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SYNTHESIS AT AMBIENT PRESSURE AND SUPERCONDUCTIVITY OF Hg-DOPED Tl-BASED DOUBLE [(Tl, Hg)-O]-LAYERED CUPRATES*

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The Hg-doped Tl-based 2201 and 2212 phase layered cuprates have been successfully synthesized at ambient pressure and identified by X-ray powder diffraction and electron diffraction analysis. Compared with pure Tl-based 2212 phase compound, there are indications that the corresponding Hg-doped Tl-based compound $(Tl_{1.8}Hg_{0.2})Ba_2CaCu_2O_z$ exhibits a much higher T_c (> 132 K).

PACC: 7410; 7460; 6160

I. INTRODUCTION

Since the discovery of high-T_c superconductivity in La-Ba-Cu-O system, a variety of cuprates, including Tl-, Bi-, Pb-and Hg-based superconducting cuprates, have been synthesized and identified. Among them the Hg-based superconducting system is particularly remarkable, not only because it has a superconducting transition temperature higher than those of Tl-and Bi-based superconducting systems, but also because it shows an indication of zero-resistance around 250 K.[1,2] However, the synthesis of this kind of Hg-based cuprates requires high-pressure reaction[3–5], and the products are only single [Hg-O] layered cuprates $HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ ($n = 1-4$). Although the importance of synthesizing double-[Hg-O] layered cuprates were pointed out[6], it is a pity that there is still not any report on successful preparation.

By studying the structural types of the existing Bi-, Tl-and Pb-based superconducting compounds in detail, it is found that: (1) in Tl-based system either single-[Tl-O] layered cuprates $TlBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ or double-[Tl-O] layered cuprates $Tl_2Ba_2Ca_{n-1}Cu_nO_{2n+4+\delta}$ can be formed easily; (2) in Bi-based system double-[Bi-O] layered cuprates $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4+\delta}$ can form but single-[Bi-O] layered compounds cannot form by itself; at most single-[(Bi, M)-O] layered cuprates (M=Cu, Cd, Zn, In)[7–10] may form, i.e., it needs doping with

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other elements with a concentration more than 50% to stabilize the single [(Bi, *M*)-O] layer in Bi-based compounds; (3) in Pb-based system double [Pb-O] layers can form which has a Cu(I) layer sandwiched between them in a reducing atmosphere[11,12]; and a single [(Pb, *M*)-O] layer can form by doping in an oxidizing atmosphere.[13-18] Hence, the study of the structural type of Hg-based system becomes the remaining problem.

It is well known that the elements Hg, Tl, Pb and Bi are located side by side in the sixth period in the periodic table. They have $6s^2$, $6s^26p^1$, $6s^26p^2$ and $6s^26p^3$ electron configurations, respectively. Their normal valence states and corresponding outer-shell electron configurations (Table 1) are shown as follows:

Table 1. Normal valence states of Hg, Tl, Pb, and Bi, and their corresponding outer-shell electron configulations.

	Hg	Tl		Pb		Bi	
Valence states	2^+	3^+	1^+	4^+	2^+	5^+	3^+
Electron configulations	$6S^0$	$6S^0$	$6S^2$	$6S^0$	$6S^2$	$6S^0$	$6S^2$

Table 2. Comparison of Tl $4f_{7/2}$ binding energies in the Tl-1212, Tl-2212, Tl-2223, Tl_2O_3 and Tl_2O.

Tl $4f_{7/2}$ binding energy/eV	Tl_2O_3	$TlBa_2CaCu_2O_7$ Tl-1212	$Tl_2Ba_2CaCu_2O_8$ Tl-2212	$Tl_2Ba_2Ca_2Cu_3O_{10}$ Tl-2223	Tl_2O
	117.4	117.7	118.1	118.2	118.6

It is clear from Table 1 that only in high-valence ions, such as Hg^{2+}, Tl^{3+} and Pb^{4+}, 6s electrons are absent while all the low-valence ions have 6s electrons. Suzuki *et al.*[19,20] studied Tl 4f core level in the Tl-1212, Tl-2212 and Tl-2223 phases by XPS measurement and compared them with those of Tl_2O_3 and Tl_2O. The results, which are summarized in Table 2, show that Tl $4f_{7/2}$ binding energy of the Tl-1212 phase approaches that of Tl_2O_3, and those of Tl-2212 and Tl-2223 phase approach that of Tl_2O. This means that the Tl ion of the former is close to trivalent Tl^{3+} and that of the latter is at least between trivalent Tl^{3+} and monovalent Tl^+. In other words, the existence of 6s lone pair electrons is closely related to the formation of single or double layers. Thallium which has no lone pair electrons can form compounds with single [Tl-O] layer while thallium which has lone pair electrons can form compounds with double [Tl-O] layers. Owing to the same reason, Bi^{3+} and Bi^{5+} can form double-[Bi-O] layered compounds and single-[Bi-O] layered cuprates, respectively. Because the valence state of Bi^{5+} is too high to exist stably, single-[Bi-O] layered compounds are difficult to be synthesized, and it is possible to be stabilized only by doping with other ions. Similarly, since Hg^{2+} has no 6s lone pair electrons or has one 6s electron at most, Hg-based system can only form single-[Hg-O] layered cuprates. The pure double-[Hg-O] layered cuprates seem difficult to prepare. In addition, the structural characteristic of single-[Hg-O] layered cuprates Hg-1201 is that there exist a large number of oxygen-defects in the [Hg-O] layer. This also

explains the difficulty of forming double [Hg-O] layers. Therefore, in order to synthesize double-[Hg-O] layered compounds, it is necessary to introduce other ions having 6s lone pair electrons to stabilize the double [Hg-O] layers. On the basis of successful preparation of Hg-1201 at ambient pressure[21] and proceeding from the exploration of the synthesis of double-[(Hg, M)-O] layered compounds, we studied the preparation and superconductivity of Hg-doped double-[(Tl, Hg)-O] layered cuprates, at first, especially the 2212 phase cuprates.

II. EXPERIMENTAL

Samples were prepared by a solid state reaction method at ambient pressure.[21] Appropriate amounts of high-purity BaO, CaO and CuO powders according to the nominal composition $Tl_2Hg_{1.5}Ba_2CaCu_2O_z$ were weighed and dried at 250–300°C for 30 min in flowing oxygen, then immediately mixed with $TlNO_3$ and HgO, and pressed into pellets in a glove box with flowing dry and inert atmosphere. The pellets were put into a tube-furnace which had been preheated to 700–760°C. The mixtures were heated for 10–60 min before they were quenched in air. At the beginning and final stages of solid state reaction, a flow of nitrogen was introduced into the reaction zone. The whole reaction system was located in a stink cupboard and had a tail-gas absorber to prevent pollution. In some cases, samples were annealed at 300°C in O_2 or N_2 for 12h. A pure Tl-2212 phase compound with a starting composition $Tl_2Ba_2CaCu_2O_z$ was also prepared under the same condition as a reference sample.

X-ray powder diffraction was carried out on a RIGAKU D/MAX-rA rotating target X-ray diffractometer with Cu $K\alpha$ radiation (0.15418 nm). Peaks were indexed and cell parameters were calculated by a least square method computation program. Selected- area electron diffraction was carried out on a HITACHI-800 analytical electron microscope operated at 200 kV. At the same time, several crystal grains were selected arbitrarily for composition analysis with X-ray energy-dispersive spectrum (EDS).

The superconductivity of the samples was determined by ac susceptibility measurement. The mutual inductance bridge had a sensitivity better than 0.1 μH and the temperature was determined with a calibrated copper-constantan thermocouple and a carbon-resistance thermometer at the same time. Temperature dependence of electrical resistance was measured by a standard four-probe technique. The temperature was determined with a calibrated Rh/Fe thermocouple and the voltage was read with a Keithley 181 nanovoltemter. The resolution of voltage was 1×10^{-8} V. All the data were collected and processed by a computer.

III. RESULTS AND DISCUSSION

Figure 1 shows the X-ray powder diffraction pattern for the sample which has a nominal

composition $(Tl_1Hg_{0.75})_2Ba_2CaCu_2O_z$ heated for 30 min. Except some very weak peaks, all the peaks can be indexed by using space group of $I4/mmm$ with a tetragonal lattice: $a = 0.3860$ nm, $c = 2.930$ nm. The transmission electron microscopic bright field image of the sample clearly shows the laminar crystallization state that consists of small single crystals. In Fig. 2 [001] and [110] electron diffraction patterns of the sample are shown, from which we obtained the same cell parameters as those obtained from X-ray diffraction (XRD) analysis. The EDS results of five crystal grains selected at random reveal that all the crystal grains have significant amount of Hg but one. Except for Cu which is not analyzed as the copper grid was used, the average composition of the sample is Tl:Hg:Ba:Ca=1.8:0.2:2:1. If the gram atomic weight of Ba is taken as 2, then the chemical formula of the sample would be $(Tl_{1.8}Hg_{0.2})Ba_2CaCu_2O_z$.

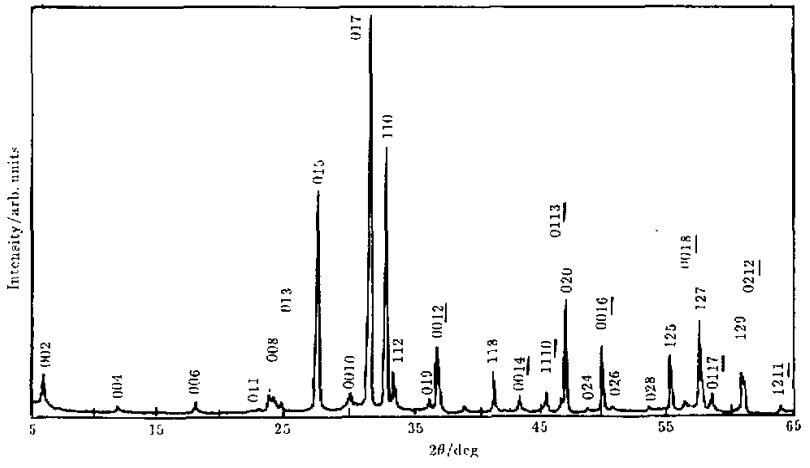
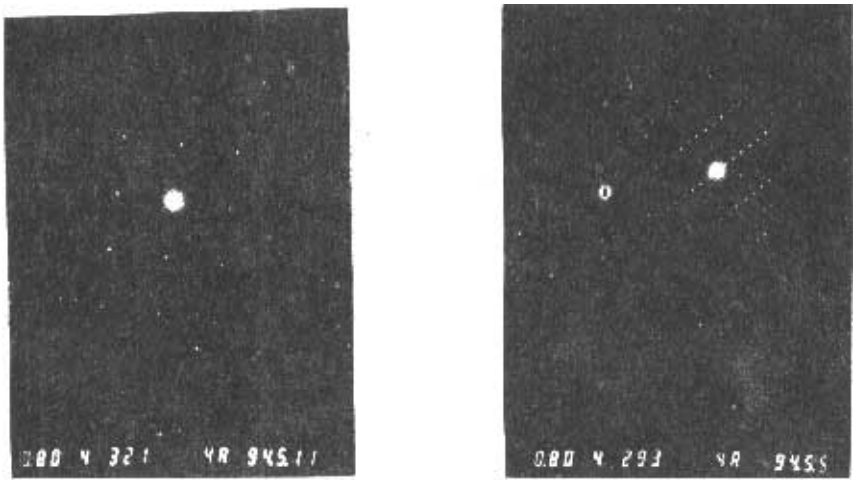


Fig. 1. X-ray powder diffraction pattern for the sample $(Tl_{1.8}Hg_{0.2})Ba_2CaCu_2O_z$.

Owing to the low decomposition temperature of HgO, it is prone to lose in the reaction process. Therefore, excess Hg is necessary to synthesize Hg-doped Tl-based 2212 phase compounds. Sheng[22] has studied the Hg-addition into $TlBaCaCuO_{4.5}$. Although the reaction temperature applied was above 900°C, it is suggested from the variation in T_c of the system that a certain amount of Hg has entered the lattice. The present work indicates that the relatively low reaction temperature and relatively short reaction time will be more favorable to Hg doping. But if the reaction temperature is too low, it will result in an increase of the amount of 2201 phase and other impurity phases such as $BaCuO_2$. We have also obtained (Tl, Hg)-based 2201 phase compound $(Tl_{1.5}Hg_{0.5})Ba_2CuO_y$ from nominal $(Tl_1Hg_{0.75})_2Ba_2CuO_y$ sample for which the reaction temperature and time is 720–730°C and

20 min, respectively. The EDS results of five crystal grains selected arbitrarily reveal that the Hg occupancy of Tl-site exceeds 25%, which is twice as much as that in the 2212 phase. Besides the low reaction temperature, the reason may be that Ca absence in the system is favorable for Hg to occupy the Tl-site.



(a) [001] (b)[110]

Fig. 2. Electron diffraction patterns of the $(Tl_{1.8}Hg_{0.2})Ba_2CaCu_2O_z$.

It should be pointed out that in the above-mentioned Hg-doped Tl-based 2212 phase compounds, the amount of Hg entering into the lattice is still not so large, but its influence upon the superconductivity of the sample is evident. Figure 3 shows the ac susceptibility vs temperature curves for the sample $(Tl_{1.8}Hg_{0.2})Ba_2CaCu_2O_z$ and the reference sample $Tl_2Ba_2CaCu_2O_z$ (pure Tl-2212) prepared under the same condition, from which we can see the obvious difference in superconductivity between the two samples as-prepared. The former has one superconducting phase, which has T_c=132.5 K (curve *a*). The latter has the T_c of 111.5 K and does not show any indication of higher T_c (curve *d*). Further study shows that as long as the samples are recycled in vacuum, the above-mentioned curves can be reproduced. But once the samples are exposed to air for a certain time and then measured, the superconductivity or the quality of the samples will change significantly. Curve *b* shows the temperature dependence of ac susceptibility of $(Tl_{1.8}Hg_{0.2})Ba_2CaCu_2O_z$ which is exposed to air for 24h. Two superconducting phases with T_c = 124.5 and 107 K, respectively, can be found in the sample. If the sample is exposed to air for 48h, the high T_c phase will vanish and only one superconducting phase with T_c = 107 K can be found (curve *c*). So we can conclude that when the as-prepared samples undergo several times of thermal recycle in a moist atmosphere, the T_c will drop step by step, although their XRD patterns do not show any significant change in phases. We believe that this change in T_c is just the result of

Hg occupying Tl-site, because the pure Hg-based superconductor is highly sensitive to the moisture and CO_2 in the environment and that will result in the degradation in quality.

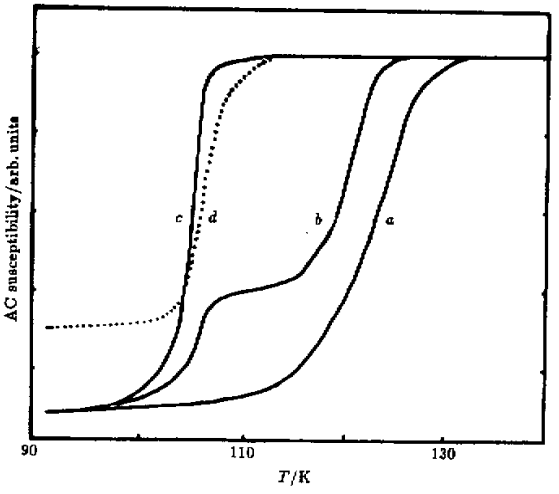


Fig. 3. Temperature dependence of ac susceptibility of some typical samples of (Tl, Hg)-2212 phase. Curve *a*: sample as-prepared; curve *b*: sample exposed to the air for 24h; curve *c*: sample exposed to the air for 48h; curve *d*: sample of pure Tl-based 2212 phase compound sample as reference.

IV. CONCLUSION

1. Hg-doped Tl-based double-[(Tl, Hg)-O] layered cuprates, $(Tl_{1.5}Hg_{0.5})Ba_2CuO_z$ (2201 phase) and $(Tl_{1.8}Hg_{0.2})Ba_2CaCu_2O_z$ (2212 phase), have been successfully synthesized at ambient pressure and identified by powder X-ray diffraction and electron diffraction analysis.

2. Compared to the pure Tl-based 2212 phase compound, Hg-doped Tl-based compound $(Ti_{1.8}Hg_{0.2})Ba_2CaCu_2O_z$ shows an indication of much higher T_c (> 132 K). But when the as-prepared samples undergo several times of thermal recycle in a moist atmosphere, the T_c will drop step by step to the usual 107 K or so.

REFERENCES

[1] J. L. Tholence, B. Souletle, O. Laborde J. J. Capponi, C. Chaillout, *Physics Letters*, **A186**(1994), 366.
[2] B. G. Levi, *Physics Today*, **47**((2)(1994), 17.
[3] S. N. Putilin, E. V. Antipov, O. Chmaissem and M. Marezio, *Nature*, **362**(1993), 226.
[4] A. Schilling, M. Carrtoni, J. D. Guo and H. R. Ott, *Nature*, **363**(1993), 56.
[5] C. W. Chu, L. Gao, F. Chen, Z. J. Huang, R. L. Meng and Y. Y. Xue, *Nature*, **365**(1993), 323.
[6] A. Umezawa, W. Zhang, A. Gurevich, Y. Feng, E. E. Hellstrom *et al.*, *Nature*, **364**(1993), 129.
[7] A. Ehmann, S. Kemmler-Sack, S. Losch, M. Schlichenmaier, W. Wischert *et al.*, *Physica*, **C198**(1992), 1.
[8] Qian Yitai, Tang Kaibin, Yang Peidong, Chen Zuyao, Li Rukang *et al.*, *Physica*, **C209**(1993), 516.

[9] T. P. Beales, C. Dineen, S. R. Hall, M. R. Harrison and J. M. Parberry, *Physica*, **C207**(1993), 1.
[10] Cao Guanghan, Qian Yitai, Yu Weichao, Wang Shizhong, Chen Zuyao, *Physica*, **C221**(1994), 278.
[11] R. J. Cava, B. Batlogg, *Nature*, **336**(1988), 211.
[12] H. W. Zandbergen, *Physica*, **C159**(1989), 81.
[13] J. Y. Lee, *J. Mater. Res.*, **4**(1989), 763.
[14] R. S. Liu, D. Groult, A. Maignan, S. F. Hu, D. A. Jefferson *et al.*, *Physica*, **C195**(1992), 35.
[15] R. S. Liu, P. T. Wu, *Physica*, **C165**(1990), 111.
[16] T. Rouillon, J. Provost M. Hervieu, D. Groult, C. Michel *et al.*, *J. Solid State Chem.*, **84**(1990), 375.
[17] T. Rouillon, A. Maignan M. Herllieu, C. Michel, D. Groult *et al.*, *Physica*, **C171**(1990), 7.
[18] H. B. Liu, D. E. Morris and A. P. B. Sinha, *Physica*, **C204**(1993), 262.
[19] T. Suzuki, M. Nagoshi, Y. Fukuda S. NakaJima M. Kikuchi *et al.*, *Physica*, **C162–164**(1989), 1387.
[20] T. Suzuki, M. Nagoshi, Y. Fukuda Y. Syono, M. Kikuchi *et al.*, *Phys. Rev.*, **B40**(1989), 5184.
[21] Zhang Yongjian, Chen Zuyao, Wei Qingqiao Qian Yitai, Ran Keqin *et al.*, *Chinese Journal of Low Temperature Physics*, **16**(1994), 179.
[22] Y. Xin and Z. Z. Sheng, *J. Appl. Phys.*, **68**(1990), 5289.