IEEE/CSC & ESAS SUPERCONDUCTIVITY NEWS FORUM (global edition), April 2016.
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Recent progress of REBCO HTS bulk

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RE in $(RE)Ba_2Cu_3O_7$	**La**	**Nd**	**Sm**	**Eu**	**Gd**	Dy	Ho	**Y**	Er	Yb
Melting point (± 5°C)	**1068**	**1085**	**1060**	**1046**	**1040**	1010	1005	**1005**	990	960
T_c (K)	**----**	**95 PO_2**	**93.5 PO_2**	**93 PO_2**	**92.5 PO_2**	92 air	92 air	**92 air**	92 air	92 air
J_c @77K; 1T x KA/cm^2	**----**	**40-50**	**40-50**		**50-60**			**20-30**		
B_{irr} (T); 77 K	**----**	**8–10**	**6 - 8**		**6 - 7**			**5 - 6**		

Better superconducting performance

Potential of LREBCO (LRE=Nd,Sm..) bulks

- Advantages compared to YBCO:

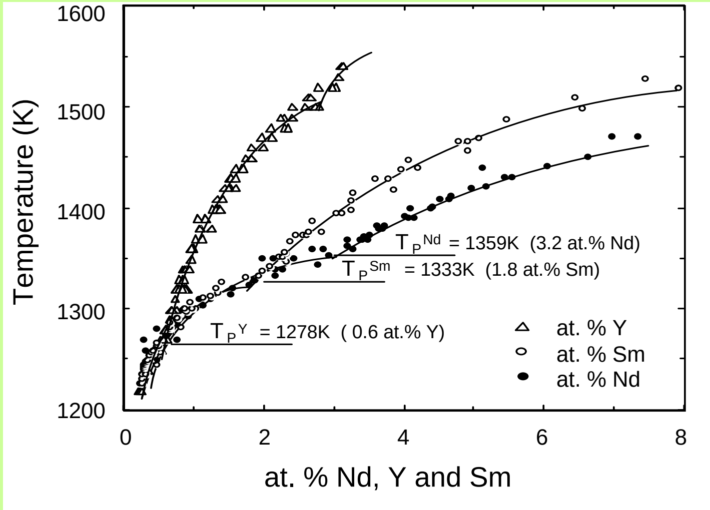
※ Exhibit better superconductivity

High T_c

High J_c at a high applied magnetic field

※ ***High growth rate***

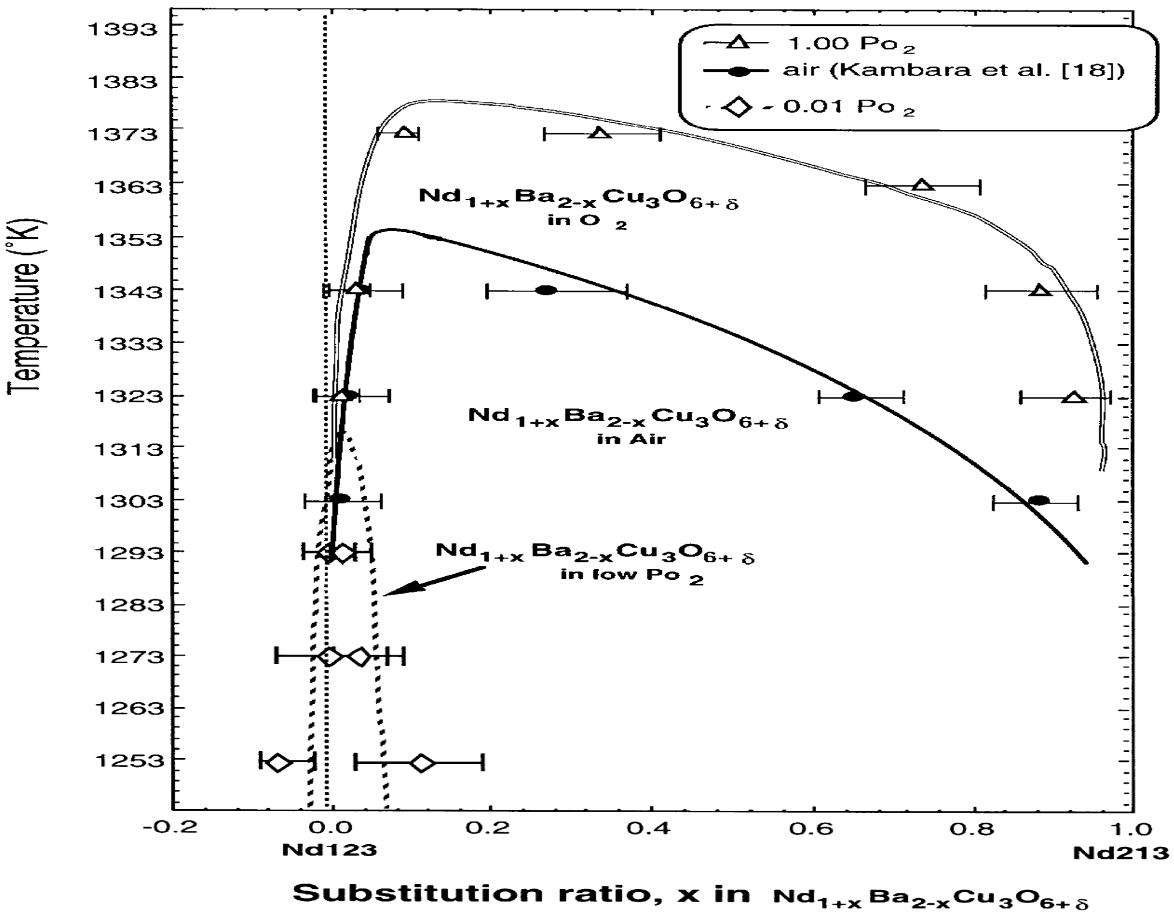
due to high RE solubility in solvent

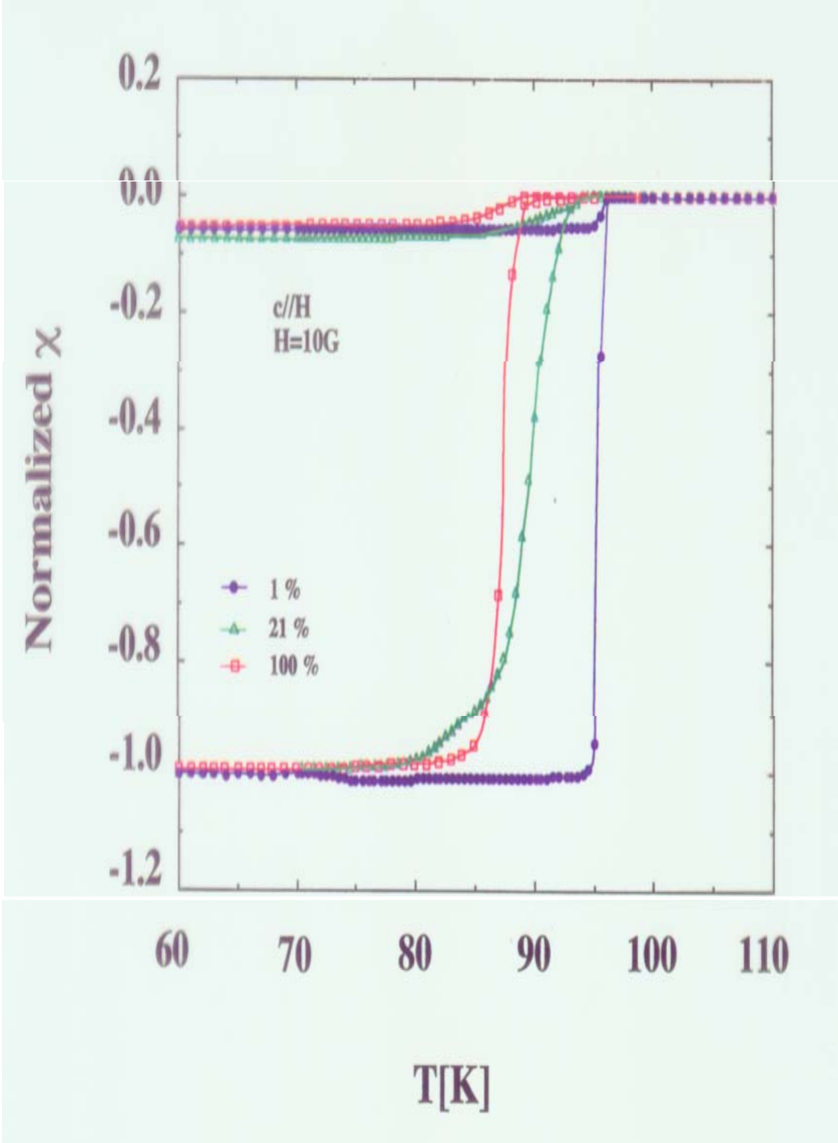


- Problems to be solved :

✓ ※ Formation of solid solution ($LRE_{1+x}Ba_{2-x}Cu_3O_y$) due to ***LRE/Ba substitution***, leading to low T_c

※ Lack of ***suitable seed*** due to high peritectic temperature T_p

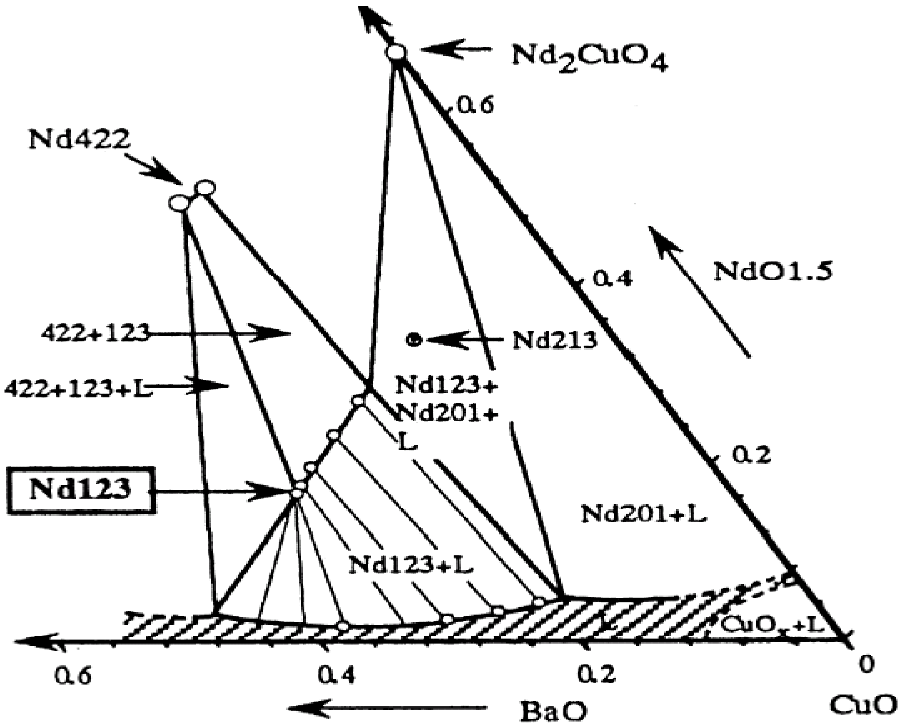


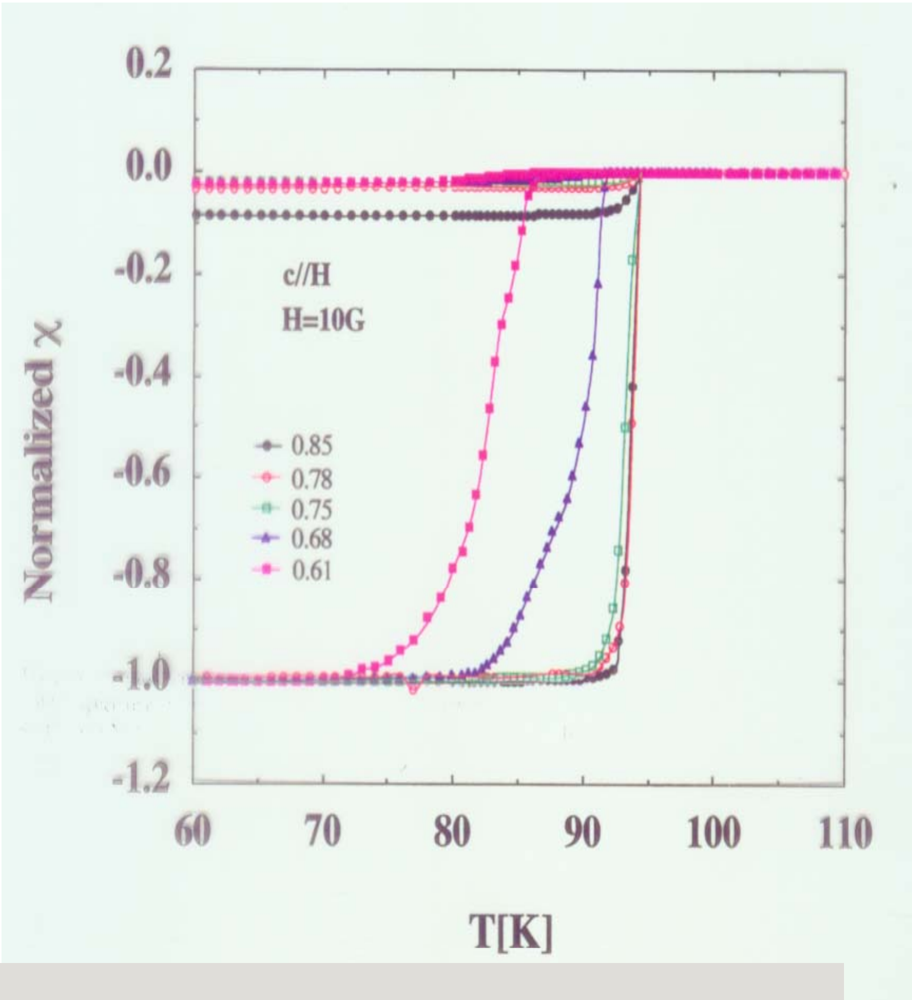


1. Oxygen-controlled growth

$Nd_{1+x}Ba_{2-x}Cu_3O_{7-y}$

Nd-Ba-Cu-O system



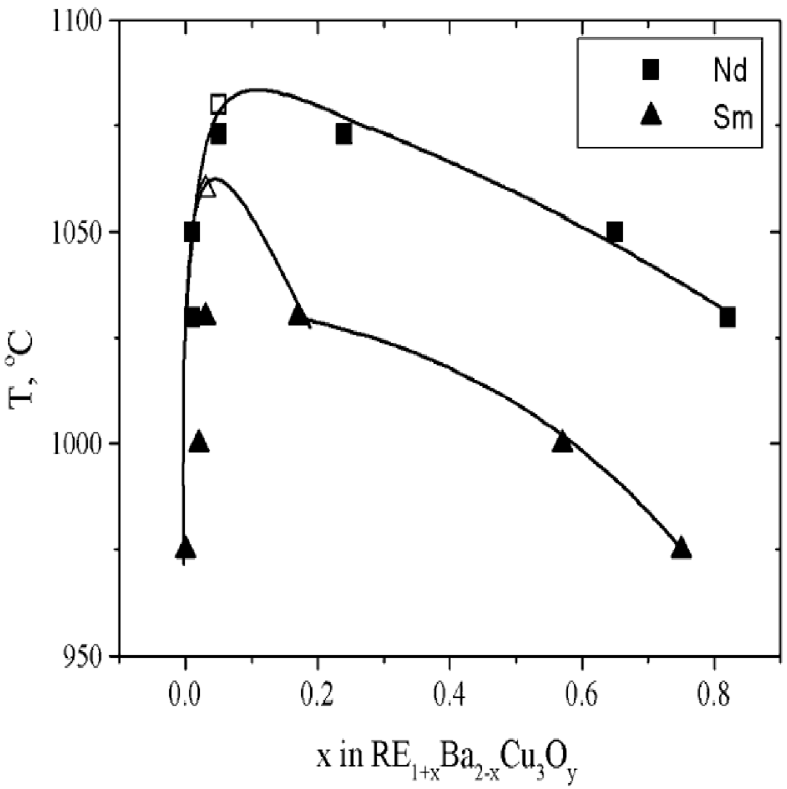


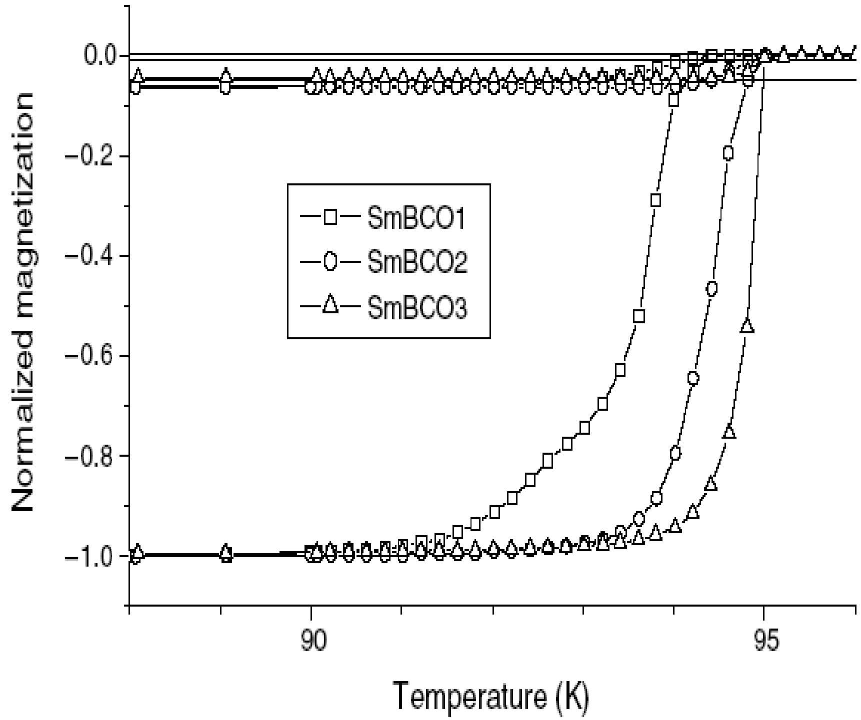
x ⟷ *p(O₂), T= constant*

2. Composition-controlled growth

95 K SmBCO grown in 1 atm oxygen pressure by TSSG

Supercond. Sci. Technol. **17** (2004) L47





SmBCO1,2,3 crystals grown from different liquid with Ba/Cu =0.50,0.52,0.54

3. Temperature-controlled growth

RE in $(RE)Ba_2Cu_3O_7$	**La**	**Nd**	**Sm**	**Eu**	**Gd**	Dy	Ho	**Y**	Er	Yb
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J_c @77K; 1T x KA/cm²	**----**	**40-50**	**40-50**		**50-60**			**20-30**		
B_{irr} (T); 77 K	**----**	**8–10**	**6 - 8**		**6 - 7**			**5 - 6**		

Cation stoichiometry of Sm123 is more controllable: Wide growth window in liquid composition and oxygen pressure

Effects of adding Ba-rich $Sm_2Ba_4Cu_2O_9$ phase on air-processed SmBCO superconductor bulks

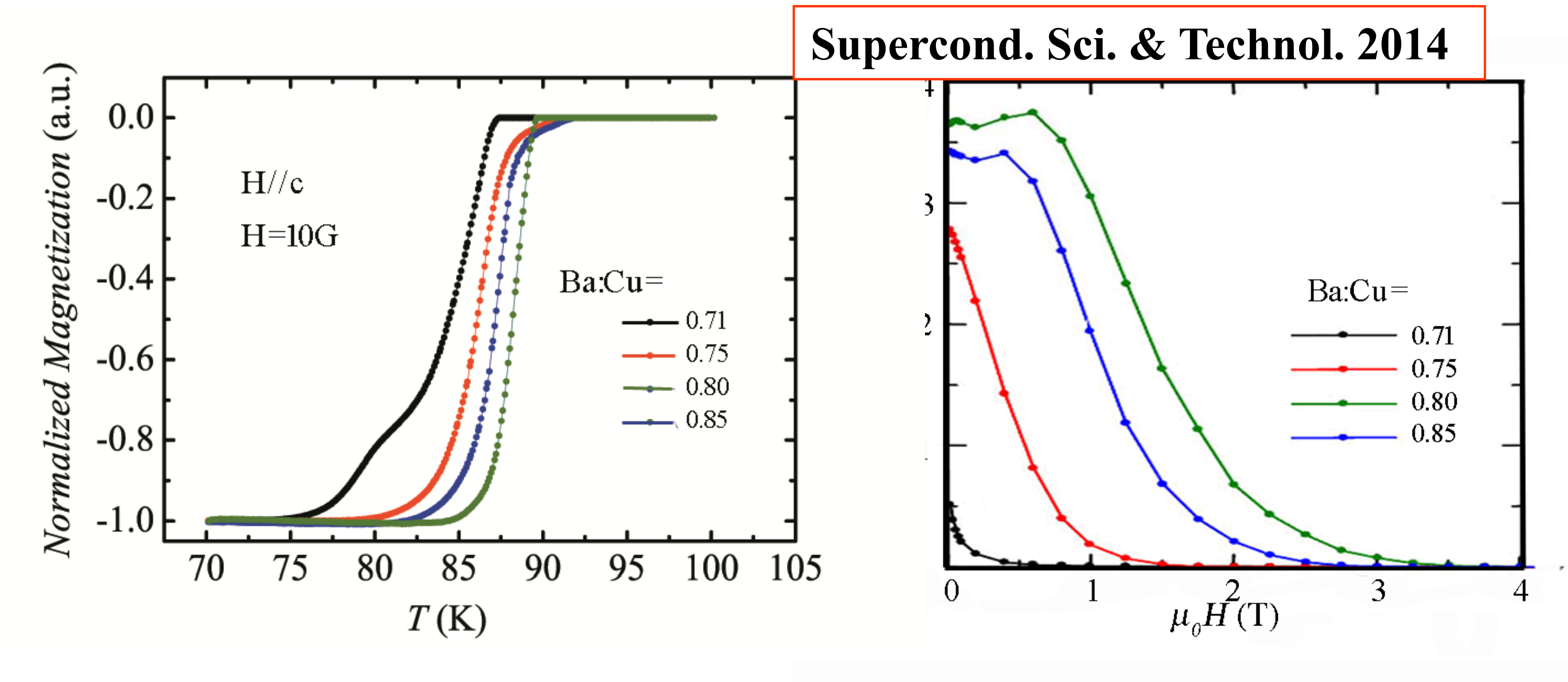
Supercond. Sci. & Technol. 2009

Optimized addition of Ba-rich phase

Ba-rich addition	pre-calcinated Ba-Cu-O compound	Sm210	BaO_2(with Sm211)	Sm242 (our lab)			
Addition amount	Ba mol% =0.3302	40 mol%	2-4 wt%	5 mol%	10 mol%	15 mol%	30 mol%
Ba/Cu ratio in precursor	0.755	0.8	0.72-0.75	0.71	0.75	0.79	0.89
T_c(K)	90	89	93	94	94	93	<88
$\triangle T_c$(K)	2	1.5	1	5	1	3	>10

the appropriate ratio of Ba:Cu ranges from 0.72 to 0.8

Effects of adding Ba-rich $Nd_2Ba_4Cu_2O_9$ phase on air-processed NdBCO superconductor bulks



T_c and J_c were effectively enhanced with increasing the Ba/Cu ratio (BCR) . Optimal properties were achieved when BCR reaches 0.80.

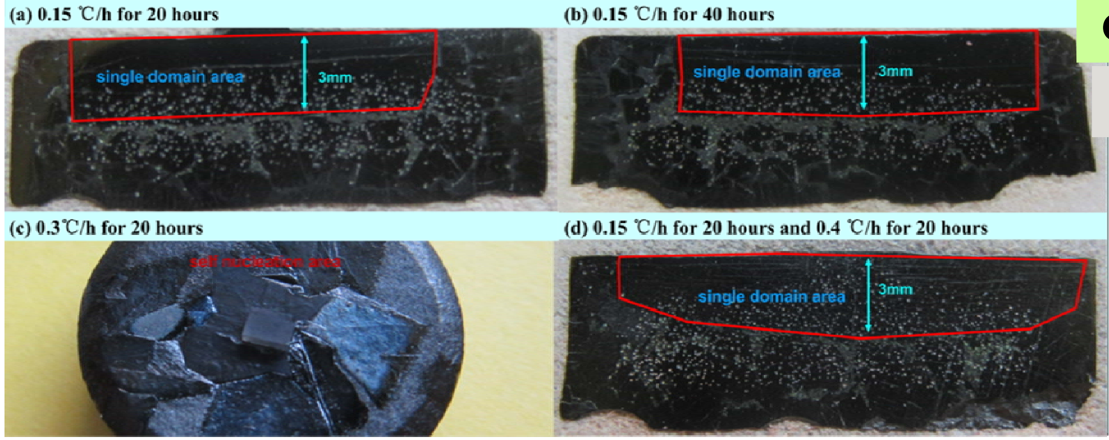
Trapping mode controlled continuous growth of SmBCO bulk

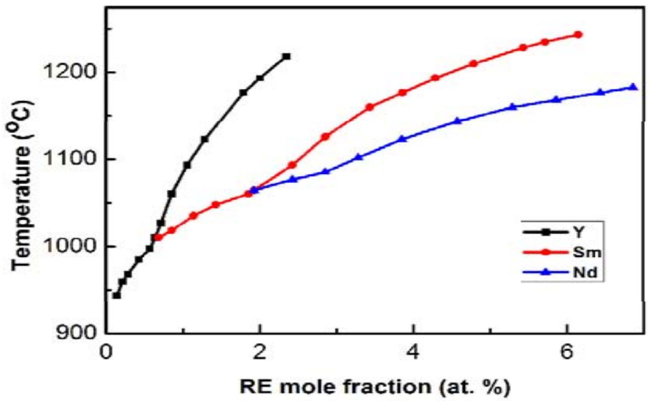
Either self-nucleation or discontinuous growth occurs in air-processed SmBCO

BN Peng Cryst. Growth & Des. (2013)

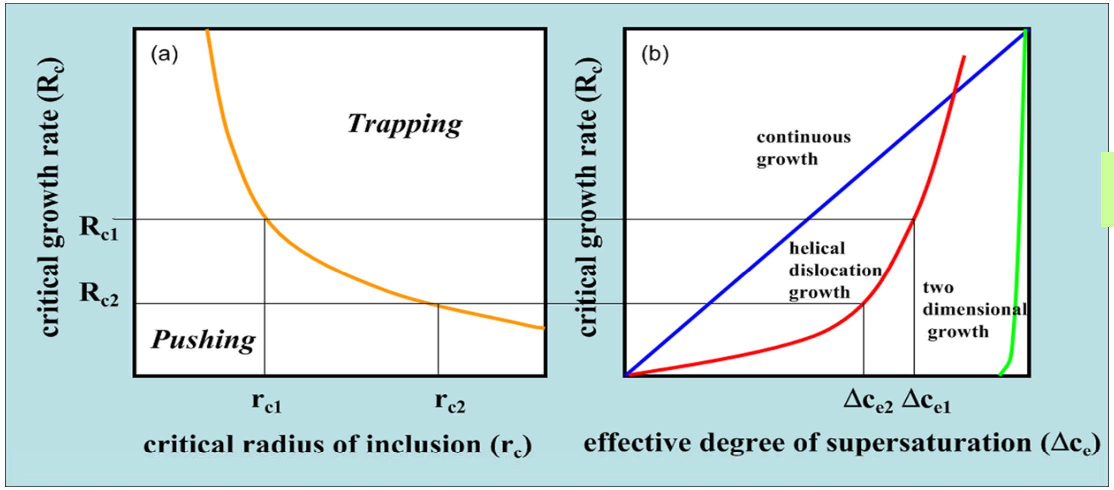
Reduction of t.c.s value caused discontinuous growth

t.c.s : temperature coefficient of solubility





211 caused discontinuous growth



$$J = \frac{\Delta c}{\Delta t} = \left(\frac{\partial c}{\partial T}\right)_T \cdot \frac{\Delta T}{\Delta t} = \left(\frac{\partial c}{\partial T}\right)_T \cdot R$$

R=constant in a normal cooling process

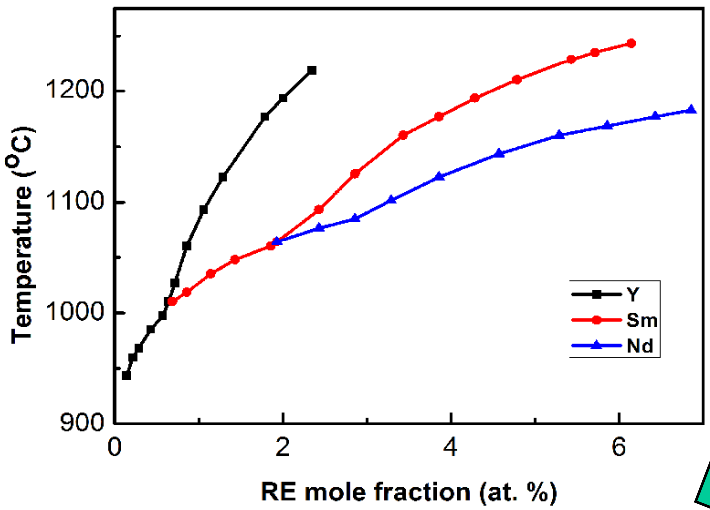
$\left(\frac{\partial c}{\partial T}\right)_T$ dereasing sharply in SmBCO system

i.e. noticeable reduction of t.c.s with decreasing temperature !!!

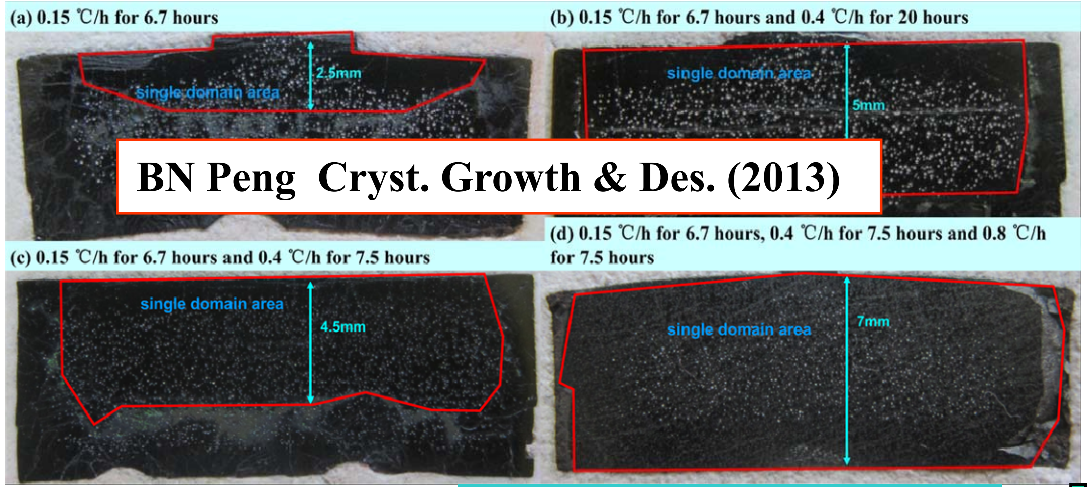
211 coarsening/ 211 segregation → **Reduction in effective supersaturation** → **Growth slows down and terminates** ← **Reduction in J (solute flux)**

$$J = \frac{\Delta c}{\Delta t} = \left(\frac{\partial c}{\partial T}\right)_T \cdot \frac{\Delta T}{\Delta t} = \left(\frac{\partial c}{\partial T}\right)_T \cdot R$$

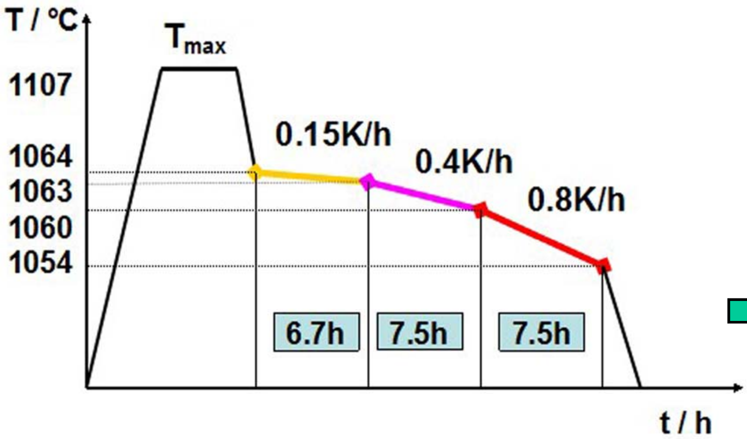
$\left(\frac{\partial c}{\partial T}\right)_T$ dereasing sharply in SmBCO system

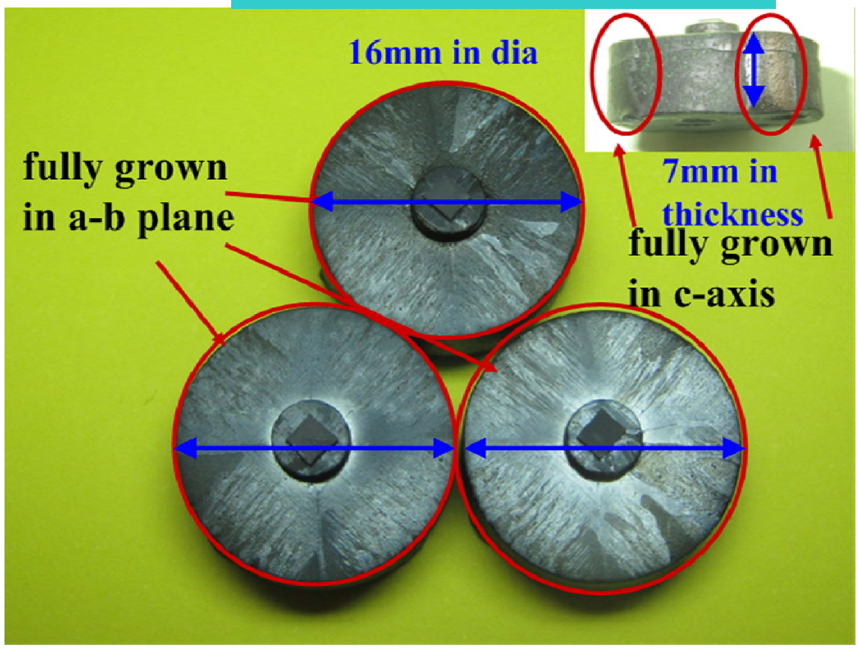


Accelerated cooling rate at a proper time



Growth continues ⟷ **211 Coarsening and segregation are partially suppressed**





Optimized profile for continuous growth of SmBCO bulks

Potential of LREBCO (LRE=Nd,Sm..) bulks

- Advantages compared to YBCO:

※ Exhibit better superconductivity

High T_c

High J_c at a high applied magnetic field

※ ***Higher growth rate***

due to high RE solubility in solvent

- Problems to be solved :

※ Formation of solid solution ($LRE_{1+x}Ba_{2-x}Cu_3O_y$) due to ***LRE/Ba substitution***, leading to low T_c

✓ ※ Lack of ***suitable seed*** → **Genetic bulk seed ; REBCO film seed**

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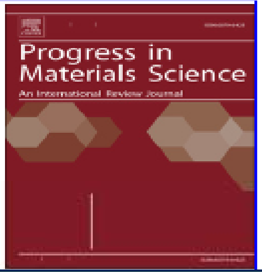


Our review paper on Prog. in Mater. Sci. 68 (2015) 97-159 (IF= 27.42）

Peritectic melting of thin films, superheating and applications in growth of REBCO superconductors

CrossMark

Amazing superheating phenomenon

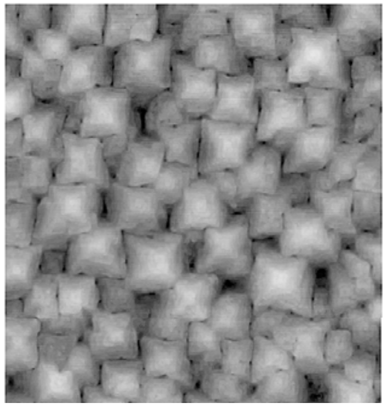
Low Peritectic Temperature (1010°C) YBCO Thin-film

↓

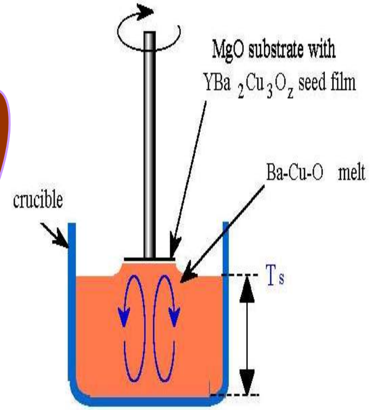
Seeding at High Processing Temperature (~1057°C)

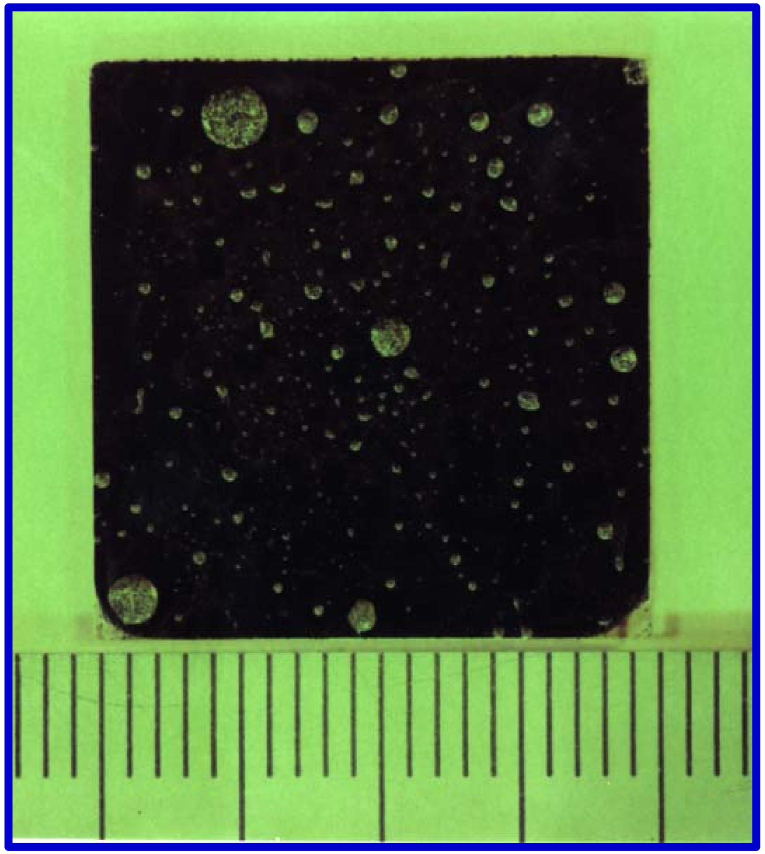
↓

Growing NdBCO Thick-films



Large Sized As-grown NdBCO LPE Thick Film

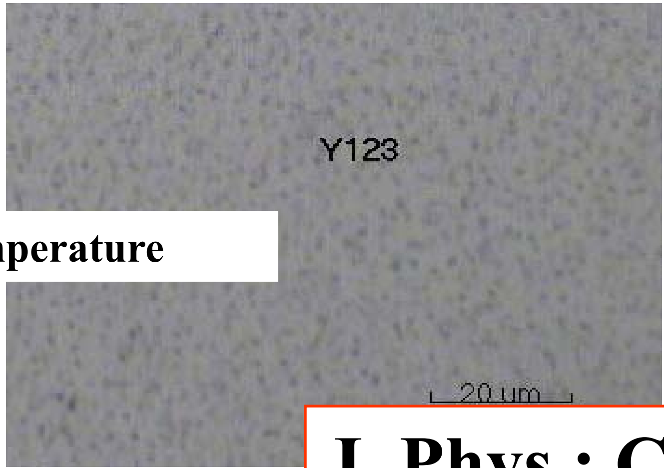




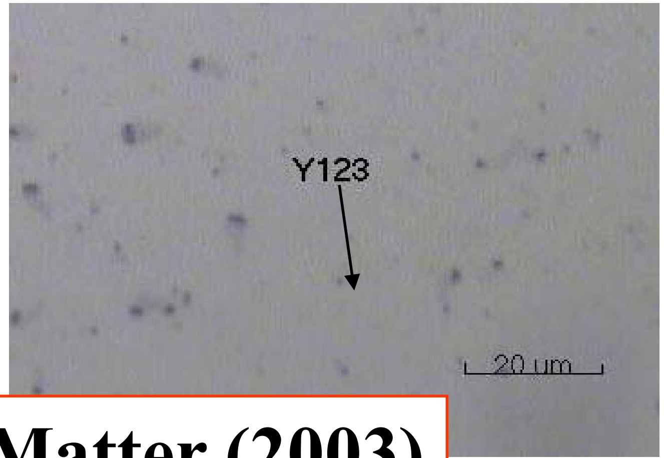
- 20x20 mm^2 in the a-b plane.
- ~ 0.1mm in the c-axis.
- Growth rate ~ 10μm/min.
- **<u>YBCO thin film seed.</u>**
- ***Growth temperature=1057°C***

In-situ observation of the YBCO melting

Room temperature

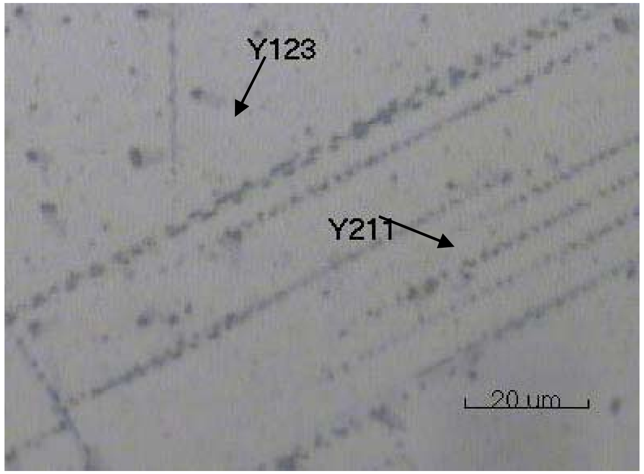


1010ºC
3min

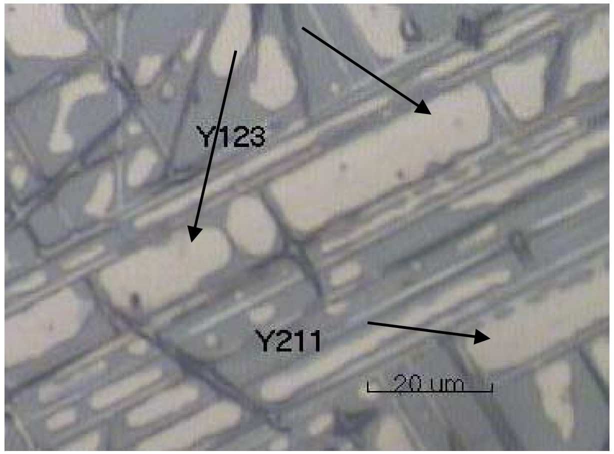


J. Phys.: Condens. Matter (2003)

1050ºC
3min



1060ºC
3min



1) YBCO thin film can superheat about 50K;

2)orientation relationship:<001>$(100)_{Y211}$ // <110>$(001)_{MgO}$

Universal superheating of thin films & Wide feasibility in seeding the growth of REBCO

1. Using YBCO film-seed, LPE growth was succeeded in various REBCO oxides

2. REBCO film-seeds were extended in various growth processes including TSMG

3. Various REBCO films universally possess high thermal stability in TSMG

4. YBCO films on various substrates

Using YBCO film-seed, LPE growth was succeeded in various REBCO oxides

RE123 systems

- NdBCO (~1057°C)
- SmBCO (1020~1055°C)

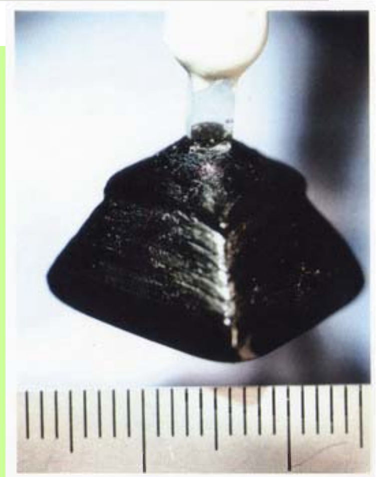
Mixed RE123 systems

- Ni-NdBCO (~1057°C)
- Sr-NdBCO (~1057°C)
- Nd-YBCO (1000~1030°C)
- Yb-YBCO (970~980°C)
- Ca-YBCO (957~980°C)
- Zn-YBCO (966~984°C)

REBCO film-seeds were extended in various growth processes

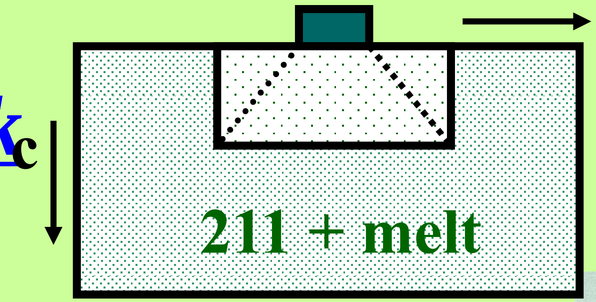
- ***Top-Seeded Solution-Growth (TSSG)***

  -Single crystal.



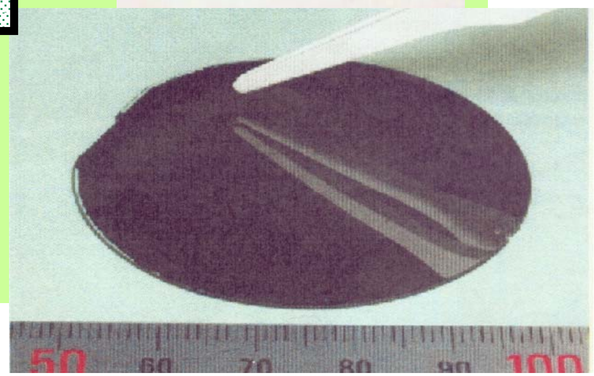
- ***Top-Seeded Melt-Growth (TSMG)***

  -single domain bulk

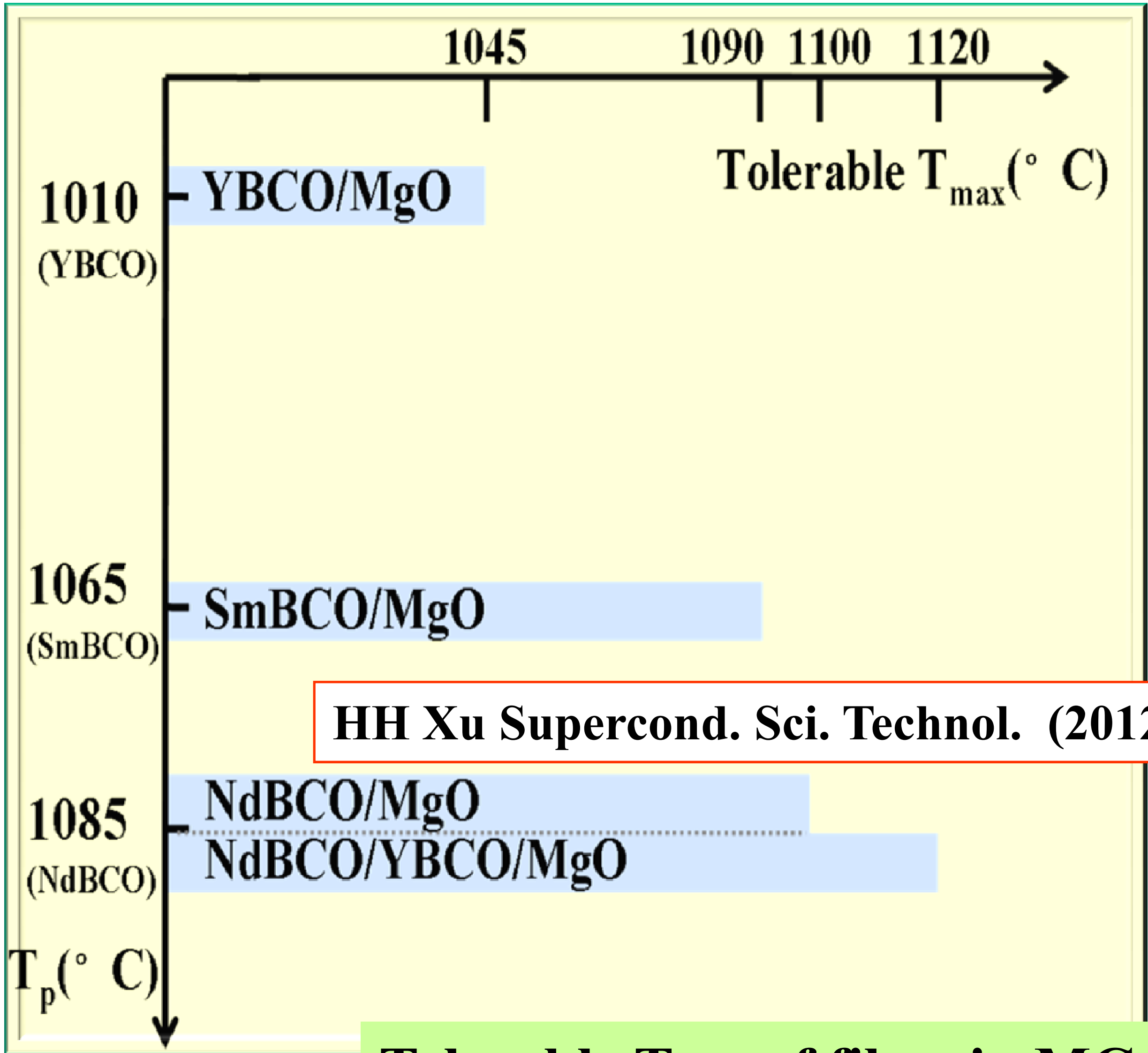


- ***Liquid phase epitaxy growth (LPE)***

  -thick film

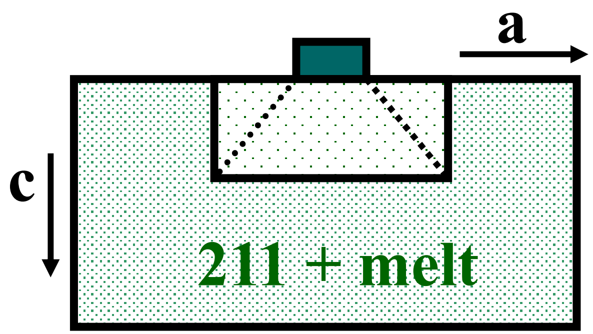


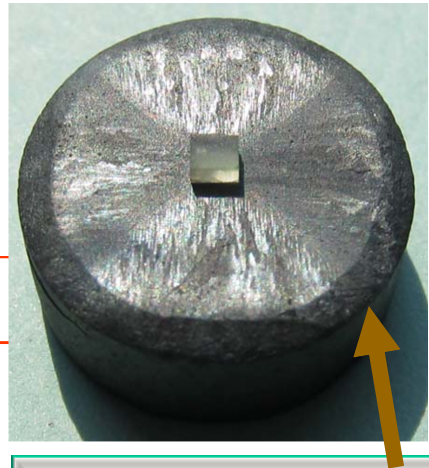
Various REBCO films universally possess high thermal stability in Top-seeded Melt-growth



HH Xu Supercond. Sci. Technol. (2012)

Tolerable T_{max} of films in MG





NdBCO bulk (16 mm in dia.)
Tmax= 1117 °C for1.5 h

YBCO films on *various* substrates

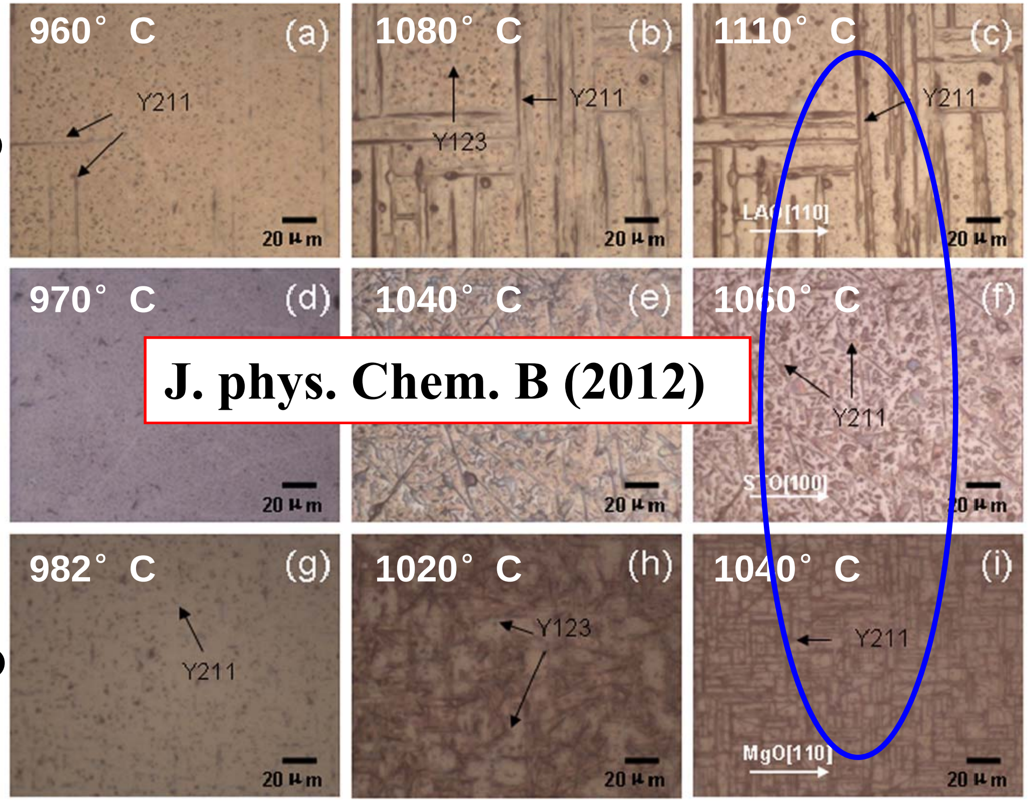
Only for Y123/MgO?

a universal superheating phenomenon

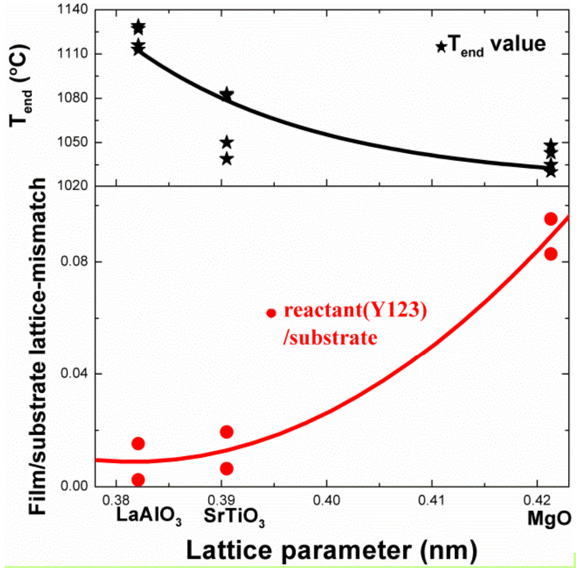
Y123/LAO

Y123/STO

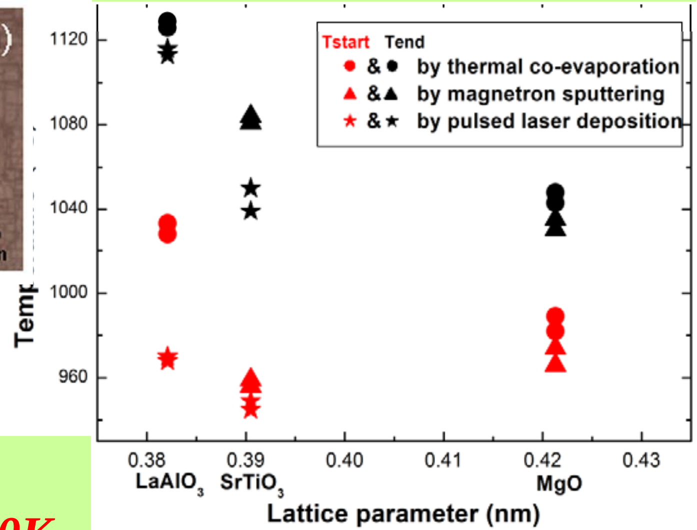
Y123/MgO



J. phys. Chem. B (2012)



Indicating a substantial superheating phenomenon



Peritectic melting: α (Y123)→β(Y211)+ Liq. on substrate

Thermal stability: Y123/LAO>Y123/STO>Y123/MgO

Extremely high level of superheating of Y123/LAO, *over 100K*

Superheating mechanism of YBCO thin film

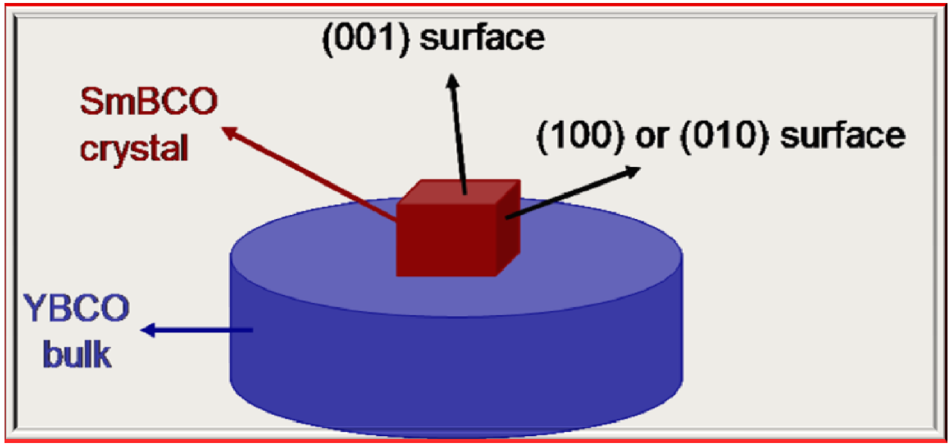
YBCO oxide: Anisotropic surface energy in crystalline plane

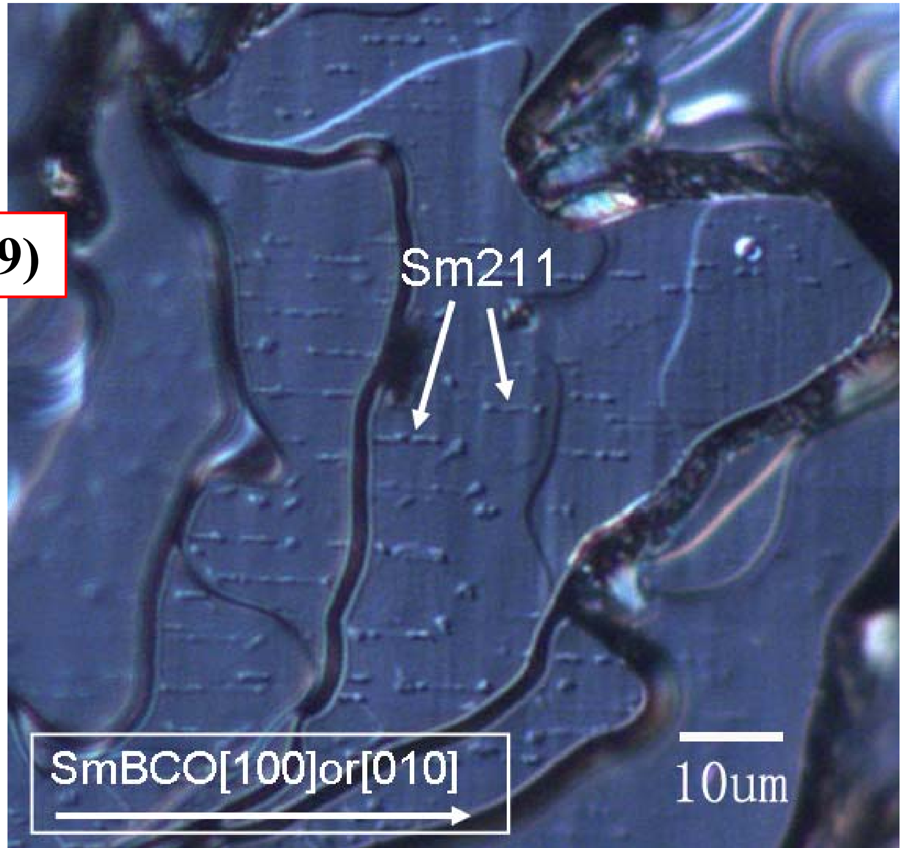
a-b plane: low surface energy, with high thermal stability

Thin film: quasi-two-dimensional structure, difficult to melt

T_{max}(~1045 °C) < T_p(SmBCO)

J. Phys. D: Appl. Phys. (2009)





Surface energies (eV nm $^{-2}$)	Values from indentation data	Calculated values for $YBa_2Cu_3O_7$	Calculated values for $YBa_2Cu_3O_6$
(100) surface	4.4	7.3	5.1
(010) surface	6.8	8.4	5.1
(001) surface	3.5	4.3	3.7

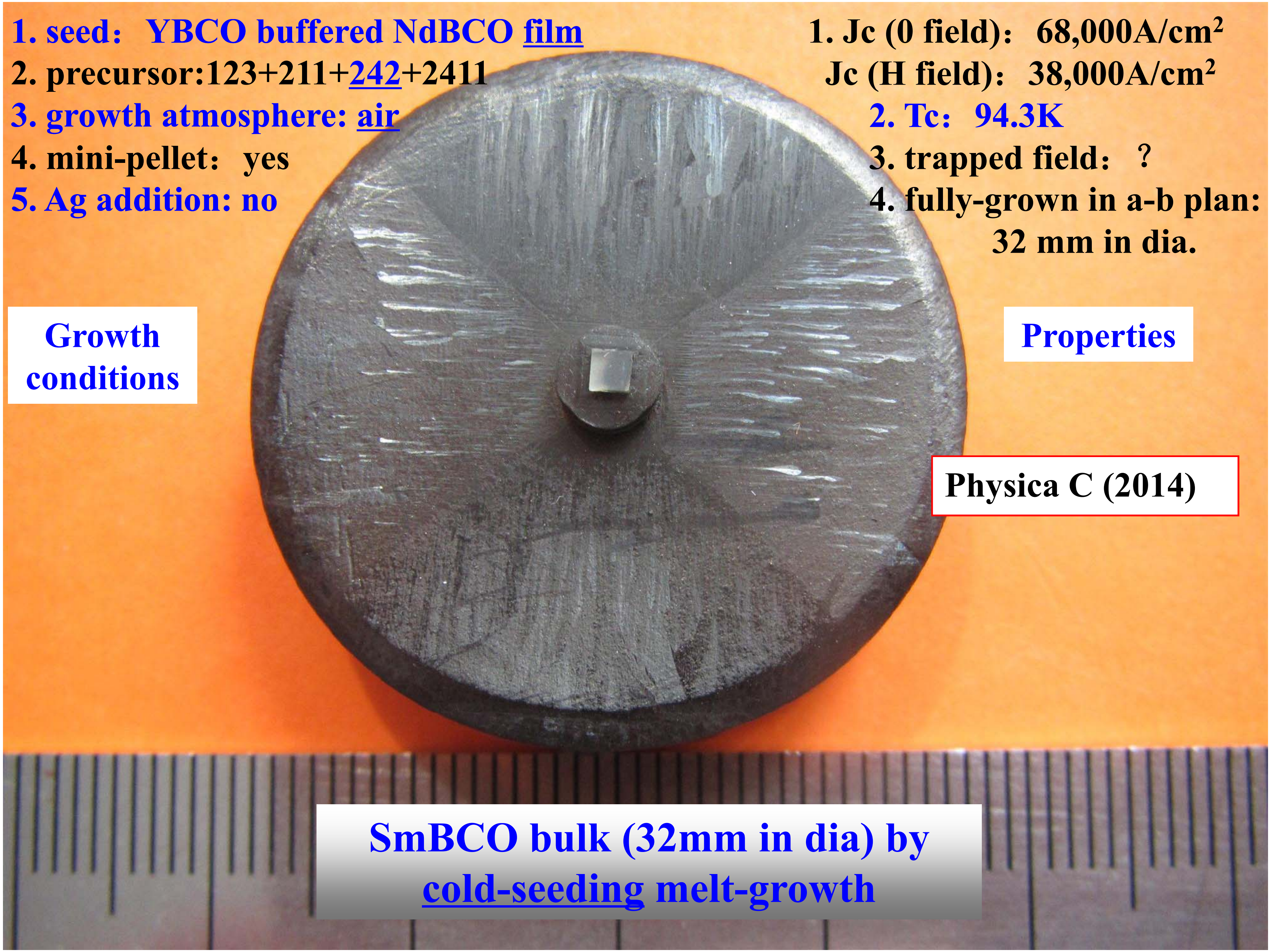
(100) or (010) surface of SmBCO crystal after MG experiment

Advantages of REBCO thin film (or buffered film) as seed materials in MG

- **Capable to endure high T_{max}**, and good for:
  - **Seeding high-performance & high T_p** REBCO bulks such as NdBCO and SmBCO
  - **Growing large-size** REBCO, since the growth window could be widened by using a higher T_{max}
  - **Recycling** failed REBCO bulks, since the remnant of solid REBCO can completely decompose by using a higher T_{max}
- **Easy to get sliced**, with highly controlled orientation i.e., a well-defined *a-b* plane and precisely known *a*-direction, which especially **benefits the control of grain boundaries in the multi-seed process**
- **Commercially available to gain large-sized film-seeds with high quality**

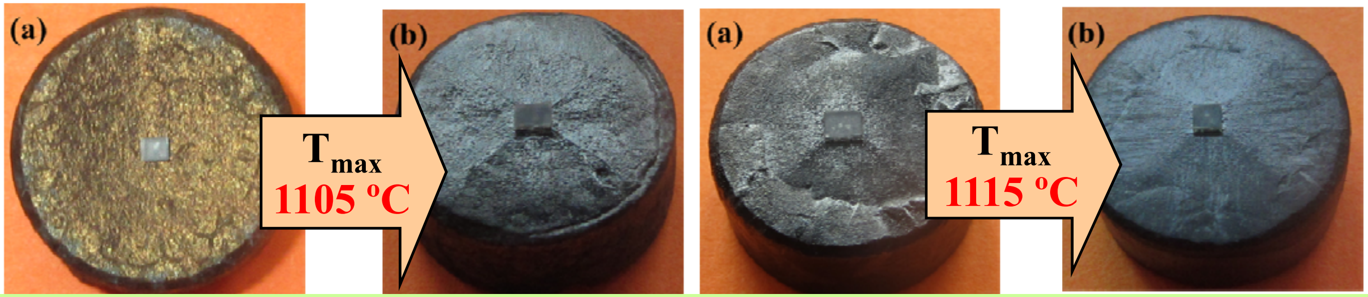
  - **seeding full-growth of large-sized** REBCO bulk with large *c*-growth sector and high performance

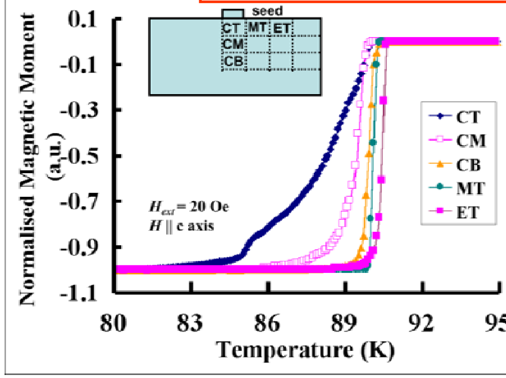
  - **processing in batch growth**


1. seed: YBCO buffered NdBCO film
2. precursor:123+211+242+2411
3. growth atmosphere: air
4. mini-pellet: yes
5. Ag addition: no
Growth conditions
1. Jc (0 field): 68,000A/cm²
Jc (H field): 38,000A/cm²
2. Tc: 94.3K
3. trapped field: ?
4. fully-grown in a-b plan: 32 mm in dia.
Properties
Physica C (2014)
SmBCO bulk (32mm in dia) by cold-seeding melt-growth

Recycling failed YBCO superconductor bulk using NdBCO/YBCO/MgO film-seeded TSMG method

HH Xu J. of Appl. Phy. (2012)





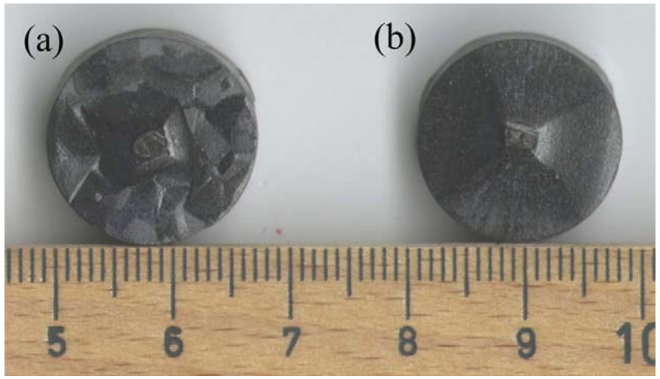
A simple & effective recycling process in this work!

Recycling failed (GdBCO/Ag) bulk

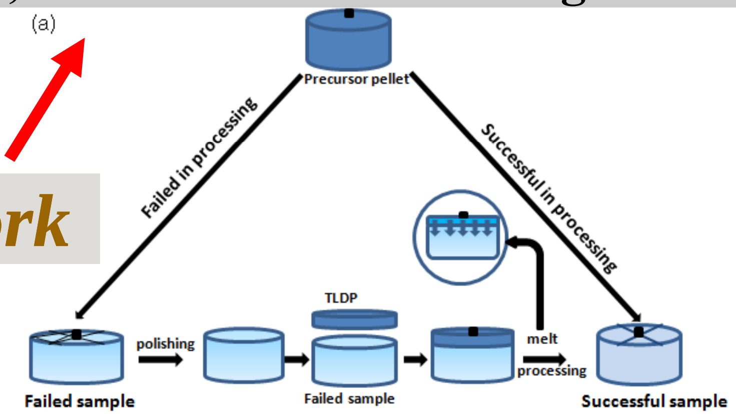
Grinding failed bulk into powder & recycling *Physica C 469 (2009) 1153*

Recycling failed YBCO bulk

Capping a liquid-rich pellet on failed bulk, Y123:Y211=10:1 in weight



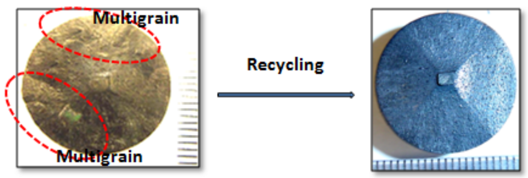
2 reported work



T_{max}=1040 °C in cold-seeding
(a) The recycled sample
(b) The reference sample

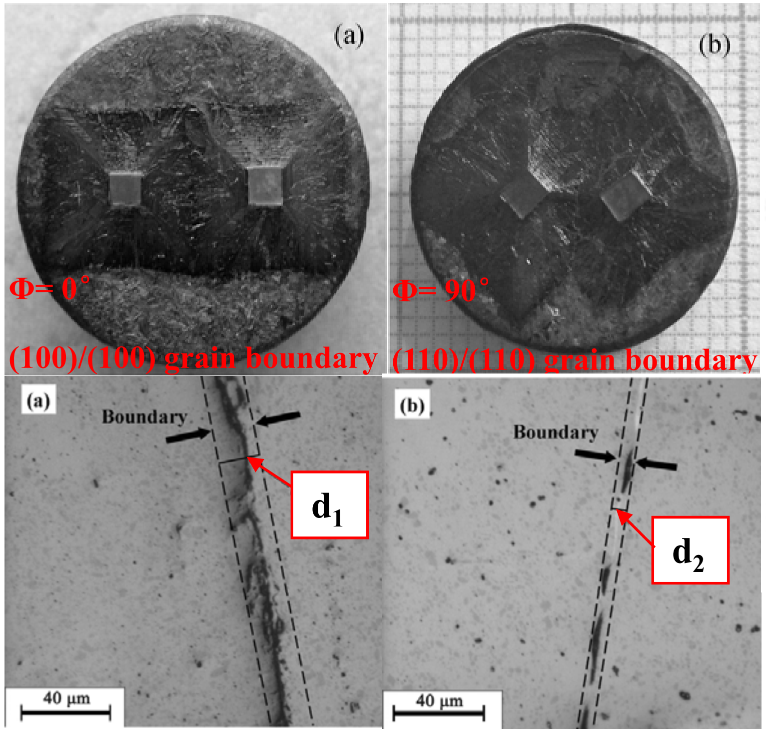
T_{max}=1100 °C in hot-seeding

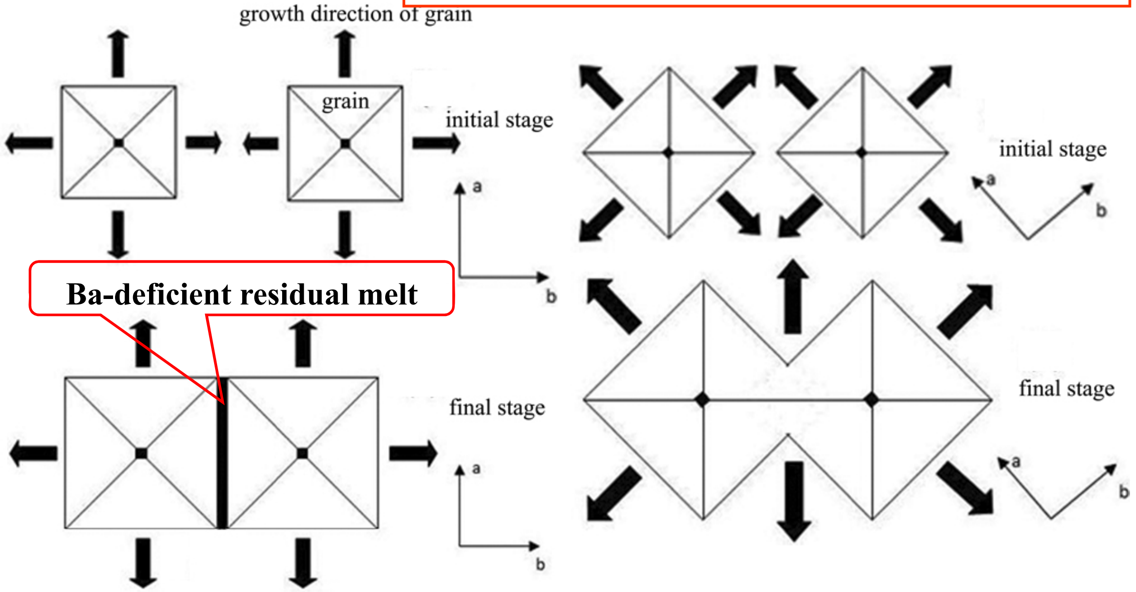
Supercond. Sci. Technol. 23 (2010) 065012



Multi-seeded melt growth of bulk YBCO using thin-film seeds

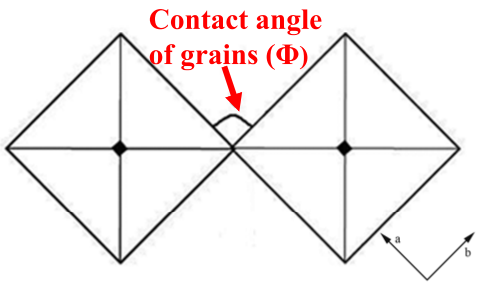
TY Li J. of Appl. Phy. (2010)

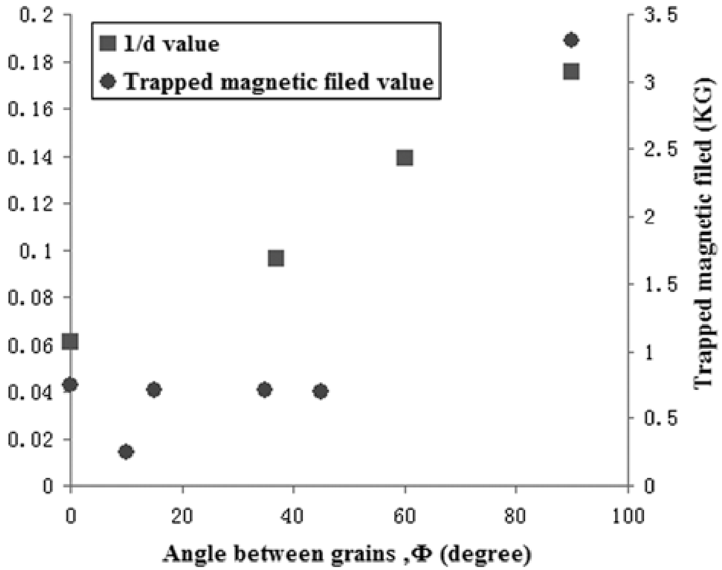




d (μm)	16.4	10.4	7.2	5.7
Φ (°)	0	37	60	90

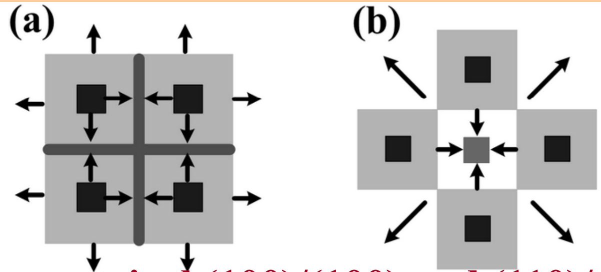
Table: Width of grain boundary for different grain contact angle.





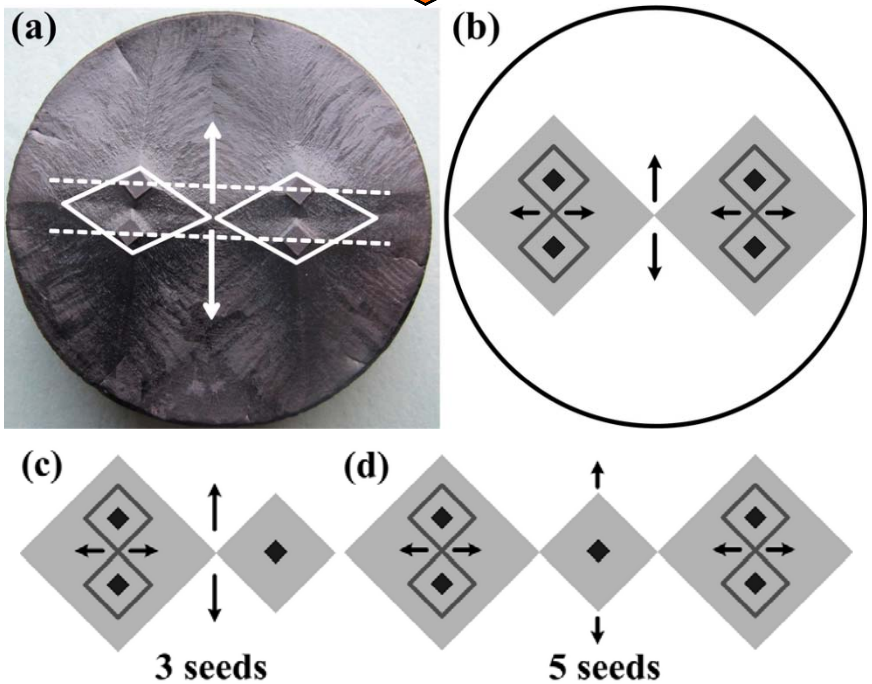
- The amount of residual melt at grain boundaries decreases with the increment in the value of "Φ" .
- Cleaner grain boundaries result directly in higher trapped fields.

multi-seed arrangement for MSMG



symmetrical (100)/(100) and (110)/(110)

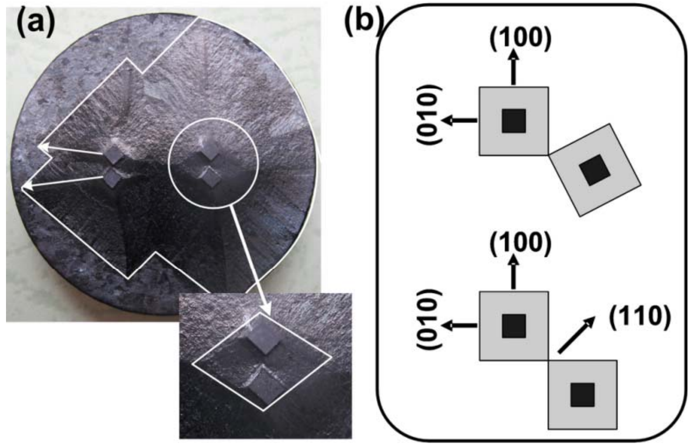
impinging region with residual melt



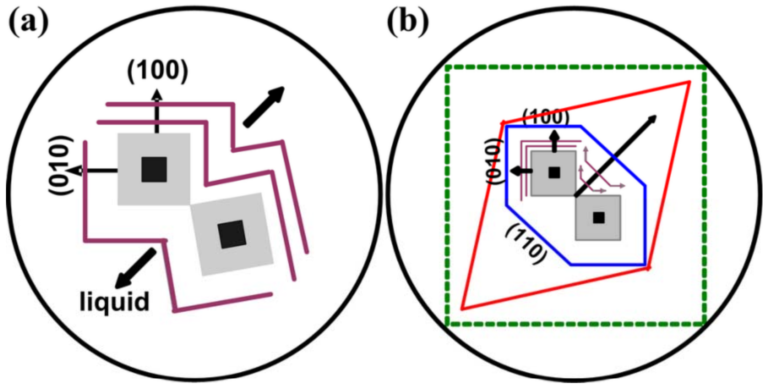
asymmetrical (110)/(110) arrangement

Clean grain boundary!

seeds with different arrangement



1)as-grown domain with different size
2)non-equilibrium shape



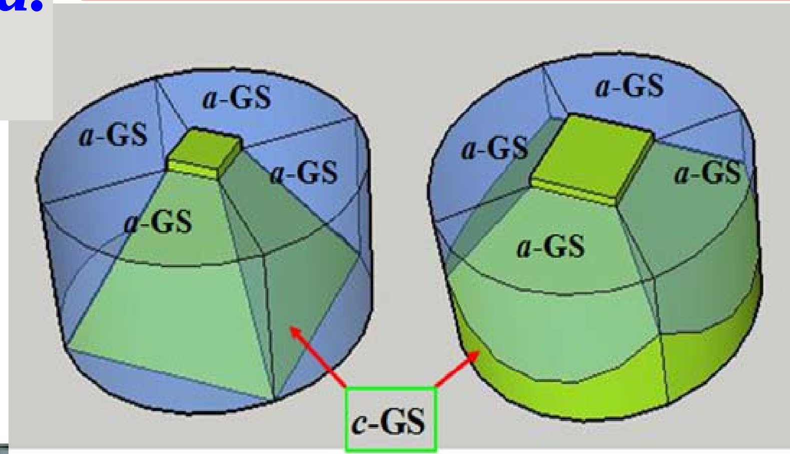
Growth rate: (110) > (100)/(010)

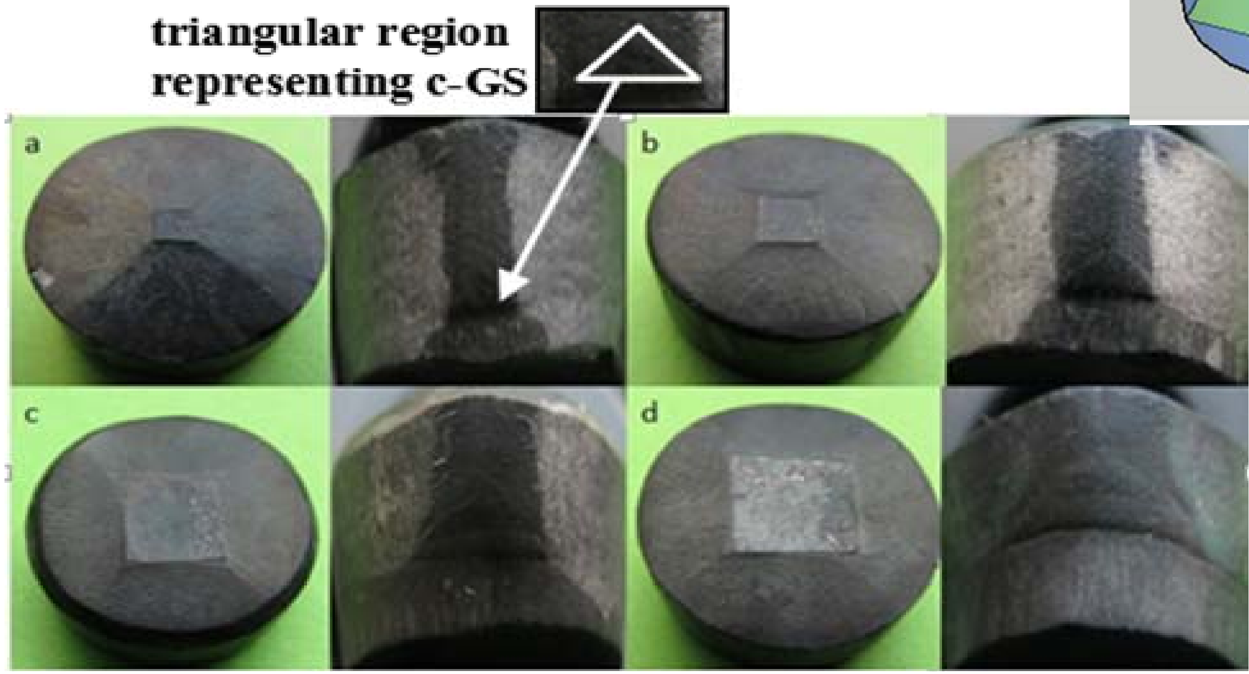
Multi-seeds arranged asymmetrically with (110)/(110) orientation leading to:
1)Enlargement of the domain size
2)Enhancement of superconducting property.

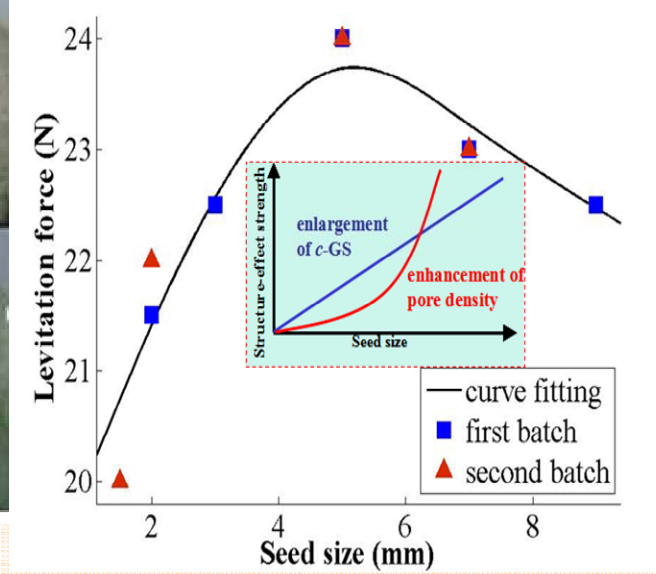
Seed-size effect on growth & supercond. Performance of YBCO bulks

HC Li Cryst. Growth & Des. (2015)

Two merits**
1. **commercial availability of the large size**
2. **superior thermal stability (T_{max} up to 1120°C)**







YBCO bulks induced by NdBCO film-seeds with different sizes of 2*2, 4*4, 7*7 and 9*9 mm^2, respectively

the triangle region (representing *c*-GS) in side views becomes increasingly larger with increasing the seed size, verifying that the grown YBCO bulk with LSS possesses a larger volume fraction of *c*-GS

REBCO thin film, as a quasi-two-dimensional structure, with low surface energy, potentially possesses high superheating capacity.

However, its thermal stability extrinsically depends on the chemical process.

First reports on superheating of REBCO thin-films

(001) Surface : low surface energy

Peritectic melting: α (Y123)➔β(Y211)+ Liq.

(001) YBCO thin-film seeding NdBCO LPE growth for ~5 seconds:

$T_{grow}^{NdBCO}(1055^oC) > T_p^{YBCO}(1005^oC)$

(001) YBCO thin film can superheat for 50°C:

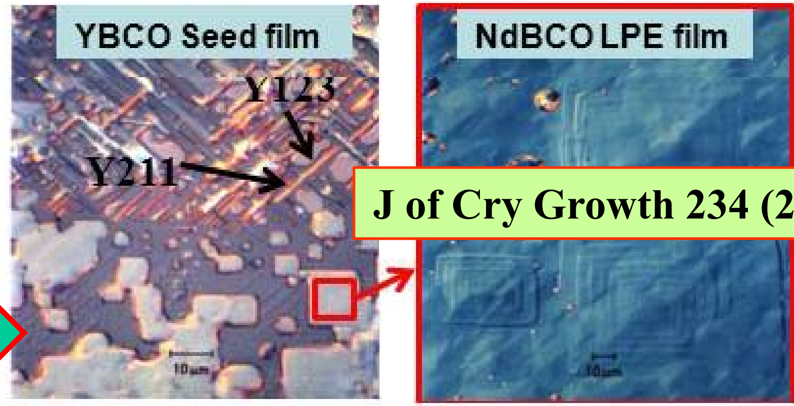
survive at 1060°C holding for 3 minutes;

<001>Y211 // <110>MgO

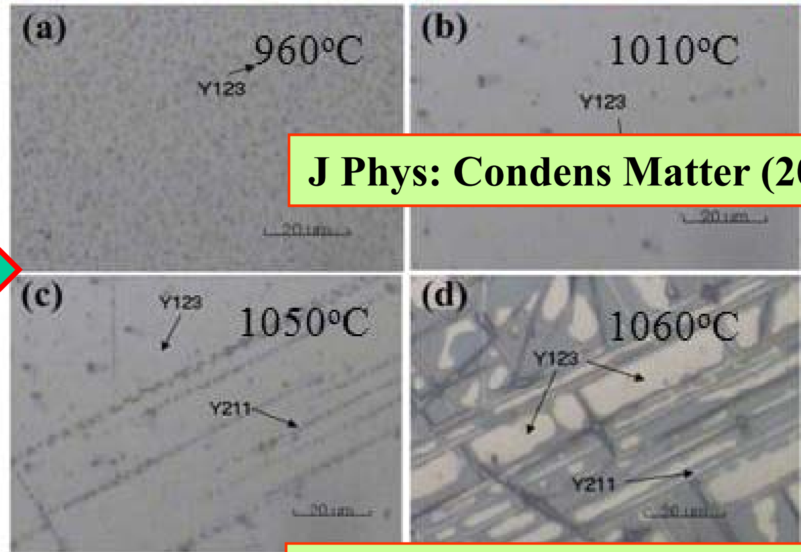
(001) YBCO thin film seeded YBCO bulk:

survive at 1045°C holding for 1.5 hours;

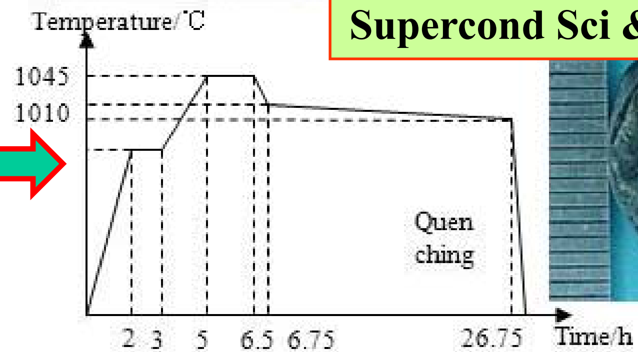
Liq. Phase Epitaxy Growth➔High Temp. Optical Microscopy➔Melt Growth

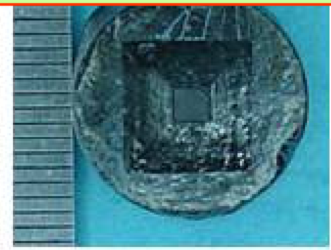


J of Cry Growth 234 (2002)



J Phys: Condens Matter (2003



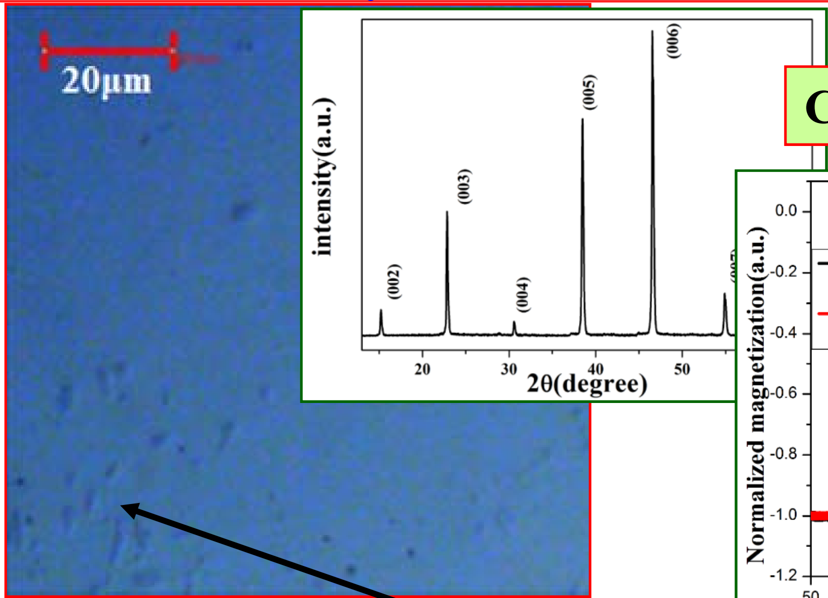


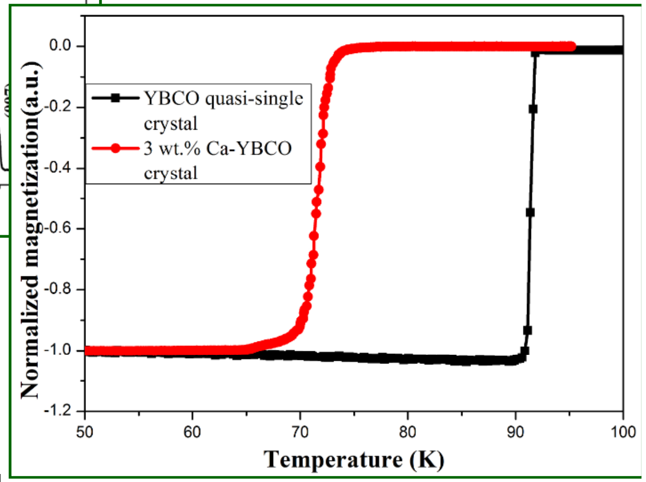
Supercond Sci & Technol (200

Modified top-seeded melt-growth for large sized YBCO and $Y_{1-x}Ca_xBa_2Cu_3O_y$ crystals

Cryst Growth & Des (2014)

CrystEngComm (2014)





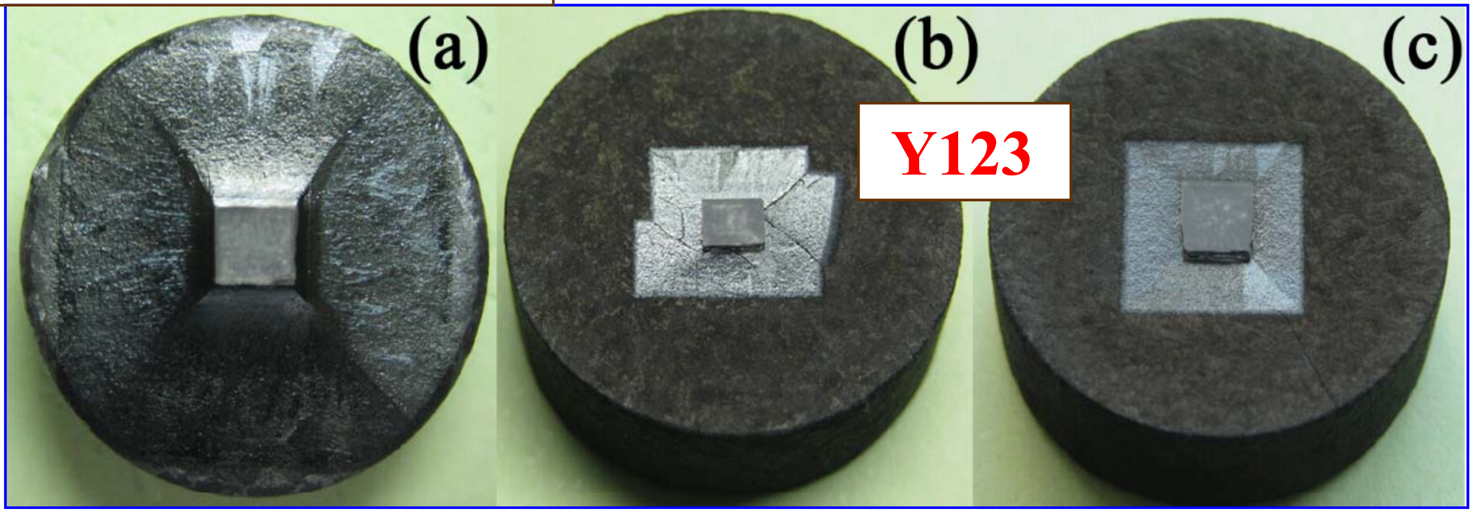
Melt Growth	Starting materials	Cooling rate K/H	Y211 trapped in grown crystal
Conventional	Y123+ 30 mol % Y211	0.5-1	~30 vol %
Modified	Y123	<0.2	~3 vol %

Large single crystals of YBCO is a matter of significant importance in study on superconductivity by Neutron Scattering Experiments !!!

Film thermal stability correlation with liquid property in growth of YBCO crystal

Conventional	Modified	Modified

Y123+30 mol % Y211



T_{max} =1120°C | T_{max} =1080°C | T_{max} =1070°C

Film thermal stability decreases in Modified MG

Summary (I) SmBCO HTS bulk

- **1. High superconducting properties T_c & J_c: Chemical composition control of (LRE)BCO; Introduction of Nano-particle**
- **2. Large size: High growth rate ;**
- **3. Reliable and repeatable process: Wide growth window (T_g, composition and $P(O_2)$);**
- **4. Cost effective: air-process; continuous growth; time-saving; batch process**

Summary (II)REBCO film-seed

1. Exploiting advantages of REBCO film-seed in MG

- **Capable to endure high T_{max},**
- **Easy to get sliced,**
- **Commercially available to gain large-sized film-seeds with high quality**

the growth of REBCO bulk superconductors is further extended for practical applications and fundamental study.

2. NdBCO thin film, as a quasi-two-dimensional structure, with low surface energy, potentially possesses high superheating capacity. However, its thermal stability extrinsically depends on the chemical process in TSMG.

Thank you