X-ray diffraction: A tool for Materials Research

Structure and Properties of functional materials

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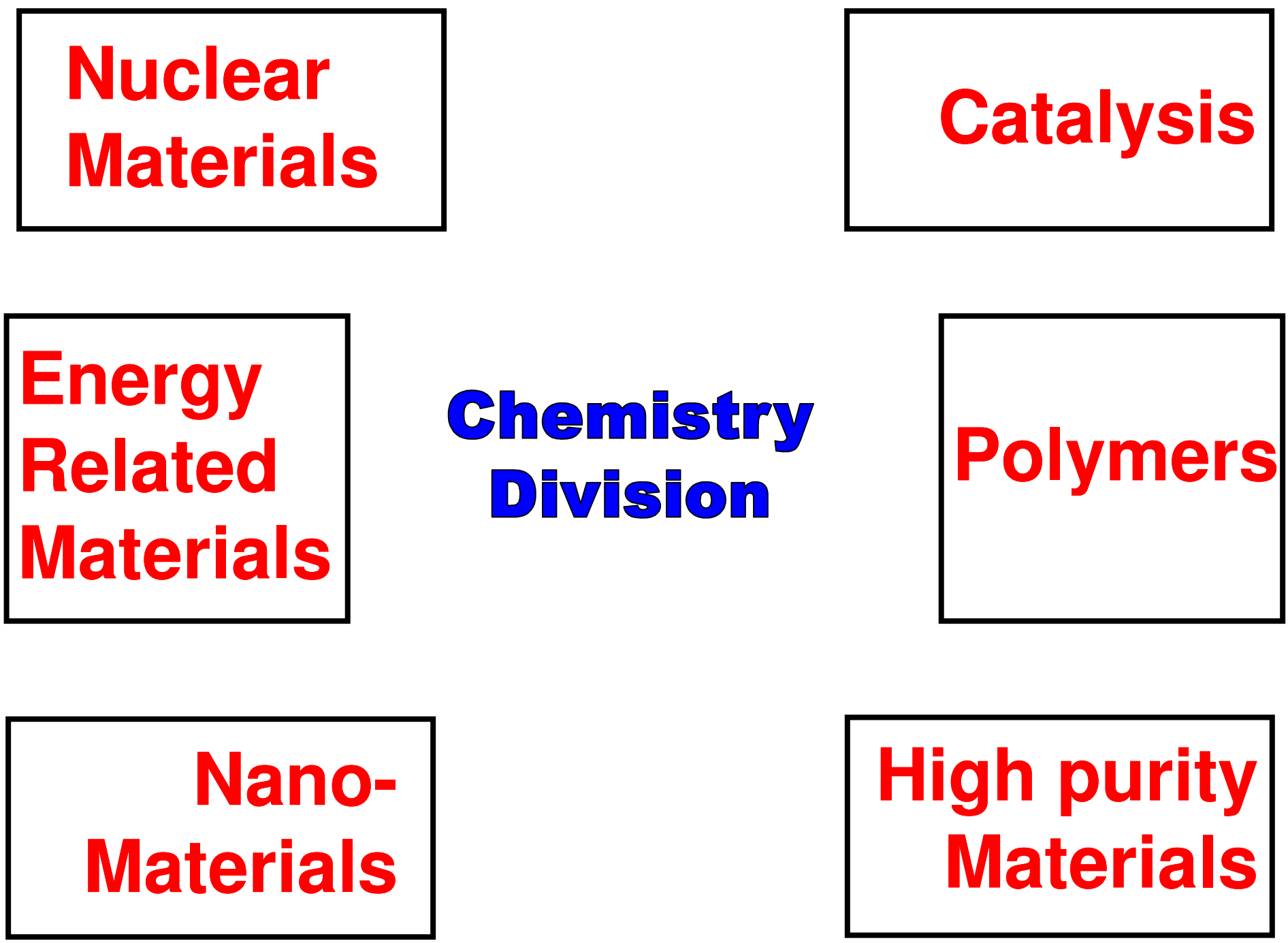
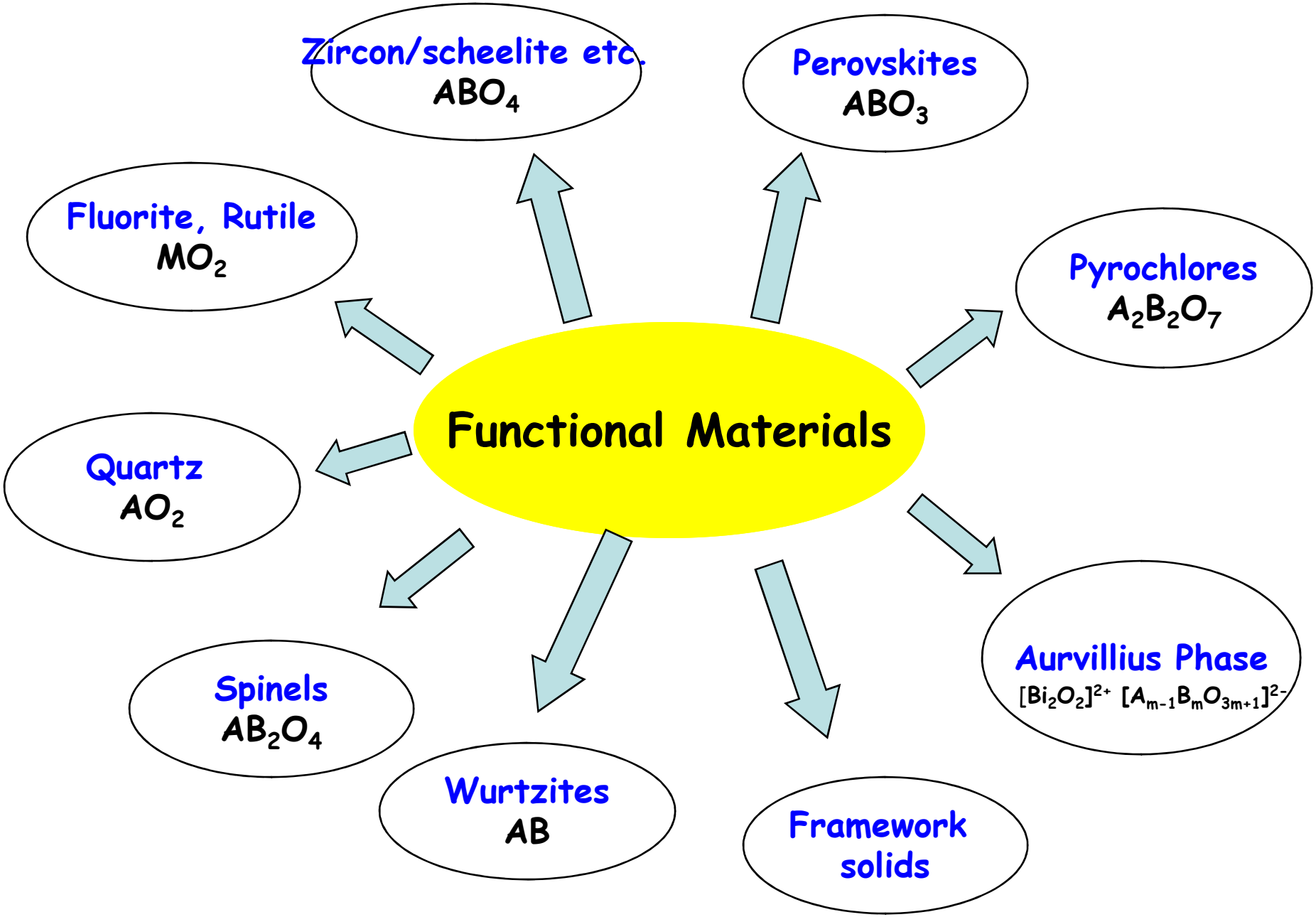
(Out lines)

- **Functional Materials**
- **Rietveld refinement**
- **Selected examples of structure and properties**

  - **Framework solids**
  - **Perovskite and related materials**
  - **Dilute magnetic semiconductor**
  - **Others**


Nuclear Materials
Catalysis
Energy Related Materials
Chemistry Division
Polymers
Nano-Materials
High purity Materials


Functional Materials
Zircon/scheelite etc.
ABO_4
Perovskites
ABO_3
Fluorite, Rutile
MO_2
Pyrochlores
$A_2B_2O_7$
Quartz
AO_2
Spinels
AB_2O_4
Wurtzites
AB
Framework solids
Aurvillius Phase
$[Bi_2O_2]^{2+}$ $[A_{m-1}B_mO_{3m+1}]^{2-}$

- Thermal expansion
- Electrical and Magnetic properties
- Compound with fission products
- High pressure/High temperature effects
- Novel and unusual compounds

Preparation methods

Ceramic method	Solid State Synthesis
Soft-chemical methods	Combustion synthesis, Template method Coprecipitation Polyol method, Sono-chemical Hydro & solvothermal methods Xero-gel method.
Other methods	Vacuum heat treatment Melt and quench technique Flux method High pressure synthesis

Data collection strategy

Just for phase identification:

10^o to 90^o; Step size 0.02^o, time per step 0.5 to 1 sec

For structural work:

5^o to 110^o; Step size 0.02^o, time per step 3 to 10 sec

Selection of step size depends on the required resolution:

A peak of 0.3^o FWHM can be nicely constructed with about 10 to 15 data points (step size 0.02^o)

What we normally expect from the diffraction studies

Accurate unit cell parameter and symmetry

Accurate structural parameters

Identification of segregated secondary phase

Correlation with physical properties

Choice of x-ray source

Wavelength (λ)

Intensity

Resolutions

Completeness of data

Weak peaks

S/N ratio

Separation of closely spaced peaks

Accurate unit cell

Symmetry

Good profile shape

Identifications of merged reflections

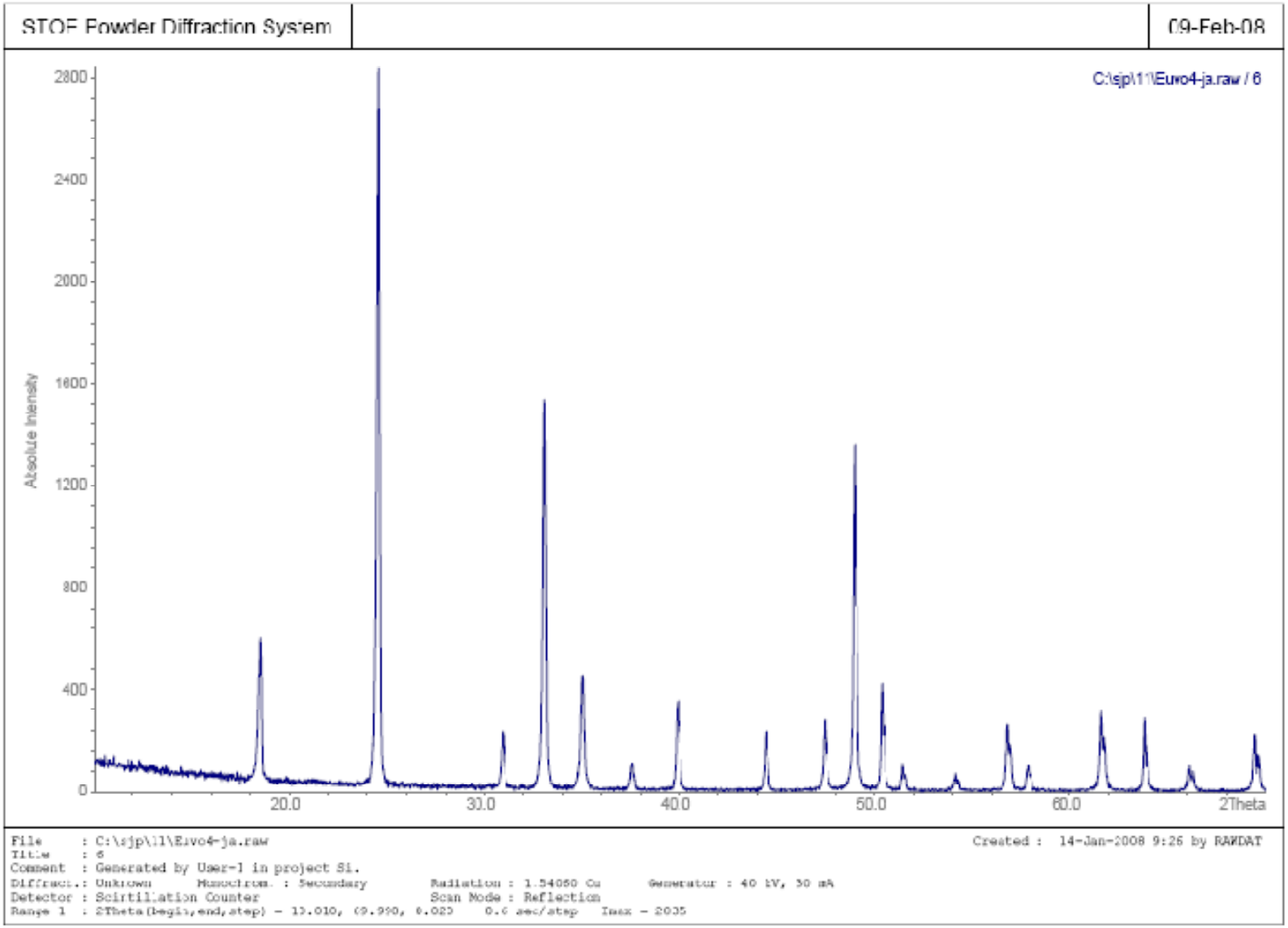
Stable refinement

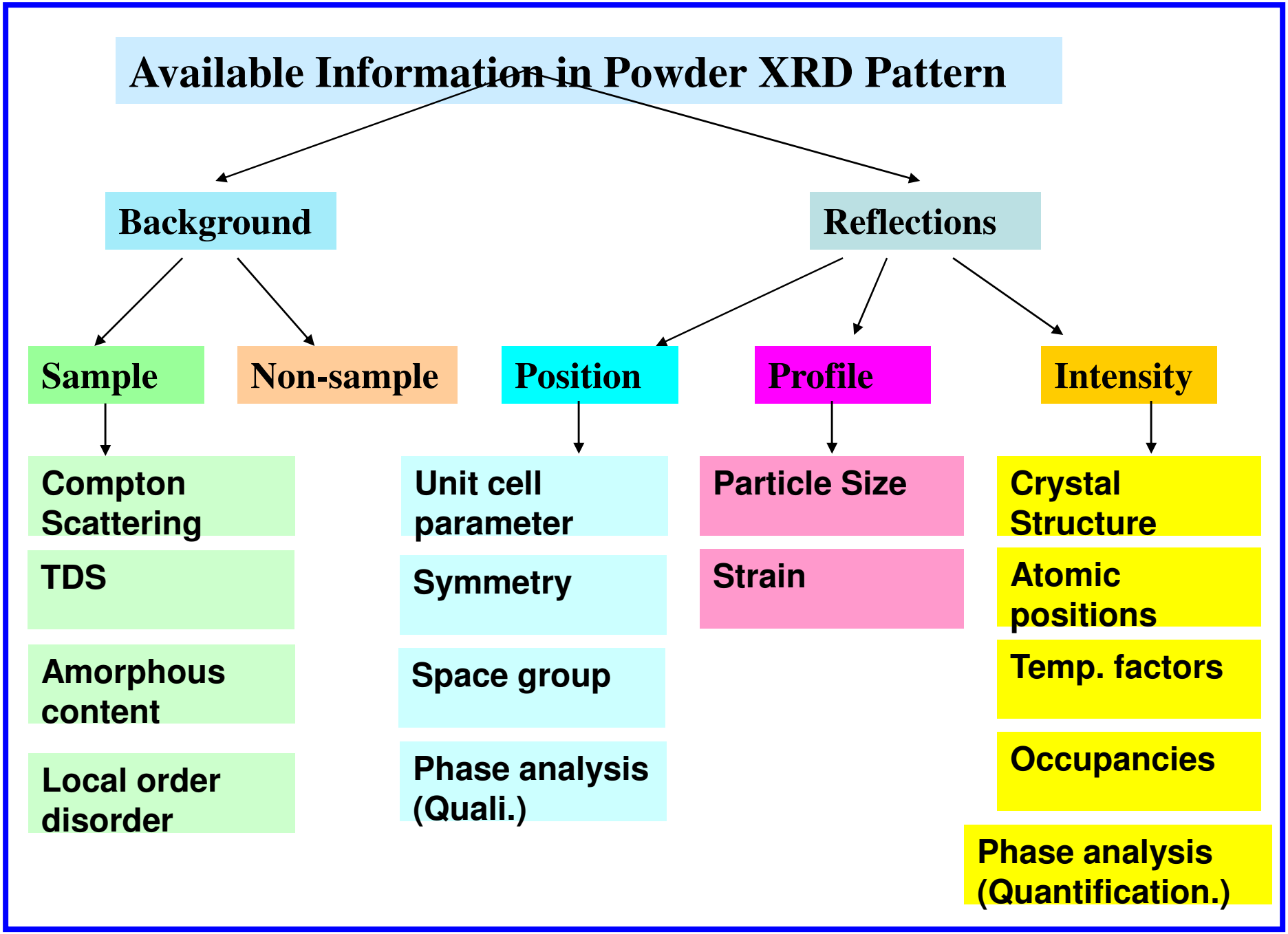
Accurate structural parameters

Comparison of PXRD data of different sources

	SEALED TUBE	RAG	SR
Wavelength	Fixed ($K\alpha_{1and\ 2}$)	Fixed ($K\alpha_{1and\ 2}$)	Tunable
Monochtrmator	Diffracted beam	Diffracted beam (incident beam)	Incident beam (double crystal)
peak-to-bkg ratio	Not good	Good	Very good
Counting time	Long (~ 1day)	Shorter (5-6 h)	Short (4-5 Mins)
Resolution (FWHM)	0.1-0.2	0.04-0.07	0.02-0.03
Detection limit	2-3 wt %	0.1 wt %	<0.1 wt %
Unit cell parameters	Ambiguous	Possible with more accuracy	Very accurate
Modulation	Below detection	Can be detected	Can be detected
Symmetry	Ambiguous	Possible	Possible
Crystal structure refinement	Possible	Possible	Possible
Crystal structure solution	Not possible	Possible	Possible

Typical XRD pattern of crystalline materials




Available Information in Powder XRD Pattern
Background
Reflections
Sample
Non-sample
Position
Profile
Intensity
Compton Scattering
TDS
Amorphous content
Local order disorder
Unit cell parameter
Symmetry
Space group
Phase analysis (Quali.)
Particle Size
Strain
Crystal Structure
Atomic positions
Temp. factors
Occupancies
Phase analysis (Quantification.)

Unit cell parameters of compounds

Determination of unit cell parameters

 # INDEXING

(Assignment of h k l to observed reflections)

 # CELL REDUCTION

(Search for other possibility of the unit cell)

 # REFINEMENT

(Minimization of errors)

Unit cell parameters of compounds

$$\frac{1}{d_{hkl}^{\,2}} = \frac{\lambda^2}{4 \times Sin^2\theta_{hkl}}$$ (From Bragg's Law)

$$\frac{1}{d^2} = \frac{\frac{h^2}{a^2}Sin^2\alpha + \frac{k^2}{b^2}Sin^2\beta + \frac{l^2}{c^2}Sin^2\gamma + \frac{2hk}{ab}(Cos\alpha \cdot Cos\beta - Cos\gamma) + \frac{2kl}{bc}(Cos\beta \cdot Cos\gamma - Cos\alpha) + \frac{2lh}{ca}(Cos\gamma \cdot Cos\alpha - Cos\beta)}{1 - Cos^2\alpha - Cos^2\beta - Cos^2\gamma + 2Cos\alpha \cdot Cos\beta \cdot Cos\gamma}$$

$$\frac{1}{d^2} = h^2(a^*)^2 + k^2(b^*)^2 + l^2(c^*)^2 + 2hka^*b^*Cos\gamma^* + 2klb^*c^*Cos\alpha^* + 2lhc^*a^*Cos\beta^*$$

$$V^2 = a^2b^2c^2\left(1 - Cos^2\alpha - Cos^2\beta - Cos^2\gamma + 2Cos\alpha \cdot Cos\beta \cdot Cos\gamma\right)$$

(h, k, l are integers, called as Miller Indices)

Unit cell parameters of compounds

Cubic System

$$\frac{1}{d_{hkl}^{\,2}} = \frac{h^2 + k^2 + l^2}{a^2}$$

$$a^2 = (h^2 + k^2 + l^2) \times d_{hkl}^{\,2}$$

Tetragonal System

$$\frac{1}{d_{hkl}^{\,2}} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$$

$$a^2 = (h^2 + k^2) \times d_{hk0}^{\,2}$$

$$c^2 = (l^2) \times d_{00l}^{\,2}$$

$$c^2 = (h^2 + k^2 + l^2) \times d_{hkl}^{\,2} - (h^2 + k^2) \times d_{hk0}^{\,2}$$

Computer Programs for unit cell determination

TREOR, VISER, ITO, CELL, UNITCELL, POWDER, INDEXING

POWD-OU.1

SrTiO3
Test PDF set
Sys.CUBIC P Lambda= 1.540600 F20=999.0(0.000, 20) X20= 0
Lo20/Lc 23 M20=999.0 A= 389.12
a= 3.9050A. V= 59.55

Line o.	c.	d-spacing A. obs.	calc.	Int. obs.	wt.	Indices h	k	l	SinSqTheta*E4 obs.	calc.	2Theta Deg. obs.	calc.	diff
1	1	3.9050	3.9050		1.0	1	0	0	389.1	389.1	22.75	22.75	0.000
2	2	2.7613	2.7613		1.0	1	1	0	778.2	778.2	32.40	32.40	0.000
3	3	2.2545	2.2546		1.0	1	1	1	1167.3	1167.3	39.96	39.96	0.000
4	4	1.9525	1.9525		1.0	2	0	0	1556.5	1556.5	46.47	46.47	0.000
5	5	1.7463	1.7464		1.0	2	1	0	1945.6	1945.6	52.35	52.35	0.001
6	6	1.5942	1.5942		1.0	2	1	1	2334.7	2334.7	57.79	57.79	0.000
7	7	1.3806	1.3806		1.0	2	2	0	3112.9	3112.9	67.83	67.83	0.000
8	8	1.3017	1.3017		1.0	3	0	0	3502.0	3502.0	72.57	72.57	0.000
						2	2	1					
9	9	1.2349	1.2349		1.0	3	1	0	3891.1	3891.2	77.19	77.19	0.000
10	10	1.1774	1.1774		1.0	3	1	1	4280.3	4280.3	81.72	81.72	0.000
11	11	1.1273	1.1273		1.0	2	2	2	4669.3	4669.4	86.21	86.21	0.000
12	12	1.0831	1.0831		1.0	3	2	0	5058.5	5058.5	90.67	90.67	0.000
13	13	1.0437	1.0437		1.0	3	2	1	5447.6	5447.6	95.14	95.14	-0.001
14	14	0.9762	0.9762		1.0	4	0	0	6225.8	6225.8	104.19	104.19	0.000
15	15	0.9471	0.9471		1.0	3	2	2	6615.0	6615.0	108.84	108.84	0.000
						4	1	0					
16	16	0.9204	0.9204		1.0	3	3	0	7004.0	7004.1	113.63	113.63	-0.001
						4	1	1					
17	17	0.8959	0.8959		1.0	3	3	1	7393.2	7393.2	118.60	118.60	0.000
18	18	0.8732	0.8732		1.0	4	2	0	7782.4	7782.3	123.81	123.81	0.001
19	19	0.8521	0.8521		1.0	4	2	1	8171.4	8171.4	129.37	129.37	0.000
20	20	0.8325	0.8325		1.0	3	3	2	8560.5	8560.5	135.41	135.41	-0.001
	21		0.7971			4	2	2		9338.8		150.20	
	22		0.7810			5	0	0		9727.9		161.01	
						4	3	0					

FINISH

Conditions	Lattice centering
$h + k = 2n$	C
$k + l = 2n$	A
$l + h = 2n$	B
$h+k,\ k + l$ and $h+l = 2n$	F
$h + k + l = 2n$	I
$-h+k+l = 3n$	R
$h-k+l = 3n$	R
No condition	P

Conditions	Symmetry elem.
hko	
$h = 2n$	a-glide
$k = 2n$	b-glide
$h+k = 2n$	n-glide
$h+k = 4n$ ($h,k = 2n$)	d-glide
hoo	
$h = 2n$	2_1 , 4_2 along <100>
$h = 4n$	4_1 , 4_3 along <100>
ool	
$l = 2n$	2_1 ,4_1, 6_3 along <001>
$l = 3n$	3_1, 3_2, 6_2, 6_4 along <001>
$l = 6n$	6_1, 6_5 along <001>

Structure refinement from Powder XRD data (Rietveld method)

Rietveld Analysis is based on

a. **Optimization of Profile parameters**

Suitable profile function defined to constrcuct the peak

b. **Optimization of Structural parameters**

Model structure (Space group, unit cell parameters, Position coordinates) are essential

Susceptible to erroneous results

a. Profile parameters

1. Background

* Can be selected by interpolation of selected points

* Can be modeled with polynomial function

2. Peak Profile

Profile is defined with specific function, like

* Gaussian

* Lorentzian

* Combination as Pseudo Voigt function

* Cauchy ***…etc.***

$$H_{hkl}^2 = U\,tan^2\,\vartheta + V\,tan\,\vartheta + W$$

3. Preferred Orientation

The preferred Orientation need to avoided as far as possible

The sample nature may some time force orientation

4. Asymmetry

Asymmetry of the peak shape

5. Displacement, Transparencies, Two theta zero

Lead to the peak shift and accurate peak positioning

Experimental and instrumental

6. Lorenz and Polarization Correction

7. Size and strain factors

b. Structural parameters

1. Chemical details
2. Scattering factor/length of various atoms
3. Unit cell parameters and space group
4. Positional details of all atoms
5. Occupancies
6. Thermal parameters *(if available)*

Structure factor calculations

$$F_{hkl} = \sum_{j \to 1}^{j \to N} f_j e^{2\pi i(hx_j + ky_j + lz_j)}$$

Where F_{hkl} : *Amplitude of scattered radiation from the plane hkl*

f_j : *Scattering factor of the atom j at the diffraction angle θ*

(x_j, y_j, z_j) : *Fractional coordinates of the atom j in the unit cell*

N : *Number of atoms in the unit cell*

$$f = f_0 e^{\frac{-B \sin^2 \vartheta}{\lambda^2}}$$

f_0 : Scattering factor of an atom when it is rest and at 0°

λ : Wavelength of x-ray

θ : Angle of diffraction

B : Isotropic temperature factor

$B = 8\pi^2 u^2$, where u^2 = mean of square displacement of the atom

(The exponential term is called Debye-Waller factor)

Intensity calculation

$$Y_{ci} = y_{bi} + s\sum_{hkl} L \times P \times n \times \left|F_{hkl}\right|^2 \phi(2\vartheta_i - 2\vartheta_{hkl}) \times P_{hkl} \times A$$

where	Y_{ci}	***: Calculated intensity at the i_{th} step***
	y_{bi}	***: Background intensity at i_{th} step***
	L	***: Lorenz factor***
	P	***: Polarization factor***
	n	***: Multiplicity***
	$\|F_{hkl}\|^2$	***: Structure factor for hkl reflections***
	$\varphi(2\theta_i - 2\theta_{hkl})$	***: Profile function***
	P_{hkl}	***: Preferred orientation function***
	A	***: Absorption correction***
	S	***: scale factor***

Error calculation and minimization

$$D = \sum_{i=1}^{n} w_i (Y_{io} - Y_{ic})^2$$

the quantity D (residual) is minimized in the least square refinements

Where ***Yio :*** ***Intensity observed at i^{th} step***

Yic : ***Intensity calculated at i^{th} step***

wi : ***weighting factor and usually $1/Y_{oi}$***

the model structure updated is applied shift $\Delta\xi$ in each step to reduce the error

Judgment of refinements

Difference plot and Residual indicator (R-Value)

Residual indicator (R-Value)

$$R_p = \frac{\sum (Y_{io} - Y_{ic})}{\sum Y_{ic}}$$ ***R. pattern***

$$R_{wp} = \left[\frac{\sum w_i (Y_{io} - Y_{ic})^2}{\sum w_i Y_{io}^{\ 2}} \right]^{1/2}$$ ***R. weighted Pattern***

$$R_{exp} = \left[\frac{N - P + C}{\sum w_i Y_{io}^{\ 2}} \right]^{1/2}$$ ***R. expected***

$$R_F = \frac{\sum \left| I_{hkl(o)}^{\ 1/2} - I_{hkl(c)}^{\ 1/2} \right|}{\sum I_{hkl(o)}^{\ 1/2}}$$ ***R. structure factor***

$$R_B = \frac{\sum \left| I_{hkl(o)} - I_{hkl(c)} \right|}{\sum I_{hkl(o)}}$$ ***R. Bragg***

$$S = \frac{W_{wp}}{W\,exp} = \chi$$ ***Goodness of fit***

$$d = \frac{\sum ((\Delta_i / \sigma_i) - (\Delta_{i-1} / \sigma_{i-1}))^2}{\sum (\Delta_i / \sigma_i)^2}$$ ***Durbin –Watson statistics***

Computer Programs for Rietveld refinements

FullProf, GSAS, Rietan, DBWS, ... etc.

Do

Try and get success

Try till no other possible solution

Keep tab on correlated parameter

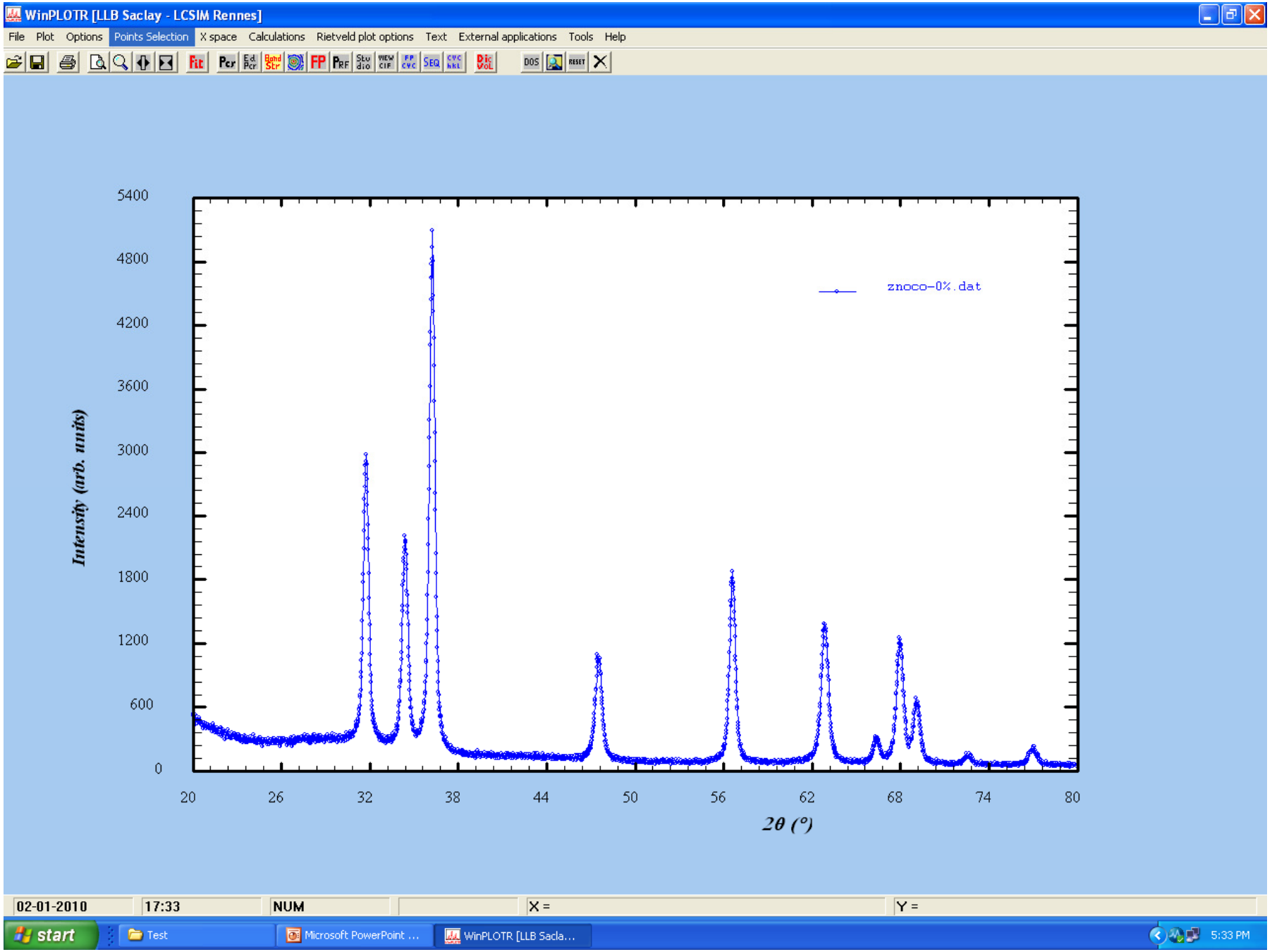
Check the chemical and physical sensibility of the refined results

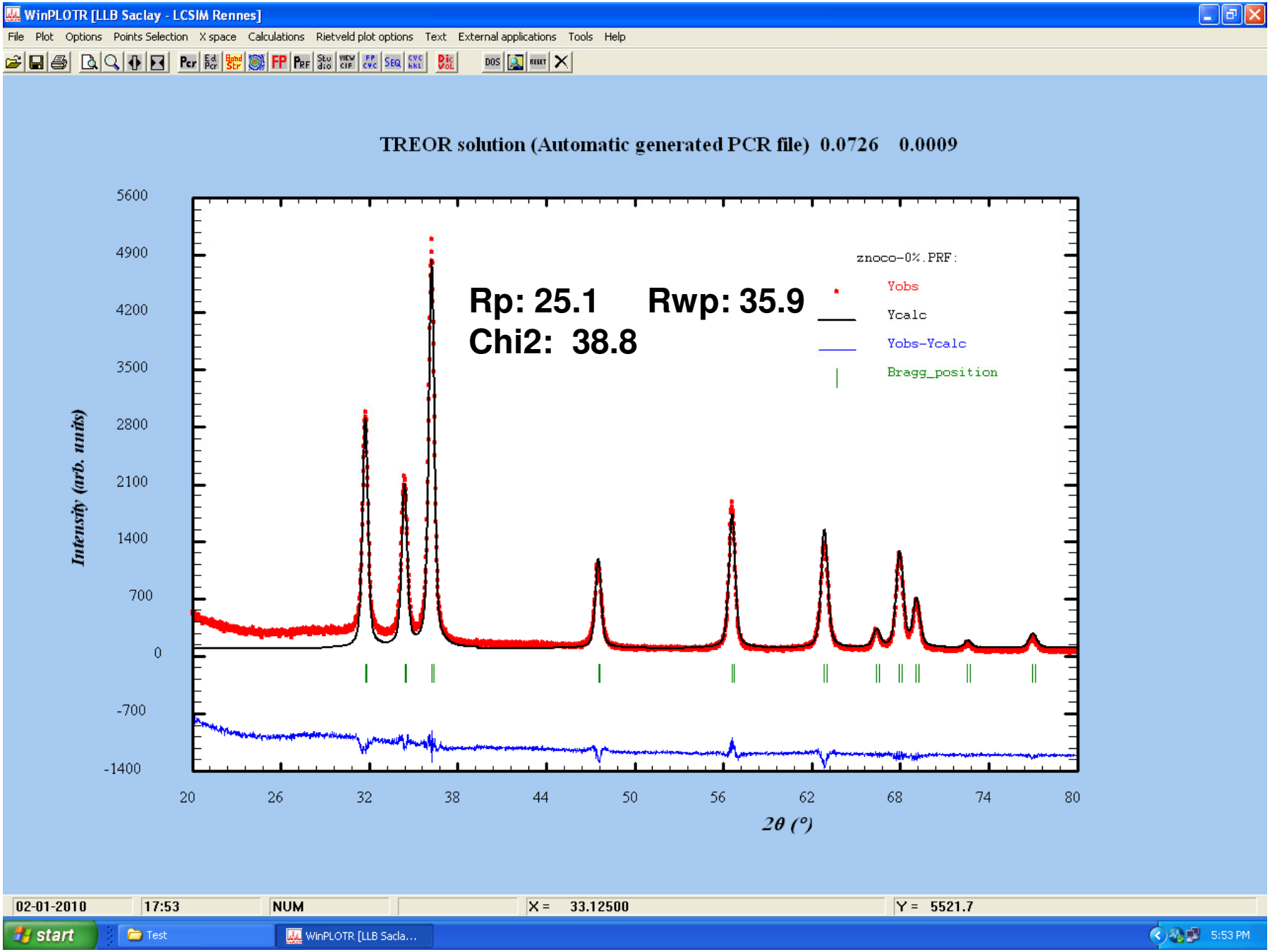
Verify if possible

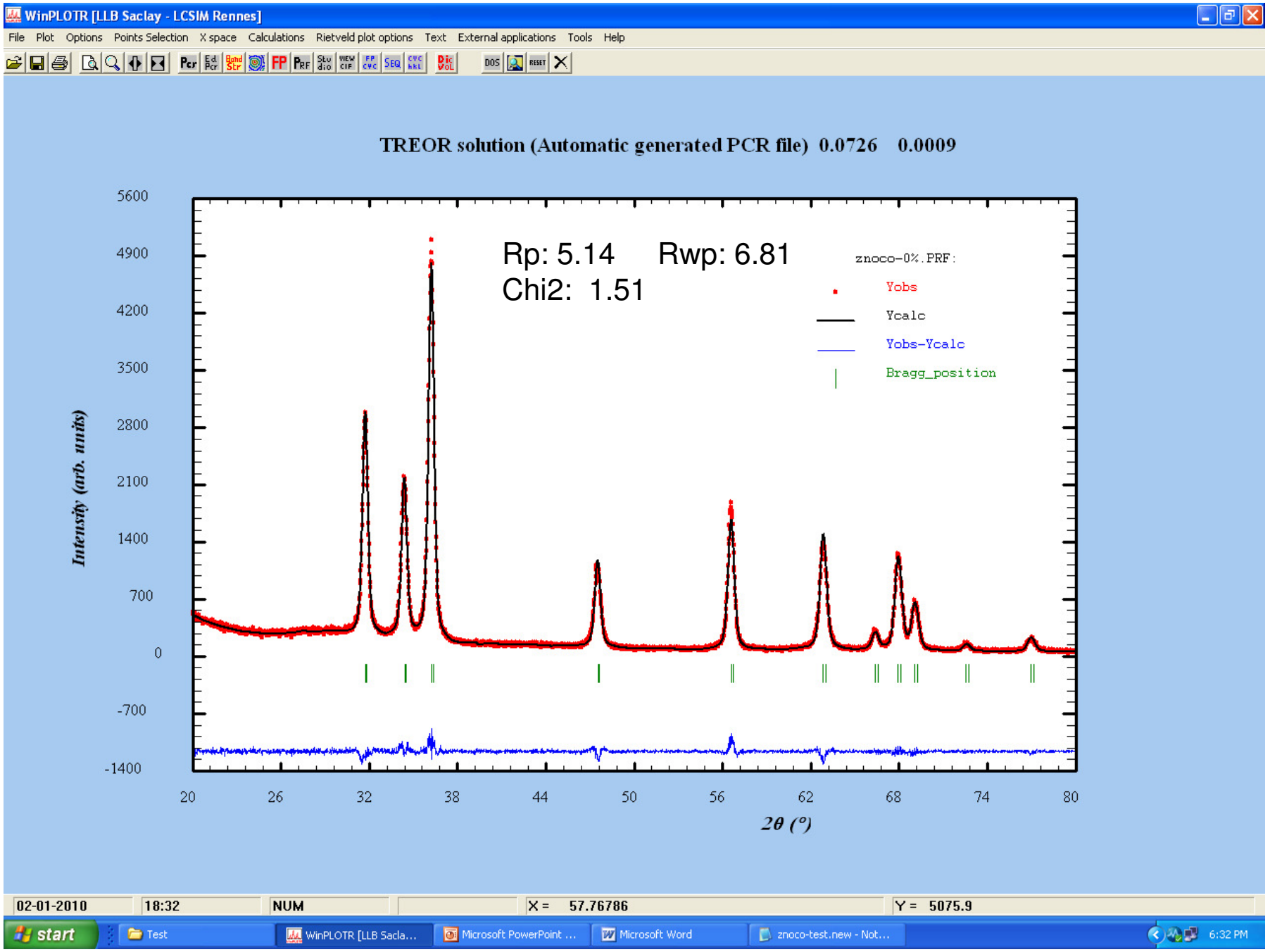
Convince yourself

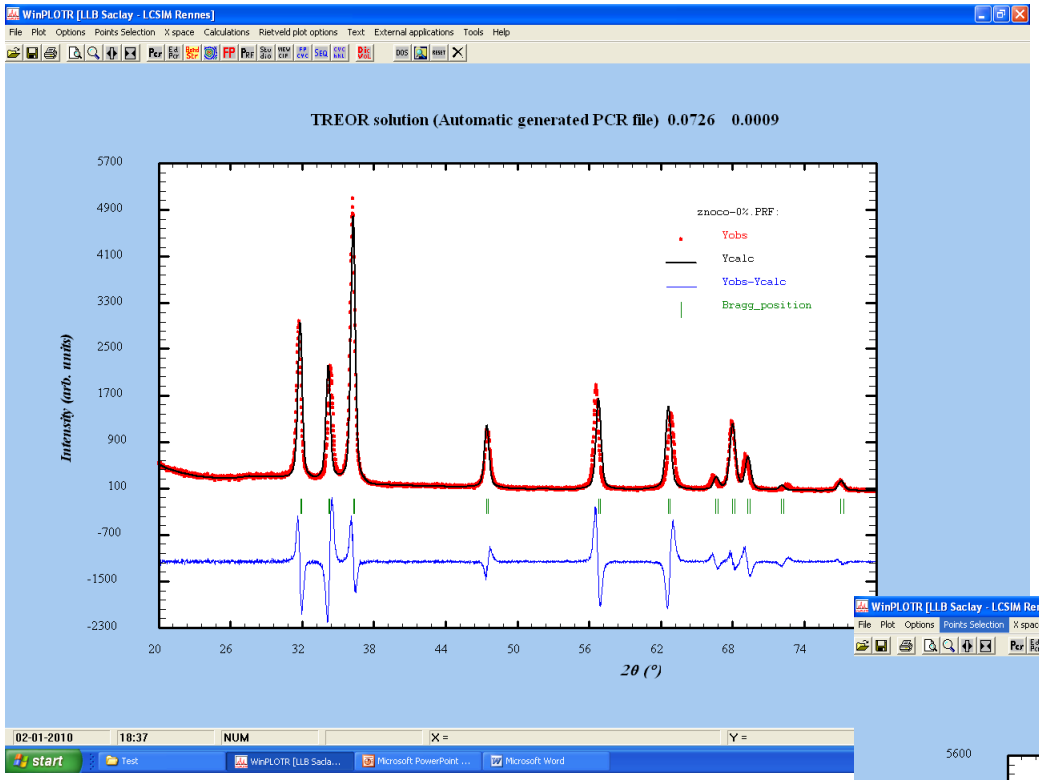
Don't

Never try with bad data and bad structural model


WinPLOTR [LLB Saclay - LCSIM Rennes]
File Plot Options Points Selection X space Calculations Rietveld plot options Text External applications Tools Help
znoco-0%.dat
Intensity (arb. units)
2θ (°)
5400
4800
4200
3600
3000
2400
1800
1200
600
0
20
26
32
38
44
50
56
62
68
74
80
02-01-2010
17:33
NUM
X =
Y =
start
Test
Microsoft PowerPoint ...
WinPLOTR [LLB Sacla...
5:33 PM


WinPLOTR [LLB Saclay - LCSIM Rennes]
File Plot Options Points Selection X space Calculations Rietveld plot options Text External applications Tools Help
TREOR solution (Automatic generated PCR file) 0.0726 0.0009
Rp: 25.1 Rwp: 35.9
Chi2: 38.8
znoco-0%.PRF:
Yobs
Ycalc
Yobs-Ycalc
Bragg_position
Intensity (arb. units)
5600
4900
4200
3500
2800
2100
1400
700
0
-700
-1400
20
26
32
38
44
50
56
62
68
74
80
2θ (°)
02-01-2010
17:53
NUM
X = 33.12500
Y = 5521.7
start
Test
WinPLOTR [LLB Sacla...
5:53 PM


WinPLOTR [LLB Saclay - LCSIM Rennes]
File Plot Options Points Selection X space Calculations Rietveld plot options Text External applications Tools Help
TREOR solution (Automatic generated PCR file) 0.0726 0.0009
Rp: 5.14 Rwp: 6.81
Chi2: 1.51
znoco-0%.PRF:
Yobs
Ycalc
Yobs-Ycalc
Bragg_position
Intensity (arb. units)
5600
4900
4200
3500
2800
2100
1400
700
0
-700
-1400
20
26
32
38
44
50
56
62
68
74
80
2θ (°)
02-01-2010
18:32
NUM
X = 57.76786
Y = 5075.9
start
Test
WinPLOTR [LLB Sacla...
Microsoft PowerPoint ...
Microsoft Word
znoco-test.new - Not...
6:32 PM

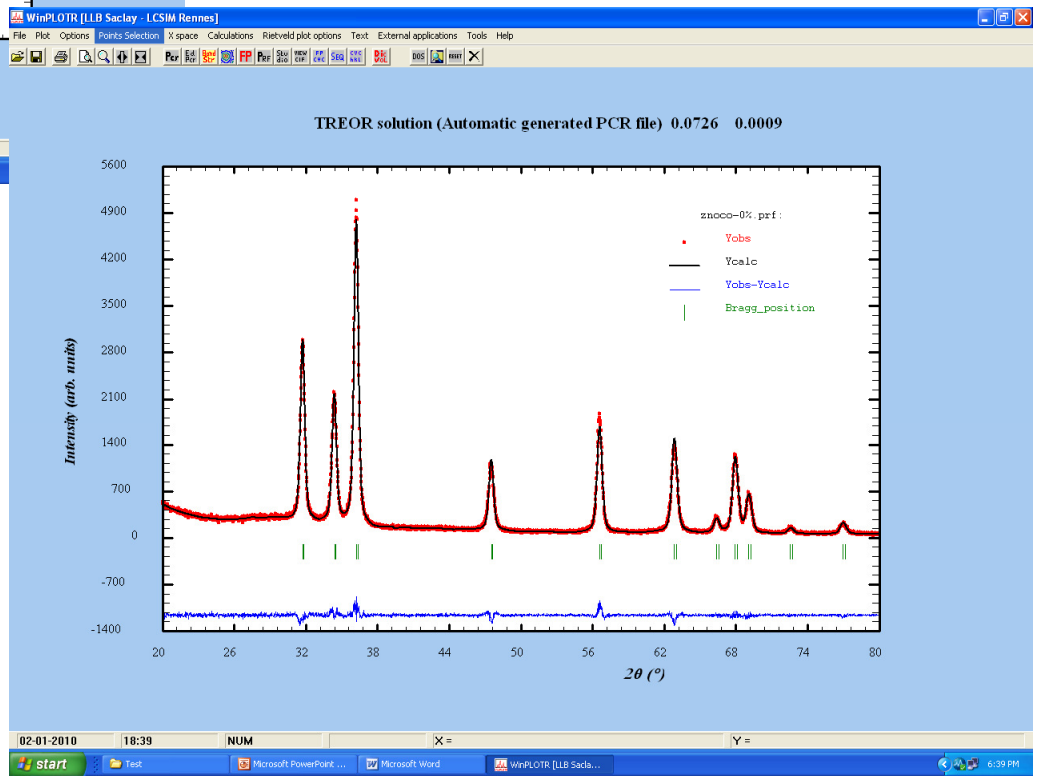


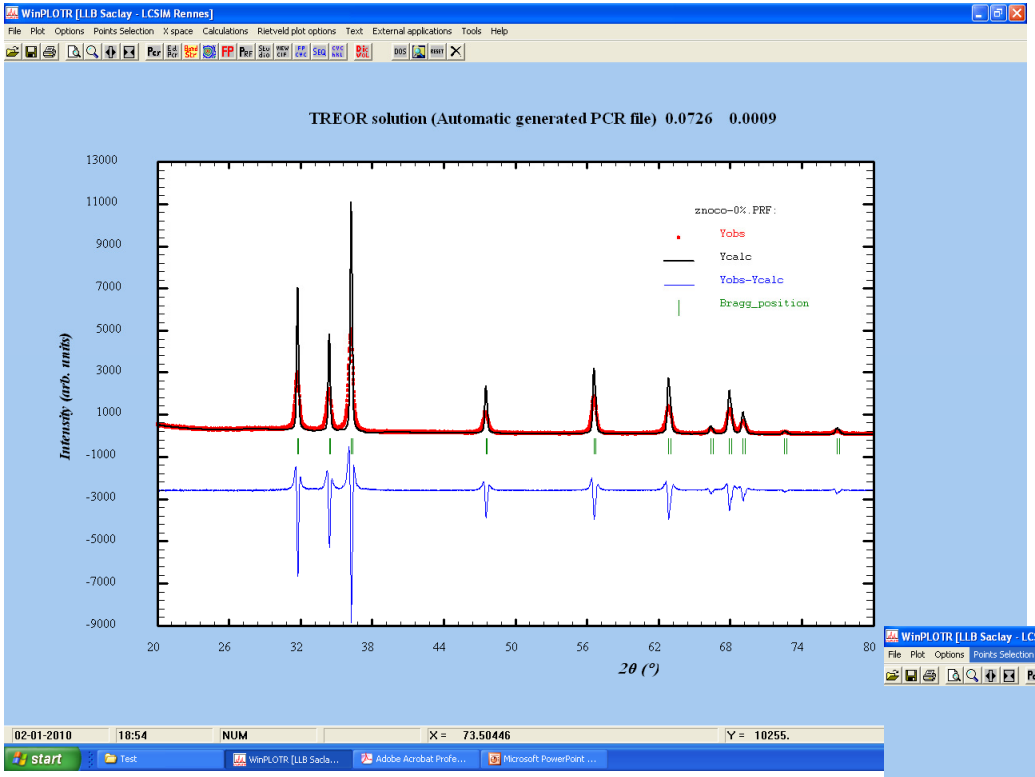
3.25019(6), c = 5.20765(16)

Rp: 5.17 Rwp: 6.80
Rexp: 5.76 Chi2: 1.39

a = 3.240189 c = 5.237664

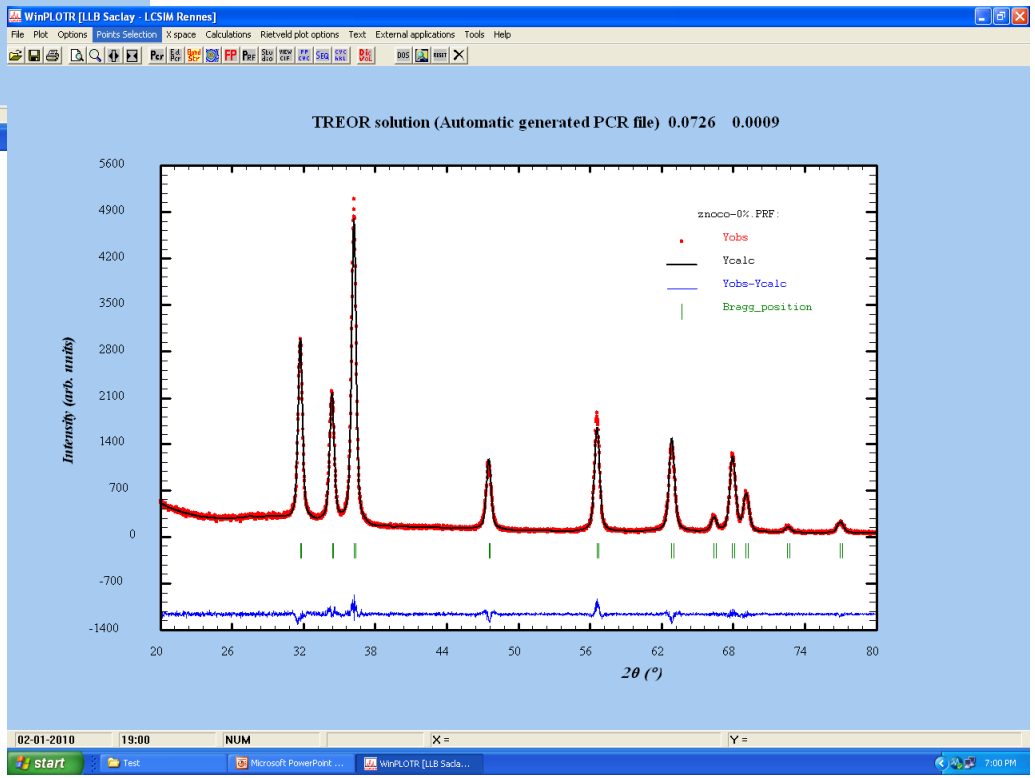
Rp: 21.5 Rwp: 33.4
Rexp: 5.76 Chi2: 33.6





0.398830 -0.218104 0.220260 0.000678

Rp: 5.17 Rwp: 6.80
Rexp: 5.75 Chi2: 1.40



0.098830 -0.018104 0.020260 0.000008

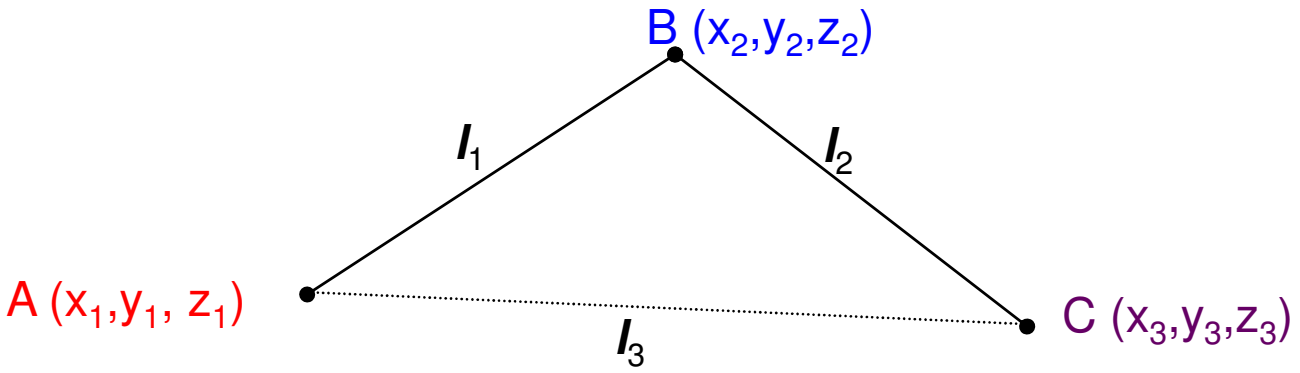
Rp: 34.6 Rwp: 46.7

Rexp: 5.76 Chi2: 65.7

$$X = ax + by\cos\gamma + cz\cos\beta \qquad Y = by\sin\gamma + \frac{cz(\cos\alpha - \cos\beta\cdot\cos\gamma)}{\sin\gamma}$$

$$Z = \frac{zV}{ab\sin\gamma}$$

$$V = abc\sqrt{1-\cos^2\alpha-\cos^2\beta-\cos^2\gamma+2\cos\alpha\cos\beta\cos\gamma}$$



$$r^2 = \overline{X}\bullet\begin{pmatrix} a\cdot a & a\cdot b & a\cdot c \\ b\cdot a & b\cdot b & b\cdot c \\ c\cdot a & c\cdot b & c\cdot c \end{pmatrix}\bullet X$$

$$l_3^2 = l_1^2 + l_2^2 - 2l_1 l_1\cos\delta$$

$$X = ((x_2 - x_1),(y_2 - y_1),(z_2 - z_1))$$

Framework Materials

$A_2(MoO_4)_3$, A = Al^{3+}, Cr^{3+}, Fe^{3+}

AMo_2O_7 (A = Zr^{4+} and Hf^{4+})

$A_2(WO_4)_3$, A = Al^{3+}, Nd^{3+} and Y^{3+}

$KScMo_2O_8$, $KAlMo_2O_8$

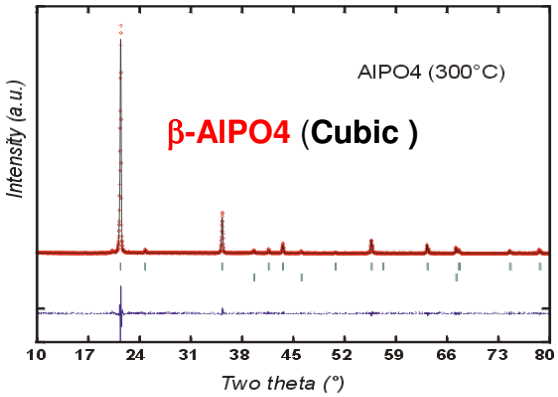
$AlPO_4$, $GaPO_4$, BPO_4

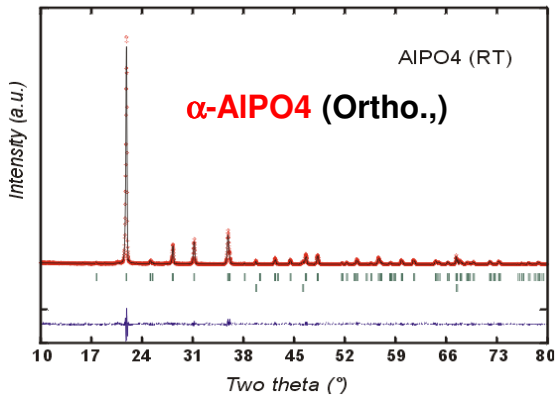
VP_2O_7

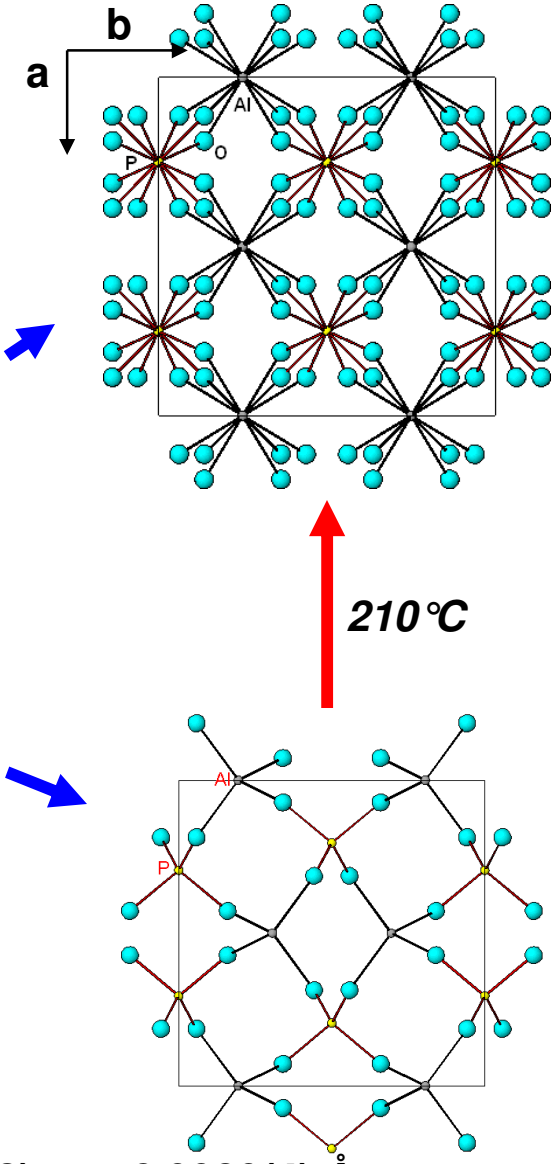
$NbOPO_4$

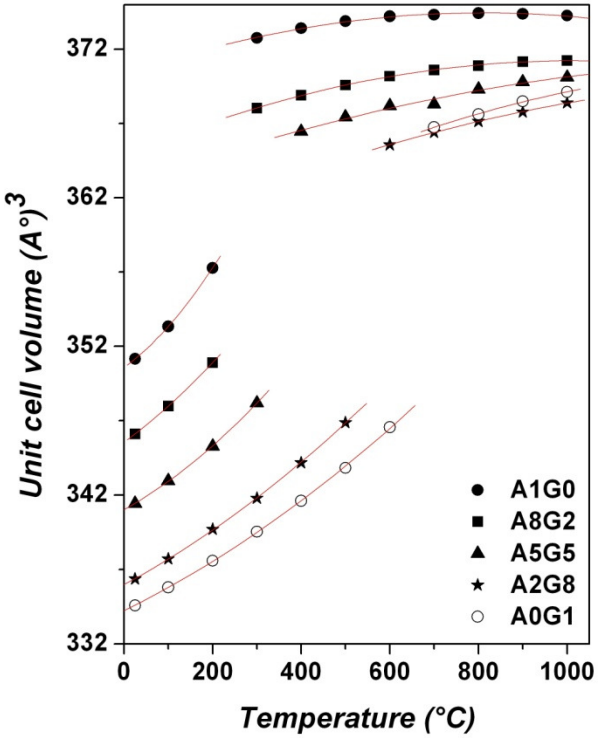
HT-XRD STUDIES ON $Al_{1-x}Ga_xPO_4$ *(cristo. type)*

Cubic, F-43m
a = 7.1969(2) Å
V = 372.77(1) Å3, Z = 4









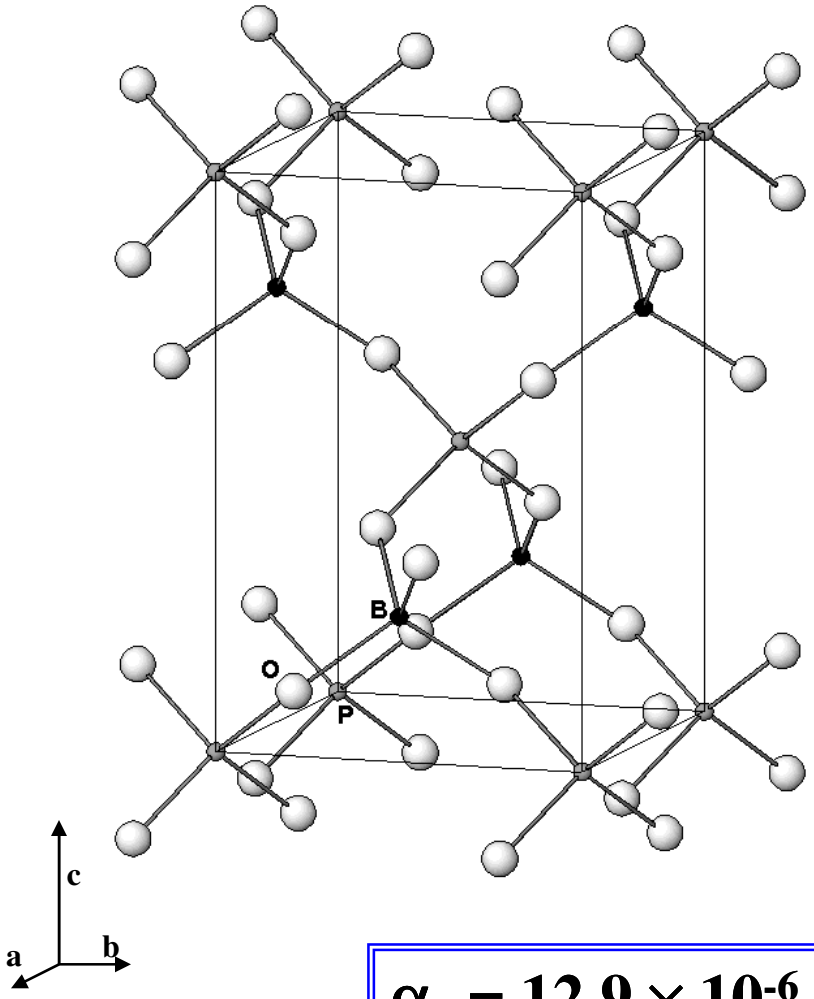
Orthorhombic, $C222_1$
a = 7.0843(14), b = 7.0823(13), c = 6.9989(4) Å
V = 351.22(1) Å3, Z = 4

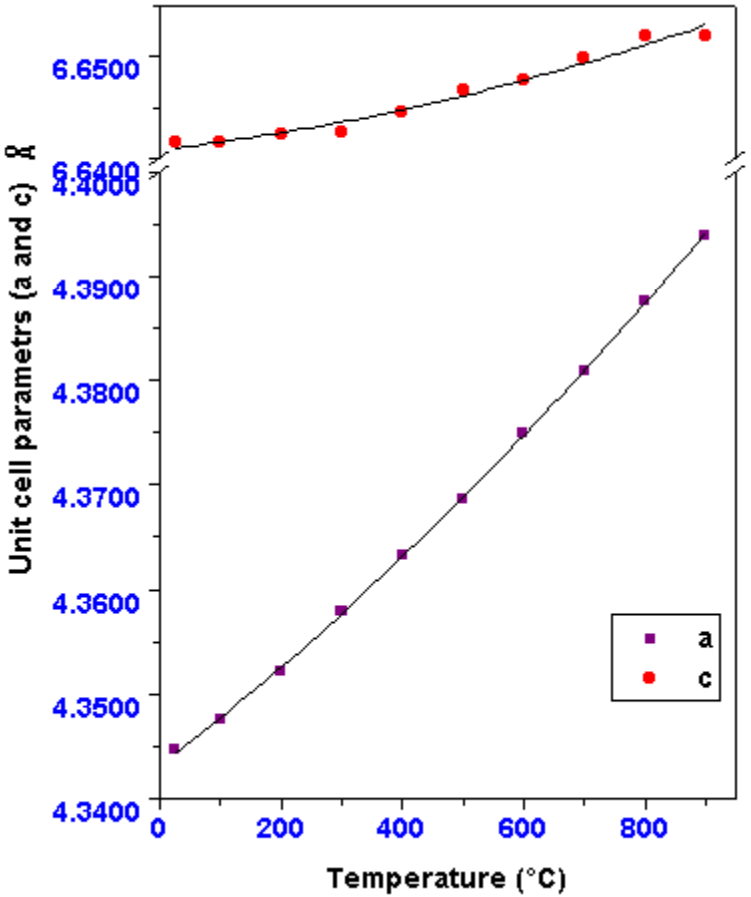
HT-XRD STUDIES ON BPO_4 (Tetragonal, cristobalite type)

Tetragonal (space group I-4. No. 82)

a = 4.3447(2), c = 6.6415(5) Å V = 125.37(1) Å^3, Z = 2.

B: *2c (0,1/2,1/4);* **P:** *2a (0,0,0);* **O:** *8g (x,y,z)*



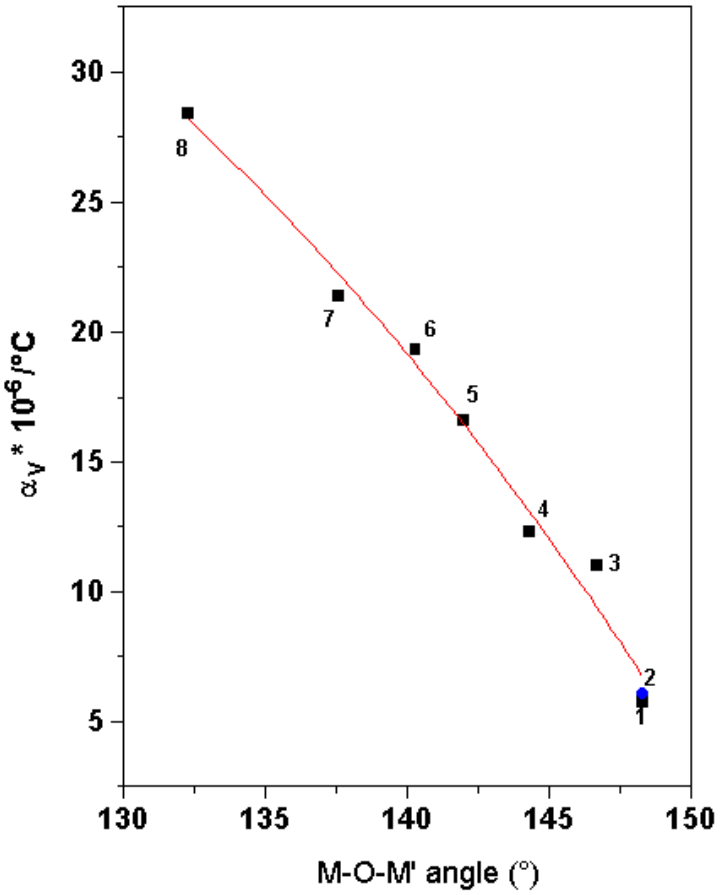


$\alpha_a = 12.9 \times 10^{-6}$ /°C ; $\alpha_c = 2.1 \times 10^{-6}$ /°C

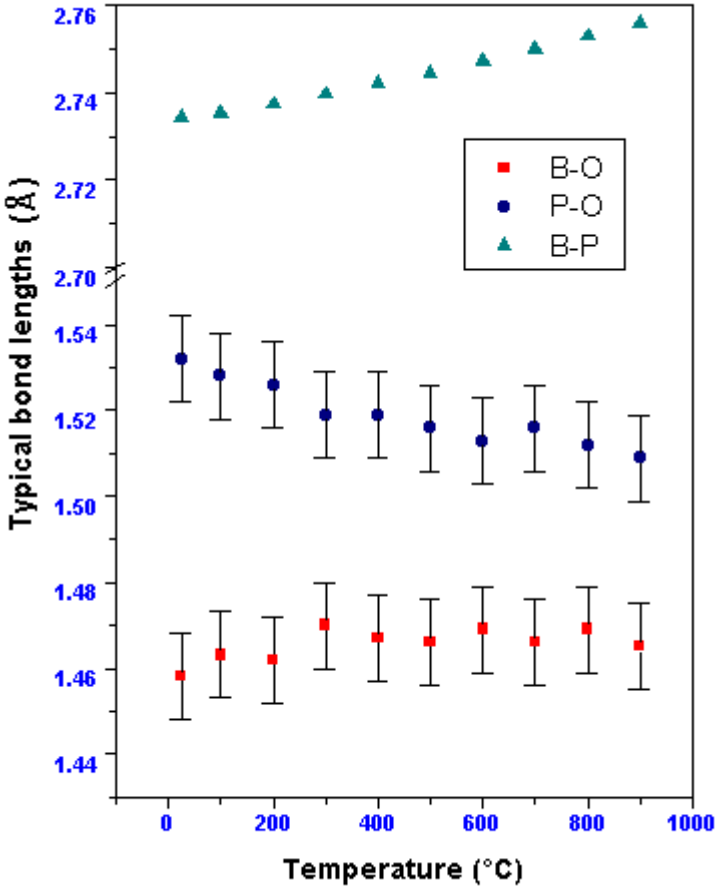
Variation thermal expansion coefficients with inter-polyhedral angle of *Cristobalite* type compounds

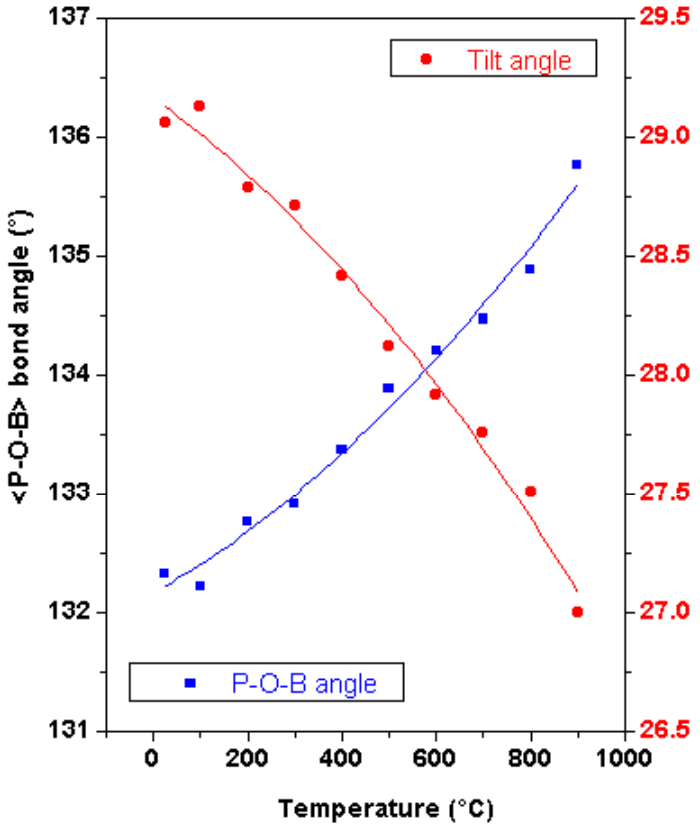
$$\alpha_V\ (/°C) = -191.32 + 4.33 \times [\theta] - 0.02 \times [\theta]^2$$

1. $AlPO_4$ (at 300°C)
2. $AlPO_4$ (at 300°C) *(lit. data)*
3. SiO_2 (at 300°C) *(lit. data)*
4. $Al_{0.8}Ga_{0.2}PO_4$ (300°C)
5. $Al_{0.5}Ga_{0.5}PO_4$ (400°C)
6. $Al_{0.2}Ga_{0.8}PO_4$ (600°C)
7. $GaPO_4$ (700°C)
8. BPO_4 (25°C)



Variation of structural parameters of BPO_4 with temperature



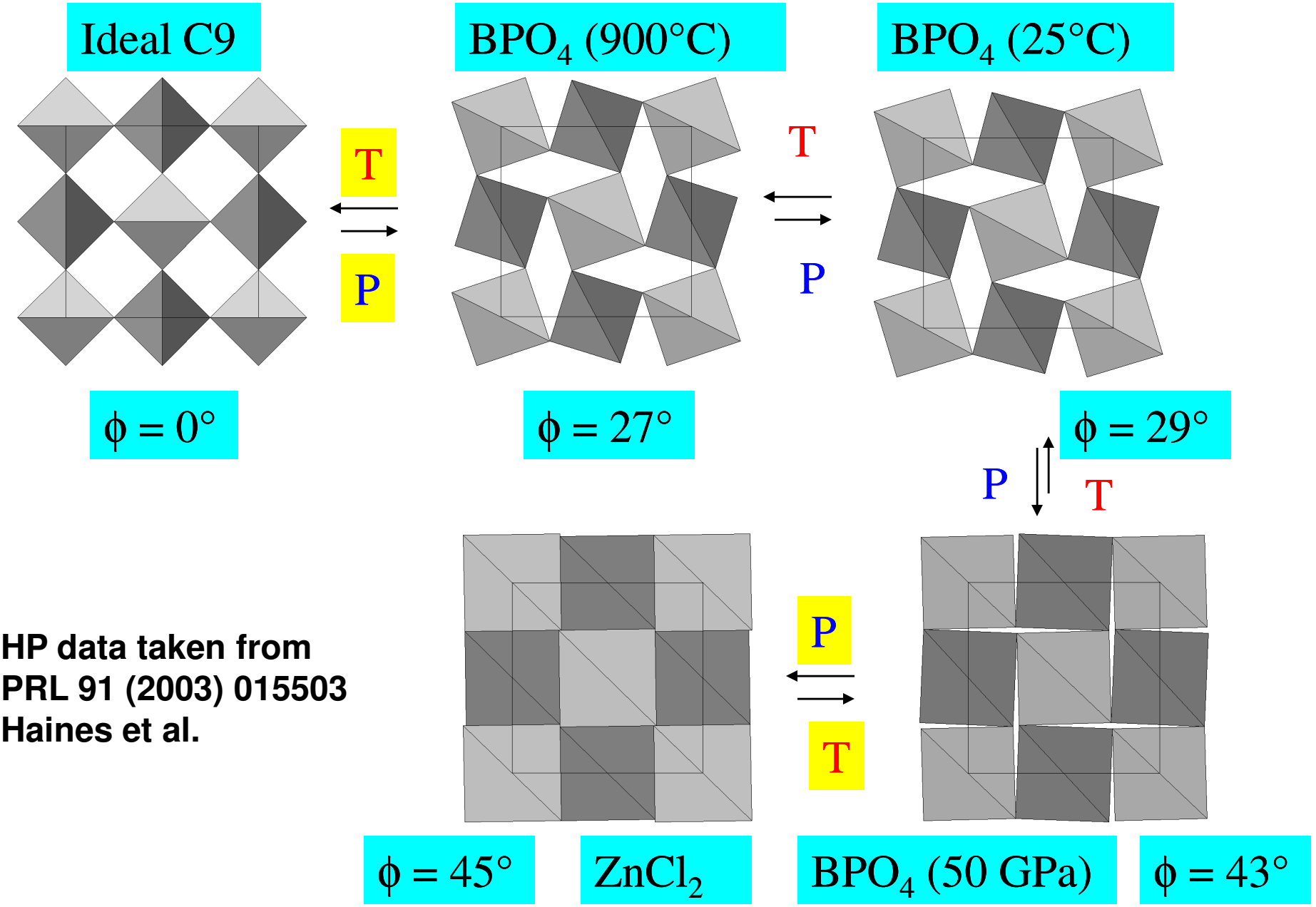


$\alpha_{B\text{-}P} = 8.99 \times 10^{-6}$ /°C

c = <B..P>$_1$ + <B..P>$_2$ + <B..P>$_3$ + <B..P>$_4$

a = <B..P>$_1$ + <B..P>$_2$

Tilt angle $\phi = \tan^{-1}(4x)$



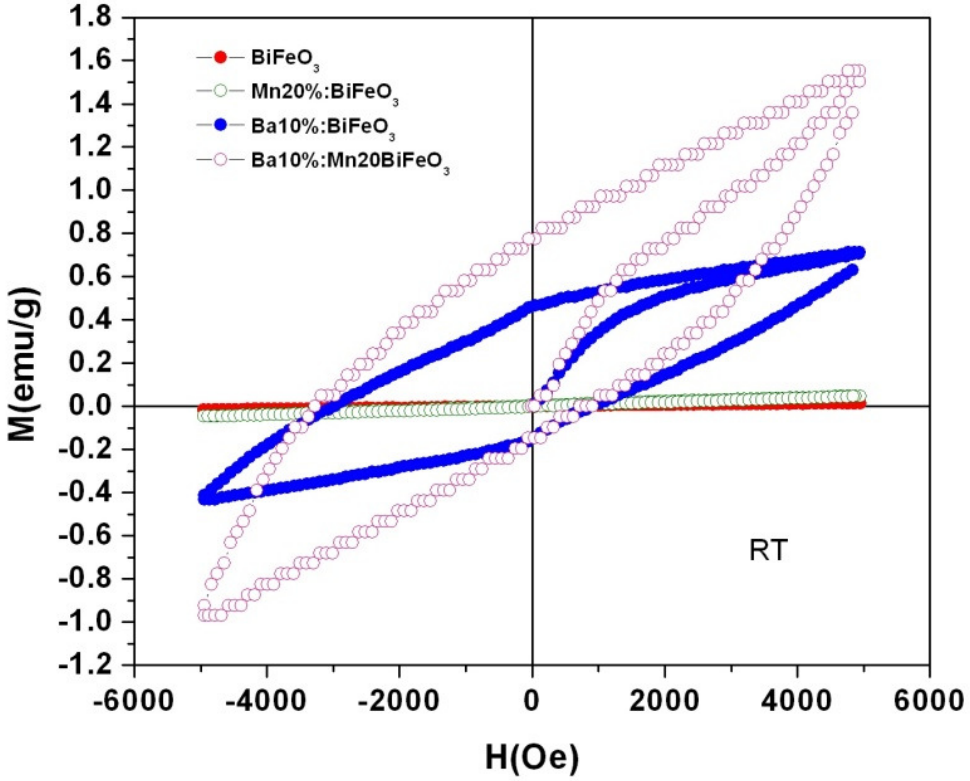
HP data taken from
PRL 91 (2003) 015503
Haines et al.

Transformation topology for cristobalite frame with Temp. /Press.

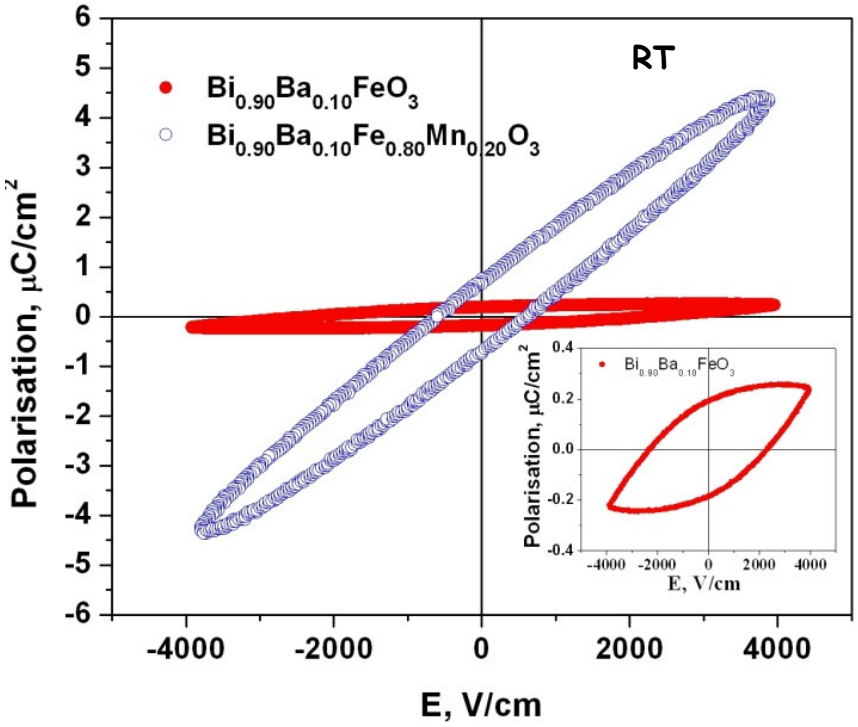
Perovskites…

Multiferroic Ba and Mn co-doped $BiFeO_3$

Preparation: Xerogel method

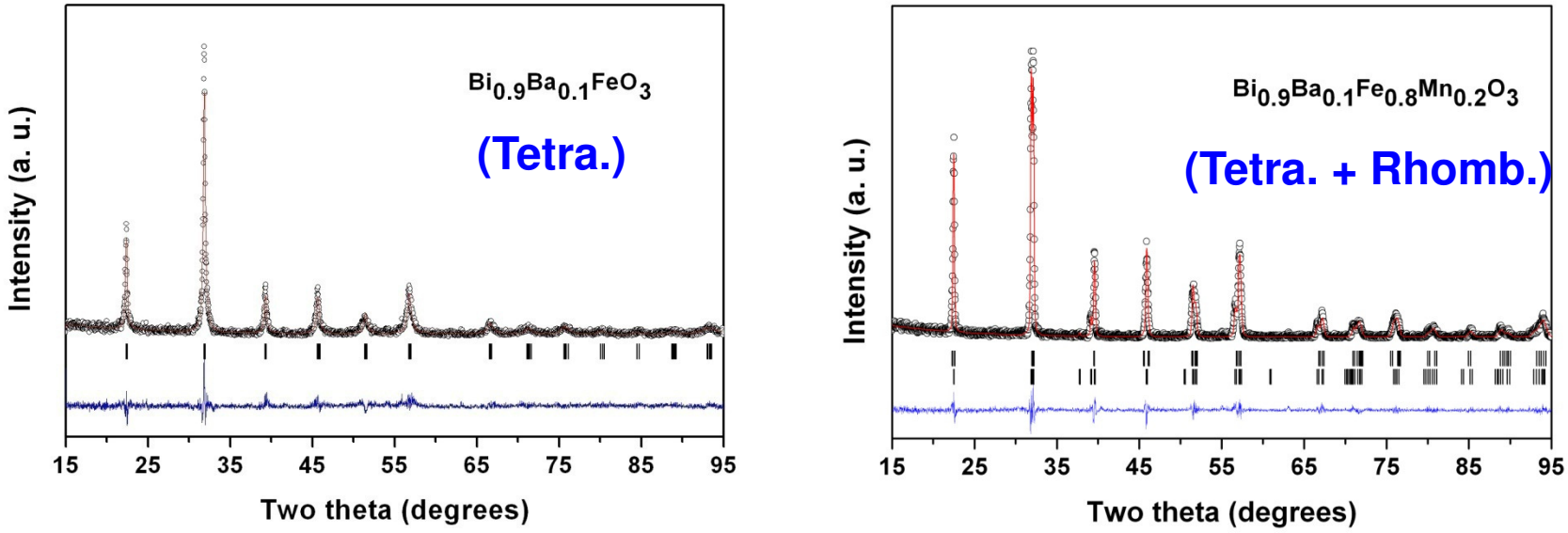


Magnetization with Field



Electric polarization with Field

Rietveld plots for XRD data

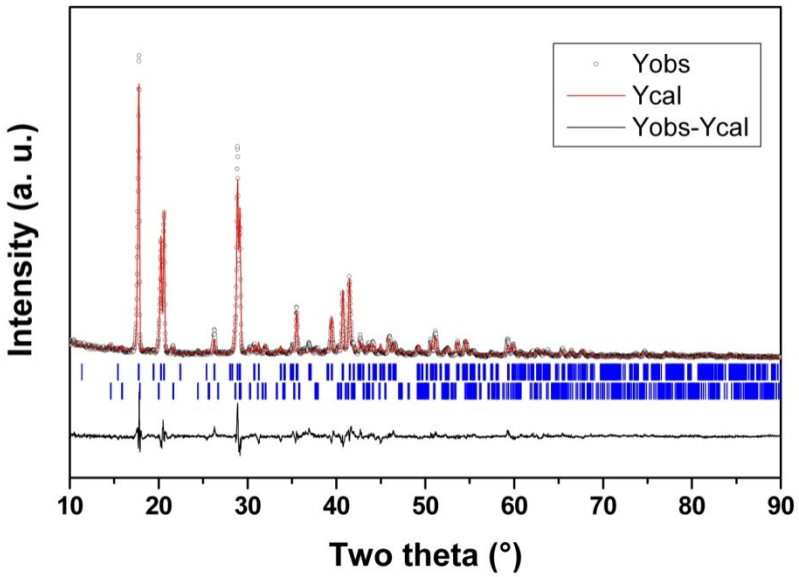


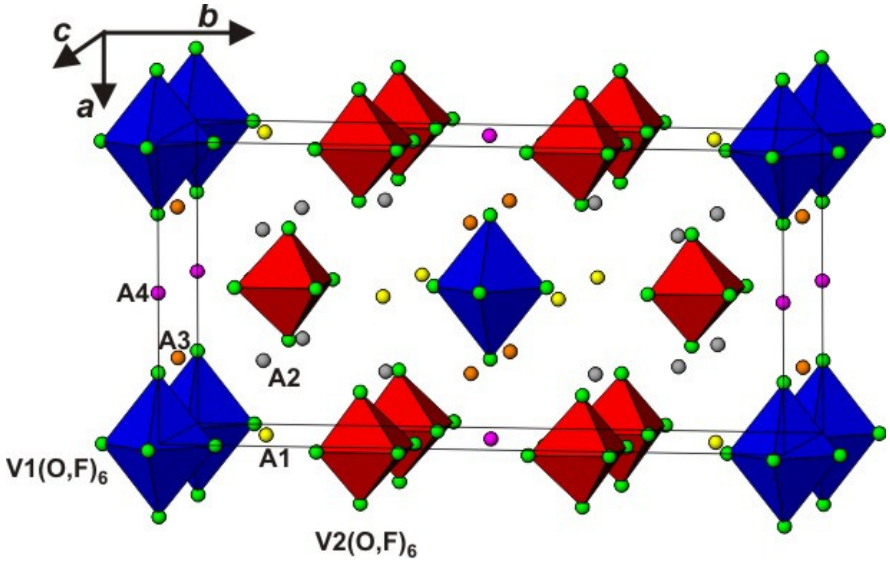
Summary of structure, electrical and magnetic properties

Sample	Symmetry	Hc (kOe)	Mr (emu/g)	Ps ($\mu C/cm^2$)
$BiFeO_3$	R3c	0.4	0.005	3.8
$BiFe_{0.8}Mn_{0.2}O_3$	R3c	0.7	0.3	3.0
$Bi_{0.9}Ba_{0.1}Fe_{0.8}Mn_{0.2}O_3$	R3c, P4mm (87:13)	4.5	3.8	4.5
$Bi_{0.9}Ba_{0.1}FeO_3$	P4mm	3.5	1.2	0.25

A new elpasolite-type $(NH_4,K)_3VO_2F_4$

Low temperature solid state reaction of KVO_3 + NH_4HF_2





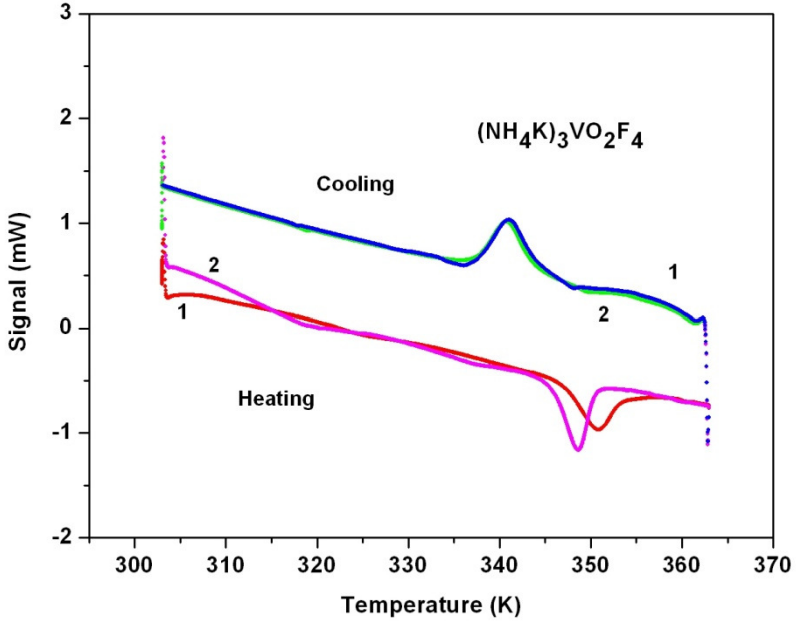
Orthorhombic (Space Group: Immm, No. 71)
a = 8.9584(4), b = 18.6910(14), c = 6.2174(4) Å, V = 1041.04(11) Å^3, Z = 6,
Rp: 10.9, Rwp: 14.1, χ2: 3.77, R_B: 12.0
Second Phase: $K_2VO_2F_3$ (Orthorhombic, Pnma, No. 62) Fraction: 7.8(4) wt %

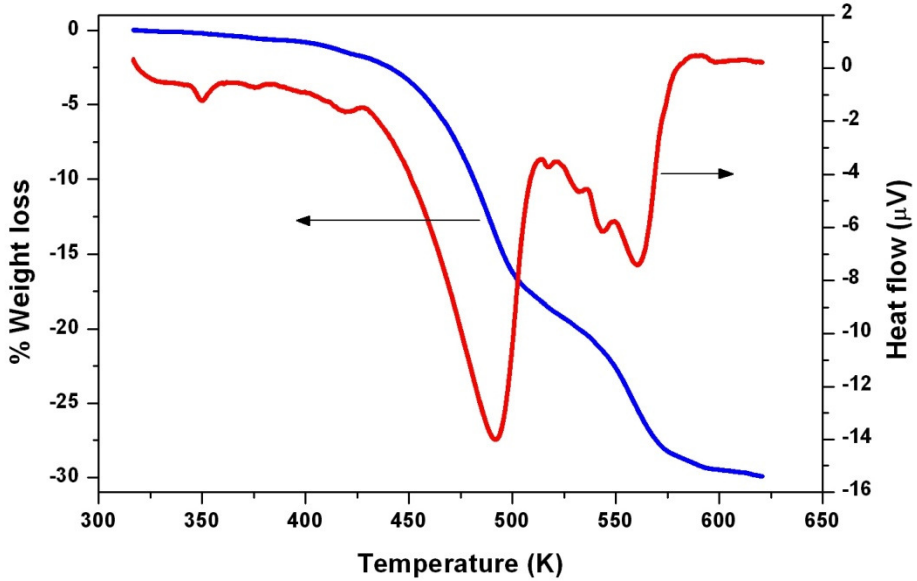
Position coordinates of $(NH_4,K)_3VO_2F_4$

Atoms	*Wyc*	x	y	z	B(Å^2)	*Occ.*
V1	*2a*	0	0	0	1.4(3)	1
V2	*4g*	0	0.6829(4)	0	3.3(2)	1
(K/N)1	*4h*	0	0.1402(6)	0.5	6.2	0.80(1) 0.20(1)
(K,N)2	*8n*	0.2836(11)	0.1679(7)	0	5.4	0.47(2), 0.53(2)
(K,N)3	*4f*	0.25	0.5	0	6.8	0.14(2), 0.86(2)
(K,N)4	*2b*	0	0.5	0.5	5.1	0.32(1), 0.68(1)
O1	*8l*	0	0.7346(7)	0.780(3)	4.8	1
O2	*8n*	0.184(1)	0.6777(9)	0	4.8	1
O3	*8l*	0	0.6042(7)	0.789(2)	4.8	1
O4	*4g*	0	0.9098(6)	0	4.8	1
O5	*4e*	0.763(2)	0	0	4.8	1
O6	*4l*	0	0	0.726(2)	4.8	1

Structural composition $(NH_4)_{1.7}K_{1.3}V(OF)_6$

Phase transition and thermal stability



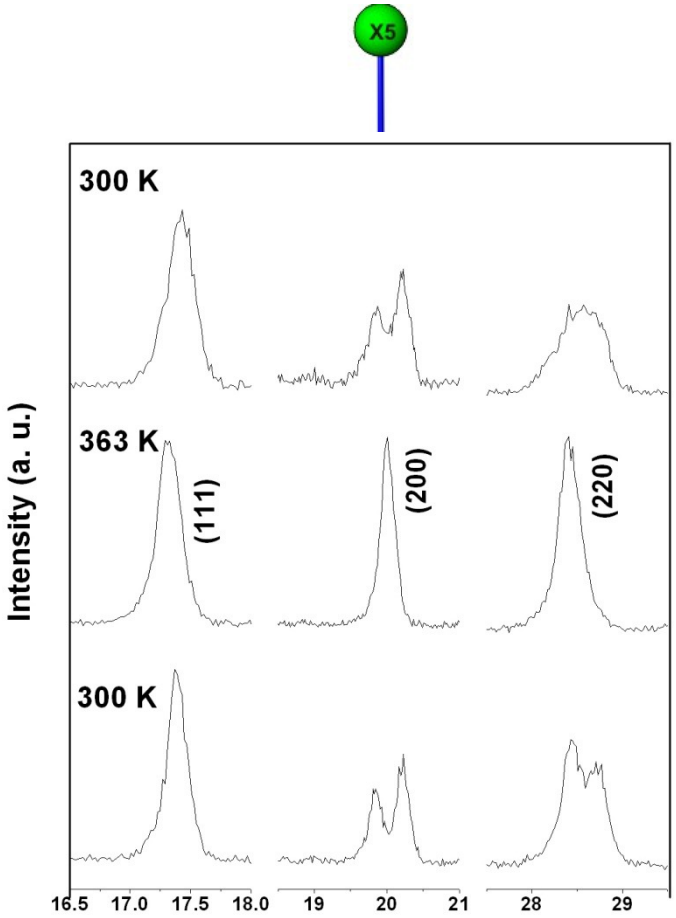


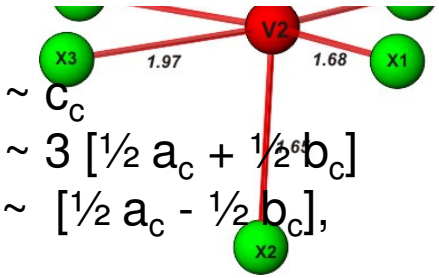
Reversible structural transition at 343 K

Weight loss (30%) between 300 to 623 K is close to that expected (26%) for the loss of 1.7 NH4F

Agrees with structural composition $(NH_4)_{1.7}K_{1.3}V(OF)_6$.

Ferroelectric properties

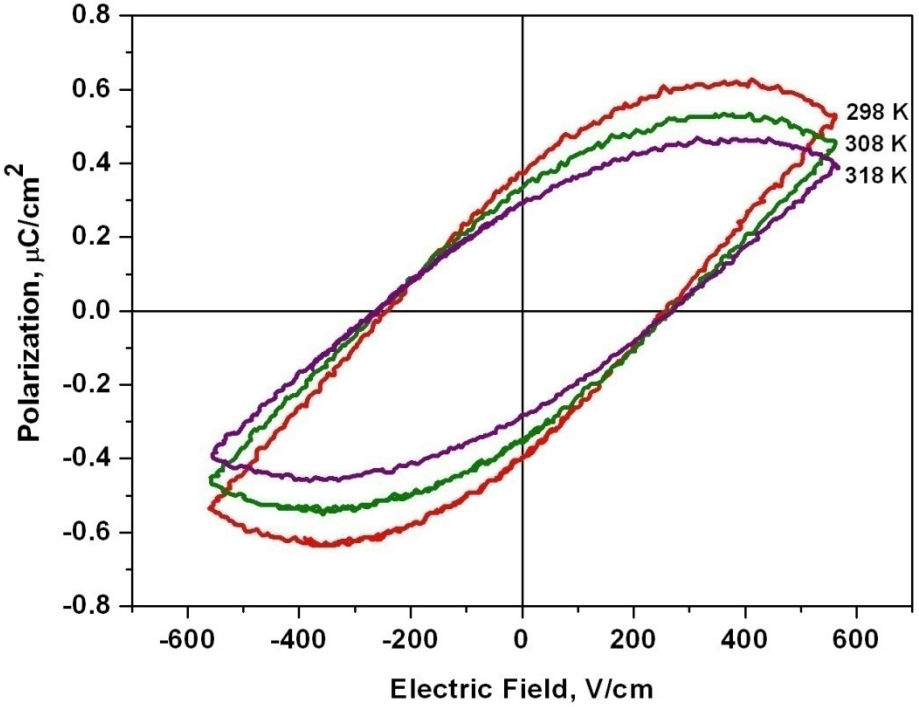




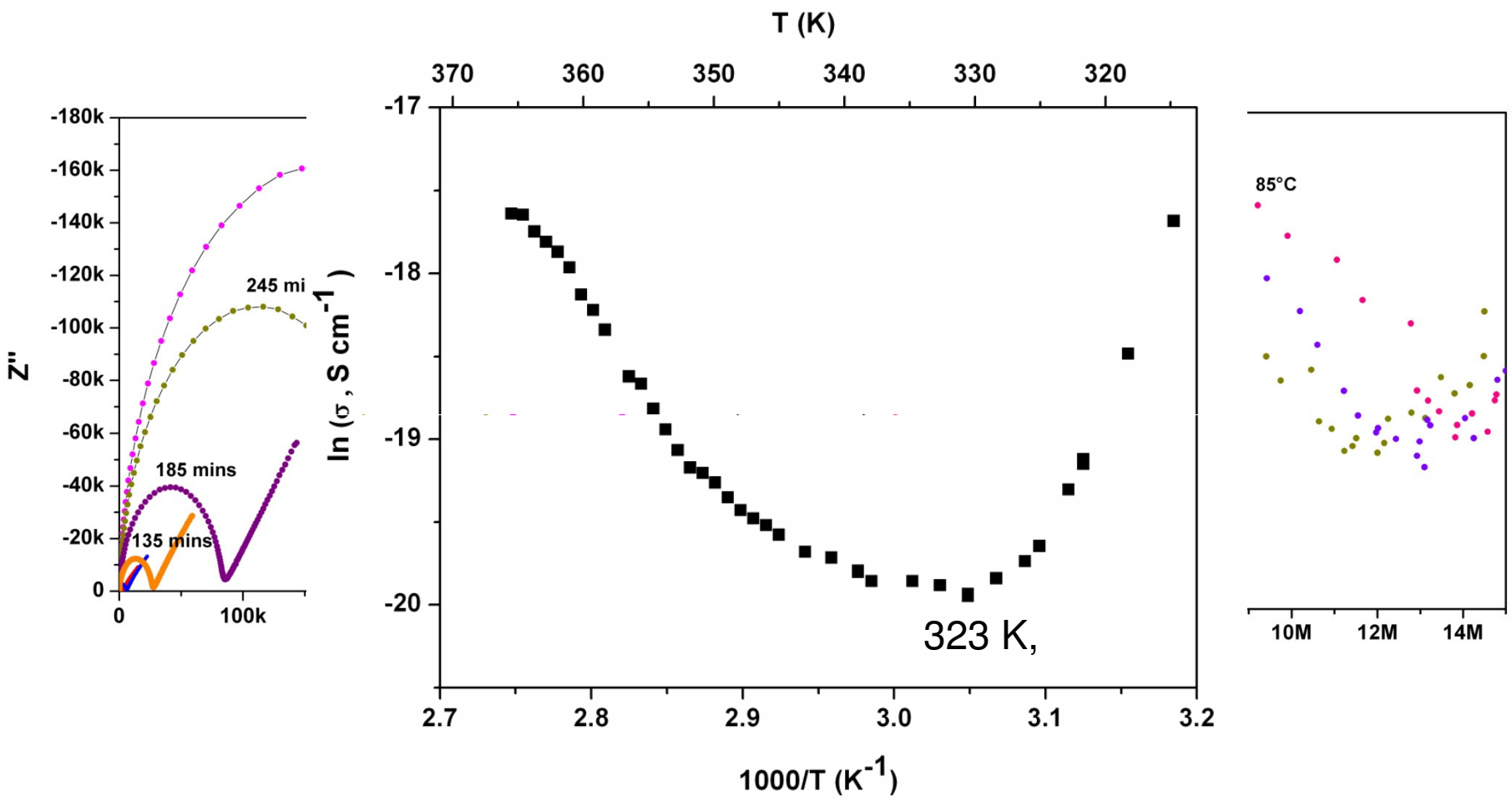
$a_o \sim c_c$

$b_o \sim 3\,[½\,a_c + ½\,b_c]$

$c_o \sim [½\,a_c - ½\,b_c]$,



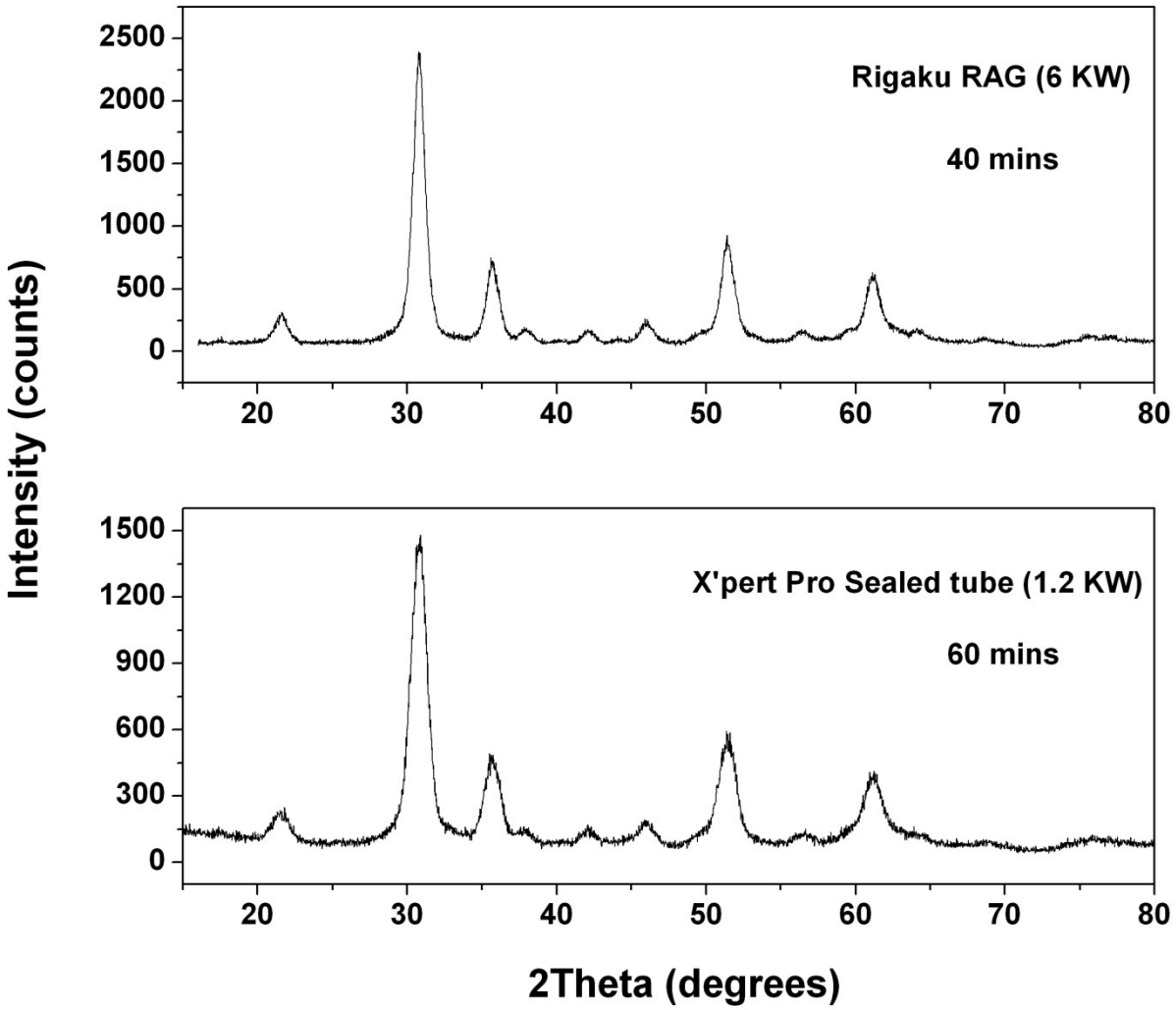
Proton conduction properties



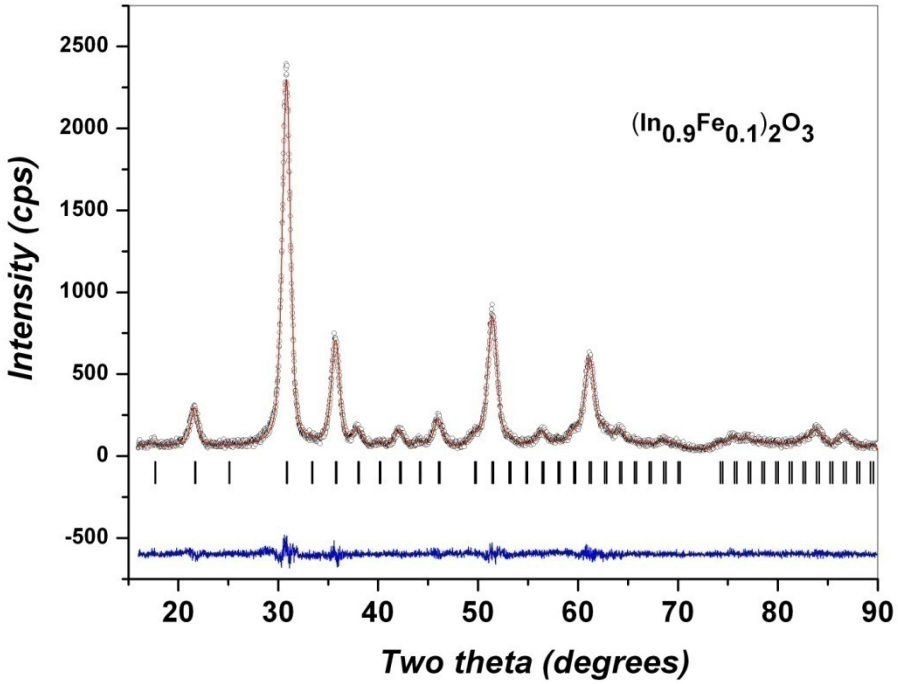
Dilute magnetic semiconductor

- ZnO-Fe
- ZnO-Co
- ZnO-Ni
- In_2O_3-Fe

Powder XRD data of In_2O_3-10 % Fe



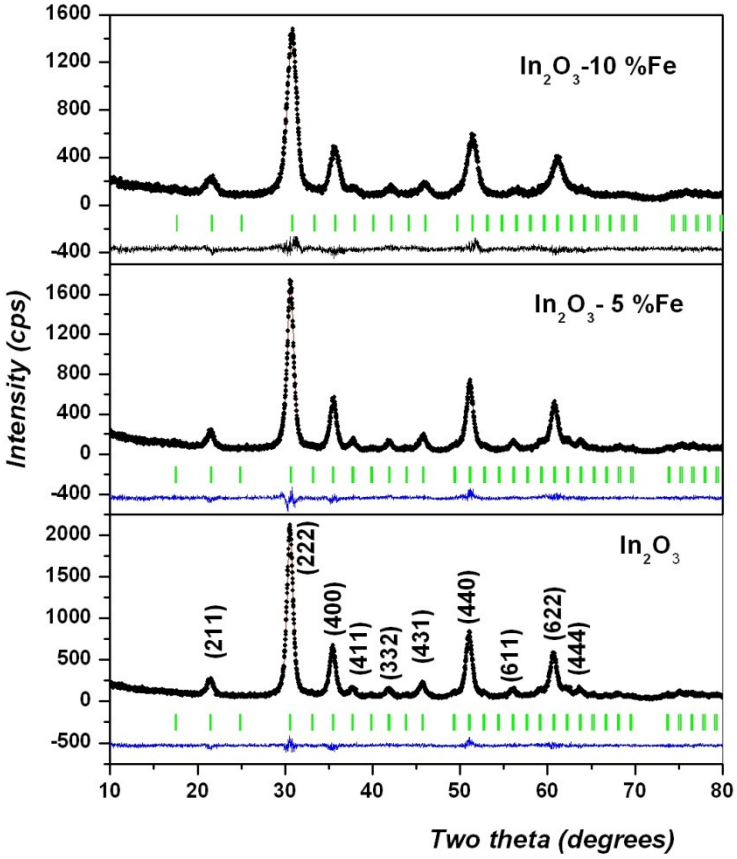
Better signal to noise ratio and peak shape in shorter time

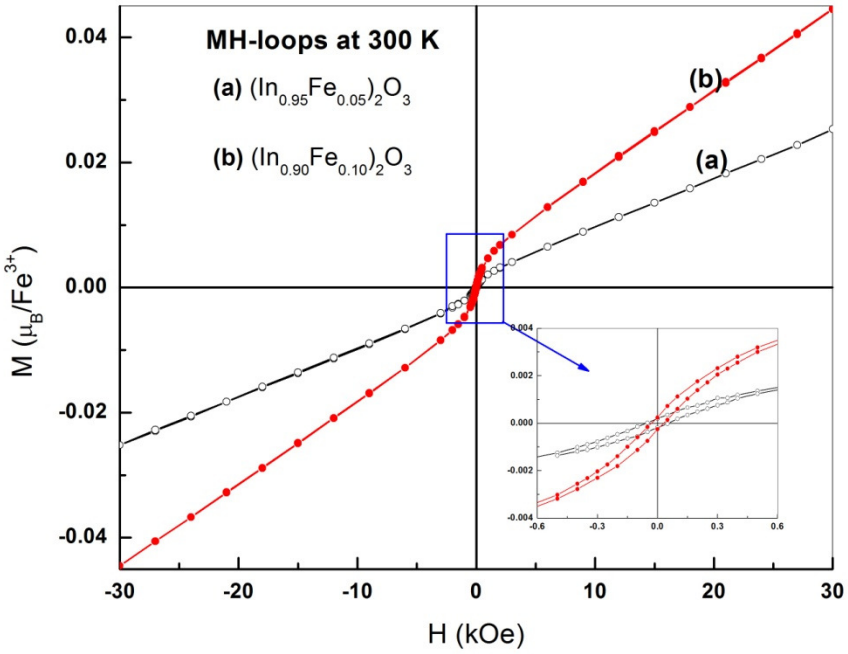


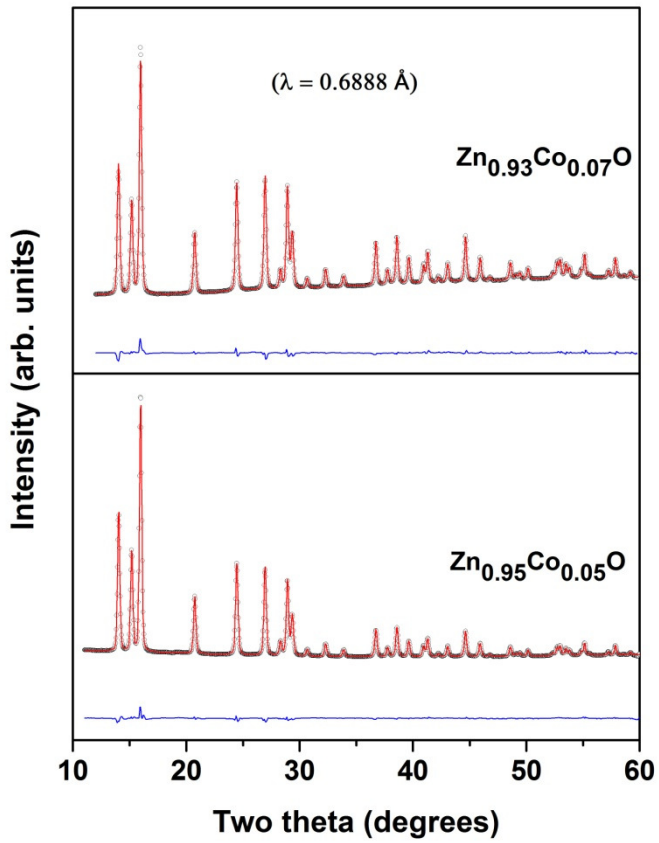
Rietveld refinement plot of x-ray data collected on rotating anode source

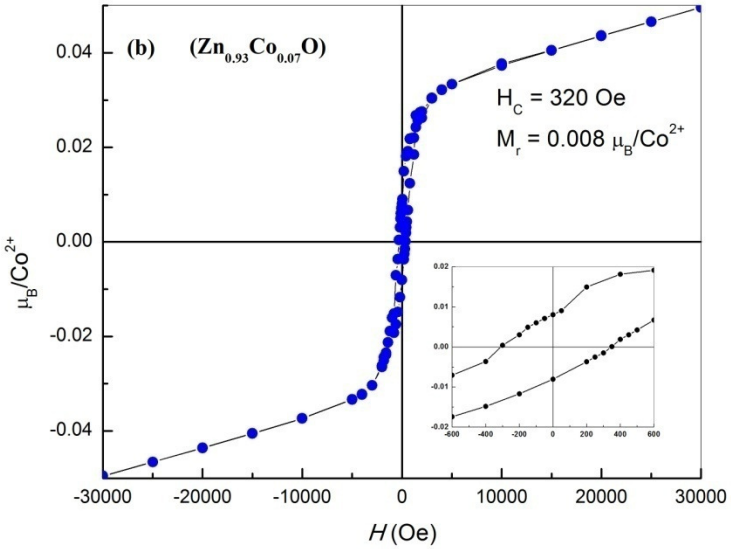
	10 % Fe In_2O_3	
Source	Sealed tube (CuKα)	Rotating anode (CuKα)
Operation power	1.2 KW	6 KW
Space group	Ia-3	Ia-3
a (Å)	10.0510(11)	10.0511(6)
V $(Å)^3$	1015.4(2)	1015.4(1)
In1 *(8b)* (¼,¼,¼)		
In2 *(24d)* (*x*,0,¼)	-0.0300(2)	-0.0323(1)
O *(48e)* (*x*,*y*,*z*)	0.3862(16) 0.1625(10) 0.3823(19)	0.3929(7) 0.1566(7) 0.3864(9)
R_{wp}	6.87	6.82
R_{wp}	9.11	9.52
X^2	1.32	1.49
R_B	2.25	1.98

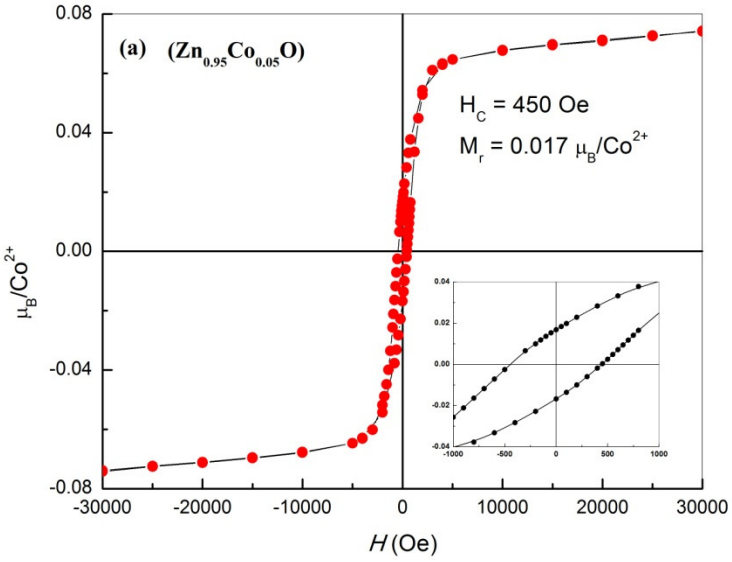
Comparison of structural parameters of two sources

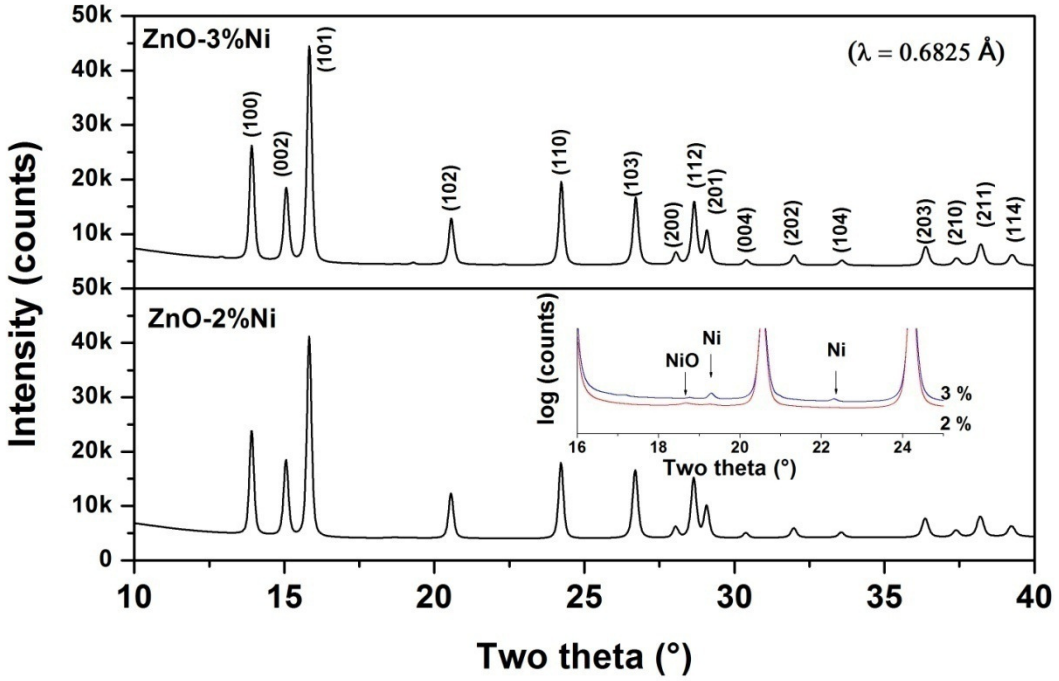

In2O3-10 %Fe
In2O3- 5 %Fe
In2O3
(211)
(222)
(400)
(411)
(332)
(431)
(440)
(611)
(622)
(444)
Intensity (cps)
Two theta (degrees)

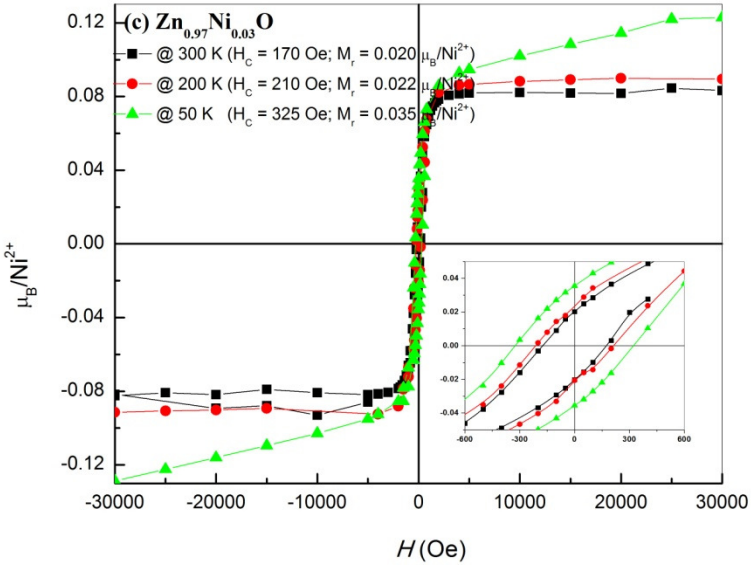

MH-loops at 300 K
(a) (In0.95Fe0.05)2O3
(b) (In0.90Fe0.10)2O3
(a)
(b)
M (μB/Fe3+)
H (kOe)

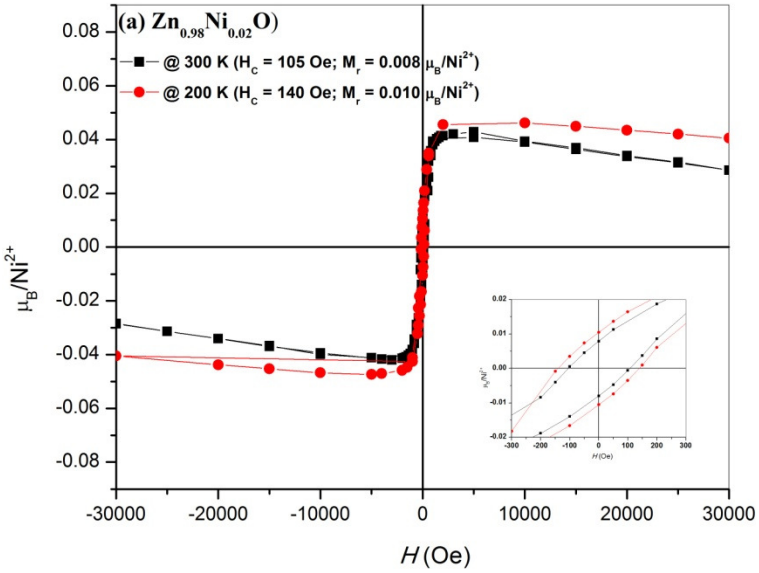

(λ = 0.6888 Å)
Zn0.93Co0.07O
Zn0.95Co0.05O
Intensity (arb. units)
10
20
30
40
50
60
Two theta (degrees)


(b) (Zn0.93Co0.07O)
HC = 320 Oe
Mr = 0.008 μB/Co2+
μB/Co2+
0.04
0.02
0.00
-0.02
-0.04
-30000
-20000
-10000
0
10000
20000
30000
H (Oe)

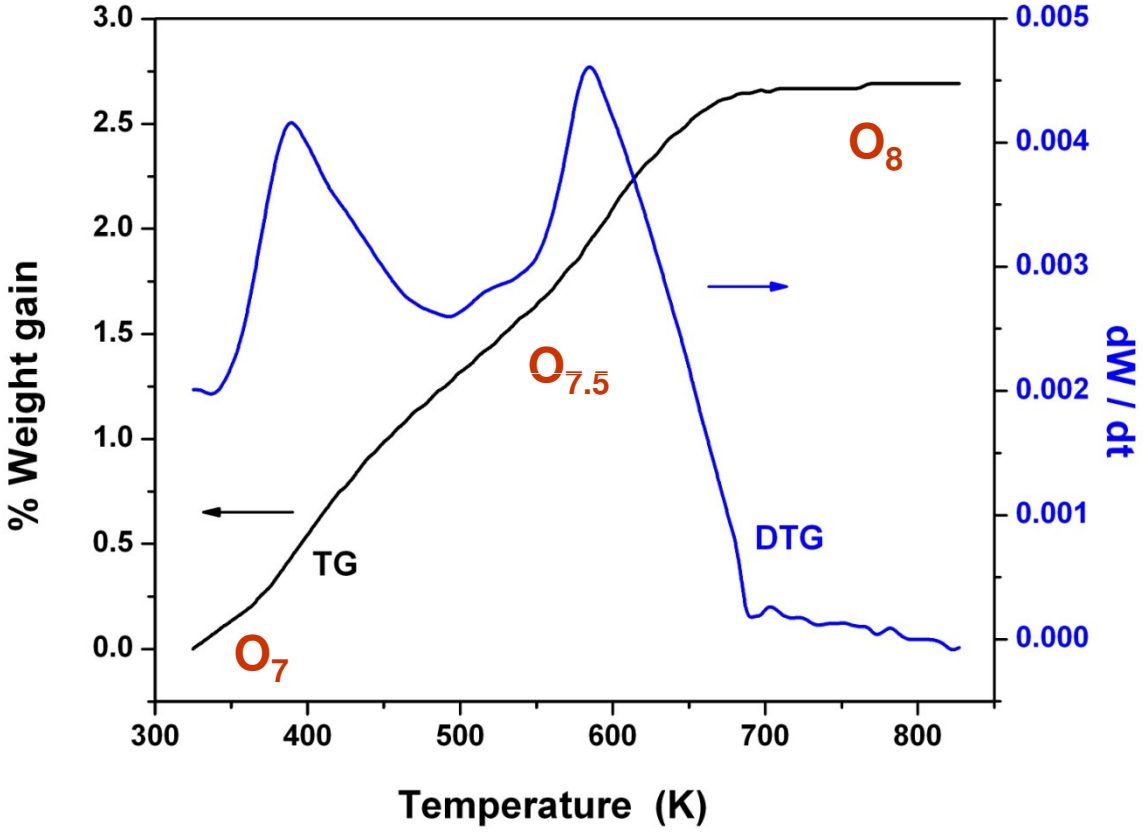

(a) (Zn0.95Co0.05O)
HC = 450 Oe
Mr = 0.017 μB/Co2+
μB/Co2+
0.08
0.04
0.00
-0.04
-0.08
-30000
-20000
-10000
0
10000
20000
30000
H (Oe)

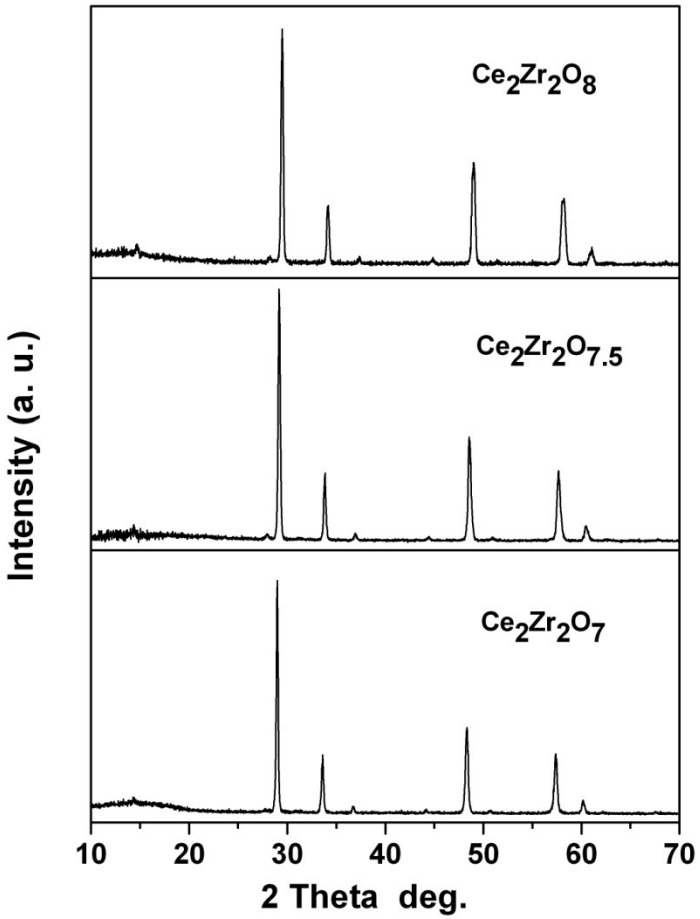

ZnO-3%Ni
(λ = 0.6825 Å)
(100)
(002)
(101)
(102)
(110)
(103)
(200)
(112)
(201)
(004)
(202)
(104)
(203)
(210)
(211)
(114)
ZnO-2%Ni
log (counts)
NiO
Ni
Ni
3 %
2 %
Two theta (°)
Intensity (counts)
Two theta (°)

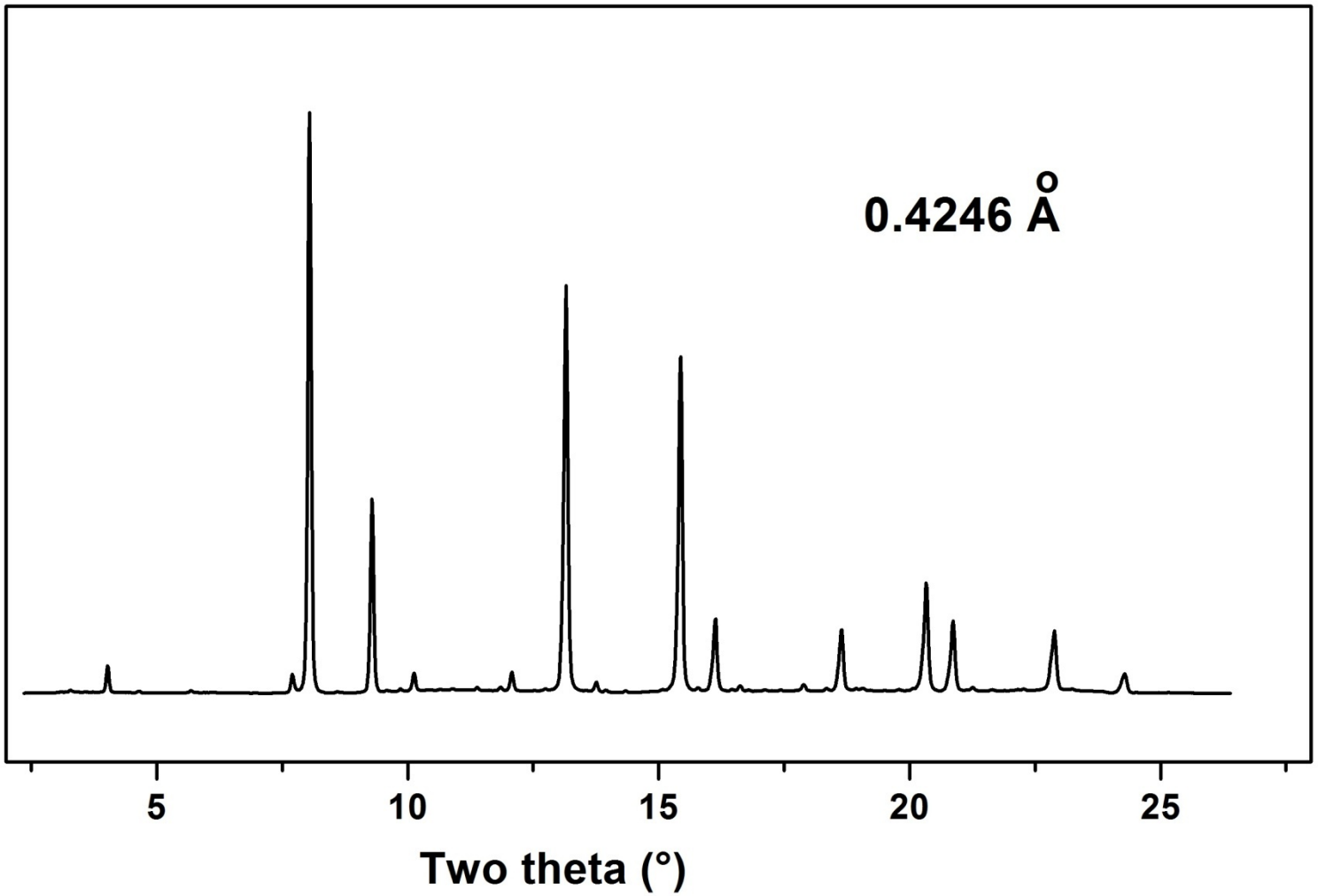

(c) Zn0.97Ni0.03O
@ 300 K (Hc = 170 Oe; Mr = 0.020 μB/Ni2+)
@ 200 K (Hc = 210 Oe; Mr = 0.022 μB/Ni2+)
@ 50 K (Hc = 325 Oe; Mr = 0.035 μB/Ni2+)
μB/Ni2+
H (Oe)


(a) Zn0.98Ni0.02O)
@ 300 K (Hc = 105 Oe; Mr = 0.008 μB/Ni2+)
@ 200 K (Hc = 140 Oe; Mr = 0.010 μB/Ni2+)
μB/Ni2+
H (Oe)

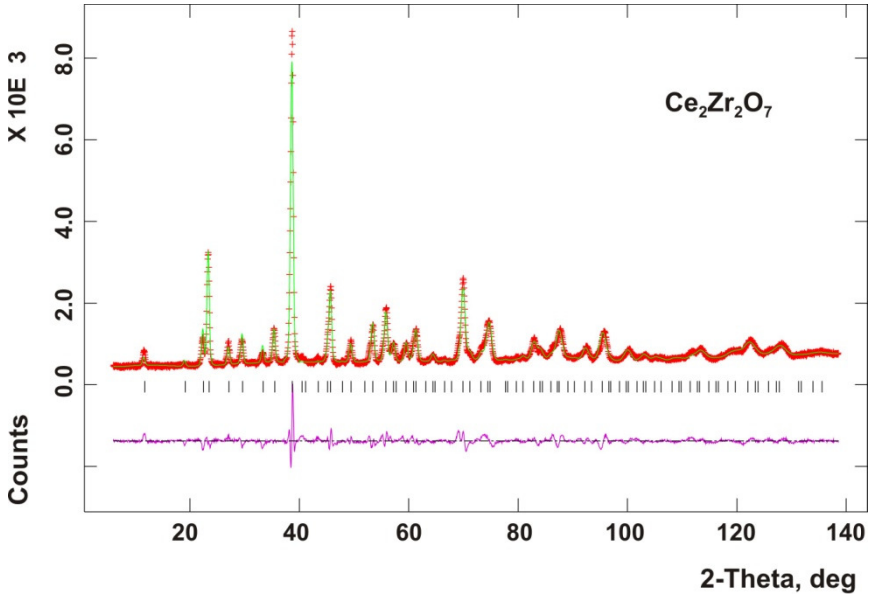
Oxidation of $Ce_2Zr_2O_7$

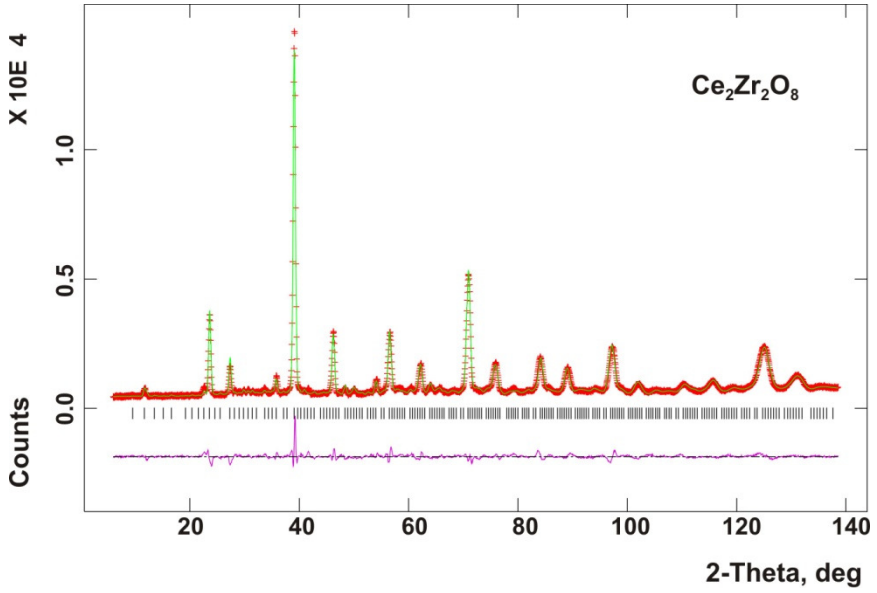





0.4246 Å
5
10
15
20
25
Two theta (°)

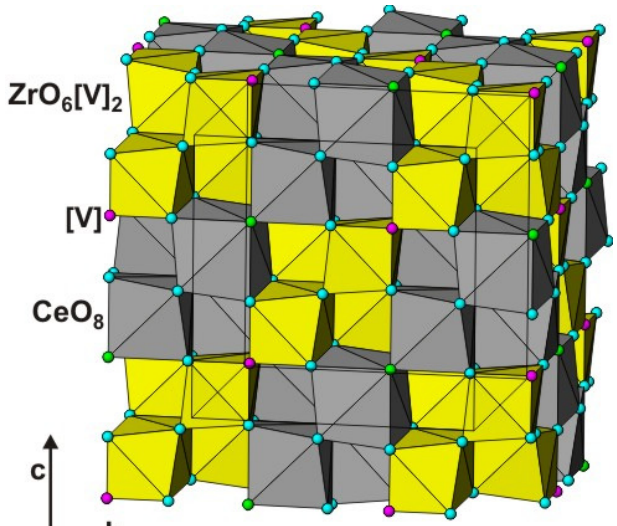
Powder neutron diffraction studies





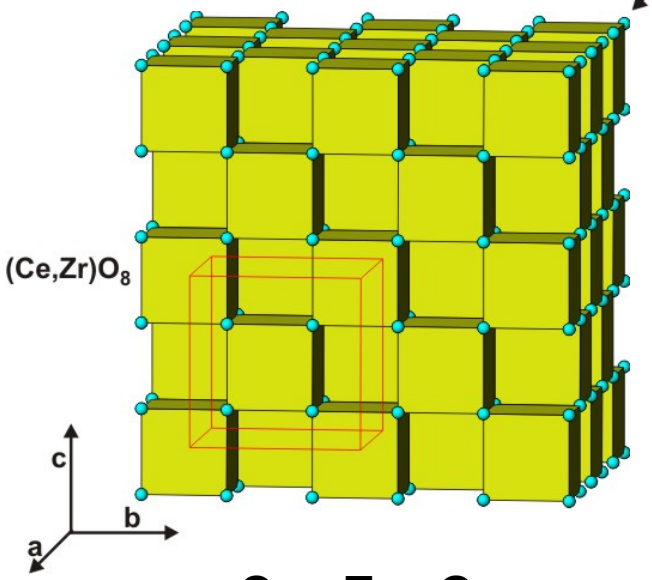
Parameters	Compositions		
Molecular formula	$Ce_2Zr_2O_7$	$Ce_2Zr_2O_{7.52}$	$Ce_2Zr_2O_8$
Color	Black	Gray	Bright yellow
Crystal system	Cubic	Cubic	Cubic
Space group	Fd3m (No. 227)	F-43m (No. 216)	$P2_13$ (No. 198)
a (Å)	10.6924(3)	10.6199(2)	10.5443(2)
V ($Å^3$)	1222.43(11)	1197.74(6)	1172.34(6)
Density (cal)	6.245 g/cc	6.466 g/cc	6.693 g/cc
R_p, R_{wp}	0.0714, 0.0533	0.0597, 0.0447	0.0664, 0.0500
χ^2	3.972	2.928	3.947
R_F^2	0.0717	0.0421	0.0519

$Ce_2Zr_2O_7$ Pyrochlore (Fd3m)

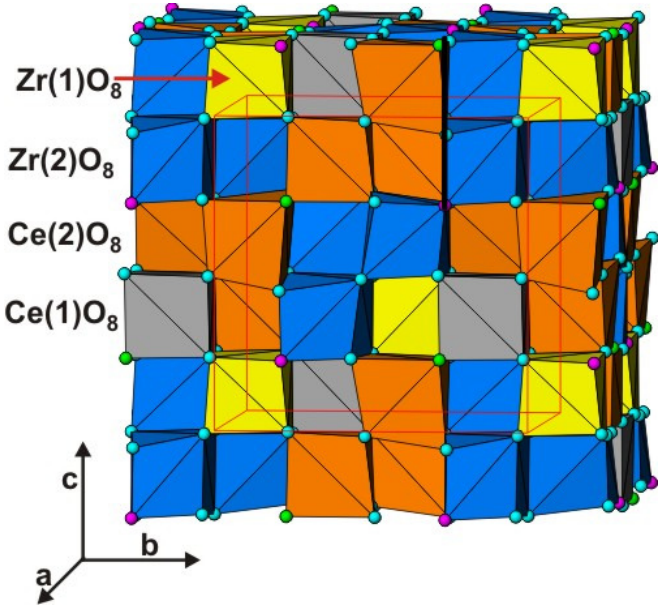


- O_2

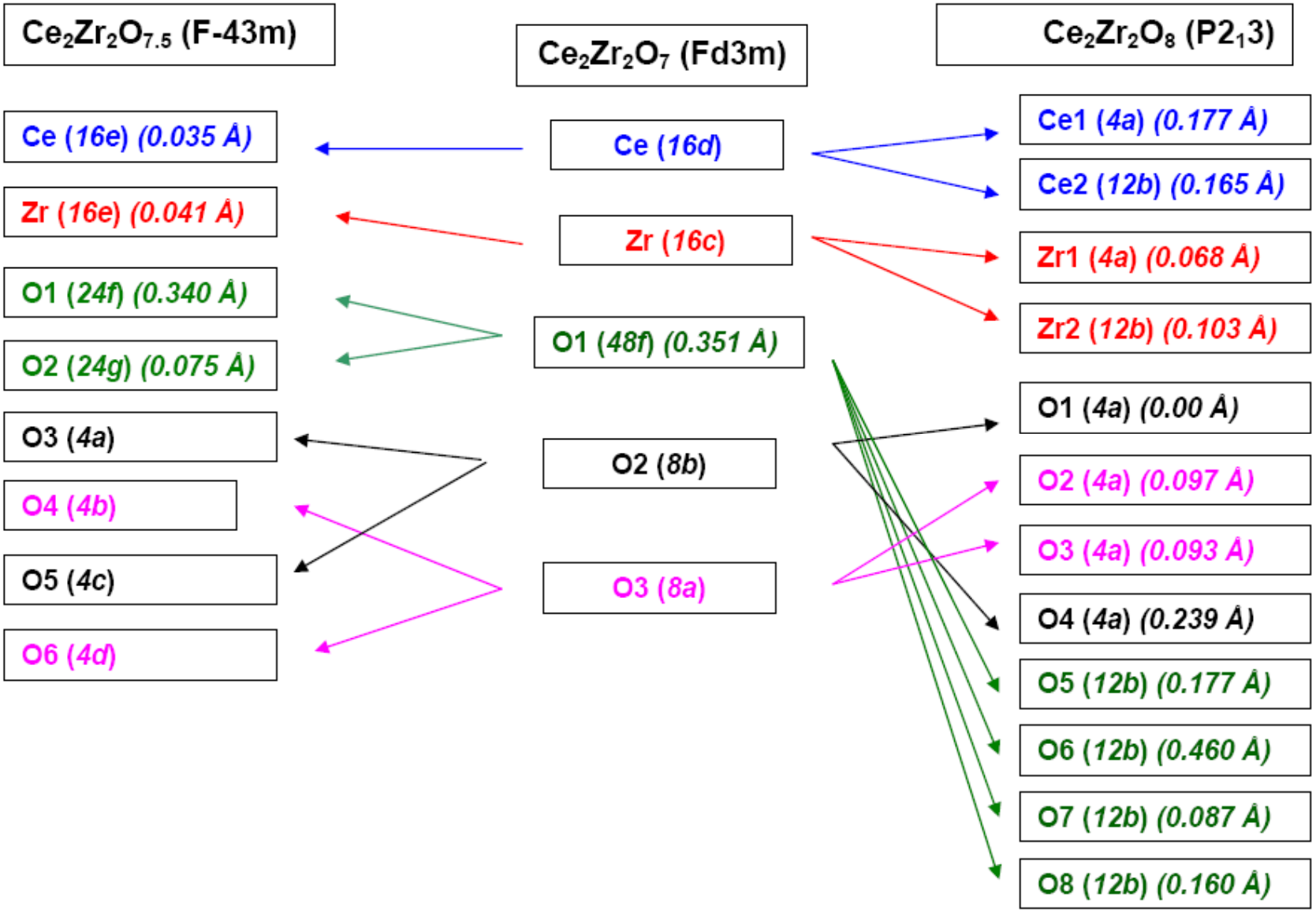
+ O_2

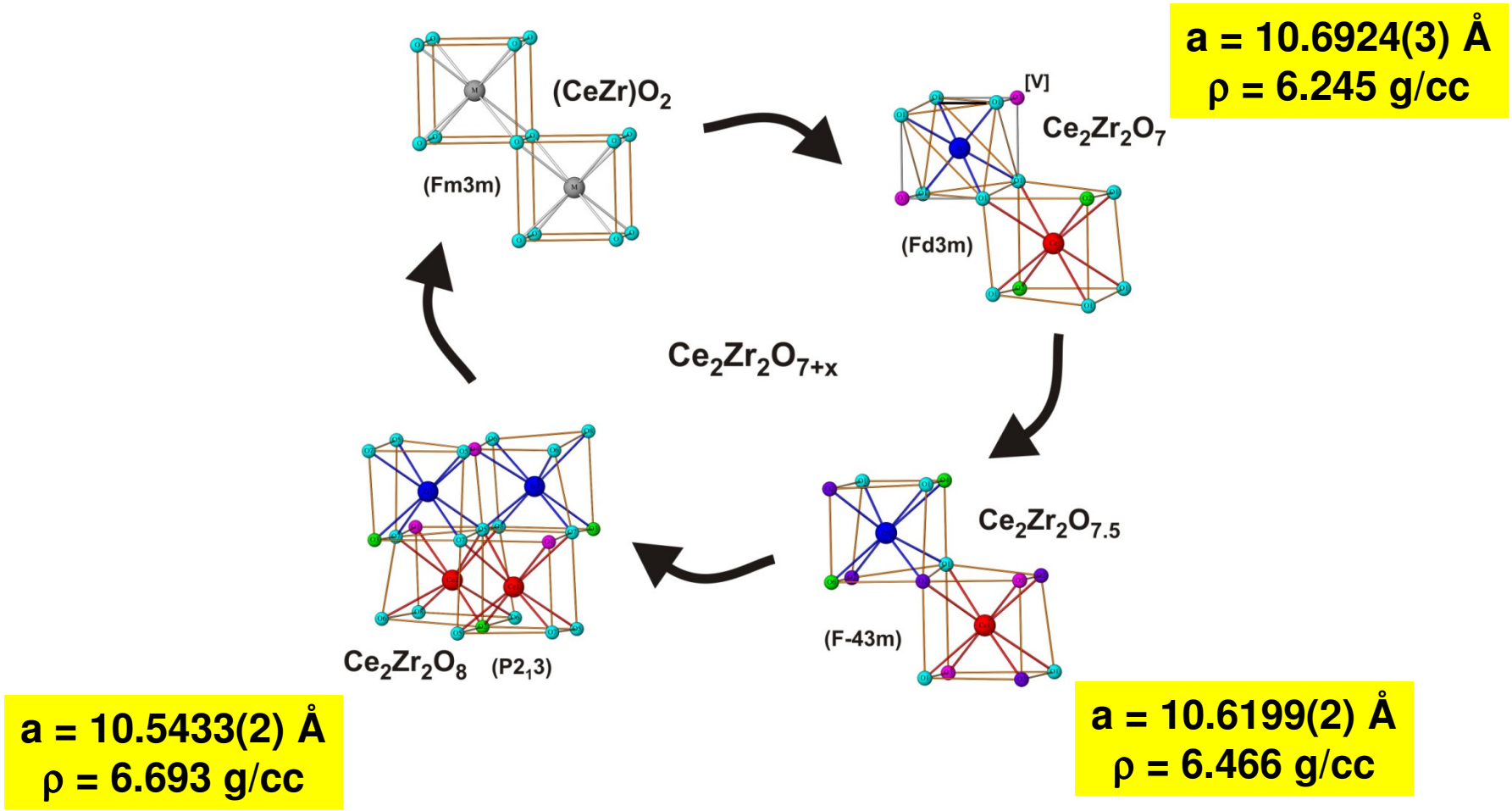


$Ce_{0.5}Zr_{0.5}O_2$
Fluroite (Fm3m)



$Ce_2Zr_2O_8$
Pyrochlore ($P2_13$)


Ce2Zr2O7.5 (F-43m)
Ce2Zr2O7 (Fd3m)
Ce2Zr2O8 (P213)
Ce (16e) (0.035 Å)
Zr (16e) (0.041 Å)
O1 (24f) (0.340 Å)
O2 (24g) (0.075 Å)
O3 (4a)
O4 (4b)
O5 (4c)
O6 (4d)
Ce (16d)
Zr (16c)
O1 (48f) (0.351 Å)
O2 (8b)
O3 (8a)
Ce1 (4a) (0.177 Å)
Ce2 (12b) (0.165 Å)
Zr1 (4a) (0.068 Å)
Zr2 (12b) (0.103 Å)
O1 (4a) (0.00 Å)
O2 (4a) (0.097 Å)
O3 (4a) (0.093 Å)
O4 (4a) (0.239 Å)
O5 (12b) (0.177 Å)
O6 (12b) (0.460 Å)
O7 (12b) (0.087 Å)
O8 (12b) (0.160 Å)



a = 10.6924(3) Å
ρ = 6.245 g/cc

a = 10.6199(2) Å
ρ = 6.466 g/cc

a = 10.5433(2) Å
ρ = 6.693 g/cc

Finally …..

- **Data quality has a significant role of the accurate structural parameters.**
- **The structure is never complete unless it is verified from single crystal data or refined from high resolution synchrotron data.**
- **The structure is never accurate if it failed to explain the properties.**
- **Though Rietveld analysis has large a number of limitation, so far this is the accepted method for ceramics oxides.**

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