Invert glasses

Louis HENNET

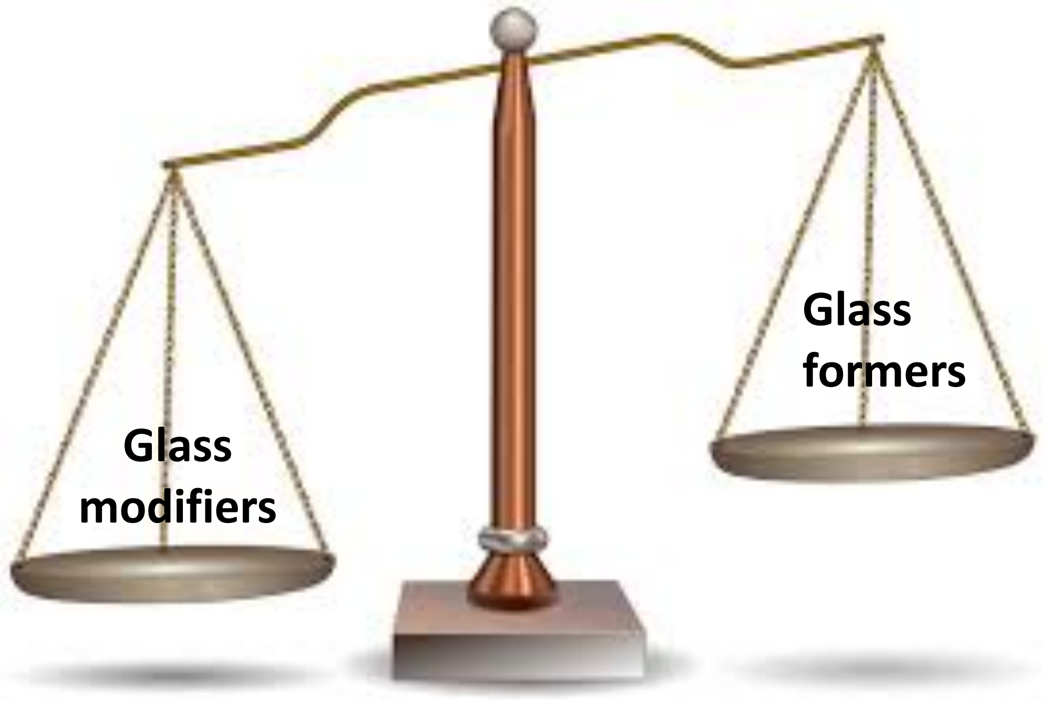
CNRS-CEMHTI
(Condition Extrêmes et Matériaux, Haute Température et irradiation)
1d avenue de la recherche Scientifique
45071 Orléans
France
louis.hennet@cnrs-orleans.fr

www.cnrs.fr

UNIVERSITE D'ORLEANS

Invert glasses

Invert glasses



Glass modifiers

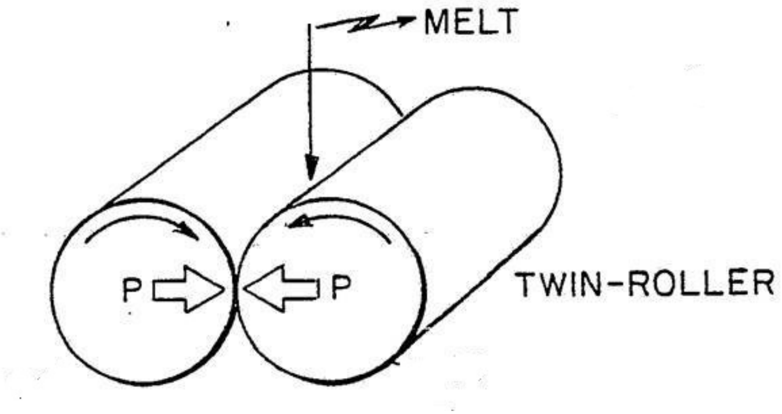
Glass formers

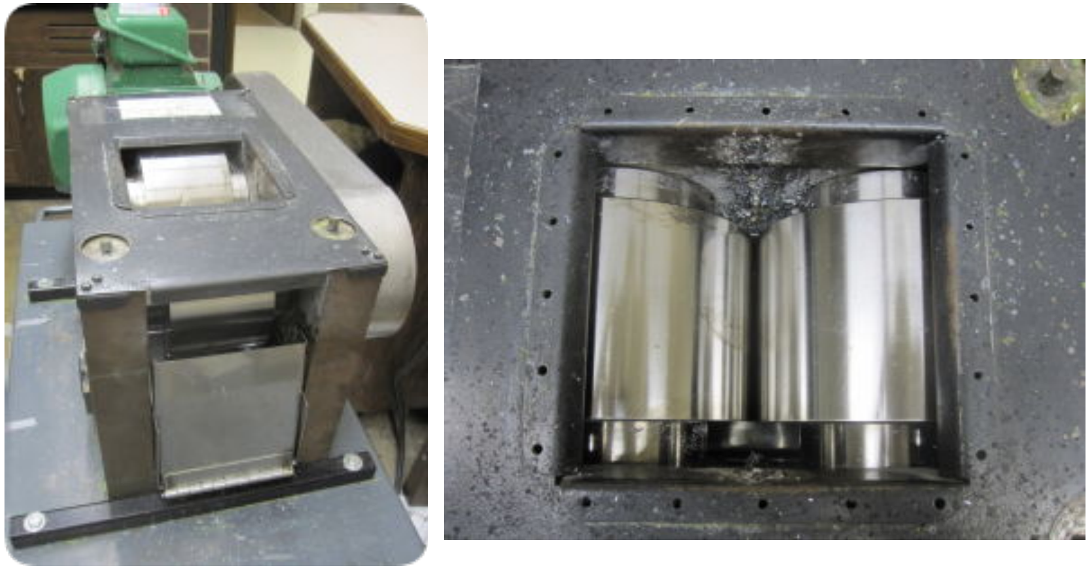
Few invert glasses can be obtained with a classical quench : C12A7 : $Ca_{12}Al_{14}O_{33}$

In most of the cases, they are obtained using fast quenching

How to quench the sample rapidely ?

1/ Roller quenching





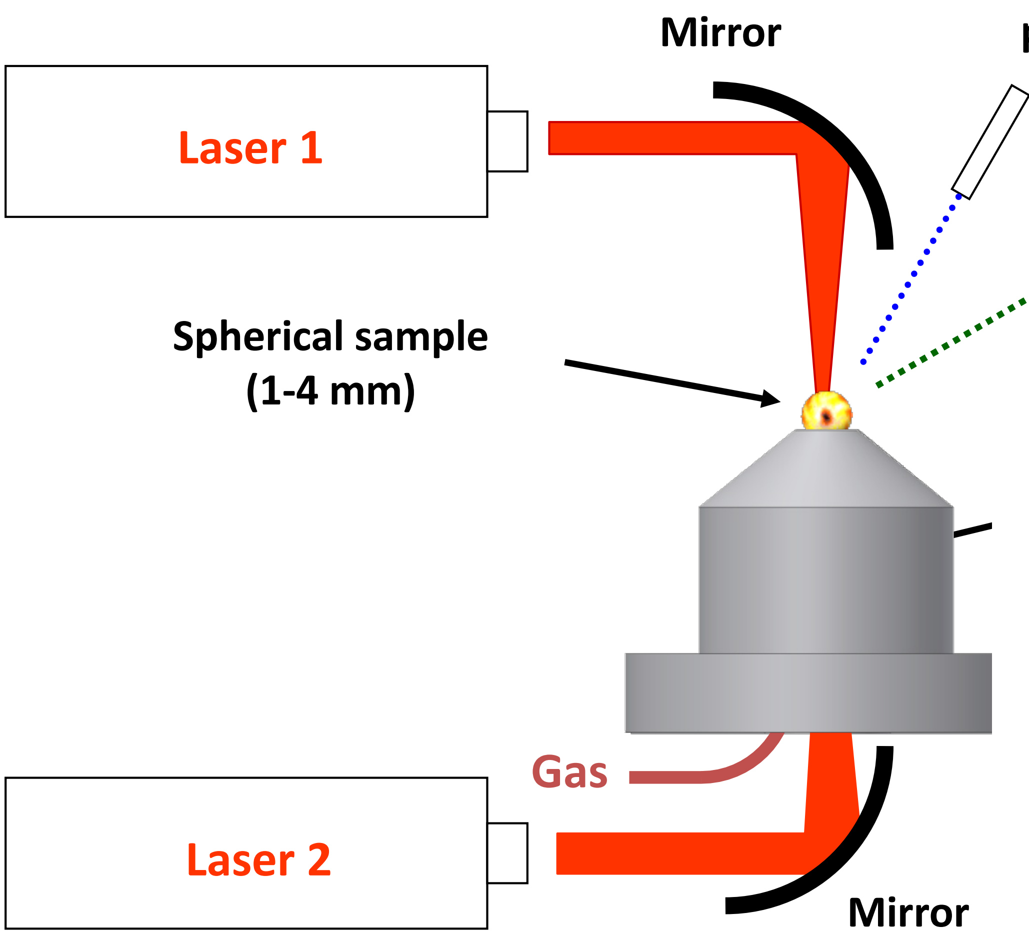
Coe College Physics Department, Warwick

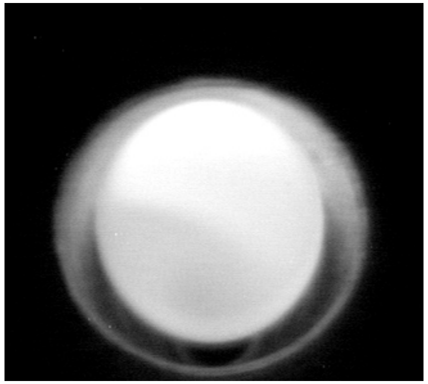
Quench rate ~10^5 K/s

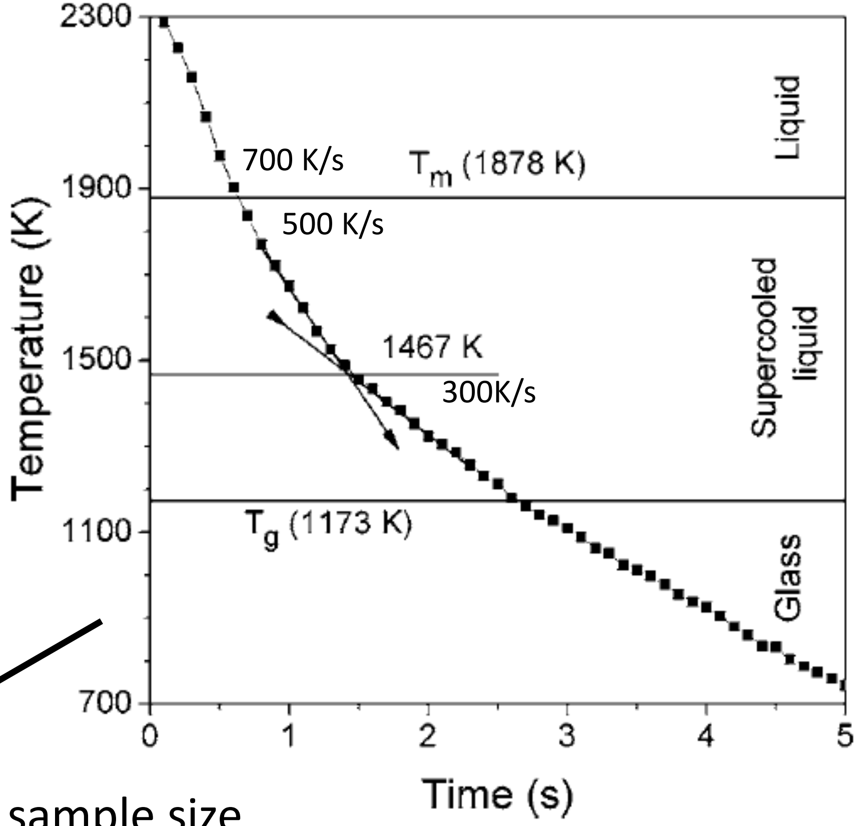
$(PbO)_{80}$-$(SiO_2)_{20}$

L. G. Alderman et al, Phys. Chem. Chem. Phys. 15, 8506 (2013)

Aerodynamic levitation and CO_2 laser heating







Cooling rates ($CaAl_2O_4$)

300-700 K/s

The rate depends on the sample size

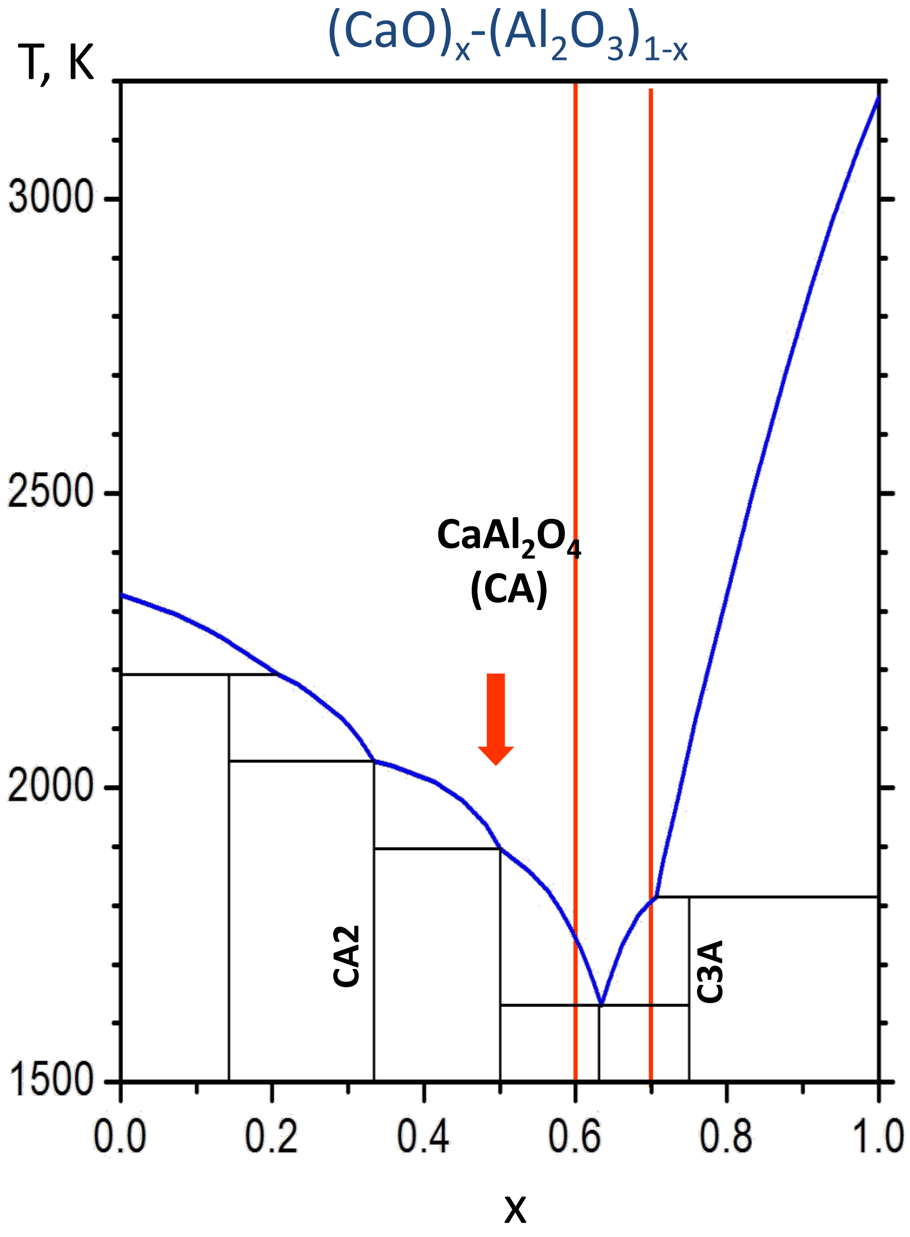
Example : $CaO – Al_2O_3$ phase diagram

With conventional methods :
Narrow vitreous domain
around the eutectic.

$Ca_{12}Al_{14}O_{33}$ (C12A7)
= invert glass

Using levitation techniques
Extension of the vitreous domain to:
$0.37<x<0.75$ (difficult below 0.4)

$Ca_2Al_6O_{11}$ (C2A3)
$CaAl_2O_4$ (CA)
$Ca_3Al_2O_6$ (C3A) = invert glass



Outline

- Silicate glasses
- with a ratio glass modifier/former >1.

What is the role played by the modifier?

  - Binary oxides: SiO_2-MO with M=Ca, Mg
- Aluminate glasses:

What explain the glass forming ability in that case?

Role of Al

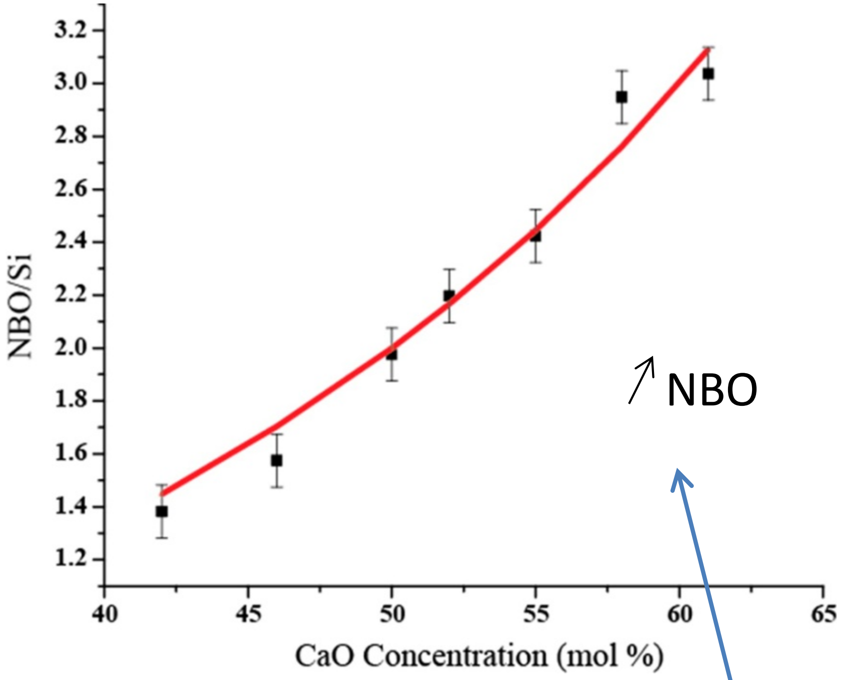
  - Aluminates: Al_2O_3-CaO
- Few words on the system SiO_2-Al_2O_3-CaO

SiO_2-CaO compositions

Glass forming system up to 63% of CaO

D. C. Kaseman et al J.Phys.Chem.B, 119, 8440 (2015)

42 mol % ≤ CaO ≤ 61 mol %

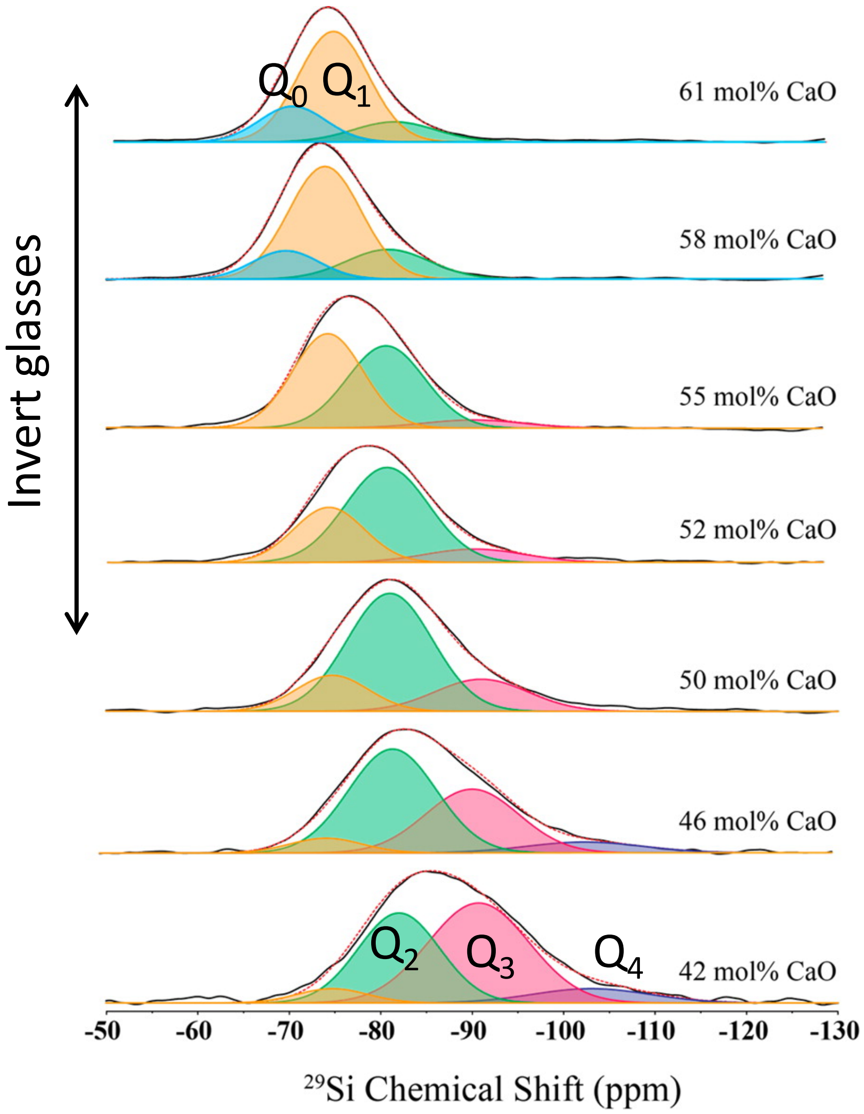


↗ NBO

Progressive replacement

Q_2,Q_3 species → Q_0,Q_1

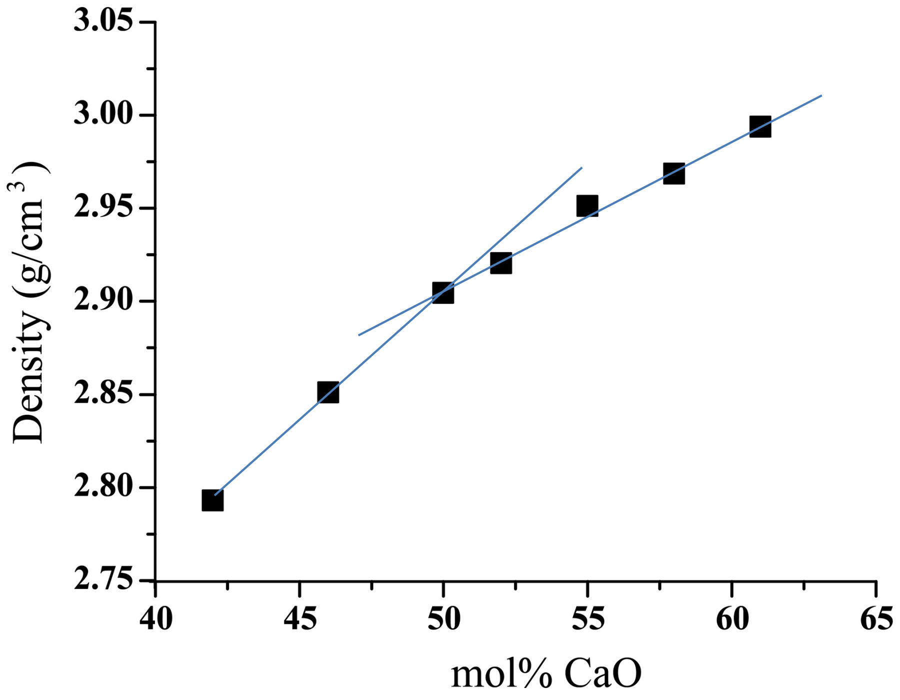
Glasses made using aerodynamic levitation



^{29}Si NMR-MAS spectra

Progressive shift of the center of gravity (increasing chemical shift)

Influence on properties



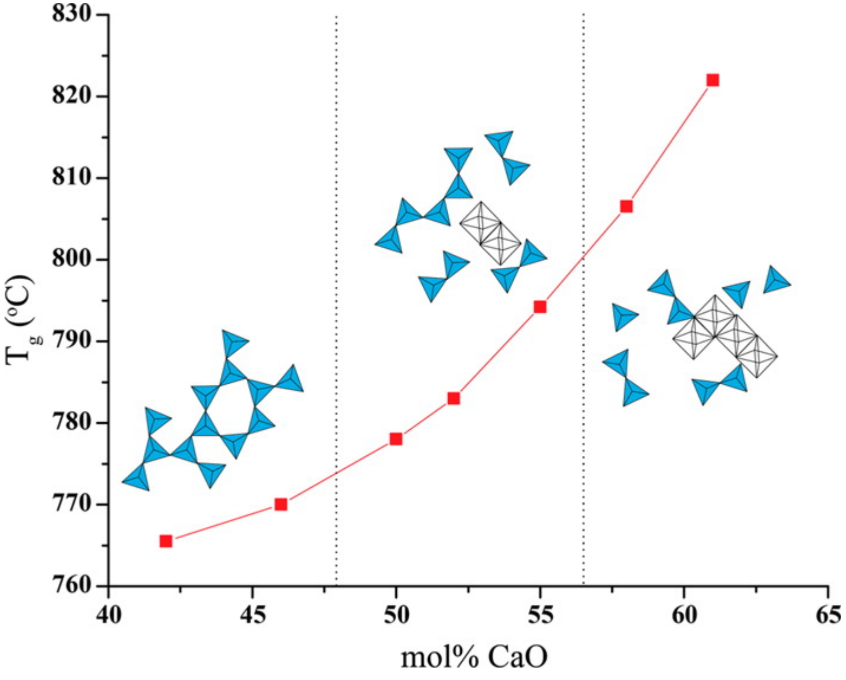
Progressive increase of the density

This increase in packing density in invert glasses is consistent with the progressive replacement of the silicate network dominated by Q_3 and Q_2 species with tightly packed corner- and edge-sharing CaO6 polyhedra in the glass structure

Progressive increase of tg

Same scenario:

At 50%, the glass structure is dominated by chains of Q_2 tetrahedra interspersed with those of CaO6 octahedra.
By increasing the CaO content the Q_2 tetrahedral chains are progressively replaced by Q_1 dimers and Q_0 monomers.
The glass structure repolymerizes via formation of percolating domains of corner and edge-sharing CaO6 octahedra with relatively strong Ca-O bonds that increases the rigidity of the structure.



SiO_2-MgO compositions

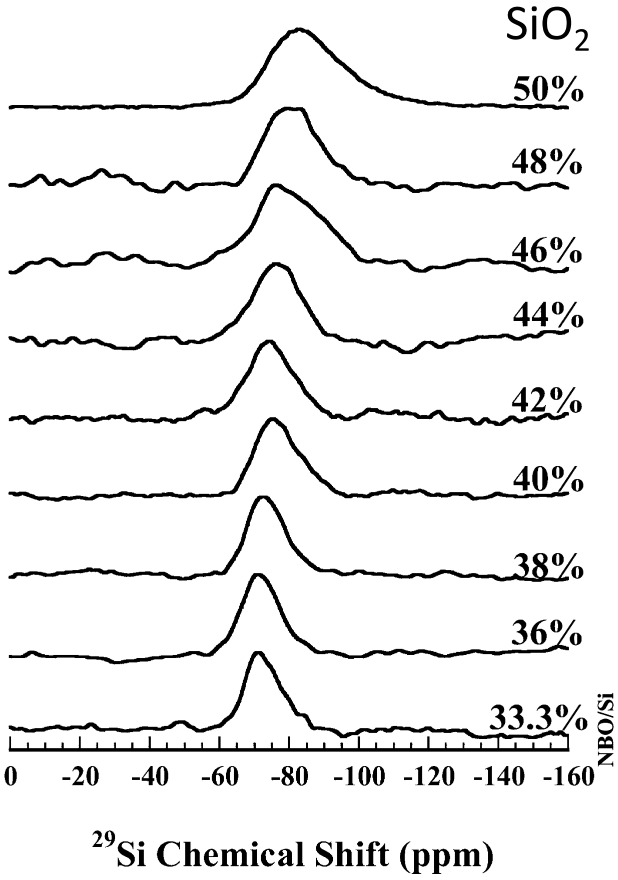
Glass forming system up to 63% of MgO

Glasses made using aerodynamic levitation

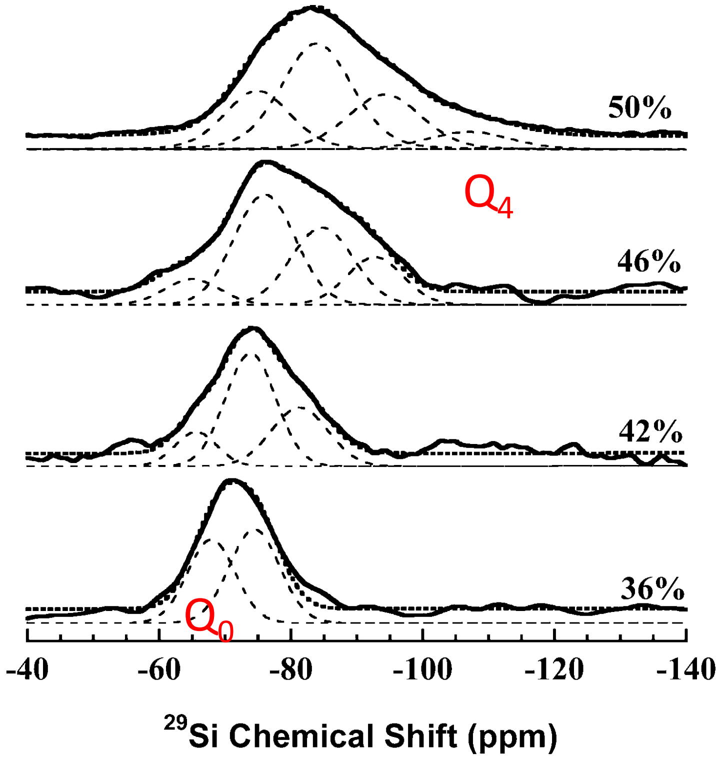
S. Sen et al, J. Phys. Chem. B 2009, 113, 15243−15248.

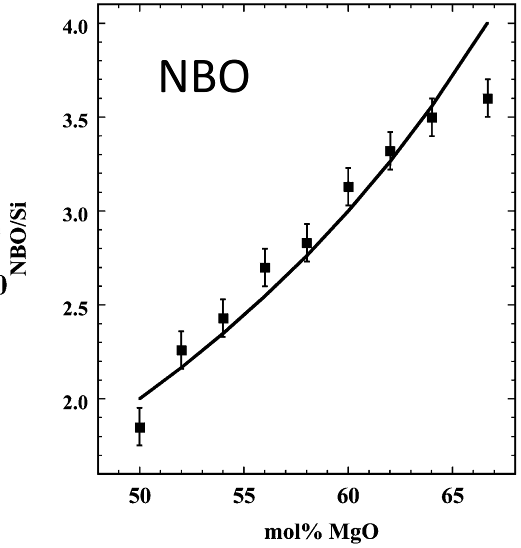
50 mol % ≤ MgO ≤ 67 mol %

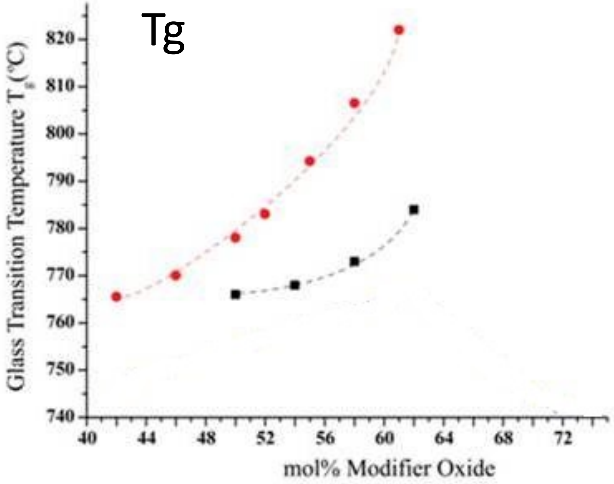
↗ MgO



^{29}Si NMR-MAS spectra



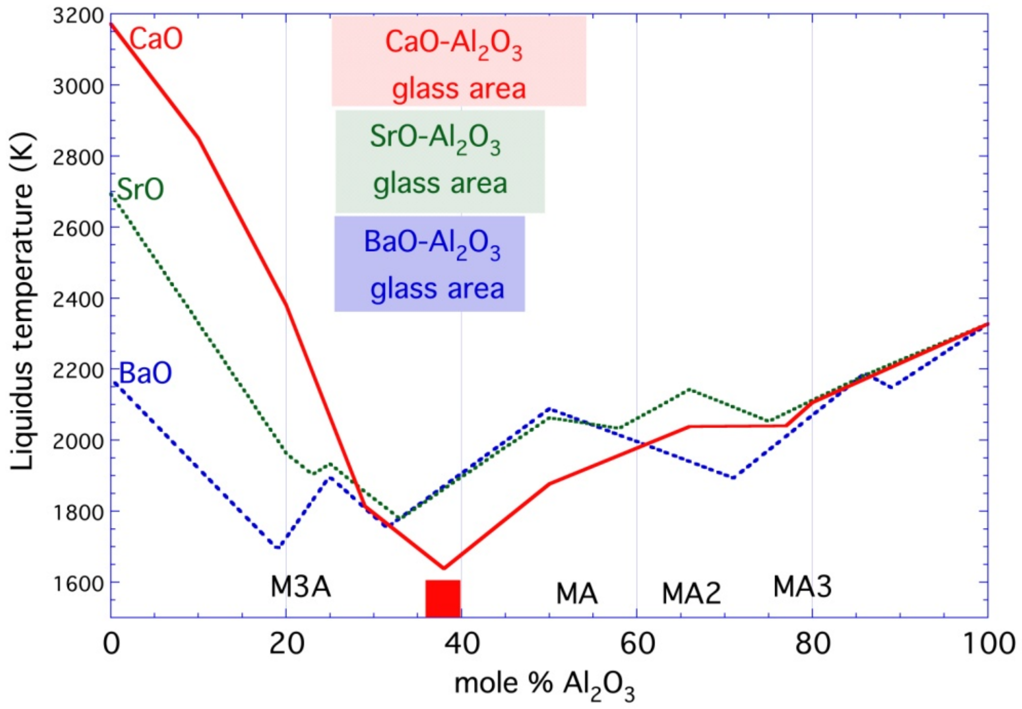




Aluminates : Al_2O_3-MO

M = Ca, Sr, Ba

Glass forming region (with levitation)



M.Licheron et al, J. Non-Cryst. Solids 357 2796–2801 (2011)

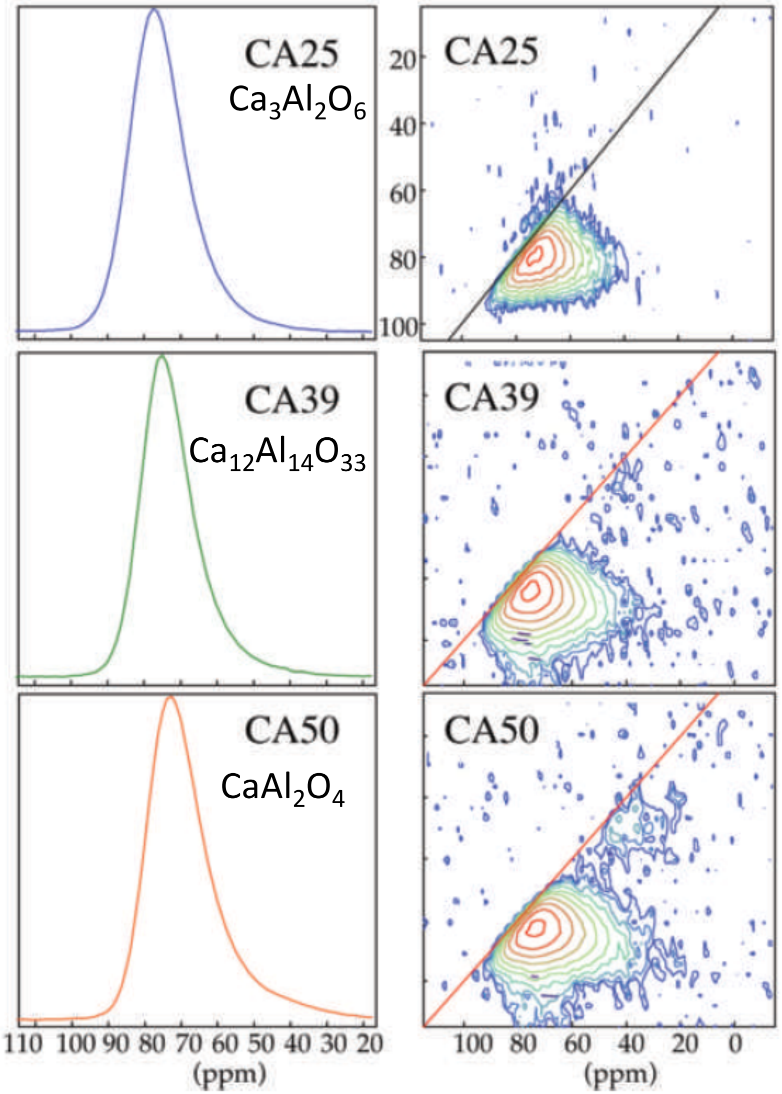
Intermediate	Modifiers
Al_2O_3	CaO SrO BaO

No traditional glass former

How is explained the glass forming ability ?

Aluminates : Al_2O_3-CaO

Glasses



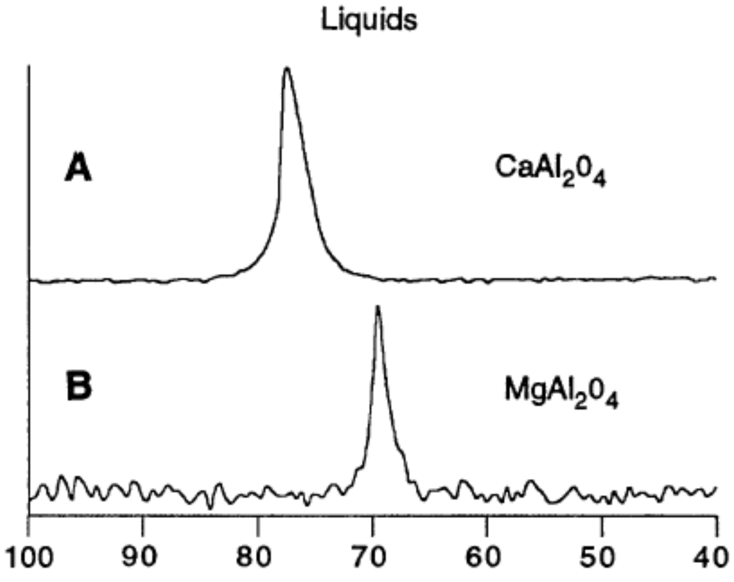
^{27}Al 3QMAS NMR spectra

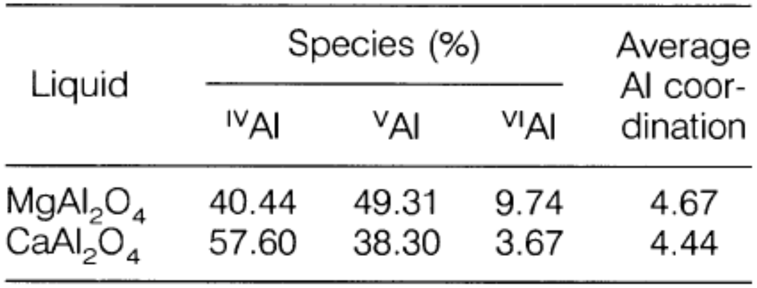
Neuville et al., Am. Min. 95, 1580–1589 (2010)

NMR

CA: CA0.50 : AlO4 (96.5%), AlO5 (3.5%) – Q_4
C12A7: CA0.39 : AlO4 (100%) – Q_3-Q_4
C3A: CA0.25 : AlO4 (100%) – Q_2

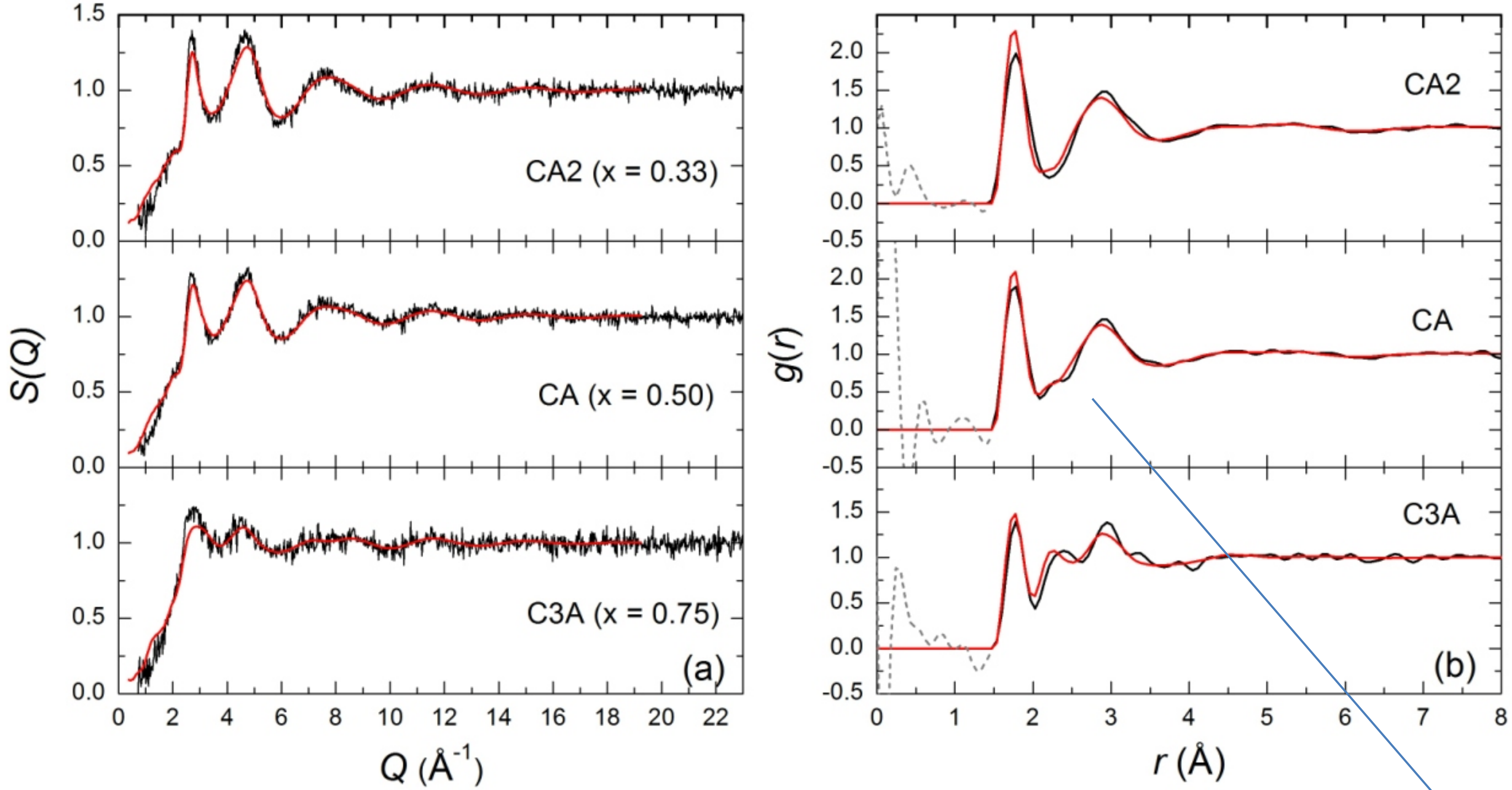
Al on tetrahedral sites.
Al_2O_3 plays a role of network former



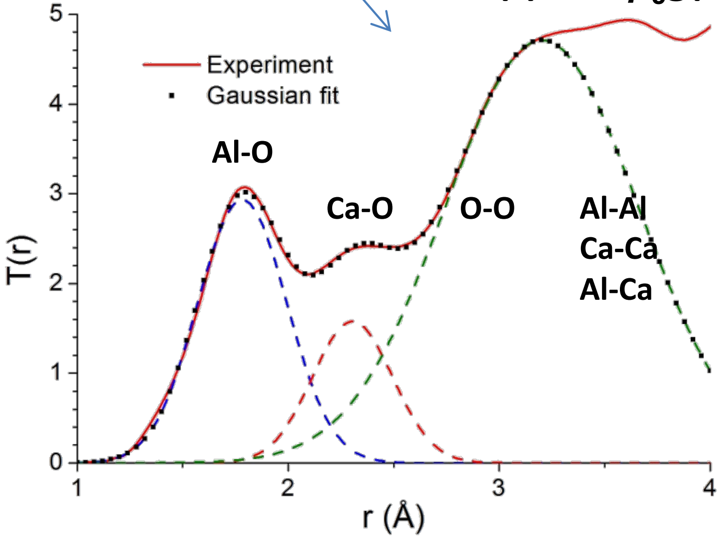


Liquid	Species (%)			Average Al coordination
	^{IV}Al	^{V}Al	^{VI}Al	
$MgAl_2O_4$	40.44	49.31	9.74	4.67
$CaAl_2O_4$	57.60	38.30	3.67	4.44

Poe et al, Science, 259, 786 (1993)



$T(r)=4\pi r\rho_0 g(r)$



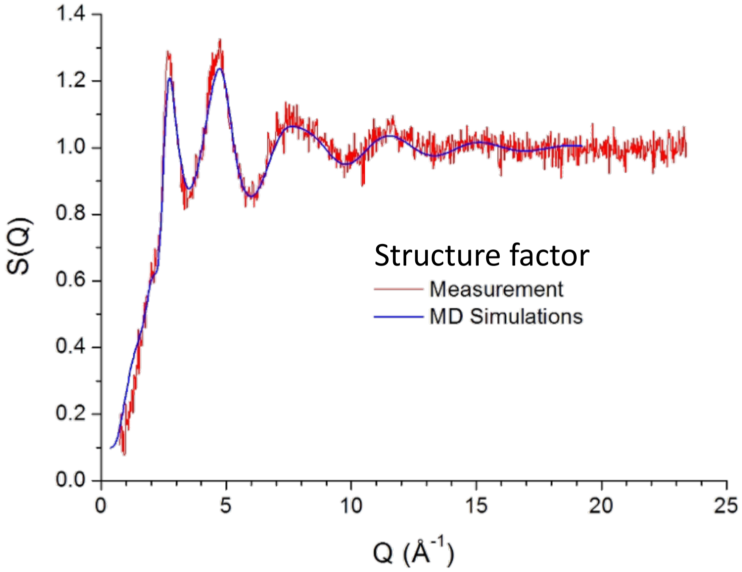
CN are calculated using a Gaussian fit to T(r)

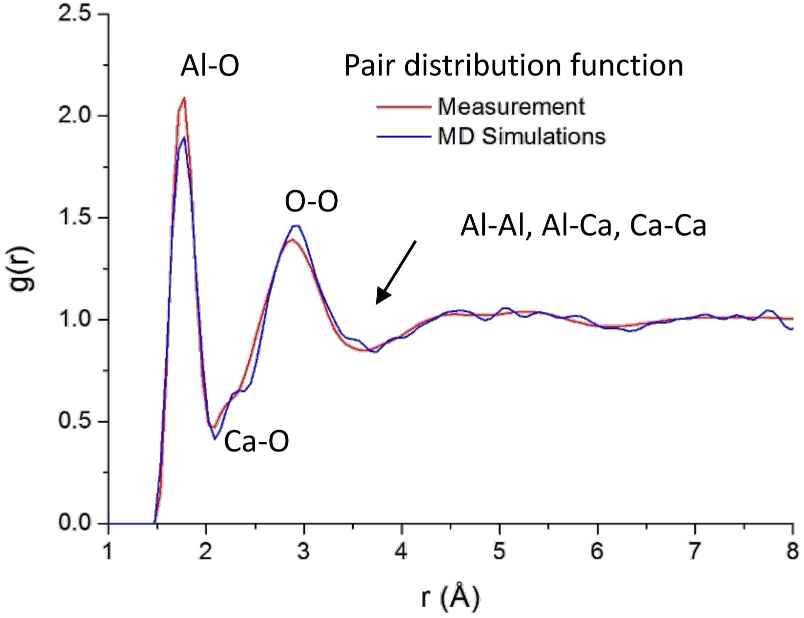
	r_{Al-O}	C_{Al-O}	r_{Ca-O}	C_{Ca-O}
X-rays	1.81 Å	4.5	2.32 Å	4.5-5.5
Neutrons	1.82 Å	4.4	2.34 Å	3.9-5.4

$CaAl_2O_4$ glass: **1.76 Å** **4.0**

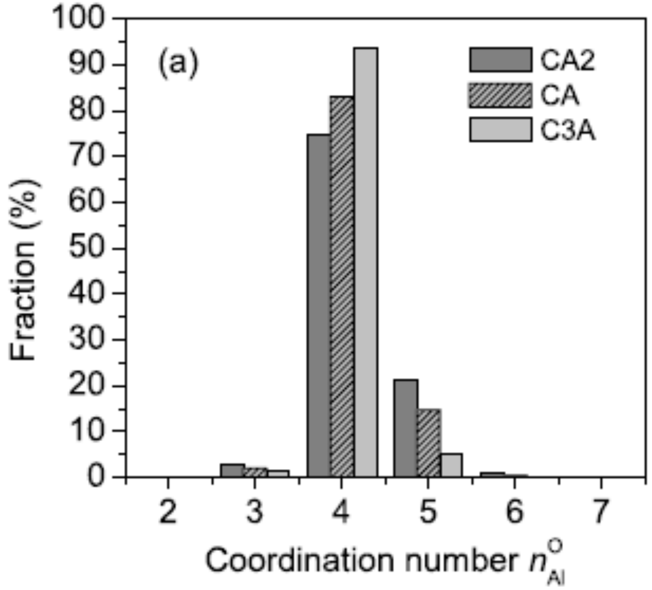
Liquid → Glass ↘ ↘

J.W.E.Drewitt et al, J. Phys. Cond. Mat., 23 155101 (2011)



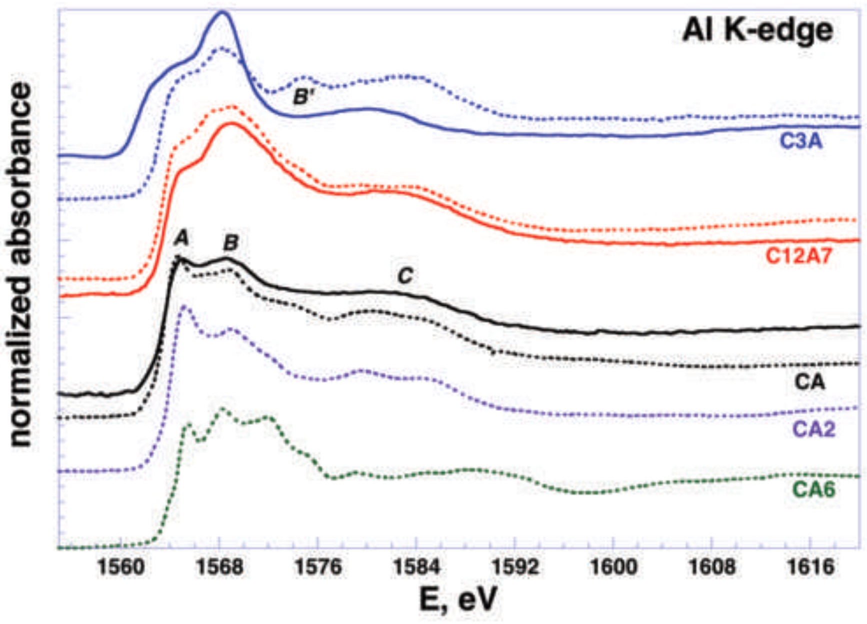


	Exp.	MD
$r_{Al\text{-}O}$	1.78 Å	1.75 Å
$r_{Ca\text{-}O}$	2.30 Å	2.29 Å
$\overline{n}_{Al}^{O}$	4.50	4.13
$\overline{n}_{Ca}^{O}$	3.90-5.5	6.20



J.W.E.Drewitt et al, J. Phys. Cond. Mat., 23 155101 (2011)

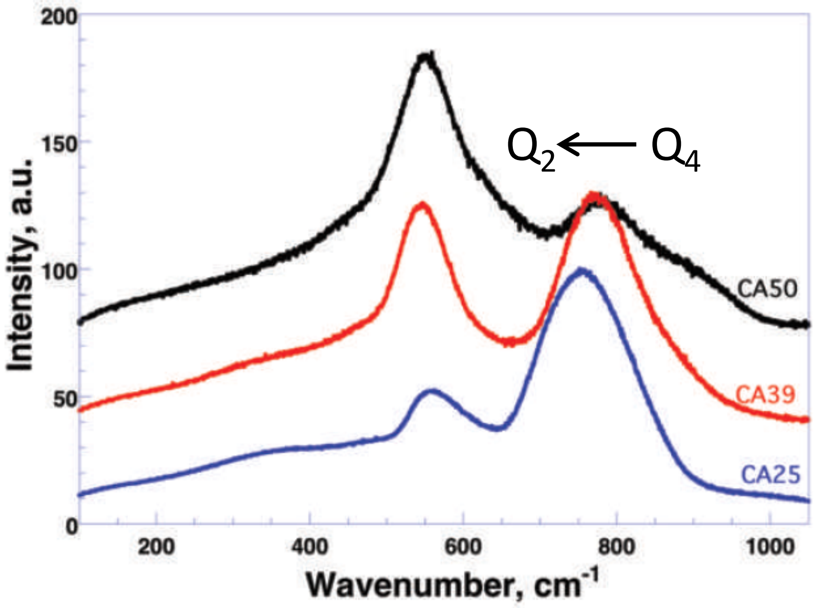
XANES at the Al K absorption edge



The spectra measured on glasses are similar to those ot the corresponding references

CA : Al in Q_4
C12A7 : Mixture Q_4,Q_3
C3A : Al in Q_2

↗ NBO with the CaO content

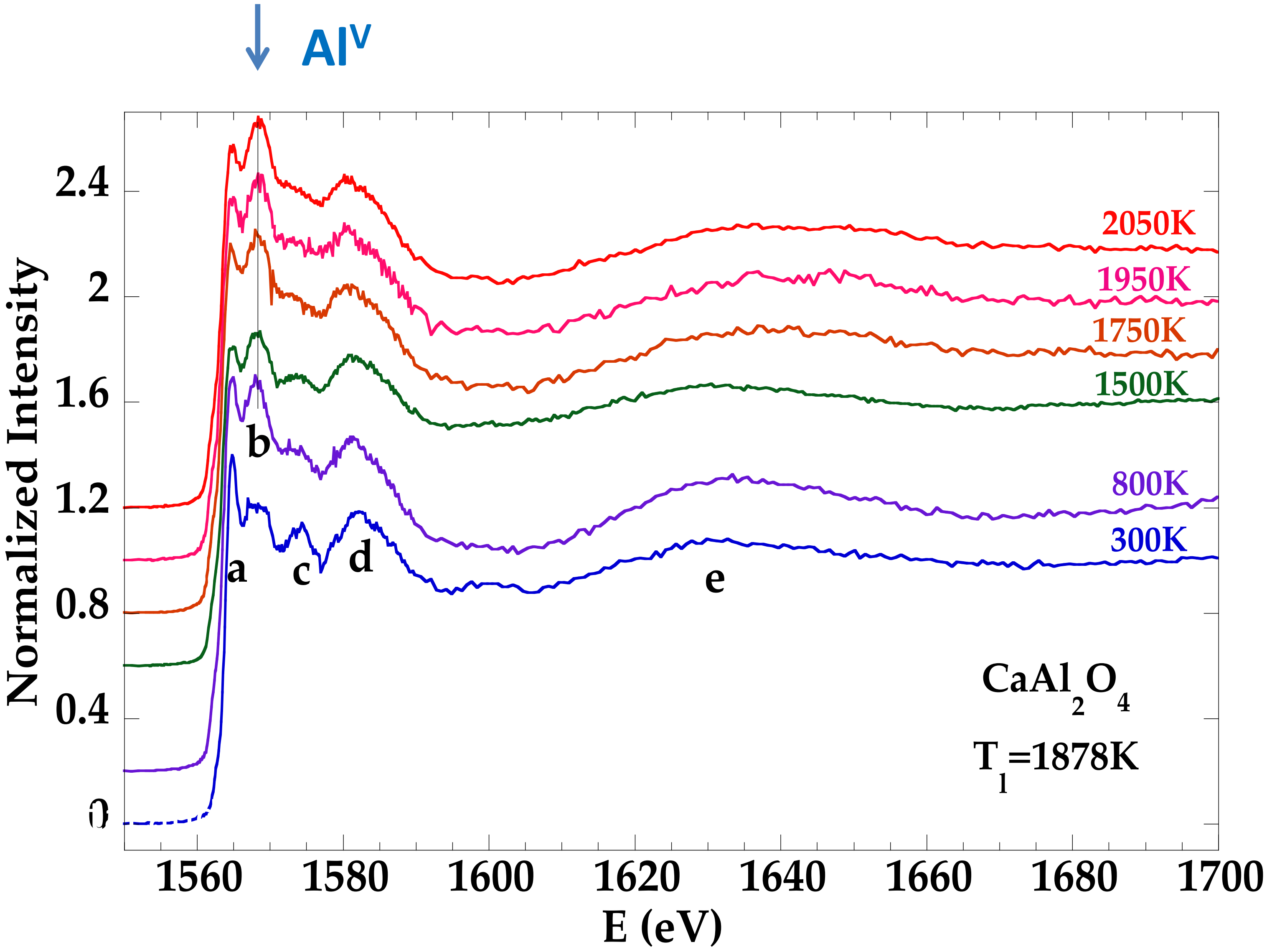


Increase of Q3 and Q2 species also visible with Raman spectroscopy

Shift of the band at 780 cm^{-1}

Neuville et al American Mineralogist, 95, 1580 (2010)

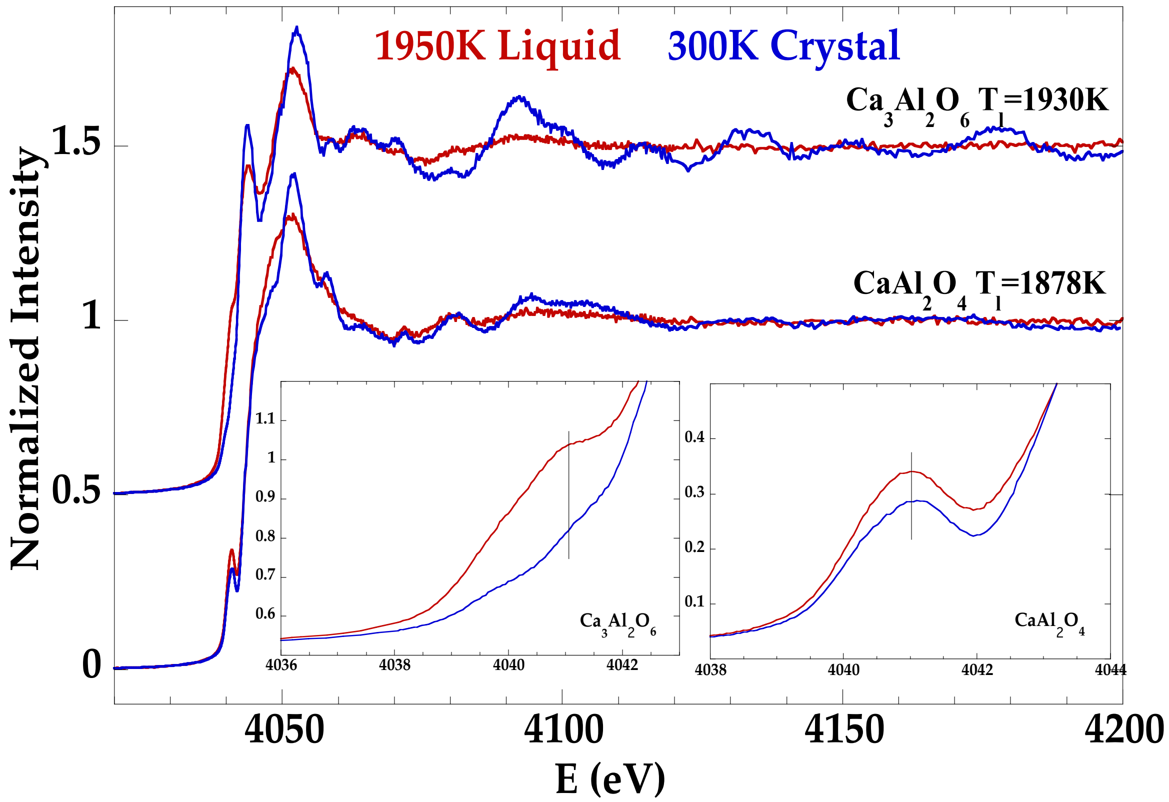
CA = $CaAl_2O_4$



Increase of $^{[5]}Al$ with increasing T
(As observed by NMR)

Neuville et al American Mineralogist, 93, 228-234 (2008)

XANES at the Calcium K absorption edge



C3A ($Ca_3Al_2O_6$)

CA = ($CaAl_2O_4$)

CA : Ca 6-7 fold coordination with a pre-edge at 4041.1eV and no change with temperature

C3A : cubic, Ca 6 fold coordination without pre-edge at RT and with a small pre-edge at 1950K – Perfect CaO6 in the glass.

ND with Isotopic substitution (NDIS)

Principle:

Total interference function :

$$F(Q) = \sum_{\alpha,\beta} c_\alpha c_\beta b_\alpha b_\beta S_{\alpha\beta}(Q) = \sum_{\alpha,\beta} w_{\alpha\beta} S_{\alpha\beta}(Q)$$

$$\alpha, \beta = Ca, Al, O$$

(coherent scattering lengths)

Isotope	**%**	**b_c (fm)**
^{nat}Ca	---	4.70
^{40}Ca	96.941	4.80
^{42}Ca	0.657	3.36
^{43}Ca	0.135	-1.56
^{44}Ca	2.086	1.42
^{46}Ca	0.004	3.60
^{48}Ca	0.187	0.39

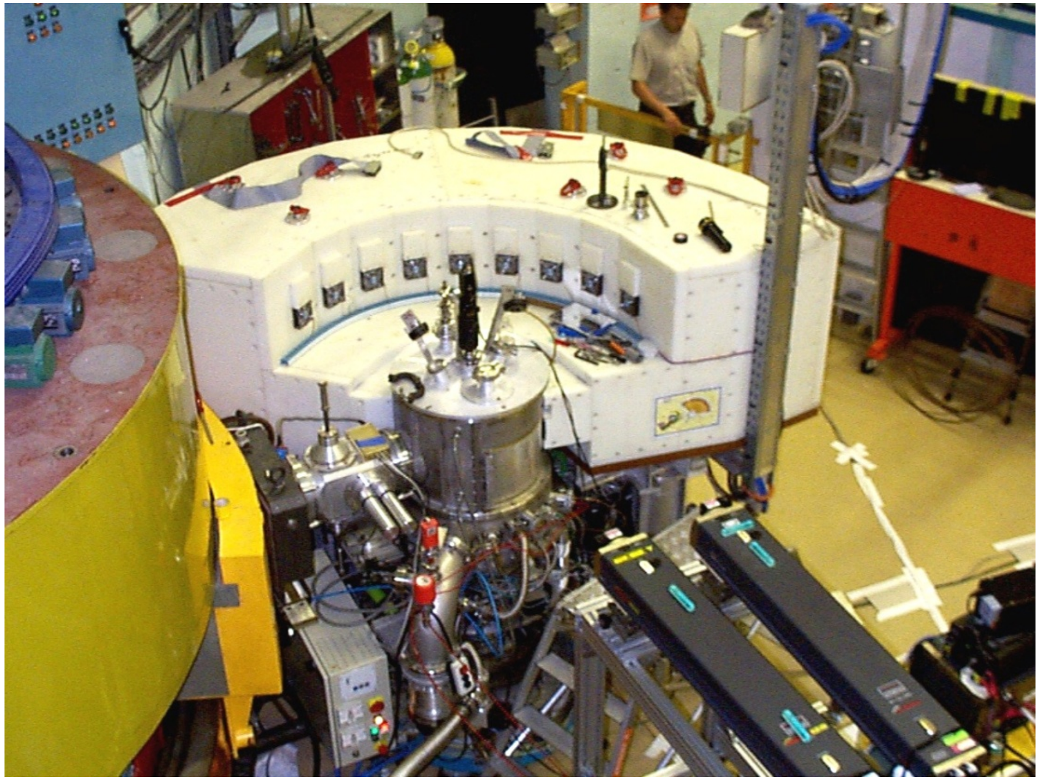
Possible to modify $w_{\alpha\beta}$ by changing $b_{\alpha,\beta}$ with the use of isotopes

In this study, we used ^{nat}Ca and ^{44}Ca

b contrast = 3.28 fm

We made 3 samples :

- $^{nat}CaAl_2O_4$
- $^{44}CaAl_2O_4$
- Mixture of the two (50/50)



$S_{\alpha\beta}(Q)$ functions with $\alpha, \beta \neq Ca$ have identical weightings and can therefore be eliminated by taking the difference function

$$\begin{aligned}\Delta^{Ca}(Q) &= {}^{nat}F(Q) - {}^{44}F(Q) \\ &= \eta\left[S_{CaCa}(Q)-1\right] + \gamma c_O b_O\left[S_{CaO}(Q)-1\right] + \gamma c_{Al} b_{Al}\left[S_{CaAl}(Q)-1\right]\end{aligned}$$

$$\eta = c_{Ca}^2\left(b_{nat}^2 - b_{44}^2\right)$$

$$\gamma = 2c_{Ca}\left(b_{nat} - b_{44}\right)$$

It is also possible to eliminate the partials functions $S_{CaO}(Q)$ and $S_{CaAl}(Q)$ by taking the difference function

$$\begin{aligned}\Delta^{x}(Q) &= \frac{b_{nat}\,{}^{44}F(Q) - b_{44}\,{}^{nat}F(Q)}{b_{nat} - b_{44}} \\ &= c_{Al}^2 b_{Al}^2\left[S_{AlAl}(Q)-1\right] + c_O^2 b_O^2\left[S_{OO}(Q)-1\right] + 2c_{Al}c_O b_{Al} b_O\left[S_{AlO}(Q)-1\right] + \eta\left[S_{CaCa}(Q)-1\right]\end{aligned}$$

Finally, by inverting the matrix equation

$$\begin{bmatrix} {}^{nat}S(Q) \\ {}^{mix}S(Q) \\ {}^{44}S(Q) \end{bmatrix} = \begin{bmatrix} c_{Ca}^2 b_{nat}^2 & 2c_{Ca} b_{nat} & 1 \\ c_{Ca}^2 b_{mix}^2 & 2c_{Ca} b_{mix} & 1 \\ c_{Ca}^2 b_{44}^2 & 2c_{Ca} b_{44} & 1 \end{bmatrix} \cdot \begin{bmatrix} S_{CaCa}(Q) \\ \delta^{Ca}(Q) \\ \delta^{x}(Q) \end{bmatrix}$$

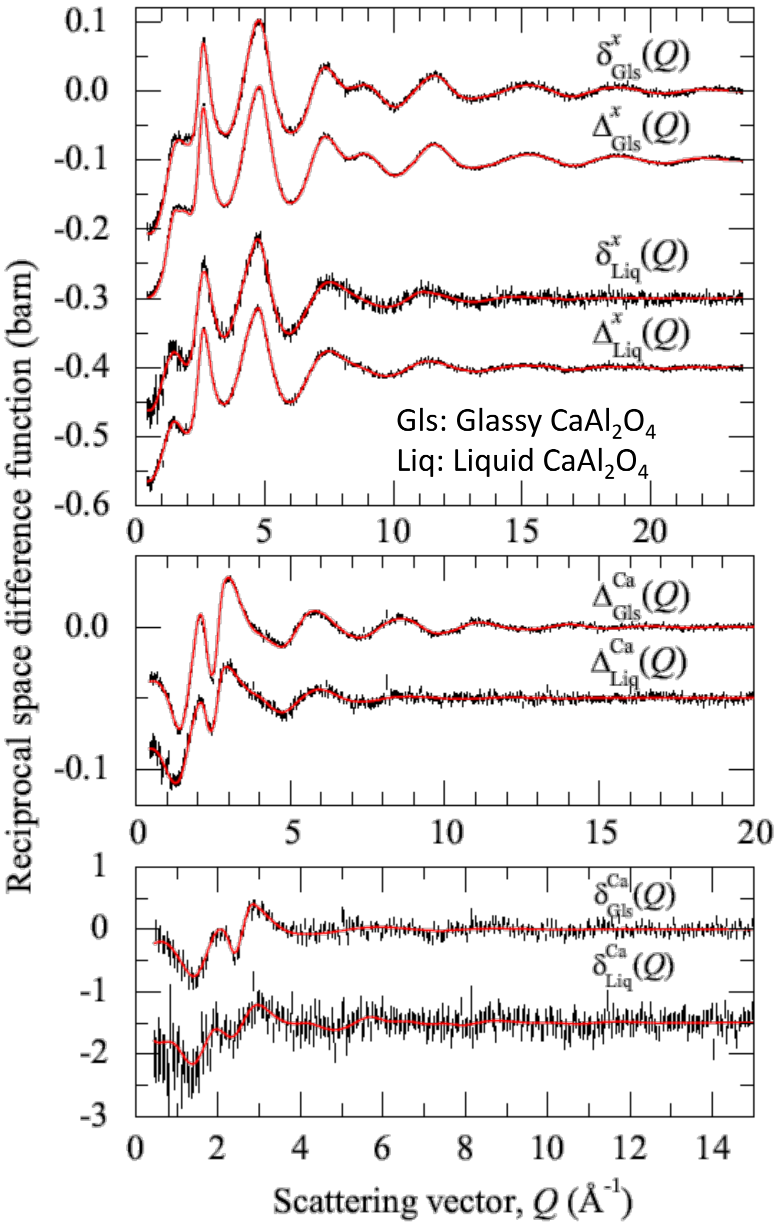
it is possible to extract the 3 functions:

$$S_{CaCa}(Q)$$

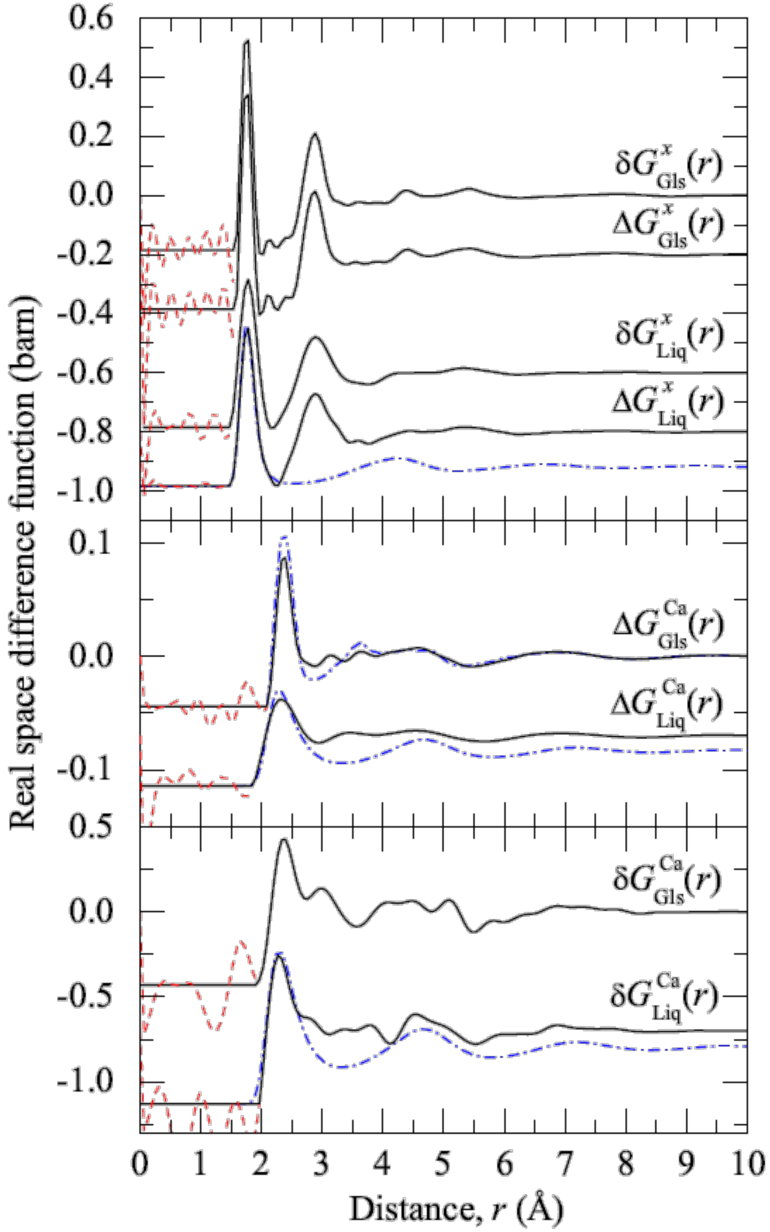
$$\delta^{Ca}(Q) = c_{Al} b_{Al}\left[S_{CaAl}(Q)-1\right] + c_O b_O\left[S_{CaO}(Q)-1\right]$$

$$\delta^{x}(Q) = c_{Al}^2 b_{Al}^2\left[S_{AlAl}(Q)-1\right] + c_O^2 b_O^2\left[S_{OO}(Q)-1\right] + 2c_{Al}c_O b_{Al} b_O\left[S_{AlO}(Q)-1\right]$$

Difference functions

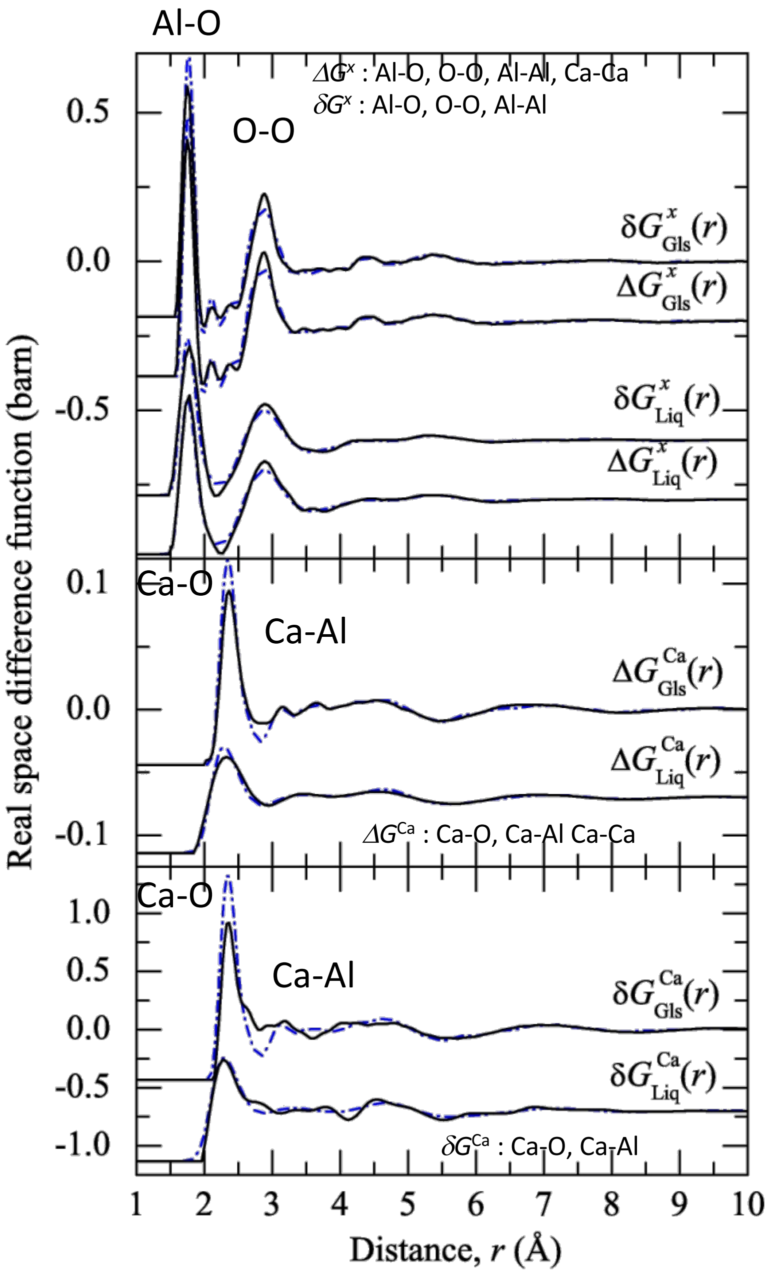


Gls: Glassy $CaAl_2O_4$
Liq: Liquid $CaAl_2O_4$



J.W.E.Drewitt et al Phys. Rev. Lett., 109 235501 (2012)

Real space difference functions



Low contribution of cation-cation pairs

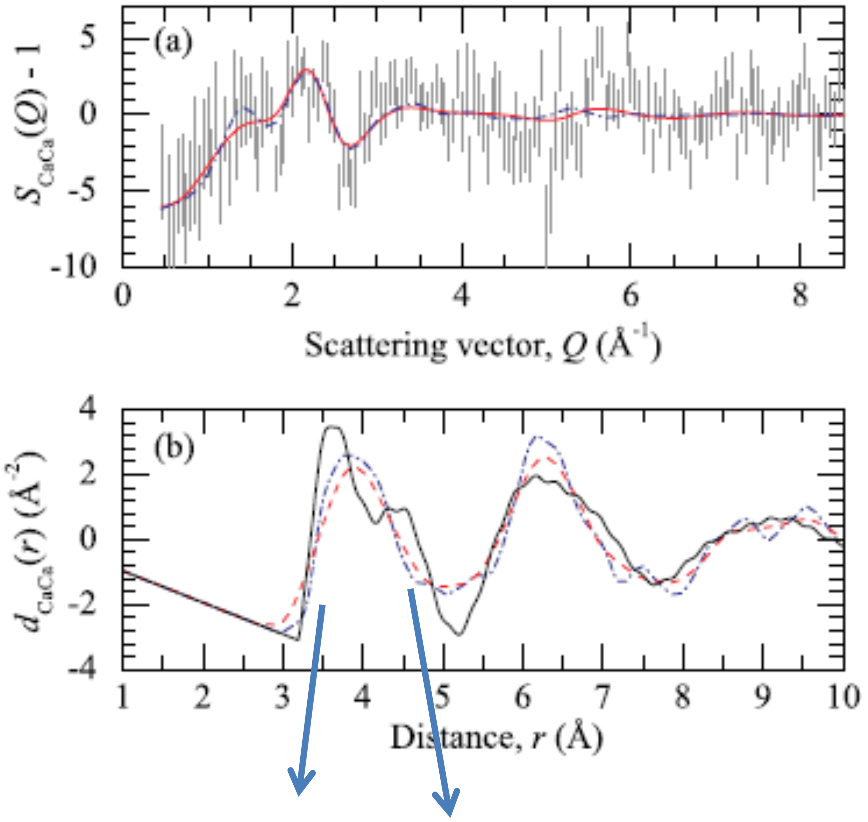
Differences : $\delta G^x(Q), \Delta G^x(Q)$ **Al-O et O-O**

	Liquid	Glass
1st peak (Al-O)		
$r_{Al\text{-}O}$	1.77 Å	1.75 Å
$\overline{n}^{O}_{Al}$	4.2 ^{IV}Al+^{V}Al (20%) few ^{VI}Al*	4.0 ^{IV}Al
2nd peak (O-O)		
$r_{O\text{-}O}$	1.88 Å	
$\widehat{\text{Al-O-Al}}$	107.99°	109.81°

Differences : $\Delta G^{Ca}(Q), \delta G^{Ca}(Q)$ **Ca-O**

1st peak (Ca-O)		
$r_{Ca\text{-}O}$	2.30 Å	2.37 Å
$\overline{n}^{O}_{Ca}$	6.0 (MD : 6.2)	6.5

Ca-Ca correlations



3.59 4.41 Å CN_{Ca}=5.22

The mean Ca-Ca distances for corner-, edge-, and face-sharing polyhedra are 4.40, 3.74, and 3.41 Å, respectively.

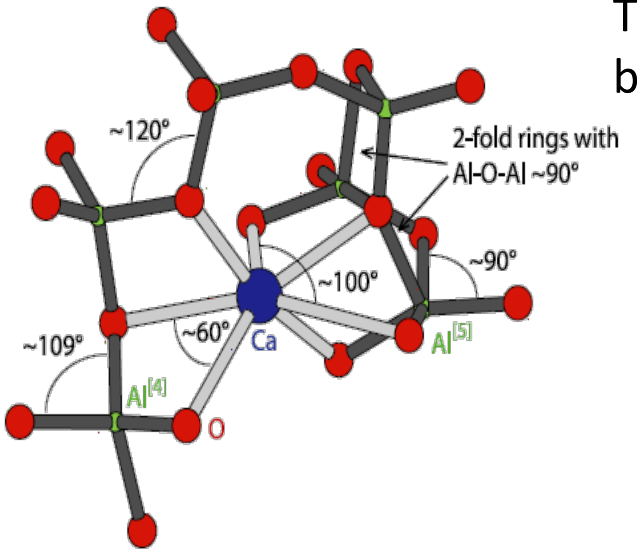
The simulated function has a single peak at rCaCa 3:81 and yields a comparable coordination number of CN_{Ca}=4.9

Formation in the glass of branched chains involving edge- and face-sharing linkages.

Some considerations on the glass forming ability of CA

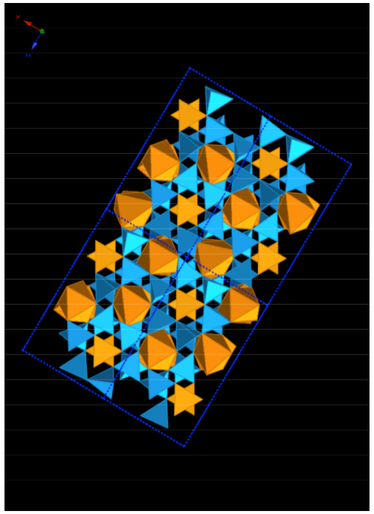
Al_2O_3 does not form a glass by itself which may be explained simply as due to insufficient oxygen atoms being available to form a tetrahedrally connected AlO_4 network and AlO6.

When CaO is added to Al_2O_3 , it increases the O:Al ratio while maintaining charge balance such that, at 50 : 50 CaO:Al_2O_3 ($CaAl_2O_4$) enough oxygen atoms are present to form a fully connected Al-O tetrahedral network.



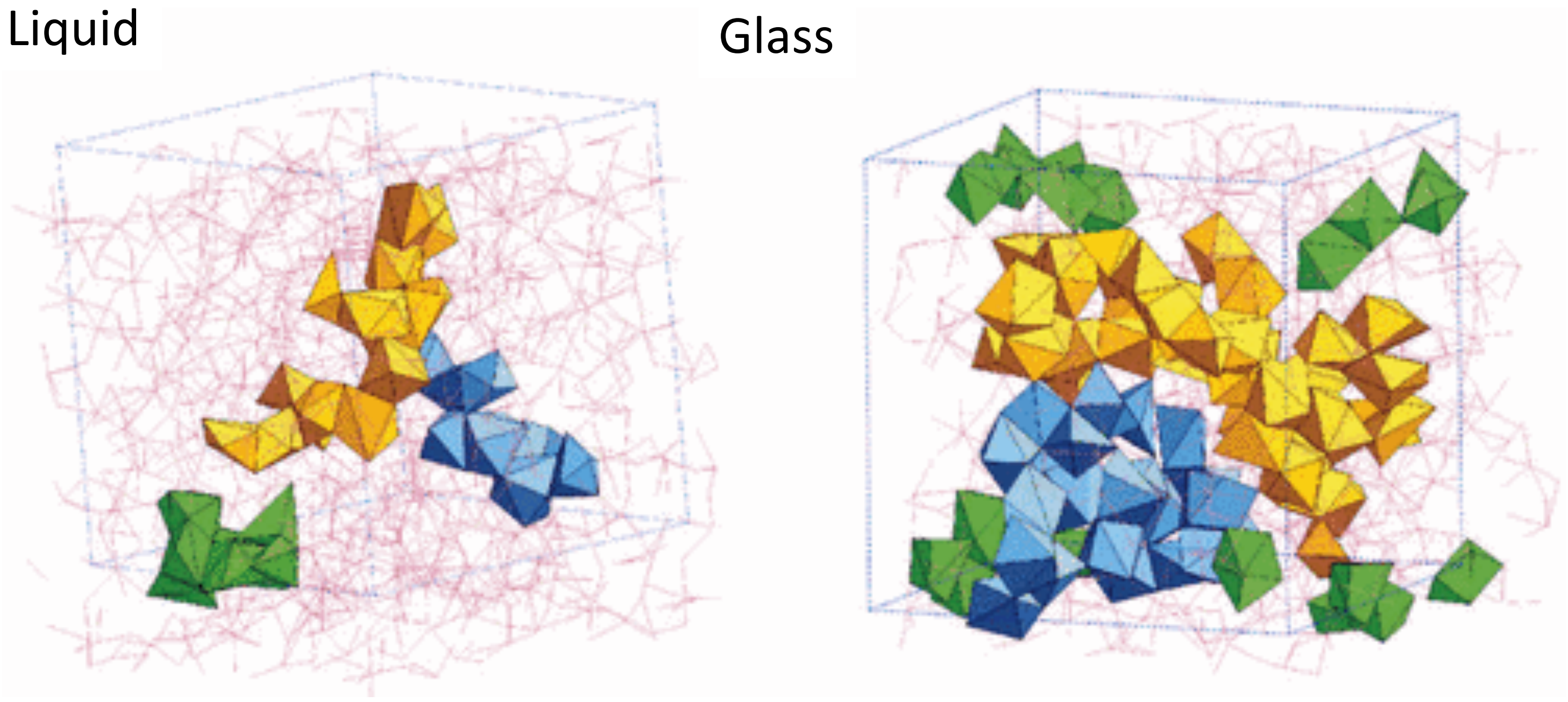
The calcium atoms then locate themselves in the voids between the tetrahedra.

Snapshot taken from the MD simulations at 2500 K



On quenching, the AlO_5 polyhedra reorganize to form a glass network made predominantly from corner sharing AlO_4 tetrahedra. In this process there is a removal of Al-centered edge-sharing motifs (Al06).

The Ca-O coordination number shows a small increase from 6.0(2) to 6.4(2), and there is a large change in the connectivity of the Ca-centered polyhedra with the formation in the glass of branched chains involving edge- and face-sharing linkages.

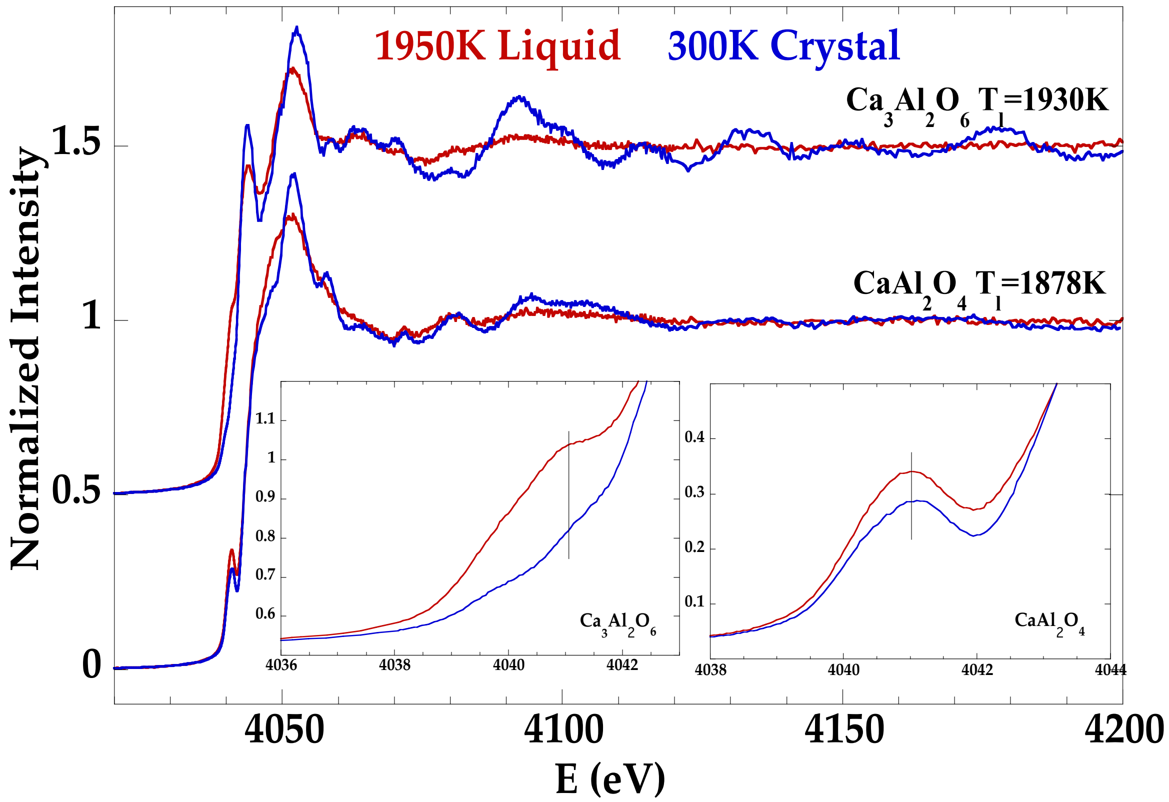

Liquid

Glass

Snapshots illustrating the largest clusters of edge-sharing Ca-centered polyhedra in the MD simulations.

J.W.E.Drewitt et al Phys. Rev. Lett., 109 235501 (2012)

XANES at the Calcium K absorption edge



C3A ($Ca_3Al_2O_6$)

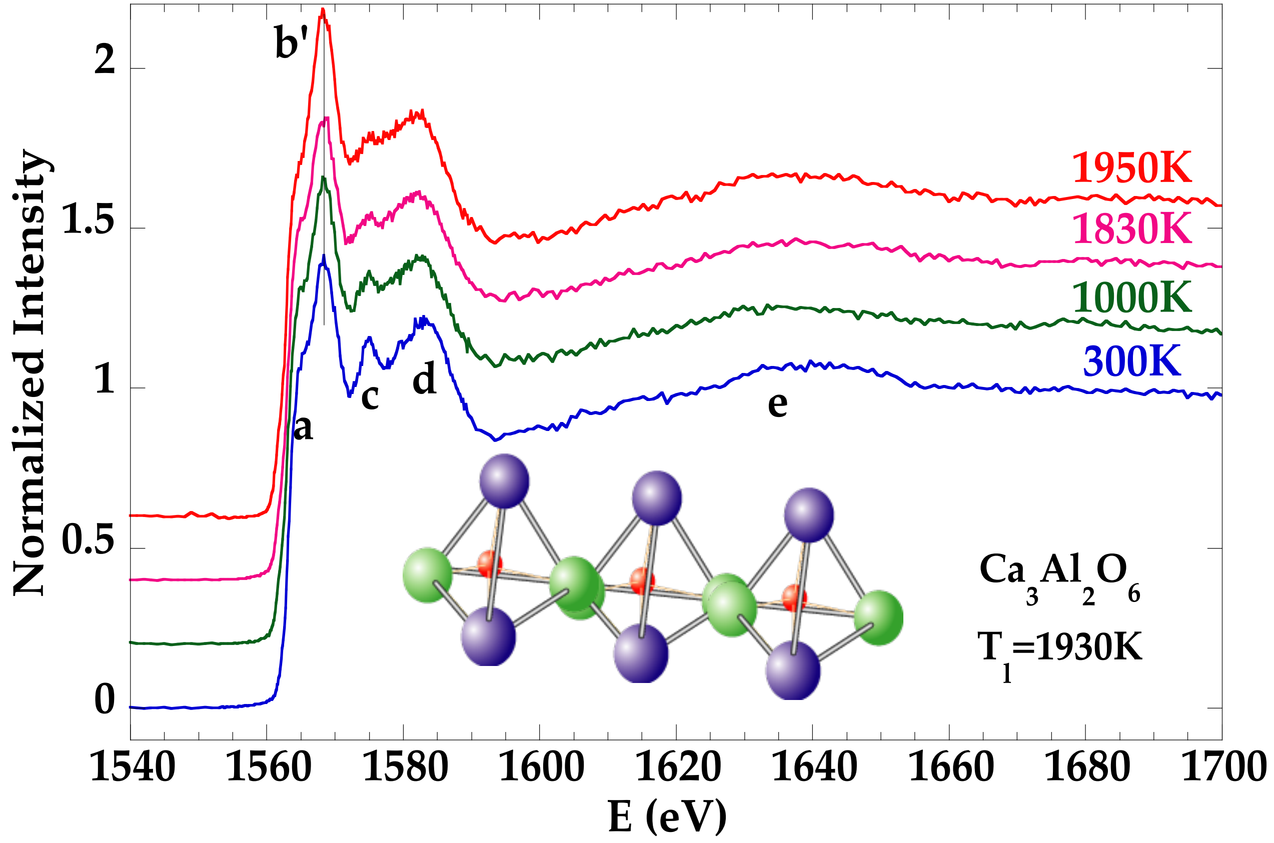
CA = ($CaAl_2O_4$)

CA : Ca 6-7 fold coordination with a pre-edge at 4041.1eV and no change with temperature

C3A : cubic, Ca 6 fold coordination without pre-edge at RT and with a small pre-edge at 1950K – Perfect CaO6 in the glass.

C3A =$Ca_3Al_2O_6$

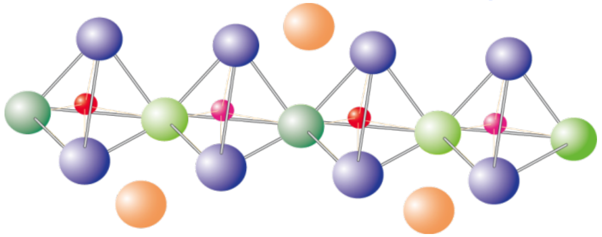
XANES at the Al K absorption edge



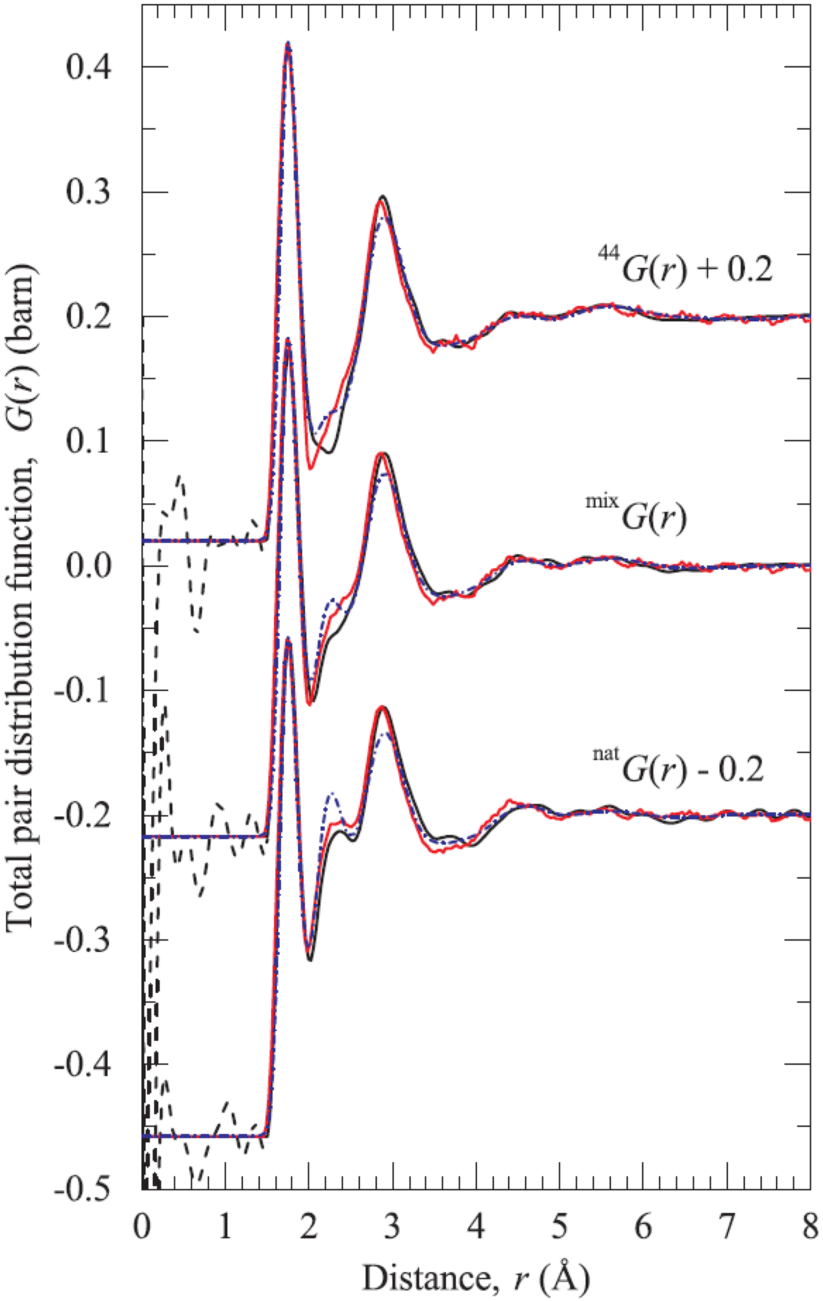
Crystal => Al in 4 fold coordination with 2 Bridging Oxygen, Q^2 species

No change observed with increasing temperature.

Al in Q^2



Neuville et al American Mineralogist, 93, 228-234 (2008)

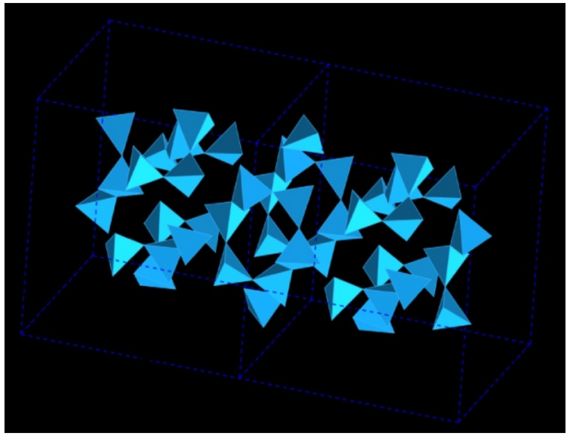


As for CA, we made neutron diffraction with isotopic substitution.

Molecular dynamics (MD) simulation and reverse Monte Carlo (RMC) refinement methods were employed to obtain a detailed atomistic model of the liquid structure.

J.W.E.Drewitt et al Phys. Rev. B., 109 235501 (2012)

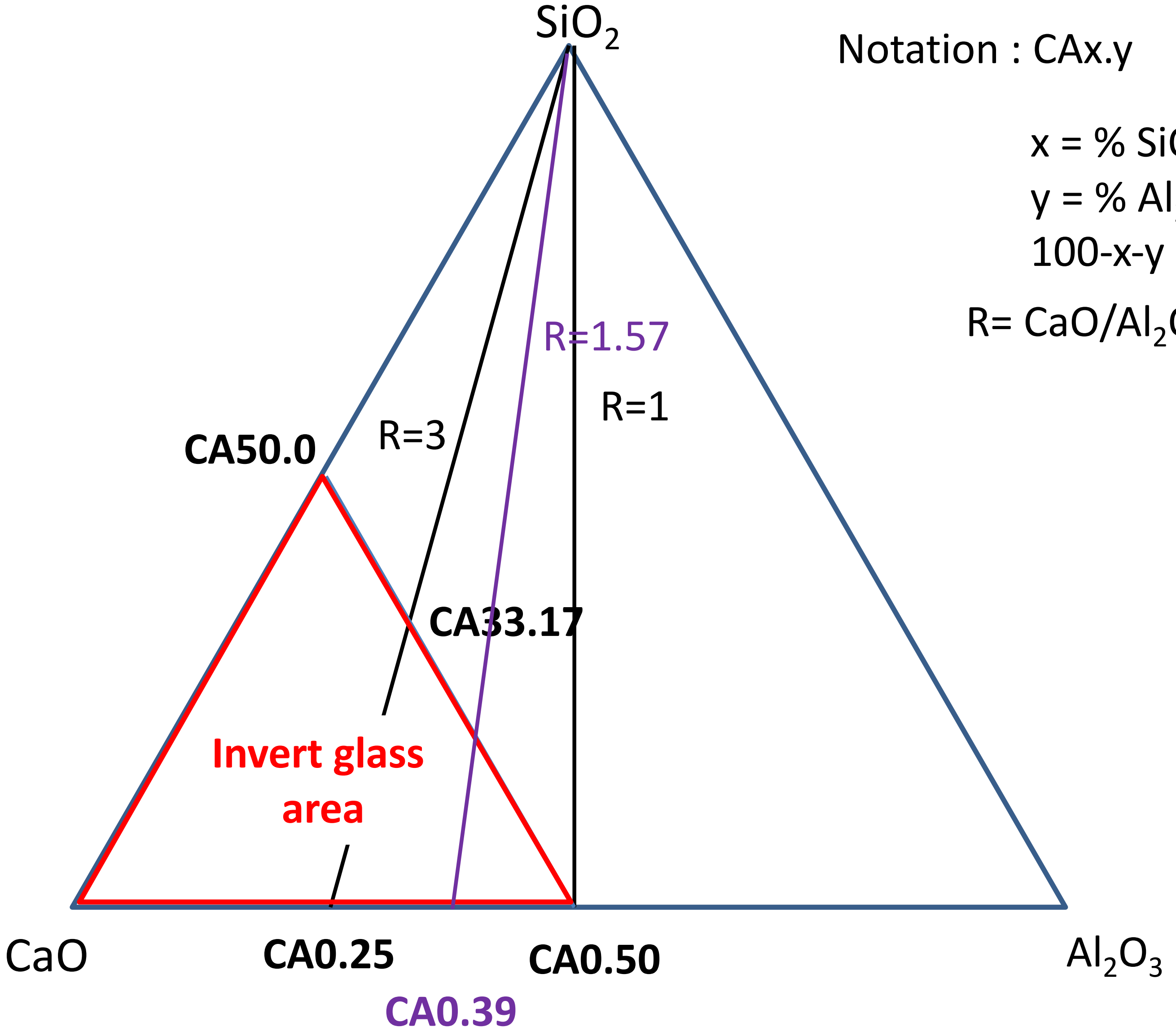
The further addition of CaO does not give rise to higher coordinated aluminum atoms but rather broadly maintains the AlO4 motifs while increasing the number of NBO atoms in the network (Al in Q_2).



As the number of NBO atoms increases, the rigidity and stability of the network will decrease, which would suggest a steady weakening of its glass-forming ability. However, the network may still, to a certain extent, be stabilized by the increased number of Ca atoms occupying voids in the network.

The composition of 75% CaO studied here appears to be the upper limit of the glass forming region for the CaO-Al_2O_3 system.
The results demonstrate that a significant number of unconnected AlO4 monomers and Al2O7 dimers which do not belong to an infinitely connected cluster are already present.
The number of these isolated units is expected to increase as the CaO content increases further.

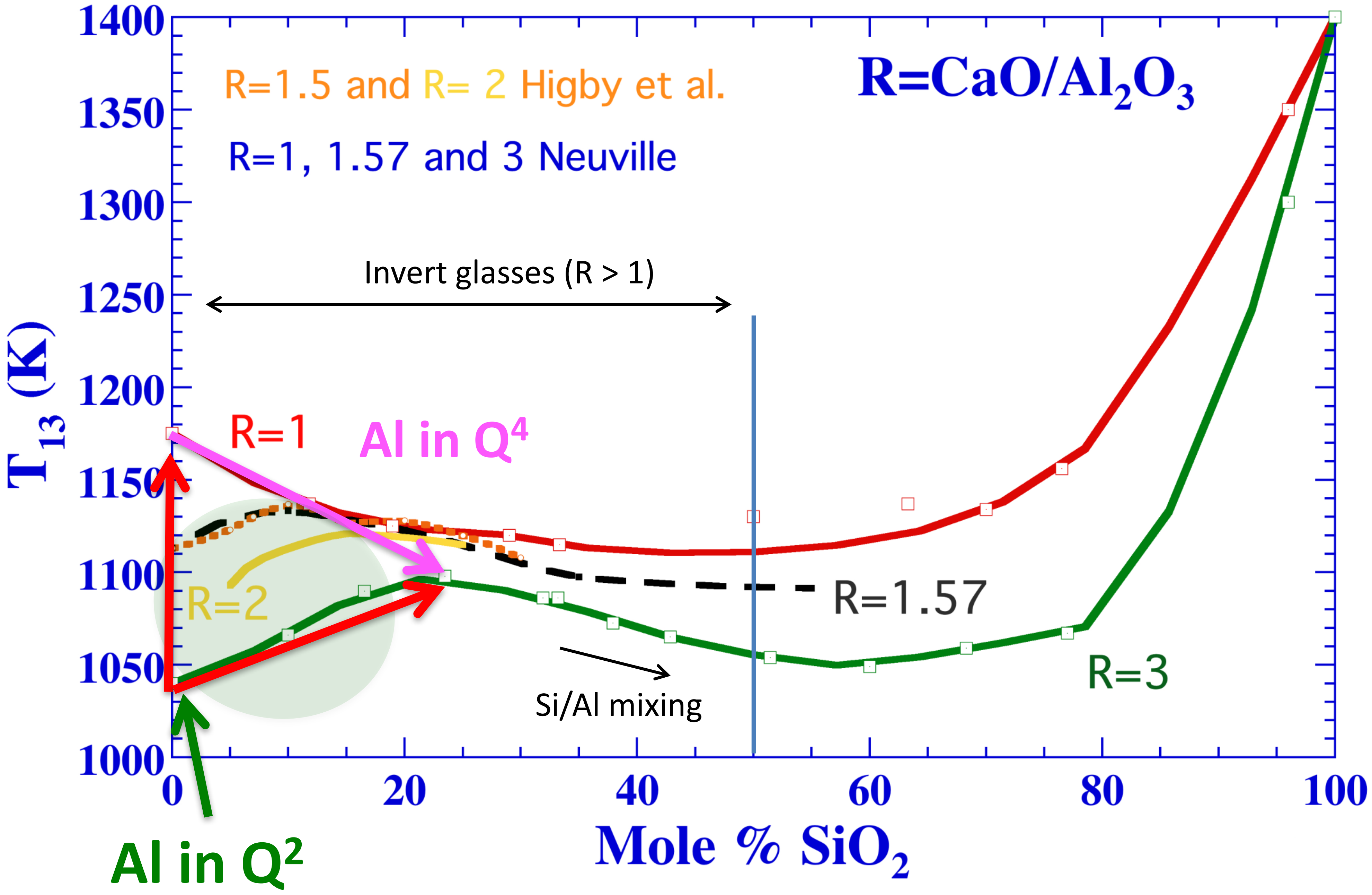
Aluminosilicates : SiO_2-Al_2O_3-CaO



Notation : CAx.y

x = % SiO_2
y = % Al_2O_3
100-x-y = % CaO

R= CaO/Al_2O_3


R=1.5 and R= 2 Higby et al.
R=1, 1.57 and 3 Neuville
R=CaO/Al$_2$O$_3$
Invert glasses (R > 1)
R=1
Al in Q^4
R=2
R=1.57
R=3
Si/Al mixing
Al in Q^2
T_{13} (K)
Mole % SiO$_2$
1400
1350
1300
1250
1200
1150
1100
1050
1000
0
20
40
60
80
100