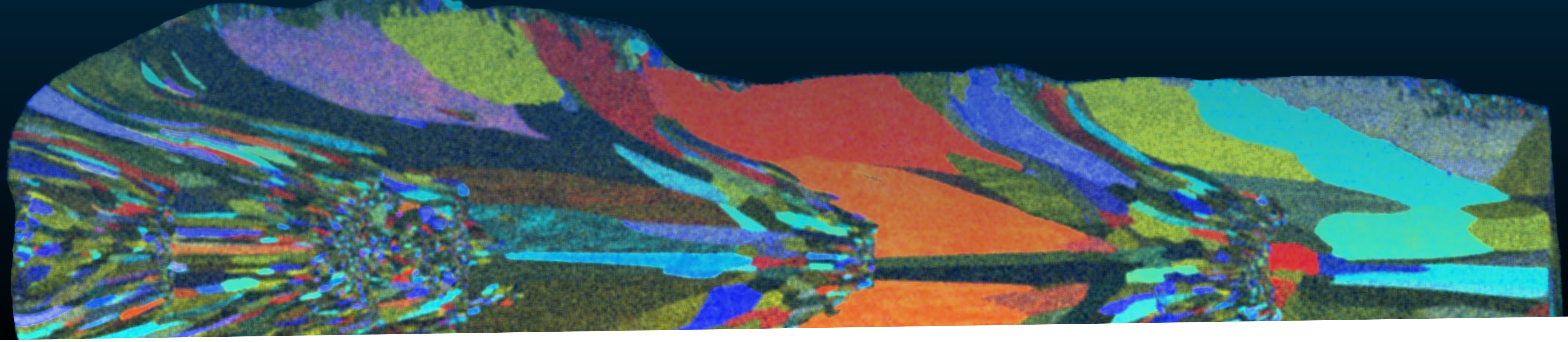
WEBINAR

Diffraction in micro-XRF
A tool, rather than a complication?

Christian Hirschle, Falk Reinhardt



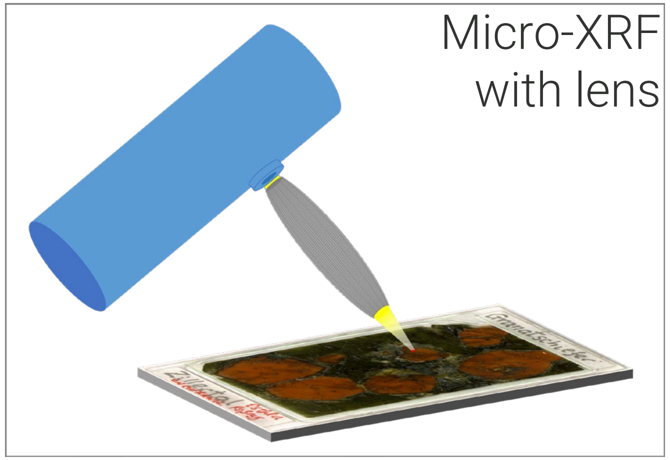
The speakers

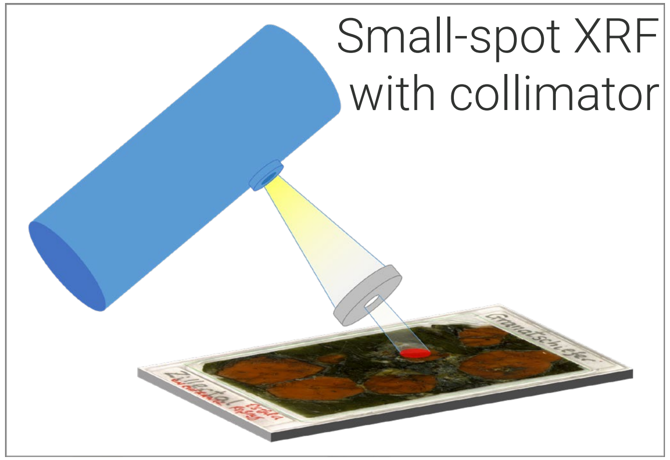
- Dr. Christian Hirschle
- Application Scientist,
  Bruker Nano Analytics, Berlin, Germany

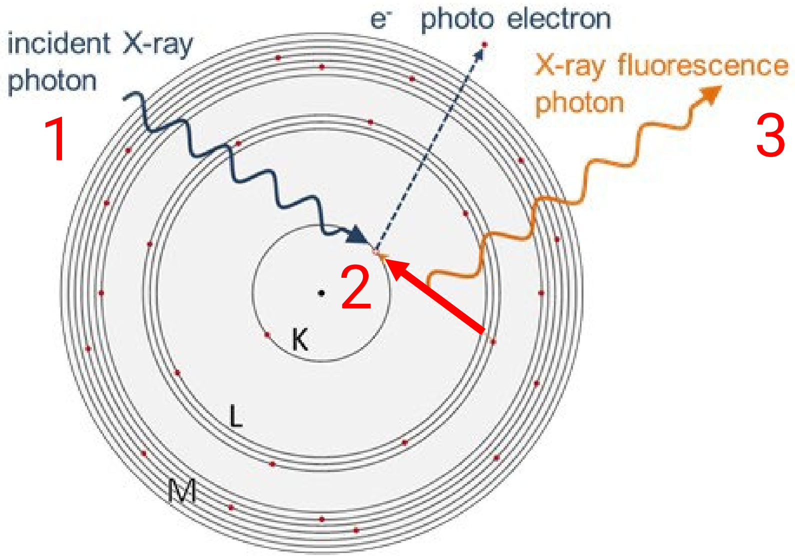
- Falk Reinhardt
- Senior Application Scientist,
  Bruker Nano Analytics, Berlin, Germany

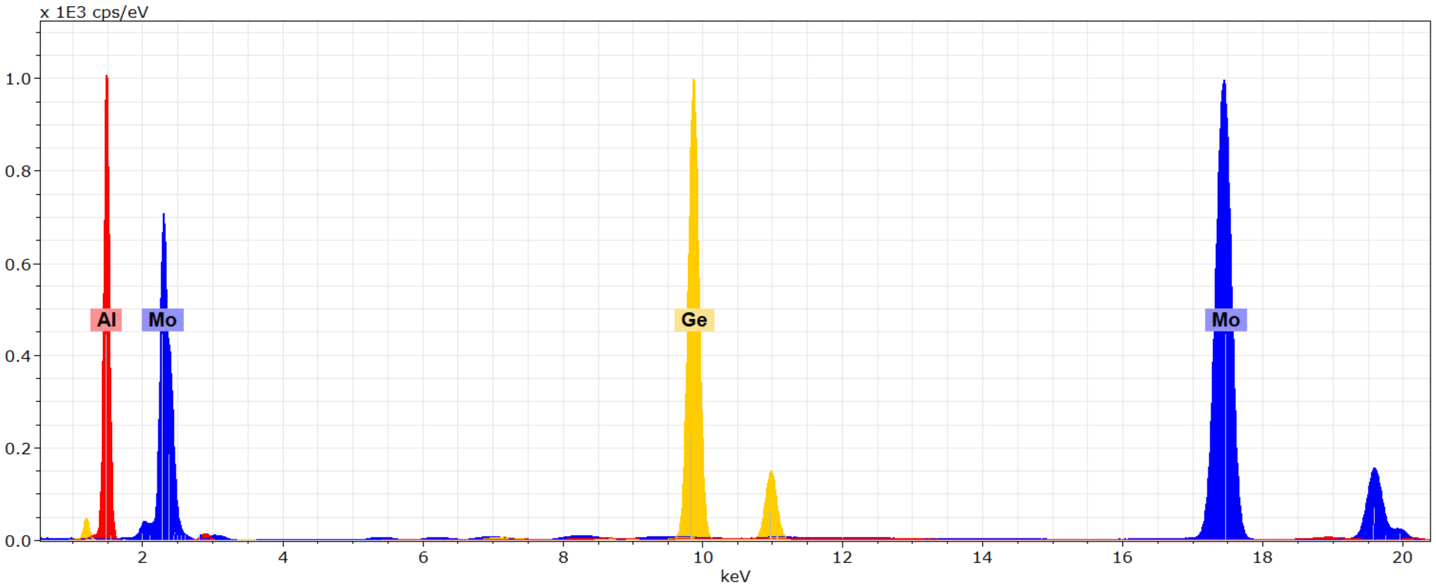
Agenda

Introduction to micro-XRF



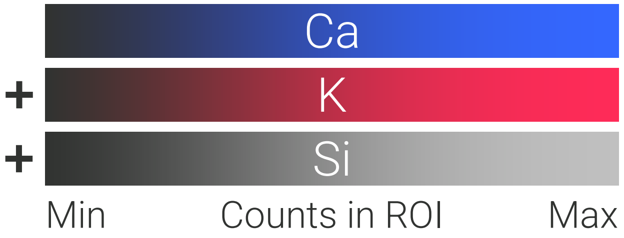


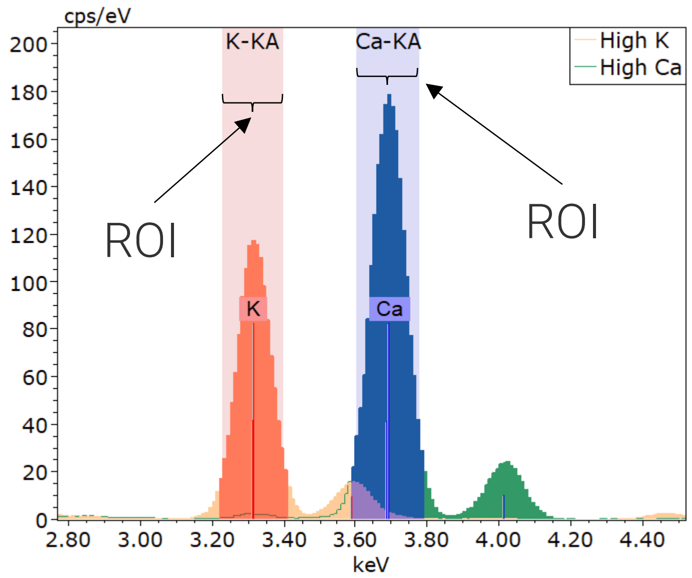


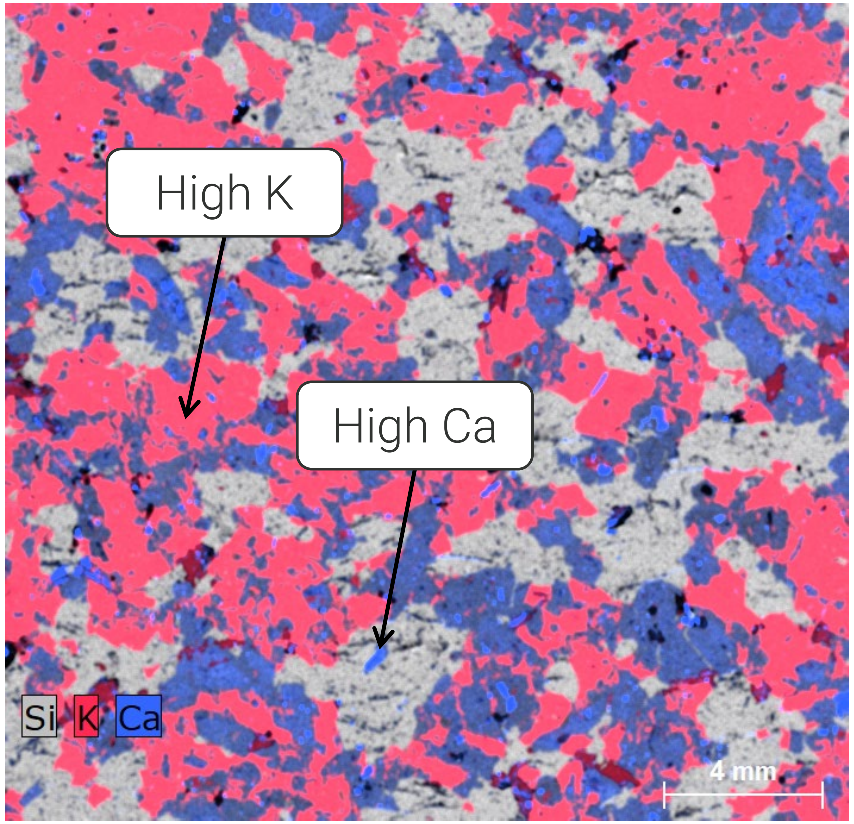


Intensity distribution maps

- Maps per default show the intensity distribution of detected radiation in specific energy regions of interest (ROI).
  - Background or overlap corrections may be applied.
- The ROI for an element is usually chosen to represent its emission line with highest detected intensity.
- Color brightness increases with increasing intensity in the ROI on a relative scale.

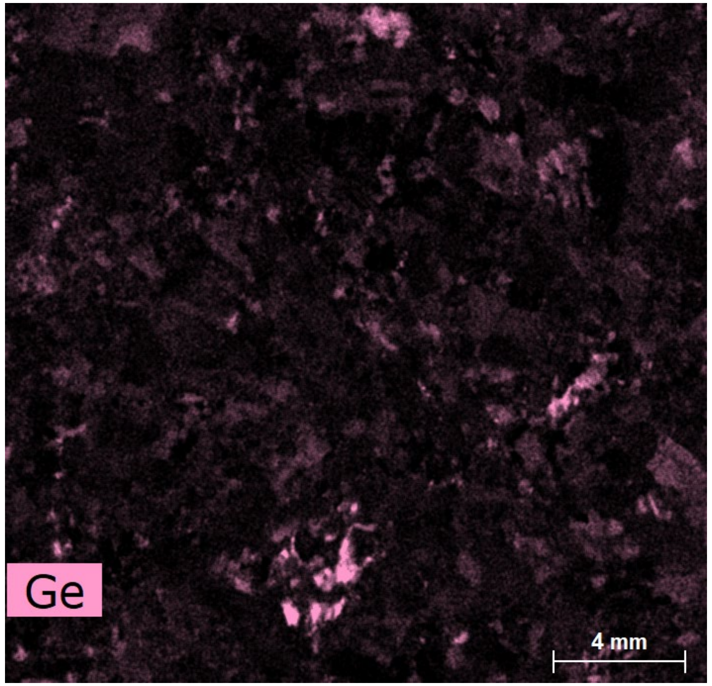


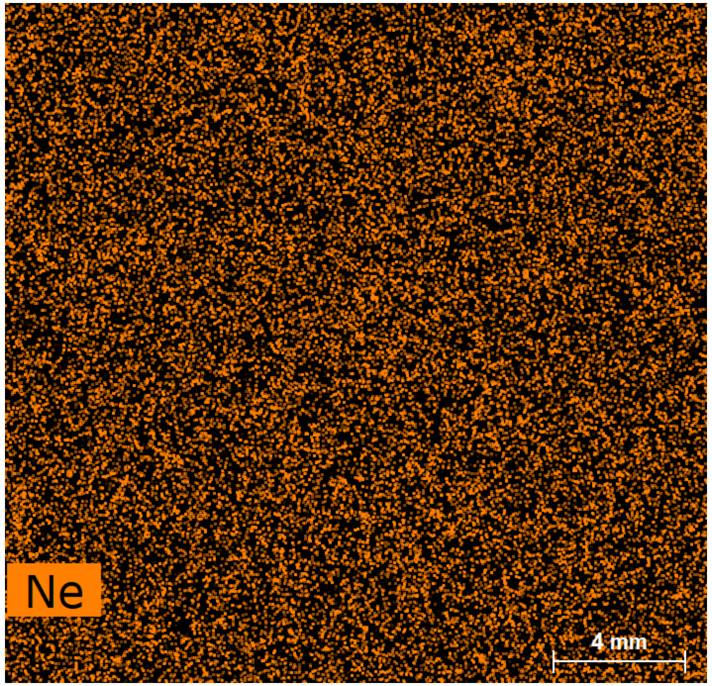




Intensity distribution maps

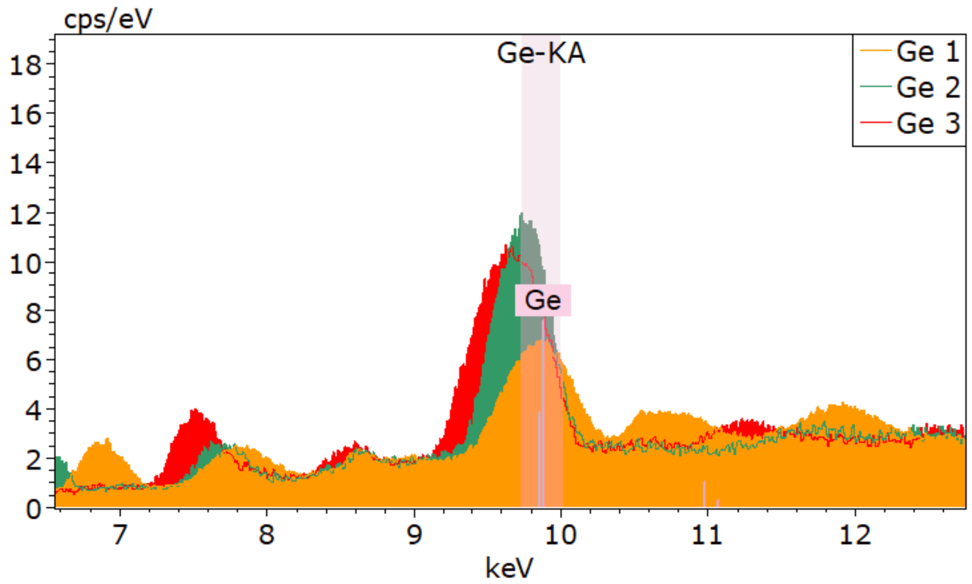
- When an element is below the limit of detection or homogeneously distributed, the intensity in the ROI will barely change
  - ➢ Maps will show random scatter from point to point, white noise.
- The Ge map here looks different from the Ne map. Do we see Ge hotspots?

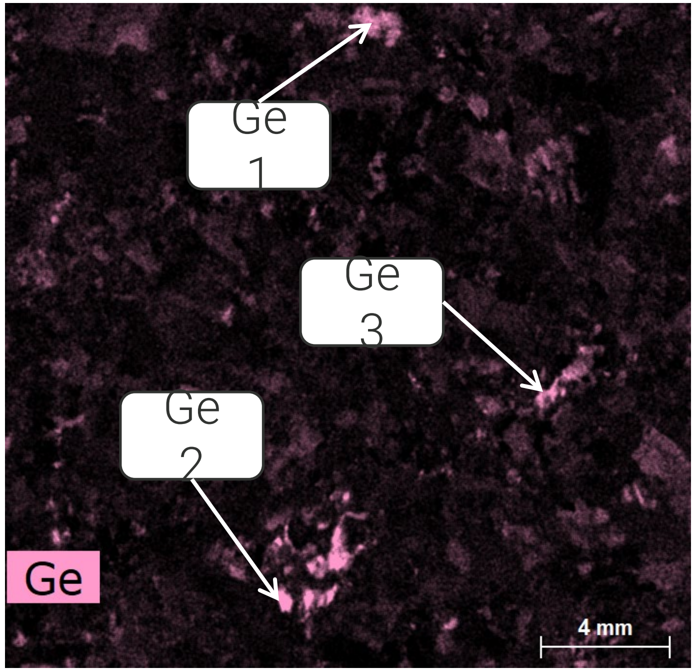




Intensity distribution maps

- Spectra from bright regions in Ge map were extracted.
- There are peaks in the Ge ROI. However, compared to regular Ge-Kα fluorescence peaks, they are centered at different energies, do not have a Gaussian shape, are wider, and they are missing distinct Ge-Kβ peaks.





➢ These peaks are not Ge fluorescence.

➢ This Ge map cannot be used to discuss the Ge distribution.

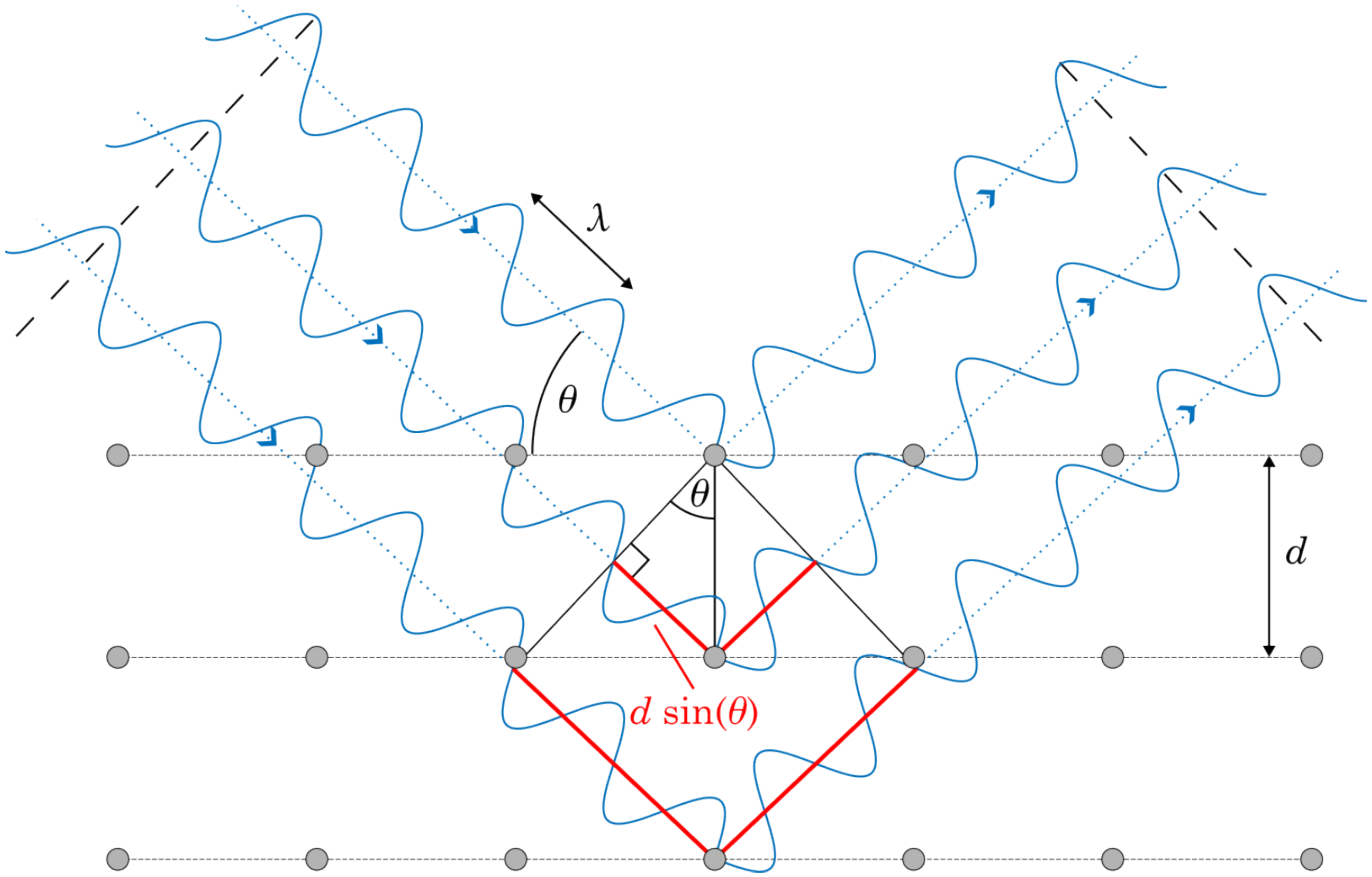
The maxima are caused by X-ray diffraction.

Diffraction: Bragg equation

How does diffraction happen?

- X-rays get scattered on the electron density; angle of incidence θ with planes of translation lattice; plane spacing *d*. Angle of incidence is equal to angle of reflection (Huygen's Principle).
- Radiation scattered from lower planes travels additional path length: $2d\sin(\theta)$.

➢ Constructive interference of reflected waves, when additional path length contains integers *n* of wavelengths λ:

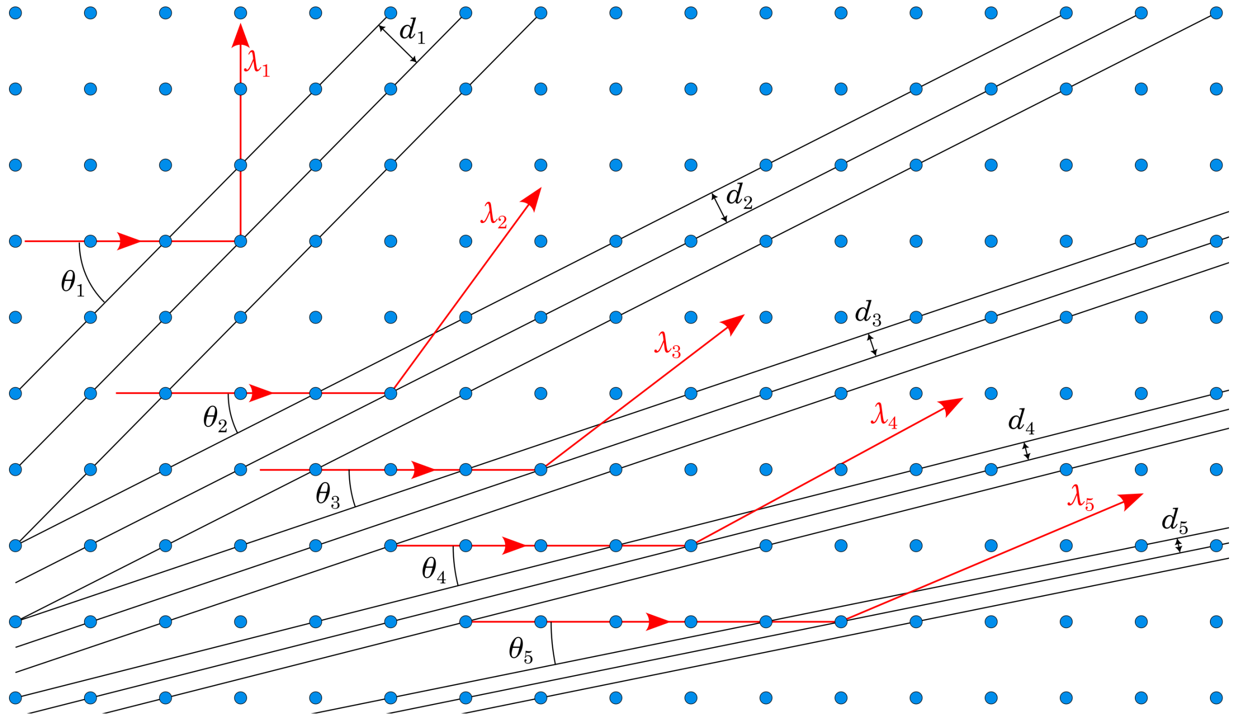


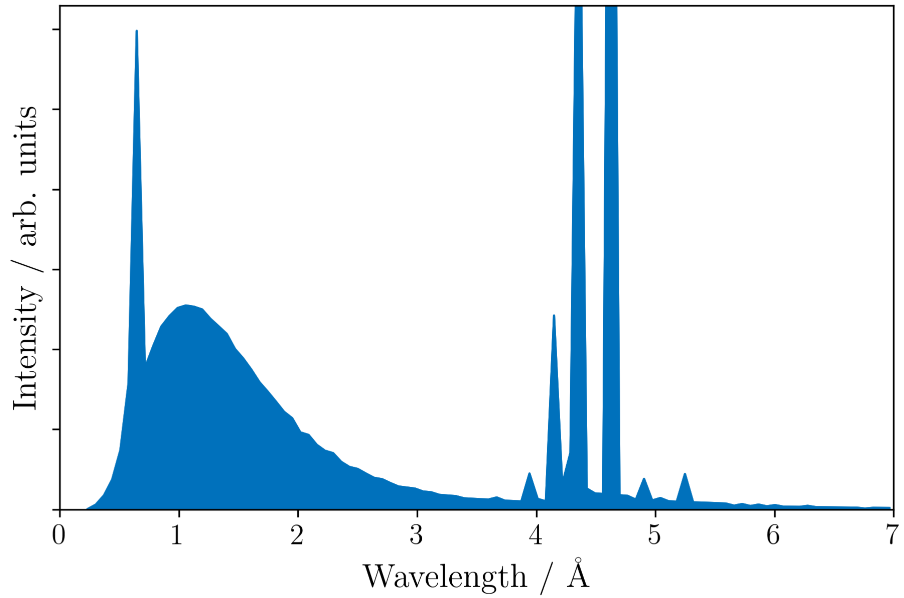
Braggs law: $2d\sin(\theta) = n\lambda$

Diffraction: Why multiple planes at once?

- X-ray tube excitation spectrum is continuous in energy range.

➢ For a given direction of incident radiation, many combinations of *d*, *θ* and *λ* fulfill Bragg‘s law!



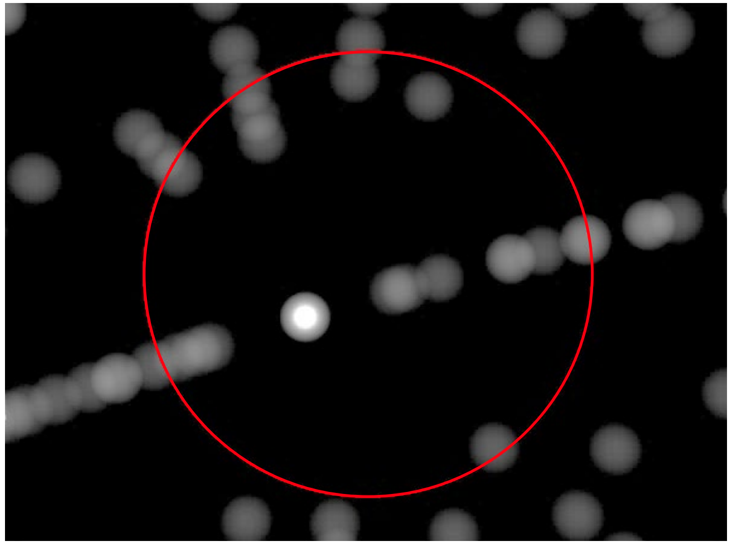


Excitation spectrum, Rh tube with polycapillary lens.

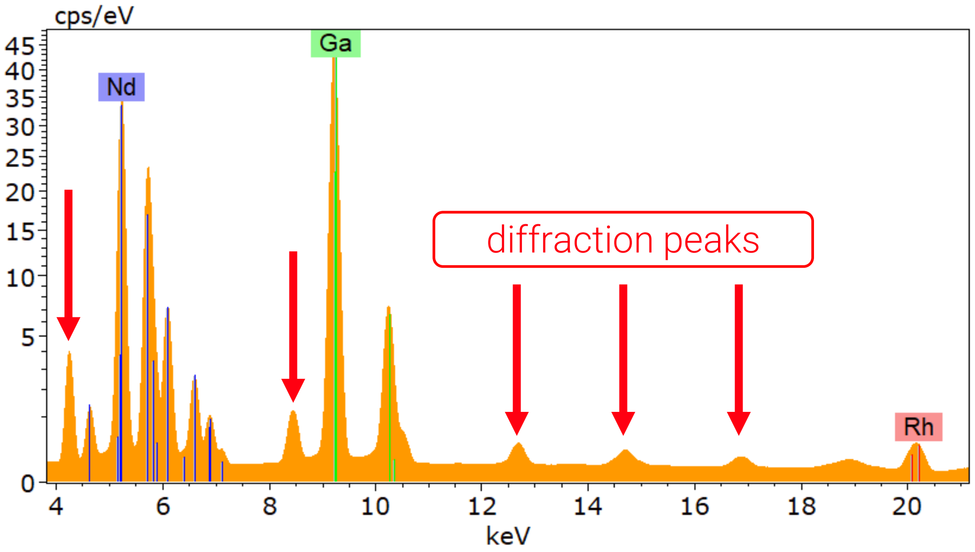
Diffraction: Why multiple planes at once?

Micro-XRF spectra often exhibit multiple diffraction peaks due to

- "white" X-rays used for excitation,
- large detectors, and
- beam divergence.



Simulated diffraction pattern for perovskite-type $NdGaO_3$ on a detector (red) of an M4 TORNADO.

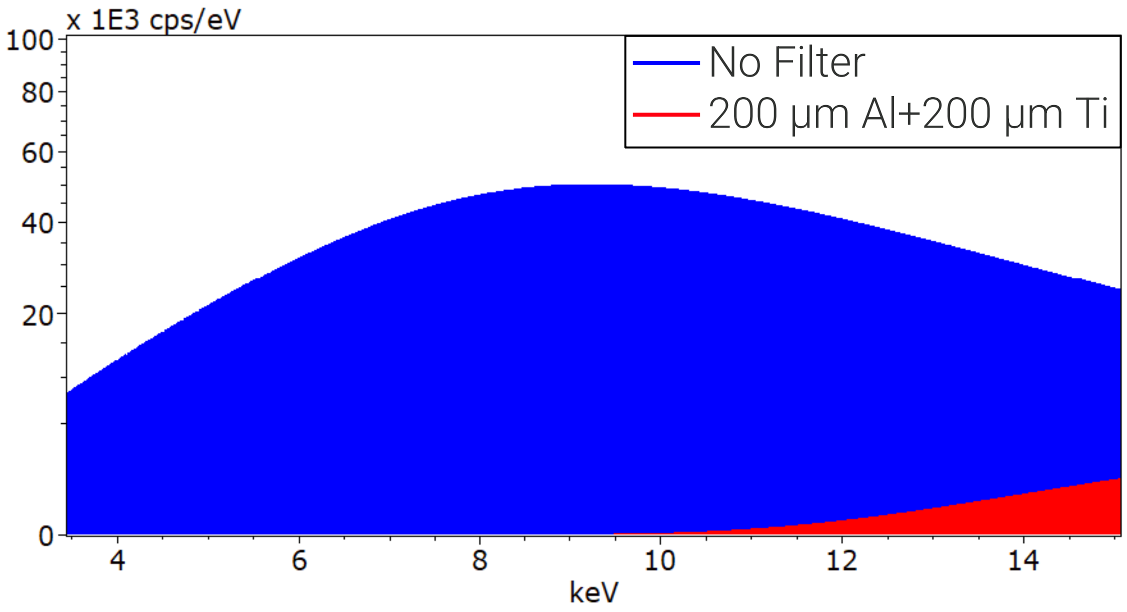


Measured spectrum for $NdGaO_3$ showing both peaks from diffracted radiation and characteristic X-rays.

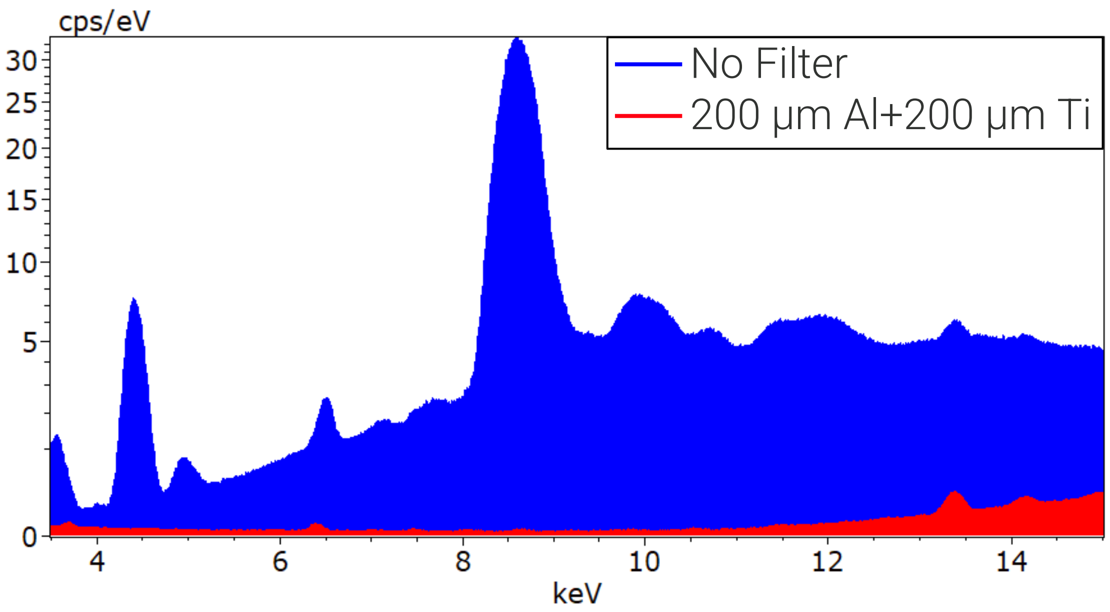
How to get rid of diffraction peaks: Filters

Diffraction relies on specific wavelengths of primary radiation for a given crystal structure/orientation.

➢ Blocking this radiation before it reaches a sample via a primary beam filter can prevent diffraction peaks.

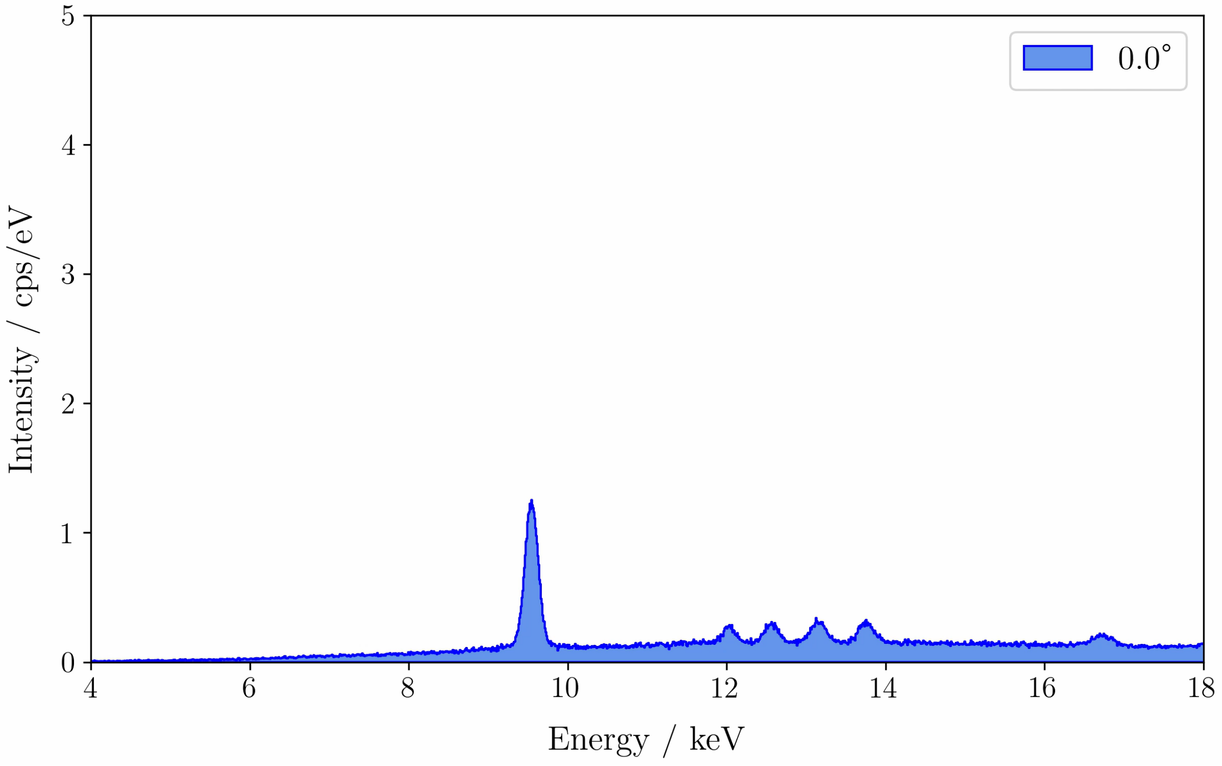


synthetic excitation spectra

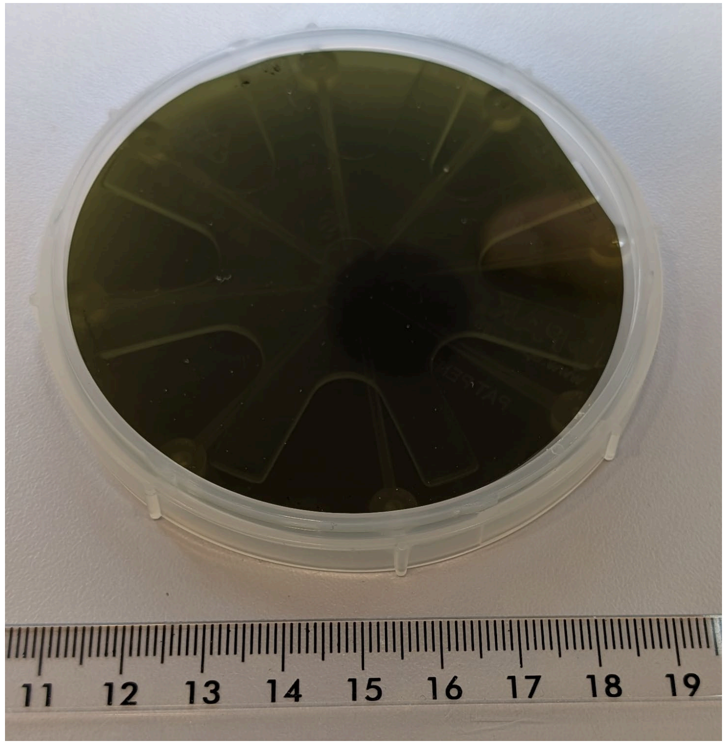


quartz in a granite

EDLM : Introduction



SiC rotating horizontally in an M4 TORNADO PLUS.
One detector, AMS 500, 120 s per measurement.

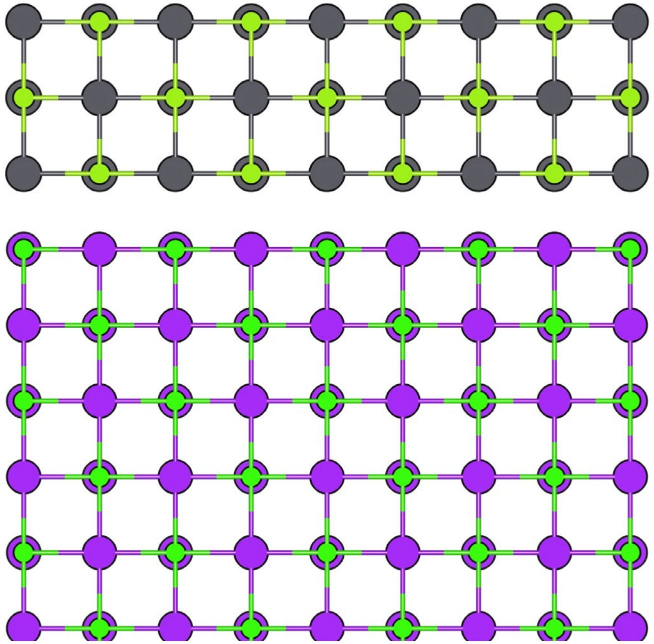


SiC wafer. Hexagonal, (001) pointing up.

➢ We can visualize changing crystal orientation by investigating diffraction peaks

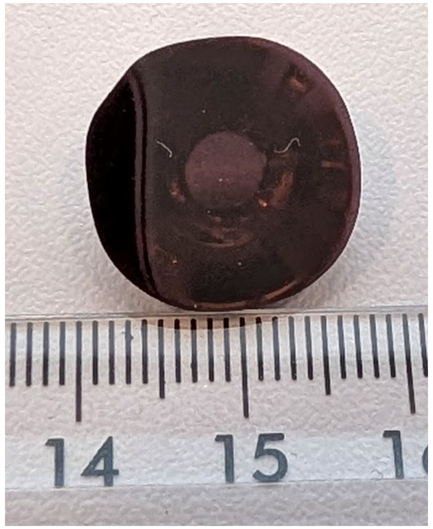
EDLM: $NdGaO_3$, twinning

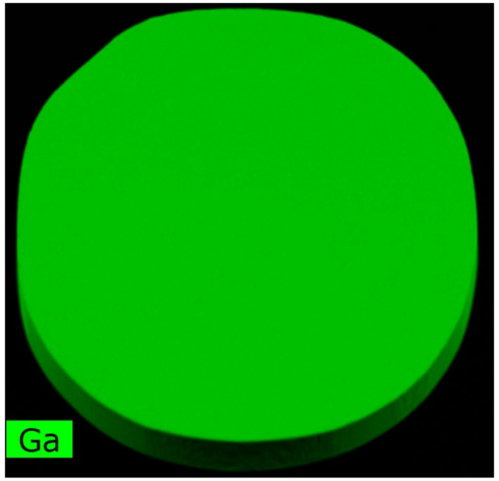
- Perovskite-type $NdGaO_3$: widely used as substrate for epitaxial growth of a variety of thin films.
- Interface/strain crucial for film properties (ferroelectricity, magnetism…).

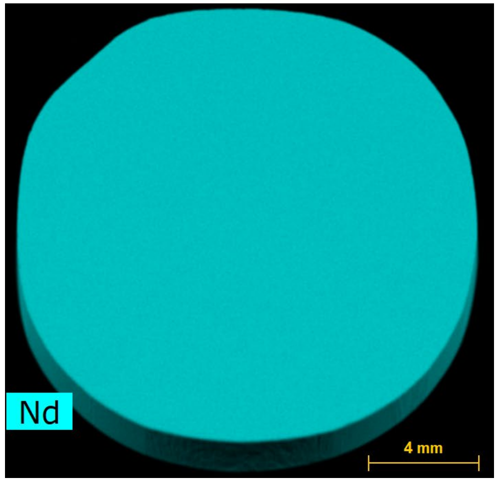


Homostructural epitaxy; NaCl structure

➢ Changing orientation of substrate generally undesirable.

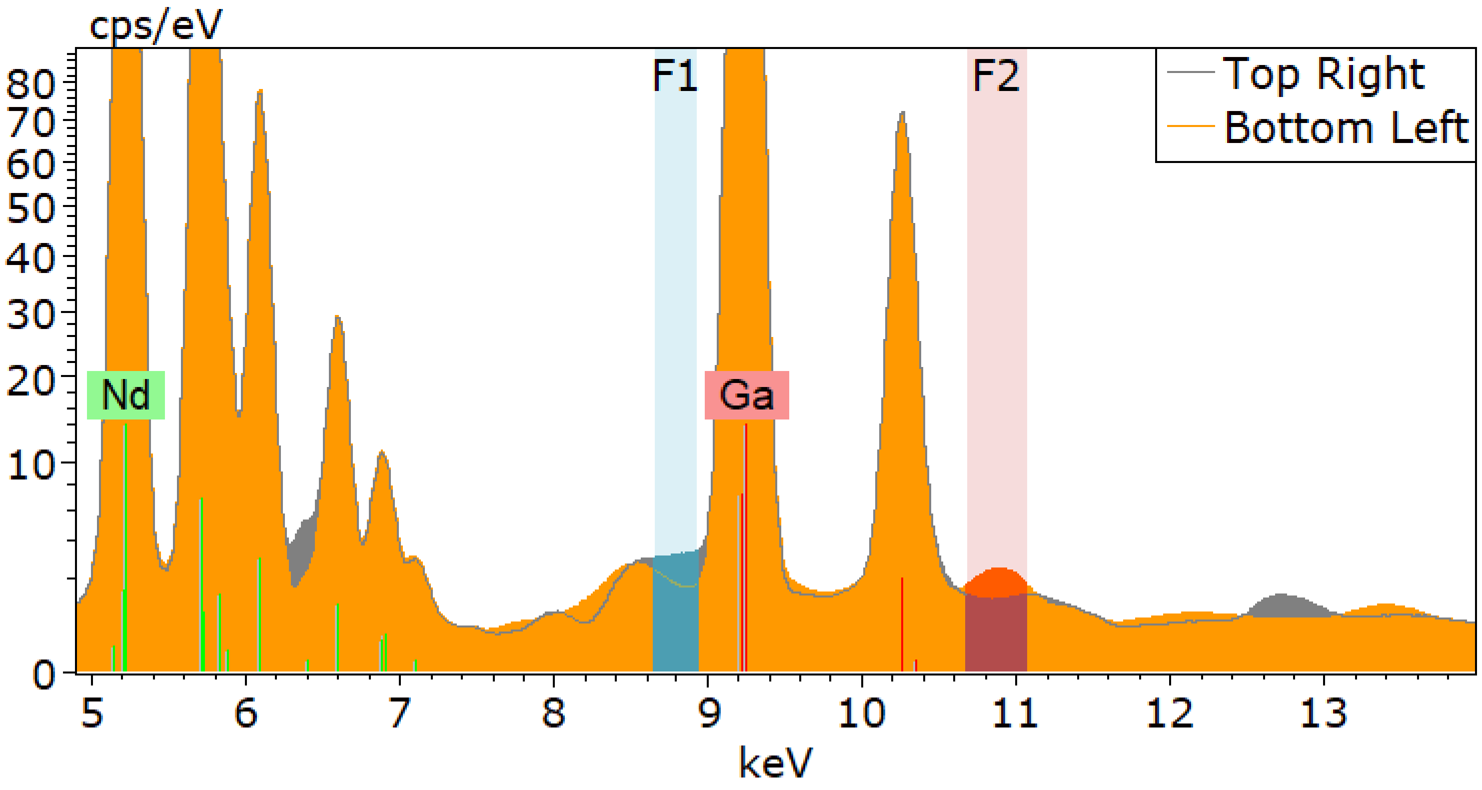


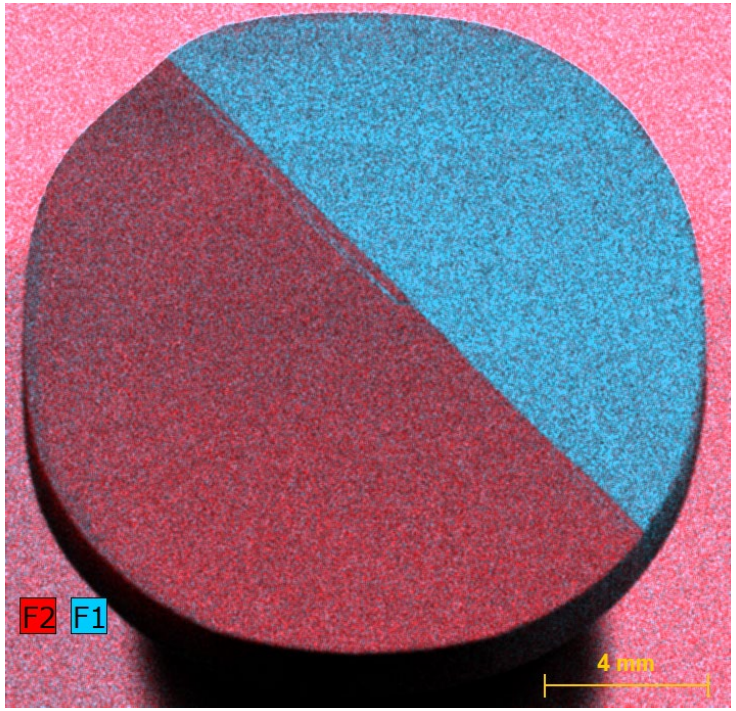




EDLM: $NdGaO_3$, twinning

- Same Map, ROI on diffraction peaks: Energy-dispersive Laue mapping (EDLM).





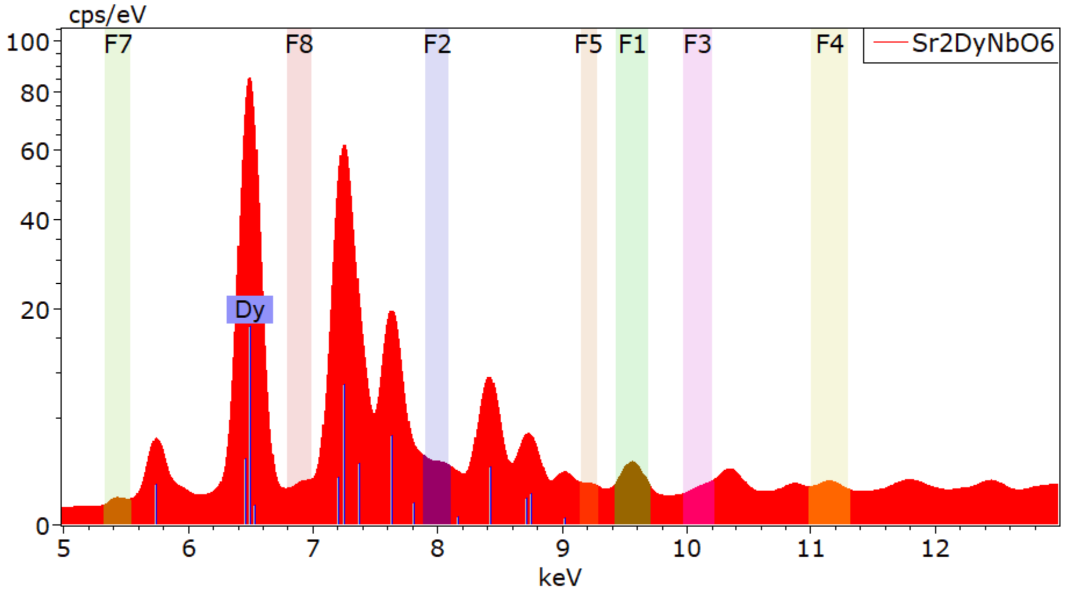
➢ EDLM reveals that the sample has two twin domains.

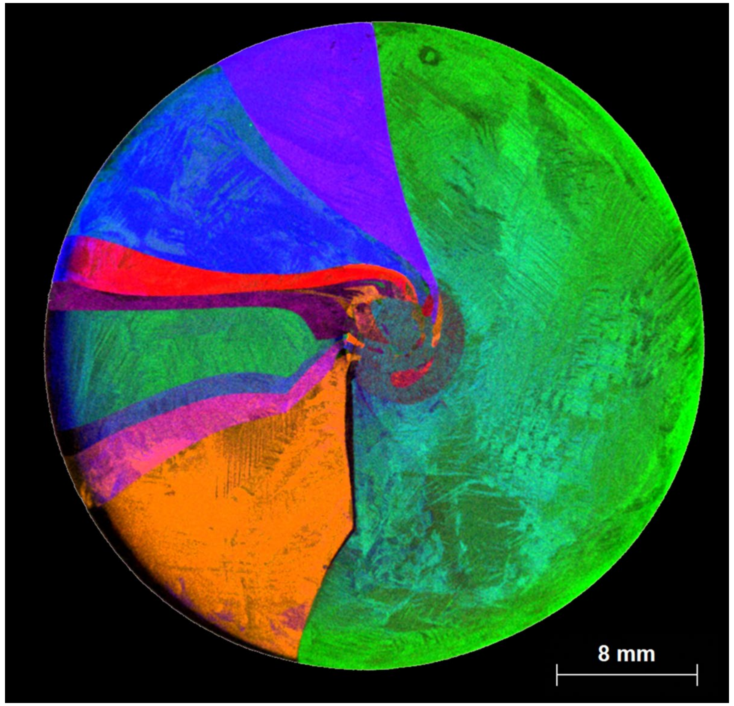
EDLM: Sr_2DyNbO_6

EDLM shows

- sudden changes to orientation, twinning following rotation during growth,
- as well as striations within the domains.

➢ Indications that rotation speed may have been too high?



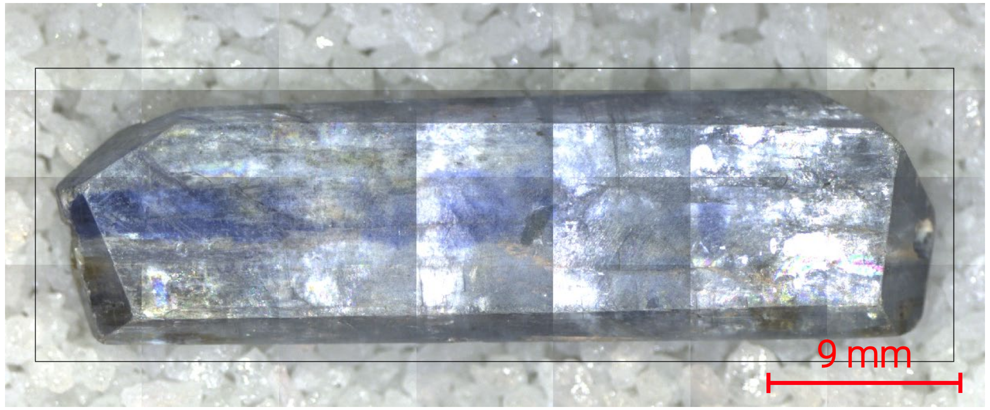


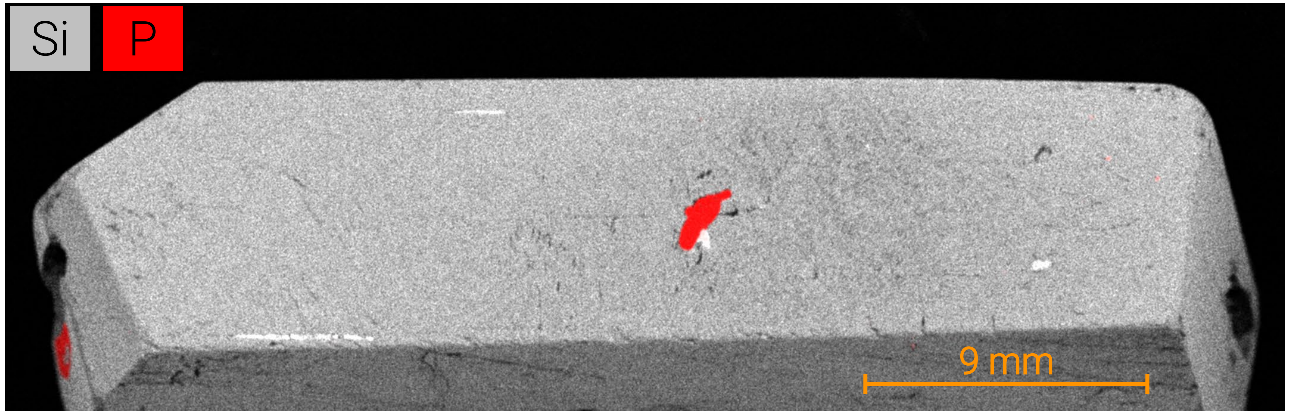
EDLM: Continuous patterns?

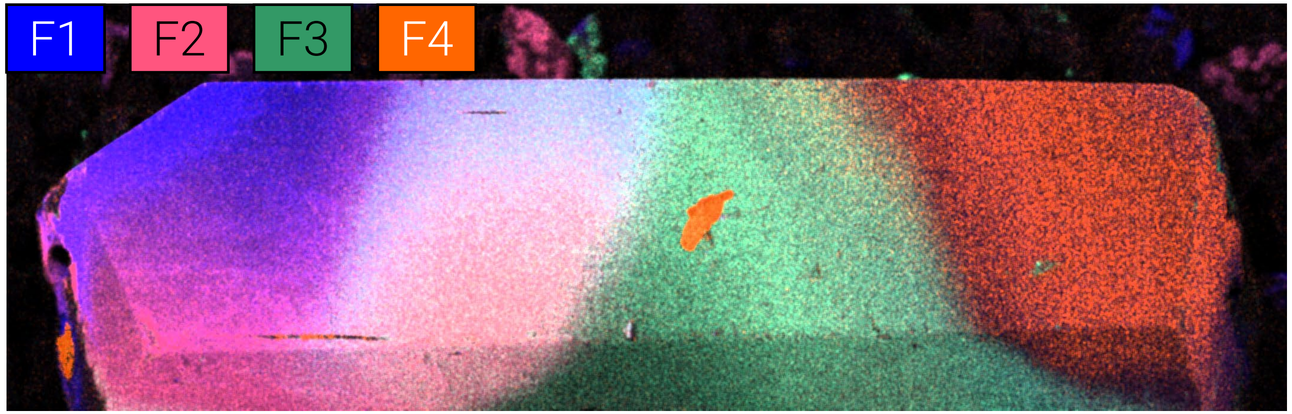
Surface-polished, flat Kyanite ($Al_2[O|SiO_4]$) sample.

- Chemically quite homogenous; one apatite inclusion close to center.

EDLM shows distinct zones, but transitions appear gradual without sharp borders?



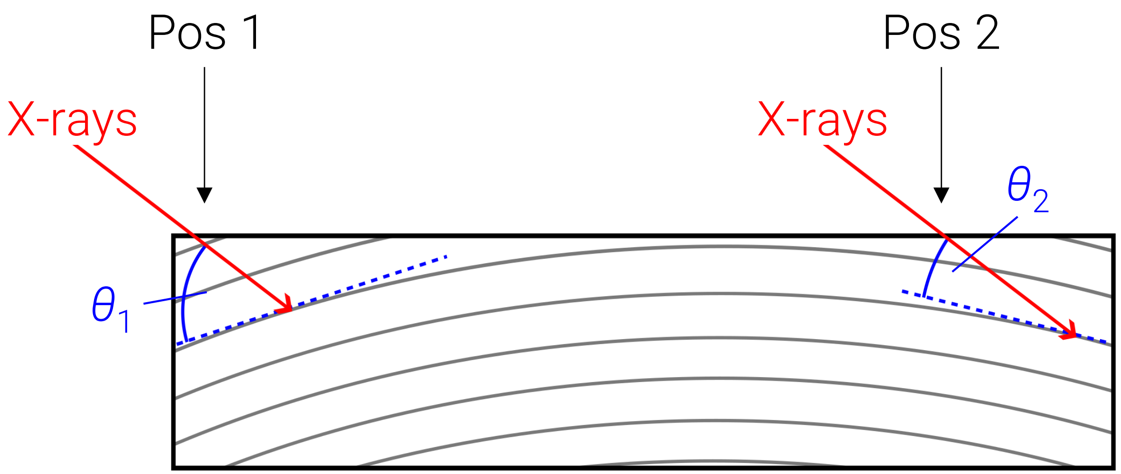




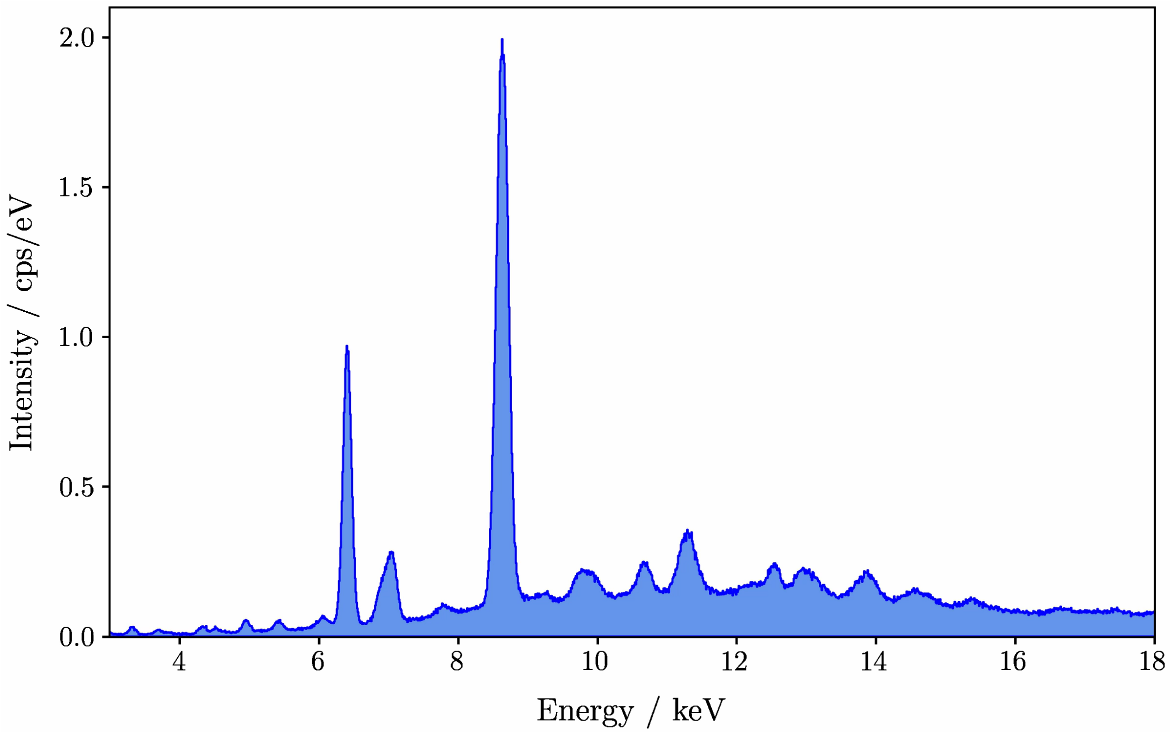
EDLM: Continuous patterns?

Spectra were extracted for ~0.9 mm wide regions from left to right on the surface.

- Diffraction pattern changes continuously, rather than abruptly
- **Grain orientation changes continuously!**



θ depends on where the X-rays hit the surface!



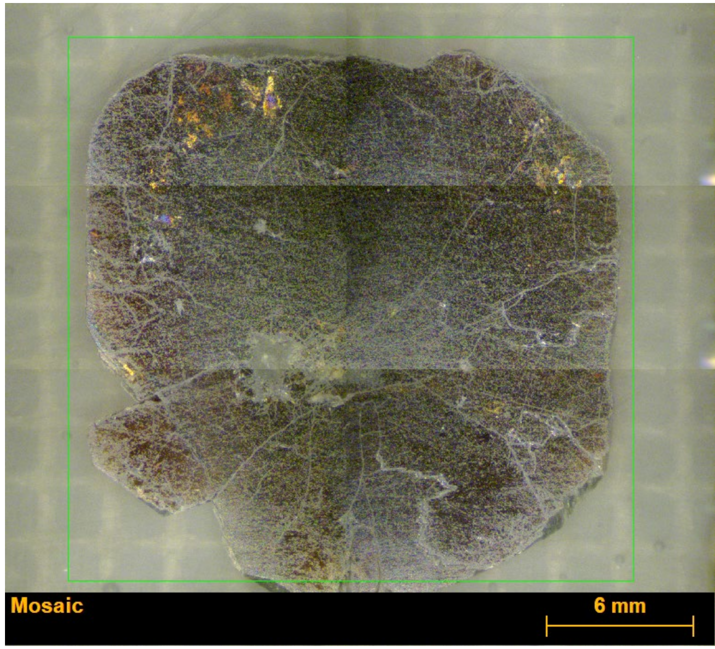
Structure of crystal was bent (Kyanite as high-pressure polymorph; metamorphism?).

When prepared as gemstone, curvature was "polished away".

EDLM: Garnet from Zillertal

universität innsbruck

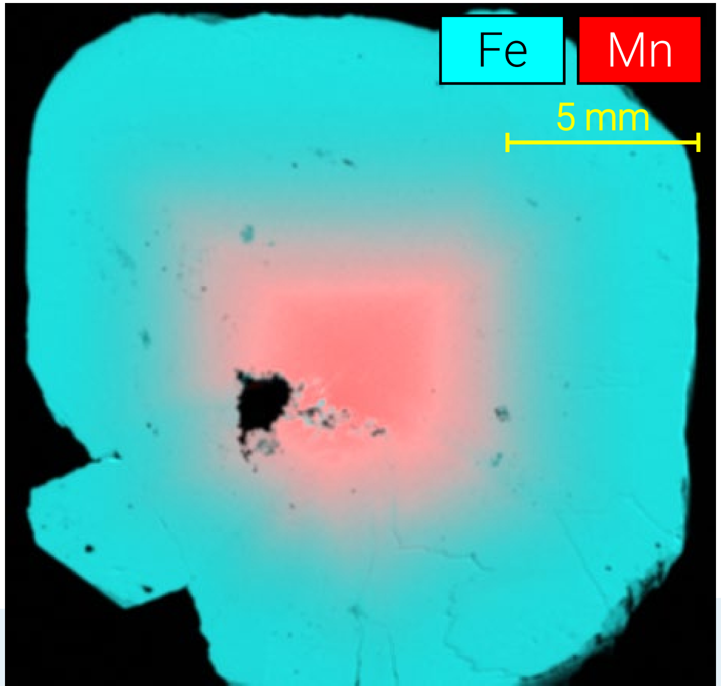
Data kindly provided by Universität Innsbruck, Institute of Mineralogy and Petrography

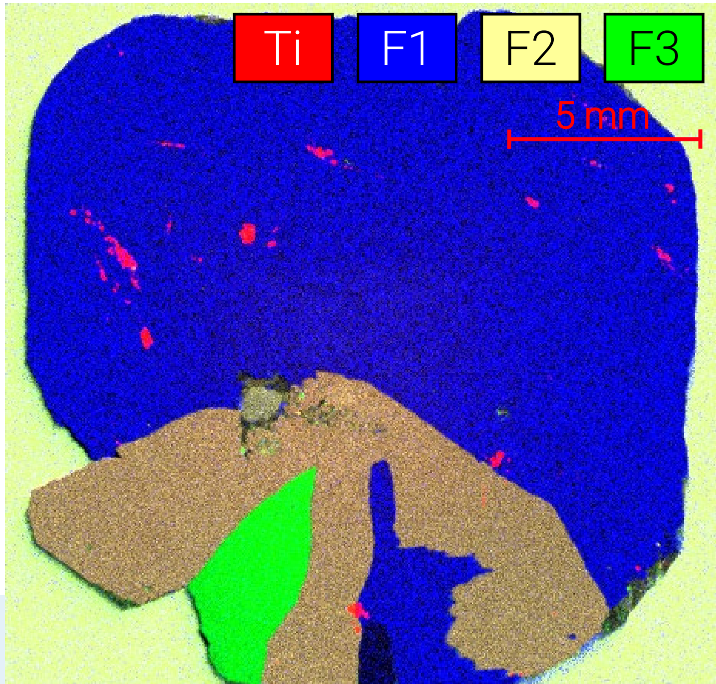


EDLM is not restricted to synthetic crystals!

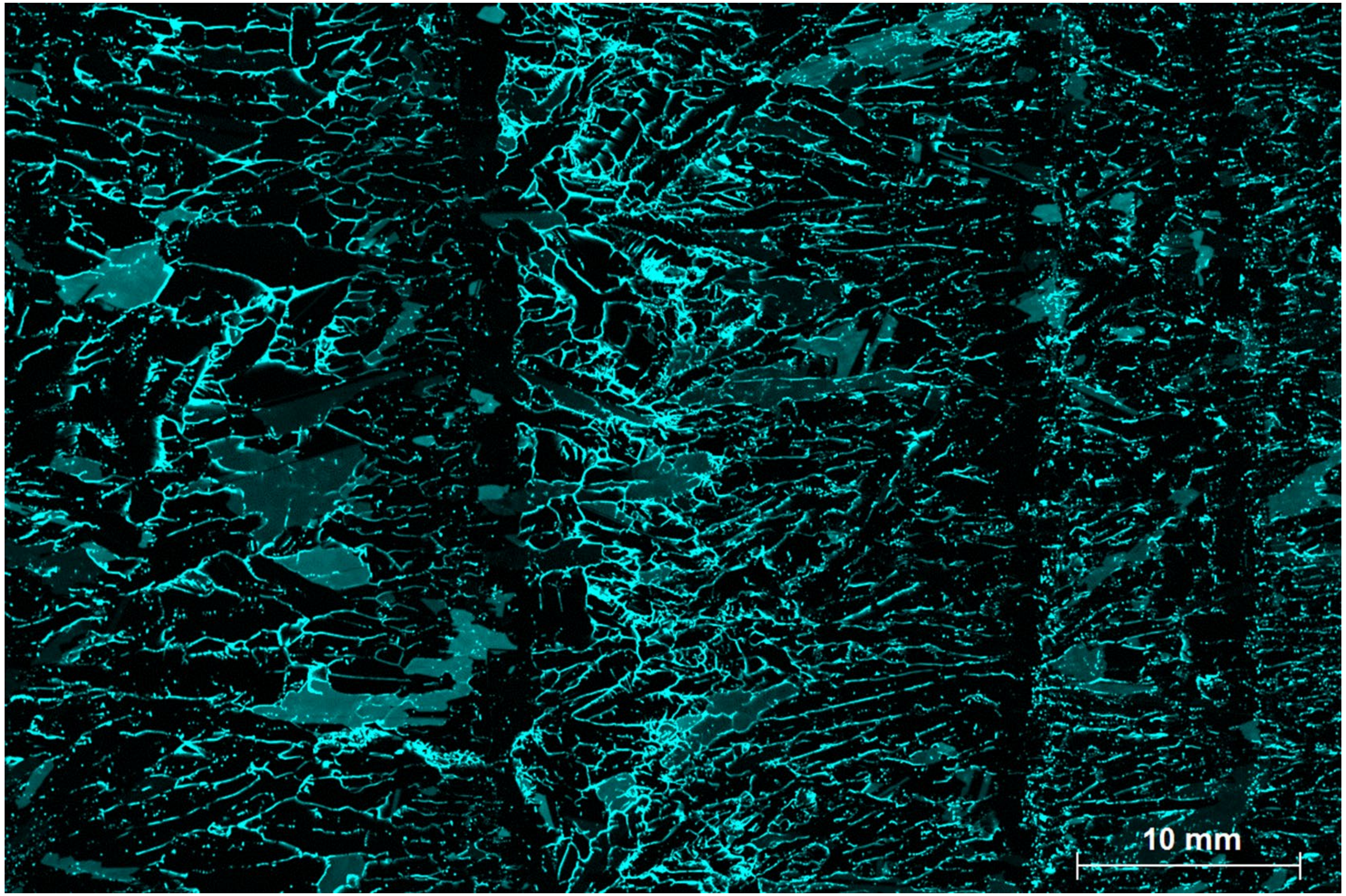
Micro-XRF map of garnet from Zillertal provides at least three different types of information:

- Chemical zonation of at least Mn, Ca, Fe, Ti, Mg and Y.
- Presence of inclusions of other phases.
- Suddenly changing grain orientation!
    - At least three different orientations.
    - Chemical zonation does not reflect changing orientation.
    - ➢ Simultaneous growth of all grains together from center.





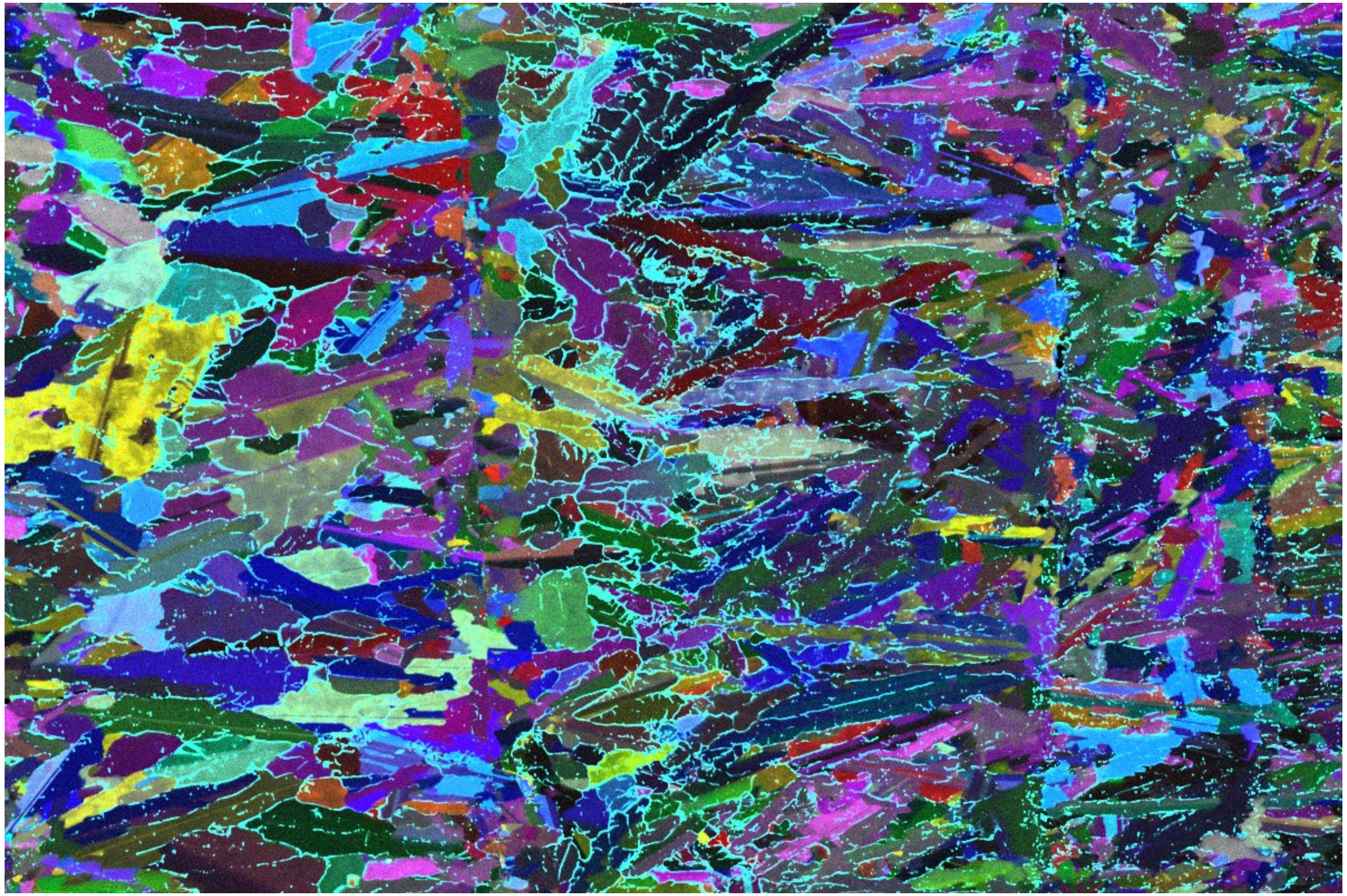
EDLM: Correspondence to chemical information



Iron in polycrystalline Si.

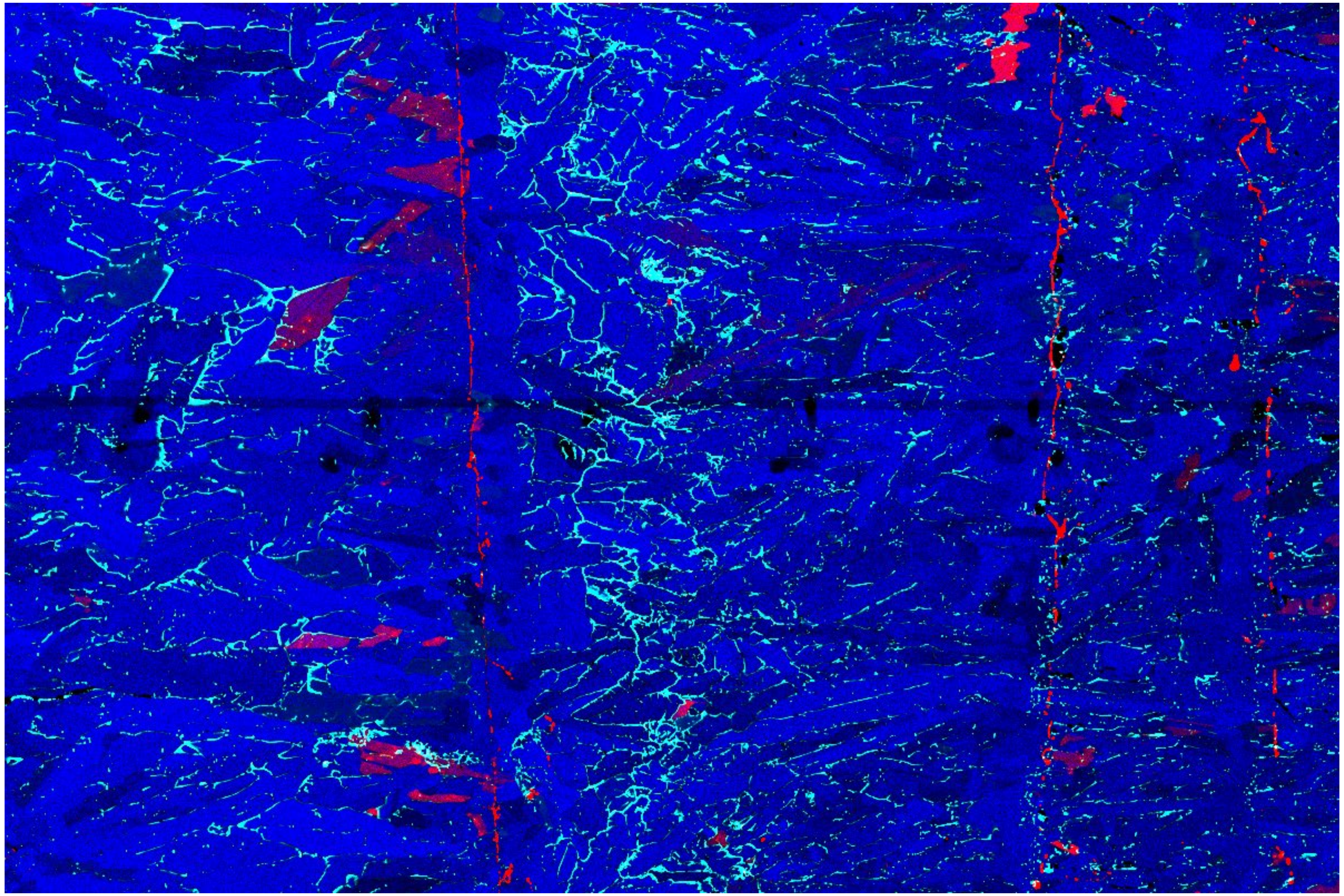
- The conspicuous pattern implies some relation with the crystal domains.

EDLM: Correspondence to chemical information



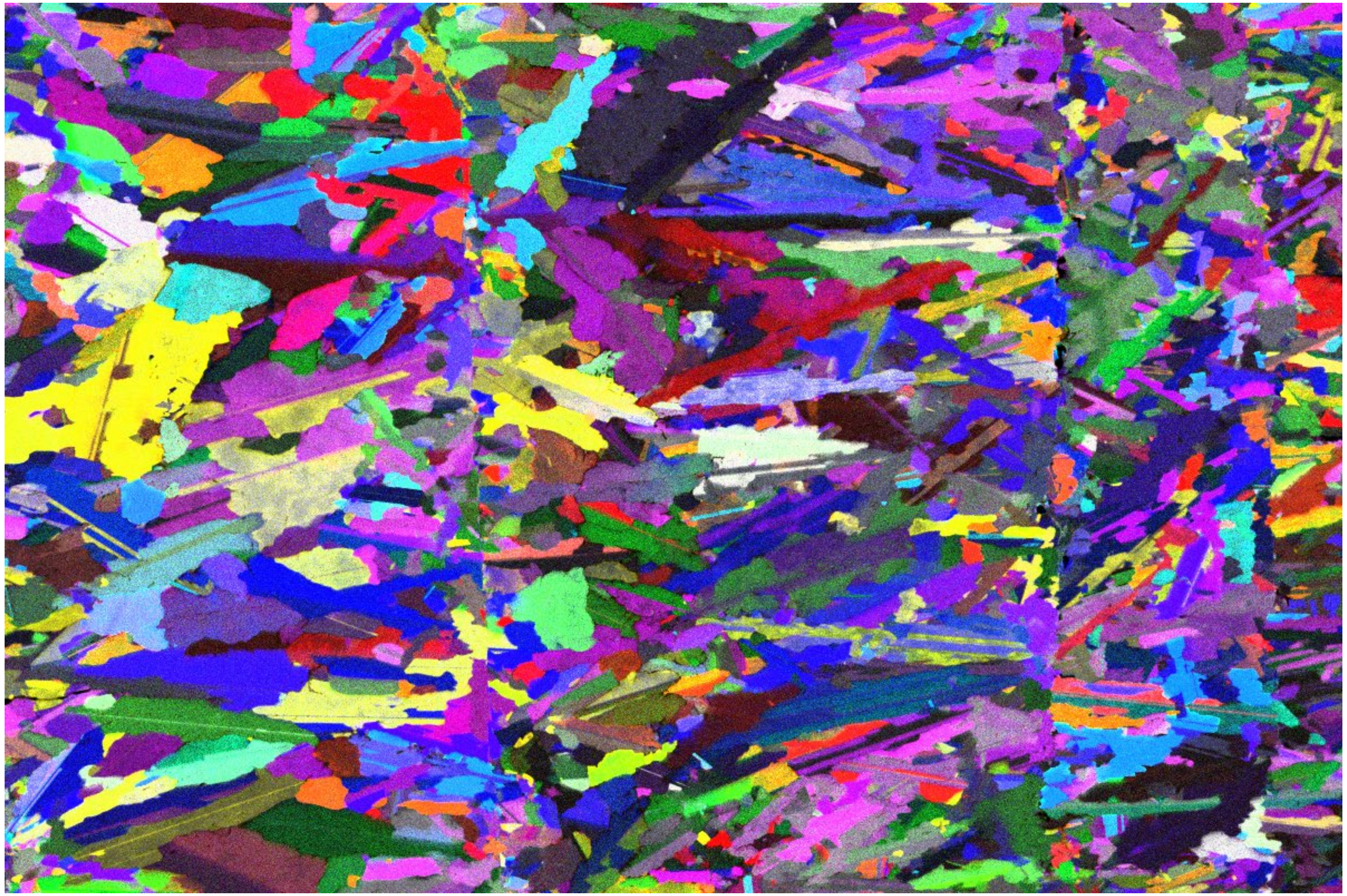
- The domain map is perfectly in line with the Fe distribution.
- During crystal growth, the inclusion of many foreign elements – traces at that time – is energetically disadvantageous. They will not be incorporated into the growing crystal but be driven forward until they hit the boundary of the next domain.

EDLM: Correspondence to chemical information



- Ca you would usually try to avoid in Si melt.
- It can be added to control crystal formation.
- In this case, one of the additives formed “horizons”.

EDLM: Correspondence to chemical information

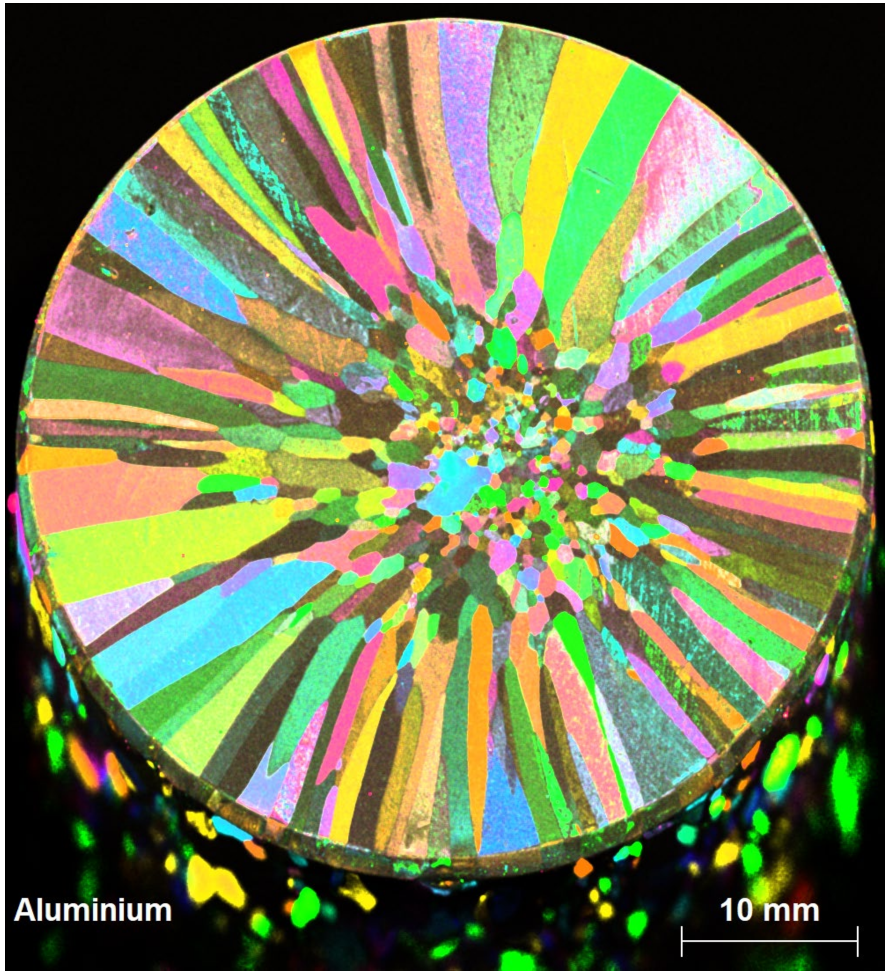


EDLM: Aluminium and mechanical properties

Almost pure aluminium

- Apparently slow cooling → large domains
- In the center many small domains ... Towards the outside some prevail and the grains get larger.

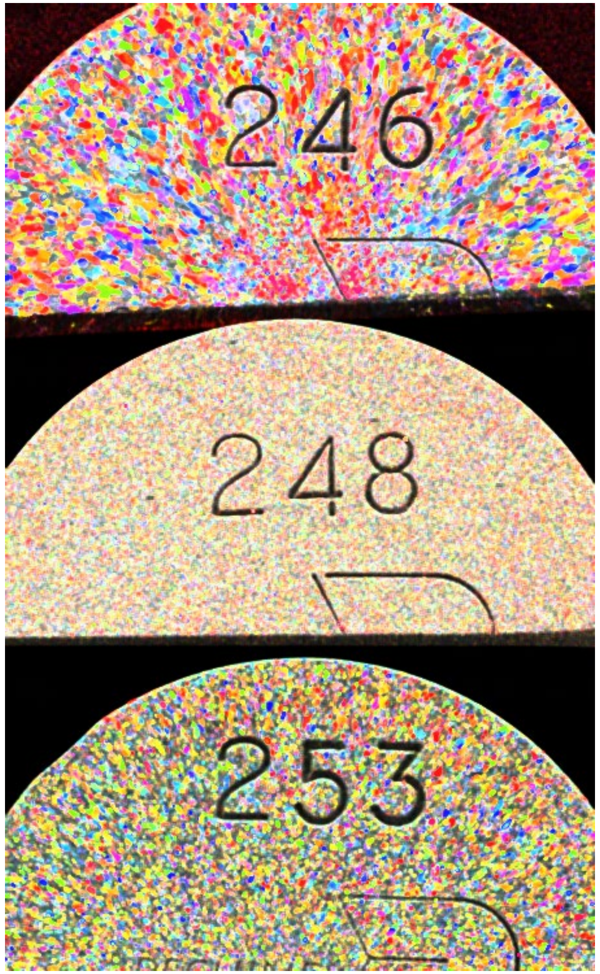
- Note: in the sidewalls the same domains can be seen “poking out” of the metal piece. This highlights once again that diffraction is not merely some sort of reflection (as the Bragg-slide might imply)



EDLM: Aluminium and mechanical properties

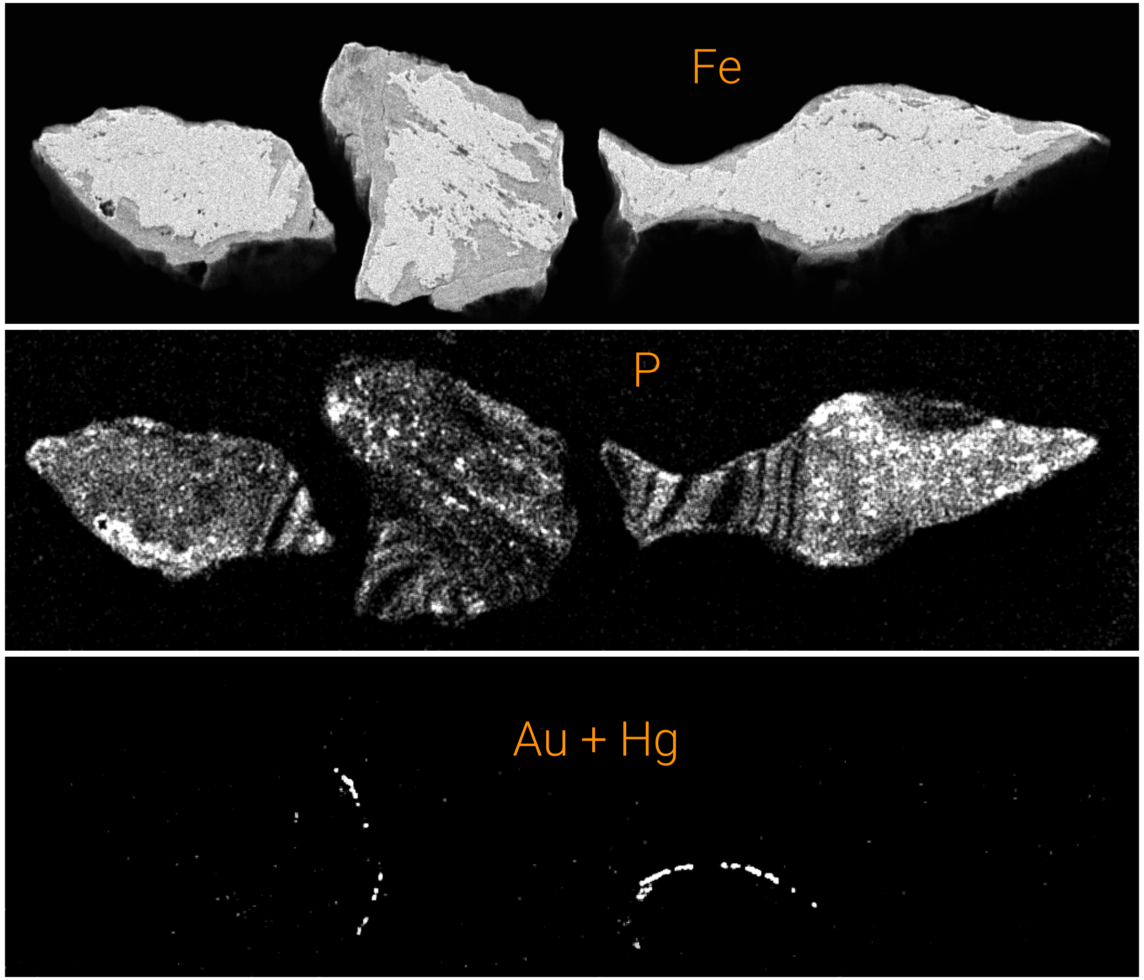
Different 7xxx Aluminium alloys with very similar composition.

- The main difference here is the crystal domain size.
- 7xxx Aluminium alloys are used in space/aerospace applications, where high mechanical strength at low weight are looked for.
- Grain refinement for grain boundary strengthening can be done either by adding suitable alloying elements, or by heat treatment. ... or both
- Finer grains in general lead to higher yield strength (Hall-Petch strengthening)!



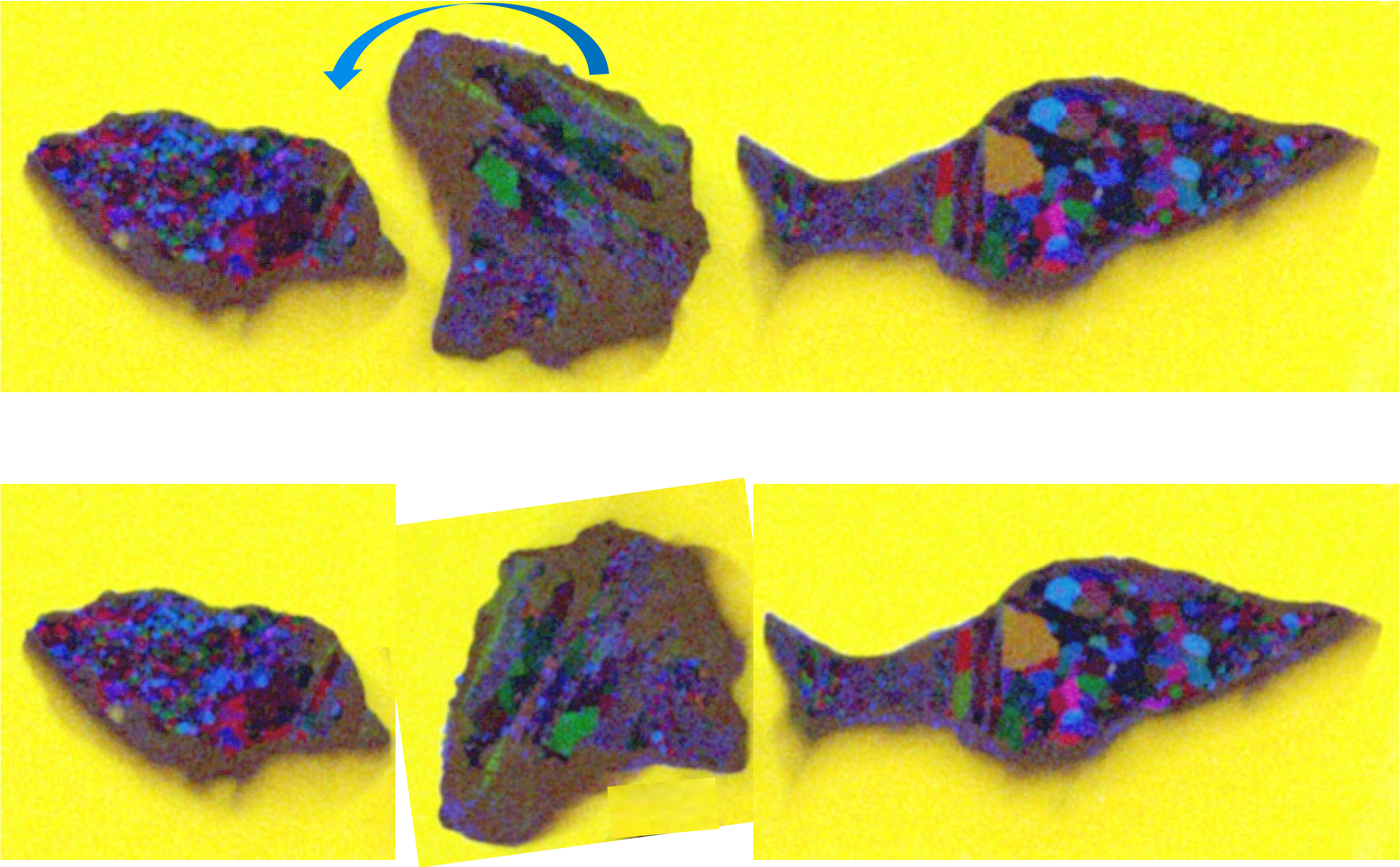
EDLM: Archaeological objects

- Fragments of a gilded dagger from the 14th century cast in epoxy.
- The gilding reveals that the central fragment is rotated against its initial orientation.



EDLM: Archaeological objects

- Domain map of the fragments.
- The center fragment rotated for this comparison.
- Clearly domains are larger on the edges → this material could be softer than the core, which is ... surprising
- Since there still is some gilding visible, this dagger may not have been intended for “real use”.



Different hardnesses of steels in traditional katana blades
https://www.artkatana.com

EDLM: Degenerate orientations

Can we see any change in orientation in the data? **No.**

- Rotation around the direction of the primary beam does not affect the angle of incidence

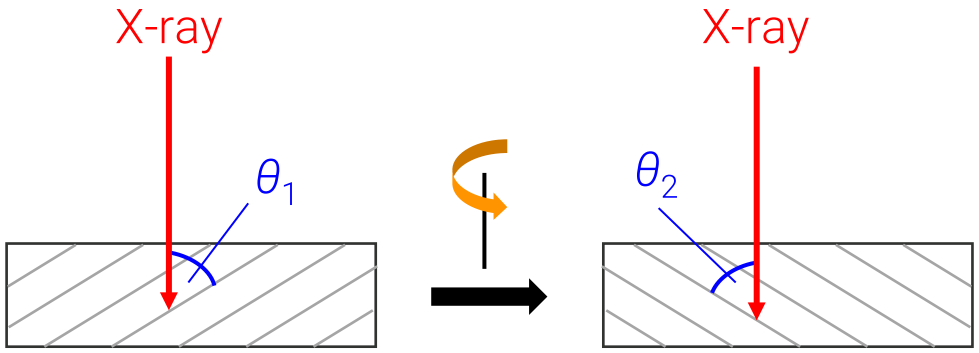
➢ This rotation does not change energy of Bragg peaks.

- Rotation around the normal direction of a lattice plane does not affect the energy of the corresponding Bragg peak.

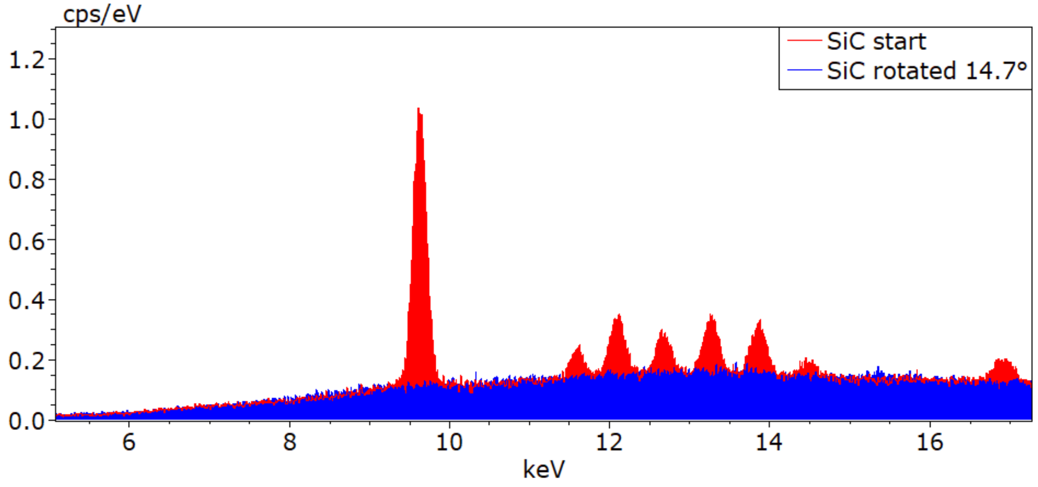
However: Detectors "see" when reflections will move off/onto them. Both rotations can still be visible in the data!

Other reasons for orientation changes to go unnoticed:

- There may be not a single Bragg peak in a spectrum.
- Bragg peaks may strongly overlap with fluorescence peaks.



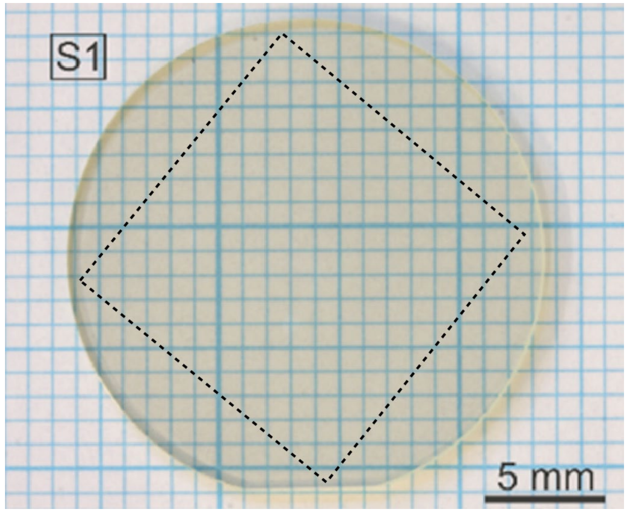
Rotation around direction of primary beam:
$\theta_1 = \theta_2$!

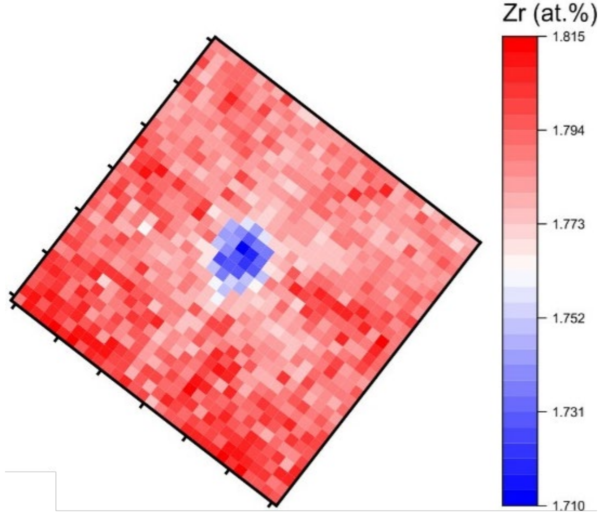


EDLM: Visualizing crystal quality

(Mg,Zr):$SrGa_{12}O_{19}$

- Substrate for epitaxial growth of hexaferrites (magnetoplumbites).
- Growth by Czochralski method.
- Doped with Mg and Zr for better growth properties.





Regular analysis by micro-XRF reveals slight inhomogeneities in dopant concentration.

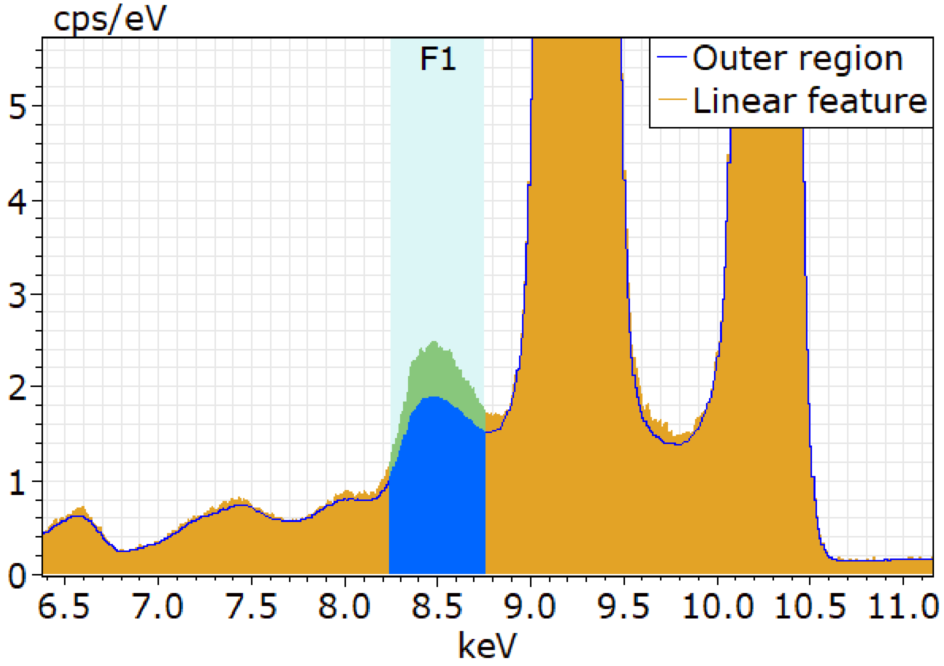
Can EDLM reveal changes to structural quality?

Guguschev *et al.* (2022) Cryst. Growth Des. **22**, 2557.

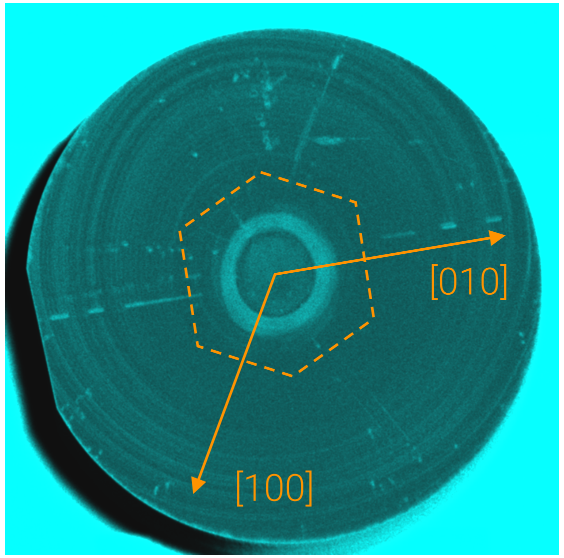
EDLM: Visualizing crystal quality

Material is a single crystal.

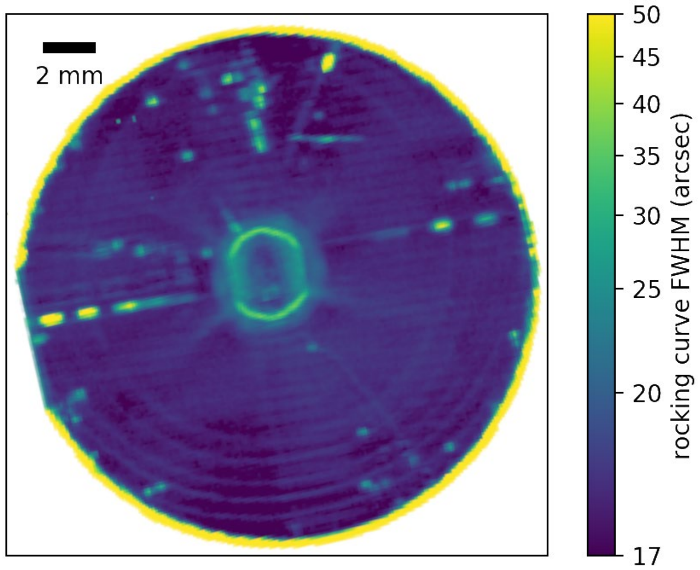
However: EDLM of just a single selected diffraction peak reveals information about structural quality!



PSG: 6/mmm



micro-XRF
(8.25 to 8.75) keV



rocking curve imaging
FWHM of (0 0 20) reflection

EDLM provides qualitatively similar results to rocking curve imaging:

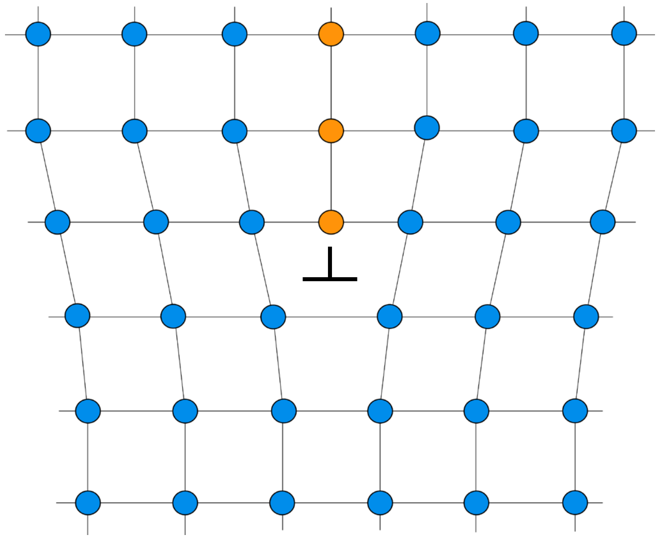
- The crystal has a strained core region.
- Concentric features indicate steps on the growth interface.
- Linear-type features following structural symmetry.

Guguschev *et al.* (2022) Cryst. Growth Des. **22**, 2557.

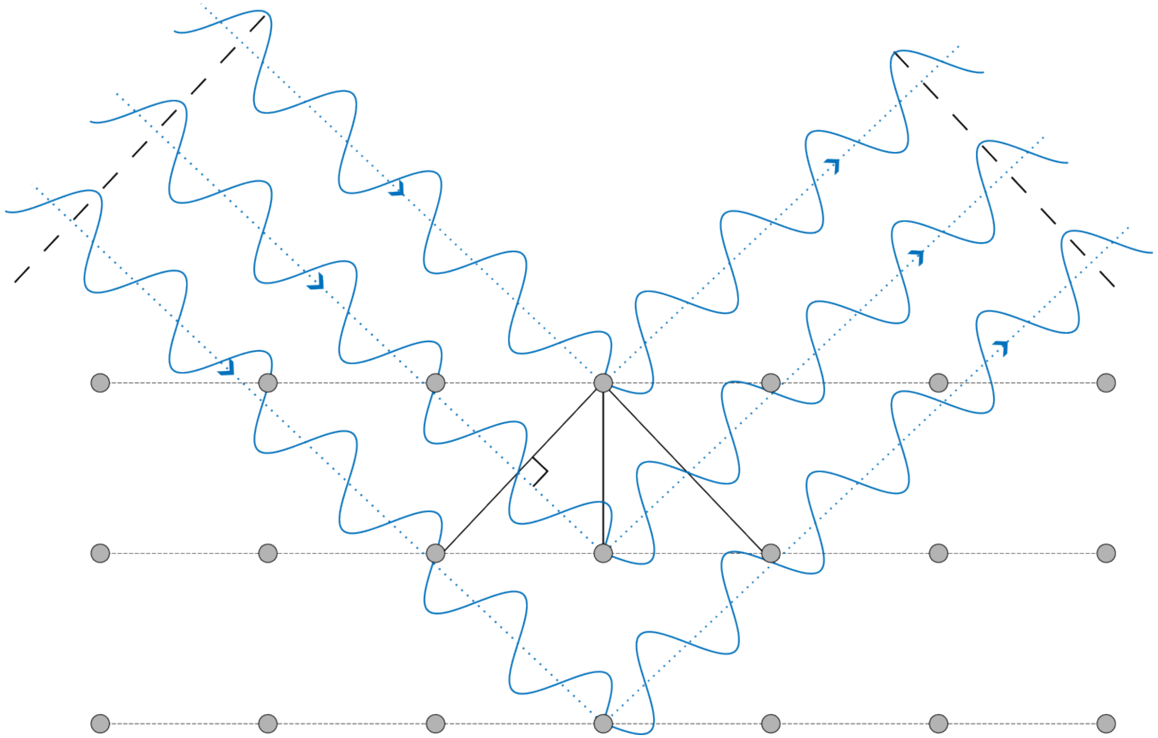
EDLM: Visualizing crystal quality

Why do intensities change in EDLM of a single crystal?

- Dislocations tend to agglomerate impurity elements.
- More varying lattice spacing (Higher mosaicity).
  - ➢ Larger parts of the excitation spectrum may contribute to intensity of diffraction peak.



- Variations in quality translate to changing secondary extinction.

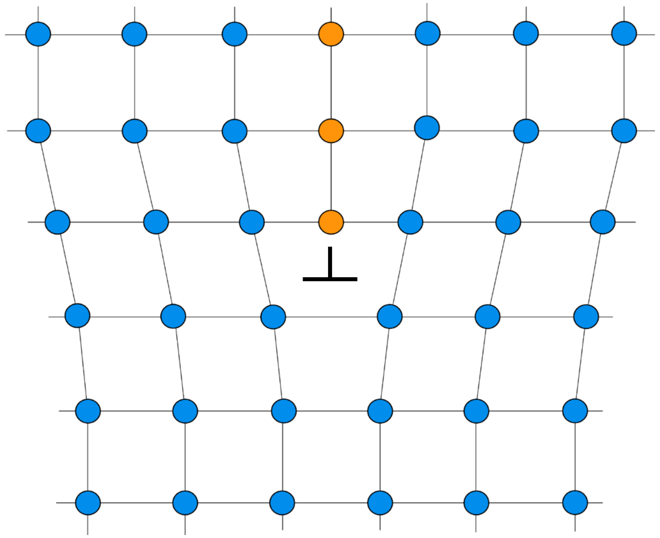


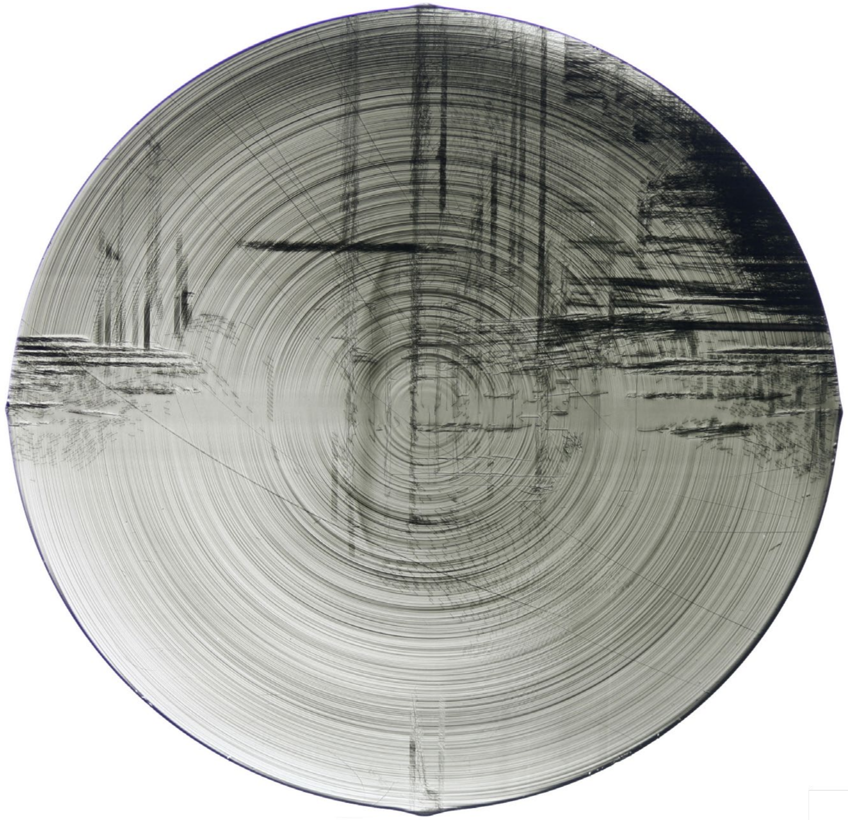
Secondary extinction: Intensity loss of primary beam when crossing a crystal owed to diffraction. Long-range effect.

Micro-XRF for X-ray topography

X-ray topography: Intensity distribution imaging of diffracted X-rays. Defects (inclusions, dislocations, …) cause local lattice strain, modulating diffracted intensity (fine structure of a Bragg peak).

→ Quite similar to EDLM! Can we get comparable data?

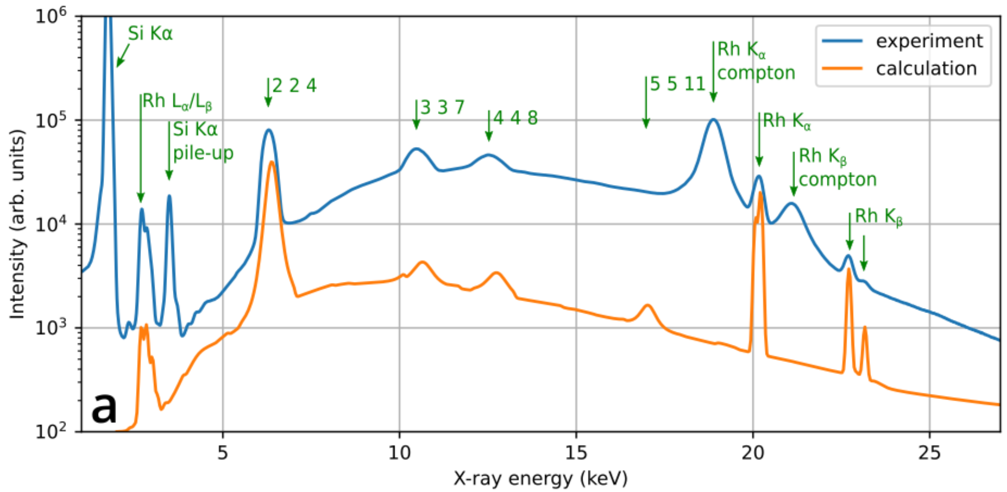


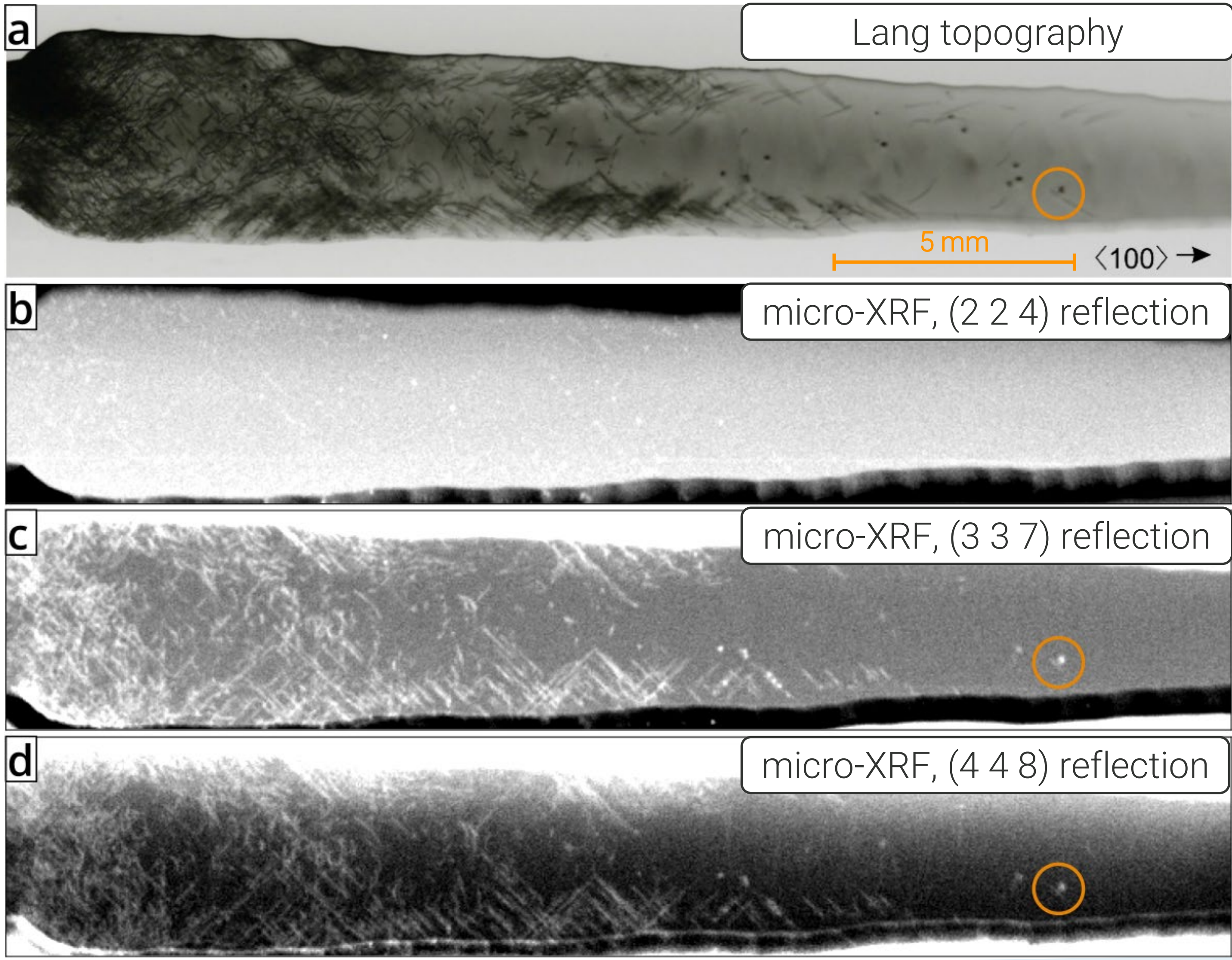


Lang topograph of Ge:Si

Micro-XRF for X-ray topography

- Dislocations in high quality silicon can be visualized!
- Results very similar to those from Lang topography can be acquired.
- Strong energy dependence of solutions.





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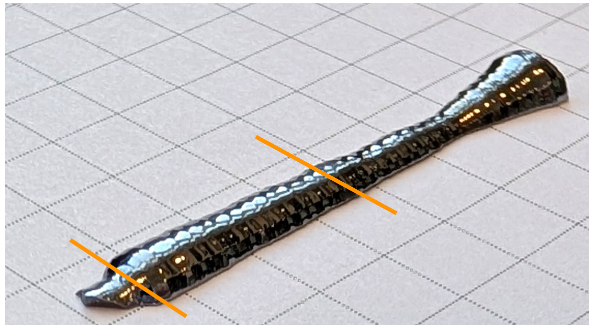
Micro-XRF for X-ray topography

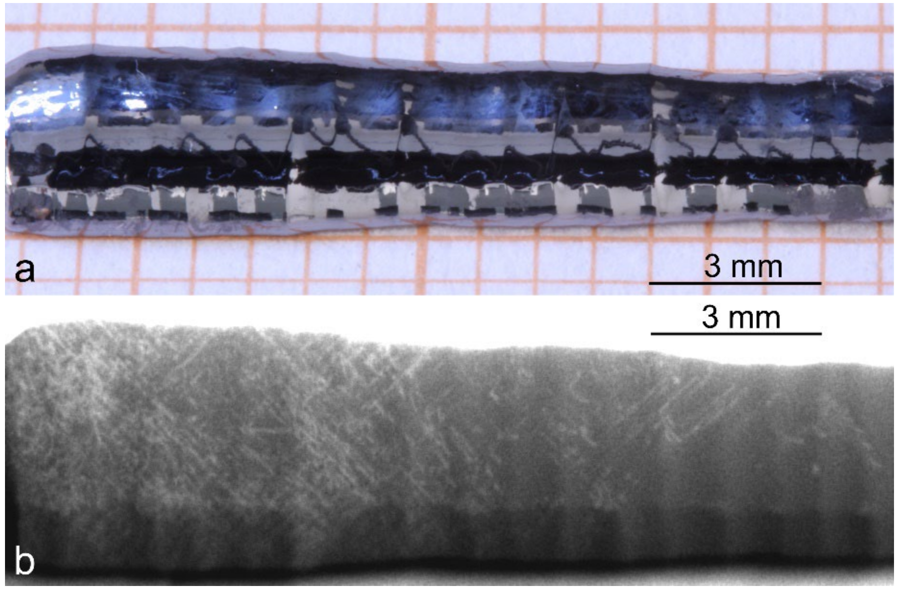
In standard XRT techniques: Curved surfaces problematic. Much smaller problem in micro-XRF due to focused convergent beam!

In micro-XRF:

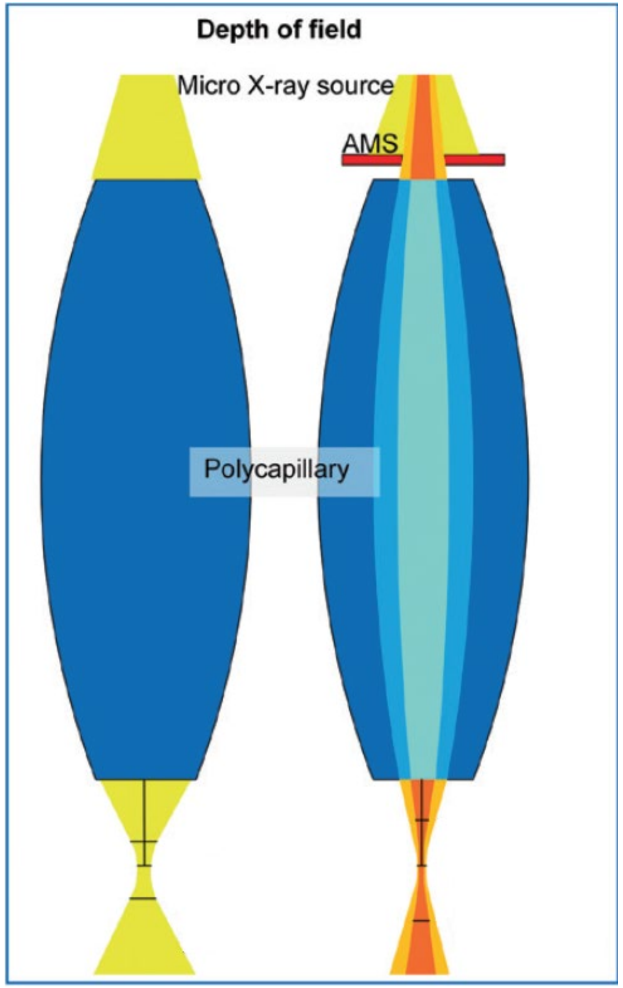
- dislocations can be visualized in curved surfaces,
- dislocations can be visualized in non-polished surfaces!

Investigation strongly aided by reducing the divergence of the primary beam by means of an aperture (AMS, Aperture management system).





Measurement on Si with AMS1000.
Flanks and maxima of (3 3 7) and (4 4 8) reflections.



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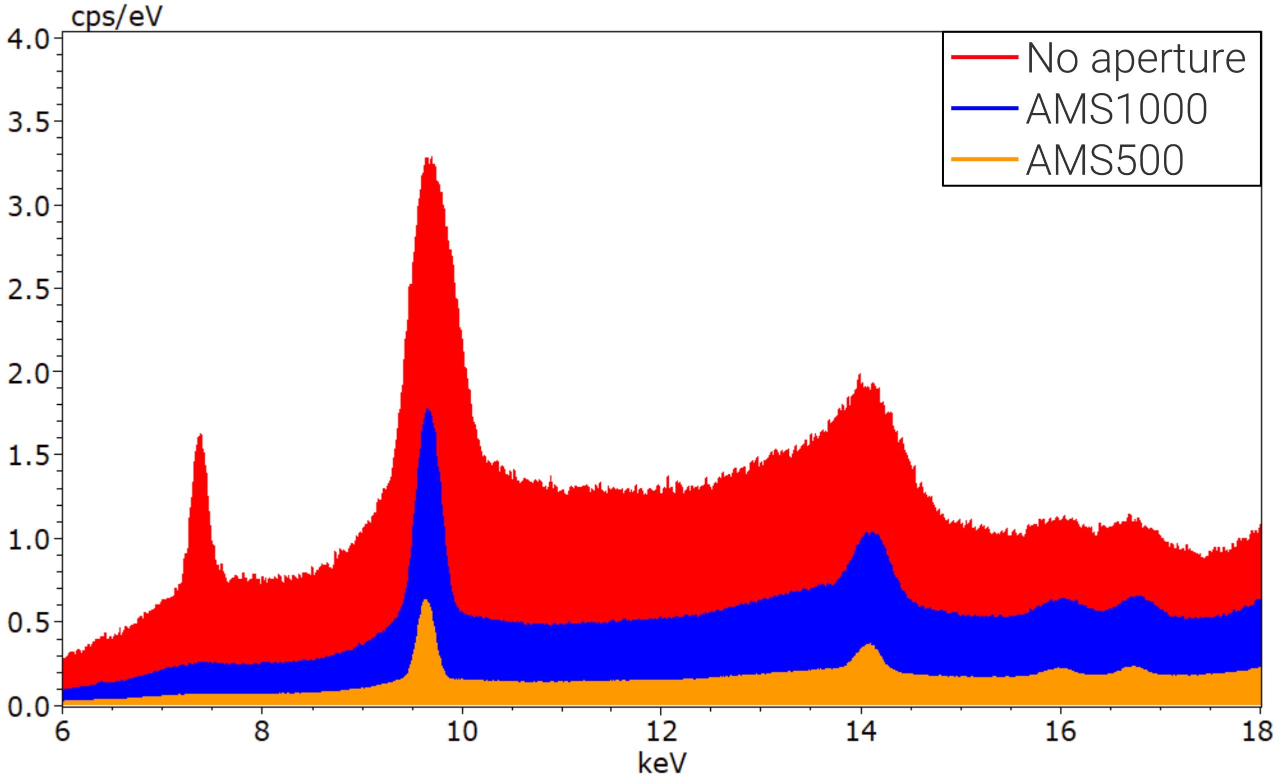
Aperture management and diffraction peaks

Consequences of using an aperture:

- Increased depth of field,
- Reduced width of diffraction peaks,
- Loss of intensity. This example, 6 keV to 18 keV: loss of 57% intensity with AMS 1000, 87% with AMS500),
- Diffraction peaks excited only by strongly divergent radiation may vanish.

In regular EDLM, using an aperture is often not recommended due to the loss of diffraction peaks/reduction in intensity.



Measurements on a silicon single crystal.

AMS1000: 1000 µm aperture.

AMS500: 500 µm aperture.

Summary

Data from micro-XRF measurements on crystalline samples contain information beyond chemistry.

Diffracted radiation can hit detectors with their energy and intensity depending on, among others, the structure type, lattice spacing, mutual orientation of detector/sample, and motif, structural perfection, intensity of primary spectrum, respectively.

Energy-dispersive Laue mapping can visualize intensity distributions of diffraction patterns to

- visualize grain, subgrain and twin boundaries,
- regions with increased defect densities in single crystals, and even
- individual dislocations in high-quality single crystals in X-ray topography applications.

While not every orientation change is necessarily visible, the data from micro-XRF can be used for rapid assessment of structural quality alongside traditional use for investigation of chemistry.

Thank you!

Are there any questions?

For more information, please contact us:
info.baxs@bruker.com

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