Coherent defocused orientation imaging of nano-crystals in second harmonic generation microscopy

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Aims & applications

Measurement of the 3D orientation of single nonlinear nano-emitters:

• To probe local electromagnetic field;

• To understand physical and chemical properties of nano-structures;

• To probe local environment of this nonlinear tag;

⇒ We use 2-photon excitation microscopy
Polarized nonlinear microscopy

Rotation of the linear polarization of the excitation beam

High numerical aperture objective

SHG or 2PF

Laser 100fs 80Mhz 690 – 1020 nm

Analysis direction

SHG mapping and local orientation information

C. Anceau et al., Chem Phys Lett (2005)
Polarized 2PE-microscopy in nano-crystals

Diagnostics of the crystalline nature of nano-crystals (2PF)


2D or 3D orientation of the crystalline structure (SHG)

Defocused orientation imaging helps to read this information!

Information about the source orientation is conserved across the microscope!

Defocused imaging helps to read this information!

Defocused orientation imaging

Image in the focal plane
No visible structure

defocused imaging 5 mm
Visible structures

defocused imaging 10 mm
Visible sub-structures

Enhancement of the defocus
Improvement of the precision of the orientation measurement
Application
Defocused orientation & position imaging (DOPI)

Figure 2. Measured defocused image of Cy5 molecules embedded in poly(vinyl alcohol) on glass near the air/polymer interface. Defocusing was achieved by moving the objective 1 μm toward the sample.

DOPI of myosin V along an actin fiber

Parameters

**Microscope:** Numerical aperture (NA=1.4), index of immersion liquid (n=1.518), magnification (m=100), Camera position (15 mm)

**Excitation:** Wavelength (\( \lambda = 945 \text{ nm} \)), polarization (linear), shape (Gaussian)

**Sample:** Orientation (Euler angles), \( \chi^{(2)} \), size (~77 nm)
Induced non-linear dipoles

The nano-crystal is smaller than the Excitation Efficiency Volume and it is centered on the focus.
Induced non-linear dipoles

Potassium Titanyl Phosphate - KTiOPO4

\[ \vec{P}_{2\omega}^{NL}(x, y, z) = \chi^{(2)}_{2\omega} : \vec{E}_\omega(x, y, z) : \vec{E}_\omega(x, y, z) \]

For KTP

\[
\begin{align*}
\chi_{15}^{(2)} &\approx 1.9 \text{ pm/V} \\
\chi_{24}^{(2)} &\approx 3.6 \text{ pm/V} \\
\chi_{31}^{(2)} &\approx 2.5 \text{ pm/V} \\
\chi_{32}^{(2)} &\approx 4.4 \text{ pm/V} \\
\chi_{33}^{(2)} &\approx 16.9 \text{ pm/V}
\end{align*}
\]

\(\chi^{(2)}\) of massive KTP

We define the KTP orientation by the Euler angles \((\theta, \varphi, \psi)\)
Far field intensity radiation pattern

10 nm long side
70 nm long side
100 nm long side

KTP along X axis
Euler angles:
\( \theta = 90^\circ, \, \phi = 0^\circ, \, \psi = 0^\circ \)
Coherent defocused orientation imaging

Polarization of the pump laser beam:

$\alpha = 0^\circ / X$ axis

$\alpha = 90^\circ / X$ axis

Experimental images

3 points to determine the KTP 3D-orientation:
- Structure & Sub-structures;
- Intensity;
- Rotation of the symmetry axis;

for the 2 polarizations of excitation.

$NA = 1.45$, $n = 1.518$, $m = 100$, $\lambda_p = 945$ nm $d = 15$ mm

Acquisition time = 10s
Coherent defocused orientation imaging

**Polarization of the pump laser beam:**

- $\alpha=0^\circ / X$ axis
- $\alpha=90^\circ / X$ axis

**Experimental images**

- Structures give information about the angle ($\theta$) between the optical axis and the axis ‘3’ of the crystal.
- The variation of the intensity and the direction of the symmetry axis allows to determine the 2 other Euler angles.
Example of image structure Vs θ angle
Coherent defocused orientation imaging

Polarization of the pump laser beam:

- $\alpha=0^\circ / X$ axis
- $\alpha=90^\circ / X$ axis

Experimental images

Calculated images

$\Rightarrow$ KTP orientation: $\theta=30^\circ \pm 5^\circ$ $\phi=115^\circ \pm 5^\circ$ $\psi=90^\circ \pm 15^\circ$
Polarization of the pump laser beam:
\[ \alpha = 60^\circ \] / X axis
\[ \alpha = 120^\circ \] / X axis
\[ \alpha = 150^\circ \] / X axis

⇒ orientation:
\[ \theta = 30^\circ \pm 5^\circ \]
\[ \phi = 115^\circ \pm 5^\circ \]
\[ \psi = 90^\circ \pm 15^\circ \]
Agreement with ellipsometric measurement

Rotation of the linear polarization of the excitation beam

High numerical aperture objective

SHG or 2PF

APD1

APD2

Laser 100fs 80Mhz
690 – 1020 nm

Analysis direction

I_X I_Y

Experimental SHG polarimetric analysis

Comparison with the modeling for a KTP orientation
(θ=30° φ=115° ψ=90°)
Diagnostic of mono-crystallinity

$\Rightarrow$ There is more than 1 nano-KTP in the excitation area.

One has an orientation close to the direction of the polarization of the exciting beam.

These nano-KTPs radiate coherently $\Rightarrow$ Images are results of an interference phenomenon.
Non-linear defocused imaging is a simply tool to determine crystalline nature and 3D-orientation of single nano-crystals with a good precision.

⇒ these nano-crystals can be used as nano-probes of local fields.

\[ \vec{P}_{2\omega}^{NL}(x, y, z) = \chi_{2\omega}^{(2)} \cdot \vec{E}_{\omega}(x, y, z) \cdot \vec{E}_{\omega}(x, y, z) \]

known To probe

⇒ to study rotational diffusion

⇒ to know radiation pattern of unknown nano-emitters…
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