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Carbonate effects in single-crystalline $YBa_2Cu_3O_{7-\delta}$

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Physical properties in the normal and superconducting states for CO_3 substituted $YBa_2Cu_3O_{7-\delta}$ single crystals are reported. From resistivity measurements in the normal state, it is obtained that the samples of the similar carrier doping, which is estimated by the *c*-axis resistivity, show a different behavior in the *ab*-plane resistivity if they have different concentrations of the carbon. The peak effects of the magnetization, which correspond to the critical current density in field, decrease with the substitution. These results suggest that the substituted carbonate affects the metallicity and superconductivity of the CuO chain layer. The substitution also suppresses the carrier doping and shortens the *c*-axis length as seen in polycrystalline samples. Some attention to purity of $YBa_2Cu_3O_{7-\delta}$ will be required because T_c can exceed 90 K for even relatively highly substituted samples, $YBa_2Cu_{3-x}(CO_3)_{0.04}O_{7-y}$.

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A small amount of impurities easily affect physical properties of high-T_c cuprates owing to the *d*-wave superconductivity. For example, a nonmagnetic metal, Zn, substitutes for Cu(2) in the CuO_2 plane of $YBa_2Cu_3O_{7-\delta}$ (YBCO) and suppresses the superconductivity and transition temperature (T_c).[1–3] On the other hand, Al substitution occurs on the Cu(1) site in the CuO chain layer, which does not contribute to the superconductivity predominantly.[4–6] The suppression of T_c for the Al substitution is smaller, because this impurity only localizes the carrier in the CuO chain layer and does not affect CuO_2 plane layer directly.[6] As even small amount of Al is supposed to obscure the intrinsic physical properties,[7,8] pure crystals without Zn, Al, or other metals are required in careful investigation. Hence, crucibles without metal impurities, such as yttria,[9] zirconia,[10] or $BaZrO_3$,[7,8] are often used in the crystal growth.

Carbonate substitution occurs in polycrystalline YBCO probably due to the low growth temperature, and the properties are different from those of the nonsubstituted. The growth at 800 °C allows a metastable phase, $YBa_2Cu_{3-x}(CO_3)_zO_{7-y}$ ($YBCO\cdot zCO_3$, $z=0.15-0.5$).[11–13] The phase shows considerably suppressed T_c (e.g., Ref. 11 reports no superconductivity above 4 K) and has a shorter *c*-axis length than that of nonsubstituted YBCO. It is also commonly proved that Cu(1) or O in the CuO chain layer is replaced with CO_3 in this phase.[11–13] Meanwhile, smaller carbonate content can remain during growth even at higher temperature ($T\sim900$ °C).[14] This phase with $z<0.08$ can reach $T_c\sim90$ K, similar to the nonsubstituted. Reference 14 suggests that substituted CO_3 in the chain layer disturbs the oxygen, or the carrier dopant, spreading in the layer, and prevents further carrier doping.

In contrast, effects of carbonate in single crystals have not been investigated so far, despite its ubiquitous presence: $BaCO_3$ is widely used as a starting reagent; the atmosphere contains 0.04% CO_2; crucibles often contain organic binders and/or dispersion agents. There are several reasons this impurity tends to be overlooked. At first, the growth temperature is normally over than 1000 °C, and carbonate is expected to escape during the growth in the form of CO_2. Second, carbon is a material hard to be detected. Chemical analysis with the commonly available inductively coupled plasma (ICP) method has difficulty in measuring carbon contamination in solids quantitatively. Moreover, compared to other metal impurities (such as Zn), the substitution effects are supposed to be small as, for single crystals, there has been no report of the large T_c degradation seen in polycrystalline samples.

In the present work, CO_3^{2-} substituted YBCO single crystals were grown and some physical properties were studied both in the normal and superconducting states. It should be noted that single crystals are required to estimate the physical properties correctly, because the carbonate in polycrystalline samples easily gathers at the grain boundary and changes the properties.[15] All experimental results obtained in this Rapid Communication agree that substituted CO_3^{2-} in the CuO chain layer induces change in the physical properties both in the normal and superconducting states, in addition to the inhibition of the carrier diffusion, which has already reported in Ref. 14 and is similarly observed in the Al substituted samples.[6]

Single crystals of carbonate substituted YBCO were prepared with a self-flux method. Y_2O_3, $BaCO_3$, and CuO were used as starting materials. The carbonate substitution was controlled by different concentrations of CO_2 in the flowing gas. The calcined powder in a $BaZrO_3$ crucible[7,8] was first heated to 1020 °C to melt the flux and then slowly cooled to 960 °C before the heater was turned off. The ICP method was applied to estimate metal impurities. The carbonate content was determined by a combustion-infrared absorption method. For physical property measurements single crystals with a size of about $0.5\times0.5\times<0.2$ mm^3 were used, and the samples were postannealed in pure O_2 at $T=T_p$ in order to control the carrier doping. Physical property characterization was performed using Quantum Design Magnetic Prop-

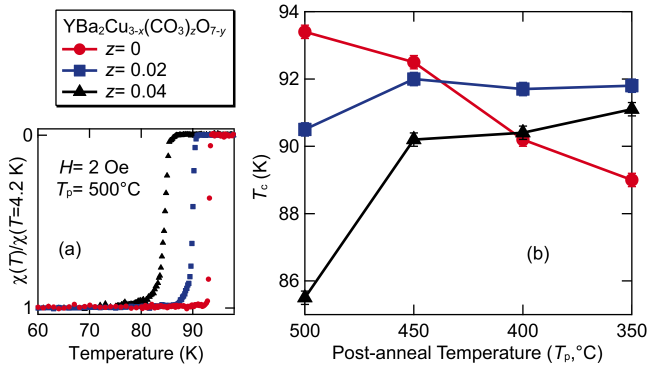

FIG. 1. (Color online) (a) Magnetic susceptibility for CO_3^{2-} substituted $YBa_2Cu_3O_{7-\delta}$ ($YBCO \cdot zCO_3$). All samples are postannealed in oxygen at 500 °C. (b) Postannealing temperature dependence of T_c for $YBCO \cdot zCO_3$ [$z=0$ (circle), 0.02 (square), and 0.04 (triangle)].

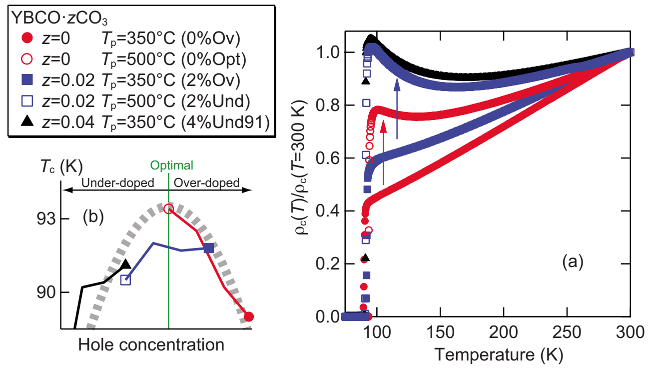

FIG. 2. (Color online) (a) c-axis resistivity for several samples of $YBCO \cdot zCO_3$ ($T_p=350$ and 500 °C). Arrows indicate change in c-axis resistivity with increasing T_p. For $z=0$, the sample at $T_p=350(500)$ °C is denoted as 0%Ov (0%Opt). (b) Carrier doping as determined from the data in (a).

erty Measurement System (MPMS) and Physical Property Measurement System (PPMS) instruments. The x-ray diffraction measurements were achieved by the 2θ-ω scan method, using a four-circle diffractometer with Mo-$K\alpha$ radiation monochromatized by graphite.

The carbon content of YBCO grown in air is estimated at ~0.3 mol % by the combustion-infrared absorption method. After taking this sample as $z=0$ for $YBCO \cdot zCO_3$, we find $z=0.02$ (2 mol %) and 0.04 (4 mol %) for the samples grown in 2% and 4% CO_2, respectively. As for impurities, the ICP results indicate slight Zr contamination of $\lesssim 0.7$ mol % both in $z=0.02$ and 0.04 samples similarly. This Zr impurity probably comes from slight damage, or melting, of crucibles. Given that the lattice constant of impurity Zr does not fit that of YBCO,[7] a small amount of dissolved $BaZrO_3$ is believed to be present on the surface of the crystal. This is also supported by experimental results mentioned later. The present ICP measurements also exhibit that Zr contamination for $z=0$, and Al and Mg impurities for all samples are lower than the detection limit (<0.3 mol %).

Figure 1(a) shows the measured magnetic susceptibility for $YBCO \cdot zCO_3$ ($z=0$, 0.02, and 0.04) annealed at $T_p=500$ °C. All samples have relatively clear superconducting transition, while their T_c values, which are determined from the onset of the transition, vary with z. In order to clarify the postannealing temperature dependence, the same measurements were performed for the samples annealed at different T_p's [Fig. 1(b)]. For $z=0$, T_c increases with increasing T_p over the observed temperature range. At $T_p=500$ °C, T_c reaches 93.4 K, suggesting the sample is optimally doped. Therefore the samples at lower T_p for $z=0$ are regarded as overdoped. The behavior of the $z=0.02$ samples is relatively flat, showing little change, except the sample at $T_p=500$ °C. For $z=0.04$, T_c decreases with increasing T_p, suggesting these samples are mostly in the underdoped region.

From Fig. 1(b), it is suggested that CO_3^{2-} substitution occurs in the CuO chain layer as seen in the polycrystalline crystals.[11–13] The highest T_c values for the substituted samples are similar to that of the nonsubstituted. If the CuO_2 plane were partially replaced with CO_3^{2-}, T_c for the substituted might have been suppressed more as seen in Zn substitution. In fact, the degree of the T_c suppression is similar to that for Al (e.g., $x=0.1$ for $YBa_2Cu_{3-x}Al_xO_{7-\delta}$ has T_c of 91.5 K),[6] which substitutes for Cu in the CuO chain layer. Moreover, the $z=0$ samples are overdoped, while the $z=0.04$ samples underdoped in the same T_p range, suggesting the carbonate substitution inhibits the oxygen, or the carrier dopant, diffusing in the CuO chain layer, as the CuO layer is supposed to provide the hole carrier to the CuO_2 layer. This agrees with Ref. 14 using polycrystalline samples.

The relative carrier doping for these materials was evaluated by measuring the c-axis resistivity. It is well known for high-T_c cuprates that the c-axis resistivity changes from semiconducting ($d\rho_c/dT<0$) to metallic ($d\rho_c/dT>0$) with carrier doping.[16] A normal method of estimating the carrier doping, such as iodometric titration, is inadequate here, because it is unknown how the substituted carbonate acts in the titration. Figure 2(a) shows the c-axis resistivity measured using a four-probe method for several samples annealed at $T_p=350$ and 500 °C. All data are normalized by the resistivity at $T=300$ K to avoid effects of the contact resistance. Due to the small size of the samples in the similar carrier doping range, the determination of the absolute value of the resistivity is difficult. From the measurements, it is found that both the $z=0$ (circle) and 0.02 (square) samples lose metallicity in the normal states with higher T_p, supporting the general behavior indicated by Ref. 16. The resistivity for $z=0.02$ at $T_p=350$ °C (filled square) lies midway between those at $T_p=350$ and 500 °C for $z=0$. As the $z=0$ samples in $T_p<500$ °C are overdoped from Fig. 1(b), the $z=0.02$ sample at $T_p=350$ °C is also overdoped (2%Ov). Similarly, the $z=0$ resistivity suggests that both samples for $z=0.02$ at $T_p=500$ °C (2%Und) and $z=0.04$ at $T_p=350$ °C (4%Und91) are underdoped. It should be noted that these 2%Und and 4%Und91 have nearly identical c-axis resistivity and T_c [Fig. 1(b)], suggesting they have quite similar carrier concentration. The data, T_c vs carrier concentration, are collected in Fig. 2(b).

In spite of the similar carrier concentration between the 2%Und and 4%Und91 samples, resistivity measurements in the ab plane display a considerably different behavior in the

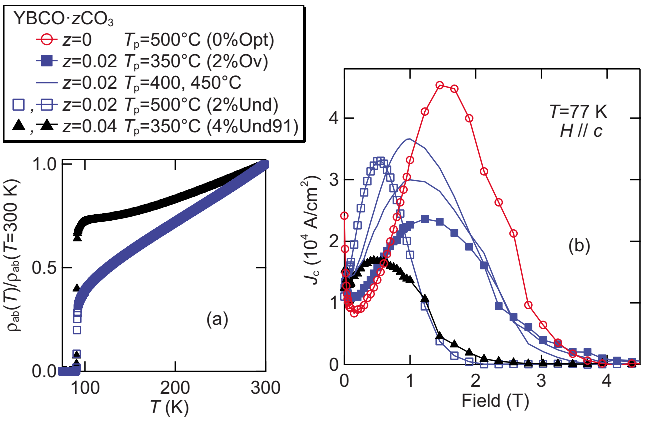

FIG. 3. (Color online) (a) *ab*-plane resistivity for YBCO$\cdot z$CO$_3$ [z=0.02, T_p=500 °C (2%Und) and z=0.04, T_p=350 °C (4%Und91)]. (b) J_c at 77 K for several YBCO$\cdot z$CO$_3$ samples. Lines without marks are the results for z=0.02 samples at intermediate T_p. The external field was applied parallel to the c axis.

normal states as seen in Fig. 3(a). Reference 14 suggests that the carbonate substitution only changes the diffusion velocity of the carrier dopant in the CuO chain layer, and consequently implies that the samples with the same carrier concentration should behave similarly even if they have different carbon contents. The discrepancy of the *ab*-plane resistivity in Fig. 3(a) indicates that substituted carbonate does not simply disturb the oxygen diffusion, but affects physical properties in the normal states. Given the CuO chain is metallic near the optimally doped for nonsubstituted YBCO, the discrepancy can be explained by chain fragmentation by the CO$_3^{2-}$ substitution hindering the metallicity.

The substitution effects beyond the carrier concentration effects can be seen in the superconducting states as well. Magnetization measurements were performed on the samples of 0%Opt, 2%Ov, 2%Und, and 4%Und91. All samples have similar T_c [within 3 K in Fig. 1(b)], suggesting tiny difference of T_c is negligible even when the measurements were performed at the same temperature (T=77 K). From the $M(H)$ measurements, the field dependence of the critical current density (J_c) is estimated [Fig. 3(b)], based on an extended Bean model.[17] For the z=0.02 samples, measurements were also achieved at intermediate T_p (lines without marks), in order to compare the results for 0%Opt, because the J_c behavior could change drastically depending on the oxygen deficiency.[7] The clear peak at $H \sim 1.5$ T for 0%Opt indicates that the oxygen deficiency creates flux-pinning centers.[7] Similar peaks are observed for the z=0.02 samples, and all of the peak heights (J_c in field) are smaller than that of 0%Opt, while one of the z=0.02 samples should be close to the optimally doped. Additionally, although 2%Und and 4%Und91 have the similar carrier doping, J_c in field for 4%Und91 is more depressed than that of 2%Und. These results suggest that the carbonate substitution depresses J_c in field irrelevant to the carrier concentration, and probably affects superconductivity in the CuO chain layer.[20]

The depression of J_c in field for the substituted supports the idea that the Zr impurity detected by ICP measurements does not enter the crystal inside. According to Refs. 18 and 19, several percents of Zr should enhance J_c in field because the introduced BaZrO$_3$ acts as a pinning center.

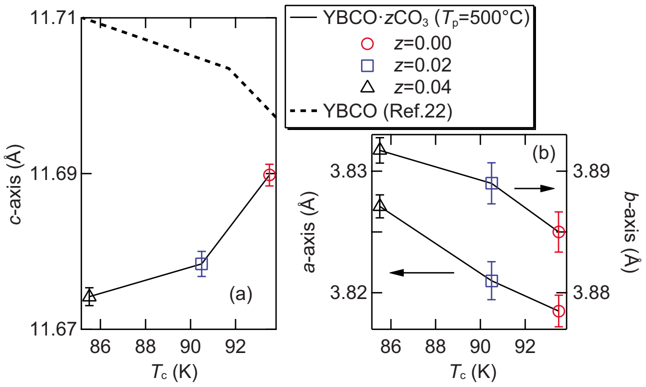

FIG. 4. (Color online) (a) c-axis length for several YBCO$\cdot z$CO$_3$ samples. All samples are postannealed at T_p=500 °C and underdoped or optimally doped. The dotted line is the c-axis length for underdoped nonsubstituted YBCO, taken from Ref. 22. (b) a and b lattice parameters for the same samples in (a).

As discussed in the polycrystalline crystals,[11–14] the CO$_3^{2-}$ substitution reduces the c-axis length. For the single crystals, x-ray diffraction was used to obtain the lattice constants of samples that were partially detwinned by heating in O$_2$ under uniaxial pressure. The lattice constants were obtained for T_p=500 °C samples using more than 250 Bragg reflections (Fig. 4). For nonsubstituted YBCO, the c-axis length in the underdoped and optimally doped regions decreases with increasing the carrier concentration[10,21,22] as shown by the dotted line[22] in Fig. 4(a). The CO$_3^{2-}$ substituted samples show the opposite behavior (solid line), although they are also underdoped or optimally doped. These results for the substituted agree with those of polycrystalline samples qualitatively.[14]

Figure 4(b) indicates that both a and b axes increase with z, or the carbonate substitution. The substitution effects on the a and b axes seem to be subtler than that on the c-axis length. References 10 and 21 exhibit for nonsubstituted YBCO that the a axis increases with decreasing T_c (or the carrier doping) in this region of the carrier doping, while the b axis is mostly unaffected. The a-axis behavior on substitution may be explained by reduction in the number of carriers. However, the increase in the b axis is not so simple. The b-axis extension with substitution is similarly implied by Ref. 14 for polycrystalline samples.

The possibility of the carbonate contamination in YBCO single crystal will give some attention in discussing the purity. Finding no impurity using the ICP method does not guarantee the purity of the samples, especially as this impurity can exist in a starting material, crucibles, and/or circumstances. For example, some controversial results are found in the two recent reports of thermal conductivity: one group says that fermion (metallic) behavior remains in nonsuperconducting YBCO,[23] while the other suggests that fermion vanishes with the disappearance of the superconductivity.[24] Both of the groups claim that they take great care of the purity of their samples, while the purity is mentioned as one of the reasons of the discrepancy, because the experimental method requires high purity of the samples. The difference of the results might be described by the difference of the carbonate contamination. A promising option to estimate crystal quality is to attempt overdoping the sample; a contaminated sample does not easily become overdoped of $T_c < 90$ K as is also seen for polycrystalline samples.

In summary, we have characterized single crystals of CO_3^{2-} substituted YBCO ($YBCO \cdot zCO_3$). The T_c suppression and *c*-axis reduction prove the carbonate substitution in the single crystals, similar to the polycrystalline samples. The common behavior implies that a particular care is required in discussing the purity even of the single crystal, because T_c of the relatively highly substituted, $z=0.04$, samples can exceed 90 K. The T_c suppression in $YBCO \cdot zCO_3$ is similar to that of Al substitution in Refs. 5 and 6, supporting the substitution that occurs in the CuO chain layer. Furthermore, the similarly carrier-doped samples with different carbon contents display different in-plane resistivities and critical current densities, meaning that carbonate does not only prevent the oxygen diffusion as suggested in the polycrystalline samples, but also affects the metallicity and superconductivity in the CuO chain layer.

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