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EXPERIMENTAL WORKSHOP ON
HIGH TEMPERATURE SUPERCONDUCTORS
(11 - 22 April 1988)

NEW HIGH T_c SUPERCONDUCTING OXIDES WITHOUT RARE EARTHS

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New high Tc superconducting oxides without rare earths ①

Bi - Sr - Ca - Cu - O superconducting oxides :

based on the Bi - Sr - Cu - O system

(michel & Raveau) —— $Bi_2 Sr_2 Cu_2 O_{7+\delta}$

105 K sharp drop in resistivity & 75 K zero resistivity (Maeda)

120 K sharp step and zero resistivity at 80 K (Chu)

103 K diamagnetic susceptibility (Zhao) and 84 K zero resistance (Xie)

Status ;

1. 110 K - 120 K sharp drop resistivity & A.c χ anomolous.
2. 85 K → 75 K zero resistivity & diamagnetic anomolous.
3. Two superconducting phases :

tetragonal (or pseudo - tetragonal) face centered unit cell with modulation along $\vec{b}$ axies.

—— 85 K phase with composition 2212 most single phase.

tetragonal unit cell without modulation. ②

—— 110 K phase 2212 or 2213

c = 30.8 Å or c = 36.8 (2223)

4. Various structure models related to Aurivilous structure : { Face centered lattice, Body centered lattice; orthorhombic, tetragonal.

What is the 85 K superconducting phase.

chemical formula	Symmetry	Lattice parameters
$Bi Sr Ca Cu_2 O_{5.5}$ (Maeda)	—	—
$Bi_2 Sr_2 Ca Cu_2 O_9$ (Hazen & chu)	A-centered	5.42 × 5.44 × 30.78
$Bi_{2.2} Sr_2 Ca_{.8} Cu_2 O_{8+x}$ (Sunshine)	F mmm	5.42 × 27.2 × 30.8
$Bi_{\frac{4}{4}} Sr_{\frac{3}{4}} Ca_{\frac{3}{2}} Cu_{\frac{4}{4}} O_{16}$ (Tarascon)	I 4/mmm	3.817 × 3.817 × 30.6
$Bi_2 Sr_2 Ca Cu_2 O_{8+x}$ (Argonne Lab.)	F 4/mmm	5.41 × 5.41 × 30.8
$Bi_2 Sr_2 Ca Cu_2 O_{8+x}$ (Institute of Physics)	I 4/mmm	3.825 × 3.825 × 30.82

possible impurity phases ③

1) * Ca_2CuO_3 type :

$(Ca_{.92}Sr_{.08})(Cu_{.96}Bi_{.08})O_3$

a = 12.234, b = 3.771, c = 3.257 Å

2) $CaCu_2O_3$ type :

$(Ca_{.6}S_{.4})Cu_{1.75}O_3$

a = 11.328, b = 12.774, c = 3.88 Å

3) $SrBiO_3$ type :

$Sr_{.9}Bi_{1.1}O_{2.55}$?

a = 13.329, c = 4.257

4) * CuO

5) $SrCuO_2$: Cmcm

a = 3.56, b = 16.32, c = 3.92 Å

6) * $CaCu_2O_3$: Pmmm

a = 9.85, b = 4.11, c = 3.47

7) * Ca_2CuO_3 : Immm

a = 12.23, b = 3.77, c = 3.25

How to prepare :

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

composition : 2212, 4334, 1112, 1113, in a wide region.

procedures :

mixing & grinding thoroughly starting materials.

calcining at 850 °C – 890 °C, in air for 8 hrs.

regrinding & pressing into pellet.

sintering at 850 °C for 12 hr in air.

quenching down to R.T or cooling in furnace

product : 85 K phase.

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

110 K phase amount increase !

50% A.C susceptibility (Tarascon)

over 70% A.C χ (Beijing)

⑤

melted sample (890°C 72 hr) showed Sandwich layers:

upper, loose, black, 110 K + 85 K phase

medium, denser, black, 85 K phase

bottom, hard, grey, NO

Maeda's procedure for 1112

1. calcining powders at 800°C for 12 hrs
2. six hours at 820°C
3. six hours at 820°C
4. sintering at 840°C
5. sintering again at 860°C
6. quenching to R. T.

Chraterization:

Resistance and A.C χ { 85 K or lower; 110 K or higher }

identification (x-ray powder diffraction & eletron microscopy)

indexing main reflections.

⑥

Body-centered lattice (I 4/mmm)

$a = a_p \doteq 3.8$ Å, $c = 30.8$ Å

Face-centered lattce (F 4/mmm)

$a = \sqrt{2}\, a_p \doteq 5.4$ Å, $c = 30.8$ Å

For 110 K phase: (orthorhombic or tetragonal)

two c parameters { 30.8 Å (Tarascon); 36.02 Å (Zhao) }

→ composition? { 2212 or 4424; 4426 (more copper); 2223 (EDX) }

Modulation: Incommensurate →(Lock-in) commensurate

incommensaurate along b axies for 85 K pha[se]

neither incommensaurate nor superlattice for 110 K phase.

Growth of single crystal: flux method.

1. synthesize the bulk sample (4334 or 1113)
2. melt the powders or bulk sample at 1100°C for 2 hrs

3. cool down to 850°C slowly (10~15 °C/hr) ⑦

4. hold sample at 850°C for 12 hrs or longer.

5. cool down to R.T. in the furnace.

products : flat superconducting crystals
plate-like (5 mm - 2 mm) : black, easily to cleavage along (a,b) plane, like mica.
minor : bar-like crystal : dark green.

flat 'single crystal' : anisotropic resistance

behavior above $T_c = 85$ K

{ metallic in (a, b) plane (semimetal)
{ semiconductive in $\vec{c}$ direction

Bar-like crystal — Bismuth-poor compound

$a = 11.84$ Å , $b = 12.37$, $c = 19.54$ Å

superconductivity uncertain ! Non-superconducting.

Growth of single crystal of Bi-compound : (modified procedure.

1. add the extra Bi_2O_3
1. hold molten sample 24 hr.
3. hold sample at 850°C 3 days
4. The bar-like crystals disappear.

structure of 85 K phase : ⑧

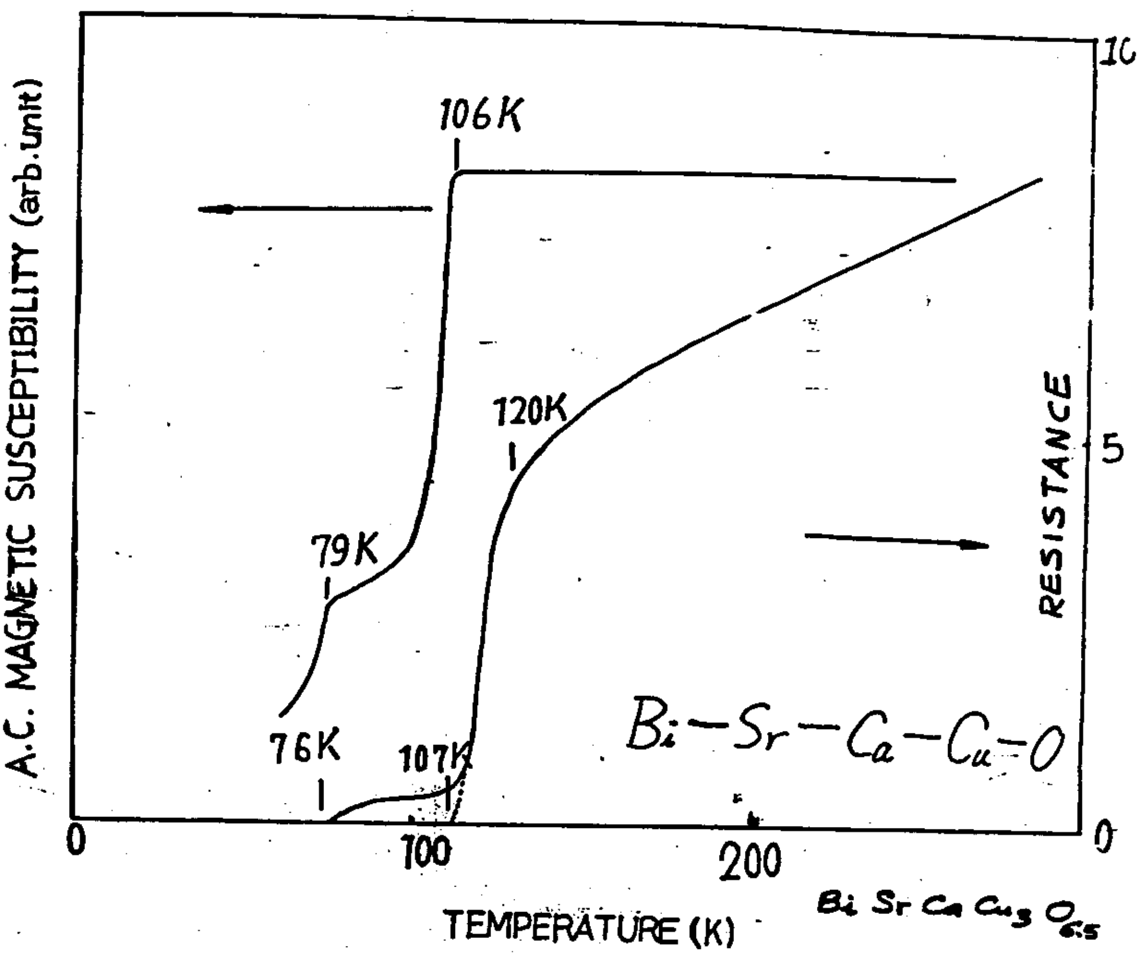
Commen in all models : alternative perovskite + double Bi_2O_2 layers (Aurivilous)
modulation along $\vec{b}$ axies or superlattice (?)
Cu-O planes exist, but are seperated by Ca Cations.

Substitution : V, Gd, Y, Pb replace Bi
→ depress T_c.
In, Cd, Sn replace Bi
→ destroy superconductivity.

Uncertain things :

1. How to isolate pure single phases of 85 K & 110 K.
2. Cu-O chain ? Bi-O chain ?
3. exact amount & distribution of Oxygen ?
4. Valences of Cu & Bi ?
   mixed valence ?
   Bi^{3+} ~ 0.96 Å , Bi^{5+} ~ 0.74 Å
   Cu^{2+} ~ 0.72 Å ,
   so, disordering of Cu^{2+} & B^{5+} ?
5. Ordering or disordering of Ba & Ca ions ?
6. Process of molten sample → amorphous → Crystalline ?

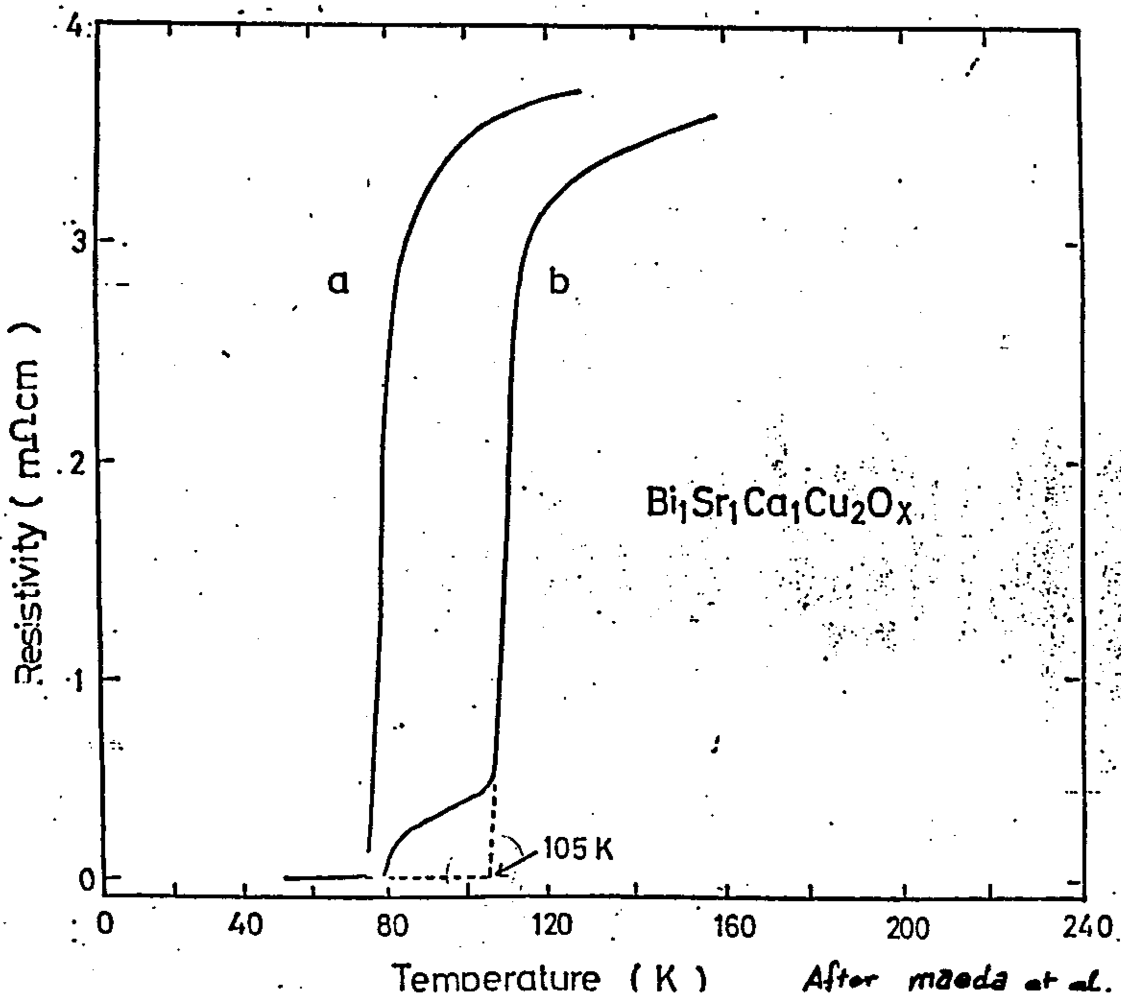
Reported in Interlaken.



Bi Sr Ca Cu_3 $O_{6.5}$

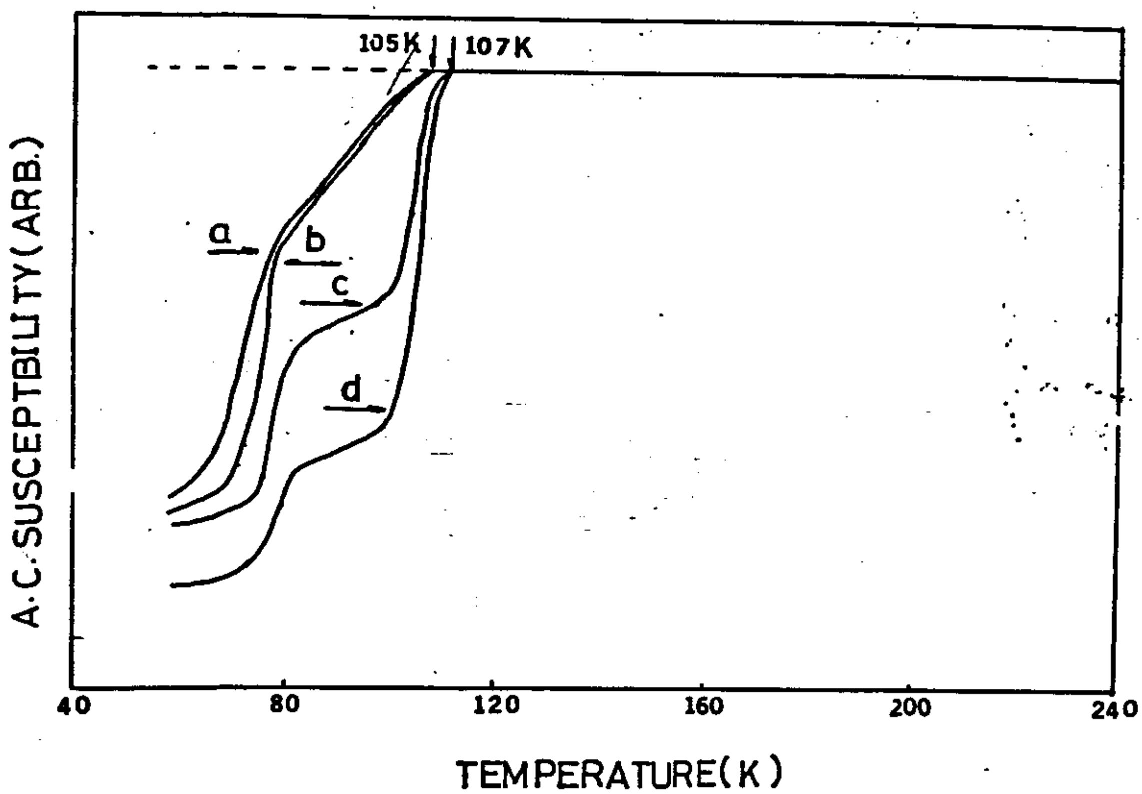
(10)

Fig. 1 II



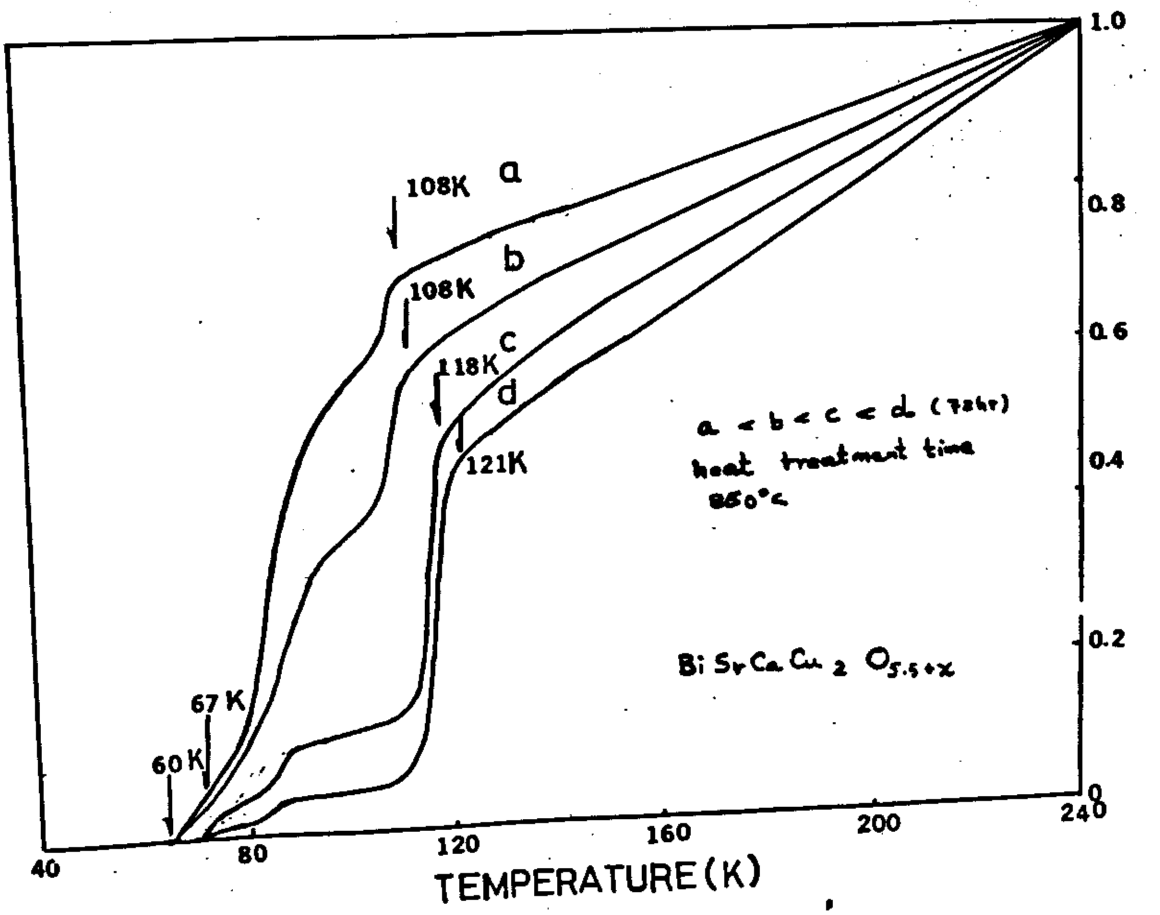
After maeda et al.

(9)



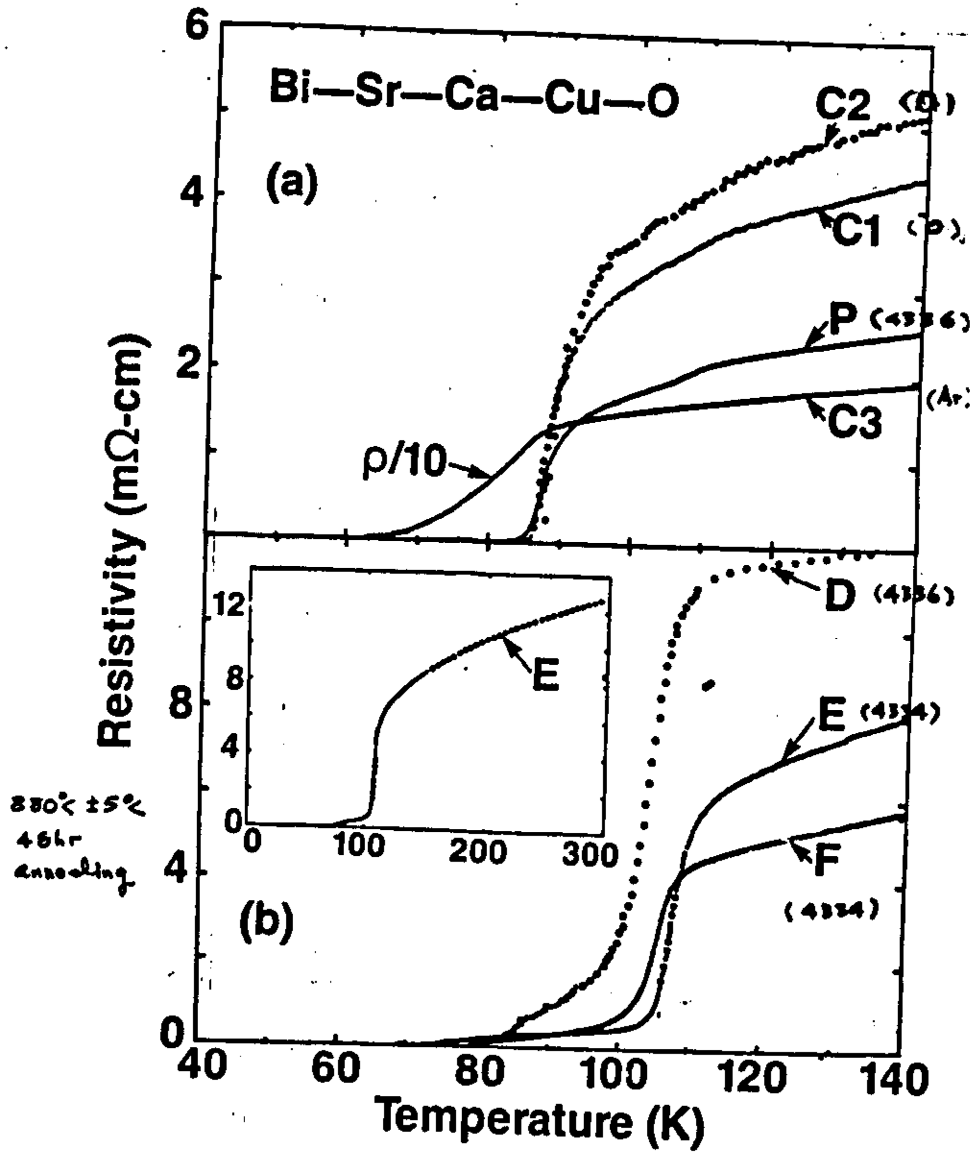
A.C. SUSCEPTBILITY (ARB.)
105K
107K
a
b
c
d
40
80
120
160
200
240
TEMPERATURE(K)

(12)

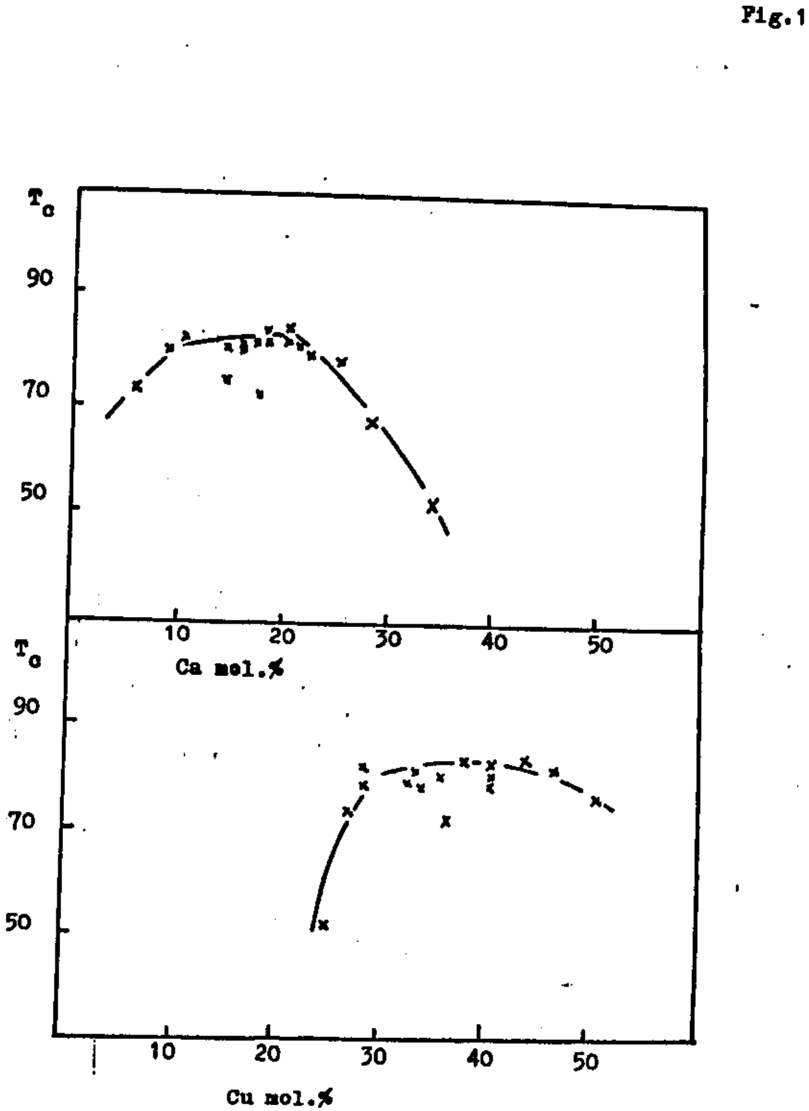


1.0
0.8
0.6
0.4
0.2
0
108K
a
108K
b
118K
c
d
121K
a < b < c < d (72hr)
heat treatment time
850°c
Bi Sr Ca Cu 2 O5.5+x
67K
60K
40
80
120
160
200
240
TEMPERATURE (K)
R(T)/R(240K)

(11)



After Tarascon



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

Fig. 2

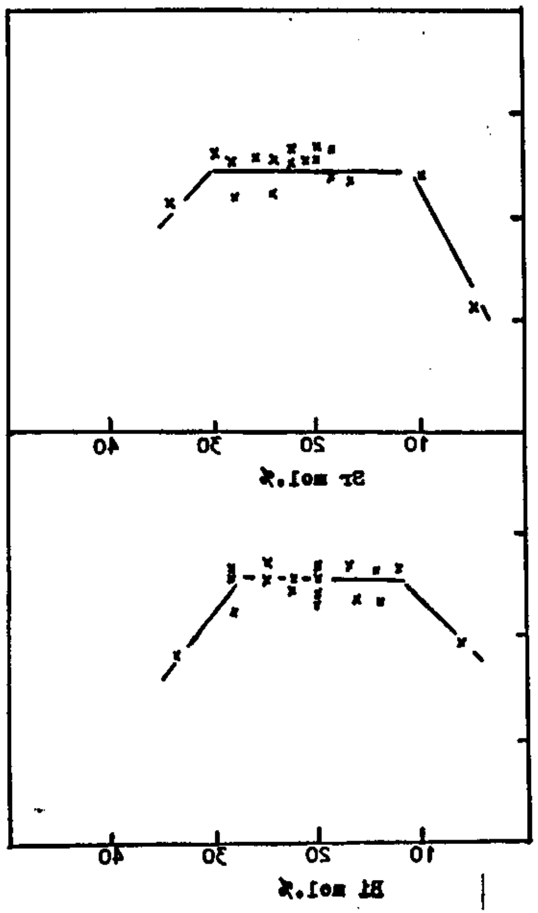
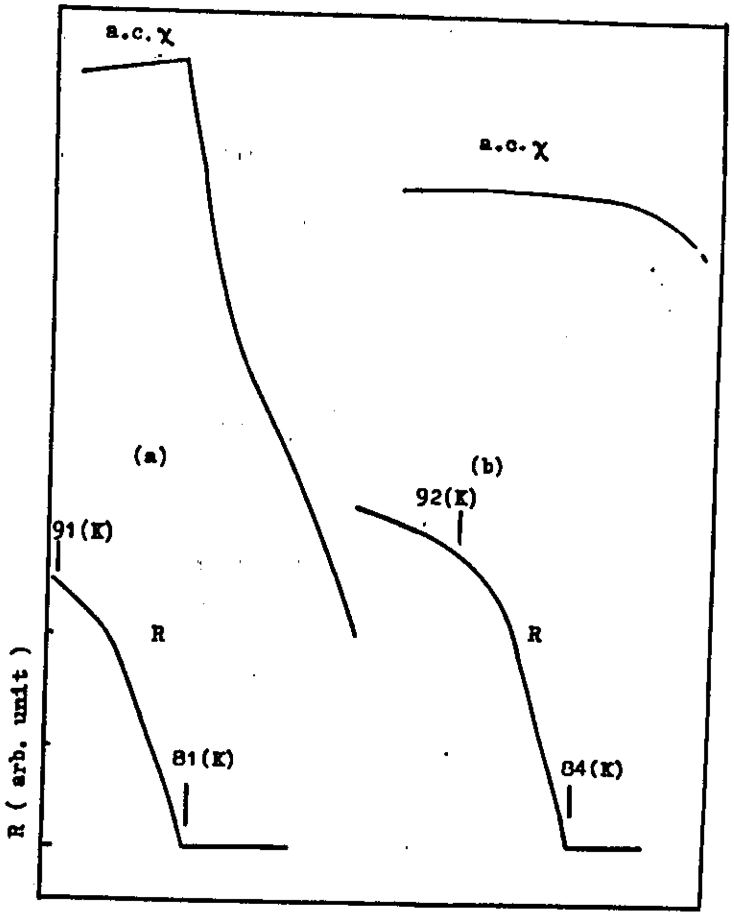
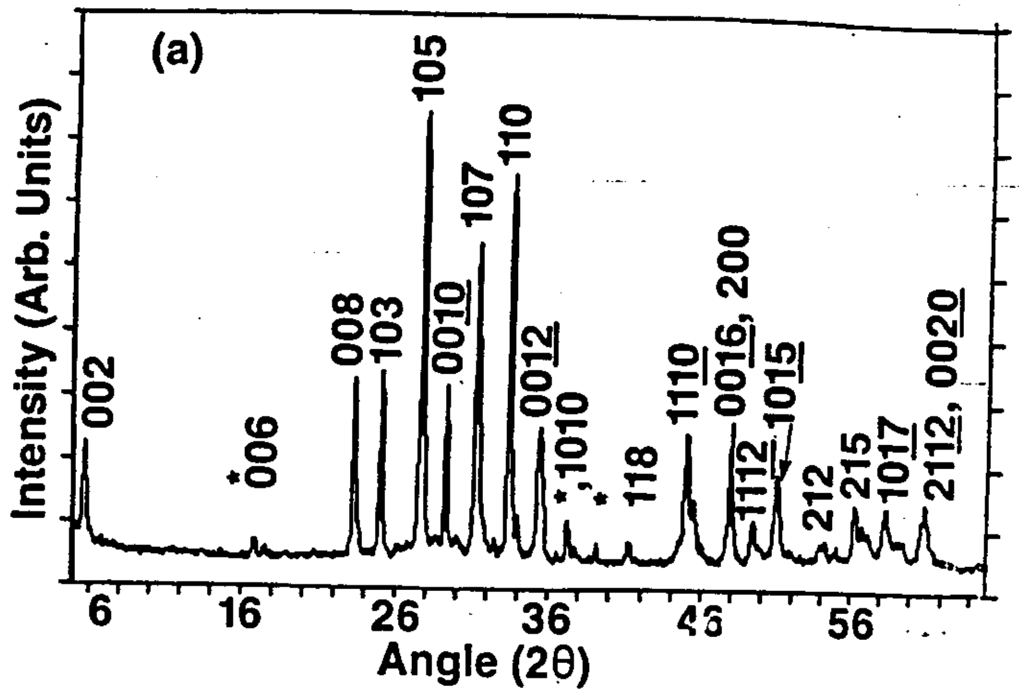


Fig. 3(a)



a) $Bi_{6.5} Sr_{6.5} Ca_{5.5} Cu_{10.5} O_{32.5+\delta}$

b) $Bi\, Sr_{1.5} Ca_{1.5} Cu_2\, O_{6.5+\delta}$



Indexing with tetragonal body centered unit cell $a = 3.817$, $c = 30.6$

a) $Bi_{17}Sr_{20}Ca_{20}Cu_{43}O_x$

b) $Bi_4Sr_3Ca_3Cu_6O_{18}$

Fig. [illegible]

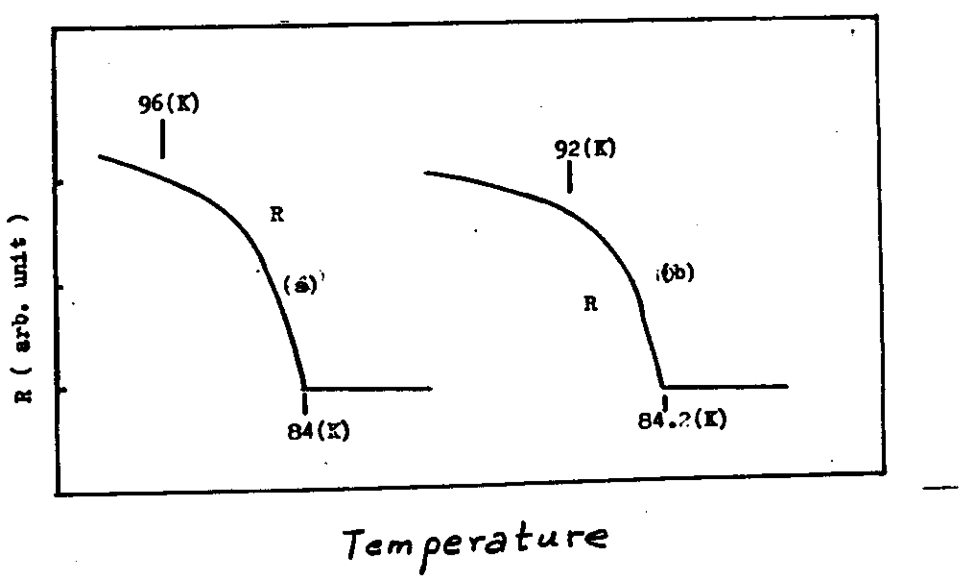
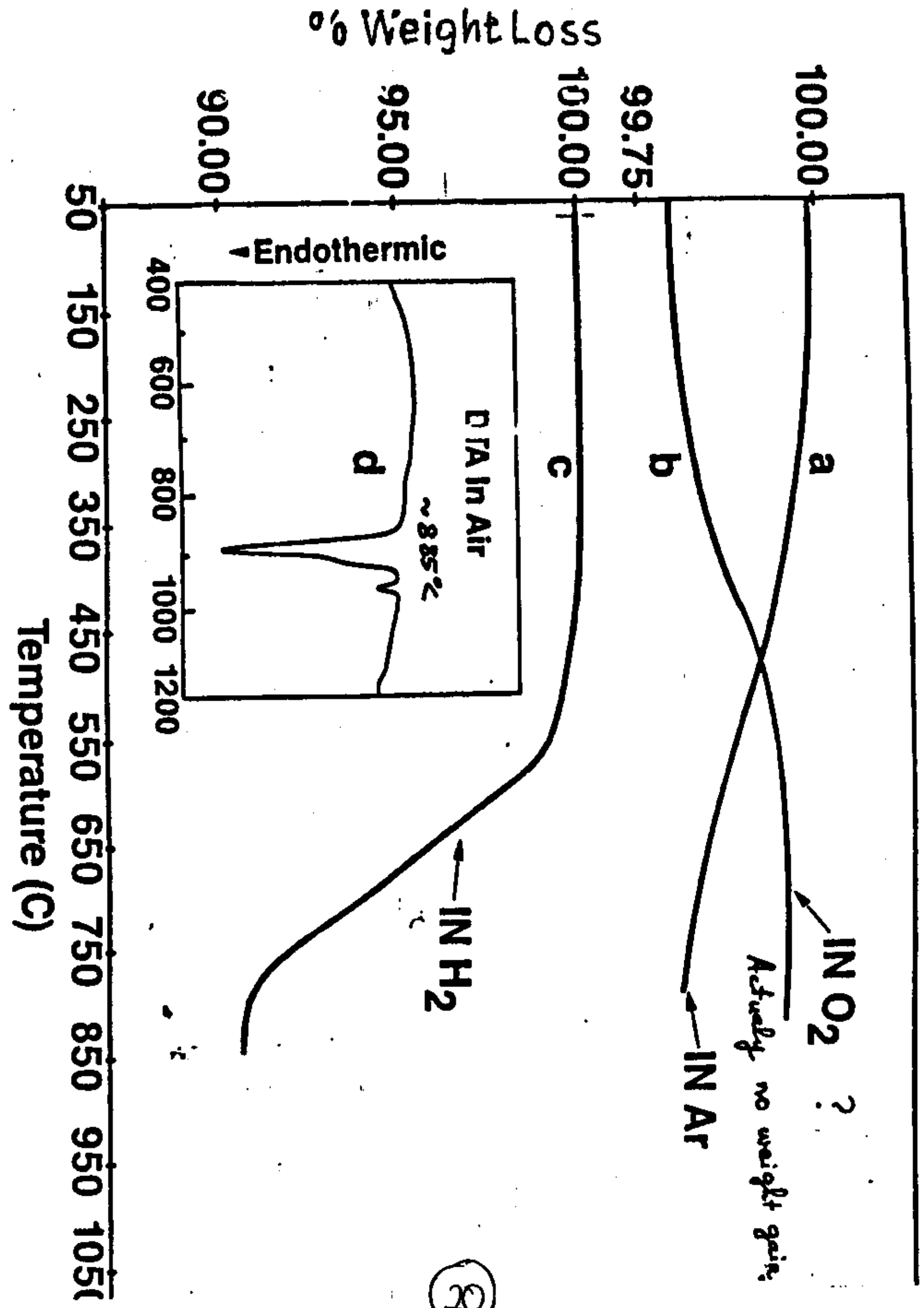
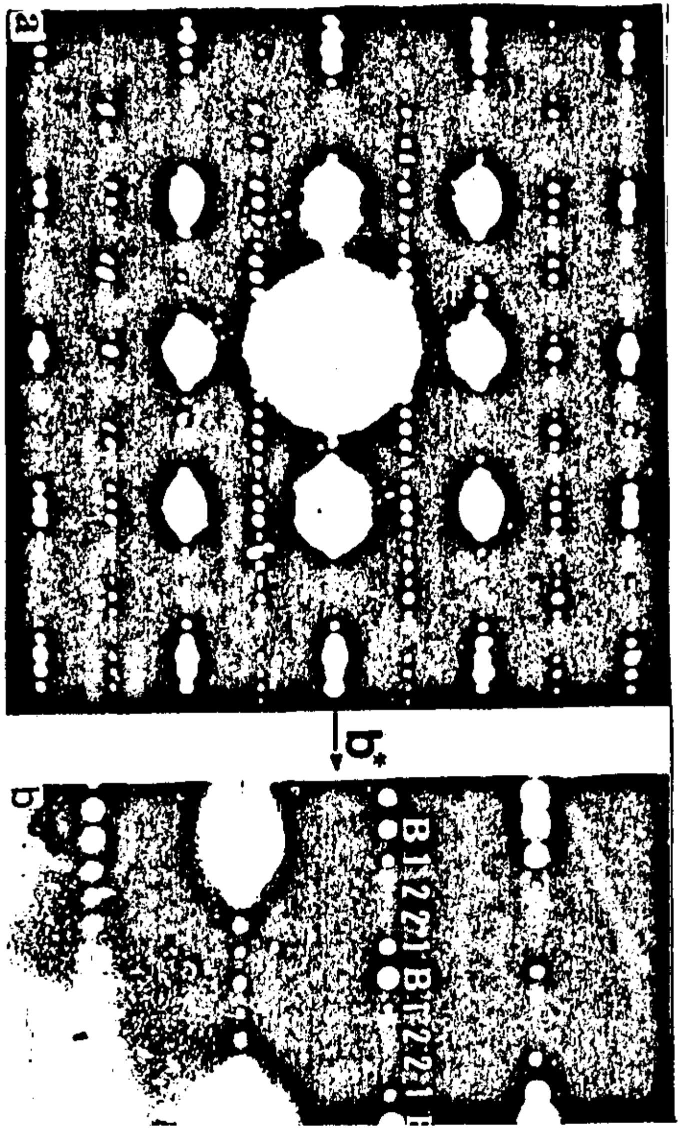


Figure B

X-ray powder diffraction pattern of the 4334 material is shown over the 2θ range from 5 to 65°. The pattern for a polycrystalline powder is shown in (a) with the Miller indices noted above each peak. Shown in (b) is the pattern for highly-c-oriented multicrystalline composite (sample C). Note that only the (00l) reflections with l even are observed. Peaks with asterisks can be indexed in a unit cell of a=5.4 and c=30.6 Å.





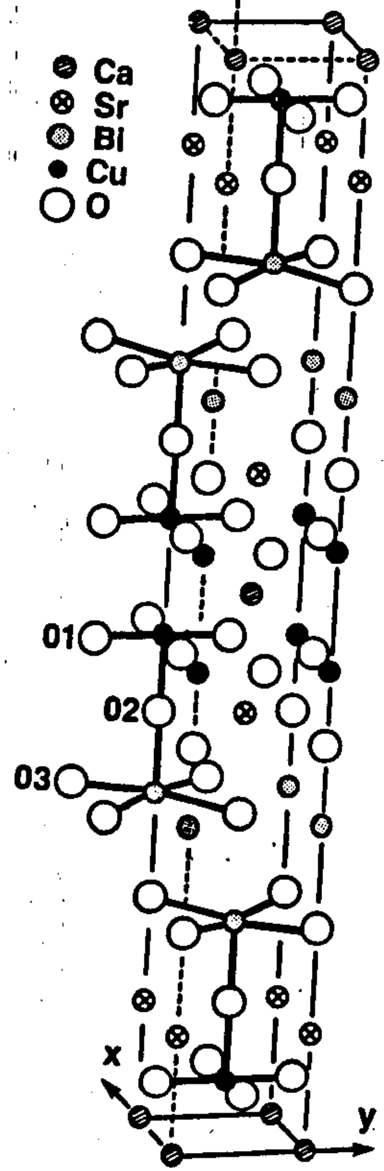
modulation structure along $\vec{b}$ axis
reported in Interlaken, submitted to J. Phys. D.
(Ref. Li)

(21)

S.G I4/mmm
$a = 3.817$ Å
$c = 30.6$ Å

$R_f = 0.16$

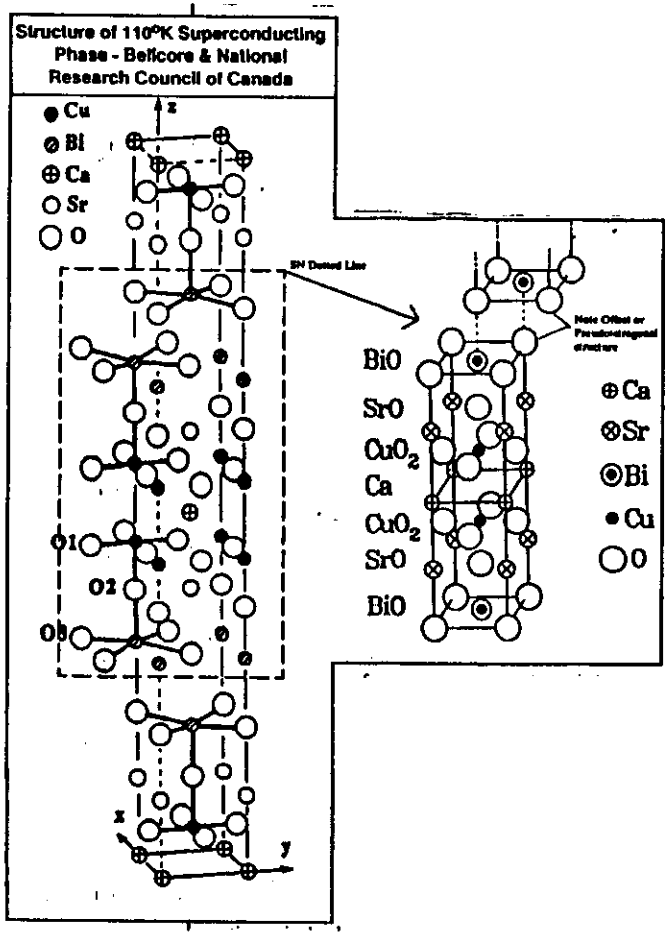
buckled crystal



$Bi_4Sr_3Ca_3Cu_4O$
or
$Bi_2Sr_2CaCu_2O$
(4424)

After Tarascon

(22)



S.G Fmmm

$a = 5.4$ Å

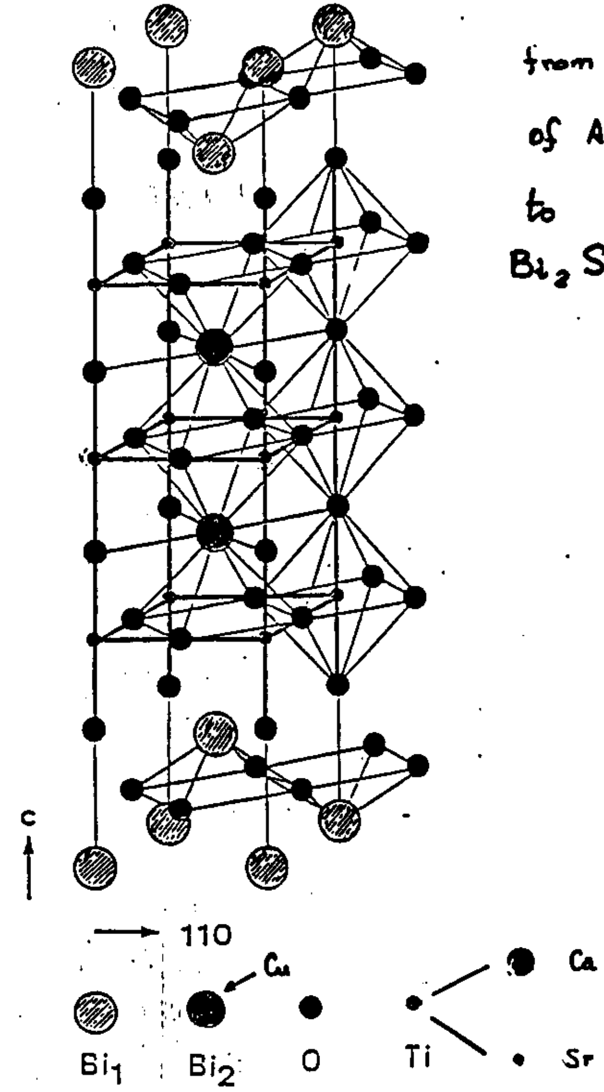
$c = 30.5$ Å

from $Bi_4Ti_3O_{10}$

of Aurivilous

to

$Bi_2Sr_2CaCu_2O_{8+}$.

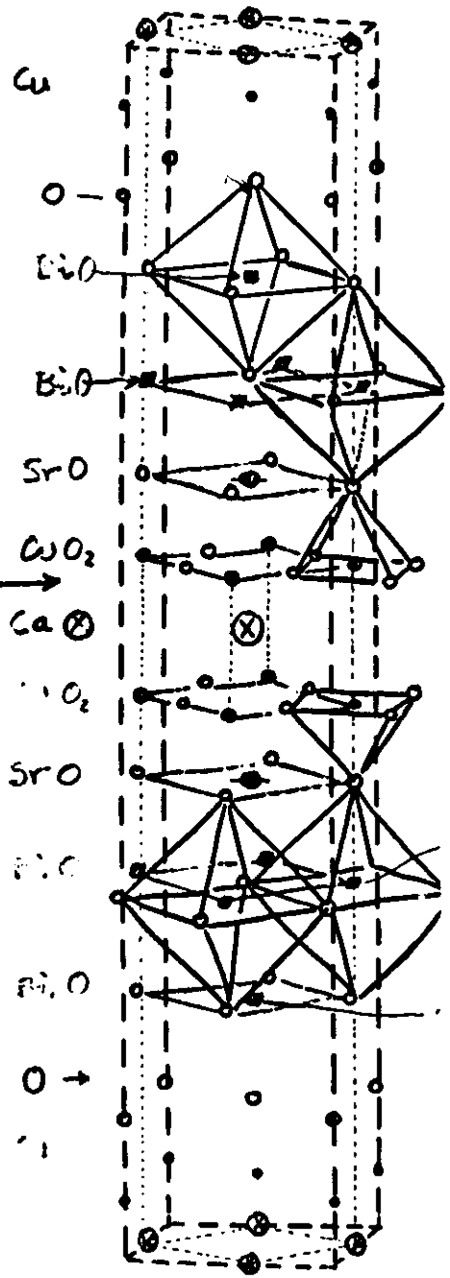


After Yasuhiko et al

$Bi_{2.2}Sr_2Ca_{0.8}Cu_2O_8$

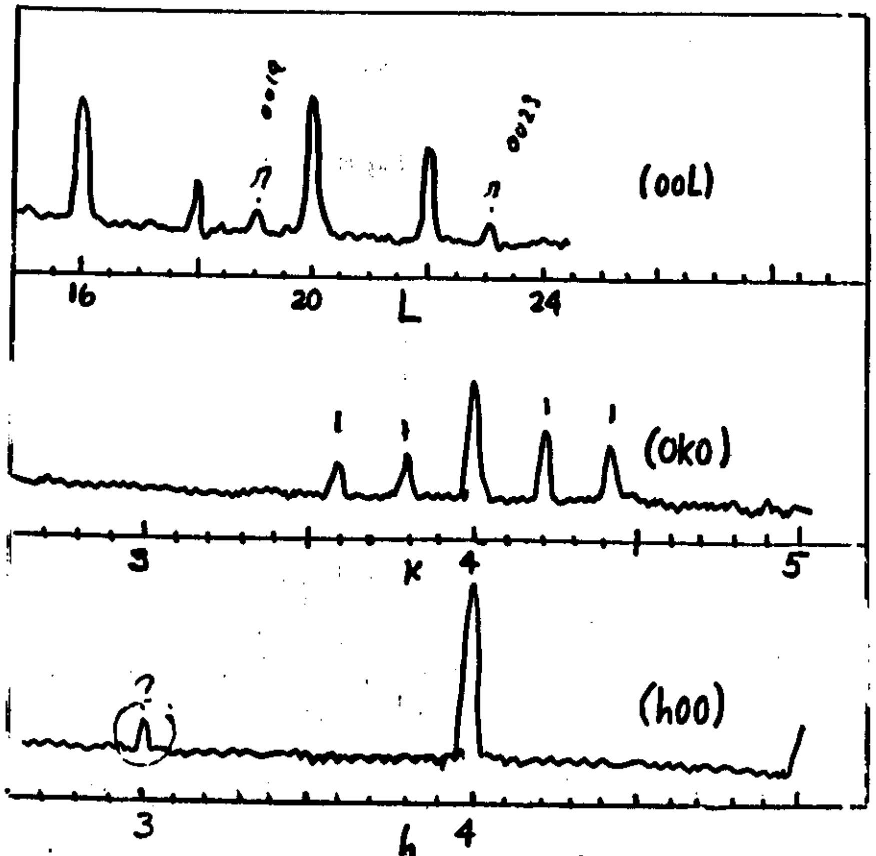
1) 5.414 × 5.428 × 30.89
2) F mmm , Z = 4
3) Incommensurate $\vec{b}$

4) Bi - O octahedra (6)
   Cu - O pyramid (5)
5) double Bi_2O_2 layer
   + perovskite
6) Face centered lattice →
   (green dot line)
7) Body centered Unit cell
   (red dot line)

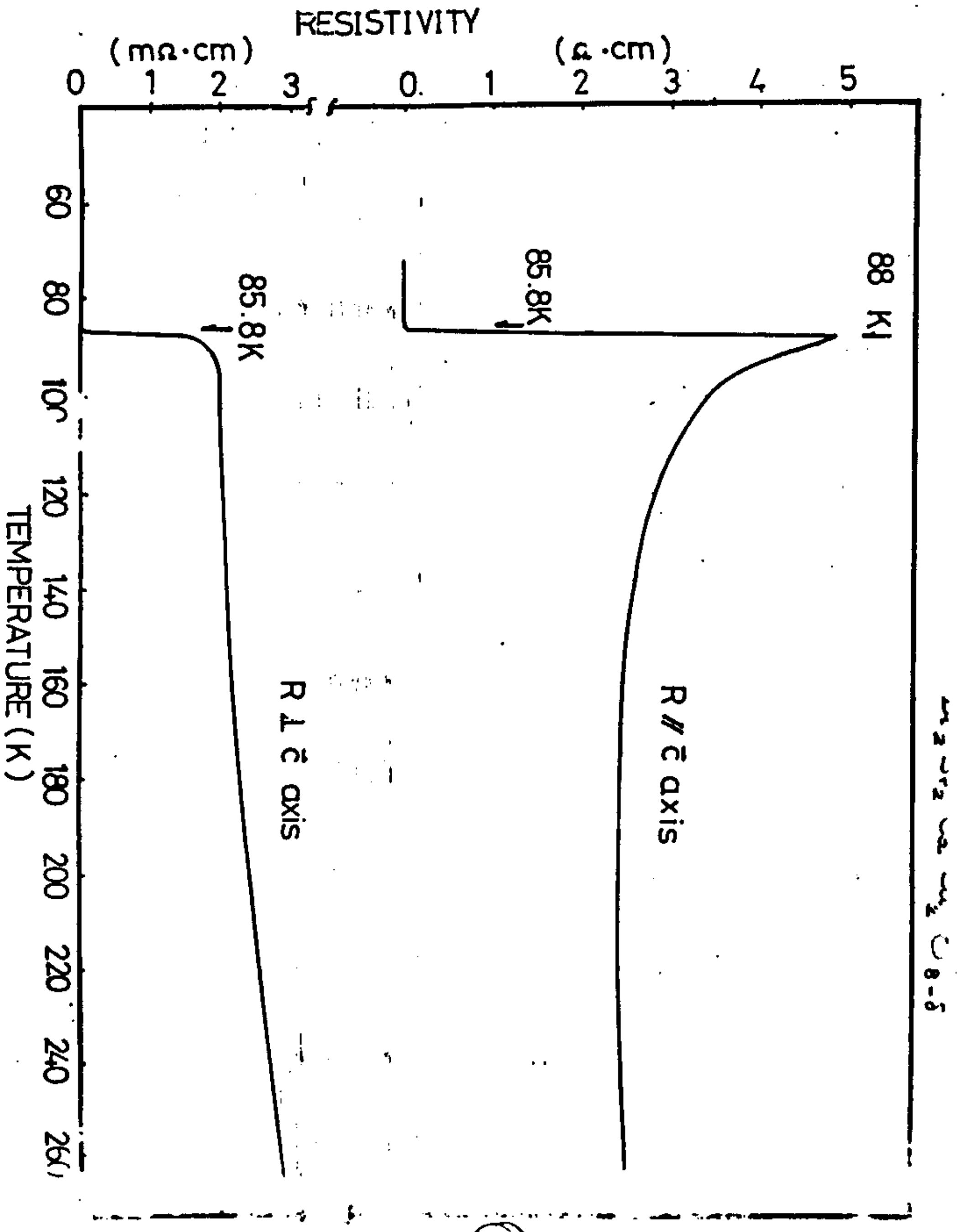


* weak peaks
  Violate Fmmm
  symmetry

After Sunshine
Bell Lab.



Weak peaks that violate Fmmm
symmetry.


RESISTIVITY
(mΩ·cm)
0 1 2 3
(Ω·cm)
0. 1 2 3 4 5
85.8K
85.8K
88 K
R ⊥ c axis
R // c axis
TEMPERATURE (K)
60 80 100 120 140 160 180 200 220 240 260

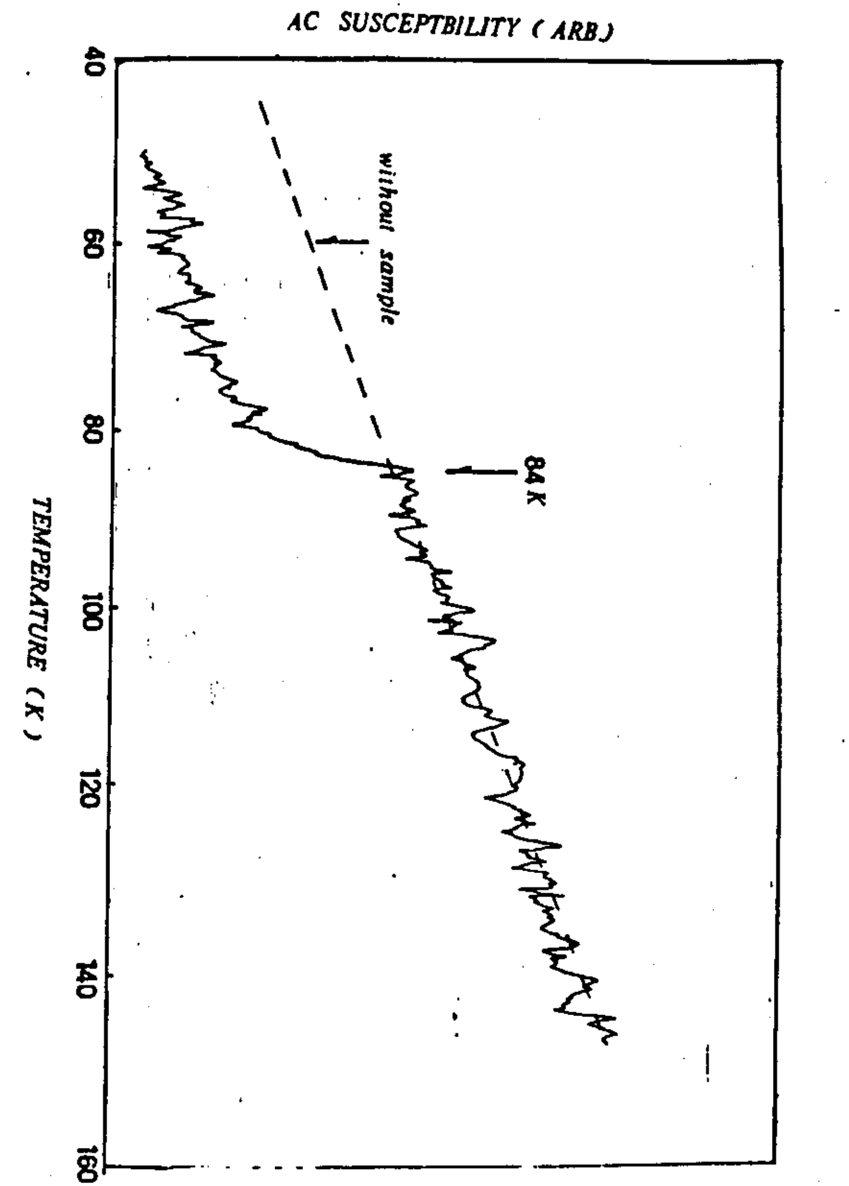
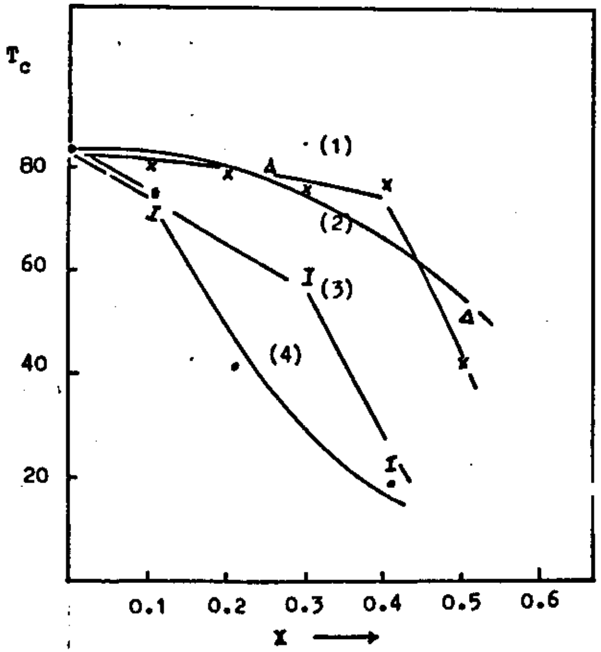

AC SUSCEPTBILITY (ARB)
without sample
84 K
TEMPERATURE (K)
40 60 80 100 120 140 160

Fig. 2

Fig. 4

$Bi_{1-x} A_x Sr Ca Cu_2 O_y$

(1) V
(2) Gd
(3) Y
(4) Pb



New high Tc superconductors above 120 K

in Tl – Ba – Ca – Cu – O system

Short history : Hermman & Sheng

Onset = 120 K, T_{zero} = 106 K

Tc to 114 K (Zhang . Xie)
120 K (Zhang . Xie)
125 K (IBM)

2212 ~ 100K phase 2213 or 2223 120K phase.

WARNING !

Thallium extreme toxic !

M.L.D ~ 12 mg / kg Tl , Tl^{3+} >> Tl^{+1} ;

How to prepare :

1. Tl_2O_3 . BaO . CaO . CuO . (1.1.1.3 or 4.3.3.6)
2. mixing and grinding
   don't calcine powder !
3. pressing into pellets (diameter 16 mm
   (5 T / cm²) thickness 2-3 mm)
4. sintering at 780°C – 800°C for 8 hrs in air.

5. Cooling to 600°c in the furnace (1.5 hr)

6. quenching to R.T.

polish a little, the surface or thin layer be clean out.

Characterization :

T_c = 117 - 120 K

strong A.C. χ anomolous.

existance region of 120K phase.

Tl/Cu ratio more critical.

Ba/(Ca + Ba) 30% - 60 %

In high pure alcohol regrinding & resintering push

J_c 80 A/cm² ⟶ 1600 A/cm².

(77K, 0 field)

Thermal analysis :

DTA no anomolous until decom.

TG no obvious weight loss

C_p at 120 K phase transformation.

anomolous !

Electron microscopy (ED. HREM) &

x-ray powder diffraction :

a = 3.847 Å (or $\sqrt{2}$ a) c = 36.02 Å

for 120 K phase

a = 3.847 Å, c = 29.43 Å

for 100 K phase.

Co-existance & intergrowth of two phases : coheren intergrowth of Both phases.

Structure :

1. $Tl_2 Ba_2 Ca Cu_3 O_9$ related to Aurivilous.

Similar to $Bi_4 Sr_3 Ca_3 Cu_4 O_{16}$

by adding extre Cu layers.

Behaviour in the magnetic field → weak link between the grains. ⟶ granulars ?

2. The structure of 100K phase with composition
$Tl_2 Ba_2 Ca Cu_2 O_{8+x}$:
almost as same as $Bi_2 Sr_2 Ca Cu_2 O_{8+x}$
(just for the preliminary framwork)

Substitution of 3^+ Valence ions :
Tl is necessary for 120 K & 100K phases.
Non successful to eleminate toxic !

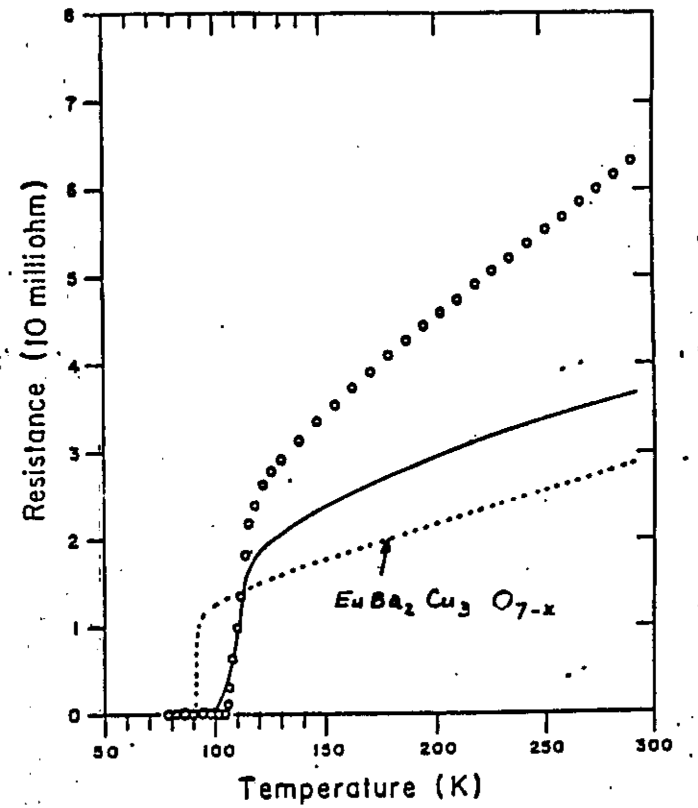
for example : In , Cd , Sn , Hf , ...

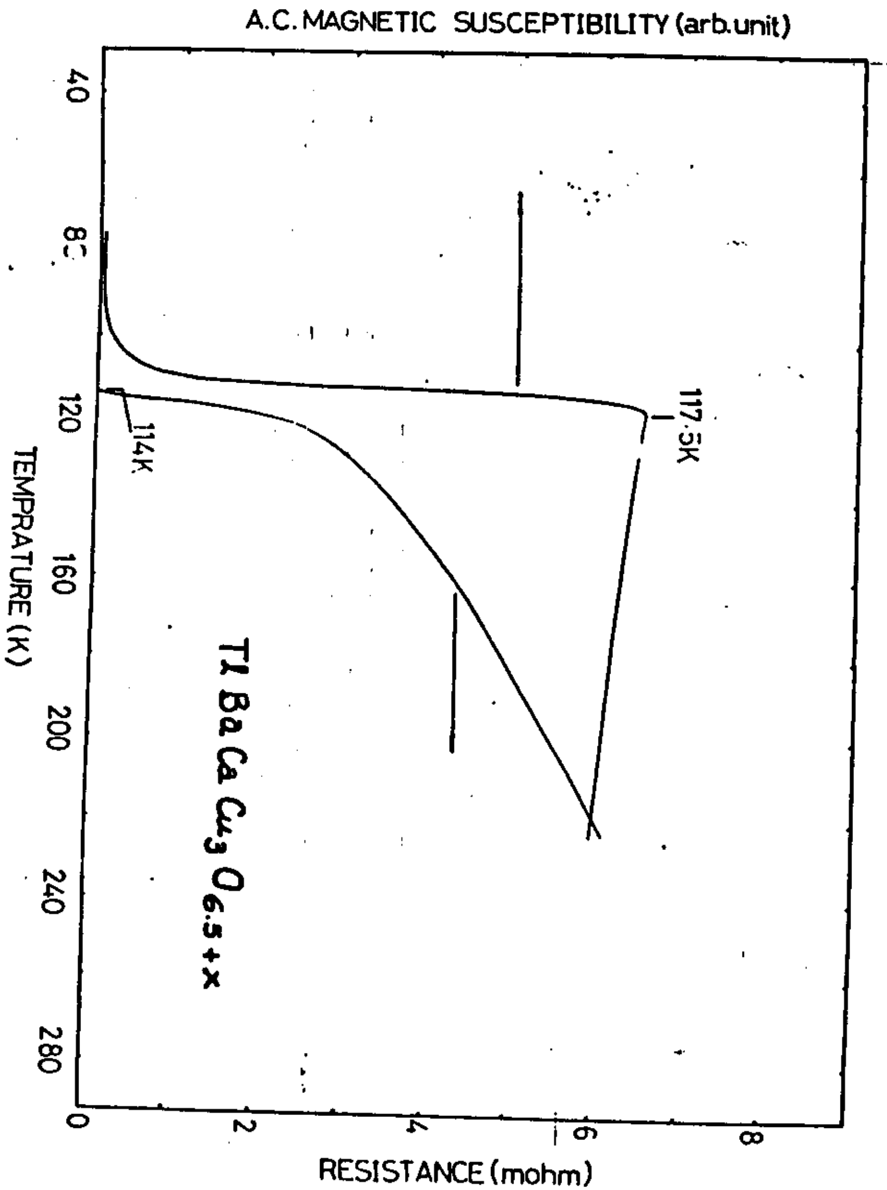
The rough idea about the relation between the Tc &

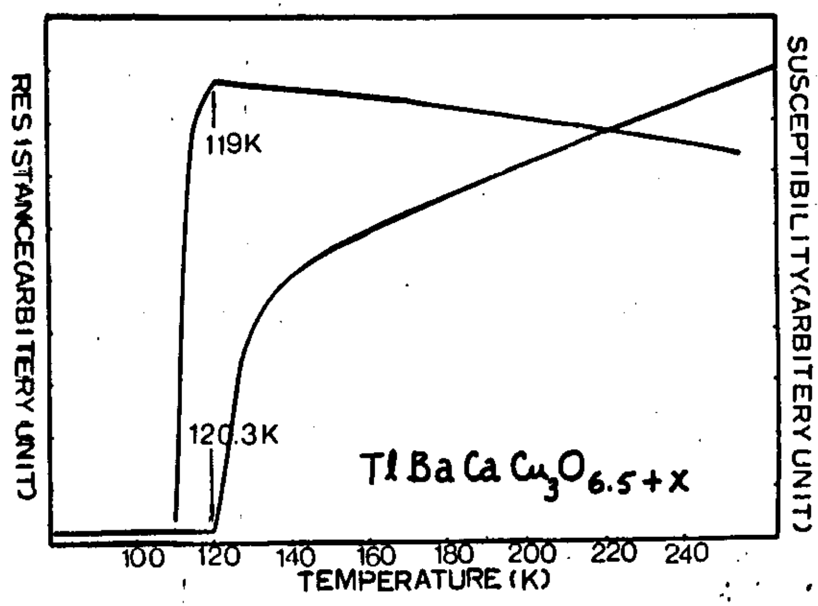
c parameters :
considering the number of moleculars or the distance between rare earths layers or Bi (Tl) layers ;
not only c parameters !

The assumption needs the experiements to support it.
1. pure single phase
2. exact determination of structure : c parameter & atomic parameters
3. setup the relation between the T_c & c :

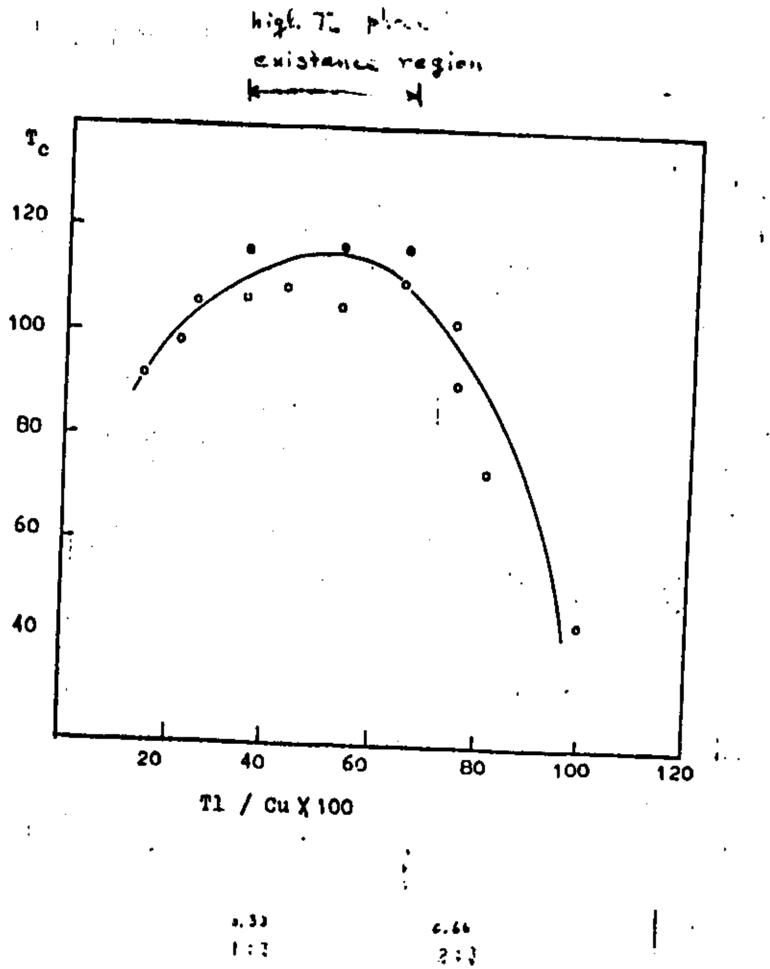
multi-phases sample
nominal composition :
$Tl_2 Ca_{1.5} Ba Cu_3 O_{8.5}$ (circle)
$Tl_{1.86} Ca . Ba Cu_3 O_{7.8+x}$ (solid line)



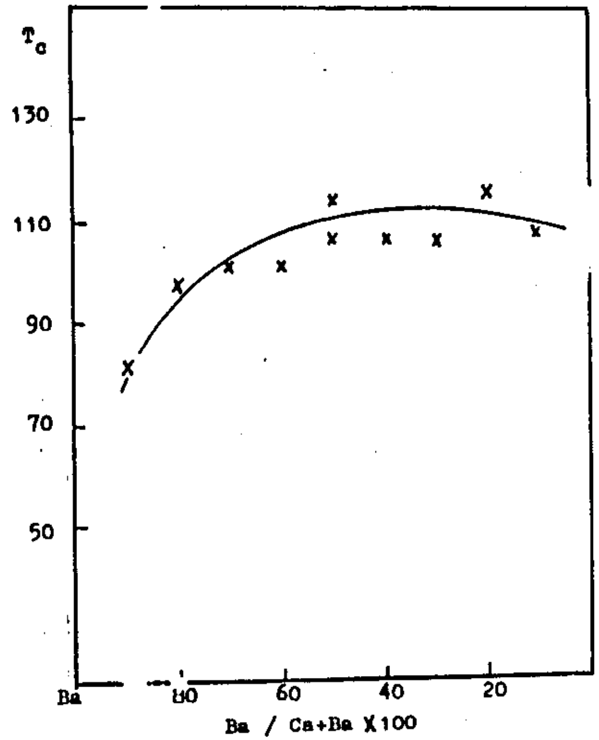




regrinding + resintering again!


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

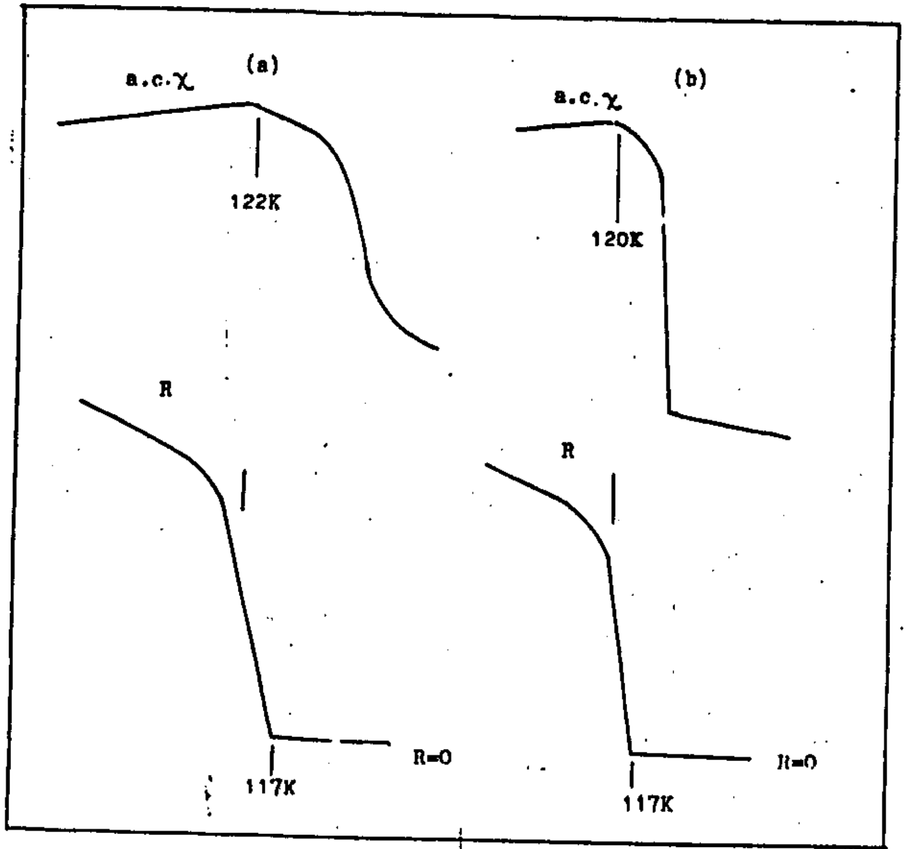
(37)


Tc
130
110
90
70
50
Ba
80
60
40
20
Ba / Ca+Ba X 100

(38)

(a) $Tl_4 Ba_3 Ca_3 Cu_4 O_{16+\delta}$

(b) $Tl_5 Ba Ca_9 Cu_{15} O_x$



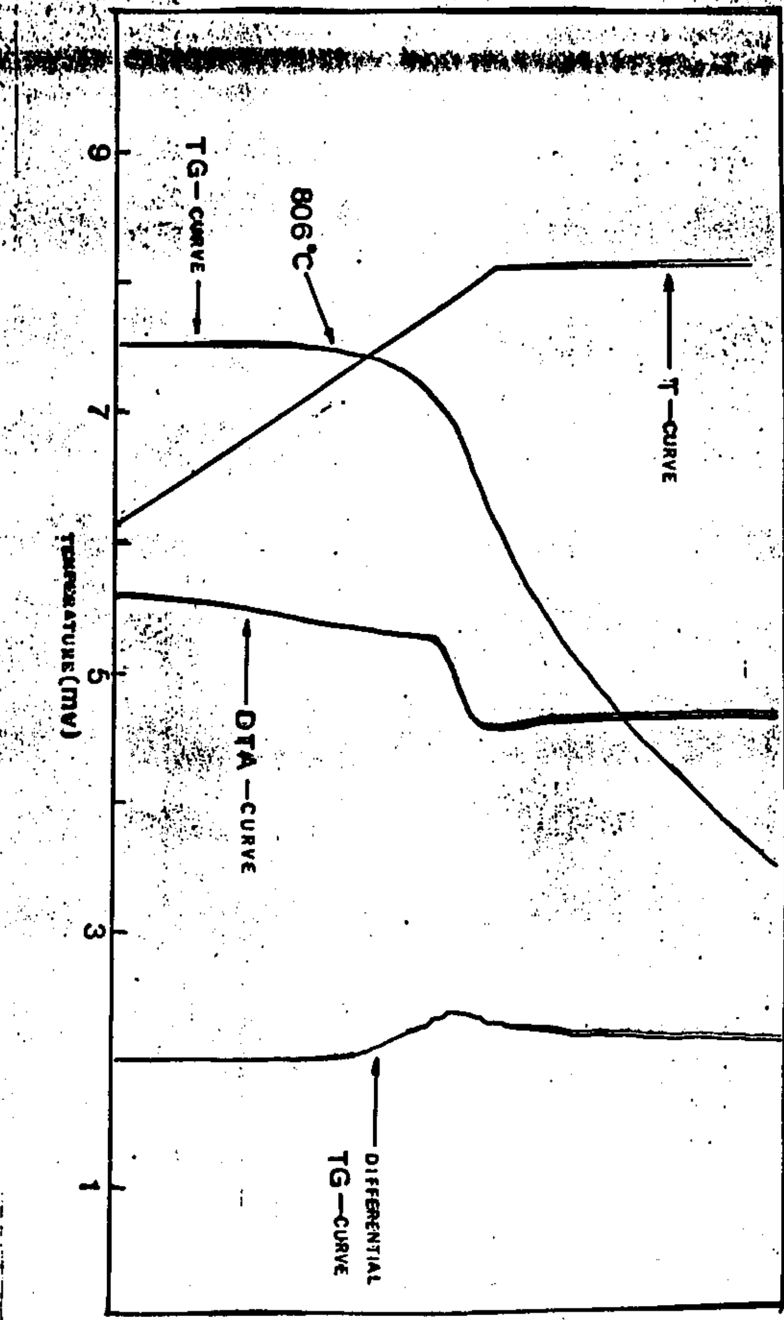
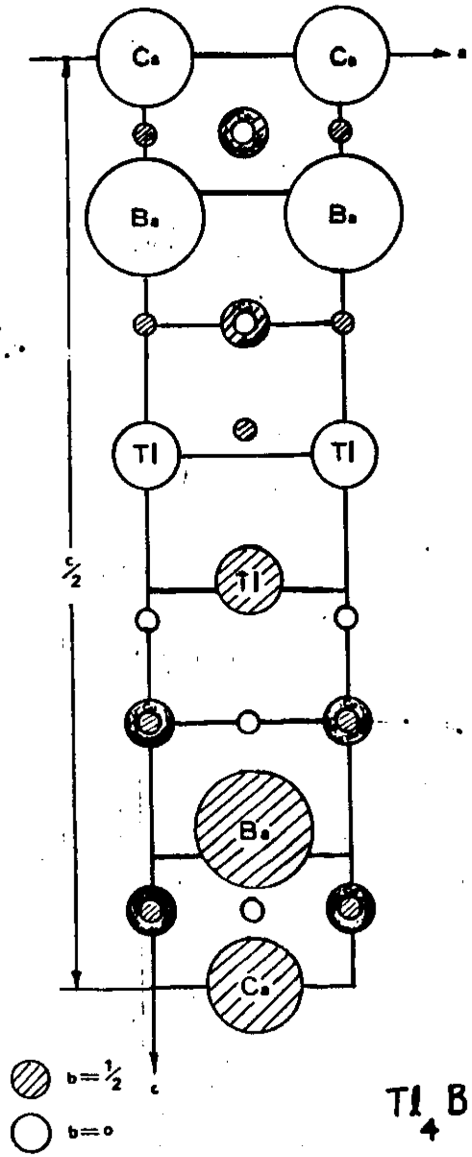


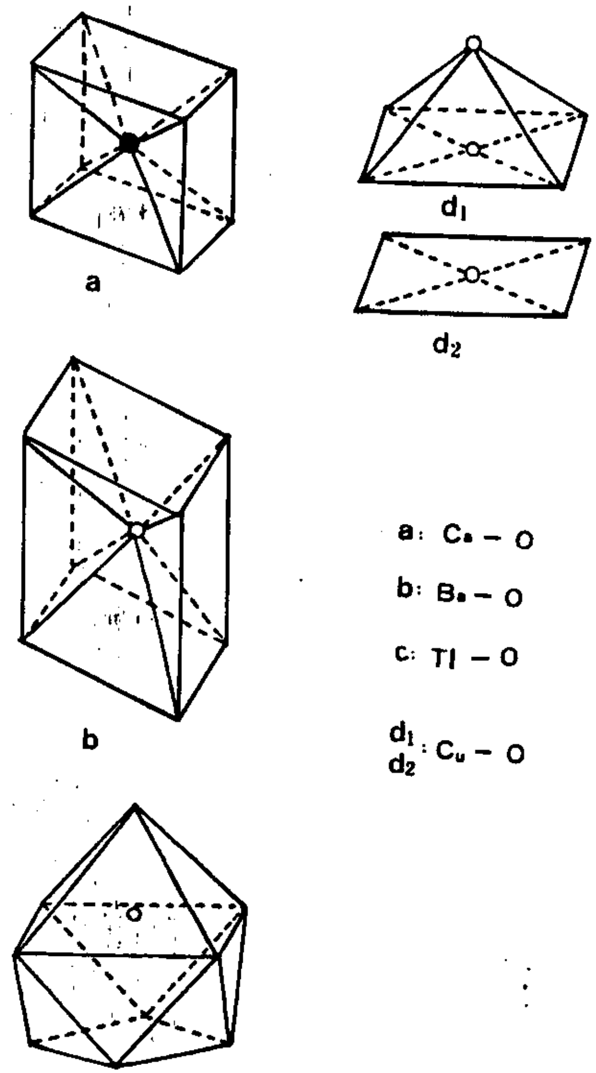
Fig 6. part of thermal analysis ~ weight loss in air.

120K phase

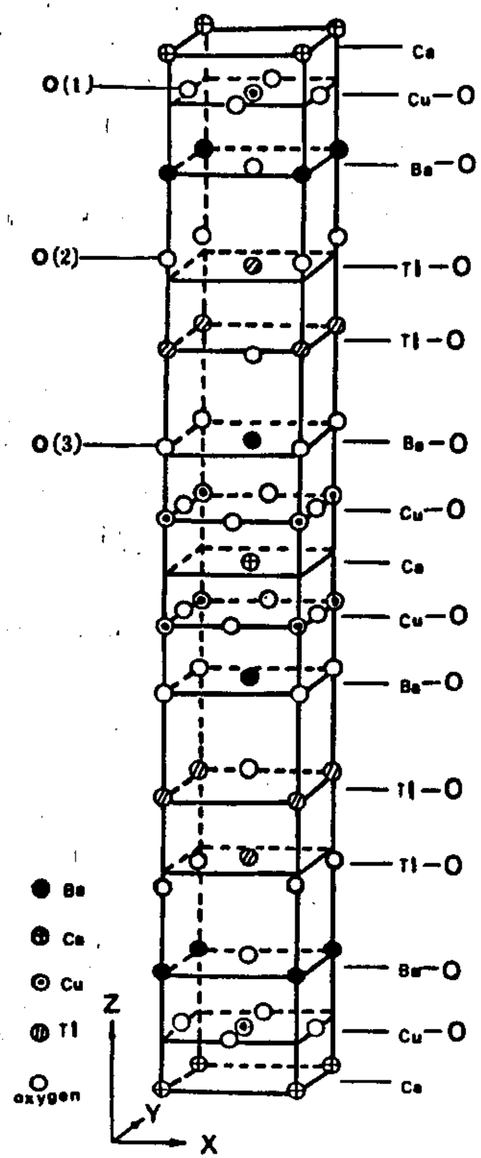


$Tl_4 Ba_3 Ca_3 Cu_6 O_{16+x}$

4 4 2 6

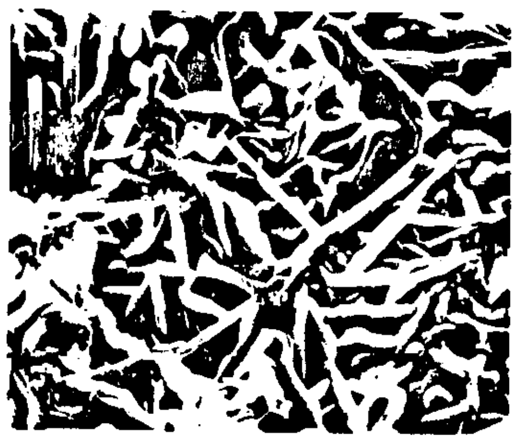


100K phase

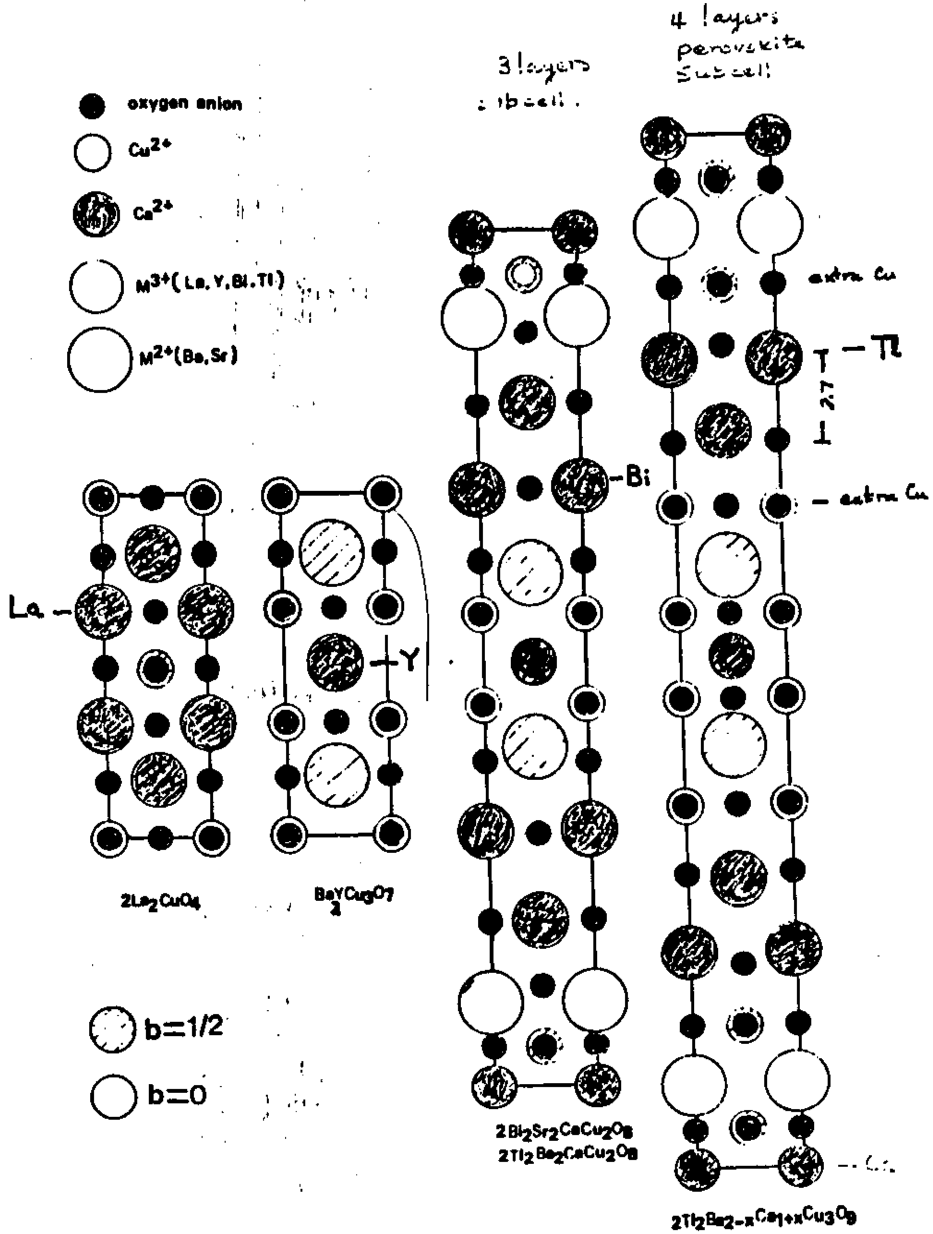


$Tl_2Ba_2CaCu_2O_{6.5}$

(43)



(44)



Ionic radius

Cu^{2+}	0.72 Å	Ba^{2+}	1.34 Å
Sr^{2+}	1.12 Å	Ca^{2+}	0.99 Å
Y^{3+}	[illegible] Å	[illegible]	0.96 Å
Tl^{+1}	1.47 Å	[illegible]	0.74 Å
Tl^{+3}	0.95 Å		

Some stable binary compound

$CaCu_2O_3$	Pmmm	a=9.85, b=4.11, c=3.47 Å
Ca_2CuO_3	Immm	a=12.23, b=3.77, c=3.25 Å
$SrCuO_2$	Cmcm	a=3.56 b=16.32, c=3.92 Å

Distances between ions

Cu - O ~1.95 Å

Bi - O ~2.75 Å

Ca - O ~2.45 Å

Sr - O ~2.50 Å