# Doping effect of Sn on superconductivity of YBa$_2$Cu$_3$O$_y$

Chen Ang†, Zhi Yu†, Li Biao-rong‡, Wang Shao-jie§ and Chen Yi-Long§

† Physics Department, Materials Science and Engineering Department, Zhejiang University, Hangzhou 310027, People's Republic of China
‡ Solid State Electronics Department, Huazhong University of Science and Technology, Wuhan 430074, People's Republic of China
§ Physics Department, Wuhan University, Wuhan 430071, People's Republic of China

**Abstract.** The superconductivity of YBa$_2$Cu$_3$O$_y$ ceramics doped with SnO$_2$ was studied. The superconducting transition temperature $T_c$ was increased slightly as the SnO$_2$ content changed from 0 to 5 wt%. The results of the Mössbauer effect and the positron annihilation spectra showed that the Sn ions did substitute for Cu(1) sites. The increase in $T_c$ may be attributed to the optimal carrier concentration as well as to the fine and dense microstructure obtained by doping with SnO$_2$.

## 1. Introduction

It is commonly recognized that the stable $T_c$ of the YBa$_2$Cu$_3$O$_y$ (YBCO) system is 90–95 K [1, 2]. A substitutional study is a meaningful way to obtain information about the electronic and crystal structure of these cuprate oxide superconductors. Much work has been performed on doped YBCO superconductors. Some much higher superconducting transition temperatures $T_c$ were reported [3, 4]. However, most of the superconducting transition temperatures $T_c$ of doped YBCO superconductors were much lower [5, 6]. The present paper reports the doping effect of Sn on the superconductivity of YBCO.

## 2. Experimental details

The samples were prepared by means of a solid state reaction. The raw materials BaCO$_3$, Y$_2$O$_3$, CuO and SnO$_2$ powders were weighed according to the nominal stoichiometry of YBa$_2$Cu$_3$O$_y$ + $x$ wt% SnO$_2$ where $x$ was equal to 0.1, 0.2, 0.5, 1, 2 and 5, respectively. The powders were carefully mixed and pre-fired on Al$_2$O$_3$ plates at 900 °C for 6 h in air and broken to powders again. The calcination was repeated several times to improve homogeneity. The pre-fired powders were pressed and sintered at 960–1000 °C for 20 h in air and then cooled by controlling carefully in a furnace. The samples were annealed at 500 °C for 24 h in air.

The crystal structure of the samples was studied by x-ray powder diffraction (XRD) at room temperature with Cu K$\alpha$ radiation. Scanning electron microscopy (SEM) was used to analyse the composition of the materials.

The samples with 0.5 wt%, 2 wt% and 5 wt% $SnO_2$ (80% enriched with $^{119}$Sn) were denoted (a), (b) and (c), respectively. The powders were pressed into discs of density 70 mg $cm^{-2}$ and mounted on the cold head of a closed-cycle refrigerator (Displex model CS-202) with an accuracy of $\pm0.1$ K. Temperature-dependent Sn Mössbauer spectra of samples (a), (b) and (c), a sample with 5 wt% natural tin (sample (a')) and $SnO_2$ in the temperature range from 12 to 300 K were recorded using a constant-acceleration spectrometer Oxford MS-500 with transition geometry. The source of 2 mCi $CaSnO_3$ was kept at room temperature. The data were analysed using the program MOSFUN.

The positron annihilation lifetime spectra of the samples were measured with a fast–slow coincidence system with a time resolution of 220 ps from $^{60}$Co. Each spectrum contained a total of $1 \times 10^6$ counts. The lifetime spectra were analysed for three components with a variance of fits less than 1.10 using the computer program POSITRONFIT EXTENDED [7].

The superconducting transition temperatures $T_c$ were measured by a traditional four-probe technique and AC susceptibility method (table 1). The accuracy of the voltmeter is $10^{-8}$ V. A calibrated Pt resistance thermometer was used to determine the temperature of the sample. The measurement of AC susceptibility was made on a mutual inductance bridge with a sensitivity better than $10^{-2} \mu$H. A calibrated carbon resistance thermometer and calibrated copper–constantan thermocouple were used to determine the temperature of the sample simultaneously.

Table 1. The superconducting transition temperature $T_c$ and the phases of the $YBa_2Cu_3O_y + x$ wt% $SnO_2$.

| $x$ | $T_c$ | Phases present |
|-----|-------|----------------|
| 0 | 92.0 | $YBa_2Cu_3O_y$ |
| 0.1 | 92.5 | $YBa_2Cu_3O_y$ |
| 0.2 | 93.0 | $YBa_2Cu_3O_y$ |
| 0.5 | 94.0 | $YBa_2Cu_3O_y$ |
| 1 | 94.5 | $YBa_2Cu_3O_y$, $BaCuO_2$, $BaSnO_3$ |
| 2 | 96.0 | $YBa_2Cu_3O_y$, $BaCuO_2$, $BaSnO_3$ |
| 5 | 96.5 | $YBa_2Cu_3O_y$, $BaCuO_2$, $BaSnO_3$ |

## 3. Results and discussion

### 3.1. Phases and superconductivity

The specimens were very hard and had a metallic lustre appearance. The relative densities of the specimens were high, up to 97.7% of the theoretical density.

The XRD results show that the single '1:2:3' structure is obtained for $x < 1$ while for $x \geqslant 1$, extra phases such as $BaSnO_3$ and $BaCuO_2$ were found (see table 1). In the dopant range of $0.1 \leqslant x \leqslant 5$, the '1:2:3' phase remains orthorhombic. No obvious variation in the lattice parameter is found. The SEM results indicate that the microstructure becomes fine and dense gradually as the $SnO_2$ content increases and a few impurities segregate at grain boundaries for $x \geqslant 1$.

The $T_c$ of samples is improved slightly as the $SnO_2$ content increases in the range of $0 \leqslant x \leqslant 5$ (see table 1). The superconducting transition is sharp and the transition region is narrow.

## 3.2. Mössbauer effect

### 3.2.1. Valence state and location of tin ions in YBCO.

The Mössbauer data are shown in table 2. The Mössbauer isomer shifts (relative to $SnO_2$) for Sn-doped YBCO in table 2 indicate a valence of $Sn^{4+}$ by comparison with that of $SnO_2$.

Table 2. Mössbauer parameter isomer shifts (IS), quadrupole splittings (QS) for YBCO samples with various Sn contents: sample (a), 5 wt%; sample (b), 2 wt%; sample (c), 0.5 wt%.

| Sample | QS (mm s$^{-1}$) | IS (mm s$^{-1}$) | $\chi^2$ |
|---|---|---|---|
| (a) | 0.79(2) | 0.11(1) | 1.13 |
| (b) | 0.65(3) | 0.07(1) | 1.25 |
| (c) | 0.52(6) | 0.04(2) | 1.09 |
| $SnO_2$ | 0.69(3) | 0.03(1) | 1.01 |

The radius of $Sn^{4+}$ is 0.69 Å, which is similar to that of $Cu^{2+}$ with a radius of 0.72 Å. From the similarity of the ionic radii and electronegativity of elements, the $Sn^{4+}$ ions were expected to substitute for Cu sites in YBCO [8–12].

### 3.2.2. Temperature dependent f(T) factor.

In the thin-absorber case, where the saturation effect can be neglected, the recoil-free fraction $f(T)$ is proportional to the absorption areas $A(T)$ under the resonance (which can be measured very precisely) and can be expressed as [13]

$$f(T) = CA(T) = \exp\left[-\frac{3E_R}{2k_B\Theta_D}\left(1 + \left(\frac{2T}{\Theta_D}\right)^2 \int_0^{\Theta_D/T} (\exp x - 1)^{-1} x \, dx\right)\right] \quad (1)$$

where $E_R$ is the recoil energy, $k_B$ is the Boltzmann constant, $C$ is a constant and $\Theta_D$ is the Debye temperature. An anomalous narrow drop of 3% near $T_c$ in the four samples (a'), (a), (b) and (c) are shown in the curves of the areas $A(T)$ versus temperature in figures 1 and 2. This implies that the phonon softening occurs in this temperature range, which may be a precursor of the onset of superconductivity in YBCO. Similar drops appear at about $T = 220$ and 200 K, as found also in other experiments [14, 15]. The temperature dependences of $A(T)$ below $T = 135$ K in figure 2 clearly demonstrate that the softening temperatures are reduced with decreasing Sn content. So the YBCO samples with 5 wt% natural tin (sample (a')) and 5 wt% enriched $^{119}$Sn (sample (a)) soften at the same temperature.

The phonon softening in the high-$T_c$ superconductors, as an anomalous diminution of the recoil-free fraction $f(T)$, has been observed in many Mössbauer measurements, but the $f(T)$-factor decreases in a different way near and below the transition temperature $T_c$. A sudden drop similar to that obtained in the present work was observed in the $^{151}$Eu Mössbauer effect for the Eu–Ba–Cu–O system [8]; in other experiments the $f(T)$-factor displays a little diminution for $T < T_c$, but no observable narrow drop.
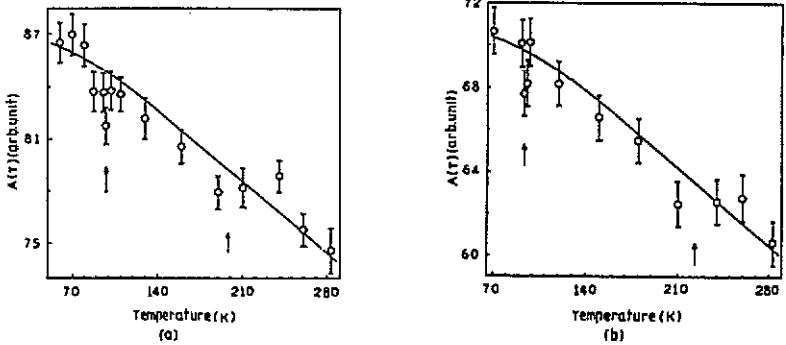
**Figure 1.** The absorption areas under the Mössbauer resonance curves as a function of temperature for superconductor YBCO samples containing (a) 5 wt% and (b) 2 wt% tin. The arrows indicate the temperature at which $A(T)$ has an anomalous drop. The full curves represent a fit to experimental $A(T)$ using the Debye model provided that the anomalous data points were rejected.
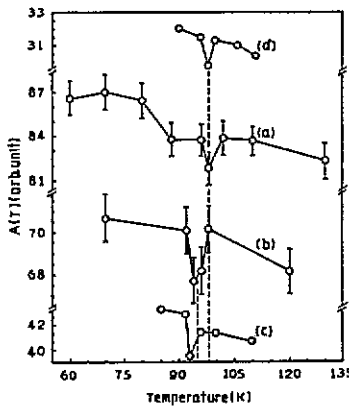


**Figure 2.** Temperature-dependent absorption areas $A(T)$ over a range from 70 to 135 K for YBCO samples containing 5 wt% natural tin (curve (a')), 5 wt% enriched Sn (curve (a)) 2 wt% enriched Sn (curve (b)) and 0.5 wt% enriched tin (curve (c)). The broken lines indicate the temperature at which $A(T)$ has an anomalous drop.
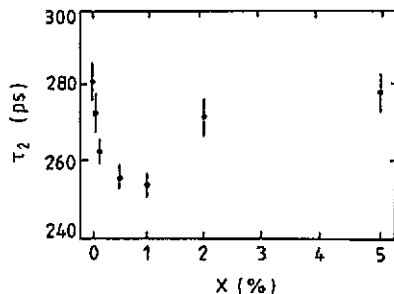


**Figure 3.** The positron lifetime as a function of the Sn content of the Sn-doped YBCO in the normal state.

*3.2.3. Debye temperature.* In the high-temperature limit, equation (1) can be reduced to the form [13]

$$\ln f(T) = \ln C + \ln A(T) = \ln C - (6E_{\rm R}/k_{\rm B}\Theta_{\rm D}^2)T. \tag{2}$$

For $T > 150$ K the temperature-dependent $\ln A(T)$ can be well fitted by a straight line, and $\Theta_{\rm D} = 320 \pm 13$ K and $\Theta_{\rm D} = 294 \pm 26$ K were obtained for samples (a) and (b) respectively. These values are in good agreement with that obtained by Tan Yuen *et al* [9].

### 3.3. Positron annihilation spectra

Three positron lifetime components $\tau_1$, $\tau_2$ and $\tau_3$ were resolved from all the obtained lifetime spectra, where $\tau_1 \simeq 170$ ps, and its intensity $I_1 \simeq 70\%$. The long lifetime $\tau_3$ and its intensities $I_3$ were found to be about 2 ns and about 1.0%, respectively. The short-lived component $\tau_1$ and the long lifetime component $\tau_3$ are assigned to the positron annihilation in the bulk and that in the source or at surfaces between the grains of ceramics. It has been reported that the intermediate-lived lifetime component $\tau_2$ is sensitive to the electronic structure of the high-$T_{\rm c}$ oxide superconductors [16]. So the following discussion is focused on this lifetime component.

The intermediate-lived component $\tau_2$ of YBCO doped with SnO$_2$ is shown in figure 3. The positron lifetime decreased quickly for $0 \leqslant x \leqslant 1$ and then $\tau_2$ increased with increasing $x$ for $x \geqslant 1$.

From the results of Mössbauer measurements on these samples, it is known that the Sn substituted for Cu sites. Did Sn replace Cu(1) or Cu(2)? Some workers reported that the Sn substituted for Cu(1) rather than Cu(2), especially when the content of Sn was small, while others reported that the Sn might occupy both Cu(1) and Cu(2) sites [8–12].

In the case of Sn doping, the experimental results show that the positron lifetime is closely related to the tin content as in figure 3. For $x < 1$, $\tau_2$ decreases with increasing $x$, i.e. the annihilation rate of positron increases. According to the results calculated by Turchi *et al* [17], the positron wavefunction is located in the vicinity of the Cu(1)–O chains and the positron mainly annihilates around the Cu(1)–O chains. The substitution of the higher-valence state Sn$^{4+}$ element for Cu(1) sites results in an increase in the overlap of the positron wavefunction with the cloud of core electrons and valence electrons of Sn$^{4+}$, i.e. the annihilation rate of the positron is increased. So the positron lifetime $\tau_2$ is decreased for $x < 1$ as in figure 3. Thus the results of the positron annihilation spectra indicate that the Sn substituted at Cu(1) sites. Further evidence and the detailed analysis will be published elsewhere [14].

The increase in the positron lifetime for $x \geqslant 1$ can be attributed to the extra phases that appeared. It is obvious that the positron annihilation lifetime is highly sensitive to the substitutional solubility; this result is in good agreement with other experimental data [18].

### 3.4. Discussion

It has been reported that the superconducting properties are directly affected by the substitution for the Cu element in YBCO compounds. This substitution will suppress the superconductivity [5, 6]. However, in Sn-doped specimens, $T_{\rm c}$ did not decrease but has been improved a little. This interesting phenomenon is briefly discussed as follows.

It is known that the carrier concentration is closely related to the superconductivity in cuprate oxide superconductors, i.e. there is an optimal value of the carrier concentration which maximizes the $T_c$ of cuprate oxide superconductors [19–22].

Neumeier *et al* [23] have studied the relation between the superconductivity $T_c$ and the substitution content of the $(Y_{1-x-y}Ca_y)Pr_xBa_2Cu_3O_{6.95}$ system superconductors in detail. The results showed that there was an occurrence of a peak in $T_c$, when the Ca content $y$ changed, for a fixed Pr content $x$. Neumeier *et al* interpreted this as the substitution of Pr and Ca together modifying the carrier density of the samples. They derive an equation which relates $T_c$ to the carrier density. According to this equation, the calculated $T_c$ may be up to 97.1 K. They supposed that, if a tetravalent element with no magnetic moment was used for solid solution substitution for the element of the '1:2:3' phase, $T_c$ may be increased. The present work indicated that $T_c$ has been increased slightly by doping Sn as a substitute for Cu. This result is in agreement with the above view.

Much work has been done to determine whether either Cu(1)–O chains or Cu(2)–O planes play the dominant role in superconductivity in the cuprate oxide superconductors. Now it is thought that the Cu(2)–O planes are responsible for the high-$T_c$ superconductivity. Tokura *et al* [19] and Tranquada *et al* [20] suggested a model in which the Cu(1)–O chains act as an electron reservoir which serves to modify the carrier concentration and $T_c$. In the present work, Sn substitutes for Cu(1) sites; so it has less influence on the Cu(2)–O planes; however, it makes the carrier concentration optimal and hence $T_c$ is improved.

The calculation results of Mössbauer spectra indicated that the Debye temperature of the sample doped with 5 wt% Sn is higher than that of the sample doped with 2 wt% Sn. On comparison with the $T_c$ data, the conclusion can be drawn that a higher Debye temperature will be favourable.

Softening phenomena near $T_c$ were observed in the temperature-dependent $f(T)$-factor, and the temperature of phonon softening increased as the amount of Sn substitution increased. This change is in good agreement with the change in superconducting transition temperature $T_c$ of the samples. From the results of the present work and the previous published data, it can be generally believed that the phonon plays an important role in the novel oxide superconductors.

On the other hand, the ceramic sintering mechanism of the materials has been improved by doping with Sn. A fine dense microstructure of the superconductors was obtained, and the weak link between the grains was improved; these contributed to the qualified superconductivity.

## 4. Conclusion

The superconducting transition temperature $T_c$ of the YBCO system ceramics has been improved slightly by doping with $SnO_2$. The results on Mössbauer and positron annihilation spectra indicate that $Sn^{4+}$ did substitute on Cu(1) sites. On the basis of the experimental results, the slight increase in $T_c$ is attributed to the optimal carrier concentration. In addition to these reasons, the improved microstructure may favour superconductivity in the materials obtained by doping with $SnO_2$.

## References

[1]   Wu M K, Ashburn J R, Torng C J, Hor P H, Meng R L, Gao L, Huang Z J, Wang Y Q and Chu

C W 1987 *Phys. Rev. Lett.* **58** 908

[2]  Chu C W, Hor P H, Meng R L, Gao L, Huang Z J and Wang Y Q 1987 *Phys. Rev. Lett.* **58** 405
[3]  Ovshinky S R, Yong R T, Allred D D, Demaggio G and Vander Leeden G A 1987 *Phys. Rev. Lett.* **58** 2579·
[4]  Cai X, Joynt R and Larbaleslier D C 1987 *Phys. Rev. Lett.* **58** 2798
[5]  Tarascon J M, Barboux P, Miceli P F, Greene L H and Hull G W 1988 *Phys. Rev.* B **37** 7458
[6]  Xiao G, Cieplak M Z, Musser D, Gavrin A, Streitz F H, Chien C L, Rhyne J J and Gotass J A 1988 *Nature* **332** 238
[7]  Kirkegaad P and Eldrup M 1974 *Comput. Phys. Commun.* **7** 401
[8]  Rongchuan Liu, Zhen Hu, Xin Jin, Huimin Shao, Duiqin Wang, Jiwan Zhao and Yuanfu Hsia 1988 *Chinese Phys. Lett.* **5** 214
[9]  Yuen Tan, Lin C L, Crow J E, Myer G N, Salomon R E and Schlottmann P 1988 *Phys. Rev.* B **37** 3770
[10]  Sharma R P and Prasad K G 1988 *Phys. Lett.* **128A** 217
[11]  Kuzmann E, Homannay Z, Vertes A, Gal M, Torkos K, Csakvari B, Solymos G K, Horvath G, Bankuti J, Kirschner I and Korecz L 1988 *Phys. Rev.* B **39** 328
[12]  Boolchand P, Enzweiler R N, Zitkovsky I, Wells J and Bresser W 1988 *Phys. Rev.* B **37** 3766
[13]  Srivastava J K, Bhargava S C, Iyengar P K and Thosar B V 1983 *Advances in Mössbauer Spectroscopy* ed B V Thosar, P K Iyengar, J K Srivastava and S C Bhargava (Amsterdam: Elsevier) p 6
[14]  Chen A, Zhi Y and Wang S J 1992 *Phys. Rev.* B submitted
[15]  Wang S J, Li X H, Chen Y L, Li S Q, Fong G H, Wang Z, Chen A and Li B R 1989 *Phys. Status Solidi* a **114** 273
[16]  Jean Y C, Wang S J, Nakaanishi H, Hardy W N, Hayden M E, Kiefl R F, Meng R L, Hor H P, Huang J Z and Chu C W 1987 *Phys. Rev.* B **36** 3994
[17]  Turchi P A E, Wachs A L, Jean Y C, Howell R H, Wetzler K H and Fluss M J 1989 *Physica* C **153–5** 157
[18]  Chen A and Zhi Y 1992 *J. Appl. Phys.* at press
[19]  Tokura Y, Torrance J B, Huang T C and Nzzal A I 1988 *Phys. Rev.* B **38** 7156
[20]·  Tranquada J M, Heald S M, Moodenbaugh A R and Xu Youwen 1988 *Phys. Rev.* B **38** 8893
[21]  Somasundaram P 1990 *Appl. Phys. Lett.* **65** 487
[22]  Shafer M W, Penney T, Olson B L, Greene R L and Koch R H 1989 *Phys. Rev.* B **39** 2814
[23]  Neumeier J J, Bjornholm T, Maple M B and Schuller I K 1989 *Phys. Rev. Lett.* **63** 2516