Hole doping in Pb-free and Pb-substituted (Bi,Pb)$_2$Sr$_2$Ca$_2$Cu$_3$O$_{10+\delta}$ superconductors

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Using single-phase samples of the (Bi,Pb)$_2$Sr$_2$Ca$_2$Cu$_3$O$_{10+\delta}$ [(Bi,Pb)-2223] high-$T_c$ superconductor and utilizing two complementary analysis techniques, i.e., coulometric redox titration and x-ray-absorption near-edge structure spectroscopy at both O K and Cu L edges, the individual charges of the (Bi,Pb)$_2$O$_{2-\delta}$ charge reservoir and the superconductive block that contains the three CuO$_2$ planes are consistently determined. Lead is found to enter the (Bi,Pb)-2223 phase with a valence close to III on average. As the oxygen content concomitantly decreases, the average CuO$_2$-plane hole concentration decreases upon substituting bismuth in the pristine Bi-2223 phase with lead.

In the structure of a high-$T_c$ superconductive copper oxide the superconductive block (SB) containing the CuO$_2$ planes is piled up with a pair of AO layers and an $M_{2-x}$O$_{m\pm\delta}$ charge reservoir (CR) with the layer sequence of -AO-CuO$_2$-(Q-CuO$_2$)$_n$-1-AO-(MO$_{1\pm\delta}$)-. The stoichiometry of the phase is described by the “chemical formula” $M_{2-x}Q_nA_2Cu_{m\pm\delta}O_{m+2n\pm\delta}$ or in short by $M-m2(n-1)n$. The group of phases with different values only for $n$ forms a “homologous series.” For each homologous series the highest $T_c$ results from the $n=3$ phase that possesses three CuO$_2$ planes stacked alternatively with two Q layers in the SB, CuO$_2$-(Q-CuO$_2$)$_{n-1}$. Among the three CuO$_2$-plane phases, Bi$_2$Sr$_2$Ca$_2$Cu$_3$O$_{10+\delta}$ (Bi-2223) is at least from the technological point of view most attractive: a majority of not only existing but also prospective wire/cable applications are based on this material. 3 The micaceous character of the (BiO$_{1\pm\delta}$O$_{2}$) double-layer CR is advantageously utilized for a grain alignment procedure. To enhance the otherwise sluggish and incomplete formation of the Bi-2223 phase partial Pb-for-Bi substitution is commonly employed. 4 Also reported is that replacing Bi partially by Pb would enhance the critical-current-density and irreversibility-field characteristics of the Bi-2223 phase as divalent and therefore Pb substitution for trivalent Bi increases the concentration of holes in the CuO$_2$ planes. 5-11 For this intuitive view a further assumption has been made that the oxygen content remains unchanged upon Pb substitution. In this work we combine two complementary analysis techniques, i.e., x-ray-absorption near-edge structure (XANES) spectroscopy and coulometric redox titration, to show that the very simple intuitive view does not hold true for (Bi,Pb)-2223.

We employ high-quality single-phase samples of (Bi$_{1-x}$Pb$_x$)$_2$Sr$_2$Ca$_2$Cu$_3$O$_{10+\delta}$ with $y=0$ and 0.15. The samples were synthesized by means of a KCl-flux technique 12 from highly homogeneous stoichiometric precursors of constituent cations, Bi, Pb, Sr, Ca, and Cu, obtained from diluted HNO$_3$ solutions of the corresponding oxides or carbonates via spray drying at 110°C. After being dried at 120°C for 20 h, the nitrate mixture was decomposed into an oxide mixture in a dynamic vacuum at 500°C. Further calcinations were performed in air at 800°C–880°C with intermediate grindings. The powder thus obtained was mixed with KCl at a molar ratio of 1:4 for the crystal-growth process which was carried out in a MgO crucible in air at 855°C or 870°C for approximately 100 h. The lower/higher temperature was used for the Pb-substituted/Pb-free sample. For both the Pb contents at $y=0$ and 0.15, the synthesis yielded numerous small platelike single-crystalline particles of approximately 100–500 µm in size (along the largest dimension) embedded in KCl flux, as confirmed by x-ray diffraction. After being separated from the flux the crystals were annealed in air at 400°C for 20 h.

For the present charge distribution analyses, three (Bi$_{1-x}$Pb$_x$)$_2$Sr$_2$Ca$_2$Cu$_3$O$_{10+\delta}$ samples were selected: (i) a $y=0$ sample with small (≤100 µm) particles, (ii) a $y=0$ sample with large (≥100 µm) particles, and (iii) a $y=0.15$ sample with large (≥100 µm) particles. Coulometric titrations were carried out for the latter two samples along the well-established protocol described in detail elsewhere. 13-15 The XANES experiments were performed for all three samples (i)–(iii), at both O K and Cu L edges. The room-temperature spectra were collected on the 6-m high-energy spherical grating monochromator beam line of the National Synchrotron Radiation Research Center in Hsinchu, Taiwan in a bulk-sensitive fluorescence-yield mode employing an ultrahigh-vacuum chamber (∼10$^{-9}$ torr) and a microchannel-plate detector system. The detector was located parallel to the sample surface at a distance of ∼2 cm. Photons were incident at an angle of 45° with respect to the sample normal. The incident photon flux ($I_0$) was monitored simultaneously by a Ni mesh located after the exit slit of the monochromator. Initially the absorption measurements were normalized to $I_0$. The photon energies were calibrated with an accuracy of 0.1 eV using the O K-edge absorption peak at...
TABLE I. Results of oxygen content and charge distribution analysis: the amount of excess oxygen ($\delta$) and the total amount of holes per (Bi,Pb)-2223 formula unit [$p(\text{SB+CR})$] are from Cu$^+$/Cu$^{2+}$ coulometric titration, the individual valences of Bi [$V(\text{Bi})_{\text{tit}}$] and Pb [$V(\text{Pb})_{\text{tit}}$], and the overall amount of holes in the charge reservoir [$p(\text{CR})$] are from Fe$^{2+}$/Fe$^{3+}$ coulometric titration; the valence of Cu is estimated based on the titration results [$V(\text{Cu})_{\text{tit}}$] and the Cu L-edge XANES data [$V(\text{Cu})_{\text{XAS}}$]. The average CuO$_2$-plane hole concentration [$p(\text{CuO}_2)_{\text{XAS}}$] is from the O K-edge XANES data.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\delta$</th>
<th>$p(\text{SB+CR})$</th>
<th>$p(\text{CR})$</th>
<th>$V(\text{Bi})_{\text{tit}}$</th>
<th>$V(\text{Pb})_{\text{tit}}$</th>
<th>$V(\text{Cu})_{\text{tit}}$</th>
<th>$V(\text{Cu})_{\text{XAS}}$</th>
<th>$p(\text{CuO}<em>2)</em>{\text{XAS}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi$_2$Sr$_2$Cu$<em>2$O$</em>{10+\delta}$ (small single-crystalline particles)</td>
<td>0.28$^a$</td>
<td>0.56(2)</td>
<td>0.14(1)</td>
<td>3.07(1)</td>
<td>2.14(2)</td>
<td>2.07(1)</td>
<td>2.07(1)</td>
<td>0.14(1)</td>
</tr>
<tr>
<td>Bi$_2$Sr$_2$Cu$<em>2$O$</em>{10+\delta}$ (large single-crystalline particles)</td>
<td>0.19$^a$</td>
<td>0.68(2)</td>
<td>0.41(1)</td>
<td>3.07$^b$</td>
<td>2.97$^c$</td>
<td>2.09(2)</td>
<td>2.05(1)</td>
<td>0.09(1)</td>
</tr>
<tr>
<td>(Bi$<em>{0.85}$Pb$</em>{0.15}$)$_2$Sr$_2$Ca$_2$Cu$<em>3$O$</em>{10+\delta}$ (large single-crystalline particles)</td>
<td>0.06$^a$</td>
<td>0.58</td>
<td>0.34</td>
<td>3.07$^b$</td>
<td>2.98$^c$</td>
<td>2.06</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$See Ref. 19.
$^b$Assumed based on the result for pristine Bi-2223.
$^c$Calculated based on an assumption, $V(\text{Bi})_{\text{tit}}=3.07$.
$^d$From Ref. 14.

530.1 eV and the Cu L$_1$ white line at 931.2 eV of a CuO reference. The monochromator resolution was set to $\sim 0.22$ and $\sim 0.45$ eV at the O K and Cu L absorption edges, respectively. The obtained spectra were corrected for the energy-dependent incident photon intensity as well as for self-absorption effects$^{16,17}$ and normalized to the tabulated standard absorption cross sections$^{18}$ in the energy range of 600–620 eV for the O K edge and 1000–1020 eV for the Cu L edge.

The precise cation compositions were analyzed by energy-dispersive x-ray (EDX) and inductively coupled-plasma (ICP) spectroscopies. For the Pb-free samples, ICP analysis indicated a slight excess of Bi and a slight deficiency of Sr when compared to the nominal stoichiometry. Since the deviations were smaller than 0.1 atoms per f.u. for both Bi and Sr, we refer to these samples as cation-stoichiometric Bi-2223 or Bi$_2$Sr$_2$Ca$_2$Cu$_3$O$_{10+\delta}$. This stoichiometry is also used for the calculation of the oxygen content and metal valence values from the redox titration data.$^{19}$ For the Pb-substituted sample (Bi$_{0.85}$Pb$_{0.15}$)$_2$Sr$_2$Ca$_2$Cu$_3$O$_{10+\delta}$, neither EDX nor ICP data suggested any deviation from the nominal stoichiometry within an error of $\pm 0.02$ atoms per f.u. Using a superconducting quantum interference device magnetometer the value of $T_c$ was determined to be 108 K for all three samples using the onset of the diamagnetic signal as the criterion.

The average hole concentration in the CuO$_2$ plane, $p(\text{CuO}_2)$, is related to the nominal valence of copper, $V(\text{Cu})$, through the relation $p(\text{CuO}_2) = V(\text{Cu}) - 2$, and can be calculated from the stoichiometry of the phase if both the exact oxygen content and the valences of cations other than Cu are accurately determined. However, we like to emphasize that the present experimental techniques—like most of the experimental techniques that are used to probe “hole concentrations” in complex oxides—do not distinguish between “charge” and “carriers.” Therefore what we measure is not necessarily “mobile holes” but rather “excess positive charge.” Here we first accurately determine the oxygen content of the (Bi,Pb)-2223 samples by coulometric Cu$^+$/Cu$^{2+}$ redox titration.$^{13-15}$ This experiment yields the total amount of high-valent copper, bismuth, and lead species, i.e., Cu$^{\text{III}}$, Bi$^{\text{V}}$, and Pb$^{\text{IV}}$, and thus the oxygen content of the sample. Upon dissolving the sample in acidic solution containing a known amount of Cu$^+$ ions, not only Cu$^{\text{III}}$ but also Bi$^{\text{V}}$ and Pb$^{\text{IV}}$ oxidize Cu$^+$ to Cu$^{2+}$ according to the following reactions:

\[ \text{Cu}^{\text{III}} + \text{Cu}^+ \rightarrow 2 \text{Cu}^{2+} \],

\[ \text{Bi}^{\text{V}} + 2 \text{Cu}^+ \rightarrow \text{Bi}^{3+} + 2 \text{Cu}^{2+} \],

\[ \text{Pb}^{\text{IV}} + 2 \text{Cu}^+ \rightarrow \text{Pb}^{2+} + 2 \text{Cu}^{2+} \].

Once the reactions described by Eqs. (1)–(3) are completed, the amount of remaining Cu$^+$ ions is accurately analyzed through coulometric titration, i.e., anodic oxidation as follows:

\[ \text{Cu}^+ (\text{excess}) \rightarrow \text{Cu}^{2+} + e^- \text{ (coulometry)} \].

From the amount of electrons produced in Eq. (4), the value of $\delta$ is calculated. With the result of the coulometric Cu$^+$/Cu$^{2+}$ titrations (Table I), it is found that the amount of excess oxygen in the Pb-substituted (Bi$_{0.85}$Pb$_{0.15}$)$_2$Sr$_2$Ca$_2$Cu$_3$O$_{10+\delta}$ sample ($\delta=0.19$) is significantly less than that in the pristine Bi$_2$Sr$_2$Ca$_2$Cu$_3$O$_{10+\delta}$ sample ($\delta=0.28$). In other words, when (Bi,Pb)-2223 samples are prepared in air of normal pressure, Pb substitution results in a decrease in the oxygen content. However, taking, respectively, the values of II and III as the “bottom valence values” for Pb and Bi in an undoped situation (where the valence of Cu is assumed at II), a simple charge-balance calculation reveals that the total number of holes per formula unit in the superconductive block plus charge reservoir $p(\text{SB+CR})$ is 0.68(2) for the (Bi$_{0.85}$Pb$_{0.15}$)$_2$Sr$_2$Ca$_2$Cu$_3$O$_{0.19}$ sample, in comparison to 0.56(2) for Bi$_2$Sr$_2$Ca$_2$Cu$_3$O$_{10.28}$ (Table I). Thus, overall the
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Pb-substituted sample is more strongly doped with holes (excess positive charge) than the pristine (Pb-free) Bi-2223 sample.

Now another question arises regarding how these holes are distributed between the CuO$_2$-(Ca-CuO$_2$)$_2$ superconductive block and the [(Bi$_{1-x}$Pb$_x$)$_2$O$_{1+y/2}$]$_2$ charge reservoir. In order to answer this question, we analyze the valence of Bi or the average valence of (Bi$_{1-x}$Pb$_x$) with another independent wet-chemical redox method, i.e., coulometric Fe$^{2+}$/Fe$^{3+}$ titration. This method allows us to detect selectively the amount of Bi$^V$ and/or Pb$^IV$ in the presence of Cu$^{III}$. The sample is dissolved in an acidic solution containing a known amount of Fe$^{2+}$ ions. Pentavalent Bi and tetravalent Pb react completely with Fe$^{2+}$ ions according to

$$\text{Bi}^{V} + 2 \text{Fe}^{2+} \rightarrow \text{Bi}^{III} + 2 \text{Fe}^{3+}, \quad (5)$$

$$\text{Pb}^{IV} + 2 \text{Fe}^{2+} \rightarrow \text{Pb}^{II} + 2 \text{Fe}^{3+}. \quad (6)$$

The valence of Bi/Pb, V(Bi/Pb)$_{\text{det}}$, is obtained by analyzing the amount of Fe$^{2+}$ ions that have not participated in the reaction given by Eqs. (5) and/or (6) through anodic oxidation:

$$\text{Fe}^{2+} (\text{excess}) \rightarrow \text{Fe}^{3+} + e^- \quad \text{(coulometry)}. \quad (7)$$

It must be noted that for Cu$^{III}$ the reaction with water, i.e.,

$$4 \text{Cu}^{III} + 2 \text{H}_2\text{O} \rightarrow 4 \text{Cu}^{II} + \text{O}_2 + 4 \text{H}^+ , \quad (8)$$

is more preferable than that with Fe$^{2+}$ ions, preventing Cu$^{III}$ from interfering with the determination of the valence of bismuth and/or lead. With the results of several parallel coulometric Fe$^{2+}$/Fe$^{3+}$ titration experiments showing excellent internal precision, we can conclude in the pristine Bi$_2$Sr$_2$Ca$_2$Cu$_3$O$_{10.28}$ sample V(Bi)$_{\text{det}}$ is not precisely III but rather 3.07(1) (Table I). For the Pb-substituted sample [(Bi$_{0.85}$Pb$_{0.15}$)$_2$Sr$_2$Ca$_2$Cu$_3$O$_{10.19}$], the present coulometric Fe$^{2+}$/Fe$^{3+}$ titration method does not distinguish the holes (=excess positive charge) located on Bi from those located on Pb, but yields only the total amount of holes in the [(Bi$_{0.85}$Pb$_{0.15}$)$_2$O$_{2.19}$] charge reservoir. Only when the valence of Bi is assumed to remain constant (at 3.07) upon Pb substitution can we reach an estimation of 2.97 for V(Pb)$_{\text{det}}$ in (Bi,Pb)-2223 (Table I). This value, being an intermediate between II and IV, i.e., clearly deviating from the intuitively assumed value of II, rather agrees with the results of the few spectroscopic studies on the valence of Pb reported for (Bi,Pb)-2223. Another comparison can be made by considering bond lengths observed for Bi and Pb in (Bi,Pb)-2223 samples [though here we need to remember that due to the incommensurate modulations typical for the (Bi,Pb)-22(n-1)n phases such bond lengths represent average values only]; using the bond lengths determined by means of neutron diffraction for a [(Bi$_{0.85}$Pb$_{0.15}$)$_2$Sr$_{1.3}$Ca$_{1.7}$Cu$_{3.1}$O$_{10+\delta}$] sample bond-valence-sum calculation reveals a valence value very close to III for both Bi and Pb, in accordance with the present result of wet-chemical analysis. In Table I, also given is the total amount of positive charge (in excess with respect to Bi$^{III}$ and Pb$^{V}$) in the charge reservoir: $p(CR)$ is 0.14(2) for Bi$_2$Sr$_2$Ca$_2$Cu$_3$O$_{10.28}$ and 0.41(2) for [(Bi$_{0.85}$Pb$_{0.15}$)$_2$Sr$_2$Ca$_2$Cu$_3$O$_{10+\delta}$]. Thus, with Pb substitution the concentration of holes in CR considerably increases. However, as already mentioned, the degree of localization of these holes is not known from the present analysis result.

Even though the distribution of the (more or less localized) holes between Bi and Pb may not be unambiguously established from the results of wet-chemical analysis, the average value of the Cu valence, V(Cu)$_{\text{det}}$, can now be calculated as

$$V(\text{Cu})_{\text{det}} = [p(\text{SB} + \text{CR}) - p(\text{CR})]/n, \quad (9)$$

from $p(\text{SB} + \text{CR})$ as determined by Cu$^{+}$/Cu$^{2+}$ redox titration and $p(\text{CR})$ as determined by Fe$^{2+}$/Fe$^{3+}$ redox titration, taking into account the number, $n = 3$, of the CuO$_2$ planes per formula unit. For the pristine Bi$_2$Sr$_2$Ca$_2$Cu$_3$O$_{10.28}$ and the Pb-substituted [(Bi$_{0.85}$Pb$_{0.15}$)$_2$Sr$_2$Ca$_2$Cu$_3$O$_{10+\delta}$], V(Cu)$_{\text{det}}$ is obtained at 2.14(2) and 2.09(2), respectively. Thus, as judged from the results of wet-chemical redox analyses, Pb substitution decreases the average valence of Cu and thereby the average CuO$_2$-plane hole concentration in (Bi,Pb)-2223. In Table I, also included is a data set previously obtained for a powder sample of [(Bi$_{0.89}$Pb$_{0.11}$)$_2$Sr$_{1.83}$Ca$_{2.05}$Cu$_3$O$_{10.06}$] ($T_c = 109$ K) by means of the two-step coulometric redox analysis. The numbers for the present Pb-substituted sample well agree with those for the previous one.

As shown previously and also confirmed in the present study through several parallel experiments, wet-chemical redox analysis can yield valence values with a high internal precision of ±0.01. However, a critical question remains, that is, how well is the atomic-scale distribution of electrons in a solid maintained upon its dissolution? To answer to this question, XANES spectroscopy is employed since it provides us with an ideal probe for the local concentration of holes in a solid: the x-ray-absorption spectrum is determined by electronic transitions from a selected atomic core level to the unoccupied electronic states near the Fermi level. Figure 1 displays the O K-edge spectra obtained for the samples in the energy range from 525 to 555 eV. The preedge peak seen around 528.3 eV for all the three samples is the well-established signature of holes in the singlet band formed upon $p$-type doping of the CuO$_2$ plane in high-$T_c$ copper-oxide superconductors. Upon Pb substitution a slight increase in the absorption energy of this peak is seen, indicating that the Fermi level moves to a higher energy, presumably due to a decrease in the CuO$_2$-plane hole concentration. The intensity of the 528.3-eV peak directly reflects the concentration of holes in the CuO$_2$ plane. To get a quantitative estimation for the hole concentration, we fitted this peak with a Gaussian function. The background was approximated by a straight line. The obtained values of spectral weight for the three [(Bi$_{1-x}$Pb$_x$)$_2$Sr$_2$Ca$_2$Cu$_3$O$_{10+\delta}$] samples are (in Mb eV per unit cell) (i) 3.31(9) for the $y = 0$ sample with small particles, (ii) 3.05(13) for the $y = 0$ sample with large particles, and (iii) 2.13(9) for the $y = 0.15$ sample. These numbers were then “standardized” against that of 1.13 obtained for a...
La$_{1.85}$Sr$_{0.15}$CuO$_4$ reference sample by an analysis parallel to that of the (Bi,Pb)-2223 samples. From the results for the Bi$_2$Sr$_2$CaCu$_2$O$_{10+\beta}$ samples, (i) and (ii), with the different particle sizes are essentially identical, whereas the value for the Pb-substituted sample is considerably lower.

Another independent estimation of the average doping state of CuO$_2$ planes is obtained from the Cu $L$-edge XANES spectra. In Fig. 2 is shown the 925–955-eV region of the Cu $L$-edge spectra for the three samples. Each spectrum exhibits a narrow peak centered at ~931.2 eV (in the $L_3$ area) as a result of divalent copper, i.e., transitions from the Cu$(2p_{3/2})3d^9O^2p^6$ ground-state configuration into the Cu$(2p_{3/2})^{-1}3d^{10}O^2p^6$ excited state, where $(2p_{3/2})^{-1}$ denotes a $2p_{3/2}$ hole. Oxidation of Cu beyond the divalent state is seen as a weak broadening or shoulder on the high-energy side of this peak. Such shoulders as a result of Cu$^{III}$ have been observed for a number of other superconductive copper oxides, e.g., Cu$_{1212}$, Bi$_{2212}$, Hg-$1(n-1)n$, and (Pb,Cu)-3212 and interpreted as transitions from the Cu$(2p_{3/2,1/2})3d^9L$ ground state into the Cu$(2p_{3/2,1/2})^{-1}3d^{10}L$ excited state, where $L$ denotes a ligand hole in the O $2p$ orbital. To obtain quantitative estimations

\[ V(Cu)_{XAS} = 2 + I(Cu^{III})/[I(Cu^{II}) + I(Cu^{III})]. \]  

For the pristine Bi-2223 with large particles, $V(Cu)_{XAS}$ was determined to be 2.07(1). Essentially the same value was obtained for the other Pb-free sample with smaller particles, i.e., 2.06(1). For the Pb-substituted sample, analysis of the Cu $L_3$-edge peak intensities gave a value of 2.05(1) for $V(Cu)_{XAS}$. These values revealed from Cu $L_3$-edge spectra are somewhat lower than the ones determined based on the wet-chemical analysis and O $K$-edge XANES data for the same samples (Table I). However, despite the deviation in absolute values, the Cu $L_3$-edge XANES results confirm our main conclusion that Pb substitution slightly decreases the valence of Cu in the present air-synthesized samples of the (Bi,Pb)-2223 phase.

In conclusion, we have employed a direct solid-state probing technique, i.e., XANES spectroscopy at both Cu $L$-edges for the CuO$_2$-plane hole concentration, we analyzed the spectra by fitting the 931.2-eV peak with a combination of Lorentzian and Gaussian functions and its shoulder with a Gaussian function. The background was fitted to an arctangent curve and subtracted from the spectrum before the peak analysis. The obtained integrated intensity of the shoulder $[I(Cu^{III})]$ was normalized against the total spectral weight in the $L_3$ area below 935 eV, i.e., the sum of the integrated intensity of the main peak $[I(Cu^{II})]$ and that of the shoulder itself $[I(Cu^{III})]$. From the normalized intensity of the shoulder, an estimation for the average valence of copper, $V(Cu)_{XAS}$, was calculated by
and O K edges, and a wet-chemical redox analysis method based on a combination of two different coulometric titration experiments, to gain complete pictures of the charge distribution in both Pb-free and Pb-substituted samples of the (Bi,Pb)-2223 phase. From all the analysis results given in Table I, it is seen that the Pb-for-Bi substitution does not increase but rather slightly decreases the average CuO$_2$-plane hole concentration. This is well explained by the facts (as concluded from the wet-chemical analysis) that Pb enters the Bi-2223 phase with a valence higher than II and furthermore decreases the oxygen content of the phase. On the contrary, the amount of excess positive charge in the charge reservoir considerably increases upon substituting Bi partly by Pb. Even though the hole concentration changed upon Pb substitution in both the SB and CR, the $T_c$ value remained constant at 108 K for the present air-synthesized samples. This agrees with the data recently reported for the variously oxygen-annealed Pb-free Bi-2223 samples: once the maximum $T_c$ of 108 K was achieved the value of $T_c$ remained constant upon further oxygen loading.\textsuperscript{13}

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\begin{thebibliography}{100}


\bibitem{2} In $M_nA_2O_{2-n}Cu_{O_{2-n}+2n}$ or $M-m2(n-1)n$, $M$ = e.g., Cu, Bi, Pb, Ti, Hg, Al, Ga, B: $m=0-3$; $A$ = e.g., Ba, Sr, La; $Q$ = e.g., Ca, rare-earth element $R$; $n=1-9$.


\bibitem{19} Even though the calculation would be carried out using slightly different Bi and Sr contents, the obtained values of metal valences and hole amounts (per formula unit or charge reservoir) would remain the same within the given accuracy. Only the absolute number for the excess oxygen content $\delta$ would change.

\bibitem{20} To indicate the valence of a species in a solid matrix, Roman numerals are used (e.g., Cu$^{III}$), whereas the charges of ions in solution are indicated by Arabic numerals (e.g., Cu$^{2+}$).


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