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Optical nanocystallography with tip-enhanced phonon Raman spectroscopy

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Here we present supplementary material to our letter. The specific Raman selection rules are derived for $BaTiO_3$ in the experimental geometry taking into account the symmetry selectivity of the Raman response and the polarization-dependent field enhancement of the tip. We calculate the experimental Raman enhancement.

Phonon TERS Selection rules

The Raman tensors for the $4mm$ space group for $BaTiO_3$ with the crystallographic c-axis along the z-direction, excluding the weak mode of B_1 symmetry are given by[1]:

$$\mathbf{A_1}(z)=\begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{pmatrix}, \mathbf{E}(x)=\begin{pmatrix} 0 & 0 & c \\ 0 & 0 & 0 \\ c & 0 & 0 \end{pmatrix}, \mathbf{E}(y)=\begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & c \\ 0 & c & 0 \end{pmatrix},$$

with x, y, and z denoting the phonon polarization directions along the corresponding crystallographic axes as seen in Fig. 1c. The tip enhancement tensors F_{ij} and F'_{kl} take, e.g., for

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$\boldsymbol{q}=\boldsymbol{k}_i-\boldsymbol{k}_s$	mode	$\boldsymbol{k}_i(\boldsymbol{e}_i\boldsymbol{e}_s)\boldsymbol{k}_s$	I_{TERS}	domain
$\mathbf{q}\parallel z$	A_1 LO	$\mathrm{z(yy)\bar{z}}=\mathrm{p_{in}p_{out}}$	$\propto \lvert a_{LO}\rvert^2(F_pF'_p)^2$	c
$\mathbf{q}\parallel y$	A_1 TO	$\mathrm{y(xx)\bar{y}}=\mathrm{p_{in}p_{out}}$	$\propto \lvert c_{TO}\rvert^2(F_pF'_p)^2$	$\mathrm{a}_{y'}$
”	E TO	$\mathrm{y(xz)\bar{y}}=\mathrm{p_{in}s_{out}}$	$\propto \lvert c_{TO}\rvert^2(F_sF'_p)^2$	”
”	E TO	$\mathrm{y(zx)\bar{y}}=\mathrm{s_{in}p_{out}}$	$\propto \lvert c_{TO}\rvert^2(F_pF'_s)^2$	”
$\mathbf{q}\parallel x$	A_1 TO	$\mathrm{x(zz)\bar{x}}=\mathrm{p_{in}p_{out}}$	$\propto \lvert b_{TO}\rvert^2(F_pF'_p)^2$	$\mathrm{a}_{x'}$
”	E TO	$\mathrm{x(zy)\bar{x}}=\mathrm{p_{in}s_{out}}$	$\propto \lvert c_{TO}\rvert^2(F_sF'_p)^2$	”
”	E TO	$\mathrm{x(yz)\bar{x}}=\mathrm{s_{in}p_{out}}$	$\propto \lvert c_{TO}\rvert^2(F_pF'_s)^2$	”

TABLE I: **TERS selection rules for tetragonal $\mathbf{BaTiO_3}$.** Here a rod is oriented parallel to the incident and scattered light. For each domain, the crystal coordinates are rotated to reflect the change in ferroelectric orientation (i.e. c||z). Contributions under the weakly enhanced $s_{in}s_{out}$ configuration, or under oblique incidence (weak E LO mode) are neglected.

the specific lab frame coordinates depicted in Fig. 1a, the form of:

$$\boldsymbol{\mathcal{F}}^{\mathbf{TERS}}_{\boldsymbol{ij}}=\begin{pmatrix} F_s & 0 & 0\\ 0 & F_p & 0\\ 0 & 0 & 0\end{pmatrix},\ \boldsymbol{\mathcal{F}'}^{\mathbf{TERS}}_{\boldsymbol{kl}}=\begin{pmatrix} F'_s & 0 & 0\\ 0 & F'_p & 0\\ 0 & 0 & 0\end{pmatrix},$$

The indices represent detected output and incident polarization, with p and s polarization defined as parallel and perpendicular with respect to the plane formed by the tip axis and incident or scattered k-vectors, respectively. The diagonal nature of our tensors reflects the lack of depolarized near-field Raman signal[2] observed with our tips. $F_p \simeq F'_p$ and $F_s \simeq F'_s$ because the amount of phonon Raman shift is in general less than or at most comparable to the plasmon linewidth[3].

For a backscattering geometry with the incident and Raman-scattered k-vectors assumed parallel with respect to the sample surface to approximate the experimental configuration (Fig. 1a), Table I shows the resulting TERS selection rules for three distinct crystallographic orientations representing the three possible orthogonal ferroelectric domain configurations. The expected TERS signal I_{TERS} under the different polarization conditions is obtained by transforming $\mathcal{F}_{\mathrm{ij}}$ and $\mathcal{F}'_{\mathrm{kl}}$ into the corresponding crystal coordinates. Modes only present under the weakly enhanced $s_{in}s_{out}$ configuration (e.g., A_1 LO for c-domain) have been omitted, as well as the E LO mode, which is weak and its excitation only possible under oblique angle of incidence (e.g., $\mathbf{q} \parallel x$ and $\mathrm{x(zx)\overline{x}}$)[1].

Enhancement factor

The underlying Raman tip-enhancement can be derived from the distance dependence and lateral scan of Fig. 2. We estimate ∼1 – 5 $BaTiO_3$ nanocrystals within the laser focus contributing to the far-field response based on nanocrystal surface density. With a near-field probe volume of $\sim 10^3$ nm^3, as determined to first order by the tip apex radius $r \sim 10 - 20$ nm, and with nanorod dimensions of $\sim 2\ \mu\mathrm{m}\times 300\ \mathrm{nm}\times 35\ \mathrm{nm}$ this corresponds to a Raman enhancement of $I \sim 10^4$–10^5. With $I \propto |E|^4$ this value is consistent with the typical field enhancement of the tips of order 10–20 as determined previously[4] in the absence of plasmonic tip-sample coupling.

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