Role of barium addition on the properties of bismuth-based superconductors

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The effect of the addition of barium on the zero resistance temperature, T_c, of $Bi_{1.6}Pb_{0.4}Sr_{1.6}Ca_2Ba_xCu_4O_y$, $x = 0.4$, 0.5, 0.6, 0.8 and 1.6 was studied. The added barium had the effect of raising T_c to a higher temperature region, although too much barium gave rise to semiconducting resistance temperature behaviour. X-ray diffraction analysis showed that as the barium concentration, x, increased from 0.4 to 0.8, a decrease in the low T_c phase and peaks due to CuO and $BaBiO_3$ appeared, whereas an increase in the peaks due to the high T_c phase and $BaCuO_2$ were seen. Critical current densities were also measured in zero field at 77 K.

1. Introduction

It has been reported [1–3] that the addition of lead to bismuth-based superconductors enhances high T_c formation. Such an effect is also expected with the addition of other elements such as antimony [4].

We have studied the effect of the addition of barium to Bi–Pb–Sr–Ca–Cu–O superconductors and found an increase in the T_c (zero) value. Barium is known to be incorporated as $(Bi_2O_3)^{2+}M_{n-1}R_nO_{3n+1}$, where M represents La^{9+}, Ba^{2+}, Pb^{2+} and K^+, and R represents Fe^{9+}, Tl^{4+}, Nb^{5+} and W^{6+} [5]. It was also interesting to study the effect of barium addition on the system Bi–Pb–Sr–Ca–Cu–O, because barium belongs to the same alkaline earth metal group as strontium and calcium, having different ionic radii.

2. Experimental procedure

A series of samples with starting composition $Bi_{1.6}Pb_{0.4}Sr_{1.6}Ca_2Ba_xCu_4O_y$ with $x = 0.4, 0.5, 0.6, 0.8$ and 1.6 were prepared by the solid state reaction technique under a normal atmosphere. The starting material Bi_2O_3, PbO, $SrCO_3$, $CaCO_3$, CuO and $BaCO_3$ (all of purity 99.9%) were mixed thoroughly in appropriate proportions using an agate mortar and pestle. The mixture was calcined at 800 °C in a porcelain boat for 20–24 h. A tube furnace was used for the heat treatment. The temperature was measured using a Pt/Pt–13% Rd thermocouple. Pellets of the calcined material of diameter 14 mm and thickness 1–2 mm were made using a die, either by applying pressure (4–6 ton cm^{-2}) or by pressing simply with the hands. The samples were sintered in a normal atmosphere at 830 ± 10 °C for different times (Table I). The visual demonstration [6] of the Meissner effect was checked before the d.c. electrical resistivity measurements by the standard four-probe technique. Silver-paste was used for the electrical contacts. The critical current density for all the specimens at 77 K was also measured using the four-probe technique.

X-ray diffractographs were taken using the JD-II series X-ray diffractometer system (Jeol). The specimens were either in the form of pellets or finely crushed pellets. CuK_α radiation was used for the experiments, and the measurements were made at room temperature.

3. Results and discussion

The electrical resistivity was measured at a current of 10 mA within the temperature range 77–300 K. High-quality silver paste was used for the electrical contacts. Fig. 1a and b show the effect of cooling rate on the temperature dependence of resistivity for $x = 0.4$. The behaviour of annealing time at an annealing temperature of 830 ± 10 °C is also represented in Fig. 1. It is clear from these plots that the ρ–T curves of the $Bi_{1.6}Pb_{0.4}Sr_{1.6}Ca_2Ba_{0.4}Cu_4O_y$ gave rise to a metallic behaviour above the superconducting transition, T_c. Only the formation of single-phase appeared. T_c(zero) increased with annealing time, and after a certain time it became stable (Fig. 1b). It is also interesting to note that the resistivity of the superconducting material decreased with increasing annealing time, showing the stability of the material. Similar behaviour was observed for the other samples with $x = 0.5$, 0.6 and 0.8, except for variation in T_c(zero).

TABLE I Effect of concentration of barium and pressure on J_c of $Bi_{1.6}Pb_{0.4}Sr_{1.6}Ca_2Ba_xCu_4O_y$ superconductors (annealing temperature 830 ± 10 °C)

Ba conc. (x)	J_c (A cm^{-2}) Hand pressed	Applied pressure (ton cm^{-2})	Annealing time (h)
0.4	12.85	35.16 (at 5)	305
0.5	11.35	–	318
0.6	12.56	–	246
0.8	16.70	32.73 (at 5)	241

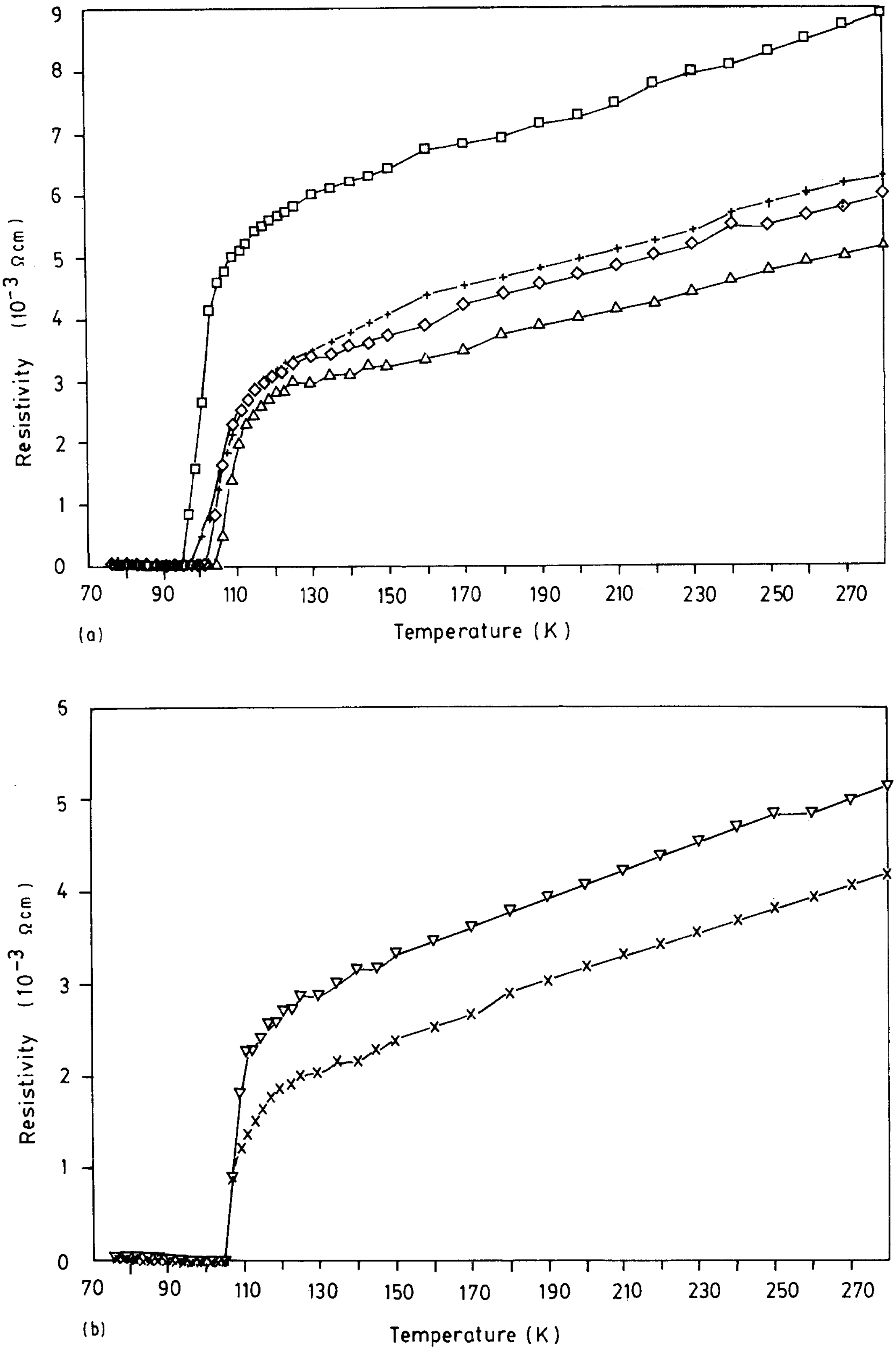

Figure 1 a, b Temperature dependence of resistivity of $Bi_{1.6}Pb_{0.4}Sr_{1.6}Ca_2Ba_{0.4}Cu_4O_y$ heated at 830 ± 10 °C for (□) 89, (+) 137, (◇) 161, (△) 233, (▽) 281 and (×) 305 h.

Fig. 2a and b show the resistivity as a function of temperature for $x = 0.8$. The curves for different annealing times are also shown. We noticed that a mixture of low-T_c(zero), and high T_c(zero) appeared below 77 K and around 110 K, respectively, in agreement with Kawai *et al.* [7]. Barium addition with values over $x = 0.8$ did not yield a superconducting effect, but gave rise to a higher resistance of the sample and the formation of a semiconductor. A resistivity–temperature curve for $x = 1.6$ is shown in Fig. 3.

Fig. 4 shows the dependence of T_c(zero) on annealing time. It is evident that longer annealing times under constant temperature contribute to the increase of T_c up to a certain time, after which T_c becomes constant within experimental error. After 50–300 days exposure of the sample to the ambient atmosphere, T_c(zero) of the samples was observed to be constant.

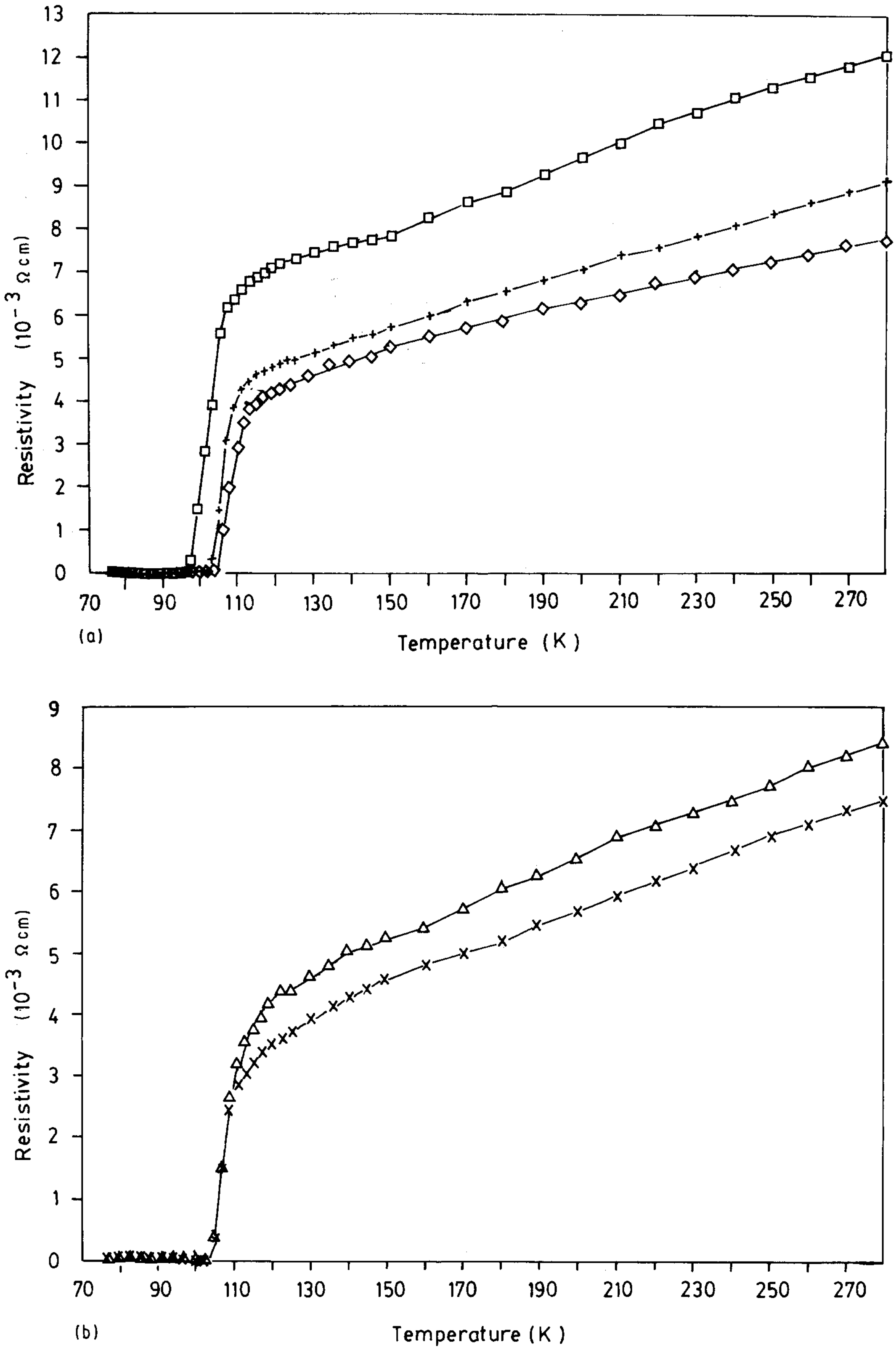

Figure 2 a, b. Temperature dependence of resistivity of $Bi_{1.6}Pb_{0.4}Sr_{1.6}Ca_2Ba_{0.8}Cu_4O_y$ annealed for (□) 97, (+) 121, (◇) 169, (△) 217 and (×) 241 h.

No ageing effect was observed in our specimens. The stability of these superconductors was studied in terms of the effect of ambient conditions, the method of preparation of the specimens, and the concentration of barium, on the critical current J_c (defined as a current, I, that generated a 1 μV signal at 77 K). To measure J_c, the I–V plots were taken for samples with $x = 0.5$, 0.6 and 0.8 at 77 K on days 1, 50 and 300 with hand-pressed and 5 ton cm^{-2} pellets. Fig. 5 shows the current density–voltage curves for hand-pressed pellets. The ambient atmosphere did not show any effect on the J_c values, but the samples which were pressed at 5 ton cm^{-2} during pellet formation showed a larger value of J_c compared to the othe samples. Table I shows the effect of concentration of barium and pressure on J_c, although the specimens prepared by both methods did not show any effect on T_c(zero).

The X-ray diffraction patterns of $Bi_{1.6}Pb_{0.4}Sr_{1.6}$

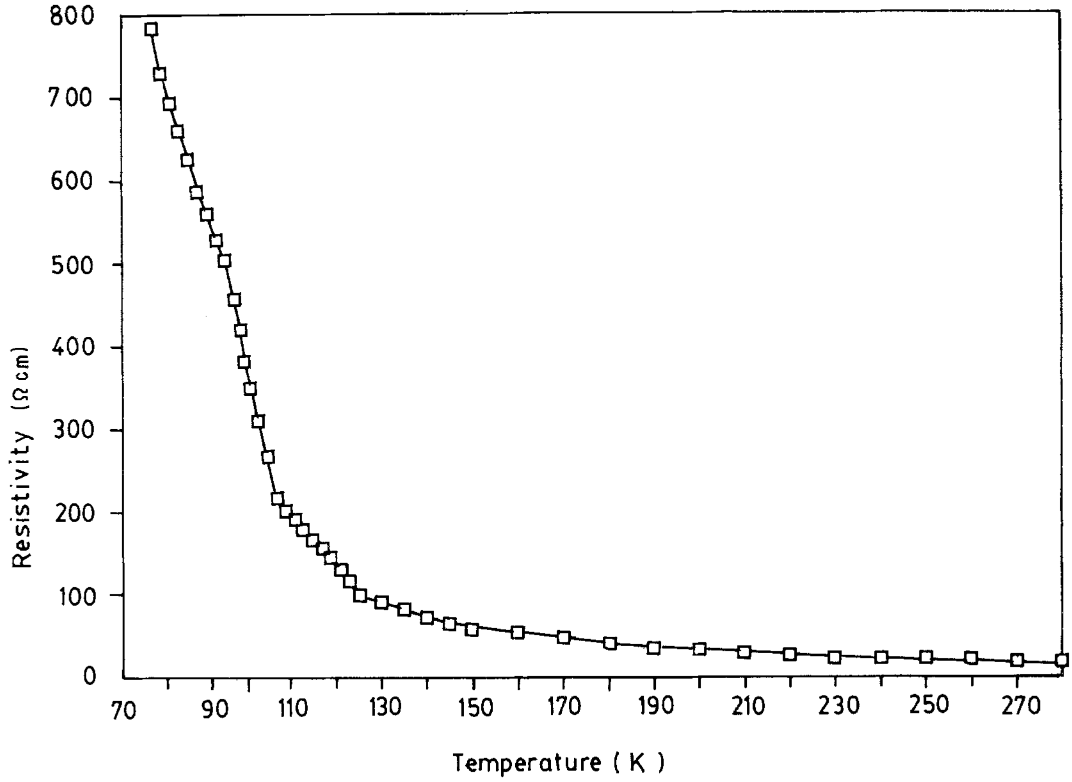

Figure 3 Temperature dependence of resistivity for $Bi_{1.6}Pb_{0.4}Sr_{1.6}Ca_2Ba_{1.6}Cu_4O_y$ heated at 830 ± 10 °C, for 150 h.

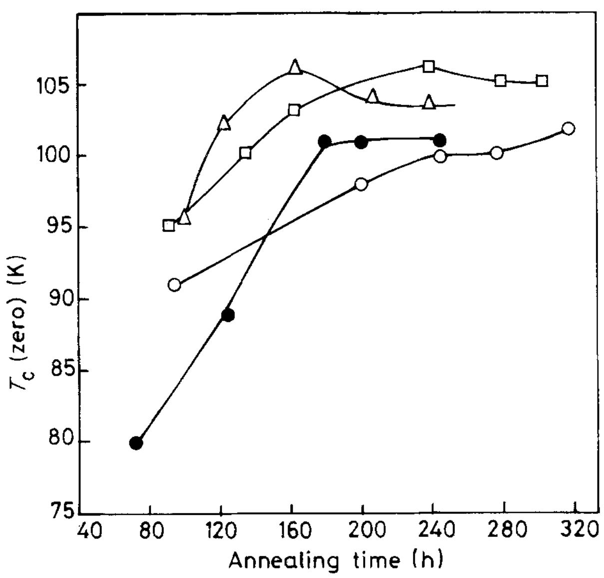

Figure 4 Annealing time versus T_c(zero) for $Bi_{1.6}Pb_{0.4}Sr_{1.6}Ca_2Ba_xCu_4O_y$ for x = (□) 0.4, (○) 0.5, (●) 0.6, (△) 0.8.

$Ca_2Ba_xCu_4O_y$ are shown in Fig. 6. All the samples with barium contents of $x = 0.4$ and 0.8 exhibited T_c(zero) above 100 K (Figs 1, 2), and the X-ray pattern showed a decrease of the low T_c phase. Barium addition of $x = 0.6$ required a longer sintering time to exhibit a positive effect. In addition to the mixture of low and high T_c phases, peaks corresponding to $BaBiO_3$, $BaCuO_2$ and CuO appeared. Barium addition with values over $x = 0.8$ did not yield a positive effect, but gave rise to a higher resistance of the sample and the formation of a semiconductor. Thus, $Bi_{1.6}Pb_{0.4}Sr_{1.6}Ca_2Ba_{0.4-0.8}Cu_4O_y$ yielded the best results.

The characteristic effect of barium addition seems to be the decomposition of the low T_c phase of Bi–Sr–Ca–Cu–O superconductors by producing $BaBiO_3$ and $BaCuO_2$ along with the formation of a high T_c phase. Accordingly, the addition of too much barium gives rise to semiconducting behaviour in the ρ–T curve, whereas a small barium addition is quite effective in decomposing the 80 K phase and producing the high T_c.

Finally, it should be pointed out that samples often show low-temperature tailing around 95 K for Bi–Pb–Sr–Ca–Cu–O [3], and that in these cases, barium addition is quite effective in producing sharp, high T_c superconductors with transition temperatures above 100 K.

4. Conclusions

The experiments show that the addition of small amounts of barium to Bi–Pb–Sr–Ca–Cu–O superconductors has the effect of decomposing the 80 K phase into a high T_c phase along with the formation of $BaCuO_2$ and $BaBiO_3$. Addition of too much barium, $x > 0.8$, results in the formation of large amounts of $BaBiO_3$ and $BaCuO_2$, producing a semiconductor material.

The annealing times show an increase in the T_c(zero) and a decrease in the resistivity up to a certain critical time, after which T_c(zero) becomes stable. Similar results have been observed in another system [8].

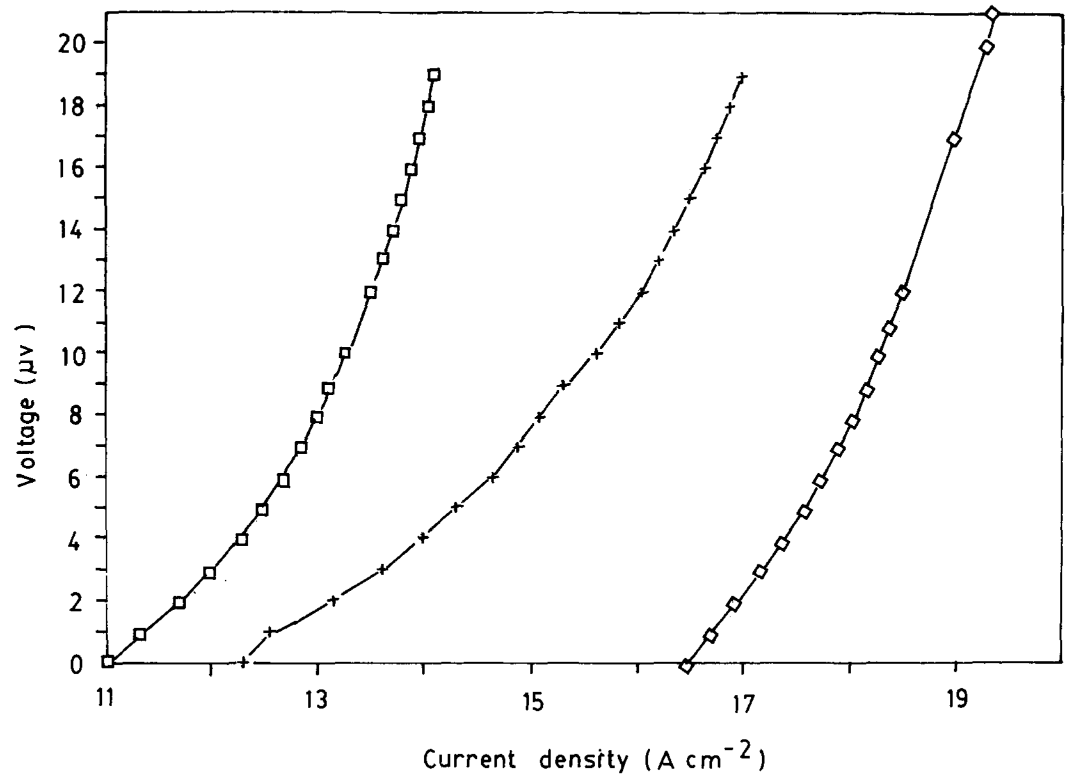

Figure 5 Current density versus voltage curves at 77 K for $Bi_{1.6}Pb_{0.4}Sr_{1.6}Ca_2Ba_xCu_4O_y$ for x = (□) 0.5, (+) 0.6, (◇) 0.8.

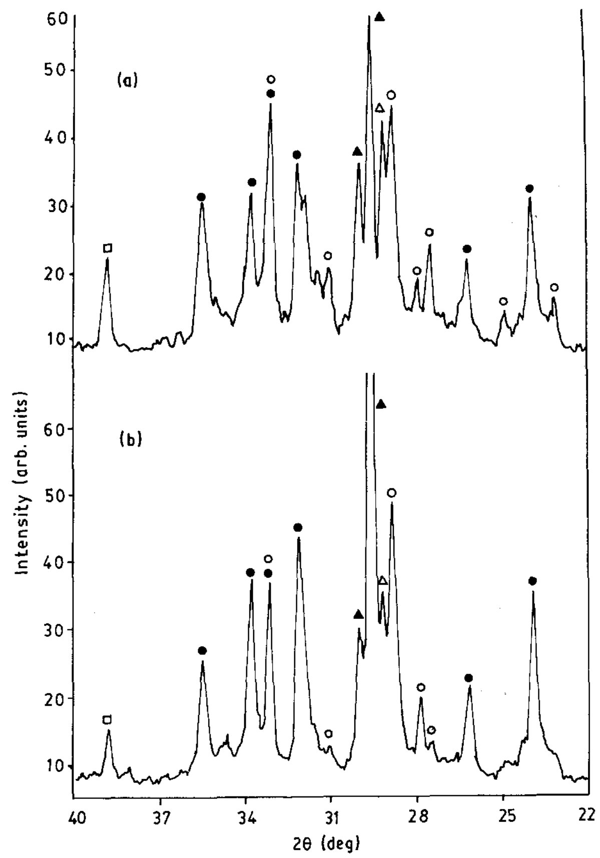

Figure 6 X-ray diffraction patterns of $Bi_{1.6}Pb_{0.4}Sr_{1.6}Ca_2Ba_xCu_4O_y$ composition for x = (a) 0.4 and (b) 0.8. (○) Low T_c phase, (●) high T_c phase, (▲) $BaCuO_2$, (△) $BaBiO_3$, (□) CuO.

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