Effect of Oxygen Doping and Cation Composition on Critical Current Densities in Polycrystalline Bi-2212 Conductors with Various Textures

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The origin of Strong **Compositional Effects on** \( J_c \) (4.2 K, sf) in Bi-2212 Wires and Dip-Coated Tapes is not clear.

It is known that significant **Overdoping** is necessary for optimizing \( I_c \) in Bulk and Round Wire conductors.

Literature data suggest that **optimum doping** (highest \( T_c \)) depends on **cation composition** of Bi-2212.

Can the difference in the doping state explain the compositional effects on \( I_c \) in Bi-2212 tapes and wires?
STRONG Effect of Cation Composition on Wire and Tape Performance

W521-524: Bi$_{2.14}$ : Sr$_{(2.86-x)}$ : Ca$_x$ :Cu$_{2.00}$
Sr/Ca = 2.25, 2.18, 1.75, 1.34


- Microstructural studies of tapes and wires did not explain a factor of four or more difference in $J_c$ of best (Sr-rich, 521) and worst (Ca-rich; 524) compositions
Overdoping $\Delta \delta_0$ is necessary for optimizing $I_c$, $T_c$ & $I_c$ vs. $\delta$ in OST 521-like RW

$\Delta \delta_0 = 0.017(6)$

$\delta_{opt} = 0.196(4)$

$\delta_0 = 0.213(4)$

Rikel et al ASC2012
OPTIMUM Doping Depends on Cation Composition

- Single Crystals grown from $\text{Bi}_{2+x}\text{Sr}_{2-x}\text{Ca}_1\text{Cu}_2\text{O}_{8+\delta}$ powders
- Annealed to vary O index
- Smaller Sr/Ca requires more overdoping

Hypothesis to Check

Can the difference in the doping state explain compositional effects on $J_c$ in Bi-2212 tapes and wires?

Program of Studies:
- Use $\text{Bi}_{2.00+z}\text{Sr}_{3.00-z-x}\text{Ca}_x\text{Cu}_{2.00}\text{O}_{8+\delta}$ based conductors (bulk, round wires, tapes)
- Vary O contents $\delta$
- Justify $T_c(\delta)$ for various $z$ & $x$
- Study effect of $\delta$ on $J_c(B)$ at various temperatures.

Proof-of-Principle Results
- $T_c$ vs. $\delta$ and $J_c$ vs. $\delta$ for bulk samples of Sr- and Ca-rich compositions

First Results for W521 wires
- $T_c$ vs. $\delta$ and $J_c$ vs. $\delta$ at 77, 66 and 4.2 K
**Melt Cast Processed (MCP) Bi-2212 Bulk**

- Easy to change cation composition in comparison with fabrication of wire and tape conductors

- 400 A class elements for FCL systems

- \( J_c(77 \text{ K}, 0 \text{ T}) \sim 5 \text{ kA/cm}^2 \)

- \( J_c(66 \text{ K} = 0.7 T_c) \sim 15 \text{ kA/cm}^2 \sim 20\% \) of best \( J_c(77 \text{ K} = 0.7 T_c) \) in Ag/Bi2223
### Compositions of 5 and 8 mm Ø MCP rods

\[
\text{Bi}_{2.00+z}\text{Sr}_{3.00-z-x}\text{Ca}_x\text{Cu}_{2.00}\text{O}_{8+\delta}
\]

<table>
<thead>
<tr>
<th>Lot</th>
<th>Bi</th>
<th>Sr</th>
<th>Ca</th>
<th>Cu</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>83</td>
<td>2.15</td>
<td>2.03</td>
<td>0.82</td>
<td>2.00</td>
<td>Sr/Ca similar to NSC bulk, but no SrSO4</td>
</tr>
<tr>
<td>82</td>
<td>2.15</td>
<td>1.95</td>
<td>0.90</td>
<td>2.00</td>
<td>~ 521</td>
</tr>
<tr>
<td>84</td>
<td>2.15</td>
<td>1.82</td>
<td>1.03</td>
<td>2.00</td>
<td>~ 522</td>
</tr>
<tr>
<td>524</td>
<td>2.15</td>
<td>1.63</td>
<td>1.22</td>
<td>2.00</td>
<td>Vintage powder 2004</td>
</tr>
<tr>
<td>85</td>
<td>2.08</td>
<td>2.07</td>
<td>0.85</td>
<td>2.00</td>
<td>Sr/Ca as in 83</td>
</tr>
<tr>
<td>86</td>
<td>2.08</td>
<td>1.68</td>
<td>1.24</td>
<td>2.00</td>
<td>Sr/Ca as in 524</td>
</tr>
<tr>
<td>148</td>
<td>2.00</td>
<td>2.11</td>
<td>0.89</td>
<td>2.00</td>
<td>Sr/Ca as in 83</td>
</tr>
<tr>
<td>149</td>
<td>2.00</td>
<td>1.70</td>
<td>1.30</td>
<td>2.00</td>
<td>Sr/Ca as in 524</td>
</tr>
<tr>
<td>147</td>
<td>1.95</td>
<td>2.01</td>
<td>0.92</td>
<td>2.02</td>
<td>NSC bulk (+ 0.1 BaO + 0.45 SrSO4)</td>
</tr>
</tbody>
</table>

- 4 similar to 521 to 524 studied in 2004-2006
  + 147 (empirically optimized at Nexans since 1990’s)
- 4 more with smaller Bi contents to double check correlations

April 08, 2015
The composition of Bi-2212 phase differs from the overall one and was determined from EDX with correction for presence of Bi-2201 intergrowth defects, whose density was assessed from XRD.
Adjusting O Contents

The $\delta$-$pO_2$-$T$ diagram of Schweizer et al (1993)


- Anneal at high $T$ for fast equilibration;
- Quench or cool down along the $pO_2$-$T$ cooling trajectory to suppress O exchange
- For $\delta > 0.230$, just annealing in air or $O_2$ at $350 \leq T \leq 550°C$

What is varied is the *nominal* O contents
Real $\delta$ are likely dependent on the cation composition (TBD).

April 08, 2015
Reversible (=> no changes in microstructure) changes in RT resistivity from ~5 to ~2 mΩ·cm suggest almost linear changes in carrier (hole) density $p$. 
Proof-of-Principle Results

- Optimum O doping $\delta_{\text{opt}}$ [maximum $T_c$]
  for Sr-rich and Ca-rich Compositions
  (the doping state that optimizes $T_c$)
$T_c$ decreases and $\delta_{\text{opt}}$ increases when decreasing Sr/Ca

- Optimum $\delta$ and maximum attainable $T_c$ depend on cation composition
The effect of cation composition on Optimum Doping

\[ \delta_{\text{opt}} = 0.282 \pm 0.033 \]

\[ \partial \delta_{\text{opt}} / \partial (\text{Sr/Ca}) = -0.10(4) \]

- The strong effect confirmed, but the precision is bad
- The predicted (average) optimum for real 524 composition requires annealing at 300°C and ~200 bar \( O_2 \) (log \( pO_2[\text{bar}] = 2.3\pm1.7 \))

April 08, 2015
Proof-of-Principle Results

- Optimum O overdoping [maximum self-field $J_c(77 \text{ K})$] as function of cation composition (the doping state that optimizes $J_c$)
$T_c$ and transport $J_c(77 \, \text{K})$

**Composition #147; Sr/Ca = 2.43(14)**

\[
\Delta \delta_{\text{ovd}} = 0.024(4)
\]

\[
\delta_{\text{opt}}(J_c) = 0.201(2)
\]

\[
\delta_{\text{opt}} = 0.177(3)
\]

\[
\text{Bi}_{1.95}\text{Sr}_{2.01}\text{Ca}_{0.92}\text{Cu}_{2.02}\text{O}_{8+\delta} + 0.1\text{BaO} + 0.4\text{SrSO}_4
\]

April 08, 2015
Overdoping $\Delta \delta_{ovd}(77 \text{ K})$ versus $T_{c, \text{ max}}$

$\Delta \delta_{ovd}(77 \text{ K}) = \delta_0 \{ J_c(77 \text{ K}) \} - \delta_{\text{opt}}$

- Overdoping $\Delta \delta_{ovd}$ at 77 K is a function of $T_{c, \text{ max}}$, tending to zero when $T_{c, \text{ max}}$ tends to 77K
Optimum Overdoping $\delta_o(J_c)$ and Cation Composition

- Optimum overdoping for $J_c(77 \text{ K, sf})$ depends on cation composition, particularly on the Sr/Ca ratio.
- Large errors in $\delta_o(J_c)$ for some compositions indicate sample-to-sample irreproducibility, likely, related to different sensitivity to solidification paths, which may lead to the scatter of the Sr/Ca ratio in the Bi-2212 phase.
Correlation between maximum $J_c$ (77 K) in 8 mm $\varnothing$ MCP rods and optimum overdoping $\delta_o(J_c)$

- The sample-to-sample scatter is almost unseen
$J_{c,\text{max}}(77\text{ K, sf})$ vs $\delta_0(J_c)$ & $T_{c,\text{max}}$ vs $\delta_{\text{opt}}$

Intentional or unintentional variations in cation composition strongly affect $J_c(77\text{K})$ vs. $\delta$ most likely because of variation in $T_c$ vs. $\delta$
Proof-of-Principle Results

- Optimum O overdoping [maximum $J_c(T, H)$]
  for Sr-rich and Ca-rich Compositions
Nexans Bulk Standard #147
Magnetization Data at 4.2 to 77 K

\[ \Delta M(77K, 0.05 \, T), \text{emu/g} \]

\[ \Delta \delta(77K) = 0.024(5) \]

\[ \Delta M(H, T) \] data for \( \varnothing5 \, \text{mm} \) rods:
- \( \delta_o(J_c) \) is strongly \( T \) dependent
- \( \Delta \delta \) increases with decreasing \( T \)

\[ \Delta \delta(40 \, K) = 0.048(7) \]

\[ \Delta \delta(4.2 \, K) = 0.061(5) \]
Bulk samples #83 [Sr/Ca = 2.37(16)] and #524 [Sr/Ca = 2.03(8)]

- No optimum is reached at 4.2 K: \( \delta_o \geq 0.252 \)
Temperature dependence of overdoping is somewhat similar to the temperature dependence of the energy gap $\Delta(T,\delta)$. 

**Overdoping $[T-\Delta\delta_o]$ Map.**
\(I_c(4.2 \text{ K})\) in OST wire with 521 composition. 
\(\text{Sr/Ca(EDX)} = 2.20(5)\)

- Composition of Bi-2212 phase in MCP #83 with \(\text{Sr/Ca} = 2.37(16)\) & #524 with \(\text{Sr/Ca} = 2.03(8)\) bracket the composition of Bi-2212 phase in W521 wires with \(\text{Sr/Ca} = 2.20(5)\)
- If \(\delta_o(J_c) = 0.234(4)\) confirmed, then not only the composition, but other factors play a role in wire samples.
Why optimizing $J_c$ requires overdoping?

- Changes with $\delta$ of the condensation energy density $U_0 = B_c^2/2\mu$
  $U_0$ depends on the carrier density $p$ and energy gap ($\sim T_c$) and peaks at $p > p_{opt}$.  
  $\Rightarrow J_c \approx U_0 \xi \quad (\xi = \text{coherence length weakly dependent on } p)$
  peaks at $\delta_o(J_c) > \delta_{opt}$


- Effect of the doping state on the transparency of GBs to supercurrent
  The doping states of GBs in general differ from that of the bulk
  O overdoping may affect the transparency of GBs to supercurrent
  Texture (dominant type of GBs) may affect $\delta_o(J_c)$


- Further studies of Bi2212 conductors with various compositions and texture should clarify what are the relative contributions of these mechanisms
Consequences for Processing Round Wires

Can the difference in the doping state explain compositional effects on $J_c$ in Bi-2212 tapes and wires?

- No answer, but
- Bi-2212 conductors need optimization of their O doping state, which opens an opportunity to independently optimize the microstructure and basic parameters dependent on the O doping:
  - The empirically optimized composition 521 (Bi$_{2.17}$Sr$_{1.94}$Ca$_{0.89}$Cu$_{2.00}$O$_{8+\delta}$) is the best for partial melt processing (PMP) round wires in 100% O$_2$.
  - Sr richer compositions may need post-annealing to have smaller $\delta$
  - Ca richer compositions may need post-annealing to have larger $\delta$
- The cation composition of Bi-2212 phase in PMP conductors is in general different from the overall precursor composition
  - The O doping state should be a processing parameter in any optimization program
Conclusion and Outlook

- It is confirmed that cation composition affects optimum O contents that maximizes $T_c$, and the effect seems **to be very strong**
  - Further work [$T_c$ vs. $\delta$] is necessary to better quantify the dependence

- $I_c$ optimization needs **significant overdoping**, which is temperature dependent.
  - Further work [M(H, T) vs. $\delta$] is necessary to quantify the temperature dependence and relate it to the basic properties of Bi-2212

- Oxygen contents $\delta_{ovd}$ optimizing $J_c$ in MCP bulk seem to differ from that for PMP wires (**to be double checked**) suggesting that not only composition, but **other factors** (e.g., texture) may affect $\delta_o(Jc)$

- **O doping state and cation composition should be considered as important parameters for optimizing performance of Bi-2212 conductors**
Thank you for your attention
Relative changes in $\delta$ are largely consistent with the phase diagram used. The slope corresponds well to presence of $\sim$10% second phases in the samples.
Why optimizing $J_c$ requires Overdoping?

- Condensation energy density $U_0 = \frac{B_c^2}{2\mu}$ peaks at $\delta > \delta_{\text{opt}}$
  Pinning force $F_p \sim \frac{B_c^2}{2\mu}$
  $U_0 \sim N(\delta, T) \times \Delta(\delta, T)$
  the density of states $N(\delta, T) \sim a\delta + b$
  the energy gap $\Delta(\delta, T) \sim T_c \sim [1-(\delta - \delta_{\text{opt}})^2]$ at least for $\delta > \delta_{\text{opt}}$
  As $a > 0$, optimum of $(a\delta + b) [1-(\delta - \delta_{\text{opt}})^2]$ is at
  $\delta_o (J_c) > \delta_{\text{opt}}$

- Transparency of GBs may depend on the doping state
  The doping state of a GB in general differs from that of the bulk
  Overdoping may affect the transparency of GBs to supercurrent
  Texture (dominant type of GBs) may affect $\delta_o (J_c)$

T Shen et al (2009) *APL* 95, 152516