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# Preparation of $Tl_2Ba_2Ca_3Cu_4O_y$ by the capillary synthetic method

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A new phase of $Tl_2Ba_2Ca_3Cu_4O_y$ with $T_c$ = 100 K was prepared by the capillary synthetic method using $Tl_2O_3$, $BaCuO_2$ and $Ca_2CuO_3$ as starting materials. The present capillary synthetic method was useful to obtain the single phase of $Tl_2Ba_2CaCu_2O_y$, $Tl_2Ba_2Ca_2Cu_3O_y$ and $Tl_2Ba_2Ca_3Cu_4O_y$ by solid state reactions using $Tl_2O_3$, $BaCuO_2$, and $Ca_2CuO_3$ as starting materials.

## 1. Introduction

Since the discovery of 40 K superconducting oxide materials in La–Ba–Cu–O system by Bednorz and Muller [1], very intensive investigations have been performed to find the superconducting oxides with higher superconducting transition temperatures $T_c$ and to clarify the mechanism of high $T_c$ superconductivity.

The $YBa_2Cu_3O_{7-z}$ with above 90 K superconductivity, which was discovered by Wu *et al.* [2], have been produced by elemental substitution of yttrium for lanthanum in La–Ba–Cu–O system. Other high $T_c$ complex copper oxides with perovskite-derivative structure have been sought. The Bi–Sr–Cu–O system and the Tl–Ba–Cu–O system have been studied by Michel *et al.* [3] and Akimitsu *et al.* [4], Kondoh *et al.* [5] and Sheng and Hermann [6]. Subsequently, the complex copper oxides with above 100 K superconductivity in the Bi–Sr–Ca–Cu–O and Tl–Ba–Ca–Cu–O systems have been discovered by Maeda *et al.* [7] and Sheng and Hermann [8].

The $Tl_2Ba_2Ca_2Cu_3O_y$ and $Bi_2Sr_2Ca_2Cu_3O_y$ were not only the highest $T_c$ materials reported so far, but also the materials containing no rare-earth elements. Among them, for the synthesis of the high $T_c$ compounds in the Tl–Ba–Ca–Cu–O system, the formation of single phase was very difficult due to the volatility of the thallium component, therefore, it is necessary to develop the advanced synthetic method to prepare the single phase oxide in this system. It is considered that the capillary method of synthesis used, can easily control the volatility of thallium component and oxygen content in compounds.

In this paper, the present authors report the capillary method of synthesis used, which is more effective for obtaining the single phase than vacuum silica tube method or normal ceramic method in air.

## 2. Experimental procedure

For the preparation of Tl–Ba–Ca–Cu–O compounds, the usual commercial powders of $Tl_2O_3$, $BaCO_3$, $CaCO_3$, $BaO_2$ and CuO with the purity of 99.99% were used as the source materials. $BaCuO_2$ and $Ca_2CuO_3$ were synthesized by calcination of mixtures of $BaCO_3$ and CuO and mixtures of $CaCO_3$ and CuO, respectively. CaO was obtained by the thermal decomposition of $CaCO_3$ at 930° C for 12 h in air. These oxide powders of $Tl_2O_3$, $BaCuO_2$, $Ca_2CuO_3$, $BaO_2$, CaO and CuO were used as the starting materials for the preparation of three kinds of high $T_c$ phases in Tl–Ba–Ca–Cu–O system. These starting materials were completely mixed in the desired proportions with ethanol for 24 h. Nominal compositions were weighed out as Tl : Ba : Ca : Cu = 2 : 2 : 1 : 2 (2212 phase), 2 : 2 : 2 : 3 (2223 phase) and 2 : 2 : 3 : 4 (2234 phase) in metal ratio, respectively. After mixing, the mixture was dried at 100° C and ground, and then pressed at 100 MPa to form pellets 8 mm in diameter and 3 mm thick. The pellet was put into a cylindrical platinum tube and inserted into the capillary silica tube as shown in Fig. 1. The capillary silica tube was put into the electrical furnace and heated at 905° C for 10 to 30 min under a stream of pure oxygen gas with heating ratio of 3° C $min^{-1}$ and cooling ratio of 10° C $min^{-1}$.

The phases of samples were identified by means of an X-ray powder diffraction (XRD). The microstructure of sample was observed by scanning electron microscope (SEM) and transmission electron microscope (TEM). The d.c. electrical resistance was measured by means of a standard four-probe method in the temperature range of 80 to 200 K.

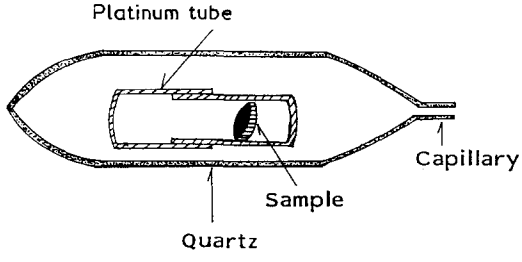


*Figure 1* Schematic diagram of the capillary cell.

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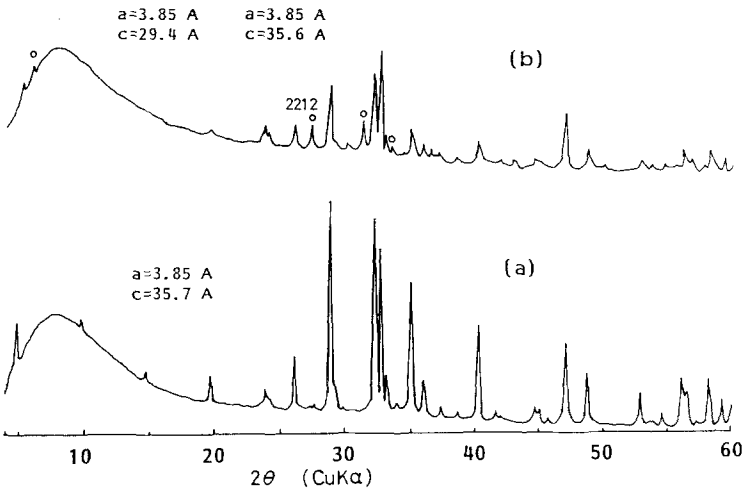


*Figure 2* X-ray powder diffraction patterns of $Tl_2Ba_2Ca_2Cu_3O_y$ prepared by different starting materials. (a) $Tl_2O_3 + 2BaCuO_2 + Ca_2CuO_3$, (b) $Tl_2O_3 + 2BaO_2 + 2CaO + 3CuO$.

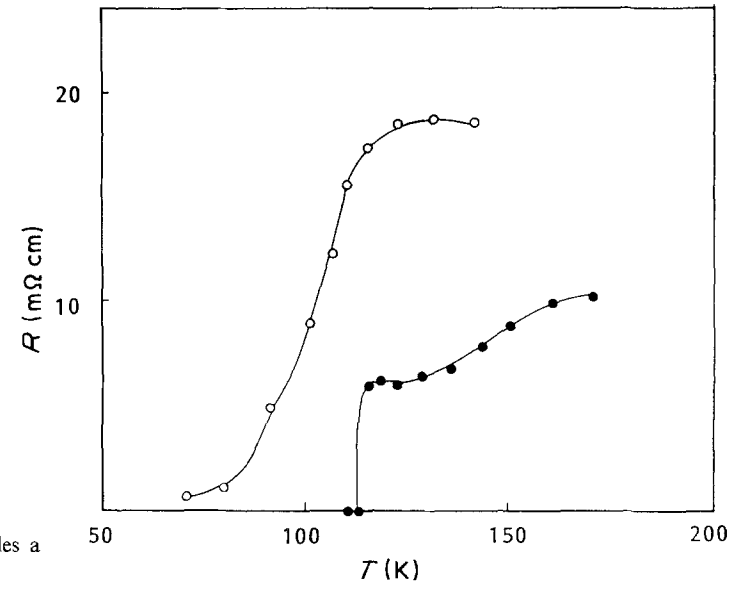


*Figure 3* Temperature dependence of resistivity of samples a (○) and b (●) illustrated in Fig. 2.

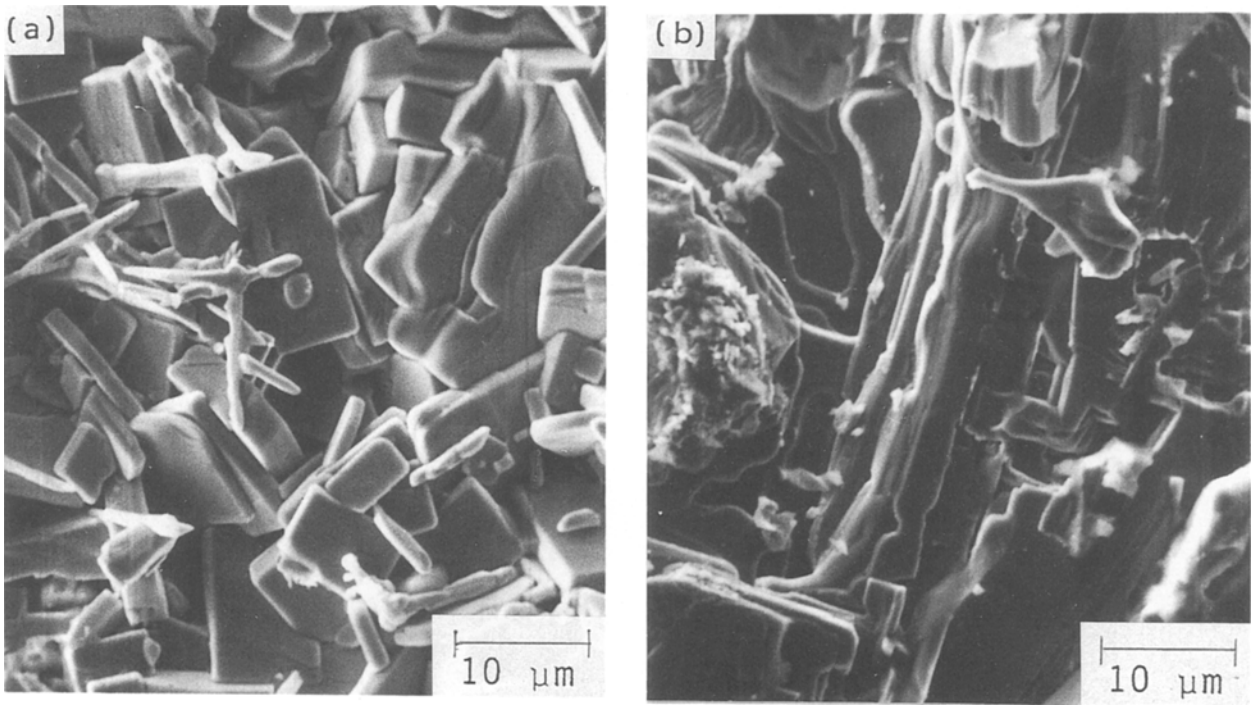


*Figure 4* SEM photographs of fracture surface of samples a and b illustrated in Fig. 2.

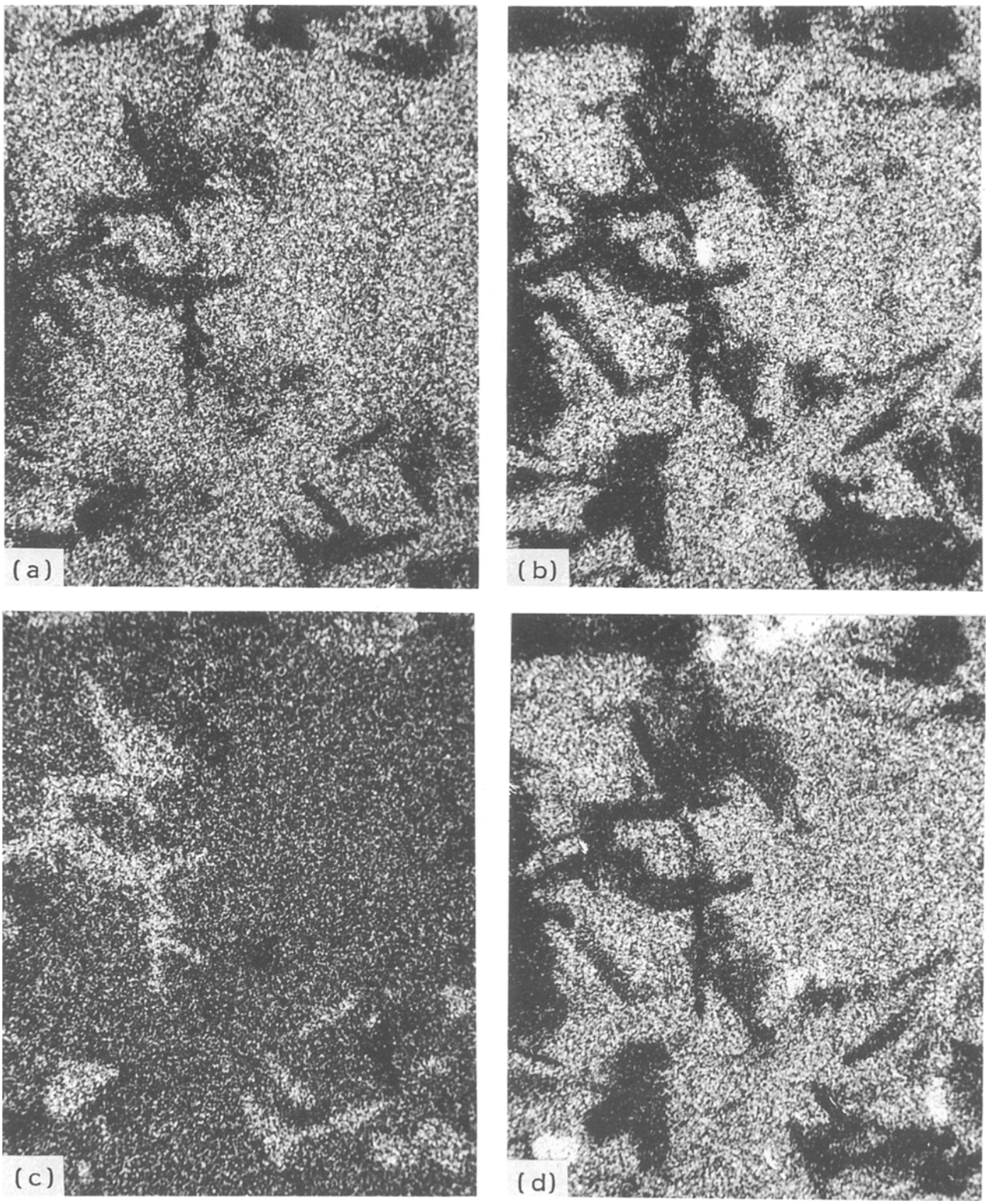


*Figure 5* Emission X-ray image of (a) Cu$K_\alpha$, (b) Ca$K_\alpha$, (c) Tl$K_\alpha$ and (d) Ba$K_\alpha$ of sample a illustrated in Fig. 2.

## 3. Results and discussion

X-ray powder diffraction pattern of two kinds of samples with composition of $Tl_2Ba_2Ca_2Cu_3O_y$ (2223 phase) synthesized at 905° C for 10 min are shown in Fig. 2. Sample a was prepared from the mixtures of $Tl_2O_3$, $BaCuO_2$ and $Ca_2CuO_3$ and sample b from the mixtures of $Tl_2O_3$, $BaO_2$, CaO and CuO. The open circles indicate the peaks corresponding to the 2212 phase. As seen in Fig. 2, sample a was the single phase of 2223 phase with lattice constants of $a = 0.385$ nm and $c = 0.357$ nm, but sample b was composed of two phases of 2223 phase with $a = 0.385$ nm and $c = 0.356$ nm and $Tl_2Ba_2CaCu_2O_y$ (2212 phase) with $a = 0.385$ nm and $c = 2.94$ nm. The present results indicate that the single phase of $Tl_2Ba_2Ca_2Cu_3O_y$ could be synthesized when the $Tl_2O_3$, $BaCuO_2$ and $Ca_2CuO_3$ were used as the starting materials in the present synthetic method. The temperature dependence of the electrical resistivity of both samples is shown in Fig. 3. The resistivity of sample a started to drop sharply at 120 K, but did not exhibit zero resistivity. On the other hand, the resistivity of sample b

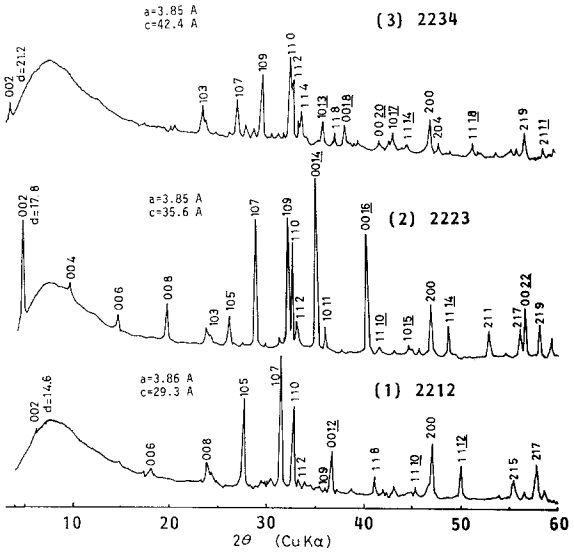


*Figure 6* X-ray powder diffraction patterns of samples 1, 2 and 3. (See Table I in sample number).

started to drop at 120 K and reached zero at 113 K. These results were remarkably different from those expected by XRD patterns shown in Fig. 2. Fig. 4 shows SEM photographs of the fracture surface of these samples. Fig. 5 shows the emission X-ray image of Cu$K_\alpha$ (Fig. 5c), Ca$K_\alpha$ (Fig 5b), Ba$K_\alpha$ (Fig. 5c) and Tl$K_\alpha$ (Fig. 5d) for sample a. As seen in Fig. 4, crystal grains with plate-like texture corresponding to the layered plate structure were observed in both samples, but small needle-like grains were found in sample a. According to the X-ray image results barium, calcium, and copper elements were uniformly distributed, but the partially concentrated distribution of thallium was found, where no other elements were observed. It is considered that the needle-like grains in sample a corresponded to the crystal of $Tl_2O_3$ or $Tl_2O$, which would be produced by recrystallization from the vapour phase of thallium oxides. Although no X-ray powder diffraction patterns corresponding to the thallium oxide phase were recognized, a small amount of thallium oxides existed in the sample a. The small number of thallium defects would introduce the change of cation distribution in 2223 phase [9], which strongly affected the superconducting transition

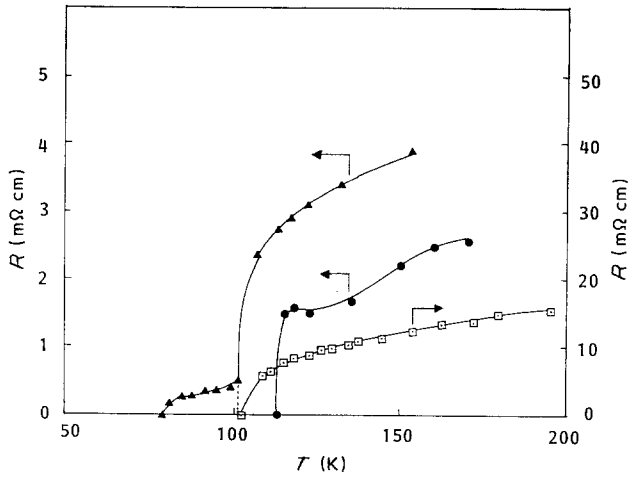


*Figure 7* Temperature dependence of resistivity of samples 1 (▲), 2 (●) and 3 (□). (See Table I in sample number).

TABLE I The synthetic conditions

| Sample | Nominal Composition | | | | Sintering Condition | |
|---|---|---|---|---|---|---|
| | | | | | Temperature (°C) | Time (min) |
| | Tl | Ba | Ca | Cu | | |
| 1 | 2 | 2 | 1 | 2 | 905 | 10 |
| 2 | 2 | 2 | 2 | 3 | 905 | 10 |
| 3 | 2 | 2 | 3 | 4 | 905 | 10 |

temperature. In order to synthesize the single phase sample in the Tl–Ba–Ca–Cu–O system, the capillary synthetic method was applied. Table I shows the synthetic conditions of three kinds of samples. The X-ray powder diffraction patterns of these samples are shown in Fig. 6. Sample 1 contained a small amount of impurity phase which has not yet been identified. Sample 2 consisted of the single phase of $Tl_2Ba_2Ca_2Cu_3O_y$. The X-ray powder diffraction patterns of sample 3 were indexed as tetragonal phase with $a = 0.385$ nm and $c = 4.24$ nm, assuming that the peak of $d = 2.12$ nm corresponded to the reflection of (0 0 2). By applying the capillary synthetic method, three kinds of almost single phases in the Tl–Ba–Ca–Cu–O system could be prepared; $a = 0.386$ nm and $c = 2.93$ nm for $Tl_2Ba_2CaCu_2O_y$, $a = 0.385$ nm and $c = 3.56$ nm for $Tl_2Ba_2Ca_2Cu_3O_y$ and $a = 0.385$ nm and $c = 4.24$ nm for $Tl_2Ba_2Ca_3Cu_4O_y$.

Temperature dependence of the electrical resistivity of these samples is shown in Fig. 7. The resistivity of sample 1 started to drop sharply at 105 K and approached zero at about 100 K, but did not reach zero resistivity until 80 K. The resistivities of both samples 2 and 3 started to drop sharply at 120 K and reached zero at 113 and 103 K, respectively. The characteristics of these three samples are listed in Table II. The SEM photograph of fracture surface of sample 3 is shown in Fig. 8. Plate-like grains were

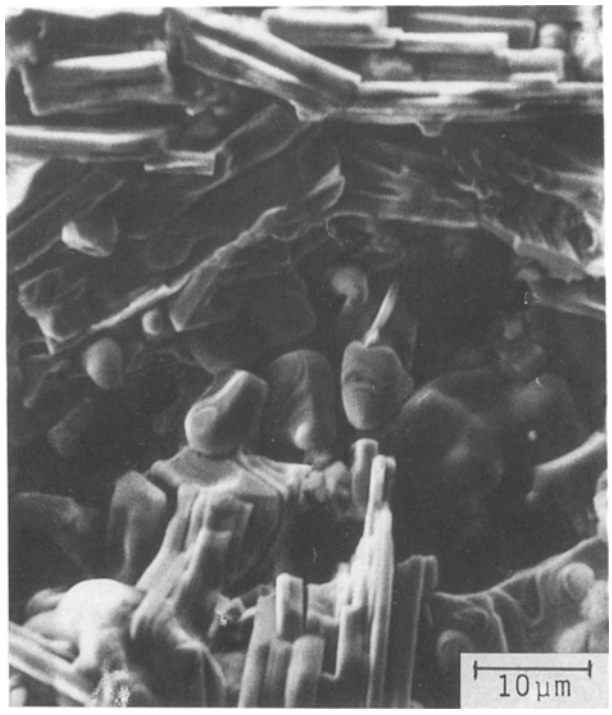


*Figure 8* SEM photograph of fracture surface of sample 3. (See Table I in sample number).

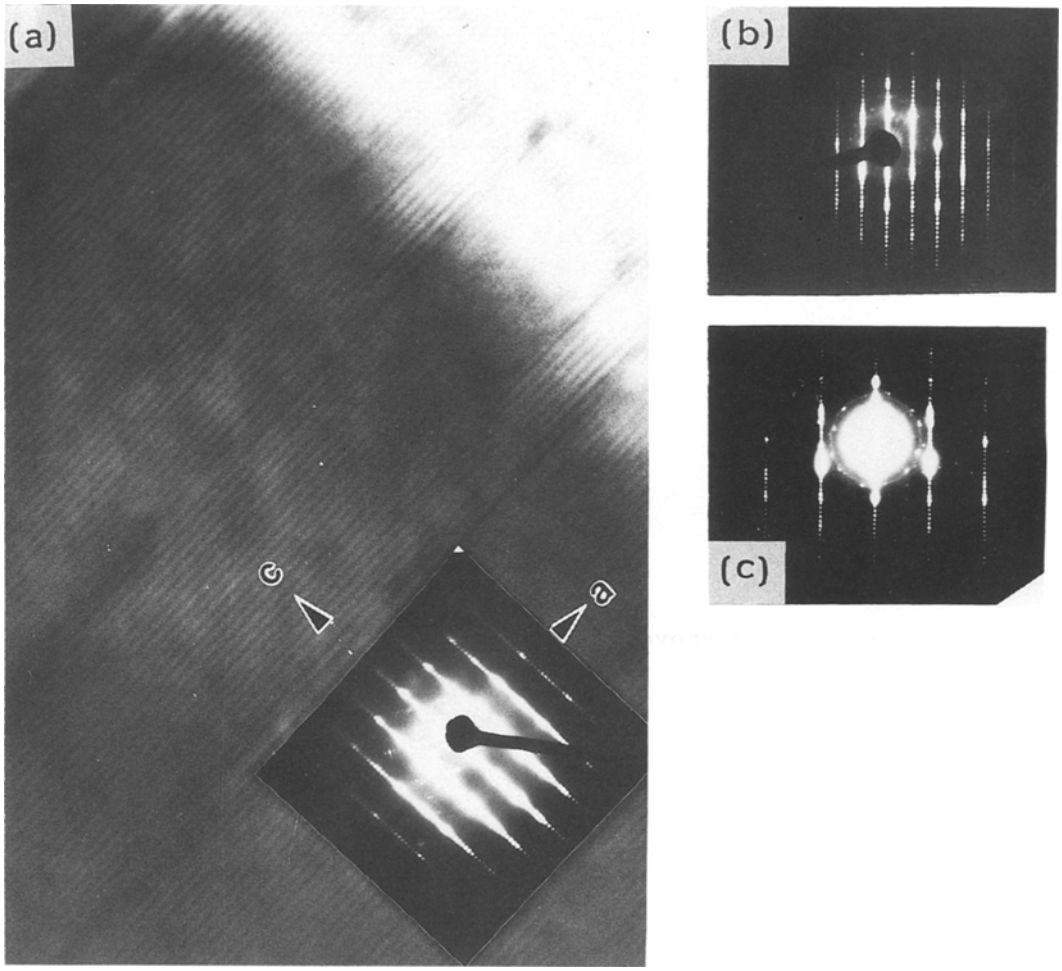


*Figure 9* Electron diffraction patterns of sample 3. (See Table I in sample number).

found in the sample. Fig. 9 shows the electron diffraction patterns of sample 3. Figs. 9a, 9b and 9c were selected-area electron diffraction patterns along [0 1 0], [1 1 0] and [3 1 0], respectively. The *c*-axis estimated from the lattice fringe image was calculated to be 4.26 nm, which was in good agreement with the value of 4.24 nm determined by X-ray diffraction analysis. Consequently, it was considered that the sample 3 was the 2234 phase with four Cu–$O_2$ layers proposed by Parkin *et al.* [10].

The relationship between $T_c$ and the number of Cu–$O_2$ layers is shown in Fig. 10, together with the literature data [8, 10–12]. Although our data were lower than those reported by about 10 K, the same tendency was found. It is believed that the superconducting transition temperature increased with increasing number of Cu–$O_2$ plates in the perovskite-derivative structure oxides such as Tl–Ba–Ca–Cu–O and Bi–Sr–Ca–Cu–O systems. It has, however, turned out that the superconducting transition temperature of sample with four Cu–$O_2$ planes was about 100 K, which was lower by about 10 K than that of sample with three Cu–$O_2$ planes.

TABLE II Characteristics of samples

| Sample | Crystal phase | Lattice constant $a$ (nm) | $c$ (nm) | $T_c$ (K) |
|---|---|---|---|---|
| 1 | 2212 | 0.386 | 2.93 | 80(100) |
| 2 | 2223 | 0.385 | 3.56 | 113 |
| 3 | 2234 | 0.385 | 4.24 | 103 |

## 4. Conclusion

The capillary synthetic method was effective for preparation of the single phase of superconductor in Tl–Ba–Ca–Cu–O system. By applying this method, the single phase of $Tl_2Ba_2Ca_3Cu_4O_y$ with $a$ = 0.385 nm and $c$ = 4.24 nm was synthesized and its superconducting transition temperature was determined to be about 100 K, which was lower about 10 K than that of $Tl_2Ba_2Ca_2Cu_3O_y$. From the results

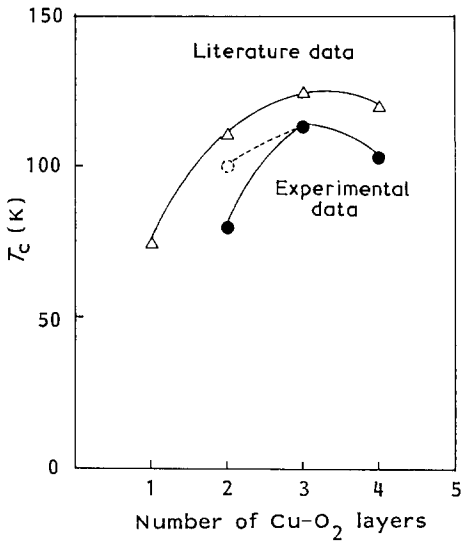


*Figure 10* Relationship between superconducting transition temperature ($T_c$) and number of Cu–$O_2$ layers. (△ literature data, ● experimental data).

on the relationship between the superconducting transition temperature and the number of $Cu–O_2$ planes in the interlayer, it was found that the increase in the number of $Cu–O_2$ planes should not increase the superconducting transition temperature.

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