Thermochimica Acta, 174 (1991) 131–151
Elsevier Science Publishers B.V., Amsterdam

HIGH-T_c SUPERCONDUCTING GLASS-CERAMICS

TAKAYUKI KOMATSU AND KAZUMASA MATUSITA

Department of Chemistry, Nagaoka University of Technology, Nagaoka 940-21 (Japan)

(Received 1 October 1989)

ABSTRACT

This paper reviews glass formation and crystallization and the superconducting properties of glass-ceramics in the Bi(Pb)–Sr–Ca–Cu–O system. There has been great progress in the superconducting glass-ceramics field in the short period following the discovery of Bi-based superconductors. Many glasses, such as those with the compositions $Bi_2Sr_2CaCu_2O_x$ and $(Bi, Pb)_2Sr_2Ca_2Cu_3O_x$, can be prepared using the conventional melt-quenching method. The glasses are crystallized by annealing at temperatures above 500 °C, and are converted into superconductors with a large amount of superconducting low-T_c phase (critical transition temperature (T_c) = 85 K) or high-T_c phase (T_c = 105 K). It has been amply confirmed that the Bi(Pb)-based glass-ceramics (i.e. crystallized glasses) exhibit superconductivity with T_c above 100 K. More extensive study will lead to the fabrication of high-performance superconductors such as fibres with high critical current densities.

INTRODUCTION

Since the first report on new high-T_c superconducting $BiSrCaCu_2O_x$ ceramics by Maeda et al. [1], many researchers have expended much effort in the preparation of high-performance superconducting Bi–Sr–Ca–Cu–O (Bi-based) ceramics. The bulk samples of Bi-based superconductors have usually been prepared by the conventional powder sintering method. Komatsu et al. [2] succeeded in preparing superconducting $BiSrCaCu_2O_x$ ceramics with a critical transition temperature T_c(zero) of 92 K using the melt-quenching method. They also found that some melt-quenched samples such as $Bi_{1.5}SrCaCu_2O_x$ and $Bi_{0.5}Pb_{0.5}SrCaCu_2O_x$ were amorphous in X-ray diffraction analyses and showed glass transition and crystallization in differential thermal analyses [3]. Since the glasses based on the Bi–Sr–Ca–Cu–O system became high-T_c superconductors as a result of annealing at temperatures above 800 °C, Komatsu et al. [3] proposed to call the superconductors prepared through the crystallization of glasses "high-T_c superconducting glass-ceramics".

Hinks et al. [4] and Minami et al. [5] also developed almost simultaneously the glass-ceramics process for the preparation of Bi-based supercon-

0040-6031/91/$03.50

ductors. The discovery of high-T_c superconducting glass-ceramics in the Bi-based system has great significance because glass-ceramics offer the possibility of fibre production. The Bi-based high-T_c superconducting glass-ceramics have been extensively studied by many research groups, and experimental data on their superconducting properties has been accumulated rapidly. In this paper, we review glass formation in the Bi(Pb)–Sr–Ca–Cu–O system, the crystallization of glasses and the superconducting properties of glass-ceramics.

Some research groups [6–9] have attempted to use the melt-quenching method for the preparation of high-T_c superconducting Ln–Ba–Cu–O ceramics (Ln: Y, Gd or Yb). Although the superconductors such as $YBa_2Cu_3O_x$ with T_c around 90 K can be prepared easily using this technique, the melt-quenched samples are not amorphous but are a mixture of crystals of compounds such as $BaCuO_2$ and Y_2O_3. Very recently, Koo et al. [10] reported that a glass precursor of $YBa_2Cu_3O_x$ has been successfully obtained by very rapid quenching from the melt. There has been no report of glass formation in the Tl–Ba–Ca–Cu–O system or on the superconducting properties of Tl-based ceramics prepared by the melt-quenching method.

GLASS-FORMATION IN THE Bi(Pb)–Sr–Ca–Cu–O SYSTEM

The composition of Bi-based ceramics exhibiting good superconductivity, reported first by Maeda et al. [1], is $BiSrCaCu_2O_x$. On the other hand, to date, it has been well established that at least three superconducting phases, $Bi_2Sr_2Ca_{n-1}Cu_nO_x$ ($n = 1$, 2 and 3), are present as stable crystal structures in the Bi-based system. $Bi_2Sr_2CuO_x$ or $Bi_2(Sr, Ca)_2CuO_x$ is generally called the very low-T_c phase ($T_c \approx 10$ K), $Bi_2Sr_2CaCu_2O_x$ is the low-T_c phase ($T_c \approx 85$ K) and $Bi_2Sr_2Ca_2Cu_3O_x$ is the high-T_c phase ($T_c \approx 105$ K). It is, therefore, very interesting and important to examine glass formation in the samples with approximately the compositions $BiSrCaCu_2O_x$, $Bi_2Sr_2CaCu_2O_x$ and $Bi_2Sr_2Ca_2Cu_3O_x$.

Figure 1 shows the X-ray powder diffraction (XRD) patterns at room temperature for some melt-quenched samples of $Bi_ySrCaCu_2O_x$ ($y = 0.5$, 1, 1.2 and 2) [11]. In this experiment, the melt-quenched samples were prepared using the conventional melt-quenching method. That is to say, commercial powders of high-purity Bi_2O_3, $SrCO_3$, $CaCO_3$ and CuO were mixed and melted in a platinum crucible at 1150–1250 °C for 30–40 min in an electric furnace. The melts were poured onto an iron plate and pressed quickly to a thickness of 1.5–3 mm. It can be seen from Fig. 1 that the melt-quenched sample of $Bi_{0.5}SrCaCu_2O_x$ is not amorphous, while the samples of $Bi_{1.2}SrCaCu_2O_x$ and $Bi_2SrCaCu_2O_x$ are amorphous. The melt-quenched sample of $BiSrCaCu_2O_x$ is not amorphous, but a weak halo at around $2\theta = 30°$ is observed. The crystalline peaks in XRD patterns for

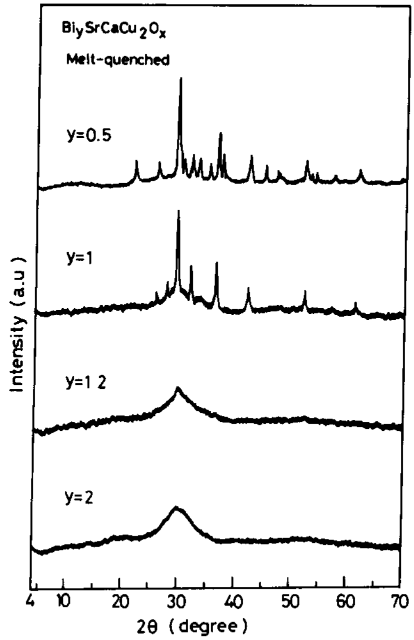

Fig. 1. XRD patterns at room temperature for some melt-quenched samples of $Bi_ySrCaCu_2O_x$ ($y = 0.5$, 1, 1.2 and 2) [11].

$Bi_{0.5}SrCaCu_2O_x$ and $BiSrCaCu_2O_x$ samples were assigned to $Bi_2(Sr, Ca)_2CuO_x$ (very low-T_c phase) and Cu_2O crystals.

A differential thermal analysis (DTA) curve for the $Bi_{1.2}SrCaCu_2O_x$ is shown in Fig. 2. An endothermic peak due to the glass transition ($T_g = 417\,°C$) and an exothermic peak (peak temperature: $T_x = 467\,°C$) due to the crystallization are clearly observed. Some other endothermic and exothermic peaks are observed at temperatures above 500 °C. These results (Figs. 1 and 2) clearly indicate that the melt-quenched samples of $Bi_{1.2}SrCaCu_2O_x$ and $Bi_2SrCaCu_2O_x$ are "glassy". The glass-forming region in the $x BiO_{3/2}$–$y SrO$–$z CaO$–$2CuO$ system ($x = 0.5$–3, $y = 0.5$–2 and $z = 0.3$–2) is shown in Fig. 3 [11]. It can be seen that the compositions in the Bi_2O_3–SrO–CaO–CuO system have a strong tendency to form a glass and that the addition of Bi_2O_3 is particularly effective in facilitating glass formation. The ratio of SrO and CaO is also important and the coexistence of SrO and CaO is necessary for glass formation.

Tohge et al. [12] also examined the glass-forming region in the pseudo-ternary system $BiO_{3/2}$–(CaO, SrO)$_{1/2}$–CuO, CaO/SrO = 1, by using a twin-roller rapid quenching method (glassy form: flakes with a thickness about 20 μm). They reported that the glassy samples were obtained in a relatively wide region including the compositions of interest, such as $BiSrCaCu_2O_x$ and $Bi_2Sr_2Ca_2Cu_3O_x$. Inoue et al. [13] reported that glassy ribbons of $BiSrCaCu_2O_x$ and $Bi_{1.3}SrCaCu_2O_x$ of about 30 μm thickness and

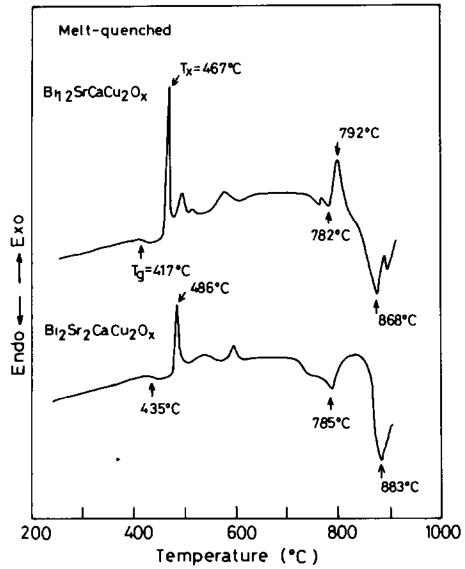

Fig. 2. DTA curves for the melt-quenched samples of $Bi_{1.2}SrCaCu_2O_x$ and $Bi_2Sr_2CaCu_2O_x$. Heating rate was 10 K min^{-1}.

2 mm width were produced by using a single-roller melt-spinning technique. Abe et al. [14] succeeded in preparing $BiSrCaCu_2O_x$ glass rods and coils by pumping the melt at 1150 °C into SiO_2 or Pyrex glass tubes. Figure 4 shows the XRD patterns at room temperature for some melt-quenched samples (bulk) of $Bi_{1.2}SrCaCu_wO_x$ ($w = 1.5$, 2.0 and 2.5). It is seen that the melt-quenched sample with $w = 1.5$ is almost a glass, but that that with $w = 2.5$ is not. These results indicate that a high Cu content is not effective for glass formation.

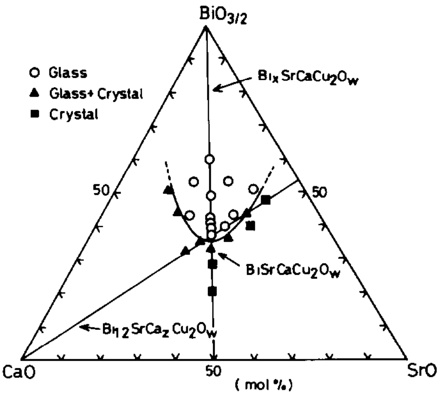

Fig. 3. The glass-forming region of the $xBiO_{3/2}$–$ySrO$–$zCaO$–$2CuO$ system ($x = 0.5$–3, $y = 0.5$–2, $z = 0.3$–2). The coordinates in the figure for the glass-forming region are the mol percentages of each oxide among $BiO_{3/2}$, SrO and CaO [11].

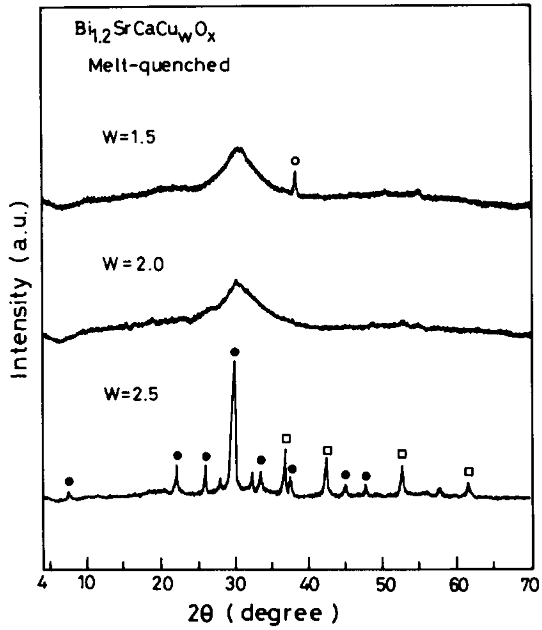

Fig. 4. XRD patterns at room temperature for some melt-quenched samples of $Bi_{1.2}SrCaCu_wO_x$ ($w = 1.5$, 2 and 2.5). ○, CaO; ●, $Bi_2(Sr, Ca)_2CuO_x$; □, Cu_2O.

The glass formation of samples with the composition of the low-T_c phase $Bi_2Sr_2CaCu_2O_x$ has been reported by several research groups [15–21]. For example, Yoshimura et al. [16] prepared $Bi_2Sr_2CaCu_2O_x$ 20 μm thick amorphous films by using a twin-roller rapid melt-quenching method. Zheng and Mackenzie [17] prepared 1 mm thick $Bi_4Sr_3Ca_3Cu_4O_x$ glass by using the conventional melt-quenching method. A DTA curve for $Bi_2Sr_2CaCu_2O_x$ glass prepared by the conventional melt-quenching method is shown in Fig. 2 [21]. The values of T_g and T_x are 435 °C and 486 °C respectively; these values are almost the same as those reported by other researchers.

The glass with the composition of the high-T_c phase $Bi_2Sr_2Ca_2Cu_3O_x$ has been successfully made by the rapid melt-quenching method [4,12,22,23]. Although many research groups have confirmed superconductivity at a temperature around 105 K in the Bi-based system, it is very difficult to prepare pure samples of the high-T_c phase. Sunshine et al. [24] and Takano et al. [25] found that the partial substitution of Pb for Bi in the Bi–Sr–Ca–Cu–O system was very effective in increasing the volume fraction of the high-T_c phase. It is, therefore, very important to examine the glass-forming region in the Bi–Pb–Sr–Ca–Cu–O system. The XRD patterns at room temperature for the melt-quenched samples of $Bi_{0.8}Pb_{0.2}SrCaCu_yO_x$ ($y = 1.5$, 1.8 and 2.0) are shown in Fig. 5. In the melt-quenched sample with $x = 1.5$, a large halo which is typical of amorphous materials was observed at around $2\theta = 30°$. The peak at around $2\theta = 37°$ is attributed to CaO. DTA curves

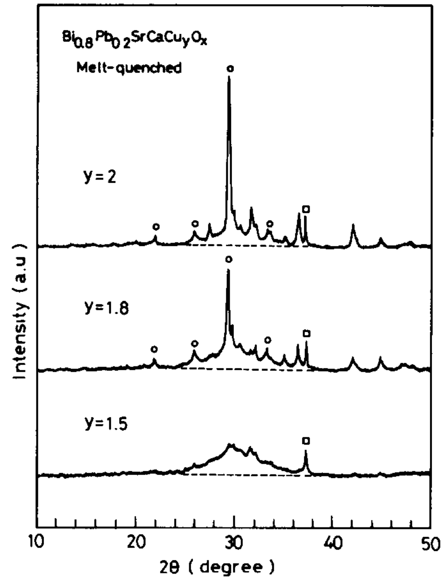

Fig. 5. XRD patterns at room temperature for the melt-quenched samples of $Bi_{0.8}Pb_{0.2}SrCaCu_yO_x$ ($y = 1.5$, 1.8 and 2). o, $Bi_2(Sr, Ca)_2CuO_x$; □, CaO.

for these melt-quenched samples are shown in Fig. 6. For the melt-quenched samples with $x = 1.5$ and 1.8, the glass transition and crystallization are clearly observed. Sato et al. [23] succeeded in preparing $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_x$ glass by using the conventional melt-quenching method. Ibara et al. [26] also reported that the melt-quenched samples of $BiPb_ySrCaCu_2O_x$ and $Bi_{0.8}Pb_ySr_{0.8}CaCu_{1.4}O_x$ ($y = 0.1$, 0.2, 0.3 and 0.4) were glass throughout.

Very recently, Tatsumisago et al. [27] measured the viscosity of $Bi_ySrCaCu_2O_x$ ($y = 1.5$ and 2.7) glasses in the glass transition region using the beam bending method and found that the Bi–Sr–Ca–Cu–O system can be characterized as a "fragile" liquid like the ZrF_4-based fluoride glasses. Varma et al. [28] have examined the dielectric properties of $Bi_2SrCaCuO_x$ and $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_x$ glasses and have found that these glasses possess relatively high dielectric constants as well as high electrical conductivity.

CRYSTALLIZATION OF Bi(Pb)–Sr–Ca–Cu–O GLASSES

To date, it has been shown that the glasses in the Bi(Pb)–Sr–Ca–Cu–O system, which were prepared by the rapid melt-quenching method, first crystallized in the $Bi_2(Sr, Ca)_2CuO_x$ phase at around 500 °C before forming the low-T_c phase $Bi_2Sr_2CaCu_2O_x$ during annealing at temperatures around 800 °C [16,20,26,29]. The exothermic peak at around 800 °C in DTA curves (see Fig. 2), which is observed just prior to the endothermic peak corre-

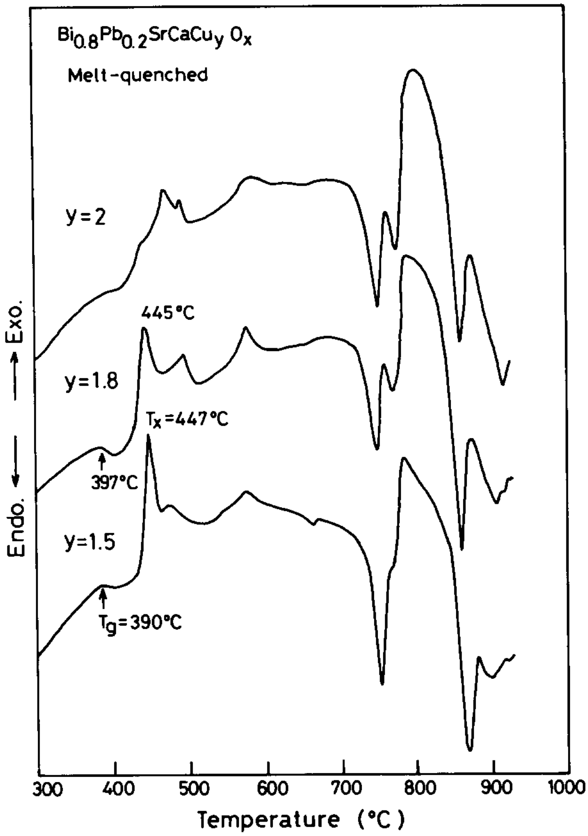

Fig. 6. DTA curves for the melt-quenched samples of $Bi_{0.8}Pb_{0.2}SrCaCu_yO_x$ ($y = 1.5$, 1.8 and 2).

sponding to the partial melting at around 870 °C, is closely related to the formation of the low-T_c phase [30]. The XRD patterns at room temperature for the annealed samples (after annealing, samples were removed from the furnace and cooled rapidly in air) of $Bi_{1.2}SrCaCu_2O_x$ are shown in Fig. 7 as an example [21]. The $Bi_2(Sr, Ca)_2CuO_x$ phase is formed in the samples annealed at 550 °C and 700 °C for 3 h. The XRD patterns for the sample annealed at 820 °C for 3 h are mainly assigned to the low-T_c phase. In this sample, the precipitation of CuO is also observed. These results are consistent with the data reported for the other Bi-based superconducting glass-ceramics.

Although the formation of the high-T_c phase in the Bi-based system is still open to question, it is well known that annealing at a temperature near the partial melting temperature is effective in increasing the volume fraction of the high-T_c phase. Recently, Shi et al. [22] examined the superconducting properties of crystallized Bi-based glasses with nominal compositions of $Bi_2Sr_2Ca_2Cu_3O_x$, $Bi_2Sr_2Ca_3Cu_4O_x$ and $Bi_2Sr_2Ca_4Cu_5O_x$, and found that

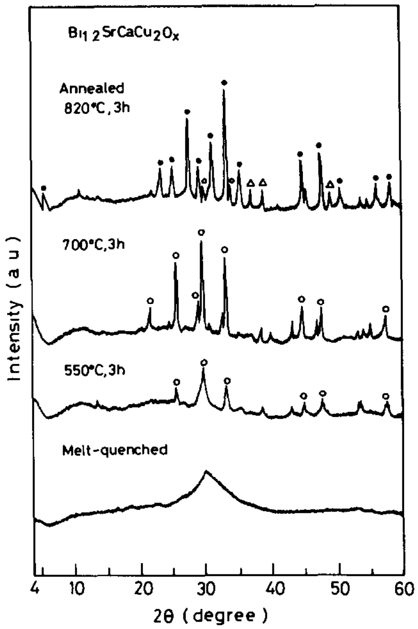

Fig. 7. XRD patterns at room temperature for the melt-quenched and annealed samples of $Bi_{1.2}SrCaCu_2O_x$ [21]. ○, $Bi_2(Sr, Ca)_2CuO_x$; ●, $Bi_2Sr_2CaCu_2O_x$; △, CuO.

the crystallized samples of $Bi_2Sr_2Ca_3Cu_4O_x$ and $Bi_2Sr_2Ca_4Cu_5O_x$ (annealed at 870 °C for 10 days) exhibited a single superconducting transition near 110 K in both resistivity and magnetic shielding experiments. Komatsu et al. [30–32] reported that prolonged annealing at 830 °C or 840 °C was very effective in increasing the volume fraction of the high-T_c phase in the Bi, Pb-based ceramics prepared by the melt-quenching method. The XRD patterns at room temperature for the annealed sample of $Bi_{0.8}Pb_{0.2}$ $SrCaCu_{1.5}O_x$ glass is shown in Fig. 8 [32]. It is seen that a high-T_c phase is clearly formed in the sample annealed for a prolonged time at 840 °C. A crystalline peak attributable to Ca_2PbO_4 was also detected.

Since the Bi-based glasses contain no pores and thus are high-density materials, it is expected that extremely tough Bi-based superconductors could be produced using the glass-ceramics process. Chaudhuri et al. [19] reported that the density of a glassy thick film of $Bi_4Sr_3Ca_3Cu_4O_x$ was 5.91 g cm^{-3} and that that of the sample annealed at 800 °C for 12 h in air was 6.08 g cm^{-3}. Sato et al. [23] reported that the density of the superconducting glass-ceramics with $T_c = 99$ K of $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_x$ was 6.42 g cm^{-3}, indicating that the annealed sample was of practically 100% theoretical density ($Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_{10+x}$: 6.25 g cm^{-3} and $Bi_{1.6}Pb_{0.4}Sr_2CaCu_2O_{8+y}$: 6.51 g cm^{-3}). The crystallization kinetics of superconducting crystals for

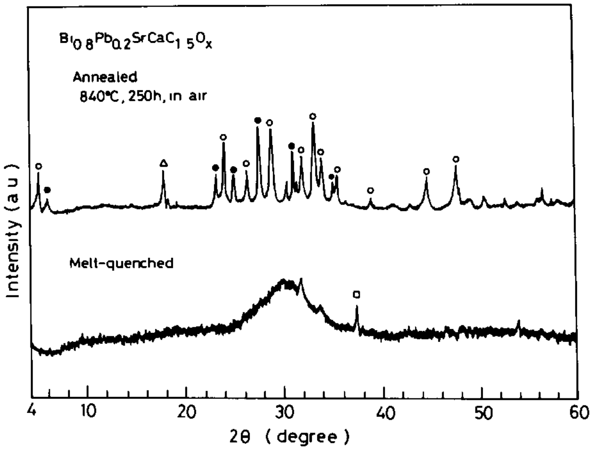

Fig. 8. XRD patterns at room temperature for the melt-quenched and annealed samples of $Bi_{0.8}Pb_{0.2}SrCaCu_{1.5}O_x$ [32]. ●, $Bi_2Sr_2CaCu_2O_x$; ○, $(Bi, Pb)_2Sr_2Ca_2Cu_3O_x$; △, Ca_2PbO_4; □, CaO.

Bi(Pb)-based glasses have not been reported yet. A detailed study of the crystallization mechanism of Bi(Pb)-based glasses is much needed.

SUPERCONDUCTING PROPERTIES OF Bi(Pb)-BASED GLASS-CERAMICS

$BiSrCaCu_2O_x$ glass-ceramics

The superconducting properties of $BiSrCaCu_2O_x$ glass-ceramics have been reported by several research groups [5,14,29]; the values of T_c(zero) are around 75 K. Komatsu et al. [2,33] examined the superconducting properties of $BiSrCaCu_2O_x$ ceramics (not glass-ceramics) prepared by the melt-quenching method and found that the ceramics exhibited superconductivity with $T_c = 92$ K and critical current density J_c (77 K, zero magnetic field) = 102 A cm^{-2} and, furthermore, that the samples annealed at temperatures above 800 °C in a nitrogen atmosphere were also superconductors with T_c above 80 K. Since the superconducting properties of Bi-based ceramics are very sensitive to the annealing and cooling conditions, it should be possible to improve the superconducting properties of $BiSrCaCu_2O_x$ glass-ceramics by finding the optimum preparation conditions. Here we report our experimental results on the superconducting properties of $Bi_{1.2}SrCaCu_2O_x$ glass-ceramics as an example [21].

The temperature dependences of the resistivity (*R–T* curves) of samples annealed at 830 °C, 850 °C and 870 °C for 20 h in air (air cooled samples) of $Bi_{1.2}SrCaCu_2O_x$ are shown in Fig. 9. In the *R–T* curves for these air-cooled samples, the large tailings are observed at temperatures below 90

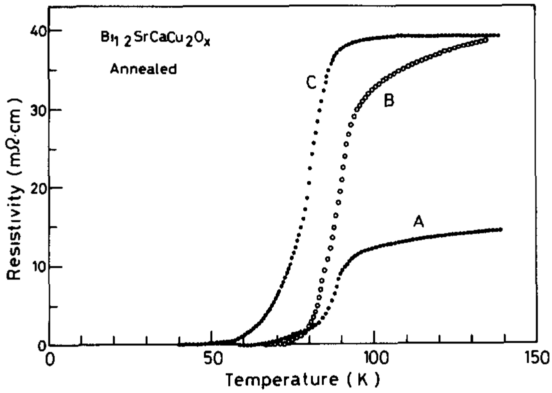

Fig. 9. Temperature dependence of resistivity for the samples of $Bi_{1.2}SrCaCu_2O_x$ annealed for 20 h in air (air-cooled samples) [21]. A, 830 °C ($T_c = 65$ K); B, 850 °C ($T_c = 71$ K); C, 870 °C ($T_c = 46$ K).

K. The values of normal-state resistivity for the samples annealed at 850 °C and 870 °C are much larger than that for the samples annealed at 830 °C. The temperature dependences of the resistivity for the samples annealed at 760 °C, 800 °C, 840 °C and 850 °C for 20 h in air (furnace-cooled samples) are shown in Fig. 10. It is seen that the values of normal-state resistivity decrease with increasing annealing temperature and the values of T_c increase from 57 K to 75 K. Furthermore, it should be pointed out that the tailings in the R–T curves for the furnace-cooled samples are smaller than those for the air-cooled samples and consequently the values of T_c for the former are higher than those for the latter.

The temperature dependences of the changes in inductance for the samples annealed at 760 °C, 800 °C and 850 °C for 20 h in air (furnace-

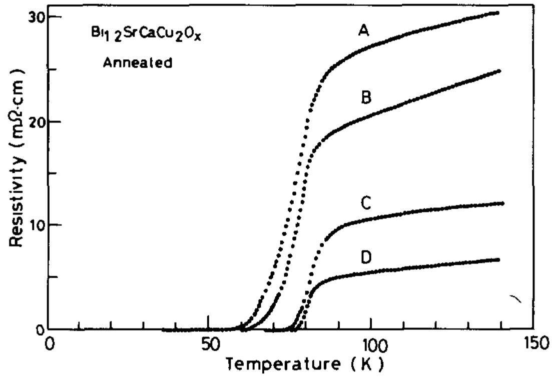

Fig. 10. Temperature dependence of resistivity for the samples of $Bi_{1.2}SrCaCu_2O_x$ annealed for 20 h in air (furnace-cooled samples) [21]. A, 760 °C ($T_c = 57$ K); B, 800 °C ($T_c = 60$ K); C, 840 °C ($T_c = 71$ K); D, 850 °C ($T_c = 75$ K).

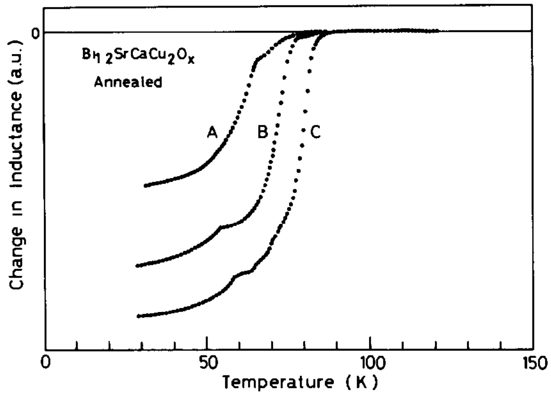

Fig. 11. Temperature dependence of changes in inductance for the samples of $Bi_{1.2}SrCaCu_2O_x$ annealed for 20 h in air (furnace-cooled samples) [21]. A, 760 °C; B, 800 °C; C, 850 °C.

cooled samples) of $Bi_{1.2}SrCaCu_2O_x$ are shown in Fig. 11. The mutual inductance of the bulk samples were measured by using an a.c. Hartshorn-type bridge, in which the frequency was 713 Hz and the a.c. field amplitude was 0.1 Oe. In all samples, the changes in inductance are clearly detected and their onsets are around 85 K. Particularly, it is noted that the changes in inductance for the sample annealed at 850 °C occur in almost one step at temperatures above 60 K and are distinct, but that for the sample annealed at 760 °C occurs in two steps and is gradual. The XRD patterns (not shown here) for these annealed samples were mainly assigned to the low-T_c phase, and no peak attributable to the high-T_c phase was observed. The results shown in Figs. 10 and 11 indicate that the volume fraction of the low-T_c phase in the $Bi_{1.2}SrCaCu_2O_x$ glass-ceramics increases with increasing annealing temperature (below 850 °C) and the value of T_c approaches that of the low-T_c phase.

In order to examine the formation of the high-T_c phase in $Bi_{1.2}SrCaCu_2O_x$ glass-ceramics, the glass was annealed at 880 °C for 20 h and then cooled rapidly in air (air-cooled) or cooled slowly in the furnace (furnace-cooled). The temperature dependences of the resistivity for these annealed samples are shown in Fig. 12. For the air-cooled sample (curve A), the value of normal-state resistivity is very large and a long tailing is observed. On the other hand, for the furnace-cooled sample (curve B), the value of normal-state resistivity is smaller than that for the air-cooled sample, and a distinct drop indicating the formation of the high-T_c phase is clearly observed at a temperature around 105 K. These results indicate that the superconducting properties in the samples annealed at temperatures near the partial melting temperature are greatly improved through the slow cooling to room temperature. The XRD patterns for these annealed samples are shown in Fig. 13. For the air-cooled sample, both the very low-T_c and the low-T_c phases are clearly observed. The unidentified peak is also observed at around $2\theta = 32°$.

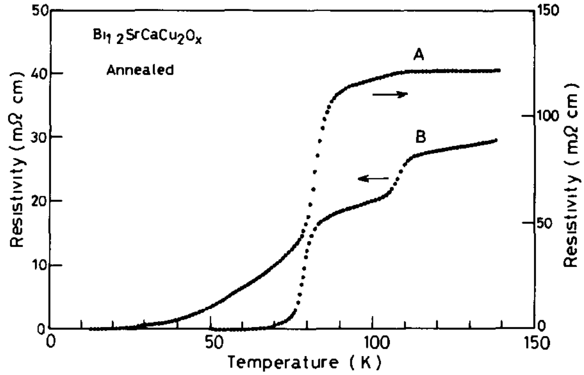

Fig. 12. Temperature dependence of resistivity for the samples of $Bi_{1.2}SrCaCu_2O_x$ annealed at 880 °C for 20 h in air [21]. A, air-cooled sample ($T_c = 17$ K); B, furnace-cooled sample ($T_c = 66$ K).

For the furnace-cooled sample, it is seen that the intensities of peaks attributable to the very low-T_c phase become weak and that of the unidentified peak at $2\theta = 32°$ becomes strong. Furthermore, a new crystalline peak, which has not been identified, appears at around $2\theta = 28°$. These results, shown in Fig. 13, indicate that some reactions occur in the sample during the slow cooling in a furnace. We believe that the main origin of the improvement in the superconducting properties of the furnace-cooled sample is due to the decrease in the volume fraction of the very low-T_c phase.

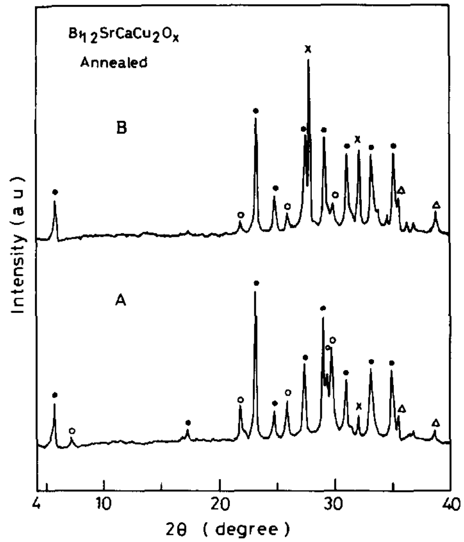

Fig. 13. XRD patterns at room temperature for the samples of $Bi_{1.2}SrCaCu_2O_x$ annealed at 880 °C for 2 h in air [21]. A, air-cooled sample; B, furnace-cooled sample. ○, $Bi_2(Sr, Ca)_2CuO_x$; ●, $Bi_2Sr_2CaCu_2O_x$; △, CuO; ×, unknown phase.

The absorption of oxygen during the slow cooling might result in the improvement of superconducting properties. Unfortunately, the formation of the high-T_c phase was not confirmed in the XRD analyses of both air-cooled and furnace-cooled samples. A study on the effect of annealing time on the formation of the high-T_c phase will be necessary.

Komatsu et al. [11] reported that the values of T_c(zero) for the glass-ceramics (annealed at 820 °C for 40 h in air; furnace-cooled samples) of $Bi_ySrCaCu_2O_x$ ($y = 1.2$–3) decrease with increasing Bi_2O_3 content. Nasu et al. [34] reported that the glass-ceramic of $Bi_{1.7}SrCa_{0.5}Cu_{2.7}O_x$ exhibited superconductivity with $T_c = 88$ K. Furthermore, Komatsu et al. [35] reported that the glass-ceramic of $Bi_{0.9}Pb_{0.1}SrCaCu_2O_x$ exhibited superconductivity with $T_c(\text{onset}) = 116$ K and $T_c(\text{zero}) = 100$ K.

$Bi_2Sr_2CaCu_2O_x$ glass-ceramics

The superconducting properties of $Bi_2Sr_2CaCu_2O_x$ or $Bi_4Sr_3Ca_3Cu_4O_x$ glass-ceramics have been reported by several research groups [15–19], and the values of T_c(zero) are 45–85 K. Because the composition of $Bi_2Sr_2CaCu_2O_x$ corresponds to that of the low-T_c phase and the melt-quenched sample with this composition becomes glass easily, it is very important to examine the superconducting properties of $Bi_2Sr_2CaCu_2O_x$ glass-ceramics in detail. Here, we show our experimental results on the superconducting properties of $Bi_2Sr_2CaCu_2O_x$ glass-ceramics (bulk sample) as an example [21]. We first checked the effect of annealing time on the superconducting properties of $Bi_2Sr_2CaCu_2O_x$ glass-ceramics. The temperature dependences of the resistivity for the samples annealed at 800 °C for 24 h and 48 h (air-cooled samples) are shown in Fig. 14. It is seen that the superconducting transition for the sample annealed for 48 h is sharp. The value of $T_c = 83$ K is similar to that of the low-T_c phase ($T_c = 85$ K). On the

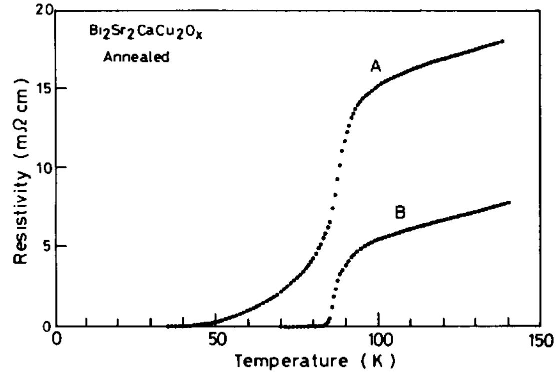

Fig. 14. Temperature dependence of resistivity for the annealed samples of $Bi_2Sr_2CaCu_2O_x$ (air-cooled samples) [21]. A, 800 °C, 24 h ($T_c = 42$ K); B, 800 °C, 48 h ($T_c = 83$ K).

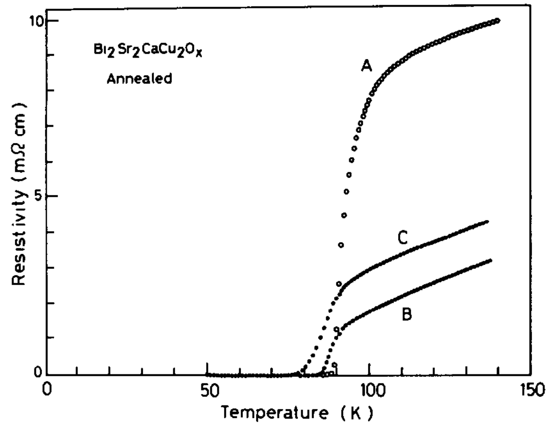

Fig. 15. Temperature dependence of resistivity for the annealed samples of $Bi_2Sr_2CaCu_2O_x$. A, 820 °C, 48 h, air-cooled ($T_c = 88$ K); B, 820 °C, 48 h, furnace-cooled ($T_c = 85$ K); C, 820 °C, 72 h, air-cooled + 400 °C, 10 h ($T_c = 78$ K).

other hand, for the sample annealed for 24 h, the normal-state resistivity is very large and a long tailing is observed. We next checked the effect of cooling conditions on the superconducting properties. The temperature dependences of the resistivity for the samples annealed at 820 °C for 48 h or 72 h are shown in Fig. 15. It is seen that the value of $T_c = 88$ K for the air-cooled sample is larger than the values for the furnace-cooled sample ($T_c = 85$ K) and for the sample obtained by annealing the air-cooled sample at 400 °C again ($T_c = 78$ K). The effect of cooling conditions obtained with the $Bi_2Sr_2CaCu_2O_x$ superconducting glass-ceramics is different from that for the $Bi_{1.2}SrCaCu_2O_x$ superconducting glass-ceramics, judging from the results obtained in the present study. The XRD pattern for the air-cooled sample is shown in Fig. 16. It is seen that the main peaks are attributable to the low-T_c phase. Some weak peaks attributable to the very low-T_c phase are also observed. It is noted that the precipitation of CuO is not detected. The XRD patterns (not shown here) for the furnace-cooled sample and for the sample annealed again at 400 °C were almost the same as that for the air-cooled sample, and no new peak appeared for these two samples. The origin of the difference in the R–T curves shown in Fig. 15 is unclear at this moment. In order to clarify the effect of cooling conditions on the superconducting properties of $Bi_2Sr_2CaCu_2O_x$ glass-ceramic, further studies, such as experiments on other samples annealed at various temperatures, will be necessary. The XRD pattern for the melt-quenched sample is also shown in Fig. 16. The melt-quenched sample of $Bi_2Sr_2CaCu_2O_x$ is a perfect glass.

The temperature dependences of the resistivity for the samples annealed at 850 °C, 860 °C and 870 °C for 48 h (air-cooled samples) are shown in Fig. 17. The value of T_c decreases on increasing the annealing temperature from 850 °C to 870 °C. A small drop in resistivity is observed at around 105 K for

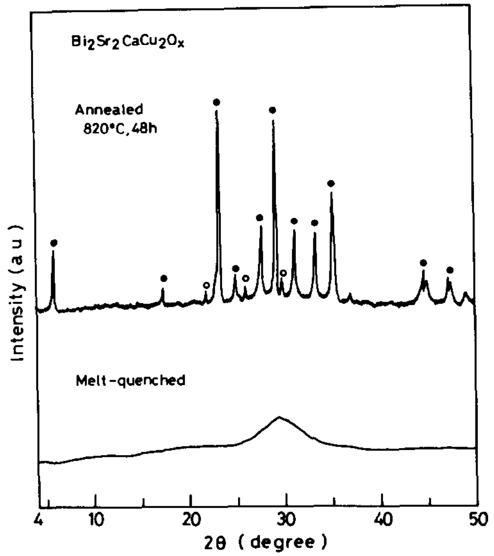

Fig. 16. XRD patterns at room temperature for the melt-quenched and annealed (820 °C, 48 h, air-cooled) samples of $Bi_2Sr_2CaCu_2O_x$ [21]. ●, $Bi_2Sr_2CaCu_2O_x$; ○, $Bi_2(Sr, Ca)_2CuO_x$.

the sample annealed at 860 °C, indicating that a small amount of the high-T_c phase is formed. For the sample annealed at 870 °C, the normal-state resistivity is very large compared with that for other annealed samples and no signal to imply the formation of the high-T_c phase is observed.

The values of T_c for the samples (air-cooled) of $Bi_2Sr_2CaCu_2O_x$ annealed at various temperatures for 48 h are summarised in Fig. 18. It is found that the $Bi_2Sr_2CaCu_2O_x$ glass-ceramics obtained by annealing at temperatures

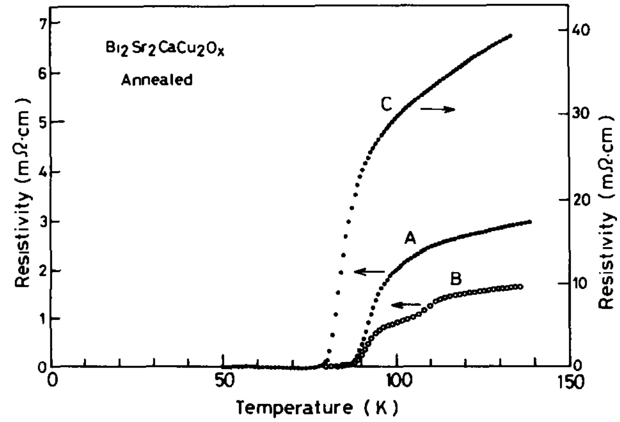

Fig. 17. Temperature dependence of resistivity for the samples of $Bi_2Sr_2CaCu_2O_x$ annealed for 48 h in air (air-cooled samples) [21]. A, 850 °C ($T_c = 86$ K); B, 860 °C ($T_c = 82$ K); C, 870 °C ($T_c = 78$ K).

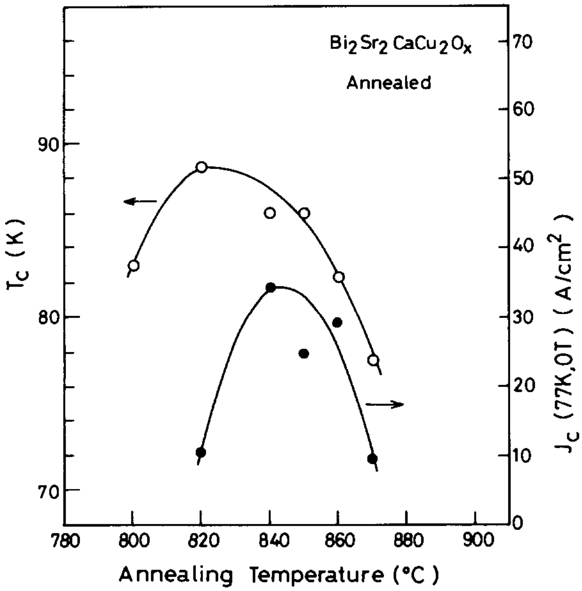

Fig. 18. Critical temperature T_c and critical current density J_c (77 K, zero magnetic field) for the annealed samples of $Bi_2Sr_2CaCu_2O_x$ (air-cooled samples). Annealing time was 48 h [21].

above 800 °C exhibit superconductivity with T_c above 80 K. The values of critical current density J_c at 77 K in zero magnetic field for these annealed samples are also shown in Fig. 18. The value of $J_c = 35$ A cm^{-2} is obtained for the sample annealed at 840 °C. Although the values of J_c for the $Bi_2Sr_2CaCu_2O_x$ superconducting glass-ceramics are not so high, it should be pointed out that these values are comparable to the values of J_c (usually below 50 A cm^{-2}) for the Bi–Pb–Sr–Ca–Cu–O ceramics with T_c above 100 K prepared by the conventional sintering method [36,37].

It is very significant that the superconducting properties of $Bi_2Sr_2CaCu_2O_x$ glass-ceramics are much better than those of $Bi_{1.2}SrCaCu_2O_x$ glass-ceramics, judging from the results obtained in the present study. Because the superconducting coupling between superconducting crystals at grain boundaries in the Bi-based ceramics is very weak [38], the coexistence of non-superconducting phases such as CuO, the concentration of ions such as Bi^{3+}, Ca^{2+} and Cu^{2+} at grain boundaries and the random orientation of superconducting crystals will enhance the weak coupling at grain boundaries. This weak coupling at grain boundaries leads to the lowering of T_c and broadening of the superconducting transition. Considering the weak coupling at grain boundaries, it is strongly desirable to make superconducting glass-ceramics with the composition of the low-T_c phase or the high-T_c phase, if one wants to obtain high-performance superconducting glass-ceramics. The above results support this idea, though the coupling nature of grain boundaries in $Bi_{1.2}SrCaCu_2O_x$ and $Bi_2Sr_2CaCu_2O_x$ superconducting glass-ceramics has not been clarified yet. Studies on the nature of coupling at grain boundaries in the Bi-based superconducting glass-ceramics will be valuable.

$(Bi, Pb)_2Sr_2Ca_2Cu_3O_x$ glass-ceramics

The superconducting properties of $Bi_2Sr_2Ca_2Cu_3O_x$ glass-ceramics have been reported by Hinks et al. [4], Tohge et al. [12], Shi et al. [22] and Sato et al. [23]. Tohge et al. [4] reported that the $Bi_2Sr_2Ca_2Cu_3O_x$ compound was successfully prepared in a glassy form using a twin-roller quenching method and that the glass-ceramics obtained by annealing at 860 °C for 4 h exhibited superconductivity with T_c(zero) = 86 K. Unfortunately, the presence of the high-T_c phase was not confirmed in their sample. Shi et al. [22] prepared the $Bi_2Sr_2Ca_2Cu_3O_x$ glass by using the rapid splat-quenching technique and examined the formation of the high-T_c phase due to the annealing at 870 °C for 1, 10 and 16 days. They reported that there was a noticeable resistivity drop near 110 K for all annealed samples, but the resistivity reached zero at 80 K. These results indicate that it is very difficult to obtain $Bi_2Sr_2Ca_2Cu_3O_x$ glass-ceramics containing a large proportion of the high-T_c phase.

On the other hand, several workers [23,26,30,32] succeeded in preparing the superconducting $(Bi, Pb)_2Sr_2Ca_2Cu_3O_x$ glass-ceramic with T_c(zero) of about 100 K. Ibara et al. [26] prepared many Bi, Pb-based glasses with compositions around $(Bi, Pb)_2Sr_2Ca_2Cu_3O_x$ using the conventional melt-quenching method and obtained the superconducting glass-ceramics with T_c(zero) of 102 K. Sato et al. [23] examined extensively the superconducting properties of $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_x$ glass-ceramics obtained by annealing under various conditions and found that the glass-ceramics annealed at 840 °c for 156 h in air exhibited superconductivity with T_c(zero) of 99 K. Here, we show our experimental results on the superconducting properties of Bi, Pb-based glass-ceramics [30,32].

Superconducting glass-ceramics of $Bi_{0.8}Pb_{0.2}SrCaCu_{1.5}O_x$ (sample A)and $BiPb_{0.2}SrCaCu_{1.5}O_x$ (sample B) were prepared by using the conventional melt-quenching method. The temperature dependences of the resistivity for the samples annealed at 830 °C and 840 °C for 250 h in air (air-cooled samples) are shown in Fig. 19. We find two features: the values of normal-state resistivity of sample A are much smaller than those of sample B and the values of critical temperature of sample A (T_c(zero): 98 K and 100 K) are much higher than those of sample B (T_c(zero): 80 K and 73 K). The temperature dependences of the changes in inductance for the sample annealed at 840 °C for 250 h are shown in Fig. 20. For sample A, a sharp drop was observed at temperatures above 100 K, indicating that the main superconducting crystals were the high-T_c phase. On the other hand, for sample B, a sharp drop was observed at temperatures around 85 K, indicating that the main superconducting crystals were the low-T_c phases. Similar

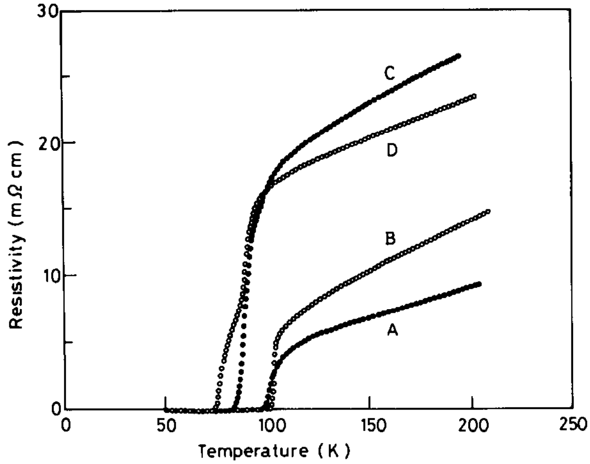

Fig. 19. Temperature dependence of resistivity for the samples of $Bi_{0.8}Pb_{0.2}SrCaCu_{1.5}O_x$ (A and B) and $BiPb_{0.2}SrCaCu_{1.5}O_x$ (C and D) annealed for 250 h in air (air-cooled samples) [32]. A, 830 °C ($T_c = 98$ K); B, 840 °C ($T_c = 100$ K); C, 830 °C ($T_c = 80$ K); D, 840 °C ($T_c = 73$ K).

temperature dependences of the changes in inductance were observed for the samples annealed at 830 °C for 250 h. These results are in accord with the results of resistivity measurements.

One of the most important results obtained in these experiments is that the volume fraction of the high-T_c phase in sample A ($Bi_{0.8}Pb_{0.2}SrCaCu_{1.5}O_x$) annealed at 830 °c or 840 °C for 250 h is much higher than that in the annealed sample B ($BiPb_{0.2}SrCaCu_{1.5}O_x$). If the Pb element substitutes for Bi in the crystal structure of the high-T_c phase, the atomic ratio of Bi(Pb), Sr, Ca and Cu in sample A would be 2 : 2 : 2 : 3, the same as that in the high-T_c phase. The chemical composition of the annealed (840 °C, 250 h)

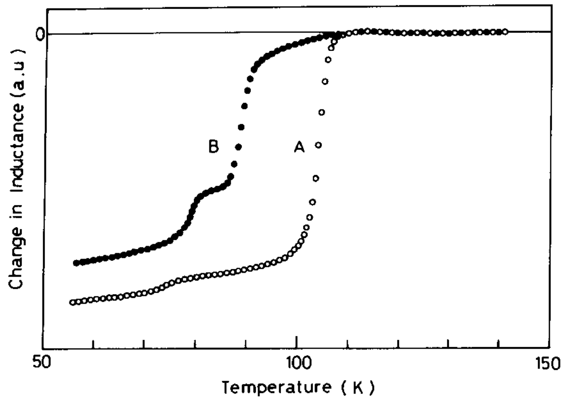

Fig. 20. Temperature dependence of changes in inductance for the samples for 250 h of $Bi_{0.8}Pb_{0.2}SrCaCu_{1.5}O_x$ (A) and $BiPb_{0.2}SrCaCu_{1.5}O_x$ (B) annealed at 840 °C.

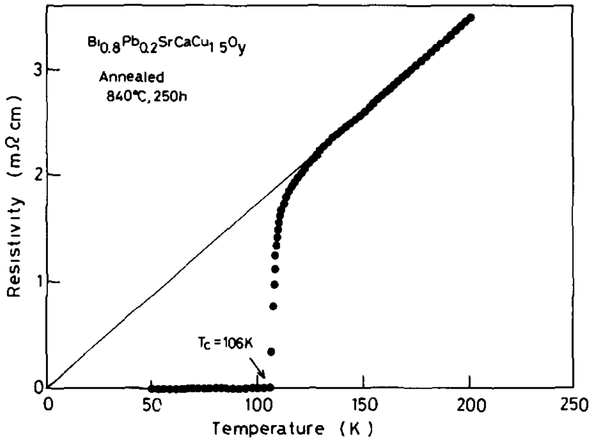

Fig. 21. Temperature dependence of resistivity for the sample of $Bi_{0.8}Pb_{0.2}SrCaCu_{1.5}O_x$ annealed at 840 °C for 250 h in air (furnace-cooled sample).

sample A was analyzed using inductively coupled plasma emission spectroscopy, and the stoichiometry $Bi_{1.6}Pb_{0.39}Sr_{1.93}Ca_{1.97}Cu_{2.85}O_x$ was inferred. This indicates that the change in the chemical composition during the melt and annealing is very small. These results imply that the Pb element substitutes for Bi in the crystal structure of the high-T_c phase in the Bi,Pb-based glass-ceramics. We obtained excellent data on the superconducting properties of $Bi_{0.8}Pb_{0.2}SrCaCu_{1.5}O_x$ glass-ceramics. The melt-quenched sample A was first annealed at 840 °C for 250 h in air and then cooled slowly (about 5 K min^{-1}) to room temperature in a furnace. The temperature dependence of the resistivity for this annealed sample A is shown in Fig. 21. The values of T_c(zero) and J_c (77 K, zero magnetic field) were 106 K and 250 A cm^{-2}, respectively. These are the highest values reported so far for Bi(Pb)-based superconducting glass-ceramics prepared by the melt-quenching method.

SUMMARY

There has been great progress in the area of Bi(Pb)-based superconducting glass-ceramics in the short period after the discovery of Bi-based superconductors. It has been demonstrated that many glasses, such as those with the compositions $Bi_2Sr_2CaCu_2O_x$ and $Bi(Pb)_2Sr_2Ca_2Cu_3O_x$, can be prepared by the conventional melt-quenching method and the glasses are converted into superconductors with a large proportion of superconducting low-T_c phase or high-T_c phase as a result of annealing at temperatures above 800 °C. However, information on the crystallization mechanism, critical current density, the nature of superconducting coupling at grain boundaries and the possibility of unidirectional orientation of superconducting crystals in the glass-ceramics is limited at this moment. Such information will be necessary for the fabrication of high-performance superconducting glass-ceramic components such as fibres with high critical current densities. More extensive study on the Bi(Pb)-based superconducting glass-ceramics is greatly needed.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge Professor T. Yamashita, Nagaoka University of Technology, for useful discussion. The authors also thank K. Imai, O. Tanaka, R. Sato, T. Ohki, C. Hirose and H. Meguro for the preparation of glasses and the measurements of superconducting properties of glass-ceramics.

REFERENCES

1 H. Maeda, Y. Tanaka, M. Fukutomi and T. Asano, Jpn. J. Appl. Phys., 27 (1988) L209.
2 T. Komatsu, K. Imai, R. Sato, K. Matusita and T. Yamashita, Jpn. J. Appl. Phys., 27 (1988) L533.
3 T. Komatsu, R. Sato, K. Imai, K. Matusita and T. Yamashita, Jpn. J. Appl. Phys., 27 (1988) L550.
4 D.G. Hinks, L. Soderholm, D.W. Capone II, B. Dabrowski, A.W. Mitchell and D. Shi, Appl. Phys. Lett., 53 (1988) 423.
5 T. Minami, Y. Akamatsu, M. Tatsumisago, N. Tohge and Y. Kowada, Jpn. J. Appl. Phys., 27 (1988) L777.
6 T. Komatsu, K. Imai, K. Matusita, M. Takata, Y. Iwai, A. Kawakami, Y. Kaneko and T. Yamashita, Jpn. J. Appl. Phys., 26 (1987) L1148.
7 T. Komatsu, K. Imai, K. Matusita, M. Ishii, M. Takata and T. Yamashita, Jpn. J. Appl. Phys., 26 (1987) L1272.
8 T. Komatsu, T. Ohki, K. Imai and K. Matusita, J. Mater. Sci. Lett., 8 (1989) 1.
9 (a) Y. Šestàk, M. Nevřiva, E. Pollert, J. Heitmàuek, A. Třiska, M. Šimeckovà, Thermochim. Acta, 132 (1988) 35.
9 (b) J. McKittrick, S. Sasayama, M.E. Mchenry, G. Kalonji and R.C. O'Handley, J. Appl. Phys., 65 (1989) 3662.
10 H.S. Koo, T.Y. Tseng, R.S. Liu, Y.T. Huang, K.S. Kuan and P.T. Wu, Jpn. J. Appl. Phys., 28 (1989) L41.
11 T. Komatsu, T. Ohki, K. Matusita and T. Yamashita, J. Ceram. Soc. Jpn., 97 (1989) 251.
12 N. Tohge, S. Tsuboi, Y. Akamatsu, M. Tatsumisago and T. Minami, J. Ceram. Soc. Jpn., 97 (1989) 334.
13 A. Inoue, H. Kimura, K. Matsuzaki, A.P. Tsai and T. Masumoto, Jpn. J. Appl. Phys., 27 (1988) L941.
14 Y. Abe, H. Hosono, M. Hosoe, J. Iwase and Y. Kubo, Appl. Phys. Lett., 53 (1988) 1341.
15 H. Sato, W. Zhu and T. Ishiguro, J. Solid State Chem., 75 (1988) 207.
16 M. Yoshimura, T.H. Sung, Z. Nakagawa and T. Nakamura, Jpn. J. Appl. Phys., 27 (1988) L1877.

17 H. Zheng and J.D. Mackenzie, Phys. Rev. B, 38 (1988) 7166.

18 K.B.R. Varma, K.J. Rao and C.N.R. Rao, Appl. Phys. Lett., 54 (1989) 69.

19 B.K. Chaudhuri, K. Som and S.P.S. Gupta, J. Mater. Sci. Lett., 8 (1989) 520.

20 Y. Oka, N. Yamamoto, H. Kitaguchi, K. Oda and J. Takada, Jpn. J. Appl. Phys., 28 (1989) L213.

21 T. Komatsu, T. Ohki, C. Hirose and K. Matusita, J. Non-Cryst. Solids, 113 (1989) 274.

22 D. Shi, M. Tang, K. Vandervoort and H. Claus, Phys. Rev. B, 39 (1989) 9091.

23 H. Sato, W. Zhu, M.M. Miller, T. Ishiguro, A.I. Schindler and C.S. Calhoun, J. Solid State Chem., 79 (1989) 146.

24 S.A. Sunshine, T. Siegrist, L.F. Schneemeyer, D.W. Murphy, R.J. Cava, B. Batlogg, R.B. van Dover, R.M. Fleming, S.H. Glarum, S. Nakamura, R. Farrow, J.J. Krajewski, S.M. Zahurak, J.V. Waszczak, J.H. Marshall, P. Marsh, L.W. Rupp, Jr. and W.F. Peck, Phys. Rev. B, 38 (1988) 893.

25 M. Takano, J. Takada, K. Oda, H. Kitaguchi, Y. Miura, Y. Ikeda, Y. Tomii and H. Mazaki, Jpn. J. Appl. Phys., 27 (1988) L1041.

26 Y. Ibara, H. Nasu, T. Imura and Y. Osaka, Jpn. J. Appl. Phys., 28 (1989) L37.

27 M. Tatsumisago, C.A. Angell, S. Tsuboi, Y. Akamatsu, N. Tohge and T. Minami, Appl. Phys. Lett., 54 (1989) 2268.

28 K.B.R. Varma, G.N. Subbanna, T.V. Ramakrishnan and C.N.R. Rao, Appl. Phys. Lett., 55 (1989) 75.

29 T. Kanai, T. Kumagai, A. Soeta, T. Suzuki, K. Aihara, T. Kamo and S. Matsuda, Jpn. J. Appl. Phys., 27 (1988) L1435.

30 R. Sato, T. Komatsu, K. Matusita and T. Yamashita, Jpn. J. Appl. Phys., 28 (1989) L583.

31 T. Komatsu, R. Sato, C. Hirose, K. Matusita and T. Yamashita, Jpn. J. Appl. Phys., 27 (1988) L2293.

32 T. Komatsu, R. Sato, K. Matusita and T. Yamashita, Appl. Phys. Lett., 54 (1989) 1169.

33 T. Komatsu, R. Sato, K. Imai, K. Matusita and T. Yamashita, Jpn. J. Appl. Phys., 27 (1988) L1839.

34 H. Nasu, Y. Ibara, S. Makida, T. Imura and Y. Osaka, J. Non-Cryst. Solids, 105 (1988) 185.

35 T. Komatsu, R. Sato, K. Imai, K. Matusita and T. Yamashita, IEEE Trans. Magn., 25 (1989) 2150.

36 K. Togano, H. Kumakura, H. Maeda, E. Yanagisawa and K. Takahashi, Appl. Phys. Lett., 53 (1988) 1329.

37 A. Kikuchi, M. Matsuda, M. Takata, M. Ishii, T. Yamashita and H. Koinuma, Jpn. J. Appl. Phys., 28 (1989) L371.

38 H. Kumakura, K. Togano, K. Takahashi, E. Yanagisawa, M. Asano and H. Maeda, Jpn. J. Appl. Phys., 27 (1988) L2059.