

## Theoretical study of the optical dispersion and anisotropy of the oxygen polarisability of PbTiO<sub>3</sub> in the tetragonal phase

K. Bammou, D. Khatib

*Laboratoire de Physique du Solide Théorique, Faculté des Sciences, BP : 28/S, Université Ibn Zohr, 80000, Agadir, Maroc*

F. Bensamka

*Laboratoire des Sciences des Matériaux, Faculté des Sciences Semlalia Université Cadi Ayyad, Marrakech, Maroc*

The optical anisotropy of the tetragonal phase of PbTiO<sub>3</sub> is discussed according to the point-dipole approach. In this microscopic model, we have taking into account of the electronic polarization and the lattice deformation, and it is shown that anisotropic electronic polarizabilities are the dominant source of the optical properties of PbTiO<sub>3</sub>. This anisotropy is attributed to the O<sub>2</sub> oxygen ion and it is due to the Ti-O<sub>z</sub> and Pb-O<sub>z</sub> overlap in the tetragonal phase. By analyzing the optical refractive index data of PbTiO<sub>3</sub> at 0.589 μm, we have determined the temperature dependence of the oxygen polarizabilities. Based on the dispersion data of the refractive index of PbTiO<sub>3</sub>, the dispersion of the oxygen polarizabilities is similarly calculated at room temperature.

### I. INTRODUCTION

Lead titanate, PbTiO<sub>3</sub>, is a crystal of the perovskite family and has been the object of many theoretical and practical investigations. This material shows a ferroelectric behavior and undergoes a cubic-tetragonal phase transition at 493 °C.<sup>1</sup>

At room temperature, PbTiO<sub>3</sub> has a much larger tetragonality<sup>2,3</sup> and a smaller birefringence<sup>4,5</sup> and shows a remarkable spontaneous polarization<sup>6,7</sup>. As for the optical anisotropy in BaTiO<sub>3</sub><sup>8</sup> and KNbO<sub>3</sub><sup>9</sup>, the origin of the optical anisotropy in PbTiO<sub>3</sub> is assumed to be the change of the dipole - dipole interaction due to the lattice deformation.

The aim of this work is to discuss about the anisotropic oxygen polarizabilities at 0.589 μm and

the dispersion of these oxygen polarizabilities at room temperature from a microscopic viewpoint.

In this article, we present in section 2 the model description, in section 3 the results of the calculation of anisotropic oxygen polarizability. Finally, in section 4 we make a summary and some discussions about the global results.

### II. MODEL DESCRIPTION

In the similar manner to the previous work on BaTiO<sub>3</sub><sup>8</sup> and KNbO<sub>3</sub><sup>9</sup> the dipole-dipole interaction acting on the constituent ions of PbTiO<sub>3</sub> is expressed as:

$$\left(\Gamma_{ij}\right)_{\beta} = \frac{3 \left[ p_j^{\beta} \cdot r_{ij}(l, m, n) \right]^2}{l, m, n \left( p_j^{\beta} \right)^2 \left[ r_{ij}(l, m, n) \right]^5} - \frac{1}{l, m, n \left[ r_{ij}(l, m, n) \right]^3} \quad (1)$$

where  $\beta$  represents a Cartesian coordinate ( $\beta = 1, 2, 3$ ),  $p_j^{\beta}$  is the dipole moment of the j-ion.

In the equation (1),  $r_{ij}$  is the distance between i and j-ions and the indices (l, m, n) represent the coordinates of a unit cell in the whole lattice.

At wavelength  $\lambda$ , the electronic polarization  $P_i^{\beta}(\lambda)$  of the i-ion in the direction  $\beta$  can be written :<sup>9</sup>

$$P_i^{\beta}(\lambda) = N_i \alpha_i^{\beta}(\lambda) \left[ 1 + \sum_{j=1}^N \left( \frac{4\pi}{3} + \frac{\Gamma_{ij, \beta}}{N_j} \right) P_j^{\beta}(\lambda) \right] \quad (2)$$

where  $\alpha_i^{\beta}(\lambda)$  represents the electronic polarizability of the i-ion, the  $N_i$  is the number of the

i-ions per unit volume and N is the number of the unit cells in the lattice.

The relation between dielectric constant  $\epsilon_r^\beta(\lambda)$ , polarization  $P^\beta(\lambda)$  and electric field  $E^\beta(\lambda)$  is:

$$\epsilon_r^\beta(\lambda) = 1 + 4\pi \frac{P^\beta(\lambda)}{E^\beta(\lambda)} \quad (3)$$

where  $P^\beta(\lambda)$  is calculated by summation of the electronic polarization  $P_j^\beta(\lambda)$  of j-ions.

$$P^\beta(\lambda) = \sum_{j=1}^N P_j^\beta(\lambda) \quad (4)$$

Considering the relation  $\epsilon_r^\beta(\lambda) = n_\beta^2(\lambda)$ , we obtain the following expression of the refractive index  $n_\beta$ :

$$n_\beta^2(\lambda) = 1 + 4\pi \sum_{j=1}^N P_j^\beta(\lambda) \quad (5)$$

By using the equation (2), the equation (5) can be written as:

$$n_\beta^2(\lambda) = 1 + 4\pi \sum_i^N \left\{ N_i \alpha_i^\beta(\lambda) \left[ 1 + \sum_{j \neq i}^N \left( \frac{4\pi}{3} + \frac{\Gamma_{ij,\beta}}{N_j} \right) P_j^\beta(\lambda) \right] \right\} \quad (6)$$

In the tetragonal phase, the term  $\mathbf{r}_{ij}$  in the equation (1) becomes:

$$\mathbf{r}_{ij} = l \cdot a \cdot \mathbf{e}_x + m \cdot a \cdot \mathbf{e}_y + \left( n + \delta_{ij} \right) \cdot c \cdot \mathbf{e}_z \quad (7)$$

where a and c are the tetragonal lattice parameters and  $\mathbf{e}_x, \mathbf{e}_y$  and  $\mathbf{e}_z$  are unit vectors. Substituting in equation (1) and taking  $P_j^\beta(\lambda)$  parallel to c-axis, the dipole-dipole coefficients in the direction of c-axis, namely  $\Gamma_{ij,c}$ , can be written as:

$$\Gamma_{ij,c} = \frac{1}{V} \left[ G_{ij}^{(o)} + \tau_c G_{ij}^{(1)} + \delta_{ij} G_{ij}^{(2)} \right] \quad (8)$$

where V is the volume of the distorted unit cell. The lattice deformation  $\tau_c$  is expressed as:<sup>10</sup>

$$G_{ij}^{(1)} = G_{ij}^{(o)} + 3 \sum_{(l,m,n)ij} \frac{n^2(3l^2 + 3m^2) - 2n^4}{(l^2 + m^2 + n^2)^{7/2}} \quad (11)$$

$$G_{ij}^{(2)} = 12 \sum_{(l,m,n)ij} \frac{3/8(l^2 + m^2)^2}{(l^2 + m^2 + n^2)^{9/2}} + \frac{n^4 - 3n^2(l^2 + m^2)}{(l^2 + m^2 + n^2)^{9/2}} \quad (12)$$

$$\tau_c = \frac{c}{a_0} - 1 \quad (9)$$

where  $a_0$  is the lattice parameter of the cubic phase.

It is found that, terms higher than  $\delta_{ij}^2$  are negligible.

In the equation (8), the terms  $G_{ij}^{(o)}, G_{ij}^{(1)}$  and  $G_{ij}^{(2)}$  represent the dipole-dipole coefficients and their explicit forms are given by the following expressions:

$$G_{ij}^{(o)} = \sum_{(l,m,n)ij} \frac{2n^2 - (l^2 + m^2)}{(l^2 + m^2 + n^2)^{5/2}} \quad (10)$$

In the table (I) are listed the calculated values of the coefficients  $G_{ij}^{(o)}$ ,  $G_{ij}^{(1)}$  and  $G_{ij}^{(2)}$ :

Table I. Calculated values of the coefficients  $G_{ij}^{(o)}$ ,  $G_{ij}^{(1)}$  and  $G_{ij}^{(2)}$ .

Position	$G_{ij}^{(o)}$	$G_{ij}^{(1)}$	$G_{ij}^{(2)}$
(0,0,0)	0	-8.071	37.297
(0.5,0.5,0.5)	0	16.325	-74.577
(0,0.5,0.5)	4.334	16.325	-112.561
(0.5,0,0.5)	4.334	16.325	-112.561
(0.5,0.5,0)	-8.667	-9.268	97.512
(0,0,0.5)	30.082	-59.691	759.550
(0,0.5,0)	-15.041	-18.278	299.445
(0.5,0,0)	-15.041	-18.278	299.445

The dipole interaction coefficients in the  $\mathbf{e}_x$  or  $\mathbf{e}_y$  direction, namely  $\Gamma_{ij,a}$ , are:

$$\Gamma_{ij,a} = \frac{1}{V} \left[ G_{ij}^{(o)} + \tau_a G_{ij}^{(1)} + \delta_{ij} G_{ij}^{(2)} \right] \quad (13)$$

where  $\tau_a$  is the lattice deformation along the a-axis, it is expressed as :<sup>10</sup>

$$\tau_a = \frac{a}{a_0} - 1 \quad (14)$$

In the cubic phase, the lattice deformation and the ionic shift are zero, then the dipole interaction coefficients  $\Gamma_{ij,0}$  can be expressed as:

$$\Gamma_{ij,0} = \frac{1}{V_0} G_{ij}^{(0)} \quad (15)$$

where  $V_0$  is the volume in the cubic phase.

### III. RESULTS OF CALCULATIONS

Considering a dipole-dipole approach carries out the calculation of the oxygen electronic polarizabilities of  $\text{PbTiO}_3$ . For our calculation, we have used the numerical data of the lattice parameters  $a_0$ ,  $a$  and  $c$  of the reference (11).

In the tetragonal phase of  $\text{PbTiO}_3$ , we can define isotropic oxygen polarizability  $\alpha_{O_z}^m$  by the following expression:

$$\alpha_{O_z}^m = \frac{1}{3} (\alpha_{O_z}^c + 2\alpha_{O_z}^a) \quad (16)$$

In the same manner, we can define an isotropic optical refractive index as:

$$n^m = \frac{1}{3} (n^c + 2n^a) \quad (17)$$

The calculated refractive index at various temperatures and  $\lambda = 0.589 \mu\text{m}$ , and that at various wavelengths and  $T = 25^\circ\text{C}$  are reported in figure 1 and figure 2 respectively.

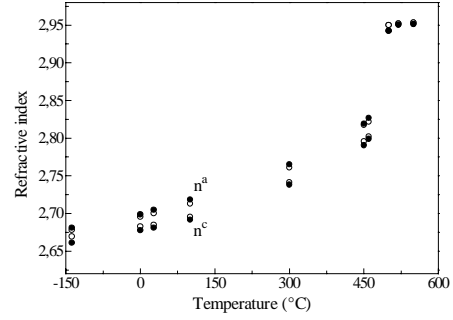


FIGURE 1: Variation of the refractive index of  $\text{PbTiO}_3$  versus temperature at  $0.589 \mu\text{m}$ . The calculated values (o) are compared to the experimental data (•) from the reference (5).

By using the theoretical results of the figure 1, we can calculate the oxygen polarizabilities of  $\text{PbTiO}_3$  at various temperatures. The results of anisotropic oxygen polarizabilities  $\alpha_{O_z}^a$ ,  $\alpha_{O_z}^c$  and those of isotropic oxygen polarizability  $\alpha_{O_z}^m$  are reported in figure 3.

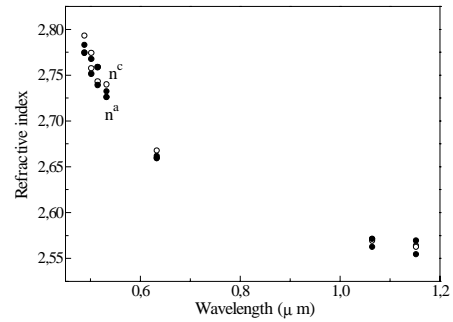


FIGURE 2: Variation of the refractive index of  $\text{PbTiO}_3$  versus wavelength at room temperature. The calculated values (o) are compared to the experimental data (•) from the reference (12).

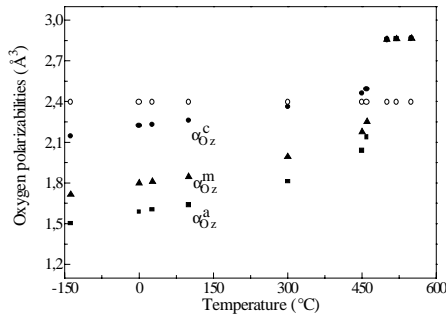


FIGURE 3 Variation of the oxygen polarizabilities  $\alpha_{O_z}^a$ ,  $\alpha_{O_z}^c$  and  $\alpha_{O_z}^m$  of PbTiO<sub>3</sub> versus temperature at 0.589  $\mu\text{m}$ . The calculated values ( $\bullet$  :  $\alpha_{O_z}^c$ ,  $\blacksquare$  :  $\alpha_{O_z}^a$ ,  $\blacktriangle$  :  $\alpha_{O_z}^m$ ) are compared to the experimental data (o) from the reference (13).

By using the theoretical results of the figure 2, we can determine the dispersion of the oxygen polarizabilities  $\alpha_{O_z}^a$ ,  $\alpha_{O_z}^c$  and  $\alpha_{O_z}^m$  at various wavelengths. The results of this calculation are reported in figure 4.

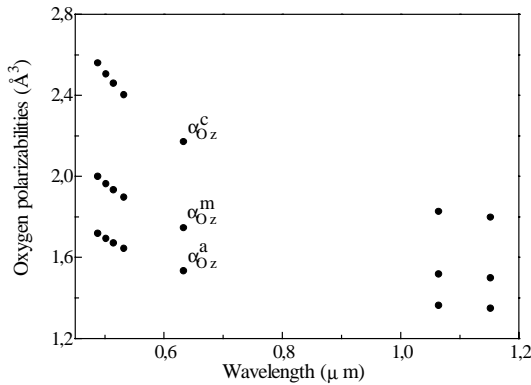


FIGURE 4: Dispersion of the oxygen polarizabilities  $\alpha_{O_z}^a$ ,  $\alpha_{O_z}^c$  and  $\alpha_{O_z}^m$  of PbTiO<sub>3</sub> at room temperature.

#### IV. SUMMARY AND DISCUSSIONS

The anisotropy of the oxygen electronic polarizabilities in the tetragonal phase of PbTiO<sub>3</sub> is discussed from a microscopic viewpoint.

At 0.589  $\mu\text{m}$ , the figure 1 and the equation (17) show that  $n^m$  increases from 2.6745 at -138 °C to 2.9503 at 493 °C.

Looking at figure 3, it is found that the oxygen polarizabilities increase with increasing temperature. In the range [ -150 °C, 460 °C ],  $\alpha_{O_z}^m$  increases from 1.7156 Å<sup>3</sup> to 2.2527 Å<sup>3</sup>. This behavior is due to the Ti - O<sub>z</sub> overlap in the tetragonal phase of

PbTiO<sub>3</sub>, which increases with decreasing temperature.<sup>14</sup>

At room temperature, the figure 2 and the equation (17) show that,  $n^m$  decreases from 2.7772 at 0.488  $\mu\text{m}$  to 2.5592 at 1.152  $\mu\text{m}$ .

Looking at figure 4, it is found that the anisotropic oxygen polarizabilities  $\alpha_{O_z}^a$  and  $\alpha_{O_z}^c$  decrease with increasing wavelength. In the range [0.488  $\mu\text{m}$ , 1.1520  $\mu\text{m}$ ],  $\alpha_{O_z}^a$  decreases from 1.7185 Å<sup>3</sup> to 1.3492 Å<sup>3</sup> and  $\alpha_{O_z}^c$  decreases from 2.5595 Å<sup>3</sup> to 1.7983 Å<sup>3</sup>.

Our theoretical results show that the oxygen polarizability and the refractive index have nearly the same behavior and show that the optical anisotropy in tetragonal phase of PbTiO<sub>3</sub> can be explained by considering an anisotropic oxygen polarizability, particularly the contribution of the oxygen O<sub>z</sub>. The comparison between these theoretical results and the measured values are generally in fairly good agreement.

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#### REFERENCES

1. J. Harada, T. Pedersen and Z. Barnea, Acta. Crystal., **A26**, 608 (1970).
2. J. Kobayashi and R. Ueda, Phys. Rev., **99**, 1900 (1955).
3. A. M. Glazer and S. A. Mabud, Acta. Cryst., **B34**, 10 (1978).
4. S. Singh, J. P. Remeika and J. R. Potopowicz, Appl. Phys. Lett., **20**, 135 (1972).
5. W. Kleeman and F. J. Schafer, Phys. Rev., **B34**, 7873 (1986).
6. V. G. Gavrilanchenko, R. I. Spinko, M. A. Martynenko and E. F. Fesenko, Sov. Phys. Sol. Stat., **12**, 1203 (1970).
7. J. G. Bergman, G. R. Crame and E. H. Turner, J. Solid State Chem., **21**, 127 (1977).
8. D. Khatib, K. Bammou, L. Hafid and F. Bensamka. Ferroelectrics Letters., **24**, 49 (1998).
9. D. Khatib, K. Bammou, F. Bensamka and L. Hafid, An. Chim. Fr., **21**, 283 (1996).
10. D. Khatib, Ferroelectrics Letters., **18**, 173 (1994).
11. S. A. Mabud and A. M. Glazer, J. Appl. Cryst., **12**, 49 (1979).
12. S. Singh, «Electro - optic materials» in handbook of lasers, Dubots ed., North Holland Pub. Co., Amsterdam (1972).
13. J. C. Slater, Phys. Rev., **78**, 748 (1950).
14. R. E. Cohen, Nature., **358**, N° 6382, 136 (1992).

