Exploring phase diagrams with neutron powder diffraction

Pr. François Goutenoire
UMR6283, IMMM (Institute of Molecules and Materials of le Mans),
University of Maine, 72085 Le Mans, Cedex 9, France

ESS-ILL User Meeting Oct. 2022

Phase diagrams and powder diffraction

Why powder vs crystal ?

**Ab-initio structure
resolution from powder diffraction**

Conclusion
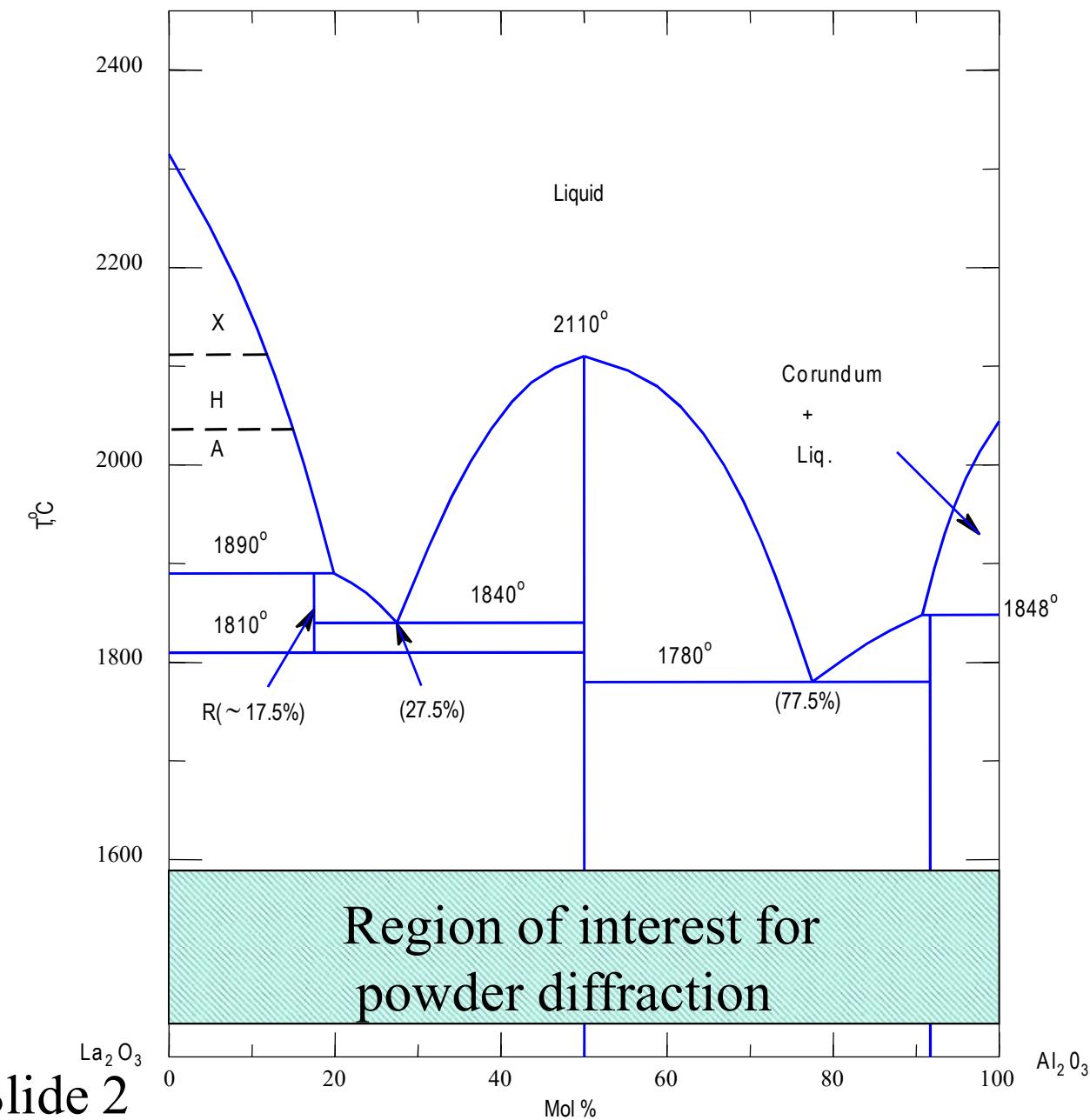
Powder Diffraction

Metallurgical
Inorganic
Organic
Pharmaceutical
Compounds

**T°C
Usual ~ 25°C
Tmax ~ 1000°C**

Slide 2
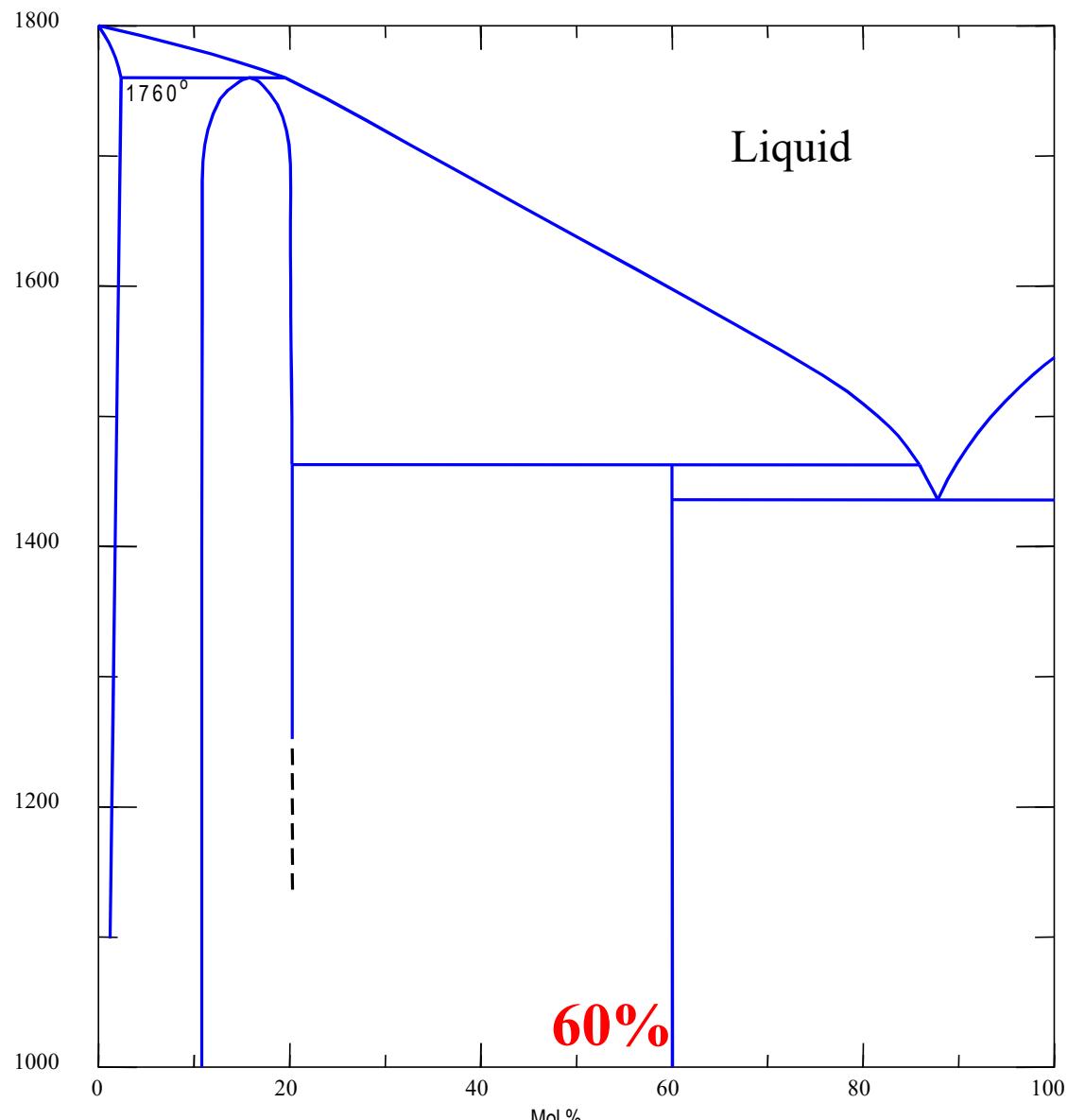
R. J. Cava, R. S. Roth, T. Negas, H. S. Parker, and D. B. Minor, *J. Solid State Chem.*, **40** [3] 318-329 (1981).

A relatively large two-phase region exists between the oxygen-rich boundary of the modulated structure and the second intermediate compound at $LaNb_{0.4}W_{0.6}O_{4.3}$, which melts incongruently. This phase is apparently unrelated to any of the oxidized variants of $CeNbO_4$. Attempts to obtain single crystals of a size suitable for X-ray study, by annealing at temperatures below the melting point for extended periods, were not successful and we were therefore unable to index the powder diffraction pattern. The five strongest lines in the powder pattern are at d = 4.263, 3.221, 2.928,

# Phase diagrams and powder diffraction

$LaNb_{0.4}W_{0.6}O_{4.3}$ **60%** $LaWO_{4.5}$ **Wrong !!!**

Structural determination from powder
(X-ray + Neutron)

$La_7Nb_3W_4O_{30}$ **57.14%** $LaWO_{4.5}$

HREM

Slide 4
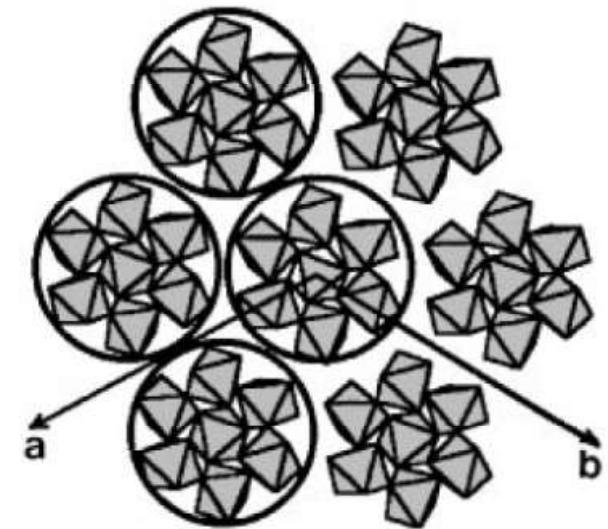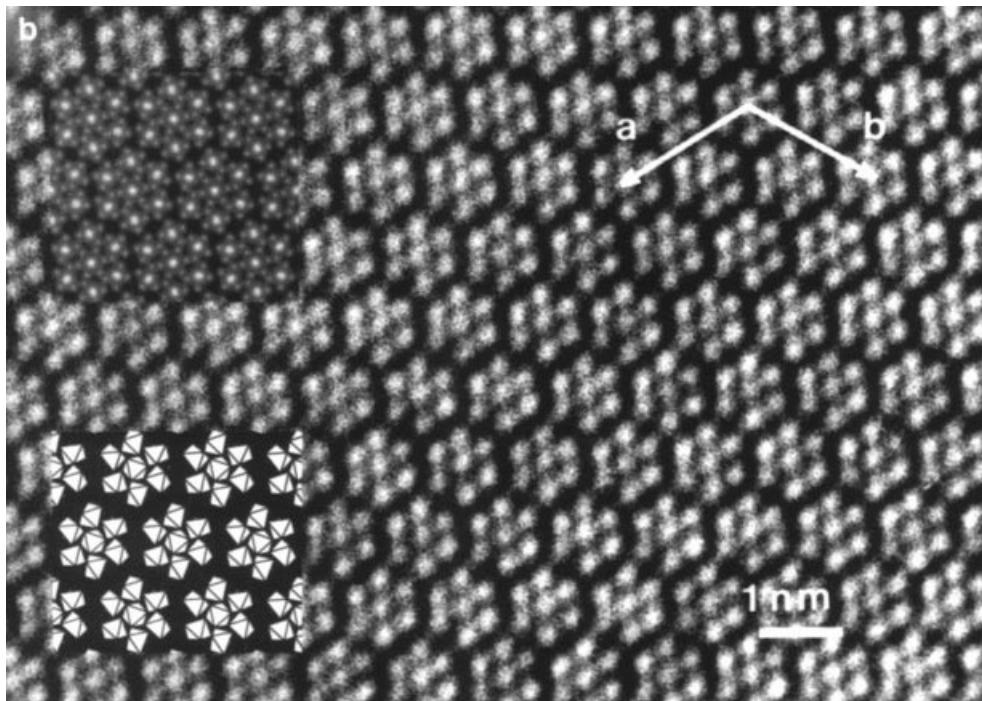
Phase diagrams and powder diffraction

$La_7Nb_3W_4O_{30}$ **57.14%** $LaWO_{4.5}$

Slide 5
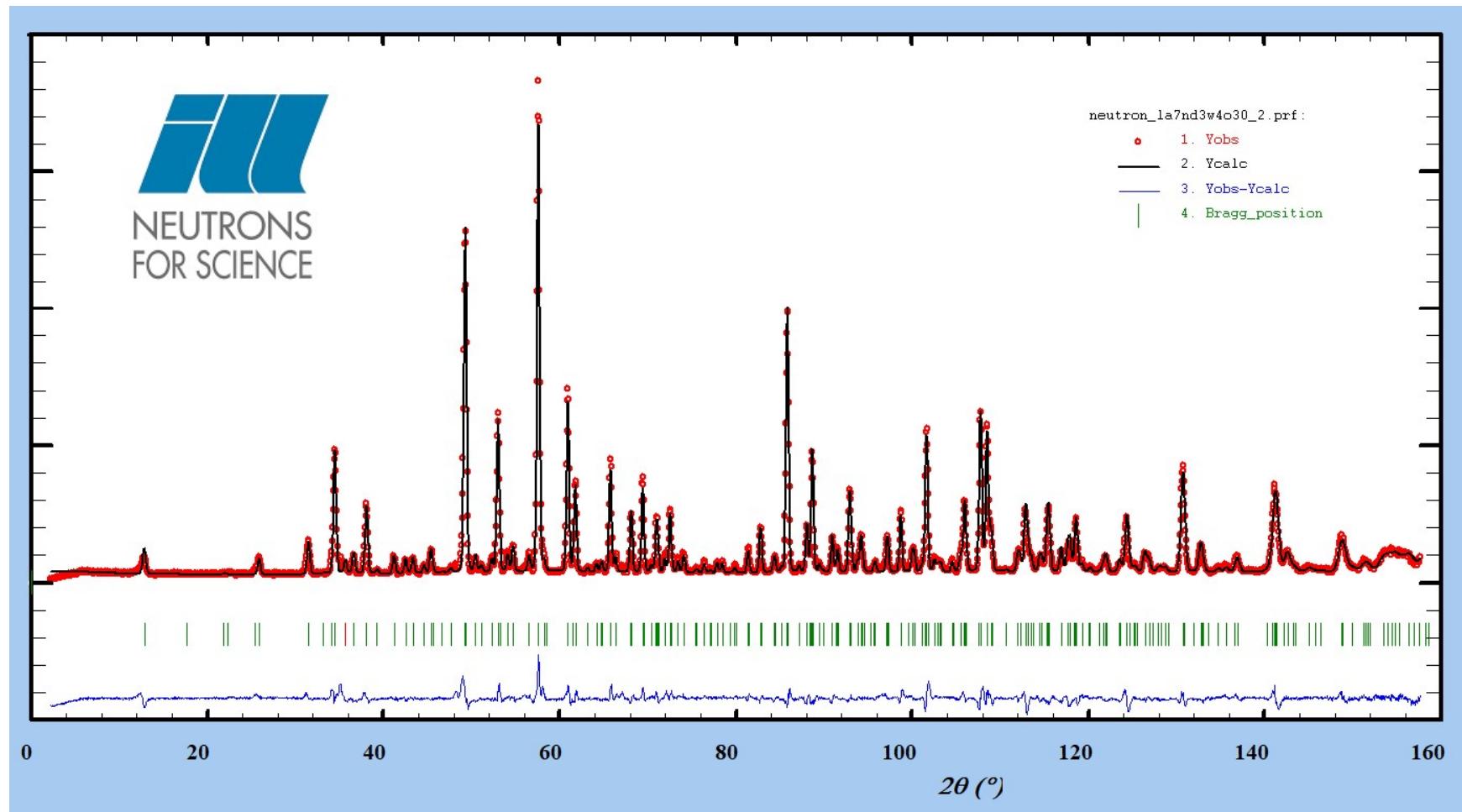
(30 atomic parameters)

Table 2
Crystallographic parameters of $La_7Nb_3W_4O_{30}$

Atom	Site	x	y	z	$B(\text{Å}^2)$
La1	3a	0	0	0	0.9(2)
Nb1	3b	0	0	0.5	1.9(2)
La2	18f	0.7773(2)	-0.0170(2)	0.3445(4)	0.88(5)
W2/Nb2	18f	0.2008(2)	0.0154(2)	0.1595(3)	0.36(6)
O1	18f	0.2458(2)	0.1003(3)	0.3550(2)	0.89(7)
O2	18f	0.2935(2)	0.0433(2)	-0.0079(2)	1.03(7)
O3	18f	0.1689(3)	0.1127(3)	0.0445(2)	1.08(7)
O4	18f	0.2045(3)	-0.0721(3)	0.3054(2)	0.86(6)
O5	18f	0.0351(2)	0.1047(2)	0.3245(2)	1.05(7)

Note : Space group R-3 (N°148), Z=3,
Cell parameters : a= 17.0640 (2) Å, c= 6.8859 (1) Å.
R_{wp}=10.7%, χ^2=3.46, R_{exp}=5.80%, R_B=4.48% (450 reflections)
Calculated density = 7.08 g.cm^{-3}, measured density = 7.03(1) g.cm^{-3}

NEUTRONS FOR SCIENCE
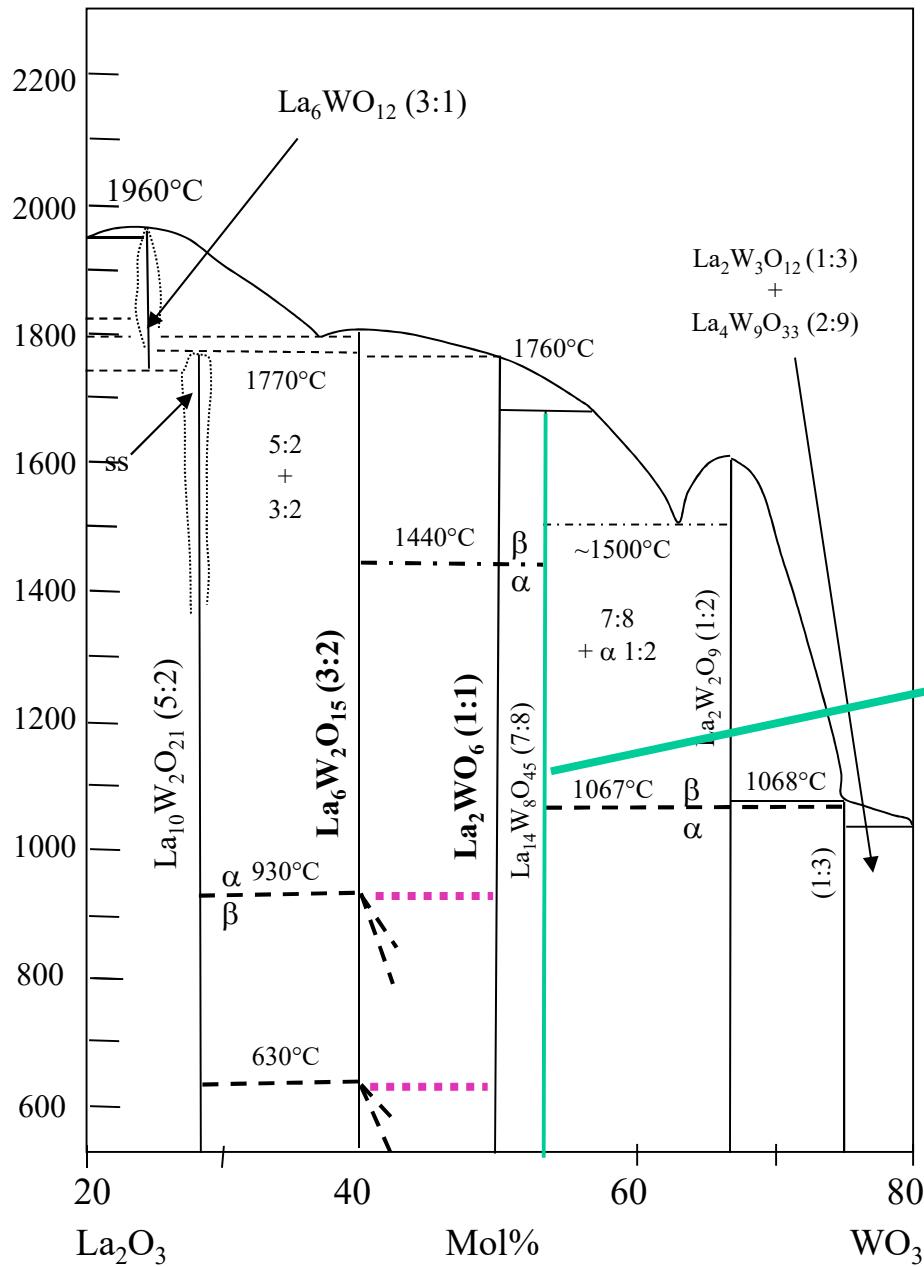
Phase diagram La_2O_3-WO_3

« Hight temperature phase relation in the system La_2O_3-WO_3 », M. Yoshiumura ; A. Rouanet ; *Mater. Res. Bull.* , vol.**11** , 151-158, (**1976**)
F. G. Casteels, M. J. Brabers, and R. DePaus, *Rev. Int. Hautes Temp. Refract.*, **16** [4] 424-436 (1980)

$La_{14}W_8O_{45}$ (7:8)
53.3 % WO_3

Slide 7

Wrong !!!

Starting formula $La_{14}W_8O_{45}$
53,3% mol. WO₃

Reformulation : $La_{18}W_{10}O_{57}$
soit **52,6%mol. WO₃**

- Hexagonal cell :
- a ≈ 9.0448(1)Å,
- c ≈ 32.6846(3)Å
- V≈ 2315,25(0,03)Å³
- Space group :
- P-62c (n°190)
- Z = 2

**SDPD Round Robin 3
2008
Armel LeBail (Univ Le Mans)**

- Structure
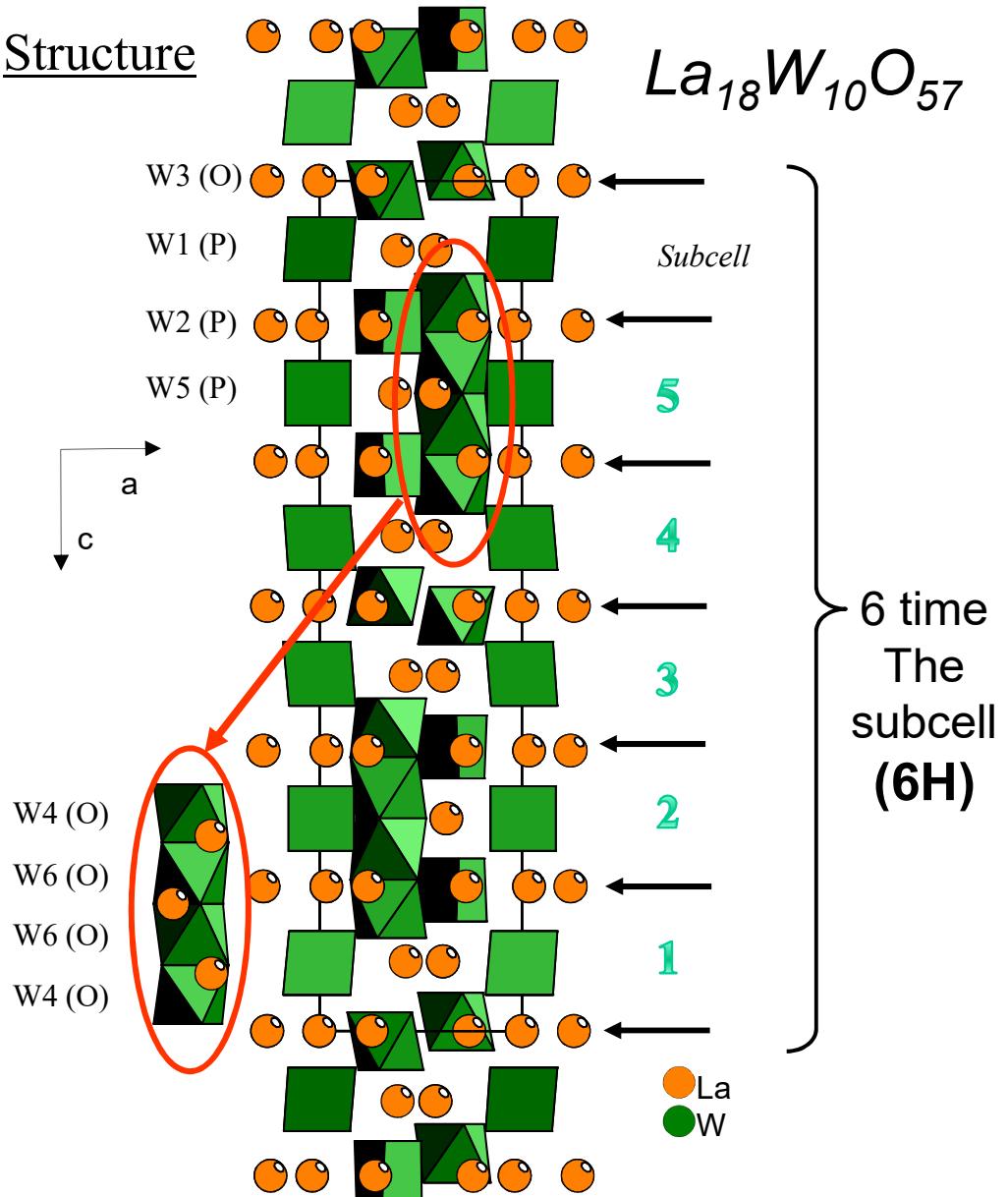
$La_{18}W_{10}O_{57}$

W3 (O)
W1 (P)
W2 (P)
W5 (P)

Subcell

5
4
3
2
1

W4 (O)
W6 (O)
W6 (O)
W4 (O)

6 time
The
subcell
(6H)

La
W

a
c

Slide 8

$La_{18}W_{10}O_{57}$

Slide 9
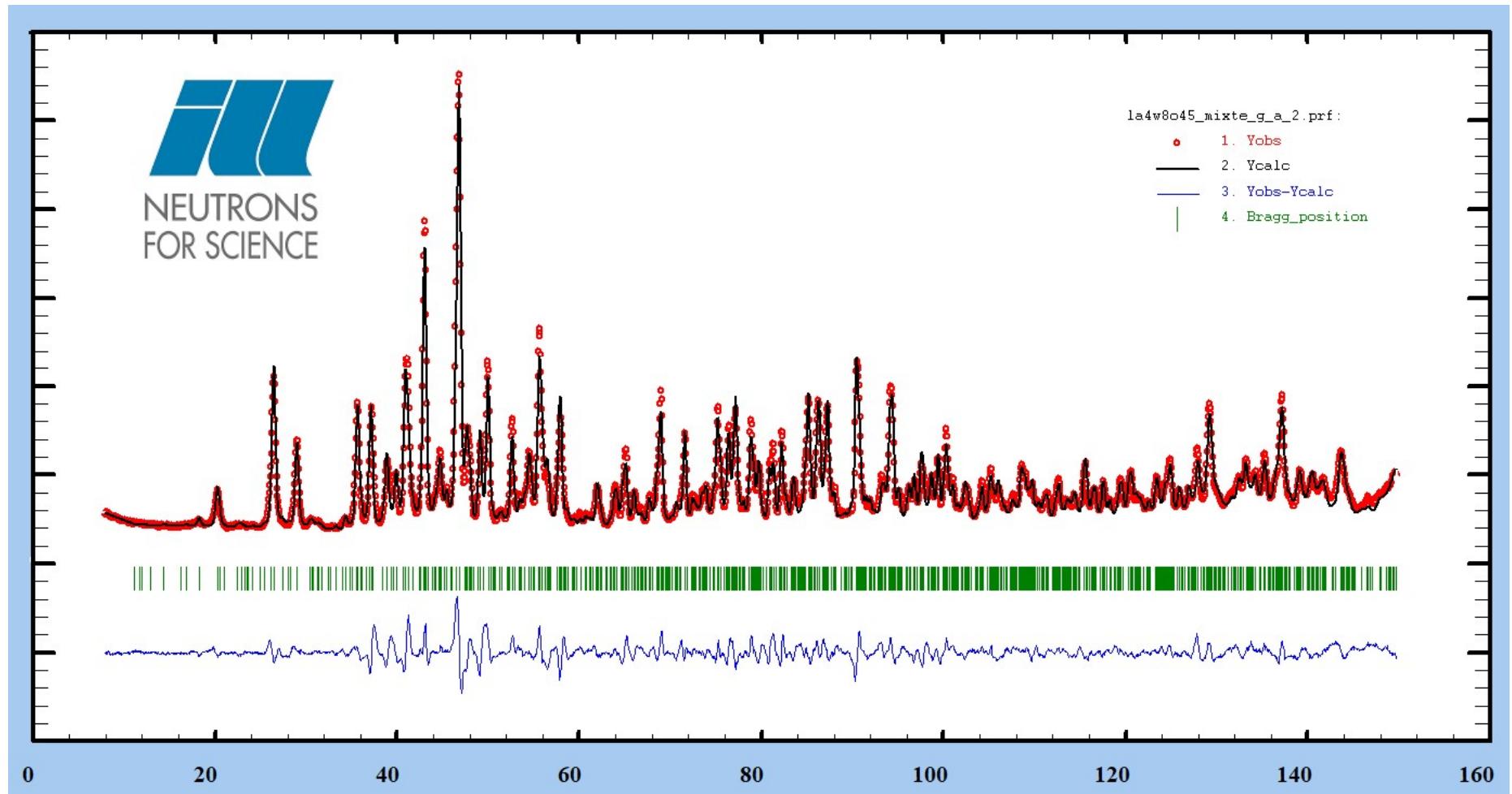
$La_{18}W_{10}O_{57}$ (64 atomic parameters)

Crystallographic parameters of $La_{18}W_{10}O_{57}$ obtained from mixed refinement

Conclusion :
crystallography
help you to get
good composition

Atom	Position	X	Y	Z	Biso(Å)
La1	12i	0.6158(7)	0.0398(6)	0.5838(2)	1.3(1)
La2	12i	0.2764(5)	0.0351(5)	0.3320(2)	0.6(1)
La3	6h	0.3711(9)	0.4295(10)	¼	0.8(1)
La4	6g	0.7434(8)	0.7434(8)	½	0.9(2)
W1	4e	0	0	0.5846(2)	0.6(1)
W2	4f	2/3	1/3	0.6670(2)	0.6(1)
W3	4f	1/3	2/3	0.0032(2)	0.6(1)
W4	4f	2/3	1/3	0.3637(2)	2.2(2)
W5	2a	0	0	¼	0.4(2)
W6	4f	2/3	1/3	0.2812(3)	0.9(2)
O1	12i	-0.169(2)	-0.016(2)	0.2121(3)	-0.05(17)
O2	12i	-0.026(2)	-0.177(2)	0.6188(4)	1.3(2)
O3	12i	0.692(2)	0.510(2)	0.7044(4)	1.1(2)
O4	12i	0.519(2)	0.709(2)	0.0454(3)	0.2(2)
O5	12i	0.678(2)	0.506(2)	0.6304(3)	0.6(2)
O6	12i	0.154(2)	0.179(2)	0.5442(4)	0.9(2)
O7	12i	0.472(2)	0.186(2)	0.3916(3)	0.00(14)
O8	12i	0.138(2)	0.594(2)	-0.0220(4)	2.5(3)
O9	6h	0.473(2)	0.180(2)	1/4	1.1(3)
O10	12i	0.516(2)	0.364(2)	0.3238(4)	1.9(3)

* half occupied site

Synchrotron: 1076 reflections, RBragg=8.75%, Rwp=20.0%

Neutron : 883 reflections RBragg=6.28%, Rwp=15.4%.

Space group P-62c (N°190), a = 9.04831(4)Å, c= 32.6975(2)Å,

Z=2, Calculated density = 7.52 g.cm^{-3}, measured density = 7.28(3) g.cm^{-3}

Slide 10
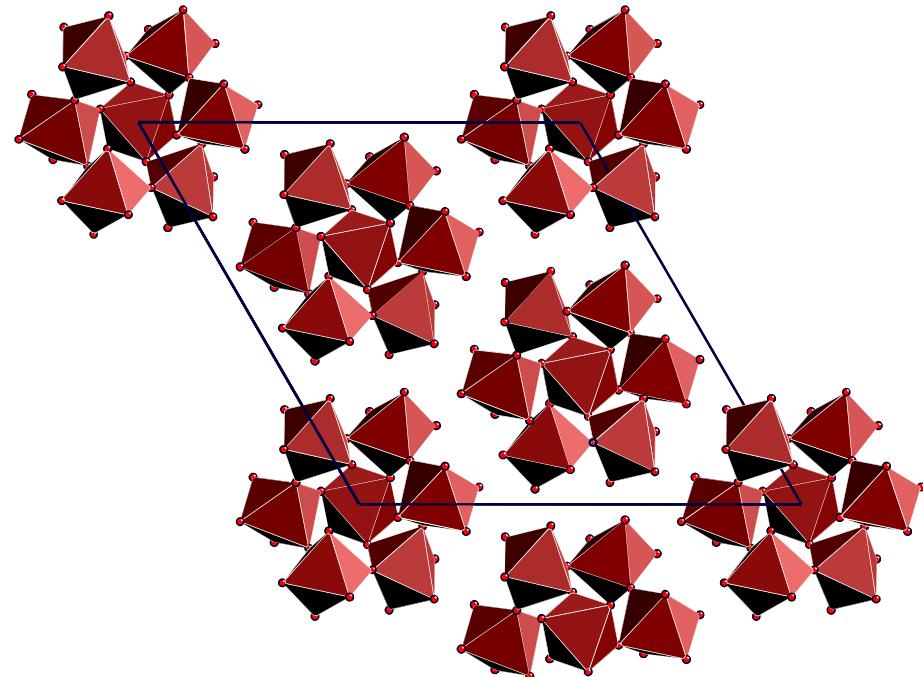
Structure

Cell parameters
$a, b, c, \alpha, \beta, \gamma$
(7 crystal systems)

Space group
Punctual symmetry + translation elements
(230 groups)

## Atomic positions
x, y, z

Slide 11

Structural data


*3D*

Single Crystal
1 000 000 resolutions

Why Powder

Structural data

3D
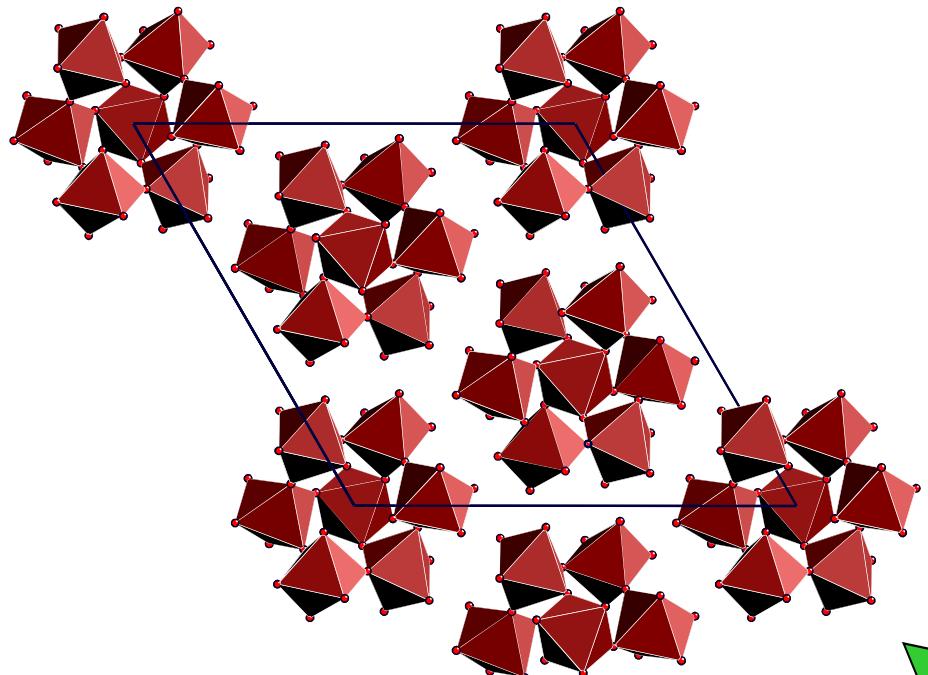
Single Crystal
~ 1 000 000 resolutions

Quick
Identification
Quantification

1D
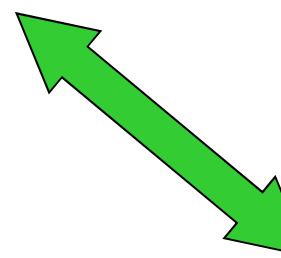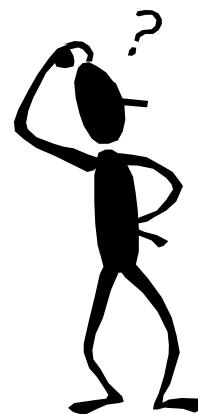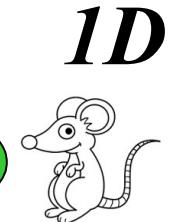
Powder

~ 30 000 resolutions

Slide 13

3 Dimensions data
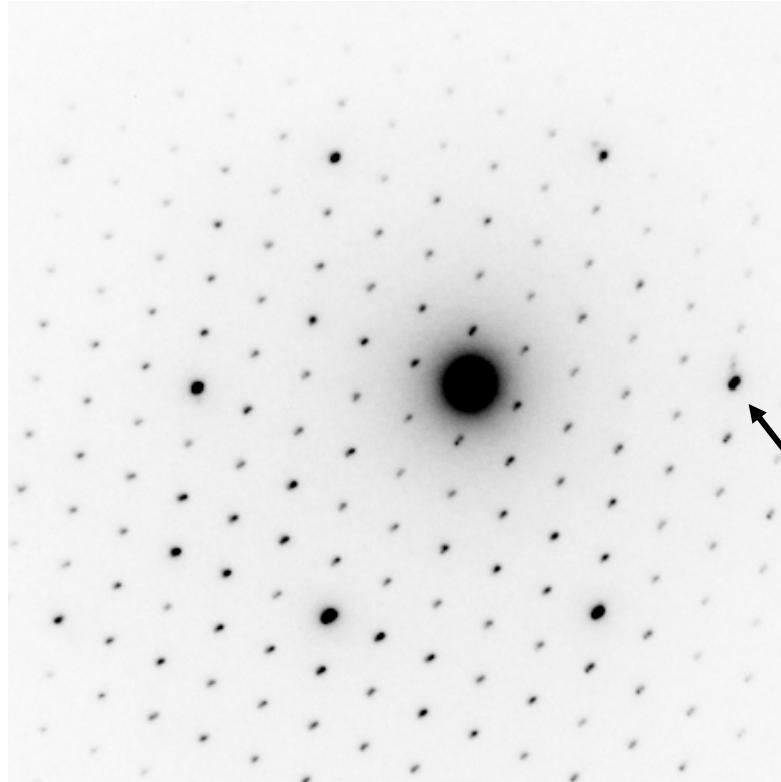
Individual intensity
I(hkl)

Electron diffraction

Slide 14

Partial structure resolution

Slide 15
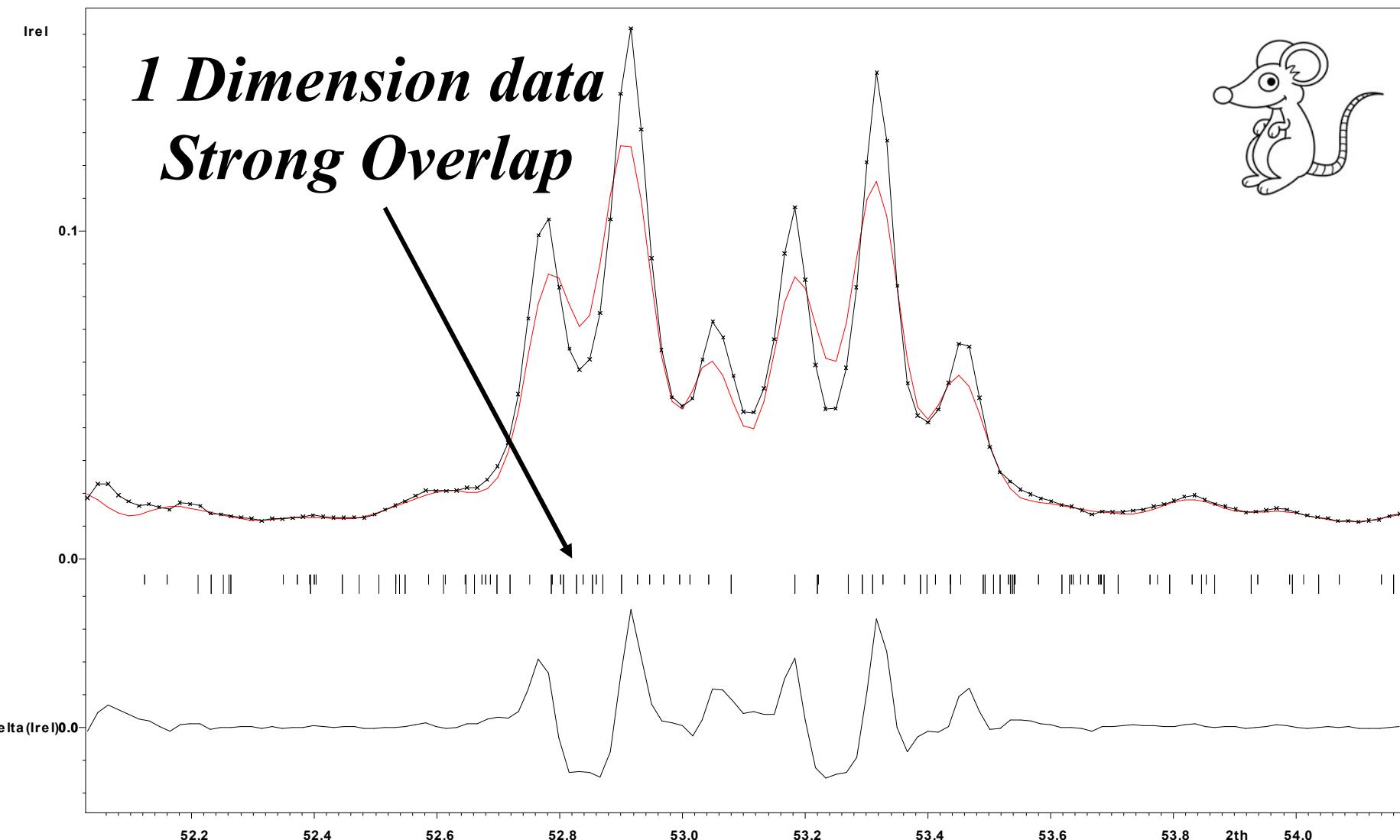
Why Powder

Single Crystal

Ideal size
100-300 μm

Powder

Ideal size
1-10 μm
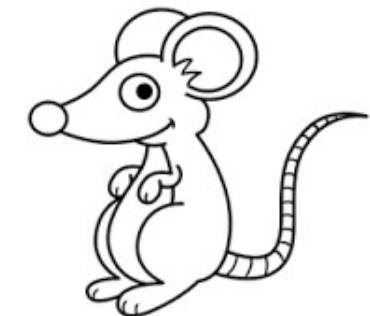
When is it difficult to obtain single crystal ?

$La_2W_2O_9$

$$(\Delta V/V)_{1060-1080} \approx 7.5\%$$

Slide 17

$La_2W_2O_9$

1366 (hkl)

Slide 18
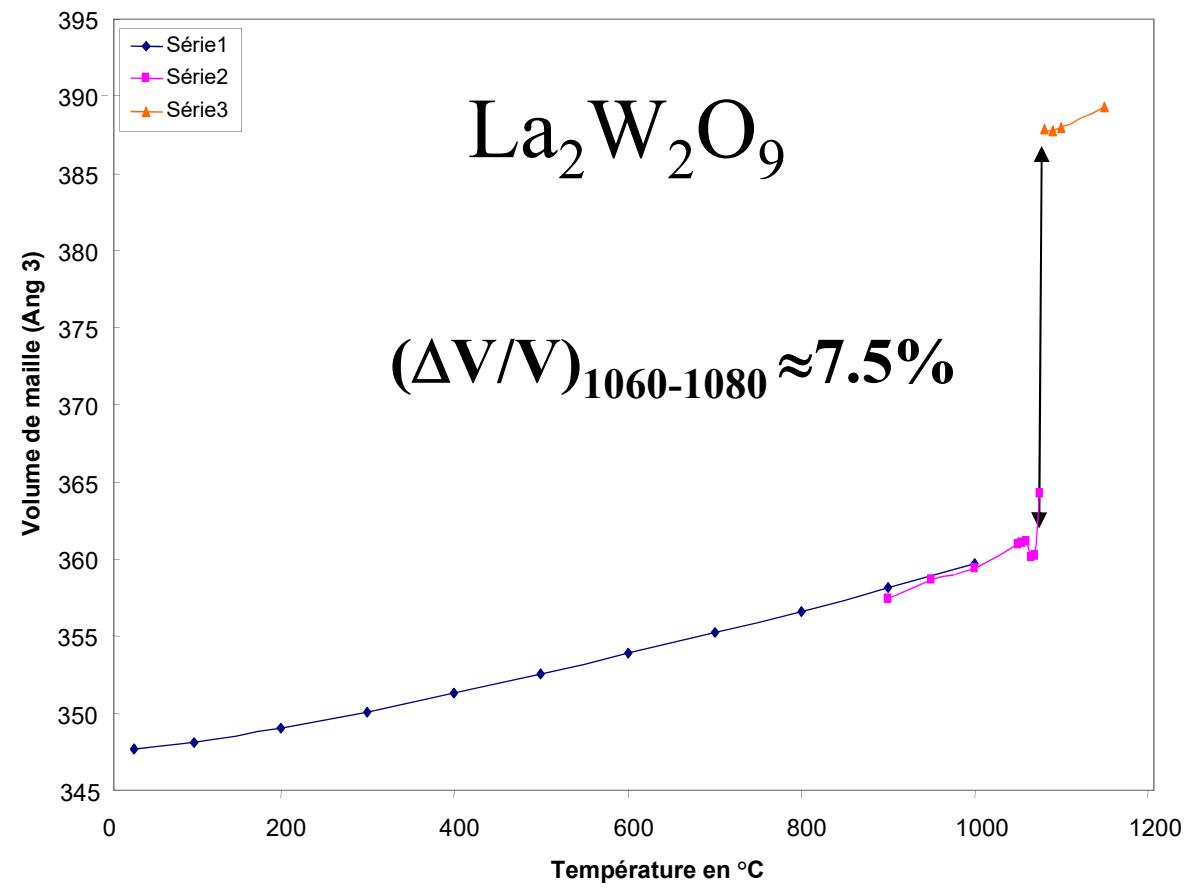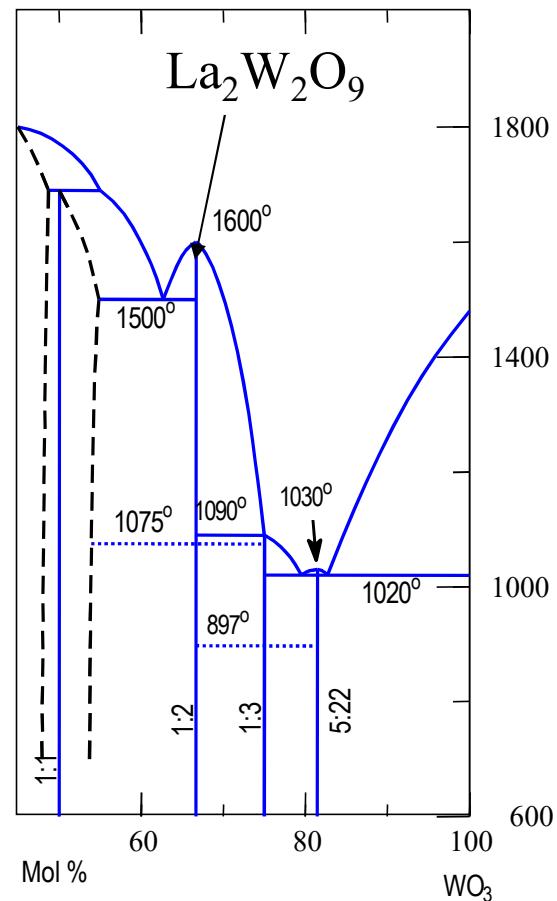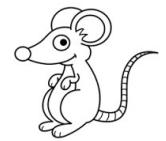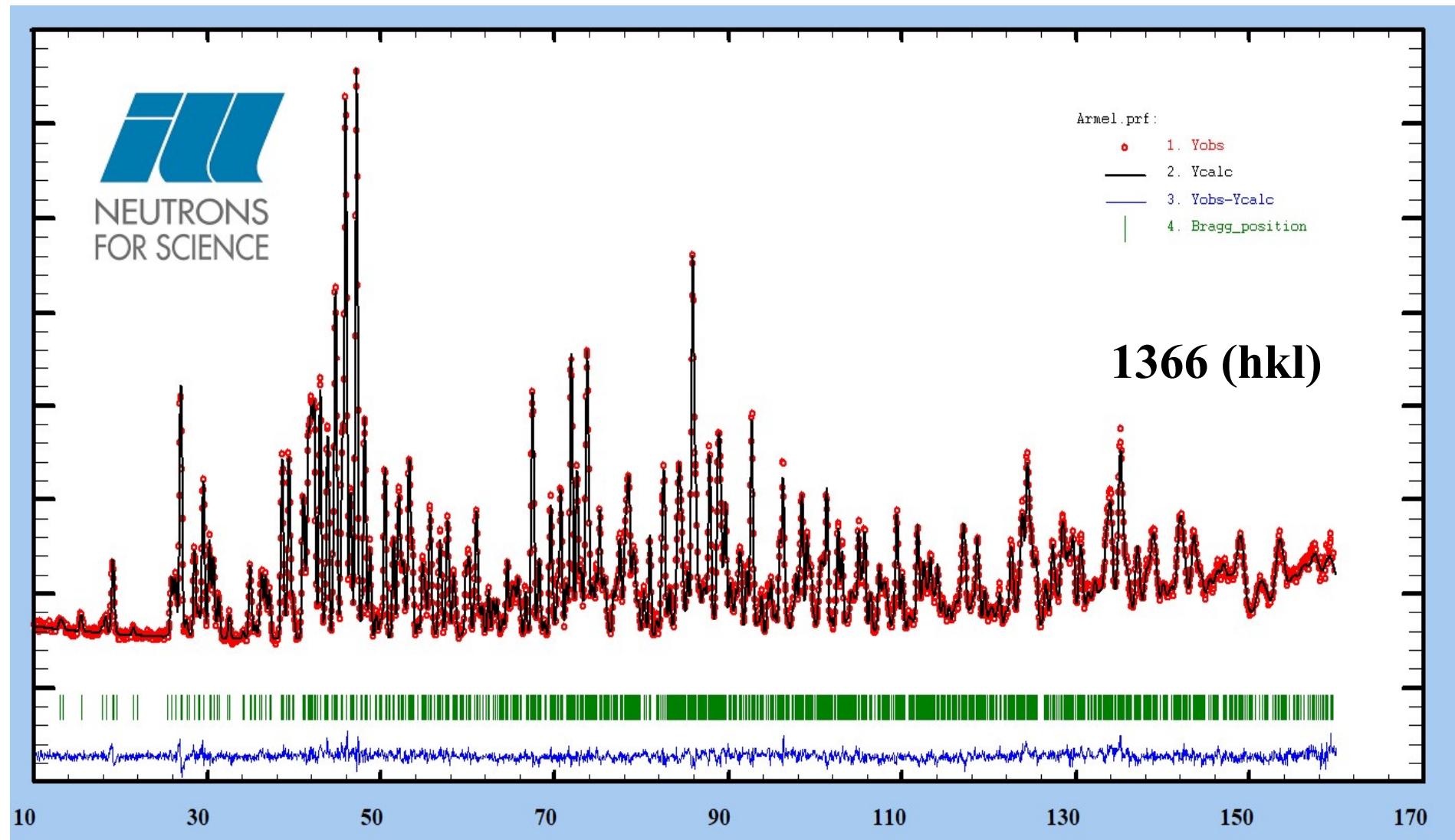
Crystal. parameters $La_2W_2O_9$ (52 atomic parameters)

|	x	y	z	B_{iso} (Å^2)
La1	0.8480(3)	0.7410(3)	0.1568(3)	0.33(3)
La2	0.5837(3)	0.7297(3)	0.6258(3)	0.57(3)
W1	0.6479(4)	0.2037(5)	0.8445(5)	0.52(5)
W2	− 0.0635(4)	0.2716(4)	0.2798(4)	
O1	0.1900(4)	0.9065(4)	0.7250(4)	
O2	0.0930(4)	0.4157(4)	0.1883(4)	
O3	0.4630(4)	0.2918(4)	0.0204(4)	
O4	0.1913(4)	0.0526(4)	0.1415(4)	
O5	0.4738(4)	0.0969(4)	0.6830(4)	
O6	0.2552(4)	0.5066(4)	0.6561(4)	0.76(5)
O7	0.0942(4)	0.2237(4)	0.4919(4)	0.93(5)
O8	0.1564(4)	0.7195(4)	0.0113(4)	0.61(5)
O9	0.3510(4)	0.6481(4)	0.3426(4)	0.76(4)

crystallographic solution found *directly* from neutron

Note. Space group $P\bar{1}$; $a = 7.2489(1)$ Å, $b = 7.2878(1)$, $c = 7.0435(1)$, $\alpha = 96.367(1)°$, $\beta = 94.715(1)°$, $\gamma = 70.286(1)°$; $Z = 2$.

Slide 19
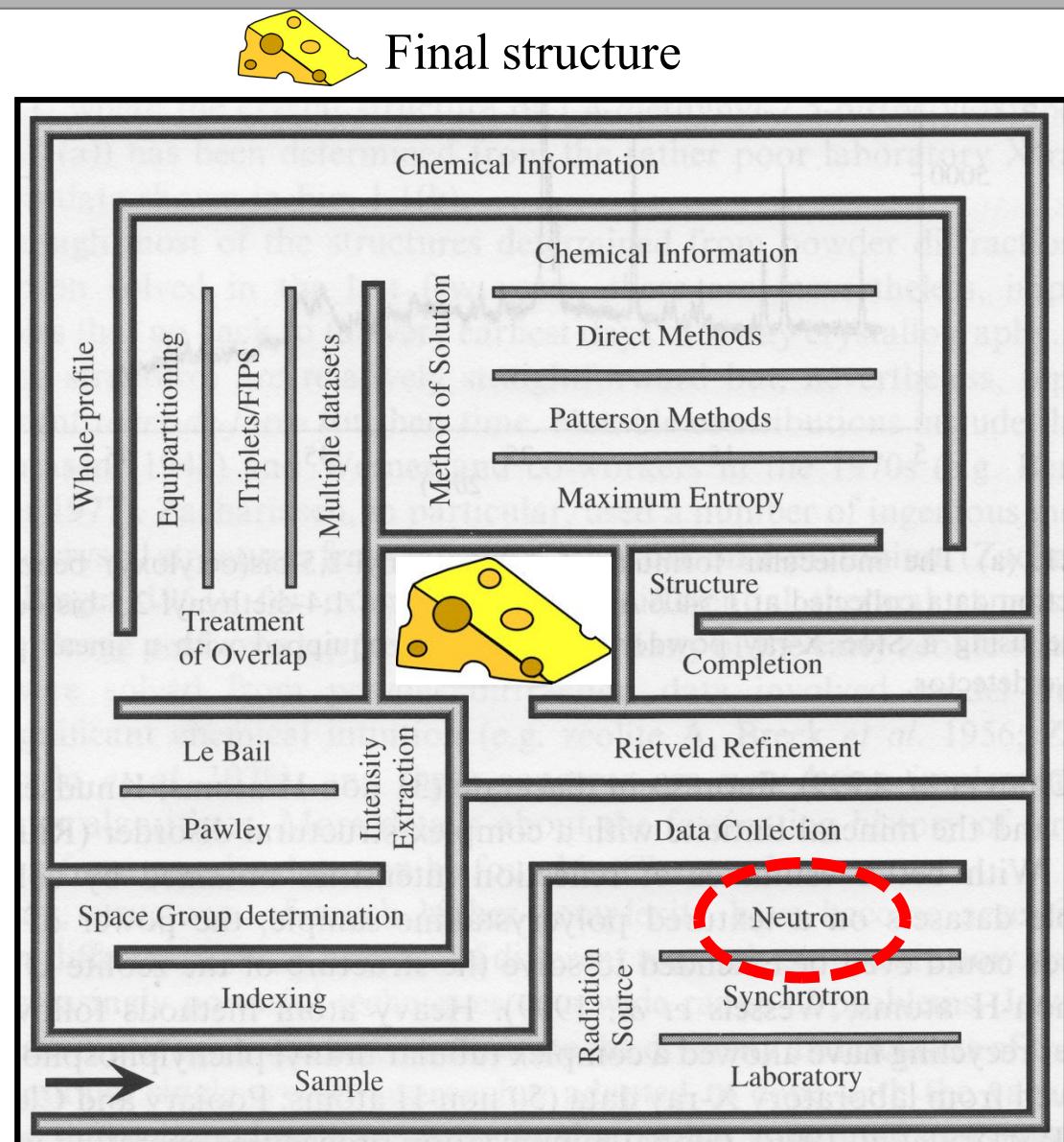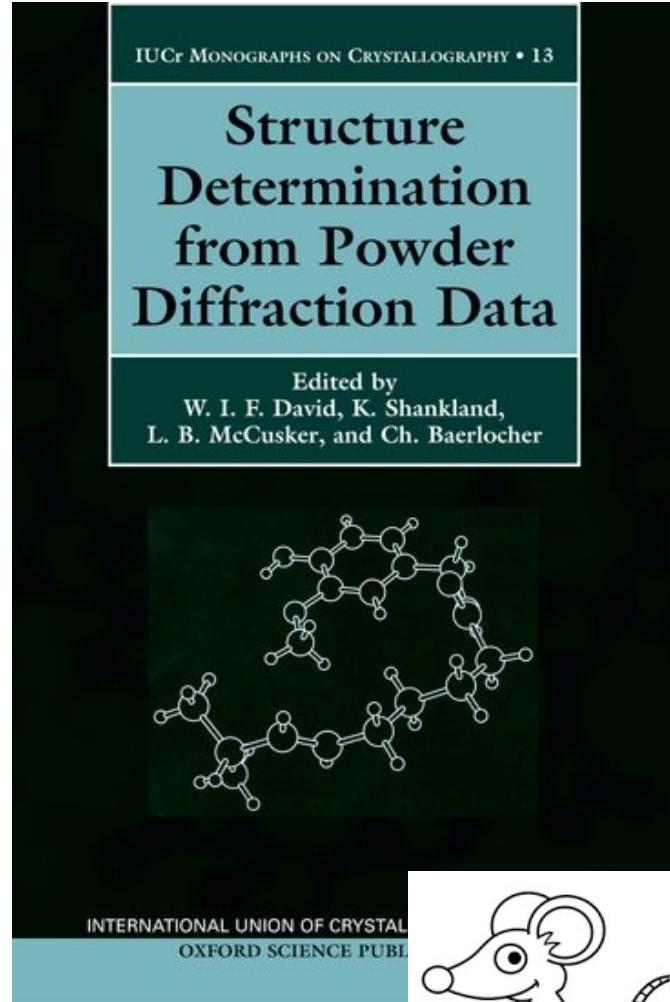
Slide 20

Introduction p4 : The structure determination maze

Ab-initio resolution from powder diffraction

X-Rays

Hydrogen
(1 electron)

Oxygen
(10 electrons)

Molybdenum
Mo6+ (36 e-)

Lanthanum
La3+ (53e-)

Tungsten
W6+ (71 e-)

Neutron

Deuterium
6.67
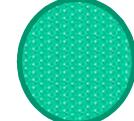
Oxygen
5.80
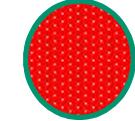
Molybdenum
6.72

Lanthanum
8.24

Tungsten
4.86

Slide 21
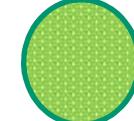
Ab-initio resolution from powder diffraction
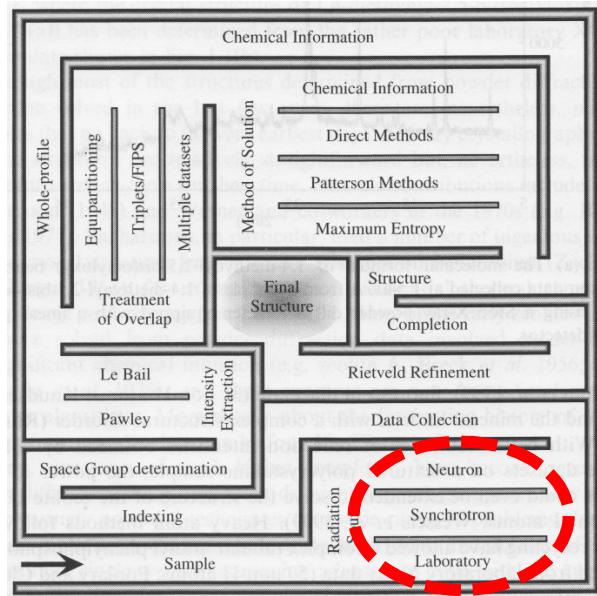
Radiation source : **laboratory high resolution powder diffractometer** in transmission/reflexion mode

Usual wavelength $\lambda=1.5406$Å Copper radiation (Low Cost)
best resolution **FWHM~ 0.040°**

If you are rich ! 10KEuros/day (Proposal)
Synchrotron Radiation
0.4Å $< \lambda < 1.6$Å **FWHM~ 0.008°**

If you are rich ! 25KEuros/day (Proposal)
Neutron Radiation
1.6Å $< \lambda < 2.3$Å **FWHM~ 0.4°**

Slide 22
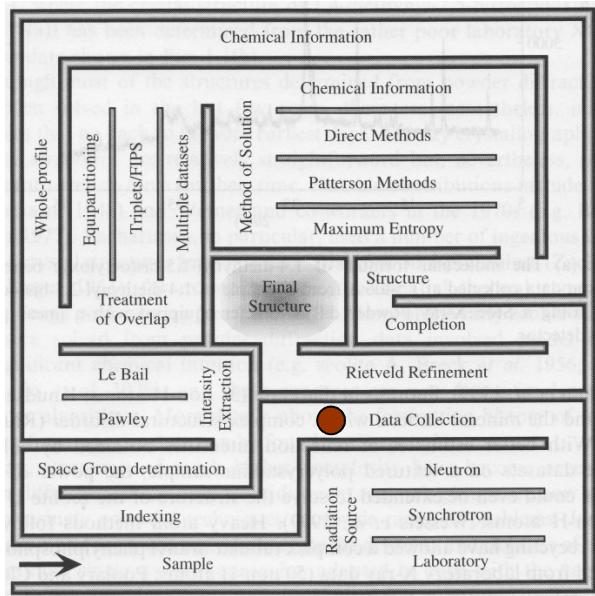
Data collection :
Two sets of data collection:
First set : for indexation
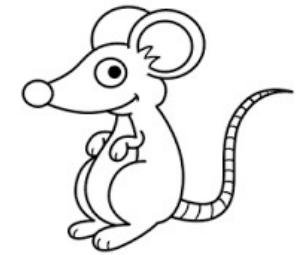
A good counting of the beginning of the diagram :
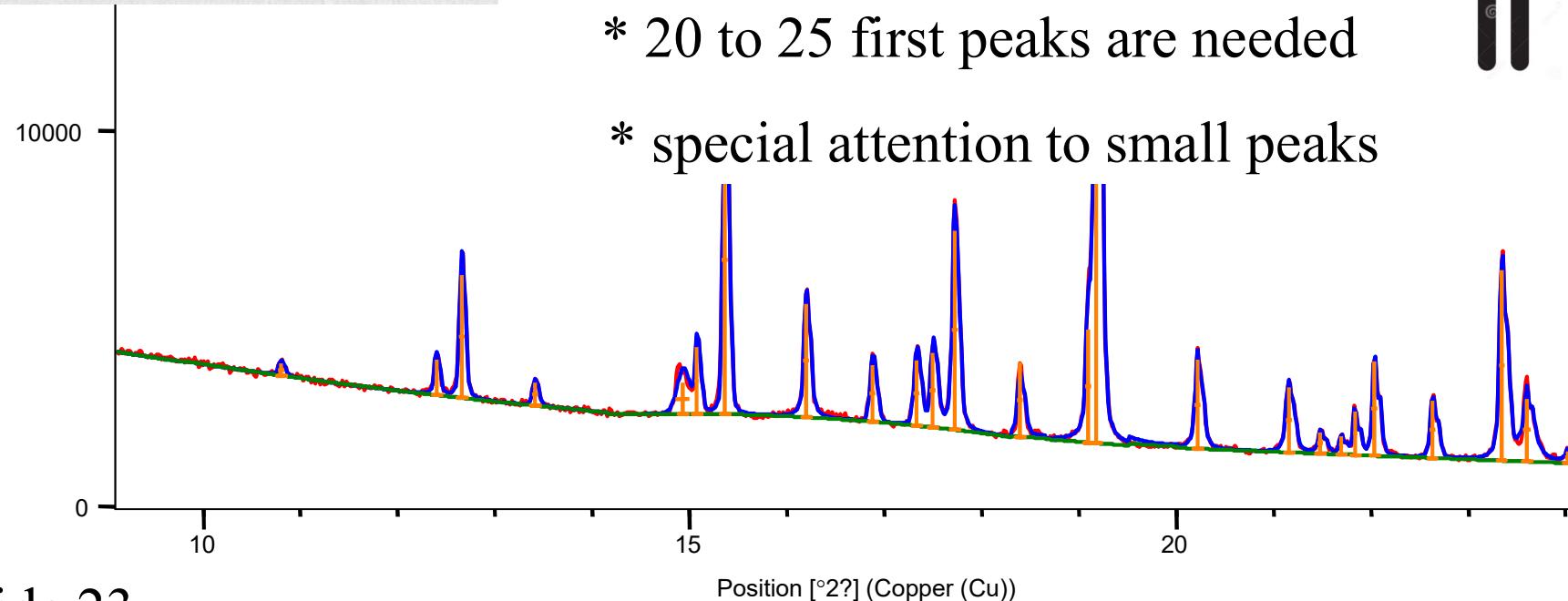
* 20 to 25 first peaks are needed

* special attention to small peaks

Position [°2?] (Copper (Cu))

Slide 23

Data collection :
Two sets of data collection:
**Second set : for structure solution
and refinement**

La_3NbWO_{10}

**A good counting statistic of a
large two-theta range**

Slide 24
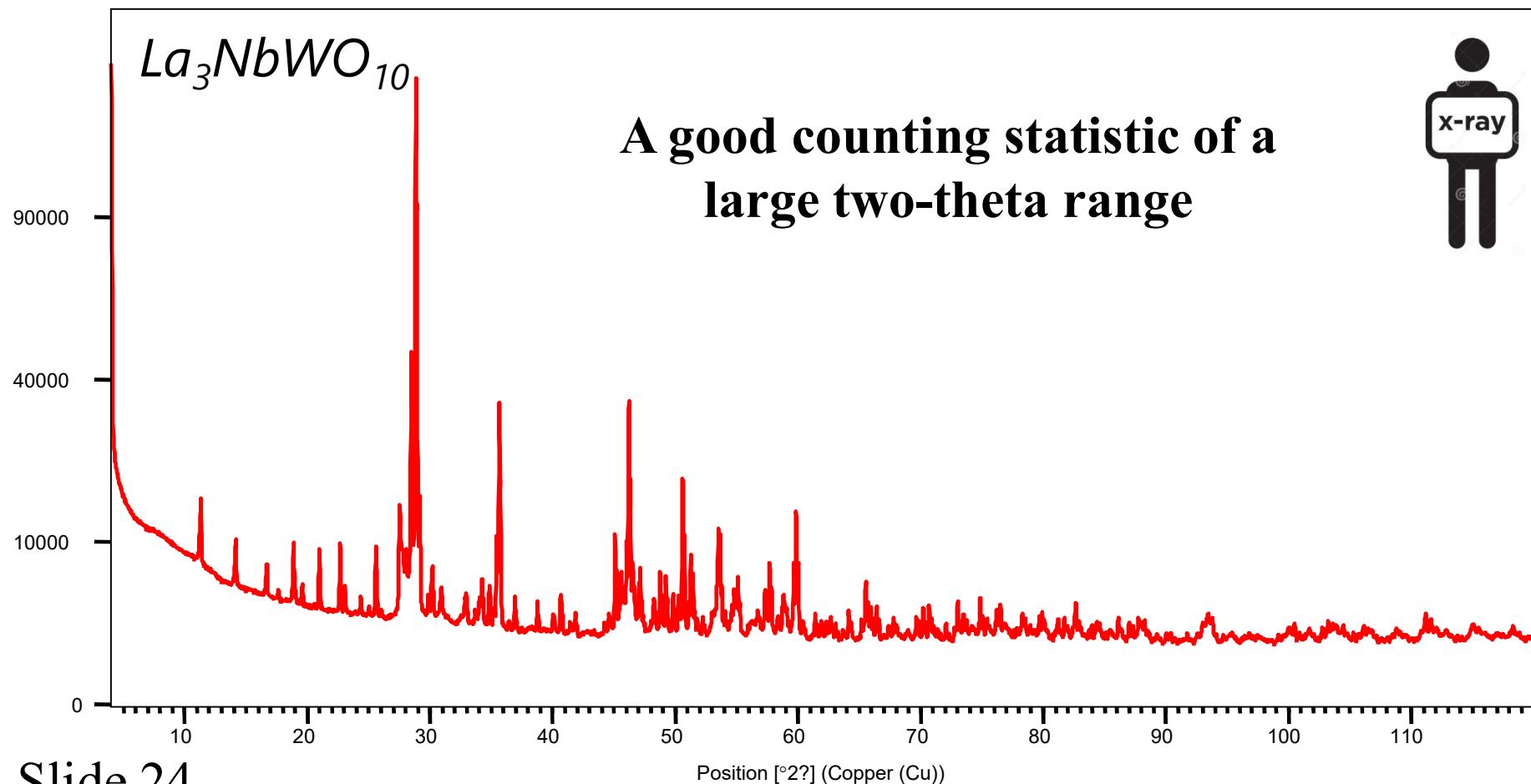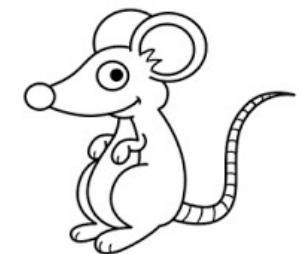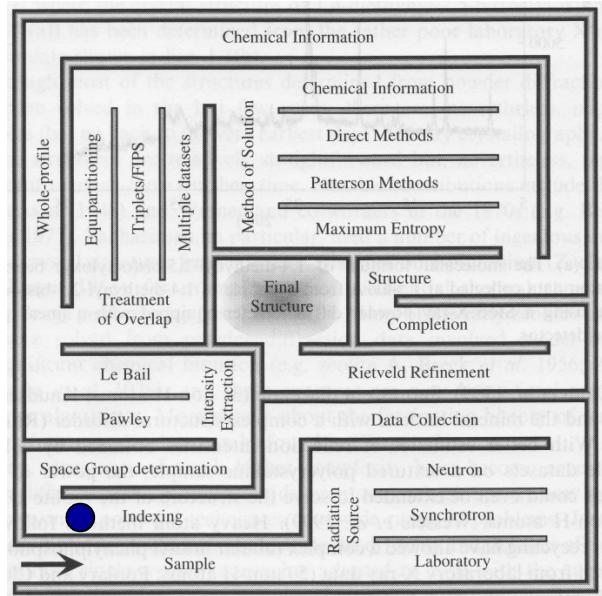
- Indexing (Autoindexation)
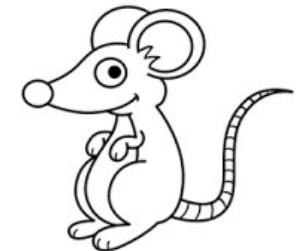
Conditions of success :

Accuracy in the peak position
better than 0.03°
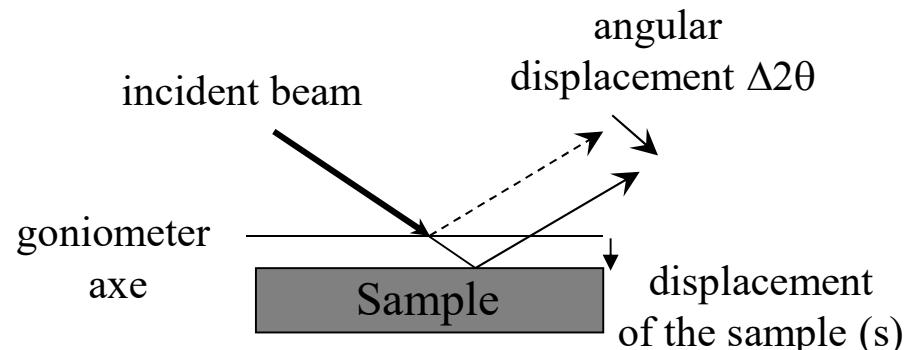
$\Delta 2\theta = (2 \times s \times \cos \theta)/R$ ($\Delta 2\theta$ in radian)

Example : R=200 mm

If $\theta = 10°$

$\Delta 2\theta = 0.03°$ if s=0.05mm = 50μm

Single phase !!

Slide 25

Space group determination
Special case of inorganic compound
Not so easy !!!

La3NbWO10

No.	a [Å]	b [Å]	c [Å]	α [°]	β [°]	γ [°]	Volume [Å3]	Indexing Method	Not indexed lines	FOM
1	12,509	10,062	10,003	90	90	90	1259,0	Treor	2	9
2	10,053	10,053	12,513	90	90	90	1264,6	Treor	**3**	20
3	10,053	10,053	12,513	90	90	90	1264,6	Treor	**3**	20
4	19,906	12,533	5,028	90	90	90	1254,4	Treor	3	8

Tetragonal

Counts

x-ray

Slide 26

Position [°2Theta] (Copper (Cu))

Ab-initio resolution from powder diffraction
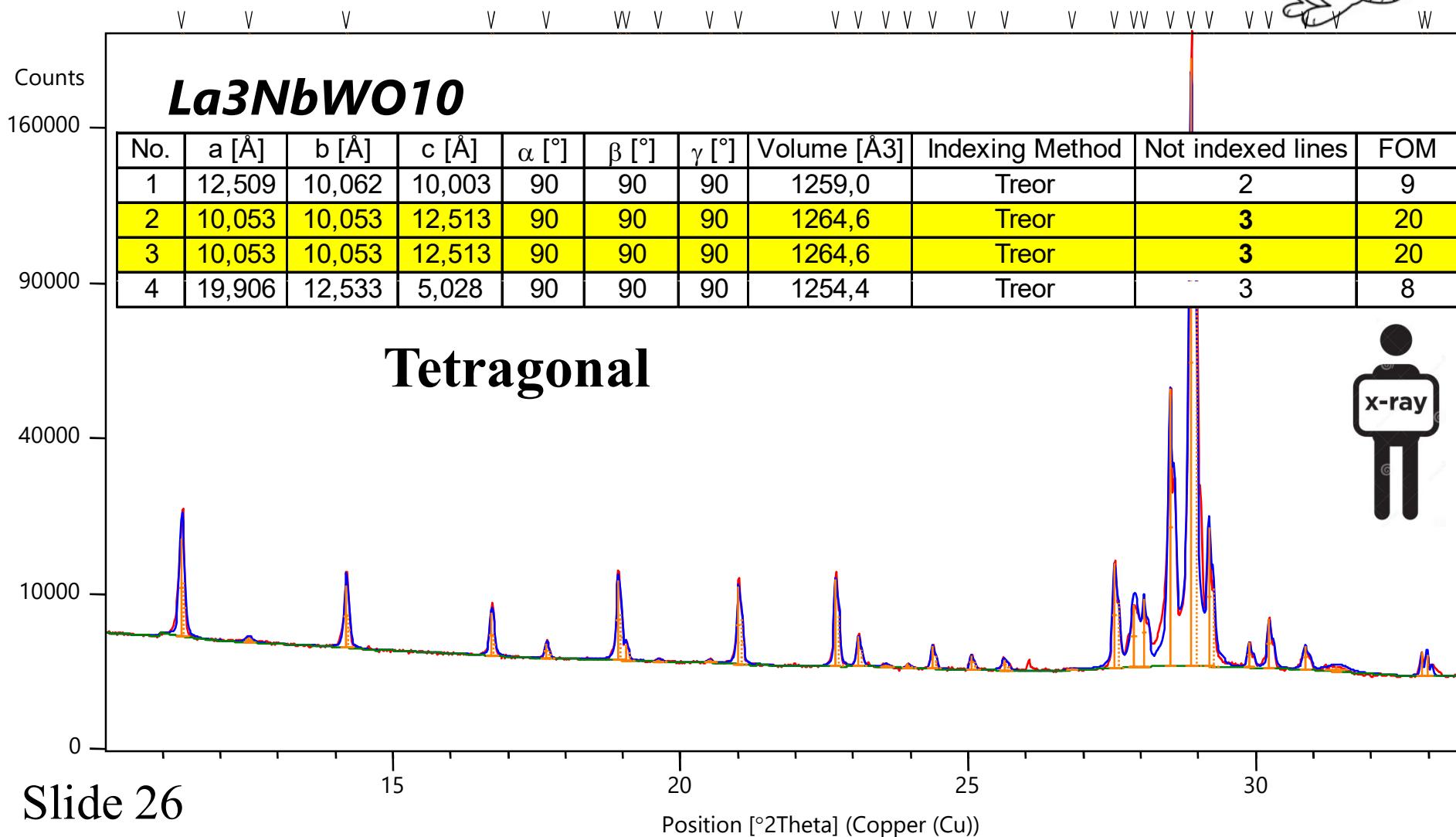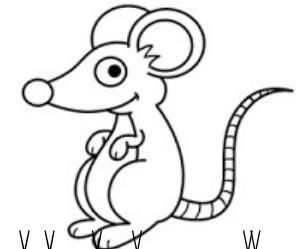
Automatic Space Group Test
(HighScore Plus)
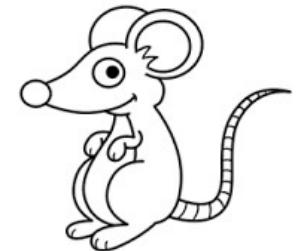
Refine Unit Cell - [Default]

Cell Refinement | Calculated and Observed Peaks | **Space Group Test**

No.	Space Group	Nmi. + Nun.	FOM	No. in ICSD	No. Unexplained Lines	No. Missing Li...
63	P 42/n m c (137)	26	24.2379	57	11	15
8	I -4 (82)	32	19.0854	97	28	4
5	I 4 (79)	32	19.0854	18	28	4
13	I 4/m (87)	32	19.0854	162	28	4
45	I -4 m 2 (119)	32	19.0854	21	28	4
47	I -4 2 m (121)	32	19.0854	51	28	4
33	I 4 m m (107)	32	19.0854	34	28	4
23	I 4 2 2 (97)	32	19.0854	10	28	4
65	I 4/m m m (139)	32	19.0854	781	28	4

La3NbWO10

Le Bail fit ~ a Rietveld refinement without structure
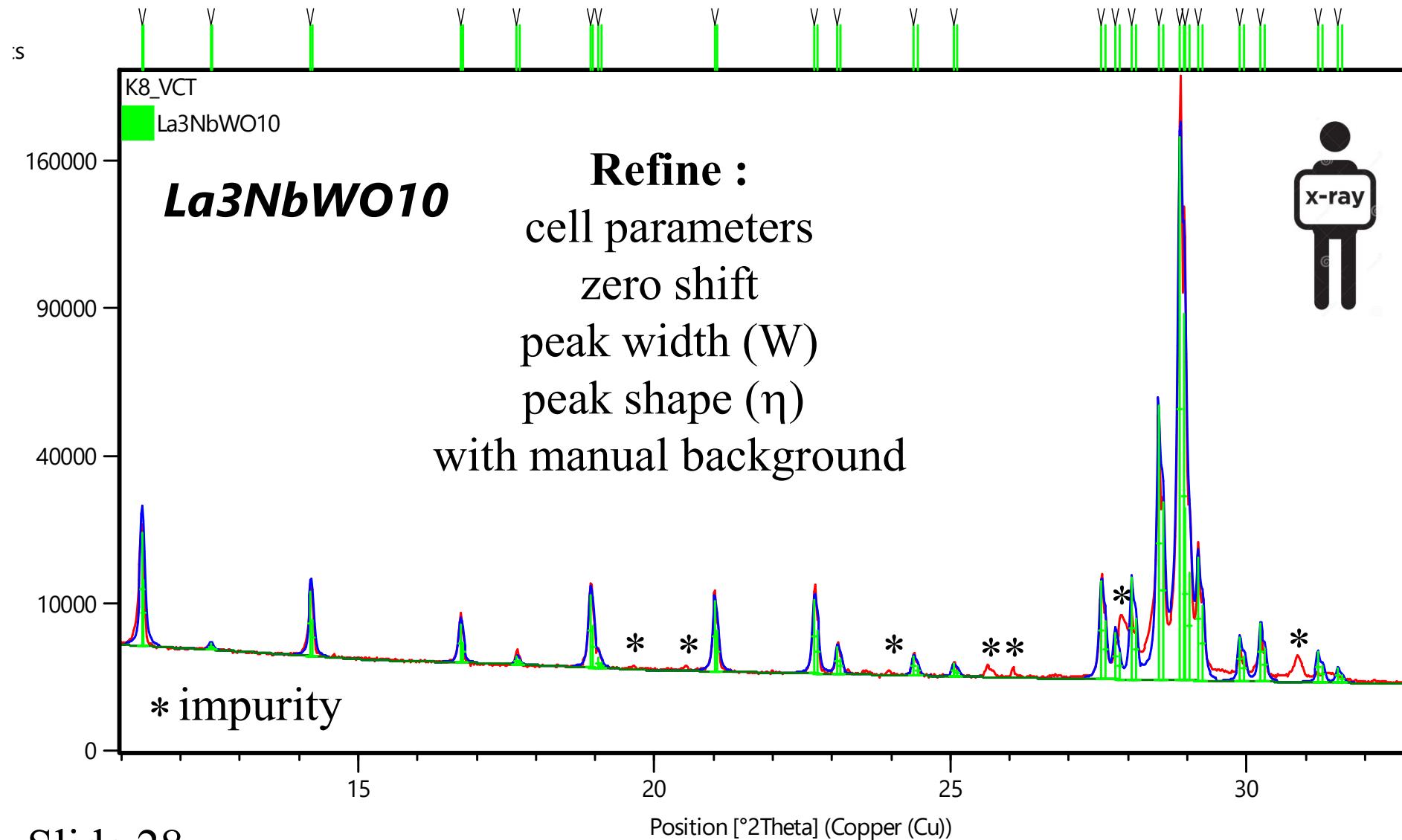
K8_VCT
La3NbWO10

La3NbWO10

Refine :
cell parameters
zero shift
peak width (W)
peak shape (η)
with manual background

∗ impurity

Position [°2Theta] (Copper (Cu))

Slide 28
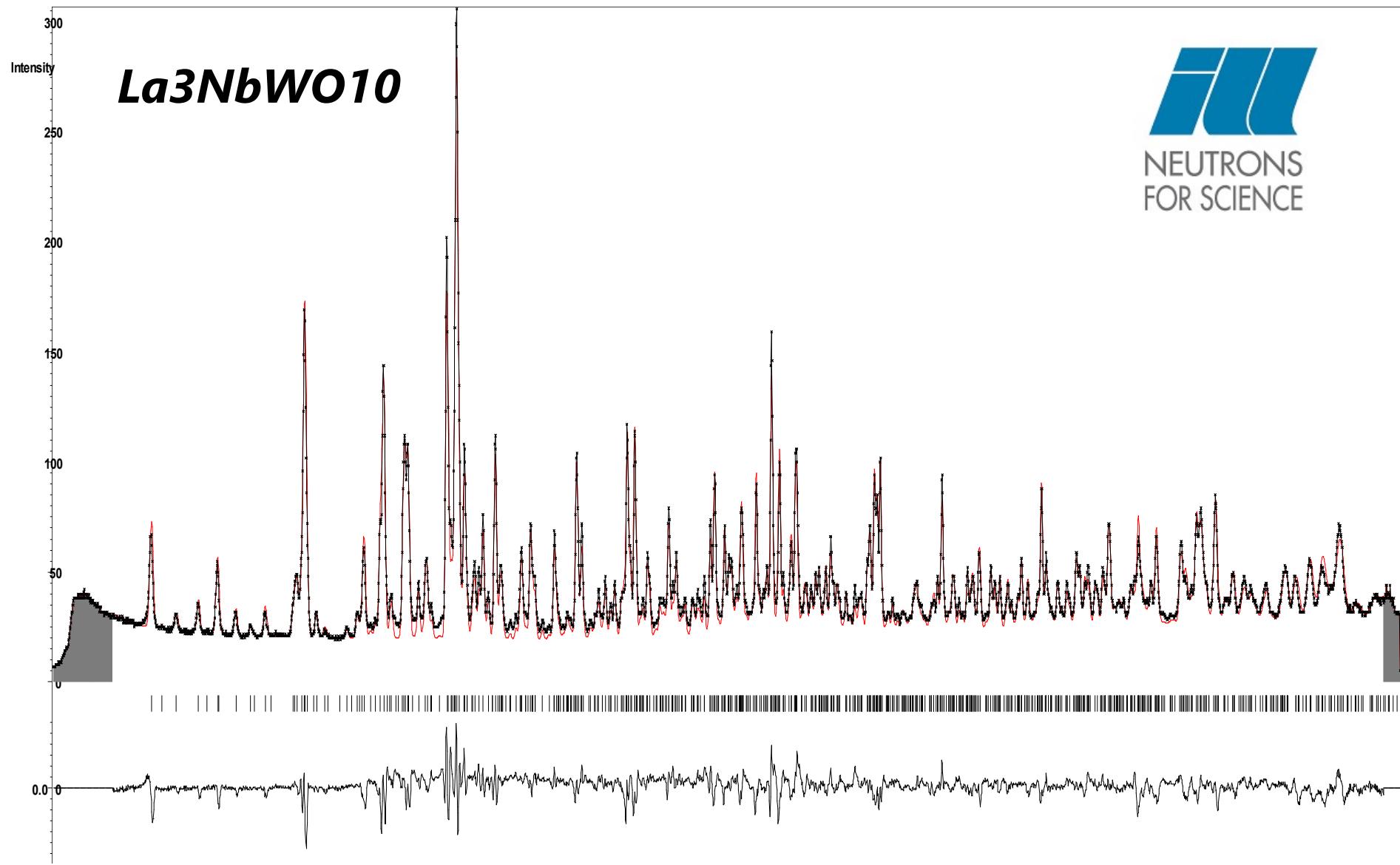
La3NbWO10

La3NbWO10 (39 atomic parameters)

Table 4
Crystallographic positions refined from mixed X-ray and neutron diffraction data of La_3NbWO_{10}: $a=b=10.0807(1)$ Å; $c=12.5540(1)$ Å; $P4_2/nmc$ (no. 137); $Z=6$.

Atom	Multiplicity	x	y	z	B_{iso} (Å^2)	Occupation
La1	8f	0.0216(1)	0.9784(1)	0.75	0.69(1)	1
La2	8g	0.75	0.9757(2)	0.5158(2)	1.62(∗)	1
La3	2a	0.25	0.75	0.25	0.28(7)	1
W1	8g	0.75	0.0538(2)	0.9796(1)	0.30(4)	0.6775(1)
Nb1	8g	0.75	0.0538(2)	0.9796(1)	0.30(4)	0.3225(1)
W2	4d	0.75	0.75	0.2937(3)	0.41(7)	0.145(1)
Nb2	4d	0.75	0.75	0.2937(3)	0.41(7)	0.855(1)
O1	16h	0.3943(4)	0.6195(4)	0.3689(3)	0.61(6)	1
O2	16h	0.5388(5)	0.3910(5)	0.4242(4)	2.28(9)	1
O3	4c	0.75	0.25	0.4867(8)	2.5(2)	1
O4	8g	0.25	0.1294(6)	0.0610(5)	1.6(1)	1
O5	8g	0.25	0.3931(6)	0.2958(5)	1.2(1)	1
O6	8g	0.75	0.5566(5)	0.3155(5)	1.1(1)	1
	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
La2	0.0083(3)	0.0014(2)	0.0015(2)	0	0	−0.0009 (2)

Mixed refinement x-ray (lab/synchrotron) + neutron

Science → Society

NEUTRONS FOR SOCIETY

La$_2$Mo$_2$O$_9$ D1B (proposal CRG O.Isnard ILL)

β La$_2$Mo$_2$O$_9$
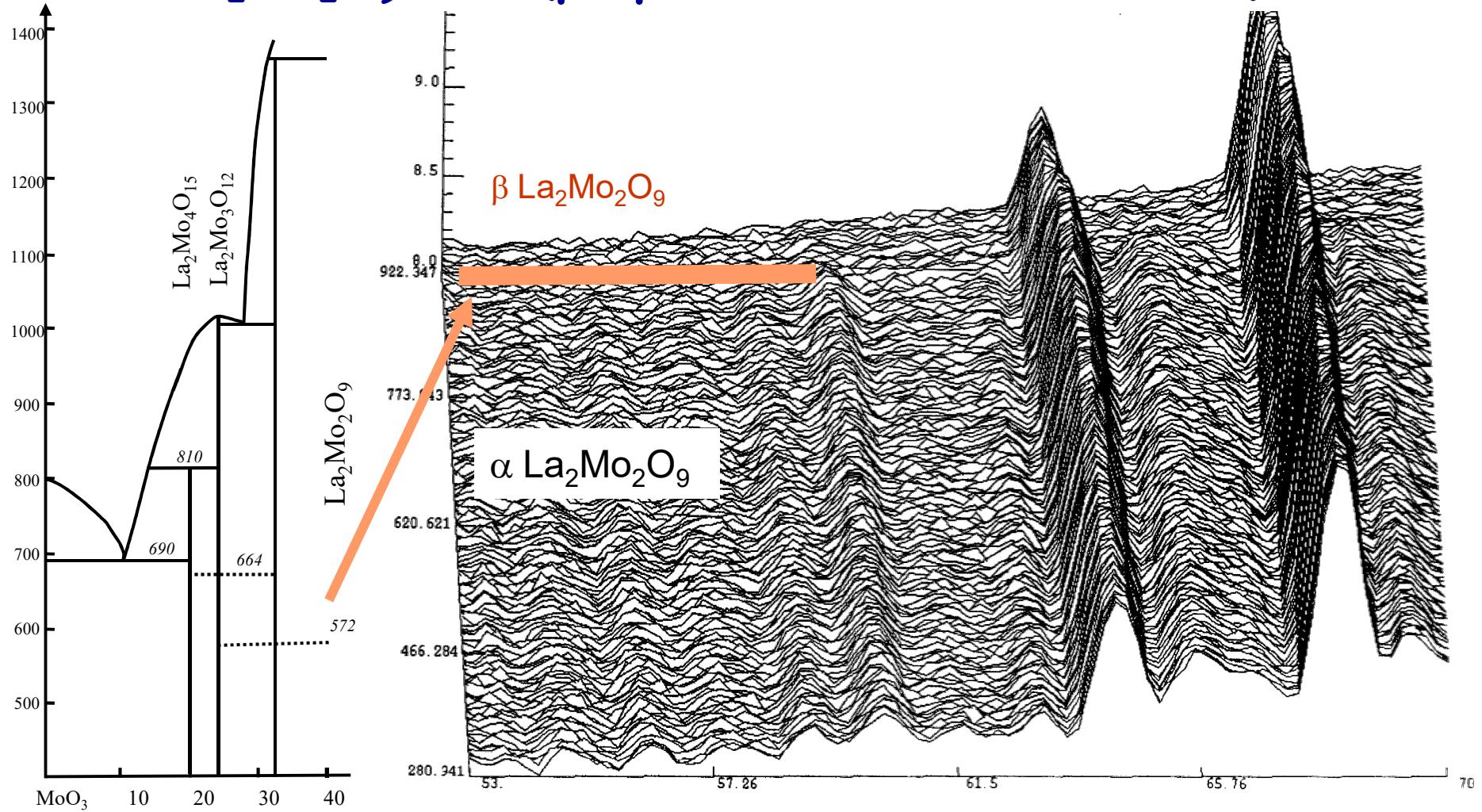
α La$_2$Mo$_2$O$_9$

Unknown structure !!

Slide 31

(13 atomic parameters)

Cubic P2$_1$3 (N° 198)

6. 10^{-2} S.cm^{-1} à 800°C

La$_2$Mo$_2$O$_9$

LAMOX

β

ZrO$_2$-10%Y$_2$O$_3$

ZrO$_2$-13%CaO

phase transition

580°C

α

log(σ) (S.cm^{-1})

1000/T(K)

La$_2$Mo$_4$O$_{15}$

La$_2$Mo$_3$O$_{12}$

La$_2$Mo$_2$O$_9$

810

690

664

572

MoO$_3$
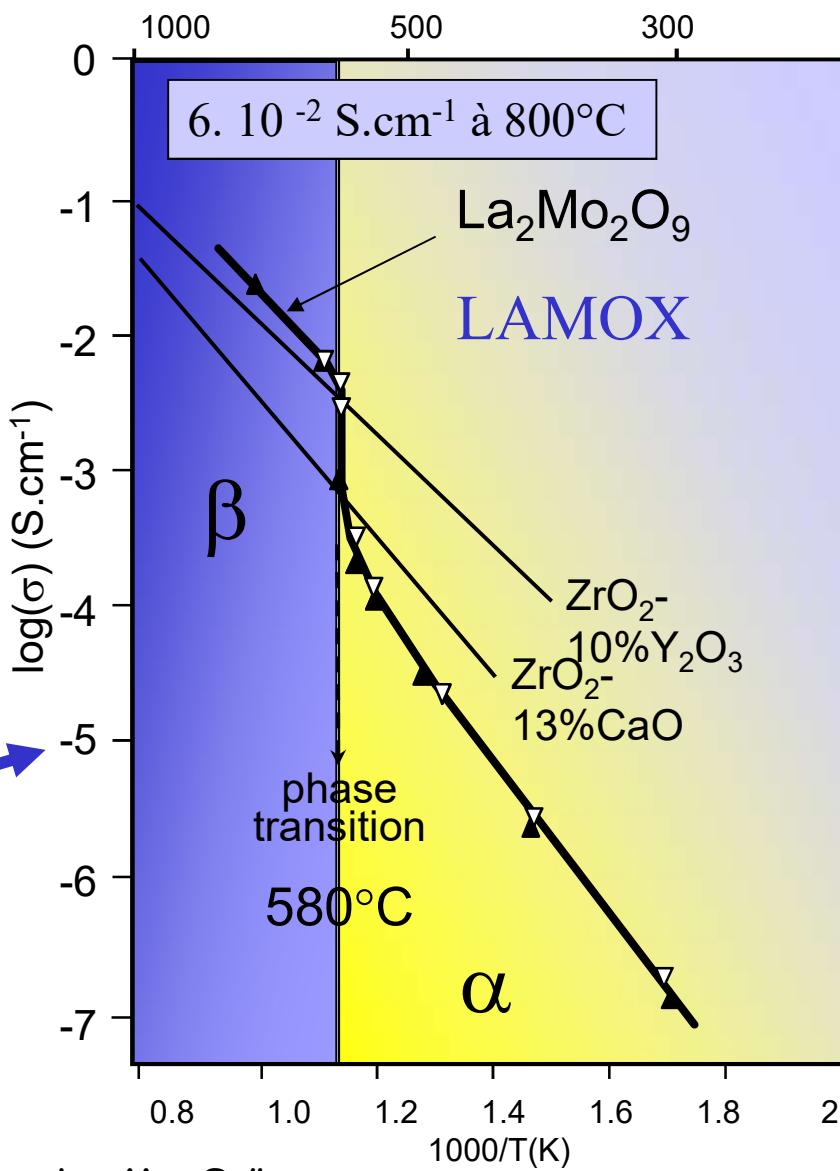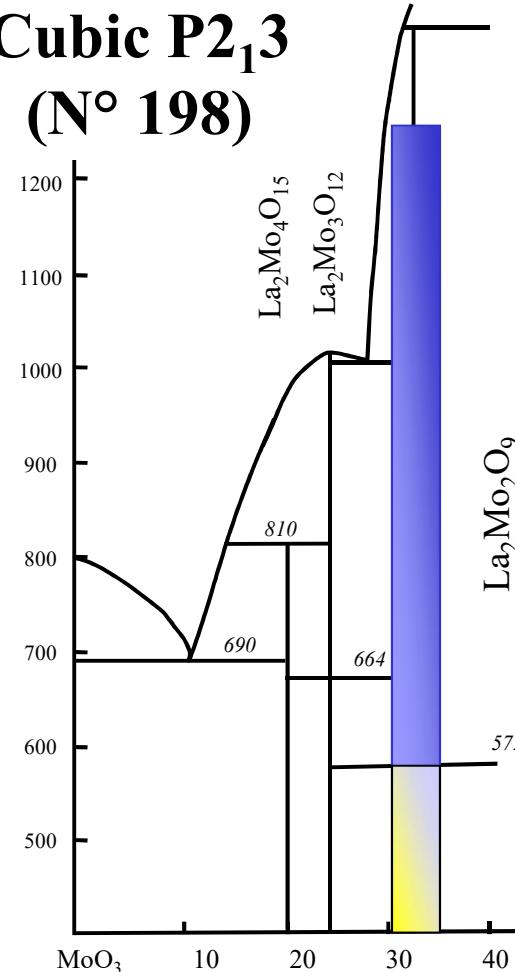
"Designing fast oxide-ion conductors based on La$_2$Mo$_2$O$_9$"
Ph. Lacorre, Nature, 2000, 404, 856-858

Michael F. Ashby
Choix de matériaux en
construction mécanique
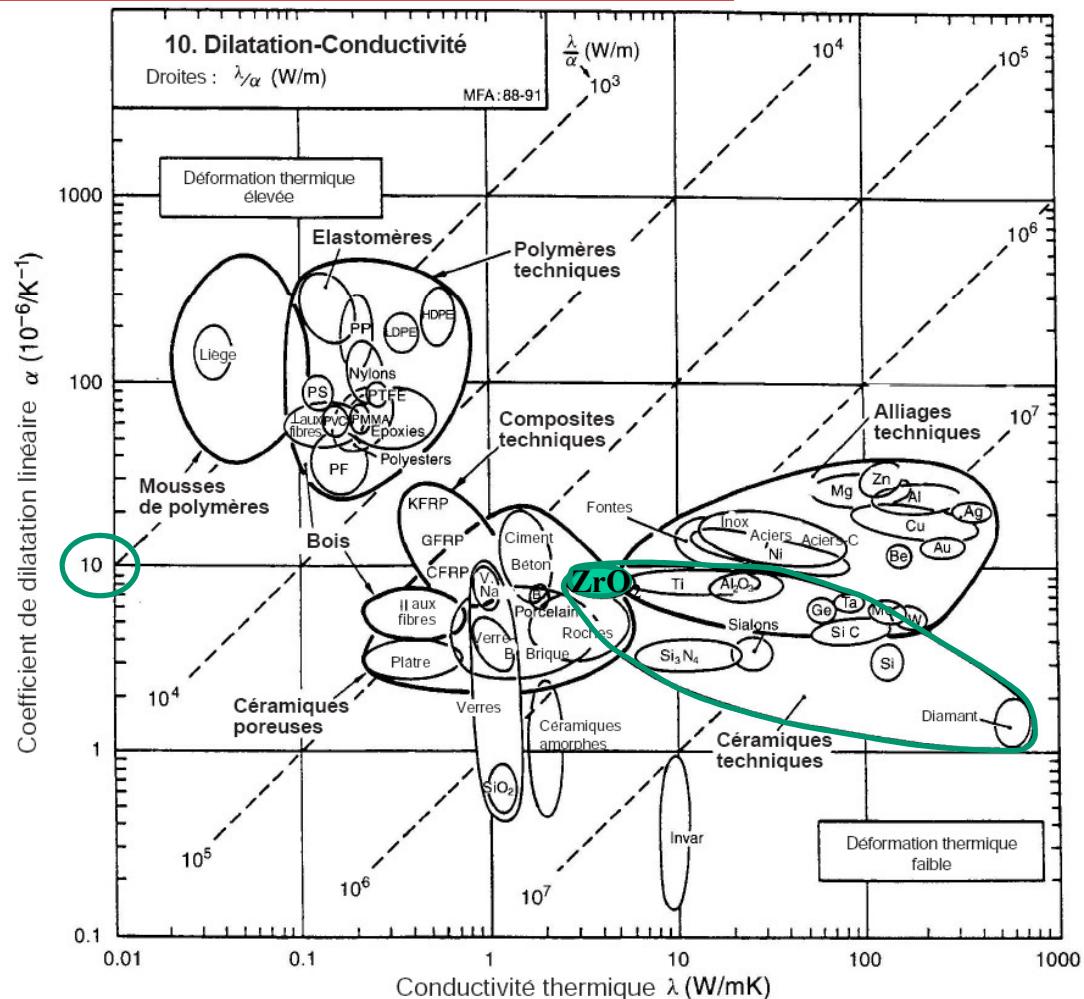
Oxide Materials with Low Thermal Conductivity

Michael R. Winter and David R. Clarke[†]

Materials Department, College of Engineering, University of California, Santa Barbara, California 93160-5050


$\alpha = 18 \times 10^{-6} K^{-1}$
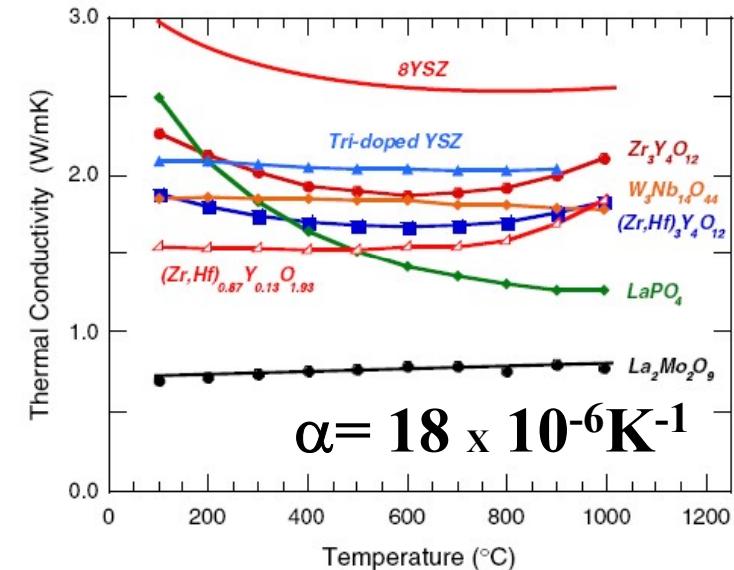
Fig. 7. Thermal conductivity of $La_2Mo_2O_9$ compared with the other materials investigated in this work. The density of the $La_2Mo_2O_9$ samples was 90%.

Giant thermally-enhanced electrostriction and polar surface phase in La$_2$Mo$_2$O$_9$ oxygen ion conductors

Qian Li,[1,2,*] Teng Lu,[3] Jason Schiemer,[4] Nouamane Laanait,[1] Nina Balke,[1] Zhan Zhang,[2] Yang Ren,[2] Michael A. Carpenter,[4] Haidan Wen,[2] Jiangyu Li,[5] Sergei V. Kalinin,[1] and Yun Liu[3,†]

[1]*Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA*
[2]*X-ray Science Division, Argonne National Laboratory, Lemont, Illinois 60439, USA*
[3]*Research School of Chemistry, The Australian National University, Canberra, ACT 0200, Australia*
[4]*Department of Earth Sciences, University of Cambridge, Cambridgeshire CB2 3EQ, United Kingdom*
[5]*Department of Mechanical Engineering, University of Washington, Seattle, Washington 98195, USA*

https://en.wikipedia.org/wiki/Electrostriction#Applications
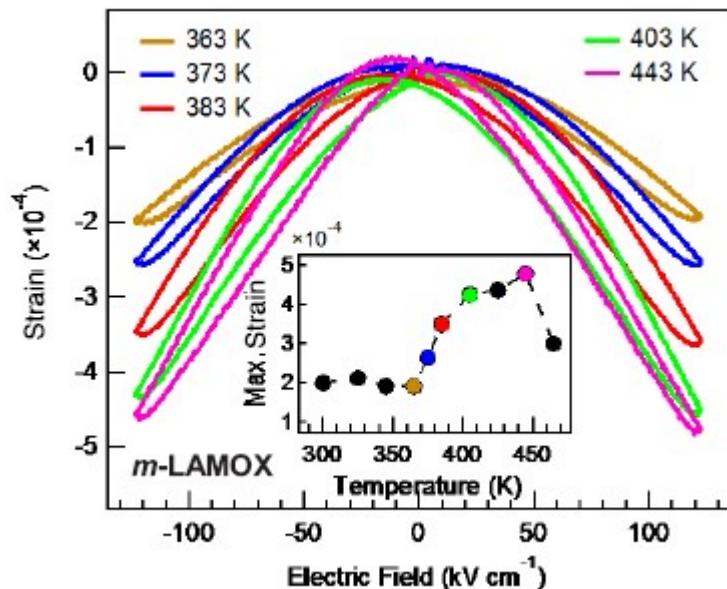
Materials [edit]

Although all dielectrics exhibit some electrostriction, certain engineered ceramics, known as relaxor ferroelectrics, have extraordinarily high constants. The most commonly used are

- lead magnesium niobate (PMN)
- lead magnesium niobate-lead titanate (PMN-PT)
- lead lanthanum zirconate titanate (PLZT)

Magnitude of effect [edit]

Electrostriction can produce a strain of 0.1% at a field strength of 2 million volts per meter (2 MV/m) for the material called PMN-15 (TRS webs references below). The effect appears to be quadratic at low field strengths (up to 0.3 MV/m) and roughly linear after that, up to a maximum fie MV/m[citation needed]. Therefore, devices made of such materials are normally operated around a bias voltage in order to behave nearly linearly. cause deformations to lead to a change of electric charge, but this is unconfirm

Applications [edit]

- Sonar projectors for submarines and surface vessels
- Actuators for small displacements

Good luck in your structure determination from powder !!!
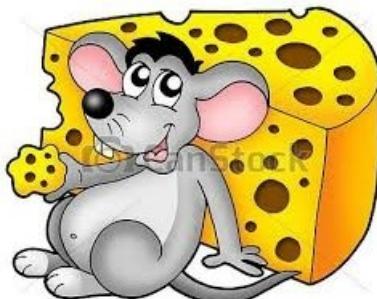
collaboration ?

Acknowledgment

Maud Barré

Philippe Lacorre

Karim Adil

Anthony Rousseau

Qiong Ye

Dan Vu

Emmanuelle Suard