

Cathodoluminescence

AMETEK



GATAN

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Journées pédagogiques GN-MEBA (PARIS), 2 & 3 décembre 2019





GATAN : world leader for TEM and SEM accessories

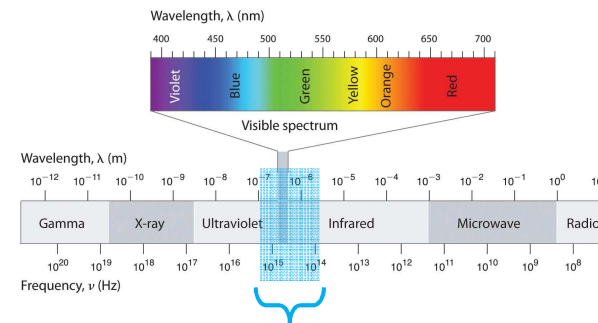
... from Specimen preparation to EELS analysis

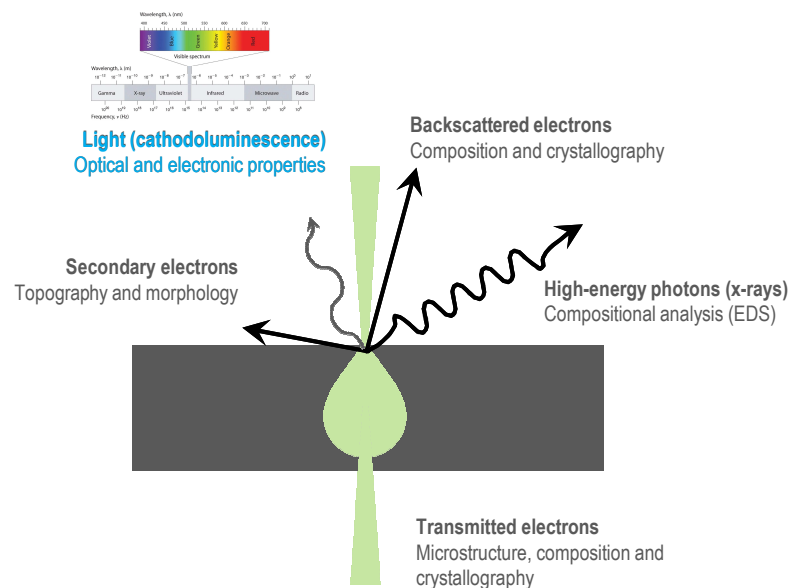
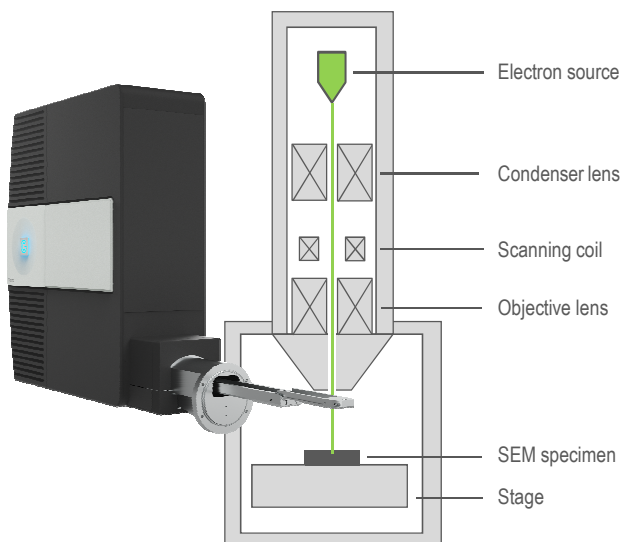
- Specimen Prep : PIPS, PECS, Ilion, Solarus, Iprep, CryoPlunge,...
- Holders : Analytical, CryoTransfer, Cooling/heating, Tensile, Tomography, multi-axes,...
- Imaging : Direct and indirect detection : Rio, Oneview, K2, K3
- Analytical : EELS spectrometers and filters, CL Systems
- SEM accessories : 3View, CL Systems (Monarc), Heating/cooling stages,...



Luminescence

- Luminescence is the emission of photons from a solid when excited by an energy source (e.g. chemical reaction, laser, electrical...)
- **Cathodoluminescence** (CL) – when exciting energy source is electrons
- Luminescence wavelengths: UV, visible, near- and mid-wavelength IR

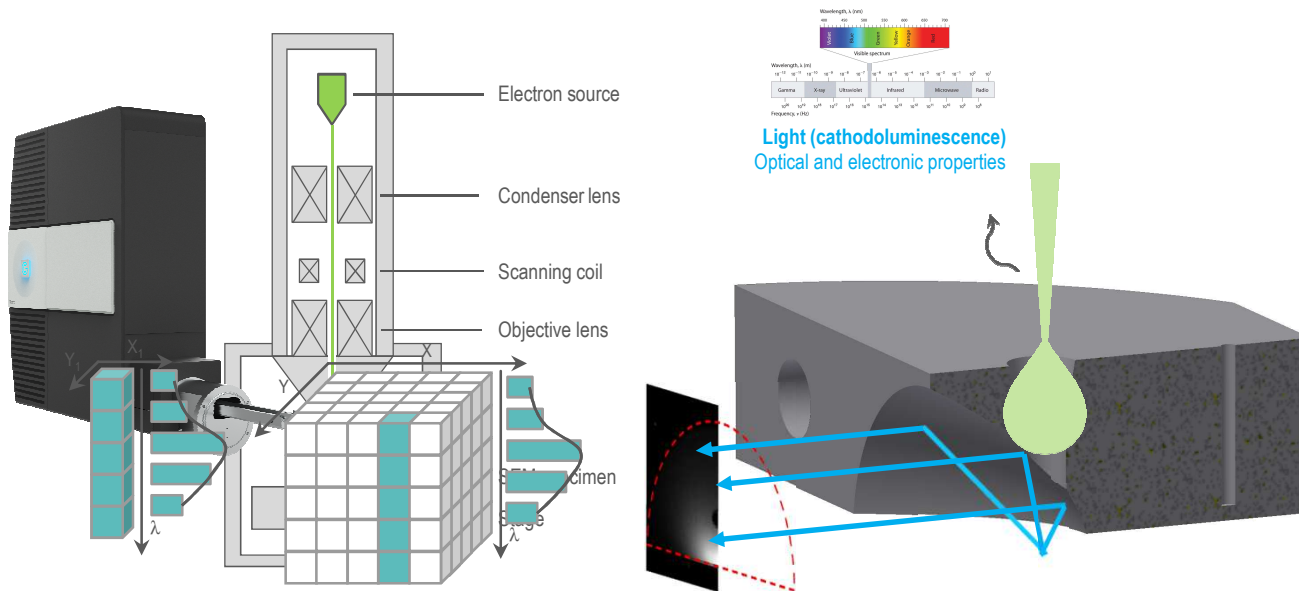




Cathodoluminescence Microscopy

- Correlate optical and, chemical and structural properties from the macro- to nano-scale
- High energy electron beam of a scanning or transmission electron microscope used
- Readily controlled – focused to sub-nanometer probe, positioned with great accuracy and rapidly scanned





Point spectra - Spectrum Image
Cathodoluminescence Microscopy
 (Hyperspectral map)

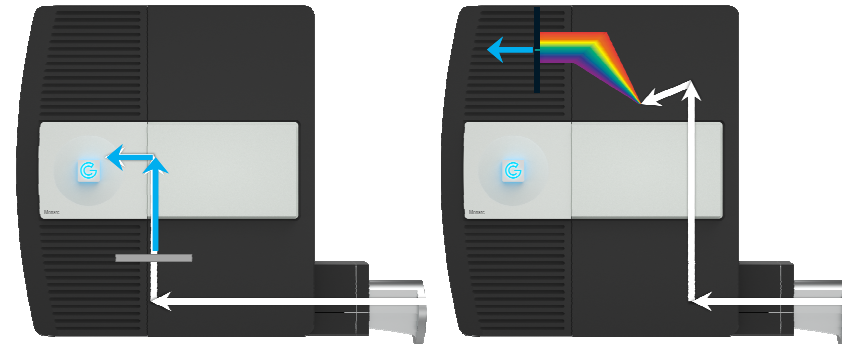
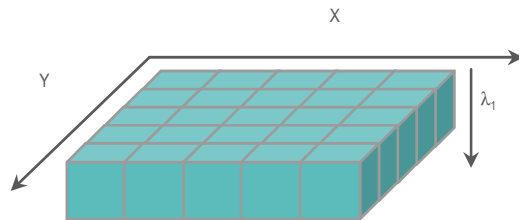


- Correlate optical and, chemical and structural properties from the macro- to nano-scale
- High energy electron beam of a scanning or transmission electron microscope used
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Wavelength-Filtered Map

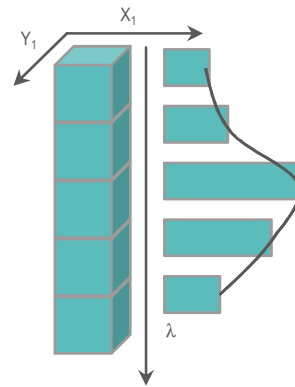
PMT – Record emitted light intensity at each location, then display in a map

Single wavelength – Reveal trace element, impurity, or compositional distributions, plus crystal defects

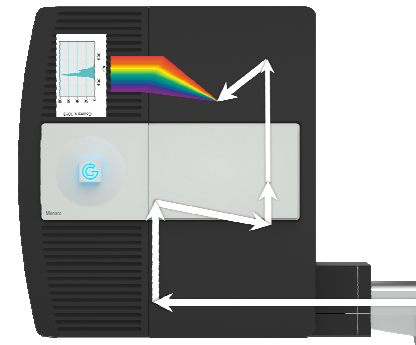


Wavelength-Resolved Spectrum

CCD – Separate the light into its constituent wavelengths, then record the intensity for each wavelength



Spectrum – Measure band gap, local density of optical states, or identifies color centers



Which groups of materials give CL?

- Elemental semiconductors
 - Compound semiconductor
 - Ceramics / insulators / oxides
 - Geological minerals and gemstones
 - Phosphors
 - Stains
 - Some metals
 - Some polymers and organic materials
 - Some food stuffs
 - Pharmaceutical compounds
- Semiconductors
- Insulators
- Metals
- Molecules



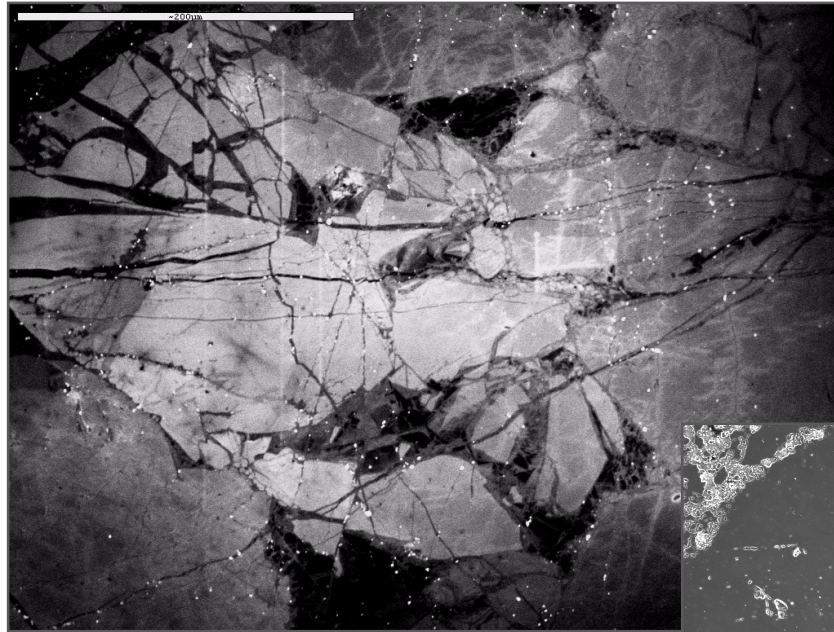
Geoscience Applications



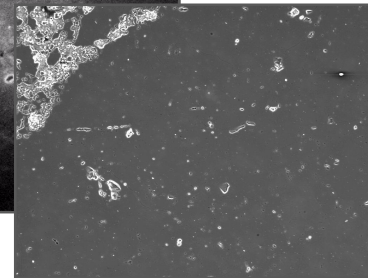
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Petrology



Panchromatic CL Image 6kV
Only CL reveals microstructure



Matching SE image



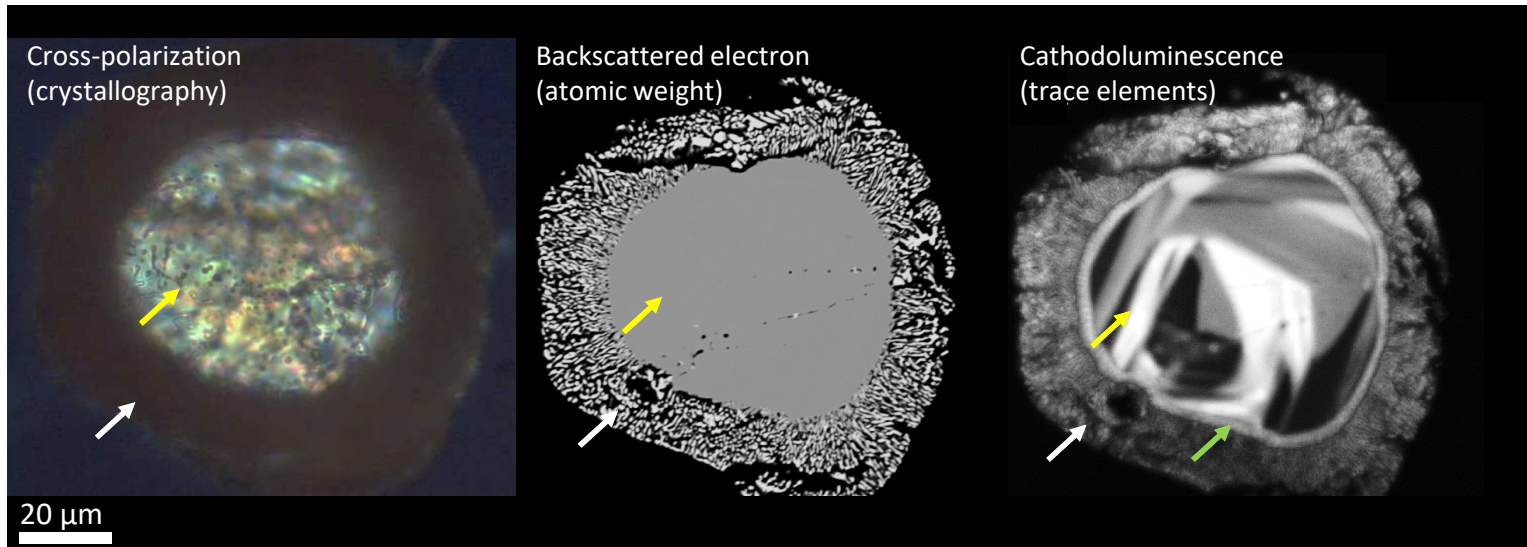
Zircons for Geochronology



Images courtesy of Dr C Loehn



- Unfiltered cathodoluminescence - Photon flux (intensity)
- Wavelength-resolved cathodoluminescence map (color or spectrum)



Reveal Mineral Texture not Observable with Other Techniques

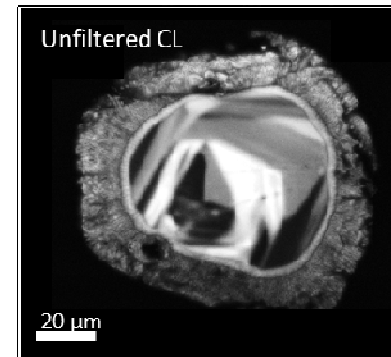
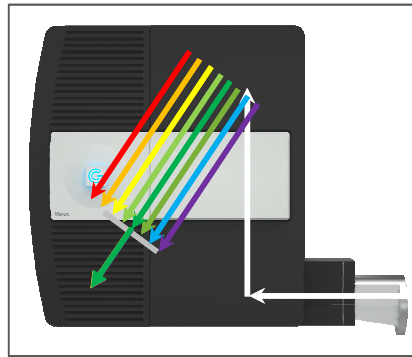
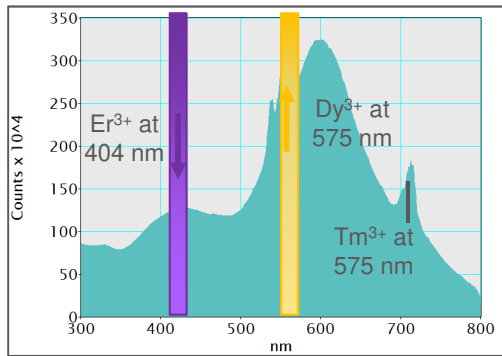
- A partially-decomposed zircon in Mistatin Lake impact melt glass
- Exceptionally well-preserved vermicular decomposition rim textures (ZrO_2 , non-crystalline SiO_2)
- Crystalline ZrSiO_4 core; only CL reveals crystallization zoning patterns
- Distinctive zoning related to the grain – impact melt interaction

Images courtesy of Michael Zanetti, Washington University in St. Louis and the McDonnell Center for the Space Sciences, Earth and Planetary Science Dept.



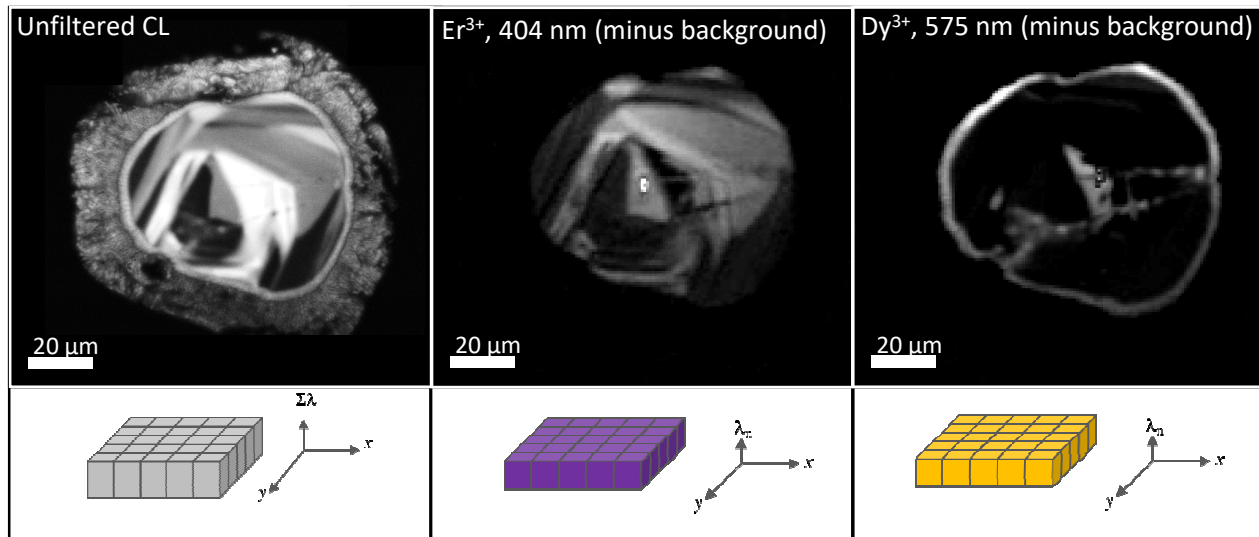
Mapping Rare Earth Element Distributions in Zircons

CL Spectrum – Zircon



Images captured using the MonoCL4™ Elite detector and provided courtesy of Michael Zanetti, Washington University in St. Louis and the McDonnell Center for the Space Sciences, Earth and Planetary Science Dept.

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Mapping Rare Earth Element Distributions in Zircons

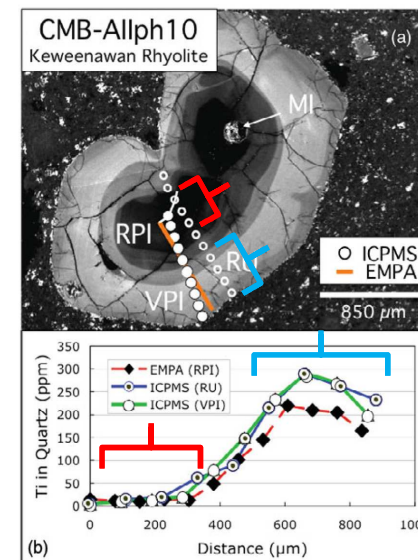
- Wavelength-filtered CL images at 404 and 575 nm corresponding to Er³⁺ and Dy³⁺ rare earth ions; images processed to remove the ZrSiO₄ background signal at 650 nm
- The Er³⁺ and Dy³⁺ concentrations were in the range 10 – 300 ppm (determined by EPMA)

Images captured using the MonoCL4™ Elite detector and provided courtesy of Michael Zanetti, Washington University in St. Louis and the McDonnell Center for the Space Sciences, Earth and Planetary Science Dept.



Quantitative Analysis of Trace Elements

- Natural quartz samples contain many trace elements (e.g., Ti, Al, Li, Fe, K)
 - Contents may vary from 0.1 – >100 ppm
- Unfiltered CL imaging reveals details of intragrain compositional variability and structure
- But limited quantitative information
- Microbeam analysis required—but is time-consuming (and costly)
- Appears that some relationship between regions of intense CL emission and Ti concentration exists



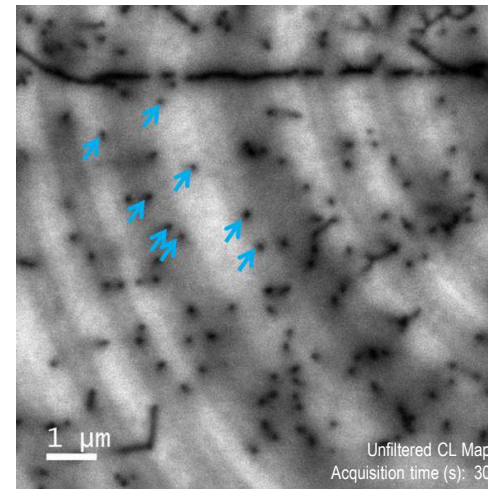
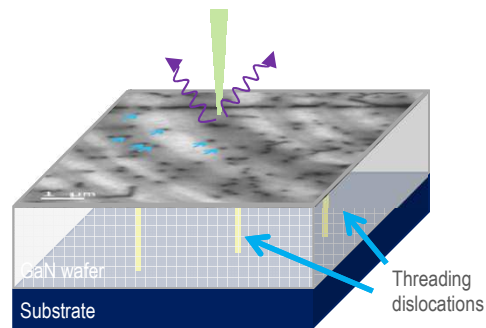
After: Leeman *et al.*, *Microsc. Microanal.* **18**, 1322–1341, 2012

Semiconductors Applications



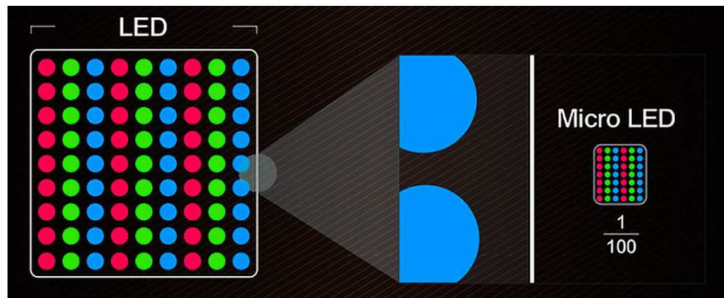
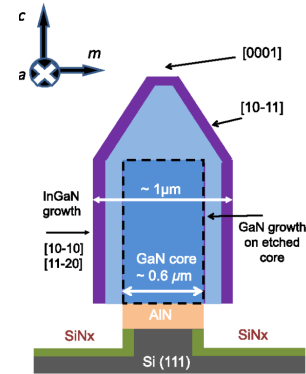
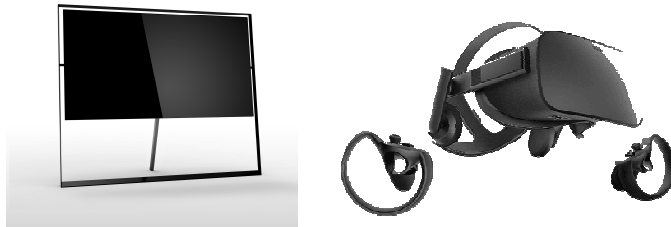
Quantify Density of Crystal Defects

- Gallium nitride – used in light emitting diodes and high power electronics
- Dislocations reduce device operating lifetimes, increase leakage current, and compromise efficiency
- Important to quantify defect density for quality assurance purposes

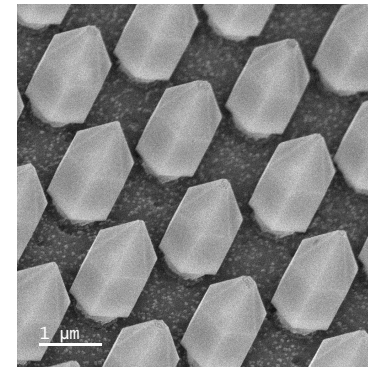


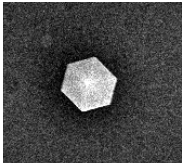
- Black spots are threading dislocations intersecting the surface
- Dislocation density: $5.2 \times 10^5 \text{ cm}^{-2}$

High resolution displays Micro-LED Hexagonal Pillar Array



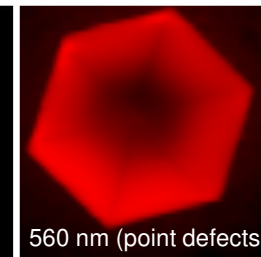
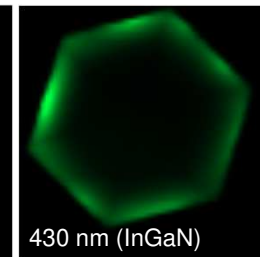
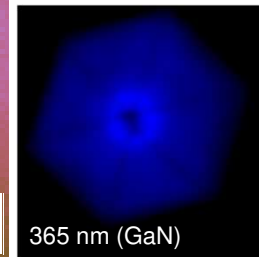
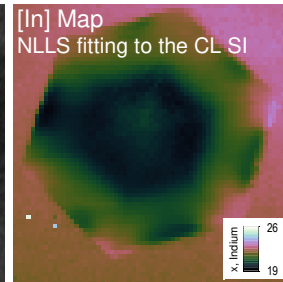
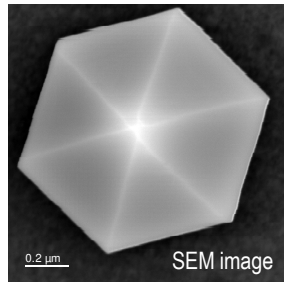
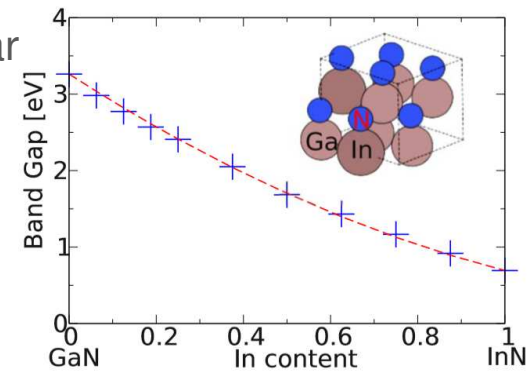
An illustration of the size difference between traditional LEDs and MicroLEDs.
Trendforce



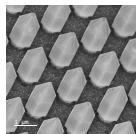


Compositional Variation and Defects

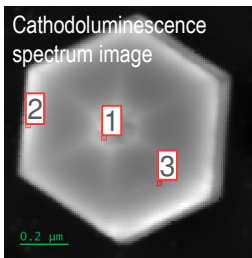
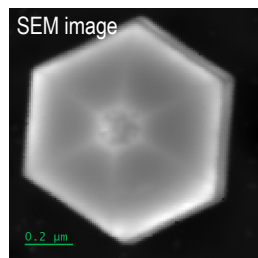
- CL Spectrum image from single pillar
 - Observe CL without effects from array
 - Compositional mapping
 - *Which direction is the light going?*



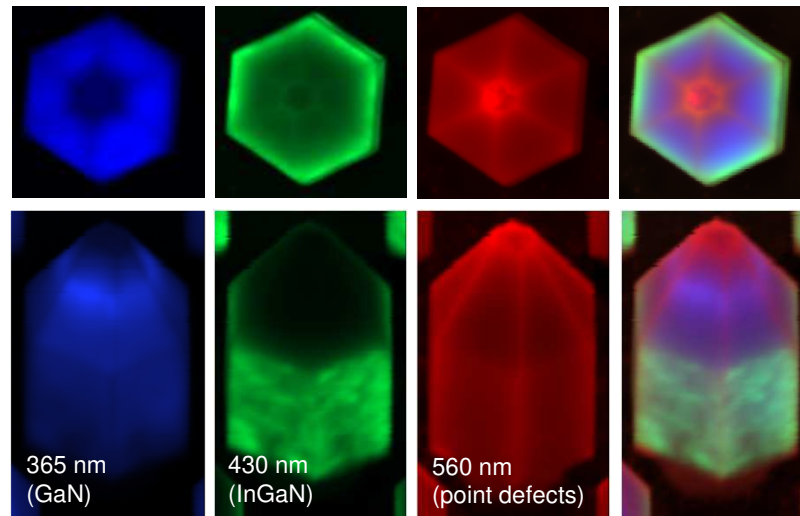
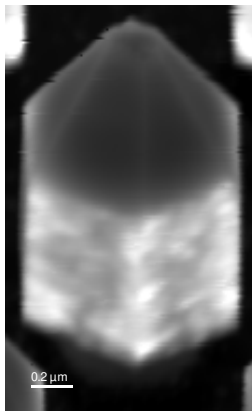
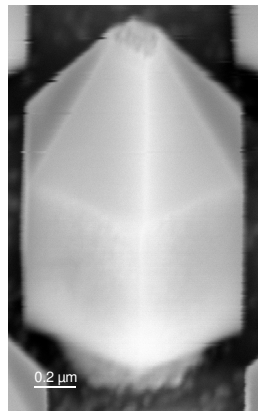
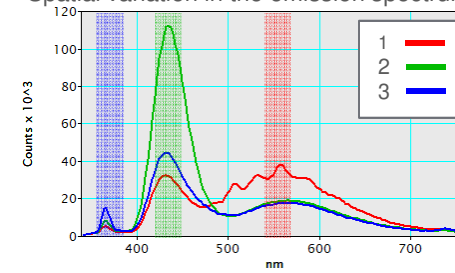
After: Moses *et al.*, Appl. Phys. Lett. **96**, 021908-1-3, 2010



Effective Compositional Variation and Defects

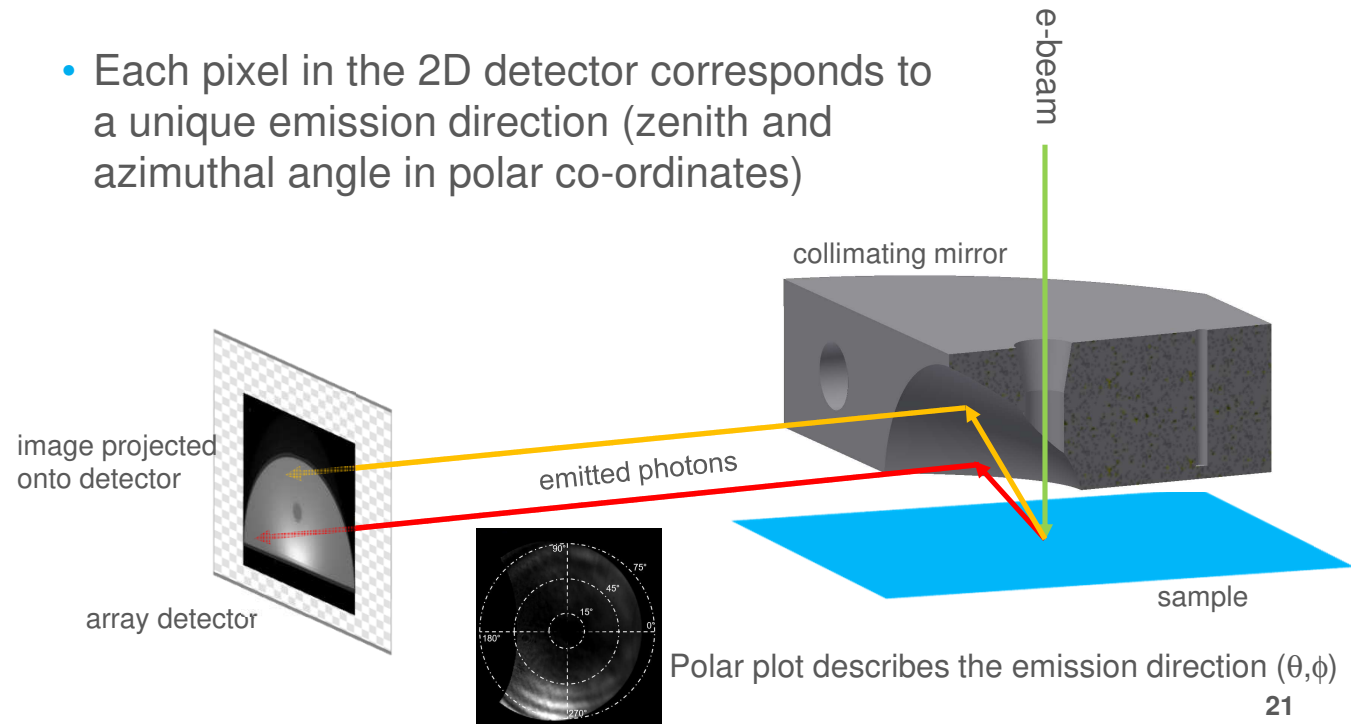


Spatial variation in the emission spectrum

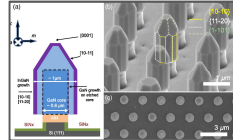
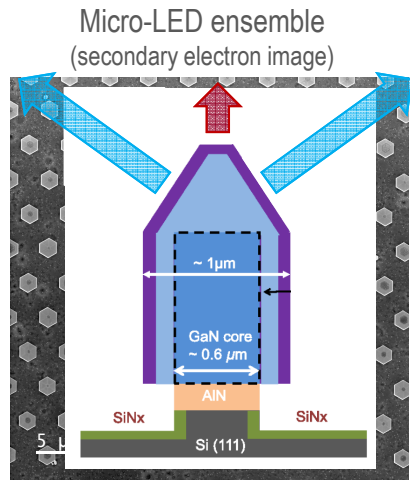


Angle-Resolved Cathodoluminescence

- Each pixel in the 2D detector corresponds to a unique emission direction (zenith and azimuthal angle in polar co-ordinates)

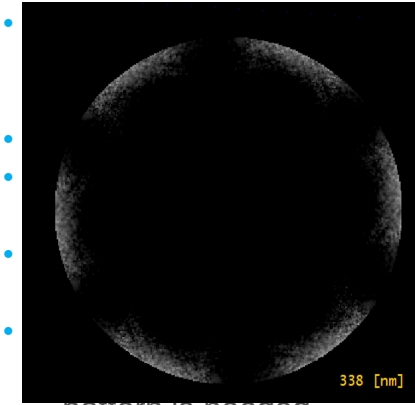
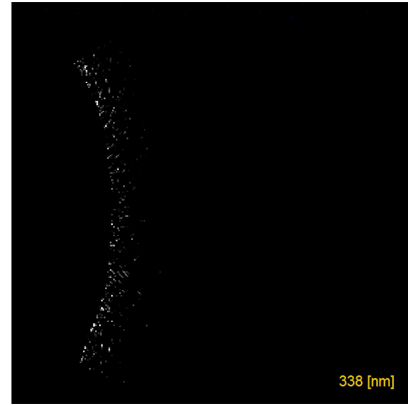


Measuring Emission Patterns with the Monarc Pro

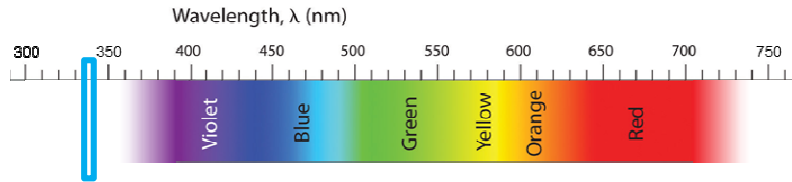


Wavelength-resolved emission pattern
(wavelength- and angle-resolved CL)

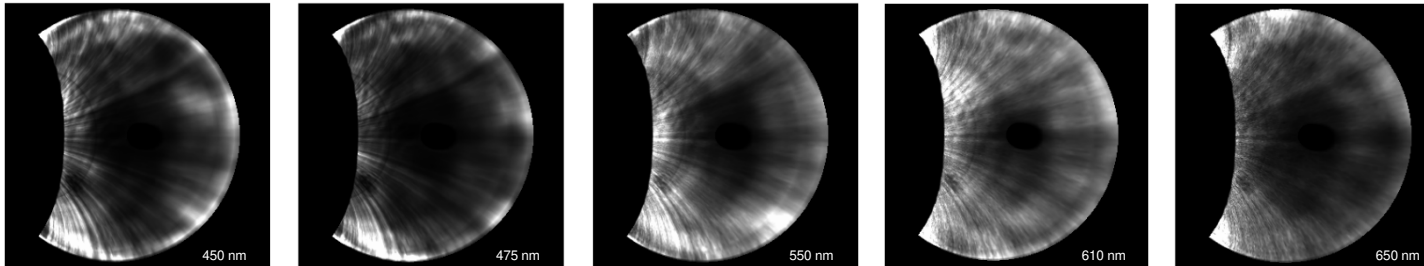
Emission pattern (angle-resolved CL) Single Array



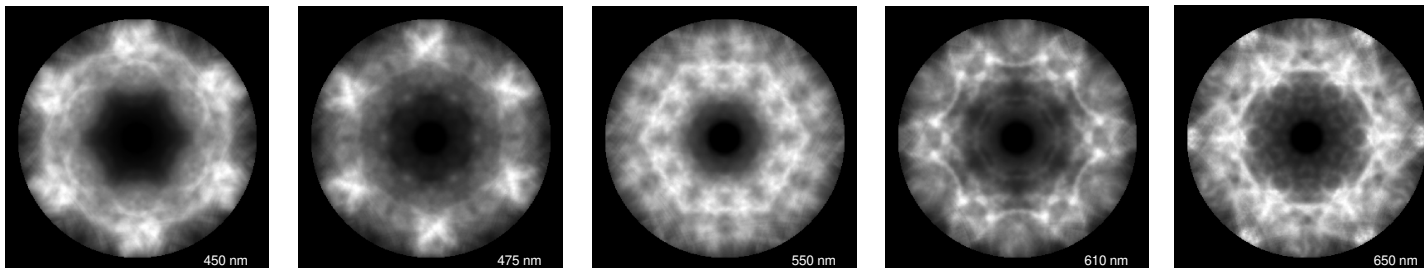
pattern is needed



Single Pillar



Array



Comparing Wavelength Angular Emission Patterns

- MicroLED pillar emits different colors at different angles in and out of the array
- Angular emission selectivity from the array ensemble is greatly enhanced by the array due to reflections, interference, or photonic effects



Summary

- Cathodoluminescence microscopy is an luminescence spectroscopy which can offer nanometer-scale spatial resolution
- Enables correlation of optical properties with material composition
- Cathodoluminescence has great many uses in reconstructing geological processes based on crystal chemistry
- Micro LEDs in array lead to enhanced emission properties as compared to single micro LED
- Light emission direction depends on LED shape, color, and array lattice

