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# Effect of annealing on properties of bismuth based high $T_c$ superconductors

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A novel method to increase the amount of the 110 K phase in the Bi–Sr–Ca–Cu–O system was examined. After the sample with composition of $Bi_2Sr_2CaCu_2O_x$ had been calcined, it was soaked in ethanol containing copper acetate and calcium acetate, the amounts of which were determined to give the composition of $Bi_2Sr_2Ca_2Cu_3O_y$ after sintering. Subsequently, annealing at about 400 °C was conducted to examine the stability of the 110 K phase. The sample containing mainly the 80 K phase and a small amount of the 110 K phase showed an increase in the amount of the 110 K phase while that containing only the 80 K phase showed no change. Therefore, it is presumed that the 110 K phase may grow when the excess calcium and copper coexist adjacent to the 80 K phase at relatively low temperatures such as 400 °C.

## 1. Introduction

Since Bednorz and Müller [1] discovered a new type of oxide superconductor with a high superconducting transition temperature ($T_c$), a great number of studies have been reported. Among them, Y–Ba–Cu–O [2], Bi–Sr–Ca–Cu–O [3] and Tl–Ba–Ca–Cu–O [4] systems attract much attention because of the high $T_c$ values. The Tl–Ba–Ca–Cu–O system exhibits the highest $T_c (\rho = 0)$, but it contains the highly poisonous element thallium which makes handling of this compound very difficult. The Bi–Sr–Ca–Cu–O system consists of less poisonous elements and includes two different superconducting phases with the $T_c$ of 80 K (the low-$T_c$ phase) and 110 K (the high-$T_c$ phase), and hence it makes this system attractive in view of practical use. One of the most serious problems in this system is, however, difficulty in obtaining the pure high-$T_c$ phase.

Up to the present time, various methods to obtain the pure high-$T_c$ phase have been proposed, including high oxygen pressure treatment at low temperatures [5], addition of excess calcium and copper [6, 7], crystallization from an amorphous state [8] as well as addition of lead [9]. The low-$T_c$ phase has the ideal composition $Bi_2Sr_2CaCu_2O_x$ and is thought to form first at ordinary sintering temperatures, while the high-$T_c$ phase has the ideal composition $Bi_2Sr_2Ca_2Cu_3O_y$ and is thought to form when the sample is held for a long time. The thermodynamic stability of compounds depends on the composition, temperature and partial pressure of constituents and so on. In order to fabricate the pure high-$T_c$ phase, it is essential to clarify its stability under preparation conditions. Although the thermodynamic stability in this system has not been clarified completely at the moment, reaction schemes concerning the formation of the high-$T_c$ phase are proposed.

According to the previous work [10], possible reactions are proposed to explain the sequential phase development during the preparation procedure

$$\begin{array}{lll} 2Bi_2Sr_2CaCu_2O_x & \rightarrow & Bi_2Sr_2Ca_2Cu_3O_y \\ (\text{low-}T_c\text{ phase}) & & (\text{high-}T_c\text{ phase}) \\ & & + Bi_2Sr_2CuO_z \\ & & (\text{semiconducting phase}) \end{array} \quad (1)$$

Reaction 1 indicates that the low-$T_c$ phase undergoes a disproportionation reaction which is presumed to take place just below the melting point. If excess CaO and CuO (or some compounds containing both elements such as $Ca_2CuO_3$) exist adjacent to the low-$T_c$ phase, the following reaction may happen

$$Bi_2Sr_2CaCu_2O_x + CaO + CuO \rightarrow Bi_2Sr_2Ca_2Cu_3O_y \quad (2)$$

Reaction 2 indicates that the low-$T_c$ phase may change to the high-$T_c$ phase when excess CaO and CuO coexist with the low-$T_c$ phase, providing that the high-$T_c$ phase is thermodynamically stable under a given condition. Furthermore, the semiconducting phase may react with adjacent excess CaO and CuO to form the high-$T_c$ phase, which is expressed by the following formula

$$Bi_2Sr_2CuO_z + 2CaO + 2CuO \rightarrow Bi_2Sr_2Ca_2Cu_3O_y \quad (3)$$

It is presumed that the high-$T_c$ phase can be formed from both the low-$T_c$ and semiconducting phases by

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choosing appropriate preparation conditions. In this study, we examined a novel method to increase the amount of the high-$T_c$ phase in the Bi–Sr–Ca–Cu–O system by annealing at low temperatures in combination with a soaking treatment.

## 2. Experimental

The mixture with composition of Bi : Sr : Ca : Cu = 2 : 2 : 1 : 2, which consists of high purity $Bi_2O_3$, $SrCO_3$, $CaCO_3$ and CuO, was calcined in the temperature range of 768 to 778 °C for 5 h. The resulting sample was pulverized and calcined again to increase the homogeneity of the composition. A part of the calcined powder was pressed to make pellets with a diameter of 20 mm and thickness of 2 to 3 mm under a pressure of 600 kg cm$^{-2}$ while the remaining powder was made into pellets after it was soaked in ethanol containing copper acetate and calcium acetate, the amounts of which were determined to give the composition of Bi : Sr : Ca : Cu = 2 : 2 : 2 : 3 after firing. The soaking treatment was carried out to add fine CaO and CuO powders to the sample which were presumed to increase the high-$T_c$ phase. The samples were sintered in the temperature range of 834 to 857 °C for 10 h. With respect to the soaked samples, annealing was conducted in the temperature range of 400 to 420 °C for 20 h. The sample obtained at each stage was examined by powder X-ray diffraction and scanning electron microscope.

After the electrodes were attached to the sample by evaporating gold, they were connected to copper lead wires with a silver paste. The resistivity was measured employing the d.c. four-probe method for the samples placed in a cryostat. The current level was maintained at 50 mA and the voltage drop was determined by averaging the values measured in the forward and reverse directions. The temperature of the sample was monitored using an Au(Fe)–chromel thermocouple.

## 3. Results

The samples without the soaking treatment showed (nominal composition $Bi_2Sr_2CaCu_2O_x$) no or very slight decrease in resistivity, indicating that they contained no or a markedly small amount of the high-$T_c$ phase. On the other hand, the high-$T_c$ phase was included more in the soaked samples (nominal composition $Bi_2Sr_2Ca_2Cu_3O_y$) than that without the soaking treatment. Since the nucleation process usually dominates crystal growth rate, it is favourable for the high-$T_c$ phase to exist in the sample in order to promote Reactions 1, 2 and 3. The soaked samples were, therefore, exclusively investigated in detail.

Figs 1a and 2a show the powder X-ray diffraction patterns for the soaked samples which showed substantially no (sample A) and slight (sample B) decrease in resistance at about 110 K, respectively. The first and second calcination and sintering temperatures for the sample A are 768, 834 and 853 °C while those for the sample B are 772, 825 and 857 °C, respectively. No other phases than the low-$T_c$ one were found in the patterns for both samples. The sintered sample B

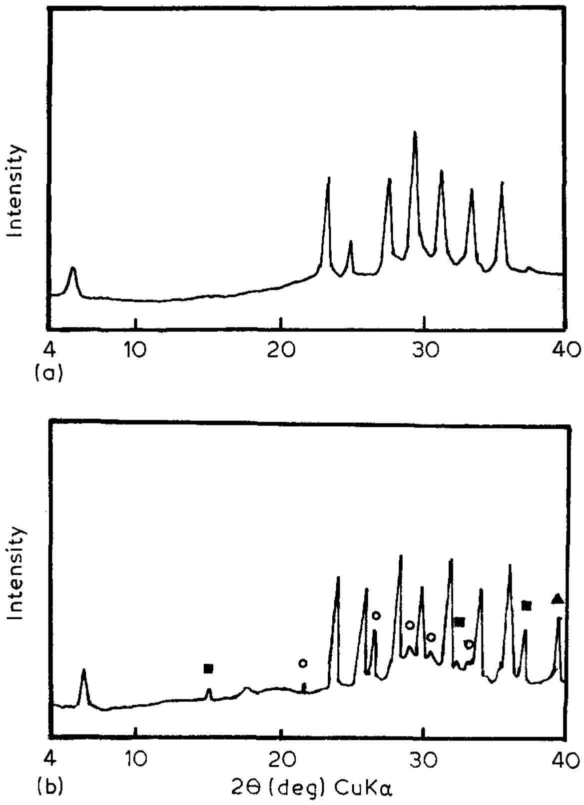

*Figure 1* Powder X-ray diffraction pattern for the sample A calcined twice at 768 and 834 °C, followed by sintering at (a) 853 °C and (b) for the same sample annealed at 400 °C for 20 h. No mark: low-$T_c$ phase, (○) $Bi_2Sr_2CuO_z$, (■) $Ca_2CuO_3$, (▲) CuO.

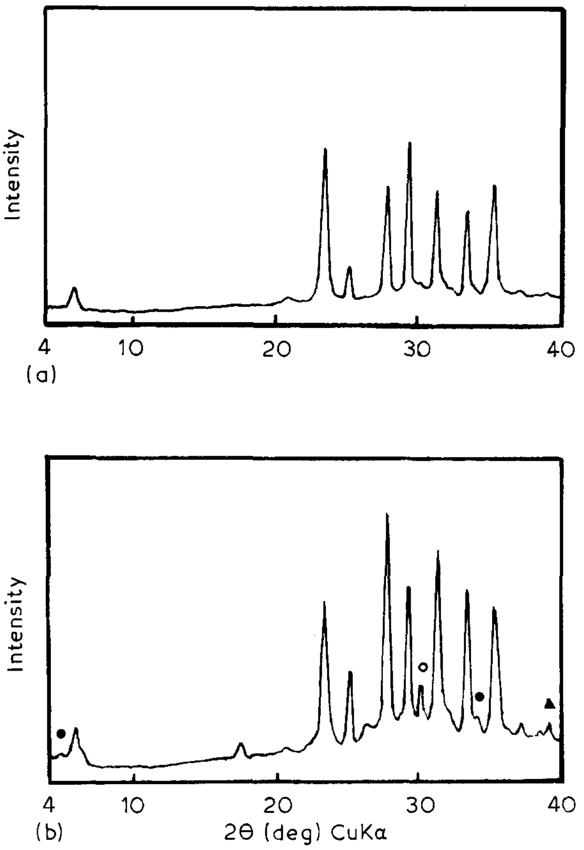

*Figure 2* Powder X-ray diffraction pattern for the sample B calcined twice at 772 and 825 °C, followed by sintering at (a) 857 °C and (b) for the same sample annealed at 400 °C for 20 h. No mark: low-$T_c$ phase, (●) high-$T_c$ phase, (○) $Bi_2Sr_2CuO_z$, (▲) CuO.

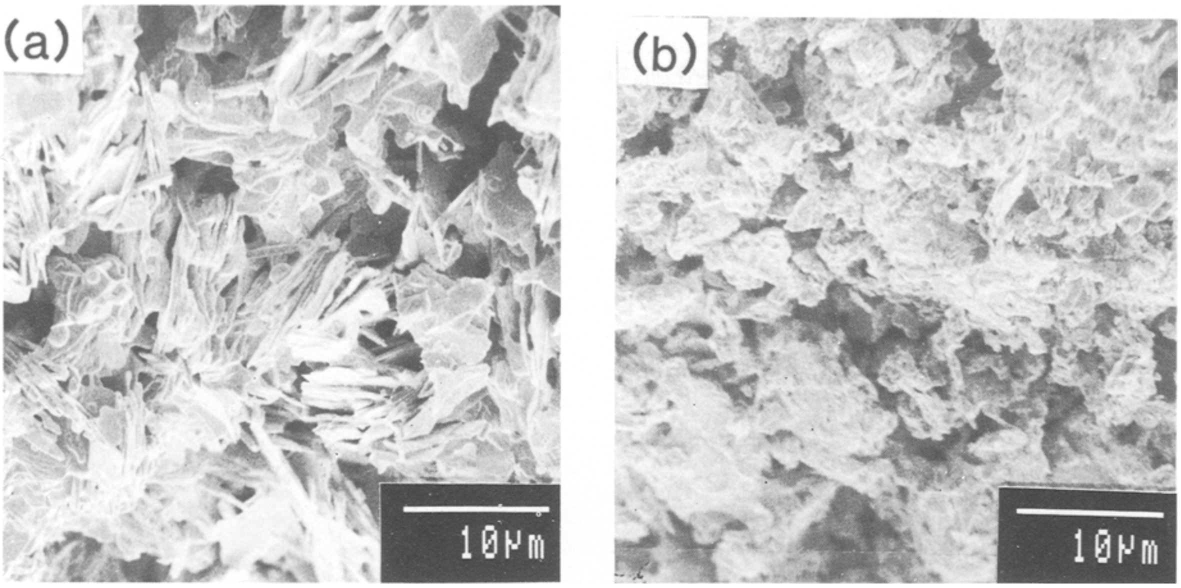

*Figure 3* Electron micrographs for sample B (a) after sintering and (b) after annealing.

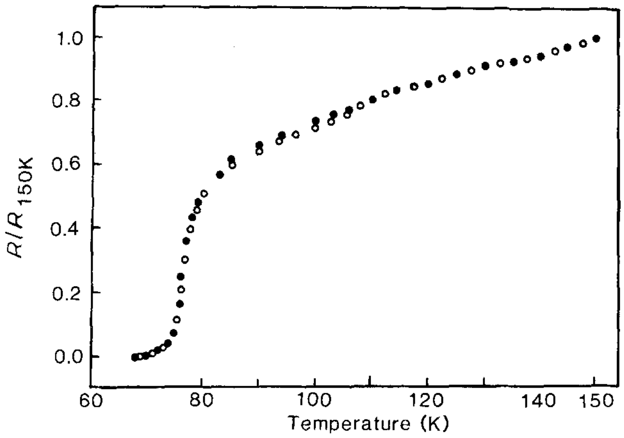

*Figure 4* Normalized resistance ($R/R_{150\,K}$) for the sample A after sintering (○) and after annealing (●).

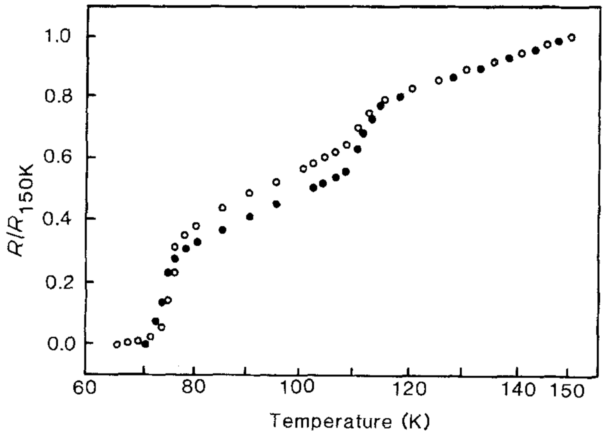

*Figure 5* Normalized resistance ($R/R_{150\,K}$) for the sample B (○) after sintering and (●) after annealing.

consisted of plate-like particles with the grain size of 10 to 20 μm and exhibited a highly porous microstructure which is shown in Fig. 3a. Sample A showed substantially the same morphology as sample B and hence is not shown here. Figs 4 and 5 show the normalized resistance ($R/R_{150\,K}$) for samples A and B, respectively. Sample B clearly exhibited the decrease in resistance at about 110 K while sample A did not show a distinct decrease in the same temperature region. The difference in characteristics may be due to the different calcination and sintering temperatures. Although the high-$T_c$ phase could not be detected for sample B by X-ray diffraction, it is clear that it contained a small amount of the high-$T_c$ phase.

If the high-$T_c$ phase acts as a nucleus for its crystal growth, Reaction 2 or 3 should be promoted by a long term annealing. Since it is suggested that the high-$T_c$ phase may be stable at low temperatures [4], annealing at low temperatures was conducted. Figs 1b and 2b show the powder diffraction patterns for the soaked samples A and B after annealing, respectively. In addition to the dominant low-$T_c$ phase, sample B contained $Bi_2Sr_2CuO_z$, CuO and a small amount of the high-$T_c$ phase while sample A contained $Bi_2Sr_2CuO_z$, CuO and $Ca_2CuO_3$. Figs 4 and 5 show the normalized resistance ($R/R_{150\,K}$) for the soaked samples A and B after annealing, respectively. It is clear that the annealed sample B exhibits a more distinct decrease than that without annealing. In contrast, the annealed sample A exhibited nearly the same characteristics as that without annealing. The microstructure for the annealed sample B differed from that without soaking and annealing as is shown in Fig. 3b. The decomposed Ca–Cu–O compounds reacted with the low-$T_c$ phase and made the grain shape round in contrast to the original plate-like shape although the low-$T_c$ phase was still dominant.

## 4. Conclusions

The $T_c$ ($\rho = 0$) was not drastically increased but it is clear that annealing effectively increases the amount of the high-$T_c$ phase within a relatively short period of time when CaO and CuO or other compounds containing both the elements exist adjacent to the high-$T_c$ phase. It is also clear, however, that annealing is not effective when the high-$T_c$ phase does not exist in the sample. It suggests that the high-$T_c$ phase would be thermodynamically stable at about 400 °C and its nucleation process would be important for the crystal growth. The reason for the small effect may be partly due to the short period of time and large grain size. Since the crystal growth rate is usually determined by a diffusion process, it takes a long time for constituent atoms to diffuse into large grains, leading to the slow reaction rate. If the sample consisting of much smaller grains were employed and annealed for a long period of time, the effect might be further enhanced. Investigation to confirm this presumption is now in progress and the results will be reported in the near future.

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## References

1. J. G. BEDNORZ and K. A. MÜLLER, *Z. Phys.* **B64** (1986) 193.
2. M. K. WU, J. R. ASHBURN, C. J. TORNG, P. H. HOR, R. J. MENG, L. GAO, Z. J. HUANG, Y. Q. WANG and C. W. CHU, *Phys. Rev. Lett.* **58** (1987) 908.
3. H. MAEDA, Y. TANAKA, M. FUKUTOMI and T.ASANO, *Jpn J. Appl. Phys.* **27** (1988) L209.
4. Z. Z. SHENG and A. M. HERMANN, *Nature* **332** (1988) 138.
5. K. KITAZAWA, S. YAEGASHI, K. KISHIO, T. HASEGAWA, N. KANAZAWA, K. PARK and K. FUEKI, *Adv. Ceram. Mater.* to be published.
6. A. SUMIYAMA, T. YOSHITOMI, H. ENDO, J. TSUCHIYA, N. KIJIMA, M. MIZUNO and Y. OGURI, *Jpn J. Appl. Phys.* **27** (1988) L542.
7. N. KIJIMA, H. ENDO, J. TSUCHIYA, A. SUMIYAMA, M. MIZUNO and Y. OGURI, *ibid.* **27** (1988) L821.
8. T. KOMATSU, K. IMAI, R. SATO, K. MATSUSHITA and T. YAMASHITA, *ibid.* **27** (1988) L533.
9. M. TAKANO, J. TAKADA, K. ODA, H. KITAGUCHI, Y. MIURA, Y. IKEDA, Y. TOMII and H. MAZAKI, *ibid.* **27** (1988) L1041.
10. H. ENDO, J. TSUCHIYA, N. KIJIMA, A. SUMIYAMA, M. MIZUNO and Y. OGURI, *ibid.* **27** (1988) L1906.

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