Multinuclear solid state NMR studies of phosphate glass samples

Samples:

- 45% P_2O_5 + 30% CaO + (25-x)% Na_2O + x% δ

Where δ = Cu_2O, CuO, ½ Cu_2O

And:

- 50% P_2O_5 + 30% CaO + (20-x)% Na_2O + x% δ

Where δ = Ag_2SO_4

Example of the Cu doped spectra obtained using the 360MHz spectrometer

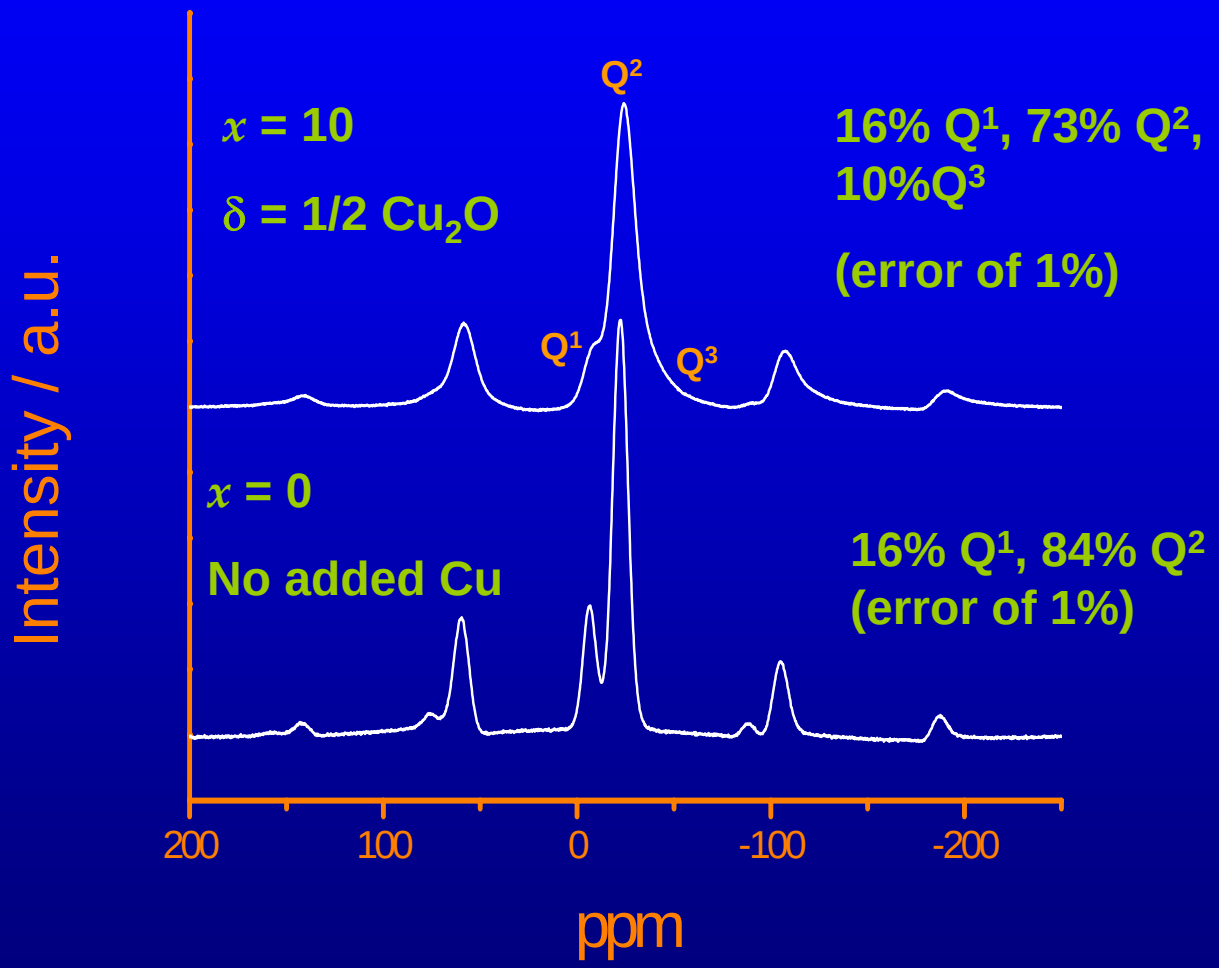
Polyphosphate glass:

55% non-P_2O_5

Thus

$f(Q^2) = (2-3y)/(1-y)$
$= 0.78$

$f(Q^1) = (2y-1)/(1-y)$
$= 0.22$



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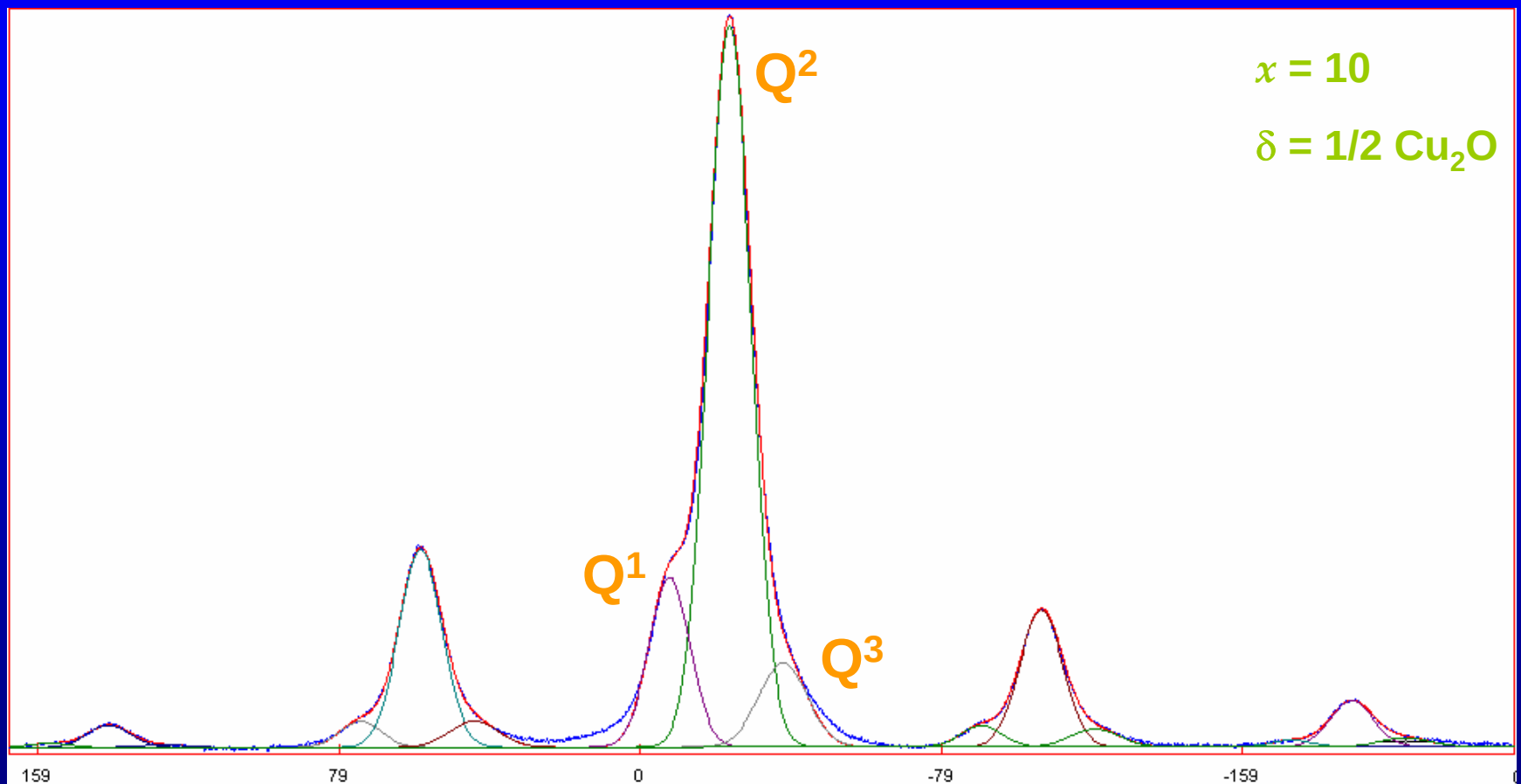
Peak Integration



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Interpretation of Cu Data (I)

CuO doped samples:

- Q^1 remains constant
- Q^2 decreases with increasing CuO
- Q^3 increases with increasing CuO

$\therefore \quad Q^2 \longrightarrow Q^3$

Cu_2O and ½ Cu_2O doped samples:

- Q^1 decreases with increasing Cu_2O
- Q^2 decreases with increasing Cu_2O
- Q^3 increases with increasing Cu_2O

Interpretation of Cu Data (II)

This correlation between increasing Cu content and the change in Q species suggests:

- As Cu % increases we are forming more bridging oxygen atoms between the ^{31}P atoms in the sample.
- This was unexpected as the Cu atoms were expected to bond to these oxygen atoms, hence reducing the number of bridging oxygen atoms to phosphorous atoms.

Interpretation of Cu Data (III)

- The ternary sample 45% P_2O_5 + 30% CaO + 25% Na_2O was found to contain less Q^1 than any of the 1% Cu doped samples which brings into question the general decreasing trend in the Q^1 species found in each case.
- $Q^2 \longrightarrow Q^3$ when more Cu is added to the system.
- The next step is to find out why…???

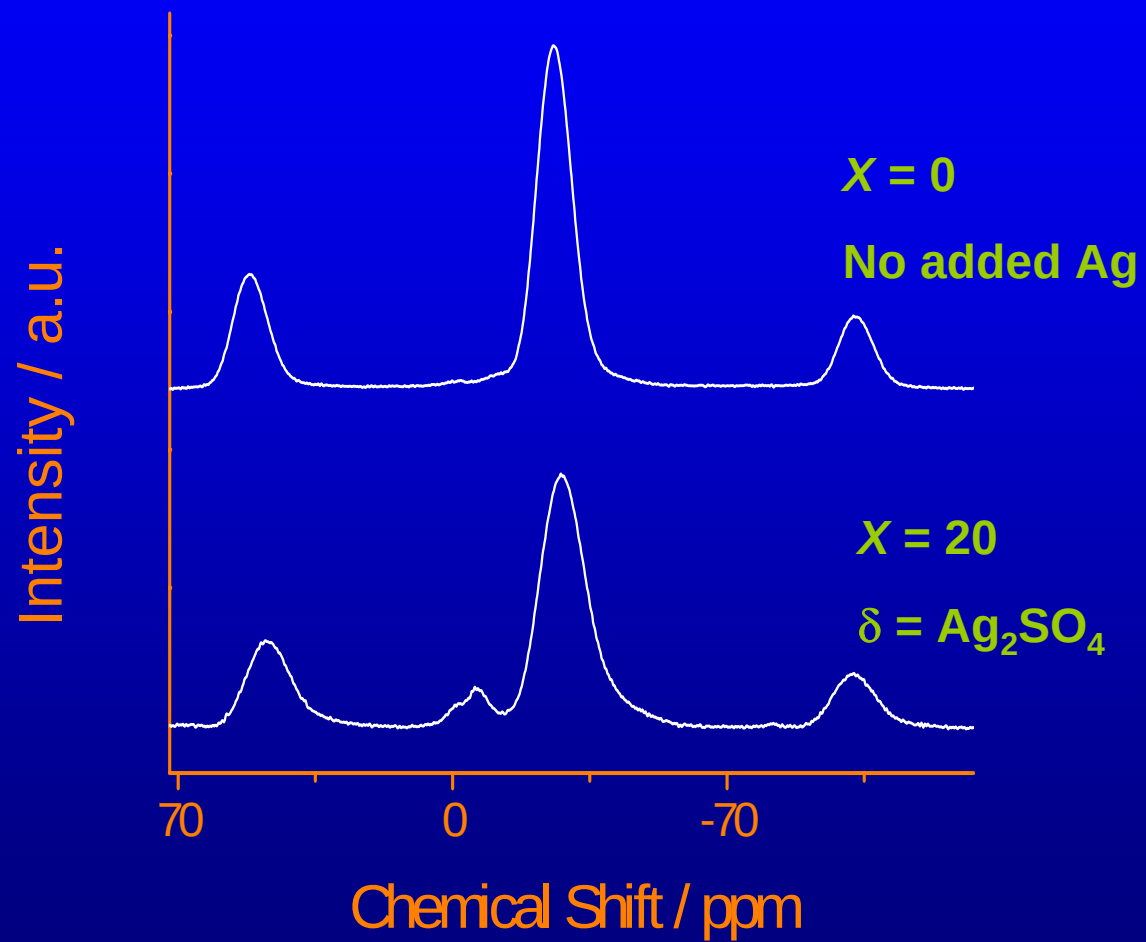
Example of the Ag doped spectra obtained using the 360MHz spectrometer

Non-crystalline samples

Metaphosphate glass:

50% non-P_2O_5

Theoretically - Networks are based entirely on Q^2 tetrahedra forming chains and rings

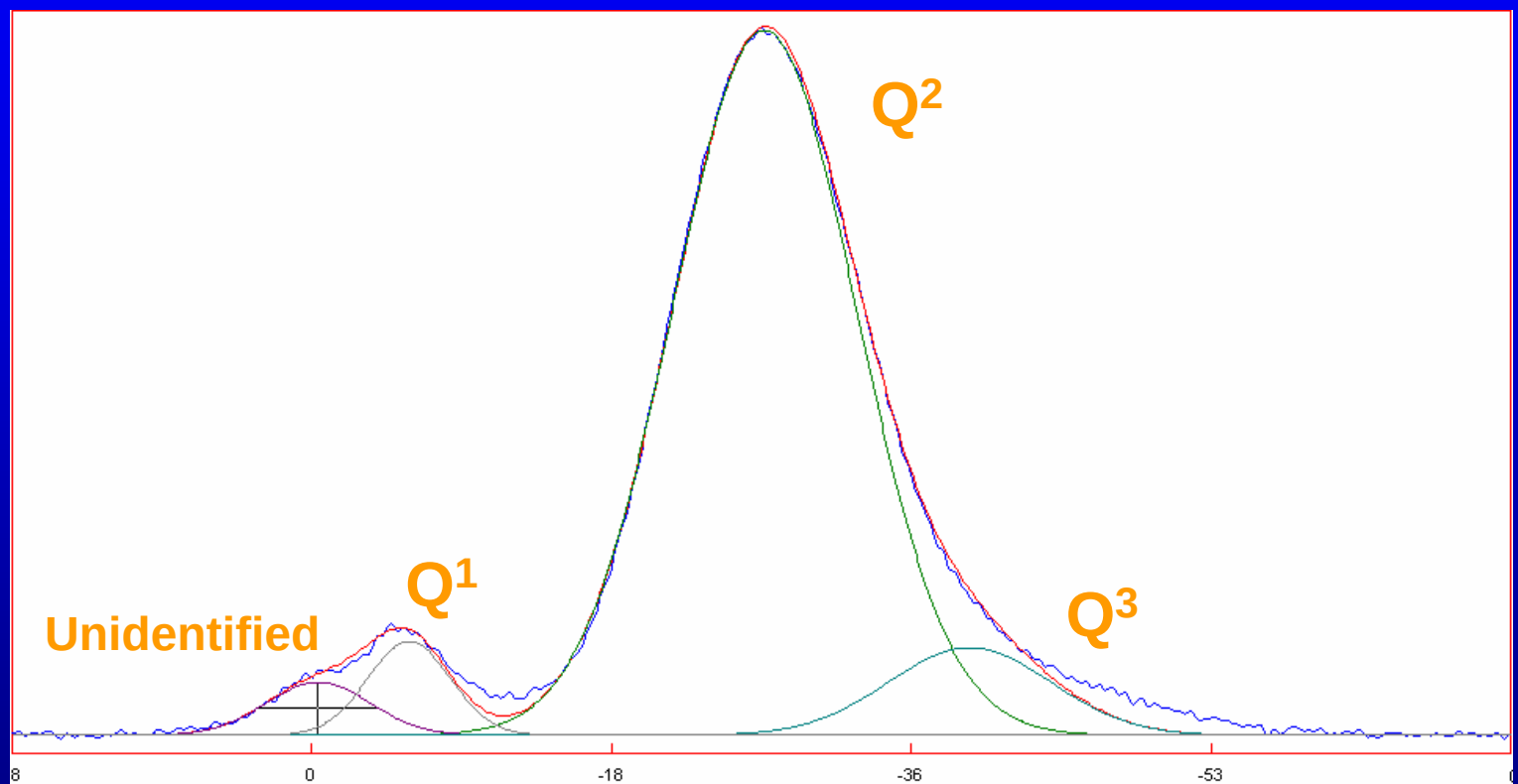


Interpretation of Ag Data (I)

Ag doped samples:

- Predicted to be all Q^2
- All 100% Q^2 species present until 20% of Ag_2SO_4 is added
- At 20% doping we have 87% Q^2,8% Q^3 and 4% Q^1
- Also present is an unidentified peak (2%)
- Why???

Peak Integration



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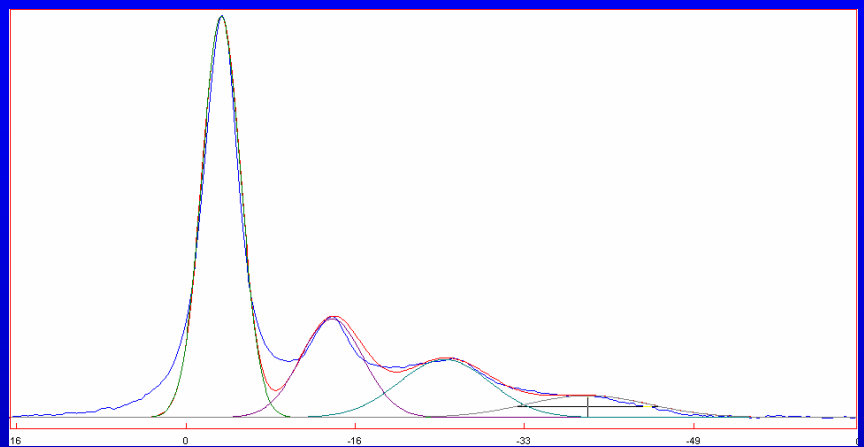
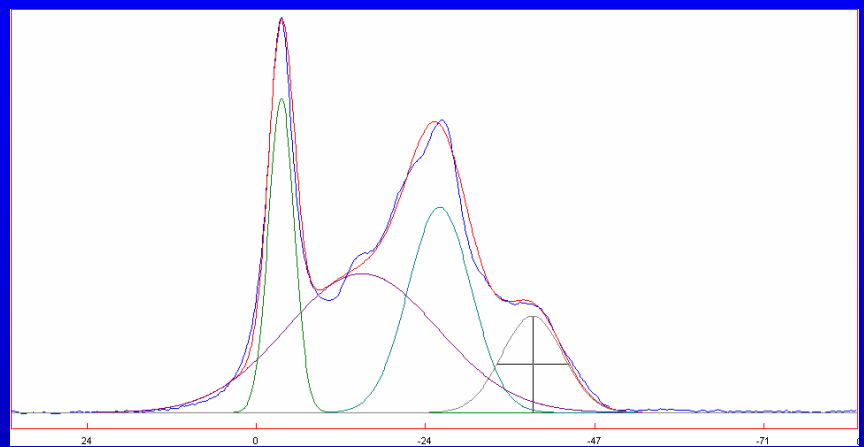
Ag doped, crystallised phosphate glasses

- The crystalline phase is less anisotropic than the glass phase, this gives rise to:
  - Narrower peaks
  - No related side bands
  - Different T_1 relaxation to the glass peak

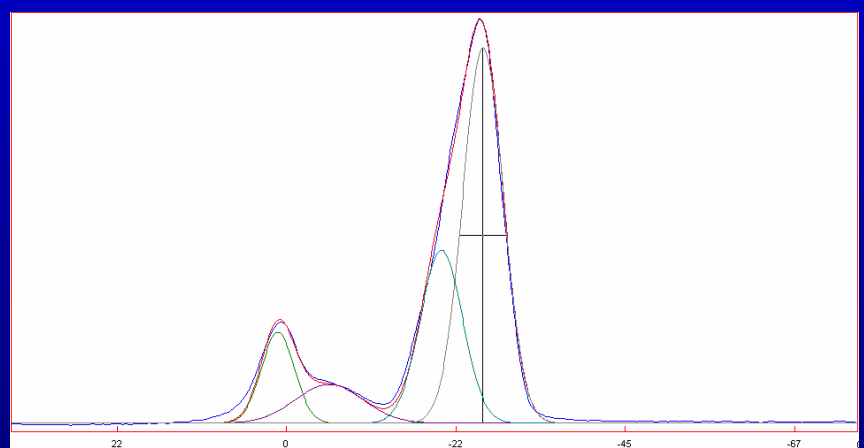
Effects of different T_1 relaxation





Pulse delay 3s

Pulse delay 30s



Pulse delay 120s

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Table of Data

Sample Cu content	Peak 1 (Q^1)			Peak 2 (Q^2)			Peak 3 (Q^3)		
	δ_{iso} / ppm ± 0.2ppm	Δ / ppm ± 0.7ppm	I / % ± 1%	δ_{iso} / ppm ± 0.2ppm	Δ / ppm ± 0.7ppm	I / % ± 1%	δ_{iso} / ppm ± 0.2ppm	Δ / ppm ± 0.7ppm	I / % ± 1%
0	-6.5	8.0	16	-22.5	9.8	84			0
CuO 1%	2.6	10.1	23	-13.5	12.1	77			0
Cu_2O 1%	2.2	10.0	24	-13.6	10.8	76			0
half Cu_2O 1%	2.2	9.5	22	-13.7	11.2	78			0
CuO 5%	-6.6	12.1	23	-22.2	12.3	69	-34.8	12.8	8
Cu_2O 5%	-6.7	10.9	18	-22.5	12.1	74	-35.9	14.3	7
half Cu_2O 5%	-7.1	10.6	17	-22.8	11.8	78	-34.8	11.6	6
CuO 10%	-7.3	13.9	22	-23.0	14.1	64	-38.0	14.6	14
Cu_2O 10%	0.4	13.1	16	-15.0	13.3	73	-28.0	12.6	10
half Cu_2O 10%	-7.7	12.7	14	-23.5	13.3	75	-37.7	15.0	10

Potential Papers

- **Nb_2O_5 - SiO_2 Sol-Gel Binary & Nb_2O_5 – TiO_2 - SiO_2 Sol-Gel Ternary XRD & EXAFS (Possibility to split into two papers)**

  All results finished, just need to write paper/papers.

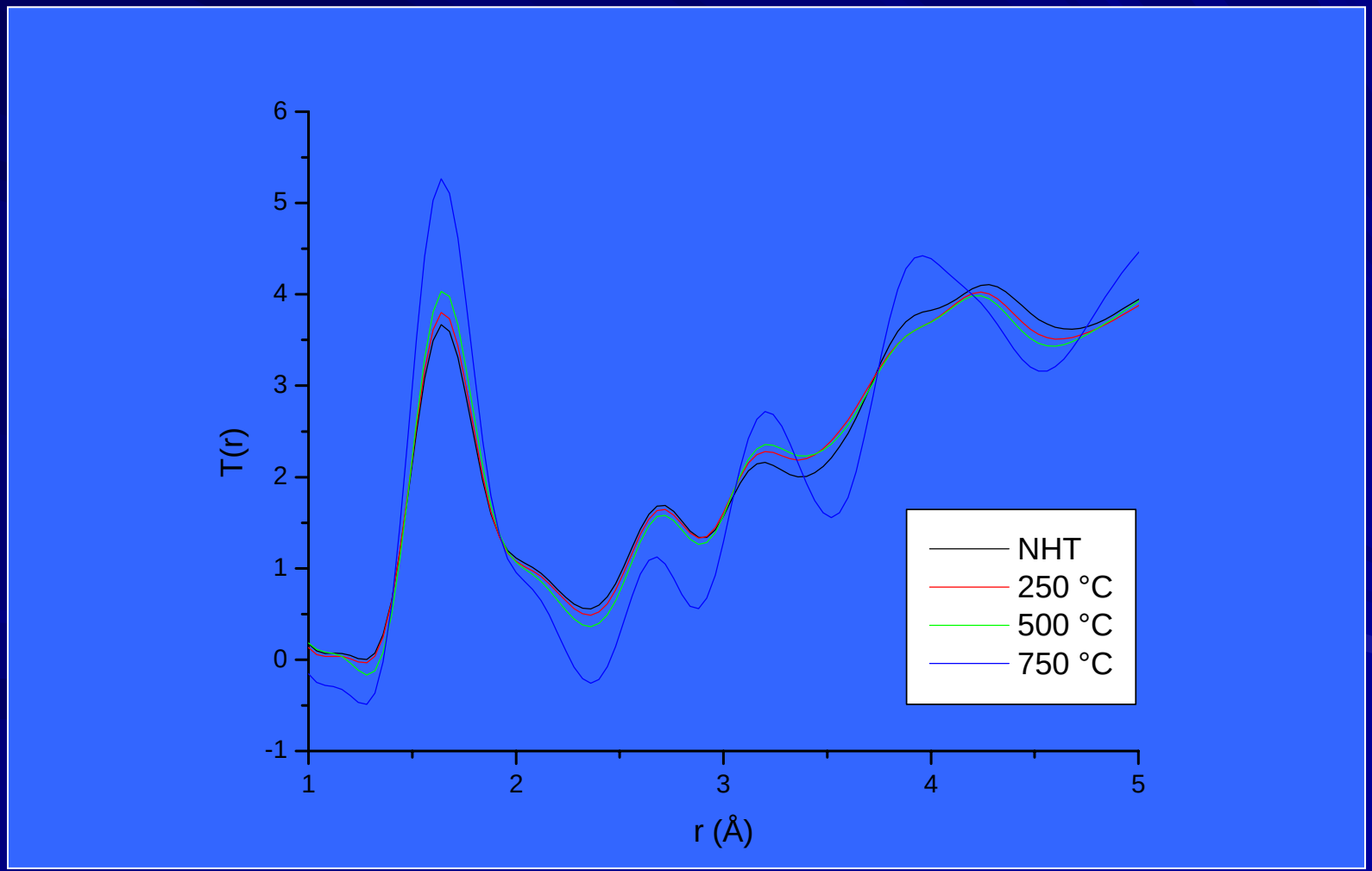
- **TiO_2 – SiO_2 in-situ gelation XRD (Not sure if the results are particularly interesting)**

  Results have been looked at and don't seem to show much change with time. Needs further work.

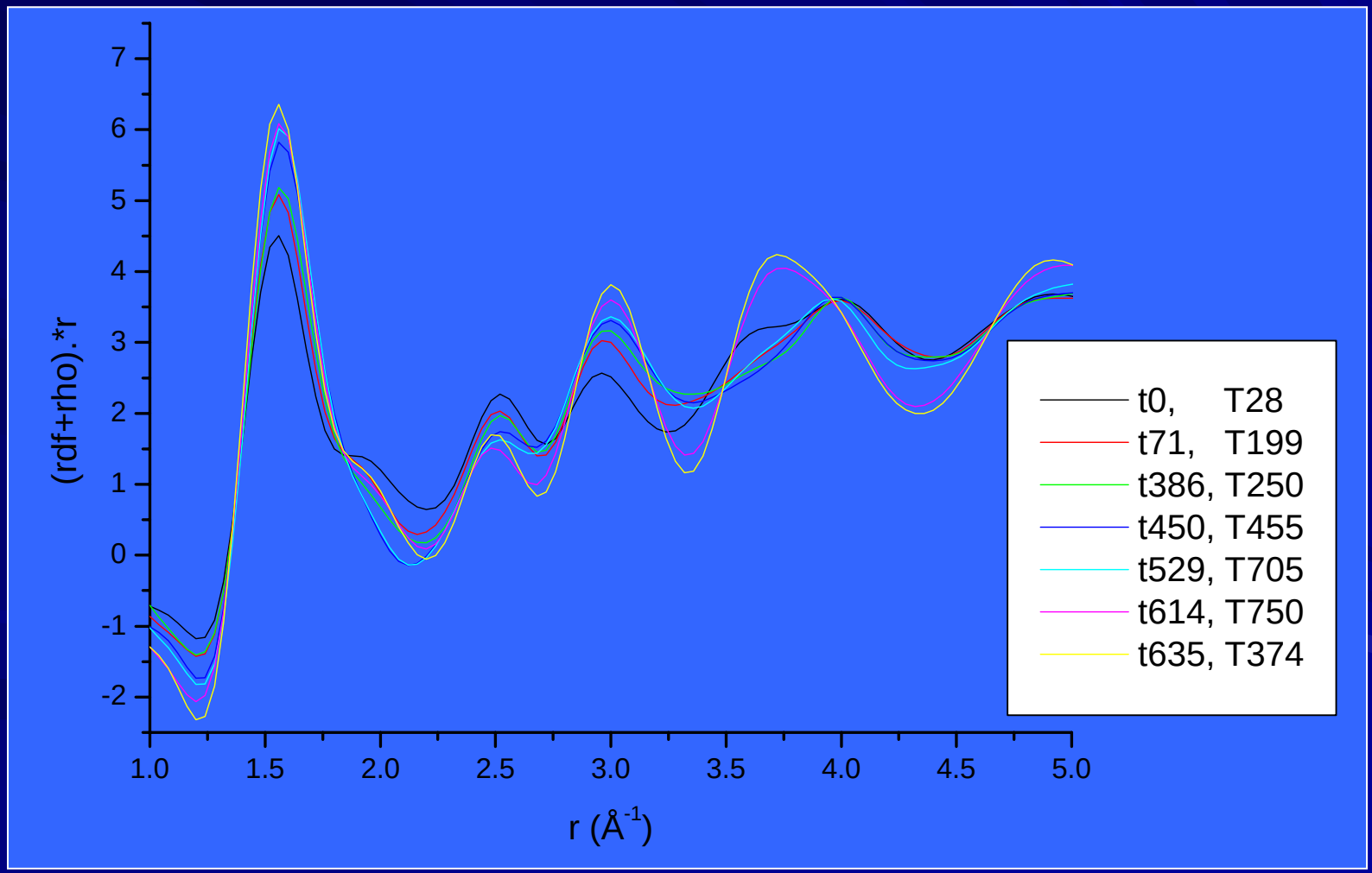
- **TiO_2 – SiO_2 in-situ heat treatment XRD**

  Results look promising. Need to fit individual scans.

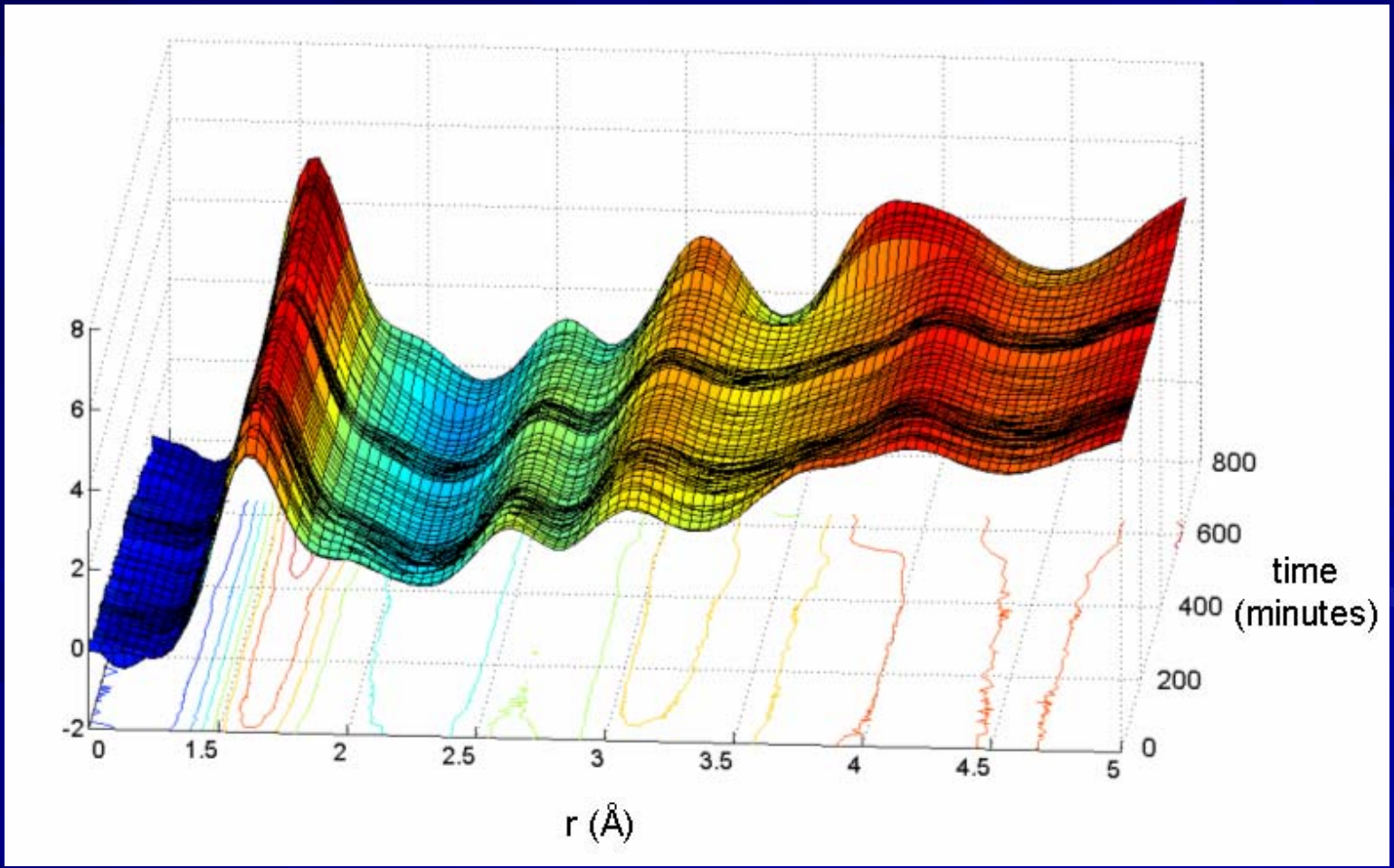
$(Nb_2O_5)_{0.0375}$ - $(TiO_2)_{0.075}$ - $(SiO_2)_{0.8875}$ heated *ex-situ*



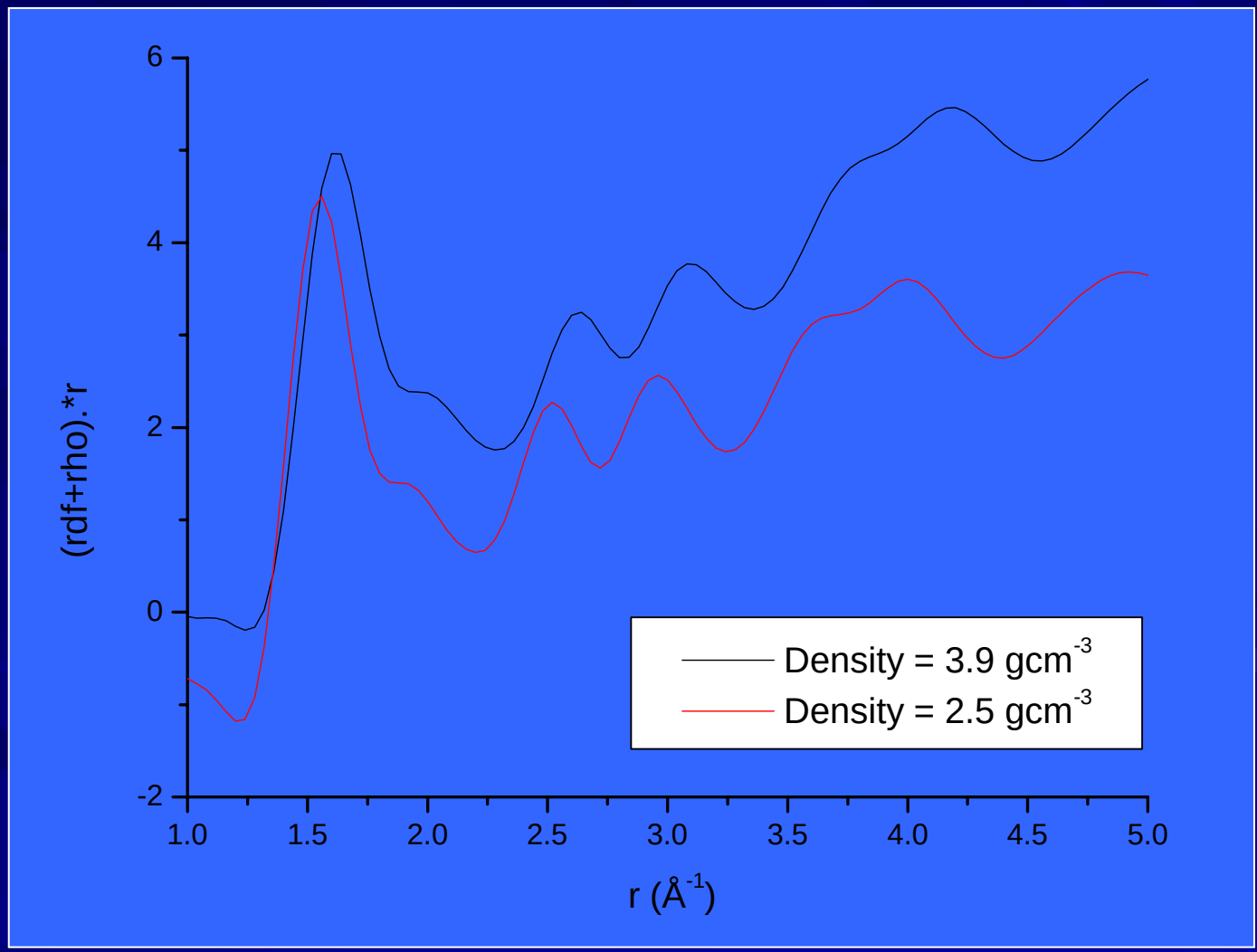
$(Nb_2O_5)_{0.0375}$ - $(TiO_2)_{0.075}$ - $(SiO_2)_{0.8875}$ heated *in-situ*



$(Nb_2O_5)_{0.0375}$ - $(TiO_2)_{0.075}$ - $(SiO_2)_{0.8875}$ heated *in-situ*



Differences caused by errors in the density



UCL (Eastman Dental Institute) - Kent-Warwick-Imperial Sol- Gel Project Meeting

Dr. Ifty Ahmed

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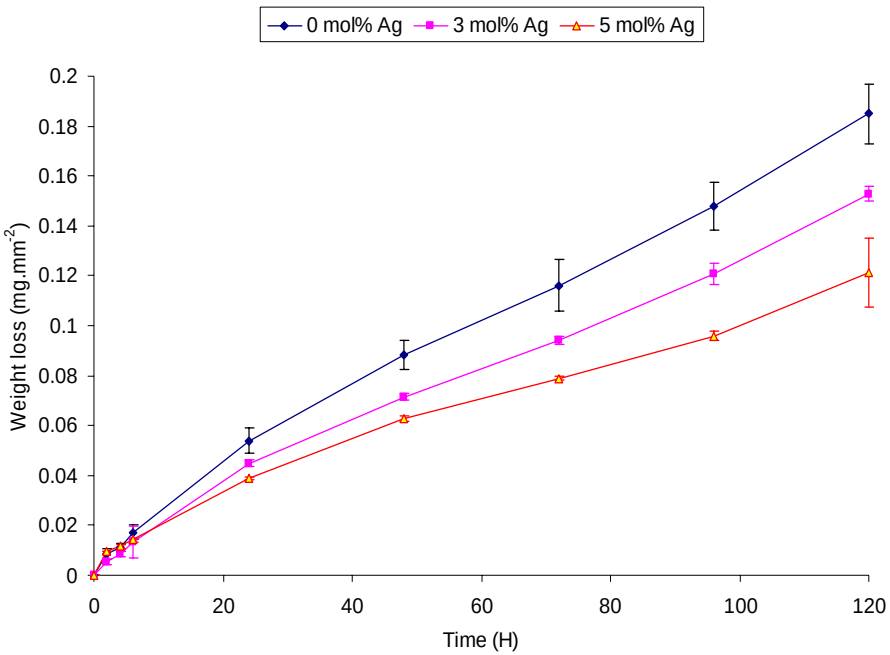
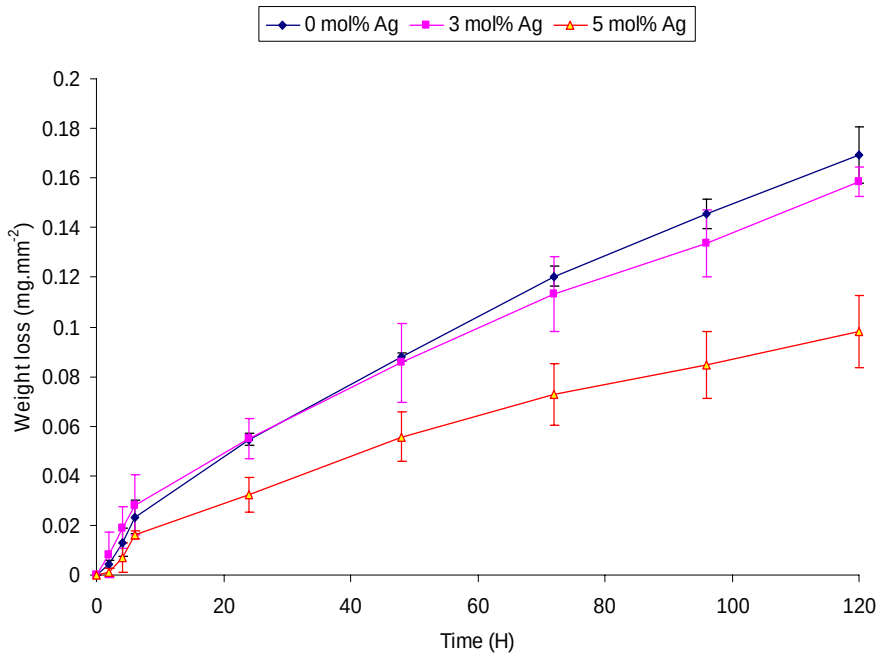
Silver-Doped Glasses Investigated:

Composition	Mol%			
	P_2O_5	CaO	Na_2O	Ag
P50 C30 N20	50	30	20	0
P50 C30 N19 + Ag = 1	50	30	19	1
P50 C30 N18 + Ag = 2	50	30	18	2
P50 C30 N17 + Ag = 3	50	30	17	3
P50 C30 N16 + Ag = 4	50	30	16	4
P50 C30 N15 + Ag = 5	50	30	15	5
P50 C30 N10 + Ag = 10	50	30	10	10
P50 C30 Ag = 20	50	30	0	20

Degradation Studies conducted in Nutrient Broth and dH2O:

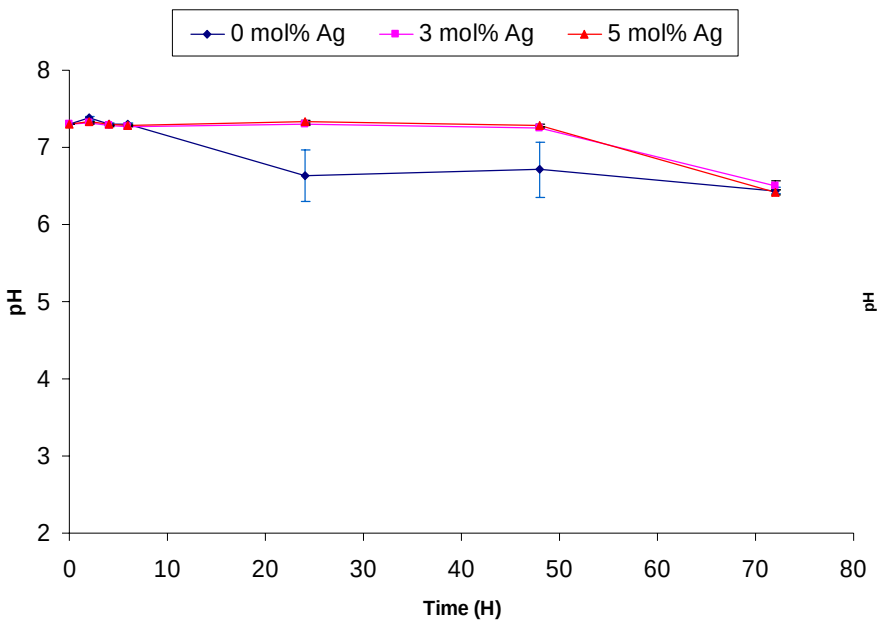


Study conducted in Nutrient Broth

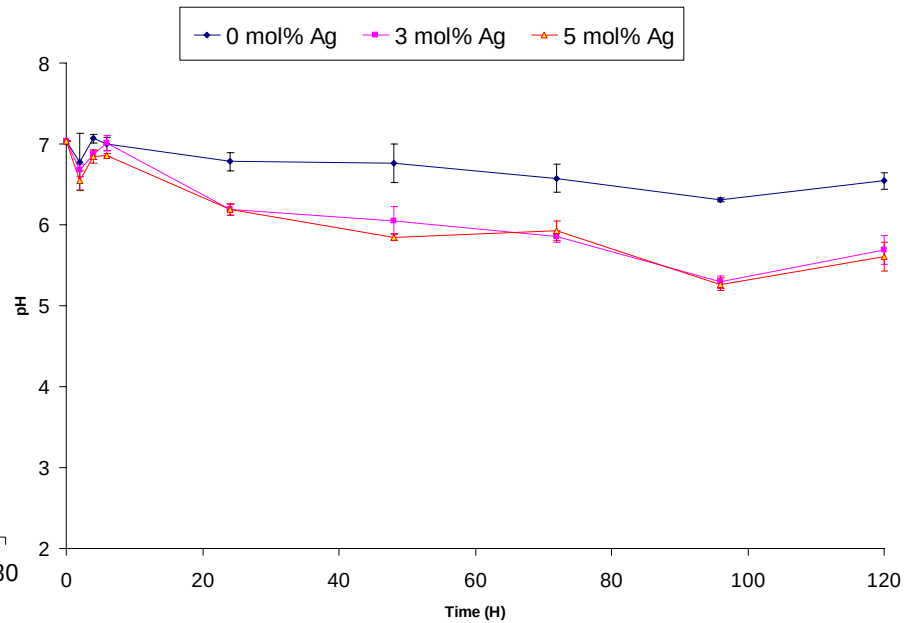


Study conducted in dH2O

pH Studies conducted in Nutrient Broth and dH2O:

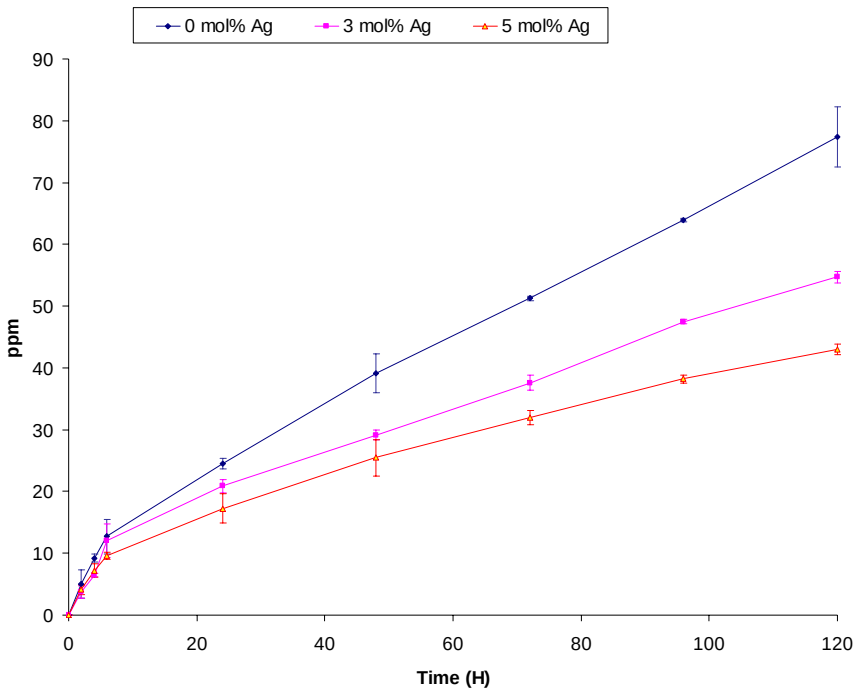


Study conducted in Nutrient Broth

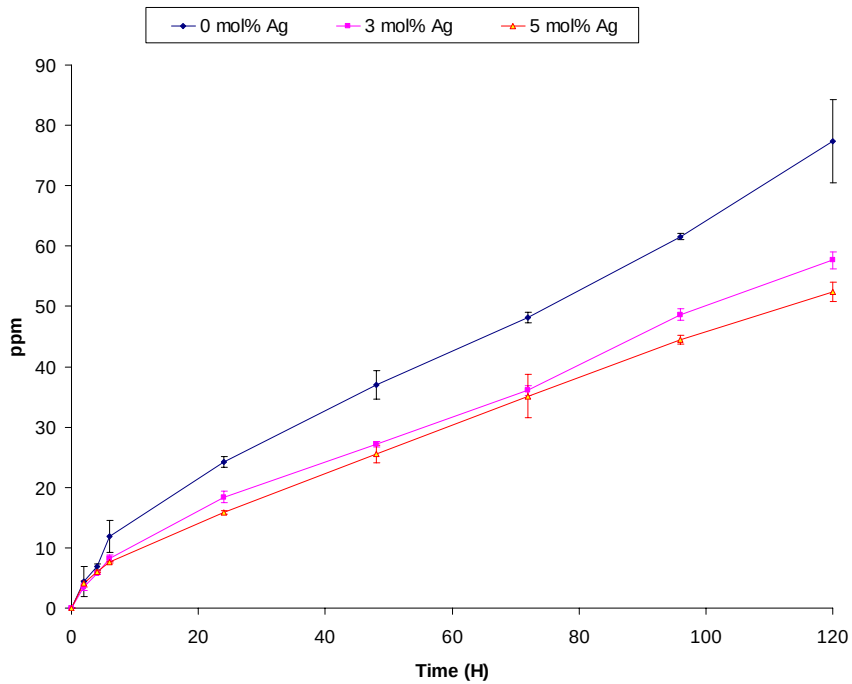


Study conducted in dH2O

Cation Release from Silver-Doped PBG's:

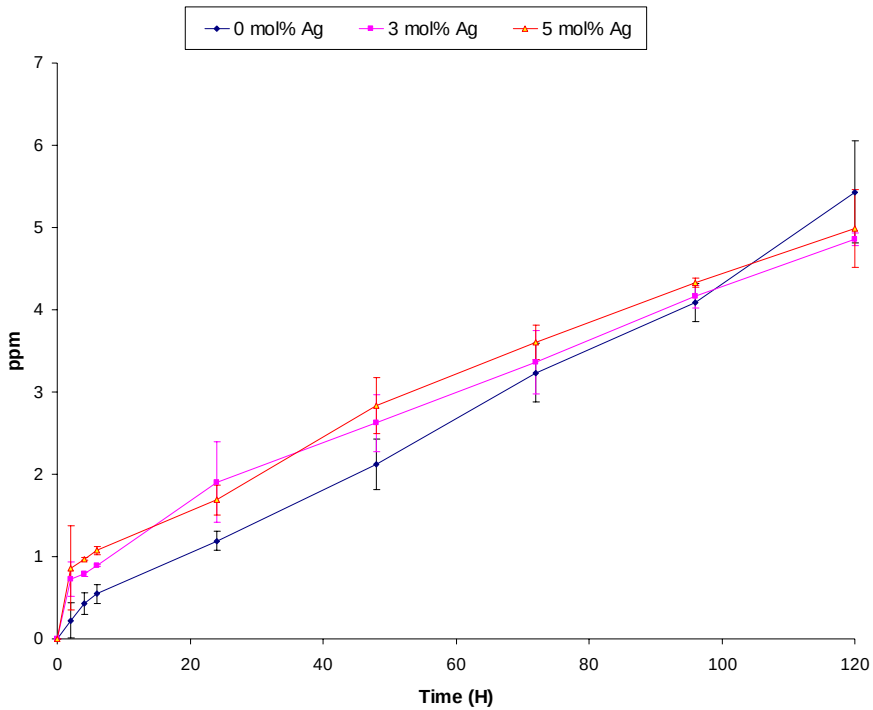


Sodium ion release profiles

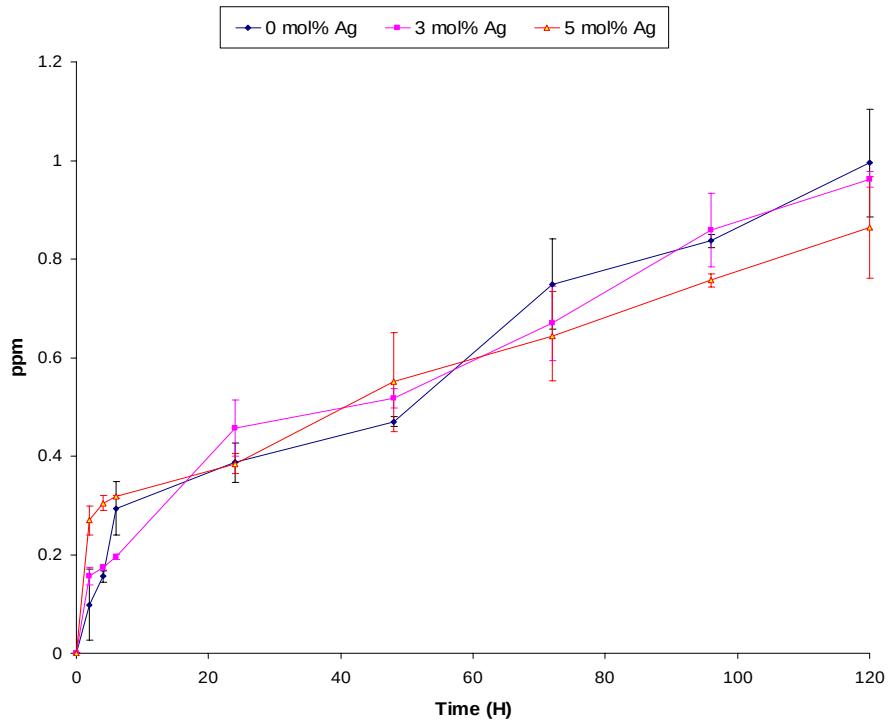


Calcium ion release profiles

Anion Release from Silver-Doped PBG's (I):

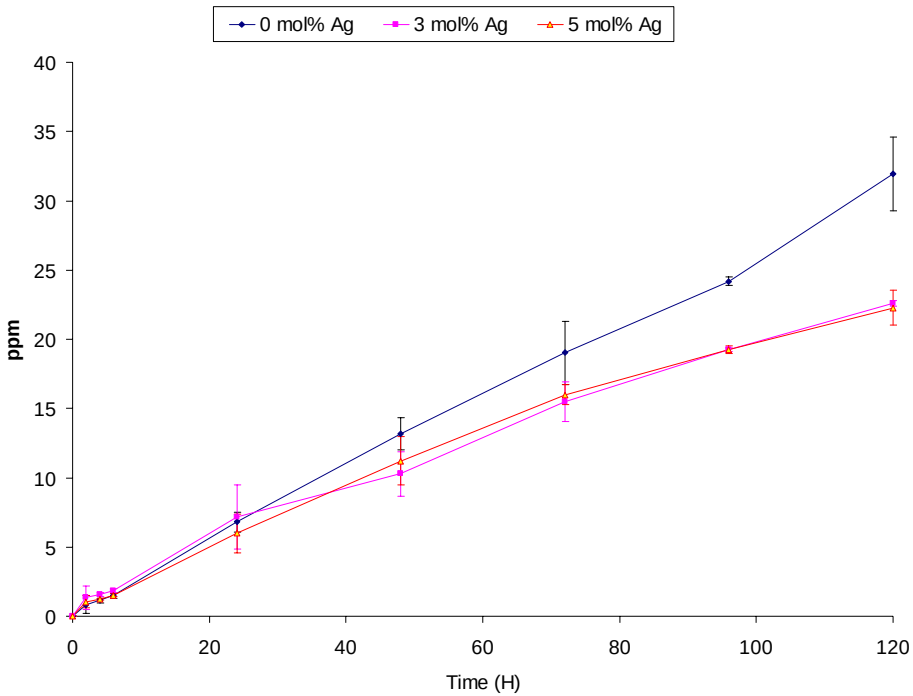


PO_4^{3-} anion release profiles

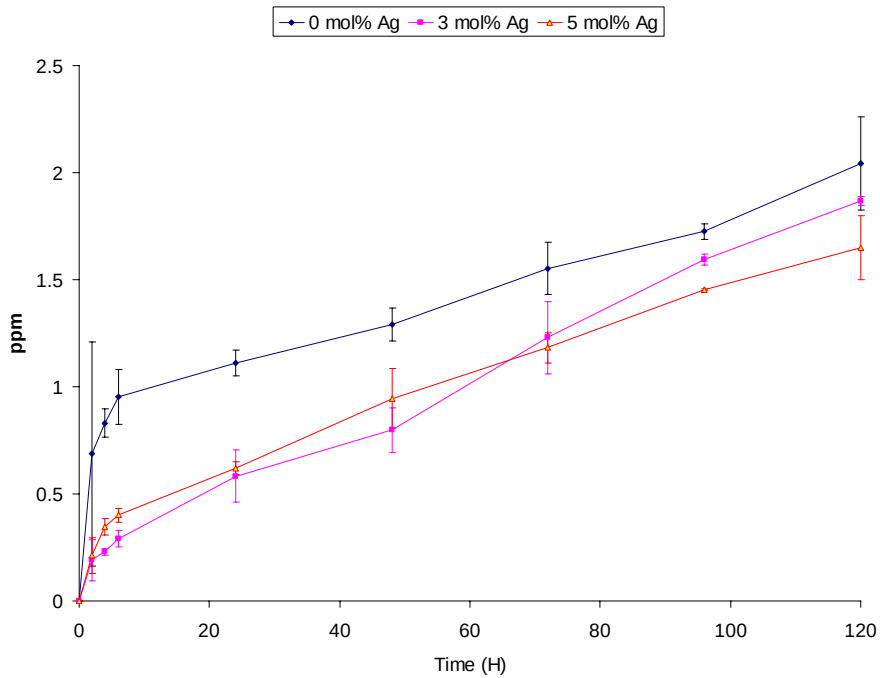


$P_2O_7^{4-}$ anion release profiles

Anion Release from Silver-Doped PBG's (II):



$P_3O_9^{3-}$ anion release profiles



$P_3O_{10}^{5-}$ anion release profiles

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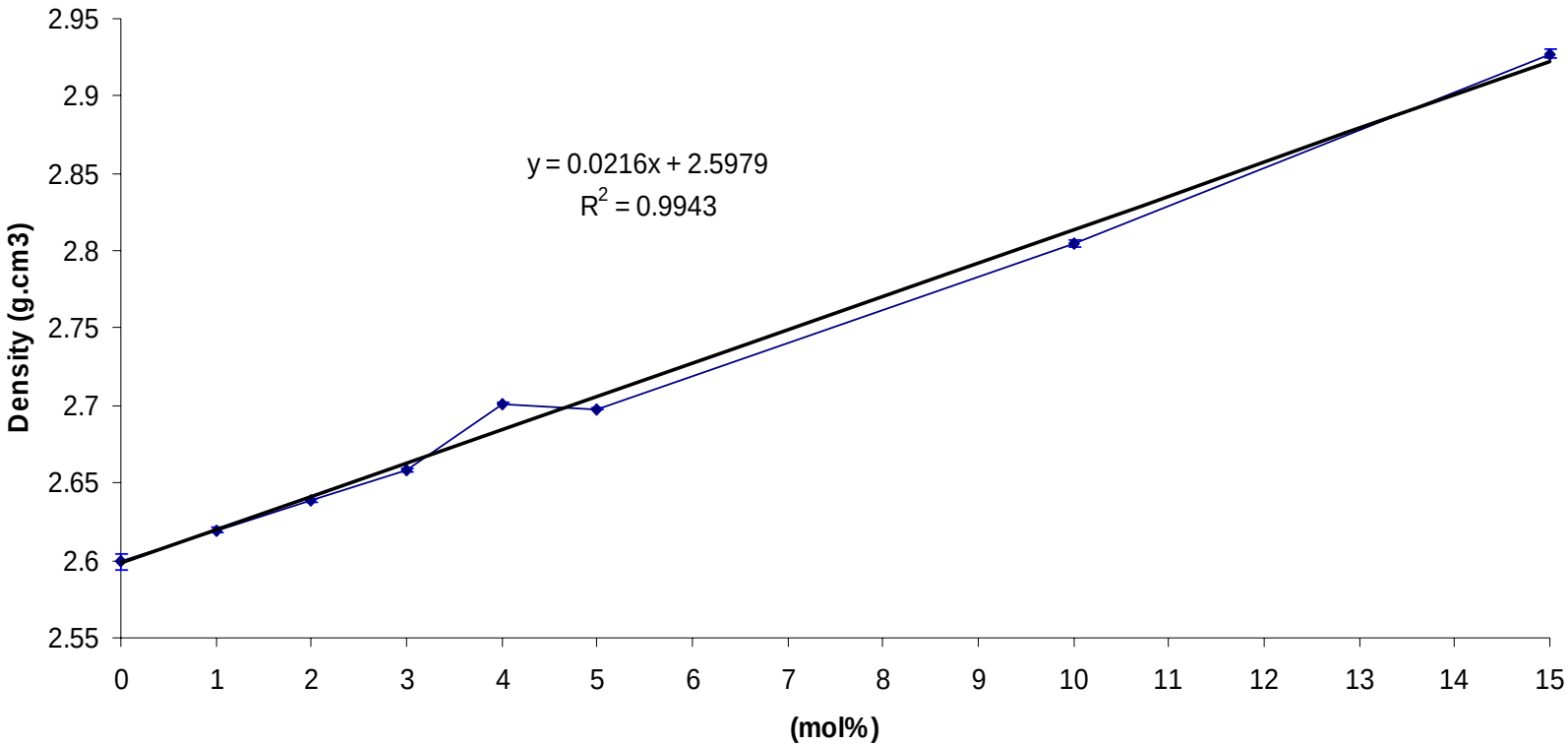
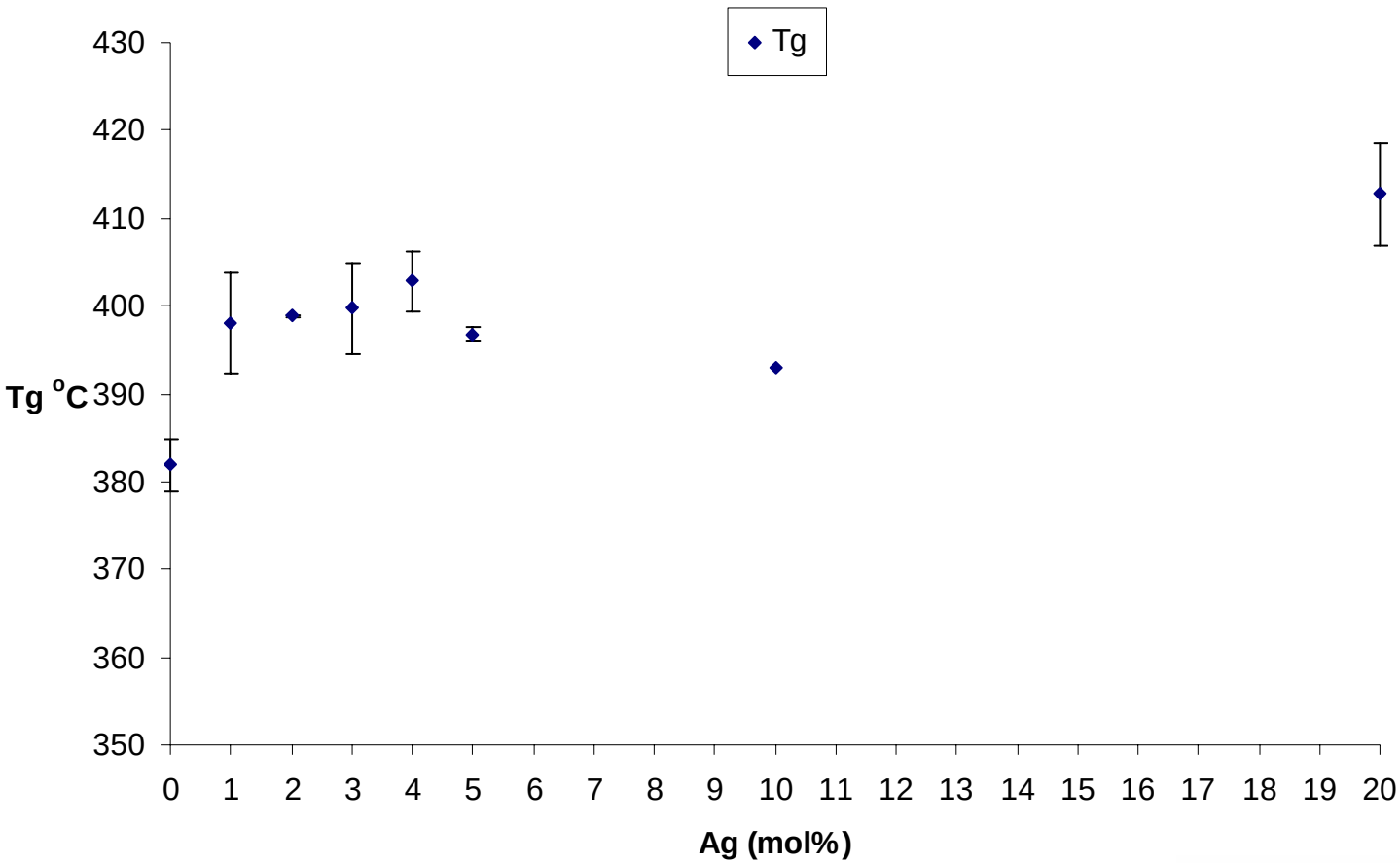
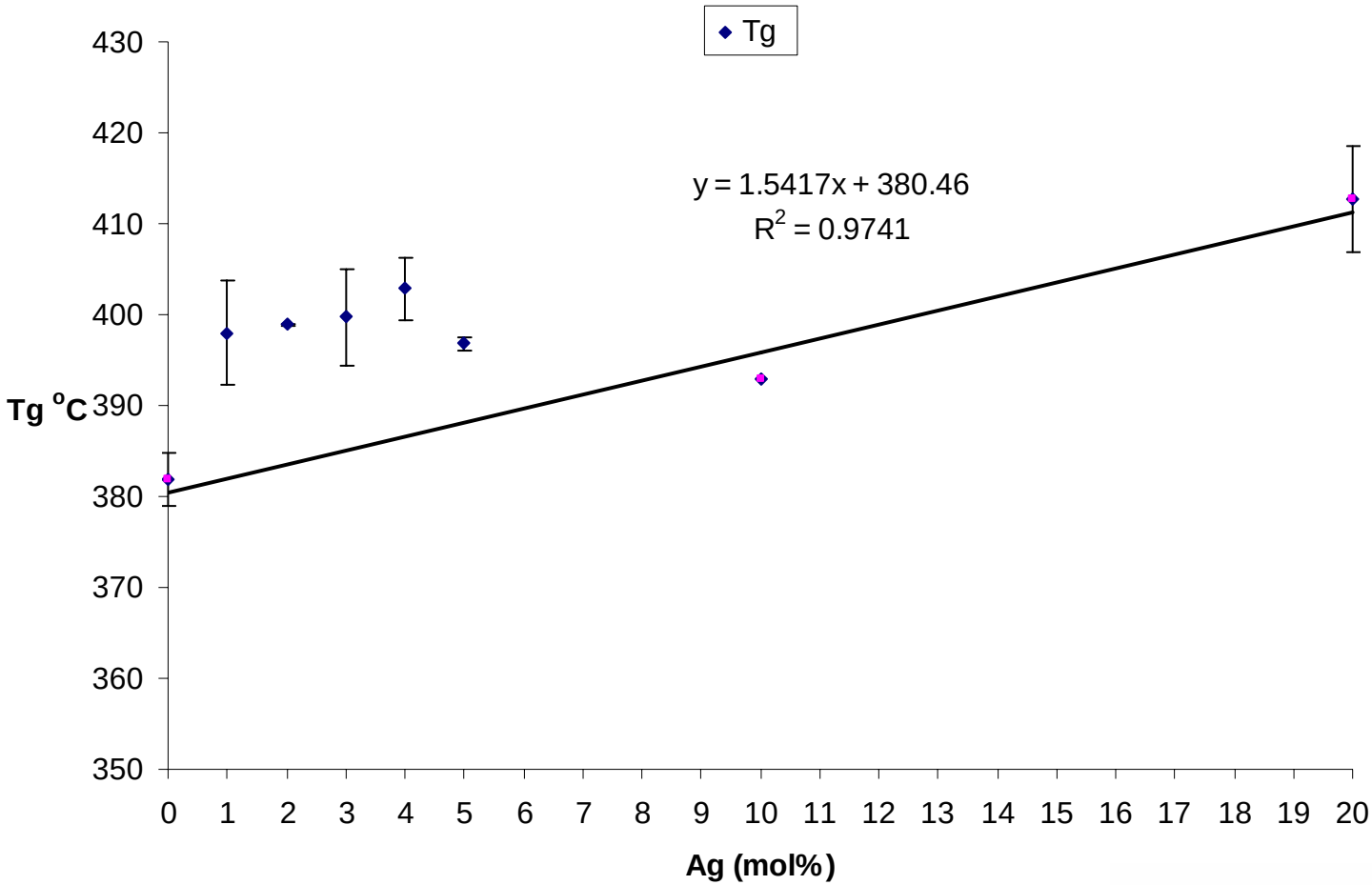
Density of Ag Compositions Investigated:



Average Tg Data Using DTA + DSC:



Average Tg Data Using DTA + DSC:



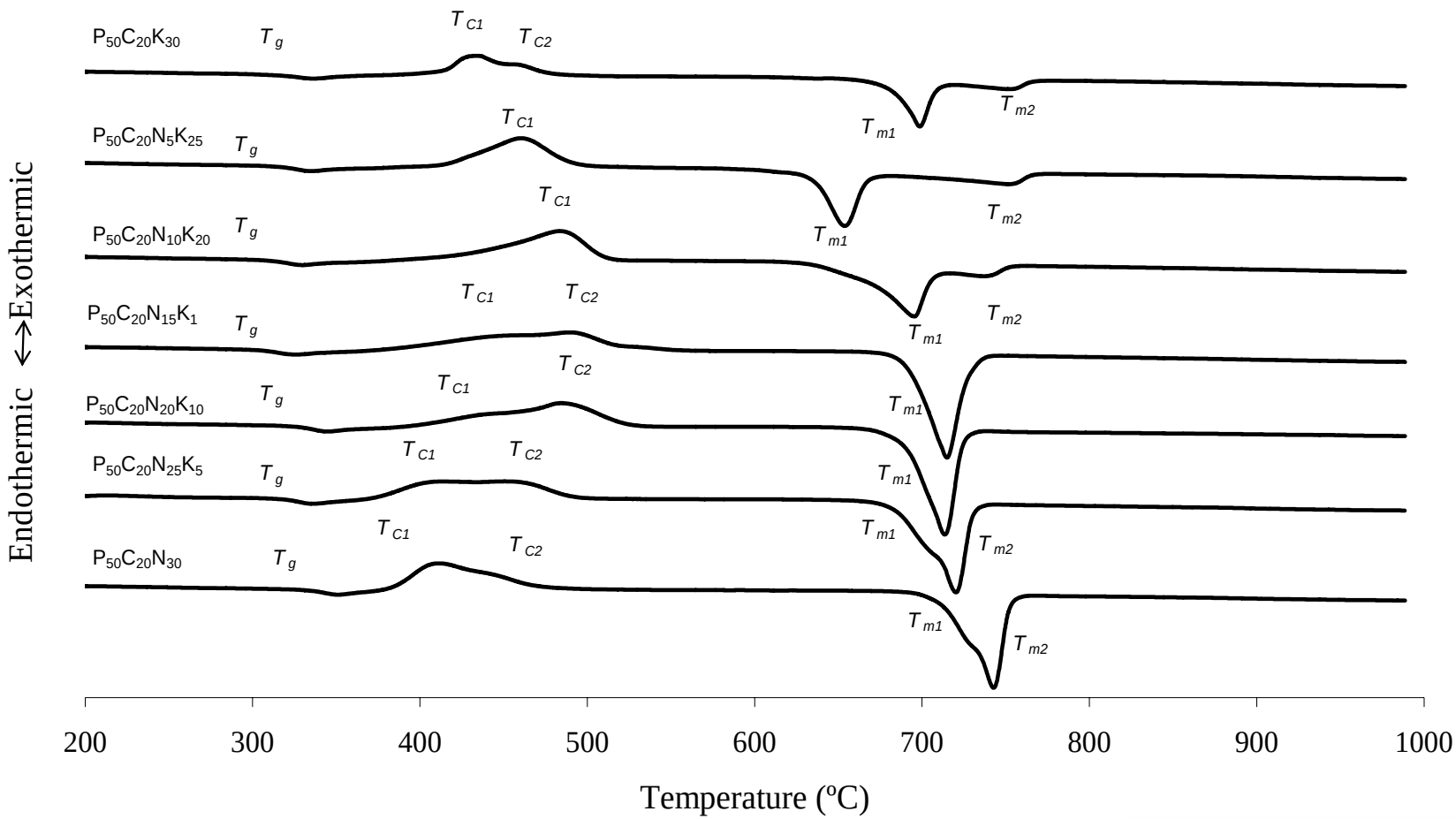
UCL (Eastman Dental Institute) - Kent-Warwick-Imperial Sol- Gel Project Meeting

E. A. Abou Neel and J.C. Knowles

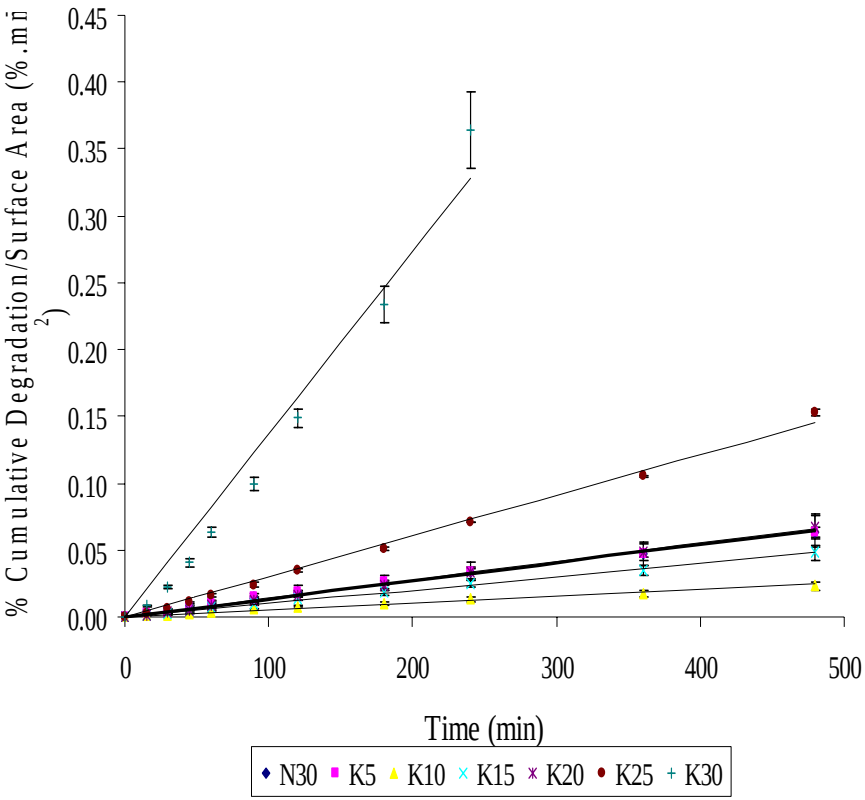
K_2O Containing Glass Code and Compositions Investigated

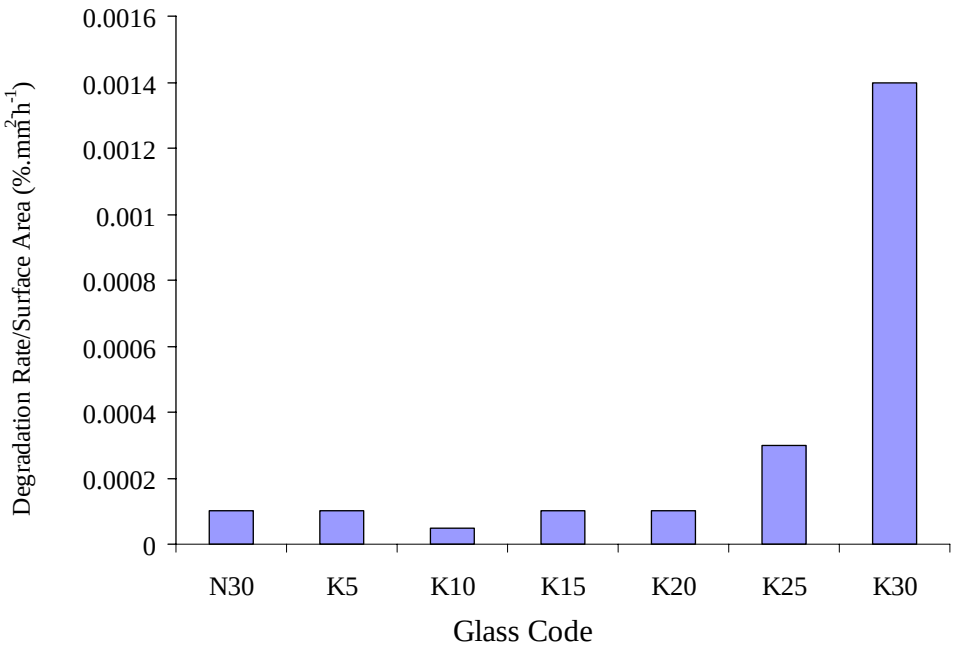
Glass code	P_2O_5 content (mol %)	CaO content (mol %)	Na_2O content (mol %)	K_2O content (mol %)
0 % K_2O	50	20	30	0
5 % K_2O	50	20	25	5
10 % K_2O	50	20	20	10
15 % K_2O	50	20	15	15
20 % K_2O	50	20	10	20
25 % K_2O	50	20	5	25
30 % K_2O	50	20	0	30

Differential Thermal Analysis

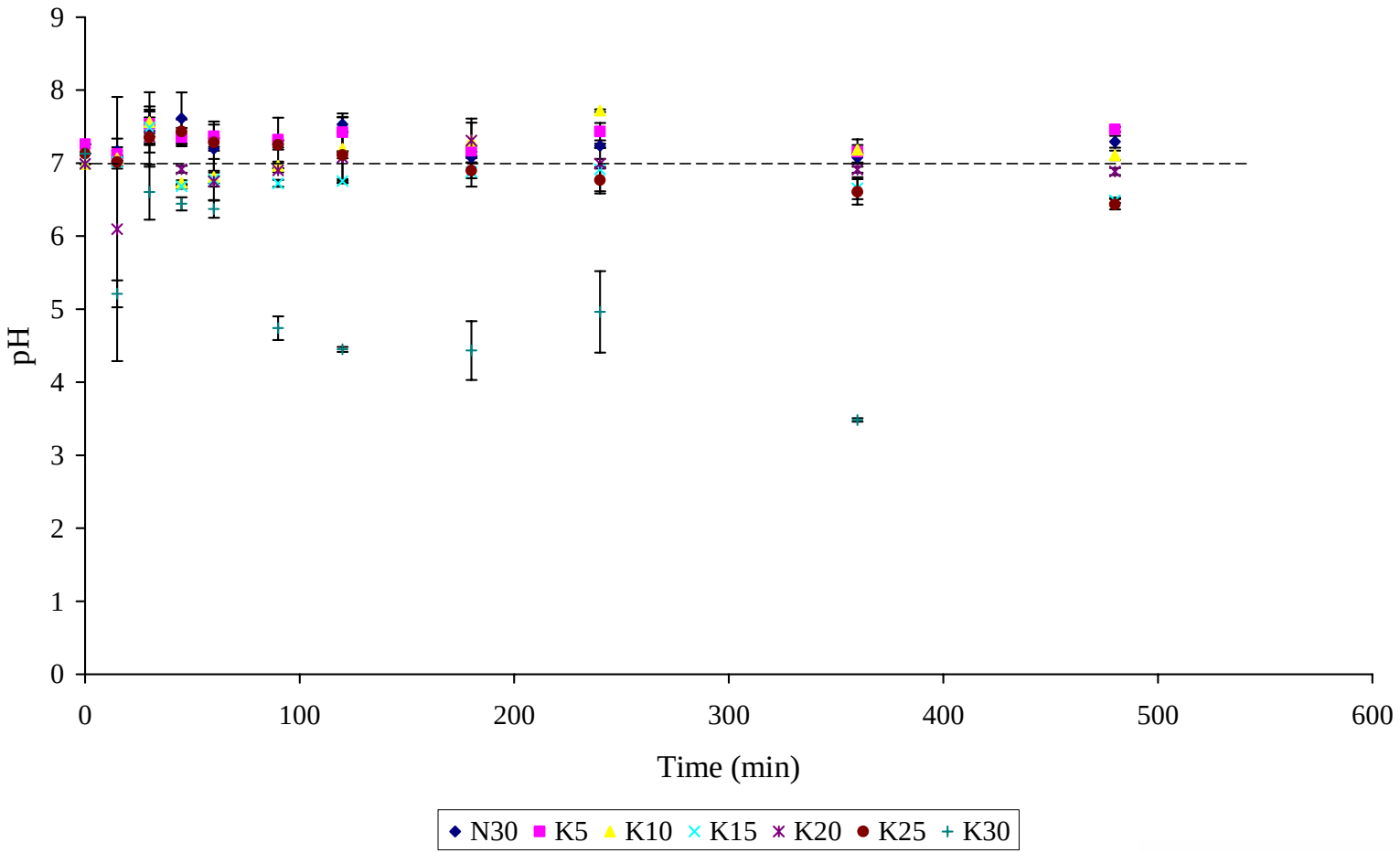


Accumulative Degradation Study in Deionised Water





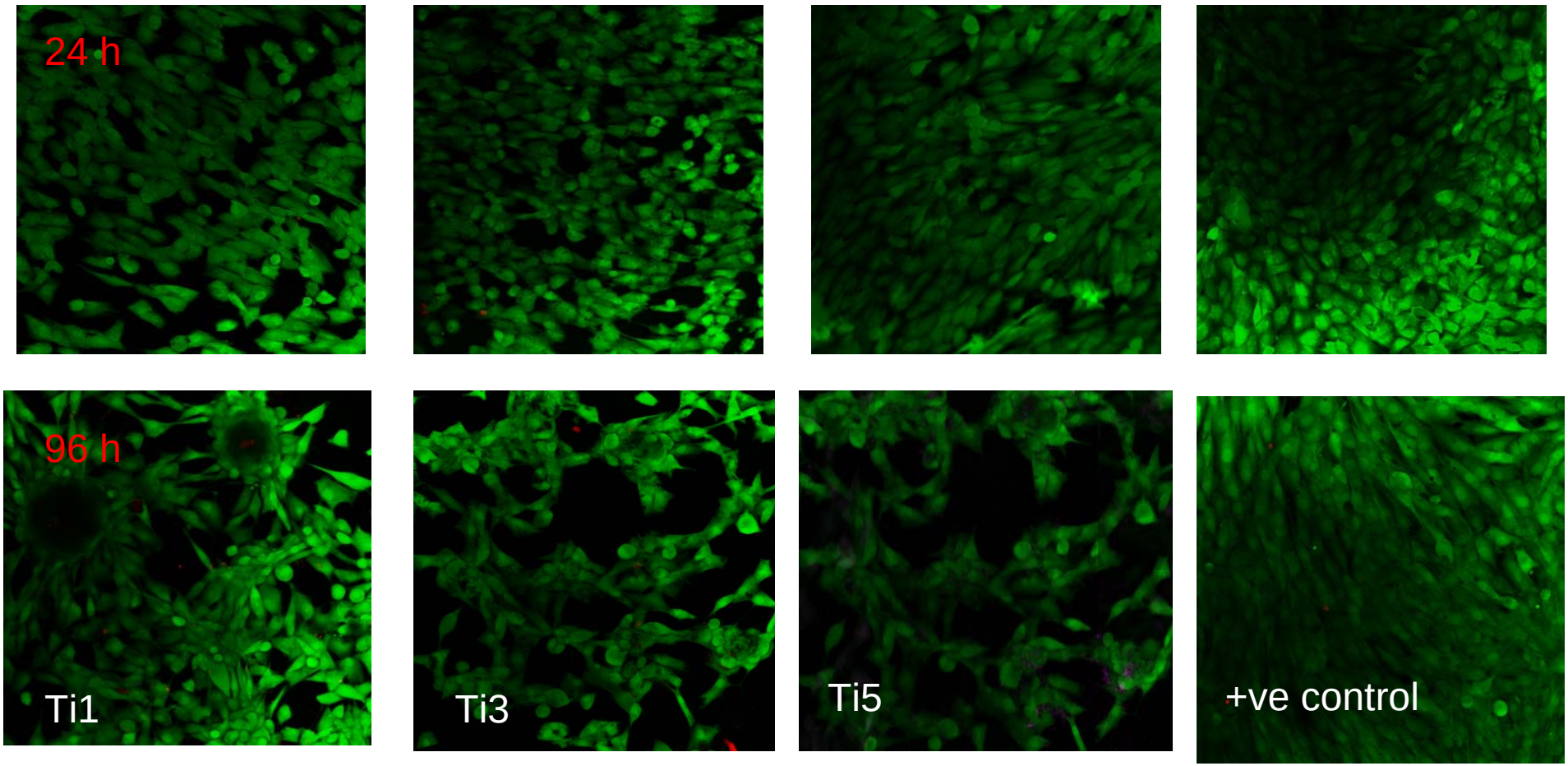
pH Change


pH
Time (min)
0
1
2
3
4
5
6
7
8
9
0
100
200
300
400
500
600
N30
K5
K10
K15
K20
K25
K30

Titanium Containing Glass Compositions under Investigation

Glass code	P_2O_5 content (mol %)	CaO content (mol %)	Na_2O content (mol %)	TiO_2 content (mol %)
1 % TiO_2	50	30	19	1
3 % TiO_2	50	30	18	3
5 % TiO_2	50	30	17	5

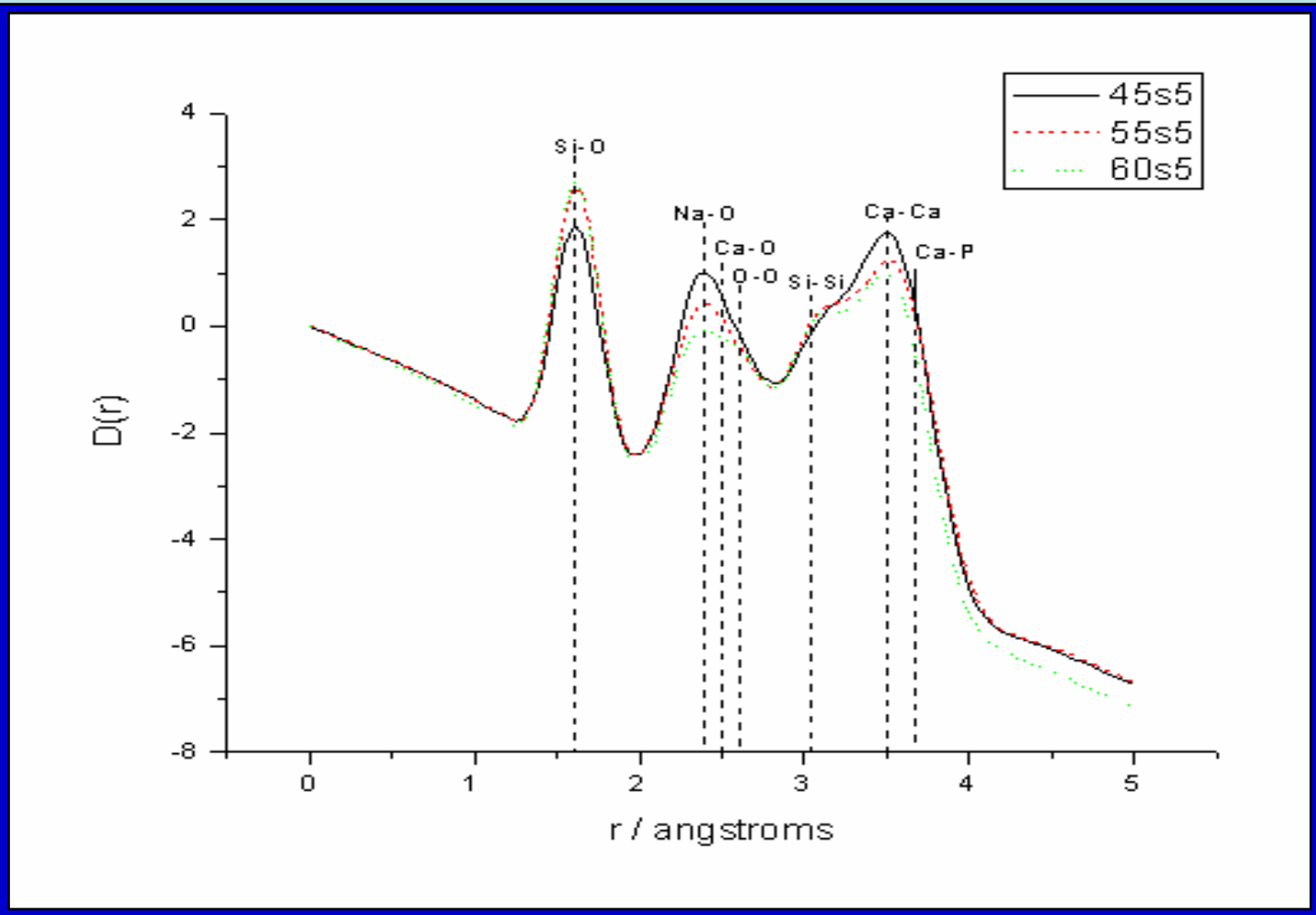
Cell Viability of MG63 on Titanium Containing Glass Discs



Sol-gel Meeting 27/01/2006

Vicky FitzGerald

Bioglass® XRD



fmg

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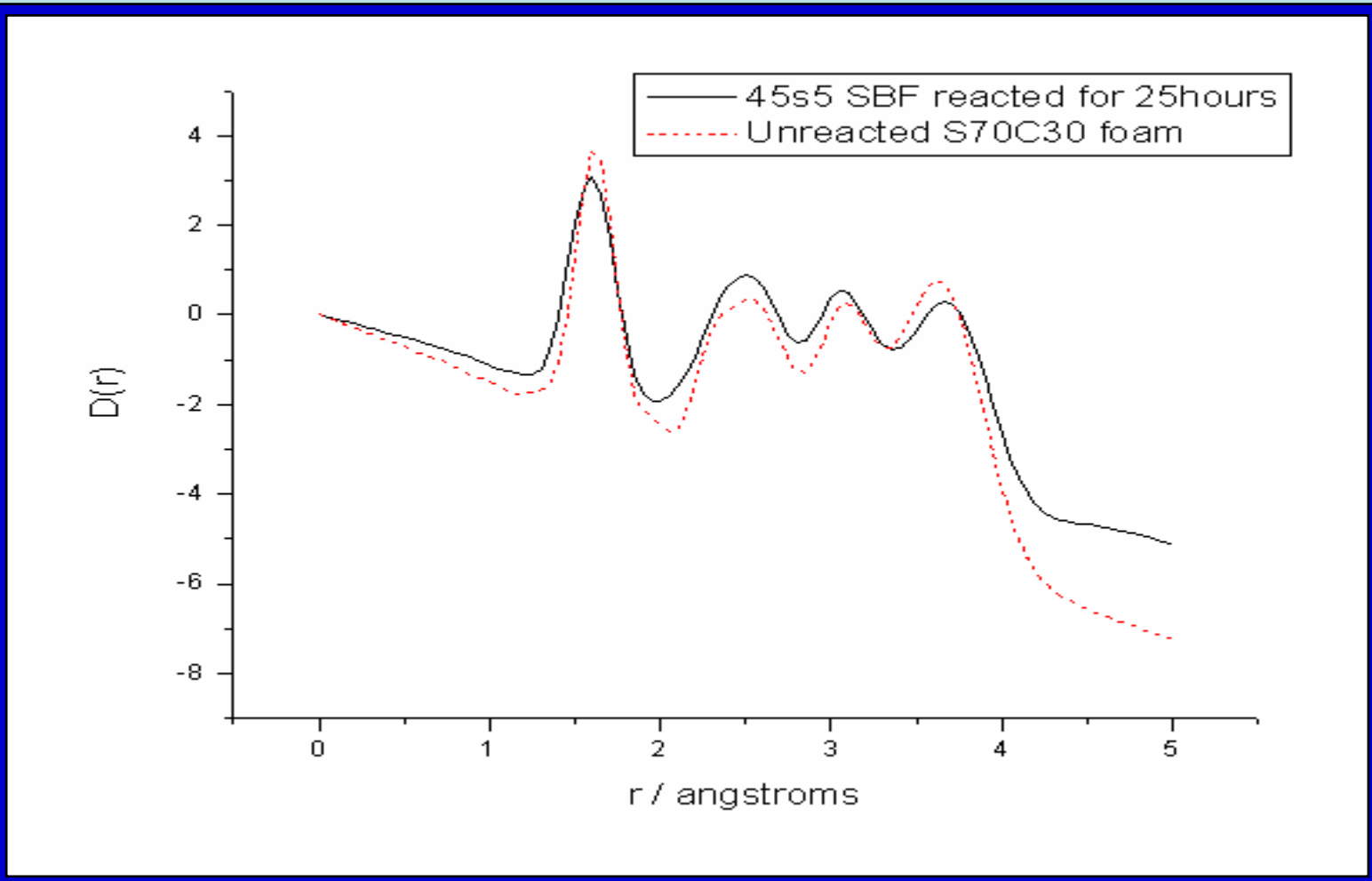
Bioglass® XRD



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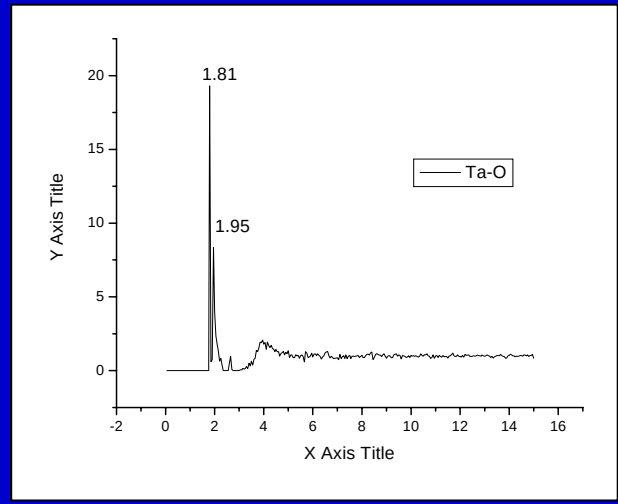
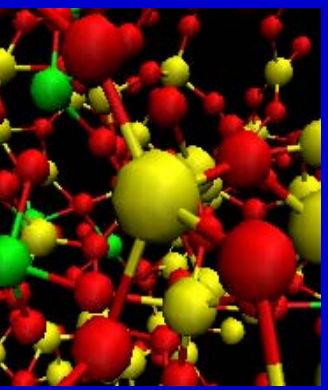
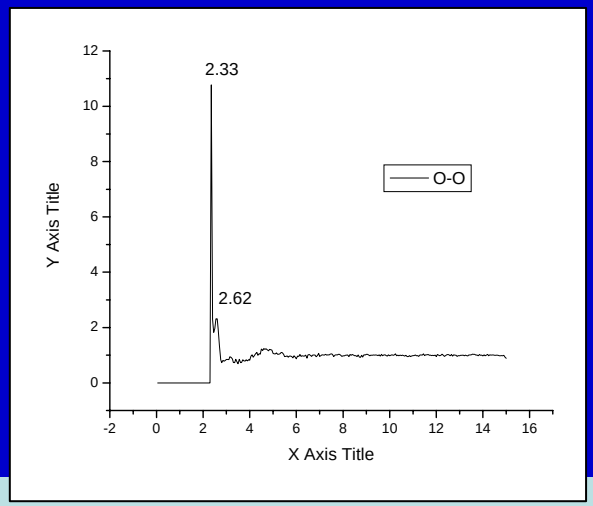
Tantalum Model 10%

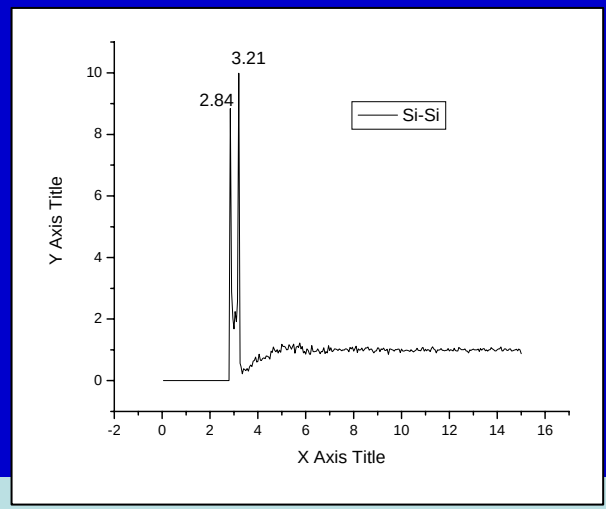
XRD Data				RMC Model		
Bond	Distance / Å	Co-ordination		Bond	Distance / Å	Co-ordination
Si - O	1.61	4.5		Si - O	1.61	3.79
Ta - O	1.91	3.6		Ta - O	1.81	4.63
Ta - O	2.06	1.1		Ta - O	1.95	
O - O	2.64	4.7		O - O	2.62	5.16
Si - Si	3.05	4.4		Si - Si	3	3.94
Si - Ta	3.38	6.1		Si - Ta	3.53	3
Ta - Ta	3.72	2.2		Ta - Ta	3.75	0.32

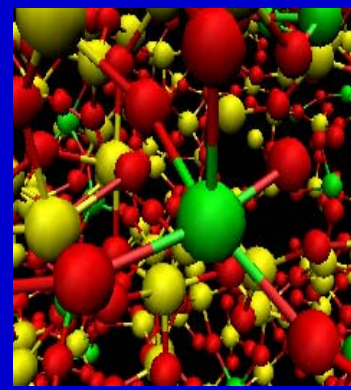




Si-O close-up







Ta-O close-up

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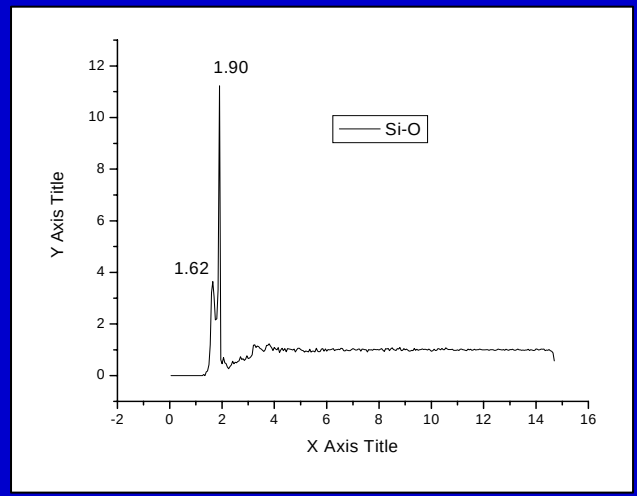
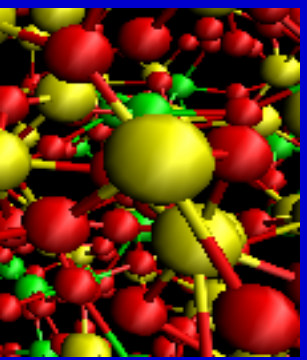
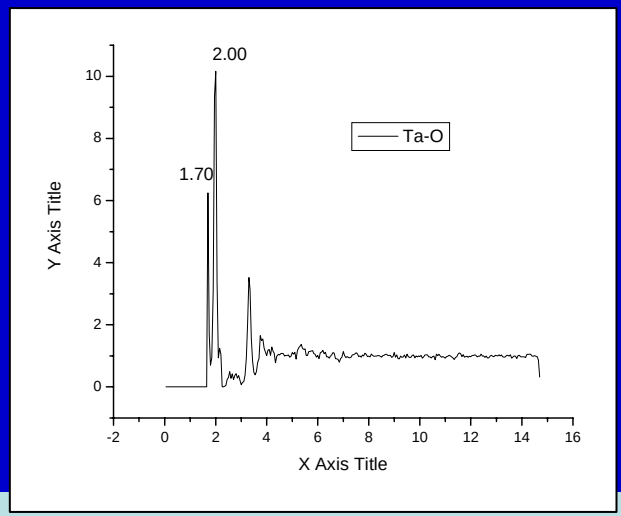
Tantalum Model 40%

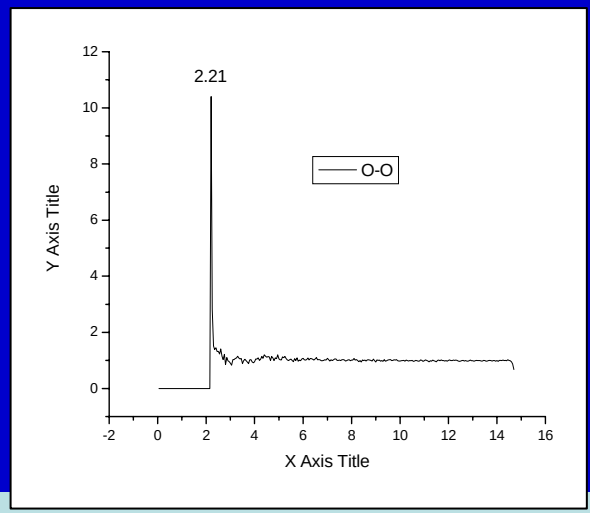
XRD Data				RMC Model		
Bond	Distance / Å	Co-ordination		Bond	Distance / Å	Co-ordination
Si - O	1.61	4.1		Si - O	1.61, 1.90	3.22
Ta - O	1.9	2.9		Ta - O	1.7	4.79
Ta - O	2.07	2		Ta - O	2	
O - O	2.57	5.1		O - O	2.21	5.13
Si - Si	3.03	3.5		Si - Si	3.21	3.86
Si - Ta	3.35	6.1		Si - Ta	3.25	3
Ta - Ta	3.75	2.7		Ta - Ta	3.55	2.75

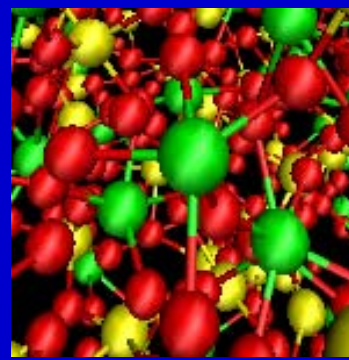




Si-O close-up







Ta-O close-up

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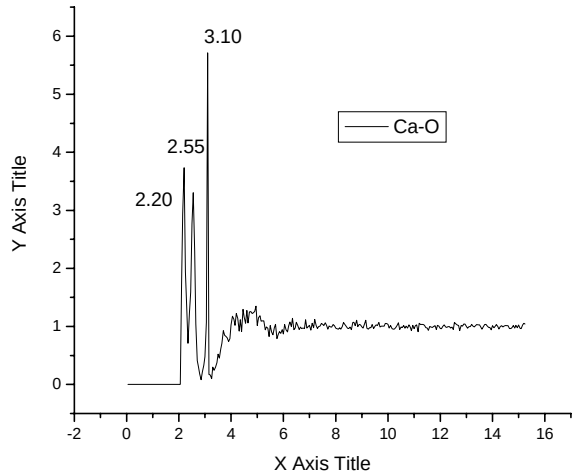
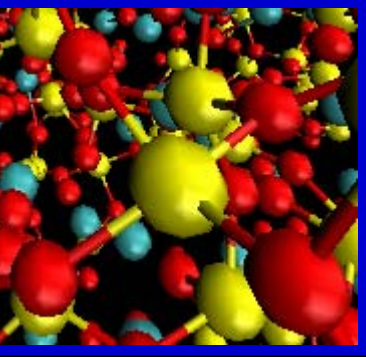
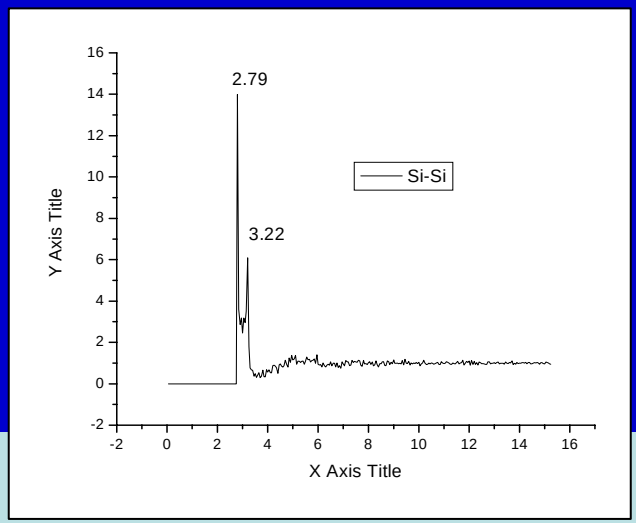
S70C30 Foam RMC

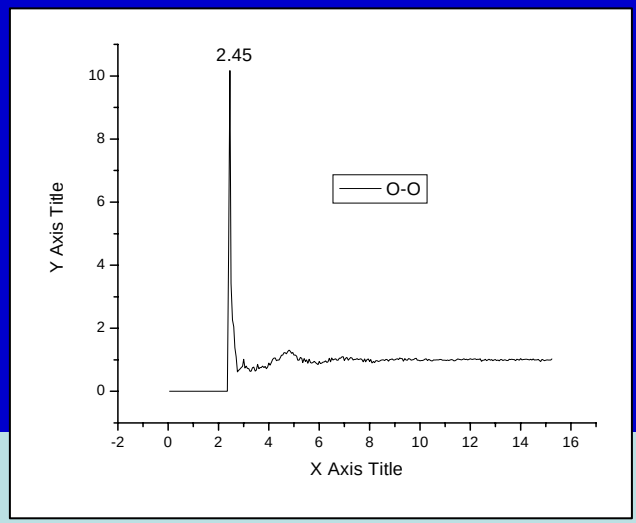
XRD Data				RMC Model		
Bond	Distance / Å	Co-ordination		Bond	Distance / Å	Co-ordination
Si - O	1.61	4.15		Si - O	1.61	3.89
Ca - O	2.32	2.4		Ca - O	2.2	Total 5.97 Ca-O
Ca - O	2.5	2.4		Ca - O	2.55	
O - O	2.63	5.7		O - O	2.45	4.77
Ca - O	2.76	1		Ca - O	3.1	
Si - Si	3.03	4		Si - Si	3	3.72
Si - Ca	3.22	not fitted		Si - Ca	3.22	1.08
Ca - Ca	3.52	not fitted		Ca - Ca	3.46	2.46





Si-O close-up





fmg

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PHOSPHOBORATE GLASSES

Sol-gel synthesis of Phosphoborate glasses without SiO_2

↓

Very few studies:

P_2O5-B_2O_3-Al_2O_3 Amorphous up to 500 C (J. Mater. Chem., 2005, 15,1640)

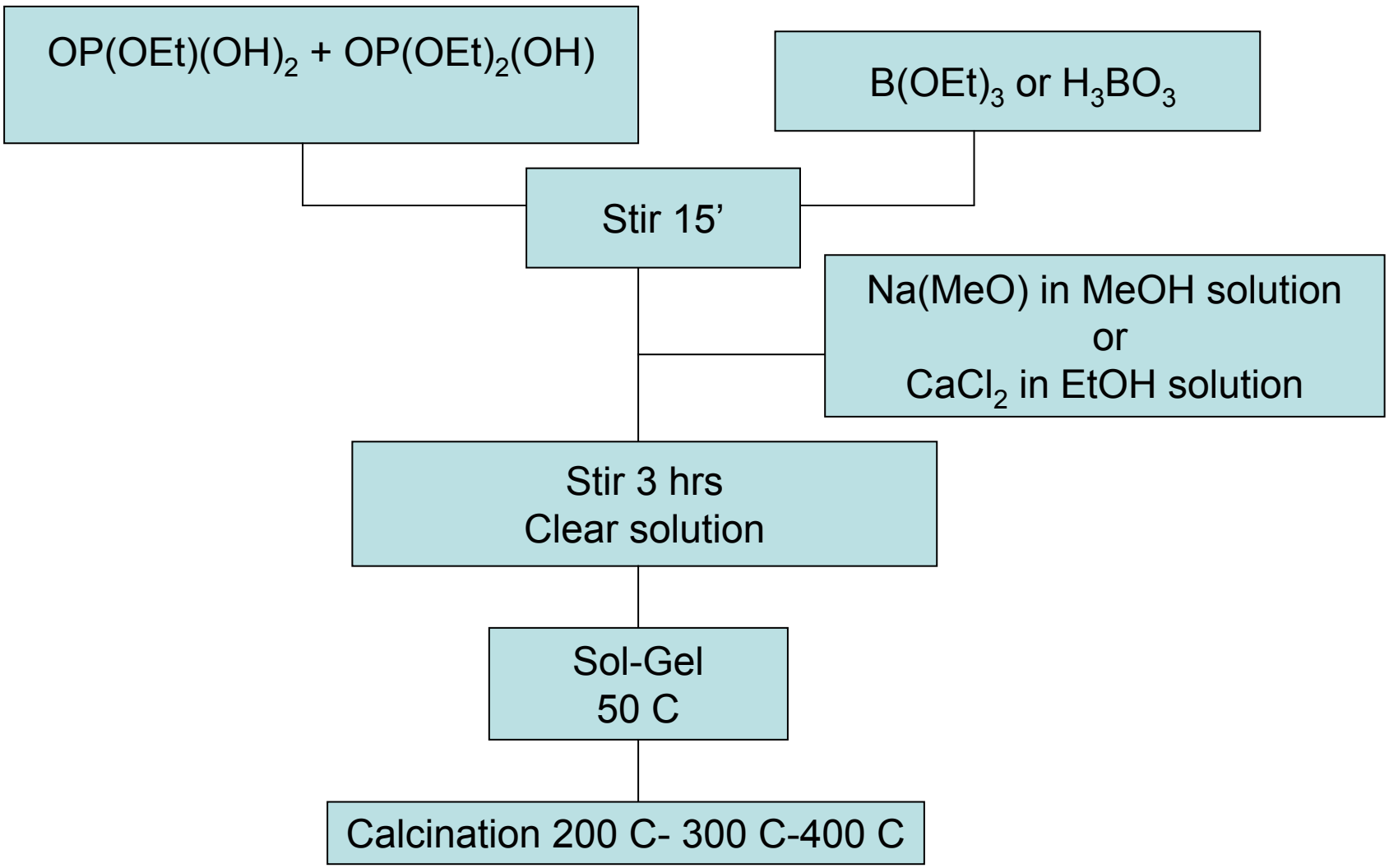
P_2O_5-B_2O_3-Li_2O Crystallise at 120 C (J. Mater. Res.., 1999, 14, 4)

P_2O_5-B_2O_3-Na_2O

P_2O_5-B_2O_3-CaO

Sol-Gel Synthesis

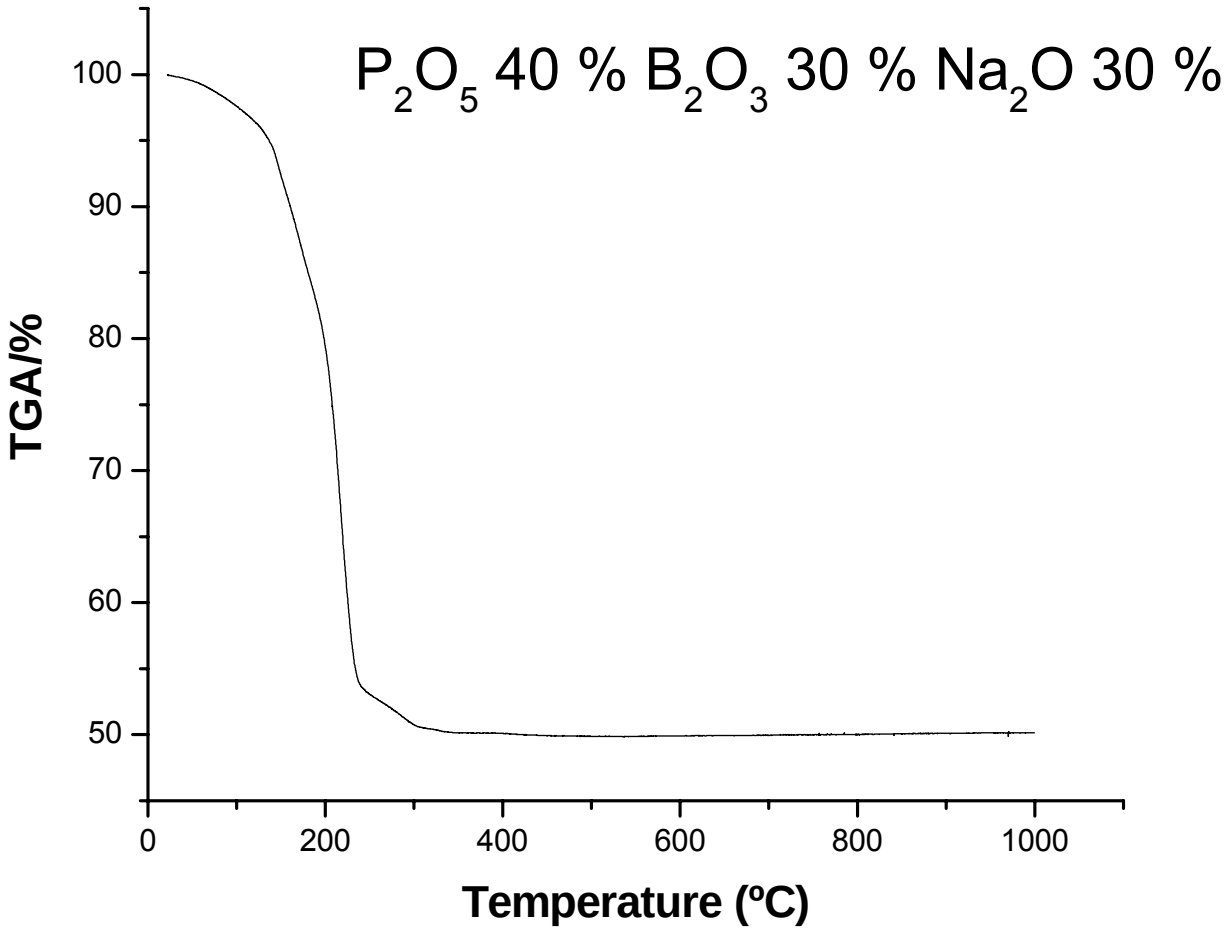
P precursor: $P_2O_5 + 3EtOH \rightarrow OP(OEt)(OH)_2 + OP(OEt)_2(OH)$



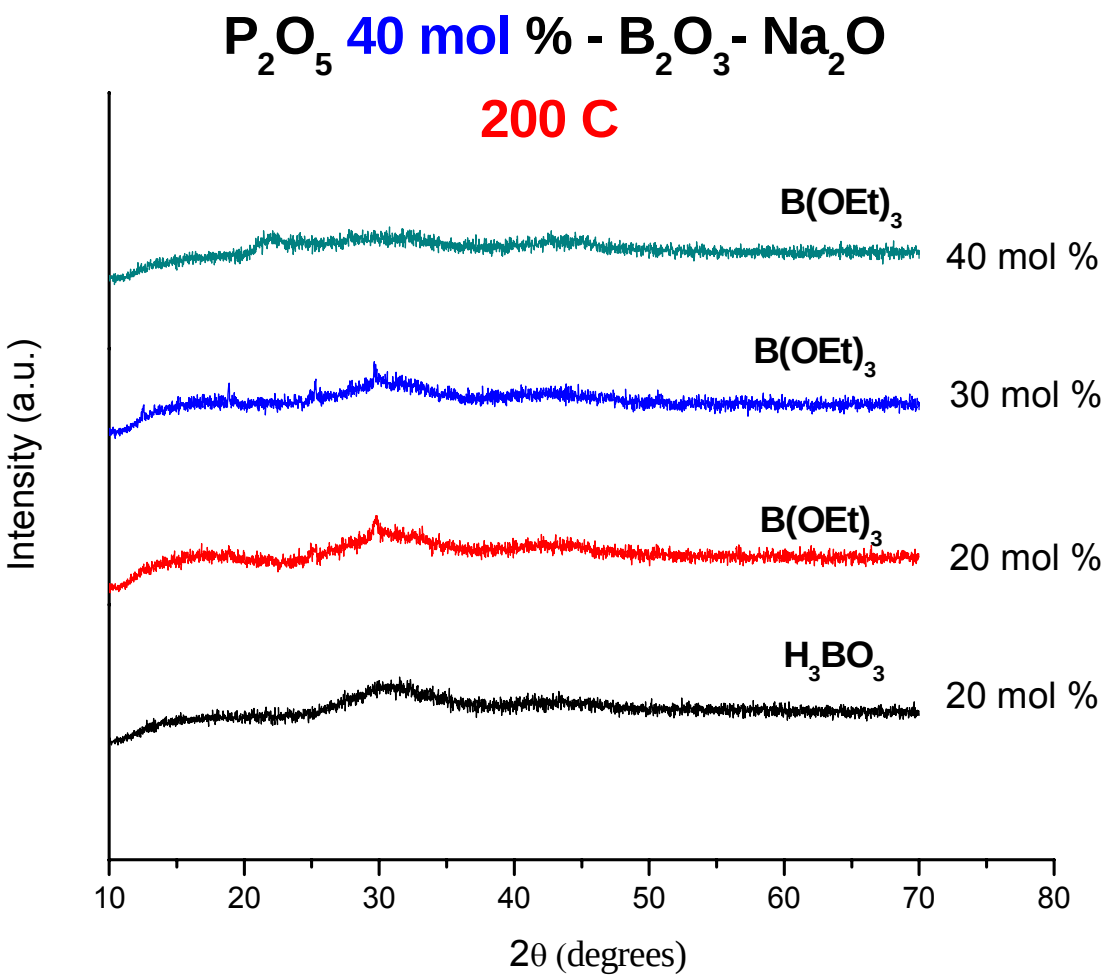
P_2O_5	B_2O_3	Na_2O	CaO	B Precursor	
30	40	30		B(OEt)3	x
30	30	40		B(OEt)3	x
40	40	20		B(OEt)3	
40	30	30		B(OEt)3	
40	20	40		H3BO3	
40	20	40		B(OEt)3	
40	10	50		B(OEt)3	x
45	10	45		B(OEt)3	
50	40		10	B(OEt)3	
50	30		20	B(OEt)3	

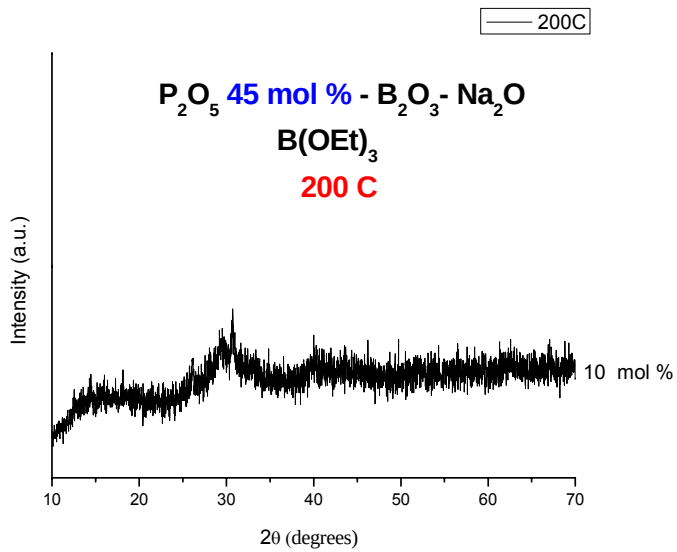
Gelation time 10-15 days

TGA gel

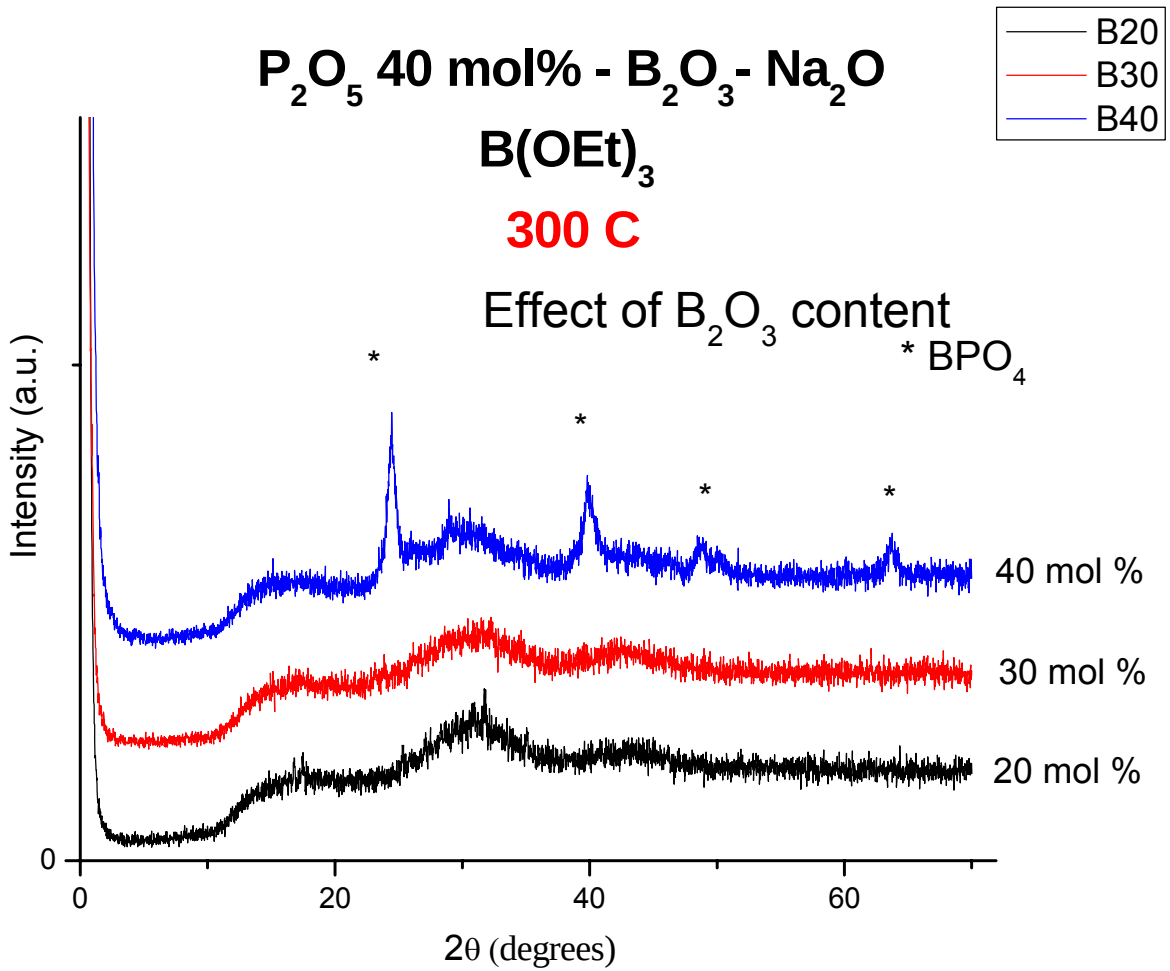

P_2O_5 40 % B_2O_3 30 % Na_2O 30 %
TGA/%
100
90
80
70
60
50
0
200
400
600
800
1000
Temperature (ºC)

XRD 200 C

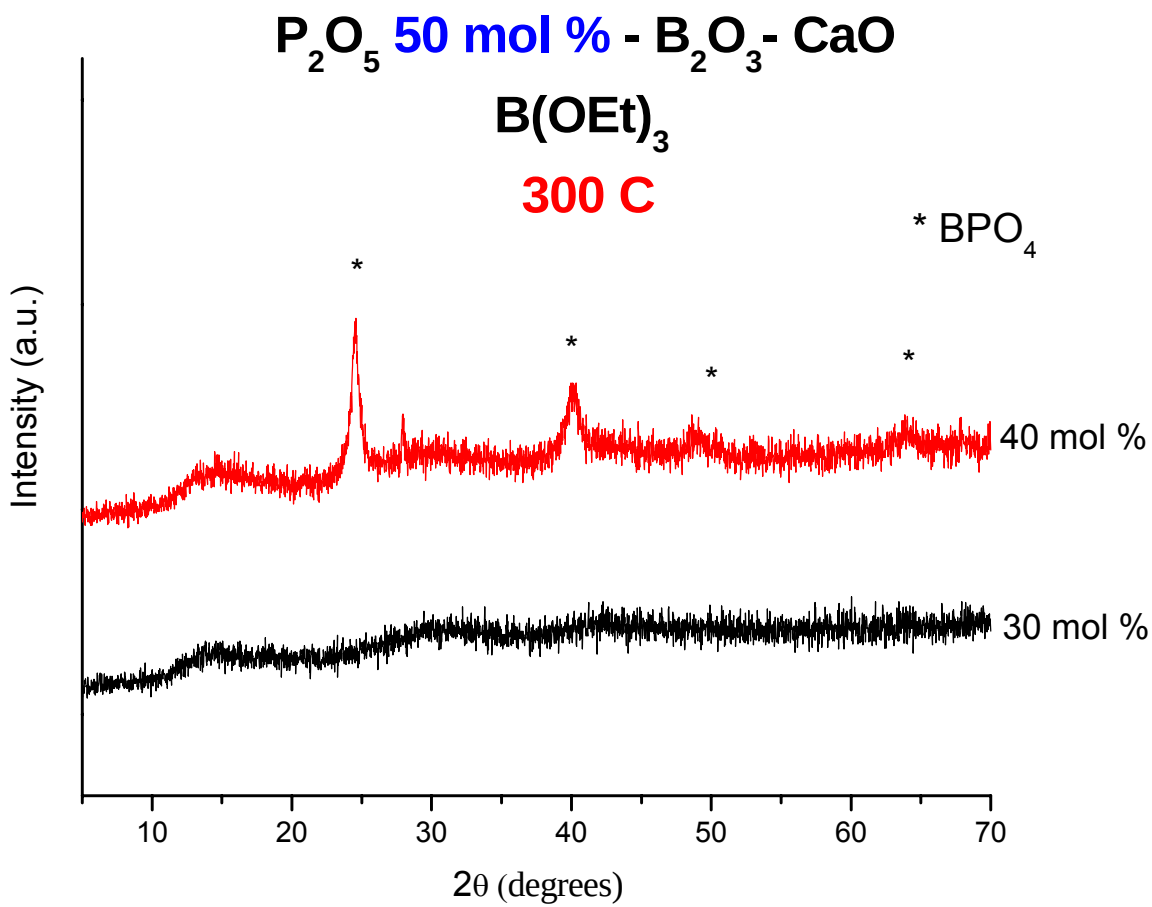

P2O5 40 mol % - B2O3- Na2O
200 C
B(OEt)3
40 mol %
B(OEt)3
30 mol %
B(OEt)3
20 mol %
H3BO3
20 mol %
Intensity (a.u.)
10
20
30
40
50
60
70
80
2θ (degrees)


200C
P2O5 45 mol % - B2O3- Na2O
B(OEt)3
200 C
Intensity (a.u.)
10 mol %
10
20
30
40
50
60
70
2θ (degrees)

XRD 300 C


B20
B30
B40
P2O5 40 mol% - B2O3- Na2O
B(OEt)3
300 C
Effect of B2O3 content
* BPO4
Intensity (a.u.)
0
0
20
40
60
2θ (degrees)
40 mol %
30 mol %
20 mol %

XRD 300 C


P2O5 50 mol % - B2O3- CaO
B(OEt)3
300 C
* BPO4
Intensity (a.u.)
40 mol %
30 mol %
10
20
30
40
50
60
70
2θ (degrees)

Conclusions

P_2O_5-B_2O_3-Na_2O

and

P_2O_5-B_2O_3-CaO

All mainly amorphous up to 200C

Samples with B_2O_3 < 40 mol% amorphous up to 300C

Samples with B_2O_3 > 40 mol% BPO_4 phase ppt

Future Work

P_2O_5-B_2O_3-Na_2O with P_2O_5 50 mol%

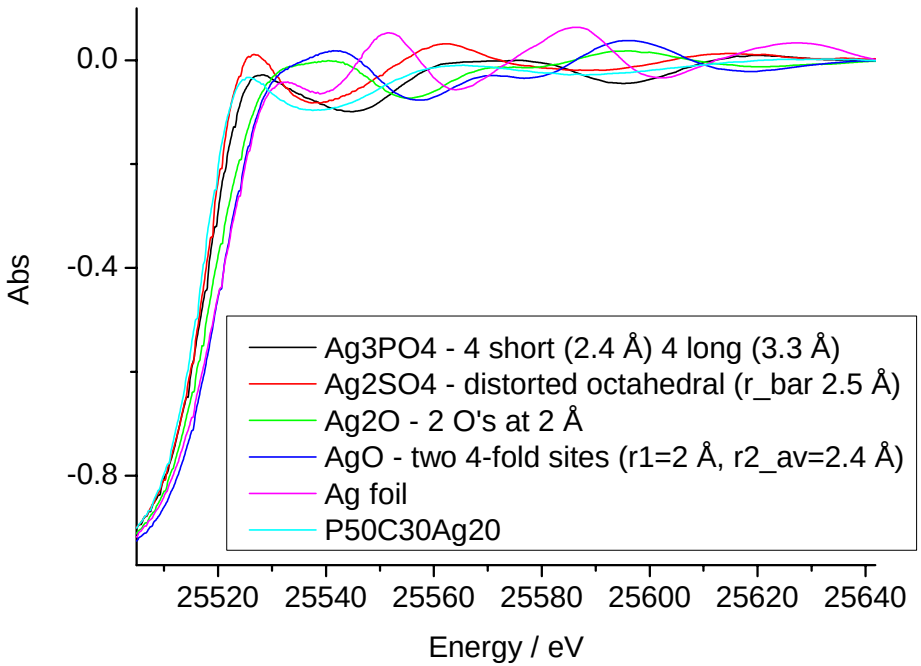
Add small amount of SiO_2

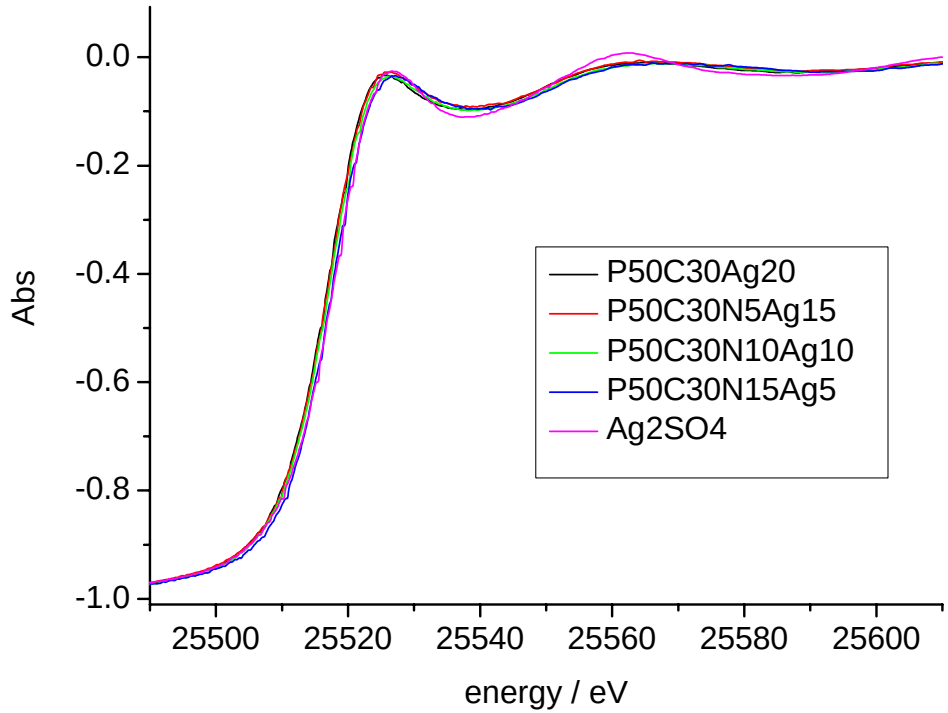
Characterise BPO_4 phase (nanocrystalline?)
BPO_4 Li-doped for Li-ion batteries
Low dielectric constant

↓

Samples sent for TEM

Ag K-edge XANES

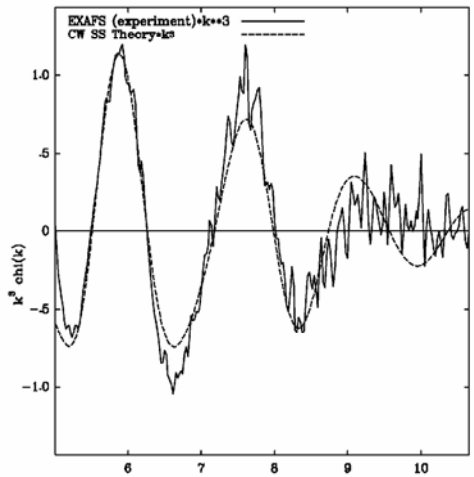


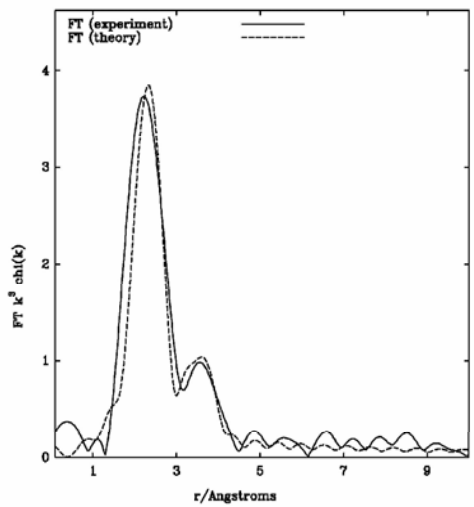


Problem: Ag K-edge XANES not sensitive to small changes in geometry of Ag site (*Sipr et al. Phys. Rev. B* ***69*** *134201)*

Ag K-edge EXAFS

P50N10Ag20

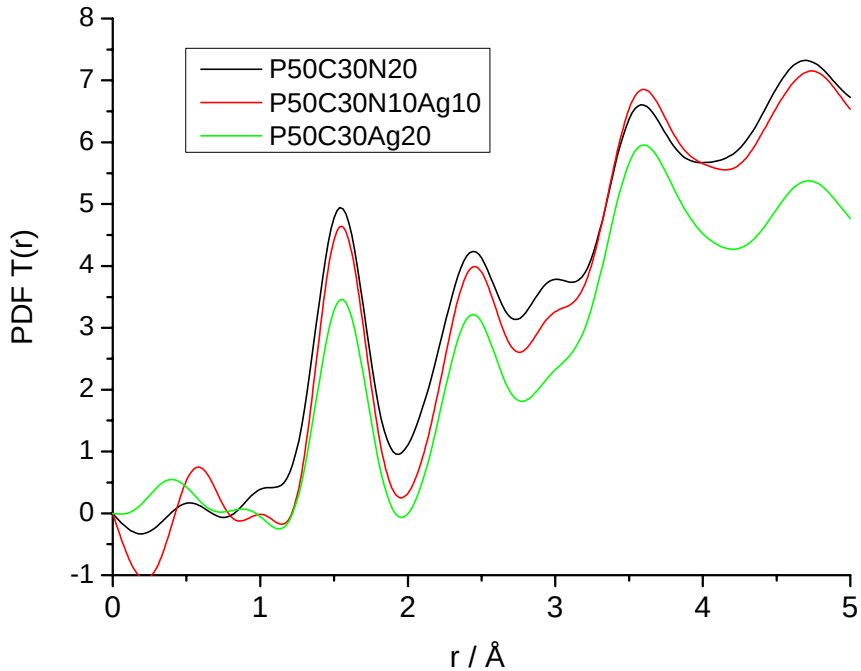





```
EF      13.8  VPI     0.00  AFAC     0.93
EM N    66.4  EMAX    661.  SPARE7  -1.00
LMAX    25.0  MTR1    1.44  MTR2     1.00
MTR3    1.28  MTR4    1.97  MTR5     1.44

FI  0.00086   R    35.68

N0    1.0 T0  1 (AG) R0   0.000  A0  0.010  -1   0
N1    4.1 T1  2 (O )  R1   2.277  A1  0.029   1   0
N2    3.9 T2  2 (O )  R2   2.626  A2  0.040   1   0
N3    6.0 T3  3 (P )  R3   3.630  A3  0.052   1   0

Experiment     r25506.prn
Parameters     r25506.par
Phaseshifts    exphsa1.agc
               exphsa1.o
               exphsa1.p
               exphsa1.ca
               exphsa1.ag
```

Sample	Shell	N	R / Å	A / Å^{-2}	*R* / %
P50C30N10Ag10	Ag-O Ag-O Ag-P	**4** **2** **6**	2.22 2.55 3.41	0.024 0.021 0.042	35.5
P50C30Ag20	Ag-O Ag-O Ag-P	4.1 3.9 **6**	2.28 2.63 3.63	0.029 0.040 0.052	35.7

High energy XRD on Ag-doped samples



Sample		R /ang	N	sigma/ang
P50C30N20	PO	1.47	1.89	0.05
	PO	1.60	2.50	0.07
	CaO	2.34	5.50	0.14
	NaO	2.37	5.99	0.11
	OO	2.54	5.27	0.10
	PP	2.94	3.72	0.12
P50C30N10Ag10	PO	1.49	2.00	0.02
	PO	1.60	3.00	0.04
	CaO	2.34	5.50	0.10
	NaO	2.36	5.30	0.11
	AgO	2.50	5.10	0.12
	OO	2.54	3.60	0.11
	PP	2.93	3.72	0.12

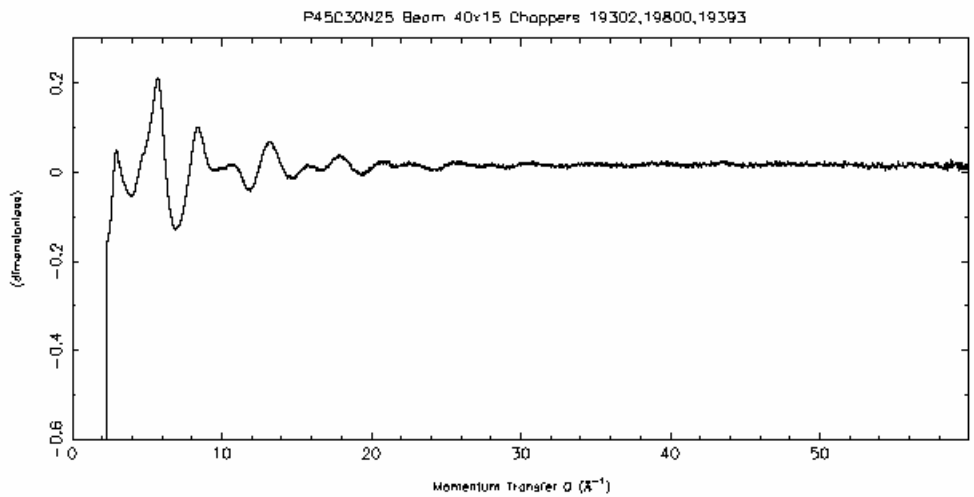
Sample	Density /gcm^{-3}	
	UKC	UCL
P50C30N20	2.52	2.60
P50C30N10Ag10	2.78	2.81
P50C30Ag20	2.42	

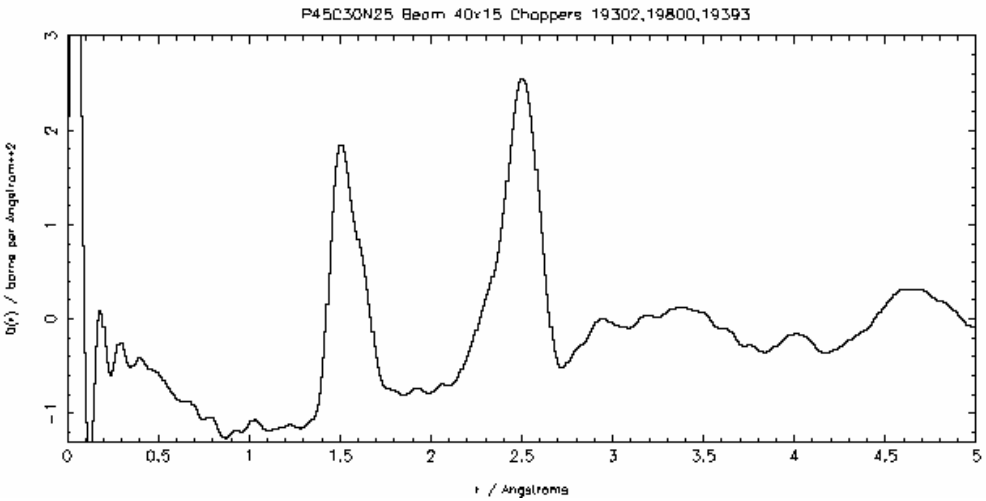
Neutron diffraction

ISIS

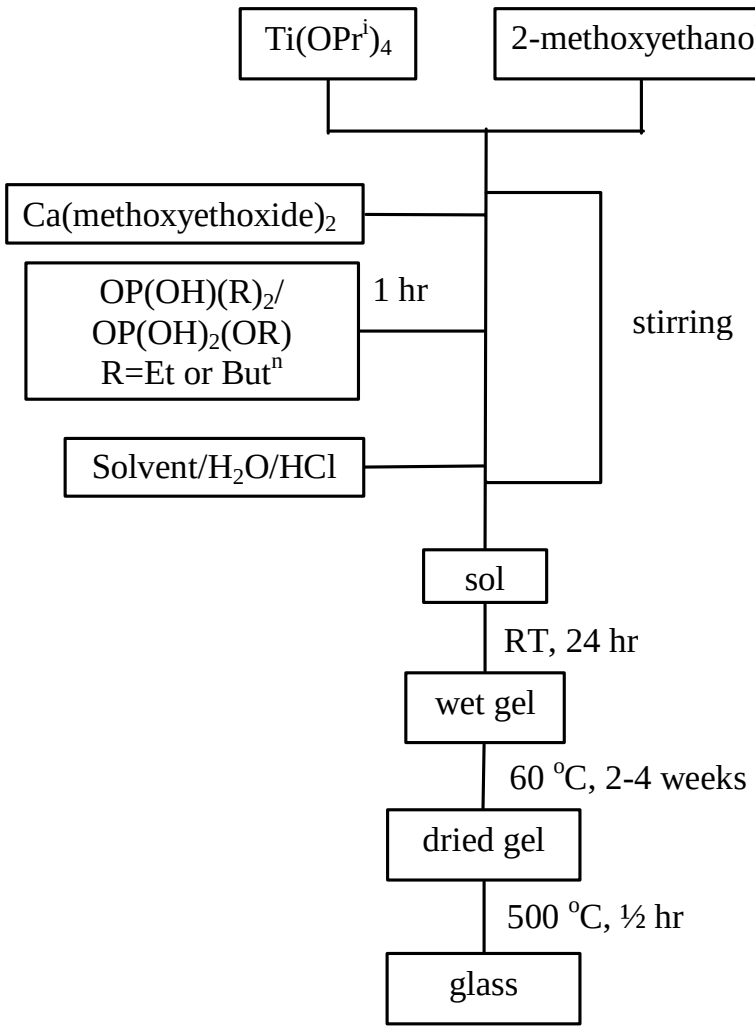
Instrument: GEM
Run number 27231
Spectrum 8
Location: C:\TOPAS\Nov05\GEM27231.dcs01

User Newport
Run start time 24-Nov-2005 10:56:12
Plot date: 26-Jan-2006 17:36:29+0100
Grouping: 1





Sample Preparation



$(TiO_2)_{0.5}(P_2O_5)_{0.5}$ samples

Sample	Heat treatment	Composition / mol%		
		TiO_2	P_2O_5	SiO_2
50T50P15	none	62.1	37.3	0.6
50T50P15	500 ^{o}C	60.1	39.3	0.6
50T50P16A	none	63.0	36.4	0.6
50T50P16A	500 ^{o}C	61.4	38.1	0.6
50T50P16B	none	61.6	37.7	0.7
50T50P16B	500 ^{o}C	60.3	39.0	0.6