



Enhancement of the superconducting critical temperature in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ by controlling disorder outside CuO_2 planes

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We investigate the effect of disorder at various lattice sites outside the CuO_2 plane on the superconducting critical temperature T_c of the cuprate superconductor $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ (Bi2212). The most effective disorder turns out to be that at the Sr site in the neighboring blocks, which contain apical-oxygen atoms. The Sr-site disorder reduces T_c and also produces a residual component (ρ_0) in the in-plane resistivity, the magnitude of which is found to be proportional to the magnitude of T_c reduction. We demonstrate that both the T_c -degradation rate and ρ_0 decrease as the number of the CuO_2 planes increases in the unit cell, that is, as the number of the neighboring SrO blocks decreases. In real crystals of Bi-based cuprates, main source of disorder is Bi atoms randomly occupying the Sr sites. We have succeeded in reducing the Bi content at Sr sites as much as possible and achieved $T_c=98$ K, a high- T_c record in Bi2212.

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I. INTRODUCTION

Sixteen years have passed since the maximum superconducting critical temperature $T_c \sim 135$ K was recorded in 1993.¹ Although many researchers have tried to raise T_c , no successful results have yet been reported and the question of which factors determine T_c in cuprates has not been fully understood. In spite of having the same CuO_2 structural unit and similar structure, T_c of cuprates is strongly material dependent, ranging from ~ 30 to 135 K, indicating that T_c is not determined by a single parameter or a few parameters which characterize the electronic or phononic systems. So many parameters have so far been known to affect T_c , e.g., (i) doping level, (ii) superfluid density,² (iii) number of CuO_2 planes in a unit cell,³ (iv) disorder in the CuO_2 plane,⁴ and (v) distance of the apical-oxygen atoms from the CuO_2 plane.⁵ Eisaki *et al.*⁶ pointed out that disorder caused by dopant atoms outside the CuO_2 planes also has influence on T_c . As a good demonstration, T_c is enhanced to 95 K for a single-layer cuprate $\text{Sr}_2\text{CuO}_{3+\delta}$ when randomly distributed dopant atoms, apical-oxygen atoms in this material, form an ordered array.⁷ Fujita *et al.*⁸ quantitatively examined the effect of this type of disorder in the single-layer system $\text{Bi}_{2.0}\text{Sr}_{1.6}\text{Ln}_{0.4}\text{CuO}_{6+\delta}$ (Ln-Bi2201) in which disorder is controllably introduced by the partial substitution of the rare-earth element (Ln) for Sr and the degree of disorder is varied by changing Ln with different ionic radii.⁹ They showed that T_c appreciably decreases with increasing degree of disorder at Sr sites.

In this paper we focus on the bilayer $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ (Bi2212), and examine the effect of disorder at various sites outside the CuO_2 planes (out-of-plane disorder). Based on this result we explore methods of enhancing and maximizing T_c of Bi2212. In addition, by comparison with the available data on single-layer and trilayer cuprates, we elucidate how the reduction in T_c due to out-of-plane disorder depends on the number of CuO_2 planes in a unit cell.

The crystal structure of Bi2212 is composed of three building blocks other than two CuO_2 planes: (1) Bi_2O_2 block, (2) SrO block, and (3) Ca block. These three blocks are charge reservoirs and, at the same time, sources of disorder. The excess oxygen atoms are located in or near the Bi_2O_2 block which act as the hole dopant. A fairly large amount of Pb can replace Bi which acts to suppress the structural supermodulation of the BiO layers. Bi^{3+} ions tend to replace the Sr^{2+} ions in the SrO block (sometimes called “site mixing”). The Ca^{2+} ions in the plane sandwiched by two CuO_2 planes can easily be replaced by rare-earth (Y or Ln^{3+}) ions with relatively small ionic radii. Bi^{3+} and Ln^{3+} substituted for Sr^{2+} and Ca^{2+} decrease the hole density in the CuO_2 plane. Normally grown single crystals of Bi2212 contain these three types of disorders. In this regard Bi2212 is a highly disordered system, but is a good ground for studying and discriminating the effects of disorder at different sites on superconducting T_c . Usually increasing or decreasing disorder in one particular block changes the doping level in the CuO_2 planes, but in Bi2212 the doping level can be controlled also by the other two blocks. This gives an opportunity to examine the pure disorder effect from an individual block without changing the doping level upon which T_c depends very sensitively.

We show below that the disorder in the SrO block is most influential on T_c , while disorder in other two blocks has very small effect on T_c . In real crystals of Bi2212 a certain fraction of Bi ions occupy the Sr sites in the SrO block which are the dominant source of disorder that reduces T_c . Therefore, the reduction in Bi content in the SrO block is an effective way to increase T_c . In the present work we have succeeded in reducing Bi content as much as possible and increasing T_c up to 98 K, a record value in Bi2212. Finally, we illustrate that the T_c degradation due to this type of disorder weakens as the number of CuO_2 planes in a unit cell increases, which explains why the single-layer system is most strongly material dependent.

TABLE I. ICP-analyzed compositions and maximum T_c (onset) of the crystals (most of them containing Pb) in this study. The molar ratio of Cu composition is set to 2.

Nominal composition	Compositions (ICP) Bi/Pb/Sr/Ca/Y/Cu	T_c^{\max} (K)
$\text{Bi}_{2.2}\text{Sr}_{1.8}\text{CaCu}_2\text{O}_{8+\delta}$	2.16/0.00/1.85/1.06/0.00/2	92.0
$\text{Bi}_{2.0}\text{Sr}_{2.0}\text{Ca}_{0.92}\text{Y}_{0.08}\text{Cu}_2\text{O}_{8+\delta}$	2.02/0.00/1.98/0.85/0.08/2	96.0
$\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$	1.69/0.33/1.96/0.92/0.00/2	96.0
$\text{Bi}_{1.4}\text{Pb}_{0.8}\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$	1.42/0.55/1.97/0.96/0.00/2	97.5
$\text{Bi}_{1.3}\text{Pb}_{0.9}\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$	1.31/0.66/1.94/1.08/0.00/2	94.0
$\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_{0.9}\text{Y}_{0.1}\text{Cu}_2\text{O}_{8+\delta}$	1.58/0.36/1.92/0.93/0.11/2	94.0
$\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_{0.95}\text{Y}_{0.05}\text{Cu}_2\text{O}_{8+\delta}$	1.50/0.37/1.97/0.92/0.05/2	96.0
$\text{Bi}_{1.4}\text{Pb}_{0.7}\text{Sr}_2\text{Ca}_{0.97}\text{Y}_{0.03}\text{Cu}_2\text{O}_{8+\delta}$	1.33/0.65/2.00/0.98/0.03/2	98.0

II. EXPERIMENTAL METHODS

High-quality single crystals of Bi2212 were grown using the traveling-solvent-floating-zone (TSFZ) method. In this study, we made the samples (1) $\text{Bi}_{2+x}\text{Sr}_{2-x}\text{CaCu}_2\text{O}_{8+\delta}$, (2) $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-y}\text{Y}_y\text{Cu}_2\text{O}_{8+\delta}$, (3) $\text{Bi}_{2-w+x}\text{Pb}_w\text{Sr}_{2-x}\text{CaCu}_2\text{O}_{8+\delta}$ and (4) $\text{Bi}_{2-w}\text{Pb}_w\text{Sr}_2\text{Ca}_{1-y}\text{Y}_y\text{Cu}_2\text{O}_{8+\delta}$ from well-dried powders of Bi_2O_3 , PbO , SrCO_3 , CaCO_3 , Y_2O_3 , and CuO . The crystal growth was carried out in air and at growth speeds of 0.15–0.2 mm/h for Pb-free Bi2212 and 0.5 mm/h for Pb-doped Bi2212. For Pb-doped crystals the actual Pb content tends to be smaller than the nominal one since Pb is easily evaporated out during the TSFZ growth. Inductively coupled plasma (ICP) spectroscopy was used for the composition analysis and a superconducting quantum interference device (SQUID) magnetometer was used for measurement of T_c . Table I lists both nominal and actual compositions of the crystals containing Pb in this study. T_c was defined as the onset temperature at which the zero-field-cooled susceptibility starts to drop. In-plane resistivity was measured by the six-probe method with current kept constant (1 mA). We measured the resistivity for more than ten samples for each composition to reduce uncertainty in the magnitude and to check homogeneity of the crystals.

T_c of each sample or the doped hole density can be varied by annealing it under different atmospheres. Oxidation annealing was performed in air or under oxygen gas flow, and deoxidation annealing was done in vacuum or under nitrogen gas flow. T_c^{\max} in Table I is the maximum T_c which was attained by changing the excess oxygen content δ under various annealing conditions. In the following, T_c means T_c^{\max} , if not otherwise mentioned. The annealing condition giving T_c^{\max} is attached to the caption of the result. We can vary two parameters, operating temperature and oxygen partial pressure, for annealing. From thermogravimetric analysis, we found that for Pb- and Y-doped crystals δ can be varied over a wider range than the reported one,¹⁰ $0.20 < \delta < 0.26$ for Bi2212 without Pb or Y. In fact, we found that T_c shows a maximum value when the annealing condition or atmosphere is in extreme reduction or extreme oxidation attainable in this study.

III. EXPERIMENTAL RESULTS

A. Effect of out-of-plane disorder on the in-plane resistivity

The Bi/Sr-site mixing, the dominant source of disorder in Bi2212, occurs easily at the Sr site in Bi2212 due to following reasons: (1) Bi^{3+} cations tend to be attracted to CuO_2 planes and replaced to the A site (nominally the Sr site in Bi2212) because the CuO_2 bilayer is negatively charged, $[\text{CuO}_2\text{-Ca-CuO}_2]^{2-}$, and (2) the apical-oxygen block allocating Sr^{2+} at the A site is relatively unstable as compared with that allocating Ba^{2+} because of smaller ionic radius of Sr^{2+} and hence smaller tolerance factor.^{11,12} These make the Sr site vulnerable to the intrusion of Bi^{3+} . Normally, Bi2212 crystals grown by the TSFZ method contain an appreciable amount of excess Bi, $x=0.10\text{--}0.20$ in the formula $\text{Bi}_{2+x}\text{Sr}_{2-x}\text{CaCu}_2\text{O}_{8+\delta}$, and T_c is, at its highest, 92 K even for optimal doping. From the previous works,^{6,8} it is likely that T_c is reduced due to this Sr-site disorder.

Figures 1(a) and 1(b) show the temperature dependences of the in-plane resistivities for optimally doped Ln-Bi2201 and Bi2212 (~ 0.2 holes/Cu) with disorder in the SrO block: (a) rare-earth element Ln substitution for Sr in Bi2201, and (b) Bi/Sr-site mixing in Bi2212. The resistivity shown in Fig. 1(c) is for a sample in which the Sr-site disorder is reduced, but the Ca site sandwiched by two CuO_2 planes is disordered due to partial Y substitution. Note that disorder due to excess oxygen atoms and structural supermodulation always exists near or inside the Bi_2O_2 block. It is demonstrated for Ln-Bi2212 that Ln disorder induces residual resistivity component ρ_0 in the in-plane resistivity and the magnitude of ρ_0 (vertical shift of the resistivity curve) is correlated well with the degree of disorder in the SrO block.⁸ Figure 1(b) shows that this is also the case with Bi2212 with Bi in the Sr sites. In Fig. 2(c) we show a plot of the T_c -degradation rate (T_c/T_{c0}) against the magnitude of two-dimensional residual resistivity per CuO_2 plane for disorder in the SrO block in both Bi2201 and Bi2212. We see that the reduction in T_c due to disorder at Sr sites roughly scales with the magnitude of ρ_0 . Note that the disorder in the Ca block due to Y substitution and that near the Bi_2O_2 block due to excess oxygen atoms produce almost no residual resistivity. Hence, we infer that disorder in these two blocks has negligible effect on T_c , even though the location of the Ca site is close to the CuO_2 planes.

Further insight into the effect of out-of-plane disorder is gained by a comparison with single-layer and trilayer cuprates. For this comparison, we use σ^2 (variance of ionic radii of cations at the Sr site) as a measure of the degree of disorder.¹⁴ σ^2 is determined by two factors: one is the fraction of different cations intruding the A site, x , and the other is the ionic radius r of the cations substituted at the A site—ionic radius mismatch between intruding cations and Sr. Specifically, in the case of $\text{Bi}_2\text{Sr}_{2-x}\text{Ln}_x\text{CuO}_{6+\delta}$, $\sigma^2(r, x)$ is determined by

$$\sigma^2(r, x) = \frac{x}{2}r_{\text{Ln}^{3+}}^2 + \left(1 - \frac{x}{2}\right)r_{\text{Sr}^{2+}}^2 - \left[\frac{x}{2}r_{\text{Ln}^{3+}} + \left(1 - \frac{x}{2}\right)r_{\text{Sr}^{2+}}\right]^2,$$

where $r_{\text{Ln}^{3+}}$ and $r_{\text{Sr}^{2+}}$ are the radii of rare-earth Ln^{3+} and Sr^{2+} ions, respectively. For $\text{Bi}_{2+x}\text{Sr}_{2-x}\text{CaCu}_2\text{O}_{8+\delta}$, assuming that

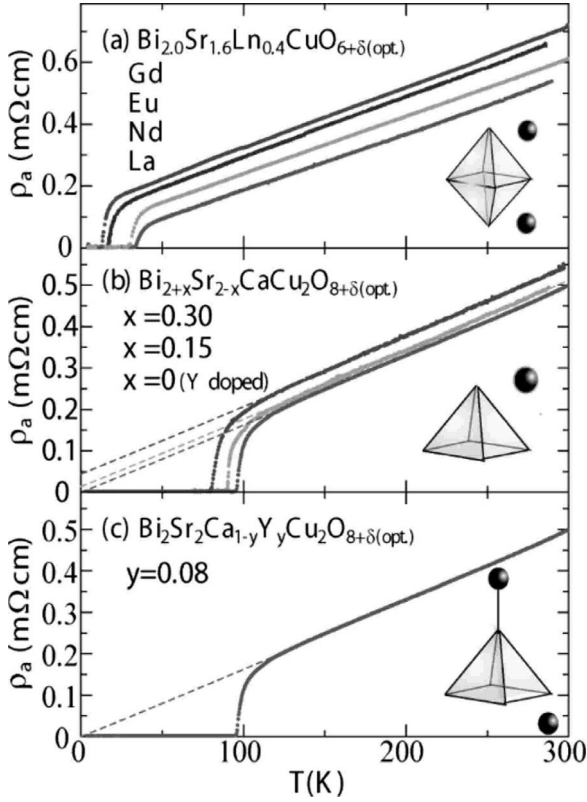


FIG. 1. (a)–(c) Effect of disorder at out-of-plane sites of optimally doped Bi cuprates on the in-plane resistivity with the current flowing along the a axis. We define the residual resistivity component ρ_0 by the extrapolation of the temperature-linear resistivity to 0 K. (a) Single-layer $\text{Bi}_2\text{Sr}_{1.6}\text{Ln}_{0.4}\text{CuO}_{6+\delta(\text{opt})}$ with various rare-earth Ln substituted for Sr (Ln=Gd, Eu, Nd, and La from top to bottom). Disorder is introduced by the 20% substituted rare-earth (Ln) element in the SrO block. The data of Ln-Bi2201 are from Ref. 8. (b) $\text{Bi}_{2+x}\text{Sr}_{2-x}\text{CaCu}_2\text{O}_{8+\delta(\text{opt})}$ with disorder due to Bi atoms occupying the Sr sites ($x=0.30, 0.15,$ and 0 from top to bottom). The data for $x=0$ are the same as that in (c). (c) $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-y}\text{Y}_y\text{Cu}_2\text{O}_{8+\delta(\text{opt})}$ (Y-Bi2212) with disorder both in the Ca and near the Bi_2O_2 block. The hole density is set near optimal (~ 0.2 holes/in-plane Cu) in each sample by adjusting oxygen content. Near-optimal doping is guaranteed by the magnitude and the slope of the temperature-linear resistivity.

the intrusion of Bi is a major source of Sr-site disorder,

$$\sigma^2(r,x) = \frac{x}{2}r_{\text{Bi}^{3+}}^2 + \left(1 - \frac{x}{2}\right)r_{\text{Sr}^{2+}}^2 - \left[\frac{x}{2}r_{\text{Bi}^{3+}} + \left(1 - \frac{x}{2}\right)r_{\text{Sr}^{2+}}\right]^2,$$

where $r_{\text{Bi}^{3+}}$ is the ionic radius of Bi^{3+} .

One sees in Fig. 1 that a small but finite residual resistivity appears and increases with increasing Sr-site disorder in both Bi2201 and Bi2212. For quantitative comparison, plotted in Fig. 2(a) is a relationship between disorder-induced two-dimensional residual resistivity per CuO_2 plane (ρ_0^{2D}) and $\sigma^2(r,x)$ for Bi2201 and Bi2212. We see that the magnitude of ρ_0^{2D} for $n=1$ is roughly twice as large as that for $n=2$ at the same σ^2 , which indicates that the Sr-site disorder works as an elastic scatterer only for the carriers in the adjacent CuO_2 plane. That is, the difference between $n=1$ and

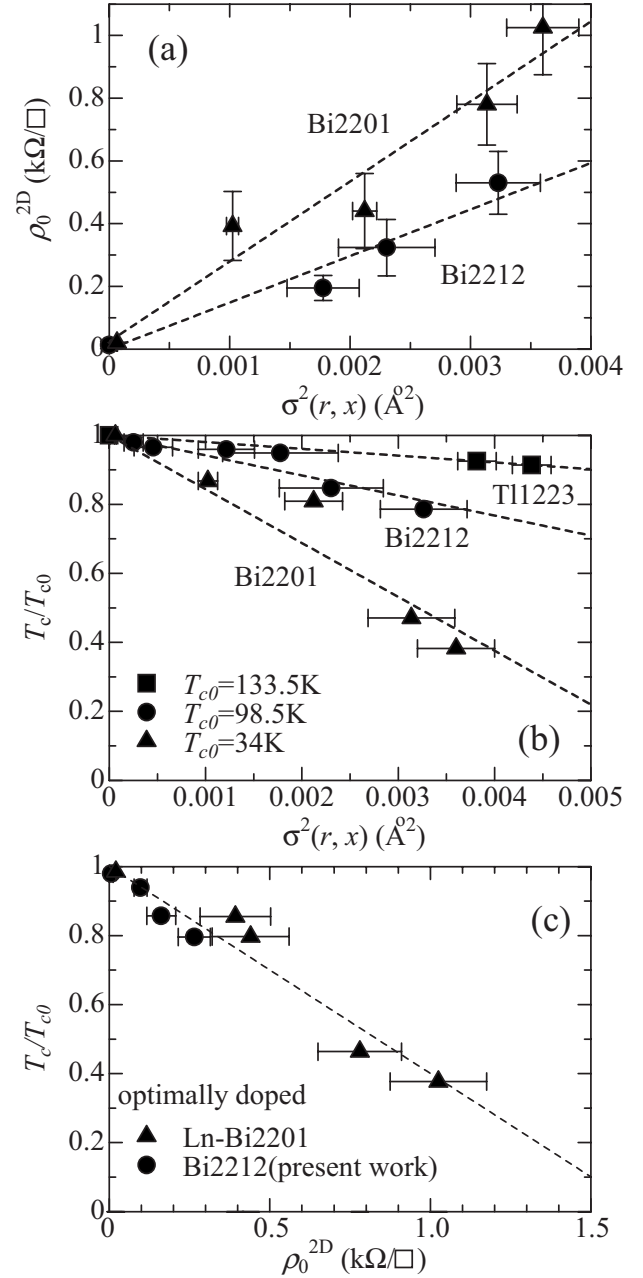


FIG. 2. (a) Residual resistivity per CuO_2 plane, ρ_0^{2D} , vs degree of disorder defined in the text. Broken lines are the least-squares fits to the data. (b) T_c normalized by T_{c0} (defined in the text) plotted against $\sigma^2(r,x)$ for $n=1$ (Bi2201) (Ref. 8), $n=2$ (Bi2212), and $n=3$ (Tl1223) (Ref. 13). (c) T_c degradation against two-dimensional residual resistivity (per CuO_2 plane) induced by disorder.

$n=2$ is naturally explained by the fact that the number of SrO blocks adjacent to a CuO_2 plane is two in Bi2201 and one in Bi2212.

T_c degradation (T_c/T_{c0}) with increasing disorder (σ^2) is plotted in Fig. 2(b) for $n=1, 2,$ and 3 . Here we use the data for $\text{Tl}_{1+x}\text{Ba}_{2-x}\text{Ca}_2\text{Cu}_3\text{O}_{6+\delta}$ (Tl1223) (Ref. 13) as a representative trilayer system since no systematic study has ever been done for Bi2223. In Fig. 2(b), T_c is normalized by the value T_{c0} , which is obtained by extrapolating T_c to $\sigma^2(r,x)=0$ for each system (see Fig. 5). The T_c -degradation rate against

$\sigma^2(r, x)$ is found to be roughly 1:1/2:1/3 for $n=1, 2$, and 3 , respectively. The result of T_c degradation against σ^2 combined with the result of the residual resistivity in Fig. 2(a) leads to the “universal” relationship between T_c degradation and residual resistivity per plane, shown in Fig. 2(c). Then, we conclude that the charge carriers or the electronic state in the CuO_2 plane is affected predominantly by the disorder in the adjacent SrO block and T_c decreases in response to the disorder-induced change in the electronic state.

B. Enhancing T_c

Because the Bi/Sr-site mixing easily occurs in Bi2212 and decreases T_c , an effective way to improve T_c is to minimize the Bi/Sr-site mixing. The best way to do this would be replacing Ba^{2+} for Sr^{2+} , but we cannot make use of this way because Ba in combination with Bi tends to form impurity phases such as BaBiO_3 . Then, the second best way is to minimize disorder in the SrO block at the expense of disorder in other building blocks, either the Bi_2O_2 or Ca block, or both blocks because we know that the effect of disorder in these blocks on T_c is very small. To do this, we substitute Pb for the Bi site in the Bi_2O_2 block and Y for the Ca site in the Ca block. As Pb^{2+} substitution for Bi^{3+} increases the hole density in the CuO_2 planes, whereas Y^{3+} substitution for Ca^{2+} decreases it, these substitutions have to be done to the extent that one can compensate for the change in hole density by decreasing/increasing excess oxygen content near the Bi_2O_2 block. In what follows, we show how T_c changes with these processes.

Figure 3(a) shows how T_c changes by substituting Y for the Ca site, $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-y}\text{Y}_y\text{Cu}_2\text{O}_{8+\delta(\text{opt})}$, with δ adjusted to give maximum T_c (or to keep the hole density constant). T_c increases up to $y=0.08$, but stops with further substitution of Y. The reason why substituting Y increases T_c is supposed to be that Y^{3+} makes $[\text{CuO}_2\text{-Ca-CuO}_2]$ bilayers more electropositive and hence drives Bi^{3+} away from the neighboring SrO blocks. In fact, the ICP-analyzed compositions (Table I) of Bi and Sr in the Y-substituted crystal are close to the ideal values, evidencing that the Bi/Sr-site mixing is considerably reduced. However, too much Y substitution ($y > 0.08$) does not improve T_c anymore probably because the decrease in hole density cannot be compensated for by oxygen annealing.

Next, we substitute Pb for Bi in the form $\text{Bi}_{2-w+x}\text{Pb}_w\text{Sr}_{2-x}\text{CaCu}_2\text{O}_{8+\delta}$ [Fig. 3(b)]. Pb substituted for Bi is considered to take the Pb^{2+} ionic state which donates a hole into the CuO_2 planes. Then, T_c is maximized or the hole density is kept at the optimal value by reducing excess oxygen content δ . T_c goes up to $T_c=97.5$ K until $w=0.55$. Another known effect of Pb substitution is to relax the structural supermodulation in the BiO planes running along b axes.^{15,16} However, according to the above analysis, diminishing the supermodulation would have minor effect on T_c because of its location far away from the CuO_2 planes. Rather, we ascribe a reason for increased T_c as the decrease in the total amount of Bi, which results in the decrease in Bi content in the SrO block. The ICP analysis gives evidence for this trend (Table I). We also have to take into account possible Pb/Sr-

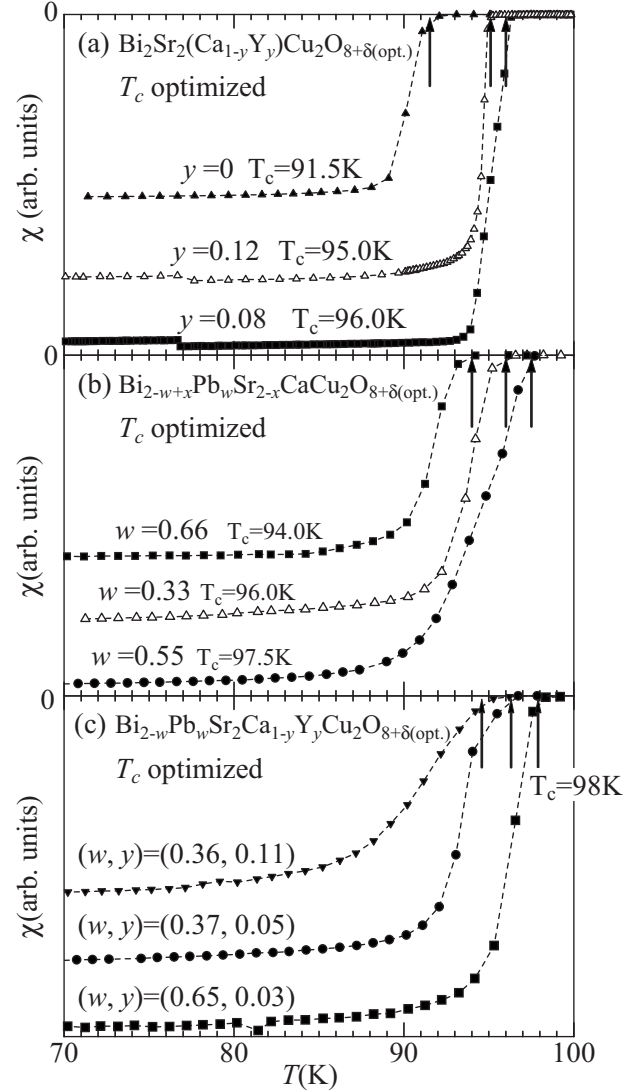


FIG. 3. (a) Superconducting transition temperature measured by magnetic susceptibility for Y-substituted Bi2212. For each Y content y , shown are the data optimized by annealing. T_c is maximized by changing excess oxygen content δ by suitable annealing: for $y=0$, 750 °C annealing in atmosphere; for $y=0.08$, 400 °C Ar-flow annealing; and for $y=0.12$, without annealing. (b) Change in T_c for Pb-substituted Bi2212. For each sample, T_c is maximized by adjusting the excess oxygen content δ under the following annealing conditions: for $w=0.33$, 600 °C annealing under N_2 flow; for $w=0.55$, 650 °C annealing in vacuum; and for $w=0.66$, 550 °C annealing under N_2 flow. (c) Enhancement of T_c with both Y and Pb substitutions in Bi2212. For each sample (w, y) , T_c is maximized by adjusting excess oxygen content. As the Pb-substituted crystals are naturally overdoped, the annealing was made under reducing atmosphere, and the oxygen content was varied by changing the annealing (T_A). The optimal conditions are for $(w, y)=(0.34, 0.11)$, 400 °C annealing under N_2 flow; for $(w, y)=(0.37, 0.05)$, 650 °C annealing in vacuum; and for $(w, y)=(0.65, 0.03)$, 425 °C annealing under N_2 flow, as shown in Fig. 4.

site mixing. However, fortunately the ionic radius of Pb^{2+} is nearly equal to that of Sr^{2+} , and the valence of Pb^{2+} is as the same as that of Sr^{2+} , so we speculate that Pb/Sr-site mixing is harmless for T_c .

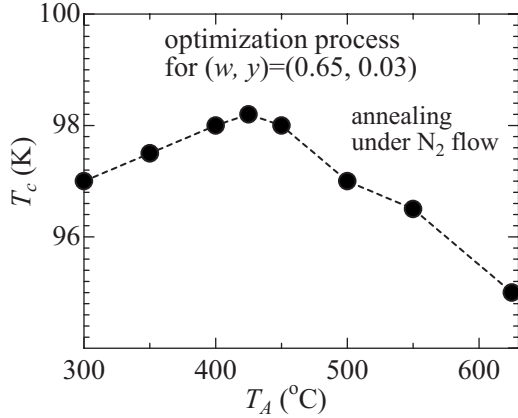


FIG. 4. T_c is plotted against annealing temperature for $(w, y) = (0.65, 0.03)$. As T_A increases, the excess oxygen content decreases; that is, the doping level changes from overdoping to underdoping, attaining optimal doping at $T_A = 425$ °C

From the results shown in Figs. 3(a) and 3(b) we know that both Y and Pb substitutions are effective in reducing the Bi/Sr-site mixing. Then, we made simultaneous substitutions of Pb for Bi and Y for the Ca site in the form of $\text{Bi}_{2-w}\text{Pb}_w\text{Sr}_2\text{Ca}_{1-y}\text{Y}_y\text{Cu}_2\text{O}_{8+\delta}$. Figure 3(c) shows the results of the simultaneous substitution. The maximum T_c (=98 K, at onset) was achieved for $w=0.60-0.65$ and $y=0.03-0.05$, as shown in Fig. 4.

IV. DISCUSSIONS

Finally, we discuss a maximum T_c value of Bi2212. T_{c0} in Fig. 2(b) is determined by extrapolating the T_c vs σ^2 plot to $\sigma^2=0$ (shown in Fig. 5). T_{c0} is, in this sense, an upper limit of T_c realized when the disorder in the SrO or BaO block is completely diminished. $T_c=98$ K achieved in the present work should be very close to the limit T_{c0} . Although the

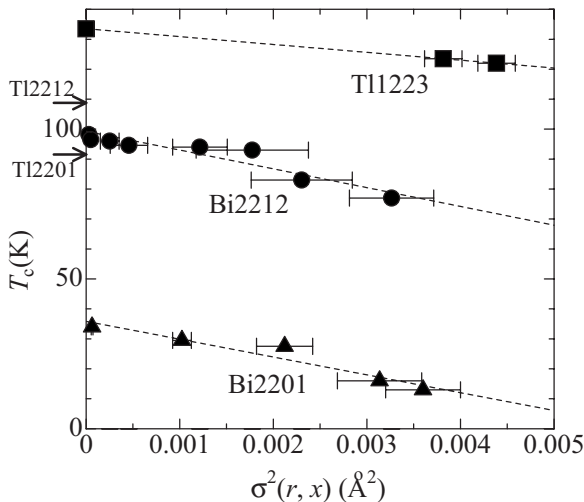


FIG. 5. T_c vs $\sigma^2(r, x)$ for single-layer, bilayer, and trilayer cuprates. The arrows indicate the highest T_c values of $\text{Tl}_2\text{Ba}_2\text{CuO}_{6+\delta}$ (Tl2201) and $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_{8+\delta}$ (Tl2212), which probably have disorder-free BaO block.

sample is optimally doped and the disorder in the SrO block is minimized (as also suggested by the ICP analysis listed in Table I), there remains disorder in the Ca and near the Bi_2O_2 blocks. However, in view of the negligibly small residual resistivity produced by these types of disorders, we expect that the T_c reduction would be very small due to these disorders. In this regard, $T_c=98.0 \pm 0.5$ K would be the maximum T_c attainable in Bi2212.

In the case of Bi2212, when the Bi/Sr-site mixing is suppressed, the charge disorder is also reduced. This is not the case with Bi2201. $\sigma^2 \sim 0$ is attained for $\text{Ln}=\text{La}$ with least mismatch in the ionic radius with that of Sr^{2+} . However, because the ionic state of Ln is Ln^{3+} (as compared with Sr^{2+}), disorder due to this charge mismatch remains even in the “optimized” La-Bi2201. It was reported that T_c increases to ~ 40 K when the content of substituted Ln is reduced as much as possible by partial substitution of Pb for Ln/Bi.¹⁷ Nevertheless, T_c is much lower than $T_c=90-98$ K realized in the isostructural Tl2201 and other single-layer systems. This suggests that the charge disorder at the Sr site equally or more seriously reduces T_c .

If T_c of 98 K is the maximum T_c value of Bi2212, then the question is why it is lower by 10 K than the maximum T_c [~ 110 K (Ref. 18)] of isostructural Tl2212. We infer that other factors might be responsible for the T_c difference between the two systems. A plausible candidate is the distance of an apical oxygen from the CuO_2 plane. The apical-oxygen distances are $d \sim 2.43$ Å for Bi2212, $d \sim 2.70$ Å for Tl2212, and $d \sim 2.80$ Å for another bilayer compound [$\text{HgBa}_2\text{CaCu}_2\text{O}_{6+\delta}$ (Hg1212)] with highest $T_c=127$ K.¹⁹ Apparently, the maximum T_c values are correlated with the apical-oxygen distance, which is also suggested by the empirical relationship based on the local-density approximation (LDA) band calculation.⁵ If we could develop any method to increase the apical-oxygen distance, T_c of Bi2212 would be enhanced to the levels of Tl2212 and of Hg1212.

We speculate that the disorder effect in the SrO block might be intimately connected with the local tilt of the CuO_6 octahedron or CuO_5 pyramid and/or the local change in the apical-oxygen distance. Local distortions, such as the tilt of CuO_6 octahedra, would lead to local modulation of transfer integrals (overlap integrals of the electronic wave functions of neighboring atoms) and/or superexchange interaction between neighboring Cu spins in the CuO_2 plane. These modulations would result in the modulation of local pairing interactions or locally stabilize some orders competing with the superconducting order, as suggested by the recent scanning-tunneling-microscopy (STM) observations²⁰⁻²³ and their theoretical interpretations.²⁴⁻²⁶

V. SUMMARY

We examined the effect of disorder at various out-of-plane lattice sites on T_c in the prototypical high- T_c cuprate $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$. From the T_c -degradation rate and the magnitude of induced residual resistivity and also from the comparison with the results for single-layer and trilayer Bi cuprates, we conclude that the disorder in the SrO block substantially reduces T_c , while disorder in the Bi_2O_2 and Ca

blocks has very small effect on T_c . The grown crystals of Bi2212 normally contain disorder in the SrO block due to Bi/Sr-site mixing and thus their T_c values are appreciably reduced. So, the effective way to enhance T_c of Bi2212 is reducing Bi/Sr-site mixing as much as possible, and $T_c = 98$ K is achieved by simultaneous substitutions of Pb for Bi and Y for Ca. The present result gives a good lesson on increasing cuprate T_c based on detailed investigation of the factors that influence T_c .

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