First-Principles Study of the Electro-Optic Effect in Ferroelectric Oxides

Marek Veithen,[1] Xavier Gonze,[2] and Philippe Ghosez[1]
[1]*Département de Physique, Université de Liège, B-5, B-4000 Sart-Tilman, Belgium*
[2]*Unité PCPM, University College of London, place Croix du Sud, 1, B-1348 Louvain-la-Neuve, Belgium*

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We first present a method to compute the electro-optic tensor from first principles, explicitly taking into account the electronic, ionic and piezoelectric contributions. We then study the nonlinear optic behavior of three paradigmatic ferroelectric oxides. Our calculations reveal the dominant contribution of the soft mode to the electro-optic coefficients in $LiNbO_3$ and $BaTiO_3$ and its minor role in $PbTiO_3$. We identify the coupling between the electric field and the polar atomic displacements along the B-O chains as the origin of the large electro-optic response in perovskite ABO_3 compounds.

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The electro-optic (EO) effect describes the change of refractive index of a material in a static electric field and is exploited in various technological applications [1]. Ferroelectric ABO_3 compounds exhibit unusually large EO coefficients and are therefore materials of choice for optical devices. Since the 1970s, $LiNbO_3$ EO modulators have been widely used in fiber-optic transmission systems [2]. More recently, there has been increasing interest in epitaxially grown $BaTiO_3$ thin films for optical waveguide modulators [3]. The EO effect is the origin of the photorefractive effect, exploited in nonvolatile holographic data storage in $LiNbO_3$ [4].

Finding better EO materials is a desirable goal. However, the experimental characterization of optical nonlinearities requires high-quality single crystals that are not always directly accessible nor easy to make. Input from accurate theoretical calculations allowing us to predict the nonlinear optical behavior of crystalline solids would therefore be particularly useful.

For many years, theoretical investigations of nonlinear optical phenomena were restricted to semiempirical approaches such as shell models [5] or bond-charge models [6,7]. In the last decade, significant theoretical advances have been reported concerning first-principles density functional theory (DFT) calculations of the behavior of periodic systems in an external electric field [8,9] and opened the way to direct predictions of various optical phenomena. Recently, particular attention has been paid to the calculation of nonlinear optical (NLO) susceptibilities and Raman cross sections [10,11].

In this Letter, we go one step further and present a method to predict the *linear EO coefficients* of periodic solids within DFT. Our method is very general, and can be applied to paradigmatic ferroelectric oxides : $LiNbO_3$, $BaTiO_3$, and $PbTiO_3$. We find that first-principles calculations are fully predictive, and provide significant new insights into the microscopic origin of the EO effect. In particular, we highlight the *predominent role of the soft mode* in the EO coupling of $LiNbO_3$ and $BaTiO_3$, in contrast with *its minor role* in $PbTiO_3$.

At linear order, the dependence of the optical dielectric tensor ε_{ij} on the static (or low frequency) electric-field $\mathcal{E}_\gamma$ is described by the linear EO tensor $r_{ij\gamma}$:

$$\Delta(\varepsilon^{-1})_{ij} = \sum_{\gamma=1}^{3} r_{ij\gamma}\mathcal{E}_\gamma. \qquad (1)$$

Throughout this Letter, we follow the convention of using Greek and Roman indexes (respectively) to label static and optical fields (respectively). We write all vector and tensor components in the system of Cartesian coordinates defined by the principal axes of the crystal under zero field. We also refer to the atomic displacements $\tau_{\kappa\alpha}$ [κ labels an atom and α a Cartesian direction] within the basis defined by the zone-center transverse optic (TO) phonon eigendisplacements $u_m(\kappa\alpha)$: $\tau_{\kappa\alpha} = \sum_m \tau_m u_m(\kappa\alpha)$.

Let us first consider the *clamped* (zero strain) EO tensor, $r^{\eta}_{ij\gamma}$, in which all electric field induced macroscopic strains η are forbidden. This is achieved experimentally by working at a frequency sufficiently high to avoid strain relaxations but low compared to the frequency of the TO modes. Within the Born-Oppenheimer approximation, we express the *total* derivative of ε_{ij} as the sum of two *partial* derivatives with respect to $\mathcal{E}_\gamma$ and τ_m:

$$\frac{d\varepsilon_{ij}}{d\mathcal{E}_\gamma} = \frac{\partial\varepsilon_{ij}}{\partial\mathcal{E}_\gamma}\bigg|_{\tau=0} + 4\pi\sum_m \frac{\partial\chi^{(1)}_{ij}}{\partial\tau_m}\bigg|_{\mathcal{E}=0}\frac{\partial\tau_m}{\partial\mathcal{E}_\gamma}. \qquad (2)$$

The derivative in the first term of the right-hand side of Eq. (2) is computed at clamped atomic positions. It describes the *electronic* contribution to the EO tensor and is proportional to the NLO susceptibilities $\chi^{(2)}_{ijl}$. The second term represents the *ionic* contribution. It depends on the first-order change of the linear dielectric susceptibility due to atomic displacements, and is related to the Raman susceptibility $\alpha^m_{ij} = \sqrt{\Omega}\sum_{\kappa\alpha}\frac{\partial\chi^{(1)}_{ij}}{\partial\tau_{\kappa\alpha}}u_m(\kappa\alpha)$ of mode m [Ω is the unit cell volume], as well as to the amplitude of the ionic relaxation induced by the field $\mathcal{E}_\gamma$. $\partial\tau_m/\partial\mathcal{E}_\gamma$ can be expressed in terms of (i) the TO phonon mode frequencies ω_m and (ii) the TO mode polarities $p_{m,\gamma} = \sum_{\kappa,\beta} Z^*_{\kappa,\gamma\beta} u_m(\kappa\beta)$, directly linked to the infrared (IR) intensities [12]. Combining this with the previous equations, we obtain the clamped EO tensor [13]

$$r^{\eta}_{ij\gamma} = \frac{-8\pi}{n_i^2 n_j^2} \chi^{(2)}_{ijl}\Big|_{l=\gamma} - \frac{4\pi}{n_i^2 n_j^2 \sqrt{\Omega}} \sum_m \frac{\alpha^m_{ij} p_{m,\gamma}}{\omega_m^2} \tag{3}$$

where n_i and n_j are the principal refractive indices.

Let us now consider the *unclamped* (zero stress) EO tensor, $r^{\sigma}_{ij\gamma}$. It can be shown [13] that the macroscopic expression proposed in Ref. [14] is still valid at the microscopic level so that the piezoelectric contribution to $r^{\sigma}_{ij\gamma}$ can be computed from the elasto-optic coefficients $p_{ij\alpha\beta}$ and the piezoelectric strain coefficients $d_{\gamma\alpha\beta}$

$$r^{\sigma}_{ij\gamma} = r^{\eta}_{ij\gamma} + \sum_{\alpha,\beta=1}^{3} p_{ij\alpha\beta} d_{\gamma\alpha\beta}. \tag{4}$$

An expression similar to Eq. (3) was previously used by Johnston [15] to estimate the clamped EO tensor of $\mathrm{LiNbO_3}$ and $\mathrm{LiTaO_3}$ from IR and Raman measurements. However, this semiempirical approach was limited by the indeterminacy of the relative sign of $\mathbf{p}_m$ and α^m. As discussed below, the direct evaluation of Eq. (3) and (4) from first principles provides an *easier* and *more accurate* estimate of the EO tensor.

We have implemented this formalism in the ABINIT open software [16], within the local density approximation (LDA) to the DFT. The optical dielectric tensor, Born effective charges, phonon frequencies and eigendisplacements are computed from linear response [12]. The piezoelectric strain coefficients $d_{\gamma\alpha\beta}$ are deduced from the piezoelectric stress coefficients $e_{\gamma\alpha\beta}$ and the elastic constants. These two quantities, as well as the elasto-optic tensor $p_{ij\alpha\beta}$, are obtained from finite differences. The nonlinear response functions $\chi^{(2)}_{ijl}$ and $\partial\chi^{(1)}_{ij}/\partial\tau_{\kappa\alpha}$ are computed from a perturbative approach using a new implementation based on the $2n+1$ theorem [8,13].

For $\mathrm{BaTiO_3}$ and $\mathrm{PbTiO_3}$, we use extended norm-conserving pseudopotentials [17], a plane wave kinetic energy cutoff of 45 hartree and a $10\times10\times10$ k-point grid. For $\mathrm{LiNbO_3}$, we use the same norm-conserving pseudopotentials as in Ref. [18] as well as the Born effective charges, phonon frequencies and eigenvectors already reported in that paper. For this compound, an $8\times8\times8$ k-point grid and a plane wave kinetic energy cutoff of 35 hartree give converged values for $\chi^{(2)}_{ijl}$ and $\partial\chi^{(1)}_{ij}/\partial\tau_{\kappa\alpha}$.

First, we study $\mathrm{LiNbO_3}$. This compound has a trigonal symmetry with 10 atoms per unit cell. The theoretical lattice constants and atomic positions are reported in Ref. [18]. $\mathrm{LiNbO_3}$ undergoes a single transition at 1480 K from a centrosymmetric high-T paraelectric $R\bar{3}c$ phase to a ferroelectric low-T R3c ground state. The form of the EO tensor depends on the choice of the Cartesian axes. Here, we follow the standards on piezoelectric crystals [19].

With this choice of axes, the EO tensor in the ferroelectric phase of $\mathrm{LiNbO_3}$ has four independent elements (Voigt notations): r_{13}, r_{33}, r_{22}, and r_{51}. The TO modes can be classified into $4A_1 + 5A_2 + 9E$. The A_1 and E modes are Raman and IR active. Only the A_1 modes couple to r_{13} and r_{33}, while the E modes are linked to r_{22} and r_{51}. Table I gives these four clamped coefficients [22], as well as the contribution of each optical phonon. For comparison, we mention the coefficients computed by Johnston [15] from measurements of IR and Raman intensities (IR + R) as well as the results of a bond-charge model (BCM) calculation by Shih and Yariv [7]. The first-principles calculations correctly predict the sign of the four EO coefficients [19]. The absolute values are also well reproduced by our method, especially if we take into account the fact that NLO properties are generally difficult to determine accurately. The experimental values are sensitive to external parameters such as temperature changes [23] and the stoichiometry of the samples. For example, using crystals of various compositions, Abdi and co-workers measured absolute values between 1.5 pm/V and 9.9 pm/V for r^{σ}_{22} [21]. These difficulties support the need for sophisticated theoretical tools to predict NLO properties. In contrast to the models of Refs. [7,15], our method is predictive and does not use any experimental parameters. Moreover, it

TABLE I. EO tensor (pm/V) in $\mathrm{LiNbO_3}$: electronic, ionic and piezoelectric contributions, and comparison with experiment, for the clamped and unclamped cases. The ionic part is split into contributions from TO modes (ω_m in $\mathrm{cm^{-1}}$).

		A_1 modes			E modes		
		ω_m	r_{13}	r_{33}	ω_m	r_{22}	r_{51}
Electronic			1.0	4.0		0.2	1.0
Ionic	TO1	243	6.2	18.5	155	3.0	7.5
	TO2	287	−0.2	−0.4	218	0.4	1.5
	TO3	355	−0.1	0.0	264	0.6	1.3
	TO4	617	2.8	4.8	330	−0.3	1.2
	TO5				372	−0.2	0.4
	TO6				384	−0.1	−0.2
	TO7				428	0.2	0.2
	TO8				585	0.7	2.1
	TO9				677	0.0	0.0
	Sum of ionic		8.7	22.9		4.4	13.9
Strain			0.8	0.1		3.0	13.7
Clamped	Present		9.7	26.9		4.6	14.9
	Exp. [20]		8.6	30.8		3.4	28
	IR + R [15]		12	39		6	19
	BCM [7]			25.9			20.5
Unclamped	Present		10.5	27.0		7.5	28.6
	Exp. [20]		10.0	32.2		6.8	32.6
	Exp. [21]					9.9	

reproduces r^{η}_{13}, r^{η}_{33}, and r^{η}_{22} better than the semiempirical models.

Our approach also provides some insight into the origin of the high $LiNbO_3$ EO response. All EO coefficients are dominated by the ionic contribution of the A_1 TO1 and the E TO1 modes. This can be explained as follows. At the paraelectric-ferroelectric phase transition, the unstable A_{2u} and E_u modes of the paraelectric phase transform to *low-frequency* and *highly polar* modes in the ferroelectric phase [18], generating a large EO response if they exhibit, in addition, a *large Raman susceptibility.* The A_1 TO1 and E TO1 modes of the ferroelectric phase have a strong overlap of, respectively, 0.82 and 0.68 with the unstable A_{2u} and E_u modes of the paraelectric phase and combine giant polarity [18] and large Raman susceptibility (see below for the A_1 mode).

In Table I, we also report the unclamped EO coefficients in $LiNbO_3$. As the piezoelectric coefficients d_{31} (-1 pC/N) and d_{33} (6 pC/N) are small compared to d_{15} (55.9 pC/N) and d_{22} (21.6 pC/N), the piezoelectric effect is important for r^{σ}_{22} andr^{σ}_{15} and negligible for r^{σ}_{13} and r^{σ}_{33}. The unclamped EO coefficient r^{σ}_{51} is nearly twice as large as the clamped one. Moreover, its theoretical value is in better agreement with the experiment than that of the clamped one. This suggests that the piezoelectric contribution was not entirely eliminated during the measurement ofr^{η}_{51}; the correct value of the clamped coefficient might be closer to the theoretical 14.9 pm/V.

Second, we study $PbTiO_3$ and $BaTiO_3$. Both compounds are stable at room temperature in a ferroelectric distorted perovskite structure of tetragonal $P4mm$ symmetry with 5 atoms per unit cell [24]. In the $P4mm$ phase, the TO modes can be classified into $3A_1 + 4E + B_1$. The EO tensor has only three independent elements: r_{13}, and r_{33}, coupling to the A_1 modes, and r_{42}, linked to the E modes. The results are shown in Table II.

For $PbTiO_3$, we found only measurements of r^{η}_{13} and r^{η}_{33}, which agree well with our theoretical results. Moreover, our calculation predicts that $PbTiO_3$ exhibits a large r^{η}_{42}, in spite of its low r^{η}_{33}. Combined with other advantageous features, such as small thermo-optic coefficients [27], this suggests that $PbTiO_3$ *might be* an interesting candidate for EO applications *if properly oriented.*

In $BaTiO_3$, the low temperature structure is rhombohedral. The $P4mm$ phase is unstable and exhibits, in the harmonic approximation, an unstable E mode that prevents the use of Eq. (3) to compute r^{η}_{42}. The theoretical estimates of r^{η}_{13} and r^{η}_{33} are reasonably accurate despite an underestimation of the theoretical r^{η}_{33}. The origin of the error can be attributed to various sources. First, the values computed for the $P4mm$ phase correspond to an extrapolation of the EO tensor to 0 K, while experimental results are obtained at room temperature. Also, linear and NLO susceptibilities can be relatively inaccurate within the LDA. In this context, note the use of the LDA optical refractive indexes in Eq. (3), overestimating the experimental values by about 10%.

TABLE II. Electronic and ionic contributions of individual TO modes (ω_m in cm^{-1}) to the clamped EO tensor (pm/V) in the $P4mm$ phase of $PbTiO_3$ and $BaTiO_3$.

	$PbTiO_3$					$BaTiO_3$		
	A_1 modes			E modes		A_1 modes		
	ω_m	r^{η}_{13}	r^{η}_{33}	ω_m	r^{η}_{42}	ω_m	r^{η}_{13}	r^{η}_{33}
Elec.		2.1	0.5		2.2		1.0	2.1
TO1	151	3.9	2.9	79	16.4	161	1.0	1.0
TO2	357	1.4	0.7	202	10.5	300	5.7	16.3
TO3	653	1.6	1.8	269	0.2	505	1.2	2.9
TO4				484	1.2			
Tot		9.0	5.9		30.5		8.9	22.3
Exp. [25]		13.8	5.9					
Exp. [14]							10.2	40.6
Exp. [26]							8	28

We compare now the NLO response of the three compounds. r^{η}_{13} is similar for all of them, while r^{η}_{33} is significantly smaller in $PbTiO_3$ than in $LiNbO_3$ and $BaTiO_3$. In the latter two compounds, the magnitude of r^{η}_{33} is dominated by one particular phonon mode. In $BaTiO_3$, the TO2 mode at 300 cm^{-1} has a similar strong overlap (92%) with the unstable mode in the paraelectric phase than the TO1 modes in $LiNbO_3$, as previously discussed. In $PbTiO_3$, all A_1 modes contribute almost equally to r^{η}_{33}. The TO2 mode at 357 cm^{-1} has the strongest overlap (73%) with the soft mode in the cubic phase. Surprisingly, its contribution to r^{η}_{33} is *23.5 times smaller* than the contribution of the TO2 mode in $BaTiO_3$.

To identify the origin of the distinctive behavior of $PbTiO_3$, we report in Table III the mode polarities and Raman susceptibilities of the A_1 TO modes. In the three compounds, α has two independent elements α_{11} and α_{33} that determine the amplitude of r^{η}_{13} and r^{η}_{33}. α_{33} is large for the TO1 mode in $LiNbO_3$ and the TO2 mode in $BaTiO_3$. On the other hand, it is the smallest for the TO2 mode in $PbTiO_3$, in agreement with experiments [28]. Combined with a higher frequency ($\omega^2_{\mathrm{PbTiO_3}}/\omega^2_{\mathrm{BaTiO_3}} = 1.41$), a lower polarity ($p_{\mathrm{BaTiO_3}}/p_{\mathrm{PbTiO_3}} = 1.49$), and a larger value of the refractive index ($n^4_{\mathrm{PbTiO_3}}/n^4_{\mathrm{BaTiO_3}} = 1.35$), this weak Raman susceptibility ($\alpha_{\mathrm{BaTiO_3}}/\alpha_{\mathrm{PbTiO_3}} = 8.27$) explains the weak contribution of the TO2 mode to r^{η}_{33} in $PbTiO_3$.

TABLE III. Raman susceptibilities and mode polarities (10^{-2} a.u.) of the A_1 TO modes in $LiNbO_3$, $BaTiO_3$, and $PbTiO_3$.

	$LiNbO_3$			$BaTiO_3$			$PbTiO_3$		
	p_3	α_{11}	α_{33}	p_3	α_{11}	α_{33}	p_3	α_{11}	α_{33}
TO1	3.65	-0.70	-2.02	1.22	-0.16	-0.13	1.25	-0.67	-0.43
TO2	0.45	0.30	0.53	3.25	-1.18	-2.73	2.18	-0.75	-0.33
TO3	0.67	0.18	-0.05	1.74	-1.26	-2.55	2.68	-2.42	-2.28
TO4	3.82	-1.96	-3.23						

TABLE IV. Decomposition of the Raman susceptibility of the A_1 TO2 mode in $BaTiO_3$ and $PbTiO_3$ into contributions from the individual atoms in the unit cell [24].

	$BaTiO_3$			$PbTiO_3$		
κ	$\sqrt{\Omega}\frac{\partial\chi^{(1)}_{33}}{\partial\tau_{\kappa 3}}$ (a.u.)	$u(\kappa,3)$ (10^{-2} a.u.)	$\alpha_{33}(\kappa)$	$\sqrt{\Omega}\frac{\partial\chi^{(1)}_{33}}{\partial\tau_{\kappa 3}}$ (a.u.)	$u(\kappa,3)$ (10^{-2} a.u.)	$\alpha_{33}(\kappa)$
Ba/Pb	0.45	−0.014	−0.01	−1.00	−0.006	0.01
Ti	−6.46	0.257	−1.66	−2.64	0.216	−0.57
O_1	5.15	−0.167	−0.86	3.69	0.059	0.22
O_2/O_3	0.43	−0.240	−0.10	−0.02	−0.316	0.01
Tot			−2.73			−0.32

The microscopic origin of the lower A_1 TO2 mode Raman susceptibility in $PbTiO_3$, compared to $BaTiO_3$, is explained by the decomposition of α_{33} into contributions of the individual atoms in the unit cell (see Table IV). In both perovskites, the major contributions to the Raman susceptibility of the A_1 TO2 modes are $\alpha_{33}(\mathrm{Ti})$ and $\alpha_{33}(\mathrm{O}_1)$ [24]; α_{33} is mostly due to the atomic displacements of the atoms located on the Ti–O chains oriented along the polar direction. First, the derivatives of $\chi^{(1)}_{33}$ versus atomic displacement are of opposite sign for Ti and O_1 atoms, and significantly larger in $BaTiO_3$ than in $PbTiO_3$. Second, the opposing displacements of Ti and O_1 atoms in the TO2 mode in $BaTiO_3$ produce contributions that add to yield a giant α_{33}. On the other hand, the in-phase displacements of Ti and O_1 in $PbTiO_3$ produce contributions that cancel out, giving a small α_{33}. This distinct behavior goes beyond a simple mass effect. Changing the mass of Pb to that of Ba in the dynamical matrix of $PbTiO_3$ has no significant effect on the relative Ti–O displacement. Large atomic displacements of opposite direction along the Ti–O chains are therefore needed to generate a large α_{33} and potentially a large r_{33}.

In summary, we presented a method to compute the EO tensor from first principles. In $LiNbO_3$ and $BaTiO_3$, the large EO response originates in the giant contribution of the successor of the soft mode, which combines low-frequency, high polarity and high Raman susceptibility. In comparison, the contribution of the similar mode in tetragonal $PbTiO_3$ is rather weak due to its low Raman susceptibility. In the perovskites, the Raman susceptibility is principally determined by the atomic displacements along the B–O chains in the polar direction. This suggests that the search for new perovskite oxides with good EO properties should focus on compounds with large relative B–O atomic displacements along the chains.

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[24] Reduced coordinates of *P4mm* $BaTiO_3$ and $PbTiO_3$: Ba/Pb (0, 0, 0), Ti $(0.5, 0.5, 0.5 + \delta_{\mathrm{Ti}})$, O_1 $(0.5, 0.5, 0 + \delta_{\mathrm{O}_1})$, O_2 $(0.5, 0, 0.5 + \delta_{\mathrm{O}_2})$, and O_3 $(0, 0.5, 0.5 + \delta_{\mathrm{O}_2})$. Relaxation at experimental lattice constants yields for $BaTiO_3$ ($PbTiO_3$): $\delta_{\mathrm{Ti}} = 0.0136$ (-0.0478), $\delta_{\mathrm{O}_1} = -0.0273$ (-0.1205), $\delta_{\mathrm{O}_2} = -0.0167$ (-0.1278).

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