DE LA RECHERCHE À L'INDUSTRIE

cea

www.cea.fr

Molecular Dynamics of nuclear waste glasses

J.-M. Delaye[1]

with the contributions of

S. Ispas[2], L.-H. Kieu[1], D. Kilymis[1,2], S. Peuget[1]

[1]Service d'Etudes de Vitrification et procédés hautes Températures (SEVT), CEA Marcoule, France

[2]Laboratoire Charles Coulomb (L2C), Université de Montpellier, France

afaq QSE Qualité Sécurité Environnement AFNOR CERTIFICATION ISO 9001 - OHSAS 18001 ISO 14001

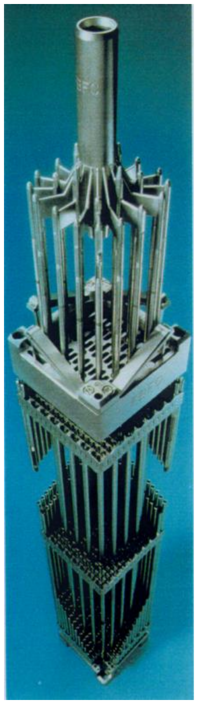
Joint ICTP – IAEA Workshop

6-10 November 2017, Trieste, Italy

Outline

- Similarities between radiation effects in real and simplified glasses (10')
- Ballistic effects in simplified nuclear glasses (15')
- Fit of an interatomic potential to simulate the mechanical property (5')
- Mechanical property changes under ballistic effects (15')
- Some works taking H_2O into account (5')
- Conclusions – Perspectives

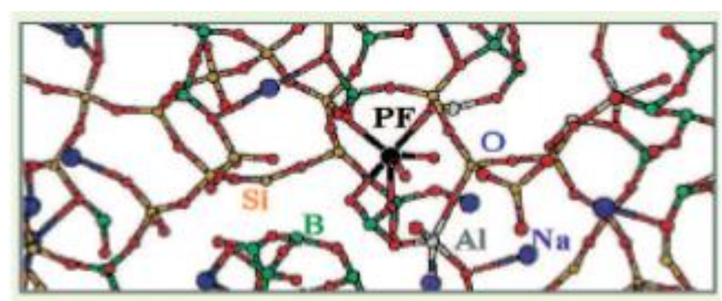
Similarities between radiation effects in real and simplified glasses



Spent fuel rods

<u>Reprocessing of the spent fuel rods exited from the reactors</u>

- U, Pu recycling ⇨ MOX fuels
- the non valorisable high level and long lived radioactive waste are confined in Nuclear Glasses
    - <u>Minor actinides</u> (Am, Np, Cm) : 500g for 500kg of U ➡ α disintegrations
    - <u>Fission products</u> (Tc, Zr, Cs, Pd, Sn, Se …) : 20kg for 500kg of U ➡ β/γ irradiations



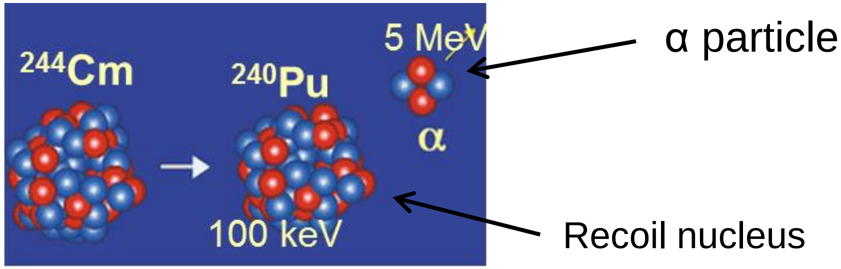
<u>Advantage of glass storage</u>: reduction of the waste volume

Similarities between radiation effects in real and simplified glasses

The French Nuclear Glass (R7T7)

	Composition nominale
SiO_2	45,1
B_2O_3	13,9
Al_2O_3	4,9
Na_2O	9,8
CaO	4,0
Fe_2O_3	2,9
NiO	0,4
Cr_2O_3	0,5
P_2O_5	0,3
Li_2O	2,0
ZnO	2,5
Ox(PF + Zr + actinides)	12,8
+ Suspension de fines Oxydes d'actinides	0,9
$SiO_2+B_2O_3+Al_2O_3$	

- **Alumino borosilicate glass**
- **More the 30 components**
- **Minor actinides content (current specification: $10^{19}\alpha/g$)**

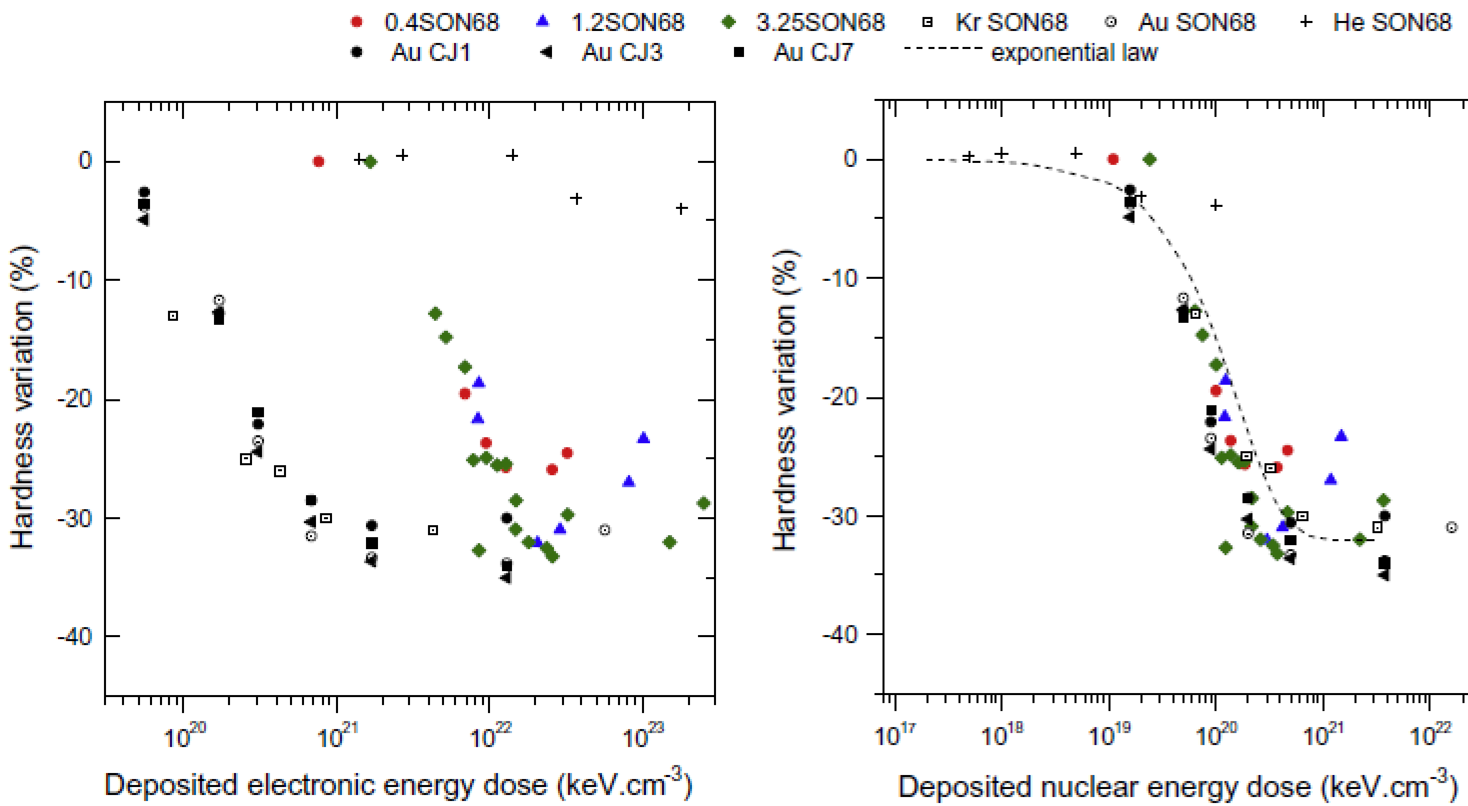


Radiation	Range	Atomic displacements per event
α (4–6 MeV)	20µm	100 to 200
Recoil nucleus (0.1MeV)	30nm	**<u>1000 to 2000</u>**
β particle	1mm	~1
γ particle	few cms	<<1

Irradiation by recoil nuclei (Nuclear Energy): ballistic effects
Irradiation by α particles and β/γ irradiations (Electronic Energy): electronic excitations

Similarities between radiation effects in real and simplified glasses

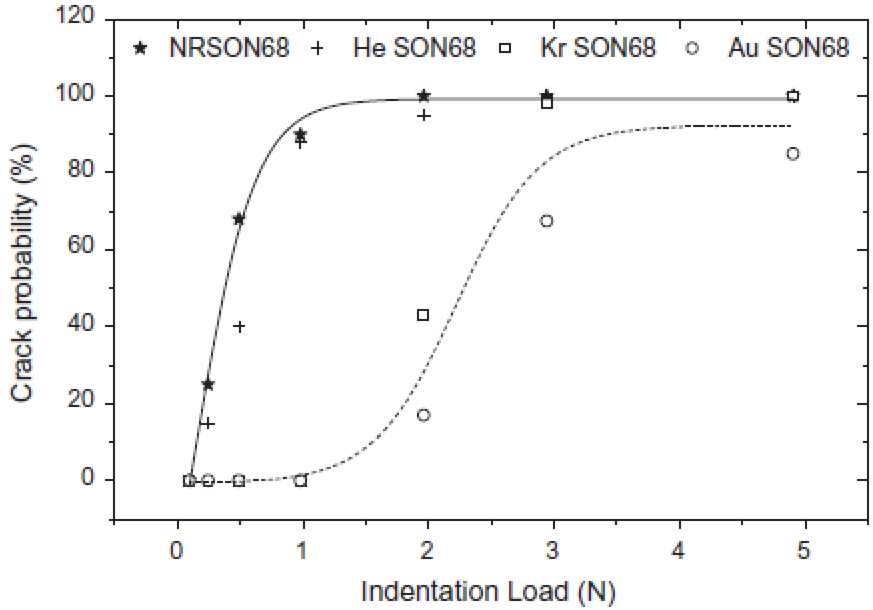
- **Ballistic effects are preponderant to explain the hardness decrease**: a nuclear glass has been irradiated by different radiation sources [doped glasses and external irradiation by light (He) and heavy ions (Au)]



S. Peuget et al., J. Nucl. Mat. 444 (2014) 76

Similarities between radiation effects in real and simplified glasses

- **Ballistic effects are preponderant to explain the fracture toughness increase**: a nuclear glass has been irradiated by light or heavy ions



The fracture toughness doesn’t change after irradiation by light ions (electronic effects)
The fracture toughness increases after irradiation by heavy ions (ballistic effects)

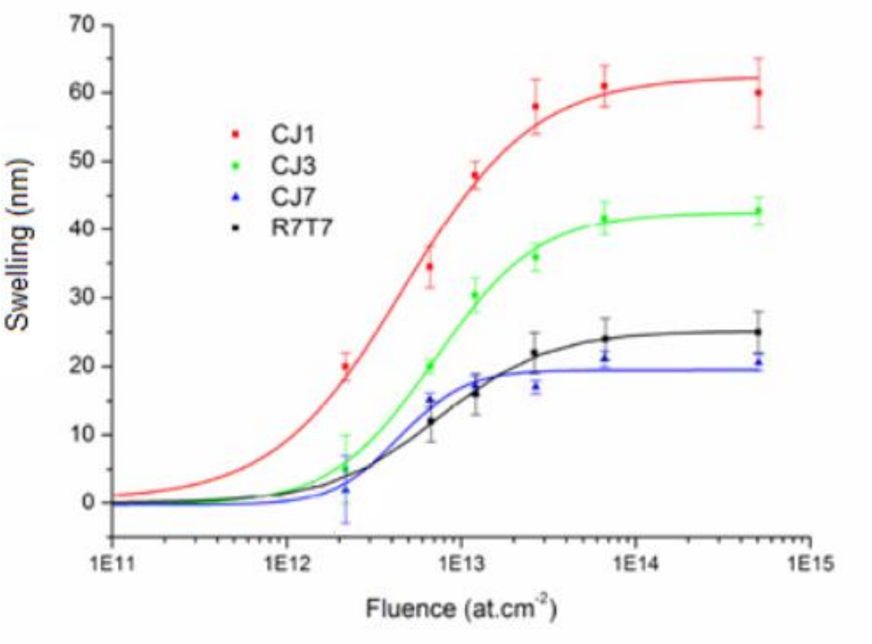
Similarities between radiation effects in real and simplified glasses

- Simplified Nuclear glasses have been studied:

% mol	SiO_2	B_2O_3	Na_2O	Al_2O_3	ZrO_2
SBN14 = CJ1	67.7	18.1	14.2	-	-
CJ7	63.8	17.0	13.4	4.0	1.8

External irradiation by heavy ions (Au)

- The swelling is qualitatively the same as in the real Nuclear Glass

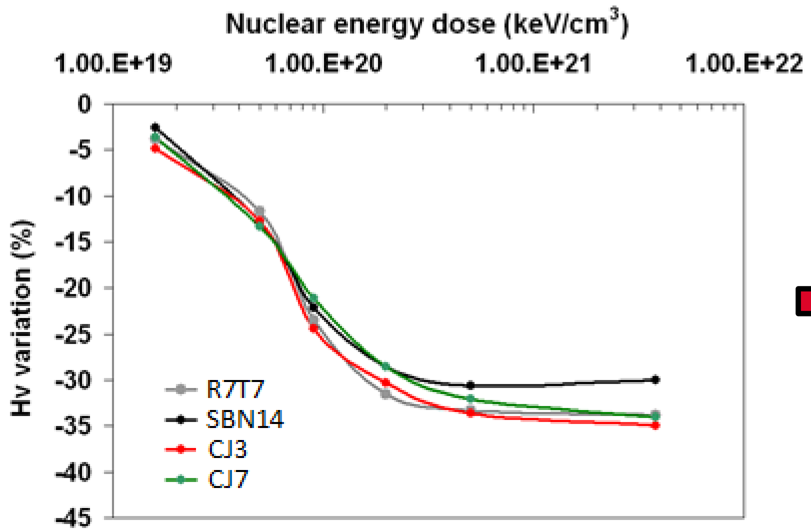


Saturation of the swelling with the dose

The saturation doses are the same in the simplified and real glasses

J. De Bonfils et al., J. Non-Cryst. Solids, 356 (2010) 388

Similarities between radiation effects in real and simplified glasses



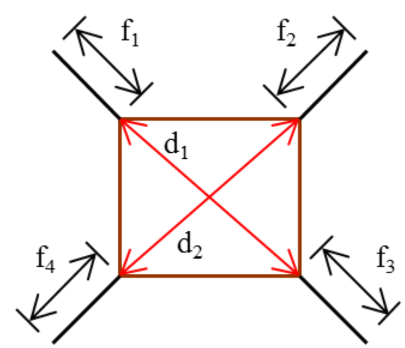
HARDNESS

Decrease of the hardness after irradiation by heavy ions:

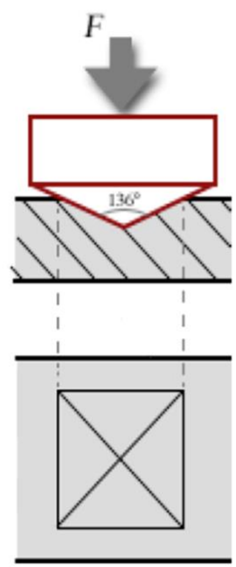
- **Saturation with the dose**
- **The saturation doses are the same**

FRACTURE TOUGHNESS

SBN14: Increase of the fracture toughness (+16%) after irradiation by neutrons



$$K_{IC} = 0{,}057 H \sqrt{a} \left(\frac{E}{H}\right)^{2/5} \left(\frac{c}{a}\right)^{-3/2}$$



J. De Bonfils et al., J. Non-Cryst. Solids, 356 (2010) 388

To conclude about this part

- Mechanical property changes under irradiation in real glasses are due to ballistic effects

- Simplified nuclear glasses behave in the same way as the real one

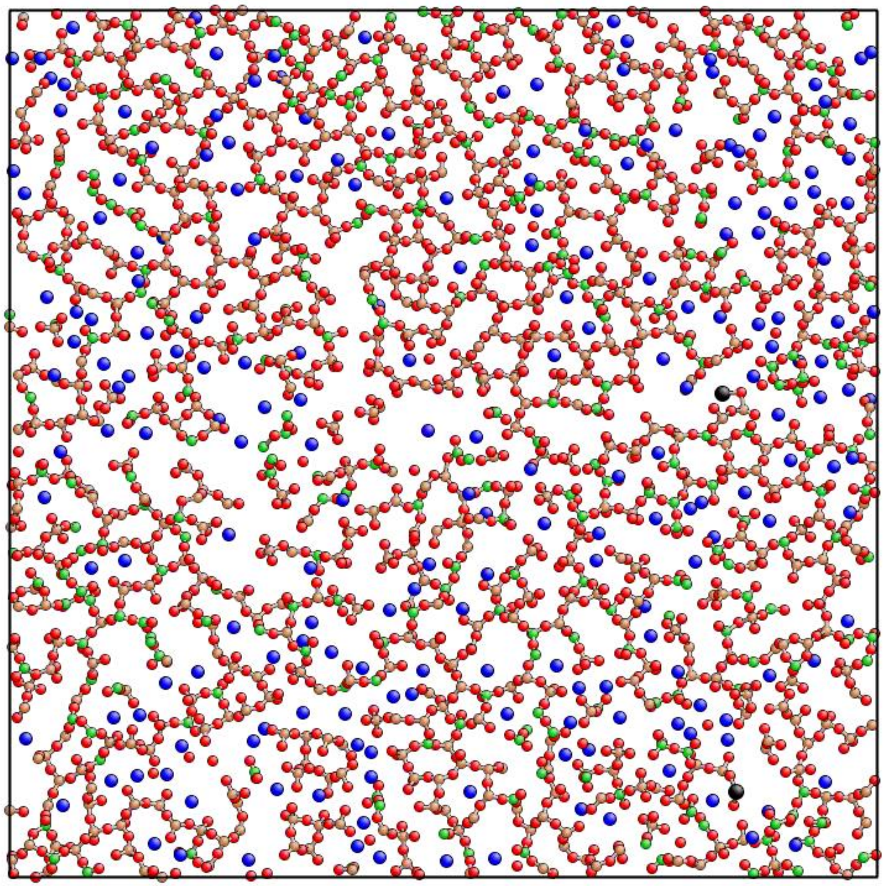
- It is justified to use classical molecular dynamics to try to understand the origin of the mechanical property changes under the ballistic effects

Atomistic modeling of ballistic effects

- Two different interatomic potentials have been used:
  - Buckingham type + three body terms (formal charges) fitted on experimental data (local coordination and first neighbour distances, structure factors), but not precise to represent the elastic properties
  - A new Buckingham type potential (partial charges) has been fitted to better represent both the glassy structure and the elastic properties
- No significant differences have been observed when displacement cascades are simulated with one or another potential: the results will not be separated in the following of this presentation

What is a displacement cascade?

- **A projectile is accelerated in a simulation box**



- **A series of ballistic collisions is generated**
- **By accumulating a large number of displacement cascades, the complete structure is irradiated and a new metastable state is reached**

Example of a displacement cascade (4keV) in a SBN14=CJ1 glass

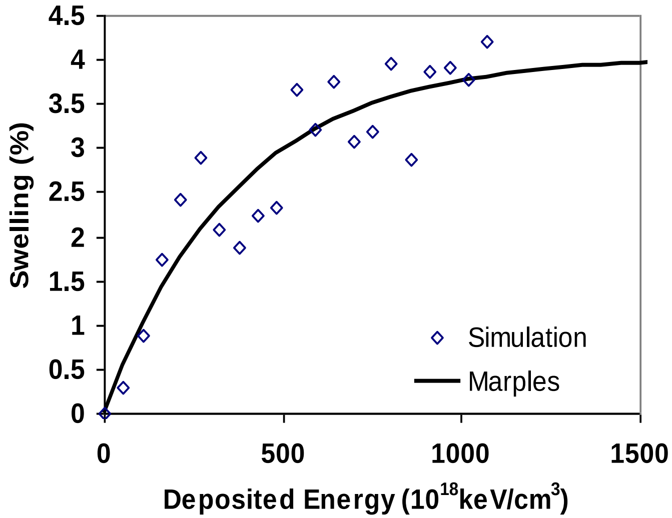
% mol	SiO_2	B_2O_3	Na_2O
SBN14 = CJ1	67.7	18.1	14.2

J.-M. Delaye et al., J. Non-Cryst. Solids, 357 (2011) 2763

Displacement cascades (600eV) in the SBN14 glass

Series of 600eV displacement cascades have been simulated to completely irradiate the volume

Swelling under ballistic effects



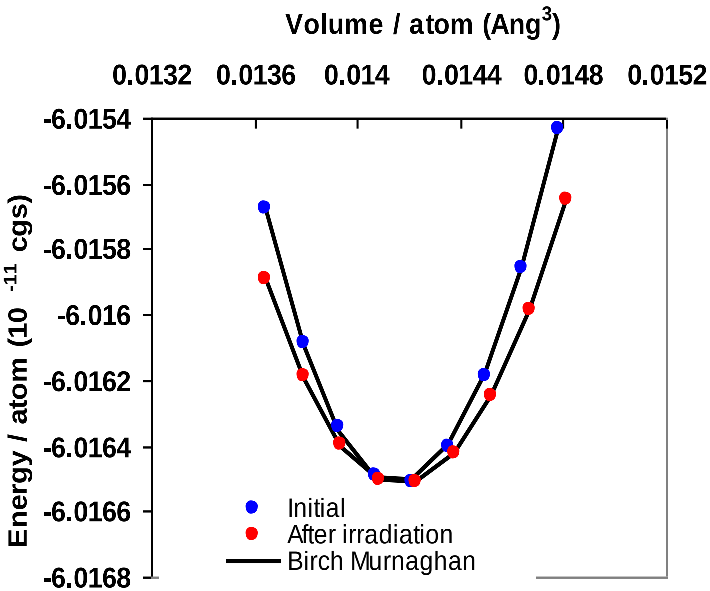
Equivalence

4.0 10^{20} keV/cm^3	2 10^{18} α/g

Experimental swelling in SBN14 irradiated by heavy ions: ~4.0%
Saturation dose: 5 10^{20}keV/cm^3

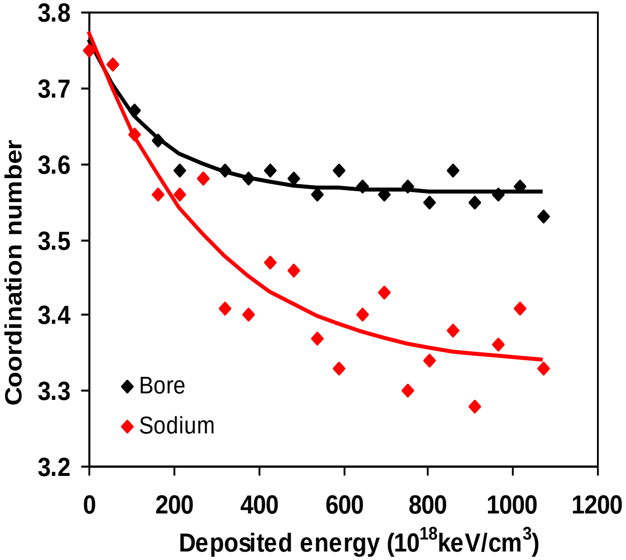
Decrease of the bulk modulus

Bulk modulus decreases from 85GPa to 61GPa (-28%)
(the decrease of the elastic moduli in the real glass is equal to -30%)



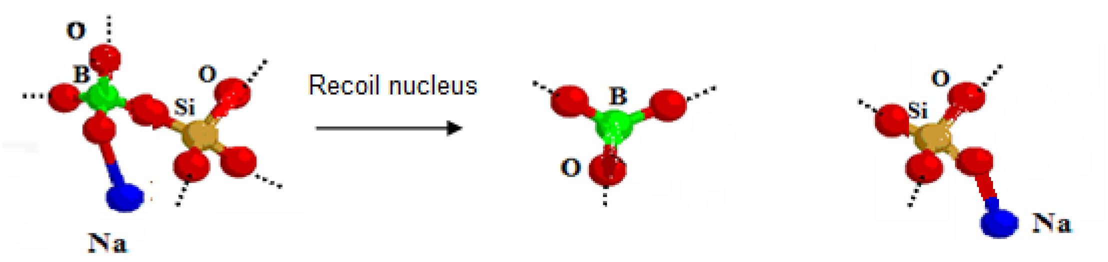
Displacement cascades (600eV) in the SBN14 glass

Depolymerization



	%B[3]	%B[4]	Q_4	Q_3
Initial	25%	75%	**95.8%**	**4.2%**
Final	47%	53%	**85.2%**	**14.6%**

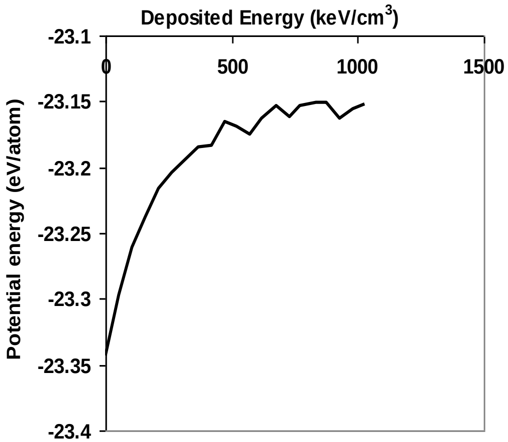
Formation of Non-Bridging Oxygens on the SiO_4 entities



Displacement cascades (600eV) in the SBN14 glass

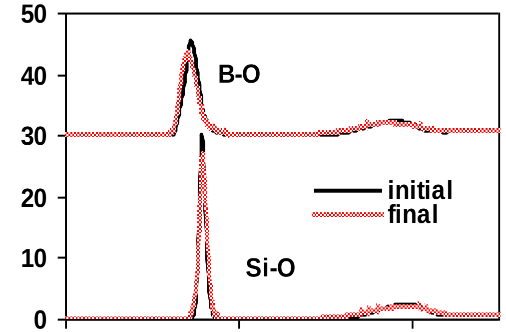
Increase of the disorder

Increase of the internal energy

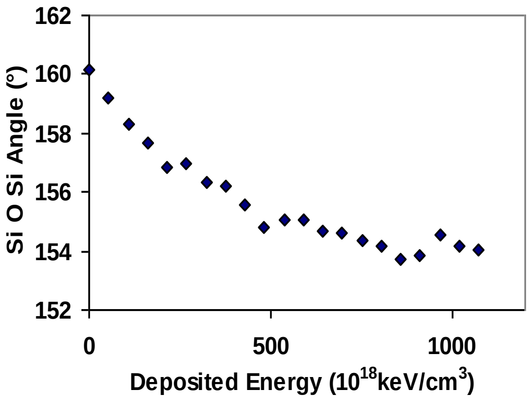


Widening of the distributions

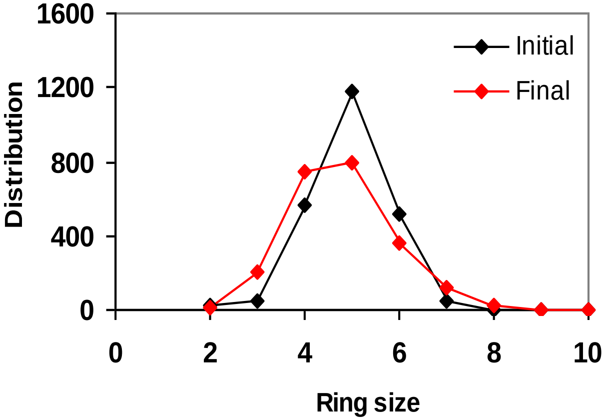
Radial distribution functions



Decrease of Si-O-Si (and Si-O-B) angles

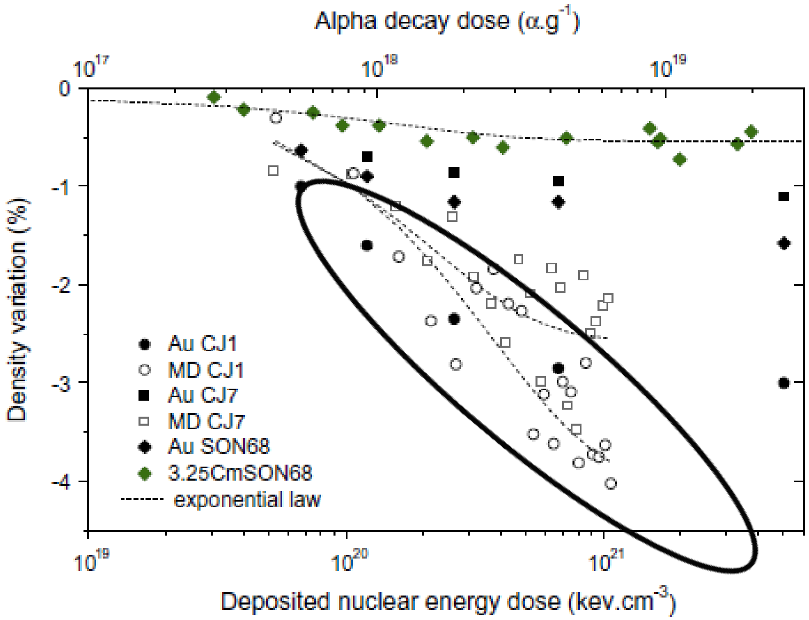


Rings



Comparison with experiments

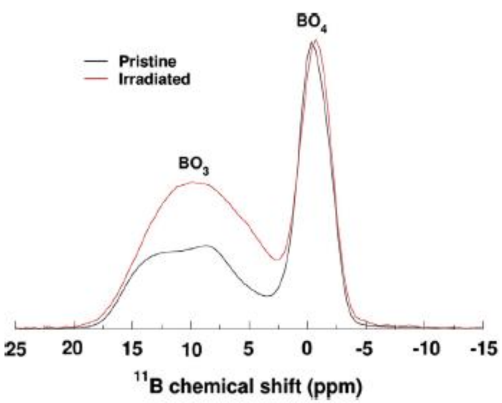
Swelling



% mol	SiO_2	B_2O_3	Na_2O	Al_2O_3	ZrO_2
CJ7	64.1	16.8	13.3	4.0	1.8

Boron coordination

Decrease of B coordination has been observed experimentally by ^{11}B NMR



% mol	SiO_2	B_2O_3	Na_2O	Al_2O_3	ZrO_2	CaO
CJ4	60.1	16.0	12.6	3.8	1.7	5.7

The radiation effects can be partly reproduced by increasing the quench rate

- By playing on the thermal history for the glass preparation, it is possible to reproduce qualitatively the ballistic effects

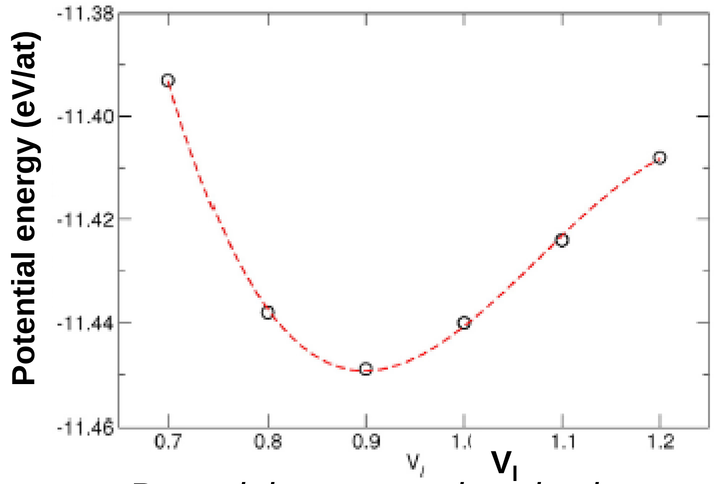
SBN14 glass	Glass quenched at 10^{14} K/s compared to the one quenched at 5 10^{12}K/s	Effect of displacements cascade accumulation (600eV)
Swelling	+7 %	+4 %
Increase of $^{[3]}$B percentage	+10 %	+17 %
Increase of NBO percentage	+3%	+4%
Decrease of Si-O-Si angle	-2°	-4°

General model proposed to explain the saturation effect under irradiation

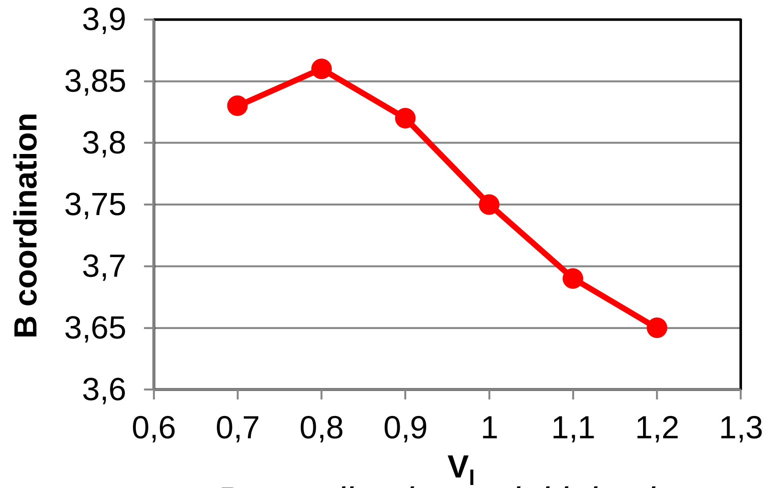
1. Inside the core of the cascade, the structure is melt and quenched very rapidly
2. A new local configuration, independent of the initial structure, is built
3. When the total volume has been irradiated, a new saturation state is reached

Confirmation of the model by using different initial configurations (SBN14 glass)

- 6 configurations have been simulated with different initial densities [2.25g/cm^3 – 3.03g/cm^3]

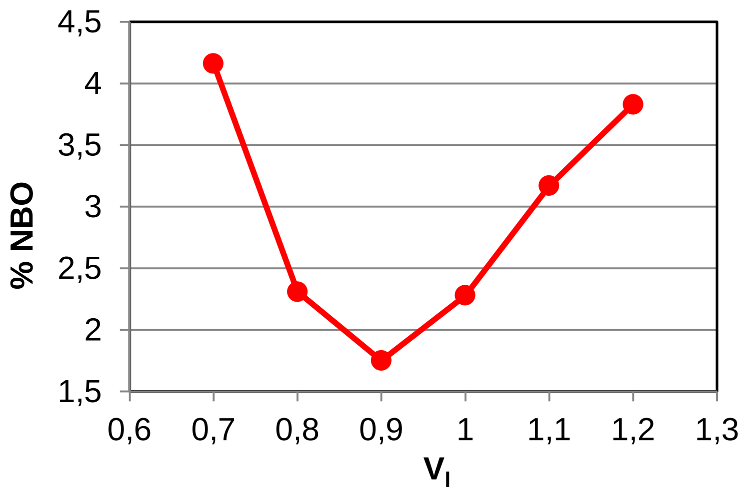


Potential energy vs initial volume

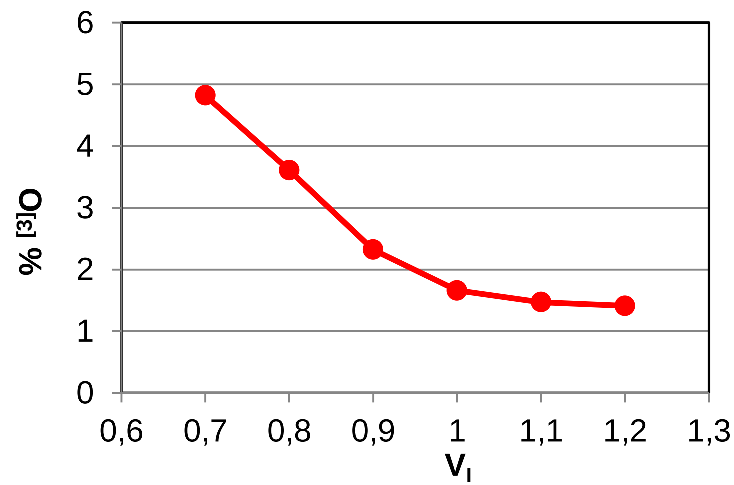


B coordination vs initial volume

VI	Density
0.7	3 .03
0.8	2.90
0.9	2.72
1.0	2.56
1.1	2.42
1.2	2.25



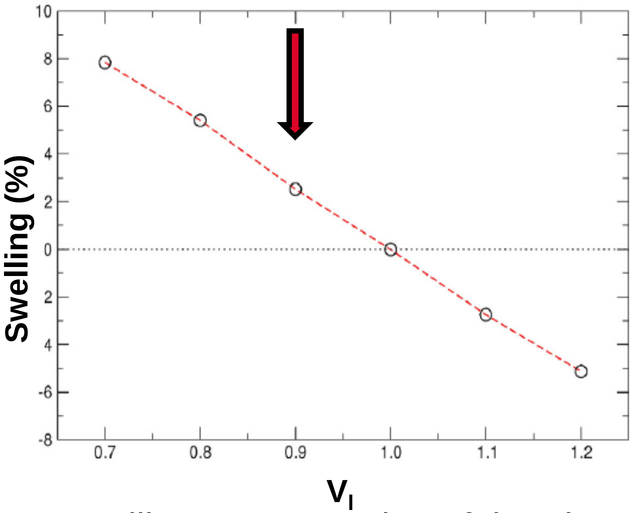
% NBO vs initial volume



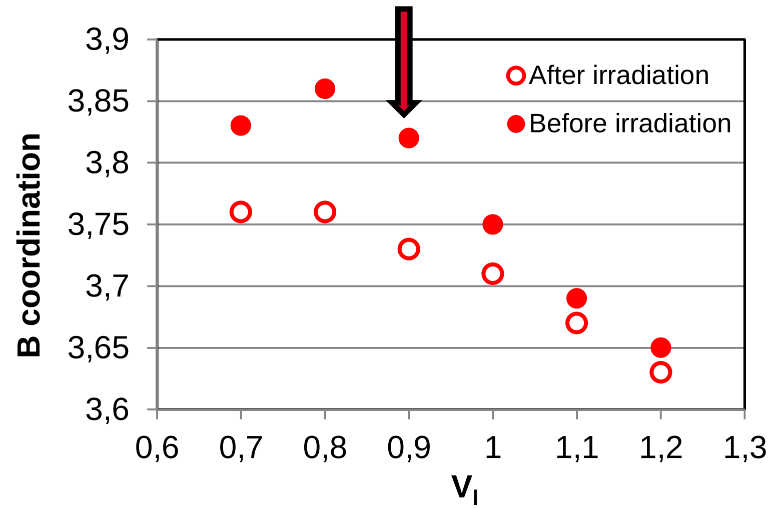
% [3]O vs initial volume

Confirmation of the model by using different initial configurations (SBN14 glass)

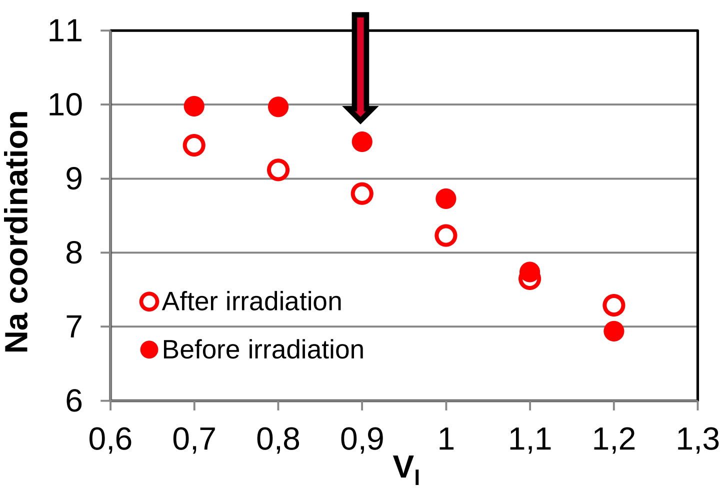
- 190 displacement cascades (800eV)



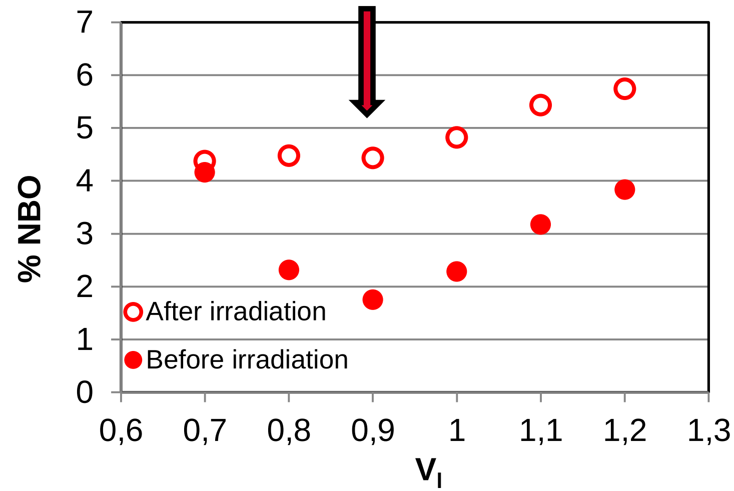
Swelling or contraction of the glass



Decrease of the B coordination



Decrease of the Na coordination



Increase of the %NBO

Confirmation of the model by using different initial configurations (SBN14 glass)

- The six final SBN14 structures get closer one to another

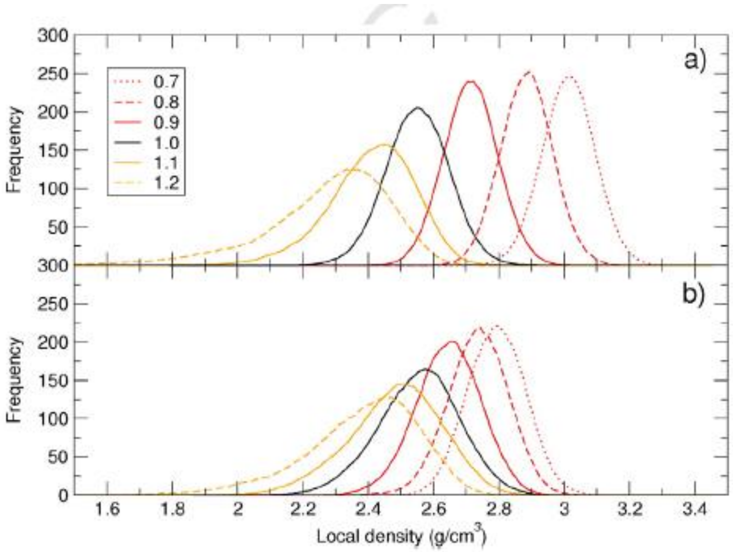
	Initial range	Final range
Density (g/cm^3)	[2.25 - 3.03]	[2.38 – 2.81]
B coordination	[3.65 - 3.86]	[3.63 – 3.76]
Na coordination	[6.94 – 9.98]	[7.29 – 9.45]
% NBO	[1.75 – 4.16]	[4.37 – 5.74]

Local density distributions

Definition of the local density:
Average atom number in a 8Å radius

Before irradiation

After irradiation



The initial memory of the structure is partly lost to converge towards a unique metastable structure (energy is too low?)

The local density distributions are less dispersed after irradiation but an increase of the disorder can be noticed

D.A. Kilymis et al., J. Non-Cryst. Solids, 432 (2015) 354

To conclude about this part

- Under ballistic effects, a new metastable structure is reached: increase of the potential energy, increase of the disorder, depolymerization …

- The swelling is associated to the decrease of the B coordination

- The initial memory is (partly?) lost and the final irradiated structure seems to be independent of the initial one → analogy with the quench rate effects

Fit of a Buckingham type potential

- A new Buckingham type potential has been fitted to study the mechanical property changes under ballistic effects
- Potential fitted for SiO_2 – B_2O_3 – Na_2O glasses
- Fit on experimental data
  - Boron coordination, structure factors
  - Macroscopic properties (density, elastic moduli)
  - The ionic charges depend on the molar composition

$$\phi(r_{ij}) = \frac{q_i q_j}{r_{ij}} + A_{ij} \exp\left(-\frac{r_{ij}}{\rho_{ij}}\right) - \frac{C_{ij}}{r_{ij}^6}$$

Buckingham potentials

L.H. Kieu et al., J. Non-Cryst. Solids, 357 (2011) 3313

Fit of a Buckingham type potential

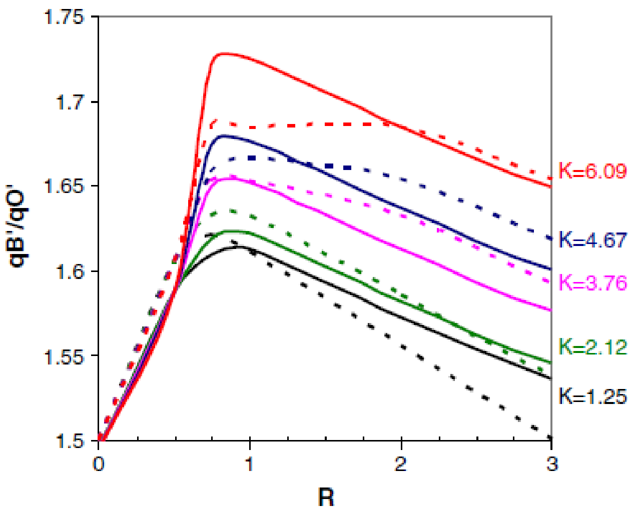
- A set of glass compositions has been used for the potential fit

	Glass composition (mol%)			ρ (g/cm³)	E (GPa)	K_b (GPa)	C_B
	SiO_2	B_2O_3	Na_2O				
SB[a]	69.5	30.5	0	2.042	34.31	23.74	3
SBN3[a]	48	48.7	3.3	2.069	35.65	23.47	3.07
SBN10[a]	44.4	46.1	9.6	2.181	45.63	28.17	3.21
SBN12	59.66	28.14	12.20	2.37	71.8	42	3.43
SBN14	67.73	18.04	14.23	2.45	82	45	3.73
SBN55	55.30	14.71	29.99	2.54	69.4	48.6	3.62
Reed[b]	75	12.5	12.5	2.78	110.4	68.7	4

$$\phi(r_{ij}) = \frac{q_i q_j}{r_{ij}} + A_{ij}\exp\left(-\frac{r_{ij}}{\rho_{ij}}\right) - \frac{C_{ij}}{r_{ij}^6}$$

$$K = \frac{[SiO_2]}{[B_2O_3]} \qquad R = \frac{[Na_2O]}{[B_2O_3]}$$

- The ionic charges depend on the composition



In the literature: $\frac{q_{B_3}}{q_O} = -1.5$ $\quad \frac{q_{B_4}}{q_O} = -1.71$

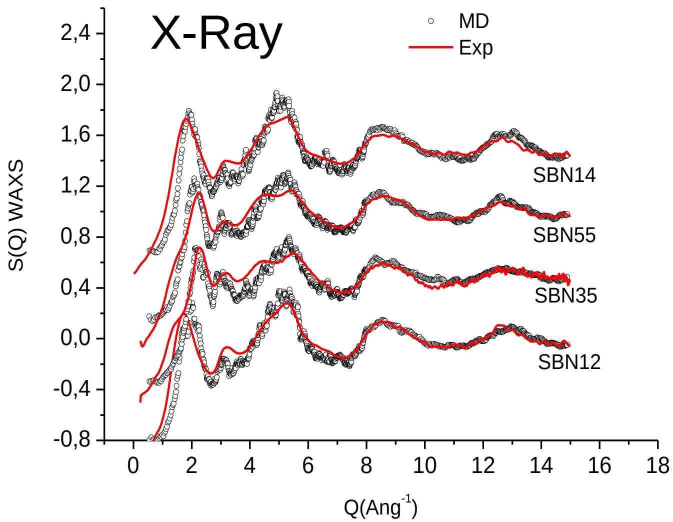
First condition $\left|\frac{q'_B}{q'_O}\right|_{YB} = f_{B3}\left|\frac{q_{B3}}{q_O}\right| + f_{B4}\left|\frac{q_{B4}}{q_O}\right|$

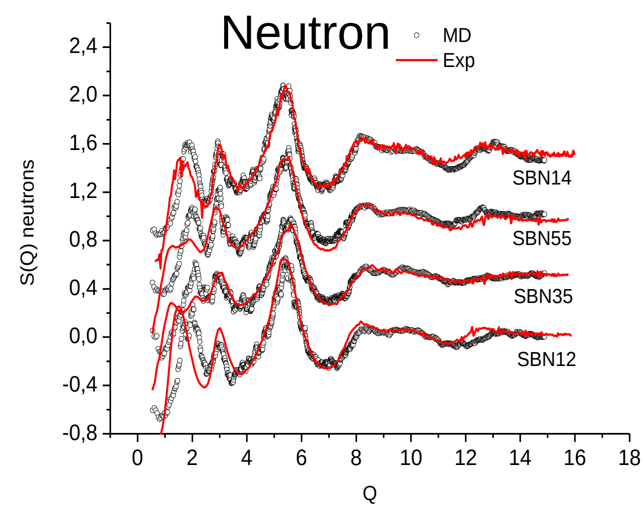
$$\Rightarrow \quad q'_B = -q'_O\left(C_6K^2 + \sum_{i=1}^{5} C_iR^i + C_0\right)$$

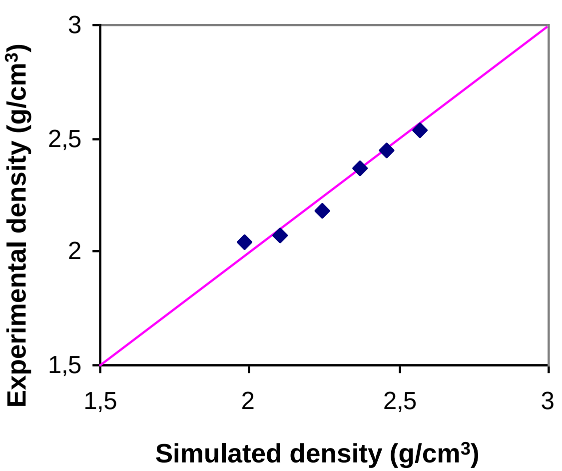
Fit of a Buckingham type potential

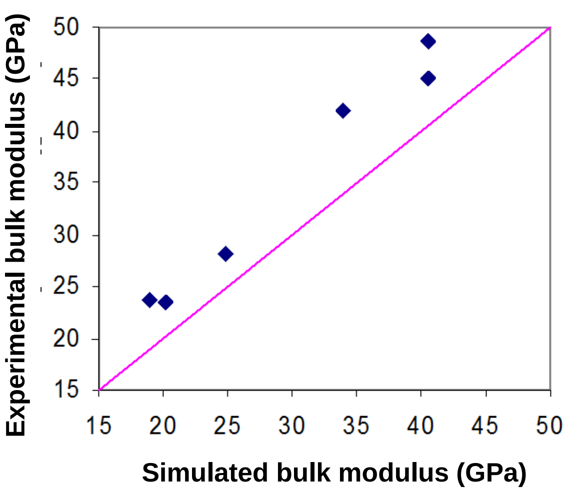
- Boron coordination, S(Q), density, bulk moduli, Young moduli

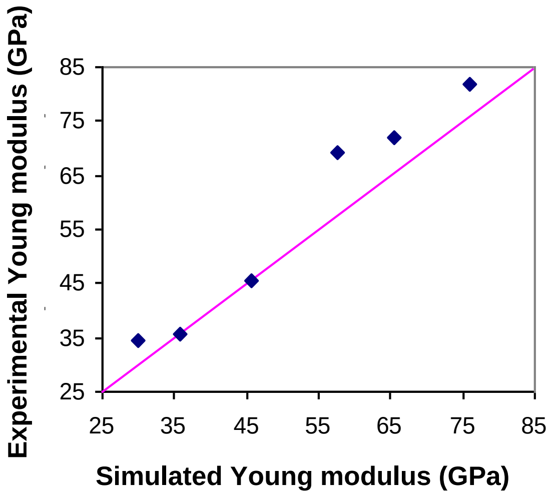
Glasses	C_B (Y&B)
SB	3.01 (3.0)
SBN3	3.09 (3.07)
SBN10	3.23 (3,21)
SBN12	3.41 (3,43)
SBN14	3.72 (3,73)
SBN55	3.58 (3,62)





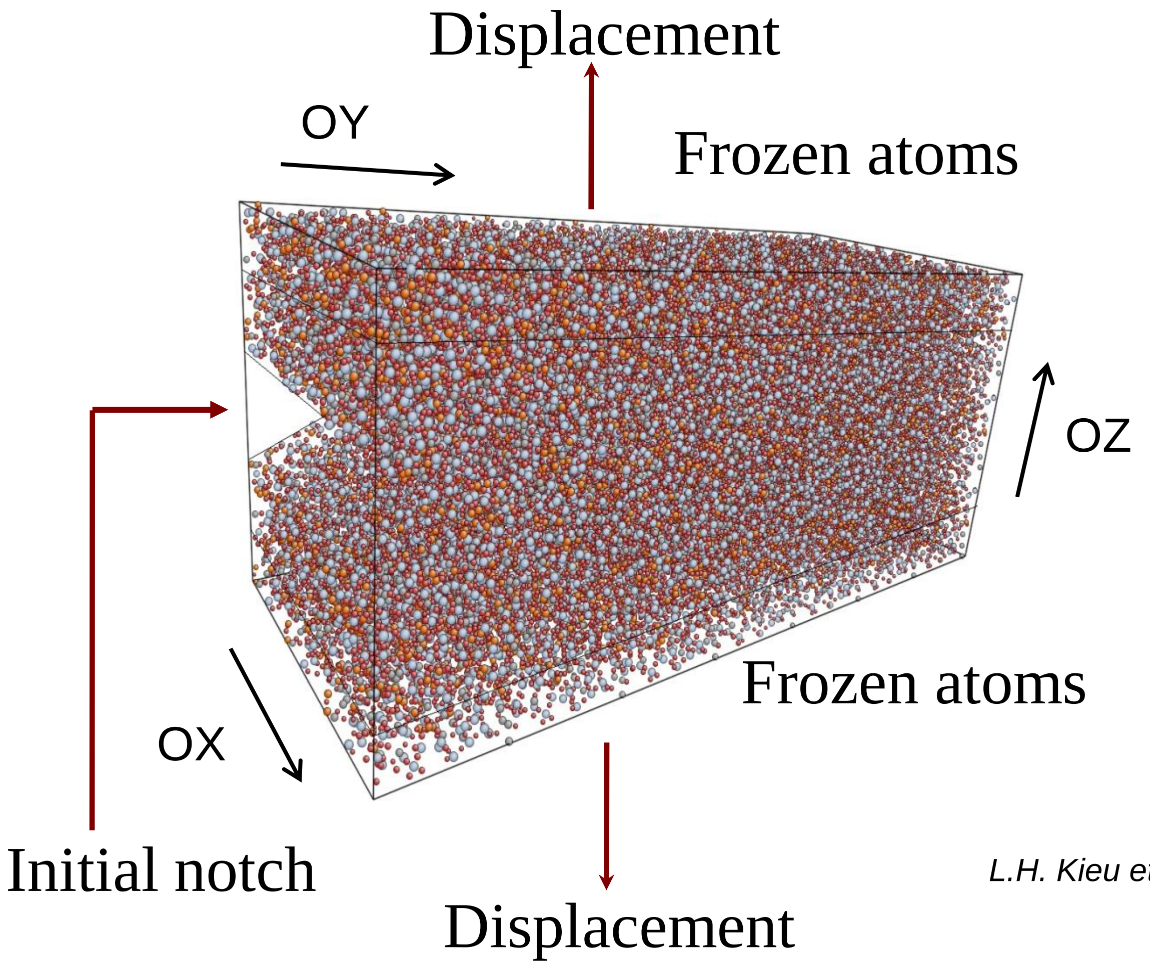






Origin of the fracture toughness increase under nuclear irradiation

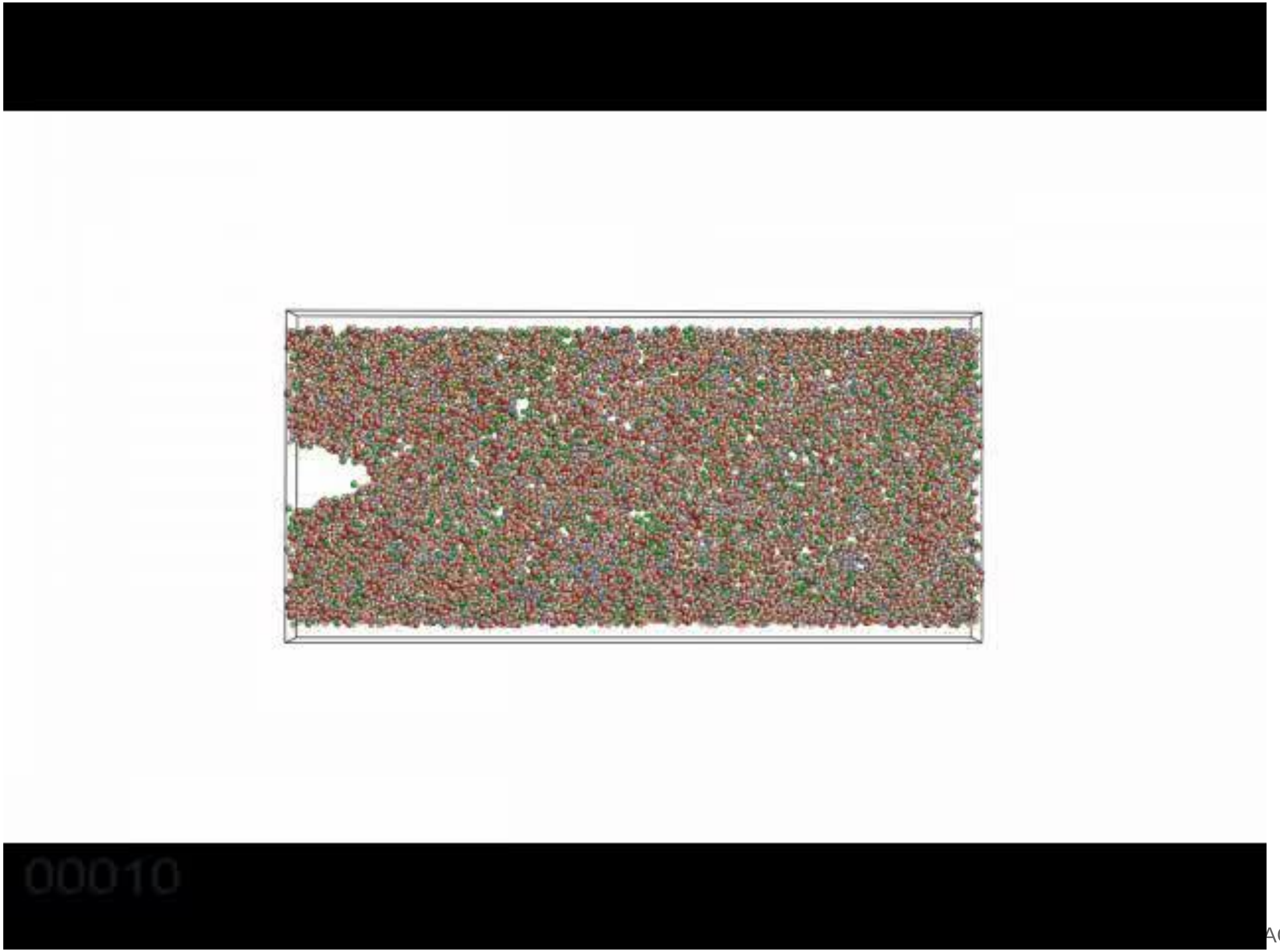
- Simulation box: rectangular parallelepiped box (10^5 atoms) of 250 x 50 x 100 $Å^3$
- 3D initial notch: 30Å deep (X direction), 20Å high (Z direction), Ly (Y direction)
- 2 layers of frozen atoms (top and bottom)



Tensile rate : 40m/s
Temperature fixed at 5K

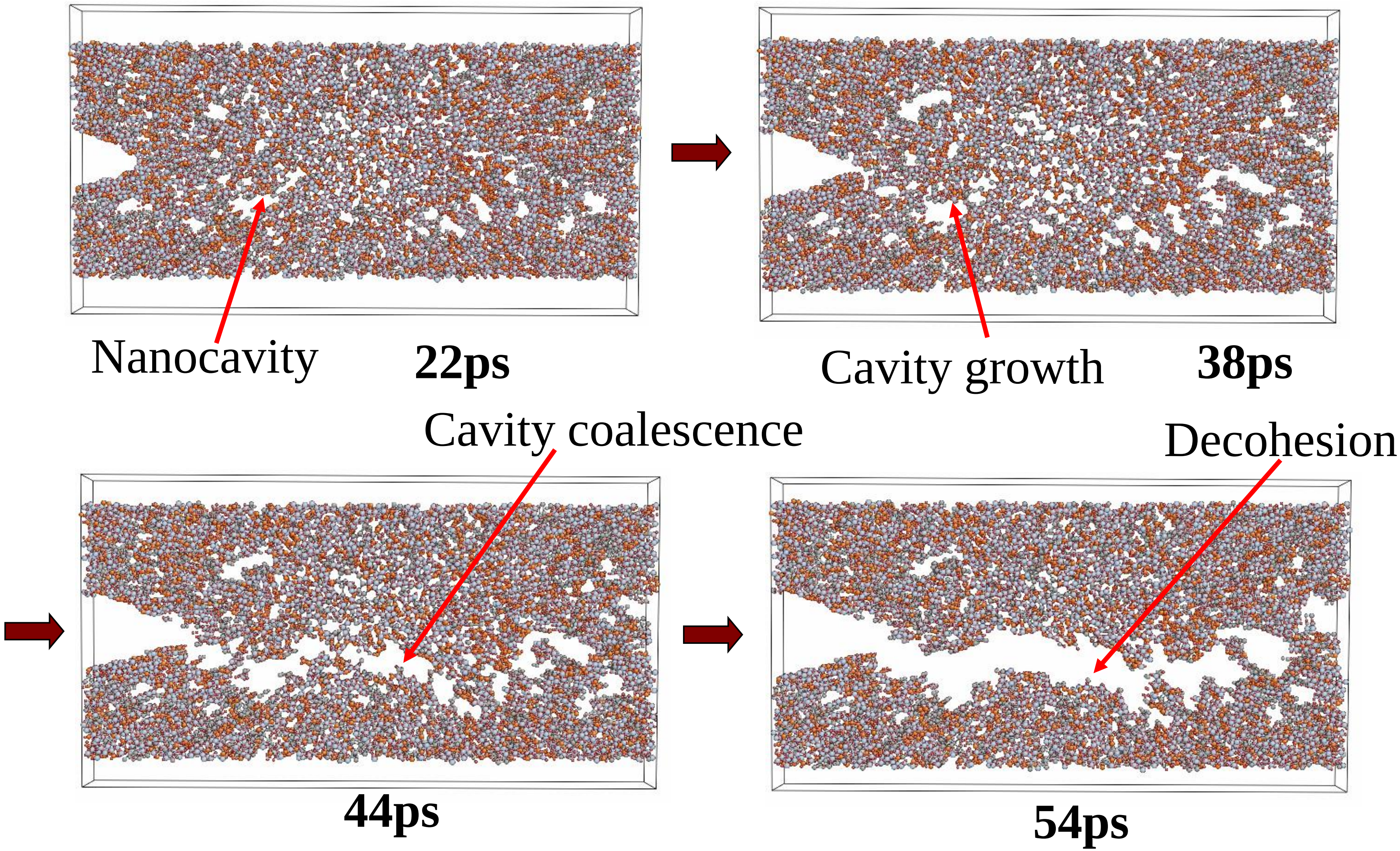
L.H. Kieu et al., J. Non-Cryst. Solids, 358 (2012) 3268

Crack propagation in a SBN14 glass



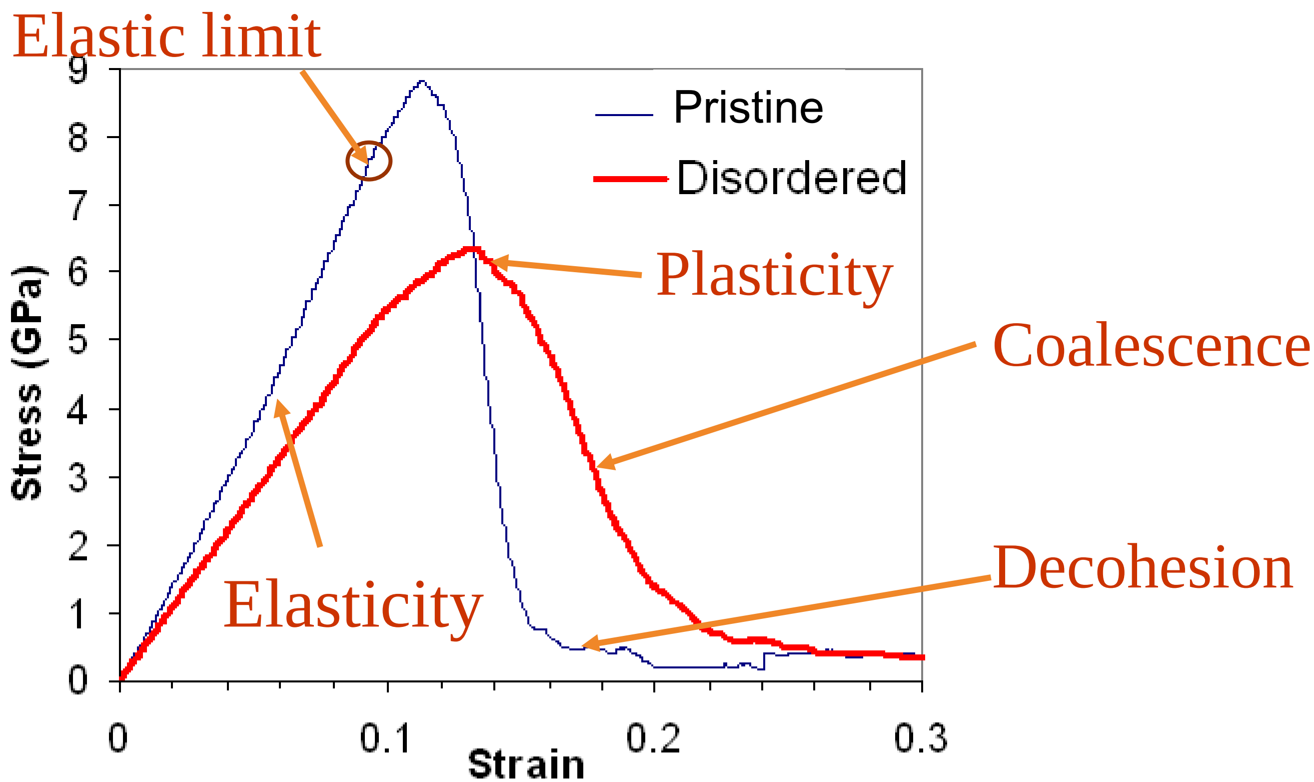
Four steps during the crack propagation

- Nucleation / Growth / Coalescence / Decohesion (67.7%SiO_2 – 18.0%B_2O_3 – 14.2%Na_2O glass)



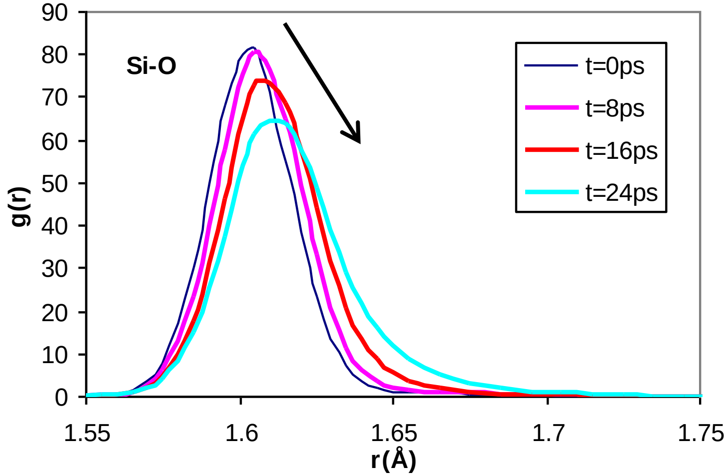
Stress – Strain curves

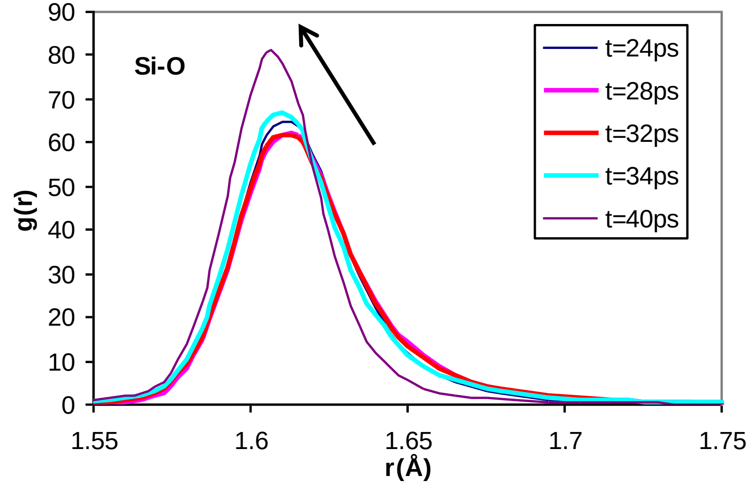
- Differences between pristine and « irradiated » (= disordered) SBN14 glass
  - Decrease of the Young modulus from 74.0GPa to 51.6GPa (-30%)
  - Decrease of the elastic limit
  - Widening of the plasticity region (the non linear part of the stress – strain curve)



RDFs versus time in the pristine glass: Si-O and [4]B-O

- The cations behave differently depending on their local coordination
  - *Tetracoordinated elements : Si and [4]B → « strong » elements*

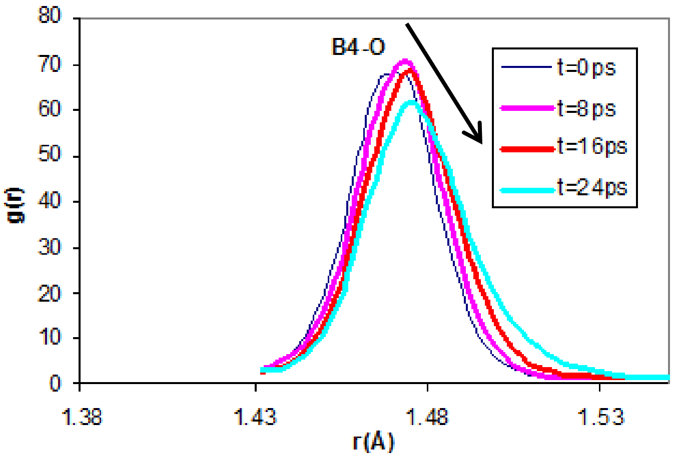


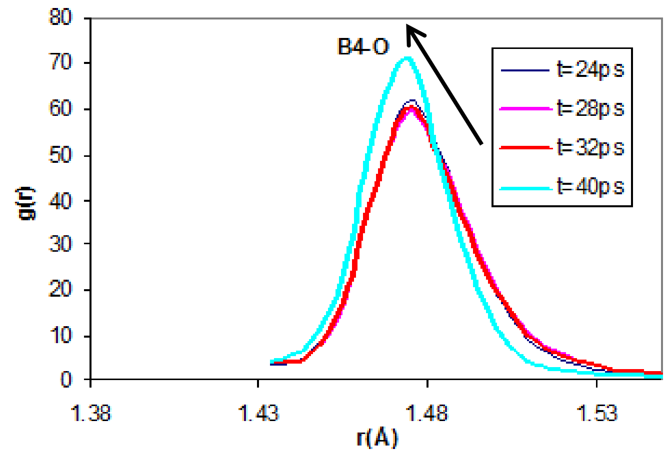


RDF Si-O

0 to 24ps : Stretching of the Si-O and ^{4}B-O distances

24 to 40ps : Relaxation of the Si-O and ^{4}B-O distances

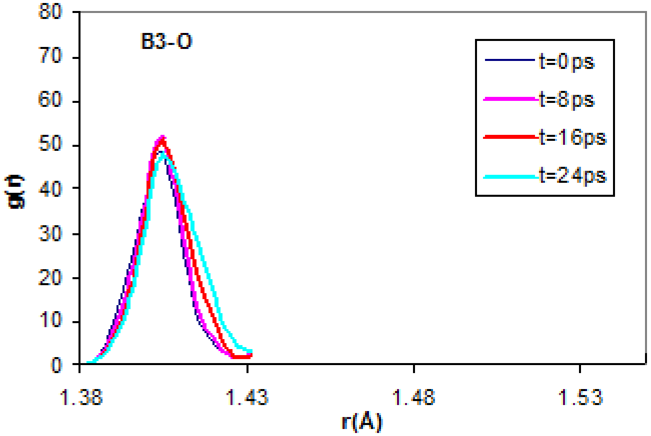


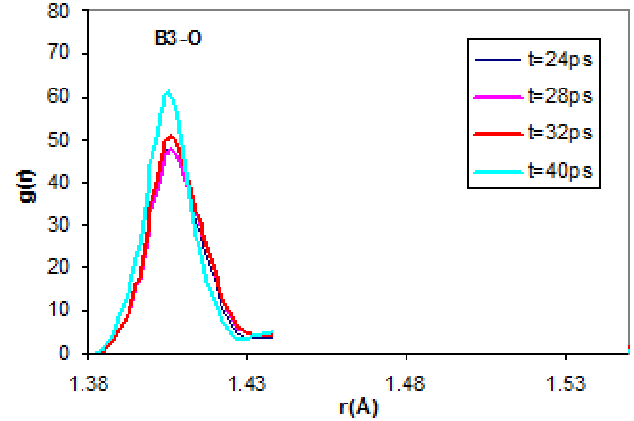


RDF [4]B-O

RDFs versus time in the pristine glass: [3]B-O and Na-O

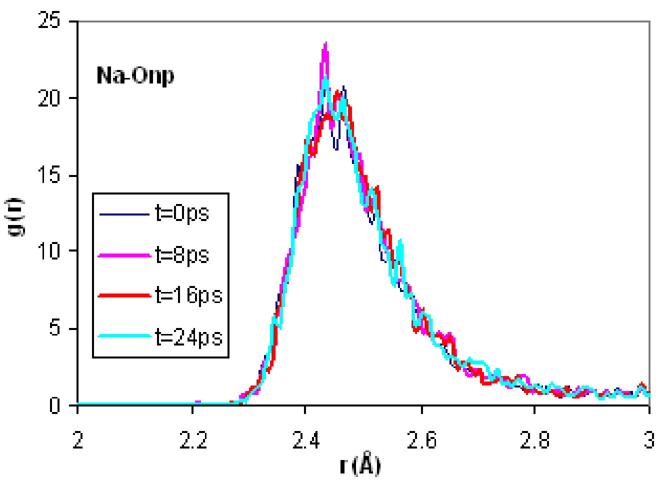
- The cations behave differently depending on their local coordination
  - *[3]B and Na → « Soft » elements*

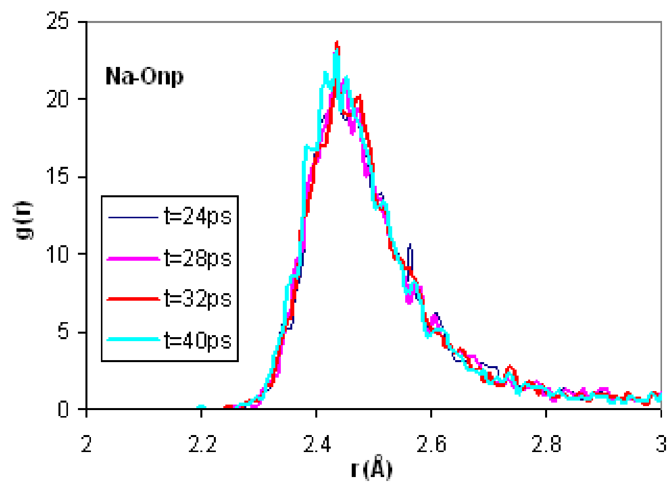




RDF [3]B-O

No stretching of [3]B-O or Na-O distances





RDF Na-O

Origin of the fracture toughness increase under nuclear irradiation

- After irradiation:

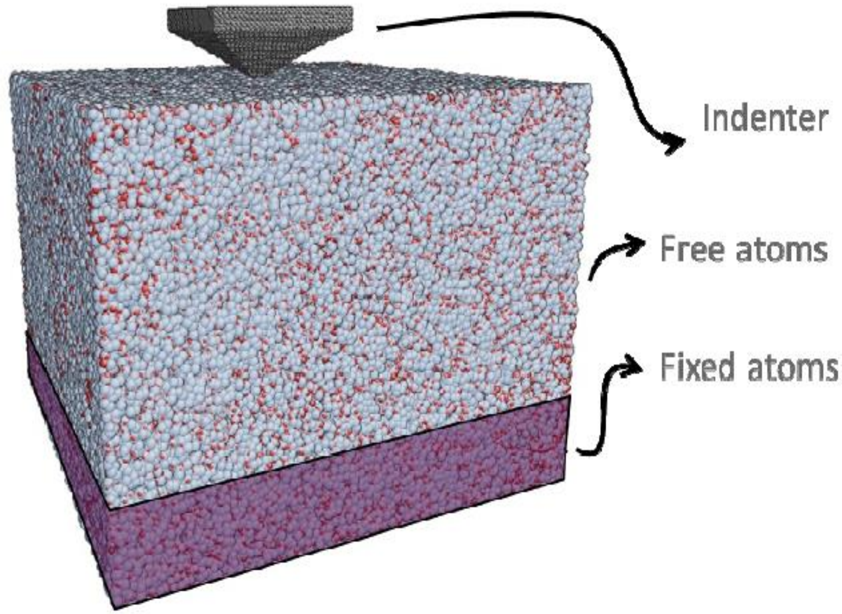
  - *Increase of the [3]B concentration relative to the [4]B concentration*
    → it explains why the pastic phase increases in the irradiated glass: the [3]B atoms enhance the plastic processes

  - *The enhancement of the plastic processes consumes a larger energy*
    → it explains why the fracture toughness increases after irradiation

Hardness measurement

Method

- 35nm x 35nm x 25nm (<>2 10^6 atoms)
- Indenter: diamond Vickers tip (angle: 136°)
- Temperature : 300K
- Indentation speed: 10m/s
- Indentation step: 0.1Å
- Holding phase at the maximum load: 50ps

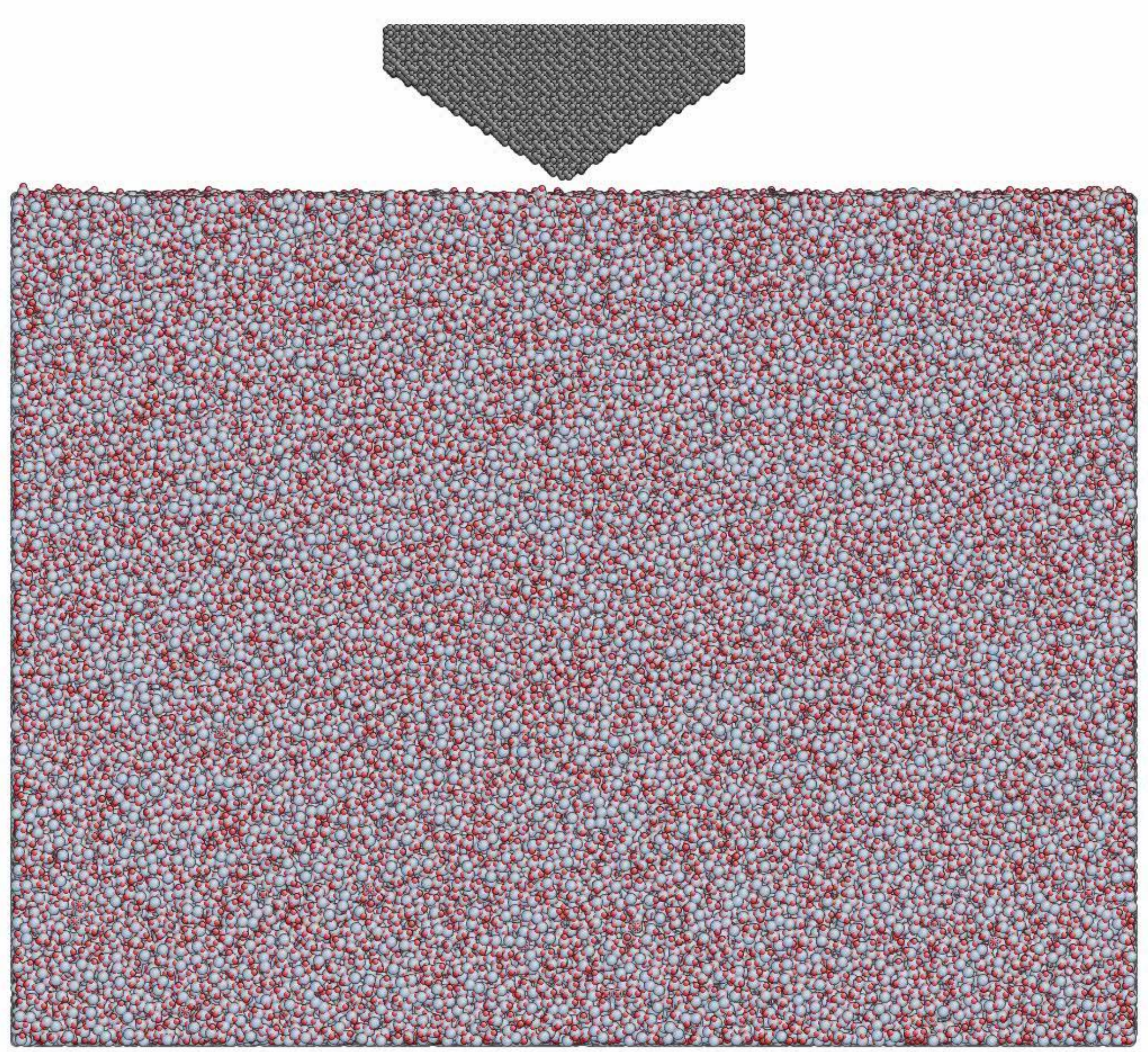


D.A. Kilymis et al., J. Chem. Phys. 141 (2014) 014504
D.A. Kilymis, J. Chem. Phys. 145 (2016) 044505

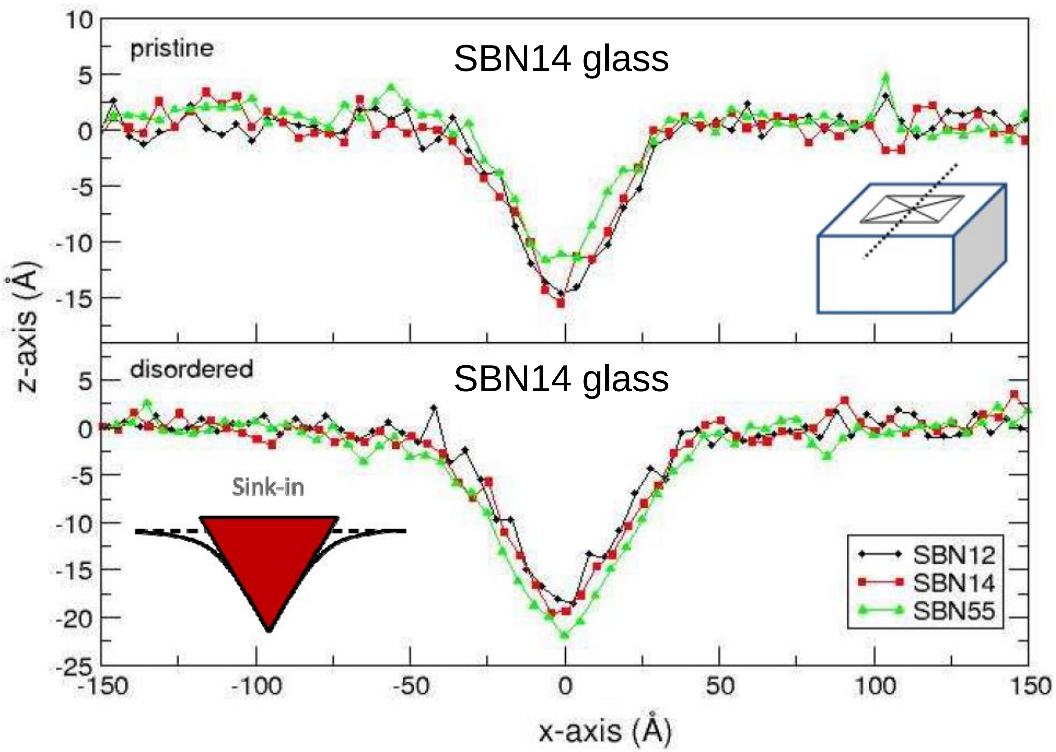
Glasses	Chemical compositions (mol%)		
	SiO_2	B_2O_3	Na_2O
SBN12	59.66	28.14	12.20
SBN14	67.73	18.04	14.23
SBN55	55.30	14.71	29.99

The heavy ion irradiation is simulated by accelerating the quench rate
=> swelling, depolymerization ($BO_4 \rightarrow BO_3$, NBO), increase of disorder

Nanoindentation in silica



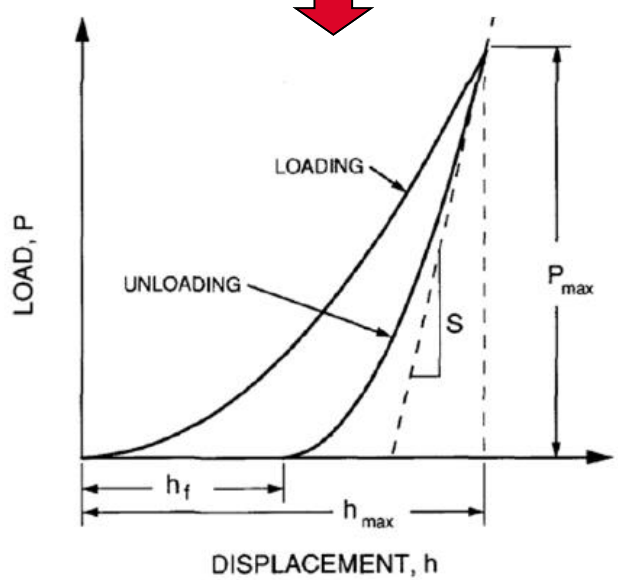
Profiles around the imprints



Indentation profiles

Hardness decrease (qualitative)

Oliver and Pharr method to calculate the surface contact then the hardness



$$h_c = h_{max} - \varepsilon \frac{P_{max}}{S}$$

$$H = \frac{P_{max}}{A_c} = \frac{P_{max}}{4h_c^2 \tan^2 \theta}$$

Harness in the pristine and « irradiated » glasses

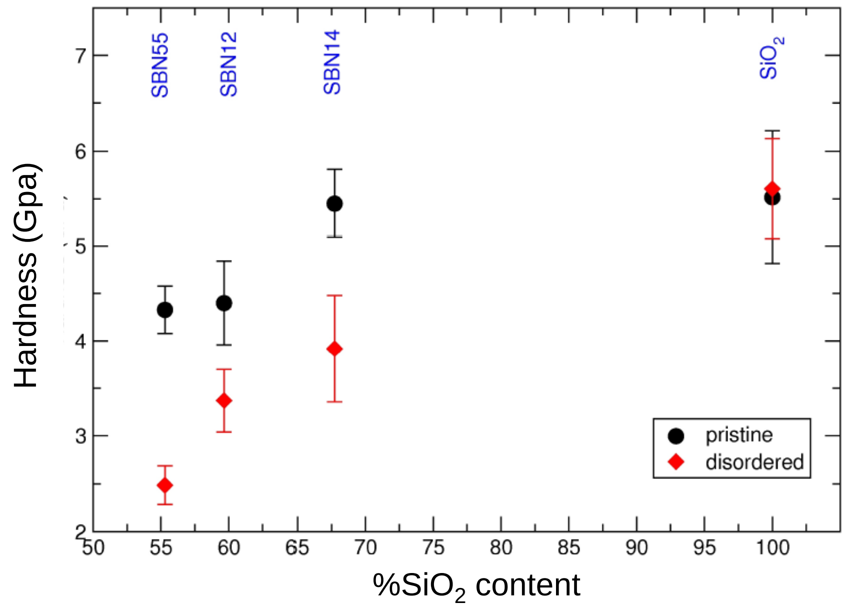
- Comparison between simulated and experimental values

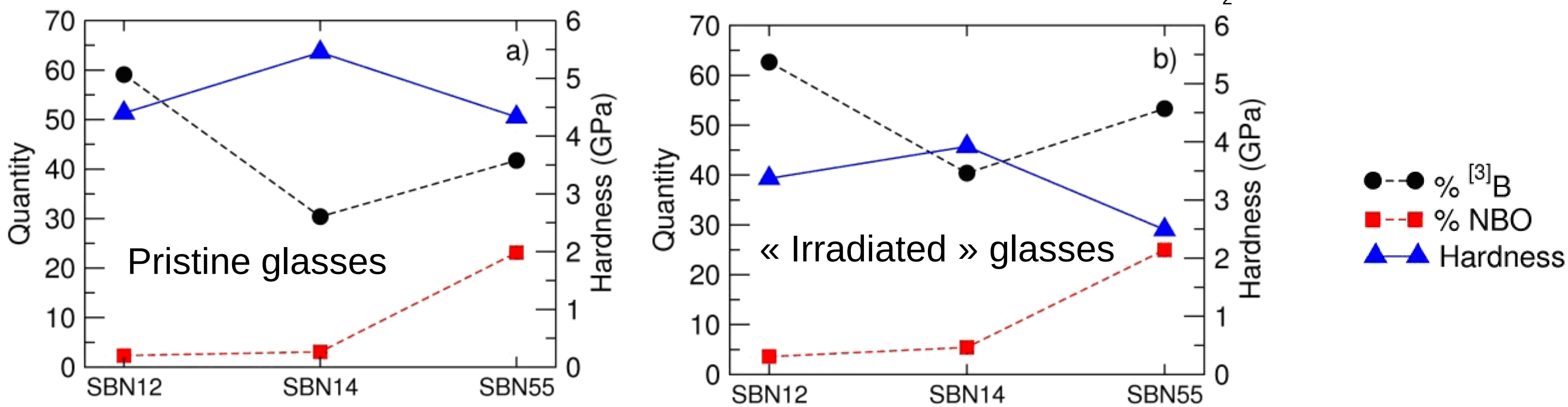
Hardness	Pristine glasses *(shift with the experiment)*	« Irradiated » glasses	Experiment (non irradiated glasses)
SBN12	4.40GPa *(-43%)*	-23.4%	5.2GPa – 8.2GPa
SBN14	**5.45GPa *(-13%)***	**-28.1%**	**6.30GPa**
SBN55	4.33GPa *(-15%)*	-42.5%	5.1GPa

- Experimental hardness is better reproduced when the Na_2O concentration increases
- Hardness decreases in the « irradiated » glasses (in agreement with the experimental observations)

Origin of the hardness decrease under irradiation

- Hardness increase with the $\%SiO_2$
- Hardness decreases in the « irradiated » glasses
- Correlations with the %[3]B and %NBO
  - *Hardness decreases with the %[3]B*
  - *Hardness decreases with the %NBO*





<u>Irradiation: increase of the [3]B and NBO concentrations and increase of the free volume → hardness decrease</u>

Investigation of the relative effects of free volume and depolymerization on the hardness decrease

- Three SBN14 glasses have been studied
  - *The pristine SBN14 glass (glass G1)*
  - *A SBN14 glass quenched rapidly (glass G1qch)*
  - *A SBN14 glass irradiated by 4keV displacement cascades (glass G1irr)*

Glass	Initial density (g/cm^3)	Hardness (GPa)	Boron coordination
G1	2.72	9.25	3.82
G1qch	2.61	6.82	3.73
G1irr	2.67	7.17	3.73

- If the glasses are compared two by two

	Swelling	Hardness change	Boron coordination change
G1 and G1qch	+4%	-26.3%	3.82 → 3.73
G1 and G1irr	+1.8%	-22.5%	3.82 → 3.73
G1irr and G1qch	+2.2%	-4.9%	3.73 → 3.73

  - *Swelling without C_B change → small decrease of the hardness*
  - *Swelling and C_B change → large decrease of the hardness*

↳ The depolymerization is the predominant effect to explain the hardness decrease

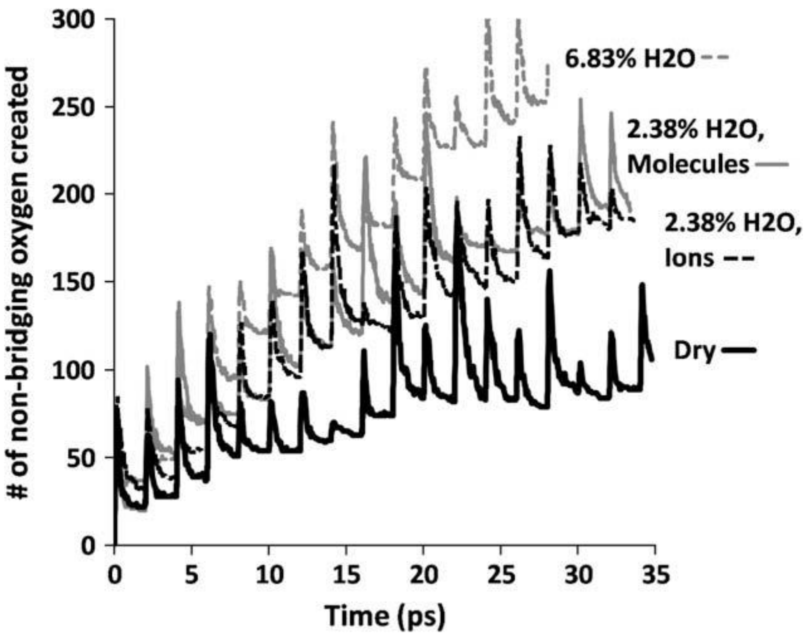
To conclude about this part

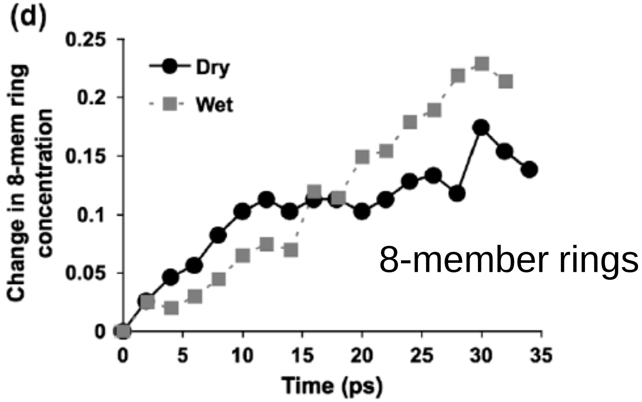
- Hardness decrease is reproduced in irradiated glasses

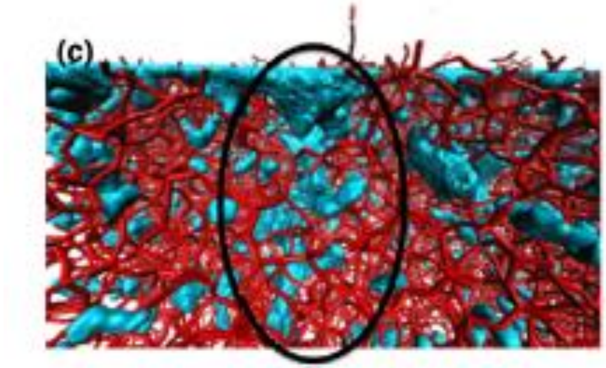
- The hardness decrease is associated to network depolymerization and not to free volume formation

Recent studies in hydrated silicate glasses (classical molecular dynamics)

- Simulation of displacement cascades (1keV) in an hydrated silica







Depending on the water content, the non-bridging oxygen concentration increases.
The modification of the ring size distribution is different depending on the water content.

In a silica / water system, when the projectiles are accelerated from the water inside the silica, channels can form and their healing is prevented by the Si-OH group formation

G.K. Lockwood, S.H. Garofalini, J. Nucl. Mater. 400 (2010) 73
G.K. Lockwood, S.H. Garofalini, J. Nucl. Mater. 430 (2012) 239

Recent studies in hydrated silicate glasses

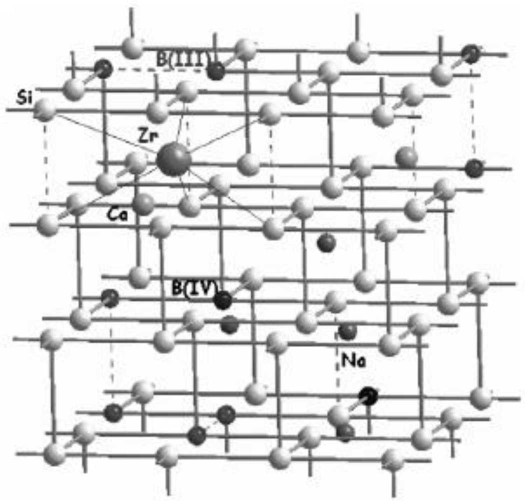
S. Kerisit, E.M. Pierce, Geochim. Cosmochim. Acta 75 (2011) 5296
S. Kerisit, E.M. Pierce, J. Non-Cryst. Solids 358 (2012) 1324

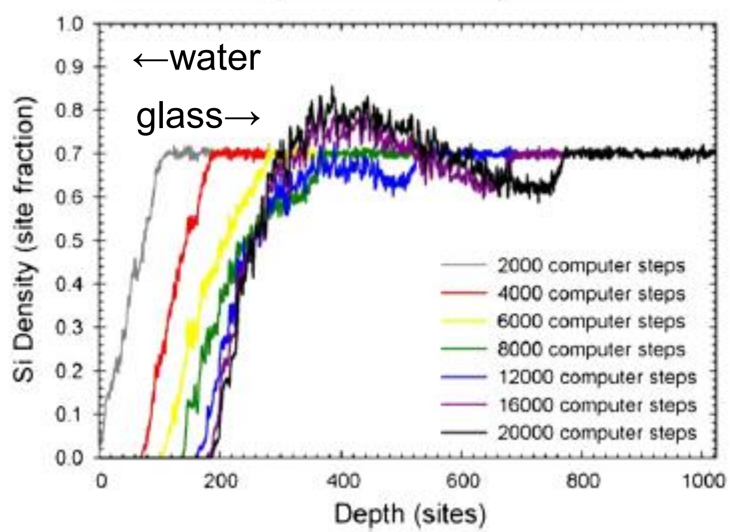
Monte Carlo simulation of glass alteration

A glass is formed by projecting a diamond network on a cubic one. Si, B, Al are located on the network. The glass is in contact with water.

Probabilities are defined to simulate the alteration rate (Si, Al, B hydrolysis and redeposition).

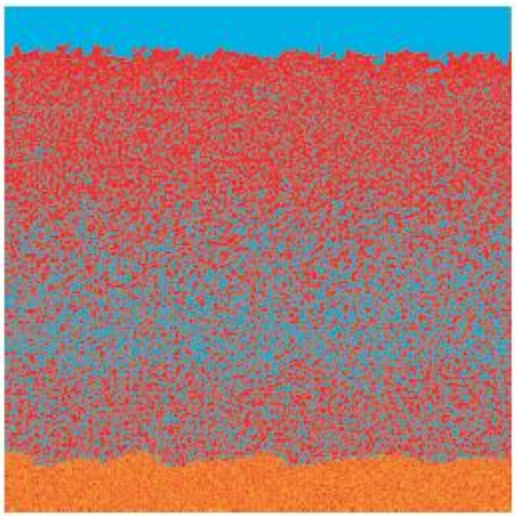
The alteration is stopped when an external layer rich in Si is formed to protect the glass.





Alteration of a 70%SiO_2-15%B_2O_3-15%Na_2O glass with S/V = 2000m^{-1}.

The formation of the alteration layer between the solution and the glass is simulated



Possibility to simulate the impact of Si/Al or Si/B ratios.

Conclusions - Perspectives

- Classical Molecular Dynamics is able to reproduce the radiation effects in simplified nuclear glasses

- Structural modifications induced by the ballistic effects:
  - *depolymerization, formation of non-bridging oxygen*
  - *increase of the disorder*
  - *increase of the internal energy*

- These structural modifications are correlated to the macroscopic property changes:
  - *Increase of the fracture toughness ↔ increase of the « plastic » element concentration*
  - *Decrease of the hardness ↔ network depolymerization*

- Perspectives: Application of classical molecular dynamics to simulate the structure and behavior under radiation and alteration of more complex glasses. For the ISG glass, the interatomic potentials are now available (J. Du et al.)

%wt	SiO_2	B_2O_3	Na_2O	Al_2O_3	ZrO_2	CaO
ISG	56.2	17.3	12.2	6.1	3.3	5.0

THANK YOU FOR YOUR ATTENTION

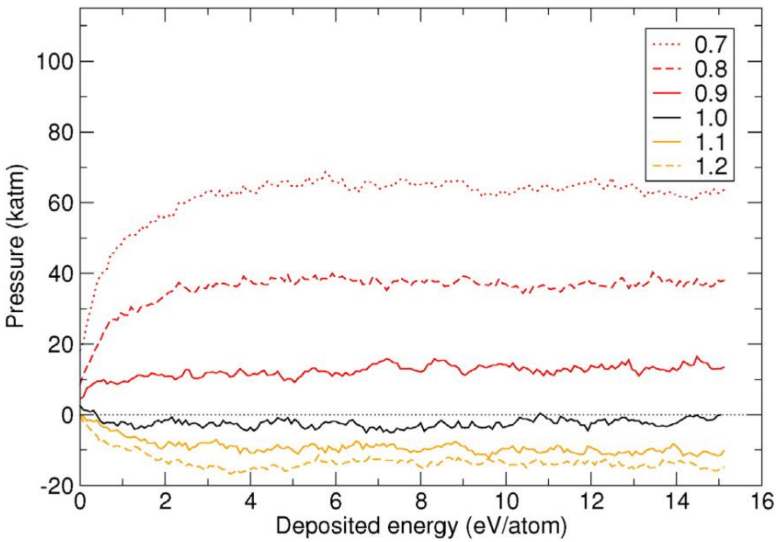
Acknowledgments
O. Bouty (CEA Marcoule / SEVT)
T. Charpentier (CEA Saclay / IRAMIS)
L. Cormier (UPMC / IMPMC)
B. Penelon (CEA Marcoule /SEVT)
C. Stolz (Ecole Polytechnique / LMS)

DE LA RECHERCHE À L'INDUSTRIE

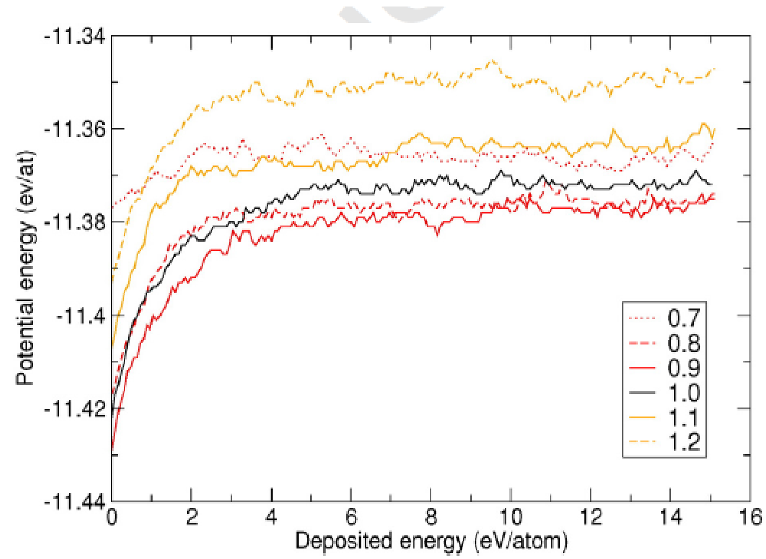
Accumulation of displacement cascades in the six SBN14 glasses

- The six SBN14 glasses have been subjected to series of 190 displacement cascades (800eV)

- Saturation of the effects above a threshold dose (<> 7-8eV/at): density, potential energy, structural characteristics



Increase and saturation of the pressure



Increase and saturation of the potential energy

D.A. Kilymis et al., J. Non-Cryst. Solids , 432 (2016) 354

Conclusion about the displacement cascade accumulation study

- Case closer to the real case (SBN14 with V_l=0.9)
  - The swelling is equal to 2.5% (3.5% experimentally with heavy ion irradiation)
  - The swelling is associated to the decrease of B and Na coordination ($BO_4 \rightarrow BO_3$), and to an increase of %NBO, potential energy and internal disorder

- More general observations
  - When a set of initial structures are irradiated, the final structures get closer one to another → there is a trend to lose the initial memory of the structure
  - Depending on the initial density, a swelling or a contraction can occur
  - A decrease of the B and Na coordinations is systematically observed
  - An increase of the potential energy and internal disorder is systematically observed

Model proposed to explain the saturation effect in the nuclear glasses

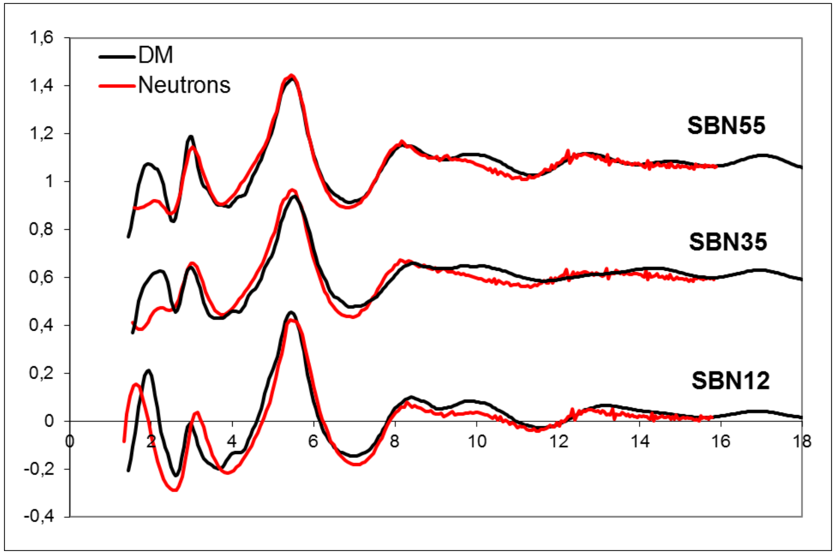
1. Inside the core of the cascade, the structure is melt and quenched very rapidly
2. A new local configuration, independent of the initial structure, is built
3. When the total volume has been irradiated, a new saturation point is reached

Fit of a Buckingham type potential

- Neutron spectra are recorded at LLB (7C2 spectrometer, λ = 0.723Å)

Glass compositions studied

Glasses	Chemical compositions (mol%)		
	SiO_2	B_2O_3	Na_2O
SBN12	59,66	28,14	12,20
SBN14	67,73	18,04	14,23
SBN35	43.95	20.63	35.42
SBN55	55,30	14,71	29,99



Glasses with a Na_2O concentration around 10% – 15% (mol%) are better reproduced