

Peculiar hole doping by Ca substitution in cuprate superconductors

J.-Y. Lin¹, P. C. Chung¹, S. J. Liu², C. C. Hsiang¹, P. H. Lin¹,
J. M. Lee³, J. M. Chen³, K. H. Wu², and Y. S. Gou²

¹*Institute of Physics, National Chiao Tung University, Hsinchu 300,
Taiwan ROC*

²*Department of Electrophysics, National Chiao Tung university, Hsinchu 300,
Taiwan ROC*

³*Synchrotron Radiation Research Center (SRRC), Hsinchu 300,
Taiwan ROC*

The doping effect of Ca substitution in $Y_{0.7}Ca_{0.3}Ba_2Cu_3O_y$ has been studied for $y=6.9$ and 6 by the x -ray absorption near edge spectroscopy (XANES). While Ca doping leads to an obvious increase in hole concentration in the CuO_2 planes in $Y_{0.7}Ca_{0.3}Ba_2Cu_3O_{6.9}$, XANES indicates absence of this doping effect in $Y_{0.7}Ca_{0.3}Ba_2Cu_3O_6$. These two contradict results suggest that the doping effect by Ca substitution could be sensitive to the oxygen content when $y \sim 6.0$. Comparisons with others' works are made.

PACS numbers: 78.70.Dm, 74.72.Bk, 74.62.Dh, 74.25.Jb.

Carrier doping is essential to the superconductivity and many other important physical properties of cuprate superconductors. It is well known that there are several ways of doping hole carriers to cuprates. For example, in the $YBa_2Cu_3O_y$ (YBCO) system, holes can be doped either by varying the oxygen content y or by the substitution of 2+ alkaline earth elements like Ca for the 3+ rare earth Y. Since YBCO is a layered compound, the distribution of the doped carriers on specific sites through different doping mechanisms is an interesting issue. Furthermore, There are controversies on some of the fundamental features of Ca-doped YBCO, especially for the highly oxygen deficient samples. For example, Ref. 1 reported the observation of superconductivity in $YCa_xBa_2Cu_3O_y$ with $x=0.2$ and $y \sim 6$, while absence of superconductivity in samples with the same nominal composition was claimed by others^{2,3}. In a recent work on similar compounds

$\text{Yb}_{1-x}\text{Ca}_x(\text{Ba}_{0.8}\text{Sr}_{0.2})_2\text{Cu}_3\text{O}_6$, there was no superconductivity for x up to 0.20. However, occurrence of superconductivity was observed for $x \geq 0.25^4$. Another related puzzle is the doping effect of Ca for $x \sim 6$. For oxygenated YBCO, it is established that Ca doping leads to an increase in the hole concentration *only* in the CuO_2 planes, in contrast with the change of the hole concentration in all the CuO_2 plane, CuO chain, and apical oxygen sites by variation of the oxygen content³. Nevertheless, whether Ca doping would lead to the same effect in the deep underdoped regime $y \sim 6$ is not clear at the moment.

These issues mentioned above are fundamentally significant. Without complete knowledge of doping mechanism and the effect of doped carriers on T_c , one can not claim the basic understanding of cuprates, let along the superconductivity mechanism behind them. The x-ray absorption near edge spectroscopy (XANES) has proven to be a powerful tool to investigate the site-specific carriers in cuprate³⁻⁶. In this paper, we focus on XANES studies of $\text{Y}_{1-x}\text{Ca}_x\text{Ba}_2\text{Cu}_3\text{O}_y$.

$\text{Y}_{1-x}\text{Ca}_x\text{Ba}_2\text{Cu}_3\text{O}_y$ thin films with nominal composition $x=0.3$ were deposited on SrTiO_3 (100) substrates by laser pulsed ablation. A KrF excimer laser was employed. The substrate temperature was kept at 750 °C during deposition and the oxygen partial pressure was 300 mtorr. Thickness of the films is about 200 nm. X-ray diffraction patterns show that the films are highly c-axis oriented. This allows the studies of the crystalline direction dependence of the electronic structure by XANES. XANES in florescence mode is a powerful tool to investigate the unoccupied (hole) electronic states in complex materials and is bulk sensitive. In particular, polarized XANES can give information about the distribution of the site specific carriers. Energy resolution of the monochromator is about 0.2 eV for the O K -edge energy range. The saturation (or "self-absorption") effects were corrected for all measured spectra normalized to the tabulated standard absorption cross section in the energy range 600 to 620 eV.

The as-prepared thin films were annealed at 450 °C in oxygen atmosphere for 30 minutes together with a YBCO thin film. The oxygen content y was thus assign as 6.9 according to T_c of YBCO. The oxygen depleted $\text{Y}_{1-x}\text{Ca}_x\text{Ba}_2\text{Cu}_3\text{O}_y$ was prepared by annealing at 450 °C in the vacuum of $\sim 10^{-6}$ torr for 1 hour. The sample was insulating and the resistivity ρ was beyond the limit of our instrument to measure. The oxygen content y was then assigned to be 6. It is noted that $\text{Y}_{0.7}\text{Ca}_{0.3}\text{Ba}_2\text{Cu}_3\text{O}_6$ is much easier to prepare in the thin film form than in the bulk or single crystals for oxygen is relatively easy to remove from the interior of the sample. After XANES experiments the $\text{Y}_{0.7}\text{Ca}_{0.3}\text{Ba}_2\text{Cu}_3\text{O}_6$ thin film was annealed again at 400 °C in oxygen atmosphere for 30 minutes. Both T_c and $\rho(T)$ revert to almost

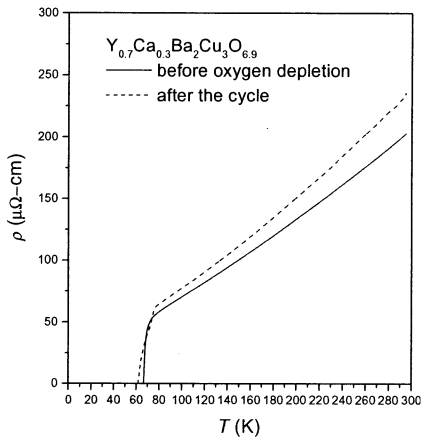


Fig. 1. $\rho(T)$ of the Ca-doped YBCO shows a nearly complete recovery from the oxygen depletion.

the same as those of the oxygenated sample (Fig. 1). This demonstrates that the annealing in the vacuum simply removed the oxygen from the CuO chains and the basic 123 structure remained its integrity even with $y \sim 6$. If the integrity of the structure had been diminished during the process, it could not have reverted to the original form by annealing at such a low temperature 400 °C.

Figs. 2 and 3 show XANES of $Y_{0.7}Ca_{0.3}Ba_2Cu_3O_{6.9}$ and $Y_{0.7}Ca_{0.3}Ba_2Cu_3O_6$ with the electric field of the light $\mathbf{E} \perp c$ and $\mathbf{E} // c$, respectively. XANES of $YBa_2Cu_3O_{6.9}$ was also included in both Figures for comparisons. XANES in Fig. 1 manifests the electronic structure of the ab plane. The peak centered around 528.4 eV is related to the Zhang-Rice (ZR) band, the peak around 529.7 eV is associated with the upper Hubbard band (UHB) and the feature around 527.9 eV is attributed to the electronic states of the CuO chain^{3,5,6}. Fig. 2 clearly shows that Ca doping leads to a significant increase in the spectral weight of the peak at 528.4 eV for the oxygenated sample, which manifests an increase in the hole number in the CuO₂ plane. However, this doping effect is clearly absent in $Y_{0.7}Ca_{0.3}Ba_2Cu_3O_6$, for there is no ZR spectral weight. Normally, a decrease in XANES contribution from

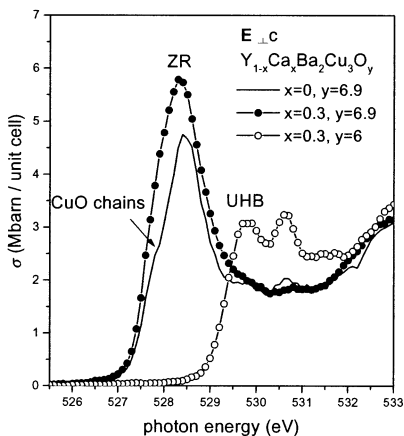


Fig. 2. O *K*-edge XANES for $\mathbf{E} \perp c$. While Ca doping leads to an increase in the ZR band spectral weight associated with the CuO₂ planes in $\text{Y}_{0.7}\text{Ca}_{0.3}\text{Ba}_2\text{Cu}_3\text{O}_{6.9}$, this doping effect is absent in $\text{Y}_{0.7}\text{Ca}_{0.3}\text{Ba}_2\text{Cu}_3\text{O}_6$.

ZR band would be accompanied by an increase in the spectral weight of UHB due to the strong correlation effects in the CuO₂ planes. This correspondence was also observed in $\text{Y}_{0.7}\text{Ca}_{0.3}\text{Ba}_2\text{Cu}_3\text{O}_6$. The peak at 530.8 eV can be associated to the oxygen depletion in the CuO chains. Actually, XANES of $\text{Y}_{0.7}\text{Ca}_{0.3}\text{Ba}_2\text{Cu}_3\text{O}_6$ in Fig. 2 is nearly identical to that of $\text{YBa}_2\text{Cu}_3\text{O}_6$ ³. All the clear features in the spectrum of $\text{Y}_{0.7}\text{Ca}_{0.3}\text{Ba}_2\text{Cu}_3\text{O}_6$ again suggest a decent structure of this oxygen deficient sample.

Fig. 3 shows the features associated with the *c*-axis direction. the peak around 528 eV is assigned to be the spectral weight of the apical holes. Ca doping does not lead to an increase in the apical hole number, consistent with the previous report³. The $\mathbf{E} // c$ spectrum of $\text{Y}_{0.7}\text{Ca}_{0.3}\text{Ba}_2\text{Cu}_3\text{O}_6$ does not show any spectral weight of the apical holes, and is very similar to that of $\text{YBa}_2\text{Cu}_3\text{O}_6$ ³.

To summarize, we have studied XANES of both $\text{Y}_{0.7}\text{Ca}_{0.3}\text{Ba}_2\text{Cu}_3\text{O}_{6.9}$ and $\text{Y}_{0.7}\text{Ca}_{0.3}\text{Ba}_2\text{Cu}_3\text{O}_6$. The spectra suggest that Ca doping leads to an increase in the hole concentration in the CuO₂ planes in $\text{Y}_{0.7}\text{Ca}_{0.3}\text{Ba}_2\text{Cu}_3\text{O}_{6.9}$, while no hole doping effect is found in $\text{Y}_{0.7}\text{Ca}_{0.3}\text{Ba}_2\text{Cu}_3\text{O}_6$. These results is

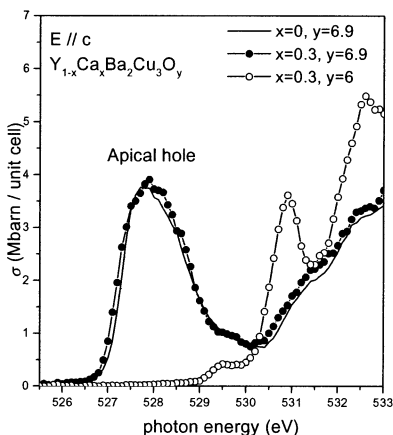


Fig. 3. O K -edge XANES for $\mathbf{E} // c$.

in consistent with those of Ref. 4, while in contrast to those of Ref. 3. The absence of the doping effect by Ca in $\text{Y}_{0.7}\text{Ca}_{0.3}\text{Ba}_2\text{Cu}_3\text{O}_6$ may reveal a subtle oxygen content dependence for y close to 6. In principle, XANES of Cu L -edge could provide indispensable information which helps to resolve the present puzzle, and is currently under investigation.

This work was supported by National Science Council of Republic of China under contract No. NSC90-2112-M-009-025.

REFERENCES

1. C. Bernhard and J. L. Tallon, *Phys.Rev. B* **54**, 10 201 (1996).
2. J. Hejtmaník, Z. Jiráček, K. Knížek et al., *Phys.Rev. B* **54**, 10 226 (1996).
3. M. Merz, N. Nucker, P. Schweiss et al., *Phys.Rev. Lett.* **80**, 5192 (1998).
4. M. Karppinen, H. Yamauchi, T. Nakane et al., *J. Solid State Chem.* **166**, 229 (2002).
5. J. M. Chen, R. S. Liu, J. G. Lin et al., *Phys.Rev. B* **55**, 14 586 (1997).
6. I. P. Hong, J.-Y. Lin, J. M. Chen et al., *Europhys. Lett.* **58**, 126 (2002).