X-ray Absorption Spectroscopy in the study of irradiated glasses

FRANCESCO D’ACAPITO
CNR-IOM-OGG C/O ESRF

F. d’Acapito, dacapito@esrf.fr
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 symmetry
- Valence state

Bad news:
- U need a synchrotron

F. d'Acapito, dacapito@esrf.fr
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

F. d’Acapito, dacapito@esrf.fr
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 $R$.

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

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

Reduction of the second neighbors
Shrinking of the coordination length

F. d’Acapito, dacapito@esrf.fr
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 SiO4 tetrahedral neighboring Zr
  - Shrinking of the Zr-Si coordination distances
- Formation of Zr oxide is ruled out.
Structure of $\beta$-irradiated glasses studied by X-ray absorption and Raman spectroscopies

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


Bulk calcium-alumino-silicate glasses
Irradiation 2.5 MeV electrons $3.8 \times 10^9$ Gy

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

**XAS:** Al K edge

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<thead>
<tr>
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<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>CaO</th>
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<td>CA68.08</td>
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</tbody>
</table>

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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.
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

F. d’Acapito, dacapito@esrf.fr
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
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

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

Blind to oxidized forms of Ag.

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

F. d’Acapito, dacapito@esrf.fr
As-exchanged glass

Ag in glass forms a single shell with O

$\text{RAg-O} = 2.28-2.20$ depending on the
preparation conditions.
No Ag-Ag shell
He irradiation

Formation of met-Ag (about 70±10 %)

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

Battaglin et al. NIM B 200 (2003), 185.
He irr. + laser treatment

Reduction of the metal peak in the FT

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

Battaglin et al. NIM B 200 (2003), 185.
H2 treatment

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

Battaglin et al. NIM B 200 (2003), 185.
He treatment + laser

Formation of Ag metal

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

Clusters not seen by diffraction

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

Scheme of the effects of the various treatments
2 step process
Ion irradiation of Ag-exchanged glasses, 600 MeV Au @ $10^{11}$-$10^{13}$ at/cm$^2$
Annealing reducing atmosphere 30', 340 C, Ar-H$2$

Small cluster, < 20nm
RE-doped Al-B glasses

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

Examples from crystals: Eu-doped SrAl2O4

The 2+ and 3+ valence state have White Lines at different energy values.
Process A: X-ray Irradiation

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

F. d’Acapito, dacapito@esrf.fr
Process B: UV irradiation

No change of the spectrum upon UV irradiation.

F. d’Acapito, dacapito@esrf.fr
Eu-doped borate glasses

**Composition**
(70-90) B2O3, (10-30) Na2O, 10 Eu2O3

**Irradiation**
X-rays (6941 eV, before L3 edge) 30' and 60'

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*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
Eu-doped borate glasses

Slight growth of Eu$^{3+}$ 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)

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

F. d’Acapito, dacapito@esrf.fr
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

<table>
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<tr>
<th>Sample</th>
<th>F shell</th>
<th>Ca Shell</th>
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<tr>
<td></td>
<td>N</td>
<td>R (Å)</td>
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<td>CaF_2</td>
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<tr>
<td>0.5 NI</td>
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<td>2.28(2)</td>
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<tr>
<td>0.5 I</td>
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<td>2.28(2)</td>
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<tr>
<td>5.0 NI</td>
<td>8</td>
<td>2.27(2)</td>
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<td>2.29(2)</td>
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<tr>
<td>Er^{Ca}</td>
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</tbody>
</table>

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Perspectives
Molecular Dynamics

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

Strong similarity with simulated spectra of $\text{Er}_2\text{Ca}$.
Poor agreement with $\text{Er}_2\text{Ca} + \text{F}_1$.

F. d’Acapito, dacapito@esrf.fr
By collecting fluorescence with an energy resolution lower than the core-hole width spectra with finer details can be collected.
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-38013 Grenoble, France

Analysis of the emission lines: info on the spin state

(Mn, Mg):GaN
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