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On the Question of Overlap between Tl : 6*s* and Cu : 3*d* Bands in the $Tl_{1-y}LaBa_{1-z}Sr_zCuO_{5-x}$ System*

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IN HONOR OF C. N. R. RAO ON HIS 60TH BIRTHDAY

Wet-chemical analysis was used to charcterize the thallium and oxygen contents *y* and *x* of the system $Tl_{1-y}LaBa_{1-z}Sr_zCuO_{5-x}$ before and after annealing in an O_2 atmosphere at 500°C. The values of *y* and *x* were found to vary sensitively with the conditions of the initial synthesis, and the oxygen content increased after the 500°C anneal in O_2. Single-phase samples were obtained for $y \leq 0.36$; the CuO_2 sheets were never reduced below $(CuO_2)^{2-}$, and the ability to reduce to this state decreased with increasing *y*. Bulk superconductivity may be obtained for all values of *z* in the range $0 \leq z \leq 1$, and the change in Meissner fraction and superconductive onset temperature T_{on} varies with the oxidation state of the CuO_2 sheets in the same manner as the system $La_{2-x}Sr_xCuO_4$ in the range $0 \leq x \leq 0.16$, provided the oxidation state of the CuO_2 sheets is calculated on the basis that all the thallium are present as Tl^{3+}. There is no evidence of an electron transfer from the CuO_2 sheets to Tl-6*s* states at low temperatures in this Tl monolayer system, which distinguishes it from the Tl bilayer systems. These observations are at variance with speculation in the literature; they also demonstrate how experimental observations in the thallium cuprates may be misleading if they are not accompanied by chemical analysis.

INTRODUCTION

It is now well established that *p*-type superconductivity in the high-T_c copper oxides occurs in a narrow range of oxidation of the parent $(CuO_2)^{2-}$ sheets centered near $p = 0.16$ holes per Cu atom (*1*, *2*) and that the oxidation must be accomplished without changing the oxygen coordination at some of the CuO_2 sheets (*3*). In the case of thallium cuprates, a lack of chemical characterization of the thallium and oxygen contents led the early investigators of these compounds to speculate as to the origin of the oxidation of the CuO_2 sheets. The oxidation in these compounds may, in principle, be accomplished without changing the oxygen coordination at the Cu atoms not only by cation substitution outside the CuO_2 sheets, but also by changing the thallium content and/or the Tl/O ratio in the Tl–O layers, or by an overlap of the band of Tl-6*s* states and the top of the highest occupied band of the CuO_2 sheets. Given the volatility of Tl–O species at the reaction temperatures, it is not possible to know what combination of mechanisms is responsible for oxidation of the CuO_2 sheets of a given thallium copper oxide, even if it is prepared in a sealed tube, without an analysis of the thallium and oxygen contents of the product.

We have developed a reliable wet-chemical method for obtaining the thallium and oxygen contents of a thallium cuprate (*4*), and we have applied this method to clarify several aspects of the $Tl_{2-y}Ba_2Ca_{n-1}Cu_nO_{2n+4-x}$ family of compounds (*5*, *6*). For example, we demonstrated that the Tl–O layers contain a deficiency of both thallium and oxygen that varies sensitively with the processing conditions, a transfer of electrons from the CuO_2 sheets to 6*s* states of the Tl–O bilayers that decreases with decreasing Tl concentration, and an apparent intercalation/distintercalation of Tl and O atoms into/from a $y = 0.5$ composition. At smaller *y*, oxygen vacancies $3x > 2y$ compensate for the loss of thallium, and the CuO_2 sheets can only be oxidized *p*-type by transfer of electrons from the CuO_2 sheets to the Tl–O bilayers; at higher $y > 3x/2$, the *p*-type doping of the CuO_2 sheets is enhanced by the internal electron-transfer redox reaction. Where electron transfer from the CuO_2 sheets is to itinerant electron states of a Tl-6*s* band, which occurs for smaller values of $y < 0.5$, extrusion of Tl as Tl_2O_3 occurs above 70°C. Moreover, the upper limit of the thallium concentration $(2 - y)$ is a function of the reaction temperature, the heating time, the manner of quenching from the reaction temperature, and the number of CuO_2 sheets per formula unit. For example, reaction in sealed tubes at ambient air pressure followed by quenching into liquid nitrogen gave thallium contents as high as $(2 - y) = 1.89$ for $n = 1$, but only 1.80 and 1.65 for the $n = 2$ and 3 members above 70°C (*6*, *7*).

In this paper, we apply our wet-chemical analysis to the Tl–O monolayer system $Tl_{1-y}LaBa_{1-z}Sr_zCuO_{5-x}$. We have chosen this Tl–O monolayer system for study because of speculations (*8*) that observed changes in the superconductive properties as a function of *z* are due to

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changes in the Cu–O bond length rather than to changes in y and/or x; reduction of the mean Cu–O bond length with increasing z should raise the highest occupied antibonding band of the CuO_2 sheets relative to the Tl-6s states of a Tl–O layer, thus increasing any electron transfer from the CuO_2 sheets to the Tl-6s band. Although applicable to the Tl–O bilayer system, the internal redox reaction is to be considered suspect in the Tl–O monolayer system. Nevertheless, such a mechanism was invoked (8) to account not only for the dramatic decrease in T_c with increasing Sr content observed in the Tl–O bilayer systems $Tl_2Ba_{2-z}Sr_zCa_{n-1}Cu_nO_{2n+4}$, $n = 1, 2$, (8, 9), but also for the fact that in the Tl–O monolayer system $TlLaBa_{1-z}Sr_zCuO_5$ the $z = 0$ end member is not a superconductor whereas the $z = 1$ end member is superconductive (10). On the other hand, Maignan *et al.* (11) found superconductivity for all values of z in the system $TlLa_{0.8}Ba_{1.2-z}Sr_zCuO_5$, whereas Subramanian and Whangbo (10) reported that $TlLaBa_{1-z}Sr_zCuO_5$ is superconducting only for $z < 0.3$. In the nominal $TlLa_{0.8}Ba_{1.2-z}Sr_zCuO_5$ system, the apical Cu–O bond length was found to decrease with z along with the in-plane Cu–O bond length (11).

The variation in T_c with Sr substitution for Ba also depends on the value of n in the series $TlBa_{2-z}Sr_zCa_{n-1}Cu_nO_{2n+3}$. The $n = 1$ phase $TlSr_2CuO_5$ is metallic, but not superconductive (12, 13), whereas the $n = 2$ metallic phase may or may not become superconductive depending on the oxygen stochiometry (14).

Whereas $TlLaBaCuO_5$ is not a superconductor, the nominal system $TlLa_{1-x}Ba_{1+x}CuO_5$ is reported (15, 16) to have a narrow superconductive compositional range between an antiferromagnetic semiconductive parent phase ($x = 0$) and a metallic overdoped phase. However, the superconductive phase field was variously reported to be $0.01 < x < 0.04$ by Manako *et al.* (15) and $0.4 < x < 1.0$ by Ku *et al.* (16).

All these studies fail to address the influence of Tl and O stochiometry since no chemical analyses were carried out. Without a chemical analysis of the product of a reaction, it is not possible to resolve the extent to which variations in T_c are due to variation in Tl concentration and the Tl/O ratio rather than to variations in an internal electron transfer from the CuO_2 sheets to Tl-6s state in the Tl–O monolayer as a result of the changing mean Cu–O bond length. Therefore, we have undertaken a systematic study of the nominal monolayer thallium cuprate, $TlLaBa_{1-z}Sr_zCuO_{5-x}$. It involves the synthesis of single-phase samples of $Tl_{1-y}LaBa_{1-z}Sr_zCuO_{5-x}$, wet-chemical determination of y and x before and after an anneal in O_2 atmosphere at 500°C, and determination of the changes in the superconductive onset temperature T_{on} as a function of the hole concentration p per Cu atom as determined from the chemical analysis and the assumption that all the thallium remain Tl^{3+} for all the values of z. We find that there is little or no loss of thallium during an O_2 anneal at 500°C in the monolayer thallium cuprates. We disregard the possibility of cation disorder on the cation sites (17–21) because the larger cations are not stable in the Cu sites, the amount of any Cu in the Tl–O layers is small, and any exchange of Tl with the larger cations does not influence our interpretation of the data. The assumption that all the thallium remain Tl^{3+} in the monolayer Tl systems can be tested by comparison of superconductive properties as a function of the calculated hole concentrations p per Cu atom with the evolution of these properties with p found in other high-T_c copper-oxide systems. We show that there is no evidence for a reduction of thallium from the Tl^{3+} state at any value of z, which implies that the Tl-6s states of a Tl–O monolayer remain too high in energy to accept electrons at the lowest temperature from the CuO_2 sheets even at the smallest mean Cu–O bond lengths attained with maximum Sr content.

In independent studies of the monolayer Tl systems $TlBa_{2-z}Sr_zCa_{n-1}Cu_nO_{2n+3}$, corresponding to $n = 2$ and a nominal 2.5+ Cu valence, the lattice a parameter changes from 3.833 Å for $z = 0$ (22) to 3.785 Å for $z = 2$ (14). Nevertheless, the superconductivity found in this system does not depend on the Sr content z or the mean Cu–O bond length; but it varies critically with the hole concentration p per Cu atom in the CuO_2 sheets, depending on the oxygen stochiometry (11, and the references given therein). This finding is consistent with our results for the $n = 1$ system.

EXPERIMENTAL

Nominal compositions $TlLaBa_{1-z}Sr_zCuO_5$ for $z = 0.00$, 0.25, 0.50, 0.75, and 1.0 were synthesized by heating at 860–890°C for 4–6 hr and quenching in air intimately ground, pelletized mixtures of Tl_2O_3, BaO_2, SrO, La_2O_3, and CuO wrapped in a gold foil and sealed in a silica tube 10 mm long and 15 mm wide at ambient air pressure. Subsequent annealings were done at 500°C in oxygen atmosphere for 4 hr followed by quenching in air.

X-ray powder diffraction patterns were recorded with a Philips diffractometer and silicon as the internal standard. Superconductive critical temperatures are the diamagnetic onset temperatures T_{on} obtained with a SQUID magnetometer. The thallium and oxygen contents were determined on single-phase (as determined by X-ray diffraction) samples by the wet-chemical procedures described elsewhere (4).

RESULTS

The system $Tl_{1-y}LaBa_{1-z}Sr_zCuO_5$ forms a complete solid solution over the compositional range $0 \leq z \leq 1$; the

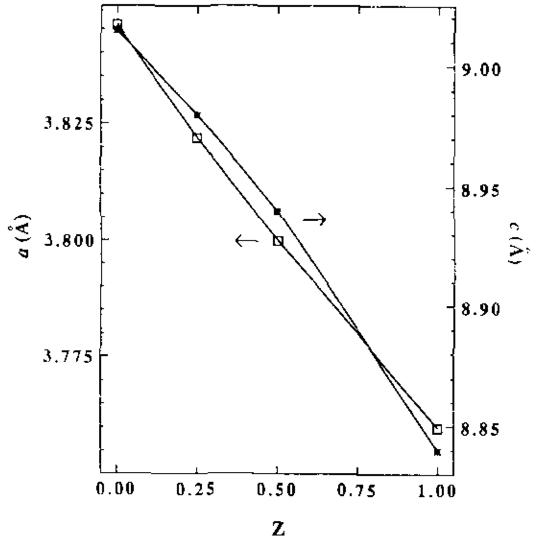

FIG. 1. Variation of unit-cell parameters a and c with z, the strontium content, for the $Tl_{1-y}LaBa_{1-z}Sr_zCuO_{5-x}$ sample.

room-temperature tetragonal ($P4/mmm$) unit cell parameters a and c decrease with z as shown in Fig. 1. The preparation of homogeneous single-phase samples was achieved by repeated grinding and heating. Any filamentary superconductivity observed in our sample was not due to the presence of either La_2CuO_4 or $La_{2-x}(Ba, Sr)_xCuO_4$ as an impurity phase; these phases were never detected in our samples.

Table 1 gives the thallium and oxygen contents determined for all samples before and after an anneal in O_2 atmosphere at 500°C; the oxidation state of the CuO_2 sheets was calculated on the basis that all the thallium is present as Tl^{3+} and is presented in Table 1 as a formal mean valence $n+$ on a copper atom, which corresponds to $p = (n - 2)$ holes per Cu atom as the oxidation of the parent $(CuO_2)^{2-}$ sheets.

The temperature dependence of the magnetic susceptibility is shown in Fig. 2 for samples 1–6 with compositions $Tl_{1-y}LaSrCuO_{5-x}$, in Fig. 3 for samples 7–12 with

TABLE 1

Chemical Analysis Data and T_{on} for the $Tl_{1-y}LaBa_{1-z}Sr_zCu_{5-x}$ System

Sample no.	Nominal composition[a,b]	Analytical data: Thallium content	Oxygen content	Cu^{n+}	T_{on} (K)
1	$TlLaSrCuO_5$	0.76	4.66	2.05	38
2	Sample 1 annealed in O_2	0.76	4.67	2.06	38
3	$TlLaSrCuO_5$	0.81	4.73	2.03	—
4	Sample 3 annealed in O_2	0.81	4.76	2.09	38
5	$TlLaSrCuO_5$	0.64	4.52	2.12	20
6	Sample 5 annealed in O_2	0.64	4.54	2.16	25
7	$TlLaBaCuO_5$	0.84	4.76	2.00	—
8	Sample 7 annealed in O_2	0.84	4.77	2.02	—
9	$TlLaBaCuO_5$	0.85	4.78	2.01	—
10	Sample 9 annealed in O_2	0.85	4.79	2.03	—
11	$TlLaBaCuO_5$	0.73	4.64	2.09	40
12	Sample 11 annealed in O_2	0.71	4.62	2.11	40
13	$TlLaBa_{0.5}Sr_{0.5}CuO_5$	0.64	4.51	2.10	30
14	Sample 13 annealed in O_2	0.64	4.53	2.14	30
15	$TlLaBa_{0.75}Sr_{0.25}CuO_5$	0.80	4.76	2.12	37
16	Sample 15 annealed in O_2	0.79	4.77	2.16	37

[a] All the compositions reported here have the tetragonal structure with space group $P4/mmm$. The variation of unit cell constants with strontium content is given in Fig. 1. The unit cell constants do not show appreciable variation for the same nominal composition with different amounts of thallium in the final product. The sample preparation procedure is described in the experimental section.

[b] O_2 annealing were all carried out at 500°C for 4 hr.

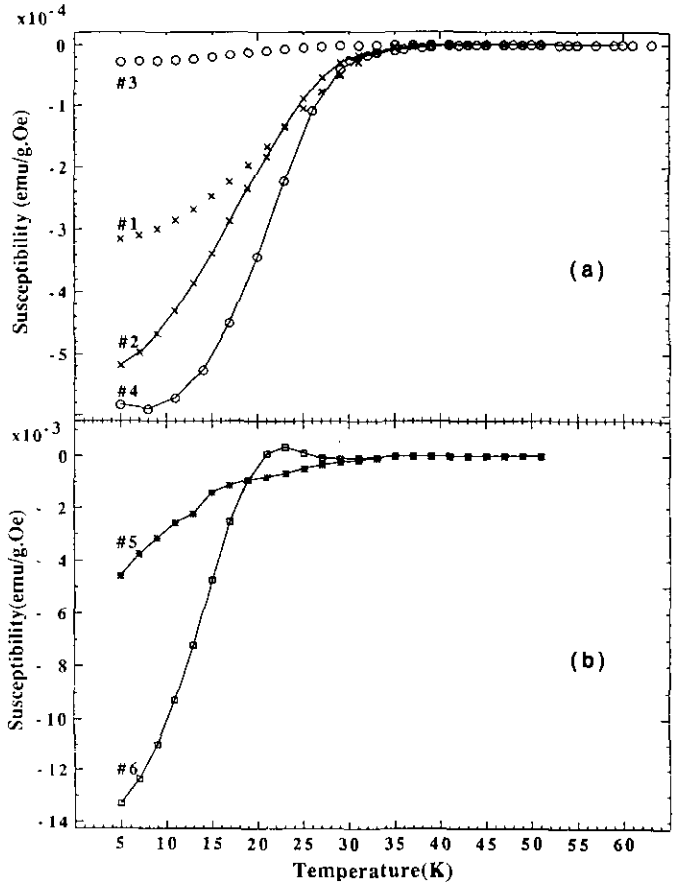

FIG. 2. Temperature dependence of magnetic susceptibility for $Tl_{1-y}LaSrCuO_{5-x}$ (numbers refer to sample numbers listed in Table 1). (a) Samples 1–4, which have diamagnetic signal intensities in the range 10^{-4} emu/g · Oe, and (b) samples 5 and 6, which have diamagnetic signal intensities in the range 10^{-3} emu/g · Oe.

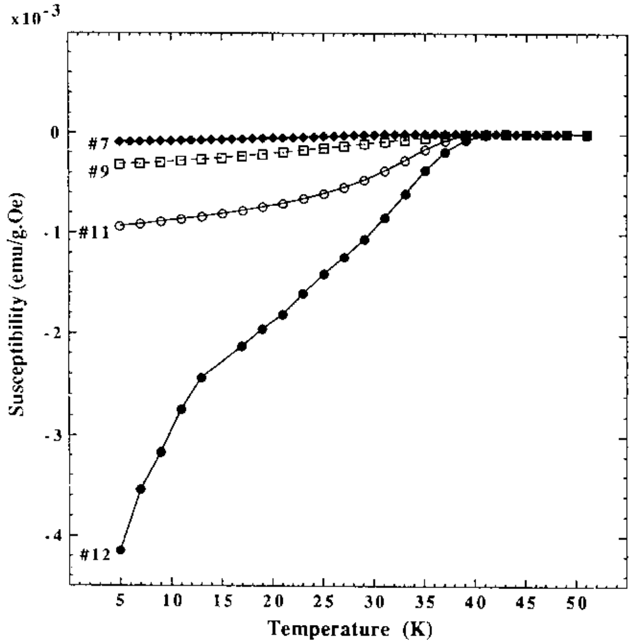

FIG. 3. Temperature dependence of magnetic susceptibility for $Tl_{1-y}LaBaCuO_{5-x}$ samples 7, 9, 11, and 12 (numbers refer to sample numbers listed in Table 1).

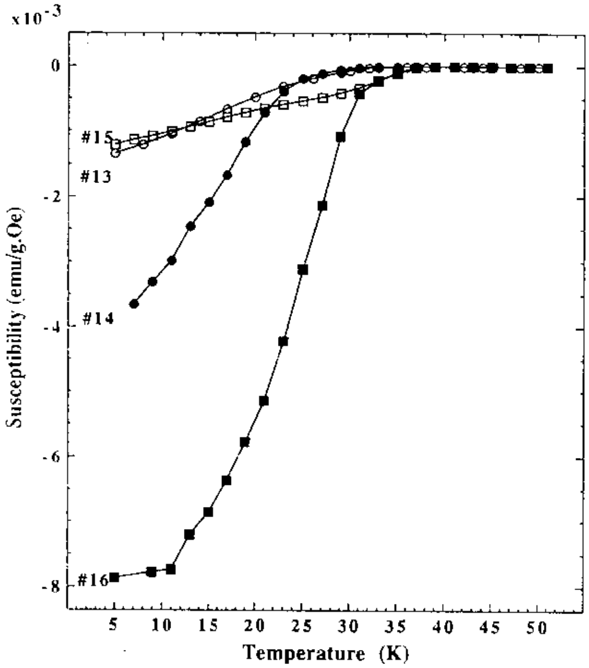

FIG. 4. Temperature dependence of magnetic susceptibility for as-prepared and oxygen-annealed samples with compositions $Tl_{1-y}LaBa_{0.5}Sr_{0.5}CuO_{5-x}$ and $Tl_{1-y}LaBa_{0.75}Sr_{0.25}CuO_{5-x}$ (numbers refer to sample numbers listed in Table 1).

compositions $Tl_{1-y}LaBaCuO_{5-x}$, and in Fig. 4 for samples 13–16 with $z = 0.50$ and 0.25.

DISCUSSION

From Table 1 and Figs. 2–4, attention is called to the following three observations:

(1) Samples with formal copper valence $n \leq 2.03$, corresponding to $p \leq 0.03$, show only a weak diamagnetic signal ($< -5 \times 10^{-5}$ emu/g · Oe) below 20 K; such a signal would be characteristic of short-range superconducting fluctuations. For such samples, the value of T_{on} is not given in Table 1. Although Manako *et al.* (15) have observed superconductivity in the system $TlLa_{1-x}Ba_{1+x}CuO_5$, we do not believe the weak diamagnetic signal found with $n \leq 0.03$ for both $z = 1$ and $z = 0$ in the system $Tl_{1-y}LaBa_{1-z}Sr_zCuO_5$ is due to an inhomogeneous distribution of La^{3+} ions. Since the weak diamagnetic signal increases with p and is not associated with any identifiable impurity phase, we believe it represents a phase segregation below room temperature typical of the type encountered in other underoxidized p-type copper oxide superconductor systems (23, and references therein). In the system $La_2CuO_{4+\delta}$ with $0 < \delta < 0.05$, for example, a static phase segregation occurs below 300 K because the interstitial oxygen atoms are mobile down to 220 K; the oxygen-rich phase ($\delta = 0.05$) is superconductive and the oxygen-poor phase ($\delta \leq 0.0$) is antiferromagnetic. In the system $La_{2-x}Sr_xCuO_4$, Seebeck data indicate a phase segregation occurring below 150 K in the range $0.02 < x < 0.10$; it is postulated to be dynamic and associated with cooperative atomic displacements that stabilize antiferromagnetic order in regions of longer mean Cu–O bond length and superconductivity in regions of shorter mean Cu–O bond length. We have not yet made Seebeck measurements on the $Tl_{1-y}LaBa_{1-z}Sr_zCuO_{5-x}$ system to determine whether a phase segregation is occurring below 300 K in the range $2.02 < n < 2.10$.

(2) Oxidation of the sample with $n < 2.03$ to $n \geq 2.05$ introduces a bulk superconductivity with a Meissner fraction that increases with n to a maximum at $n \approx 2.16$. This behavior is like that occurring in the $La_{2-x}Sr_xCuO_4$ system for $0.05 \leq x < 0.16$, which corresponds to exactly the same range of p. In the range $0.02 \leq x < 0.05$ of $La_{2-x}Sr_xCuO_4$, the superconductive regions are too small to yield a zero resistance and a bulk superconductivity, but superconductive fluctuations compete with antiferromagnetic spin fluctuations to introduce a weak diamagnetic signal.

(3) The greater the parameter y, i.e., the loss of Tl, the easier it is to oxidize the CuO_2 sheets; however, the larger the value of y, the smaller is the maximum value of

T_{on} obtained for a given value of n. For example, $Tl_{0.85}LaBaCuO_{4.78}$ (sample 9) retains an $n \leq 2.03$ even after an anneal at 500°C in O_2 atmosphere. On the other hand, as-prepared $Tl_{0.73}LaBaCuO_{4.64}$ has an $n = 2.09$ and is a bulk superconductor with $T_{on} = 40$ K (sample 11). For this sample, which has the maximum of T_{on} observed, an anneal at 500°C in O_2 atmosphere increases the Meissner fraction as n increases to 2.11. On the other hand, samples 5 and 13 with $Tl_{0.64}$, $z = 1$ and 0.5, and $n = 2.12$ and 2.10, have a sharp $T_{on} \leq 30$ K with a large Meissner fraction after an O_2 anneal at 500°C increases their respective hole concentrations to $p = 0.16$ and $p = 0.14$. The maximum T_{on} for an optimum value of p appears to decrease with decreasing Tl concentration.

(4) Whereas Subramanian and Whangbo (10) report that the system $TlLaBa_{1-z}Sr_zCuO_5$ loses its superconductivity for $z > 0.3$, we find bulk superconductivity for $z = 0.5$, 0.25, and 1.0 in our samples. Their synthetic procedure should have allowed retention of a greater concentration of thallium (smaller y), which would be consistent with a smaller value of n.

Finally, our preliminary results (24) on the Tl bilayer system $Tl_{2-y}Ba_{2-z}Sr_zCuO_{6-x}$ which formed single-phase compositions for $0.0 \leq z \leq 1.25$ show an evolution of superconductive properties with hole concentration p similar to that of the parent system with $z = 0$ (5, 25). Samples prepared in silica tubes sealed under ambient pressure and quenched into liquid nitrogen were slightly overdoped, and annealing in O_2 renders them further overdoped, which makes T_{on} decrease, whereas annealing in N_2 has the opposite effect. These results clearly contradict the speculation (8) that the variation of mean Cu–O bond length with Sr substitution for Ba is responsible for the variation in superconductive properties in this Tl bilayer system. In the Tl monolayer system the changing mean Cu–O bond length also apparently has essentially no effect on the superconductive properties.

CONCLUSIONS

Chemical analysis shows that Tl monolayer copper oxides lose varying amounts of thallium and oxygen during reaction depending upon the conditions of synthesis. Single-phase materials were obtained with up to 36% of Tl vacancies. Oxygen loss never exceeded that required to reduce the CuO_2 sheets to $(CuO_2)^{2-}$, and the greater the loss of thallium, the more difficult it is to reduce the CuO_2 sheets all the way to $(CuO_2)^{2-}$.

With the assumption that all the thallium are present as Tl^{3+} in the Tl monolayer system, the superconductive behavior as a function of hole concentration p per Cu atom in the CuO_2 sheets tracked that of the analogous $La_{2-x}Sr_xCuO_4$ system over the range $0 \leq p \leq 0.16$ found for the Tl monolayer system; this range corresponds to the underdoped to optimally doped range $0 < x \leq 0.16$ in $La_{2-x}Sr_xCuO_4$. However, no evidence was found for a suppression of T_c near $p = 1/8$ as occurs in $La_{2-x}Ba_xCuO_4$ (26). The magnitude of the maximum value of T_{on} appears to depend on the Tl concentration rather than on the value of z; a $T_{on} = 38$ K was found for $z = 1$, a $T_{on} = 40$ K for $z = 0$, and a $T_{on} = 37$ K for $z = 0.25$ provided $y < 0.30$.

Transport measurements should be able to reveal whether a phase segregation occurs below room temperature for compositions $2.02 < n < 2.10$ as in the related $La_{2-x}Sr_xCuO_4$ and $La_2CuO_{4+\delta}$ systems.

Our study shows clearly that there is no tranfer of electrons from the CuO_2 sheets to the Tl-6s band with increasing Sr content in the $Tl_{1-y}LaBa_{1-z}Sr_zCuO_{5-x}$ system, contrary to speculation in the literature (10). Whether the superconductivity occurs in the system $Tl_{1-y}LaBa_{1-z}Sr_zCuO_{5-x}$ depends on the Tl and oxygen contents and not on the Sr content.

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