Synthesis Process of the High T_c Superconductor in the $Tl_2Ca_2Ba_2Cu_3O_x$ Phase

1989 Jpn. J. Appl. Phys. 28 L587

(http://iopscience.iop.org/1347-4065/28/4A/L587)

JAPANESE JOURNAL OF APPLIED PHYSICS
VOL. 28, NO. 4, APRIL, 1989, pp. L 587–L 590

Synthesis Process of the High T_c Superconductor in the $Tl_2Ca_2Ba_2Cu_3O_x$ Phase

C. WANG, H. L. CHANG, M. L. CHU,
Y. S. GOU† and T. M. UEN†

Institute of Electro-optical Engineering, National Chiao Tung University, Hsinchu, Taiwan, R.O.C.
†Department of Electrophysics, National Chaio Tung University, Hsinchu, Taiwan, R.O.C.

(Received January 5, 1989; accepted for publication March 14, 1989)

High T_c superconductor $Tl_2Ca_2Ba_2Cu_3O_x$ were prepared by a two-stage process: prequenched after a 880°C × 12 minutes heat treatment, and then annealed at 880–890°C for 120 minutes in a flowing oxygen atmosphere. The zero-resistivity temperatures distribute in a range from 115 to 119 K. The X-ray diffraction patterns exhibit that they are all in the 2223 phase. The results indicate that the predominance of $Tl_2Ca_2Ba_2Cu_3O_x$ phase is irrelevant to whether the composition of the starting material is $TlCa_3BaCu_3O_x$ or $Tl_2Ca_2Ba_2Cu_3O_x$ by using our process. The influence of each stage in our process has also been studied.

KEYWORDS: superconductivity, high T_c superconductor, Tl-Ca-Ba-Cu-O system, quenching process, annealing process

Recently, the superconductor Tl-Ca-Ba-Cu oxide system have been of current interest, since the transition temperature of this system has been reported as the highest one up to date and this material is very easily produced by conventional ceramic method. Because the system has several phases showing different superconducting transition temperatures and because of the volatility of thallium, the formation of single phase of this system has been widely discussed. Sugise *et al.*[1] started with the nominal composition $Tl_4Ca_3Ba_2Cu_4O_x$, sintered at 885°C, and then quenched in air. Their studies indicated that, during the sintering process, the $Tl_2Ca_2Ba_2Cu_3O_x$ (2223) phase formed first and then the $TlCa_2Ba_2Cu_3O_x$ (1223) phase increased with the decrease of the 2223 one. After prolonged sintering, the $TlCa_3Ba_2Cu_4O_x$ (1324) phase increased at the expense of the 1223 phase. Parkin *et al.*[2] reported that the starting metallic compositions of $TlCa_3BaCu_3$ and $Tl_2Ca_2Ba_2Cu_3$ gave rise to the largest percentages of the 2223 and 2122 phases, respectively. Liu *et al.*[3] reported that fixed starting materials sintered at the same temperature but with different time resulted in a wide variety of superconducting transition temperatures, and sometimes gave a semiconductor. Other groups[4,5] have reported their special methods to form the Tl-Ca-Ba-Cu-O superconducting phases. In this letter we report our studies on the preparation of the bulk samples in this system. Our studies reveal that the single phase samples with 2223 structure could be formed stably by our special treatments.

Our process is described as following: appropriate amounts of high purity powders of $CaCO_3$, $BaCO_3$ and CuO were mixed, calcined at 900°C for about 16 hours in a flowing oxygen atmosphere with several intermediate grindings. Subsequently, the mixture of appropriate amounts of Tl_2O_3 and Ca-Ba-Cu-O were pressed into pellets (16 mm in diameter and 1–2 mm in thickness), wrapped in gold foils and sintered in a flowing oxygen atmosphere. The sintering process includes two stages: first the samples were fired at 880°C for 12 minutes and quenched to room temperature, then sintered at 880–890°C for 120 minutes and furnace cooled. In the furnace we used, a thermocouple with reference at 0°C was

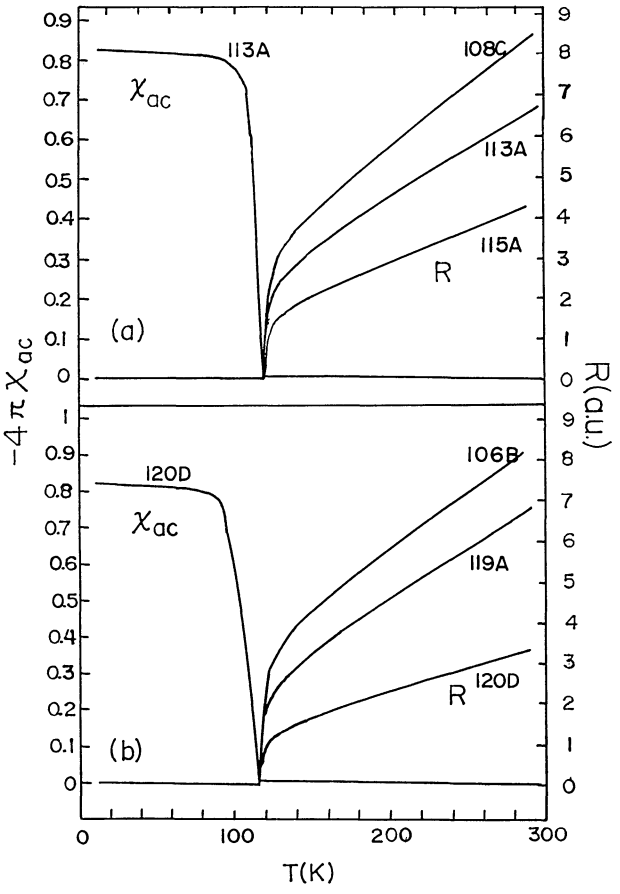

Fig. 1. Temperature dependent resistivities R and ac susceptibilities $-4\pi\chi_{ac}$ of various representative samples from TCBCO1(a) and from TCBCO2(b) by the two-stage process. The sample number was given in the neighborhood of each curve. The zero-resistivity temperatures are 118 K and 116 K for the samples from TCBCO1 and from TCBCO2 respectively and the sharp transitions of the temperature dependent χ_{ac} begin at the same temperatures.

placed directly above the samples by about 1 cm. We have studied the Tl-Ca-Ba-Cu-O system with starting materials of nominal compositions $TlCa_3BaCu_3O_x$ (TCBCO1) and $Tl_2Ca_2Ba_2Cu_3O_x$ (TCBCO2).

The electrical resistivity measurements were carried out by a standard four-probe method. The ac susceptibilities χ_{ac} were measured by a mutual inductance method at a frequency of 3 kHz. Figure 1 is the temperature dependent resistivities R of some representative samples from TCBCO1 (a) and from TCBCO2 (b) respectively. We also show the ac susceptibilities of specific samples from TCBCO1 and from TCBCO2. For the samples from TCBCO1, the resistivities vanish at $T_0=118$ K and a sharp transition which begins at the same temperature is observed on the temperature dependent χ_{ac} curve. At 90 K the $-4\pi\chi_{ac}$ is better than 0.8 and equals to 0.83 at 12 K. For the samples from TCBCO2, the zero-resistivity temperatures T_0 are 116 K and $-4\pi\chi_{ac}$ equals to 0.82 at 12 K. We have prepared a lot of samples in different batches by this two-stage process. Their T_0 distributes in the range from 117 to 119 K and from 115 to 116 K for the samples from TCBCO1 and from TCBCO2 respectively. Thus, these samples are highly reproducible by using our process and they are not sensitive to the annealing temperature from 880 to 890°C. We also found that the T_0's are very stable at the same values for repetitive measurements in a period of one month.

X-ray diffraction patterns were measured at room temperature with Cu Kα radiation to determine the structure of these samples. Figure 2 is the X-ray diffraction patterns of the representative samples from TCBCO1 (a) and from TCBCO2 (b) respectively. Compared them with previous work,[6] we conclude that only the 2223 phase, except for weak impurity peaks, is presented. These results mean that whatever the compositions of the starting materials are $TlCa_3BaCu_3O_x$ or $Tl_2Ca_2Ba_2Cu_3O_x$, the predominant phase is the 2223 one by using our process.

In order to understand the effect of each stage on the sample in our two-stage preparation process, we prepared the samples by each stage only, namely, the quenching-only process and the annealing-only process. In the quenching-only process the starting materials were fired at 880°C for 12 minutes and then quenched to room temperature. In the annealing-only process the starting materials were sintered at 880°C for 120 minutes and cooled in the furnace. For the samples with starting materials TCBCO1, Figs. 3(a), 4(a) and Figs. 3(b), 4(b) are the resistivities, ac susceptibilities and the X-ray diffraction patterns corresponding to the quenching and the annealing process respectively. Figure 3(a) shows that the T_0's of the samples by the quenching-only process distribute in the range from 98 to 108 K. The rounding behaviors of the R-T curves indicate that other phases with higher T_c may be presented. The 90% to 10% transition widths ΔT in the R-T curve at the critical temperature tell us that a perceivable amount of impurities or lower T_c phases are residual between the predominant superconducting crystallites. The temperature dependent

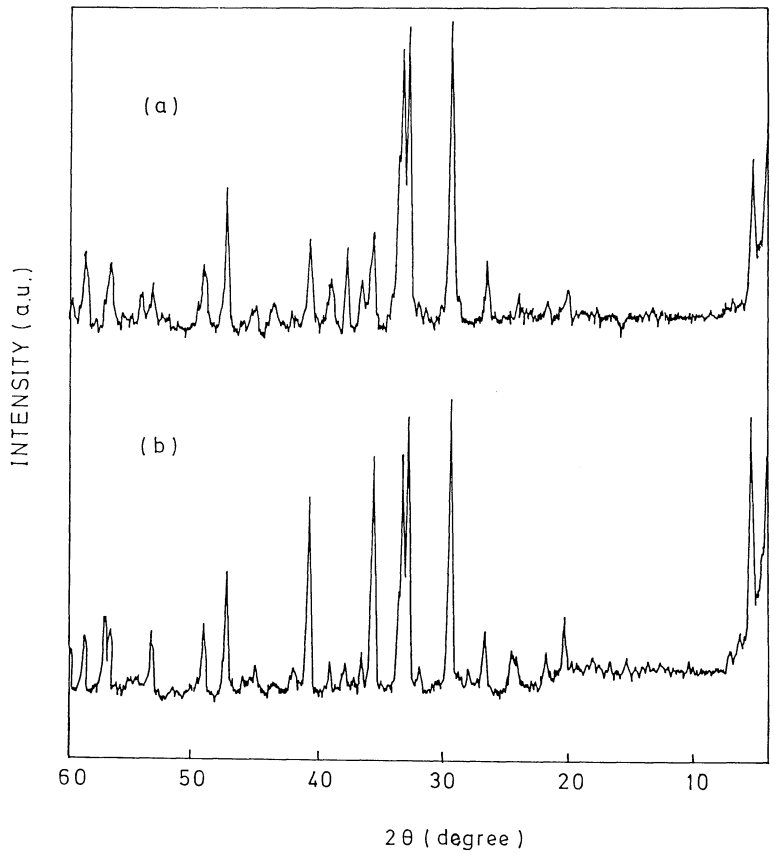

Fig. 2. The X-ray diffraction patterns of the representative samples from TCBCO1 (a: sample 113 A) and from TCBCO2 (b: sample 119 A) by the two-stage process.

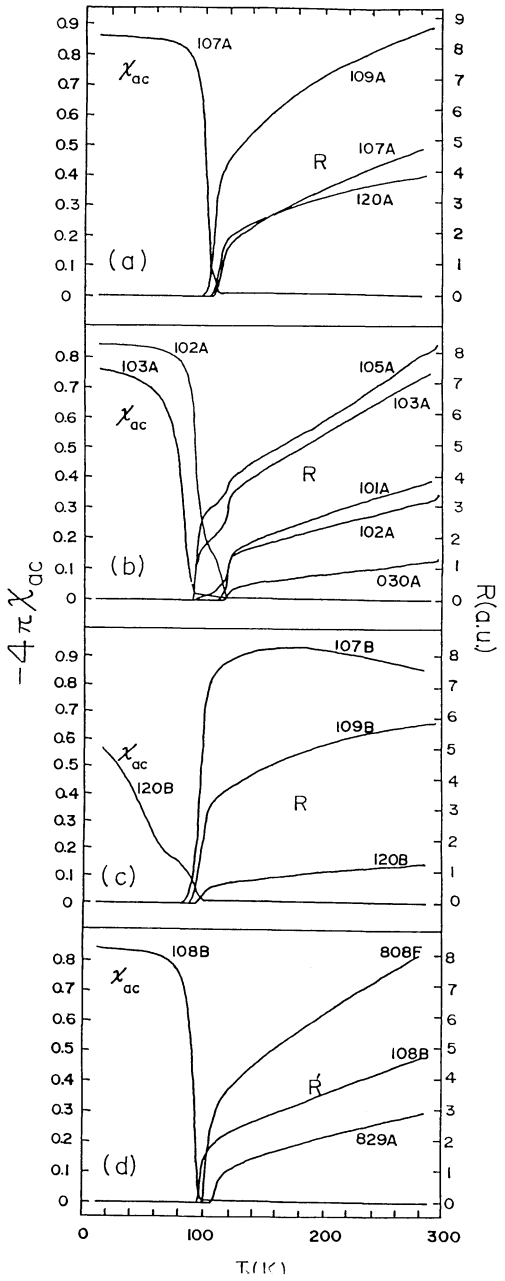

Fig. 3. Temperature dependent resistivities R and ac susceptibilities $-4\pi\chi_{ac}$ of the representative samples (a) from TCBCO1 by the quenching process, (b) from TCBCO1 by the annealing process, (c) from TCBCO2 by the quenching process and (d) from TCBCO2 by the annealing process.

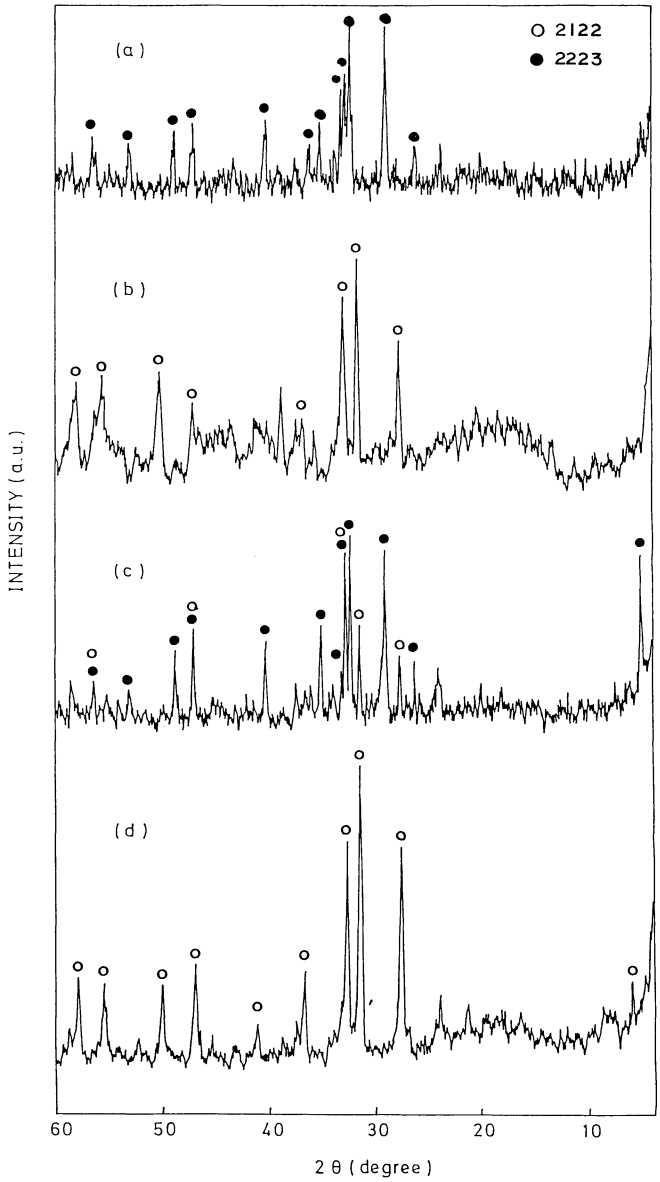

Fig. 4. The X-ray diffraction patterns of the representative samples (a) 109 A from TCBCO1 by the quenching process, (b) 101 A from TCBCO1 by the annealing process, (c) 109 B from TCBCO2 by the quenching process and (d) 108 B from TCBCO2 by the annealing process.

ac susceptibity (Fig. 3(a)) shows two transitions take place at 113 and 105 K. That is, there are at least two superconducting phases in the sample. The X-ray diffraction pattern, Fig. 4(a), however indicates that its predominant phase is the 2223 one.

For the samples prepared by the annealing-only process from TCBCO1, the zero-resistivity temperatures distribute from 90 to 118 K, as shown in Fig. 3(b). The kinks at 120 K in the R-T curves and the apparent changes in the slope at 120 K and 95 K in the χ_{ac}-T curves indicate that various amounts of the 120 K phase are present in the samples in addition to the 95 K phase. The X-ray diffraction patterns, Fig. 4(b), show the structures of these samples with $T_0 < 118$ K. The patterns exhibit the predominant phase is 2122 one for the samples with $T_0 < 118$ K. Though the kinks in the R-T and the χ_{ac}-T curves indicate there exist a phase with $T_c \sim 120$ K, there are no apparent peaks of the 2223 phase. For the sample (030A) with $T_0 = 118$ K, the X-ray diffraction pattern shows that this sample consists only of the 2223 phase. These results tell us that the conditions of formation for these two phases are possibly very close when the annealing-only process are used and therefore it is hard to control the quality of the resultant products from same starting materials by same preparation process.

Figure 3(c) and Fig. 4(c) correspond to the representative samples with the starting material TCBCO2 by using the quenching-only process. The temperature dependent resistivities (Fig. 3(c)) show considerably different behaviors and T_0's are in the range from 78 to 92 K. One of the R-T curves behaves like a semiconductor at high

temperature. It indicates that the quenching-only process may form semiconducting phases in this system. Figure 3(c) also shows the temperature dependent ac susceptibility of a selected sample from TCBCO2 by using the quenching process. The slopes of χ_{ac} below 100 K reveal that there are more than one superconducting phases in different percentages. The X-ray diffraction patterns (Fig. 4(c)) point out that there are at least two phases, 2122 and 2223, in these samples.

Figure 3(d) and Fig. 4(d) show the temperature dependent resistivities, ac susceptibility and the room temperature X-ray diffraction pattern of the representative samples from TCBCO2 by using the annealing-only process. For these samples, the T_0's vary from 97 to 107 K and a sharp transition at about same temperatures can be observed from the χ_{ac}-T curves. The X-ray diffraction patterns (Fig. 4(d)) exhibit the predominant phase is the 2122 one. These results agree with those of Parkin *et al.*,[2] that the starting material witk nominal compositions $Tl_2Ca_2Ba_2Cu_3O_x$ gave rise to the largest percentages of the 2122 phase which possesses T_c ranging from 95 K to 108 K. It is therefore very interesting that though the stable phase is the 2122 phase by using the annealing-only process, we can get a 2223 phase as a predominant one by simply adding a prequenching stage.

In summary, we developed a two-stage process for preparing the Tl–Ca–Ba–Cu–O 2223 phase and studied the effects on the samples by only using each stage of our process. With the quenching-only process we obtained multiphase samples with the starting materials $TlCa_3BaCu_3O_x$ and $Tl_2Ca_2Ba_2Cu_3O_x$. It is also possible to get a semiconductor. With the annealing-only process we obtained predominantly a 2122 phase with the starting material $Tl_2Ca_2Ba_2Cu_3O_x$, but from $TlCa_3BaCu_3O_x$ we obtained a mixture with uncertain percentages of the 2122 phase and the 2223 phase. However, the predominace of the 2223 phase in the Tl–Ca–Ba–Cu–O superconducting system was always reproduced by using our two-stage process and irrelevant to whether the compositions of the starting material is $TlCa_3BaCu_3O_x$ or $Tl_2Ca_2Ba_2Cu_3O_x$. Further investigations of the effects of the different combinations of the heat treatment times and cooling methods are being conducted. We have found different results when we changed the heat treatment time in the first stage (the quenching stage) while holding the second stage (the annealing stage) unchanged. The results and a lot of DTA (Differential Thermal Analysis) data will be reported elsewhere.

The authors wish to thank Prof. T. J. Yang and Dr. D. M. Chen for valuable discussion. This research at NCTU was supported by the National Science Council, R.O.C. under Contract NSC78-0208-M009-12.

References

1) R. Sugise, M. Hirabayashi, N. Terada, M. Jo, T. Shimomura and H. Ihara: Jpn. J. Appl. Phys. **27** (1988) L1709.
2) S. S. P. Parkin, V. Y. Lee, E. M. Eugler, A. I. Nazzal, T. C. Huang, G. Gorman, R. Savoy and R. Beyers: Phys. Rev. Lett. **60** (1988) 2539.
3) R. S. Liu, W. H. Lee, P. T. Wu, Y. C. Chen and C. T. Chang: Jpn. J. Appl. Phys. **27** (1988) L1206.
4) I. K. Gopalakrishnan, P. V. P. S. S. Sastry, K. Gangadharan, G. M. Phatak, J. V. Yakhmi and R. M. Iyer: Appl. Phys. Lett. **53** (1988) 414.
5) M. Kikuchi, N. Kobayashi, H. Iwasaki, D. Shindo, T. Oku, A. Tokiwa, T. Kajitani, K. Hiraga, Y. Syono and Y. Muto: Jpn. J. Appl. Phys. **27** (1988) L1050.
6) C. C. Torardi, M. A. Subramanian, J. C. Calabrese, J. Gopalakrishnan, K. J. Morrissey, T. R. Askew, R. B. Flippen, U. Chowdhry and A. W. Sleight: Science **240** (1988) 631.