EDX Microanalysis in TEM

a) Review (brush-up) generation and detection of X-rays, SDD detectors

b) Quantification
   EDX in SEM, Interaction volume
   ZAF matrix corrections
   EDX in TEM (Cliff-Lorimer, thin film)

c) Examples

X-ray generation:
Inelastic scattering of electrons at atoms
\[ E_{\text{electron\_in}} > E_{\text{electron\_out}} \]

- Continuum X-ray production (Bremsstrahlung, Synchrotron)
- Characteristic X-ray emission
- Inner shell ionization

SE, BSE, EELS
Efficiency of X-ray generation

Relative efficiency of X-ray and Auger emission vs. atomic number for K lines

Ionization cross-section vs. overvoltage $U = E_o/E_{\text{edge}}$
(electron in $\rightarrow$ X-ray out)

Light elements
Auger Spectroscopy

Heavy elements
EDS

Light element atoms return to fundamental state mainly by Auger emission. For that reason, their K-lines are weak. In addition their low energy makes them easily absorbed.

To ionize the incident electron MUST have an energy larger than the core shell level $U > 1$. To be efficient, it should have about twice the edge energy $U > 2$. 

Cu-K 8.1kV, HT
15kV
$U = 15/8.1 = 1.85$
Modern silicon drift (SDD) detector: no LN cooling required

Right: Si(Li) detector
Cooled down to liquid nitrogen (LN) temperature

X-Ray energy conversion to electrical charges:
3.8eV / electron-hole pair in average
Electronic noise + imperfect charge collection:
130 eV resolution / Mn Ka line

- Detector acts like a diode: at room temperature, the leak current for 1000V would be too high!
- The FET produces less noise if cooled!
- Li migration at room temperature!
- ->Detector cooling by LN
**Detection and artifacts**

Take care when looking for "trace" elements (low concentrations). Don't confuse small peaks with escape peaks!

EDX spectrum in a SEM of (K,Na)NbO$_3$

Electron beam: 10keV

Number of x-rays

```
<table>
<thead>
<tr>
<th>Number</th>
<th>Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Channel 1</td>
<td>10keV</td>
</tr>
<tr>
<td>Channel 2</td>
<td>9.955 keV</td>
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<tr>
<td>Channel 3</td>
<td>9.856 keV</td>
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<tr>
<td>Channel 4</td>
<td>9.757 keV</td>
</tr>
<tr>
<td>Channel 5</td>
<td>9.658 keV</td>
</tr>
</tbody>
</table>
```

“Channels” = Energy

Duane-Hunt limit

Characteristic X-ray peaks

Continuum, Bremsstrahlung

10keV
c) Quantification

First approach:
compare X-ray intensity with a 
standard (sample with known 
concentration, same beam current of 
the electron beam)

c_i: wt concentration of element i
I_i: X-ray intensity of char. Line 
k_i: concentration ratio

\[
\frac{c_i}{c_{i,\text{std}}} = \frac{I_i}{I_{i,\text{std}}} = k_i
\]

Yes, but…..

Quantification

Correction matrix

\[
[Z \times A \times F] \frac{C_i}{C_{i,\text{std}}} = \frac{I_i}{I_{i,\text{std}}} = k_i
\]

- "Z" describe how the electron beam 
  penetrates in the sample (Z dependant 
  and density dependant) and loose energy
- "A" takes in account the absorption of the 
  X-rays photons along the path to sample 
  surface
- "F" adds some photons when (secondary) 
  fluorescence occurs

When the going gets tough…..
Flow chart of quantification

Measure the intensities and calculate the concentrations without ZAF corrections

Calculate the ZAF corrections and the density of the sample

Calculate the concentrations with the corrections

Is the difference between the new and the old concentrations smaller than the calculation error?

no

Yes!

stop

Correction methods for EDX in SEM

ZAF (purely theoretical)
PROZA Phi-Rho-Z
PaP (Pouchou and Pichoir)
XPP (extended Puchou/Pichoir)

- with standards (same HT, current, detector settings)
- Standardless: theoretical calculation of $I_{\text{std}}$
- Standardless optimized: « hidden » standards, user defined peak profiles
Small interaction volume -> high spatial resolution for EDX Analysis!

EDS in TEM

Thin samples -> correction factors weak (A and F can be neglected)

Very weak beam broadening -> high spatial resolution ~ beam diameter (~nm)

High energy: artifacts!
\[
\frac{C_i}{C_{(i)}} = K \frac{I_i}{I_{(i)}},
\]

\(K\) is the sensitivity factor (not constant), determined (inversely) by:
- \(Z\) the atomic number
- \(A\) absorption of X-rays within the specimen
- \(F\) fluorescence of X-rays within the specimen

The correction factor for bulk analysis is referred to as ZAF correction.

- HOWEVER...for thin samples \(A\) and \(F\) are very small and can be ignored
  - Sensitivity factor proportional only to \(Z\)!

- In 1975 Cliff and Lorimer showed that a standard is not needed if intensities for two elements are gathered simultaneously and compared...

*Journal of Microscopy*
Volume 103, Issue 2, March 1975, Pages 203-207
The quantitative analysis of thin specimens(Article)
Cliff, G., Lorimer, G.W.
Department of Metallurgy, Faculty of Science, University of Manchester, Manchester, M13 9PL, United Kingdom
The weight percent of each element analysed can be related to the measured intensities.

For a binary system this gives:

\[
\frac{C_A}{C_B} = k_{AB} \frac{I_A}{I_B} \quad \text{Cliff-Lorimer equation}
\]

\[
C_A + C_B = 100\%
\]

The convention is to use wt%.

\(k_{AB}\) is another sensitivity factor, called the Cliff-Lorimer factor.

Ternary systems

\[
\frac{C_A}{C_B} = k_{AB} \frac{I_A}{I_B}
\]

\[
\frac{C_B}{C_C} = k_{BC} \frac{I_B}{I_C}
\]

\[
C_A + C_B + C_C = 100\%
\]

\[
k_{AB} = \frac{k_{AD}}{k_{BD}} \quad k_{BC} = \frac{k_{BD}}{k_{CD}}
\]

\(k_{AB}\) can be calculated from \(k_{AD}\) and \(k_{BD}\).
If the specimen is thin enough to assume no absorption and no fluorescence then $k_{AB}$ is only related to the atomic number, $Z$.

This is often true in TEM/XEDS

For bulk specimens ZAF correction is necessary

• $k$-factors can be determined experimentally (using standards) or calculated from first principles
• Remember this is not a constant, but a sensitivity factor that depends on the detector, microscope, analysis conditions...
• We only need to determine $k_{AB}$ in relation to one element. Then all other $k$-values can be calculated:

$$k_{AB} = \frac{k_{AC}}{k_{BC}}$$

• Experimental $k$-values can be obtained from single-phase compounds

• Standard spectra must be recorded for each instrument setup

STEM point analysis

PbMg$_{1/3}$Nb$_{2/3}$O$_3$ (bulk)

Processing option: Oxygen by stoichiometry (Normalised)

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>Mg</th>
<th>Si</th>
<th>Nb</th>
<th>Pb</th>
<th>O</th>
<th>Total</th>
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<tr>
<td>Spectrum 1</td>
<td>30.02</td>
<td>13.32</td>
<td>56.66</td>
<td></td>
<td>100.00</td>
<td></td>
</tr>
<tr>
<td>Spectrum 2</td>
<td>19.15</td>
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<td>11.72</td>
<td>57.06</td>
<td>100.00</td>
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<tr>
<td>Spectrum 3</td>
<td>6.03</td>
<td>12.49</td>
<td>22.13</td>
<td>59.37</td>
<td>100.00</td>
<td></td>
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<td>Spectrum 4</td>
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<td>12.39</td>
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<td>59.29</td>
<td>100.00</td>
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</tr>
<tr>
<td>Spectrum 5</td>
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<td>12.48</td>
<td>22.52</td>
<td>59.36</td>
<td>100.00</td>
<td></td>
</tr>
<tr>
<td>Spectrum 6</td>
<td>5.98</td>
<td>13.66</td>
<td>20.11</td>
<td>60.25</td>
<td>100.00</td>
<td></td>
</tr>
<tr>
<td>Spectrum 7</td>
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<td>12.45</td>
<td>22.66</td>
<td>59.34</td>
<td>100.00</td>
<td></td>
</tr>
<tr>
<td>Spectrum 8</td>
<td>5.49</td>
<td>12.96</td>
<td>21.84</td>
<td>59.72</td>
<td>100.00</td>
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</tr>
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<td>Spectrum 9</td>
<td>5.63</td>
<td>12.19</td>
<td>23.04</td>
<td>59.14</td>
<td>100.00</td>
<td></td>
</tr>
</tbody>
</table>

Max. 30.02 13.32 13.66 23.04 60.25
Min. 5.49 7.96 4.11 11.72 56.66

All results in Atomic Percent
Pb(Zr,Ti)O$_3$ Thick films for MEMS

SEM image of a wet etched (in HF/HCl solution) side-wall of 2 µm PZT film. All the 8 interfaces corresponding to the intermediate crystallization steps became visible indicating a compositional gradient (preferential etching) across the PZT layers.

CTEM dark field image

STEM dark field

TEM dark field images. Strong diffraction contrast

STEM dark field images. The ramps in the gray level indicate changes of density or chemical composition (~atomic number).
EDX Line-scan

EDX point analysis

Quantitative EDX Analysis of the points indicated in the image
Processing options: Oxygen by stoichiometry (normalised) results a Percent

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>Zr</th>
<th>Ti</th>
<th>Pb</th>
<th>O</th>
<th>Total</th>
<th>Zr/Ti</th>
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<tbody>
<tr>
<td>1</td>
<td>8.43</td>
<td>12.60</td>
<td>18.45</td>
<td>60.52</td>
<td>100.0</td>
<td>40/60</td>
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<tr>
<td>2</td>
<td>9.92</td>
<td>9.98</td>
<td>20.15</td>
<td>59.95</td>
<td>100.0</td>
<td>49/51</td>
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<tr>
<td>3</td>
<td>12.07</td>
<td>7.61</td>
<td>20.49</td>
<td>59.84</td>
<td>100.0</td>
<td>61/39</td>
</tr>
</tbody>
</table>
STEM Element Mapping
PMN/PT 90/10 (bulk)

Artifacts
how to recognize/minimize them
EDS in TEM

Thin samples -> correction factors weak (A and F can be neglected)

Very weak beam broadening -> high spatial resolution ~ beam diameter (~nm)

High energy: artifacts!

Analytical TEM of multifilament Nb$_3$Sn superconducting wires

Superconducting Nb$_3$Sn cables for high magnetic fields 10-20T:
increase current density, lower cost
Potential Applications:
NMR, Tokamak fusion reactors
Large Hadron Collider (LHC), CERN

Typical cable:
1 x 1.5mm cross-section
121x121 filaments of Nb$_3$Sn in a bronze (Cu/Sn) matrix

Prof. R. Flükiger, V. Abächerli, D. Uglietti, B. Seeber
Dept. Condensed Matter Physics (DPMC), University of Geneva
“Nano”-engineering: controlled creation of “imperfections” of nm scale (coherence length)

Cu and Ti are believed to play an important role at the grain boundaries: “dirty” grain boundaries = pinning

- Is it possible to detect Cu and Ti at the grain boundaries?
- What is the difference between the grain boundaries depending on where the additives are added to the unreacted material?

**Typical problems:**

thinning of heterogeneous specimens: selective thinning

Cross-section, polished mechanically to 30 um, ion milled until perforation

STEM, Dark field: core of filament too thick, preferential etching of bronze matrix
Specimen preparation by focused Ion Beam (FIB): large areas with uniform thickness ideally for EDX Analysis in the TEM (STEM mode).

SEM (FIB)

thickness: 40-50 nm

STEM-DF

Sample #21

EDS, element maps

Spot analysis
Line profile

<table>
<thead>
<tr>
<th>Point</th>
<th>Ti %at</th>
<th>Nb %at</th>
<th>Sn %at</th>
<th>Ta %at</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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<td>79.7</td>
<td>17.1</td>
<td>2.9</td>
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<tr>
<td>2</td>
<td>0.4</td>
<td>79.2</td>
<td>17.8</td>
<td>2.4</td>
</tr>
<tr>
<td>3</td>
<td>0.8</td>
<td>77.8</td>
<td>18.5</td>
<td>2.7</td>
</tr>
<tr>
<td>4</td>
<td>1.8</td>
<td>75.1</td>
<td>20.8</td>
<td>2.1</td>
</tr>
<tr>
<td>5</td>
<td>0.5</td>
<td>76.5</td>
<td>20.9</td>
<td>1.9</td>
</tr>
<tr>
<td>6</td>
<td>0.2</td>
<td>74.3</td>
<td>23.1</td>
<td>2.2</td>
</tr>
<tr>
<td>7</td>
<td>1.6</td>
<td>73.1</td>
<td>23.4</td>
<td>1.7</td>
</tr>
<tr>
<td>8</td>
<td>1.2</td>
<td>73.7</td>
<td>22.8</td>
<td>2.1</td>
</tr>
<tr>
<td>9</td>
<td>0.9</td>
<td>70.4</td>
<td>26.4</td>
<td>2.1</td>
</tr>
</tbody>
</table>

Sample #21

Marco Cantoni
**grain boundaries? Ti/Cu**

EDX line-scan

Cu and Ti at the grain boundaries:
width ~ coherence length (4nm)
possible pinning centers!!

**Sample #21**

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**grain boundary without Ti**

Quantitative Line-scan

Sample #24

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New possibilities due to SDD (silicon drift detector) technology

SDD Si(Li)
Thickness 300-400µm 3mm
Area 30,50,80mm² 30mm²
Det. Interval 4-10µsec. 50-100µsec.
Speed: 100’000cps 10’000cps
Cooling Peltier Liq. N

Analytical TEM
Since 2012 @ CIME
OSIRIS/TALOS/THEMIS

ChemiSTEM™ Technology
A revolution in EDX analytics

TECNAI OSIRIS
5x electrons
10x Det. area
400x400 pixels (5umx5um)  
160'000 spectra  
4msec., (10min.)  
2.5nA  

- 400x400 pixels (500nmx500nm)  
- 160'000 spectra  
- 4msec., (10min.), 2.5nA
Synthetic sapphire: $\text{Al}_2\text{O}_3$

$\text{Al}_2\text{O}_3$ with La (250ppm) in the grain boundaries

Paul Bowen, M. Stuer
EPFL-LPT
QUALITATIVE EDX Mapping:

GREAT!

October 2014: **Titan THEMIS @CIME**
Chemical analysis on atom columns

SrTiO$_3$, Raw
Ti–K
Sr–L
Pb–L

HAADF

Filtered
PbTiO$_3$
Ti–K
Sr–L
Pb–L

2 nm

EPFL Titan THEMIS
STEM HAADF atomic resolution

SrTiO$_3$

Pb(Zr, Ti)O$_3$

5 nm
EPFL Titan THEMIS
STEM HAADF (z-contrast): atomic resolution

Atomic elemental mapping ..!
TEM lamella was prepared by FIB. 30 microns wide area was lifted out next to the chromium plating. Three windows of 7 microns were thinned down to the electron transparency. 2-3 microns thick areas were kept in order to ensure the stability of the sample.

In following slides STEM EDX analysis from each of the thinned windows is presented.

Marker made by FIB to recognize the Cr side of the lamella.

1st window in TEM lamella – 3 microns from Cr plating

BF and DF HAADF images of window 1

STEM EDS mapping revealed the presence of Cr-S rich precipitates that might contain also oxygen. However, oxygen was not taken into account since its proper quantification at very low quantities is difficult.
3 spectra were analyzed in window 1 at higher magnification. 2 precipitates and the matrix.

The precipitates contain chromium and sulfur and their ratio is close to 1:1. The peaks at Kα (5.411) and Kβ (5.947) lines for chromium and Kα (2.307) for sulfur are evident.
The quantification of the spectra from matrix is showing 0.01 at.% of chromium. In order to verify chromium presence, original spectra needs to be magnified. For certain spectra the automatic background deconvolution was slightly adjusted.