

Second harmonic generation imaging of local antiferroelectric-ferroelectric phase transitions in a PbZrO_3 thin film

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Polar orders play a central role in modern technologies, spanning applications from information storage and energy harvesting to neuromorphic computing. While ferroelectric (FE) implementation into devices is more mature, the development of antiferroelectric (AFE)-based devices is still in its infancy. However, AFEs are emerging as promising candidates for multiple applications such as energy storage (supercapacitors), all-solid refrigeration (electrocaloric cooling) or thermal switches. In this work, we probe the transition between the antipolar and polar states in epitaxial layers of the prototypical antiferroelectric oxide, PbZrO_3 . We discuss operando second-harmonic generation (SHG) imaging as a powerful tool, providing spatially resolved insights into the electric-field-induced AFE–FE phase transitions. This technique enables the mapping of local symmetry-breaking and phase coexistence during switching, offering a route to unravel the microscopic mechanisms governing AFE–FE transitions in such functional oxides.

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The rapidly increasing demand for efficient data processing and storage is a major challenge in modern information and communication technologies. Sustaining this growth requires the ability to handle information at drastically reduced energy costs and at much higher operation speeds. CMOS-based artificial intelligence (AI) and the Internet of Things (IoT) could drive global electricity consumption to rise by 15% per year, reaching nearly 945 TWh annually by 2030 [1]. From an energy perspective, the manipulation of information using electric fields offers an intrinsically low-power alternative, as it avoids Joule heating losses inherent to charge transport. In this framework, electric-field tunable polar textures have emerged as a natural pathway toward low power nanoelectronics. Ferroelectric-based devices have already demonstrated technological maturity, achieving switching energies on the order of a few attojoules per bit (aJ/bit) [2].

Among electrical ferroic orders, antiferroelectrics (AFE) have recently attracted renewed attention. First introduced by Kittel in 1951 [3], AFEs are defined by an antipolar ground state that can be reversibly switched to an energetically equivalent polar phase under an applied electric field or pressure. While AFE crystals have already been implemented in various applications in bulk form [4], a major paradigm shift occurred with the advent of high-quality epitaxial thin films,

enabling the stabilization of pristine AFE phases at thicknesses of only a few tens of nanometers [5,6]. The controllable AFE–FE (antiferroelectric–ferroelectric) phase transition in such systems offers promising prospects for highly efficient data storage, sensing, and energy-harvesting technologies [4]. Furthermore, antiferroelectric tunnel junctions could be envisioned as fundamental building blocks for neuromorphic architectures. Indeed, ferroelectric tunnel junctions behave as artificial synapses [7], and antiferroelectric tunnel junctions [8] are expected to emulate neurons [9]. Despite this progress, several key issues remain under debate, and a comprehensive understanding of prototypical AFEs such as PbZrO_3 is still lacking, in particular concerning their thickness dependence and switching path [10]. A remarkable asset to tackle these issues would be the ability to image the inherent properties of electric-field-induced AFE–FE phase transition at the device level.

One of the salient differences between AFE and FE phases lies in their respective symmetry, with ferroelectric phases lacking space inversion symmetry, while antiferroelectrics do not.

Breaking space inversion symmetry is the main source of optical second-harmonic generation (SHG) [11,12], the lowest order of nonlinear optical processes. In the electron dipole (ED) approximation, SHG is largely dominated by a leading-order source term: $\vec{S}(2\omega) \propto \chi^{(2)} : \vec{E}(\omega) \otimes \vec{E}(\omega)$ where $\vec{E}(\omega)$ is the electric field of the fundamental light and $\chi^{(2)}$, the second-order nonlinear susceptibility reflecting the system's symmetry. The latter is only allowed in systems lacking spatial inversion symmetry. Therefore, SHG stands as a suitable technique to decipher the AFE–FE phase transitions. As early as the 1980s, Fujishita *et al.* [13] reported the

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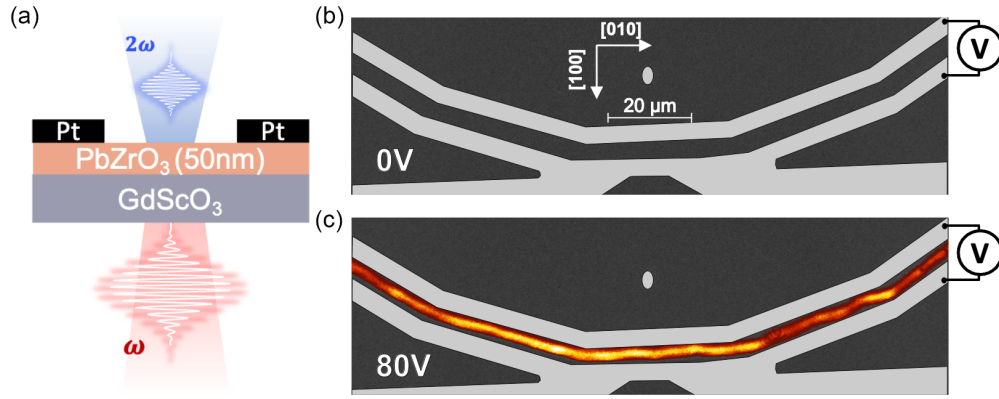


FIG. 1. (a) Sketches of the experimental setup. SHG is used to probe the phase transitions of a PbZrO₃ thin film under an applied electric field. Note that the sample is illuminated from the backside, i.e., through the GdScO₃ substrate. (b) SHG image at 0 V. (c) SHG image at 80 V. The light gray areas represent the Pt electrodes and have been reproduced by overlaying a white light image acquired in the same configuration (see Note 4 of the Supplemental Material [16]).

antiferroelectric nature of PbZrO₃ powder ceramics, referring to a private communication in which the absence of SHG was cited as evidence for the nonpolar character of this compound. More recently, SHG imaging has been employed to demonstrate the polar-to-antipolar phase transition in BiFeO₃/TbScO₃ superlattices [14]. Here, we implement SHG imaging to decipher electric-field-induced AFE–FE phase transitions in a PbZrO₃ epitaxial single layer.

The experimental setup is based on a wide-field transmission microscope where the sample is illuminated from its backside and SHG light collected from its frontside by a 40× objective lens with a 0.6 numerical aperture. Light pulses at 800 nm wavelength are generated by a Ti:Sapphire amplified laser at 1 kHz repetition rate and pulse duration of about 100 fs. An SHG image at 400 nm is formed on a Peltier-cooled CCD camera reaching an optimal submicron resolution of about 400–500 nm.

The sample under study is a 50 nm thick (001) PbZrO₃ epitaxial film grown by pulsed laser deposition on top of a (110) GdScO₃ substrate (see Ref. [5] for details). Electrodes of 50-nm-thick Pt with a 4-μm-wide gap have been subsequently designed on top of the PbZrO₃ layer [Fig. 1(a)] for the application of an external electric field, driving the AFE–FE phase transition while performing SHG imaging. The switching fields measured in capacitor design of equivalent epitaxial films are about 0.4 MV/cm in quasistatic measurements [5], so that we expect switching to occur applying few tens of volts between both electrodes. Importantly, an applied electric field acts per se as a source of SHG. In order to take it into account, the SHG source term $[\vec{S}(2\omega)]$ mentioned above is now written as

$$\vec{S}(2\omega) \propto (\chi^{(2)} + \chi^{(3)} \cdot \vec{E}_A) : \vec{E}(\omega) \otimes \vec{E}(\omega) \quad (1)$$

with $\chi^{(3)}$ the third-order susceptibility and $\vec{E}_A$ the applied electric field. This additional term is commonly named electric-field-induced SHG (EFISHG) and has already been implemented to assess DC and THz electric fields in classical nonlinear bulk crystals and thin films [15].

Experimentally, the measured quantity is the SHG intensity ($I_{2\omega}$),

$$I_{SHG} \propto |\mathcal{S}_\omega|^2 \\ \propto [\chi^{(2)^2} + 2 \cdot \chi^{(2)} \cdot \chi^{(3)} \vec{E}_A + (\chi^{(3)} \vec{E}_A)^2] : \vec{E}(\omega) \otimes \vec{E}(\omega) \quad (2)$$

One can first observe that the SHG intensity depends on three distinct components $\chi^{(2)^2}$, which corresponds to the conventional second-harmonic generation arising from the intrinsic noncentrosymmetry; $(\chi^{(3)} \vec{E}_A)^2$, which is solely the result of the application of an external electric field and varies quadratically with its magnitude; and finally, the cross term $2 \cdot \chi^{(2)} \cdot \chi^{(3)} \vec{E}_A$, which depends linearly on the applied field and on the second-order nonlinear susceptibility. This latter term is also nonzero only in the noncentrosymmetric (ferroelectric) phase.

Figures 1(b) and 1(c) present examples of two raw SHG images for applied voltages of 0 V and 80 V, respectively. Note that the 80 V is equivalent to an electric field of about 130 kV/cm in the central region between the electrodes (see Note 1 of the Supplemental Material [16]). Both polarizer and analyzer were aligned vertically, i.e., along the [100] crystal direction of the PbZrO₃ layer. Without any applied external electric field [Fig. 1(b)], no SHG intensity is detected as expected for the centrosymmetric AFE phase. However, polar antiphase boundaries or ferroelectric phases have been observed in PbZrO₃ crystals [17]. If these polar entities were isolated in the film, they could generate an observable SHG signal at zero electric field, which is not the case [Fig. 1(b)]. If we consider these entities as randomly distributed over a characteristic length scale of approximately 10–50 nm (smaller than the SHG optical resolution), their individual SHG contributions interfere destructively, resulting in the absence of a detectable signal in the SHG measurement. Nevertheless, local P–E loops and advanced STEM imaging showed that such features are not prevalent in similar PbZrO₃ samples [5,6].

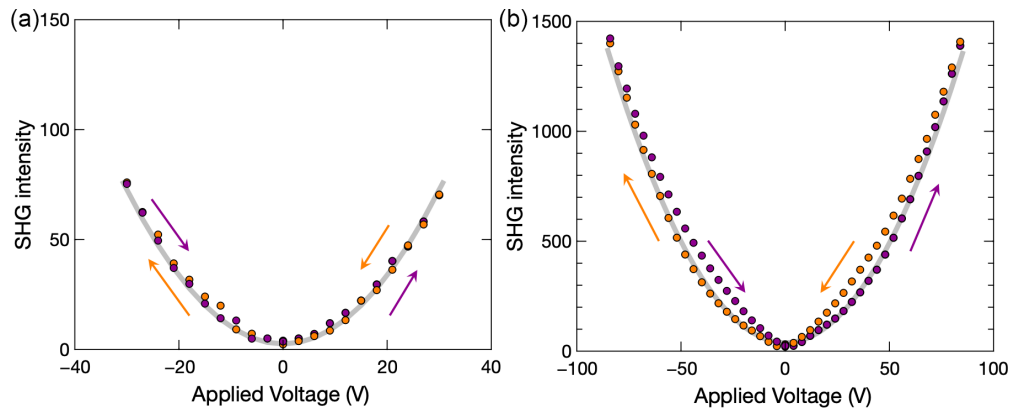


FIG. 2. SHG intensity dependences on the applied electric field from ± 30 V (a) and ± 80 V (b) acquired in 3 V steps. For each step, the voltage value is applied 3 seconds prior to the SHG image and maintained during its whole acquisition (120 sec). Their respective quadratic fits are displayed as gray lines. SHG intensities have been averaged over the whole area between the Pt electrodes and sorted for increasing (purple dots) and decreasing (orange dots) applied voltages.

In contrast, the image acquired under 80 V [Fig. 1(c)] shows a clear SHG intensity located between the Pt electrodes. When the SHG intensity, averaged over the entire region between the Pt electrodes, is plotted as a function of the applied voltage (Fig. 2), a global quadratic dependence on the external electric field is observed. This is characteristic of a dominant EFISHG contribution, $(\chi^{(3)}\vec{E}_A)^2$, to the overall SHG intensity.

However, while a perfect parabolic dependence is observed when the applied electric field remains sufficiently low [Fig. 2(a)], a clear deviation from this parabolic behavior appears at higher field strengths [Fig. 2(b)], which can be attributed to the additional $\chi^{(2)}$ source terms in Eq. (2). This indicates the loss of centrosymmetry, that is to say, the transition of PbZrO_3 to its noncentrosymmetric ferroelectric phase.

In order to visualize and spatially resolve the electric-field-induced AFE–FE phase transition, the fully quadratic EFISHG contribution can be quantified by fitting the average raw SHG intensity as a function of an applied electric field with a parabola up to a voltage threshold below which the phase transition has not occurred yet [Fig. 2(a)]. This contribution can be subsequently subtracted, singling out the finite values of $\chi^{(2)}$ associated with the ferroelectric phase. Note that this parabolic “background” removal has to be performed for each pixel as $\chi^{(3)}$ components of the EFISHG depend on the relative orientation between the crystal axis and the applied electric field direction (see Note 2 of the Supplemental Material [16]).

Subtracting this parabolic EFISHG, it is now possible to reconstruct a series of images showing the electric-field-induced phase transitions. Figure 3 presents a selection of these images as the applied voltage (electric field) is increased from 0 V to 84 V and back to 0 V. Regions with positive (red) and negative (blue) contrasts are clearly visible and dependent on the applied voltage. However, while $\chi^{(2)^2}$ will obviously add a positive contribution to the overall signal, only $2 \cdot \chi^{(2)} \cdot \chi^{(3)}\vec{E}_A$ can be responsible for a negative contribution, appearing in blue in images displayed in Fig. 3.

Coming back from high voltages, remanent “red/blue” domains are formed and persist down to 0 V depending on regions (see comparison between panels at 45 V of Figs. 3(c) (increasing voltages) and 3(g) (decreasing voltages)). To further elucidate this behavior, we analyze the corresponding hysteresis loops in selected regions of interest (Fig. 4). The analysis focuses on areas located near the center of the gap between electrodes, rather than close to the metallic edges, where spurious SHG contributions may arise and where the electric field is no longer strictly in plane (see Notes 1 and 3 of the Supplemental Material [16]).

Three representative types of antiferroelectric (AFE) and ferroelectric (FE) hysteretic responses can be identified. The first, illustrated in Fig. 4(a), corresponds to an electric field applied roughly along the [110] direction. The SHG intensity remains negligible up to a threshold of approximately 50 V, above which it increases markedly, signaling the onset of ferroelectric order through two distinct contributions. First, the emergence of a finite second-order nonlinear susceptibility (i.e., $\chi^{(2)} \neq 0$) directly reflects the breaking of inversion symmetry. Second, the third-order susceptibility ($\chi^{(3)}$) may differ between the antiferroelectric (AFE) and ferroelectric (FE) phases, in a manner analogous to the phase dependence of the permittivity [18]. Removing the quadratic contribution observed in the AFE phase allows us to better visualize the transition, even though the increase in SHG intensity is not strictly linear in the ferroelectric phase; a quadratic component can be identified, arising from the difference between two parabolic contributions stemming from different $\chi^{(3)}$ susceptibilities for the two phases. Moreover, the abrupt emergence of a measurable SHG signal appears to be consistent with an AFE–FE phase transition, rather than with the gradual expansion of a ferroelectric phase under an applied electric field.

Upon reducing the electric field, a finite remanent SHG plateau persists between roughly 60 V and 25 V, clearly indicating a remanent FE phase, before the signal vanishes. A symmetric behavior is observed for negative applied fields.

When the electric field is applied along the [100] direction [Fig. 4(b)], the SHG intensity similarly deviates from zero

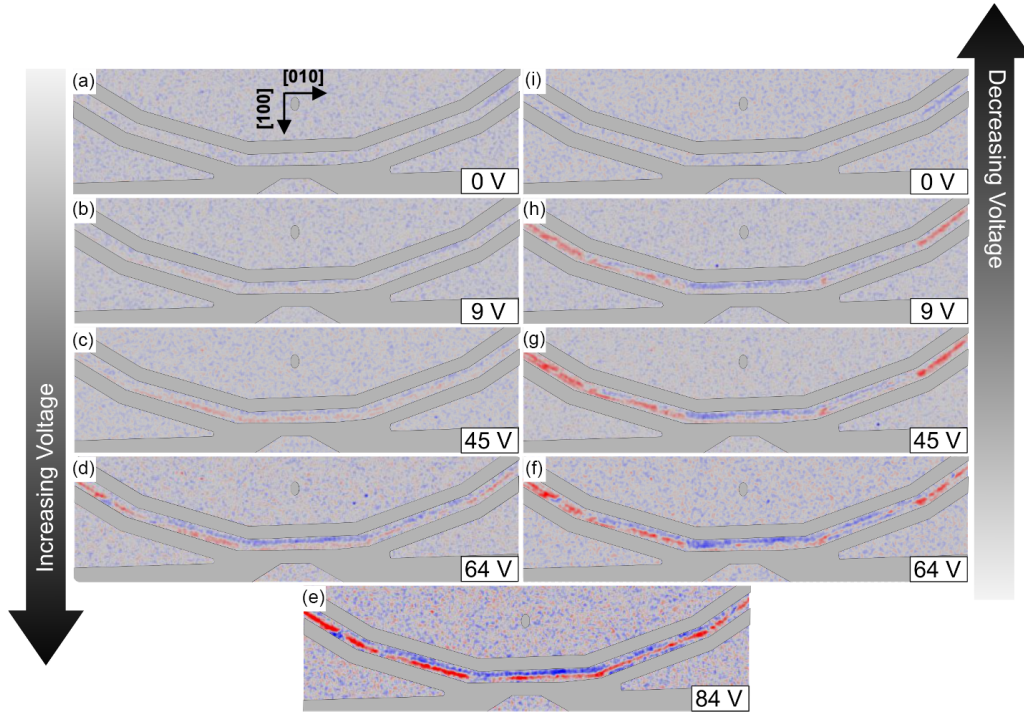


FIG. 3. (a)–(i) Set of processed SHG images as function of an applied voltage, in which the parabolic contribution has been subtracted. The voltage is increased from 0 V to 84 V (a)–(e) and then decreased to 0 V (e)–(i) as indicated by the arrows.

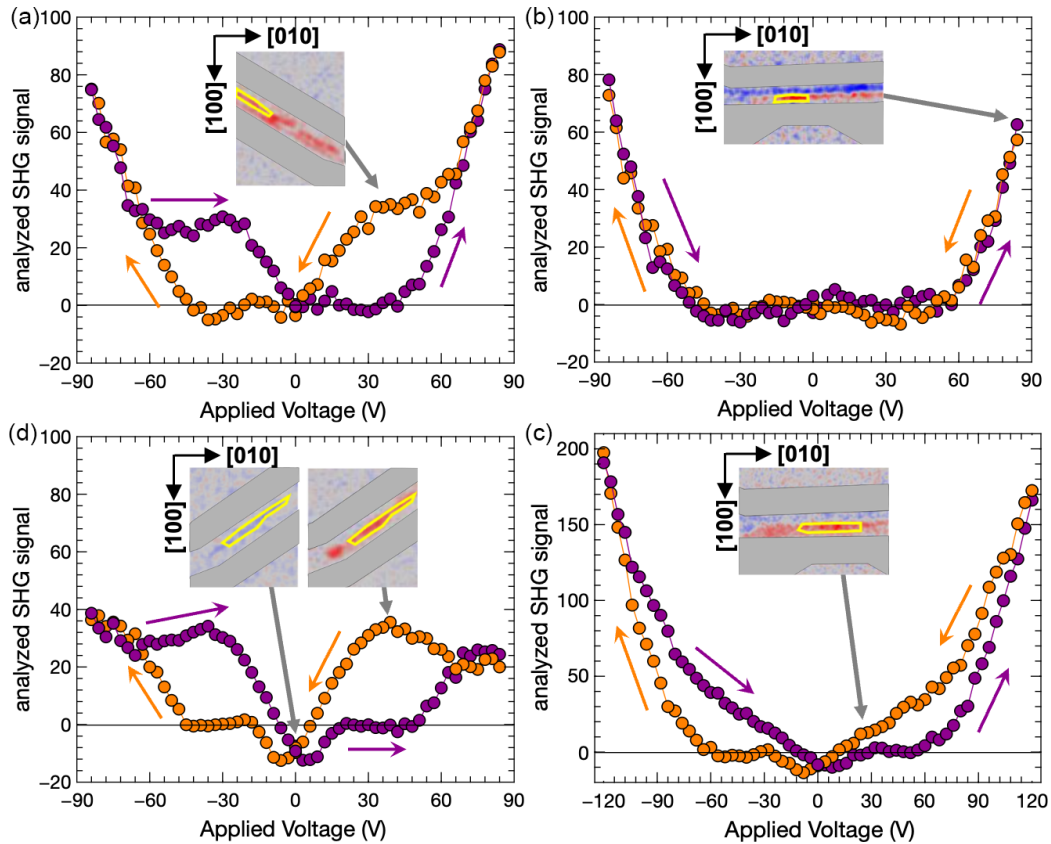


FIG. 4. (a)–(d) Typical hysteresis loops assessed at three different locations indicated by yellow square boxes displayed on the inset images. The purple (orange) solid dots indicate increasing (decreasing) applied voltages. The inset images have been chosen for an applied voltage indicated by the gray arrows. Panels (b) and (c) are taken at the same location but with different maximum electric fields.

beyond a higher threshold (~ 60 V) and increases linearly, but no remanent signal is detected upon field removal. Interestingly, applying higher voltages [Fig. 4(c)] allows one to recover a similar behavior to the one observed in Fig. 4(a). This indicates that applying an electric field along the [100] is less favorable to produce a hysteretic formation of the ferroelectric phase.

A third distinct response is shown in Fig. 4(d). Here, the SHG intensity begins to increase linearly near 50 V [just as in the case of Fig. 4(a)], followed by a change in slope around 70 V. This could suggest a saturation of the ferroelectric polarization along the direction of the applied electric field. Indeed, the PbZrO_3 texture might not undergo a complete transition at once but rather evolve progressively into the ferroelectric state through the nucleation of small domains. Such a process would result in a linear increase of $\chi^{(2)}$, dependent on the electric field strength, until the full ferroelectric saturation is achieved. When the electric field is reduced, a remanent response becomes apparent, accompanied by a slight increase of the SHG signal. Interestingly, back at zero voltage, the SHG signal exhibits a negative intensity, which is the signature of a remanent FE polarization. Indeed, as mentioned above, a negative SHG signal could only be the result of the crossed term $\chi^{(2)} \cdot \chi^{(3)} \vec{E}_A$. If the electric field is reversed as the ferroelectric polarization has not yet switched, this term will become negative. As the field continues to decrease, the signal returns to zero at about -20 V, indicating that, at this threshold, the ferroelectric polarization switches back to the AFE ground state. Such behavior is reminiscent of the double hysteresis

observed on $\text{Pt/PbZrO}_3/(\text{Ba,Sr})\text{RuO}_3$ capacitors [5], in which the reversed ferroelectric-to-antiferroelectric phase transition is often centered in the zero electric-field range. These different types of phase transitions within a given AFE layer illustrate the impact of the electrical field alignment relative to the crystal axis on the switching process.

To conclude, this work demonstrates the suitability of SHG imaging with submicron spatial resolution to investigate the electric-field-induced AFE–FE phase transition in thin epitaxial layers. The reported methodology lays the foundation for a systematic investigation of the properties of antiferroelectric thin films. We also demonstrate here the importance of the EFISHG on the SHG signals, potentially allowing a sensitive measurement of internal fields in polar materials.

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Data availability. The data that support the findings of this article are not publicly available. The data are available from the authors upon reasonable request.

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