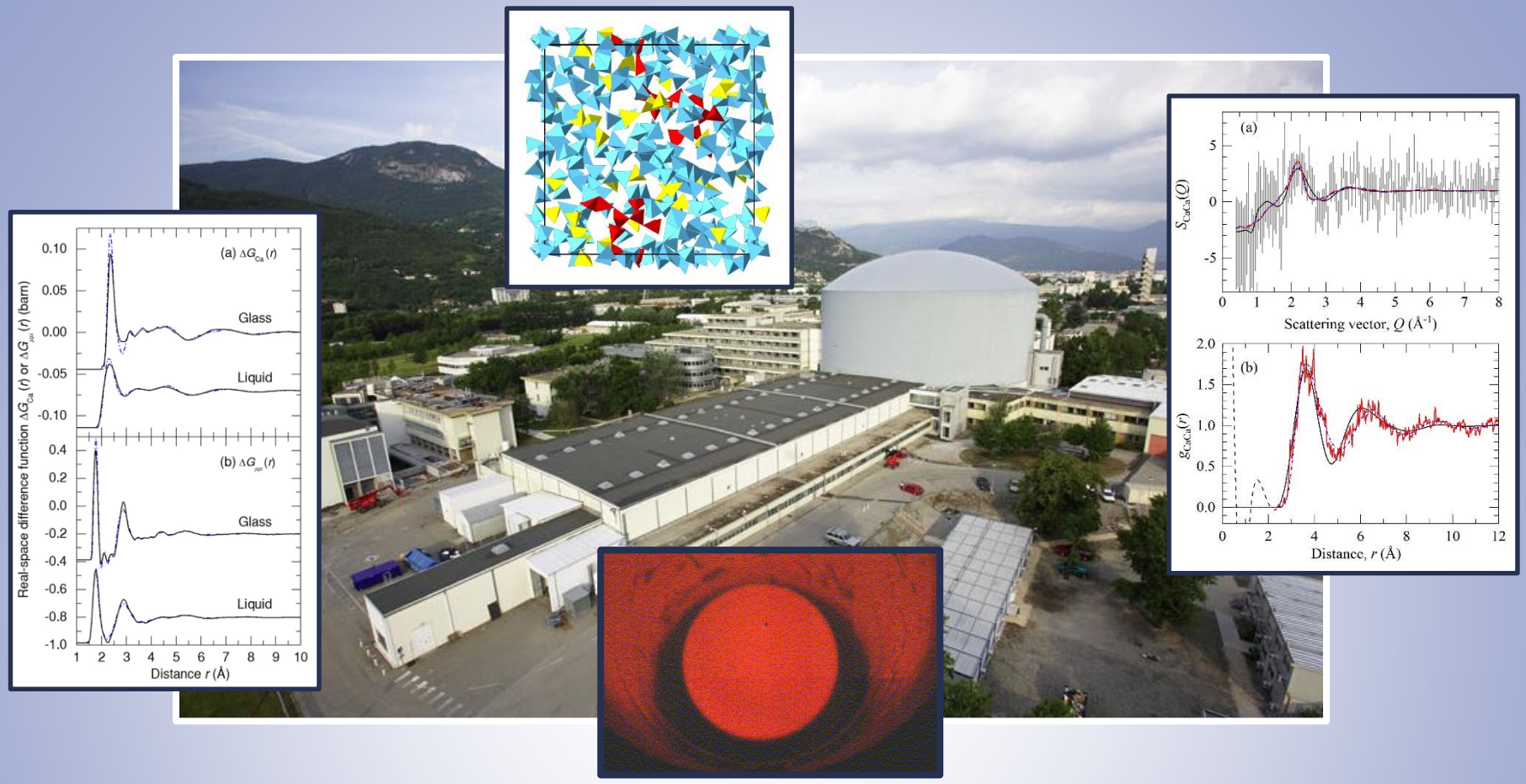

Structure of glass-forming aluminate liquids under extreme conditions by neutron diffraction with isotope substitution

James W E Drewitt | ADD 2019

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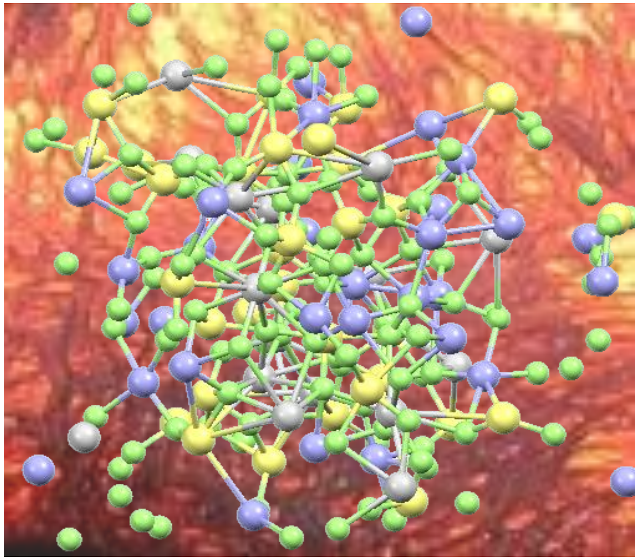
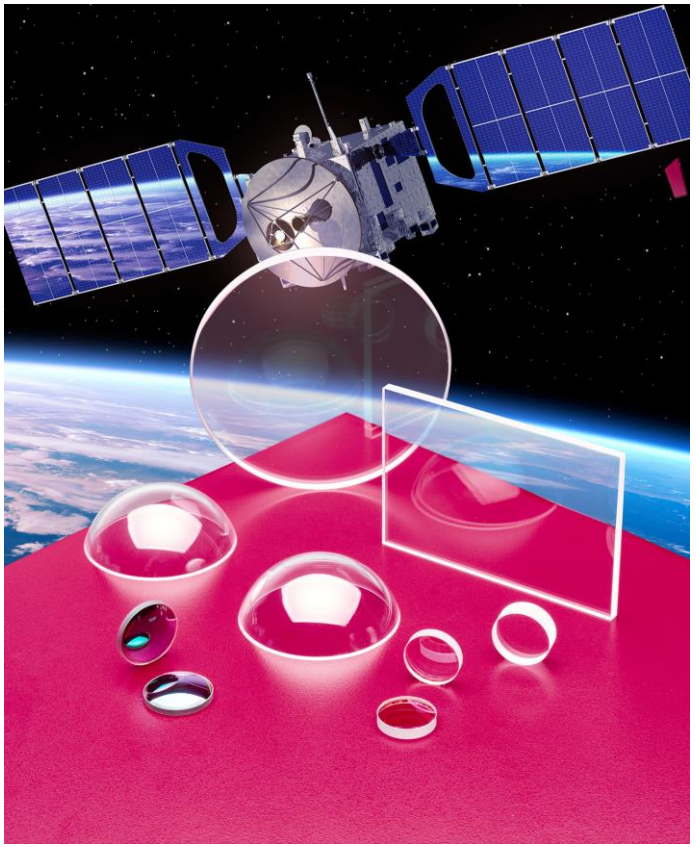
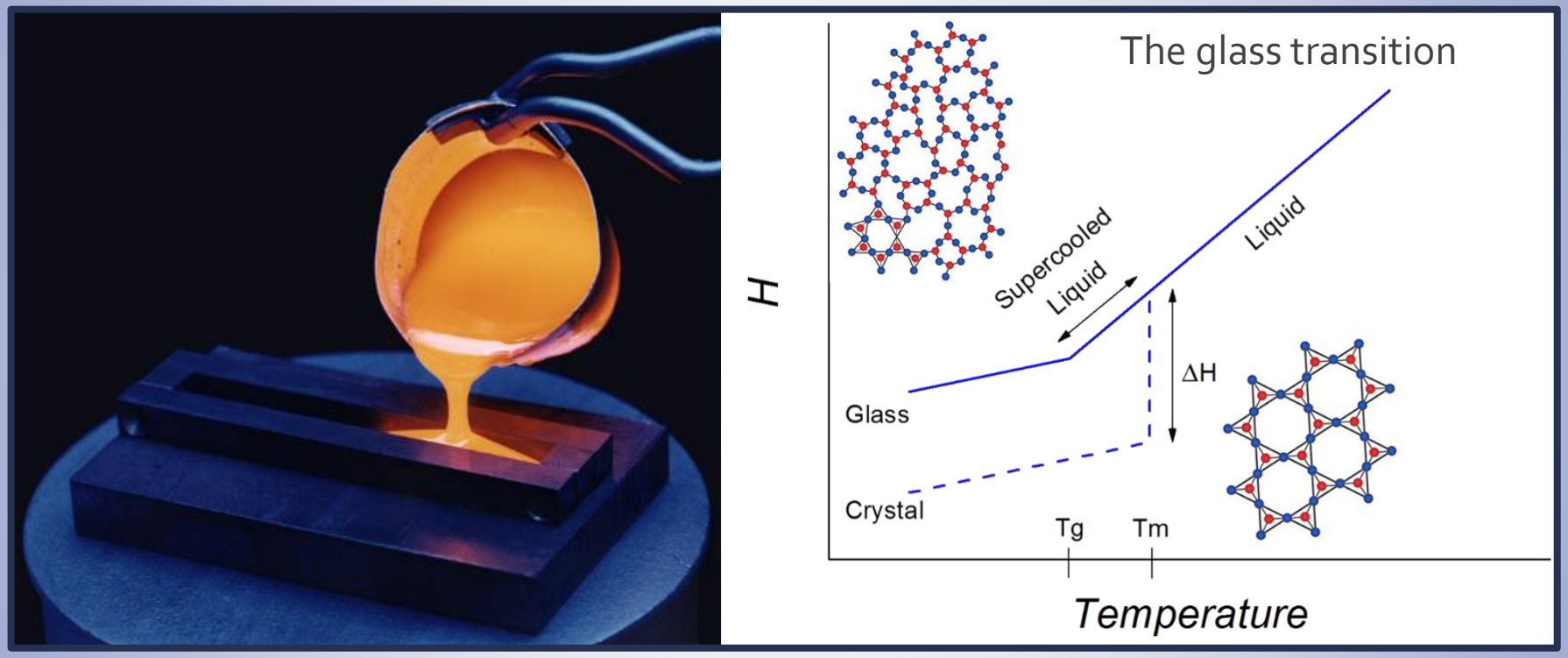
Gaston Garbarino

Aluminate liquids and glasses





Glass forming liquids



W. H. Zachariasen's rules

[CONTRIBUTION FROM THE RYERSON PHYSICAL LABORATORY, UNIVERSITY OF CHICAGO]

THE ATOMIC ARRANGEMENT IN GLASS

BY W. H. ZACHARIASEN

RECEIVED MAY 13, 1932 PUBLISHED OCTOBER 5, 1932

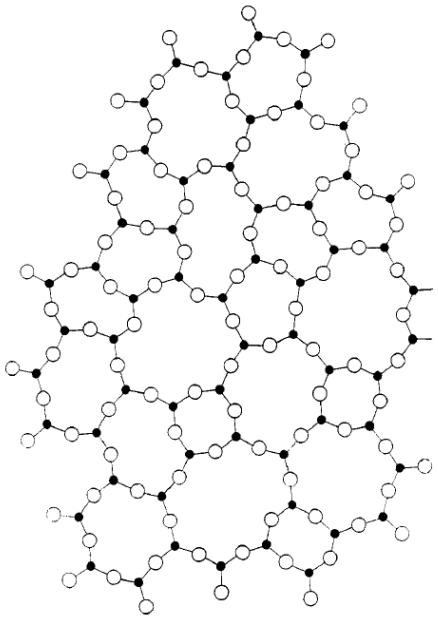
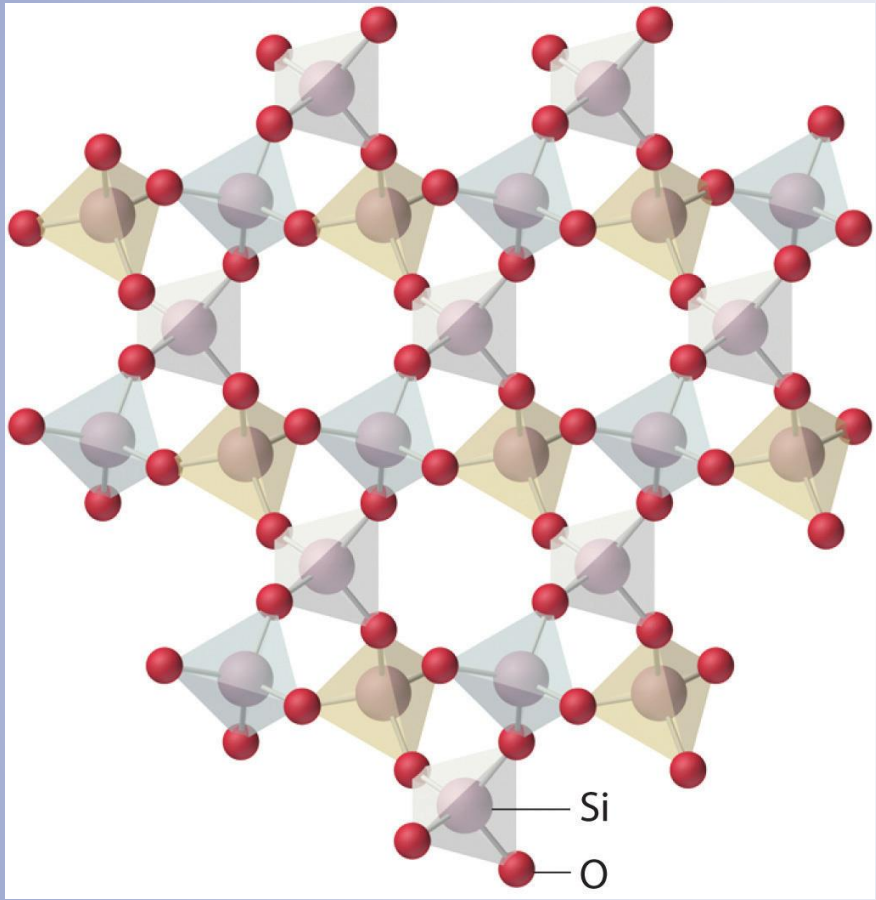


Fig. 1b.

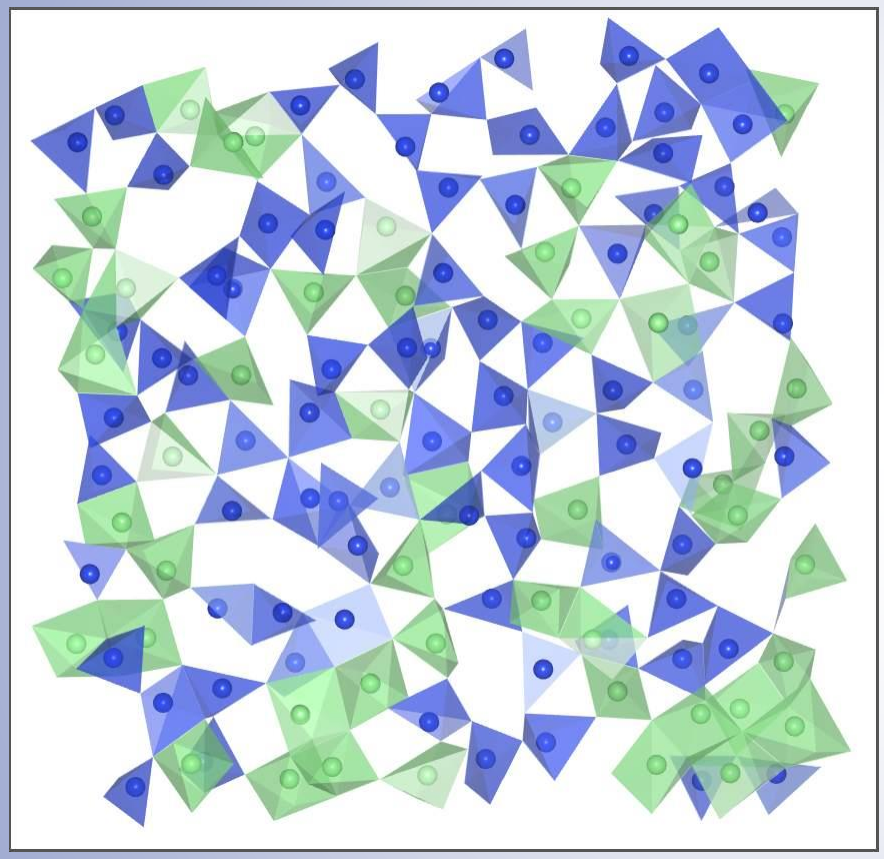
- An oxygen atom linked to no more than two glass-forming atoms
- The coordination number of the glass-forming atoms is small (3 or 4)
- The polyhedra share corners, not edges or faces
- Polyhedra linked in a 3-dimensional network

The case for liquid silica SiO_2



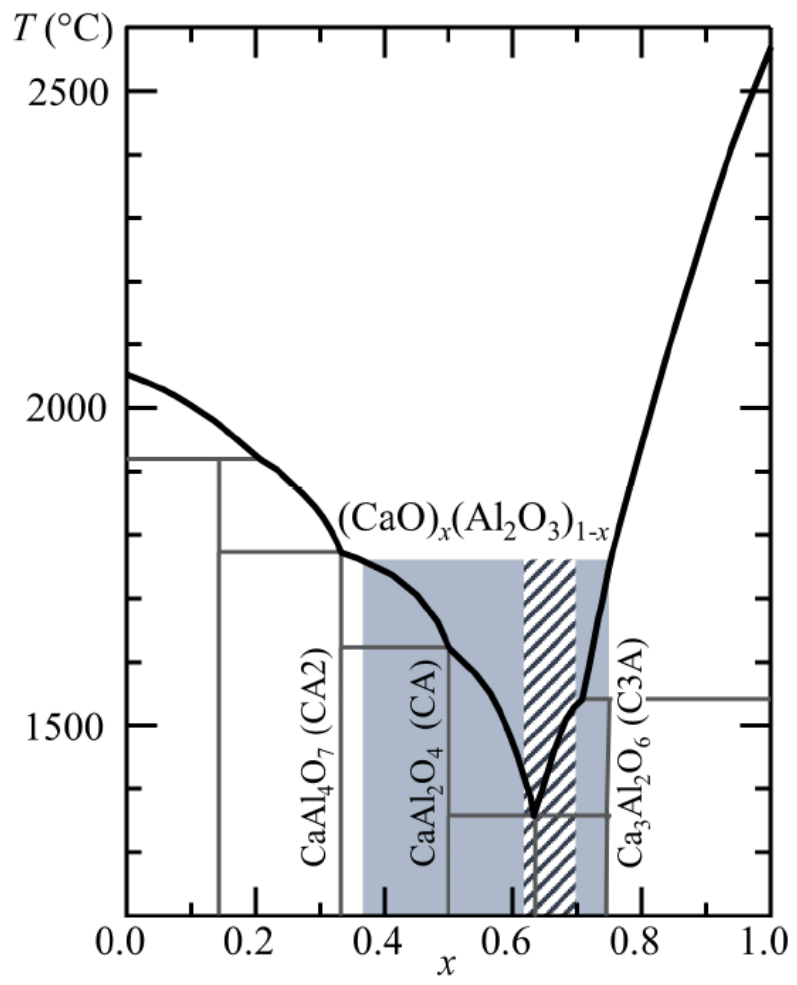
- ✓ An oxygen atom linked to no more than two glass-forming atoms
- ✓ The coordination number of the glass-forming atoms is small (3 or 4)
- ✓ The polyhedra share corners, not edges or faces
- ✓ Polyhedra linked in a 3-dimensional network

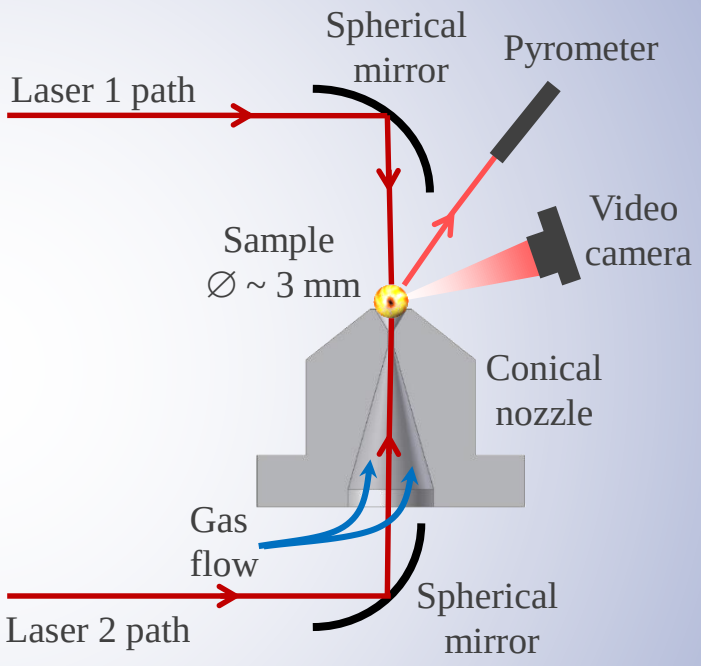
The case for liquid alumina Al_2O_3



- ✗ An oxygen atom linked to no more than two glass-forming atoms
- ✗ The coordination number of the glass-forming atoms is small (3 or 4)
- ✗ The polyhedra share corners, not edges or faces
- ✗ Polyhedra linked in a 3-dimensional network

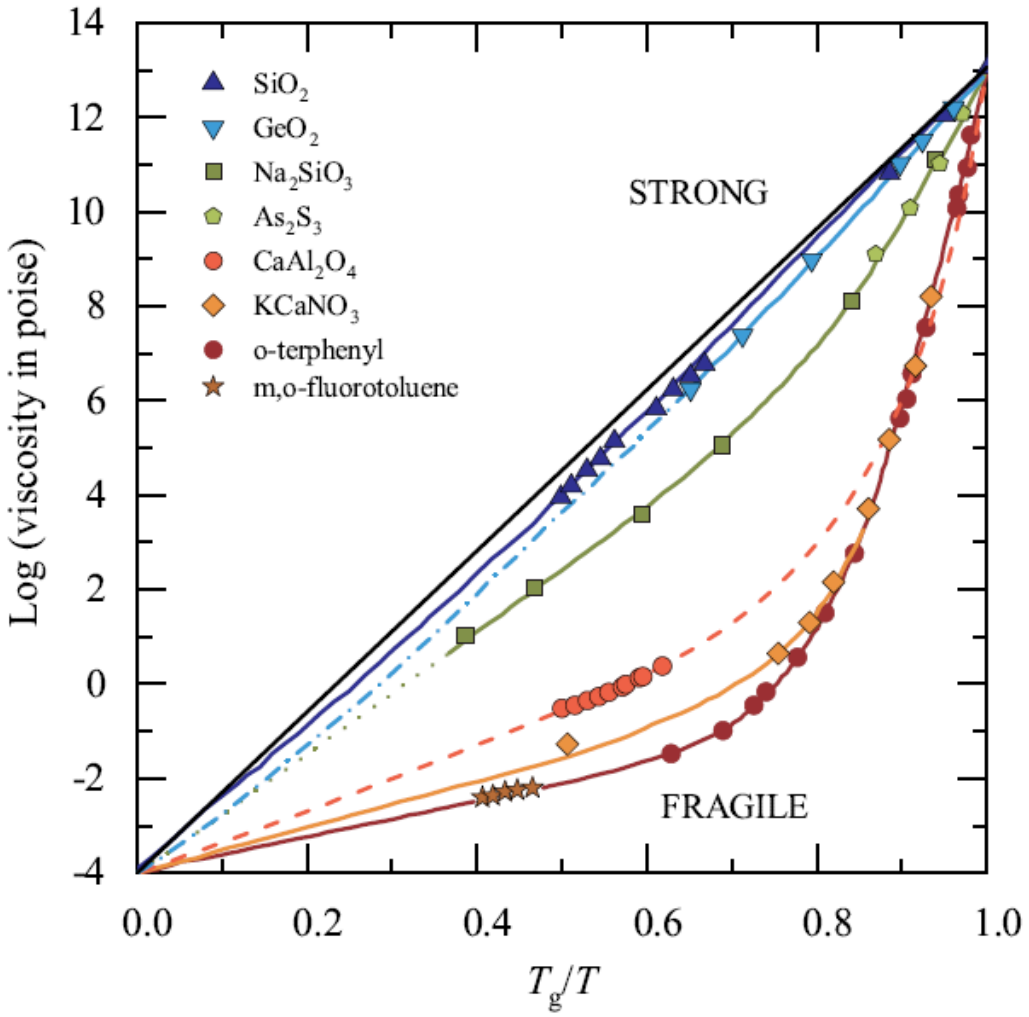
$CaO\text{-}Al_2O_3$ glass forming region





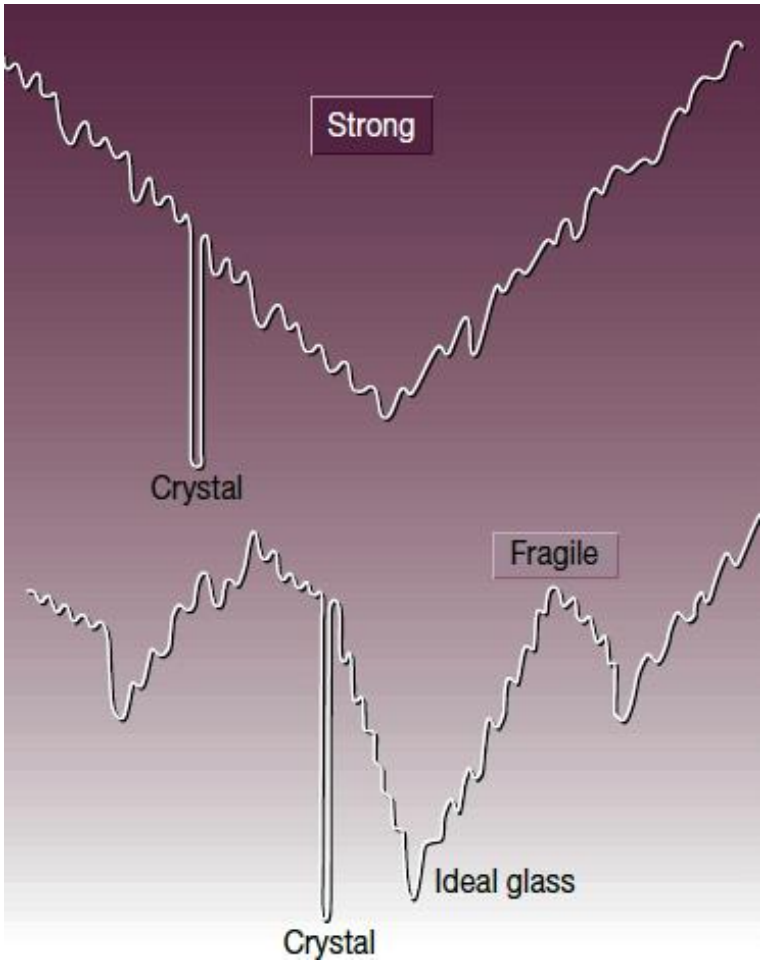
Aerodynamic levitation with laser heating

Liquid $CaO\text{-}Al_2O_3$ fragility



- Glass-forming liquids classified in terms of kinetic fragility
- "Strong" liquids exhibit approximately Arrhenius viscosity temperature dependence
- "Fragile" liquids exhibit non-Arrhenius behaviour characterised by a drastic dynamic slow-down on approach to T_g
- Vogel-Tammann-Fulcher fit to $CaAl_2O_4$ viscosity give fragility index (gradient at T_g) m = 116 characteristic of a fragile liquid (cf. m = 20 for SiO_2)

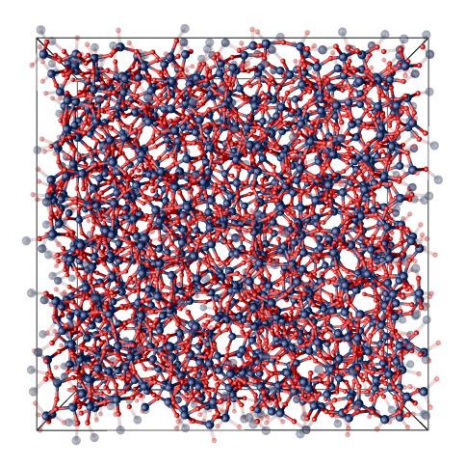
Liquid $CaO\text{-}Al_2O_3$ fragility

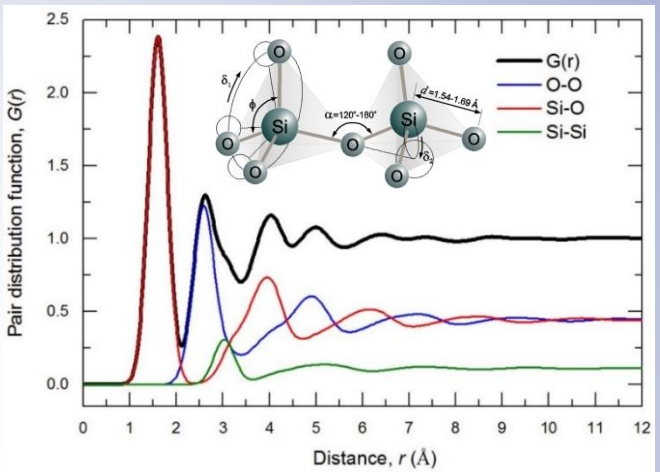


Debenetti & Stillinger 2001 *Nature* **410** 259

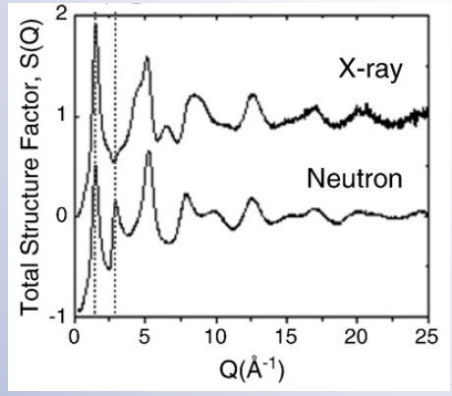
- Strong liquids (e.g. SiO_2) have deep broad minima in the potential energy landscape due to stable local coordinations and self-reinforcing 3-D networks that restrict the number of available configurations.
- Fragile liquids - larger range of potential energy minima in configurational space due to higher degree of short- and intermediate-range disorder
- On supercooling high energy barriers cf. thermal energies are encountered: increasingly unable to explore the full-range of configurational states.
- The system becomes trapped in a deep local energy minimum.

Liquid and Glass Diffraction



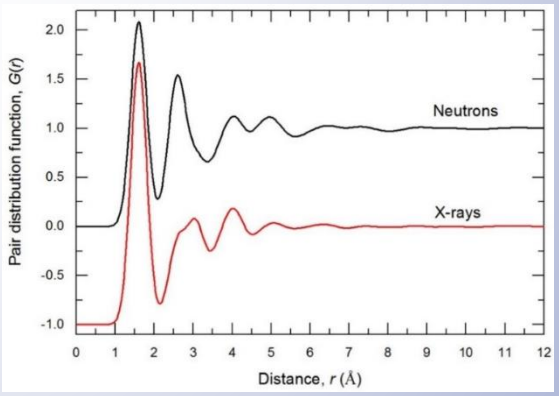


Structure factor



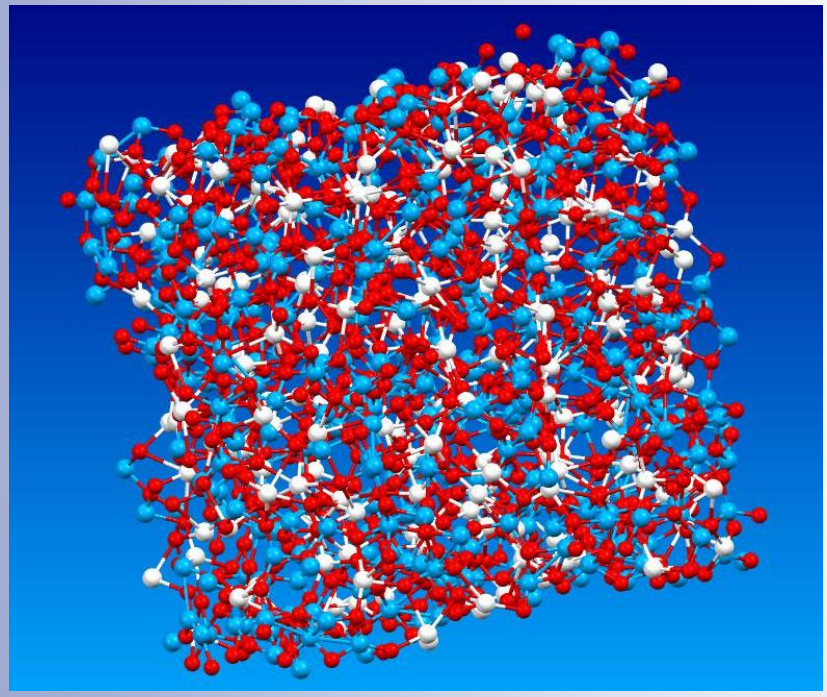
Fourier Transform

Pair distribution function



Aspherical Ion Model (AIM)

Snapshot of Liquid $CaAl_2O_4$ at 2500 K



- AIM ionic interaction potentials derived for the **Ca-Mg-Al-Si-O** system (Jahn & Madden 2007)
- Account for dipole polarisation and shape deformation

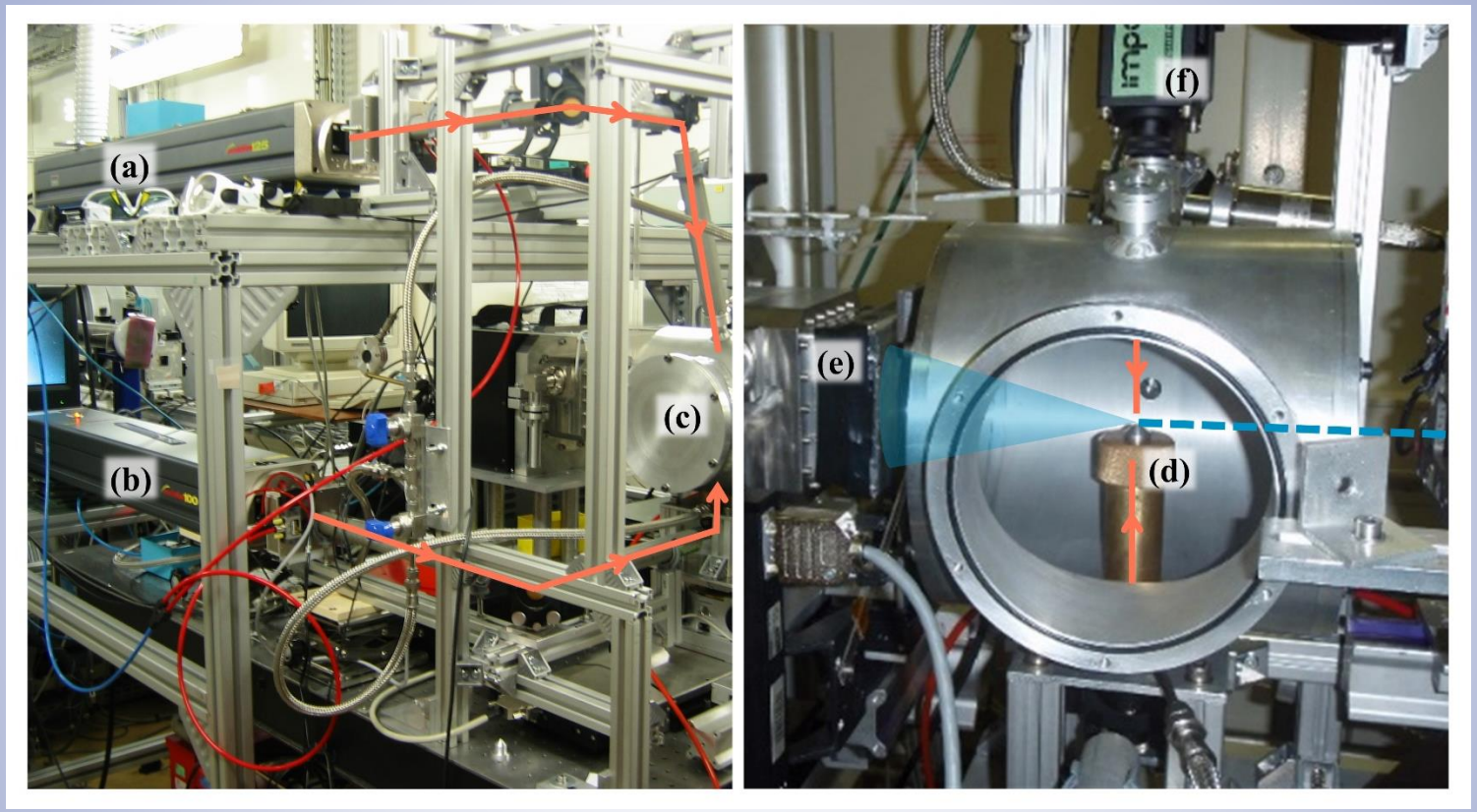
$$V = V^{qq} + V^{\mathrm{disp}} + V^{\mathrm{rep}} + V^{\mathrm{pol}}$$

V^{qq} : pair wise additive Coulomb and V^{disp} dispersion interactions

V^{rep} : short-range repulsion term

V^{pol} : dipolar and quadrupolar polarization terms

Synchrotron x-ray diffraction with aerodynamic levitation

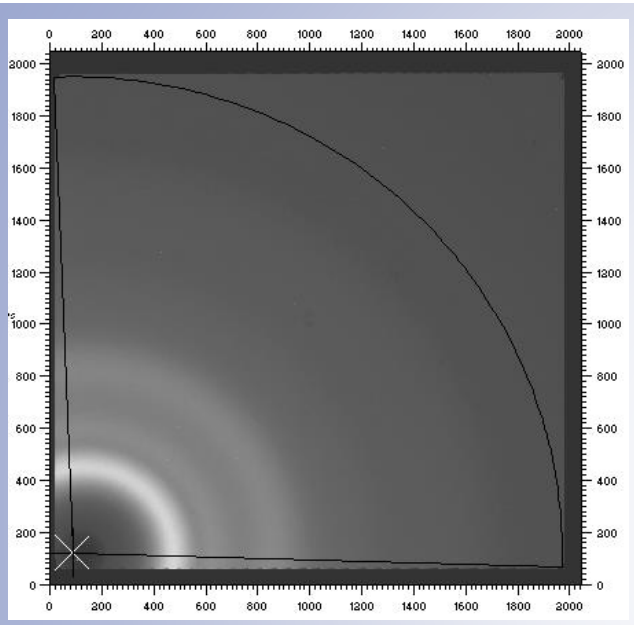


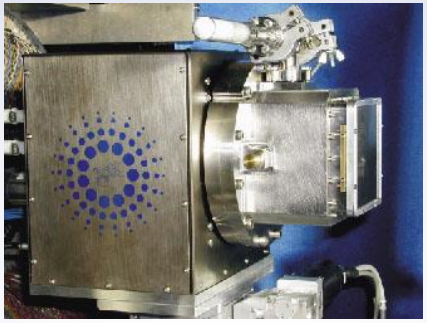
(a) + (b) : CO_2 lasers
(c) levitation chamber

(d) levitation nozzle
(e) Frelon CCD detector
(f) pyrometer

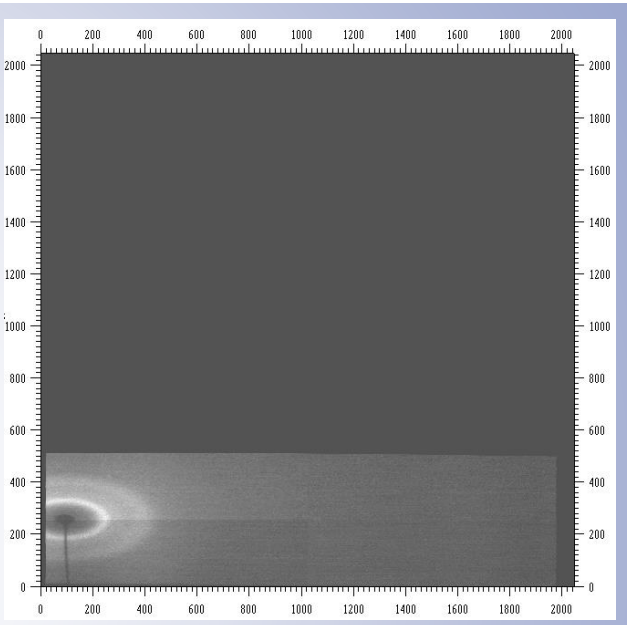
- Drewitt *et al.* 2011 *J. Phys. Condens.* **23** 155101

Static and time-resolved synchrotron x-ray diffraction





ESRF frelon camera:
Fast **R**eadout **LO**w **N**oise



Full Frame Transfer mode

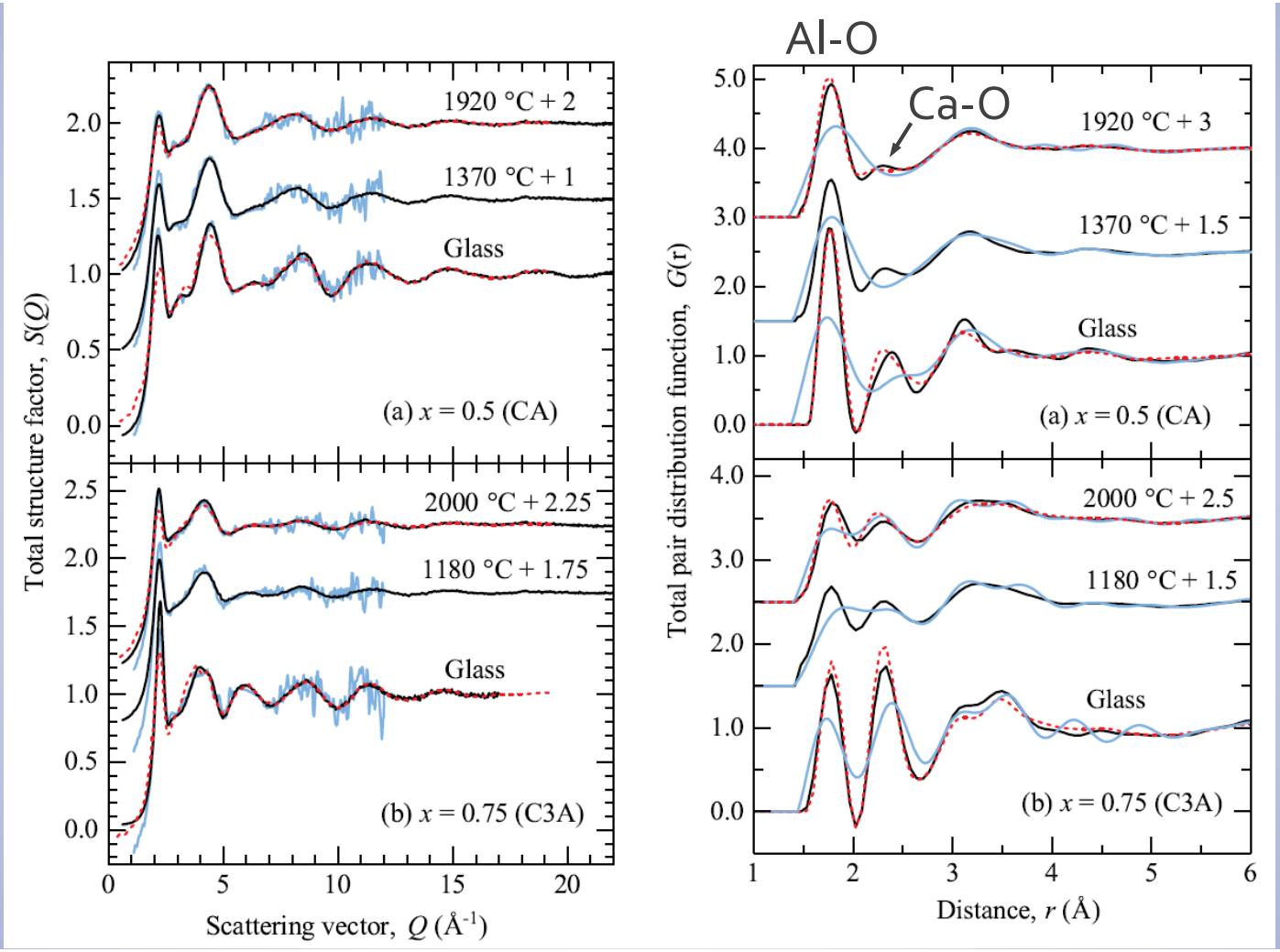
- Active image zone: 2048 X 2048 14 μm² pixels
- Static XRD 60 s acquisitions
- Beam centre at corner for large *Q*-range

Frame Transfer mode

- Active image zone: 2048 X 512 pixels
- Remainder of chip – memory buffer
- Time-resolved XRD with 30 ms acquisitions

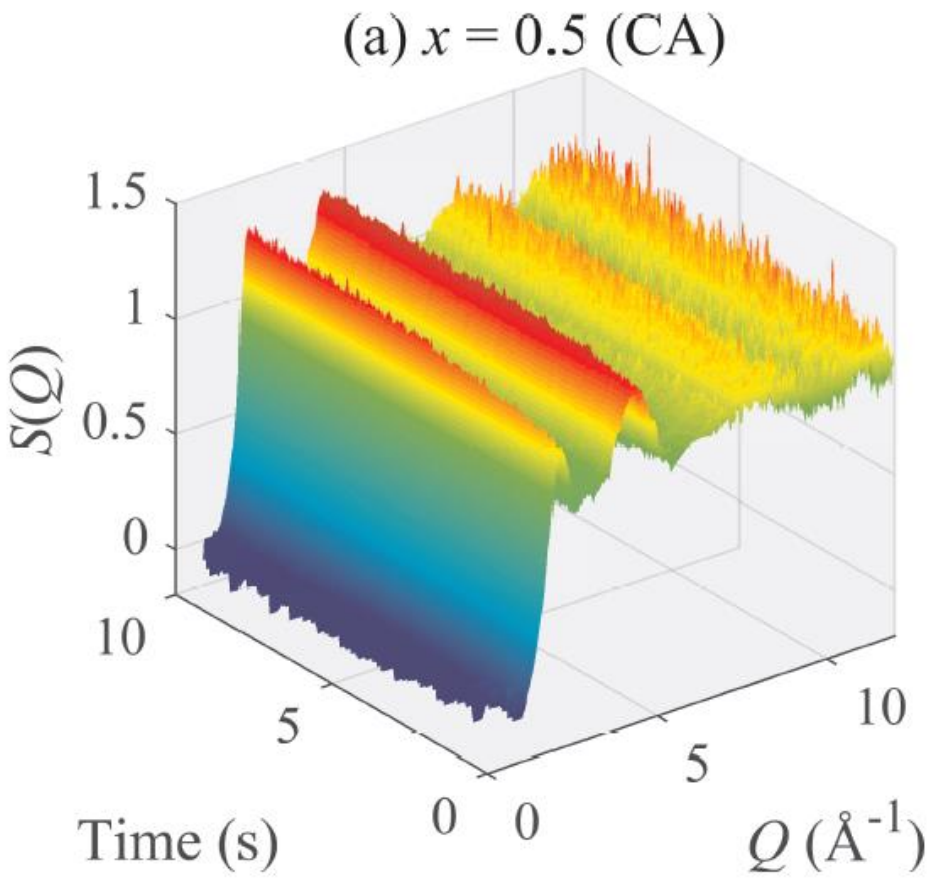
Drewitt *et al.* 2011 *J. Phys. Condens.* **23** 155101

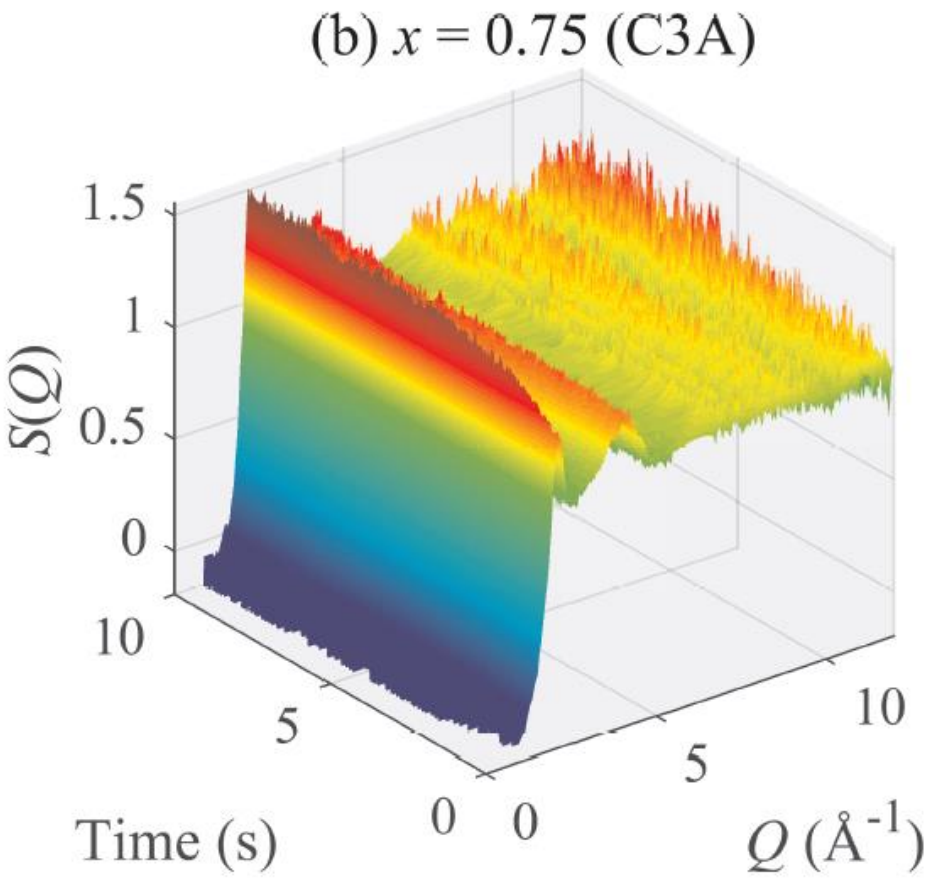
In situ vitrification of liquid $CaAl_2O_4$ and $Ca_3Al_2O_6$



- Drewitt *et al.* 2019 Submitted

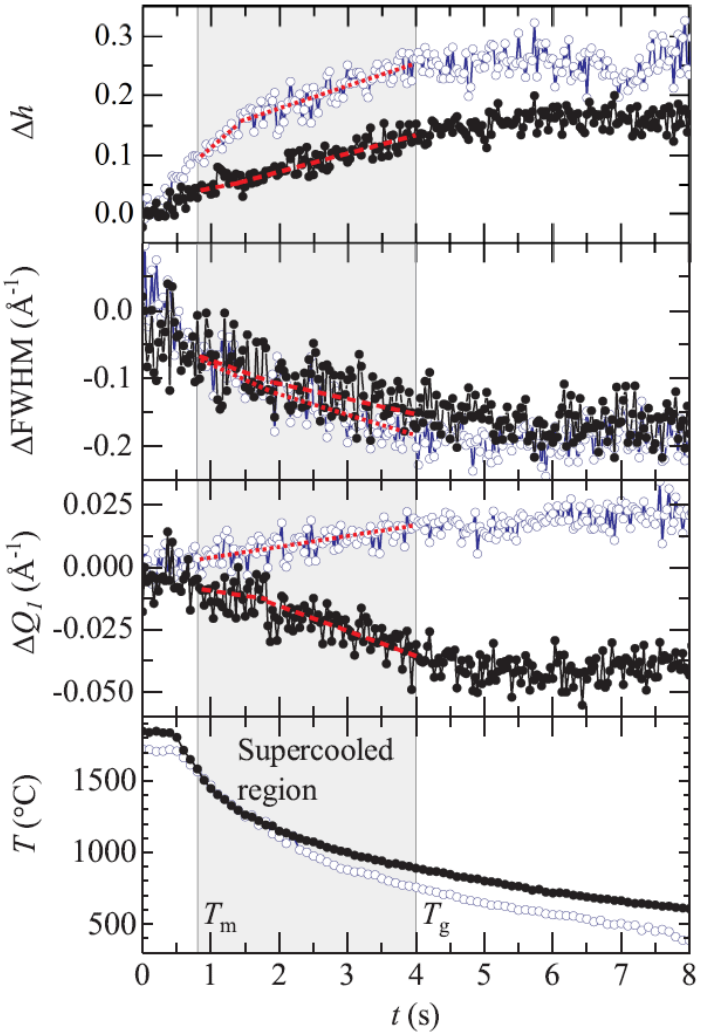
In situ vitrification of liquid $CaO\text{-}Al_2O_3$





- Drewitt *et al.* 2019 Submitted

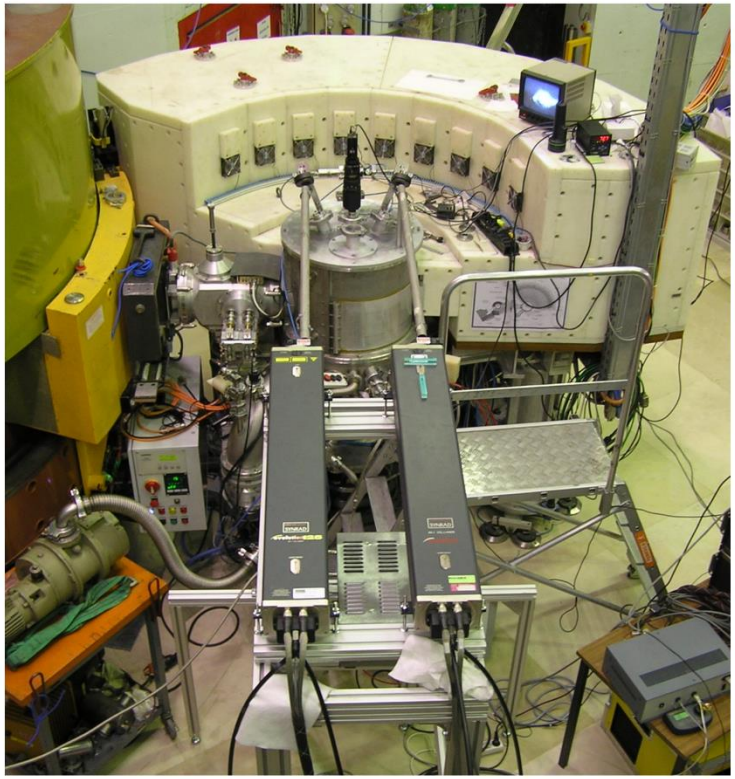
In situ vitrification of liquid $CaAl_2O_4$

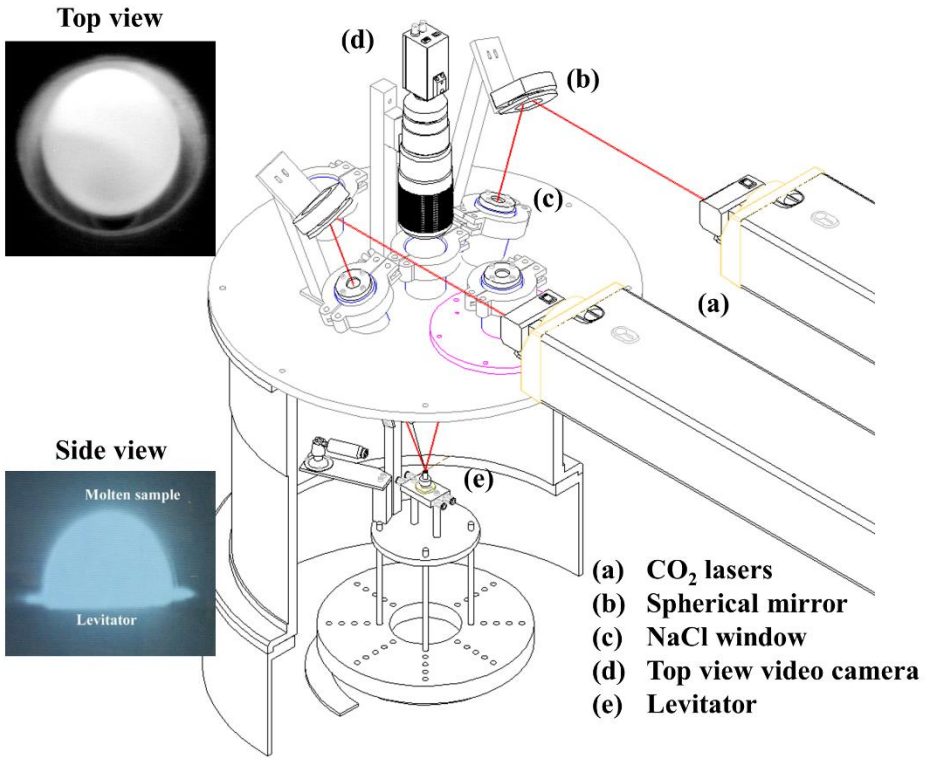


- Cooling from T_m to T_g in 3.2 s
- 96 X 30 ms acquisitions in supercooled region during glass formation
- Two distinct cooling regimes marked inflection in vicinity of dynamical cross-over temperature at ~ 1.25 T_g
- Progressive increase in height and reduction in FWHM of first peak in $S(Q)$ accompanied by shift in peak position (-ve for CA, +ve for C3A)
- Indicative of progressive ordering of cation-centred polyhedra
- No further structural organisation beyond T_g

Drewitt *et al.* 2019 Submitted

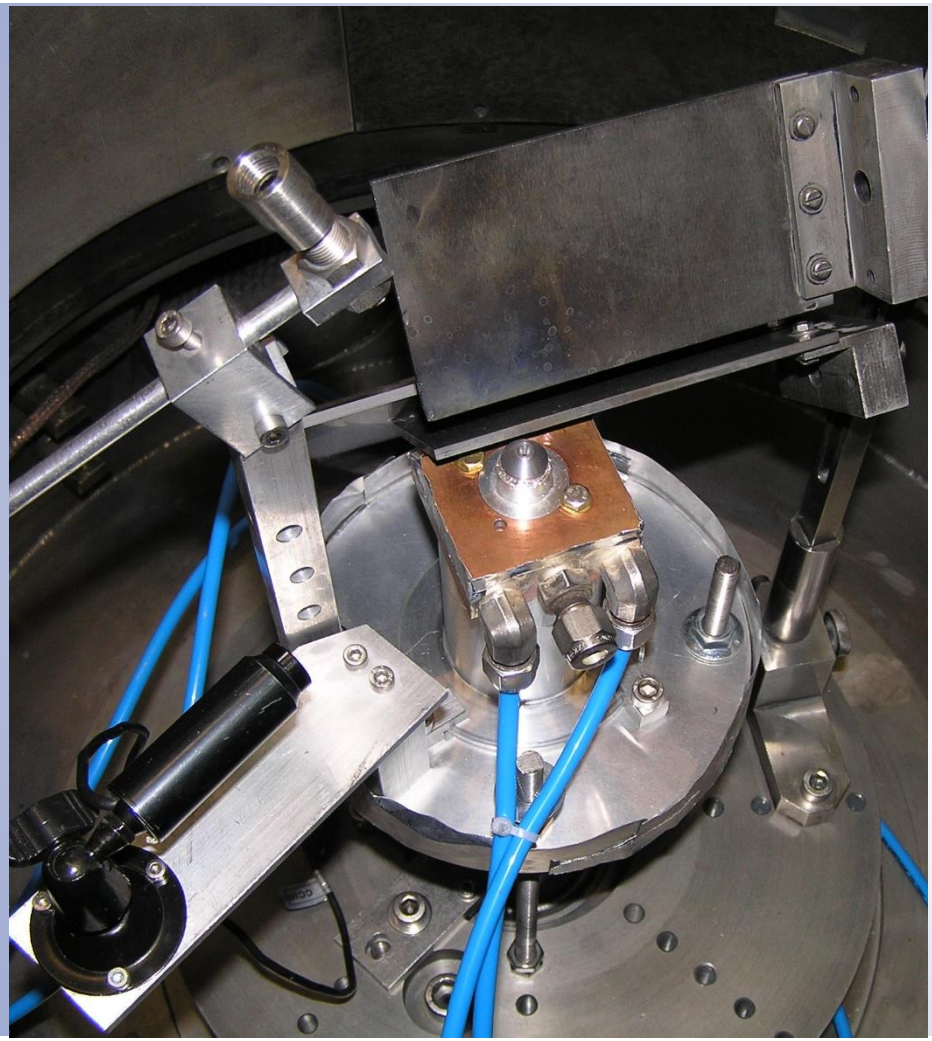
D4c Neutron Diffractometer, Institut Laue-Langevin

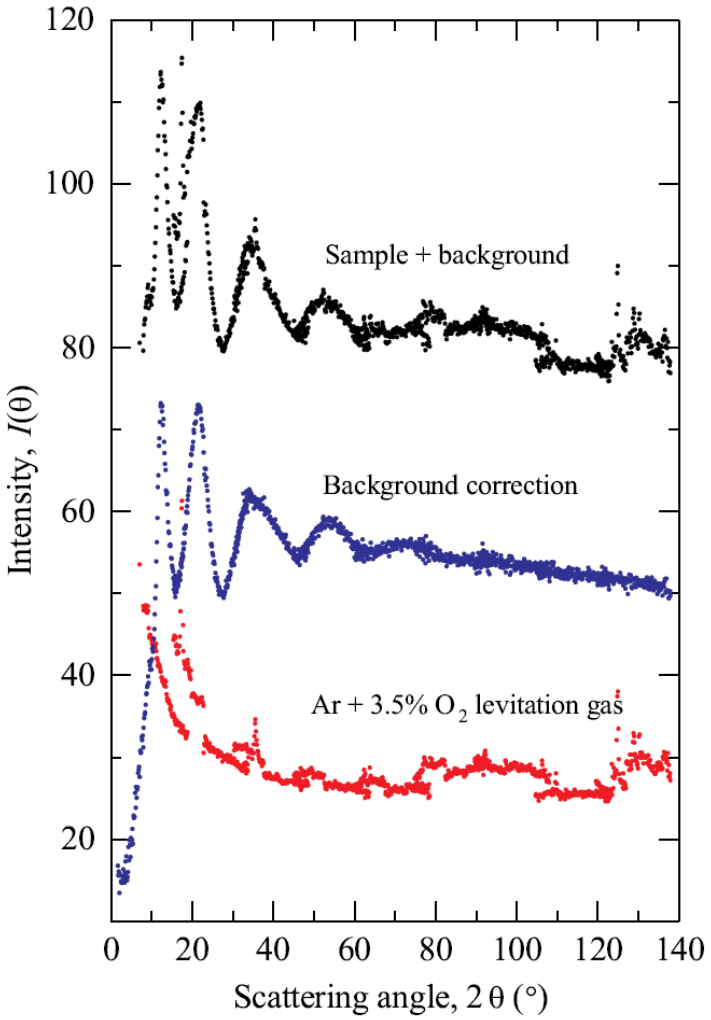




- Drewitt *et al.* 2012 *Phys. Rev. Lett.* **109** 235501

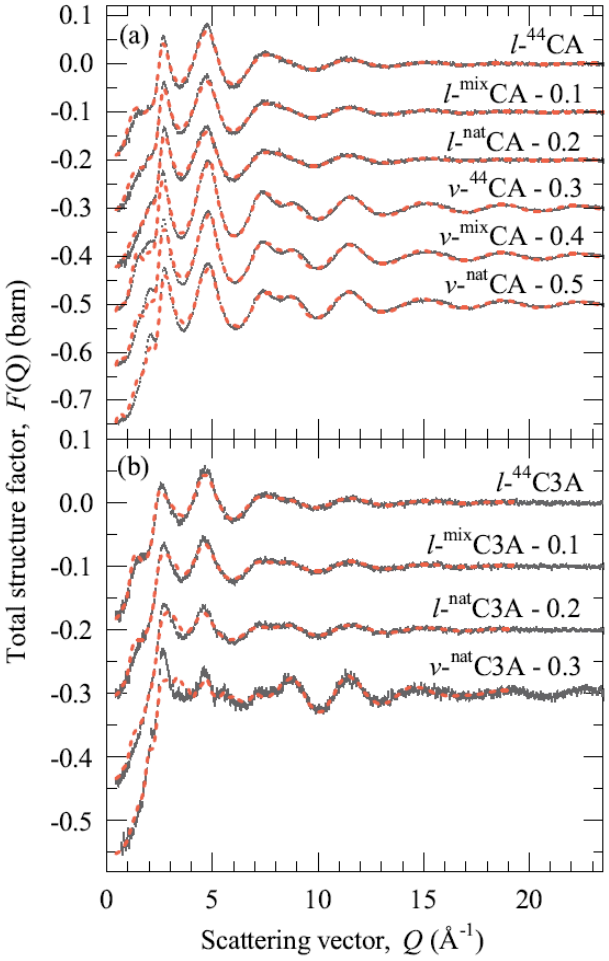
Neutron diffraction of levitated liquid $CaAl_2O_4$





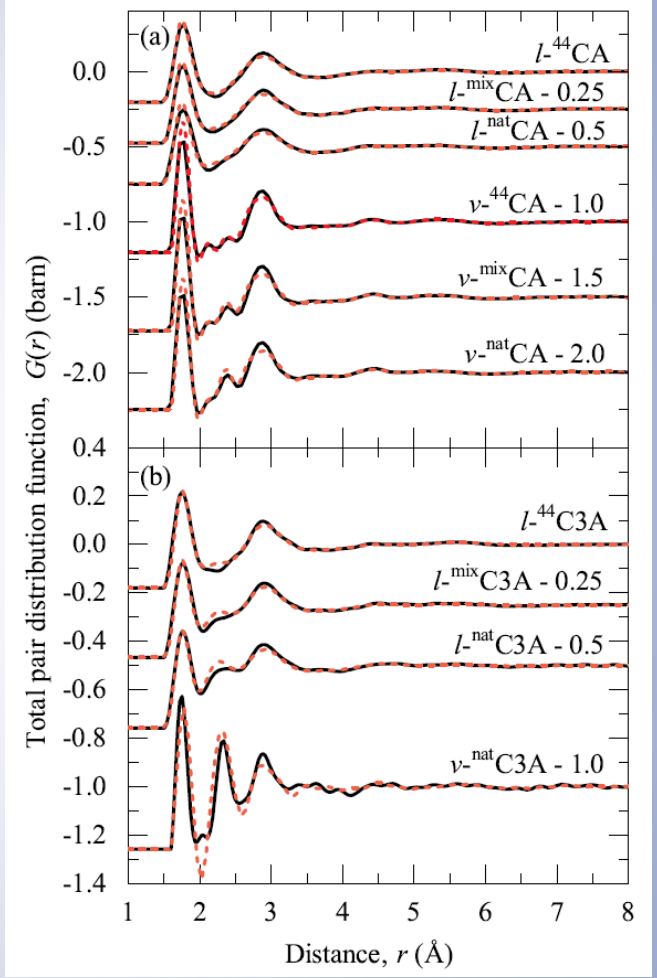
- Drewitt *et al.* 2012 *Phys. Rev. Lett.* **109** 235501

Neutron diffraction with ^{44}Ca isotope substitution



Three samples of identical composition varying only in Ca isotopic enrichment

- $b(^{44}\mathrm{Ca})$ = 1.42(6) fm
- $b(^{\mathrm{nat}}\mathrm{Ca})$ = 4.70(2) fm
- $b(^{\mathrm{mix}}\mathrm{Ca})$ = 3.06(3) fm
- Long counting times!



Drewitt *et al.* 2012 *Phys. Rev. Lett.* **109** 235501; 2017 *Phys. Rev. B* **95** 064203

Neutron diffraction with ^{44}Ca isotope substitution

$$F(Q) = \sum_{\alpha}\sum_{\beta} c_\alpha c_\beta b_\alpha b_\beta [S_{\alpha\beta}(Q) - 1]$$

Full partial structure factor analysis using NDIS most feasible for binary systems as $N(N+1)/2$ isotopically substituted samples are required.

Pseudo-binary representation Ca and μ (Al,O)

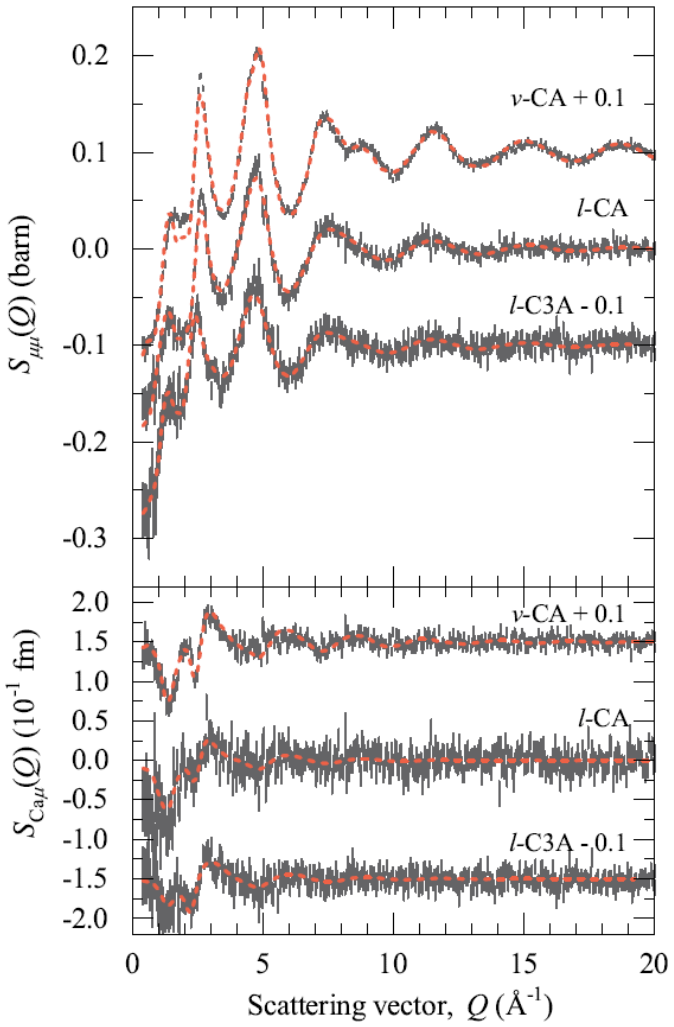
$$F(Q) = c_{Ca}^2 b_{Ca}^2 [S_{\mathrm{CaCa}}(Q) - 1] + 2c_{Ca} b_{Ca} S_{\mathrm{Ca}\mu}(Q) + S_{\mu\mu}(Q),$$

$$S_{\mathrm{Ca}\mu}(Q) = c_{\mathrm{Al}} b_{\mathrm{Al}} [S_{\mathrm{CaAl}}(Q) - 1] + c_{\mathrm{O}} b_{\mathrm{O}} [S_{\mathrm{CaO}}(Q) - 1]$$

$$S_{\mu\mu}(Q) = c_{\mathrm{Al}}^2 b_{\mathrm{Al}}^2 [S_{\mathrm{AlAl}}(Q) - 1] + c_{\mathrm{O}}^2 b_{\mathrm{O}}^2 [S_{\mathrm{OO}}(Q) - 1] + 2c_{\mathrm{Al}} c_{\mathrm{O}} b_{\mathrm{Al}} b_{\mathrm{O}} [S_{\mathrm{AlO}}(Q) - 1]$$

- Drewitt *et al.* 2012 *Phys. Rev. Lett.* **109** 235501

Neutron diffraction with ^{44}Ca isotope substitution



Pseudobinary partial structure factors isolated using the scattering matrix

$$\begin{bmatrix} S_{\mathrm{CaCa}}(Q) - 1 \\ S_{\mathrm{Ca}\mu}(Q) \\ S_{\mu\mu}(Q) \end{bmatrix} = \begin{bmatrix} c_{\mathrm{Ca}}^2 b_{44}^2 & 2c_{\mathrm{Ca}} b_{44} & 1 \\ c_{\mathrm{Ca}}^2 b_{\mathrm{mix}}^2 & 2c_{\mathrm{Ca}} b_{\mathrm{mix}} & 1 \\ c_{\mathrm{Ca}}^2 b_{\mathrm{nat}}^2 & 2c_{\mathrm{Ca}} b_{\mathrm{nat}} & 1 \end{bmatrix}^{-1} \times \begin{bmatrix} {}^{44}F(Q) \\ {}^{\mathrm{mix}}F(Q) \\ {}^{\mathrm{nat}}F(Q) \end{bmatrix}$$

Drewitt *et al.* 2012 *Phys. Rev. Lett.* **109** 235501; 2017 *Phys. Rev. B* **95** 064203

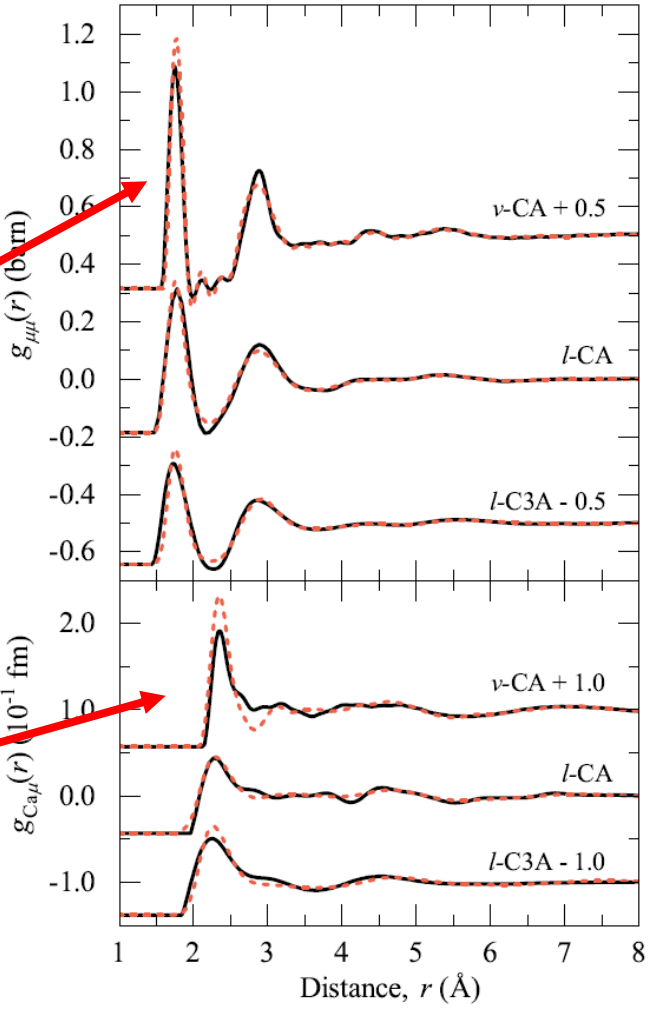
Real-space difference functions

Eliminate correlations involving Ca

$$g_{\mu\mu}(r) = c_{\mathrm{Al}}^2 b_{\mathrm{Al}}^2 [g_{\mathrm{AlAl}}(r) - 1] + c_{\mathrm{O}}^2 b_{\mathrm{O}}^2 [S_{\mathrm{OO}}(Q) - 1] + 2c_{\mathrm{Al}} c_{\mathrm{O}} b_{\mathrm{Al}} b_{\mathrm{O}} [S_{\mathrm{AlO}}(Q) - 1]$$

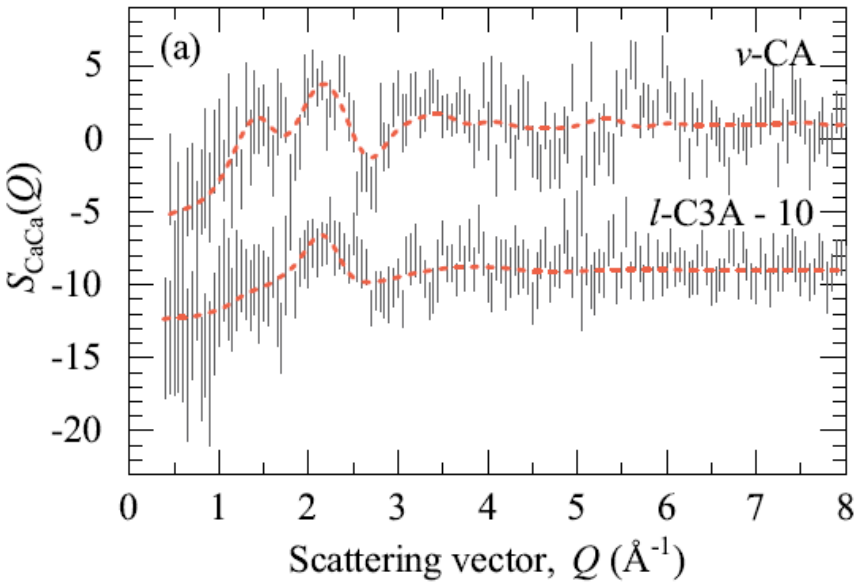
Eliminate correlations not involving Ca

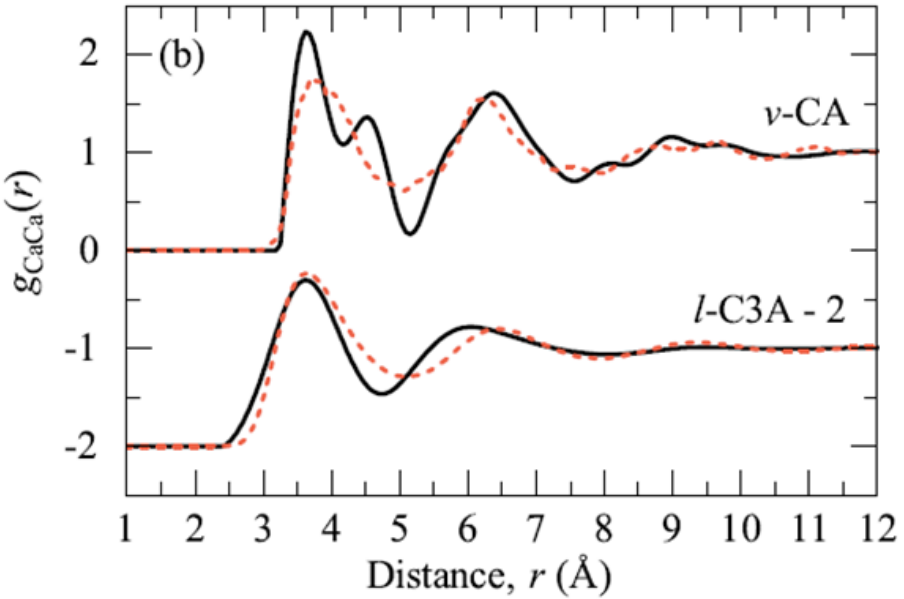
$$g_{\mathrm{Ca}\mu}(r) = c_{\mathrm{Al}} b_{\mathrm{Al}} [g_{\mathrm{CaAl}}(r) - 1] + c_{\mathrm{O}} b_{\mathrm{O}} [g_{\mathrm{CaO}}(r) - 1]$$



Drewitt *et al.* 2012 *Phys. Rev. Lett.* **109** 235501; 2017 *Phys. Rev. B* **95** 064203

Direct extraction of the Ca-Ca correlations

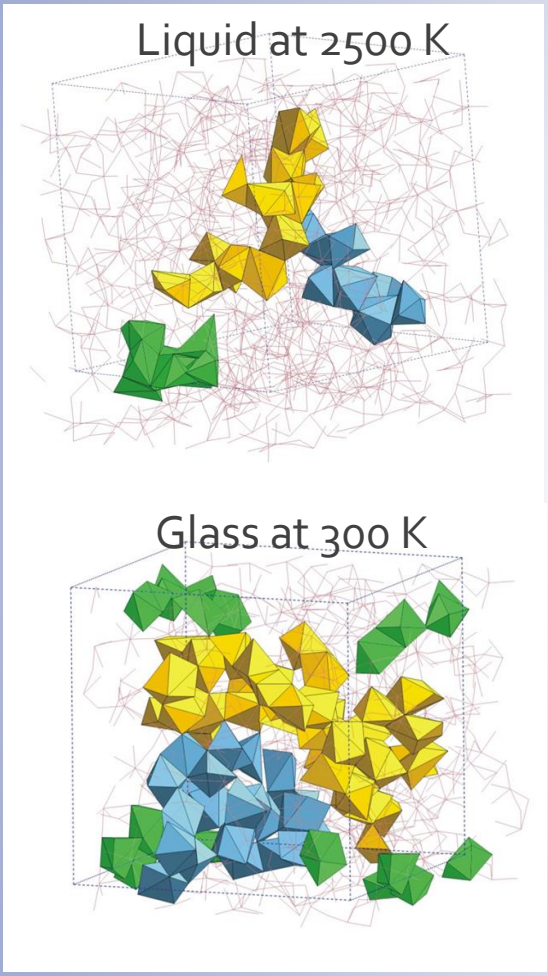




- $S_{CaCa}(Q)$ and $g_{CaCa}(r)$ isolated for equimolar CA glass and C3A liquid
- Very small samples (~ 3 mm): first double difference function for oxide liquid

Drewitt *et al.* 2012 *Phys. Rev. Lett.* **109** 235501; 2017 *Phys. Rev. B* **95** 064203

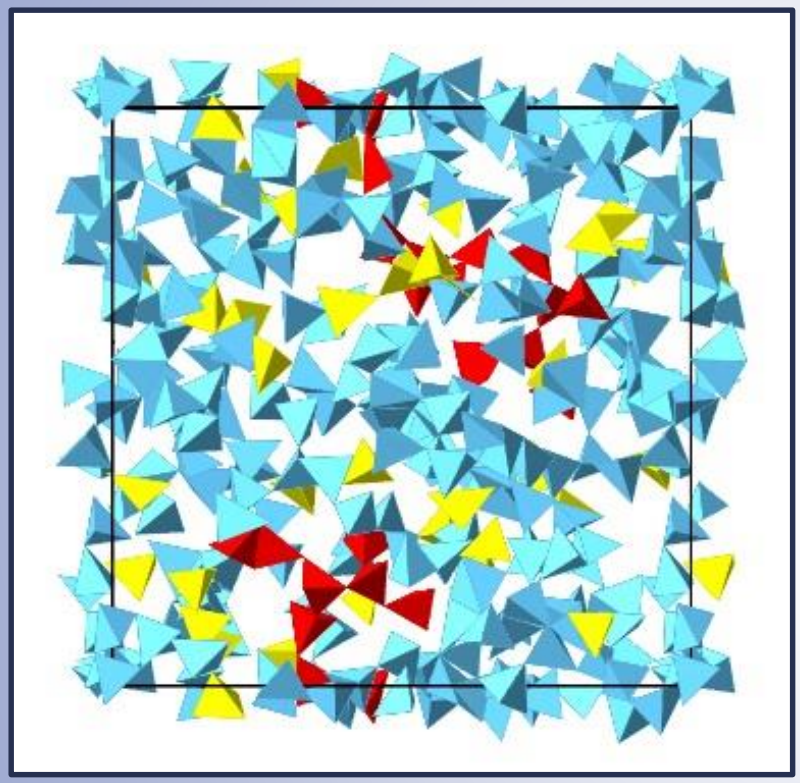
Structural reorganization on multiple length scales



- AlO_5 and oxygen triclusters present in the liquid
- On glass formation, these breakdown to form almost entirely corner shared tetrahedral glass network
- Accompanied by an increase in medium range order, associated with development of chains of edge and face shared Ca-centered polyhedra in glass
- Although $CaAl_2O_4$ liquid breaks Zachariasen's rules, on vitrification it forms a tetrahedral corner shared network

Drewitt *et al.* 2012 *Phys. Rev. Lett.* **109** 235501

AlO_4 liquid network structure

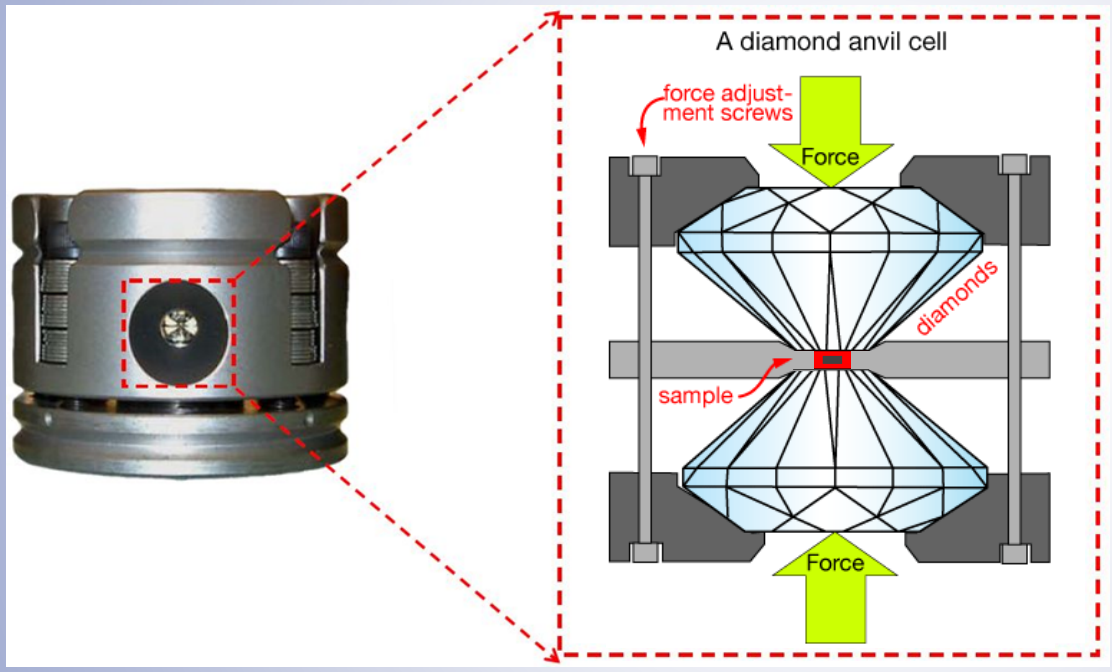


- Although depolymerised composition, liquid $Ca_3Al_2O_6$ largely composed of AlO_4 tetrahedra forming infinite network
- Around 10 % unconnected AlO4 monomers and Al_2O_7 dimers
- With increasing CaO concentration, number of isolated units increases, thus C3A composition represents a threshold beyond which glass can no longer support infinitely connected network

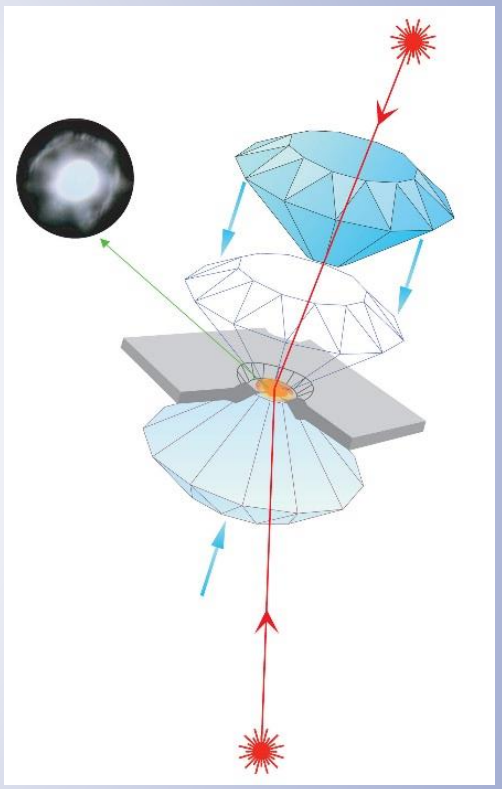
Drewitt *et al.* 2017 *Phys. Rev. B* **95** 064203

Aluminate liquids and glasses at high-pressure

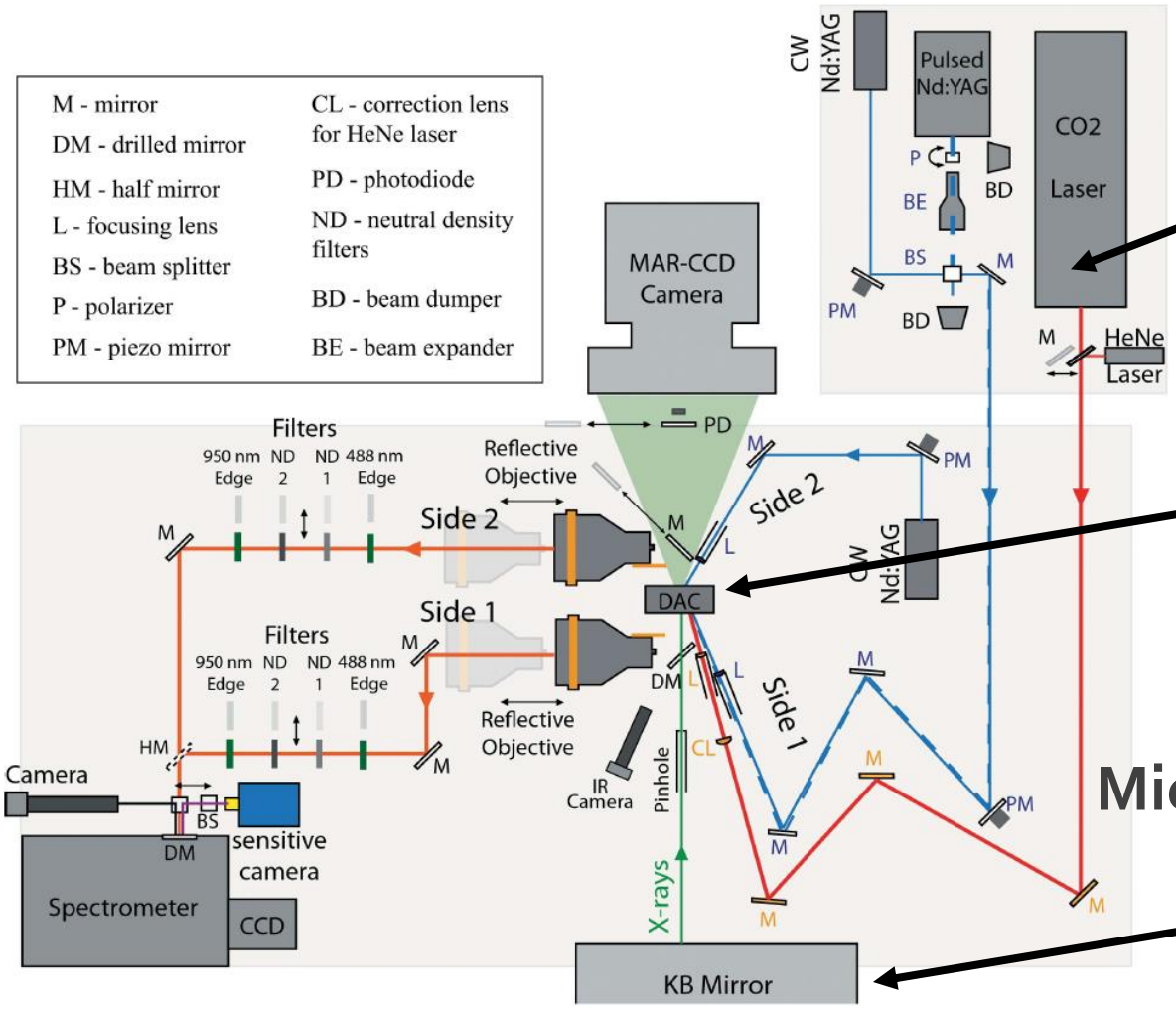
Diamond Anvil Cell (DAC)



Laser heating



Beamline ID27 - ESRF

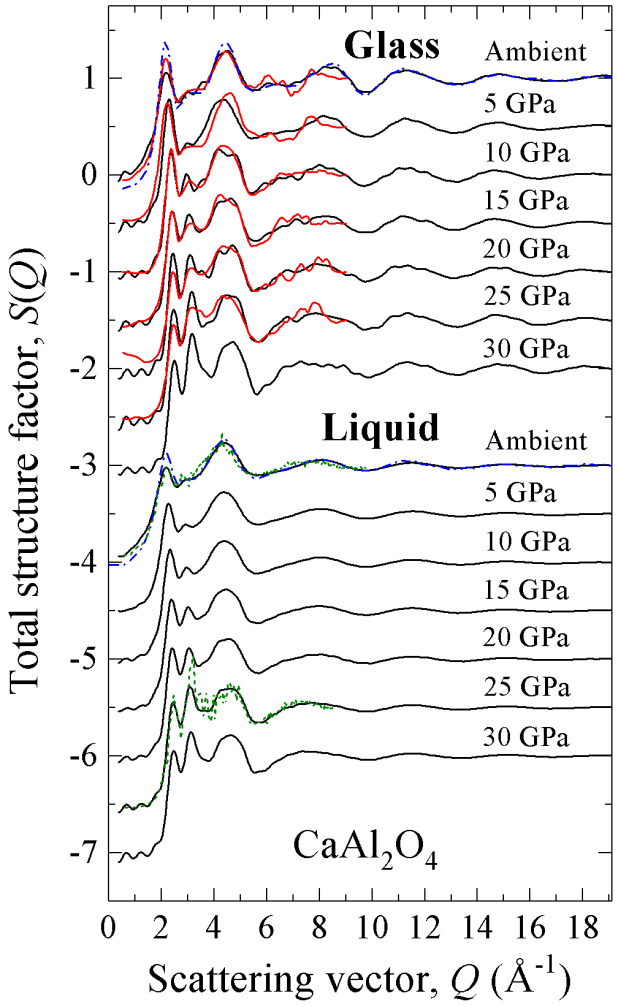


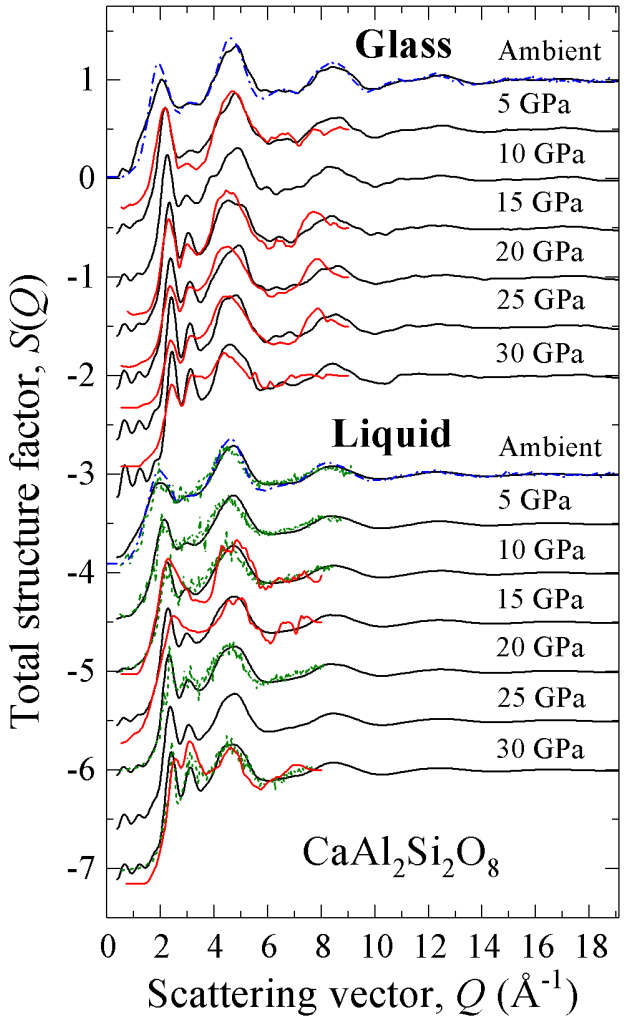
CO2 laser

DAC

Micro focussed X-rays

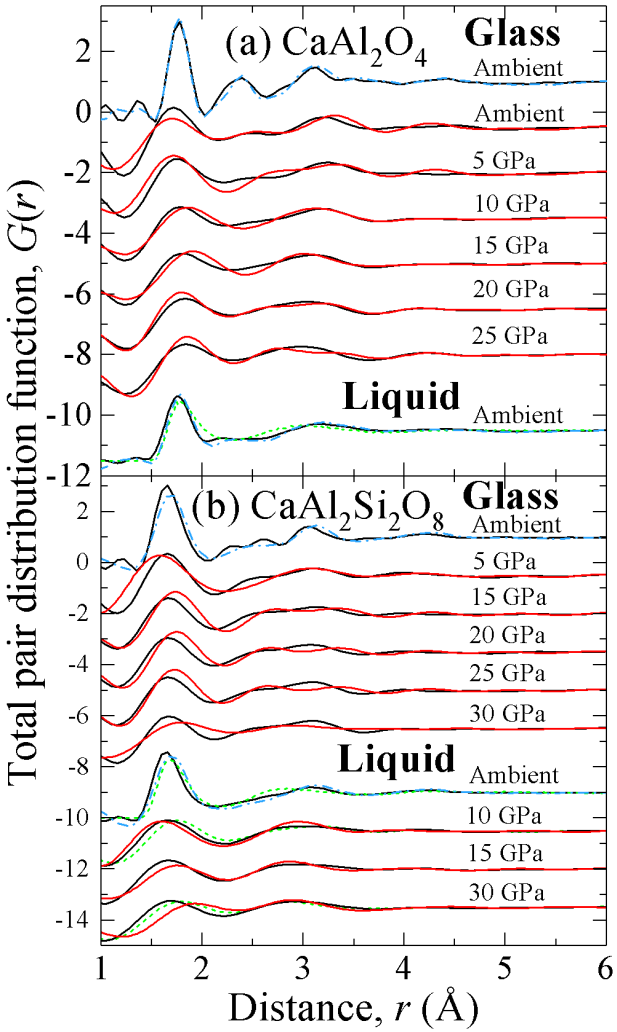
High pressure x-ray structure factors

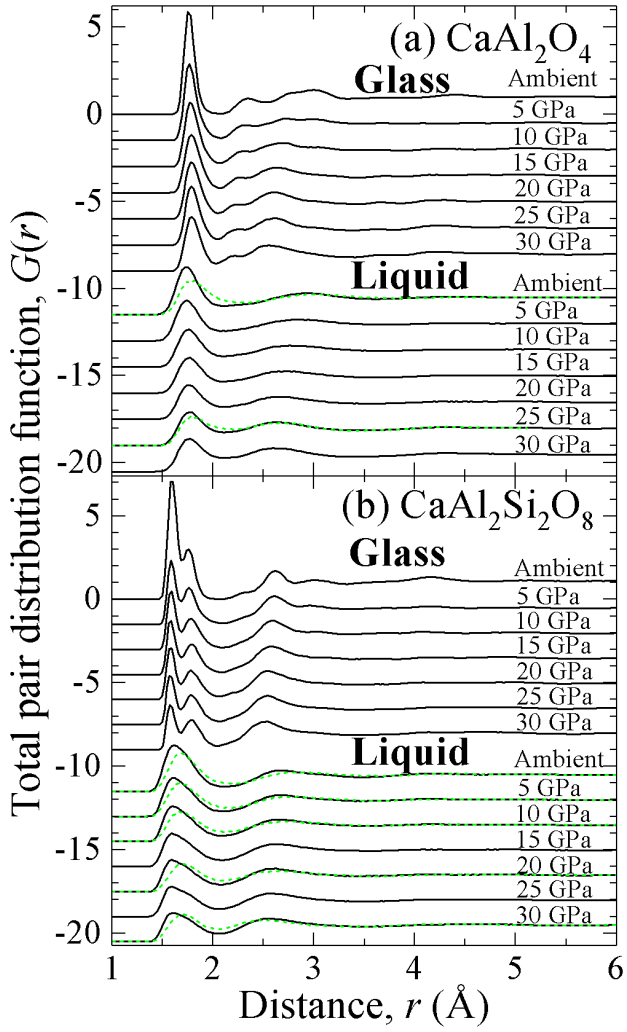




- Drewitt *et al.* 2015 *J. Phys. Condens. Matter* **27** 105103

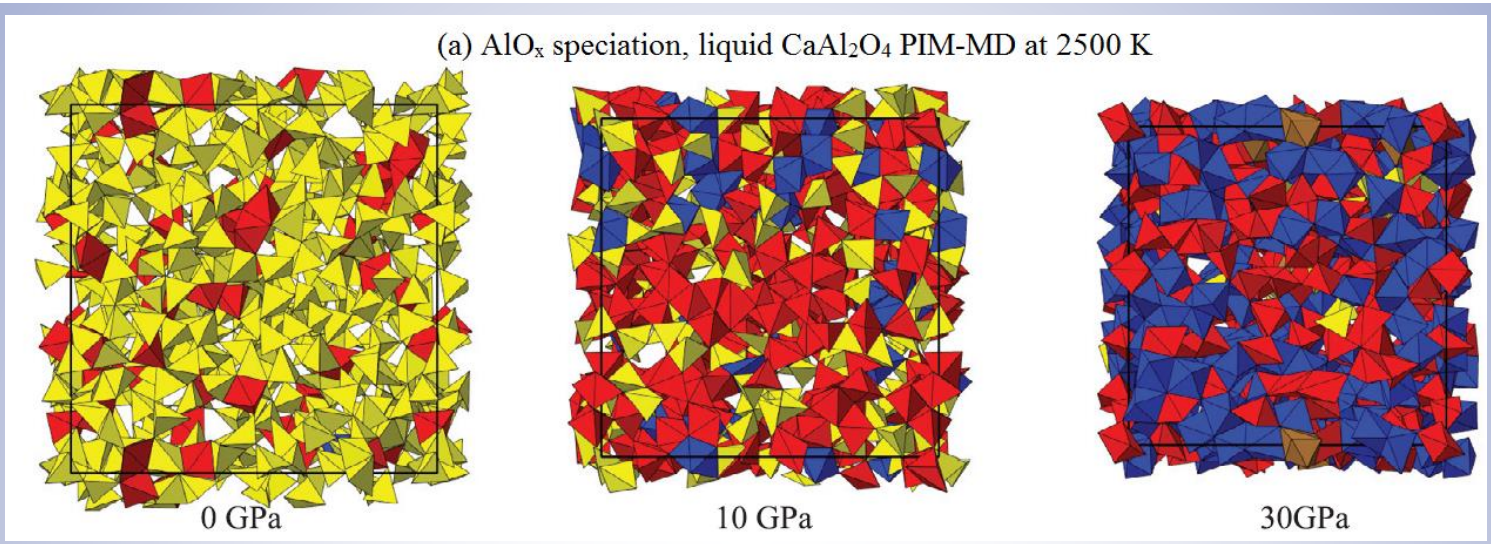
High pressure pair distribution functions





- Drewitt *et al.* 2015 *J. Phys. Condens. Matter* **27** 105103

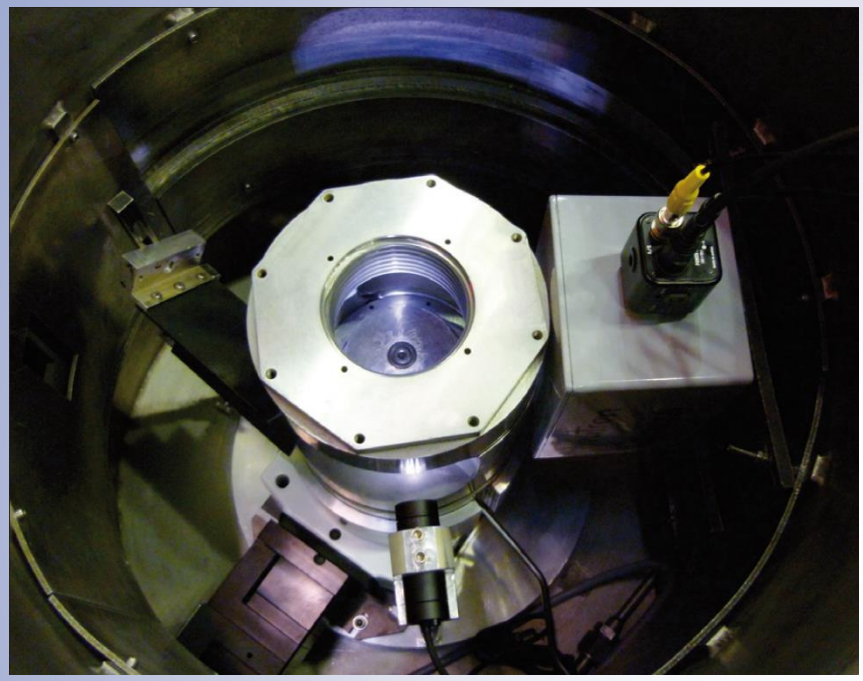
Al-O coordination and clustering with pressure

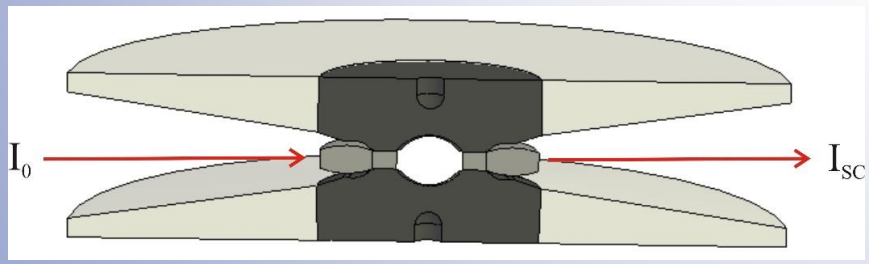


- Ambient pressure: structure is strongly determined by chemical ordering arising from network forming Al-O / Si-O tetrahedra (**yellow**).
- Elevated pressure: relatively open network structure is compressed and the Al and Si coordination increases. AlO_6 units (**blue**) become increasingly dominant above 15 GPa.
- Development of topological ordering: more closely packed structure, increase in O-O coordination number consistent with closely packed hard spheres.

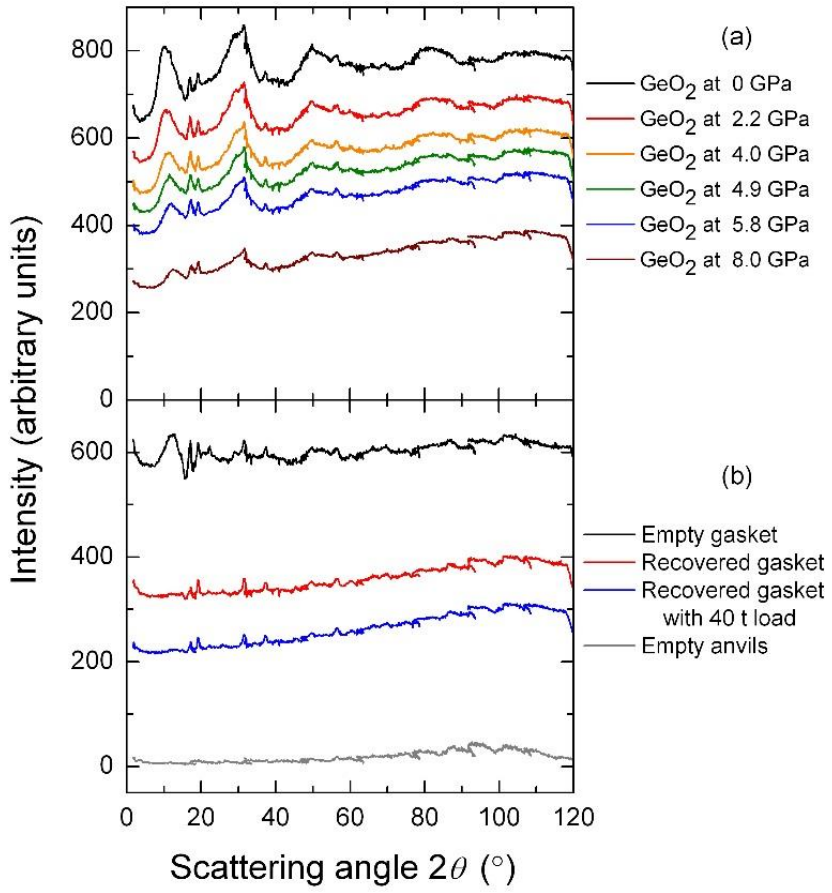
Drewitt *et al.* 2015 *J. Phys. Condens. Matter* **27** 105103

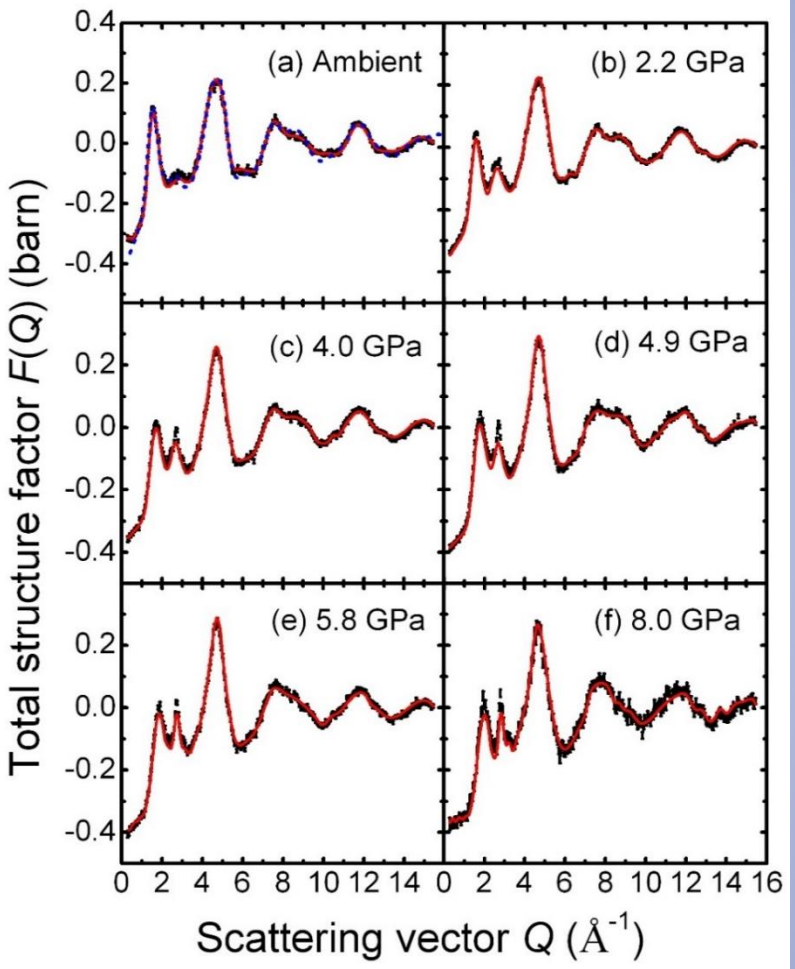
High pressure neutron diffraction with isotope substitution





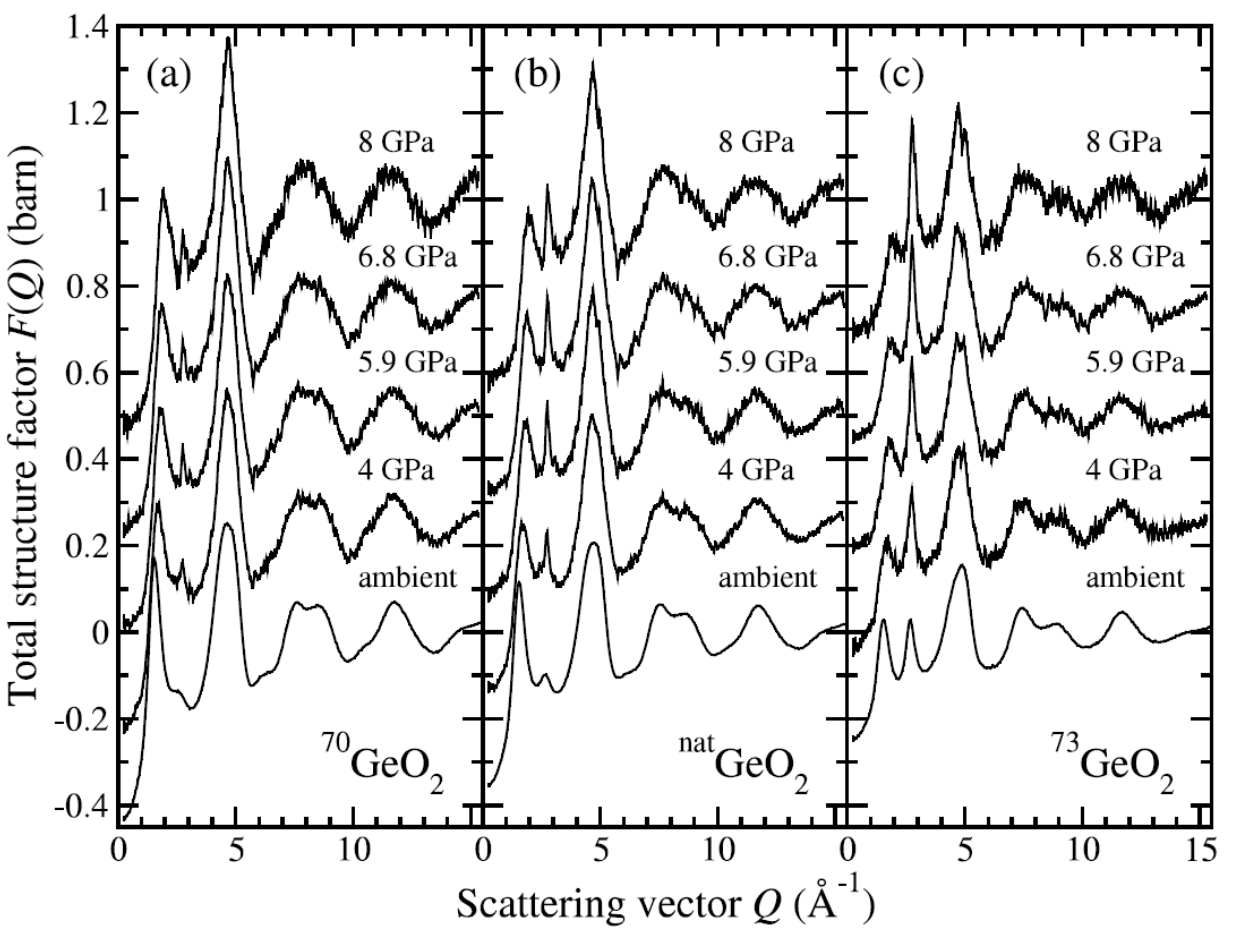
High pressure neutron diffraction with isotope substitution





- Drewitt *et al.* 2010 *Phys. Rev. B* **81** 014202

High pressure neutron diffraction with isotope substitution

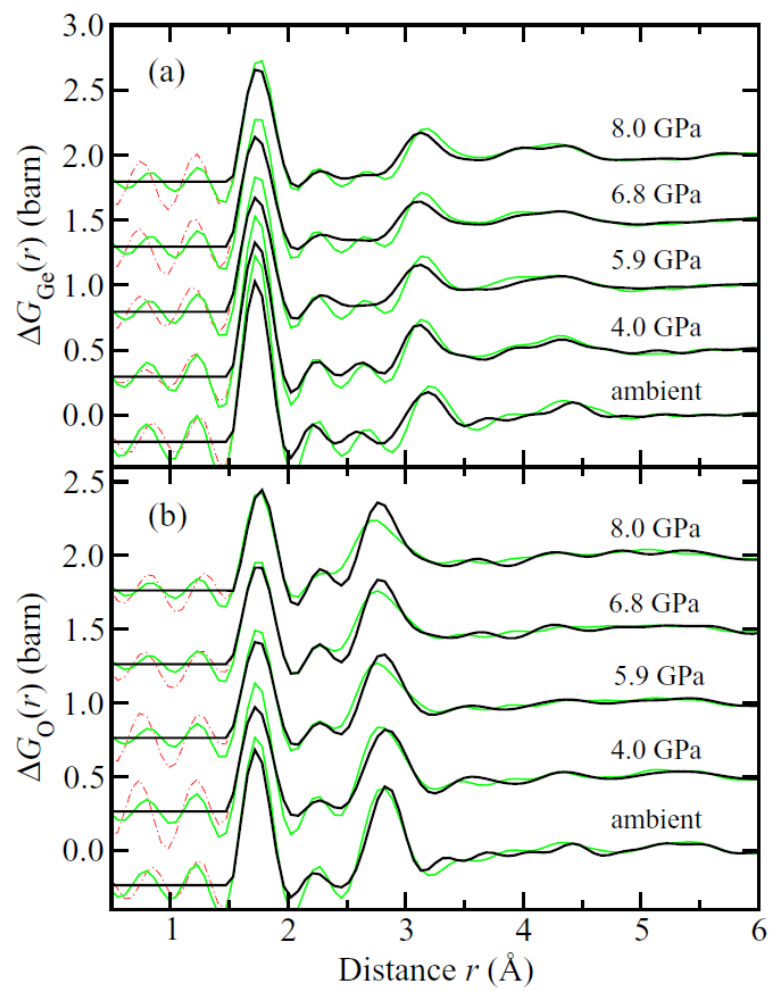


Contrast in neutron scattering lengths

- $b(^{73}Ge)$ = 5.02(4) fm
- $b(^{nat}Ge)$ = 8.185(20) fm
- $b(^{70}Ge)$ = 10.0(1) fm

- Wezka *et al.* 2012 *J. Phys. Condens. Matter* **24** 502101

High pressure neutron diffraction with isotope substitution

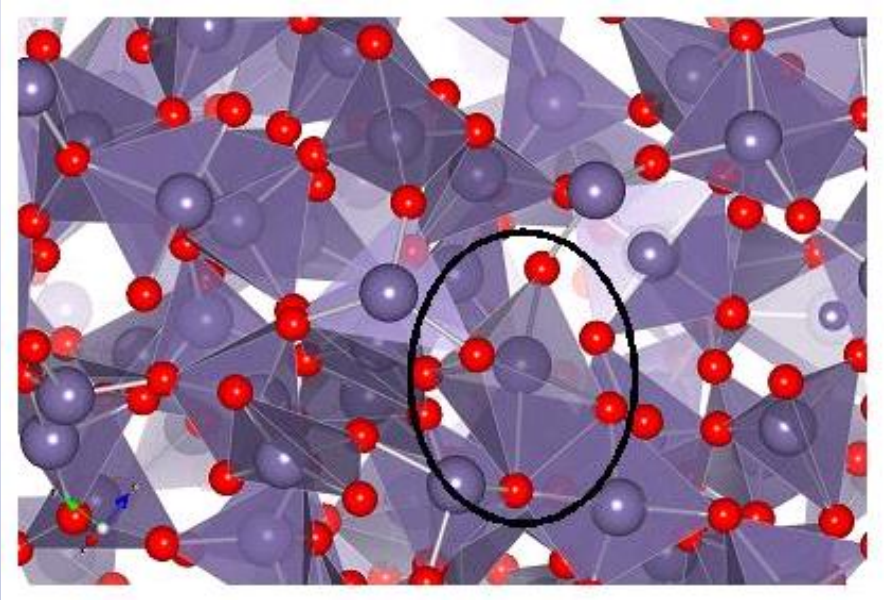


- Rigorous constraint for MD models
- DIPole-Polarisable Ion Model (DIPPIM) only model in quantitative agreement with experiment

- Wezka *et al.* 2012 *J. Phys. Condens. Matter* **24** 502101

High pressure neutron diffraction with isotope substitution

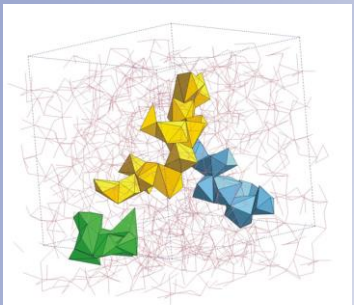
- Results consistent with operation of two densification mechanisms:
- (1) Collapse of open network structure of corner-linked tetrahedra at low *P* – evidenced by reduction and shift in first sharp diffraction peak
- (2) > 5 GPa, transformation of tetrahedra to higher coordinations

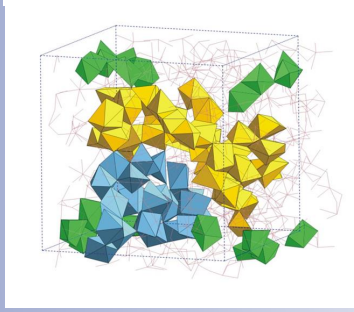


5-fold polyhedra play an essential role in *P*-driven transformations

- Wezka *et al.* 2012 *J. Phys. Condens. Matter* **24** 502101

Summary I: NDIS on small levitated liquid calcium aluminates



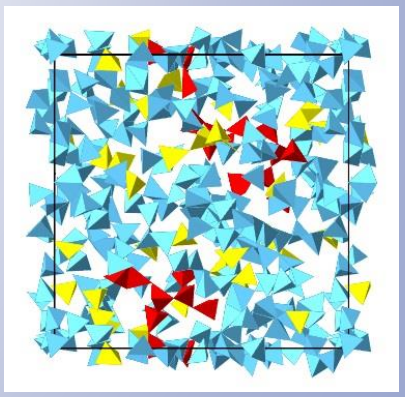


Equimolar $CaAl_2O_4$

- Liquid breaks Zachariasen's rules
- Undergoes structural reorganisation on quenching: Breakdown of AlO_5 oxygen triclusters to form corner-shared tetrahedral AlO_4 network structure
- Accompanied by changes in medium range order via formation of edge- and face-shared chains of Ca-centred polyhedra.

Glass forming end member $Ca_3Al_2O_6$

- liquid consists mostly of tetrahedral AlO_4 network
- Represents a threshold, above which isolated AlO_4 monomers or Al_2O_7 dimers prevents formation of infinitely connected network.



Summary II: Al coordination change at high pressure

Al coordination change at high pressure

- Strong chemical ordering at ambient *P:* AlO_4 + SiO_4
- AlO_5 dominant at ~10 GPa followed by AlO_6 by 30 GPa
- At 30 GPa, Ca+Al ions form large clusters of edge- or face-sharing polyhedra
- O-O coordination from 9 to 11 at 10 GPa: consistent with random close packing of hard spheres
- Pressures within accessibility region for Paris-Edinburgh press: neutron diffraction with isotope substitution…