5th International Conference on Superconductivity and Magnetism (ICSM 2016)

April 26, 2016, @Fethiye, Turkey

Potentials of HTS Superconducting Materials for Extensive Applications

Jun-ichi Shimoyama

Aoyama Gakuin University, Sagamihara, Japan

OUTLINE

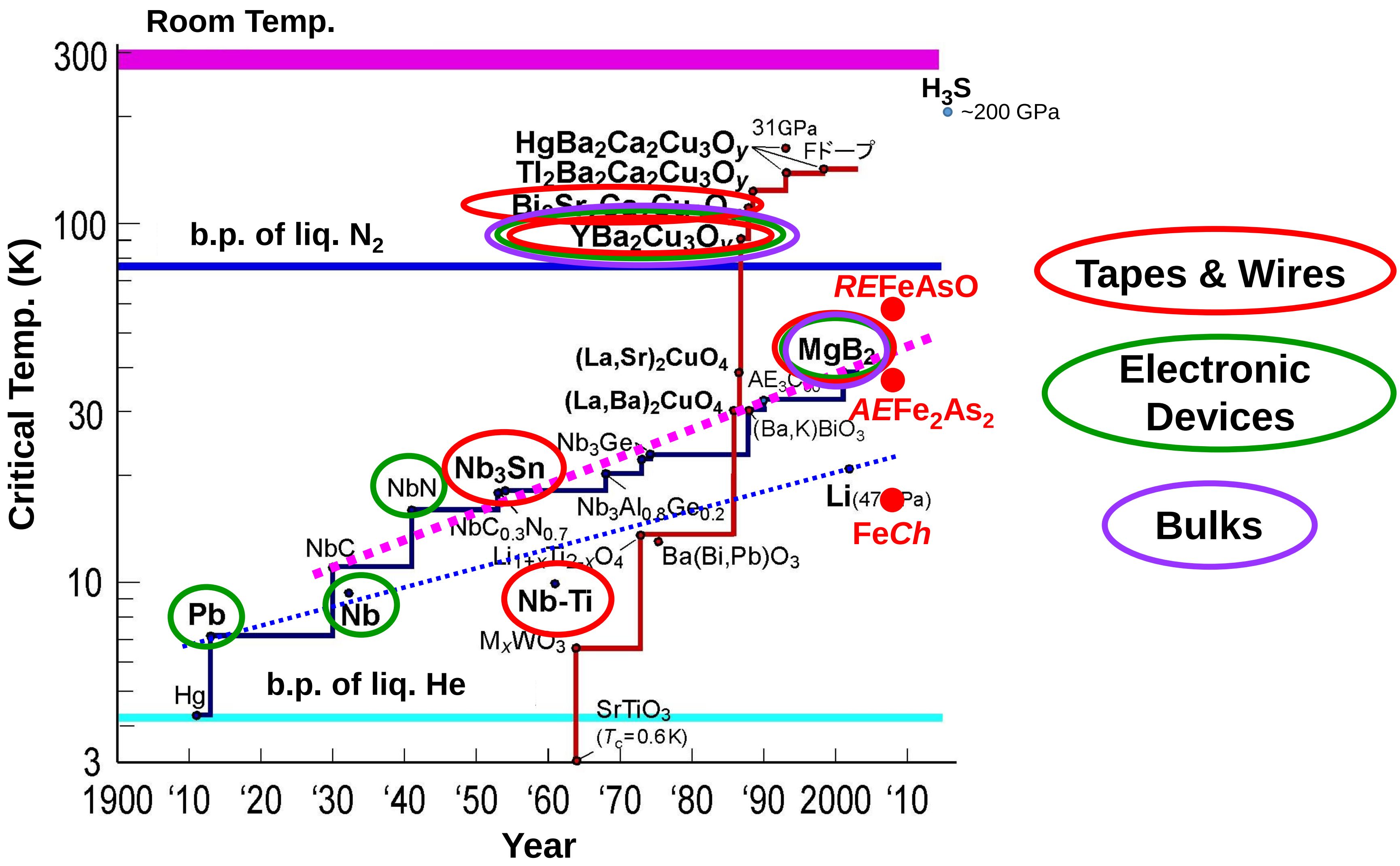
1. **What are needed for superconducting materials?**

2. **Current HTS materials partly supported by basic studies**
    - **BSCCO Tape**
    - **RE123 Coated Conductors**
    - **RE123 Melt-solidified Bulks**

3. **Potentials of new candidate materials; iron-based superconductors**

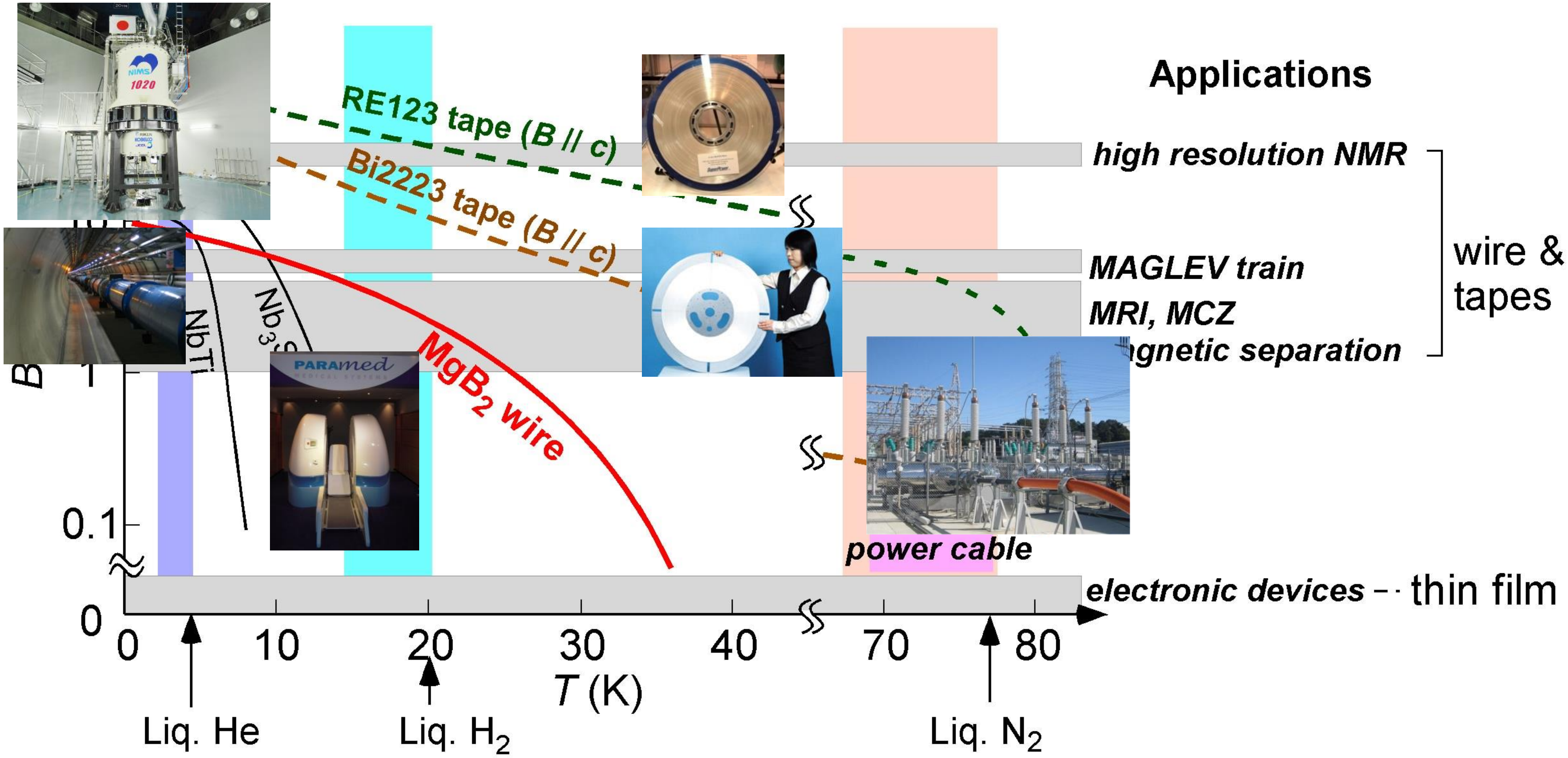
4. **Recent my anxiety**

History of superconducting materials with changes of record-high T_c



Applicable conditions of superconducting materials

J_E > 100 A/mm^2 for long length conductors



Required J_E depends on applications.

eg. MAGLEV train

by Central Japan Railway

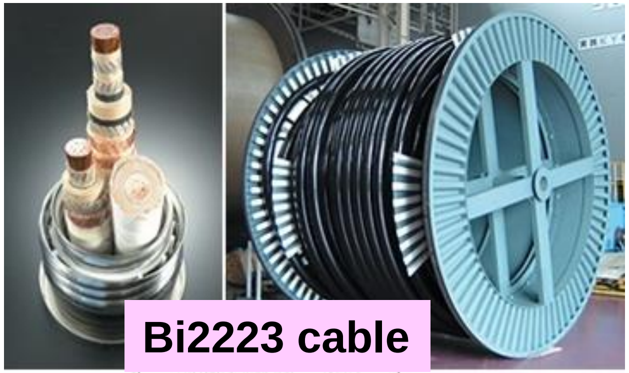
Superconducting magnet using Nb-Ti

$J_E > 400\ \mathrm{A/mm^2}$ (4.2 K, ~5 T)

+ persistent current circuit

to obtain large force for levitation and running with light magnet system

eg.: transmission cable



by Sumitomo Electric Industries

HTS high-T_c cable

$J_E > 100\ \mathrm{A/mm^2}$ (77 K, ~0.1 T)

Generic Concept of Metallic Superconductors with High J_c

Strong pinning centers with moderate density in **strong superconducting matrix**

numerous studies for introduction of pinning sites

atomic defects

dislocations

fine non-superconducting Precipitates (α-Ti in Nb-Ti)

grain boundaries
(Nb_3Sn, MgB_2)

irradiation damages

numerous studies for achieving high T_c and high H_{c2}

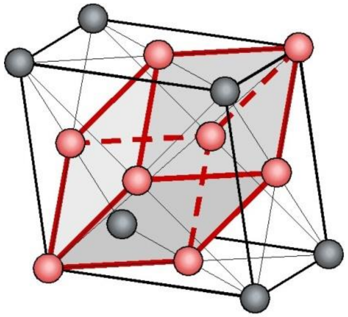
choosing best composition (alloy)

controlling chemical composition to the ideal (=integral) ratio (inter-metallic compounds)

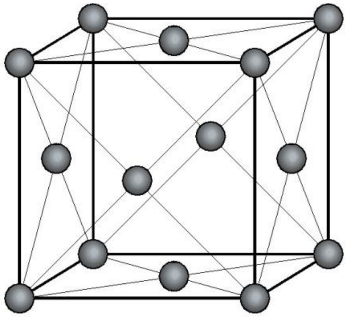
doping to improve microstructure, H_{c2} and/or workability

Crystal Structures of Representative Metallic Superconductors

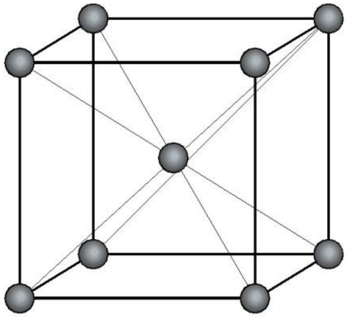
simple, highly symmetric, with a few constituent elements



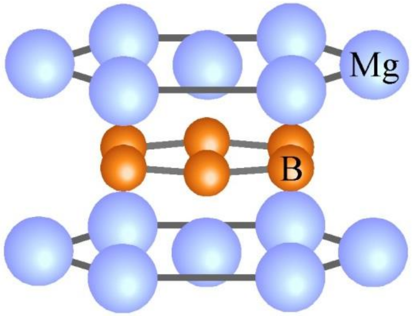
Hg
rhombohedral
A10



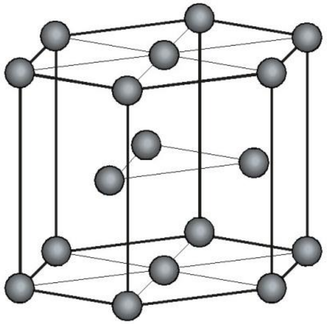
Pb
fcc
A1



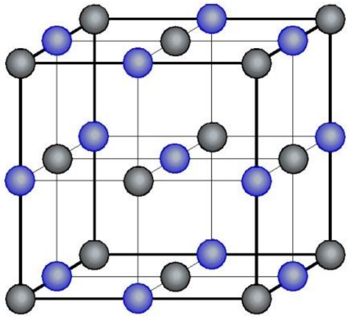
Nb, V, Nb-Ti
bcc
A2



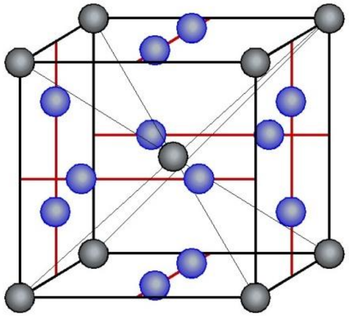
MgB_2
AlB_2-type



Tc, Bi-Pb
hcp
A3



NbC, NbN
rock salt
B1



Nb_3Sn, V_3Ga

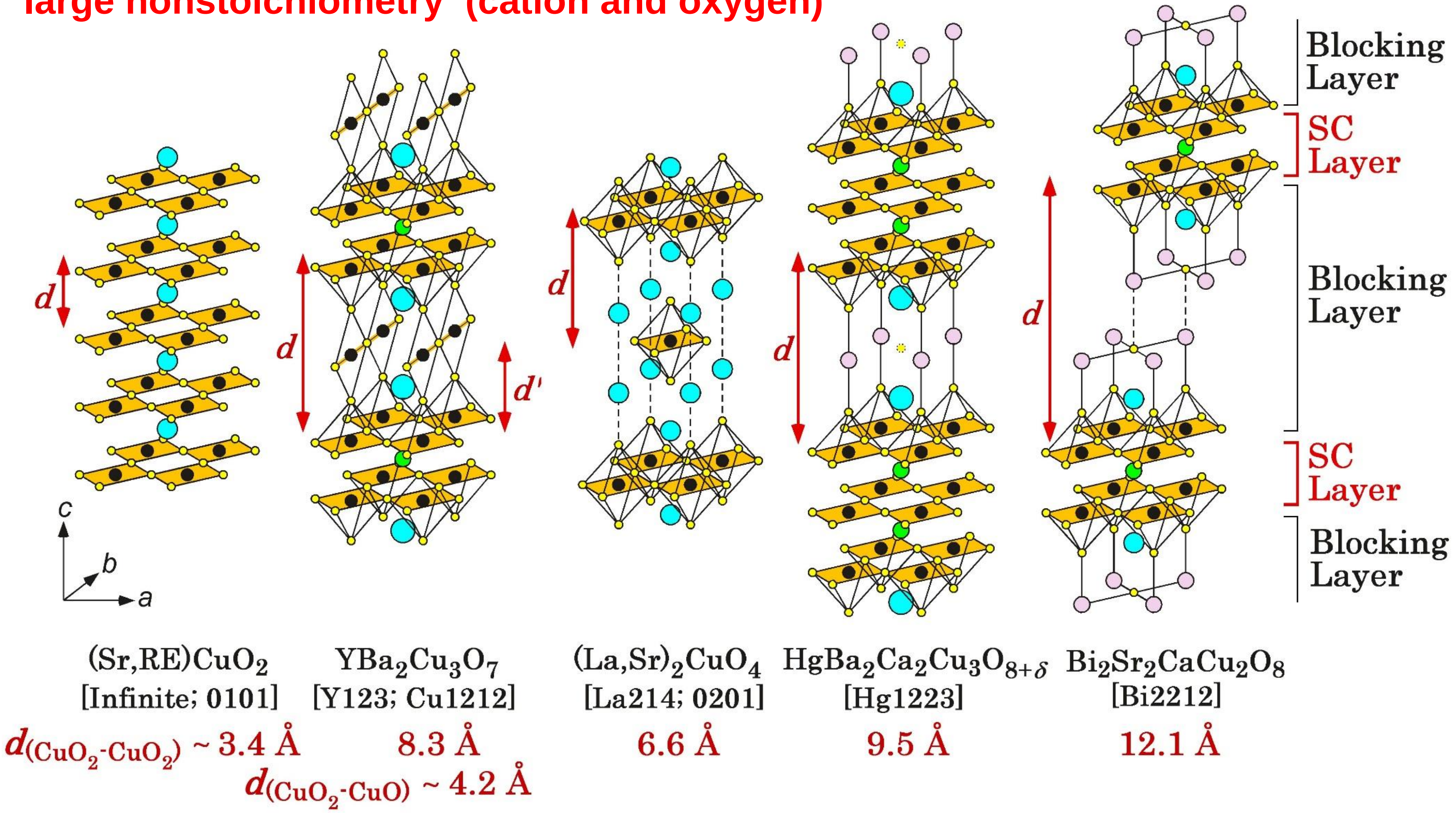
A15

Characteristic Crystal Structure of Cuprate SC

layered cuprates (containing various sites of cations and anions)

in which most of superconducting carriers spread along the CuO_2 plane

complex, highly anisotropic with d_{x2-y2} symmetry, many elements, large nonstoichiometry (cation and oxygen)

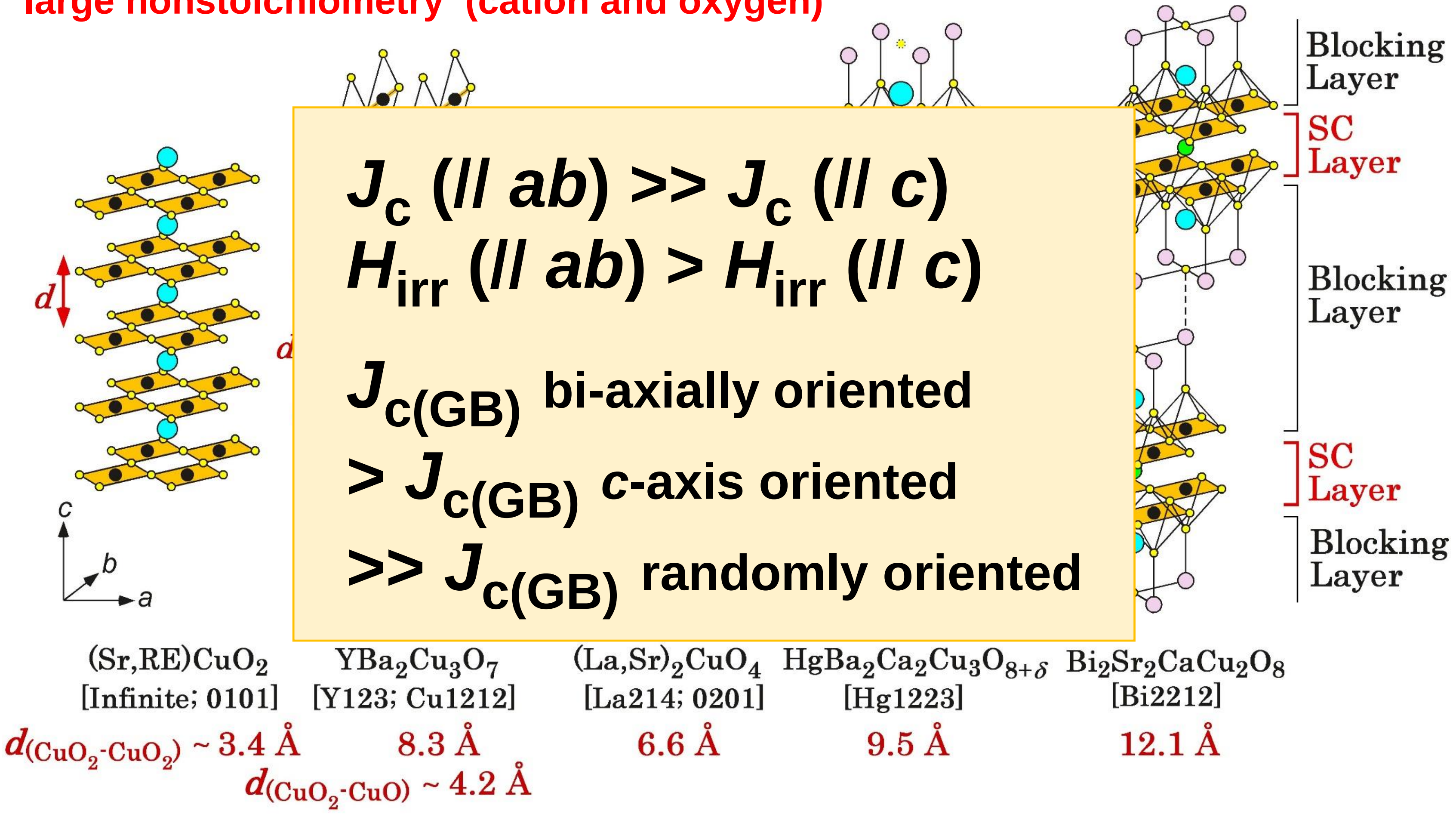


Characteristic Crystal Structure of Cuprate SC

layered cuprates (containing various sites of cations and anions)

in which most of superconducting carriers spread along the CuO_2 plane

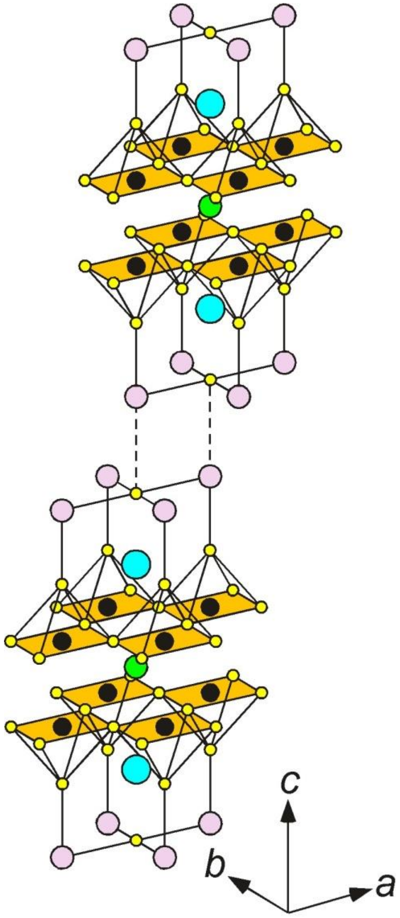
complex, highly anisotropic with $d_{x^2-y^2}$ symmetry, many elements, large nonstoichiometry (cation and oxygen)



J_c (// *ab*) >> J_c (// *c*)
H_{irr} (// *ab*) > H_{irr} (// *c*)

$J_{c(GB)}$ bi-axially oriented
> $J_{c(GB)}$ *c*-axis oriented
>> $J_{c(GB)}$ randomly oriented

Is this a crystal structure of actually existing compound?

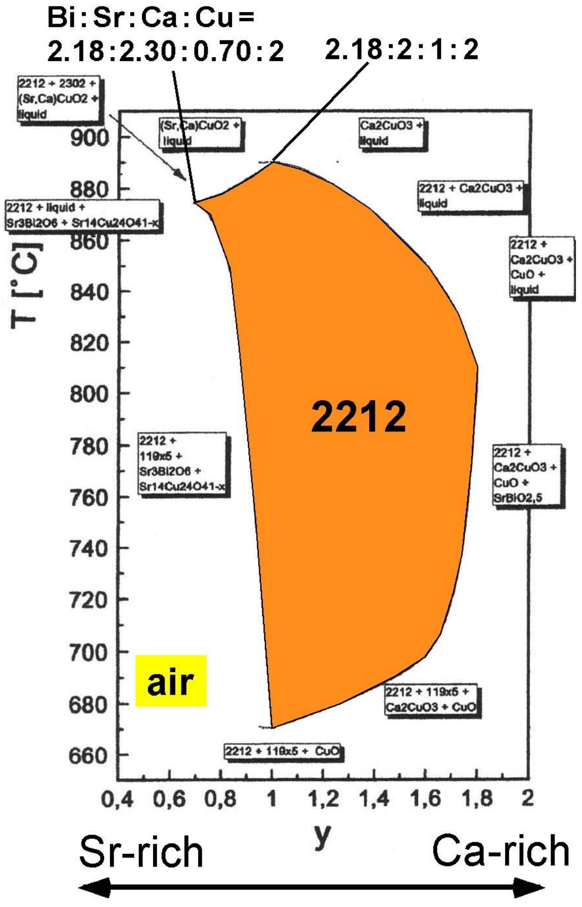


$Bi_2Sr_2CaCu_2O_8$
[Bi2212]

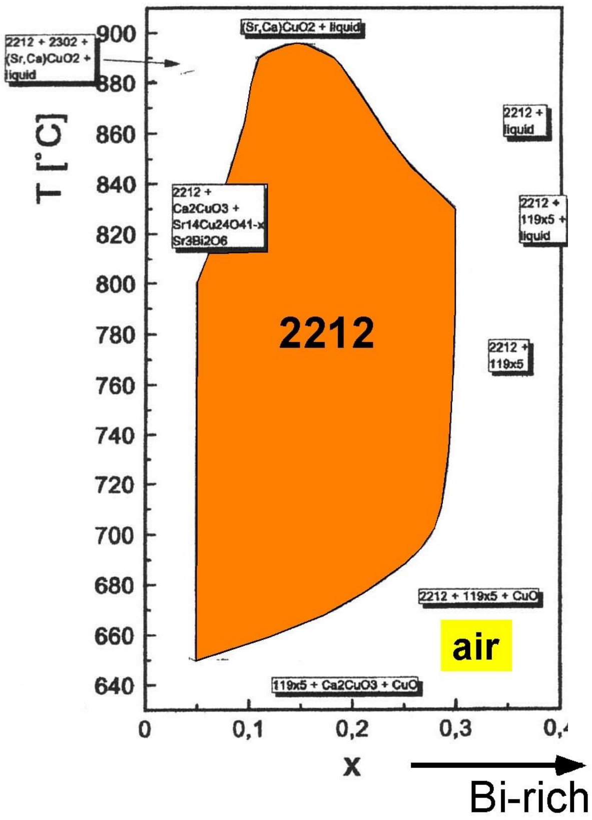
Large Cation Nonstoichiometry in Bi2212

Bi-rich & Sr-poor composition is stable ! --- Bi and Ca substitute for Sr

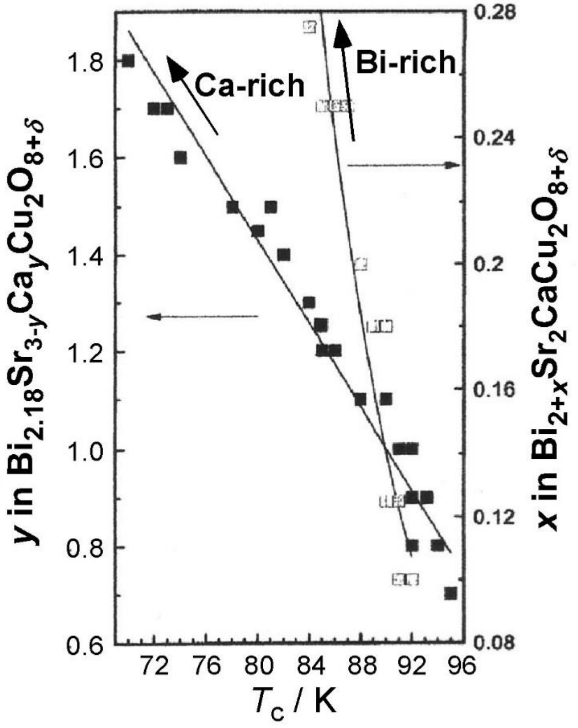
Majewski, *Supercond Sci. Technol*. 10 (1997) 453.



$Bi_{2.18}Sr_{3-y}Ca_yCu_2O_{8+\delta}$



$Bi_{2+x}Sr_2CaCu_2O_{8+\delta}$



Generic Concept of Cuprate Superconductors with High J_c

Strong pinning centers with moderate density in **strong superconducting matrix**

numerous studies for introduction of pinning sites to improve J_c-B characteristics and H_{irr}

- atomic defects
- twins
- dislocations
- fine non-superconducting precipitates
- locally weak superconducting regions by element substitutions or nonstoichiometric cation composition
- irradiation damages

numerous studies for improving grain alignment

J_c (77 K, s.f.)

c-axis alignment --- < 10^5 Acm^{-2}
bi-axial alignment --- > 10^6 Acm^{-2}

decreasing anisotropy

improving conductivity at blocking layer by carrier overdoping and/or cation substitutions

Few studies on precise control of nonstoichiometric cation compositions (unintentional)

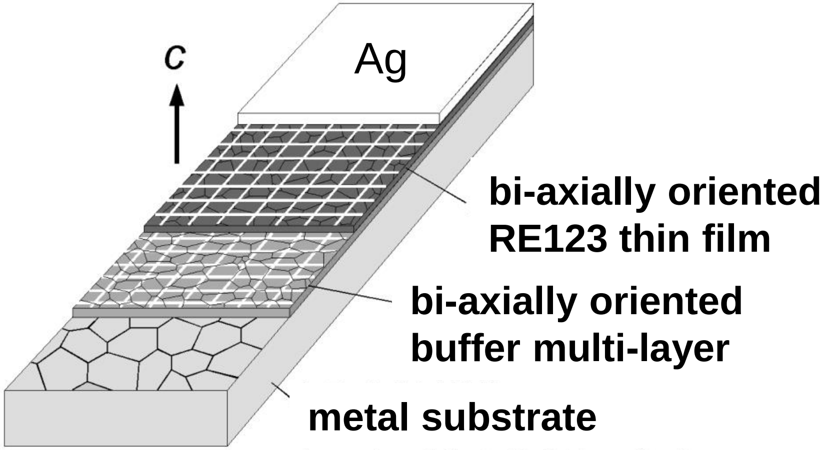
homogeneous chemical composition without site exchange between cations

Quite Difficult !

Structure of RE123 and Bi(Pb)2223 tapes

Improvement of properties
= enlargement of application fields and decreasing cost

RE123 tape (Coated Conductor)



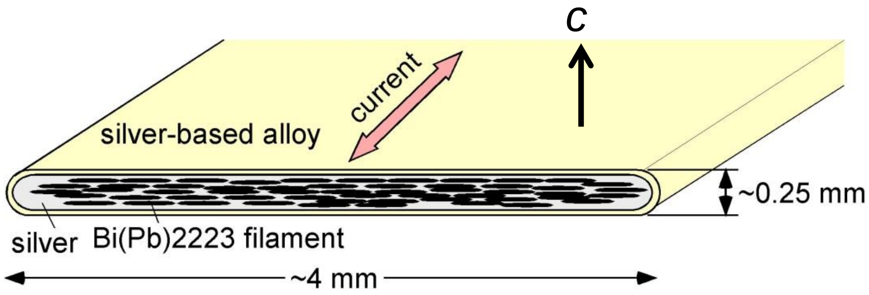
J_c ~2 x 10^6 A /cm^2 at 77 K

Thin and mono superconducting layer

Ratio of RE123 layer : 1~3%

Increases in thickness and J_c of SC layer

Bi(Pb)2223 tape (Ag-sheathed)



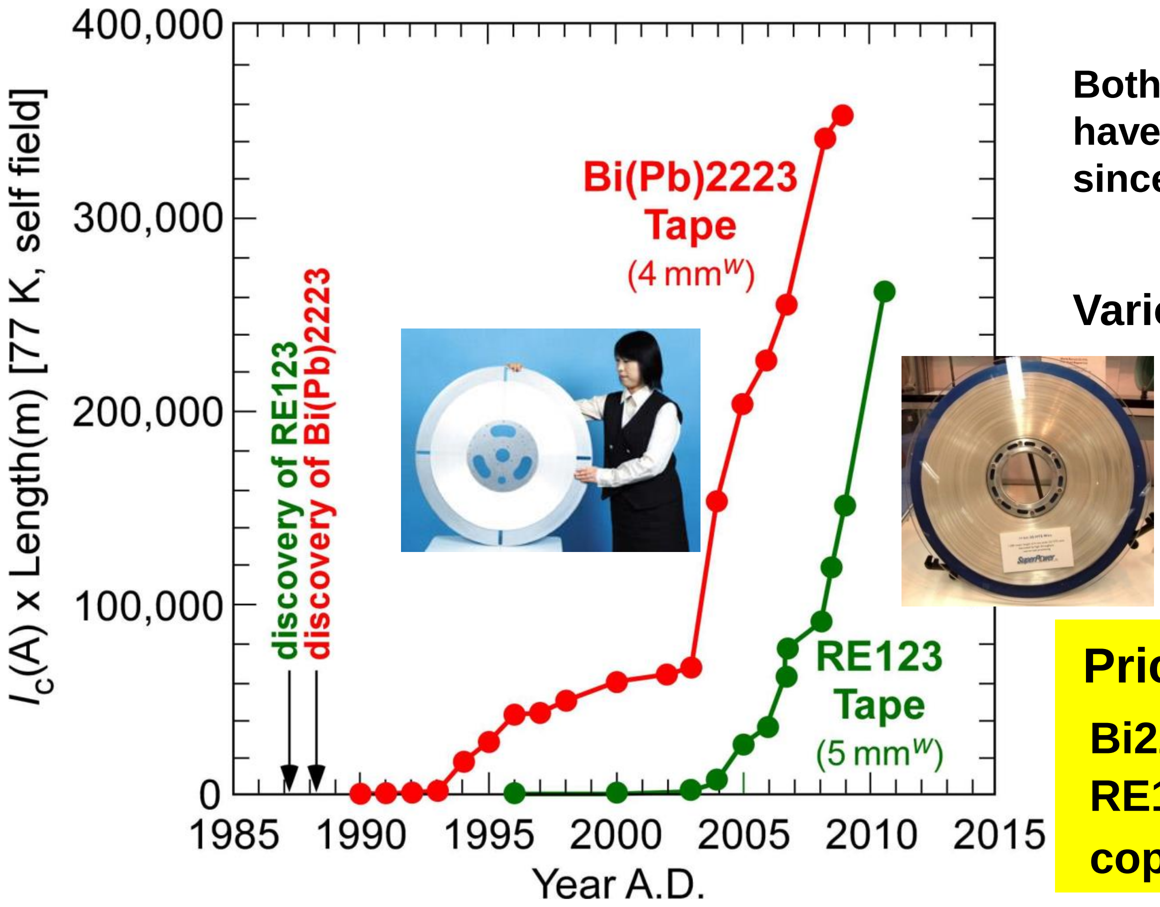
J_c ~6 x 10^4 A /cm^2 at 77 K

Multi-filament (55~121 filaments)

Ratio of Bi(Pb)2223 filament: ~40%

Increases in J_c of SC layer and mechanical strength

History of I_c x L values of high-T_c superconducting tapes



Both properties and productivity have been dramatically improved since 2004.

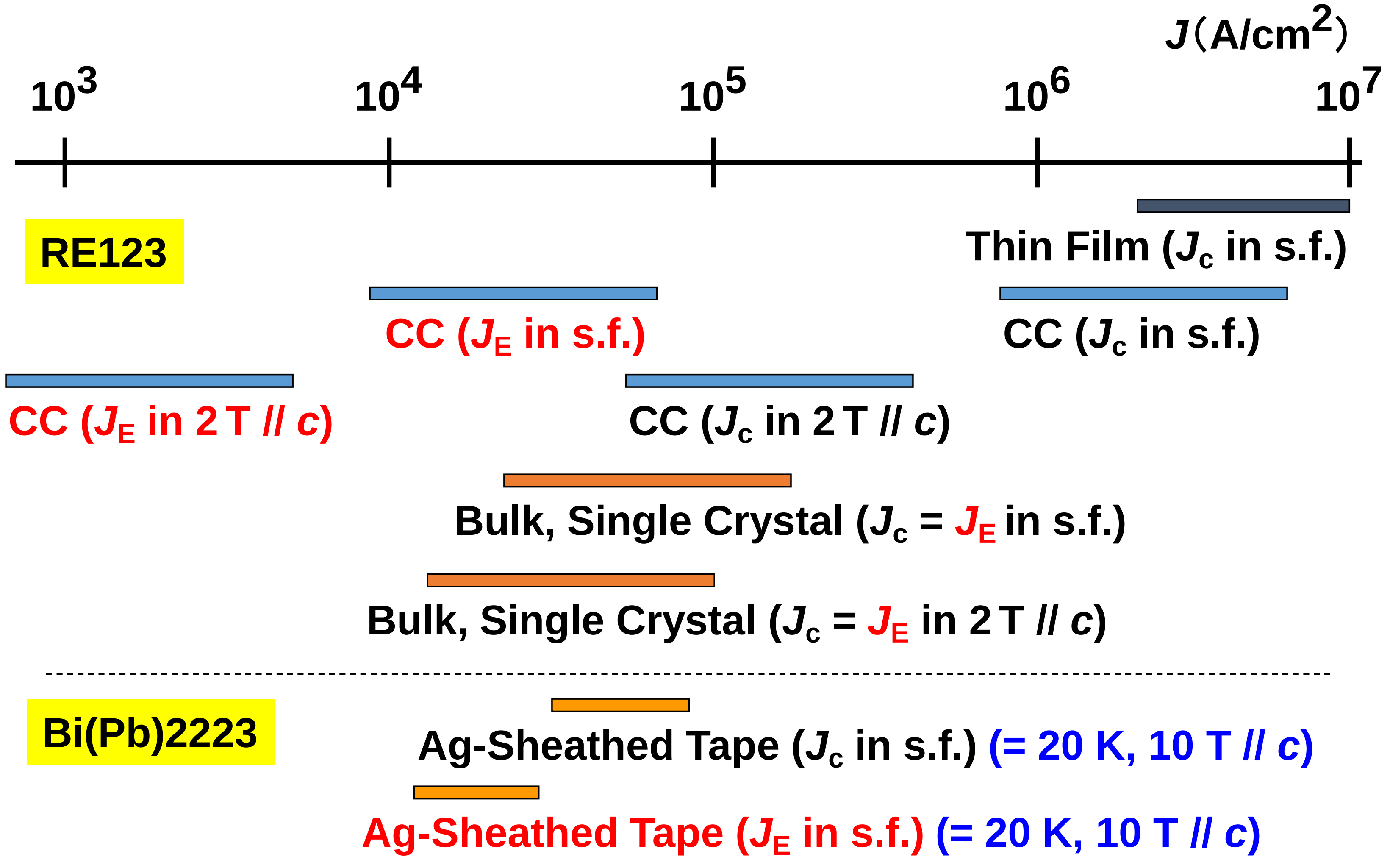
⬇

Various practical applications

Price of conductors (2013)	
Bi2223	**¥10~15 / Am**
RE123	**< ¥50 / Am**
copper	**¥~5 / Am**

At present, I_c x L index is becoming less important.
The yield rate of long length tapes is more essential.

Critical Current Properties of HTS Materials (at 77 K)



RE123

Thin Film (J_c in s.f.)

CC (J_E in s.f.)

CC (J_c in s.f.)

CC (J_E in 2 T // c)

CC (J_c in 2 T // c)

Bulk, Single Crystal (J_c = J_E in s.f.)

Bulk, Single Crystal (J_c = J_E in 2 T // c)

Bi(Pb)2223

Ag-Sheathed Tape (J_c in s.f.) (= 20 K, 10 T // c)

Ag-Sheathed Tape (J_E in s.f.) (= 20 K, 10 T // c)

These values are much lower than the pair breaking current density >10^8 Acm^{-2}.

Bi2223 Tapes (BSCCO)

Recent BSCCO Tapes: Updated Type HT-NX

DI-BSCCO

Specifications of DI-BSCCO

New release!

	Type H	Type HT-SS	Type HT-CA	Type HT-NX
Average Width	4.3+/-0.2mm	4.5+/-0.1mm	4.5+/-0.1mm	4.5+/-0.2mm
Average Thickness	0.23+/-0.01mm	0.29+/-0.02mm	0.34+/-0.02mm	0.31+/-0.03mm
Reinforcement tape	—	Stainless steel (0.02mm^t)	Copper alloy (0.05mm^t)	Nickel alloy (0.03mm^t)
Ic (77K, Self Field)	170A, 180A, 190A, 200A			
Critical Wire Tension * (RT)	80N **	230N **	280N **	410N **
Critical Tensile Stress * (77K)	130 MPa **	270 MPa **	250 MPa **	400 MPa **
Critical Tensile Strain * (77K)	0.2% **	0.4% **	0.3% **	0.5% **
Critical Double Bending Diameter * (RT)	80mm **	60mm **	60mm **	40mm **

* 95% Ic retention, * * Typical value

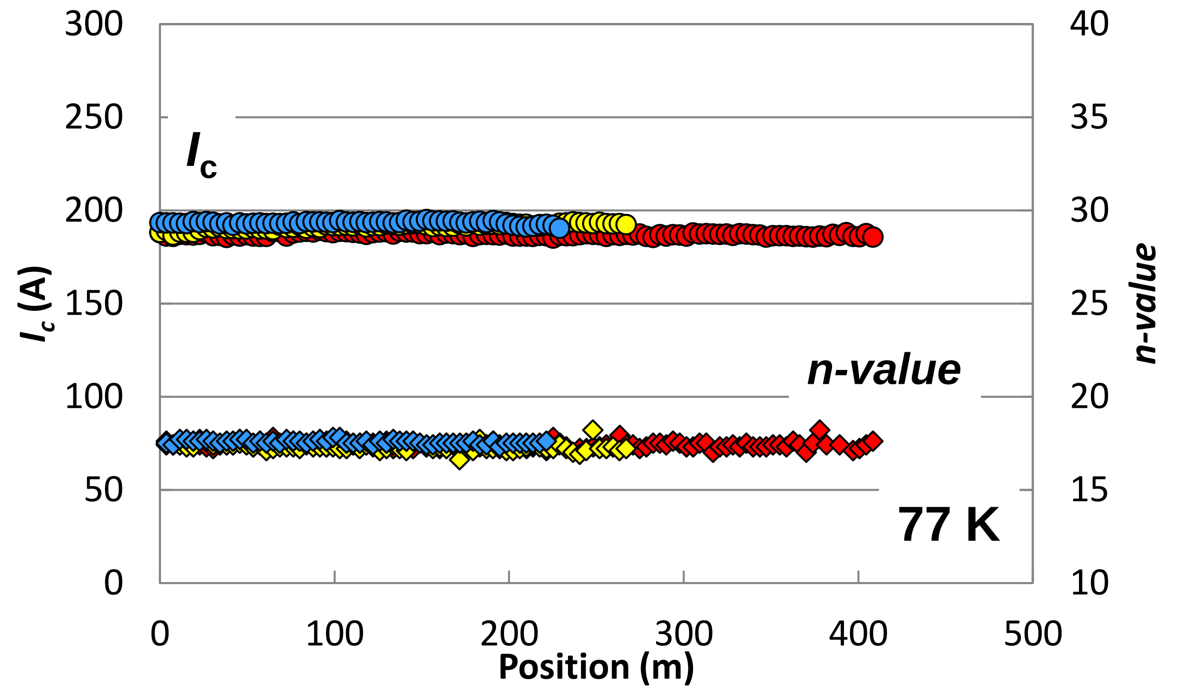
- ✓ The tensile strength of Type HT-NX is 1.5 times higher than those of Type HT-SS and Type HT-CA
- ✓ Type HT-NX has released since April, 2015
- ✓ Max. 200 m Type HT-NX is available unit length for shipment now

SUMITOMO ELECTRIC

Recent BSCCO Tapes: Updated Type HT-NX

DI-BSCCO

I_c and *n-value* distributions



- ✓ I_c and *n-value* are very uniform over the whole wire length
- ✓ The present available Type HT-NX is 200 m
- ✓ More than 500 m Type HT-NX is being experimentally produced now
  ➔ Next target unit length: Max. >500 m (in near future)

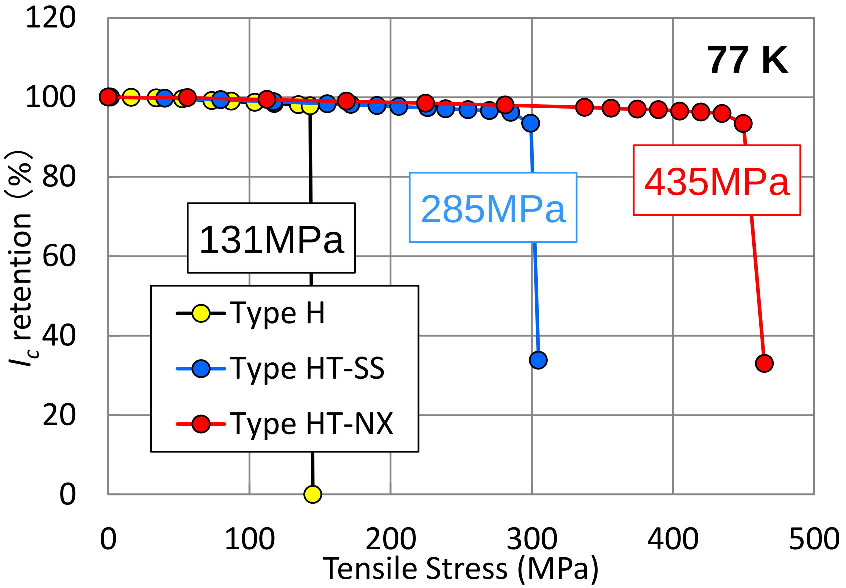
SUMITOMO ELECTRIC

Recent BSCCO Tapes: Updated Type HT-NX

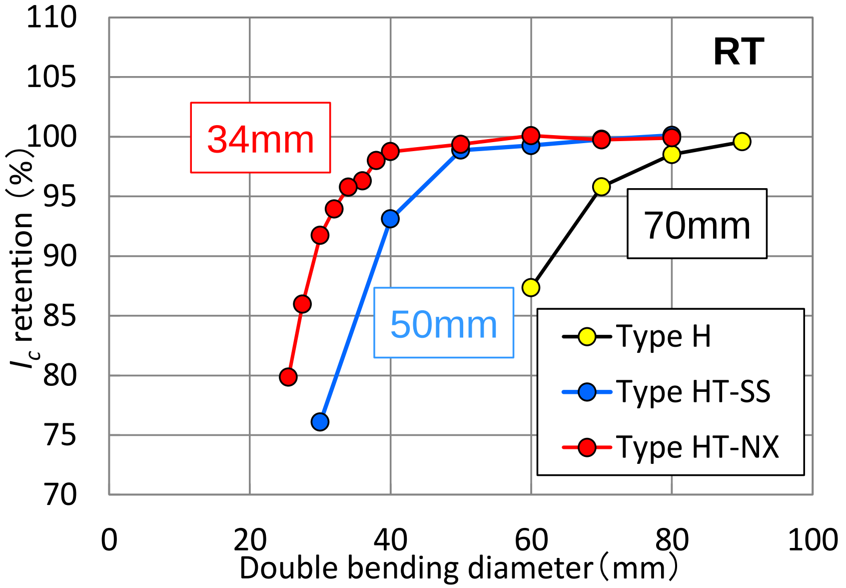
DI-BSCCO

Results of mechanical tests

① Tensile test at 77 K



② Bending test at RT



✓ **At 95% I_c retention for each test,**

Tensile stress : 435 MPa@77K
Bending diameter : 34 mm@RT

SUMITOMO ELECTRIC

Recent BSCCO Tapes: Updated Type HT-NX

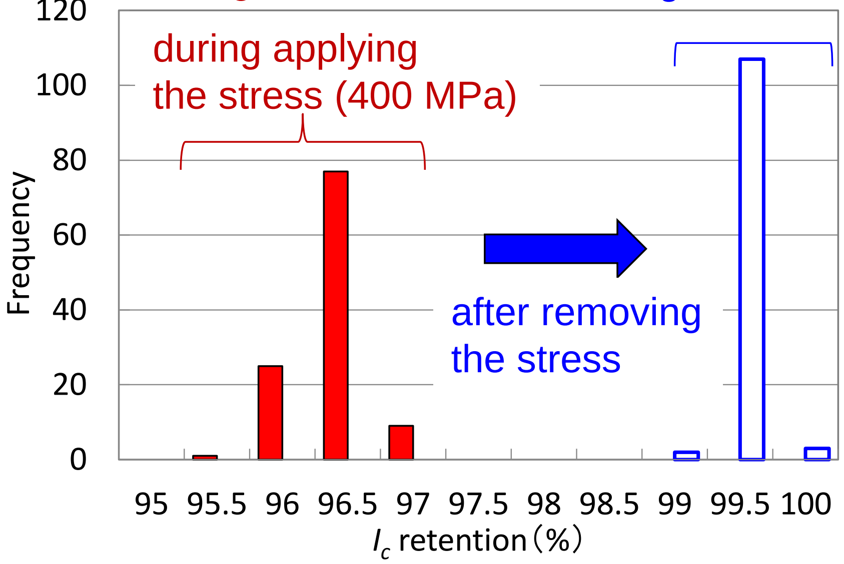
Robustness of mechanical properties

113 wires of Type HT-NX with over 100m have already produced.

① Tensile stress of 400 MPa at 77 K

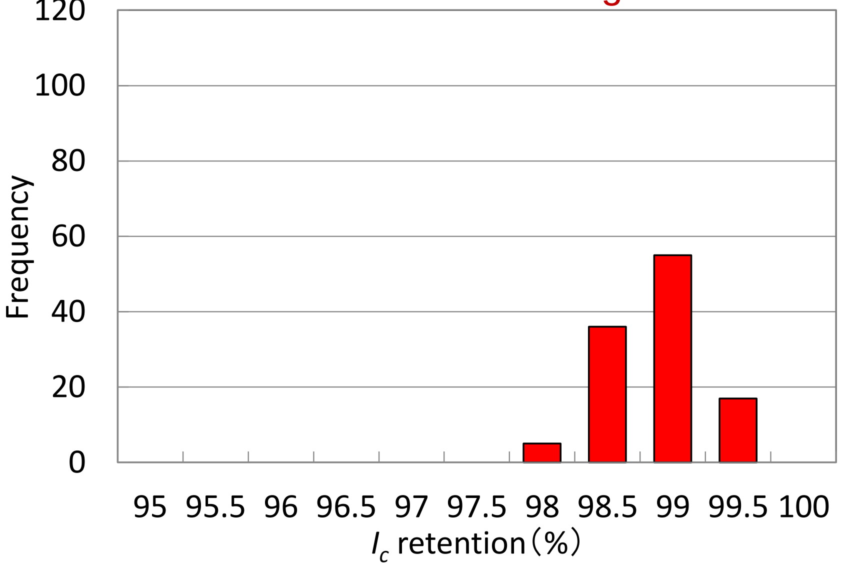
average: 96.7%
3 sigma : 0.8%

average: 99.3%
3 sigma : 0.4%



② Bending diameter of 40 mm at RT

average: 98.6%
3 sigma : 1.1%



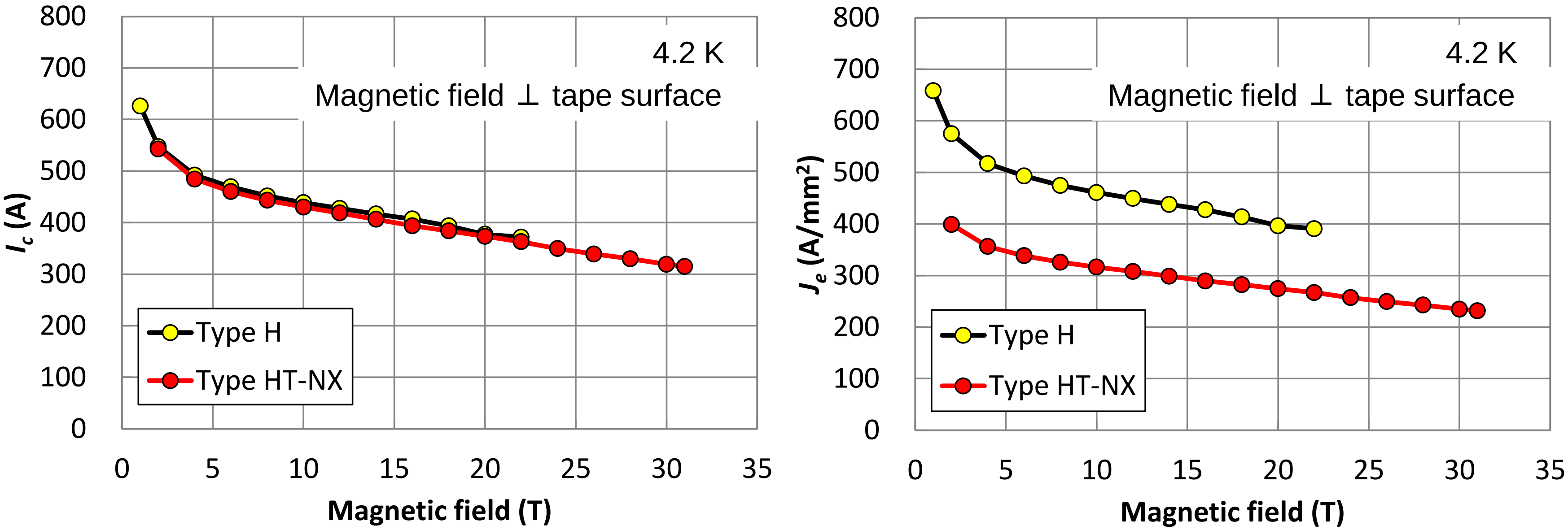
- ✓ **After removing the stress, I_c of all the wires was recovered up to 99%**
  ➔No filament fracture under the tensile stress of 400 MPa at 77 K
- ✓ **I_c maintained 98% under the bending diameter of 40mm at RT**

Recent BSCCO Tapes: Updated Type HT-NX

DI-BSCCO

in-field I_c and J_e at 4.2 K

***Measured by NIMS @ LNCMI/Grenoble for Type H, NHMFL/Florida for Type HT-NX**



- ✓ **I_c of Type H and Type HT-NX are same down to low temperature (4.2K).**
- ➔ **The lamination never affects the original Type H wire's in-field I_c.**

- ✓ **J_e at 4.2K and normal field**

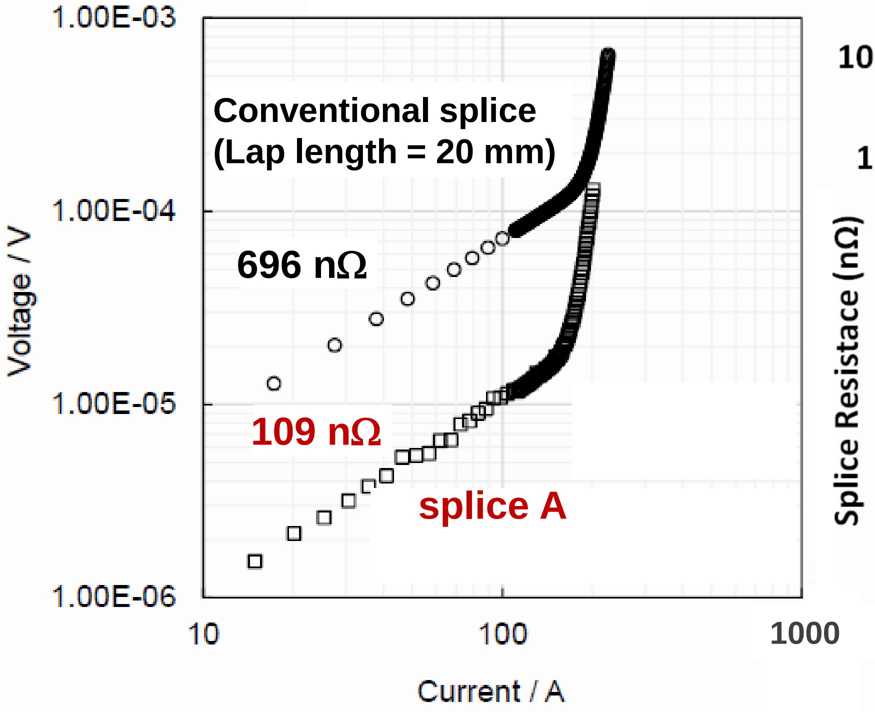
$\sim$300 A/mm^2 at 15T
$\sim$275 A/mm^2 at 20T
$\sim$250 A/mm^2 at 25T
$\sim$235 A/mm^2 at 30T

SUMITOMO ELECTRIC

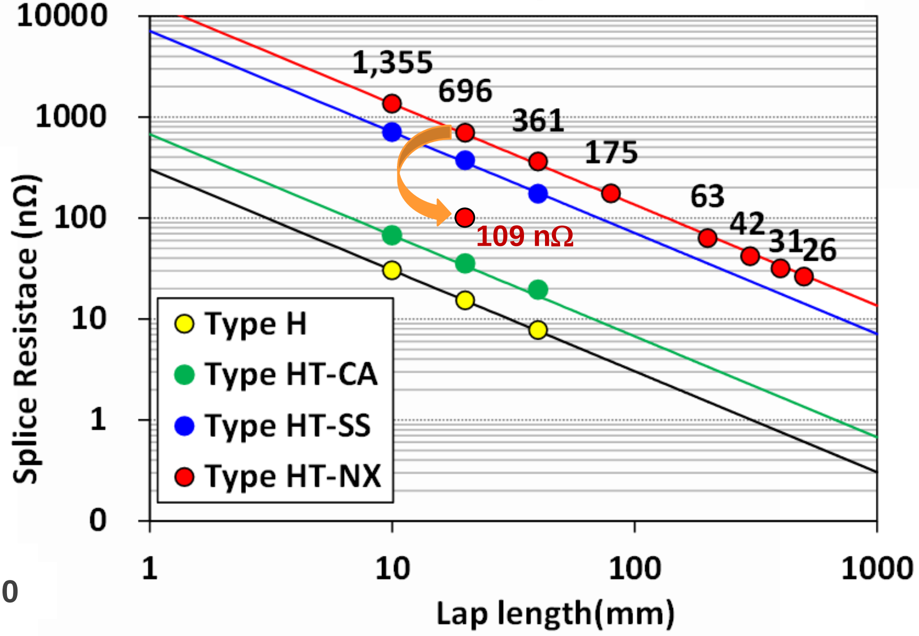
Recent BSCCO Tapes: R&D ~ new splice

DI-BSCCO

Resistance of new splice Type HT-NX



Relationship between lap length and splice resistance



✓ **The splice resistance of Type HT-NX decreased by 84 % for splice A, resulting in the comparable value of Type HT-CA**

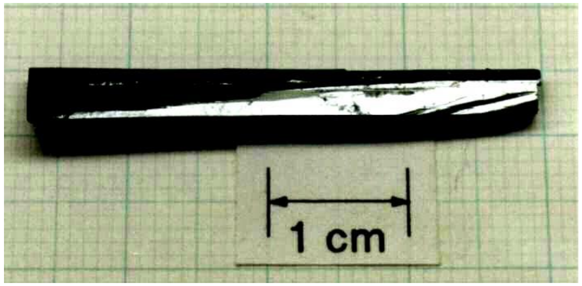
SUMITOMO ELECTRIC

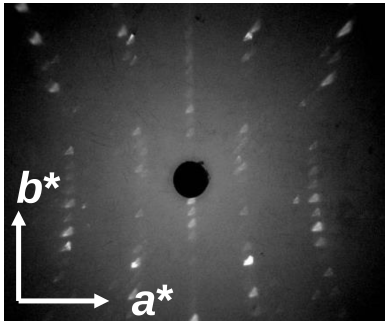
How physical properties of Bi2212 single crystal change with cation composition ?

Samples : Bi2212 single crystals grown by FZ

growth rate = 0.25~0.3 mm / h

nominal composition Bi : Sr : Ca : Cu	atmosphere during crystal growth
2.0 : 2.0 : 1.0 : 2	1% or 5%O_2 grown more than 15 boules
2.1 : 1.9 : 0.9 : 2	air
2.1 : 1.8 : 1.0 : 2	air
2.1 : 1.7 : 1.1 : 2	air
2.1 : 1.5 : 1.3 : 2	air



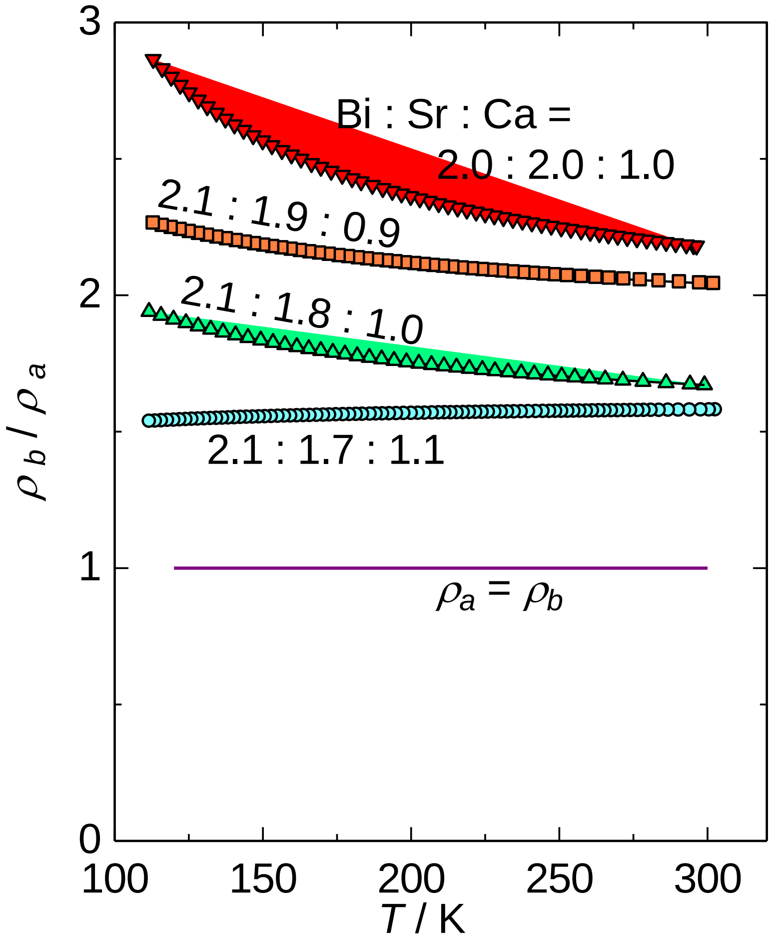


two-step post annealing

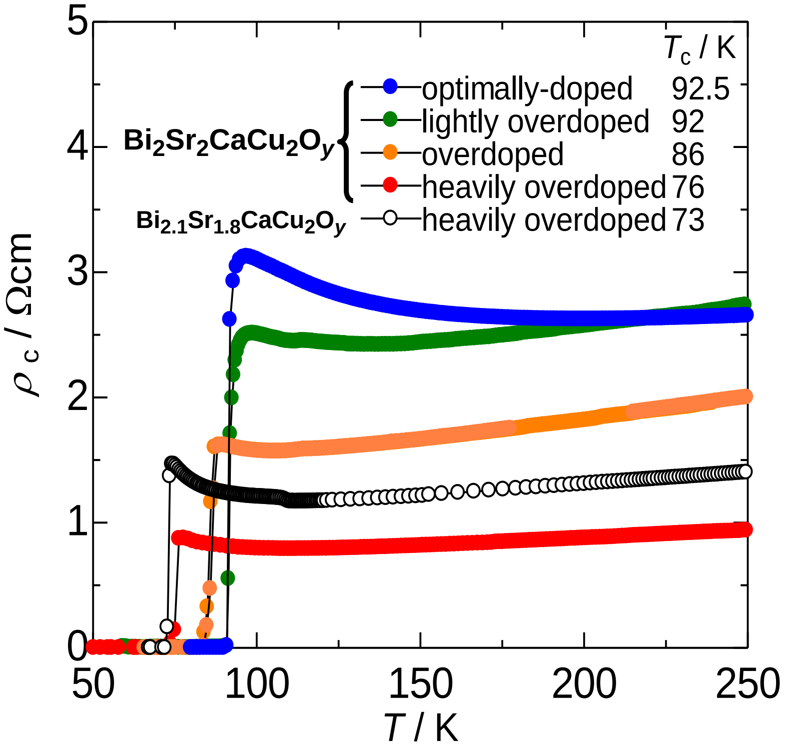
at ~800℃ in air for 72 h --- improving compositional fluctuation of cations

at <800℃ in various P_{O_2} and quenching --- control of oxygen content

Change of In-Plane Anisotropy of Bi2212 with Cation Composition



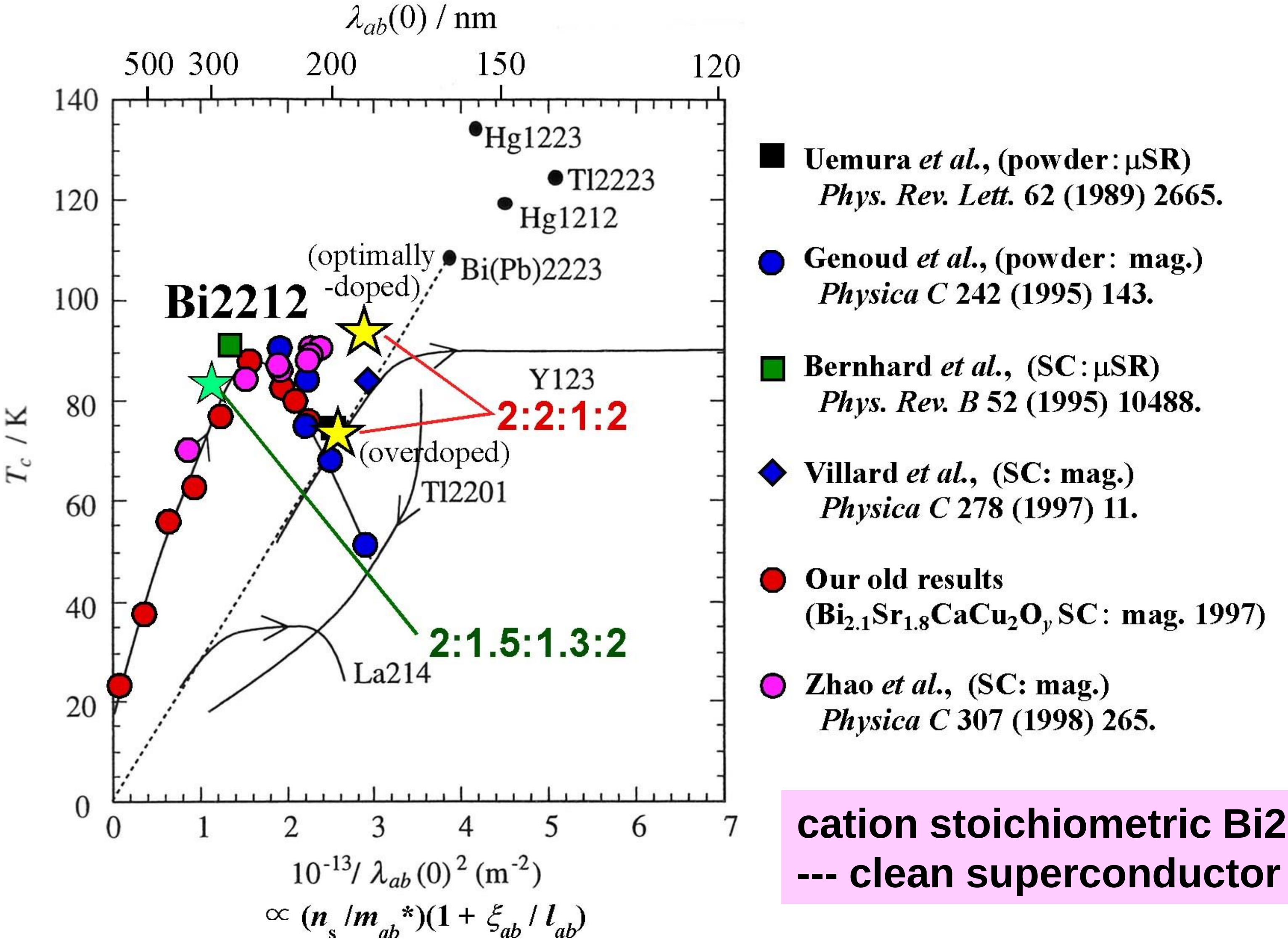
Makise *et al*., *Physica C* 460-462 (2007) 772.



cation stoichiometric Bi2212
--- large ρ_b / ρ_a , low ρ_c

due to elimination of lattice distortion

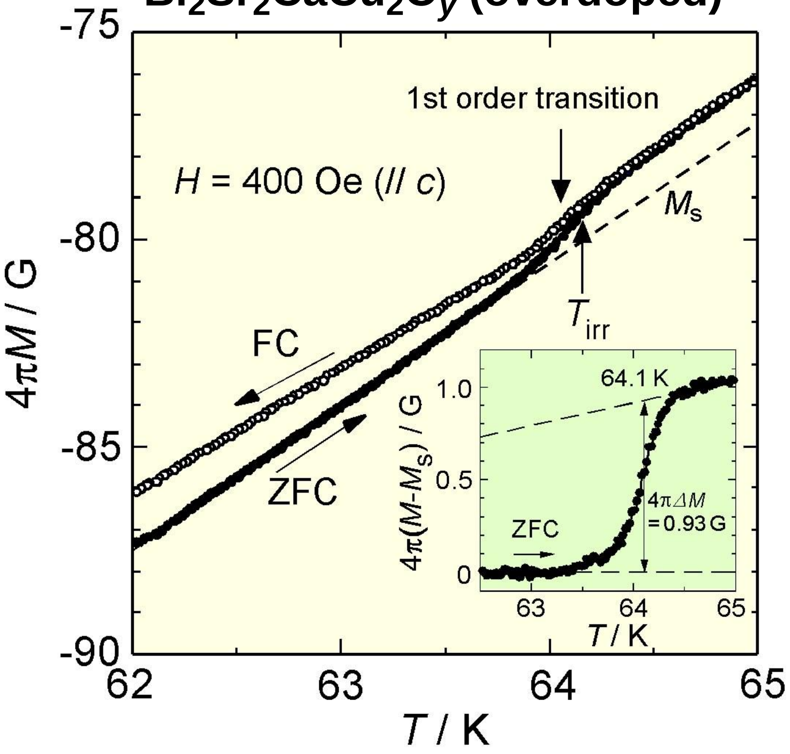
Cation Composition Dependent λ_{ab} of Bi2212



cation stoichiometric Bi2212
--- clean superconductor

First Order Transition of Vortex System of Cation Stoichiometric Bi2212

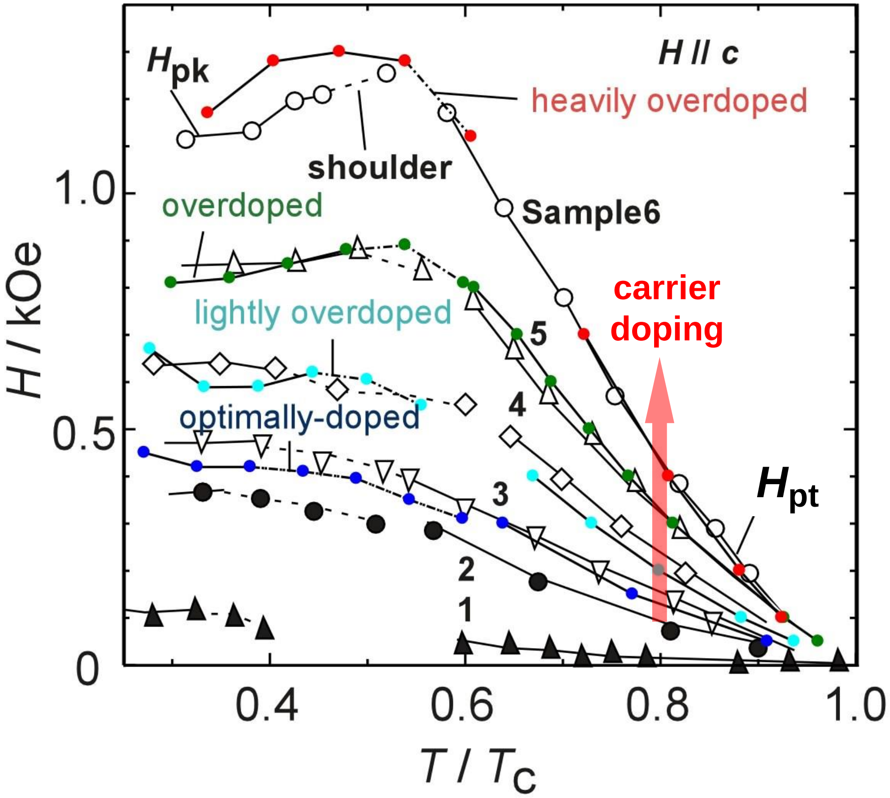
$Bi_2Sr_2CaCu_2O_y$ (overdoped)



T_{pt} ~ T_{irr}

no reversible region below T_{pt}

strong bulk pinning up to T_{pt}

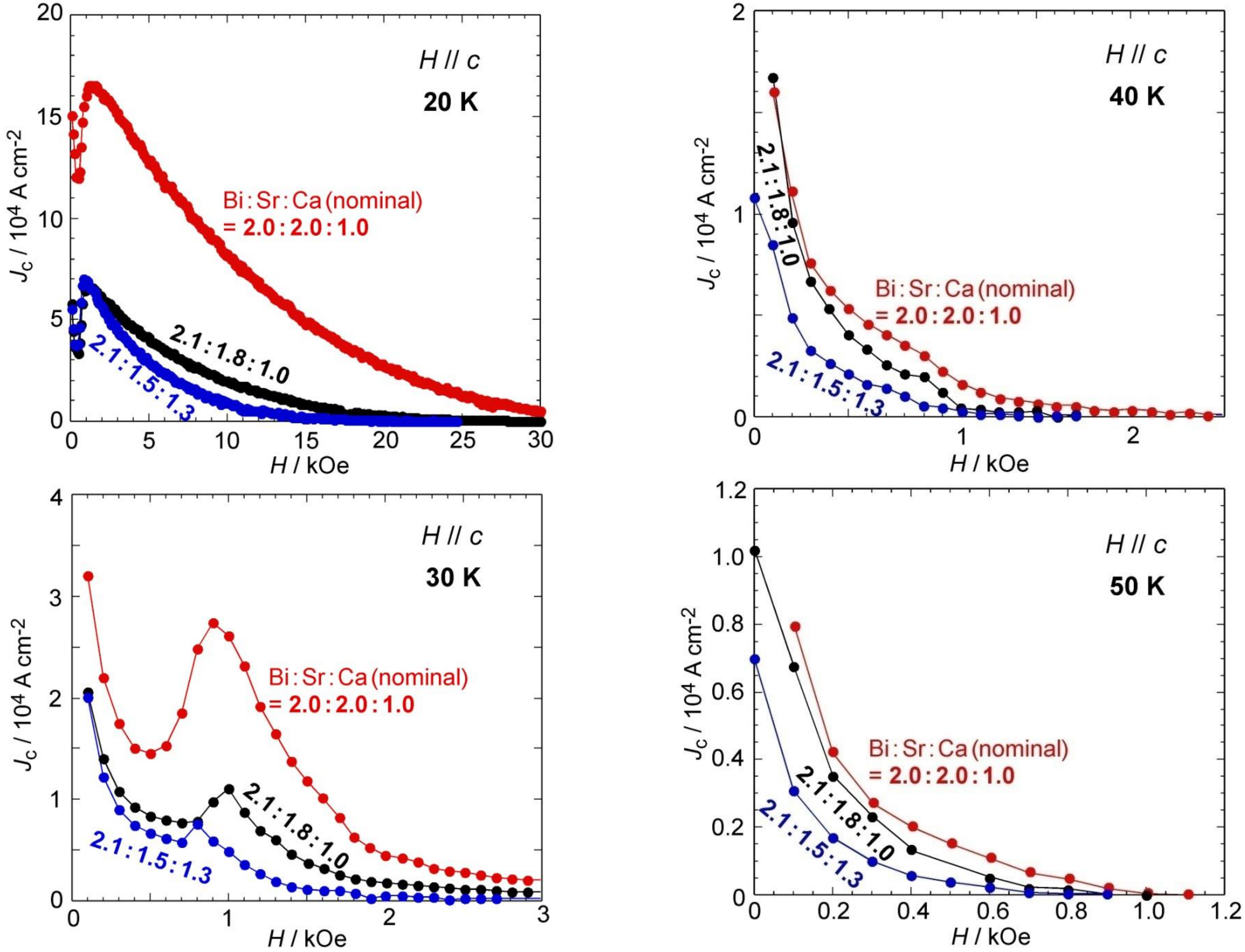


color symbols : $Bi_2Sr_2CaCu_2O_y$
black symbols : $Bi_{2.1}Sr_{1.8}CaCu_2O_y$

Cation composition does not affect second peak field, H_{pk} & H_{pt}.

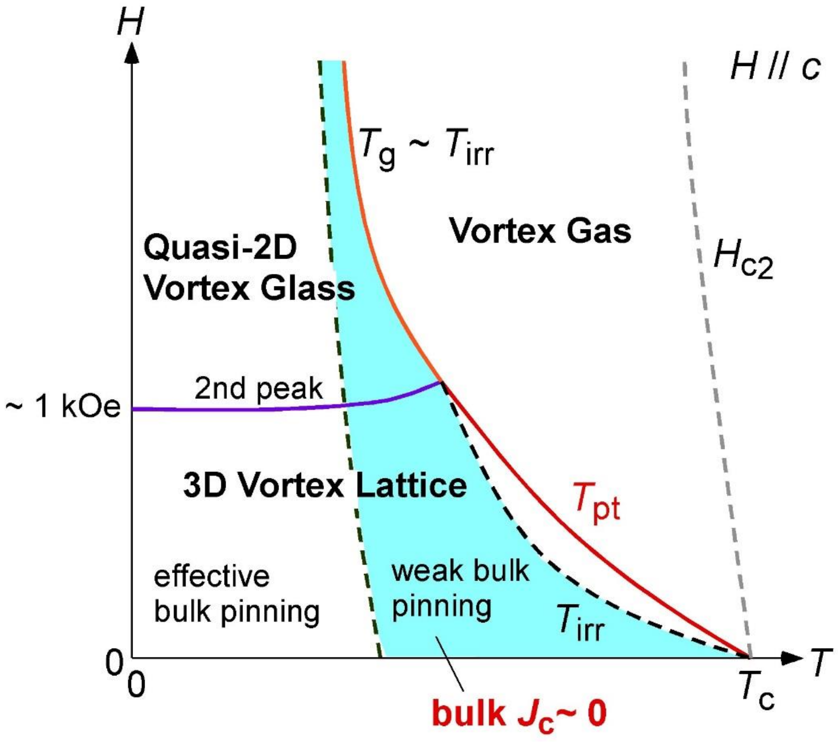
Stoichiometric Cation Ratio Gives the Best J_c

Bi2212 single crystals

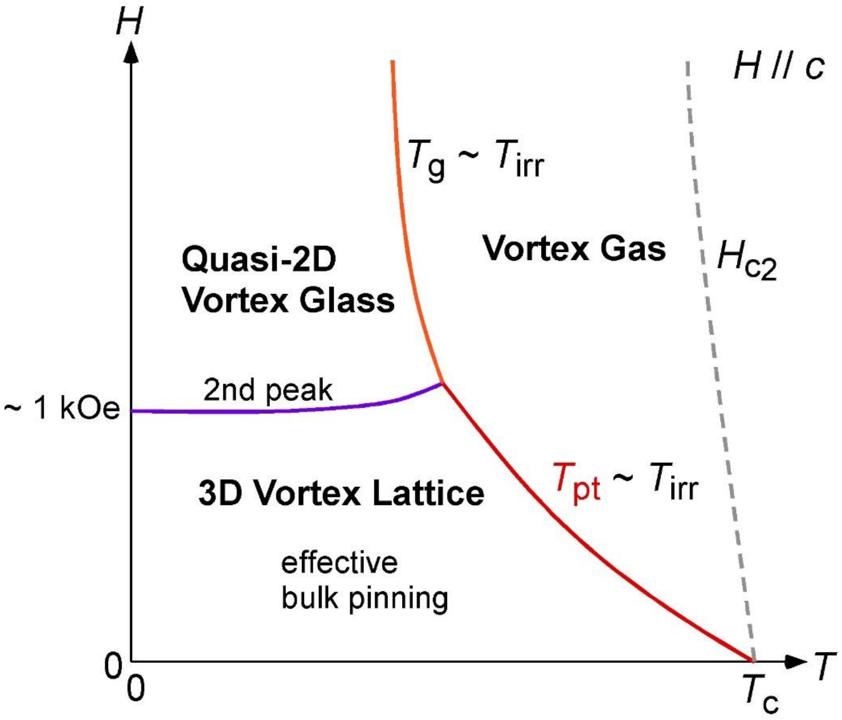


Vortex Phase Diagram of Bi2212 (*H* // *c*)

cation nonstoichiometric crystals (Bi-rich & Sr-poor: conventional)



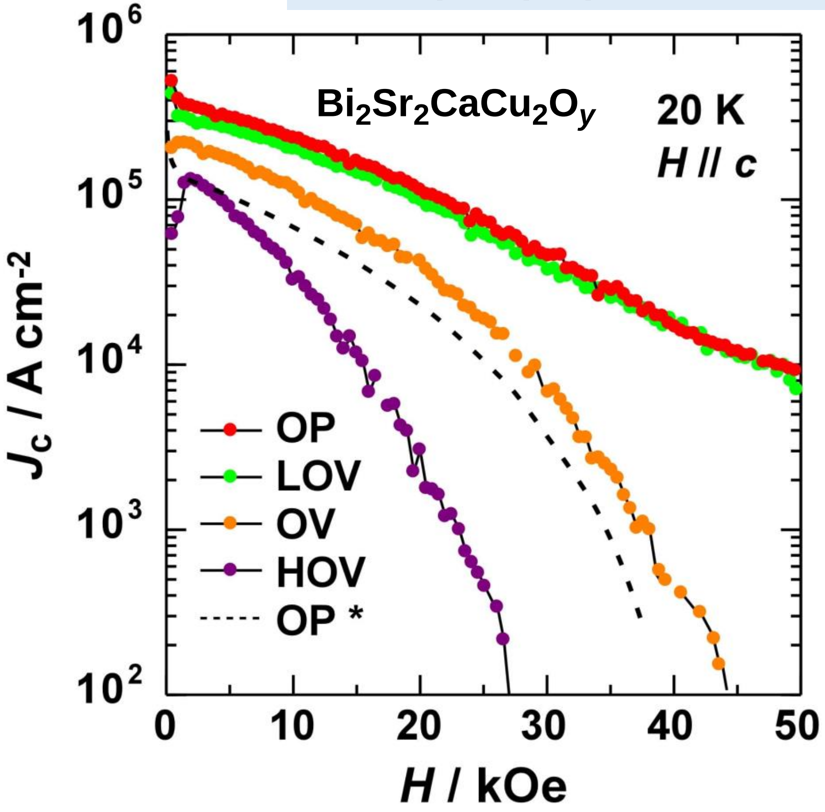
cation stoichiometric crystals (our study)

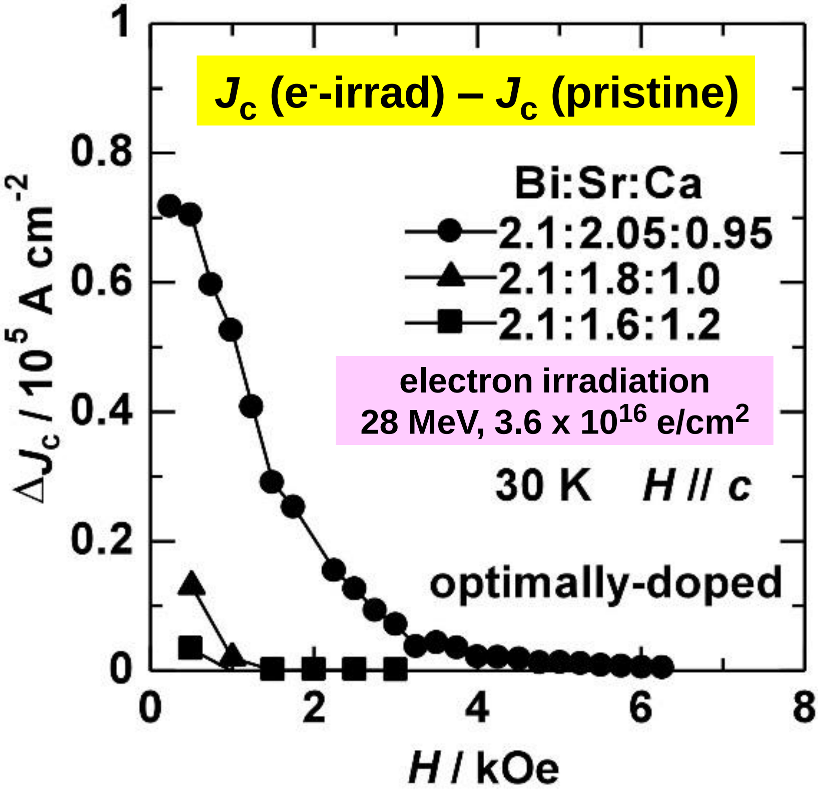


Strong Pinning Observed in Cation Stoichiometric & Carrier Concentration Controlled Bi2212

Bi2212 Single Crystals with Bi:Sr:Ca:Cu ~ 2:2:1:2

optimally-doped (OP) : lightly overdoped (LOV)
overdoped (OV) : heavily overdoped (HOV)



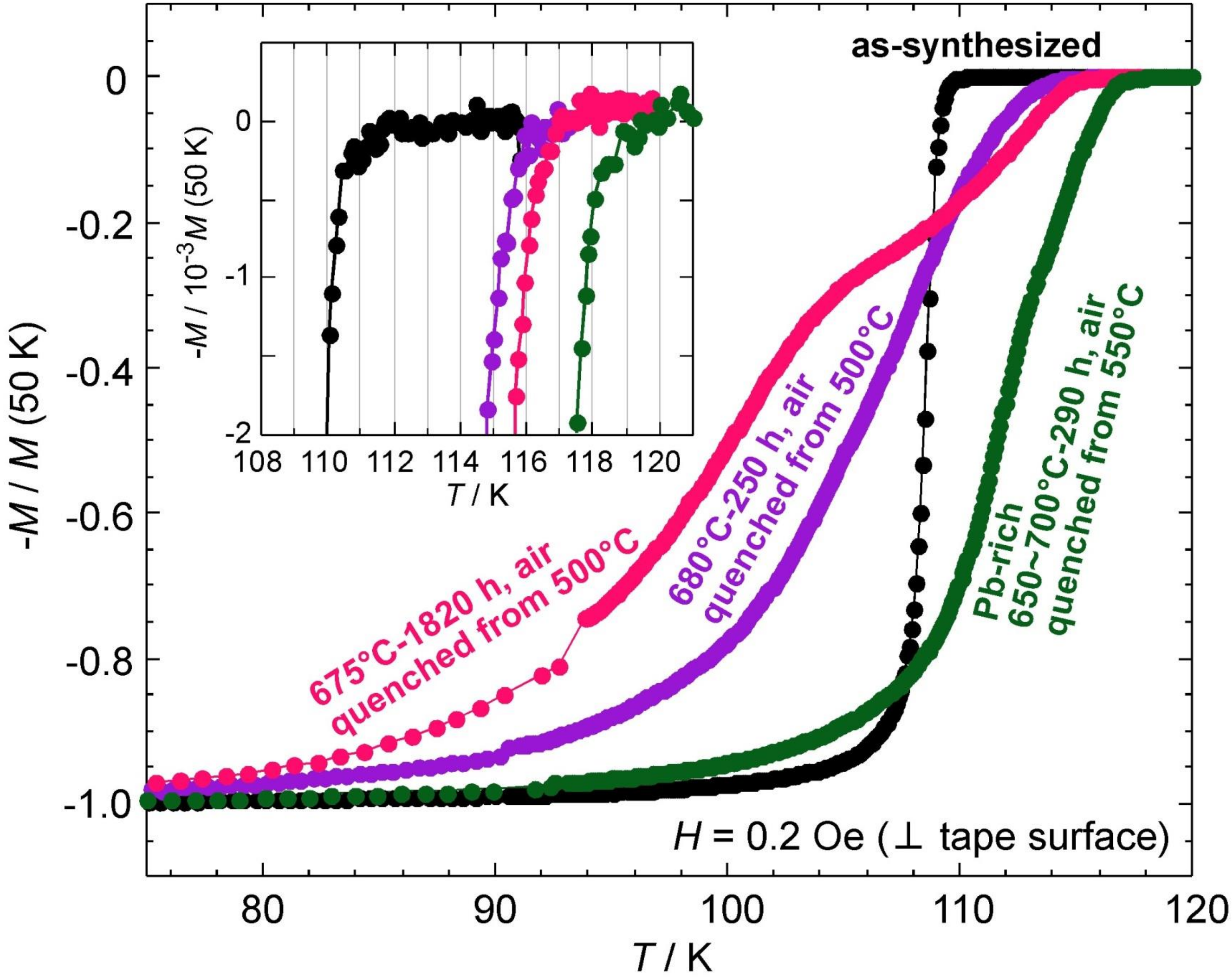


* different crystal boule

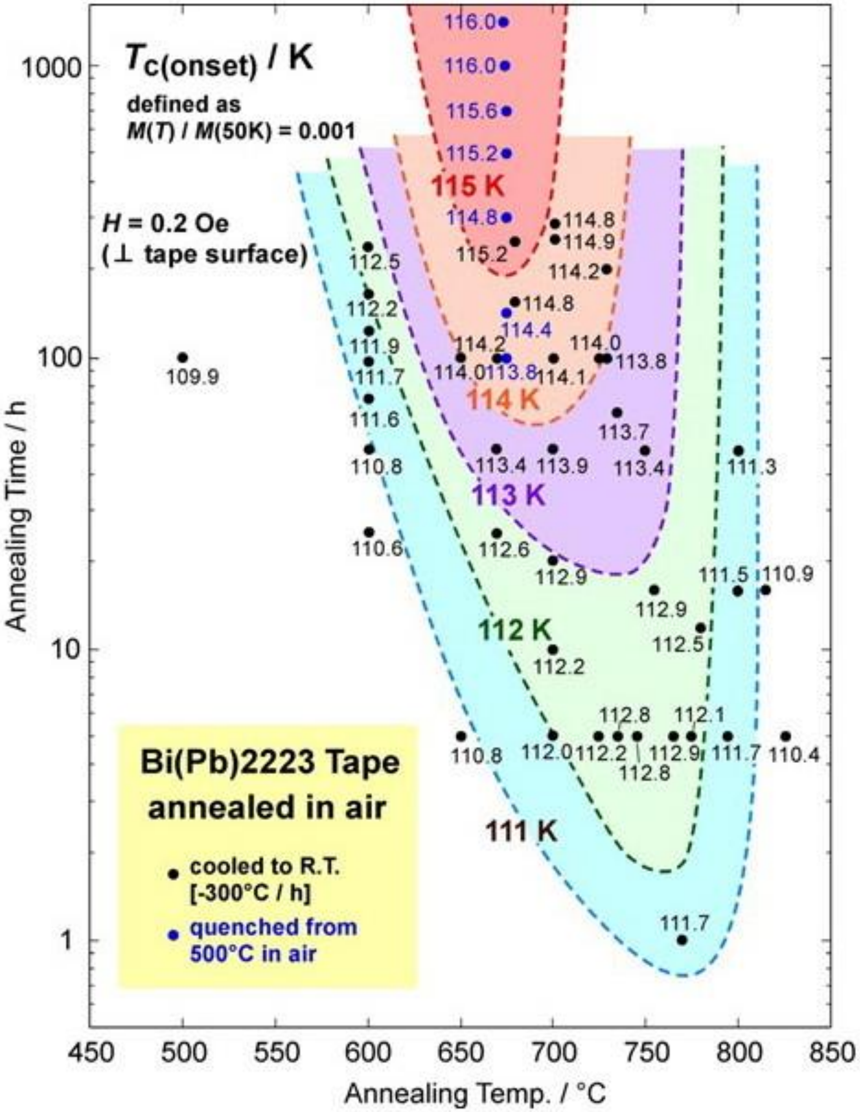
Carrier optimally-doped crystal exhibited record-high J_c-B properties!

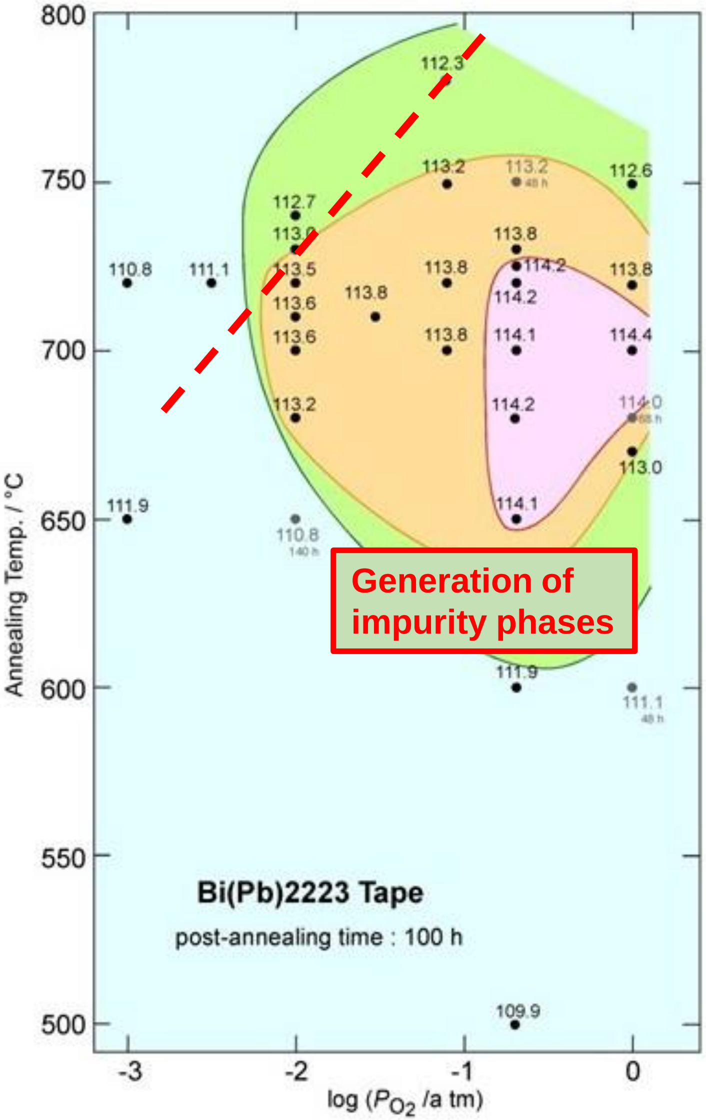
Enhancement of T_c in Bi(Pb)2223

DI-BSCCO Tape (by SEI)



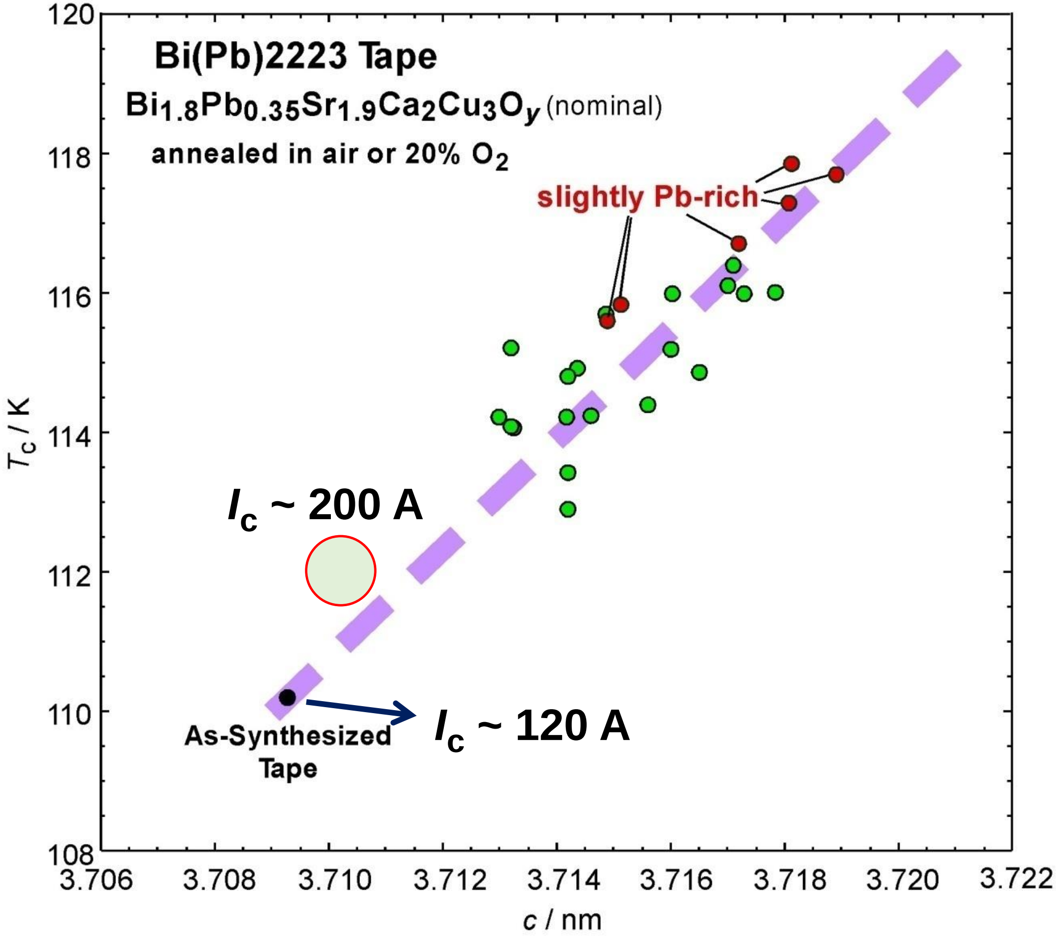
T_c Map of Bi2223 Tapes

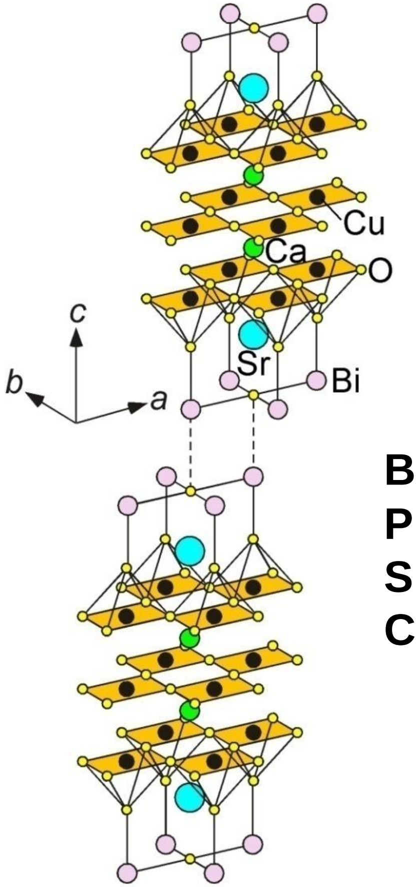




Shimoyama *et al*., *Jpn. J. Appl. Phys*. **44** (2005) L1525-L1528.

Origin of Enhanced T_c of Bi(Pb)2223



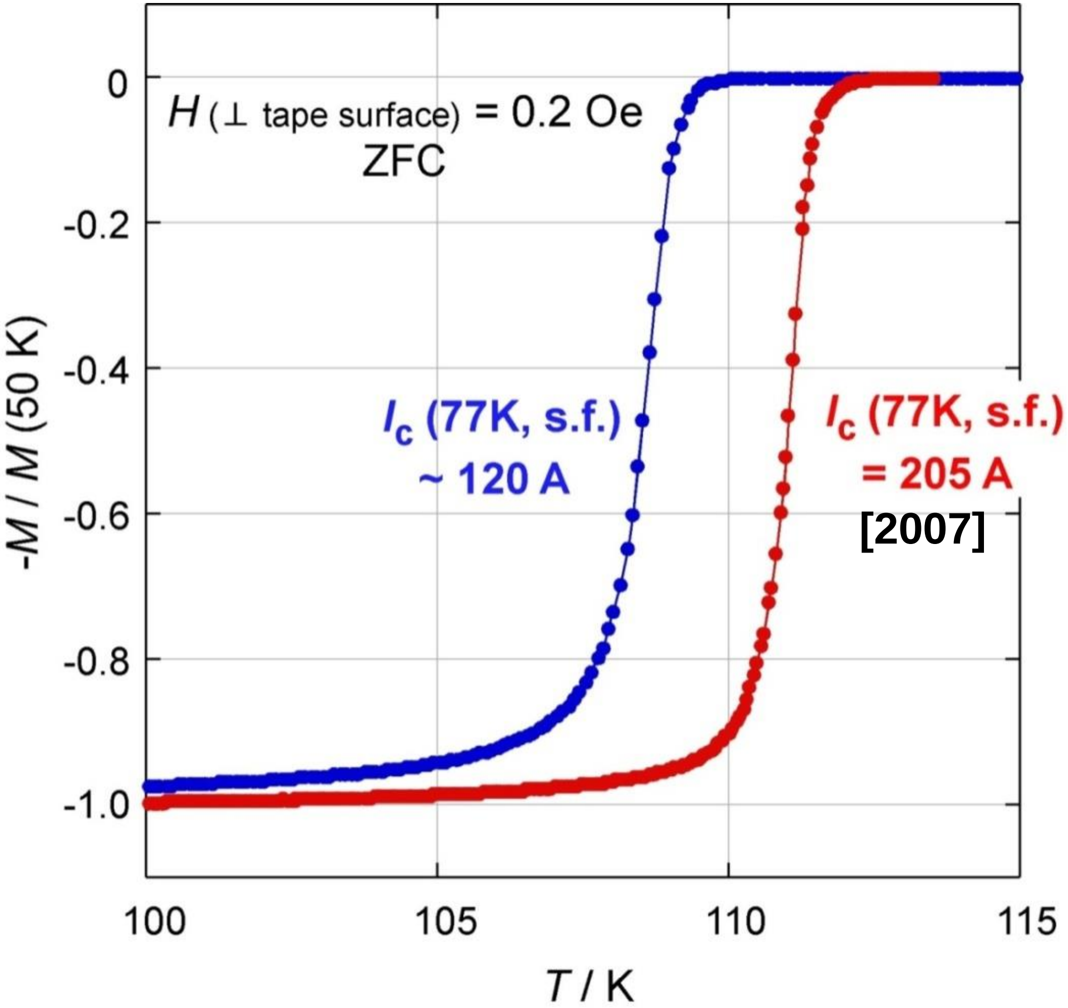


$Bi_2Sr_2Ca_2Cu_3O_{10}$
[Bi2223]

***r* / nm**
(C.N.= 8)

Bi^{3+} : 0.111
Pb^{2+}: 0.129
Sr^{2+} : 0.125
Ca^{2+}: 0.112

Partial substitutions of Bi and Ca for Sr-site is suppressed by post annealing.



best I_c (77 K, s.f.) = 273 A

DI-BSCCO has improved microstructure, cation composition and optimized carrier doping state for each application

RE123 Materials

Coated Conductors

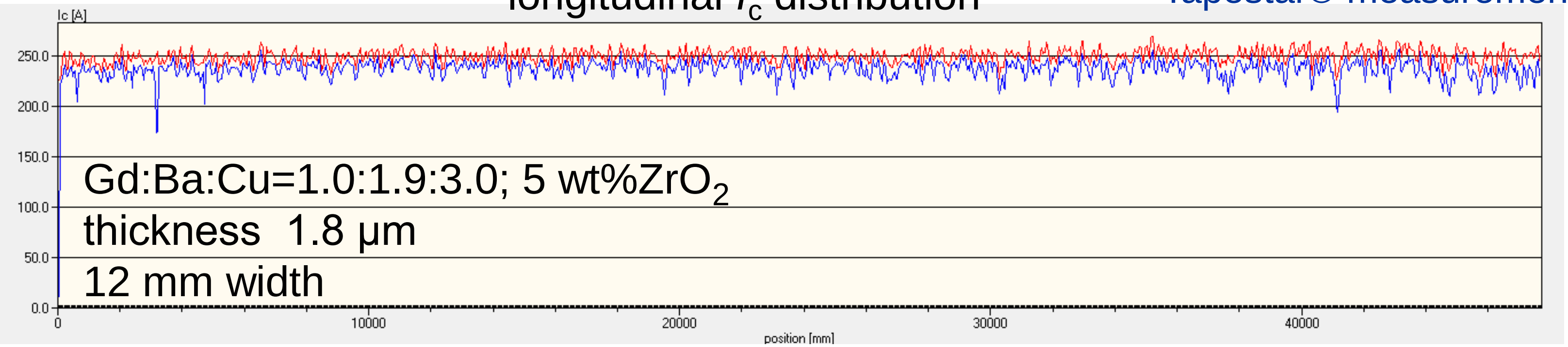
Melt-Solidified Bulks

Recent RE123 Coated Conductors

50 m long $BaZrO_3$ doped GdBCO wire

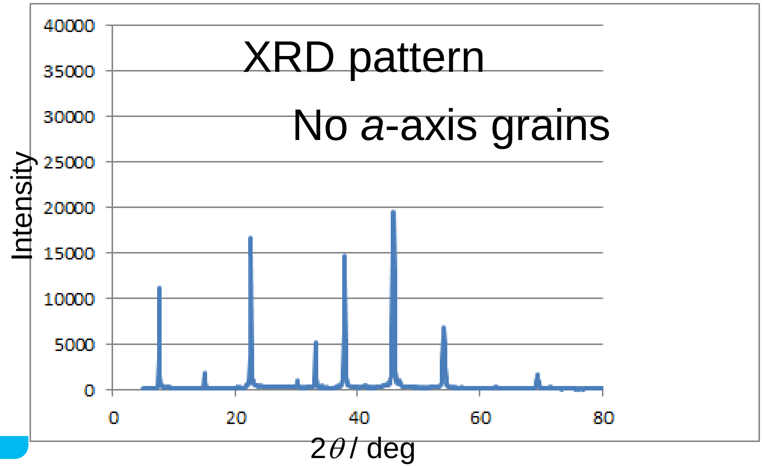
longitudinal I_c distribution

Tapestar® measurement



$Gd:Ba:Cu=1.0:1.9:3.0$; 5 wt%ZrO_2
thickness 1.8 μm
12 mm width

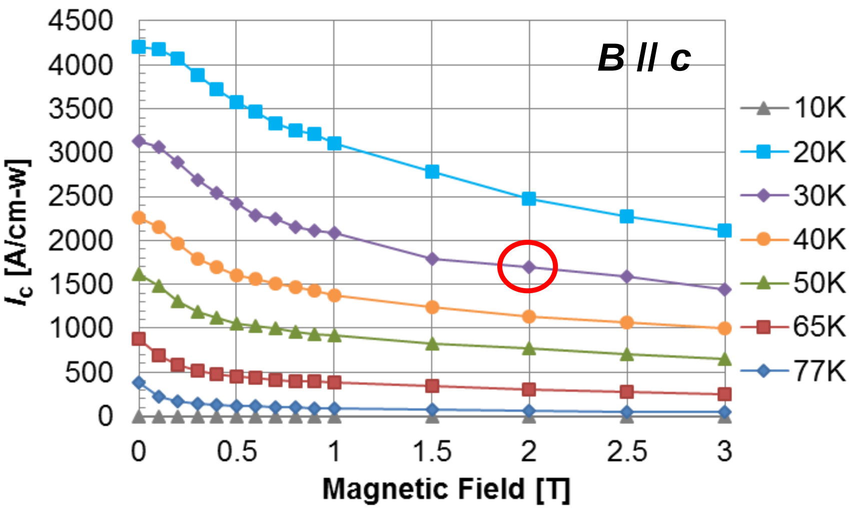
I_c=271 A (77 K,0 T)
J_c = 1.3 MA/cm^2
Uniformity (STDV/ave.I_c) =3.2 (%)



XRD pattern

No *a*-axis grains

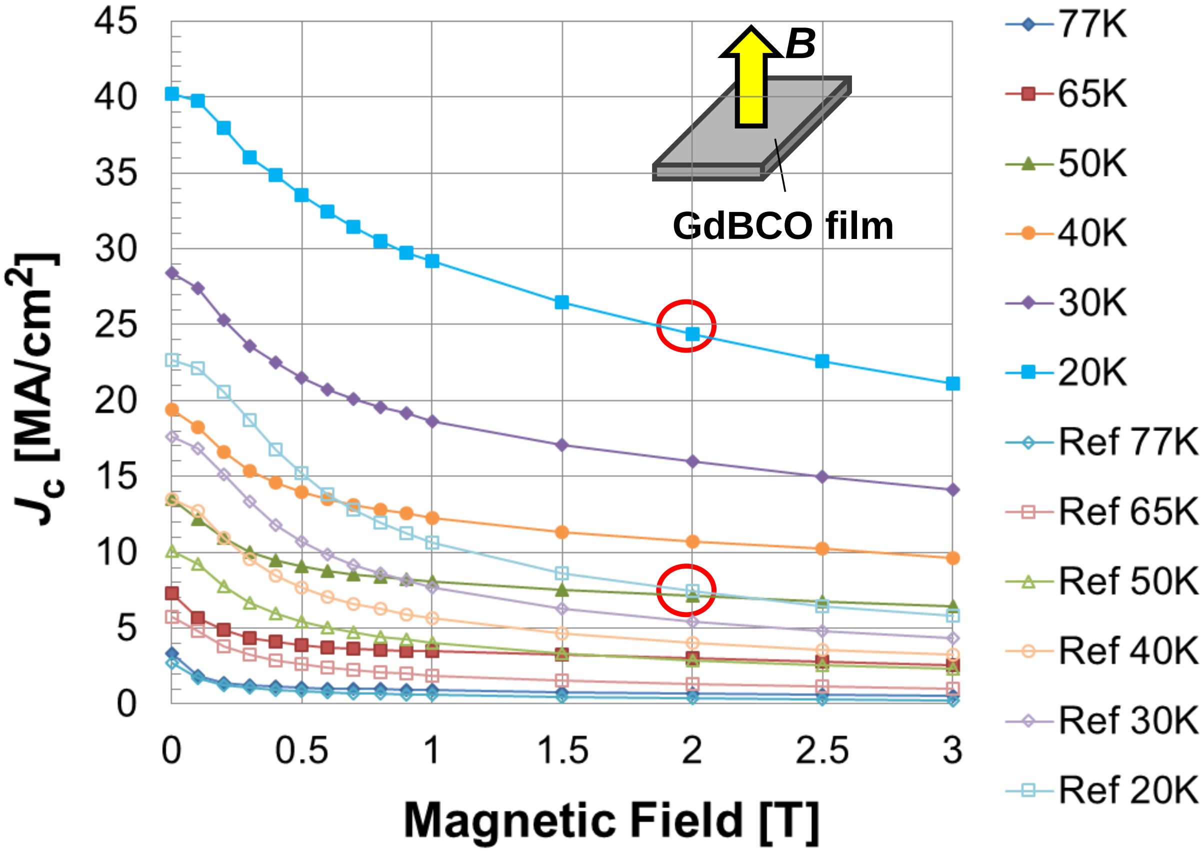
1700 A/cm (30 K 2 T)



Fujikura

Recent RE123 Coated Conductors

Enhanced J_c for BHO doped GdBCO



with APC
16 MA/cm^2
(30 K, 2 T)

> x2~3

non APC
6 MA/cm^2

Twice or further high J_c compared to non-doped wire at low temp.

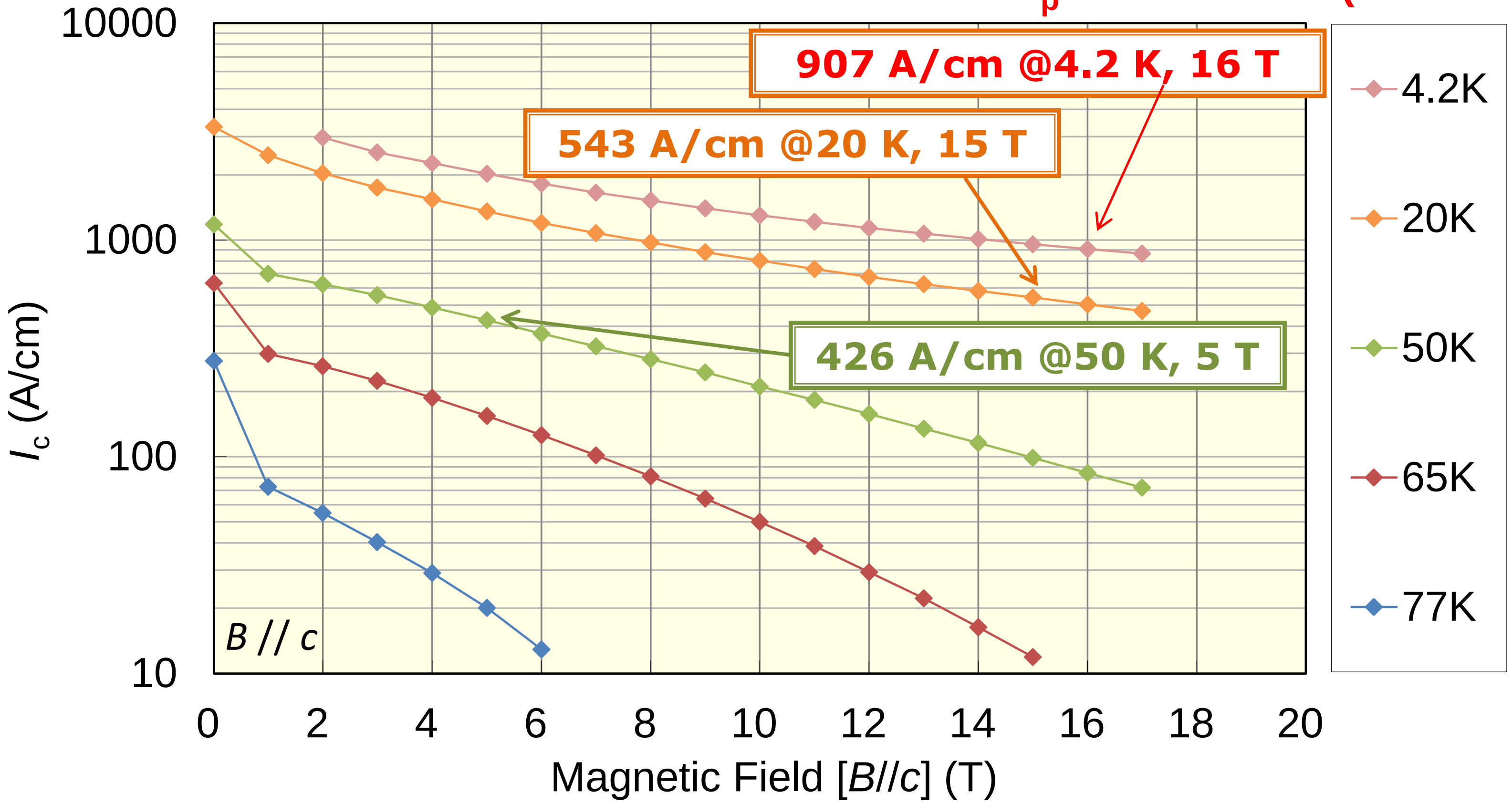
Fujikura

Recent RE123 Coated Conductors

I_c properties in high magnetic fields

Sample : GdBCO + BHO (thickness : 1.2 μm)

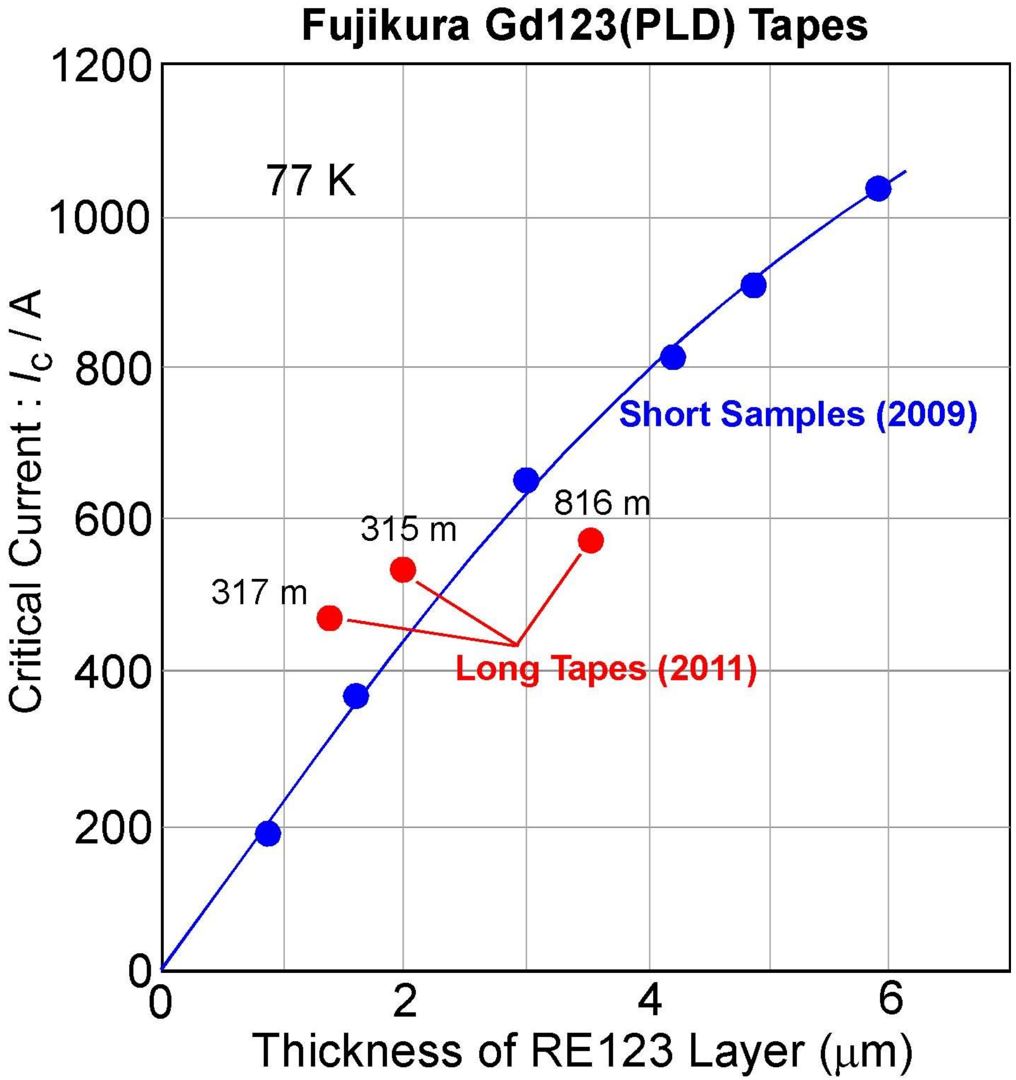
F_p= 1210 GN/m^3 (4.2K 16T)



* This work includes some data measured at High Field Laboratory for Superconducting Materials, Institute for Materials Research, Tohoku University.

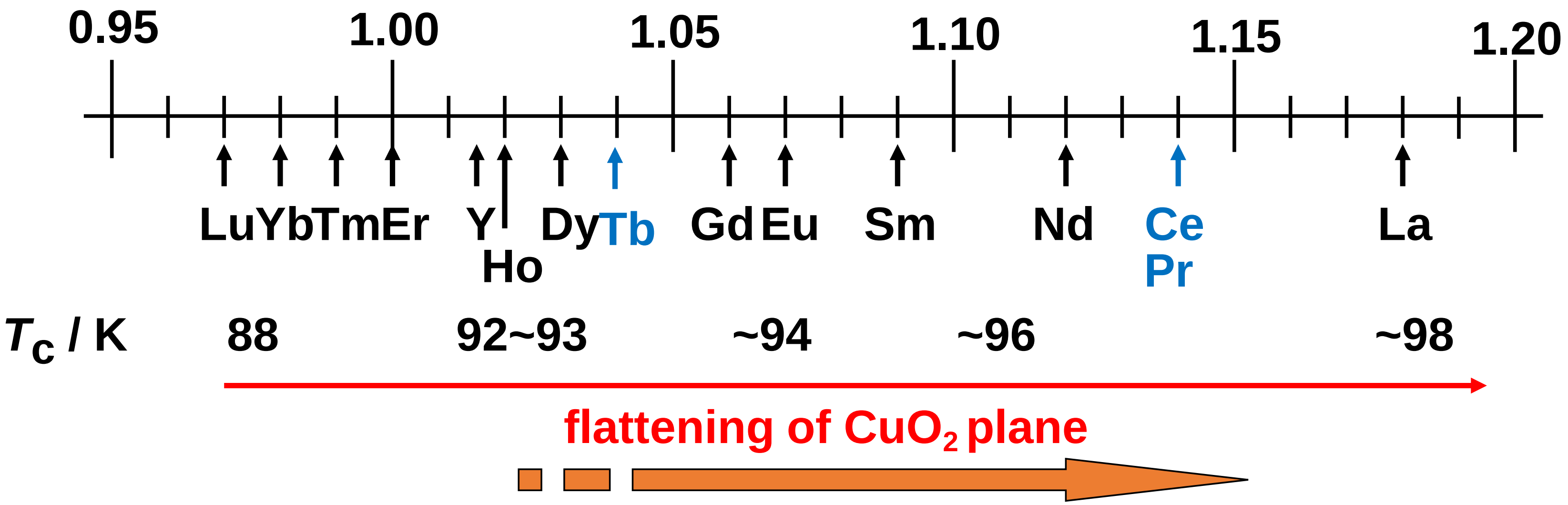
Fujikura

Simple way to increase I_c and J_e



Problem of RE123: RE substitution for Ba

Ionic radii of RE^{3+} (C.N.= 8) / Å



0.95 1.00 1.05 1.10 1.15 1.20

Lu Yb Tm Er Y Ho Dy Tb Gd Eu Sm Nd Ce Pr La

T_c / K 88 92~93 ~94 ~96 ~98

flattening of CuO_2 plane

RE substitution for Ba site

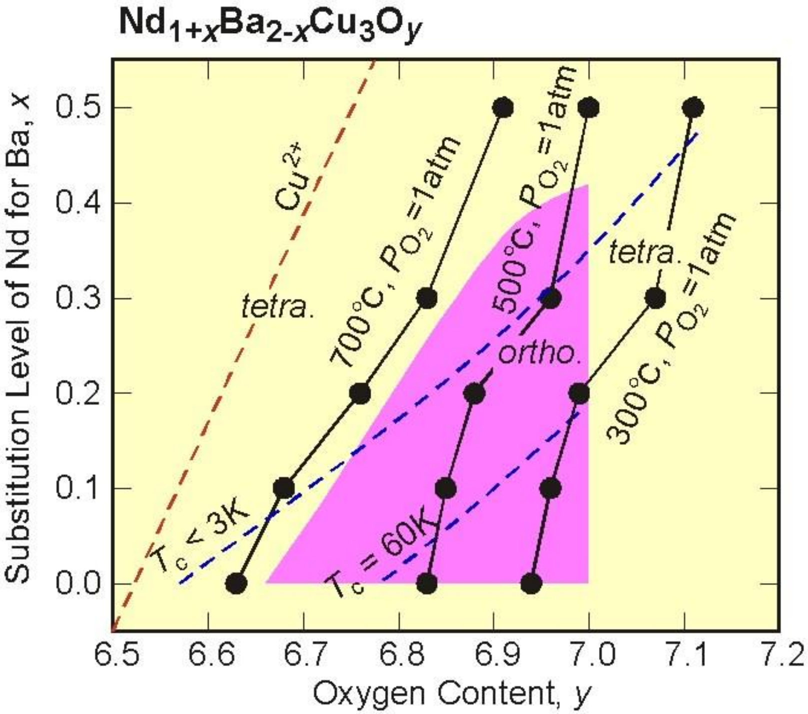
$RE_{1+x}Ba_{2-x}Cu_3O_y$

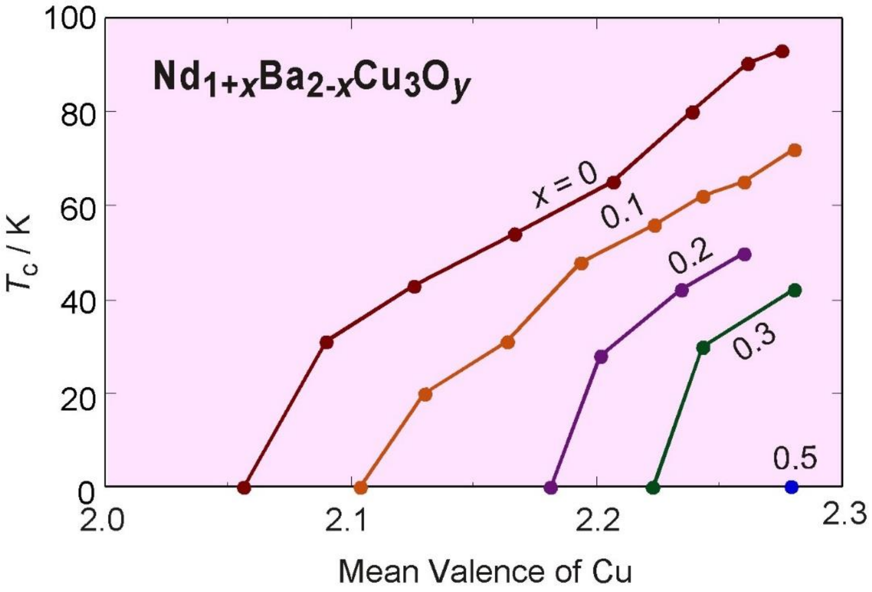
Pr eats (attracts) hall carriers.

Ce forms $BaCeO_3$.

Tb forms $BaTbO_3$, while it can form Tb(Sr)123.

Carrier Doping State and Superconductivity of Nd-rich Nd123





Nominal carrier density is unchanged by Nd composition.

T_c is essentially decreased by Nd substitution for Ba.

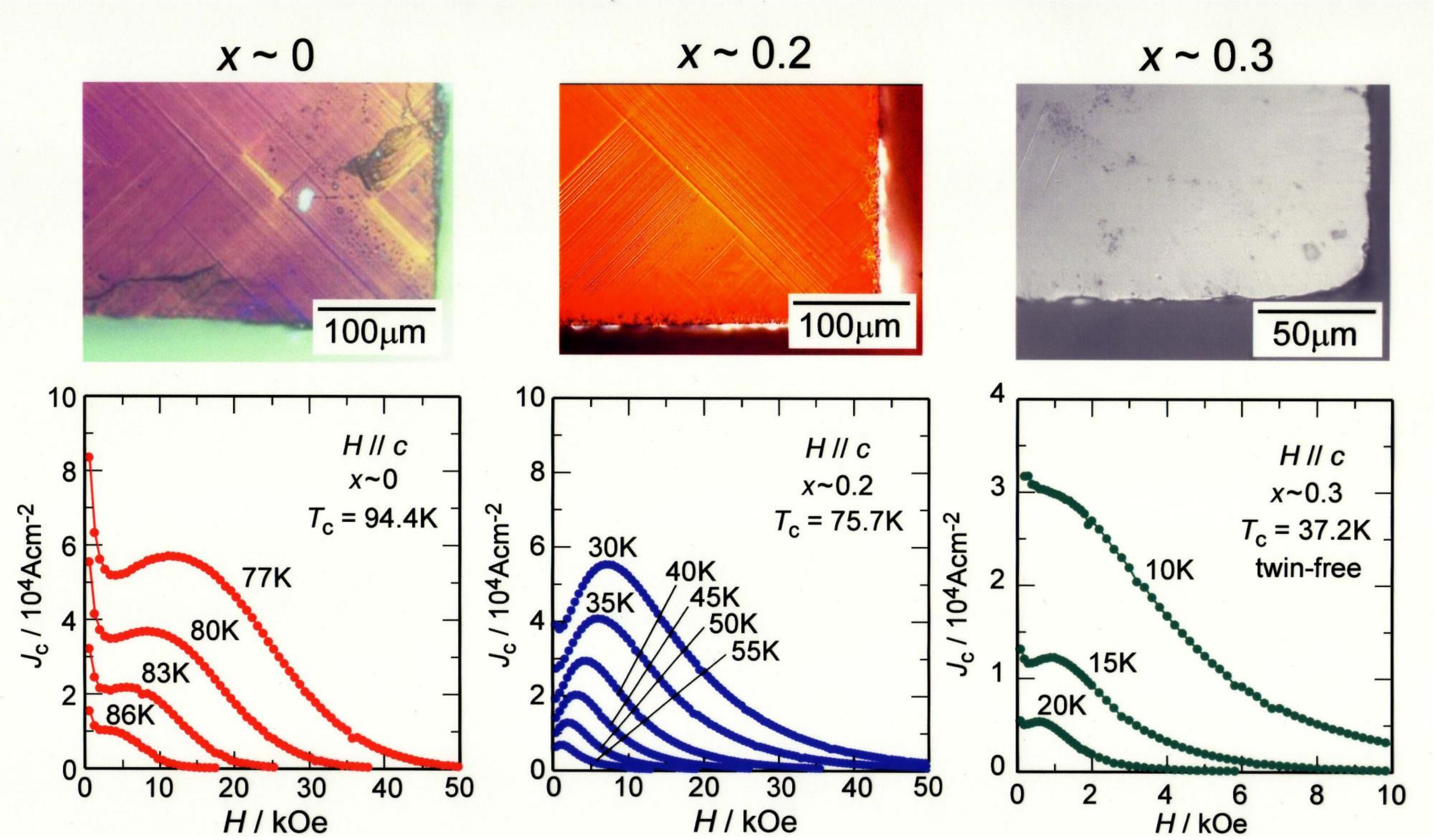
-- structural deformation
-- ineffective carrier doping

➡ **weak superconducting matrix**

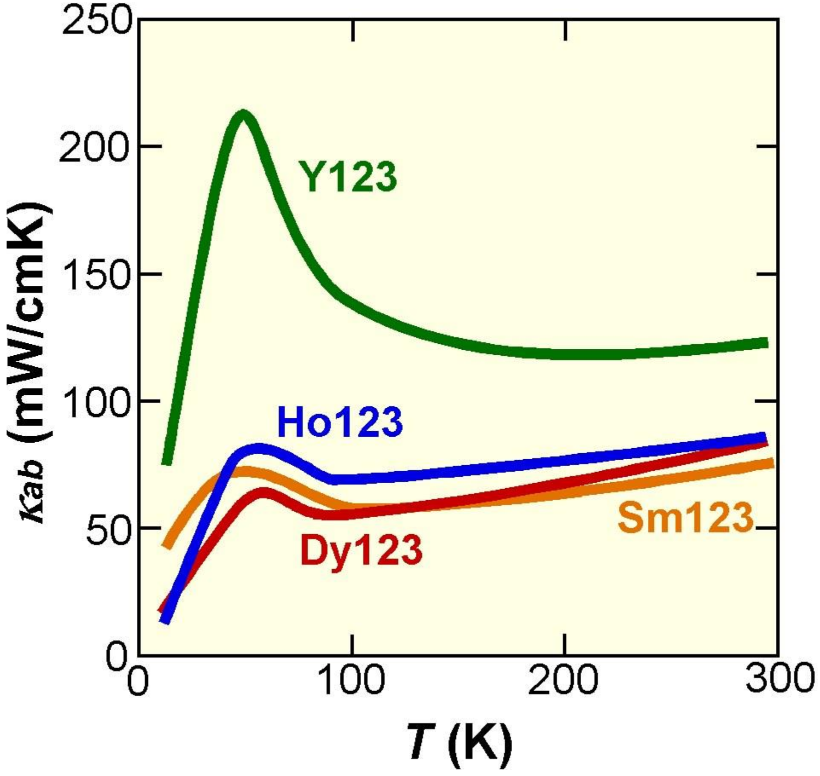
Deteriorated Critical Current Properties of Nd123 Single Crystals by Excess Nd

$Nd_{1+x}Ba_{2-x}Cu_3O_y$

Maruyama *et al*, M^2S-HTSC VII (2003)

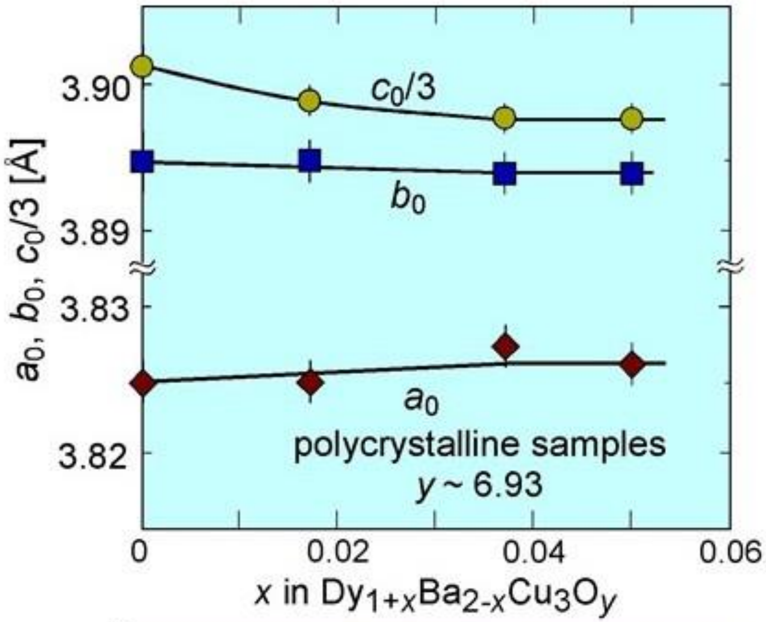


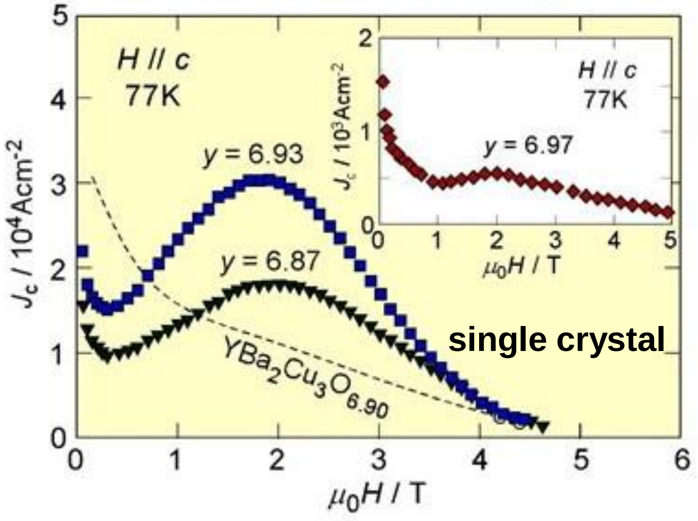
RE Substitution for Ba Site in Dy123 and Ho123



from http://ikebehp.mat.iwateu.ac.jp/database.html

low thermal conductivity
--- lattice deformation

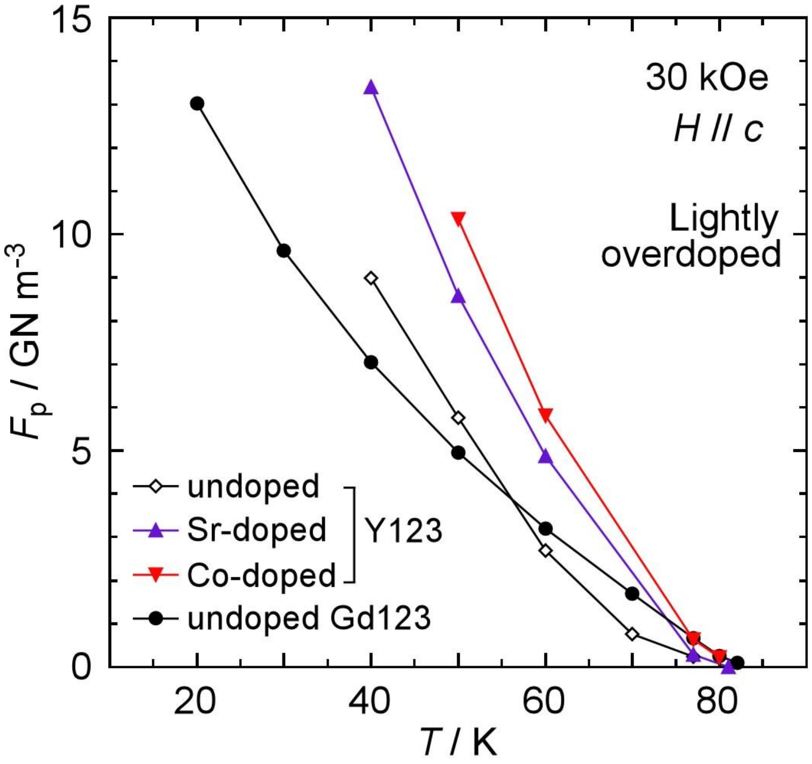


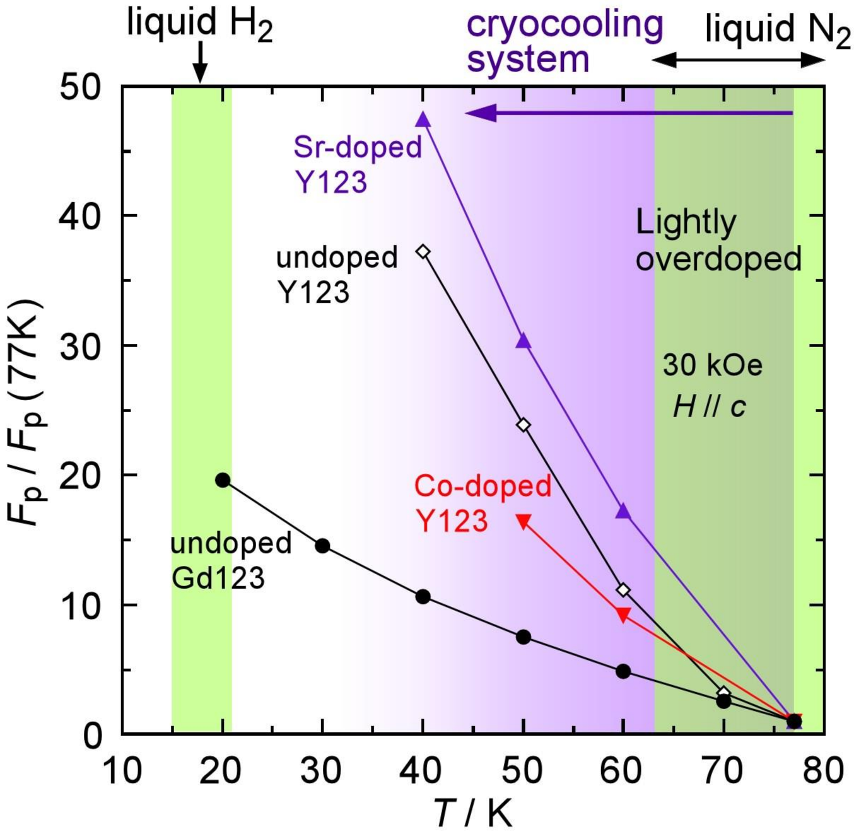


analyzed composition: $Dy_{1.02}Ba_{1.98}Cu_3O_y$

Comparison of F_p of Gd123 and Y123 Single Crystals

Ishii *et al*., *IEEE Trans. Appl. Supercond*. **19** (2009) 3487-3490.





Y123 single crystals show better performance than Gd123 at low temperatures.
Dilute impurity doping enhances J_c.

Concept of Dilute Doping

Direct substitution to superconducting layers:
to CuO_2 plane in HTSC

⟶ Dramatic Local Degradation of $|\Psi|^2$

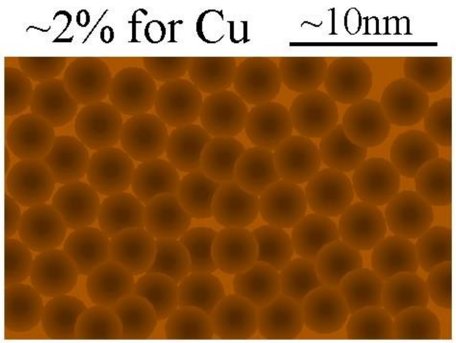
Short coherence length of HTSC enabled effective dilute doping for enhancement of pinning strength.

undoped

***ab*-plane**

good superconducting matrix

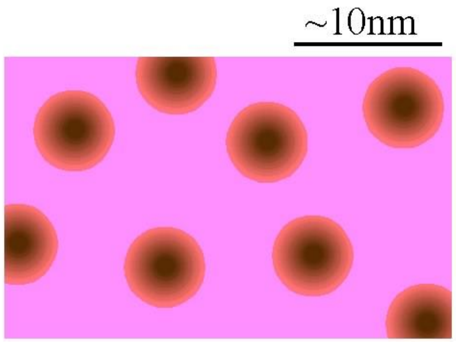
high doping level > 1%



degraded superconducting matrix

serious decrease of bulk T_c

low doping level ~ 1%



generation of local low T_c regions in good superconducting matrix

***e.g.* Zn-substituted RE123 bulk**

Krabbes et al., *Physica C* 330, 181 (2000).

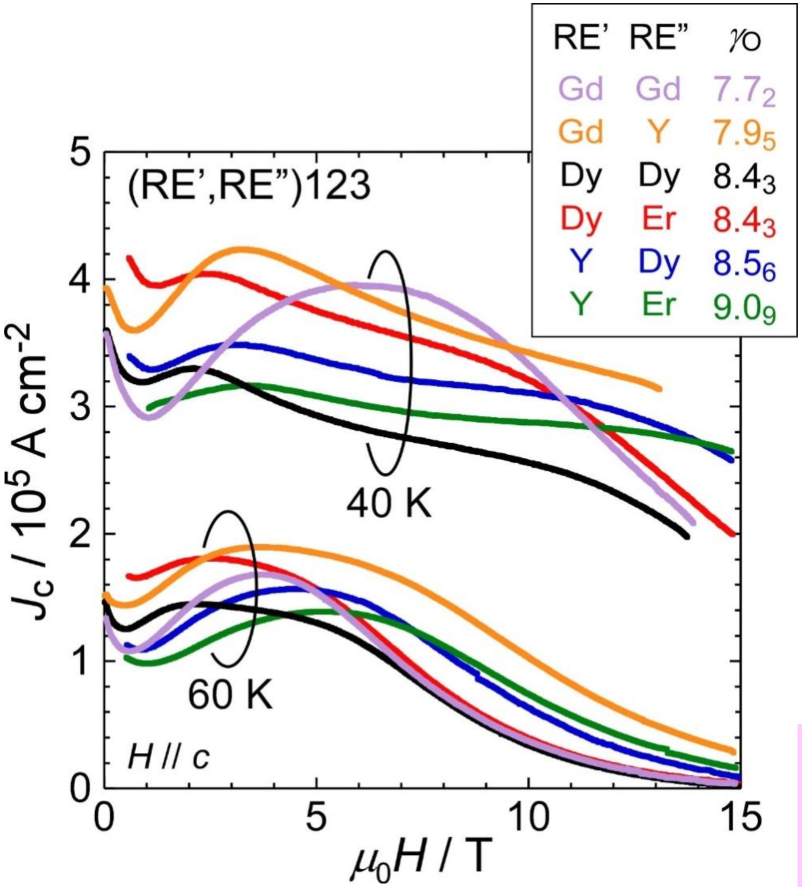
RE-Mixed RE123 Melt-Solidified Bulks; (RE'RE"123)

Setoyama *et al*., *Supercond. Sci. Technol*., **28** (2015) 015014

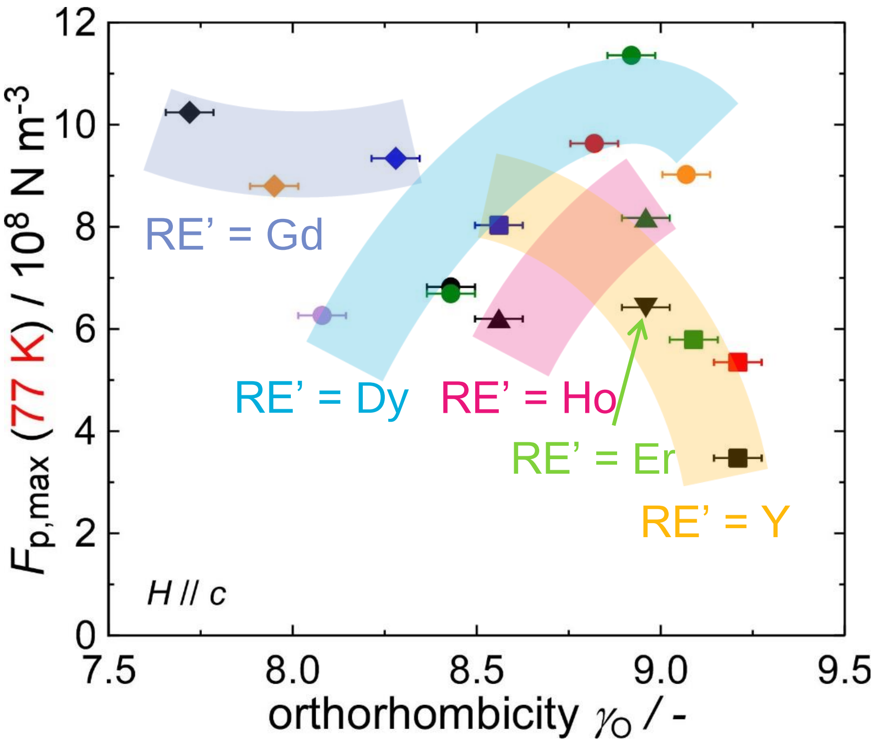
Orthorhombicity $\gamma_O = \dfrac{1000(b-a)}{b+a}$

a, *b* : *a*-, *b*-axis length (*b* > *a*)

Low γ_O ⟺ High level RE/Ba substitution

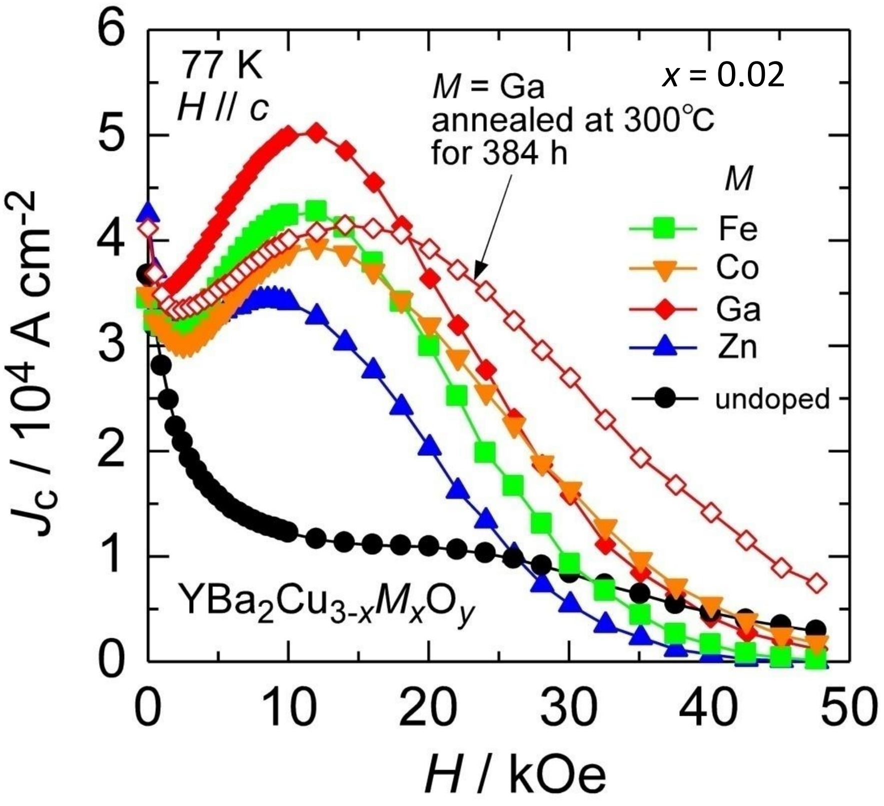


RE'	RE"	γ_O
Gd	Gd	7.7_2
Gd	Y	7.9_5
Dy	Dy	8.4_3
Dy	Er	8.4_3
Y	Dy	8.5_6
Y	Er	9.0_9

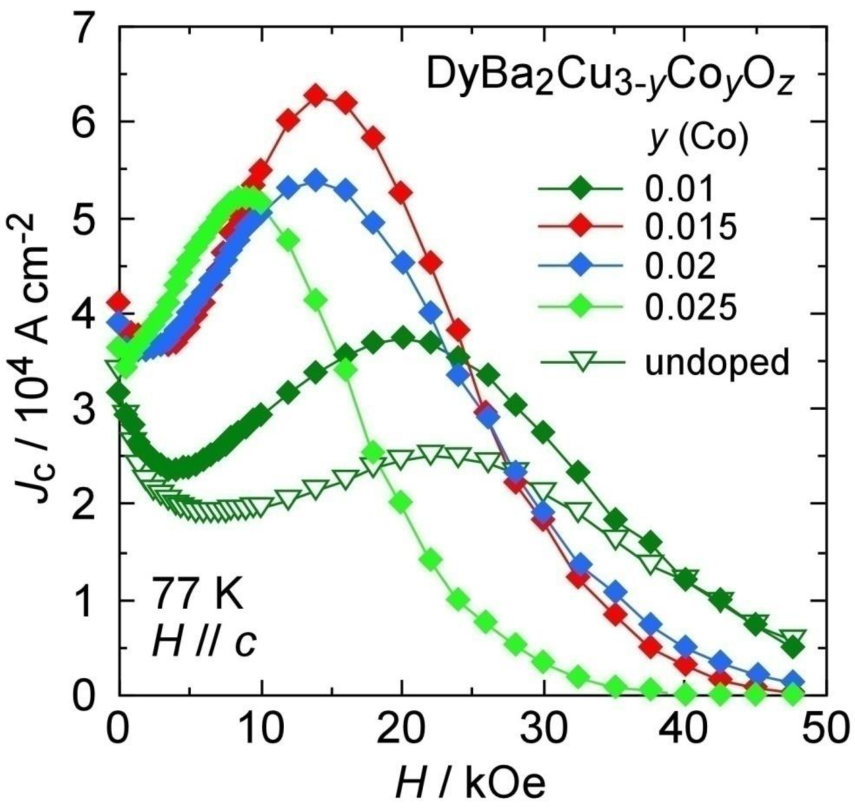


Effect of RE mixing ---
precise control of RE/Ba substitution level less than 1%

Dilute Doping for Cu in CuO Chain of RE123 Melt-Solidified Bulks



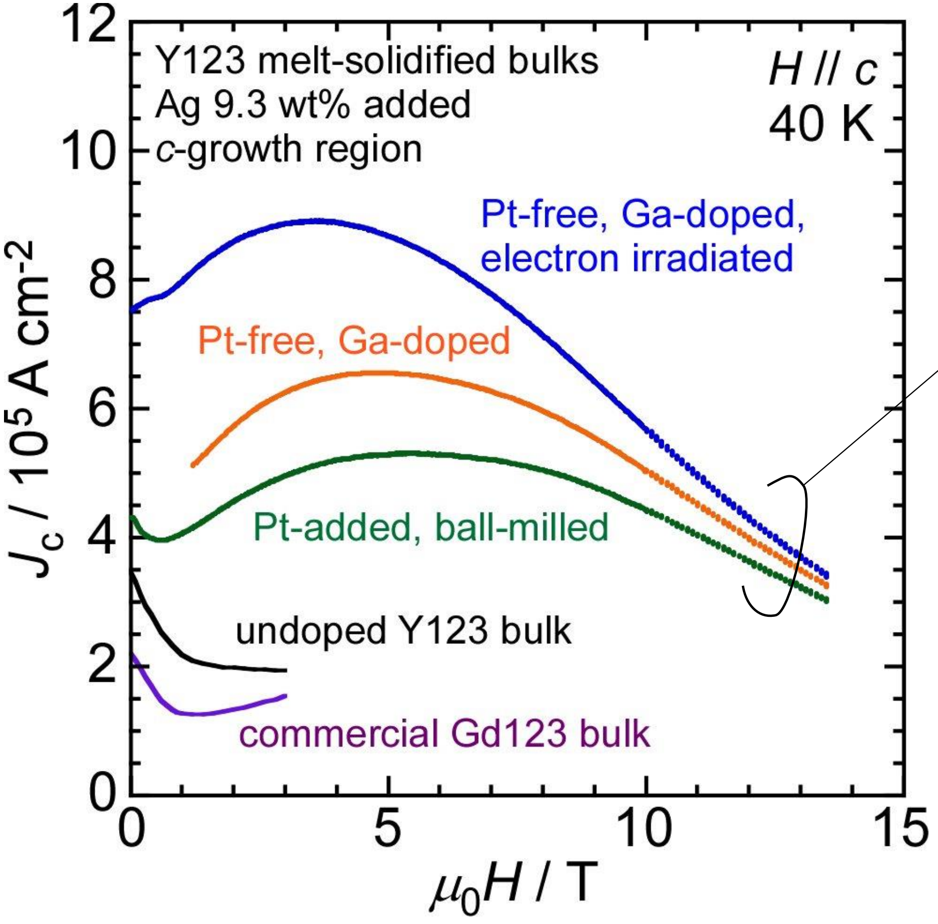
Ishii *et al.*, *APL* 89 (2006) 202513.



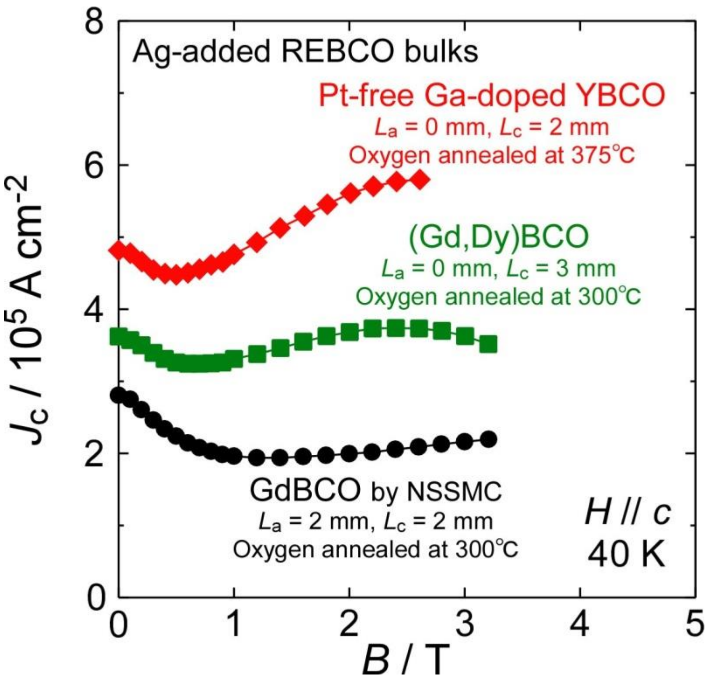
Dilute doping for Cu in Cu-O chain is the universally effective method for enhanced J_c of RE123 system.

(better than direct substitution for Cu in CuO_2 plane)

J_c-B Characteristics of Y123 Bulks at 40 K

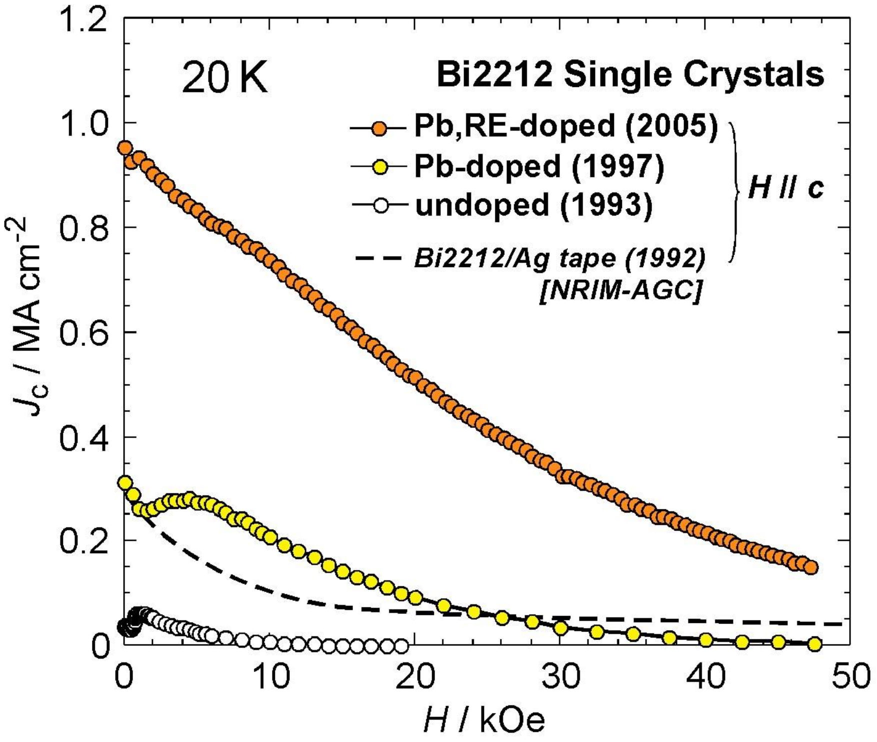


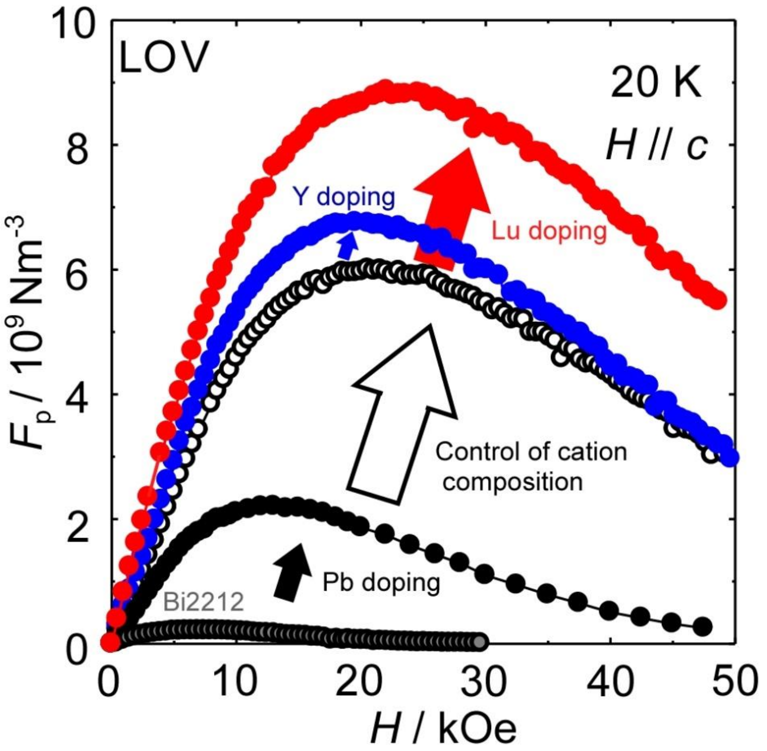
small pieces cut
from small bulks



Enhancement of J_c for Bi2212 Single Crystals by Pb-doping, Tuning of Cation Composition and Dilute Impurity Doping

Uchida *et al*., *J. Phys. Conf. Series* 43 (2006) 231-234.





Summary 1

Cation composition of cuprate superconducting materials should be the integral number ratio, 1:2:3, 2:2:2:3 etc..

--- increase in superconducting condensation energy
--- (dramatic) increase in pinning strength
--- large enhancement of J_c particularly at low temperatures

RE123 : Cation composition is already close to 1:2:3.

But it is not exact 1:2:3.

- RE211 included (=RE-rich) melt-solidified bulks
- CC prepared under non-equilibium conditions, PLD

Bi2223 : Cation composition is not well-controlled particularly for long length tapes.

- Adjusting 2:2:2:3
- increase in Pb-concentration

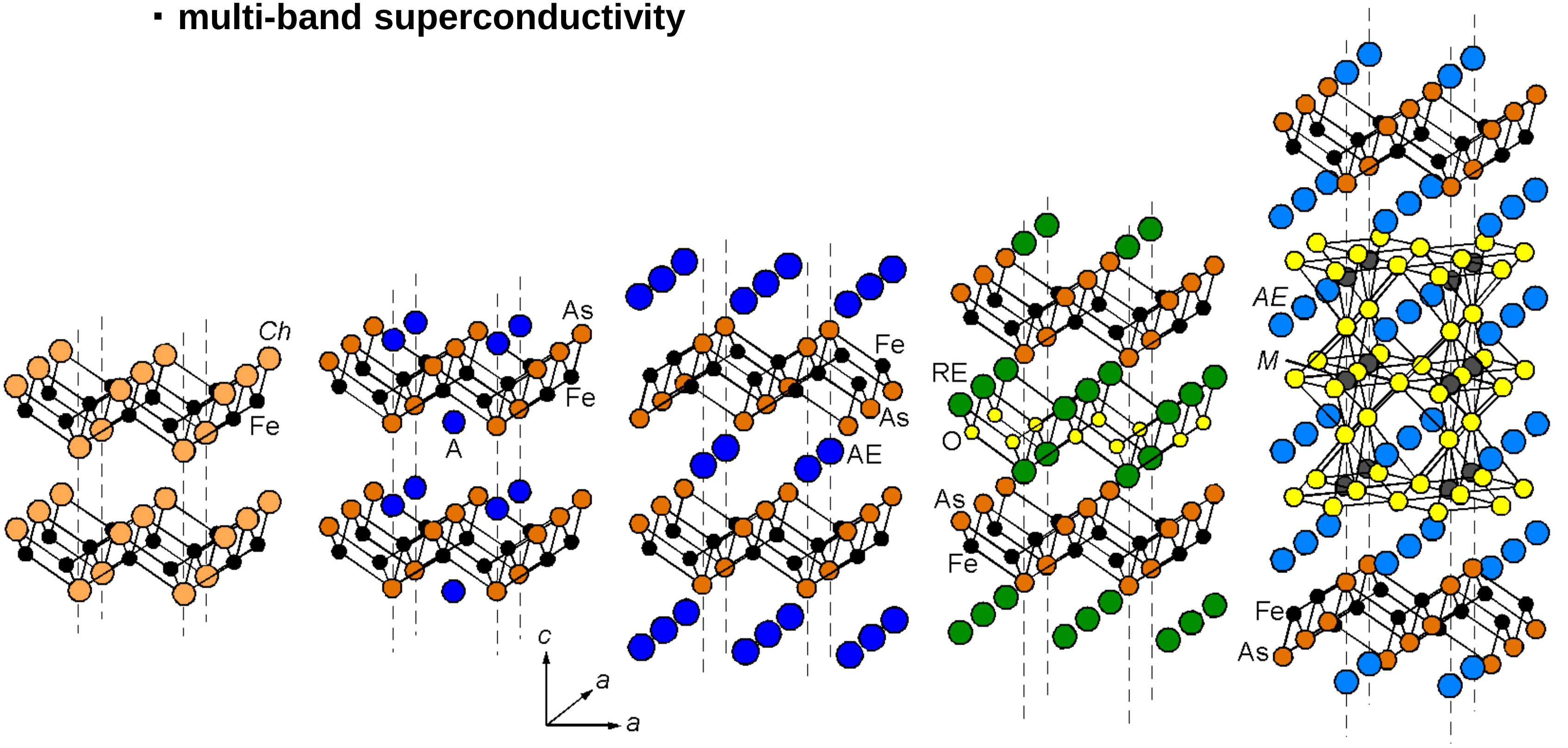
Large rooms are remaining for enhancement of J_c.

Iron-Based Superconductors

122 phase

Crystal Structures of Iron-Based Superconductors

- **basically tetragonal with long *c*-axes including one Fe plane (*ab*-direction)**
- **large structural variation at blocking layer**
- **multi-band superconductivity**



$\mathrm{Fe}Ch$
[11]
Ch: Se, Te, S

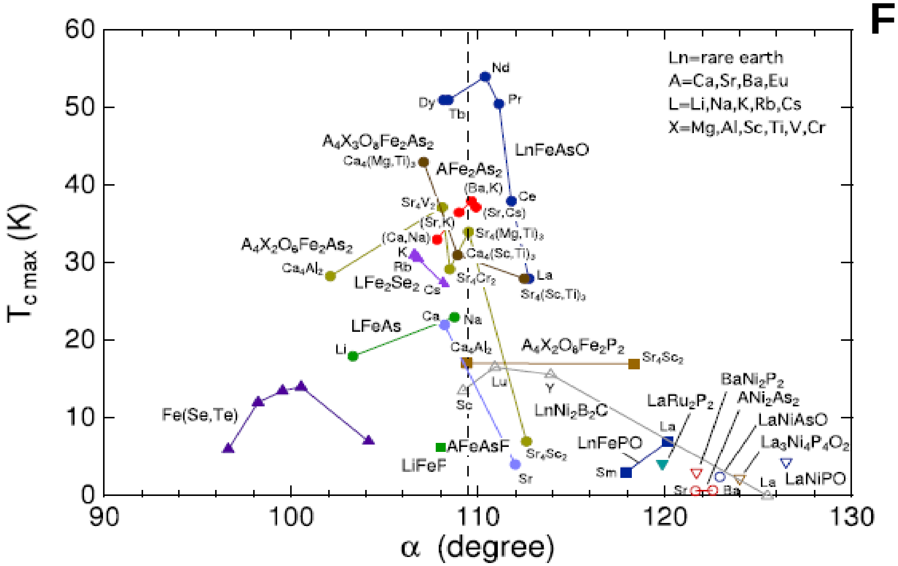
AFeAs
[111]
A: Li, Na

$\mathrm{AEFe_2As_2}$
[122]
AE: Ba, Sr

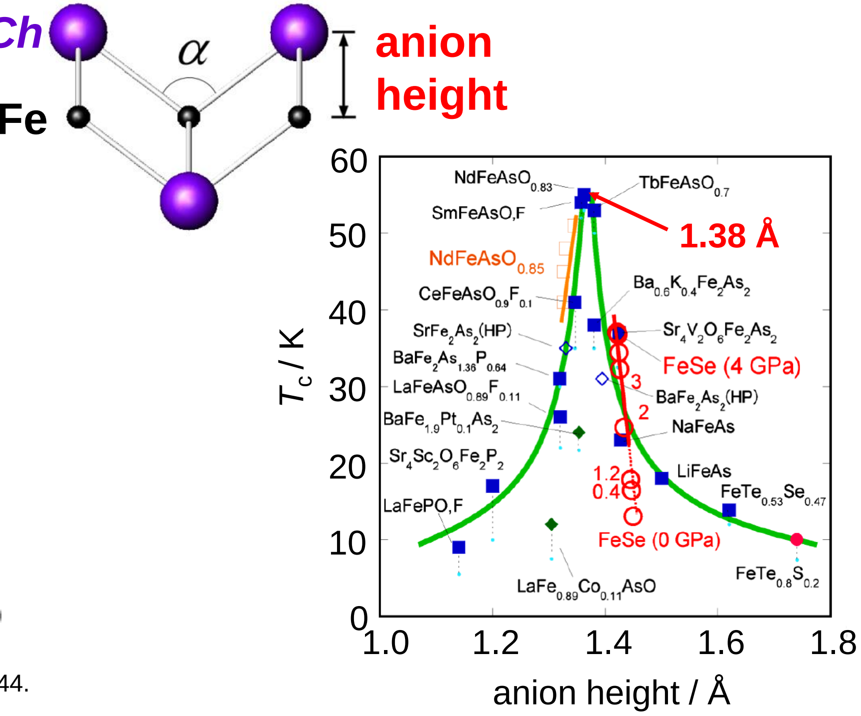
REFeAsO
[1111]
RE: rare earth

$(\mathrm{Fe_2As_2})(AE_4M_3\mathrm{O_8})$
[PB: 22438]
M : (Sc,Ti), (Mg,Ti)

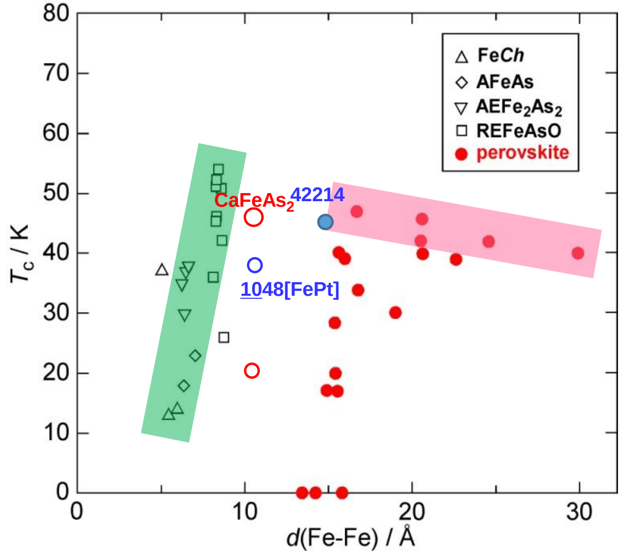
T_c



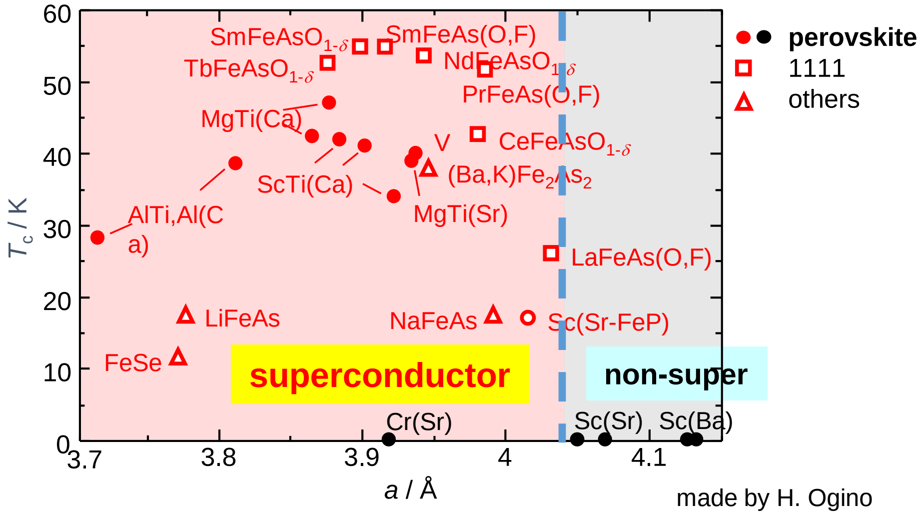
C.H. Lee *et al*., *Solid St. Comm.* **152** (2012) 644.



Y. Mizuguchi *et al*., *Supercond. Sci. Technol*. 23 (2010) 054013



H. Ogino *et al*., *Appl. Phys. Lett*. **97** (2010) 072506



made by H. Ogino

T_c of iron-based superconductor is

sensitive to local crystal structure at Fe*Pn* or Fe*Ch*, symmetry, anion height and Fe-Fe distance

not much sensitive to the carrier concentration (Wide T_c plateau often appears in the T_c vs x diagram.)

always deteriorated by impurity substitution for Fe.

Intrinsic T_c of Fe_2As_2 monolayer is ~50 K at the most. Slightly higher T_c of 1111 compounds can be explained by some additional reasons.

Bulk superconductivity with high T_c > 77 K --- long shot

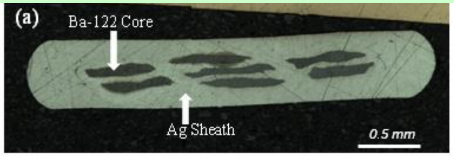
⬇

Practical applications < 30 K

122 System --- Small Anisotropy = Strong Grain Coupling

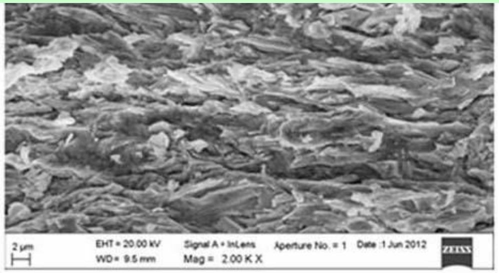
PIT method --- semi-closed tapes & wires ⇒ (AE,K)Fe_2As_2 can be used.

uniaxially-pressed 122/**Ag** tape



K. Togano *et al*., *SUPERCOM* (2013)

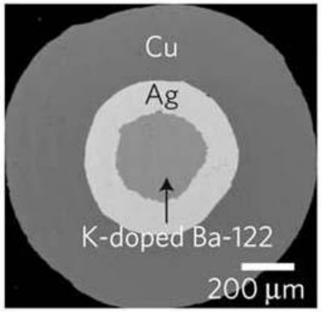
cold-rolled 122/Fe tape (0.6 mm^t)
Sn addition ⇒ texturing



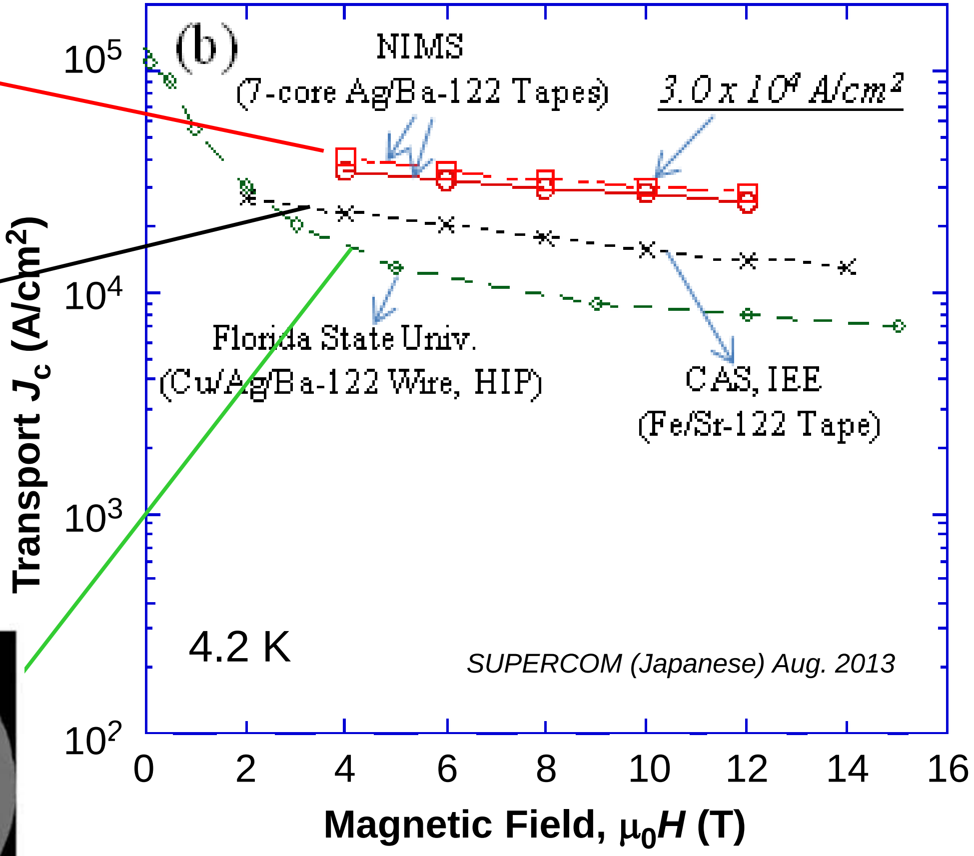
Z. Gao *et al*., *Sci. Reports*. **2** 998 (2012)

Ba122/**Ag**/Cu Round Wire

reactive ball-milling + low temp. & high pressure sintering (600°C, 2 GPa)



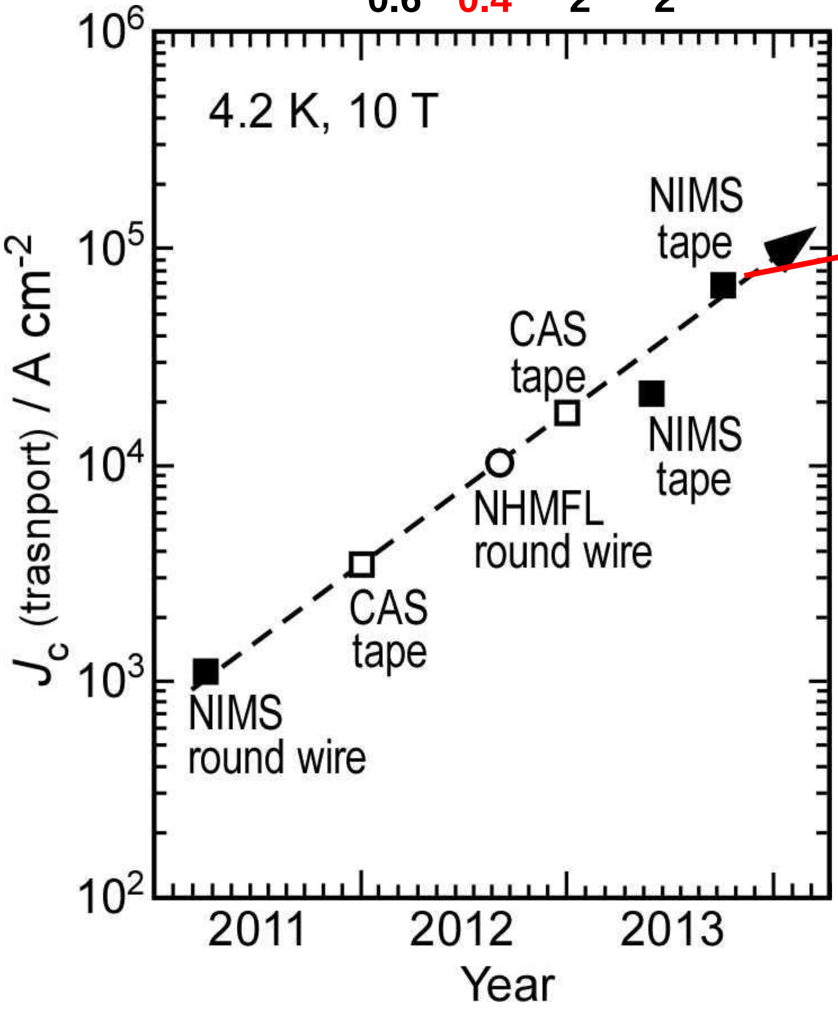
J.D. Weiss *et al*., *Nature Materials* **11** (2012) 682-685.



High I_c > 100 A at 4.2 K, 10 T

Rapid but Recently Sluggish Increase in J_c of 122 Tapes

$AE_{0.6}K_{0.4}Fe_2As_2$



Gao *et al.* (NIMS)

NIMS Tape
(2015)
SUS/Ag/122

Strategies up to the present time

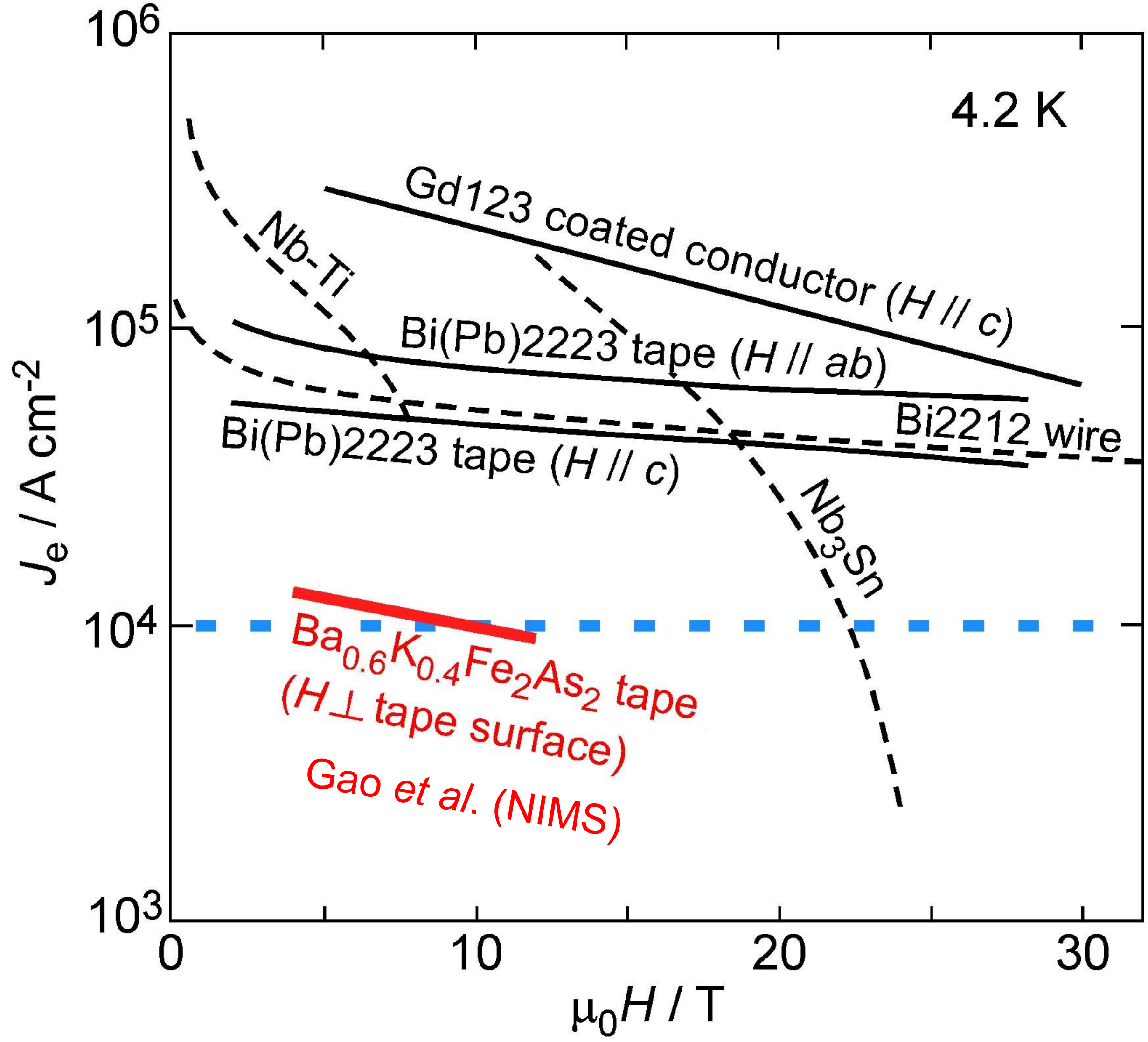
Improvement of phase purity

Increase in relative density
by uni-axial pressing with larger pressures

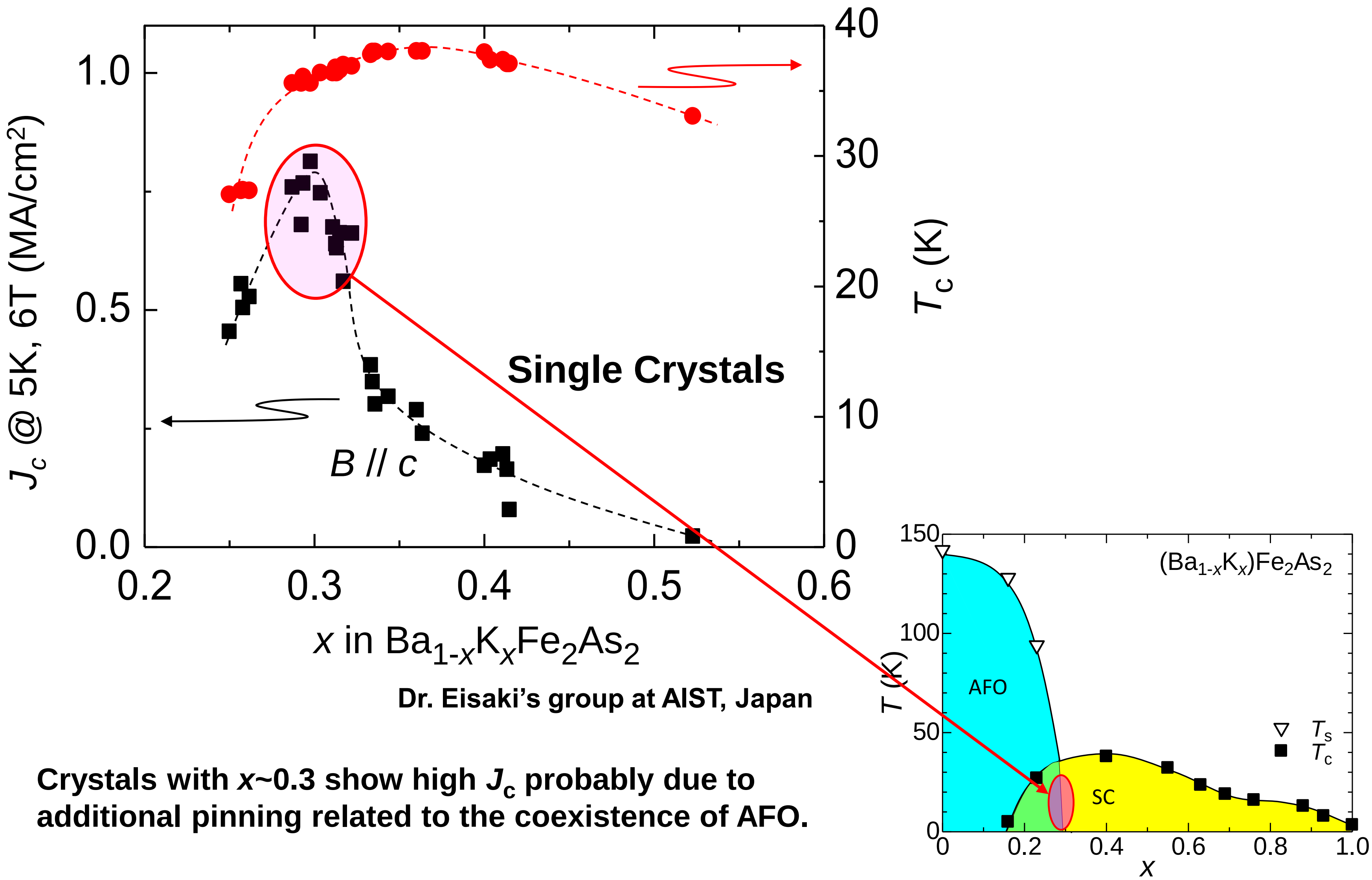
to enhance current path ratio

Another new idea is indispensable.

Comparison of Engineering J_c at 4.2 K



Optimal K composition for T_c is not best for J_c in field.

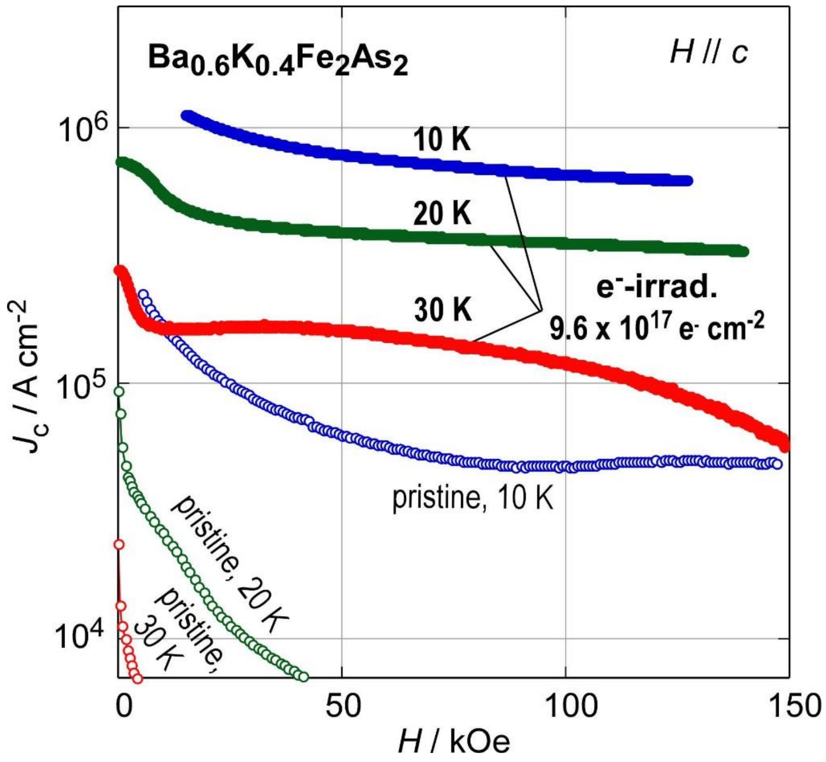


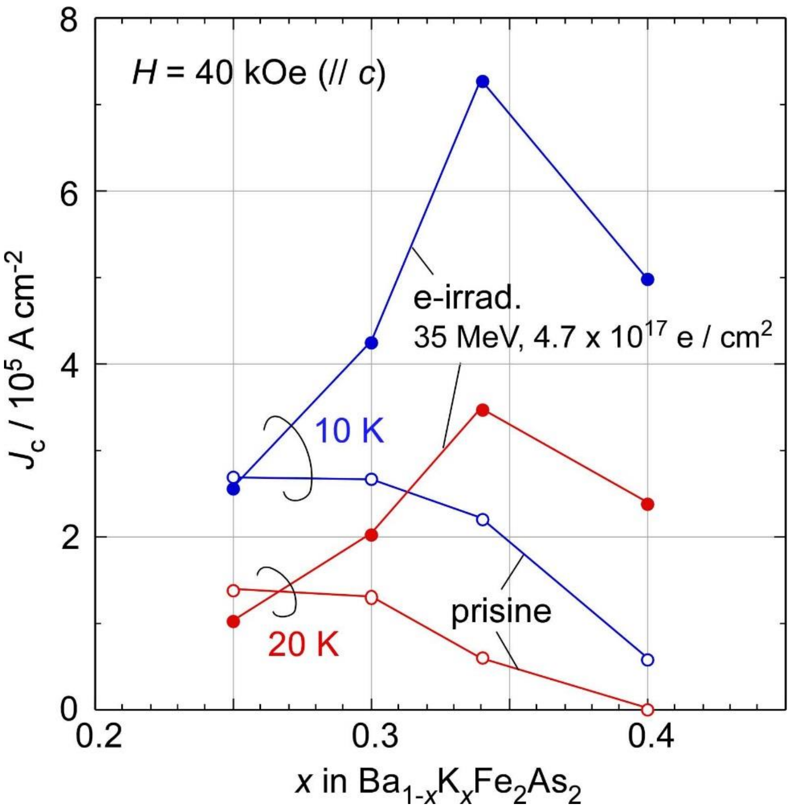
Dr. Eisaki's group at AIST, Japan

Crystals with x~0.3 show high J_c probably due to additional pinning related to the coexistence of AFO.

Electron irradiation is effective to enhance J_c of (Ba,K)122

Most effective at x = 0.35~0.40, far from AFO state

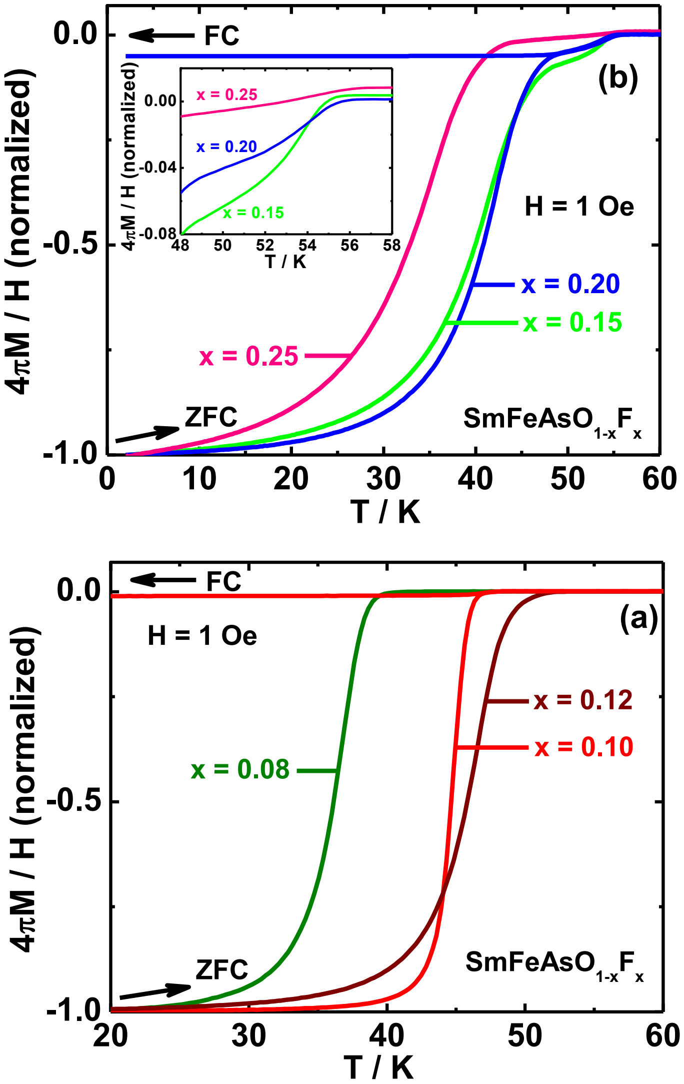




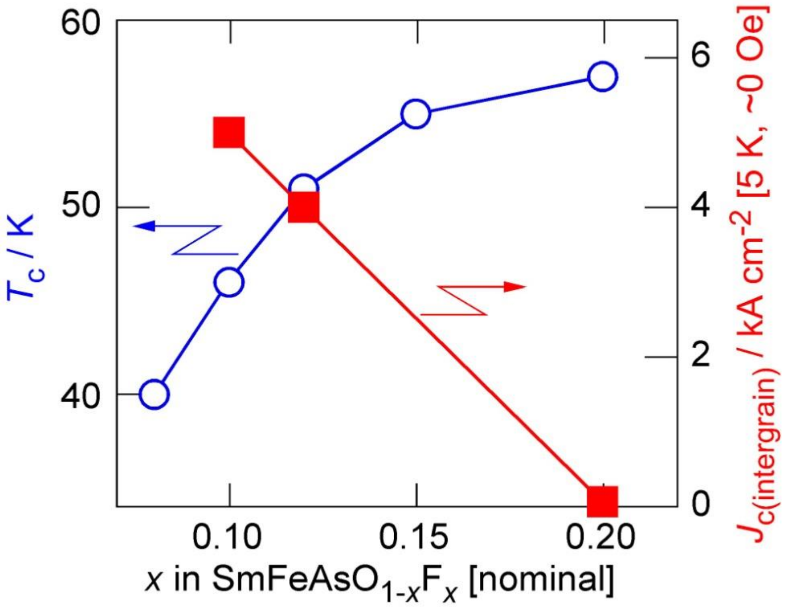
Collaboration of AIST-UT-AGU

An example of improving J_c by control of doping level

$SmFeAsO_{1-x}F_x$ sintered bulk



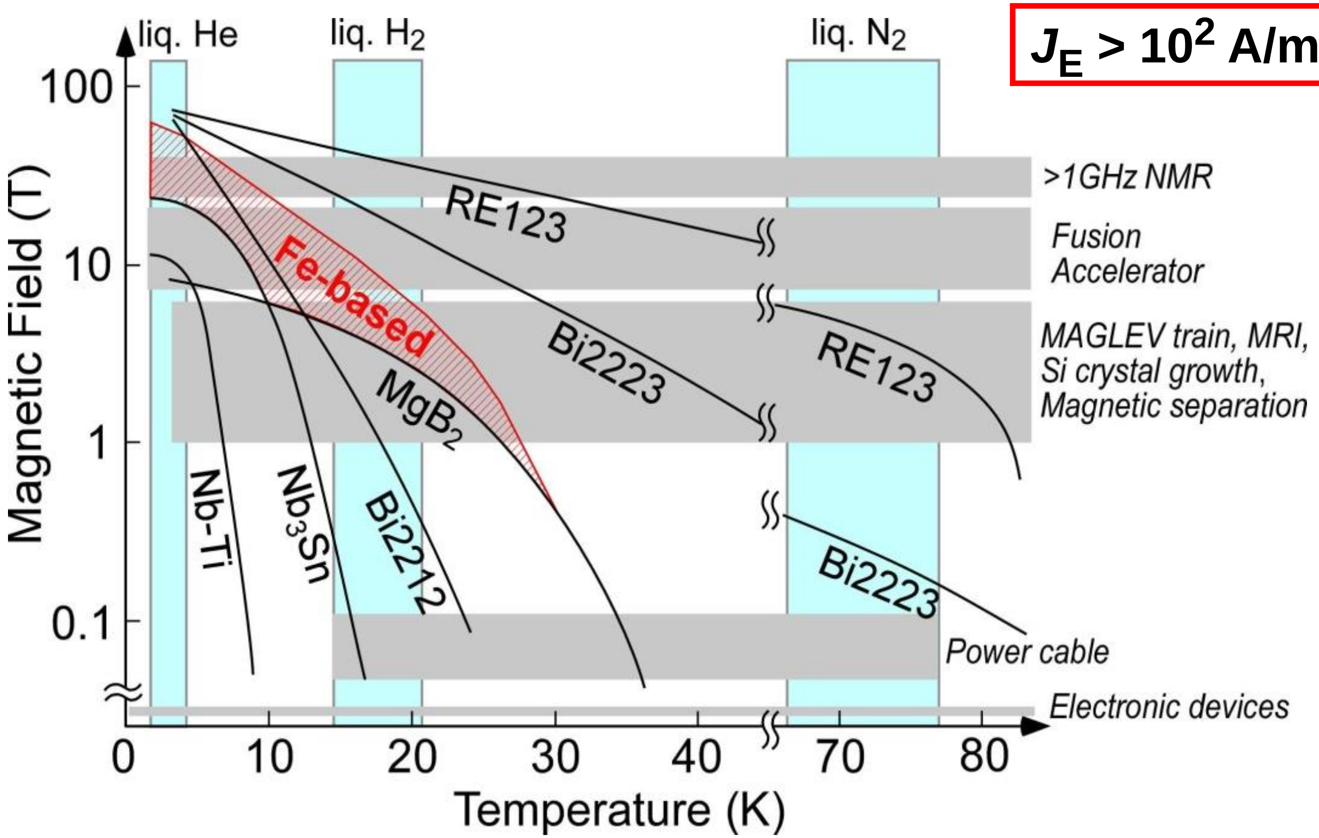
S.J. Singh *et al.*, *SuST* **26** (2013) 065006.



T_c (max) $\neq$ $J_{c,\text{intergrain}}$ (max)

Possible Application Condition of Iron-Based Superconducting Materials

$J_E > 10^2$ A/mm^2



More practical conditions for iron-based superconductors;
high performance, long length, homogeneous, high productivity, low cost, etc.

Summary 2

My opinion on iron-based superconductors

**No iron-based superconducting long tapes so far
Does it need several years more?**

**Some breakthroughs must be indispensable.
New technique besides purification and densification, what is?**

Controls of chemical composition and grain orientation might contribute to improve absolute values and homogeneity of J_c of long tapes

**We must understand;
how inhomogeneous in the superconducting state,
how inhomogeneous superconductivity should be controlled.**

These are common problems in superconductors and more serious in short ξ SC.