UCCS
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Chimie Lille
ÉCOLE NATIONALE SUPÉRIEURE DE CHIMIE

Nouvelles phases dans les systèmes Bi_2O_3-P_2O_5-MO_y : une mine d'or pour les physico-chimistes de l'état solide

O. Mentré, M. Colmont, M. Huvé

- UCCS- University of Lille I- ENSCL , France (UMR CNRS 8181)

cnrs
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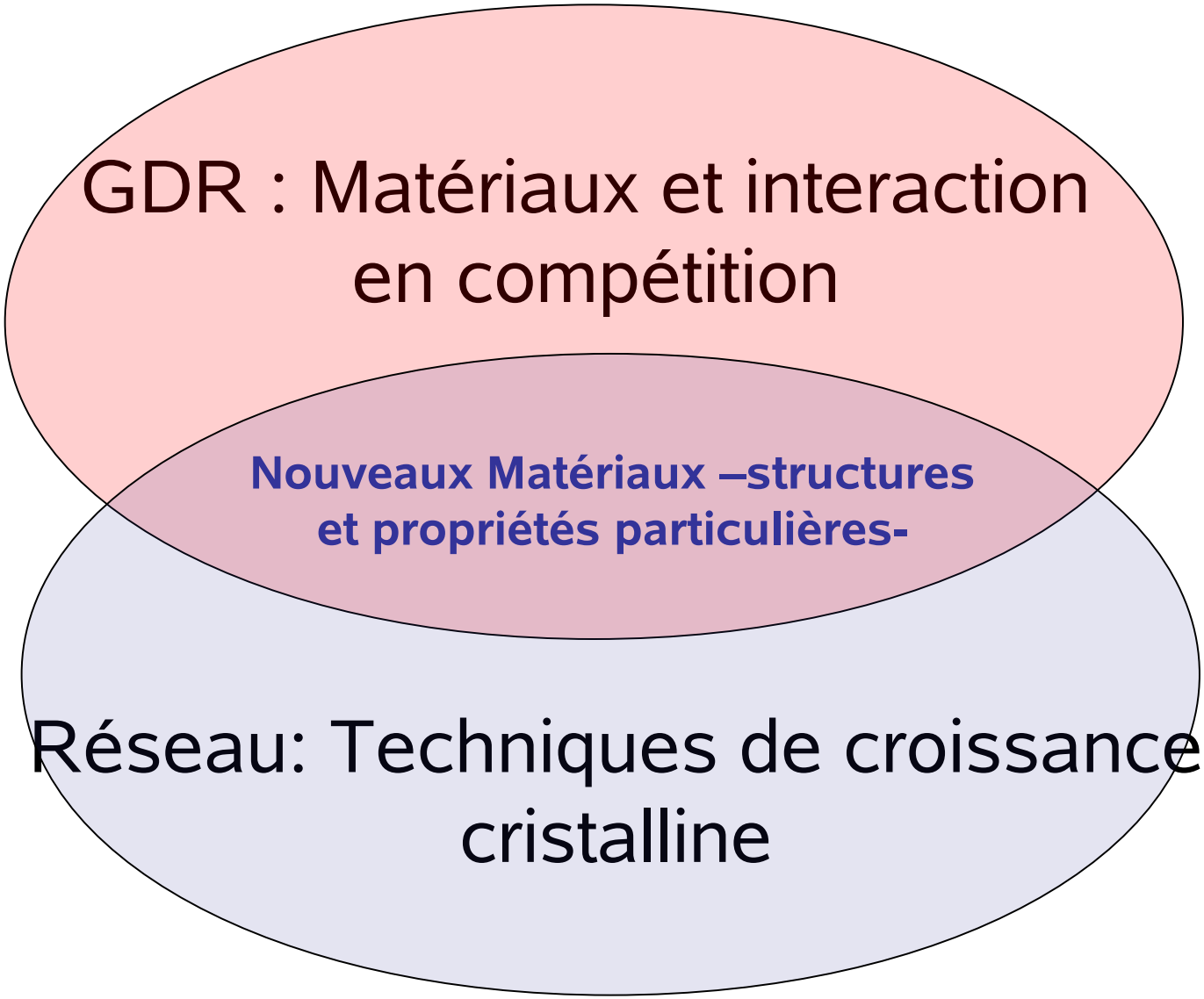
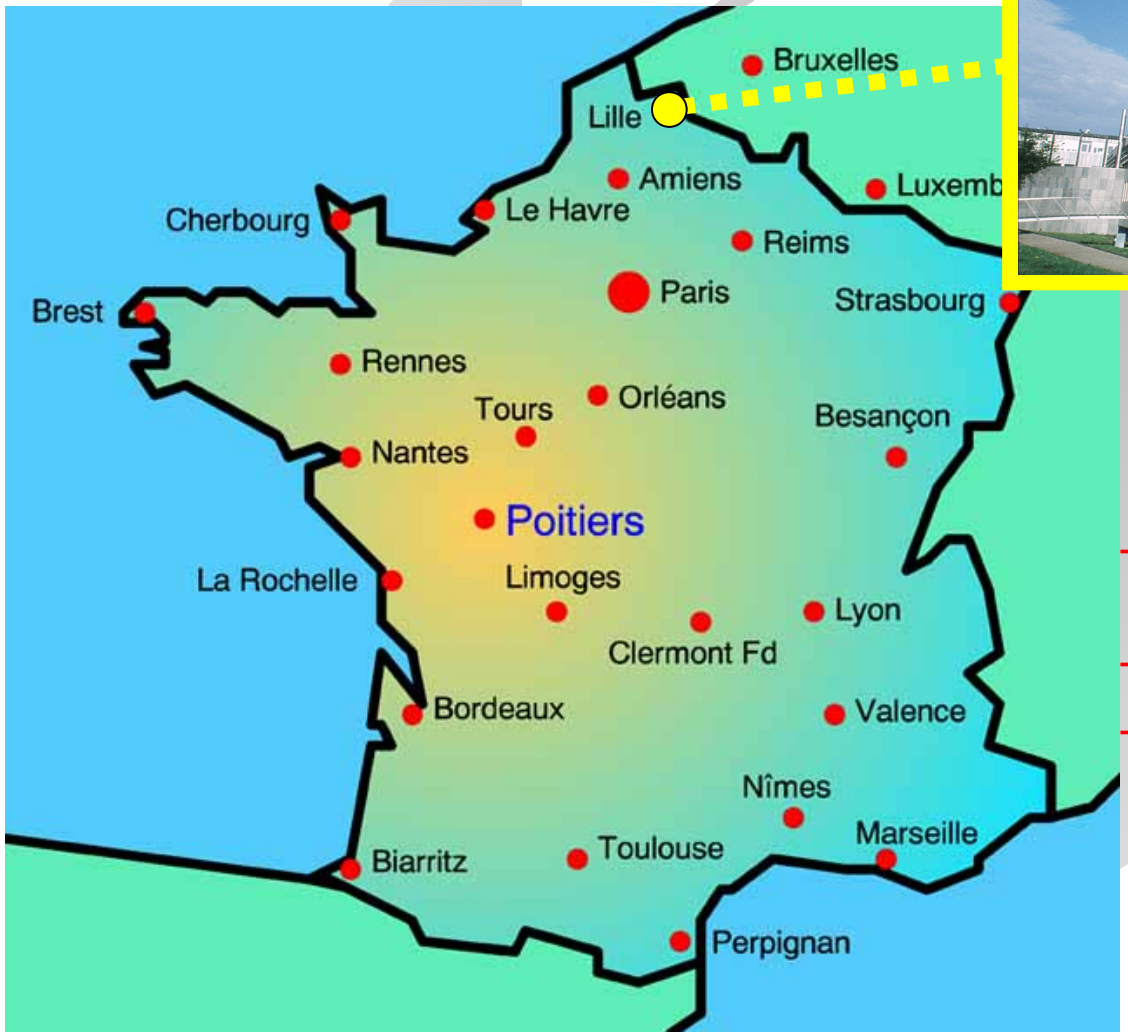

GDR : Matériaux et interaction en compétition
Nouveaux Matériaux –structures et propriétés particulières-
Réseau: Techniques de croissance cristalline

Unité de Catalyse et de Chimie du Solide de Lille, UMR CNRS 8181



groupe oxydes innovants et phases dérivées

- → Nouveaux Matériaux à propriétés ciblées (electrochimie, transport/magn …)
- → cristallochimie des composés du Bismuth
- → « Design » structural

- **Systèmes chimiques : Bi_2O_3 – MO – X_2O_5 : diagrammes de phase (M = Ca, Mg, Zn, Co, Ni, Cu, Pb …X = P, As, V …)**

✪ Approche structurale prédictive (Design)

✪ Richesse/flexibilité structurale (ordre vs désordre)

✪ Cristallochimie particulière : codes contraste en MEHR

✪ Propriétés “particulières” (non-centrosymétrie, magnetisme …)

- **Chimie du solide : challenge →approche prédictive**

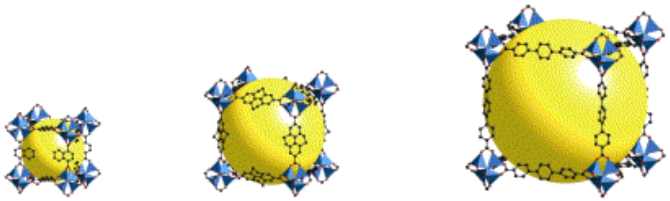
nanostructured metal oxides and chalcogenides, salt-inclusion synthesis, and a palette of preparation techniques for porous materials.

Most research efforts in current solid-state chemistry are concerned with the design and prediction of new structures and materials [2,3]. In general it is difficult to design a phase a priori. Progress has been considerable and we have many cases in which "materials design" is actually possible, e.g. simple isoelectronic elemental substitutions, the intercalation of species into solids, the synthesis of coordination solids based on solid-state structures, and the assembly of templated materials (see elsewhere in this issue). Nevertheless, in most cases the ability to broadly design and predict new phases remains a challenge [4].

« Report from the third workshop on future directions of solid-state chemistry : The status of solid-state chemistry and its impact in the physical sciences » , *Progress in Solid State Chemistry* 36 (2007) 1-133

- **Matériaux hybrides**

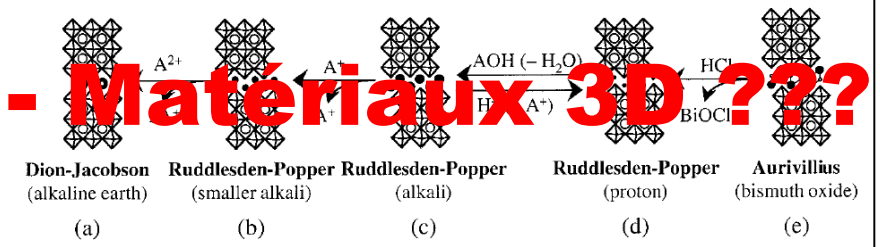
- Aimants moléculaires, MOFs (templates, Self-assembling BUs…)



J. L. C. Rowsell and O. M. Yaghi, *Microporous and Mesoporous Materials* 73 (2004)

- **inorganiques « purs »**

- Matériaux 2D (layers, blocks)

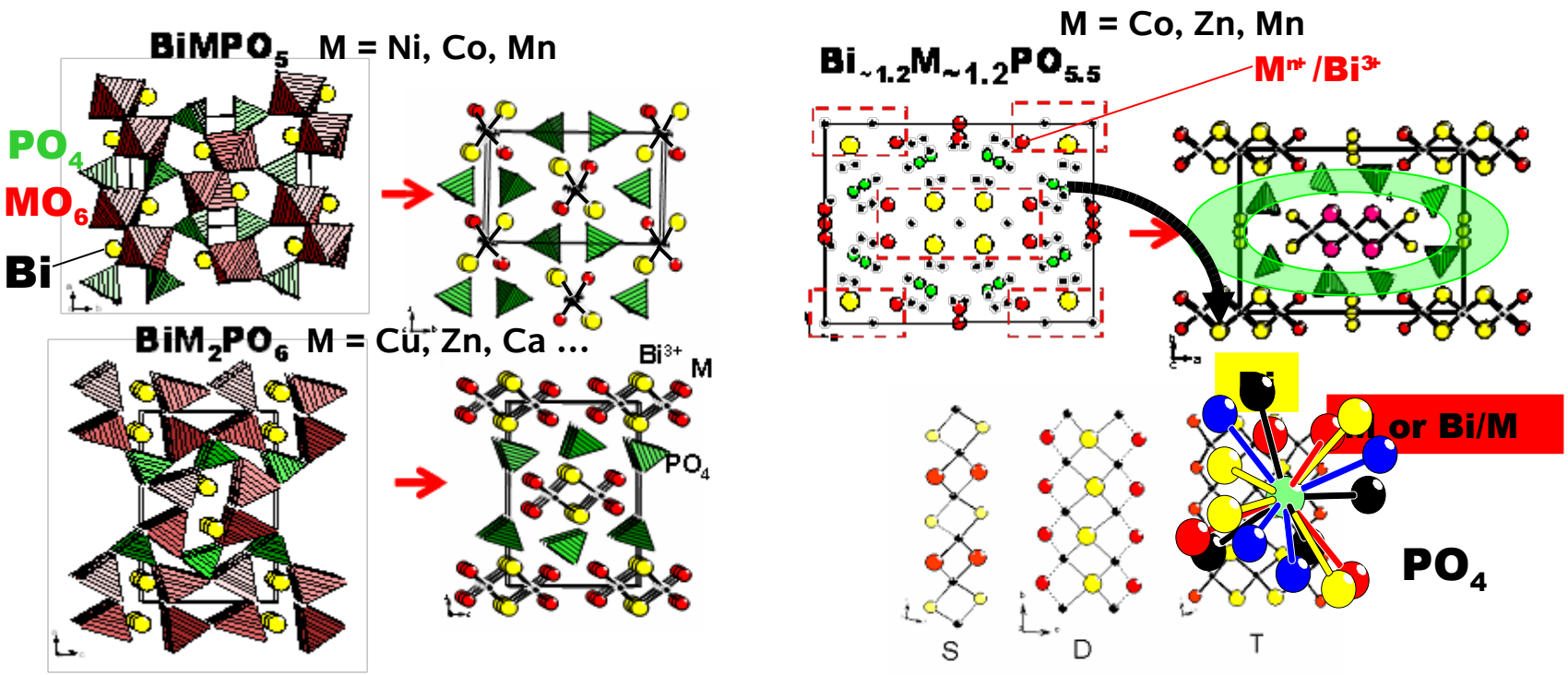


- Matériaux 3D ???

R. E. Schaak and T. E. Mallouk, *Chem. Mater* 14 (2001) 1455

Nouvelles phases 3D dans les systèmes Bi_2O_3-P_2O_5-MO_y

- **Adequate Building units**

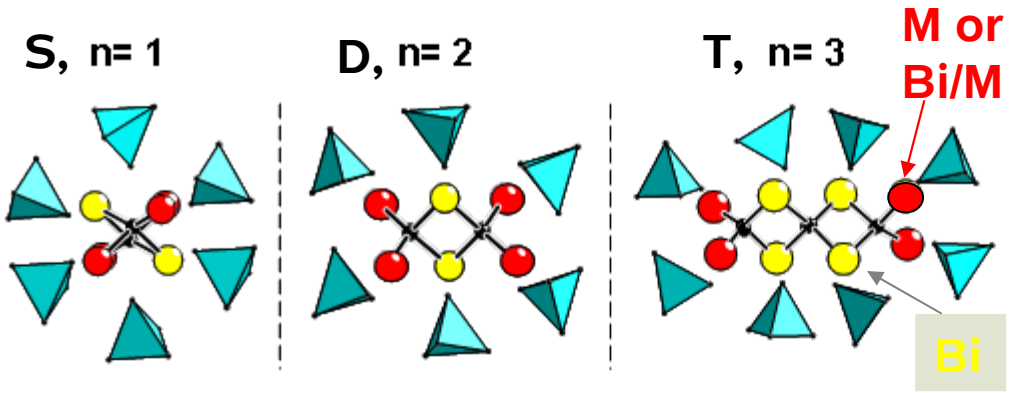


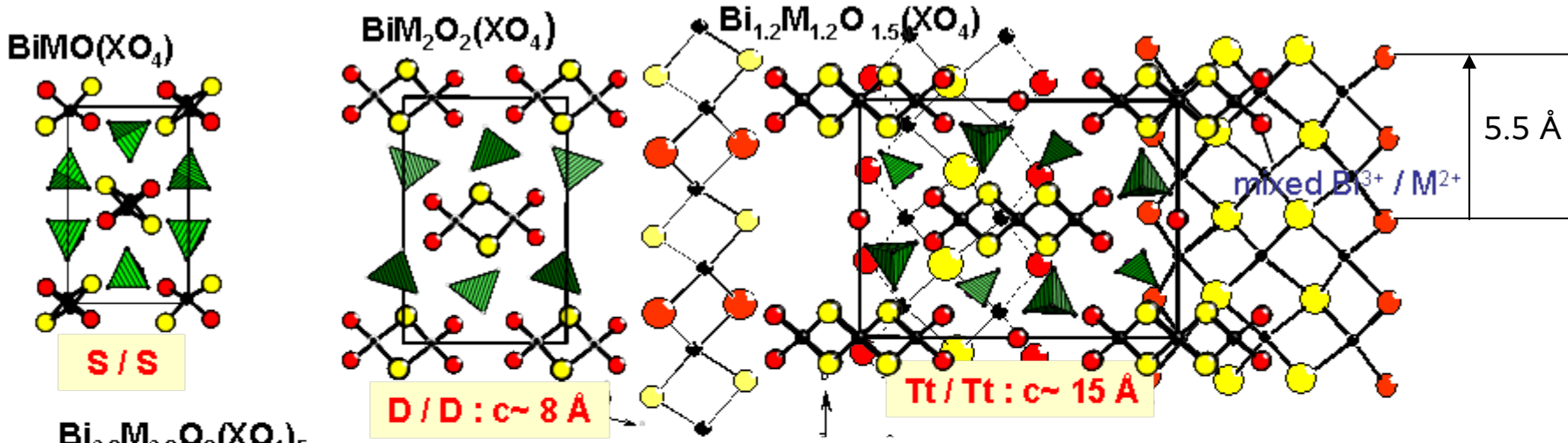
Utilisation de polyèdres oxo-centrès en cristallochimie

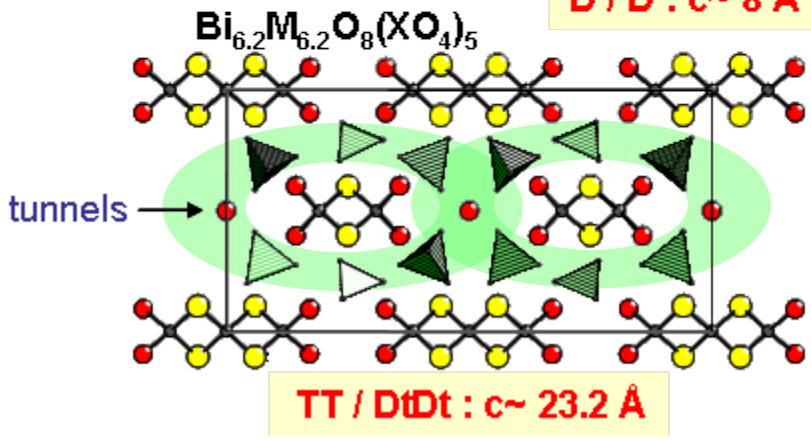
- **Sauerstoff als Koordinationszentrum in Kristallstrukturen,** G. Bergerhoff , J. Paeslack 1968. *Z. Kristallogr.*, 126, 112-123 (1968).
- **OM_4 tetrahedra and the cationic groups $(MO)^{n+}$ in rare earth oxides and Oxysalts,** P.E. Caro, *Journal of Less-Common Metals*, 16, 367-377 (1968).
- **An alternative approach to non-molecular crystal structures,** M. O' Keeffe and B.G. Hyde. *Structural and Bonding* 61, 77-177 (1985).
- **[NM_4] tetrahedra in nitride sulfides and chlorides of the trivalent Lanthanides, Th. Schleid ,** *Eur. J. Solid State Inorg. Chem.*, 33, 227-240 (1996).
- **On the influence of light anions (O^2, N^3 and F^-) on the crystal chemistry of rare-earth metal trichlorides and sesquisulfides,** Th. Schleid , *Mater. Sci. Forum*, 315,163-168(1999).
- **Types of cationic complexes on thebase of oxocentred [OM_4] tetrahedra in crystal structures of inorganic compounds.** S.V. Krivovichev, S.K. Filatov, T.F. Semenova, *Russ.Chem. Rev*. 67, 137-155 (1998).
- **Structural principles for minerals and inorganic compounds containing anion-centered tetrahedra.** S.V. Krivovichev ,S.K. Filatov , *Amer. Mineral*., 84, 1099-1106, (1999)….

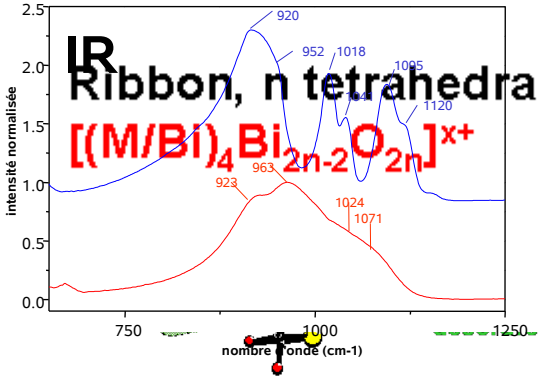
Bi_2O_3-MO-$(P, V, As)_2O_5$
(M=Zn,Co,Cu,Ca,Mg,Cd,Pb …)

→ Rubans formés de $O(Bi,M)_4$ dans des nouveaux oxo-phosphates de bismuth



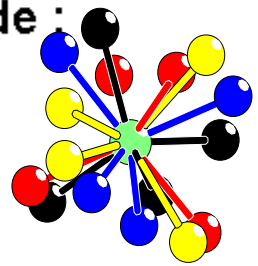






T

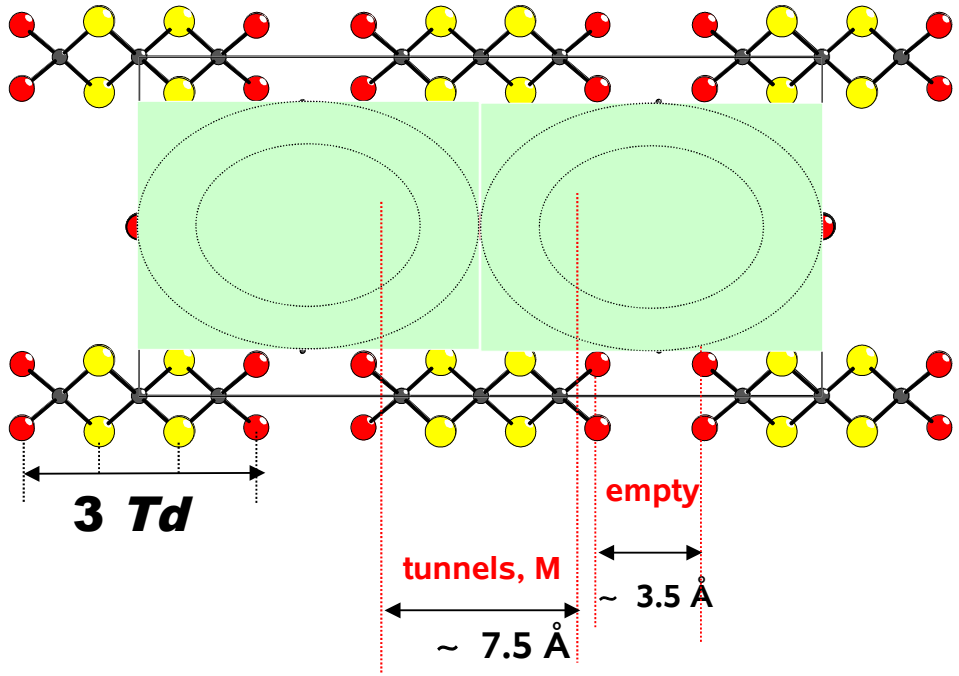
Désordre PO_4



- **association de BU's : règles structural**

par analogie avec les phases "parent

→ **prediction structurale**
→ **formulation chimique**



Ribbon with n $O(Bi,M)_4$ *Tetrahedra :*

- ***Formulation = f(n)***
- ***N surrounding PO_4 = f(n)***
- ***« tunnels » vs. « empty » : space between 2 ribbons***
- ***electroneutrality : Bi^{3+} /M^{n+} at edges ; occupancy of t***

Structural Particularities. They are listed above and detailed on Figure 1:

(i) The sizes of the ribbons vary from the single chain (n tetrahedra along the width = 1) to n = 2, 3, 4, 5, 6, then leading to a continuous series of polycations. Theoretically, the ribbon size is unlimited. Up to now, structural types with ribbons of variable width (n = 1, 2, 3, 4, 5, 6 and $n = \infty$ $O(Bi,M)_4$ tetrahedra wide) have been characterized. At this point, the question of the stability of long-sized ribbons against either their slicing in shorter ones in the materials or the creation of infinite layers remains unanswered.

(ii) The number of surrounding PO_4 groups is mathematically defined as a function of n.

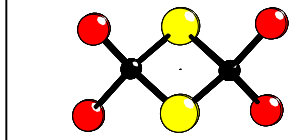
(iii) The intergrowth of different sized ribbons is one of the keys of the richness of this structural series.

(iv) Because of their similar inter- and intraribbon organization, most of these materials crystallize in an (pseudo)orthorhombic unit cell with two common parameters. The first one (conventionally, the a axis), ~11.5 Å, corresponds to the ribbons/PO_4 ordered periodicity perpendicular to the infinite dimension of the ribbons. The second, ~5.5 Å (conventionally, the b axis) is inherent to the structure of ribbons and corresponds to the height of two edge-shared $O(Bi,M)_4$ tetrahedra along the infinite axis. Finally, the c axis is variable and depends on the size and sequence of ribbons in each particular material.

(v) For $n \leq 3$, the tunnels "t" are located in between two edges of ribbons separated by in-plane distances of about 7.5 Å. Four columns of the surrounding PO_4 form their 1D cavities. The occupancy of tunnels is disordered, and at least can we empirically announce that along one b-period (~5.5 Å) t should contain a maximum of two M^{2+} cations to respect plausible M−M distances.

(vi) The cores C of ribbons are solely occupied by Bi^{3+} while their edges (E) can be suited by M^{2+} or mixed Bi^{3+}/M^{2+}. These mixed Bi^{3+}/M^{2+} positions are generally responsible for a disorder in the inter-ribbon space, namely, the competition between several orientations of the PO_4 groups depending on their local Bi/M environment.

Design of new compounds from OM_4-based building units

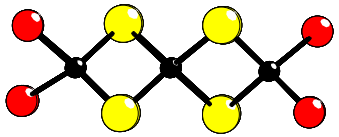


Double ribbons D

+ 6 PO_4

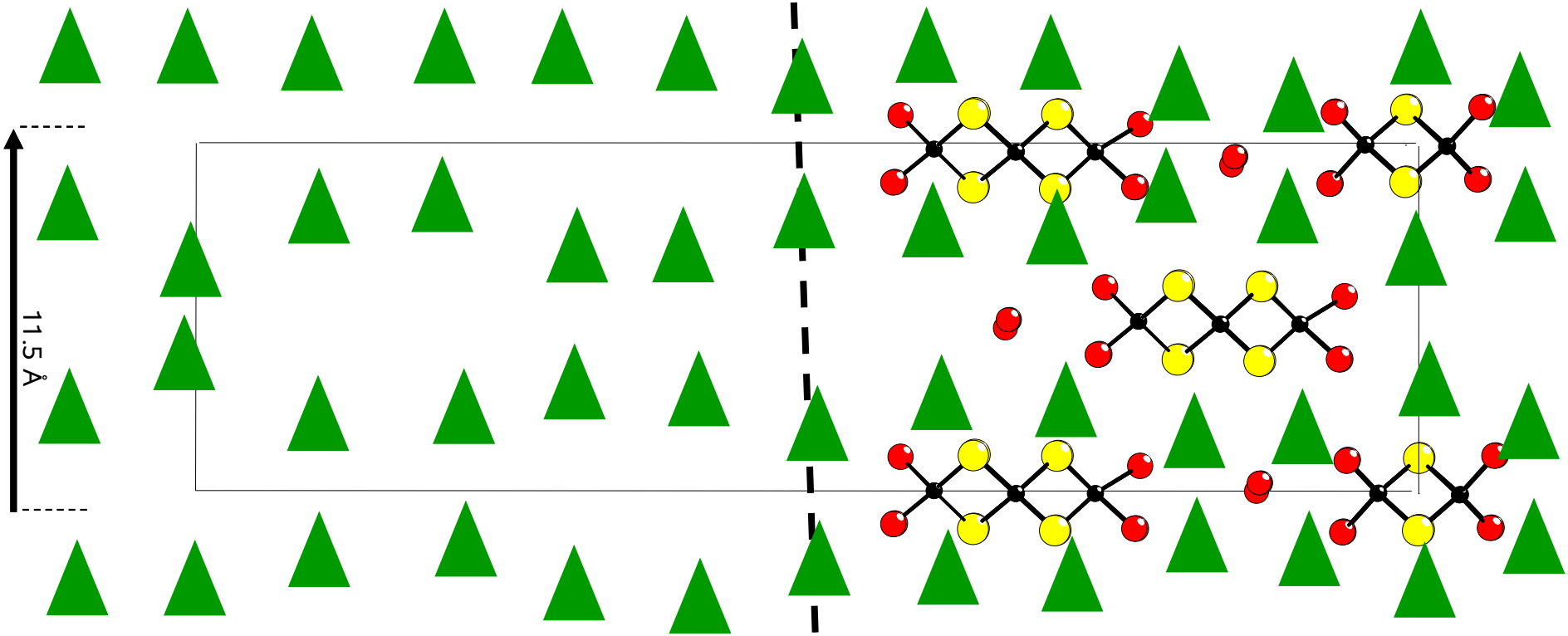
tunnels t

+ 4 PO_4



Triple ribbons T

+ 8 PO_4

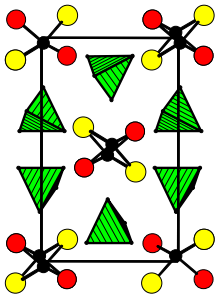


Structural type : DtTTt / TtDtT (c~ 40 Å) ,

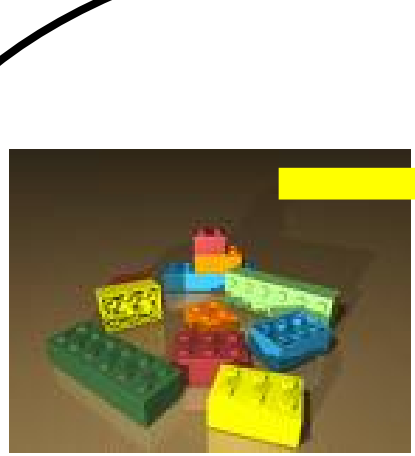
Formula : $[Bi_2(M/Bi)_4O_4]_1\ [Bi_4(M/Bi)_4O_6]_2\ M_{x<4}\ (PO_4)_{10}$

Double ribbons | tunnels | Triple ribbons

= Building Units and intergrowths



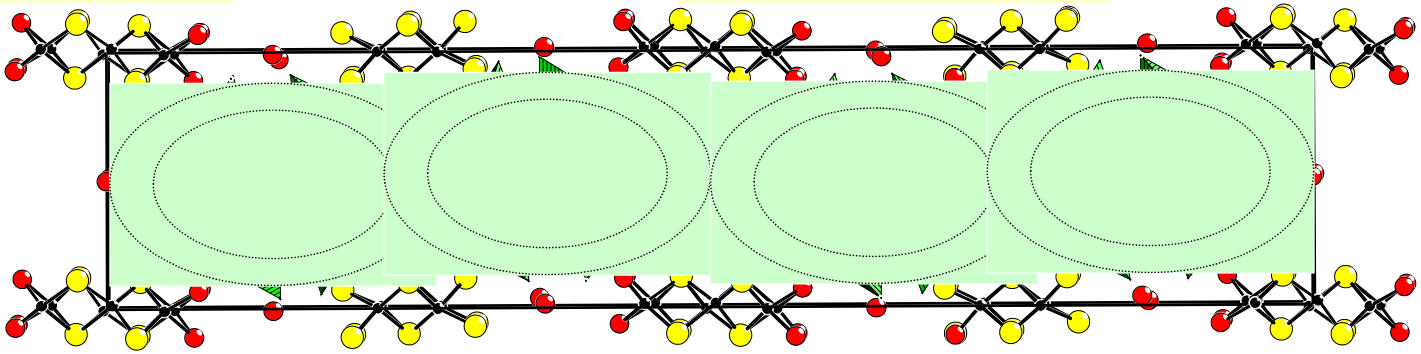
1 / 1 $BiMPO_5$



Bi^{3+} / M

33 / 2t2t : c~ 23.2 Å $Bi_{-3}Cd_{-372}Co_{-128}P_3O_{17}$

$Bi_{-62}Cu_{-62}P_5O_{28}$

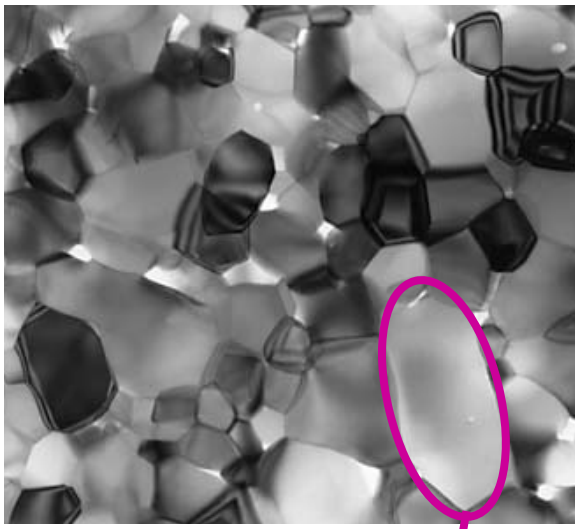


t2t3t2t3 / 33t33t : c~ 53 Å $Bi_{-38}Cd_{-36}Cu_{-15}P_{35}O_{195}$

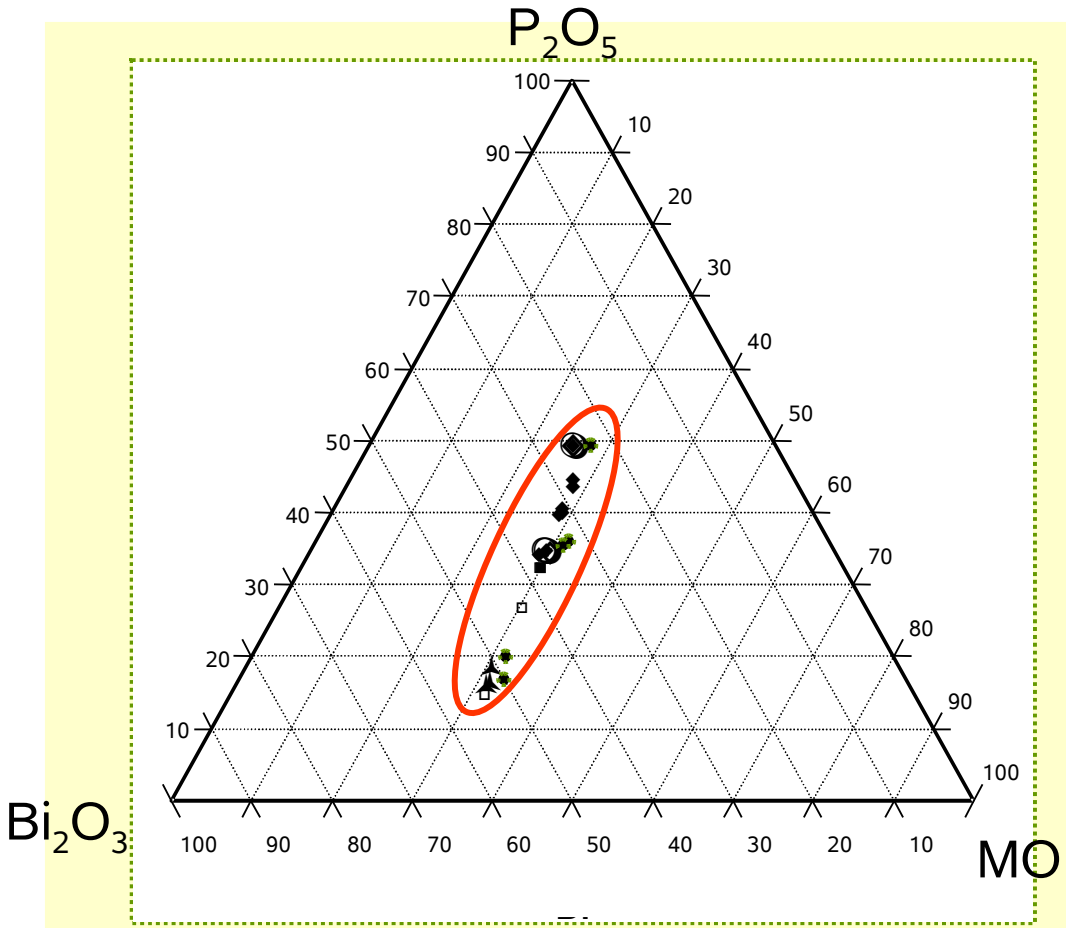
MEHR outil d' analyse structural

***Chem. Mater.*, 16, 2628 (2004).**

Multi-phased sample

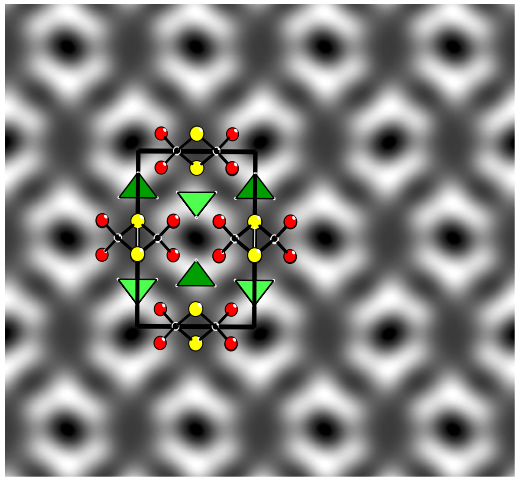


Analyse de cristallites isolées



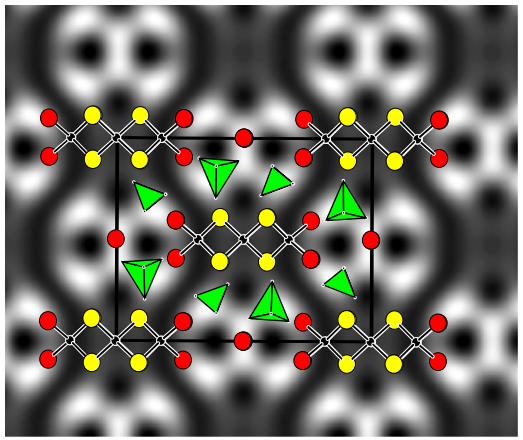
« HREM a usefull tool to formulate new members of the wide Bi^{3+}/M^{2+} oxyphosphate series »
M. Huvé, M.Colmont. and O. Mentré, *Chemistry of Materials*, **16**, 2628 (2004).

mother



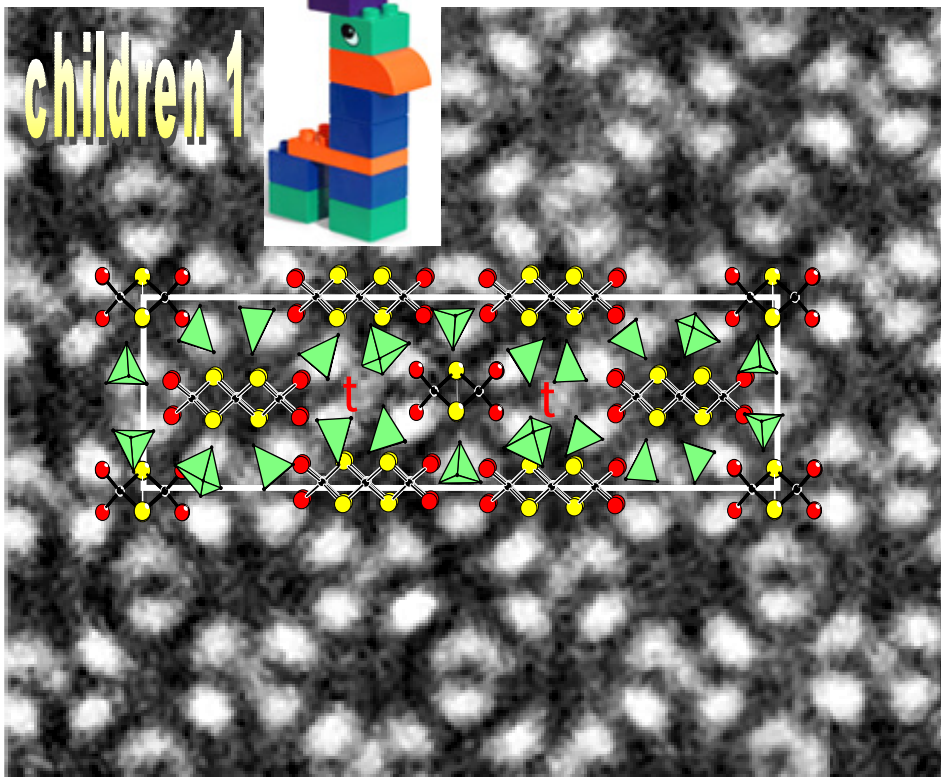
Δf= -10nm e=4.1 nm

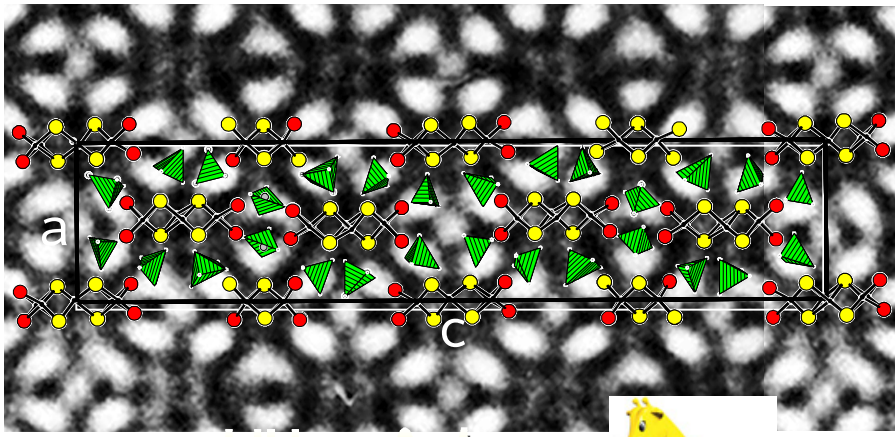
father



Δf= -10nm e=4.3 nm

children 1



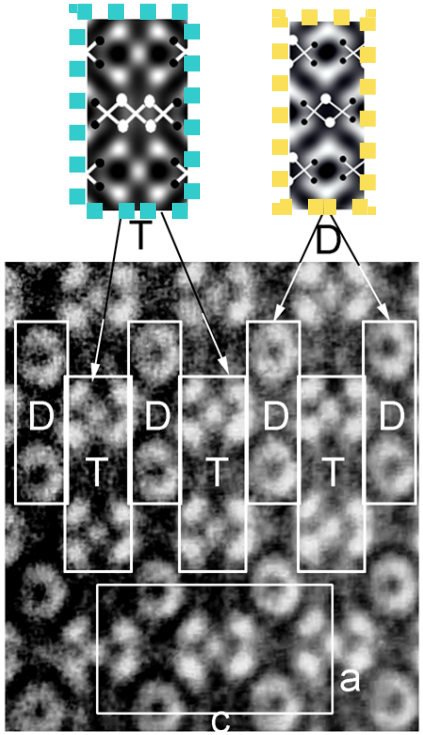


children 3, 4 ...

Structure and Formulation from HREM

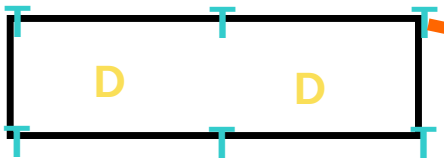
M. Huvé, M. Colmont , O. mentré,
Inorg. Chem, **45**, 6604, (2006)

M. Huvé, M. Colmont, O. Mentré,
*Chem. Mater.***16,** 2628 (2004).

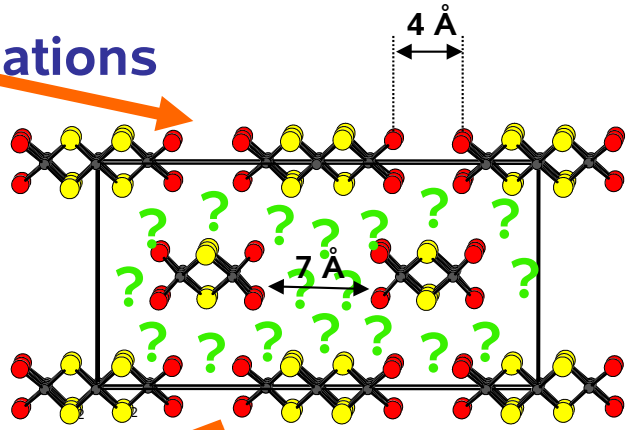


Code

HREM

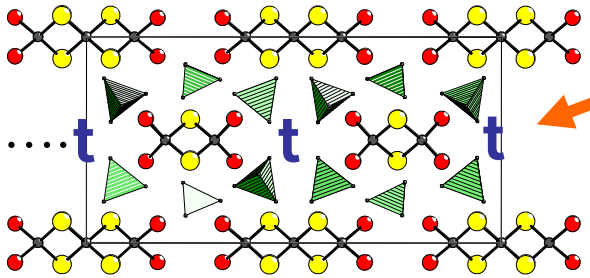


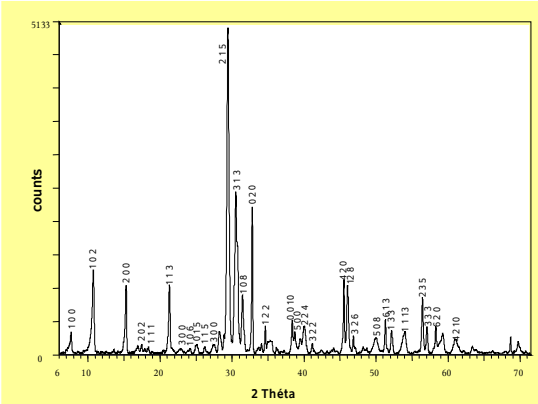
polycations



« Rules » :

PO_4 + tunnels





Formulation and synthesis

$[Bi_4(Bi,M)_4O_6]_2[Bi_2(Bi,M)_4O_4]_2t_2(PO_4)_{12}$

Single-crystal : $Bi_{\sim 3}Cd_{\sim 3.72}Co_{\sim 1.28}O_5(PO_4)_3$, R_1= 5.37% , Abmm, Z= 4

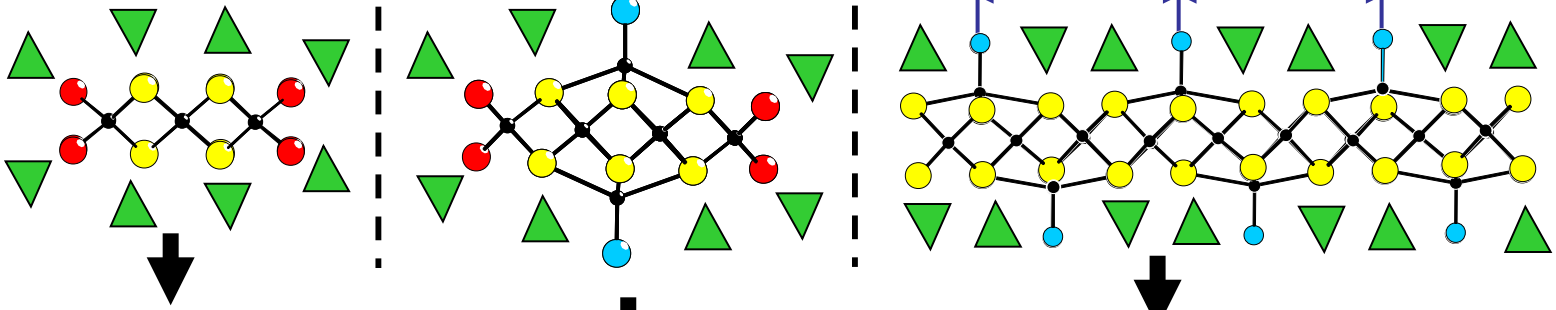
Powder : a= 11.5322(28)Å, b= 5.4760(13)Å, c= 23.2446(56)Å

n ≤ 3

n > 3

layers

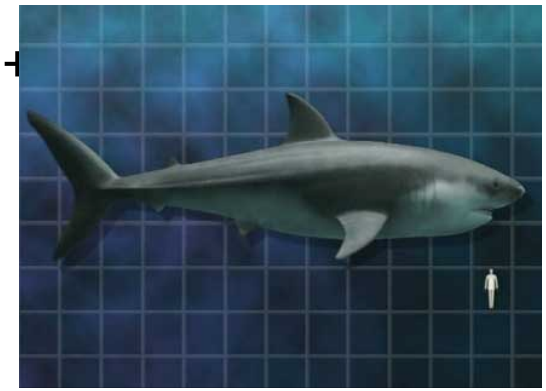
3 tetrahedra



$[(M/Bi)_4Bi_{2n-2}O_{2n}]^{n+}$

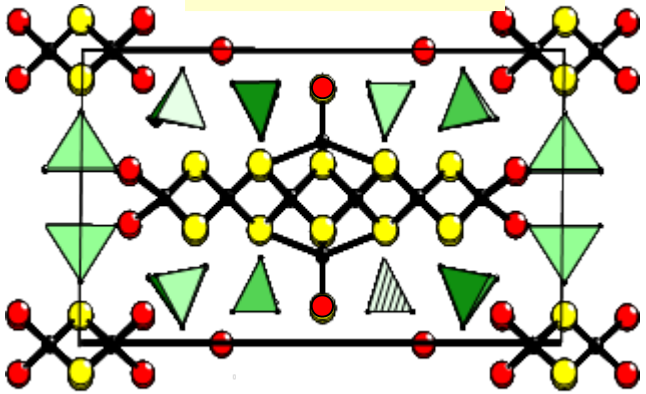
$[Bi_3MO_3]^{n+}$; 2 PO_4

$N_{surrounding}$ PO_4: 2n+

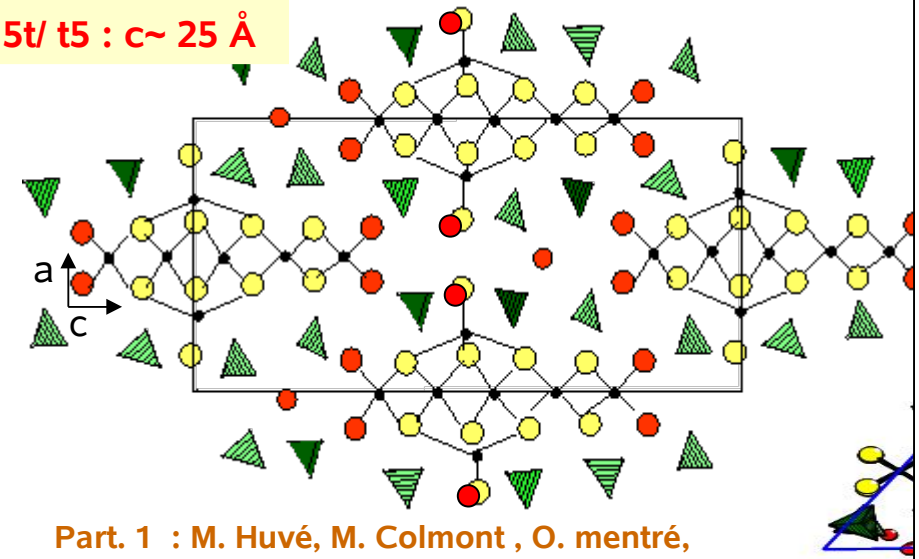


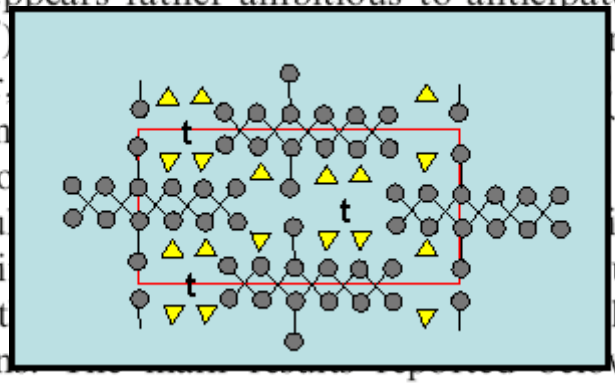
Inter

2tt/ 6 : c~ 21 Å



5t/ t5 : c~ 25 Å





It appears rather ambitious to anticipate all possible $(n)/(n')$ member that, so far ribbons has system an acentric compo predict and formu ng to $(n)/(n)$ ferro-i ures deduced from t l $n = 4$ to 12 ribbon w have been already detailed in the previous paragraph devoted to the Formulation of Compounds.

Formulas of n-sized ribbons: $[(M/Bi)^{E}{}_4Bi^{C}{}_{2n-2}Bi^{Ex}{}_{2int-[(n-1)/3]}O_{2n+2int[(n-1)/3]}]^{x+}$.

Number of neighboring PO_4 groups: $2[(n-1) - int-[(n-1)/3]]$ per ribbon.

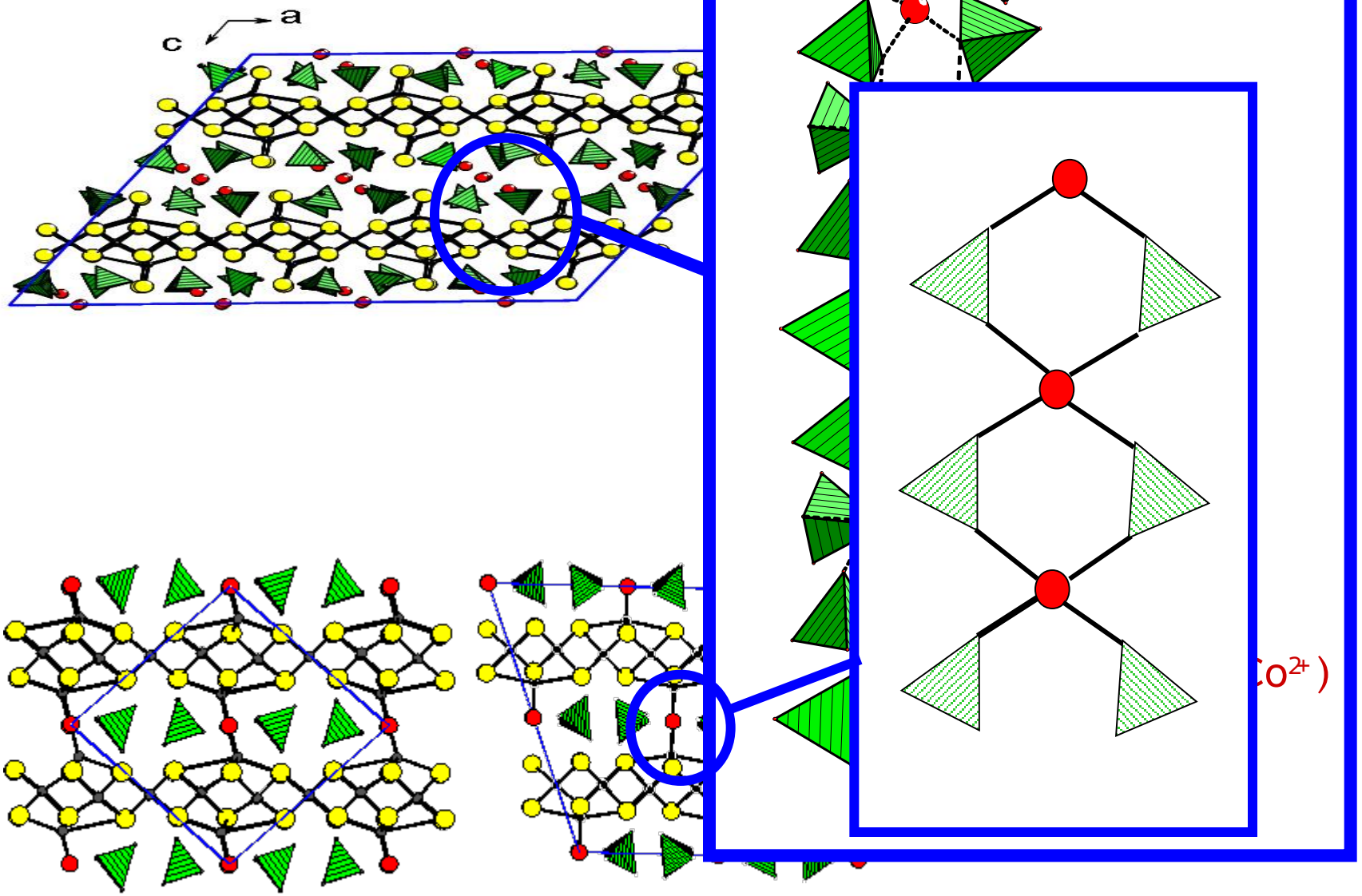
Number of created tunnels: Here, two cases should be distinguished depending on the interplay between PO_4 and excrescences and on the possibility of creating tunnels between two subsequent PO_4 groups along c:

(i) $n \neq 3n'$: there are $int[(n+1)/3] - 1$ tunnels per ribbon. The compounds are so-formulated: $(n)t_{(int[n/3]-1)}/(n)t_{(int[n/3]-1)}$ which corresponds to the global formula $[(M/Bi)_4Bi_{2n-2}Bi_{2int[(n-1)/3]}O_{2n+2int[(n-1)/3]}(PO_4)_{2[(n-1)-int[(n-1)/3]]}t_{int[(n+1)/3]-1}$, with $t = M_{x<2}$.

(ii) $n = 3n'$: there are $n/3$ tunnels per ribbon leading to the $(n)t_{n/3}/(n)t_{n/3}$ intergrowth. The general formula is $[(M/Bi)_4Bi_{2n-2}Bi_{2int[(n-1)/3]}O_{2n+2int-[(n-1)/3]}(PO_4)_{2[(n-1)-int[(n-1)/3]]}t_{n/3}$, with $t = M_{x<2}$.

Part. 1 : M. Huvé, M. Colmont , O. mentré, *Inorg. Chem*, 45, 6604, (2006)

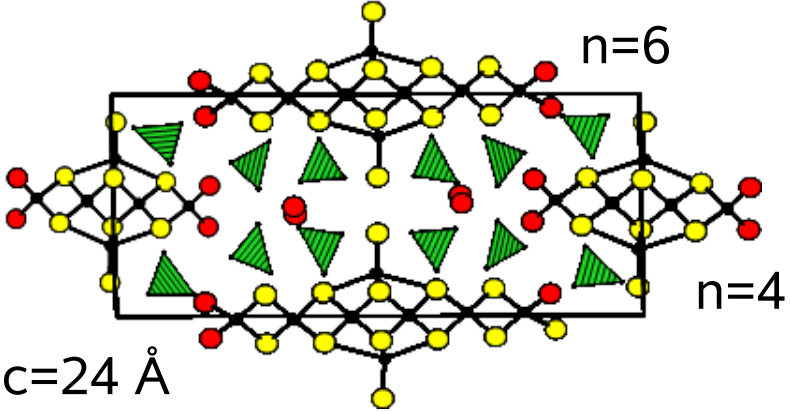
Part. 2 : M. Colmont, M. Huvé, O. Mentré, *Inorg. Chem*, 45,6612, (2006).



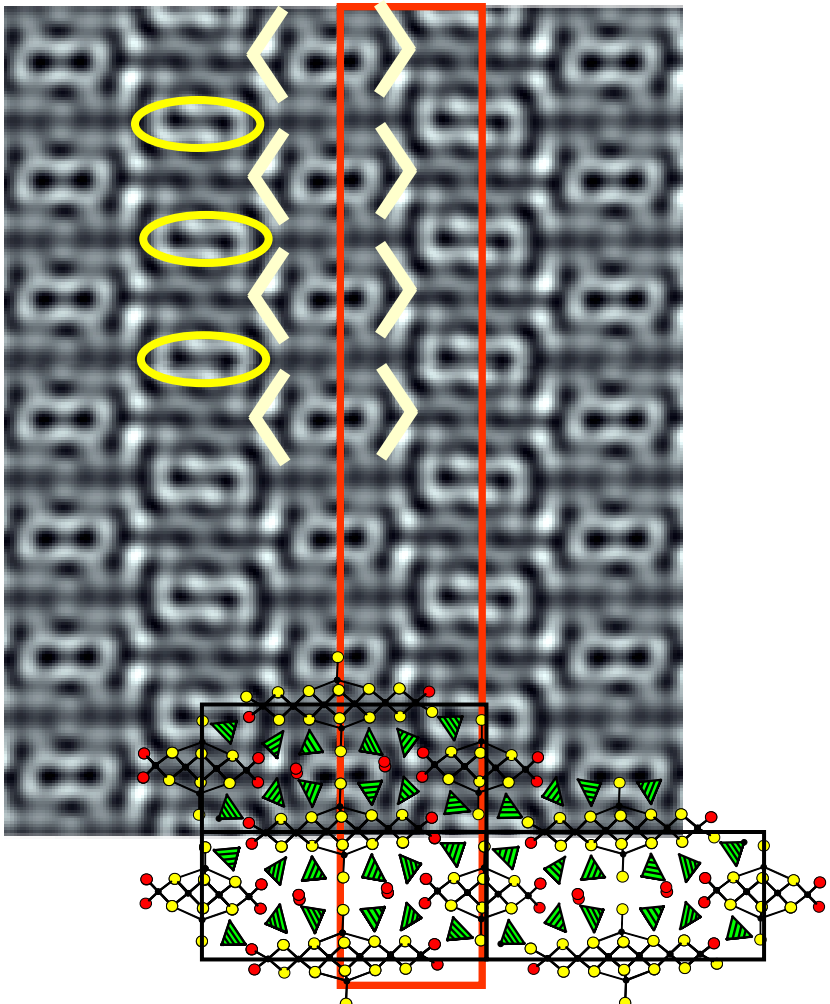
Steinfink, Lynch, JSSC, 177, 1412 (2004)

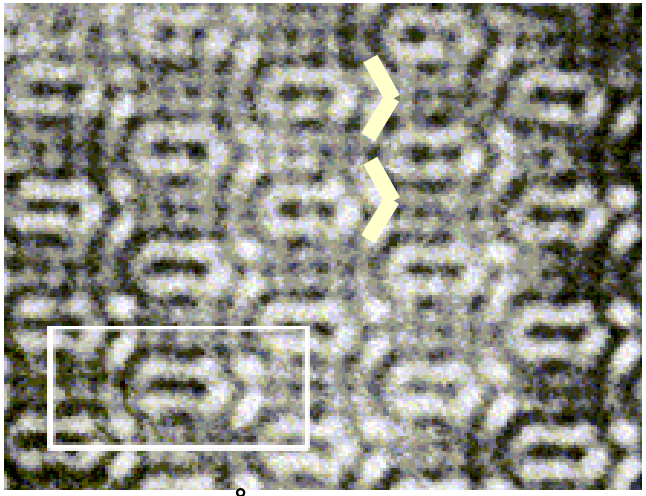
Colmont, Huvé, Ketatni, Mentré, Solid State Sciences, (2008)

MEHR : rubans polycationiques n>3

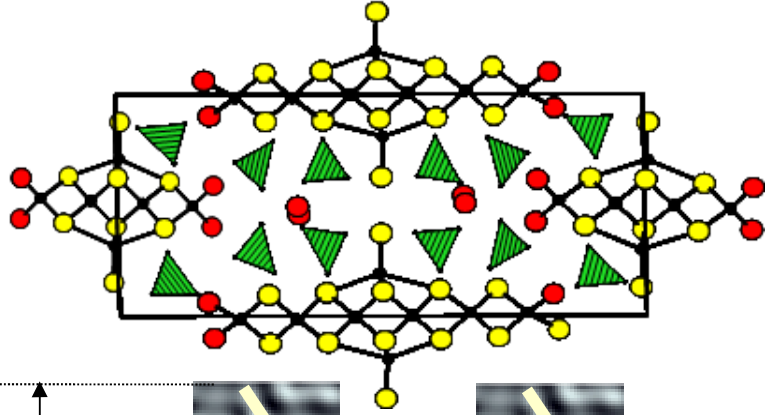


Composé inconnu ?

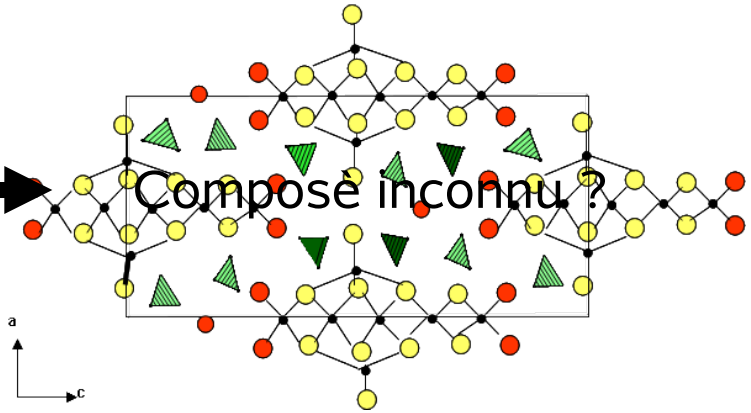




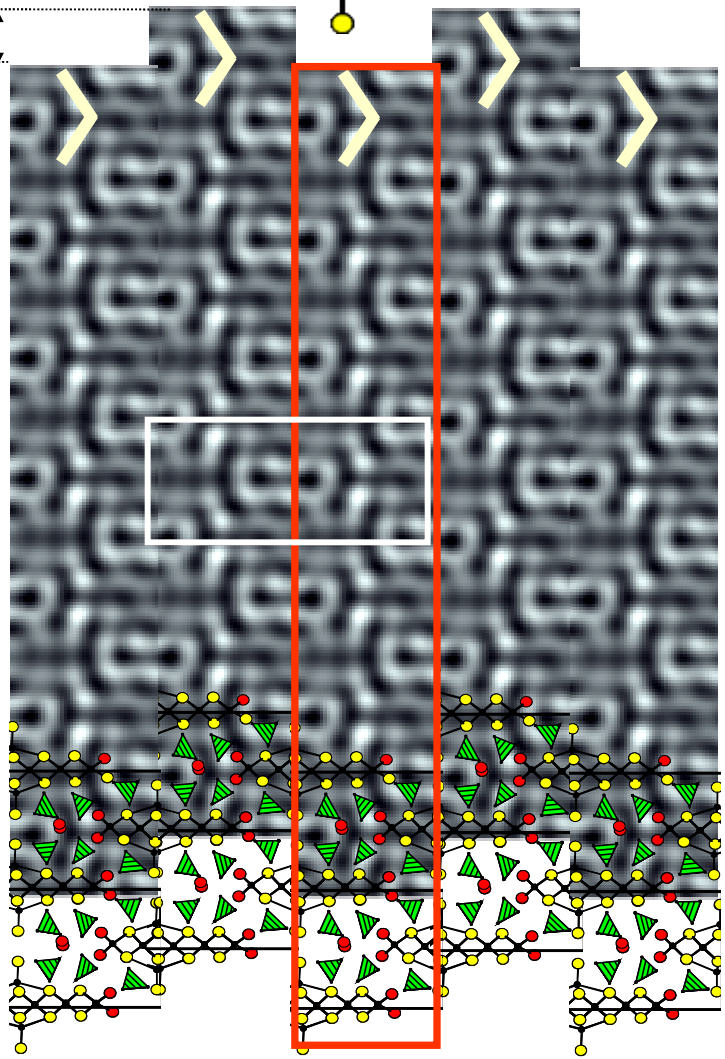
c=25 Å

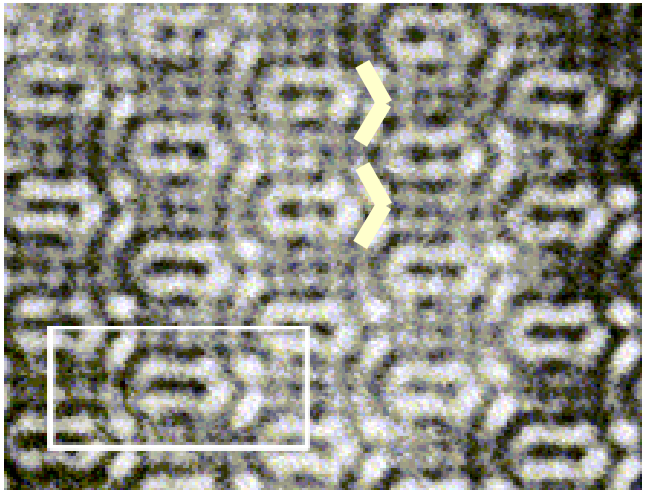


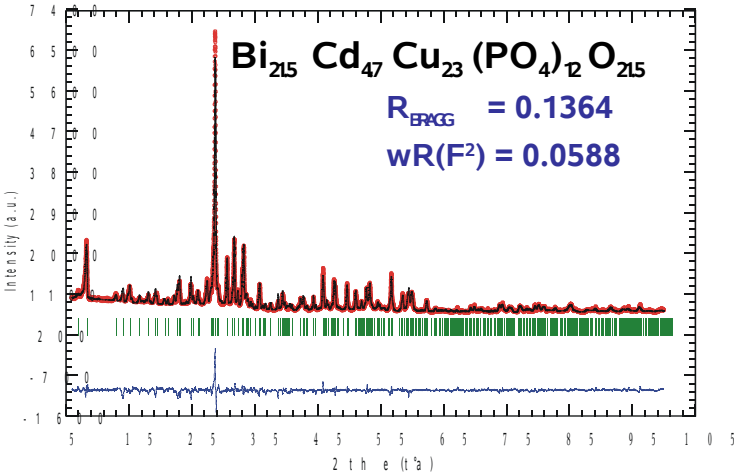
Composé inconnu ?



a/2

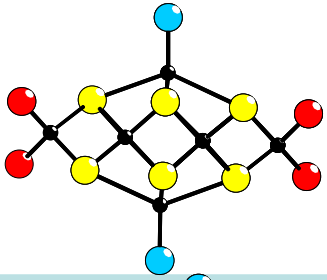




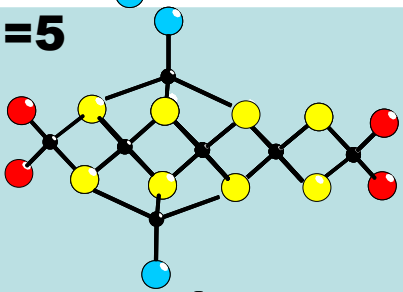


Highlight : n =3n'+2 → brique polaire

n=4

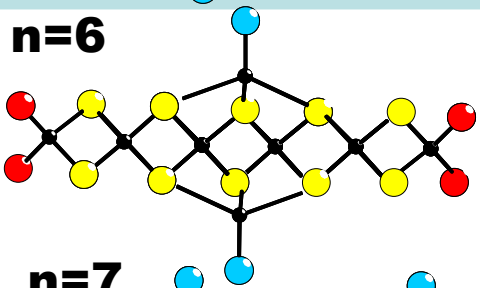


n=5

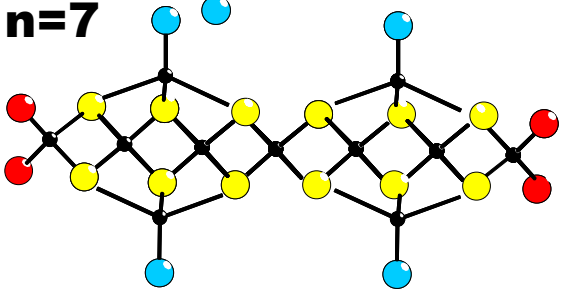


polaire

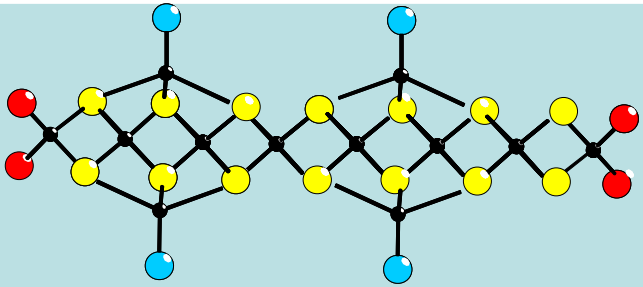
n=6



n=7

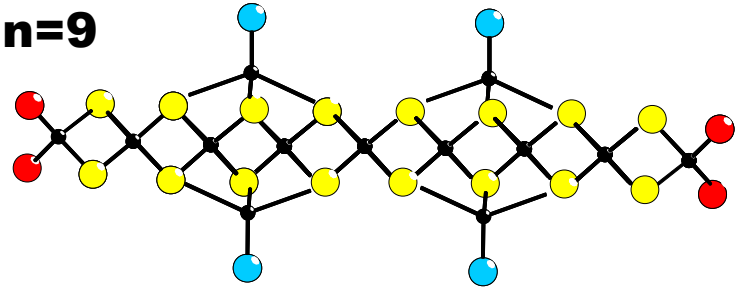


n=8

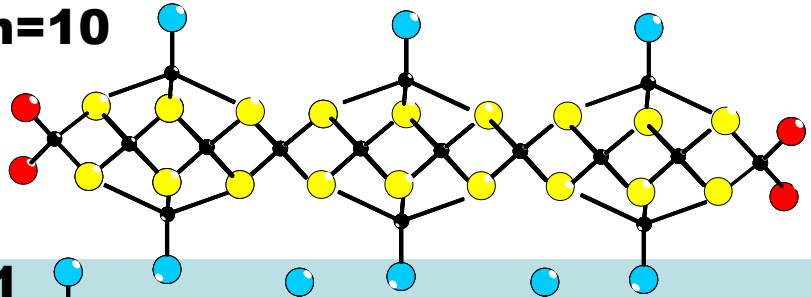


polaire

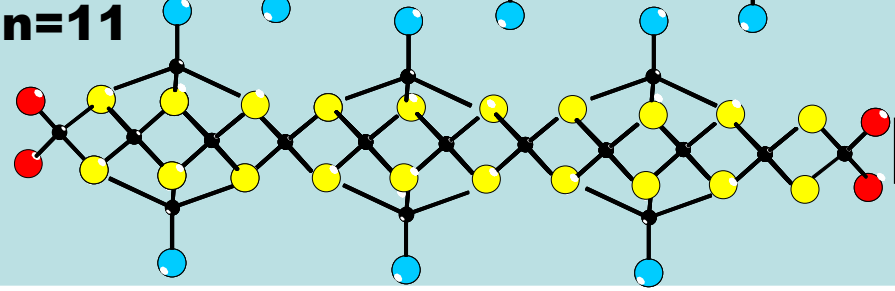
n=9



n=10



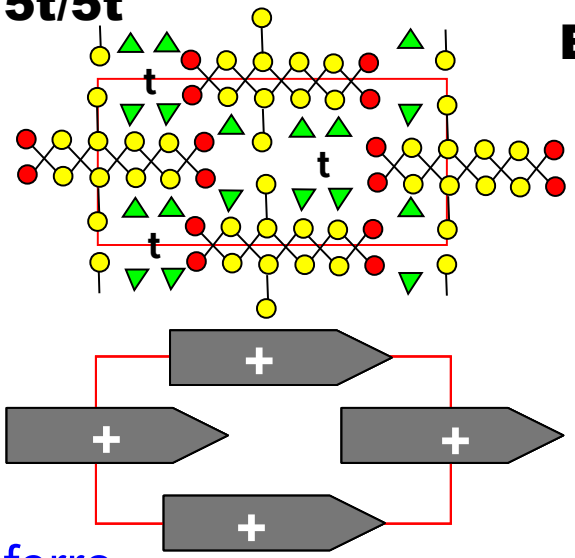
n=11



polaire

BU polaire → Matériaux non-centro ?

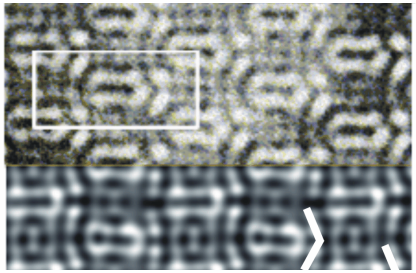
5t/5t

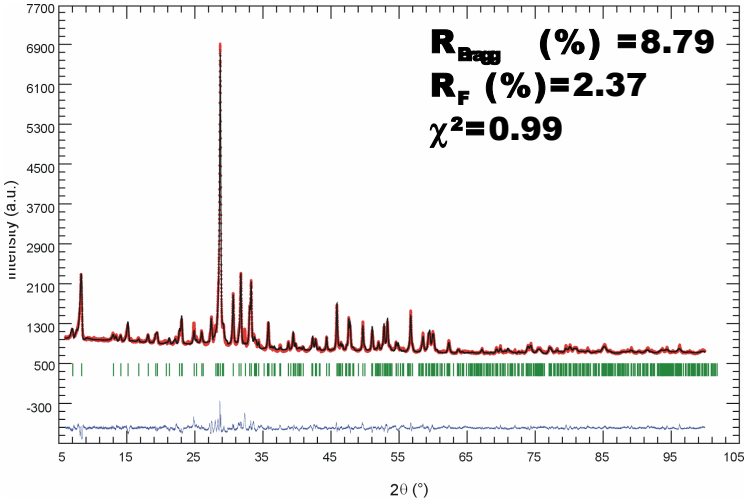


ferro

$Bi_{20}Cd_{7.42}Cu_{0.58}O_{24}(PO_4)_{12}$

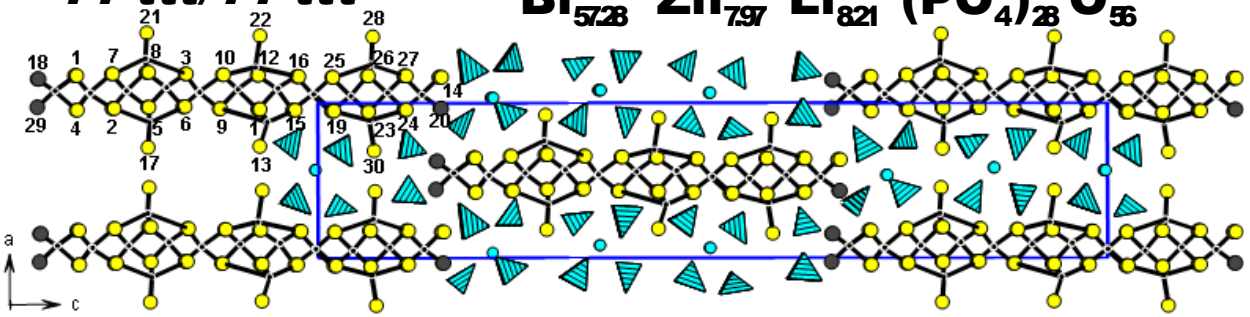
a= 11.6617 (4)
b= 5.3794 (2)
c= 25.0587 (7)
S.G. Ibm2

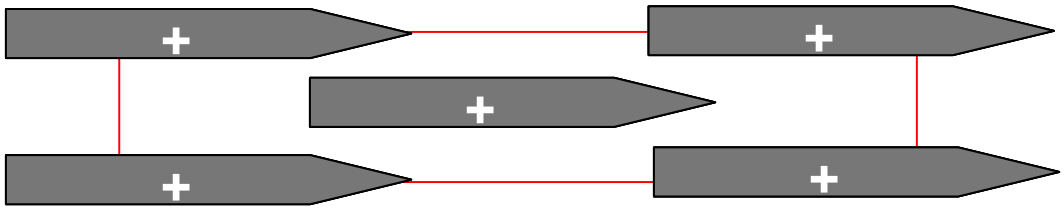




11 ttt/11 ttt

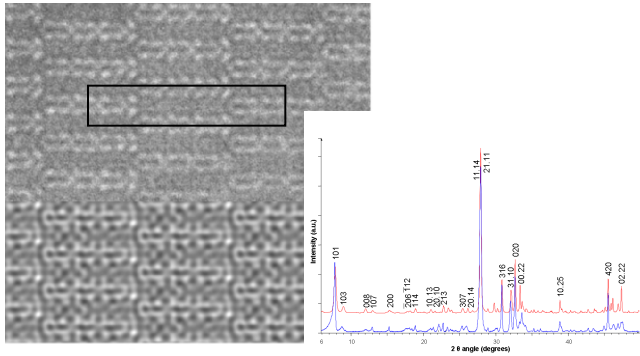
$Bi_{5.728}Zn_{7.97}Li_{8.21}(PO_4)_{28}O_{56}$





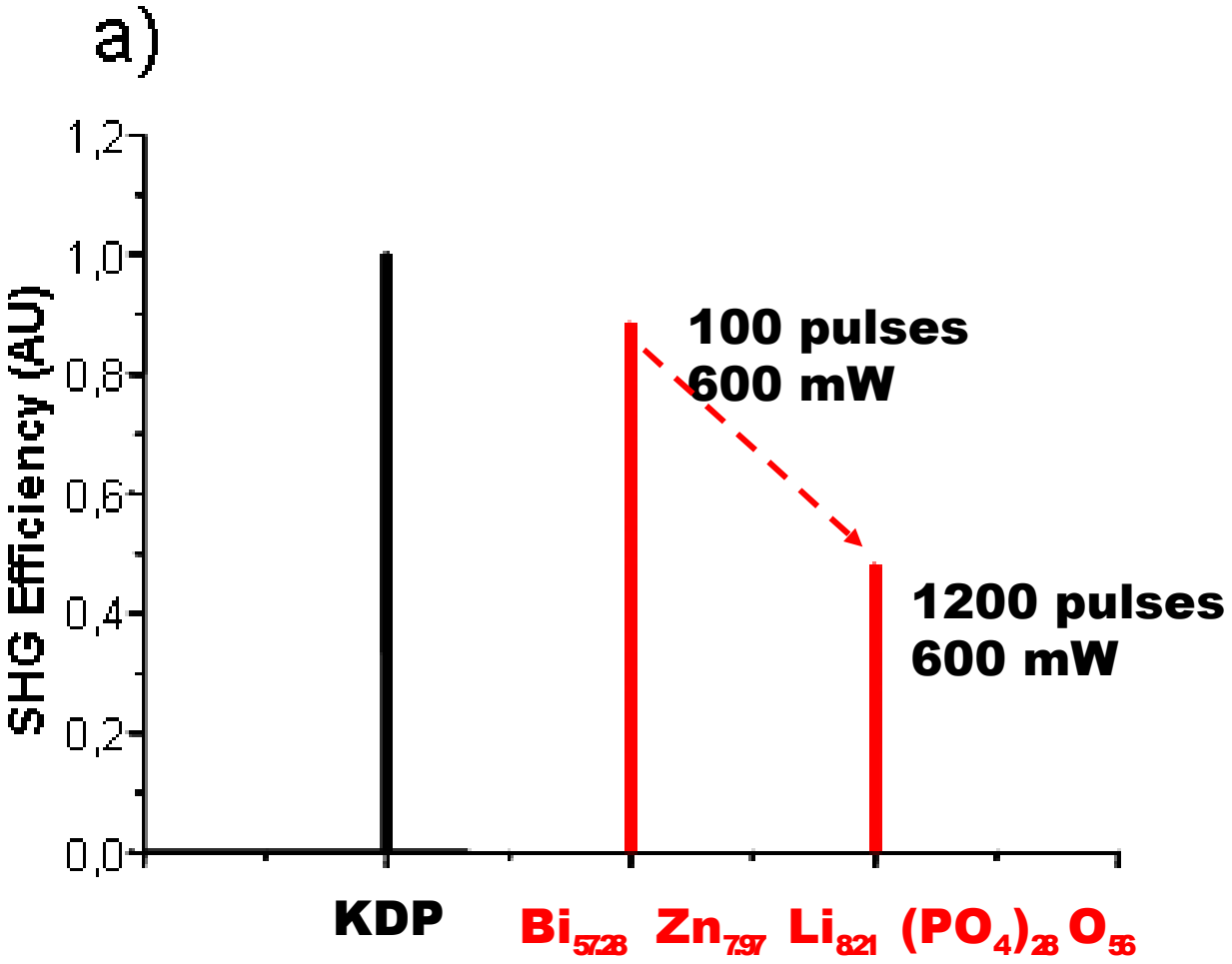
ferro

a=11.579(3) ,
b= 5.476(1), ß = 90.28(2)°
c= 59.0149(14)
S.G. Im ; R_1 = 8.17 %



Génération de 2nde Harmonique (J. Lejay)

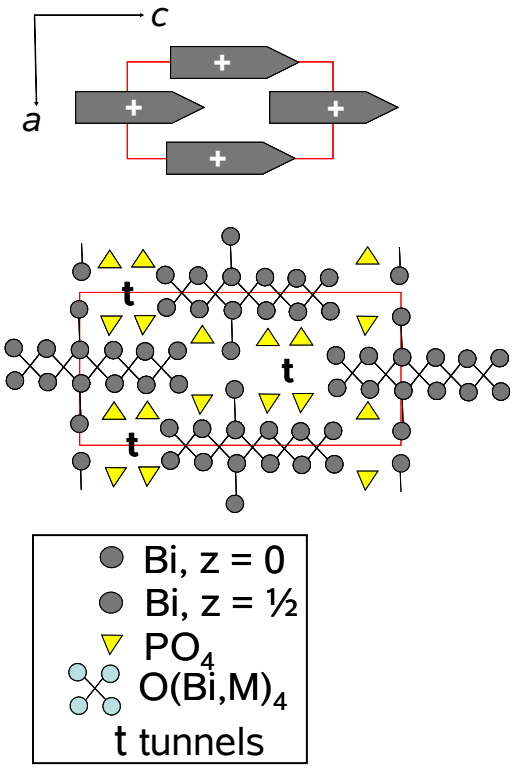
Chem. Mater., Vol. 21, No. 17, 2009 4021

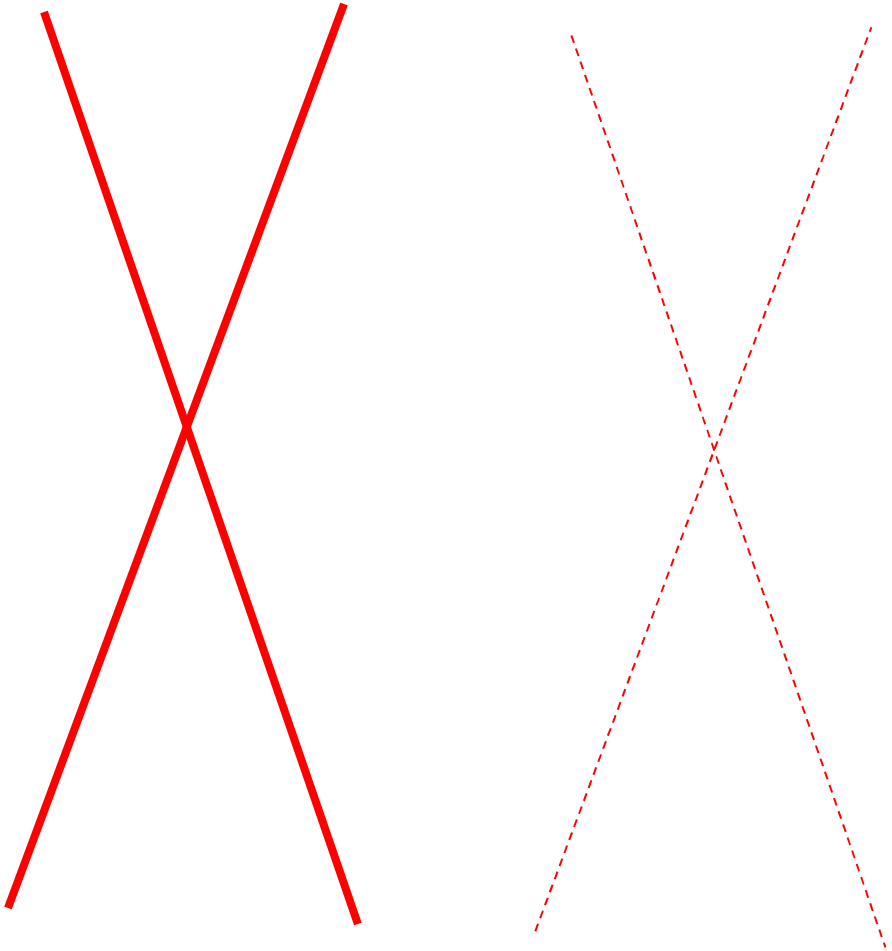


Perte de SH signal → noircissement des échantillons (Bi^{III} → Bi^{V}) ?

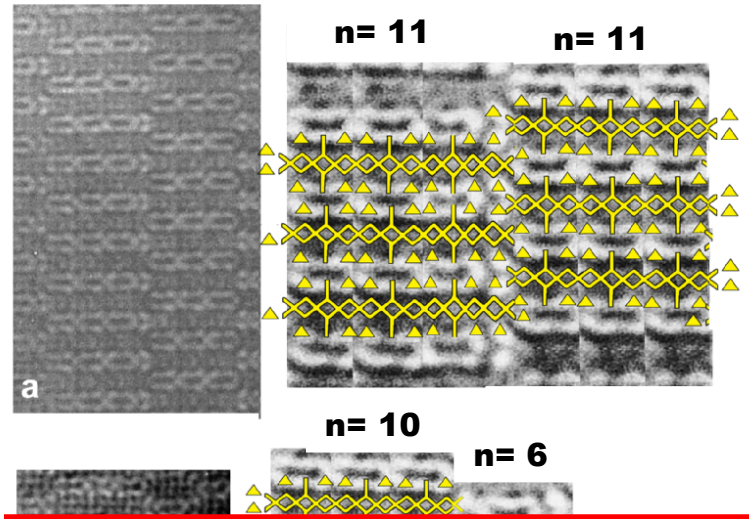
Ferro versus Antiferro

a) Ferro *(observed)*





Intercroissances non-centro Bi_2O_3-ZnO/LiO-P_2O_5



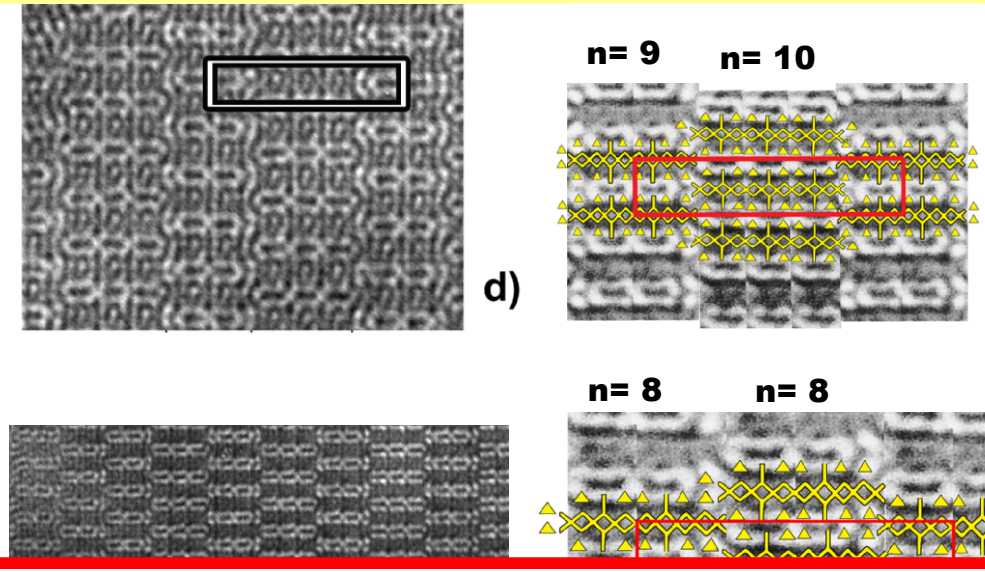
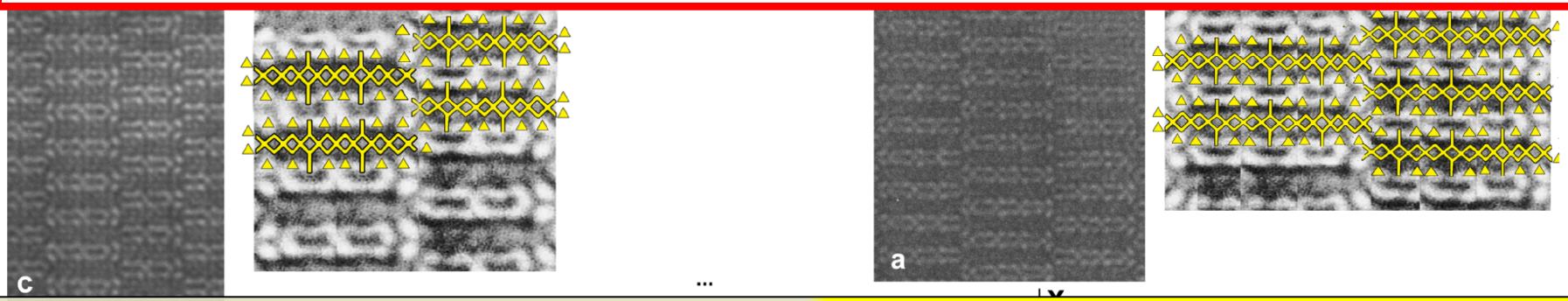
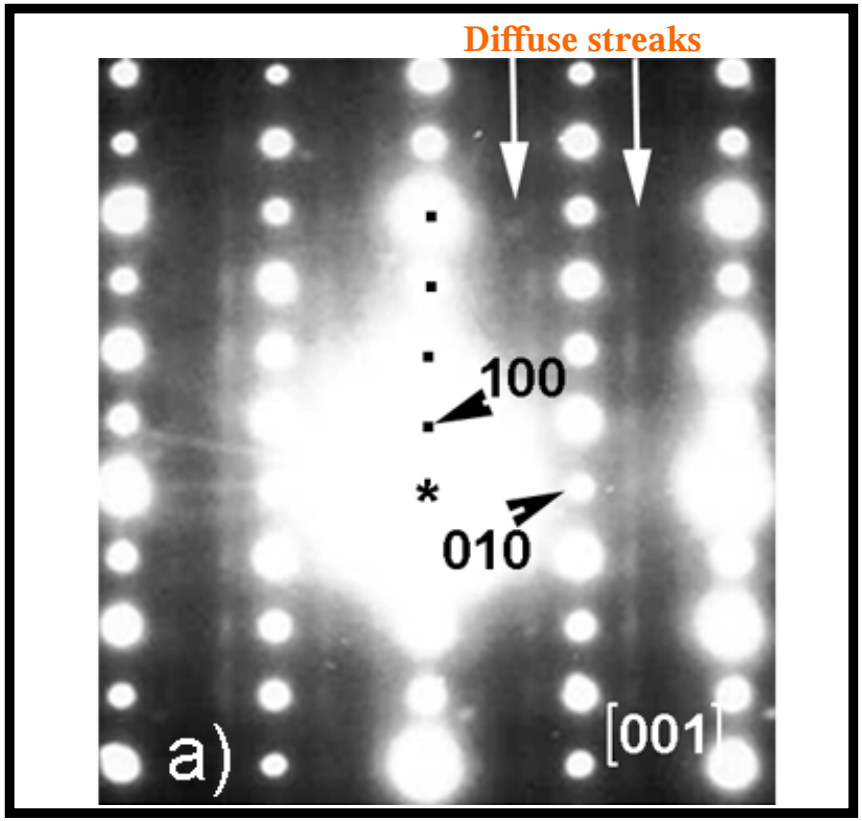


Table 3. Summary of the Different Associations of Ribbons Evidenced Is This Work

type of intergrowth	ribbon 1	ribbon 2	sequence	general formula
12,11 c~ 59Å - acentric,	$Bi_{22}M'_6(Bi,M)_4O_{30}$	$Bi_{20}M'_6(Bi,M)_4O_{28}$	(12)ttt/(11)tttt	$Bi_{42}M'_{12}(Bi,M)_8O_{58}(PO_4)_{30}M_{y<14}$
11,10 c~ 54Å - acentric,	$Bi_{20}M'_6(Bi,M)_4O_{28}$	$Bi_{18}M'_6(Bi,M)_4O_{26}$	(11)tt/(10)/ttt	$Bi_{38}M'_{12}(Bi,M)_8O_{54}(PO_4)_{26}M_{y<10}$
10,6 c~ 41Å - centro	$Bi_{18}M'_6(Bi,M)_4O_{26}$	$Bi_{10}M'_2(Bi,M)_4O_{14}$	(10)tt/(6)tt	$Bi_{40}M'_{12}(Bi,M)_8O_{56}(PO_4)_{24}M_{y<8}$
8,8 c~ 41Å - acentric,	$Bi_{14}(Bi,M)_4M'_4O_{20}$	$Bi_{14}(Bi,M)_4M'_4O_{20}$	(8)tt/(8)tt	$Bi_{28}M'_8(Bi,M)_8O_{40}(PO_4)_{20}M_{y<8}$
9,10 c~ 48Å - acentric,	$Bi_{16}(Bi,M)_4M'_4O_{22}$	$Bi_{18}M'_6(Bi,M)_4O_{26}$	(9)tt/(10)ttt	$Bi_{34}M'_{10}(Bi,M)_8O_{48}(PO_4)_{24}M_{y<10}$
11,11 c~ 57Å - acentric,	$Bi_{20}M'_6(Bi,M)_4O_{28}$	$Bi_{20}M'_6(Bi,M)_4O_{28}$	(11)ttt/(11)ttt	$Bi_{40}M'_{12}(Bi,M)_8O_{56}(PO_4)_{28}M_{y<12}$
9,8 c~ 43Å - acentric,	$Bi_{16}(Bi,M)_4M'_4O_{22}$	$Bi_{14}(Bi,M)_4M'_4O_{20}$	(9)tt/(8)ttt	$Bi_{30}M'_8(Bi,M)_8O_{42}(PO_4)_{20}M_{y<10}$



Désordre ???

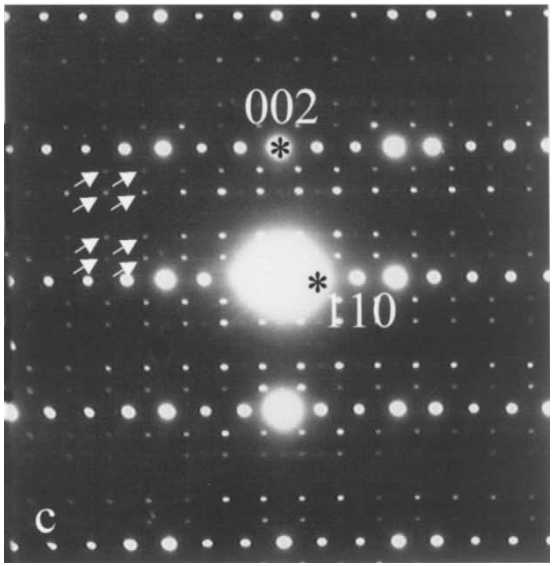


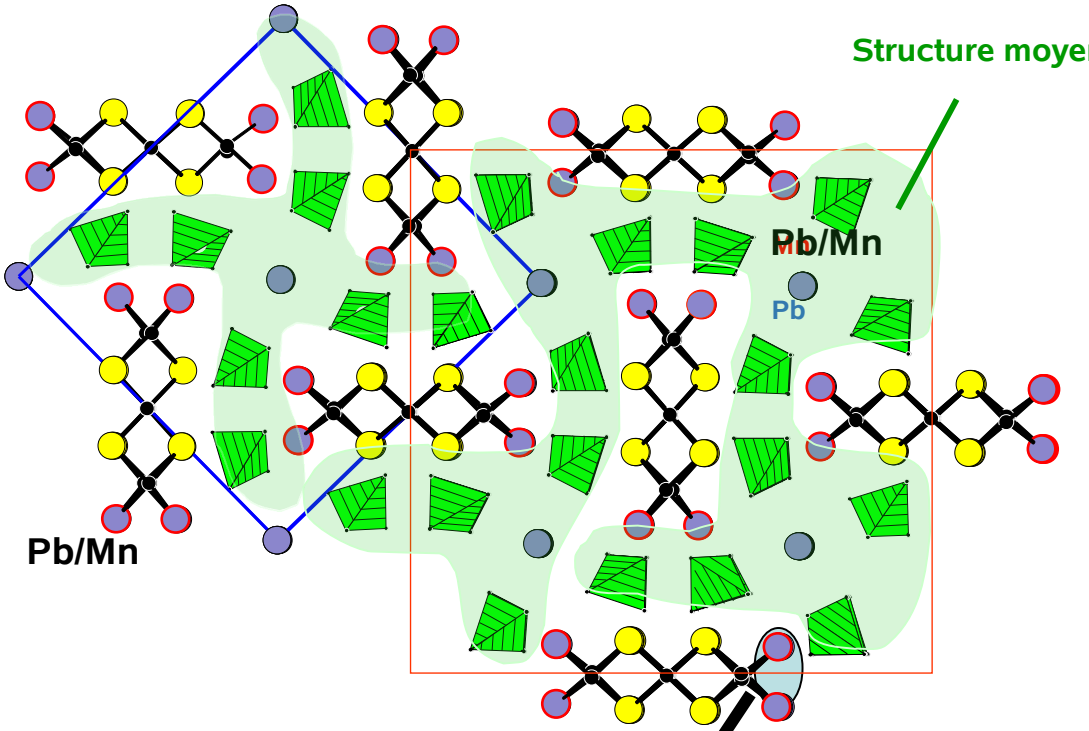
satellite spots

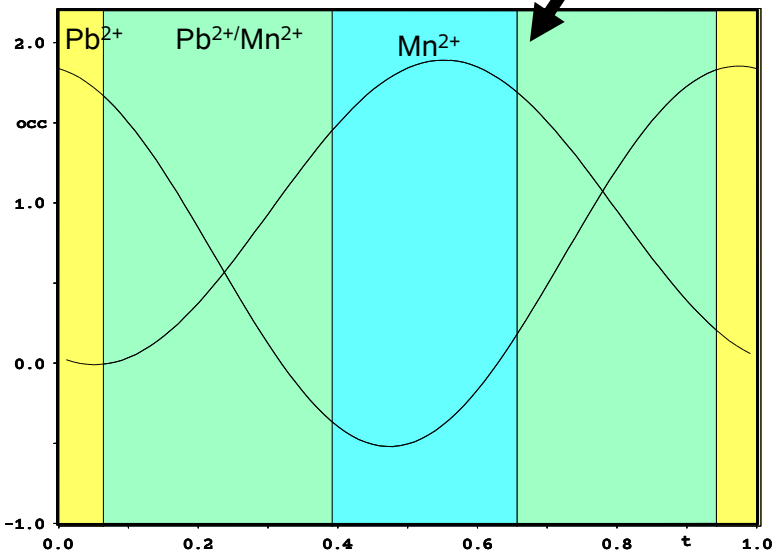
Satellites de modulation … en général perdu à l'échelle du monocristal

$Bi_2Pb_{1.05}Mn_{1.55}O_3(PO_4)_2$

modulé, q = (1/2, 0.304, 1/2)







Approche modulée

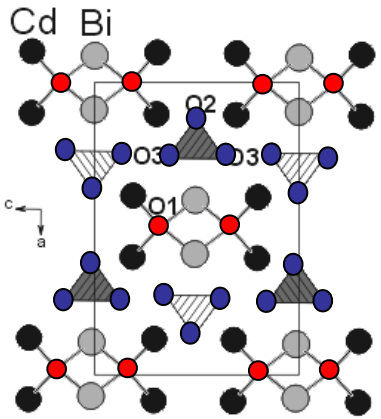
S.S.G. XCC2(00g)s0s
R_{fund} = 0.0456 et $R_{satellite}$ = 0.127

edges ribbons : Pb/M ordering along x_4

channels : Pb/M partial ordering along x_4

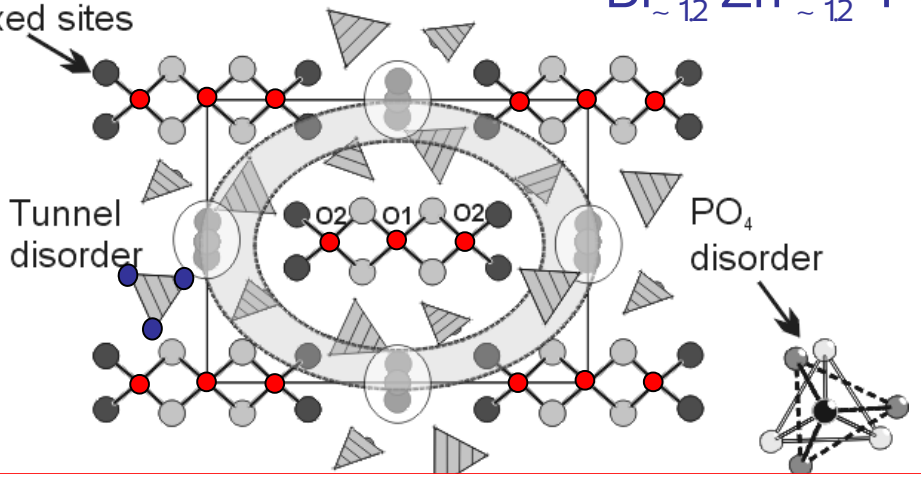
PO_4 configurations : mainly disordered

$BiCd_2PO_6$



Bi^{3+}/Zn^{2+} mixed sites

$Bi_{\sim 1.2}Zn_{\sim 1.2}PO_5$



LETTER www.rsc.org/njc | New Journal of Chemistry

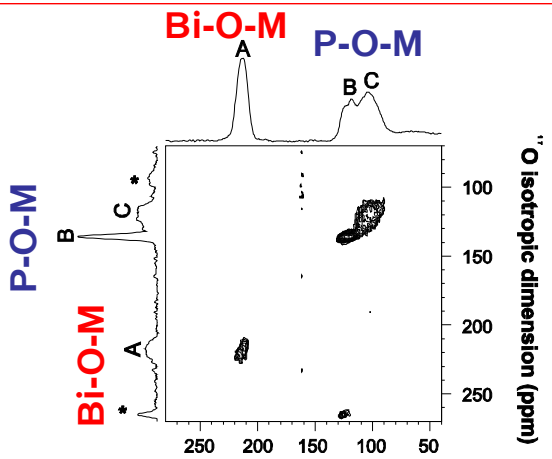
Evidence of crystalline/glassy intermediates in bismuth phosphates

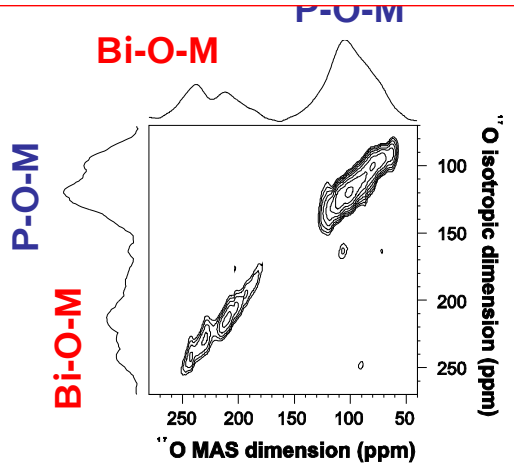
Marie Colmont,* Laurent Delevoye and Olivier Mentré

Received (in Montpellier, France) 3rd September 2008, Accepted 27th October 2008
First published as an Advance Article on the web 14th November 2008
DOI: 10.1039/b815388b

a

MQMAS- 18.8 T -





M. Colmont, L. Delevoye, O. Mentré, New J. Chem. (2008)

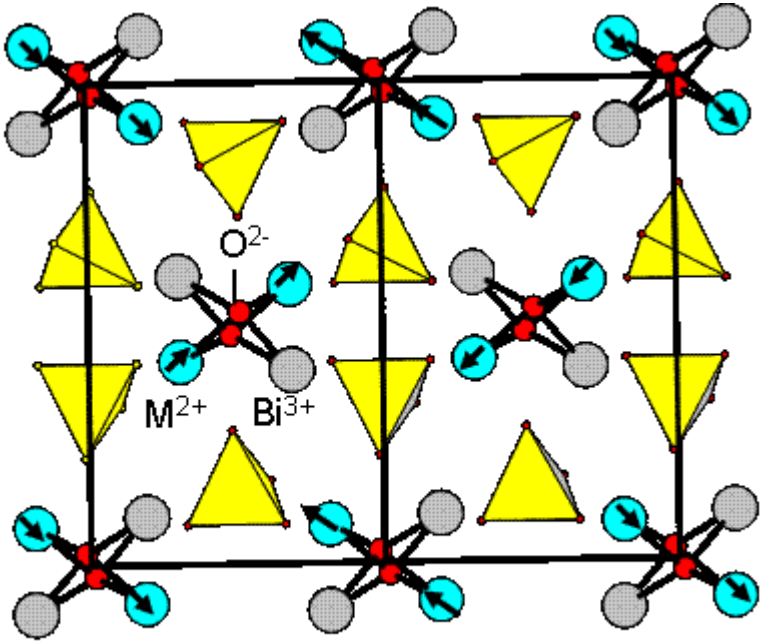
Propriétés magnétiques :

Structures complexes (Bi/M/O)

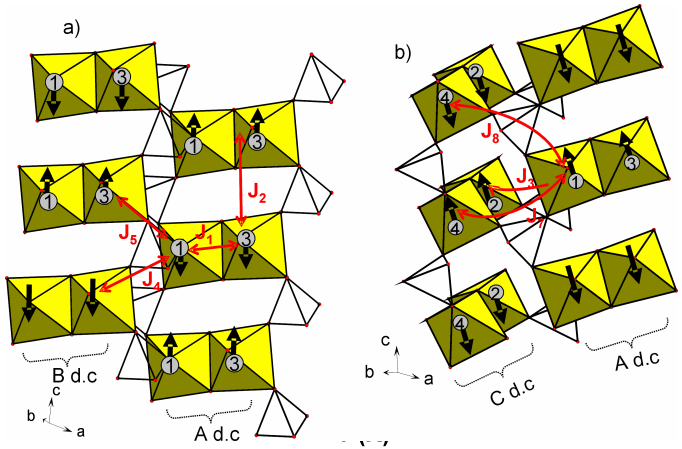
→ topologies particulières des cations paramagnetiques

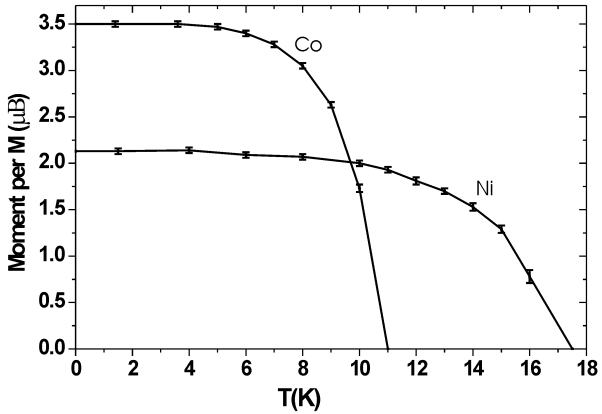
→ flexibilité structurale (substitution facile Cu^{2+} , Ni^{2+} , Co^{2+} , Zn^{2+} , Ca^{2+} , Mg^{2+} …)

n=1



$BiMPO_5$ M = Ni^{2+} , Co^{2+}

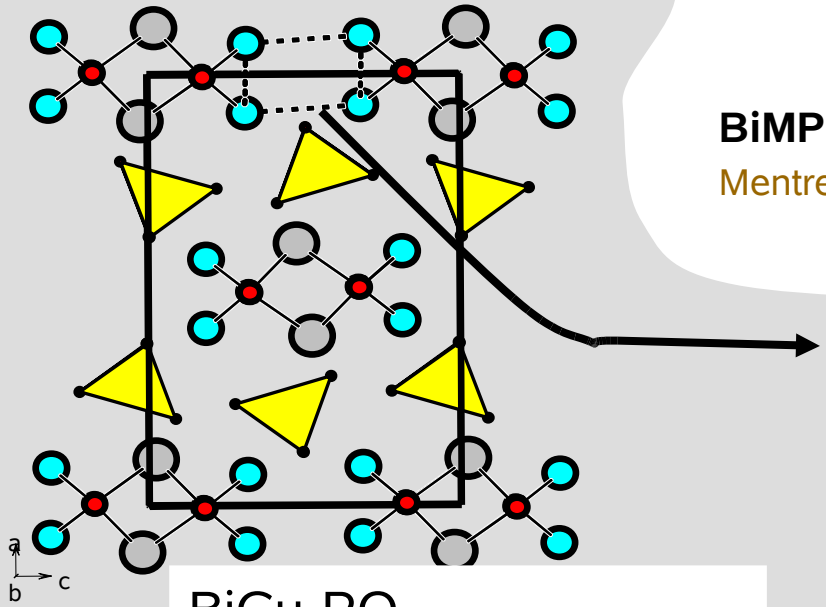




$BiMPO_5$ (M=Co, Ni) : AF ordering of F dimers

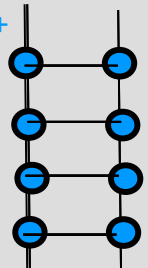
Mentre, Bourree, Carjaval, J. Phys. Cond Mater. 20, 2008, 415211

n=2



$BiCu_2PO_6$

Cu^{2+}

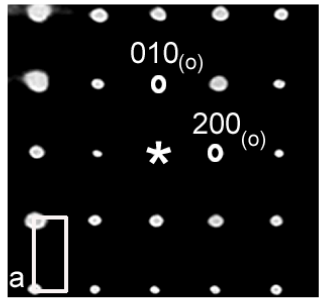


$BiCu_2PO_6$:
S=1/2 two-leg ladder

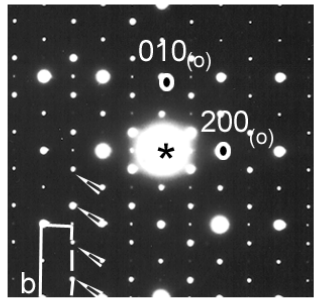
Modulation dans $BiCu_2P_{1-x}V_xO_6$: effets de taille des XO_4

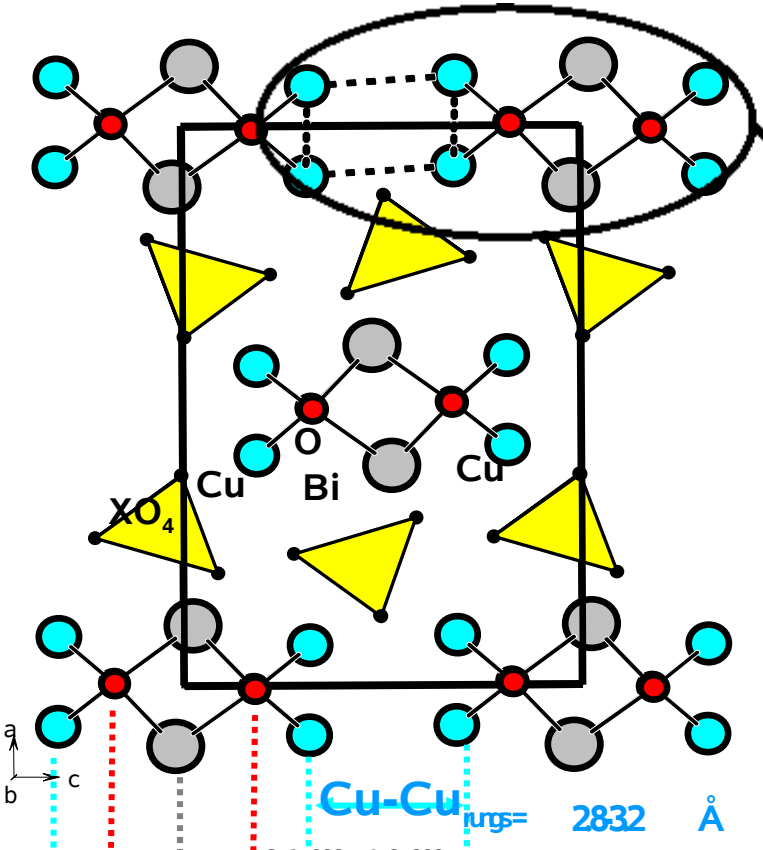
O. Mentré, M. Ketatni, M. Colmont, M. Huvé, F. Abraham, V. Petricek, *JACS*, **33**,128 (2006).

X = 0 – 0.7 : structure moyenne, S.G. Bbmm
Gap de spin

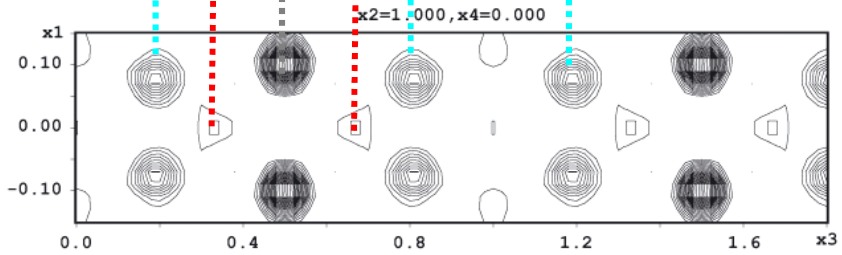


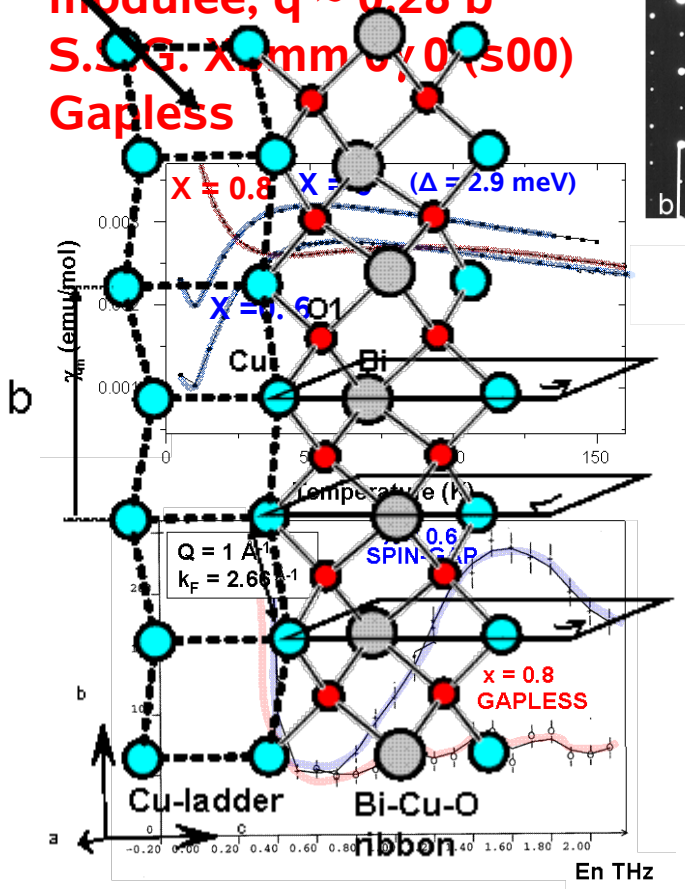
X = 0.7 – 0.9 : structure modulée, q ~ 0.28 b*
S.G. X2mm 0, 0, (s00)
Gapless





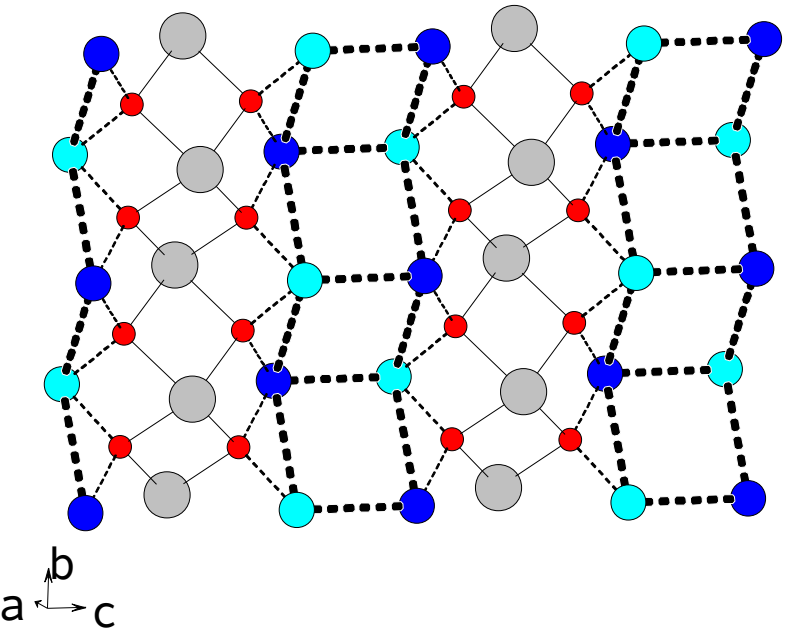
Cu-Cu$_{\text{rungs}}$ = 2.832 Å

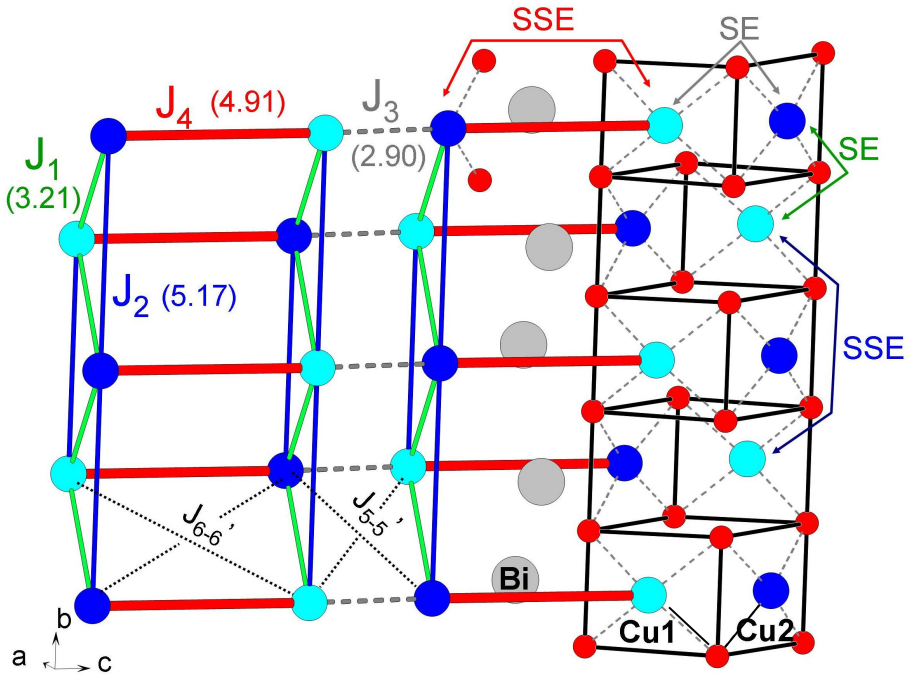




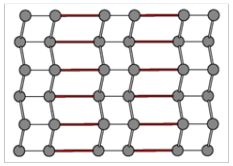
gap

gapless

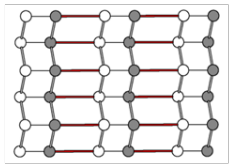

b
a
c


SSE
SE
J4 (4.91)
J3
(2.90)
J1
(3.21)
SE
J2 (5.17)
SSE
J6-6'
J5-5'
Bi
Cu1
Cu2
b
a
c

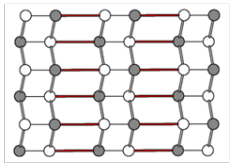
Cu1-O-Cu2 = 92°



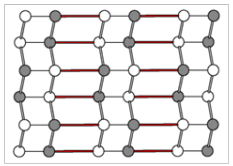
FM (0, 0, 0)



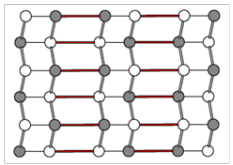
AF1 (-115.7, -74.3, -44.2)



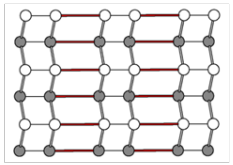
AF2 (-231.1, -157.8, -102.1)



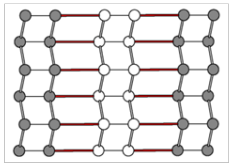
AF3 (-259.4, -180.8, -118.7)



AF4 (-166.0, -113.2, -72.9)

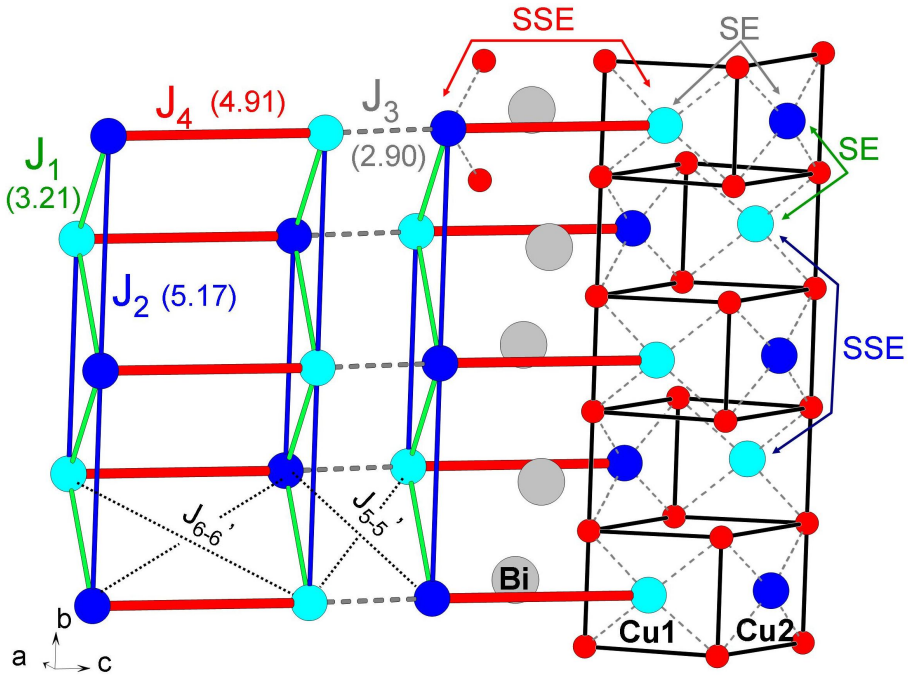


AF5 (-139.5, -84.5, -57.1)



AF6 (-89.9, -45.1, -28.2)

$E(FM) = (-8J_1 - 8J_2 - 4J_3 - 4J_4 - 8J_5 - 8J_6)N^2/4$
$E(AF1) = (-8J_1 - 8J_2 + 4J_3 + 4J_4 + 8J_5 + 8J_6)N^2/4$
$E(AF2) = (+8J_1 - 8J_2 + 4J_3 + 4J_4 - 8J_5 - 8J_6)N^2/4$
$E(AF3) = (+ 8J_2 + 4J_3 + 4J_4)N^2/4$
$E(AF4) = (+8J_1 - 8J_2 + 4J_3 - 4J_4 - 8J_5 + 8J_6)N^2/4$
$E(AF5) = (+8J_1 - 8J_2 - 4J_3 - 4J_4 + 8J_5 + 8J_6)N^2/4$
$E(AF6) = (-8J_1 - 8J_2 - 4J_3 + 4J_4 - 8J_5 + 8J_6)N^2/4$



Cu1-O-Cu2 = 92°

GGA + U

→ Échelle frustrée J1/J4

→ Frustration J2/J1 = 0.7-0.8

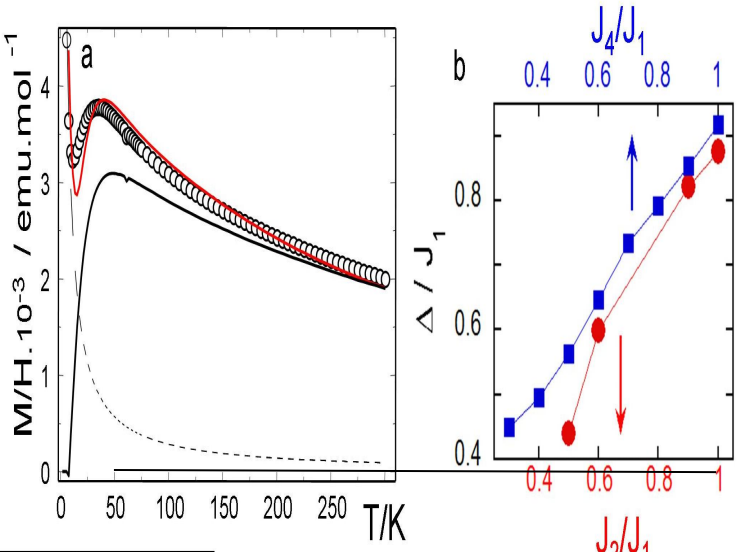
→J3 non dominant

	U = 4 eV	U = 6 eV	U = 8 eV	Phys. Rev. B **76**, 052402, (2007)
J_1	**31.87 (0.82)**	**21.01 (0.94)**	**14.37 (1.00)**	**(1.00)**
J_2	**21.49 (0.55)**	**16.20 (0.72)**	**11.40 (0.79)**	**(0.34)**
J_3	13.06 (0.34)	14.47 (0.64)	7.98 (0.56)	(1.00)
J_4	**38.76 (1.00)**	**22.43 (1.00)**	**14.34 (1.00)**	**(0.74)**
J_5	-0.08 (0.00)	0.06 (0.00)	0.02 (0.00)	(0.04)
J_6	3.10 (0.08)	0.07 (0.00)	-0.13 (-0.01)	(0.03)

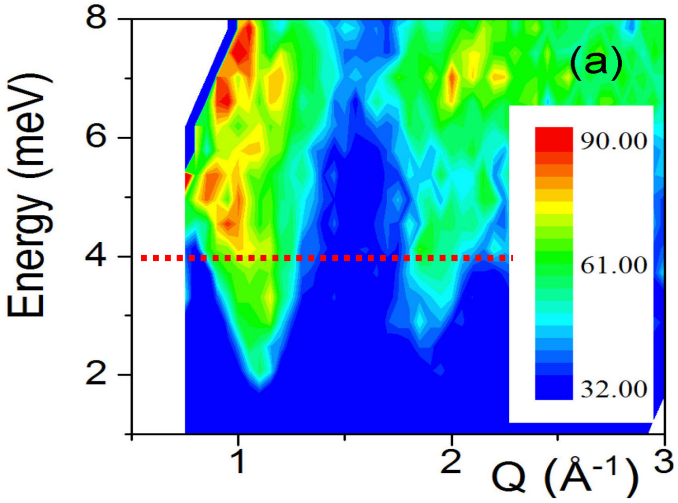
Fit de la susceptibilité

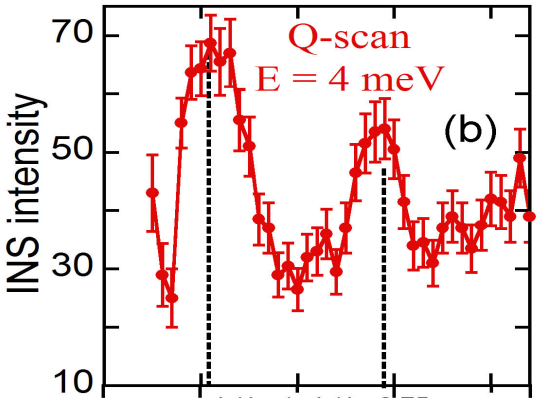
$$\hat{H}_{ex} = \sum_{i,j=1}^{N} J_{ij}\hat{S}_i \cdot \hat{S}_j + g\mu_B \sum_{i=1}^{N} \hat{S}_i \cdot \vec{H}$$

avec $= J_1, J_2, J_4$ *et cluster 12 spins*

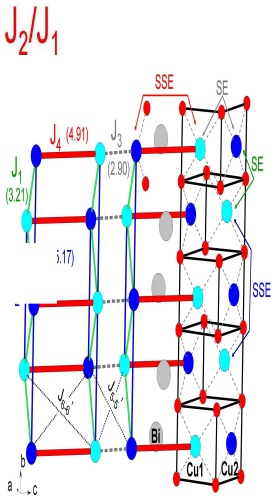


Diffusion des neutrons (LLB)





Δ = 4 meV



Frustration $\alpha > \alpha_c$: Lifshitz point

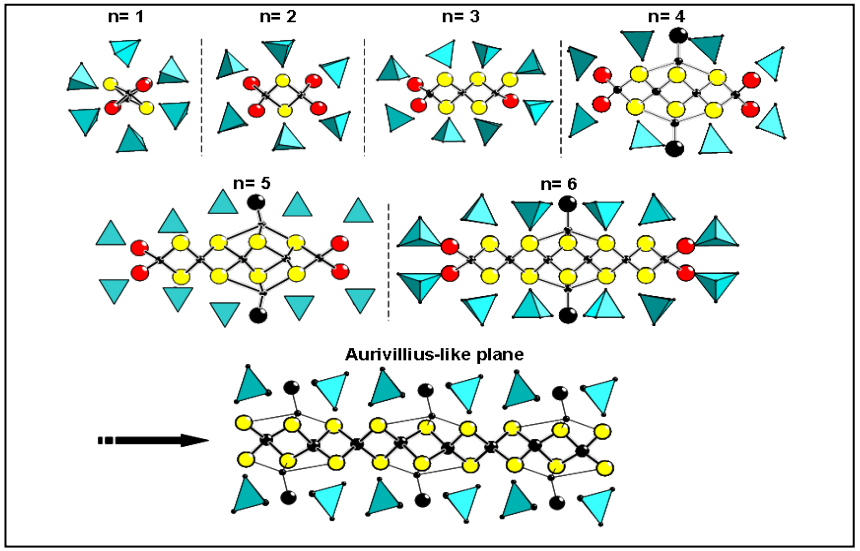
Split de S(Q) → incommensurable

O. Mentré, E. Janod, P. Rabu, M. Whangbo, S. Petit, PRB-rapid comm. 2009

Conclusion : Rich systems, building units and intergrowths

unlimited number of new intergrowths (→ non-centro)

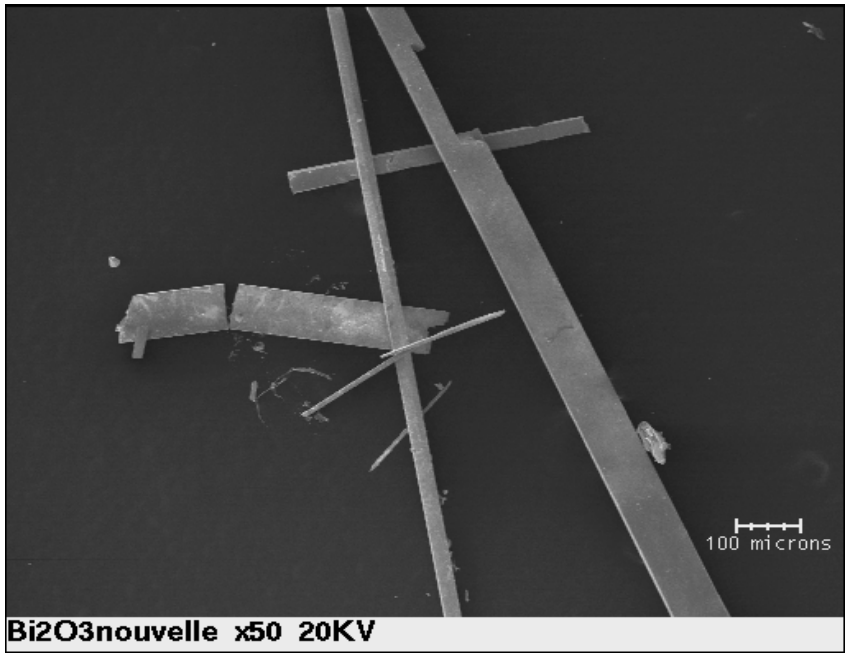
Towards new properties

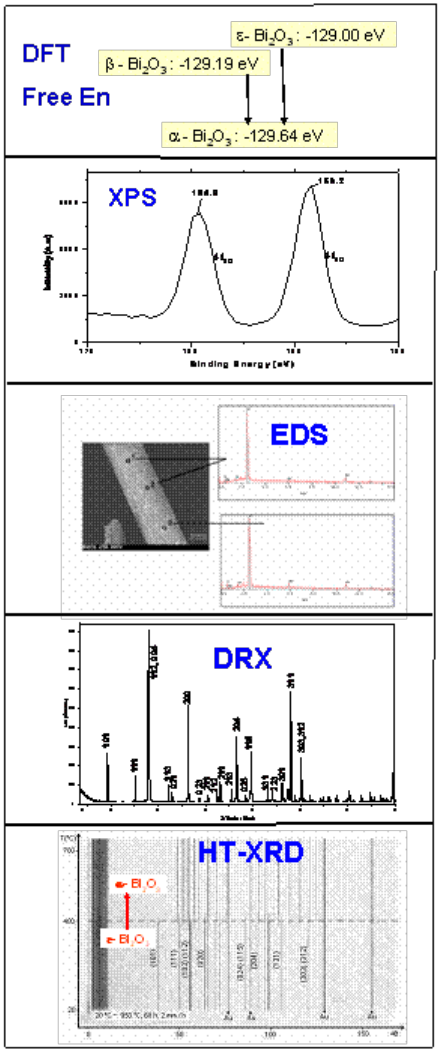


ε -Bi_2O_3 Synthesis, characterization

-Autogeneous pressure, KOH solution

→ new metastable Bi_2O_3 polymorph

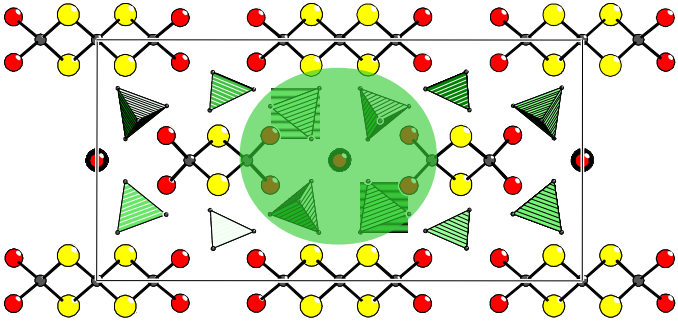


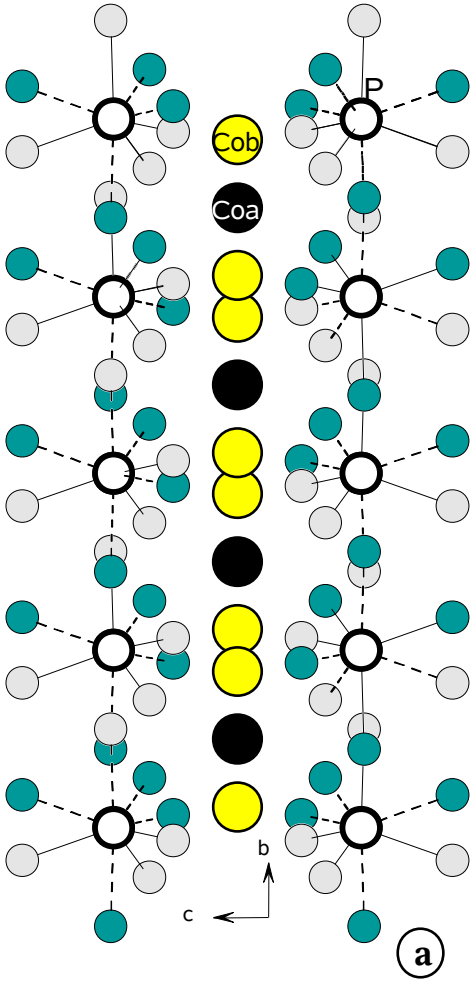


N. Cornei, N. Tancret, F. Abraham, O. Mentré, *Inorg. Chem.* **45**, (2006), 4886

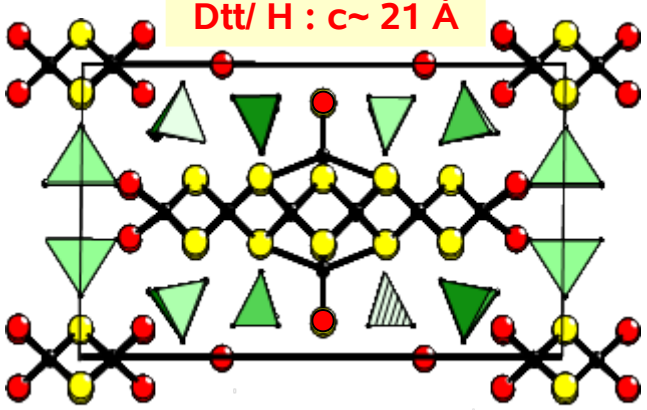
general cases : ordered fragments

+ local XO_4 ordering

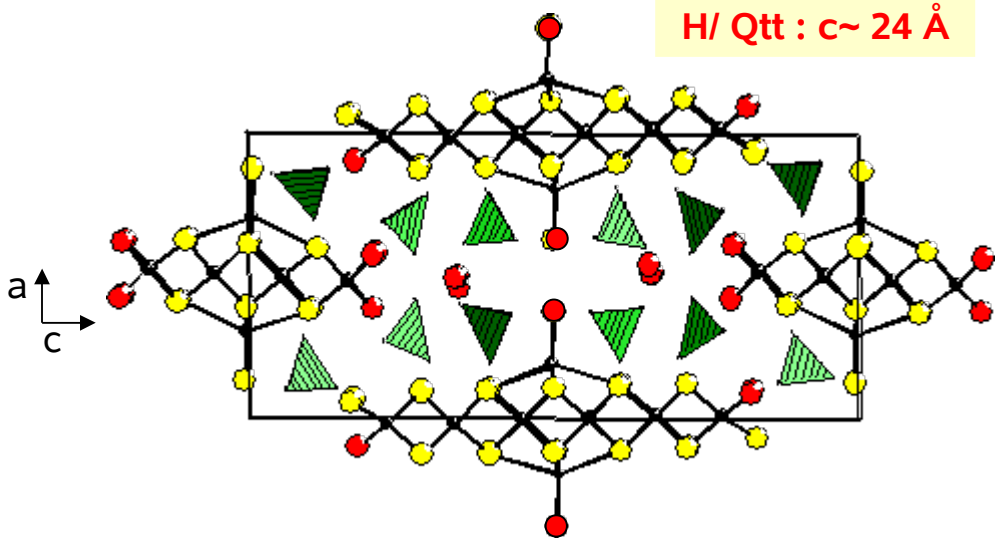




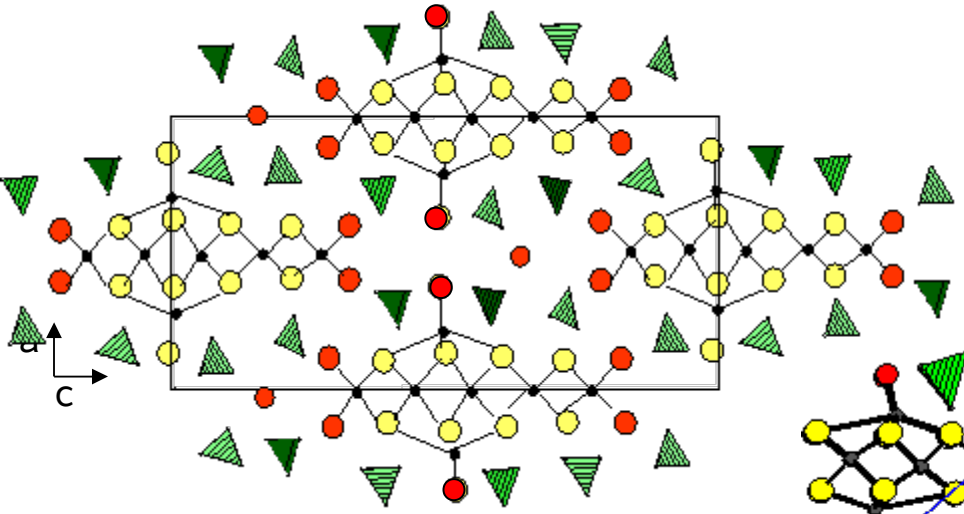
Dtt/ H : c~ 21 Å



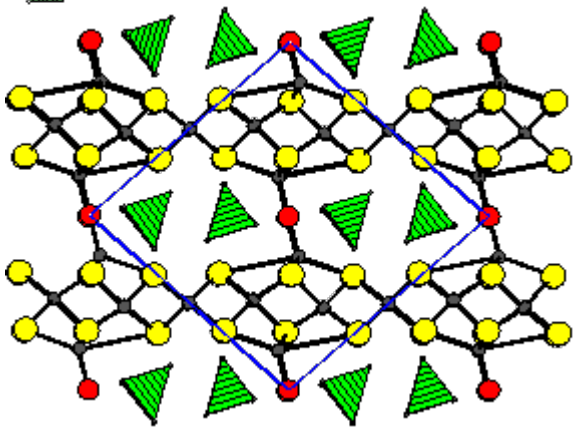
H/ Qtt : c~ 24 Å



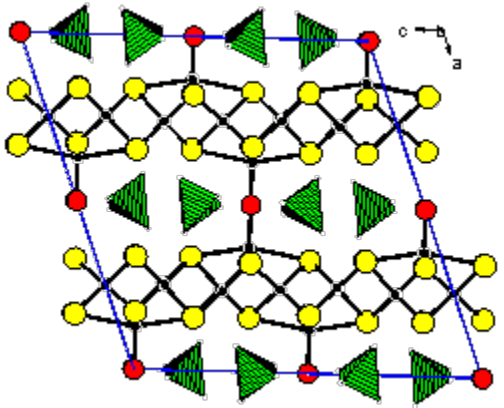
tP/ Pt : c~ 25 Å



Two polymorphs for infinite planes



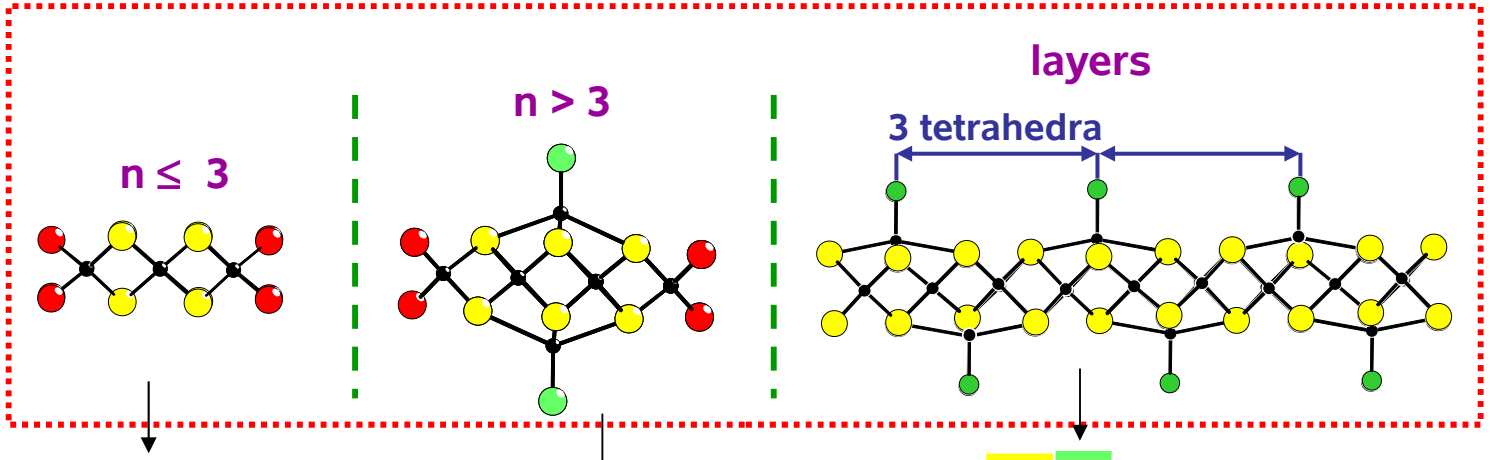
Steinfink, Lynch, JSSC, 177, 1412 (2004)



Colmont, Huvé, Ketatni, Mentré, Solid State Sciences, online (2008)

Part. 1 : M. Huvé, M. Colmont , O. mentré, *Inorg. Chem*, 45, 6604, (2006)

Part. 2 : M. Colmont, M. Huvé, O. Mentré, *Inorg. Chem*, 45,6612, (2006).



$[(M/Bi)_4Bi_{2n-2}O_{2n}]^{n+}$

n PO_4: 2n+2

$[Bi_3MO_3]^{n+}$; 2 PO_4

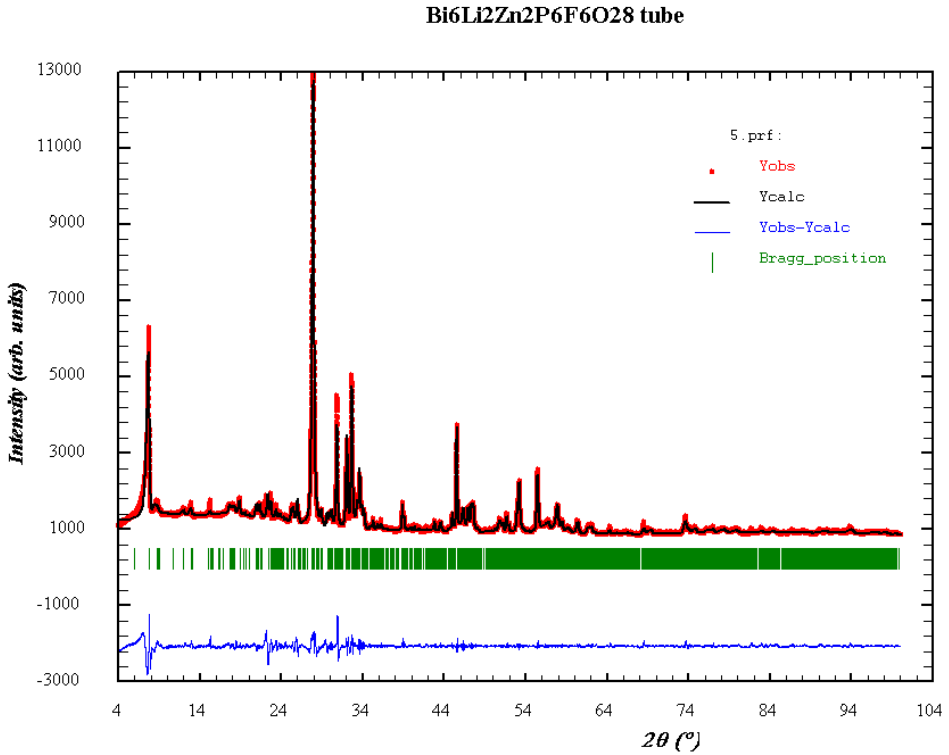
$[(M/Bi)_4Bi_{2n-2}M'_{2int[(n-1)/3]}O_{2n+2int[(n-1)/3]}]^{n+}$

n PO_4: 2[(n+1)-(int(n-1)/3))]

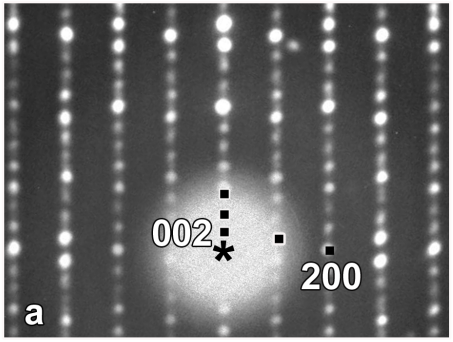
Highlight : $n_{tetrahedra} \neq 3n$: non-centrosymmetric buliding units !!!

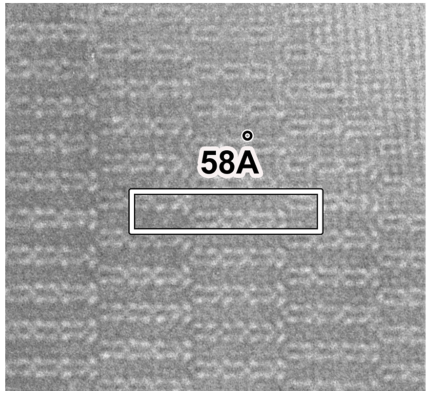
sample $Bi_6LiZn_2P_4O_{22}$

M. Colmont, M. Huve, O. Mentre, JACS, subm.2008



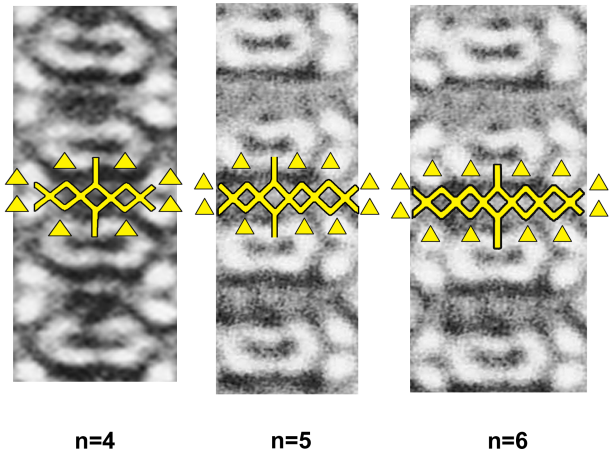
Most of the crystallite

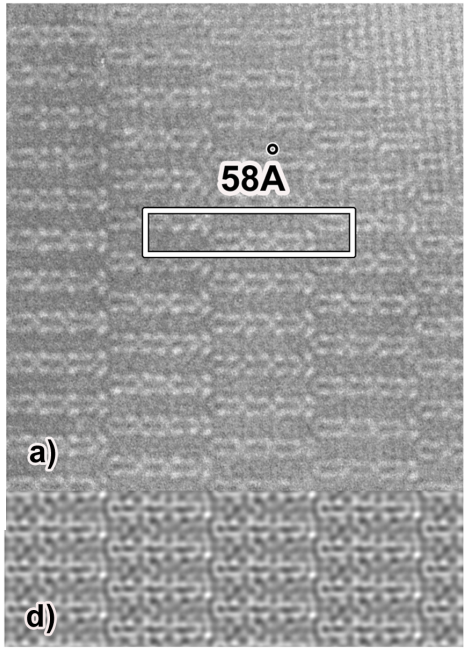




a= 11.5826(3), b= 5.4736(2), c= 58.9041(19)Å and β= 90.55(1)°

Starting contrasts

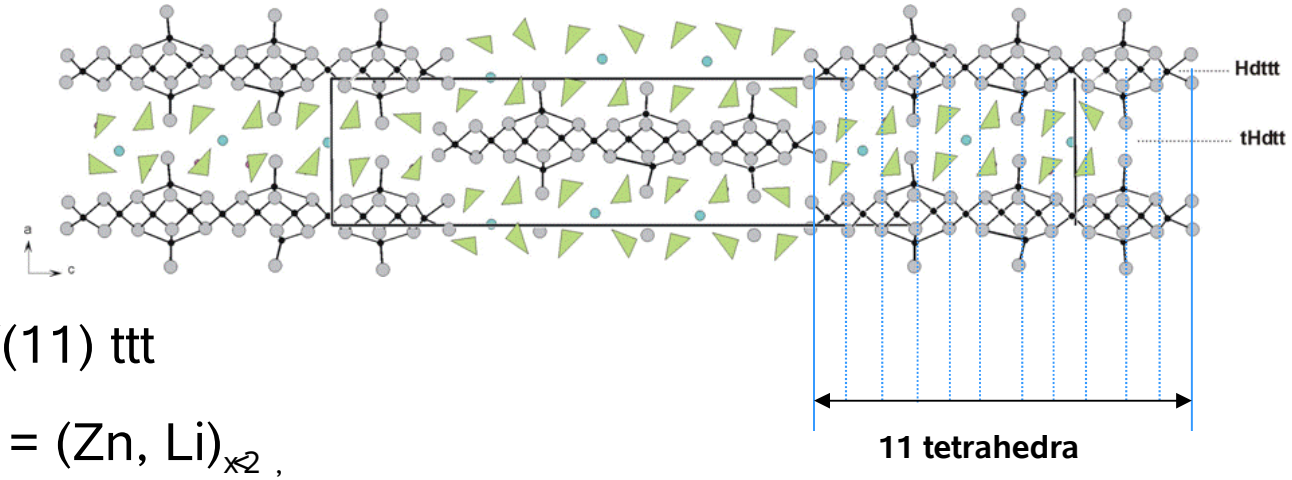




XRD Single crystal

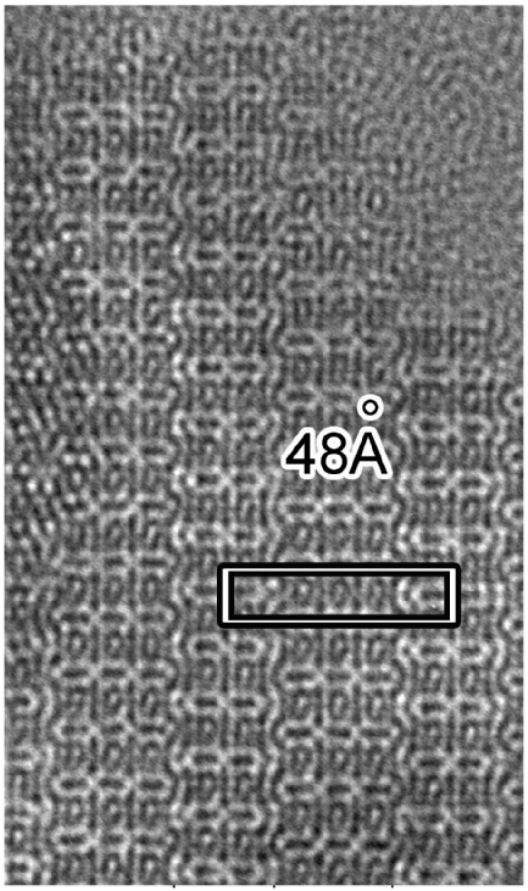
$Bi_{5.68}\ Zn_{0.48}\ Li_{0.36}\ (PO_4)_2\ O_{5.5}$.

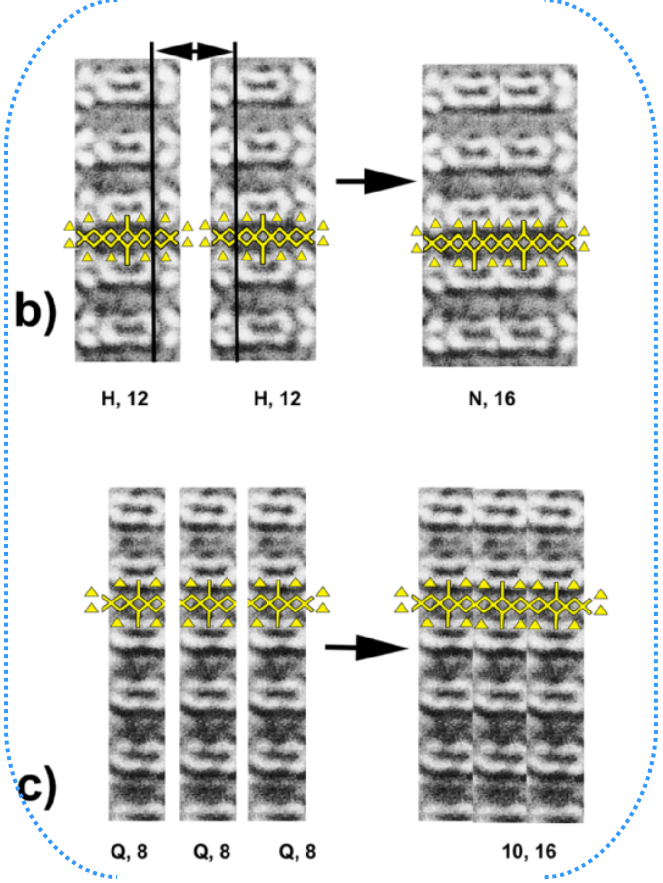
R_1 = 8.7%, wR_2 = 10.34%

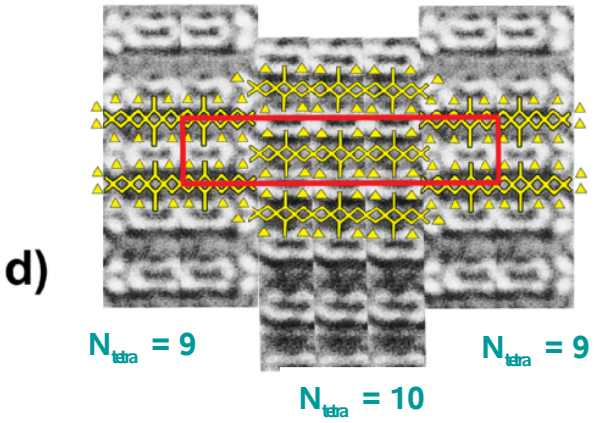


intergrowth type : (11) ttt/(11) ttt

(11) = $Bi_2\ (Bi,Zn)_4Bi_6O_{2.8}$, t = $(Zn, Li)_{x<2}$,



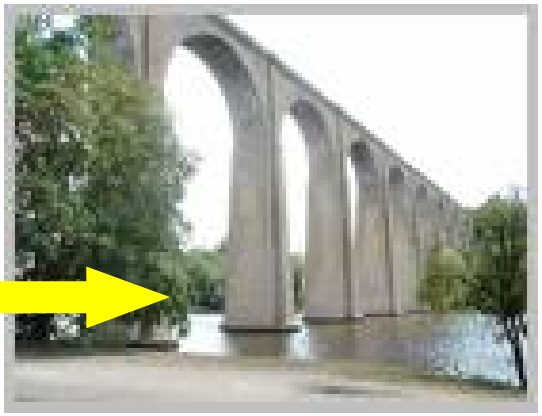




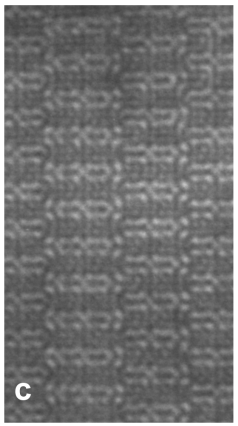
intergrowth type :

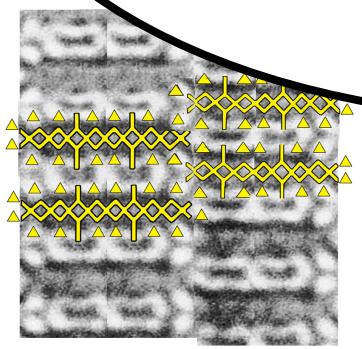
(9) tt/(10) ttt

N size intergrowth	Ribbon1	Ribbon2	Sequence	General formula
12,11	$Bi_{22}M'_6(Bi,M)_4O_{30}$	$Bi_{20}M'_6(Bi,M)_4O_{28}$	(12)tt/(11)ttt	$Bi_{42}M'_{12}(Bi,M)_8O_{58}(PO_4)_{30}M_{y<14}$
11,10	$Bi_{20}M'_6(Bi,M)_4O_{28}$	$Bi_{18}M'_6(Bi,M)_4O_{26}$	(11)ttt/(10)/tt	$Bi_{38}M'_{12}(Bi,M)_8O_{54}(PO_4)_{26}M_{y<10}$
10,6	$Bi_{18}M'_6(Bi,M)_4O_{26}$	$Bi_{10}M'_2(Bi,M)_4O_{14}$	(10)tt/(6)t	$Bi_{40}M'_{12}(Bi,M)_8O_{56}(PO_4)_{24}M_{y<6}$
8,8	$Bi_{14}(Bi,M)_4M'_4O$			$O_{40}(PO_4)_{20}M_{y<8}$
9,10	$Bi_{16}($			<10
11,11				
9,8				



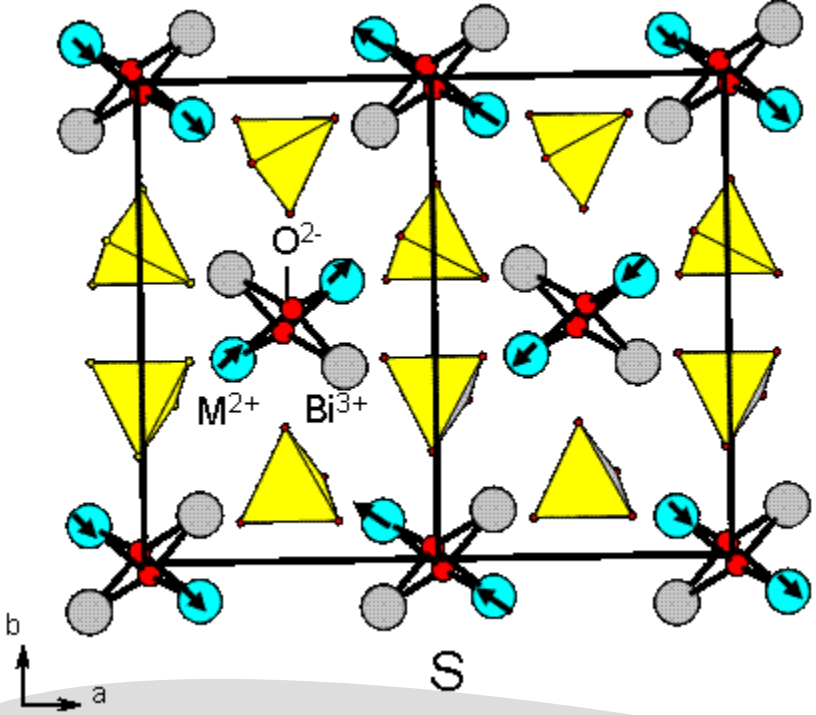
N_{tetra}

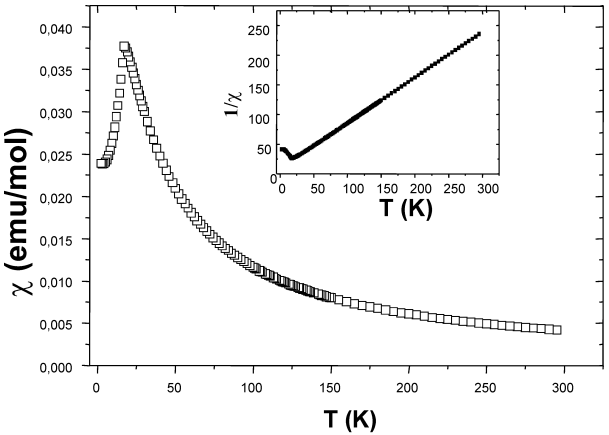


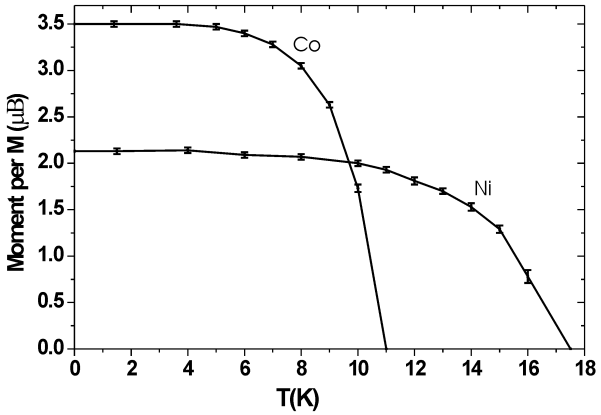


...

N_{tetra} =9 N_{tetra} =8

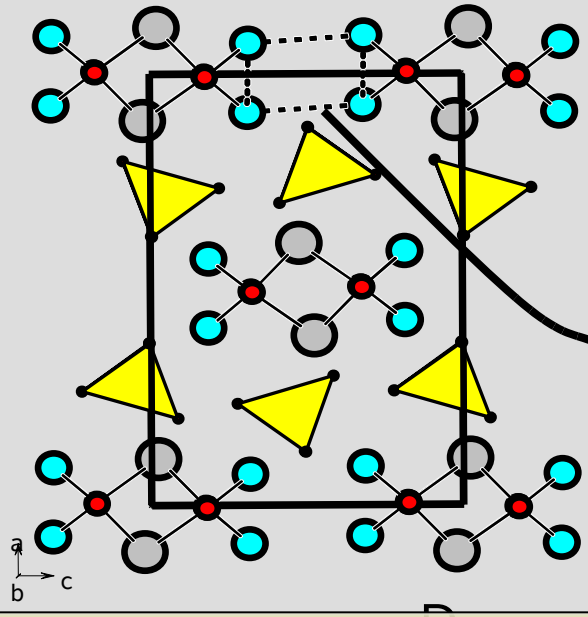


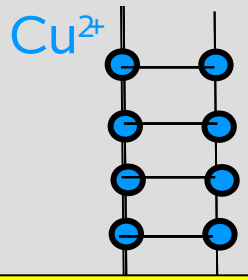




$BiMPO_5$ (M=Co, Ni) : AF ordering of F dimers

O.Mentre, Bourree, Carjaval, J. Phys. Cond Mater. 20, 2008, 415211



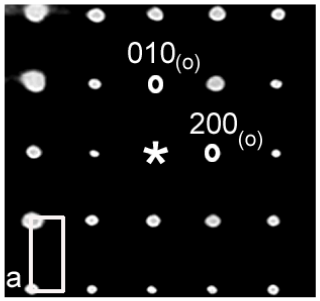


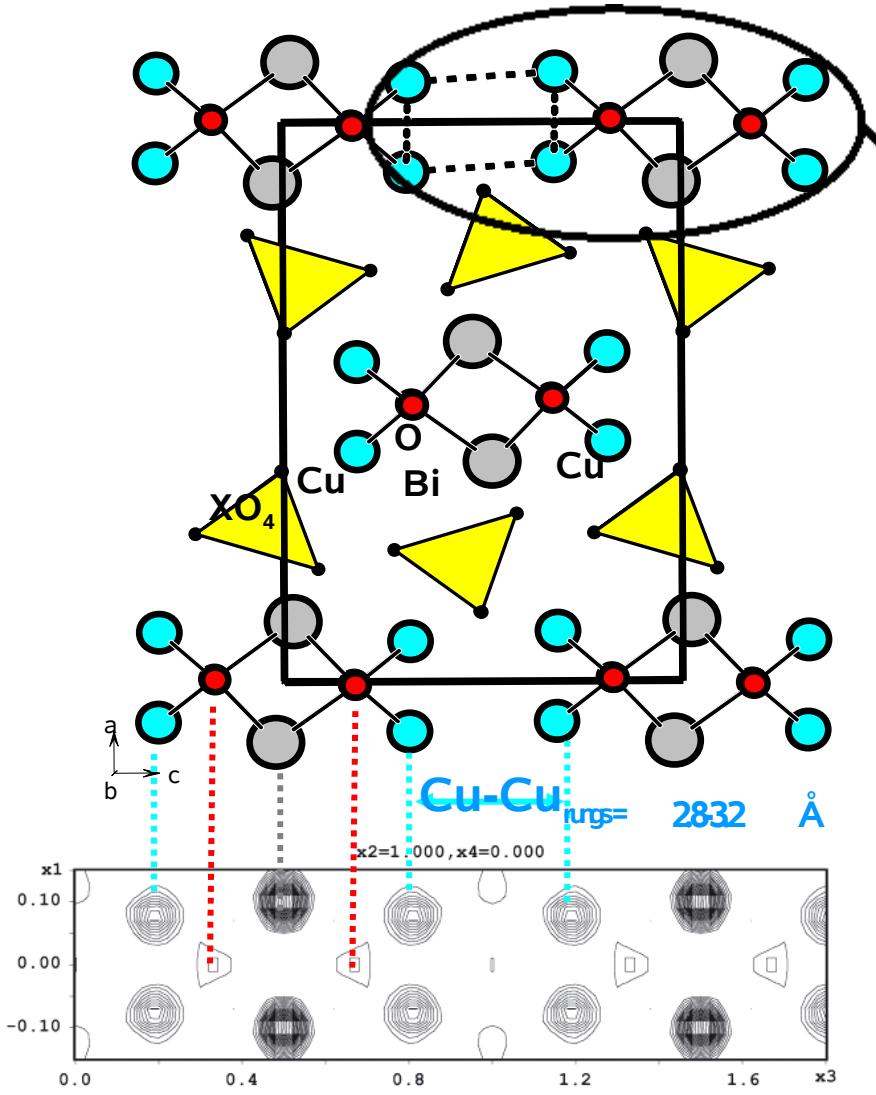
$BiCu_2PO_6$:
S=1/2 two-leg ladder

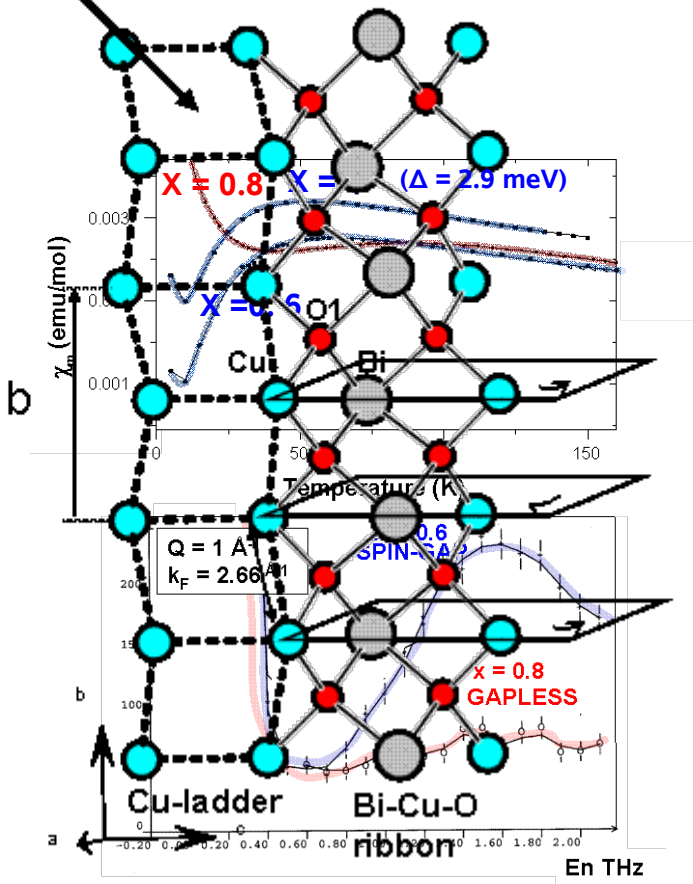
Modulation of the ribbons
$BiCu_2P_{1-x}V_xO_6$: effects of the XO_4 size

O. Mentré, M. Ketatni, M. Colmont, M. Huvé, F. Abraham, V. Petricek, *JACS*, **33**,128 (2006).

X = 0 – 0.7 : average structure, S.G. Bbmm
SpinGap

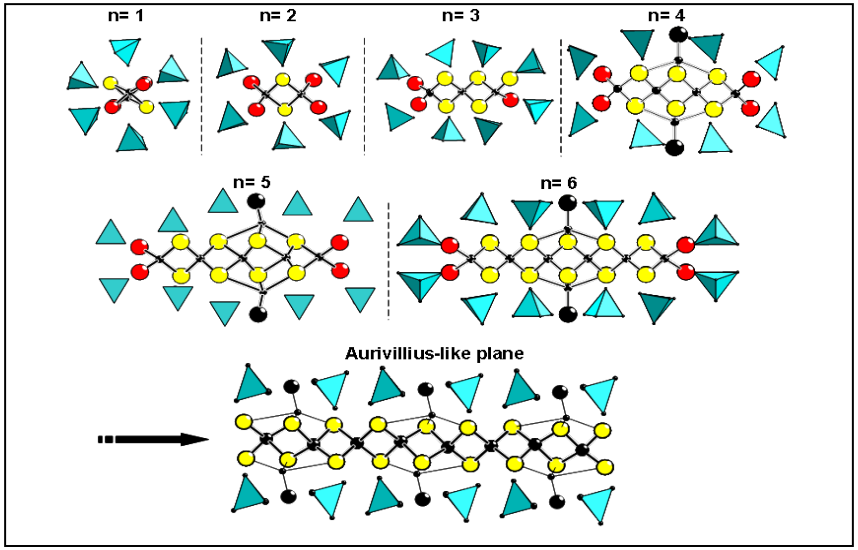






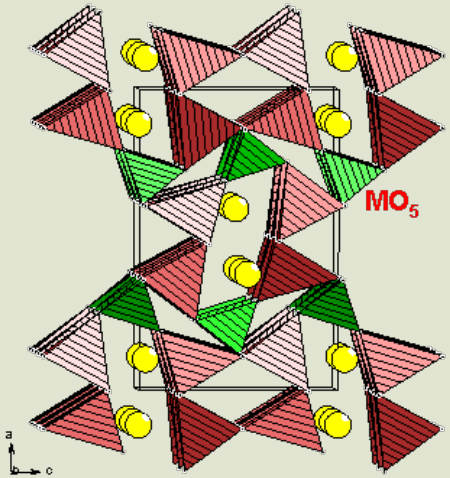
Conclusion : Rich system, buiding units and intergrowths

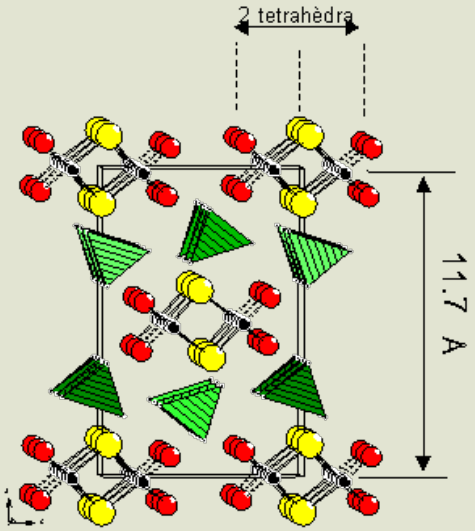
infinite number of new intergrowths (→ non-centro)



Advice (anti-structure)

MO_x contre OM_z





→ 2 complementary views of the same system

… make sure to check both !!!

Chimie Lille
ÉCOLE NATIONALE SUPÉRIEURE DE CHIMIE
USTL Lille 1
UCCS
U.M.R. CNRS 8181
Unité de Catalyse et de Chimie du Solide - UMR CNRS 8181
ENSCL – Bât. C7 – BP 90108 - 59652 Villeneuve d'Ascq Cedex - France - ☎ +33 (0)3.20.43.65.87
Email : mentre@ensc-lille.fr
CNRS CENTRE NATIONAL DE LA RECHERCHE SCIENTIFIQUE

… collaborators …

Marie Colmont, UCCS, France

Marielle Huvé, UCCS, France

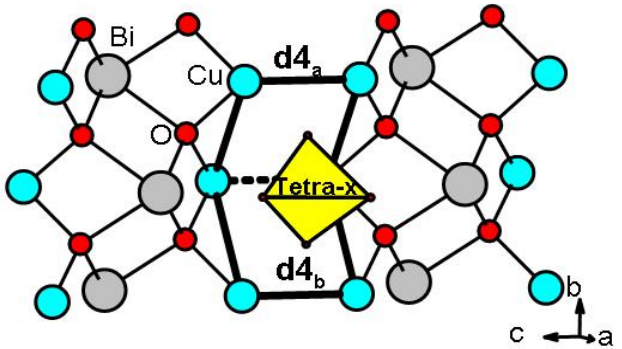
Nicoletta Cornei, Iasi, Romania

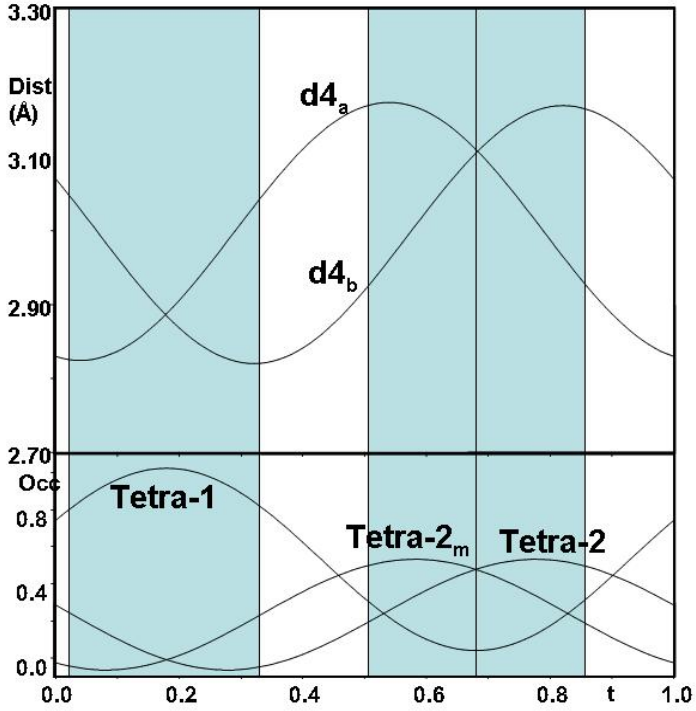
Mostafa Ketatni, Beni-Mellal, Morocco

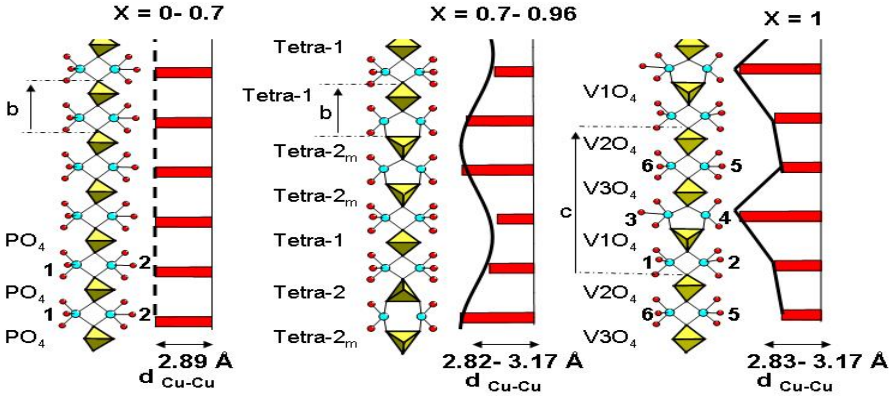
Vacek Petricek, Praha, Czech Republic

Francis Abraham, UCCS, France

F. Bouree, J.R. Carvajal, LLB-IMN

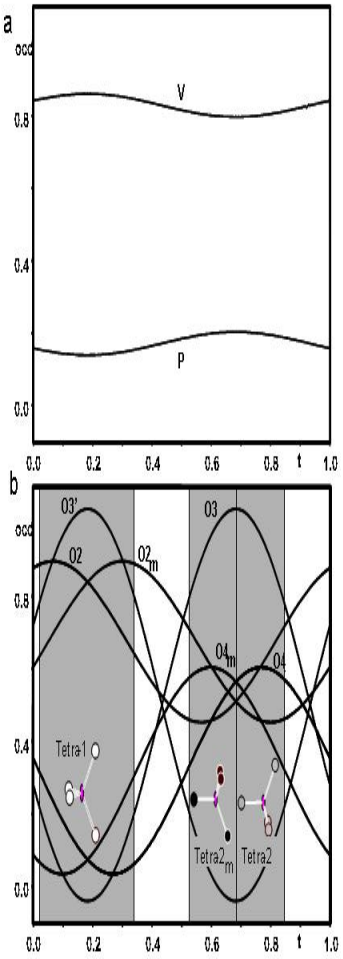

Bi
Cu
O
d4a
Tetra-x
d4b
b
c
a

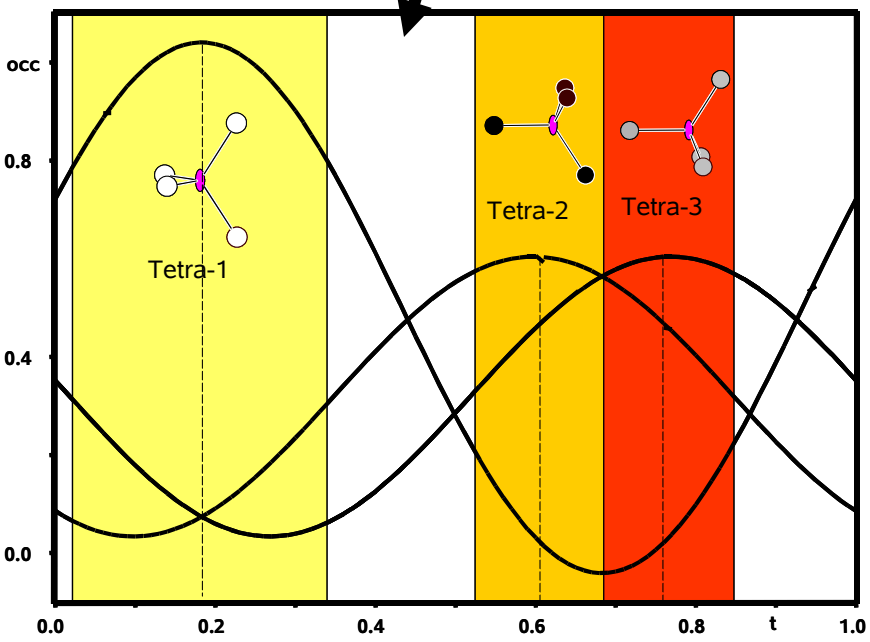

3.30
Dist
(Å)
3.10
2.90
2.70
d4a
d4b
Occ
0.8
0.4
0.0
Tetra-1
Tetra-2m
Tetra-2
0.0
0.2
0.4
0.6
0.8
t
1.0


X = 0- 0.7
b
PO4
1
2
PO4
1
2
PO4
2.89 Å
d Cu-Cu
X = 0.7- 0.96
Tetra-1
Tetra-1
b
Tetra-2m
Tetra-2m
Tetra-1
Tetra-2
Tetra-2m
2.82- 3.17 Å
d Cu-Cu
X = 1
V1O4
V2O4
6
5
V3O4
c
3
4
V1O4
1
2
V2O4
6
5
V3O4
2.83- 3.17 Å
d Cu-Cu

$BiCu_2(V_{1-x}P_x)O_6$; x = 0.13

q = (0, 0.268, 0)





S.S.G. Xbmm(0γ0) s00

R_{fund} = 0.0445et $R_{satellite}$ = 0.066