Raman mapping: Introduction and application to the imaging of zircon textures

Dr. Tamás VÁCZI
Department of Mineralogy
Eötvös Loránd University, Budapest
C.V. Raman’s spectrographs
Sir Chandrasekhara Venkata Raman

inelastic scattering of visible light, experimental proof: 1928

Nobel Prize: 1930

"... the new field of spectroscopy has practically unrestricted scope in the study of problems related to the structure of matter."

(Nobel lecture, 1930)
Today’s laboratory spectrometers

Not shown:

• computer driving motorised/piezo-driven stage that enables collecting and processing multidimensional data sets
• user (!!!)
HOW?
Mapping

Mapping using **point focus**: “0D” illumination, spot stepped in a raster
- “true confocal” microscopy
- best optical performance at the cost of throughput
- excellent to good spectral selectivity
- good depth selectivity
Fast mapping

One of several fast mapping options: **line focus**
“instantaneous” in 1D; line profile stepped across surface
- “pseudo-confocal” microscopy
- used for high-speed mapping (or less beam damage)
- excellent to good spectral selectivity
- good depth selectivity
Imaging

Multispectral or hyperspectral direct imaging: “instantaneous” 2D images.

• homogeneous, global illumination
• needs special band pass filter device (e.g. LCTF)
• good for high-throughput screening, remote sensing etc.
• moderate to poor spectral selectivity
• no depth selectivity, no below-surface imaging
Mapping vs. imaging

modified from Lee (2012)
Sampling methods

We map a surface through rastering the sampling spot (map).

- Stage (sample) moves under a stationary beam
- Laser beam stepped over sample – limited by FOV, vignetting
- Combined techniques can cover gaps between steps or decrease damage

3D: raster — focus — raster — focus — raster …
Choosing step sizes

Nyquist criterion: signal variation should be sampled at half the intervals of the *smallest expected feature size* (originally frequency).

- **undersampling**: fast & good to cover large area at the risk of missing small features
- **par-sampling**: best match to spot size
- **oversampling**: best definition of shapes

\[
\lambda = 532 \text{ nm}; (a) 1 \mu\text{m}; (b) 0.5 \mu\text{m}; (c) 0.1 \mu\text{m}
\]

Similar concerns exist for \( z \) (depth). There is an ugly time penalty for small step sizes!
Data reduction

Purpose: convert data to information (spatial info from a large number of spectra). To create informative imagery from raw data several steps may be necessary:

• [CRE/spike elimination, smoothing]
• background subtraction – you may want to use the background (PL) signal!
• image generation
• corrections, adjustments
• analysis
• publication
• happiness!
Data reduction: creating images

Raman maps are multidimensional data sets: each $x,y$ pixel/$x,y,z$ voxel contains a Raman spectrum. Raw maps are only viewable with dedicated spectroscopy software, to visualize chemical/physical content we need to process them.

1. **Integral intensities:** uses the integral of the signal between two limits (cursors), with or without “baseline” subtraction, to display a *basic distribution of a few components* – only good for intensities.
Data reduction: creating images

Raman maps are multidimensional data sets: each $x,y$ pixel/$x,y,z$ voxel contains a Raman spectrum. Raw maps are only viewable with dedicated spectroscopy software, to visualize chemical/physical content we need to process them.

2. **Spectral parameters** (position, intensity, FWHM): uses parameters from individual, fitted analytical profiles to display phase distribution, quantitative physical and chemical properties and their changes.
Data reduction: creating images

Raman maps are multidimensional data sets: each $x,y$ pixel/$x,y,z$ voxel contains a Raman spectrum. Raw maps are only viewable with dedicated spectroscopy software, to visualize chemical/physical content we need to process them.

3. **Multivariate analysis:** uses entire spectra to decompose multiple/mixed spectra, to display subtle variations or a distribution of many phases — good treatment of mixed spectra and broad bands

![Supervised DCLS fitting of a linear combination of model spectra](image1.png)

schwertmannite, goethite
Image smoothing (blurring)

May show a more appealing view of the same image by blurring pixel edges (similar to antialiasing) — no change in data!

Myrmekite from the Duluth Complex (Minnesota). A DCLS fit can distinguish between quartz, feldspar and different feldspar orientations. (532 nm, ~40 mW, 2×2.5 s, 85×85 steps/1 µm)
The best achievable resolution is determined by the spot size and the desired contrast.

Black inclusion in serpentine: hematite in magnetite.

The thickness of the marked lamella is 0.29 µm (473 nm, N.A. 0.9, \( d_R = 0.32 \) µm, 4 s, 109×80 steps/0.2 µm).
WHAT?
We create images in which contrast comes from identity. You can display a distribution of anything that can be derived from single spectra: intrinsic chemical and/or physical properties.

- structure
- composition
- strain
- order, defects
- crystal orientation
- grain size
- grain shape
- ...
- ...
- ...

Through mapping you may get location bias out of the picture and move towards representative and quantitative distribution information.
Phase distribution

Tree opal from Megyaszó (NE Hungary): no detail in reflected-light microscope, but very well distinguishable on a chemical image (mixed Raman/PL map, 473 nm).

red: opal
green: strong PL emission
blue: C–H$_x$ vibrations (artefact?)
Iron-rich crust on a rock fragment from the Bányabérc waste dump, Mátra Mts., Hungary. As a result of subaerial weathering processes in an acidic environment, crusts of iron oxide-hydroxides, oxy-hydroxide-sulfates and sulfates formed. (633 nm, ~1.3 mW, 2×10 s, 90×115 steps/0.4 µm)

Phase map (goethite, schwertmannite)
Phase distribution

Submicrometre association of pyrite and marcasite (colloform pyrite) from Parádfürdő (Recsk Ore Complex, NE Hungary). Due to minor band shifts (heating?), DCLS fitting was inappropriate. Note that optical resolution is insufficient for this material. (633 nm, ~3.3 mW, 2×10 s, 100×100 steps/0.2 µm)
Chemical zoning, crystal orientation

*Pyrite* with anomalously high Pb content (Bor area, Serbia, sample courtesy A. Pacevski). The two Raman maps show the same area!
Crystal defects

*Chalcedony growth zones:* map constructed from the intensity of the Si—OH defect band (@503 cm⁻¹) (Schmidt et al., 2012)
Strain map

*Nanoindenter impression in single-crystal silicon* (Berkovich tip, 20 mN). Assuming uniaxial stress, band shift is convertible into strain: \( +1 \text{ cm}^{-1} = -500 \text{ MPa} \).

Nanoindenter impression in single-crystal silicon (Berkovich tip, 20 mN). In addition to strain haloes, further analysis reveals deviatoric stress and amorphous Si. (633 nm, ~4 mW, 2×1.5 s, 108×106 steps/0.1 µm)
3D mapping: new mineral!

*Salt melt inclusion* in an unusual, Cu-free Au-porphyry deposit (Biely Vrch, Javorie Stratovolcano, Slovakia). 3D mapping was helpful to locate the purest spectra of salts (still, spectrum subtraction was necessary). Raman analysis confirmed the analogy of the *new mineral javorieite* (IMA 2016-020) with synthetic KFeCl$_3$.

(532 nm, ~40 mW, 4×3 s, 32×29 x-y steps/0.3 µm, 3 z steps/1.0 µm)

P. Koděra et al., in prep.
Raman imaging of zircon
Zircon

zircon

- $\text{ZrSiO}_4 (Z = 4)$
- $I4_1/amd$
- ortho/nesosilicate

- $\text{Zr site: ZrO}_8$
  compatible with large HFS elements (Hf, REE, U, Th)
- $\text{Si site: SiO}_4$
  P, 4H
- interstitial sites
Zircon textures

PLM

CL

BSE

Nasdala et al. (2005)

J.W. Valley (Peck et al., 2000)

Geisler et al. (2005)

Ireland & Williams (2003)

Arizona LaserChron Center

50 µm

4404 Ma

m-(Zr,U)O₂

50 µm

100 µm
Raman spectroscopy: structural state

Increasing radiation damage:
- intensity loss
- peak shift
- band broadening
- amorphous fraction
- (new peaks)

Dose \((D)\): \(10^{18}\) alpha events/g
- U & Th concentrations
- age

Naturally accumulated damage
- dose
- thermal history (!)
Raman spectroscopy: structural state

A: Saxonian rhyolite
B: Moon
C: Meissen massif monzonite
D: Frankenstein gabbro

+ : un-annealed zircon
○: Sri Lankan zircon (effective dose, corrected for thermal annealing)

\[
\nu_3(\text{SiO}_4) \text{ FWHM} [\text{cm}^{-1}] = \alpha \text{ dose } [10^{16}/\text{mg}]
\]

\[
\text{Damage [dpa]}
\]

\[
\text{Dose } (\times 10^{15} \alpha\text{-events/mg})
\]

Nasdala et al. (2001)
Pilenik et al. (2003)
Raman spectroscopy: structural state

A: Saxonian rhyolite
B: Moon
C: Meissen massif monzonite
D: Frankenstein gabbro

Nasdala et al. (2001)

\[ v_3(\text{SiO}_4) \text{ FWHM} \text{ [cm}^{-1}\text{]} \]

\[ \alpha \text{ dose [10}^{16}/\text{mg]} \]

\[ \text{Irradiation dose [10}^{18} \alpha/\text{g]} \]

\[ \nu_3(\text{SiO}_4) \text{ FWHM [cm}^{-1}\text{]} \]

\[ 0 \text{ to } 0.10 \text{ dpa} \]

\[ +: \text{un-annealed zircon} \]
\[ \circ: \text{Sri Lankan zircon (effective dose, corrected for thermal annealing)} \]

Váčzi & Nasdala, in prep.
BSE contrast in zircon

BSE contrast

Sources of contrast in back-scattered electron (BSE) images

- BSE signal intensity is *qualitative* and *relative*: brightness, contrast are adjusted until *image looks just fine*
  
  backscattering coefficient \( \eta \): fraction of primary electrons emitted from sample surface

- BSE yield is a strong function of the average atomic number (\( \bar{Z} \)): "composition contrast"

\[
\bar{Z} = \left( \sum_i c_i \sqrt{Z_i} \right)^2
\]

\[
\bar{\eta} = 1.75 \cdot 10^{-3} \bar{Z} + 0.37 \left[ 1 - \exp\left( -0.015 \cdot \bar{Z}^{1.3} \right) \right]
\]

according to Pouchou & Pichoir (1991)
BSE contrast

Sources of contrast in back-scattered electron (BSE) images

• crystallographic contrast

orientation contrast

phase contrast
BSE contrast in zircon

BSE images of (unaltered) zircon single crystals:

- no orientation contrast
- average Z contrast?

Nasdala et al. (Am. Mineral., 2006)

- Bluffpoint quartz diorite, Ontario (2732 Ma)
- Mulkahy Lake gabbro, Ontario (2733 Ma)
- Afella gneis, Algeria (1983 Ma)
- Leucogranite, Adirondacks (1045 Ma)
- Granite, Demitz, Saxony (530 Ma)
- Tuff, Hungary (19 Ma)
- Synthetic zircon (0 Ma)
BSE contrast in zircon

- take a crystal
- cut it in two halves
- anneal one half
- mount and observe the two halves together
BSE contrast in zircon

zircon crystal from Mulkahy Lake, Canada (sample D.W. Davis, Toronto)

**BSE:** grayscale image of backscattering coefficient

**Raman map:** Colour-coded representation of crystallinity

Nasdala et al. (Am. Mineral., 2006)
BSE contrast in zircon

- direct correlation between BSE intensity and the degree of radiation damage is observed.

The contrast seen in BSE images of radiation-damaged, unaltered zircon crystals reflects the structural state, not chemical composition!
Electron-beam annealing

Electron-beam annealing

Electron microprobe analysis irradiates samples with moderate-energy electrons (typically 15–20 keV, up to 200 nA and 1000s of s).

Raman spectroscopy: Irradiation with an electron beam induces an ordering of damage in zircon.
Electron-beam annealing

- Samples: gem-quality, homogeneous zircon fragments from Sri Lanka
- Note that Sri Lankan zircons do not show the damage corresponding to their calculated actinide content and age, a ca. 0.55× correction is needed (Nasdala et al., 2004)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Effective α dose (10^{18}/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>G4</td>
<td>2.46–2.70</td>
</tr>
<tr>
<td>OR1</td>
<td>1.44–1.61</td>
</tr>
<tr>
<td>M146</td>
<td>1.06–1.12</td>
</tr>
<tr>
<td>M144</td>
<td>0.47–0.50</td>
</tr>
<tr>
<td>syn</td>
<td>0</td>
</tr>
</tbody>
</table>

![Raman shift vs. Intensity graph](image1)
![Effective α dose graph](image2)
Electron-beam annealing

- **Aim**: a systematic evaluation of electron beam–zircon interaction
- **EPMA (JEOL JXA-8600 Superprobe)**
- fixed energy (20 keV) beam current (,,flux“): 10 nA–200 nA irradiation time: 10–500 s
Electron-beam annealing
Electron-beam annealing

IF-deconvoluted and position-corrected data

electron-beam annealing  thermal annealing

Geisler et al. (2001)
Electron-beam annealing

A detailed map can show annealing spots without positioning errors. (632.8 nm, ~13 mW, 46×40 steps/0.3 μm)

sample M144:
• 200 nA/500 s, 100 nA/500 s, 100 nA/200 s
• FIB-milled crosses
Electron-beam annealing

3D mapping: imaging of damage distribution in the depth of the electron-beam interaction volume

• surface focus is satisfactory
• small electron energies still appear to anneal damage
  (633 nm, ~13 mW, 20×40 steps/0.2 µm x-y, 8 steps/0.5 µm z)

x-z section of 3D FWHM map

CASINO MC simulation of energy transfer
PL mapping
REE PL emissions probe the crystal field around the $^{\text{VIII}}\text{Zr}$ site.

PL mapping

PL map (532 nm, 4 mW, 2×8 s, 114×70 steps/1 µm)
Free advice: NEVER forget the “f”!