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Zero resistance of quenched $Bi_{1.5}Pb_{0.4}Sb_{0.1}Sr_2Ca_2Cu_3O_x$ at 140 K

J. A. A. KHAN, N. M. BUTT, A. MAHMOOD, R. SHAHEEN, G. BASHIR*, K. A. SHAHID*
*Nuclear Physics Division, and *Nuclear Materials Division, Pinstech, Nilore, Pakistan*

A glass-ceramic of nominal composition $Bi_{1.5}Pb_{0.4}Sb_{0.1}Sr_2Ca_2Cu_3O_x$ was prepared by the melt-quenching method. The subsequent heat treatment of the sample at 860 ± 5 °C showed T_c(zero) at 94 K. Exposure of the sample for 4 days in air improved its T_c(zero) to 140 K. In another similarly heat-treated sample, a two-step transition in the ρ–T curve at 140 K and at 111 K, was observed. The superconducting transition appeared to be of a percolative nature.

1. Introduction

Since the report of superconductivity in Bi–Sr–Ca–Cu–O ceramic with two different transition temperatures of 110 K (high-T_c phase) and 80 K (low-T_c phase) by Maeda *et al.* [1], considerable attention has been paid to these materials. It has been shown that substituting a part of the bismuth by lead enhances the formation of the high-T_c phase in the Bi–Sr–Ca–Cu–O system [2, 3]. Komatsu *et al.* [4–6] have succeeded in preparing high-T_c superconductive glass-ceramics based on Bi–Sr–Ca–Cu–O and Bi–Pb–Sr–Ca–Cu–O systems using the melt-quenching method. This method is attracting much attention because it gives greater compositional homogeneity [7, 8] and seems to eliminate pores. It is, therefore, expected to give higher zero resistance temperature, T_c (zero).

In this study we report the effect of partial substitution of bismuth by lead and antimony, in melt-quenched glass samples with starting composition $Bi_{1.5}Pb_{0.4}Sb_{0.1}Sr_2Ca_2Cu_3O_x$, on the superconducting transition temperature, T_c.

2. Experimental procedures

2.1. Sample preparation

Analytical grade powders, Bi_2O_3, Pb_3O_4, Sb_2O_3, CuO, $SrCo_3$ and $CaCo_3$ (99.999% pure), in atomic ratio Bi:Pb:Sb:Sr:Ca:Cu = 1.5:0.4:0.1:2:2:3, were mixed, ground and calcined in a platinum crucible in air at 820 °C for 20 h. The calcined material was reground, mixed and melted in a platinum crucible at 1200 °C for 20 min. The melt was rapidly cooled to 1090 °C, heated for 2 h and then poured on to a stainless steel plate at room temperature to make disc-like samples: Sample 1 ~ 1 mm thick and ~ 8 mm diameter, sample 2 ~ 2.5 mm thick and ~ 12 mm diameter. These samples are called "as-quenched". The as-quenched samples were then heat treated at 860 ± 5 °C for 24 h in air and furnace cooled.

2.2. Measurements

The temperature, T, dependence of electrical resistivity, ρ, was measured by the d.c. four-probe method, using a closed cycle helium refrigeration system, under a vacuum $\approx 10^{-5}$ torr (1 torr = 133.322 Pa). The electrical contacts were made with silver paint. The measuring current was 10 mA. The temperature was measured using a calibrated type-K thermocouple placed in close proximity to the sample, with an accuracy of ± 0.5 K. ρ and T were simultaneously measured as T decreased or increased slowly: with cooling/heating rates as slow as 4 K h^{-1} in the superconducting transition region. The resistance was measured with an accuracy of 0.1 mΩ. The X-ray diffraction (XRD) patterns were recorded at room temperature using CuK_α radiation for $2\theta = 3°$–$60°$.

3. Results and discussion

The as-quenched samples showed semiconductive behaviour and no superconducting transition was seen above 40 K (Fig. 1). After heat treatment, the sample showed a metallic behaviour with T_c(zero) at 94 K (Fig. 2, curve 1). The temperature dependence of the same heat-treated sample after a stay of 4 days in air at room temperature also showed metallic behaviour but with T_c(zero) at 140 K (Fig. 2, curve 2). At this stage the ρ–T measurements were repeated six times over a period of 10 days and always the same T_c(zero) = 140 K ± 0.5 K was observed during the heating and cooling cycles. In fact, no significant change in the ρ–T curve from 300–140 K was observed. It may be of interest to mention that the two-point resistance (contact resistance and sample resistance) remained 2–3 Ω during all this time when measured using a digital multimeter. Thus the electrical contacts remained stable throughout the experiment and the observed drop in resistivity could not be attributed to the effect of humidity, as reported by Kitazawa *et al.* [9]. Therefore, this drop in resistivity can only be attributed to superconductivity. Sample 2, after heat treatment, showed a two-step transition: a drop in resistivity between 147 and 138 K with T_c(mid-point) at 140 K and zero resistivity at 111 K (Fig. 2, curve 3). The drop of resistivity around 140 K in this sample is thus due to the same 140 K phase which was responsible for

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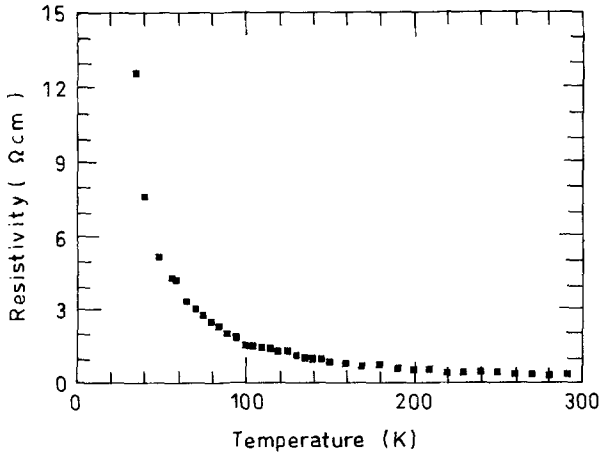

Figure 1 Temperature dependence of resistivity for $Bi_{1.5}Pb_{0.4}Sb_{0.1}Sr_2Ca_2Cu_3O_x$ glass-ceramic quenched from 1090 °C to room temperature. It shows a semiconductive behaviour.

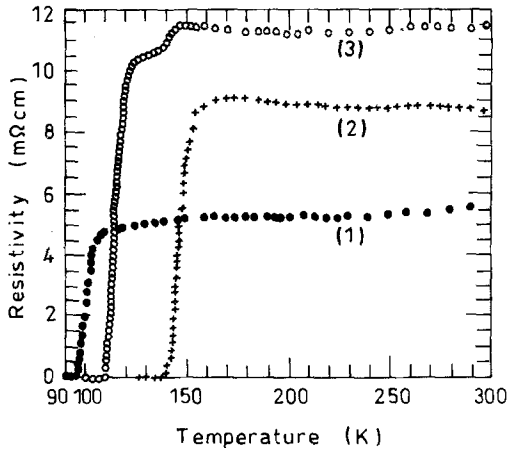

Figure 2 Temperature dependence of resistivity for $Bi_{1.5}Pb_{0.4}Sb_{0.1}Sr_2Ca_2Cu_3O_x$ glass-ceramic annealed at 860 ± 5 °C in air. (1) The as-annealed Sample 1 with T_c(zero) = 94 K. (2) The behaviour of the same sample after 4 days stay in air at room temperature, T_c(zero) = 140 K. (3) The behaviour of the as-annealed Sample 2 of the same composition, T_c(zero) = 111 K.

zero resistance at 140 K in Sample 1 as seen in Fig. 2, curve 2.

From the results shown in Fig. 2, it appears that a new superconducting phase may exist at 140 K which is stable over several days. This is the first time that zero resistivity has been observed at 140 K.

The observation of superconducting transition at 140 K, is in agreement with Liu *et al.* [10] who reported a kink in the resistance between 150 and 140 K in a $BiCaSrCu_2O_x$ sample quenched from 915 °C and heat treated at 820 °C for 40 h. Hongbao *et al.* [11] have recently examined superconducting properties of $Bi_{1.9-x}Pb_xSb_{0.1}Sr_2Ca_2Cu_3O_y$ ceramics prepared by the conventional sintering method. They reported that the samples annealed at 865 °C for 60 h in air with $x = 0.4$, and quenched in air, exhibit a drop in a.c. susceptibility at 140 K. They also reported that the resistivity measurements of this sample show T_c(zero) = 132 K, which degraded to 106 K. Komatsu *et al.* [12] also studied the superconducting properties for $Bi_{1.6}Pb_{0.4}Sb_xSr_2Ca_2Cu_3O_y$ with $x = 0.1$ and 0.2 prepared by the melt-quenching method, and sintered at 860 °C for 100 h in air followed by rapid cooling in air. They observed, for sample with $x = 0.1$, T_c(zero) at 75 K which improved to 102 K after annealing at 400 °C for 10 h in air.

By comparing Fig. 2 with previous studies [10–12], it is obvious that the 140 K phase exists and its formation is assisted by doping the material with a small amount of antimony. Moreover, the zero resistivity achieved at 140 or 111 K in our case is much higher than that reported earlier [11, 12]. Slow cooling also appears to be beneficial for achieving higher T_c(zero). Rapid cooling was reported in [11, 12] for the same composition to exhibit T_c(zero) at 106 and 75 K, while our sample which was slowly cooled showed T_c(zero) much higher (Fig. 2) than those referred to above.

The XRD patterns of the as-quenched samples did not show any crystalline peaks; thus the samples are considered amorphous. The XRD studies of the heat-treated samples showed weak crystalline peaks at $2\theta \geq 27°$, along with a broad halo around $2\theta = 30°$, which indicate that long-range order is not yet complete. From this it is suggested that a 140 K superconducting phase is developing together with the glassy state. In addition, the kinetics of the superconducting phase appear to be very slow. The XRD studies also show that the volume fraction of 140 K phase is very small, therefore, it is difficult to determine the structure by XRD. The 140 K phase may be a filamentary type existing along the grain-boundary region [10, 12]. Because of the disconnected grains, we did not observe zero resistivity (only a drop in resistivity) at 140 K in Sample 2, shown in Fig. 2, curve 3. However, the zero resistivity, observed in Sample 1 (Fig. 2, curve 2) reflects the percolative nature of the superconducting transition and is not due to the bulk superconductivity. The addition of antimony, therefore, seems to assist the formation of a 140 K superconducting phase.

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