Direct Observation of Large Flexoelectric Bending at the Nanoscale in Lanthanide Scandates

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Supporting Information

ABSTRACT: There is a growing interest in the flexoelectric effect, since at the nanoscale it is predicted to be very large. However, there have been no direct observations of flexoelectric bending consistent with current theoretical work that implies strains comparable to or exceeding the yield strains of typical materials. Here we show a direct observation of extraordinarily large, two-dimensional reversible bending at the nanoscale in dysprosium scandate due to the converse flexoelectric effect, with similar results for terbium and gadolinium scandate. Within a transmission electron microscope, thin features bend up to 90° with radii of curvature of about 1 μm, corresponding to very large nominal strains. Analysis including independent experimental determination of the flexoelectric coefficient is semiquantitatively consistent with interpreting the results as due to flexoelectricity. These results experimentally demonstrate large flexoelectric bending at the nanoscale.

KEYWORDS: Flexoelectricity, in situ, transmission electron microscopy, lanthanide scandates

Higher order electromechanical couplings in materials are an area of substantial current research since they involve spatial gradients of applied fields which activate traditionally forbidden responses, such as mechanically induced polarization in centrosymmetric materials. One of these is the flexoelectric effect, which couples polarization and strain gradient. Though typically small at the macroscale, the size scaling of strain gradients is expected to lead to large flexoelectric responses at the nanoscale. Understanding the fundamental science of this phenomenon will help expedite its inclusion in existing devices and could open possibilities for new applications.

First observed in solids by Bursian and Zaikovskii, the term flexoelectricity was coined in the field of liquid crystals and subsequently adopted for solids and also biological membranes. The current resurgence of interest in the flexoelectric effect in oxide systems, largely sparked by measurements made by Cross and Ma on relaxor ferroelectrics, has led to major experimental and theoretical progress in understanding flexoelectricity. From these experimental and theoretical advances, it has been found that flexoelectric couplings in oxides have profound impacts on mechanical and dielectric properties, can change domain walls and interfaces in ferroelectrics and ferroelastics, and can control defect formation among many other discoveries. Advances in our understanding of this phenomenon have led to a number of promising applications including flexoelectric energy harvesting, actuation, and strain sensing. Improving the efficacy of flexoelectric-based devices requires advancing the understanding of the underlying science of flexoelectricity.

In their pioneering work, Bursian and Zaikovskii observed curvature in a BaTiO$_3$ film due to the application of an electric field. A 2.5 μm thick film of BaTiO$_3$ was measured to have a curvature of 150 m$^{-1}$ under an applied potential of 20 V. In films of nanometer thickness, it was predicted that the curvature would be on the order of 10$^6$ to 10$^{10}$ m$^{-1}$, which equates to strains comparable to or exceeding typical oxide yield strains. This occurs because the flexural rigidity of a plate scales as the elastic thickness cubed, dropping precipitously at small sizes. None of the existing literature includes direct experimental evidence demonstrating the predicted high curvature and strain values, although there are some indirect measurements of comparable curvatures (e.g., ref 34). A subtle question is whether such large effects are physically realistic or just nominal extrapolations.

In this Letter, we report direct experimental observations of large, two-dimensional reversible flexoelectric bending at the nanoscale in DyScO$_3$ with similar results for TbScO$_3$ and GdScO$_3$. Within a transmission electron microscope (TEM), thin features of these single crystal oxides bend up to 90° with radii of curvature ~1 μm when positively charged by the loss of secondary electrons. The bending scales with electron beam flux and is not associated with any dislocations, twinning, or...
similar changes in the oxide. Extensive additional analyses of these materials to better define the source of this bending are presented, including atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), reflection electron energy loss spectroscopy (REELS), ex situ measurements of flexoelectric coefficients, and theoretical modeling using density functional theory (DFT) with hybrid exact-exchange functionals. The results semiquantitatively indicate that the observed bending is a consequence of large charging coupled to curvature via a high flexoelectric coupling voltage. In most cases, the magnitude of the bending is not limited by yield strength, but by the achievable potential across the oxide as set by the band gap in the limit of a thin insulator.

Figure 1 shows a number of frames from Video V1 in the Supporting Information, in which a thin DyScO₃ sample bends under the illumination of a TEM electron beam. Increasing the electron flux by converging the beam increased bending, while decreasing the electron flux had the opposite effect. If the electron beam was not centered on the sample, it bent away from the beam (Supporting Information, Figure S1 and Video V2). In general, the bending was reversible, although too severe bending could cause fracture (Supporting Information, Video V3).

While bending along the length of the sample is clearest in Figure 1, it was definitively two-dimensional, occurring along both the length and width of the sample. As the electron flux was increased, the sample shape approached that of a spherical zone. An illustration of this two-dimensional bending is shown in Figure 2a. By comparing the projected length and width of the sample in Figure 1 at various fluxes to the reference frame (lowest flux used), we extracted the curvature along the sample length and width as a function of incident electron beam flux (J). As shown in Figure 2b, the relationship between flux, estimated assuming a quantum yield of 0.2, and curvature is well described by an empirical fit of the form \( \kappa = A \left(1 - \exp \left(-\frac{J}{B}\right) \right) + \kappa_0 \) where \( \kappa \) is the curvature, \( J \) is the flux, \( A \) and \( B \) are constants, and \( \kappa_0 \) is the (unmeasured) curvature of the reference frame. This implies saturation of the curvature as a function of flux and, as discussed later, is consistent with saturation of sample charging as a function of flux.
DyScO$_3$ has a work function of 5.8 eV and the band gap, in agreement with previously reported values and help aware of (Supporting Information, Video V4), it is important to understand the underlying charging mechanism. UPS results (Supporting Information, Figure S2) indicated that the surface of a DyScO$_3$ sample. After the surface was disordered, the charging was less severe and the bending was minimal to none. This indicates that the surface plays some role in the observed charging and bending.

The bending and associated charging were observed for about 50 different features from 20 different samples, including TbScO$_3$ and GdScO$_3$ samples. We did not observe any dependence upon the crystallographic direction of the features with the caveat that the thin direction was always [110]. The process appeared to be elastic with no evidence of dislocations or phase transitions and was often on the time scale of the video recordings. We looked for similar charging and bending in SrTiO$_3$, KTaO$_3$, NdGaO$_3$, and LaAlO$_3$. There was some charging in NdGaO$_3$ and LaAlO$_3$ (significantly less than in the lanthanide scandates), but little to no bending.

Our observations indicate that the curvature in the DyScO$_3$ samples saturates as a function of flux, the bending is a consequence of large charging in this material, and the nature of the surface plays some role in the charging. Now we turn to establishing the origin of this charging, the role of the surface, and how these observations are attributed to the converse flexoelectric effect.

For high incident electron energies (as typically used in TEM) charging in insulators will be net positive, involving the loss of secondary electrons. The charging will scale with the electron flux and be partially compensated by competing neutralization processes, such as the capture of secondary electrons from other locations in the microscope. The spatial distribution of this charge does not have to be symmetric, and in fact, one would anticipate the top surface of the sample to charge positive with respect to the bottom surface (Supporting Information). This asymmetric charge distribution induces a potential across the sample. In the limit of a thin insulator, the maximum potential (and the maximum amount of charging) is set by the band gap of the material; i.e., once the potential is sufficiently large, any additional charging is mitigated by Zener tunneling. Thus, if the flux is sufficiently high, one would expect the charging and potential to saturate, as we observed.

Since these materials charged more than any materials we are aware of (Supporting Information, Video V4), it is important to further understand the underlying charging mechanism. UPS results (Supporting Information, Figure S2) indicated that DyScO$_3$ has a work function of 5.8 eV and the band gap, experimentally measured with REELS (Supporting Information, Figure S2), was found to be 5.7 ± 0.1 eV. These values are in agreement with previously reported values and help explain the large charging: the band gap and work function of DyScO$_3$ are approximately equal, so almost every secondary electron produced by inelastic scattering in the bulk has sufficient energy to escape the material. As a direct confirmation of this hypothesis, Figure 3 compares secondary electron images of GdScO$_3$ and KTaO$_3$ nanoparticles. As can be seen in this image, the GdScO$_3$ nanoparticles have less topographic contrast than the KTaO$_3$ nanoparticles, and a significantly lower secondary electron signal except near the conducting carbon support or KTaO$_3$ nanoparticles. The lack of topographic contrast directly indicates a long mean free path of the electrons; the lower secondary electron signal is because the GdScO$_3$ has charged significantly more positive than the KTaO$_3$. The relatively short distance over which the contrast from the GdScO$_3$ varies indicates very poor conduction even for the relatively large electric field gradients present.

It is also important to elucidate the role of the surface (and rule out the possibility of an anomalous surface structure or phase which, for instance, could lead to misfit stresses). XPS measurements were used to determine if water was present on the DyScO$_3$ TEM samples, since hydroxides often occur at oxide surfaces and could lead to surface dipoles. Results indicated that the annealed samples prior to TEM experiments had minimal chemisorbed hydroxide (Supporting Information, Figure S3). For the surface structure, the diffraction patterns in Figure 4 show a low diffuse background with no evidence of additional reflections. This indicates few bulk defects and a well-ordered 1 × 1 surface, with no surface reconstructions or additional phases. Based on the annealing conditions, we expect this surface to be valence neutral. AFM imaging (Supporting Information, Figure S4) confirmed that the surface was flat with monatomic steps of a height of 0.15 nm. Angle-resolved XPS measurements indicated that the surface is a Sc rich double-layer dominated by ScO$_{10}^-$ octahedra with a vacant site (Supporting Information, Figure S4), similar to the well-established double-layer reconstructions on SrTiO$_3$ (001). This is anticipated because the 1 × 1 (110) surface of DyScO$_3$ (a Pbnm orthorhombic perovskite) is similar to the 2 × 2 (001) surface of a cubic perovskite. DFT calculations performed with the all-electron augmented plane wave and local orbitals WIEN2k code for different surface configurations indicated that the lowest energy structure contained three rows of...
scandium oxide (Supporting Information, Figure S5). Except for a small density of unoccupied states associated primarily with one of the surface Sc atoms, there was nothing unusual in the surface band structure, consistent with the experimental UPS and REELS data. These results allow us to exclude anomalous surface structures or phases as the source of the bending and suggest that disordering the surface decreased charging (and therefore bending) because ion-beams will differentially sputter oxygen and lead to a reduced, disordered, and more conductive surface which helps neutralize charging, similar to coating with carbon.

Our TEM observations as well as structural and electronic characterizations were all consistent with the sample bending as a result of a charging-induced potential across the sample, i.e., a converse flexoelectric response. To further establish the origins of the bending, ex situ characterization of the bulk flexoelectric effect in DyScO$_3$ was carried out using a three-point bending method. Polarization versus strain gradient for a [110] oriented DyScO$_3$ sample is shown in Figure 5. To validate the setup, the flexoelectric coefficients of [100] and [110] oriented SrTiO$_3$ were measured to have magnitudes of 12.4 nC/m and 8.3 nC/m, respectively, consistent with literature values which range from 1 to 10 nC/m; see ref 9. Flexoelectric coefficients were found to minimally vary with static force and oscillatory frequency. The magnitude of the flexoelectric coefficient for [110] oriented DyScO$_3$ was measured to be $8.4 \pm 0.4$ nC/m, using the standard error for 13 different measurements. The signs for [110] oriented DyScO$_3$ and SrTiO$_3$ were negative, which agree with the sign of the flexoelectric coefficient deduced from in situ TEM observations (Supporting Information). Although the flexoelectric coefficient in DyScO$_3$ is of the same order of magnitude as the measured flexoelectric coefficient in SrTiO$_3$, the dielectric constant of DyScO$_3$ at room temperature is an order of magnitude smaller than that of SrTiO$_3$. Therefore, the flexocoupling voltage (ratio of the flexoelectric coefficient to the dielectric constant) is an order of magnitude larger in DyScO$_3$ than in SrTiO$_3$ at $42 \pm 2$ V. This is larger than typical flexocoupling voltages of 1–10 V; see ref 6.

It is possible to quantitatively connect the ex situ flexoelectric measurements with the in situ TEM observations via an expression developed by Bursian and Trunov. Assuming a plate geometry and constant electric field across the thickness of the sample, the curvature is given by $\kappa = \frac{\mu V}{D - \nu Y}$, where $\kappa$ is the curvature, $\mu$ is the flexoelectric coefficient, $D$ is the flexural rigidity, $V$ is the potential, $\nu$ is the Poisson's ratio, $Y$ is the Young's modulus, and $d$ is the elastic thickness, which we will take as the sample thickness. Using the measured flexoelectric coefficient, band gap (as discussed previously, once the charging in a thin insulator has saturated, it is reasonable to estimate the saturated potential across the sample with the band gap), literature Young's modulus, and thickness from the in situ observations, we can arrive at an estimate for the curvature arising from the flexoelectric effect in the saturated regime.

First, it is necessary to estimate the elastic thickness to use in this calculation because there are inherent thickness gradients in the TEM samples, and the above expression was derived for a plate of uniform thickness. From the TEM experiments, we found that the thickness in the DyScO$_3$ samples varied from approximately 50 nm at the base of the features (based upon electron energy loss measurements) to 5 nm or less at the edges. Taking an average elastic thickness of 22.5 nm, the measured band gap of 5.7 eV, a Poisson's ratio of 0.25, and a Voigt–Reuss–Hill average for the Young's modulus of 183 GPa, we obtain a curvature of $2.5 \times 10^5$ m$^{-3}$. We note that although the sample is a single crystal with known elastic tensor coefficients, we used the Voigt–Reuss–Hill average to estimate the Young's modulus as it is ambiguous what elastic tensor components it is proper to use for the effective modulus. We argue that the agreement with our observed saturated curvature ($\sim 3 \times 10^5$ m$^{-3}$) is semiquantitative especially given the approximations made in deriving the above expression and in the thickness and modulus estimations. It is worth noting that estimating the saturated potential across the sample as the band gap corresponds to a surface charge density of 0.3 electrons/ nm$^2$. This is a large, but reasonable, charge density that is seen in a number of other insulating systems.

To verify that these observations were not associated with an electron optics artifact, we collected diffraction patterns while varying the electron flux after tilting to the [110] zone axis of a DyScO$_3$ sample. As shown in Figure 4 (Supporting Information, Video V5) as the electron flux is decreased from panels a–h, changes in the Laue circle indicate that the sample
is bending. While there was a slight deflection of the beam, it was several orders of magnitude smaller than the bending of the sample. For completeness, changing the microscope focus did not lead to large shifts in the beam, which is consistent with minimal bending of the electron beam.

A second possibility is that the ∼2 T magnetic fields in the microscope play a role in the observed bending; DyScO$_3$ changes from a paramagnetic to an antiferromagnetic state below 4 K and measurements have shown that a magnetic field of a few T can rotate DyScO$_3$ samples around this transition temperature. We performed experiments in low-field electron microscopes that exposed the samples to ∼5 Oe magnetic fields and observed similar bending (Supporting Information, Figure S6), ruling out magnetic contributions as the dominant term.

A number of other remote possibilities are briefly discussed in the Supporting Information; they are orders of magnitude too small to account for the magnitude of the observed bending. We note that these unlikely effects can also be ruled out as they would have led to bending in other samples of different materials and be well-known in the existing literature.

With nominal strains comparable to or exceeding the yield strains of typical oxides, these experimental observations of reversible bending in lanthanide scandates are quite extraordinary; extraordinary, but consistent with what one expects for the flexoelectric effect at the nanoscale and the large reduction of the flexural rigidity. Theoretical predictions have claimed very large flexoelectric responses should exist at the nanoscale due to how flexoelectricity scales with size; however, prior to this work, there have been no direct observations of such scaling, leaving this size extrapolation open to question. Our results provide direct experimental evidence that this size extrapolation is physically reasonable.

In terms of application, these observations experimentally demonstrate the feasibility of constructing nanoscale devices with quite large mechanical motions relative to their size. In terms of the fundamental science, many questions remain regarding the detailed physical origin of the large flexoelectric coupling in these materials as well as general features of the flexoelectric effect, since it is in many respects the least explored electromechanical coupling. To date, theoretical and experimental studies of flexoelectricity have focused on relatively simple oxides. These lanthanide scandates contain strongly correlated 4f electrons (We note that Dy has two minority 4f electrons in DyScO$_3$, Tb has one in TbScO$_3$, and Gd has none in GdScO$_3$, and all three scandates showed approximately the same bending, so the minority 4f states may play a role, but their presence is not required.). Significant octahedral rotations, strong and anomalous polar phonons, as well as other physical terms such as Rashba spin–orbit coupling when electric fields are present and probably additional complex couplings between spin and orbital moments and atomic positions (Supporting Information). They are much more complex systems with rich and, as of yet, relatively unexplored science compared to simpler materials such as SrTiO$_3$ or BaTiO$_3$, where flexoelectric phenomena have been previously studied. Dissecting the interplay between electronic, phonon, and spin–orbit terms in these strongly correlated materials is a challenge which we will pose to the larger community.
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