

Photoemission Study of Electronic Structure of Tl-1223 Superconductors Synthesized under Ambient- and High-Pressure

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A change of electronic structure of $\text{TlBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{9.8}$ [Tl-1223] superconductors synthesized under ambient and a high pressure, as a function of vacuum-annealing temperature has been studied by *in-situ* photoemission spectroscopy, in order to elucidate a mechanism of a significant increase of superconducting transition temperature T_c up to 133.5 K in the high pressure Tl-1223 by reduction. For the high pressure Tl-1223, systematic shifts of core binding energy of the cations around the charge reservoirs with increase of the annealing temperature indicate a selective oxygen-depletion around the reservoirs and a decrease of Tl-valence, while a charging state of CuO_2 planes was rather robust in the reduction. This phenomena is interpreted as a majority of the electrons left by the reduction should be absorbed into the Tl ions and some electrons might be pulled out from CuO_2 planes. It should lead the moderate change of the hole-content of the CuO_2 planes by the reduction, while intra-unit-cell potential-distribution should be modified. An utilization of this charge redistribution mechanism should be an excellent way to optimize the hole-distribution among the nonequivalent CuO_2 planes without a fatal decrease of the hole-content.

Key Words: Tl-1223, high pressure synthesis, photoemission spectroscopy, valence-change.

1. INTRODUCTION

$\text{Cu}_{1-x}\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4\pm\delta}$ system (Cu-system) and $\text{TlBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+3\pm\delta}$ system (Tl-O single-layer system) are classes of high temperature superconductors (HTS) with structural similarity [1]-[3]. For ceramics of these systems synthesized by sintering under ambient pressure, the highest superconducting transition temperature T_c , so far, is in the range of 122 ~ 123 K [4]. Any oxidation-reduction treatments subsequent to the synthesis resulted in a slight increase of the T_c . Recently, in high pressure-synthesized (Cu, Tl) $\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{9\pm\delta}$ [(Cu, Tl)-1223] and $\text{TlBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{9\pm\delta}$ [Tl-1223], one of the members and relatives of the Cu system superconductors, a significant increase of T_c from below 100 K in each as-grown state to above 130 K by the reduction-annealing has been discovered by our group [5], [6]. The highest T_c of (Cu, Tl)-1223 and Tl-1223 so far are 132.5 and 133.5 K, respectively, which are comparable to the record of T_c under ambient pressure in $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{9\pm\delta}$. These results reveal an importance of these materials for practical application above 77 K. Elucidation of the mechanism of these change of electronic structure, which finally leads the optimized states for superconductivity, therefore, becomes a subject of study attracting a great interest.

We have recently performed *in-situ* X-ray photoemission spectroscopy (XPS) on Tl-1223 ceramics grown under high pressure and ambient pressure, as a function of the vacuum-annealing temperature. Systematic changes of the photoelectron spectra with the annealing temperature

have been observed. These reveal that, for the ambient pressure samples, valence of Tl and Cu ions should seriously decrease with a rise of the annealing temperature. On the other hand, for the high pressure specimens, CuO_2 planes is in an over-doped state and a charging state of them is robust in this treatment, whereas the valence of Tl also decreases with the annealing temperature. The results of the high pressure specimen is interpreted as a majority of the electrons left by the reduction should be absorbed into the Tl ions in their charge reservoir, which consequently should lead the much moderate change of the hole-concentration of the CuO_2 planes. It means that a potential distribution within an unit cell can be controlled without a fatal decrease of the hole concentration of the CuO_2 planes. These results indicate that an utilization of this charge-redistribution mechanism present in the over-doped specimens should be an advantageous way to optimize electronic structure of HTS with nonequivalent CuO_2 planes for high T_c .

2. EXPERIMENTAL PROCEDURE

The high pressure (HP) samples were prepared from almost carbon-free (Ba, Ca)-Cu-O precursors and Tl-O powders by sintering at 850 °C under 4 GPa. This procedure resulted in randomly oriented polycrystalline ceramics with very low porosity. The ambient pressure (AP) ones were obtained by a conventional powder process. Chemical formula of both kinds of the samples was $\text{TlBa}_2\text{Ca}_2\text{Cu}_3\text{O}_y$. Details of the sample-preparation were

described previously [1], [7]. As shown in Table I, in as-sintered state, T_c of the HP and AP samples were 100 K and 123 K, respectively. The increase T_c of the former beyond 130 K and little change of T_c of the latter were confirmed in a separated experiment.

Figure 1 shows a change of Ba 4d signals with surface-treatments. Ba 4d signals of the fractured surfaces were dominated with the intrinsic component which exhibits a binding energy of the $4d_{5/2}$ peak of 87.5 eV. For the HP samples, a simple fracturing in ultra high vacuum successfully yielded a clear photoelectron Fermi edge. The AP samples contained a lot of pores of which inner walls were degraded. The fracturing of such structure resulted in not only fresh planes but also an exposure of the contaminated walls. An in-situ annealing under the atomic oxygen beam with flux density of 5×10^{15} atoms/cm²sec was adopted to the AP samples subsequently to the fracturing. This cleaning procedure also developed the Fermi edge and the single component feature of their Ba 4d signals.

The samples were, then, transferred into an analysis system. XPS has been performed at room temperature. Monochromatized Al-K α radiation were used for excitation. Electron binding energies were calibrated by using *in-situ* deposited Au layer. Overall energy resolution was 450 meV estimated from the slope of the Fermi edge of the Au. After the initial measurement of the clean surfaces, they were annealed in UHV and a subsequent measurement was performed. The treatment temperature T_{ann} was elevated by 100 °C every anneal-measurement cycle.

Table I T_c of the Tl-1223 specimens synthesized under a high pressure (HP) and ambient pressure (AP) at as-grown state and after reduction above 500 °C in flowing nitrogen.

sample	T_c (K)	
	as-grown	after the reduction
HP	~ 100	133.5
AP	123	123

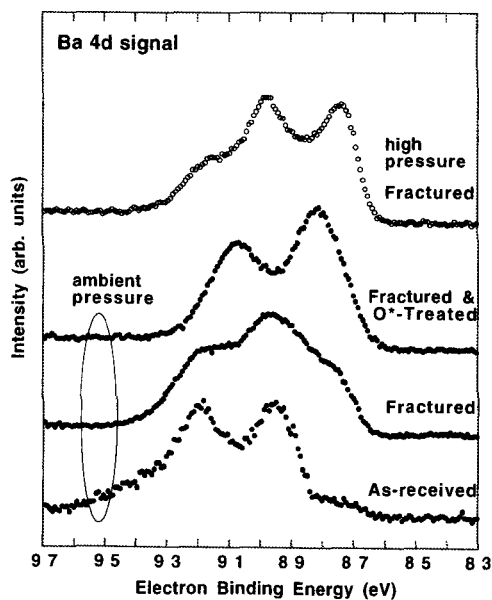


Fig.1 A change of Ba 4d signals of the high-pressure and ambient pressure samples with surface treatments.

3. RESULTS AND DISCUSSION

For both kinds of the specimens, the Fermi edges were detectable up to T_{ann} of 500 °C, though heights of the Fermi edges were reduced with an increase of T_{ann} . A valence band main peak, which should have Cu 3d character, around binding energy of 3 eV and O 1s signal of both samples exhibited almost coherent shift towards higher energy side with a rise of T_{ann} . The shift of the HP and AP samples by the annealing of 500 °C amounted 0.25 and 0.4 eV, respectively. These results indicate that the metallic nature of the specimens should be conserved close to

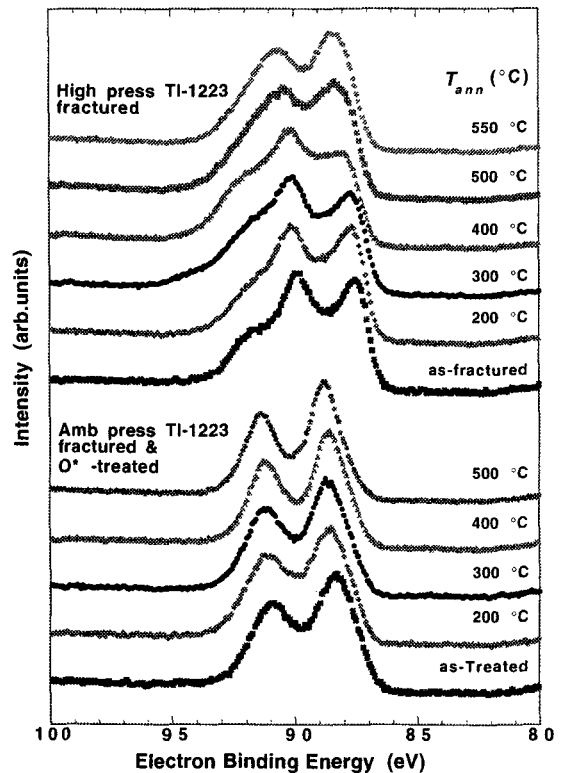


Fig.2 A change of Ba 4d signals of the Tl-1223 grown under the high- and ambient-pressure with vacuum annealing temperature T_{ann} .

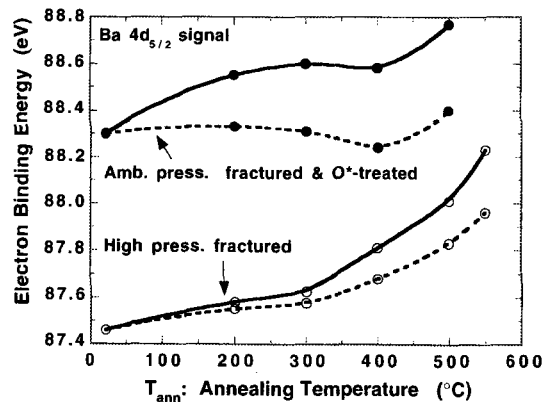


Fig.3 T_{ann} dependence of binding energy of Ba $4d_{5/2}$ peak of the Tl-1223 synthesized under the high- and ambient-pressure. The dashed lines show the binding energy relative to the Fermi level of the non-annealed state ($T_{ann} = 27$ °C) of each sample.

their decomposition, and that the Fermi energy should increase by some tenths of eV with a rise of T_{ann} .

T_{ann} dependences of the Ba 4d spectra and of binding energy of Ba $4d_{3/2}$ peak of the HP and the AP samples are shown in Fig.2 and Fig.3, respectively. Before the vacuum annealing, electron binding energy of the intrinsic (bulk) component of the $4d_{5/2}$ peak of the HP specimen was 87.4 eV, while that of the AP specimen exceeded 88 eV. This difference means that an effective oxygen-coordination number of the Ba ions in the HP sample should be higher with respect to that in the AP one. Both of peak exhibited a positive shift with an increase of T_{ann} . Though it is well known that the binding energy of Ba core signals of HTS is dominated by an initial state electrostatic effects due to closely packed oxygen ligands [8], the shifts observed in the present study should include the binding energy reference effects due to the increase of the Fermi level. Dashed lines in Fig.3 represent the binding energy of the $4d_{3/2}$ peaks with respect to the original Fermi level of each sample before the vacuum annealing. In the region of T_{ann} below 300 °C, the corrected binding energy of both kinds of the samples is almost independent of T_{ann} , which means that the chemical potential shift should be dominant in this region. In the region of T_{ann} above 300 °C, the positive slope of the HP sample remains still, whereas the corrected binding energy of the AP sample does not show any significant change all over the annealing conditions. These results indicate that the oxygen coordination number or valence bond sum of the Ba ions in the HP sample should be rather high and it should be lowered as a function of T_{ann} . Contrarily, that in the AP sample stayed at its low initial value.

Figure 4 shows changes of Tl 4f signals with T_{ann} . For the as-fractured state, The $4f_{7/2}$ peak of the HP and AP samples located at a binding energy of 117.4 and 117.9 eV, respectively. Taking into account that reported binding energies of Tl $4f_{7/2}$ peak of Tl_2O_3 and Tl_2O are 117.4 and 118.6 eV, respectively [9], [10], the Tl ions of the non-annealed HP sample is trivalent, while those in the as-grown AP samples are already in a mixed-valence state. Positive shifts of these peaks with an increase of T_{ann} were observed. In the present study, the maximum T_{ann} where the metallic feature was still conserved was 500 °C. After this high temperature annealing, the Tl $4f_{7/2}$ peaks moved

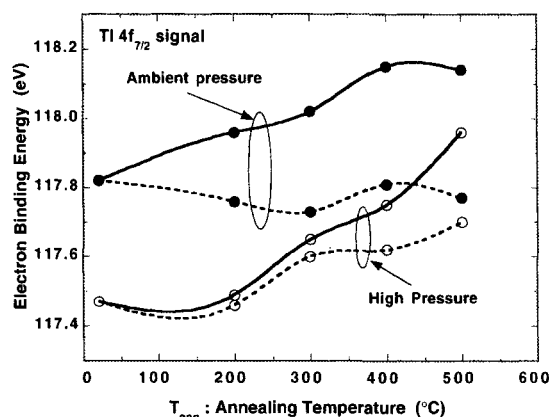


Fig.4 T_{ann} dependence of binding energy of Tl $4f_{7/2}$ peak of Tl-1223 synthesized under the high- and ambient-pressure. The dashed lines show the binding energy relative to the Fermi level of the non-annealed state of each sample.

to 118.0 ~ 118.1 eV. These results indicate that a decrease of valence of the Tl ions by this reduction. This is also consistent with the decrease of an effective oxygen coordination numbers of the Ba ions, which are adjacent to the Tl-O layers. Some parts of excess electrons left in the reduction should be absorbed into the Tl ions in the charge reservoir blocks of the 1223 structure. The difference between the amounts of the shifts suggests that this phenomenon in the HP samples should be more remarkable than in the AP ones.

Figure 5 and 6 show T_{ann} dependences of Cu $2p_{3/2}$ spectra and of binding energy of the main peak in this signal

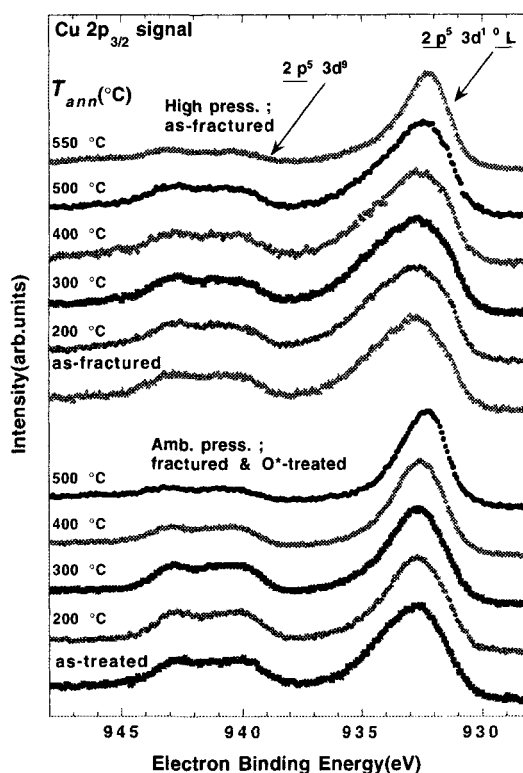


Fig.5 A change of Cu $2p_{3/2}$ signals of Tl-1223 synthesized under the high- and ambient-pressure with vacuum annealing temperature T_{ann} .

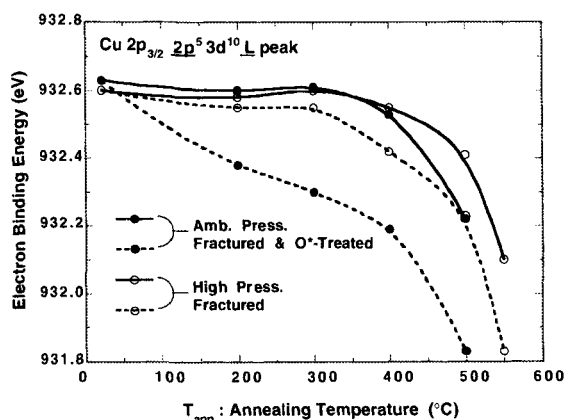


Fig.6 T_{ann} dependence of binding energy of Cu $2d_{3/2}$ $2p^5 3d^{10} \underline{L}$ (\underline{L} : ligand hole) peak of Tl-1223 synthesized under the high- and ambient-pressure. The dashed lines show the binding energy relative to the Fermi level of each non-annealed state.

which has $2p^53d^{10}\underline{L}$ (L: hole in ligand) final state, respectively. With an increase of T_{ann} , the main peak of both kinds of the samples becomes narrower. The narrowing in the AP sample looks steeper than the other. For the AP sample, a remarkable decrease of the binding energies of this peak with respect to the Fermi level of the non-annealed state (filled symbol-dashed line in Fig.5) was observed even in a low region of T_{ann} . On the other hand, the binding energy of the HP sample exhibited a much slower decrease even in a high region of T_{ann} up to 500°C. A ratio of an integrated intensity of the $2p^53d^9$ peak to that of the $2p^53d^{10}\underline{L}$ one of the AP samples decreases faster than that of the HP one. It has been reported that the valence of the CuO_2 planes should be positively correlate with the binding energy, and that a deviation of the valence of Cu from 2+ should result in a decrease of ratio [10], [11]. These results mean the moderate decrease of the hole concentration of the CuO_2 planes in the HP sample against the reduction annealing, while the reduction of the AP sample even at the low temperature should cause a serious decrease of the concentration. A structure refinement of the two kinds of Tl-1223 showed the charge-reservoir of the AP specimen should have a lower oxygen-concentration and a higher degree of Ca-substitution for Tl than those of the HP one. The remarkable difference in the annealing effect on the electronic structure should originate in the initial deviations of the microstructure between the charge-reservoirs.

In conventional ceramics of Tl-1223 grown under ambient pressure, a fatal decrease of the hole concentration was observed even by the low temperature annealing. The porous structure and the low hole-concentration with respect to the high pressure one might dominate this phenomenon. On the other hand, for the high pressure-synthesized Tl-1223, a majority of the electrons left by the high temperature reduction should be absorbed into their charge reservoir, which consequently should lead the much more moderate change of the hole-concentration of the CuO_2 planes. The changes of the charging states of the charge reserving blocks and the variations of a distribution of intra-unit cell static potentials should also affect a hole-distribution of the CuO_2 planes. Since the effect on the two outer CuO_2 planes, which were over-doped in the as-grown states should be more significant than on the optimally or slightly under doped inner one in the 1223 structure [12]. Such a change of potential-distribution without a fatal fall of hole-content should be advantageous for optimizing electronic structure of the 1223 phases including the hole-distribution among the CuO_2 planes.

4. SUMMARY

A change of electronic structure of $\text{TlBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{9.8}$ [Tl-1223] superconductors synthesized under ambient and a high pressure as a function of reduction-annealing temperature has been investigated by *in-situ* XPS. Systematic shifts of binding-energy of core signals of the constituents around the charge reservoir-blocks with increase of the annealing temperature indicate a selective oxygen-depletion around the charge-reservoir blocks, and a decrease of Tl-valence, while spectra of Cu were robust with the treatment. The phenomena in the high temperature-treated specimens is interpreted as a majority of the electrons left by the reduction should be absorbed into the Tl ions in

their charge reservoirs and some electrons might be also pulled out from CuO_2 planes. It should lead the much more moderate change of the hole-concentration of the CuO_2 planes, while intra-unit cell potential-distribution should be modified by the reduction. The steep decrease of the hole concentration with T_{ann} on the ambient pressure samples may be caused by a structural difference of the Tl-O charge reservoirs and the low hole-content in their non-annealed state. Taking into account that the high T_c above 133 K is realized by reducing these systems above 350 °C, utilization of this charge redistribution mechanism, starting from the over doped state, should be an excellent way to optimize the hole distribution among the nonequivalent CuO_2 planes without a fatal decrease of total concentration of holes.

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