Deformation of a bismuth ferrite nanocrystal imaged by coherent X-ray diffraction

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Abstract. Perovskite materials that contain transition metal-oxides often exhibit multifunctional properties with considerable utility in a device setting. $BiFeO_3$ is a multiferroic perovskite material that exhibits room temperature anti-ferromagnetic and ferroelectric ordering. Optical excitation of $BiFeO_3$ crystals results in an elastic structural deformation of the lattice with a fast response on the pico-second time scale. Here we report on dynamic optical excitation coupled with Bragg coherent X-ray diffraction measurements to investigate the structural properties of $BiFeO_3$ nanoscale crystals. A continuous distortion of the diffraction speckle pattern was observed with increasing illumination. This was attributed to strain resulting from photo-induced lattice deformation.

1. Introduction

Transition metal oxides with perovskite crystal structure are emerging as enabling materials for next generation photovoltaics, power electronics, energy harvesting, light emitting diodes and multiferroic devices.[1–3]. Bismuth Ferrite ($BiFeO_3$) is a perovskite metal-oxide semiconducting material with a band-gap of 2.8 eV that shows both antiferromagnetic and ferroelectric ordering at room temperature due to its two differing Fe-O bond lengths. Coexistence of antiferromagnetic and ferroelectric ordering is generally observed in perovskite structures where the ferroelectric displacement from centrosymmetry occurs in the non-magnetic ion. In the case of $BiFeO_3$, the ferroelectric displacement is primarily due to a distortion of the Bi ions from a centrosymmetry configuration. In $BiFeO_3$ each Fe ion is surrounded by six neighbouring Fe ions with antiparallel spin orientation leading to G-type antiferromagnetic ordering and a coupled long-range incommensurate spin-cycloid antiferromagnetic ordering along the [110] direction. Light-mediated photostriction is also observed in $BiFeO_3$ with magnitude dependent on the intensity and polarisation of the impinging light.[4]

Bragg coherent X-ray diffraction imaging (BCXDI) is a lens-less imaging technique suited to the study of nanoscale crystals. It is largely non-destructive and provides information on how atoms are displaced from a reference position at the surface and throughout the bulk of a material.[5] BCXDI experiments are performed by illuminating a sample with a spatially coherent X-rays that exceed the dimensions of the crystal. Coherent light scattered from the entire volume of the nanoscale crystal will interfere and produce a speckle pattern, the

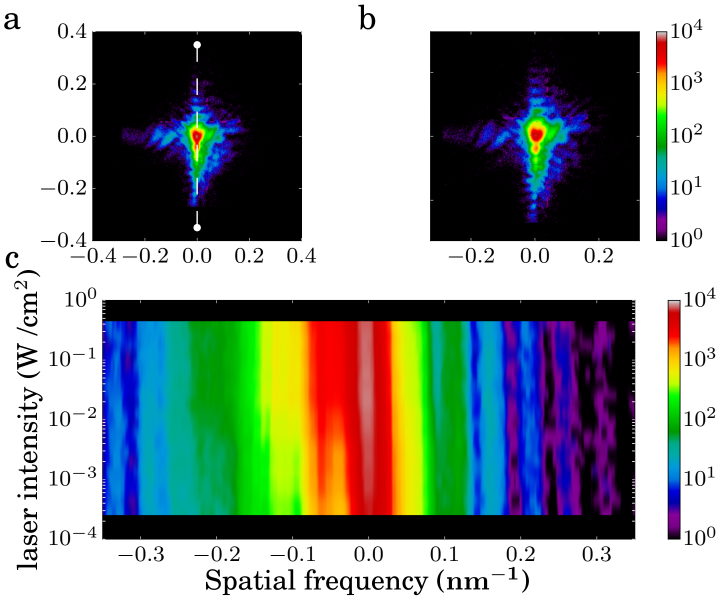

Figure 1. Two-dimensional slices of the speckle pattern of a single $BiFeO_3$ nanocrystal unilluminated (**a**) and illuminated with maximum intensity of 4.0 W/cm^2 of 632.8 nm wavelength laser light (**b**). (**c**), Collated line scans of each speckle pattern along the path indicated in (**a**)for increasing laser illumination intensity.

intensity of which is routinely acquired using a photon counting area detector.[6] If the detector is positioned far enough away from the sample so that the finest fringes are resolved and the speckle pattern is sufficiently oversampled, inversion of the speckle pattern by using iterative projection phase retrieval techniques permits recovery of the complex three-dimensional electron density of the object and its phase information.[7–10] We are then able to directly relate the recovered phase information to lattice displacements in the direction of the wave transfer vector $\mathbf{Q}$ as $\phi(\mathbf{r}) = \mathbf{Q} \cdot \mathbf{u}(\mathbf{r})$, where $\mathbf{u}(\mathbf{r})$ is the average unit cell displacement vector.[11–14]

2. Experiment

$BiFeO_3$ nanocrystals were synthesised on r-plane sapphire substrates using a pulsed laser deposition (PLD). The source material consisted of a solid target of $BiFeO_3$. The target was ablated using a 248 nm, 20 mJ KrF excimer laser system in an oxygen partial pressure of 0.03 hPa. X-ray diffraction measurements confirmed single phase $BiFeO_3$ growth constituents when PLD synthesis was performed at 550°C. The distribution of nanocrystal sizes was largely uniform and dependent on the duration of the synthesis process and the laser fluence. Synthesis performed for 30 minutes with a repetition rate of 200 Hz produced highly faceted nanocrystals of $BiFeO_3$ approximately 200 nm in size. Experiments were performed in air at the coherence branch of beamline I13 at the Diamond Light Source using 9.1 keV photons.[15] A sample of sparsely arranged $BiFeO_3$ nanocrystals was mounted onto the goniometer assembly, a single nanocrystal aligned to the eucentric point and the (110) specular reflection located. A polarised 632.8 nm Helium-Neon (HeNe) laser was focussed via a 0.28 NA microscope objective on to the eucentric point of the sample goniometer and aligned to the X-ray beam. The intensity was attenuated using a linearly graded neutral density filter. The X-ray beam was condensed to 10 µm using a defocussed zoneplate assembly (D = 400 µm, Δr = 150 nm, efficiency 35%). Data was acquired using the 3 mega-pixel photon counting Excalibur detector[16]. Experimental results were gathered by identifying the speckle pattern of a single nanoscale crystal of $BiFeO_3$

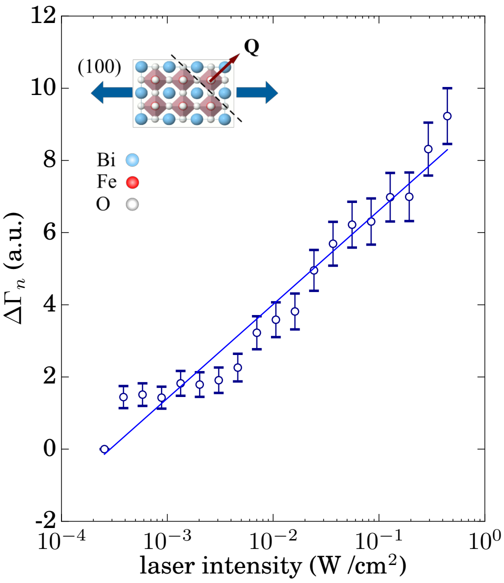

Figure 2. The change in intensity of the cross-correlation measure ($\Delta\Gamma_n$) for each speckle pattern.

on the area detector and then acquiring speckle patterns at varying laser illumination intensity.

3. Results and discussions

Two-dimensional speckle patterns in the absence of laser illumination and with maximum laser illumination are shown in figure 1(**a**) and (**b**). Figure 1(**c**) shows collated line scans of each speckle pattern along the path indicated in (**a**) for increasing laser illumination intensity. A progressively asymmetric distortion of the speckle pattern is clearly observed with increasing illumination intensity. This asymmetry is understood to result from lattice strain in the material.[14] Photo-induced structural deformation will therefore result in an atomic displacement field $\mathbf{u}(\mathbf{r})$.

We can quantify changes in each speckle pattern by contrasting the intensity sum of the cross-correlation for each successive speckle pattern with that of the unperturbed speckle pattern. If the cross-correlation of the n^{th} successive speckle pattern $I_n(\mathbf{q})$ with that of the unperturbed is denoted as $\Gamma_n(\mathbf{q}) = I_n(\mathbf{q}) \otimes I_0(\mathbf{q})$, then the normalised change in sum $\Delta\Gamma_n$ is given by:

$$\Delta\Gamma_n = \sum_{\mathbf{q}} \frac{\Gamma_n(\mathbf{q}) - \Gamma_0(\mathbf{q})}{\Gamma_0(\mathbf{q})}. \tag{1}$$

Here, $\Gamma_0(\mathbf{q})$ is the auto-correlation for the unperturbed speckle pattern. This result is shown in figure 2 along with a linear fit to the change in correlation sum with the logarithm of the laser intensity. Deformation of the speckle pattern appears to rapidly increase with an increase in the intensity of the laser. Our observations suggest that structural distortion results from photo-excitation as a result of light-mediated photostriction. This effect is thought to result from photo excited electron-hole pairs that are separated by the ferroelectric polarisation field within the crystal. Their separation yields an internal voltage that further induces a reverse piezoelectric effect. The photostrictive effect is also known to occur with below band-gap excitation.[4, 17]

This can be understood if a magneto-electric coupling component that additionally couples to Fe^{3+} ions in the lattice is included. [18–21]

4. Conclusion

The possibility of harnessing multiferroic compounds such as $BiFeO_3$ that can operate at room temperature is desirable for the realisation of numerous technological applications. We have demonstrated that photostriction can occur in nanocrystals of $BiFeO_3$ and results in lattice strain that increases with illumination intensity.

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