A new aspect of single-layered cuprate superconductors — 90 K superconductors for Ca-doped Bi$_2$Sr$_2$CuO$_{6+\delta}$ single crystals

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Abstract. We found that the highest $T_c$ ($T_{c\text{ max}}$) of the superconductors in Bi-2201 phase was 80–90 K for the partially Ca substituted Bi$_2$Sr$_2$CuO$_{6+\delta}$ for Sr. The superconductivity was confirmed to be bulk effect from a specific heat jump around $T_c$. By the findings the correlation between the structure and $T_{c\text{ max}}$ has been made clear and simple with respect to the distance between Cu and the apical oxygen for the single-layered cuprate superconductors in the hole doped system.

1. Introduction
The mechanism of the high-temperature superconductivity in the hole-doped cuprates is still open. The single-layered cuprate superconductors are one of the most interesting materials for studying the problems from the crystal-structural point of view since the significant difference in the highest transition temperature $T_c$ in the hole-doped system. The $T_{c\text{ max}}$ values and the structures for the representative single-layered superconductors of La$_{2-x}$Sr$_x$CuO$_4$ (LSCO) [1] and Tl$_2$Ba$_2$CuO$_{6+\delta}$ (TBCO) [2] have been almost settled, whereas the $T_{c\text{ max}}$ for Bi$_2$Sr$_2$CuO$_{6+\delta}$ (BSCO) has been still controversial [3, 4, 5, 6].

The introduction of inhomogeneity associated with the carrier doping is needed for the cuprate superconductors. Then there are many extrinsic factors which will degrade the $T_c$ of the superconductivity [7]. Therefore, the $T_{c\text{ max}}$ value is thought to be the most close to the intrinsic one. In the present experiment, we report that the $T_{c\text{ max}}$ for BSCO is 80–90 K for the single crystals with partial Ca substitution for Sr (Ca-BSCO). We find the almost linear dependence of $T_{c\text{ max}}$ with respect to the distance between Cu and the apical oxygen for the single-layered cuprate superconductors in the range of $T_c < 100$ K.

2. Experimental
Preparation of single crystals was carried out by employing a traveling-solvent floating-zone (FZ) method. Starting materials of Bi$_2$O$_3$, SrCO$_3$, CaCO$_3$ and CuO were mixed according to the chemical formula of Ca-BSCO ($i.e.$, Bi$_{2+x}$Sr$_{2-x-y}$Ca$_y$CuO$_{6+\delta}$ with $x = 0.1, 0.15$ or $0.2$ and $y = 0.05, 0.4, 0.5$ or $0.6$ which will be expressed by $(x, y)$). The mixed powders were calcined at 700 ºC for 24 h. The product was reground, pelletized and calcined again at 800 ºC for 48 h.

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The calcined pellets were reground. The powders were pressed into a bar-shape rod and sintered at 800 °C for 48 h. The sintered rod was pre-melted in the FZ furnace at a traveling velocity of 10~25 mm/h. The final growth of crystals was done at the traveling velocity of 0.3 mm/h. All growth experiments were performed in air.

X-ray diffraction was measured by an XRD system (X’Pert PRO, PANalytical). Magnetic properties of samples were measured by a SQUID magnetometer (MPMS, Quantum Design). The applied magnetic field was 10 Oe (1 mT). The heat capacity was measured by a SQUID equipment (PPMS, Quantum Design). The same single crystal was used for the measurements with respect to each composition of the sample throughout the present experiment.

3. Results and discussion
Figure 1 is the X-ray diffraction pattern of the (00\(\ell\)) reflection peaks for the sample of (\(x, y\)) = (0.15, 0.4). The lattice parameter \(c = 2.442\) nm is consistent with the results of single-crystal analysis for the Ca-BSCO with the similar composition [8]. The inset of Fig. 1 indicates the negligibly small amount of impurity phases. Indeed, the single crystal was confirmed for the sample from the same batch from the precise XRD measurement [9].

The magnetization measurement was carried out for the same sample as measured in Fig. 1. The result is shown in Fig. 2, where the shielding effect is measured with raising temperature after cooling the sample in zero magnetic field (ZFC) and the Meissner effect was measured with cooling the sample in magnetic field (FC). The bulk effect of the superconductivity was confirmed by heat capacity measurement for the same sample as shown in the inset of Fig. 2. The magnitude of the jump is approximately 10 mJ/K\(^2\)mol, which is almost the same value for the sintered material [10]. The heat capacity jump is obtained as a broad peak below the magnetic \(T_c\) that is defined by the crossing temperature for the linear extrapolation of \(M/H\) data at \(-1\times10^{-3}\) emu/gOe and the \(M/H\) at the normal state. The broadness of the peak is about 10 K, and the value is comparable with the broad transition width observed in Meissner curve in Fig. 2. Those profiles of the broadness suggest the presence of the inhomogeneity of the superconductivity.

In the present experiment the optimal doping is observed at \((x, y) = (0.15-0.2, 0.4-0.5)\), and the \(T_{c\,\text{max}}\) is 87.2 K at \((x, y) = (0.15, 0.5)\) as shown in Fig. 3. The highest onset temperature of the transition, \(T_{c\,\text{onset}}\), is 91.1 K for the sample of \((x, y) = (0.2, 0.4)\) exhibited in the inset of Fig. 3. This tendency is consistent with the preceding results for the sintered crystals in which the \(T_{c\,\text{max}}\) is obtained at \((x, y) = (0.1, 0.4)\) [11, 12]. Thus the \(T_{c\,\text{max}}\) of BSCO is concluded to be 87.2 K.

The \(T_{c\,\text{max}}\) of the single-layered cuprate superconductors are summarized in Fig. 4 with...
Figure 2. Temperature dependence of $M/H$ for the single crystal of Ca-BSCO in the external field of 1 mT. The magnetic field is applied perpendicular to the CuO$_2$ plane. The inset is the heat capacity $C/T$ vs. $T$ for the same sample in the main panel.

Figure 3. Temperature dependence of $M/H$ for the single crystal of Ca-BSCO with the highest $T_c$ and Tconset (inset) measured in 10 mT.

Figure 4. The observed $T_c\ max$ plotted with respect to the Cu-apical oxygen distance for the single-layered cuprate superconductors. The dashed line is the guide for the eyes.

respect to the distance between Cu and the apical oxygen (Cu-O(2) distance), where 5 types of superconductors are indicated, LSCO [1], BSCO [3], La-doped BSCO (La-BSCO) [5], TBCO [2], HgBa$_2$CuO$_{4+\delta}$ (HBCO) [13] and Sr$_2$CuO$_2$F$_2$ (apical F) [14]. We plot the present result of Ca-BSCO at the Cu-O(2) distance obtained by Imai et al. [7] because of the similarity of the Ca doping level. We tried to synthesis Bi$_2$Sr$_2$CuO$_{6+\delta}$ ((x, y) = (0, 1)) whose $T_c$ was reported as 80 K [4], but it was difficult to grow single phase of Bi-2201 for this composition [15]. It is known that the $T_c\ max$ of LSCO increases up to 51.6 K with increasing the Cu-O(2) distance by applying pressure [16]. This tendency is also observed for the thin film of LSCO [17]. The Cu-O(2) distance is, however, not reported for those experiments, and the position of $T_c\ max$ for LSCO (stressed) is presumably shift to the longer distance as indicated by the arrow. Thus the $T_c\ max$ is well correlated to Cu-O(2) distance and looks like to be proportional to the distance in the region of $T_c\ max < 100$ K. The correlation between $T_c\ max$ and Cu-O(2) distance is theoretically studied [18, 19], and the results are consistent with the experimental results in Fig. 4 quantitatively.
The following two points should be commented about the correlation between $T_c$ and the inhomogeneity surrounding CuO$_2$ plane. One is the modulation structure along the crystal $b$-axis: The CuO$_2$ plane is not flat for the present case of Ca-BSCO due to the presence of the modulation [10]. The other is the doping of the isovalent element of Ca with respect to Sr: This doping will suppress the randomness of the potentials at the Sr crystallographic site. Those two points suggest the important role of the Cu-O(2) distance of the mean structure upon $T_{c \text{ max}}$.

4. Conclusion
The highest $T_c$ of the single-layered cuprate superconductors in the hole doped system was studied for the partially Ca-substituted BSCO for Sr. The experiment has been done for the single crystals prepared by using a floating-zone method. Much attention has been paid to measure the physical properties of X-ray diffraction, magnetization and heat capacity for the same crystal. We obtained $T_c$ of 87.2 K and onset temperature of 91.1 K for $(x, y) = (0.15, 0.5)$ and $(0.2, 0.4)$, respectively. The present work gives a linear dependence of highest $T_c$ with respect to the Cu-apical oxygen distance for the single-layered cuprates in the range of $T_c < 100$ K.

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