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Preparation of the $Bi_{1.8}Pb_{0.4}Ca_2Sr_2Cu_3O_y$ Superconductor with a Citrate Precursor Method

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The $Bi_{1.8}Pb_{0.4}Ca_2Sr_2Cu_3O_y$ superconductor is prepared by a citrate precursor method. Nitrate salts of the constituent metals are dissolved in deionized water, and citric acid and ethylene glycol are added. The pH of the solution is adjusted to 6.8. The solution is then dried at 80°C, pyrolyzed at 200°C, calcined at 810°C, pressed into pellets and sintered at 860°C for 20 min, and lowered to 850°C for different periods and cooling in the furnace or quenching in the air. The highest $T_{c(zero)}$ is 114 K, observed in a sample which is sintered for 24 hr and resintered for 96 hr with furnace cooling. The X-ray diffraction pattern shows that it contains 95% high T_c phase of $Bi_{2-x}Pb_xCa_2Sr_2Cu_3O_y$ superconductor.

INTRODUCTION

Maeda *et al.* have discovered the first non-rare-earth-containing superconductor in the Bi–Ca–Sr–Cu–O system (1) where two superconducting phases are identified, a low T_c phase of $Bi_2CaSr_2Cu_2O_{8+\delta}$ (abbreviated as 2122) and a high T_c phase of $Bi_2Ca_2Sr_2Cu_3O_{10+\delta}$ (abbreviated as 2223) (2). However, it is very difficult to obtain a pure 2223 phase with the stoichiometric amount of Bi–Ca–Sr–Cu–O mixture (3). With the partial substitution of the PbO for Bi_2O_3 (4), sintering in the reduced oxygen partial pressure (5), or modification of starting nominal composition with excess Ca and Cu (6), the formation of 2223 is accelerated.

High T_c oxide superconductors are usually prepared by the solid state reaction method. Due to the inhomogeneity of the reactant mixture, repeated grinding and heat treatment are needed to accelerate the reaction. In general, single phase 2223 can only be prepared by prolonged heat treatment for several days (7). Recently, Pandey *et al.* (8) prepared the 2223 single phase (free from 2021 and 2122 phases) in 48-hr heat treatment using a semiwet route with a stoichiometric composition, $Bi_{1.6}Pb_{0.4}Ca_2Sr_2Cu_3O_y$, but no T_c was reported. Using the same method, they also obtained a sample with $T_{c(zero)} = 120$ K, but which contained a large quantity of 2122 and 2021 phases (9). Interestingly, a sample containing more than 90% of 2223 phase with stoichiometric composition has a sharp fall around 120 K in the resistivity measurement (10). However, the transition has a tail with $T_{c(zero)}$ at 112 K. It seems that their sample contains two superconducting phases. The high T_c and high purity are not easy to attain simultaneously by using the semiwet method.

In our laboratory, a citrate precursor method has been employed in preparing the 2122 (11) phase. Owing to the homogeneity of this method, with 12-hr heat treatment, we have successfully obtained a record high $T_{c(zero)}$ of 95 K in the single phase 2122 sample (12). We have also reported a T_c of 106 K in a sample with a stoichiometric nominal composition of $Bi_{1.7}Pb_{0.3}Ca_2Sr_2Cu_3O_{10+d}$ which is prepared by the same method with only 8-hr calcination and 24-hr sintering (13). We believe that the citrate precursor method is a valuable route in preparing high T_c superconductors. Nevertheless, Chen and Hu (14) adopt the same method to obtain 2223 phase superconductors with $T_{c(zero)} < 100$ K. In this paper, we report a nearly single phase 2223 with $T_{c(zero)} = 114$ K using the citrate precursor method.

EXPERIMENTAL

The 2223 superconductors were prepared by a citrate precursor method which was basically the same as previously reported (11). All chemicals used were of reagent grade. The molar ratio of Bi : Pb : Ca : Sr : Cu was 1.8 : 0.40 : 2.0 : 2.0 : 3.0. $Bi(NO_3)_3 \cdot 5H_2O$ (3.49 g, 7.20 mmole) was first dissolved in 0.5 ml concentrated nitric acid. $Pb(NO_3)_2$ (0.53 g), $Ca(NO_3)_2 \cdot 4H_2O$ (1.89 g), $Sr(NO_3)_2$ (1.69 g), and $Cu(NO_3)_2 \cdot 3H_2O$ (2.90 g) were then added and dissolved together in 20 ml deionized water. 11.60 g citric acid (CA) and 5.14 ml ethylene glycol (EG) were added and dissolved in the nitrate solution. The molar ratio of CA/metal ions was 1.50 and that of EG/metal ions was 2.50. The pH value of the citrate solution was adjusted to 6.8 by adding an appropriate amount of ammonia water or triethylamine. The solution was then

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heated and stirred at 80°C for 2–3 hr in order to form a blue viscous mixture, and then pyrolyzed at 200°C for 0.5 hr to decompose the organic constituents and inorganic salts. At such temperature, spontaneous combustion was initiated by the nitrate salts. The deep-grey residue consisted of homogeneous flakes with very fine particles. The residue was precalcined in a furnace for 20 min at 500°C. The reaction mixture was ground and calcined at 810°C for 8 hr with one intermittent grinding. It was then pressed into pellets at a pressure of 5.2 kbar, and sintered at 860°C for 20 min; then the temperature was lowered to 850°C for different periods, from 24 to 264 hr. Some of the samples were ground and resintered again for different periods. The samples were either quenched in air or cooled in the furnace. The cation concentration was analyzed by the inductively coupled plasma–atomic emission spectroscopy (ICP–AES).

The X-ray diffraction pattern was obtained by a rotating anode Rigaku Diffractometer with CuK_α radiation. We chose the intensity ratio of the (00*10*) diffraction of 2223 phase at 24.0° to the (008) diffraction of 2122 phase at 23.2° as a standard for the determination of the ratio of these two phases. Due to the preferred orientation found in the *c*-axis on the 2223 pellet, which is stronger than that in the 2122 phase, we took the XRD patterns on the powdered samples instead of the sintered pellets. We believe that the intensity ratio calculated in this way was more reliable.

The electrical resistivity was measured by the standard four-probe method. A rectangular-shaped sample was cooled in a closed cycle refrigerator and its temperature was measured by a silicon diode sensor near the sample. The magnetic susceptibility was measured by a Quantum Design SQUID Magnetometor with a field of 20 Oe between 5 and 120 K.

TABLE 1

Sintering Conditions and the $T_{c(zero)}$ of the 2223 Superconductor

Sintering (hr)	Cooling[a]	Resintering (hr)	Cooling	$T_{c(zero)}$ (K)
24	Q			88
24	F			101
24	Q	72	F	106
24	F	72	F	108
24	F	96	F	114
48	F			101
48	F	240	F	113
72	F			103
96	Q			103
96	F			105
120	F			108
264	F			111

[a] F, furnace cooling; Q, air quenching.

RESULTS AND DISCUSSION

We have tried to sinter the 2223 compound with different periods and to cool the samples by either furnace cooling or quenching in air in order to find better processing conditions. The $T_{c(zero)}$ of twelve samples with different sintering periods is listed in Table 1. It is clear that a furnace-cooled sample has a higher T_c than an air-quenched one regardless of whether the sintering period is 24 or 96 hr. Comparing the T_c with the sintering period, it is found that the longer the sintering period is, the higher the T_c is. This suggests that the amount of the high T_c phase existing in these samples increases with the sintering period. In addition, resintering the sample accelerates the formation of the 2223 phase. For example, a sample sintered for 96 hr has a T_c at 105 K, but another sample sintered for 24 hr and resintered for 72 hr has a T_c at 108 K. Similar results are also found in other samples sintered for 120 hr. The highest $T_{c(zero)}$ at 114 K is found in the sample which is sintered for 24 hr and resintered for 96 hr. In conclusion, furnace cooling and resintering the samples result in a higher T_c.

The X-ray powder diffraction pattern of the 114-K sample is shown in Fig. 1. Examining the small angle diffractions, there is no (002) reflection at 5.75° belonging to the 2122 phase, but a small (002) peak at 7.14° belonging to the 2021 phase is observed. Also, a few diffraction peaks attributed to the 2122 phase are clearly present. These are marked "×" on the top of the peaks. From the intensity ratio of (00*10*) diffraction of 2223 with (008) diffraction of 2122, about 95% of the high T_c phase is obtained in this 114 K sample.

The temperature-dependent magnetic susceptibility of the 114-K sample is plotted in Fig. 2 with a field of 20 Oe. Only one superconducting transition is observed, though a small amount of the low T_c phase is detected by the XRD, which cannot be clearly seen in this figure. Because the sample is ground into powder for measurement, the magnetic moment of the field cooled (FC) and zero field cooled (ZFC) curves are quite close together due to the disappearance of the super current produced by the intergrain boundary or the destruction of the flux pinning in the powdered sample.

The temperature-dependent resistivity of the 114-K sample is plotted in Fig. 3. Only one superconducting transition is observed. A linear dependence of the resistivity vs temperature is observed before the superconducting transition occurs. It has a quite small room temperature resistivity of 1.01 mΩ-cm and a large resistivity ratio, ρ_{290}/ρ_{150} of 1.60 among the high-T_c superconductors. The $T_{c(onset)}$, $T_{c(zero)}$, and ΔT_c are 122, 114, and 6 K, respectively. The transition width, ΔT_c, is large in comparison with the $YBa_2Cu_3O_{7-x}$ compound, for which ΔT_c is 1–2

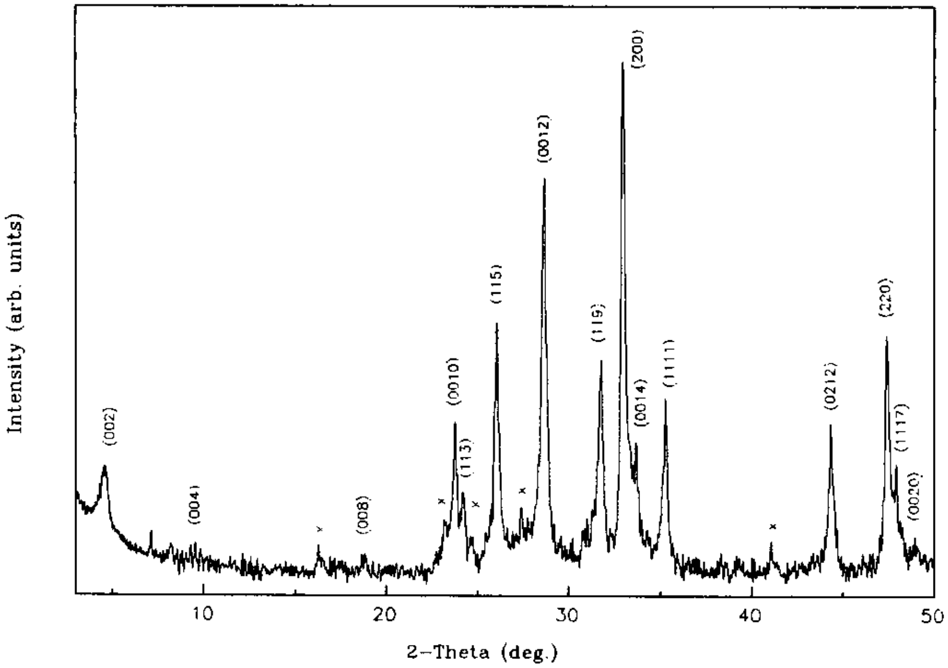

FIG. 1. XRD of the 114-K $Bi_{1.8}Pb_{0.4}Ca_2Sr_2Cu_3O_y$ powder; "×" is marked on the top of peaks belonging to 2122 and 2121 phases.

K. This may be caused by the existence of the impurities and other factors.

A zero resistivity of 122 K with a nonstoichiometric nominal composition of $Bi_{1.6}Pb_{0.535}Ca_{2.675}Sr_{2.675}Cu_3O_y$ is prepared by Pandey *et al.* (15) via a semiwet route using $Pb_{0.2}CaSr(CO_3)_{2.2}$ as a precursor. It is probably the highest $T_{c(zero)}$ reported in the 2223 phase without antimony. Although T_c is high, they obtain more 2122 than 2223 phase in their sample, as well as other impurities. A zero resistivity of 116-K sample with a nominal composition of

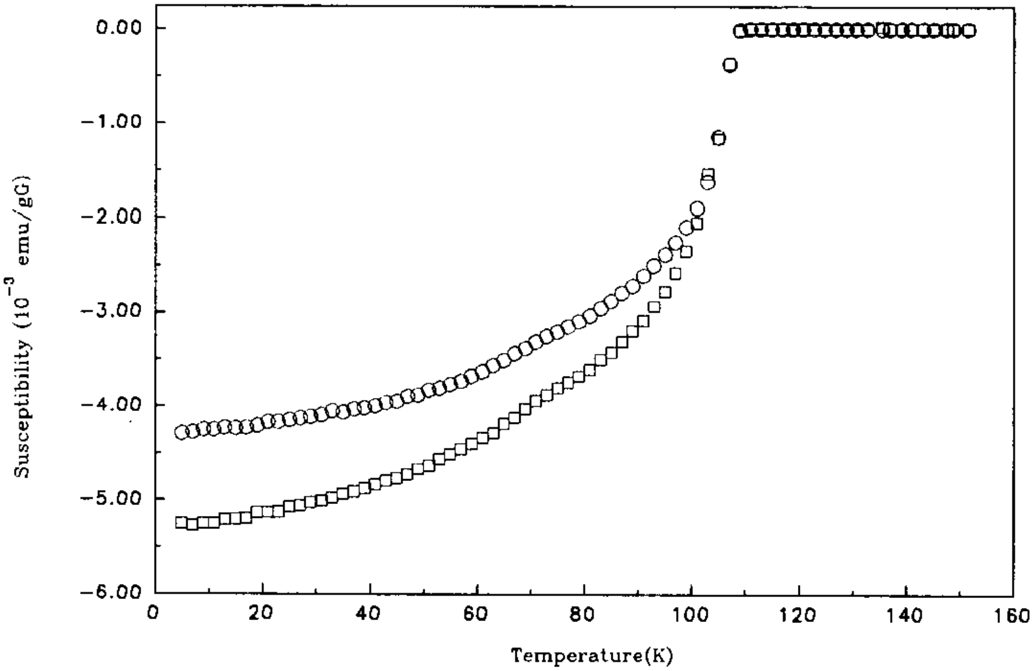

FIG. 2. Temperature-dependent magnetic moment of the 114-K $Bi_{1.8}Pb_{0.4}Ca_2Sr_2Cu_3O_y$ (○) for FC and (□) for ZFC.

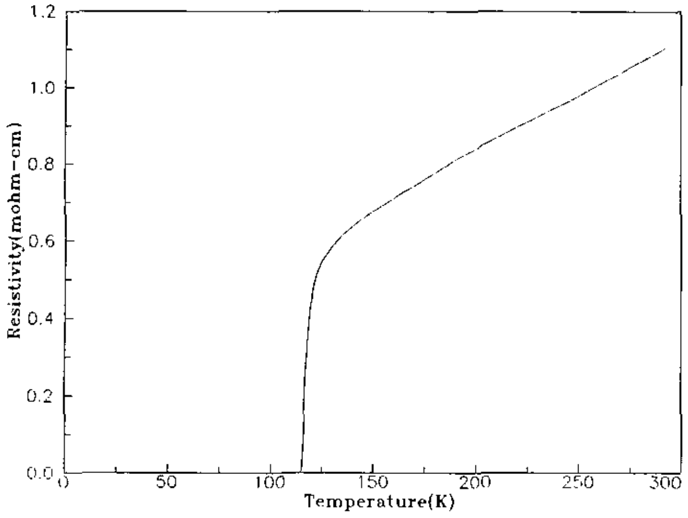

FIG. 3. Temperature-dependent resistivity of the 114-K $Bi_{1.8}Pb_{0.4}Ca_2Sr_2Cu_3O_y$.

$Bi_{1.546}Pb_{0.864}Ca_2Sr_2Cu_{3.4}O_y$ is reported by Takada *et al.* (16), in which a small amount of 2122 phase is observed. Takada *et al.* believe that a starting composition of Pb/(Bi+Pb) $\geq$ 0.30 is required for obtaining high T_c. Again, large deviation of starting composition is employed in the preparation of the 2223 phase. The existence of the unwanted impurities may cause unexpected problems in many application cases. Obviously, the T_c of the 2223 phase is dependent on the starting composition, and the exceptional high T_c is found in the off-stoichiometry samples. In order to avoid the unwanted impurities presented with the superconducting phase, it is better to keep the composition as close to the 2223 as possible.

A report by Chen and Hu (14) on the starting composition of $Bi_{1.5}Pb_{0.5}Ca_2Sr_2Cu_3O_y$ had a $T_{c(zero)} < 100$ K prepared with the same method as ours. The low T_c found by them is probably due to the following reasons: The volatility of the PbO that causes the shortage of the Pb is not accounted for. The sintering period is too short to have a higher T_c value. The sample is sintered in the flowing oxygen, which is not recommended for the synthesis of the 2223 phase (17). We have found that an appropriate amount of oxygen stoichiometry optimizes the T_c of the 2223 phase (18). Synthesis of the 2223 superconductor in the oxygen atmosphere probably intercalated too much oxygen to obtain the high T_c.

In our experiment, the total starting composition of Bi and Pb is 2.20. From the analysis by the ICP–AES on the 114-K sample, we find the molar ratio of Bi : Pb : Ca : Sr : Cu = 1.79 : 0.28 : 2.00 : 2.01 : 3.00. Thus, 30% of the Pb is vaporized during the preparation. In comparison, a $T_{c(zero)}$ of 107 K with a composition of Bi : Pb : Ca : Sr : Cu = 1.80 : 0.20 : 2.20 : 1.90 : 3.00, very close to that of our starting material, is reported by Donnelly *et al.* (19). This is prepared by the solid state reaction method, with a 200 hr-sintering period. Its T_c is still lower than ours.

In this report, we demonstrate the polymeric CA/EG-derived precursor method as a valuable method in preparation of the 2223 superconducting phase with high purity and high T_c.

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