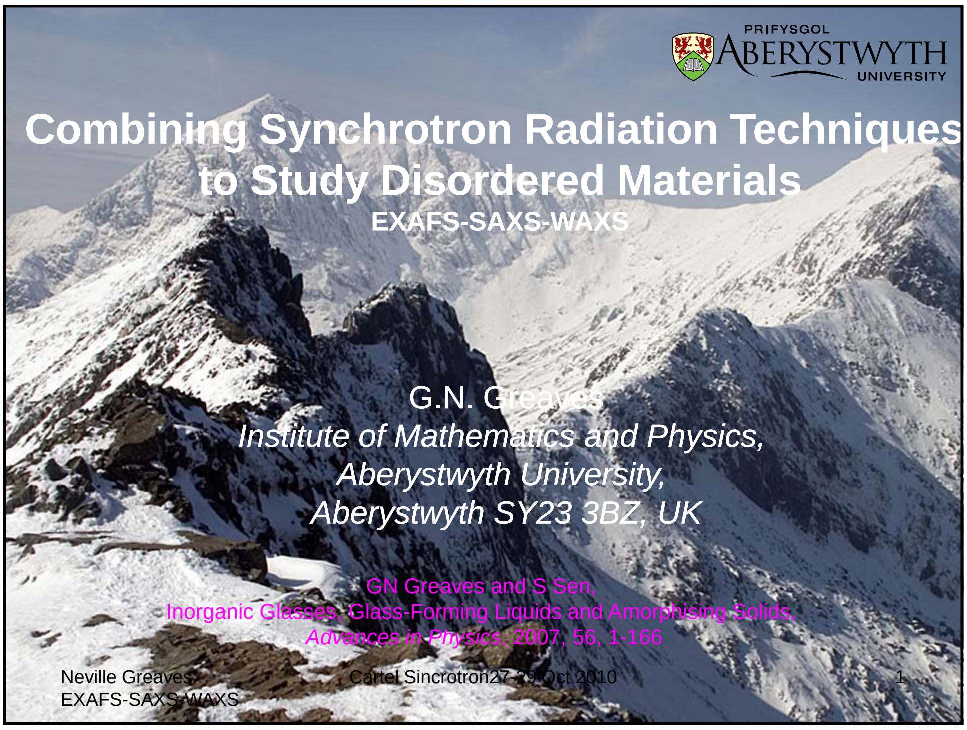
PRIFYSGOL ABERYSTWYTH UNIVERSITY
Combining Synchrotron Radiation Techniques to Study Disordered Materials
EXAFS-SAXS-WAXS
G.N. Greaves
Institute of Mathematics and Physics,
Aberystwyth University,
Aberystwyth SY23 3BZ, UK
GN Greaves and S Sen,
Inorganic Glasses, Glass-Forming Liquids and Amorphising Solids,
Advances in Physics, 2007, 56, 1-166
Neville Greaves
EXAFS-SAXS-WAXS
Cartel Sincrotron27-29 Oct 2010
1


PRIFYSGOL ABERYSTWYTH UNIVERSITY
• Combining x-ray techniques
• EXAFS – modifier channels in glasses
• SAXS – Long range order and diffusion
• WAXS – Glasses and zeolite stability
• SAXS-WAXS – Liquid-liquid transitions
• EXAFS-SAXS-WAXS–formation of glass ceramics

Combining x-ray techniques

SAXS/WAXS
Bras W, Derbyshire G E, Ryan AJ, Mant G R, Felton A, Lewis R A, Hall C J and Greaves G N
*Nucl. Instr. and Methods. A*326, 587-591 (1993)

EXAFS/WAXS
Sankar G, Wright P A, Srinivasa N, Thomas J M, Greaves G N, Dent A J, Dobson B R, Ramsdale C A and Jones R H,
J. Phys. Chem. 97, 9550-9554 (1993)

Glasses and liquids
Inorganic Glasses, Glass-Forming Liquids and Amorphising Solids,
GN Greaves and S Sen,
Advances in Physics, 2007, 56, 1-166

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combined x-ray techniques

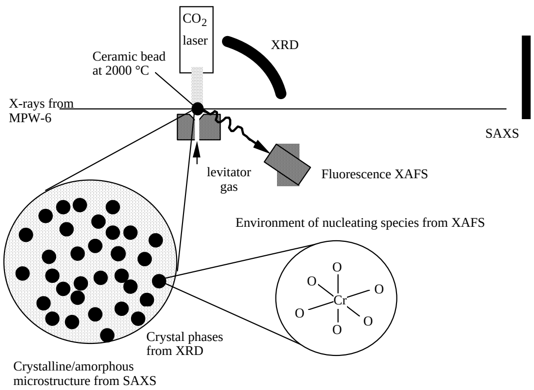

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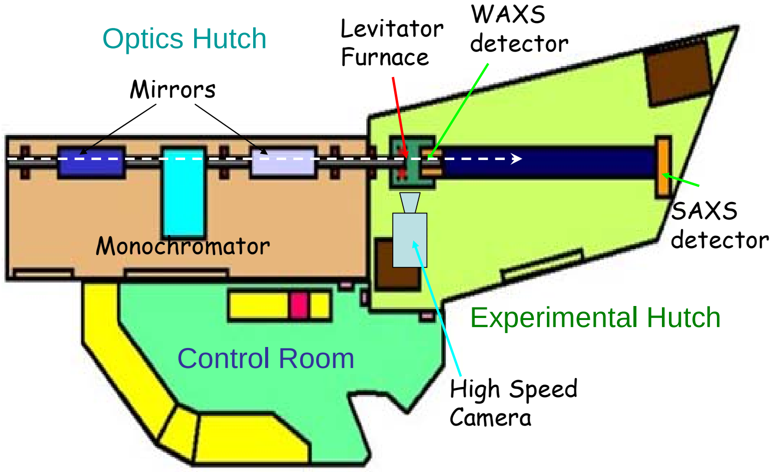
Figure 2

Arrangement on I22 at Diamond Light Source



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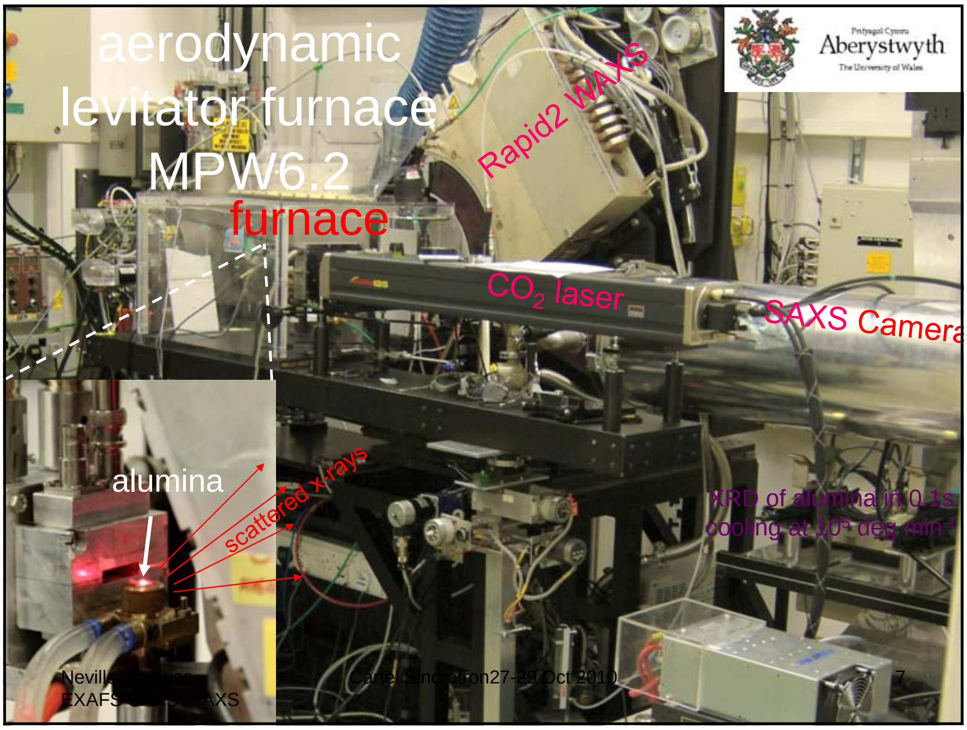

EXAFS

Modifier channels in glasses

The Local Structure of Silicate Glasses
Greaves G N, Fontaine A, Lagarde P, Raoux D and Gurman S J
***Nature*, 293, p611-616 (1981)**

Cation Microsegregation and Ionic Mobility in Mixed Alkali Glasses
Vessal B, Greaves G N, Marten P T, Chadwick A V, Mole R, Houde-Walter S
***Nature* 356, 504-507 (1992)**

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EXAFS - basics

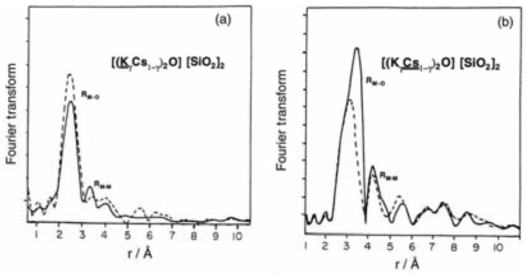
Element specific:

Coordination Number, N   Inter-atomic Distance, R   Debye-Waller Factor ,σ

$$\chi(Q) = \sum_{\beta} \frac{-A(Q)}{Q} \frac{N}{R^2_{\beta}} \left| f_{\beta}(Q,\pi) \right| \exp\left(\frac{-2R_{\beta}}{\lambda}\right) \exp\left(-2\sigma^2 Q^2\right) \sin 2\left(QR_{\beta} + 2\delta + \phi\right)$$

N and R

Modifiers adopt well-defined sites in oxide glass networks

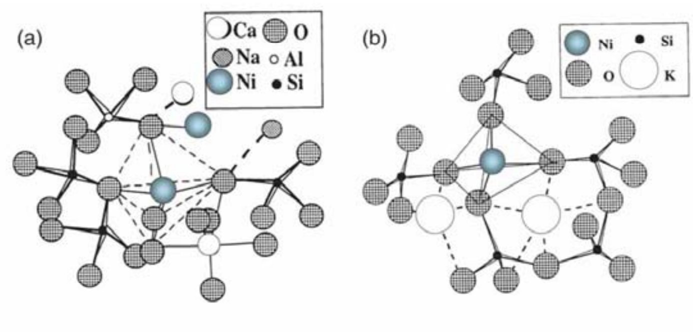


modifier polyhedra →

A Structural Basis for Ionic Diffusion in Oxide Glasses
Greaves G N, Gurman S J, Catlow C R A, Chadwick A V, Houde-Walter S, Dobson B R and Henderson C M B
Phil. Mag. A65, 1059-1072 (1991)

N and R

Environments of intermediates in silicates



L. Galoisy and G. Calas, Geochimica et Cosmochimica **57** 3613 (1993); ibid **57** 3627.

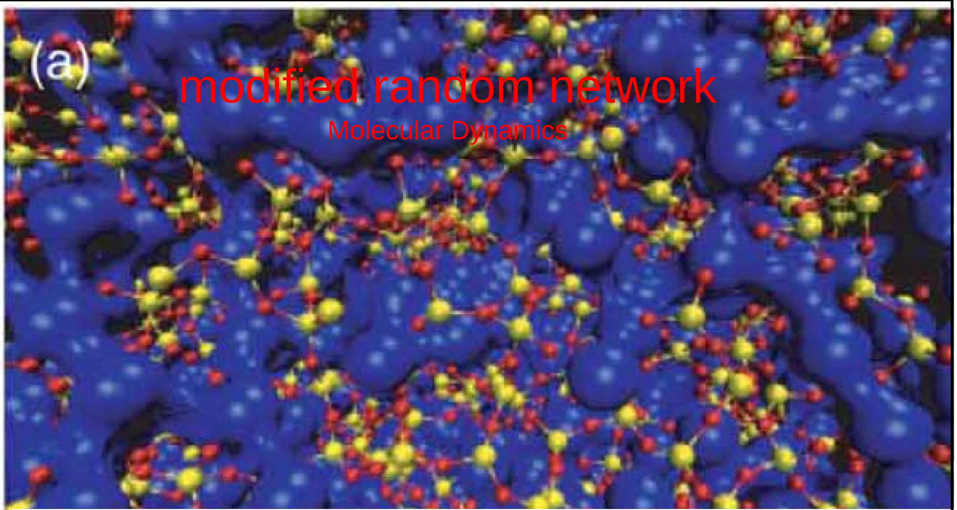
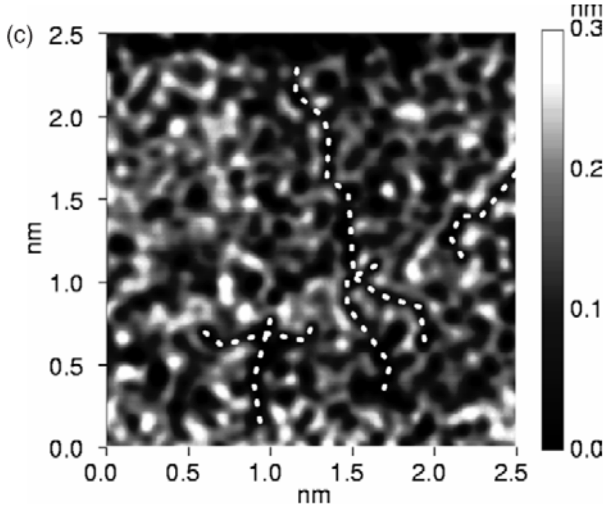


Figure 19. Static alkali channels modelled with molecular dynamics in alkali silicate glasses. (a) 'Snapshot' of the structure of the $Na_2Si_3O_7$ glass silicate with the Na atoms (blue) emphasized with an enlarged equipotential isosurface. Reproduced with permission from Meyer *et al.*

Meyer, J. Horbach, W. Kob, F. Kargl and H. Schobler, Phys. Rev. Lett. **93** 027801,1–4 (2004).

AFM

modified random network



G.H. Frischat, J.-F. Poggemann and E. Heide, J. Non-Cryst. Solids **345–346** 197 (2004).

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EXAFS-SAXS-WAXS
Cartel Sincrotron27-29 Oct 2010
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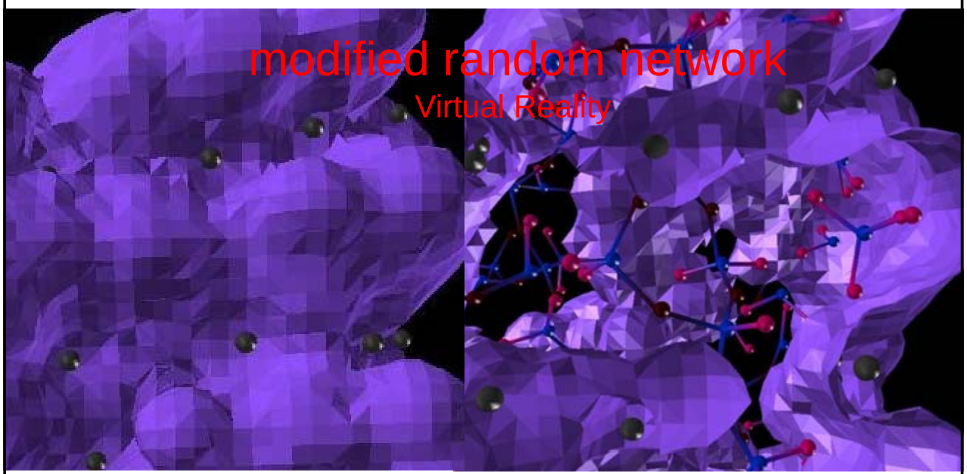

network isosurface and cutaway for Na2Si2O5

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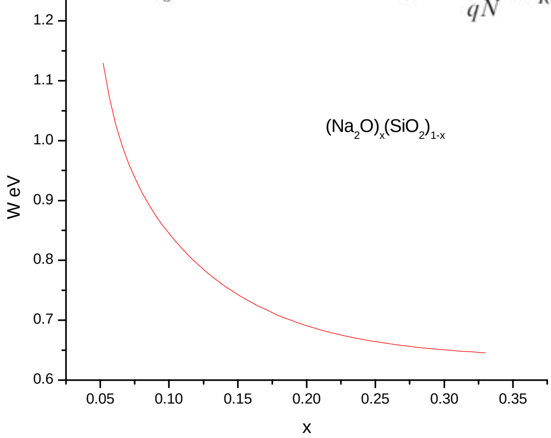
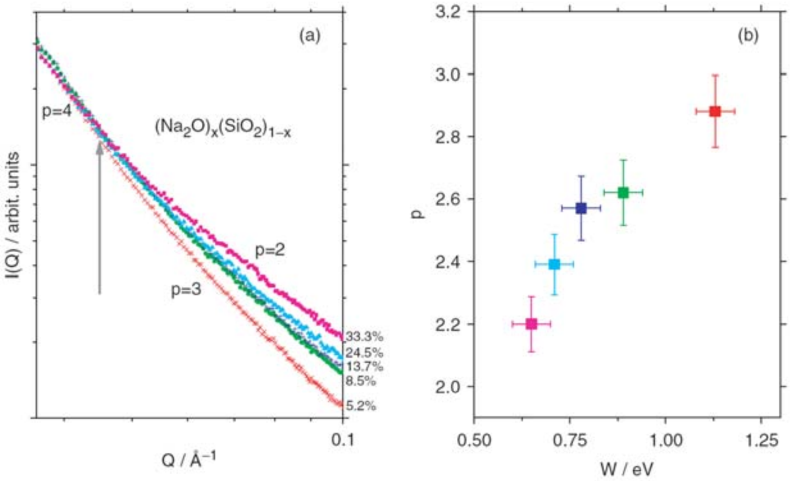
ionic diffusion/electrical conductivity

Single alkalis

$$D = D_0 e^{-W/k_B T} \qquad D = \frac{\sigma k_B T}{qN} H_R$$



SAXS and dimensionality and ionic diffusion



Inorganic Glasses, Glass-Forming Liquids and Amorphising Solids, GN Greaves and S Sen,
***Advances in Physics*, 2007, 56, 1-166**

Solids,

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SAXS

Long range order and diffusion

Inorganic Glasses, Glass-Forming Liquids and Amorphising Solids,
GN Greaves and S Sen,
***Advances in Physics*, 2007, 56, 1-166**

G.N. Greaves, M.C. Wilding, S. Fearn, D. Langstaff, F. Kargl, S. Cox, Q. Vu Van, O. Majérus, C.J. Benmore, R. Weber, C.M. Martin, L. Hennet ***Science 2008, 322, 566-570.***

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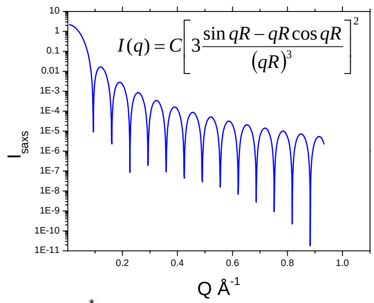
SAXS - basics

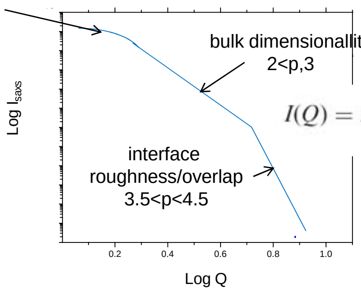
monodispersed particles



Guinier

$$I(Q) = I(0)e^{-R_{R_g}^2 Q^2/3}$$

fractal structures



Porod

$$I(Q) = K_1 + \frac{K_2}{Q^p} \quad Q > \frac{1}{R_g}$$

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18

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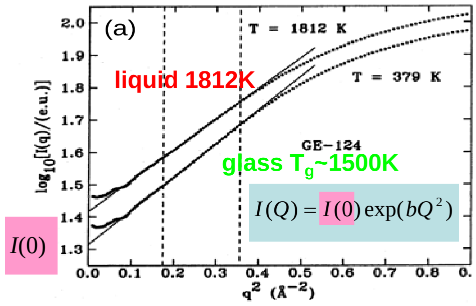
density fluctuations & compressibility

SAXS from **liquid** and **glassy** SiO_2 **Q independent**

$$V < \Delta\rho^2 > / \rho_0^2 = S(0)/\rho_0 = I(0)/(\rho_0 \sum_{\alpha}^{N} W_{\alpha\beta...}^2) = k_B T K_T$$



***K_T*, compressibility**

R. Bruning, C. Levelut, A. Faivre, R. LeParc, J.-P. Simon, F. Bley, and J.-L. Hazemann: Europhys. Lett. Vol. 70, (2005), p.211.

V.V. Golubkov, J. Non-Cryst. Solids **192–193** 463 (1995).

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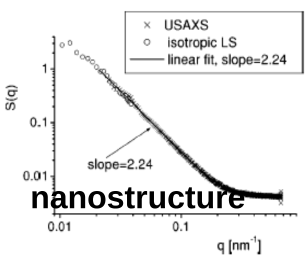
nanostructure & long range fluctuations in OTP

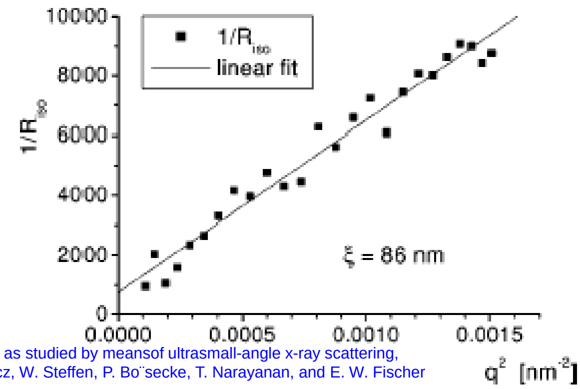
Ornstein-Zernike approximation

H.E. Stanley, Introduction to phase transitions and critical phenomena, Oxford University press Oxford, 1971

$$I(Q) = \frac{I_0}{1 + Q^2\xi^2}$$

ξ correlation length





Long-range density fluctuations in orthoterphenyl as studied by meansof ultrasmall-angle x-ray scattering, A. Patkowski, Th. Thurn-Albrecht, E. Banachowicz, W. Steffen, P. Bo¨secke, T. Narayanan, and E. W. Fischer (2000) Phys Rev E, 61, 6909-6912

Figure 5

Yttria-alumina liquids & L-L Transitions

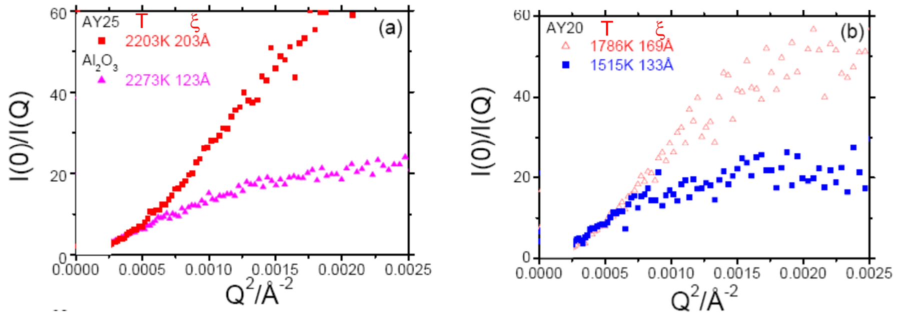


Fig. 6 Ornstein-Zernike plots of SAXS data $I(0)/I(Q)$ v Q^2, including the correlation lengths ξ of long range fluctuations analysed from the slopes at low Q for different temperatures. (a) SAXS data for liquid Al_2O_3 and AY25 at temperatures above T_m taken from Fig. 3(a) and the very different ξ values for these liquids of different strength. (b) AY20 data from Fig. 3(b), showing the increase in ξ at the liquid-liquid transition around 1788K (Fig. 4(a)) and the shift in the maximum to larger wavevectors.

$$I(Q) = \frac{I_0}{1 + Q^2\xi^2}$$

ξ correlation length

Liquid-liquid transitions, crystallisation and long range fluctuations in supercooled yttrium oxide-aluminium oxide.
G.N. Greaves, M.C. Wilding, L. Hennet, W. Bras, O. Majérus, S. Fearn, F. Kargl
Journal of Non-Crystalline Solids 355, 715-721 (2009)

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EXAFS-SAXS-WAXS

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WAXS

Glasses and Zeolite stability

Rheology of collapsing zeolites amorphised by temperature and pressure
GN Greaves, F Meneau, A Sapelkin, LM Colyer,I ap Gwynn, S Wade, G Sankar,
Nature Materials 2, 622-629 (2003)

Zeolite collapse and polyamorphism
G.N. Greaves, F. Meneau, F. Kargl, D. Ward,P.Holliman and F. Albergamo:
*J. Phys. Condens. Matter.*19, (2007), 415102.

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WAXS - basics

Element specific:

Structure Factor, S(Q) Partial Structure Factors, $S_{\alpha\beta}(Q)$ Radial Distribution Factor, J(r)

$$S(Q) = \sum_{\alpha}^{N} \sum_{\beta}^{N} W_{\alpha} W_{\beta} S_{\alpha\beta}(Q)$$

$$S_{\alpha\beta}(Q) = \frac{\sin Q r_{\alpha\beta}}{Q r_{\alpha\beta}}$$

$$J(r) = \frac{2r}{\pi} \int_{0}^{\infty} [Q\{S(Q)-1\} \sin Qr] dQ + 4\pi\rho_0 r^2$$

Partial structure factors
in silica glass -
RMC from XRD and ND

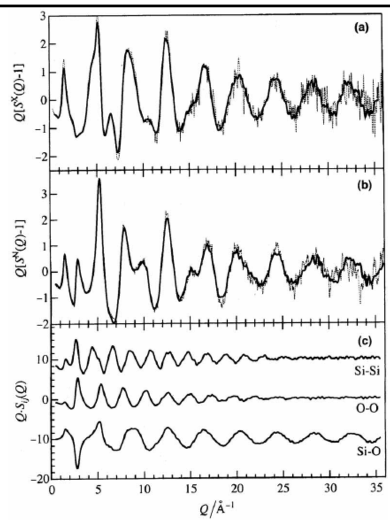


Figure 6. Reverse Monte Carlo simulation of silica glass compared to high-energy X-ray scattering (a) and neutron scattering (b). The interference functions, $Q(S(Q)-1)$ differ because of the different cross-section weightings. Dashed lines are experimental and solid lines the result of RMC modelling. The partial structure factors for Si–Si, O–O and Si–O obtained from RMC modelling are given in (c), displaced vertically. Reproduced with permission from [60] © 2001 Elsevier.

H. Ohno, S. Kahara, N. Umesaki and K. Suzuya, J. Non-Cryst. Solids **293–295** 125 (2001).

Polyhedra in silicate glasses

EXAFS, ND and Molecular Dynamics

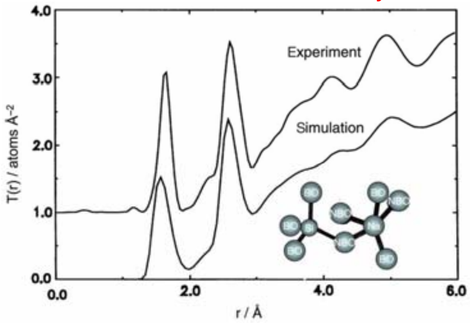


Figure 10. The total RDF $T(r) = J(r)/r$ (a) for $Na_2Si_2O_5$ glass obtained from neutron scattering (Exp) [132] compared to the predictions from an MD model (Sim) at 1000 K [125, 126]. A Si, Na, BO and NBO configuration is illustrated. Reproduced with permission from [126] © 1995 Elsevier.

Cation Microsegregation and Ionic Mobility in Mixed Alkali Glasses
Vessal B, Greaves G N, Marten P T, Chadwick A V, Mole R, Houde-Walter S
Nature 356, 504-507 (1992)

Inorganic Glasses, Glass-Forming Liquids and Amorphising Solids,
GN Greaves and S Sen,
***Advances in Physics*, 2007, 56, 1-166**

Prifysgol Cymru
Aberystwyth
The University of Wales

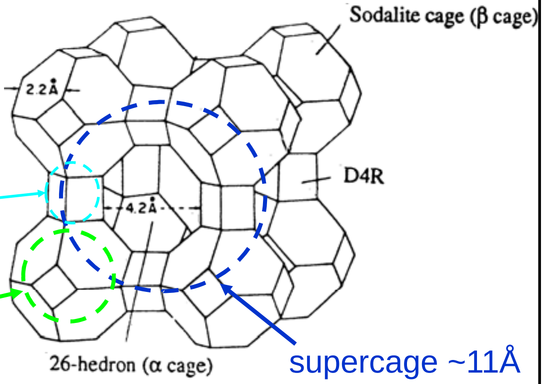
Zeolite Structure and Secondary Building Units

density 1.5 gcm^{-3}

NB density of glass 2.5 gcm^{-3}
ΔV_A ~ 40%

Double ring
~6Å diameter

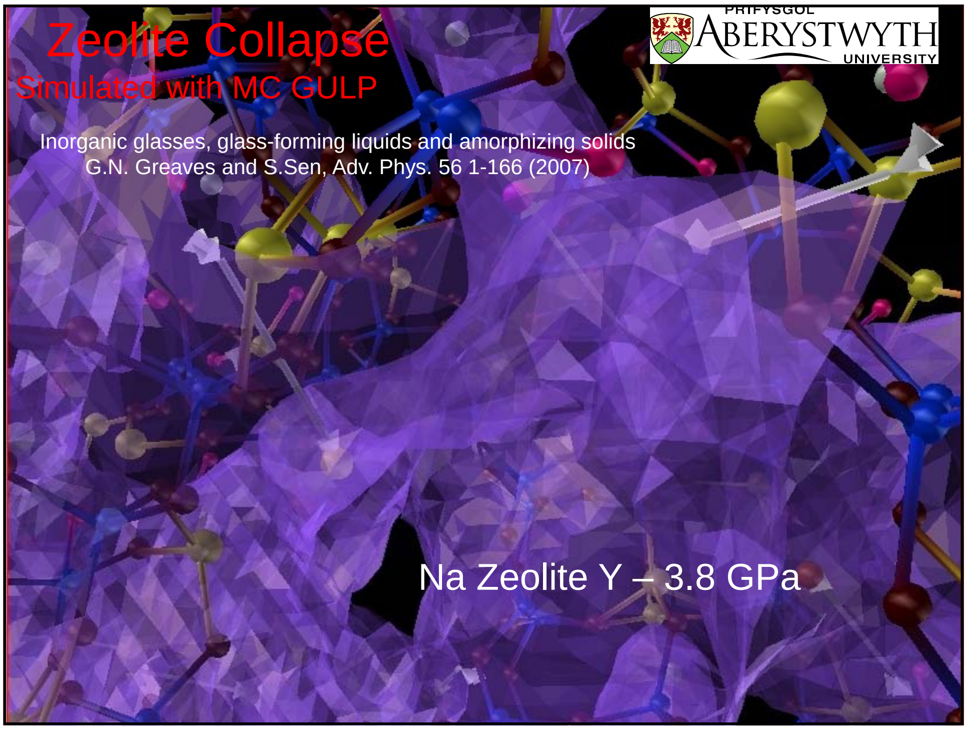
Sodalite cage
~7Å diameter



supercage ~11Å diameter

Zeolite A: $Na_{12}Al_{12}Si_{12}O_{48}$


Zeolite Collapse
Simulated with MC GULP
Inorganic glasses, glass-forming liquids and amorphizing solids
G.N. Greaves and S.Sen, Adv. Phys. 56 1-166 (2007)
Na Zeolite Y - ambient pressure


Zeolite Collapse
Simulated with MC GULP
Inorganic glasses, glass-forming liquids and amorphizing solids
G.N. Greaves and S.Sen, Adv. Phys. 56 1-166 (2007)
Na Zeolite Y – 3.8 GPa

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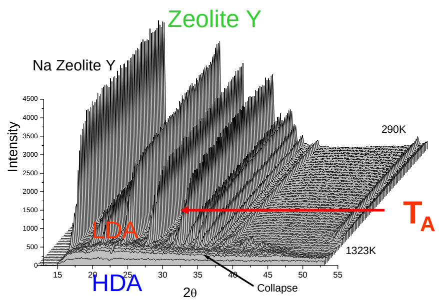
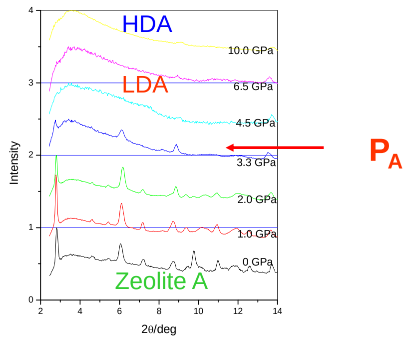
Zeolite amorphisation

via a low density amorphous phase (LDA)
to a high density amorphous phase (HDA)
-similar to a melt-quenched glass

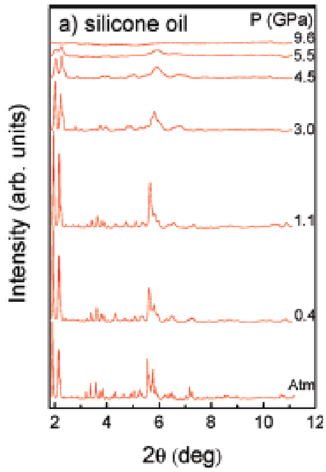
GN Greaves et al
Nature Materials, **2**, 622-629 (2003)

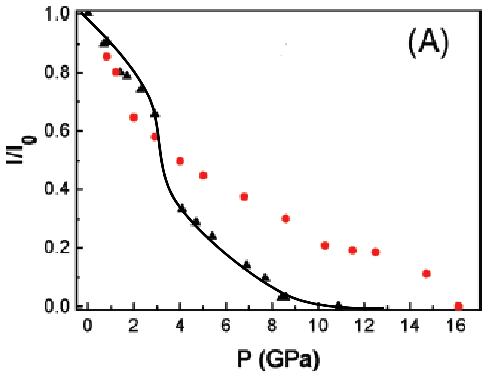


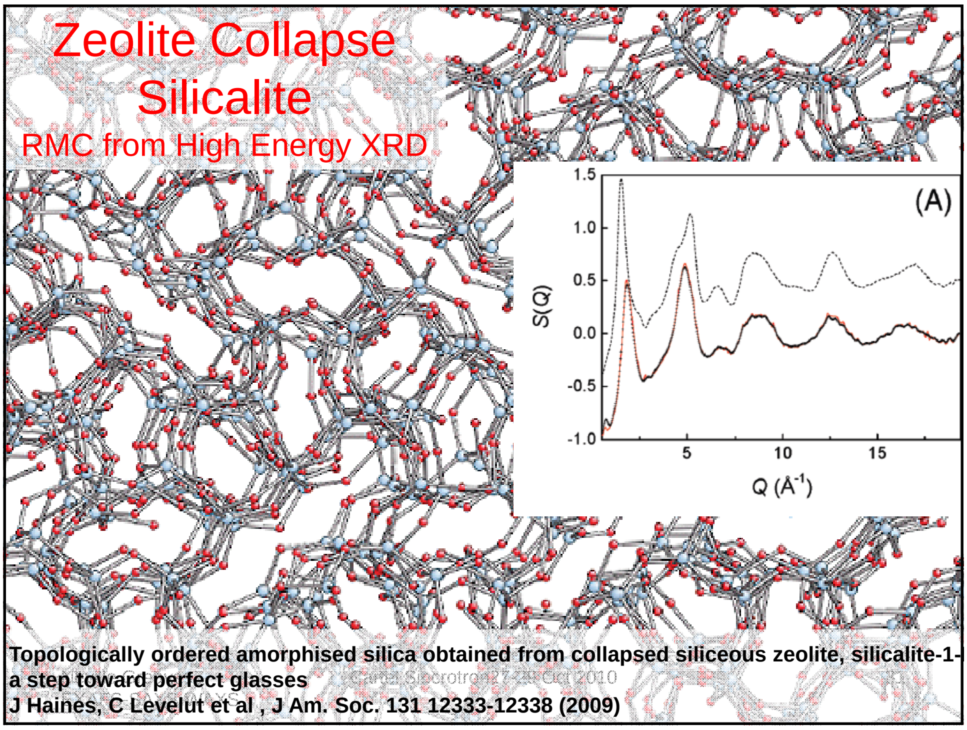


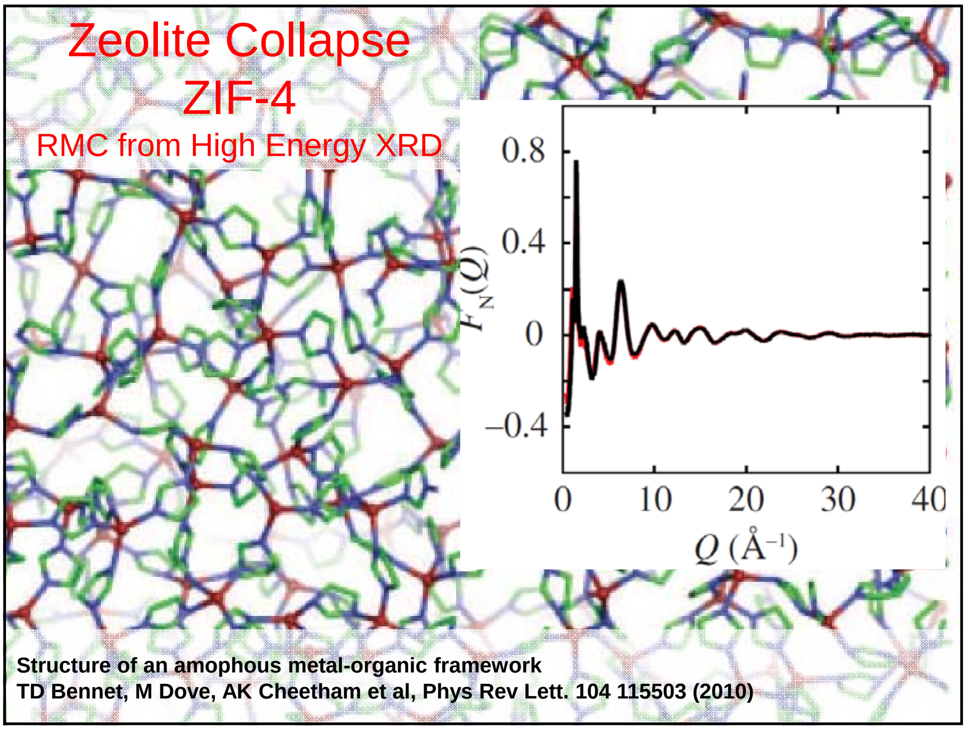
Silicalite-F-1 amorphisation

Harries J et al J. AM. CHEM. SOC. VOL. 132, 8860-8861






Zeolite Collapse
Silicalite
RMC from High Energy XRD
(A)
S(Q)
1.5
1.0
0.5
0.0
-0.5
-1.0
5
10
15
Q (Å^{-1})
Topologically ordered amorphised silica obtained from collapsed siliceous zeolite, silicalite-1-
a step toward perfect glasses
J Haines, C Levelut et al , J Am. Soc. 131 12333-12338 (2009)


Zeolite Collapse
ZIF-4
RMC from High Energy XRD
$F_N(Q)$
0.8
0.4
0
−0.4
0
10
20
30
40
Q (Å^{-1})
Structure of an amophous metal-organic framework
TD Bennet, M Dove, AK Cheetham et al, Phys Rev Lett. 104 115503 (2010)

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SAXS-WAXS

Liquid-liquid transitions

Detection of First-Order Liquid/Liquid Phase Transitions in Yttrium Oxide–Aluminum Oxide Melts
G.N. Greaves, M.C. Wilding, S. Fearn, D. Langstaff, F. Kargl, S. Cox,
Q. Vu Van, O. Majérus, C.J. Benmore, R. Weber, C.M. Martin, L. Hennet
Science 2008, 322, 566-570

Polyamorphism and liquid-liquid phase transitions: challenges for experiment and theory.
McMillan, P. F. M Wilson, MC Wilding, D Daisenberger, M Mezouar, GN Greaves,
J. Phys.: Condens. Matter **19** 415101 (2007).

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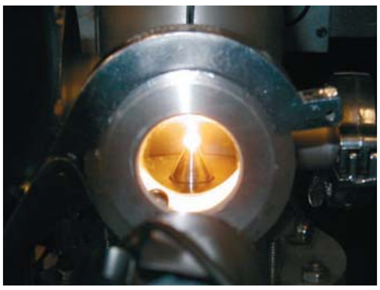
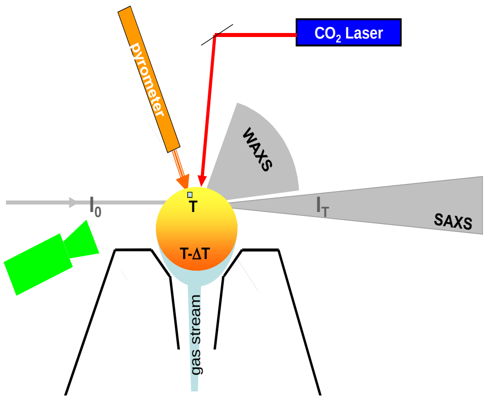
d





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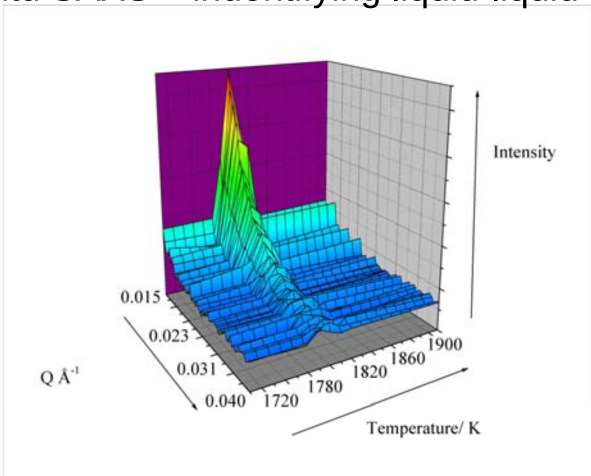
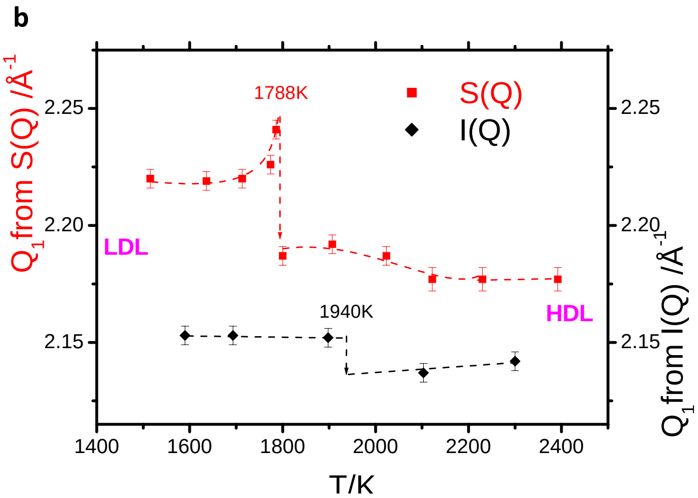
In situ SAXS – indentifying liquid-liquid transition



Detection of First-Order Liquid/Liquid Phase Transitions in Yttrium Oxide–Aluminum Oxide Melts
G.N. Greaves, M.C. Wilding, S. Fearn, D. Langstaff, F. Kargl, S. Cox,
Q. Vu Van, O. Majérus, C.J. Benmore, R. Weber, C.M. Martin, L. Hennet
Science 2008, 322, 566-570

Neville Greaves Cartel Sincrotron27-29 Oct 2010 35
EXAFS-SAXS-WAXS

In situ WAXS – position of principal peak and L-L Transition



Composition and polyamorphism in supercooled yttria-alumina melts
Greaves G N, Wilding M C, Langstaff D, Kargl F, Hennet L, Benmore CJ, Weber JKR, McMillan PF
J.Non-Cryst.Solids in press 2010.

Neville Greaves Cartel Sincrotron27-29 Oct 2010 36
EXAFS-SAXS-WAXS

EXAFS-SAXS-WAXS

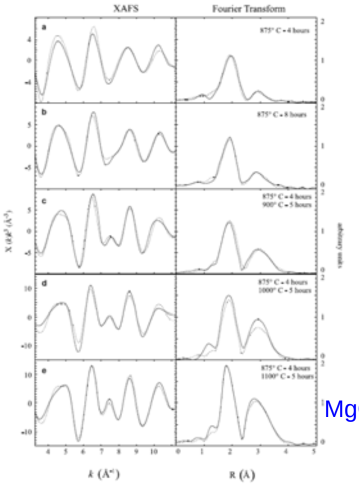
processing of glass ceramics

Bras, W.; Greaves, G. N.; Oversluizen, M.; Clark, S. M.; Eeckhaut, G. The development of monodispersed alumino-chromate spinel nanoparticles in doped cordierite glass, studied by in situ X-ray small and wide angle scattering, and chromium X-ray spectroscopy. *J. Non-Cryst. Solids* **2005**, *351* (27−29), 2178–2193.

Bras, W, Clark, SM, Greaves, GN, Kunz, M, van Beek, W, Radmilovic, V, Nanocrystal growth in cordierite glass ceramics studied with x-ray scattering *Crystal Growth & Design* 9, 1297-1305 (2009).

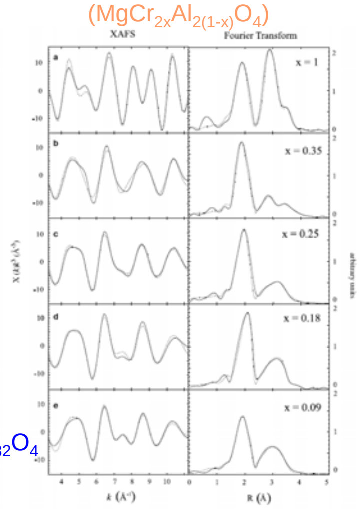
Cr EXAFS

cordierite ($Mg_2Al_4Si_5O_{18}$) glass doped with 0.34 mol% Cr_2O_3



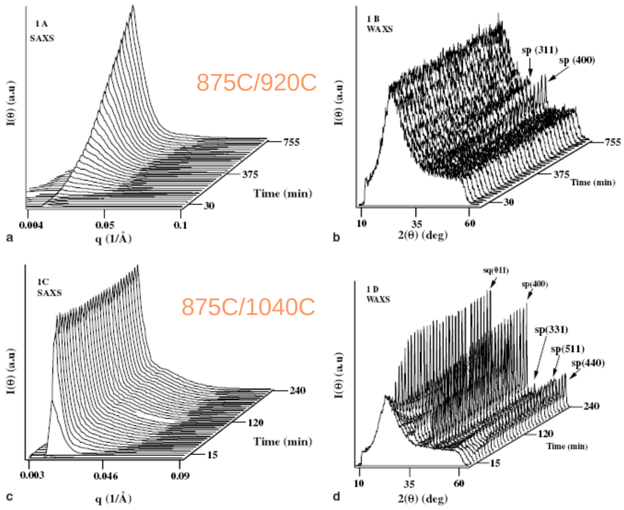
chromo-aluminate spinels ($MgCr_{2x}Al_{2(1-x)}O_4$)

$MgCr_{0.18}Al_{1.82}O_4$



In situ SAXS/WAXS

cordierite ($Mg_2Al_4Si_5O_{18}$)
glass heat treated
at different temperatures



Neville Greaves
EXAFS-SAXS-WAXS

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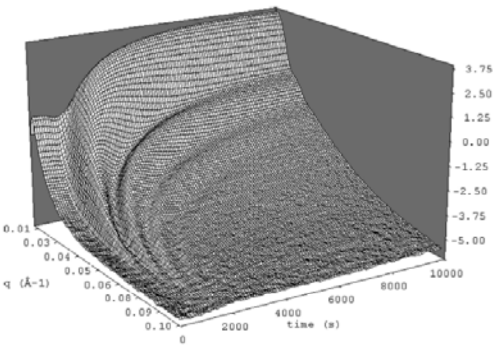
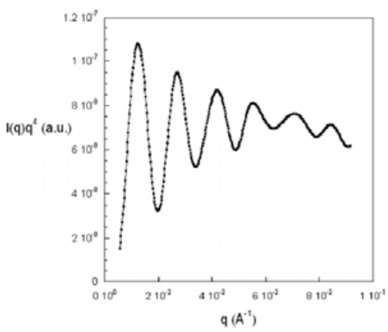
SAXS and form factor

cordierite/Cr glass
875C/925C

ln I_{saxs} v Q



I_{saxs} Q^4 v Q
i.e with thermal fluctuations removed



20nm crystallites highly monodispersed

Neville Greaves
EXAFS-SAXS-WAXS

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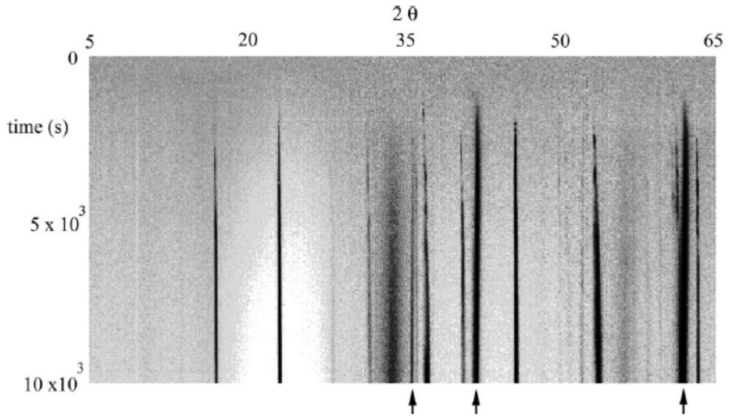
$MgCr_{0.18}Al_{1.82}O_4$ 40

distinguishing nanocrystalline phases

spinel ($MgCr_{0.18}Al_{1.82}O_4$) in bulk & stuffed quartz (μ- cordierite) at surface



in situ spinel particle growth and internal strain

Guinier radius

$$R_g = \sqrt{\frac{3}{5}}R$$

Particle radius

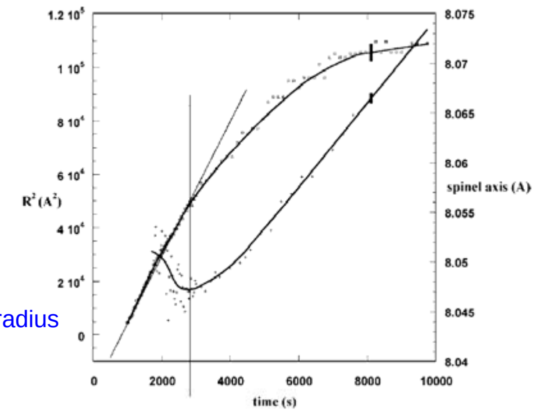


Figure 7. The correlation between the R^2 of the particle and time (□). The vertical bar at time = 8000 s indicates the error margin at the later stages of development. At the early stages, a linear fit can be made to the R^2 data. This confirms the predictions that we are dealing with a diffusion-limited growth process. The development of the spinel unit cell volume as function of time (◇). The changeover from shrinking to growing coincides with the moment when the particle size leaves the $(t)^{1/2}$ growth regime. Also noteworthy is that this is the moment when the noise is much reduced.


PRIFYSGOL
ABERYSTWYTH
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• Combining x-ray techniques
• EXAFS – modifier channels in glasses
• SAXS – Long range order and diffusion
• WAXS – Glasses and zeolite stability
• SAXS-WAXS – Liquid-liquid transitions
• EXAFS-SAXS-WAXS–formation of glass ceramics
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EXAFS-SAXS-WAXS
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