homogeneous solution. The slurry mixture was cast under dr. blade's technique into green sheets of thickness ranging between 35 to 60 μm. Tape samples of a size of about $1 \times 4\ mm^2$ were cut and then pressed onto the substrate. Different substrates were used here, some of which were not favorable for producing a superconductor texture under a partial melting technique. The samples were then subjected to arious heat treatments. The heat treatment profile of the samples is shown in figure (1). The tape was first heated at the rate of 2 to 4 °C/min. to 500 °C in order to remove the organics. At this temperature, the sample was annealed for two hours to assure the removal of all the organic compounds. Then the temperature was increased, depending on the substrate type, to 890 or 900 °C. At this temperature, where it is partially melted, the sample remained for 12 minutes. The sample temperature was then slowly cooled to 840°C at a rate of 0.1°C/min. The superconductor was sintered for 6 hours, then the sample was either quenched to room temperature or cooled slowly to room temperature at the rate of 3 to 5 °C/min.

Figure 1



Some samples were annealed in a nitrogen atmosphere at 500 to 550 °C for about 14 hours. This annealing temperature was found by Dimesso et al. (1992) to be effective in increasing both the critical temperature and critical current density. The SEM (Scanning Electron Microscopy) and EDS (Energy Dispersive x-ray Spectroscopy) analysis of the surface and cross section of the samples showed the composition of the Bi-2212 system in most areas, and very few colonies of some other second phases. Optical microscopy showed that the grain size and the orientation of the **ab** plane is dependent on heat treatment conditions.

The AC susceptibility and the electrical resistivity measurements were used to determine the superconductivity behavior of the samples. A more detailed description of the systems used in measuring the AC susceptibility and the resistance of the samples is described elsewhere (Schindler et al. 1994). The resistance of the samples was measured using the four-lead technique. The zero-point transition temperature of the samples was observed to be between 80 to 90 K depending on the heat treatment conditions, and the externally applied magnetic field. Also the critical current density was dependent on the heat treatment conditions, the annealing conditions and grain size.

A platinum thermometer was used to determine the temperature of the sample. The temperature, and the resistance of the sample, were measured using a four-lead method. The resistance measurements, R(T), were taken using a computerized Keithely 224 current source. A scanner allowed a simultaneous measurement of up to four samples with different bias currents. A Keithley 195-A voltmeter with a 1 μ

V resolution was used to measure the voltage drop of the sample. The current-voltage characteristics (IVC) were taken using a current source driven by a ramp generator with a maximum output of ± 100 mA. The samples were mounted on a dip-stick which could be inserted in a liquid helium container. A small magnetic field could be applied to the sample. The samples may be mounted either parallel, or perpendicular to the field.

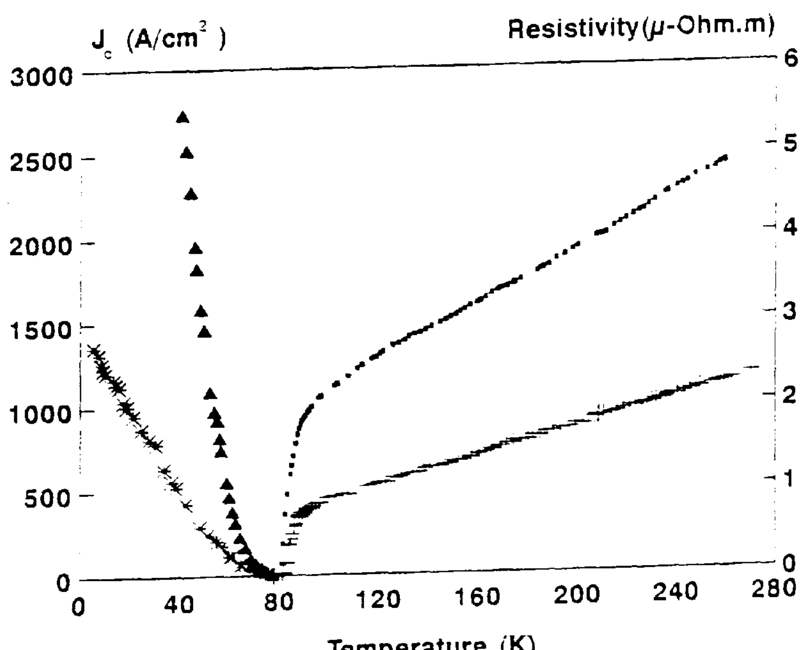
Results & Discussions

The electrical parameters (resistivity, critical current density, J_c, and IV characteristics) and the critical transition temperature, T_c, of BSCCO superconductor tapes were found to be dependent on several factors. These factors include the growth conditions, heat treatments, substrate material, and annealing conditions. In the following sections, these factors are discussed separately and their effect on the electrical, thermal, and structural properties of the superconductor is presented.

1. The effect of substrate Material.

Different materials were used as substrate to grow tapes of the BSCCO (Bi-2212) superconducting phase. The type of substrate material was found to be very critical in the formation of the superconducting phase. Silver foil, single crystal MgO and single crystal MgO covered by thin silver layer were good environment for the formation of the Bi-2212 phase. The superconducting phase of BSCCO did not form on polycrystalline MgO, saphire, and single-crystal or polycrystalline Al_2O_3 when the samples were partially melted at 890 °C, in addition, the superconducting phase did not form when a thin layer (0.5 μm) of silver covered these materials. This may be attributed to the interaction of sample material with these substrates, hence, preventing the formation of the superconducting phase. The size of grains was found to be dependent on the substrate material. In this work the largest grain size obtained in this laboratory was of about 400 μm when the sample was grown on silver foil, while smaller grains (about 200-300 μm) were obtained when using single crystal MgO or MgO covered by a thin silver layer of thicknesses between 0.5 to 1 μm. The silver layer on MgO was dissolved completely throughout the superconductor. Then, tiny colonies of the superconductor were observed outside the bulk tape of BSCCO. As pointed out, by Kase et al. (1991), Zhang et al. (1992), and Dimesso et al. (1992), silver plays an important role in grain alignment by lowering the melting point of the BSCCO sample and forming a highly textured microstructure. Grain size and their orientation also have a major effect in the determination of the critical current density, the transition temperature to the superconducting state, and the resistivity in the normal state. Figure (2) displays the resistivity and critical currents of two samples: one with grain size of about 300 μm, and the other of a size of about 100 μ m. Referring to figure (2), larger grains have lower resistivity in the normal state and igher critical current, Jc, and critical transition temperature, T_C, than do smaller grains.

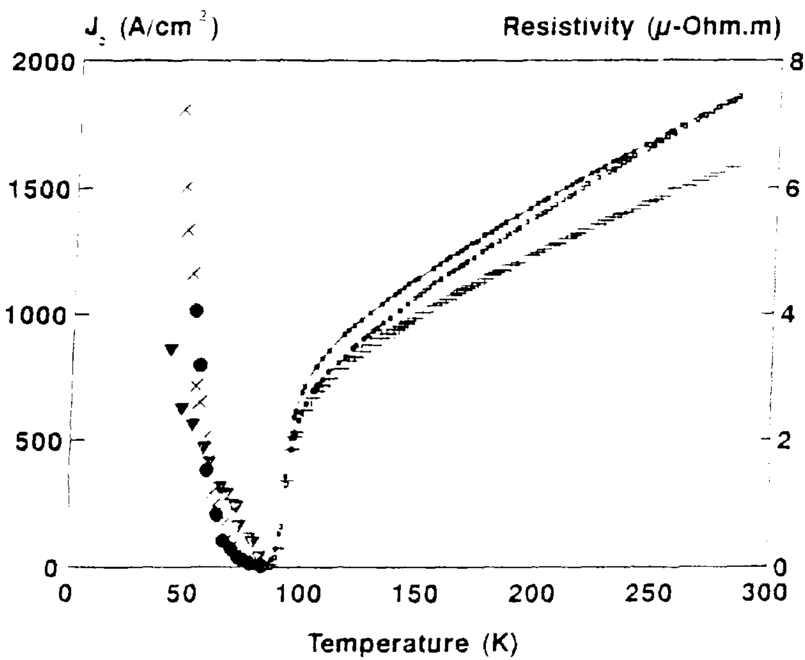
Figure 2



The concentration of second phases and grain boundaries are greater in samples with small grain size, hence suppressing the supercurrent in the superconducting state and increasing the resistivity of the sample in the normal state.

When the superconducting phase on a certain substrate was formed, it was found that the material of the substrate had a small or even negligible effect on the resistivity of the normal state, critical current density, and the transition temperature to the BSCCO (Bi-2212) superconducting phase. The resistivities and critical currents of three samples, grown under the same heat treatment conditions, and of almost equal grain sizes but different substrates, are shown in figure (3). Two samples were grown on single-crystal MgO, coated by 0.5-

Figure 3

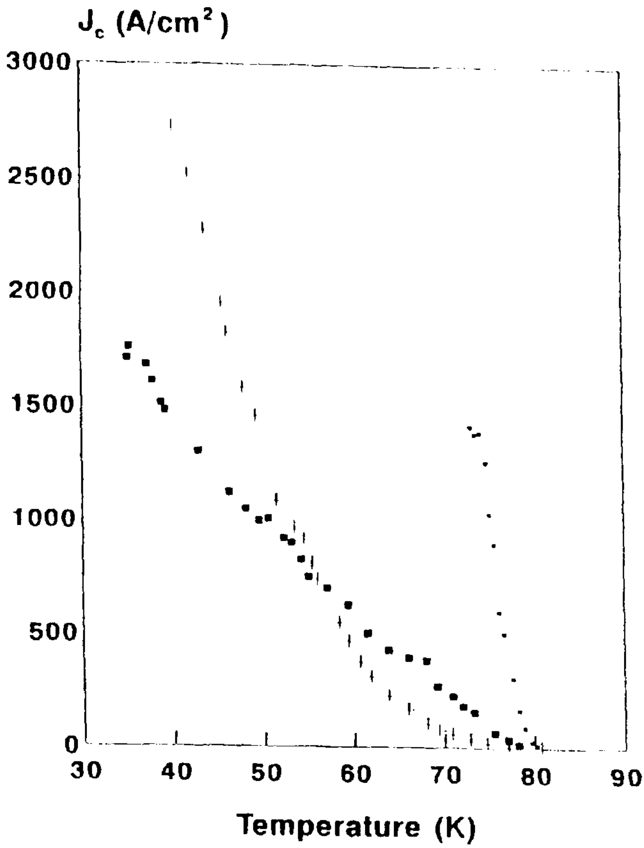


or 1-μm silver layer, the third was grown on only MgO. As can be seen in the figure, the resistivities of two of the samples are the same, and about 10% greater than the resistivity of the third sample. This difference is most probably due to other second phases and microcracks, rather than to the substrate type. By studying the effect of the heat treatment conditions on the properties of BSCCO thick films, Dimesso et al. (1992) confirmed that the presence of non-superconducting layers would weaken the links at the interface between grains and then degrade the superconducting properties. These non-superconducting layers were found to be effective in suppressing the supercurrent flowing in the sample. Also, the critical current density, J_c, values were found to depend on the microstructure in the core of the sample not on the film surface (Zhang et al. 1992). Their results clearly indicate that any microcracks or non-superconducing phase may greatly affect the resistivity of sample in the normal state. The transition temperatures and the critical current densities (see figure 3) are almost the same for those three samples as they should be. This implies that the critical current density and the transition temperature to the superconducting phase depend on the quality of the superconductor sample but not on the substrate material.

2- The effect of heat treatment.

The heat-treatment conditions have an important effect, not only on the electrical parameters of the sample, but also on the microstructure texturing of the specimen. Slow cooling (at the rate of 3 to 5 ° C/min) from the sintering temperature of 840 °C generates a low transition temperature [T(off-set) = 80 K], and a low critical current density, J_c. Quenching the specimen from 840 °C to room temperature drastically increases the electrical parameters of the superconductor, it results in a higher T_c = 89K, and higher J_c. In figure (4), the critical current densities of three samples are displayed. These samples were grown under different heat-treatment conditions. The critical current density of the superconductor was improved by

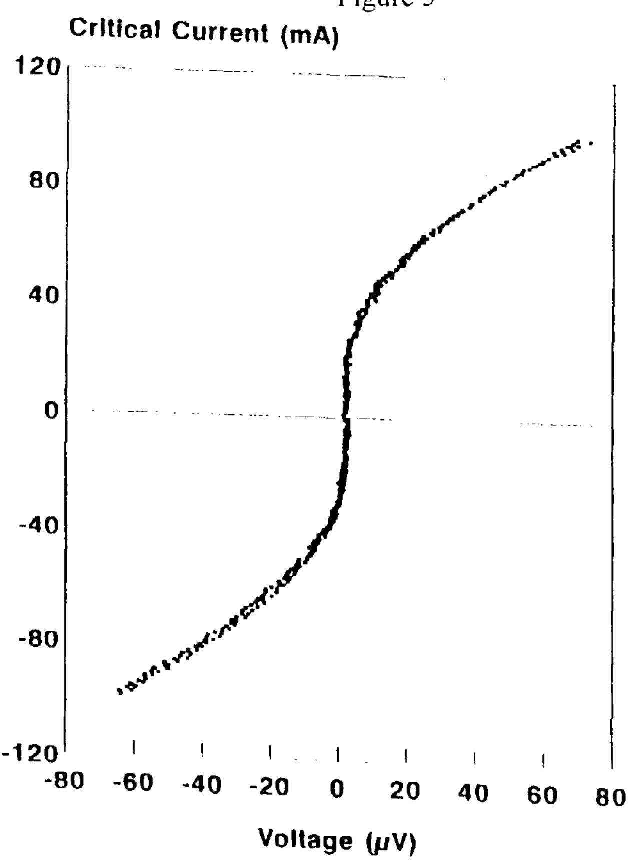
Figure 4



J_c (A/cm²)
3000
2500
2000
1500
1000
500
0
30
40
50
60
70
80
90
Temperature (K)

annealing the specimen in a nitrogen atmosphere at 500 to 600 °C. Annealing in nitrogen reduces the excess of oxygen content in the specimen, hence increasing both T_c and J_c (Noji et al. 1993, Dimesso et al 1992, Bock et al. 1991), also affecting the lattice parameters, especially the c-axis value (Dimesso et al. 1992, Maeda et al. 1989). In addition, it was found (Ishizuka et al. 1991) that the oxygen content could help in the crystalline orientation by controlling the flux of activated oxygen in preparing BSCCO thin films. As shown in figure (4), the highest critical current is obtained for a quenched then annealed sample, while the J_c of a slowly cooled sample is low; the latter .case was improved by annealing the superconductor sample in a nitrogen atmosphere. The critical current was determined from the current-voltage characteristics (IVC). A typical IVC curve for the Bi-2212 phase is shown in figure (5). The I_c of the sample was obtained by taking the average value at both ends of the curve when the voltage starts to develop across the sample. Analysis of different samples grown under various heat-treatment conditions showed that at a certain temperature, the critical current, I_c, depends on both grain size and heat-treatment conditions. Our results are in good qualitative agreement with other researchers' results on thin films and bulk BSCCO samples grown under various heat treatment conditions. The heat-treatment conditions, the annealing atmosphere, and the cooling

Figure 5



rate from 840 °C to room temperature were found to have great influence not only on T_c and J_c of thick BSCCO films, but also on the intergranular coupling of the sample (Noji et al. 1993, Dimesso et al. 1992, Shimoyama et al. 1992a). Ishizuka et al. (1991) also observed this phenomena was in thin BSCCO films prepared on $SrTiO_c$ substrates by coevaporation using a molecular beam epitaxy machine .

Summary and Conclusion

The electrical and thermal parameters of $Bi_2Sr_2CaCu_2O_x$ (Bi-2212) high temperature superconductor tapes, grown on silver foil, MgO single crystal or MgO covered by a thin layer of silver, were found to depend on the heat-treatment conditions and grain size. The resistivity of the normal state decreases with the increase of grain size and is independent of the substrate material when the superconducting phase is formed. Samples of large grains showed higher critical current densities and higher critical temperatures than did those of small grains. The critical current density and critical temperature could be improved by quenching the sample from the sintering temperature (840 °C) to room temperature, and then annealing it in a nitrogen atmosphere. Annealing in a nitrogen atmosphere helps in removing the excess of oxygen in the sample, hence affecting the lattice parameters. Some substrates were found not to be good ground for the formation of the superconducting BSCCO (Bi-2212) phase by partial melting of the sample at a temperature of 890 °C.

Acknowledgments

We would like to thank Dr. A. I. Kingon and Dr. C. C. Koch for allowing us to use the facilities of their laboratory in Materials Science and Engineering Department of North Carolina State University, and for their useful suggestions. Also, many thanks to Dr. G. Schindler and C. Sarma for their help in measurements, as well as useful discussions and critical comments and suggestions.

Figure Captions:

1- **Figure 1:** A typical heat treatment profile of BSCCO (2212) superconductor tape grown by partial melting on single crystal MgO r Ag/MgO.

2- **Figure 2:** Grain size effect on the resistivity of the normal state and the critical current of the superconducting state: + , R(T) for large grains; ■ , R(T) or small grains; ▲ , Jc(T) for large grains; and, * , c (T) for small grains.

3- **Figure 3:** Dependence of the resistivity of the normal state and the critical current on the substrate type: ▒ , R(T) for a sample on MgO; + , R(T) for a sample on 0.5-micron Ag layer on MgO; -■- , R(T) for a sample on 1- micron Ag layer on MgO; and, × , ▼ , ● the corresponding Jc(T) respectively.

4- **Figure 4:** The effect of heat treatment conditions on the critical current density of BSCCO tapes: ▪ Jc for a quenched then annealed sample in N2 atmosphere; Jc for a slowly cooled sample then annealed in N2 ; and, ▒ , Jc for a quenched sample.

5- **Figure 5:** A typical current-voltage characteristics (IVC) curve of SCCO tape at 77 K.

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