Ultrafast Three-Dimensional X-ray Imaging of Deformation Modes in ZnO Nanocrystals

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ABSTRACT: Imaging the dynamical response of materials following ultrafast excitation can reveal energy transduction mechanisms and their dissipation pathways, as well as material stability under conditions far from equilibrium. Such dynamical behavior is challenging to characterize, especially operando at nanoscopic spatiotemporal scales. In this letter, we use X-ray coherent diffractive imaging to show that ultrafast laser excitation of a ZnO nanocrystal induces a rich set of deformation dynamics including characteristic “hard” or inhomogeneous and “soft” or homogeneous modes at different time scales, corresponding respectively to the propagation of acoustic phonons and resonant oscillation of the crystal. By integrating the 3D nanocrystal structure obtained from the ultrafast X-ray measurements with a continuum thermo-electro-mechanical finite element model, we elucidate the deformation mechanisms following laser excitation, in particular, a torsional mode that generates a 50% greater electric potential gradient than that resulting from the flexural mode. Understanding of the time-dependence of these mechanisms on ultrafast scales has significant implications for development of new materials for nanoscale power generation.

KEYWORDS: ZnO, nanocrystal, ultrafast X-ray, power generation
nanocrystalline ZnO that cannot be obtained by either approach alone.

Figure 1 shows the setup for the ultrafast CDI experiments, which we performed at beamline 7-ID-C at the Advanced Photon Source (APS). ZnO nanocrystals on a SiO2 substrate (see Methods) were placed on a sample stage at the center of a diffractometer. A laser system (Duetto, time-bandwidth) with a repetition rate of 6.5 MHz was used to generate ~10 ps 1064 nm optical pulses. The output of the laser is frequency tripled to 355 nm for above-band gap excitation with an incident laser flux of 1.16 mJ/cm². Optical pulses were synchronized to the X-ray pulses of the APS and timed electronically to arrive at the sample at specified temporal offsets from the probe X-ray pulses. The X-ray pulses were focused by a Kirkpatrick–Baez (K–B) mirror pair to a 50 μm spot on the sample with a transverse coherence length of 10 μm, larger than individual crystals. The APS was operated in 24 bunch mode with a temporal spacing of 153 ns between X-ray pulses, which matched the laser repetition rate. The X-ray photon energy was set to 9.0 keV using a diamond (111) monochromator. Diffracted X-ray pulses were collected by an Amsterdam Scientific Instruments (ASI) Timepix detector in the (100) Bragg geometry. By employing iterative phase retrieval algorithms, a complex 3D electron density ρ(r) was retrieved from the data, where the phase φ(r) yielded a projection of the atomic displacement field onto the reciprocal lattice vector of the measured Bragg peak. The phase of the image is related to the distortion of the lattice through the relationship φ(r) = 〈Q·u(r)〉 where u(r) is the atomic displacement and Q̂ equals the scattering vector. To perform the pump–probe experiments, the sample was excited with a laser pulse at time t_laser. The sample was subsequently probed with an X-ray pulse arriving at a predetermined time t_ray. From the 3D diffraction pattern obtained at t_ray, the structure and lattice displacement in the crystal were obtained. By varying the delay between the laser and X-ray pulses (δt = t_ray − t_laser), it is possible to image the time-varying structure and displacement field in the crystal.

To gain an overall picture of the dynamical response of the material, we performed continuum multiphysics simulations to complement the experimental observations. The X-ray imaged crystal structure was used as an input to the simulation model. The imported crystal volume was meshed with tetrahedral units of sizes between 1 and 50 nm, as illustrated in the Finite Element Model (FEM) shown in Figure 1. To mimic experimental conditions, a multiphysics simulation including electrostatics, solid mechanics, and heat transfer in a piezoelectric material was performed in COMSOL (see Methods). A detailed description of the simulation, the crystallographic orientations, and the simulation boundary conditions are provided in the Supporting Information (see Supplementary Figures S1 and S2).

We first analyze the various homogeneous deformation modes in the laser-excited sample. Figure 2a–c show 2D slices through the 3D coherent diffraction pattern around the (100) Bragg peak at select delay times. Motion of the Bragg peak was observed relative to the static sample scattering vector. We denote these motions as parallel (q∥) and perpendicular (q⊥) to the static ZnO (100) Bragg condition (Supplementary Movie S1). The peak shift along q∥ can be interpreted as a homogenous strain (breathing arising from volumetric expansion and contraction) in the lattice, while the peak shift along q⊥ can be interpreted as the rotational homogeneous deformation mode of the crystal. However, the distortion in the peak is due to the time-varying inhomogeneous strain in the lattice. This inhomogeneous strain in the lattice is a consequence of the propagation of acoustic phonons in the lattice. As expected, with decreasing laser fluence, both the Bragg peak shift (lattice breathing and rotation) as well as the distortion in the Bragg peak (inhomogeneous strain) becomes less pronounced (Supplementary Figure S7). Figure 2d shows the measured angular deviation of the Bragg peak as a function of delay time for a laser fluence of 1.16 mJ/cm², while Figure 2ef shows the Fourier transform of the same time signature. We observed dominant/characteristic breathing frequency of 230 ± 38 MHz, which corresponds to the lattice expansion/contraction along the ZnO crystal’s long axis (see Figure 2e). In addition, two low-intensity frequency peaks are seen at 77 and 383 MHz. These correspond to lattice deformations in the lateral plane perpendicular to the [0001] long axis. In Figure 2f, we show that the rotational/flexural deformation is characterized by two fundamental modes, the dominant mode at 230 MHz (flexural deformation along the crystal’s long axis) and a low-intensity mode at 77 MHz (rotational deformation about an axis normal to the substrate). Importantly, the Bragg peak motion is also observed at negative times, where the X-ray arrives before the laser pulse. This is evidence of the crystal not returning to a rest state between the individual pump–probe pulses spaced 153 ns apart. Effectively the crystal is a driven harmonic oscillator with a primary natural frequency of ~230 MHz.

The average displacement calculated from the FEM simulation, projected along the [100] crystallographic direction, of the ZnO crystal upon the third cycle of pulsed excitation is...
shown in Figure 2g. The [100] projected average displacement represents the homogeneous breathing deformation mode of the sample and is expected to correlate with \( q_\parallel \) peak shift deviation from CDI measurements. In our simulation, the projected lattice deformation is representative of the breathing mode and oscillates with a characteristic time period of \( \sim 260 \) MHz (Figure 2h), which matches reasonably well with the experiments. (g) Fourier transform of the time signal in (h) reveals a characteristic breathing mode frequency of \( 260 \pm 40 \) MHz, which agrees very well with the experiments. (i,j) Dominant rotational modes and their corresponding frequencies as obtained from the eigen-mode and eigen-frequency analysis (see Supporting Information Figure S3 for details). The shapes in brown denote the maximum extent of deviation for that mode from the base structure in gray.

Figure 2. Time-resolved Bragg coherent diffraction data from a single ZnO crystal. Experimentally measured coherent diffraction images recorded at (a) 0 ps, (b) 500 ps, and (c) 2000 ps delay from the laser. Measured intensity is depicted on a log scale. The dotted horizontal and vertical lines are provided for visual reference. (d) Experimentally measured time-dependent shift in the Bragg peak; and (e) Fourier transform of time signal in (d) for the \( q_\parallel \) deviations, which corresponds to the homogeneous breathing deformation mode, reveals a characteristic frequency of \( 230 \pm 38 \) MHz. (f) Fourier transform of time-signal in (d) for \( q_\parallel \) deviations representing the homogeneous rotational deformation mode. (g) Temporal evolution of the average crystal deformation projected along the [100] direction computed from the finite element model. This deformation corresponds to the homogeneous breathing mode. (g) Fourier transform of the time signal in (h) reveals a characteristic breathing mode frequency of \( 260 \pm 40 \) MHz, which agrees very well with the experiments. (i,j) Dominant rotational modes and their corresponding frequencies as obtained from the eigen-mode and eigen-frequency analysis (see Supporting Information Figure S3 for details). The shapes in brown denote the maximum extent of deviation for that mode from the base structure in gray.

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To identify the homogeneous rotational deformation modes in the crystal, we perform an eigenmode analysis on the simulated crystal (see Supporting Information Figure S3 for details). The crystal deformation corresponding to the first two dominant flexural/rotational modes, with characteristic frequencies at \( \sim 290 \) and \( 200 \) MHz, respectively, are depicted in Figure 2j. Fourier transform of time-signal in (d) for \( q_\perp \) deviations has a dominant peak in the range \( \sim 230 \) MHz, which agrees well with our eigenmode analysis. The meshed wireframe in each panel depicts the original crystal and the crystal distortion is amplified for visualization. It is worth noting that the frequency of the observed dominant deformation at \( \sim 290 \) MHz is consistent with an analytical solution for the flexural (rotational) mode of a hexagonal prism cantilever given by

\[
 f_{\text{flex}} = \frac{\beta^2 d}{4EI} \sqrt{\frac{SE}{6p}}
\]

(see Supporting Information for more details). The calculated value of \( f_{\text{flex}} = 242 \) MHz from the analytical solution is in agreement with experimental observation (230 \( \pm 38 \) MHz) and FEM simulations (290 \( \pm 40 \) MHz).

In addition to rotational modes, there exists faster/higher frequency inhomogeneous deformation modes that propagate axially and radially within the ZnO crystal. These so-called “hard” deformation modes are a consequence of the propagation of acoustic phonons through the crystal lattice. Such modes cannot be identified directly by analyzing the position of the Bragg peak. Instead, we turn to the real space three-dimensional images of the displacement field in the crystal obtained from the coherent diffraction imaging to identify local variations in the strain field corresponding to these modes. Figure 3a–c shows the measured displacement field in 2-D slices of the ZnO nanocrystal at representative...
delay times following laser excitation. The measured displacement fields show the propagation of strain waves axially (Figure 3a–c) and radially (Figure 3g). The simulated inhomogeneous deformation fields show close agreement with the experimentally observed displacement fields (Figure 3d–f,h).

As is evident from the axial and radial slices in Figure 3, the time-varying deformation field shows a complex interplay between different axial (Figure 3a–c), radial (Figure 3g), and torsional deformation modes (see Supplementary Movies S2 and S3). To better understand the nature of these various inhomogeneous deformation modes and the relative contributions of each to the observed displacement fields, we obtain a Fourier transform of the time-varying 3-D displacement field both for the experimentally measured fields as well as the simulated. This is equivalent to solving the eigenvalue problem for the deformation modes as done for Figure 2h (see Supplementary Figure S4). From this analysis, we obtain a 3-D representation of the local contribution to different inhomogeneous deformation modes. For instance, Figure 4a,c shows a flexural mode that results from a combination of torsion and alternating tensile-compressive waves. Black arrows describe the deformation direction. This flexural mode repeats with a frequency of ∼1.5 GHz wherein the ends and the midpoints of the crystal show a maximum in lattice displacement (volume in red), while the regions in blue are relatively unperturbed. Figure 4b,d describes a similar deformation mode, which again is a combination of higher harmonic torsional mode and axial deformation modes. This mode has a frequency of ∼2 GHz, where the lattice displacement is maximum at the ends of the nanorod (volume in red), while the bulk of the nanocrystal shows little lattice deformation (volume in blue). In good agreement with the X-ray diffraction data, our finite element simulations also shows the existence of such high frequency deformation modes that are a combination of higher harmonic torsional and axial tensile/compressive deformations as shown in Figure 4c,d.

The implications of such higher frequency inhomogeneous deformation modes for practical applications can be significant. Recent studies have described piezoelectric energy harvesting devices that work by exploiting the homogeneous flexural deformation mode to convert mechanical energy into electrical energy.3,26 Our experimentally informed finite element model could further be used as a predictive tool to identify other deformation modes (Figure 5) that generate higher potential output and hence open up new opportunities for mobile/portable electronics applications. Figure 5a shows the time

![Figure 3](image-url) Time-resolved imaging of inhomogeneous deformation along the axial and radial directions in an isolated nanocrystal. (a–c,g) Cuts through the ZnO nanocrystal showing the projected displacement along the [100] direction as a function of delay time. Red arrows in (g) denote the direction of the lab x-axis lying on the slice plane. (d–f,h) Displacement fields projected along the [100] direction as predicted by the FEM simulation.

![Figure 4](image-url) Imaging and simulation of the modal response of a ZnO nanocrystal. Representative high frequency deformation modes with frequency (a) 1.5 GHz and (b) 2.0 GHz imaged through CDI. Corresponding simulated deformation modes at (c) 1.56 GHz and (d) 1.98 GHz are also shown. Images represent volume renderings of the local contribution to the deformation modes at a particular frequency. Regions in blue show regions that do not oscillate at the noted frequency, while regions in red show regions that oscillate strongly at that frequency. Arrows are guides to the eye to show the nature of deformation.
In summary, we find that ultrafast laser excitation of a ZnO nanocrystal triggers multiple homogeneous (breathing and rotational) and inhomogeneous (axial, radial, and torsional) deformation modes with different characteristic time scales. Ultrafast X-ray coherent diffractive imaging enabled three-dimensional operando study of these modes on spatiotemporal scales and with a lattice strain resolution (∼0.01 Å) relevant to nanoscale power generation. Integration of experiment-informed multiphysics simulations with the X-ray imaging data enabled identification of a torsional mode that yields an electric potential gradient across the crystal 50% higher than that resulting from the homogeneous flexural mode utilized up to now in piezoelectric based nanoscale power-generation devices. This effect could be exploited to achieve higher efficiency nanoscale power generators than existing ones that rely solely on homogeneous deformation modes. Beyond a better understanding of the dynamic behavior of materials, this powerful approach can aid in tailoring and design of mechanical, optical, and piezoelectric responses of materials for the next generation of sensors, actuators, and energy harvesting devices.

**Methods.** Sample Preparation. ZnO crystals were prepared through a modified chemical vapor deposition process where the growth occurred in the gas phase and crystals are subsequently deposited on a substrate downstream. A mixture of zinc carbonate (ZnCO$_3$·2Zn(OH)$_2$·H$_2$O) and graphite powder were placed in a silica boat at the center of a quartz tube within a Carbolite furnace maintained at 900 °C. Argon was used as the carrier gas. The decomposition of the carbonate resulted in the formation of ZnO via the reaction:

$$\text{ZnCO}_3 \xrightarrow{\text{heat}} \text{ZnO} + \text{CO}_2$$
**FINITE ELEMENT SIMULATION** An exposed surface of ZnO (see Figure S1) is heated with a 50 ps pulsed laser of 96 mW every 150 ns. The heat power is chosen to reproduce the experimental laser fluence of 1.16 mJ/cm², such that the energy delivered to the nanocrystal over the heating cycle is the same (2.9239 nJ). The laser absorption coefficient is taken to be 0.5 in our calculations, considering the spectral emissivity of ZnO coatings at the pump laser wavelength of ~350 nm.}

**ASSOCIATED CONTENT**

* Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nanolett.6b04652.

Details of the analytical and coupled finite element model, the experimental Bragg peak response for different laser fluences, and a description of the supplementary movies (PDF)

Supplementary movies (ZIP)

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**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This work was supported by Argonne LDRD 2015-149-R1 (Integrated Imaging, Modeling, and Analysis of Ultrafast Energy Transport in Nanomaterials). Work at the Advanced Photon and the Center for Nanoscale Materials was also supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357. Sample preparation was supported by EPSRC Grant No. EP/D052939/1.

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