I. INTRODUCTION

The enhancement of the superconducting transition temperature \( T_c \) is one of key concerns for the studies of high-temperature superconductors (HTS). Crystallographically HTS consists of CuO₂ plane that supports superconducting current as well as charge reservoir layer where doping takes place. In the hole-doped high-\( T_c \) cuprates the charge reservoir is composed of two parts. That immediately outside the CuO₂ plane is called as the apical oxygen (apical-O) layer since the oxygen atoms here are at the apical sites of a CuO₆ octahedron or a CuO₂ pyramid, and that outside the apical-O layer, is named the second nearest charge-reservoir layer. The cation in the apical-O layer is termed as the A-site cation. The apical-O and A-site cation are expected to be more heavily involved in the electronic state of the CuO₂ plane in order to achieve a higher \( T_c \). The effect of dopant disorder on \( T_c \) has become a recent concern. The effect of the out-of-plane disorder was systematically studied for La₃CuO₅⁺δ. It was demonstrated that the introduction of cation disorder in the apical-O layer, A-site disorder, gives rise to an appreciable decrease in \( T_c \). The scanning-tunneling spectroscopy (STS) has revealed variations in the measured gap on nanometer scale. This gap inhomogeneity is shown also by STS to be correlated with the out-of-plane disorder.

Tuning oxygen stoichiometry is another usual way to dope CuO₂ plane as typically found for YBCO 123, Bi₂₂(\( n-1 \))₄Sr₂Ca₅Cu₂O₧₊₄ where \( n \) is controlled by the oxygen amount in the second nearest charge-reservoir layer. Since there is a direct connection with CuO₂ plane, tuning apical oxygen is expected to have stronger effect than those at the second charge-reservoir layer on superconductivity. This was supported by recent theoretical work that indicates correlation of \( T_c \) with the distance between apical oxygen and CuO₂ plane. However, for almost all the hole-doped HTS the apical oxygen sites are fully occupied. Searching for a system with tunable apical oxygen content would be effective for studying the superconducting mechanism of HTS. The hole doped Sr₂CuO₄⁺δ superconductor synthesized under high pressure is a unique cuprate that crystallizes into an oxygen-deficient La₂CuO₄ (i.e., K₂NiF₄) structure with partially occupied apical sites as shown in Fig. 1. Interestingly the apical oxygen acts as hole dopant, i.e., the carrier density of Sr₂CuO₄⁺δ is determined by the amount of additional oxygen \( \delta \) that is located at the apical site. Recently, using SrO₂ as an oxidizer, we have succeeded in fab-
The samples were synthesized in two steps. In the first step, a series of Sr$_{2}$-$x$Ba$_{x}$CuO$_{3}$ (0 ≤ $x$ ≤ 0.6) precursors were prepared by conventional solid-state reaction method from high-purity raw materials SrCO$_{3}$, BaCO$_{3}$, and CuO. The powder mixture in an appropriate ratio was ground together in an agate mortar and then calcined at 950 °C for approximately three days in air with two intermediate grindings in order to obtain single-phase samples. In the second step, the precursors were mixed with SrO and CuO to form the nominal composition of Sr$_{2}$-Ba$_{x}$CuO$_{3}$+$\delta$ in a dry glove box that was used to prevent the degradation of hygroscopic reagents. The materials were then subjected to high-pressure synthesis under 6 GPa pressure and at 1000 °C for 30 min using a cubic-anvil-type high pressure facility, and then quenched to room temperature before releasing the pressure. The role of SrO$_{2}$ is to create an oxygen atmosphere during the high-pressure synthesis as previously described in the related Cl series$^{22-23}$ or Sr$_{2}$CuO$_{3}$+$\delta$ (Ref. 16) superconductors. Here the excess oxygen content $\delta$ is controlled by the oxidizer amount SrO$_{2}$ in the nominal starting materials. In order to study the ordering effect of the dopant atoms (apical oxygen distribution), we also annealed several samples in the temperature range between 150 and 300 °C for 12 h under 1 atm N$_{2}$ atmosphere in a tube furnace.

The structure of obtained polycrystalline samples was identified by powder x-ray diffraction (XRD) collected with 2θ steps of 0.02° and 3 s counting time in the range of 5° ≤ 2θ ≤ 120° using Cu Kα radiation. The x-ray diffraction pattern was refined with Rietveld method using WINGROD program. The DC magnetic susceptibility was measured using a superconducting quantum interference device magnetometer in an external magnetic field of 20 Oe for both zero-field-cooling and field-cooling (FC) modes.

III. RESULTS AND DISCUSSION

By changing the Sr to Ba ratio and keeping a constant hole concentration (fixed $\delta$), a series of Sr$_{2}$-Ba$_{x}$CuO$_{3}$+$\delta$ (0 ≤ $x$ ≤ 0.6) superconductors were prepared using the high-pressure and high-temperature synthesis. Since a maximum $T_c$ is attained in SrCuO$_{3}$+$\delta$ at nominal $\delta$ = 0.4, we keep all the Sr$_{2}$-Ba$_{x}$CuO$_{3}$+$\delta$ samples with the same oxygen content in order to separate out the A-site effects. The x-ray diffraction patterns show purely tetragonal $K_{2}NiF_{4}$-type phase with space group I4/mmm in the entire $x$ range up to 0.6. Note that no information on the apical-O configuration can be extracted directly from the x-ray diffraction. Assuming the La$_{2}$CuO$_{4}$ prototype tetragonal structure but with partially occupied apical oxygen, we refined the crystal structure of Sr$_{2}$-Ba$_{x}$CuO$_{3}$+$\delta$ using the Rietveld method. Figure 2 shows the XRD pattern of a sample with the nominal composition Sr$_{1.84}$Ba$_{0.16}$CuO$_{3}$+$\delta$, together with the results of Rietveld refinement. A reasonable $R_{wp}$ (weighed-profile $R$ factor) factor of 8.76% was obtained as shown in Table I, indicating that the structural model is a reasonable one. Figure 3 shows the cell parameters of the samples as a function of Ba content $x$ for Sr$_{2}$-Ba$_{x}$CuO$_{3}$+$\delta$. As compared with Sr$_{2}$CuO$_{3}$+$\delta$ both $a$- and $c$-axis lattice constants of Sr$_{2}$-Ba$_{x}$CuO$_{3}$+$\delta$ are expanded...
due to larger Ba ion incorporated to the Sr sites. For example, the lattice parameters increased from $a=3.79$ Å, $c=12.50$ Å for Sr$_2$CuO$_3$+ (Ref. 16) to $a=3.89$ Å, and $c=12.78$ Å for Sr$_{1.3}$Ba$_{0.6}$CuO$_{3.4}$, respectively.

In Fig. 4(a) we present the temperature dependence of magnetic susceptibility measured for the as-prepared samples Sr$_{2-x}$Ba$_x$CuO$_{3.6}$ with $x=0.16$, 0.32, and 0.6 in the FC mode at an external field of 20 Oe. The superconducting transition temperature $T_c$ increases with increasing Ba content. Starting from $T_c=75$ K for Sr$_2$CuO$_{3.6}$ a maximum $T_c=98$ K is reached at $x=0.6$. The Meissner volume fraction of Sr$_{2-x}$Ba$_x$CuO$_{3.6}$ sample is more than 10% at 5 K, suggesting the nature of bulk superconductivity. The Sr$_{2-x}$Ba$_x$CuO$_{3.6}$ sample with $x>0.6$ are mixed phases, showing no superconducting transition.

In the case of Sr$_2$CuO$_{3.6}$, $T_c$ can be enhanced to 95K by post-annealing at relatively low temperatures ($\sim 250$ °C), probably because the apical-O atoms order optimally. However, the Ba substituted samples very easily decomposes upon heating at ambient pressure. It is found that Sr$_{2-x}$Ba$_x$CuO$_{3.6}$ becomes unstable with increasing Ba content due to the fact that the high-pressure synthesized materials with larger unit cell is usually thermodynamically meta-stable at ambient pressure. In Fig. 4(b) we show the post-annealing effect on Sr$_{1.9}$Ba$_{0.1}$CuO$_{3.4}$. $T_c$ increases from the initial 80K (as prepared) to 91K by annealing at 250 °C but its superconducting volume fraction appreciably decreases. With increasing Ba content to $x=0.32$, $T_c=88$ K of as-prepared sample is enhanced to 92K by annealing at 200 °C, but annealing at higher temperatures results in degradation of superconductivity [Fig. 4(c)]. Though the nominal composition is also Sr$_{1.68}$Ba$_{0.32}$CuO$_{3.4}$, the $T_c$ of the sample is a little lower than the $T_c$ of the sample in Fig. 4(a). In fact, besides the nominal composition, the $T_c$ of the material varies a little depending on the synthesis temperature. In the case of $x=0.6$, as prepared $T_c$ reaches 98K, already exceeding the maximum $T_c=95$ K of Sr$_2$CuO$_{3.6}$ with optimally ordered apical-O atoms. We annealed the sample of Sr$_{1.3}$Ba$_{0.7}$CuO$_{3.4}$ but its superconductivity is lost immediately upon heating even at 150 °C indicating the heavily metastable nature of the Ba substituted sample. It seems that the highest $T_c$ of the present superconductor is realized in the vicinity of a structural instability.

For Sr$_2$CuO$_{3.6}$ the electron diffraction (ED) and high-resolution transmission electron microscopy (TEM) measurements are possible to investigate the evolution of the structural modulation associated with the apical-O ordering with post-annealing temperature. A modulated structure with $C2/m$ symmetry is found for as-prepared sample with $T_c=75$ K which evolves into a $Pmnm$ modulation structure with $T_c=95$ K after annealing at 250 °C. Supposing that the as-prepared samples have the same $C2/m$ modulated structure as that of Sr$_2$CuO$_{3.6}$, then the result indicates that $T_c$ is

![FIG. 3. (Color online) The lattice parameters $a$ and $c$ as a function of $x$ value for Sr$_{2-x}$Ba$_x$CuO$_{3.6}$.](image)

![FIG. 2. (Color online) The Rietveld refinement results of powder XRD patterns for Sr$_{1.84}$Ba$_{0.16}$CuO$_{3.4}$ sample. Dots and lines show the observed and calculated patterns, respectively. The difference between the observed and fitted patterns is displayed at the bottom of the figures.](image)

### TABLE I. Results of structure refinements for the superconductor Sr$_{1.84}$Ba$_{0.16}$CuO$_{3.4}$ using the Rietveld method. Space group: $I4/mmm$. $R_w=8.76\%$, $R_p=6.15\%$. The lattice parameters: $a=3.8152(2)$ Å, $c=12.5665(3)$ Å. The refinement range of 2θ is $5^\circ-120^\circ$, CuKα1 radiation was used.

<table>
<thead>
<tr>
<th>Atom (Sr/Ba)</th>
<th>Site</th>
<th>$X$</th>
<th>$Y$</th>
<th>$Z$</th>
<th>Occupancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sr/Ba</td>
<td>4e</td>
<td>0</td>
<td>0</td>
<td>0.35590(14)</td>
<td>1</td>
</tr>
<tr>
<td>Cu</td>
<td>2a</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>O1</td>
<td>4c</td>
<td>0</td>
<td>0.5</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>O2</td>
<td>4e</td>
<td>0</td>
<td>0</td>
<td>0.172072(0)</td>
<td>0.58(2)</td>
</tr>
</tbody>
</table>
Remarkably enhanced by Ba substitution without changing the ordering pattern of apical-O atoms. Unfortunately, the neutron or ED and TEM investigation are not possible at the moment for the Ba-substituted materials since it is difficult to obtain sufficient amount of samples, and they are unstable against heating due to exposure to high-density electron beam flux. So, we cannot rule out the possibility that the Ba incorporation tends to stabilize the Pmmn modulation corresponding to the “optimal” apical-O ordering in Sr2CuO3+δ with Tc=95 K. In either case since Tc=98 K achieved in the as-prepared sample of x=0.6 exceeds the highest Tc of Sr2CuO3+δ, it is certain that the larger A-site cation size leads to higher Tc in the present system.

It is also noted that the substituted Ba in the Sr2CuO3+δ plays dual roles: one is to expand the unit cell size and the other is to create disorder due to cation size mismatch between Sr2+ and Ba2+. The previous investigation of La2CuO4-related superconductors suggested that Tc depends both on the average cation size and the A-site cation disorder.

It was also suggested that, if the degree of disorder does not change, Tc tends to increase with increasing A-site cation size ⟨rA⟩, while Tc decreases with increasing the A-site disorder at the constant average ⟨rA⟩. In the present Sr2−xBaxCuO3+δ system, Tc of as-prepared sample increases with A-site cation size, achieving 98 K at x=0.6. The result suggests that the larger A-site cation size is an important ingredient for the enhancement of Tc in Sr2CuO3+δ while the A-site disorder arising from cation size mismatch between Sr and Ba appears to have relatively small effect on Tc. Since Sr and Ba are isovalent alkaline earth element, their substitution does not change the carrier density, nor introduce charge disorder, which is different from ordinary A-site substitution with heterovalence ions such as that in La2−xSrxCuO4.17-19 From the Shannon table,25 the ionic radius for Ba2+ (Sr2+) is 1.47 Å (1.31 Å). The calculated disorder parameter σ2 = ⟨rA⟩2-⟨rA⟩2 for Sr2−xBaxCuO3+δ is 0.005 for x=0.6. In the case of other single-layer cuprates, such as La-based 214 and rare-earth substituted Bi2201 compounds, this value is so large that it would have lead to a considerable reduction in Tc—more than 50% reduction, or Tc reduction of more than 30K, from the Tc value of disorder-free (σ=0) material.4 It is likely that a similar Tc reduction took place in Sr2CuO3+δ by Ba substitution, and an ideal Tc value of “disorder free” Sr1.8Ba0.6CuO3+δ would be 130 K or higher. Note that in the La214 and Bi2201 systems the A-site disorder is accompanied with charge disorder. So, it is inferable that dominant effect of A-site disorder on Tc is from charge disorder introduced by substitution of heterovalent cations which is not the case with the present system.

If there were a small but finite reduction in Tc due to the cation-size disorder then the Tc enhancement in Sr2−xBaxCuO3+δ is indicative of substantial contribution from the expansion of the unit cell size. There might be two factors associated with the increase in lattice parameters which would affect the electronic parameters in the CuO2 plane: (1) increase in the apical-O distance, possibly caused by the increase in the c-axis lattice constant and (2) increase in the Cu-O in-plane bond length. The correlation between Tc and apical-O distance is empirically pointed out in the two contexts, a change in the second (third) nearest-neighbor hop-
ping parameter and a change in the Madelung energy. In a different context, Geballe suggests a possible role of apical-O atoms as negative-\(U\) centers which promote pair formation.\(^6\)

The in-plane \(\text{Cu-O}\) bond length changes from 1.89 Å for \(\text{Sr}_2\text{CuO}_3\) to 1.95 Å for \(\text{Sr}_{2-x}\text{Ba}_x\text{CuO}_3\) at \(x=0.6\). The simplest copper oxide containing \(\text{CuO}_2\) plane is the so-called infinite-layer compound \(\text{CaCuO}_2\) wherein \(\text{CuO}_2\) plane alternatively stacks with \(\text{Ca}\) spacer along the \(c\) axis. The \(\text{CuO}_2\) plane in the infinite-layer compound is thus “free-standing” suffering only weak compressive or tensile stresses from the \(\text{Ca}\) layer. The \(\text{Cu-O}\) bond length in the infinite-layer compound is thus “free-standing” with expanded dimension provides a stage favorable for \(T_c\) enhancement with \(\text{Ba}\) substitution might be a consequence of this work].

\(\text{Sr}_2\text{CuO}_3^+\) the increasing \(\text{Cu-O}\) bonding length from 1.89 Å for \(\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8\); Ref. 29 \(\text{HgBa}_2\text{CuO}_4^+\) and \(\text{Sr}_1\text{Ba}_0.6\text{CuO}_3\) in Fig. 5. In this sense, the \(T_c\) enhancement with \(\text{Ba}\) substitution might be a consequence of the increasing \(\text{Cu-O}\) bond length from 1.89 Å for \(\text{Sr}_2\text{CuO}_3\) toward 1.93 Å. In the context a much higher \(T_c\) can be expected for \(\text{Ba}_2\text{CuO}_3\).

IV. SUMMARY

In conclusion, we have successfully synthesized Ba-doped \(\text{Sr}_{2-x}\text{Ba}_x\text{CuO}_{3+y}\) \((0 \leq x \leq 0.6)\) with a \(\text{K}_2\text{NiF}_4\)-type structure using a high-pressure and high-temperature synthesis. The superconducting transition temperature with \(T_c^{\text{max}} = 98\) K is achieved for \(x=0.6\). The increase in the unit cell size due to incorporation of large-size \(\text{Ba}\) cation is likely responsible for the enhancement of \(T_c\) in this material. Since \(\text{Ba}\) is isovalent to \(\text{Sr}\), the result also suggests that the disorder

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