

**PREPARATION OF HIGH PURITY BI- AND Tl-BASED SUPERCONDUCTORS
WITH THREE Cu-O LAYERS**

P.T. WU and W.H. LEE
Materials Research Laboratories,
Industrial Technology Research Institute,
Chutung, Hsinchu 31015, Taiwan, Republic of China

ABSTRACT

High purity three Cu-O layered superconductors in both (Bi,Pb)-Sr-Ca-Cu-O ($T_c = 110$ K) and (Tl,Pb,Bi)-Sr-Ca-Cu-O ($T_c = 118$ K) systems have been successfully made by using either solid state reaction or solution method. Better performance in regard to obtaining a nearly monophasic high- T_c superconducting phase was found in the samples with the Ca/Sr ratio close to 2.4/1.6 for these two systems. Via the solution method, the mass production of pure, homogeneous precursor powders of high- T_c superconductor is anticipated.

1. INTRODUCTION

For the past two years, a large body of experimental research have been focused on trying to fabricate the monophasic $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ ("2223" phase, $T_c = 105$ K) and $\text{TlSr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ ("1223" phase, $T_c = 100$ K) superconductors because of their competitively high critical temperatures, T_c s. However, owing to the complexity of these five component systems, specimens prepared by using the ideal composition (2223 or 1223) of the high- T_c phase and the routine ceramic fabrication techniques always consisted of mixtures with an amount of low- T_c ($\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_y$ "2212", $T_c = 75$ K, $\text{TlSr}_2\text{CaCu}_2\text{O}_y$ "1212", $T_c = 75$ K) and/or other additional phases that can not be ignored. So far, it has been demonstrated that at least four methods: (1) the partial substitution of Pb for Bi (or Tl) [1-5], (2) the observant control of heat treatment [6], (3) sintering under suitable gas atmosphere [7-8], (4) the modification of starting nominal composition [9-12] can promote and stabilize the formation of high- T_c phase. One interesting phenomenon is that the low T_c phase tends to appear without a small surplus of Ca and Cu, while a large surplus of Ca and/or Cu leads to the formation of Ca_2CuO_3 , Ca_2PbO_4 and the semiconducting phase. Therefore, it is thought that to single out the high- T_c phase ("2223" or "1223") is a most challenging task due to its special synthetic condition.

In this paper we make a noteworthy and brief review that has been successfully studied at our laboratory on the synthesis of Bi- and Tl-based

systems with three Cu-O layered structure. We put more emphasis on expediting the formation of the high- T_c phase on both systems. In addition, the solution method using metal nitrates plus certain amount of oxalic acid for chelating the metal cations has also been proven to be thriving in singling out the high- T_c phase as well as for the mass production of precursor powders.

2. EXPERIMENTAL AND RESULTS

All samples investigated for this work were synthesized from high purity starting materials by solid state reaction or solution method. A microcomputer-controlled Philips APD PW1700 x-ray diffractor equipped with copper target and graphite monochromator for CuK_α radiation was used to get the powder x-ray diffraction patterns at a continuous scan rate of 0.04 $^\circ/\text{sec}$. Differential thermal analysis (DTA) of calcined powders were carried out in air using an ULVAC 7000 type thermoanalyzer. The atomic concentrations of the samples were determined by an EDAX 9100/70 energy dispersive spectrometer (EDS). The surface morphology of these samples was monitored by Cambridge S360 scanning electron microscopy (SEM). AC electrical resistivity measurements were made using a standard four-probe technique in a LR400 system fully automated for data acquisition. Resistivity data are taken for warming curve. However, since the resistivity data are devoid of any interesting features, they are not presented here. The low field temperature dependence of the magnetization data were taken in a superconducting quantum interference device (SQUID) magnetometer developed by Quantum Design, Inc., San Diego, California. To eliminate the residual magnetic field, the approximate zero field was calibrated by measuring a conventional superconductor Pb within an accuracy of ± 0.2 gauss. The temperature control module (TCM) has an accurate temperature control within 0.1 % between 1.8 and 400 K. The total calibration error is estimated well within 0.5 % for the magnetic property measurement system (MPMS). Table 1 presents the sources and purities of the starting materials used in this study. Details of the sample preparation and physical characterization are given in each of the sections which follow.

TABLE 1
The sources, purities of the starting materials.

Starting Materials	Source	Purity
Bi_2O_3	Gredmann	99.9 %
PbO	Cerac	99.9 %
SrCO_3	Cerac	99.5 %
CaCO_3	Gredmann	99.98 %
CuO	Aldrich	99.99+ %
Tl_2O_3	Gredmann	99.5 %
$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$	Merk Chemical Co.	99 %
$\text{Pb}(\text{NO}_3)_2$	Merk Chemical Co.	99.5+ %
$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	Merk Chemical Co.	98.5+ %
$\text{Sr}(\text{NO}_3)_2$	Merk Chemical Co.	99 %
$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$	Frank Berlin	99.5 %

2.1 (Bi,Pb)-Sr-Ca-Cu-O system

2.1 (a) Solid State Reaction Method

The samples were synthesized following the flow of the process shown in fig. 1. The nominal composition $(\text{Bi}_{1.7}\text{Pb}_{0.4})\text{Sr}_{1.6}\text{Ca}_{2.4}\text{Cu}_{3.6}\text{O}_y$ was selected

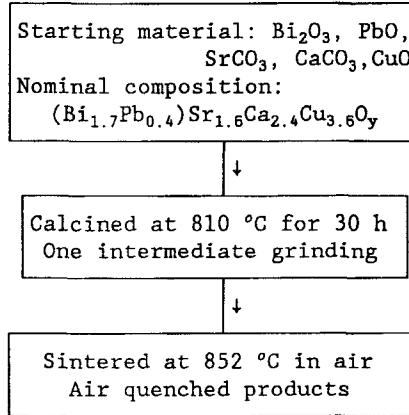


Figure 1. Flow chart of the solid state reaction preparation procedure of the superconductor $(\text{Bi}_{1.7}\text{Pb}_{0.4})\text{Sr}_{1.6}\text{Ca}_{2.4}\text{Cu}_{3.6}\text{O}_y$.

from the phase diagram reported by Lee et al [13]. Powder x-ray diffraction patterns indicated that a nearly single-phased 110 K high- T_c superconductor could be obtained for the sample sintered at 852 °C for 20 hours [14]. This characterization was also corroborated with the static magnetization data as displayed in fig. 2. It is seen that the temperature dependent magnetization curve of the sample sintered at 852 °C for 20 h (or

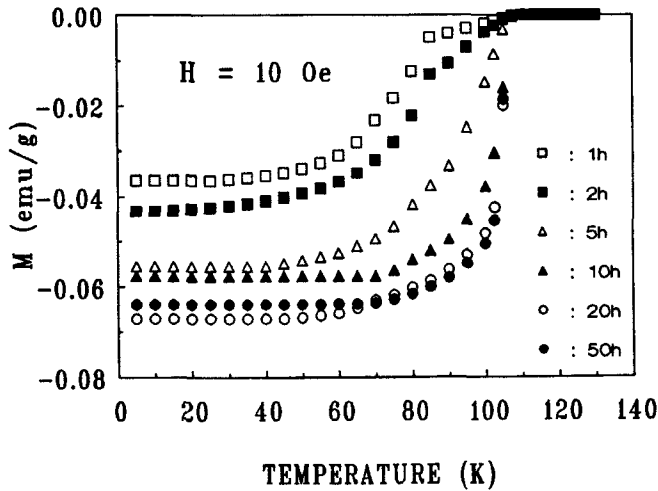


Figure 2. DC magnetization vs T for $(\text{Bi}_{1.7}\text{Pb}_{0.4})\text{Sr}_{1.6}\text{Ca}_{2.4}\text{Cu}_{3.6}\text{O}_y$ sintered at 852 °C for 1 ~ 50 h. The measuring field is 10 Oe.

above) exhibits the sharpest transition into the superconducting state around 110 K among the investigated samples. And no appreciable second step making the other superconducting phase transition is observed. To illustrate the formation mechanism of ("2223") high- T_c superconducting phase in the Ca- and Cu-rich (Bi,Pb)-Sr-Ca-Cu-O system, Differential Thermal Analysis (DTA) was employed to investigate the partial melting phenomenon. An evidence that the partial melting resulted from the coexistence of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_y$, Ca_2PbO_4 and CuO phases is strongly responsible for the large grain growth and the acceleration of the formation of the ("2223") high- T_c phase was observed [15,16].

2.1 (b) Solution Method [17]

Fig. 3 depicts the flow of the solution method for preparing the ("2223") high- T_c phase in (Bi,Pb)-Sr-Ca-Cu-O system. The finally mixed

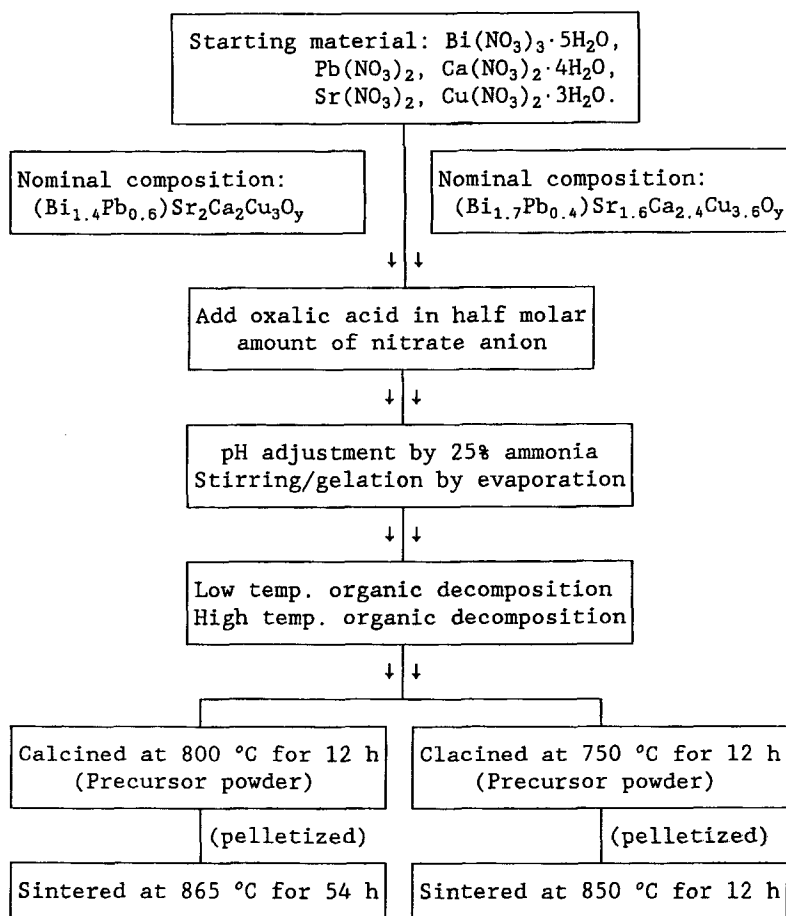


Figure 3. Flow chart of the solution method for preparing the high- T_c (Bi,Pb)-Sr-Ca-Cu-O superconductor with $T_c = 110$ K.

solution was placed in a 120 °C oil bath for gelation. With the increasing pH value, the gel color changes from light to deep blue.

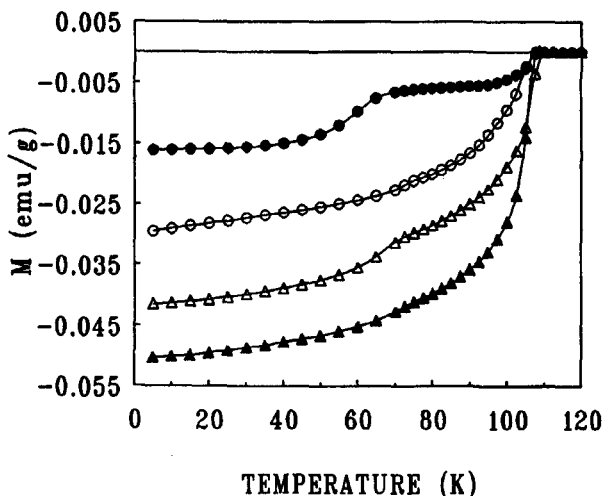


Figure 4. Temperature dependence of zero-field-cooled magnetization data measured in a field of 10 Oe between 5 and 130 K. Three symbols (●, ▲, △) correspond to $(\text{Bi}_{1.4}\text{Pb}_{0.6})\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ with pH = 5.6, 6.7 and 7.8. The open circle (○) corresponds to $(\text{Bi}_{1.7}\text{Pb}_{0.4})\text{Sr}_{1.6}\text{Ca}_{2.4}\text{Cu}_{3.6}\text{O}_y$ with pH = 6.7.

Fig. 4 displays the zero-field-cooled (ZFC) magnetization data for $(\text{Bi}_{1.4}\text{Pb}_{0.6})\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ (pH = 5.6, 6.7, 7.8) and $(\text{Bi}_{1.7}\text{Pb}_{0.4})\text{Sr}_{1.6}\text{Ca}_{2.4}\text{Cu}_{3.6}\text{O}_y$ (pH = 6.7) measured in an applied field of 10 Oe between 5 and 130 K. It is seen that the 110 K phase dominates for the sample of pH = 6.7. Structure and resistivity analyses also support the magnetic measurements. We must point out here that the high purity 110 K superconducting phase can be synthesized at the lowest calcination temperature (750 °C) and the shortest sintering time (12 h) as far as we know by using the solution method and the recipe $(\text{Bi}_{1.7}\text{Pb}_{0.4})\text{Sr}_{1.6}\text{Ca}_{2.4}\text{Cu}_{3.6}\text{O}_y$ as elucidated in 2.1 (a).

2.2 (Tl,Pb,Bi)-Sr-Ca-Cu-O system

2.2 (a) Solid State Reaction Method

As described above, the formation of the three Cu-O layered phase ("2223") in the (Bi,Pb)-Sr-Ca-Cu-O system could be accelerated by taking the appropriate ratio (2.4 : 1.6) of Ca to Sr. When this rule was applied to the Tl-based system, we found that it was surprisingly successful [18]. For comparative study with the recent reports [19,20] in synthesizing the nearly ("1223") single-phase compound using an off-stoichiometric nominal composition of $(\text{Tl}_{0.64}\text{Pb}_{0.2}\text{Bi}_{0.16})\text{Sr}_2\text{Ca}_3\text{Cu}_4\text{O}_y$, several samples are prepared according to the flow chart of fig. 5.

As shown in fig. 6, the temperature dependence of dc magnetization curves measured in a field of 10 Oe between 5 and 130 K indicate that the samples with modified Ca/Sr ratio; namely, $(\text{Tl}_{0.5}\text{Pb}_{0.5})\text{Sr}_{1.6}\text{Ca}_{2.4}\text{Cu}_3\text{O}_y$ and $(\text{Tl}_{0.64}\text{Pb}_{0.2}\text{Bi}_{0.16})\text{Sr}_{1.6}\text{Ca}_{2.4}\text{Cu}_3\text{O}_y$, are nearly single phase superconductors with T_c s among 115 and 120 K irrespective of their short heat treatment time. However, an obvious second superconducting phase ("1212") transition around 80 K is seen for the sample with the starting nominal composition $(\text{Tl}_{0.64}\text{Pb}_{0.2}\text{Bi}_{0.16})\text{Sr}_2\text{Ca}_3\text{Cu}_4\text{O}_y$. In our XRD analyses [21], the two intermediate phases, $(\text{Ca,Sr})_2\text{CuO}_3$ and $(\text{Ca,Sr})\text{CuO}_2$, may play an important role in accelerating the formation of the ("1223") high- T_c phase in Tl-based system.

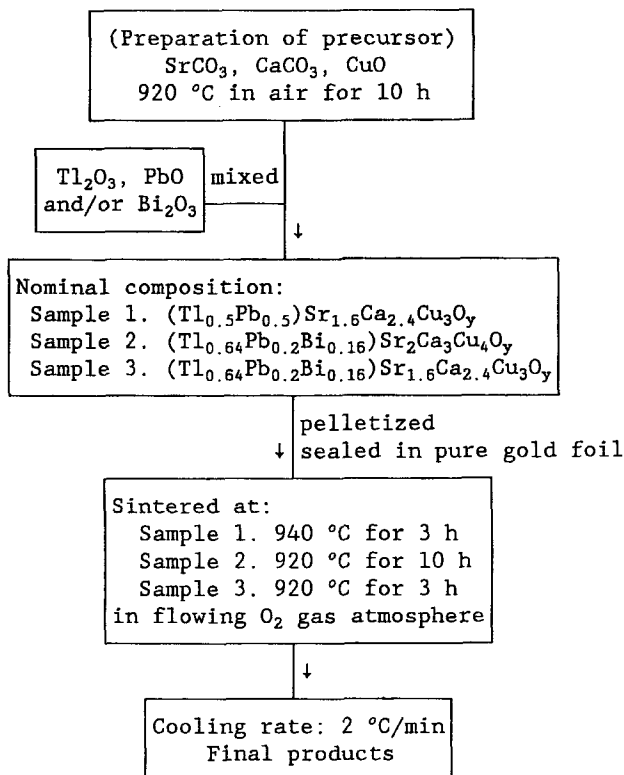


Figure 5. Flow chart of the solid state reaction preparation procedure for Tl-based superconductor with ("1223") phase.

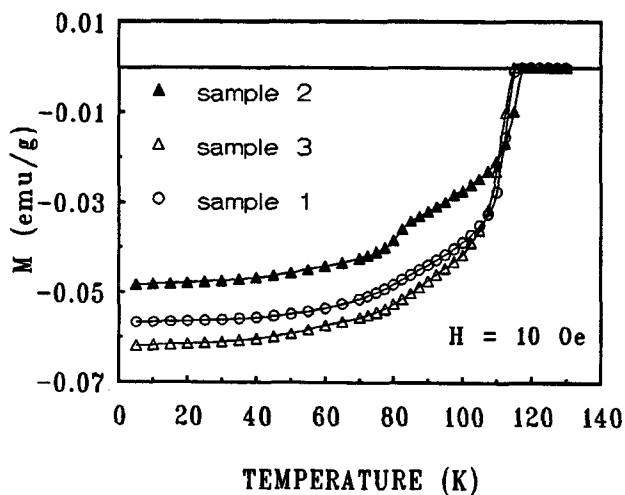


Figure 6. Temperature dependence of dc magnetization of samples 1, 2 and 3 measured in a cooling field of 10 Oe between 5 and 130 K.

2.2 (b) Solution Method [22]

This method is similar to that described in section 2.1 (b), a modified Pechini process. Tl_2O_3 and other metal nitrates are dissolved in aqueous solution plus certain amount of oxalic acid for chelating the metal cations. The final solution was put in an oil bath for gelation at 100 ~ 120 °C. The blue complexed gel turned out to be black because of the addition of Tl_2O_3 . Detailed flow chart of the preparation of the high- T_c ("1223") phase in Tl-based system is shown in fig. 7.

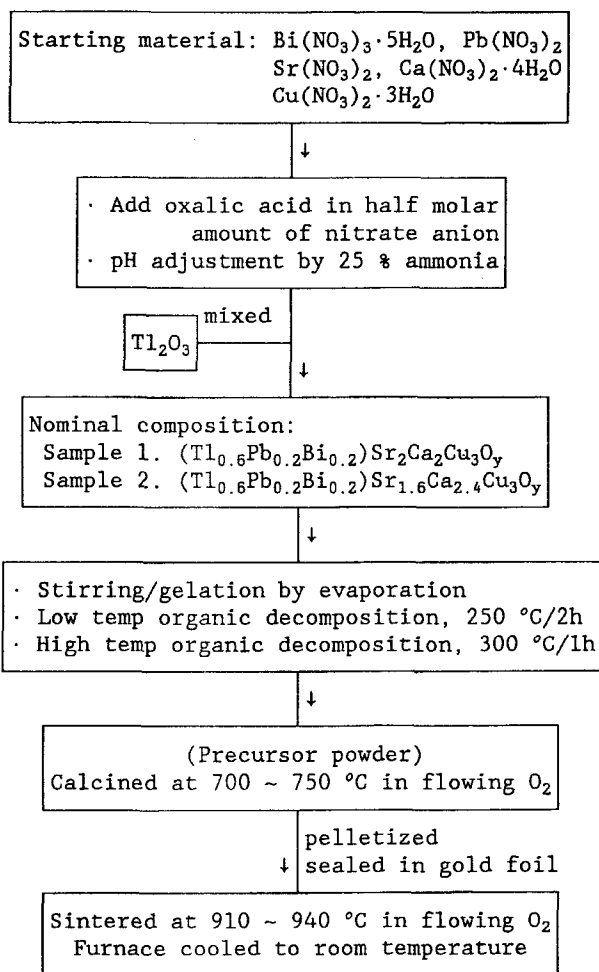


Figure 7. Flow chart of solution method for synthesizing ("1223") high- T_c superconductor in Tl-based system.

Fig. 8 presents the temperature dependence of zero-field-cooled (ZFC) magnetization data of samples $(Tl_{0.6}Pb_{0.2}Bi_{0.2})Sr_{1.6}Ca_{2.4}Cu_3O_y$ and $(Tl_{0.6}Pb_{0.2}Bi_{0.2})Sr_2Ca_2Cu_3O_y$ measured in an applied field of 10 Oe. As well as in the (Bi-Pb)Sr-Ca-Cu-O system, the (Tl,Pb,Bi)-Sr-Ca-Cu-O sample with the Ca/Sr ratio of 2.4/1.6 has a better performance regarding to high- T_c ("1223") phase purity. This property also has been consistently observed

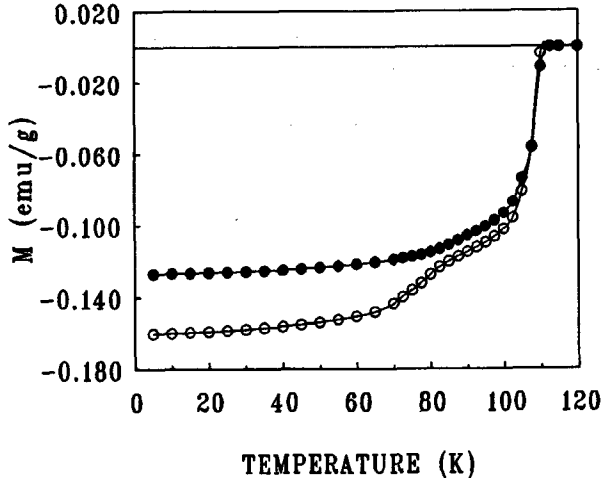


Figure 8. Zero-field-cooled magnetization for two samples measured in a field of 10 Oe between 5 and 120 K. The open circle (O) and solid circle (●) correspond to $(\text{Tl}_{0.6}\text{Pb}_{0.2}\text{Bi}_{0.2})\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ and $(\text{Tl}_{0.6}\text{Pb}_{0.2}\text{Bi}_{0.2})\text{Sr}_{1.6}\text{Ca}_{2.4}\text{Cu}_3\text{O}_y$.

in the x-ray diffraction patterns and resistivity measurements.

3. SUMMARY

In general, the ratio of Ca/Sr > 1 is a very important factor in accelerating the formation of ("2223") (Bi-Pb)-Sr-Ca-Cu-O or ("1223") (Tl,Pb,Bi)-Sr-Ca-Cu-O high- T_c phase. For the Bi-based system, the partial melting due to the coexistence of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_y$, Ca_2PbO_4 and CuO phases are found very helpful to the grain growth and promotion of forming ("2223") phase. As to the Tl-based system, the formation mechanism is still unclear and further investigation is required. Via the solution method, successful mass production of high purity and homogeneous ("2223") and ("1223") phase precursor powders is expected.

ACKNOWLEDGEMENTS

We are grateful to our colleagues of superconducting materials lab, MRL for their assistance in experiments. This research was supported by the Ministry of Economic Affairs, Republic of China, under contract number 34S1100 and 34S1200 to the Industrial Technology Research Institute.

REFERENCES

1. Sunshine, S.A., Siegrist, T., Schneemeyer, L.F., Murphy, D.W., Cava, R.J., Batlogg, B., van Dover, R.B., Fleming, R.M., Glarum, S.H., Nakahara, S., Farrow, R., Krajewski, J.J., Zahurak, S.M., Waszczak, J.V., Marshall, J.H., Rupp, L.W. and Feck, W.F., Structure and physical properties of single crystals of the 84 K superconductor $\text{Bi}_{2.2}\text{Sr}_2\text{Ca}_{0.8}\text{O}_{8+x}$. *Phys. Rev. B*, 1988, 38, 893-900.

2. Yamada, Y. and Murase, S., Pb introduction to the high- T_c superconductor Bi-Sr-Ca-Cu-O. Jpn. J. Appl. Phys., 1988, 27, L996-L998.
3. Takano, M., Takada, J., Oda, K., Kitaguchi, H., Miura, Y., Ikeda, Y., Tomii, Y. and Mazaki, H., High- T_c phase promoted and stabilized in the (Bi,Pb)-Sr-Ca-Cu-O system. Jpn. J. Appl. Phys., 1988, 27, L1041-L1043.
4. Mizuno, M., Endo, H., Tsuchiya, J., Kijima, N., Sumiyama, A. and Oguri, Y., Superconductivity of $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{Pb}_x\text{O}_y$ ($x = 0.2, 0.4, 0.6$). Jpn. J. Appl. Phys., 1988, 27, L1225.
5. Green, S.M., Jiang, C., Mei, Y., Luo, H.L. and Politis, C., Zero resistance at 107 K in the (Bi,Pb)-Ca-Sr-Cu oxide system. Phys. Rev. B, 1988, 38, 5016-5018.
6. Uzamaki, T., Yamanaka, K., Kamehara, N. and Niwa, K., Preparation and magnetic properties of Bi-Pb-Sr-Ca-Cu-O superconducting ceramics. Appl. Phys. Lett., 1989, 54, 2253-2255.
7. Endo, U., Koyama, S. and Kawi, T., Preparation of high- T_c phase of Bi-Sr-Ca-Cu-O superconductor. Jpn. J. Appl. Phys., 1989, 27, L1476-L1479.
8. Koyama, S., Endo, U. and Kawi, T., Preparation of single 110 K phase of the Bi-Pb-Sr-Ca-Cu-O superconductor. Jpn. J. Appl. Phys., 1988, 27, L1861-L1863.
9. Endo, U., Koyama, S. and Kawi, T., Composition dependence on the superconducting properties of Bi-Pb-Sr-Ca-Cu-O system. Jpn. J. Appl. Phys., 1989, 28, L190-L192.
10. Sasakura, H., Minamigawa, S., Nakahigashi, K., Kogachi, M., Nakanishi, S., Fukuoka, N., Yoshikawa, M., Noguchi, S., Okuda, K. and Yanase, A., Single high- T_c phase region of the Bi-Pb-Sr-Ca-Cu-O system. Jpn. J. Appl. Phys., 1989, 28, L1163-L1166.
11. Tanaka, A., Kamehara, N. and Niwa, K., Composition dependence of high T_c phase formation in pb-doped Bi-Sr-Ca-Cu-O thin films. Appl. Phys. Lett., 1989, 55, 1252-1254.
12. Lu, S.W., Lee, W.H. and Wu, P.T., Promotion of 110 K superconducting phase in the Bi(Pb)-Sr-Ca-Cu-O system. MRL Bull. Res. Dev., 1990, 4, 43-46.
13. Lee, C.L., Chen, J.J., Wen, W.J., Perng, T.P., Wu, J.M., Wu, T.B., Chin, T.S., Liu, R.S. and Wu, P.T., Phase relations of equilibrium compounds in the Bi-Ca-Sr-Cu-O system. Prog. High Temp. Superconductivity, 1989, 19, 331-340.
14. Huang, Y.T., Liu, R.G., Lu, S.W., Wu, P.T. and Wang, W.N., Accelerated formation of 110 K high T_c phase in the Ca- and Cu-rich Bi-Pb-Sr-Ca-Cu-O system. Appl. Phys. Lett., 1990, 56, 779-781.
15. Huang, Y.T., Shei, C.Y., Wang, W.N., Chiang, C.K. and Lee, W.H., Formation mechanism of 110 K high- T_c superconducting phase in the Ca- and Cu-rich Bi-Pb-Sr-Ca-Cu-O system. Physica C, 1990, 169, 76-80.
16. Huang, Y.T., Wang, W.N., Wu, S.F., Shei, C.Y., Hurng, W.M., Lee, W.H.

- and Wu, P.T., Formation of the liquid phase in the system Bi-Pb-Sr-Ca-Cu-O. J. Am. Cer. Soc., 1990, 73, 3507-3510.
17. Chiang, C., Shei, C.Y., Huang, Y.T., Lee, W.H. and Wu, P.T., Preparation of high purity 110 K phase in the (Bi,Pb)-Sr-Ca-Cu-O superconductor system using a solution method. Physica C, 1990, 170, 383-387.
 18. Huang, Y.T., Wu, S.F., Chiang, C.K. and Lee, W.H., Accelerated formation of the three Cu-O layered Tl-(Pb,Bi)-Sr-Ca-Cu-O compound. Appl. Phys. Lett., 1990, 57, 2354-2355.
 19. Kaneko, T., Wada, T. and Yamauchi, H. and Tanaka, S., (Tl,Pb,Bi)Sr₂Ca₂Cu₃O_z superconductors with zero resistance at 120 K. Appl. Phys. Lett., 1990, 56, 1281-1283.
 20. Wada, T., Kaneko, T. and Yamauchi, H., Recent progress in the development of Tl-Sr superconductors-highlighting (Tl,Pb,Bi)Sr₂Ca₂Cu₃O₉ superconductors which exhibit zero resistance at 123 K. ISTEC Journal, 1990, 3, 21-24.
 21. Unpublished work.
 22. Chiang, C., Shei, C.Y., Wu, S.F. and Huang, Y.T., Preparation of high purity Tl-based "1223" superconductor phase by modified Pechini process in water solution. Submitted.