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Chemistry and Superconductivity in Thallium-Based Cuprates

By

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## CHEMISTRY AND SUPERCONDUCTIVITY OF THALLIUM-BASED CUPRATES

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### 1. Introduction

Following the discoveries of high temperature superconductivity in the rare-earth copper oxide systems at  $\sim 40\text{K}$  by Bednorz and Müller in 1986[1] and at  $\sim 90\text{K}$  by other researchers[2,3] in 1987, Sheng and Hermann, in 1988, discovered superconductivity in the thallium-alkaline-earth copper oxide systems with critical temperatures as high as  $\sim 120\text{K}$ [4,5]. All of the Tl-based compounds can be described by the general formula,  $\text{Tl}_m\text{A}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+m+2}$ , where  $m=1$  or  $2$ ;  $n=1\sim 5$ ;  $\text{A}=\text{Ba}, \text{Sr}$ . For convenience, the names of these compounds are abbreviated as 2223 for  $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ , where each number denotes the number of Tl, Ba(Sr), Ca and Cu ions per formula, respectively. The compounds with  $m=1$  and  $m=2$  are usually referred to as single and double Tl-O layered compounds, respectively. The highest superconducting transition temperature known so far was found in  $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$  at  $\sim 125\text{K}$ [6,7].

The thallium-based compounds are structurally related to the rare-earth-based cuprates and present more interesting chemical and physical features. To date, about twenty-five thallium-copper oxide systems have been investigated. A summary of those studies is given in Table 1. Current investigations of these Tl-based high  $T_c$  superconducting oxides have mostly focused on the synthesis, structural and electronic properties and the correlations between the chemistry and their superconducting properties.

Unlike the rare-earth-based compounds, the Tl-based copper oxides are thermally unstable phases, and hence, are difficult to prepare as pure phases. Moreover, the thallium compounds are severely nonstoichiometric and

Table 1. Superconducting Thallium-copper-oxides and Related Systems

Compound	$T_c$ (K)	Related Systems [ $T_c$ (K)]	Ref.
$Tl_2Ba_2CuO_6$	0-90		8-14
$Tl_2Ba_2CaCu_2O_8$	110		10,11,15,16
		$Tl_2Ba_{2-x}Sr_xCaCu_2O_8$ [40-110]	17-19
		$Tl_{2-x}K_xBa_2CaCu_2O_8$ [110-130]	20
		$Tl_{2-x/3}Tl_{1-x}Ba_{1+x}LnCu_2O_8$ [0]	21
$Tl_2Ba_2Ca_2Cu_3O_{10}$	115-125		6,7,10,11,16,22,23
		$Tl_2Ba_{2-x}Sr_xCa_2Cu_3O_{10}$ [114]	19
$Tl_2Ba_2Ca_3Cu_4O_{10}$	104-110		24,25
$TlBa_2CuO_5$	metallic		10,11,26
		$TlBa_{2-x}Ln_xCuO_5$ [-40]	27
$TlBa_2CaCu_2O_7$	50-90		10,11,26,28,29
		$TlBa_2LnCu_2O_7$ [0]	30,31
		$TlSr_2(Ln,Ca)Cu_2O_7$ [60-90]	32-35
$TlBa_2Ca_2Cu_3O_9$	110-117		36,37
$TlBa_2Ca_3Cu_4O_{11}$	-120		38-41
$TlBa_2Ca_4Cu_5O_{13}$	-110		42-44
$(Tl,Bi)Sr_2CuO_5$	metallic		45
		$(Tl,Bi)Sr_{2-x}Ca_xCuO_5$ [-50]	46
$(Tl,Bi)Sr_2CaCu_2O_7$	90		47,48
$(Tl,Bi)Sr_2Ca_2Cu_3O_9$	-120		49
$(Tl,Pb)Sr_2CuO_5$	0-20		45,50
		$(Tl,Pb)-Sr-Ln-Cu-O$ [20-70]	51-54
$(Tl,Pb)Sr_2CaCu_2O_7$	80-85		55,56
$(Tl,Pb)Sr_2Ca_2Cu_3O_9$	115		55
$TlSr_2CaCu_2O_7$	100		57
		$Tl-Sr-Ca-Cu-O$ [20-100]	58-60
		$Tl-Sr-Ln-Cu-O$ [0-40]	61
phases with $n \geq 4$	110-160?		62,63

contain a considerable concentration of structural defects, which significantly affects the physical properties. The copper and thallium chemistry are particularly interesting in terms of the Cu and Tl valences and the correlations between their valences and superconductivity of Tl-based cuprate materials.

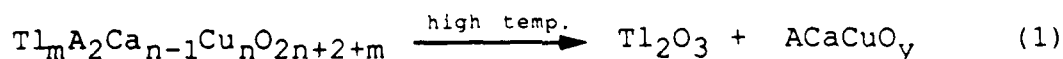
This article is intended to review the present status of the chemistry of the thallium based high  $T_c$  superconducting oxides, including their syntheses, structures, nonstoichiometries, Tl and Cu valences and their correlations with the superconducting properties. In view of the extensive studies carried out on these phases, it is not possible to include all the results in this paper.

## 2). Synthetic Chemistry of $Tl_m A_2 Ca_{n-1} Cu_n O_{2n+m+2}$

Thallium and its compounds are among the most toxic inorganic materials. Safety procedures are extremely important in the preparation of Tl-containing compounds.  $Tl_2O_3$ , which is one of the starting oxides used to prepare the high  $T_c$  superconducting thallocuprates, is highly volatile at temperatures above its melting point of  $\sim 710^\circ C$ . In preparing these high  $T_c$  superconducting oxides, prevention of thallium loss is the most important factor, not only for safety purposes, but also for maintaining the stoichiometry of the products to ensure the formation of the desired phase.

### i. Reactions in Open Systems

The thallium based high temperature superconducting compounds were first synthesized by Sheng and Hermann[4-5], by heating a Ba-Ca-Cu-O precursor oxide with  $Tl_2O_3$  powder at  $\sim 880-910^\circ C$  for  $\sim 3-5$  minutes in flowing oxygen. This technique is extremely simple, convenient and unusually quick for a solid state reaction; and it is now generally used with modifications of the reaction temperature, time and the starting chemical composition, to prepare most of the well characterized thallium based compounds[18,19,22-24,64,65]. However, this method carries some difficulties inherent in the synthesis of pure phase samples due to the volatility of the thallium component and severe decomposition of products at the high reaction temperatures as described by:



In order to prevent severe thallium loss during the reaction, samples have been wrapped in noble metal foils, such as Au, Ag, Pt. Ni foils have also been used in the synthesis of thallium-based superconductors, however, in our experience, Ni foils become highly reactive at the temperatures needed to synthesize those compounds. We have found that very thin ( $\leq 0.025$ mm thick) Au foil works better than other foils, in terms of preventing Tl loss, because it is very inert and melts slightly at the high reaction temperatures, forming a tight seal which prevents severe thallium loss.

In open reaction systems, phase transformation from a Tl-rich to a relatively Tl-poor phase was observed as a result of Tl loss. For example, starting with a 2223 stoichiometry, continuous transformations of 2201 $\rightarrow$ 2212 $\rightarrow$ 2223[65] and 2223 $\rightarrow$ 1223 $\rightarrow$ 1234[40,44,65] phases as a function of time have been observed by powder X-ray diffraction. Under controlled reaction conditions, single phase samples can be obtained.

### ii. Reactions in Closed Systems

Thallium-copper oxide samples can also be prepared using a completely sealed reaction system, which was developed by researchers at DuPont[7,15,36]. In this method, starting materials are sealed into a gold tube and heated at  $\sim 900^\circ\text{C}$  for a period of 0.5-3 hours; both pure powder samples and single crystals can be prepared, since a much longer reaction time may be used under closed reaction conditions. This technique is, in our experience, the best way to reproducibly prepare pure phase samples with nearly the desired stoichiometry. Silver tubes have also been used successfully as a less expensive substitute for gold tubes.

Sealed quartz tubes[6,10,11,26,66-68] or autoclave-like inert metal containers[69] have also been employed for the preparation of Tl-based compounds. However, the quartz tube can be severely attacked by the thallium oxide vapor, resulting in deviation from the desired stoichiometry. In addition, there is always a danger of explosion at high temperatures due to the high vapor pressure of thallium oxides in the quartz tube. Special precautions should be taken when using this route. Preparing materials in an autoclave, in principle, should work as well as the sealed-gold tube technique, however, in conventional autoclaves, the sealing does not hold at the reaction temperatures used ( $840\sim 930^\circ\text{C}$ ), resulting in deviations from the stoichiometry. The advantage of using quartz tubes is obvious when vacuum conditions are required.

Using the above techniques,  $\text{Tl}_2\text{Ba}_2\text{CuO}_6$ [8-14],  $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$ [10,11,15,16] and  $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ [7,10,11,16] (2201, 2212 and 2223, respectively),  $(\text{Tl,Pb})\text{Sr}_2\text{CaCu}_2\text{O}_7$ [55,56], and  $(\text{Tl,Pb})\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_9$ [55] have been successfully prepared in both bulk pure powder and single crystal forms.  $\text{TlBa}_2\text{Ca}_2\text{Cu}_3\text{O}_9$  (1223) single crystals have also been grown by the sealed-gold tube technique[36]. Although single crystal growth of  $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$  and  $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$  were reported using an open reaction system[70] with excess CaO and CuO, it is very difficult to reproducibly obtain good quality single crystals this way.

### iii. Synthetic Chemistry

All of the members of  $\text{Tl}_m\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+m+2}$  are thermally unstable. At  $\sim 820^\circ\text{C}$ , they begin to form at a relatively rapid rate, but decomposition occurs

almost simultaneously (decomposition can take place slowly even at 750°C). At approximately 880-900°C, the compounds melt incongruently, according to equation (1). If an open reaction system is used, thallium loss in this temperature region is severe and irreversible. The ideal temperature region, in our experience, for the preparation of single phase samples is ~840-870°C for 1-6 hours, regardless of the nature of starting materials and the composition of products.

The single Tl-O layered compounds are much less stable than the double layered counterparts, and therefore, the preparation of pure single Tl-O layered compounds is extremely difficult. Although, the existence of  $\text{TlBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+3}$  with  $n$  up to 5 has been observed [10,11,26,62,63,71-75] by means of high resolution electron microscopy, none of the compounds has been prepared in pure powder form. The exception is  $\text{TlSr}_2\text{CaCu}_2\text{O}_7$  [57], which was prepared by a hot press technique from a nonstoichiometric starting composition. However, single phase analogues of these unstable compounds can be prepared by partial substitutions of Tl by Bi or Pb, or Ca by rare-earth elements, forming  $(\text{Tl,Bi,Pb})\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{4n+1}$  ( $n=1, 2$  and  $3$ ) [45-56] and  $\text{TlBa}_2(\text{Ca}_{1-x}\text{Ln}_x)_{n-1}\text{Cu}_n\text{O}_{4n+1}$  ( $0.0 \leq x \leq 1.0$ ;  $n=1$  and  $2$ ) [30-35]. The reason for the instability of the single Tl-O layered compounds is probably due to the high formal valence (much higher than 2+) of copper in these compounds. The existence of strontium analogues in the  $\text{Tl}_2\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4}$  family has not been reported; although there is evidence of  $\text{Tl}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$  in a mixed phase sample [17].

Another way to prevent severe loss of Tl is by the use of Tl-containing precursor oxides [14,45,47]. Unlike the Ba-Ca-Cu-O precursors, which have to be prepared at high temperatures prior to the reaction with  $\text{Tl}_2\text{O}_3$ , the Tl-containing precursors can be prepared by preheating all of the starting oxides at ~580-600°C for 1-2 hours. CuO does not react with the other components at such low temperatures. The Tl-containing precursor oxides observed include  $\text{Ba}_2\text{Tl}_2\text{O}_5$ ,  $\text{Sr}_4\text{Tl}_2\text{O}_7$  and an unidentified Ca-Tl-O phase, all of which are relatively less volatile than  $\text{Tl}_2\text{O}_3$  at the high reaction temperatures.

Most preparations of Tl-based cuprates are carried out in pure oxygen atmosphere. However, post-annealing of samples in controlled atmosphere has been reported to be an important factor for the preparation of pure phase samples and the enhancement of the superconducting properties for some of the Tl-based cuprates [14,68,69,76]. For example, the preparation of the superconducting  $\text{Tl}_2\text{Ba}_2\text{CuO}_6$  phase ( $T_c \sim 80-90\text{K}$ ), which has a tetragonal crystal symmetry, requires an oxygen-poor atmosphere or fast quenching in air from the reaction temperature (~820-850°C) to room temperature [14]. If the sample of 2201 is prepared in pure oxygen atmosphere or in a closed reaction system, the product has an orthorhombic symmetry and either lower  $T_c$  (~20K) or metallic behavior [10-14]. The nonsuperconducting (or low  $T_c$ ) phase can be converted into a superconducting phase (or with enhanced  $T_c$ ), by post-annealing the sample in an inert atmosphere at ~300°C [14]. This transformation is

accompanied by an orthorhombic to tetragonal phase transition, which is believed to be related to the oxygen content and/or ordering in  $Tl_2Ba_2CuO_6$  and is critical in determining the superconducting properties. The effects of controlled atmosphere on the superconductivity of Tl-based cuprates were also found in other systems, such as in the 2223 and will be discussed later in detail.

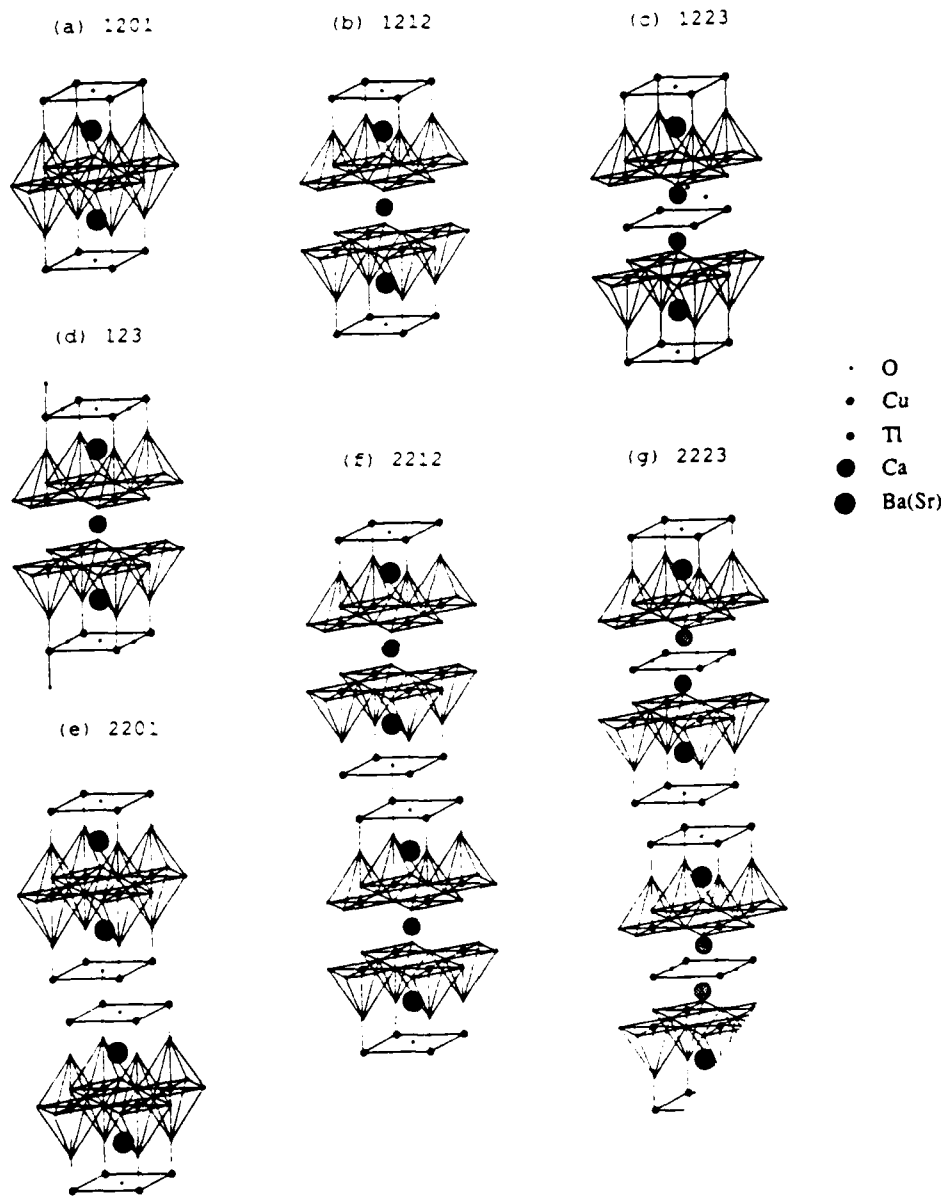


Figure 1. Schematic presentation of crystal structures of 1201, 1212, 1223, 123, 2201, 2212 and 2223.

### 3. The Structural Properties of $Tl_m A_2 A'_{n-1} Cu_n O_{2n+m+2}$

#### i. Basic Structural Properties

Characterization of the new thallium copper oxides were carried out by single crystal X-ray diffraction, Rietveld analysis of powder neutron/X-ray diffraction, electron diffraction and high resolution electron microscopy. The structures of  $Tl_2 Ba_2 Ca_{n-1} Cu_n O_{2n+4}$  phases ( $n=1, 2,$  and  $3$ )[7-9,15,16],  $(Tl,Pb)Sr_2 Ca_{n-1} Cu_n O_{4n+1}$  ( $n=2$  and  $3$ )[55,56] and  $TlBa_2 Ca_2 Cu_3 O_9$ [36] have been well established by single crystal X-ray and/or powder neutron diffraction analyses. Figure 1 illustrates schematically the crystal structures of these compounds. The structure of  $YBa_2 Cu_3 O_7$  (denoted as 123) is shown for comparison. Figure 2 shows the powder X-ray diffraction patterns of pure 1201, 1212, 2201, 2212 and 2223 phases prepared in our laboratory[14,45,47,77]. The structures of the other members of this family were characterized only by high resolution electron microscopy, powder X-ray analysis and electron diffraction techniques, especially for the phases with  $m=1$  or  $n>4$ [62,63,71-75] (also see Table 2). High resolution electron microscopy studies have shown that the phases with  $n\geq 4$  consist of intergrowths of the phases with  $n\leq 3$ , and exist only in microscopic regions of the samples[73].

In general, the Tl-based superconducting oxides can be considered to form oxygen deficient perovskite or Aurivillius related structures. The unit cell is made up of alternating arrays of one to  $n$  Cu-O corner-sharing square-planar and/or square-pyramidal layer(s) and one single or double edge-sharing Tl-O octahedral layer. The Cu-O and Tl-O polyhedra are interconnected to form covalent framework slabs; the A cations are located in the interstices of Tl-O and Cu-O slabs and the  $Ca^{2+}$  ions are between the Cu-O layers (Figure 1). The oxygen coordination number of Tl is 6, of Cu is 4 or 5, of Ca is 8, and of A is 9 in the double and 12 in the single Tl-O layered compounds. In all of these compounds, the Tl-O bond length is  $\sim 2.0\text{\AA}$  along the 001 and  $\sim 2.5-3.0\text{\AA}$  along the 110 direction; the Cu-O bond length is  $\sim 1.90-1.92\text{\AA}$  in the  $ab$  plane; the distance of adjacent Cu-O layers is  $\sim 3.1-3.2\text{\AA}$ . The apical Cu-O distance is  $\sim 2.7\text{\AA}$  in  $Tl_m Ba_2 Ca_{n-1} Cu_n O_{2n+4}$  and  $\sim 2.3\text{\AA}$  in  $(Tl,M)Sr_2 Ca_{n-1} Cu_n O_{2n+3}$  ( $M=Pb$  or  $Bi$ ). The Cu-O-Cu bond angle is close to  $180^\circ$  in all the structurally characterized phases, indicating that the Cu-O layer is almost ideally planar.

Table 2 summarizes the lattice parameters of the known thallium copper oxides. Tetragonal symmetry was found to be common in all of these compounds, as determined by X-ray and neutron diffraction. However, there are some uncertainties about the oxygen or thallium positions in the structure. In the double Tl-O compounds, the oxygen atom in the basal plane of the Tl-O layer can be refined only at the  $16(n)$  position of space group  $I4/mmm$  with  $1/4$  occupancy, instead of the ideal, fully occupied  $4(e)$  site[7-9,15]. In the single Tl-O layer compounds, the oxygen refines best at  $4(n)$ , not the ideal  $2(g)$  position; and Tl must be placed at a position slightly deviating from the ideal  $4(l)$  site[55]. The displacements of the oxygen and thallium atoms from their ideal locations, in

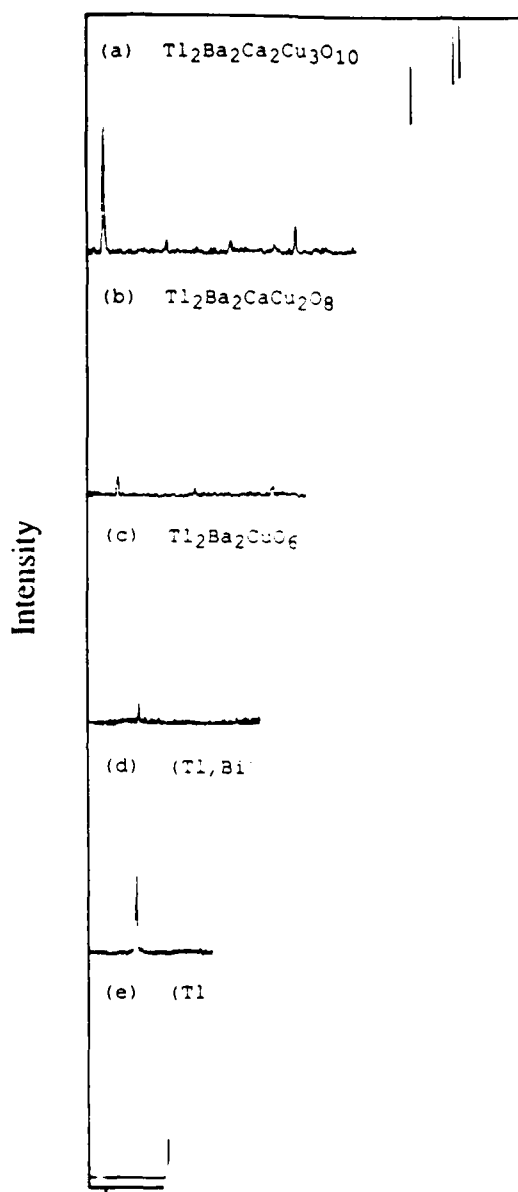


Figure 2. Powder X-ray diffraction patterns of *a.*  $Tl_2Ba_2Ca_2Cu_3O_{10}$ , *b.*  $Tl_2Ba_2CaCu_2O_8$ , *c.*  $Tl_2Ba_2CuO_6$  (tetragonal), *d.*  $(Tl,Bi)Sr_2CaCu_2O_7$ , and *e.*  $(Tl,Bi)Sr_2CuO_6$ .

Table 2. Lattice parameters of thallium copper oxides

Compound	a(Å)	b(Å)	c(Å)	SG	Refs.
Tl <sub>2</sub> Ba <sub>2</sub> CuO <sub>6</sub> (ortho)	5.4967(3)	5.4651(3)	23.2461(1)	Abma <sup>‡</sup>	9
Tl <sub>2</sub> Ba <sub>2</sub> CuO <sub>6</sub> (tetra)	3.866(1)		23.239(6)	I4/mmm <sup>†</sup>	8
Tl <sub>2</sub> Ba <sub>2</sub> CaCu <sub>2</sub> O <sub>8</sub>	3.8550(6)		29.318(4)	I4/mmm <sup>†</sup>	15
	3.8559(1)		29.4199(10)	I4/mmm <sup>‡</sup>	16
Tl <sub>2</sub> Ba <sub>2</sub> Ca <sub>2</sub> Cu <sub>3</sub> O <sub>10</sub>	3.8503(6)		35.88(3)	I4/mmm <sup>†</sup>	7
	3.8487(1)		35.6620(15)	I4/mmm <sup>‡</sup>	16
Tl <sub>2</sub> Ba <sub>2</sub> Ca <sub>3</sub> Cu <sub>4</sub> O <sub>12</sub>	3.854(1)		42.070(11)	I4/mmm <sup>†</sup>	24
TlBa <sub>2</sub> CuO <sub>5</sub>	3.896(2)		9.694(9)	P4/mmm <sup>†</sup>	10,26
TlBa <sub>2</sub> CaCu <sub>2</sub> O <sub>7</sub>	3.8505(7)		12.728(2)	P4/mmm <sup>†</sup>	10,11
TlBa <sub>2</sub> Ca <sub>2</sub> Cu <sub>3</sub> O <sub>9</sub>	3.8429(6)		15.871(3)	P4/mmm <sup>†</sup>	10,37
TlBa <sub>2</sub> Ca <sub>3</sub> Cu <sub>4</sub> O <sub>11</sub>	3.85		18.73	P4/mmm <sup>†</sup>	41
TlSr <sub>2</sub> CaCu <sub>2</sub> O <sub>7</sub>	3.805(6)		12.14(6)	P4/mmm <sup>†</sup>	57
(Tl,Bi)Sr <sub>2</sub> CuO <sub>5</sub>	3.759(1)		9.01(1)	P4/mmm <sup>†</sup>	45
(Tl,Bi)Sr <sub>2</sub> CaCu <sub>2</sub> O <sub>7</sub>	3.796(1)		12.113(1)	P4/mmm <sup>†</sup>	47,48
(Tl,Pb)Sr <sub>2</sub> CuO <sub>5</sub>	3.731(1)		9.01(1)	P4/mmm <sup>†</sup>	45
(Tl,Pb)Sr <sub>2</sub> CaCu <sub>2</sub> O <sub>7</sub>	3.80		12.05	P4/mmm <sup>†</sup>	55
(Tl,Pb)Sr <sub>2</sub> Ca <sub>2</sub> Cu <sub>3</sub> O <sub>9</sub>	3.808		15.232	P4/mmm <sup>†</sup>	55
phases with n≥4	3.80~3.85		*	?	38,39

†: Single crystal X-ray diffraction data

‡: Powder X-ray diffraction data

‡: Neutron diffraction data

\*: The *c* lattice parameters can be estimated by formulae  $c = 23.2 + 6.4(n-1)$  for the *m*=2 phases;  $c = 9.6 + 3.2(n-1)$  for the *m*=1, A=Ba phases; and  $c = 9.0 + 3.1(n-1)$  for the *m*=1 A=Sr phases. The structural symmetry is suggested to be tetragonal.

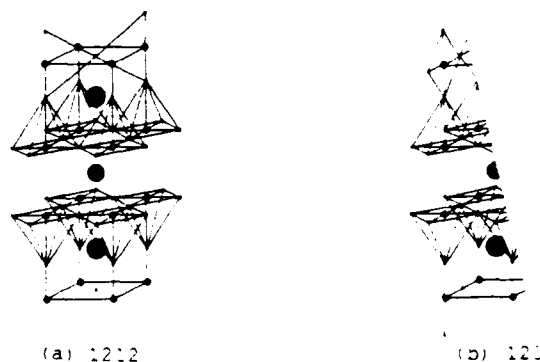


Figure 3. Structure of 1212(a), considering oxygen ordering in the Tl-O basal plane. A Tl-O chain is shown and compared with the Cu-O chain in the 123 structure(b).

all of the Tl-based cuprates, result in the formation of four different Tl-O bonds in the basal plane and severely distorted Tl-O octahedra. It is assumed that the  $16(n)$  oxygens in the double layered compounds and the Tl atoms in the single layered compounds are randomly distributed around the ideal sites of the tetragonal lattice. Ordering of these atoms will lead to the formation of a local Tl-O chain, as shown in Figure 3, and a concomitant change in the structural symmetry and/or formation of a superlattice. However, both X-ray and neutron diffraction studies lack conclusive evidence for oxygen ordering in  $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$  and  $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ [16].

### ii. Local Structural Distortions and Cation Deficiencies

High resolution electron microscopy and electron diffraction techniques have been used to investigate the local structural properties of Tl-based superconductors. Reports of structural modulations, similar to those found in the Bi-based high  $T_c$  superconducting oxides, have not been unambiguously confirmed[78-84]. The origin of such modulations and their correlations with the physical properties are not well understood. It has been suggested that the modulated structure is due to the local ordering of cation defects or oxygen atoms in the Tl-O basal plane[84,86]. However, these effects are not reproducible, and the presence of the modulations is dependent upon the sample exposure to the electron beam[81-84].

Consistent with X-ray and neutron diffraction results, high resolution electron microscopy and microprobe chemical analysis show significant Tl and Ca deficiencies in most of the thallium copper oxides[67,85,86]. The amounts of Tl/Ca deficiencies depend on the preparation conditions and the type of structure. In general, the deficiencies tend to increase with more Cu-O layers in the structure[87]. Hibble et al. reported that in  $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$  and  $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ , the deficiencies are 12%Tl/30%Ca and 8.5%Tl/28%Ca, respectively. No Tl/Ca deficiencies were observed in  $\text{TlBa}_2\text{Ca}_2\text{Cu}_3\text{O}_9$ [85]. However, in these studies, barium and copper deficiencies were not observed. The Tl/Ca deficiencies cause deviations from the ideal stoichiometry and are likely to have significant effects on the superconducting properties of these compounds. Partial occupancies of Tl and Ca on each other's sites have also been observed by the X-ray and neutron diffraction analyses [7,15,16,55]. Nominally, 50 percent of Tl could be substituted by Ca in 2223[88].

### iii. Structural Phase Transition

All of the Tl-based cuprates crystallize with tetragonal symmetry, except  $\text{Tl}_2\text{Ba}_2\text{CuO}_6$ , which exists in both tetragonal and orthorhombic form, depending on the preparation condition and/or the post annealing treatment. Ramanujachary *et al.*[14] reported a reversible structural phase transition under controlled atmosphere at  $\sim 300^\circ\text{C}$  by high temperature X-ray diffraction techniques. A small but measurable oxygen loss was observed, by both DTA and

TGA analysis (Figure 4), accompanying the phase transition from orthorhombic to tetragonal symmetry. Figure 5 illustrates the X-ray powder diffraction peak profiles of the 200/020 reflection of the tetragonal phase as a function of temperature when the tetragonal sample is heated in oxygen. As the temperature exceeds 300°C, the reflection splits into a doublet, which clearly indicates the tetragonal-orthorhombic transition. The oxygen-rich phase is orthorhombic with lower  $T_c$  (or only metallic if the samples are prepared in the closed reaction system), while the oxygen-poor phase is tetragonal with high  $T_c$  (55-85K). Although the difference in the oxygen content of these two phases is small, estimated at  $<0.1$  oxygen atom per formula unit, it appears to be a very important factor in determining the superconducting and structural properties of 2201. Oxygen ordering may also be important in effecting the physical properties of this compound. The correlation between superconductivity and preparation conditions of the 2201 phase is well illustrated in Figure 6.

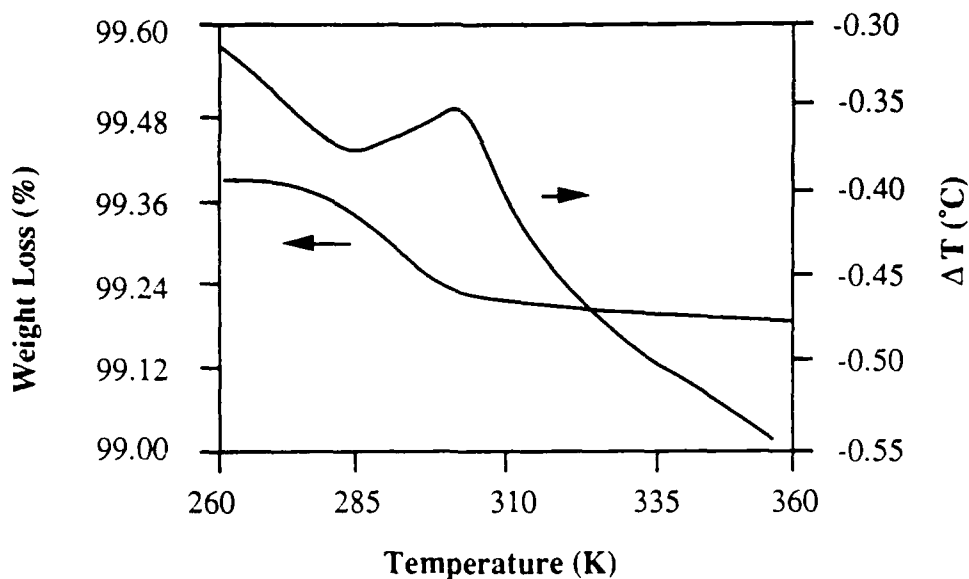


Figure 4. TGA(left) and DTA(right) profiles of a 2201 sample heated in Ar atmosphere.

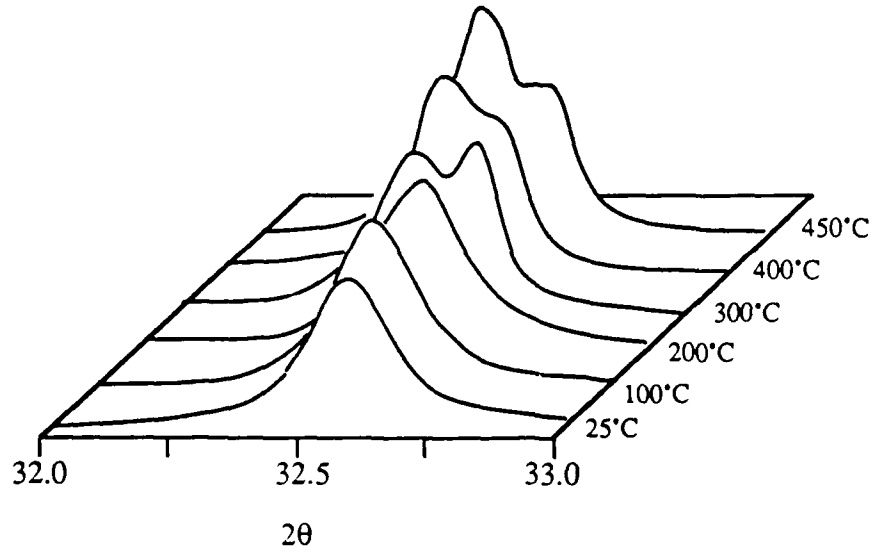


Figure 5. Peak profiles of 200/020 reflection of a tetragonal 2201 sample when heated in oxygen atmosphere at various temperatures.

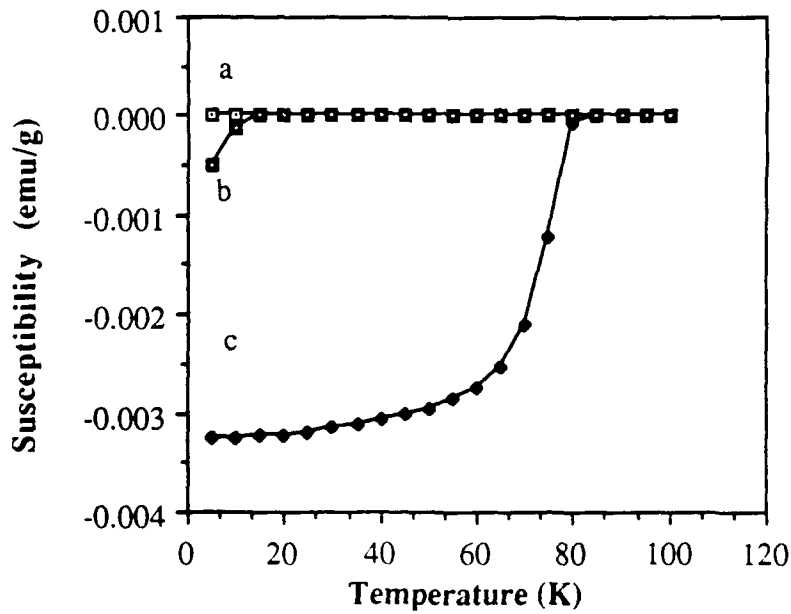


Figure 6. Superconductivity of 2201 samples prepared at different conditions. *a.* prepared in closed reaction system, which is orthorhombic and metallic, *b.* furnace cooled in air, which is orthorhombic with  $T_C \sim 20\text{K}$ , and *c.* quenched in air to room temperature, which is tetragonal and  $T_C$  is  $\sim 85\text{K}$ .

The structural difference between the orthorhombic and tetragonal phases is attributed to differences in the local symmetry around the thallium atoms. According to crystallographic studies[8,9], in the orthorhombic form of 2201, the deviation from the tetragonal symmetry is essentially restricted in the Tl-O layers. The oxygen coordination of Tl in the orthorhombic form of 2201 is nearly a square-pyramid[9]. Bordet et al. noted differences in the superlattice structure of these two phases by means of electron diffraction: the superlattice correlation length in the orthorhombic phase is much larger than that in the tetragonal phase[80]. It was suggested that the tetragonal-orthorhombic phase transition is related not only to the oxygen content, but also to the oxygen ordering in the Tl-O basal plane[14].

#### *iv. Nonstoichiometry of Oxygen*

The importance of oxygen nonstoichiometry in Tl-based cuprates has been reported in several studies[14,68,69,76]. However, there is no general consensus on how the oxygen nonstoichiometry affects the superconductivity. Hervieu et al.[68] and Ramanujachary et al.[14] reported that argon annealing of 1212 and 2201 samples enhances the  $T_C$ , while other investigators found that oxygen annealing can improve the superconducting properties of 2223 and that heat treatment in an inert atmosphere is detrimental to superconductivity[69,76]. These results imply that the effects of oxygen nonstoichiometry on superconductivity might be different in different compounds, depending upon the structure, oxygen content/ordering and other nonstoichiometric factors.

The presence of excess oxygen in all of the Tl-based compounds seems questionable, because wherever excess oxygen is presumed to be in the lattice, unacceptably short metal-oxygen bonds appear to form. Neutron diffraction studies[16] showed that oxygen deficiencies are possible in the 2223 phase and are most likely to be located in the Tl-O basal plane, which is disordered in the tetragonal lattice.

The effects of oxygen nonstoichiometry were observed in only a few phases, most profoundly in the 2201 and 2223 systems. Figure 7 shows the effects of the cooling and the post-annealing conditions on the superconductivity of 2201 samples. These effects are related to the oxygen content in the structure as mentioned earlier. In contrast, when a 2223 sample is annealed in Ar atmosphere at low temperatures, the  $T_C$  is depressed; and an oxygen post-annealing will restore the  $T_C$  back to  $\sim 120\text{K}$ [76]. In 2212, oxygen/Ar annealing at temperatures between 250-450°C has no significant effect on  $T_C$ .

Due to the complexity of the thallium-copper systems, the oxygen content of these compounds has not been directly determined by chemical methods. Schilling et al. reported[69] a qualitative evaluation on the correlation between the oxygen content and the superconducting transition temperature, using TG

measurements, but the exact oxygen content in the samples could not be determined from the study.

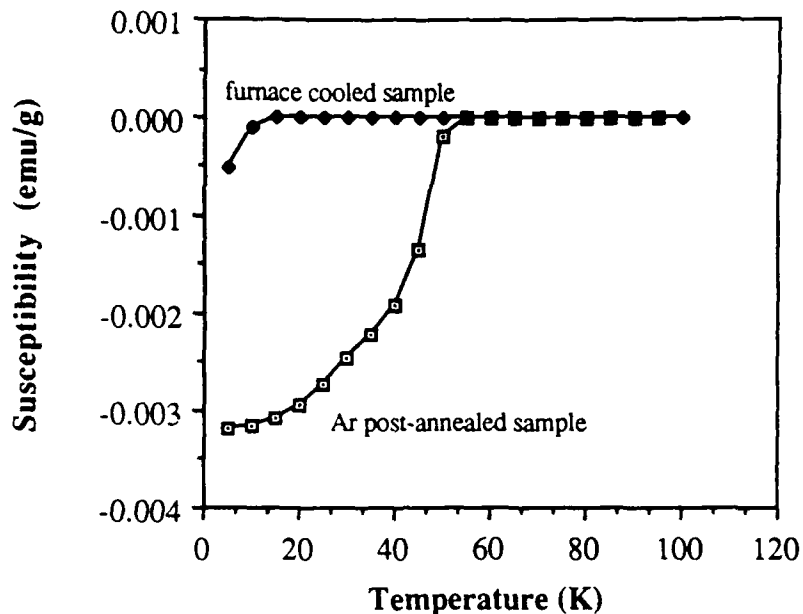


Figure 7. Enhancement of  $T_c$  by Ar post-annealing of a 2201 orthorhombic low  $T_c$  sample.

#### 4. Formal Oxidation States of Copper and Thallium

The formal oxidation states of copper and thallium are by far the most interesting features of the thallium-copper oxide superconductors. In the high  $T_c$  superconducting cuprate materials (except in the newly found electron-doped cuprate superconductors [89,90]), the existence of  $\text{Cu}^{2+\delta}$  ( $\delta$  is equivalent to the hole concentration in the compound) has been considered to be a critical factor for superconductivity. One of the central issues concerning the Tl-based cuprate superconductors is how  $\text{Cu}^{2+\delta}$  is generated in these compounds and how it is correlated with superconductivity.

In  $\text{TlBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+3}$ , (assuming  $\text{Tl}^{3+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Ca}^{2+}$  and  $\text{O}^{2-}$ ), the valence of the copper cation is  $(2+1/n)^+$ , as calculated from the ideal stoichiometry, and varies with the number of Cu-O layers in the structure. However, for the ideal stoichiometry of  $\text{Tl}_2\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4}$ , the copper valence is  $2+$  for all the members of this family. The origin of  $\text{Cu}^{2+\delta}$  in  $\text{Tl}_2\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4}$  has been attributed to the following: *a.* the Tl/Ca deficiencies in the structure; *b.* partial

occupancy of Ca on the Tl sites; *c.* the internal redox reaction  $Tl^{3+} + Cu^{2+} \longrightarrow Tl^{3-\delta} + Cu^{2+\delta}$  (details will be discussed in later sections); and *d.* possibly, although not proven, excess oxygen in the structure (like in the Bi-based high  $T_c$  materials).

The crystallographic data[7,8,15,36,55,61] show that in the Tl-O octahedra, there are two very short Tl-O bonds( $\sim 2.0\text{\AA}$ ) along the *c* crystallographic direction; two nearly regular ( $\sim 2.5\text{\AA}$ ) and two extremely long Tl-O bonds( $3.0\text{\AA}$ ) in the basal plane. Compared with known  $Tl^{3+}$ -O and  $Tl^{1+}$ -O bond distances( $\sim 2.4\text{\AA}$  and  $\sim 3.0\text{\AA}$ , respectively), the formal valence of Tl in these materials appears to be between 3+ and 1+ and/or corresponds to a very anisotropic electronic charge distribution on the Tl cation. XPS results indicate[91-93] that the effective charge on the Tl cations could be less than 3+ in several Tl-based cuprates. These results suggest mixed valency of Tl, which is consistent with the band structure calculations and the crystallographic data.

Table 3. Calculated Copper and Thallium Valences in Selected Compounds

Valence & $T_c$	Compounds					
	1201 <sup>*</sup>	1223 <sup>†</sup>	1223 <sup>‡</sup>	2201	2212	2223
$V_{Tl-O1}$	0.67	0.83	0.97	1.02	1.05	1.19
$V_{Tl}$	2.09	2.35	3.10	2.65	2.60	2.86
$V_{Cu}$	2.76	2.07	2.29	2.07	2.07	2.08
$T_c$ (K)	0-40	110	120	80-90	110	125
Reference	61	55	36	8	15	7

‡:  $(Tl,Pb)Sr_2Ca_2Cu_3O_9$

†:  $TlBa_2Ca_2Cu_3O_9$

\*:  $TlSr_{2-x}Pr_xCuO_5$

Others are Tl-Ba-Ca-Cu-O phases.

Calculations are based on the equation  $V = \sum(d/d_0)^{-N}$ .  $d_0$  and  $N$  values for both  $Tl^{3+}$  and  $Cu^{2+}$  are from ref. 94. Bond distances,  $d$ , are from the corresponding references.

The valences of copper and thallium ions can be estimated using the relationship between bond-order and bond-length in oxide materials[94]. Selected values calculated from the crystallographic data are tabulated in Table 3, together with the superconducting transition temperature of each compound. It is seen that the valence of Tl is less than 3 (less than 3.5 at the Tl

site for the  $(\text{Tl}_{0.5}\text{Pb}_{0.5})\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_9$ ) and that the copper valence is greater than 2 in all of the selected compounds. In addition, the copper valences are much higher in the single Tl-O layered compounds than those in the double Tl-O layered compounds. It is interesting to note that the superconducting transition temperatures of these compounds are related to the Tl-O<sub>1</sub> (the Tl-O bond along the *c* crystallographic direction) bond order. In both single and double Tl-O layered compounds,  $T_c$  increases with increasing Tl-O<sub>1</sub> bond order. Since the Tl-O<sub>1</sub> bonds are connected to the Cu-O layer(s) where the holes are presumably located, the correlation between the Tl-O<sub>1</sub> bond order and the  $T_c$  may imply that the internal electronic communication between the Tl-O and Cu-O layers is an important factor in effecting superconductivity in the Tl-based cuprates.

### 5. Substitutional Studies

Substitutional studies have been carried out in all of the known Tl-based cuprate phases, in part, to explore new superconducting oxides in the Tl-related system, and in part, to understand the relationship between the chemistry of these oxides and superconductivity. The major focus of substitutional studies has been to manipulate the formal oxidation states of copper and thallium, alternatively, to vary the concentration of holes by chemical substitution. Because of the complexity and thermal instability of Tl-based compounds, cationic substitution often leads to mixed phase products. In the single Tl-O layered compounds, substitutions at the Tl site by Bi or Pb appears to stabilize the phases via reducing the formal copper valence, and hence, have been studied more extensively than the double Tl-O layered compounds.

#### i. Substitutions in the $\text{TlA}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+3}$ Family ( $A=\text{Ba}, \text{Sr}$ )

As previously discussed, in the ideally stoichiometric  $\text{TlBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+3}$  ( $n=1, 2$  and  $3$ ), the formal copper valence is always higher than  $2+$ , while in  $\text{Tl}_2\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4}$ , it is always  $2+$ . The copper valence in  $\text{TlBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+3}$  is nominally  $3.0+$  for  $n=1$ ,  $2.50+$  for  $n=2$  and  $2.33+$  for the  $n=3$  phase respectively. The high copper valence may be one of the reasons for the structural instability observed in the single Tl-O layered compounds. With the exception of single crystal  $\text{TlBa}_2\text{Ca}_2\text{Cu}_3\text{O}_9$ [36], pure phase powder materials have not been obtained for  $\text{TlA}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+3}$  family without substitution. The  $\text{TlA}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+3}$  system is an ideal system for studying the correlations between the copper valence/hole concentration and superconductivity, provided that pure phase samples can be obtained. Replacement of  $\text{Tl}^{3+}$  by  $\text{Pb}^{4+}/\text{Pb}^{2+}$ , or  $\text{Bi}^{5+}/\text{Bi}^{3+}$ , or  $\text{Ca}^{2+}$  by  $\text{Ln}^{3+}$  ( $\text{Ln}=\text{rare-earth elements}$ ) would be expected to reduce the copper valence with concomitant stabilization of the structure.

$\text{Tl}^{3+}$ ,  $\text{Pb}^{4+}$  and  $\text{Bi}^{5+}$  have identical electronic configuration and similar chemistry. Substitutions of Tl by Bi and Pb in the Tl-Sr-Ca-Cu-O systems were

carried out very successfully.  $(\text{Tl,Bi})\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+3}$  ( $n=1$  and  $2$ )[45,47,48] and  $(\text{Tl,Pb})\text{Sr}_2\text{CuO}_5$ [45] were prepared as pure polycrystalline phases, and  $(\text{Tl,Pb})\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4}$  ( $n=2$  and  $3$ )[55] in both powder and single crystal forms. In the substituted  $(\text{Tl,M})\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+3}$  ( $M=\text{Pb}$  or  $\text{Bi}$ ) compounds, the  $\text{Tl/Pb(Bi)}$  ratio is close to 1.0. No solid solution region was reported in the  $(\text{Tl,M})\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+3}$  phases, except in nonsuperconducting  $\text{Tl}_{1-x}\text{Bi}_x\text{Sr}_2\text{CuO}_5$ [45], where  $0.0 < x \leq 0.50$ .

The Pb and Bi valences are of interest in the  $(\text{Tl,Pb(Bi)})\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+3}$  series. There is no direct method available to determine the formal valence of Bi and Pb in these compounds. The existence of  $\text{Bi}^{3+\delta}$  is apparent in  $\text{Tl}_{1-x}\text{Bi}_x\text{Sr}_2\text{CuO}_5$  by a careful analysis of lattice parameters as a function of  $x$ . As shown in Figure 8, the lattice parameters of  $\text{Tl}_{1-x}\text{Bi}_x\text{Sr}_2\text{CuO}_5$  decrease in the region  $0.0 \leq x \leq 0.20$ , and then increase with  $x$  in the region  $0.20 < x \leq 0.50$ . The initial decrease of the lattice parameter  $a$  is attributed to the substitution of  $\text{Tl}^{3+}$  by  $\text{Bi}^{3+\delta}$ , while the increase is due to the substitution of  $\text{Tl}^{3+}$  by  $\text{Bi}^{3+}$  since both  $\text{Bi}^{5+}$  and  $\text{Tl}^{3+}$  are smaller than  $\text{Bi}^{3+}$  ( $r_{\text{Bi}^{3+}}=1.17\text{\AA}$ ,  $r_{\text{Bi}^{5+}}=0.90\text{\AA}$  and  $r_{\text{Tl}^{3+}}=1.03\text{\AA}$  for  $\text{CN}=6$ ). Therefore, in the region  $0.20 \leq x \leq 0.50$ ,  $\text{Bi}^{3+\delta}$  and  $\text{Bi}^{3+}$  are likely to coexist.

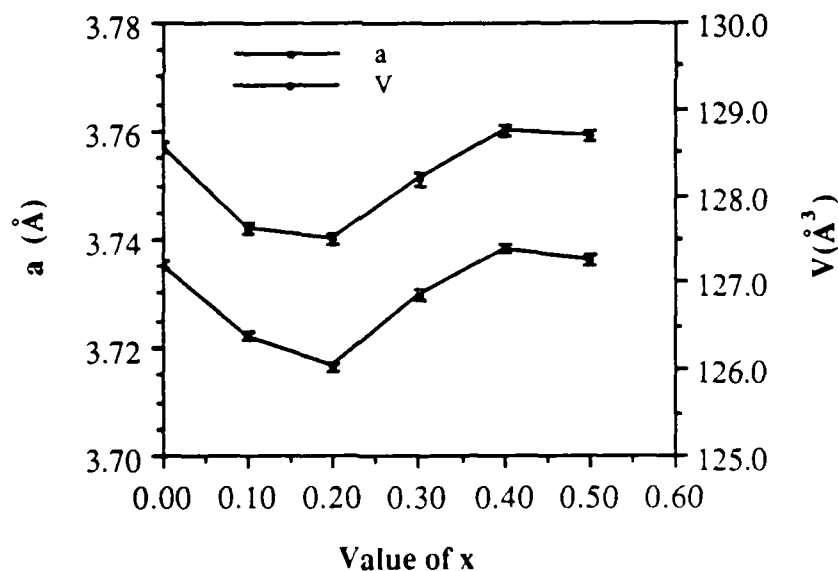


Figure 8. Lattice parameter of  $\text{Tl}_{1-x}\text{Bi}_x\text{Sr}_2\text{CuO}_5$  as a function of Bi content  $x$ .

Substitution of trivalent rare-earth cations for  $\text{Ca}^{2+}$  would also be expected to reduce the copper valence and stabilize the single  $\text{Tl-O}$  layered phases. A complete substitution of Ca by rare-earth cations in  $\text{TlA}_2\text{CaCu}_2\text{O}_7$  ( $A=\text{Ba}$  or  $\text{Sr}$ ) stabilizes the phase but destroys the superconductivity, resulting in semiconducting compounds[30,31]. Partial substitutions of Ca by rare-earth ions

yield superconductivity with a lower  $T_C$  than that of the parent compounds[32-35]. However, Yb substitution for Ca was reported to be not deleterious to superconductivity[33]. Although  $TlBa_2CuO_5$  is only metallic[10], superconductivity was reported in  $TlBa_{2-x}Ln_xCuO_5$  ( $Ln=La, Nd$ ) with  $T_C \sim 40K$ [27]. Reports of superconductivity in the  $Tl-Ln-Ba(Sr)-Ca-Cu-O$  mixed phase systems[35,51-54] may be due to the presence of either  $TlA_{2-x}Ln_xCuO_5$  or  $TlA_2CaCu_2O_7$  or both[33,52].

### ii. Substitutions in the $Tl_2Ba_2Ca_{n-1}Cu_nO_{2n+4}$ Family

Following the discovery of superconductivity in the  $Tl-Ba-Ca-Cu-O$  systems, attempts to prepare Sr analogues have been undertaken. Superconductivity was reported[57-60] in some  $Tl-Sr-Ca-Cu-O$  phases, however, further confirmation of this is needed. Partial substitutions of Ba by Sr in the 2212 and 2223 system were studied by Hayri et al[17] and Soeta et al.[19], respectively. It has been found that in both systems, increasing the Sr content will decrease the  $T_C$  and that the lattice parameters of 2212 and 2223 decrease linearly with increasing Sr content. The reasons for the depression of  $T_C$  by Sr substitution in both 2212 and 2223 oxides are not clear at present. It is possible that the substitution of Ba by Sr alters the  $Tl-O-Cu$  bonding characteristics, resulting in an unfavorable electronic communication between the  $Tl-O$  and  $Cu-O$  layers, and subsequent depression in the superconducting properties.

Substitutions of Tl by Bi or Pb in the double  $Tl-O$  layer compounds were without success, due to the formation of  $BaBiO_3$  or  $BaPbO_3$ [82,95]. Attempts to substitute  $K^+$  for Tl, in the  $Tl-O$  layers were carried out by Sequeira et al[20]. These authors supposed that the valence of Tl in  $Tl-O$  layers is a strong admixture of  $Tl^{3+}$  and  $Tl^{1+}$  and hence assumed that  $K^+$  can be used to replace mono-valent thallium. However, their work does not provide conclusive evidence that such substitutions do take place, since there are no corresponding changes in the structural parameters as inferred from their neutron diffraction study[20]. Potassium sublimes at the high reaction temperatures employed in their synthesis, and an off-stoichiometric composition can still yield 2212 or 2223-type oxides, which can account for the superconducting properties of  $K^+$  "substituted" phases.

Bourgault et al. reported partial substitution of  $Ba^{2+}$  by  $Tl^+$  in the  $Tl^{III}_{2-x/3}Tl^I_{1-x}Ba_{1+x}LnCu_2O_8$  ( $Ln=Pr$  and  $Nd$ ) system[21]. A nonsuperconducting pure phase sample was isolated corresponding to  $x \sim 0.25$ . Based on powder X-ray diffraction data, the authors concluded that  $Tl^+$  and  $Ba^{2+}$  ions are randomly distributed at the Ba sites in the 2212 related structure. This observation implies that partial occupancies of  $Tl^+$  at the Ba sites provide another source of nonstoichiometry in addition to: a) apparent  $Tl^{3+}$  and  $Ca^{2+}$  deficiencies, and b) partial occupancy of  $Ca^{2+}$  on the  $Tl^{3+}$  site in the  $Tl$ -based cuprates.

### iii. Others

Most substitutional studies focused on various replacements in the Tl, Ba and Ca sites. A few investigations were also carried out on substitution for the Cu site, primarily by Fe ions for Mössbauer spectroscopic studies[96]. One of the reasons for the lack of other transition metal substitutions at the Cu-sites may be related to the difficulty in preparing samples at the relatively low reaction temperatures and short reaction times that are required to prevent the loss of Tl. However, if the synthetic difficulties can be overcome, it would be worthwhile to study substitutions at the Cu site, which would provide clues, vital for the understanding of electronic correlations between the Tl-O and Cu-O layers.

## 6. Physical Properties and $T_c$ Correlations

Due to the difficulties encountered in preparing high quality samples and growing large single crystals of thallium-copper oxide superconductors, the physical properties have not been well established. There are some discrepancies surrounding the superconductivity and other related physical properties of these compounds, probably due to subtle differences (such as inhomogeneity and nonstoichiometry) in the samples and measurement conditions. For instance, in the 2201 system, regardless of the crystal symmetry, the superconducting transition temperatures have been reported to be anywhere between 0-90K. In addition, there is no general agreement on the superconducting transition temperatures of polycrystalline 2212 and 2223 specimens. Measurements on impure/mixed phase samples can often lead to misleading conclusions and compound the confusion, which is already present in thallico-cuprates. Although the correlations between the chemistry and superconductivity in these phases are far from being established, most of the known physical properties of the thallium-copper oxides are at least qualitatively comparable with those of the rare-earth based copper oxides.

### *i. Transport and Magnetic Properties*

The thallium copper oxides are metallic in their normal state, including the nonsuperconducting members of  $TlA_2CuO_5$  ( $A=Ba$  and  $Sr$ ).  $TlBa_2LnCu_2O_y$  is the only known exception, which is semiconducting between 4-300K. The normal state resistivity of thallico-cuprates is very similar to that of the 123-type materials (of the order of  $\sim 10^{-3} \Omega \cdot cm$  at room temperature). Thermoelectric power measurements[97,98] on polycrystalline 2223 samples show a positive Seebeck coefficient, which indicates that the dominant charge carriers in these compounds are holes. The thermoelectric power is small, about 2-4  $\mu V/K$ , and increases linearly with decreasing temperature upto  $T_c$ . A small value of thermal power is in agreement with the observed metallic property, however, the temperature dependence of the Seebeck coefficient can not be explained by simple band models.

Hall effect measurements[99,100], provide further evidence that holes are the major charge carriers in the superconducting thallium cuprates. The charge carrier concentration in a 2223 sample, calculated from the Hall coefficient, was estimated to be  $\sim 2 \times 10^{21} / \text{cm}^3$ , somewhat smaller than that of rare-earth-based high  $T_c$  compounds ( $n \approx 6 \times 10^{21} / \text{cm}^3$ ). The complex  $R_H \propto 1/T$  temperature dependence, however, has not been explained.

Although the thermoelectricity and Hall effect measurements indicate that the major charge carriers are holes in 2212 and 2223 phases, Vijayaraghavan et al., recently, reported possible electron superconductivity in  $\text{TlCa}_{1-x}\text{Ln}_x\text{Sr}_2\text{Cu}_2\text{O}_{7-\delta}$  when  $x=0.25$ [33]. Superconductivity was found in this system and the  $T_c$  and the type of the charge carriers were found to be dependent on the composition and the nature of the rare-earth ions.

The measured transport properties are somewhat qualitative, because the polycrystalline powder samples used for the measurements usually contain impurities, which may affect the quantities of physical properties and their temperature dependencies. Measurements on single crystal samples are preferred.

Critical current densities for 2212 and 2223 phases were measured in thin film and polycrystalline powder samples. In a 2212 thin film[101], the transport critical current densities  $J_c$  are  $10^3 \text{ A/cm}^2$  at 95K,  $10^{4-5} \text{ A/cm}^2$  at 77K and  $\sim 10^6 \text{ A/cm}^2$  at 4K; while in a powder sample[102],  $J_c$  is only  $\sim 300 \text{ A/cm}^2$ . The lower critical field  $H_{c1}$  is about  $\sim 3 \times 10^{-2} \text{ T}$ , and the upper critical field  $H_{c2}$  is about 50 T at 77K for a 2223 sample. The critical fields  $H_{c1}$  and  $H_{c2}$  are estimated to be  $\sim 5 \times 10^{-2} \text{ T}$  and 100~130 T, respectively at 0K. The upper critical field of 2223 is much lower than 205 T, estimated as the Pauli paramagnetic limiting field. From the magnetization studies on 2223[103,104], the coherence length  $\xi$  was estimated to be  $\sim 26 \text{ \AA}$  at 77K and  $16\text{--}18 \text{ \AA}$  at 0K. The penetration depth,  $\lambda$  is at out  $\sim 2200 \text{ \AA}$  at 77K and  $1400 \text{ \AA}$  at 0K. Magnetic relaxation[105] and flux pinning[102] have also been investigated.

Surprisingly, in most of the thallium-copper oxides, evidence of antiferromagnetic ordering was not found, except in  $\text{TlBa}_2\text{YCu}_2\text{O}_7$ . Low temperature neutron diffraction study on semiconducting  $\text{TlBa}_2\text{YCu}_2\text{O}_7$  shows evidence of antiferromagnetic ordering[106]. A three dimensional magnetic ordering, similar to that seen in  $\text{YBa}_2\text{Cu}_3\text{O}_6$  and  $\text{Bi}_2\text{Sr}_2\text{YCu}_2\text{O}_x$ , was established in this compound with the Néel temperature  $>350\text{K}$ . The absence of magnetic ordering in most of the thallium cuprates raises concern about the proposed relationship between superconductivity and antiferromagnetic ordering.

## ii. Electronic Structures

The electronic band structures of  $\text{Tl}_2\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4}$  ( $n = 1, 2$  and  $3$ ) series were calculated by several groups[107-109]. In general, the electronic band

structures are similar to those of the Bi-based compounds[110,111]. The focus of these studies has been on the special features of electronic structure introduced by the Tl-O layers. Although, in the various calculations, different approximation schemes were used, the calculated results are comparable and uniform in some features. Figure 9 shows a schematic diagram of the  $\text{Tl}_2\text{Ba}_2\text{CuO}_6$  band structure.

Bands I and II are the Tl-O antibonding bands, consisting of Tl6s and O2p orbitals. III and IV are the Cu-O bands, made up of Cu3d and O2p orbitals. As the number of Cu-O layers increases in the structure, all the corresponding bands remain at essentially the same energies, but the degeneracy of Cu-O bands (III and IV) increases. The presence of two Cu-O bands is a distinctive feature in all of the thallium-copper oxides. The broad band (band III, in Fig. 9) is essentially the Cu-O band arising from the Cu-O equatorial plane which disperses across the Fermi level, indicating that this band is the main conduction band. The narrow Cu-O band is of interest. It is very close to or possibly slightly overlaps with the Fermi level. If this narrow band does overlap with the Fermi level, it may provide electrons to the Fermi level. The most important feature of the Tl-O bands is that they may cross  $E_f$ , and provide holes to the Cu-O bands. If this is the case, the Tl-O layers are expected

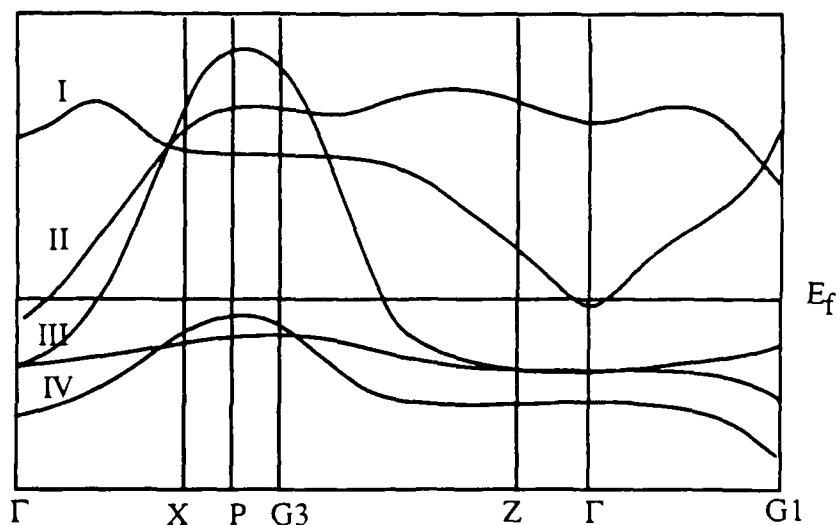


Figure 9. Schematic band diagram of  $\text{Tl}_2\text{Ba}_2\text{CuO}_6$  (after ref. 109).

to be metallic. The broad Cu-O conduction bands are relatively insensitive to structural changes, such as deviation from the ideal stoichiometry, local

distortion or substitutions. However, the Tl-O bands and the narrow Cu-O bands are very sensitive to small structural changes. An isoelectronic substitution of Sr for Ba will dramatically change the band structure near the Fermi level, as revealed by the test calculations[109].

The calculated electronic band structures provide some insight for the understanding of the physical properties of thallium-copper oxide superconductors. First, they present a mechanism by which  $\text{Cu}^{2+\delta}$  might be produced, in addition to the nonstoichiometry or structural defects. Second, the coexistence of broad Cu-O and narrow Tl-O bands near the  $E_f$  reveal that electronic conduction in these compounds may occur by plasmon-like(or exciton)[109] or charge fluctuation(transfer)-like mechanisms[112]. Third, the band structures show that the sizes of either the hole reservoir(the Tl-O bands) or the electron reservoir(the narrow Cu-O bands) are not monotonic functions of the number of Cu-O layers[109], which indicates that the basic band structure does not change with the number of Cu-O layers. Finally, these calculations demonstrate great similarities among the band structures of cuprate superconductors; this implies that they all may have a similar conduction mechanism.

Herman et al.[113] reported band structure calculations on the single Tl-O layer compounds. Their results show features of the Cu-O band which are comparable to those seen in the double Tl-O layer compounds. It was suggested that the Tl-O narrow band can be moved away from  $E_f$  without significantly altering the Fermi surface, implying that the Tl-O layers are not necessarily the hole reservoirs.

The band structures, however, can provide only very qualitative information about the relationship between the chemistry and superconductivity in these compounds, given the fact that these calculations oversimplify the complex structural features, such as nonstoichiometry and local structural distortions. Therefore, oversimplification of the actual structure in order to perform the calculation may lead to ambiguities. For example, most of the calculations do not take into consideration the electronic spin functions, so that a calculated metallic state could actually be an antiferromagnetic insulating state.

Electron photoemission experiments[91-93] often provide some confirmation of the calculated band structures. These experiments indicate that the electronic states near the Fermi level are composed of mainly  $\text{Cu}3d$ ,  $\text{O}2p$  and the Tl6s orbitals.

### iii. $T_c$ Correlations

The discovery of high  $T_c$  superconductivity in the cuprate materials has challenged the conventional BCS theory of superconductivity, because BCS

theory fails to predict such high critical temperatures. It has been established by flux quantization measurements that in these high  $T_c$  materials the superconducting current carriers are paired holes/electrons. To date, there has not been a general consensus on the superconducting mechanisms and correlations between the chemistry of materials and the superconductivity.

However, some common features have been fairly well established in the superconducting cuprates: *a)* all the cuprates are nonstoichiometric compounds, containing oxygen or cation defects; *b)* mixed Cu valence in the compounds provides the charge carriers; *c)* all of the compounds have orthogonal (tetragonal or orthorhombic) symmetry, providing the most effective metal  $3d$ -oxygen  $2p$  overlapping for conduction; *d)* the superconducting cuprates are poor metals ( $\rho \sim 10^{-3} \Omega\text{-cm}$  at room temperature) in their normal state, which indicates that they are near a metal-semiconductor boundary; and *e)* in some cases, the semiconducting form of the superconducting phase orders antiferromagnetically at ambient temperatures, which implies that the superconducting mechanism may be related to the magnetic properties.

In the thallium-copper oxides, all of the above features are present, in addition to the effects due to the Tl-O layers. It appears that the superconductivity is correlated with electronic interactions between the Tl-O and Cu-O layers. Many structural properties could also be considered to be related to the transition temperature, including the in-plane and apical Cu-O distances, the polarizability of the lattice, the distance between Cu-O layers, number of Cu-O layers, the location and concentration of charge carriers. Although, there have been insufficient data to support any of these correlations, such empirical data could provide further understanding of these materials.

## 7. Future Work

The new superconducting oxide family of  $\text{Tl}_m\text{A}_2\text{A}'_{n-1}\text{Cu}_n\text{O}_{2n+2+m}$  presents many structural and electronic features in common with other superconducting cuprates and provides new opportunities for understanding the chemical, structural and electronic property relationships required for high temperature superconductivity. However, more work is needed to fully understand details of the structural defects including oxygen content/ordering and distribution of cation deficiencies in these compounds. Novel substitution studies would be helpful in clarifying some of these issues.

Synthetic techniques, which can reproducibly yield pure phase samples with controlled stoichiometry, need to be developed. Investigations of new ternary layered thallium transition metal oxides would be useful for modeling the role of Tl-O layers in the Tl-based cuprate materials.

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