Modélisation des propriétés thermodynamiques - Prise en compte des effets de pression et de volume

Dominique de Ligny

FRIEDRICH-ALEXANDER
UNIVERSITÄT
ERLANGEN-NÜRNBERG
TECHNISCHE FAKULTÄT

iLM
INSTITUT LUMIÈRE MATIÈRE

UCBL Lyon 1

2 countries - 2 towns - 2 years

DGG ↔ USTV
JOINT MEETING
2019 - 2020

UNION POUR LA SCIENCE ET LA TECHNOLOGIE VERRIÈRES

NÜRNBERG

13-15 of May 2019

MARITIM Hotel Nürnberg
Frauentorgraben 11
D-90443 Nürnberg
http://www.hvg-dgg.de/en/

ORLÉANS

15-19 of June 2020

Orléans University
http://www.ustverre.fr

International School: Thermodynamic of Glass
(TC3 ICG, USTV, DGG)
Erlangen Sunday 12 May 2019

Comity of organization:
Reinhard Conradt, Natalia Vedishscheva, Daniel Neuville, Dominique de Ligny

www.hvg-dgg.de/en/

Content

- Généralité sur le volume
- Evolution de la densité avec la composition
- Volume et temperature fictive
- Densification et pression fictive
- Anomalie elastique et composition

Pressure and Volume with the Gibbs free energy

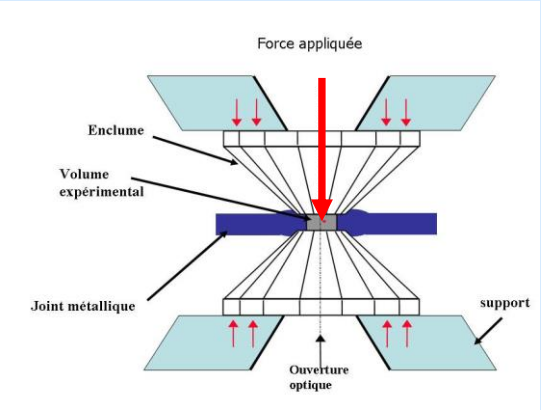
dG=VdP-SdT+$\sum \mu_i \, dn_i$

Volume is the derivative of G by the Pressure

We need: Equation of State
V=f(T,P)

Direct determination or by integration of the bulk modulus **K**

in situ Brillouin



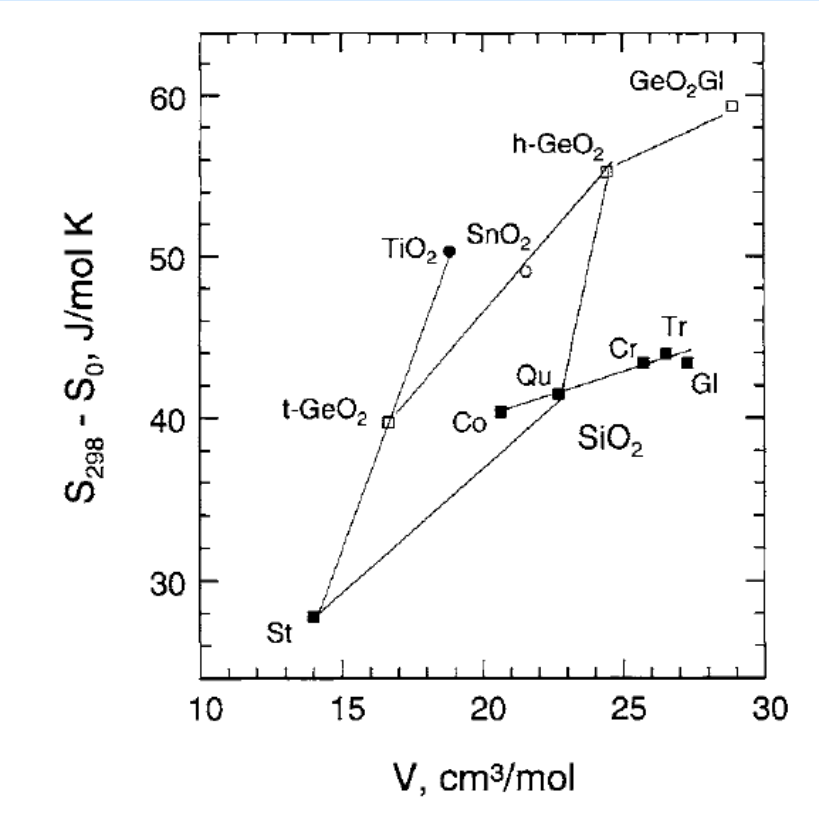
$$\Delta\nu_{180} = \frac{2n \,.\, c}{\lambda}$$

$$c_l = \sqrt{\frac{K + \frac{4}{3}G}{\rho}}$$

Entropy versus Volume

Entropy is sensitive:
- Vibrational properties
- Short range order
- Coordination number

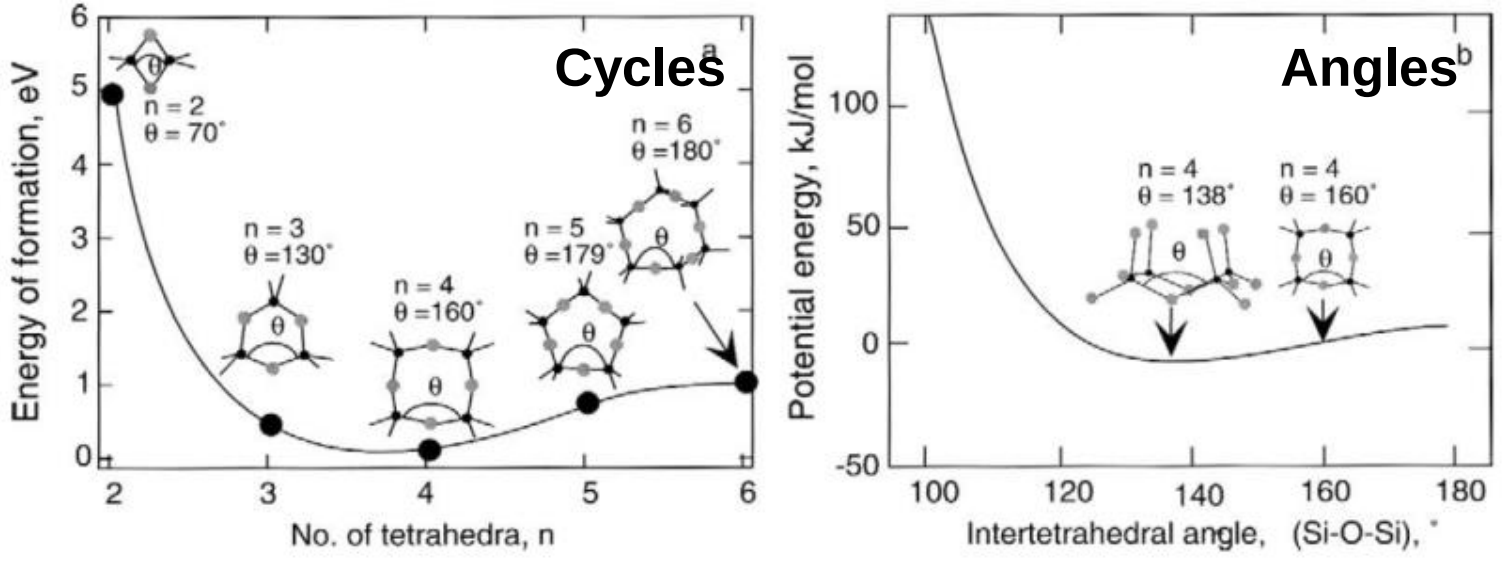
Sens of evolution known



Volume is sensitive:
- Short range order
- Medium range order
- Angles between units

Sens of evolution unknown

Why so much possibilities for SiO_2?

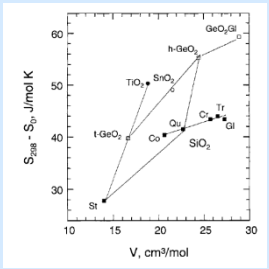


Galeener 82

Gibbs et al. 81

Network very flexible as shown with SiO_2 polymorphs:

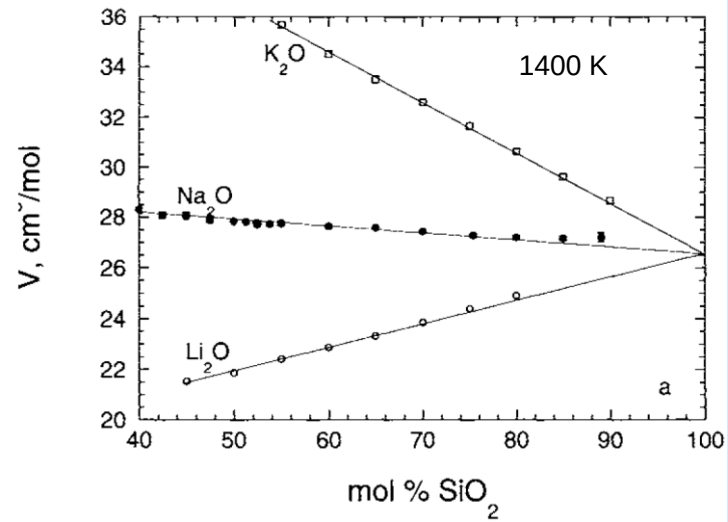
- coesite (n=4)
- quartz (spiral of 6)
- tridymite (n=6)
- cristobalite (n=6)
- zeolites (n=6)



No significant energetic effect

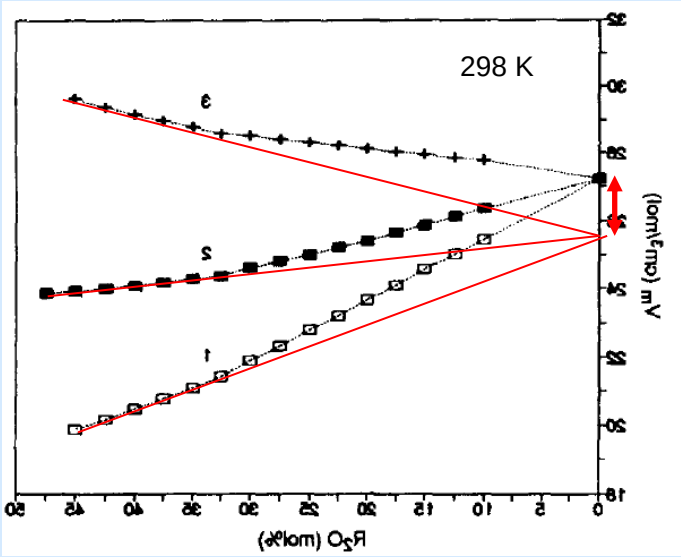
Evolution of volume with the composition

Liquid



Bockris et al. 1956

Glass



H. Doweidar / Journal of Non-Crystalline Solids 194 (1996) 155–162

Liquid additivity of oxides

$$v(T) = \sum_i x_i \overline{v}_i(T)$$

no additivity from oxides

Modelisation of the volume with composition

Using the database SciGlass Priven and Fluegel

$$\text{Density} = b_o + \sum_{i=1}^{n}\left[b_i C_i + \sum_{k=i}^{n}\left(b_{ik} C_i C_k + \sum_{m=k}^{n} b_{ikm} C_i C_k C_m\right)\right]$$

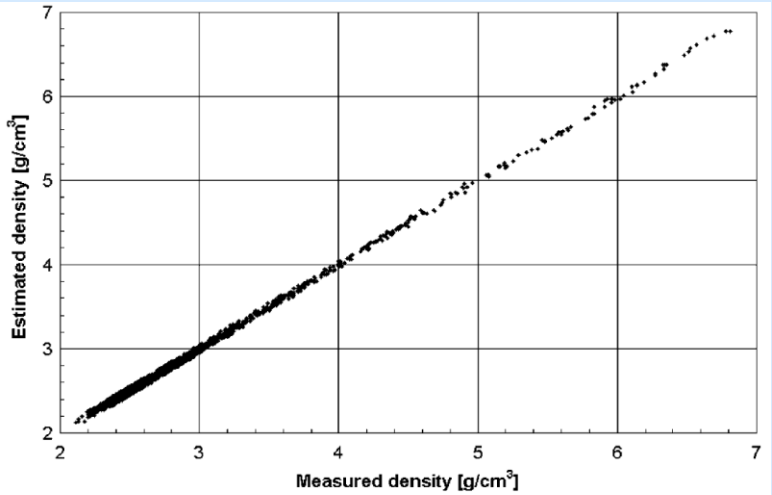


Fig. 2. Plot of 6719 measured versus estimated density values according to the model in Table II.

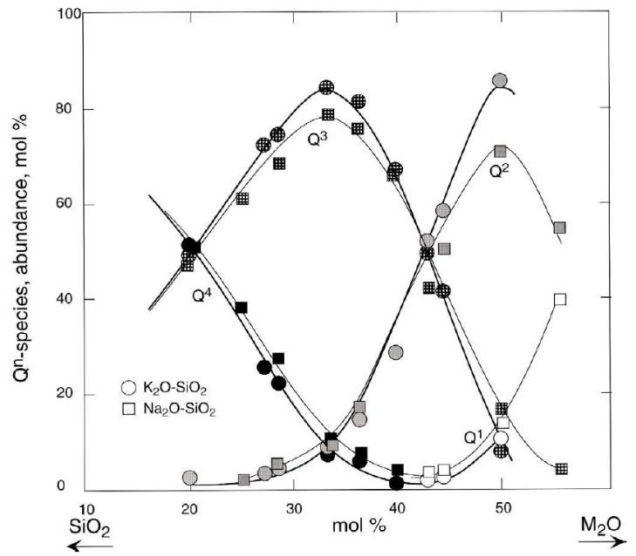
J. Am. Ceram. Soc., **90** [8] 2622–2625 (2007)

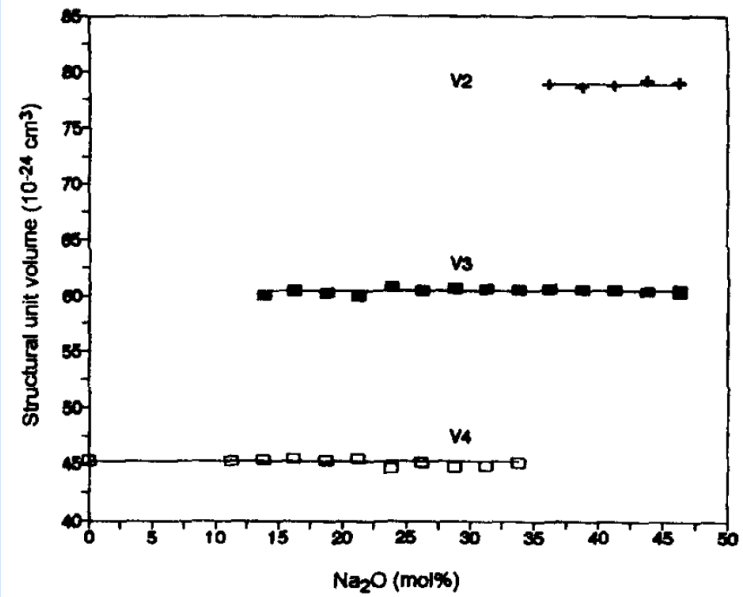
Variable	Coefficient	Variable	Coefficient	Variable	Coefficient
Intercept	2.121560704	CdO	0.052945783	$K_2O \times MgO$	−0.000337747
Al_2O_3	0.010525974	La_2O_3	0.10643194	$K_2O \times CaO$	−0.000349578
$(Al_2O_3)^2$	−0.000076924	Nd_2O_3	0.090134135	$K_2O \times SrO$	−0.000425589
B_2O_3	0.00579283	NiO	0.024289113	$K_2O \times BaO$	−0.000392897
$(B_2O_3)^2$	0.000129174	ThO_2	0.090253734	$Al_2O_3 \times CaO$	−0.000102444
$(B_2O_3)^3$	−0.000019887	U_xO_y	0.063297404	$Al_2O_3 \times PbO$	−0.000651745
Li_2O	0.012848733	Sb_xO_y	0.044258719	$Al_2O_3 \times TiO_2$	−0.000563594
$(Li_2O)^2$	−0.000276404	SO_3	−0.044488661	$Al_2O_3 \times BaO$	−0.000273835
$(Li_2O)^3$	0.00000259	F	0.00109839	$Al_2O_3 \times SrO$	−0.000177761
Na_2O	0.018129123	Cl	−0.006092537	$Al_2O_3 \times ZnO$	−0.000109968
$(Na_2O)^2$	−0.000264838	Remainder†	0.02514614	$Al_2O_3 \times ZrO_2$	−0.002381651
$(Na_2O)^3$	0.000001614	$Na_2O \times K_2O$	−0.000395491	$Na_2O \times PbO$	−0.000036455
K_2O	0.019177312	$Na_2O \times Li_2O$	−0.00031449	$Na_2O \times TiO_2$	−0.00014331
$(K_2O)^2$	−0.000319863	$K_2O \times Li_2O$	−0.000329725	$Na_2O \times ZnO$	−0.000155275
$(K_2O)^3$	0.00000191	$Na_2O \times B_2O_3$	0.000242157	$Na_2O \times ZrO_2$	−0.000126728
MgO	0.01210604	$K_2O \times B_2O_3$	0.000259927	$Na_2O \times Fe_2O_3$	−0.000371343
$(MgO)^2$	−0.000061159	$Li_2O \times B_2O_3$	0.000106359	$K_2O \times PbO$	−0.000525213
CaO	0.017992367	$MgO \times B_2O_3$	−0.000206488	$K_2O \times TiO_2$	−0.000386587
$(CaO)^2$	−0.00005478	$CaO \times B_2O_3$	−0.000032258	$K_2O \times ZnO$	−0.000329812
SrO	0.034630735	$PbO \times B_2O_3$	−0.000186195	$CaO \times PbO$	−0.00084145
$(SrO)^2$	−0.000086939	$Fe_2O_3 \times B_2O_3$	−0.000720268	$ZnO \times Fe_2O_3$	−0.001536804
BaO	0.049879597	$ZrO_2 \times B_2O_3$	−0.000697195	$Na_2O \times K_2O \times B_2O_3$	−0.000032967
$(BaO)^2$	−0.000168063	$Al_2O_3 \times B_2O_3$	−0.000735749	$Na_2O \times MgO \times CaO$	−0.000009143
ZnO	0.025221567	$Li_2O \times Al_2O_3$	−0.000116227	$Na_2O \times MgO \times Al_2O_3$	−0.000012286
$(ZnO)^2$	0.000099961	$Na_2O \times Al_2O_3$	−0.000253454	$Na_2O \times CaO \times Al_2O_3$	−0.000005106
PbO	0.070020298	$K_2O \times Al_2O_3$	−0.000371858	$Na_2O \times CaO \times PbO$	0.000100796
$(PbO)^2$	0.000214424	$MgO \times CaO$	0.000057248	$K_2O \times MgO \times CaO$	−0.00001217
$(PbO)^3$	−0.000001502	$MgO \times Al_2O_3$	0.000167218	$K_2O \times MgO \times Al_2O_3$	−0.000041908
Fe_xO_y	0.036995747	$MgO \times ZnO$	0.000220766	$K_2O \times CaO \times Al_2O_3$	−0.000012421
Mn_xO_y	0.016648722	$Li_2O \times CaO$	−0.00008792	$K_2O \times CaO \times PbO$	0.000125759
TiO_2	0.018820343	$Na_2O \times MgO$	−0.000300745	$MgO \times CaO \times Al_2O_3$	−0.000011236
ZrO_2	0.043059714	$Na_2O \times CaO$	−0.000228249	$CaO \times Al_2O_3 \times Li_2O$	−0.000016177
$(ZrO_2)^2$	−0.000779078	$Na_2O \times SrO$	−0.00023137	$Al_2O_3 \times B_2O_3 \times PbO$	0.000030116
Ce_xO_y	0.061277268	$Na_2O \times BaO$	−0.000171693		

Modelisation of the volume with composition

Molecular Approach
Doweidar

Additive model on the Qn species

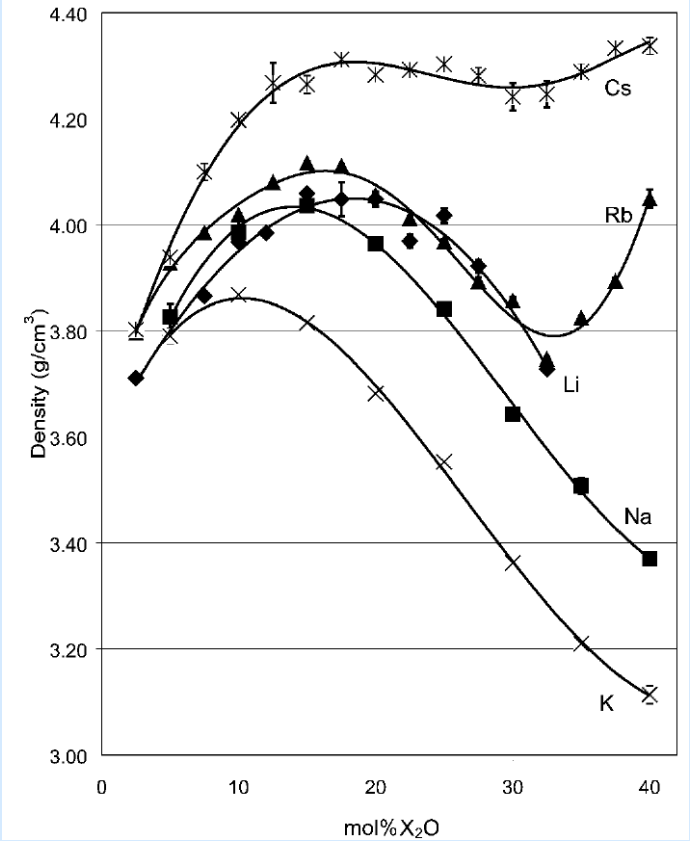




H. Doweidar / Journal of Non-Crystalline Solids 194 (1996) 155–162

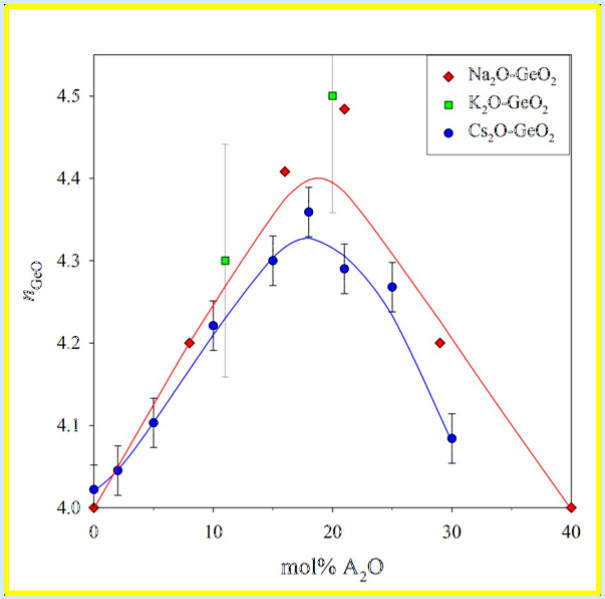
Here a structural model is needed

Modelisation of the volume with composition



Effect more complex with change of coordination

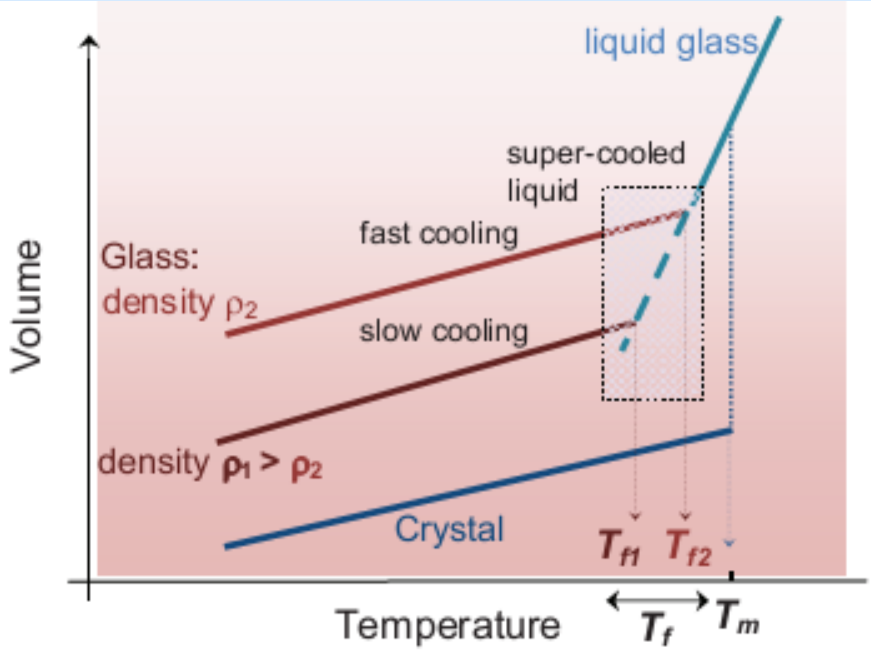
Hendersen and Wang
Eur. J. Mineral.
2002, 14, 733-744

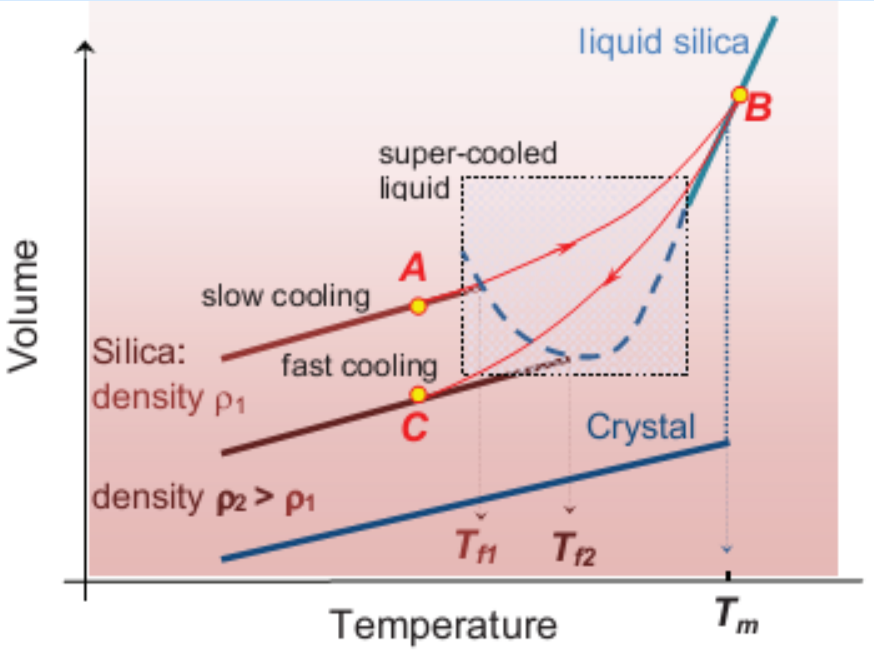


Na_2O: *(Ueno et al, Physica B, 1983)*
K_2O: *(Hoppe et al, J Non-Cryst Sol, 1999)*
Cs_2O: *(Hannon et al, J Phys Chem B, 2007)*

Mixing terms can take in account these variations

Variation of volume with cooling rate

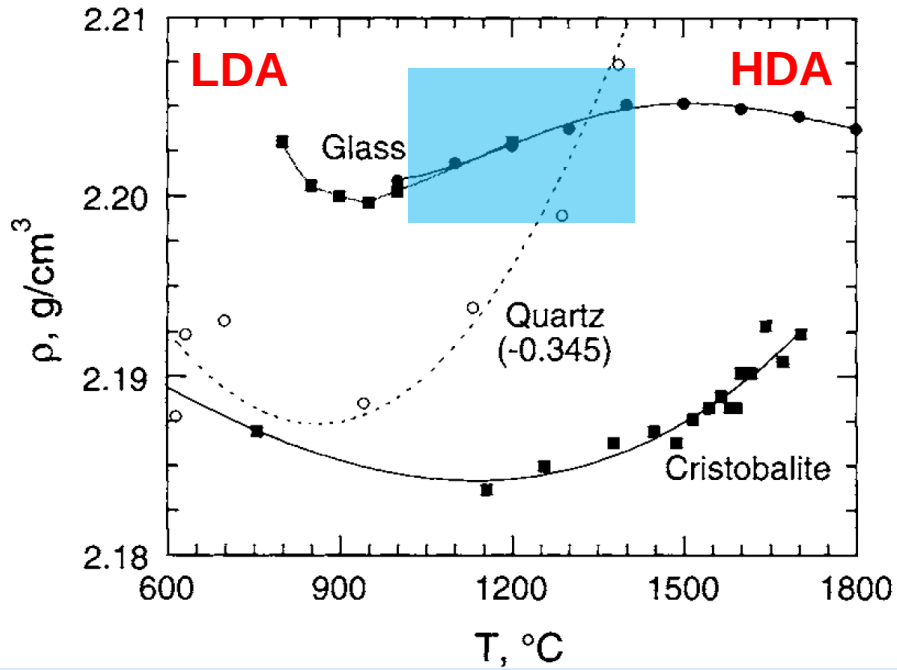




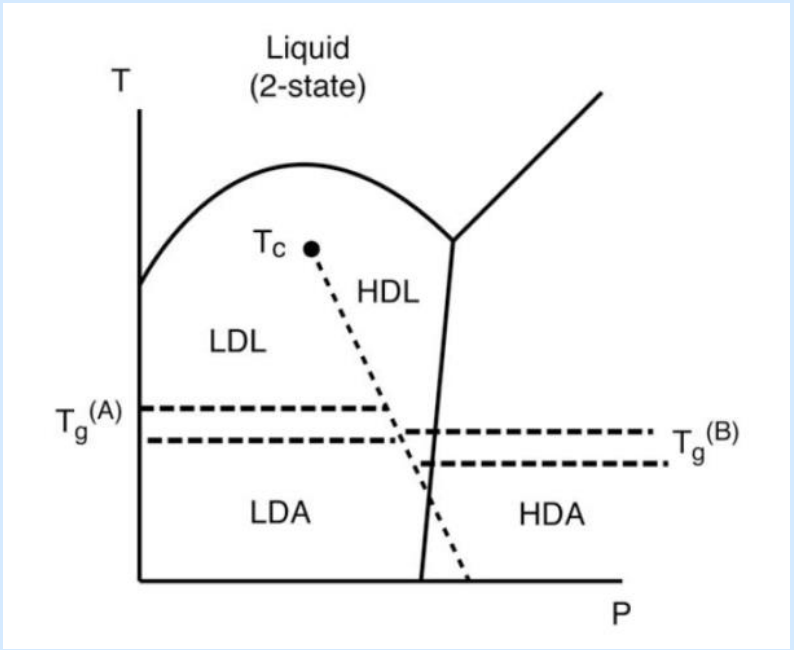
Normal (GeO_2) **Anormal (SiO_2)**

Anomalous relationship of silica glass with cooling rate explain by Sen with polyamorphism

Silica glass and polyamorphism



Mysen Richet 08
Sen et al. PRL 04

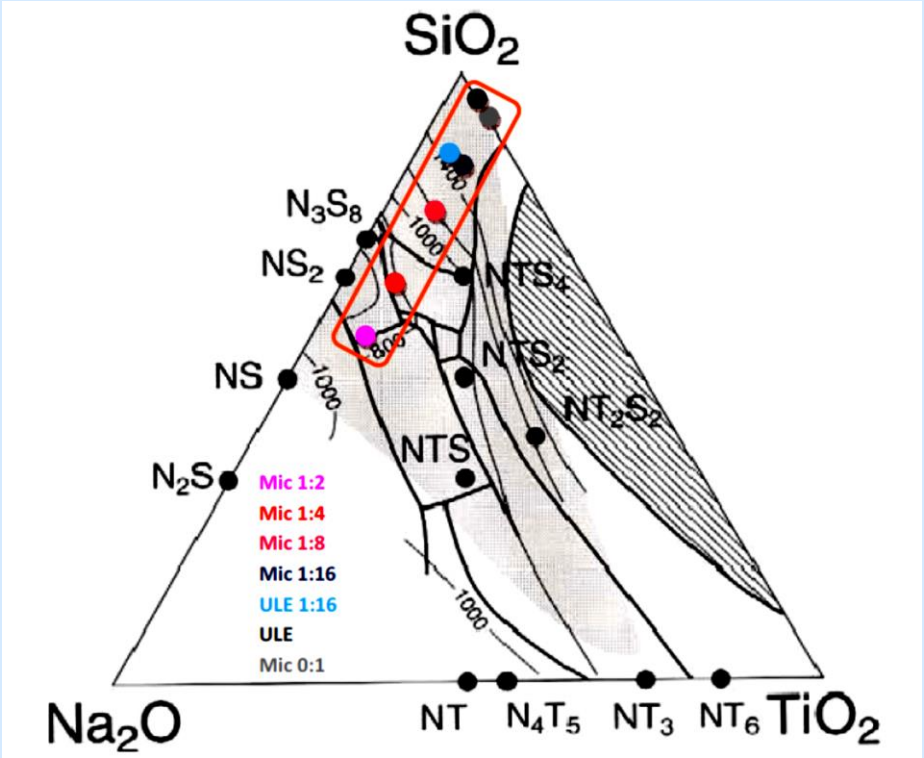


McMillan et Wilding JNCS09

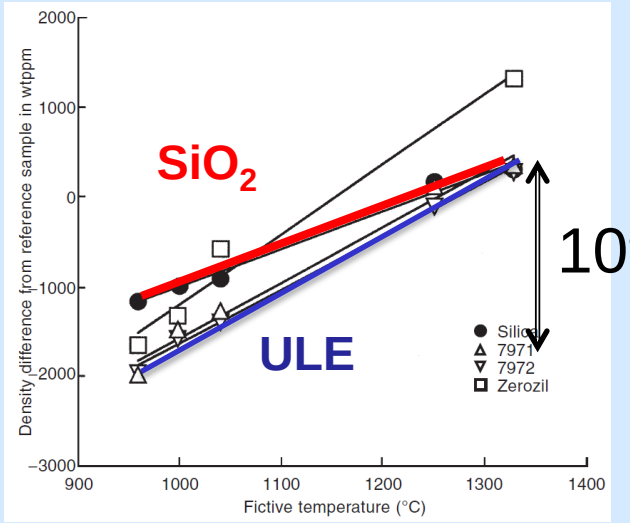
Silica polyamorphic transition smeared on a large T range?
Continuous evolution?

Titanosilicates

Sample	Na_2O /mol%	SiO_2 /mol%	TiO_2 /mol%	M /g mol^{-1}
Mic 1:2	35	56	9	43,91
Mic 1:4	22	68	10	45,00
Mic 1:8	12	78	10	45,79
Mic 1:16	6	85	9	46,20
ULE 1:16	6	87	7	46,05
ULE	0	94	6	46,45



Mysen and Richet 2005

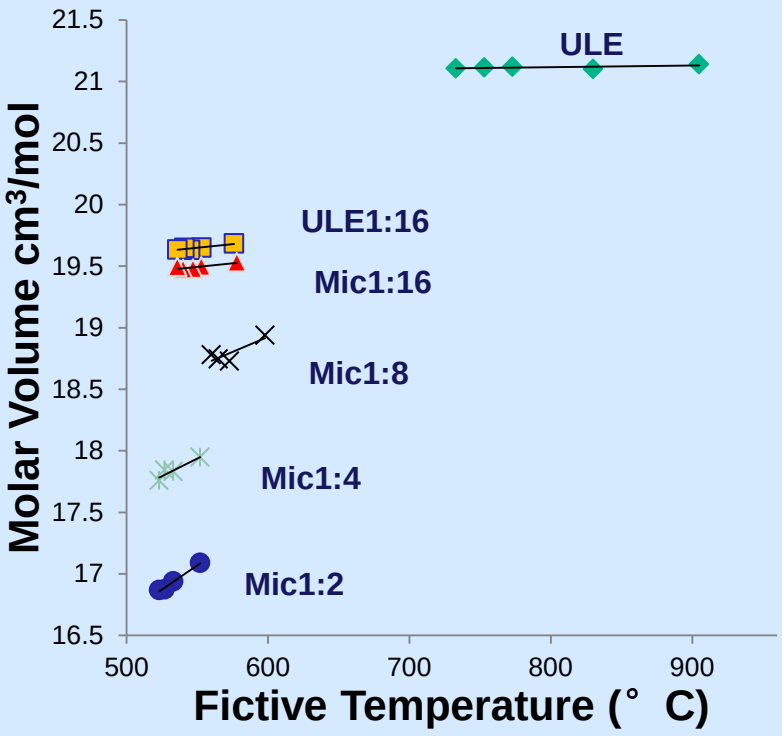


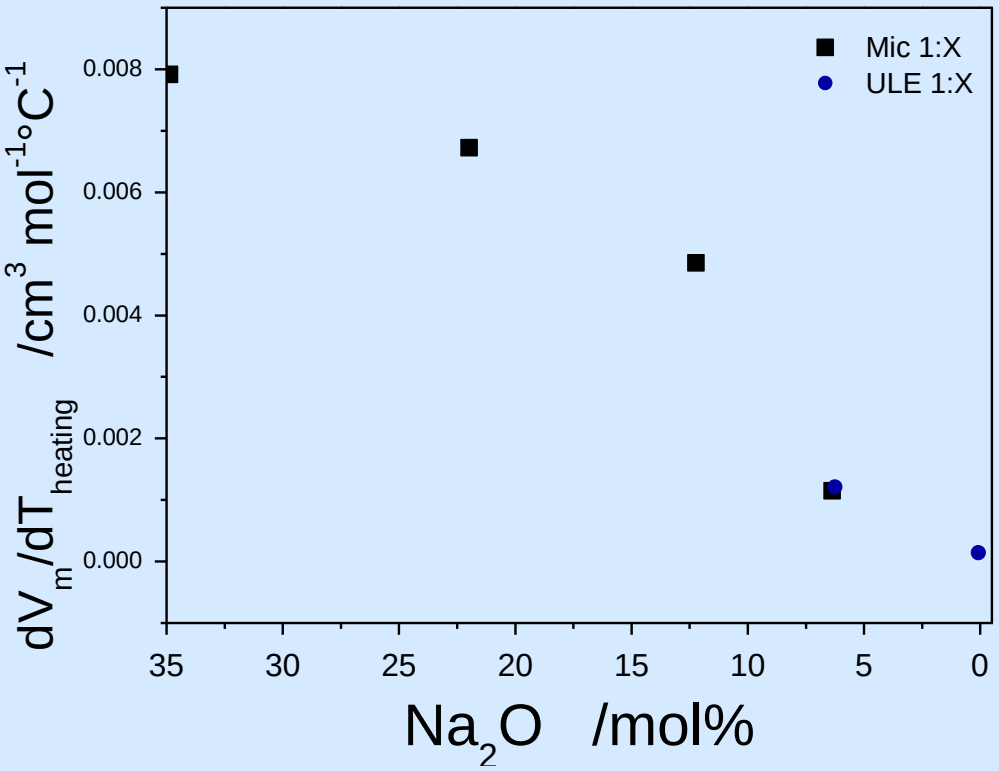
Shelby Phys. Chem. of Glasses 205

FRIEDRICH-ALEXANDER UNIVERSITÄT ERLANGEN-NÜRNBERG
TECHNISCHE FAKULTÄT

TECHNISCHE HOCHSCHULE NÜRNBERG
GEORG SIMON OHM

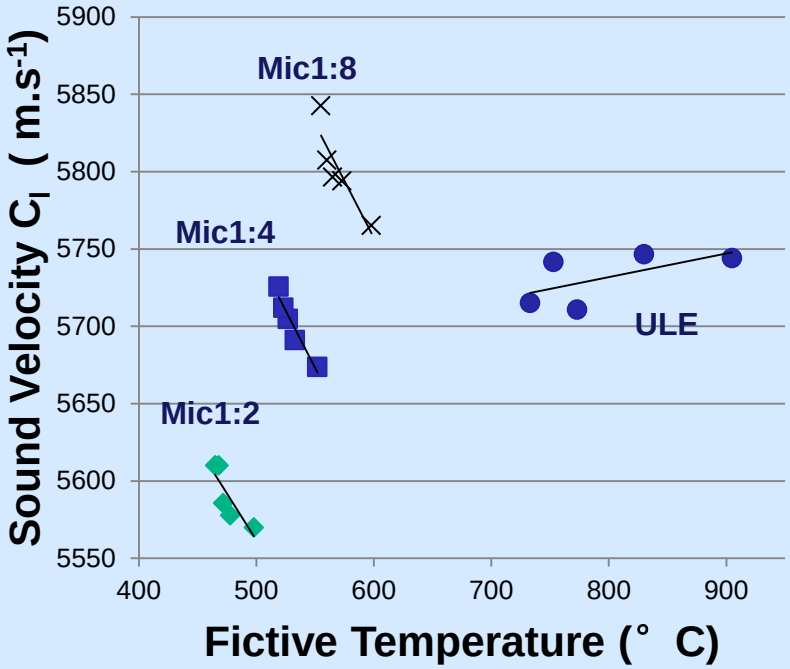
Molar volume versus fictive temperature

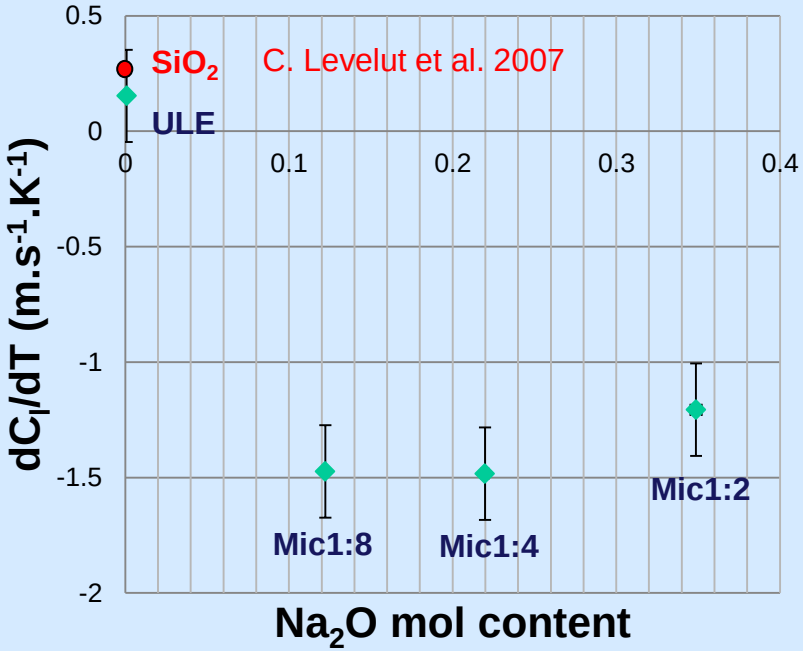




- The variation of the Molar volume with T_f is increasing with the concentration of Na_2O
- Due to the precision of the buyancy measurement the ULE glass here appears constant

Evolution of longitudinal sound velocity

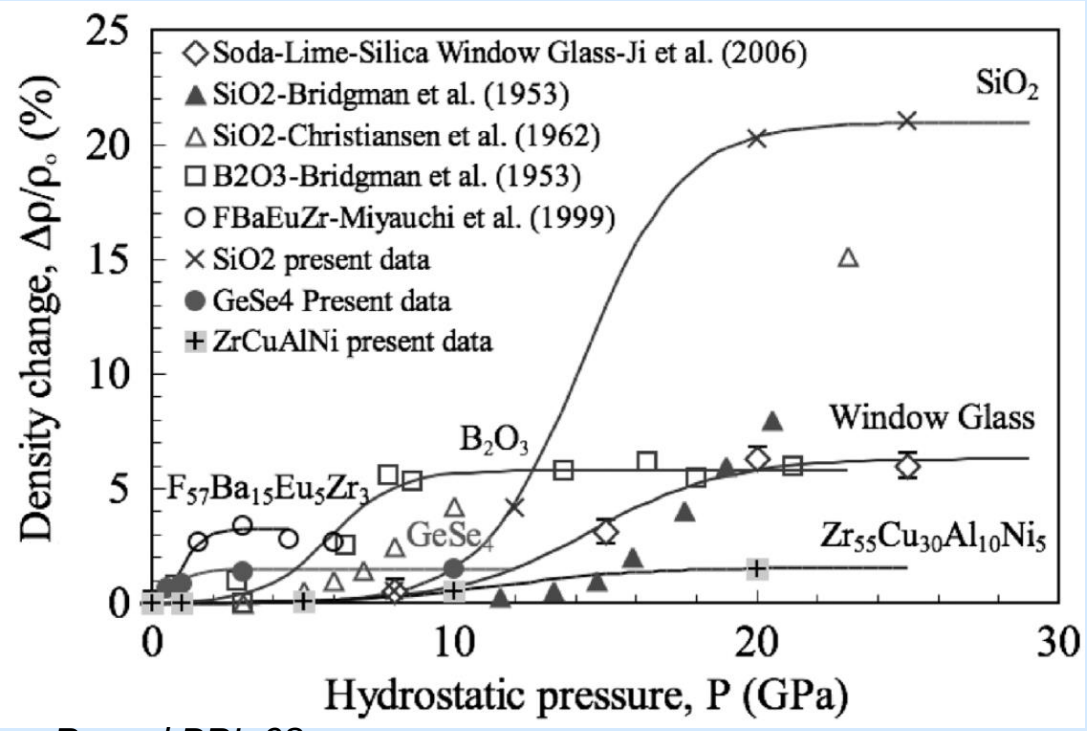




ULE glass behaves very differently from the Na containing glasses

ULE has more or less the same behavior than pure silica glass
Could it be associated with HDA to LDA transition?

Densification and Energy



Rouxel PRL 08

Variations with density (g/cm^3) of the enthalpy (kJ/mol) of oxide glasses

Glass	$\partial H/\partial \rho$
GeO_2	−32.3 (14.1)
SiO_2	−44 (20)
$K_2Si_4O_9$	−105.2 (10.7)
$Na_2Si_4O_9$	−52.1 (13.6)
$NaAlSi_3O_8$	−9.1 (10.4)

P. Richet et al. / Chemical Geology 213 (2004) 41–47

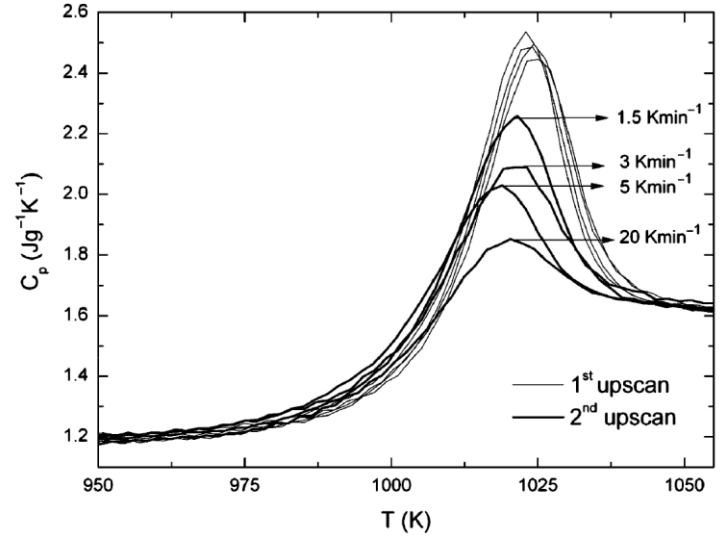
$$T_{\text{fictive}} = \left(\frac{\partial U}{\partial S}\right)_V = T - A\left(\frac{\partial \xi}{\partial S}\right)_V ,$$

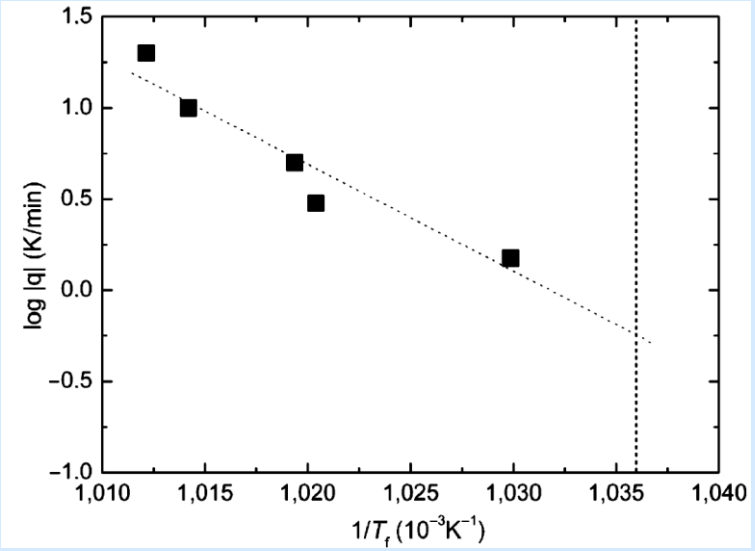
$$p_{\text{fictive}} = -\left(\frac{\partial U}{\partial V}\right)_S = p + A\left(\frac{\partial \xi}{\partial V}\right)_S .$$

Schmelzer and Gutzow 2011

Evolution of Tg with densification

$CaMgSi_2O_6$ densified at 500MPa at 1040K for 10 min



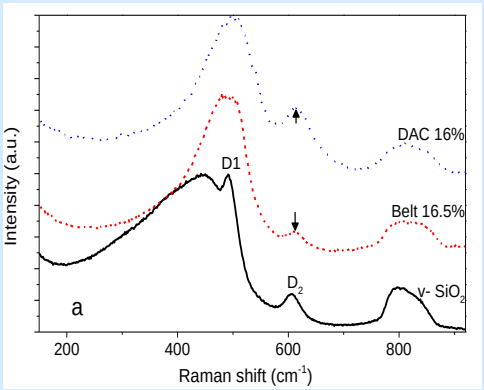


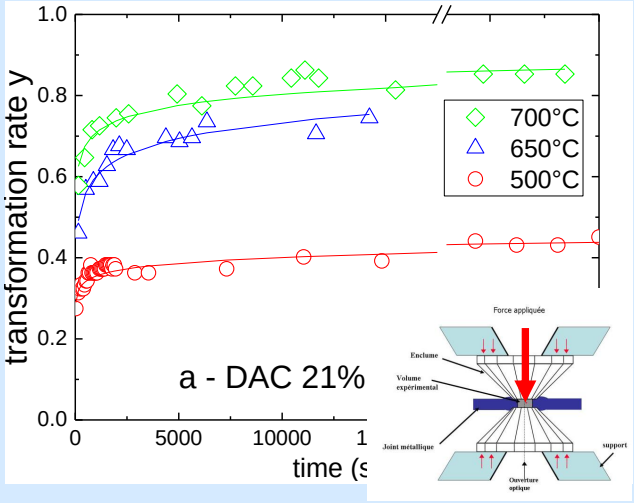
Wondraczek et al. *J. Am. Ceram. Soc.*, **90** [5] 1556–1561 (2007)

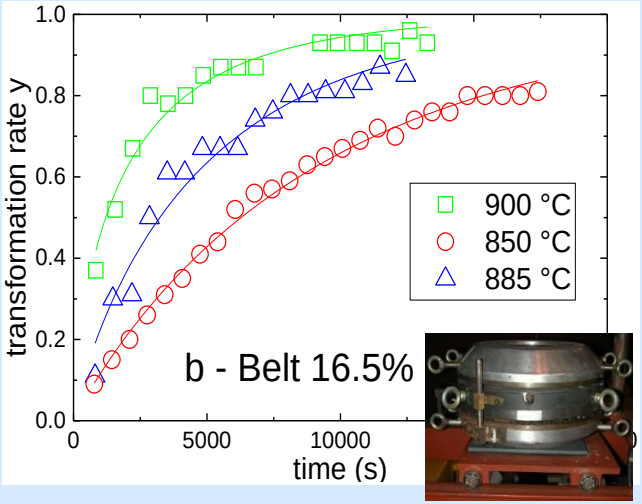
$$T_{f0} = T_{fA}\left[1 + \frac{V(p_0 - p)\,(\alpha_{Vl} - \alpha_{Vg})}{C_{pl} - C_{pg}}\right]$$

Continuity between Tf and Pf

Relaxation of densified silica glass







Cold and hot compression lead to two different glass with the same density

Very fast evolution at temperature a lot below Tg

Transformation does not reach the final relaxation state

Slow evolution at higher temperature but still below Tg

Transformation reachs the final relaxation state

At least two order parameters are needed to define the densified state

No link with Tg….

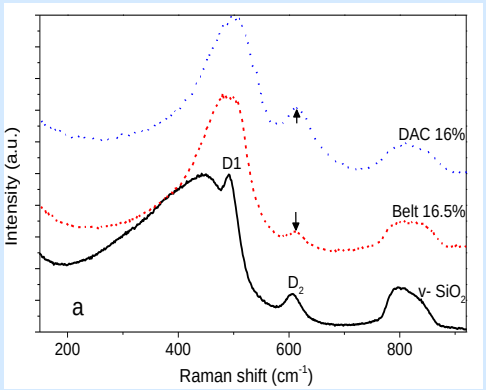
Cornet et al. J. Chem. Phys. 146 (2017)

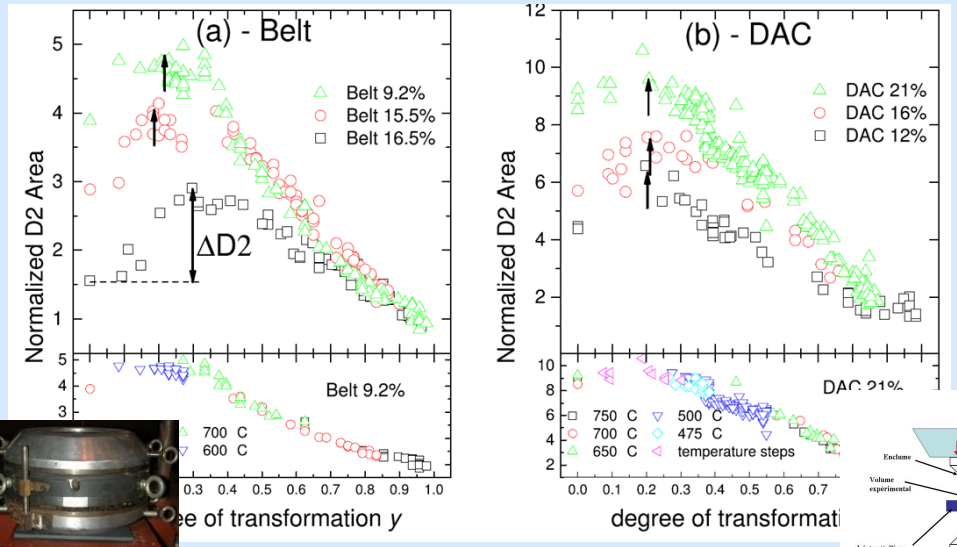
FRIEDRICH-ALEXANDER UNIVERSITÄT ERLANGEN-NÜRNBERG
TECHNISCHE FAKULTÄT

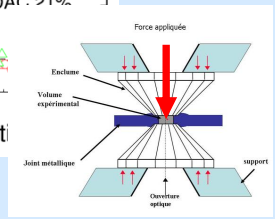
INSTITUT LUMIÈRE MATIÈRE

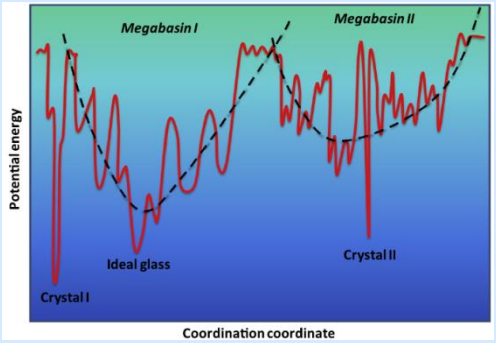
Lyon 1

Existence of an intermediate exited state





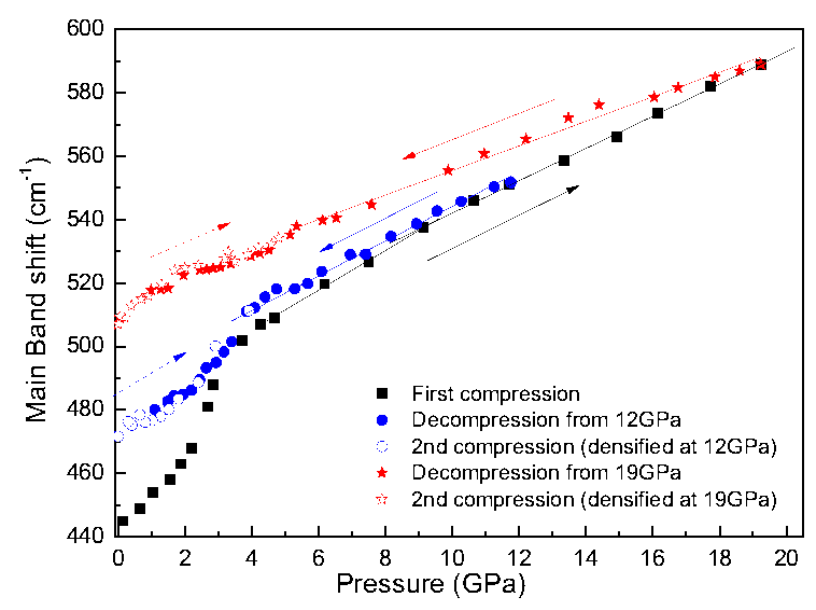


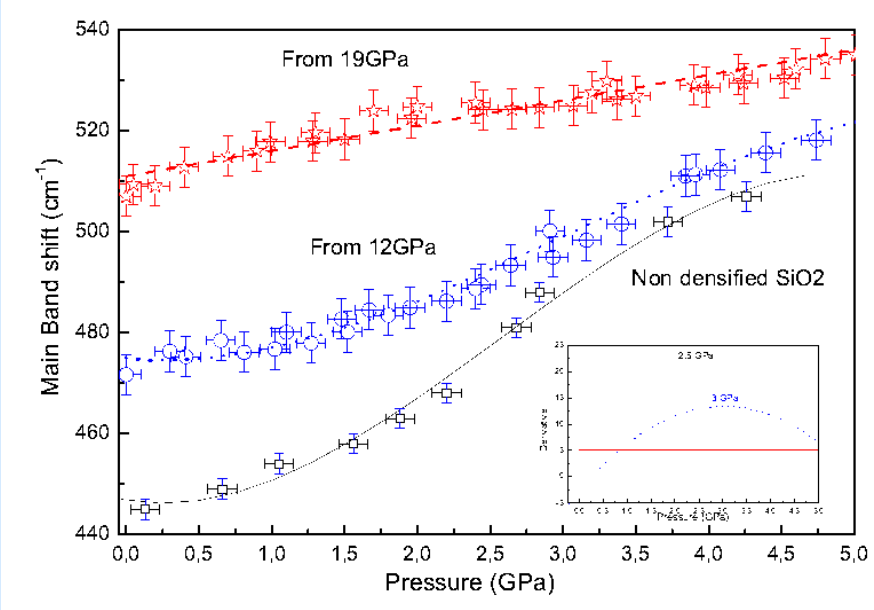


Existence of at least two megabassins

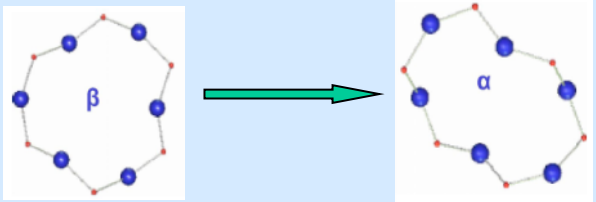
Perhaps then change of the order parameter

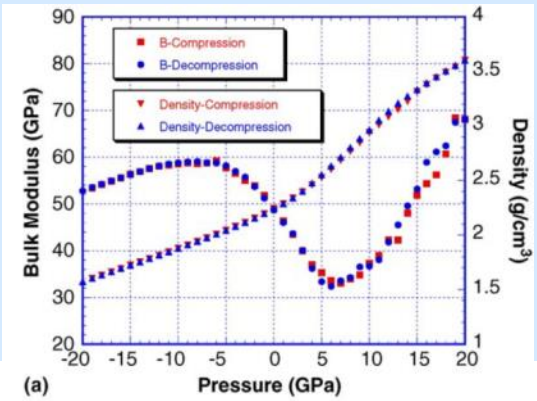
Elastic anomaly of SiO_2 glass





$$LDA_\beta \rightarrow LDA_\alpha$$





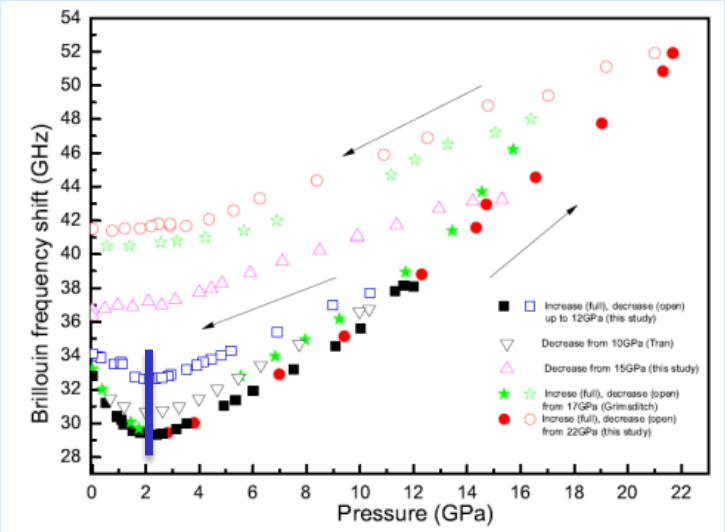
L. Huang et al. / Journal of Non-Crystalline Solids 349 (2004) 1–9

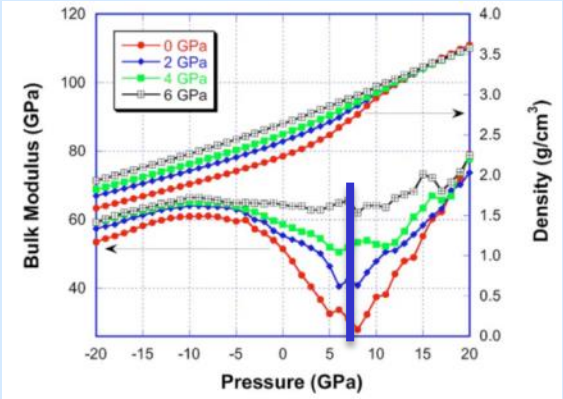
FRIEDRICH-ALEXANDER UNIVERSITÄT ERLANGEN-NÜRNBERG
TECHNISCHE FAKULTÄT

INSTITUT LUMIÈRE MATIÈRE

Lyon 1

Densification and elastic anomaly





L. Huang and J. Kieffer Appl. Phys. Lett. **89**, 141915 (2006)

progressive densification

LDA $\rightarrow$ ***HDA***

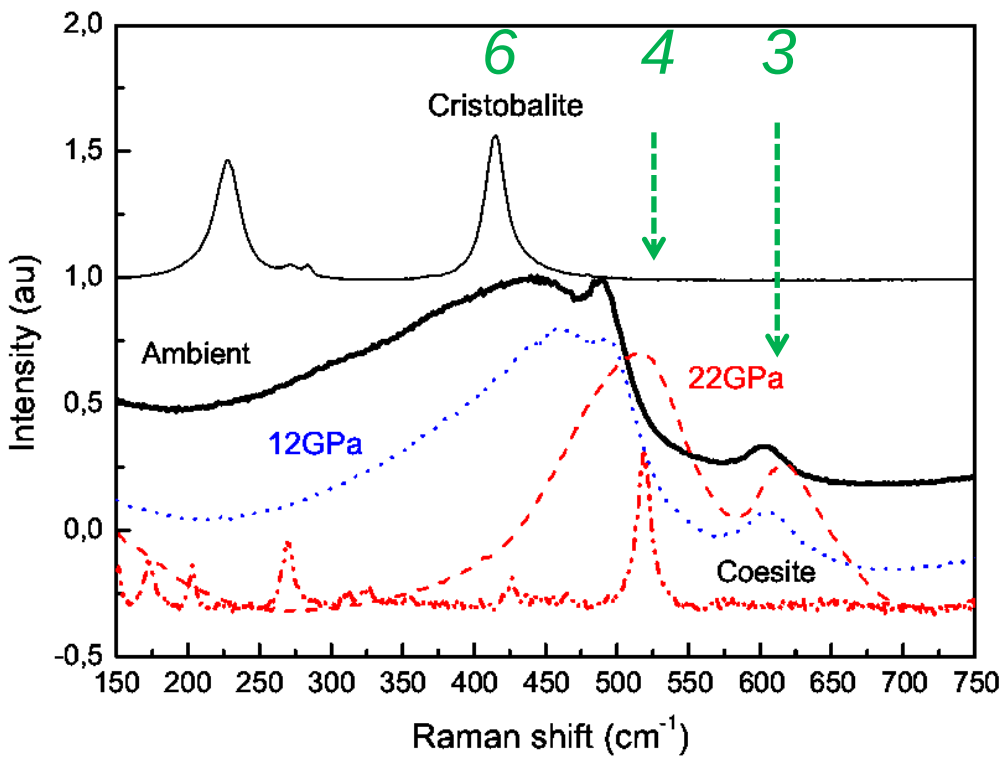
$2{,}20 gcm^{-3}$

$2{,}66 gcm^{-3}$

Disappearance of elastic anomaly
at 40% of the maximum densification
The minimum does not shift

SiO_2 glass ex situ

Raman measurements ex situ



LDA → ***HDA***

2,20gcm^{-3}

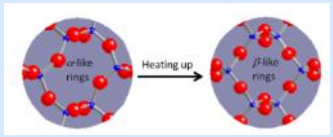
2,66gcm^{-3}

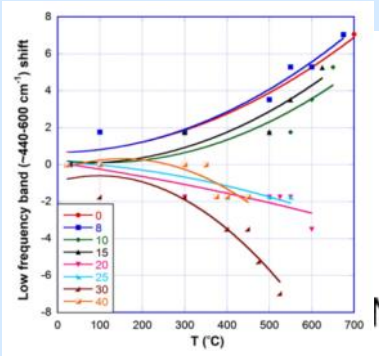
6 membered rings

to 4 membered rings

Could be a good candidate for a change of mega basin

Na_2O-Al_2O_3-SiO_2 system and samples





Q. Zhao et al. / Journal of Non-Crystalline Solids 358 (2012) 3418–3426

Chemically induced transition LDA-HAD Limit for NS4

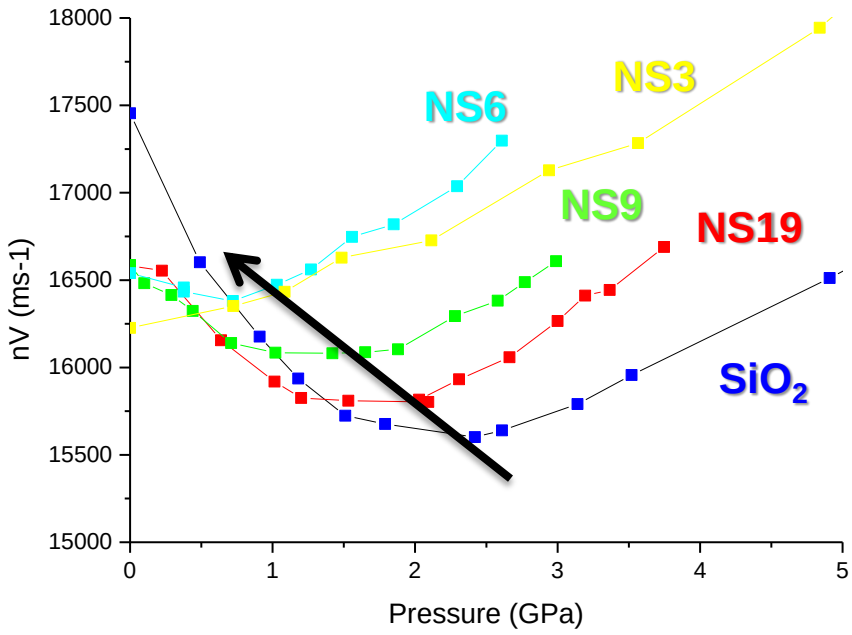
Cristobalite
6 membered ring

Albite
4 membered ring

Dehydrated Analcite(Stoffel et al. ZAAC 2016)
4 membered ring

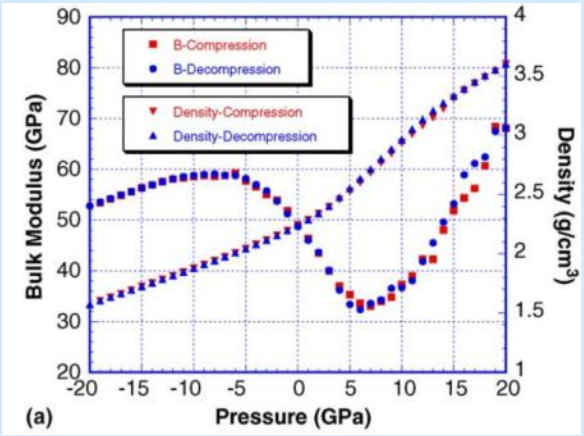
Nepheline
6 membered stuffed ring

Binary SiO_2-Na_2O



Two possible interpretations:

- Same slope at high pressure shift of the position of the minimum with increasing Na content: shift of the 0
- Progressive increase of HDA with Na content

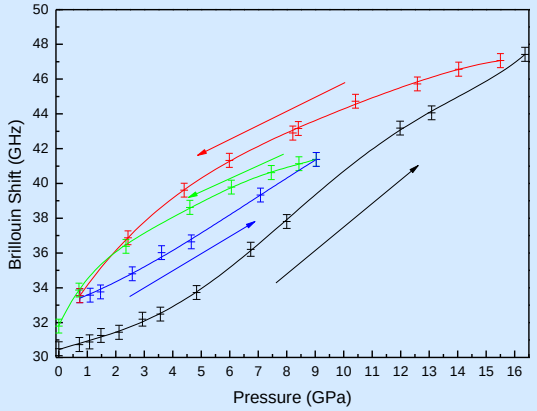


L. Huang et al. / Journal of Non-Crystalline Solids 349 (2004) 1–9

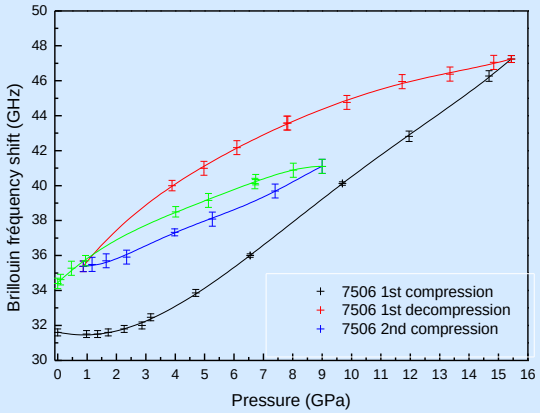
The prediction of Huang‘s group is correct

Effect of the Na/Al ratio on permanent densificaton

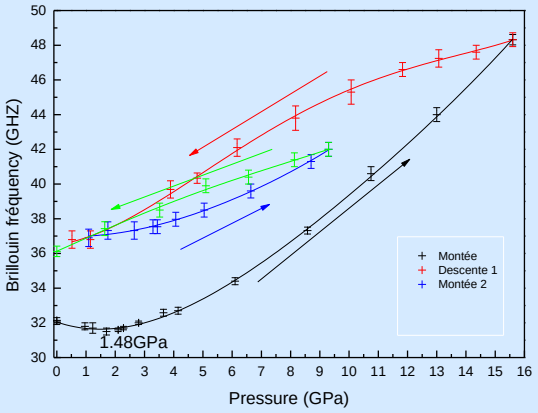
NA 75.00 / NS3



NA 75.06

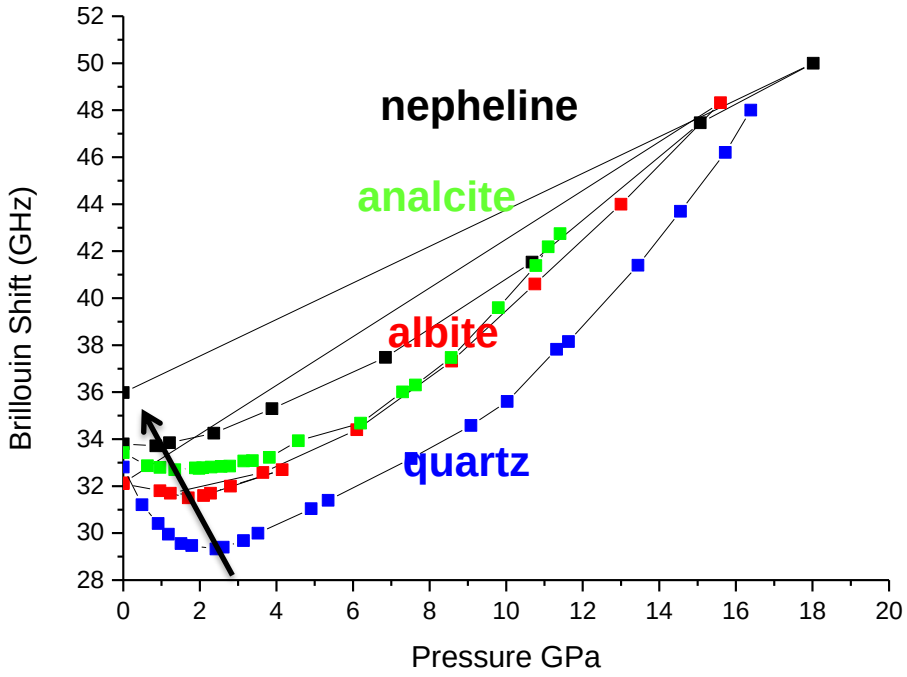


NA 75.12 / Albite



- Elastic hardening with densification higher for polymerized compositions
- NS3 no significant densification so already 100% HDA
- Hysteresis cycles: probably coordination change of Si and Na, bigger when depolymerized

Decreasing SiO_2 at Al/Na=1



Three possible effects:

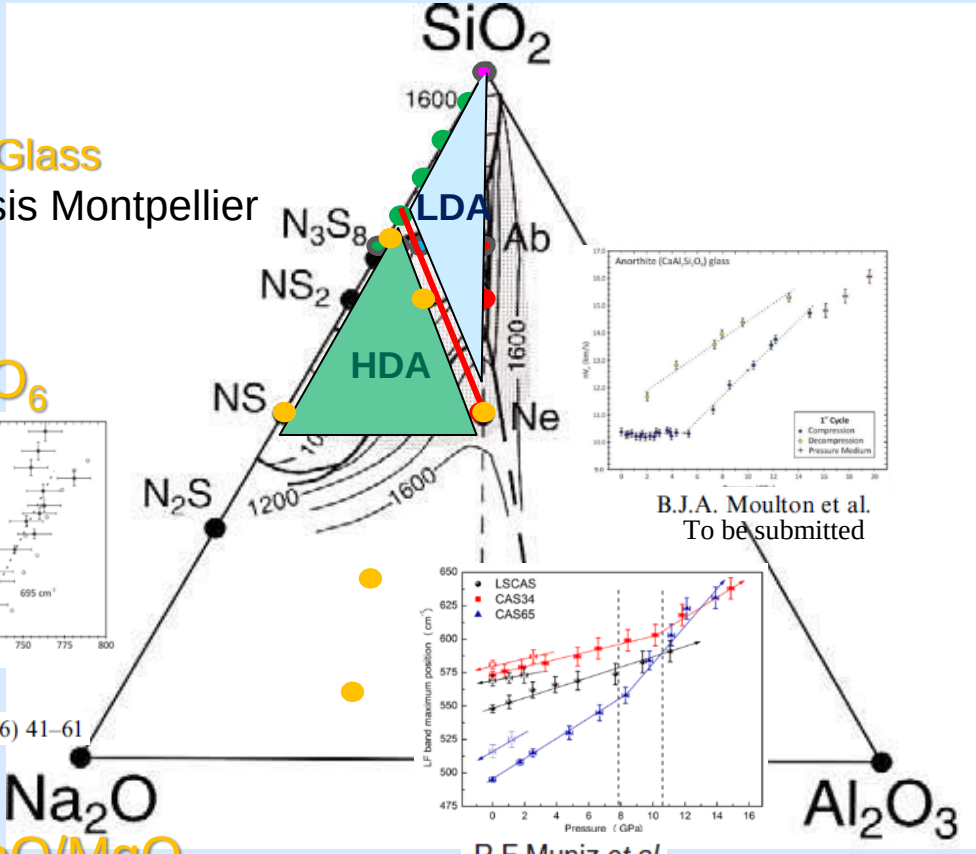
- Anomaly can take place with smaller rings
- Al is as good as Si in rings
- Filling the holes by Na

Here the minimum strongly flatted suggesting the disappearance of the structure responsible of the elastic anomaly… HDA formation?

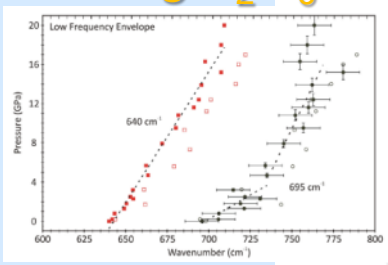
Limit of the elastic anomaly

Window Glass

Tran thesis Montpellier



$CaMgSi_2O_6$



B.J.A. Moulton et al.

Geochimica et Cosmochimica Acta 178 (2016) 41–61

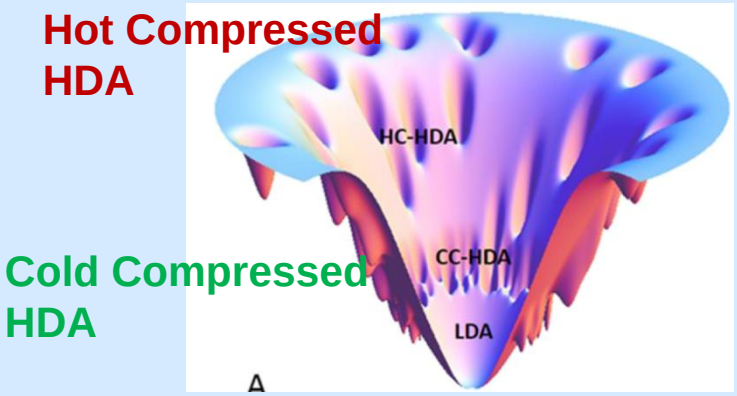
B.J.A. Moulton et al.
To be submitted

R F Muniz *et al*

J. Phys.: Condens. Matter **28** (2016) 315402

Conclusion

- Modélisation compliquée
- Evolution en Pression très riche en information
- Volume et temperature fictive liée à la polymerisation
- Polyamorphisme multiple
- HAD/LDA approche qui pourrait peut être aussi aider à la modélisation?



Guerette et al. J. Chem. Phys. 148 (2018)