

Preparation of Bi-Pb-Sr-Ca-Cu-O Superconductors by the Spray Pyrolysis Method Using Ultrasonic Atomization Techniques

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The high T_c oxide superconductor of the Bi-Pb-Sr-Ca-Cu-O system was prepared by spray pyrolysis. X-ray diffraction patterns of the sample show a perfectly isolated 110 K phase. Superconducting transition with zero-resistance temperature at $T_c = 101$ K was achieved for a sample calcined at 850°C for 18 hr and sintered at the same temperature for 12 hr. The heat treatment time required to form the pure 110 K phase could be minimized by spray pyrolysis. The critical current density at 77 K in zero magnetic field was 528 A/cm². © 1990 Academic Press, Inc.

Introduction

The discovery of the high T_c oxide superconductor of the Y-Ba-Cu-O system (1) was soon followed by the discovery of superconductivity at 105 K in the Bi-Sr-Ca-Cu-O system (2). In the latter system, three superconducting phases with T_c at about 10, 80, and 110 K are known and great efforts (3, 4) have been made to obtain the pure 110 K phase. Takano *et al.* (5) succeeded in increasing the volume fraction of the 110 K phase by partial substitution of Pb for Bi in this system using a coprecipitation method. Escudero *et al.* (6) presented X-ray powder diffraction patterns of a 90% single phase bulk sample of the 110 K phase. Koyama *et al.* (7) reported that the pure 110 K phase was obtained by the code-

composition of metal nitrates and the solid reaction under low oxygen pressure. The pure 110 K phase was also obtained by a conventional solid state reaction in which the starting powders were calcined at 800–810°C for 12 hr, and then sintered at 870–880°C for 240 hr, in air (8). It has been known that the formation of the pure 110 K phase at a given temperature was influenced by the heat treatment time (5, 9).

This letter presents the results of a study in which the pure 110 K phase in the Bi-Pb-Sr-Ca-Cu-O system was obtained during a short time of heat treatment.

Experimental Procedure

A powder was prepared by the spray pyrolysis of metal nitrates. Details of the apparatus for spray pyrolysis were previously reported (10). High purity Bi₂O₃,

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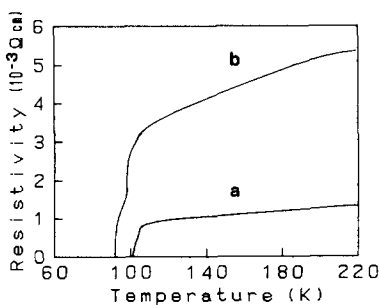


FIG. 1. Temperature dependences of the electrical resistivity. (a) Sample calcined at 850°C for 18 hr and sintered at the same temperature for 12 hr. (b) Sample sintered at 850°C for 30 hr without the process of calcination.

PbO, SrCO₃, CaCO₃, and CuO with the ratio Bi_{0.8}Pb_{0.2}Sr₁Ca₁Cu_{1.5}O_y were dissolved in dilute nitric acid with the aid of heat. This solution was atomized into fine droplets using an ultrasonic atomizer. The droplets were carried into the furnace maintained at 800°C with air; the flow rate of the air was about 5.5 cm/sec. The powder obtained was calcined at 850°C for various spans of time, thoroughly ground, and pressed into pellets at 40 MPa. The pellet samples were sintered at 850°C for various spans of time. All the heat treatments were conducted in air. After heat treatment, all the samples were air quenched.

Electrical resistance was measured as a function of temperature by a standard four-

probe technique on a slab sample 10 mm in length and 6 mm² in cross section cut from the sintered pellet. Sample contacts were made with silver paste.

A source current of 10 mA was used over the temperature range of 77–300 K. Critical current densities, J_c , were measured by a standard four-probe resistive method in a zero magnetic field.

The reaction process was measured by X-ray diffraction (Rigaku) with CuK α radiation.

Results and Discussion

Figure 1 shows the relation between resistivity and temperature for samples with different heat treatments. Sample (a) was calcined at 850°C for 18 hr, and then sintered at the same temperature for 12 hr. Sample (b) was sintered at the same temperature for 30 hr without the process of calcination. The normal state resistivity of sample (b) was about three times as large as that of sample (a). As the temperature is lowered, the resistances of samples (a) and (b) initially decreased almost linearly and deviated from linear behavior below the temperature of about 124 K. It can be recognized that sample (b) had two resistance drops at near 94 and 100 K, and zero resistance is obtained at 92 K. However, sample (a) had only one resistance drop at near 106 K, and zero resistance was obtained at 101 K. The critical current densities at 77 K in zero magnetic field of samples (a) and (b) were about 528 and 8 A/cm², respectively.

Figure 2 shows the variation of the critical current densities for the pellet samples calcined at 850°C for 18 hr and sintered at the same temperature for various spans of time. It is seen that the critical current densities when the sintering time varied from 1 to 12 hr increased slowly and almost linearly, and after reaching a maximum at about 12 hr ($J_c = 528$ A/cm²), J_c began to decrease rapidly.

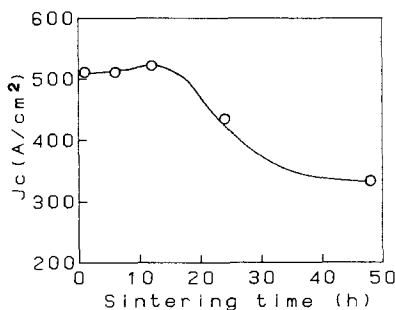


FIG. 2. Critical current densities versus sintering time for the pellet samples obtained by the spray pyrolysis method.

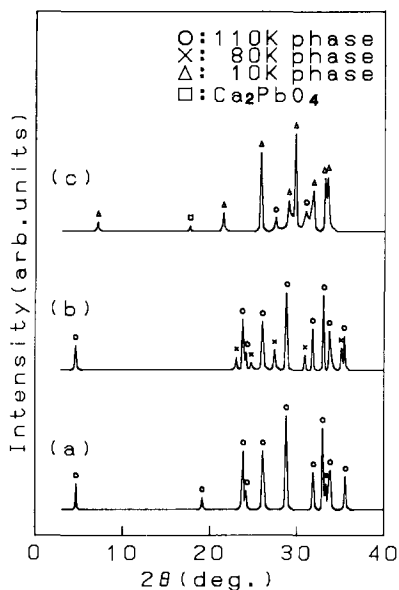


FIG. 3. X-ray powder diffraction patterns. (a) Sample calcined at 850°C for 18 hr and sintered at the same temperature for 12 hr. (b) Sample sintered at 850°C for 30 hr without the process of calcination. (c) Powder sample obtained by the spray pyrolysis.

Figure 3 shows the XRD patterns for samples (a), (b), and (c), where the circles, crosses, and triangles indicate the peaks due to the 110 K phase, the 80 K phase, and the 10 K phase, respectively. Sample (c) was powder spray-pyrolyzed at 800°C, in which the mixed XRD peaks of the 10 K phase and the 80 K phase were detected. However, the major superconducting phase is the 10 K phase. Sample (b) was sintered at 850°C for 30 hr, without the process of calcination. The results show that the peak intensity of the 110 K phase is much greater than that of the 80 K phase. Sample (a) was calcined at 850°C for 18 hr, and then sintered at the same temperature for 12 hr. It is

noteworthy that all the peaks observed in this sample were attributed to the 110 K phase.

The heat treatment required to form the pure 110 K phase can be minimized by using the spray pyrolysis method. It is much shorter than those reported by other groups using different methods (8, 9, 11). A possible reason may be the fact that the starting powder spray-pyrolyzed using ultrasonic atomization techniques could be mixed uniformly.

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