X-ray Absorption Spectroscopy in the study of irradiated glasses

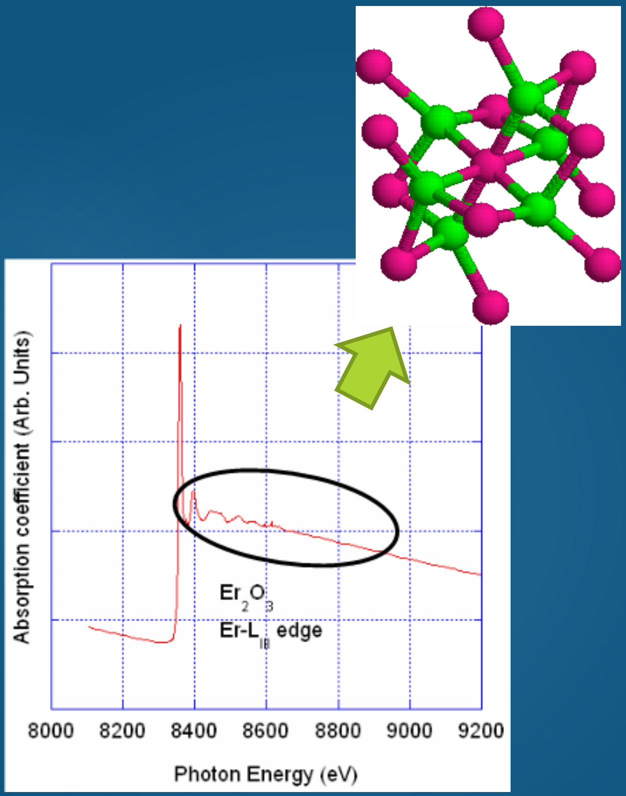
FRANCESCO D'ACAPITO

CNR-IOM-OGG C/O ESRF

Layout

- Intro to XAS
- Damage on the main components
- Damage on dopants
- Perspectives
- Conclusions

X-ray Absorption Spectroscopy



The information is retrieved from the oscillations above core level absorption edge

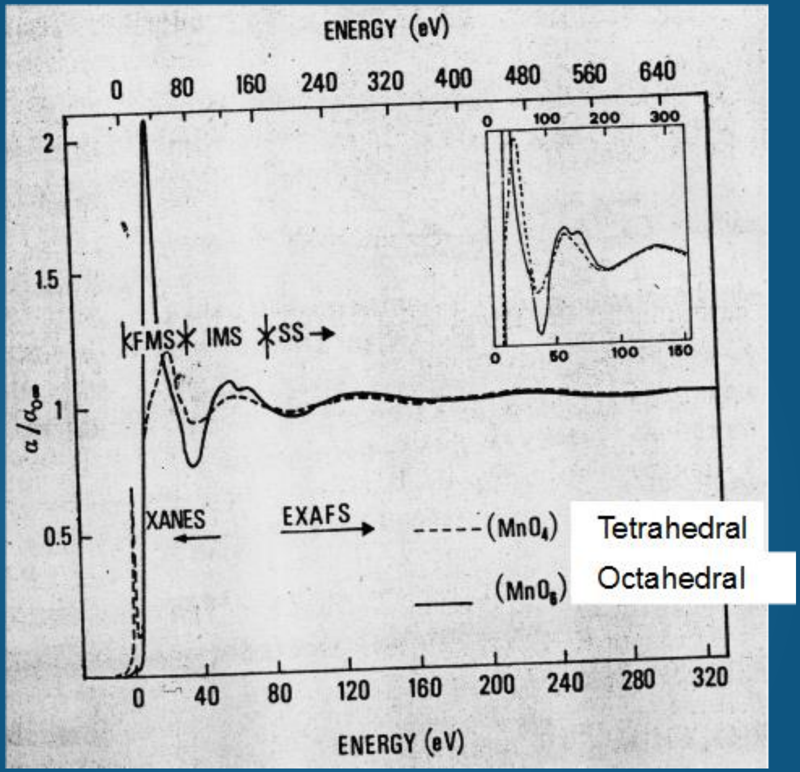
Local parameters

- Nature and distance of ligands
- Site simmetry
- Valence state
-

Bad news:

- U need a synchrotron

Regions of a XAS spectrum



XANES

- Up to 50 eV
- Long photoelectron wavelength
- Electronic structure
- Local geometry, symmetry
- Complex scattering processes

- EXAFS
  - Short photoelectron wavelength
  - Quantitative
  - Dominated by single scattering

American Mineralogist, Volume 76, pages 60–73, 1991

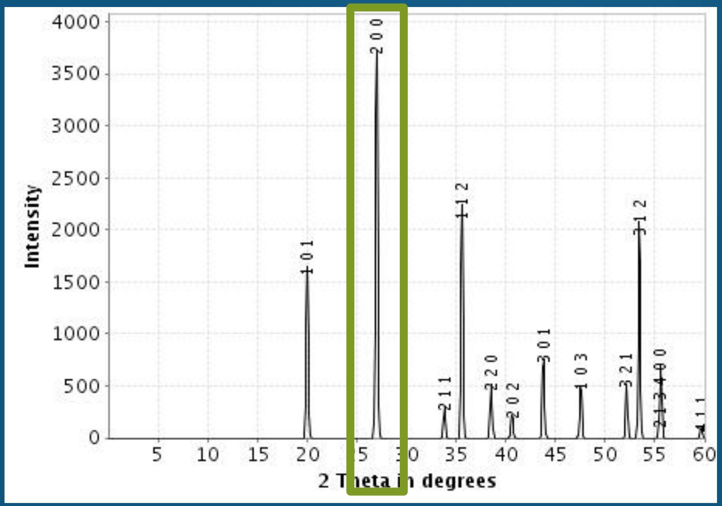
Structural analysis of radiation damage in zircon and thorite: An X-ray absorption spectroscopic study

François Farges, Georges Calas

Some minerals (ex. ZrSiO4) can undergo amorphization (metamictization) due to the radiation damage (α particles, recoils) from the actinides they contain.

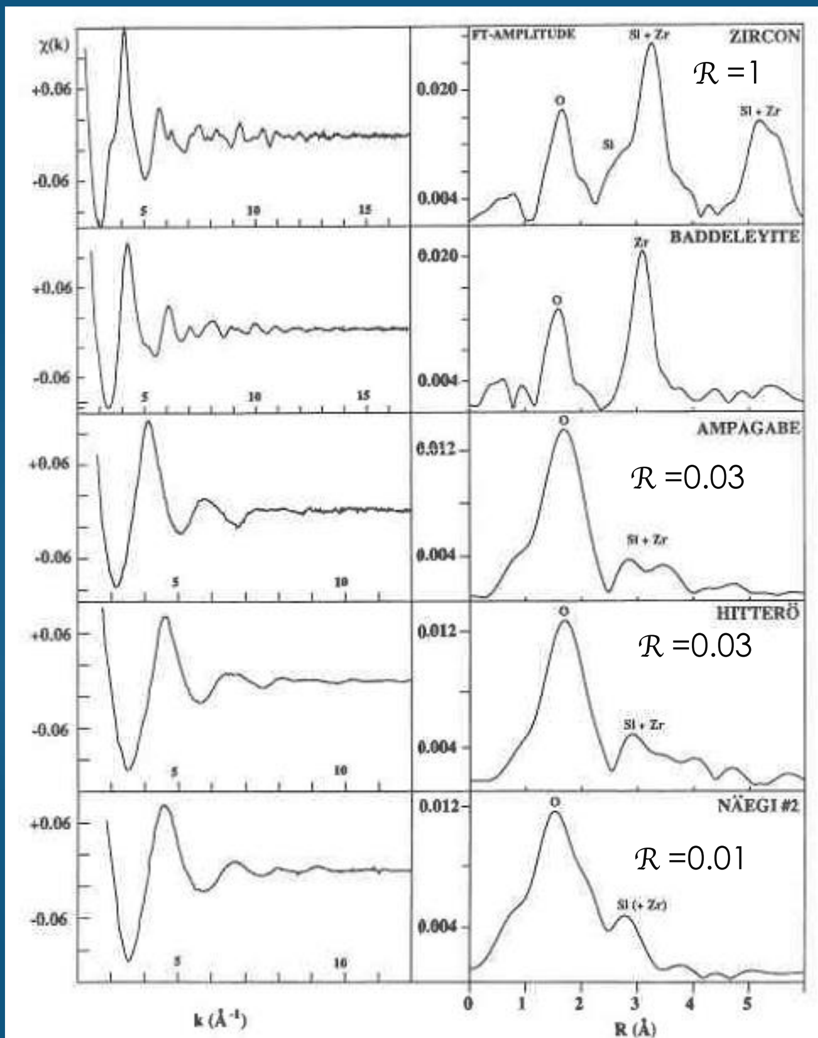
In the case of Zircon the disorder level is measured as the ratio of the 200 diffraction line respect a reference perfect crystal $\mathcal{R}$

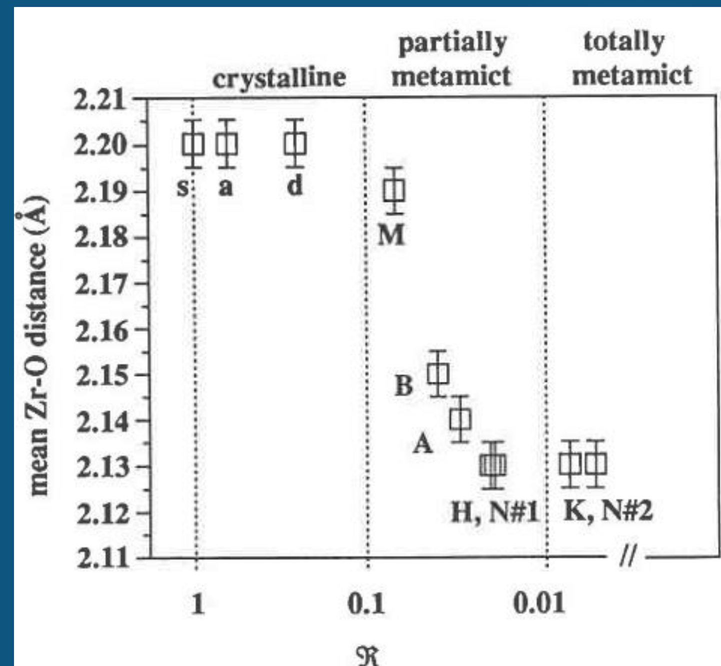
XAS at the Zr-K edge has revealed details of the metamictization process.



XAS data analysis

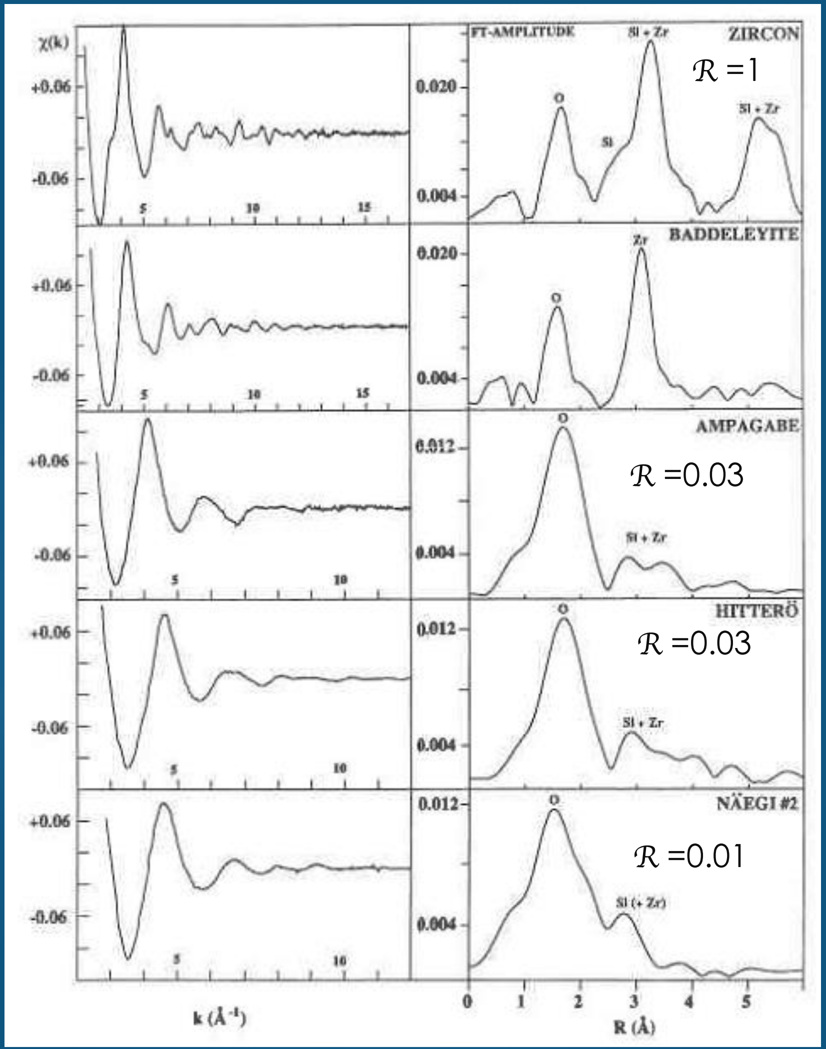
	O	
	R (Å)	N
Crystalline Australia	2.20	8.0
Crystalline Brazil	2.19	8.0
Metamict Miask	2.19	8.0
Metamict Betafo	2.15	7.0
Metamict Ampagabe	2.14	6.9
Metamict Hitterö	2.13	7.1
Metamict Näegi no. 1	2.13	6.8
Metamict Näegi no. 2	2.13	7.1
Metamict Kinkle's Quarry	2.13	7.2





First shell Zr-O
Reduction of the NN
Shrinking of the bond length

XAS data analysis



	Si			Zr	
	R (Å)	*N*	Δσ (Å)	*R* (Å)	*N*
Crystalline Australia	2.95	2.3	0.03	3.62	4.0
Crystalline Brazil	2.95	1.8	0.03	3.64	3.4
Metamict Miask		UM*		3.62	2.7
Metamict Betafo	2.82	1.1	0.04	3.31	0.9
Metamict Ampagabe	2.86	0.9	0.04	3.34	1.1
Metamict Hitterö	2.86	0.6	0.02	3.34	0.5
Metamict Näegi no. 1	2.90	0.4	0.00	3.34	0.9
Metamict Näegi no. 2	2.88	0.9	0.00		UM*
Metamict Kinkle's Quarry	2.86	0.5	0.00		UM*

Reduction of the second neighbors
Shrinking of the coordination length

Conclusion

Model for metamictization

- Displacement of O atoms due to bombardement
- Adaptation of Zr to a lower coordination
    - Shrinking of the Zr-O bond length
- Tilting of the SiO_4 tetrahedral neighboring Zr
    - Shrinking of the Zr-Si coordination distances
- Formation of Zr oxide is ruled out.

Structure of β-irradiated glasses studied by X-ray absorption and Raman spectroscopies

Daniel R. Neuville [a,*], Laurent Cormier [b], Bruno Boizot [c], Anne-Marie Flank

Journal of Non-Crystalline Solids 323 (2003) 207–213

Istituto Officina dei Materiali

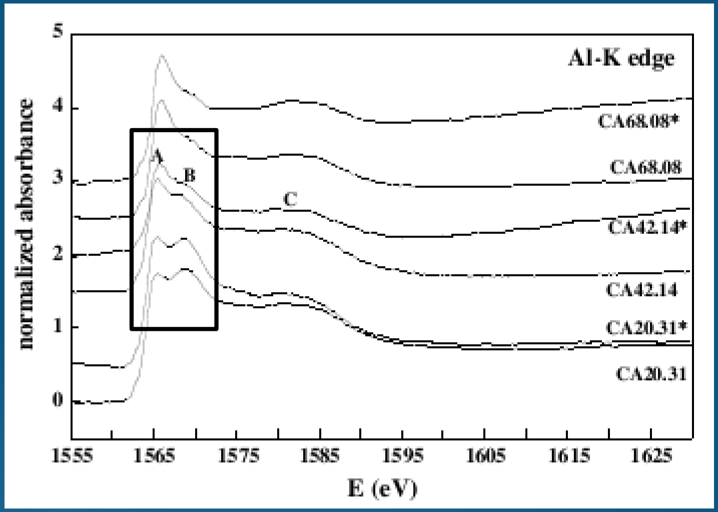
Bulk calcium-alumino-silicate glasses
Irradiation 2.5 MeV electrons 3.8*10^9 Gy

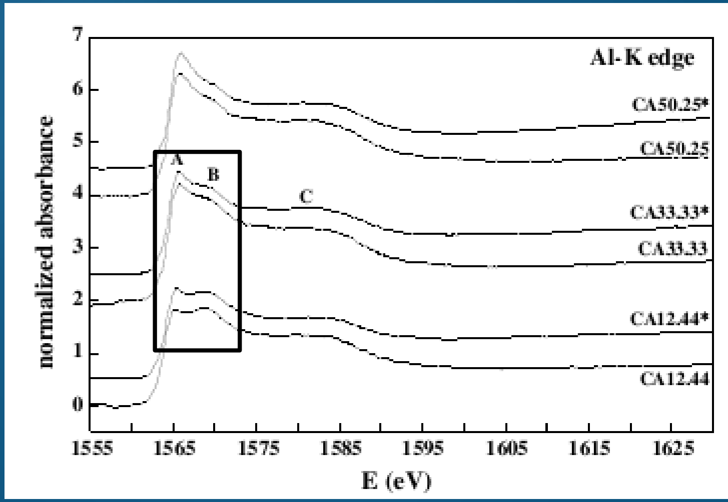
RAMAN:
- presence of O2 in irradiated samples
- increase of the Q3/Q2 ratio

XAS: Al K edge

	SiO_2	Al_2O_3	CaO
CA12.44	11.82	44.10	44.10
CA20.31	20.00	31.00	49.00
CA33.33	33.33	33.33	33.33
CA42.14	42.86	14.28	42.86
CA50.25	50.00	25.00	25.00
CA68.08	68.30	8.71	22.97

β-irradiated glasses





More evident effect on low-silica samples.

Feature A: position related to the Al-O bond length (and to polymerization)
Feature B attributed to Q3 species

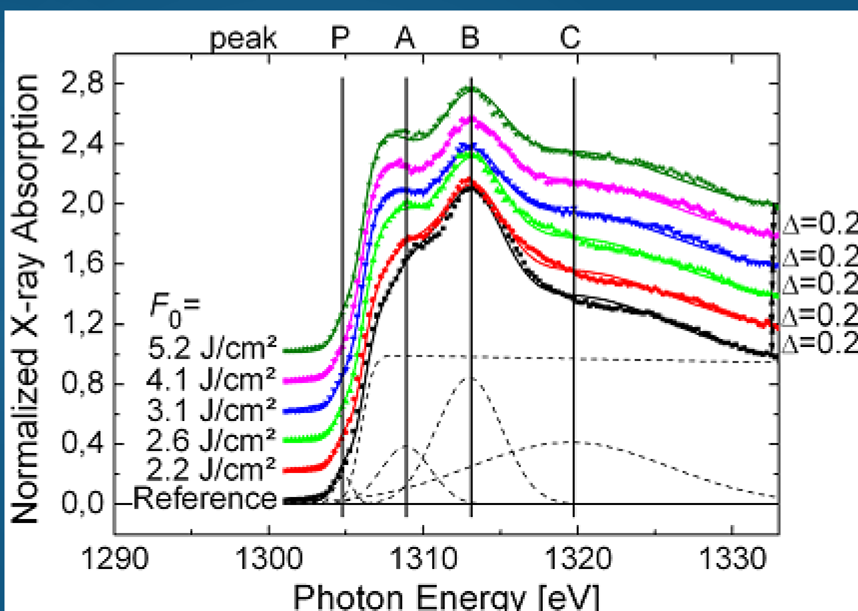
Blue shift of A
Increase of B in the irradiated samples
Both signs of increased polymerization.

APPLIED PHYSICS LETTERS 100, 224101 (2012)

Femtosecond laser-induced modification of potassium-magnesium silicate glasses: An analysis of structural changes by near edge x-ray absorption spectroscopy

T. Seuthe,[1] M. Höfner,[2] F. Reinhardt,[3] W. J. Tsai,[4] J. Bonse,[5] M. Eberstein,[1] H. J. Eichler,[2] and M. Grehn[2,a)]

Glasses 20K2O, 20MgO, 60SiO2
Laser irradiation 800nm 130 fs, 2 -> 5.2 J/cm^2



Evolution of the peak A respect to B with irradiation.
'Red' shift of the edge
By comparison with several Mg minerals
shortening of the Mg-O distance from 2.08 to 2.01 Å.
Densification of the matrix

Ag-doped glasses

- Ag frequently used in the realization of waveguides to locally rise the index of refraction.
- Irradiation processes used for promoting Ag aggregation in clusters.
- Clusters possess interesting optical properties
  - Surface Plasmon Resonance
  - Nonlinear optical response
- Useful to create devices ‘in waveguide’.
- Several methods used to create clusters

SEVIER Nuclear Instruments and Methods in Physics Research B 200 (2003) 185–190
www.elsevier.com/locate/ni

Silver nanocluster formation in ion-exchanged glasses by annealing, ion beam and laser beam irradiation: An EXAFS study

G. Battaglin [a], E. Cattaruzza [a], F. Gonella [a], R. Polloni [a], F. D'Acapito [b], S. Colonna [c], G. Mattei [d], C. Maurizio [d], P. Mazzoldi [d], S. Padovani [d,*], C. Sada [d], A. Quaranta [e], A. Longo [f]

Soda lime glasses doped with Ag by ion exchange

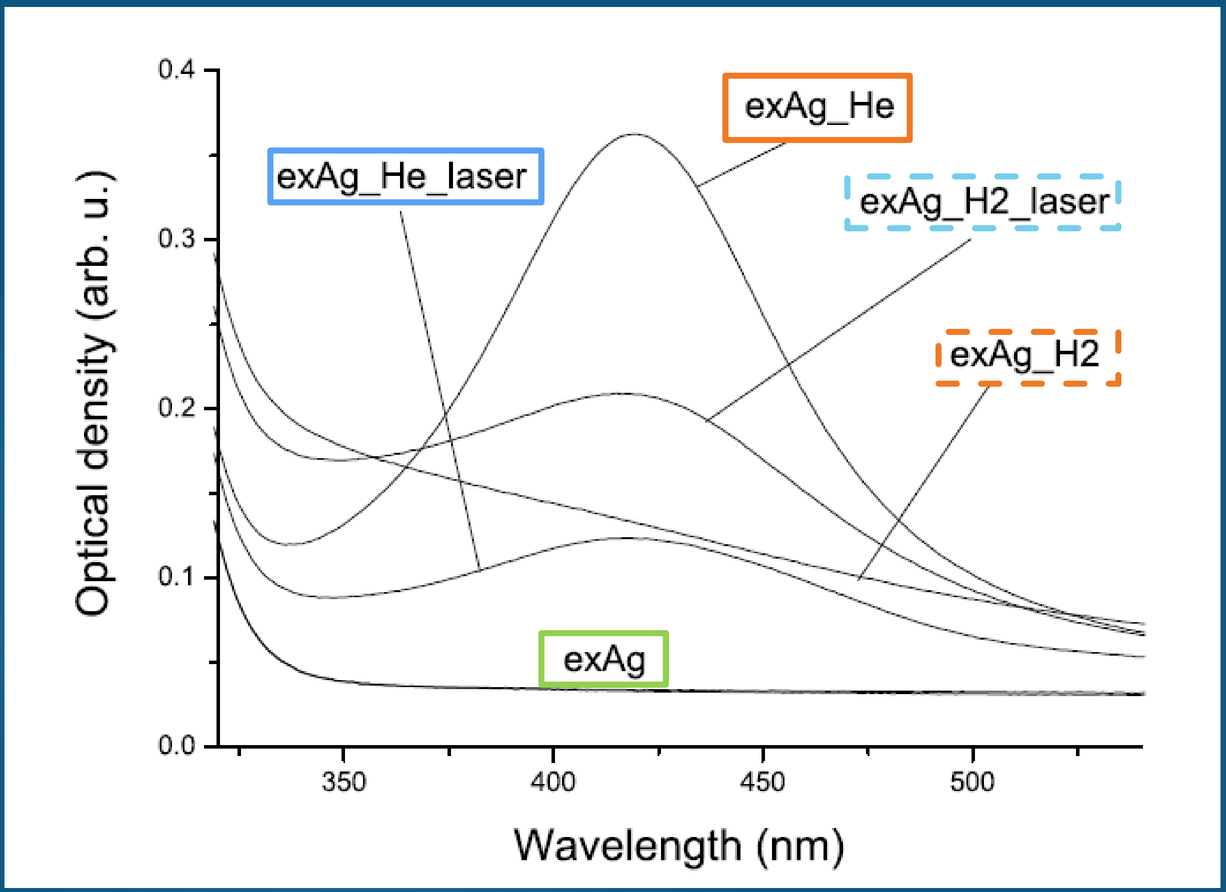
Different treatments:

- Laser irradiation 532nm, 10ns, 0.5 J/cm2
- He irradiation 1.5 MeV, 2*10^16 at/cm2
- Annealing 5h, 250 C, (Ar+5%H2)

Experimental techniques

- Optical absorption
- X-ray Absorption Spectroscopy (XAS)

Optical absorption



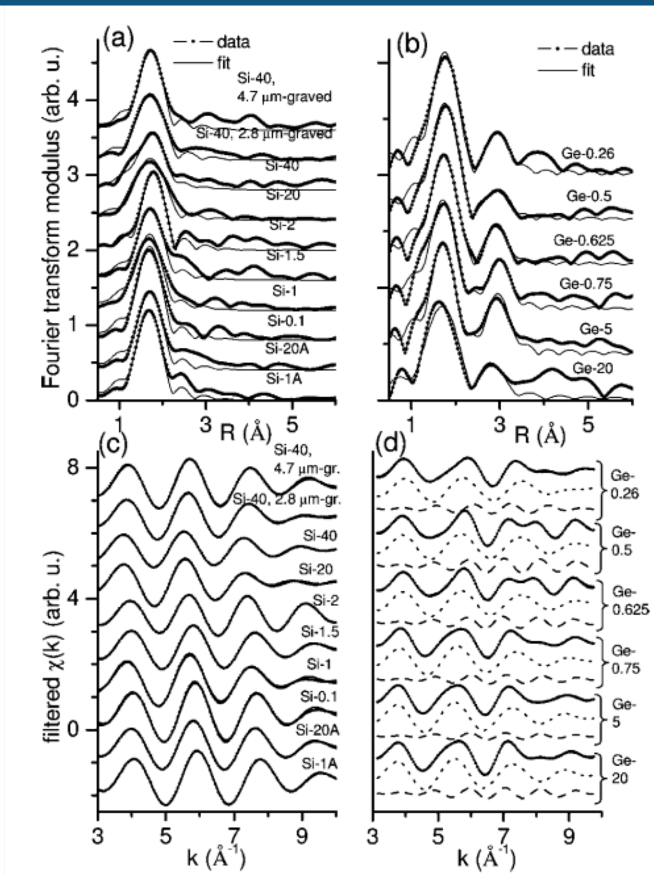
Battaglin et al. NIM B **200** (2003), 185.

Peaks due to the Surface Plasmon Resonance (SPR) of Ag clusters.

Blind to oxidized forms of Ag.

As-exchanged glass

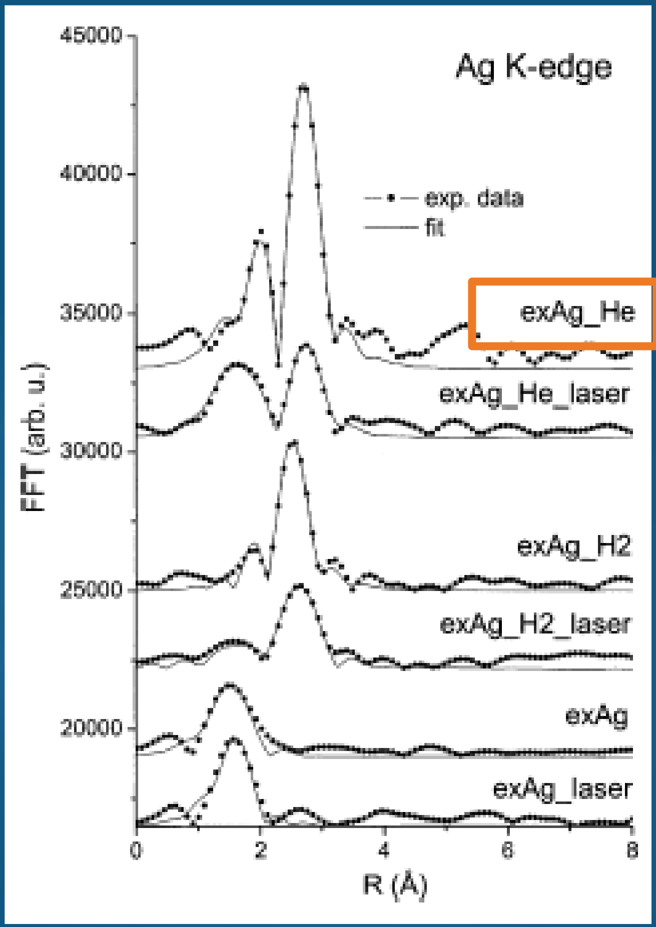
C. Maurizio,*,† A. Quaranta,‡ E. Ghibaudo,§ F. D'Acapito,† and J.-E. Broquin§



J. Phys. Chem. C **2009**, *113*, 8930–8937

Ag in glass forms a single shell with O
RAg-O = 2.28-2.20 depending on the preparation conditions.
No Ag-Ag shell

He irradiation



Battaglin et al. NIM B **200** (2003), 185.

Coordination	R (Å)	N	σ^2 (10^{-4} Å^2)
Ag–O	2.08 ±0.06	1 ± 2	128 ± 354
Ag–Ag	2.86 ±0.02	8 ± 1	98 ± 11

Formation of met-Ag (about 70±10 %)

Bulk clusters, the Ag-Ag spacing is near the bulk value (2.88 Å)

He irr. + laser treatment

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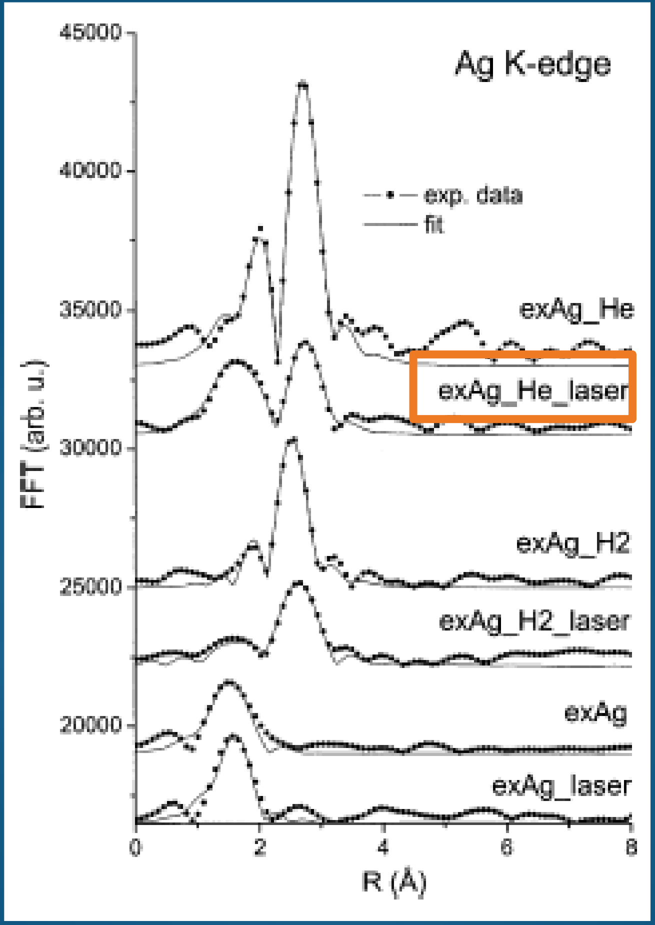


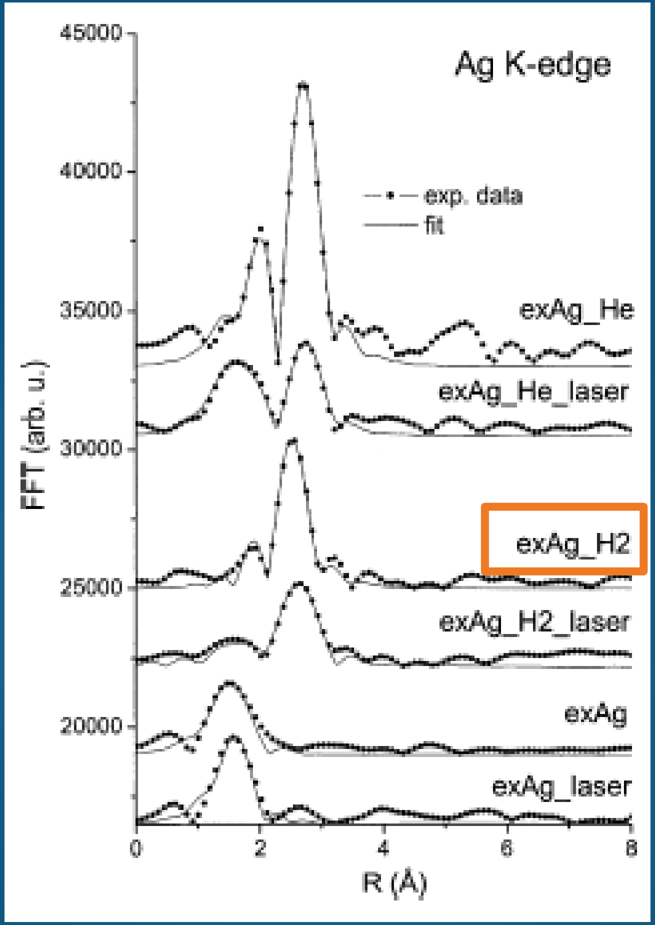
Battaglin et al. NIM B **200** (2003), 185.

Coordination	R (Å)	N	σ^2 (10^{-4} Å^2)
Ag–O	2.10 ±0.02	1.3±0.5	87±63
Ag–Ag	2.84 ±0.02	3.2±0.7	114±27

Reduction of the metal peak in the FT

Nanometric clusters, the Ag-Ag spacing is shorter than the bulk value.

H2 treatment



Battaglin et al. NIM B **200** (2003), 185.

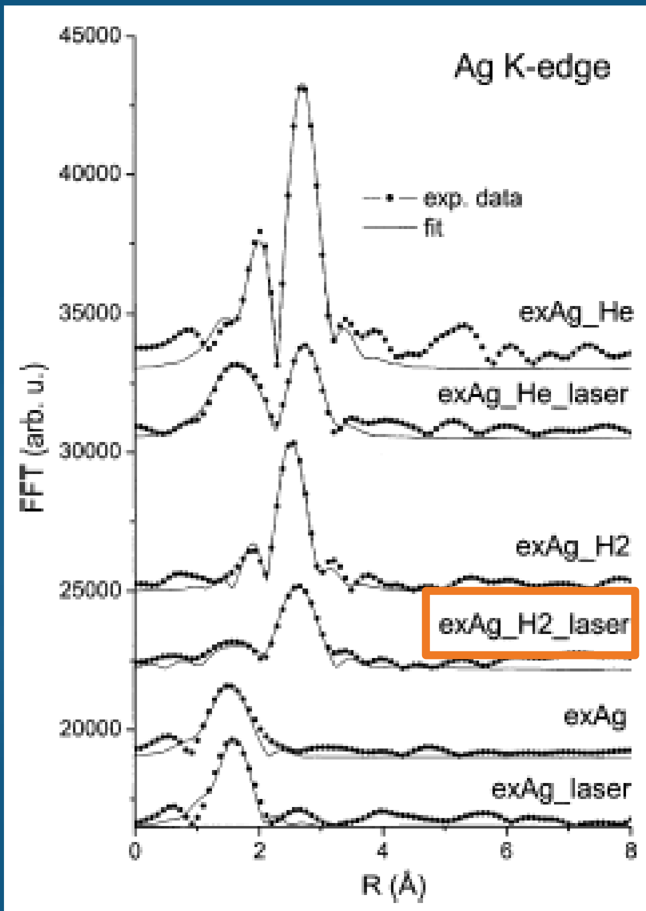
Coordination	R (Å)	N	σ^2 (10^{-4} Å^2)
Ag–O	2.26 ± 0.06	0.5 ± 0.4	52 ± 47
Ag–Ag	2.70 ± 0.02	3.4 ± 0.7	93 ± 20

Formation of Ag metal

Again , nanometric clusters, the Ag-Ag spacing is shorter than the bulk value.

Clusters not seen by diffraction nor exhibit SPR

He treatment + laser



Battaglin et al. NIM B **200** (2003), 185.

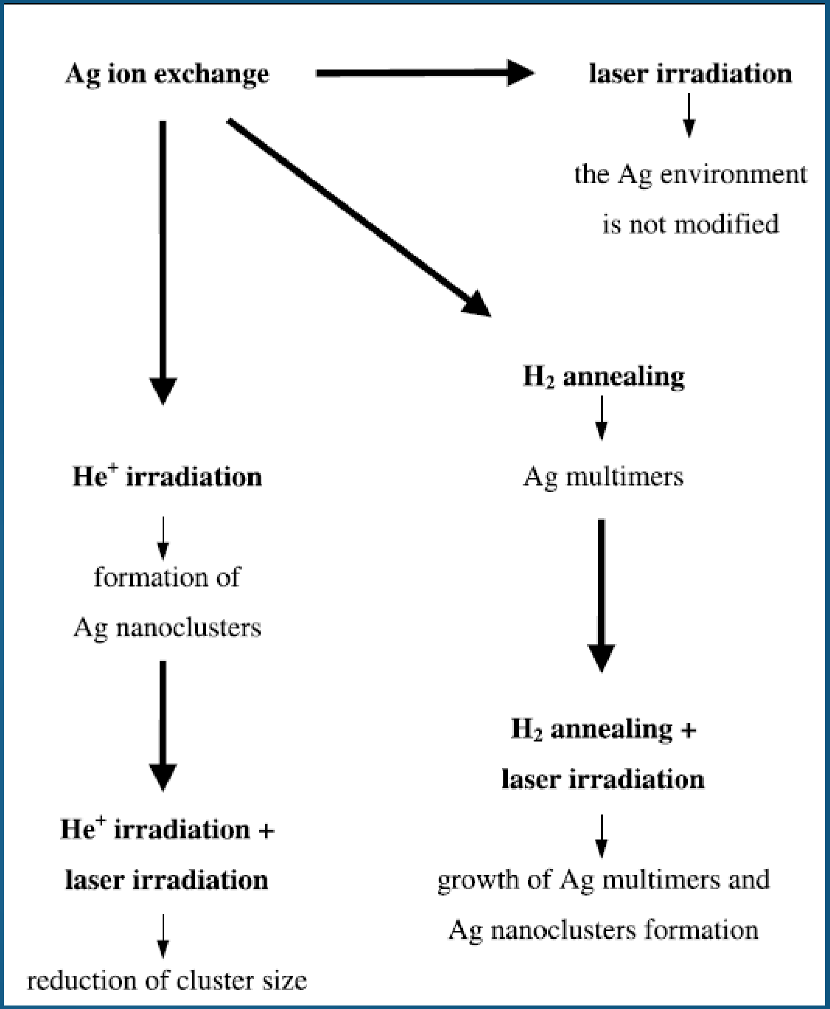
Coordination	R (Å)	N	σ^2 (10^{-4} Å^2)
Ag–O	2.20 ±0.06	0.5 ± 0.4	57 ± 52
Ag–Ag	2.76 ±0.02	5 ± 1	198 ± 32

Formation of Ag metal

Growth of the nanoclusters, the Ag-Ag spacing is longer than before.

Clusters not seen by diffraction

Conclusion



Scheme of the effects of the various treatments

Nuclear Instruments and Methods in Physics Research B 245 (2006) 222–224

www.elsevier.com

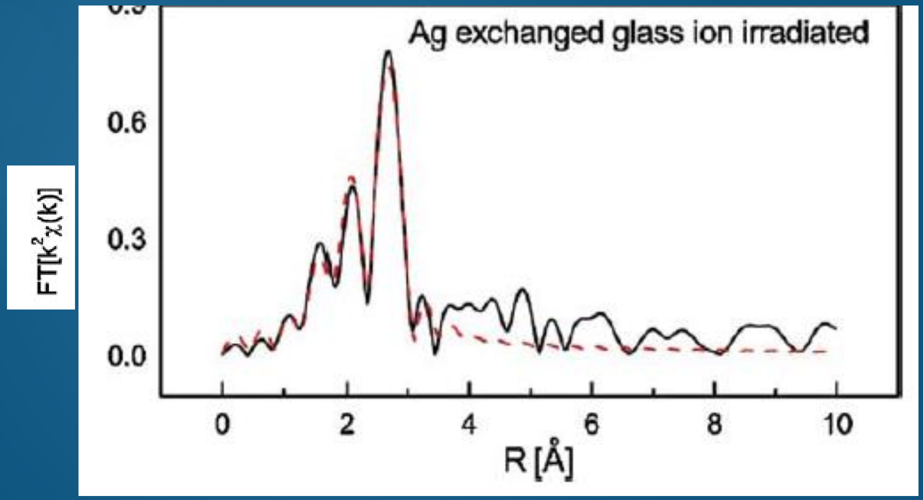
Ion beam induced nanosized Ag metal clusters in glass

H.-E. Mahnke [a,*], B. Schattat [a], P. Schubert-Bischoff [a], N. Novakovic [a,b]

2 step process

Ion irradiation of Ag-exchanged glasses, 600 MeV Au @ 10^11-10^13 at/cm2

Annealing reducing atmosphere 30', 340 C, Ar-H2



System	Shell 1
Ag in glass	2.85(2)
	2.25(10)

Small cluster, < 20nm

RE-doped Al-B glasses

X-ray induced reduction of rare earth ion doped in Na_2O-Al_2O_3-B_2O_3 glasses

Yutaka Shimizugawa,[a*] Norimasa Umesaki,[a] Katsumi Hanada,[b] Ichiro Sakai[b] and Jianrong Qiu[c]

J. Synchrotron Rad. (2001). 8, 797–799

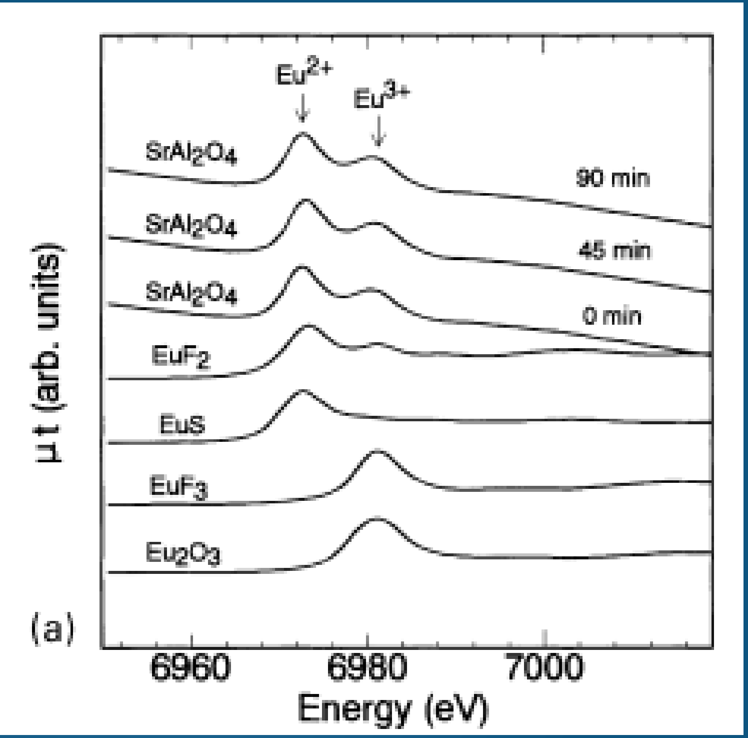
Composition 5Na2O-10Al2O3-85B2O3
RE (Sm, Eu) 0.05 mol %
Irradiation:
A: 10 and 100 min, X-rays before LIII edge
B: UV (254 nm) for 30’.

Effects of the two processes on the balance RE3+/ RE2+

RE valence states

JIANRONG QIU[a]†*, M. KAWASAKI[b], K. TANAKA[b], Y. SHIMIZUGAWA[c] and K. HIRAO

J. Phys. Chem Solids Vol 59, No. 9, pp. 1521–1525, 1998



Examples from crystals: Eu-doped SrAl2O4

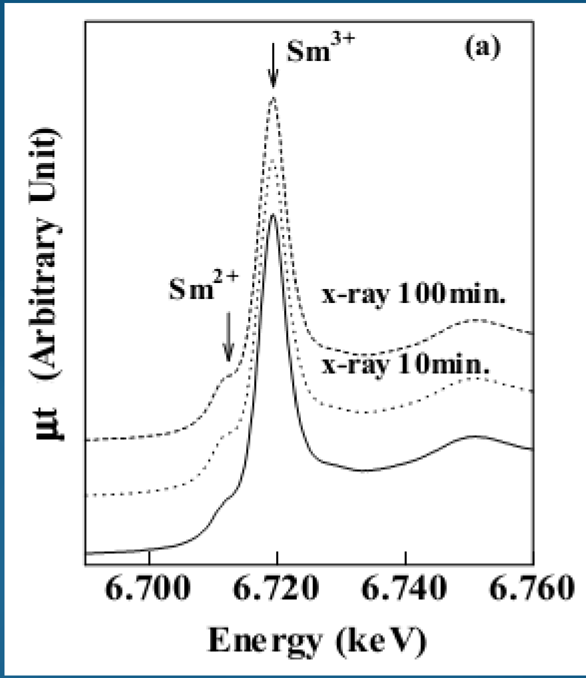
The 2+ and 3+ valence state have White Lines at different energy values.

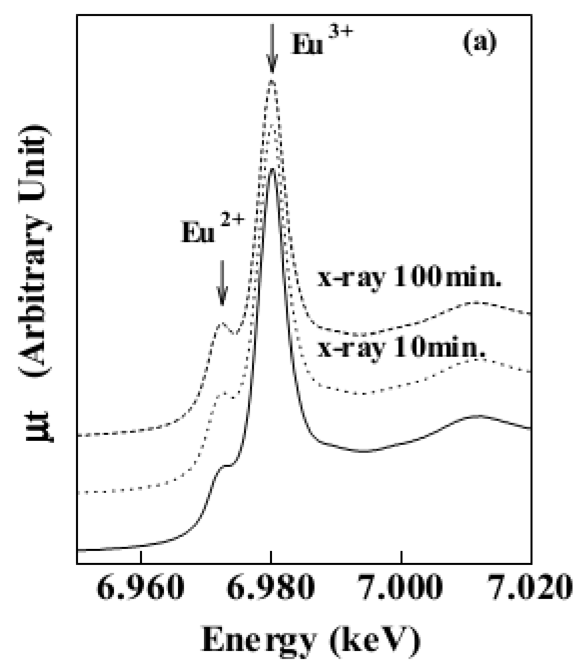
Process A: X-ray Irradiation

X-ray induced reduction of rare earth ion doped in Na_2O-Al_2O_3-B_2O_3 glasses

Yutaka Shimizugawa,[a*] Norimasa Umesaki,[a] Katsumi Hanada,[b] Ichiro Sakai[b] and Jianrong Qiu[c]

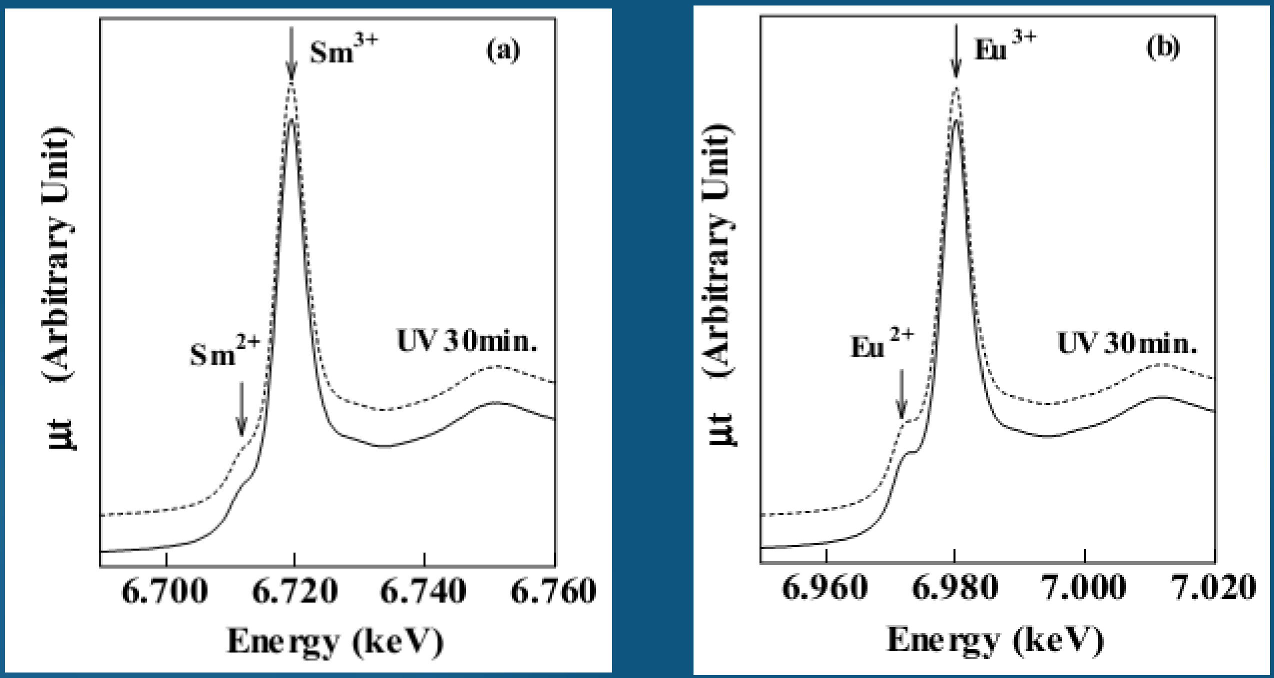
J. Synchrotron Rad. (2001). 8, 797–799





Clear increase of a peak before the white line for increasing irradiation times.
Peak due to RE2+ state.

Process B: UV irradiation



No change of the spectrum upon UV irradiation.

Eu-doped borate glasses

J. Synchrotron Rad. (1999). 6, 624–626

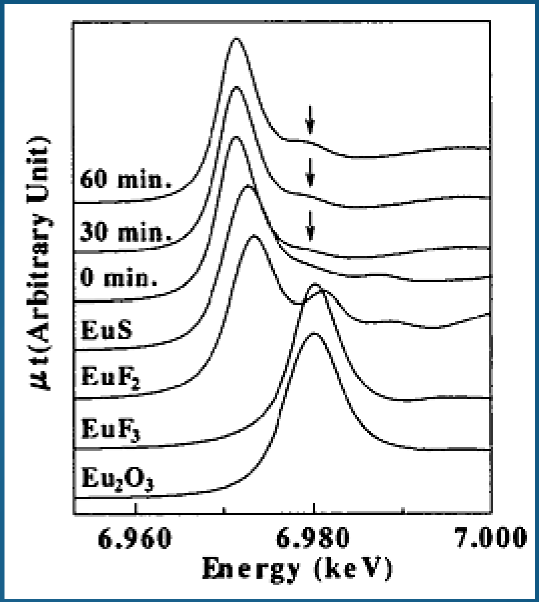
Local structure around europium ions doped in borate glasses

Yutaka Shimizugawa,[a*] Norimasa Umesaki,[a] Jianrong Qiu[b] and Kazuyuki Hirao[bc]

Composition
(70-90) B_2O_3, (10-30) Na_2O, 10 Eu_2O_3

Irradiation
X-rays (6941 eV, before L3 edge) 30’ and 60 ‘

Eu-doped borate glasses



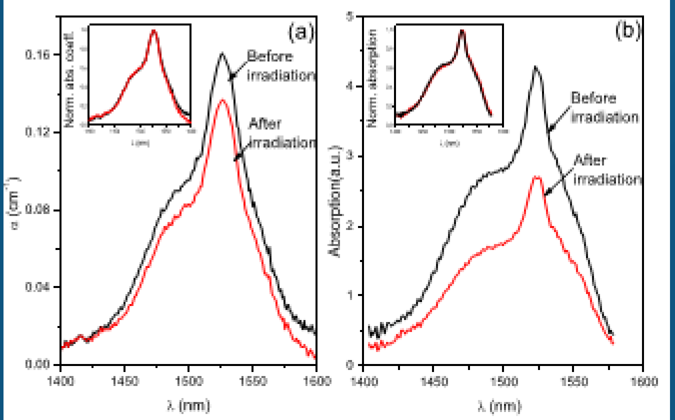
Slight growth of Eu3+ species upon X-ray irradiation .

Er:CaF2

CaF2 is known as a host for 2+ RE
RE takes the place of a Ca ion and coordinates with a charge compensating defect
Preliminary study for the investigation of highly damaged Er-doped silica fibres.

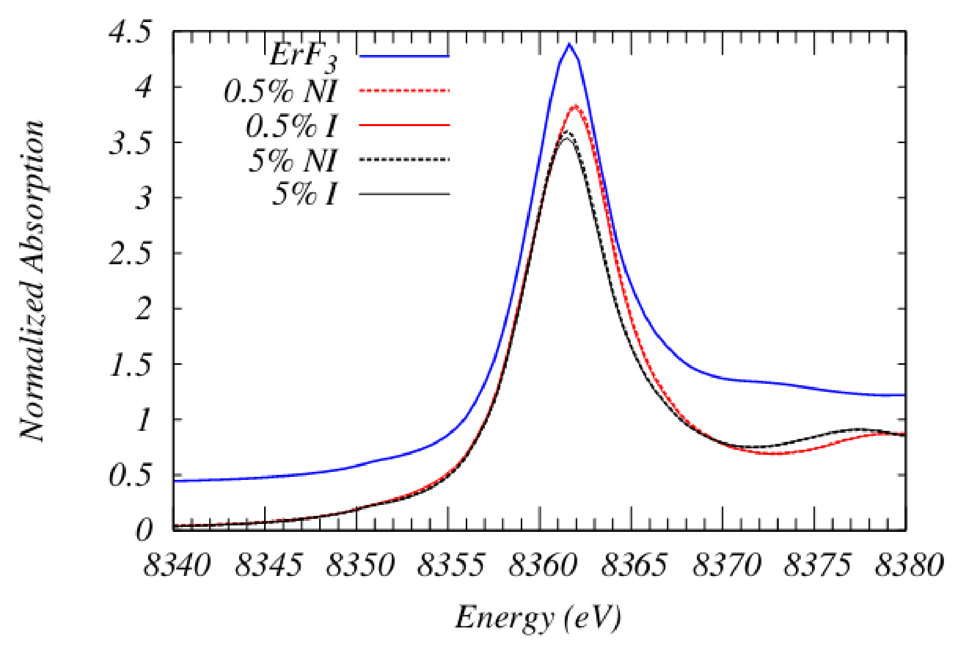
Irradiation: low energy X-rays, (RX 45 kV - 5 min., 1,83 kGy)

OPTICS LETTERS / Vol. 39, No. 21 / November 1, 2014



Yasmine Mebrouk,* Franck Mady, Mourad Benabdesselam, Jean-Bernard Duchez, and Wilfried Blanc

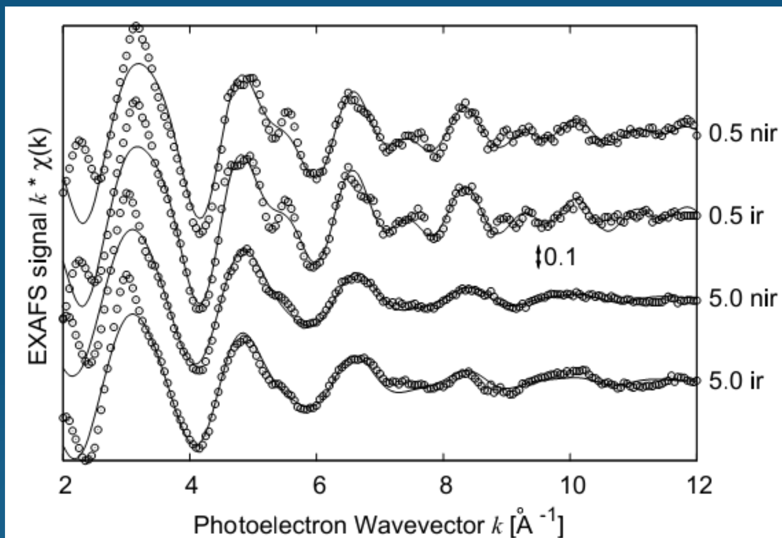
XANES data

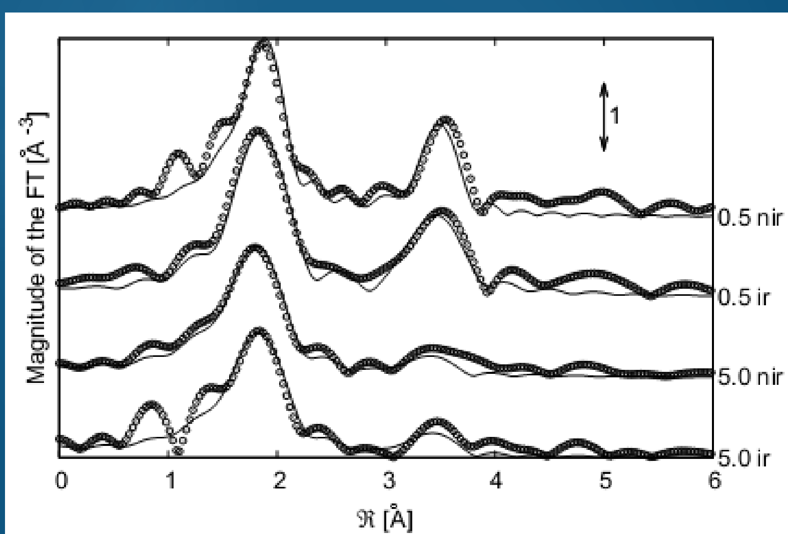


No difference between I and NI samples.

Considerable difference between high and low conc samples.

EXAFS and DFT





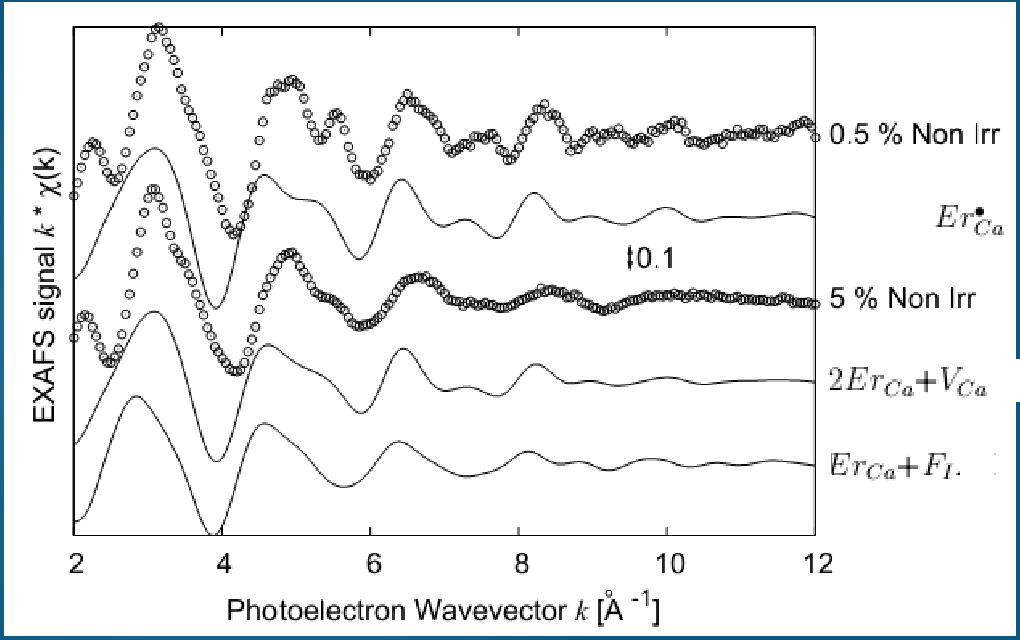
DFT, Structural simulation, supercell 81 atoms

Sample	F shell			Ca Shell		
	N	R (Å)	σ^2(Å^2)	N	R (Å)	σ^2(Å^2)
CaF_2	8	2.381	-	12	3.888	-
0.5 NI	8	2.28(2)	0.002(1)	12	3.89(2)	0.006 (2)
0.5 I	8	2.28(2)	0.002(1)	12	3.89(3)	0.006 (2)
5.0 NI	8	2.27(2)	0.004(2)	12	3.89(5)	0.03 (2)
5.0 I	8	2.29(2)	0.005(2)	12	3.89(5)	0.03 (1)
$Er^{\bullet}_{Ca}$	8	2.282	-	12	3.92	-
$2Er_{Ca}+V_{Ca}$	2	2.19	-	4	3.87	-
	6	2.31	-	7	3.93	-
$2Er_{Ca}+F_I$	4	2.28	-	4	3.72	-
	5	2.38	-	4	3.94	-
			-	4	4.02	-

Perspectives

Molecular Dynamics

Simulation of XAS spectra via MD-DFT.
300K, NVT, step 2fs, total 8.5 ps
EXAFS: average over 1ps
Easy comparison between different test sites



Strong similarity with simulated spectra of $Er^{\bullet}_{Ca}$ or $2Er_{Ca}+V_{Ca}$.

Poor agreement with $Er_{Ca}+F_{I}$

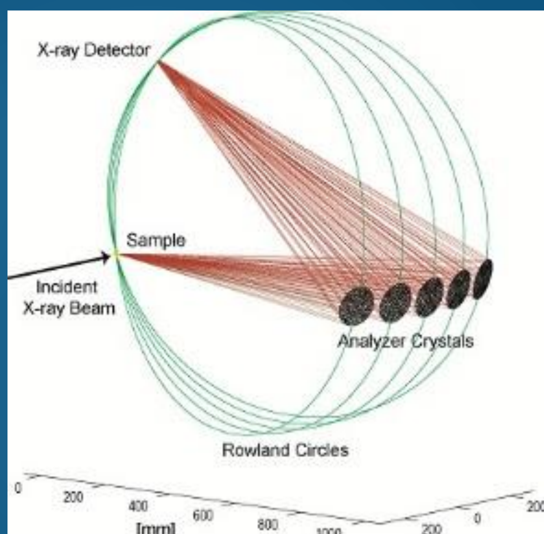
VOLUME 67, NUMBER 20 PHYSICAL REVIEW LETTERS 11 NOVEMBER 1991

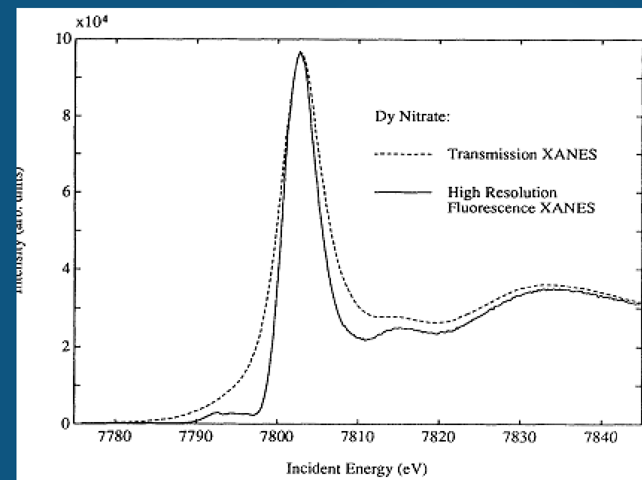
Elimination of the Inner-Shell Lifetime Broadening in X-Ray-Absorption Spectroscopy

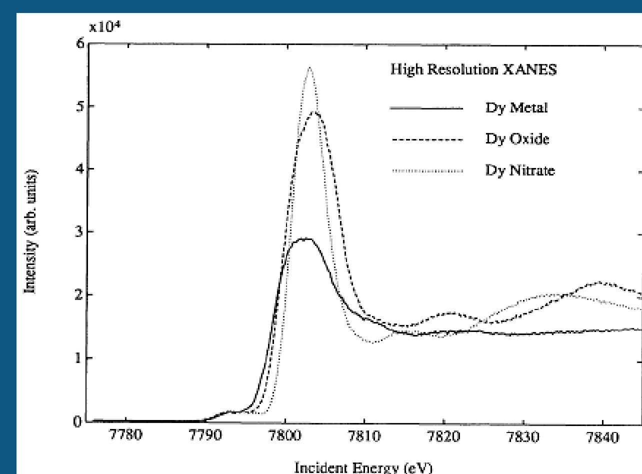
K. Hämäläinen,[a] D. P. Siddons, J. B. Hastings, and L. E. Berman

By collecting fluorescence with an energy resolution lower than the core-hole width spectra with finer details can be collected.

http://www.pieter-glatzel.de/XASXES.html







Semicond. Sci. Technol. 29 (2014) 023002 (19pp) doi:10.1088/0268-1242/29/2/023002

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Invited Review

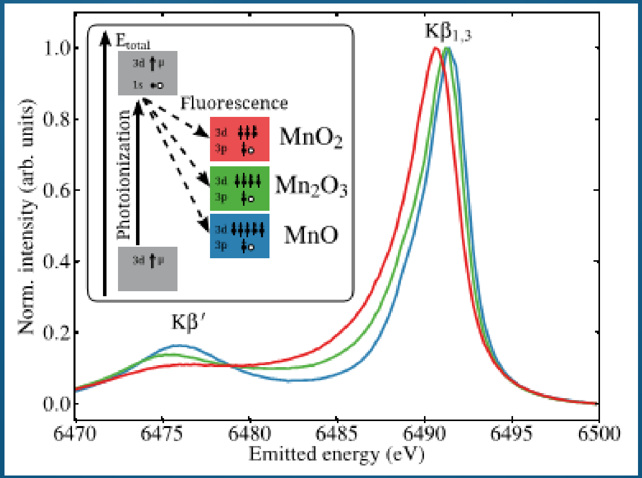
Hard x-ray emission spectroscopy: a powerful tool for the characterization of magnetic semiconductors

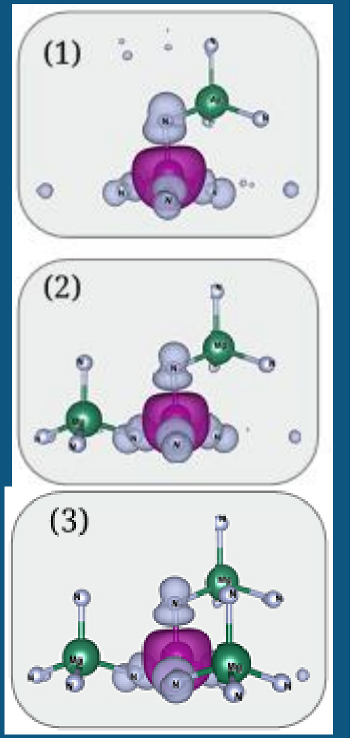
M Rovezzi and P Glatzel

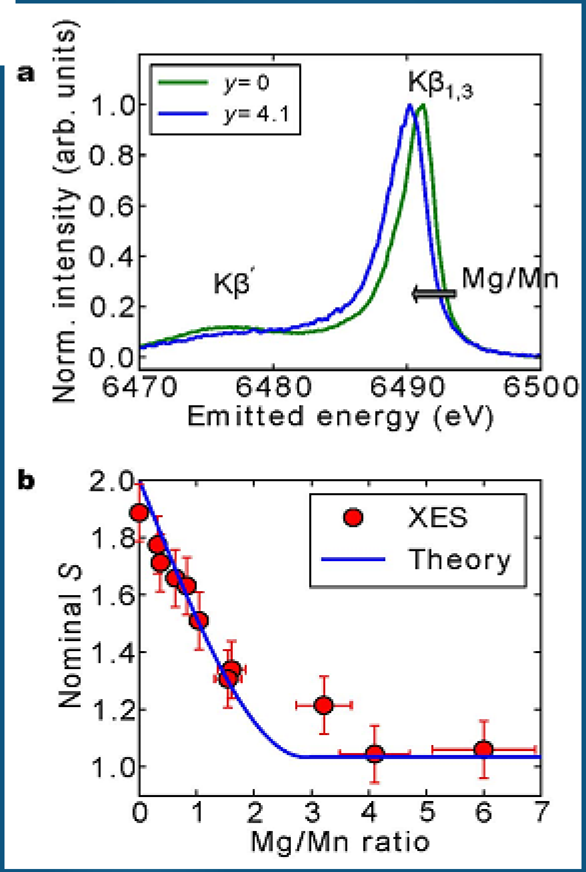
European Synchrotron Radiation Facility, 6 rue Jules Horowitz, F-38043 Grenoble, France

(Mn, Mg):GaN

Analysis of the emission lines: info on the spin state







Conclusion

- XAS useful complement for other techniques (RAMAN, XRD, Mossbauer, …)
- Direct determination of local structural parameters
- Determination of valence states
- Increased capability of ab-initio simulations of structures and XAS spectra
- Novel experimental techniques
  - RIXS, HERFD