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Preparation of high-T_c superconducting film in the system of Bi–Sr–Ca–Cu–O from sol–gel process and its properties

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High-T_c superconducting $Bi_2Sr_2CaCu_2O_x$ films with $T_c^{off} = 80$ K were prepared by the dipping method of sol–gel processing using inorganic salts. The influence of the preparation conditions on the superconducting properties of the derived material is reviewed. Bi, Sr, Ca and Cu nitrates were used as raw materials. Glycerol was used as solvent. The thickness of films made by the dip method was about 0.5 μm. The films were crystallized by heat-treatment at 830 °C for 10 min. T_c^{off} of the films was 80 K and J_c at 77 K was more than 8 kA cm^{-2}. Synthesis of high-T_c superconducting films was very easy and the crystallization of films was possible with a relatively low heat-treatment temperature.

1. Introduction

$BiSrCaCu_{1.5}O_x$ (BSCCO) high-T_c oxides having T_c (end) = 105 K have been reported in many independent investigations [1–3]. Furthermore, the following favourable points have been established: apparent durability against humid atmosphere, insensitivity to the concentration of oxygen defects, and no need for rare-earth elements.

In recent years the sol–gel process, based on the polycondensation and other reactions of metal alkoxides and/or reactive metal salts, has been widely hailed as an important new process for the preparation of glasses and ceramics [4]. The sol–gel process permits the preparation of glasses or ceramics [5] at relatively low temperature and hence their compositions are more controllable.

It is well known that a Josephson device with submicrometre dimensions has great potential for electronic devices with ultrafast logic operation (~ 1 ps) [6]. In this case, film preparation by the dipping method is a very useful technique for preparing BSCCO as electronics devices. The influence of the starting material on superconduction properties is a very important factor and the superconducting transition temperature significantly depends on the preparation conditions. Preparation by the sol–gel process consists basically of three steps: elimination of water, solvent and metal oxygen interaction by condensation, and formation of high-T_c crystal phase [7].

2. Experimental procedure

Fig. 1 shows the flow sheet in the system BSCCO = 2:2:1:2. Bi, Sr, Ca and Cu nitrates were used as raw materials. Each nitrate salt was weighed so as to give Bi:Sr:Ca:Cu = 2:2:1:2 in molar ratio [8, 9] and dissolved into a solvent such as ethylene glycol, glycerol or diethylene glycol. The concentration of each nitrate was approximately 0.02 M. After being mixed, they were stirred for 1 h at room temperature. The starting solution was then divided in two: one solution was heated at 250 °C, and then the powders obtained were pressed and annealed at 800 to 870 °C in air in an electric furnace. After annealing for 48 h, each specimen was prepared by three different cooling conditions; in liquid nitrogen, in air, and in the furnace from 850 °C.

On the other hand, thin films were prepared by dipping into the solution of substrate. Yttria-stabilized zirconia (YSZ) was used as substrate. The substrates were cleaned with ethyl alcohol and acetone before the experiments.

The films and sintered bodies obtained were completely black in colour. The temperature dependence of resistance was measured by the four-point probe technique under a constant d.c. current with a digital voltmeter of 1 μV resolution. The d.c. current applied was dependent on the d.c. resistance of the sample. For instance, 3.0 mA was applied for the samples prepared from pellets, and 1.0 mA was applied for the samples prepared from thin films. The separations of electrodes were approximately 1 and 3 mm, respectively. The resistivity at each temperature was measured for two opposite current directions after the time-differentials of temperature and resistivity for the samples fell to zero. The superconducting transition curves were obtained from both the raising and decreasing temperature processes, and the mean values were taken as the experimental results.

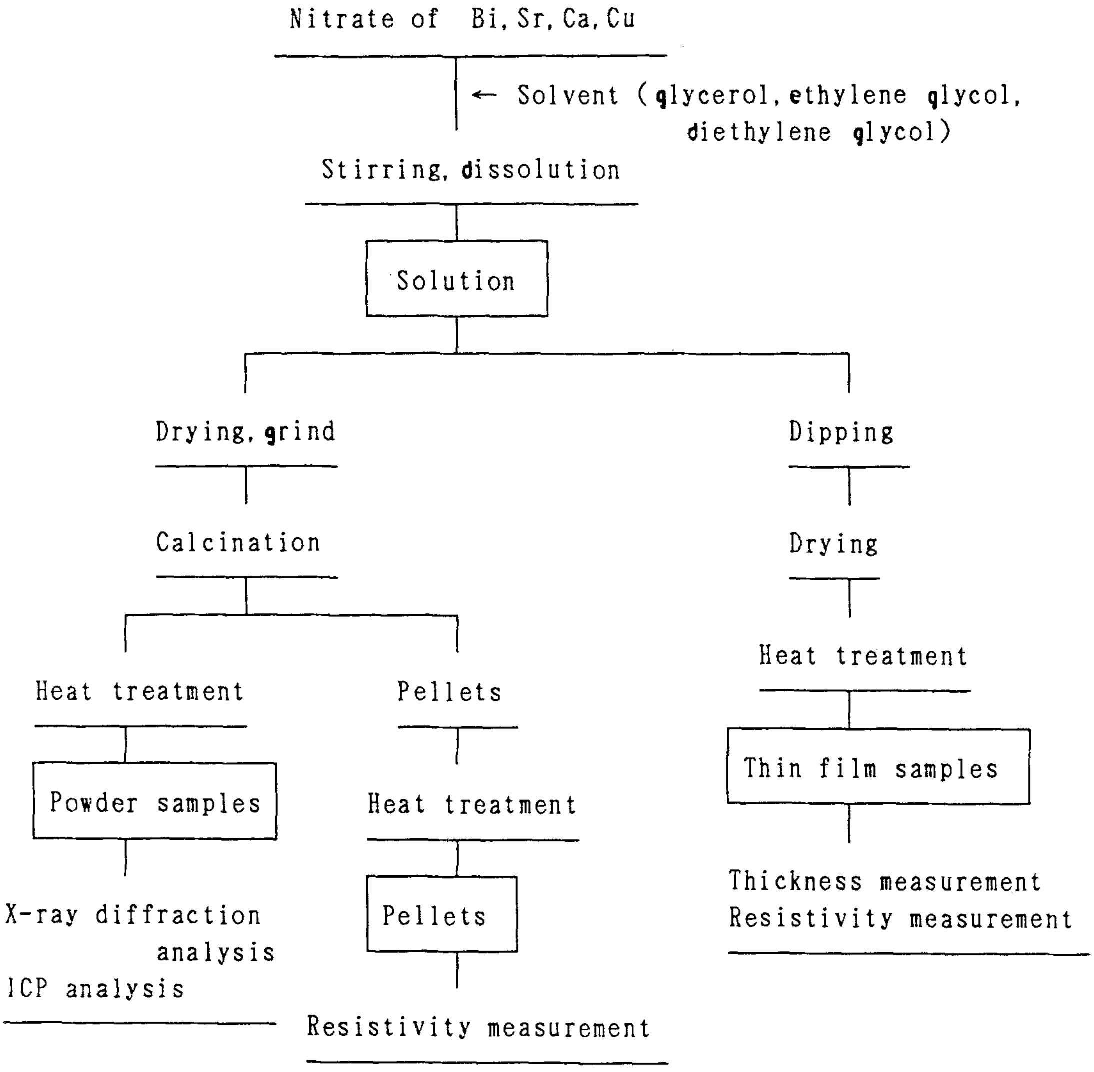

Figure 1 Flow sheet.

3. Results and discussion

Fig. 2 shows thermogravimetric analysis (TGA) and differential thermal analysis (DTA) results for $Bi_2Sr_2Ca_1Cu_2O_x$. Three steps in decreasing weight can be seen in this figure. The first and second decreases were partially overlapped with each other from 350 to 450 °C. The third step of the decrease began at 480 °C and finished at 530 °C. From this figure, the first, second and third falls seem to correspond to the successive pyrolysis of BSCCO. The DTA curve obtained was quite complicated. A sharp exothermic peak at 470 °C followed the three exothermic peaks which started from nearly 300 °C, and a broad exothermic peak appeared at 570 °C. This broad and large exothermic peak is mostly attributed to oxidation.

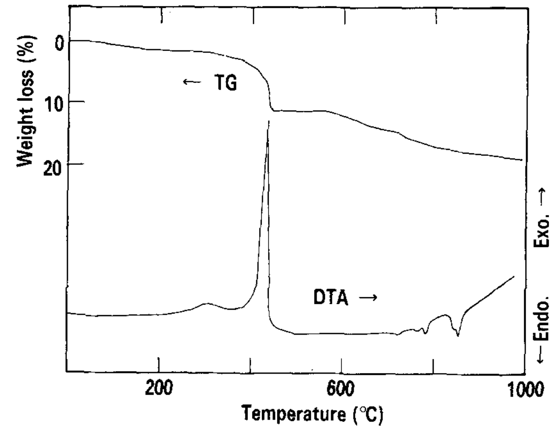

Figure 2 DTA and TG in the system $Bi_2Sr_2Ca_1Cu_2O_x$ dried at 300 °C for 2 h. Glycerol was used as solvent.

Fig. 3 shows XRD patterns for the BSCCO = 2:2:1:2 system prepared by the sol–gel process, heat-treated at 750 to 870 °C for 24 h. The peaks due to high-T_c (80 K) Bi–Sr–Ca–Cu–O crystal phase were seen. From the XRD results it can be concluded that approximately 800 °C annealing in air was necessary to form the superconducting crystal as the main phase. However, CaBiO impurity phase was precipitated by heat-treatment above 870 °C.

Fig. 4 shows XRD patterns for samples heat-treated at 850 °C for 24 to 96 h. The superconducting phase was observed for each heat-treatment time, but CaBiO was precipitated by heat-treatment for longer than 72 h.

Fig. 5 shows the changes of XRD intensity for different cooling conditions in samples heat-treated at 850 °C for 48 h. The highest value of T_c was obtained in the specimen quenched from 850 °C to liquid

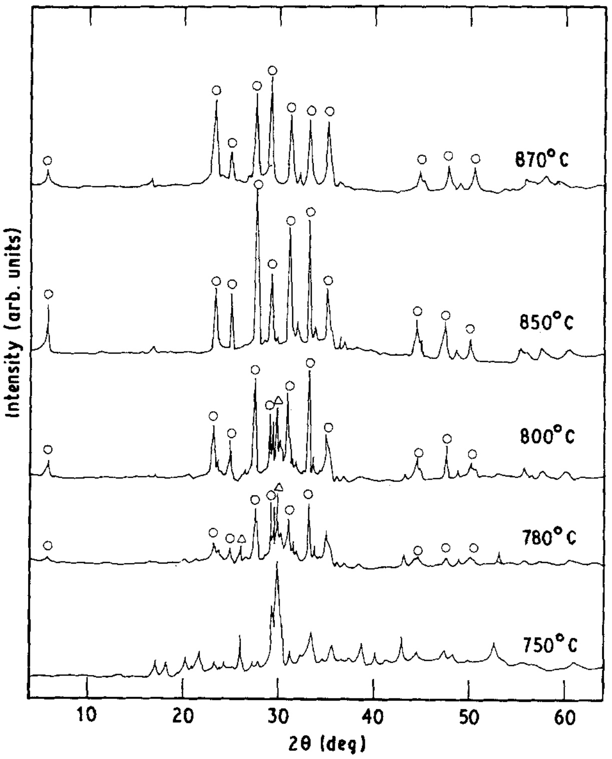

Figure 3 X-ray diffraction patterns (CuK_α) in the $Bi_2Sr_2Ca_1Cu_2O_x$ system heat-treated at different temperatures for 24 h. (○) 80 K, (△) impurity.

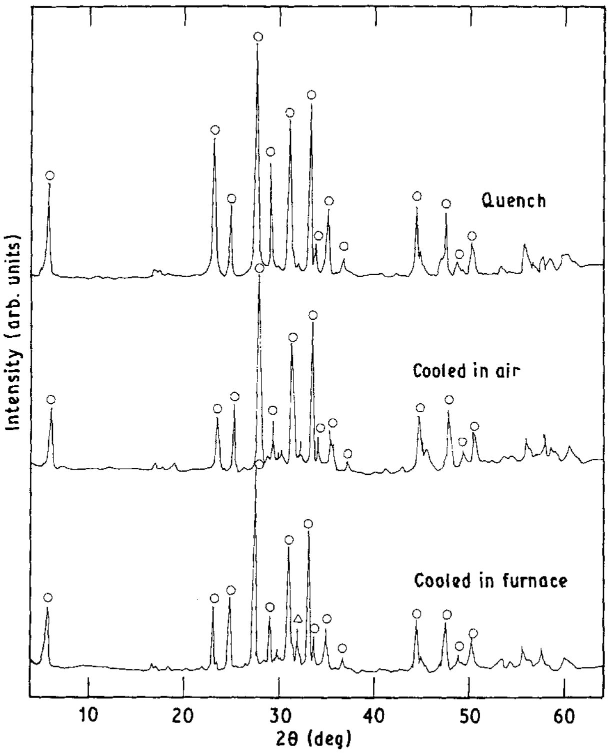

Figure 5 Changes of X-ray diffraction intensity (CuK_α) for different cooling conditions in the $Bi_2Sr_2Ca_1Cu_2O_x$ system heat-treated at 850 °C for 48 h. (○) 80 K, (△) impurity.

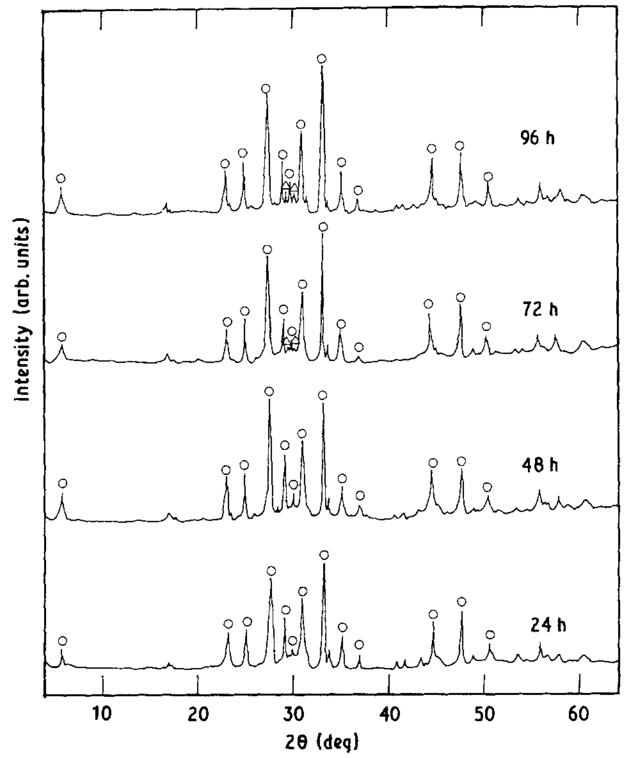

Figure 4 X-ray diffraction patterns (CuK_α) in the $Bi_2Sr_2Ca_1Cu_2O_x$ system heat-treated at 850 °C for different times. (○) 80 K, (△) impurity.

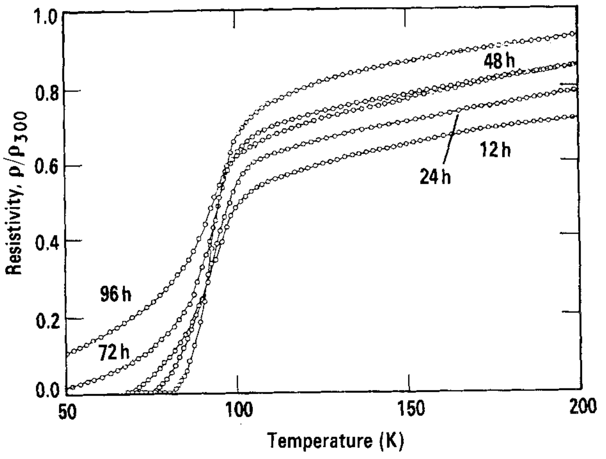

Figure 6 Temperature dependence of the electrical resistivity of pellet samples in the $Bi_2Sr_2Ca_1Cu_2O_x$ system heat-treated at 850 °C for different times. Each sample was quenched from 850 °C.

nitrogen, and T_c decreased in the order of cooled in air and cooled in the furnace from 850 °C.

Fig. 6 shows the temperature dependence of electrical resistivity of pellet samples heat-treated at 850 °C for 24 to 96 h. Each sample was quenched to room temperature from 850 °C. The highest value of T_c was observed after heat-treatment at 850 °C for 48 h; for heat-treatment below 24 h, the value of T_c decreased below that for heat-treatment for 48 h. It is suggested that in this case the heat-treatment is insufficient. T_c decreased largely for heat-treatment above 72 h and a long tail was observed. The lowest H_c at 77 K, $-$ 0.25 e.m.u. g^{-1} at 0.15 kOe, was observed by heat-treatment at 850 °C for 48 h.

Fig. 7 shows the thickness of films and dipping times. Glycerol was used as solvent. The thickness of films shows a linear relationship with dipping time. The film thickness for a single dipping was about 0.5 μm.

Fig. 8 shows the temperature dependence of the

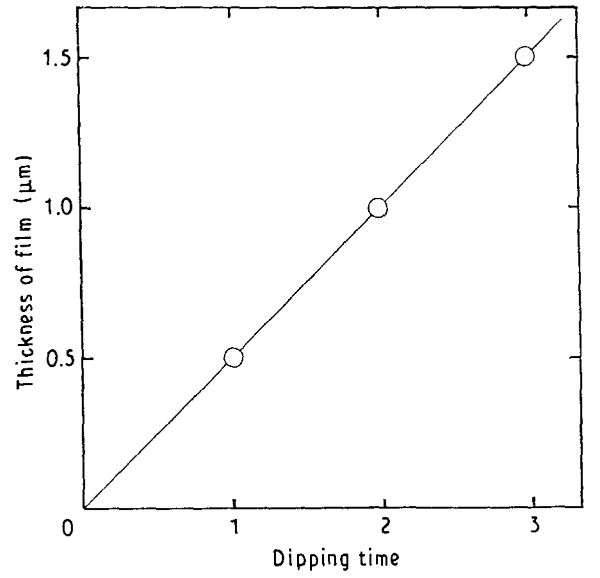

Figure 7 Thickness of films and dipping times in the $Bi_2Sr_2Ca_1Cu_2O_x$. Glycerol was used as solvent.

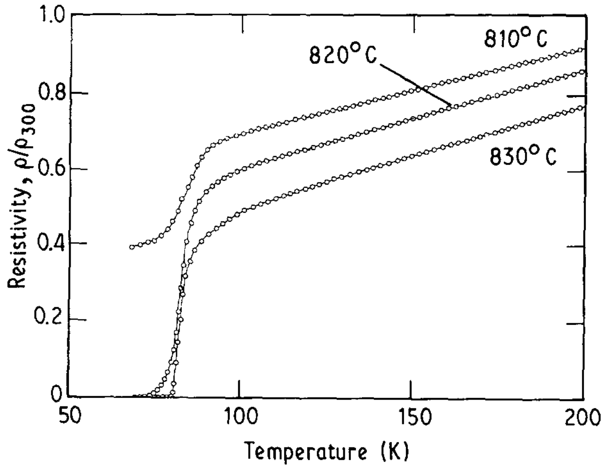

Figure 8 Temperature dependence of the electrical resistivity of thin films in the $Bi_2Sr_2Ca_1Cu_2O_x$ system heat-treated at different temperatures for 10 min.

TABLE I ICP analyses for nominal composition Bi:Sr:Ca:Cu = 2.00:2.00:1.00:2.00

Heat-treatment temperature (°C)	Heat-treatment time (h)	Results			
		Bi	Sr	Ca	Cu
700	24	1.98	2.00	1.01	1.97
750	24	1.98	2.00	1.00	2.05
800	24	1.96	2.00	0.97	2.00
850	24	2.06	2.00	1.09	2.16
870	24	1.94	2.00	1.00	2.02
870	216	1.90	2.00	1.00	2.04

electrical resistivity of thin films. The superconducting crystal phase of thin films was obtained at a lower temperature of heat-treatment than for sintered specimens. The optimum conditions of heat-treatment were 830 °C for 10 min. T_c^{off} of this film was 80 K and J_c at 77 K was more than 8 kA cm^{-2}.

Table I shows the results of elemental analysis determined by inductively coupled plasma (ICP) spectrometry for thin films. The nominal composition of the starting material was BSCCO = 2:2:1:2. This table shows the values when Sr contents were normalized to 2.00. From this table it can be concluded that the Bi content is vaporized with increasing heat-treatment temperature. The composition of each film obtained was quite close to that of the starting solution. These results imply that adjustment of the composition is not necessary, unlike for the sol–gel route for transparent conductive films [10, 11].

4. Conclusions

The sol–gel process using nitrate salts to form BSCCO = 2:2:1:2 superconducting films was investigated in detail.

1. Each raw material was mostly decomposed and oxidized below 550 °C, which was the temperature of pre-heating.
2. The optimum condition of thin films was obtained by the sol–gel process when Bi, Sr, Ca and Cu nitrates were used as raw materials and glycerol, ethylene glycol and diethylene glycol were used as solvents.
3. Superconducting films having a high T_c were obtained by heat-treatment at 830 °C for 10 min and crystallization of films was possible at a relatively low heat-treatment temperature compared with sintered pellets.
4. T_c^{off} of these films was 80 K and J_c at 77 K was more than 8 kA cm^{-2}.
5. From ICP measurements, the composition of the films obtained was quite similar to that of the starting solution.

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