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

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Motivation

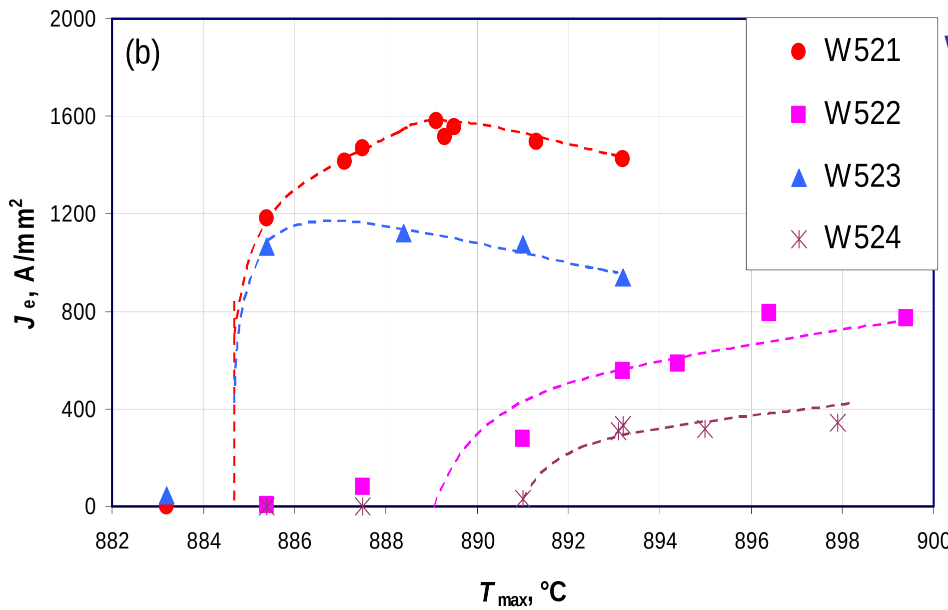
- The origin of Strong **Compositional Effects on J_c (4.2 K, sf)** in Bi-2212 Wires and Dip-Coated Tapes is not clear.

- 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.

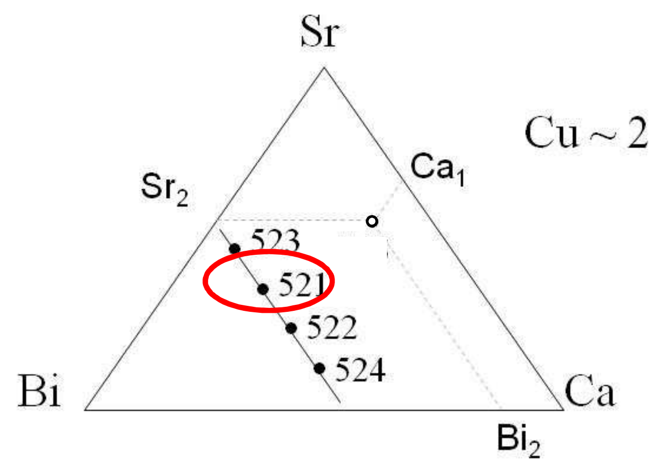
- Can the difference in the doping state explain the compositional effects on I_c in Bi-2212 tapes and wires?

STRONG Effect of Cation Composition on Wire and Tape Performance



W521-524: $Bi_{2.14}$: $Sr_{(2.86-x)}$: Ca_x :$Cu_{2.00}$

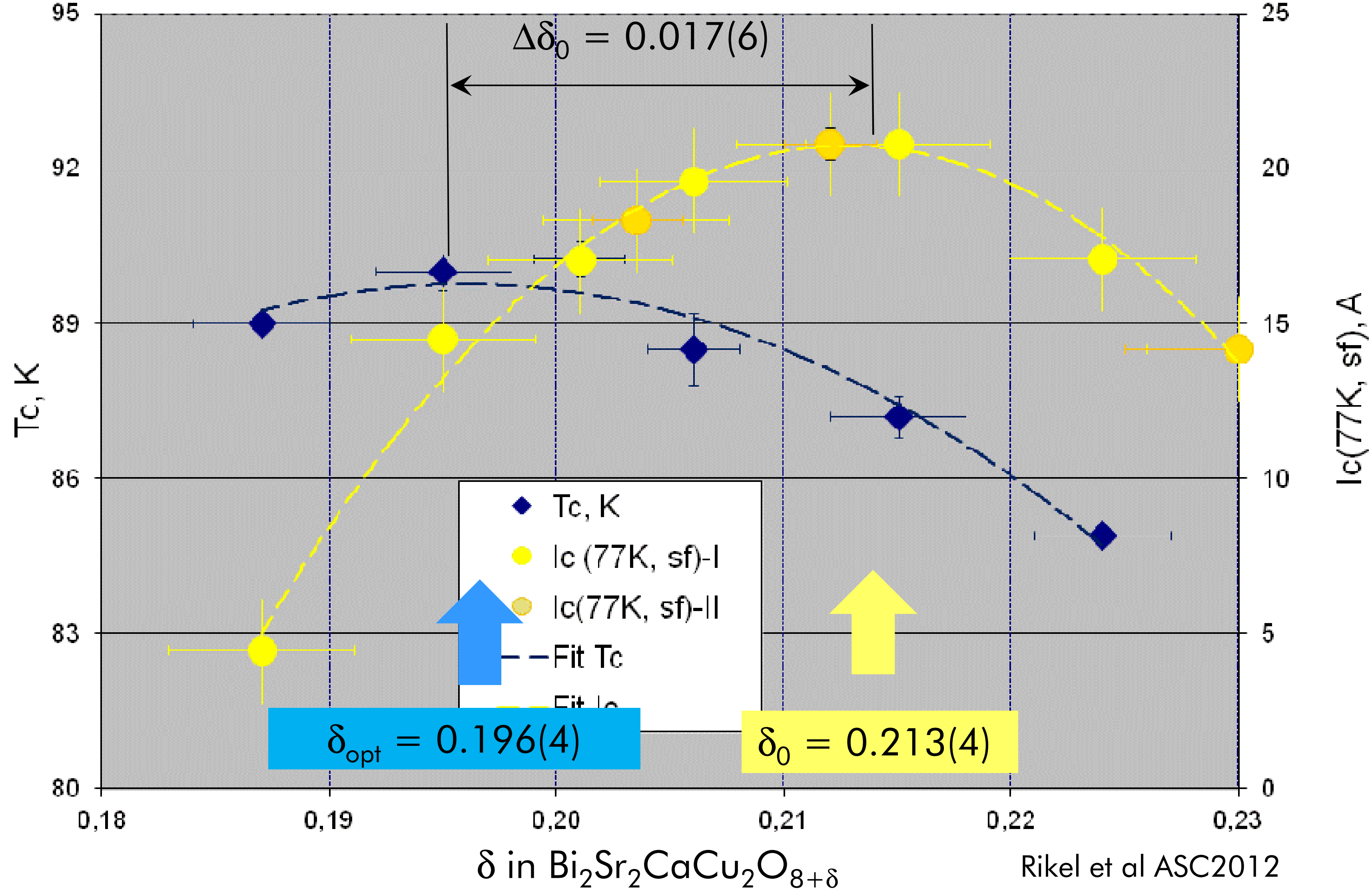
Sr/Ca = 2.25, 2.18, 1.75, 1.34



H. Miao et al 2006 *Adv Cryo Eng*. 52B, p. 673, (2006) [Proc. ICMC 2005]
M. Rikel et al 2006 *J Phys: Conf Ser.,* 43 (2006) 51–54 [Proc. EUCAS 2005]

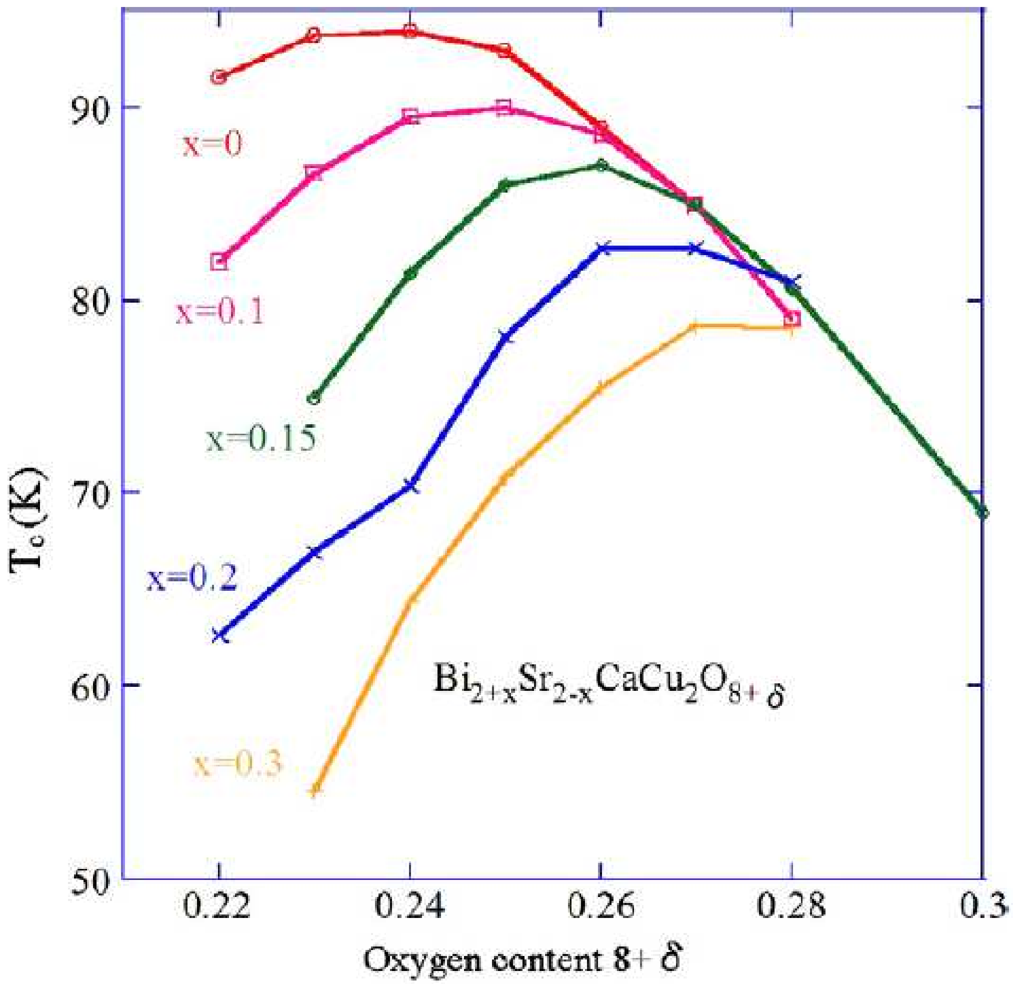
- Microstructural studies of tapes and wires did not explain a factor of four or more difference in J_c of best (Sr-rich, 521) and worst (Ca-rich; 524) compositions

Overdoping $\Delta\delta_o$ is necessary for optimizing I_c. T_c & I_c vs. δ in OST 521-like RW



Rikel et al ASC2012

OPTIMUM Doping Depends on Cation Composition



Yamashita *et al.* Physica C 470 (2010) p.170

- Single Crystals grown from $Bi_{2+x}Sr_{2-x}Ca_1Cu_2O_{8+\delta}$ 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 $Bi_{2.00+z}Sr_{3.00-z-x}Ca_xCu_{2.00}O_{8+\delta}$ based conductors (bulk, round wires, tapes)
- Vary O contents δ
- Justify $T_c(\delta)$ for various z & x
- Study effect of δ on $J_c(B)$ at various temperatures.

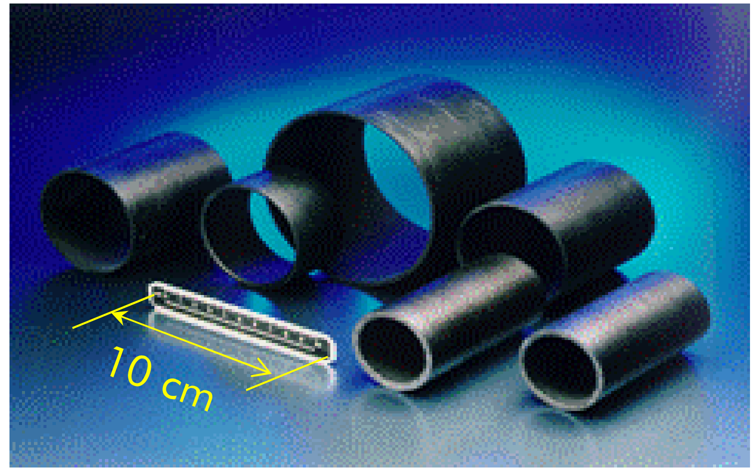
Proof-of-Principle Results

- T_c vs. δ and J_c vs. δ **for bulk samples** of Sr- and Ca-rich compositions

First Results for W521 wires

- T_c vs. δ and J_c vs. δ at 77, 66 and 4.2 K

Melt Cast Processed (MCP) Bi-2212 Bulk



400 A class elements for FCL systems

J_c(77 K, 0 T) ~ 5 kA/cm^2

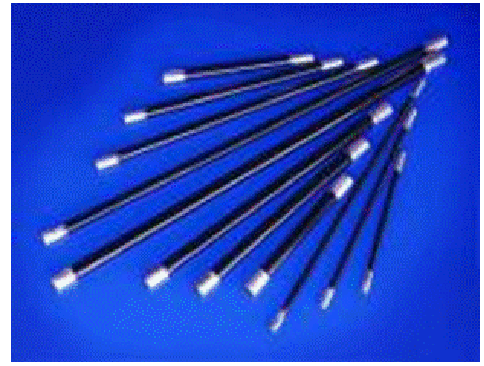
J_c(66 K = 0.7T_c) ~ 15 kA/cm^2 ~ **20%** of best J_c (77 K = 0.7T_c) in Ag/Bi2223

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

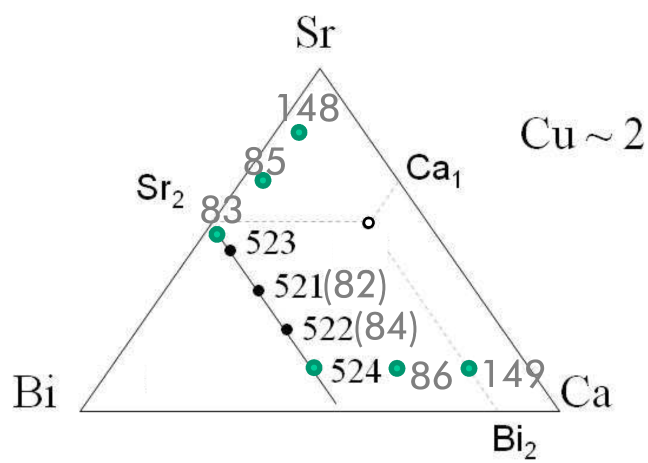
Compositions of 5 and 8 mm ∅ MCP rods

$Bi_{2.00+z}Sr_{3.00-z-x}Ca_xCu_{2.00}O_{8+\delta}$

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



- 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

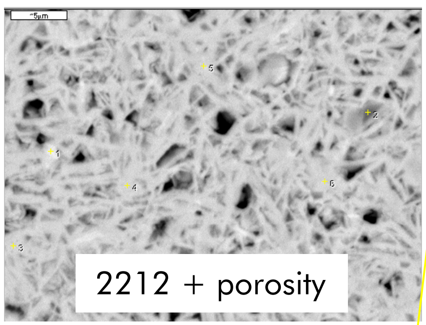


Melt Cast Processed Bi-2212. Nonequilibrium Microstructure

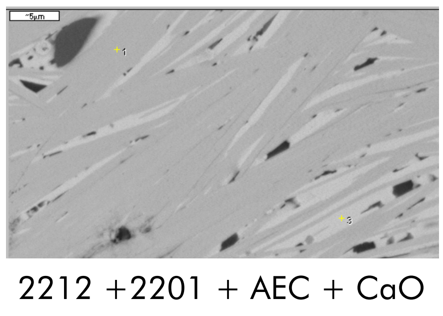
524: Single-Phase in Equilibrium

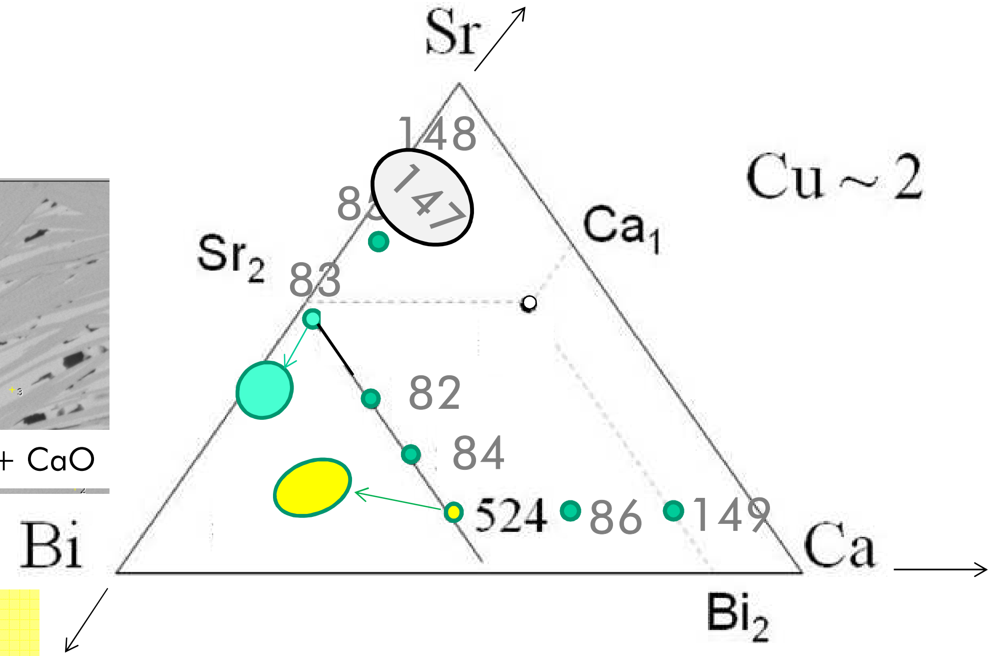
$Bi_{2.15}Sr_{1.63}Ca_{1.22}Cu_{2.00}O_{8+\delta}$

Precursor granule



MCP Bulk



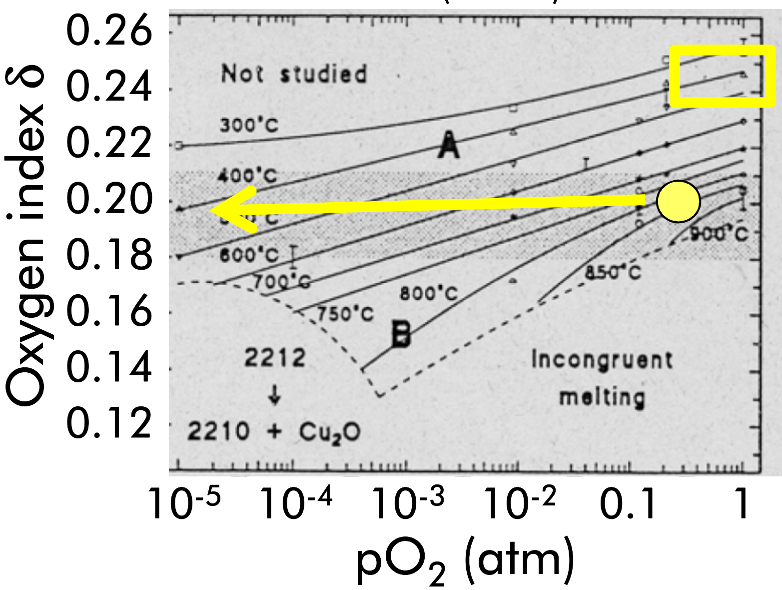


EDX +XRD of Bi-2212 phase:

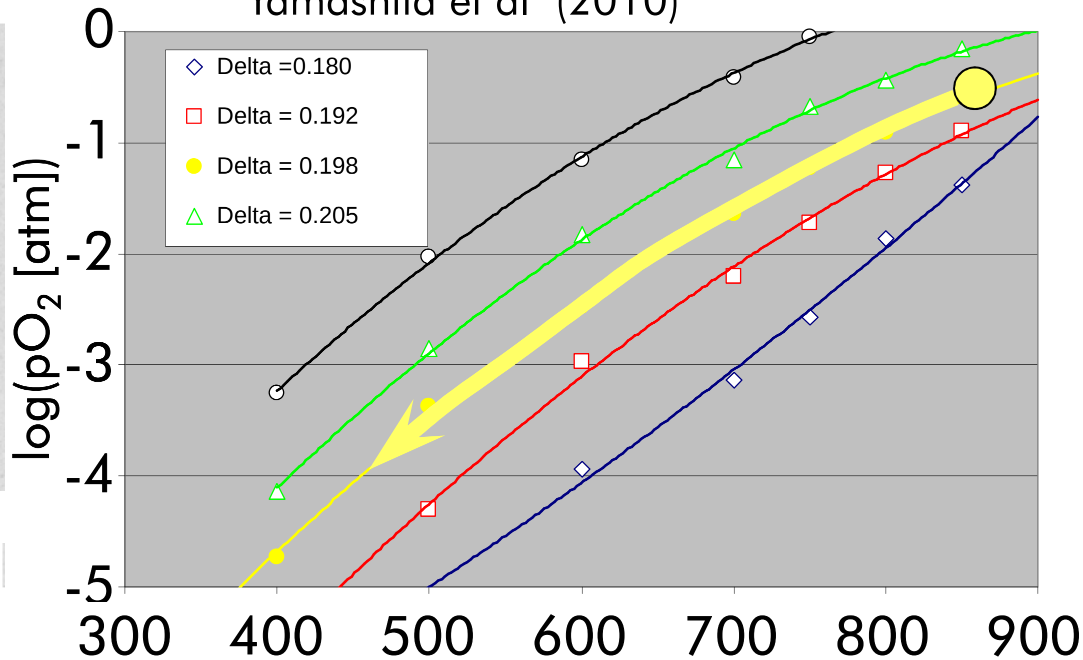
$Bi_{2.21(3)}Sr_{1.86(3)}Ca_{0.92(2)}Cu_{2.00(4)}O_{8+\delta}$

- 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

The δ-pO_2-T diagram of Schweizer et al (1993)



Approach of Glowacki et al (2003) , Yamashita et al (2010)

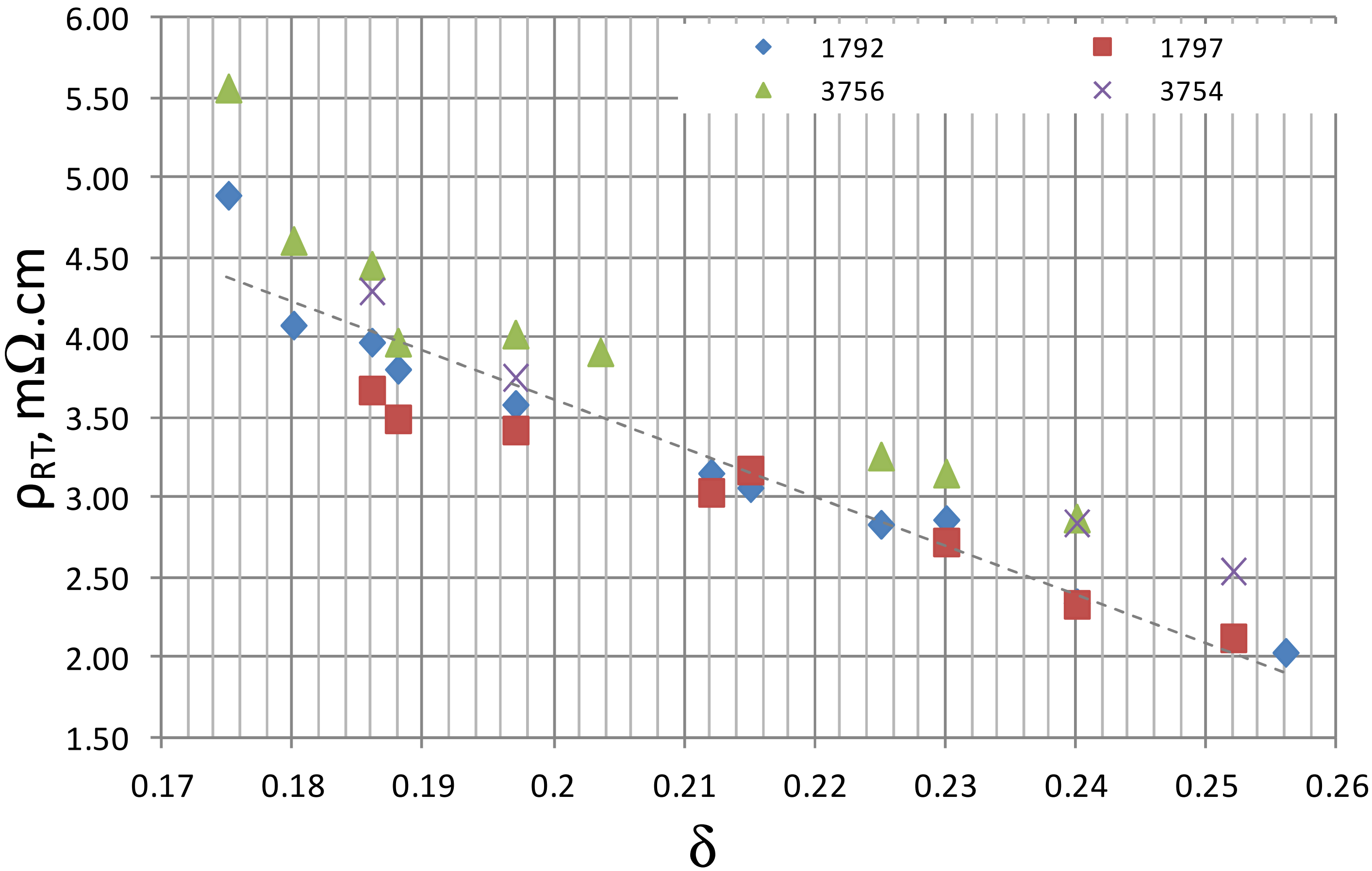


- Anneal at high T for fast equilibration;
- Quench or cool down along the pO_2-T cooling trajectory to suppress O exchange
- For $\delta > 0.230$, just annealing in air or O_2 at $350 \leq T \leq 550$°C

What is varied is the *nominal* O contents

Real δ are likely dependent on the cation composition (TBD).

Room Temperature Resistivity
5 mm ∅ rods. Composition #147

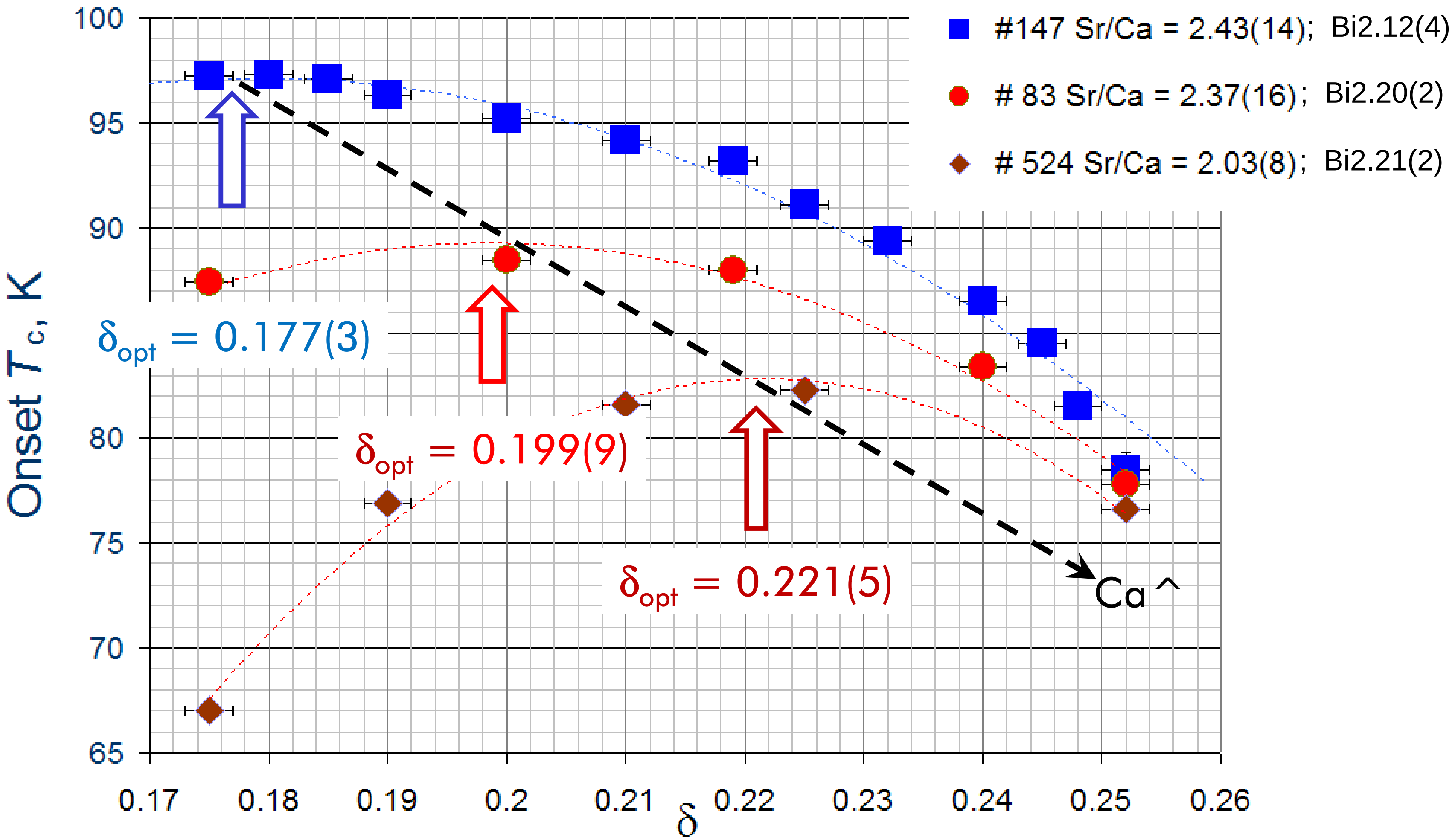


- Reversible (=> no changes in microstructure) changes in RT resistivity from ~5 to ~2 mΩ·cm suggest almost linear changes in carrier (hole) density ***p***

Proof-of-Principle Results

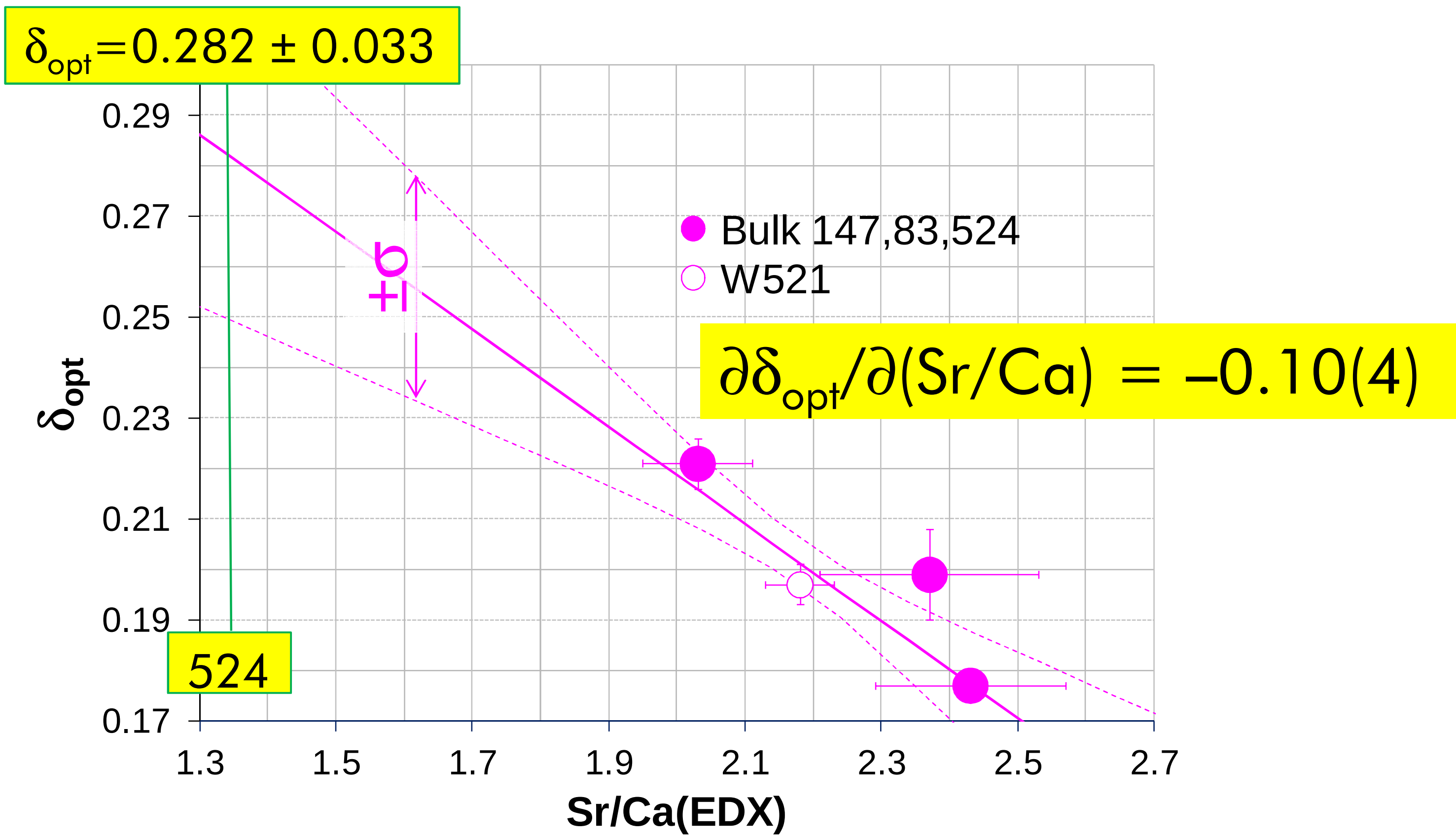
- Optimum O doping δ_{opt} [maximum T_c]
  for Sr-rich and Ca-rich Compositions
  (the doping state that optimizes Tc)

T_c decreases and δ_{opt} increases when decreasing Sr/Ca



- Optimum δ and maximum attainable T_c depend on cation compostion

The effect of cation composition on Optimum Doping

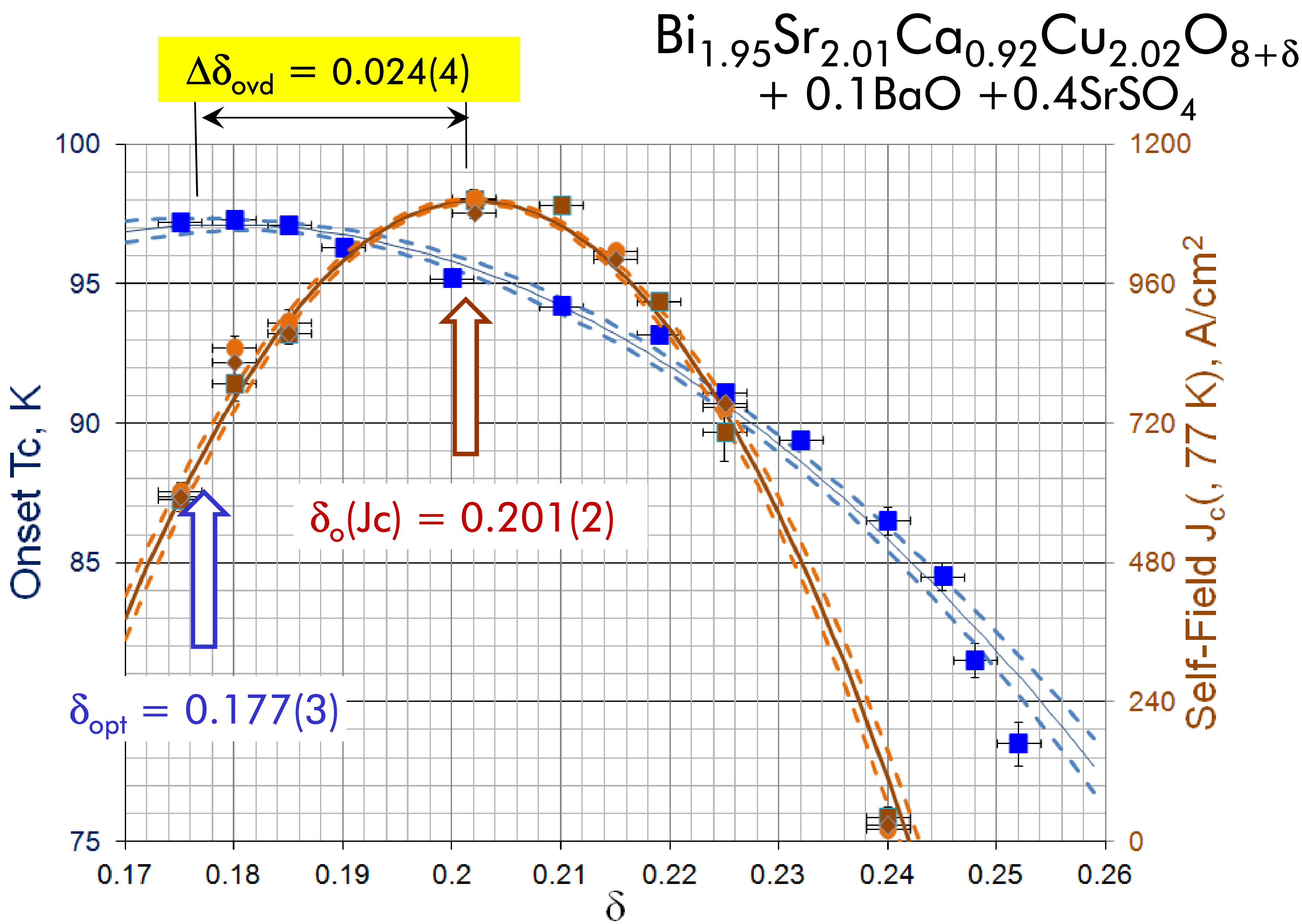


- The strong effect confirmed, but the precision is bad
- The predicted (average) optimum for real 524 composition requires annealing at 300°C and ~200 bar O_2 (log pO_2[bar] = 2.3±1.7)

Proof-of-Principle Results

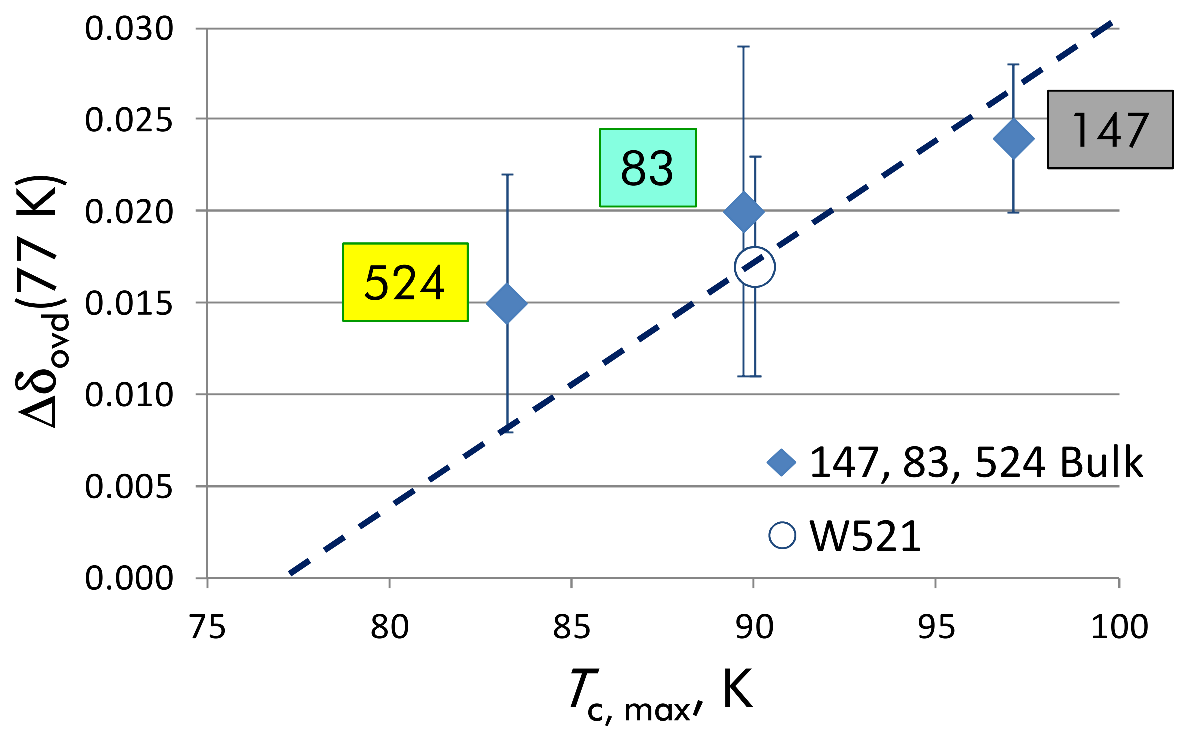
- Optimum O overdoping [maximum self-field J_c(77 K)] as function of cation composition
  (the doping state that optimizes Jc)

T_c and transport J_c(77 K)
Composition #147; Sr/Ca = 2.43(14)



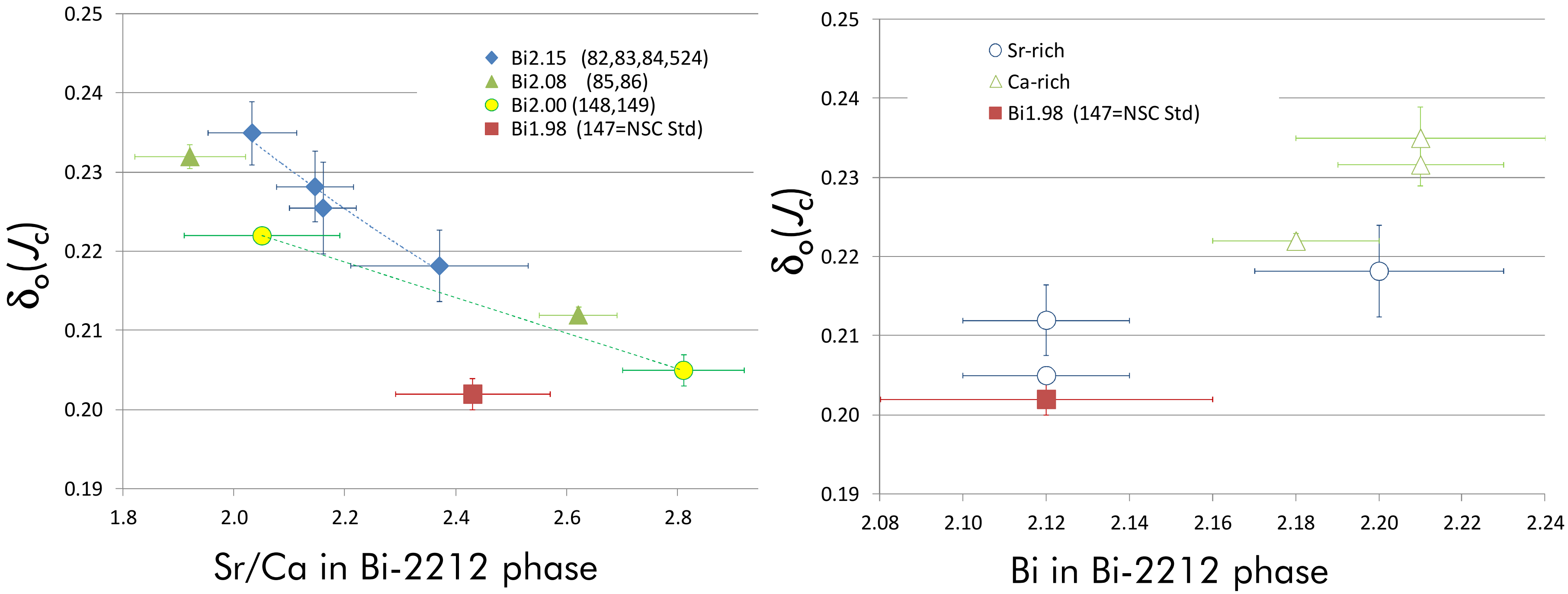
Overdoping $\Delta\delta_{ovd}$(77 K) versus $T_{c,\,max}$

$$\Delta\delta_{ovd}(77\ \mathrm{K}) = \delta_o\{J_c(77\mathrm{K})\} - \delta_{opt}$$



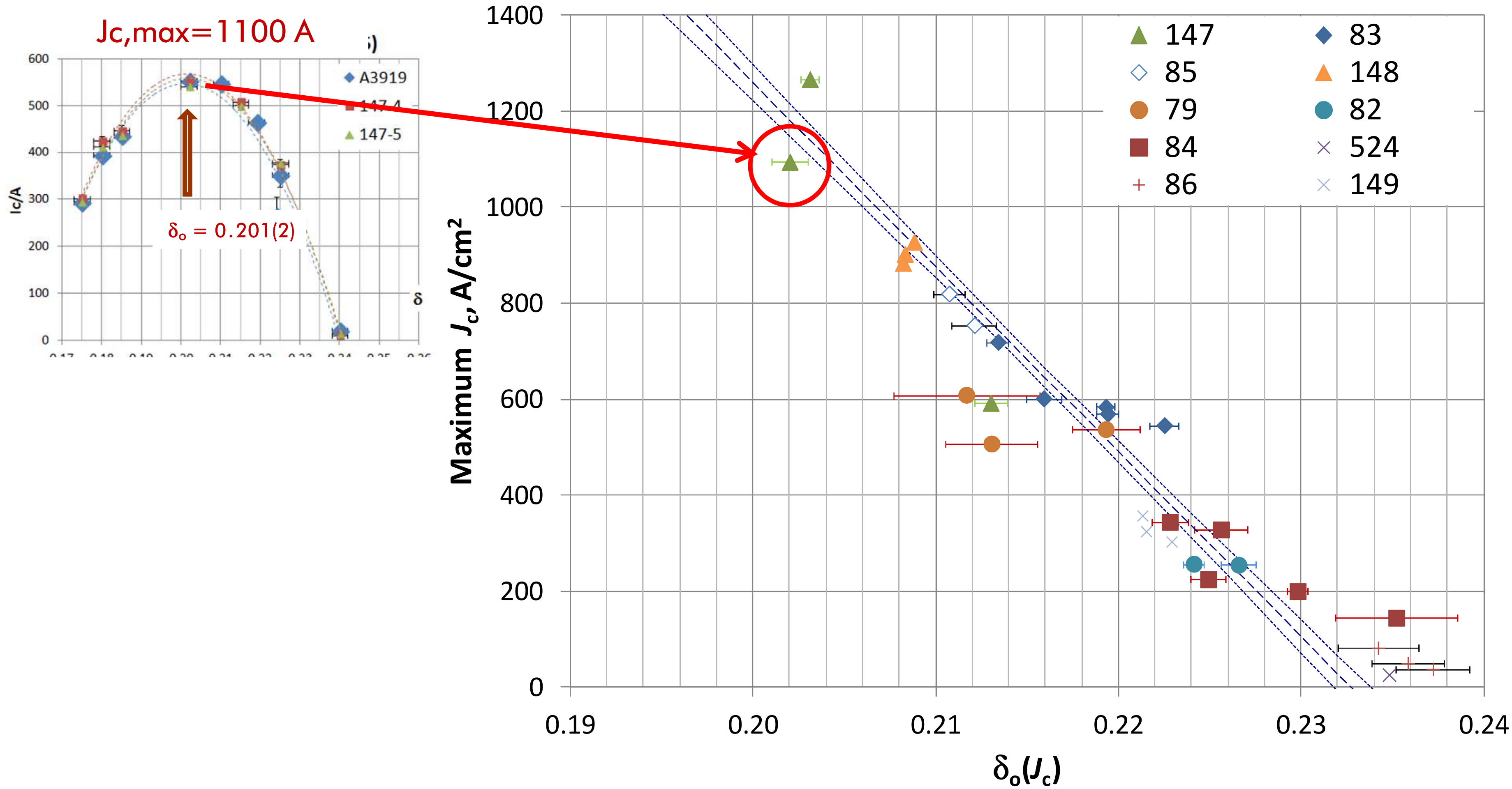
- Overdoping $\Delta\delta_{ovd}$ at 77 K is a function of $T_{c,max}$, tending to zero when $T_{c,max}$ tends to 77K

Optimum Overdoping δ_o (J_c) and Cation Composition



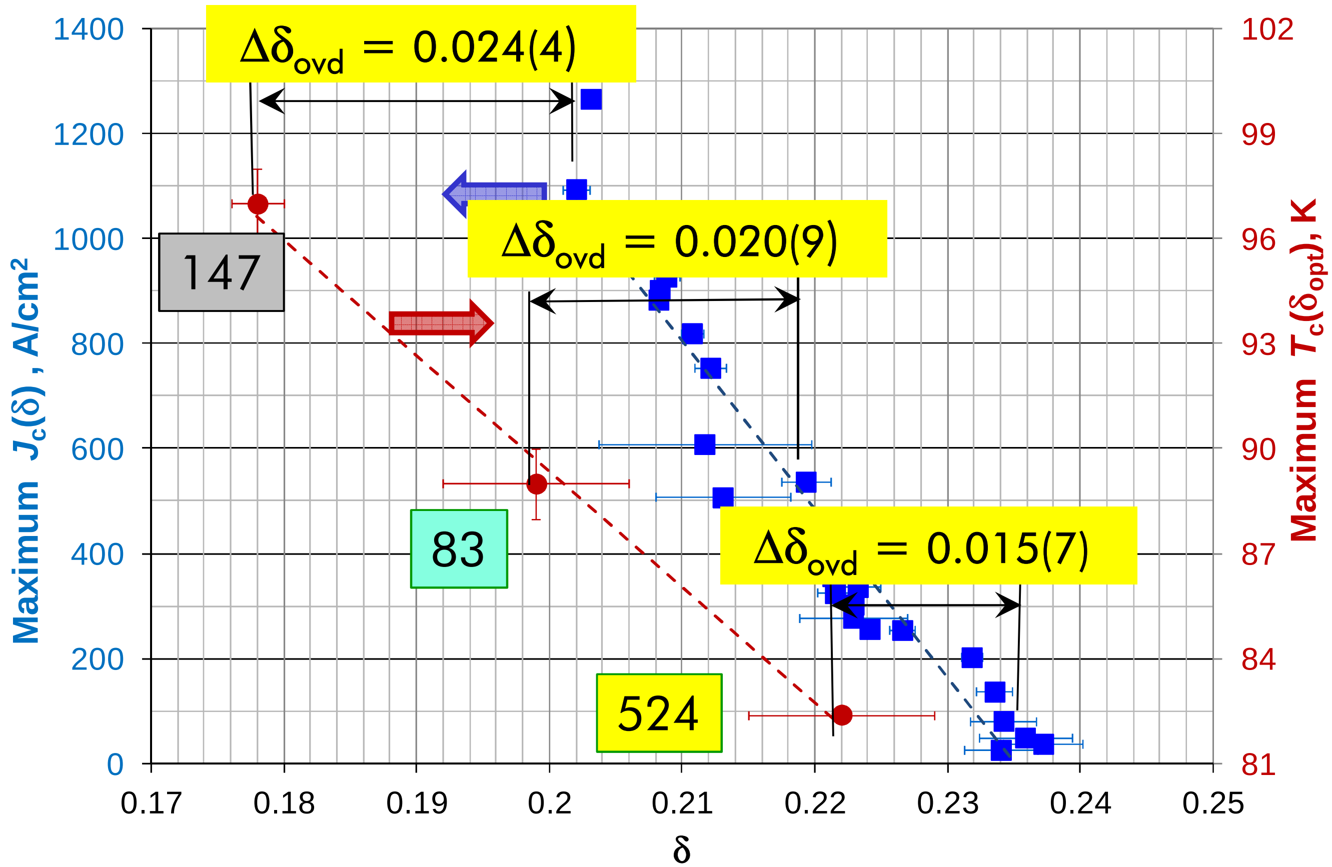
- Optimum overdoping for J_c(77 K, sf) depends on cation composition, particularly on the Sr/Ca ratio
- Large errors in $\delta_o(J_c)$ for some compositions indicate sample-to-sample irreproducibility, likely, related to different sensitivity to solidification paths, which may lead to the scatter of the Sr/Ca ratio in the Bi-2212 phase.

Correlation between maximum J_c (77 K) in 8 mm ∅ MCP rods and optimum overdoping $\delta_o(J_c)$



- The sample-to-sample scatter is almost unseen

$J_{c,max}$(77 K, sf) vs $\delta_o(J_c)$ & $T_{c,max}$ vs δ_{opt}

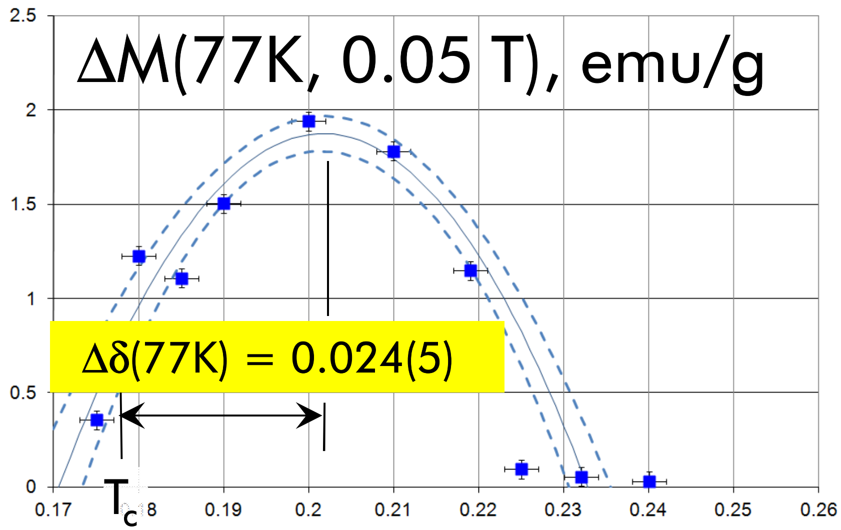


Intentional or unintentional variations in cation composition strongly affect J_c(77K) vs. δ most likely because of variation in T_c vs. δ

Proof-of-Principle Results

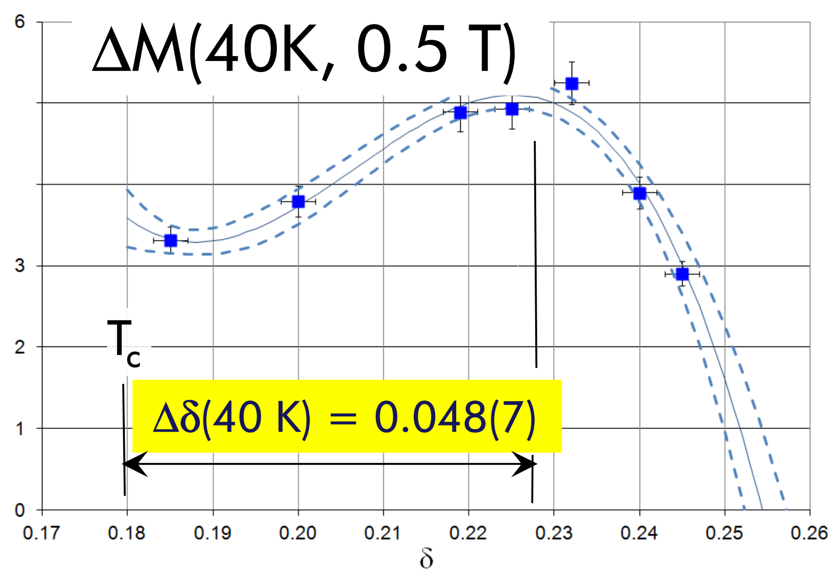
- Optimum O overdoping [maximum $J_c(T, H)$] for Sr-rich and Ca-rich Compositions

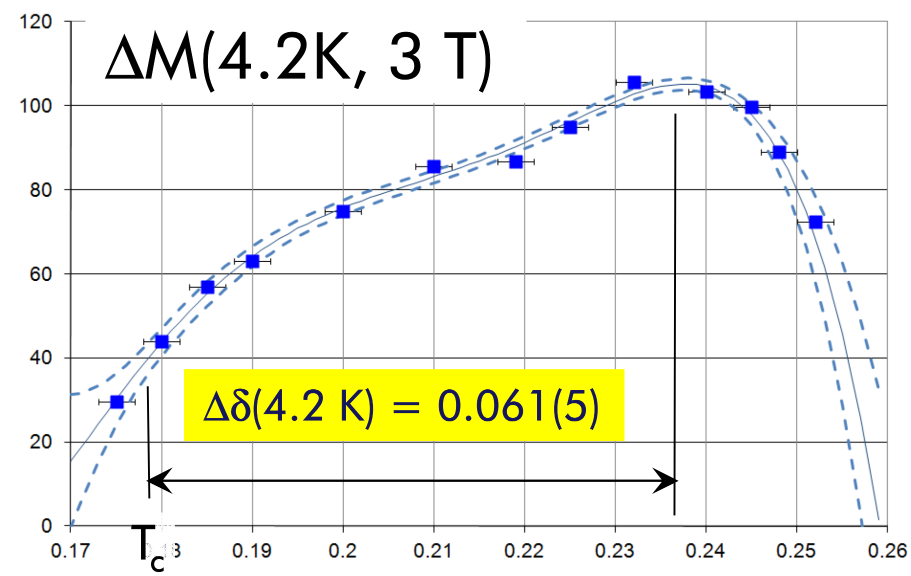
Nexans Bulk Standard #147
Magnetization Data at 4.2 to 77 K



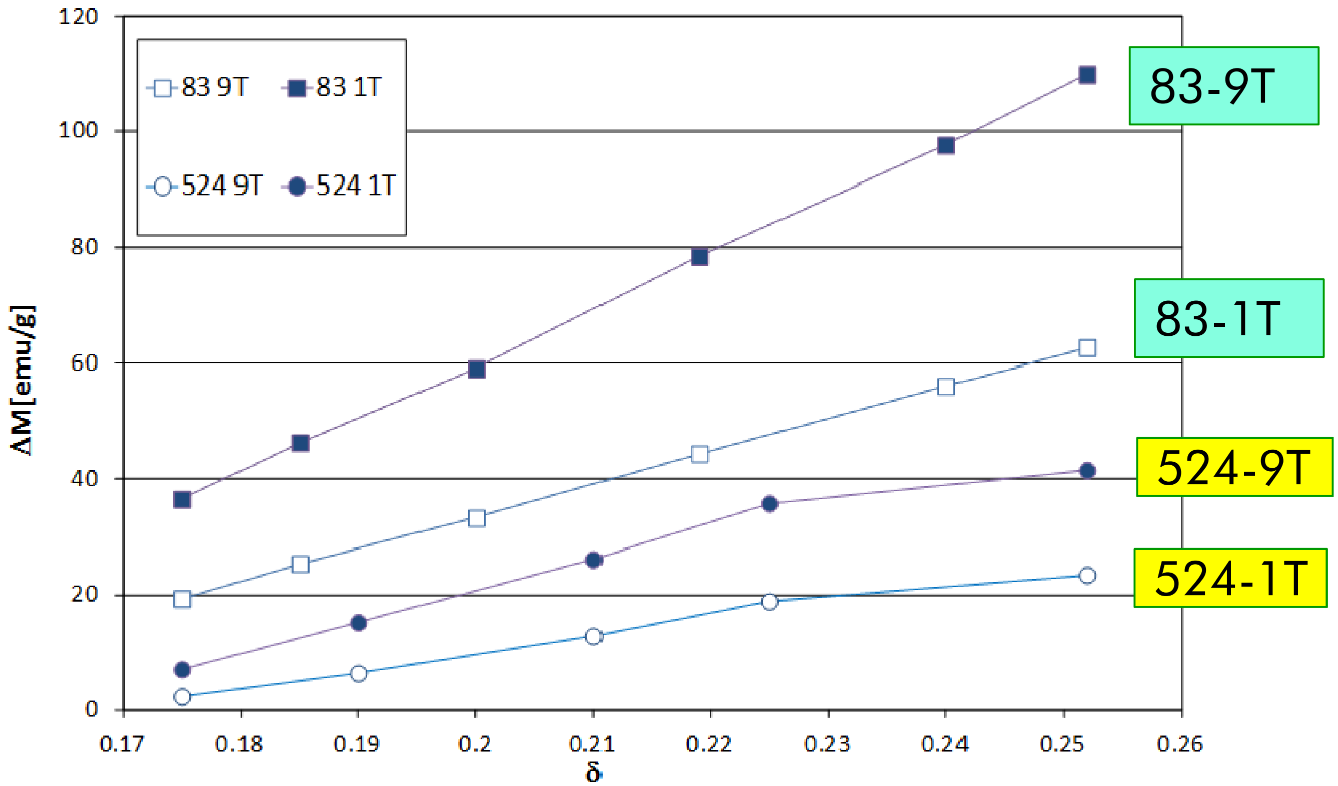
Δ*M*(*H*, *T*) data for ∅5 mm rods:

- **$\delta_o(J_c)$ is strongly *T* dependent**
- **Δδ increases with decreasing *T***



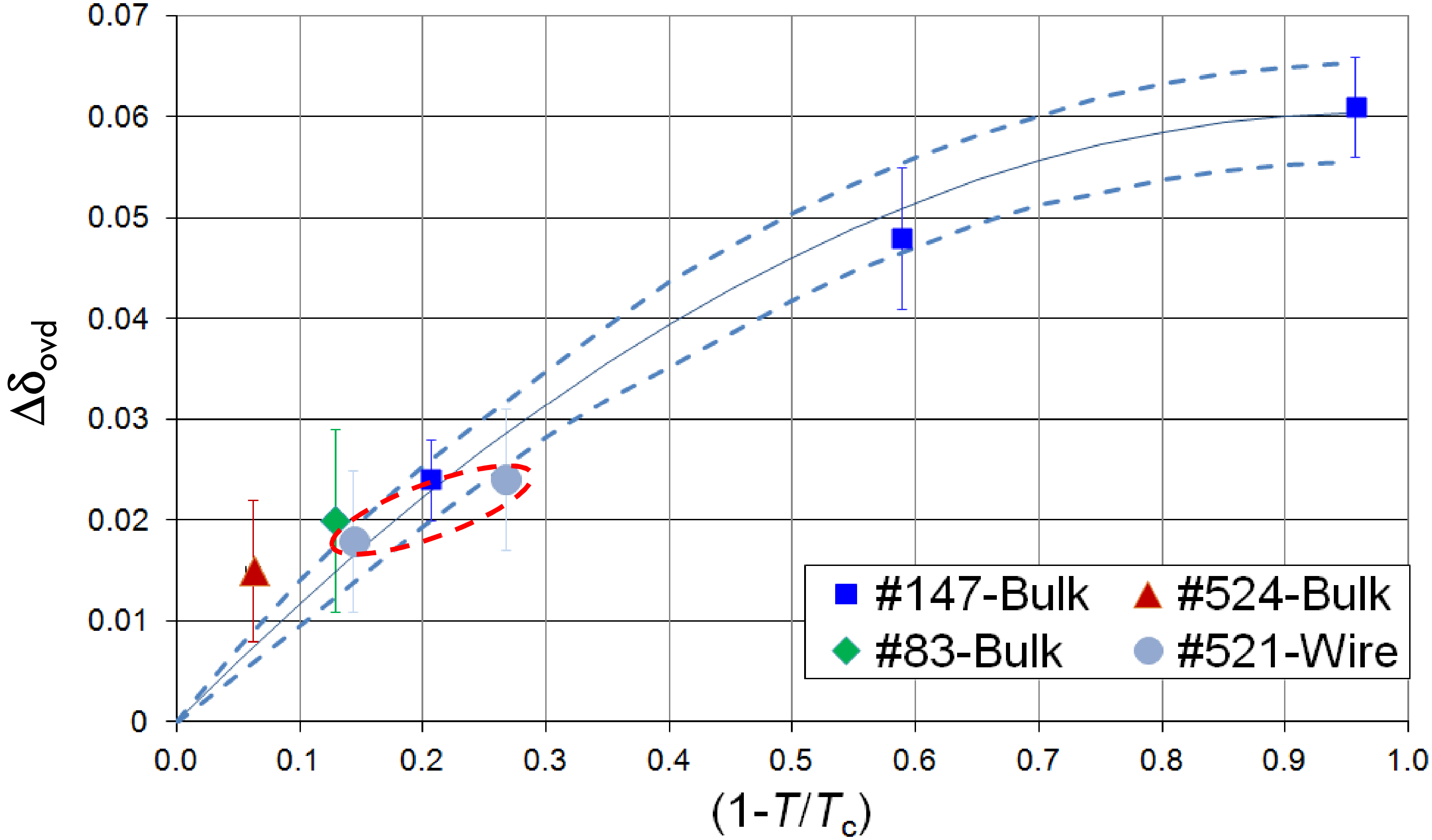


Bulk samples #83 [Sr/Ca =2.37(16)] and #524 [Sr/Ca = 2.03(8)]



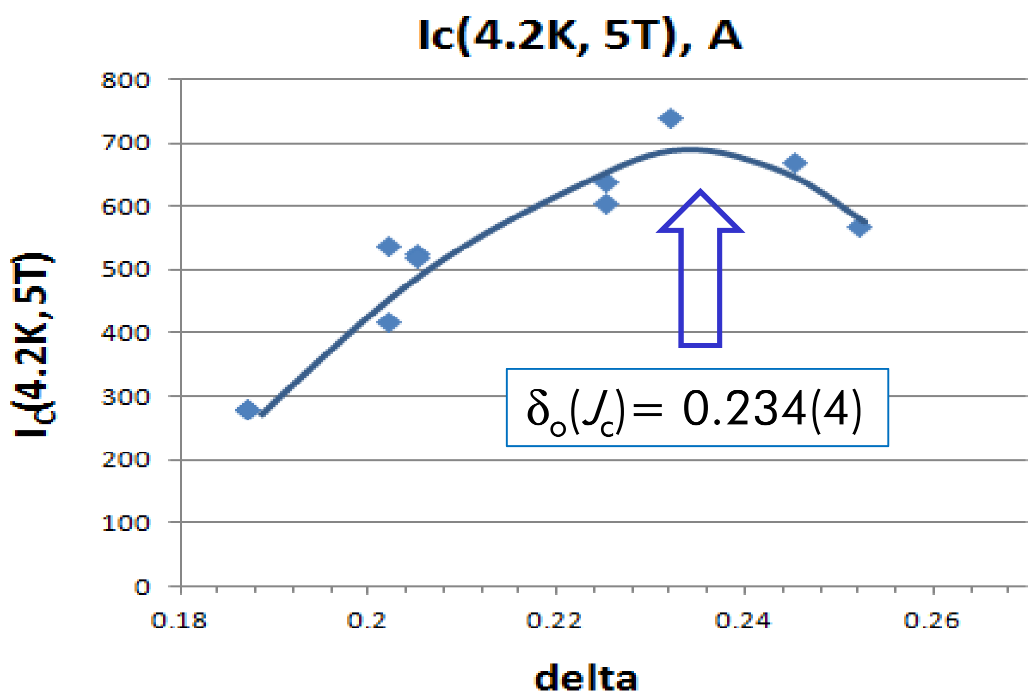
- No optimum is reached at 4.2 K: $\delta_o \geq 0.252$

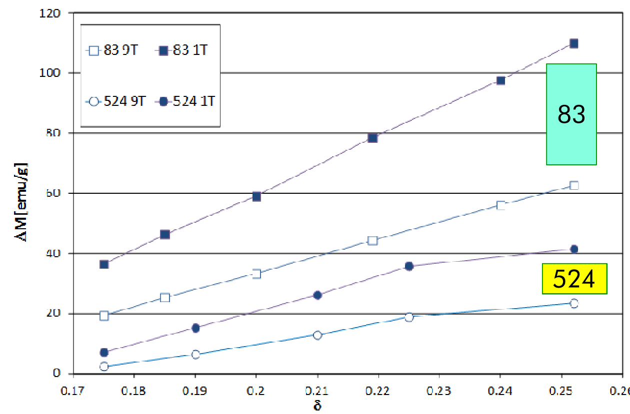
Overdoping [T - $\Delta\delta_o$] Map.



- Temperature dependence of overdoping is somewhat similar to the temperature dependence of the energy gap $\Delta(T,\delta)$

I_c(4.2 K) in OST wire with 521 composition. Sr/Ca(EDX) = 2.20(5)





- Composition of Bi-2212 phase in MCP #83 with **Sr/Ca = 2.37(16)** & #524 with **Sr/Ca = 2.03(8)** bracket the composition of Bi-2212 phase in W521 wires with **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 δ 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 $p > p_{opt..}$

  => $J_c \approx U_0\,\xi$ (ξ = coherence length weakly dependent on p) peaks at $\delta_o(J_c) > \delta_{opt}$

  J L Tallon et al (2000), *Physica C*, **338** 9-17

  T Matsushita et al (2006) SuST, **19**, 200-205

- 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 δ_o (J_c)

  H Claus et al (2007) PRB **76,** 014529

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

- 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?

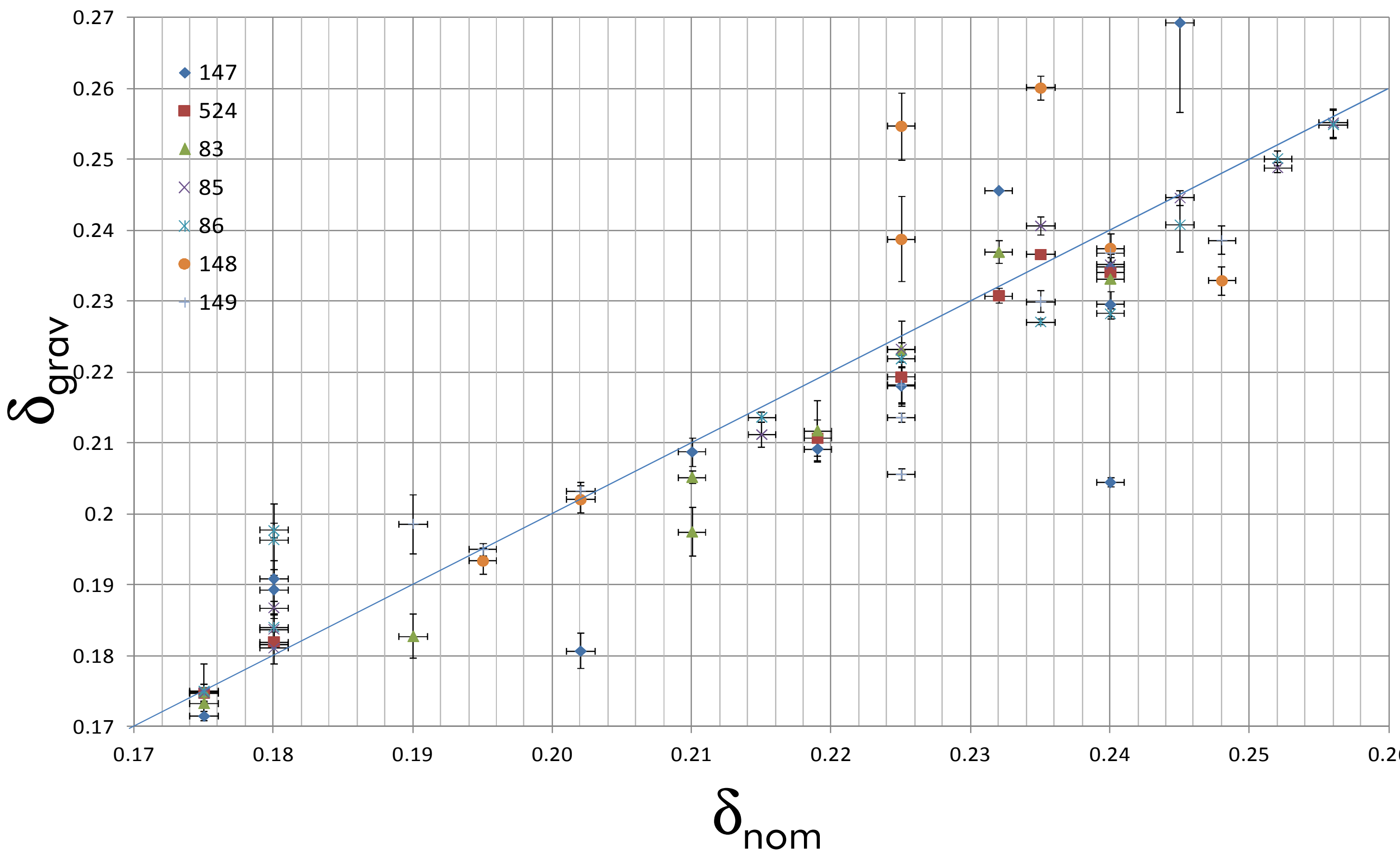
- No answer, but
- Bi-2212 conductors need optimization of their O doping state, which opens an opportunity to **independently** optimize the **microstructure** and basic parameters dependent on the **O doping**:
  - The empirically optimized composition 521 ($Bi_{2.17}Sr_{1.94}Ca_{0.89}Cu_{2.00}O_{8+\delta}$) is the best for partial melt processing (PMP) round wires in 100% O_2.
  - Sr richer compositions may need post-annealing to have smaller δ
  - Ca richer compositions may need post-annealing to have larger δ
- 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 Tc, and the effect seems **to be very strong**
  - Further work [Tc vs. δ] is necessary to better quantify the dependence
- I_c optimization needs **significant overdoping**, which is temperature dependent.
  - Further work [M(H, T) vs. δ] is necessary to quantify the temperature dependence and relate it to the basic properties of Bi-2212
- Oxygen contents δ_{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 δ_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

δ from gravimetry versus nominal



- Relative changes in δ are largely consistent with the phase diagram used. The slope corresponds well to presence of ~10% second phases in the samples

Why optimizing J_c requires Overdoping?

- Condensation energy density $U_0 = B_c^2/2\mu$ peaks at $\delta > \delta_{opt}$

  Pinning force $F_p \sim B_c^2/2\mu$

  $U_0 \sim N(\delta,T) \times \Delta(\delta,T)$

  the density of states $N(\delta,T) \sim a\delta + b$

  the energy gap $\Delta(\delta,T) \sim T_c \sim [1-(\delta - \delta_{opt})^2]$ at least for $\delta > \delta_{opt}$

  As $a > 0$, optimum of $(a\delta + b)\,[1-(\delta - \delta_{opt})^2]$ is at

  $$\delta_o\,(J_c) > \delta_{opt}$$

  J L Tallon et al (2000), *Physica C*, 338 9-17

- Transparency of GBs may depend on the doping state

  The doping state of a GB in general differs from that of the bulk

  O overdoping may affect the transparency of GBs to supercurrent

  Texture (dominant type of GBs) may affect $\delta_o\,(J_c)$

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