INDUCED SUPERCONDUCTIVITY IN TETRAGONAL YBa$_2$Cu$_3$O$_{6+\delta}$ BY INCORPORATION OF Ca


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The effects of the substitution of Y$^{3+}$ by Ca$^{2+}$ in semiconducting, tetragonal YBa$_2$Cu$_3$O$_{6+\delta}$ ($\delta=0.10 \pm 0.01$) were studied by electrical resistivity, X-ray diffraction (XRD), energy dispersive X-ray spectrometry (EDS), selected area electron diffraction (SAED) and heat capacity measurements. The maximum $T_c$ (20K) was found for 25-30% Ca incorporation in the YBa$_2$Cu$_3$O$_{6.10}$ compound; we find that this is also the maximum solubility limit for Ca doping. SAED patterns are consistent with disorder between the Ca and Y ions along the crystal c axis. The specific heat anomaly around 23K was observed with $\Delta C(T_c)/T_c \sim 2$ mJ/g.at K$^2$ and $\gamma(0) \sim 1.3$ mJ/g.at K$^2$.

INTRODUCTION

RECENTLY McCarron et al. [1,2] discovered that the substitution of Y$^{3+}$ by Ca$^{2+}$ in semiconducting (antiferromagnetic) tetragonal YBa$_2$Cu$_3$O$_{6+\delta}$ ($\delta \leq 0.2$) could induce superconductivity with $T_c$ up to 44K. Based on their neutron powder X-ray studies, the idealized structural model for this high $T_c$ superconducting material, (Y$_{1-x}$Ca$_x$)Ba$_2$Cu$_3$O$_{6+\delta}$ ($\delta \leq 0.2$), can be characterised by slabs of two planes of square pyramidal Cu(2)O$_2$ separated by Y and/or Ca ions in which each slab is an intergrowth of [[Cu(1)O](BaO)] layers as shown in Fig.1. Calcium substitution for yttrium in YBa$_2$Cu$_3$O$_6$ presumably results in the partial oxidation of the Cu(2)-O sheets, leaving the O-Cu(1)-O chains unaffected. [1,2] We have developed a rapid-quench technique to study the effects of Ca incorporation in samples leaving the oxygen stoichiometry close to six. Superconductivity with $T_c$ around 20K in (Y$_{1-x}$Ca$_x$)Ba$_2$Cu$_3$O$_{6+\delta}$ ($\delta \leq 0.1$) was achieved. This superconducting transition temperature is about 20K lower.

Fig. 1. The idealized structural model for the high $T_c$ superconducting material (Y$_{1-x}$Ca$_x$)Ba$_2$Cu$_3$O$_{6+\delta}$ ($\delta \leq 0.2$).
than the previous reports [1,2], which we believe to be due to the smaller δ value in our samples.

**EXPERIMENTAL**

Samples with nominal compositions of \((Y_{1-x}Ca_x)Ba_2Cu_3O_{6+δ}\) were prepared by solid state reaction from stoichiometric mixture of high purity \(Y_2O_3\), \(CaO\), \(BaO_2\) and \(CuO\) powders. The powders were weighed, mixed and pressed into pellets with dimensions of 10mm diameter and 2mm thick using a pressure of 5 ton/cm\(^2\). The pellets were sintered in air at 950°C for 20-25 h and then quenched to room temperature in air. Subsequently, the pellets were then annealed in \(Ar\) at 730°C for 20-25 h in a vertical furnace and then rapidly quenched into air or liquid nitrogen within 1 sec.

Both Iodometric titration [3] and thermogravimetric analysis under hydrogen [4] (10% \(H_2\) in \(Ar\)) were used to determine the δ values in \((Y_{1-x}Ca_x)Ba_2Cu_3O_{6+δ}\). Both analytical techniques lead to consistent results for the oxygen concentration. A standard four point probe method was used for the electrical resistivity measurement, and was fully automated for data acquisition. The electrical contacts to the samples were made by fine copper wires with a conductive silver paint, the temperature being recorded by a calibrated silicon diode sensor located close to the sample. X-ray diffraction (XRD) studies were carried out with CuK\(\alpha\) radiation using a Spectrolab CPS-120 diffractometer. Lattice parameters were determined by least square procedures from X-ray diffraction patterns recorded at ambient conditions using a focusing Guinier camera. Variant compositions were examined by energy dispersive X-ray spectrometry (EDS) in a Jeol EM-200CX electron microscope. Molybdenum specimen grids were used and background spectra were studied to ensure no Cu signals being detected from sample free areas. The selected area electron diffraction (SAED) patterns were recorded in the same electron microscope operating at 200 KeV in which a ±45° double tilt stage was used. A high-precision continuous-heating differential calorimeter[5] (1:10⁴ resolution) operating over the temperature range 1.5K to 300K was used to measure the specific heat of the \((Y_{1-x}Ca_x)Ba_2Cu_3O_6\) compounds. We measure directly the difference in specific heat between the sample and a non-superconducting reference (\(YBa_2Cu_3O_6\)). This reference was chosen and found to have a similar phonon specific heat to the sample allowing the small superconducting anomaly to be found.

**RESULTS AND DISCUSSION**

Figure 2 shows the temperature dependence of the resistivity of \((Y_{0.75}Ca_{0.25})Ba_2Cu_3O_{6+δ}\) quenched from (a) air (950°C) to air (room temperature) (b) \(Ar\) (730°C) to air (room temperature) and (c) \(Ar\)(730°C) to liquid nitrogen with the δ values of 0.37, 0.21 and 0.10, respectively. The superconducting transition temperature in \((Y_{0.75}Ca_{0.25})Ba_2Cu_3O_{6+δ}\) is varied from 74K to 20K by quenching at different annealed conditions. It seems clear that the smaller δ values in \((Y_{0.75}Ca_{0.25})Ba_2Cu_3O_{6+δ}\) lead to lower \(T_c\) values which is consistent with the observed superconductivity in \(YBa_2Cu_3O_7-δ\). Importantly, the \(T_c\) curve in \((Y_{0.75}Ca_{0.25})Ba_2Cu_3O_{6+δ}\) [Fig. 2(b)] is similar to the previous results [1,2] with the semiconducting behaviour in normal state and \(T_c\)(onset) = 57K, \(T_c\)(mid-point) = 43K and \(T_c\)(zero) = 38K. We consider that the oxygen content (6.21) in this Ca substituted \(YBa_2Cu_3O_{6+δ}\) is still high which may possible contribute a little hole from the O-Cu(1)-O chains to the Cu(2)-O planes. In order to minimize this effect we performed a rapidly quenched technique to insure the intrinsic properties of Ca incorporation in \(YBa_2Cu_3O_{6+δ}\).
Now, the oxygen content could be controlled within $\delta = 0.10 \pm 0.01$ in $(Y_{1-x}Ca_x)Ba_2Cu_3O_6+\delta$ by this approach. Fig 2(c) shows the $T_c$ curve of $(Y_{0.75}Ca_{0.25})Ba_2Cu_3O_6.10$ in which the sample has more semiconductor-like behaviour, larger resistivity in normal state and lower $T_c$ [$T_c$(onset) = 34K; $T_c$(mid-point) = 20K and $T_c$(zero) = 15K] than the $(Y_{0.75}Ca_{0.25})Ba_2Cu_3O_6.2$ [Fig. 2(b)] sample.

The normalized resistivity as a function of temperature in $(Y_{1-x}Ca_x)Ba_2Cu_3O_6+\delta$ ($\delta= 0.10 \pm 0.01$ and the $\delta$ values are independent of the increasing of the $x$ value) is shown in Fig. 3. The substitution of Ca$^{2+}$ in Y$^{3+}$ within $x=0.2$ - 0.4 induces superconductivity from the parent semiconducting $YBa_2Cu_3O_6\delta_1$ compound. With a further increase in $x$, viz $x > 0.4$, in $(Y_{1-x}Ca_x)Ba_2Cu_3O_6.1$, the material becomes semiconductor. Figure 4 shows the room temperature resistivity and $T_c$(mid-point) dependence of the $x$ in $(Y_{1-x}Ca_x)Ba_2Cu_3O_6.10$. The substitution of 2+ valence of Ca in 3+ valence of Y in the $(Y_{1-x}Ca_x)Ba_2Cu_3O_6.10$ system, we propose that the hole concentration in the Cu(2)-O planes is increased via the removal of electrons from the $\sigma^*x^2-y^2$ orbital. This is partially confirmed by the sharp decrease in the room temperature resistivity by which reflects the introduction of holes through the Ca doping from $x=0$ to 0.3. However, between $x=0.3$ and 1.0, the rapid increase in the room temperature resistivity is attributed to a decrease in the mean free path of hole carriers resulting from an increase in the concentration of the impurity phase. The presence of impurity phases (e.g. BaCuO$_2$), at the same time, prevents further increase in hole concentration. It is worth noting that the $T_c$(mid-point) as a function of $x$ in the $(Y_{1-x}Ca_x)Ba_2Cu_3O_6.1$ system behaves an analogous fashion to that found in the $La_{2-x}Sr_xCuO_4$ system [6]; here antiferromagnetic ordering of the parent (semiconductor) compound $La_2CuO_4$ is rapidly destroyed by Sr doping and induced superconductivity occurs with maximum $T_c$ of 32K at $x=0.15$.

Figure 5 shows the XRD powder diffraction pattern of the $(Y_{0.70}Ca_{0.30})Ba_2Cu_3O_6.1$ sample. Almost all of the peaks can be indexed on the basis of the $YBa_2Cu_3O_6$-like structure having the tetragonal unit cell (P4/mmm) and lattice parameters $a=3.860\pm0.004\text{Å}$ and $c=11.826\pm0.002\text{Å}$ except for small amounts of BaCuO$_2$ impurity. Lattice parameters are calculated over the homogeneity range $x =0$-0.4 with the cell volume showing a maximum $(176.2\text{Å}^3)$ at $x=0.3$. This is because the larger Ca$^{2+}$ ion (0.99Å) replaces the slightly smaller Y$^{3+}$ ion (0.93Å) in the range between $x=0$ and 0.3. McCarron et al. [1] proposed that the Cu(2)-O sheets are buckled in $YBa_2Cu_3O_6$.

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**Fig. 3.** The normalized resistivity as a function of temperature in $(Y_{1-x}Ca_x)Ba_2Cu_3O_6+\delta$ ($\delta= 0.10 \pm 0.01$).

**Fig. 4.** The room temperature resistivity and $T_c$(mid-point) dependence of the $x$ in $(Y_{1-x}Ca_x)Ba_2Cu_3O_6.10$. 
Fig. 5. The XRD powder diffraction pattern of the \((\text{Y}_{0.7}\text{Ca}_{0.3}\text{Ba}_2\text{Cu}_3\text{O}_6.1)\) sample.

Figure 6. The SAED (inset) and EDS results of the (a) \(\text{YBa}_2\text{Cu}_3\text{O}_6.10\) and (b) \((\text{Y}_{0.7}\text{Ca}_{0.3})\text{Ba}_2\text{Cu}_3\text{O}_6.10\).
which possible lead to a limited maximum solid solubility of Ca in \((Y_{1-x}Ca_x)Ba_2Cu_3O_{6.10}\) at \(x = 0.3\). However, in the Bi and Tl systems the Cu-O sheets are nearly flat and may therefore accept higher doping levels between Y and Ca yielding higher \(T_c\). For example, the Ca\(^{2+}\) substitution of \(Y^{3+}\) over the homogeneity range \(x=0-1\) in the \((Tl_{0.5}Pb_{0.5})Sr_2(Y_{1-x}Ca_x)Cu_2O_{7-\delta}\) system [7], this chemical substitution lead to increase the hole concentration and the \(T_c\). The decreasing of the cell volume from \(x = 0.3\) to 0.4, we propose that the excess smaller Ca\(^{2+}\) ions may substitute into the larger Ba\(^{2+}\) \((1.35\text{Å})\) sites which lead to decrease of the cell volume. This was confirmed by our XRD results in which the BaCuO\(_2\) impurity peak at \(x = 0.4\) is stronger than \(x = 0.3\) because of the excess Ca\(^{2+}\) ions substitution into the Ba\(^{2+}\) sites and the depleted Ba\(^{2+}\) ions combining with the Cu\(^{2+}\) ions to form the BaCuO\(_2\). When \(x > 0.5\), the multiple phases were exhibited in the sample.

The inset in Figures 6 (a) and (b) show the electron diffraction patterns of the \(YBa_2Cu_3O_{6.10}\) and \((Y_{0.7}Ca_{0.3})Ba_2Cu_3O_{6.10}\), respectively. The streaking of the diffraction spots is along the \(c^*\) axis of the \((Y_{0.7}Ca_{0.3})Ba_2Cu_3O_{6.1}\) sample. This suggests that, in the case of \((Y_{0.7}Ca_{0.3})Ba_2Cu_3O_{6.1}\) there exists considerable disorder in the stacking of layers along the \(c\) axis. We propose that the occupation of the \(Y^{3+}\) sites by Ca\(^{2+}\) ions may cause the random variation of \(c\) periodicity along the \(c\) axis would lead to disorder. Figure 6 (a) and (b) shows the EDS results of the samples whose chemical compositions are \(YBa_2Cu_3O_{6.10}\) and \((Y_{0.7}Ca_{0.3})Ba_2Cu_3O_{6.10}\), respectively.

Figure 7 shows a specific heat anomaly in \((Y_{0.95}Ca_{0.25})Ba_2Cu_3O_{6.10}\) determined against \(YBa_2Cu_3O_{6.10}\) as a reference. The specific heat anomaly at 8K and a rather broad superconducting specific heat anomaly [height \(\Delta C(T) / T_c \sim 2 \text{ mJ/g.at K}^2\)] extending from 12K to 23K with mid-point \(T_{c} = 15K\), which is consistent with the electrical measurement. This anomaly is about half the size of that found in \(YBa_2Cu_3O_7\) [8]. The superconducting pair density [\(\alpha \Delta C(T_c)\)] in \((Y_{0.95}Ca_{0.25})Ba_2Cu_3O_{6.10}\) is approximately \(~8\%\) of that in \(YBa_2Cu_3O_7\). We find \(\gamma(0) \sim 1.3\) mJ/g.at K\(^2\) and a small magnetic term of similar magnitude to that observed in \(YBa_2Cu_3O_7\). The introduction of Ca to \(YBa_2Cu_3O_{6.10}\) leads to a hardening of phonons at around 8 meV and softing of phonons at around 20 meV.

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REFERENCES