Étude structurale de matériaux sous forme de couches minces par diffraction des rayons X en incidence rasante

G. Baldinozzi, D. Simeone
SPMS, LRC Carmen, CNRS-CEA-CentraleSupélec
J-F Bérar
Néel, Grenoble

Collaborations et examples d’applications:
S. Bouffard (Cimap, Caen), P. Lecoeur (IEF, Orsay)
C. Laberty-Robert, C. Sanchez (LCMC, Jussieu)

ANR-06-BLAN-0292, C’nano IDF Solnac 2009,
Triangle de la Physique Instrumat 2011-074T, ANR-10-LABX-0039
Outline

- Diffraction basics – Glancing angle (incidence) XRD
- Rietveld method and GA-XRD
- Structures & microstructures
- Examples
- Conclusion
Conventional X-ray diffraction

+ Reliable information on
  - the preferred orientation of crystallites
  - the crystallite size and lattice strain (in one direction)

  - No information on the residual stress (constant direction of the diffraction vector)

  - Low scattering from the layer (large penetration depth)
Penetration depth of X-rays


\[ n = \sqrt{1 + \chi} \approx 1 + \frac{\chi}{2} = 1 - \frac{r_e \lambda^2}{2\pi} \rho \]

\[ n \approx 1 - \frac{r_e \lambda^2}{2\pi} \rho \left( f_0 + f' - if'' \right) \]

\[ n \approx 1 - \delta + i\beta \leq 1 \]

Example: Gold (CuKα)

\[ \delta = 4.2558 \times 10^{-5} \]

\[ \beta = 4.5875 \times 10^{-6} \]

\[ n_v \cos \theta = n_j \cos \theta_j \quad ; \quad n_j = \cos \theta_c \]

\[ 1 - \frac{r_e \lambda^2}{2\pi} \rho \equiv 1 - \frac{\theta^2}{2} \quad ; \quad \theta_c = \sqrt{\frac{r_e \lambda^2}{\pi} \rho} \]
Snell, Fresnel laws for X-rays (GAXRD)

\[ \psi_j = a_j e^{i \mathbf{k}_j \cdot \mathbf{r}}; \quad j = I, T \text{ or } R \]
\[ k = |\mathbf{k}_I| = |\mathbf{k}_R| = \frac{1}{n} |\mathbf{k}_T| \]

\[ C^1 \begin{cases} 
  a_T = a_I + a_R \\
  a_T k_T = a_I k_I + a_R k_R 
\end{cases} \]

\[ n \cos \alpha' = \cos \alpha \]
\[ (a_I + a_R) n \sin \alpha' = (a_I - a_R) \sin \alpha \]

\[ n = 1 - \delta + i \beta \equiv 1 - \frac{\alpha_c^2}{2} + i \beta; \quad \alpha_c^2 \equiv \left( \frac{4\pi}{k^2} \right) \rho, \quad \beta = \frac{\mu}{2k} \]

\[ \left( 1 - \frac{\alpha_c^2}{2} + i \beta \right) \left( 1 - \frac{\alpha'^2}{2} \right) = \left( 1 - \frac{a^2}{2} \right) \rightarrow \alpha'^2 = \alpha^2 - \alpha_c^2 + 2i \beta \]

Snell’s Law

\[ \left( 1 + \frac{a_R}{a_I} \right) \alpha' = \left( 1 - \frac{a_R}{a_I} \right) \alpha \rightarrow R \equiv \frac{a_R}{a_I} = \frac{\alpha - \alpha'}{\alpha + \alpha'} \]

Fresnel’s Law
Glancing angle X-ray diffraction (GAXRD)

\[ t \cdot \frac{dI}{dz} = I_0 \cdot \frac{1}{e} \]

\[ x_e = \frac{\sin \theta_i \cdot \sin \theta_o}{\mu (\sin \theta_i + \sin \theta_o)} \]

Penetration depth (\(\mu\)m)

Gold, CuK\(\alpha\),
\(\mu \approx 4000 \text{ cm}^{-1}\)
Parallel, monochromatic X-ray beam impinges on a sample surface at a fixed angle of incidence ($\alpha_1$) and diffraction profile is recorded by detector-only scan.

When the angle of incidence ($\alpha_1$) of X-ray beam decreases, since the refractive index in the sample is less than unity, total external reflection of X-rays occurs below the critical angle of incidence $\alpha_C$. The diffracted and scattered signals at the angle $2\theta$ arise mainly from a limited depth below the surface of the specimen.
Analyzer Crystal

Polycrystalline Thin Film

Sample rotation, $\phi$

Diffraction angle, $2\theta$

Sample Normal

Sample inclination, $\psi$

Diffraction vector

Angle of incidence $\alpha$

Goebel mirror

X-ray source

IRRSUD@Ganil
Snell’s law for XRD

$1 + R(\alpha) = T(\alpha) \rightarrow T(\alpha) = \frac{2\alpha}{\alpha + \alpha'}$

$T(\alpha) = \frac{2\alpha / \alpha_c}{\alpha / \alpha_c + \sqrt{\left(\frac{\alpha^2}{\alpha_c^2} - 1\right)}}$ for $\alpha > \alpha_c$

$T(\alpha) = \frac{2\alpha}{\alpha_c}$ for $\alpha \leq \alpha_c$

- Quantitative phase analysis
- Symmetry
- Crystal structure (Rietveld)
- Crystallite size and strain determination

Isothermal annealing

Microstructure vs. depth
Reflections shape and breadth …

- **Instrumental broadening**
- **Specimen-related broadening**
  - Crystallite finite size
  - Microstrain
    - Non-uniform Lattice Distortions
    - Faults
    - Dislocations
    - Antiphase domain boundaries
    - Surface Relaxation
    - …

- The peak profile is a convolution of the effects from all of these contributions
Typical sources of instrumental broadening

- **X-ray Source Profile**
  - Natural emission linewdths of Kα₁ and Kα₂ lines
  - Size of the X-ray source

- **Goniometer Optics**
  - Divergence and Receiving Slit widths
  - Imperfect focusing
  - Beam size
  - Penetration into the sample
  - ...
Specimen broadening

**Crystallite size**
- Fourier transformation of finite objects (with limited size)
- Constant line broadening (with increasing diffraction vector)

**Lattice strain**
- Local changes in the d-spacing
- Line broadening increases with increasing $q$ (a result of the Bragg equation in the differential form)
Empirical profile matching is sometimes difficult:
- overlapping peaks
- a mixture of nanocrystalline phases
- a mixture of nanocrystalline and microcrystalline phases

Rietveld profile analysis (more information about the sample)
- how much of each phase is present in a mixture
- lattice parameter refinement
  - nanophase materials often have different lattice parameters from their bulk counterparts
- atomic structure, site occupancy, thermal displacement parameters, …
- better compensation of profile-related errors
Rietveld analysis of multi-phase thin films

- Accurate retrieval of “domain” size and microstrain once instrumental broadening is corrected for
- Increased sensitivity to layers immediately below the surface
- In-situ measurements (irradiation and/or annealing phases)

Fe$^{+2}$Ti$_2^{+4}$O$_5$
a.k.a. Fe$_{0.3}$Ti$_{0.7}$O$_{1.67}$

J. Mat. Chem A 2 6567-6577 (2014)
Measuring structure and strain in a thin layer: thin films & the problem of ion irradiation

- The GAXRD setup
  - Accurate retrieval of “domain” size and microstrain once instrumental broadening is corrected for
  - Increased sensitivity to layers immediately below the surface
  - In-situ measurements (irradiation and/or annealing phases)

Typical GAXRD pattern obtained on a fluorite phase
## Structural evolution of spinels under irradiation

### Behavior of spinel under irradiation: Modification of Diffraction patterns

<table>
<thead>
<tr>
<th></th>
<th>MgAl$_2$O$_4$</th>
<th>MgCr$_2$O$_4$</th>
<th>ZnAl$_2$O$_4$</th>
</tr>
</thead>
</table>
| **High E. ions @ RT** | Vanishing of odd Bragg reflexions  
D. Simeone, J. Nucl. Mat. 2002  
K Yasuda, MINB 2006, JNM 2007... | Vanishing of odd Bragg reflexions  
G. Baldinozzi, Nucl. Inst Meth B. 2007 | Non vanishing of odd Bragg reflexions  
D. Simeone, J. Nucl. Mat. 2002 |
| **Low E. ions @ 140 K** | Vanishing of odd Bragg reflexions  
D. Gosset, J. Eur Ceram Soc, 2005 | Non vanishing of odd Bragg reflexions  
D. Gosset, J. Eur Ceram Soc, 2005 |
| **Low E. ions @ RT** | Non vanishing of odd Bragg reflexions  
D. Gosset, J. Eur Ceram Soc, 2005 | Non vanishing of odd Bragg reflexions  
G. Baldinozzi, Nucl. Inst Meth B. 2005 |
Spinel irradiation at room temperature

Simulation of neutron irradiation by low energy ions (cascades) and of fission products by swift heavy ions

GAXRD

GAX-Ray diffraction:
Asymmetric reflection setup (fixed, grazing impinging beam)

MgCr$_2$O$_4$: Au @ 4 MeV
MgCr$_2$O$_4$: thermal annealing after irradiation

- Temperature restores the normal structure.
- The annealing of the extended defects increases the size of the coherent diffracting domains.
Electron density from X-ray diffraction

Fourier syntheses derived from the observed diffracted intensities indexed in the Fd3m space group
How to reconcile LRO & SRO?

- Ion irradiation produces changes in the structures of spinels:
  - At the atomic scale:
    - Cations are interchanged as in the thermal picture
    - The local structure consists of octahedra and tetrahedra
    - The “true” space group is unchanged
  - The existence of extended defects produces
    - A broadening of (000) peaks
    - An apparent symmetry change to the Fm3m \((a' = a/2)\)

- Antiphase domain boundaries?
  - Formed during the ordering of a material that goes through an order-disorder transformation
  - The fundamental peaks are not affected
  - The superstructure peaks are broadened
    - the broadening of superstructure peaks varies with \(hkl\)
Mesoporous ceria layers (coarsening)

μ-SOFC

Cermet: Ni/Ce₀.₉Gd₀.₁O₂₋ₓ porous

\[ \text{H}_2 + \text{O}^{2-} \rightarrow \text{H}_2\text{O} + 2 \text{e}^- \]

Ceramic: Ce₀.₉Gd₀.₁O₂₋ₓ dense

\[ \text{O}_2 + 4 \text{e}^- \rightarrow 2\text{O}^{2-} \]

Total Thickness ≤ 1 μm

Composite: LSCF/Ce₀.₉Gd₀.₁O₂₋ₓ porous

Fuel

Anode ≈ 200 nm

Electrolyte ≈ 600 nm

Cathode ≈ 200 nm

Air

NiO/CGO

CGO

LSCF/CGO

200 nm

600 nm

200 nm
Finite crystallite size and lattice strain in nanocrystalline ceria

Strain

Parabolic growth mechanism

\[ \frac{dR}{dt} = \frac{k(T)}{R} \]

\[ k(T) = \frac{k_0}{T} \exp \left( -\frac{Q_m}{k_B T} \right) \]

\[ \ln[T(d^2-d_0^2)] \]

\[ (k_B T)^{-1} (\text{eV}^{-1}) \]

\[ d_0 = 1.7 \text{ nm} \]

Monitoring the particle contacts in mesoporous ceria as a function of the annealing $T$
Inhomogeneous strain in films

But the regular $\psi$-scan method unfortunately probes a volume that changes as a function of $\psi$, averaging out the strain in the film, and preventing a mapping of the local strain.
Measuring the local strain in glancing geometry

\[ \psi = \alpha - \theta(hkl) \]

\[ \tau = \frac{\sin \alpha \sin (2\theta - \alpha)}{\mu [\sin \alpha + \sin (2\theta - \alpha)]} \]

\[ \langle \epsilon_{\varphi\psi} \rangle = \frac{\int_0^t \epsilon_{\varphi\psi}(z) \exp \left( -\frac{z}{\tau} \right) dz}{\int_0^t \exp \left( -\frac{z}{\tau} \right) dz} \]

\[ \langle \epsilon_{\varphi\psi} \rangle = \frac{1}{\tau} \int_0^\infty \epsilon_{\varphi\psi}(z) \exp \left( -\frac{z}{\tau} \right) dz = \frac{1}{\tau} \mathcal{L} \left( \epsilon_{\varphi\psi}(z), \frac{1}{\tau} \right) \]

\[ \epsilon_{\varphi\psi}(z) = \mathcal{L}^{-1} \left( \tau \langle \epsilon_{\varphi\psi} \rangle, z \right) \]

\( \psi \) angle should be re-encoded in glancing geometry

The depth \( \tau \) probed by X-rays is a now a function of the impinging angle

The average strain in a film of thickness \( t \) is still averaged by the way we measure (Fredholm’s integral)

If \( t \) is larger than the probed depth \( \tau \) the Fredholm’s integral becomes a Laplace transform that can be inverted, thus providing the value of the local strain at each value \( z \) in the film
Glancing geometry: asymmetric impinging beam on a W film

\[
e_{zz} = (a_3 \tau^3 + a_2 \tau^2 + a_1 \tau + a_0)^{-1}
\]

\[a_0 = 31.5573 \quad a_1 = 475.271 \quad a_2 = 207.828 \quad a_3 = 1\]
Conclusion

- GAXRD & materials modelling - global approach to understand complex systems:
  - Elementary mechanisms
  - Chemistry, crystal structure
  - (Meso) Microstructures

- Understand the property changes
- Point out the key issues to design new/better materials for advanced technologies