

Theory of optical anisotropy and spontaneous polarization in the tetragonal phase of ABO_3 perovskite type structure

H. Chaib and D. Khatib

Laboratoire de Physique du Solide Théorique, Faculté des Sciences, B.P. 28/S, Université Ibn Zohr, 80000 Agadir, Maroc

W. Kinase

Department of Physics, School of Science and Engineering, Waseda University, 3, Okubo, Shinjuku-ku, Tokyo 169, Japan

The microscopic mechanism of optical anisotropy and spontaneous polarization in the tetragonal phase of ABO_3 perovskite type structure, in particular BaTiO_3 , KNbO_3 and PbTiO_3 , are discussed by using a microscopic model. For the optical anisotropy, we have taking into account of the dipole-dipole effect due to the ionic and electronic polarizations of the crystal and the spontaneous Kerr effect. The last effect is a cause of the strong local field acting on the constituent ions. For the spontaneous polarization we use only the dipole-dipole effect. In this microscopic model, only the Ti ions for BaTiO_3 and PbTiO_3 and Nb ions for KNbO_3 localized at the center of the unit cells of the lattice are assumed to have the spontaneous shift. The cubic-tetragonal phase transition in the three compounds above mentioned is also analyzed. It is found that the optical anisotropy, the spontaneous polarization and the nature of the phase transition are in good agreement with the experimental data.

I. INTRODUCTION

The oxygen-octaedra ferroelectrics ABO_3 perovskite structure constitute a very attractive class of compounds for various properties. The cases of barium titanate BaTiO_3 , potassium niobate KNbO_3 and lead titanate PbTiO_3 are given as illustrative examples. These three materials have similar structure and exhibit a sequence of ferroelectric phase transitions. At high temperature all materials above mentioned are paraelectric with the cubic structure. Their unit cell is reported in the Fig. 1.

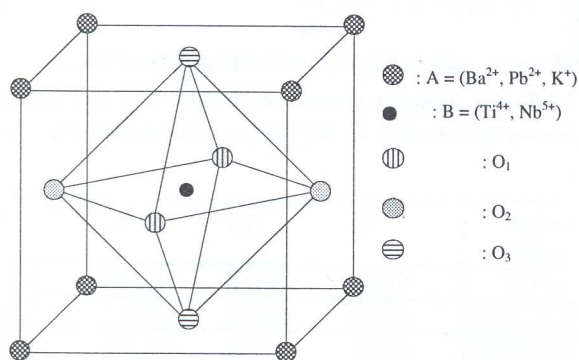


FIG. 1. Unit cell of ABO_3 perovskite structure.

On cooling these materials undergo successive structural phase transitions. The symmetries, the direction of the spontaneous polarization and the phase transitions temperatures of the three oxygen-octaedra above mentioned are reported in Fig. 2.

In the Fig. 2 the upper indices ('), (') and (') correspond to BaTiO_3 , KNbO_3 and PbTiO_3 respectively. All these phase transitions are strongly of first-order character and related to a large thermal hysteresis,^{1,2} a remarkable optical anisotropy³ and a large spontaneous polarization.⁴

In tetragonal phase, BaTiO_3 and KNbO_3 have a much

large birefringence⁵ and a large spontaneous polarization.⁴ In both materials the birefringence and the spontaneous polarization decrease with increasing temperature to the next phase transition.⁶ Whereas PbTiO_3 of the same family, as BaTiO_3 and KNbO_3 , it has a much larger tetragonality and a smaller birefringence⁷ and shows a remarkable spontaneous polarization.⁸ The birefringence of PbTiO_3 first increases (absolutely) with decreasing temperature, passes through a maximum at about 400 °C, and then decreases.⁹

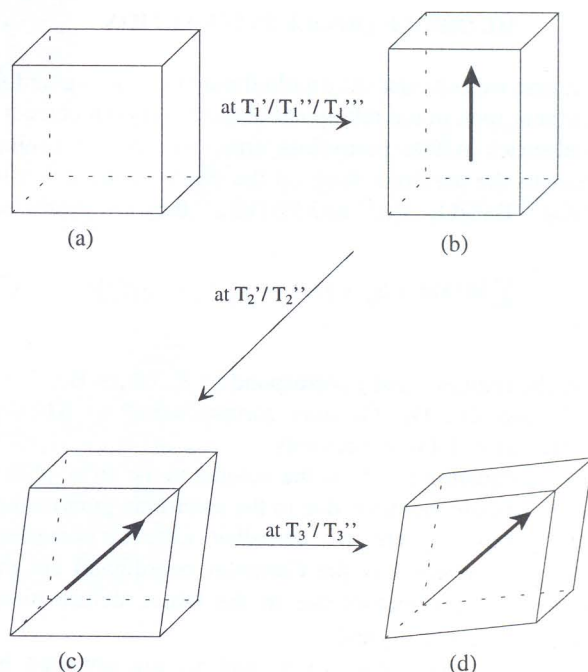


FIG. 2. Symmetries, direction of the spontaneous polarization and the phase transition temperatures.

The unusual nature of the birefringence of PbTiO_3 compared to BaTiO_3 and KNbO_3 appears strange and so it

will be interesting to examine it.

The aim of this article is to discuss quantitatively about the birefringence, the spontaneous polarization and the nature of the cubic tetragonal phase transition of BaTiO₃, KNbO₃ and PbTiO₃ from a microscopic viewpoint.

In this article, we discuss, in section 2 the origin of the optical anisotropy, in section 3 the dipole-dipole interaction, in section 4 the spontaneous Kerr effect based upon a quantum approach. Finally, in section 5 we make a summary and some discussions about the global results.

II. ORIGIN OF THE OPTICAL ANISOTROPY

Following Kinase *et al.*, The origin of the optical anisotropy is considered as the results of three main mechanisms^{10,11,12}:

- (i) The change of the dipole-dipole interaction due to

the lattice deformation by the piezoelectric effect ;

- (ii) The modification of the electronic polarizabilities due to the lattice deformation by the piezoelectric effect.

- (iii) The variation of the electronic polarizabilities by the Kerr effect due to the perturbation of the local field acting on the constituent ions when the sample is biased by an external field.

These three processes are specified by a diagram in Fig. 3.

The process (ii) is not discussed in this work. It has a close relation to the elasto-optic effect and requires a precise knowledge about the chemical bonds. In the case of BaTiO₃ for example the value of the birefringence in the tetragonal phase is known with an absolute uncertainty of $\pm 20\%$.¹³ So the contribution of this process is negligible with respect to the accuracy of the experimental data.

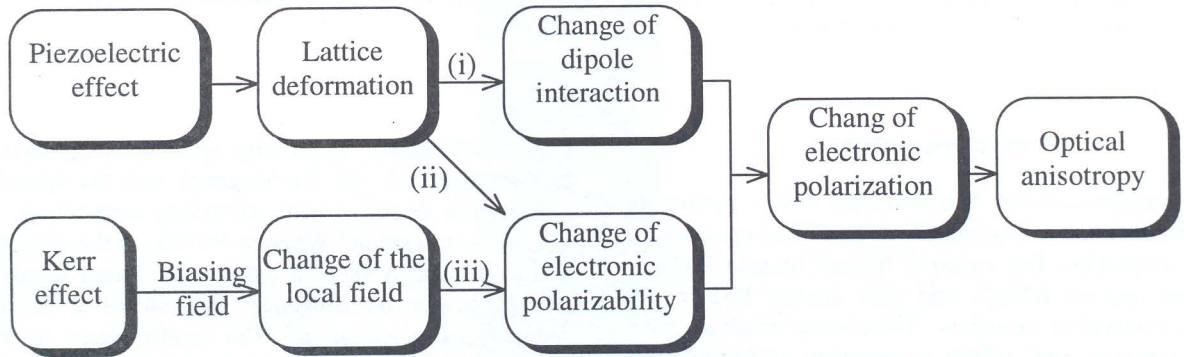


FIG. 3. The diagram of the mechanism of optical anisotropy.

III. DIPOLE-DIPOLE INTERACTION

At first we consider the dipole-dipole field acting on the constituent ions in the tetragonal phase of oxygen-octaedra ferroelectrics ABO₃ perovskite structure. In the similar manner to the previous work on the electro-optic effect in BaTiO₃,¹⁴ BaTiO₃ : Fe,¹⁵ and PbTiO₃,¹⁶ they are expressed as :

$$E_i^{dip} = \frac{1}{V_0} \sum_j \left(4.1888 + S_{ij} + \gamma_{ij1}\tau_1 + \gamma_{ij2}\tau_2 + \gamma_{ij3}\tau_3 \right) p_j \quad (1)$$

where the indices i and j correspond to K, Nb or Ba, Ti or Pb, Ti and O₃, O₂, O₁ ions corresponding to KNbO₃, BaTiO₃ and PbTiO₃ respectively.

In the equation (1), V_0 is the volume in the cubic phase, p_j are the dipole moments due to the electronic polarization of the j -ions ; S_{ij} are the so-called Lorentz correction factors ; γ_{ijk} (where k is the Cartesian coordinate) are the further correction factors due to the lattice deformations corresponding to τ_1 , τ_2 and τ_3 .

The numerical values of S_{ij} and γ_{ijk} are obtained by performing a calculation over the whole lattice. The results in the case of ABO₃ crystals are listed in Table I which was calculated in the earlier article by Kinase.¹⁷

The local fields E_i^{loc} acting on the respective ions in the tetragonal phase are obtained by the summation of the dipole-dipole fields and the bias E_i^{bias} . They are expressed as :

$$E_i^{lo} = E_i^{dip} + E_i^{bias} = \frac{p_i}{\alpha_i} \quad (2)$$

where α_i represent the electronic polarizabilities.

TABLE I. Lorentz correction factors (S_{ij}) and further correction factors due to the lattice deformation (γ_{ij1} , γ_{ij2} , γ_{ij3}).

Lattice point	S_{ij}	γ_{ij1}	γ_{ij2}	γ_{ij3}
(0,0,0)	0.000	2.156	2.156	-16.879
($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$)	0.000	-10.062	-10.062	7.558
(0, $\frac{1}{2}$, $\frac{1}{2}$)	4.334	-1.579	-27.173	3.184
($\frac{1}{2}$, 0, $\frac{1}{2}$)	4.334	-27.173	-1.579	3.184
($\frac{1}{2}$, $\frac{1}{2}$, 0)	-8.668	11.423	11.423	-9.408
(0, 0, $\frac{1}{2}$)	30.082	-2.116	-2.116	-98.581
(0, $\frac{1}{2}$, 0)	-15.041	1.595	43.007	-12.045
($\frac{1}{2}$, 0, 0)	-15.041	43.007	1.595	-12.045

The equation (1), can be rearranged as :

$$\mathbf{E}^{dip} = \frac{1}{V_0} \tilde{\mathbf{B}} \mathbf{p} \quad (3)$$

where \mathbf{E}^{dip} and \mathbf{p} are column vectors arranged in order of K, Nb or Ba, Ti or Pb, Ti and O₃, O₂, O₁ ions and $\tilde{\mathbf{B}}$ is the dipole interaction matrix.

If we consider only the Lorentz correction factors in equation (1), we obtain the results already calculated by Slater for BaTiO₃.¹⁸

By taking account of the lattice deformation, the matrix $\tilde{\mathbf{B}}$ can be written :

For BaTiO₃ :

$$\tilde{\mathbf{B}} = \begin{pmatrix} 4.0438 & 4.2955 & -4.6070 & 8.6144 & 8.6144 \\ 4.2955 & 4.0438 & 33.4919 & -11.0512 & -11.0512 \\ -4.6070 & 33.4919 & 4.0438 & 8.6144 & 8.6144 \\ 8.6144 & -11.0512 & 8.6144 & 4.0438 & -4.6070 \\ 8.6144 & -11.0512 & 8.6144 & -4.6070 & 4.0438 \end{pmatrix} \quad (4)$$

For KNbO₃ :

$$\tilde{\mathbf{B}} = \begin{pmatrix} 3.9937 & 4.3944 & -4.7208 & 8.7412 & 8.7412 \\ 4.3944 & 3.9937 & 33.3223 & -11.2614 & -11.2614 \\ -4.7208 & 33.3223 & 3.9937 & 8.7412 & 8.7412 \\ 8.7412 & -11.2614 & 8.7412 & 3.9937 & -4.7208 \\ 8.7412 & -11.2614 & 8.7412 & -4.7208 & 3.9937 \end{pmatrix} \quad (5)$$

For PbTiO₃ :

$$\tilde{\mathbf{B}} = \begin{pmatrix} 3.3281 & 4.8652 & -5.2860 & 9.7412 & 8.1321 \\ 4.8652 & 3.3281 & 29.7150 & -12.1308 & -12.1308 \\ -5.2860 & 29.7150 & 3.3281 & 9.1321 & 8.7412 \\ 9.1321 & -12.1308 & 9.1321 & 3.3281 & -5.2860 \\ 9.1321 & -12.1308 & 9.1321 & -5.2860 & 3.3281 \end{pmatrix} \quad (6)$$

when the bias field is only of optical origin, the equation (2) can be written :

$$\mathbf{E}^{loc} = \mathbf{E}^{opt} + \frac{1}{V_0} \tilde{\mathbf{B}} \mathbf{p} \quad (7)$$

Considering the relation $p_i = \alpha_i E_i^{loc}$, we obtain the following expressions of the electronic dipole moments p_i induced by the incident light :

For BaTiO₃ :

$$\begin{aligned} p_{Ba} &= 4.6821 E^{opt} (1 - 1.2861\tau_1 - 1.2861\tau_2 - 1.7360\tau_3) \\ p_{Ti} &= 0.6027 E^{opt} (1 - 0.1781\tau_1 - 0.1781\tau_2 - 6.4758\tau_3) \\ p_{O_3} &= 7.2778 E^{opt} (1 - 1.2317\tau_1 - 1.2317\tau_2 - 2.9943\tau_3) \\ p_{O_2} &= 5.8964 E^{opt} (1 - 1.1066\tau_1 - 1.1066\tau_2 - 2.0998\tau_3) \\ p_{O_1} &= 5.8964 E^{opt} (1 - 1.1066\tau_1 - 1.1066\tau_2 - 2.0998\tau_3) \end{aligned} \quad (8)$$

For KNbO₃ :

$$\begin{aligned} p_K &= 4.0671 E^{opt} (1 + 0.1471\tau_1 + 0.1471\tau_2 - 2.0282\tau_3) \\ p_{Nb} &= 0.4637 E^{opt} (1 + 0.4457\tau_1 + 0.4457\tau_2 - 5.2332\tau_3) \\ p_{O_3} &= 5.1014 E^{opt} (1 - 0.8636\tau_1 - 0.8636\tau_2 - 2.2519\tau_3) \\ p_{O_2} &= 4.3898 E^{opt} (1 - 0.9474\tau_1 - 0.9474\tau_2 - 1.4971\tau_3) \\ p_{O_1} &= 4.3898 E^{opt} (1 - 0.9474\tau_1 - 0.9474\tau_2 - 1.4971\tau_3) \end{aligned} \quad (9)$$

For PbTiO₃ :

$$\begin{aligned} p_{Pb} &= 6.0211 E^{opt} (1 - 1.5955\tau_1 - 1.5955\tau_2 - 1.8758\tau_3) \\ p_{Ti} &= 0.6291 E^{opt} (1 + 0.1842\tau_1 + 0.1842\tau_2 - 6.0678\tau_3) \\ p_{O_3} &= 7.6724 E^{opt} (1 - 1.4246\tau_1 - 1.4246\tau_2 - 2.8880\tau_3) \\ p_{O_2} &= 6.5256 E^{opt} (1 - 1.5983\tau_1 - 1.5983\tau_2 - 2.1169\tau_3) \\ p_{O_1} &= 6.5256 E^{opt} (1 - 1.5983\tau_1 - 1.5983\tau_2 - 2.1169\tau_3) \end{aligned} \quad (10)$$

The expression of the lattice deformations τ_1 , τ_2 and τ_3 for an optical field acting along the (001) direction, namely the 3-direction are :

$$\tau_1 = \tau_2 = \frac{a}{a_0} - 1 \quad \tau_3 = \frac{c}{a_0} - 1 \quad (11)$$

In the same manner, when the optical field is along the (010) direction, namely the 2-direction, the lattice deformations being :

$$\tau_1 = \tau_3 = \frac{a}{a_0} - 1 \quad \tau_2 = \frac{c}{a_0} - 1 \quad (12)$$

where a_0 is the lattice parameter in the cubic phase and a and c are the lattice parameters in the tetragonal phase.

For our calculations, we have used the data reported in Tables II, III and IV corresponding to BaTiO₃, KNbO₃ and PbTiO₃ respectively where Z_i are the ionic effective charge, $\delta\xi_i$ the ionic shifts, n_0 the optical index in the cubic phase, Δn the birefringence and P_s the spontaneous polarization in the tetragonal phase.

TABLE II. Numerical data for BaTiO₃ at 25°C.

$a=3.992 \text{ \AA}$	$c=4.035 \text{ \AA}$	$a_0=4.001 \text{ \AA}$
$\delta\xi_{Ba}=0.000 \text{ \AA}$	$\delta\xi_{Ti}=0.140 \text{ \AA}$	$\delta\xi_{O}=0.000 \text{ \AA}$
$Z_{Ba}=1.48$	$Z_{Ti}=2.72$	$Z_O=-1.40$
$n_0=2.4$	$\Delta n=-0.100$	$P_s=0.26 \text{ Cm}^{-2}$

TABLE III. Numerical data for KNbO₃ at 350°C.

$a=3.997 \text{ \AA}$	$c=4.063 \text{ \AA}$	$a_0=4.023 \text{ \AA}$
$\delta\xi_K=0.103 \text{ \AA}$	$\delta\xi_{Nb}=0.18 \text{ \AA}$	$\delta\xi_{O_1}=\delta\xi_{O_2}=0.018 \text{ \AA}$
$Z_K=0.75$	$Z_{Nb}=2.85$	$Z_O=-1.2$
$n_0=2.36$	$\Delta n=-0.119$	$P_s=0.30 \text{ Cm}^{-2}$

TABLE IV. Numerical data for PbTiO₃ at 25°C.

$a=3.902 \text{ \AA}$	$c=4.156 \text{ \AA}$	$a_0=3.97 \text{ \AA}$
$\delta\xi_{Pb}=0.000 \text{ \AA}$	$\delta\xi_{Ti}=0.157 \text{ \AA}$	$\delta\xi_{O}=0.114 \text{ \AA}$
$Z_{Pb}=1.20$	$Z_{Ti}=3.78$	$Z_O=-1.66$
$n_0=2.659$	$\Delta n=-0.012$	$P_s=0.60 \text{ Cm}^{-2}$

The total electronic polarization induced by the incident light is obtained by summation of the p_j divided by the volume of the distorted unit cell that is written :

$$V = V_0 (1 + \tau_1)(1 + \tau_2)(1 + \tau_3) \quad (13)$$

$$P^{opt} = \frac{1}{V_0} \sum_j P_j \quad (14)$$

For BaTiO₃ :

$$P^{opt} = 0.2872E^{opt} (1 - 1.6419\tau_1 - 1.6419\tau_2 - 3.1666\tau_3) \quad (15)$$

For KNbO₃ :

$$P^{opt} = 0.2828E^{opt} (1 - 0.6472\tau_1 - 0.6472\tau_2 - 1.9185\tau_3) \quad (16)$$

For PbTiO₃ :

$$P^{opt} = 0.2452E^{opt} (1 - 0.0878\tau_1 - 0.0878\tau_2 - 1.1729\tau_3) \quad (17)$$

The birefringence $(\Delta n)^{dip}$ due to the change of the dipole-dipole interaction caused by the lattice deformations is given by :

$$(\Delta n)^{dip} = \frac{4\pi(\delta P^{opt})}{2n_0 E^{opt}} \quad (18)$$

By taking account of the ionic polarization, the equation (1) can be written :

$$E_i^{dip} = \frac{1}{V_0} \sum_j (4.1888 + S_{ij} + \gamma_{ij1}\tau_1 + \gamma_{ij2}\tau_2 + \gamma_{ij3}\tau_3) (P_j + Z_j e \delta \xi_j) \quad (19)$$

The spontaneous polarization is calculated by summation of the ionic and the electronic polarizations :

$$P_s = \frac{1}{V} \sum_j (p_j + p_j^o) \quad (20)$$

where $p_j^o = Z_j e \delta \xi_j$ correspond to the ionic moment dipole of the j ion.

The calculated value of P_s and corresponding $(P_s)^{exp}$ obtained at the cubic-tetragonal transition temperature of the three crystals above mentioned are reported in Table V.

TABLE V. Calculation values of P_s and $(P_s)^{exp}$

	P_s	$(P_s)^{exp}$
BaTiO ₃ at 25°C	0.28 Cm ⁻²	0.26 Cm ⁻²
KNbO ₃ at 350°C	0.35 Cm ⁻²	0.30 Cm ⁻²
PbTiO ₃ at 25°C	0.50 Cm ⁻²	0.60 Cm ⁻²

IV. SPONTANEOUS KERR EFFECT

The spontaneous Kerr effect was first discussed in the scope of a quantum approach. By using the variational method, the variation of the electronic polarizabilities of the constituent ions due to the local field was calculated by the determination of the change of the Slater-type orbitals.¹⁹

The electronic polarizabilities of the constituent ions are expressed as :

$$\alpha_{3j} = \alpha_j^0 \left[1 - \theta_{3j} (E_j^{loc})^2 \right] \quad (21)$$

$$\alpha_{2j} = \alpha_j^0 \left[1 - \theta_{2j} (E_j^{loc})^2 \right] \quad (22)$$

where θ_{3j} and $\theta_{2j} = \theta_{3j}/3$ are the Kerr coefficients and refer to the polarizabilities respectively parallel and perpendicular to the 3-axis. α_j^0 is the free electronic

polarizability of the j -ion without any local field.

Equation (21) and (22) represent the non-linear and anisotropic effect of the electronic polarizability due to the local field.

In the case of oxygen-octaedra ABO₃ perovskite structure, we calculated the electronic polarizabilities of the constituent ions as :

For BaTiO₃ :

$$\begin{aligned} \alpha_{3Ba} &= 1.9460 \left[1 - 18.1785 \cdot 10^{-15} (E_{Ba}^{loc})^2 \right] \text{ \AA}^3 \\ \alpha_{3Ti} &= 0.1859 \left[1 - 17.1039 \cdot 10^{-16} (E_{Ti}^{loc})^2 \right] \text{ \AA}^3 \\ \alpha_{3O} &= 2.3940 \left[1 - 8.1059 \cdot 10^{-14} (E_O^{loc})^2 \right] \text{ \AA}^3 \end{aligned} \quad (23)$$

For KNbO₃ :

$$\begin{aligned} \alpha_{3K} &= 1.9460 \left[1 - 18.5156 \cdot 10^{-14} (E_K^{loc})^2 \right] \text{ \AA}^3 \\ \alpha_{3Nb} &= 0.1859 \left[1 - 11.1297 \cdot 10^{-16} (E_{Nb}^{loc})^2 \right] \text{ \AA}^3 \\ \alpha_{3O} &= 2.0877 \left[1 - 6.5628 \cdot 10^{-14} (E_O^{loc})^2 \right] \text{ \AA}^3 \end{aligned} \quad (24)$$

For PbTiO₃ :

$$\begin{aligned} \alpha_{3Pb} &= 2.2520 \left[1 - 6.5256 \cdot 10^{-14} (E_{Pb}^{loc})^2 \right] \text{ \AA}^3 \\ \alpha_{3Ti} &= 0.1859 \left[1 - 17.1039 \cdot 10^{-16} (E_{Ti}^{loc})^2 \right] \text{ \AA}^3 \\ \alpha_{3O} &= 2.3940 \left[1 - 8.1059 \cdot 10^{-14} (E_O^{loc})^2 \right] \text{ \AA}^3 \end{aligned} \quad (25)$$

The birefringence $(\Delta n)^{Kerr}$ due to the modification of the electronic polarizabilities induced by the local field, that is the spontaneous Kerr effect can be written as :¹²

$$(\Delta n)^{Kerr} = -\frac{1}{2\epsilon_0 n_0 V_0 E^{opt}} \sum_{ij} \frac{\partial p_i}{\partial \alpha_j} \alpha_j^0 \theta_{3j} (E_j^{loc})^2 \quad (26)$$

where ϵ_0 is the permittivity of the free space and the indices i and j represent the sort of the constituent ions.

The local fields acting on the respective ions were calculated as :

For BaTiO₃ :

$$\begin{pmatrix} E_{Ba}^{loc} = -0.0139 \\ E_{Ti}^{loc} = 0.3753 \\ E_{O_3}^{loc} = 2.2884 \\ E_{O_2}^{loc} = 0.0112 \\ E_{O_1}^{loc} = 0.0112 \end{pmatrix} \times e \times 10^{16} \text{ in CGS esu} \quad (27)$$

For KNbO₃ :

For PbTiO₃ :

$$\begin{pmatrix} E_K^{loc} = -0.0075 \\ E_{Nb}^{loc} = 0.3979 \\ E_{O_3}^{loc} = 0.3404 \\ E_{O_2}^{loc} = 0.0119 \\ E_{O_1}^{loc} = 0.0119 \end{pmatrix} \times e \times 10^{16} \text{ in CGS esu} \quad (28)$$

$$\begin{pmatrix} E_{Pb}^{loc} = -0.0139 \\ E_{Ti}^{loc} = 0.3753 \\ E_{O_3}^{loc} = 0.2884 \\ E_{O_2}^{loc} = 0.0112 \\ E_{O_1}^{loc} = 0.0112 \end{pmatrix} \times e \times 10^{16} \text{ in CGS esu} \quad (29)$$

$\frac{\partial p_i}{\partial \alpha_j}$ is the rate of the electronic dipole moment of the i -ion by the change of the electronic polarizability of the j -ion which was expressed as the following matrix (ij) :

For BaTiO₃ :

$$\left(\frac{\partial p_i}{\partial \alpha_j} \right)_{ij} = \begin{pmatrix} 2.8326 & -0.1901 & -0.0130 & 0.7288 & 0.7288 \\ -0.0169 & 2.7713 & 0.3252 & -0.0092 & -0.0092 \\ -0.0169 & 3.3579 & 3.7847 & 0.7906 & 0.7906 \\ 0.7785 & -0.1102 & 0.9183 & 2.8994 & -0.0111 \\ 0.7785 & -0.1102 & 0.9183 & -0.0111 & 2.8994 \end{pmatrix} \times E^{opt} \quad (30)$$

For KNbO₃ :

$$\left(\frac{\partial p_i}{\partial \alpha_j} \right)_{ij} = \begin{pmatrix} 2.8326 & -0.1901 & -0.0130 & 0.7288 & 0.7288 \\ -0.0169 & 2.7713 & 0.3252 & -0.0092 & -0.0092 \\ -0.0169 & 3.3579 & 3.7847 & 0.7906 & 0.7906 \\ 0.7785 & -0.1102 & 0.9183 & 2.8994 & -0.0111 \\ 0.7785 & -0.1102 & 0.9183 & -0.0111 & 2.8994 \end{pmatrix} \times E^{opt} \quad (31)$$

For PbTiO₃ :

$$\left(\frac{\partial p_i}{\partial \alpha_j} \right)_{ij} = \begin{pmatrix} 2.8326 & -0.1901 & -0.0130 & 0.7288 & 0.7288 \\ -0.0169 & 2.7713 & 0.3252 & -0.0092 & -0.0092 \\ -0.0169 & 3.3579 & 3.7847 & 0.7906 & 0.7906 \\ 0.7785 & -0.1102 & 0.9183 & 2.8994 & -0.0111 \\ 0.7785 & -0.1102 & 0.9183 & -0.0111 & 2.8994 \end{pmatrix} \times E^{opt} \quad (32)$$

The calculated values of $(\Delta n)^{Kerr}$ and those of $(\Delta n)^{dip}$ are reported in Table VI :

TABLE VI. Calculated values of $(\Delta n)^{dip}$ and $(\Delta n)^{Kerr}$ of BaTiO₃, KNbO₃ and PbTiO₃.

	$(\Delta n)^{dip}$	$(\Delta n)^{Kerr}$
BaTiO ₃ at 25°C	-0.034	-0.057
KNbO ₃ at 350°C	-0.036	-0.102
PbTiO ₃ at 25°C	-0.0078	-0.004

V. SUMMARY AND DISCUSSION

The total birefringence Δn is obtained by taking account of two effects discussed above. We obtain the calculated value as :

$$(\Delta n)^{cal} = (\Delta n)^{dip} + (\Delta n)^{Kerr} \quad (33)$$

The value of $(\Delta n)^{cal}$ and the corresponding $(\Delta n)^{exp}$ obtained at the cubic-tetragonal transition temperature of the three crystals above mentioned, are reported in Table VII.

TABLE VII. Comparison between $(\Delta n)^{cal}$ and $(\Delta n)^{exp}$ of BaTiO₃, KNbO₃ and PbTiO₃.

	$(\Delta n)^{cal}$	$(\Delta n)^{exp}$
BaTiO ₃ at 25°C	-0.091	-0.100
KNbO ₃ at 350°C	-0.138	-0.119
PbTiO ₃ at 25°C	-0.011	-0.012

Table V and Table VII show that the measured values

of the spontaneous polarization and those of the birefringence respectively obtained at the cubic-tetragonal transition temperature of BaTiO₃, KNbO₃ and PbTiO₃ are very close to our calculated results.

These theoretical results show that the experimental spontaneous polarization can be explained by considering the contribution of the dipole-dipole effect alone. The birefringence is reproduced by considering the contribution of the Kerr effect which contributes for about 60 %, 74 % and 36 % for BaTiO₃, KNbO₃ and PbTiO₃ respectively.

¹J. A. Gonzalo, R. Ramirez, G. Lifante and M. Koralewski, *Ferroelectrics Letters*, **15**, 9 (1993).
²B. Noheda, M. Karalewski, G. Lifante and J. A. Gonzalo, *Ferroelectrics Letters*, **17**, 25 (1994)
³M. E. Line et A. M. Glass, *Principle and applications of ferroelectrics and related materials*, Oxford, Clarendon (1977).
⁴F. Jona and J. Shirane, *Ferroelectrics crystals*, Pergamon-Press (1962).
⁵M. D. Fontana, Ph.D. Thesis, University of Metz, France (1985).
⁶S. H. Wemple, M. Didomenico and M. Camlibel, *J. Phys. and Chim.*, **29**, 1797 (1968).
⁷W. Kleeman and F. J. Schäfer, *Phys. Rev. B*, **34**, 7873 (1986).
⁸J. G. Bergman, G. R. Grane and E. H. Turner, *J. Solid State Chem.*, **21**, 127 (1977).
⁹J. Shirane, R. Pepinsky and R. Frazer, *Acta Crysta.*, **2**, 131 (1956).
¹⁰W. Kinase and K. Mori, *Ferroelectrics*, **29**, 235 (1980).

¹¹W. Kinase, N. Ohnishi, M. Yoshikawa and K. Mori, *Ferroelectrics*, **56** (1984).
¹²W. Kinase, M. Yoshikawa and N. Ohnishi, *Ferroelectrics*, **67**, 159 (1986).
¹³P. Jullien, A. Lahlafi and A. Maillard, *Ferroelectrics*, **108**, 147 (1990).
¹⁴D. Khatib, B. Jannot and P. Jullien, *Ferroelectrics Letters*, **15** (1993).
¹⁵D. Khatib, P. Jullien and B. Jannot, *Ferroelectrics*, **145** (1993).
¹⁶D. Khatib, B. Jannot and L. Lifsal, *Advanced Materials Research*, **1-2** (1994).
¹⁷W. Kinase, Y. Uemura and M. Kikuchi, *J. Phys. and Chem. Solids*, **30**, 441 (1969)
¹⁸J. C. Slater, *Phys. Rev.*, **78**, 748 (1950).
¹⁹J. C. Slater, *Phys. Rev.*, **36**, 57 (1930).