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Tl valence change and T_c enhancement $(>130\ \mathrm{K})$ in $(\mathrm{Cu,Tl})\mathrm{Ba_2Ca_2Cu_3O}_y$ due to nitrogen annealing

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Annealing effects in a reducing environment (flowing nitrogen) in the temperature range of 200–600 °C are reported on the high Tl content $(\mathrm{Cu}_{1-x}\mathrm{Tl}_x)\mathrm{Ba_2Ca_2Cu_3O}_y$ system, synthesized under high pressure (4.5 GPa). A considerable enhancement in T_c from 97 K (as-synthesized) to >130 K (annealed at 550 °C) and an anomalous behavior in the resistivity with annealing is found. The results have been analyzed in the context of the loss of oxygen and Tl valence change.

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I. INTRODUCTION

Since the time of their discovery, both $\mathrm{CuBa_2Ca}_n\mathrm{Cu}_{n+1}\mathrm{O}_y$ (Refs. 1–5) and $\mathrm{TlBa_2Ca}_n\mathrm{Cu}_{n+1}\mathrm{O}_y$ (Refs. 6–9) systems, designated as Cu-12$n(n+1)$ and Tl-12$n(n+1)$, respectively, have been under extensive investigation. Both the systems are found to be isostructural to each other except for the position of oxygen in the charge reservoir layer. Interestingly, Cu-12$n(n+1)$ is synthesized at high pressure and high temperatures while Tl-12$n(n+1)$ is obtained at relatively low temperature and ambient pressure.[1–5,10,11] It is likely that a hybrid charge reservoir layer with both Tl and Cu might lead to moderate synthesis conditions, maintaining the low superconducting anisotropy.[3] Such trials have earlier been attempted by us in thin films.[12,13] We designate this system as (Cu,Tl)-1223. A higher member $(n=3)$ of this family, (Cu,Tl)-1234 has in fact been found to yield a rather high T_c of 126 K.[10] Besides affecting the synthesis parameters, Tl by changing its valence state is thought to vary the number of carriers and oxygen content in conventional Tl-based superconductors.[14,15] The role and dynamics of the Tl valence change due to annealing in relation to T_c and the electronic structure have also been reported for conventional Tl-based superconductors.[14–17] However, such a study has not been undertaken on the (Cu,Tl)-12$n(n+1)$ system to look for a possible effect on T_c and Tl-valence change. The present results on the nitrogen annealing of (Cu,Tl)-1223 synthesized at high pressure indicate a substantial increase in T_c and a change in the Tl valence state.

II. EXPERIMENT

Polycrystalline samples of nominal $(\mathrm{Cu_{0.5}Tl_{0.5}})\mathrm{Ba_2Ca_2Cu_3O}_y$ were synthesized through a $\mathrm{Ba_2Ca_2Cu_3O}_y$ precursor with CuO(0.5 mole), $\mathrm{Tl_2O_3}$ (0.25 mole), and oxidizer AgO (0.6 mole) under high pressure at 4.5 GPa (Riken CAP-07) and 850 °C temperature for 2 h in a Au capsule.[10] Phase purity of the as-synthesized sample (s-0) was checked through powder x-ray diffraction (XRD) (Rigaku RINT 1000 Diffractometer with monochromated CuKα) and the chemical composition was analyzed through energy dispersive spectrometry (EDS) in a scanning electron microscope (JEOL JSM-6301F). These samples were then annealed in flowing nitrogen for 12 h at different temperatures in the range of 200–600 °C (Table I) and cooled in the furnace (i.e., furnace cooling). Resistivity below 280 K was measured using the four probe method and the Hall number (N_H) was measured at room temperature for several samples. Oxygen loss in the as-synthesized sample below 800°C was measured by thermogravimetric analysis (TGA) (Rigaku TAS 100) in flowing nitrogen. X-ray photoemission spectroscopy (XPS) for the as-synthesized sample (s-0) and the sample annealed at 550 °C (s-550) was carried out at room temperature using a Surface Science Spectra SSX-100 spectrometer with monochromatized AlKα (1486.6 eV) on their freshly fractured surfaces in ultrahigh vacuum (UHV) conditions. Au was sputtered to ~10 Å thickness on these samples to serve as a core level energy calibrator with Au-4$f_{7/2}$ of 83.95 eV.

TABLE I. Summary of the experimental results with annealing. T_A is the annealing temperature, T_c refers to the onset of superconducting transition, ρ is the resistivity at 280 K, and N_H /CuO$_2$ is the Hall number per CuO$_2$ plane at room temperature.

Sample name	T_A(°C)	T_c (K)	R (mΩ cm)	N_H /CuO$_2$
s-0	as-synthesized	97.6	0.68	0.50
s-200	200	103.5	0.86	
s-300	300	104.9	1.7	
s-330	330	124.5 (115.4)	7.4	
s-350	350	125.6	45	
s-380	380	129	140	<0.05
s-400	400	129.2	69	0.11
s-450	450	128.9	25	
s-500	500	129.3	18	
s-550	550	131.4	11	0.19
s-600	600	131.2	15	

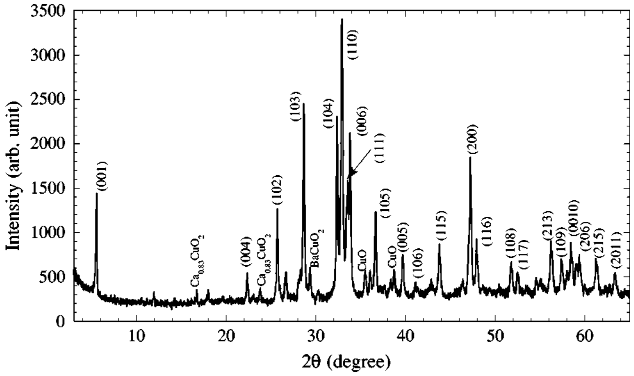

FIG. 1. XRD pattern of the as-synthesized (Cu,Tl)-1223 sample prepared under high pressure.

III. RESULTS

From the XRD pattern of the s-0 sample (Fig. 1) all the characteristic peaks of the (Cu,Tl)-1223 superconducting system could be identified. There were also some low intensity minor peaks corresponding to nonsuperconducting oxides of Ba, Ca, and Cu. Lattice parameters of the tetragonal (Cu,Tl)-1223 system were determined to be $a = 3.854$ Å and $c = 15.890$ Å. XRD patterns of s-0 and s-550 did not yield any noticeable difference except for < 0.02 Å change in the c-parameter. EDS measurements carried out on a number of crystallites of typically $5 \times 5 \times 1$ μm^3 size indicated an average composition of $Tl_{0.79}Ba_2Ca_{1.84}Cu_{3.37}O_y$ with Ba stoichiometry fixed to 2. Tl content was seen to be distributed in the range of 0.4 to 1.

The temperature dependence of the resistivity (ρ) of the various samples is depicted in Figs. 2(a) and 2(b). The room temperature ρ increases with annealing temperature T_A up to 380° C, decreases continuously for T_A between 400–550 °C and shows an increasing trend at 600 °C. The sample annealed at 550°C (s-550) showed a $T_{c,onset}$ of over 130 K, possibly the highest ambient pressure value reported for any high T_c system without Hg. While the s-300 sample depicts a signature of a second transition at 123 K, both s-330 and s-350 samples show clear double transitions. The Hall number (N_H) at room temperature for the samples s-0, s-400 and s-550 were estimated to be 0.5, 0.11, and 0.19 per CuO_2 plane, respectively (Table I).

It would be worth mentioning that the results reported here are typical of a number of (Cu,Tl)-1223 samples containing varying oxidizer (AgO) contents between 0 and 0.65 mole with a maximum T_c of ~ 110 K. These samples, when annealed in flowing nitrogen between 550–600 °C, gave a T_c of around 130 K and it was seen to be a common feature of (Cu,Tl)-1223 synthesized under high pressure. The highest $T_c \sim 133$ K obtained in such material was confirmed by sharp resistivity and magnetic transitions.[18] These samples, however, were not found to be highly stable in ambient conditions with T_c lowering to 128 K in a week's time with a tendency to deteriorate further. The unannealed sample, however, showed long term stability in ambient conditions. The relation of such metastability to CO_2 or moisture in the ambient is still not clear at present.

TGA data for the s-0 sample (Fig. 3) show a small weight loss in the temperature range of 30–650 °C and a large weight loss above 650 °C. The former was ascribed to the release of oxygen. The latter to the escape of Tl (or Tl oxide) vapor from the system[19,20] and the sample starts to decompose around that temperature simultaneously. Significantly, a distinct weight loss of about 0.5 wt% also occurred around 350 °C (inset) and a larger one around 530°C. On the preliminary experiment this process was not reversible even under the oxygen annealing.

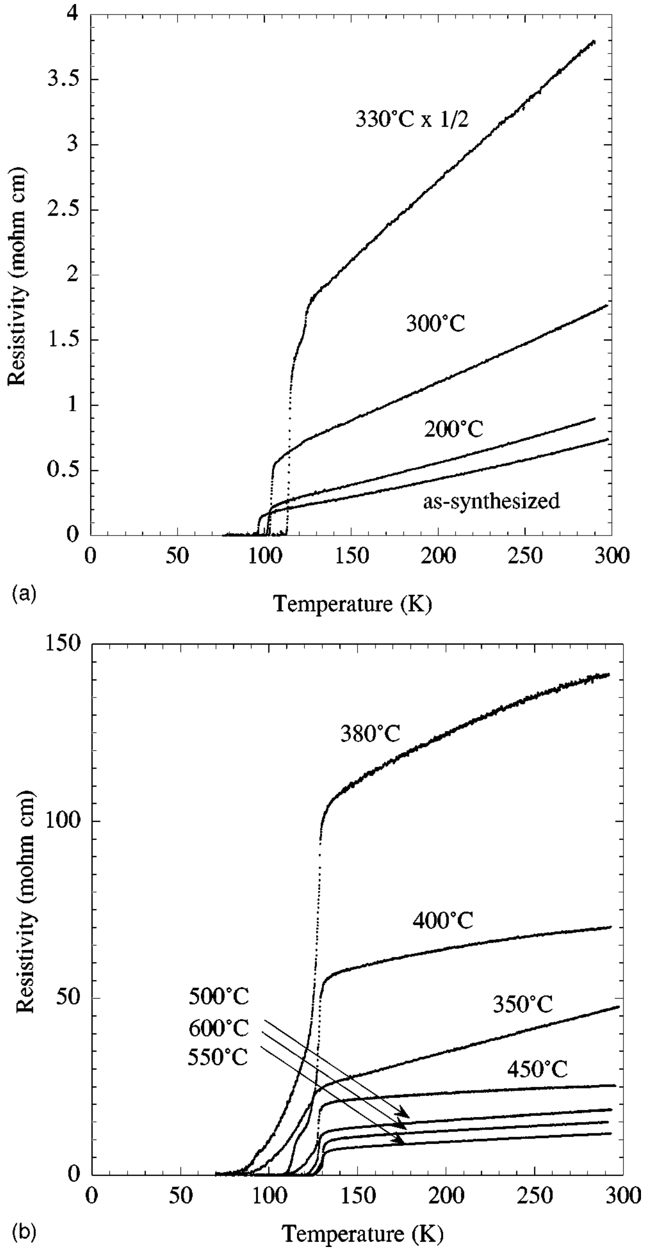

FIG. 2. (a) Resistivity behavior with annealing in N_2 below 330 °C. (b) Resistivity behavior with annealing in N_2 above 350 °C.

The surfaces of both the samples s-0 and s-550 fractured under UHV conditions were of high quality as the photoelectron Fermi edge could be clearly observed in their XPS spectra.[21,22] The Tl-4$f_{7/2}$ core level, calibrated with the Au-4$f_{7/2}$ core level of 83.95 eV, was clearly seen to shift in the s-550 sample (Fig. 4). The Tl-4$f_{7/2}$ core-level binding

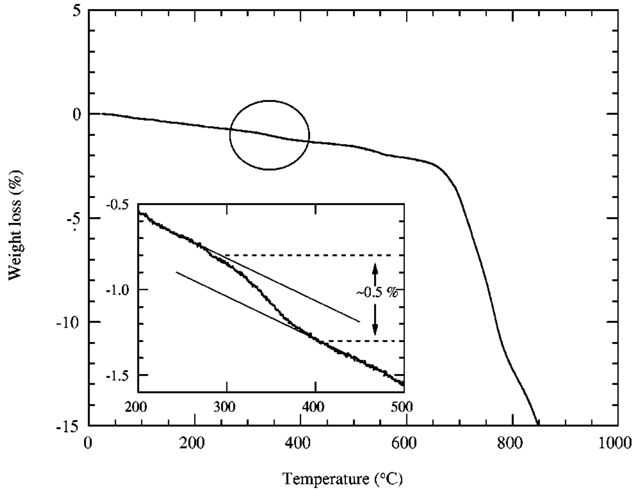

FIG. 3. TGA of the as-synthesized sample. Inset shows the weight loss at ∼350 °C.

energies and T_c values of the s-0 and s-550 samples when compared with those reported[17,23] for Tl-1212, Tl_2O_3 and Tl_2O (Table II) indicate a clear shift of Tl valence from 3+ towards the 1+ state due to annealing.

IV. DISCUSSION

A. Overall annealing behavior and importance of thallium valence change

The decrease of room temperature resistivity with annealing temperature with T_A between 380°C and 550°C [Fig. 2(b)] and the loss of oxygen above 380°C appear to present an abnormal situation of carrier density enhancement despite oxygen removal. Another interesting case is that of s-300 and s-550 samples possessing different T_c values in spite of being both in the nearly optimally doped state. We deal with such a situation in the next section in terms of competing sources of hole addition and depletion. The observed two transitions have been categorized as the 100 K phase and 130 K phase, generated below and above $T_A \sim 380$ °C. Both these phases may have the respective changes in their resistivity and T_c with the varying of hole concentration (n_h) and may apparently cross over near 380 °C as suggested in Fig. 2(b).

The recovering of the resistivity on the annealing above 380 °C was not observed on the $(Cu_x,C_{1-x})Ba_2Ca_2Cu_3$ [(Cu,C)-1223] in which there is not any thallium element.[24] The resistivity of (Cu,C)-1223 monotonically increased with increasing of the annealing temperature. We think the recovering of the resistivity cannot be explained without the supplying holes relating to the Tl valence change, as mentioned in the next section, though we cannot rule out the effect of the local depression of oxygen in grain boundaries.

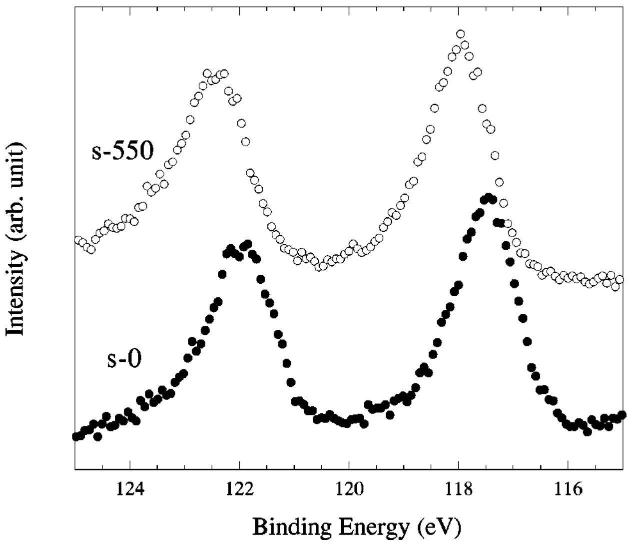

FIG. 4. XPS spectra of Tl core-level binding energy in s-0 and s-550 samples.

We notice that the highest T_c of the as-prepared samples was about 110 K, just varying the nominal oxygen contents without annealing, as mentioned in Sec. II. After annealing, the highest T_c was about 133 K. We believe that the phase induced by the annealing is different from that of the as-prepared sample. On both of the s-300 and s-550 samples, T_c seems to be nearly equal to that of the optimum one or the highest ones. As we will discuss in Secs. IV B 1 and IV B 3, we believe both of them are in the nearly optimally doped situation.

The XRD pattern of the as-synthesized sample can be indexed as (Cu,Tl)-1223 with a basic structure equivalent to that of (Cu,C)-1223 and Tl-1223. The charge reservoir layer here comprises Cu, Tl, and O. The occupancy of these ions is still not determined for want of a large enough single crystal of this material. Even though the crystal structures of (Cu,Tl)-1223 and Tl-1223 might be similar, the annealing effects observed in the two cases are entirely different. Moreover, if only Tl-1223 had formed, impurity phases like Ba_2CuO_3, $CaCuO_2$, and CuO would have shown up in large quantities, contrary to observation (Fig. 1). We also rule out

TABLE II. Comparison of Tl-4$f_{7/2}$ core-level binding energy in different systems.

Material	T_c (K)	Condition	Tl-4$f_{7/2}$ (eV)	Ref.
(Cu,Tl)-1223	97	as-synthesized	117.5	this work
	131	annealed at 550 °C	118.0	this work
Tl-1212	74.5∼87		117.66∼117.83	17
	73		117.7	23
Tl_2O_3			117.4	23
Tl_2O			118.6	23

the possibility of the formation of a double Tl-O layer on the basis of a low anisotropy seen in the as-synthesized sample.[25]

In view of the complicated stoichiometries seen in all Tl-based compounds, the possibility of antisite occupancies of Cu and/or Ca at Tl or vice versa have been suggested.[26–29] The average composition observed in the as-synthesized samples may have two candidates with some variation in their occupancy levels. Either Cu occupies Tl vacancies as $(\mathrm{Tl}_{0.79}\mathrm{Cu}_{0.21})\mathrm{Ba}_2\mathrm{Ca}_{1.84}\mathrm{Cu}_{3.16}\mathrm{O}_y$, or Tl occupies Ca vacancies as $(\mathrm{Tl}_{0.63}\mathrm{Cu}_{0.37})\mathrm{Ba}_2(\mathrm{Ca}_{1.84}\mathrm{Tl}_{0.16})\mathrm{Cu}_3\mathrm{O}_y$. Since there is not much change observed in its c parameter compared with that of Tl-1223, and in the absence of any conclusive evidence about Tl at Ca-sites on this system, it can safely be conjectured that only a part of Cu occupies Tl sites in the charge reservoir layer. It would be worthwhile mentioning here that the single superconducting transitions seen in the annealed samples suggest that the distributed Tl content may not be present in the annealed samples or at least in the superconducting grains. We think that there is no chance of the intergrowth like Tl-1234 up to about 650°C where the Tl loss started as observed in the TGA data. Efforts are being made to synthesize single crystals of this material for a precise determination of its crystal structure.

B. Analysis of the annealing process

In this section we focus our attention on the possible Tl valence state conversion. The observed anomalous $\rho(T)$ behavior with increasing T_A demands that the suppression of charge carriers in the CuO_2 planes resulting from the oxygen removal, should be compensated by some other counter process. This we believe is provided by the possible Tl valence change. These two processes have competing rates with oxygen removal being dominant at temperatures below 400°C and the Tl valence effect becoming predominant at around 550°C, where a single phase high T_c (>130 K) superconductor is obtained. For a further in-depth inspection we divide the annealing range into three regions as below.

1. Annealing effect below 300°C

The change of $\rho(T)$ with T_A in this region is rather normal and can simply be explained on the basis of a decrease of n_h due to oxygen removal. The as-synthesized material (s-0) was a heavily doped one. It was found that the density of states at the Fermi level $[D(E_F)]$ measured by XPS, is about twice as high as that of an optimally doped conventional Tl-1223.[21,22] Hall number (N_H) of 0.5 per one CuO_2 plane and the nominal composition are also consistent with its heavily doped situation. Tl is considered to be in the 3+ state as estimated by the Tl-$4f_{7/2}$ core-level binding energy spectra. The s-0 sample being already in the overdoped state may not accept any further carrier increase created by the Tl valence change. The large amount of excess oxygen, which may be in the neighborhood of Tl ions, would also inhibit formation of the higher ionic radius Tl^{1+}.

The resistivity ρ of the s-300 sample is seen to be about three times that of the s-0 sample. A nearly optimally doped state is suggested by the observed nearly linear $\rho(T)$. The improvement of T_c with increasing T_A indicates the approach to the optimally doped regime from the overdoped one.

The ~0.85% weight loss was detected up to 300 °C annealing. It corresponds to a loss of oxygen of 0.43 mole for a unit formula. The lost holes due to annealing are ~0.28 per one CuO_2 plane when all of the lost oxygen is relevant to the supply of holes. This large amount of missing holes may mainly contribute to the suppression of the conductivity with increasing T_A between room temperature and 300 °C. (The absolute value of the resistivity of s-300 is still low as a sintered polycrystalline sample[30]).

On this estimation, the doping level of the s-0 seems to be slightly too large compared to that of $\mathrm{La}_{1-x}\mathrm{Sr}_x\mathrm{CuO}_4$ and $\mathrm{YBa}_2\mathrm{Cu}_3\mathrm{O}_y$. It has been well known that T_c depends on the number of CuO_2 planes between the charge reservoir layer. We have to mention that the doping level where T_c disappears does also depend on this number of CuO_2 planes, though it has not been widely recognized yet.[31–46]

2. Annealing effect between 330°C *and* 380°C

The broad transitions in the s-350 and s-380 samples seem to indicate some inhomogeneity in the systems. We observed a huge resistivity increase in the s-380 and its recovery in the higher annealed sample s-550. This recovery of the conductivity following the increased resistivity was not observed in (Cu,C)-1223 where there is no thallium element. We cannot explain these phenomena only by the removal of the oxygen and its inhomogeneity. One has to look for some other mechanism. Taking a cue from the observed XPS spectra, we turn to a Tl valence effect. A change of valence of Tl ions has been proposed in earlier reports on conventional Tl-based superconductors synthesized under ambient conditions.[14–16,47] By this model, Tl valence changes so as to compensate for the change of carriers due to oxygen content, and such a mechanism would maintain a constant number of carriers in the sample. In a different report on Tl-1212 thin film,[48] such compensation appears to be rather incomplete where the T_c of the film was seen to increase and decrease with annealing temperature up to 400 °C and stabilized to a higher T_c value for $T_A > 500$ °C. It is therefore suggested in the present case that the above compensation is not established under the possible nonequilibrium conditions prevailing below 400°C where the competing rate of the Tl valence change is not rapid enough to match the change in oxygen. The competition of the removal of oxygen with the Tl valence change may be the origin of the huge resistivity increase and the inhomogeneity.

3. Annealing effect above 400°C

The observed decrease of resistivity ρ with increasing T_A between 400 °C and 550 °C implies an increase in the carrier density and is inexplicable on the basis of the loss of oxygen alone. $D(E_F)$ measured by XPS of s-550 is nearly equal to that of the optimally doped conventional Tl-1223.[22] N_H of 0.19 per one CuO_2 plane and the highest T_c are consistent with the optimally doped situation. The Tl valence effect seemingly becomes more prominent in this temperature regime to overcome the number of holes (n_h) lost by oxygen removal. The total n_h supplied by the Tl valence change can be estimated from the n_h lost by annealing. When we consider that the total weight loss is due to oxygen release only, the amount of the Tl valence conversion is estimated to be

$$\Delta n_h(300\text{–}550\,^\circ\mathrm{C}) + n_h(s-550) - n_h(s-300) \sim 0.8 \sim \Delta n_h(\mathrm{Tl}^{3+} \rightarrow \mathrm{Tl}^{1+})$$

as a crude approximation. $\Delta n_h(300\text{–}550\,^\circ\mathrm{C})$ is the loss of carriers due to oxygen release between 300°C and 550 °C. We believe that both s-550 and s-300 are in an optimally doped situation as discussed above and in Sec. IV B 1 and the n_h of each is nearly equal to the other. It means that about 0.4 mole of Tl^{3+} gets converted to Tl^{1+}, which seems consistent with the XPS estimation of 1:1 for Tl^{3+} and Tl^{1+} states, with the occupancy of Tl sites in the charge reservoir being 0.8 where we linearly interpolate the shift of Tl-$4f_{7/2}$ core level binding energy using that of $\mathrm{Tl_2O_3}$ and $\mathrm{Tl_2O}$ to make a rough estimation.

We stress again that the oxygen weight loss up to 550 °C is ~2% corresponding to one mole oxygen lost per a unit formula. It indicates the missing of ~2 holes for three $\mathrm{CuO_2}$ planes. Without the large valence change of thallium we never expect the emergence of the superconductivity with high T_c. We speculate that an occupancy and location of oxygen in the charge reservoir layer can affect the size and valence of the thallium ion as described in Sec. IV B 1. The removal of oxygen makes room to accept an enlargement of the size of the thallium ion due to its valence change.

The sample annealed at 380 °C (s-380) yielded a T_c of 125 K which is higher than the maximum T_c of 110 K seen in the as-synthesized samples.[49] The conventional Tl-1223 system also shows a $T_c \sim 120$ K by annealing in a reducing environment.[50] This, however, is still lower than the T_c of the s-380 sample.

A small change in T_c of the conventional Tl-1223 by annealing in oxidizing/reducing environments[14] indicates its insensitivity towards the amount of oxygen in the system. A nearly optimum carrier doping level seems to be maintained here. However, in the present case of (Cu,Tl)-1223 it is possible to optimize T_c by optimizing n_h through annealing conditions. The electronic band structure here does not seem to be as rigid as in Tl-1223 or it has an instability against a large Tl valence change which is the most typical feature of (Cu,Tl)-1223, not seen in Tl-1223 where the $\mathrm{Tl}^{3+} \rightarrow \mathrm{Tl}^{1+}$ change is less than 0.1.[16]

A correlation between oxygen content and electronic structure on Tl-1201 and Tl-1212 systems has earlier been reported.[17,51] According to band structure calculations and the XPS measurements on Tl-1212, Vasquez *et al.*[17] argued that the oxygen content changes the Fermi level but not the Tl valence. The change of Tl-$4f_{7/2}$ binding energy was attributed to a change in the chemical potential as all other core-level binding energies shifted in the same direction as that of Tl-$4f_{7/2}$. However, in the case of (Cu,Tl)-1223 we did observe the other core-level binding energies to have a different doping dependence as compared to that of Tl-$4f_{7/2}$[21,22] which gives credence to the Tl valence shift model. We think that the valence change is dominant in this shift even though the chemical potential shift has a contribution. One therefore has to take into account the Tl valence change in the band structure model proposed earlier[17] to explain the abnormal annealing effects in (Cu,Tl)-1223.

V. CONCLUSION

Synthesis of the (Cu,Tl)-1223 compound with a Cu and Tl hybrid charge reservoir layer under high pressure has been attempted. Treatment of the material in flowing $\mathrm{N_2}$ yields a considerable enhancement of T_c (>130 K). The observed anomalous decrease of resistivity with increasing annealing temperature, and the different T_c values obtained for the nearly optimally doped materials at 300 °C and 550 °C, present intriguing situations. These results, unlike in conventional Tl systems, have been explained on the basis of hole depletion and addition by oxygen removal and $\mathrm{Tl}^{3+} \rightarrow \mathrm{Tl}^{1+}$ conversion below and above 380 °C respectively. XPS corroborates the nearly 1:1 conversion of the Tl valence state in the 550 °C sample with $T_c \sim 130$ K. There is seemingly a need to consider the Tl valence change in the band structure model proposed earlier[15] to account for the abnormal annealing effects seen in the (Cu,Tl)-1223 system.

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[1] H. Ihara, K. Tokiwa, H. Ozawa, M. Hirabayashi, A. Negishi, M. Matsuhata, and Y.S. Song, Jpn. J. Appl. Phys., Part 2 **33**, L503 (1994).

[2] H. Ihara, K. Tokiwa, H. Ozawa, M. Hirabayashi, A. Negishi, M. Matsuhata, and Y.S. Song, Jpn. J. Appl. Phys., Part 2 **33**, L303 (1994).

[3] H. Ihara, in *Advances in Superconductivity VII*, edited by K. Yamafuji and T. Morishita (Springer-Verlag, Tokyo, 1995), p.225.

[4] K. Tokiwa, Y. Tanaka, A. Iyo, T. Tsubaki, K. Tanaka, J. Akimoto, Y. Oosawa, N. Terada, M. Hirabayashi, M. Tokumoto, S.K. Agarwal, T. Tsukamoto, and H. Ihara, Physica C **298**, 209 (1998).

[5] S.K. Agarwal, A. Iyo, K. Tokiwa, Y. Tanaka, K. Tanaka, M. Tokumoto, N. Terada, T. Saya, M. Umeda, H. Ihara, M. Hamao, T. Watanabe, and A.V. Narlikar, Phys. Rev. B **58**, 9504 (1998).

[6] H. Ihara, R. Sugise, M. Hirabayashi, N. Terada, M. Jo, K. Hayashi, A. Negishi, M. Tokumoto, Y. Kimura, and T. Shimomura, Nature (London) **334**, 510 (1988).

[7] H. Ihara, R. Sugise, K. Hayashi, N. Terada, M. Jo, M. Hirabayashi, A. Negishi, N. Atoda, H. Oyanagi, T. Shimomura, and S. Ohashi, Phys. Rev. B **38**, 11 952 (1988).

[8] R. Sugise, M. Hirabayashi, N. Terada, M. Jo, T. Shimomura, and H. Ihara, Jpn. J. Appl. Phys., Part 2 **27**, L1709 (1988).

[9] S.S.P. Parkin, V.Y. Lee, A.I. Nazzal, R. Savoy, R. Beyers, and S. J. La Placa, Phys. Rev. Lett. **61**, 750 (1988).

[10] H. Ihara, K. Tokiwa, K. Tanaka, T. Tsukamoto, T. Watanabe, H. Yamamoto, A. Iyo, M. Tokumoto, and M. Umeda, Physica C **282-287**, 957 (1997).

[11] H. Yamamoto, K. Tanaka, K. Tokiwa, H. Hirabayashi, M. Tokumoto, N.A. Khan, and H. Ihara, Physica C **302**, 137 (1998).

[12] H. Ihara, Y. Sekita, F. Tateai, N.A. Khan, K. Ishida, E. Harashima, T. Kojima, H. Yamamoto, K. Tanaka, Y. Tanaka, N. Terada, and H. Obara, IEEE Trans. Appl. Supercond. **9**, 1551 (1999).

[13] N.A. Khan, Y. Sekita, F. Tateai, T. Kojima, K. Ishida, N. Terada, and H. Ihara, Physica C **320**, 39 (1999).

[14] B. Morosin, E.L. Venturini, R.G. Dunn, and P.P. Newcomer, Physica C **288**, 255 (1997).

[15] B. Morosin, E.L. Venturini, and D.S. Ginley, Physica C **175**, 241 (1991).

[16] B. Morosin, E.L. Venturini, and D.S. Ginley, Physica C **183**, 90 (1991).

[17] R.P. Vasquez, D.L. Novikov, A.J. Freeman, and M.P. Siegal, Phys. Rev. B **55**, 14 623 (1997).

[18] K. Tanaka, A. Iyo, Y. Tanaka, K. Tokiwa, N. Terada, M. Tokumoto, M. Ariyama, M. Tsukamoto, S. Miyashita, T. Watanabe, and H. Ihara, Physica B **284-288**, 1079 (2000).

[19] W.L. Holstein, J. Phys. Chem. **97**, 4224 (1993).

[20] M. Jergel, F. Hanic, G. Plesch, V. Strbik, J. Liday, C.F. Guajardo, and G.S.C. Puente, Supercond. Sci. Technol. **7**, 931 (1994).

[21] N. Terada, K. Tanaka, Y. Tanaka, A. Iyo, K. Tokiwa, T. Watanabe, and H. Ihara, Physica B **284-288**, 1079 (2000).

[22] N. Terada (unpublished).

[23] T. Suzuki, M. Nagoshi, Y. Fukuda, S. Nakajima, M. Kikuchi, Y. Syono, and M. Tachiki, Physica C **162-164**, 1387 (1989).

[24] A. Iyo (unpublished).

[25] K. Tanaka, A. Iyo, Y. Tanaka, K. Tokiwa, M. Tokumoto, M. Ariyama, M. Tsukamoto, T. Watanabe, and H. Ihara, Physica B **284-288**, 1081 (2000).

[26] D.C. Sinclair, M.A.G. Aranda, P. Attfield, and J. Rodriguez-Carvajal, Physica C **225**, 307 (1994).

[27] M. Karpinnen and H. Yamauchi, J. Supercond. **11**, 39 (1998).

[28] M. Onada, S. Kondoh, K. Fukuda, and M. Sato, Jpn. J. Appl. Phys., Part 1 **27**, 1234 (1988).

[29] R.S. Liu, S.D. Hughes, R.J. Angel, T.P. Hackwell, A.P. Mackenzie, and P.P. Edwards, Physica C **198**, 203 (1992).

[30] H. Takagi, B. Batlogg, H.L. Kao, J. Kwo, R.J. Cava, J.J. Krajewski, and W. F. Peck, Phys. Rev. Lett. **69**, 2975 (1992).

[31] Y. Tokunaga, K. Ishida, Y. Kitaoka, K. Asayama, K. Tokiwa, A. Iyo, and H. Ihara, Phys. Rev. B **61**, 9707 (2000).

[32] Y. Tokunaga, H. Kotegawa, K. Ishida, G.-q. Zheng, Y. Kitaoka, K. Tokiwa, A. Iyo, and H. Ihara, J. Low Temp. Phys. **117**, 473 (1999).

[33] M. Ogino, T. Watanabe, H. Tokiwa, A. Iyo, and H. Ihara, Physica C **258**, 374 (1996).

[34] T. Watanabe, S. Miyashita, N. Ichioka, K. Tokiwa, K. Tanaka, A. Iyo, Y. Tanaka, and H. Ihara, Physica B **284-288**, 1075 (2000).

[35] A. Iyo and M. Tokumoto, Physica C **311**, 35 (1999).

[36] A. Iyo, T. Saya, K. Tokiwa, Y. Tanaka, N. Terada, M. Tokumoto, and H. Ihara, Physica C **282-287**, 509 (1997).

[37] A. Iyo, K. Tokiwa, N. Terada, M. Tokumoto, and H. Ihara, Czech. J. Phys. **46**, Suppl. S3, 1481 (1996).

[38] A. Iyo, K. Tokiwa, N. Terada, M. Tokumoto, M. Hirabayashi, and H. Ihara, in *Advances in Superconductivity VIII*, edited by H. Hayakawa and Y. Enomoto (Springer-Verlag, Tokyo, 1996), p. 289.

[39] A. Iyo, T. Saya, K. Tokiwa, N. Terada, M. Tokumoto, and H. Ihara, in *Advances in Superconductivity IX*, edited by S. Nakajima and M. Murakami (Springer-Verlag, Tokyo, 1997), p. 349.

[40] A. Iyo and H. Ihara, Bulletin of the Electrotechnical Laboratory **12**, 701 (1998) [in Japanese] (http://www.etl.go.jp/jp/results/bulletin/62.html).

[41] N. Hamada and H. Ihara, Physica B **284-288**, 1073 (2000).

[42] K. Tokiwa, C. Kunugi, H. Kashiwagi, T. Nibe, H. Aota, N. Ichioka, T. Watanabe, A. Iyo, Y. Tanaka, S.K. Agarwal, and H. Ihara, J. Low Temp. Phys. **117**, 903 (1999).

[43] T. Watanabe, H. Kashiwagi, S. Miyashita, N. Ichioka, K. Tokiwa, A. Iyo, Y. Tanaka, S.K. Agarwal, and H. Ihara, J. Low Temp. Phys. **117**, 753 (1999).

[44] K. Tokiwa, H. Aota, C. Kunugi, K. Tanaka, Y. Tanaka, A. Iyo, H. Ihara, and T. Watanabe, Physica B **284-288**, 1077 (2000).

[45] C. Kunugi, S. Kuwata, K. Tokiwa, A. Iyo, T. Watanabe, and H. Ihara, Physica C **307**, 17 (1998).

[46] T. Watanabe, T. Tonozuka, H. Ihara, K. Tokiwa, and M. Hirabayashi, Physica C **235**, 1495 (1998).

[47] B. Morosin and E.L. Venturini, Phys. Rev. B **46**, 510 (1992).

[48] M.P. Siegal, E.L. Venturini, P.P. Newcomer, B. Morosin, D.L. Overmyer, F. Dominguez, and R.G. Dunn, Appl. Phys. Lett. **67**, 3966 (1995).

[49] K. Tanaka and H. Ihara (unpublished).

[50] C. Martin, A. Maignan, J. Provost, C. Michel, M. Harvieu, R. Tournier, and B. Raveau, Physica C **168**, 8 (1990).

[51] L.F. Mattheiss, Phys. Rev. B **42**, 10 108 (1990).