Comparative Study of the Effects of La-Substituted Ca in (Bi, Pb):2212 and (Bi, Pb):2223 Superconductors

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Abstract
We report here a comparative study of the effects of La-substituted Ca on (Bi, Pb):2212 and (Bi, Pb):2223 superconductors with various La content (0.00 ≤ x ≤ 0.30). Regardless of the effects of La, it is evident that the superconducting volume fraction, excess of oxygen, critical concentration for quenching superconductivity, Vickers hardness, anisotropy, interlayer coupling, critical magnetic fields, and critical current were higher for the 2212 series than the 2223 series. In contrast, orthorhombic distortion, c-parameter, crystallite diameter, doping distance, distance between two Cu atoms, hole carrier/Cu ion ratio, melting temperature $T_m$, critical temperature $T_c$, onset of diamagnetic $T_{cM}$, surface energy, elastic component, resistance pressure, and c-axis coherence length were higher for the 2223 series than the 2212 series. An inverse linear relationship between $T_m$ and $T_c$ was estimated for both series, and for room-temperature (RT) bismuth–strontium–calcium–copper–oxide (BSCCO) superconductors, the required $T_m$ values should be 1048.03°C for the 2223 series and 784.48°C for the 2212 series. Surprisingly, the difference in temperature between zero resistivity and diamagnetic onset $|T_{cR} - T_{cM}|$ for La = 0.30 samples is 30 K. In the critical field region (CFR), the exponents of order parameters (OPD) are two-dimensional (2D), but their values were higher for the 2212 series than the 2223 series. Further, they became three-dimensional (3D) as La increased to 0.30 due to the reduced effective length in highly substituted samples. Our results were discussed with the help of the differences in the physical parameters between the considered series. These findings revealed that the 2212 series is more suitable for applications that need higher hardness and critical fields and currents. In contrast, the 2223 series is more suitable for research for higher $T_c$ and altering plastic deformation. To our knowledge, the present systematic investigation has not been reported elsewhere, which highlights the present work.

Keywords BSCCO phases · excess oxygen · hole carrier/Cu · excess conductivity · Vickers hardness · melting point · critical temperature

Introduction

The (Bi, Pb):2212 orthorhombic unit cell consists of two units of (Bi, Pb)$_2$Sr$_2$CaCu$_2$O$_8$ and 15 layers. The oxygen atoms of (8O$^{2-}$) need 16 electrons, which are supplied by the 2Bi$^{3+}$+2Sr$^{2+}$+1Ca$^{2+}$+2Cu$^{2+}$. To be a superconductor, the cell is over-doped with excess oxygen δ of 0.10–0.23. The extra atom requires two more electrons through transforming two Cu$^{2+}$ ions into two Cu$^{3+}$ ions, and therefore, the electronic arrangement in the unit cell has two CuO$_2$ planes and becomes 2Bi$^{3+}$+2Sr$^{2+}$+1Ca$^{2+}$+2Cu$^{3+}$+9O$^{2-}$. In contrast, the unit cell of the Bi (Pb):2223 compound consists of a Bi$_{1.7}$ Pb$_{0.30}$Sr$_2$Ca$_2$Cu$_3$O$_{10+δ}$ unit and about 19 layers and planes. The chemical formula of ten oxygen atoms (10 O$^{2-}$) requires at least 20 electrons, which are supplied by 1.7Bi$^{3+}$+0.30Pb$^{2+}$+2Sr$^{2+}$+2Ca$^{2+}$+3Cu$^{2+}$. To be a superconductor, it is over doped with excess oxygen by transforming three Cu$^{2+}$ ions into three Cu$^{3+}$ ions, and therefore, the electronic arrangement having three CuO$_2$ planes becomes 1.7Bi$^{3+}$+0.30Pb$^{2+}$+2Sr$^{2+}$+2Ca$^{2+}$+3Cu$^{3+}$+11O$^{2-}$. The Bi (Pb):2212 and Bi (Pb):2223 superconductors, with critical temperatures ($T_c$) of 87 and 110 K, respectively, have been widely used in the fabrication of wires and tapes due to their high critical fields and currents. Usually, the low Bi:2201 and Bi:2212 phases tend to coexist as minority phases with (Bi, Pb):2212 and (Bi, Pb):2223 majority phases, but the calcination process...
depresses as much as possible the number of minority phases.\textsuperscript{5–7}

Numerous studies on the effects of RE\textsuperscript{3+} substitutions at the Ca\textsuperscript{2+} site in the BSCCO system (RE\textsuperscript{3+} rare earth element in the lanthanide series)\textsuperscript{8–13} have been reported. It has been proved that such a substitution decreases the density of superconducting carriers in BSCCO systems, and consequently, the critical concentration $x_c$ required for quenching superconductivity is decreased.\textsuperscript{14–16} Further, the $x_c$ decreases as the ionic size of RE\textsuperscript{3+} increases towards the La series. Meanwhile, other reports show an increase in the $x_c$ by Y substitution in place of Ca.\textsuperscript{17–19} But most of the research has been focused on the Y, Gd, Sm, and Nd elements,\textsuperscript{20–24} and a few of them are based on the La element due to the poor superconductivity of La: 123.

However, the excess of positive charge for trivalent RE\textsuperscript{3+} cation, as compared to divalent Ca\textsuperscript{2+} cation, causes repletion between CuO\textsubscript{2} planes, thereby the separation between these planes may be increased. Furthermore, the increase in RE content induces excess oxygen to be incorporated between the Bi\textsubscript{2}O\textsubscript{3} double layers.\textsuperscript{25} In this respect, the oxygen stoichiometry of BSCCO systems is relatively invariant with respect to RE\textsuperscript{3+} when prepared in an identical environment.\textsuperscript{26–28}

Recently, Sedky et al. presented individual studies on the structural, thermal, mechanical, electrical, magnetic, and excess conductivity properties of the Bi\textsubscript{1.7}Pb\textsubscript{0.3}Sr\textsubscript{2}Ca\textsubscript{1−x}La\textsubscript{x}Cu\textsubscript{2}O\textsubscript{y} (2212) and Bi\textsubscript{1.3}Pb\textsubscript{0.7}Sr\textsubscript{2}Ca\textsubscript{1−x}La\textsubscript{x}Cu\textsubscript{2}O\textsubscript{4} (2223) series.\textsuperscript{25–32} It has been proved that La significantly improves the superconducting parameters related to both series and also extends the superconductivity above 0.30. This study presents a comparative analysis of the effects of La-substituted Ca in (Bi, Pb):2212 and (Bi, Pb):2223 superconductors. Regardless of the effects of La, it is concluded that superconducting volume friction, excess oxygen, $x_c$, Vickers hardness, critical fields, and currents are higher for the 2212 series than the 2223 series. In contrast, the melting temperature $T_m$, critical temperature $T_c$, onset of diamagnetic $T_{cm}$, surface energy, elastic component, and resistance pressure are higher for the 2223 series than the 2212 series. In addition, the order parameter exponents in the critical field region (CFR) are two-dimensional (2D) for both series, but their values are higher for the 2212 series than the 2223 series. Further, they become three-dimensional (3D) as La is increased to 0.30 due to the expected reduced effective length in highly substituted samples. Our results are discussed in terms of differences in the most calculated and measured superconducting parameters between the two series. To our knowledge, the present investigation has not been reported elsewhere, which highlights the present work.

**Experimental Details**

The Bi\textsubscript{2}O\textsubscript{3}, PbO, SrO, La\textsubscript{2}O\textsubscript{3}, CaCO\textsubscript{3}, and CuO oxides and carbonates of 4N purity were thoroughly mixed in the required proportions and calcined at 825°C in air for 24 h. This exercise was repeated three times, with intermediate grinding at each stage. The resulting powder was reground, mixed, and pressed into pellets at a force of up to 10 tons. The pellets of (Bi, Pb):2212 were sintered in air at 840°C for 36 h and left in the furnace for slow cooling to room temperature at a rate of 5°C/min. (Bi, Pb):2223 pellets were also sintered in air at 850°C, but for 150 h and then left in the furnace for slow cooling at the same rate of 5°C/min. The phase purity of the samples was examined using an X-ray diffraction pattern (XRD) using a Philips PW-1700 with Cu-K\textalpha radiation of wavelength $\lambda = 1.5418$ Å at 40 KV and 30 mA settings and a diffraction angle range of 20°–70° with a step of 0.06°. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) of the samples in powder form were performed in the temperature range of 30–1000°C with a heating rate of 10°C/min. The electrical resistivity of the samples was obtained using the standard four-probe technique in a closed-cycle cryogenic refrigerator within the range of 18–300 K (Displex) employing helium gas. Direct-current (DC) magnetization was carried out by means of a SQUID magnetometer (Quantum Design) in both field cooling (FC) and zero-field cooling (ZFC) at a field of 20 Oe in the temperature range of 10–150 K. More precisely, the samples were first cooled to 20 K in the absence of the applied field, then the field was switched on and the data was acquired for increasing temperature (ZFC) up to 150 K. After that, the samples were cooled again and FC magnetization was acquired in the presence of the field. Finally, the Vickers microhardness of the samples at room temperature was determined using the manual microhardness tester model IN-412A with an applied load of 0.49–10 N for 10 s.

**Results and Discussion**

**XRD and DTA Analysis**

The XRD patterns of the samples shown in Fig. 1a and b show that the 2212 H (hkl) and 2223 H (hkl) superconducting phases were responsible for the majority of the obtained peaks, which correspond to $T_c = 89$ K and 110 K, respectively. In contrast, the minority peaks of very low intensity indicated by L (hkl) belong to the minority superconducting phases of Bi (Pb):2201 and Bi (Pb):2212, with $T_c$ of 23 and 89, respectively, which are normally formed
The superconducting volume fractions of the 2212 ($V_{2212}$) and 2223 ($V_{2223}$) series were determined by $^{7,33,34}$

$$V_{2212} = \frac{\Sigma I_{2212}(\text{peaks})}{\Sigma I_{2212}(\text{peaks}) + \Sigma I_{2201}(\text{peaks}) + \Sigma I_{\text{other}}(\text{peaks})}$$

and

$$V_{2223} = \frac{\Sigma I_{2223}(\text{peaks})}{\Sigma I_{2223}(\text{peaks}) + \Sigma I_{2212}(\text{peaks}) + \Sigma I_{\text{other}}(\text{peaks})},$$

respectively.

It is also clear from Fig. 2a that $V_{2212}$ is higher than $V_{2223}$. This is because the 2201 minority phase formed in the 2212 series at 750°C, whereas the minority 2212 phase formed at 825–850°C in the 2223 series. As the temperature increased to the sintering point (850°C), the majority of the 2201 phases were transferred to 2212, and therefore $V_{2212}$ was increased. In the case of the 2223 series, the amount of the 2212 minority phase was not completely transferred to the 2223 phase, which in turn decreased the 2223 majority phase. The porosity of the samples was calculated as $PS = [1 - (\rho_{\text{exp}}/\rho_{\text{th}})]$ and shown in Fig. 2b. It is seen that $PS$ was decreased by La for both series, but it was higher for the 2223 series than the 2212 series. This behavior may be related to the ratio of dislocation density and oxygen vacancies between them, which may be higher for the 2223 series than for the 2212 series.

The c-parameter and orthorhombic distortion $OD = [(b - a)/a]$ against La are shown in Fig. 3a and b for both series. It was found that the OD for pure 2212 was generally higher than that for 2223, while the opposite was true for the La-substituted samples. However, this was related to the amount of excess oxygen and the length of the Cu–O bond in the Cu–O$_2$ planes in both series, as reported elsewhere. $^{36-39}$ Consequently, the length of the in-plane Cu–O bond was decreased, which is helpful for more effectively reducing the a-parameter of pure 2212 as compared to pure 2223. Otherwise, the change in the b-parameter is related to the
change in the hole carrier concentration per Cu ion, which is induced by La doping within these planes.\textsuperscript{40–43} Thus, the rate of decrease or increase in the (a/b) ratio for La-substituted samples is responsible for the further increase of OD in the 2223 series than that of the 2212 series. On the other hand, the c-parameter of the 2223 series was higher than that of the 2212 series. This was due to increasing the number of CuO\textsubscript{2} planes in 2223 (three planes) as compared to 2212 (two planes).

The average crystallite diameter, \(D_{\text{hkl}}\), evaluated by Scherrer’s equation, and also the dislocation density, \(\beta = 1/D_{\text{hkl}}^2\), against La content are shown in Fig. 4a and b. \(D_{\text{hkl}}\) values are higher for pure 2212 and La = 0.05 samples than for similar samples of the 2223 series, while the opposite is true for La-substituted samples. This may be related to the behavior of \(V_{2212}\) and \(V_{2223}\) against La for both series. \(\beta\) values were decreased by La, and they were slightly higher for the 2223 series than the 2212 series. This behavior indicated that La samples have very few lattice defects and good crystalline quality.\textsuperscript{44,45} Further, the increase in the 2223 series may be related to increasing both the c-parameter, OD, and \(D_{\text{hkl}}\).

Figure 5a and b shows the DTA patterns of the samples. It is worth noting that when \(T\) was raised to around 800°C, the crystallization tendencies for 2201 in the 2212 series and 2212 in the 2223 series almost vanished. Figure 6a and b shows the heat loss and melting temperature \(T_m\) at the peak against the La content for both series. The heat loss of pure 2212 was higher than that of pure 2223 and decreased by La for both series, but it was higher for the 2223 series than the 2212 series. This result indicated that the amount of 2201 minority phase formed in the 2212 series was melted below 800°C and after that it decomposed into the 2212 majority phase.\textsuperscript{46} In contrast, the 2212 minority phase formed in the 2223 series was melted above 800°C, and after that, it decomposed into the 2223 majority phase.\textsuperscript{47} The \(T_m\) was increased by La for both series, but it was higher for the 2223 series than the 2212 series even for pure samples. This may be attributed to increasing the optimum temperature required for melting the mixture due to La, which facilitated the growth of majority phases.\textsuperscript{47,48} Such an observed increase in \(T_m\) emphasizes the role of La addition in the internal structure of the examined samples.
Oxygen Content Analysis

Figure 7a shows the oxygen content $y$ against the La content for both series, and it is seen that for pure samples, there is an excess of oxygen above the stoichiometric values of 8 and 10 for both systems ($y = 8.1$ for 2212 and 10.07 for 2223). Furthermore, values of $y$ were gradually increased by La for the two series, but it is higher for the 2223 series than the 2212 series, which indicates that La helps with more excess oxygen for the two series. For more clarity, the excess oxygen is 0.10, 0.17, 0.47, and 0.58 for 2212, which is higher than 0.07, 0.12, 0.37, and 0.53 determined for 2223, as well as the OD behavior obtained from XRD. However, according to the mechanism of excess oxygen in a pure BSCCO system, the electrons were transferred from Cu to the BiO layer, leading to the formation of holes on Cu and electrons on Bi according to $\text{Bi}^{3+} + \text{Cu}^{2+} \rightarrow \text{Bi}^{3-x} + \text{Cu}^{2+x}$. These changes in the valence state of Bi are due to excess oxygen and are reflected as the changes of hole carriers in the Cu–O$_2$ planes. Since the superconductivity of copper-oxide systems is localized in the Cu–O$_2$ planes where the majority of holes are supposed to reside, it is believed or expected that the majority of excess of oxygen will be in the Cu–O$_2$ planes.

The effective Cu$_{\text{eff}}$ valance was obtained by

$$
\text{Cu}_{\text{eff}} = \frac{2y - [9.7 + 2(1-x) + 3x]}{2} ; \text{ for } 2212 \text{; and }
$$

$$
\text{Cu}_{\text{eff}} = \frac{2y - [9.7 + 2(2-x) + 3x]}{2} ; \text{ for } 2223
$$

Figure 7b shows the Cu$_{\text{eff}}$ against La for the two series. It was found that the values of Cu$_{\text{eff}}$ are higher for the 2223 series than the 2212 series. This can be explained in terms of increasing the number of holes which may be introduced by La as a result of such substitution. Thus it is illogical to replace Ca$^{2+}$ by La$^{3+}$, and therefore, Cu$_{\text{eff}}$, should be decreased, but this is discussed in the next paragraph.
The excess oxygen in the form of excess doping density $\Sigma^{-1}$ is converted into a doping distance $d$ as follows:

$$d = a\sqrt{\Sigma}$$

(3a)

where $a$ is lattice parameter, and $\Sigma$ given by

$$\Sigma = \frac{1}{(1 - 8y^{-1})}; \quad \text{for 2212;} \quad \text{and}$$

$$\Sigma = \frac{1}{(1 - 10y^{-1})}; \quad \text{for 2223}$$

(3b)

It is evident from Fig. 8 that $\Sigma^{-1}$ is higher for the 2212 series than the 2223 series, while $d$ is higher for the 2223 series than the 2212 series; see Fig. 8a and b. This, of course, is clear evidence of changing the hole carrier concentrations between the series as a result of such substitution. Increasing $d$ for the 2223 series rather than the 2212 series is related to the difference in the $c$-axis between them. The distance $z$ between the two nearest Cu atoms was calculated by

$$z = \sqrt{(2a)^2 + a^2} = a\sqrt{5}$$

(4)

Moreover, the crystal geometry factor (CGF) of the area of superconducting planes can be obtained from

$$\text{CGF(Jm}^2\text{kg)} = [(2d)^2n\pi^2K_Bm_{\text{eff}}] = 6.31 \times 10^{-54}d^2n\pi^2$$

(5)

where $n$ is the number of CuO$_2$ planes, and $m_{\text{eff}}$ is the effective mass of the hole ($m_{\text{eff}} = 2m_e = 18.210^{-31}$ kg).

It is evident from Fig. 9a and b that $z$ is higher for the 2223 series than the 2212 series. The CGF factor is higher for pure 2223 than for pure 2212, and the difference in CGF between them is gradually decreased by La until it becomes zero for La = 0.15 and 0.30 samples. This behavior can be considered good evidence for hole carrier behavior between the series, as presented in the next paragraph.

**Resistivity Analysis**

Figure 10a and b depicts the electrical resistivity versus temperature for the two series. Figure 11a depicts the critical $T_c$, onset temperature $T_{\text{on}}$, and transition width $\Delta T_c$ for the samples. It was found that $T_c$ and $T_{\text{on}}$ were higher
for the 2223 series than the 2212 series. This was due to
the difference in $T_c$ for pure samples (94 K for 2212 and
119 K for 2223). The reduced $T_c \{T_c(x)/T_c(0)\}$ against La
is also shown in Fig. 11b. It was found that the critical
concentration $x_c$ of La for quenching superconductivity
can be extended above 0.30 for both series, which is higher
than that reported (0.25).\textsuperscript{8–16,18–22,26,52,53} It was also clear
that La slightly had a higher solubility in the 2212 series,
and it was less detrimental to the superconductivity as
compared to the 2223 series; that is $[T_c(x)/T_c(0)] \propto (1/T_c)$
for BSCCO systems.

An inverse linear relation could be obtained between $T_m$
obtained from DTA and $T_c$ as shown in Fig. 12b. The linear
relations are given by

\[
T_c(K) = -3.406 \cdot T_m + 2963.3 \text{ for 2212 and } T_c(K) =
-2.5413 \cdot T_m + 2963.3 \text{ for 2223, which is consistent with}
\text{reported values for high-$T_c$ systems.}^{54,55}\]

This finding suggests that to achieve a higher $T_c$, an eutectic compound with
a lower melting point should be looked into. Based on the
above data, a composition of $T_m = 784.48^\circ C$ for 2212 and
1048.03$^\circ C$ for 2223 is required for RT superconductivity
with $T_c = 300 K$.

The phase diagram of high-$T_c$ systems is well described
by\textsuperscript{56}

\[
\frac{T_c^m}{T_c^\circ} = 1 - 82.6(p - 0.16)^2
\]

where $T_c^\circ$ and $T_c^m$ are the critical and maximum $T_c$, respec-
tively, and $p$ is the hole carrier concentration per Cu ion. It
is evident from Fig. 12a that $p$ is higher for the 2223 series
than the 2212 series due to the extra positive charges trans-
ferred to the CuO$_2$ planes, which disagrees with the role
of substitution for decreasing $P$ due to replacing Ca$^{2+}$ by
La$^{3+}$.\textsuperscript{57,58} To clarify this point, we suppose that La decreases
the hole carrier concentration due to replacing Ca$^{2+}$ by La$^{3+}$,
but in contrast, the excess oxygen introduces some excess
holes in the Cu–O$_2$ planes, and consequently, the effective

\textbf{Magnetic Measurements}

Figure 13a–d shows the magnetic moment as a function of
temperature in the field cooling (FC) and zero field cooling
(ZFC) for the samples. Although the diamagnetic signal is

\textbf{Fig. 9} (a) Distance between two nearest Cu atoms (z) versus La content for the samples. (b) Crystal geometry factor (CGF) versus La content for the samples.

\textbf{Fig. 10} Resistivity versus temperature for the samples (a) Bi (Pb) 2212 and (b) Bi (Pb) 2223.
zero at $T_{cM}$ for both series, the area of diamagnetic is higher than zero, indicating the presence of a superconducting state with an expected critical current, as previously reported.$^{59,60}$

As shown in Fig. 14a and b, the onset of diamagnetism $T_{cM}$ decreases with increasing La for both series, followed by a sharp increase to 80 K for La = 0.30 samples. $T_{cM}$ average values for 2223 are higher than for 2212, as well as for $T_{cR}$ ($R = 0$). Interestingly, as La increased to 0.15, the temperature difference $|T_{cM} - T_{cR}|$ also increased, and it was greater for the 2223 series than for the 2212 series. However, when La was increased to 0.30, the $|T_{cR} - T_{cM}|$ sharply increased up to 30 K for both series. This was because it was possible to determine the $T_{cM}$ of the first islands due to pure clusters that were present essentially and appeared in the superconducting sample using high-accuracy magnetic measurements.$^{59,61,62}$ This is, of course, impossible in the case of resistivity measurements, because they are measured across the sample’s cross-sectional area.

**Microhardness Analysis**

It is evident from the curves of microhardness $H_v$ versus $F$ shown in Fig. 15a and b that they were decreased by increasing $F$ for the two series, and at fixed $F$, the $H_v$ is higher for the 2212 series than the 2223 series. The higher values of $H_v$ for 2212 are due to the decreased porosity of the 2212 series and therefore alter the point of plastic deformation.$^{37,63,64}$

The diagonal length $d_p$ is related $F$ according to$^{15,65}$

$$\frac{F}{d_p} = H_t d_p + \gamma$$

(7)

$H_t$ is true hardness, and $\gamma$ is surface energy. The plots of $F/d_p$ against $d_p$ are shown in Fig. 16a and b. Figure 17a and b shows that $H_t$ is greater for the 2212 and 2223 series, as is $H_v$. But, the values of $\gamma$ are higher for the 2223 series than the 2212 series, indicating that a more compacted surface...
has higher hardness, and thus lower surface energy was obtained. Firstly, the indentation size effect assumes that the indentation contains an elastic portion of the deformation besides plastic deformation. This is explained by adding an elastic component $d_e$ to the measured elastic component $d_p$ as follows:

Fig. 13  Magnetic moment versus temperature for the samples (a) FC of Bi (Pb) 2212, (b) FC of Bi (Pb) 2223, (c) ZFC of Bi (Pb) 2212, and (d) ZFC of Bi (Pb) 2223.

Fig. 14  (a) Onset of diamagnetism ($T_{CM}$) versus La content for the samples. (b) Width of transition ($\Delta T_{CM}$) and temperature difference $|T_{CR} - T_{CM}|$ versus La content for the samples.
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Fig. 15  Vickers hardness ($H_v$) against applied load ($F$) for the samples (a) Bi (Pb):2212 and (b) Bi (Pb):2223.

Fig. 16  The plot of $F/d_p$ against indentation $d_p$ for the samples (a) Bi (Pb):2212 and (b) Bi (Pb):2223.

Fig. 17  (a) The plot of true hardness ($H_t$) against La content for the samples. (b) Surface energy ($\gamma$) against La content for the samples.
The plot of $d_p$ versus $F^{1/2}$ is shown in Fig. 18a and b for the two series where the slope represents $\left[(1854.4)^{1/2}(H_t)^{-1/2}\right]$, and the vertical intercept represents $d_e$.

Secondly, the effect of energy dissipative processes and therefore $H_t$ was obtained by subtracting dissipative part $F_0$ from applied load $F$ as follows:

$$H_t = 1854.4 \left[ \frac{F}{(d_p + d_e)^2} \right]$$

$$d_p = [(1854.4)^2 H_t^{-2}]^{1/2} - d_e \quad (8)$$

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$$F = \left( \frac{H_t}{1854.4} \right) d_p^2 + F_0 \quad (9)$$

The slope of the linear plot of $F$ against $d_p^2$ is shown in Fig. 19a and b for the two series, in which $H_t/1854.4$ is the slope, and the intercept is the resistance pressure $F_0$. Also, $H_t/1854.4$ is the mean field temperature $T_{c mf}$.

Fluctuation Analysis

The linear fit of normal resistivity $\rho_n$ versus $T$, shown in Fig. 21a and b, follows the formula. The mean field temperature ($T_{c mf}$) was estimated from the peak of $d\rho/dT$ against the $T$ plot, which is shown in Fig. 22a and b. By using the values of excess conductivity $\Delta\sigma$ and reduced temperatures $\xi$, we plotted $\ln\Delta\sigma$ against $\ln\xi$ as shown in Fig. 23a and b. However, the linear fit of each curve in the normal field region (NFR), mean field region (MFR), and critical field region (CFR) is mentioned. In Fig. 24, the crossover temperatures, $T_{c1}$ and $T_{c2}$, and $T_{c mf}$ against $La$ are shown in Fig. 24a and b. It is noted that their values are higher for the 2223 series than the 2212 series, which emphasizes the hardness suppression indicated above.

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Comparative Study of the Effects of La-Substituted Ca in (Bi, Pb):2212 and (Bi, Pb):2223…

Figure 25a and b shows the behaviors of $J$ and $\xi_c(0)$ against La content. It is clear that the values of $J$ are higher for the 2212 series than the 2223 series, whereas the opposite is true for $\xi_c(0)$.

The dimension exponent $\lambda$ was well determined using the relation

$$\Delta \sigma = A \epsilon - \lambda \ln \epsilon \quad (10)$$

$$J = \ln \left( \frac{T_0}{2T_m} \right) \quad \xi_c(0) = \left( \frac{dJ}{2} \right)$$

Figure 20 (a) Elastic component ($d_e$) versus La content for the samples. (b) Surface energy ($F_{so}$) versus La content for the samples.

Figure 21 The linear fit of resistivity ($\rho_{m}$) versus temperature for the samples (a) Bi (Pb):2212 and (b) Bi (Pb):2223

However, the values of $\lambda$ in the CFR for the 2212 series are 0.90 (2D), 0.78 (2D), 0.70 (2D), and 0.35 (3D), whereas they are 0.53 (2D), 0.99 (2D), 0.65 (3D), and 0.38 (2D) for the 2223 series. This means that the OPD is 2D for both series, but it becomes 3D for La = 0.30 samples rather than 2D as reported for BSCCO systems.71,72 This behavior is related to another generated reduced length

\[ \ln \Delta \sigma = \ln A - \lambda \ln \epsilon \quad (11) \]
or dimension perpendicular to the direction of current flow. In addition, anisotropy is given by

\[
\gamma = \left[ \frac{0.71 K_B}{\sqrt{N_G H_c^2(0) \xi_c^4(0)}} \right]^{\frac{1}{2}} = \frac{\xi_{c}(0)}{\xi_{c}(0)}
\]

\[N_G \] is the Ginzberg reduced number given by \[N_G = \frac{T_{c0} - T_{cR}}{T_{cR}}\], and \[H_c(0)\] is the thermodynamic critical field at 0 K given by;

\[H_c(0) = \frac{\phi_0}{2 \sqrt{2 \tau_c(0) \xi_c(0)}}\], and \(\tau_c(0)\) is the London penetration depth at 0 K which is about 250 nm and 300 nm for 2212 and 2223 superconductors, respectively.

The upper critical fields at 0 K along the c-axis \(H_{c2}(c \text{- axis})\) and along the a-b plane \(H_{c2}(ab \text{- plane})\), and also the critical current density at 0 K and \(J_c(0)\) were calculated by using the following relations:

\[H_{c2}(c \text{- axis}) = \frac{\phi_0}{2 \pi \xi^2_c(0)}; \quad H_{c2}(ab \text{- plane}) = \frac{\phi_0}{2 \pi \xi^2_{ab}(0) \xi_{c}(0)}\]

\[H_{c2}(0) = \sqrt{[H_{c2}(ab \text{- plane})]^2 + [H_{c2}(c \text{- axis})]^2}\]
\[ J_c(0) = \frac{2\varphi_0}{\sqrt{6\pi} \lambda^2(0) \xi(0)} \] (13)

As indicated in Fig. 26a, the values of anisotropy are higher for the 2212 series than the 2223, while the values of NG shown in Fig. 26b are higher for the 2223 series than the 2212. On the other hand, Fig. 27a and b shows the critical field and critical current for both series, in which they are higher for the 2212 series than the 2223 series. In light of these observations, one can say that the increase in excess oxygen and hole carrier/Cu ions introduced by La into the CuO2 planes of the BSCO system may also affect the path of current flow in the system and improve the critical fields and currents. This leads to electronic

Fig. 25  (a) Interlayer coupling \((J)\) versus La content for the samples. (b) c-axis coherence length \((\xi_c(0))\) versus La content for the samples.

Fig. 26  (a) Anisotropy \((\gamma)\) versus La content for the samples. (b) Ginzberg reduced number \((N_G)\) versus La content for the samples.

Fig. 27  (a) Critical current \((J)\) versus La content for the samples. (b) Upper critical fields \((H_{c2})\) versus La content for the samples.
or chemical inhomogeneity in the charge reservoir layer (BiO/SrO), which supplies the charge carriers to the CuO2 planes through which the actual super-current is believed to flow.\textsuperscript{31,76,77}

However, and regardless of the effects of La discussed in detail in Refs. 29–32, it is found that $\chi_1$ for quenching superconductivity, Vickers hardness, critical magnetic fields, and critical current density are higher for the 2212 series than the 2223 series. In contrast, the melting temperature $T_m$, critical temperature $T_c$, onset of diamagnetic $T_{cM}$, surface energy, elastic component, and resistance pressure are higher for the 2223 series than the 2212 series. These findings are due to the differences in superconducting volume fraction, crystallite diameter, porosity, excess oxygen, hole carrier/Cu ion ratio, doping distance, spacing between two neighboring Cu atoms, anisotropy, and interlayer coupling between the two series. For example, superconducting volume fraction, excess of oxygen, anisotropy, and interlayer coupling are higher for the 2212 series, and they are responsible for the former performance of the 2212 series, while the orthorhombic distortion, c-parameter, crystallite diameter, doping distance, distance between two neighboring Cu atoms, hole carrier/Cu ion ratio, and c-axis coherence length, which are higher for the 2223 series, are responsible for the latter performance of the 2223 series. To our knowledge, the present systematic investigation has not been reported elsewhere, which highlights the present work.

### Conclusion

A comparative study between the effects of La-substituted Ca in (Bi, Pb):2212 and (Bi, Pb):2223 superconductors has been well investigated. We have shown that the critical concentration for quenching superconductivity, Vickers hardness, critical fields, and critical current $J_c$ are higher for the 2212 series than the 2223 series. In contrast, the critical temperature $T_c$, melting temperature $T_m$, onset of diamagnetism $T_{cM}$, and resistance pressure are found to be higher for the 2223 series than the 2212 series. An inverse linear relationship between $T_m$ and $T_c$ could be obtained for both series. The 1048.03°C and 784.48°C $T_m$ values are required for RT superconductors of 2223 and 2212. Surprisingly, for both series, the temperature difference between zero resistivity and diamagnetic onset, $|T_{cM} - T_{cRL}|$ for La = 0.30 samples is 30 K. The order parameter exponents in the critical field region are 2D for both series, but they become 3D as La increases to 0.30 due to the expected reduced effective length in highly substituted samples. The preference of the 2212 over the 2223 for the former parameters is mainly attributed to the superconducting volume fraction, excess of oxygen, anisotropy, and interlayer coupling, which are higher for the 2212 series than the 2223 series. Meanwhile, orthorhombic distortion, c-parameter, crystallite diameter, doping distance, distance between two Cu atoms, hole carrier/Cu ion ratio, and c-axis coherence length, which are higher for the 2223 than the 2212, are responsible for the latter preference of the 2223 series. These findings reveal that the 2212 series is more suitable for research for higher $T_c$ and altering plastic deformation. In contrast, the 2223 series is more suitable for research for higher $T_c$ and applications that need higher hardness and critical fields and currents. In this article, we have shown that the critical concentration for quenching superconductivity, Vickers hardness, critical magnetic fields, and critical current density are higher for the 2212 series than the 2223 series. These findings are due to the differences in superconducting volume fraction, crystallite diameter, porosity, excess oxygen, hole carrier/Cu ion ratio, doping distance, spacing between two neighboring Cu atoms, anisotropy, and interlayer coupling between the two series. For example, superconducting volume fraction, excess of oxygen, anisotropy, and interlayer coupling are higher for the 2212 series, and they are responsible for the former performance of the 2212 series, while the orthorhombic distortion, c-parameter, crystallite diameter, doping distance, distance between two neighboring Cu atoms, hole carrier/Cu ion ratio, and c-axis coherence length, which are higher for the 2223 series, are responsible for the latter performance of the 2223 series. To our knowledge, the present systematic investigation has not been reported elsewhere, which highlights the present work.

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