JOURNAL OF MATERIALS SCIENCE 30 (1995) 1827–1831

Rapid formation of the high-T_c phase in (Bi,Pb)–Sr–Ca–Cu–O superconductor via the sol-gel method

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Bi–Pb–Sr–Ca–Cu–O powder was synthesized by the oxalate gel method. A sample with the composition of $Bi_{1.7}Pb_{0.4}Sr_{1.6}Ca_{2.4}Cu_{3.6}O_y$ was used in this study. After pyrolysis of the gel precursor at 500 °C for 5 h, the resulting powder was calcined at 850 °C for another 5 h. The black powder was pressed into pellets and sintered at 852 °C for 5 h. The high-T_c phase was formed more easily in the sample with excess calcium and copper than in the theoretical composition. $(Bi,Pb)_2Sr_2Ca_2Cu_3O_y$ (above 90%) was prepared as above within a relatively short time. Characterization of $(Bi,Pb)_2Sr_2Ca_2Cu_3O_y$ superconductor by X-ray diffraction, scanning electron microscopy, electron probe microanalysis, resistivity measurement and magnetic measurement, is reported.

1. Introduction

Since the discovery of Bi–Sr–Ca–Cu–O superconductors by Maeda *et al.* [1], extensive work has been devoted to the processing of this material. One of the problems with the bismuth cuprates is the difficulty in obtaining phase purity. Recently, several methods, such as lead-doping [2], usage of the organic precursor [3], spray pyrolysis [4, 5] and freeze-drying [6], have been used to enhance the high-T_c phase in a relatively short time. In this paper we report on the enhancement of the high-T_c phase, obtained through a well-mixed solution and control of the calcination temperature.

2. Experimental procedure

The starting precursors were prepared from oxalate solution as described elsewhere [7]. The molar ratio of Bi:Pb:Sr:Ca:Cu was adjusted to 1.7:0.4:1.6:2.4:3.6. After pyrolysis of the resulting powder at 500 °C for 5 h, the black powder was calcined at 850 °C for 5 h. It was then ground and pressed into pellets at a pressure of 500 kg cm^{-2} and sintered at various temperatures for 5 h in static air. X-ray diffraction patterns (XRD) of various heat-treated samples were taken on a MAC MXP^3 X-ray diffraction unit with CuK_α radiation. The surface morphology of the sintered samples was examined using a Jeol JSM-840A SEM. The resistivity of the ceramic samples was measured by the four-probe method using a direct current density of 0.5–2 A cm^{-2}. The magnetic behaviour of the sintered sample was examined using a commercial superconducting quantum interference device (SQUID) magnetometer (Quantum Design) with an external magnetic field of 20 G.

3. Results and discussion

Fig. 1 shows the X-ray diffraction results of starting powders and the heat-treated samples after sintering at different temperatures for 5 h. After calcination at 850 °C for 5 h (Fig. 1a), the 2212 phase and 2223 phase had begun to crystallize. The ratio of high-T_c phase was about 31% at this stage. The sample sintered at 850 °C consisted mainly of the 2223 phase and 30% of the 2212 phase was detectable in the powder X-ray diagram. Sintering at a temperature higher than 852 °C for 5 h resulted in samples (Fig. 1b–e) which consisted of almost only the high-T_c phase with minor impurity. The impurity was identified as the 2201 phase in the bismuth cuprated system and Ca_2PbO_4. Fig. 2 shows the relationship between relative volume of the high-T_c phase and sintering temperature. The 2223 phase increases as the sintering temperature

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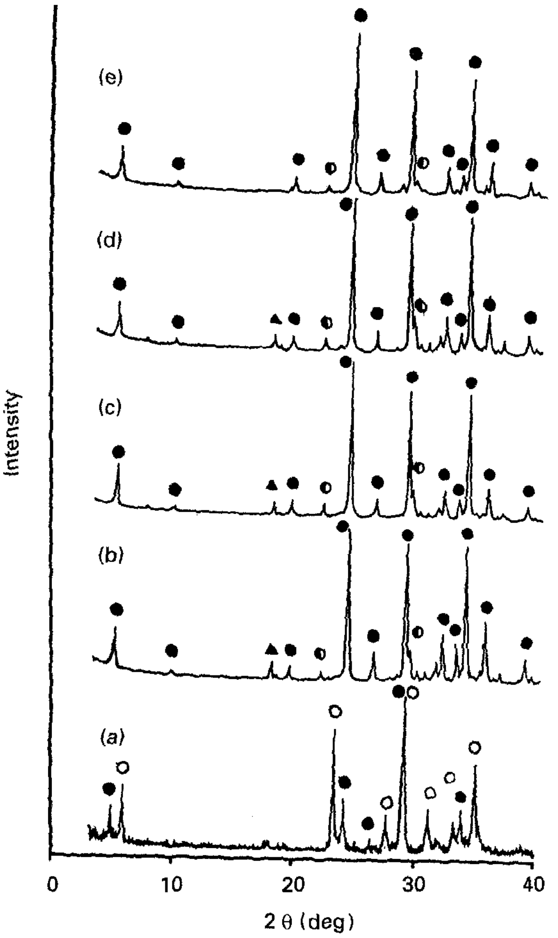

Figure 1 X-ray diffraction patterns of the samples sintered at various temperatures for 5 h: (a) starting powder, calcined at 850 °C, and those sintered at (b) 852 °C, (c) 855 °C, (d) 857 °C and (e) 852 °C then quenched from a high temperature. (●) Bi2223, (○) Bi2212, (◐) Bi2201, (▲) Ca_2PbO_4.

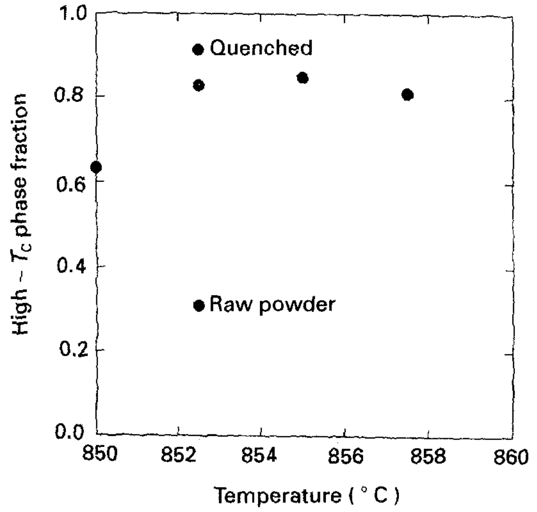

Figure 2 Sintering-temperature dependence of the volume fraction for the Bi2223 phase.

increases and reaches a maximum at a temperature of 857 °C. Further sintering at a temperature above 860 °C will cause melting of the pellets. From Fig. 2, we found that the sintering temperature is crucial to

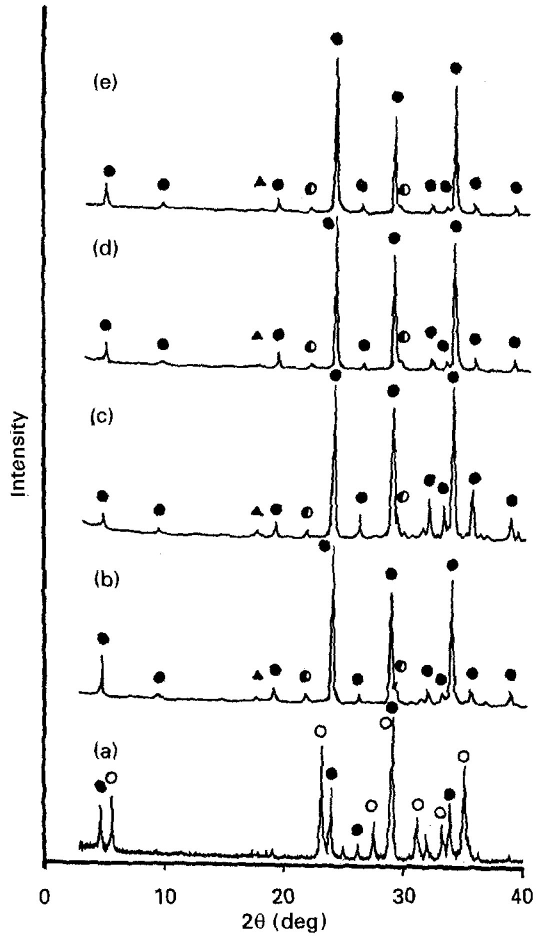

Figure 3 X-ray diffraction patterns of the sintered samples sintered at 852 °C in static air atmosphere: (a) 2 h, (b) 24 h, (c) 72 h (d) 96 h and (e) 120 h. For key, see Fig. 1.

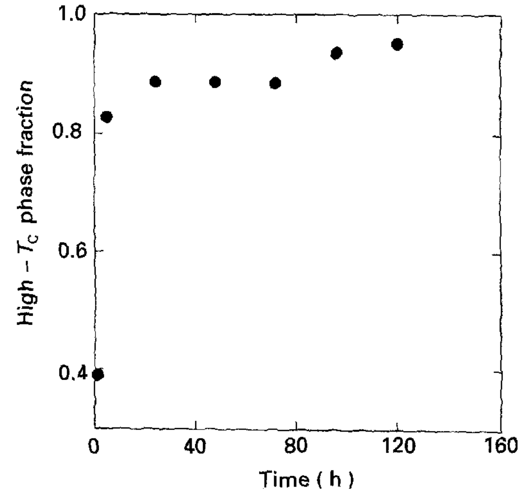

Figure 4 The sintering-time dependence of the high-T_c phase fraction for the samples sintered at 852 °C.

the formation of the high-T_c phase. The 2223 phase can only be synthesized within a narrow temperature window of about 10 °C for the rapid formation of this phase. A sample sintered at 852 °C and subsequent

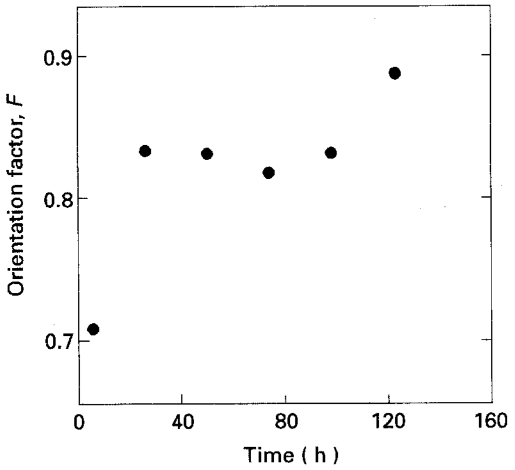

Figure 5 The sintering-time dependence of the orientation factor of Bi2223 phase for the samples sintered at 852 °C.

quenching from high temperature was compared with the other samples. The amount of 2201 phase in the quenched sample was lower than that in the as-prepared sample.

The sintering time was also examined using isothermal sintering processes. Fig. 3 shows XRD patterns of the samples sintered for various times at 852 °C. It was found that the high-T_c phase was produced almost completely by sintering at 852 °C for 5 h, while prolonged sintering time only changed the relative intensity of the diffraction peaks. The relative amount of high-T_c phase to the 2201 phase was estimated from the X-ray intensity of both phases. Fig. 4 shows the sintering-time dependence on the ratio of high-T_c phase. The high-T_c phase increases as the sintering time increases. After sintering at 852 °C for 24 h the high-T_c phase was about 90%. The intensity of the (0 0 1) plane increases with increasing sintering time. This indicates that an oriented structure exists in which the *c*-axis is aligned parallel to the surface of the sintered sample. Using the orientation factor, *F*, presented by Lotgerling [8], we can evaluate the textured alignment of the samples. The value of *F* increases with increasing reaction time, as shown in Fig. 5 and reaches a value of 0.83 after sintering at 852 °C for 24 h. Fig. 6 shows a scanning electron micrograph of the (Bi,Pb)–Sr–Ca–Cu–O sample prepared at 852 °C for 5 h. From the micrograph and energy dispersive analysis of X-rays (EDAX), the plate-like crystals were 2223 phase and the sample was less homogeneous. From the electron probe microanalysis (EMPA) compositional maps, it was found that the calcium ions segregated from other metal ions and became clusters. The segregation of metal ions could result from the improper heat treatment at higher temperature.

Results of the resistivity measurements for specimens subjected to different heat treatments are shown in Fig. 7. The temperature dependence of resistivity for the samples sintered at 852 °C for 5 h (curve a) and 24 h (curve b) is illustrated. The superconducting transition did not occur in one step for the sample sintered at 852 °C for 5 h. The effect of the formation of monoclinic phase on the superconductivity of 2223 phase in the bismuth-based system had been reported by Wang *et al.* [9]. Prolonging the sintering will improve the superconducting transition as shown in the sample which was treated at 852 °C for 24 h. Table I summarizes the resistivity of the samples, as prepared in this report. Fig. 8 shows the temperature dependence of the magnetic susceptibility of the superconducting oxides sintered at 852 °C for 5 h. Abrupt change in the magnetization curves are observed at 107 K for zero-field-cooled (ZFC) and field-cooled (FC) curves for the sample which is consistent with the resistivity measurement. The relative volume [10] of the high-T_c superconducting phase is estimated from the susceptibility and the volume of the high-T_c phase is about 91.3% for the sample sintered at 850 °C for 5 h. Comparison ofthe zero-field cooled magnetization curve of the sintered sample and the magnetization of the ideal superconductor, the superconducting volume of the sintered pellet was estimated to be about 89%.

In summary, we have reported the synthesis of the 110 K (Bi,Pb)–Sr–Ca–Cu–O oxide superconductor with a high volume fraction of the high-T_c phase in a relatively shorter period. More detailed studies on the chemical processes, chemical compositions and heat treatment (calcination, sintering temperature and atmosphere) are in progress.

Acknowledgement

This research was supported by the National Science Council of Taiwan, under contract nos NSC82-0208-M-007-81 and NSC82-0511-M-007-140 to National Tsing Hua University.

TABLE I The critical temperature of the specimens sintered at several temperatures and different reaction times.

No.	Sintering conditions		T_c(onset) (K)	T_c(zero) (K)
	°C	h		
1	850	5	110	80[a]
2	852	5	110	95
3	855	5	106	88
4	857	5	110	94
5	852	5[b]	110	82
6	860	5	Melt	
7	852	24	115	102

[a] Two phases.

[b] Quenched from a high temperature.

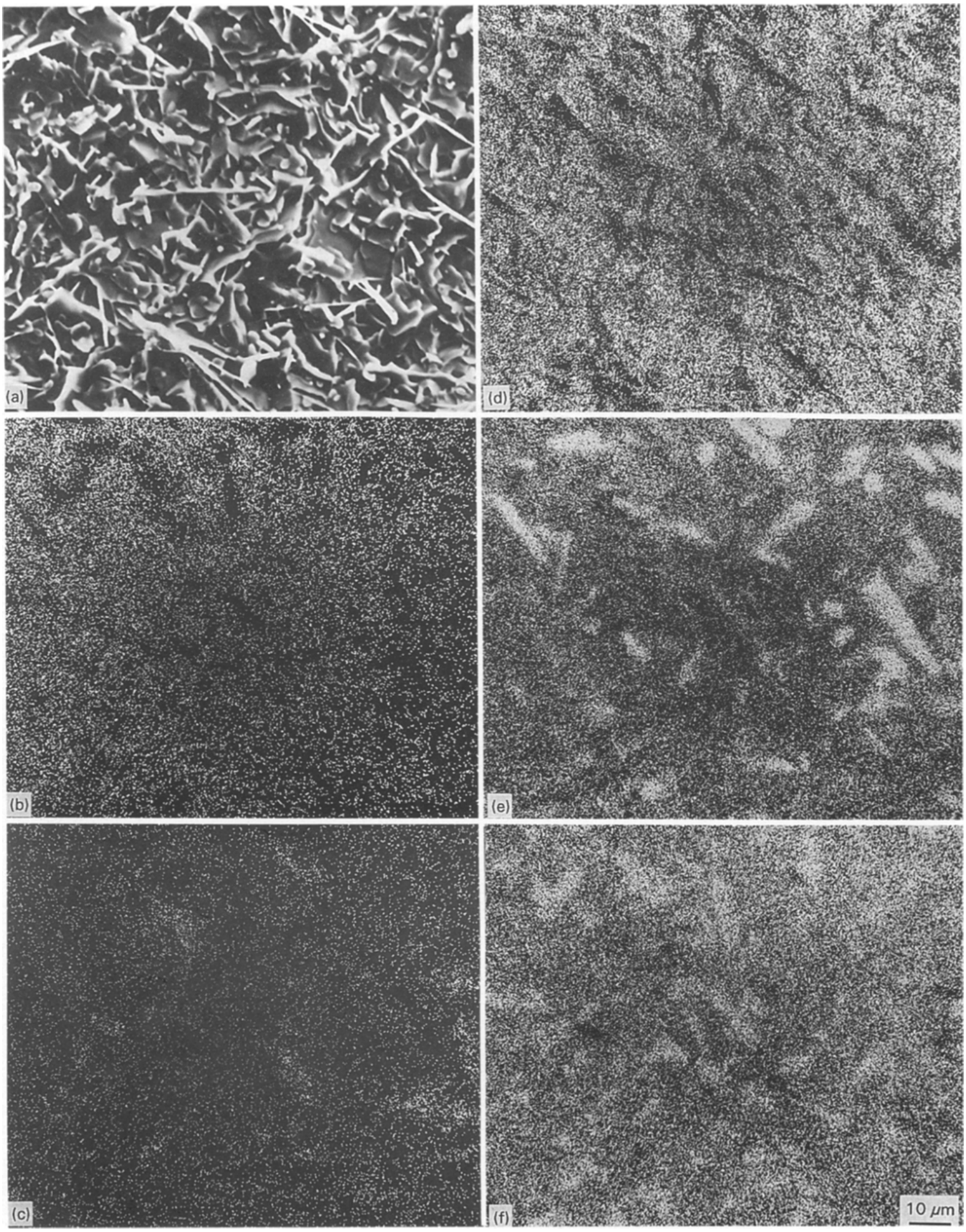

Figure 6 (a) Scanning electron micrograph, and the corresponding EPMA compositional maps of (b) Bi, (c) Pb, (d) Sr, (e) Ca and (f) Cu for the sample sintered at 852 °C for 5 h.

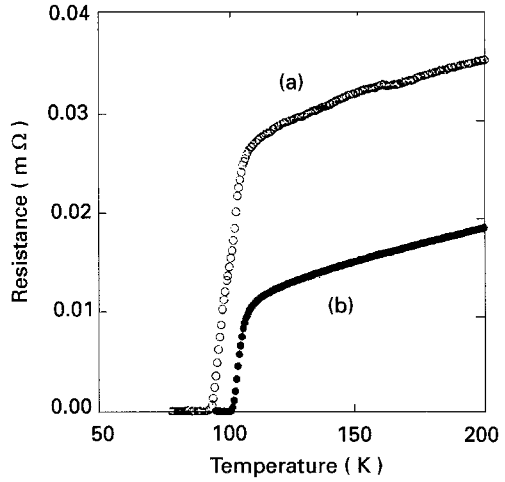

Figure 7 Temperature dependence of the electrical resistance for samples sintered at 852 °C for (a) 5 h, and (b) 24 h.

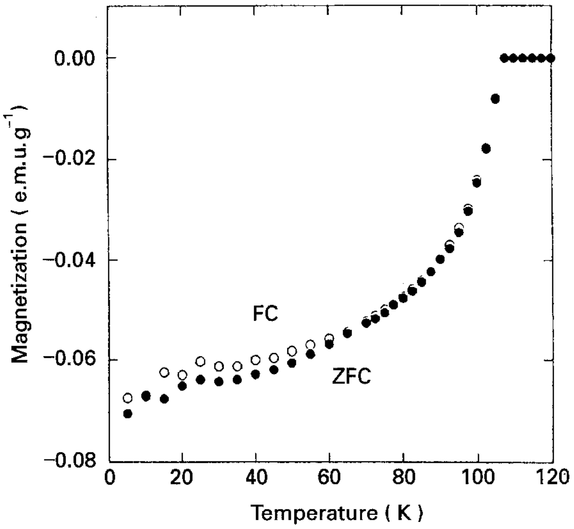

Figure 8 Temperature dependence of magnetization for a sample sintered at 852 °C for 5 h.

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Received 1 September 1993
and accepted 8 September 1994