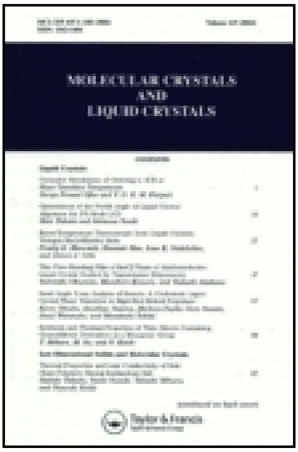

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

# X-ray Photoelectron Spectroscopic Evidence for $Cu^{3+}$ Valence State in Superconducting Phase, $YBa_2Cu_3O_{7-\delta}$

Jin-Ho Choy [a] , Duk-Young Jung [a] & Q. Won Choi [a]
[a] Department of Chemistry, College of Natural Sciences, Seoul National University, Seoul, 151-742, Korea

To cite this article: Jin-Ho Choy , Duk-Young Jung & Q. Won Choi (1990): X-ray Photoelectron Spectroscopic Evidence for $Cu^{3+}$ Valence State in Superconducting Phase, $YBa_2Cu_3O_{7-\delta}$ , Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 184:1, 61-67

To link to this article: http://dx.doi.org/10.1080/00268949008031739

*Mol. Cryst. Liq. Cryst.*, 1990, vol. 184, pp. 61–67
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

# X-ray Photoelectron Spectroscopic Evidence for $Cu^{3+}$ valence state in superconducting phase, $YBa_2Cu_3O_{7-\delta}$

Jin-Ho Choy, Duk-Young Jung and Q. Won Choi
Department of Chemistry, College of Natural Sciences, Seoul National University
Seoul 151-742, Korea

Abstract X-ray photoelectron spectra of the Cu 2p and O 1s core levels of $YBa_2Cu_3O_{7-\delta}$ ($\delta$=0.09 and 0.40) provide us with the evidence of the mixed valency of $Cu^{2+}$ and $Cu^{3+}$ in $YBa_2Cu_3O_{6.91}$. The binding energies of Cu $2p_{3/2}$ and $2p_{1/2}$ states in $YBa_2Cu_3O_{7-\delta}$ samples are compared with those of $La_2CuO_4$, $Y_2BaCuO_5$ and $La_4LiCuO_8$ which contain $Cu^{2+}$ and $Cu^{3+}$, exclusively. The O1s XPE spectra disclosed at least two, possibly three, with the major contribution at the binding energies of 529.6 and 532.0 eV. We have found no evidence for the existence of $O_2^{2-}$ species (Binding Energy $\geq$ 533 eV) in the prepared Y-Ba-Cu oxides. Additionally, absence of peroxide ion ($O_2^{2-}$) in $YBa_2Cu_3O_{7-\delta}$ has been confirmed by colorimetric test using $Ti^{4+}$ solution.

## INTRODUCTION

The recently discovered high temperature superconductor $YBa_2Cu_3O_7$ has been studied extensively after the first report in the La-Ba-Cu-O system by Bednorz and Müller[1] in order to understand how the crystal structure and superconductivity correlate to each other. Although the real mechanism leading to such a high Tc of about 90 K is now under debate, it has become more evident that the content of oxygen and the mixed valency of Cu or O play an important role in the superconductivity.

There have been contradictory results on the determination of the electronic states of Cu, which lead to the conclusions confirming or ruling out the existence of $Cu^{3+}$ even in the samples with $\delta$ close to zero. The confirmation of $Cu^{3+}$ has been achieved by means of chemical analysis,[2] X-ray photoelectron spectrosopy[3-6] and X-ray absorption spectroscopy.[7-8] However, it has been also reported that $Cu^{3+}$ ion is clearly excluded in the phase by the similar experiments.[9-20] Recent reports[17-20] for XPE spectroscopic measurement on O 1s insisted that there exists peroxide ion in $YBa_2Cu_3O_{7-\delta}$. Therefore it is of interest to reveal the presence of either $Cu^{3+}$ or $O_2^{2-}$ in the high Tc oxides because the high oxygen content ($\delta$<0.5) could induce a high oxidation state for copper, that is, $Cu^{3+}$, or unusual oxygen species(e.g. $O_2^{2-}$) in $YBa_2Cu_3O_{7-\delta}$.

## EXPERIMENTAL SECTION

Superconducting phase $YBa_2Cu_3O_{7-\delta}$ was prepared by thermal decomposition reaction of corresponding metal nitrate precursors, which were obtained by dissolution of stoichiometric mixture of $Y_2O_3$, $Ba(NO_3)_2$ and Cu metal in an aqueous solution of nitric acid. After the heat treatment at 400 °C, the sample was well-ground, pelletized and transferred to the furnace for the calcination. Sample I and II were calcined at 910 °C in $O_2$ for 25 hrs twice, and then sample I was annealed at 300 °C whereas sample II was quenched from 910 °C. $La_2CuO_4$, $Y_2BaCuO_5$ and $La_4LiCuO_8$ were prepared for the reference materials in the XPE spectroscopic measurement. The samples were characterized by powder X-ray diffractometer with JEOL DX-GO-2 equipped with Ni filtered Cu-K$\alpha$ radiation ($\lambda$= 1.5418 Å). The average oxidation state of copper was estimated by iodometric titration as previously reported.[21] The electrical resistance of Sample I was measured by DC-four probe method from 77 to 300K. Its magnetic susceptibility data were obtained from liquid helium to room temperature.

XPE spectra were obtained by PHI 5100 Perkin-Elmer spectrometer which has been calibrated by $Ag3d_{5/2}$, $Ag3p_{3/2}$, $Au4f_{7/2}$ and carbon(graphite) 1s core level energies. Unmonochromated Mg-K$\alpha$ radiation of 1253.6 eV was used and the resolution of X-ray beam is about 0.8 eV. The base pressure in the spectrometer chamber was lower than $2.0 \times 10^{-9}$ Torr. In order to authenticate the existence of arguing $O_2^{2-}$ in $YBa_2Cu_3O_{7-\delta}$, absorption spectroscopic tests were performed semi-quantitatively by dissolving about 0.1g of the sample in 4 ml of 0.013 M $Ti^{4+}$ in aqueous sulfuric acid solution.

## RESULTS AND DISCUSSION

The electrical resistivity of sample I shows a sharp transition to zero resistance at 90 K. Magnetic measurement from 4 to 150 K is illustrated in Figure 1, in which

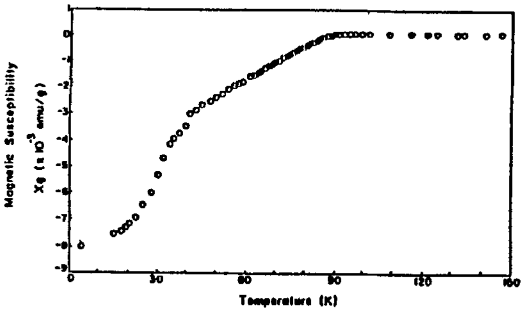

FIGURE 1 Temperature Dependent Magnetic Susceptibility of $YBa_2Cu_3O_{6.91}$ (Sample I).

Meissner effect appeared at 90 K in accordance with the result of the resistivity measurement. Structural analysis of the prepared $YBa_2Cu_3O_{7-\delta}$ confirm the fine preparation of samples and their lattice parameters are given in Table 1. Up to now, it is rather well established that the crystal structure of superconducting $YBa_2Cu_3O_7$ contains two types of copper, one in the corner shared $[CuO_4]$ chains(square planar-Cu(1)) between two Ba-O planes and the other in $[CuO_5]$ layers(square pyramidal-Cu(2)) between Ba-O and Y planes, respectively perpendicular to the c axis direction.[22-23] Simple calculations of crystal field stabilization energies (CFSE) [24] of copper ions($Cu^{2+}$and $Cu^{3+}$) were performed in the reduced symmetries of $C_{4v}$ and $D_{4h}$, respectively. It is quite evident that square planar site prefers $Cu^{3+}$(-24.56Dq) to $Cu^{2+}$(-12.28Dq). Therefore $Cu^{2+}$ fails to keep in the $D_{4h}$ site and presumably is forced to occupy the $C_{4v}$ site. It should be noted that $Ni^{2+}$, $Pd^{2+}$, $Pt^{2+}$ and $Au^{3+}$ with $d^8$ electron configurations are stabilized in square planar complexes. On the bonding charateristics, the unexpectedly short Cu(1)-O(4) bond length of 1.843 A, simliar to that found in alkali metal cuprates such as $KCuO_2$ and $NaCuO_2$, suggests that the $Cu^{3+}$ ions preferentially occupy the sqaure planar Cu(1) site. Locating $Cu^{2+}$ and $Cu^{3+}$ ions on Cu(2) and Cu(1) sites, respectively, yields

TABLE 1. Lattice parameters(Å) and Chemical analysis for $YBa_3Cu_3O_{7-\delta}$

| | a | b | c | formula $YBa_2Cux^{2+}Cuy^{3+}O_z$ x | y | z | $Cu^{3+}/Cu^{2+}$ |
|---|---|---|---|---|---|---|---|
| Sample I | 3.8242 | 3.8872 | 11.683 | 2.18 | 0.82 | 6.91 | 0.38 |
| Sample II | 3.8343 | 3.8782 | 11.703 | 2.80 | 0.20 | 6.60 | 0.07 |

the ideal formulae $YBa_2Cu_3O_7$.

The XPE spectra of Cu-2p level show the $2p_{1/2}$-$2p_{3/2}$ spin-orbit doublet, accompanied by shake-up lines which are shifted by 8 - 9 eV to the higher binding energy site from the main 2p peaks(Figure 2). Such satellites are frequently observed[25] in core-level photoemission from divalent copper compounds and are attributed to a ligand-to-metal charge transfer ($2p^63d^9 \rightarrow 2p^53d^{10}$) in the final state of photoemission process, thereby effectively screening the excited core-hole. The observation of these satellites provides strong evidence for a $Cu^{2+}$ or higher valence state in the presently studied quaternary oxides. The ratio of satellite to 2p in Sample I ($YBa_2Cu_3O_{6.91}$) is smaller than in Sample II ($YBa_2Cu_3O_{6.60}$), which indicate the lower content of $Cu^{2+}$ in Sample II. The spectrum of $Y_2BaCuO_5$ is very similar with that of Sample II, showing that Sample II includes Cu ion in the valence of 2+, exclusively. After 10 minutes ion etching of $YBa_2Cu_3O_{6.91}$, however, the satellite peaks become strongly suppressed while the Cu 2p signals become very narrow and their positions are shifted to lower binding energy site. This change of Cu 2p spectra is due to the local reduction of $Cu^{2+}$ and $Cu^{3+}$ to $Cu^+$ by the ion bombardment under high vacuum.[26] Therefore, the surface cannot be cleaned by sputtering due to decomposition of sample by the ion beam. Mechanical scraping also causes a great damage to the crystal structure. In our experiment, all samples have been managed with great care to prevent from surface contamination. As shown in Figure 2, the area of $2p_{3/2}$ peak where the binding energy is approximafely 934

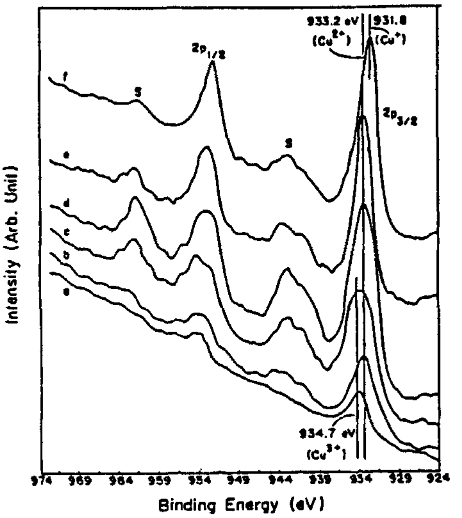

FIGURE 2 XPE Spectra in the Region of the Binding Energy for Cu2P Electron in a) $La_4LiCuO_8$ b) $La_2CuO_4$ c) $YBa_2Cu_3O_{6.91}$ d) $YBa_2Cu_3O_{6.60}$ e) $Y_2BaCuO_5$, and f) after 10 mins. sputtering of sample (c).

eV increases obviously in the Sample I with high oxygen content, which is expected to be from $Cu^{3+}$.

The comparison among the $2p_{3/2}$ peaks of Sample I, II, $La_2CuO_4(Cu^{2+})$, $Y_2BaCuO_5(Cu^{2+})$ and$La_4LiCuO_8(Cu^{3+})$[27] makes it possible to prove the mixed valence of Cu in $YBa_2Cu_3O_{6.91}$. The binding energies were 933.2 eV for the Cu $2p_{3/2}$ electrons in $Y_2BaCuO_5$ and $La_2CuO_4$ with only $Cu^{2+}$ and 934.7 eV in $La_4LiCuO_8$ in which only $Cu^{3+}$ ions exist. $La_4LiCuO_8$ has been prepared at 800 °C under the high oxygen pressure (1 kbar) for this measurement, which specifies $Cu^{3+}(d^8)$ with no shake-up peaks. According to these results, the spectra for Sample I are consistent with a mixture of $d^8(Cu^{3+})$ and $d^9(Cu^{2+})$ configurations as a ground state. Also it can be deduced that in Sample II there are small amounts of $Cu^{3+}$ ions, as shown in Figure 2-(d). Such an investigation technique is only valid for the surface anlysis, therefore, it could not be completely excluded for $Cu^{3+}$ to be stabilized on the surface due to the decrease of coordination number. $Cu^{3+}$ in $d^8$ low spin state configuration$(t_{2g}{}^6d_{z^2}{}^2)$ is stabilized in a strongly distorted octahedra($La_4LiCuO_8$) or in square planar surrounding($NaCuO_2$).

The O1s spectra consist of two main contribution at 530 and 532 eV, as shown in Figure 3. Though they are not fully assigned, it is certain that the overlapping shape result from the different coordination environments. Recent days, there are several reports[17-20] that XPE spectra exhibit an extra O1s peaks showing direct contact between oxygen atoms($O_2{}^{2-}$) in the $YBa_2Cu_3O_{7-\delta}$ structure. The photoemission data of O1s for $YBa_2Cu_3O_{7-\delta}$ (Sample I and II) provide no evidence of such peroxide-like species. They insisted the extra peak

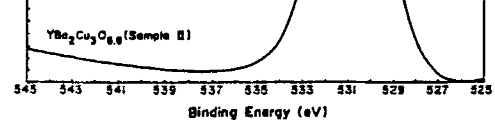

FIGURE 3 XPE Spectra of Oxygen 1s for $YBa_3Cu_3O_{6.91}$ and $YBa_2Cu_3O_{6.60}$

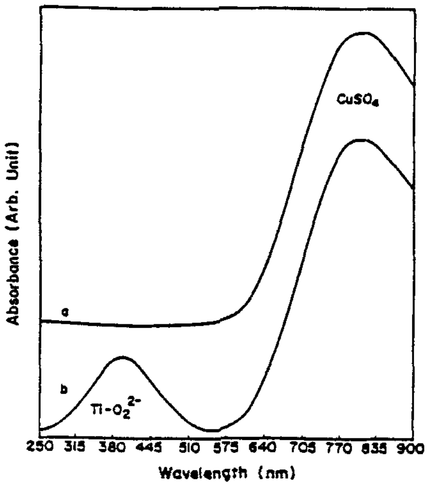

FIGURE 4 Absorption Spectra of the $Ti^{4+}$-Solutions.

a) $YBa_2Cu_3O_{6.91}$ dissolved in $Ti^{4+}$-solution.

b) 2 mM $H_2O_2$ in $Ti^{4+}$-solution (a).

(533-534 eV) should correspond to peroxide ion ($O_2^{2-}$), excluding the existence of $Cu^{3+}$ ion in the superconducting phase. Colorimetric analysis is applied to $YBa_2Cu_3O_{6.91}$ superconductor in order to verify the possible existence of $O_2^{2-}$ ion in the lattice. Assuming that $O_2^{2-}$ions exist in Sample I with a formula of $YBa_2Cu_3(O^{2-})_6(O_2^{2-})_{0.46}$, the expected concentration of of peroxide ion in 4 ml of $Ti^{4+}$ solution is 2 mM, where 126 mg of Sample I is dissolved. The expected $[O_2^{2-}]$ is larger than the detection limit ($10^{-5}$ M) of the titanium-complex technique. However, as shown in Figure 4, there is no absorbance around 405nm in the sample solution. On the contrary, the reference solution containing 2 mM of hydrogen peroxide shows the relatively strong absorbance in the same region.

It clearly shows the absence of $Ti^{4+}$-$O_2^{2-}$ complex in the sample solution, supporting the XPE spectroscopic data for oxygen 1s core-electron. Therefore the peaks at high binding energy (533-534 eV) in O 1s XPE spectra, which others have reported, must come from surface interaction with adsorbed oxygen, water, or from the other oxygen containing impurities. From the results of XPE spectroscopic and colorimetric analyses, the stably isolated $O_2^{2-}$ in the lattice could be excluded.

## ACKNOWLEDGEMENT

The financial support for this work from Korean Ministry of Science and Technology is greatly appreciated.

## REFERENCES

1. J. G. Bednorz and K. A. Müller, Z.Phys., B64, 189 (1986).
2. S. X. Dou, H. K. Liu, A. J. Bourdillon, N. Savvides, J. P. Zhou and C. C. Sorrell, Solid State Commun., 68, 221 (1988).
3. H. Eikenbusch, W. Paulus, R. Schöllhorn and R. Schlogl, Mat. Res. Bull., 22, 1505, (1987).
4. A. Balzarotti, M. De Crescenzi, N. Motta, F. Patella and A. Sgarlata, Phys. Rev., B38, 6461 (1988).
5. P. Steiner, S. Hufner, V. Kisinger, I. Sander, B. Siegwart, H. Schmitt, R. Schulz, S. Junk, G. Schwitzgebel, A. Gold, C. Politis, H. P. Muller, R. Hoppe, S. Kemmler-Sack and C. Kruz, Z. Phys., B69, 449 (1988).
6. E. Sacher and J. E. Klemberg-Sapieha, Phys. Rev., B39, 1461 (1989).
7. H. Oyanag, H. Ihara, T. Matsubara, M. Tokumoto, T. Matsushita, M. Hirabayashi, K. Murata, N. Terada, T. Yao, H. Iwasaki and Y. Kimura, Jpn. J. Appl. Phys., 26, L1561 (1987).
8. J. B. Boyce, F. Bridges, T. Claeson, R. S. Howland and T. H. Geballe, Phys. Rev., B36, 5251 (1987).
9. T. A. Sasaki, Y. Baba, N. Masaki and I. Takano, Jpn. J. Appl. Phys., 26, L1569 (1987).
10. D. D. Sarma and C. N. R. Rao, Solid State Commun., 65, 47 (1988).
11. H. Fjellvag, P. Karen, A. Kjekshus and J. K. Grepstad, Solid State Commun., 64, 917 (1987).
12. E. D. Crozier, N. Alberding, K. R. Bauchspiess, A. J. Seary and S. Gygax, Phys. Rev., B36, 8288 (1988).
13. S. Horn, J. Cai, S. A. Shaheen, Y. Jeon, M. Croft, C. L. Chang and M. L. denBoer, Phys. Rev., B36, 3895 (1987).
14. J. A. Yarmoff, D. R. Clarke, W. Drube, U. O. Karlsson, A. Taleb-Ibrahimi and F. J. Himpsel, Phys. Rev., B36, 3967 (1987).
15. P. Kuiper, G. Kruizinga, J. Ghijsen, M. Grioni, P. J. W. Weijs, de F. J. F. Groot, G. A. Sawatzky, H. Verwij, L. F. Feiner and H. Peterson, Phys. Rev., B38, 6483 (1988).
16. P. Thiry, G. Rossi, Y. Petroff, A. Revocolevschi and J. Jegoudez, Europhys. Lett., 5, 55 (1988).
17. Y. Dai, A. Manthiram, A. Campion and J. B. Goodenough, Phys. Rev., B38, 5091 (1988).
18. C. N. R. Rao, P. Ganguly, J. Gopalakrishnan and D. D. Sarma, Mat. Res. Bull., 22, 1159 (1987).
19. D. D. Sarma, K. Sreedhar, P. Ganguly and C. N. R. Rao, Phys. Rev., B36, 2371 (1987).
20. C. N. R. Rao, P. Ganguly, M. S. Hegde and D. D. Sarma, J. Am. Chem. Soc., 109, 6893 (1987).
21. J. H. Choy, S. Y. Choi, S. H. Byeon, S. H. Chun, S. T. Hong, D. Y. Jung, W. Y. Choe and Y. W. Park, Bull. Korean Chem.Soc., 9, 289 (1988).
22. D. R. Clarke, Adv. Cer. Mat., 3B, 273 (1987).
23. W. I. F. David, W. T. A. Harrison, J. M. F. Gunn, O. Moze, A. K. Soper, P. Day, J. D. Hinks, M. A. Beno, L. Soderholm, D. W. Capone II, I. K. Schuller, C. U. Segre, K. Zhang and J. D. Grace, Nature, 327, 310 (1987).
24. J. H. Choy, S. H. Byeon, S. T. Hong, D. Y. Jung, S. Y. Choi, B. W. Kim, J. T. Kim, D. Y. Noh, H. I. Yoo, D. N. Lee, D. Y. Seung and T. S. Park, J. Korean Ceramic Soc., 25, 154 (1988).
25. A. Reller and Ber Bunsenges, Phys. Chem., 90, 742 (1986).
26. H. M. Meyer III, D. M. Hill, T. J. Wagener, Y. Gao, J. H. Weaver, D. W. Capone II and K. C. Goretta, Phys. Rev., B38, 6500 (1988).
27. G. Demazeau, C. Parent, M. Dovchard and P. Hagenmuller, Mat. Res. Bull., 7, 913 (1972).