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Thermal instability of Bi–Pb–Sr–Ca–Cu–O superconductor around 650 °C

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$Bi_{0.85}Pb_{0.15}Sr_{0.8}CaCu_{1.4}O_y$ superconductor was quenched to room temperature after annealing at several temperatures in air. From the initial magnetization curve measurement for the annealed samples, it was found that the volume fraction of superconducting phases of the sample annealed at 650°C greatly decreased. TEM observation revealed that a second phase often appeared in the grain-boundary region for the sample annealed at 700 °C. The second phase was identified as $Bi_1Pb_2Sr_{2.6}Ca_1Cu_{1.6}O_y$ by energy dispersive spectroscopy.

1. Introduction

It has been found that the partial lead substitution for bismuth is an effective method for preparing a single phase with a critical temperature (T_c) of 110 K (the high T_c phase) in the Bi–Sr–Ca–Cu–O system [1]. However, superconducting phases with T_c < 100 K exist, although these phases show the same X-ray diffraction pattern as the high T_c phase. It is thought that such behaviour is due to stacking faults, compositional fluctuation in the solid solution, cation deficiency, oxygen deficiency [2] and thermal instability. A narrow range of solid solutions exists in the Bi–Pb–Sr–Ca–Cu–O system [3]. Strontium, calcium and copper ratios affect T_c strongly, and even a small surplus of calcium and copper is enough to decrease T_c to around 95 K [4]. Experiments were carried out to examine oxygen deficiency and thermal instability. For a phase with T_c = 80 K (the low T_c phase), oxygen loss and the *c*-axis increase with increasing temperature [5]; for the high T_c phase, T_c is reported to be insensitive to quenching temperature below 650 °C [6]. This is in marked contrast with the drastic T_c variation of the low T_c phase [7]. Matsuda *et al.* [8, 9] investigated the effect of annealing on the high T_c phase. A tailing phenomenon was observed in the resistivity–temperature (*R–T*) curve for all samples annealed at 600–825 °C. It was supposed that this phenomenon was closely related to the appearance of an unknown peak at $2\theta = 17.9°$ in the X-ray diffraction pattern (CuK_α) which is close to the main peak ($2\theta = 17.6°$) of the Ca_2PbO_4 phase. Furthermore, from the a.c. susceptibility measurements, it was elucidated that the tailing phenomenon was caused by the weak coupling between the high T_c grains during annealing.

In the present work, in order to clarify the origin of the weak coupling due to annealing, we estimate the volume fraction of the superconducting phase of annealed samples through initial magnetization curve measurement, and investigate their microstructure and crystallographic properties.

2. Experimental procedure

Superconducting ceramic powder with the starting composition of $Bi_{0.85}Pb_{0.15}Sr_{0.8}CaCu_{1.4}O_y$ was prepared by a solid-state reaction. Appropriate amounts of Bi_2O_3, PbO, $SrCO_3$, $CaCO_3$ and CuO of high purity (99.9%) were wet-mixed in ethanol and calcined at 800 °C. The sample was ground, then pressed and heated at 835 °C, and cooled to room temperature in a furnace, and finally ground. This process (from pressing to grinding) was repeated several times to ensure a complete solid-state reaction; the total firing time was about 50 h. All firing was done in air. Thermogravimetric (TG) analysis was carried out in air with heating and cooling rates of 5 °C min^{-1} between room temperature and 800 °C, and subsequently between room temperature and 830 °C. The pressed samples were quenched to room temperature after annealing at several temperatures in air for 24 h. The initial magnetization curves were measured at 77, 90 and 100 K for the powder, which was obtained by grinding the quenched bulk sample, using a vibrating sample magnetometer. X-ray powder diffraction (XRD) data were taken at room temperature with graphite-monochromatized copper radiation. Dense samples were prepared by hot pressing in air at 830 °C at 300 kg cm^{-2} for 2 h. Then, the sample was annealed at 700 °C in air for 50 h. Microstructural and compositional analyses were performed with transmission electron microscopy (TEM) equipped with energy dispersive spectroscopy (EDX).

3. Results and discussion

The low T_c phase or an unknown phase was not appreciably observed in the XRD pattern for the sample before annealing. Fig. 1 shows the TG curve for the powder before annealing. Only during the first heating was weight loss observed below 500 °C, apparently due to moisture included in the sample. A considerable weight loss occurred above about 800 °C,

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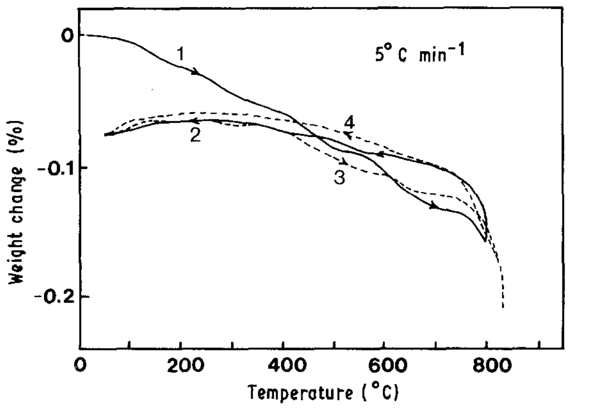

Figure 1 Thermogravimetric curve in air for the sample before annealing. The starting composition was $Bi_{0.85}Pb_{0.15}Sr_{0.8}CaCu_{1.4}O_y$. Temperature was changed successively, 1 → 2 → 3 → 4.

due to a release of oxygen from the sample, because the weight change of the sample is reversible.

Fig. 2 shows the lattice constants of quenched samples. The *a*-axis remained almost unchanged, and the smallest value was observed in the sample annealed at 650 °C. On the other hand, the *c*-axis of the quenched sample tended to increase with increasing annealing temperature, except that the *c*-axis of the sample annealed at 650 °C decreased. Fig. 3 shows the

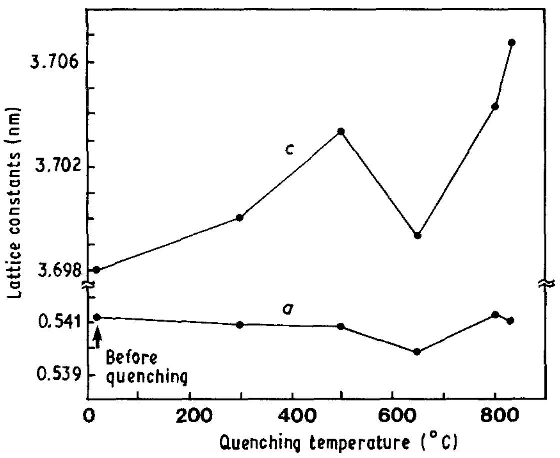

Figure 2 The lattice constants of quenched samples with the starting composition of $Bi_{0.85}Pb_{0.15}Sr_{0.8}CaCu_{1.4}O_y$.

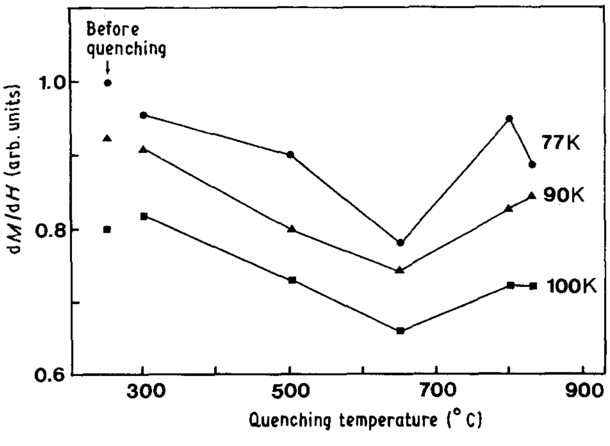

Figure 3 XRD patterns (CuK_α) for quenched samples with the starting composition of $Bi_{0.85}Pb_{0.15}Sr_{0.8}CaCu_{1.4}O_y$.

slope of initial magnetization curve ($-$ dM/dH) at 77, 90 and 100 K for the quenched samples. When the measurement temperature and grain size were constant, the value of $-$ dM/dH was proportional to the volume fraction of superconducting phases. As shown in Fig. 3, the volume fraction of the high T_c phase decreased sharply at 650 °C.

Fig. 4 shows the XRD patterns for the quenched samples in the diffraction angle range $2\theta = 17.0°–18.5°$. In the sample annealed at 650 °C, an unknown phase was observed, which showed a peak at $2\theta = 17.95°$. This result was similar to that in the previous study [8]. At 800 °C, the peak for the unknown phase disappeared, and Ca_2PbO_4 was formed in small amounts. At 830 °C, both the unknown phase and the Ca_2PbO_4 phase disappeared in the XRD pattern.

Fig. 5 shows transmission electron micrographs for the hot-pressed samples. In the annealed sample, a second phase (A in Fig. 5b) was often observed between the high T_c phase grains. The second phase was identified as $Bi_1Pb_2Sr_{2.6}Ca_1Cu_{1.6}O_y$ by EDX. It is known that the lead-rich high T_c phase was not stabilized around 700 °C and small amounts of $(Sr, Ca)_2CuO_3$ and Ca_2PbO_4, not pure but including both strontium and bismuth, precipitate after annealing around 700 °C [10]. It seems that the unknown peak in Fig. 4 is due to the second phase, and the high T_c phase locally decomposes in the grain-boundary region around 650 °C.

Matsuda *et al.* [9] measured the temperature dependence of the a.c. susceptibility for the powder sample obtained by crushing after annealing at 700 °C

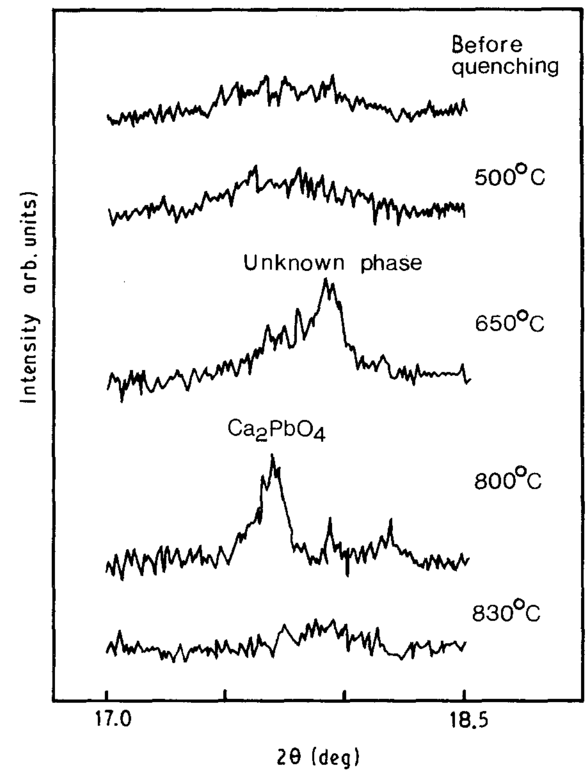

Figure 4 Slope of the initial magnetization curve ($-$ dM/dH) at 77, 90 and 100 K for quenched samples with the starting composition of $Bi_{0.85}Pb_{0.15}Sr_{0.8}CaCu_{1.4}O_y$.

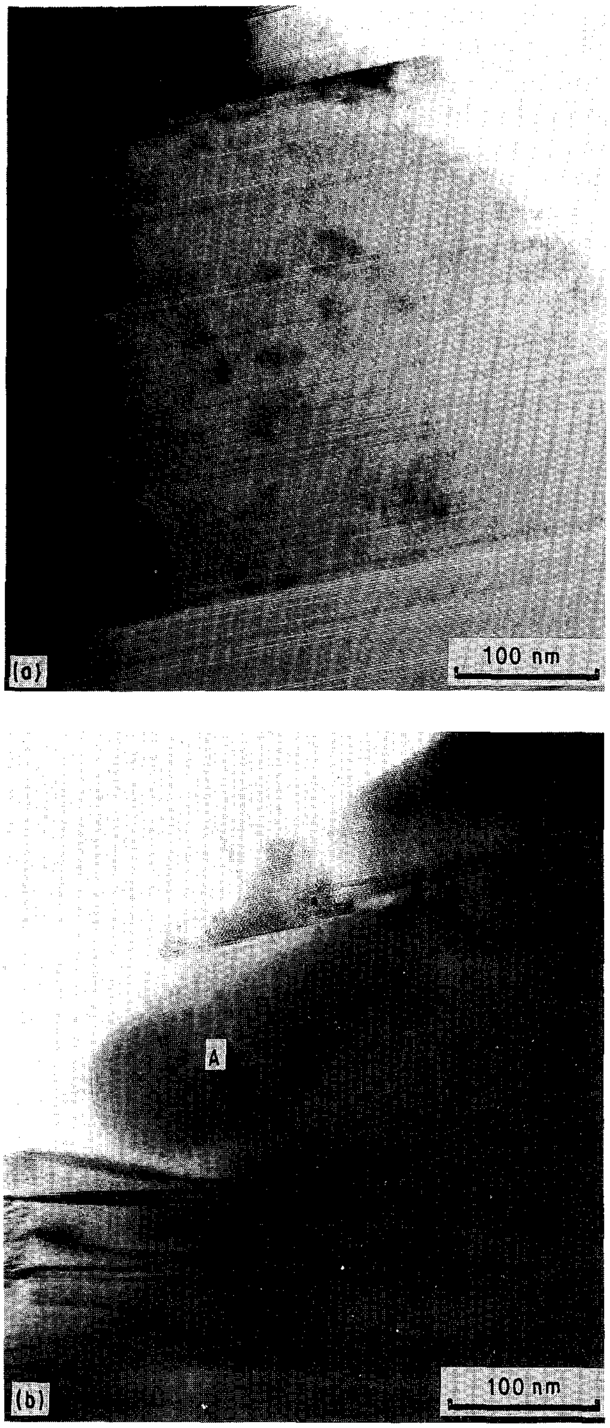

Figure 5 Transmission electron micrographs for hot-pressed samples (a) before annealing and (b) after annealing at 700 °C in air for 50 h.

and only one step was observed around 112 K in the magnetization–temperature curve. They concluded that the annealed sample did not contain a low T_c phase. Taking this into account, it is considered that the second phase is not a superconducting phase and is the origin of the weak coupling between the high T_c grains, which results in the tailing phenomenon in the R–T curve.

4. Conclusions

Oxygen loss occurred abruptly above 800 °C in air for the lead-stabilized high T_c phase. The *c*-axis tended to increase with increasing temperature. However, at about 650 °C, the *c*-axis of the high T_c phase decreased. From the initial magnetization curve measurement for the annealed samples, it was found that the volume fraction of superconducting phases of the sample annealed at 650 °C decreased greatly. TEM observation revealed that the second phase often appeared in the grain-boundary region for the sample annealed at 700 °C. The composition of the second phase was $Bi_1Pb_2Sr_{2.6}Ca_1Cu_{1.6}O_y$. It seems that the high T_c phase locally decomposes around 650 °C and the second phase appears in the grain-boundary region.

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