Theoretical Study of Ferroelectric and Optical Properties in the $180^\circ$ Ferroelectric Domain Wall of Tetragonal BaTiO$_3$

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The microscopic mechanism of spontaneous polarization and refractive indices in $180^\circ$ ferroelectric domain walls of tetragonal Barium titanate (BaTiO$_3$) is discussed by using a microscopic model. This model bases on the orbital approximation in correlation with the dipole–dipole interaction due to the local field acting on all constituent ions within the domain wall. It is found that the behavior of both the spontaneous polarization and the refractive indices depends on the thickness of the domain wall which was varied between 5 and 20 Å. Moreover, the spontaneous polarization shows a hyperbolic tangent shape for domain walls of a larger thickness which then vanishes at the center of the domain wall. The refractive indices suggest the domain wall to act like a biaxial crystal resulting in refractive index profiles of a Gaussian shape for domain walls of $\sim 20$ Å. This dramatically affects optical transmission through the domain wall especially for light being polarized parallel to the domain wall.

1. Introduction

Barium titanate (BaTiO$_3$) is one of the most well known ferroelectric materials. After the discovery of its ferroelectric properties, it was intensively studied as a representative of compounds having a first order ferroelectric phase transition [1] and field reversible spontaneous polarization below the Curie point. BaTiO$_3$ and comparable materials) exhibit a sequence of ferroelectric phase transitions: At high temperature, BaTiO$_3$ is paraelectric having a cubic structure. On cooling, this material undergoes successive structural phase transitions [1] all of them being strictly of the first order showing a large thermal hysteresis [2, 3], a remarkable optical anisotropy [4], a large spontaneous polarization [1, 4], as well as electrooptic [5, 6] and photorefractive activity [7].

In recent years, a number of experimental investigations was reported focusing on characterizing the ferroelectric domains and domain walls in BaTiO$_3$ [8–16] as well as in other ferroelectric materials [17–20]. Transmission electron microscopy, X-ray spectroscopy, as well as scanning force microscopy have been applied with very limited success though: In fact, none of these inspections was able to deliver some experimental data on the physical properties within the $180^\circ$ domain wall of BaTiO$_3$. To our knowledge the few data available on the domain wall properties have been deduced from theoretical calculations mainly focussing on the domain wall thickness, the (elastic) domain wall energy [21], or the domain wall structure and character [22]. More recent theoretical work in this respect reports on first principle calculations in order to compute the energy and thickness of the ferroelectric domain wall [23]. The common con-
clusion from these theoretical investigations claims that the 180° domain wall in BaTiO₃ must have a width of less than 20 Å. Most probably it is this very small thickness which so far might be the main reason for the difficulties in obtaining reliable experimental data on the physical properties within the domain wall.

Here we present a somewhat different theoretical approach for computing the spontaneous polarization and refractive indices within the 180° domain wall of tetragonal BaTiO₃. The microscopic model takes into account the anisotropy in the electronic polarizability of all ions within the domain wall, their ionic shifts as well as the crystalline deformations. The model was previously tested for the calculation of bulk properties of ferroelectric crystals like ferroelectricity and optical anisotropy [24–26], as well as their linear electro-optical coefficients [27–29] in mono-domain BaTiO₃ and KNbO₃. Based on those experiences which agree excellently well with the corresponding experimental data, we initiate here the application of the orbital approximation in correlation with the dipole–dipole interaction for the ferroelectric domain wall in BaTiO₃. Further motivation for these calculations stems from today’s perspective in applying optical measurement techniques in the optical near-field [8] to directly investigate the local absorption properties [30] as well as the chemical nature of bonding within the domain wall via tip-enhanced Raman spectroscopy [31].

The paper is structured as follows: In Section 2 the dipole–dipole interaction due to the local field acting on the constituent ions taking into account the individual ionic shifts and crystalline deformations is discussed. Also a summary on the electronic polarizability of ions in the BaTiO₃ unit cell is given for completeness, as well as the basic approach to our quantum mechanical calculation. In Section 3 then the results of the spontaneous local electric field, the anisotropy of electronic polarizability, the spontaneous polarization, and local refractive index calculated over the 180° domain wall in BaTiO₃ are presented. We clearly differentiate these results for different widths of the domain wall. This section also contains the discussion of the above mentioned findings.

2. Description of the Model

As mentioned above the model is based on the dipole–dipole interaction in correlation with the quantum mechanical orbital approximation where every ion is modeled as consisting of a single electron and the effectively charged nucleus [26–28]. The model therefore accounts for the possible anisotropy in the electronic polarizability, the crystalline deformations, as well as the ionic shifts both in the bulk and over the domain wall.

The latter are of uttermost importance when modeling the 180° domain wall in a ferroelectric system. We therefore write the strains parallel to the pseudo-cubic [100], [010], and [001] directions as Δ₁, Δ₂, and Δ₃, respectively, while the shearing concerning the (100), (010), and (001) planes are denoted as δ₁, δ₂, and δ₃, respectively. The distance \( r(\vec{n}_{i}, \vec{m}_{j}) \) between the \( i \)-ion sitting in the \( \vec{n}(n_x, n_y, n_z) \) unit cell (the indices \( n_x, n_y, n_z \) represent the coordinates of a unit cell in the whole lattice) and the \( j \)-ion which is found in the \( \vec{m}(m_x, m_y, m_z) \) unit cell follows as

\[
\begin{pmatrix}
1 + \Delta_1 / \delta_1 & \delta_3 / \delta_2 \\
\delta_2 & 1 + \Delta_2 / \delta_1 \\
\delta_1 & 1 + \Delta_3 / \delta_1 
\end{pmatrix}
\begin{pmatrix}
\vec{n}_{i} \\
\vec{m}_{j}
\end{pmatrix}
+ \begin{pmatrix}
(\vec{s}_{i}) - (\vec{s}_{j})
\end{pmatrix},
\]

(1)
with \( \mathbf{r}^{(n, \hat{m})}_i \) representing the interionic distance in the cubic phase between \( i \)-ion in unit cell \( \hat{n} \) and \( j \)-ion in unit cell \( \hat{m} \), and \( \mathbf{s}^{(n)}_i \) and \( \mathbf{m}^{(\hat{m})}_j \) denoting the shifts of the \( i \)-ion of the \( \hat{n} \) unit cell and the \( j \)-ion of the \( \hat{m} \) unit cell, respectively.

The unit cell volume \( v \) then becomes
\[
v = a_0^3 \left[ (1 + A_1) (1 + A_2) (1 + A_3) - (1 + A_1) (\delta_1)^2 - (1 + A_2) (\delta_2)^2 - (1 + A_3) (\delta_3)^2 + 2\delta_1\delta_2\delta_3 \right],
\]
where \( a_0 \) is the lattice constant in the cubic phase.

The local field acting on \( i \)-ion of the \( \hat{n} \) unit cell in the \( k \)-direction is expressed as [32]
\[
E^{\text{loc}}_k (\hat{n}_i) = E^{\text{ext}}_k + \sum_{j=1}^{5} \left( \sum_{k'=1}^{3} \sum_{n=0}^{m} 3r_k (\hat{n}_i, \hat{m}_j) r_{k'} (\hat{n}_i, \hat{m}_j) - \delta_{kk'} r^2 (\hat{n}_i, \hat{m}_j) \right) / 4\pi\varepsilon_0 \left\| \mathbf{r} (\hat{n}_i, \hat{m}_j) \right\|^5 
\times p_k (\hat{n}_i, \hat{m}_j) + \frac{1}{3\varepsilon_0 v} \frac{r^2 (\hat{n}_i, \hat{m}_j)}{p_k (\hat{n}_i, \hat{m}_j)} \right).
\]

In the last equation, \( E^{\text{ext}} \) represents an external electric field which is in general the sum of the bias electric field \( E^{\text{bias}} \) and the optical electric field \( E^{\text{opt}} \), \( E^{\text{ext}} = E^{\text{bias}} + E^{\text{opt}} \). \( \delta_{kk'} \) denotes the Kronecker symbol, and \( p_k (\hat{n}_i, \hat{m}_j) \) the dipole moment along the \( k' \)-direction, which can be expressed as
\[
p_k (\hat{n}_i, \hat{m}_j) = p^c_k (\hat{m}_j) + p^l_k (\hat{n}_i, \hat{m}_j),
\]
with the two contributions \( p^c_k (\hat{m}_j) \) and \( p^l_k (\hat{n}_i, \hat{m}_j) \) specifying the electronic dipole moment and the relative ionic dipole moment in the \( k' \)-direction of the \( j \)-ion as seen by the \( i \)-ion, respectively. These dipole moments are calculated as
\[
p^c_k (\hat{m}_j) = \sum_{i=1}^{3} a_{k'l} (\hat{m}_j) E^{\text{loc}}_i (\hat{m}_j)
\]
and
\[
p^l_k (\hat{n}_i, \hat{m}_j) = Z^*_{k'l}(j) e \left( s_k (\hat{m}_j) - s_k (\hat{n}_i) \right) .
\]

In Eq. (5), \( a_{k'l} (\hat{m}_j) \) represents the \( (k'l) \) element of the electronic polarizability tensor of the \( j \)-ion of the \( \hat{m} \) unit cell given by [26–28]
\[
a_{k'l} (\hat{m}_j) = \alpha_{\text{exp}} (\hat{m}_j) \left[ \delta_{k'l} - \theta_{k'l}(j) \left( E^{\text{loc}}_i (\hat{m}_j) \right)^2 \delta_{k'l} + 2E^{\text{loc}}_i (\hat{m}_j) E^{\text{loc}}_j (\hat{m}_j) \right] .
\]

Here \( \alpha_{\text{exp}} (j) \) represents the measured free electronic polarizability of the \( j \)-ion. These values are reported in Table 1, for completeness, together with the coefficients \( \theta_{k'l}(j) \). Note that in order to obtain Eq. (7) which expresses the electronic polarizabilities of tetragonal BaTiO₃ as a function of electric field, we used the quantum mechanical orbi-
Approximation. This manifests in treating the electrostatic energy of the core-shell system, introduced by the presence of the electric field, as a small perturbation within the Schrödinger equation. The quantum mechanical problem then is solved by applying the variational method. As a result we obtain the wave functions of the core-shell system under the presence of the electric field, which then in turn are used to compute the components of the electronic polarizability tensor for all orbitals involved for one specific ion. Finally, the total electronic polarizability of an ion is obtained by summing over all orbitals.

In Eq. (6), \( Z_k^*(j) \) represents the effective ionic charge along the \( k' \) direction of the \( j \)-ion. With this, Eq. (3) may then be rewritten as

\[
E_{\text{loc}}^k(\mathbf{n}_i) = E_{k}^{\text{ext}} + \sum_{j=1}^{5} \sum_{k'=1}^{3} \left( \frac{3r_k(\mathbf{n}_i, \mathbf{m}) r_k(\mathbf{n}_i, \mathbf{m}) - \delta_{kk'}r^2(\mathbf{n}_i, \mathbf{m})}{4\pi\epsilon_0 \| \mathbf{r}(\mathbf{n}_i, \mathbf{m}) \|^5} + \frac{1}{3\epsilon_0 \epsilon V} \delta_{kk'} \right)
\times p_k^j(\mathbf{n}_i, \mathbf{n}_j) + \delta E_{\text{loc}}^k(\mathbf{n}_i),
\]

where

\[
\delta E_{\text{loc}}^k(\mathbf{n}_i) = \sum_{j=1}^{5} \sum_{k'=1}^{3} \sum_{m} \frac{3r_k(\mathbf{n}_i, \mathbf{m}) r_k(\mathbf{n}_i, \mathbf{m}) - \delta_{kk'}r^2(\mathbf{n}_i, \mathbf{m})}{4\pi\epsilon_0 \| \mathbf{r}(\mathbf{n}_i, \mathbf{m}) \|^5}
\times \left( p_k^j(\mathbf{n}_i, \mathbf{m}) - p_k^j(\mathbf{n}_i, \mathbf{m}) \right).
\]

Here \( \delta E_{\text{loc}}^k(\mathbf{n}_i) \) represents the contribution to the local field of the \( i \)-ion of the \( \mathbf{n} \) unit cell in \( k \)-direction due to the variation of the relative dipole moment between the unit cell \( \mathbf{n} \) and the unit cell \( \mathbf{m} \).

To evaluate the components of the local field of every ion in the \( \mathbf{n} \) unit cell we first consider the local field \( E_{\text{loc}}^k(\mathbf{n}_i) \), neglecting the contribution from \( \delta E_{\text{loc}}^k(\mathbf{n}_i) \) completely. \( \delta E_{\text{loc}}^k(\mathbf{n}_i) \) will be added later, because this last contribution depends on the dipole moments of all other unit cells within the crystal (i.e. their local fields). Once \( E_{\text{loc}}^k(\mathbf{n}_i) \) is evaluated for all unit cells in the crystal, we then superimpose \( \delta E_{\text{loc}}^k(\mathbf{n}_i) \) to all the corresponding local field contributions \( E_{\text{loc}}^k(\mathbf{n}_i) \) which makes a self-consistent calculation necessary.

<table>
<thead>
<tr>
<th>( j )-ion</th>
<th>( \alpha^{\text{exp}}(j) )</th>
<th>Ref.</th>
<th>( \theta_1(j) )</th>
<th>( \theta_2(j) )</th>
<th>( \theta_3(j) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba(^{2+})</td>
<td>1.9460</td>
<td>[33]</td>
<td>4.3662</td>
<td>4.3662</td>
<td>6.9311</td>
</tr>
<tr>
<td>Ti(^{4+})</td>
<td>0.1859</td>
<td>[33]</td>
<td>0.3429</td>
<td>0.3429</td>
<td>0.6353</td>
</tr>
<tr>
<td>O(^{2-})</td>
<td>2.3940</td>
<td>[33]</td>
<td>16.9844</td>
<td>16.9844</td>
<td>31.7611</td>
</tr>
</tbody>
</table>
Thus the local field present along the $k$-direction acting on $i$-ion of the $\hat{n}$ unit cell can be written as
\[
\sum_{j=1}^{5} \sum_{l=1}^{3} S_{kl}(\hat{n}_{i,j}) E_{i}^{loc}(\hat{n}) = \mathit{Q}_{k}(\hat{n}_{i}) ,
\] (10)
with
\[
S_{kl}(\hat{n}_{i,j}) = \delta_{kl} \delta_{ij} - \sum_{k'=1}^{3} T_{kk'}(\hat{n}_{i,j}) \alpha_{k'l}(\hat{n})
\] (11)
and
\[
\mathit{Q}_{k}(\hat{n}_{i}) = E_{k}^{ext} + \sum_{j=1}^{5} \sum_{k'=1}^{3} T_{kk'}(\hat{n}_{i,j}) p_{k}^{i}(\hat{n}_{i,j}) ,
\] (12)
where
\[
T_{kk'}(\hat{n}_{i,j}) = \sum_{m} \frac{3r_{k'}(\hat{n}_{i,m}) r_{k}(\hat{n}_{i,j})}{4\pi e_{0} \rho(\hat{n}_{i,j})} - \delta_{kk'} \frac{r_{k}(\hat{n}_{i,j})^{2}}{4\pi e_{0} \rho(\hat{n}_{i,j})^{3}} + \frac{1}{3 e_{0} \rho(\hat{n}_{i,j})} \delta_{kk'} .
\] (13)

By solving Eq. (10) for each unit cell $\hat{n}$, we obtain the $(l,j)$ component, $E_{i}^{loc}(\hat{n})$, for the local field after adding the contribution $\delta E_{i}^{loc}(\hat{n})$. The total polarization $P_{k}(\hat{n})$ of the $\hat{n}$ unit cell is expressed as
\[
P_{k}(\hat{n}) = \frac{1}{v} \sum_{j=1}^{5} \left( p_{k}^{e}(\hat{n}_{j}) + p_{k}^{ion}(\hat{n}_{j}) \right) ,
\] (14)
with
\[
p_{k}^{ion}(\hat{n}_{j}) = Z_{k}(j) e_{sk}(\hat{n}_{j}) .
\] (15)
representing the absolute ionic dipole moment in the $k$-direction of the $j$-ion in the $\hat{n}$ unit cell.

The connection between the optical dielectric constant $\varepsilon_{opt}^{kl}(\hat{n}_{j})$ in the $\hat{n}$ unit cell, polarization $P_{k}(\hat{n})$ and the optical electric field $E_{p}^{opt}$ is expressed in the following way:
\[
\varepsilon_{opt}^{kl}(\hat{n}_{j}) = \delta_{kl} + \frac{1}{\varepsilon_{0}} \frac{\partial P_{k}(\hat{n}_{j})}{\partial E_{p}^{opt}} .
\] (16)
Here we have
\[
\frac{\partial P_{k}(\hat{n}_{j})}{\partial E_{p}^{opt}} = \frac{1}{v} \sum_{j=1}^{5} \frac{\partial p_{k}(\hat{n}_{j})}{\partial E_{p}^{opt}} .
\] (17)

By using Eq. (5), the term $-\frac{\partial p_{k}(\hat{n}_{j})}{\partial E_{p}^{opt}}$ can be written as
\[
\frac{\partial p_{k}(\hat{n}_{j})}{\partial E_{p}^{opt}} = \sum_{l=1}^{3} \alpha_{kl}(\hat{n}) \frac{\partial E_{i}^{loc}(\hat{n}_{j})}{\partial E_{p}^{opt}} .
\] (18)
Note that \( \frac{\partial E_{loc}^j}{\partial E_{opt}^l} \), representing the local electric field induced along the \( l \)-direction of the \( j \)-ion in the \( \mathbf{n} \) unit cell, in units of the \( l' \)-component of the optical electric field, also consists of two contributions. The first one is obtained by solving the following equation:

\[
\sum_{j=1}^{5} \sum_{l=1}^{3} S_{kl}(\mathbf{n}_{i,j}) \frac{\partial E_{loc}^j(\mathbf{n}_{i,j})}{\partial E_{opt}^l} = \delta_{kl},
\]

which is deduced from Eq. (10). The second contribution is given as follows:

\[
\frac{\partial \delta_{loc}^j(\mathbf{n}_{i,j})}{\partial E_{opt}^l} = \sum_{j=1}^{5} \sum_{l'=1}^{3} \sum_{m} \frac{3r_{kl'}(\mathbf{n}_{i,j}, \mathbf{m}_{i,j}) r_k(\mathbf{n}_{i,j}) - \delta_{kk'}r^2(\mathbf{n}_{i,j})}{4\pi \varepsilon_0 \| \mathbf{r}(\mathbf{n}_{i,j}) \| ^3}
\times \sum_{l=1}^{3} \left( \alpha_{kl}(\mathbf{m}_{i,j}) \frac{\partial E_{loc}^j(\mathbf{m}_{i,j})}{\partial E_{opt}^l} - \alpha_{kl}(\mathbf{n}_{i,j}) \frac{\partial E_{loc}^j(\mathbf{n}_{i,j})}{\partial E_{opt}^l} \right).
\]

In the electromagnetic theory [34], one proves that for light being polarized along the direction of the unit vector \( \mathbf{u}(u_1, u_2, u_3) \) and impinging on a dielectric medium characterized by the optical dielectric impermeability tensor \( \tilde{\eta}_{opt} = \tilde{\varepsilon}_{opt}^{-1} \), the refractive index \( n \) may be expressed as

\[
n = \left( \sum_{k=1}^{3} \sum_{l=1}^{3} \eta_{kl}^opt u_k u_l \right)^{-1/2}.
\]

In the special case of light being polarized along the \( k \)-direction, the refractive index thus becomes

\[
n_k = (\eta_{kk}^opt)^{-1/2}.
\]

### 3. Results and Discussion

The calculation of the spontaneous polarization and the refractive indices over the 180° domain wall in BaTiO\(_3\) are carried out using available experimental data at room temperature reported in Table 2. In this study we consider the 180° domain wall to coincide with the \( yz \) plane in the bulk. The change of the spontaneous ionic shifts near the domain wall is given by Ref. [35]

\[
s_k(\mathbf{m}_{i,j}) = (s_k(j))^0 \tanh \left( \frac{x(\mathbf{m}_{i,j})}{2r_c} \right),
\]

where \( x(\mathbf{m}_{i,j}) \) is the \( x \)-position of the \( j \)-ion within the \( \mathbf{m} \) unit cell; \( (s_k(j))^0 \) are the spontaneous ionic shifts in a homogeneous ideal crystal, and \( r_c \) represents the effective thickness of the domain wall (also called the correlation radius of the order parameter). These calculations are performed for a variety of effective thicknesses of the domain wall ranging between 5 and 20 Å [4] as stated in an earlier work by Zhirnov [21].
The spontaneous local field $E_{\text{sp}}$ corresponds to the value of the local electric field $E_{\text{loc}}$ of the $j$-ion in the $\tilde{n}$ unit cell in absence of any external electric field ($E_{\text{ext}} = 0$). The calculation shows that the values of the spontaneous local electric field acting on the constituent ions of BaTiO$_3$ along the 1 and 2-direction are exactly zero. On the other hand, values of the local electric field along the 3-direction are non-zero and are reported in Fig. 1 for four different values of the effective thickness $r_c$ of the domain wall ($r_c = 5, 10, 15, 20$ Å).

**Fig. 1.** Variation of the 3-direction component of the spontaneous local field $E_{\text{loc}}$ passing through the $180^\circ$ domain wall of BaTiO$_3$ at room temperature for a) $r_c = 5$, b) 10, c) 15, and d) 20 Å. Different symbols correspond to Ba$^{2+}$ ions (open circles), Ti$^{4+}$ (full circles), O$_{2\times}$ (cross +), O$_{2\times}$ (cross ×) and O$_z^-$ ions (full diamonds). The domain wall (at $x = 0$) coincides with the Ti–O$_2$(100) plane.

### Table 2
Numerical data of BaTiO$_3$ at room temperature: lattice parameters ($a = a_0(1 + (\Delta_1)^0)$ and $c = a_0(1 + (\Delta_2)^0)$), effective ionic charges $Z^*_k(j)$, spontaneous ionic shifts $(s_k(j))^0$. $a_0$ represents the lattice constant in the cubic phase.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$ (Å)</td>
<td>3.992</td>
<td>[36]</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>4.035</td>
<td>[36]</td>
</tr>
<tr>
<td>$(s_3(Ba))^0$ (Å)</td>
<td>0.00</td>
<td>[1]</td>
</tr>
<tr>
<td>$(s_3(Ti))^0$ (Å)</td>
<td>0.05</td>
<td>[1]</td>
</tr>
<tr>
<td>$(s_3(Ox))^0$ (Å)</td>
<td>-0.05</td>
<td>[1]</td>
</tr>
<tr>
<td>$(s_3(Oy))^0$ (Å)</td>
<td>-0.05</td>
<td>[1]</td>
</tr>
<tr>
<td>$(s_3(Oz))^0$ (Å)</td>
<td>-0.09</td>
<td>[1]</td>
</tr>
</tbody>
</table>

$E_{\text{loc}}$ is expressed as $E_{\text{loc}} = Z^*_j(j)(\tilde{n})$ in the $\tilde{n}$ unit cell. $Z^*_j(j)$ is the effective ionic charge of the $j$-ion and $(s_k(j))^0$ is the spontaneous ionic shift of the $j$-ion along the $k$-direction.
As seen in Fig. 1 for small values of $r_c$, the 3-direction component of the spontaneous local field undergoes a small increase (in absolute value) before then decreasing towards the center of the domain wall (at $x = 0$). This holds for all ions in BaTiO$_3$, also approaching the domain wall from both sides. In fact the 3-component of the local electric field $E_{\text{loc}}(\vec{n})$ measures exactly zero at the center of the domain wall with the absolute values left and right having opposite sign (see Fig. 1). For large values of $r_c$, the behavior of the spontaneous local field becomes like that of the hyperbolic tangent function while for smaller $r_c$, the increase in $E_{\text{loc}}(\vec{n})$ is very pronounced, as reported above. Please note that $x = 0$ was set to coincide with the Ti–O$_2$ (100) plane (see later).

In the tetragonal phase, the amplitude of the anisotropy of the electronic polarizability $\delta\alpha(\vec{n})$ of the $j$-ion in the $\vec{n}$ unit cell may be defined as follows:

$$\delta\alpha(\vec{n}) = \alpha_{33}(\vec{n}) - \alpha_{11}(\vec{n}).$$

(24)

All the elements of the electronic polarizability tensor in the spontaneous state ($E_{\text{ext}} = 0$) are evaluated by considering Eq. (7), Table 1, and Fig. 1. The calculation shows that only diagonal elements $\alpha_{kk}(\vec{n})$ are non-zero. The calculated values of the amplitude of the anisotropy of the electronic polarizability $\delta\alpha(\vec{n})$ are reported in Fig. 2.

The analysis of these results shows that far away from the domain wall center in tetragonal BaTiO$_3$, only the oxygen O$_2^-$ presents a remarkable anisotropy of the elec-

![Fig. 2. Variation of the anisotropy amplitude $\delta\alpha$ of electronic polarizability (given in absolute values) passing through the 180° domain wall of BaTiO$_3$ at room temperature for a) $r_c = 5$, b) 10, c) 15, and d) 20 Å. Symbols indicate Ba$^{2+}$ ions (open circles), Ti$^{4+}$ (full circles), O$_2^-$ (cross +), O$_{xy}^-$ (cross ×) and O$_z^-$ ions (full diamonds). The domain wall (at $x = 0$) coincides with the Ti–O$_2$ (100) plane](image-url)
tronic polarizability. Our findings are in good agreement with results from Lawless [38] reporting the amplitude of the electronic polarizability $\delta \alpha$ of the oxygen $O_2^-$ in monodomain BaTiO$_3$ to be approximately $-0.225 \, \text{Å}^3$. Approaching the domain wall (see Fig. 2), the anisotropy increases in absolute numbers and then decreases to zero in the middle of the domain wall for small values of $r_c$. This behavior is different for big values of $r_c$ for which the amplitude of anisotropy decreases directly without showing any increase (see Fig. 2d). The same behavior is found for the other oxygen-ions (i.e. $O_2^-$ and $O_2^{2-}$) for which an anisotropy of electronic polarizability appears when approaching the domain wall, which then vanishes again at $x = 0$.

Next we present and discuss the results obtained for the spontaneous polarization $P_{sp} (\mathbf{n})$ in the $\mathbf{n}$ unit cell. $P_{sp} (\mathbf{n})$ is defined as the total polarization, with the components $P_k (\mathbf{n})$ being deduced from Eq. (14), in absence of any external field. The calculation shows that only the 3-component of the spontaneous polarization $P_{sp}^3 (\mathbf{n})$ is non-zero. The calculated values are reported in Fig. 3 and show that for $|x| \gg 0$, the spontaneous polarization measures $-0.30$ and $+0.30 \, \text{C/m}^2$ for the ($-$) region and the ($+$) region, respectively, in excellent agreement with the experimental data [39] of $\pm 0.28 \, \text{C/m}^2$. Close to the domain wall $P_{sp}^3 (\mathbf{n})$ behaves quite similar to the spontaneous local field, namely, increases with a small amount (in absolute numbers) for small $r_c$ values, and then decreases towards $x = 0$. For larger $r_c$ values $P_{sp}^3 (\mathbf{n})$ simply decays to approach zero at the center of the domain wall (at $x = 0$) in all cases. Again we

![Fig. 3. Variation of the 3-component of spontaneous polarization $P_{sp}^3 (\mathbf{n})$ passing through the 180° domain wall of BaTiO$_3$ at room temperature for a) $r_c = 5$, b) 10, c) 15, and d) 20 Å. The domain wall (at $x = 0$) coincides with the Ti-O$_2$ (100) plane](image-url)
deduce the point symmetrical behavior of \( P_3^{\text{spont}}(\hat{n}) \) similar to \( \mathbf{E}_{\text{loc}}(\hat{n}) \) with contributions left and right of the domain wall center having opposite signs.

Figure 4 finally reports the calculated values for the refractive indices \( n_1, n_2, \) and \( n_3 \) for the same domain wall thicknesses as considered above. Far away from the domain wall and whatever its thickness, the crystal possesses only two refractive indices, one called the ordinary refractive index \( n_o \) \((n_1 = n_2)\), and the second called extraordinary refractive index \( n_e \) \((n_3)\). The calculated values of these refractive indices are \( n_o = 2.3704 \) and \( n_e = 2.2839 \), respectively, which are in good agreement with experimental data \((n_o = 2.398 \) and \( n_e = 2.312\) given by Johnston and Weingart [5] for mono-domain BaTiO\(_3\) at room temperature.

Approaching the domain wall, however, the refractive indices \( n_1 \) and \( n_2 \) become different from each other, and hence the crystal in this region can be characterized as a biaxial crystal having three different refractive indices. The refractive index \( n_1 \) remains almost constant when passing through the domain wall for all values of \( r_c \), while the other two indices show a dramatic thickness dependence. For a small thickness \( r_c \) they decrease before rising again, hence forming peaks centered in the domain wall at \( x = 0 \). For large \( r_c \) the refractive indices centered at \( x = 0 \) show a broadened Gaussian-like behavior.

These theoretical calculations show that the behavior of all magnitudes studied here, like spontaneous local electric field, anisotropy of electronic polarizability, spontaneous polarization, or local refractive index, drastically depend on the thickness of the domain wall. Whatever this thickness is, the spontaneous polarization changes its sign passing from the (\(-\)) domain to the (\(+)\) domain having a value of exactly zero at the center of

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**Fig. 4. Variation of the refractive indices** \( n_1 \) (full triangles), \( n_2 \) (full diamonds), and \( n_3 \) (full circles) passing through the 180° domain wall of BaTiO\(_3\) at room temperature. The domain wall \((at x = 0)\) is pinned at the Ti–O\(_2\) (100) plane.
the domain wall. On the other hand, the refractive indices are symmetrical with respect to the domain wall center showing important peaks in the middle of the domain wall. This might be the reason for observing an optical contrast at 180° domain walls, as recently reported from near-field optical investigations [40].

Furthermore, the above reported calculations have been repeated, considering this time a domain wall being centered at the Ba–O (100) plane, instead of the Ti–O2 plane considered above. This effectively results in shifting the domain wall at $x = 0$ by half the unit cell. It is found that the behavior of all quantities studied here remains the same, except that in the case of a domain wall centered at the Ba–O (100) plane (Fig. 5), the peaks of the refractive indices are slightly lowered compared to the values reported in Fig. 4 (domain wall centered at the Ti–O2 (100) plane), particularly for small values of the domain wall thickness.

### 4. Conclusions

By using a microscopic model taking into account a quantum method based on the orbital approximation and the dipole–dipole interaction due to the local field acting on the constituent ions, we have studied the ferroelectric and optical properties within 180° ferroelectric domain walls of tetragonal BaTiO3. The calculations show a dramatic dependence of spontaneous polarization, local spontaneous electric field, anisotropy of electronic polarizability, and refractive indices on the effective domain wall thickness. For a large domain wall width, the behavior of the spontaneous polarization within the domain wall is quite similar to the former theoretical work based on a three dimensional Landau–Ginzburg model [41]. However, the model presented here allows to
evaluate the microscopic properties even for a very small width of the domain wall. Moreover, we find the anisotropy of electronic polarizability of the $O^{2-}$ ions as well as the spontaneous polarization to vanish in the middle of the domain wall. On the other hand, the BaTiO$_3$ 180° domain wall behaves like a biaxial crystal resulting in dramatic changes of the refractive indices $n_2$ and $n_3$. Therefore, the optical propagation properties over the domain wall should be changed dramatically using light with polarization parallel to the domain wall.

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**References**