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Irradiation Induced Phenomena in Nuclear Glass

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Introduction

In France, non-recoverable radioactive wastes coming from spent nuclear fuels are stored in alumino borosilicate glassy matrices. It is envisaged to store them in a deep geological repository to isolate them from the rest of the environment. These glasses will be subjected to internal irradiations, and after some hundreds of years, to water corrosion due to the arrival of the groundwater in contact with them. Studies are carried out to quantify the radiation and water corrosion effects to characterize the long-term waste package behavior. Experimental and numerical approaches have been considered in order to study the variations of the structural and mechanical properties under irradiation.

Experimentally, it has been shown, on industrial and simplified glasses doped with short lived actinides or irradiated externally by heavy ions, that the elastic effects lead to different structural (decrease of the polymerization glass networks, increase of the disorder) and mechanical modifications (swelling, decrease of the hardness, increase of the fracture toughness, increase of the internal energy). A computational approach using classical molecular dynamics has been developed in parallel to clarify the correlations between the structural and mechanical property changes. This presentation will expose the main results from our simulations.

Computational method

An empirical pair potential of the Buckingham form has been developed recently to model atomic interactions [1]. Hence the interaction between any *(i,j)* pair of constituent atoms is modelled using the following relation:

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

The adjustable parameters have been determined in order to reproduce structural and elastic properties of a set of SiO_2-B_2O_3-Na_2O glasses. A dependence between the ionic charges and the glassy compositions has been introduced in order to reproduce the Boron anomaly, i.e. the nonlinear evolution of the B coordination versus the R(=[Na_2O]/[B_2O_3]) and K(=[SiO_2]/[B_2O_3]) ratios. These potentials were then used to study fracture mechanisms and nanoindentation in pristine and irradiated simplified nuclear glasses.

Results

The three simulated glass compositions are the following:
SBN12 glass: 59.6%SiO_2 – 28.2%B_2O_3 – 12.2%Na_2O
SBN14 glass: 67.8%SiO_2 – 18.0%B_2O_3 – 14.2%Na_2O, this glass is characterized by the same molar ratios as the real nuclear glass
SBN55 glass: 55.3%SiO_2 – 14.7%B_2O_3 – 30.0%Na_2O

For each glassy composition, pristine structures (quenched from the liquid state with a rate equal to 5×10^{12}K/s) and disordered structures have been prepared. The disordered structures have been obtained after the heating of the pristine ones and their faster quench (with a rate equal to 10^{14}K/s) in order to reproduce the main radiation effects, i.e. depolymerization and increase of the internal disorder. The disordered glasses are considered as models of irradiated ones and their mechanical properties have been compared to those of the pristine glasses.

The fracture simulations have made possible to identify the different steps leading to the cracking of the materials [2]. Under the application of an external tensile stress, nano cavities are firstly formed. Then they begin to coalesce as the external stress increases forming increasingly large voids until the complete opening of the structure. During the fracture process, two different behaviors have been noticed: the Si and 4-coordinated B atoms on one hand accumulating stresses in their local environments, and, on the other hand, the 3-coordinated B and Na atoms adapting themselves much more easily to the local stress changes and then facilitating the viscous flow. This observation has made possible to propose an explanation of the origin of the fracture toughness increase in the simplified SBN14 glass. The radiation effects induce a decrease of the average B coordination, with a rise of the 3-coordinated B concentration. In consequence, the plasticity of the material increases, and the energy cost needed for the sample breakage is larger, hence the fracture toughness increase.

Concerning the nanoindentation simulations [3], a Vickers indenter in diamond has been pushed then removed from a simulation box and, using the loading – unloading curves, the hardness values have been quantified (Fig. 1). With the increase of the disorder, a systematic hardness decrease is observed [4] in the three glassy compositions that has been correlated to an increase of the 3-coordinated B and non-bridging oxygen concentrations.

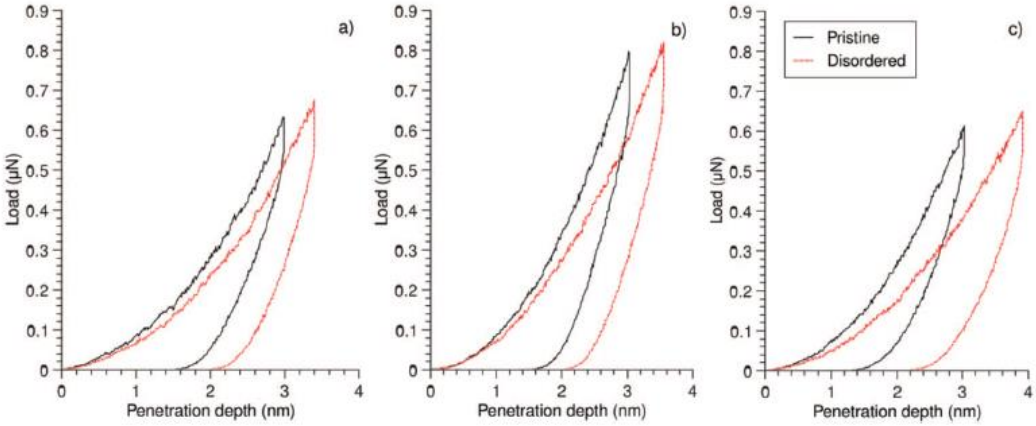

Fig. 1: Loading – unloading curves during nanoindentation simulated in the SBN12 (a), SBN14 (b) and SBN55 (c) glasses.

Taking into account the disordering and depolymerization effects, this study using the classical molecular dynamics method has therefore allowed reproducing changes of the mechanical properties analogous to what has been observed in simplified nuclear glasses irradiated externally by heavy ions. Thus, the structural origins of these changes have been better understood.

References

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[3] D. A. Kilymis, J.-M. Delaye, “Deformation mechanisms during nanoindentation of sodium borosilicate glasses of nuclear interest”, J. Chem. Phys., 141 (2014) 014504.

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Irradiation Induced Phenomena in Nuclear Glass

Contributors

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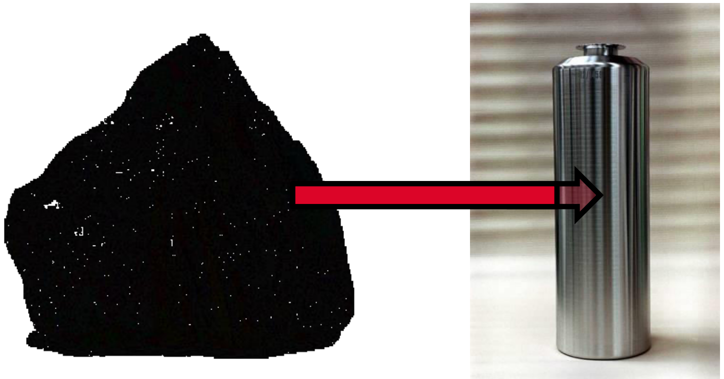
OUTLINE

- Context: Analogy between the behaviors of complex and simplified nuclear glasses under irradiation (ballistic effects)

- Classical molecular dynamics simulations
  - Empirical potentials
  - Series of displacement cascades
  - Fracture: origin of the fracture toughness increase under irradiation
  - Hardness: origin of the hardness decrease under irradiation

- Conclusions

R7T7 glass: the French nuclear glass to confine the high level radioactive wastes



Borosilicate R7T7 glass

- The nuclear glasses will be subjected to internal irradiations (α disintegrations from minor actinides and β/γ radiations from fission products)

- It's important to understand the radiation effects on the macrocopic properties to certify the long term behavior of the glass

R7T7 glass composition: more than 30 components

	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) + Suspension de fines	12,8
Oxydes d'actinides	0,9
$SiO_2+B_2O_3+Al_2O_3$	

SiO_2, B_2O_3 and Na_2O are the major components

Swelling under irradiation in R7T7 glass

R7T7 glass has been irradiated internally by ^{244}Cm with different doses and dose rates

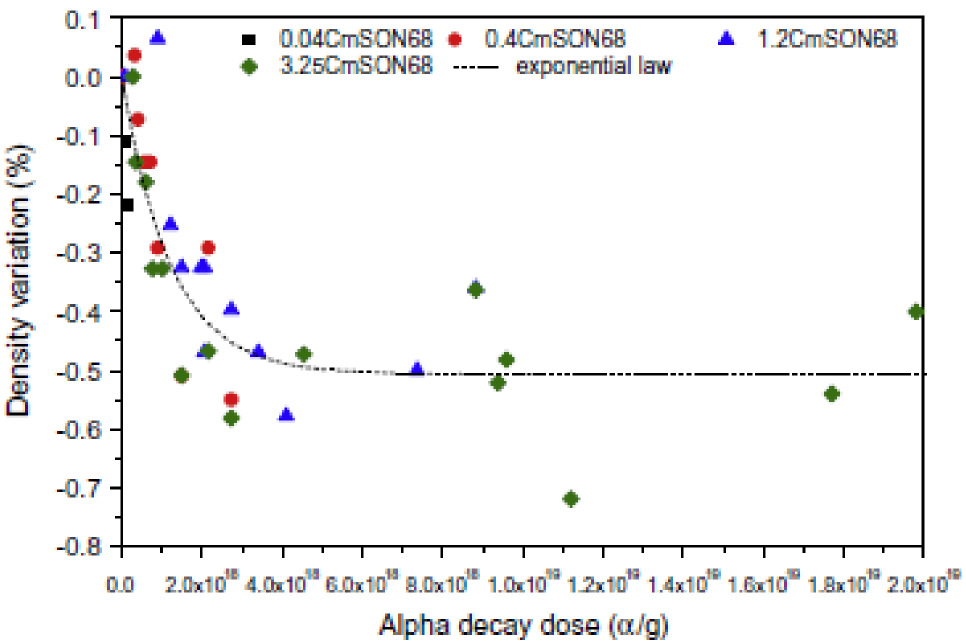


Fig. 1. Density versus alpha decay dose in CmSON68 glass.

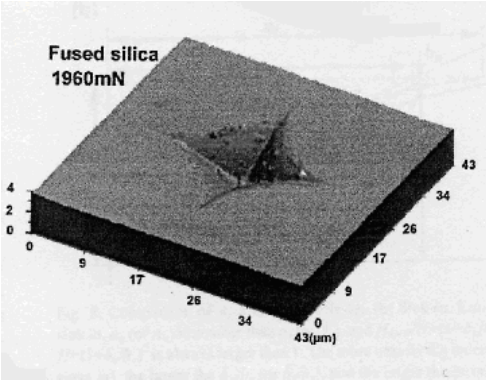
Saturation of the swelling after a critical dose (4 10^{18} α/g)

Final swelling is around 0.6% for each dose rate

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

Fracture toughness increase – Hardness decrease

R7T7 glass has been irradiated externally by heavy ions (Kr, Au)



Microindentation is used to measure the critical charge P_c for which the fracture probability is equal to 50% → the fracture toughness can be deduced

$$P_c = A\frac{K_{IC}^4}{H^3}$$

→ **Fracture toughness increases by around 25% in the R7T7 glass irradiated by Au ions**

R7T7 glass has been doped by short lived actinides (^{244}Cm) or irradiated externally by heavy ions (Kr, Au, Si)

Hardness is measured by Vickers micro indentation

→ **Hardness decreases by around 30%**

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

S. Peuget et al. Nucl. Instr. Meth. Phys. Res. B 246 (2006) 379

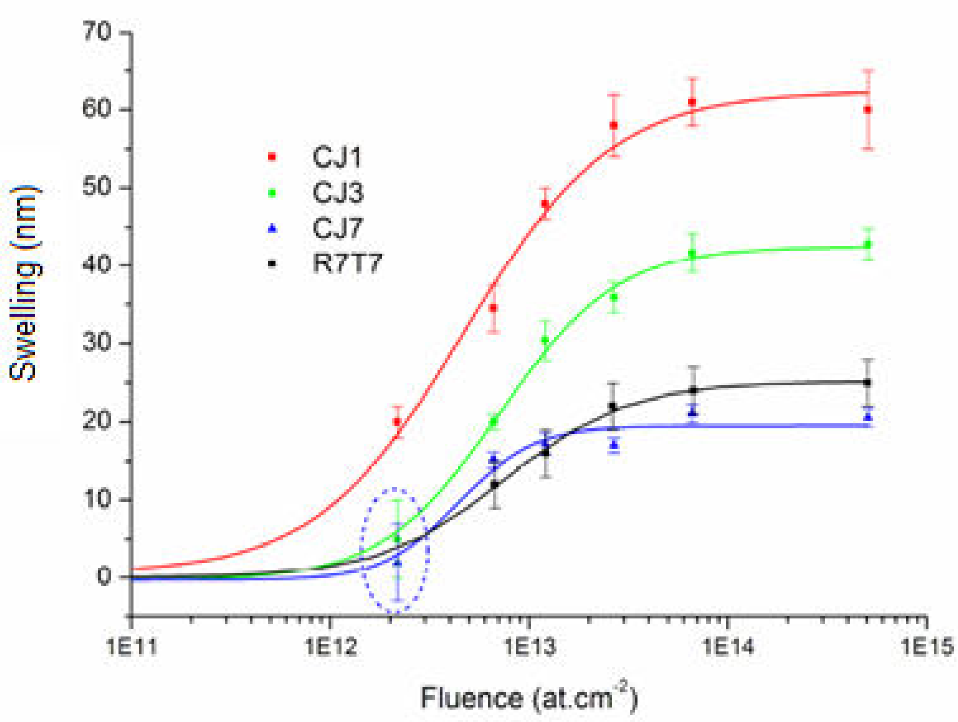
Anology between R7T7 glass and simplified glasses: density

- Three simplified glasses have been prepared:

%mol	SiO_2	B_2O_3	Na_2O	Al_2O_3	CaO	ZrO_2
SBN14 = CJ1	**67.73**	**18.04**	**14.23**	-	-	-
CJ3	61.16	16.29	12.85	3.89	5.81	-
CJ7	63.77	16.98	13.39	4.05		1.81

Irradiated by Au ions

- The swelling is qualitatively the same as in the R7T7 glass



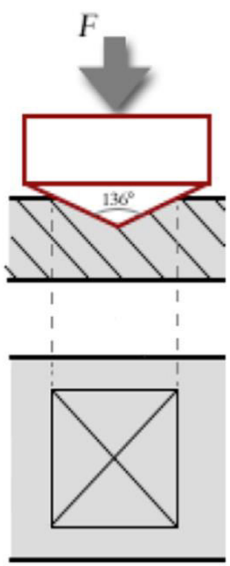
Saturation of the swelling with the dose

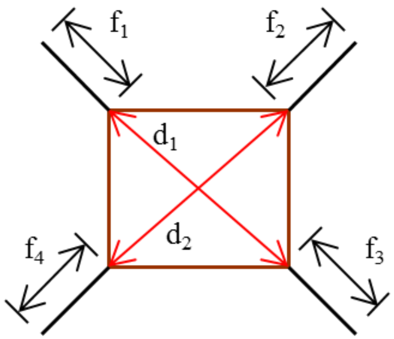
The swelling is larger in the simplified glasses

Anology between R7T7 glass and simplified glasses: fracture toughness and hardness

- Fracture toughness and hardness have been measured in the three simplified glasses (SBN14 = CJ1, CJ3, CJ7) subjected to heavy ion or neutron irradiations

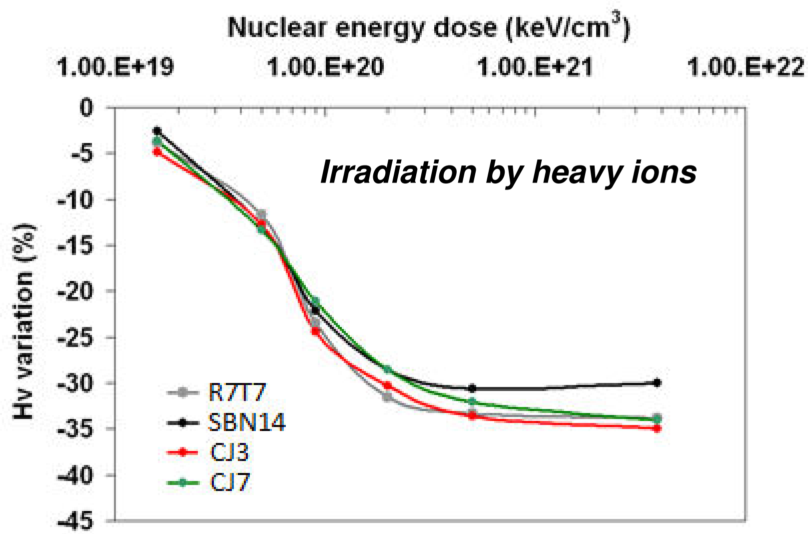
- The fracture toughness and hardness changes are qualitatively the same as in the R7T7 glass





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

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



Decrease of the hardness after irradiation by heavy ions

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

Use of classical molecular dynamics to investigate the consequences of ballistic effects

- Atomistic modeling of simplified nuclear glasses based on $SiO_2 - B_2O_3 - Na_2O$

- Objective: To understand the atomistic origin of the swelling, fracture toughness increase and hardness decrease under irradiation

- Empirical interatomic potentials are used
  - fitted on structural data (Boron coordination, structure factors) and macroscopic properties (density, elastic moduli):

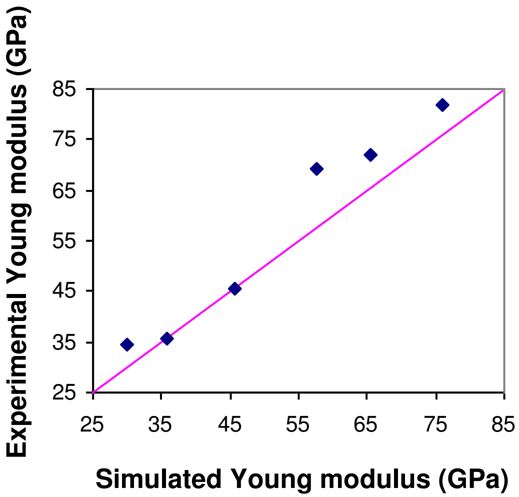
$$\phi(r_{ij}) = \frac{q_i q_j}{r_{ij}} + A_{ij} \exp\left(-\frac{r_{ij}}{\rho_{ij}}\right) - \frac{C_{ij}}{r_{ij}^6}$$

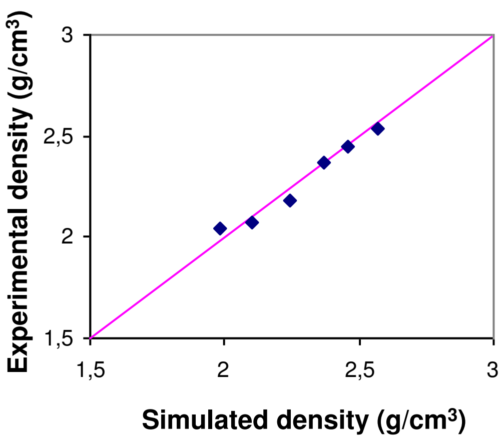
Buckingham potentials

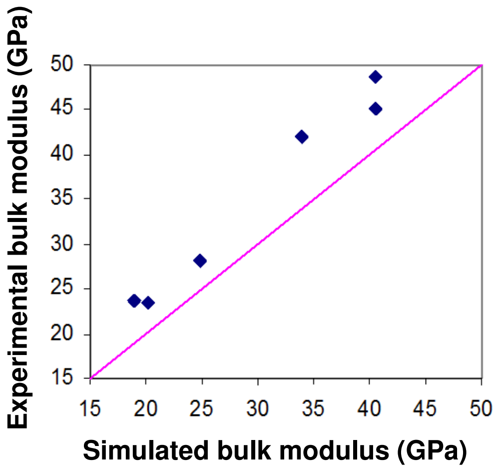
Empirical potentials: macroscopic properties

- A series of simple glasses are simulated to validate the potentials

Glasses	Chemical compositions (mol%)			C_B (Y&B)
	SiO_2	B_2O_3	Na_2O	
SB	69.5	30.5	0	3.01 (3.0)
SBN3	48	48.7	3.3	3.09 (3.07)
SBN10	44.4	46.1	9.6	3.23 (3,21)
SBN12	59.66	28.14	12.20	3.41 (3,43)
SBN14	67.73	18.04	14.23	3.72 (3,73)
SBN55	55.30	14.71	29.99	3.58 (3,62)







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

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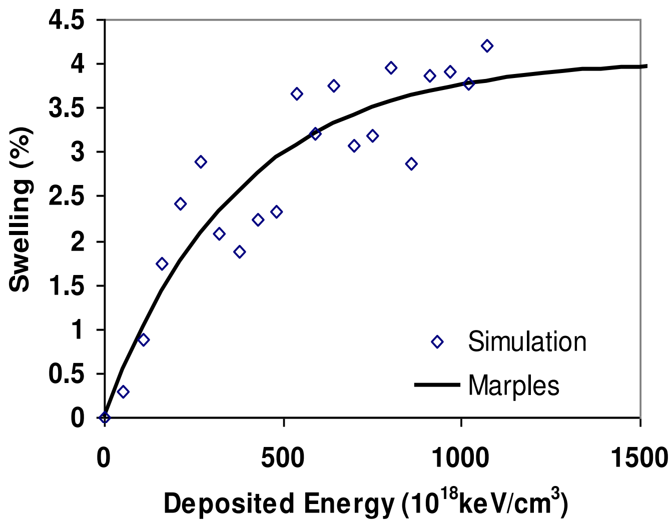
Series of displacement cascades simulated by classical molecular dynamics

DISPLACEMENT CASCADES IN THE SBN14 GLASS (SIO_2-B_2O_3-NA_2O, SIMPLIFIED NUCLEAR GLASS) (1)

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

Swelling under ballistic effects



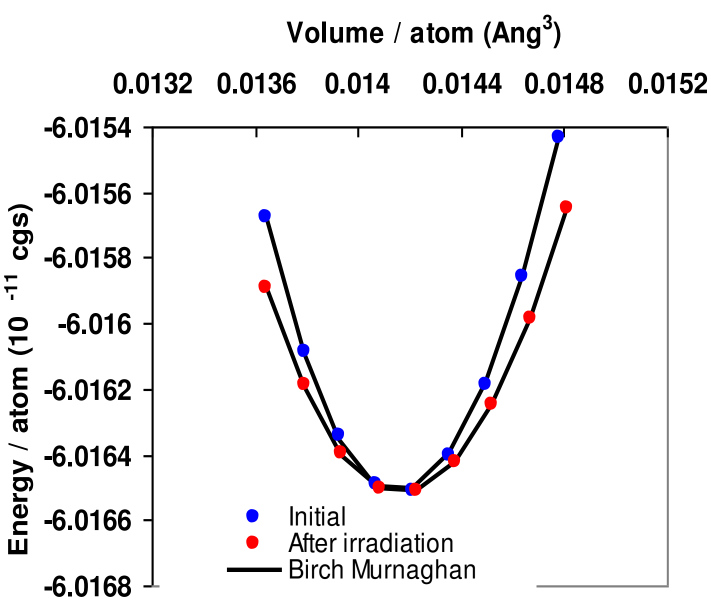
Equivalence

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

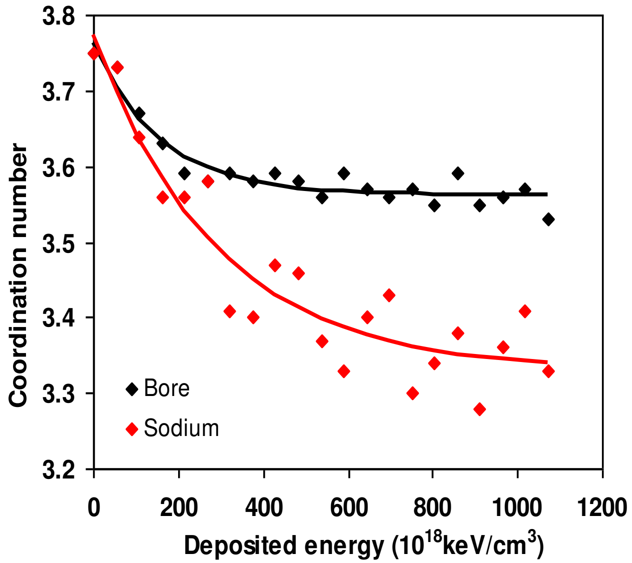
Decrease of the bulk modulus

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



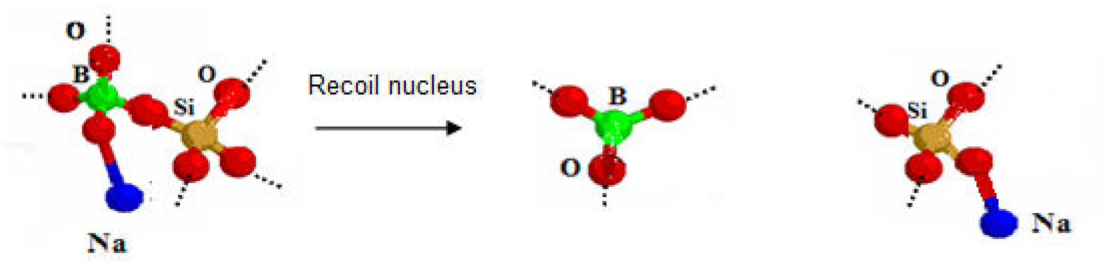
DISPLACEMENT CASCADES IN THE SBN14 GLASS (SIO_2-B_2O_3-NA_2O, SIMPLIFIED NUCLEAR GLASS) (2)

Depolymerization



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

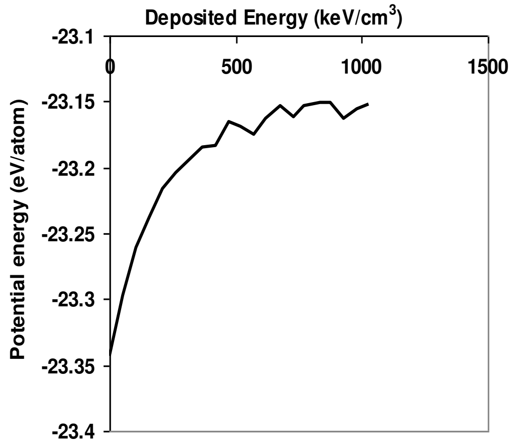
Formation of Non-Bridging Oxygens on the SiO_4 entities



DISPLACEMENT CASCADES IN THE SBN14 GLASS (SiO_2-B_2O_3-Na_2O, SIMPLIFIED NUCLEAR GLASS) (3)

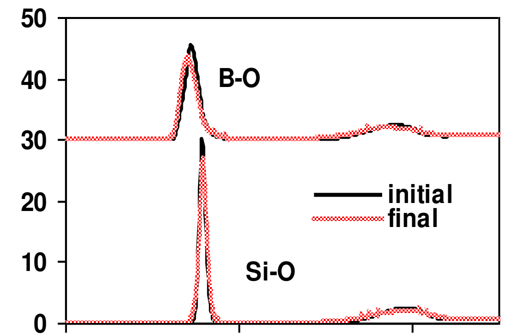
Increase of the disorder

Internal energy increases

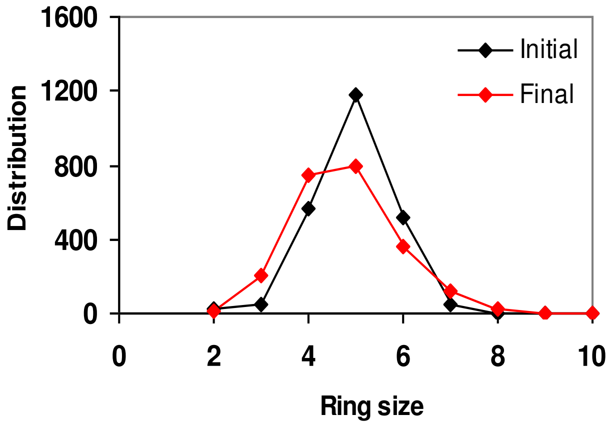


Widening of the distributions

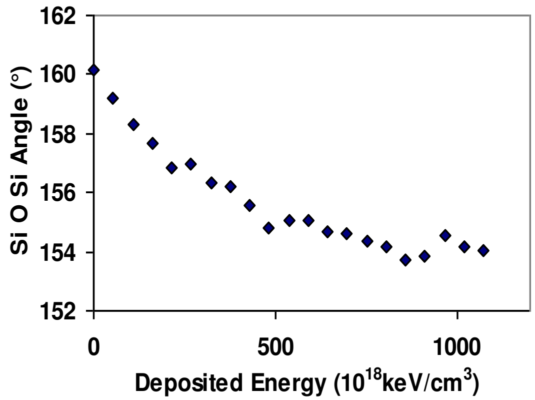
Radial distribution functions



Rings



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



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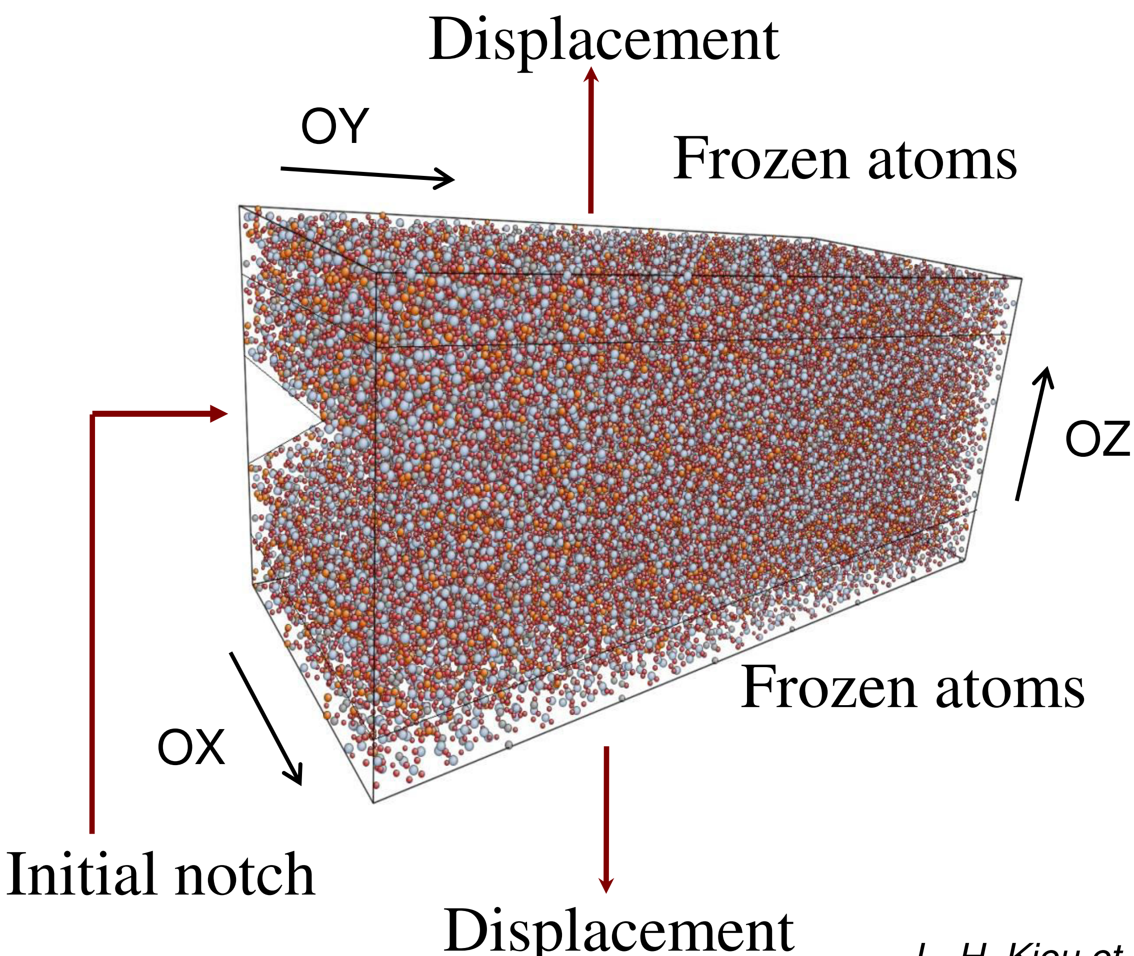
Simulation of fracture behavior by classical molecular dynamics

Fracturation method

- 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

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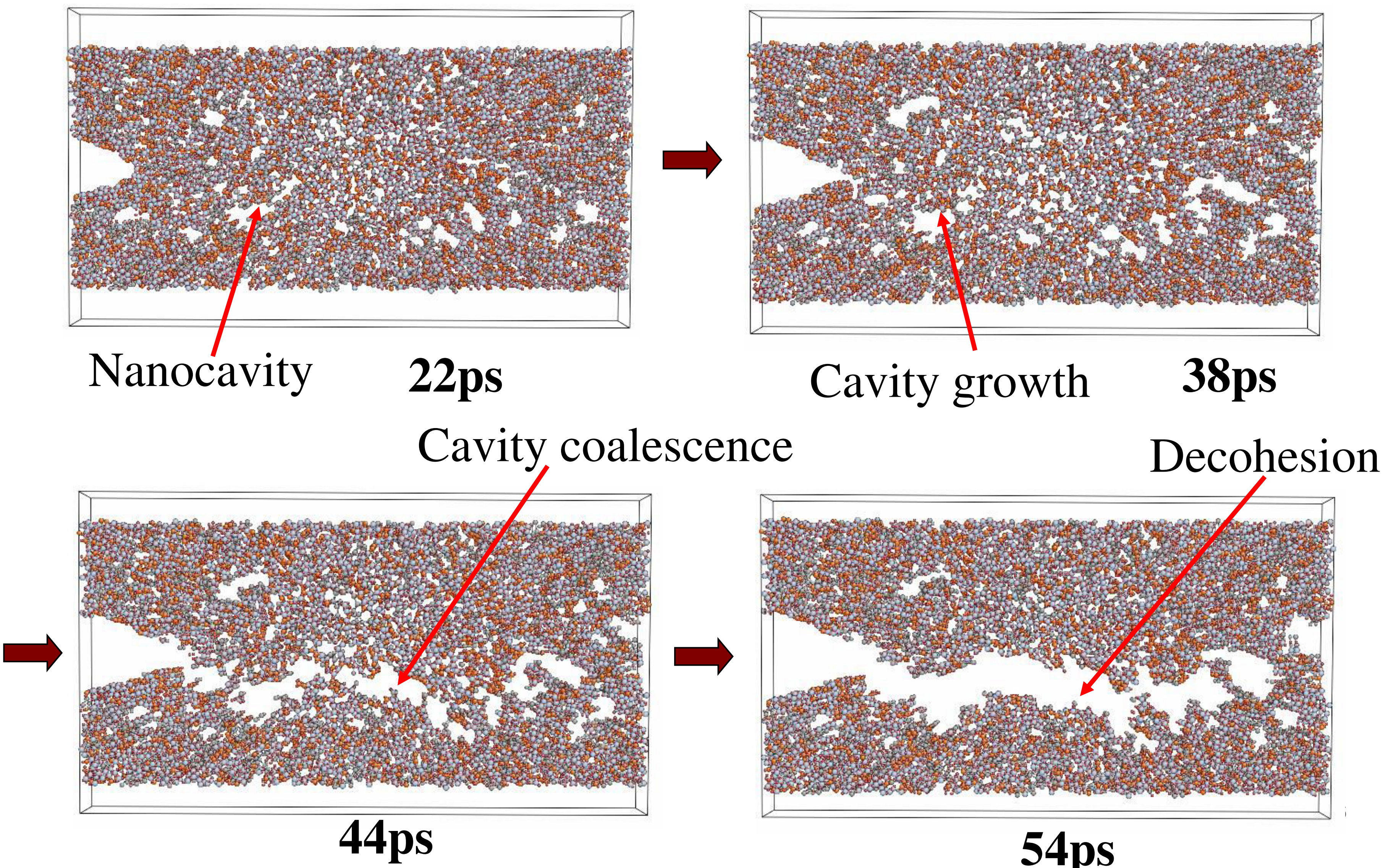
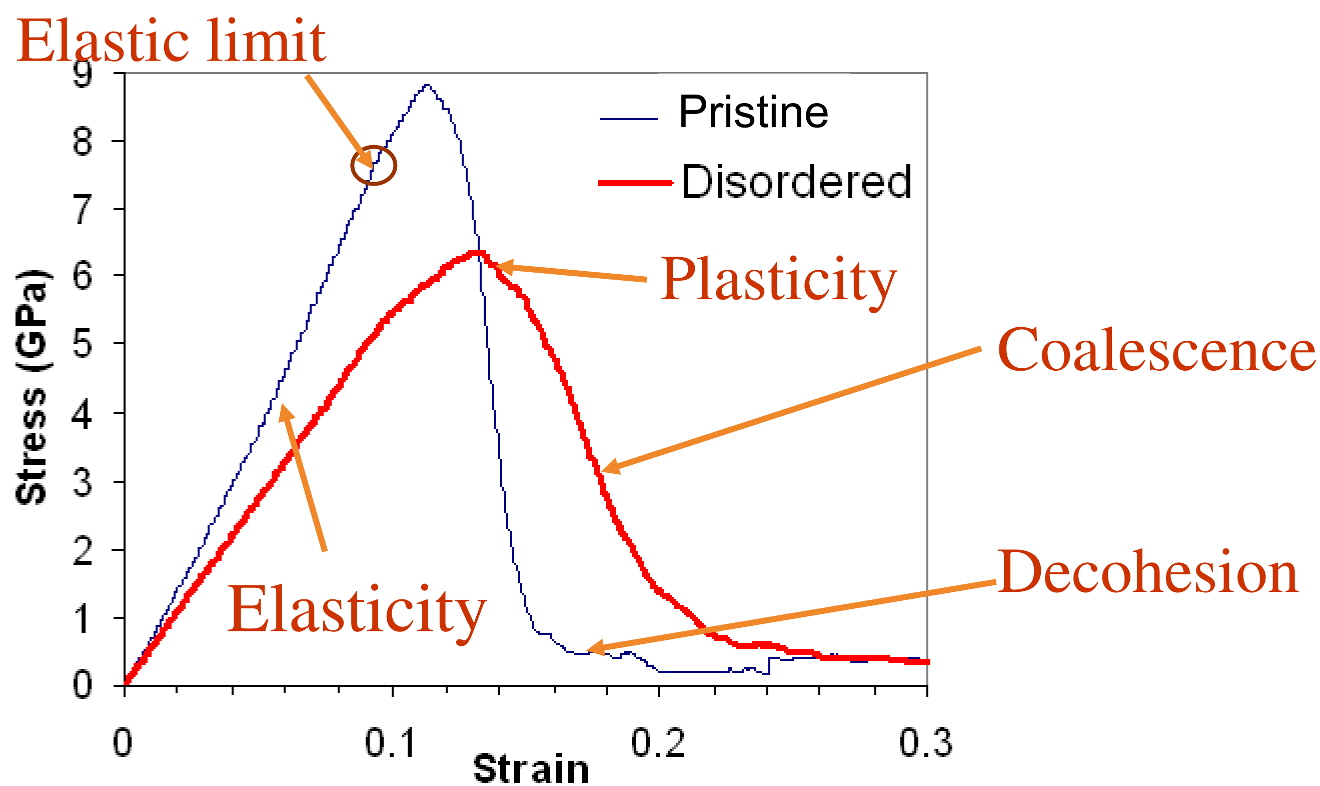
The four steps of fracture mechanisms

- Nucleation / Growth / Coalescence / Decohesion (SBN14 glass)



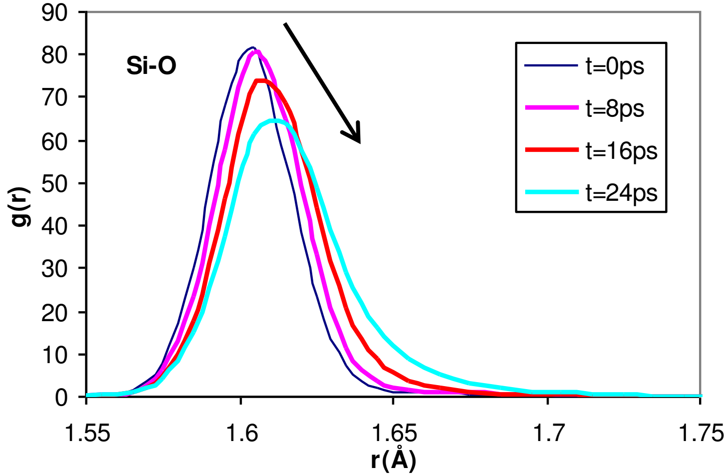
Stress – Strain curves

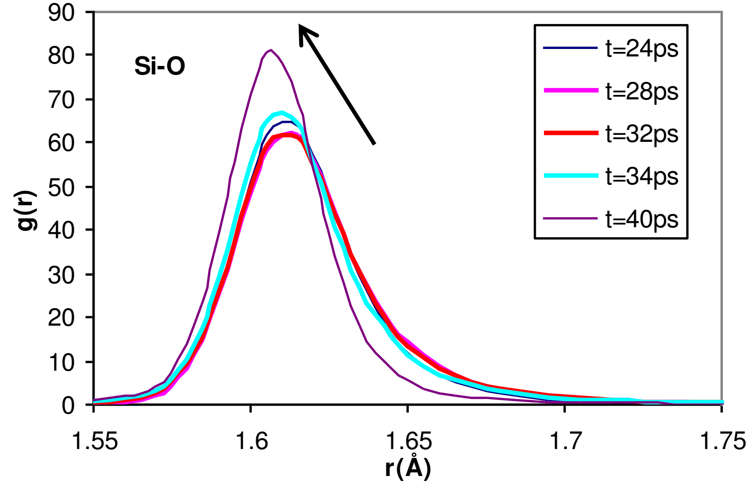
- **Differences between pristine and disordered SBN14 glass**
  - **Decrease of the Young modulus from 74.0GPa to 51.6GPa (-30%)**
  - **Decrease of the elastic limit**
  - **Increase of the plasticity region (the non linear part of the stress – strain curve): duration from 10ps to 13ps**



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**

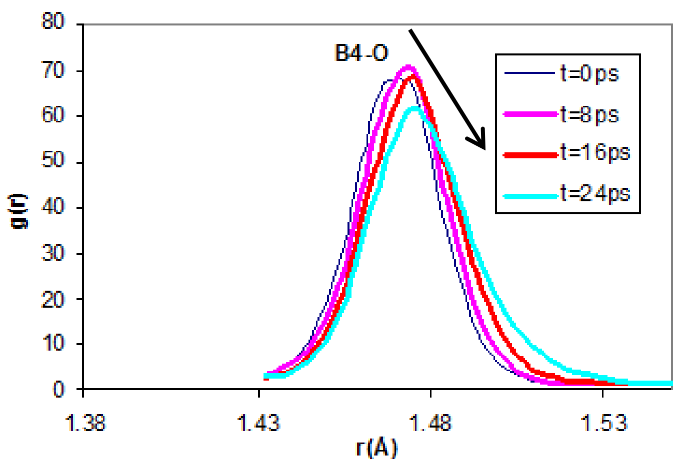


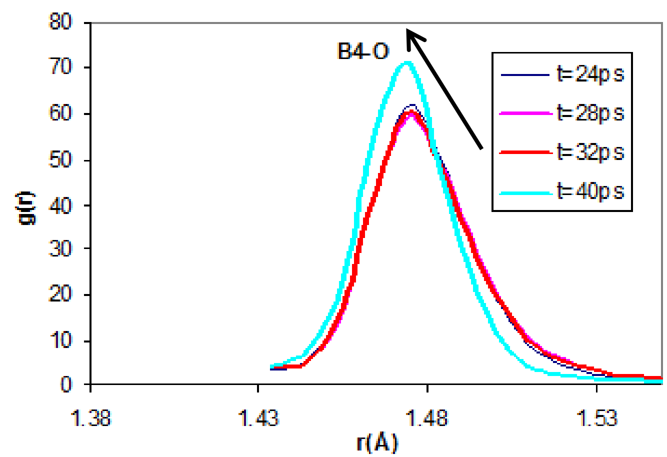


RDF Si-O

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

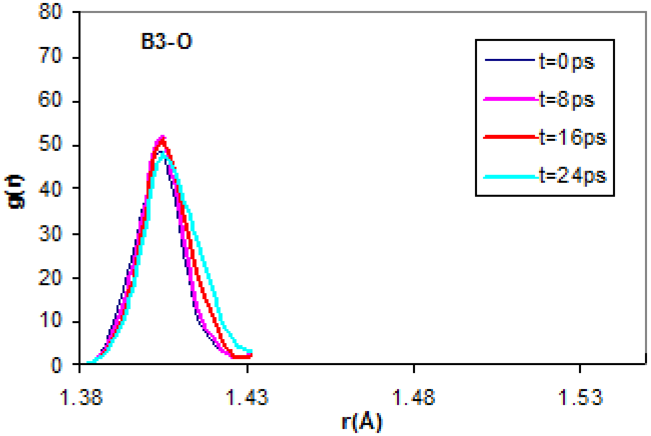


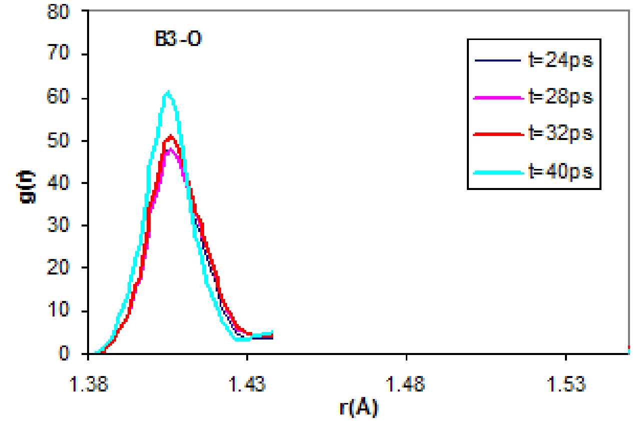


RDF [4]B-O

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

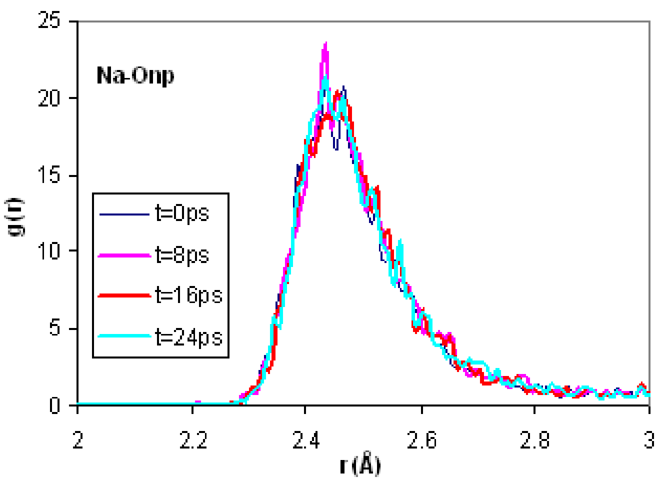
- **The cations behave differently depending on their local coordination**
  - **^{3}B and Na → « Soft » elements**

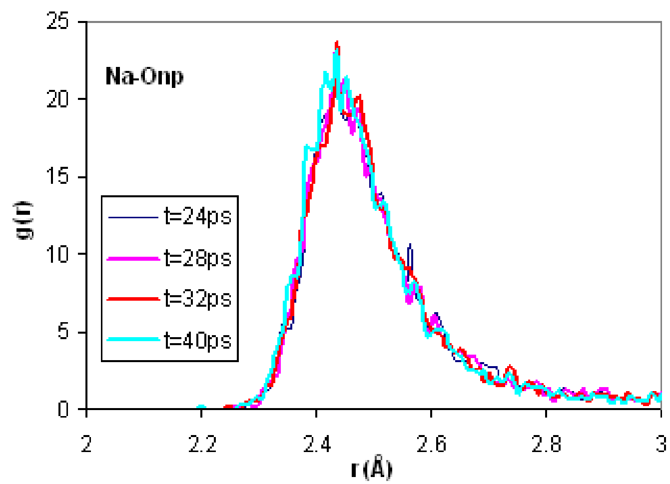




RDF [3]B-O

No stretching of ^{3}B-O or Na-O distances





RDF Na-O

Origin of the fracture toughness increase in the disordered glasses

- In the disordered (i.e. irradiated) glasses:

  - Increase of the [3]B relative to the [4]B
  $\rightarrow$ it explains why the pastic phase increases in the disordered glass because the [3]B atoms enhance the plastic processes

  - The enhancement of the plastic processes consumes a larger energy
  $\rightarrow$ it explains the fracture toughness increase under irradiation

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Simulation of nanoindentation by classical molecular dynamics

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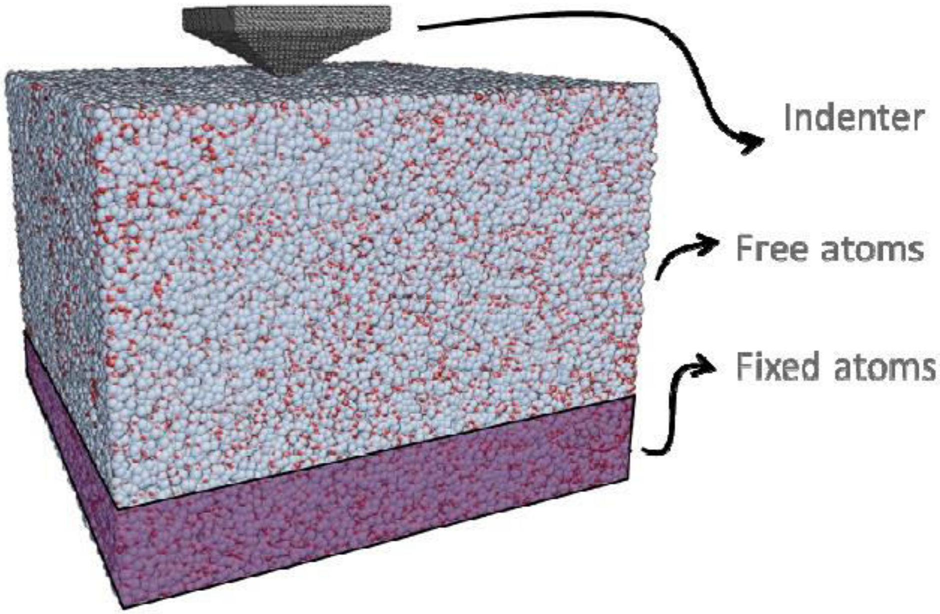
Simulation of hardness: Method

- 35nm x 35nm x 25nm (<>2 10^6 atoms)
- Indentation speed : 10m/s
- Step of indentation : 0.1Å
- Temperature : 300K
- Indentor : Vickers diamond tip (136° apex angle)
- At full loading, a 50ps relaxation period is applied by keeping the indenter still



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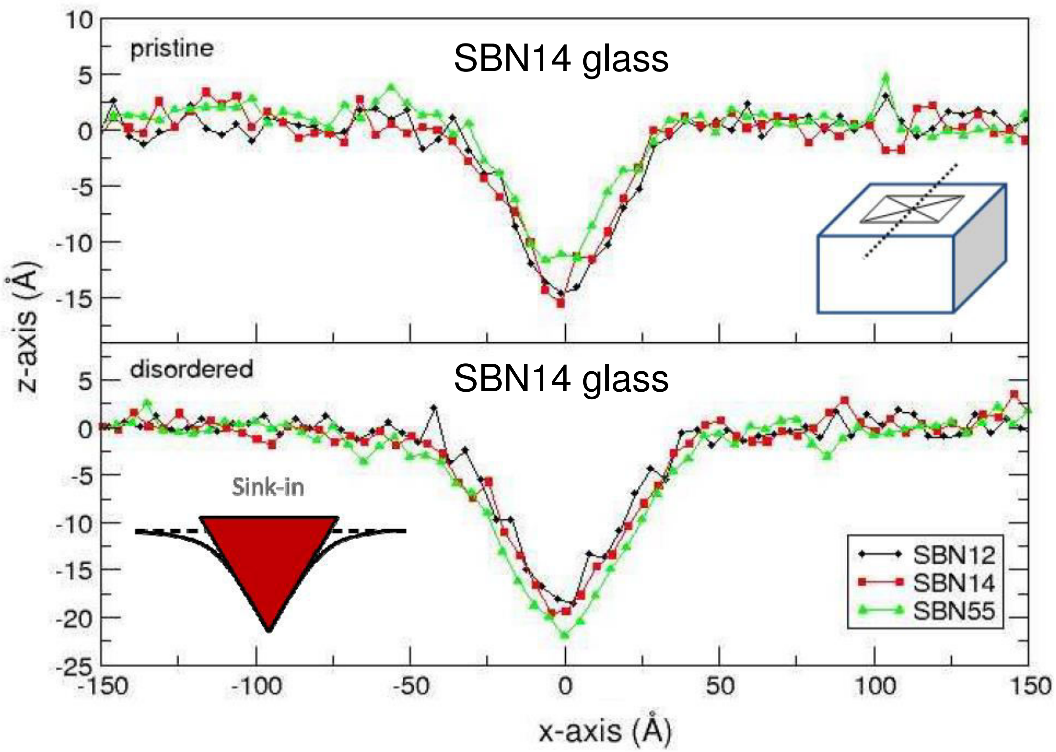
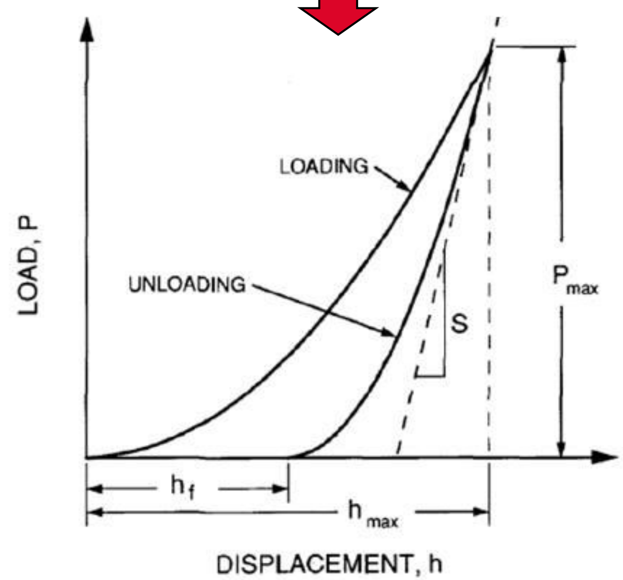
Simulation of hardness: indentation profiles



Indentation profiles

Hardness decreases (qualitative observation)

Oliver-Pharr method to determine the contact surface, then the hardness



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

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

Quantitative hardness measurements

- **Comparison between simulated and experimental values**

Hardness	Pristine *(difference with experimental value)*	Disordered	Experiment (pristine glasses)
Silica	5.5GPa	+1.8%	7.45GPa
SBN12	4.40GPa *(-43%)*	-23.4%	7.7GPa (?)
SBN14	**5.45GPa *(-13%)***	**-28.1%**	**6.30GPa**
SBN55	4.33GPa *(-15%)*	-42.5%	5.1GPa

- *Hardness in silica doesn't change much between pristine and disordered structures*
- *Experimental hardness is better reproduced when the Na_2O concentration increases*
- **Hardness decreases in the disordered (i.e. irradiated) SBN14 glass (experimental behavior is reproduced)**

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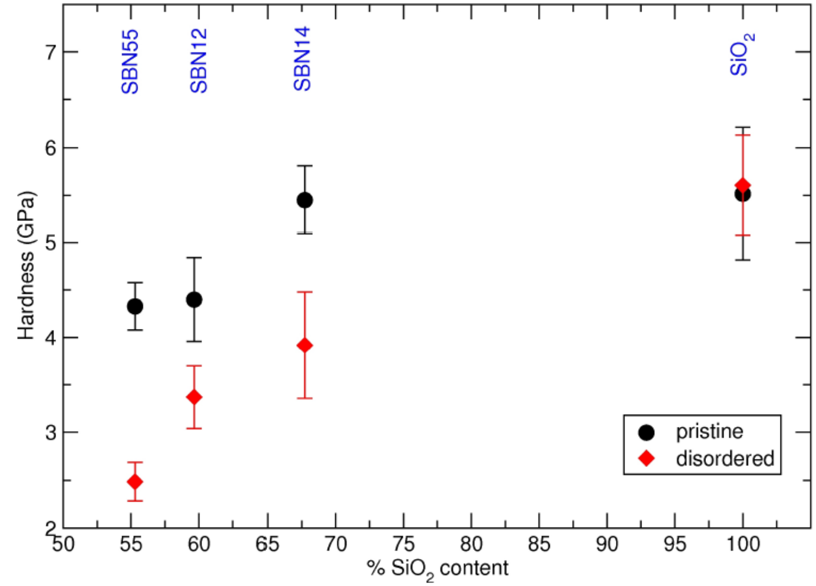
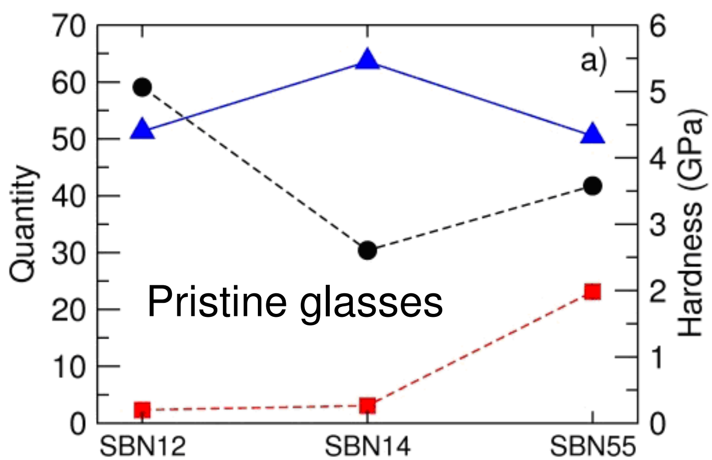
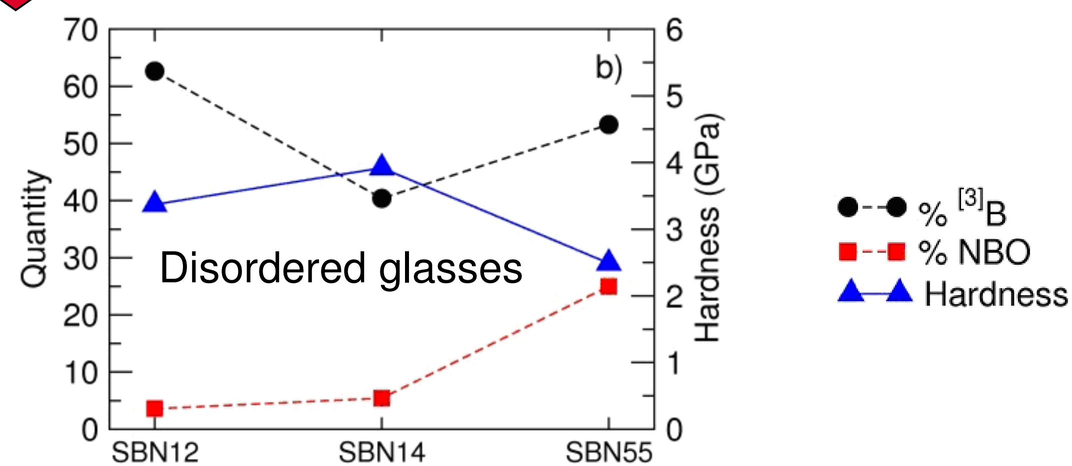
Origin of the hardness decrease

- Increase of the hardness with the $\%SiO_2$
- Decrease of the hardness in the disordered glasses
- Correlations with the $\%^{[3]}B$ and %NBO
  - Hardness decreases with the $\%^{[3]}B$
  - Hardness decreases with the %NBO







<u>Irradiation: increase of [3]B concentration and %NBO + increase of free volume → hardness decrease</u>

Conclusion

- Experimentally, in the complex and simplified nuclear glasses subjected to ballistic effects:

  density decreases, hardness decreases, fracture toughness increases

- Classical molecular dynamics has been used …
  … to simulate displacement cascades in SBN14 glass

  swelling is associated with depolymerization and increase of disorder

  … to simulate fracture behavior

  the increase of the $^{[3]}B$ concentration favors plasticity → origin of the fracture toughness increase

  … to simulate nano indentation

  the increase of the $^{[3]}B$ and NBO concentrations facilitates indenter penetration → origin of the hardness decrease

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