Growth and hole density control through equilibrium oxygen annealing of optimally doped $Y_{1-x}Ca_xBa_2Cu_3O_7-\delta$ single crystals

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Abstract

We have grown calcium and oxygen co-doped $Y_{1-x}Ca_xBa_2Cu_3O_7-\delta$ (CD-Y123) single crystals using a self-flux method. A process of fine tuning the oxygen content to reach the equilibrium state through in situ monitoring of the conductivity change is established. Structural, compositional and electronic property characterizations of optimal CD-Y123 crystals indicate that they are high quality equilibrium crystals with a sharp superconducting transition width of 0.2 K.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

High temperature superconductivity is induced by doping holes into $CuO_2$ planes using either cation dopants or anion dopants. $La_{2-x}Sr_xCuO_4+\delta$, for instance, can be doped by either the cation dopant strontium ($Sr^{2+}$) or the anion dopant oxygen ($O^{2-}$). Dopant Sr replaces La and occupies the lattice site such that it behaves as a quenched disorder. Dopant O enters into interstitial sites and is mobile down to $\sim 200$ K so that it behaves as an annealed disorder. In Sr and O co-doped $La_{2-x}Sr_xCuO_4+\delta$ (CD-L214) different disordering effects, quenched disorder versus annealed disorder, can be tuned at a fixed hole density by tuning Sr content versus O content. A true intrinsic physical property will reveal itself as a property that depends only on planar doped hole density $P_{pl}$, defined as the holes per Cu atom on the $CuO_2$ planes; it should be independent of the nature, cation or anion, and the ordering of the dopants. Systematic studies of the preparation and oxygen doping efficiency of CD-La214 polycrystalline samples indicated that delicate electrochemical oxidation performed at elevated temperature and long time post-annealing are required in order to achieve thermodynamically equilibrated samples [1, 2]. Equilibrium polycrystalline samples have only two superconducting transitions with $T_c = 15$ and 30 K [2], which was independently confirmed later [3]. Systematic high pressure studies of pure oxygen doped $La_{2}CuO_4+\delta$ (OD-La214) and CD-La214 show that these two intrinsic superconducting transitions are manifestations of two intrinsic electronic superconducting phases that are independent of the content of anion and cation dopants; they depend only on $P_{pl}$ [4]. High pressure Hall effect measurements of OD-La214 at room temperature exhibit consistent hole localization at $P_{pl} = 0.06$ ($\sim 1/16$) and $P_{pl} = 0.100$ ($\sim 1/9$) under various pressures [5]. Indeed, far infrared charge dynamic studies of CD-La214 suggested that a small number of free holes coexist with charged ordered states formed at $P_{pl} = 1/16$ and $P_{pl} = 2/16$ with $T_c = 15$ K and $T_c = 30$ K, respectively [6]. Furthermore, in a series of specifically prepared high quality pure Sr doped $La_{2-x}Sr_xCuO_4$ (SrD-214) single crystals (see figure 2 in [7]) we observed a much sharper $T_c = 15$ K at $P_{pl} = 0.063$ and $T_c = 30$ K at $P_{pl} = 0.11$ transition width ($\Delta T \sim 2$ K) than that ($\Delta T \sim 6$ K) for transition temperatures other than these two intrinsic superconducting transitions. Charge dynamic studies on these single crystals are intrinsically consistent with the picture obtained from polycrystalline CD-La214 [8]. All these results strongly suggest that there are intrinsic superconducting phases around magic doping concentrations $P_{pl} = m/n^2$. 

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where \( m \) and \( n \) are positive integers and \( n = 3 \) or \( 4 \) with \( m \leq n \). Detailed studies of these intrinsic electronic superconducting phases will shed light on the mechanism of high \( T_c \) cuprates. Unfortunately, preparation of equilibrium high quality CD-La214 crystals turns out to be if not impossible then extremely difficult; micro-cracks developed upon oxygen charging and the crystal can even disintegrate at high oxygen doping [9]. This shortfall has seriously hindered detailed studies of the intrinsic superconducting phases. The crystal is not in an electronic equilibrium state and results derived from CD-La214 crystals with \( T_c \) different from these two intrinsic transitions should be interpreted with care.

A parallel situation occurred in the \( Y_1Ba_2Cu_3O_{7−δ} \) (Y123) high \( T_c \) superconductor system. For pure oxygen doped \( YBa_2Cu_3O_{7−δ} \) (OD-Y123), the doped hole density of the \( CuO_2 \) plane can be tuned from almost zero doping up to a slightly overdoped regime by adjusting the oxygen content and the chain ordering [10, 11]. Two intrinsic transitions are identified in the OD-Y123 system at \( T_c = 60 \) K or \( T_c = 90 \) K and the \( T_c \) versus doping behavior depends only on the hole density [12]. Calcium and oxygen co-doped \( Y_{1−x}Ca_Ba_2Cu_3O_{7−δ} \) (CD-Y123) can extend the doping well into the overdoped regime with reduced orthorhombic strain due to oxygen ordering, at the price of increasing out-of-plane disorder due to Ca dopant. Different disordering effects, quenched disorder versus annealed disorder, can be tuned at a fixed hole density by tuning Ca content versus O content. Therefore, preparing high quality equilibrium CD-Y123 single crystals and fine tuning their oxygen content provides a unique opportunity to study the intrinsic electronic properties of high \( T_c \) cuprates.

In this paper we present the growth, post-annealing, and characterization of \( CuO-BaO \) self-flux grown optimal CD-Y123 crystals. All the total full-widths at half-maximum (FWHM) of the x-ray rocking curves (006 peak) of the crystals used in this study were less than 0.05°. Based on an established oxygen annealing process, we obtained sharp superconducting transitions with a width of 0.2 K, defined as the temperature interval for a drop of normal state value from 10% to 90%, by thermoelectric power (TEP) and resistivity measurements. The magnetic measurements show that the shielding (zero-field-cooled) signal is about 100% and the Meissner (field-cooled) signal is as large as 45% of that of a perfect superconductor. To the best of our knowledge, those are best results for optimal CD-Y123 crystals that can be found in the literature so far.

2. Experimental details

The \( Y_{1−x}Ca_Ba_2Cu_3O_{7−δ} \) single crystals were grown using a self-flux method, which has proven to be the best method for growing OD-Y123 single crystals. BaZrO\(_3\) crucibles were used since they do not react with the melts and consistently yield high quality OD-Y123 crystals [13, 14].

High purity \( Y_2O_3 \) (99.999%), \( BaCO_3 \) (99.997%), \( CuO \) (99.995%), and \( CaCO_3 \) (99.995%) were used as starting materials. We fix the composition of the flux at the eutectic point of BaO and CuO with molar ratio BaO:CuO = 28:72. The starting compositions to grow \( Y_{1−x}Ca_Ba_2Cu_3O_{7−δ} \) single crystals are 10–12% \([1/6(Y_{1−x}Ca_Ba_2Cu_3O_7)]\) and 90–88% \([BaO]_{0.28}(CuO)_{0.72}\) which are located on the line between points of \( 1/6(Y_1Ba_2Cu_3O_7) \) and \( (BaO)_{0.28}(CuO)_{0.72} \) in the \( 1/2(Y_2O_3)−BaO−CuO \) ternary phase diagram. A mixture of the starting composition was first ball milled and calcined at \( 850^\circ C \) for 10 h followed by another thorough ball milling before being packed into the crucible. About 50 g of mixed powder was pressed into a \( \sim 19 \) ml BaZrO\(_3\) crucible using a pestle. The crucible was placed in a muffle furnace with heating elements mounted on four side walls. A temperature gradient \( \Delta T = 6–8 \) K was established over the crucible (\( φ = 30 \) mm) by adjusting the distance between the crucible and the back wall of the furnace. The temperature gradient was monitored by a Pt/Pt-10Rh thermocouple configured such that the temperature difference was measured directly to reduce random noise and improve the signal-to-noise ratio. The typical temperature fluctuation observed was \( ±0.1^\circ C \). The molten mixture was held at \( 1040^\circ C \) for 16 h then fast cooled at a rate of \( 4^\circ C \) \( min^{-1} \) to \( 1000^\circ C \). After \( \Delta T \) was established, the furnace was cooled at a rate of \( 0.5–2^3^\circ C \) \( h^{-1} \) from 1000 to 945\(^\circ C \) where the flux was decanted inside the furnace.

The perfection of the crystal was examined by rocking curves using a Rigaku Geigerflex x-ray powder diffractometer equipped with a curved graphite single-crystal monochromator. The chemical compositions of the crystals were analyzed by wavelength dispersive spectrometry (WDS) using a JEOL JXA8600 electron probe microanalyzer (EPMA). An ac thermoelectric power measurement method [15] was employed to determine the planar hole density. The anisotropic resistivity of crystals was measured by an eight-lead method [16]. DC magnetization data were measured using a Quantum Design Magnetic Properties Measurement System (MPMS).

3. Results and discussions

All of the crystals were characterized by measuring the rocking curves of the (006) peak before further studies. In figure 1...
we show a crystal’s rocking curve for the (006) peak with FWHM = 0.046°. One can expect a smaller FWHM if the rocking curve was determined by a system equipped with a double-crystal monochromator.

Composition analysis using a high-precision EPMA with WDS showed that cation stoichiometry of (YCa):Ba:Cu was 1:2:3 within the experimental accuracy of ±2%. The crystals have a calcium content ranging from x = 0.07 to 0.18. The variation of Ca content from point to point on one crystal is less than ±1.8%.

In the CD-Y123 system \( P_{pl} \) depends on both Ca content \((x)\) and O content \((7 - \delta)\). Although, without ambiguity, there are \(x/2\) holes coming from Ca doping, the determination of holes contributed by the oxygen dopant is non-trivial. The doping efficiency of oxygen depends on the Ca doping level and the relation \( P_{pl} \) is not well established. We have proposed a universal hole scale based on the TEP value at 290 K \( (5^{290} K) \) which determines the \( P_{pl} \) in the CuO planes \([17]\). \( P_{pl} \) is a true measure of planar hole density, which works for all cuprate superconductors \([18]\). All the \( P_{pl} \) values reported in this paper were determined based on our universal hole scale \([17]\).

For a crystal with a specific \(x\), its \( P_{pl} \) can be tuned from \(x/2\) to the overdoped regime by adjusting the oxygen deficiency \(\delta\) by annealing the crystal under a specific oxygen partial pressure \( (P_{O2}) \) and temperature \( (T) \). \(\delta\) can be adjusted by fixing either one of the parameters and changing the other. In figure 2(a) we summarize various equilibrium temperatures of OD-Y123 reported in the literature into the \( P_{O2} - T - \delta \) phase diagram. Open symbol is equilibrium temperature and oxygen partial pressure at several specific oxygen contents \([19]\). Among them, open stars \((\delta = 0.5)\) are where O-T transition taking place \([20, 21]\). The annealing temperature at each \( P_{O2} \) is limited by the decomposition temperature \([22]\) which is also plotted (cross) in the phase diagram. We adjusted \(\delta\) by fixing the \( P_{O2} \) and changed the annealing temperature. To achieve a certain \(\delta\), we fixed \( P_{O2} \) at 1 atm, 8.0% O2–92.0%Ar, 1.0% O2–99.0%Ar, and pure Ar (with O2 < 0.3 ppm) gases for different target regions. In figure 2(b), we plot \(T\) versus \(\delta\) for OD-Y123 at various \( P_{O2} \) collected from the literature \([19, 23]\). These two figures serve as a starting point for us to design an annealing process for adjusting \(\delta\) in CD-Y123 crystals. The real oxygen content of CD-Y123 crystal is less than OD-Y123 at the same annealing conditions, since both oxygen content \([24]\) and oxygen doping efficiency \(1\) change with calcium concentration when annealing at fixed \(T\) and \( P_{O2} \).

To ensure an equilibrium oxygen distribution we monitored the annealing process by in situ resistance measurement. Oxygen diffusion is mainly along the \(ab\)-plane direction which is about five to six orders of magnitude faster than in the \(c\)-axis direction \([25, 26]\). Therefore, we only need to be concerned with \(ab\)-plane diffusion. We assume that the initial oxygen concentration \((C_i)\) of the crystal is uniform and all surfaces are kept at a constant concentration \((C_i)\). The

\[
\frac{C - C_i}{C_i - C_i} = 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} \cos \left[ \frac{2(n+1)}{2l} \pi x \right] e^{-\left(\frac{4n+4}{4l}\right)^2 \pi^2 t} \]

(1)

where the sample thickness, along the diffusion direction \((x\)-axis), is \(2l\) with the center at \(x = 0\) and \(D\) is the diffusion coefficient.

The electrical conductivity for mobile hole carriers can be written as

\[
\sigma = P_{pl} \mu e
\]

where \(\mu\) is the hole mobility and \(e\) is the electron charge. At fixed \(x\) we assume that \( P_{pl} \) changes linearly with oxygen concentration and \(\mu\) stays constant in the studied range of oxygen concentration at any time instant \(t\), \( C(t) = C \) is \([27]\)
oxygen concentration during isothermal annealing; we have

\[
\frac{\sigma(x, t) - \sigma_i}{\sigma_i - \sigma_f} = \frac{C(x, t) - C_i}{C_f - C_i}.
\]

(2)

We take \( l \) to be much shorter than the distance from the sample edge to the nearby voltage contact so that the diffusion along the current direction will not contribute to the resistance between voltage contacts. Under this condition, measured resistance can be treated as a parallel connection of infinitesimal \( d\sigma(x, t) \). Thus, the measured conductance \( G \) is the integration of \( dG(x, t) \), which is proportional to \( \sigma(x, t) \) \( dx \), over the sample dimension along the diffusion direction \( x \) (width of the crystal). Therefore, the conductance varies with time as

\[
\frac{G(t) - G_i}{G_i - G_f} = 1 - 8 \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} e^{-(2n+1)^2 / \tau} \quad \text{(3)}
\]

where the diffusion time (relaxation time) constant \( \tau = \frac{2l^2}{\pi^2 D} \) is determined by the geometric parameter \( l \) and the diffusion coefficient \( D \).

In figures 3(a) and (b) we present examples of normalized conductance change versus time in units of time constant \( \tau \) for crystals annealed in flowing oxygen and flowing argon environments, respectively. The solid (red) lines are the fitted to equation (3) with a diffusion coefficient of \( D = 4.86 \times 10^{-9} \text{ cm}^2 \text{ K}^{-1} \) in flowing oxygen at 490°C and \( D = 4.7 \times 10^{-11} \text{ cm}^2 \text{ K}^{-1} \) in flowing argon at 489°C. The oxygen out-diffusion in flowing Ar is two orders of magnitude slower than that of in-diffusion in flowing oxygen. The insets in figure 3 are the plots of resistance versus time during the annealing process. Note that the resistance in flowing argon (inset of figure 3(b)) appears to be changing linearly with time during the initial several hundred hours; the linear change in resistance was also observed in OD-Y123 single crystals [28, 29]. It was attributed to a surface reaction limited out-diffusion process [30]. However, for long time annealing, 2000 h in our case, we find that the overall resistance followed a bulk diffusion limited process if we plot the result as normalized conductance change versus time constant (figure 3(b)). Equation (3) describes the experimental data for both in- and out-diffusion very well and can be used to judge the oxygen homogeneity in the crystal. Based on equation (3), the oxygen concentration at the center is 99.5% of that at the surface when the annealing time is five times \( \tau \) (93.7% for 3\( \tau \)). We conclude that it is necessary to express the monitoring process by plotting normalized conductance change versus the diffusion time constant \( \tau \). Thus, the oxygen distribution is only related to \( \tau \) regardless of the differences in sample dimension and diffusion coefficient. Otherwise, without knowing the dimensions of the sample, it is difficult to assess the annealing process and the homogeneity of the final state. We monitor annealing processes in \textit{situ} and quench the crystals to room temperature when the 5\( \tau \) criterion is satisfied.

An optimal CD-Y123 with \( x = 0.10 \) (rocking curve is presented in figure 1) was obtained by annealing the crystal in flowing oxygen at several temperatures higher than the final temperature 500°C step by step. In each step, the annealing time was long enough to ensure an oxygen equilibrium state was reached. Figure 4(a) shows the temperature dependence of TEP. The hole density is \( P_{pl} = 0.256 \) which is very close to the optimal doping concentration \( P_{pl} = 0.25 \). The anisotropy resistivity is shown in figures 4(b) and (c). Both TEP and resistivity (in-plane and out-of-plane) exhibit sharp transitions with transition width, defined as a 10%–90% drop from normal state value, of ~0.2 K (insets of figures 4(a)–(c)). The temperature dependence of in-plane resistivity is linear from room temperature down to \( T_c \), similar to that of the optimal OD-Y123. The resistivity value is smaller than but close to that along the \( a \) direction and larger than that along the \( b \) direction (oxygen chain direction) of the optimal OD-Y123 [31, 32]. Out-of-plane resistivity is much larger (1.6 times that at room temperature) than that of optimal OD-Y123 [32], which can be attributed to the increase in the \( c \)-axis lattice constant due to the increase of both \( x \) [33] and \( \delta \) [21].

We also performed magnetization measurements on an optimally doped crystal (\( P_{pl} = 0.247 \)) with \( x = 0.11 \).
Figure 4. TEP (a), in-plane (b), out-of-plane (c) resistivities, and anisotropy versus temperature for a Y1−xCaxBa2Cu3O7−δ crystal with $x = 0.10$ doped close to the optimal hole density. Insets of (a)–(c) show sharp transition widths of 0.2 K for TEP, in-plane, and out-of-plane resistivities.

Figure 5. Zero-field-cooled and field-cooled susceptibilities versus temperature for a Y1−xCaxBa2Cu3O7−δ with $x = 0.11$ doped close to the optimal hole density. Insets show the superconducting transition of TEP and in-plane resistivity. We obtained 0.3 K and 1 K transition widths (with the same definition as that used for TEP and resistivity) for shielding (zero-field-cooled) and Meissner (field-cooled) signals, respectively. The absolutely susceptibility of shielding signal was about 100% and the Meissner signal was as large as 45% of that of a perfect superconductor (figure 5) after demagnetization factor correction.

4. Conclusions

We have grown high quality calcium and oxygen co-doped Y1−xCaxBa2Cu3O7−δ single crystals using a self-flux method. A quantitative in situ monitoring procedure has been established which allows us to fine tune the oxygen content and ensure the preparation of equilibrated crystals. The crystals prepared following this procedure show that the superconducting transition widths of TEP and resistivities are the smallest and the Meissner signal is the largest for CD-Y123 to date. These results indicate we have achieved equilibrium crystals of high quality. Study of the hole density dependence of the physical properties of CD-Y123 crystal will provide an alternative route for studying the intrinsic physical properties of high $T_c$ cuprates.

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