

Chemical Methods to Identify the Origin of Oxidation in the Thallium Cuprate Superconductors

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Creation of mixed valency in the CuO_2 sheets of the copper oxide superconductors is a necessary condition to suppress long-range antiferromagnetic order and promote superconductivity. The oxidation/reduction of the $(\text{CuO}_2)^{2-}$ sheets is generally achieved by suitable ionic substitutions and/or oxygen intercalation/disintercalation. The mechanism for such an oxidation in the thallium cuprate superconductors has, however, not yet been established. We have adopted a simple wet chemical method to obtain the Tl content and a modified iodometric procedure to determine the total oxygen content. Our wet chemical analyses combined with thermogravimetric analysis demonstrate for the first time that oxidation of the CuO_2 sheets in $\text{Tl}_2\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4}$ is primarily due to an overlap of the Tl-6s band with the σ_{2p}^* and/or π^* bands of the CuO_2 sheets. Neither Tl vacancies nor excess oxygen in the Tl_2O_2 blocks is required to render the thallium cuprates superconductive. © 1990 Academic Press, Inc.

Creation of mixed valency in the CuO_2 sheets of the copper oxide superconductors is believed to be a necessary condition to suppress long-range antiferromagnetic order and promote superconductivity. The oxidation/reduction of the $(\text{CuO}_2)^{2-}$ sheets is generally achieved by suitable ionic substitutions and/or oxygen intercalation/disintercalation. The possibility that an alternate mechanism may be operative in the thallium cuprate superconductors has remained untested because of inadequate analytical procedures. We have adopted a simple wet chemical method (1) to obtain the absolute Tl content, and a modified iodometric procedure (2) to obtain the total oxygen content; the analysis for both thallium and oxygen has allowed us to demonstrate for the first time that oxidation of the CuO_2 sheets occurs by an overlap of the Tl-6s band.

Although the oxidation of the $(\text{CuO}_2)^{2-}$ sheets in the $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4+x}$ ($n = 1-3$) family has been shown to be due to the excess x oxygen in the $\text{Bi}_2\text{O}_{2+x}$ blocks (3, 4), the mechanism for such an oxidation in the analogous p -type " $\text{Tl}_2\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4}$ " family has yet to be established. The lack of any adequate chemical characterization is due to (1) a volatilization of Tl during synthesis and (2) the dissolution problems encountered in the usual iodometric determination of the oxygen content. In the absence of firm analytical data, it has not been possible to distinguish (5) between the several sources of oxidation that have been suggested: the presence of Tl vacancies (6), of mixed-valent Tl in a Tl_2O_2 layer (7), and/or of excess oxygen in the Tl_2O_2 layer (8). We report the application of our wet chemical methods combined with ther-

mogravimetric analysis (TGA) to the systems $\text{Tl}_2\text{Ba}_2\text{CuO}_6$ and $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$ to demonstrate that oxidation of the CuO_2 in stoichiometric $\text{Tl}_2\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4}$ is primarily due to an overlap of the Tl-6s band with the $\sigma_{x^2-y^2}$ and/or π^* bands of the CuO_2 sheets, where the Tl content is close to two per formula unit. Neither Tl vacancies nor excess oxygen in the Tl_2O_2 blocks is required to render the thallium cuprates superconductive.

$\text{Tl}_2\text{Ba}_2\text{CuO}_6$ and $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$ were obtained by introducing into a muffle furnace maintained at 900°C in air an intimate mixture of stoichiometric quantities of Tl_2O_3 , BaO_2 , CuO , and/or CaO pelletized and wrapped in a gold foil. The mixture was fired at 900°C for 10 min with one intermittent grinding and then quenched in liquid nitrogen. Formation of single-phase materials was confirmed by X-ray powder diffraction recorded with a Philips diffractometer and $\text{Cu K}\alpha$ radiation. Quenching the product in liquid nitrogen proved essential as air-quenching or furnace-cooling results in phase separation with the formation of impurity phases such as BaCO_3 , BaCuO_2 , and Tl_2O_3 .

The Tl content was determined by a volumetric method (1). A known amount (~ 100 mg) of " $\text{Tl}_2\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4}$ " was dissolved in 10 ml of 3.5 N HCl. The solution was diluted with water and perchloric acid to 30 ml so that the resulting solution contained 2% perchloric acid. An equal volume of 10% thiourea solution was added, and the white precipitate that formed—perchlorate–thiourea complex—was stirred for 2 hr on a magnetic stirrer; other cations such as Ba, Ca, and Cu form soluble perchlorate–thiourea complexes and remain in solution. The precipitate was filtered on a sintered-glass crucible, washed with a 5% thiourea solution containing about 0.5% perchloric acid, and dissolved in hot water. The solution was acidified with 3 ml of concentrated HCl

and boiled with 1 ml of bromine until the color of the bromine disappeared. The solution was cooled, and a few drops of bromine were added until the color turned yellow to ensure a complete oxidation of all Tl to Tl^{3+} . The excess bromine was removed by adding 5 ml of 5% phenol; and the solution was treated with 15 ml of 10% KI and titrated against 0.03 N sodium thiosulfate solution with starch as an indicator. The Tl content was estimated from the titer value. The validity of the procedure was confirmed by carrying out the experiment under identical conditions with Tl_2O_3 . Alternatively, the Tl content in the solution of perchlorate–thiourea complex could be determined by precipitating Tl as Tl_2CrO_4 with K_2CrO_4 as precipitant in an ammoniacal medium (9).

The total oxidizing power of the system was determined by the modified iodometric procedure (2). A known amount (~ 100 mg) of " $\text{Tl}_2\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4}$ " was dissolved in 10 ml of ice-cold 2 N HBr in a 250-ml Erlenmeyer flask fitted with a ground-glass stopper. The solution was shaken well and cooled in an ice bath; 15 ml of 10% KI was added to this solution, shaken well, and warmed up to room temperature. The liberated iodine was then titrated against 0.03 N thiosulfate solution with starch as an indicator.

The analytical results for $\text{Tl}_{2-y}\text{Ba}_2\text{CuO}_{6-x}$ obtained by quenching in liquid nitrogen and after annealing in N_2 or O_2 are given in Table I. The quenched sample is deficient in thallium ($y = 0.08$) and oxygen ($x = 0.41$) and has a formal Cu oxidation state of $1.41 +$ if all Tl is assumed to be Tl^{3+} . The observation of *p*-type conduction suggests that the CuO_2 sheets are oxidized beyond the formal oxidation Cu^{2+} . The observation of a concentration of Tl vacancies smaller ($y = 0.08$) than that needed to compensate for the concentration of oxygen vacancies ($x = 0.41$) unambiguously demonstrates that the oxidation of the CuO_2^- sheets in the quenched

TABLE I
ANALYTICAL DATA AND LATTICE PARAMETERS OF $Tl_{2-y}Ba_2CuO_{6-x}$ ^a

Sample no.	Preparative conditions	Total redox power ^b	Formal oxidation state of Cu ^c	Oxygen content (6 - x)	$T_c(K)$ ^d	Lattice parameters ^e (Å)	Volume (Å ³)
1.	Fired at 900°C and quenched in liquid N ₂	4.25	1.41 +	5.59	63	$a = 5.479(3)$ $c = 23.203(9)$	696.5
2.	Sample 1 annealed in O ₂ at 350°C, 1 hr ^f	4.98	2.14 +	5.95	Normal metal	$a = 5.451(1)$ $b = 5.505(1)$ $c = 23.152(6)$	694.8
3.	Sample 2 reannealed in N ₂ at 350°C, 1 hr	4.92	2.08 +	5.92	26	$a = 5.458(1)$ $b = 5.500(1)$ $c = 23.180(6)$	696.1

^a All samples showed a Tl content of 1.92 with $y = 0.08$.

^b Obtained by assuming all Tl⁺, Cu⁺, and O²⁻ at the end of the titration.

^c Assuming all Tl³⁺ and O²⁻ in the solid sample.

^d Diamagnetic onset obtained from susceptibility data.

^e $a = \sqrt{2} a_{tet}$ for the tetragonal samples.

^f Annealing of sample 1 in O₂ to obtain sample 2 was accompanied by an extrusion of a smaller amount of Tl₂O₃.

samples is primarily due to a mixed Tl valency; it is not due to Tl vacancies or to excess oxygen in the Tl₂O₂ layer. A mixed Tl valency implies an overlap of the Tl-6s band with the conduction band.

The TGA plots recorded with a Per-

ken-Elmer Series 7 thermal analysis system for Tl_{1.92}Ba₂CuO_{6-x} are shown in Fig. 1. Tl_{1.92}Ba₂CuO_{5.59}, obtained by quenching in liquid nitrogen, picks up oxygen above 80°C and reaches a maximum $x = 0.04$ close to 300°C; this oxidation is accompanied by a

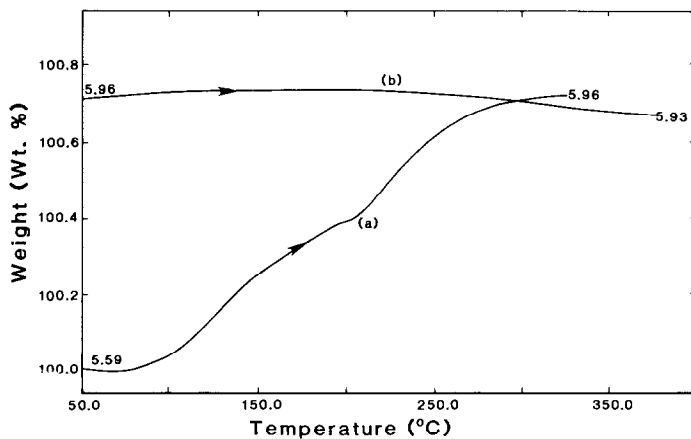


FIG. 1. TGA plots at 1°C/min of Tl_{1.92}Ba₂CuO_{5.59} (sample 1 in Table I) (a) in O₂ atm and (b) followed by cooling to ambient temperature in O₂ (not shown) before heating in N₂ atm. The numbers refer to oxygen content.

topotactic extrusion of some Tl; only Tl_2O_3 appears as a small second phase. The fully oxidized sample with $x \approx 0.05$ is a normal metal and is not superconducting, as has been observed by Shimakawa *et al.* (6); the suppression of T_c is due to a higher concentration of holes in the CuO_2 sheets. The fully oxidized sample loses about 0.03 oxygen in N_2 around 350°C (Fig. 1b) and exhibits a $T_c \approx 26$ K. These observations clearly establish that T_c vanishes at higher hole concentrations in this system, as also in $\text{La}_{2-y}\text{Sr}_y\text{CuO}_4$ (10). Furthermore, the sample quenched in liquid nitrogen is generally tetragonal; it transforms to the orthorhombic symmetry upon annealing in O_2 . The fully oxidized, orthorhombic sample retains orthorhombic symmetry upon annealing in N_2 at 350°C , but it shows a $T_c \approx 26$ K. Superconductivity thus appears to be independent of the room temperature crystal symmetry, as was also found by Shimakawa *et al.* (6). Similar observations of T_c being independent of the room temperature orthorhombic vs tetragonal symmetry have also been reported for some cation-substituted $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ systems (11, 12).

Similar experiments on $\text{Tl}_{2-y}\text{Ba}_2\text{CaCu}_2\text{O}_{8-x}$ showed $y = 0.10$ and $x \approx 0.45$ in the quenched sample; this sample also oxidizes rapidly above 80°C and reaches a maximum weight with $x \approx 0.10$ around 350°C . Unlike the $\text{Tl}_{2-y}\text{Ba}_2\text{CuO}_{6-x}$ system, the quenched and O_2 -annealed samples exhibit only a small difference in the value of T_c . Since the oxidation process is accompanied by a topotactic extrusion of some Tl from the lattice as Tl_2O_3 impurity, it is difficult to know the actual increase in hole concentration upon oxidation and to correlate the variation of T_c with oxygen content.

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