Crystal Chemistry Design for Discovery of New Superconductors

__Road2RTS__, Loen, Norway, 17 - 23 June 2007

Outline:

- *Layered cuprates:*
  Hg-based Cu mixed oxides
  Cu-based oxyfluorides
- *Bismuthates*
- *Borides and vanadites*

RESEARCHERS FIND EXTRAORDINARILY HIGH TEMPERATURE SUPERCONDUCTIVITY IN BIO-INSPIRED NANOPOLYM

Paul M. Grant
May 2028

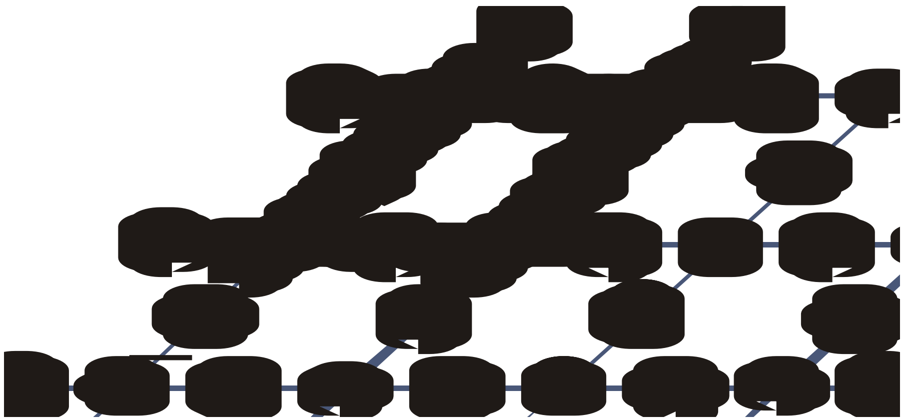
Forty-two years ago, Johannes Georg Bednorz and Karl Alex Müller startled the world with their unexpected discovery of superconductivity in layered copper oxide perovskites at temperatures substantially higher than previously thought possible. The history of this breakthrough is well known, and a large number of related compounds were found over the succeeding years, culminating in 2002 with **Au-2223**—a triple-layer CuO complex with an ambient-pressure transition temperature of **175 K**, synthesized by Paul Chu and his collaborators in Houston. Such materials have found a number of communications and electric power applications, especially in distribution cables, transformers and passive RF filters, but remain limited by the need for cryogenic packaging.

of Stanford University envisioi possibility of very high temp superconductivity in specia signed organic chain system that time, the prevailing Ba Cooper–Schrieffer (BCS) theo cessfully explained all known conductivity as being media electron–phonon coupling. Li served that BCS could apply fermion pairing sustained by eral boson field, including, fo ple, one derived from excitons nons. In the weak-coupling li BCS transition temperature, typically about 10 K. Ev strong-coupling variant of BC oped by William McMilla Gerasim Éliashberg suggest superconductivity mediated b vibrations would not be possib 30–40 K: To paraphrase

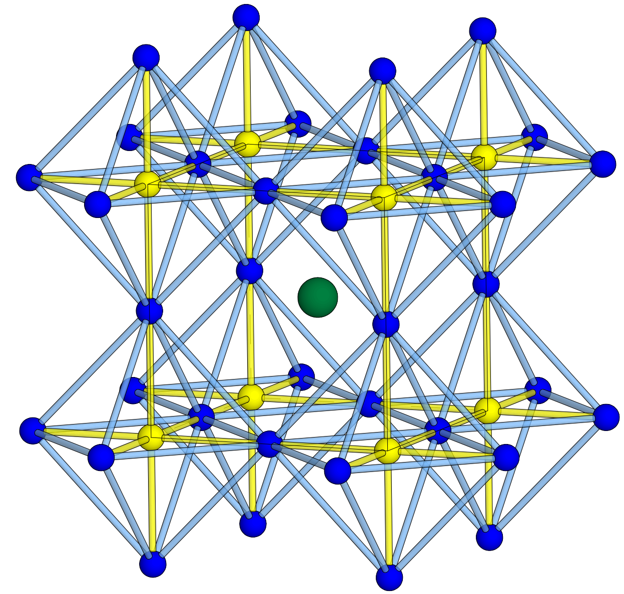
Paul Grant, Physics Today, May 1998

Au –2223
"Au2Ba2Ca2Cu3O8"
VCu = +2

Double chains of the AuO4 squares ⇒ orthorhombic symmetry
dAu-O = 2.06 Å in AuBa2Y0.6Ca0.4Cu2O7 (Tc=80K)
(P. Bordet et al. Physica C 276 (1997) 237)

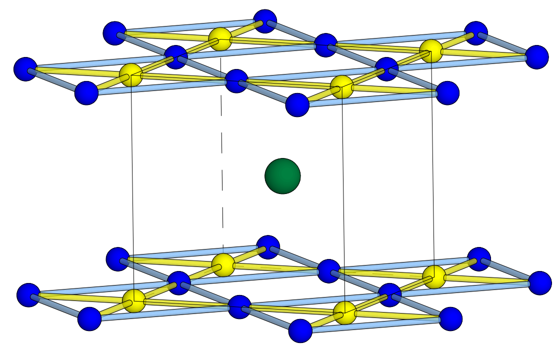


CuO_2 layer



Perovskite structure

Empirical criteria for superconductivity in layered cuprates:



"infinite layer" structure
$CaCuO_2$ ($LaNiO_2$)

1) Filling of the s* conducting band (formal Cu valence)

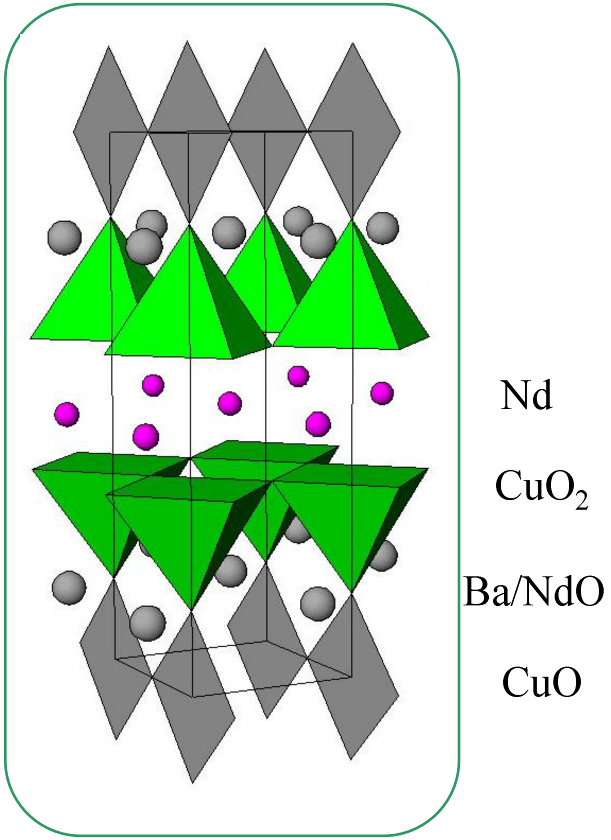
- $+2.05 \leq V_{Cu} \leq +2.25$ - *p*-type SC (carriers - holes)
- $+1.8 \leq V_{Cu} \leq +1.9$ - *n*-type SC (carriers - electrons)

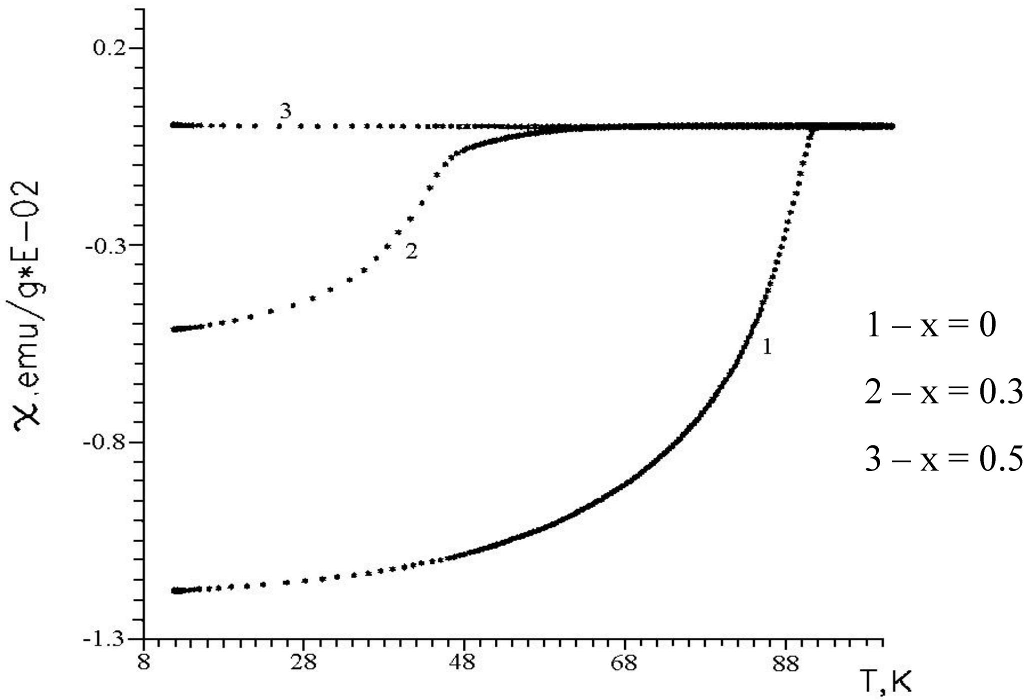
2) $3d_{x^2-y^2}$(Cu) and $2p_{x,y}$(O) overlap: $1.9Å \leq d_{eq}(Cu\text{-}O) \leq 1.97Å$, $\angle$Cu-O-Cu $\approx 180°$

3) nearly two-dimensional structure: $d_{ap}(Cu\text{-}O) \geq 2.2Å$

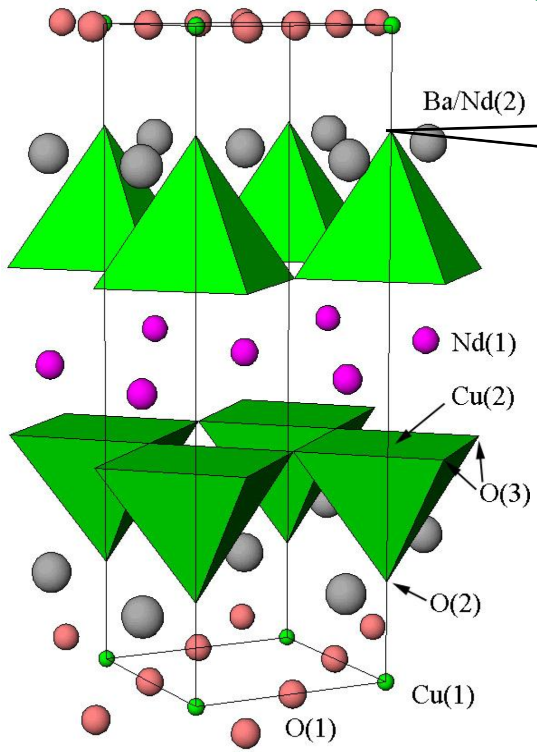
Influence of cation disorder: $Nd_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$

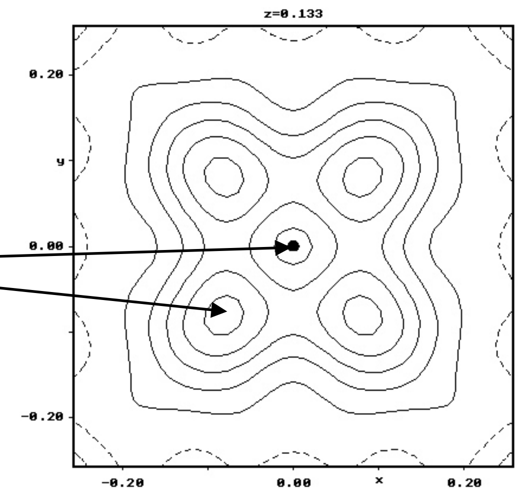
$NdBa_2Cu_3O_{7-\delta}$	$\delta = 0.19$	a=3.8633(9) Å	b=3.916(1) Å	c=11.745(7) Å	VCu = 2.21
$Nd_{1.2}Ba_{1.8}Cu_3O_{7-\delta}$	$\delta = 0.09$	a=3.8902(7) Å		c=11.684(6) Å	VCu = 2.21
$Nd_{1.5}Ba_{1.5}Cu_3O_{7-\delta}$	$\delta = -0.05$	a=3.8803(8) Å		c=11.636(7) Å	VCu = 2.20
$Nd_{1.7}Ba_{1.3}Cu_3O_{7-\delta}$	$\delta = -0.15$	a=3.883(1) Å		c=11.541(6) Å	VCu = 2.20

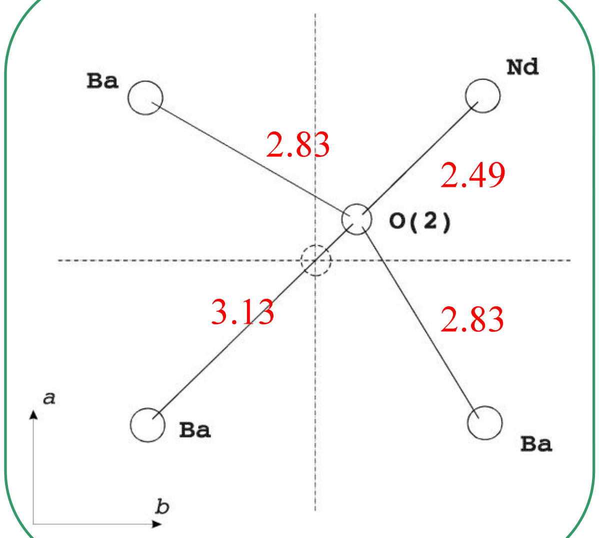


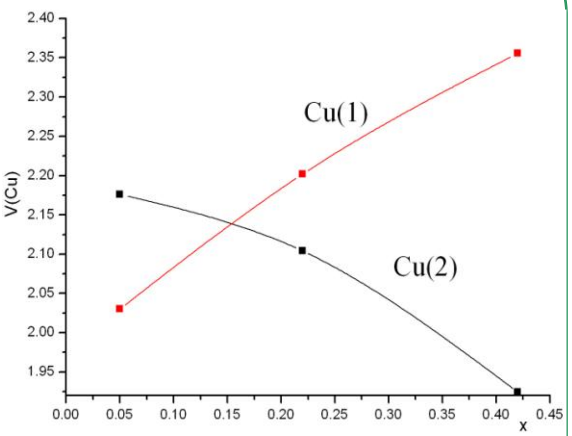


$Nd_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$

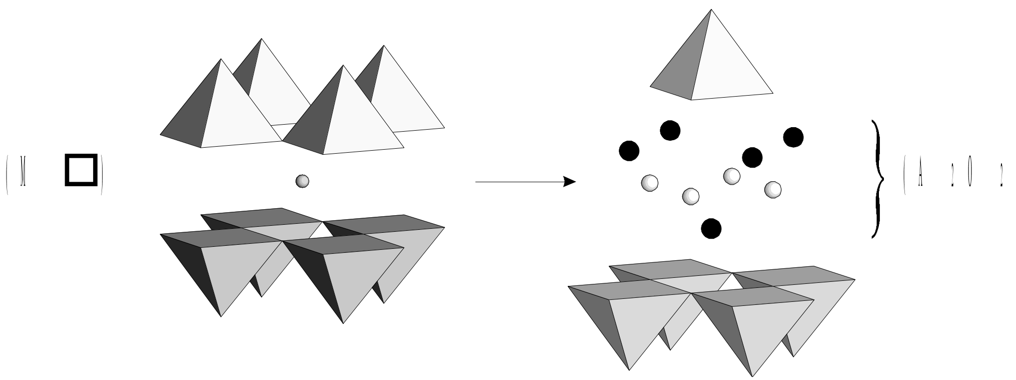


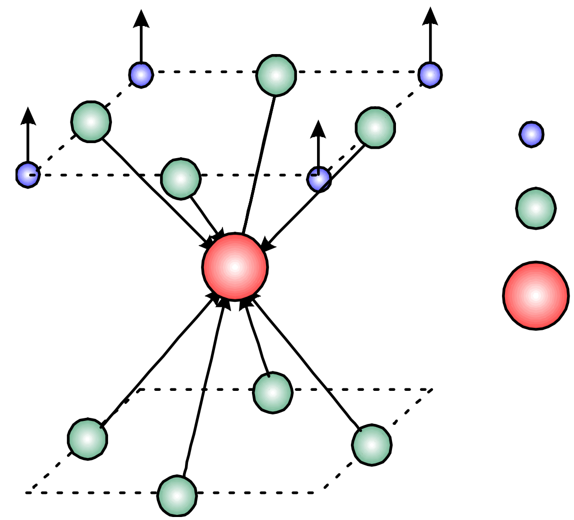






Cu mixed oxides with fluorite slab





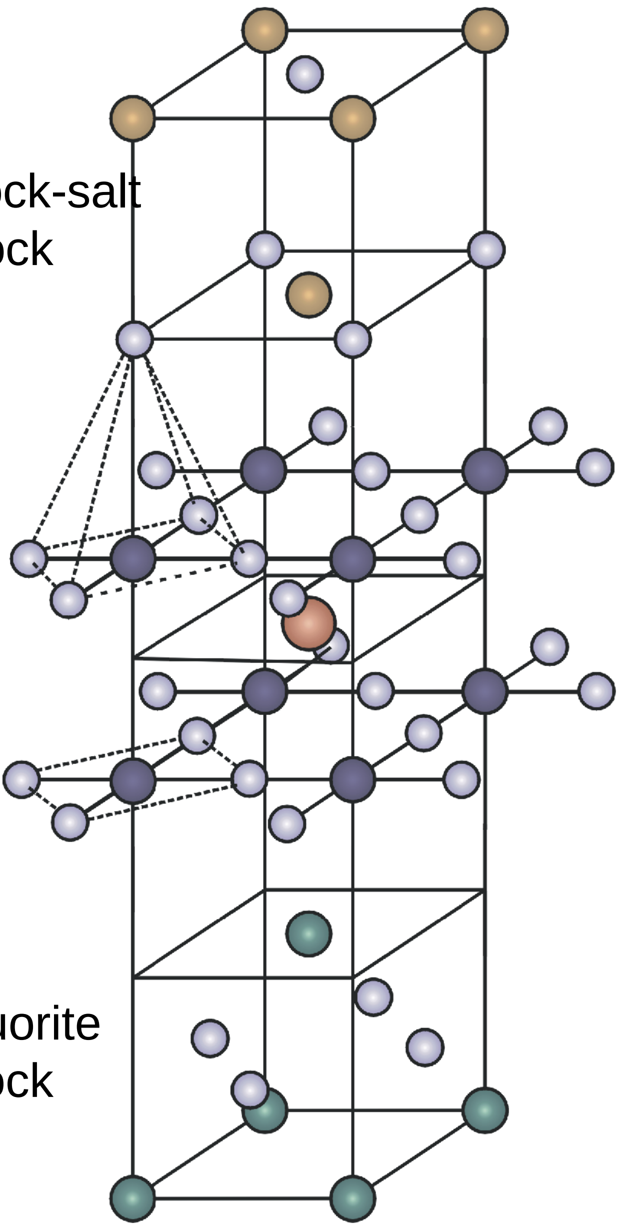
Phase with fluorite slab	T_c	Parent structure	T_c
$La_{0.9}Sm_{0.9}Sr_{0.2}CuO_{3.97}$	27K	$La_{1.6}Sr_{0.4}CaCu_2O_6$	60K
$Pb_2Sr_2Eu_{1.33}Ce_{0.67}Cu_3O_{10}$	24K	$Pb_2Sr_2Y_{0.6}Ca_{0.4}Cu_3O_8$	70K
$Bi_2Sr_2Eu_{1.7}Ce_{0.3}Cu_2O_{10+\delta}$	28K	$Bi_2Sr_2CaCu_2O_{8+\delta}$	80K
$Eu_{1.7}Sr_{1.7}Ce_{0.6}Cu_3O_{8+\delta}$	36K	$YBa_2Cu_3O_{7-\delta}$	94K

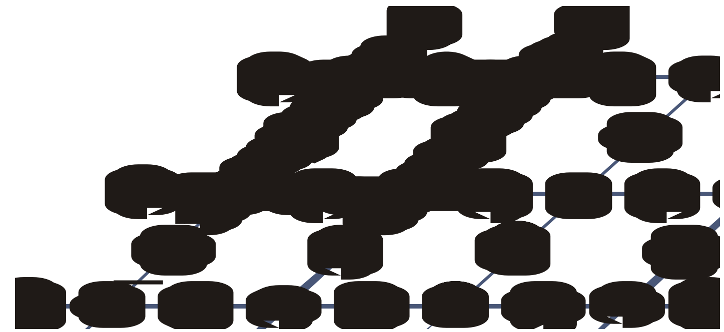
Intergrowth structures

Rock-salt block

Perovskite block

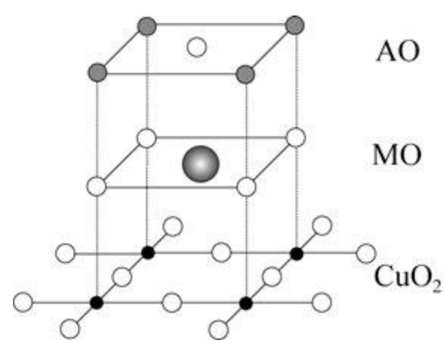
Fluorite block

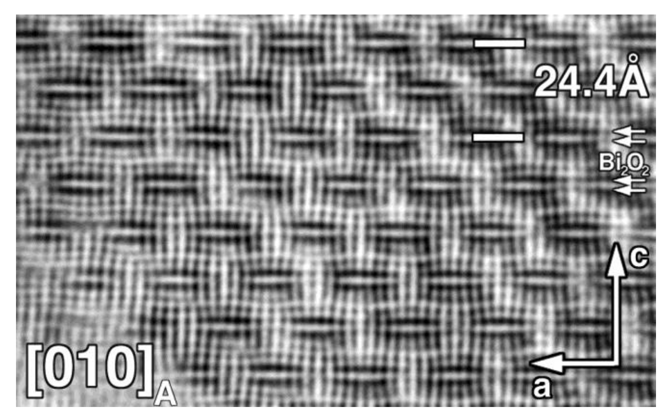




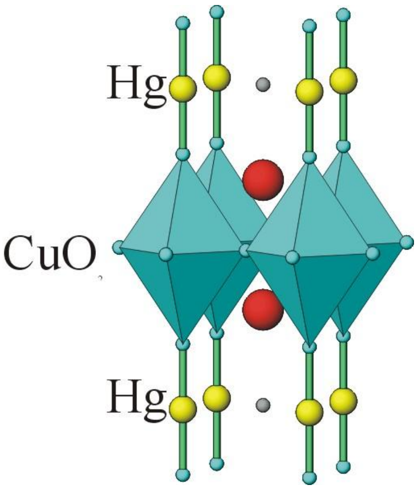
CuO_2 layer

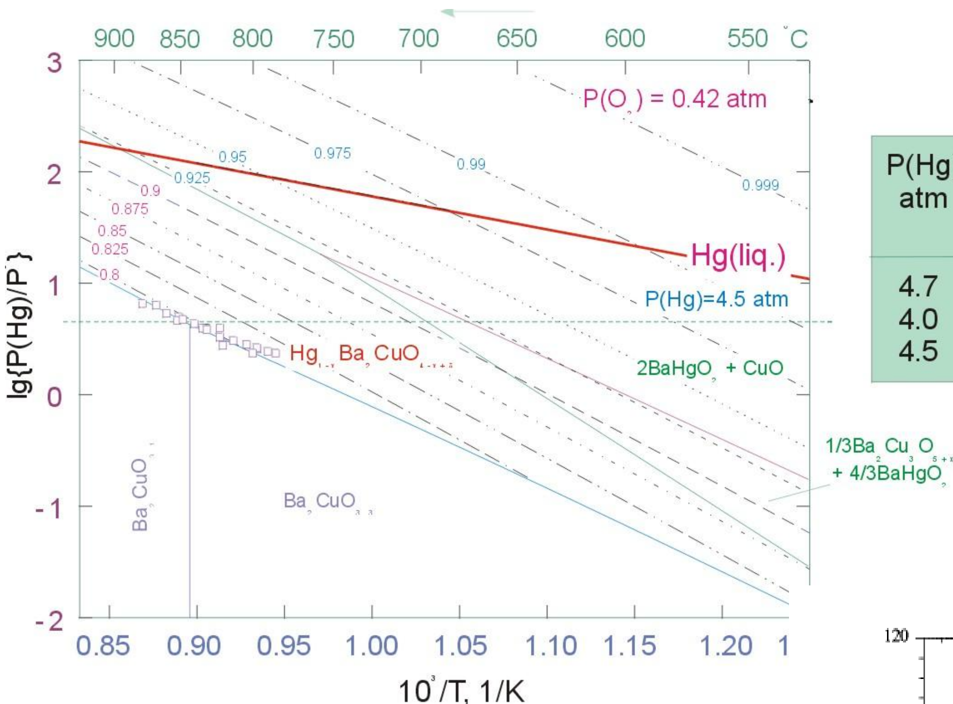
Chemical bonding/coordination,
distance matching,
electro neutrality,
chemical co-existence





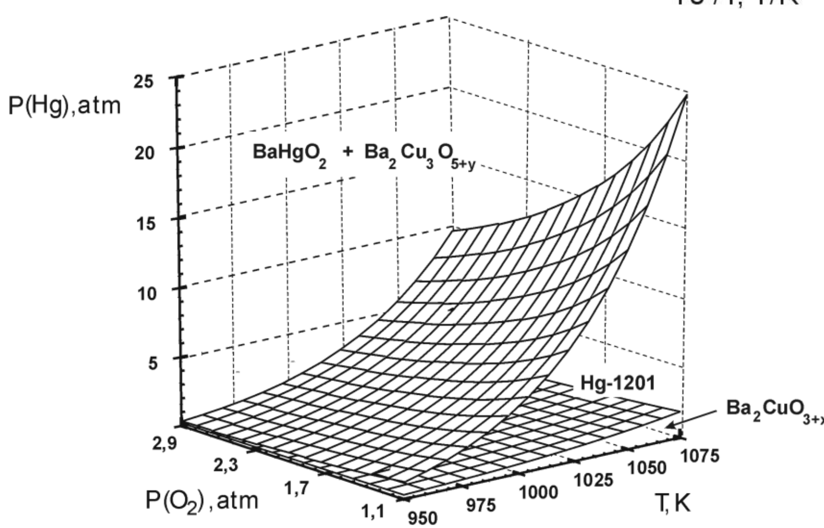
$HgBa_2CuO_{4+\delta}$ (Hg-1201)

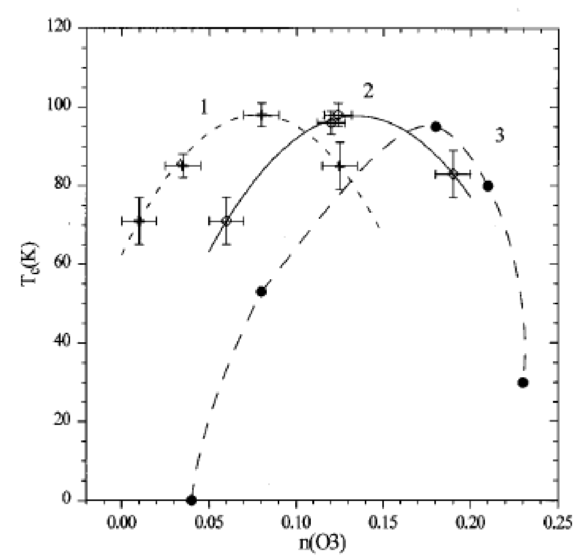




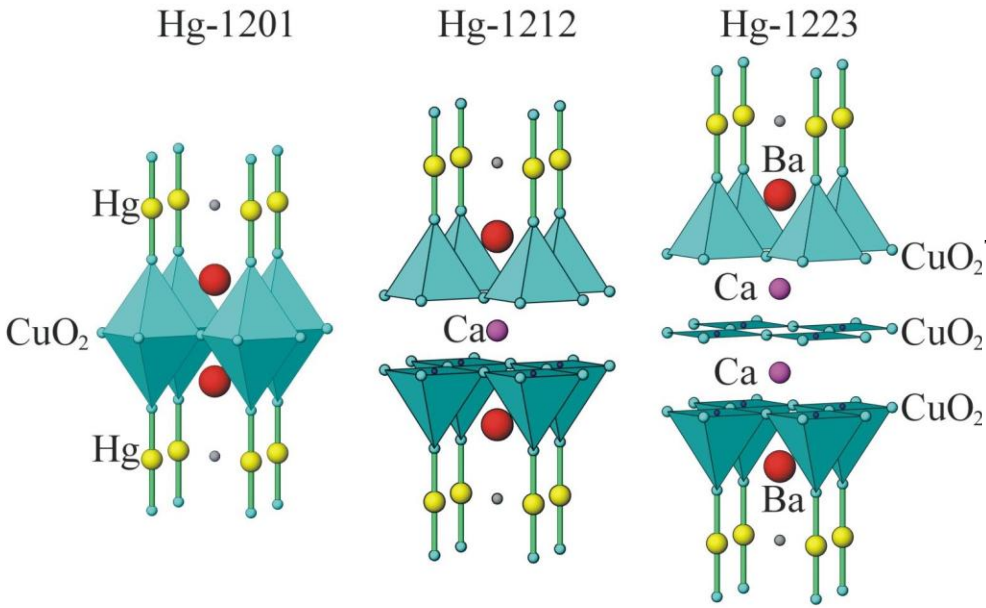
Results of Hg-1201 synthesis
($P(O_2)$ = 0.42 atm)

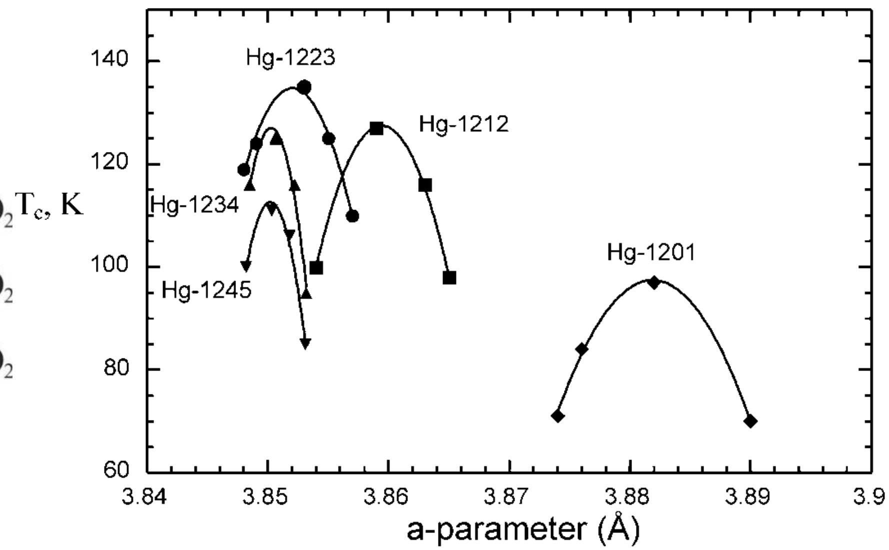
P(Hg) atm	T, °C	mercury content, 1-x	
		experimental	expected from P(Hg)-T diagram
4.7	700	0.91(2)	0.90(1)
4.0	650	0.96(2)	0.94(1)
4.5	600	0.98(2)	0.97(1)





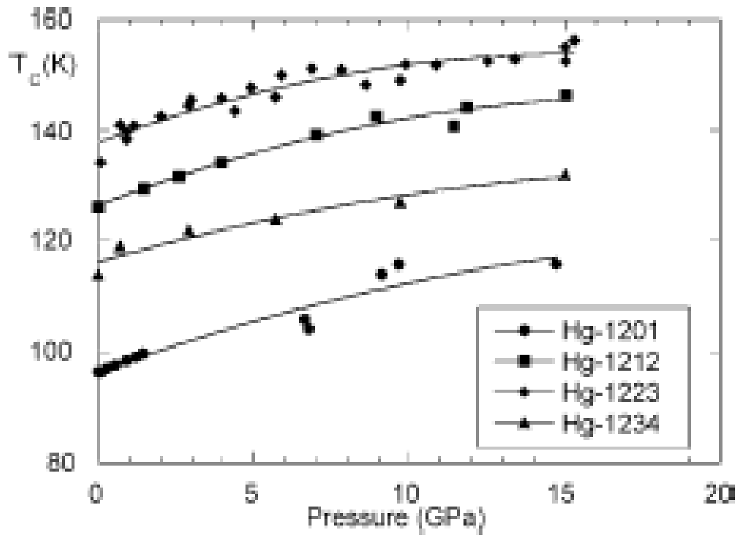
Hg-based superconducting Cu mixed oxides
$HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$

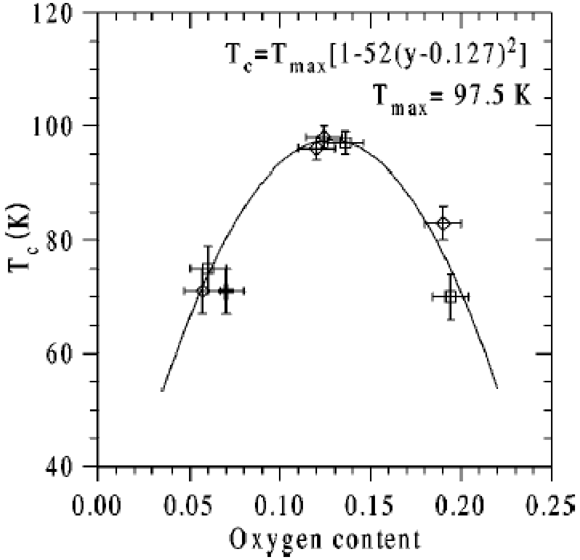


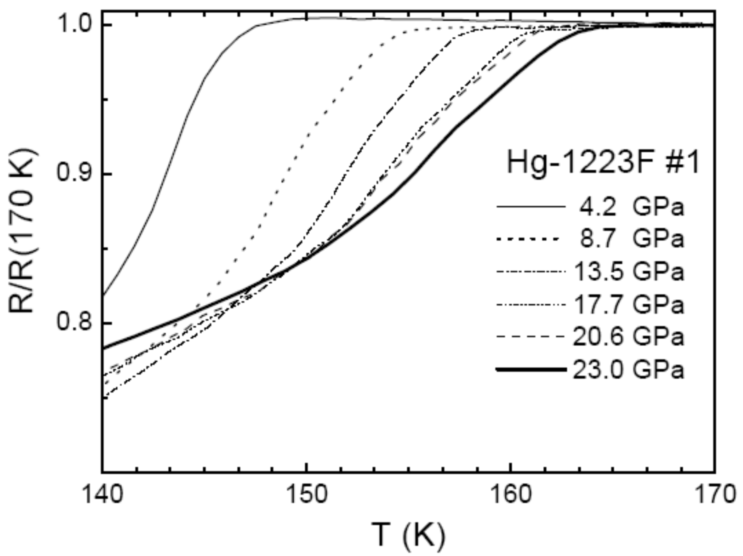


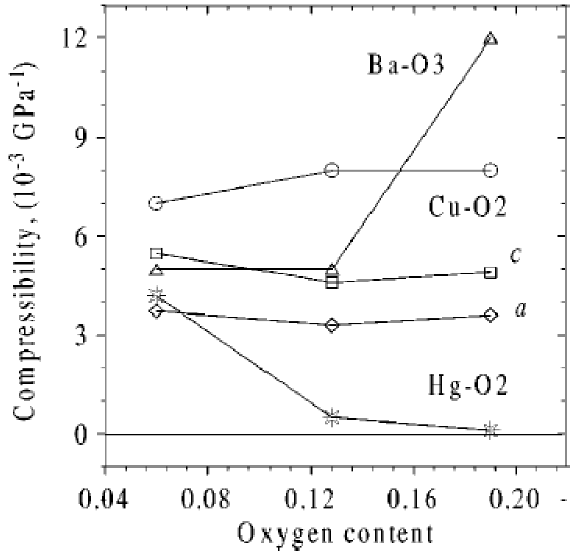
The dependence of *T*c vs. *a*-parameter for the $HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ series

Influence of high pressure









Fluorination of $HgBa_2Ca_2Cu_3O_{8+\delta}$

Ti, 500 °C →

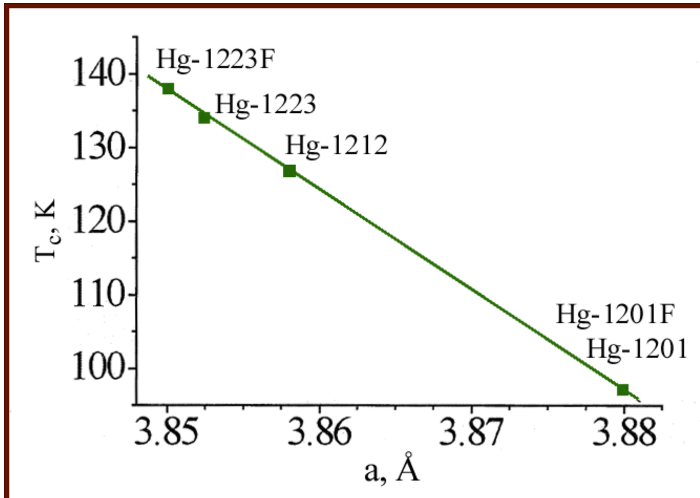
T_c= 100K
a = 3.8560(4)Å
c = 15.839(5)Å

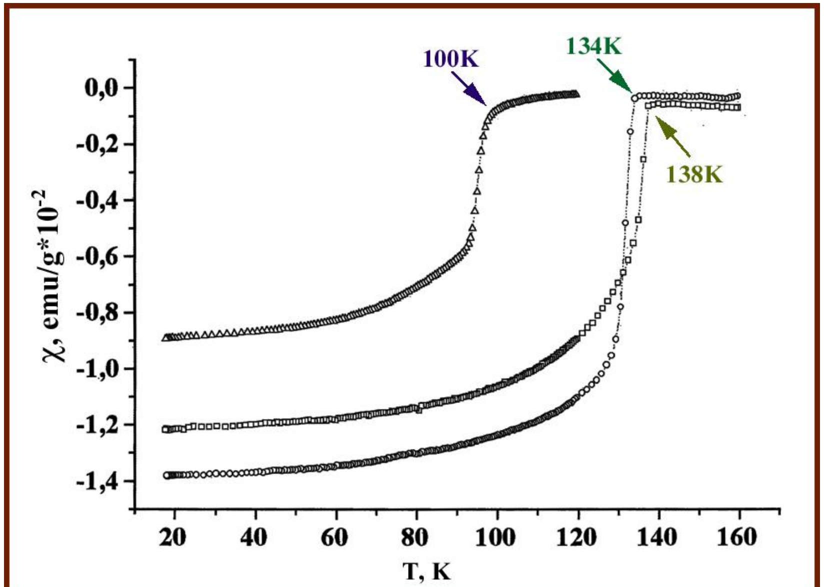
O_2, 300 °C →

T_c= 134K
a = 3.8524(4)Å
c = 15.819(4)Å

XeF_2, 200°C →

T_c= 138K
a = 3.8501(2)Å
c = 15.773(3)Å





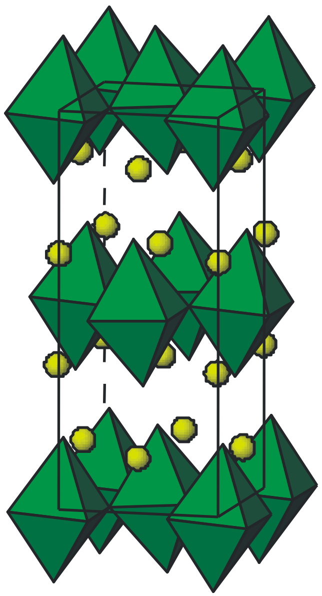
The dependence of T_c *vs a* parameter for oxygenated and fluorinated $HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ phases, n=1-3

$dT_c/da \approx$ **-1.35×10^3** K/Å for Hg-bearing HTSC
∠Cu2-O2-Cu2 = **177.3 - 178.4°** for Hg-1223

$dT_c/da \approx$ **-1.0×10^3** K/Å for epitaxial $La_{1.9}Sr_{0.1}CuO_4$ thin films (J.-P. Locquet et. al., Nature, 394, 453(1998))

$dT_c/da \approx$ **-1.6×10^2** K/Å under pressure
∠Cu2-O2-Cu2 = **175.0°** for Hg-1223 under 2GPa

Fluorination of La_2CuO_4



La_2CuO_4

a = 5.352Å

b = 5.400Å

c = 13.157Å

I. $La_2CuO_4F_d$ (δ≤0.18)

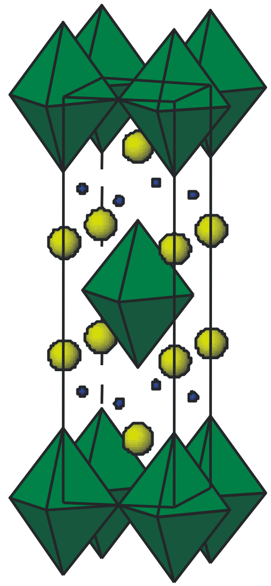
T_c = 35 – 40K

XeF_2, t = 150 – 200 °C

a = 5.328Å

b = 5.427Å

c = 13.194Å

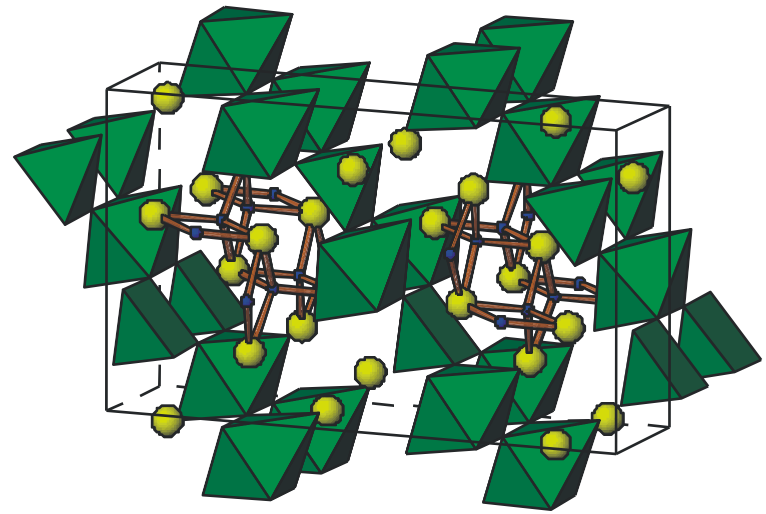


II. $La_2CuO_{4-x}F_y$

XeF_2, t = 230 – 250 °C

a = 4.038Å

c = 13.093Å



III. $La_2CuO_{3.6}F_{0.8}$

XeF_2, t = 300 – 400 °C

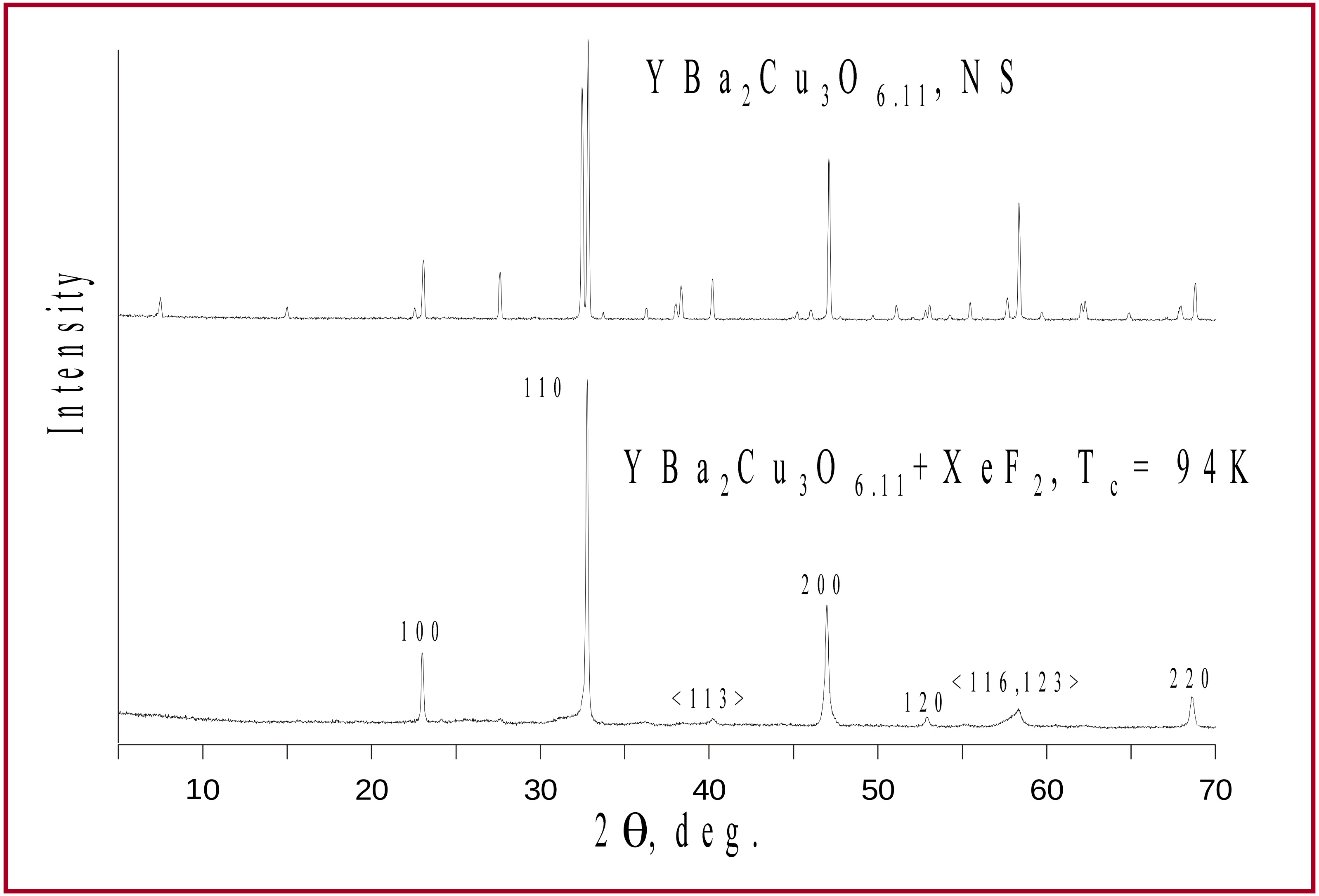
a = 17.36Å

b = 5.62Å

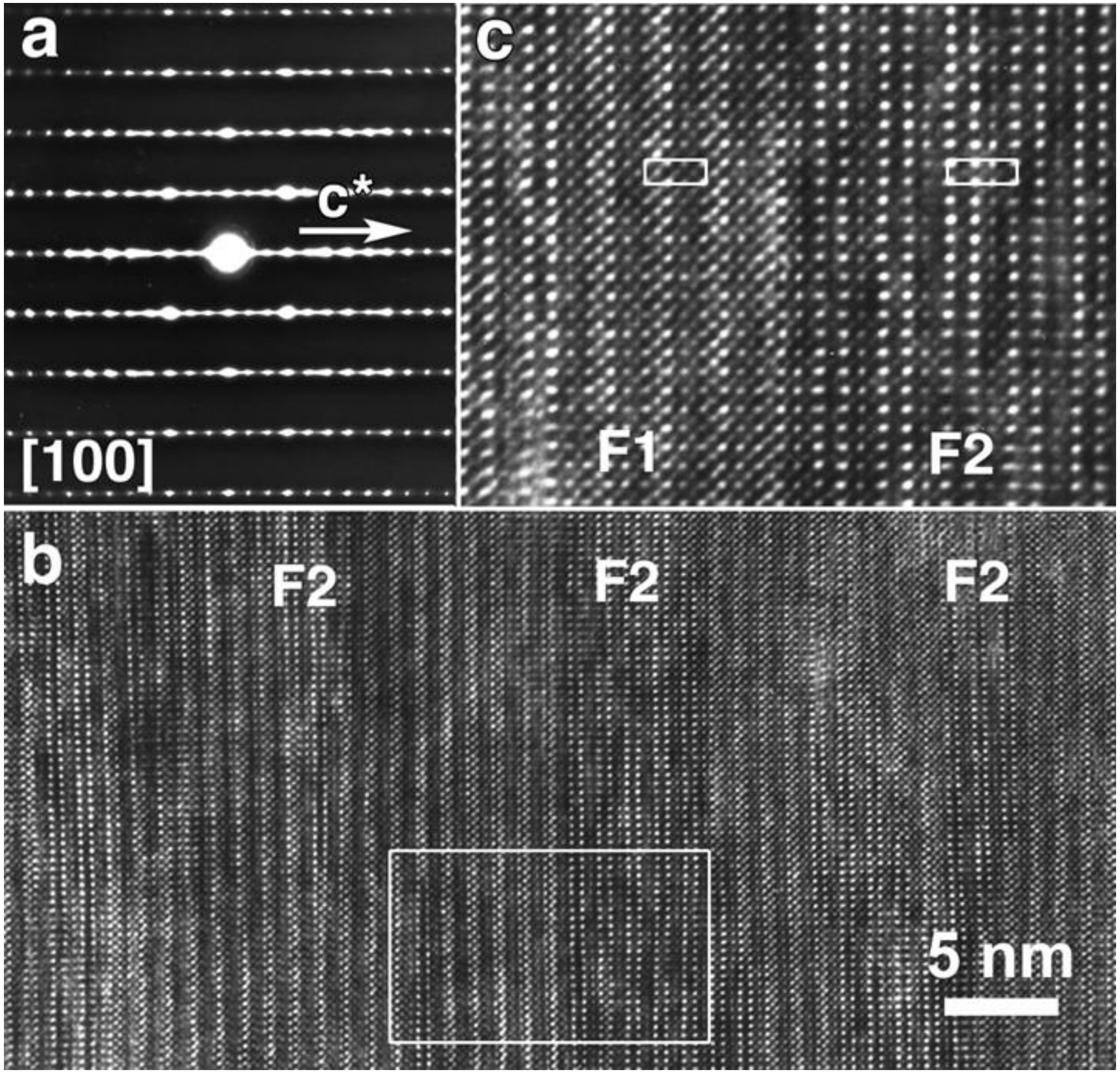
c = 10.59Å

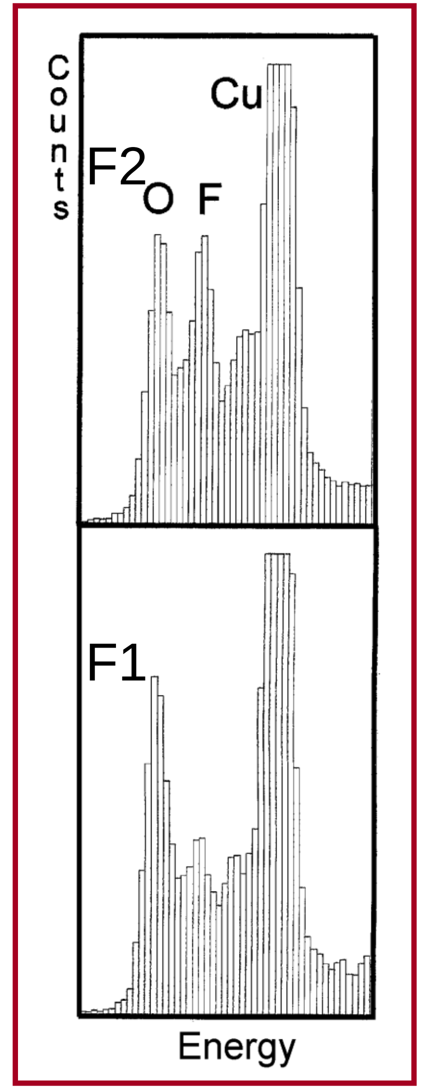
b = 91.5°

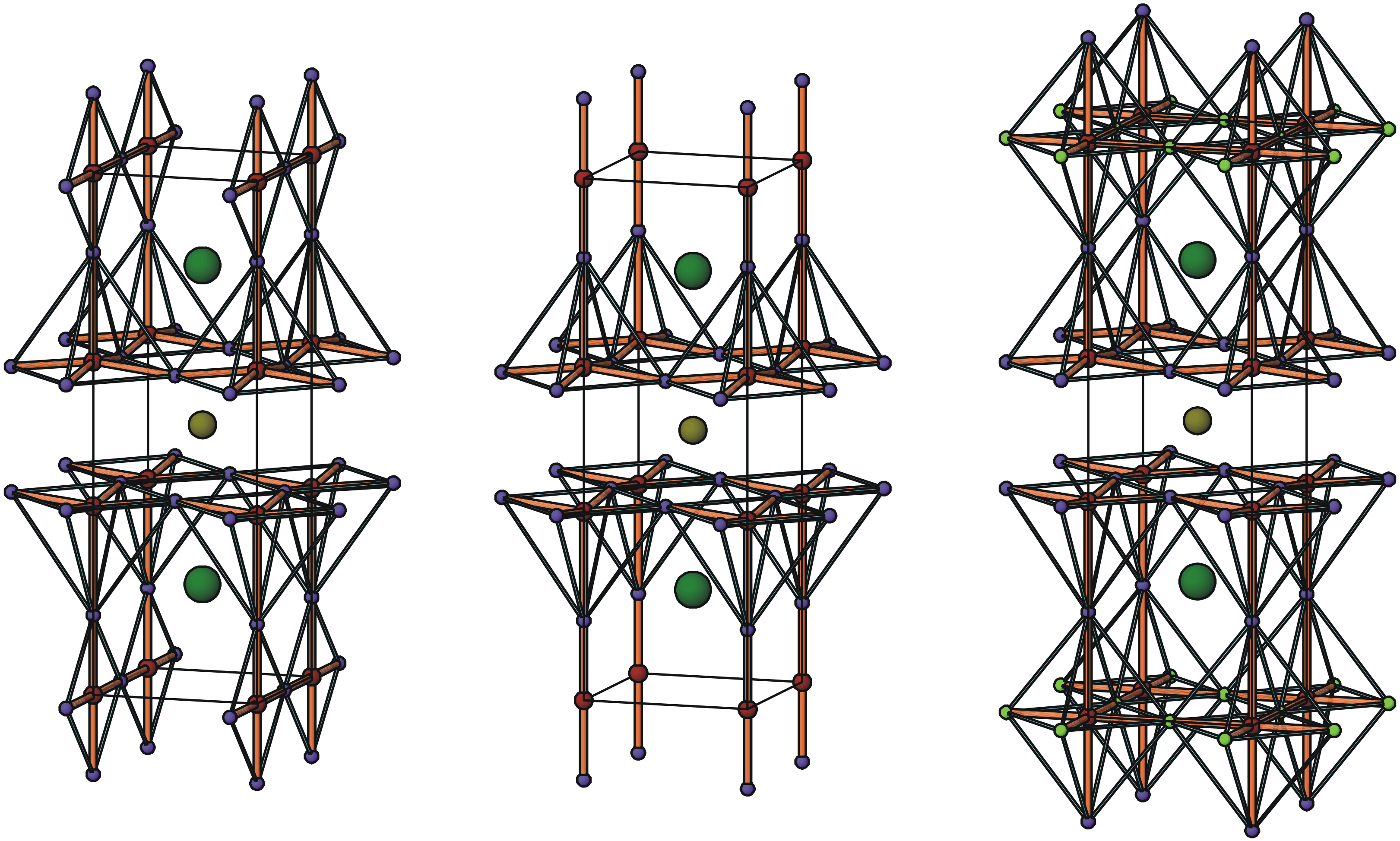
Fluorination of $YBa_2Cu_3O_{6.11}$



$YBa_2Cu_3O_6F_2$





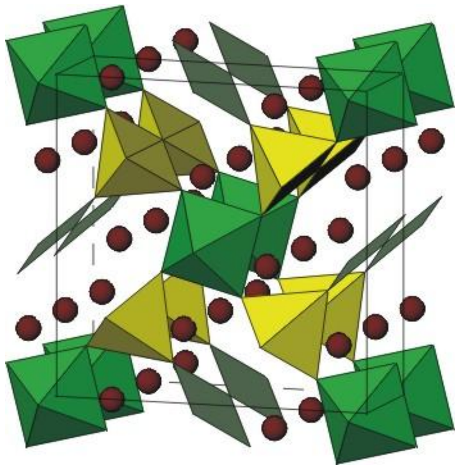


$YBa_2Cu_3O_7$ ← O^{2-} — $YBa_2Cu_3O_6$ — $2F^-$ → $YBa_2Cu_3O_6F_2$

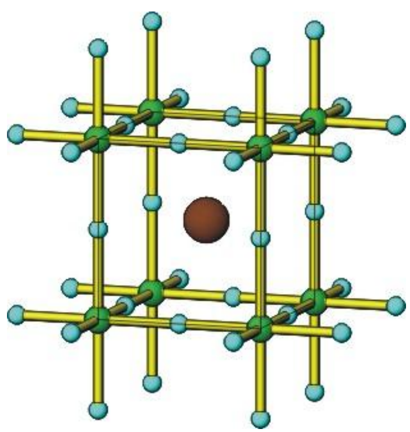
c = 11.7Å | c = 11.8Å | c = 13Å

Anion-deficient perovskites $La_{8-x}Sr_xCu_8O_{20-\delta}$ (x~1.5)

a=10.8269(4)Å
c=3.8665(2)Å



XeF_2

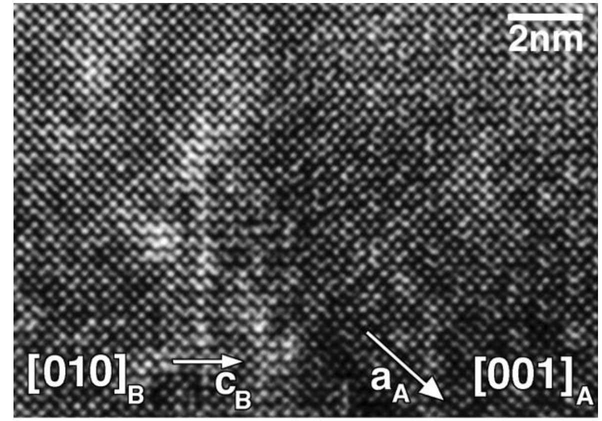


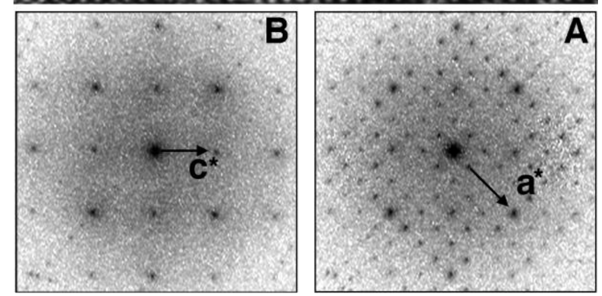
CuO_2

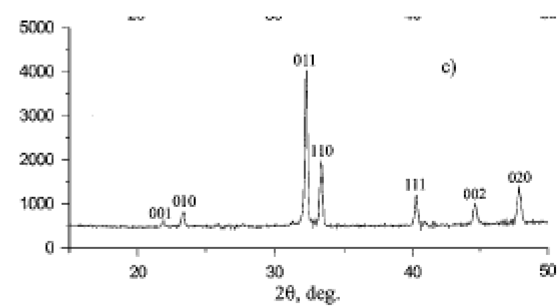
(La,Sr)(F,O)

CuO_2

a=3.7921(3)Å
c=4.0515(4)Å

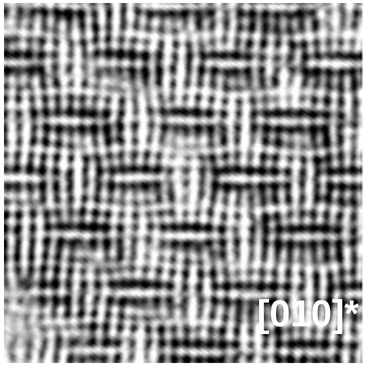


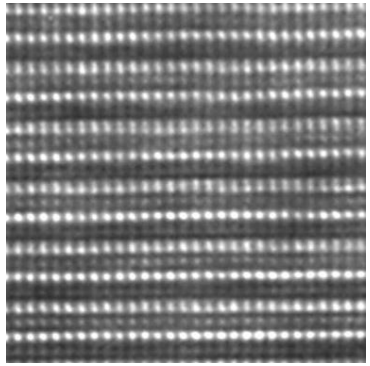


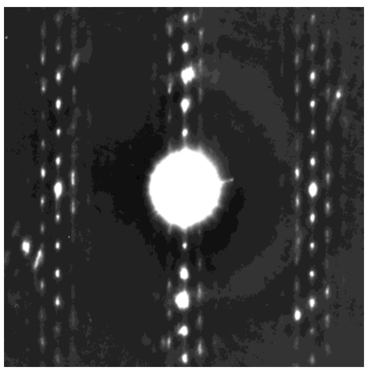


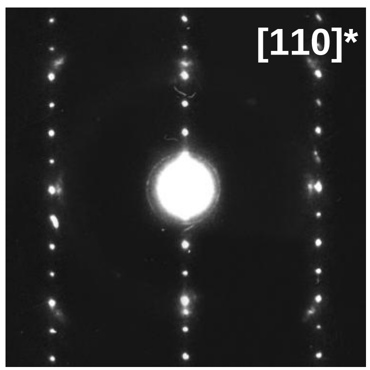
Fluorination of Bi-2201

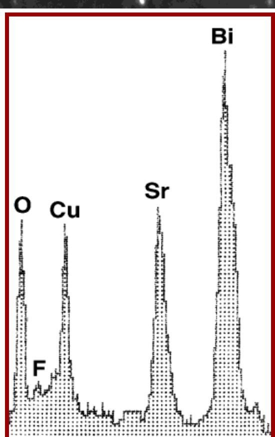
Bi-2201	Bi-2201F

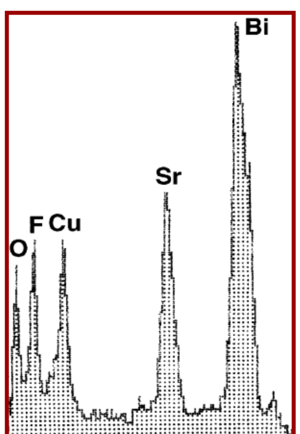










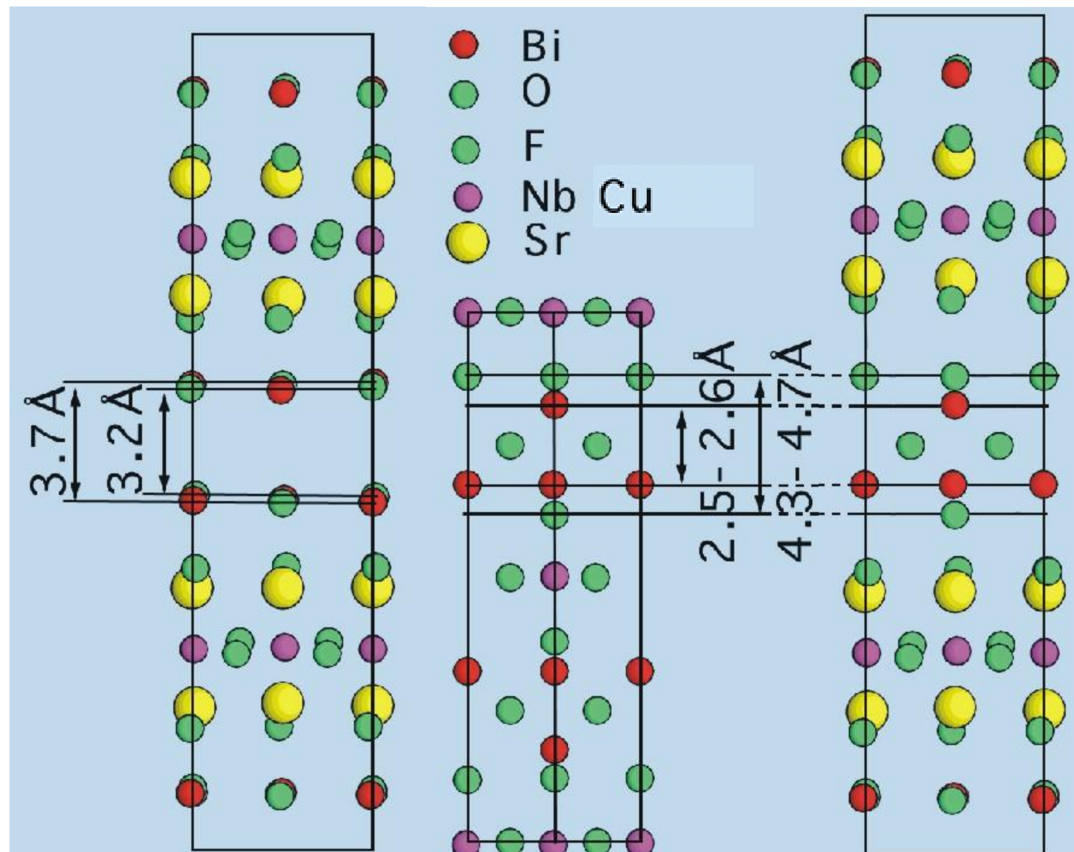


a = 5.398Å
b = 5.368Å
c = 24.349Å

$\xrightarrow{XeF_2,\ 200^oC}$

a = 3.837Å, c = 26.18Å

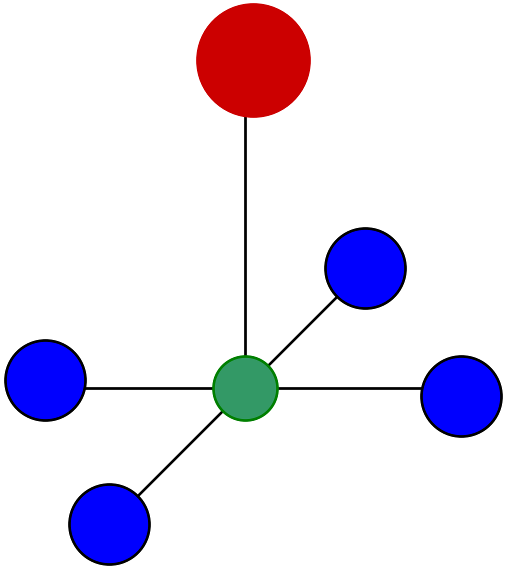
Bi-2201 | Bi_2NbO_5F | Bi-2201F



Superconducting properties of fluorinated and oxygenated layered cuprates

Compound	T_c (K), oxyfluoride	T_c (K), oxygenated prototype
$YBa_2Cu_3O_6F_2$	94	92
$Y_2Ba_4Cu_7O_{14}F_2$	62	80
$HgBa_2CuO_4F_{0.24}$	97	97
$HgBa_2CaCu_2O_6F_\delta$	128	127
$Hg_{0.8}Ba_2Ca_2Cu_{3.2}O_8F_\delta$	**138**	134
$Sr_2CuO_2F_{2+\delta}$	**46**	-
$La_2CuO_4F_\delta$, $\delta \leq 0.18$	35 - 40	38
$Nd_2CuO_{3.7}F_{0.3}$	27	24
$Sr_2CaCu_2O_{4.6}F_2$	99	-
$Sr_2Ca_2Cu_3O_{6.2}F_{3.2}$	111	-
$Sr_2Nd_{0.2}Ca_{0.8}Cu_2O_5F$	85	-
$La_{1.6}Sr_{0.4}CaCu_2O_6$ **$Sr_2CaCu_2O_{4+x}Cl_{2-x}$**	 **80**	60

Problems of synthesis of oxyhalogenides



Metastable compounds (easily decompose or redox reactions):

1) by soft chemistry:
   a) LT fluorination of parent compounds
   b) anion exchange

2) under high pressure

3) by electrochemistry

Bi-based superconducting oxides

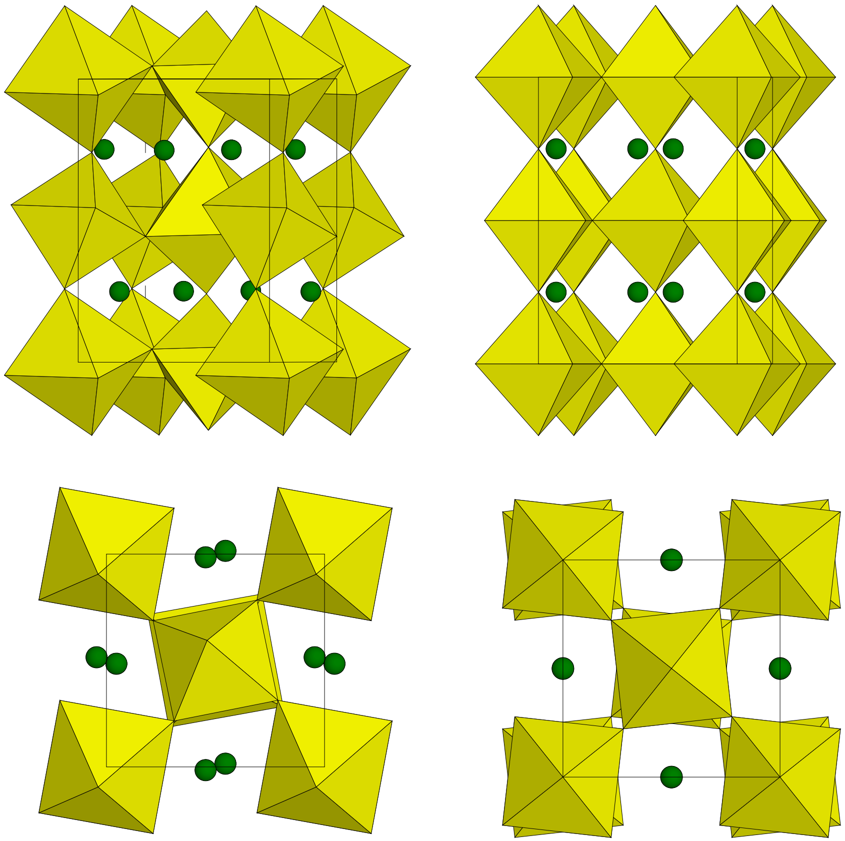
Compound	T_c	Reference
$BaPb_{0.75}Bi_{0.25}O_3$	12K	Sleight A.W. et al., SSC 17 (1975) 17
$Ba_{0.6}K_{0.4}BiO_3$	30K	Mattheiss L.F. et al., PRB 37 (1988) 3745 Cava R.J. et al., Nature 332 (1988) 814
$BaPb_{0.75}Sb_{0.25}O_3$	3.5K	Cava R.J. et al., Nature 339 (1989) 291
$Sr_{0.4}K_{0.6}BiO_3$	12K	Kazakov S.M. et al., Nature 390 (1997) 147
$K_{0.9}Bi_{1.1}O_3$	10K	Khasanova et al., Physica C 305 (1998) 275
$La_{0.2}K_{0.8}BiO_3$	12K	Khasanova N.R et al., JSSC 144 (1999) 205

Superconductivity vs. structure distortions

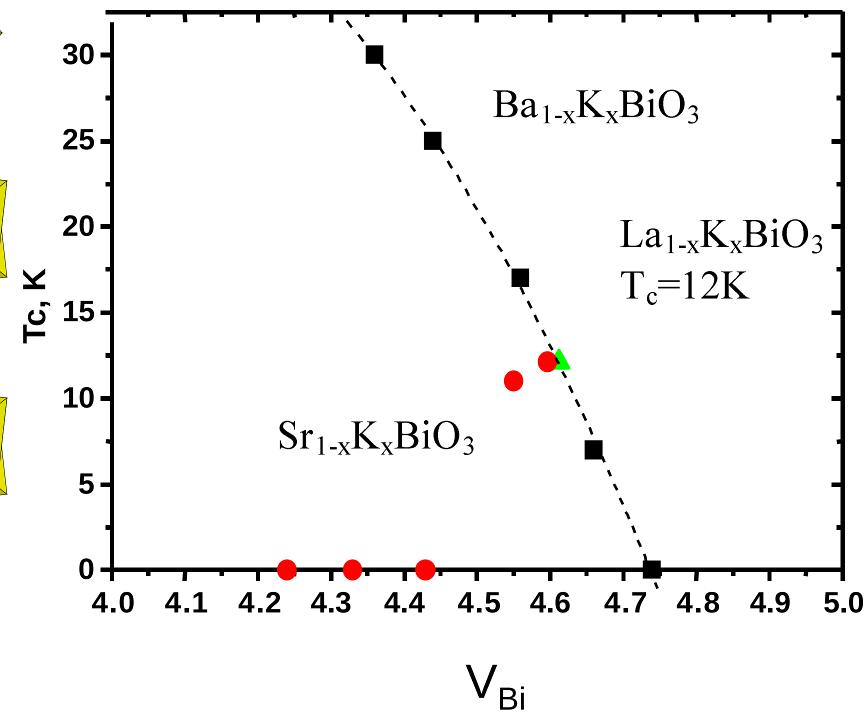
P2$_1$/n
$a \approx b = a_{per}\sqrt{2}$
$c = 2a_{per}$

$Sr_{1-x}K_xBiO_3$

I4/mcm
$a = a_{per}\sqrt{2}$
$c = 2a_{per}$



K content	t	∠Bi-O-Bi, deg.	Superconductivity
0.0	0.795	149.1	NS
0.33	0.903	166.3	NS
0.43	0.923	170.0	NS
0.60	0.944	173.5	T_c = 12K



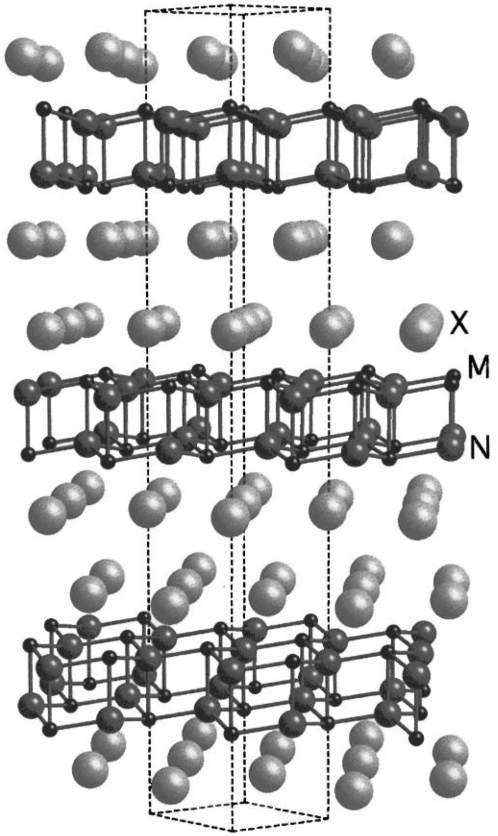
Bi1 - $O_{aver.}$ - 2.31Å   V(Bi1) = 3.21

Bi2 - $O_{aver.}$ - 2.11Å   V(Bi2) = 4.57

From 3d to 2d structures

HfN Tc = 8.8 K

$Li_{0.48}(THF)_y HfNCl$ T_c = 25.5 K



L.F. Mattheiss (RPB 45 (1992), 12528): Superconductivity in layered bismuthates?

Layered Bismuthates

$A_{n+1}Bi_nO_{3n+1}$:

$n = 1 \Rightarrow A_2BiO_4$, $n = 2 \Rightarrow A_3Bi_2O_7$, $n = \infty \Rightarrow ABiO_3$

$A_3Bi_2O_7$ (n=2)

K(Rb)-Sr(Ba)-Bi-O

450°C, 40-80 atm O_2

$Sr_{1.6}K_{1.4}Bi_2O_7$

a = 4.155 Å
c = 21.83 Å

500°C,
5-150 atm O_2

$(Sr,Rb)_3Bi_2O_7$

a = 4.184 Å
c = 22.188 Å

500°C
5 atm O_2

$Ba_{1.7}Rb_{1.3}Bi_2O_7$

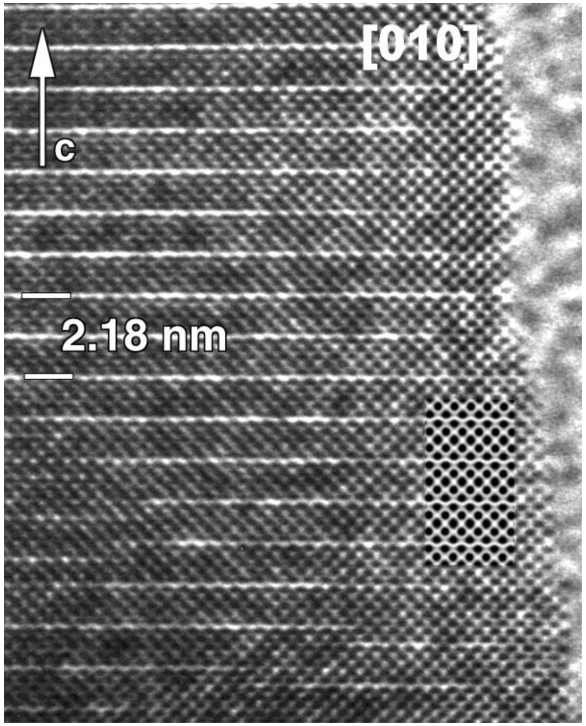
a = 4.263 Å
c = 22.27 Å

450°C, 2-3 atm O_2

$Ba_{1.7}K_{1.3}Bi_2O_7$

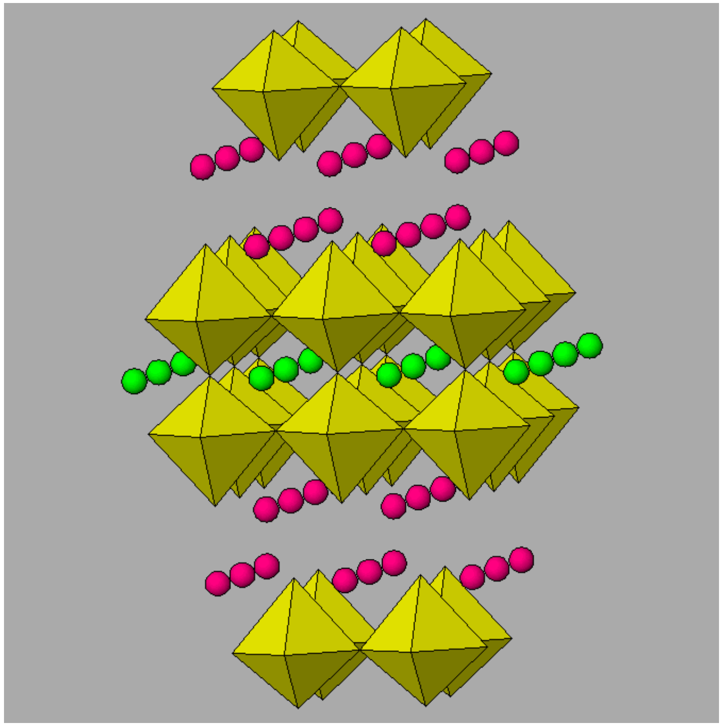
a = 4.252 Å
c = 21.89 Å

$A_3Bi_2O_7$ (A = Ba, Sr, K, Rb)



$Ba_{1.9}K_{1.1}Bi_2O_7$

Ba/K ratio = 1.4 -1.8

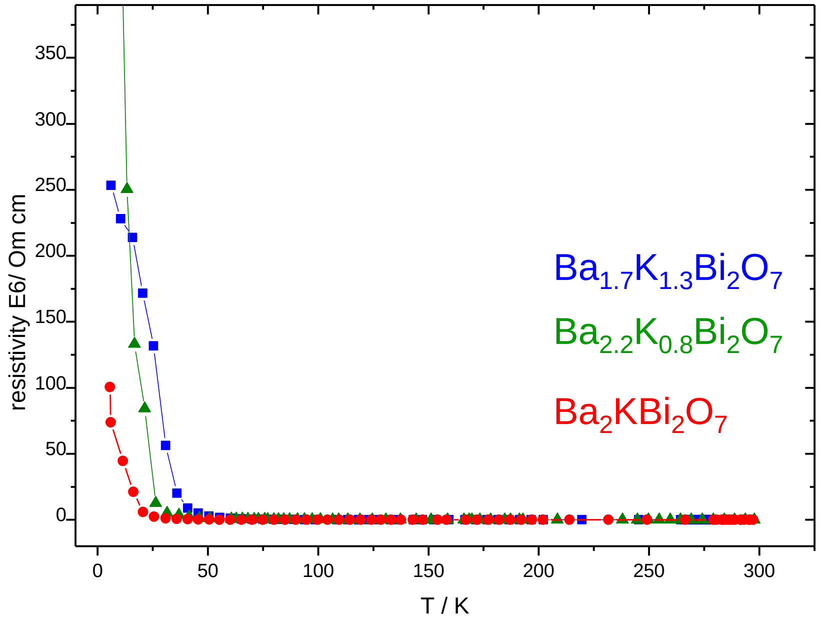


$Sr_{1.6}K_{1.4}Bi_2O_7$

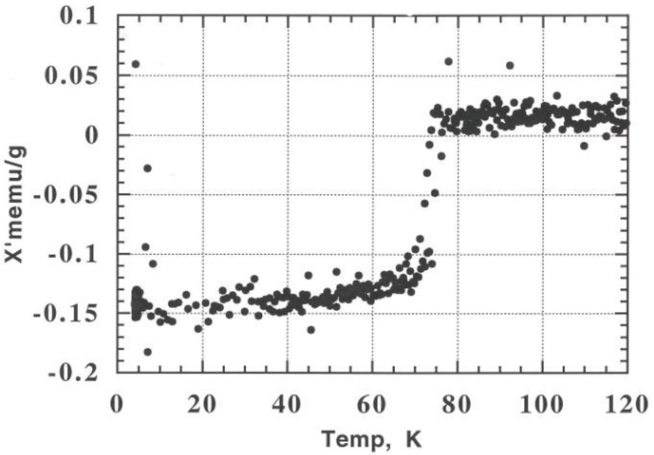
Ordering Sr and K cations

Properties

$(Ba,K)_3Bi_2O_7$

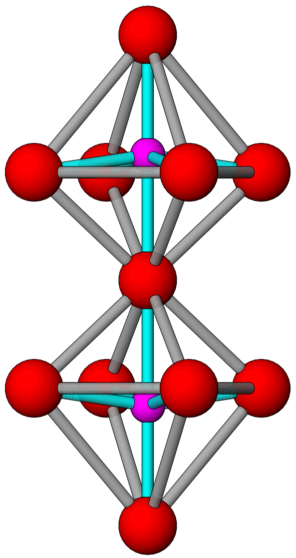


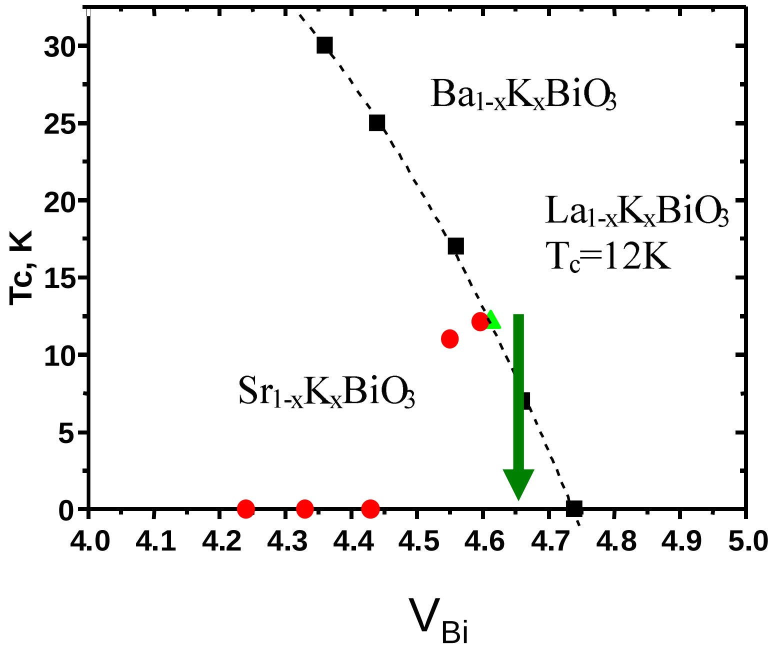
$(Sr,Rb)_3Bi_2O_7$

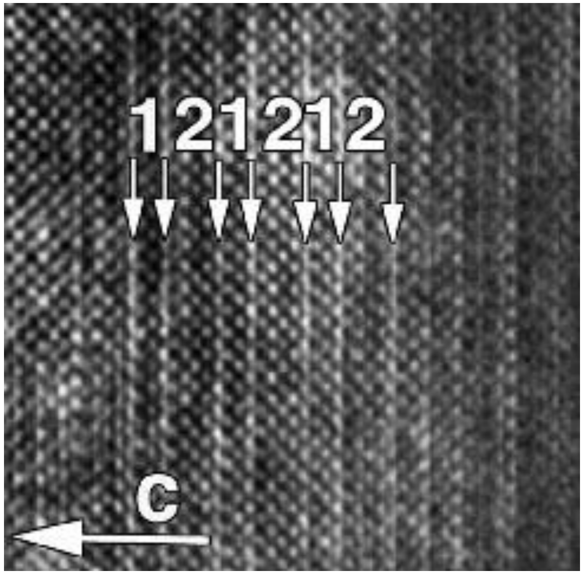


Structure features

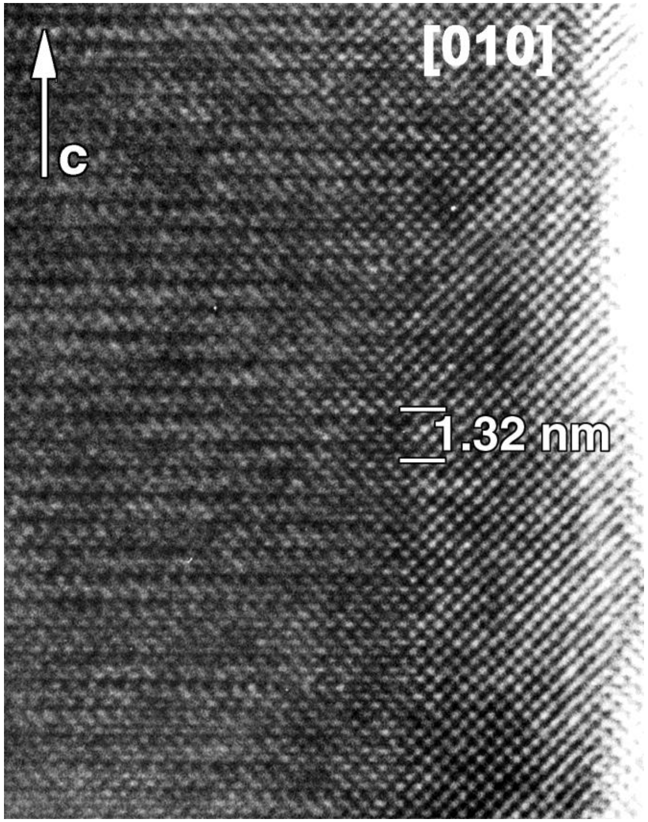
	$Ba_{1.7}K_{1.3}Bi_2O_7$	$Sr_{1.6}K_{1.4}Bi_2O_7$	$(Sr,Rb)_3Bi_2O_7$
Bi – $O1_{ap}$ (Å) Bi – $O3_{ap}$ (Å) Bi – $O2_{eq}$ (Å)	2.174 2.035 2.131	2.154 2.040 2.098	2.128 2.030 2.110
< Bi – O >(Å)	2.12	2.10	2.10
∠(Bi-O2-Bi) (°)	170	163.5	165
V_{Bi}	4.65	4.7	~4.7

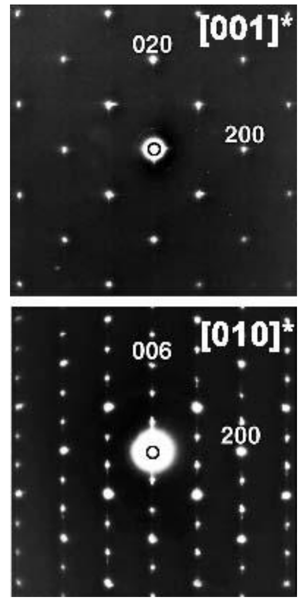


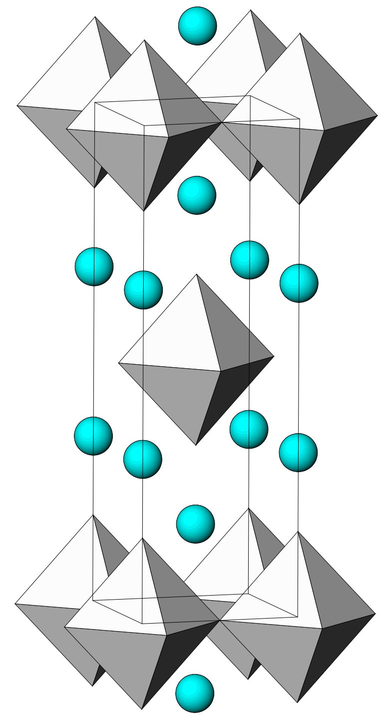




$(Ba,K)_2BiO_4$ - 0201



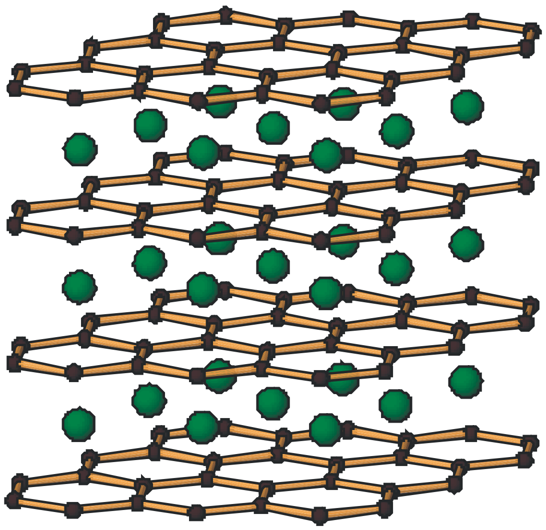




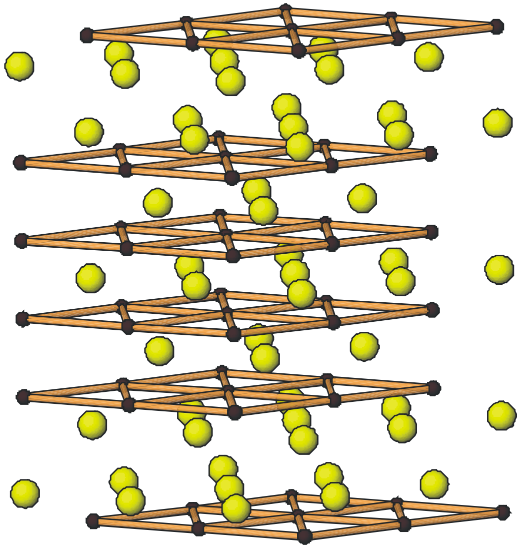
S.G. *I* 4/mmm
a = 4.3Ǻ
c = 13.2Ǻ

EDX:
Ba/K/Bi = 1.3/0.7/1.0
(VBi = + 4.7)

Search for new B-based superconductors



MgB_2
P 6/mmm
a=3.086 Å
c=3.521 Å



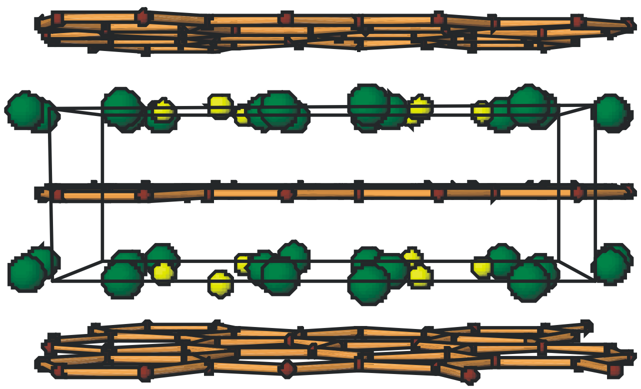
Rh_5B_4
P 6_3/mmc
a=3.306 Å
c=20.394 Å

Mg_3RhB_8

$$3Mg + RhB + 7B_{cr} \xrightarrow[\text{2) } 1100^0\text{C, 200 h}]{\text{1) } 1150^0\text{C, 80 h}} Mg_3RhB_8$$

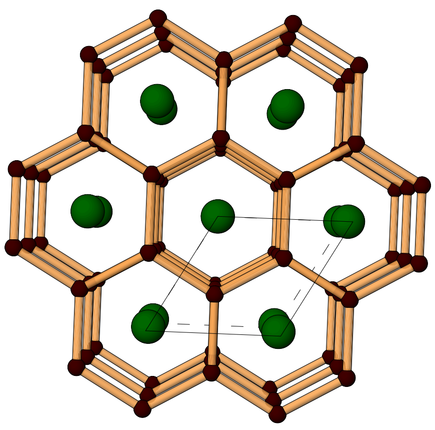
EDX: Mg/Rh=2.97(5)/1.03(5)

Pbam, Z = 3
a = 8.7855(5) Å
b = 11.0599(6) Å
c = 3.5465(3) Å

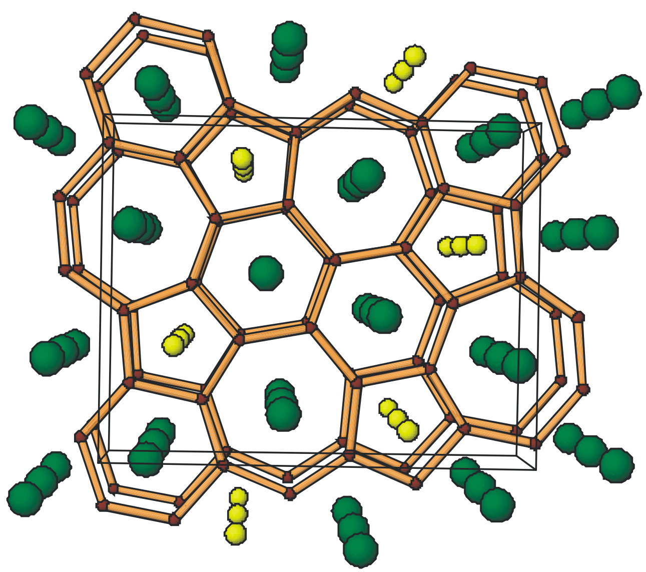


-Mg, -"$Rh_{0.75}Mg_{0.25}$", -B.

MgB_2

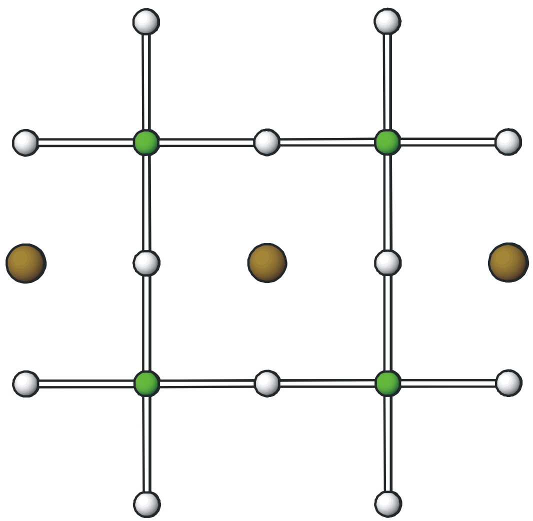


d_{Mg-B}=2.50Å
d_{B-B}=1.78Å
d_{Mg-Mg}=3.08Å

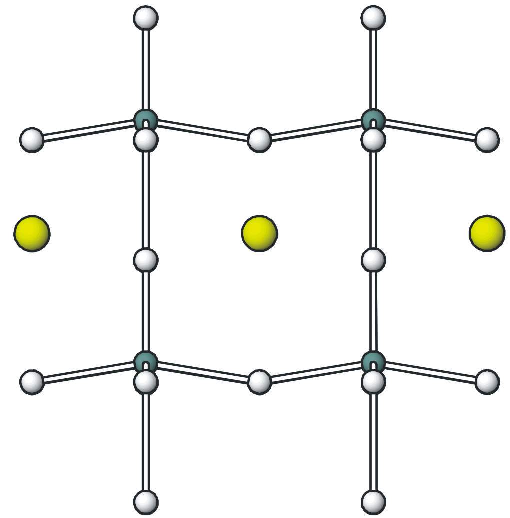


d_{Mg-B}=2.524(8)Å
d_{B-B}=1.69(1)-1.79(1)Å
d_{Mg-Mg}=2.961(5)-3.377(5)Å

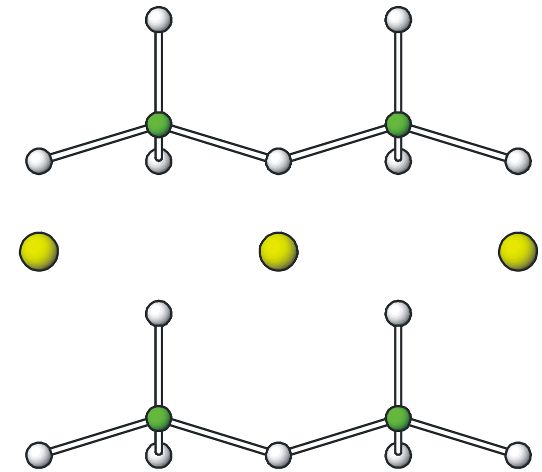
$PbVO_3$. Comparison with other ABO_3 perovskites



$SrVO_3$
$c/a = 1.000$
V in ideal octahedron



$PbTiO_3$
$c/a = 1.064$
V in distorted octahedron



$PbVO_3$
$c/a = 1.229$
V in square pyramid

Lone pair of Pb^{2+} localization

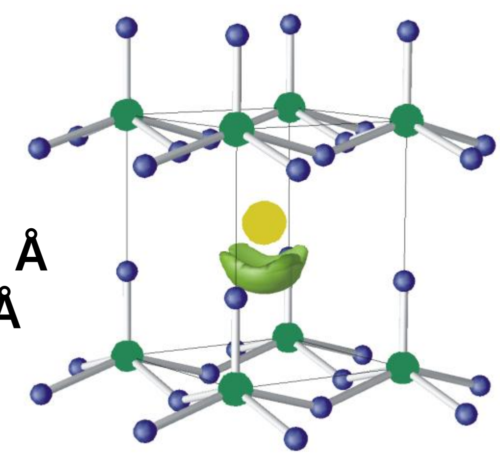
+

Stable square pyramidal coordination for V^{4+}

=

layered structure

P4mm
a=3.80005(6) Å
c=4.6703(1) Å



ELF isosurface ($\eta = 0.85$)

Synthesis:

At ambient pressure:

$PbO + VO_2 \Rightarrow$ mixture of known phases

But at 40-60 kbar/700°C:

$PbVO_3$

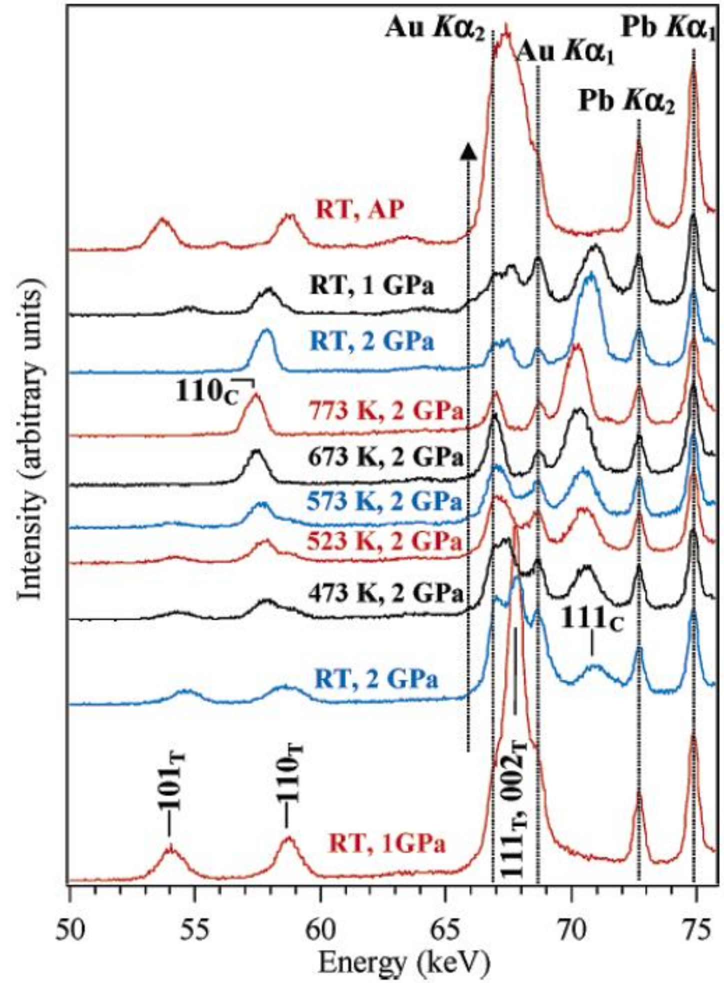
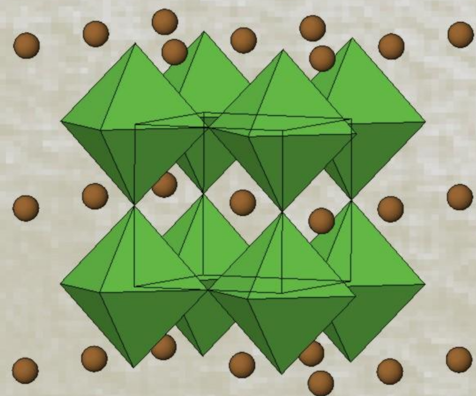


Figure 4. Energy-dispersive X-ray powder diffraction patterns for $PbVO_3$ at different pressure and temperatures. (*hkl*) of the tetragonal (T) and cubic (C) phases are given.

A.A. Belik et al. *Chem. Mater.* **2005,** *17,* 269

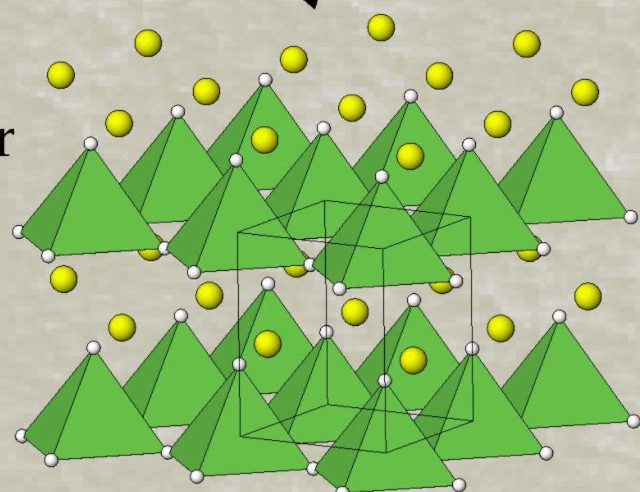
$PbVO_3$. Comparison with strontium vanadium oxides

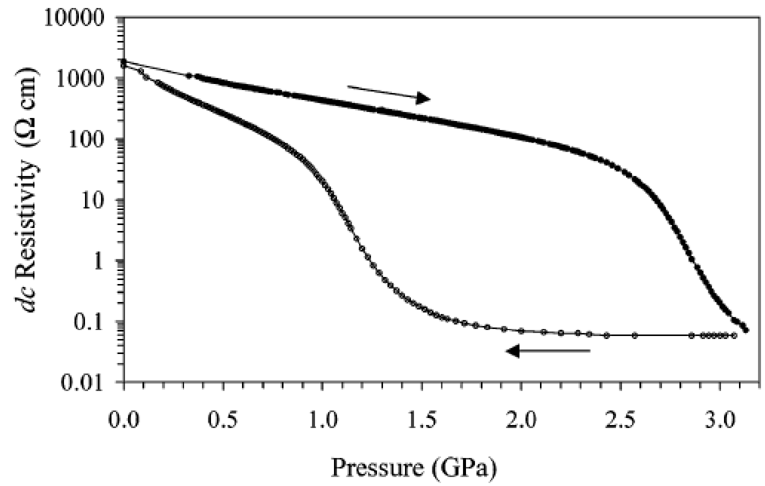


$SrVO_3$

$PbVO_3$

semiconductor





Pressure dependence of resistivity of $PbVO_3$ at room temperature

from: *A.A. Belik et al. Chem. Mater.* ***2005,*** *17, 269*