Photostriction and elasto-optic response in multiferroics and ferroelectrics from first principles

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Abstract

The present work reviews a series of recent first-principles studies devoted to the description of the interaction of light and strain in ferroelectric and multiferroic materials. Specifically, the modelling schemes used in these works to describe the so-called photostriction and elasto-optic effects are presented, in addition to the results and analysis provided by these *ab-initio* calculations. In particular, the large importance of the piezoelectric effect in the polar direction in the photostriction of ferroelectric materials is stressed out. Similarly, the occurrence of low-symmetry phases in lead titanate thin films under tensile strain is demonstrated to result in large elasto-optic constants. In addition, first-principle calculations allow to gain microscopic knowledge of subtle effects, for instance in the case of photostriction, where the deformation potential effect in directions perpendicular to the polar axis is shown to be almost as significant as the piezoelectric effect. As a result, the numerical methods presented here could propel the design of efficient opto-mechanical devices.

1 Introduction

1.1 Ferroelectric and Multiferroic Materials

Perovskite ferroelectrics possess a spontaneous electrical polarization and form an important class of materials [1]. Such compounds exhibit properties of technological relevance, since they can, e.g., convert various forms of energies. For instance, some ferroelectric (FE) systems can efficiently convert mechanical to electrical energies and *vice-versa*, because of their large piezoelectric coefficients, which is at the heart of piezoelectric transducers and actuators. Ferroelectric

materials are also of importance for other applications, such as non-volatile memories, dielectrics for microelectronics and wireless communication, and pyroelectric arrays

Perovskite multiferroics (MFEs) constitute another intensively studied type of materials because of the inherent coexistence between ferroelectricity and magnetism. The primary initial interest of MFE materials resides in the promise of designing new devices exploiting the magnetoelectric coupling between magnetic and electrical properties [2]. As a matter of fact, controlling magnetic properties by an electric field would be of large technological interest.

There are properties and phenomena of FEs and MFEs that have been much less studied than, e.g., piezoelectricity and magnetoelectricity, despite the numerous studies devoted to these two types of materials. Such properties and phenomena are related to the *interaction of light and matter*, and hold promise for exciting discoveries – such as the use of ferroelectrics as novel and efficient photovoltaic or photoconductive materials [3, 4, 5].

In this Review article, we will concentrate on recent computational, *ab-initio* efforts devoted to two specific light-matter interactions, that are photostriction and elasto-optic effects.

1.2 Photostriction

Most ferroelectric materials are semiconductors or insulators, and thus have a finite bandgap. As such, when light made of photons with energy higher than the bandgap hits a ferroelectric material, it is partially absorbed. Its absorption can convert the energy carried by light into:

- (i) Electrical energy, i.e., the photovoltaic effect, whose origin may stem from various contributions [6, 7]: the so-called Bulk Photovoltaic Effect (BPVE) generated by the lack of inversion symmetry inherent to all ferroelectric materials [8, 9, 10, 11], the ferroelectric-metal Schottky interface, the presence of internal electric fields caused by defects, etc.
- (ii) Chemical energy, i.e., the photocatalysis effect [12].
- (iii) Mechanical energy, i.e., the photostriction effect, which is the main focus of this subsection.

Photostriction in ferroelectric materials was studied as early as in 1966 in SbSI crystals, with a 0.04 % change in the length of the polar axis under white light illumination [13]. An order of magnitude larger effect was observed later on by Xiao *et al.* in Fe-doped lithium niobate crystals [14]. Interestingly, the photostrictive properties of ferroelectrics have mostly been interpreted as being driven by their piezoelectric properties (strain linearly induced by a change in polarization or electric field) [15]. As a result, investigations of materials with large piezoelectric properties, such as the ones usually found in so-called Morphotropic Phase Boundaries (MPBs), were at the forefront of research in the 90's. In particular, $(\text{Pb}_{1-x}\text{La}_x)(\text{Zr}_{1-y}\text{Ti}_y)\text{O}_3$ (PLZT) was comprehensively studied [16, 17, 18], and devices based on the photostriction effect and PLZT were

designed to take advantage of its large coupling of light and strain [19]. However, most classical ferroelectric materials, including PLZT, have large bandgaps that often rise above 3 eV [20], which lies at best at the extreme side of the visible range, and most often, in the ultraviolet (UV) domain. As a result, research on the conversion of solar energy into mechanical energy (but also into electrical energy) using ferroelectrics has been at a standstill for a decade or so. Recently though, new prospects have appeared in the field, mainly driven by the appearance of low band-gap FE and MFE materials. For instance, Nechache *et al.* have achieved a low band-gap of 1.5 eV in multiferroic $\text{Bi}_2\text{FeCrO}_3$, eventually resulting in one of the most efficient perovskite oxide-based solar cell [4]. Most recent photostriction experiments have been conducted on multiferroic bismuth ferrite, whose band-gap ranges from 2.2 to 2.7 eV [2, 21], and is therefore suitable for visible light absorption. As of right now, photostriction of 0.004% was reported in bismuth ferrite [22, 15]. The photostriction effect in bismuth ferrite has recently been used to increase the coercivity of a Nickel film deposited on a BiFeO_3 single crystal by 50% [23], opening the way to strain-mediated optical control of magnetic properties. Note also that the photostriction effects described so far are taking place at the scale of seconds or even minutes in the case of lithium niobate [14]. On the other hand, pump-probe experiments have demonstrated the occurrence of photo-generated strain fields at the scale of picoseconds and below [24, 25, 26, 27, 28, 29, 30, 31]. Interestingly, Ref. [27] showed the possibility, depending on the orientation of BiFeO_3 grains with respect to the probe, to generate preferentially shear or longitudinal acoustic waves.

There is a variety of mechanisms contributing to photostriction [32, 33, 34]. First, light-matter interaction, through the interaction of photoexcited carriers with the lattice, creates heating of the material, resulting in thermal dilation. Second, the electronic density redistribution generated by the excitation causes lattice to deform through a mechanism known as the deformation potential [35, 36, 34] (often termed electronic pressure as well). Third, in materials lacking inversion symmetry, such as ferroelectrics, the converse piezoelectric effect caused by the appearance of a photo-induced electric field results in the appearance of a photo-induced deformation [15, 32, 34]. The latter mechanism is particularly appealing, as it provides polar materials (and ferroelectric materials in particular) with an additional handle compared to centrosymmetric materials. In addition, it is known how to design large piezoelectric and ferroelectric materials, by mixing a ferroelectric material (such as lead titanate) with a relaxor or antiferroelectric material (such as lead magnesium niobate or lead zirconate). Such mixing results in the appearance of low symmetry (often monoclinic, sometimes orthorhombic) phases for a specific compositional range defining the aforementioned MPB [37, 38, 39, 40]. The existence of these low-symmetry phases in the phase diagram has been demonstrated to host giant piezoelectric properties [41].

The origin of photostriction can be qualitatively captured using a simple Landau model [15, 42]. Consider a uniaxial ferroelectric material. Its thermodynamic potential $\Phi_F(T, \mathbf{P}, \boldsymbol{\eta})$, in the dark, can be expressed as a Taylor expansion in terms of the order parameters (polarization $\mathbf{P}$ and strain $\boldsymbol{\eta}$) with

respect to the reference paraelectric phase,

$$\begin{aligned}\Phi_F(T, \mathbf{P}, \boldsymbol{\eta}) &= \Phi_P(T) + \frac{\alpha(T)}{2} \mathbf{P}^2 + \frac{\beta}{4} \mathbf{P}^4 \\ &+ \frac{\gamma}{6} \mathbf{P}^6 + \frac{C}{2} \boldsymbol{\eta}^2 + \frac{Q}{2} \mathbf{P}^2 \boldsymbol{\eta}.\end{aligned}\quad (1)$$

In this equation, $\alpha(T)$ is a second rank tensor. β and γ are fourth and sixth rank tensors, which are considered temperature independent. Q is the fourth-rank electrostrictive tensor, and C is the second-rank stiffness tensor. At equilibrium, the thermodynamic potential must reach a stationary point, and thus the following set of equations must be solved,

$$\frac{\partial \Phi_F}{\partial \mathbf{P}} = 0 = \alpha(T) \mathbf{P} + \beta \mathbf{P}^3 + \gamma \mathbf{P}^5 + Q \mathbf{P} \boldsymbol{\eta}, \quad (2)$$

$$\frac{\partial \Phi_F}{\partial \boldsymbol{\eta}} = 0 = C \boldsymbol{\eta} + \frac{1}{2} Q \mathbf{P}^2. \quad (3)$$

The perturbation caused by illumination can be considered as adding the energy of the photo-excited electrons and subtracting those of the holes [15], in a similar fashion to what has been done to study heavily doped ferroelectric materials [43]. As a result, the thermodynamic potential of the gas of photoexcited electrons and holes must be considered alongside that of Eq. (1). The total thermodynamic potential is therefore

$$\Phi(T, \mathbf{P}, \boldsymbol{\eta}) = \Phi_F(T, \mathbf{P}, \boldsymbol{\eta}) + \Phi_{ph}(T, \mathbf{P}, \boldsymbol{\eta}), \quad (4)$$

with

$$\Phi_{ph}(T, \mathbf{P}, \boldsymbol{\eta}) = \sum_{n, \mathbf{k}} \delta n_{n\mathbf{k}} \varepsilon_{n\mathbf{k}}. \quad (5)$$

In Eq. (5), $\delta n_{n\mathbf{k}}$ is the change of occupancy of the Bloch state $n\mathbf{k}$ with respect to the system in the dark, and $\varepsilon_{n\mathbf{k}}$ is the energy of that state. Since photon absorption creates the same amount of holes and electrons, the condition $\sum_{n, \mathbf{k}} \delta n_{n\mathbf{k}} = 0$ must be satisfied. In the simple case of a two-level system, for which holes are created at the top of valence band ε_v while electrons are photoexcited at the bottom of the conduction band ε_c , the former equation can be simply written as,

$$\Phi_{ph}(T, \mathbf{P}, \boldsymbol{\eta}) = \delta n_e E_{v \rightarrow c}, \quad (6)$$

with δn_e being the number of photoexcited electrons in the conduction band, and $E_{v \rightarrow c} = \varepsilon_c - \varepsilon_v$. The latter is a function of temperature, polarization and strain. Assuming that the perturbation introduced by switching on the light is small, the order parameters can be expanded around their equilibrium in the dark. That is, they can be written $\mathbf{P} = \mathbf{P}_0 + \delta \mathbf{P}$ and $\boldsymbol{\eta} = \boldsymbol{\eta}_0 + \delta \boldsymbol{\eta}$, with the

quantities having the subscript "0" referring to the equilibrium values in the dark, which are solutions of Eqs. (2) & (3). It is then straightforward to define, as done in Ref. [42], a photo-induced stress σ_{photo} and photo-induced electric field $\mathbf{E}_{photo}$,

$$\sigma_{photo} = -\delta n_e \left. \frac{\partial E_{v \rightarrow c}}{\partial \eta} \right|_{\mathbf{P}_0, \eta_0}, \quad (7)$$

$$\mathbf{E}_{photo} = -\delta n_e \left. \frac{\partial E_{v \rightarrow c}}{\partial \mathbf{P}} \right|_{\mathbf{P}_0, \eta_0}, \quad (8)$$

allowing to re-write Eq. (6) as

$$\Phi_{ph}(T, \mathbf{P}, \eta) = \Phi_{ph}(T, \mathbf{P}_0, \eta_0) - \sigma_{photo} \delta \eta - \mathbf{E}_{photo} \cdot \delta \mathbf{P}. \quad (9)$$

As a result, the equilibrium conditions under illumination, in this simple model, are

$$\frac{\partial \Phi}{\partial \mathbf{P}} = 0 = \alpha(T) \mathbf{P} + \beta \mathbf{P}^3 + \gamma \mathbf{P}^5 + Q \eta \mathbf{P} - \mathbf{E}_{photo}, \quad (10)$$

$$\frac{\partial \Phi}{\partial \eta} = 0 = C \eta + \frac{1}{2} Q \mathbf{P}^2 - \sigma_{photo}, \quad (11)$$

which, under the assumption that $\delta \mathbf{P}$ and $\delta \eta$ are indeed small compared to the equilibrium values in the dark, can be linearized, leading to [42]

$$\delta \mathbf{P} = \chi_{ph} \mathbf{E}_{photo} + d_{ph}^T \sigma_{photo}, \quad (12)$$

$$\delta \eta = S_{ph} \sigma_{photo} + d_{ph} \mathbf{E}_{photo}. \quad (13)$$

In those latter equations, χ_{ph} is the dielectric susceptibility under illumination, d_{ph} is the piezoelectric constant under illumination, and S_{ph} the elastic compliance under illumination.

From Eq. (13), the contribution of the potential deformation mechanism (through the photo-induced stress σ_{photo}) and the piezoelectric mechanism (caused by the photo-induced electric field $\mathbf{E}_{photo}$) appear naturally. To be exhaustive, one should also include the contribution of lattice heating and thermal dilatation. This can be done by adding the energy of the lattice/phonon gas, $\Phi_L = \sum_{n, \mathbf{q}} \delta n_{ph, n\mathbf{q}} \hbar \omega_{n\mathbf{q}}$, in which $\delta n_{ph, n\mathbf{q}}$ and $\hbar \omega_{n\mathbf{q}}$ represent the change in population and energy of the n^{th} phonon mode at wavevector $\mathbf{q}$ [33].

1.3 Elasto-optic effect

Elasto-optic effect describes the change of permittivity, ε , due to mechanical strain, η . It can be used for creating or designing acousto-optic modulators,

acousto-optic tunable filter, electro-optic deflection, etc [44]. Such effect can be quantified by the elasto-optic tensor, p_{ij} , that is defined via

$$\Delta\left(\frac{1}{\tilde{\varepsilon}}\right)_i = \sum_j p_{ij}\eta_j, \quad (14)$$

where i and j are both integers that can vary from 1 to 6 (when adopting the Voigt notation). Introducing the extinction coefficient k and refractive index n tensors via

$$\tilde{\varepsilon} = \varepsilon' + i\varepsilon'' = (n + ik)^2, \quad (15)$$

Under low-frequency field (the Pockels effect), ε'' is about zero, and Eq. (14) can be rewritten as

$$\Delta\left(\frac{1}{n^2}\right)_i = \sum_j p_{ij}\eta_j. \quad (16)$$

Eq. (16) was used in Ref. [45] to compute the elasto-optic coefficient. Note that, as indicated above, both refractive index n and strain η have 6 components when using the Voigt notation, implying that there are 36 components for the elasto-optic coefficient p_{ij} . However, common elasto-optic materials (such as SiO_2 and LiNbO_3) have relatively high symmetry, and, as a result, only a few of the elasto-optic tensor components are finite.

2 Methods

2.1 Photostriction using the ΔSCF method

When performing Density Functional Theory (DFT) calculations, one is typically minimizing the energy functional with respect to density by self-consistently resolving the ground state density, in accordance with the two Hohenberg-Kohn theorems at the foundation of DFT [46]. There are several schemes to achieve such calculations, however one simple, popular and practical way is to assume that one can find a system of non-interacting electrons with the same energy and ground state density as the true system of fully interacting electrons. Such approximation is called the Kohn-Sham (KS) ansatz [47], and provides a physically intuitive one-electron picture, within which one is left to fill monoelectronic orbital states (determined from a monoelectronic Schrödinger equation) by increasing levels of energy. As described in Fig. (1), a KS calculation would start by guessing an input potential V_{in} , thereby fully determining the one-electron Hamiltonian. This Hamiltonian is then solved, resulting in a set of monoelectronic orbitals φ_i with eigenvalues ε_i . The lowest energy lying states would then be filled in order to determine the ground state, and the new potential V_{out} generated by the distribution of electrons in these occupied orbitals becomes the input for a new cycle, until convergence of the ground state density is reached up to a desired accuracy.

Figure 1: (a) Regular Kohn-Sham calculation to find the ground state electronic density: from an input potential V_{in} , the now known Kohn-Sham Hamiltonian can be diagonalized. Its lowest eigenstates (“orbitals”) are then filled with electrons, and a new potential is calculated based on the latter electronic distribution. The output potential is then plugged in as input potential until convergence to a reasonable accuracy is reached. (b) Δ SCF calculation: at filling, not all low energy lying eigenstates are filled, but some electrons are imposed to occupy excited orbitals. An output potential is then calculated based on this electronic distribution, and the density is self-consistently solved under the constraint of certain occupation numbers. Reproduced from Ref. [42]. Copyright 2017 American Physical Society.

The Δ SCF method [48] is essentially analog to a regular Kohn-Sham calculations: starting from an input potential V_{in} , the monoelectronic Schrödinger equation is solved. The main difference arises when the filling of the orbitals is performed. As sketched in Fig. (1.b), some electrons are constrained to occupy excited states in the conduction band, while leaving holes in the valence band. Therefore, the system is converged under the constraint of having some electrons lying in higher energy states, and holes in lower energy states. This rather simple approach has been proven to be rather successful in describing resonance level in finite systems such as molecules adsorbed on metallic surfaces [49], or the ligand-field splitting in Fe-phthalocyanine [50]. In infinite systems however, the Δ SCF method does not improve much the description of excited states energies such as the bandgap energy when using traditional functionals [51]. One should resort to more accurate models, such as the GW approximation [52] or Time Dependent DFT (TD-DFT) [53], which are rather computationally expensive. Performing structural relaxation with the former technique is even practically untractable. Furthermore, we note that many GW calculations are typically used as corrections to eigenenergies and wavefunctions determined with a more traditional functional [54]. As a result, the Δ SCF method is a useful tool to apprehend photostrictive phenomena.

During Δ SCF calculations, a k -point A belonging to the valence band is emptied, meanwhile a k -point B belonging to the conduction band is filled with electrons, mimicking what we call a $A \rightarrow B$ transition. In the following works described below, only cases for which the photoexcited holes (electrons resp.) are sitting at the top (bottom) of the valence (conduction) band are considered. This amounts to assume that electron-phonon scattering, responsible for the thermalization of the photo-excited carriers, is extremely fast compared to other processes such as optical recombination of electrons with holes, the latter typically ranging in the nano- to microsecond according to Ref. [33], while electron-phonon thermalization processes typically occur on a picosecond time scale. In other words, the influence of the non-thermalized electrons, which are known to be responsible for ballistic photovoltaic current in ferroelectrics [8, 10, 11], is neglected.

2.2 Elasto-optic coefficients

First-principle techniques were used in Ref. [45] to calculate the frequency-dependent dielectric tensor once the electronic ground state was determined. More precisely, the imaginary part of dielectric function was computed via the following equation [55]

$$\begin{aligned} \varepsilon''(\omega) = & \frac{4\pi^2 e^2}{\Omega} \lim_{q \rightarrow 0} \frac{1}{q^2} \sum_{c,v,\mathbf{k}} 2\omega_{\mathbf{k}} \delta(\epsilon_{c\mathbf{k}} - \epsilon_{v\mathbf{k}} - \hbar\omega) \\ & \times \langle u_{c\mathbf{k}+\mathbf{e}_\alpha\mathbf{q}} | u_{v\mathbf{k}} \rangle \langle u_{c\mathbf{k}+\mathbf{e}_\beta\mathbf{q}} | u_{v\mathbf{k}} \rangle^*, \end{aligned} \quad (17)$$

where c and v refer to band indices of the conduction and valence bands, respectively. $u_{c\mathbf{k}}$ is the cell periodic part of the Bloch orbitals at the reciprocal space point $\mathbf{k}$; $\mathbf{e}_\alpha$ and $\mathbf{e}_\beta$ are unit vectors along the α and β Cartesian direction, respectively; and the asterisk symbol denotes complex conjugate. The real part of the dielectric tensor $\varepsilon'_{\alpha\beta}$ is then extracted through the Kramers-Kronig transformation

$$\varepsilon'(\omega) = 1 + \frac{2}{\pi} P \int_0^\infty \frac{\varepsilon''_{\alpha\beta}(\omega')\omega'}{\omega'^2 - \omega^2} d\omega', \quad (18)$$

where P denotes the so-called principal value [55].

In the low frequency range, complex refractive index, with real part (n) and imaginary part (k), and complex dielectric function, with real part (ε') and imaginary (ε''), follow the relation

$$\tilde{\varepsilon} = \varepsilon' + i\varepsilon'' = \tilde{n}^2 = (n + ik)^2 \quad (19)$$

Reference [45] concentrated on energies $\hbar\omega'$ smaller than the electronic band gap, which implies that, as consistent with the delta function appearing in Eq.(17), $\varepsilon''(\omega)$ vanishes for the selected energies. The refractive index is thus simply equal to the square root of $\varepsilon'(\omega)$. Our first-principles computations of the refractive index within its band gap are found to be rather accurate. This is demonstrated by the prediction in Ref. [45] of an average refractive index, $(n_{11} + n_{22} + n_{33})/3$ of 2.8 for PbTiO₃ for an energy about 40% smaller than the band gap, which compares well with the measured value of 2.7 at a wavelength of 633 nm.

Reference [45] then computed the elasto-optic coefficient, p_{ij} , via the aforementioned Eq. (16). Only the ‘1’ and ‘2’ components of the strain tensor (with the ‘1’, ‘2’ and ‘3’ axes being along the pseudo-cubic [100], [010] and [001] directions, respectively) were considered in this formula, with $\eta_1 = \eta_2$, to reflect epitaxial growth of the film. The resulting effective elasto-optic coefficients are thus obtained from the following relations: $1/(n_1^2(\eta_1)) - 1/(n_1^2(0)) = (p_{11} + p_{12})\eta_1$, $1/(n_2^2(\eta_1)) - 1/(n_2^2(0)) = (p_{21} + p_{22})\eta_1$, and $1/(n_3^2(\eta_1)) - 1/(n_3^2(0)) = (p_{31} + p_{32})\eta_1$. Note that for the tetragonal, orthorhombic, rhombohedral and the monoclinic Cm phases of epitaxial PbTiO₃ films (see Section 4 for a description of these phases), $n_1 = n_2 = n_o$, which is known as the ordinary refractive index, and $n_3 = n_e$, which is termed the extraordinary refractive index. Note that first-principles methods can predict elasto-optic coefficients accurately. For example, for bulk LiNbO₃ (using the hexagonal setting), one gets $p_{31} = 0.17$ for a photon energy being roughly half-way within its band gap [45], which is in very good agreement with the corresponding experimental value of 0.18 [56].

3 Modelling photostriction in multiferroic and ferroelectric materials

3.1 Photostriction in classical ferroelectric materials

Among the vast family of ferroelectric materials, barium and lead titanate emerge as prototypical examples. Both are perovskite oxides, with barium or lead ions occupying the A-sites of the perovskite structure while titanium ions sit on the B-sites. Barium titanate undergoes three successive phase transitions, from the high-symmetry $Pm\bar{3}m$ paraelectric phase at high temperature to a ferroelectric tetragonal $P4mm$ phase at 390 K, before transforming to an orthorhombic ferroelectric phase around 280 K, and eventually goes into a ferroelectric rhombohedral $R3m$ phase below 180 K [57]. Lead titanate is even simpler, as it experiences only one transition from the high-symmetry cubic $Pm\bar{3}m$ phase to a ferroelectric tetragonal $P4mm$ phase at 766 K [1].

Both compounds have been successfully described in first-principles calculations using the Local Density Approximation (LDA) functional, and this was the starting point of Ref. [42], in which other technical details are provided. We describe here only the photostriction induced in the ground state of those compounds, that is the $R3m$ and $P4mm$ phases of barium and lead titanate respectively. The band structure of both compounds are presented in Fig. (2). The considered “transitions” are $Z \rightarrow Z$, $Z \rightarrow \Gamma$, $X \rightarrow \Gamma$ and $X \rightarrow Z$ for PbTiO_3 (PTO) and $Z \rightarrow \Gamma$ and $\Gamma \rightarrow \Gamma$ for rhombohedral BaTiO_3 (BTO). Again, the assumption is made that the thermalization of the phonons is sufficiently fast as compared to the photoexcitation and recombination processes to consider that the hole and electrons are located at the top and bottom of valleys in the valence and conduction bands. According to Ref. [33], the relaxation time of the electron to the bottom of the conduction band is typically of the order of 1 ps, while recombination has a much larger (1 ns-1 μ s) relaxation time, justifying this approximation. Note also that the first-principle description of ultra-fast phenomena such as those occurring in Refs. [25, 26, 28, 29] is out of the scope of this review because of the above mentioned approximation.

The results obtained for the aforementioned transitions in PbTiO_3 are presented as filled symbols in Fig. (3). Because of the same $d_{x^2-y^2}$ character of the conduction states at Γ and X [see Fig. (4) in Ref. [42]], the results are insensitive to the location of the electrons in Γ - Z branch of the conduction band. This can be seen as transitions involving electrons at Γ or Z show the same behavior, provided the hole is located at the same point in the valence band. When the hole sits at X in the valence band, the change of lattice constant in the polar direction is small compared to that induced when the hole sits at Z . In the direction normal to the polar axis (left panel of Fig. (3)), the hole sitting at Z generates a significant expansion, while when located at X , only a minor reduction is found. Note that at X (which is the top of the valence band), the hole has a combined Pb 6s and O $2p_x$ character, while at Z it has Pb 6s and O $2p_z$ character [42].

Figure 2: Band structures of (a) tetragonal lead titanate, and (b) rhombohedral barium titanate. The reference energy is placed at the middle of the Kohn-Sham gap. The arrows represent the different transitions that are considered. Adapted from Ref. [42]. Copyright 2017 of the American Physical Society.

Figure 3: Change of lattice constant orthogonal (left panel) and parallel (right panel) to the tetragonal axis in the $P4mm$ phase of lead titanate, as obtained from Δ SCF calculations (filled symbols) and as estimated from the converse piezoelectric model (open symbols). Reproduced from Ref. [42]. Copyright 2017 from the American Physical Society.

As described in Section 1.2, photostriction in polar materials can be understood as originating from three main contributions: potential deformation, converse piezoelectric effect following a photo-induced electric field, and thermal dilatation following photo-induced heating. During Δ SCF calculations, the temperature is 0 K. As a result, thermal dilatation is not taken into account in those calculations. We now address the question of which of the two former mechanisms, between potential deformation and piezoelectric effect, is the dominant mechanism.

First, it is noted that the ionic relaxation can be translated into a change of polarization through the Born approximation,

$$\delta P_i = \frac{e}{V_0} \sum_{\alpha,j} Z_{ij}^{\alpha*} \delta u_j^\alpha. \quad (20)$$

In Eq. (20), e is the elementary electric charge, α denotes the atom number in the unit cell, δu_j^α its displacement in the j -th direction with respect to a reference configuration (here the ground-state structure), and $Z_{ij}^{\alpha*}$ is the Born effective charge tensor of atom α . Of course, a major approximation is made here: it is assumed that the Born effective charge does not change between the ground state and the excited state, which is, in principle, questionable. However, as discussed in Ref. [42], because the amount of excited charges is quite small, this approximation seems reasonable. The change of polarization in lead titanate, using Born charges calculated with Density Functional Perturbation Theory (DFPT) [42], is depicted in the left panel of Fig. (4). For all considered transitions, the polarization decreases. The strongest decrease rate happens for the $Z \rightarrow Z$ and $Z \rightarrow \Gamma$ transitions, and also correspond to the strongest photostriction effect calculated in Fig. (3).

This change in polarization can be directly related to a change of strain state by the third rank converse piezoelectric tensor $\mathbf{g}$,

$$\delta \boldsymbol{\eta} = \mathbf{g} \cdot \delta \mathbf{P}. \quad (21)$$

The converse piezoelectric tensor $\mathbf{g}$ is trivially related to more well-known piezoelectric tensor $\mathbf{d}$ (which relates the change of strain to an electric field) by $\mathbf{g} = \mathbf{d} \cdot \boldsymbol{\chi}^{-1}$, with $\boldsymbol{\chi}$ being the dielectric susceptibility. After calculating the piezoelectric tensor from DFPT calculations [42], the piezoelectric-induced change of lattice constant, as estimated from Eq. (21) and Fig. (4), was plotted as open symbols in Fig. (3). It can be observed there that along the polar axis, the piezoelectric model accounts for most of the calculated effect, for all transitions. In the direction perpendicular axis, the situation is not as clear. On one hand, the calculated results agree well with the piezoelectric model for the $Z \rightarrow Z$ and $Z \rightarrow \Gamma$ transitions, which are the ones with the strongest change of polarization. On the other hand, due to the negative value of the g_{13} component, a weak expansion of the lattice is predicted in the plane orthogonal to the polar axis from the converse piezoelectric model for the two transitions departing from the X point (for which the induced change in polarization is weaker) while the Δ SCF data rather shows a small contraction. This latter

Figure 4: Change of polarization against the concentration of excited carriers, for different transitions in (left) tetragonal lead titanate and (right) rhombohedral barium titanate. Reproduced from Ref. [42]. Copyright 2017 American Physical Society.

difference might result from the action of a different mechanism, for instance the potential deformation (also sometimes coined electronic pressure).

To check whether the potential was of any influence in the obtained results, ΔSCF calculations were performed at fixed atomic positions. In other words, only the volume of the cell is allowed to relax, and thus the polarization is kept approximately constant (up to the change of volume and the minor electronic dipole induced [42]). The results, plotted as open blue circles in Fig. (5) in the case of a $Z \rightarrow Z$ transition in PTO, show that along the polar axis the potential deformation mechanism is a negligible contribution compared to the piezoelectric effect. The picture is however different in the directions perpendicular to the polarization, for which the associated piezoelectric constant is smaller. It is found then that the potential deformation contribution could account for as much as a third of the calculated effect. More importantly, in the case of the $X \rightarrow Z$ transition, although the electronic pressure mechanism brings again a small contribution to the photostriction of the polar axis, it actually now competes and overcomes the (small) expansion caused by the piezoelectric effect, and results in an overall contraction of the a axis [see Fig. (6)]. Because the electronic pressure competes with the converse piezoelectric effect in the case of the $X \rightarrow Z$ transition, the c axis contraction is also reduced compared to that found in the $Z \rightarrow Z$ transition [see Fig. (6.b)]. Actually, observing Fig. (6.b), the ΔSCF data are found to lead to a larger contraction than predicted using the piezoelectric model, despite the competition of the electronic pressure mechanism. It must however be noted that both the piezoelectric model and frozen ion ΔSCF calculations can only be taken as qualitative estimates of the

Figure 5: Photo-induced change of lattice constant in tetragonal PbTiO_3 for a $Z \rightarrow Z$ transition, as calculated from a fully relaxed ΔSCF calculation (black squares), as estimated from the piezoelectric model (open black diamonds) and as calculated using frozen atomic position calculations (open blue circles), for the polar axis direction (right panel) and the direction perpendicular to it (left panel). Adapted from Ref. [42].

importance of the piezoelectric and potential deformation contributions to photostriction, as they rely on quite strong assumptions. Typically, we compute the change of polarization necessary to evaluate the converse piezoelectric effect by using ground state Born charges and finite displacement. As a result, it is most likely that only orders of magnitude and qualitative trends may be safely discussed when decomposing the photostriction effect in terms of those basic mechanisms.

In the case of barium titanate, depicted in Fig. (7), the pseudo-cubic lattice constant is found to decrease with increasing concentration of photoexcited for both the $\Gamma \rightarrow \Gamma$ and the $Z \rightarrow \Gamma$. Meanwhile, the pseudocubic angle slightly increases. A similar analysis in terms of piezoelectric and electronic pressure source terms for the calculated photostriction was conducted in Ref. [42]. It was shown there that the piezoelectric effect was the dominant mechanism in the

Figure 6: Photo-induced change of lattice constant in tetragonal PbTiO_3 for a $X \rightarrow Z$ transition, as calculated from a fully relaxed ΔSCF calculation (black squares), as estimated from the piezoelectric model (open black diamonds) and as calculated using frozen atomic position calculations (open blue circles), for the polar axis direction (right panel) and the direction perpendicular to it (left panel). Adapted from Ref. [42].

Figure 7: Change of pseudo-cubic lattice constant (left panel) and pseudocubic angle (right panel) versus concentration of excited electrons for different transitions in rhombohedral barium titanate. Reproduced from Ref. [42]. Copyright 2017 American Physical Society.

case of the $\Gamma \rightarrow \Gamma$ transition, but that potential deformation actually competes with the photo-induced piezoelectric effect for the $Z \rightarrow \Gamma$ transition.

3.2 Photostriction in bismuth ferrite

Bismuth ferrite has a rhombohedral structure with space group $R3c$ below 1103 K [2], whose unit cell is sketched in green in Fig. (8). It is made of two pseudocubic 5-atom perovskite cells (depicted as black cubes in Fig. (8)) along the $[111]_{pc}$ pseudocubic direction because of the $a^-a^-a^-$ tilting pattern (in Glazer notation [58]) of the oxygen octahedra [59, 60, 61]. The $[111]_{pc}$ direction is also associated with a large polarization of about $100 \mu\text{C}\cdot\text{cm}^{-2}$ [62, 63]. BiFeO_3 (BFO) also exhibits a G -type antiferromagnetic order convoluted with cycloidal arrangement of the antiferromagnetic vector, propagating in the $[1\bar{1}0]_{pc}$ whilst the antiferromagnetic vector rotates in the plane spanned by $[1\bar{1}0]_{pc}$ and $[111]_{pc}$ with a period of 62-64 nm [64, 65, 66, 2].

BiFeO_3 , among ferroelectrics and multiferroics, has a relatively low bandgap, estimated to be of the order of 2.7 eV [67]. However, possible defect bands at 2.2 eV, as observed in photoconductivity spectroscopy experiments [68], have for a long time shed confusion on the true value of the bandgap. This relatively "small" bandgap has made BFO one of the prominent multiferroics for the study and application of the coupling between light and ferroic order parameters, such

Figure 8: Bismuth ferrite rhombohedral unit cell (green) and pseudocubic 5-atom unit cell.

as photovoltaics [69, 70, 71], photocatalysis [72, 73, 21] and photostriction [22, 15, 26]. Steady photostriction in BiFeO_3 was studied in Ref. [74] using the ΔSCF method in a similar fashion to lead and barium titanates, except that the $\text{LSDA}+U$ functional was used, with $U = 3.87$ eV. The band structure of bismuth ferrite is plotted in Fig. (9). The bottom of the conduction band (CBM) is located at the Z point, while the top of the valence band (VBM) is located in-between B and Z points. Three transitions, depicted by different arrows in Fig. (9), are considered: $Z \rightarrow Z$ (denoted direct CBM, in green), $\text{VBM} \rightarrow Z$ (in red, denoted indirect VBM-CBM) and a vertical transition from the VBM (in blue, denoted direct VBM).

The results, shown in Fig. (10), show that the pseudocubic directions are shrinking upon photoexcitation. Generally speaking, pseudocubic directions “close” to the polar axis (such as $[100]$, $[110]$ and $[111]$) tend to shorten. On the other hand, due to the opening of the pseudocubic angle with the increase of photo-excited carriers, the directions “away” from the polar axis (such as $[1\bar{1}0]$ or $[1\bar{1}1]$) lengthen [74].

Interestingly, experiments on single crystals of BiFeO_3 under UV light report an elongation of $+2.7 \times 10^{-3}\%$ along the $[101]$ pseudocubic direction [15]. According to our calculations, an expansion is only possible if this $<101>$ direction is actually a $[10\bar{1}]$ direction (i.e., perpendicular to the spontaneous polarization), in which case such expansion would occur for a concentration of photoexcited electrons of roughly $1.6 \times 10^{19} \text{ cm}^{-3}$. Note that, according to literature reports, concentration of photoexcited carriers ranging from 5×10^{17} to $5 \times 10^{19} \text{ cm}^{-3}$ were measured or estimated [27, 75].

To answer the question about whether the origin of the calculated photostric-

Figure 9: Band structure of *R3c* bismuth ferrite, and the different transitions considered in Ref. [74]. Copyright 2016 American Physical Society.

Figure 10: Change of (a) pseudocubic lattice constant, (b) pseudocubic angle and (c) length along the pseudocubic $[1\bar{1}0]$ direction with the number of photoexcited carriers in rhombohedral bismuth ferrite. Taken from Ref. [74]. Copyright 2016 American Physical Society.

Figure 11: Calculated photo-induced change in pseudocubic lattice constant (filled symbols) and estimated change in lattice constant caused by reduction of the polarization and converse piezoelectric effect (open symbols) in $R3c$ BiFeO₃. Taken from Ref. [74]. Copyright 2016 American Physical Society.

tive effect was driven by the piezoelectric effect or not, we conducted a similar analysis as in lead and barium titanates. The polarization was shown to diminish with the number of photoexcited carriers n_e . Meanwhile, the piezoelectric tensor $\mathbf{d}$ and the dielectric susceptibility χ , taken from molecular dynamics simulations [76], allowed the estimation of the piezoelectric constant $\mathbf{g}$ and therefore of the piezoelectric photo-induced strain (see open symbols in Fig. (11)). It is found that for the direct CBM and indirect VBM-CBM transitions, the piezoelectric model is rather accurate. Performing frozen ion Δ SCF calculations indeed proves that the electronic pressure was a minor (cooperating) contribution in those cases [74]. On the other hand, the photo-induced change of lattice constant in the direct VBM transition case is predicted to be stronger in the piezoelectric model than the calculated values, which was found later to be the result of the competition of the piezoelectric mechanism (which in this case favors shrinking) with the potential deformation (which for this transition favors expansion). Overall, the piezoelectric effect still prevails, but its influence is reduced.

3.3 Conclusions about photostriction in ferroelectrics

Overall, the use of first-principles tends to confirm the scenario of a converse piezoelectric effect-driven photostriction in ferroelectric materials. This seems to be particularly true along the polar axis, for which the piezoelectric constant is larger. However, in directions perpendicular to the polar axis, the

Figure 12: (left panel) Photo-induced change of length in tetragonal PTO, rhombohedral BTO and rhombohedral BFO along several directions, for different transitions; (right panel) Change in pseudocubic angle in rhombohedral BTO *versus* rhombohedral BFO. Taken from Ref. [42]. Copyright 2017 from the American Physical Society.

photo-induced potential deformation can become a sizable contribution or competition as demonstrated in the case of lead titanate. Comparing PTO, BTO and BFO in Fig. (12), it appears that lead titanate, at least in the case of the $Z \rightarrow Z$ transition, has the largest photostriction potential, which results mostly from (i) strong photo-induced change of polarization and (ii) large piezoelectric constant. Note also that two dimensional ferroelectric compounds, such as in the monochalcogenide family (SnS, SnSe), have also been predicted to be good photostrictive materials using the same methods [77].

4 Elasto-optic effects in ferroelectrics

Reference [45] investigated elasto-optic effects in PTO films under epitaxial strain. For that, it first computed the total energy of different phases, as shown in Figure (13a). Note that these calculations also predicted that bulk PTO adopts a tetragonal (T) phase with a space group of $P4mm$, and having a lattice constant a equal to 3.87 Å as well as an axial ratio of 1.04. Such computational results are rather consistent with experimental results of 1.02 - 1.06 [78]), and the fact that PTO bulk adopts a $P4mm$ state below 760 K [79]. As shown in Fig. (13a), this tetragonal T phase is also predicted to be the ground state (i.e., it has the lowest energy) for strains ranging from 0% to 1%. Its out-of-plane polarization (P_z) decreases from 0.87 C/m² to 0.80 C/m² [see Fig. (13d)], and its axial ratio reduces from 1.04 to 1.02 as the strain increases from 0 to 0.75% [see Fig. (13b)].

In the strain window from 0.75% to 1.75%, a monoclinic Cm phase first has a very low energy close to that of the T phase and then becomes the ground state [see Fig. (13a)]. Another monoclinic Pm phase exhibits a very similar energy than the Cm phase, indicating that both Cm and Pm can likely be stabilized in PTO films by, e.g., applying epitaxial strain and/or electric field. Interestingly, both Pm and Cm phases have been observed for PTO films grown on a DyScO₃ substrate (corresponding to a biaxial strain of 1.4%) [80]. As shown Fig. (13b), the Cm phase decreases its axial ratio from 1.022 to 0.988 when the epitaxial strain ranges from 0.75% to 1.75%. Unlike the T phase that has only an out-of-plane component of polarization, the Cm phase has both out-of-plane and in-plane components of polarization. When this strain varies from 0.75% to 1.75%, the in-plane polarization (P_x) of Cm increases from about zero to 0.66 C/cm² while the out-of-plane polarization P_z concomitantly decreases from 0.75 C/cm² to almost zero. In other words and as shown in Fig. (14a), the polarization of the Cm state continuously rotates from the out-of-plane [001] direction towards the in-plane [110] direction when increasing strain in this intermediate strain range. Regarding the Pm monoclinic phase, the axial ratio decreases from values larger than 1 to less than 1 when the strain is enhanced between 0.75% to 1.75%, and is qualitatively (and even quantitatively) very similar to the axial ratio of the Cm phase. As shown in Figs. (14c) and (14d), the P_z out-of-plane polarization of Pm decreases and the P_x in-plane polarization increases in this tensile strain range. Note that P_y is zero for the Pm phase, which differs from the case of the

Figure 13: Total energy (a), axial ratio (b), x-component of the polarization, P_x (c), and out-of-plane component of the polarization, P_z (d), of PTO films as a function of tensile strain. Note that $P_y = P_x$ for the *O* and *Cm* phases, $P_y = 0$ for the *T* and *Pm* phases. Taken from Ref. [45]. Copyright 2016 from the American Physical Society.

Figure 14: Schematic representations of polarization directions of the Cm , Pm , O , and T phases. Polarization of the T phase is along the $[001]$ direction, of the O phase is along the $[110]$ direction. Polarization of Cm is along a $[uvw]$ direction (with u being different with v), which rotates from the $[100]$ direction to the $[110]$ direction under strain, and polarization of Pm is along a $[u0v]$ direction (with u being different with v), which rotates from the $[001]$ direction to the $[100]$ direction under strain.

Cm phase for which $P_y = P_x$ is non-null. As shown in Fig. (14b), the polarization of the Pm phase rotates from the pseudo-cubic $[001]$ to $[100]$ directions when increasing the tensile strain. These different in-plane polarization can induce different optical properties and elasto-optic effects between the Cm and Pm phases, as we will see below.

At the large strain $>1.75\%$, an orthorhombic (O) phase has the lowest energy and thus becomes the ground state. This O phase has an axial ratio smaller than 1, a large in-plane polarization and a null out-of-plane polarization.

Optical properties and elasto-optic effects were considered in Reference [45] for these different phases of PTO under tensile strain. The predicted refractive index n for an $\hbar\omega$ energy being 0.3 eV below the computed band gap is shown in Fig. (15). n_o and n_e represent the refractive index for ordinary ray and extraordinary ray, respectively. As shown in Fig. (15a), n_o is larger than n_e in the T phase, while the reverse situation holds for the O phase. The hierarchy between n_o and n_e in the Cm and Pm phases depends on strain. At strain less than about 1.25%, n_o is higher than n_e , while n_o is less than n_e for strain larger than $\simeq 1.25\%$. To further investigate the hierarchy of n_o and n_e , Fig. (15b) shows the refractive index as a function of the axial ratio c/a . In first approximation, n_o is equal to n_e when c/a is 1, and n_o is larger (smaller) than n_e when c/a is larger (smaller) than 1. Therefore, the hierarchy between n_o and n_e is dependent on the c/a axial ratio. Such facts may be useful for discovering materials with large elasto-optic effects.

Furthermore, both n_o and n_e increase with strain in the T phase and decrease

Figure 15: Panel (a): Refractive index n of ordinary (open symbols) and extraordinary rays (filled symbols) for PTO in its T (squares), O (dots) and Cm (up triangles) phases as a function of strain. Note that for the monoclinic Pm phase, the x- and y-directions are not equivalent by symmetry (due to the polarization direction), and therefore n_1 and n_2 differ. In-plane and out-of-plane refractive indices of the Pm phase (down triangles) are also shown. Panels (b) and (c): Similar to Panel (a) but as a function of the axial ratio and magnitude of the polarization, respectively. Taken from Ref. [45]. Copyright 2016 American Physical Society.

in the O phase [see Fig. (15a)]. This different behavior is related to polarization. As a matter of fact and as shown in Fig. (15c), both n_o and n_e decrease when the polarization increases in the T and O phases. As Cm and Pm phases structurally bridge the T and O phases, the refractive n_o and n_e indices of these monoclinic state have to continuously evolve between those of the corresponding refractive indices of the T and O phases. n_o at strain 0.75% of the T phase and at the strain 1.5% in the O phase are very similar, therefore n_o in Cm and Pm phases does not need to change too much to bridge the T and O phases at the intermediate strain of 0.75%-1.5%. In contrast, n_e at strain 0.75% of the T phase is much smaller than n_e at the strain 1.5% in the O phase. n_e in the Cm and Pm phases thus have to sharply increase in the intermediate strain to bridge the n_e 's of the T and O phases. This sharply changing n_e with strain can induce large elasto-optic effects, according to Eq. (16).

As a matter of fact and as revealed in Table 1, the effective elasto-optic coefficient $(p_{31} + p_{32})/2$ for the monoclinic Cm and Pm phases indeed has very large values. It is at least two times that of the T phase and three times that of the O state. The large elasto-optic coefficient is related to n_e in Cm and n_3 in Pm , which significantly change with strain. These value appear to be the largest elasto-optic coefficient predicted or reported. For instance, they are about twice as large as the coefficient of lithium niobate, for which $p_{31} = 0.18$, and 30-60%

Table 1: Elasto-optic coefficients for the four studied phases of epitaxial (001) PTO films under a tensile strain of 1.2%, for an $\hbar\omega$ energy being 0.3 eV smaller than the computed band gap. The number in parentheses corresponds to $(p_{21} + p_{22})/2$ of the Pm phase, which, due to symmetry and unlike in the T , O and Cm phases, differs from $(p_{11} + p_{12})/2$. Note that $p_{31} = p_{32}$ in the T , O and Cm states, therefore making $(p_{31} + p_{32})/2 = p_{31}$ in these three phases. Taken from Ref. [45]. Copyright 2016 American Physical Society.

Phase	T	O	Pm	Cm
$(p_{11} + p_{12})/2$	-0.10	0.20	-0.09 (-0.13)	-0.04
$(p_{31} + p_{32})/2$	-0.22	0.10	-0.43	-0.35

bigger than that of quartz ($p_{31} = 0.29$) [81].

In this part of the review, we described the four phases of PbTiO_3 under tensile strain, and their refractive indices behavior under strain. The fast increase of refractive index n_e of the monoclinic Cm and Pm phases with epitaxial strain induces very large elasto-optic effects. Further analysis reveals that such rapid change of refractive index is also related to a sharp change of the axial ratio with strain [see Fig. (15b)]. These results may provide a new route to discover large elasto-optic effect materials by searching for low-symmetry phases possessing a rapid evolution of the axial ratio and polarization with strain. Note that this rapid evolution can occur in epitaxial ferroelectrics films [82, 83] but also in the morphotropic phase boundaries of some solid solutions[84, 85, 86, 87, 88] when varying composition or hydrostatic pressure. Note also that a recent work demonstrated that large elasto-optic coefficients can occur in epitaxial thin films made of the multiferroic BiFeO_3 [89].

5 Conclusion

In summary, this review provided details about (i) the methods used to recently predict photostriction and elasto-optic effects in ferroelectrics and multiferroics from first principles; and (ii) their concomitant results and analyses aimed at microscopically understanding such effects. We hope that these methods and analyses can be used as starting points to design novel FE and MFE materials exhibiting giant couplings between light and physical properties. Such interesting general topic is at its infancy stage, and therefore further developments (such as tackling these couplings using the more sophisticated and complex GW [52] and time-dependent DFT [90] schemes as well as exciting related discoveries are likely to occur in a near future.

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