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Chemical state of Tl in the superconductor $Tl_2Ba_2Ca_2Cu_3O_{10}$ studied by x-ray photoelectron spectroscopy

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Tl $4f$ core levels of $Tl_2Ba_2Ca_2Cu_3O_{10}$, Tl_2O_3, and Tl_2O were measured by x-ray photoelectron spectroscopy in order to elucidate the chemical state of Tl ions in the superconducting oxide. The Tl $4f_{7/2}$ level is found to be at 117.4, 118.2, and 118.6 eV for Tl_2O_3, $Tl_2Ba_2Ca_2Cu_3O_{10}$, and Tl_2O, respectively. This result reveals that the Tl valence is between +3 and +1. The creation of holes in $Tl_2Ba_2Ca_2Cu_3O_{10}$ is discussed in terms of a charge transfer between Tl ions and Cu-O layers. Furthermore, the stabilization of double Tl-O layers is also discussed from the viewpoint of structural chemistry.

INTRODUCTION

Since the discovery of the Cu-O-based superconducting oxides,[1-4] a number of studies have been carried out in order to elucidate the mechanism of high-temperature superconductivity. It is fundamentally important to understand the origin of superconducting carriers (holes) in the pyramidal Cu-O layers which are considered to be the superconducting paths. In $La_{2-x}Sr_xCuO_4$ and $YBa_2Cu_3O_{7-\delta}$ compounds, the origin of hole creation has been rather easily explained, that is, holes are created by the substitution of Sr^{2+} for La^{3+} and by excess oxygens ($\delta \simeq 0$) in the structure, respectively. On the other hand, in Tl-Ba-Ca-Cu-O and Bi-Sr-Ca-Cu-O systems, the origin of holes cannot be explained by assuming nominal valence and stoichiometric composition.

The crystal structure of both $Tl_2Ba_2Ca_{n-1}Cu_nO_{2n+4}$ ($n=1$, 2, and 3) (Refs. 5-7) and $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}$ ($n=1$, 2, and 3) (Refs. 7-9) has double Tl-O or Bi-O layers. From the viewpoint of structural chemistry, it is rather surprising that Tl^{3+} with the electron configuration $[Xe]4f^{14}5d^{10}$ forms the same layered structure as Bi^{3+} with $[Xe]4f^{14}5d^{10}6s^2$, because a metal ion with s electrons in the outer shell forms a polarized chemical bonding which would explain a layered structure.[10] Therefore, it is worthwhile to investigate the chemical composition and the valence of Tl in this system.

In this paper, we will first report a piece of evidence that the valence of Tl ions in the superconductor is between +3 and +1. The creation of holes will be discussed in terms of a charge transfer between Tl ions and Cu-O layers. Furthermore, the stabilization of double Tl-O layers will also be discussed.

EXPERIMENT

The samples investigated here were prepared by mixing appropriate amounts of Tl_2O_3, $BaCuO_2$, BaO, CaO, and CuO. The mixture was pressed into a pellet of 10-mm diam and 1-mm thickness. The pellets were wrapped with gold foil and heated in a silica tube at 910 °C for 7 min under oxygen flow of 120–150 ml/min, followed by cooling with a rate of 10 °C/min. The samples obtained were characterized by x-ray powder diffraction, dc magnetization, and four-probe resistivity measurements, which indicated the compounds were $Tl_2Ba_2Ca_2Cu_3O_{10}$. The oxygen content was estimated to be ten on the basis of the crystal structure, because it is difficult to determine the exact oxygen content.

X-ray photoelectron spectroscopy (XPS) was carried out at room temperature under ultrahigh vacuum conditions ($\sim 1\times10^{-8}$ Pa) using a surface science instruments spectrometer with a monochromatized x-ray source of Al $K\alpha$ ($h\nu=1486.6$ eV). Spectra were taken with an energy resolution of 0.7 eV which was determined by the full width at half maximum of the Au $4f_{7/2}$ line. The surface of the samples was scraped with a file to clean it *in situ* under ultrahigh vacuum conditions. Standard materials of Tl_2O_3 and Tl_2O were used to obtain the standard XPS spectra of Tl^{3+} and Tl^{1+}, respectively.

RESULTS AND DISCUSSION

Before carrying out the XPS measurements, the $Tl_2Ba_2Ca_2Cu_3O_{10}$ sample was characterized by x-ray powder diffraction, dc magnetization, and four-probe resistivity measurements. The x-ray-diffraction pattern showed that the sample is nearly of single phase with the space group $I4/mmm$ and lattice parameters of $a=3.8502(2)$ Å and $c=35.572(2)$ Å. Figure 1 shows the temperature dependence of the dc magnetization in a magnetic field of 10 Oe. An onset of the Meissner signal appears at 114 K, coinciding with the temperature at which zero resistivity was observed by four-probe resistivity measurements. Smooth variations in the Meissner sig-

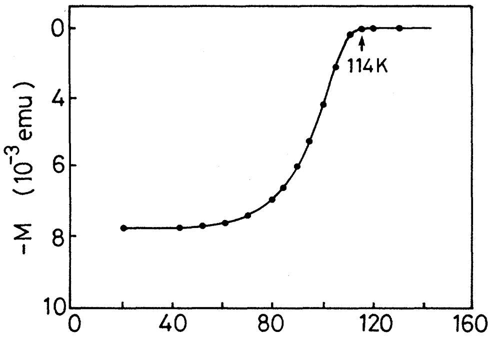

FIG. 1. Temperature dependence of dc magnetization of $Tl_2Ba_2Ca_2Cu_3O_{10}$ measured in a field of 10 Oe. Onset temperature was 114 K which corresponds to T_c determined by transport measurement.

nals are found and no steps are observed, showing a single superconducting phase. Furthermore, we estimated the volume fraction of high-T_c superconducting phase, from the initial slope of the magnetization curve at 4.2 K, to be larger than at least 90% that of perfect diamagnetism. These results also indicate that the sample is nearly of single phase with a T_c of 114 K and is suitable for XPS measurements.

We show Tl 4*f* core-level spectra of $Tl_2Ba_2Ca_2Cu_3O_{10}$, Tl_2O_3, and Tl_2O in Fig. 2. An electron flood gun was employed at 2 eV for the binding-energy measurements of Tl_2O because it is an insulator. However, since it was difficult to neutralize the charge completely, the binding energy of Tl 4*f* for Tl_2O was corrected by using the C 1*s* 284.9-eV line (due to hydrocarbon contaminant) obtained in the slightly contaminated $Tl_2Ba_2Ca_2Cu_3O_{10}$ as a reference. The binding energies of Tl $4f_{7/2}$ along with C 1*s* measured under various conditions are listed in Table I.

It was previously reported that the binding energy of Tl $4f_{7/2}$ is 117.7 eV for Tl^{3+} in Tl_2O_3 and is between 118.7 and 119.4 eV for Tl^{1+} depending upon the ligands.[11] This tendency is in good agreement with our results: 117.4 and 118.6 eV for Tl_2O_3 and Tl_2O, respectively. It should be emphasized here that the binding energy of Tl $4f_{7/2}$ in $Tl_2Ba_2Ca_2Cu_3O_{10}$ is significantly higher than that in Tl_2O_3 but slightly lower than that in Tl_2O. Judging from the previous data and our results, it is revealed that the valence of Tl in the superconductor $Tl_2Ba_2Ca_2Cu_3O_{10}$ is between +3 and +1.

It was reported that T_c is largely dependent on the hole concentration in a Cu-O layer and that its optimum value, determining the highest T_c in $YBa_2Cu_3O_{7-\delta}$, is 0.2–0.3.[12] In the case of $Tl_2Ba_2Ca_2Cu_3O_{10}$ with T_c higher than 100 K, the hole concentration in a Cu-O layer around room temperature was experimentally estimated to be 0.2–0.3.[13] We will discuss two possibilities for hole creation in the Tl-Ba-Ca-Cu-O system. First, if a nominal valence is assumed, partial substitution of Ca^{2+} for Tl^{3+} would provide holes. This was confirmed by electron probe microanalysis (EPMA) (Ref. 10) and the analysis of high-resolution images taken by transmission electron microscope (TEM),[14] that is, about 15% of Tl in $Tl_2Ba_2Ca_2Cu_3O_{10}$ is substituted for Ca.[10] This result shows that the hole concentration caused by the substitution would not be sufficient for superconductivity with T_c higher than 100 K, because an averaged hole concentration in a Cu-O layer is estimated to be 0.1. The second possibility is a charge transfer of $Tl^{3+}+(\text{Cu-O})^0 \rightarrow Tl^{(3-\delta)+}+(\text{Cu-O})^{\delta+}$, which leads to a formation of holes in Cu-O layers. Our XPS result exactly supports this possibility, because the valence of Tl is found to be between +3 and +1, although it is difficult to estimate the exact valence. If this system requires an optimum hole concentration for high

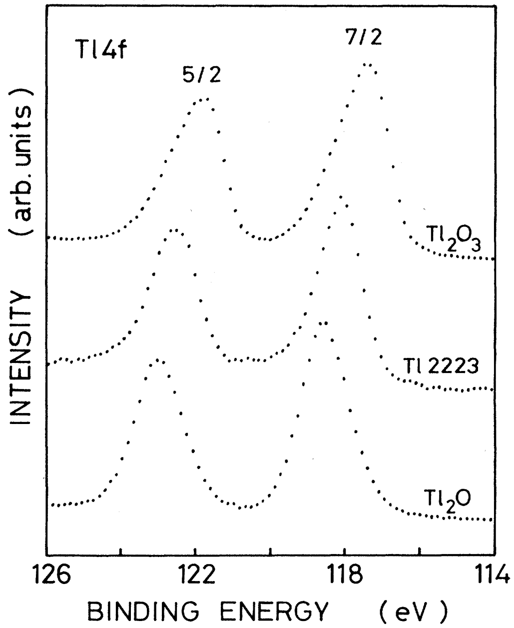

FIG. 2. XPS spectra of the Tl 4*f* core levels in Tl_2O_3, $Tl_2Ba_2Ca_2Cu_3O_{10}$, and Tl_2O. The energy scale of the spectrum for Tl_2O is corrected by using C 1*s* (284.9 eV) obtained in $Tl_2Ba_2Ca_2Cu_3O_{10}$ as a reference in order to cancel out a charge up shift.

TABLE I. Electron binding energies of C 1*s* (hydrocarbon) and Tl $4f_{7/2}$ for $Tl_2Ba_2Ca_2Cu_3O_{10}$, Tl_2O_3, and Tl_2O. The peak energy of Tl $4f_{7/2}$ for Tl_2O is corrected by using the energy of C 1*s* for slightly contaminated $Tl_2Ba_2Ca_2Cu_3O_{10}$.

Sample	C 1*s* (hydrocarbon) (eV)	Tl $4f_{7/2}$ (eV)
$Tl_2Ba_2Ca_2Cu_3O_{10}$ (slightly contaminated)	284.9	118.3
$Tl_2Ba_2Ca_2Cu_3O_{10}$ (scraped in vacuum)	not observed	118.2
Tl_2O_3 (scraped in vacuum)	not observed	117.4
Tl_2O flooded electrons (slightly contaminated)	282.2	115.9
Tl_2O (corrected)	284.9	118.6

T_c as does $YBa_2Cu_3O_{7-\delta}$,[12] the Tl^{1+} valence would produce too many holes to create the high-T_c superconductivity. This is consistent with the structural stability discussed later. We emphasize here that the charge transfer would operate as an origin of hole creation as does the substitution of Ca for Tl.

The other point under discussion is stabilization of the double Tl-O layered structure. It is empirically known that if the outer shells of metal ions in the oxides have *s* electrons, the enhanced polarizability results in stabilizing peculiar covalently bonded structures.[10] There are three cases which take such electronic configuration in simple oxides, i.e., $[Ar]3d^{10}4s^2$ (As_2O_3 and SeO_2), $[Kr]4d^{10}5s^2$ (SnO, Sb_2O_3, and TeO_2), and $[Xe]4f^{14}5d^{10}6s^2$ (Tl_2O, PbO, and Bi_2O_3) which take layer or chain structures.[15] For example, in case of PbO, it was pointed out that the dielectric dipole moment originating from the inert pair of 6*s* electrons[15,16] localized at Pb ions electrostatically attracts two Pb-O layers, hence lamellate fractures occur between the layers. On the other hand, Tl ions in Tl_2O have the same electronic configuration as Pb ions in PbO, which could explain why Tl_2O has a layered structure[17] and shows lamellate fractures. Accordingly, we can qualitatively understand the double Tl-O layered structure in $Tl_2Ba_2Ca_2Cu_3O_{10}$ from our XPS results which show that the Tl ions in $Tl_2Ba_2Ca_2Cu_3O_{10}$ partially have 6*s* electrons. However, $Tl_2Ba_2Ca_2Cu_3O_{10}$ does not show lamellate fractures along a Tl-O layer in spite of its layered structure. This fact suggests that Tl in $Tl_2Ba_2Ca_2Cu_3O_{10}$ has a different valence from that of Tl_2O, which is consistent with our XPS results. Furthermore, it should be pointed out that if the Tl ions in $Tl_2Ba_2Ca_2Cu_3O_{10}$ take an exact valence of +1, an ionic radius of Tl^{1+} would be too large ($r = 1.50$ Å for Tl^{1+}, $r = 0.89$ Å for Tl^{3+}) to stabilize the structure.

In summary, we have measured the 4*f* core spectra of Tl in $Tl_2Ba_2Ca_2Cu_3O_{10}$, Tl_2O_3, and Tl_2O by XPS in order to elucidate the chemical state of Tl in the superconductor. We conclude that the valence of Tl in $Tl_2Ba_2Ca_2Cu_3O_{10}$ is between +3 and +1. This result could explain both the origin of holes in Cu-O layers due to a charge transfer between Tl ions and Cu-O layers, and the stability of the double Tl-O layered structure.

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