New insights into the optical control of macroscopic polarization in ferroelectric crystals

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ABSTRACT

Recent research in the field of ferroic materials has proved ferroelectric domain wall motion induced by polarized light. Further research showed that this phenomenon leads to the ability to tune macroscopic polarization and their related properties by means of polarized light in a ferroelectric crystal. This brand-new light-matter coupling supposes a non-contact external control of dielectric and other related properties in ferroelectrics.

The aim of this work is to answer some of the many issues which remain unknown concerning this brand-new phenomenon. For this purpose a custom-made versatile setup was built up. The effect was studied as a function of wavelength, time, power and crystalline orientation to determine some of the dependencies of the phenomenon.

The results showed that the phenomenon seems to be wavelength-independent, it has a non-negligible response time and no power threshold. Also an important result was to discover that the power dependence is linear, which makes the phenomenon suitable for creating transducers. Additionally, the effect has a strong dependence on crystalline orientation, as expected.

The presented results are of great interest for future research and may open a pathway to find a next generation of photo-stimulated ferroelectric devices.
This thesis is written as part of the Bachelor's Degree in Engineering Physics at Universitat Politècnica de Catalunya. The research described herein was conducted under the supervision of Jose Eduardo Garcia at the Department of Physics, Universitat Politècnica de Catalunya, between February and June 2017. This work is to the best of my knowledge original, except where acknowledgements and references are made to previous work.

First and foremost, I have to thank my supervisor Jose Eduardo Garcia for giving me the opportunity to work on this project and providing me with all the facilities for the research. I would also like to thank him for introducing me to this field and for his kindness, making my research period so comfortable. I am also grateful to Diego Alejandro Ochoa from the Department of Physics for his help during my research.

I take this opportunity to express gratitude to my friends, who gave me the support I needed these years. The time I spent at university was not easy in academic and personal terms, and they helped me to carry on. I am indebted to them for their friendship, which sometimes I did not deserve.

Most importantly, none of this could have happened without my family. I am grateful to my parents for giving me the education I have nowadays. I would also like to especially thank my grandmothers, who raised me with the love I can't return. They would be very proud if they could see me now. This thesis is dedicated to you.
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Ferroic materials (e.g., ferroelectric, ferromagnetic and ferroelastic) have aroused huge interest since its discovery on 19th century, due to their switchable properties under the effect of an external stimulus. In the case of ferroelectrics, discovered at early 20th century, a spontaneous polarization of the material is observed in a certain range of temperatures, which can be reverted 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 and the attention they get in science and technology is easily proved, since they already have so many applications as sensors and actuators in many fields. For instance, they are used in instrumentation, industry, biomedicine, sound devices and they are starting to be important in terms of energy harvesting and green electric power generation.

The optical control of ferroic properties is of great interest for the scientific community, as it involves the establishment of new paradigms for technology. Referring to the field of ferroelectric devices such as the nonvolatile ferroelectric random access memory (FeRAM), optical control could solve one of the drawbacks of the implementation of these memories: circuitry. Unlike electrical control, optical control needs no contact at all. It is also speculated with possible applications as photo-actuators, i.e. devices capable of producing optically stimulated reversible deformations.

Recent research in this field has proved that macroscopic polarization and their related properties can be tuned by means of polarized light in a ferroelectric crystal. This
brand-new light-matter coupling supposes a non-contact external control of dielectric and other related properties in ferroelectrics. Although this discovered phenomenon may open a pathway to find a next generation of photo-stimulated ferroelectric devices, the previous studies carried out and the ones that are included in this thesis are only a first step in this long way.

1.1 State of the art

It all started with the article *Ferroelectric domain wall motion induced by polarized light* [1], by Fernando Rubio-Marcos¹, Adolfo Del Campo¹, Pascal Marchet² and Jose F. Fernández¹. The authors showed a surprising ability to move ferroelectric domain walls of a BaTiO$_3$ single crystal by varying the polarization angle of a coherent light source. They stated that this unexpected coupling between polarized light and ferroelectric polarization modifies the stress induced in the BaTiO$_3$ single crystal at the domain wall. The effect could potentially lead to the non-contact remote control of ferroelectric domain walls by light.

The study was followed by Fernando Rubio-Marcos, Diego A. Ochoa³, Adolfo Del Campo, Miguel A. García¹, Germán R. Castro⁴, Jose F. Fernández and Jose E. García³ [2]. After the discovery of the phenomenon, they demonstrated that reversible optically change of ferroelectric domain configuration is possible. This effect leads to tune macroscopic polarization and their related properties by means of polarized light, i.e. it supposes a non-contact external control. Hence, it was not only a microscopic effect, but a macroscopic one. It was discovered that the local movement of domain walls is noted in the macroscopic scale as a change in dielectric properties. Thus, new perspectives were open in using this phenomenon in the future as a photo-actuator or sensor.

After the discovery and the first and crucial step, more stages of this long pathway will be needed. It is a complex process of understanding the phenomenon and maybe finding a next generation of photo-stimulated ferroelectric devices. In this context, the next step of the pathway includes this work. Due to the novelty of the phenomenon, this work was necessary to answer some questions related to the macroscopic behaviour of this light-matter coupling.

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1.2 Aim of the thesis

The main goal of this work is to answer some of the many issues which remain unknown concerning this brand-new phenomenon. For this purpose, some objectives were addressed to step-by-step accomplish the aim of this thesis.

First of all, it was needed to design and assemble a versatile setup to carry out the experiments. Once the setup was ready, the next stage would be to investigate some questions about the phenomenon. Does the incident light wavelength affect the change of macroscopic polarization in a 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 vary with optical power of incident light? How does the phenomenon evolve with time? This work tried to solve these questions analyzing and discussing the experimental results in order to gain insight into the theoretical frame of the studied effect.

As can be seen, this project has a great experimental character, as it requires self-made setups to carry out different experiments. The collected data will be of great help to acquire more knowledge about this new phenomenon. Furthermore, this may open up the possibility of a new field inauguration in science and technology.
In this chapter we are going to see the theoretical background needed to understand the physics involved in this work, starting from what is a ferroelectric crystal. The main characteristics of these materials will be briefly explained to give a general idea about the field too. Additionally, since the phenomenon we are focusing on is a new light-matter coupling, we present here some basic concepts about already known light-matter interactions. Finally, details of the previous research on the new phenomenon are stated at the end of this chapter, placing the reader at the starting point of this work.

2.1 Introduction to ferroelectric crystals

Ferroelectric crystals are substances in which a built-in spontaneous polarization $P_s$ exists in a certain range of temperatures and isotropic pressures in the absence of an external electric field [3]. The spontaneous polarization can be switched between its two or more orientational states by applying an external electric field or a mechanical stress. This is called ferroelectric switching, which is an important feature to distinguish ferroelectric and pyroelectric crystals. Pyroelectric materials show a flow of charge to and from its surfaces upon a temperature change, which changes the spontaneous polarization. In fact, all ferroelectric materials are pyroelectric, but not the other way around (see Figure 2.1).
CHAPTER 2. BACKGROUND

Crystal systems
(32 Point Groups)

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Figure 2.1: A schematic tree of the different classes of crystal systems and their property classifications. Piezoelectricity refers to elastic strains in the material in response to an external electric field. Pyroelectricity refers to a presence of spontaneous polarization in the material that can be changed in magnitude with temperature, resulting in a charge flow to and from the material surfaces. A ferroelectric material therefore is pyroelectric, piezoelectric, and non-centrosymmetric [4]. Figure adapted from [5].

2.1.1 Characteristics

Non-centrosymmetry

As it can be seen in Figure 2.1, ferroelectric materials (in their ferroelectric phase) are pyroelectric, piezoelectric and non-centrosymmetric. Non-centrosymmetry, i.e. lack of inversion symmetry in their crystalline structure, endows this materials with possible nonlinear optical responses which would disappear in a centrosymmetric material. Some examples are spontaneous polarization, electro-optic effect or sum-difference frequency generation. In fact, some of the best-known electro-optic and nonlinear optical materials in lasers and optics are ferroelectrics.

Polarization and domains

Ferroelectric materials typically exhibit separate regions called *domains* which differ in their spontaneous polarization direction. The number of distinct spontaneous polarization directions in a ferroelectric depends on its point group symmetry. All polar classes can be potentially ferroelectric because they contain at least one unique axis that does not change with the symmetry operations of the point group [5] (see Table A.1 from Appendix A for detailed information).

Each region in a ferroelectric with uniform polarization, $P$, is called a *ferroelectric domain*. For each polarization in direction $+P$, there can be a polarization in the direction $-P$, which means at least two degenerate polarization states. There can be additional...
2.1. INTRODUCTION TO FERROELECTRIC CRYSTALS

Figure 2.2: Schematic examples of some common types of ferroelectric domain walls. Broad arrows indicate the direction of polarization, $P_s$ in each domain, and the hatched plane indicates the domain wall. Figure adapted from [5].

degeneracies, from the number of distinct polarization directions possible in a crystal system. When two domains with distinct polarization directions $P$ meet within a crystal, they form domain walls that separate the two domains.

The domain walls are also restricted by symmetry to distinct crystallographic planes within the crystal depending on the nature of the walls (see Table A.1). As can be deduced from the $\pm P$ degeneracy, all ferroelectrics can possess 180°domain walls, or antiparallel domain walls, that separate $+P$ and $-P$ polarization domains. For uniaxial trigonal and hexagonal materials only 180° can exist, while for tetragonal, orthorombic, monoclinic and triclinic more orientations can be found, such as 60°, 90° or 120° (see Figure 2.2).

The most common symmetries among materials in nature are the low symmetries, such as monoclinic, triclinic and orthorombic systems [6].

Note that a fictitious, infinite ferroelectric crystal (without surfaces) in equilibrium state would be composed of a single domain, since creation of domain walls costs energy. However, the formation of domains and domain walls in real life ferroelectric can be understood considering a slab of a uniaxial ferroelectric crystal with its polarization direction perpendicular to the slab surfaces. From a single domain state, the surfaces will be charged with charge density $\sigma = +P$ and $\sigma = -P$ and an electric field (called depolarizing field), $E_d = -P/\varepsilon_0$, will be created between these uniformly charged surface sheets of opposite polarities. This field destabilizes the spontaneous polarization and a way for the crystal to compensate it is to split up into a multi-domain state. Energy balance between domain walls energy and the decrease in polarization energy through multi-domain creation determines the final domain structure.
DOMAIN REVERSAL

As explained before, ferroelectrics are distinguished by the fact that its polarization direction can be changed by an externally applied electric field. Domains with polarization direction closer to the applied field are favored, and they grow by nucleation and growth or by the movement of existing domain walls.

PHASE TRANSITIONS

As the temperature is increased, a ferroelectric undergoes a phase transition, which is accompanied by the disappearance of spontaneous polarization and by a change in the symmetry of the crystal lattice. This temperature is called the Curie temperature, denoted by \( T_c \). Above \( T_c \) the material becomes paraelectric, i.e. it has the ability to become polarized under an applied electric field but unlike ferroelectricity, the removal of the field results in the polarization in the material returning to zero [7]. This phase with the highest symmetry is called the prototype phase. In most, but not all cases, this phase is non-polar and occurs in the highest temperature phase [5].

2.1.2 Barium titanate

Barium titanate oxide (BaTiO\(_3\)), also called BTO, is the ferroelectric crystal we will put the spotlight on, since it is the one for which the new light-matter interaction has been reported. It was discovered by Wainer and Salomon in 1942 [8] and is the most widely used ferroelectric material [9]. Figure 2.3 shows the basic perovskite-like structure of barium titanate crystal with the titanium ion occupying the octahedrally coordinated site and the barium ion in the twelve coordinated site in a high temperature cubic symmetry. The ferroelectric phase at room temperature is tetragonal with oxygen and titanium ions shifting to produce spontaneous polarization. Kay and Vousden [10] showed that BaTiO\(_3\) has a series of ferroelectric-ferroelectric transitions from tetragonal to orthorhombic at 5°C and a transition from orthorhombic to rhombohedral at -90°C. These transitions can be seen in Figure 2.4.

DIELECTRIC PROPERTIES

Discussions of the dielectric properties of BaTiO\(_3\) crystals and polycrystals must recognize that no "true" values can be quoted. Almost every chemical and physical deviation from purity and perfection has a substantial effect on the dielectric properties [11].
2.1. INTRODUCTION TO FERROELECTRIC CRYSTALS

Figure 2.3: Perovskite structure of BaTiO$_3$. (a) Representation with the Ba ion in the center of the cell and Ti ions inside the oxygen octahedra. Figure reproduced from [9]. (b) Alternative representation as a network of corner-linked oxygen octahedra, with titanium filling the octahedral holes and barium filling the dodecahedral holes. Figure reproduced from [5].

As the single crystal is strongly anisotropic (Figure 2.4), the values commonly found for unpoled polycrystals should be some average of these. The low dielectric constant in the $c$-direction for the single crystal is due to the fact that the displaced atoms are tightly bound by the ferroelectric displacement along the polar axis, while they are relatively free to vibrate perpendicular to it [11]. Actually, measured values for BTO samples will be lower in the case of a-plane orientation and higher for c-plane orientation. This is due to the contribution of c-plane domains in an a-plane sample and the other way around.

Figure 2.4: Dielectric permittivity for single crystal BaTiO$_3$ as a function of temperature. Equivalent polar directions under an applied electric field (E) for the polymorphic phases related to the cubic prototype perovskite structure. Figure reproduced from [12].
CHAPTER 2. BACKGROUND

2.2 Light-matter interactions/optical properties

Matter consists of atoms which are comprised of charges particles and therefore when an electromagnetic field is incident in matter significant interactions can take place. Atoms are also particles and due to particle nature of light, not only electromagnetic interactions take place, there are particle collision phenomena. However, this work does not deal with situations where particle-like treatment of light becomes essential. In this context, we will focus on the range of electromagnetic spectrum corresponding of visible light, i.e. we treat with optics. In this field, two big groups of phenomena can be established regarding the linearity of the phenomenon: linear optics and nonlinear optics.

2.2.1 Linear optics

An insulating material for which polarization $P$ is proportional to the electric field $E$, with a scalar constant of proportionality is called an isotropic linear dielectric. In crystals while there may be a linear relation between $P$ and $E$, in general it is a tensor equation because in a crystal $P$ may have nonzero components perpendicular to $E$ [13]. For instance ferroelectric crystals, which in fact are nonlinear dielectrics.

Only one parameter is needed to relate $P$ and $E$ in an isotropic linear dielectric. However, three constants are conventionally used for the constitutive equation: susceptibility $\chi_e$, permittivity $\epsilon$ and relative permittivity $\epsilon_r$. They are defined in Table 2.1. These parameters are not independent; any one determines the other two. For example, from $D = \epsilon_0 E + P$ and $D = \epsilon E$, we derive a relation between $\epsilon$ and $\chi_e$, $\epsilon = \epsilon_0 (1 + \chi_e)$; then by the definition of $\epsilon_r$, $\epsilon_r = 1 + \chi_e$. Note that $\chi_e$ is always $> 0$, because the atomic dipoles align with $E$ so that $P$ points in the same direction as $E$. Therefore $\epsilon > \epsilon_0$ and $\epsilon_r > 1$ for any dielectric material [13].

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<th>Parameter</th>
<th>Symbol</th>
<th>Defining equation</th>
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<tr>
<td>susceptibility</td>
<td>$\chi_e$</td>
<td>$P = \chi_e \epsilon_0 E$</td>
</tr>
<tr>
<td>permittivity</td>
<td>$\epsilon$</td>
<td>$D = \epsilon E$</td>
</tr>
<tr>
<td>relative permittivity</td>
<td>$\epsilon_r$</td>
<td>$\epsilon_r = \epsilon / \epsilon_0$</td>
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Table 2.1: Parameters for an isotropic linear dielectric with their definitions. Table reproduced from [13].

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$^1D$ stands for the electric displacement field and $\epsilon_0$ is the permittivity in vacuum $= 8.85 \cdot 10^{-12} F/m$
In terms of electromagnetic waves, the net effect of introducing a homogeneous, isotropic dielectric into a region of free space is to change $\epsilon_0$ to $\epsilon$ and $\mu_0$ to $\mu$ in Maxwell’s Equations. The phase speed in the medium now becomes $v = 1/\sqrt{\epsilon \mu}$. The ratio of the speed of an electromagnetic wave in vacuum to that in matter is known as the absolute index of refraction $n$; $n \equiv c/v = \sqrt{\epsilon \mu/\epsilon_0 \mu_0}$ [14]. Actually $\epsilon_r$ and therefore $n$ are frequency dependent. For instance, the dependence of $n$ is a well-known effect since Sir Isaac Newton dispersed white light into its constituent colors. In this context, relative permittivity can be expressed in its real and imaginary parts, and we will use the following notation from now on: $\epsilon_r = \epsilon' + i\epsilon''$.

It is in this linear and frequency-dependent terms where the basic light-matter interactions appear. This is the case of scattering, absorption, dispersion, reflection, refraction and other well-known phenomena from geometrical optics.

### 2.2.2 Nonlinear optics

Nonlinear optics is the study of phenomena that occur as a consequence of the modification of the optical properties of a material system by the presence of light. Typically, only laser light is sufficiently intense to modify the optical properties of a material system. The beginning of the field of nonlinear optics is often taken to be the discovery of second-harmonic generation by Franken et al. [15], shortly after the demonstration of the first working laser by Maiman [16] in 1960. However, some nonlinear effects were discovered prior to the advent of the laser, such as the observation of saturation effects in the luminescence of dye molecules reported by G.N. Lewis et al. [17].

When susceptibility is not a function of the field, linear relationship between the polarization and the electric field can no longer be applied and we can speak of nonlinear optics. In this case, the susceptibility itself becomes dependent on the electric field and the relation between $P$ and $E$ is:

$$P(t) = \chi^{(1)}(t)E(t) + \chi^{(2)}E^2(t) + \chi^{(3)}E^3(t) + ...$$

(2.1)

$$= P^{(1)}(t) + P^{(2)}(t) + P^{(3)}(t) + ...$$

where the first term is the usual linear polarization and the others are referred to as the nonlinear polarization. The quantities $\chi^{(2)}$ and $\chi^{(3)}$ are the second- and third-order nonlinear optical susceptibilities, respectively [18]. In Equation 2.1, $\chi^{(n)}$ may be regarded as the response function of the material. The polarization can be expressed in
the frequency domain like:

\[
P_l(\omega_i) = \chi_{lm}^{(1)}(\omega_i)E_m(\omega_i)
+ 2\chi_{lmn}^{(2)}(\omega_i;\omega_j,\omega_k)E_m(\omega_j)E_n(\omega_k)\delta(\omega_i;\omega_j + \omega_k)
+ 6\chi_{lmno}^{(3)}(\omega_i;\omega_j,\omega_k,\omega_h)E_m(\omega_j)E_n(\omega_k)E_o(\omega_h)\delta(\omega_i;\omega_j,\omega_k,\omega_h)
+ \text{higher terms in } E \text{ and other terms involving magnetic field } B + ...
\]

(2.2)

where the subscripts \(l, m, n, o\) indicate cartesian components and \(\omega_i, \omega_j, \omega_k, \text{etc.}\), represent the frequencies of interest. Factor ‘2’ in Equation 2.2 comes from the definition of the electric field: 
\[E(t) = E e^{-i\omega t} + c.c.\]
This notation follows the one used in [17]. The delta function assumes the value of unity when the frequencies in its argument satisfy: \(\omega_i = \omega_j + \omega_k\).

From Equation 2.2 we can identify different phenomena in each term. For example, from the second term, \(P_l^{(2)}(\omega_i) = 2\chi_{lmn}^{(2)}(\omega_i;\omega_j,\omega_k)E_m(\omega_j)E_n(\omega_k)\delta(\omega_i;\omega_j + \omega_k)\), we may have one of the following nonlinear effects:

- \(\chi_{lmn}^{(2)}(\omega_i;\omega_j,\omega_k)\): optical three-wave mixing, which includes sum- and difference-frequency generation
- \(\chi_{lmn}^{(2)}(2\omega;\omega,\omega)\): optical second-harmonic generation or frequency doubling
- \(\chi_{lmn}^{(2)}(\omega;0,\omega)\): linear electro-optic or Pockels effects
- \(\chi_{lmn}^{(2)}(0;\omega,\omega,\omega)\): optical rectification
- \(\chi_{lmn}^{(2)}(\omega_j + \omega_k;\omega_j,\omega_k)\): frequency upconversion, or
- \(\chi_{lmn}^{(2)}(\omega_j - \omega_k;\omega_j,\omega_k)\): parametric oscillation

Or more examples, from the third term in equation 2.2 we may have:

- \(\chi_{lmno}^{(3)}(\omega_i;\omega_j,\omega_k,\omega_h)\): optical four-wave mixing
- \(\chi_{lmno}^{(3)}(3\omega;\omega,\omega,\omega)\): optical third-harmonic generation
- \(\text{Re}\chi_{lmno}^{(3)}(\omega;\omega,\omega,\omega)\): a nonlinear refractive index
- \(\text{Im}\chi_{lmno}^{(3)}(\omega;\omega,\omega,\omega)\): two-photon absorption, or
- \(\text{Im}\chi_{lmno}^{(3)}(\omega_s;\omega_l,-\omega_l,\omega_s)\): stimulated Raman scattering
2.3 New light-matter interaction

As mentioned on section 1.2, two stages of previous research have been carried out in the last months. First, the article by F. Rubio-Marcos et al. [1] was presented as a discovery of a surprising ability to move ferroelectric domain walls of BaTiO$_3$ using a coherent light source. They characterized the domain structure using X-Ray Diffraction and Confocal Raman Microscopy. They found that their sample presented a tetragonal symmetry with two different crystallographic orientations: (001) or c-plane and (100) or a-plane. In addition, using Raman microscopy they found other regions between a- and c-plane domains, which they called b-domain regions, that were a combination of a-domains and c-domains. These regions appeared at domain boundaries and were found to be complex domains which reduce domain wall stress. Focusing on one of these domain boundaries, the research group found that when illuminating with polarized light, domain wall moved some microns. Hence, they were able to module the motion of ferroelectric domain walls by varying the polarization angle of a coherent light source$^2$. The schematic behaviour is shown on Figure 2.5(a), where domains represented by colours appear displaced when laser is on.

Then, the already mentioned subsequent research [2] demonstrated tuning of macroscopic polarization and their related properties by means of polarized light. The aim of this second step was to investigate what was the extent of this coupling between polarized light and ferroelectric polarization. Figure 2.5 is a summary of their research. They proposed, as in the previous article, that complex domain structure is composed of out-of-plane polarization (c-domains) and in-plane polarization (a-domains) with head-to-head configuration of the polarization vectors. Hence, the head-to-head configuration maximizes the internal stress at the domain wall, so the c/a-domain wall is hindered by b-domains. The complex b-domain structure was not resolved macroscopically in [1], and this is one of the main results that this later study offers. High-resolution Synchrotron X-Ray Diffraction was used to resolve those complex structures.

The research group thought that different domain configurations should lead to different values of functional properties, such as dielectric permittivity, piezoelectric constants, and so on. A light induced change in the macroscopic dielectric permittivity of the BTO crystal can be seen in Figure 2.5. A notable variation of the real permittivity value occurs when the ferroelectric crystal is illuminated (Fig. 2.5(b)), which is related to the difference in its macroscopic polarization. Negligible differences in imaginary

$^2$Green 532 nm laser was the light source used in the article and in the following research
permittivity are shown (Fig. 2.5(c)). The observed change in permittivity is a conclusive proof of the light-controlled macroscopic polarization in ferroelectrics.

Figure 2.5: Reversible domain structure change evidenced through monitoring the macroscopic dielectric response. (a) Schematic view of the phenomenon, where the crystal is represented with its top ITO transparent electrical contact and its internal domain structure. Red colour represents a-domains, blue represents c-domains and green b-domains. The domain walls move when polarized light strikes the sample, and this is monitored measuring impedance change. (b),(c) Real relative permittivity $\epsilon'$ and imaginary relative permittivity $\epsilon''$ of the BTO crystal before and after optical excitation, as a function of the frequency. Figure extracted from [2]

To sum up, it has been shown that reversible optical change of ferroelectric domain configuration is possible. This is the starting point of this work. The aim was to gain insight about this phenomenon and try to bring it closer to future technological applications. This electric polarization switching driven by light will have the opportunity to compete with or to complement the previous-known electric polarization switching by an electric field or by an applied strain. All of this seems to lead to a new generation of ferroelectric devices, such as the already mentioned photo-actuators.
This chapter contains the information related to the methods used all along the thesis. All the relevant information about the samples used is presented at the beginning. The custom-made experimental setup designed is also detailed next. Finally, the procedure followed to obtain the pertinent measures is explained, as well as the final data processing used to visualize the results, which will be seen on Chapter 4.

3.1 Samples

The BaTiO$_3$ single crystals used in this work were produced by top-seeded solution growth and provided by PIKEM Ltd (UK). The $5 \times 5 \times 0.5$ mm BTO crystals were grown with two different crystalline orientations. The first sample, hereafter referred as 'sample a', was grown with (100) orientation or a-plane. The second sample, hereafter referred as 'sample c', was grown with (001) orientation or c-plane. The single-crystals were covered with a indium tin oxide (ITO) layer on the top face$^1$ and with a gold layer on the bottom face$^2$ as electrical contacts. ITO was chosen as a transparent contact in order to let the laser light reach the BTO crystal.

These two samples would theoretically have a single domain of a-plane in case of sample a, or c-plane in case of sample c. But actually this is not what is found analyzing

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$^1$Via sputtering at Research Group on Solar Energy Materials and Systems in the Department of Advanced Materials for Energy of the Catalonia Institute for Energy Research (IREC)

$^2$Via sputtering using Quorum Sputter Coater SC7620, at Department of Physics, UPC
BTO samples. As it can be seen in Figures 3.1 and 3.2 the domain structure is much more complicated.

Figures 3.1 and 3.3(a) show the domain structure we find on sample \(a\), which is the same crystal used on previous research. Figure 3.3(a) displays a schematic view of the domain structure, combining AFM and Raman mapping information. It shows a domain structure composed of a-domain and c-domain, which are represented in red and blue colours. The head-to-head configuration maximizes the internal stress at close to the domain wall. As a consequence of these stresses the a-c-domains are hindered by b-domains, which are represented in green. The insert of the b-domains structure shows how internal stress at the domain wall is minimized by a bundle of alternate a-domain and c-domain [1].

\[\text{Figure 3.1: Mapping of the domain structure of the BTO single crystal through confocal Raman microscopy for sample } a. (a) \text{ Image I is an optical micrograph of the BTO single crystal. The white rectangle shows the scanned area. Image II is a Raman image showing the domain distribution at the surface by colour code and so does III in the depth scan, cross section. Raman spectra having same spectral shift for the Raman modes are identified using the same colour. The intensity of the colour is correlated with the Raman intensity. (b) Main Raman spectra of BTO Raman image associated with the three different colours: red=a-domain, blue=c-domain, green=b-domain, which are collected in the points marked as } A, C \text{ and } B \text{ in (a.II) respectively. Figures extracted from [1].}\]

Figures 3.2 and 3.3(b) show the domain structure we find on sample \(c\), which is obviously different from sample \(a\). This difference allowed us to compare between crystal orientations for our phenomenon\(^3\). More specifically, Figure 3.3(b) shows a domain

\(^3\text{Characterization and images of sample } c \text{ (Figures 3.2 and 3.3(b)) supplied by laboratory of confocal raman microscopy of CSIC’s Instituto de Cerámica y Vidrio}\)
structure composed of c-domain and b-domain, which are represented in blue and green colours. In this case simply the absence of a single domain in the crystal, which would be energetically unfavorable, causes an internal stress. As a consequence, the material breaks down into a multi-domain structure and b-domains appear, represented in green, between the different c-domains.

![Figure 3.2](image1)

**Figure 3.2:** Mapping of the domain structure of the BTO single crystal through confocal Raman microscopy for sample c. (a) As in Figure 3.1(a), (a) shows the optical micrograph, the Raman image showing the domain distribution at the surface and in depth. (b) Main Raman spectra of BTO Raman image associated with two different colours in this case: blue=c-domain, green=b-domain, which are collected in the points marked as C and B in (a,II) respectively.

![Figure 3.3](image2)

**Figure 3.3:** (a) Scheme of the BTO complex domain structure for sample a. Figure extracted from [1]. (b) Scheme of the BTO complex domain structure for sample c.
CHAPTER 3. METHODOLOGIES

3.2 Experimental setup

The experimental setup idea was, as explained on the introduction section, to design and assemble a versatile setup to carry out the desired experiments. The setup needed to be able to hold the sample on a certain spot to irradiate it with the lasers. Three different laser diodes were chosen: the same green 532 nm wavelength laser used in previous research, a red 658 nm laser and a blue-violet 405 nm laser. These laser diodes should be placed at some constant distance to the sample and they needed to be switched on and off easily. Also, the optical power of the laser had to be monitored and controlled, by means of increasing and decreasing its value as desired. For the red and blue-violet laser diodes some lenses were used to focus the laser beams, which diverge too much for the foreseen experiments (and compared to our standard, the green laser). All this also requires a power supply for the laser, the impedance analyzer to take the measures, and a computer to obtain and process the experimental data. The resulting full experimental setup is shown on Figure 3.4, with the designed main part in the center, connected to the power supply and impedance analyzer on the right and to the computer on the left.

![Figure 3.4: General overview of the setup](image)

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3.2. EXPERIMENTAL SETUP

3.2.1 Setup overview

The main part of the setup is shown on Figure 3.5. It has different configurations depending on the laser used and on the experiment to perform. The main components are the following (see Appendix B for more information and photographs):

- (A) Laser Diode -LD- mount: holds and controls the laser diodes. Laser diodes can be quickly and easily changed in the mount, simply inserting the laser diode into the socket and fastening a clamp ring with two screws. The mount is connected to the power supply, which is controled by the computer\textsuperscript{4}. In case of using red or blue-violet lasers, an aspheric lens is mounted on the LD mount to focalize the laser beam.

- (B) Support micropositioners: help to position the neutral density filter precisely.

- (C) Neutral Density -ND- filter: reduces the optical power that reaches the sample. This continuously variable reflective neutral density filter provides linear, adjustable attenuation within the coated region via translation.

- (D) Iris: cuts the laser beam when necessary. It avoids switching on and off the laser diode to illuminate or not the sample.

- (E) Powermeter: measures the optical power incident onto the sample. The measured values are displayed on the computer as a function of time\textsuperscript{5}.

- (F) Plano-convex lens: focalizes the laser beam in case of using red or blue-violet laser diodes, aided by the aspherical lens on the LD mount.

- (G) Sample holder: 3D printed custom-made piece with a copper contact to place and hold the BTO sample.

- (H) Contact micropositioners: place two tungsten tips to make electrical contact with the sample and measure impedance thanks to the impedance analyzer.

\textsuperscript{4}Using LabVIEW\textsuperscript{TM} 2016, National Instruments
\textsuperscript{5}Using Thorlabs Optical Power Meter Utility software, Thorlabs, Inc.
CHAPTER 3. METHODOLOGIES

Figure 3.5: Main setup component with the LD mount (A), support micropositioners (B) for the ND filter (C), iris (D), powermeter (E), plano-convex lens (F), sample holder (G) and contact micropositioners (H).

3.3 Measures and data processing

3.3.1 Procedures for measures

Frequency sweep

Frequency sweep experiments were performed to obtain the on/off behaviour of the phenomenon, as in the previous research. In order to do that, the impedance analyzer was set with frequency as a sweep variable. Settings also include taking 101 point measures from 100Hz to 1MHz in logarithmic scale, so that in a semilogarithmic plot measures were linearly spaced along the frequency axis. For each laser, one frequency sweep with laser off was measured, then the sample was illuminated for some minutes and another frequency sweep was made, with the laser still on. More measures were
taken after one or two minutes with the laser still on to ensure that there was no temporal drift\textsuperscript{6}. Optical power was measured just after obtaining the data.

**Time dependent**

In this case, to determine time response of the phenomenon, impedance analyzer was set to take time as the sweep variable, taking 801 measure points with 2 seconds between measure and measure, at constant frequency. Each time-dependent experiment consisted in start the measure with the analyzer, then start irradiating the sample and after 800 s, stop illuminating it and wait another 800 s, while all the process is measured. This was repeated with four different frequencies for each laser. Optical power was measured before and after the measure to detect if there was some significant change.

**Power dependent**

With the same configuration as the frequency sweep case, different experiments were made with different optical power. A frequency sweep with the laser off was taken first, then after five minutes with the laser on the 'on' frequency sweep was taken. After each measure, using the ND filter, incident light power was reduced for the next one and after waiting another five minutes -to have the sample on its original state-, the process was repeated for a new power value.

### 3.3.2 Data processing

#### Obtaining relative permittivity

To explain how to measure the relative permittivity of a ferroelectric crystal sample, it is useful to briefly remind the concept of admittance. Admittance, $Y$, is defined as the reciprocal of the impedance, $Z$, and it can be seen as a measure of how easily a material will let electrical current flow. In our case, we are interested in another interpretation of the admittance, i.e. its interpretation as a phasor that represents the dynamic effect of the material’s susceptance to polarization:

\begin{equation}
Y = G + j \cdot B
\end{equation}

where $Y$ is the admittance, $G$ is the conductance, $B$ is the susceptance and $j = \sqrt{-1}$.

\textsuperscript{6}Once a time dependent experiment was made, the timeouts were set to 5 minutes between on and off measures so that the relaxation time did not affect frequency sweep measures.
With the Impedance Analyzer, we can display and collect different variables from the impedance measures, including those $G$ and $B$. From the $G$ and $B$ data (real and imaginary parts of the admittance) for each frequency, the following transformations can be applied\footnote{This transformation can be applied if we consider the sample with the two electrical contacts as a parallel resistor-capacitor (RC) circuit.}:

$$
\epsilon' = \frac{B \cdot t}{\epsilon_0 \cdot \omega \cdot A} \quad ; \quad \epsilon'' = \frac{G \cdot t}{\epsilon_0 \cdot \omega \cdot A}
$$

where $\epsilon'$ and $\epsilon''$ are the real and imaginary parts of the relative permittivity $\epsilon$ respectively, $t$ is the thickness of the sample, $A$ is the area of the electric contact of the sample, $\omega$ is angular frequency and $\epsilon_0$ is the electrical permittivity in vacuum ($\epsilon_0 = 8.85 \cdot 10^{-12} \text{F/m}$).

So, we are able to obtain real and imaginary parts of the relative permittivity, although we are only interested in the real part\footnote{The imaginary part of the relative permittivity, $\epsilon''$, has been proven to be unaltered no matter if the laser incides the sample or not. The phenomenon seemed to affect only $\epsilon'$, which has been tested also in our results but will not be shown since it lacks of useful information.}. This data processing was implemented on MATLAB\footnote{MATLAB and Statistics Toolbox Release 2016b, The MathWorks, Inc.}. Also using MATLAB, some fittings were made using $nlinfit$ function for discussion chapter (Chap. 5).

**Obtaining power values**

One fact that has not been commented yet is that the powermeter is at certain distance from the sample. Thus, optical power measurements could be wrong due to dispersion in the air between the powermeter and the sample. This problem is fixed by removing the powermeter from its standard position and placing it at the sample site, before performing an experiment. Ensuring that the laser diode is providing a constant optical power\footnote{This is immediately reached with red laser diode, but in the case of green and blue-violet lasers some time must be waited until this condition is reached.}, a measure is taken at the sample site and then at the powermeter original position. Hence, we can obtain the power loss empirically and exactly, without having to include theoretical calculations. This has to be repeated for each laser, since their characteristics are different.
In this section the results of the experiments are shown. Only direct results of the measures are plotted because any interpretation is included on the discussion chapter, so the reader can distinguish between the obtained data and the processed or interpreted data. Two main sections appear, one for the sample with crystalline orientation (100), or sample a, and the other for the sample with crystalline orientation (001), or sample c. Whithin this sections, results are also divided by the colour (wavelength) of the laser diode used\(^1\).

### 4.1 Sample with crystalline orientation (100)

#### 4.1.1 Green laser

##### 4.1.1.1 Frequency sweep

Here are the results for the frequency sweep experiments to show the simple switch on/switch off behaviour of the phenomenon. As it can be seen in Figure 4.1, the real relative permitivity of the crystal has a value of 2750 at 100Hz with laser off and reduces its value to 2295 with laser on. Both the ON and OFF measured values decrease as a straight line in the plot with increasing frequency, until 100kHz\(^2\). For instance, at

---

\(^1\)If not otherwise stated, measures were made with an optical power value of 40mW.

\(^2\)Our results will be reliable until we reach 100kHz frequency. This is due to poor calibration of higher frequencies, where reliability is lost.
100kHz, OFF permittivity has lowered to a value of 2671 and its corresponding ON value is now 2229. However, measures maintain their relative distance on the plot until 100kHz.

![Figure 4.1: Frequency sweep for green laser and sample a. Absolute values for real relative permittivity $\epsilon'$ as a function of frequency for ON and OFF states.](image)

To clearly view the relative change between ON and OFF permittivity, Figure 4.2(a) shows normalized values of $\epsilon'$. These are calculated as follows:

$$\epsilon'_n = \frac{\epsilon'}{\epsilon'_{f0}}$$

(4.1)

where

- $\epsilon'_n$ is the normalized $\epsilon'$
- $\epsilon'$ is the real relative permittivity
- $\epsilon'_{f0}$ is the value of real relative permittivity at 100Hz with laser off

At 100Hz, permittivity decreases to 0.835 times its OFF value and a 16.5% in percentage, as shown in Figure 4.2. This percentage change is approximately constant along the frequencies, maintaining its value between 16.5% and 16.8% in the range 100Hz to 100kHz.
4.1. SAMPLE WITH CRYSTALLINE ORIENTATION (100)

Figure 4.2: Normalized values of $\epsilon'$ (a) and percentage change (b) of frequency sweep for green laser and sample a.

As the effect is important only in a relative sense, i.e. the phenomenon reduces the permittivity between ON and OFF, we will focus on relative or normalized data. This is the reason why from now on the frequency sweep plots will be shown only with normalized $\epsilon$ and/or relative percentage change, but not in absolute values of relative permittivity.

4.1.1.2 Time dependent

Time dependent experiments show the result of switching on the laser and maintaining it for 800 s before switching it off and wait another 800 s. This allows seeing the time response of the switch on/switch off phenomenon. Figure 4.3(a) displays how permittivity goes from 2779 to 2321 in the first 800 s period and returns to a high value of 2762 in the second 800 s period. We see that once $\epsilon'$ reaches certain low or high value, it stabilizes there. As in the frequency sweep experiments, Figure 4.3(b) shows the normalized $\epsilon'$, now relative to the first value in time, not in frequency.

(4.2) $\epsilon'_n = \frac{\epsilon'}{\epsilon'_{t=0}}$

where

- $\epsilon'_n$ is the normalized real relative permittivity
- $\epsilon'$ is the real relative permittivity
- $\epsilon'_{t=0}$ is the value of real relative permittivity at $t = 0$ s with laser off
CHAPTER 4. RESULTS

Figure 4.3: Time dependence for green laser and sample $a$. (a) Absolute real relative permittivity $\epsilon'$. (b) Normalized values of real relative permittivity $\epsilon'$. Measures taken at 1kHz.

Like in the previous case, this relative plots are the way that time dependent experiments will be shown from now on, as they again involve only relative information.

4.1.1.3 Power dependent

Figure 4.4(a) shows different values of the relative permittivity taken at 1kHz with decreasing optical power reaching the sample from the laser. It can be seen that every measure decreases the absolute value of relative permittivity in OFF state. Also it can be seen that less power implies less change in $\epsilon'$.

The behaviour, which seems to be linear, is better displayed in Figure 4.4(b). We may see that at 40mW normalized permittivity is 0.836 with the laser on and at 1mW this value is now 0.994, almost reaching the OFF $\epsilon'$. In that figure $\epsilon'$ is taken relative to the OFF values to take into account some existent losses from one measure to the next one (otherwise we can not set a common OFF reference value).

$$
\epsilon'_{n,ON} = \frac{\epsilon'_{ON}}{\epsilon'_{OFF}} \quad ; \quad \epsilon'_{n,OFF} = \frac{\epsilon'_{OFF}}{\epsilon'_{OFF}} = 1
$$

where

- $\epsilon'_{n,ON}$ is the normalized real relative permittivity with laser on
- $\epsilon'_{n,OFF}$ is the normalized real relative permittivity with laser off
- $\epsilon'_{ON}$ is the value of real relative permittivity with laser on
- $\epsilon'_{OFF}$ is the value of real relative permittivity with laser off
4.1. SAMPLE WITH CRYSTALLINE ORIENTATION (100)

4.1.2 Red laser

4.1.2.1 Frequency sweep

In this case, it seems in that relative permittivity behaves very similar to the green laser case (see Figure 4.5). With the laser on, $\epsilon'$ decreases to 0.83 times its OFF value. In percentage this is a 17%, as shown in Figure 4.5(b). This percentage change is again approximately constant, diminishing as it reaches 100kHz, where change is 16.4%.

Figure 4.4: Power dependence for green laser and sample a in absolute values (a) and normalized values (b) of permittivity $\epsilon'$.

Figure 4.5: Frequency sweep for red laser and sample a in normalized values (a) and percentage change of permittivity $\epsilon'$ (b).
CHAPTER 4. RESULTS

4.1.2.2 Time dependent

Figure. 4.6(a) displays the time dependent experiment with the red laser. The result is similar to the one for green laser, reaching an ON state of $\epsilon' = 0.834$.

4.1.2.3 Power dependent

Again a linear relation seem to appear for power dependence. Figure 4.6(b) displays the results with power going from 1mW to almost 35mW. In this case, optical power does not go up to 40mW because of technical problems with the laser, causing power losses.

![Graphs showing time and power dependence](image)

Figure 4.6: (a) Time dependence for red laser and sample a. Measure taken at 1kHz. (b) Power dependence for red laser and sample a.

4.1.3 Blue-violet laser

4.1.3.1 Frequency sweep

Figure 4.7 displays that relative permittivity behaves very similar to the green and red cases. With the laser on, $\epsilon'$ decreases to 0.839 times its OFF value. In percentage this is a 16.1%, as shown in Figure 4.7(b). This time, percentage maintains its value between 16.1% and 16.8% in 100Hz to 100kHz range.
4.1. SAMPLE WITH CRYSTALLINE ORIENTATION (100)

Figure 4.7: Frequency sweep for blue-violet laser and sample a in normalized values (a) and percentage change of permittivity $\epsilon'$ (b).

4.1.3.2 Time dependent

Figure 4.8(a) displays that the result is similar as the one for green and red lasers, going from OFF state to an ON state of $\epsilon'_n = 0.8357$.

4.1.3.3 Power dependent

Figure 4.8(b) shows the results with power going from 1mW to almost 43mW, again with a linear behaviour. In this case optical power goes above 40mW due to few power losses. For instance, at 1mW we have 0.993 $\epsilon'_n$ value and at 42.5mW $\epsilon'_n = 0.8337$.

Figure 4.8: (a) Time dependence for blue-violet laser and sample a. Measure taken at 1kHz. (b) Power dependence blue-violet laser sample a.
CHAPTER 4. RESULTS

4.2 Sample with crystalline orientation (001)

4.2.1 Green laser

4.2.1.1 Frequency sweep

For sample c absolute values are again displayed instead of normalized. This is done in order to appreciate that c-plane oriented BTO crystals do not have the same relative permittivity value but a considerably lower one. In Figure 4.9 we see that these values are, for example, 884 at 100Hz with the laser off and 808.8 with the laser on. As in the case of sample a, values decrease with increasing frequency and at 100kHz, $\epsilon' = 781.1$ with the laser off and $\epsilon' = 715.5$ with the laser on.

![Graph](image)

**Figure 4.9:** Frequency sweep for green laser and sample c in absolute values of permittivity $\epsilon'$.

We also observe that there is a different shape in Figure 4.9 with respect to sample a. This shape is also displayed in Figure 4.10(a) which shows normalized $\epsilon'$ calculated as before. In Figure 4.10(b) the percentage change is between 8.4% and 8.5% in the 100Hz - 100kHz range, except in 91.2kHz, which goes out of this margin.

4.2.1.2 Time dependent

Despite the different $\epsilon'$ values for sample c and the different shape in frequency sweep experiments, time dependent experiments seem to be very similar to the previous cases,
as we may see in Figure 4.11(a). The only appreciable difference is the reached ON value for $\epsilon'_n$, which now it is 0.9212.

![Frequency sweep for green laser and sample c in normalized values (a) and percentage change (b).](image)

**Figure 4.10:** Frequency sweep for green laser and sample c in normalized values (a) and percentage change (b).

### 4.2.1.3 Power dependent

For power experiments we have the same situation as time dependence, the behaviour is similar to the previous measurements but the reached values are now 0.9277 at 40mW and 0.9954 at 1mW. See Figure 4.11(b).

![Time dependence for green laser and sample c. Measure taken at 1kHz. (b) Power dependence green laser sample c.](image)

**Figure 4.11:** (a) Time dependence for green laser and sample c. Measure taken at 1kHz. (b) Power dependence green laser sample c.
The results are discussed in this chapter, analyzing the behaviour of the phenomenon as a function of different variables. These variables are wavelength, time, power and crystalline orientation. Each dependence has its own section and there is also a section for discussing power threshold, which was indicated before as another aim of this work, together with the mentioned variables dependencies.

5.1 Wavelength dependence

As it has been told all along Chapter 4, results for different wavelengths are very similar. This can be easily seen on Figures 5.1(a) and 5.1(b), where no significant difference is appreciated between the graphs of the green, red and blue-violet lasers. It may be seen that there is some difference above 100kHz but, as we mentioned earlier on the previous chapter, measures above that value are not reliable at all, so results must be taken into account in the 100Hz-100kHz region.

The change of real relative permittivity in all three cases is between 16% and 17% with no clear correlation between wavelength and percentage change. For this reason, the phenomenon seems to be wavelength-independent, or, at least, the dependence could not be found with the precision of our setup.
Figure 5.1: Wavelength dependence. (a) Frequency sweep for all three wavelengths in ON and OFF states. (b) Percentage change in real relative permittivity for the different wavelengths.

5.2 Time dependence

We saw that the phenomenon has a non-negligible response time. Plots seem to correspond (and actually they do) to an exponential decay, reaching some approximately constant equilibrium value. Analyzing different realizations and plots for time dependent experiments, a linear background was detected. This was later corroborated taking measures with the laser off and constant frequency for some minutes. These tests showed that $\epsilon'$ was slightly decreasing through time, so a linear background was present. It was also considered that time response would not necessarily be the same going from OFF state to ON state than vice versa, so two different coefficient functions were used. Taking all this into account, the following functions were the models for which data was fitted:

\begin{align*}
F_{ON}(t) &= A_{ON} + B_{ON} \cdot e^{(t-t_{ON})/\tau_{ON}} + C_{ON} \cdot t \\
F_{OFF}(t) &= A_{OFF} + B_{OFF} \cdot e^{(t-t_{OFF})/\tau_{OFF}} + C_{OFF} \cdot t
\end{align*}

where $A_{ON,OFF}, B_{ON,OFF}, C_{ON,OFF}$ are coefficients to fit, $t$ is time in seconds, $t_{ON}$ and $t_{OFF}$ are the initial times for each half of the measure\(^1\) and $\tau_{ON}$ and $\tau_{OFF}$ are time constants to fit for the exponential decays.

\(^1\)F$_{ON}$ begins at time equals zero and finishes at time 800 seconds, where F$_{OFF}$ begins
5.3 Power threshold

One of the initial questions of this thesis was if there is a power threshold for the phenomenon. The answer is no. At least in the milliwatt range, which is the range we can explore with our setup, no threshold seems to exist. As Figure 5.3 demonstrates, if we reduce incident optical power the change in relative permittivity decreases, reaching the OFF value as optical power approaches zero.
CHAPTER 5. DISCUSSION

Figure 5.3: Non-existence of power threshold. Real relative permittivity $\epsilon'$ for different incident light power, showing that no power threshold is observed in the phenomenon.

5.4 Power dependence

From the results chapter we know that power dependent experiments show a linear relation between normalized relative permittivity and laser power. Knowing this linear relation and taking into account that at zero incident optical power, change in $\epsilon'$ should be zero because we are in laser off conditions, the following function was used to fit power dependence:

$$F(P) = k \cdot P + \epsilon'_{n,0},$$

where $P$ is optical power in mW, $k$ is the coefficient to fit and $\epsilon'_{n,0}$ is the value of $\epsilon'_n$ at $P = 0$, or, in other words, $\epsilon'_n = 1$.

The result of fitting a power dependent plot, for instance the green laser one, is shown in Figure 5.4(a). The obtained coefficients with confidence intervals and coefficient of determination $R^2$ for the different lasers are shown in Table 5.2. Although results differ depending on the laser used, $k$ seems to be around -0.004mW$^{-1}$. Those differences in $k$ coefficient can also be seen in Figure 5.4(b), where only at higher values of optical power the divergence seems to be appreciable.
5.5. CRYSTALLINE ORIENTATION DEPENDENCE

Figure 5.4: Power dependence. (a) Linear fitting (in black) of the normalized real relative permittivity experimental data as a function of incident optical power (in green). (b) Fitted linear relations between incident optical power and change in normalized $\epsilon'$. Each wavelength used is represented in its colour.

<table>
<thead>
<tr>
<th>Laser</th>
<th>$k$</th>
<th>95% confidence interval</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Green</td>
<td>-0.00431</td>
<td>(-0.00439,-0.00423)</td>
<td>0.9947</td>
</tr>
<tr>
<td>Red</td>
<td>-0.00375</td>
<td>(-0.00380,-0.00370)</td>
<td>0.9963</td>
</tr>
<tr>
<td>Blue-violet</td>
<td>-0.0040</td>
<td>(-0.0041,-0.0039)</td>
<td>0.9876</td>
</tr>
</tbody>
</table>

Table 5.1: Fitted coefficients

5.5 Crystalline orientation dependence

Sample $c$ exhibited some different behaviours compared to sample $a$. The first one noticed was the different shape in frequency sweep plot. This may be caused by some instrumentation effect, because this shape not only appeared with sample $c$ but also with the last experiments with sample $a$ (that are not shown in this work). However, this is not studied in depth, as the studied effect is relative, in the sense that the shape is the same on both ON and OFF states and therefore it does not affect relative changes.

Another difference, which in this case is remarkable, is that the change in relative permittivity is around half the value in sample $c$ than in sample $a$, as we can see in Figure 5.5(b). This is easily explained if we remind that c-plane domains have out-of-plane polarization vectors and the electric field associated to the incident polarized light has an in-plane direction on the sample. This explanation should lead to zero change in permittivity, but the sample with crystalline orientation (001) has also domains with
crystalline orientation (100). This means that there are regions where the polarization vector is also in-plane, so the electric field of the incident polarized light can interact with these regions and move the domain walls as in [1].

Figure 5.5: Crystalline orientation dependence. (a) Frequency sweep for both crystalline orientation samples. (b) Percentage change in real relative permittivity for both samples.

Figure 5.6: Crystalline orientation dependence (bis). (a) Time constants for sample c. (b) Power dependence for samples a and c.
5.5. CRYSTALLINE ORIENTATION DEPENDENCE

5.5.1 Time constant

The same functions used for time fitting in section 5.2 were used for sample c. The resulting time constants seem to have similar values for sample c than for sample a, even though $\tau_{\text{OFF}}$ seems to have a value of 40 seconds instead of 45. Since $\tau_{\text{ON}}$ maintains its 30 seconds value, $\tau_{\text{ON}}$ and $\tau_{\text{OFF}}$ are closer for the new sample.

5.5.2 Power relation

Power relation is again linear with power, although $\epsilon_n$ for sample of crystalline orientation (001) reaches half the value of sample a at 40mW. The linear coefficients, fitted as in section 5.4, are shown in Table 5.2 with the corresponding confidence intervals and $R^2$ parameter for both samples. The coefficient $k$ for sample c is near half the value for the case of sample a, which is in agreement with the difference in relative change observed.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$k$</th>
<th>95% confidence interval</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>-0.00431</td>
<td>(-0.00439,-0.00423)</td>
<td>0.9947</td>
</tr>
<tr>
<td>c</td>
<td>-0.00183</td>
<td>(-0.00191,-0.00175)</td>
<td>0.9876</td>
</tr>
</tbody>
</table>

Table 5.2: Fitted coefficients
After seeing the results and discussing them, some conclusions can be made with respect to the phenomenon and its future. First, we have seen that the phenomenon is wavelength-independent, which means that its future applications will have obviously nothing to do with distinguishing between wavelengths or with having different wavelength to activate the device. This also means that a photo-actuator could work with any wavelength, i.e. it could work with the cheapest laser diode, reducing the cost of the device. The device could be suitable for any ambit where a laser is present, no matter the wavelength, even though until now only low-power lasers have been tested. Of course, this statements are only speculations but the objective is to highlight the pros and cons of the phenomenon.

We have also observed that the phenomenon has a non-negligible response time, which makes it non-viable for a FeRAM application. This random access memories based on ferroelectrics need a very fast time response, which this phenomenon does not have, since time constants are of the order of a minute.

Another notable result is that the light-matter coupling has no power threshold and, what is more remarkable, the dependence in optical power is linear. This fact is very promising in the field of transducers, like sensors or actuators. The reason is that a linear relation is a simple mathematical relation between the input and the output, also making it simple to detect abnormal response and to make a linear regression for calibration purposes. In this area, the next step is to measure power dependence for higher optical power lasers. This could lead to find a higher limit of the linear response
or to find a different and, why not, interesting behaviour for those higher values.

The last significant result is that the phenomenon also exists for BTO samples with out-of-plane crystalline orientation. Moreover, the behaviour was the same, except for the relative change values. This provides two different linear coefficients that could be used for different requirements of future applications. With different crystalline orientation samples we could have devices with different sensitivity. In regards to this, more samples with different ratios of a- and c-domains could be tested to see if the relative change strongly depends on this relation or not. If it were demonstrated that different proportions of domains lead to different changes, we could have the ability to build custom-sensitivity transducers for a desired application. Apart from making devices, if there is a clear relation between proportions of domains and the phenomenon, one could think of an easy way of identifying the amount of a- and c-domains in a sample by comparing to some known values.

Future perspectives are based on performing more research to keep unveiling the secrets of this phenomenon and trying to find a theoretical explanation for its behaviour. There are many issues and problems that have not been treated in this work. One of these issues is the joint dependence on some variables, for example optical power and time. Also more wavelengths can be introduced to glimpse if some of the studied dependencies actually have a weak relation with wavelength or if there is some feature conditioned to wavelength that has not been treated yet. More variables can be modified, like the aforementioned increase in optical power, or maybe trying to modify the sample characteristics. Some different types of BTO samples can be introduced, such as polycrystalline samples, thin films, different thickness or area samples, different top and bottom contacts, and so on.

As it has been said since the beginning of this work, this is just the starting point to discover and try to understand the phenomenon and therefore much more study is needed in this field. We don't know where this phenomenon will lead us, but the truth is that a great step has been taken to find it out.
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