Matériaux vitreux sous irradiation: le rôle des centres colorés

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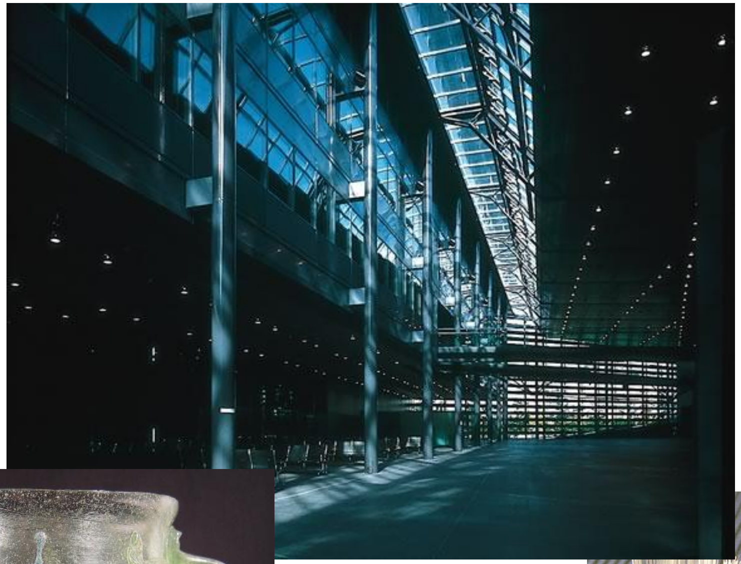
Verres : domaine d'applications

Optique (lentilles, prisme, fibres…), télecommunication, architecture, médecine…

verres plats, Verres d'emballage, verres de stockage, verres bioactifs (prothèses), verre pour l'isolation ou renforcement mécanique



Verres en milieu radiatif

Nuclear, medical applications

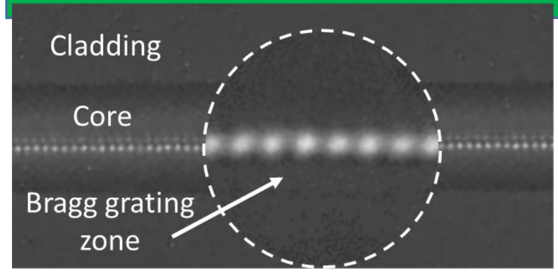
HLW storage glass
Glass fiber:sensor,
Dosimeters, radiation
shielding

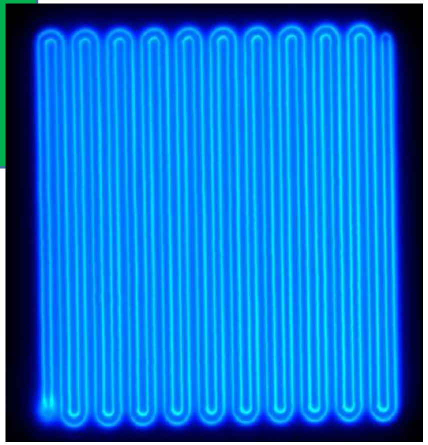
Space applications

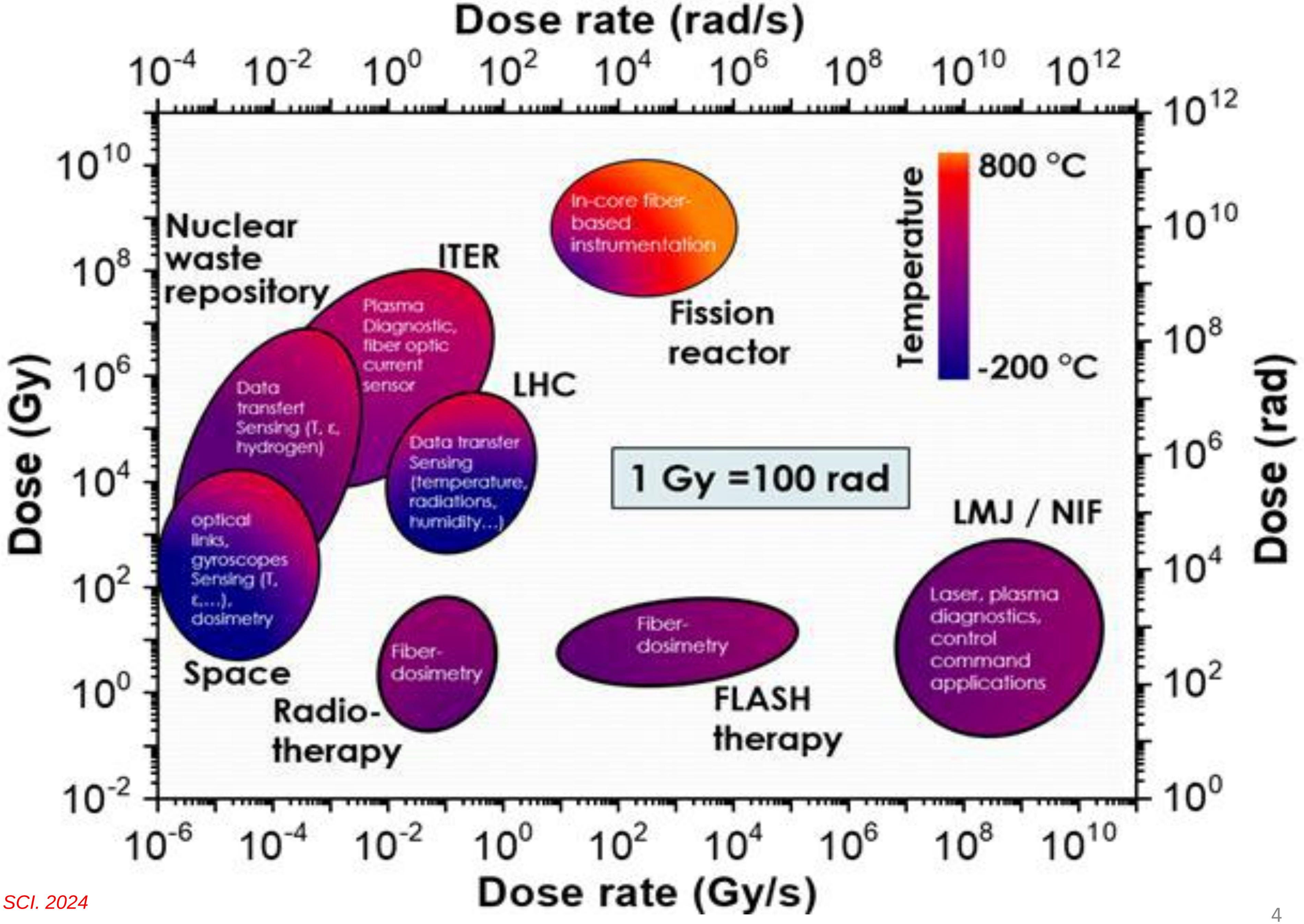
Optical fibers

Glass structuring

Ion, electron beams
UV, fs laser







S Girard et al IEEE TRANS. NUCL. SCI. 2024

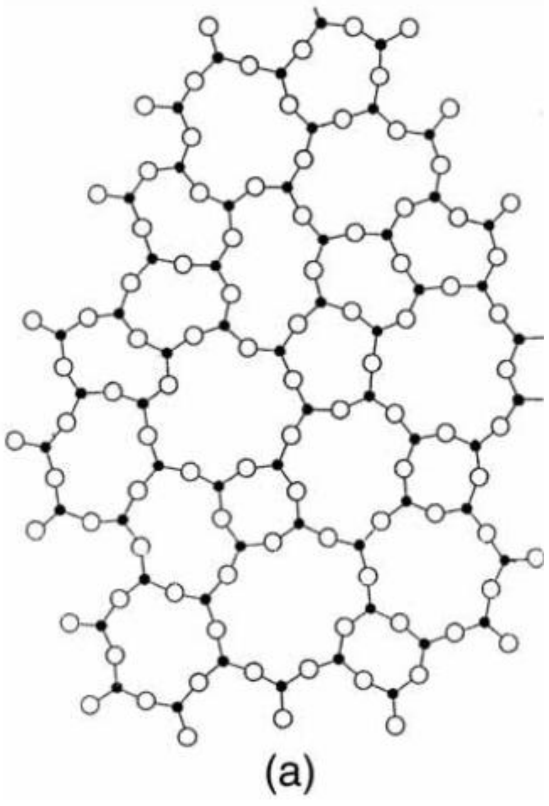
Plan

- **Défauts ponctuels dans la silice**
- **Impact des centres colorés sur les propriétés des verres et leur utilisation**
  - **Coloration, indice, RIA (propriétés optiques)**
  - Propriétés mécaniques (verres nucléaires)
  - **Structuration sous irradiation**
  - **Dosimétrie**

Défauts ponctuels dans la silice

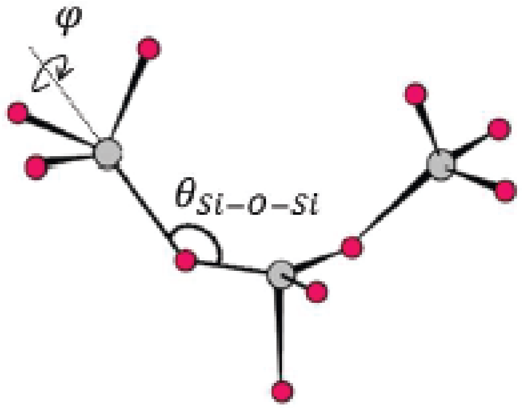
La silice SiO_2

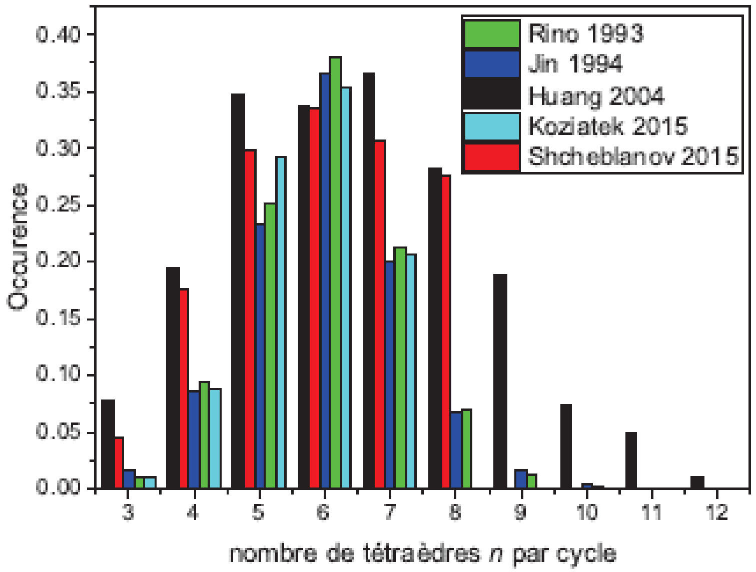
CRN-SiO_2



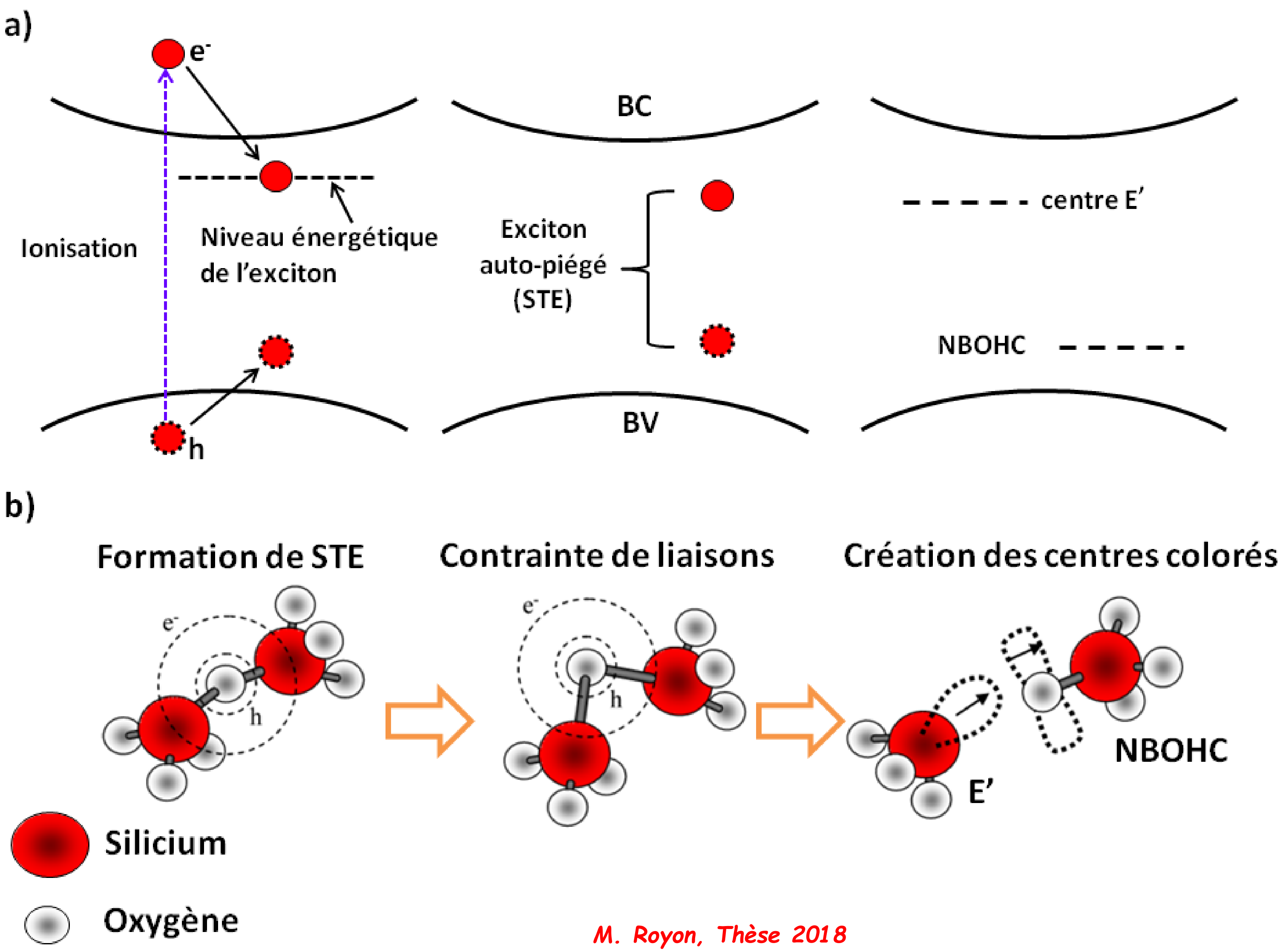
Modèle de Zachariasen 1932

Advances in Physics,
Vol. 56, No. 1, January–February 2007, 1–166

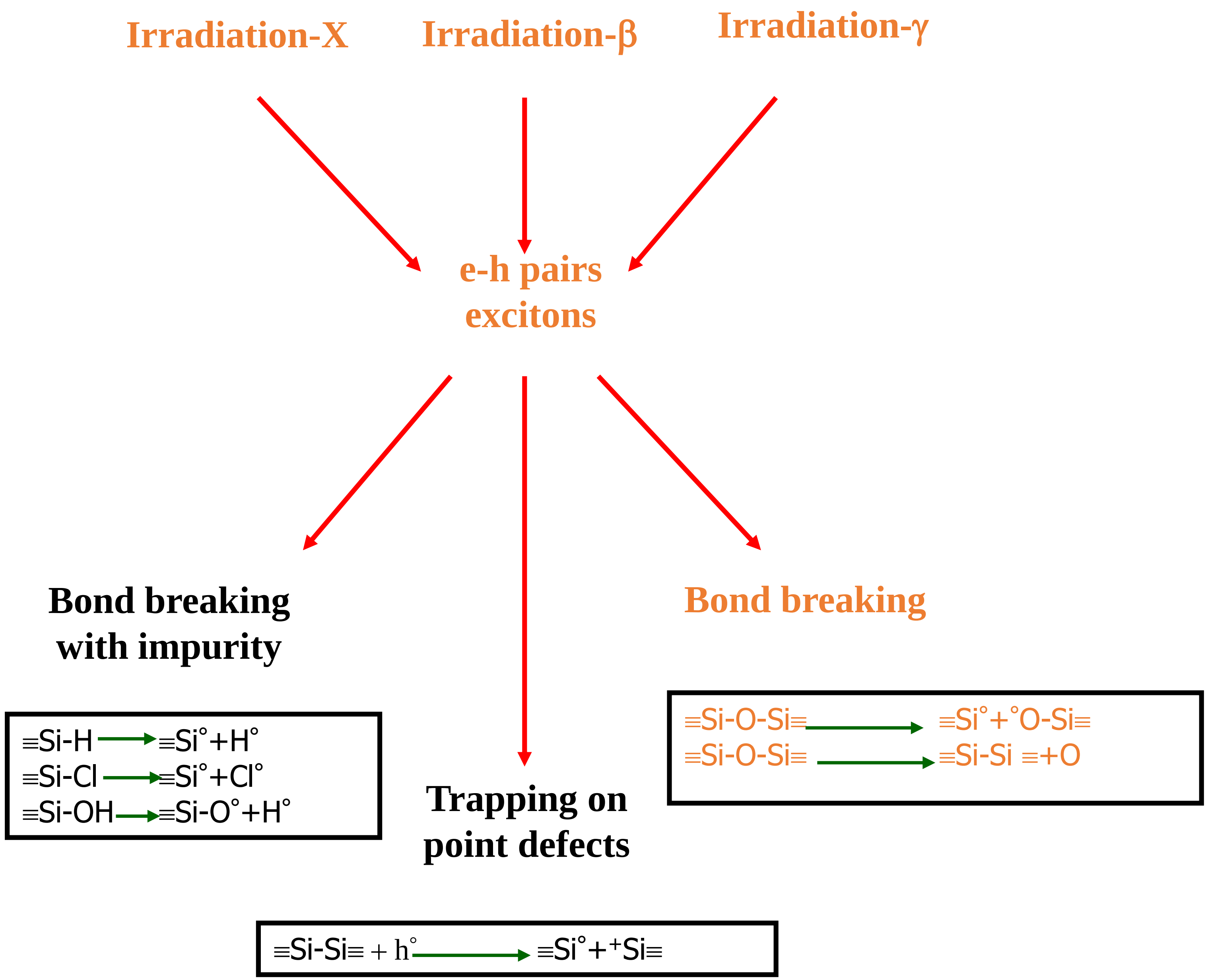




Formation des défauts ponctuels dans la silice



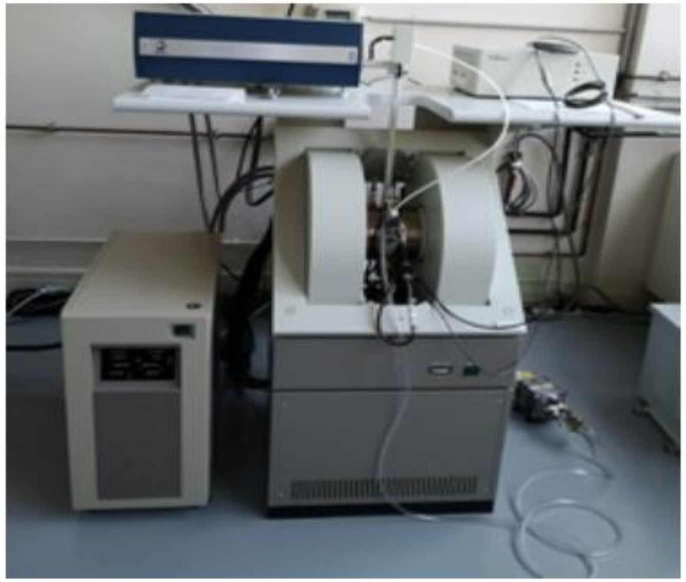
M. Royon, Thèse 2018

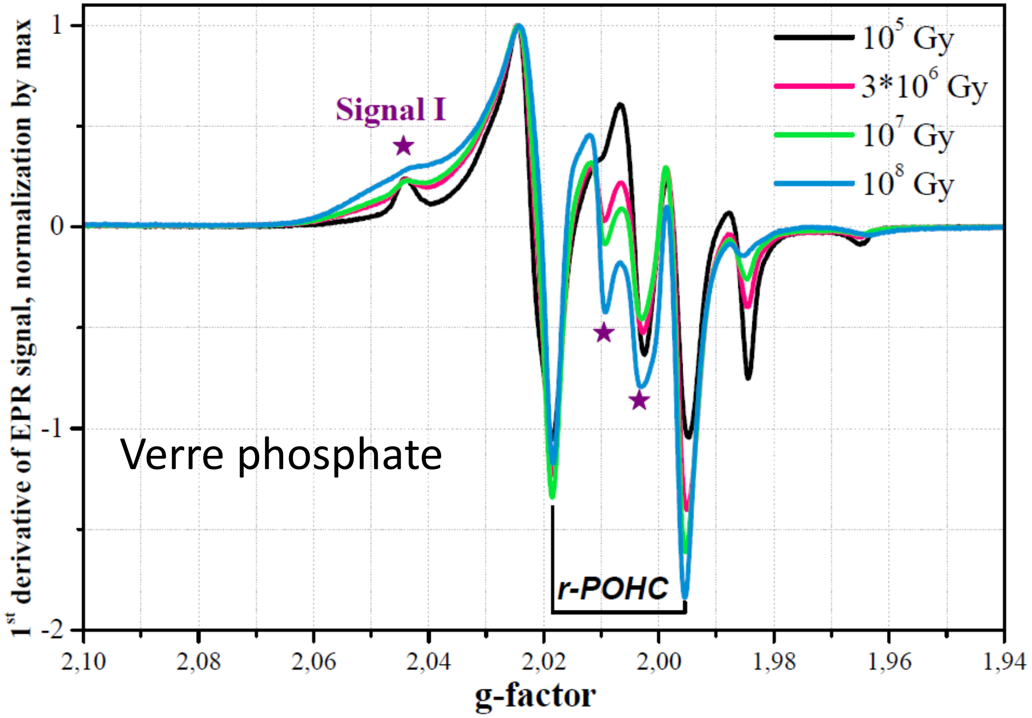


Irradiation-X
Irradiation-β
Irradiation-γ
e-h pairs
excitons
Bond breaking
with impurity
≡Si-H → ≡Si°+H°
≡Si-Cl → ≡Si°+Cl°
≡Si-OH → ≡Si-O°+H°
Trapping on
point defects
≡Si-Si≡ + h° → ≡Si°+⁺Si≡
Bond breaking
≡Si-O-Si≡ → ≡Si°+°O-Si≡
≡Si-O-Si≡ → ≡Si-Si ≡+O

Methods to characterize point defects

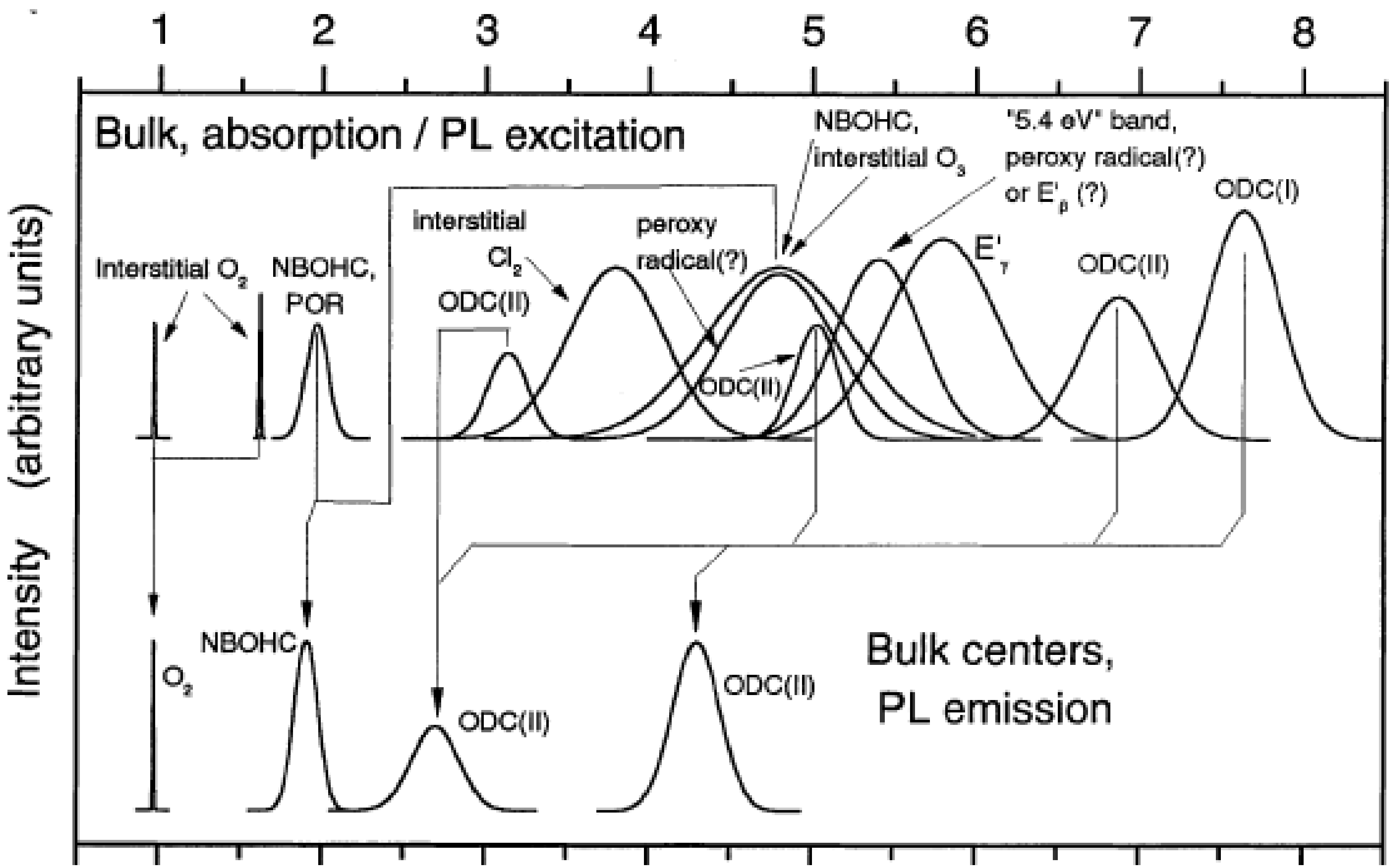
- Absorption optique (quantification)
- Photoluminescence
- **RPE: Résonance Paramagnétique Electronique (identification et quantification)**





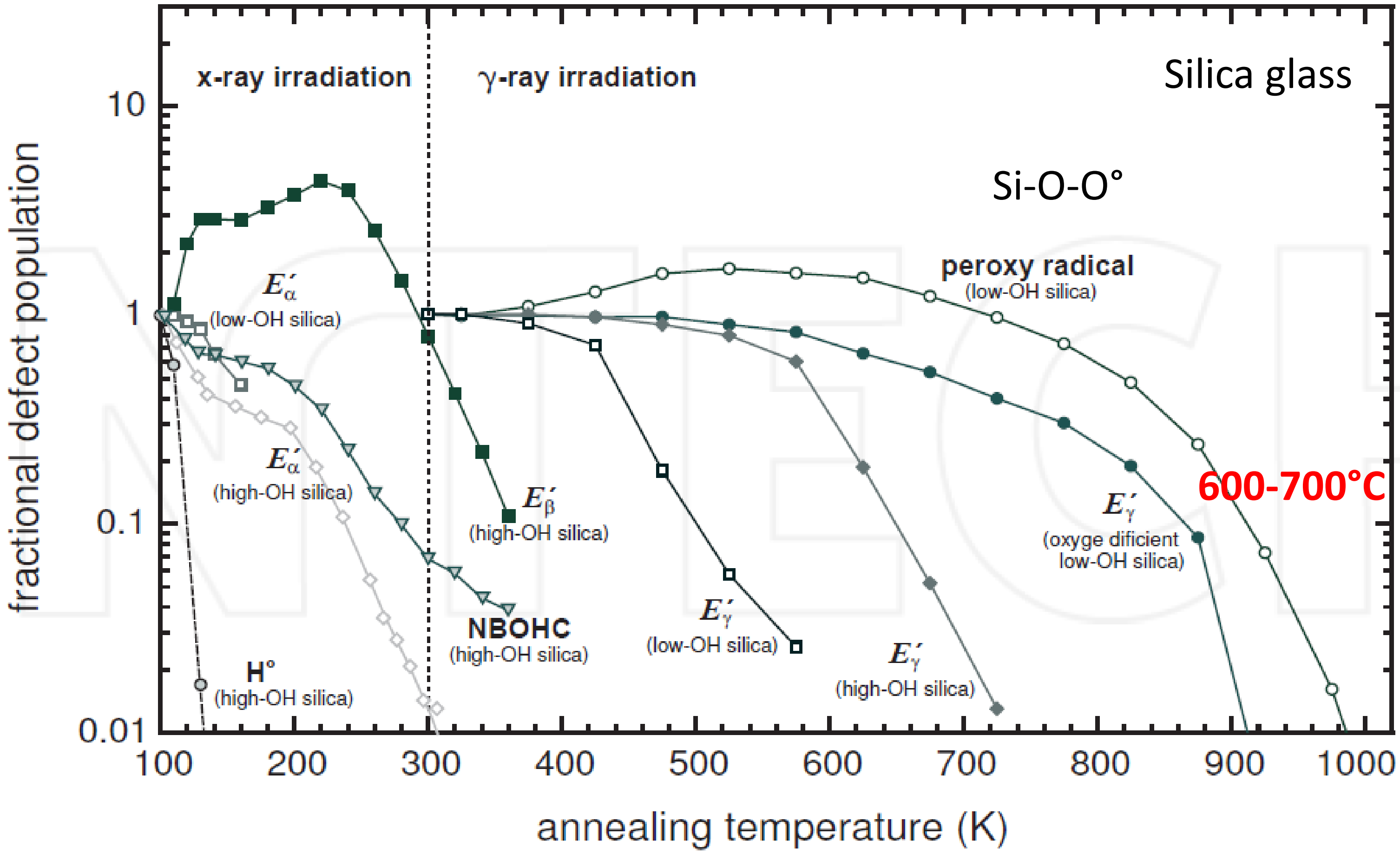
Pukhkaya PhD 2013

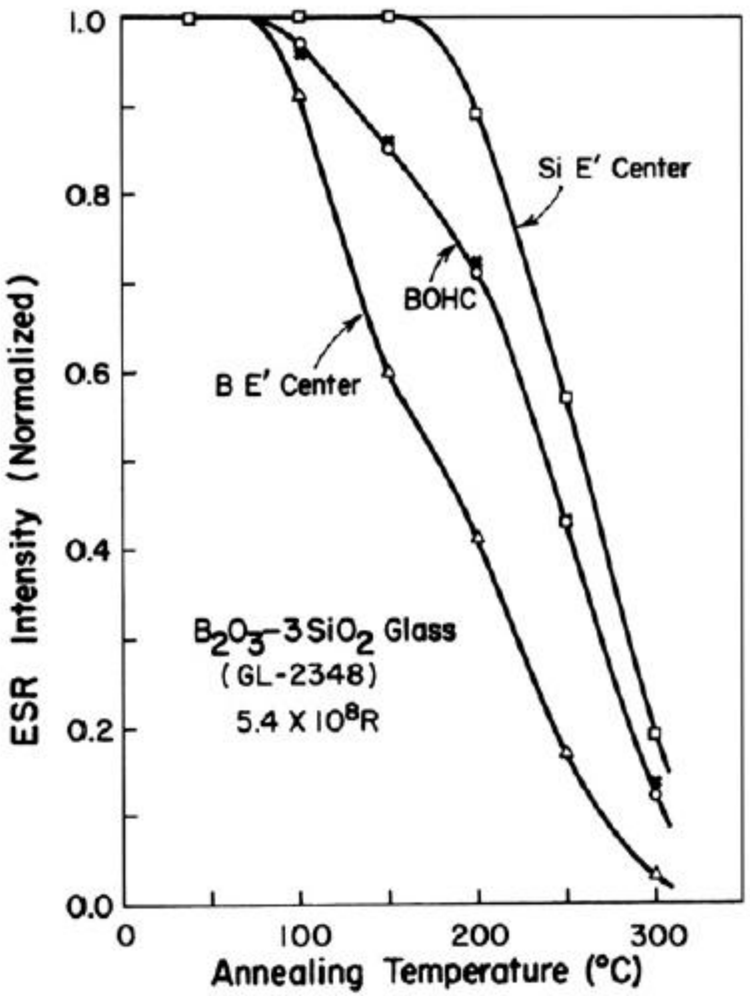
Absorption et emission des défauts dans la silice



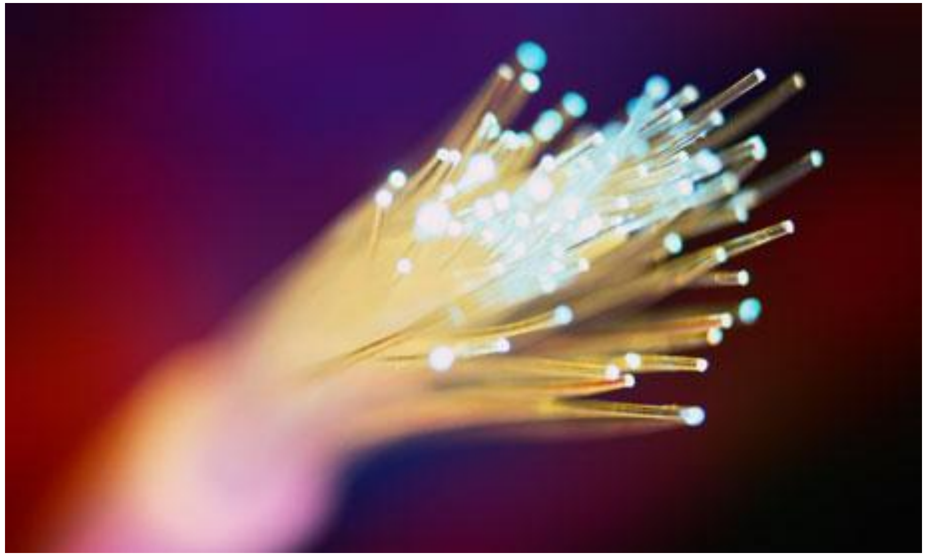
L. Skuja, JNCS 1998

Thermal stability

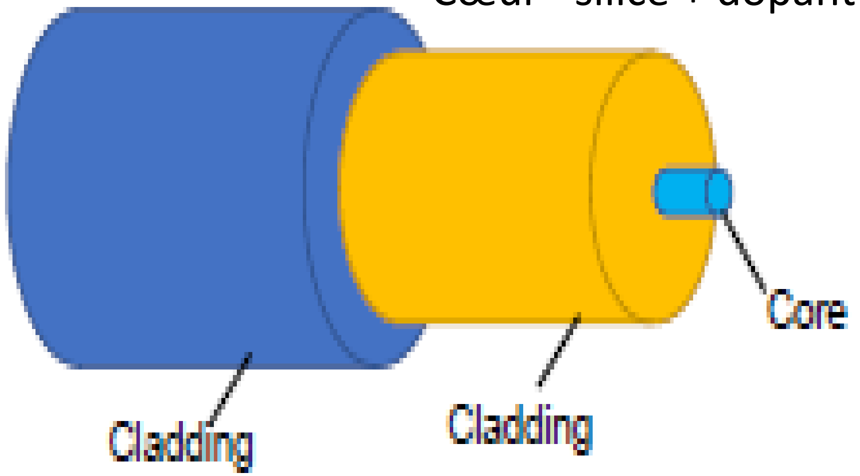




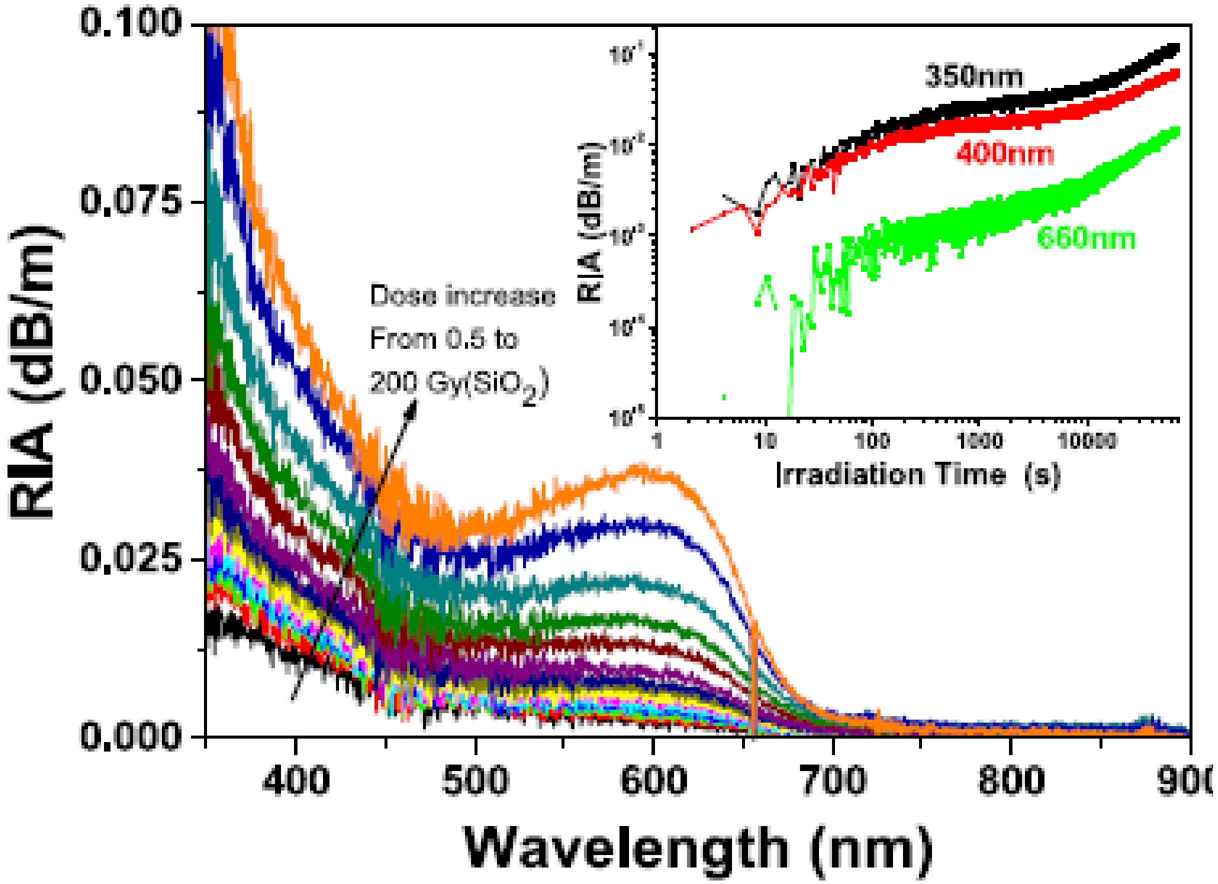
Impact des défauts ponctuels sur les fibres optiques



Cœur= silice + dopant (Ge, P, Al….)



Radiation-Induced Attenuation (RIA)



S. Girard et al. J. Opt 2018

Radiation effects

Mainly RIA

But RIE (Cerenkov effect…)

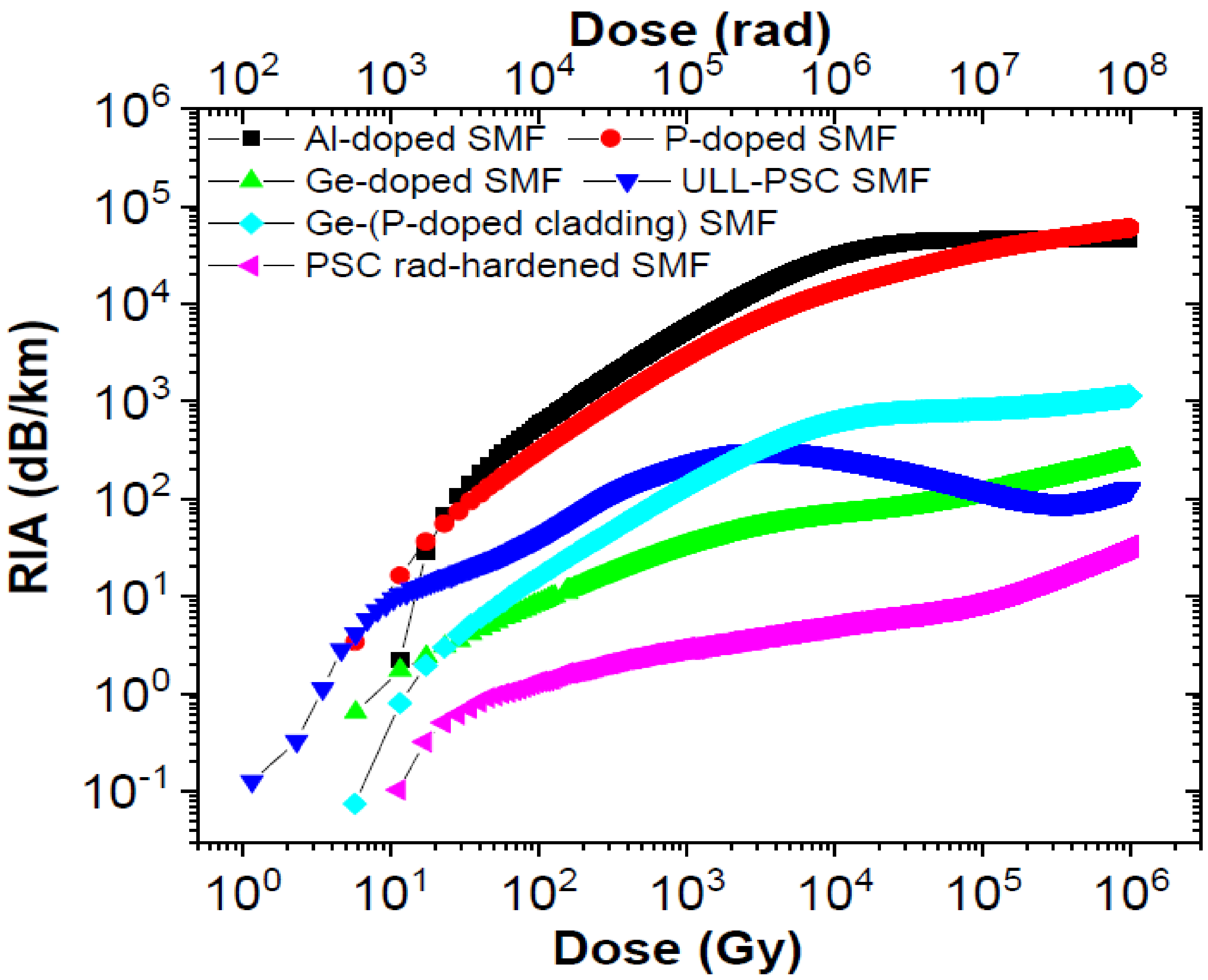
And silica glass compaction so refractive index is modified !

IEEE TRANS. NUCL. SCI. 2024

Overview of Radiation Effects on Silica-Based Optical Fibers and Fiber Sensors

S. Girard, *IEEE Senior Member*, J. Kuhnhenn, A. Gusarov, A. Morana, *Member, IEEE*, P. Paillet, *IEEE Fellow*, T. Robin, L. Weninger, *IEEE Student Member*, F. Fricano, *IEEE Student Member*, M. Roche, *IEEE Student Member*, C. Campanella, G. Mélin, D. Lambert, *IEEE Senior Member*, E. Marin, A. Boukenter, and Y. Ouerdane

RIA depends on ionizing dose, dose rate, temperature, wavelength, and nature of **dopants in the fiber**



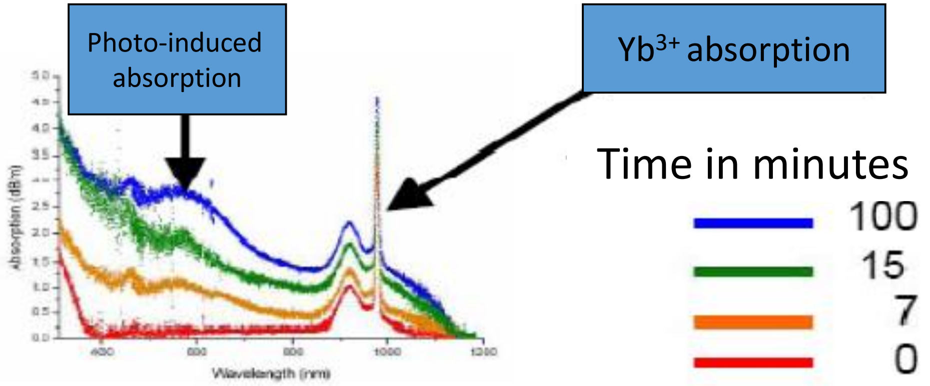
Petrie et al JNCS 2019

P, Al, Ge give rises to specific point defects

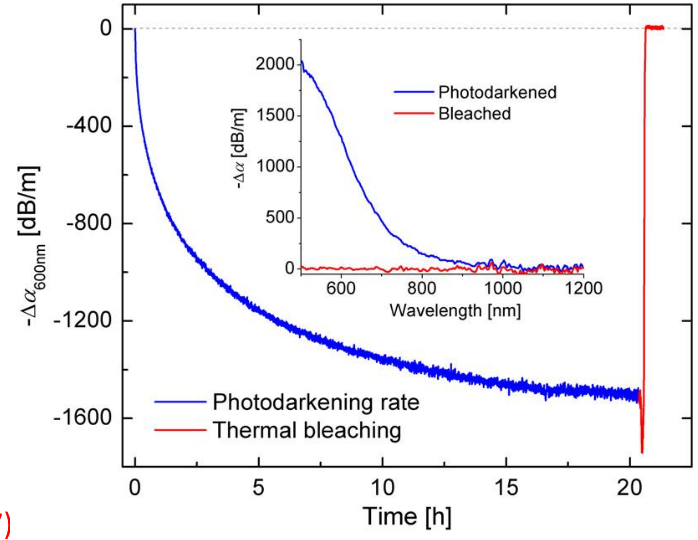
Photodarkening/Radiodarkening: Yb doped laser fibers

- High power laser fiber (1 µm)
- **Photodarkening**

Formation of color centers under the IR laser pump: decrease of laser efficiency

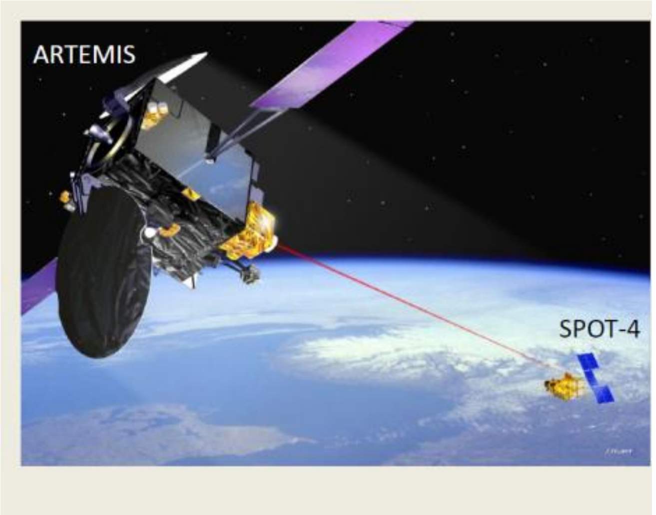


I. Mannek-Hönninger *et al*, OE **15**, 1606 (2007)

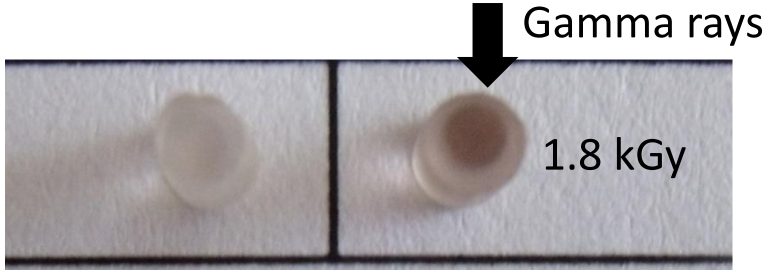


Joan J. Montiel i Ponsoda PhD 2013

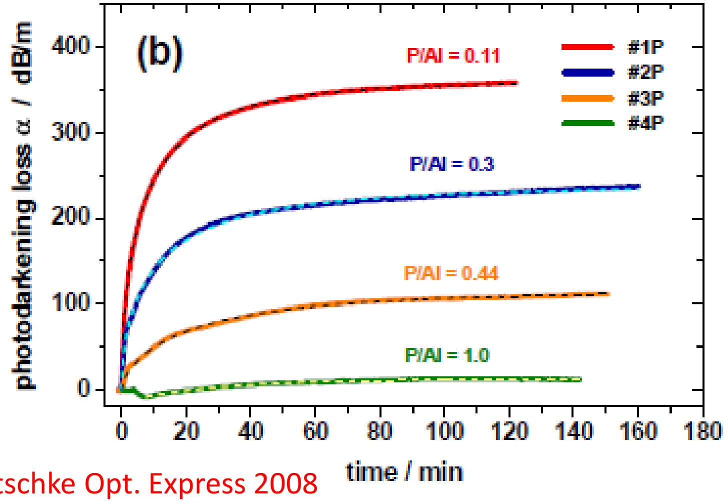
- **Radiodarkening:** spatial or nuclear applications



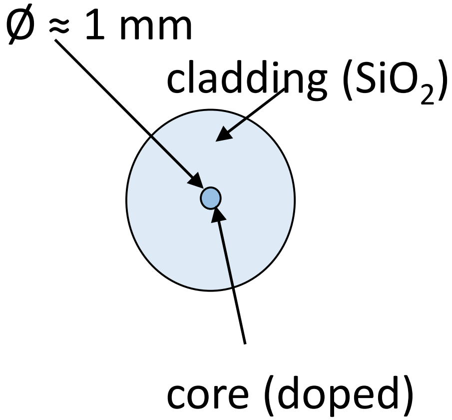
Optical fiber preforms



P/Al doped silica preform



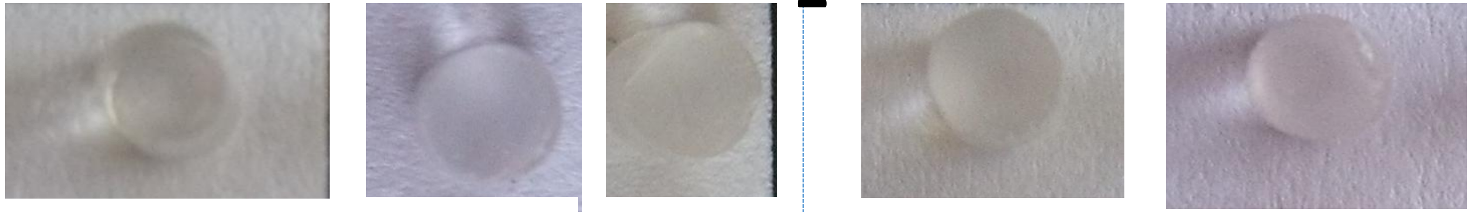
Jetschke Opt. Express 2008



Al/P decrease

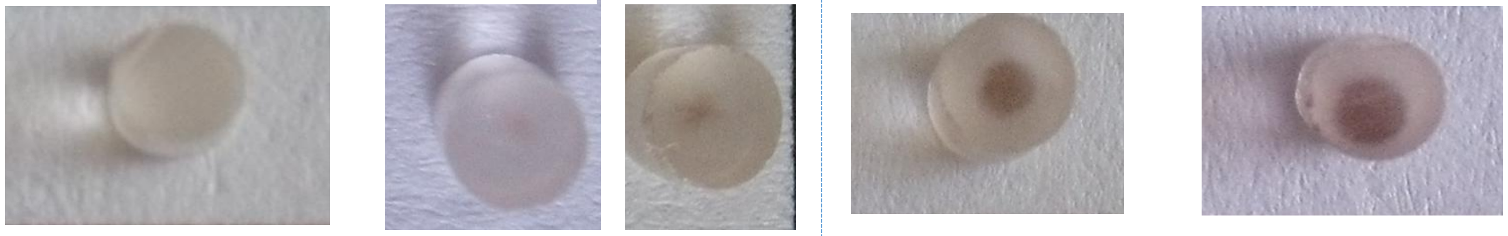
P **0.3** **1** **2.8** **Al**

before gamma irradiation



Deschamps et al. Opt. Exp 2013

After gamma irradiation

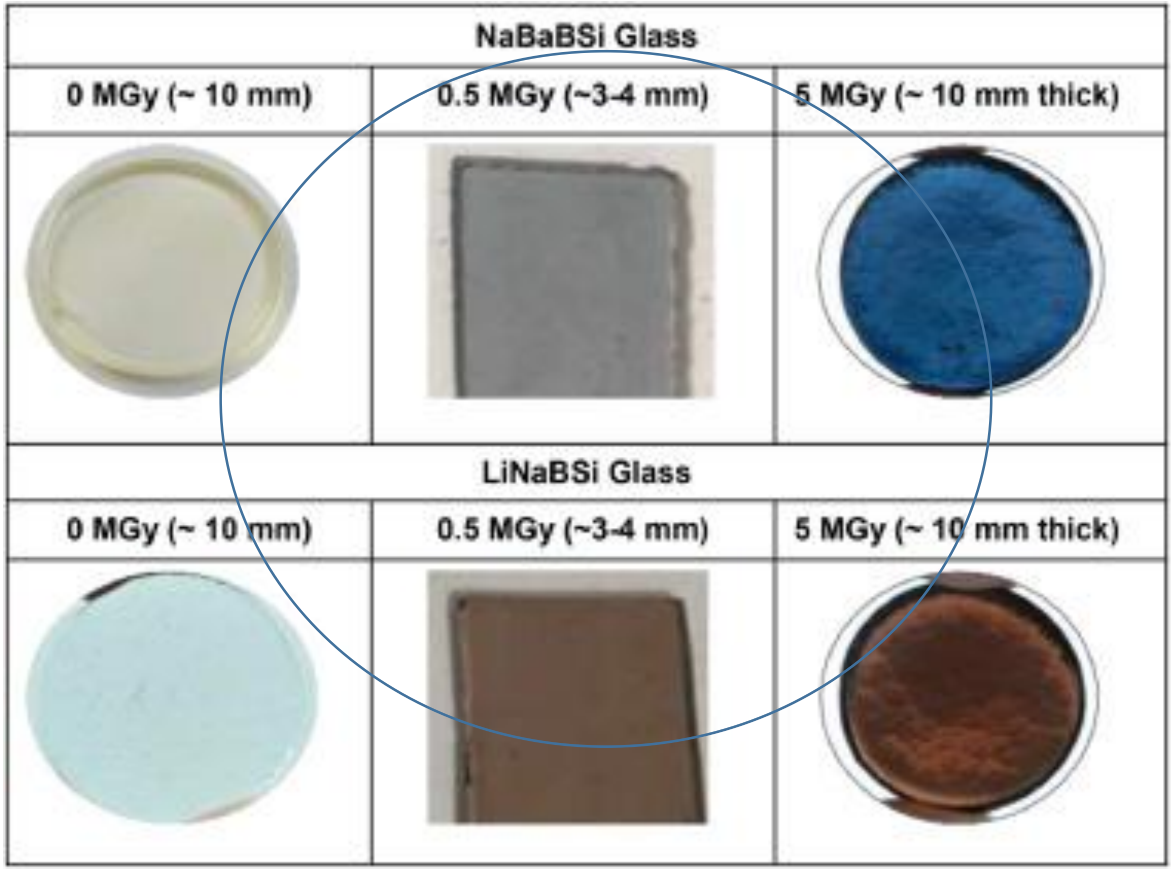


Al/P <1 low coloration of the core under gamma radiation at 1800 Gy

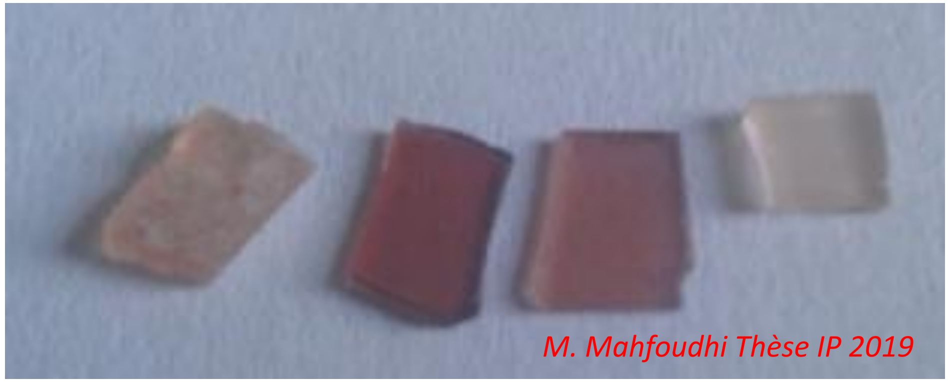
Impact des centres colorés sur les propriétés des verres

Changement de couleur lié aux défauts ponctuels

Borosilicates



Verres phosphates



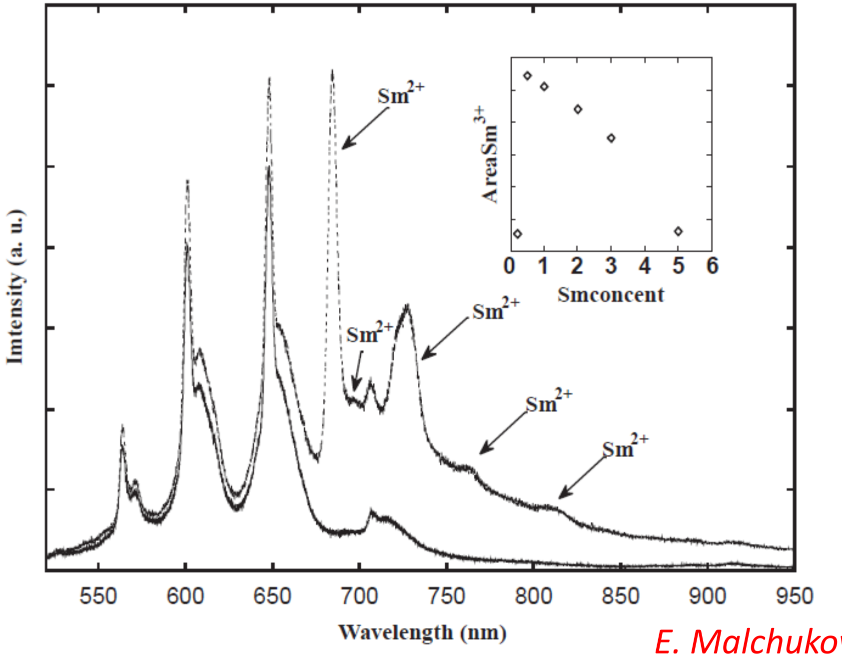
P. Rautiyal, G. Gupta, R. Edge, L. Leay, A. Daubney, M.K. Patel, A.H. Jones, P.A. Bingham, Journal of Nuclear Materials, Volume 544 2021

Verres dopés (ions de transition ou ions TR)

Irradiation: **modification des degrés d'oxydation (réduction ou oxydation)**

4+/3+ Ce, Tb
3+/2+ **Sm, Eu**, Tm, Yb…

$Sm^{3+} + e \rightarrow Sm^{2+}$



E. Malchukova NIMB 2005

Fe^{3+} / Fe^{2+}

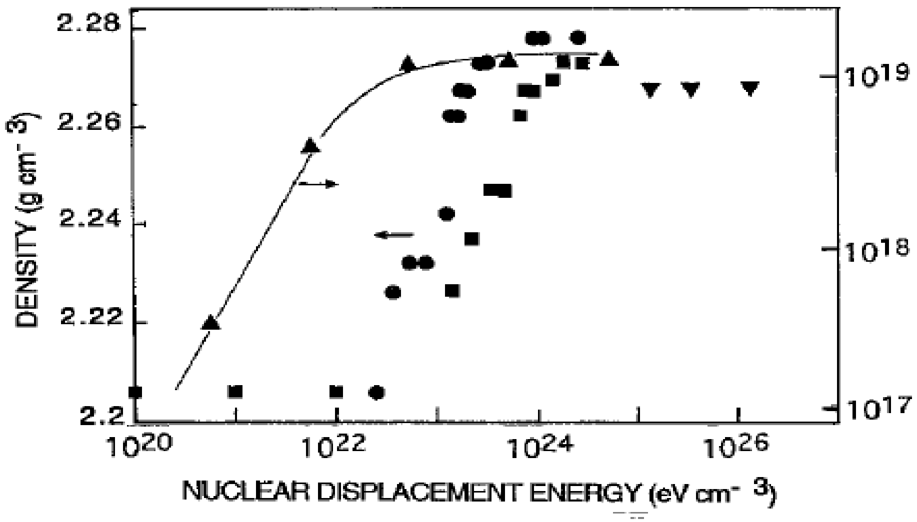
Verre lunaire

Densificaton de la silice par irradiation

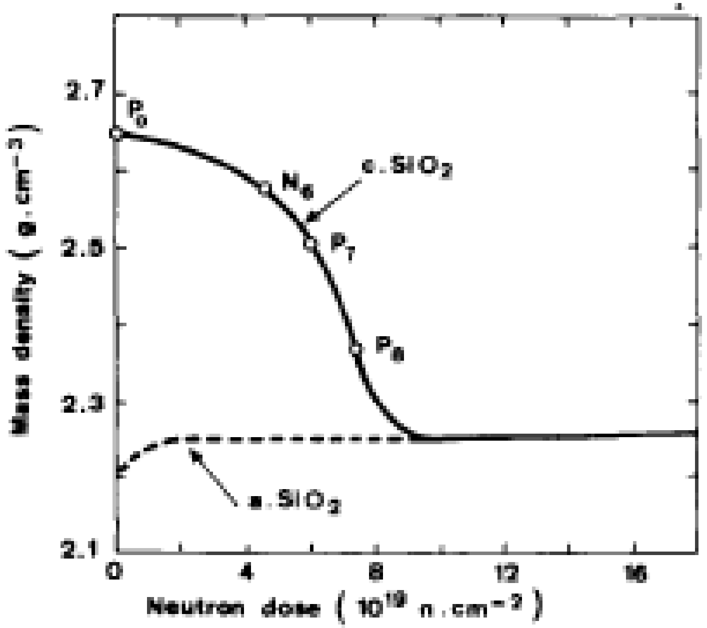
Fast neutrons

Ions

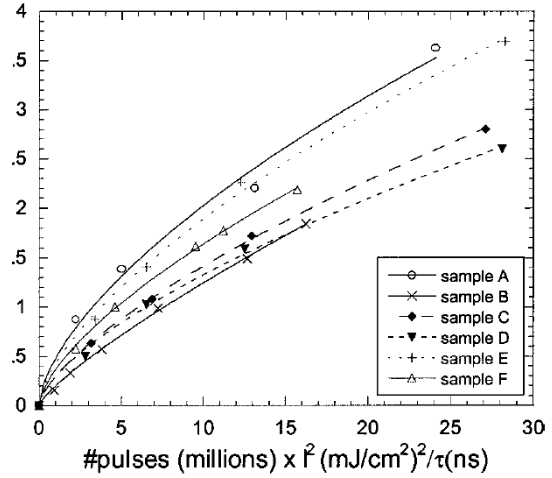
UV laser



R.A.B. Devine / Nucl. Instr. and Meth. in Phys. Res. B 91 (1994) 378–390



Journal of Non-Crystalline Solids 167 (1994) 199–204



J. Appl. Phys., Vol. 87, No. 7 2000

Density increment < 3-4 %

Ionization or knock on mechanisms

D^n with n=1 for neutrons and 2/3 for ionizing irradiation

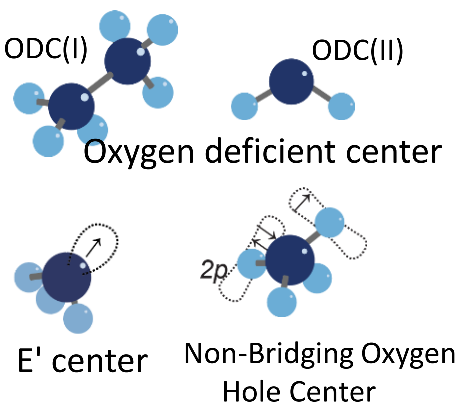
Densification of silica (and relaxation) under radiation

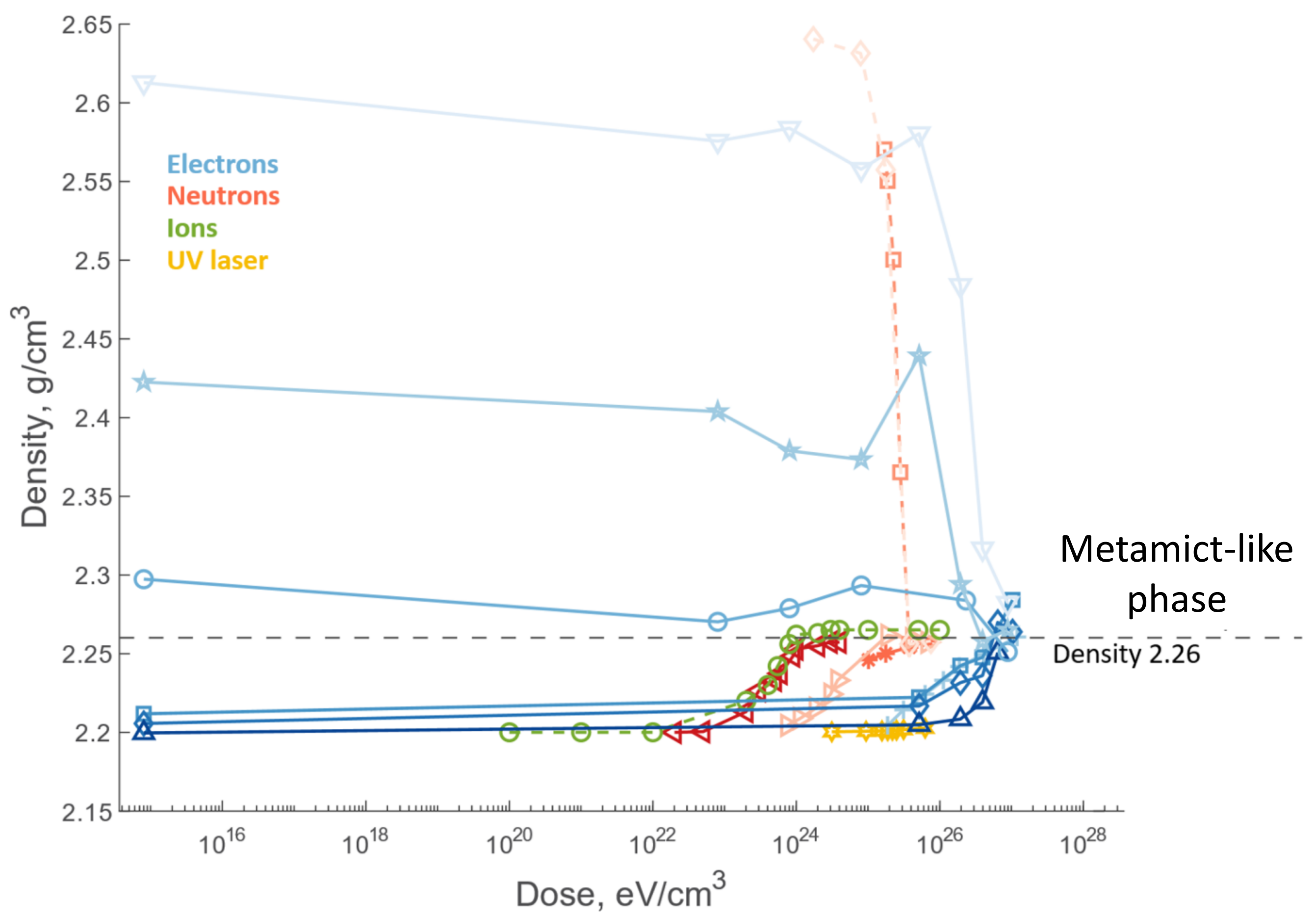
Gamma, X-rays, neutrons, electrons, and ions irradiation

Densification limited to 3%

But also relaxation of densification

Defects formation



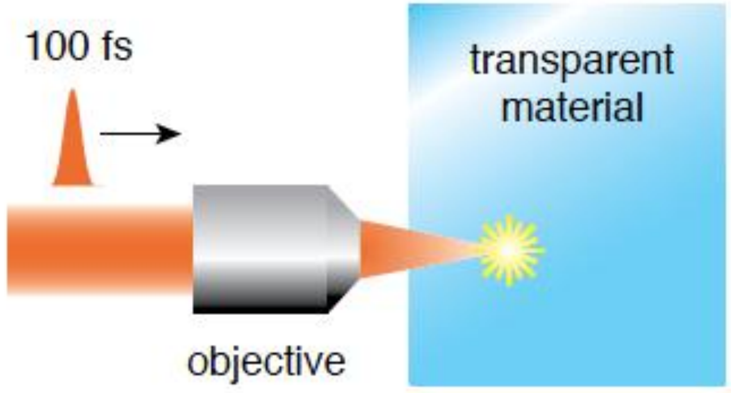


Dependence of silica density on the irradiated dose

Mobasher M.et al. JNCS, 597 (2022)

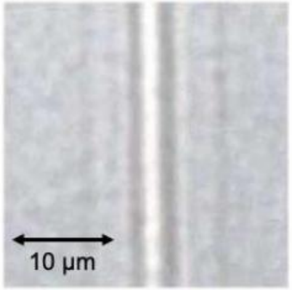
Shchedrina et al. 2025 JNCS

SiO_2 refractive index modification under fs laser

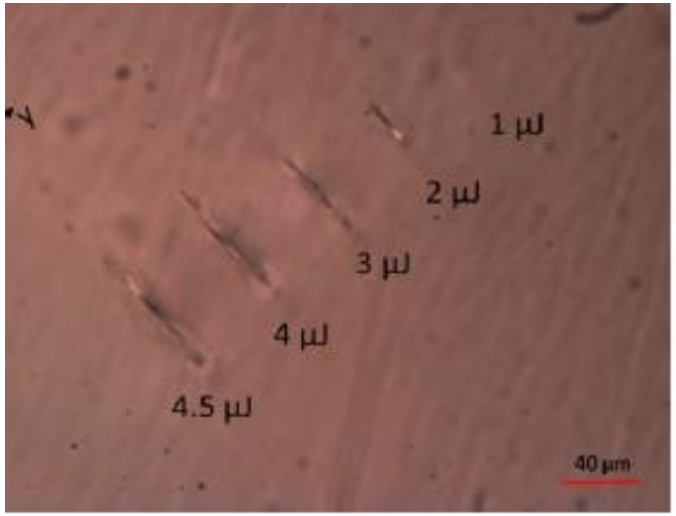


Miura. al, Opt. Lett. (1996)

Type I



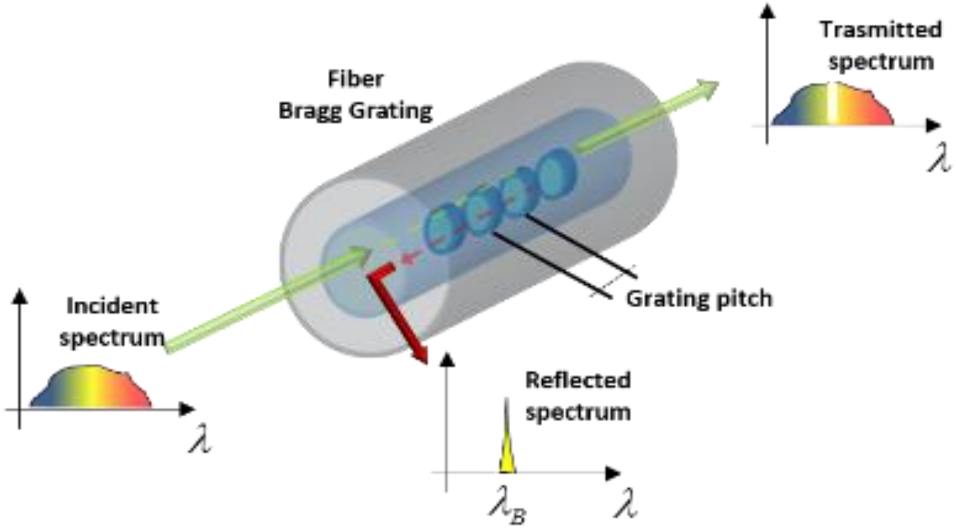
Low irradiance



Mahfoudhi PhD (2019)

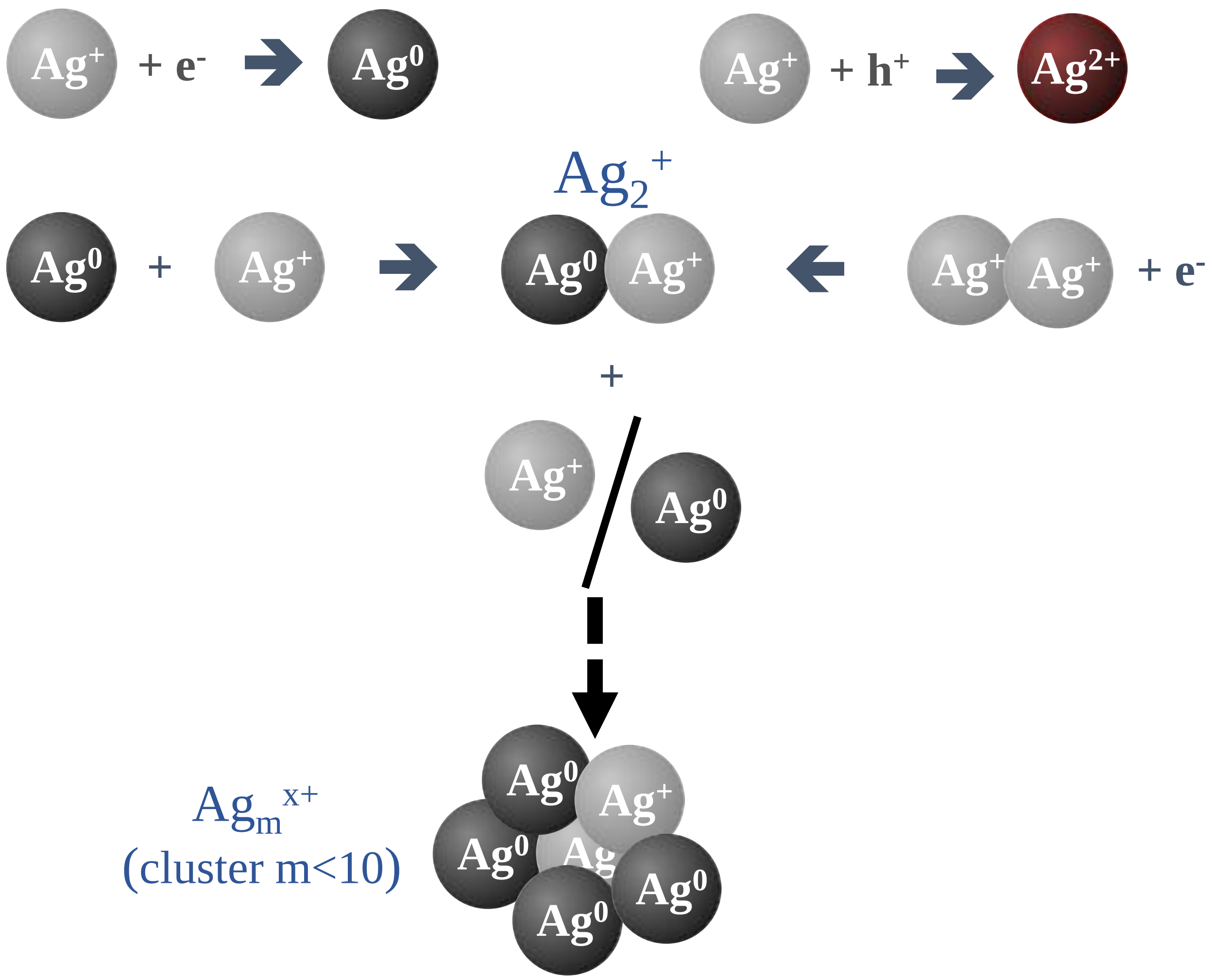
Defects assisted densification

Fabrication des capteurs (P, T)
de type fibre optique à réseau de Bragg

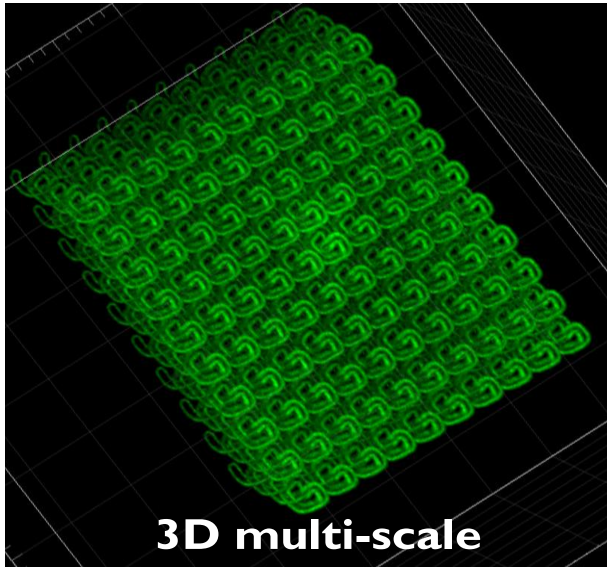


Photostructuration des verres dopés Ag

Glass host + ionizing irradiation ➔ $e^- + h^+$



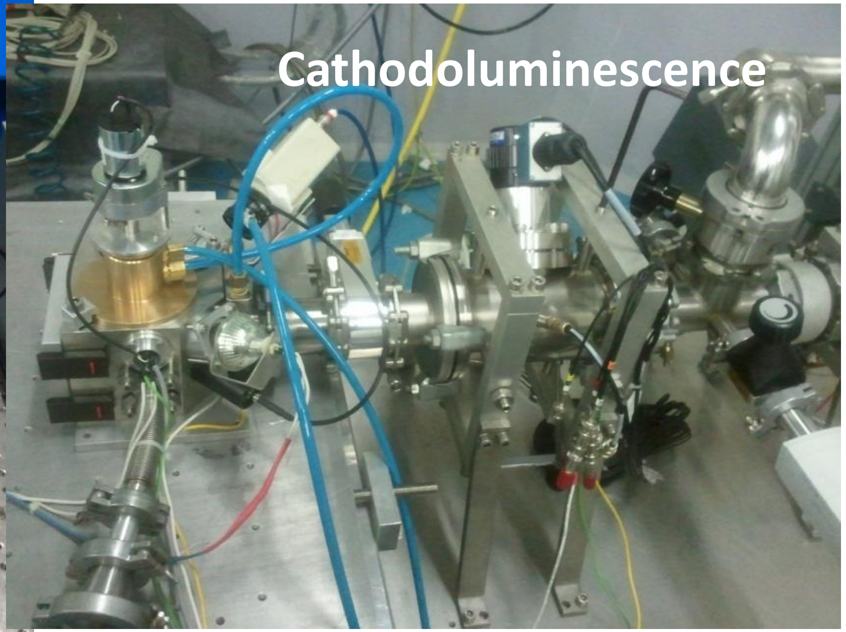
fs DLW



$Ag_m^{\ x+}$

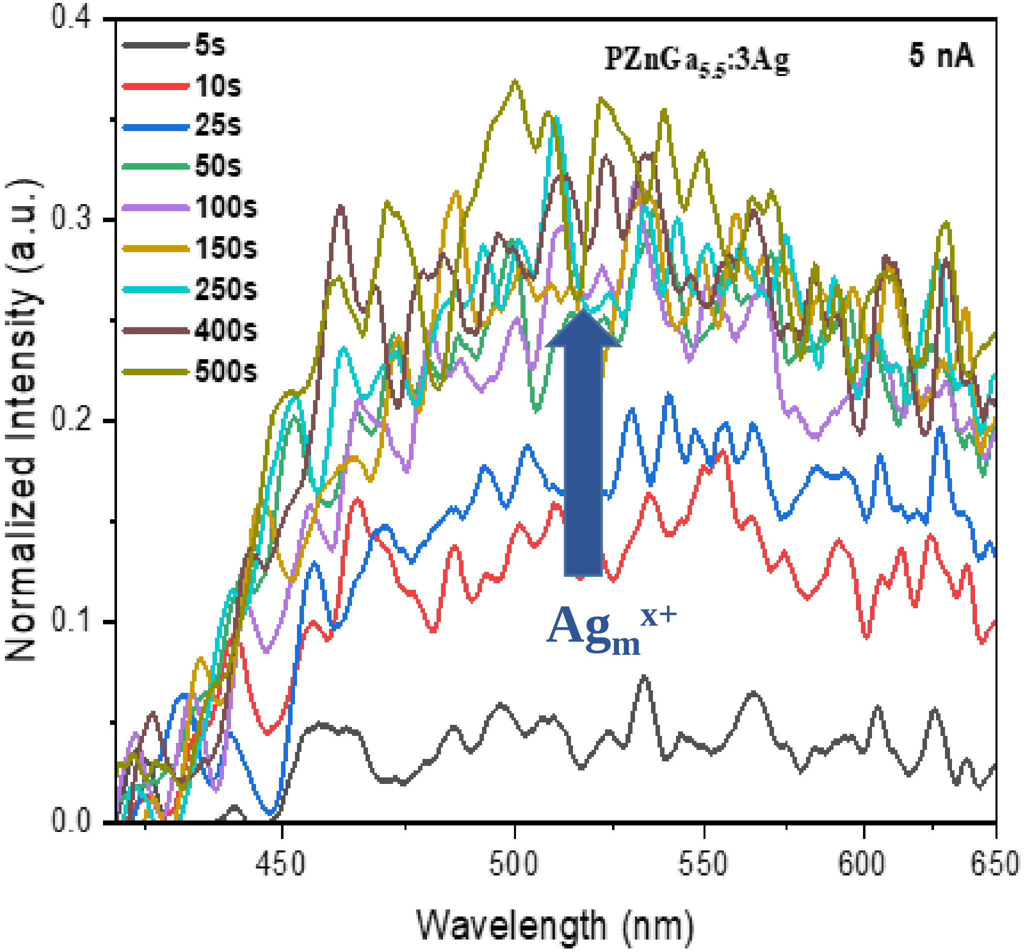
N. Marquestaut et al., *Avd. Funct. Mat. 24(37) 5824–5832 (2014)*

Electron Irradiation



- Accelerator High energy electrons
- Electron energy : 150KeV-2.5MeV

Cathodoluminescence of PZnGa5.5:3Ag



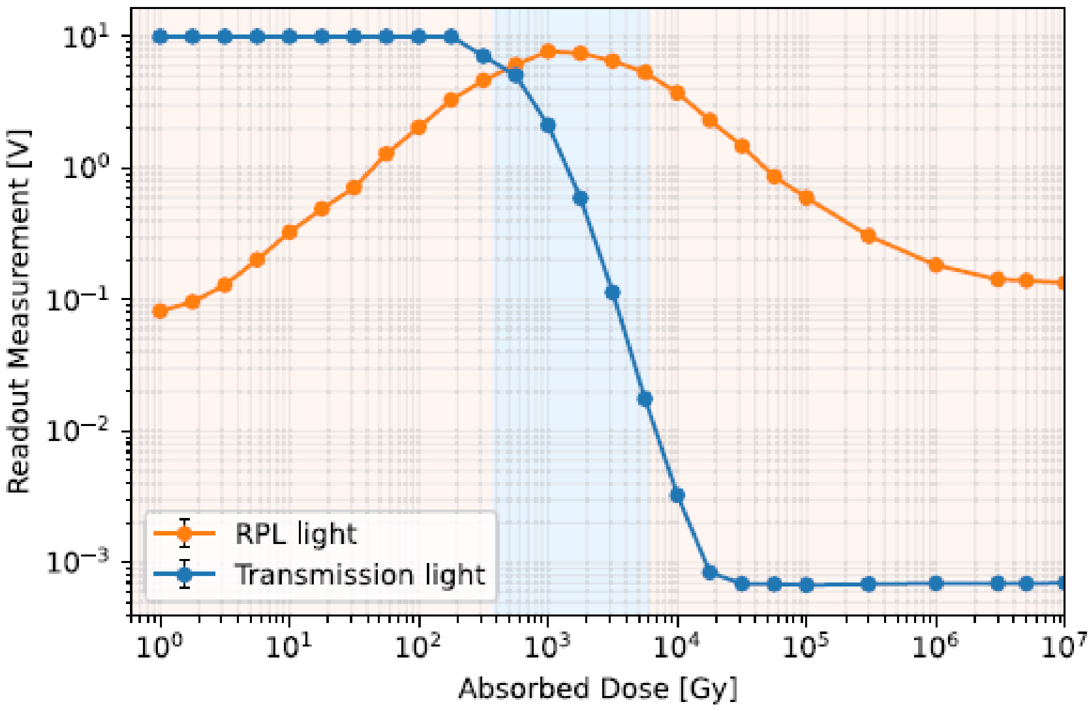
Formation of Ag_m^{x+} clusters during the first steps of electron irradiation

F. Alassani et al JNCS 600(1):122009 (2023)

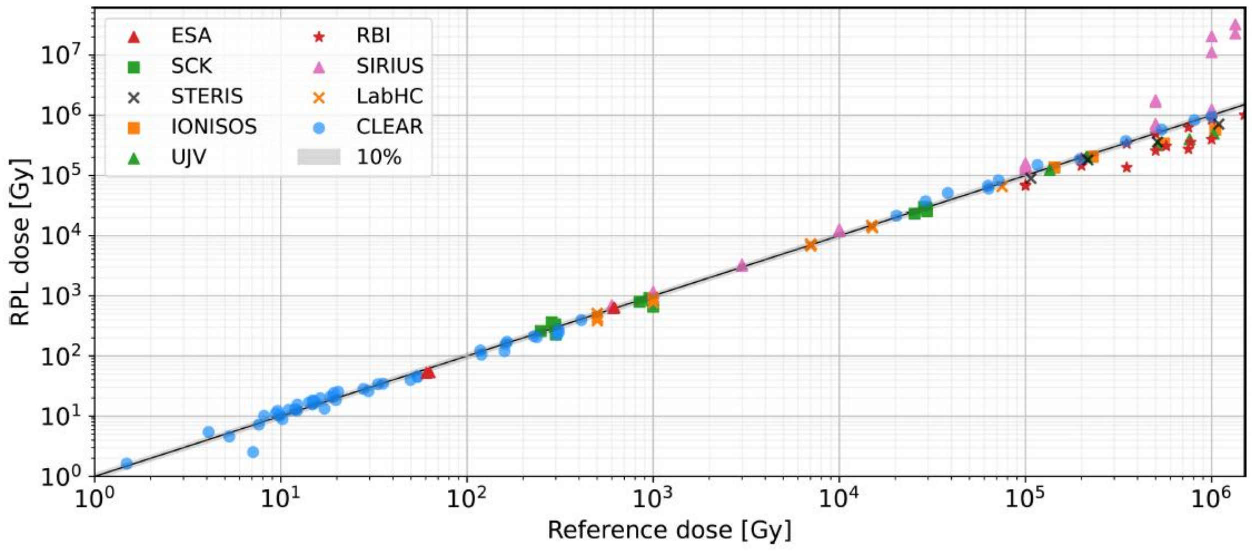
Dosimetrie par RadioPhotoluminescence

LHC-CERN

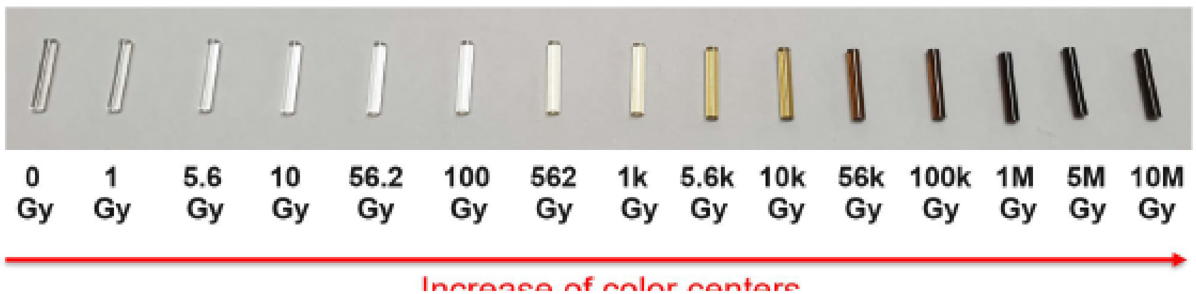
Verres métaphosphates dopés Ag



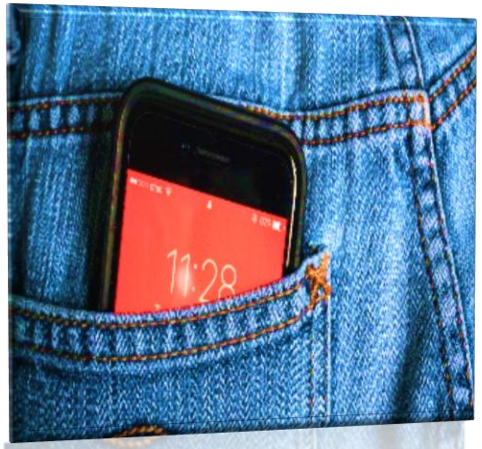
(a)



IEEE TRANSACTIONS ON NUCLEAR SCIENCE, VOL. 72, NO. 8, AUGUST 2025

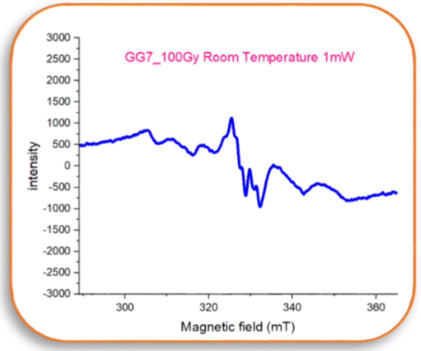


Dosimetrie par RPE



Verre de smartphone

Irradiation

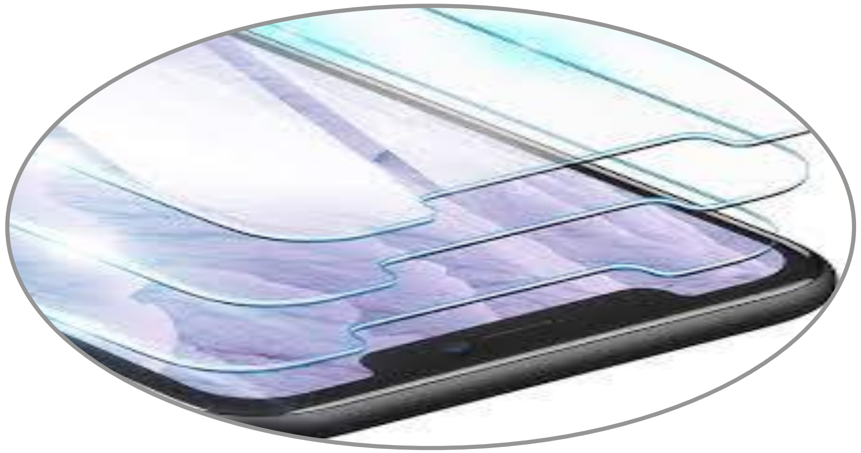


Evaluation de la dose

Méthode automatisée

Verre de type Alkali Alumino-silicate

Ecrans tactiles

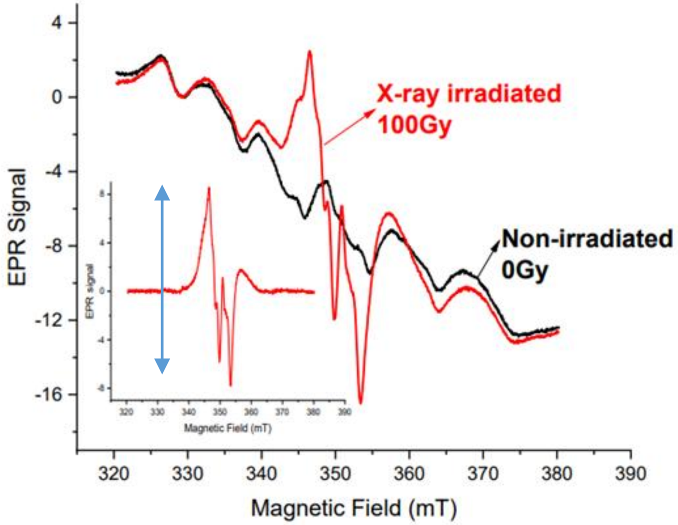


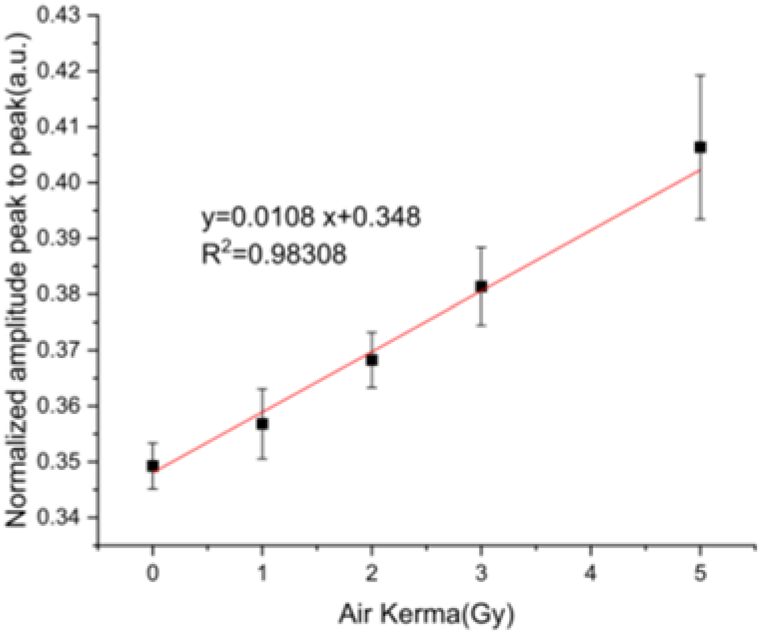
Ecrans de protection

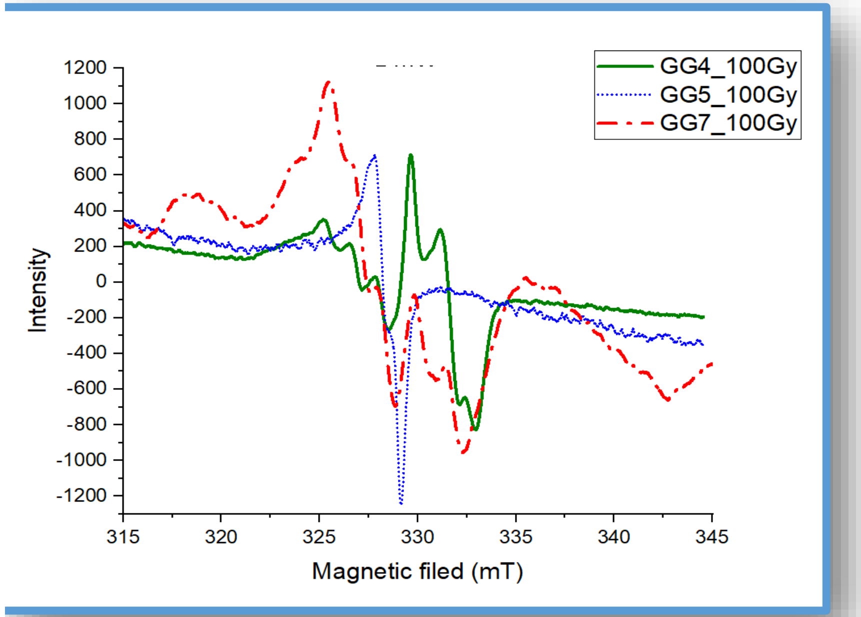
Dosimétrie
accident radiologique de grande ampleur

Thèse M. Mobasher, IP 2024
Thèse A. Gaborit en cours
Collab. ASNR

Mobasher et al. Rad. Measurements 2024







Projet dosimétrie RPE

Merci pour votre attention !

Future collaboration avec GenF (start-up de Thalès)/ réacteur à fusion par confinement inertiel

Besoin d'irradiation avec des faisceaux pulsés (ions, électrons..)

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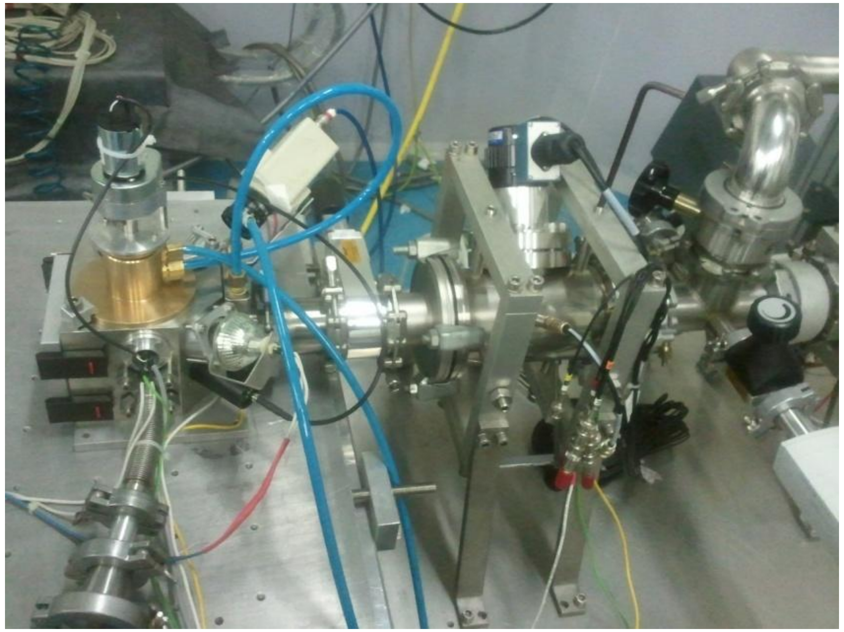
Electron Irradiation

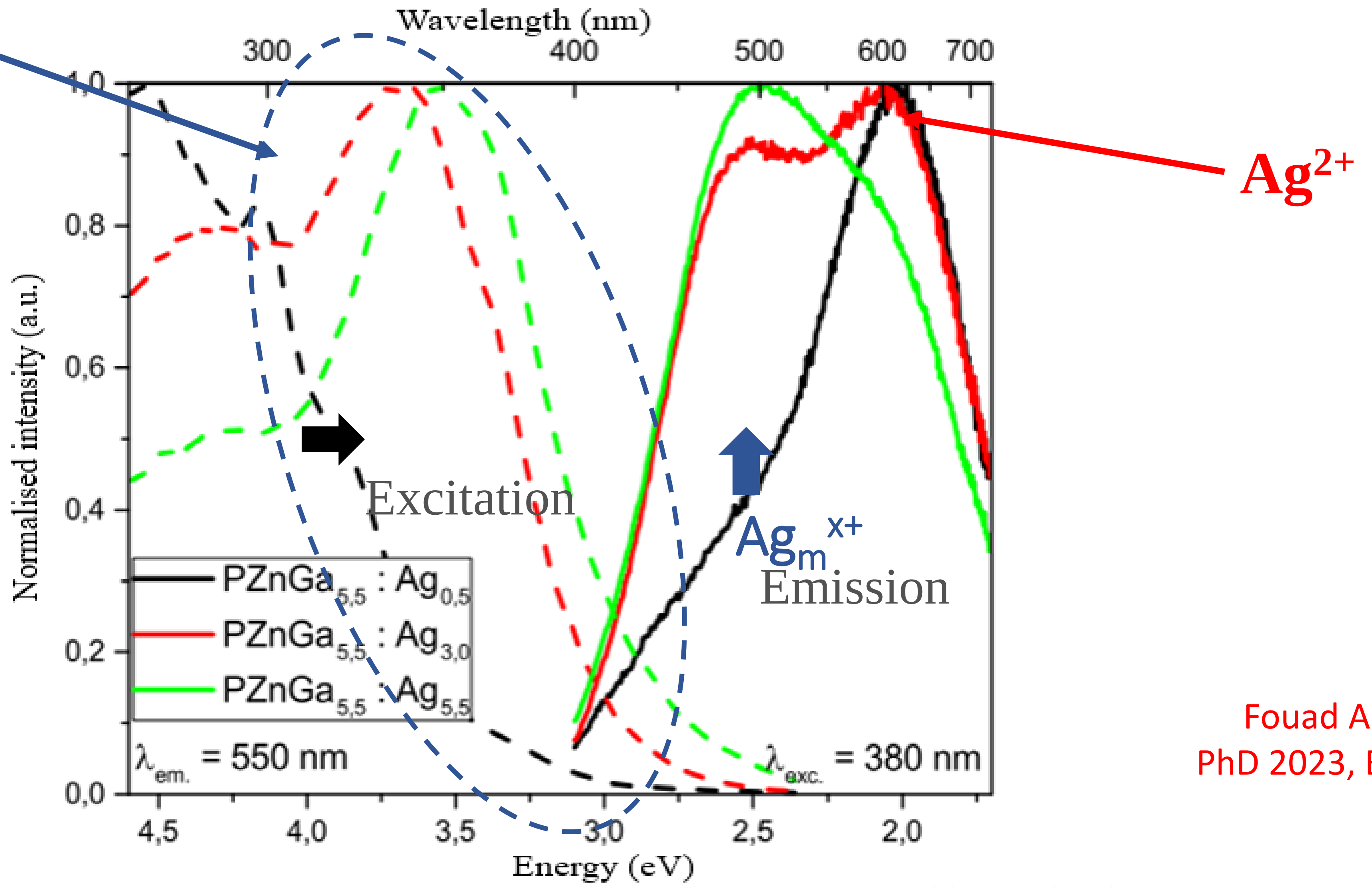


Proposal: octobre de chaque année

- Irradiation Plateform with high energy electrons
- Electron energy : 150 keV-2.5MeV
- Temperature 20 K-1200 K
- Current : 5 nA-10 mA

Excitation and emission spectra of the electron irradiated PZn glass

Ag_m^{x+} and Ag^{2+}



F. Alassani et al JNCS 600(1):122009 (2023)

Fouad Alassani
PhD 2023, Bordeaux

Solarisation des verres au Mn (verres du patrimoine)

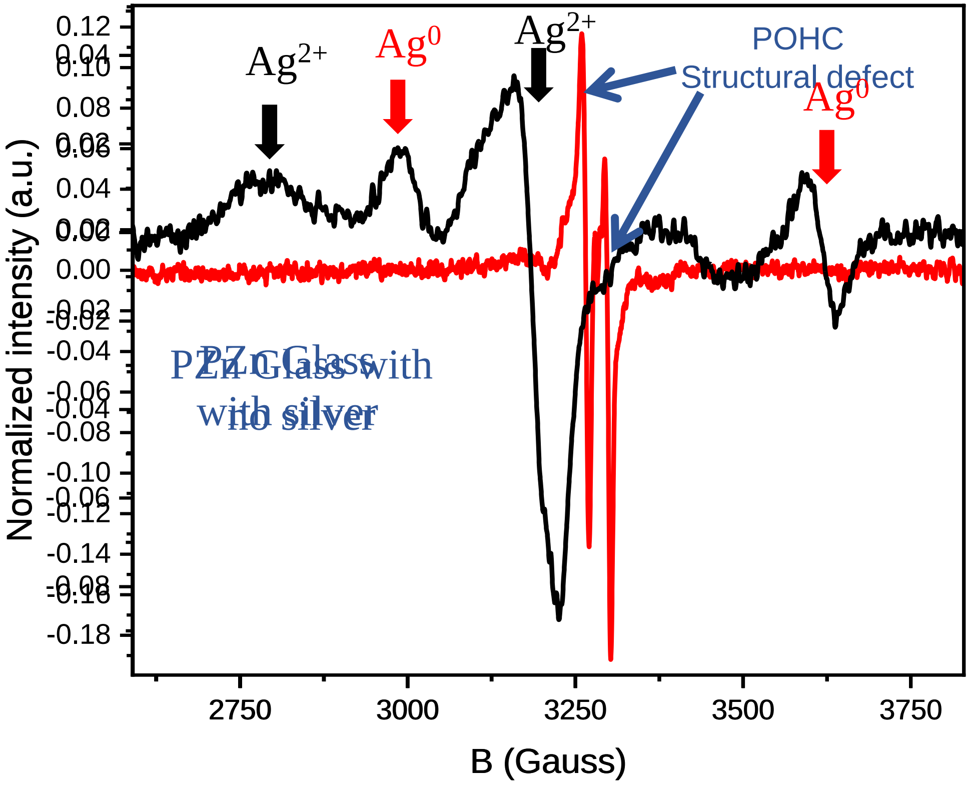
Le verre peut se solariser et virer au violet, sous l'effet des photons UV
Réduction de Fe^{3+} en Fe^{2+} et oxydation de Mn^{2+} en Mn^{3+}
$Fe^{3+} + Mn^{2+} \rightarrow Fe^{2+} + Mn^{3+}$

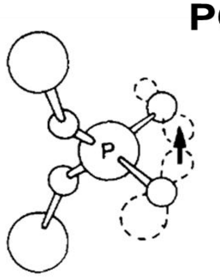
Verre Lalique (1931)
chapelle de Douvre-la-Délivrande

Couleur violette
Ions Mn^{3+}

Restauration du verre avec un recuit
le manganèse revient alors à son état d'oxydation stable Mn^{2+} (incolore)
Et pour protéger ces verres d'une nouvelle solarisation: nouveau vitrage classique qui absorbe les UV.

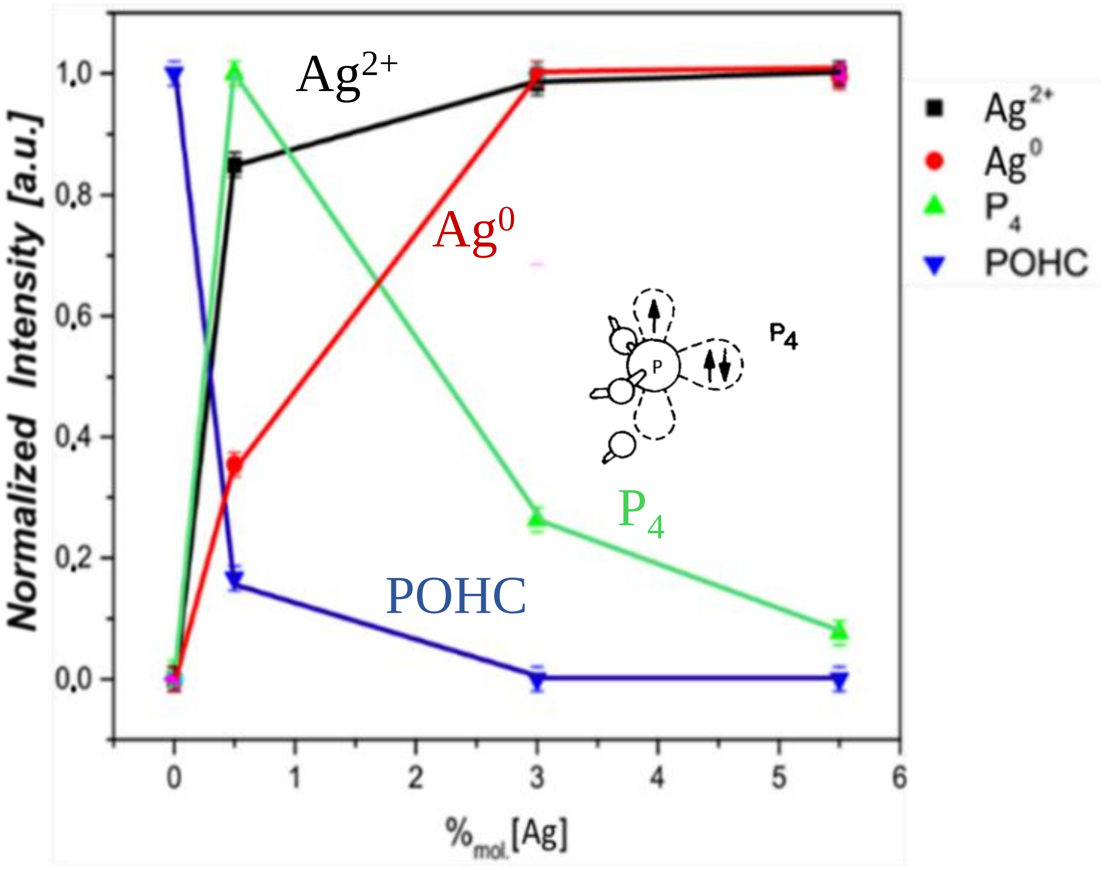
Electron irradiated Zn Phosphate





POHC

Evolution of defects with silver content



Inversion of defect populations at high silver concentration

F. Alassani et al JNCS 600(1):122009 (2023)

Le verre de la pyramide du Louvre

Transparent, incolore, pas de solarisation

~~Mn~~ pour décolorer
Se (Se^{6+}, Se^{4+}, $Se°$, Se^{2-})

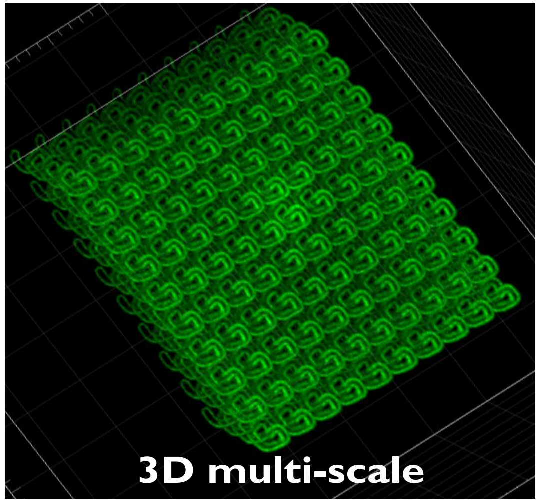
une teneur en sélénium de l'ordre de 1 ppm a été suffisante pour décolorer le verre de la pyramide qui contenait 150 ppm de fer

Le verre de la pyramide du Louvre
P. Lehuédé Techné 49 2020

Ag doped phosphate glasses

Interaction of femtosecond laser with glass

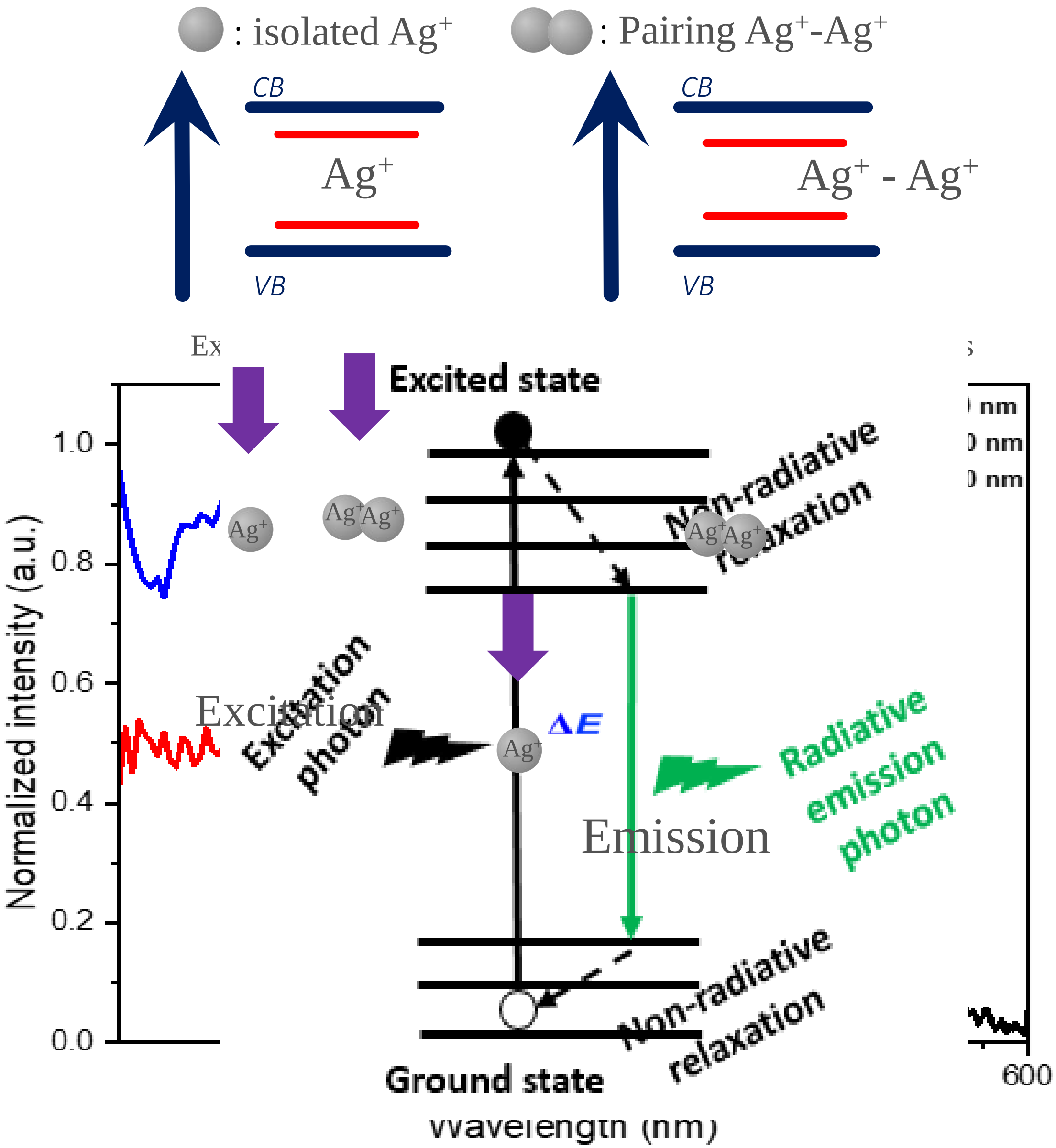
fs DLW



N. Marquestaut et al., Avd. Funct. Mat. 24(37) 5824–5832 (2014)

Ag_m^{x+}

Under UV



Initial processes of silver clusters formation ?
Higher glass volume: electron irradiation

Aknowledgements

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SIRIUS

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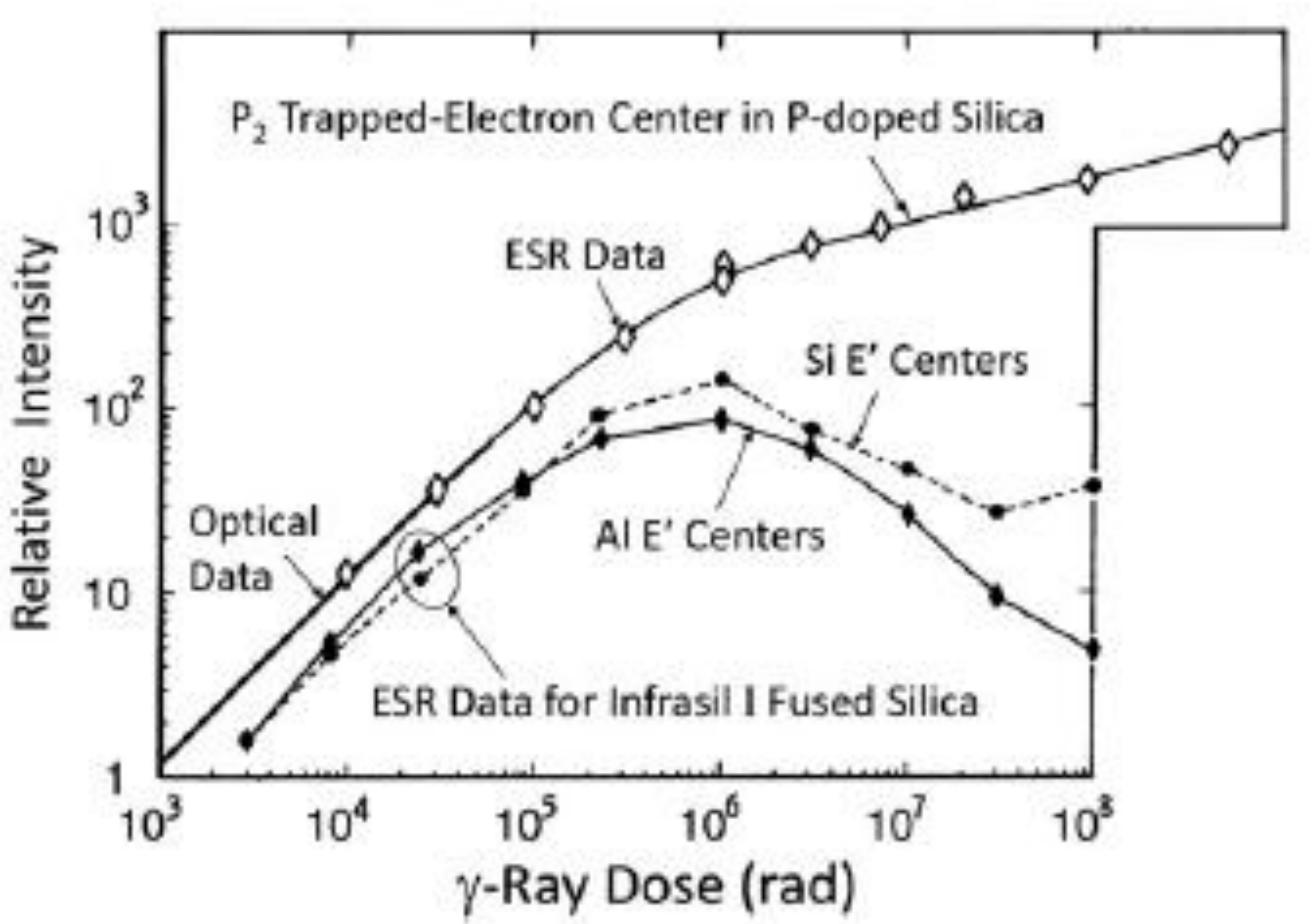
Dose effect in silica glass



D. Griscom Journal of Non-Crystalline Solids 2011

D^n : n<1 doses >10^4 Gy