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# Effect of copper content on glass formation and superconductivity in the Bi–Pb–Sr–Ca–Cu–O system

T. KOMATSU, R. SATO, H. MEGURO, K. MATUSITA, T. YAMASHITA*
*Department of Chemistry and *Department of Electronics, Nagaoka University of Technology, Nagaoka 940-21, Japan*

High-$T_c$ superconducting ceramics of formula $Bi_{0.8}Pb_{0.2}SrCaCu_xO_y$ ($x = 1.5$, 1.8 and 2.0) were prepared by using the melt-quenching method, and the effect of copper content on glass formation and superconductivity was examined. It was found that the composition with $x = 1.5$ had a tendency to form a glass and $Bi_2(Sr, Ca)_2CuO_y$ crystals tended to precipitate easily during the rapid quenching of melts in the compositions with $x = 1.8$ and 2.0. It was found from the temperature dependence of a.c. complex susceptibility that the intergrain coupling of superconducting crystals in the samples obtained was weak, but the weak coupling was improved by increasing the annealing time. The superconducting glass–ceramics $Bi_{0.8}Pb_{0.2}SrCaCu_{1.5}O_y$ exhibited superconductivity with a $T_c$ (zero) of 106 K and a $J_c$ of 250 A cm$^{-2}$.

## 1. Introduction

Since the first report on the new high-$T_c$ superconducting $BiSrCaCu_2O_x$ ceramics with different critical temperatures $T_c$ of 105 K (high-$T_c$ phase) and 80 K (low-$T_c$ phase) by Maeda *et al.* [1], many researchers have expended much effort to prepare high-performance superconducting Bi–Sr–Ca–Cu–O ceramics with a large amount of the high-$T_c$ phase. Sunshine *et al.* [2] and Takano *et al.* [3] found that the partial substitution of lead for bismuth in the Bi–Sr–Ca–Cu–O system was very effective in increasing the volume fraction of the high-$T_c$ phase. Bulk samples of Bi(Pb)-based superconductors have usually been prepared by the conventional powder sintering method.

Komatsu and co-workers [4–11] developed the melt-quenching method as a new preparation technique of Bi(Pb)-based superconducting ceramics. Other groups [12–27] have also tried to prepare high-performance superconducting ceramics and thick films by using a rapid melt-quenching method. To date, some authors [7, 9–11, 23, 27] have already succeeded in preparing Bi(Pb)-based superconducting ceramics with $T_c$ above 100 K by using the melt-quenching method. It has been thought that the melt-quenching method can be applied to the production of the samples with various shapes and fibres. At the present time, however, experimental data on the superconducting properties and characterization of superconductors prepared by the melt-quenching method are very scarce. The purpose of the present study is to examine the effect of copper content on glass formation and superconductivity in the Bi–Pb–Sr–Ca–Cu–O system.

## 2. Experimental procedure

The nominal compositions examined in this study are $Bi_{0.8}Pb_{0.2}SrCaCu_xO_y$ ($x = 1.5$, 1.8 and 2.0). Commercial powders of guaranteed reagents $Bi_2O_3$, $Pb_3O_4$, $SrCO_3$, $CaCO_3$ and CuO were mixed and calcined at 800 °C for 10 h in air. The calcined powders were melted in a platinum crucible at 1250 °C for 20 min in an electric furnace. The melts were poured on to an iron plate and pressed quickly to a thickness of about 1.5 mm. The melt-quenched samples were heated to 840 °C at a heating rate of 7 K min$^{-1}$ and annealed for 250 h in air. Some samples were annealed for 100 and 300 h. After annealing, the samples were removed from the furnace and cooled rapidly in air.

Measurements of $T_c$ and critical current density $J_c$ (at 77 K, zero magnetic field) were made by using a four-point probe method. Metallic indium was used for the electrodes. The measuring current was 5 mA (i.e. current density $\sim 150$ mA cm$^{-2}$). Measurements of the complex susceptibility $\chi'$–i$\chi''$ for the annealed samples (bulk) were carried out by using an a.c. Hartshorn-type bridge, in which the frequency was 713 Hz and the a.c. field amplitudes were 0.1 and 2.0 Oe. The sample temperature was monitored with a Au(Fe)–Chromel thermocouple. X-ray powder diffraction (XRD) analyses at room temperature using Cu$K\alpha$ radiation were performed to determine the phases present in the melt-quenched and annealed samples. Differential thermal analyses (DTA) for the melt-quenched samples were made at a heating rate of 10 K min$^{-1}$.

## 3. Results and discussion

### 3.1. Glass formation and crystallization

The chemical composition of an annealed (840 °C, 250 h) sample with a nominal formula $Bi_{0.8}Pb_{0.2}SrCaCu_{1.5}O_y$ was first analysed by using inductively

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coupled plasma emission spectrometry, and the formula $Bi_{0.8}Pb_{0.195}Sr_{0.965}Ca_{0.985}Cu_{1.425}O_y$ was obtained. This indicates that the change in the chemical composition during the melt and annealing is very small.

The XRD patterns at room temperature for the melt-quenched samples are shown in Fig. 1. In the melt-quenched sample of $Bi_{0.8}Pb_{0.2}SrCaCu_{1.5}O_y$ (hereafter referred to as sample A), a large halo which is typical of amorphous material was observed at around $2\theta = 30°$. The peak at around $2\theta = 37°$ is attributed to CaO [13]. This assignment was confirmed by electron probe microanalysis. In the melt-quenched sample of $Bi_{0.8}Pb_{0.2}SrCaCu_{1.8}O_y$ (sample B), several crystalline peaks were observed and some peaks were attributed to $Bi_2(Sr,Ca)_2CuO_y$ (a very low-$T_c$ phase with $T_c \approx 10$ K). A small halo was also observed in sample B. The XRD pattern for a melt-quenched sample of $Bi_{0.8}Pb_{0.2}SrCaCu_2O_y$ (sample C) is similar to that of sample B and indicates the presence of $Bi_2(Sr,Ca)_2CuO_y$ crystals. The other crystalline peaks with no mark in Fig. 1 have not been identified at this moment.

DTA curves for the melt-quenched samples A, B and C are shown in Fig. 2. The patterns of DTA curves for these samples are very similar, though the endothermic and exothermic temperature peaks are different in each sample. In the melt-quenched samples A and B, the glass transition $T_g$ and crystallization $T_x$ are clearly observed. The results shown in Figs 1 and 2 indicate that the compositions in the Bi(Pb)–Sr–Ca–Cu–O system have a tendency to form a glass as the copper content decreases and, furthermore, $Bi_2(Sr,Ca)_2CuO_y$ crystals tend to precipitate easily during the rapid quenching of melts. It is noted that the melt-quenched sample with a composition corresponding to the high-$T_c$ phase $(Bi,Pb)_2Sr_2Ca_2Cu_3O_y$ is nearly a glass. Some authors [12, 24, 27] have reported that the melt-quenched sample with a formula $Bi_2Sr_2Ca_2Cu_3O_y$ was a glass. These results are very important in the application of the glass–ceramic process to superconducting fibre production.

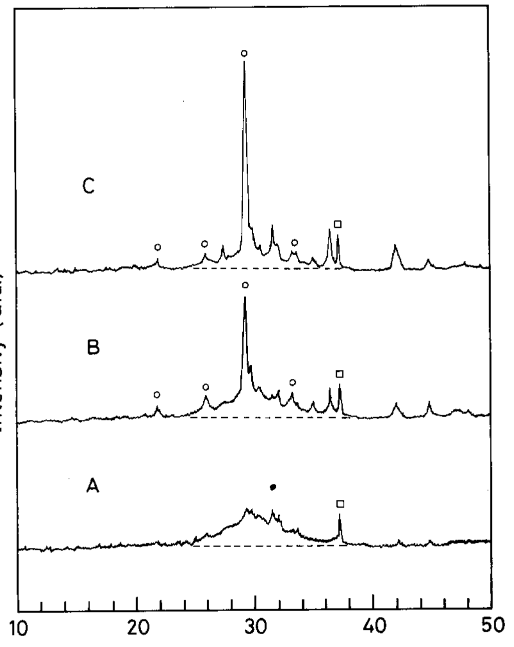


*Figure 1* XRD patterns at room temperature for melt-quenched samples of $Bi_{0.8}Pb_{0.2}SrCaCu_xO_y$ (A: $x = 1.5$, B: $x = 1.8$ and C: $x = 2.0$). (○) $Bi_2(Sr,Ca)_2CuO_y$, (□) CaO.

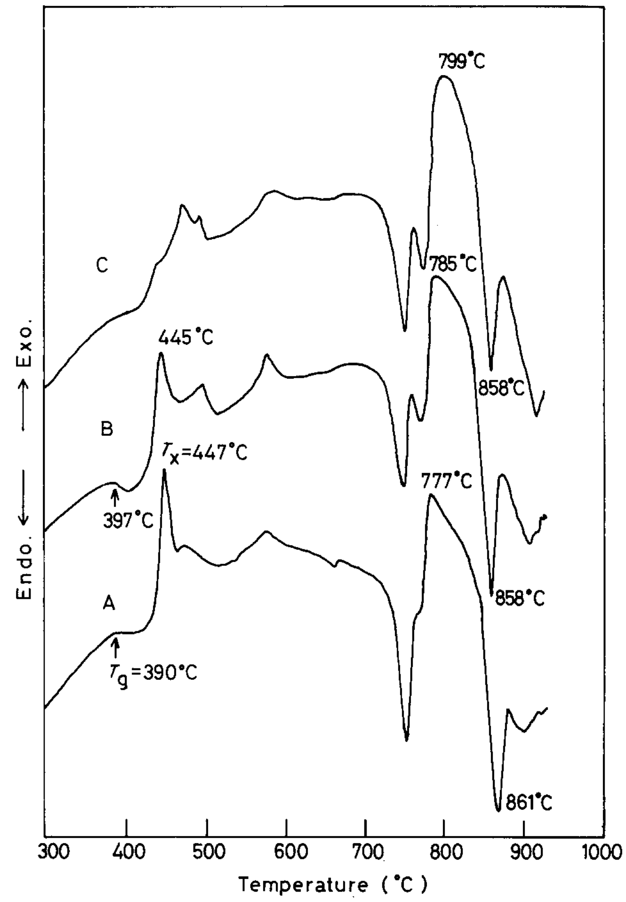


*Figure 2* DTA curves in air for melt-quenched samples of $Bi_{0.8}Pb_{0.2}SrCaCu_xO_y$ (A: $x = 1.5$, B: $x = 1.8$ and C: $x = 2.0$). $T_g$ and $T_x$ are glass transition and crystallization temperatures, respectively. Heating rate was 10 K min$^{-1}$.

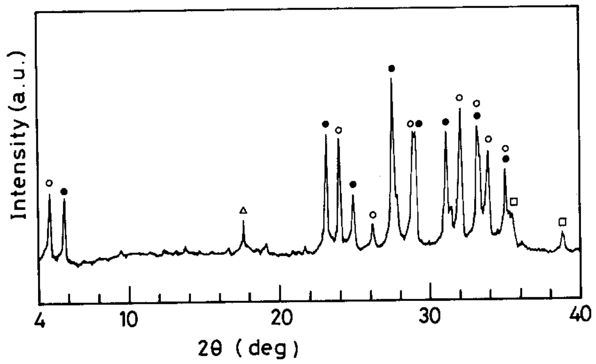
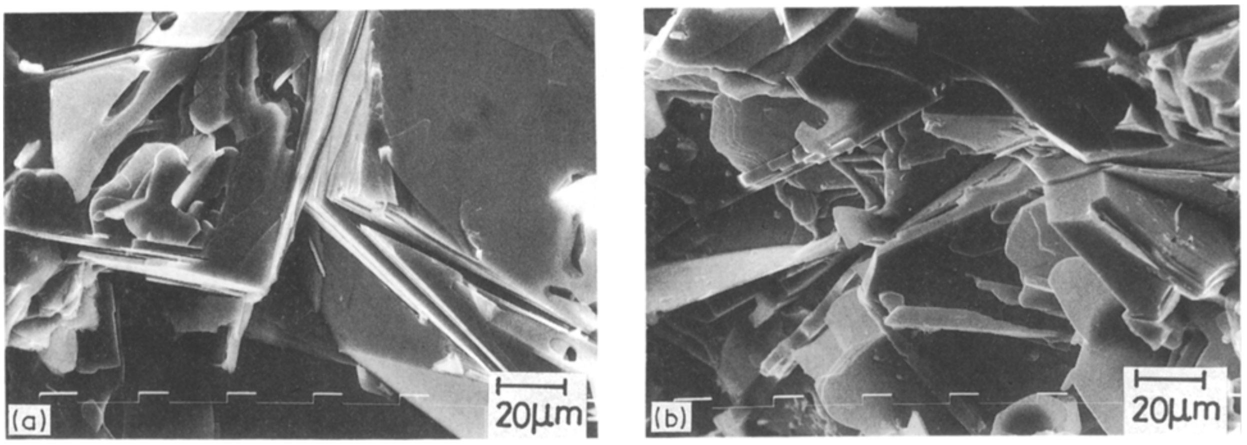


*Figure 3* XRD pattern at room temperature for annealed (840 °C, 250 h, in air) sample of $Bi_{0.8}Pb_{0.2}SrCaCu_2O_y$ (sample C): (○) high-$T_c$ phase, (●) low-$T_c$ phase, (△) $Ca_2PbO_4$, (□) CuO.

To date, it has been well confirmed that glasses in the Bi(Pb)–Sr–Ca–Cu–O system, prepared by the rapid melt-quenching method, first crystallize in the $Bi_2(Sr,Ca)_2CuO_y$ phase at around 500 °C, then the low-$T_c$ phase $Bi_2Sr_2CaCu_2O_y$ is formed during annealing at temperatures around 800 °C [18, 19, 23, 25]. Although the formation mechanism of the high-$T_c$ phase in the melt-quenching method is still open to



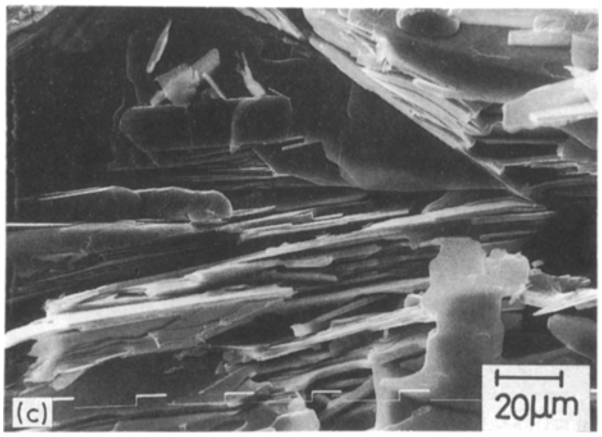


*Figure 4* SEM photographs of annealed (840 °C, 250 h, in air) samples of $Bi_{0.8}Pb_{0.2}SrCaCu_xO_y$: (a) A, $x = 1.5$; (b) B, $x = 1.8$; (c) C, $x = 2.0$.

question, it has been clarified that a prolonged annealing at temperatures around 830 or 840 °C is very effective in increasing the volume fraction of the high-$T_c$ phase [11]. In this paper, we focus our attention on the superconducting properties of the ceramics obtained by a prolonged annealing at 840 °C.

The XRD pattern for sample C annealed at 840 °C for 250 h in air is shown in Fig. 3 as a typical example. It is seen that both the high-$T_c$ and low-$T_c$ phases are present. Crystalline peaks attributable to $Ca_2PbO_4$ and CuO were also detected. Similar XRD patterns were observed for samples A and B annealed at 840 °C for 250 h. Scanning electron micrographs for the fracture surfaces of the annealed samples A, B and C are shown in Fig. 4. All samples consist of plate-like crystals. In particular, it is seen clearly in sample C that plate-like crystals about 3 μm thick are piled up. These SEM photographs indicate that the morphology of bismuth-based superconducting crystals prepared by the melt-quenching method is almost the same as for those prepared by the conventional sintering method.

### 3.2. Superconducting properties

The intergrain coupling nature of superconducting crystals in the annealed sample A was examined through measurements of a.c. complex susceptibility. To our knowledge, there has so far been no report on the coupling at grain boundaries of superconducting glass–ceramics. The temperature dependences of the a.c. susceptibility for sample A annealed at 840 °C for 100 h are shown in Fig. 5. In the real-part $\chi'$ against temperature curve, two transitions were clearly observed at around 110 and 75 K, indicating the presence of both high-$T_c$ and low-$T_c$ phases. It is seen that a small shoulder at around 100 K in $\chi'$–$T$ curve for a large a.c. amplitude ($H = 2.0$ Oe) disappears in the curve for a small a.c. amplitude ($H = 0.1$ Oe). In the imaginary-part $\chi''$ against temperature curves, a peak at around 110 K was observed. In particular, it is noted that this peak shifts to higher temperature and becomes sharper on decreasing the a.c. amplitude from 2.0 to 0.1 Oe. Furthermore, it seems that a large shoulder located in the temperature range between 70 and 100 K becomes weak on decreasing the a.c. amplitude.

The temperature dependences of the a.c. susceptibility for sample A annealed at 840 °C for 300 h are shown in Fig. 6. The real-part $\chi'$–$T$ curve indicates that the low-$T_c$ phase is still present in sample A annealed for a prolonged time (300 h). In the $\chi''$–$T$ curve, a sharp peak at 110 K and a small peak at around 70 K were observed, and these peaks shift to higher temperatures and become sharper with decreasing a.c. amplitude. It is found that the peaks at around 110 K in the $\chi''$–$T$ curve shown in Fig. 6 are sharper than those shown in Fig. 5.

Several authors [28–30] have carried out a.c. susceptibility measurements on bismuth-based superconductors prepared by the sintering method in order to examine the coupling nature at grain boundaries. As discussed by Kumakura *et al.* [30], the shoulder in the $\chi'$–$T$ curve and the peak in the $\chi''$–$T$ curve, which are sensitive to the a.c. amplitude, are attributed to weak intergrain coupling. Furthermore, they reported that the intergrain coupling in bismuth-based superconductors is very weak compared with that in thallium-based superconductors. The strong effect of a.c. amplitude on the temperature dependence of susceptibility obtained in the present study indicates that the intergrain coupling of superconducting crystals in samples prepared by the melt-quenching method is weak. It is considered that the coexistence of non-superconducting phases such as $Ca_2PbO_4$ and CuO shown in Fig. 3 and the random orientation of superconducting crystals shown in Fig. 4 cause the weak coupling at grain boundaries. The difference between the $\chi''$–$T$ curves shown in Figs 5 and 6 means that the intergrain weak coupling of superconducting crystals is improved by increasing the annealing time.

The temperature dependences of the resistivity for samples A, B and C annealed at 840 °C for 250 h in air are shown in Fig. 7, and the values of $T_c$ (zero) and $J_c$ (77 K, zero magnetic field) for these annealed samples are summarized in Fig. 8 as a function of copper content. It is seen that $Bi_{0.8}Pb_{0.2}SrCaCu_{1.5}O_y$ ceramics exhibit good superconductivity. This means that an excess amount of copper, which is estimated as a deviation from the nominal composition of the high-$T_c$ phase $(Bi, Pb)_2Sr_2Ca_2Cu_3O_y$, causes a degradation of superconducting properties. A similar tendency has been reported in a previous paper [11], though the preparation method of the melt-quenched samples was different.

Very recently, Endo *et al.* [31] examined the superconducting properties of ceramics (prepared by the sintering method) with a nominal composition close to the ideal high-$T_c$ phase. They found that the deviation from the ideal composition delicately affected the value of $T_c$ (zero) and that even a small surplus of

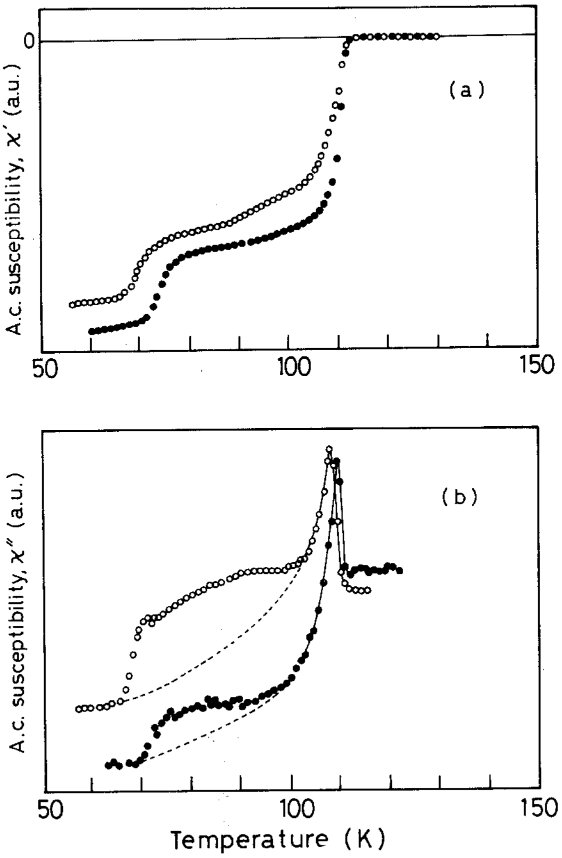


*Figure 5* Temperature dependences of (a) the real part $\chi'$ and (b) the imaginary part $\chi''$ of a.c. complex susceptibility obtained with a.c. field amplitudes of (●) 0.1 and (○) 2.0 Oe for annealed (840 °C, 100 h, in air) sample of $Bi_{0.8}Pb_{0.2}SrCaCu_{1.5}O_y$ (sample A).

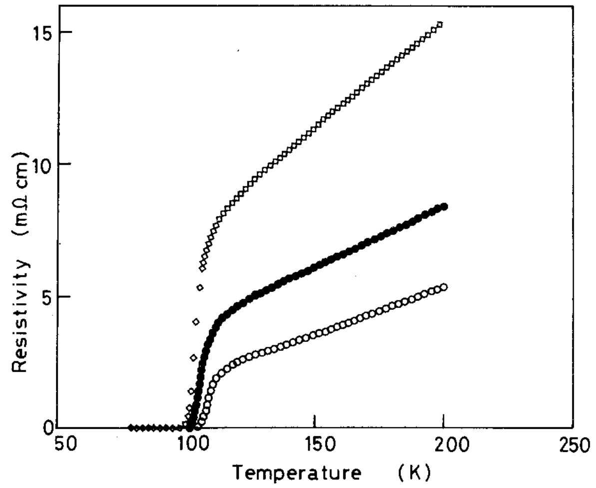


*Figure 7* Temperature dependences of the resistivity for annealed (840 °C, 250 h, in air) samples of $Bi_{0.8}Pb_{0.2}SrCaCu_xO_y$: (○) A, $x = 1.5$; (●) B, $x = 1.8$; (◇) C, $x = 2.0$).

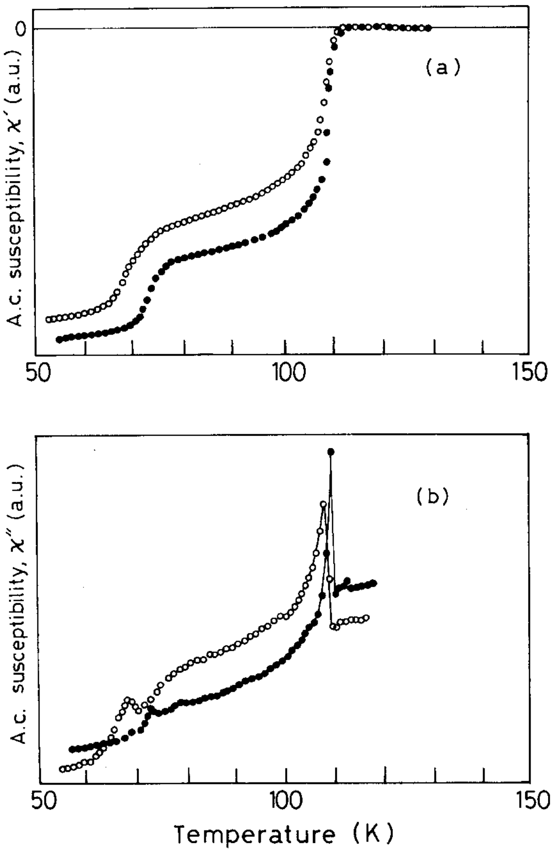


*Figure 6* Temperature dependences of (a) the real part $\chi'$ and (b) the imaginary part $\chi''$ of a.c. complex susceptibility obtained with a.c. field amplitudes of (●) 0.1 and (○) 2.0 Oe for annealed (840 °C, 300 h, in air) sample of $Bi_{0.8}Pb_{0.2}SrCaCu_{1.5}O_y$ (sample A).

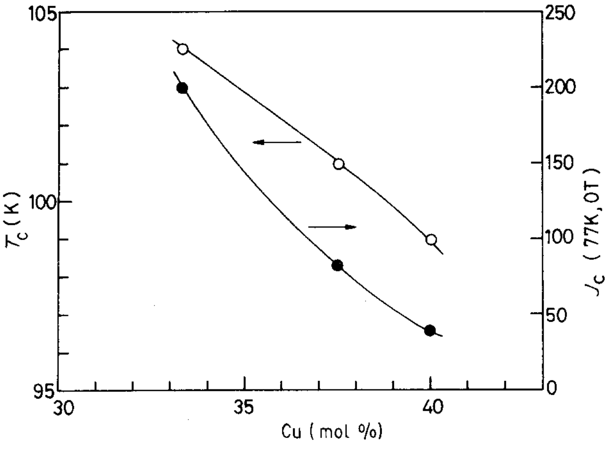


*Figure 8* Values of (○) critical temperature $T_c$ and (●) critical current density $J_c$ (77 K, zero magnetic field) for annealed (840 °C, 250 h in air) samples of $Bi_{0.8}Pb_{0.2}SrCaCu_xO_y$ ($x = 1.5$, 1.8 and 2.0).

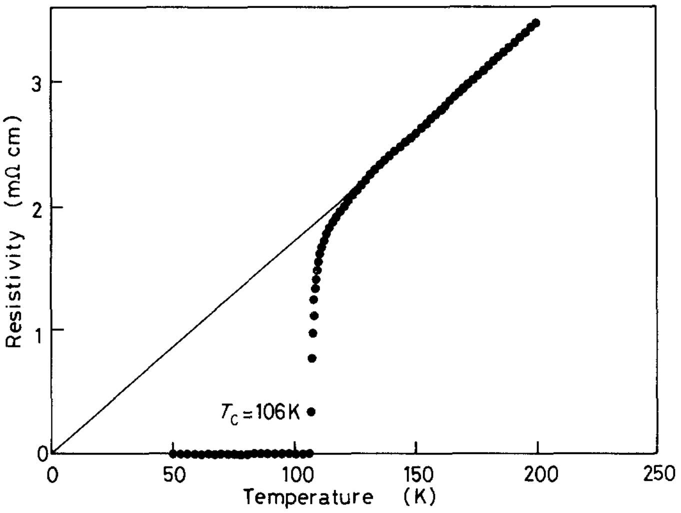


*Figure 9* Temperature dependence of resistivity for annealed (840 °C, 250 h, in air) sample of $Bi_{0.8}Pb_{0.2}$-$SrCaCu_{1.5}O_y$ (sample A). After annealing, the sample was cooled slowly in the furnace.

calcium and copper was enough to make it fall to around 95 K. The value of $T_c = 104$ K for sample A obtained in this study is almost the same as that for sintered ceramics prepared by the conventional sintering method [1], but the value of $J_c = 200\ \mathrm{A\,cm^{-2}}$ is larger than those (usually below $50\ \mathrm{A\,cm^{-2}}$) reported previously for sintered ceramics [32, 33].

Finally, we show the best data on the superconducting properties of bismuth-based ceramics obtained in the present study. The melt-quenched sample A (nearly glass) was first annealed at 840 °C for 250 h in air and then cooled slowly (about $5\ \mathrm{K\,min^{-1}}$) to room temperature in a furnace. The temperature dependence of the resistivity for this annealed sample A is shown in Fig. 9. The values of $T_c$ (zero) and $J_c$ were 106 K and $250\ \mathrm{A\,cm^{-2}}$, respectively. These values are the highest among the values reported so far for high-$T_c$ bismuth-based superconducting glass–ceramics prepared by the melt-quenching method. Further study on the effect of cooling conditions on the superconducting properties of glass–ceramics is now in progress.

## 4. Conclusions

High-$T_c$ superconducting ceramics of formula $Bi_{0.8}Pb_{0.2}SrCaCu_xO_y$ ($x = 1.5$, 1.8 and 2.0) were prepared by using the melt-quenching method, and the effect of copper content on glass formation and superconductivity was examined. The results are summarized as follows.

1. The melt-quenched sample with $x = 1.5$ was nearly glass.
2. The temperature dependences of a.c. complex susceptibility showed that the intergrain coupling of superconducting crystals in the glass–ceramics was weak, but the weak coupling was improved by increasing the annealing time.
3. Values of both $T_c$ and $J_c$ for samples annealed at 840 °C for 250 h in air decreased with increasing copper content.
4. The superconducting glass–ceramics $Bi_{0.8}Pb_{0.2}$-$SrCaCu_{1.5}O_y$ exhibited superconductivity with a $T_c$ (zero) of 106 K and a $J_c$ of $250\ \mathrm{A\,cm^{-2}}$.

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