

Light-Induced Capacitance Tunability in Ferroelectric Crystals

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ABSTRACT: The remote controlling of ferroic properties with light is nowadays a hot and highly appealing topic in materials science. Here, we shed light on some of the unresolved issues surrounding light-matter coupling in ferroelectrics. Our findings show that the capacitance and, consequently, its related intrinsic material property, i.e. the dielectric constant, can be reversibly adjusted through the light power control. High photodielectric performance is exhibited across a wide range of the visible light wavelength because of the wavelength-independence of the phenomenon. We have verified that this counterintuitive behaviour can be strongly ascribed to the existence of ‘locally free charges’ at domain wall.

Ferroic materials (e.g., ferroelectric, ferromagnetic and ferroelastic) have aroused huge interest since their discovery as a result of their switchable properties under the effect of an external stimulus. In particular, ferroelectric materials exhibit a spontaneous polarization in a certain range of temperatures that can be switched by applying an electric field. Ferroelectrics belong to a larger group of materials called ferroelastoelectrics, better known as piezoelectrics, which allow the conversion of mechanical stress into voltage and vice versa. The usefulness of such materials is clearly endorsed by the attention they have received in science and technology, since they already have many applications as sensors and actuators in many fields. For instance, they are used in instrumentation, industry, biomedicine and sound devices, as well as gaining importance in terms of energy harvesting and green electric power generation.¹⁻³

The optical control of ferroic properties is of great interest for the scientific community, since it involves the establishment of new paradigms for technology.⁴⁻¹⁶ For instance, optical control could solve one of the main drawbacks of the implementation of ferroelectric devices; namely, the circuitry. Unlike electrical control, optical control needs no contact at all. Recent research in this field has proved that macroscopic polarization and, consequently, its related properties can be tuned by means of polarized light in a ferroelectric crystal.¹⁷ This brand new light-matter coupling supposes a non-contact external control of functional properties in ferroelectrics. While this newly discovered phenomenon may open a pathway to the next generation of photo-stimulated ferroelectric devices, the studies carried out so far are still in their early stages.

The surprising ability to move ferroelectric domain walls by a coherent, low-power light source was recently proved.^{17,18} It was demonstrated that reversible optical change in ferroelectric domain configuration is possible. The implication of this discovery for the macroscopic properties of a ferroelectric crystal has also been explored, showing that the local movement of domain walls is

noted on the macroscopic scale as a change in dielectric properties.¹⁷ This phenomenon turns ferroelectric crystals into active optical materials for a new generation of photo-stimulated ferroelectric devices. However, given the novelty of this new manifestation of light-matter coupling, further stages of this long pathway still remain to be covered, and fundamental questions are still unanswered: Does the incident light wavelength affect the change of macroscopic polarization in the ferroelectric crystal? Does the crystalline orientation affect the phenomenon? Is there a power threshold for which the change of macroscopic polarization is not observable? How does the phenomenon evolve with time? The main goal of this work is to address some of the many issues that remain unexplored concerning this brand new phenomenon.

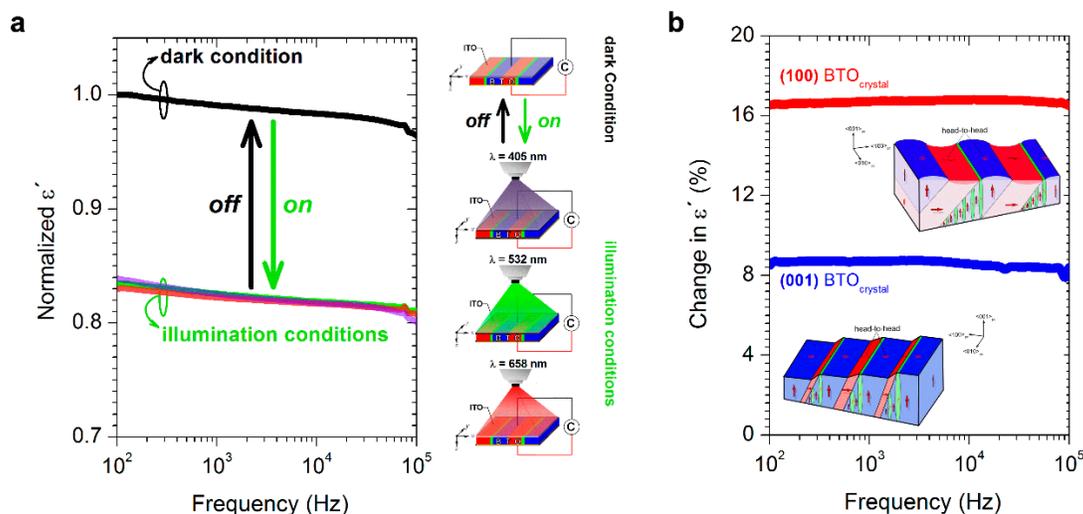


Figure 1. Wavelength and frequency dependence of dielectric constant for the (100) BTO crystal, and the impact of the crystalline orientation on the light-activated phenomenon. (a) Frequency sweep for all three wavelengths in dark and illumination conditions. The dielectric constant values are normalized by taking into account the value in the dark condition at 100 Hz. On the right of the panel, a schemes sequence showing a simplified experimental setup to determine the capacitance response is displayed. (b) Percentage change of dielectric constant for the (100) and (001) BTO crystals. The incident light power is 40 mW in all cases. Schematic domain wall structures showing out-of-plane polarization (*c*-domains, in blue), in-plane polarization (*a*-domains, in red), and combined out-of-plane and in-plane regions (*b*-domains, in green), corresponding to both crystalline orientations, are illustrated below each curve. (More information about ferroelectric domain structure for both (100) and (001) BTO crystals can be found in the Supporting Information 3 and 4).

The frequency dependence of dielectric constant of the (100) BTO crystal in dark and illumination conditions was recently reported,¹⁷ showing a reversible light-induced change in the capacitance of the sample that is not related to the previously observed photo-effects in BTO crystals.¹⁹ Here we go a step further and explore the capacitance behavior under three different wavelengths of the light source, fairly outside of the absorption spectra of the BTO.¹⁹ Figure 1(a) shows that no significant difference is appreciated between the frequency dependence of dielectric constant for the green (532 nm), red (658 nm) and blue-violet (405 nm) lasers, which imply a wide range of the visible light wavelength. A dielectric constant change of ca. 17% is displayed in all cases, thereby establishing that the phenomenon is wavelength-independent.

In order to determine how crystalline orientation impacts on this light-activated phenomenon, we carry out the same experiment, with a fixed wavelength (532 nm), but taking into account the crystalline growth direction of the BTO single crystal. BTO single crystals with (100) and (001) crystallographic orientations (i.e., in-plane polarization and out-of-plane polarization, respectively) are studied. Both single crystals develop a domain structure in which 90° domain occurrence produces a different domain density. Moreover, the appearance on localized domain regions with a polarization that combines in-plane and out-of-plane polarizations (so-called *b*-domains) is relatively higher in (100) BTO single crystal (Figure S4 and S5). As expected, this observation provides enlightening information; thus, for (001) BTO crystal the change in the dielectric constant is significantly lower than the value for (100) BTO sample, as may be observed in Figure 1(b). This result shows that the domain structure configuration, and in particular domain walls, determine the magnitude of the light-induced capacitance change. As was hypothesized,¹⁷ the key factor lies in the existence of ‘locally free charges’ at domain wall, i.e. charged domain wall. The head-to-head configuration between *a*- and *c*-domains leads to the formation of a charged

domain wall by the appearance of compensatory ‘locally free charges’ at the domain walls to balance the pressure of the bound polarization charge at the wall.²⁰⁻²³ More specifically, the stack of *b*-domains (that is, *b*-domain density) caused by the domain wall between *a*- and *c*-domains in the (001) BTO crystal is lower than the *b*-domain density in the (100) BTO crystal, as the result of a lower accumulation of local stress in the (001) BTO crystal (see Supporting Information 3 and 4). Consequently, a minor domain wall motion is triggered by the same power light. In this way, and in view of the results obtained, it is conceivable that this captivating phenomenon driven by light-matter interaction can be improved by means of domain engineering; that is, encouraging the occurrence of charged domain walls. Otherwise, no photo-induced response should be observed in a single-domain crystal, since the light-induced change in the capacitance of the crystal is related to the existence of charged domain walls.

In order to effectively evaluate the capability of a ferroelectric crystal as optical material for tuning the capacitance of a light-controlled ferroelectric-based device, light power dependent experiments were carried out, the results of which are shown in Figure 2. As may be observed, a linear relation between normalized dielectric constant and light power is displayed across all the frequency range. Thus, an effective and easy reversible control of capacitance is demonstrated to be possible. Taking into account that at zero incident optical power, the change in the capacitance should be zero, a linear fit enables the light power sensitivity of the BTO crystal to be obtained for sensor applications. The sensitivity values of 0.43 and 0.18 percentage of dielectric constant decrease per milliwatt of light power are in agreement with the observed difference in the relative changes in dielectric constant shown in Figure 1(b). It is important to note that, as may be observed in Figure 2(a), light power threshold is absent, which suggests that ferroelectric crystals could be used as active optical material for high performance photodetector systems. It is worth pointing out that

the light-activated process of the capacitance can be controlled with a high resolution, which is detectable for light power density values as low as 0.06 Wcm^{-2} . This result is over six orders of magnitude smaller than the lower light power density required for the thermally induced ferroelectric switching,^{16,24,25} which is a very promising value for high performance photodetector systems.

The following step is to consider the time-response capability of the system. In this regard, time-dependent measurements were performed, as shown in Figure 3, where one may observe that the reversible change in dielectric constant has a non-negligible response time. Thus, when the light is on, a temporal dielectric constant decrease is displayed until a constant equilibrium value is achieved, whereas a temporal increase is exhibited when the light is off until reaches the dielectric constant value for the light-off condition. The transient response of dielectric constant seems to correspond to an exponential decay/growth when the light is on/off. An exponential fitting with a high goodness of fit reveals two clearly different time constants for off-on and on-off processes. The time constants were computed for four different frequencies and the resulting values are shown in Figure 3(b). Time constants are frequency-independent, with values higher than 30 seconds. Similar time responses are obtained when analyzing the system for the red and blue-violet incident light, which shows no correlation between the light wavelength and the transient response of the observed phenomenon. In principle, the time needed to reach a new reversible state of macroscopic polarization in the material is conditioned by the domain size. Domain widths in single crystals are in the range of tens of micrometers and the domain wall area could exceed 2 mm^2 . A large volume of materials is involved in the domain switching effect and may limit the range of applications in which the technology could benefit from the phenomenon. Nevertheless, the

transient response could probably be improved by tailoring the electrode-material interface and/or exploring the material response by modifying its dimensionality.

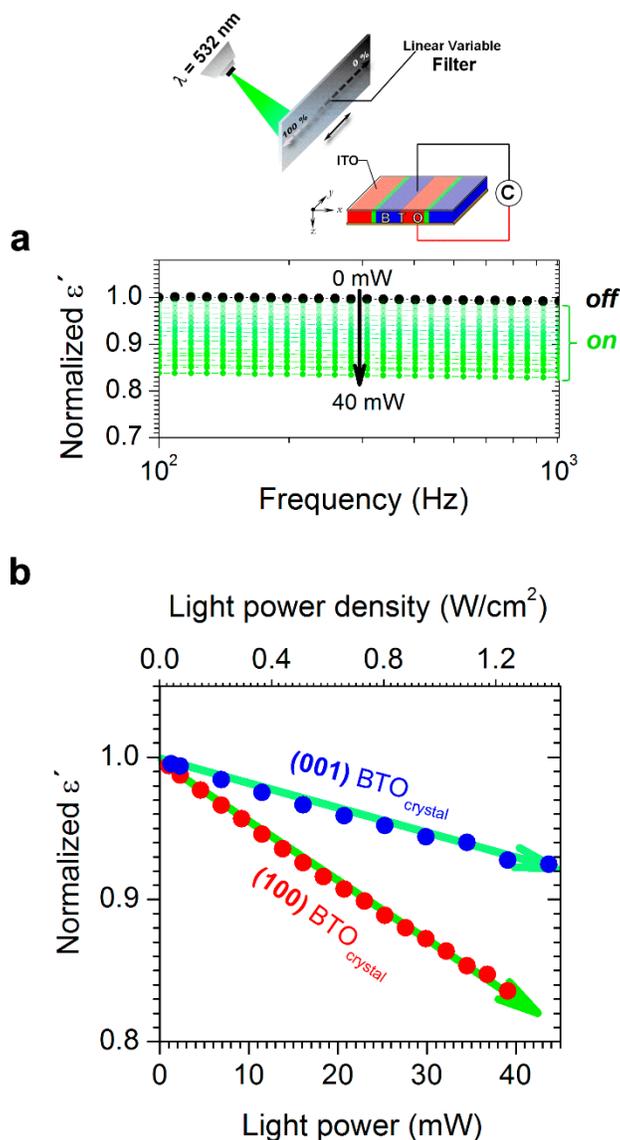


Figure 2. Light-activated dielectric constant tunability. (a) Light power dependence of the dielectric constant in illumination conditions for the (100) BTO crystal. The light power is controlled by a linear variable filter, ranging from 0 (dark condition) to 40 mW, with a light power step of 2 mW. The dielectric constant values are normalized for each frequency by taking into account the value in the dark condition. A simplified experimental scheme is shown in the upper part of the image. (b) Evolution of the normalized dielectric constant as a function of both light power and light power density, and its dependence with the crystalline orientation of the BTO crystal. The light power density was calculated according to the light spot diameter, which is 2 mm. For both crystals, the behavior shows a linear trend, the decay slope being greater for the (100) BTO crystal than for the (001) BTO crystal.

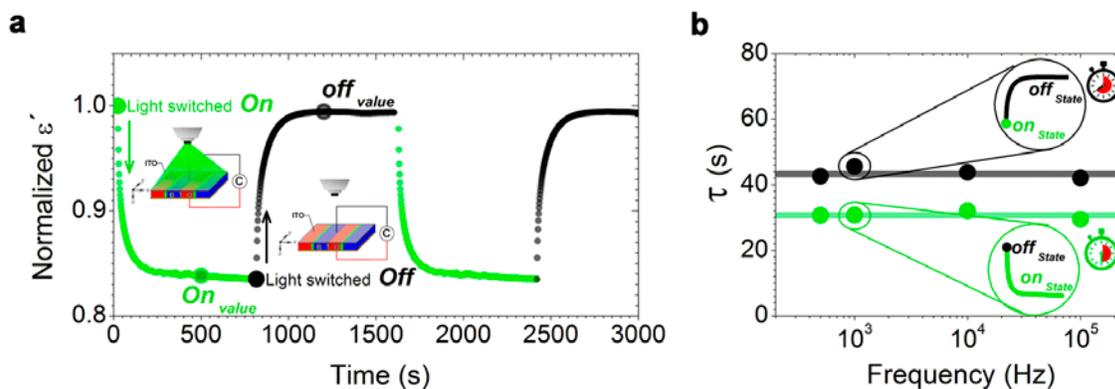


Figure 3. Time dependence and reversibility on the light-induced dielectric constant change for the (100) BTO crystal. (a) Normalized dielectric constant evolution as a function of the time, at 1 kHz. Dielectric constant transient dependence seems to correspond to an exponential decay/growth when the light is turned on/off. A similar behavior is observed (not shown) at another measurement frequency. The measurements were taken every two seconds. Additionally, a simplified experimental setup used in dark/illumination conditions is represented within the image. (b) Time constant for on and off dynamic processes at several frequencies. The inserts indicate the form of the fitted curves corresponding to decay/growth of the dielectric constant induced by the on/off light process. The error bars are not visible because the symbol size is greater than the error calculated from standard deviation.

In conclusion, here we have successfully resolved some issues concerning light-matter coupling in ferroelectric materials, although there still remain subjects waiting to be explored. Specifically, our results reveal that the capacitance of BaTiO₃ single crystals can be reversibility modified by the light power control. This precise photo-control and its wavelength-independence enable subtle fluctuations in the dielectric response to be detected with light power density as low as 0.06 Wcm⁻². More importantly, we have demonstrated that the light-activated process is intimately bound up with the crystalline orientation of the crystal. In other words, in order to improve the efficiency and effectiveness of the photo-response in ferroelectric materials, it is necessary to foster the occurrence of charged domain walls by domain engineering. Finally, we are convinced that these results will serve as an inspirational source for further studies based on light-induced processes in ferroelectric materials.

ASSOCIATED CONTENT

Supporting Information.

The following files are available free of chargeThe Supporting Information is available free of charge on the ACS Publications website at DOI:

Details of the BTO samples, experimental methods, experimental setup for capacitance measurements, and domain structure characterization of the samples (PDF).

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Author Contributions

J.E.G. and D.A.O. planed the research. D.P.-M. performed the capacitance measurements. F.R.-M. and A.D.C. performed the domain structure characterization. Data processing was carried out by D.P.-M., A.D.C. and F.R.-M. All the authors contributed to the discussion of the results. D.P.-M., J.E.G. and F.R.-M. wrote the manuscript with inputs from J.F.F. The work was supervised by J.E.G. and J.F.F. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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