

## The Chemical Control of Superconductivity in $\text{Bi}_2\text{Sr}_2(\text{Ca}_{1-x}\text{Y}_x)\text{Cu}_2\text{O}_{8+\delta}$

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The chemical substitution of  $\text{Y}^{3+}$  for  $\text{Ca}^{2+}$  in  $\text{Bi}_2\text{Sr}_2(\text{Ca}_{1-x}\text{Y}_x)\text{Cu}_2\text{O}_{8+\delta}$  leads to the overdoped, optimum doped and underdoped states. The hole distribution in the series compounds 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  $\text{CuO}_2$  planes. The intensity of the pre-edge peak decreases with the Y doping. This demonstrates that the chemical substitution of  $\text{Y}^{3+}$  for  $\text{Ca}^{2+}$  in  $\text{Bi}_2\text{Sr}_2(\text{Ca}_{1-x}\text{Y}_x)\text{Cu}_2\text{O}_{8+\delta}$  gives rise to a decrease in hole concentration within the  $\text{CuO}_2$  planes.

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### I. Introduction

A 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. One of such systems is the so-called Bi-2212 system,  $\text{Bi}_2\text{Sr}_2(\text{Ca}_{1-x}\text{Y}_x)\text{Cu}_2\text{O}_{8+\delta}$  [1-3]. The crystal structure of  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$  can be described in terms of the half unit cell of an intergrowth of triple rock salt-type layers  $\{[\text{BiO}][\text{SrO}]\}$  with double  $[\text{Sr}(\text{Ca},\text{Y})\text{Cu}_2\text{O}_5]$  oxygen deficient perovskite layers, formed by sheets of corner-sharing  $\text{CuO}_5$  pyramids interleaved with calcium (yttrium ions substitute into the Ca sites) as shown in Fig. 1. The square pyramidal  $\text{CuO}_5$  arrangement between Cu and O is exhibiting in  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ . Due to the orthorhombic unit cell of  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ , the material has two Cu-O bonds [denoted by Cu-O(1) and Cu-O(2)] within the  $\text{CuO}_2$  planes and one Cu-O bond [denoted by Cu-O(3)] in the apical direction. A relatively sharp metal-insulator transition takes place between  $x \sim 0.5$ , giving rise to the antiferromagnetic order. The normal-state resistivity systematically increases with increasing Y concentration, implying a decreased number of charge carriers consistent with reported Hall-effect measurements [4, 5]. 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  $\text{Y}^{3+}$  ion relative to the divalent  $\text{Ca}^{2+}$  ion.

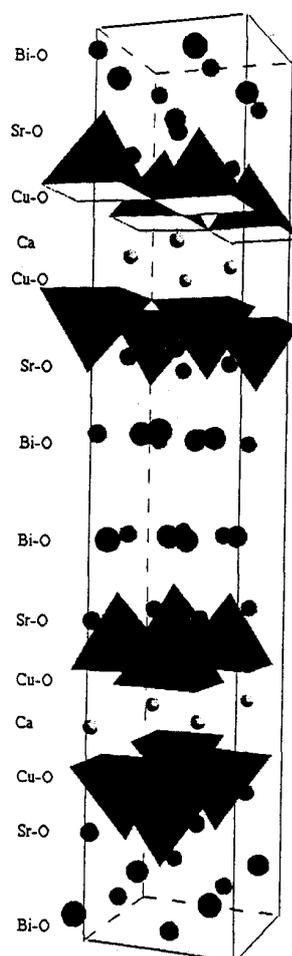


FIG. 1. The idealized crystal structure of  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ .

It has been experimentally demonstrated that hole states play an important role for superconductivity in the p-type cuprates materials. Therefore, a knowledge of the unoccupied electronic structure near the Fermi level of these compounds is a crucial step toward comprehensive understanding of the mechanism of superconductivity. 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  $\text{Bi}_2\text{Sr}_2(\text{Ca}_{1-x}\text{Y}_x)\text{Cu}_2\text{O}_{8+\delta}$  system. 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.

## II. Experimental

The polycrystalline sample of  $\text{Bi}_2\text{Sr}_2(\text{Ca}_{1-x}\text{Y}_x)\text{Cu}_2\text{O}_{8+\delta}$  with Y content in the range  $0.0 \leq x \leq 1.0$  were synthesized by the conventional solid state reaction as follows: at first, the powder reagents of  $\text{Bi}_2\text{O}_3$ ,  $\text{SrCO}_3$ ,  $\text{CaCO}_3$ ,  $\text{CuO}$  and  $\text{Y}_2\text{O}_3$  were mixed with a molar ratio of  $\text{Bi} : \text{Sr} : \text{Ca} : \text{Y} : \text{Cu} = 2 : 1 : 1-x : x : 2$ . Then, the powders were calcined at  $816^\circ\text{C}$  for 16 h and  $840^\circ\text{C}$  for 10 h in air. Next, due to the melting points are different with no Y-doped samples, the calcined and sintered temperatures are divided into two parts. For  $x = 0.0$ , the pre-fired material was calcined again at  $870^\circ\text{C}$  for 90 h with intermittent grindings. After that, the powders were pressed into 1 cm disk-shaped pellets with  $2 \text{ ton/cm}^2$  pressure, and finally sintered at  $870^\circ\text{C}$  for 50 h in air. For those  $x = 0.1 \sim 1.0$  compounds, these pre-fired powders were calcined at  $870^\circ\text{C}$  for 30 h and  $880^\circ\text{C}$  for 10 h with intermittent grindings. After that, the powders were pressed into disk-shaped pellets and sintered at  $890^\circ\text{C}$  for 10 h in air.

Structural properties and phase purity were characterized by powder X-ray diffraction (XRD). The powder X-ray diffraction data were collected with a step-scan procedure on a Scintag-X1-type diffractometer using  $\text{Cu K}\alpha$  radiation and solid state detector. All the samples are confirmed by XRD as a single phase. The superconducting transition temperature was determined by zero field cooled susceptibility measurements with a Quantum Design SQUID magnetometer.

The facility of the synchrotron radiation was supported from Synchrotron Radiation Research Center (SRRC), Hsinchu, Taiwan. All spectra of XANES were carried out at room temperature. The XANES measurements of O-K-edge were performed at the 6-m high-energy spherical grating monochromator (HSGM) beamline. All samples were pressed into pellets and attached by conducting tape. Then these samples were put into an ultra high vacuum chamber ( $10^{-9}$  torr) in order to avoid the surface contamination. The X-ray-fluorescence yield spectra were recorded with a microchannel plate (MCP) detector. This detector consists of a dual set of MCPs with an electrically isolated grid mounted in front of them. For X-ray fluorescence yield detection, the grid was set to a voltage of 100 V while the front of the MCPs was set to  $-2000$  V and the rear to  $-200$  V. The grid bias insured that positive ions would not be detected while the MCP bias insured that no electrons were detected. The MCP detector was located  $\sim 2$  cm from the sample and oriented parallel to the sample surface. Photons were incident at an angle of  $45^\circ$  with respect to the sample normal. The incident photon flux ( $I_0$ ) was monitored simultaneously by a Ni mesh located after the exit slit of the monochromator. All the absorption spectra were normalized to  $I_0$ . The photon energies were calibrated within an accuracy of  $\sim 0.1$  eV by using the known O K-edge absorption peak of the  $\text{CuO}$  compound. The energy resolution of the monochromator was set to  $\sim 0.22$  eV for the O K-edge absorption measurements.

## III. Results and discussion

In Figure 2, we show the  $T_c$ 's (as obtained from the SQUID measurement) as a function of the compositional parameter  $x$  in  $\text{Bi}_2\text{Sr}_2(\text{Ca}_{1-x}\text{Y}_x)\text{Cu}_2\text{O}_{8+\delta}$ . This system has superconductivity over the homogeneity range  $x = 0 \sim 0.5$ , with the superconducting transition temperature showing a maximum of 92 K at  $x = 0.2$ . However, towards the high end of the Y doping ( $0.2 < x < 0.6$ ), the  $T_c$ 's of these compounds decreases which leads to a dome-shaped curve as shown in Figure 2.

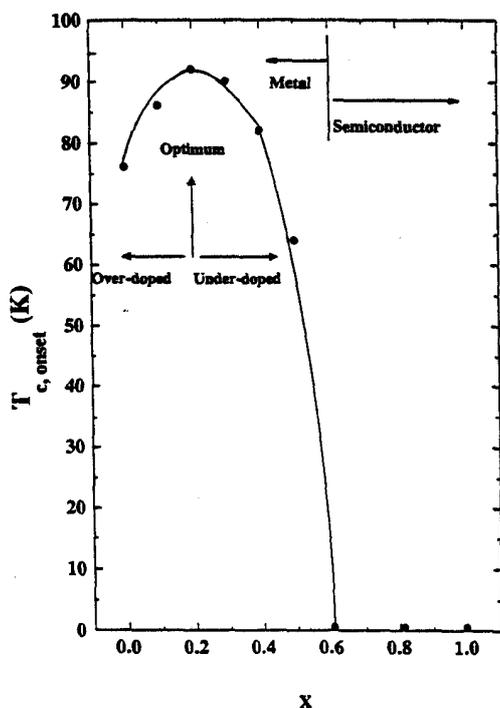


FIG. 2.  $T_c$ 's as a function of compositional parameter  $x$  in  $\text{Bi}_2\text{Sr}_2(\text{Ca}_{1-x}\text{Y}_x)\text{Cu}_2\text{O}_{8+\delta}$ .

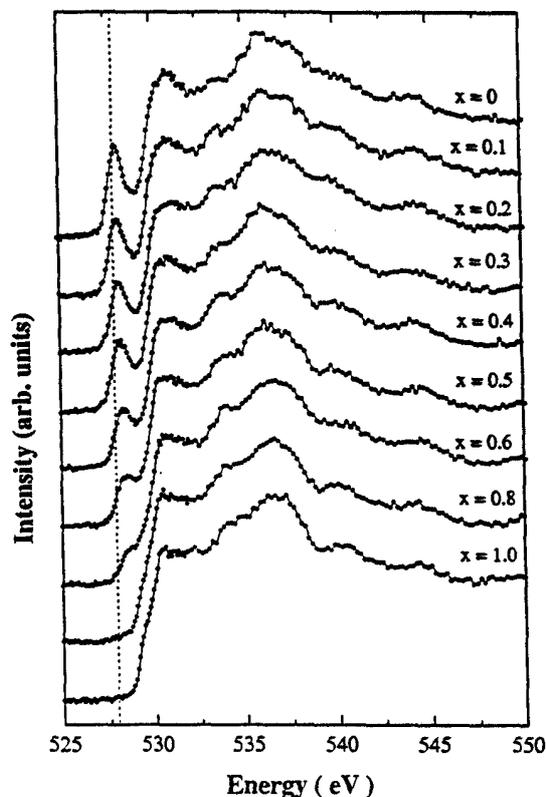


FIG. 3. O K-edge XANES spectra for the series of  $\text{Bi}_2\text{Sr}_2(\text{Ca}_{1-x}\text{Y}_x)\text{Cu}_2\text{O}_{8+\delta}$  samples with  $x = 0 \sim 1.0$  in the energy range of 525 - 555 eV obtained with a bulk-sensitive total X-ray-fluorescence yield technique.

Moreover, across the homogeneity range  $x = 0.5 \sim 1.0$ , the materials undergo a Metal-Insulator Transition based on our resistivity measurement. The great attraction of such system is able to control the hole concentration in the  $\text{CuO}_2$  planes with a simple chemical substitution involving other layers in the unit cell. Therefore, the detailed studies of the electronic structure near the Fermi level via XANES are particular importance.

In Figure 3, we show the O K-edge XANES spectra for the series of  $\text{Bi}_2\text{Sr}_2(\text{Ca}_{1-x}\text{Y}_x)\text{Cu}_2\text{O}_{8+\delta}$  samples with  $x = 0 \sim 1.0$  in the energy range of 525 - 555 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 3, 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 3 can be ascribed to the transition from  $3d^9\bar{L}$  to  $\text{O}1s3d^9$  ( $\bar{L}$  denotes a hole in an  $\text{O}2p_{x,y}$  orbital) states corresponding to creation of a

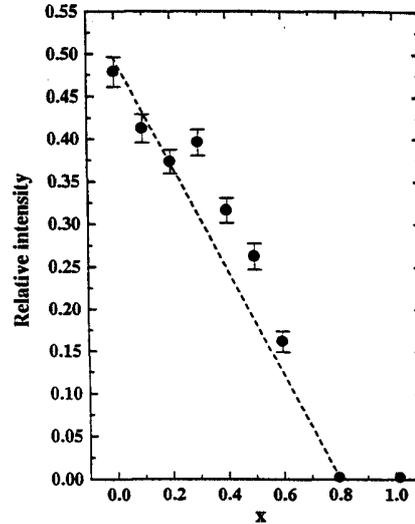


FIG. 4. The integrated intensity of the pre-edge at  $\sim 528.3$  eV as a function of Y content  $x$  in  $\text{Bi}_2\text{Sr}_2(\text{Ca}_{1-x}\text{Y}_x)\text{Cu}_2\text{O}_{8+\delta}$ . Line through data points is guide to the eyes.

core hole on the O1s level and a filling of the  $\text{O}2p_{x,y}$  states admixed to the upper Hubbard band [6]. The transition is strongly related to the variation of the hole concentration within the  $\text{CuO}_2$  planes [6]. The contribution of the broad peak above 530 eV is due to the wide antibonding  $\text{Bi}6p_{x,y,z}-\text{O}(1)$  and  $\text{O}(2)2p_{x,y}-\text{O}(3)2p_z$  band [6]. The pre-edge peaks were analyzed by fitting Gaussian functions to each spectrum. In Figure 4 the integrated intensity of the pre-edge peaks is plotted as a function of compositional parameter  $x$  in  $\text{Bi}_2\text{Sr}_2(\text{Ca}_{1-x}\text{Y}_x)\text{Cu}_2\text{O}_{8+\delta}$ . It can be seen from Figure 4 that the intensity of the pre-edge peak at  $\sim 528$  eV originating from the  $\text{CuO}_2$  planes decreases in intensity as the Y doping increases. This effect may indicate that the hole concentration within the  $\text{CuO}_2$  plane sites decreases with increasing Y doping.

#### IV. Conclusions

The hole distribution in the  $\text{Bi}_2\text{Sr}_2(\text{Ca}_{1-x}\text{Y}_x)\text{Cu}_2\text{O}_{8+\delta}$  series compounds has been investigated by high-resolution O K-edge X-ray-absorption near-edge-structure (XANES) spectra. The intensity of the pre-edge peak ( $\sim 528.3$  eV) decreases with the Y doping which is ascribed to the excitations of O 1s electron to O 2p hole states located in the  $\text{CuO}_2$  planes. This demonstrates that the chemical substitution of  $\text{Y}^{3+}$  for  $\text{Ca}^{2+}$  in  $\text{Bi}_2\text{Sr}_2(\text{Ca}_{1-x}\text{Y}_x)\text{Cu}_2\text{O}_{8+\delta}$  gives rise to a decrease in hole concentration within the  $\text{CuO}_2$  planes and controls the superconductivity.

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