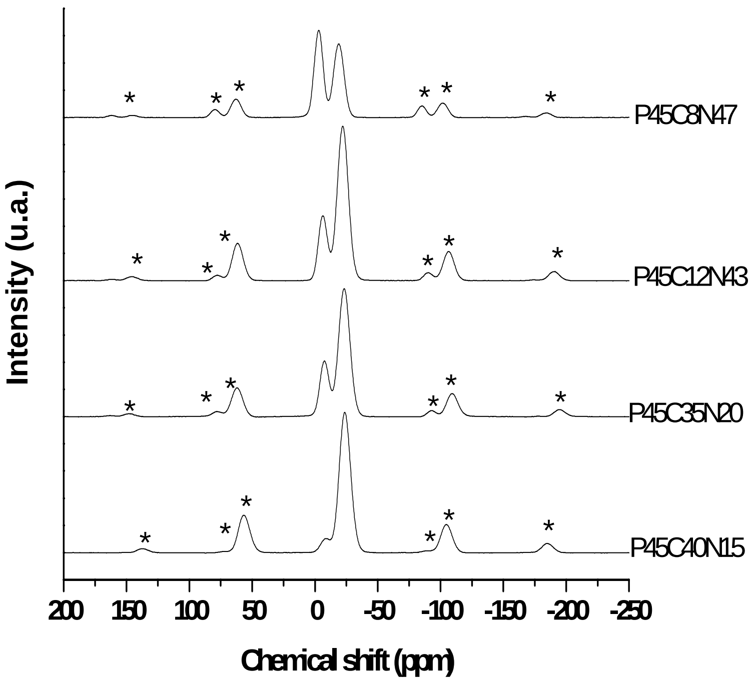
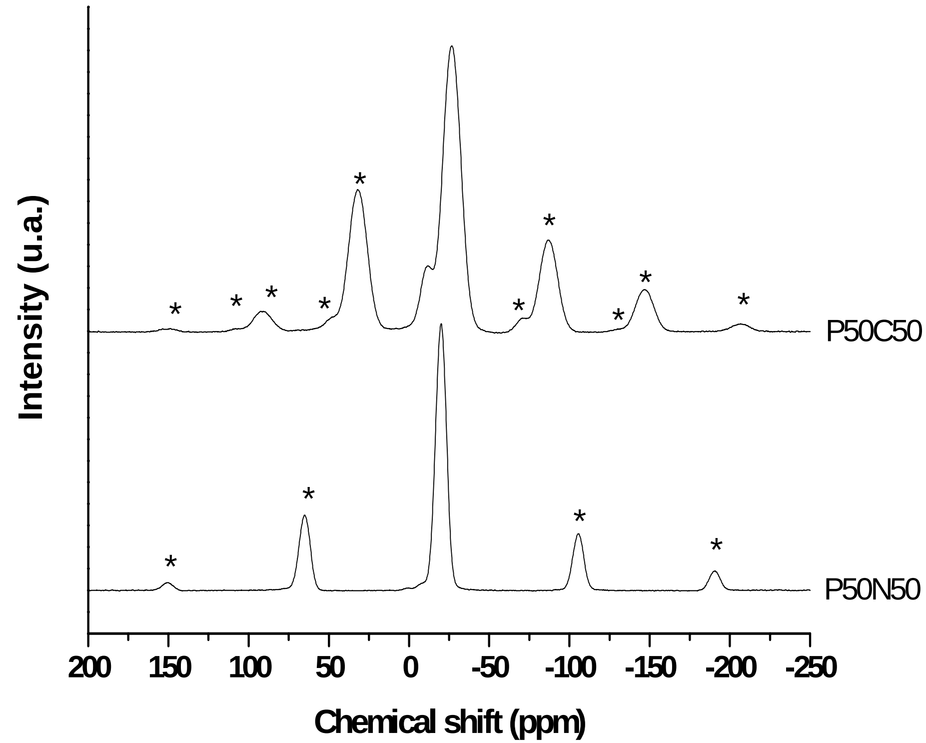
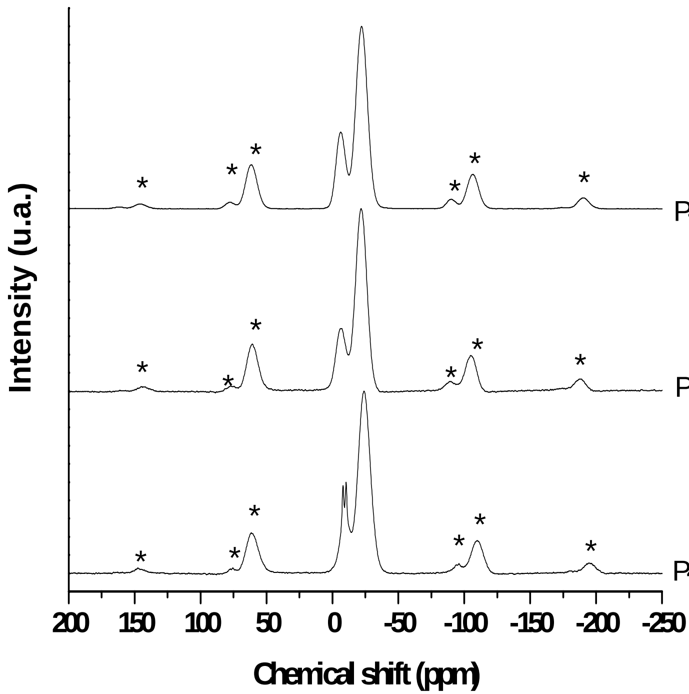
^{31}P MAS NMR Melt-quenched glasses

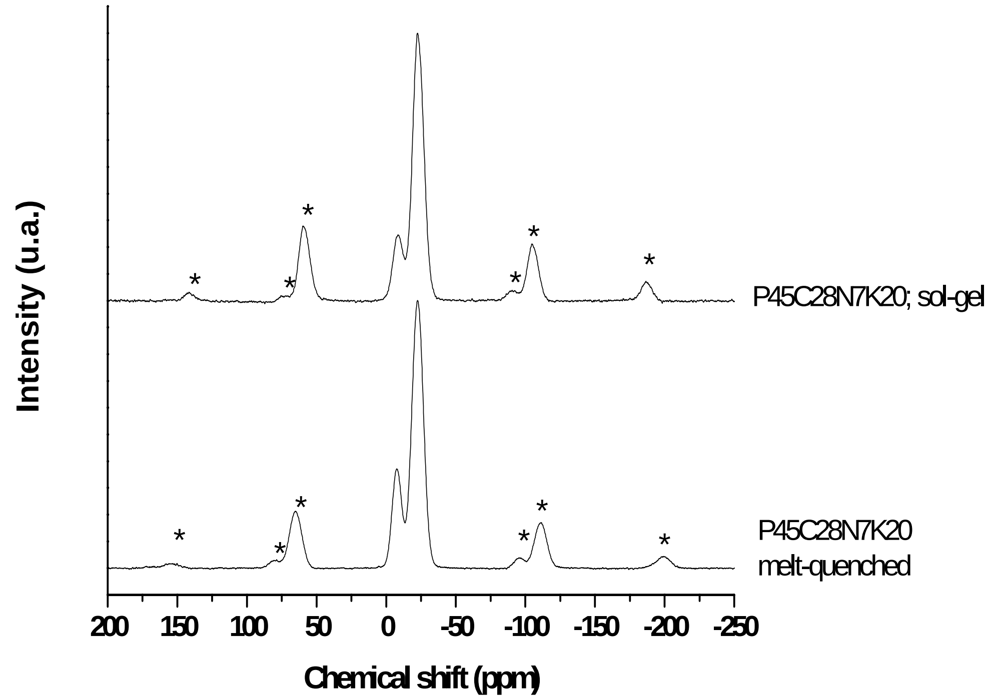




	Q^1 ppm	Q^2 ppm	Q^1 %	Q^2 %
MQ-P45C8N47	-2.89	-19.01	45.3	54.7
MQ-P45C30N25	-6.24	-21.94	21.71	78.29
MQ-P45C35N20	-7.68	-23.35	22.57	77.45
MQ-P45C40N15	-8.26	-23.58	5.97	94.03
MQ-P50C50	-11.48	-26.54	9.85	90.16
MQ-P50N50	-7.78	-19.99	3.0	97.0

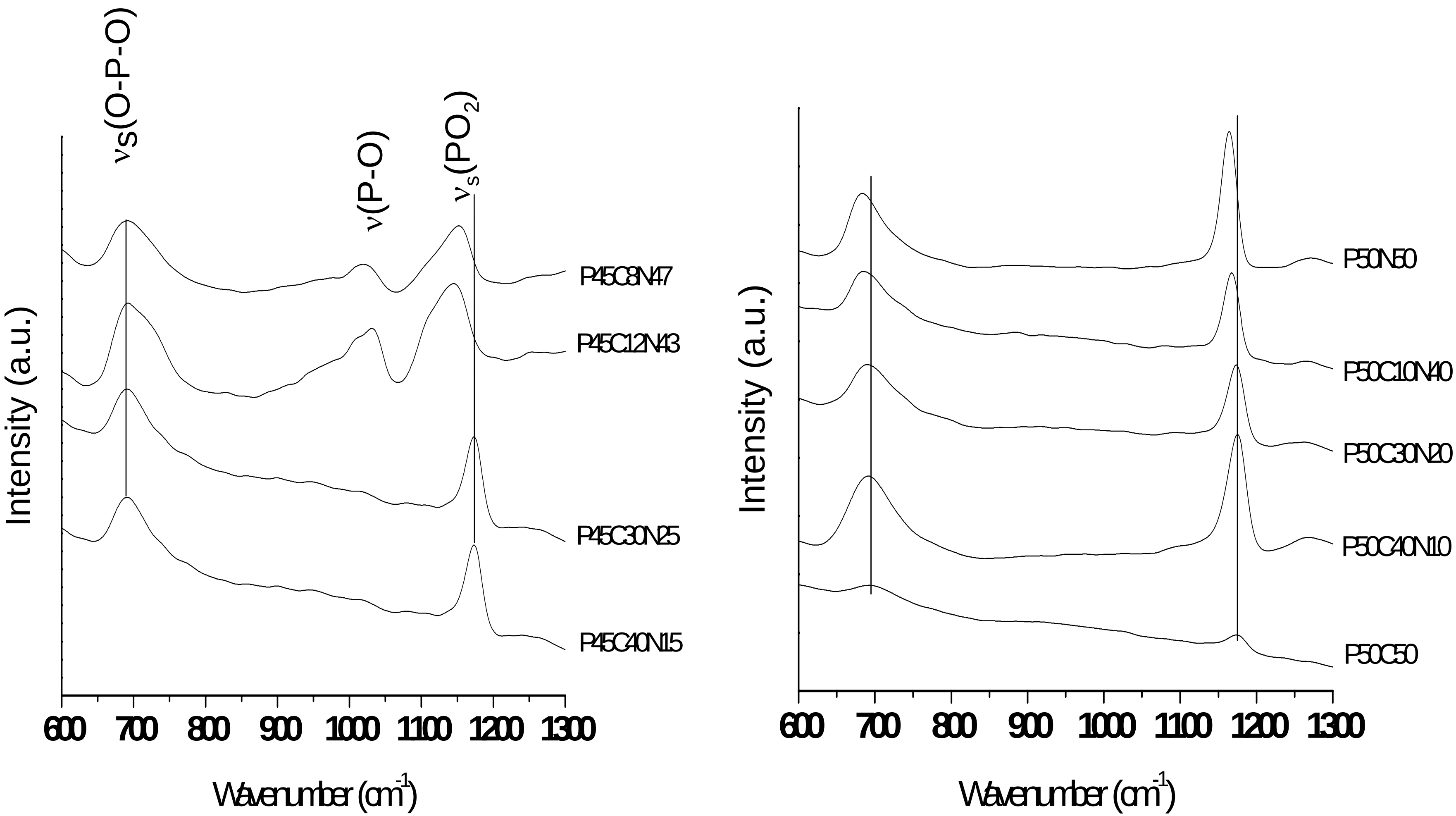
^{31}P MAS NMR



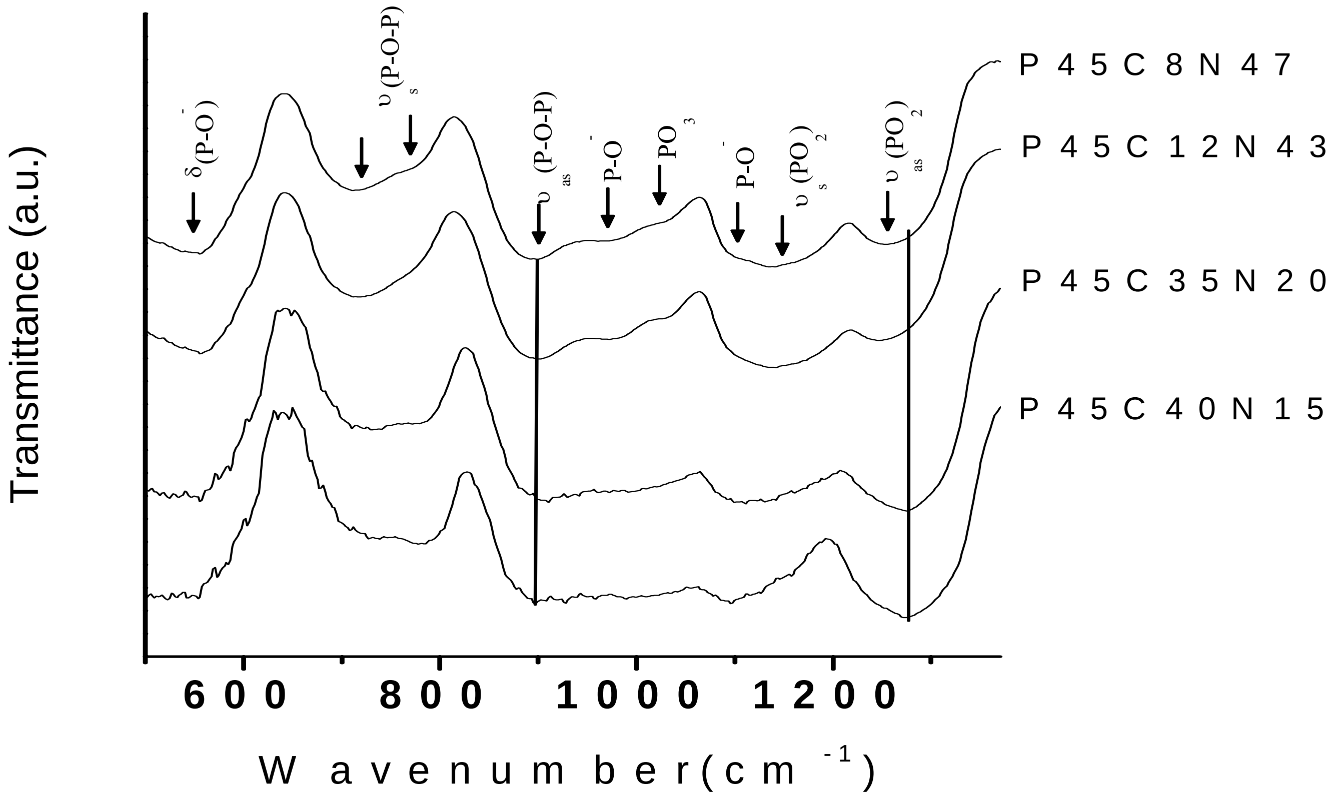


	Q^1 ppm	Q^2 ppm	Q^1 %	Q^2 %
SG- P45C28N7K20	-8.38	-22.7	19.35	80.65
SG- P45C30N25	-6.75	-21.94	24.0	76.0
SG-P45C40N15	-8.01 -10.31	-23.93	23.37	76.63
MQ-P45C30N25	-6.24	-21.94	21.71	78.29
MQ-P45C28N7K20	-7.70	-22.53	20.50	79.50

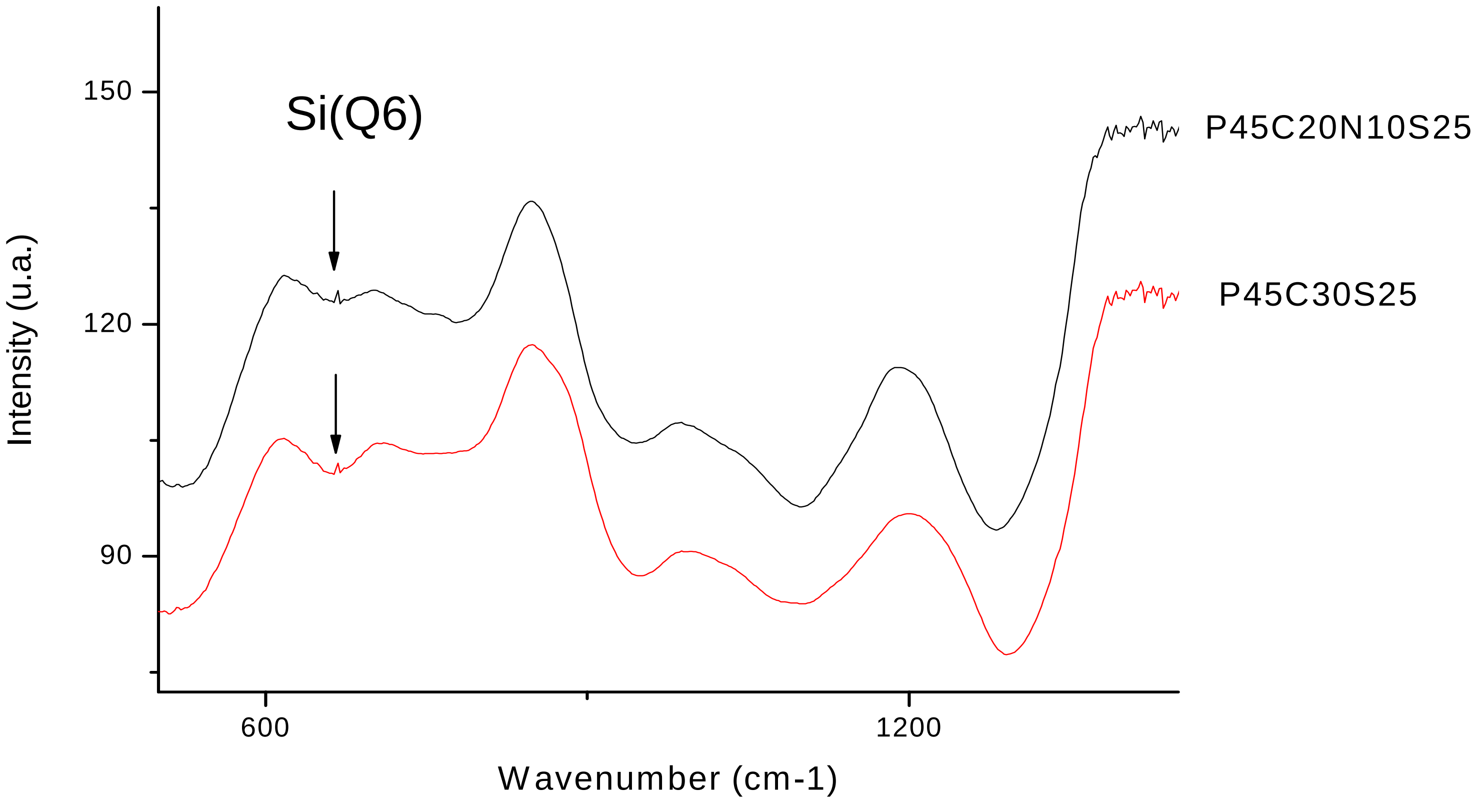
Raman spectroscopy Melt-quenched glasses



Infrared-spectroscopy-Melt-quenched glasses

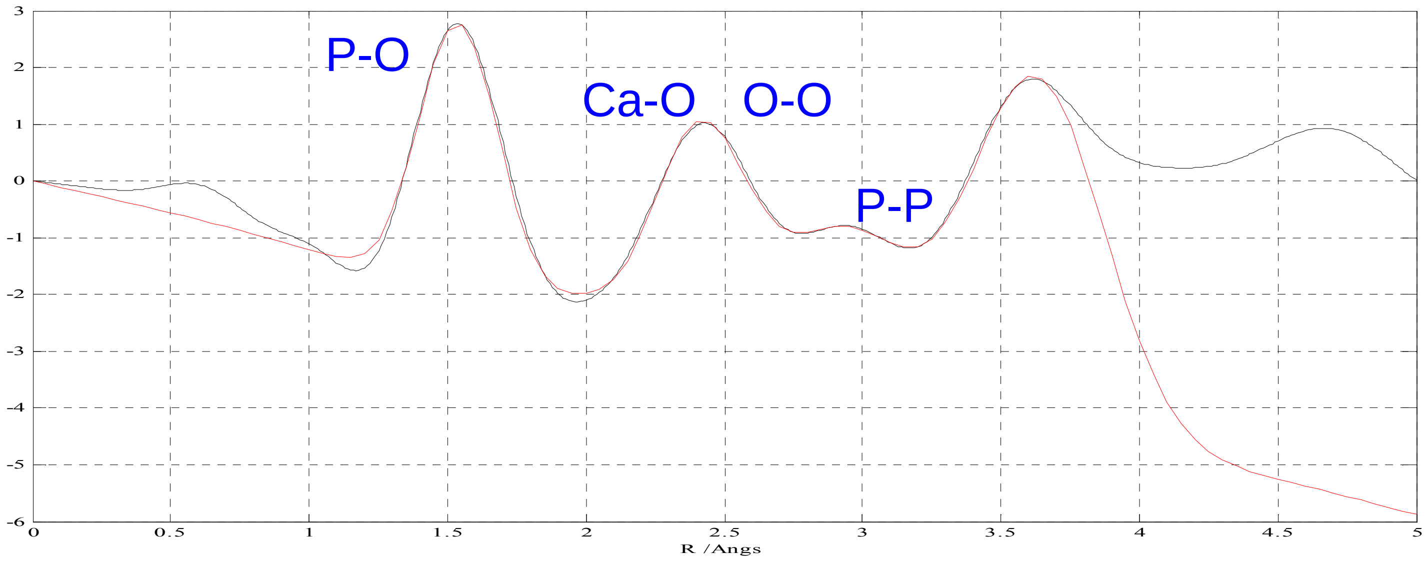


Infra-red sol-gel with 25 mol % SiO_2



High-Energy XRD -Daresbury-Station 9.1

P50C50 MQ



	R/Å	n	δ
P-O	1.54	3.5	0.085
Ca-O	2.39	4.2	0.1
O-O	2.51	4.5	0.15
P-P	2.98	4.75	0.2

^{31}P NMR

- Ternary MQ: As the CaO increases and the Na2O decreases, the Q2 site fraction increases the Q1 decreases.
- Binary MQ: P50C50 < Q2 than P50N50
- SG and MQ same compositions show similar Q distributions and chemical shifts

Raman / IR

- Q1 peak in Raman P45 with more than 43% Na2O
- Shift to higher wavenumbers as CaO increases and Na2O decreases
- Si(Q6) in sol-gel with 25 mol% SiO2

XRD

P-O, Me-O distances and Ca^{2+} coordination numbers are typical for methaphosphate glasses.

Further exp work:

^{29}Si MAS NMR (Warwick January)

9.1 XRD (Daresbury February)

Data analysis:

Thermal Analysis

Ca^{2+} EXAFS

High Energy XRD

Papers:

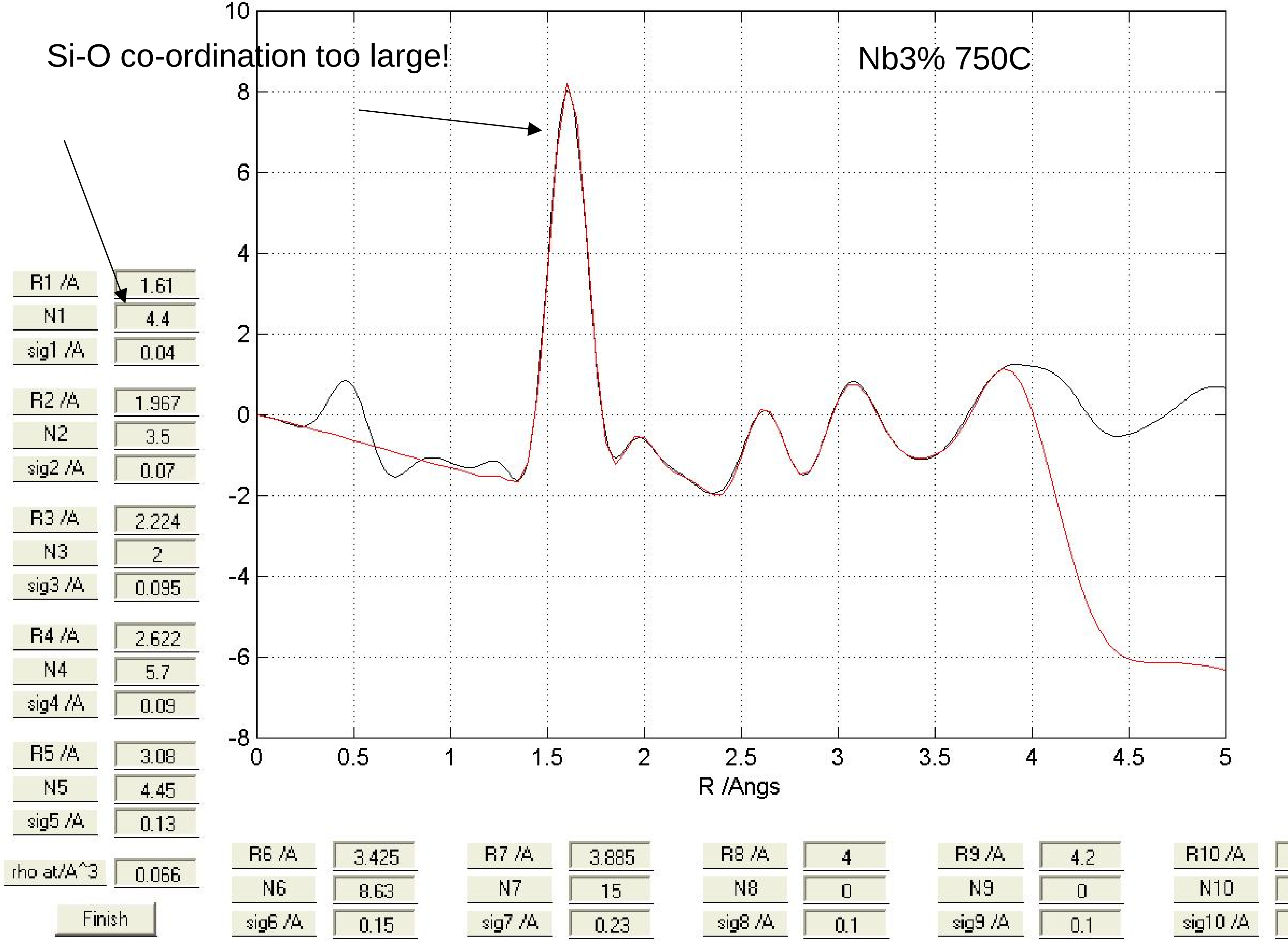
Comparison MQ and SG (Physics and Chemistry of glasses) **(submitted)**

Synthesis (Journal of Materials Chemistry) **(submitted)**

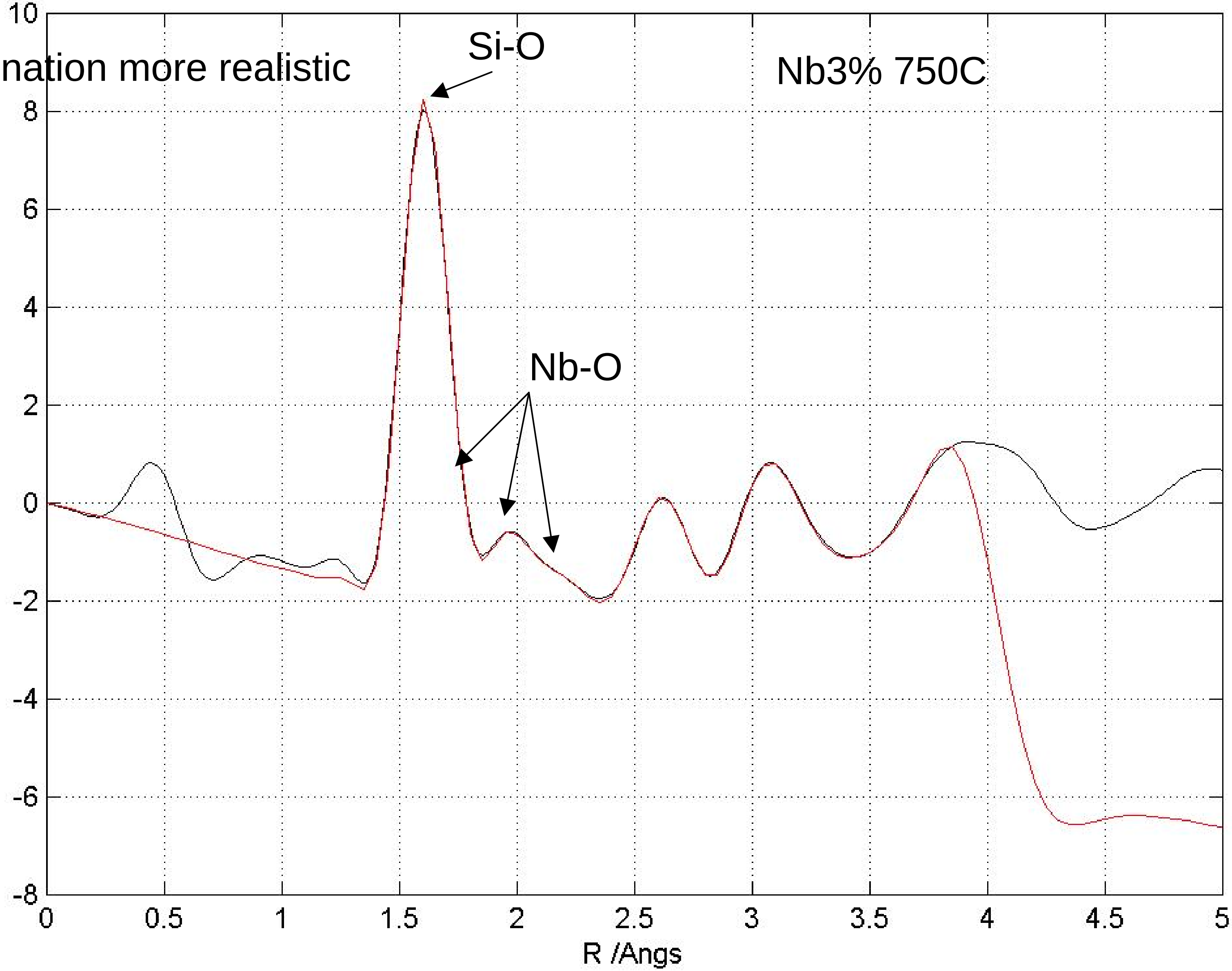
Vibrational spectroscopy (IR and Raman)

^{31}P MAS NMR (in progress)

Sample	Oxide Content (mol%)	
	Nb_2O_5	SiO_2
$(Nb_2O_5)_{0.03}$ - $(SiO_2)_{0.97}$ unheated	-	-
$(Nb_2O_5)_{0.03}$ - $(SiO_2)_{0.97}$ 250°C	3.8	96.2
$(Nb_2O_5)_{0.03}$ - $(SiO_2)_{0.97}$ 500°C	4.4	95.6
$(Nb_2O_5)_{0.03}$ - $(SiO_2)_{0.97}$ 750°C	3.8	96.2
$(Nb_2O_5)_{0.30}$ - $(SiO_2)_{0.70}$ unheated	41.7	58.3
$(Nb_2O_5)_{0.30}$ - $(SiO_2)_{0.70}$ 250°C	39.1	60.9
$(Nb_2O_5)_{0.30}$ - $(SiO_2)_{0.70}$ 500°C	41.7	58.3
$(Nb_2O_5)_{0.30}$ - $(SiO_2)_{0.70}$ 750°C	41.7	58.3


Si-O co-ordination too large!
Nb3% 750C
10
8
6
4
2
0
-2
-4
-6
-8
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5
5
R /Angs
R1 /A 1.61
N1 4.4
sig1 /A 0.04
R2 /A 1.967
N2 3.5
sig2 /A 0.07
R3 /A 2.224
N3 2
sig3 /A 0.095
R4 /A 2.622
N4 5.7
sig4 /A 0.09
R5 /A 3.08
N5 4.45
sig5 /A 0.13
rho at/A^3 0.066
Finish
R6 /A 3.425
N6 8.63
sig6 /A 0.15
R7 /A 3.885
N7 15
sig7 /A 0.23
R8 /A 4
N8 0
sig8 /A 0.1
R9 /A 4.2
N9 0
sig9 /A 0.1
R10 /A
N10
sig10 /A

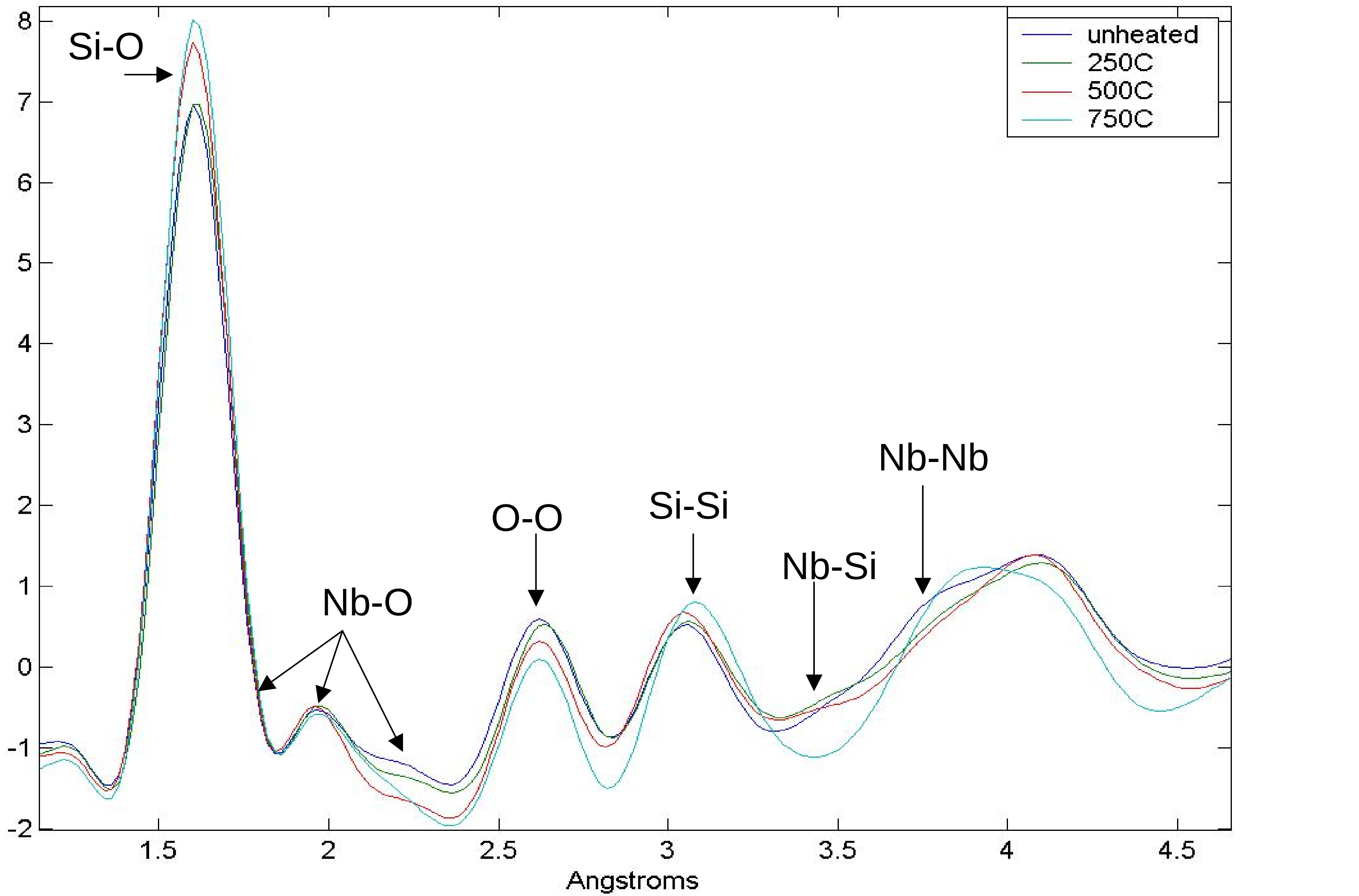
Si-O co-ordination more realistic



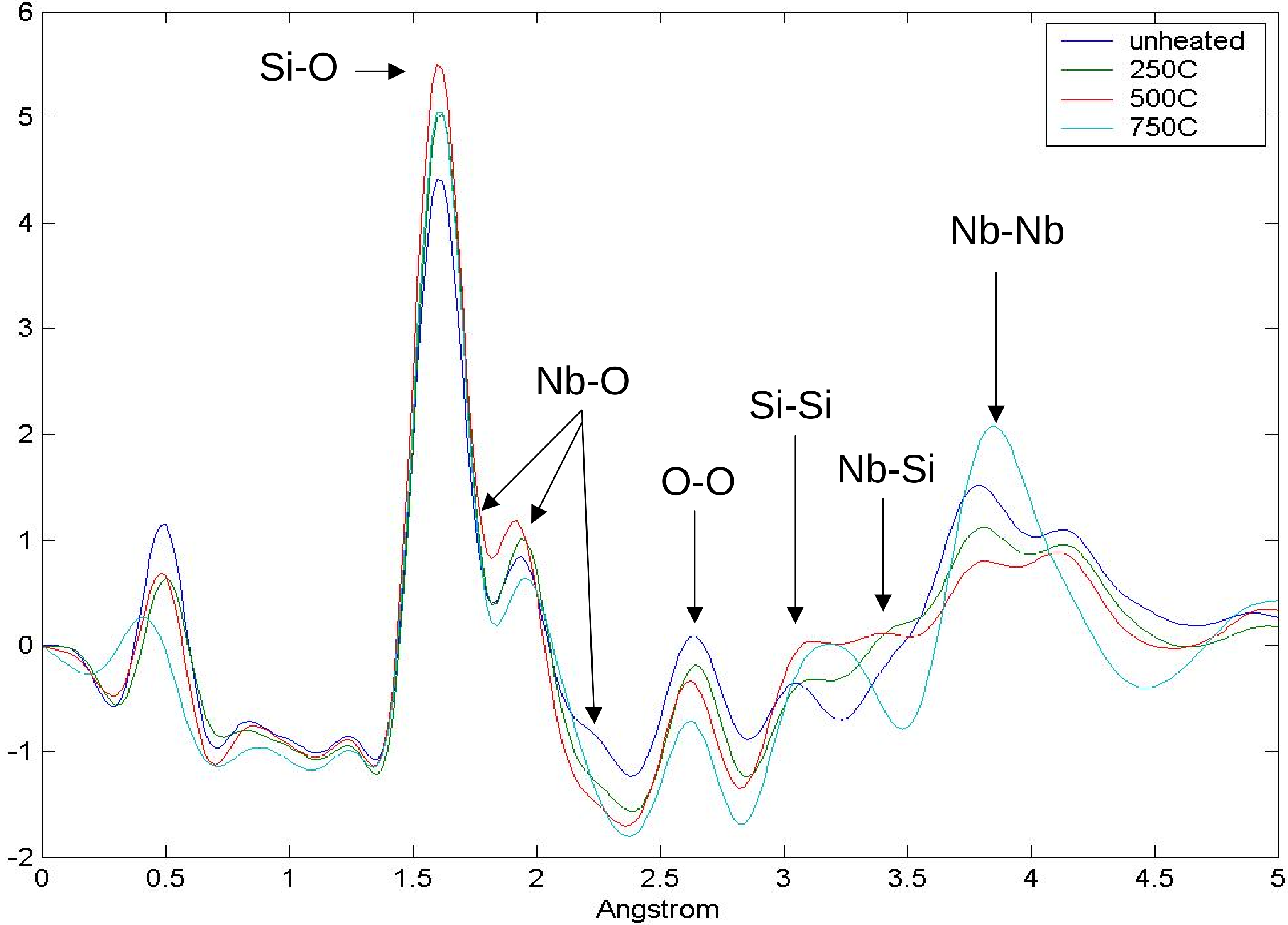
R1 /A	1.6
N1	3.95
sig1 /A	0.03
R2 /A	1.7
N2	1.9
sig2 /A	0.04
R3 /A	1.95
N3	2.92
sig3 /A	0.05
R4 /A	2.165
N4	2.4
sig4 /A	0.095
R5 /A	2.625
N5	7.2
sig5 /A	0.11
rho at/A^3	0.066
R6 /A	3.035
N6	3.83
sig6 /A	0.1
R7 /A	3.2
N7	1.1
sig7 /A	0.1
R8 /A	3.48
N8	1.2
sig8 /A	0.19
R9 /A	3.875
N9	12
sig9 /A	0.17
R10 /A	[illegible]
N10	[illegible]
sig10 /A	[illegible]

Finish

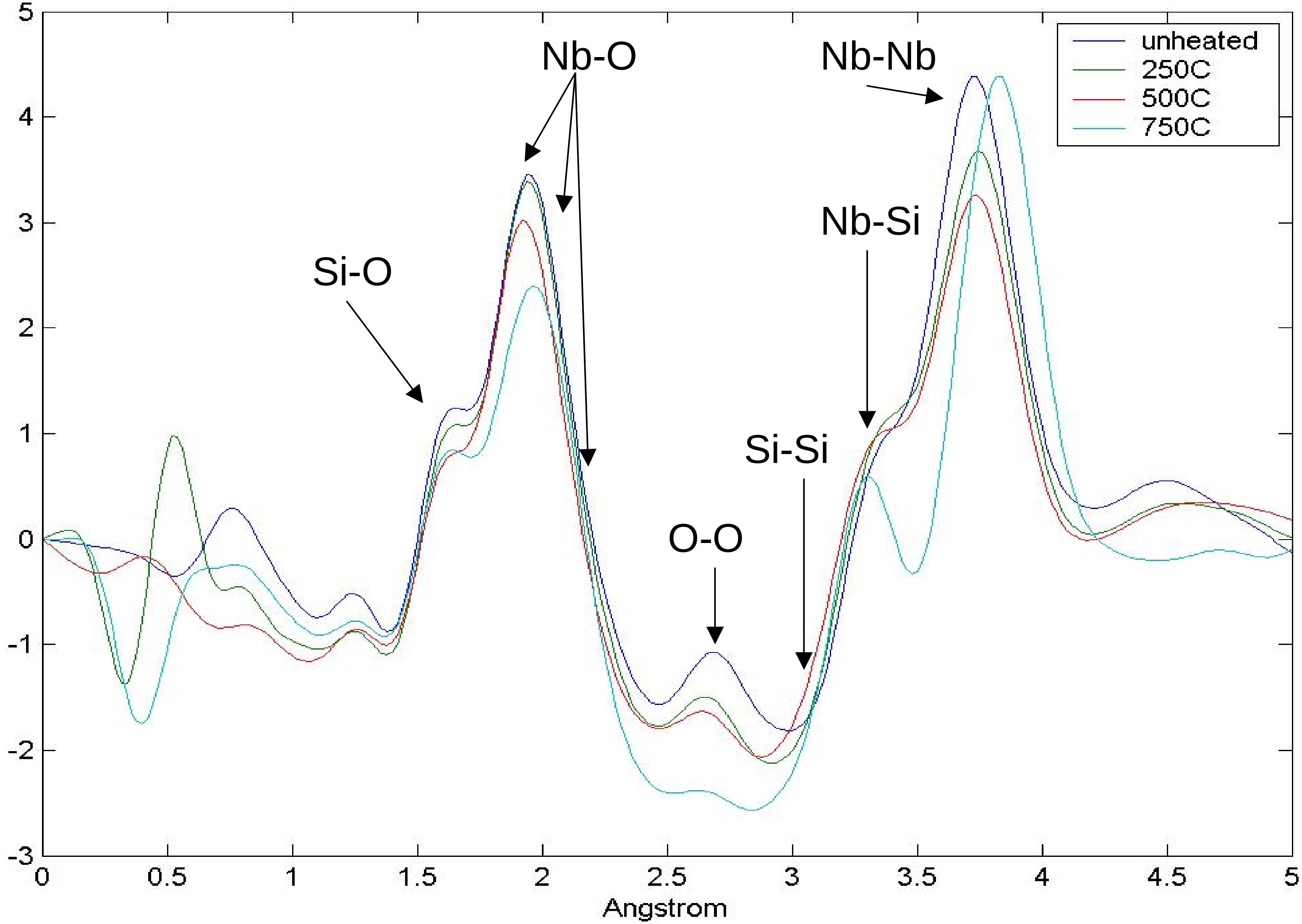
$(Nb_2O_5)_{0.03}$ - $(SiO_2)_{0.97}$



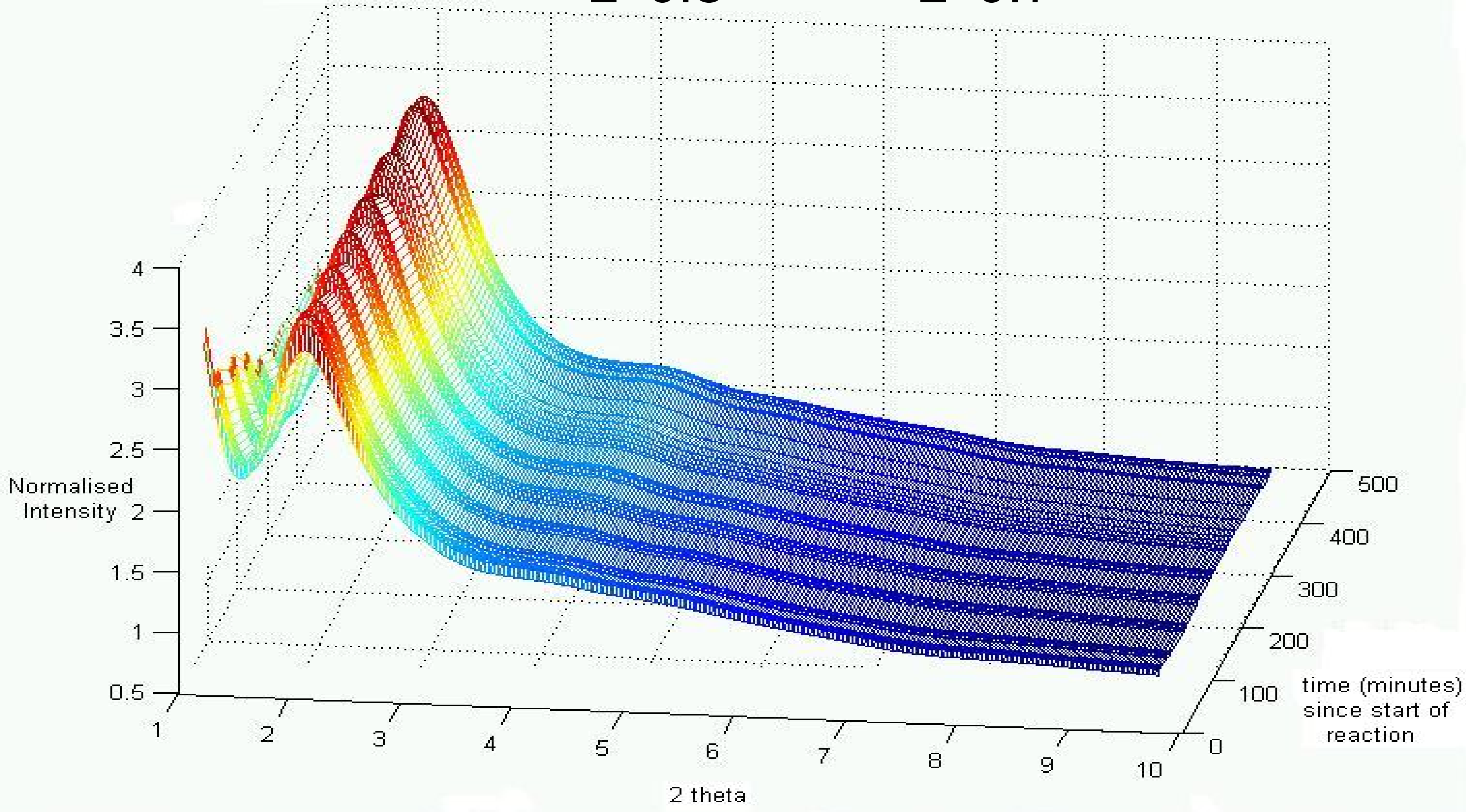
$(Nb_2O_5)_{0.075}$ - $(SiO_2)_{0.925}$



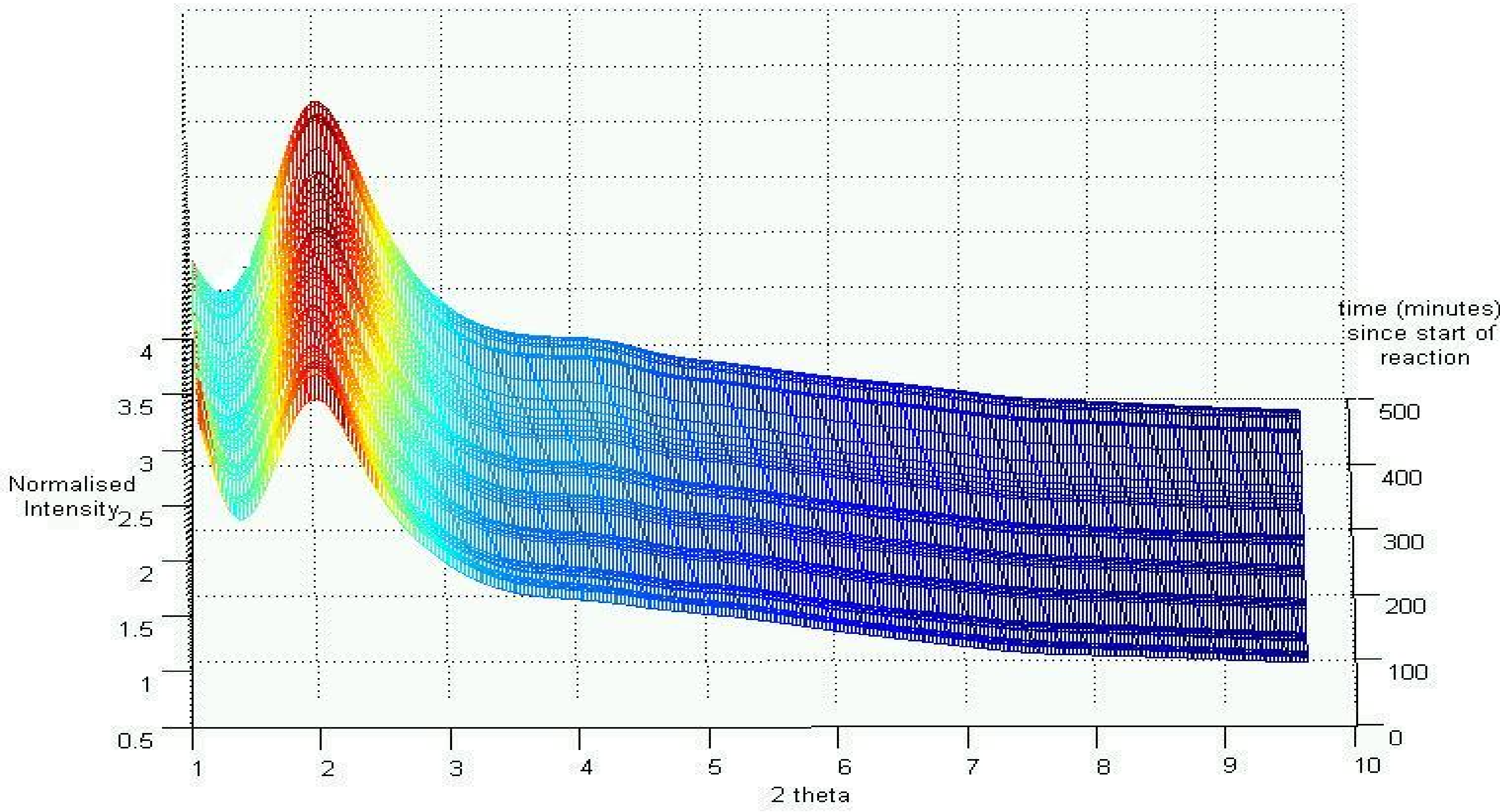
$(Nb_2O_5)_{0.30}$ - $(SiO_2)_{0.70}$



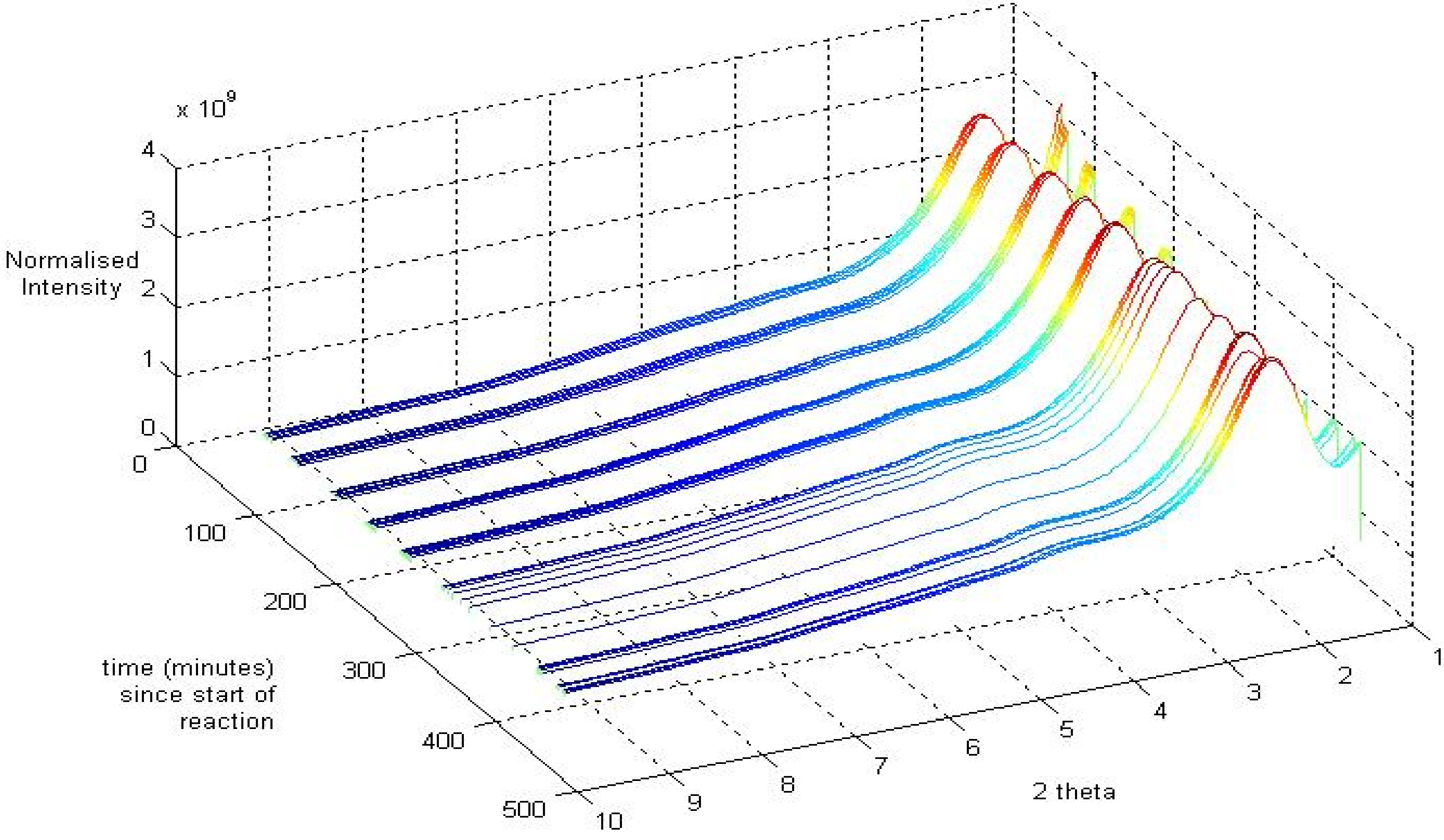
X-Ray diffraction data showing the in-situ sol-gel reaction for $(TiO_2)_{0.3}$-$(SiO_2)_{0.7}$



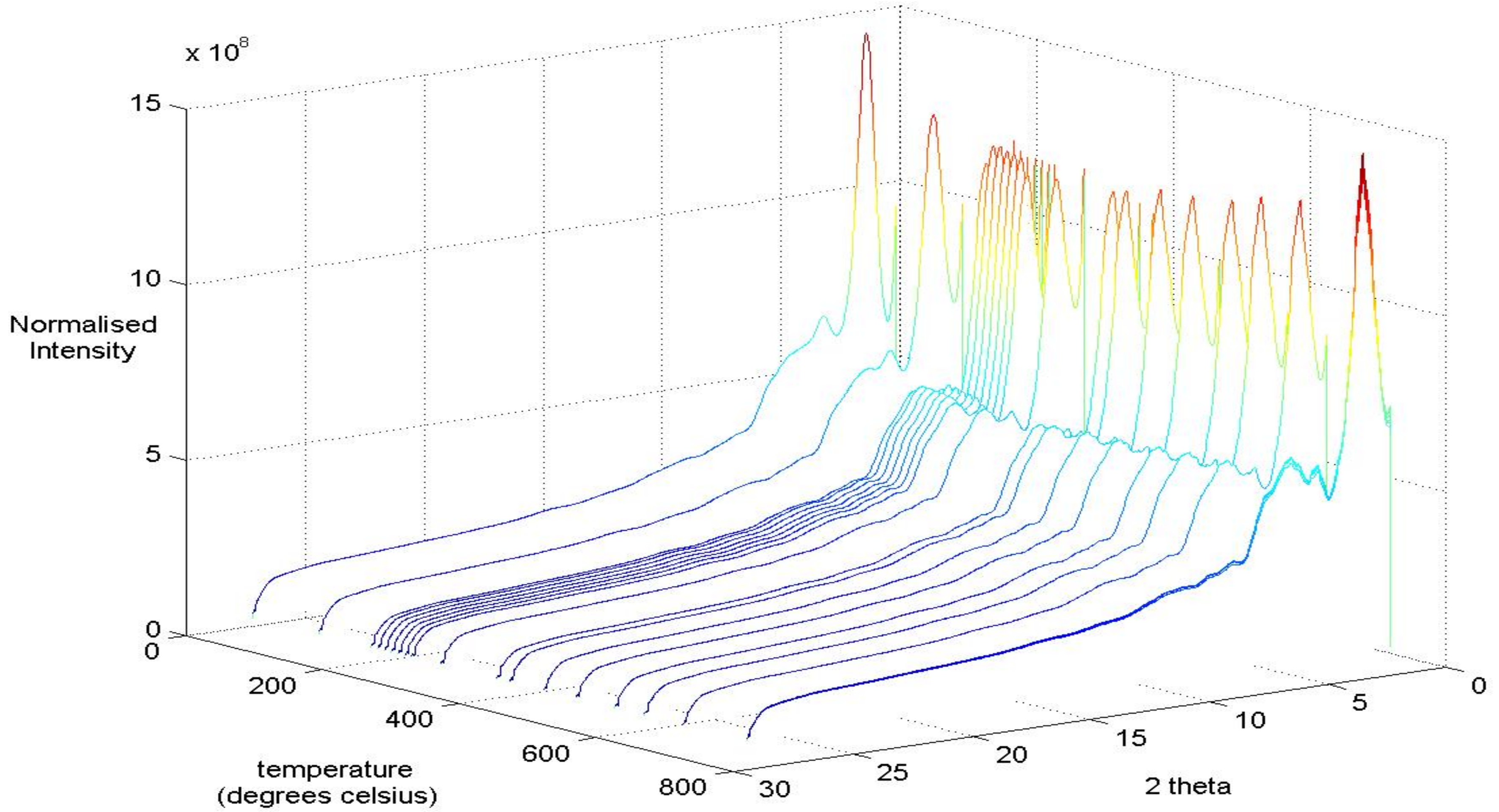
X-Ray diffraction data showing the in-situ sol-gel reaction for $(TiO_2)_{0.3}$-$(SiO_2)_{0.7}$



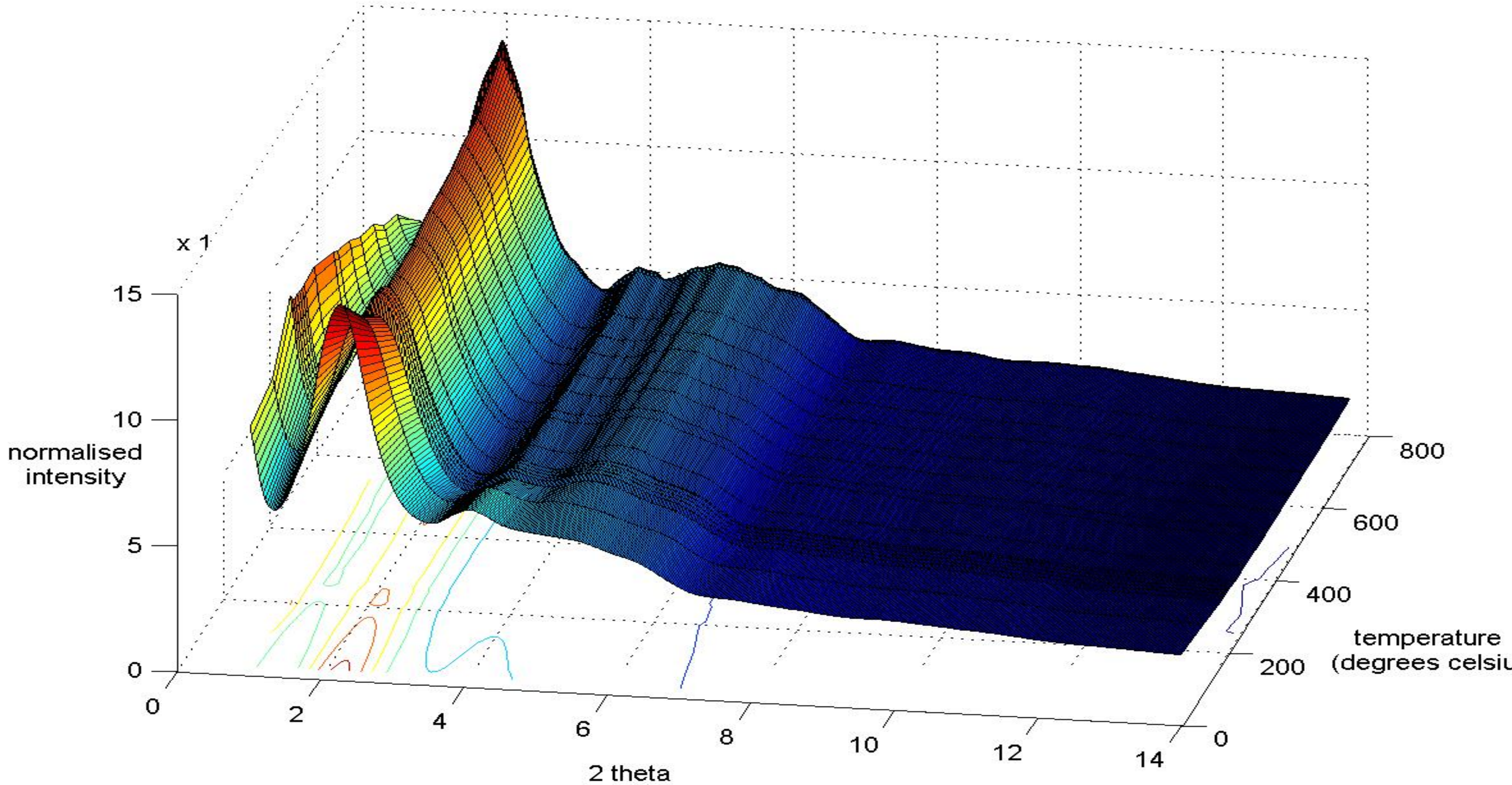
X-Ray diffraction data showing the in-situ sol-gel reaction for $(TiO_2)_{0.3}$-$(SiO_2)_{0.7}$



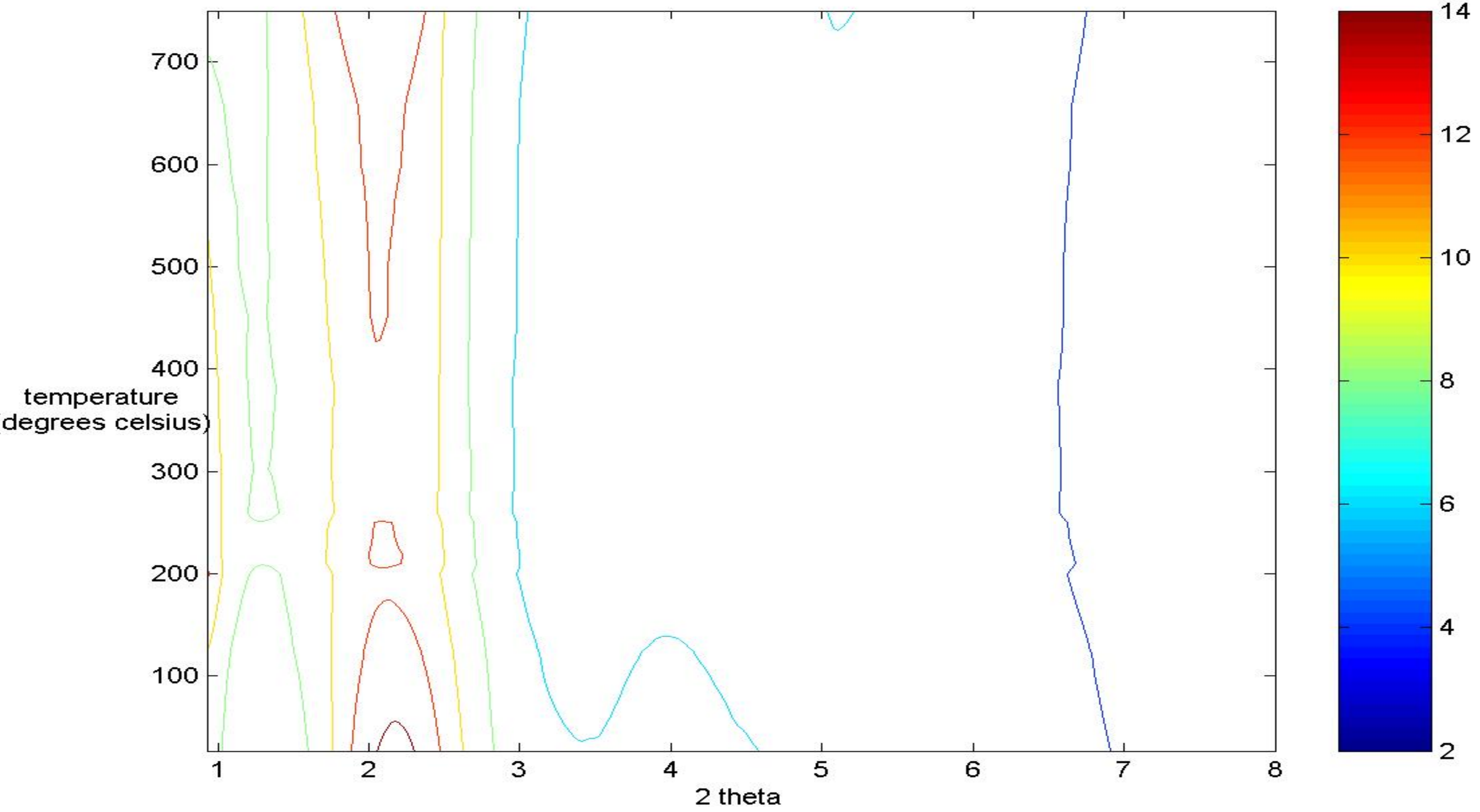
X-Ray diffraction data showing the in-situ heating of $(TiO_2)_{0.3}$-$(SiO_2)_{0.7}$



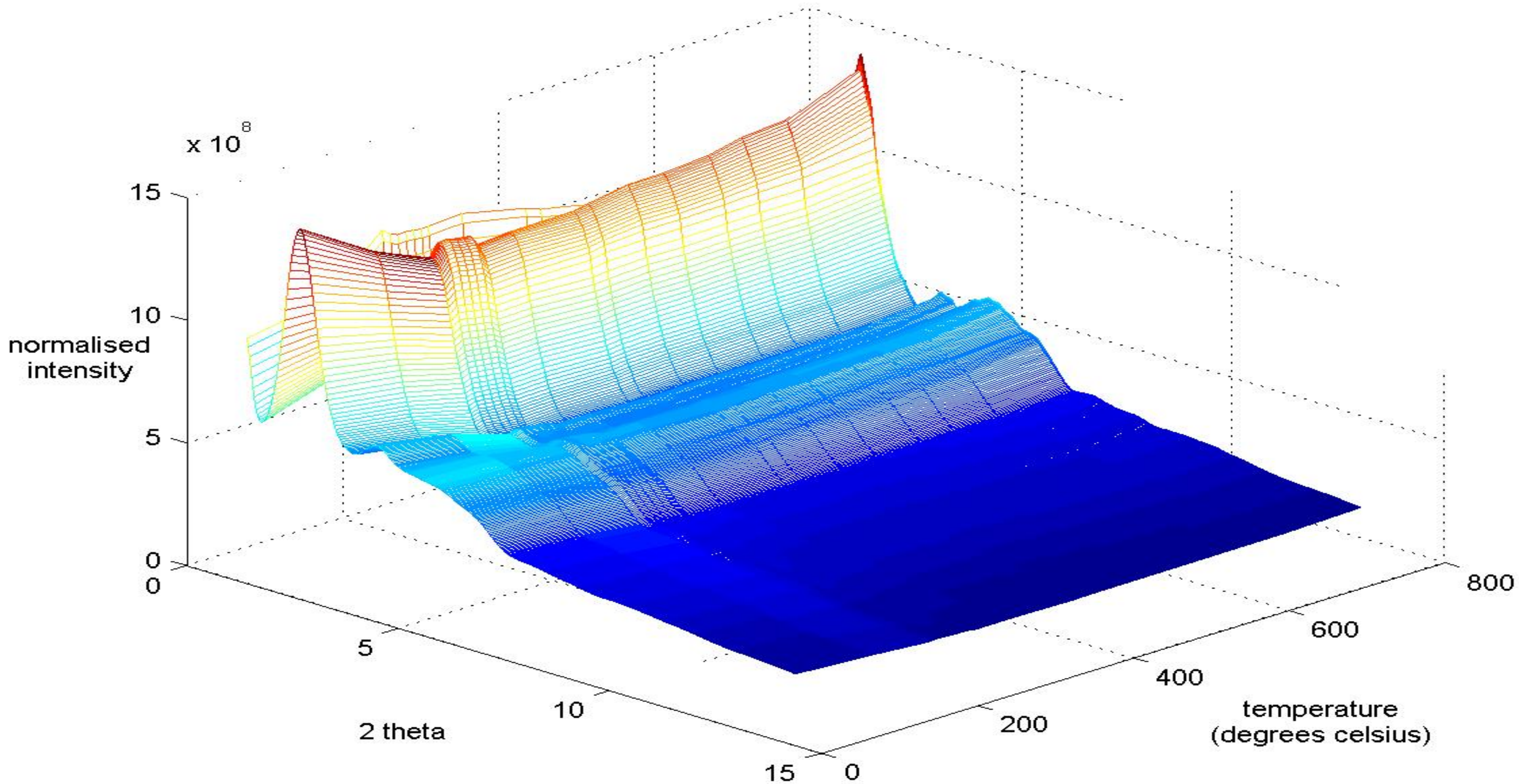
X-Ray diffraction data showing the in-situ heating of $(TiO_2)_{0.3}$-$(SiO_2)_{0.7}$



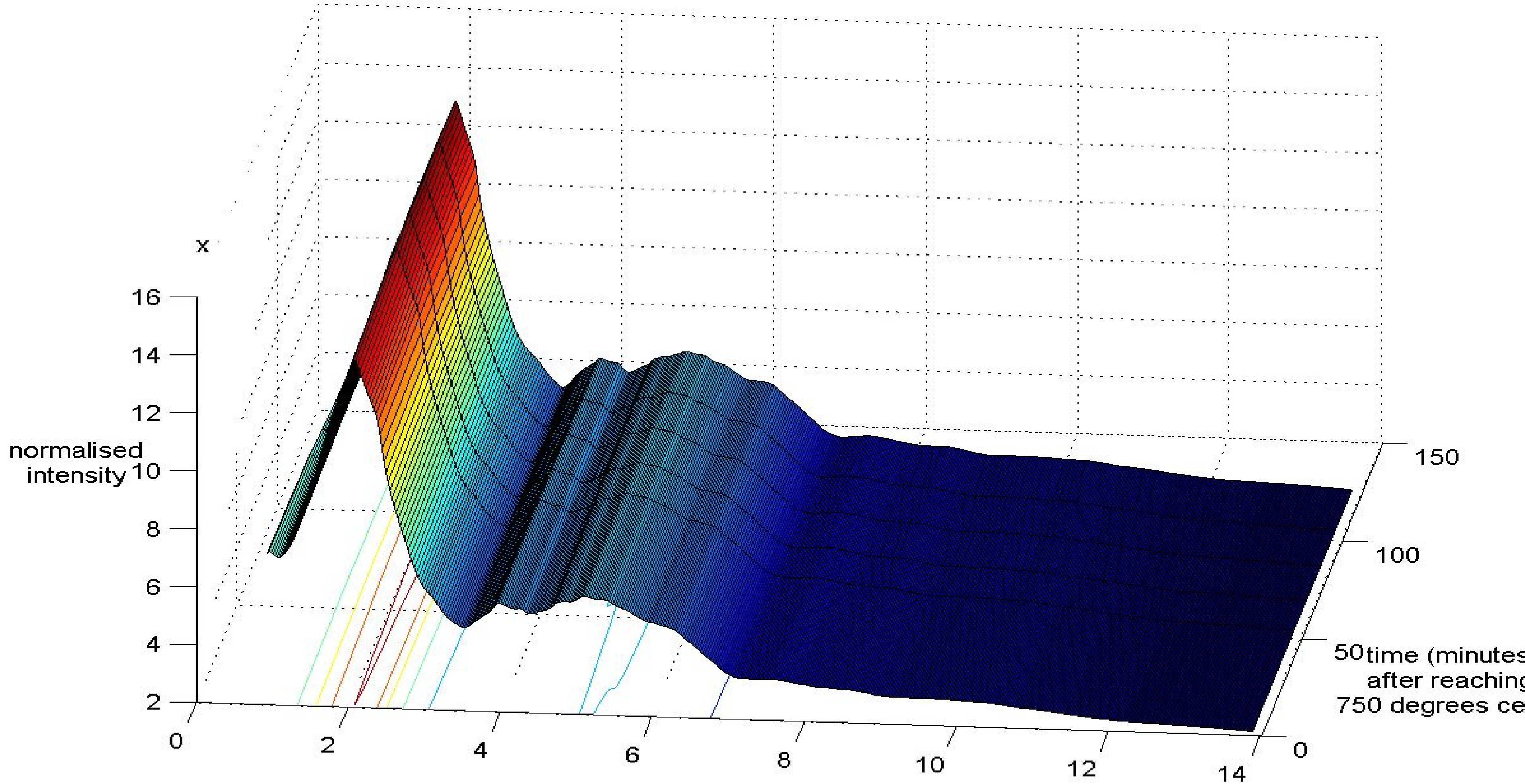
X-Ray diffraction data showing the in-situ heating of $(TiO_2)_{0.3}$-$(SiO_2)_{0.7}$



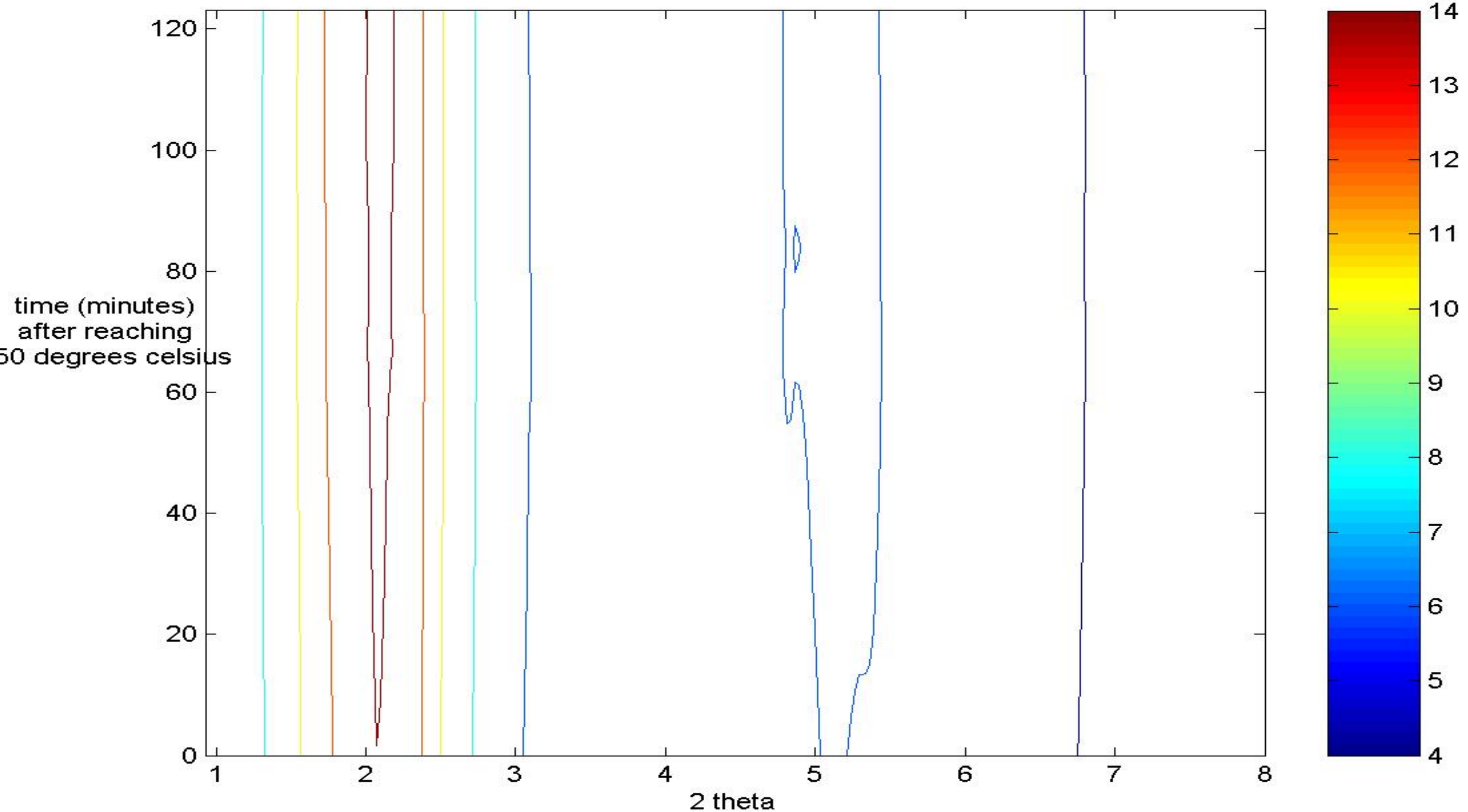
X-Ray diffraction data showing the in-situ heating of $(TiO_2)_{0.3}$-$(SiO_2)_{0.7}$



X-Ray diffraction data showing the in-situ heating of $(TiO_2)_{0.3}$-$(SiO_2)_{0.7}$



X-Ray diffraction data showing the in-situ heating of $(TiO_2)_{0.3}$-$(SiO_2)_{0.7}$



SAXS

- 70:30 Powders (1 minute-30 days)
- Ahmad’s powders
- Thin films on a mica window
- Un-reacted 70:30 Powder in SBF through a capillary, normal concentration of sample
- Un-reacted 70:30 powder in SBF through a capillary, higher concentration of sample

Results

- Powders went fine, first peak changed and Bragg peaks occurred from 5hr sample
- Thin films of sample on mica washed off but sample holder worked
- No bragg peaks occurred in any of the capillary runs that could be seen, not even with greater amount of sample in SBF

Future work

- Films that are thicker or with more layers are being made by Ahmad (daresbury)
- Capillary can be increased in diameter to 2mm to increase amount of sample in the beam (daresbury)
- Solid piece of sample with SBF flowing over (ESRF)

Neutron Data

- Ta Si neutron data is now giving correct Si-O bond length
- Once data is re-analysed it will be included in MPhys project student’s RMC modelling along with XRD data

Turbidity

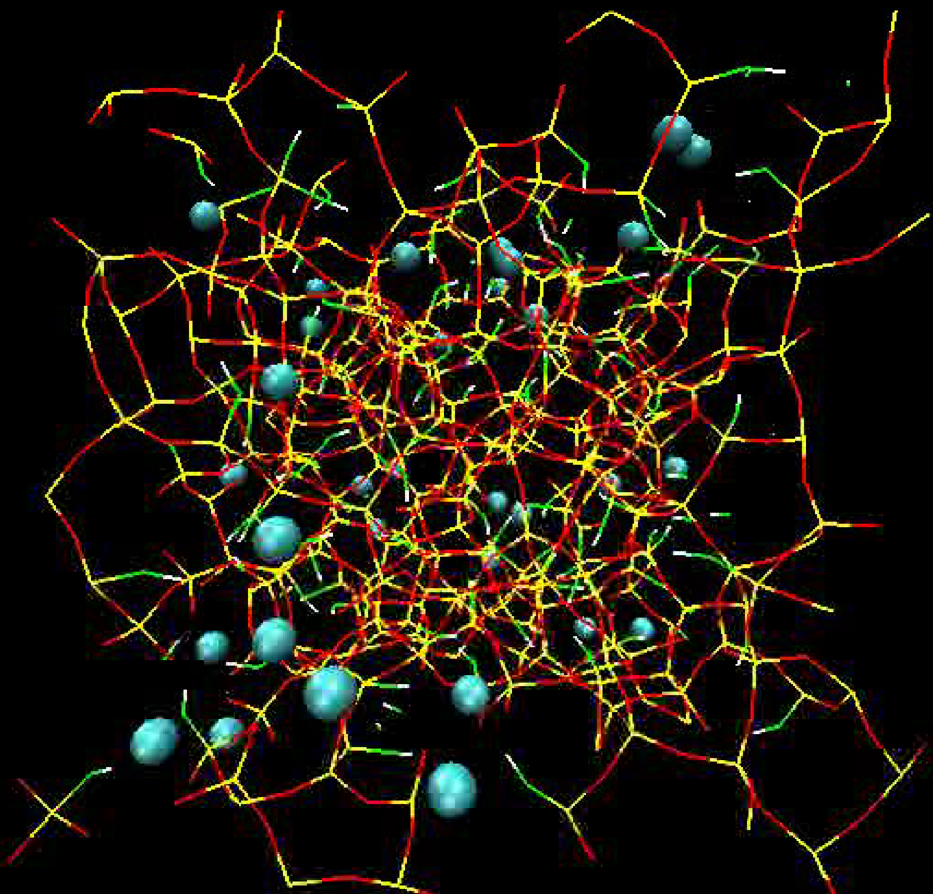
- In house turbidity experiments on Calcium silicate glasses in-situ
- Build an in-situ cell for UV-visible-NIR spectrophotometer

Models:

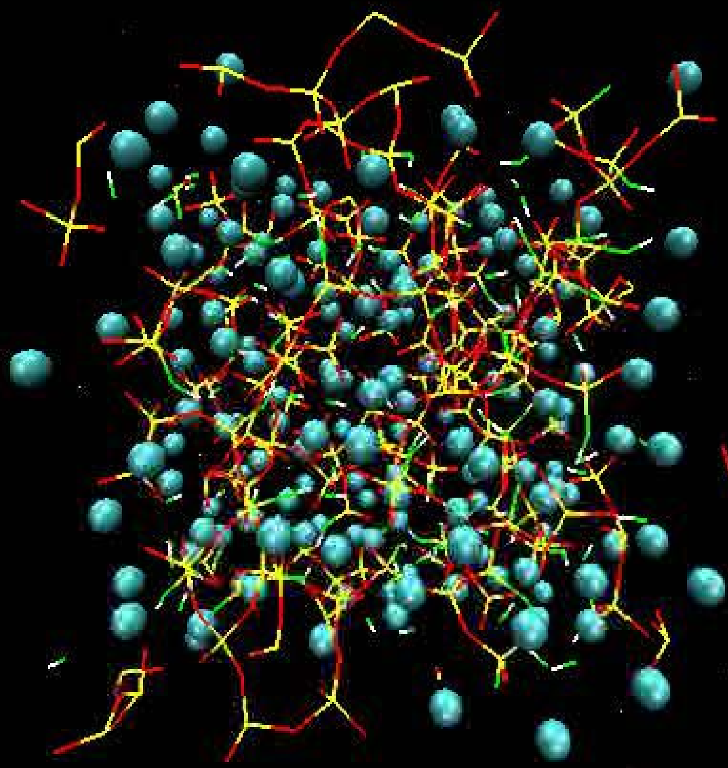
	Model 00	Model 10	Model20	Model30	Model40	Model 50
g/cm3	1.99	2.11	2.22	2.37	2.50	2.67
box L (Å)	25.72	25.19	24.67	24.11	23.62	23.08
box atm	1152	1120	1088	1056	1024	992
num Si	320	288	256	224	192	160
num Ca	0	32	64	96	128	160
num O_{total}	704	672	640	608	576	544
O_{bO} / O_{nb} only	576	544	512	480	448	416
num H / O_h	128	128	128	128	128	128

- Can have any density / composition
- Density 90% of Bulk Glass
- OH Content 40% of Ca+Si Value

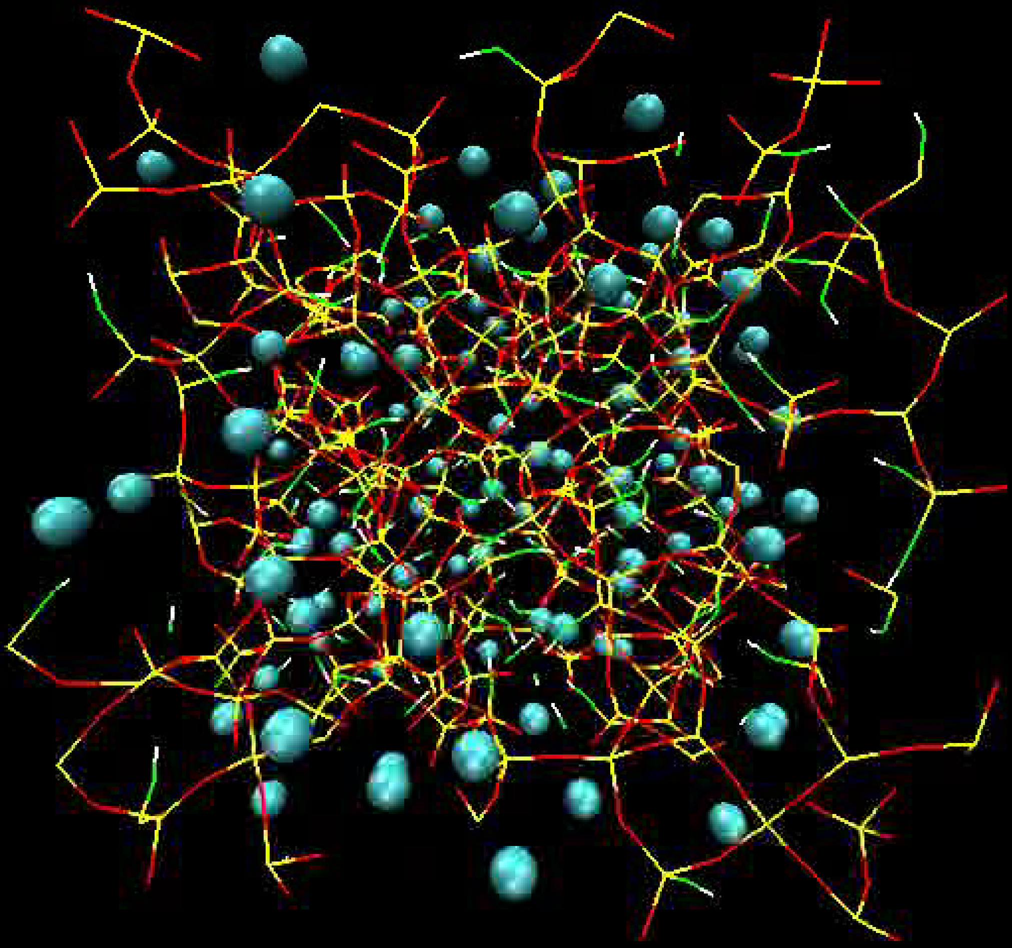
M10, x = 0.1



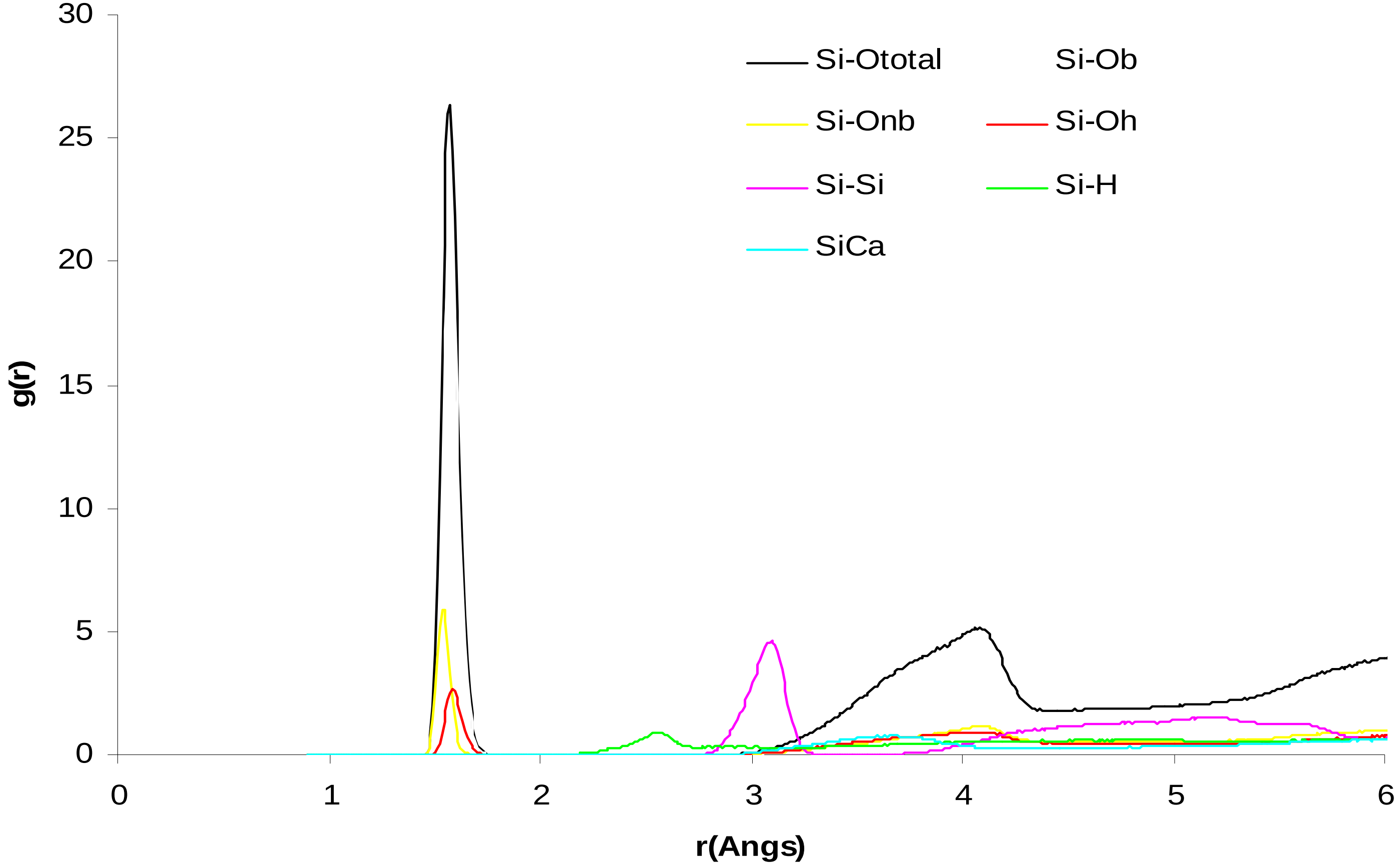
M50, x = 0.5



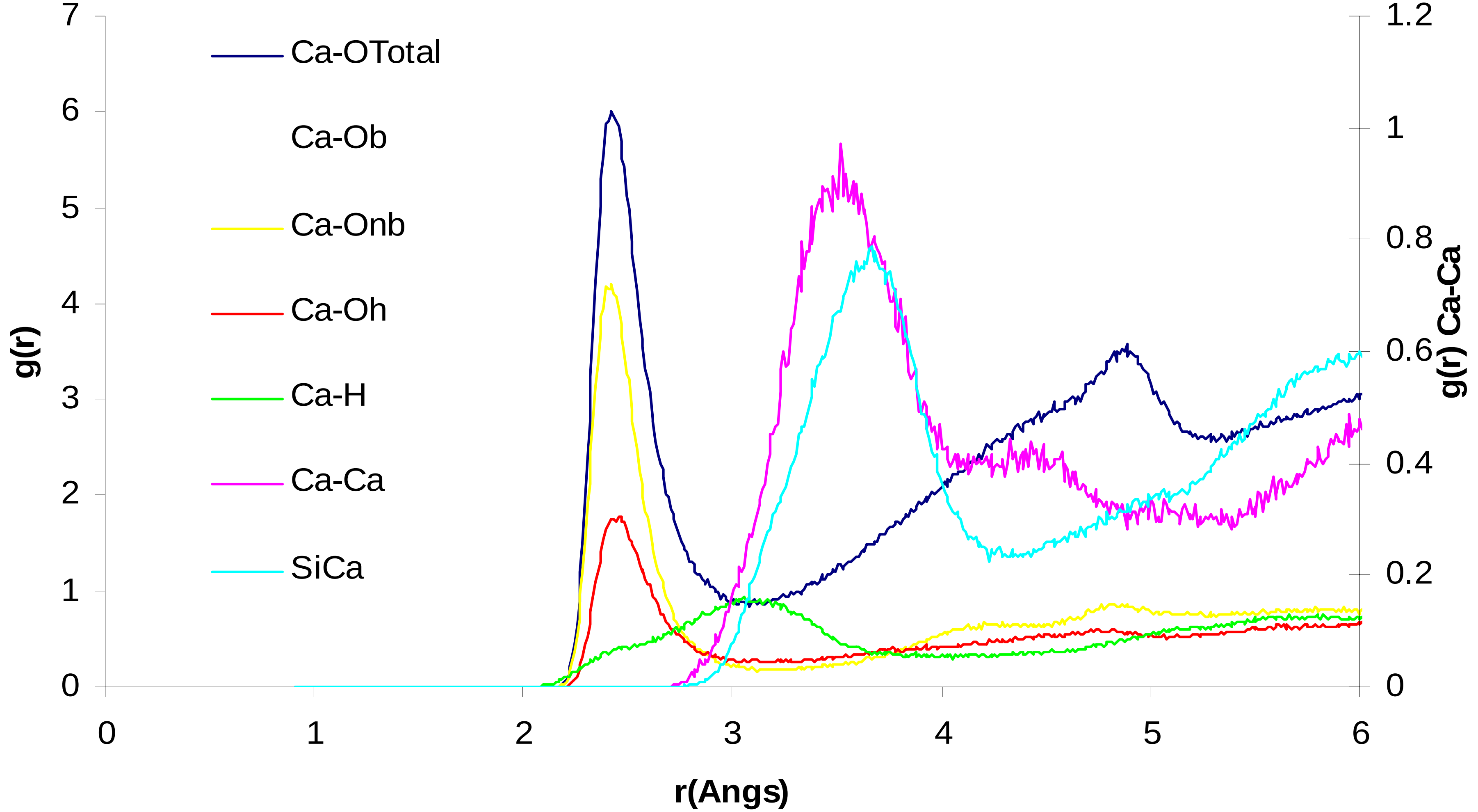
M30 (x = 0.3)



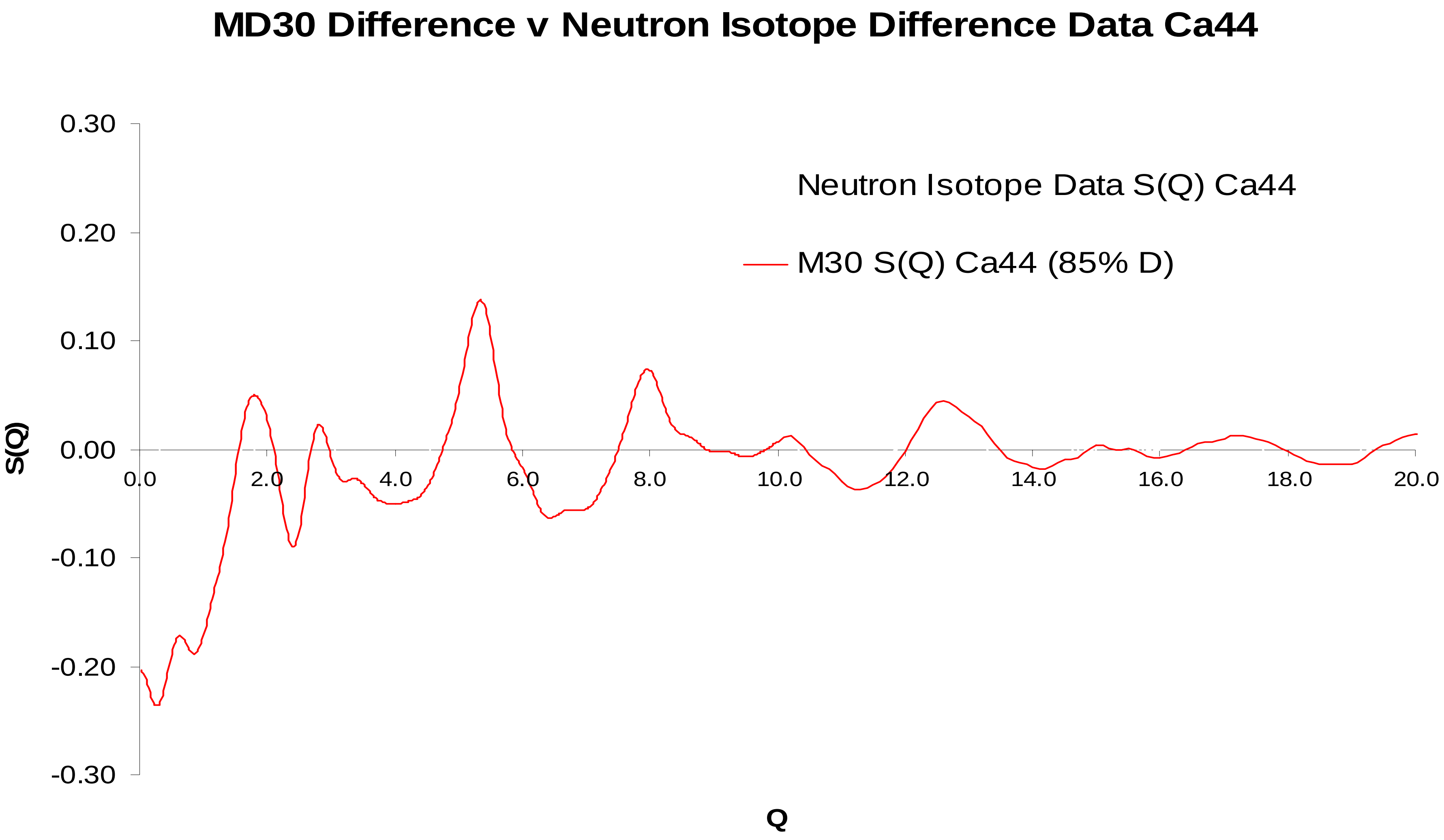
The distribution functions g(r) for Si-O_{total}, Si-O_b , Si-O_{nb} Si-O_h, Si-H and Si-Si (left hand axis) for M30 (x = 0.3)



The Distribution Functions g(r) for Ca-O_{total}, Ca-O_b, Ca-O_{nb}, Ca-O_h and Ca-Ca (left hand axis) for M30 (x = 0.3)



Neutron Diffraction



Silicon & Oxygen Coordination

Si-(O_{total} / $O_{b\&nb}$ / O_h)

- Si – O_{total} is 100% 4 coordinated
- Si - $O_{b\&nb}$ 6% N=2, 32% N=3, 63% N=4.
- Si – Oh 64% N=0, 30% N=1, 6% N=2. **So 64% of Si has no O_h coordination.**
- The values don't change much as Ca is added (M00 – M50).

(O_{total} / $O_{b\&nb}$ / O_h)- Si

- **There is a growth of O_{nb} as you add Ca.**
- O_b- Si for M00 98% and M50 39%.
- O_{nb}- Si M00 2% and M50 60%
- Due to deploymerisation by the Ca.
- **There is a preference for Oh to go to Ca region.**
- Initially M00 O_h-Si is 96% N = 1, As Ca is added, M50 has 50% 0, 50% 1.

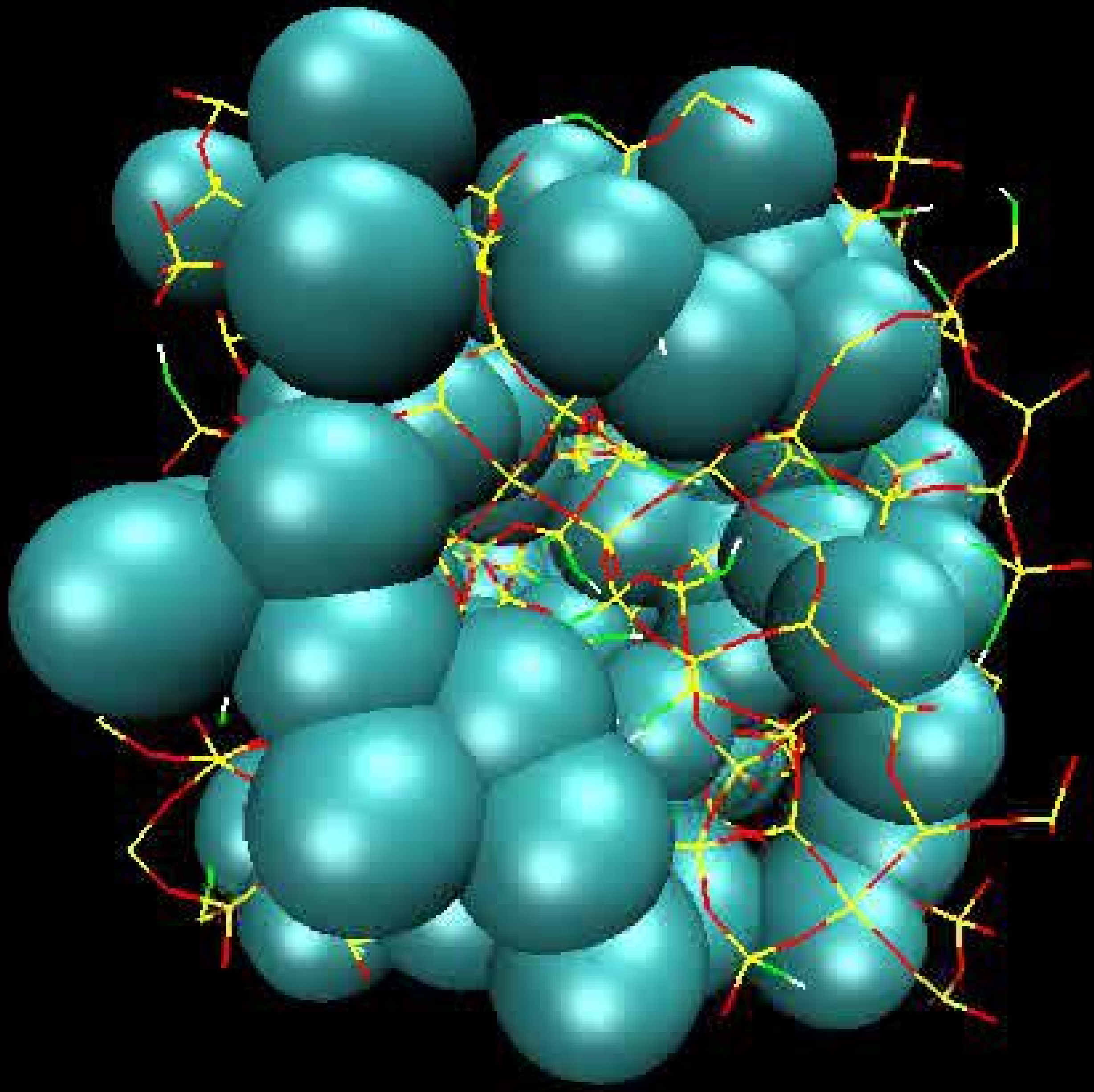
Calcium & Oxygen Coordination

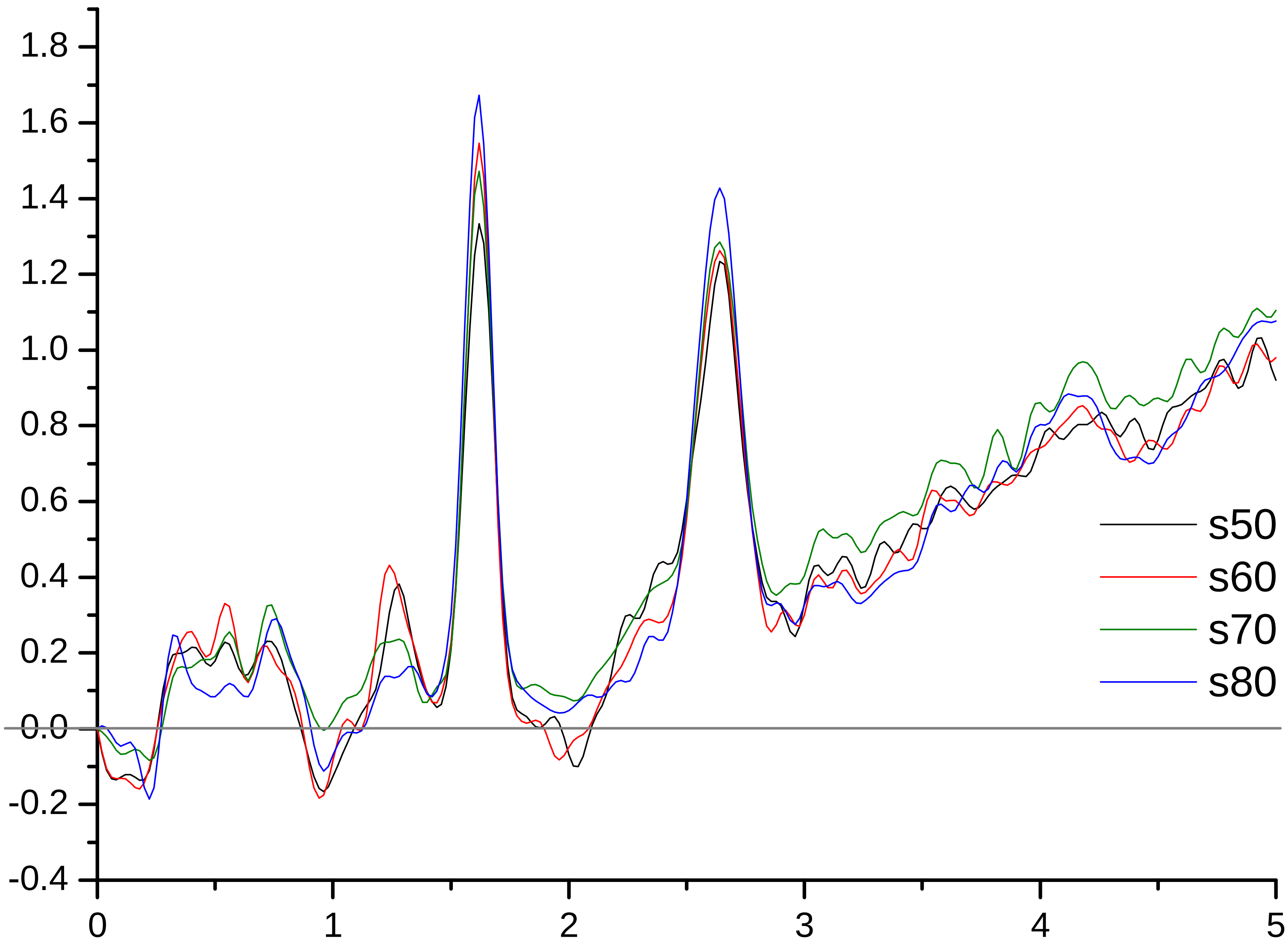
- Total Ca – O_{total} changes from 4.5 to 6 as Ca is added. A similar trend to the bulk glass results for variation in Ca content.

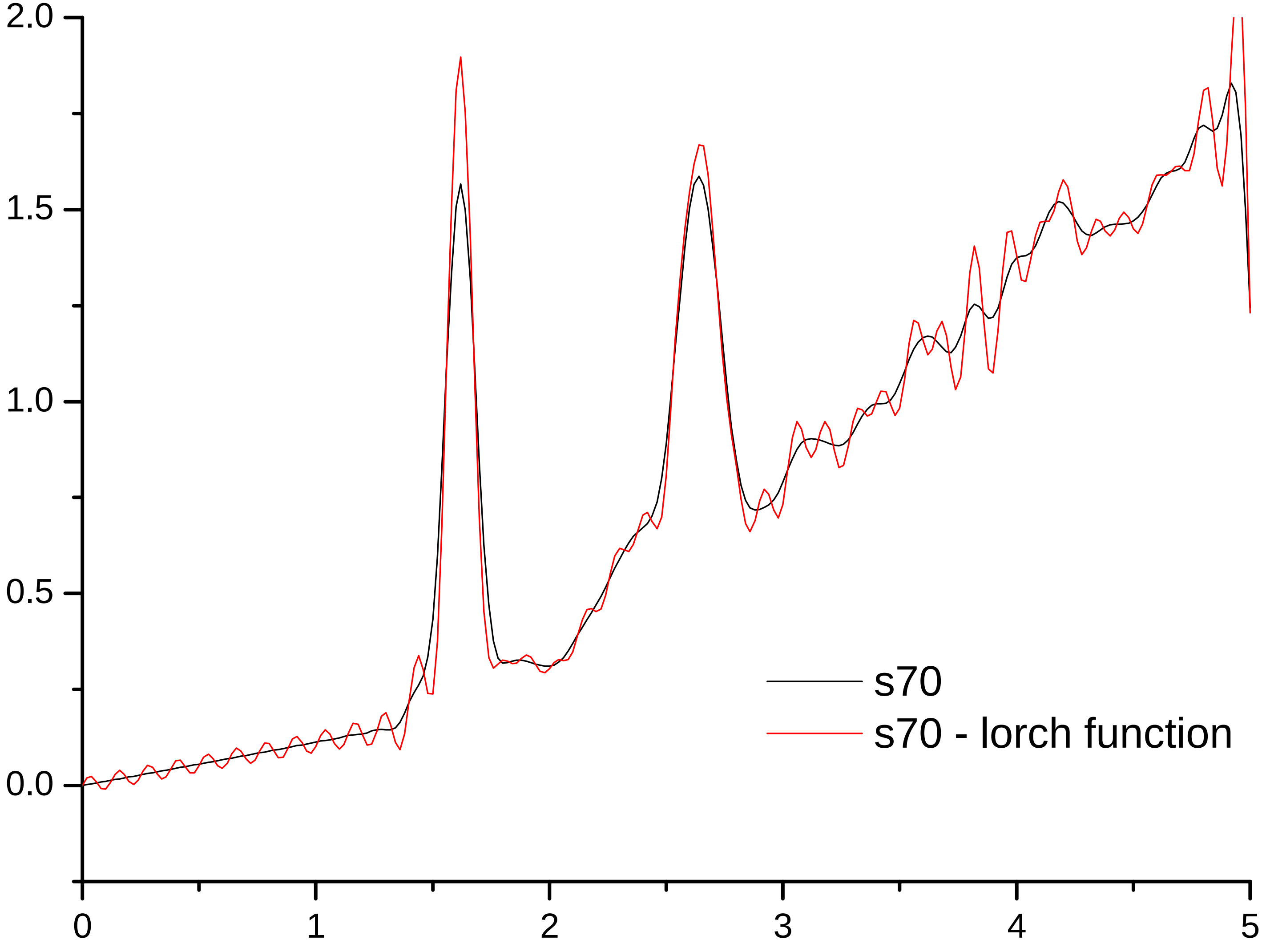
- The change in Ca Coordination is due to the increase in O_{nb} rather than changes to the Ca-O_h which remain steady as the Ca content is altered.

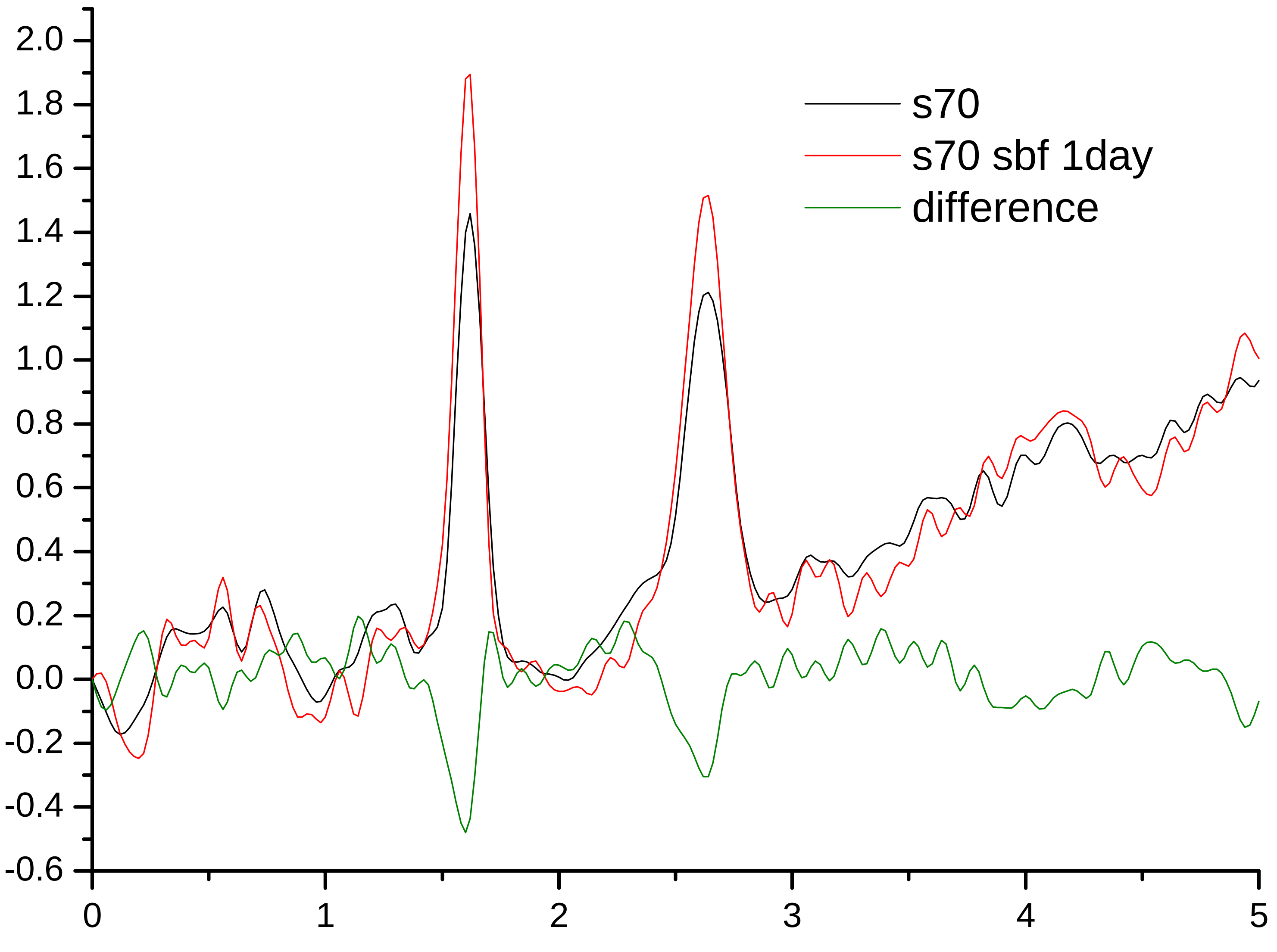
- There are no N = 0 for Si-$O_{b/nb}$ thus there are no isolated O_{nb}'s in the Ca region.

- By comparing ratios for avg. CN's Si-$O_{b/nb}$ / Si-O_h and Ca-$O_{b/nb}$ / Ca-O_h the former ratios are 4 times greater than the latter. Hence there is a preference for more O's in Si region and more O_h's in the Ca region.




1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
0
1
2
3
4
5
s50
s60
s70
s80


2.0
1.5
1.0
0.5
0.0
0
1
2
3
4
5
s70
s70 - lorch function



2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
0
1
2
3
4
5
s70
s70 sbf 1day
difference

	NDIS		s50		s60	
Si-O	*1.61*	3.8	*1.62*	3.85	*1.62*	3.8
Si-H	*2.2*	0.7	*2.2*	0	*2.2*	0
Ca-O	*2.32*	2.3	*2.32*	2.1	*2.32*	2.1
Ca-O	*2.51*	1.65	*2.51*	0.8	*2.51*	1.4
O-O	*2.64*	4.65	*2.635*	3	*2.635*	3.1
Ca-O	*2.75*	1.05	*2.75*	1.5	*2.75*	1.5
Ca-H	*2.95*	0.6	*2.95*	0.6	*2.95*	0.6
sum Ca-O		**5**		**4.4**		**5**
	s7010h		**s805h**		**sbf1day**	
Si-O	*1.62*	3.9	*1.62*	3.85	*1.61*	3.85
Si-H	*2.2*	0	*2.2*	0	*2.2*	0
Ca-O	*2.33*	2.9	*2.33*	2.6	*2.32*	2
Ca-O	*2.51*	1.2	*2.51*	1.4	*2.51*	1.1
O-O	*2.635*	3.85	*2.635*	4.3	*2.63*	3.95
Ca-O	*2.75*	1	*2.75*	0.9	*2.75*	0.7
Ca-H	*2.95*	0.2	*2.95*	0.2	*2.95*	0.2
sum Ca-O		**5.1**		**4.9**		**3.8**