Substitution effects in Bi$_2$Sr$_2$(Ca$_{1-x}$Y$_x$)Cu$_2$O$_{8+\delta}$ studied by X-ray absorption spectroscopy

R. S. Liu*, I. J. Hsu*, J. M. Chen* and R. G. Liu*

*Department of Chemistry, National Taiwan University, Taipei, Taiwan, R.O.C.

The Bi$_2$Sr$_2$(Ca$_{1-x}$Y$_x$)Cu$_2$O$_{8+\delta}$ system over the homogeneity range $x = 0 \sim 1.0$ has a maximal superconducting transition temperature ($T_c$) of around 92 K at $x = 0.2$. The hole distribution of overdoped, optimum doped and underdoped states in Bi$_2$Sr$_2$(Ca$_{1-x}$Y$_x$)Cu$_2$O$_{8+\delta}$ has been investigated by high-resolution O K-edge X-ray-absorption near-edge-structure (XANES) spectra. Near the O 1s edge, a well-pronounced pre-edge peak with maximum at $\sim$528.3 eV is found, which is ascribed to the excitations of O 1s electron to O 2p hole states located in the CuO$_2$ planes. The intensity of this pre-edge peak decreases as the Y doping increases, demonstrating that the chemical substitution of Y$^{3+}$ for Ca$^{2+}$ in Bi$_2$Sr$_2$(Ca$_{1-x}$Y$_x$)Cu$_2$O$_{8+\delta}$ gives rise to a decrease in hole concentrations within the CuO$_2$ planes. Moreover, the correlation between $T_c$ and critical current density ($J_c$) as a function of doping concentration has been studied. It is important to point out that the highest $J_c$ across the system is appeared at the overdoped side with $x = 0$ in Bi$_2$Sr$_2$(Ca$_{1-x}$Y$_x$)Cu$_2$O$_{8+\delta}$.

1. INTRODUCTION

The Bi$_2$Sr$_2$(Ca$_{1-x}$Y$_x$)Cu$_2$O$_{8+\delta}$ system exhibiting a composition-induced metal-superconductor-insulator transition may offer a great potential for investigating the important structural and electronic characteristic, which can lead to superconductivity at such extraordinary high temperature [1]. The system over the homogeneity range $x = 0 \sim 1.0$ has a maximal superconducting transition temperature ($T_c$) of around 92 K at $x = 0.2$. The depression of $T_c$ and the decreasing carrier concentration have been interpreted as a result of hole filling due to the additional electrons contributed by the trivalent Y$^{3+}$ ion relative to the divalent Ca$^{2+}$ ion. The X-ray absorption spectra are determined by electronic transitions from a selected atomic core level to the unoccupied electronic states near the Fermi level. X-ray absorption near edge structure (XANES) is therefore a direct probe to the character and local density of hole states responsible for high-$T_c$ superconductivity.

In this study, an attempt was made to use XANES for providing electronic structural
information across the system. Moreover, the correlation between \( T_c \) and critical current density (\( I_c \)) as a function of doping concentration has also been studied. The results reported here may be able to stimulate further experiments and theories, since the titled system offers a remarkable opportunity of testing and evaluating a theory of high-\( T_c \) superconductivity.

2. EXPERIMENTAL

The polycrystalline samples of Bi\(_2\)Sr\(_2\)(Ca\(_{1-x}\)Y\(_x\))Cu\(_2\)O\(_{6+\delta}\) with Y content in the range 0.0 \( \leq x \leq 1.0 \) were synthesized by the conventional solid state reaction [2]. All the samples are confirmed by powder X-ray diffraction (XRD) as a single phase. The magnetic properties of the samples were measured by a Quantum Design SQUID magnetometer. The facility of the synchrotron radiation was supported from Synchrotron Radiation Research Center (SRRC), Hsinchu, Taiwan. The XANES measurements of O-K-edge were performed at the 6-m high-energy spherical grating monochromator (HSGM) beamline [2].

3. RESULTS AND DISCUSSION

In Figure 1 we show the O K-edge XANES spectra for the series of Bi\(_2\)Sr\(_2\)(Ca\(_{1-x}\)Y\(_x\))Cu\(_2\)O\(_{6+\delta}\) samples with \( x = 0 \sim 1.0 \) in the energy range of 525 - 540 eV obtained with a bulk-sensitive total X-ray-fluorescence yield technique. The O K-edge X-ray absorption spectrum for the sample with \( x = 0 \), as shown in Figure 1, mainly consists of a pre-edge around 528 eV and a broad peak above 530 eV. The pre-edge peak at \( \sim 528.3 \) eV in Figure 1 can be ascribed to the transition from 3d\(_L\) to O1s3d\(_L\) (\( L \) denotes a hole in an O2p\(_{x,y}\) orbital) states corresponding to creation of a core hole on the O1s level and a filling of the O2p\(_{x,y}\) states admixed to the upper Hubbard band [3]. The transition is strongly related to the variation of the hole concentration within the CuO\(_2\) planes. The contribution of the broad peak above 530 eV is due to the wide antibonding Bi6p\(_{x,y}\) - O(1) and O(2)2p\(_{x,y}\) - O(3)2P\(_z\) band [3].
The pre-edge peaks were analyzed by fitting Gaussian functions to each spectrum. In Figure 2 the integrated intensity of the pre-edge peaks is plotted as a function of compositional parameter $x$ in Bi$_2$Sr$_2$(Ca$_{1-x}$Y$_x$)Cu$_2$O$_{8+y}$. It can be seen from Figure 2 that the intensity of the pre-edge peak at $\sim 528$ eV originating from the CuO$_2$ planes decreases in intensity as the Y doping increases. This effect may indicate that the hole concentration within the CuO$_2$ plane sites decreases with increasing Y doping.

Assuming the grains are spherical, then

$$J_c (A/cm^2) = 30 \Delta M/d$$

Where $\Delta M$ (emu/cm$^3$) is the difference in magnetization for increasing and decreasing field ($H > H_{cl}$), and $d$ is the average diameter (cm) of the grains ($d \sim 10 \mu m$ for the series Bi$_2$Sr$_2$(Ca$_{1-x}$Y$_x$)Cu$_2$O$_{8+y}$ powdered samples).

In Figure 4 we show the critical current, $J_c$, at $T = 5$ K and $H = 1$ Tesla as a function of the chemical composition $x$ in Bi$_2$Sr$_2$(Ca$_{1-x}$Y$_x$)Cu$_2$O$_{8+y}$. The intragrain critical current of the series Bi$_2$Sr$_2$(Ca$_{1-x}$Y$_x$)Cu$_2$O$_{8+y}$ samples decreases as the Y doping increases, demonstrating that a decrease in hole concentrations within the CuO$_2$ planes may effect the critical current of the material.
Figure 4. Critical current ($J_c$) at $T = 5 \text{ K}$ and $H = 1 \text{ Tesla}$ and critical temperature ($T_c$) as a function of the chemical composition $x$ in Bi$_2$Sr$_2$(Ca$_{1-x}$Y$_x$)Cu$_2$O$_{8+\delta}$.

Moreover, both $T_c$ and $J_c$ dependence of $x$ in Bi$_2$Sr$_2$(Ca$_{1-x}$Y$_x$)Cu$_2$O$_{8+\delta}$ are shown in Figure 4. The sample with the highest $T_c$ ($\sim 92 \text{ K}$) is appeared at $x = 0.2$ in Bi$_2$Sr$_2$(Ca$_{0.8}$Y$_{0.2}$)Cu$_2$O$_{8+\delta}$. However, the sample with the highest $J_c$ is exhibited at $x = 0$ in Bi$_2$Sr$_2$(Ca$_{0.8}$Y$_{0.2}$)Cu$_2$O$_{8+\delta}$. This means that the highest $T_c$ sample is not corresponding to the highest $J_c$ one and the highest $J_c$ is appeared in the overdoped region in Bi$_2$Sr$_2$(Ca$_{0.8}$Y$_{0.2}$)Cu$_2$O$_{8+\delta}$. Such controversial effect can be explained by Liang [5] using the condensation energy, $U(0) = H_{c2}(0)/8\pi$ (where $H_{c2} \sim H_{c1}H_{c2}$ is the thermodynamic critical field) of the materials. They demonstrate that $T_c$ varies more or less symmetrically with doping about a broad maximum at $x = x_{\text{opt}} = 0.68$ (optimal doping) in Y$_{0.8}$Ca$_{0.2}$Ba$_2$Cu$_3$O$_{8+\delta}$. This is similar to the $x = 0.2$ sample with the maximum $T_c$ in Bi$_2$Sr$_2$(Ca$_{0.8}$Y$_{0.2}$)Cu$_2$O$_{8+\delta}$. In contrast, the condensation energy $U(0)$ has a sharp maximum situated at $x = x_{\text{crit}} \sim 0.77$ (the overdoped site) in Y$_{0.8}$Ca$_{0.2}$Ba$_2$Cu$_3$O$_{8+\delta}$, which is corresponding to the highest $J_c$ sample ($x = 0$) in Bi$_2$Sr$_2$(Ca$_{0.8}$Y$_{0.2}$)Cu$_2$O$_{8+\delta}$. Further experiments (e.g. specific heat etc.) are needed in order to offer an important way forward in understanding the mechanism of high-temperature of superconductivity.

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**REFERENCES**

(4) C.P. Bean, Rev. Mod. Phys. 36 (1964) 31.