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EXPERIMENTAL WORKSHOP ON
"HIGH TEMPERATURE SUPERCONDUCTORS"
(30 March - 14 April 1989)

PREPARATION AND CHARACTERIZATION OF HIGH T_c SUPERCONDUCTORS
Part II

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High T_c superconductors without rare earths

Bi - Sr - Ca - Cu - O system.

Pb - Sr - (RE, Ca) - Cu - O system.

Tl - Ba - Ca - Cu - O system

(Tl Pb) - Sr - Ca - Cu - O system

- Bi - Sr - Ca - Cu - O system.
  (Michal & Raveau , Maeda)

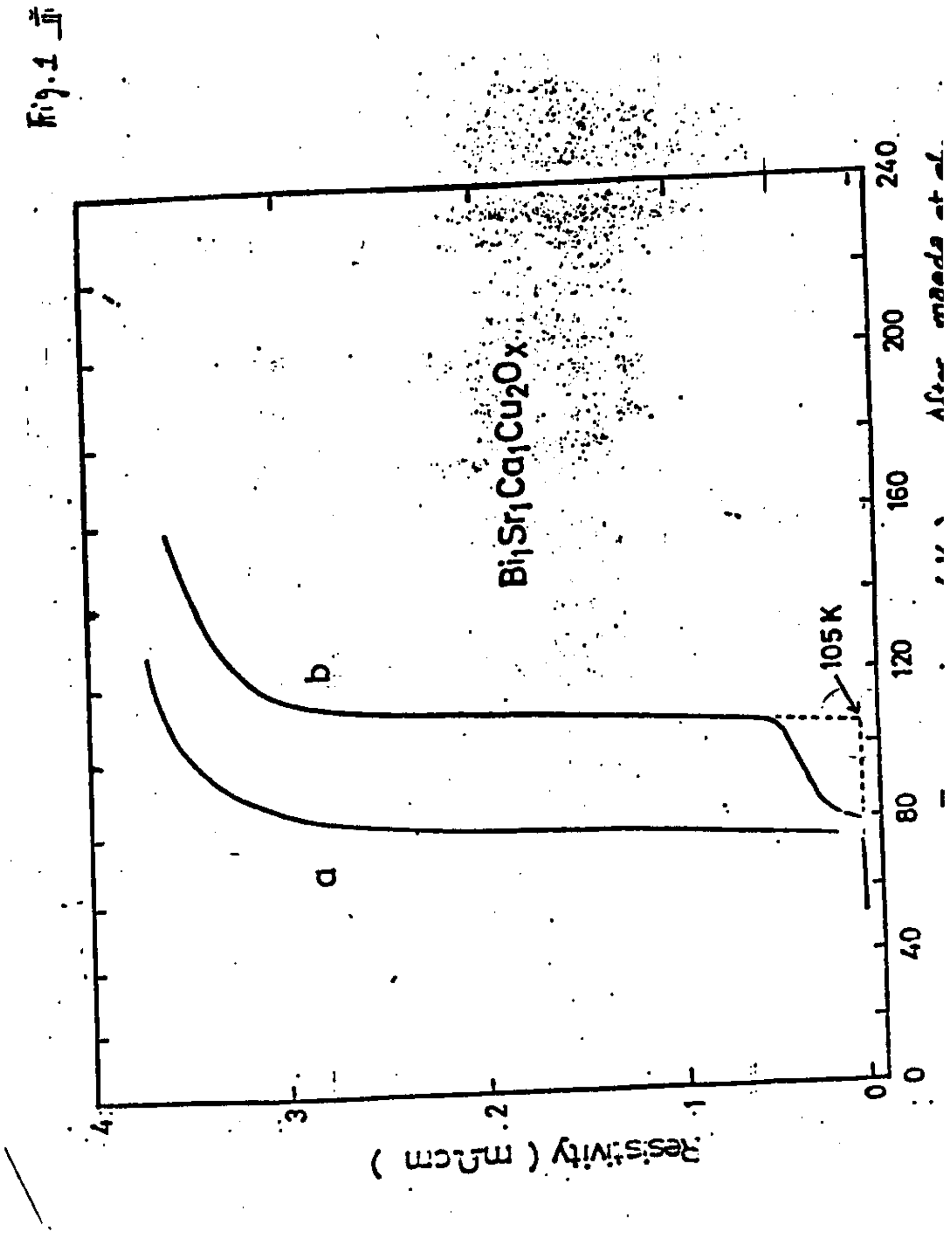
1. $Bi_2\ Sr_2\ Cu\ O_6$ ~ 12K
   $Bi_2\ Sr_2\ Ca\ Cu_2\ O_8$ ~ 90K
   $Bi_2\ Sr_2\ Ca_2\ Cu_3\ O_{10}$ ~ 110K

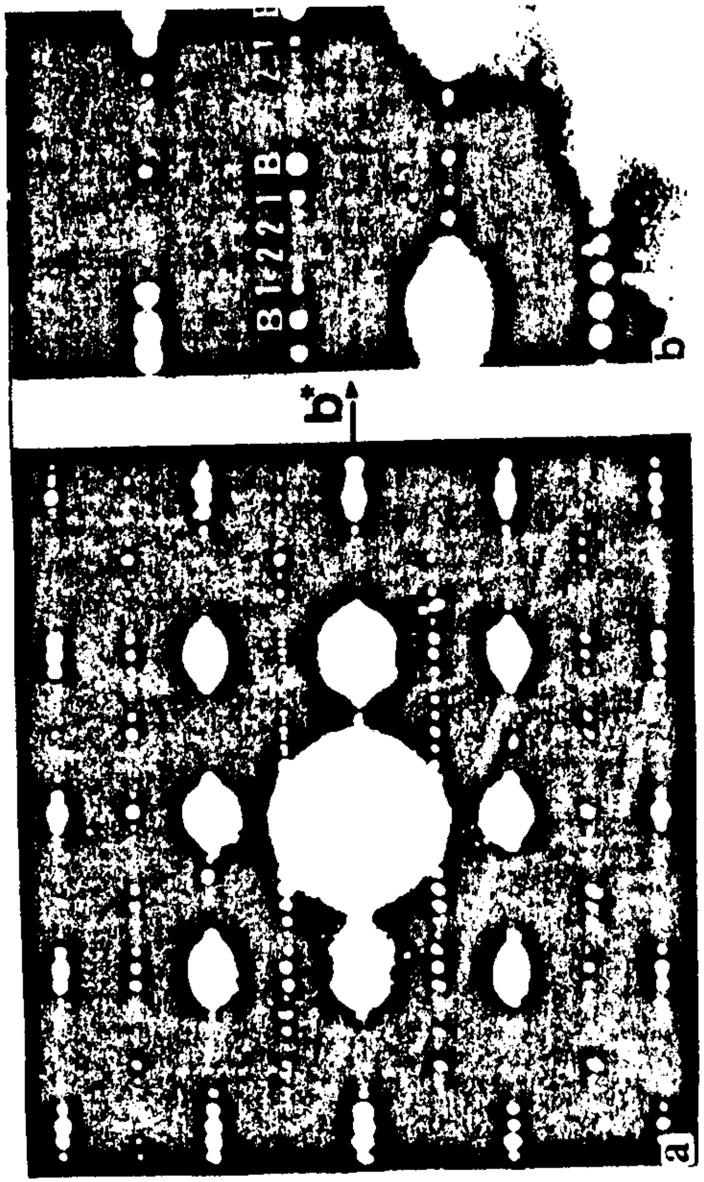
2. structure :
   2212 has most complex structure.
   So far, different space groups were cited.
   F 4/mmm , I 4/mmm , Fmmm , Aman .

   a = 5.42 Å , c = 30.8 Å (F 4/mmm)
   a = 3.825 Å , c = 30.8 Å (I 4/mmm)
   a = 5.42 Å , b = 27.2 Å , c = 30.8 Å (Fmmm)
   a = 5.42 Å , b = 5.44 Å , c = 30.8 Å (Aman)

* modulation along b axis (F lattice) or
<110> (I lattice) always.

comparing with RE - cuprates — No modulations,
and Tl - cuprates - very few.





modulation structure along 1Δ axis
reported in Interlaken. submitted to J. Phys. D.
(Ref. ii)

2223 phase has the similar structure

2223 = 2212 + perovskite slab of $CaCuO_2$

a = 3.835 Å , c = 36.82 Å .

3. Resistance measurement :

For 2212 phase, single phase polycrystalline & large single crystal were easy to obtain.

T_c^{zero} = 85 K ~ 90K .

anisotropic behavior above & below T_c

{ Semiconducting ∥ c axis
{ metallic ⊥ c axis

For 2223 , single phase ? No large single crystal.

T_c^{zero} = 105 ~ 110 K ,

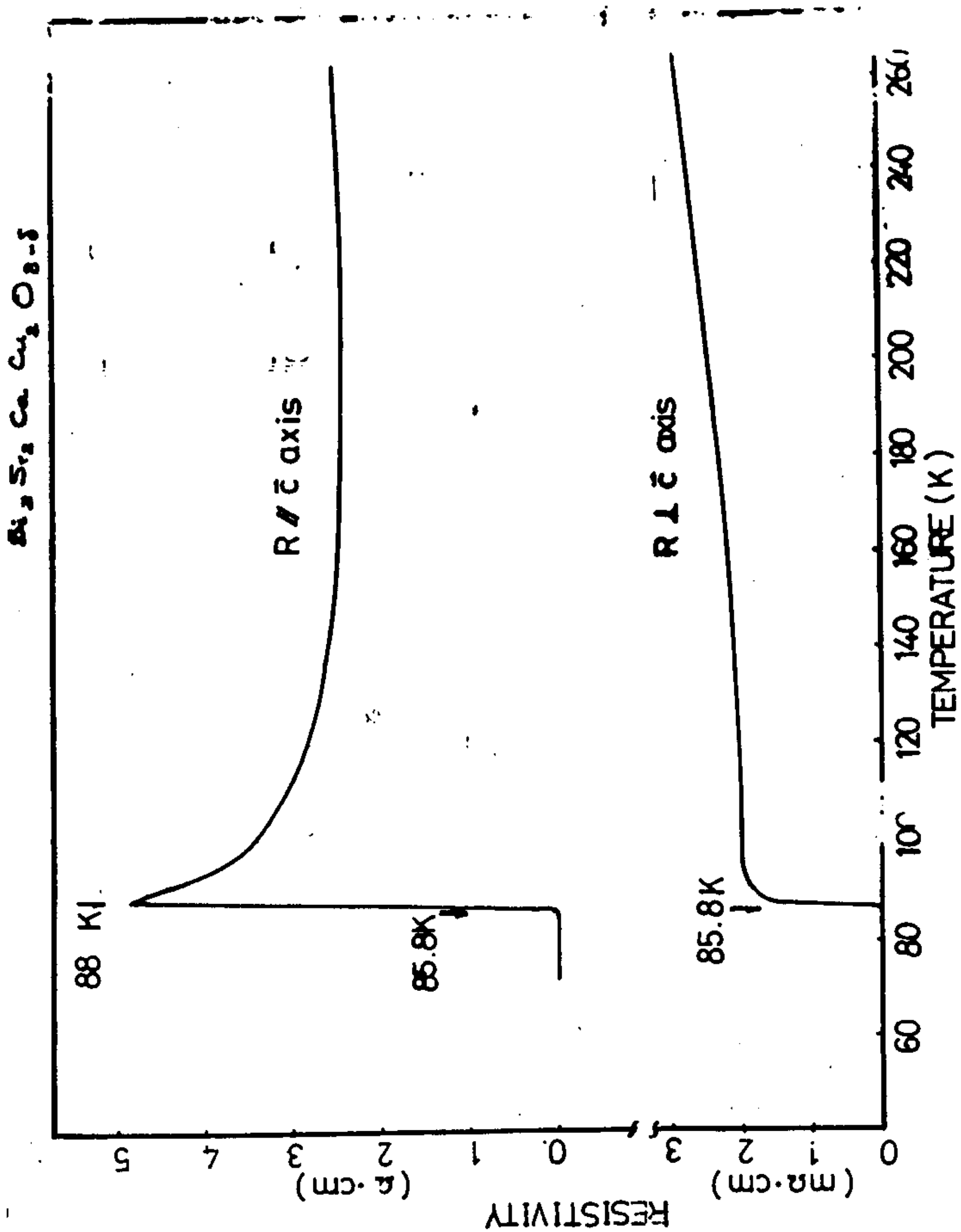
4. A.C. Magnetic susceptibility :

25 % ~ 30% meissner effect for single crystal.

5. J_c is very low for bulk sample.

J_c ≈ 3000 A/cm² or little more for single crystal from electrical measurement, (Beijing)

J_c ≈ 10^4 A/cm² (Japan)



$J_c = 2\times10^5$ A/cm^2 for single crystal from magnetic measurement (Beijing) ($H=0$, $T=1.5$ K)

J_c drops strongly when the magnetic field was applied.

6. Thermal analysis:

No heat peak from DTA & TG.

→ not sensitive to O_2 pressure.

No obvious specific heat jump was observed at T_c for 85 K phase. but there is a kink.

How to prepare the sample:

1. Starting materials: Bi_2O_3, CuO, $CaCO_3$, $SrCO_3$

2. Composition: stoichiometric composition.

Acturely, there is a wide region, in which it is possible to get the superconducting phase.

→ Some kind disordering of Bi, Sr, Ca &

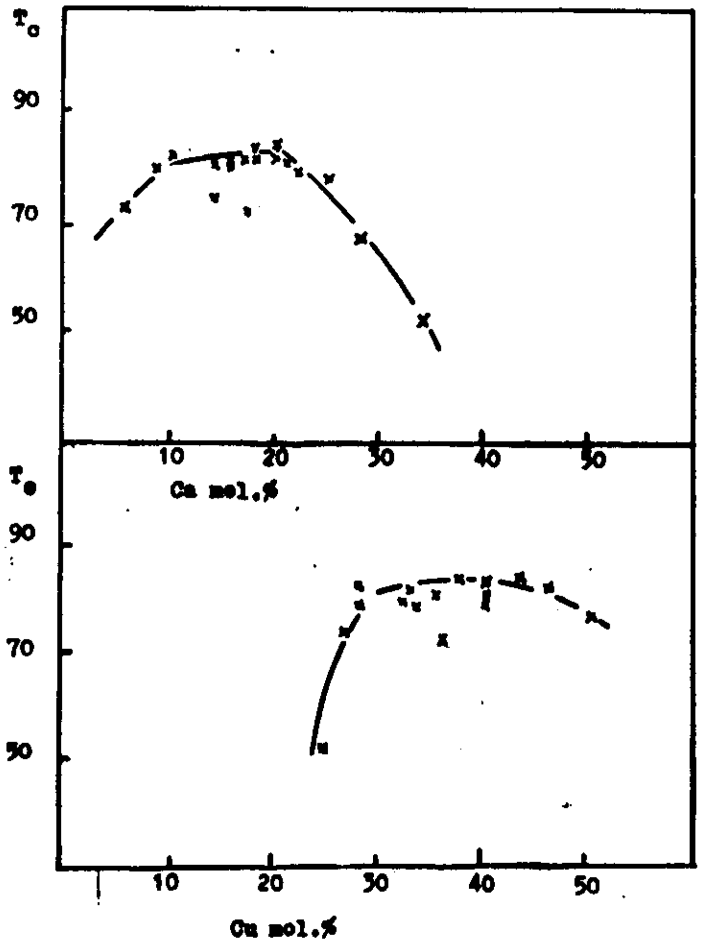
3. Procedure:

85K phase:

- mixing & grinding thoroughly.
- Calcining at 850°C – 880°C in air for 8 h.
- Regrinding & pressing into pellets
- Sintering at 880°C in air for 12 hrs
- Quenching in air down to RT.

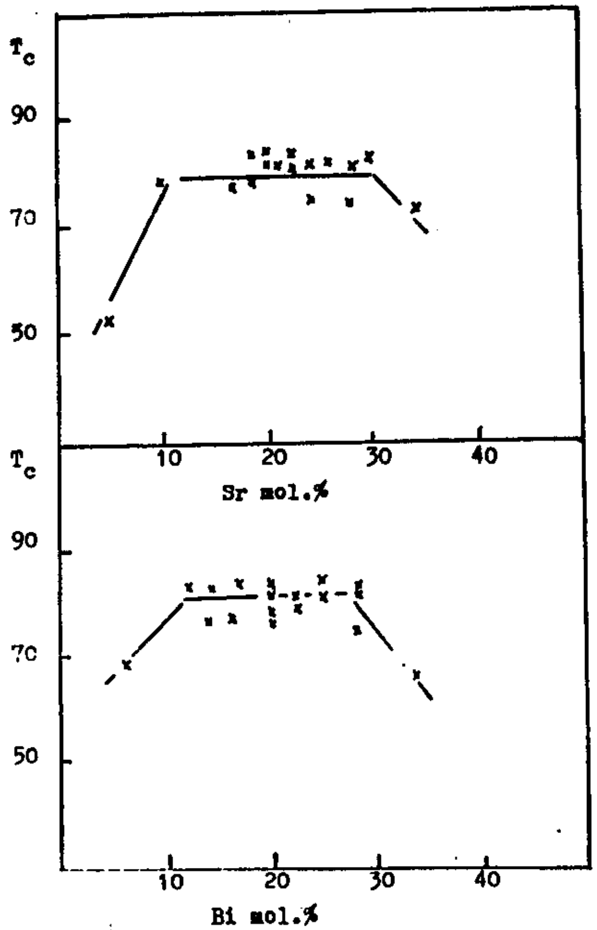
— 4 —

Fig.1



Institute of Physics,
submitted to J. of Physics. D

Fig. 2



3.

single phase, $T_c = 85$ K, but contain the intergrowth.

110 K phase:

Keeping sample at high temperature for a day. (very close, but not above the melting point)

110 K phase amount increase.

- low temperature annealing at 700 ~ 750 °C, repeated several time. $T_c^{zero} = 107$ K.

  Almost single phase, but reproducibility is low.

- doping Pb in $Bi_2 Sr_2 Ca_2 Cu_3 O_{10}$.

  $Bi_{2-x} Pb_x Ca_2 Sr_2 Cu_3 O_{10}$

  $0.2 \leq x \leq 0.6$

  starting materials: Bi_2O_3, PbO, $CaCO_3$, $SrCO_3$ & CuO.

  prefired powders in air at 800 °C ~ 850 °C for 24 h.

  Reground and pressed into pellets.

  Sintered at 860 ~ 865 °C for 60 h.

  furnace-cooling to 400 °C, then quenched to RT.

  It is very sensitive to sintering temperature.

N.D & Electron micrography reavels:

Bi, Pb planes exist.

Single phase ceramics & single crystal are needed to determine structure and understand superconductivity.

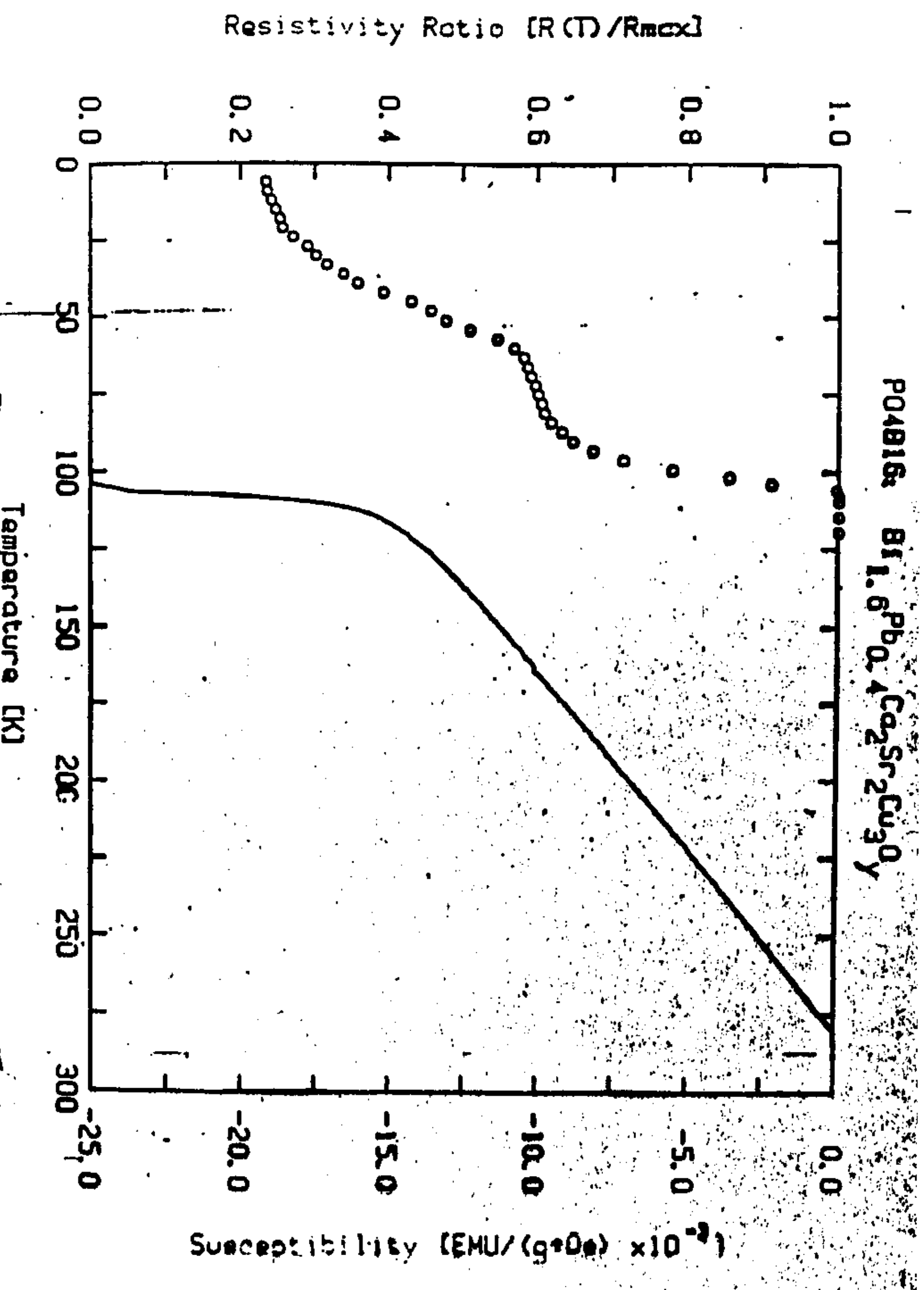


Fig. 1c

Growth of 2212 single crystal :

Self - flux Method

- Synthesize the bulk sample of 2212 phase.
- Melt the bulk sample (100g ~ 200g) at 1065°C, add 10% extra Bi_2O_3
- Hold molten sample at 1065°C for 24h. in air to avoid sandwich structure solution.
- Rapid cooled to 925°C
- Slow down to 825°C at 1°~2°/hr. hold it at 825°C 3 days.
- furnace - cooled down to RT in 6hr.

Product :

flat superconducting crystal, black, shining. easily to cleavage along (a,b) plane, like mica. size ranged from 10 mm ~ 20 mm.

T_c = 85K.
Strong unisotropic behavior.

Minor impurity phase : bar - like, dark green crystal.
Bi - poor compound : a = 11.84, b = 12.37, c = 19.581

Magnetic behavior in the applied magnetic field.

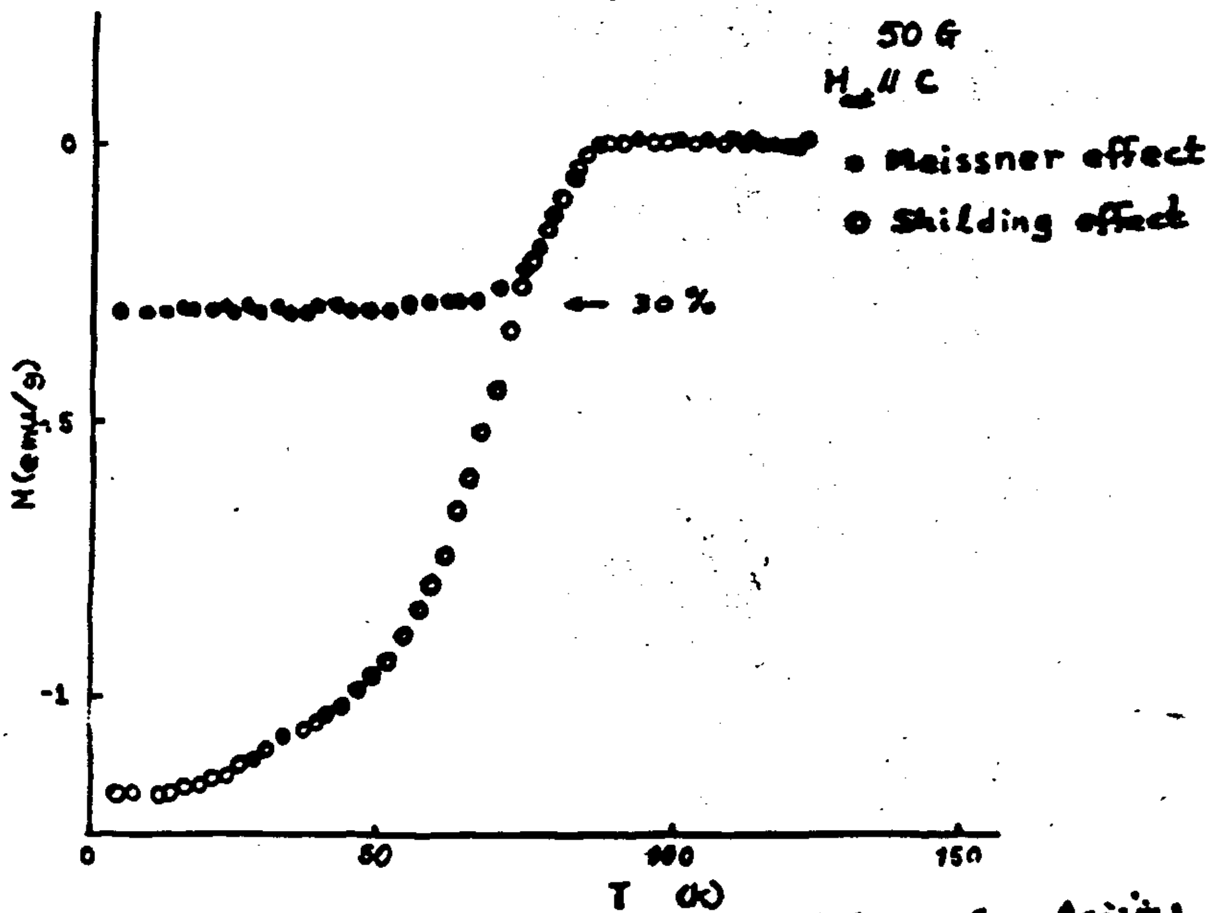
- meissner effect only 25% ~ 30%
- Magnetization loops :

$H_{c1}^{\parallel}$ = 2.9 KOe , $H_{c1}^{\perp}$ = 480 Oe

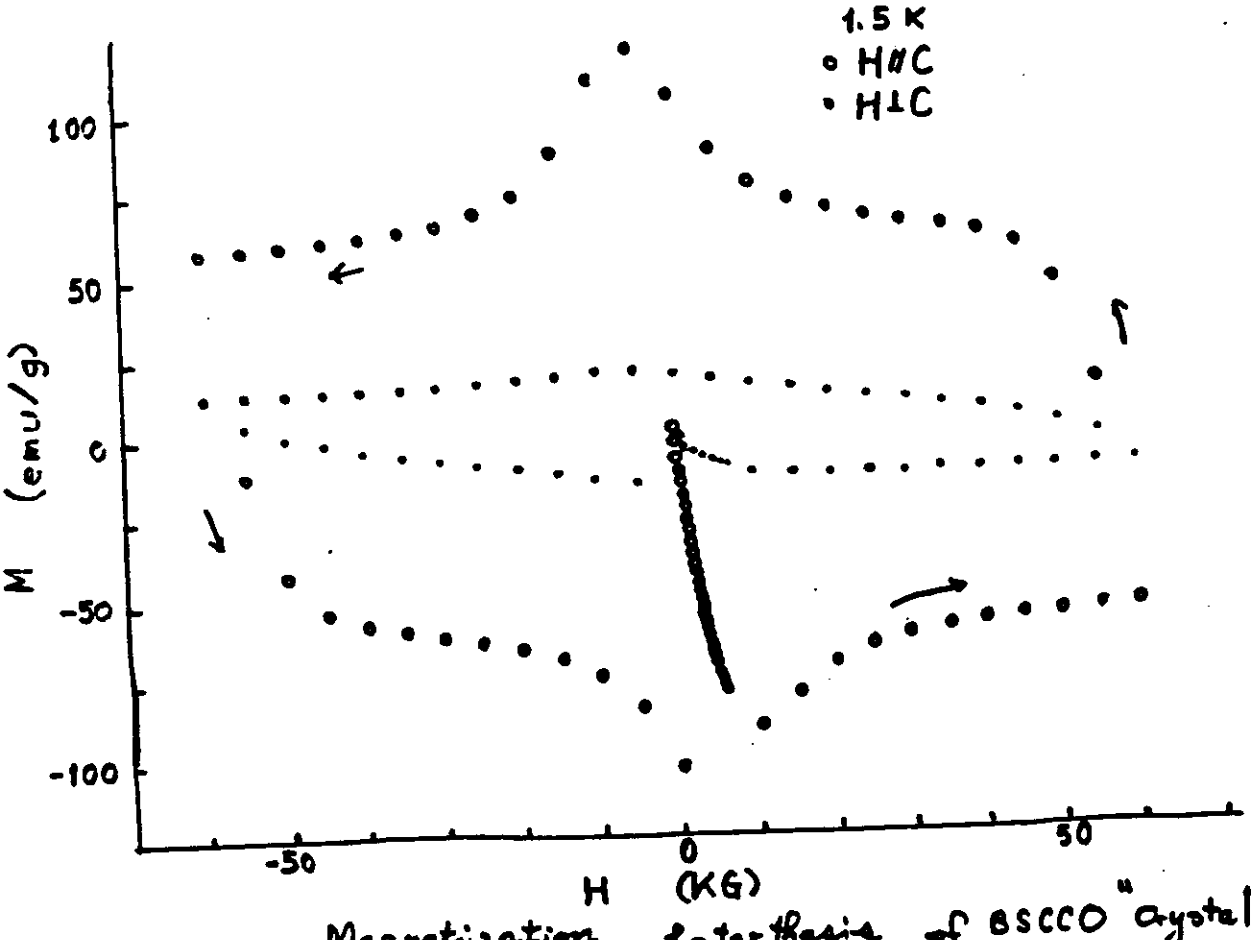
show anisotropy.

* * *

1. High quility single crystal for 2212
2. 2223 phase : single crystal.
3. Origin of modulation, and relation to SC.
4. Increase J_c & H_{c1}, H_{c2}.



Cui et al, Beijing



Magnetization hysteresis of BSCCO "crystal"

Amorphous of Bi-cuprates;

Unlike YBCO, quenching the solution of Bi-cuprate and annealing it at low temperature.
The superconductivity goes back.

- 2212 phase molten solution was splat quenched on copper plate at 0°C

- 2223, quenching the solution to 200°C.

Amount of amorphous varies with the temperature of copper plates.

- Crystallization of Amorphous;

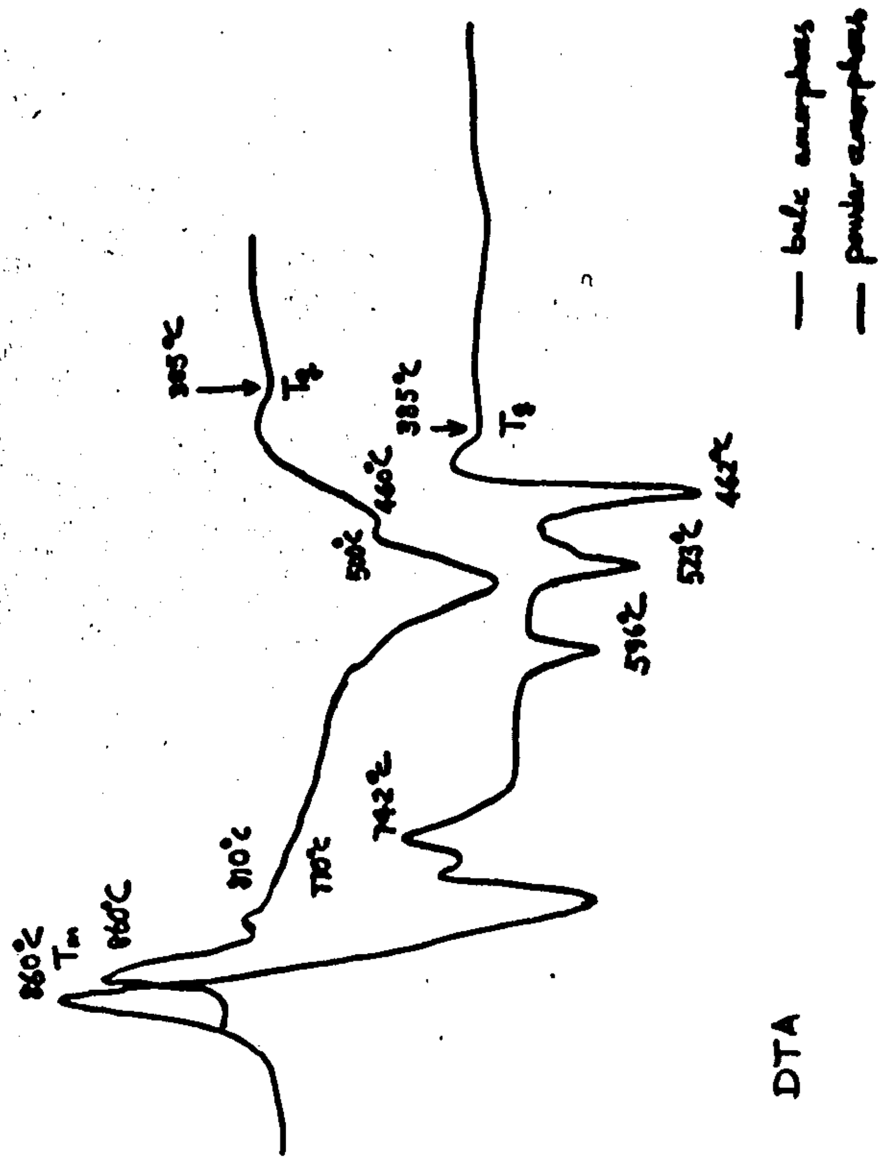
  Three steps of Crystallization from DTA;

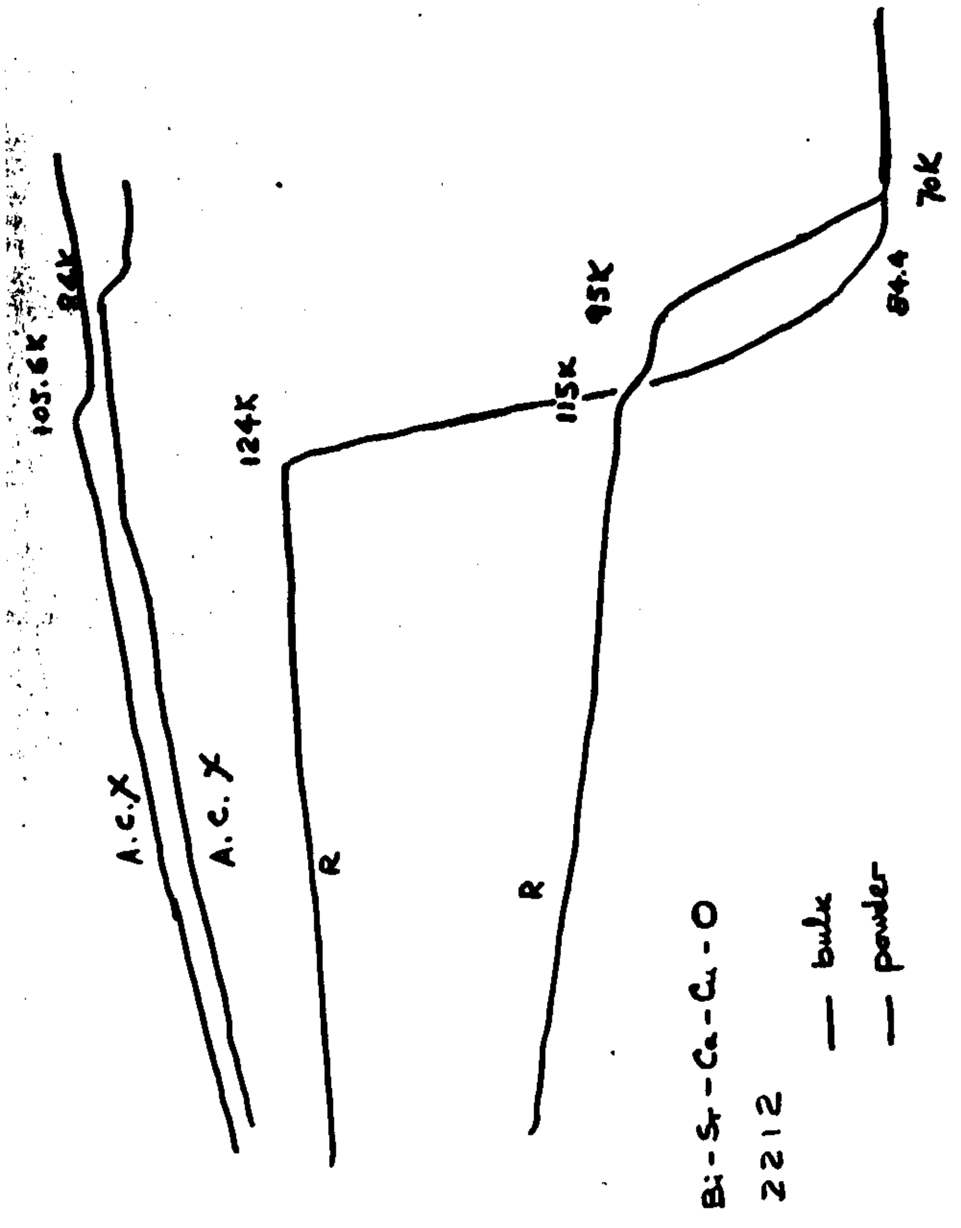
  450°C, 525°C, 583°C.

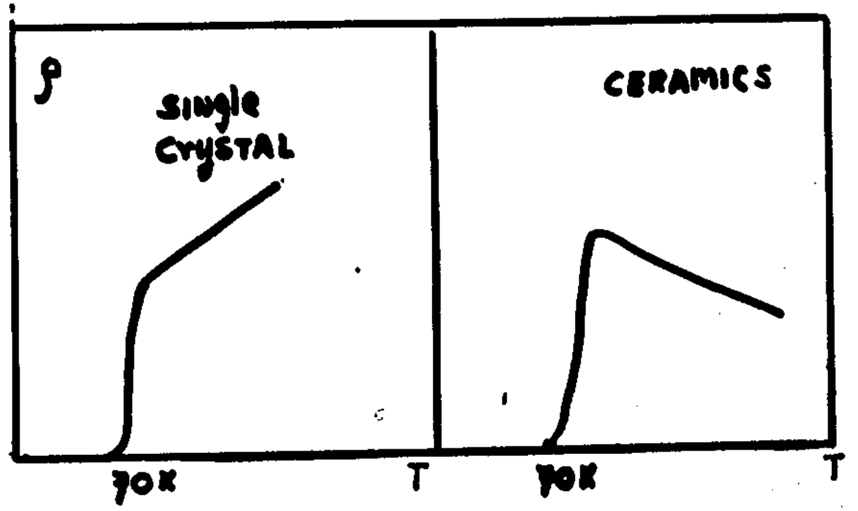
  Three crystalline phases have similar tetragonal structures;

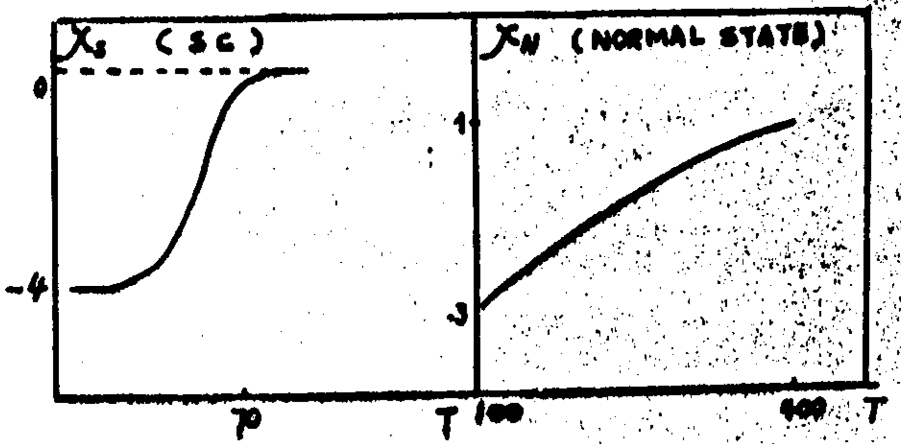
  a parameters almost same

  c parameters change.









$Pb_2 Sr_2 Y_{.5} Ca_{.5} Cu_3 O_{8+\delta}$

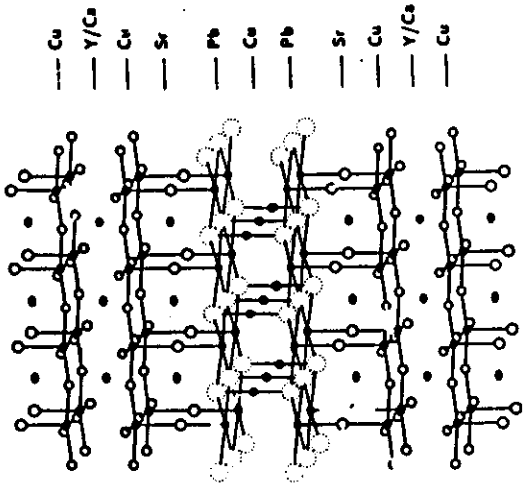


Fig. 6. The structure of $Pb_2Sr_2(Ca,Y)Cu_3O_8$. Metal atoms are shaded; Cu–O and Pb–O bonds are shown. Oxygen atoms in the PbO sheets are dotted because they are not localized on the ideal sizes.

Tl - cuprates & related superconducting compounds

Dicovery. Hermman & Sheng first synthesize Tl-based superconducting compound ;

$Tl_2 Ba_2 Cu O_6$ (T_c = 60 ~ 84 K) is not isostructural to 123 phase, but rather to $Bi_2 Sr_2 Cu O_6$.

WARNING

Thallium extreme toxic

M.L.D 12 mg / kg Tl ions

Tl^{3+} >> Tl^{+1}

Don't heat Thallium oxides in the Open furnace !

$Tl_2O_3 \xrightarrow{860°C} Tl_2O$

Tl_2O oxide melts between 300°C & 600°C

Status :

- Synthesis & structure :

1. All of Tl - cuprate superconductors can be represent as

$(TlO)_m Ba Ca_{n-1} Cu_n O_{2n+2}$

m = 1, 2

n = 1, 2, 3, 4,

They can be divited into two classes.

m=1. primitive tetragonal phases: (P4/mmm)

$Tl Ba_2 Ca_{n-1} Cu_n O_{2n+3}$

n = 2, 3, 4

m=2. Body-centered tetragonal phases: (I4/mmm)

$Tl_2 Ba_2 Ca_{n-1} Cu_n O_{2n+4}$

n = 1, 2, 3.

2. Lattice constants of Tl-cuprates.

All of phases have almost same a parameters: 3.847 Å

Different c parameters:

Compounds	c parameters (Å)	Tc (K)
1202	9.70	—
1212	12.73	85
1223	15.89	110
1234	18.73	115
2201	23.18	85
2212	29.42	105
2223	35.82	120~125
2234	41.80	120

When n value increase by one, adding CuO_2 plane & CaO plane, c parameter increase, and Tc increases & saturates.

3.1 Å (P4/mmm)

6.2 Å (I4/mmm)

3. Structures:

All structures of Tl-cuprates are related to each other and connected with Aurivilous type structures.

Perovskite slabs + Rock salt sheet

Cu-layered perovskite-like slabs were separated by either Mono-layer Tl-O sheet or Bi-layers Tl-O sheet.

Same sequences of Cations

Same spacings between the adjacent layers

Ca - Cu	1.57 Å
Cu - Ba	1.64 Å
Ba - Tl	2.01 Å
Tl - Tl	2.06 Å (for I4/mmm only)

4. Preparation.

starting materials: only oxides or peroxides

Tl_2O_3 (99.9%), BaO (BaO_2), CaO (CaO_2), CuO.

Composition:

① In the wide range of the metal atom ratio

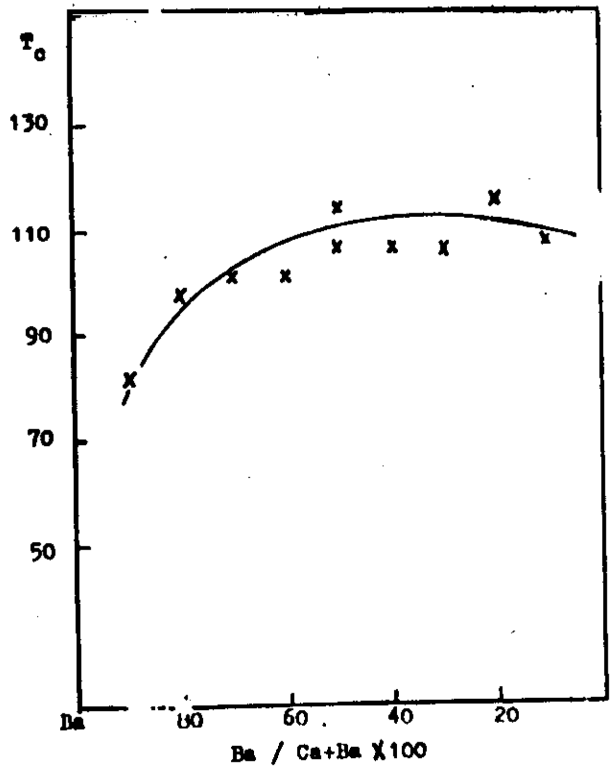
ex. 1112, 1113, 2212, 2223, 2234.

② Most stable superconducting phase: 2212 (Tc ≈ [illegible]

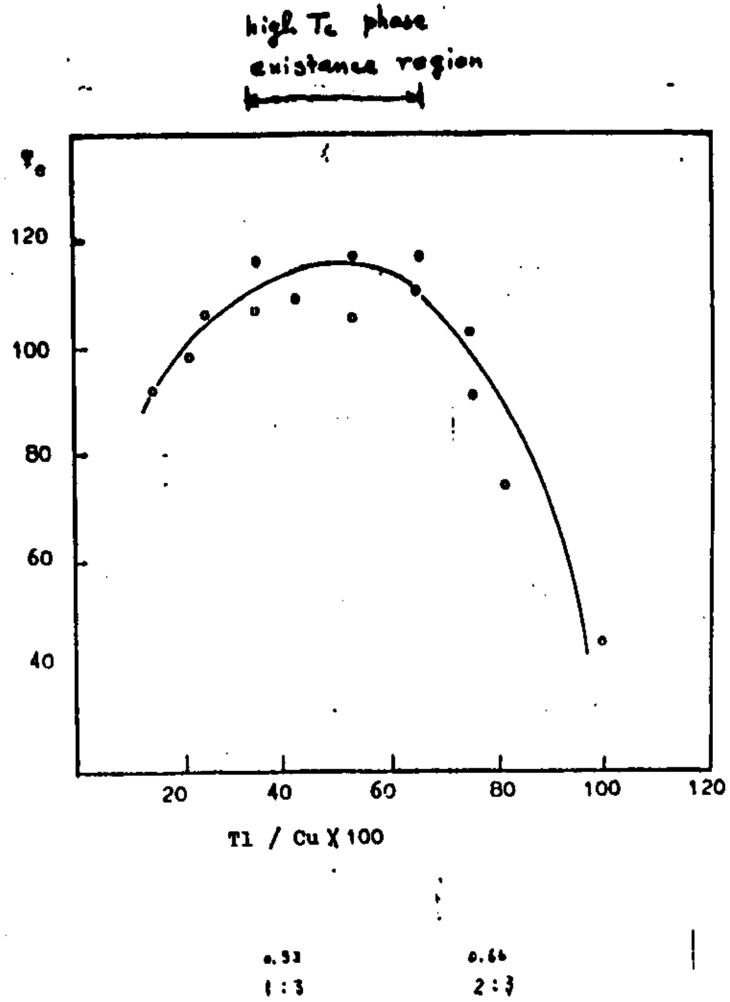
③ when Ca and Cu excess.

ex. 2234 or 2245 for making multi-phase samples with Tc ≥ 120 K mostly.

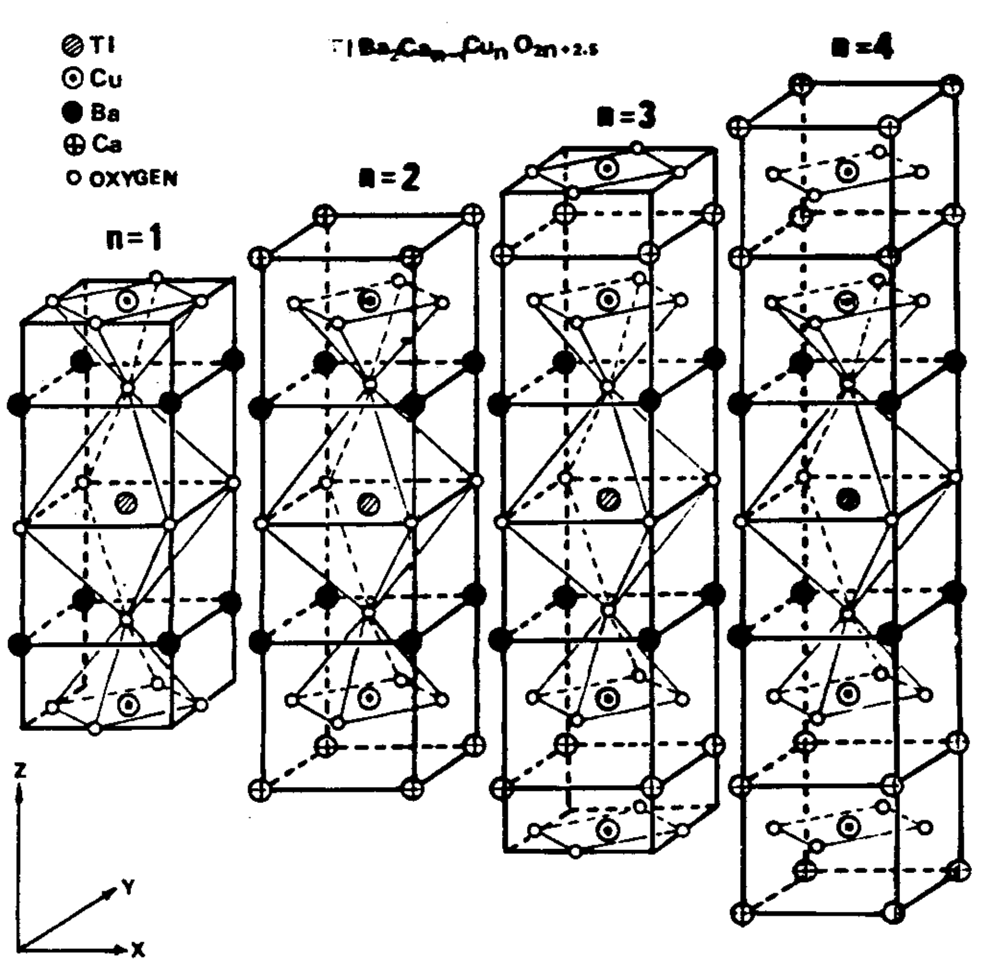
Du Pont's work:

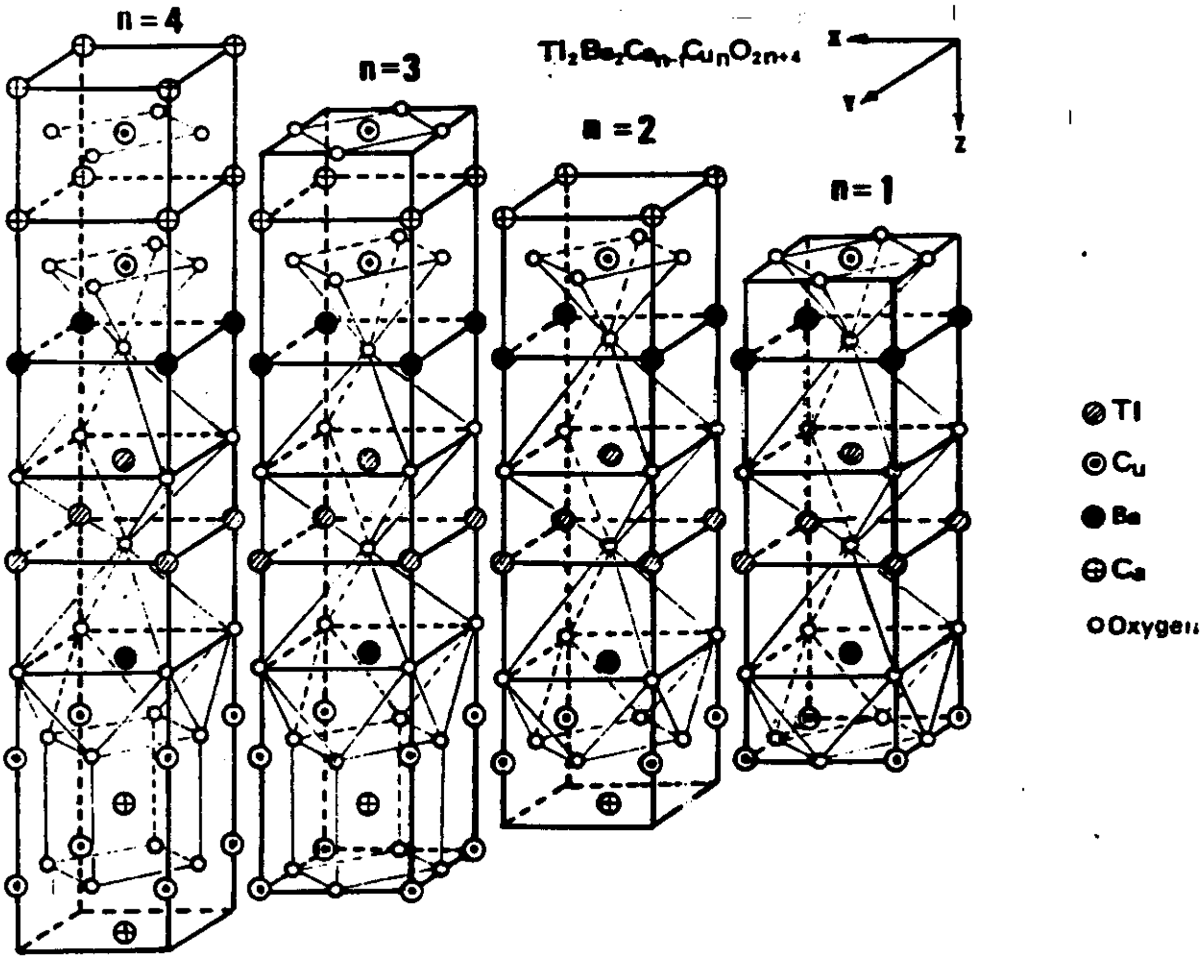


T_c
130
110
90
70
50
Ba
80
60
40
20
Ba / Ca+Ba X100



high T_c phase
existance region
T_c
120
100
80
60
40
20
40
60
80
100
120
Tl / Cu X 100
0.33
1 : 3
0.66
2 : 3


Tl
Cu
Ba
Ca
OXYGEN
Tl Ba2Can-1Cun O2n+2.5
n=1
n=2
n=3
n=4
Z
Y
X


n=4
n=3
n=2
n=1
Tl2Ba2Can-1CunO2n+4
X
Y
Z
Tl
Cu
Ba
Ca
Oxygen

①

starting oxides were sealed into gold tube
(½" dia. × 4" long)

Synthesis conditions are following:

Compounds	conditions (in gold tube)	T_c
2 2 0 1	875°C, 3 hrs.	90K
2 2 1 2	900°C., 6 hrs.	110K
2 2 2 3	890°C, 1 hr.	125 K
2 1 3 4	860°C, 3 hrs.	119K
2 2 4 5	880°C, 6 hrs.	?

Our work;

800°C ~ 820°C in air, 2h → furnace-cooled down to 600°C
→ hold sample at 600°C, 2h → quenched in air to RT.

2223 phase with T_c 115 ~ 120K
2212 phase with T_c 105 ~ 110K.

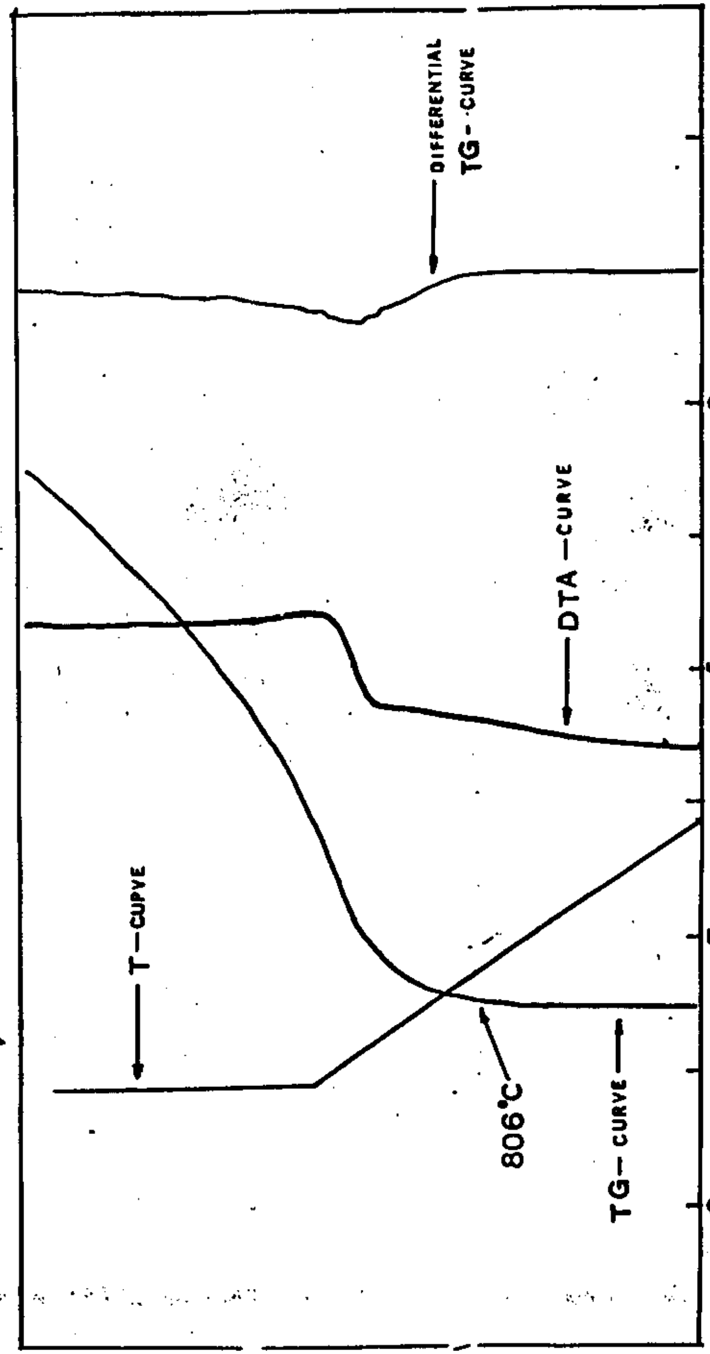
Other way;

EX making precusor ($Ba_2Ca_2Cu_3O_7$) by firing
$BaCO_3$, $CaCO_3$ and CuO stoichiometric mixture
at 930°C in air for 24 hrs.
Mixing Tl_2O_3 & precusor powder and pressing into pellet.
Firing pellets at 850°C ~ 860°C for 5 min.

Single crystal growth; (2223 phase)

① starting composition, 2234, containing extra Ca & Cu
② In sealed tube (gold)
③ heating at 920°C for 3hrs.
④ cooling down to 300°C at 5°C/min.
⑤ Size of crystal is about (0.1 × 0.1 × 0.01 mm³)

... part of thermal analysis in air.



⑤

- Thermal analysis :
  1. DTA : No thermal peak until Tl_2O_3 decomposes into Tl_2O at 810°c
  2. TG : No obvious weight change peak until 810°c
  3. Cp : Very small specific heat jump was found at about 110 c.

- Microstructure & disorder : (HREM)
  1. Coherent intergrowth ,
  2. domain structure
  3. very few modulate structure (along b direction)
  4. Tl / Cu ratio is more critical
  5. Ba / Ca ratio is not sensitive.
  6. Tl & Cu , Ca & Cu can be replaced by each other.
  7. Some disorder in Tl-O plane.
- Jc :

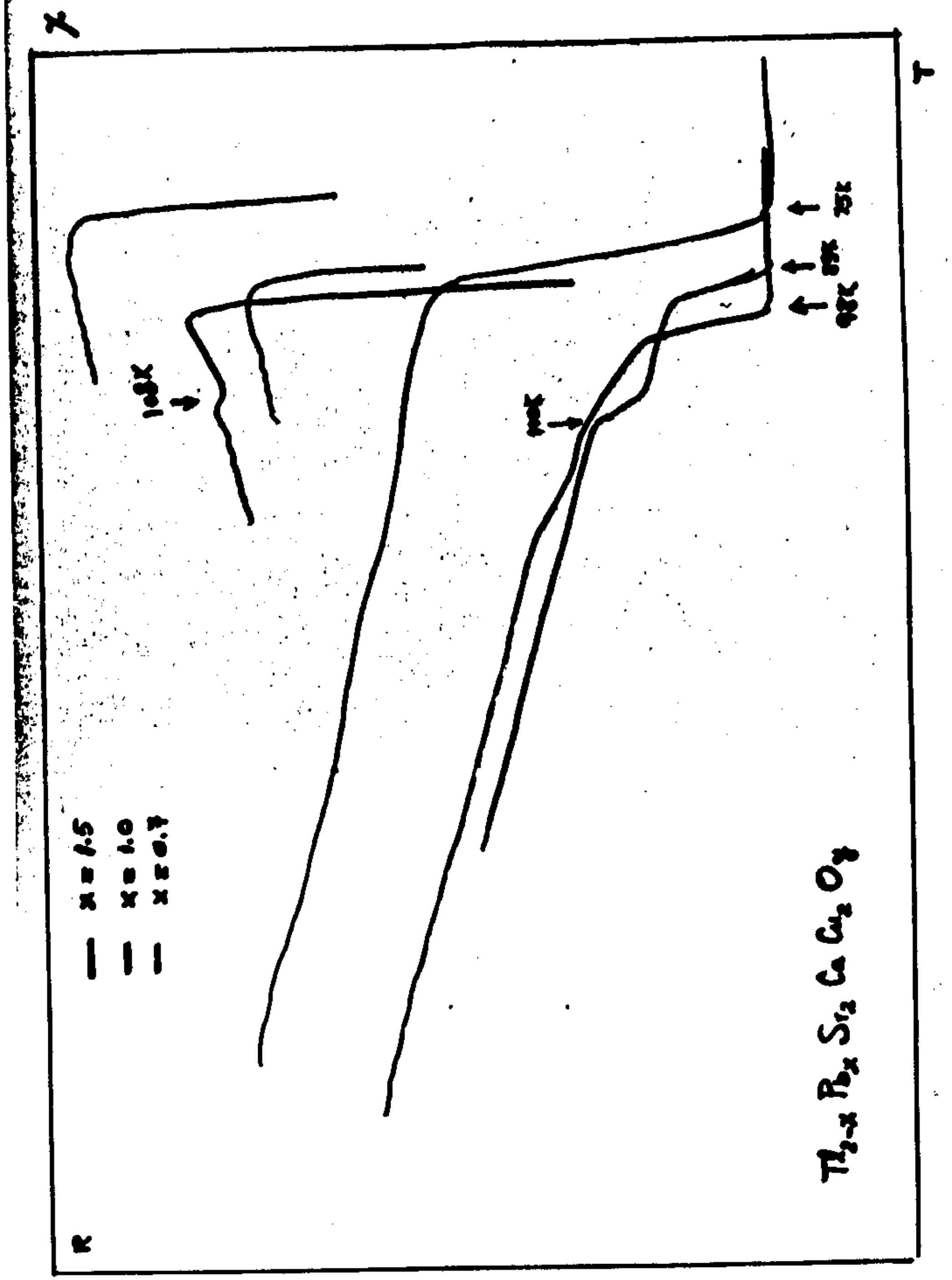
  In high pure alcohol regriding & resintering twice. Jc reaches to 1000 A / cm².

  Now, bulk specimen reaches Jc = 27,000 A / cm². but it is not highly reproducible.

- $(Tl_{.5} Pb_{.5})_m Sr_2 Ca_{n-1} Cu_n O_x$

  m = 1, 2 n = 2, 3

Compounds	Lattice constants	Tc (K)
1 2 0 1	3.73 × 8.98	–
1 2 1 2	3.80 × 12.05	80 ~ 90
1 2 2 3	3.81 × 15.23	115 ~ 120



- $TlBa_2Ca_{1-x}R_xCu_2O_y$:
  R = Nd, Sm, Er, Gd, La,
  T_c = 40K – 70K

  T_c varies with synthesis condition,

- Other substitution work :
  In, Cd, Sn, Sb, ... to replace Tl, always decrease or destroy SC.