Determination of oxygen content and cation valences in superconducting Tl-based cuprates by a wet chemical method

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A wet chemical route based on constant-potential electrolysis and different reactivities of Cu^{3+} and Tl^{3+} with water is proposed to distinguish the average valences of Cu and Tl in superconducting thallium cuprates. The validity of the method is demonstrated using $YBa_2Cu_3O_y$, Tl_2O_3, and Tl_2O as reference materials for Cu^{3+}, Tl^{3+}, and Tl^+, respectively. Furthermore, the oxygen contents and the cation valences have been determined for various Tl-22$(n-1)n$ phases (where $n = 1-4$). With increasing n value the Cu valence is found to decrease, while the valence of thallium remains rather constant at ca. $+3$, regardless of the value of n. Based on these results, the possible carrier doping mechanisms in the Tl-22$(n-1)n$ phases are discussed.

I. INTRODUCTION

The value of the copper valence in superconducting cuprates has been considered to be one of the crucially important factors for the occurrence of superconductivity. A great variety of mechanisms, such as cation and/or anion substitution, excess oxygen or charge transfer, have been proposed for doping charge carriers into the CuO_2 planes. The iodometry has proven to be an effective method for the determination of oxygen contents in superconducting cuprates.[1] However, it is not a suitable method for determining the distinct metal valences in a compound which contains two different kinds of multivalent cation. This is because iodide which is used as a reducing agent simultaneously reacts with both kinds of cation. In the bismuth cuprate superconductors both copper $(Cu^{2+/3+})$ and bismuth$(Bi^{3+/5+})$ may exhibit mixed valence states. Kurusu, Takami, and Shintomi[2] developed a constant-current coulometric method, based on the different oxidation powers of Cu^{3+} and Bi^{5+}, to separately analyze the average valences of the both metals. Recently, we[3,4] by slightly modifying the method, extended it applicability to the lead-containing materials as well.

In the case of Tl-based layered cuprate superconductors, the oxygen contents can be analyzed either by iodometry proceeding via HBr (Ref. 5) or by an electrochemical method developed by us.[6] In the electrochemical method monovalent copper is used as a reductant. It has been suggested from the band calculations[7] that in the double Tl layer cuprates, the Tl $6s$ orbitals overlap the Cu $3d$ orbitals resulting in the charge transfer from the double TlO layers to the CuO_2 layers and, furthermore, in the mixed $Cu^{2+/3+}$ and $Tl^{+/3+}$ valence states. This hypothesis is consistent with observations by x-ray photoemission spectroscopy[8] (XPS) and chemical analysis.[9] If it was possible to separately determine the average valences of both Tl and Cu, the results would be useful for clarifying the mechanism of hole doping into the CuO_2 planes. Unfortunately, the coulometric method

cannot be employed for the Tl-based layered cuprates, because of the too small difference between the standard potentials of the $Tl^{+/3+}$ and $Cu^{+/2+}$ couples. So it is necessary to use the constant-potential electrolysis technique which allows us to oxidize Cu^+ selectively in the presence of Tl^+.[6] The present study confirms that for the separation of the Cu and Tl valences different reactivities with water can be utilized: Tl^{3+} is relatively stable in acidic solutions, while Cu^{3+} is reduced immediately. The selectivities of the proposed method are demonstrated using $YBa_2Cu_3O_y$, Tl_2O, and Tl_2O_3 as reference materials for Cu^{3+}, Tl^+, and Tl^{3+}, respectively. Furthermore, the oxygen contents and the average Cu and Tl valences are studied in several superconducting double TlO layer cuprates.

II. EXPERIMENTAL

A. Sample preparation and properties

The $YBa_2Cu_3O_y$ reference sample was synthesized by a solid-state reaction of high purity $(3N)$ Y_2O_3, $BaCO_3$, and CuO powders. The oxygen content of this sample was established by both the conventional iodometric method and the coulometric method described in Ref. 3. High purity $(3N)$ Tl_2O_3 and Tl_2O powders were used as references for the Tl^{3+} and Tl^+ ions, respectively. Four kinds of superconducting Tl-based layered cuprates, whose nominal compositions are shown in Table I, were

TABLE I. Stoichiometric data for the studied Tl double-layer cuprates.

Nominal starting composition	Observed Tl content	Observed oxygen content
$Tl_{1.8}Ba_2Cu_{1.2}O_z$	1.75	5.98
$Tl_{1.7}Ba_2Ca_{1.3}Cu_2O_z$	1.63	7.94
$Tl_{1.7}Ba_2Ca_{2.3}Cu_3O_z$	1.62	9.92
$Tl_{1.7}Ba_2Ca_{3.3}Cu_4O_z$	1.60	11.89

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prepared by a conventional solid-state reaction method using high purity ($3N$) Tl_2O_3, BaO, CaO, and CuO powders as starting materials. In order to obtain single-phase samples, the Tl-site was partially substituted by Ca or Cu, so that the nominal starting compositions were shifted from the stoichiometric ones, i.e., $Tl:Ba:Ca:Cu=2:2:n-1:n$. The powder mixtures were sintered at temperatures between 865 and 890°C in air or in flowing O_2 gas. The single-phase character of the synthesized samples was confirmed by powder x-ray diffraction. The Tl contents of the sintered samples were determined by means of induction coupled plasma (ICP) analysis. The valences of Tl and Cu were calculated using the observed Tl contents. The superconducting properties of the samples were characterized by measuring electrical resistivities and the dc magnetic susceptibilities.
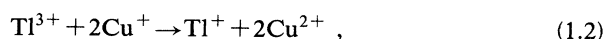
B. Potentiostatic electrolysis

Careful control of the potential was achieved with a conventional three-electrode technique. A constant potential of 400 mV from a potentio-controlled source (HZ-1A:Hokuto Denko) was applied between a working electrode (Pt-plate) and a saturated Ag/AgCl reference electrode (6861-10C:Horiba). The response current was measured between the working electrode and a Pt-counter electrode which was separated from the test solution by a KCl/agar-salt bridge. The electrolyses were carried out in flowing nitrogen gas in a cell containing ca. 150 ml of 0.5 M HCl solution, from which dissolved oxygen had been taken away.
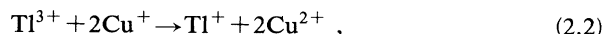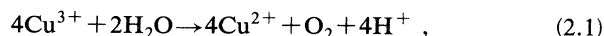
III. RESULTS AND DISCUSSION

A. Procedure for the oxygen content and metal valence determinations

The oxygen contents and the average valences of Cu and Tl can be determined by two redox experiments using CuCl as a reducing agent and applying constant-potential electrolysis of excess Cu^+ as a final analysis step in both experiments. Experiment 1: determination of the oxygen content

$$Cu^{3+}+Cu^+\rightarrow 2Cu^{2+} , \tag{1.1}$$

$$Tl^{3+}+2Cu^+\rightarrow Tl^+ +2Cu^{2+} , \tag{1.2}$$

$$Cu^+\rightarrow Cu^{2+}+e^-: \text{ electrolysis }. \tag{1.3}$$

Experiment 2: determination of the Tl valence

$$4Cu^{3+}+2H_2O\rightarrow 4Cu^{2+}+O_2+4H^+ , \tag{2.1}$$

$$Tl^{3+}+2Cu^+\rightarrow Tl^+ +2Cu^{2+} , \tag{2.2}$$

$$Cu^+\rightarrow Cu^{2+}+e^-: \text{ electrolysis }. \tag{2.3}$$

The difference between the two experiments is only the order in the addition of the sample material and CuCl. Namely, in Experiment 1 the sample is added into the cell after CuCl, while in Experiment 2 this order is reversed. In Experiment 1, both Tl^{3+} and Cu^{3+} are reduced by a known amount of Cu^+. From the total number of electrons being produced in the electrolysis of excess Cu^+, the oxygen content of the sample can be calculated. In Experiment 2, Cu^{3+} is allowed to completely react with water before CuCl is added to determine the remaining oxidation power of the solution and thus the valence of thallium. Finally, the value for the Cu valence can be calculated as the difference between the results of these two measurements.

The calculation procedure is in the following demonstrated using the data observed for the $Tl_{1.63}Ba_2Ca_{1.3}Cu_2O_z$ sample as an example. The valences of Tl and Cu are denoted with $+(1+a)$ and $+(2+b)$, respectively. Thus the oxygen content can be expressed by $z=6.115+(1.63a+2b)/2$. The amount of CuCl found to have been reacted per 1 mol of the sample materials in Experiments 1 and 2 were 3.69 and 3.31 mol, respectively. In Experiment 1 the total oxidation power of the sample above the valences of $+1.00$ for Tl and $+2.00$ for Cu, i.e., the sum $1.63a+2b$, is determined [Eqs. (1.1) and (1.2)]. This means that the oxygen content $z=6.115+3.69/2=7.96$. Experiment 2 gives directly the value of $1.63a$ and thus the Tl-valence value of $+(1+3.31/1.63)=+3.03$, since only Tl is allowed to oxidize CuCl [Eq. (2.2)]. Finally, from the difference between the results of the two experiments the valence value of Cu can be calculated to be $+(2+0.38/2)=+2.19$.

B. Measurements on the reference materials ($YBa_2Cu_3O_y$ and Tl_2O_3)

The experimental results for the studied $YBa_2Cu_3O_y$ and Tl_2O_3 reference samples are summarized in Table II. The experiments on $YBa_2Cu_3O_y$ were carried out in the presence of Tl_2O. According to Experiment 1, the oxy-

TABLE II. The observed Cu and Tl valences and the resulting oxygen contents in $YBa_2Cu_3O_y$ and Tl_2O_3 according to the potentiostatic electrolysis in experiments 1 and 2. The sequence of added reactants is given in parentheses.

Measurement	Cu valence	Tl valence	Oxygen content
Experiment 1 (CuCl → Tl_2O → $YBa_2Cu_3O_y$)	+2.25		6.88
Experiment 2 (Tl_2O → $YBa_2Cu_3O_y$→ CuCl)	+1.99		
Experiment 1 (CuCl→Tl_2O_3)		+3.03	3.03
Experiment 2 (Tl_2O_3→ CuCl)		+2.97	2.97

gen content of $YBa_2Cu_3O_y$ is 6.88. This value is in good agreement with the results of 6.87 and 6.86 obtained for the same sample by iodometric and coulometric titrations, respectively.[3,6] Thus it is evident that Cu^{3+} in $YBa_2Cu_3O_y$ reacts quantitatively with Cu^+. In Experiment 2 for $YBa_2Cu_3O_y$, the observed Cu valence value was $+1.99$. The result means that Cu^{3+} completely reacts with water before CuCl is added. In the case of Tl_2O_3, a Tl valence value of $+3.0$ was obtained in both experiments indicating that (1) the Tl^{3+} and Cu^+ ions stoichiometrically reacted and (2) the stability of Tl^{3+} against H_2O is high enough to permit the successful separation of the Cu and Tl valences.

C. Oxygen contents and valences of Tl and Cu in double TlO layer cuprate superconductors

When thallium cuprate superconductors are studied the tendency of Tl to evaporate during the high-temperature synthesis may cause remarkable errors in the determined oxygen content values if the concentration of Tl vacancies is not known and included in the calculations. In the present study ICP analyses revealed that 3–6 % of Tl had evaporated out of the samples during

the sintering of the studied double TlO layer cuprates (Table I). In Fig. 1 the resistivity and the dc magnetic susceptibility data for the same samples are shown. All the samples exhibit a sharp superconducting transition. The following zero-resistance temperatures (T_c^{zero}) are obtained: 26 K for the $n=1$ member, 91 K for $n=2$, 113 K for $n=3$, and 103 K for $n=4$.

The observed oxygen contents are summarized in Table I. All the values are close to or a little less than the stoichiometric ones. This confirms that unlike in $YBa_2Cu_3O_y$ and the Bi-based cuprate superconductors, excess oxygen is *not* the main source of holes in the Tl-based cuprate superconductors. Shimakawa and co-workers[10,11] have, however, reported, based on neutron diffraction and gravimetric studies, that their $Tl_2Ba_2CuO_y$ phase contained excess oxygen corresponding to $y=6.1$ and that the extra oxygen atoms are located between the two TlO layers. We have also previously found excess oxygen [$y=8.09$ (Ref. 6)] in our $Tl_{1.92}Ba_2CaCu_2O_y$ sample in which the Tl site was not substituted by Ca. The partial replacement of trivalent Tl by divalent Ca or Cu (Table I) might explain the some-
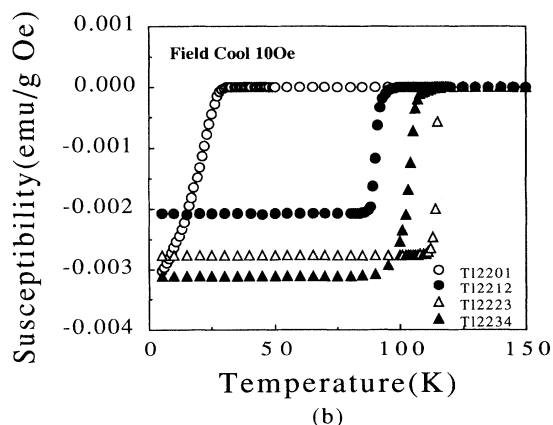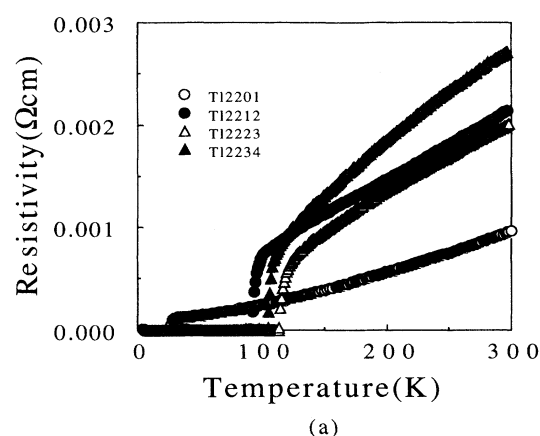

FIG. 1. Temperature dependence of (a) electrical resistivity and (b) dc magnetic susceptibility of the studied double TlO layer cuprates.
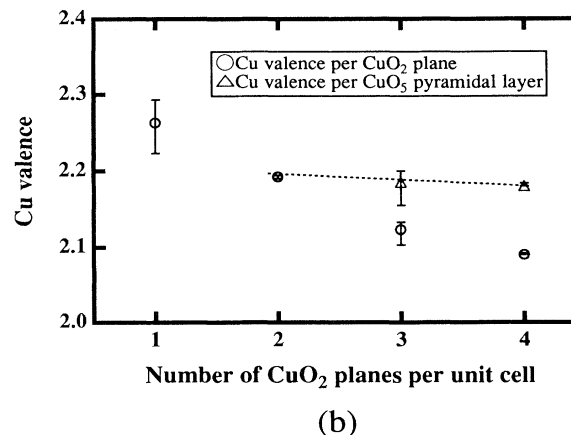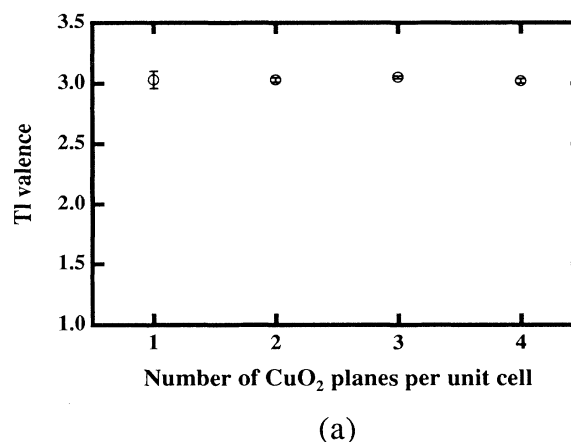

FIG. 2. Observed (a) Tl and (b) Cu valences in the studied double TlO layer cuprates.

what lower oxygen content values observed in the present study.

The experimental results for the Tl and Cu valences are shown in Figs. 2(a) and 2(b), respectively. The average Cu valence values represented by open circles in Fig. 2(b) have been calculated by assuming that all the CuO_2 planes are equivalent. With increasing n this average value of the Cu valence was found to decrease from $+2.26$ to $+2.09$. On the other hand, the Tl valence remains rather constant and close to $+3.0$ in each phase. This observation is not consistent with the XPS data of Suzuki et al.[8] showing Tl peaks between those of Tl_2O and Tl_2O_3 for the double TlO layer cuprates. The above discrepancy might be explained either (1) by the fact that the XPS method does not necessarily reflect the bulk properties but measures sample surfaces in ultrahigh vacuum conditions, or (2) by the conclusion that solid-state valence values are possibly changed during the dissolution step in the wet chemical analysis route used in present work.

If an overlapping of the Tl 6s and the Cu 3d orbitals occurs, the Tl valence should be less than $+3$ and the Cu valences higher than the observed values. Since the Cu valence values determined by the wet chemical method are in the range of $+2.09$ and $+2.26$, and thus sufficient for exhibiting superconductivity, the extent of charge transfer from the double TlO layers to the CuO_2 layers is most probably quite small. Consequently, the main hole doping mechanisms of the studied samples are thought to be the substitution of the Tl site by Ca^{2+} and/or Cu^{2+} and also by the deficiency of Tl.

According to the present data, the number of carriers per CuO_2 plane, i.e., the average valence of Cu decreases with increasing n. However, the charge may be inhomogeneously distributed between the fivefold- and fourfold-coordinated Cu atoms, and according to the generally accepted opinion only the pyramidal CuO_5 layers are doped with holes. Therefore, if the total carrier number is attributed only to these two CuO_5 layers, an almost equal Cu

valence value of $+2.19$ is obtained for all the phases with $n = 2-4$ [triangles in Fig. 2(b)]. Furthermore, if the total number of carriers supplied from the double TlO layers is supposed to be constant, the actual doping level being responsible for superconductivity is more or less the same for the $n = 2$, 3, and 4 phases. The reason why the T_c's are, however, different among these three phases, is not clearly understood but could be related to some other feature than the carrier density, e.g., the spin system.

IV. CONCLUSION

The valences of Cu and Tl in the $Tl_2Ba_2Ca_{n-1}Cu_nO_z$ samples with $n = 1-4$ were separately determined using a potentiostatic electrolysis method. For each of the $Tl_2Ba_2Ca_{n-1}Cu_nO_z$ phases, the oxygen content is close to the stoichiometric value. The Tl valence has been found to be approximately $+3.0$ for all the phases, and thus independent of the number of CuO_2 planes in the unit cell. On the contrary, the determined value of the Cu valence decreases from $+2.26$ to $+2.09$ as n increases from 1 to 4. However, if only the pyramidal CuO_5 layers are supposed to accommodate charge carriers, the Cu valence in these planes is around $+2.19$ regardless of the value of n. Since T_c depends on n, the obvious conclusion is that some features other than the carrier density also contribute to the magnitude of T_c.

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