**Fluorescence**

Absorption of light at one wavelength and its re-emission in any direction at a longer wavelength

Phosphorescence – relaxation occurs via an intermediate state and so is delayed

The electron knocked out in EDS is not a photoelectron, but in XPS it is...

**EDS/EDX**

**Energy Dispersive X-Ray Spectroscopy**

Penetration depth:

\[ P = R(E_0^{1.68} - E_c^{1.68}) \]

- \( P \) = penetration depth [µm]
- \( R \approx 10^{-2} \) for average \( Z \)
- \( E_0 \) = energy of beam [keV]
- \( E_c \) = energy of x-ray [keV]
**EDS - Phase Analysis**

Pb$_{1.33}$Nb$_{2}$O$_{6.67}$

BSI

**MSE 321 Structural Characterization**

---

**WDS**

Wavelength Dispersive X-Ray Spectroscopy

- **Proportional counter**
  - High V causes gas amplification
  - Current in wire is proportional to number of x-rays (intensity)
  - Reduce V to ~200V, lose gas amplification (ionisation chamber - obsolete)
  - Increase V to ~1500V, get Geiger counter, low count rate, also obsolete for diffractometry

**MSE 321 Structural Characterization**
**EDS vs WDS**

BaL$_\alpha$ = 4.467 keV  
TiK$_\alpha$ = 4.508 keV  
$\Delta E = 41$ eV  

BaL$_\beta_1$ = 4.828 keV  
TiK$_\beta$ = 4.931 keV  
$\Delta E = 103$ eV

**EDS - Elemental Mapping**

Energy Dispersive X-ray Micro Analysis  
Calcium map of Oxalis seed coat
Detection Limits

MDC = Minimum detectable concentration

\[
MDC = \frac{100(2\sqrt{Bt})}{pt - Bt} = \frac{200B}{(p - B)t} \quad \text{wt}%
\]

- \(B\) = average background count rate
- \(p\) = peak count rate in standard reference material
- \(t\) = acquisition time

Operator only has control of \(t\), but it is not feasible to count for longer than ~15 mins (beam intensity does not remain stable that long).

Parameters \(p\) and \(B\) depend on design/condition of analysis system

EDS has poorer signal-to-noise ratio than WDS

EDS and WDS have poorer signal-to-noise ratios for light elements

MDC ~0.1wt% for EDS, ~0.01wt% for WDS

\[C_a / C_b = k_{ab} \left( \frac{N_a}{N_b} \right)\]

where values of \(k_{ab}\) are the Cliff-Lorimer constants for TEM (no A or F correction)

Cathodoluminescence (CL)

Electrons knock out outer electrons, emitting visible/UV photons upon relaxation

Emission is modified by impurities or defects

Resolution fairly poor (whole interaction volume), but can be improved by using low kV or narrower beams (FEG)

Traditional polishing techniques employed for thin geological sections create a "dead layer" that prevents work at low kV and higher spatial resolution.

Remnants of polishing compound can be very much brighter than the area of interest, saturating the detectors at the gain required to image the region of interest.

Peak in photon energy corresponds to \(E_g\), and width of peak decreases at low \(T\)

At liquid He temperatures (~3 K) alterations in \(E_g\) due to composition (> 10 ppb) can be detected - CL is several orders of magnitude more sensitive than EDS or other x-ray techniques
Chemical Analysis - PEELS

![Graph showing PEELS analysis of TiO₂ particle](image)

20nm TiO₂ particle

End of Lecture