Synthèse et structure de $BiMO_3$ (M=Mn, Cr) du local au monocristal

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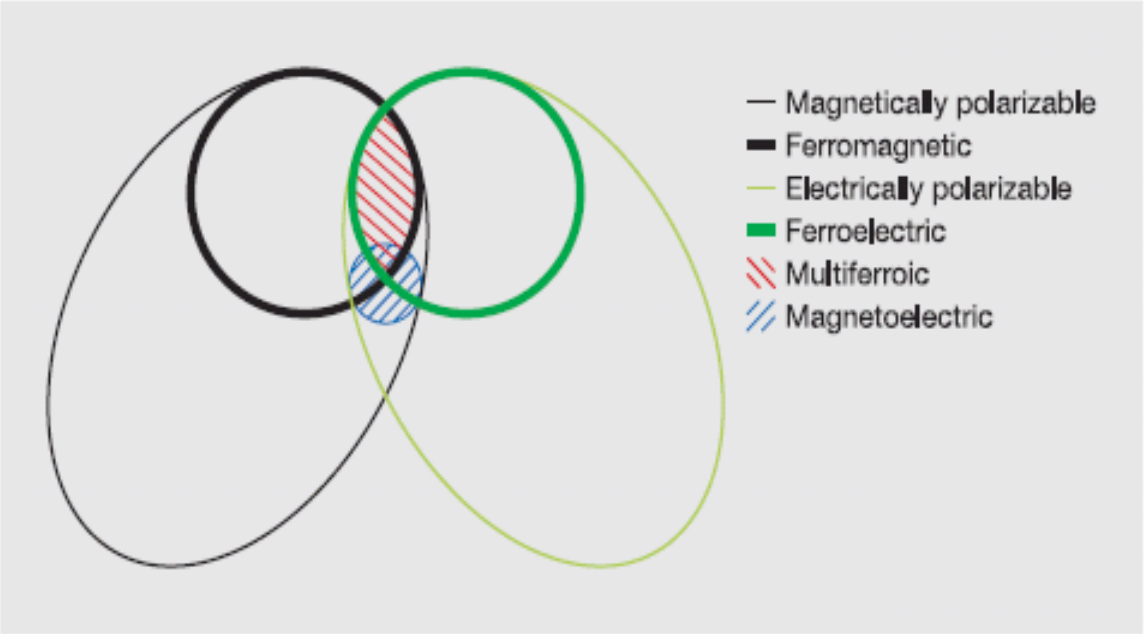
Le Multiferroïsme



✓ *2 ordres "ferroïques":*
ferromagnetique
ferroelectrique
ferroelastique

✓ *Définition + large : coexistence de ferroélectricité et ordre magnétique (antiferro…)*

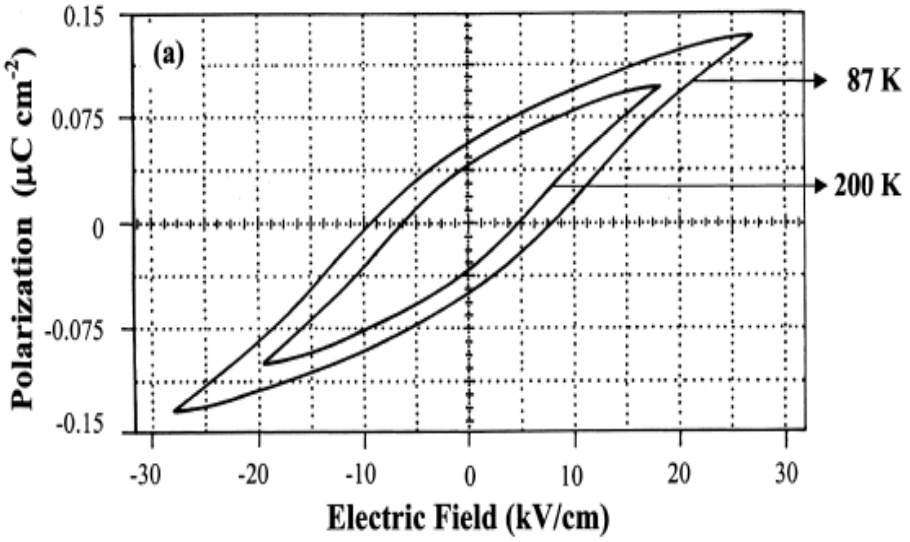
✓ *1ère espèce : ferroélectrique qui s'ordonne magnétiquement*
2ème espèce : l'ordre magnétique induit la ferroélectricité

✓ *applications possibles :*
- *mémoires à 4 états*
- *écriture/lecture électrique/magnétique*
- *piloter une propriété par l'autre…*

Pérovskites multiferroïques de 1ère espèce : $BiMnO_3$: ferromagnétique et ferroelectrique ?

synthèse HP

Pbnm (GdFeO3-type) -> C121,
a = 9.53 Å. *b* = 5.61 Å. *c* = 9.85Å. ß = 110.7°

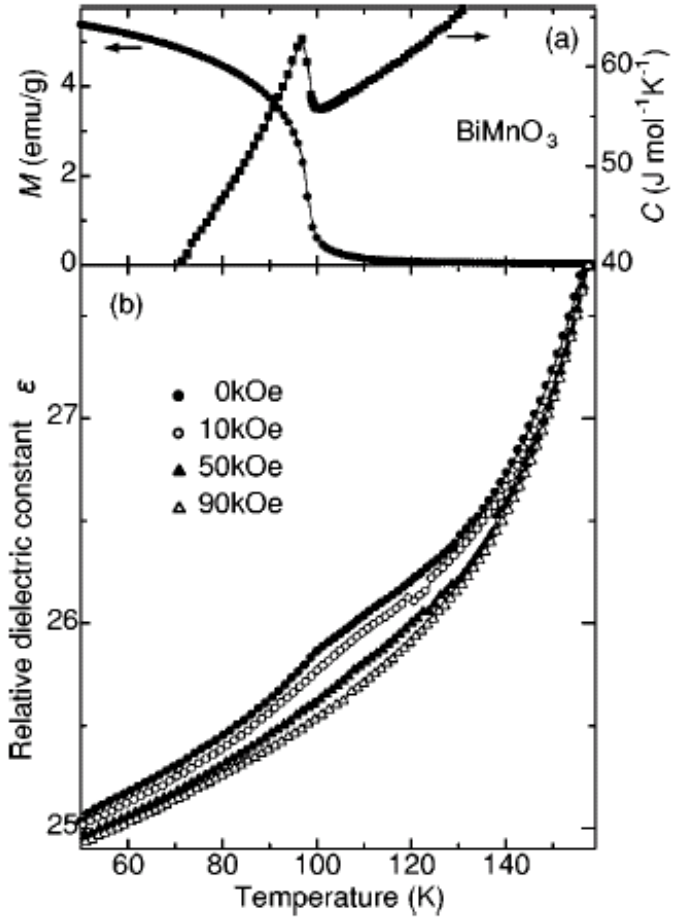


A. M. dos Santos et al.
Solid State Commun. ***122****, 49 2002.*

polarisation elect. mesurée = 0.04 $C.cm^{-2}$
vs
Calculée (LSDA+U)= 0.5 $C.cm^{-2}$

T. Shishidou et al., J. Phys.: Condens. Matter ***16****, S5677 2004*

T(FE)≈760K, T(FM)≈105K



Kimura et al.,PRB ***67****, 180401,2003*
Moreira dos Santos et al., PRB ***66****, 64425, 2002*

$BiMnO_3$: ferromagnétique et ferroélectrique ???

Belik et al. : SG = *C2/c* !!
(CBED + PND)

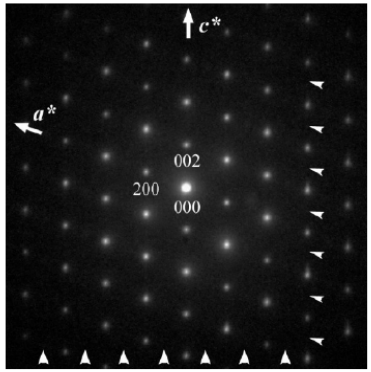


Figure 3. SAED pattern taken along the [010] zone axis. The *h0l* ($h = 2n + 1$ and $l = 2n + 1$) reflections are absent due to the existence of the *C*-centered lattice and *c*-glide plane as indicated by arrows.

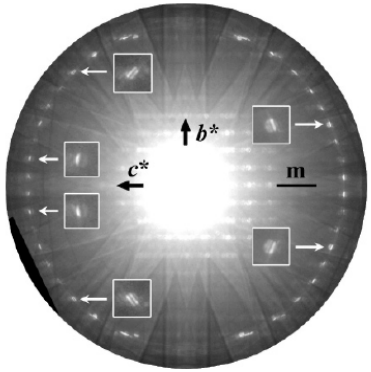
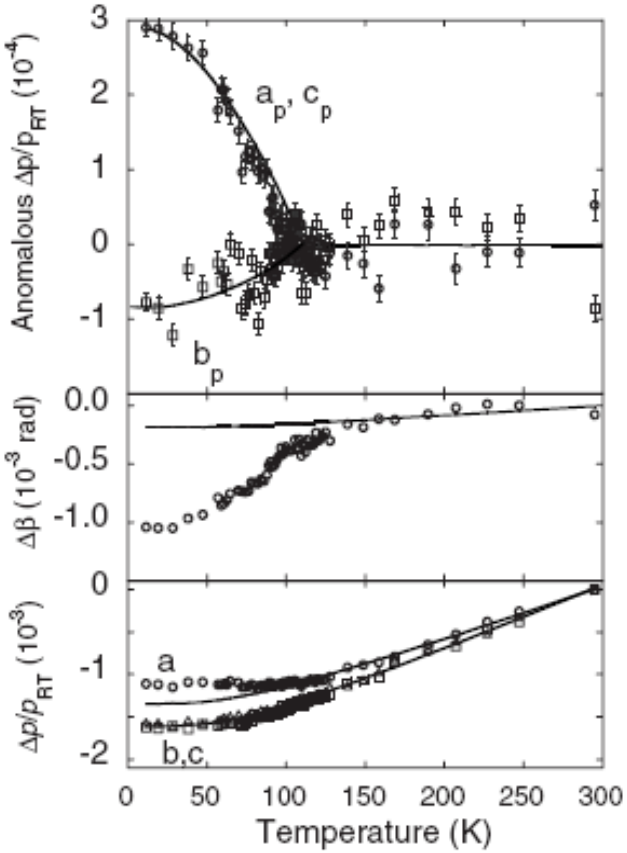


Figure 4. CBED pattern taken along the [100] zone axis. The HOLZ reflections clearly show the mirror-plane symmetry of this pattern perpendicular to the *b**-axis as indicated by the arrows.

Montanari et al. confirment… (PND)
+ effet magnetoelastique



11A. Belik et al., J. Am. Chem. Soc. ***129****, 971 2007*

=> $BiMnO_3$ n'est pas ferroélectrique ?

et $BiCrO_3$???

T("FE")=430K, T(AFM)=120K
AF (θ≈360K) "parasitic FM"

Pbnm => C121 at 430K
a=9.47Å, b=5.48Å, c=9.59Å, β =108.58°
isostructural à $BiMnO_3$??

=>synthèse de poudres/cristaux HP
de $BiCrO_3$ et $BiMnO_3$

⇒Étude structurale
⇒Structure magnétique

⇒***Structure locale ≠ structure moyenne ?***

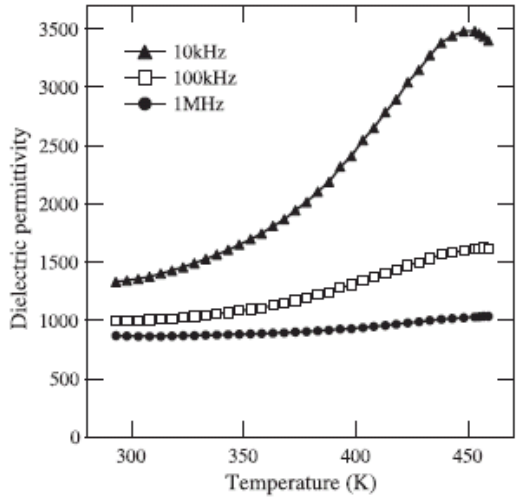


Fig. 3. Temperature dependence of dielectric permittivity of $BiCrO_3$ at 10 kHz, 100 kHz and 1 MHz.

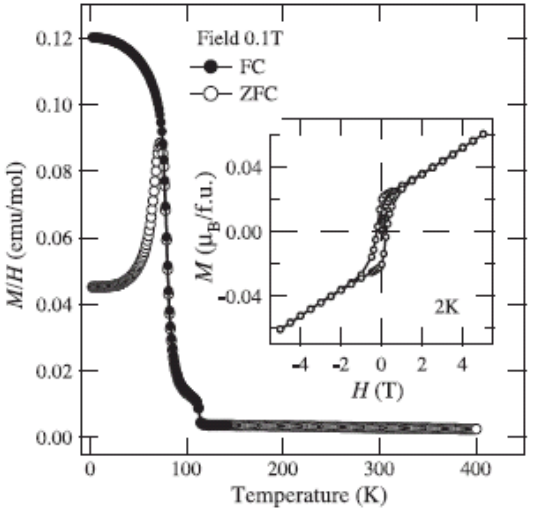
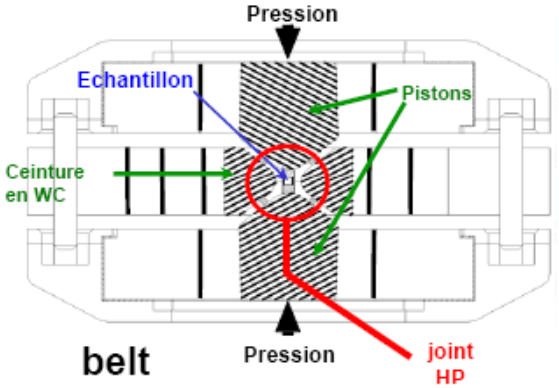


Fig. 4. Temperature dependence of magnetic susceptibility of $BiCrO_3$ measured at H=0.1 T. Open and solid marks represent ZFC and FC measurements, respectively. The inset shows the magnetization curve at 2 K.

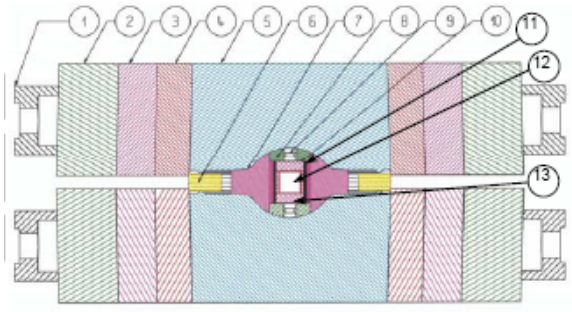
Niitaka et al., Solid State Ionics 172 (2004) 557–559

Institut Néel - synthèses Hautes Pressions

	Belt		Conac	
Diamètre utile des cellules	12 mm	16 mm	40mm	28mm
Volume des capsules (Au,Pt,acier,CuBe,Ta,BN)	0.04 cm^3	0.17 cm^3	0.8 cm^3	0.2 cm^3
Masse de produit (moy.)	160 mg	450 mg	2 g	0.5 g
Gamme de pression	0 - 8 GPa	0 - 4 GPa	0 - 6 GPa	0 - 7.5 GPa



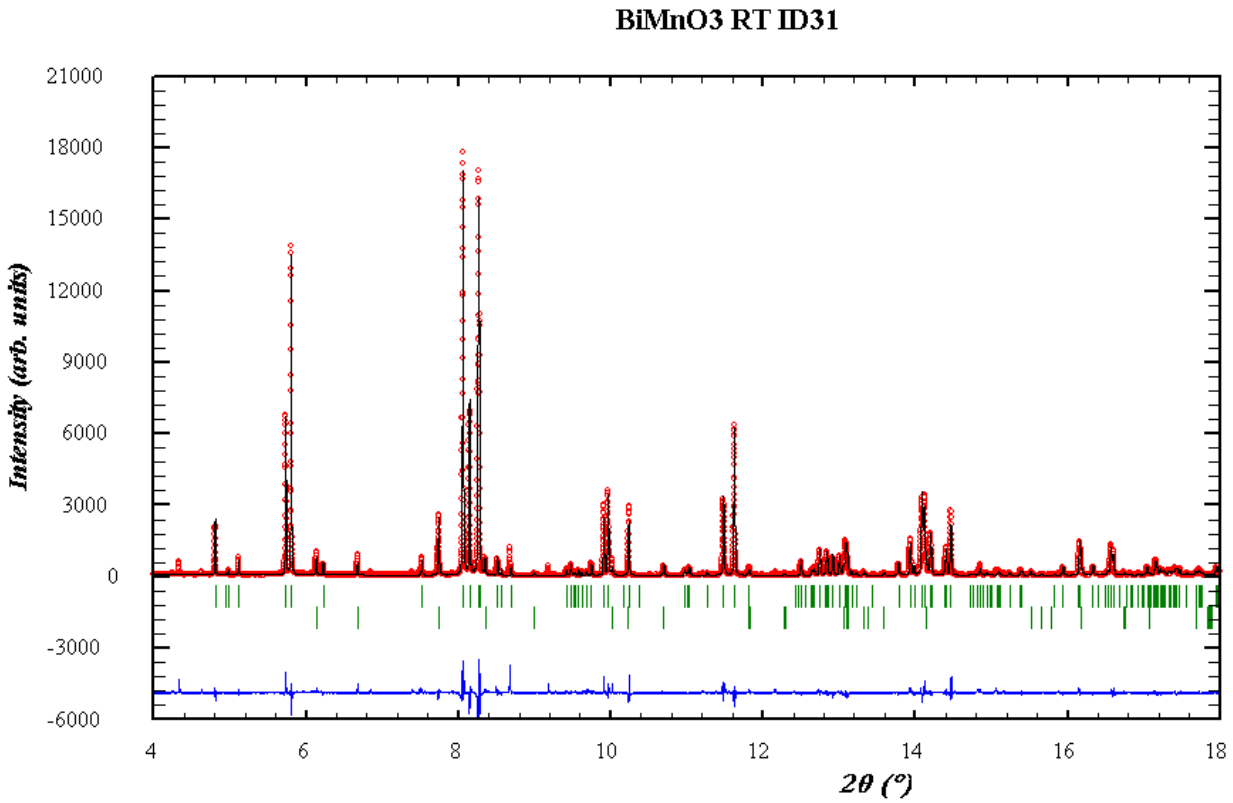
belt



Conac

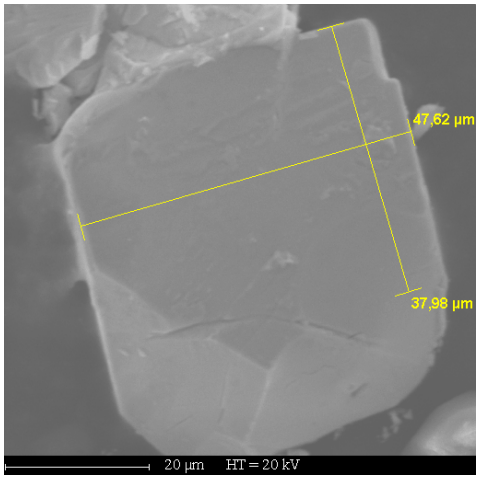
Structure moyenne de BiMnO3 ,
Poudre ID31 ESRF à 30keV

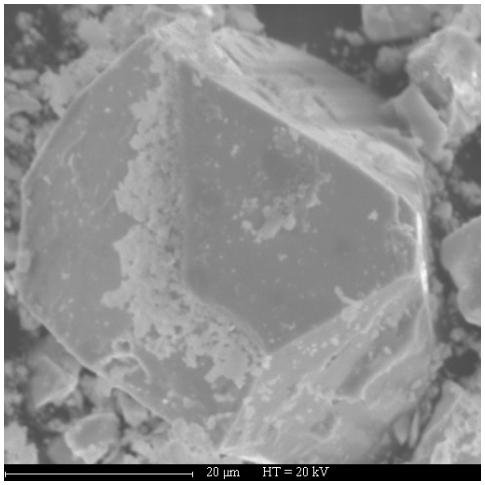
Affinement C2/c et C2 équivalents
Pas de réflexions (hkl) h+k=2n+1; (h0l) l=2n+1

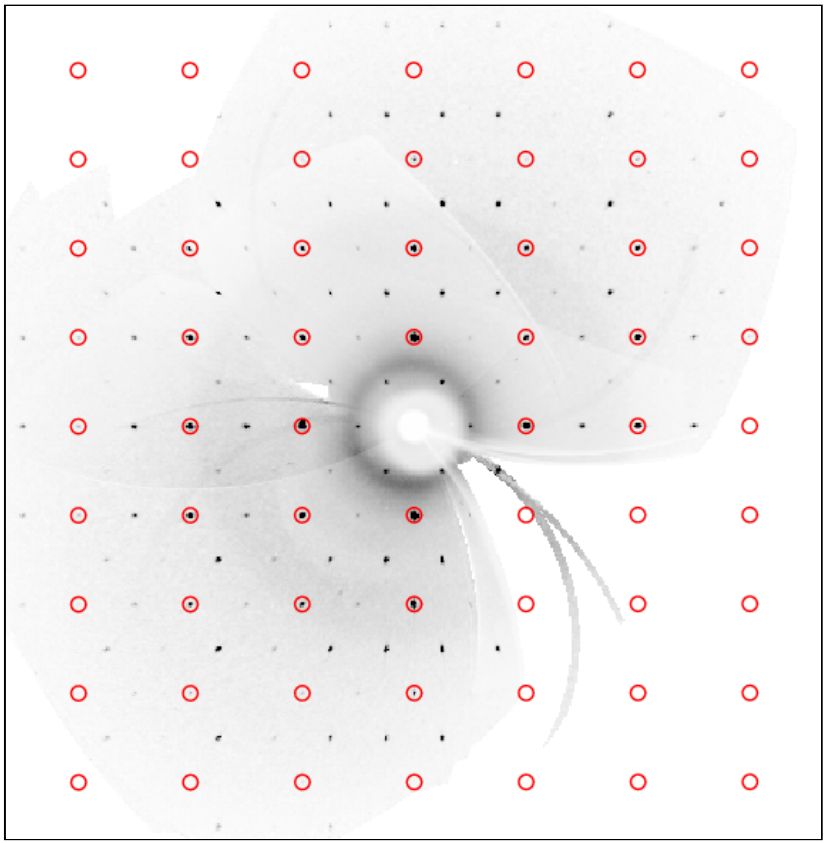


Structure moyenne de $BiMnO_3$, Monocristaux, kappaApex, λ=AgKα

Affinements C2/c et C2 équivalents
Pas de réflexions (hkl) h+k=2n+1; (h0l) l=2n+1







Crystal data

Crystal system monoclinic
Space group ***C* 1 2/c 1 (no. 15)**
Unit cell *a* = 9.566 Å *b* = 5.624 Å
c = 9.889 Å b = 110.63 °

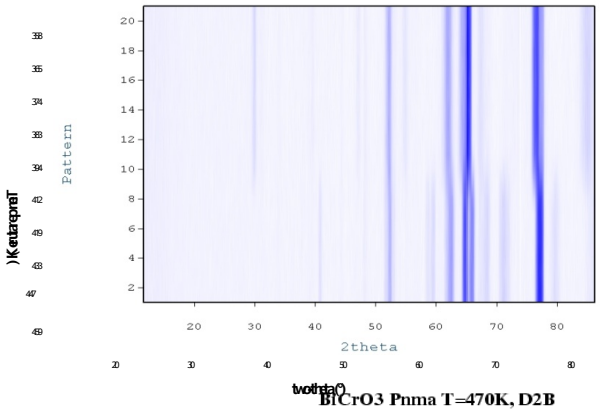
Robs=2.3%, Rwobs=2.6%

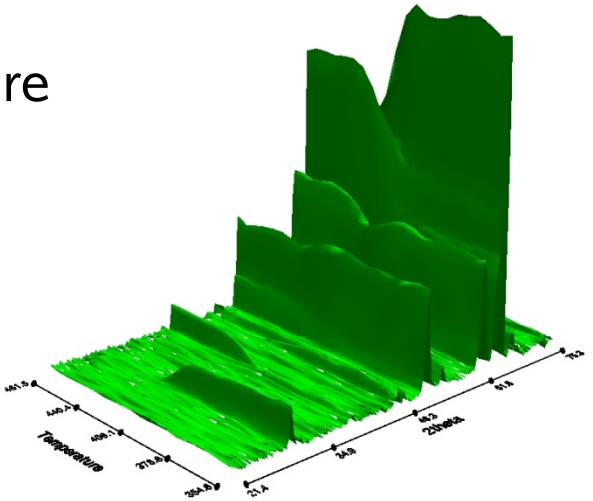
Atomic coordinates

Atom	Wyck.	x	y	z
Bi	8*f*	0.13671(4)	-0.21969(8)	0.12672(4)
Mn1	4*e*	0	0.2127(5)	1/4
Mn2	4*c*	1/4	1/4	0
O1	8*f*	0.1010(8)	0.1717(15)	0.0832(9)
O2	8*f*	0.3544(8)	0.4549(14)	0.1634(7)
O3	8*f*	0.1453(8)	0.4295(14)	0.3666(9)

Structure moyenne de $BiCrO_3$,
Poudre neutrons D20/D2B ILL vs T

Transition de phase haute température



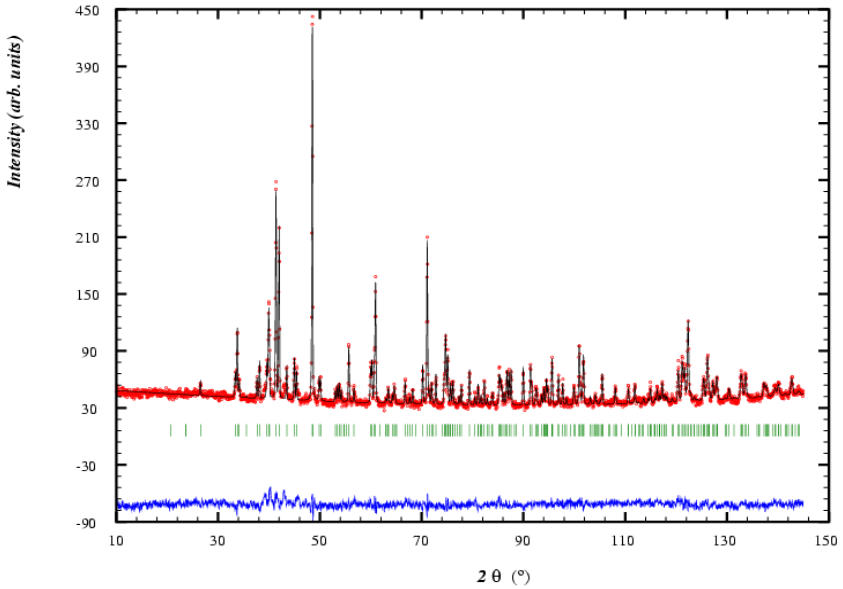


D20

Tc≈430K(warm)

Tc≈415K(cool)

Pnma



D2B

Pnma **a=5.5427(1), b=7.7524(2), c=5.4255(1)**

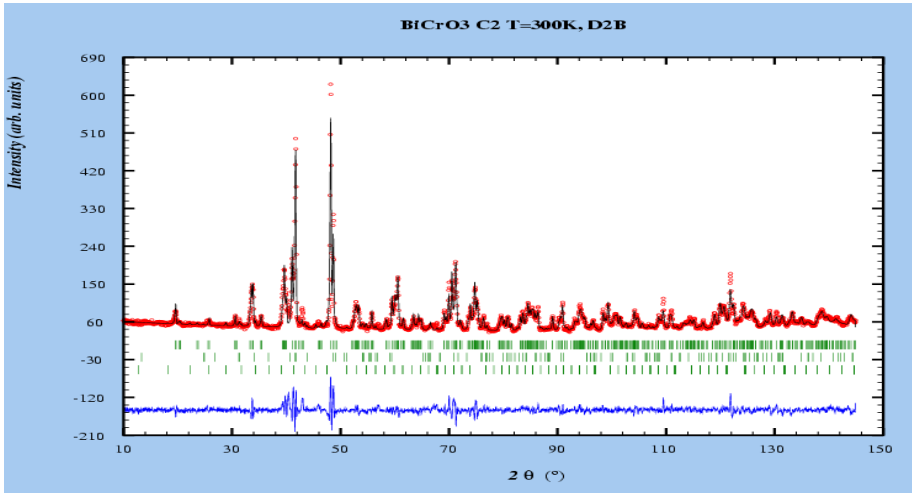
Bi1	0.0432(4)	¼	-0.0051(6)	1.31(5)
Cr1	½	½	0	0.67(8)
O1	0.4793(6)	¼	0.0811(6)	0.97(6)
O2	0.2948 (5)	0.0390(3)	0.7015(5)	1.22(5)

Bi1-O1: 3.160(4)
Bi1-O1: 2.462(4)
Bi1-O1: 3.145(5)
Bi1-O1: 2.328(5)
Bi1-O2 (x2): 2.675(3)
Bi1-O2 (x2): 2.389(3)
Bi1-O2 (x2): 3.353(3)
Bi1-O2 (x2): 2.661(3)
Average: ***2.77***

Cr1-O1 (x2): 1.9906(7)
Cr1-O2 (x2): 1.989(3)
Cr1-O2 (x2): 2.002(3)
Average: ***1.99***

Structure à T ambiante

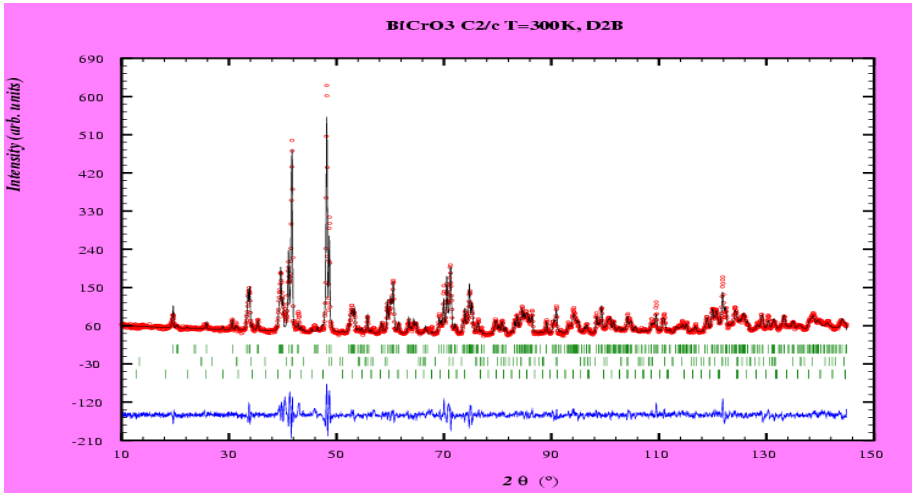
C121



Rp: 20.2, Rwp: 21.3, Rexp: 9.83, Chi2: 4.71, RBragg: 7.11

Atom	x	y	z	Biso
Bi1	0.1250(9)	-0.046(4)	0.3813(1)	0.334(2)
Bi2	0.3596(8)	0.019(5)	0.1185(1)	0.334(2)
Cr1	0	0	0	0.341(6)
Cr2	0.235(2)	-0.010(6)	0.741(2)	0.341(6)
Cr3	½	0.021(4)	½	0.341(6)
O1	0.083(2)	-0.042(6)	0.832(2)	0.79(5)
O2	0.408(2)	0.049(5)	0.657(2)	0.79(5)
O3	0.160(2)	0.284(5)	0.612(2)	0.79(5)
O4	0.359(2)	0.274(6)	0.409(2)	0.79(5)
O5	0.358(2)	0.223(6)	0.909(2)	0.79(5)
O6	0.148(2)	0.239(6)	0.114(2)	0.79(5)

C12/c1

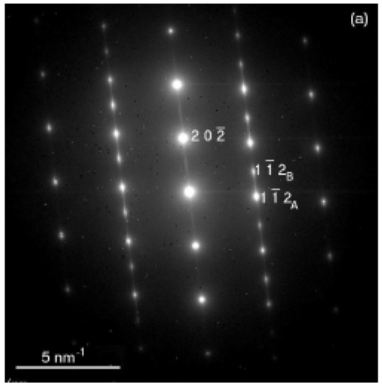


Rp: 21.5, Rwp: 22.1, Rexp: 10.14, Chi2: 4.76, RBragg: 7.47

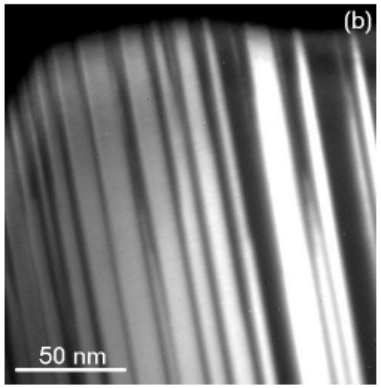
Atom	x	y	z	Biso
Bi1	0.1331(4)	0.2166(6)	0.1313(4)	0.74(7)
Cr1	¼	¼	1/2	0.63(18)
Cr2	0	0.2366(18)	¾	0.82(19)
O1	0.0860(5)	0.2037(11)	0.5869(5)	0.91(9)
O2	0.1552(6)	0.5226(12)	0.3643(6)	1.17(11)
O3	0.3582(6)	0.5256(10)	0.1590(5)	0.47(8)

Biso contraints

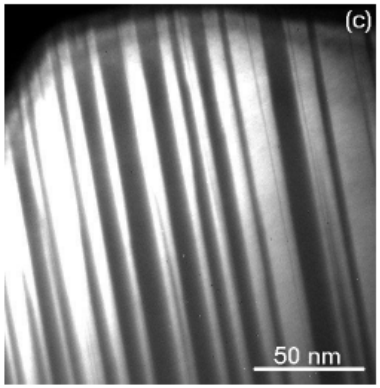
Formes de raies difficiles à décrire à T< transition



(a) Electron diffraction pattern of the [1 3 1] zone axis of monoclinic $BiCrO_3$.

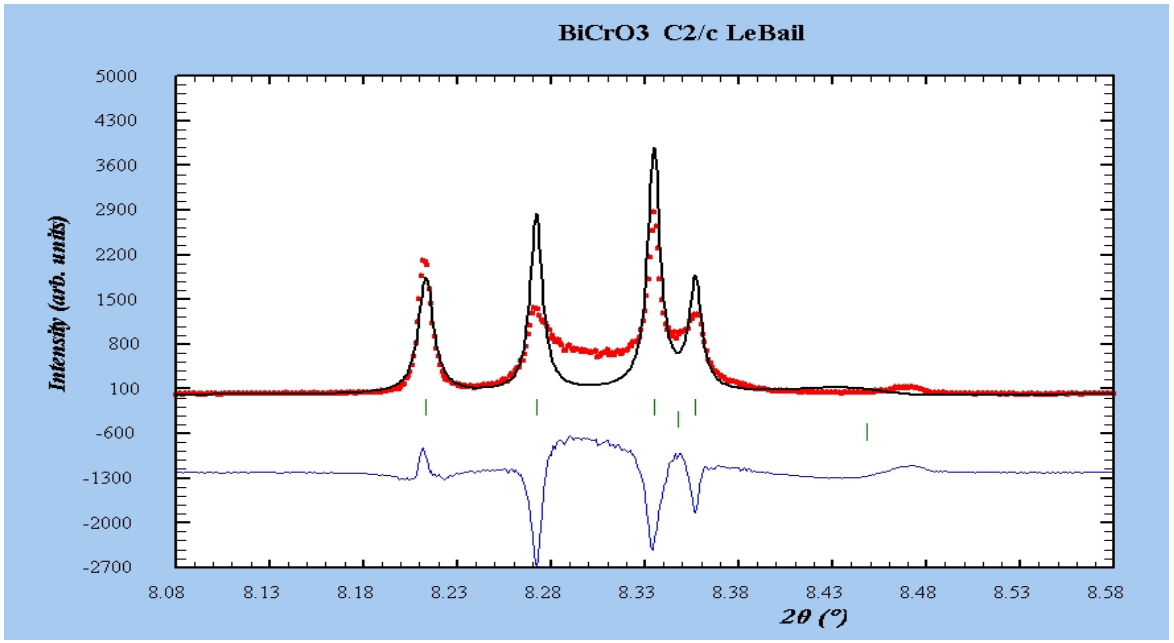


(b) Dark field image of $BiCrO_3$ selecting a spot of family A.



(c) Dark field image of $BiCrO_3$ selecting a spot of family B.

TEM
Macles
Qques nanomètres



ESRF-ID31
Diffusion diffuse

Structure moyenne

=> **$BiMnO_3$** (poudres, cristaux)

C2/c centrosymétrique non ferroélectrique
(affis de même qualité, pas de refl. Interdite)

=>**$BiCrO_3$**

idem, mais nano-domaines de macles,
difficile de conclure

Structure locale ≠structure moyenne ?

=> distortions locales désordonnées=>ferroélectricité?

⇒étude par analyse PDF de données RX sur ID31-ESRF

Utilisation de la fonction de distribution de paires pour l'études structurale de composés partiellement désordonnés

A partir de données de diffraction de poudres :

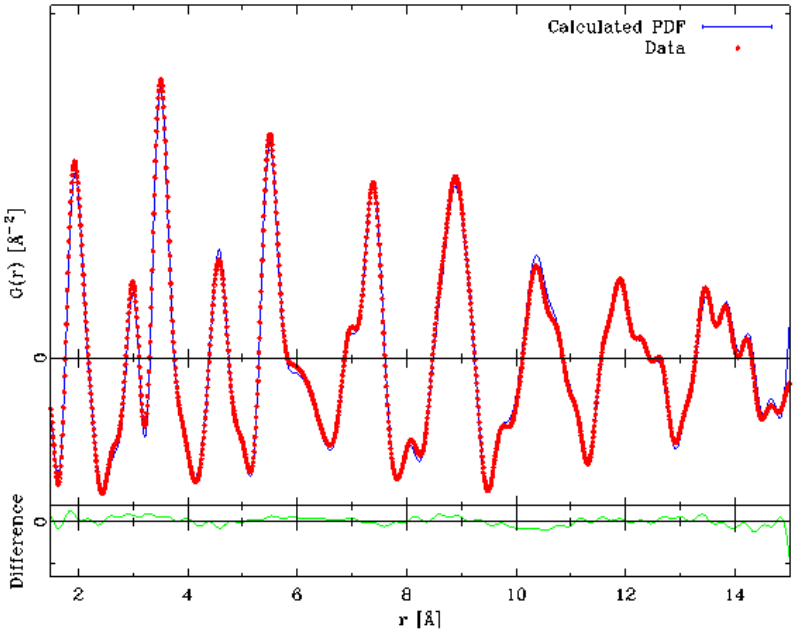
$$G(r) = 4\pi r[\rho(r) - \rho_0] = \frac{2}{\pi}\int_0^{\infty} Q[S(Q) - 1]\sin(Qr)dQ$$

r = distance interatomique

$\rho(r)$ = densité de paires, $\rho 0$: densité numérique moyenne

$S(Q)$=intensité de diffusion cohérente normalisée,

$Q=4\pi\sin(\theta)/\lambda$



A partir d'un modèle structural :

$$G_{calc}(r) = \frac{1}{r}\sum_i\sum_j\left[\frac{b_i b_j}{\langle b\rangle^2}\delta(r - r_{ij})\right] - 4\pi r\rho_0,$$

r_{ij} = distance interatomique

b_i : pouvoir diffusant

=> **"Rietveld" dans l'espace direct** (PDFFIT *Proffen et al.,. Appl. Cryst.,1999)*

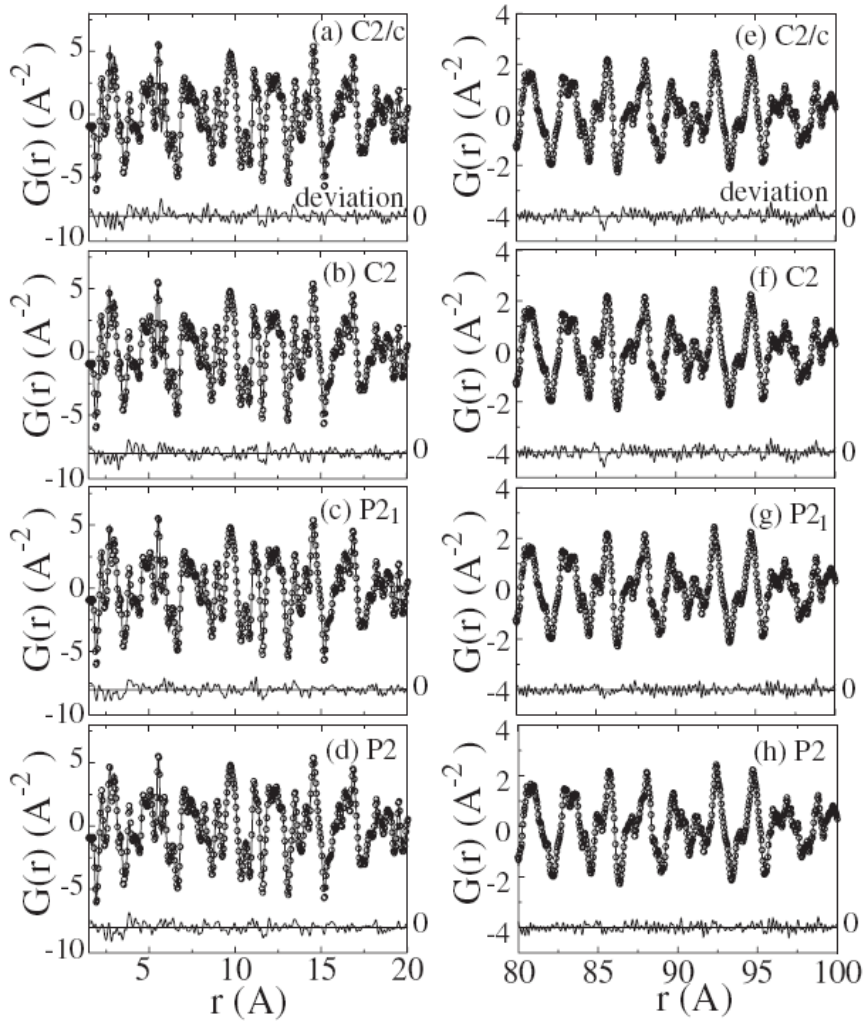
=> **fit RMC de la PDF** (DISCUS, *Proffen et al.,. Appl. Cryst.,1997*)

de S(Q) (RMCPow, *Mellergard et al., Acta Cryst. A 1999*)

des deux (RMCProfile, *Keen et al., JPCM 2005)*

Th. Proffen, S. J. L. Billinge, T. Egami and D. Louca, Z. Kristallogr. 218 (2003) 132–143

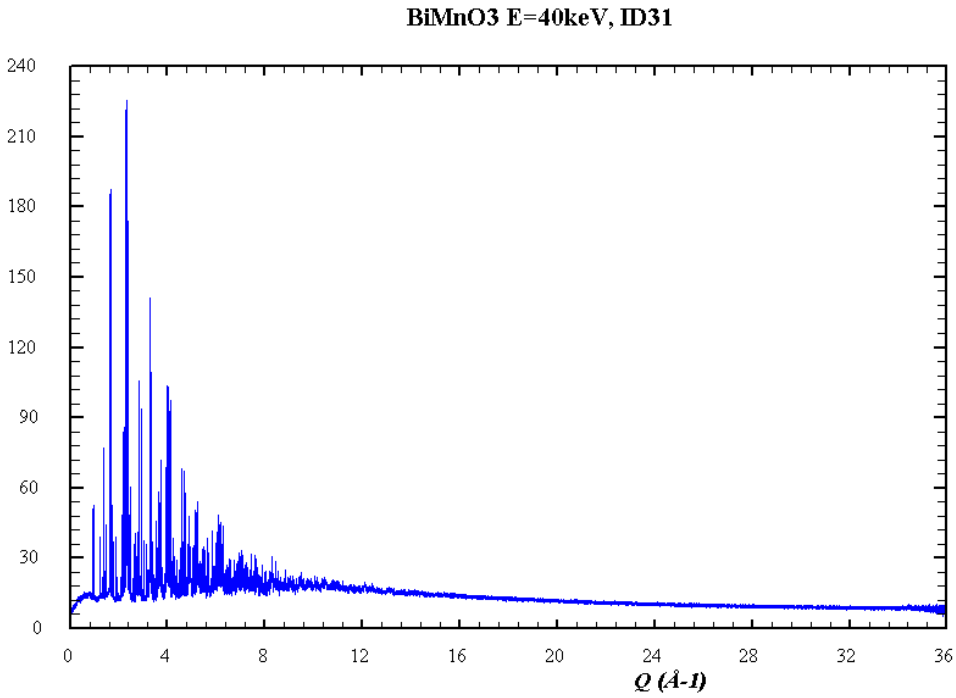
Kodoma et al.,
PDF sur BiMnO3 (NPD)
=> P21 ou P2

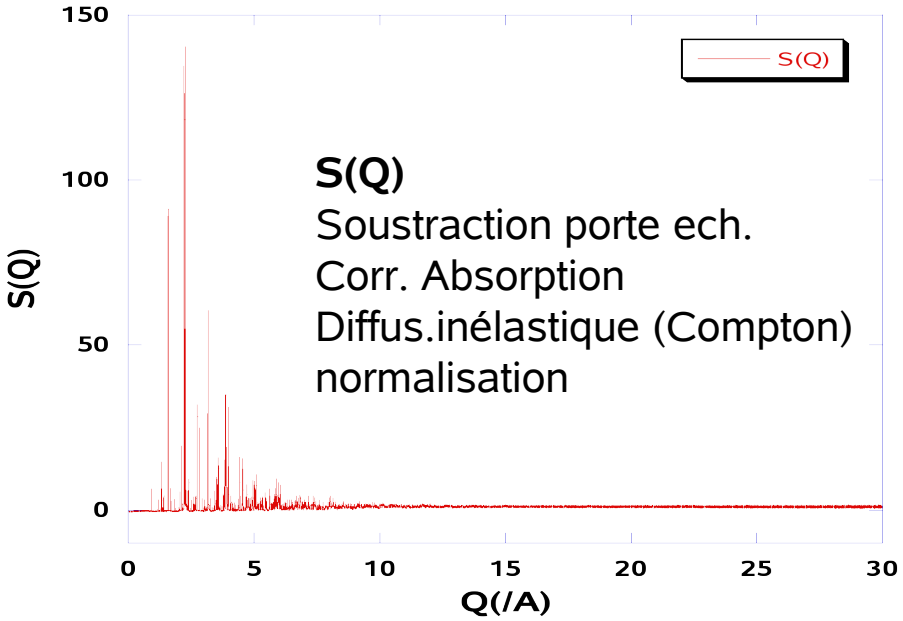


Kodoma et al. J. Phys. Soc. Jpn., Vol. 76, No. 12

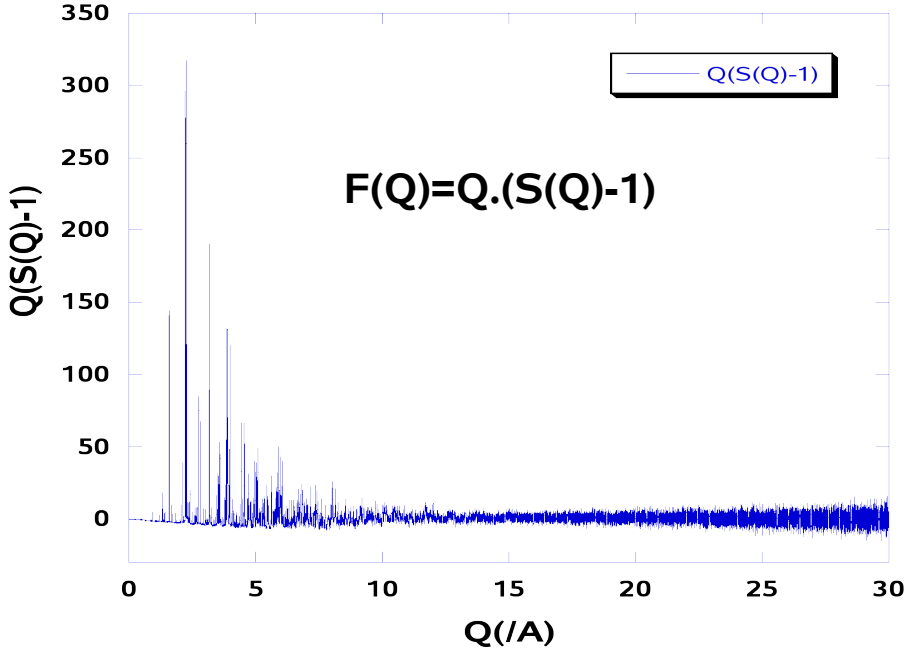
Mesures sur ID31

λ≈40keV≈0.3 Å,
Debye-Scherrer + multianalyseur,
2θmax=117°, Qmax>30 Å^{-1}





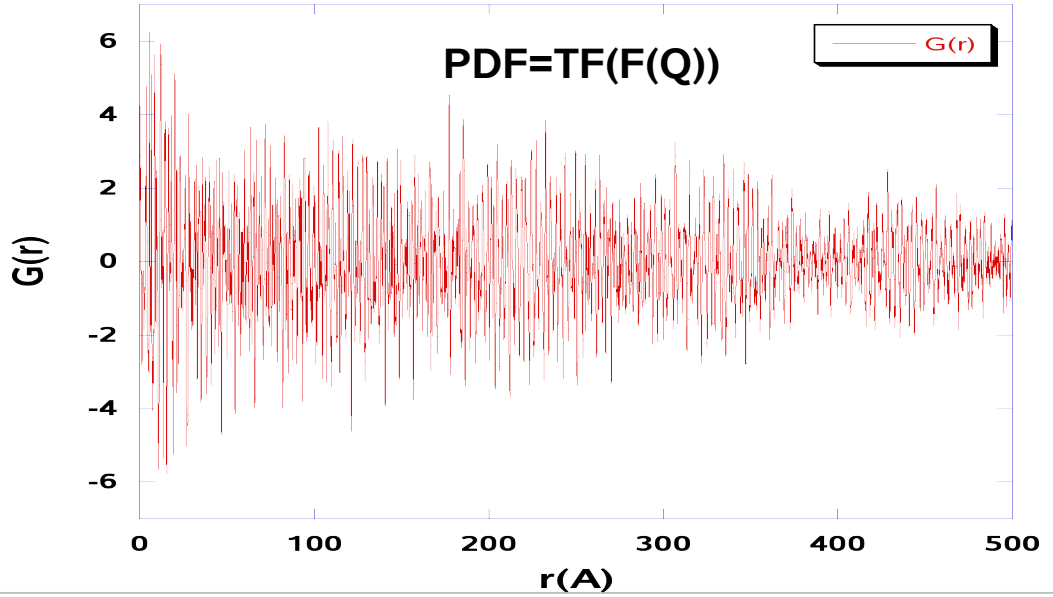
S(Q)
Soustraction porte ech.
Corr. Absorption
Diffus.inélastique (Compton)
normalisation



F(Q)=Q.(S(Q)-1)

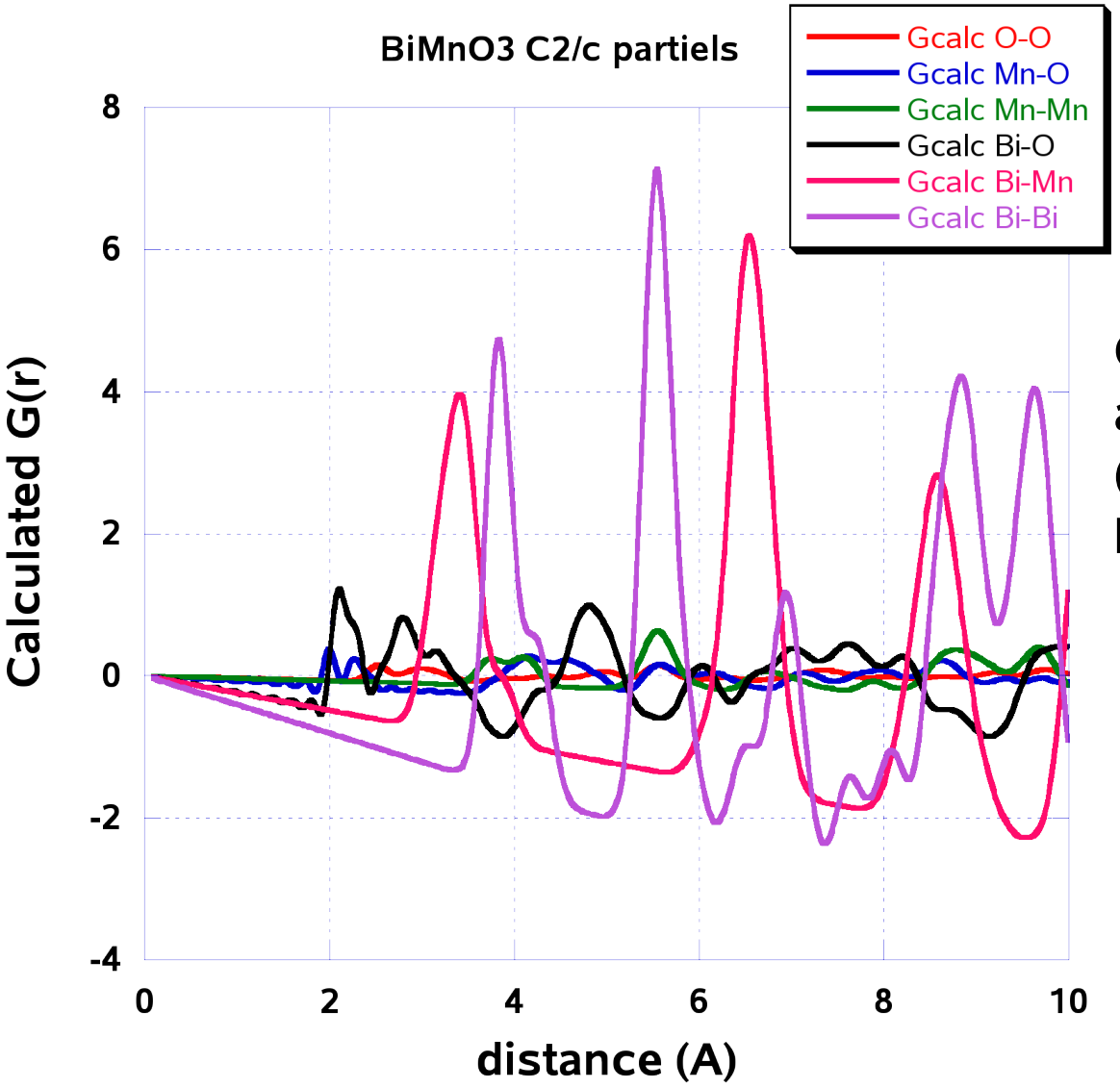
$$G(r) = \frac{2}{\pi}\int_0^{\infty} Q[S(Q)-1]\sin(Qr)dQ,$$

$BiMnO_3$



PDF=TF(F(Q))

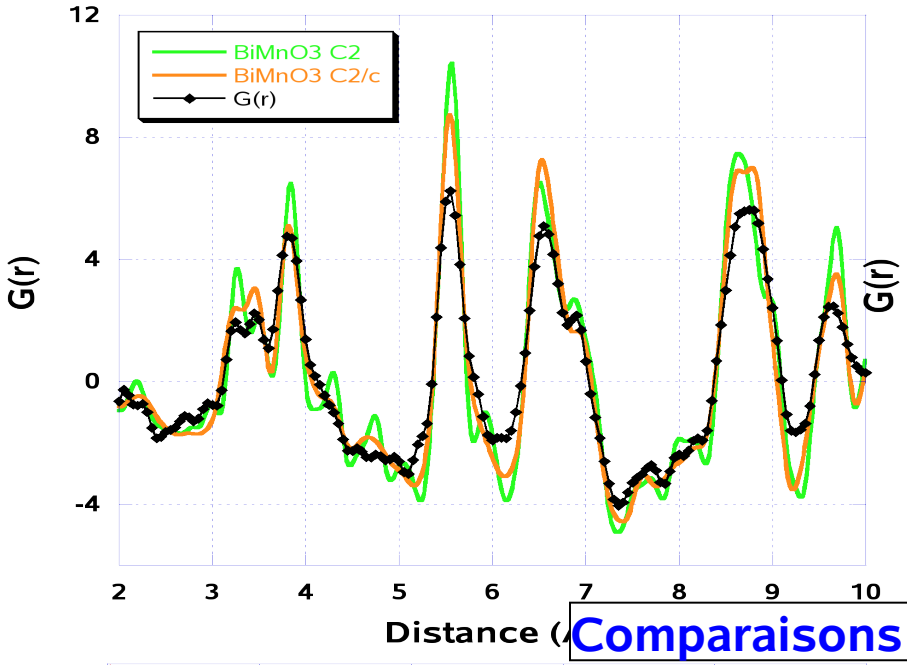
X. QIU,et al. PDFgetX2: J. Appl. Cryst. (2004), **37**, 678–678

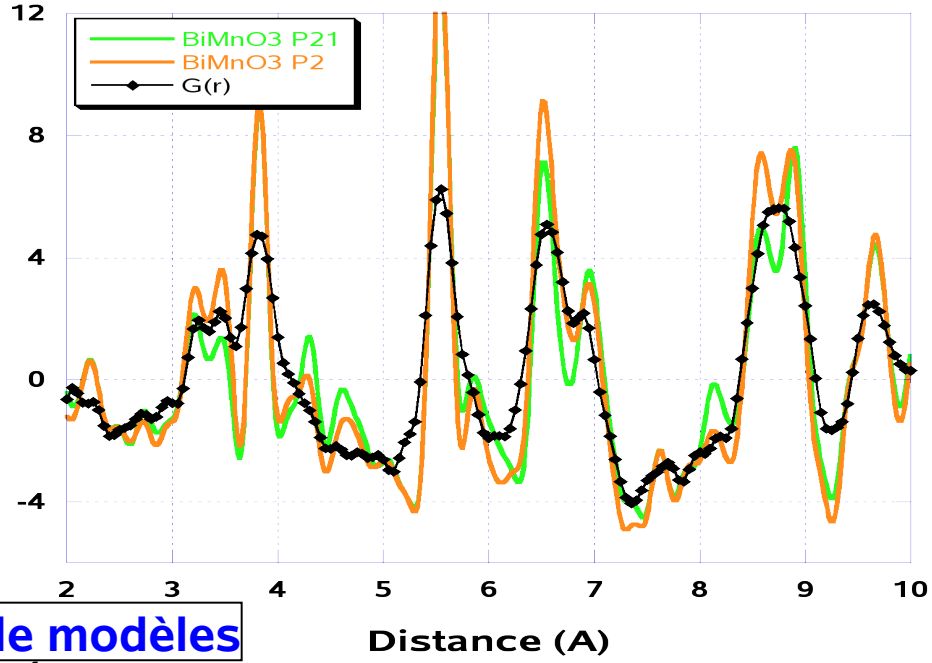


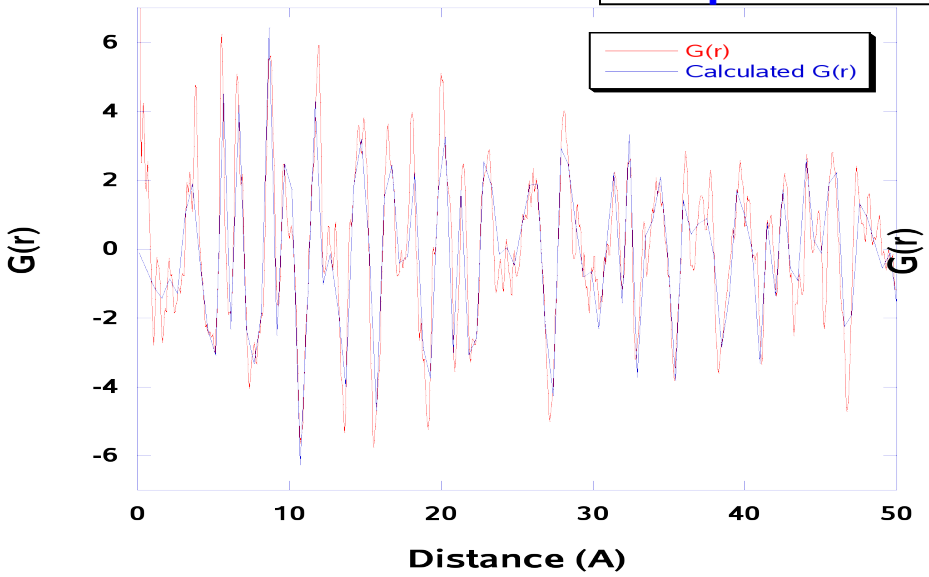
Calculs et affinnements avec PDFGUI (Billinge group, Michigan State Univ.)

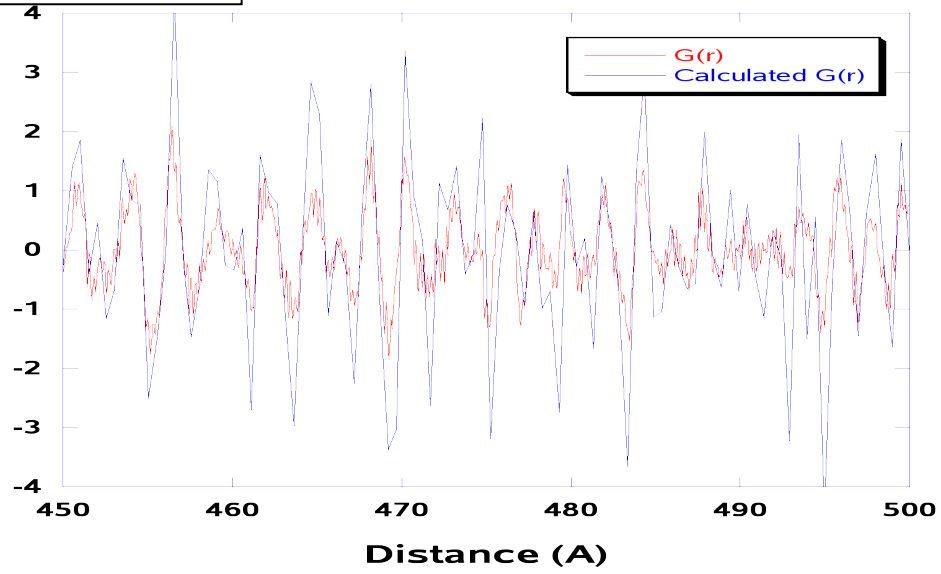
PDFGUI, C.L. Farrow et al.
J. Phys.: Condens. Matter 19 (2007) 335219

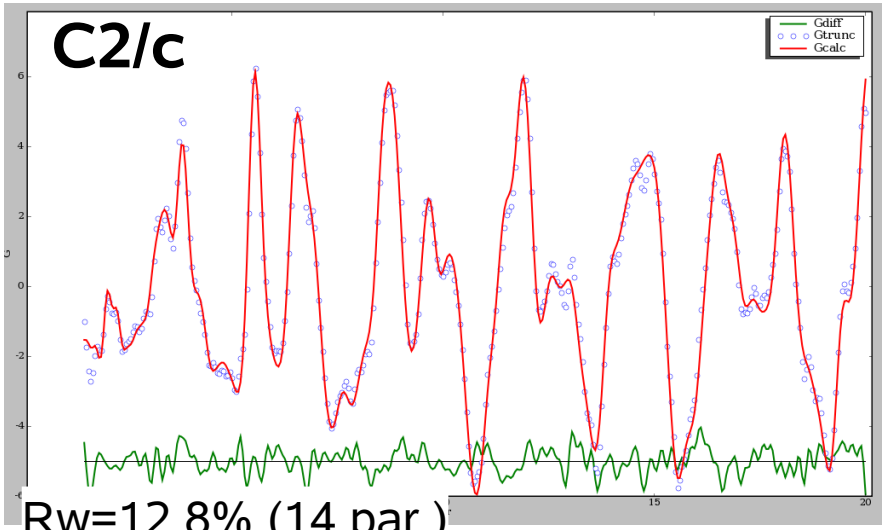
Comparaisons de modèles



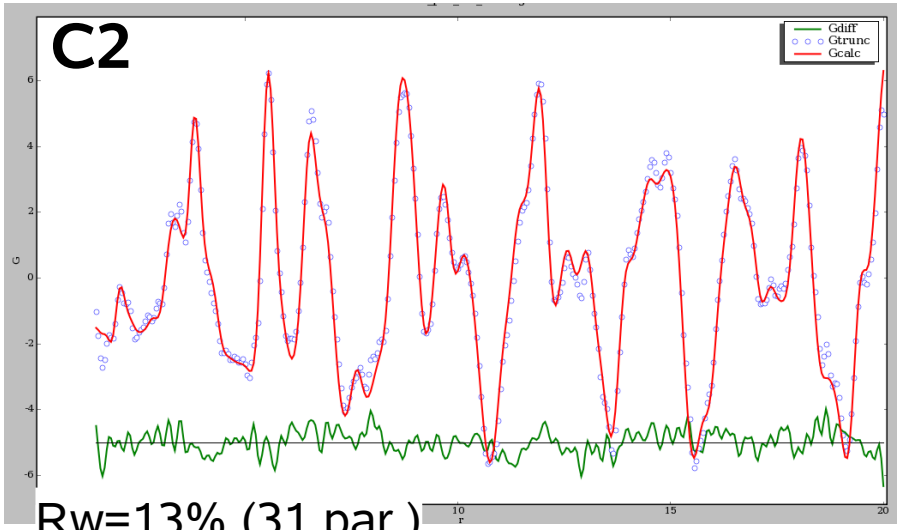








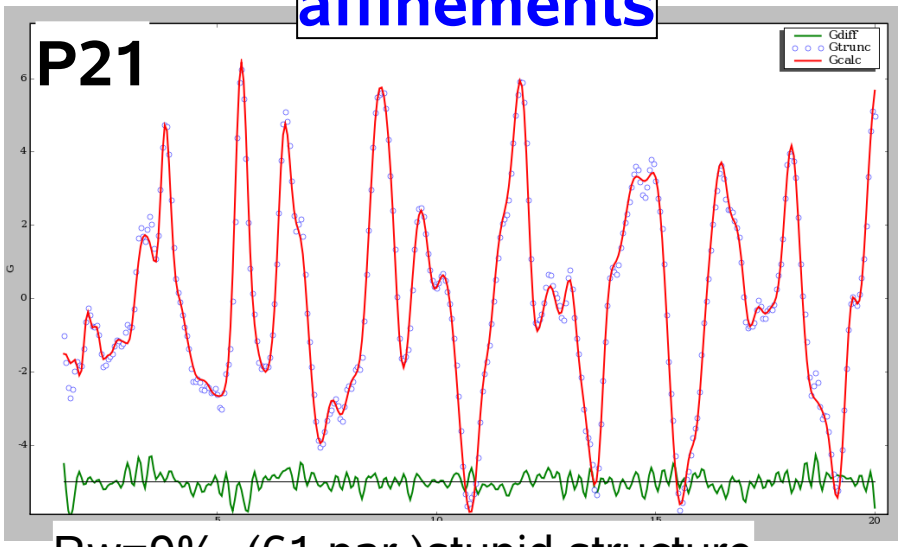
Rw=12.8% (14 par.)



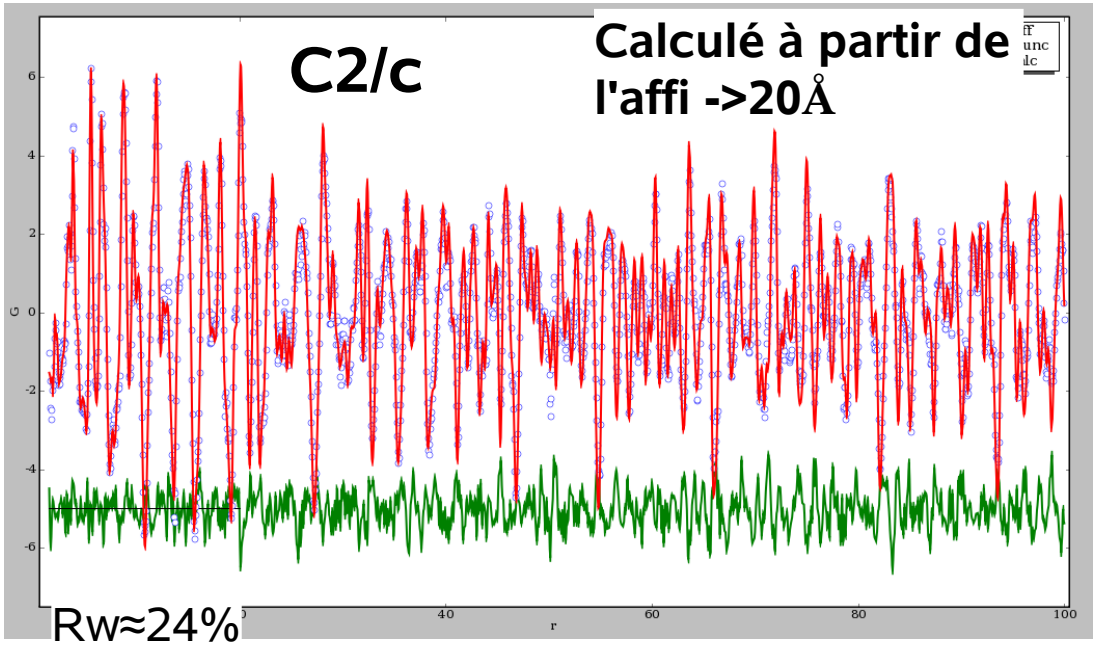
Rw=13% (31 par.)

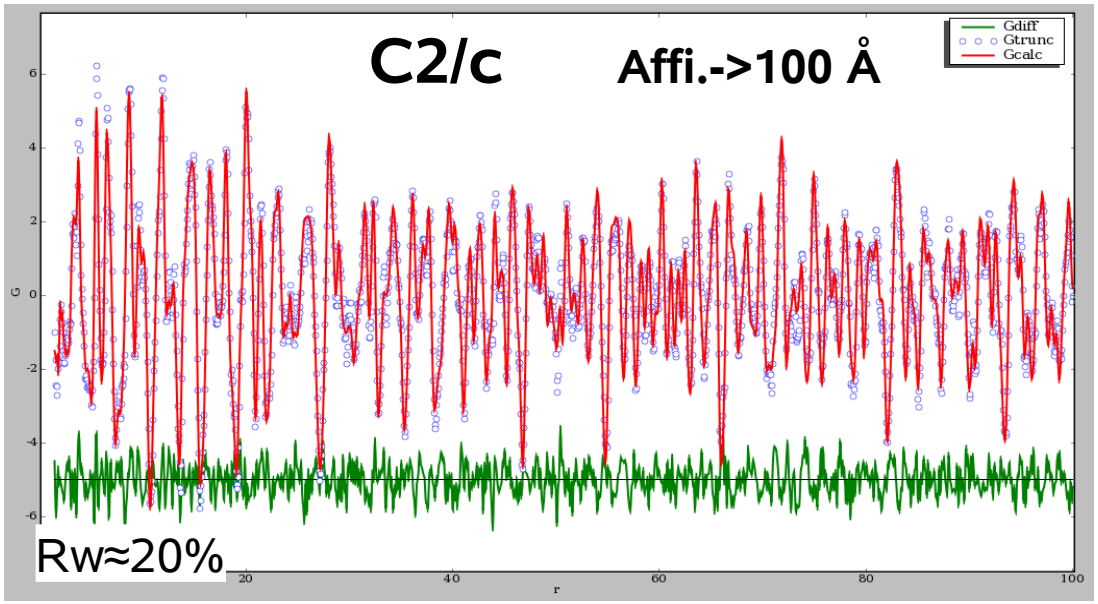
affinements

$BiMnO_3$



Rw=9%, (61 par.)stupid structure



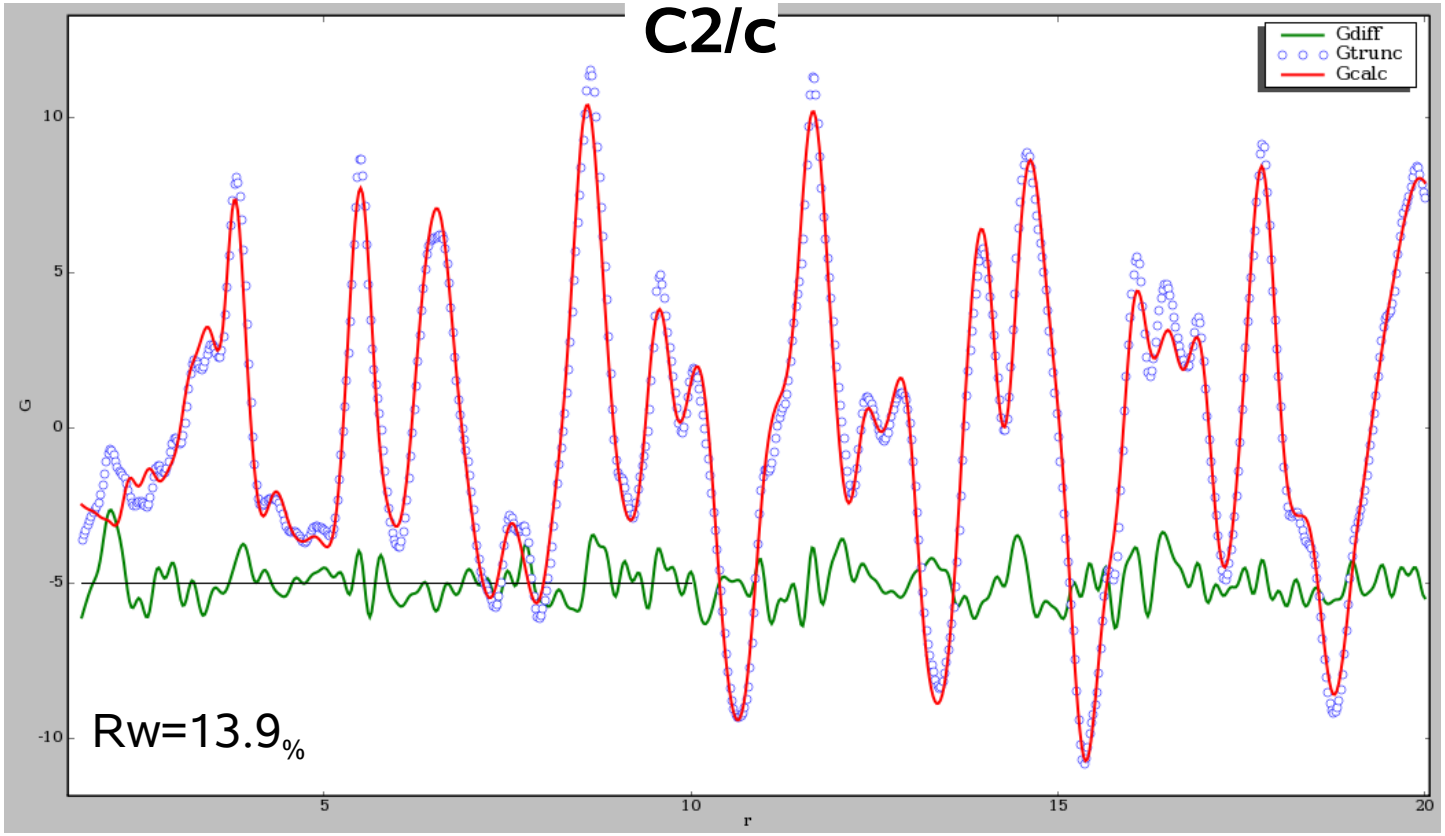


$BiMnO_3$

Structure locale
≈ structure moyenne

pas de désordre

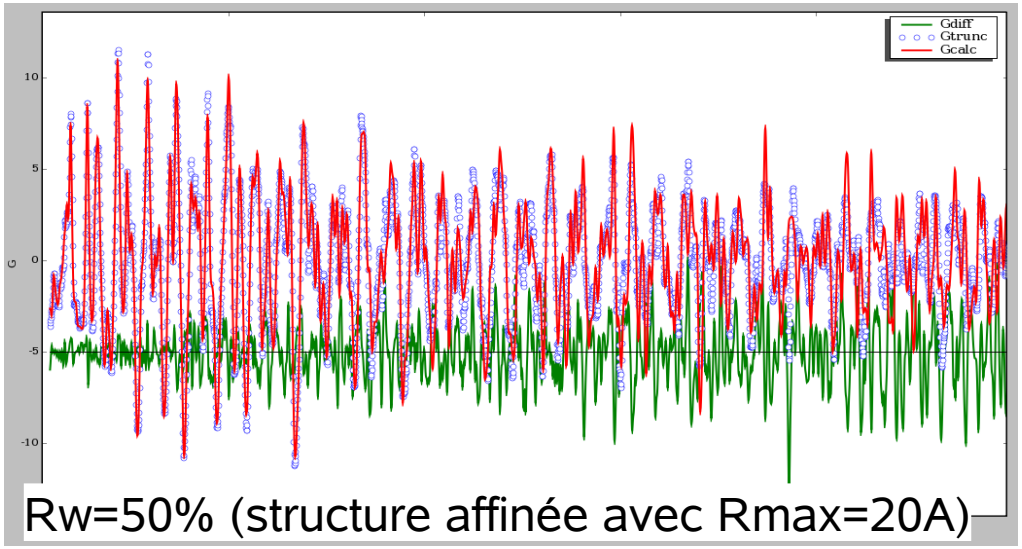
$BiCrO_3$



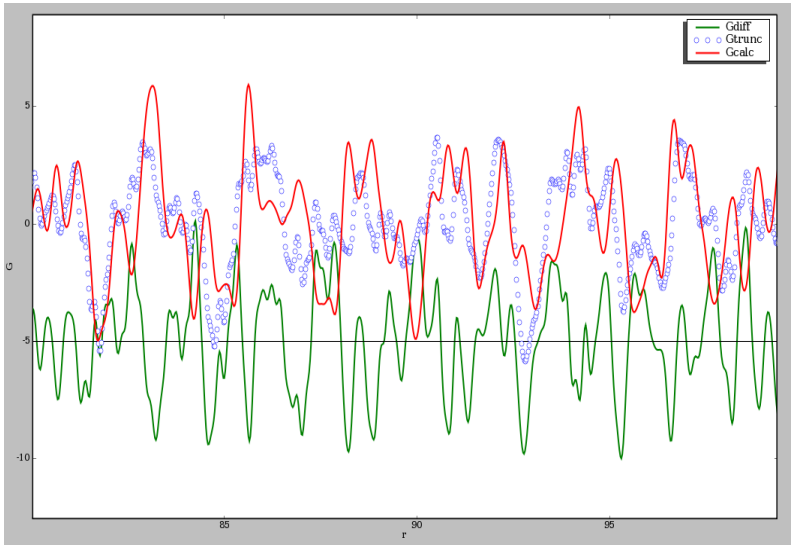
Affinement correct avec C2/c (pas mieux en C2)

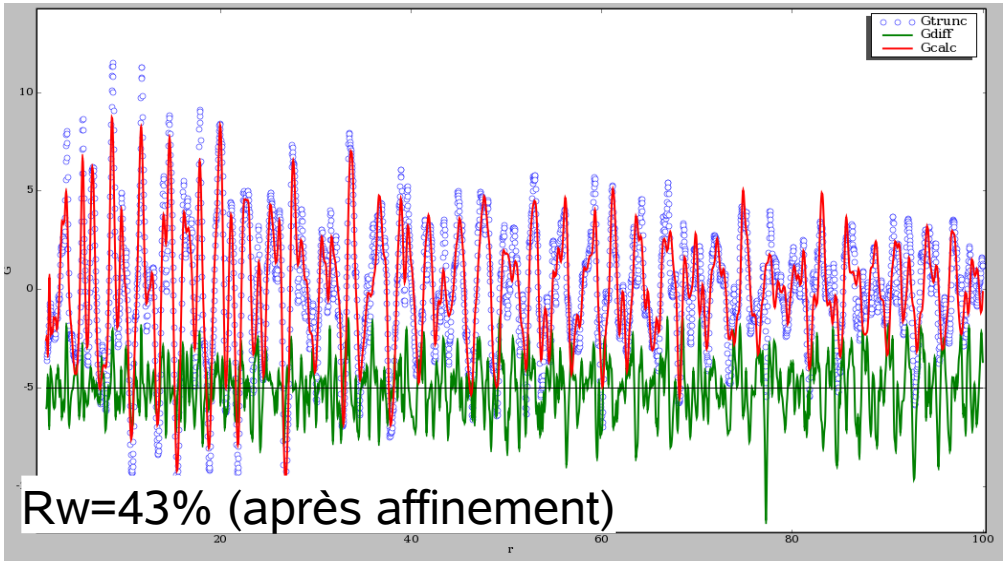
Qualité comparable (un peu moins bonne) que $BiMnO_3$

=> structure locale



Rw=50% (structure affinée avec Rmax=20A)





Rw=43% (après affinement)

Structure locale
≠structure moyenne

=> influence des macles

=> étudier la structure
des parois de macles

Conclusions

✓structure moyenne C2/c $BiMnO_3$, $BiCrO_3$

✓données haut Q/haute résolution =>PDF à grandes distances

✓structure locale C2/c $BiMnO_3$, $BiCrO_3$

✓effet des domaines visible sur la PDF de $BiCrO_3$

✓$BiMnO_3$ = multiferroïque de type 2 ?,

Cc en dessous de T(FM)

(**I. V. Solovyev, *b and Z. V. Pchelkina*** *JETP Letters, 2009, Vol. 89, No. 12, pp. 597–602)*

⇒RX monocristal BT

⇒PDF BT