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Optical crystallography and ferroelectric domain imaging of BaTiO₃ nanocrystals with tip-enhanced phonon Raman spectroscopy SAMUEL BERWEGER, CATALIN C. NEACSU, Department of Chemistry, University of Washington, Seattle, WA, 98195, YUANBING MAO, HONGJUN ZHOU, STANISLAUS S. WONG, Department of Chemistry, State University of New York at Stony Brook, Stony Brook, NY, 11794-3400, MARKUS B. RASCHKE, Department of Chemistry, University of Washington, Seattle, WA, 98195 — The capability of probing phase transitions, stress, electron-phonon coupling, or doping via their effect on the vibrational structure of crystals has positioned phonon Raman spectroscopy as a powerful tool for the study of semiconductors and dielectrics. In extending the technique to the near-field, the symmetry selectivity of the phonon Raman response allows for optical crystallography on the nanoscale in tip-enhanced Raman spectroscopy taking advantage of the local field enhancement provided by the nanometer size apex of a plasmonic scanning probe tip. The general selection rules that provide the necessary degrees of freedom are derived as a superposition of the crystal Raman tensor, momentum conservation for phonon and light emission, and the symmetry of the near-field tip scattering geometry. The capabilities are demonstrated for the spectrally and spatially resolved identification of intrinsic ferroelectric domains of individual BaTiO₃ nanocrystals by probing the A₁ TO and E TO phonon modes with nanometer spatial resolution.

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