

Thermoelectric power of high-pressure synthesized $\text{CuBa}_2\text{Ca}_3\text{Cu}_4\text{O}_{11-\delta}$

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We report measurements of thermoelectric power (TEP) for high-pressure synthesized $\text{CuBa}_2\text{Ca}_3\text{Cu}_4\text{O}_{11-\delta}$ superconductors. The magnitude of TEP for the sample with $T_{c,\text{zero}} = 115.9$ K is very small and shows a sign crossover at ~ 160 K. The TEP shows a peak behavior and displays an approximately linear temperature dependence with a negative slope $-0.033 \mu\text{V}/\text{K}^2$ for $120 \leq T \leq 240$ K. These features resemble those for other known high- T_c cuprate superconductors, in particular S_a in the a direction for an untwinned $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystal and polycrystalline Tl-2201 samples. A brief discussion is given on the TEP behavior in comparison with $\text{CuBa}_2\text{YCu}_2\text{O}_{7-\delta}$ cuprate superconductors by considering their similar structure of building blocks and type of charge reservoir.

The cuprate superconductor $\text{CuBa}_2\text{Ca}_3\text{Cu}_4\text{O}_{11-\delta}$ (Cu-1234) with transition temperature of 117 K has recently been synthesized using high-pressure synthesis techniques by several groups.¹⁻⁴ The crystal structure of $\text{CuBa}_2\text{Ca}_3\text{Cu}_4\text{O}_{11-\delta}$ is known to be in the category of $(\text{ACuO}_{3-x})_m(\text{BO}_{1-y})_n$ intergrowth structure.⁵ So far, there are no data available on the thermopower of this high-pressure synthesized $\text{CuBa}_2\text{Ca}_3\text{Cu}_4\text{O}_{11-\delta}$ superconductor. The thermopower behavior of $\text{CuBa}_2\text{Ca}_3\text{Cu}_4\text{O}_{11-\delta}$ superconductor is thus of interest for identifying its similarities and differences as compared to other perovskite-based cuprate superconductors.

Among the normal-state transport properties, thermoelectric power (TEP) is known to be a sensitive probe to the energy dependence of the electron relaxation processes and topology of Fermi surface. A number of studies⁶ have shown that the TEP for cuprate superconductors tends to show peak behavior and a more positive value with decreasing hole carrier concentration regardless the number of CuO_2 planes per unit cell. Virtually all the Bi- and Tl-based cuprates in the normal state well above T_c display an approximately linear temperature dependence in TEP with a negative slope of -0.024 to $-0.03 \mu\text{V}/\text{K}^2$.⁶ In this paper, we present the first measurements of TEP on high-pressure synthesized $\text{CuBa}_2\text{Ca}_3\text{Cu}_4\text{O}_{11-\delta}$ superconductors. Our general finding is that our nearly single-phase sample has the universal behavior characteristic of ab plane of optimally doped or overdoped high- T_c cuprates, particularly reminiscent of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (Ref. 7) and $\text{Tl}_2\text{Ba}_2\text{CuO}_{6+\delta}$.⁸

Polycrystalline samples of $\text{CuBa}_2\text{Ca}_3\text{Cu}_4\text{O}_{11-\delta}$ were synthesized following the procedure described in Ref. 1. In brief, $\text{CuBa}_2\text{Ca}_3\text{Cu}_4\text{O}_{11-\delta}$ was synthesized at 950°C under 5 GPa for 1 h by using the starting materials of BaO_2 , CaO , and CuO with stoichiometric composition. Electrical resistivity was measured using the standard four-probe technique. Thermoelectric power was measured between 80 and 340 K by employing two pairs of copper-constantan thermocouples. Data were taken only after the system reached thermal equilibrium, which was monitored by a calibrated Si diode and the voltage response across Cu Seebeck probes. Temperature gradients were typically between 0.3 and 0.5 K. The uncertainty of measurements is $\pm 0.1 \mu\text{V}/\text{K}$.

As shown in Fig. 1, the powder x-ray diffraction pattern indicates that the sample is a nearly single phase of $\text{CuBa}_2\text{Ca}_3\text{Cu}_4\text{O}_{11-\delta}$. Most of the peaks can be indexed based on a tetragonal unit cell with the lattice constants of $a = 3.859(2) \text{ \AA}$ and $c = 18.000(12) \text{ \AA}$. In common with other high- T_c cuprate superconductors, the sample displays a linear temperature dependence of resistivity, and shows a zero resistivity at 115.9 K (Fig. 2). The onset diamagnetic transition measured at a field of 10 Oe is found to be 117 K. In Fig. 3 we plot the thermoelectric power data against temperature, which has been corrected for the contribution of Cu leads. A trace amount of carbon content was detected in our sample by chemical analysis. The possibility of the existence of minor phase of $(\text{Cu}_{1-x}\text{C}_x)\text{Ba}_2\text{Ca}_3\text{Cu}_4\text{O}_{11-\delta}$ is not excluded.^{1,4,9} We, however, believe this situation would not affect our TEP results. The main features of the TEP data for our $\text{CuBa}_2\text{Ca}_3\text{Cu}_4\text{O}_{11-\delta}$ ($T_{c,\text{zero}} = 115.9$ K) ceramic sample are (1) a crossover to negative sign at $T \geq 160$ K, (2) a positive and sharp peak near T_c , and (3) an approximately linear temperature dependence with a negative slope of $-0.033 \mu\text{V}/\text{K}^2$ in the temperature range 120–240 K. These features are typical of high- T_c cuprate superconductors with optimized or overdoped carrier concentration. The peak behavior is quite similar to the ab -plane TEP, S_{ab} , for Bi- and Tl-based cuprates, and is generally considered to be intrinsic to the CuO_2 planes. This view is also supported by our recent measurements on polycrystalline (Bi,Pb)-2223 cuprates with $2a \times 2b \times c$ superstructure as a result of one-fourth of oxygen missing in the CuO_2 planes.¹⁰ We note that the TEP curve, specifically the sharp peak with a sign crossover at much lower temperature (i.e., 160 K) and an inflection point at ~ 240 K marking a decrease of slope to $-0.0137 \mu\text{V}/\text{K}^2$ for $240 \leq T \leq 340$ K, is similar to S_a in the a direction for an untwinned $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystal⁷ (see inset of Fig. 3) and polycrystalline Tl-2201 samples,⁸ suggesting some common transport mechanism to contribute the temperature dependence of TEP and opposite sign for these cuprates.

For the Bi-,⁸ Tl-,⁸ and Hg-based¹¹ superconductors, TEP often shows a positive shift in magnitude which is nearly temperature-independent as the hole carrier concentration decreases (e.g., by reducing the oxygen content). Nevertheless,

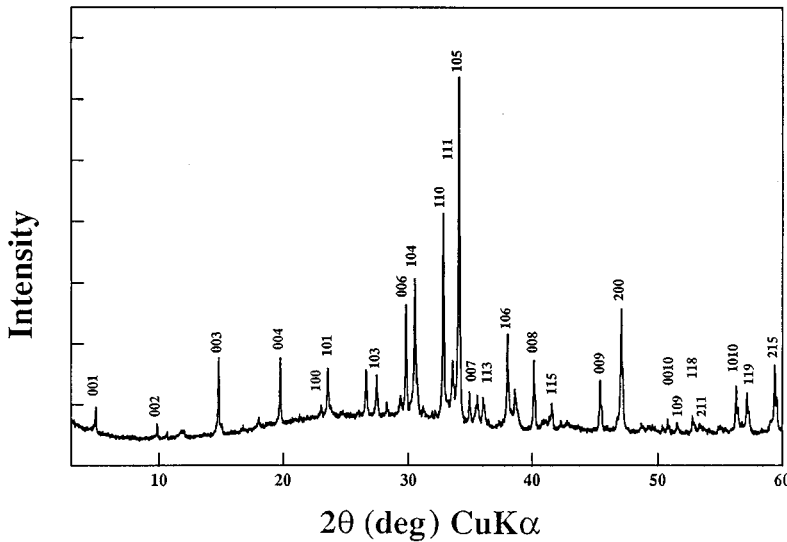


FIG. 1. X-ray diffraction pattern for $\text{CuBa}_2\text{Ca}_3\text{Cu}_4\text{O}_{11-\delta}$ with $T_{c,\text{zero}} = 115.9$ K.

TEP for $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ appears to have a more complicated sensitivity to the oxygen stoichiometry than other cuprate superconductors. This complication has been ascribed to the CuO chains contribution by a simplified two-band model with a CuO_2 -plane-related, quasi-two-dimensional (2D) band and a CuO -chain-related, quasi-1D band.^{7,12} Therefore, the CuO chains contribution to both the electrical conductivity¹³ and TEP appears to be unique among the high- T_c cuprate superconductors.

As we write down the chemical formula of Y-123 cuprate in the four number naming scheme as $\text{CuBa}_2\text{YCu}_2\text{O}_{7-\delta}$ (Cu-1212), one can readily find its structural similarity to $\text{CuBa}_2\text{Ca}_3\text{Cu}_4\text{O}_{11-\delta}$. The CuO chainlike coordination exists between the BaO bilayers in both $\text{CuBa}_2\text{Ca}_3\text{Cu}_4\text{O}_{11-\delta}$ and $\text{CuBa}_2\text{YCu}_2\text{O}_{7-\delta}$ cuprates.⁵ Due to their similar CuO chain configuration in the structure, which is also the charge reservoir for both compounds, it is worthwhile to compare our data with those of $\text{CuBa}_2\text{YCu}_2\text{O}_{7-\delta}$ in the literature in order to gain some insight. It should also be noted that the TEP of $\text{La}_{1.8}\text{Sr}_{0.2}\text{CaCu}_2\text{O}_{6-\delta}$ behaves similarly to that of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ because of their similar structures of building blocks and similar sources of charge reservoir.¹⁴ Despite the controversy whether the CO_3 groups are partially substitut-

ing the CuO sites in $\text{CuBa}_2\text{Ca}_3\text{Cu}_4\text{O}_{11-\delta}$,^{1,4,5,9} one could reasonably expect similar contributions of CuO chains to the electrical conductivity for $\text{CuBa}_2\text{Ca}_3\text{Cu}_4\text{O}_{11-\delta}$, if the oxygen content in the CuO chains is sufficient. One could further expect that TEP for $\text{CuBa}_2\text{Ca}_3\text{Cu}_4\text{O}_{11-\delta}$ would be dominated by the most conductive paths from both the CuO_2 planes and the CuO chains due to their comparable electrical conductivity, e.g., $\sigma_{\text{chain}} = 0.0084$ ($\mu\Omega \text{ cm}$)⁻¹ and $\sigma_{\text{plane}} = 0.0056$ ($\mu\Omega \text{ cm}$)⁻¹ in the case of $\text{CuBa}_2\text{YCu}_2\text{O}_{7-\delta}$ single crystal.¹³ However, it appears that a small deviation of oxygen vacancy could result in different magnitude of TEP and even a sign change, particularly in S_b , which has contributions from CuO chains.^{7,15,16} This could be due to one-dimensional conduction nature of Cu-O chains which is extremely sensitive to the broken segments of chains as a result of oxygen defects. It has been demonstrated that more oxygen deficiency (larger probability of broken chains) reflects more positive TEP of CuO chains.⁷ Therefore, more positive TEP of the

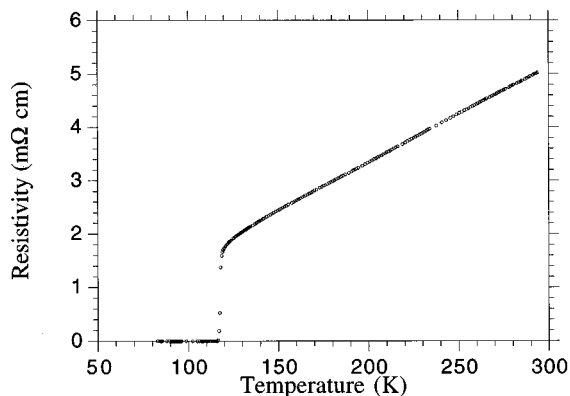


FIG. 2. The temperature dependence of resistivity for $\text{CuBa}_2\text{Ca}_3\text{Cu}_4\text{O}_{11-\delta}$. The zero resistivity is found to be 115.9 K.

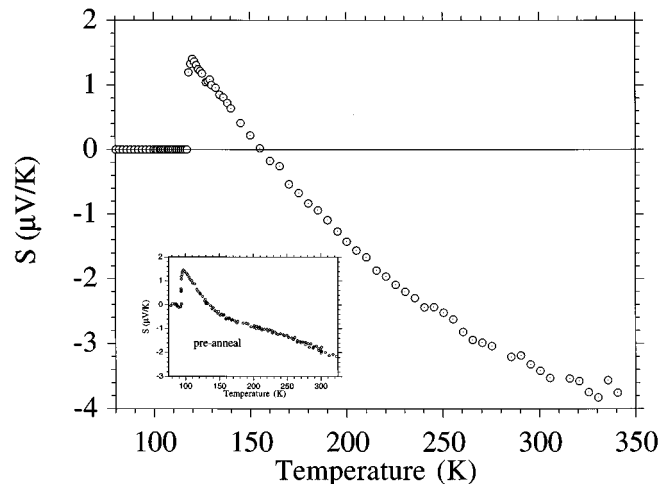


FIG. 3. The temperature dependence of thermoelectric power for $\text{CuBa}_2\text{Ca}_3\text{Cu}_4\text{O}_{11-\delta}$ with $T_{c,\text{zero}} = 115.9$ K. This behavior resembles S_a in the a axis for an untwinned $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystal (inset) (Ref. 7).

sample would suggest more broken segments of CuO chain configuration. With this picture in mind, by comparing with untwinned single crystal data of $\text{CuBa}_2\text{YCu}_2\text{O}_{7-\delta}$, it could give us a hint on whether the CuO chains play a role in the TEP behavior.

Turning to our TEP data in Fig. 3, it seems to indicate that the conduction for this $\text{CuBa}_2\text{Ca}_3\text{Cu}_4\text{O}_{11-\delta}$ sample ($T_{c,\text{zero}}=115.9$ K) is mainly from the carriers in the CuO_2 planes. For polycrystalline samples, the random arrangement of grain orientations would have TEP contributions from all three crystallographic axes. It is quite natural to expect that the TEP data in Fig. 3 are mainly contributed from ab planes like other cuprate superconductors due to their anisotropic nature. In fact, both the peak behavior above T_c and the sign crossover are quite similar to the ab -plane TEP of other high- T_c cuprate superconductors. One could argue that the crystal structure of $\text{CuBa}_2\text{Ca}_2\text{Cu}_4\text{O}_{11-\delta}$ may either involve the CuO chains or CuO_2 planes charge reservoir between BaO bilayers. Nevertheless, one can readily see that it is unlikely to have CuO_2 planes exist between BaO bilayers because that would give the valence state of Cu to be +5 if one takes +2.25 as the valence state of Cu for the rest of the CuO_2 planes. The arrangements of Cu and O atoms between the BaO bilayers of $\text{CuBa}_2\text{Ca}_3\text{Cu}_4\text{O}_{11-\delta}$ are most likely either in the form of CuO chains in one direction or defect chain segments in both a and b directions. However, the possibility of partial substitution of CuO sites by CO_3 groups is not excluded.^{4,9} In any event, the role of CuO chains conduction seems to be downplayed by the broken chain segments and the CO_3 group substitutions for this sample, particularly when we consider the high pressure synthesis which involves a process similar to quench from high temperature after a short period of one-hour sintering. This might be able to explain the similarity between our TEP data in Fig. 3 and S_a of the a direction for an untwinned $\text{CuBa}_2\text{YCu}_2\text{O}_{7-\delta}$ single crystal in Ref. 7. It could also support our argument that our TEP data in Fig. 3 is mainly contributed from the CuO_2 planes.

With regard to the effects of carrier concentration on TEP, unfortunately, it is not available to us due to the metastability of this high-pressure phase of $\text{CuBa}_2\text{Ca}_3\text{Cu}_4\text{O}_{11-\delta}$, which tends to decompose upon further heat treatment both in the oxygen and argon atmosphere. However, in another high-pressure synthesized $\text{CuBa}_2\text{Ca}_3\text{Cu}_4\text{O}_{11-\delta}$ sample with $T_{c,\text{zero}}=102$ K (Fig. 4) and $T_{c,\text{onset}}=117$ K, TEP in the normal state remains positive at $T \leq 340$ K (Fig. 5). The broad superconducting transition in both resistivity ($T_{c,\text{onset}}=117$ K) and TEP may indicate the oxygen inhomogeneity from one grain to another across the sample. As compared to the data of Fig. 3, the relatively large positive values of TEP imply a lower hole carrier concentration for this sample, assuming that it follows the same systematic trend of high- T_c cuprate superconductors. Higher sample resistivities (Fig. 4) might also suggest a lower carrier concentration than that of the $T_{c,\text{zero}}=115.9$ K sample. There are two possibilities for the origin of a lower hole carrier concentration. Either the oxygen loss or CO_3 substitution in the charge reservoir of $\text{CuO}_{1-\delta}$ layers could reduce the hole carrier concentration of $\text{CuBa}_2\text{Ca}_3\text{Cu}_4\text{O}_{11-\delta}$. Although our TEP curve is quite similar to those of pre-oxygen-annealed S_b in Ref. 7 (inset of Fig. 5) and some other $\text{CuBa}_2\text{YCu}_2\text{O}_{7-\delta}$ samples,^{17,18} it is unlikely

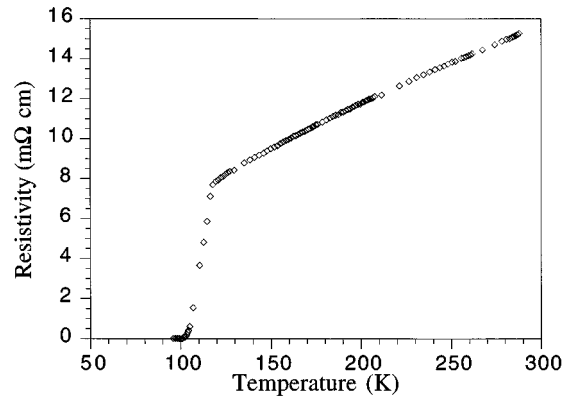


FIG. 4. The temperature dependence of resistivity for $\text{CuBa}_2\text{Ca}_3\text{Cu}_4\text{O}_{11-\delta}$. The $T_{c,\text{onset}}$ and $T_{c,\text{zero}}$ are 117 and 102 K, respectively.

that the positive values of TEP in Fig. 5 is due to the extra contributions from the CuO chains as in the case of S_b $\text{CuBa}_2\text{YCu}_2\text{O}_{7-\delta}$ in Ref. 7. The reasoning is given as follows. One can readily notice some differences of TEP at high temperatures between them. Our sample displays a slightly broader peak behavior and a minimum TEP above T_c is shifted to higher temperature at ~ 230 K. Furthermore, TEP at $T \geq 250$ K in our data continues to increase with increasing temperature, whereas the S_b of $\text{CuBa}_2\text{YCu}_2\text{O}_{7-\delta}$ in Ref. 7 decreases at $T \geq 250$ K. The derived chain contribution was found to be nearly saturated and independent of temperature at $T \geq 240$ –250 K as a result of narrow band conduction.⁷ The sum of weighted contribution from CuO_2 plane and $\text{CuO}_{1-\delta}$ contributions would therefore result in a less positive TEP with increasing temperature, for the TEP of CuO_2 planes (S_a) becomes more negative with increasing temperature at $T \geq 250$ K. In addition, TEP of $\text{CuBa}_2\text{YCu}_2\text{O}_{7-\delta}$ with large oxygen deficiency often displays a positive broad hump. In the light of increasing sample TEP for temperatures above 250 K in Fig. 5, it is therefore unlikely that CuO chain

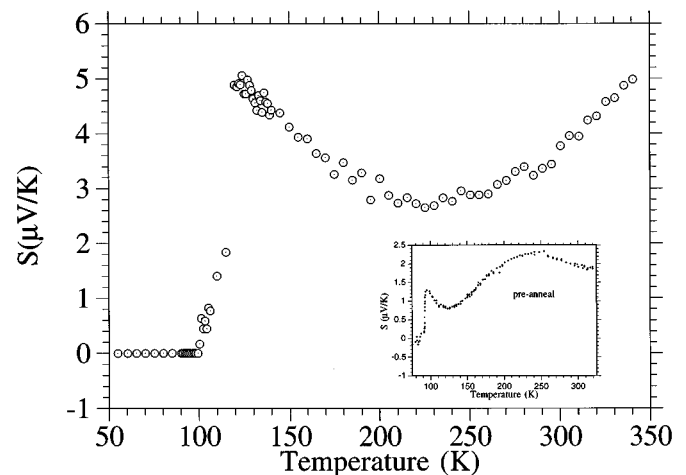


FIG. 5. The temperature dependence of thermoelectric power for $\text{CuBa}_2\text{Ca}_3\text{Cu}_4\text{O}_{11-\delta}$ with $T_{c,\text{onset}}=117$ K and $T_{c,\text{zero}}=102$ K. Inset shows the TEP of S_b in the b axis of an untwinned $\text{CuBa}_2\text{YCu}_2\text{O}_{7-\delta}$ single crystal (Ref. 7).

conduction plays a significant role to be responsible for the TEP behavior in the $T_{c,zero} = 102$ K sample. It is more plausible that positive TEP results of Fig. 5 are a combination of higher oxygen content grains with a negative (or less positive) TEP and less oxygen content grains (more broken CuO chain segments) with a positive TEP as a result of oxygen inhomogeneity within the sample. However, partial insertion of CO_3 groups between BaO bilayers could also possibly result in positive TEP results. The effect of CO_3 groups insertion on TEP is discussed in the following.

We now turn to the question of the effects on TEP if CO_3 groups are inserted between the BaO bilayers and partially substitute the CuO chain sites. Since the CO_3 group itself is not expected to contribute the electrical conduction, one could also expect no direct contribution from CO_3 groups to TEP. However, CO_3 groups could effect the carrier concentration of $(\text{Cu}_{1-x}\text{C}_x)\text{Ba}_2\text{Ca}_3\text{Cu}_4\text{O}_{11-\delta}$. If we take +4 and +2.25 as the valence state for C and Cu of the CuO_2 planes, respectively, for $(\text{Cu}_{0.68}\text{C}_{0.32})\text{Ba}_2\text{Ca}_3\text{Cu}_4\text{O}_{11.06}$ with the formula determined by the time-of-flight neutron-powder-diffraction data,⁹ the valence state of Cu in the CuO chains would be +2.71, as compared to +3.12 for $\text{CuBa}_2\text{Ca}_3\text{Cu}_4\text{O}_{11.06}$ without containing CO_3 groups. One can readily see that the CO_3 groups act as electron donors instead of hole donors. The CO_3^{2-} anion seems to introduce holes because of its anionic nature; however, it should be noted that two oxygen atoms of the CO_3 group are shared by the rocksalt layers of BaO. The net effect of inserted CO_3 groups is merely CO^{2+} unit which would reduce the hole carrier concentration in the system. While the partial substi-

tution of CO_3 groups would most likely change the occupancy number of oxygen in the CuO chains, it is more plausible that the oxygen stoichiometry of $\text{CuBa}_2\text{Ca}_3\text{Cu}_4\text{O}_{11-\delta}$ is not greater than 11, because the valence state of Cu would be +3 for $\delta=0$ if we again take +2.25 as the valence state of Cu in the CuO_2 planes. It is now quite clear that the effect of CO_3 insertion would reduce the hole carrier concentration. Although we are not clear how the reduced hole carrier concentration would be distributed in the CuO chains and CuO_2 planes, TEP should become more positive as a result of CO_3 insertion either by taking hole concentration away from the CuO chains or CuO_2 planes assuming the oxygen stoichiometry remains the same.

In conclusion, we have measured thermoelectric power for high-pressure synthesized $\text{CuBa}_2\text{Ca}_3\text{Cu}_4\text{O}_{11-\delta}$ cuprates. The nearly single phase sample with $T_{c,zero} = 115.9$ K is found to show common TEP characteristics with other high- T_c cuprates. By comparing with an untwinned single crystal of $\text{CuBa}_2\text{YCu}_2\text{O}_{7-\delta}$, it is conceivable that the carrier conduction in the CuO_2 planes is responsible for the TEP behavior of $T_{c,zero} = 115.9$ K sample without significant CuO chain contributions. Similarities can be found in both the structure and TEP behavior between the $\text{CuBa}_2\text{Ca}_3\text{Cu}_4\text{O}_{11-\delta}$ and $\text{CuBa}_2\text{YCu}_2\text{O}_{7-\delta}$ cuprates. We suggest that the TEP behavior of high- T_c cuprate superconductors is closely associated with the type of charge reservoir which has effects on the carrier characteristics.

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