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An Improved Coprecipitation Method for Preparation of Superconducting Bi,Pb-Sr-Ca-Cu-O Material

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Superconducting Bi,Pb-Sr-Ca-Cu-O material has been prepared by an improved coprecipitation method; mixed metal oxalates as the precursor were precipitated from a homogeneous acetic acid solution of the constituent metal acetates and dimethyl oxalate. This method permits easier fabrication of the superconducting material which is almost free from low-Tc phase.

The preparation methods of high-Tc superconducting oxides have been extensively investigated, since superconducting properties such as transition temperature, critical current density, and percent flux expulsion in oxide superconductors depend sensitively on their preparative method parameters. Superconducting Bi,Pb-Sr-Ca-Cu-O material has been usually prepared by the conventional solid-state reactions of the mixtures of either the constituent metal oxides/carbonates.[1] However, this method necessitates repeated sintering-grinding operations, but it is nevertheless difficult to prepare chemically homogeneous material. In such circumstances, particular attention has been paid to the other methods such as coprecipitation of the oxalates of the constituent metal ions from solution[2,3] and co-decomposition of nitrates of those.[4] These methods can give a more homogeneous mixture accompanied by an improvement in superconducting properties. But, some problems still remain. In the oxalate coprecipitation method, aqueous oxalic acid or ammonium oxalate solution as a precipitating reagent has been added dropwise into an aqueous nitric acid solution containing the constituent metal nitrates, followed by calcining and sintering(designated as OC

method). However, a material having a stoichiometric composition could hardly be obtained without sophisticated modification such as adjustment of the final pH and/or the initial metal composition, addition of organic compounds, etc., because certain metal oxalates have moderate solubilities in the nitric acid solution and hence remain partially in the filtrate. To overcome these difficulties, we have developed an alternative coprecipitation method using metal acetates dissolved in acetic acid solution and aqueous dimethyl oxalate solution instead of the solutions of the metal nitrates and oxalic acid described above(designated as DMOC method). The present paper describes the improved coprecipitation technique and some superconducting properties of the samples of the Bi,Pb-Sr-Ca-Cu-O system.

The samples by the DMOC method were prepared as follows. $Bi(NO_3)_3 \cdot 5H_2O$, $Sr(CH_3COO)_2 \cdot 1/2H_2O$, $Ca(CH_3COO)_2 \cdot H_2O$, $Cu(CH_3COO)_2 \cdot H_2O$, and $Pb(CH_3COO)_2 \cdot 3H_2O$ were dissolved in 250 ml of 41% acetic acid solution in this order so as to reach a mole ratio of Bi:Sr:Ca:Cu:Pb = 0.016:0.020:0.020:0.030:0.004(solution A). As a source of Bi-compound $Bi(NO_3)_3 \cdot 5H_2O$ was used since chemically pure grade bismuth acetate was not obtained. Separately, 17.7 g of dimethyl oxalate was dissolved in 150 ml of distilled water(solution B). After adding the solution B to the solution A, the resultant solution was stirred for 1 week at room temperature till a complete precipitation occurred. Then this solution was filtered without any pH adjustment, washed by distilled water, and dried at 120 °C for 12 h. The precursor thus obtained was calcined at 500 °C for 5 h. The calcined mass was ground, pelletized (10 mm in diameter and 2 mm in thickness), sintered at 835 °C in air for 12 h, and then cooled at the rate of 2.8 °C/min to room temperature(this sample is denoted as DMOC-1). Since the details of the OC method,[2,3] especially of the coprecipitation conditions have not been reported, the following procedure was attempted. 150 ml of 9.1% aqueous oxalic acid solution was added to 150 ml of 13% nitric acid solution containing the same amounts of the corresponding metal nitrates as mentioned above. Normally the final pH was adjusted by using ammonia water. Subsequently, each resultant precipitate was treated in the same manner as described above. Structural characterization of sintered mass was carried out by X-ray diffraction and SEM studies. The compositions of the sintered mass and the corresponding filtrates were determined by atomic absorption spectroscopic analysis.

The chemical composition(Table 1) of the DMOC-1 was substantially coincident with that of the starting solution, but the OC samples showed non-stoichiometric

Table 1. Composition of samples[a] and property of the corresponding filtrates

Sample	Filtrate		Atomic ratio of sample				
	pH	Color	Bi	Pb	Sr	Ca	Cu
DMOC-1	0.9	colorless	1.69	0.38	1.88	1.97	3.00
OC-1-1	5.7[b]	blue	2.82	0.63	3.23	2.65	3.00
OC-1-2	3.6[b]	blue	1.94	0.48	2.38	2.42	3.00
OC-1-3	0.1	colorless	1.61	0.37	0.85	0.75	3.00
Nominal composition			1.60	0.40	2.00	2.00	3.00

a) Normalized for Cu as 3.00. b) After pH adjustment.

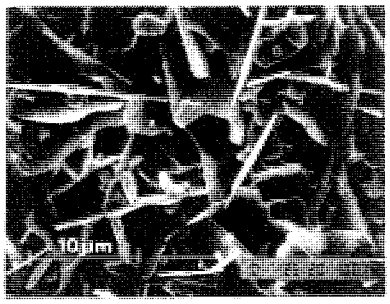

Fig. 1. SEM of DMOC-1 disk.

compositions. Thus, the two wet-chemical processes did not lead to the same result. This discrepancy will arise from the differences of solubilities of each precipitate(metal oxalates) in each mother liquor. The filtrates corresponding to OC-1-1 and OC-1-2 were bluish in color, indicating incomplete precipitation of at least Cu^{2+}. In the case of OC-1-3 Cu^{2+} and Bi^{3+} precipitated completely but the other metal ions, particularly Sr^{2+} and Ca^{2+}, incompletely. On the other hand, the filtrate corresponding to the DMOC-1 was colorless. The proportion(mol%) of each metal ion in the filtrate was as follows: Bi 0.0, Pb 0.0, Sr 10.2, Ca 1.2, and Cu 0.3. This result clearly indicates that in the DMOC method most of metal oxalates are scarcely soluble in the acetic acid solution. In fact the filtrate produced no precipitate, even if its portion was mixed with aqueous oxalic acid solution. In addition, in the case of the OC method the precipitation occurred immediately each time oxalic acid solution was added by portions whereas in the DMOC method it occurred gradually 5-10 min later depending upon the temperature of the solution. The latter precipitation behavior suggests that the coprecipitation from the homogeneous solution can occur simultaneously everywhere, where coexisting uniformly-dissolved dimethyl oxalate produces oxalic acid and methanol as a result of its controlled hydrolysis. Methanol may also participate in the precipitation like ethanol in $YBa_2Cu_3O_{7-x}$ superconductor.[5] The presence of the Meissner-Ochsenfeld effect was demonstrated for the DMOC-1 but not for the OC samples. For the latter samples sintering time of 12 h may be too short for this effect to occur. A scanning electron micrograph of the DMOC-1 disk is shown in Fig. 1. Thin leaves of crystals, which are characteristic for the Bi,Pb-Sr-Ca-Cu-O system, are observed.

As seen from Fig. 2, the X-ray diffraction pattern of powdered DMOC-1 reveals the presence of at least two different phases; the dominating phase was identified as high-Tc phase(e.g. 2θ = 4.7 deg), and the diffraction lines of another phases as

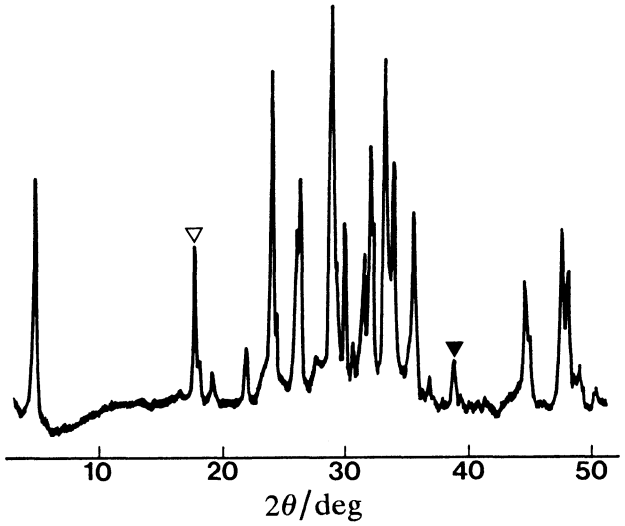

Fig. 2. X-Ray powder diffraction pattern of DMOC-1. ▽: Ca_2PbO_4, ▼: CuO

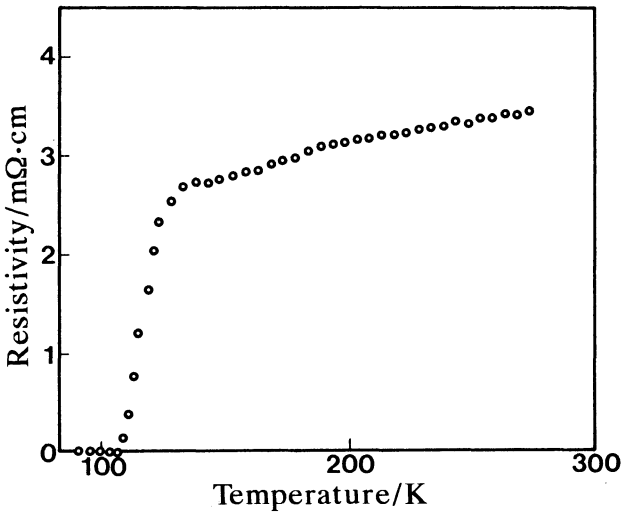

Fig. 3. Temperature dependence of the resistivity of DMOC-1.

Ca_2PbO_4 and CuO. It should be noted that the formation of low-Tc phase(e.g. 2θ = 5.7 deg) was successfully suppressed by sintering for only 12 h. The X-ray profile due to Ca_2PbO_4 disappeared when the amount of Pb in the starting solution was reduced to one-half(not shown). The temperature variation of the resistivity of the DMOC-1 was also examined by using alternative current of 3 mA. As seen in Fig. 3, the temperature at which zero resistance state is attained was 108 K.

In conclusion, the improved coprecipitation procedure permits easier preparation of superconducting Bi,Pb-Sr-Ca-Cu-O compounds with a predominant fraction of high-Tc phase, a considerable reduction in sintering time, and the avoidance of repetitive sintering-grinding operations.

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