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TESTING A POINT-DIPOLE ELECTRO-OPTIC
MODEL BY AN APPLICATION TO LEAD
TITANATE

August S. Sanchez

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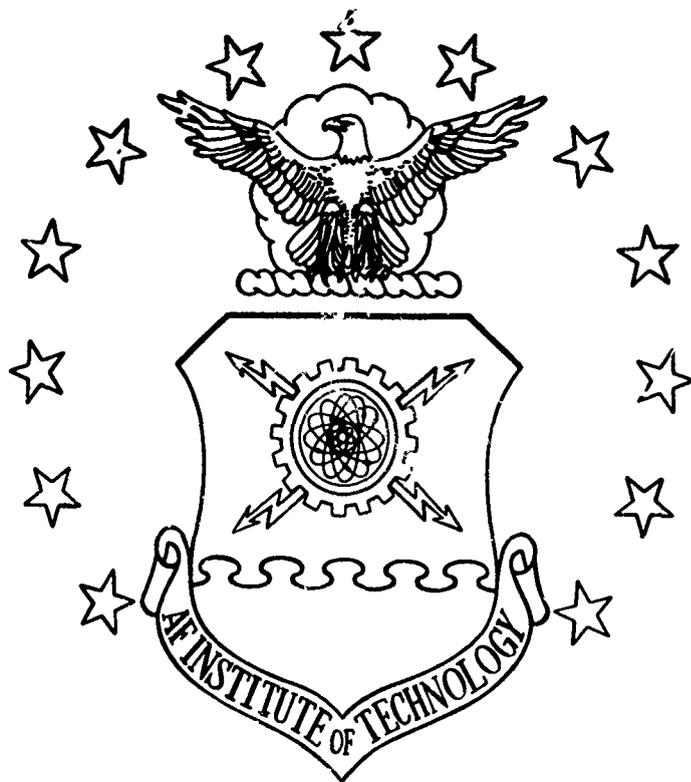
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THESIS

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13. ABSTRACT A molecular point-dipole model that has been used successfully to calculate ferroelectric and electro-optic properties of the perovskite barium titanate ($BaTiO_3$) is further tested here by an application to lead titanate ($PbTiO_3$). The model calculates Lorentz factors by the method of Rama Rau and the crystal's internal electric fields by the Ewald method of lattice sums. The model further treats the polarizabilities of ions as field-dependent and simulates covalency in bonds by replacing the full ionic charge by an "effective" charge. The Kerr and Pockel electro-optic constants are determined by the anisotropy induced in the refractive index by an external electric field.

The calculations done showed that the model could match the experimental refractive index and dielectric constant and calculate satisfactory electro-optic constants in the cubic (paraelectric) phase, but was unable to calculate correctly the natural birefringence or dielectric anisotropy of the tetragonal (ferroelectric) phase. The model's failure in the tetragonal phase was investigated by determining the contribution to the natural birefringence by each of the different mechanisms in the model. It was found that at room temperature the contribution to the natural birefringence by the crystal lattice tetragonality or the ion displacements alone, through the Lorentz factors, was at least an order of magnitude larger than the experimentally measured birefringence.

The conclusion drawn is that the large c/a axis ratio and highly unsymmetrical positions of the ions in $PbTiO_3$ incorrectly dominate the model's behavior in its present form.

Recommendations are to consider an explicit dependence of the polarizabilities on both the electric field and bond length.

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TESTING A POINT-DIPOLE ELECTRO-OPTIC MODEL
BY AN APPLICATION TO LEAD TITANATE

THESIS

Presented to the Faculty of the School of Engineering
of the Air Force Institute of Technology
Air University
in Partial Fulfillment of the
Requirements for the Degree of
Master of Science

by

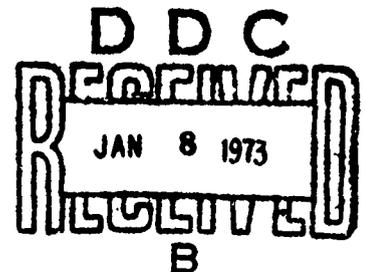
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Preface

In the late 1940's, the study of ferroelectricity received a new momentum and direction with the discovery of ferroelectric barium titanate (BaTiO_3) and identification of its crystal structure. The new interest lay in the fact that the tetragonal crystal structure of ferroelectric BaTiO_3 was simple in comparison to the structure of other ferroelectrics and might lend itself to an explanation of its ferroelectricity through a description of its physical structure. Lead titanate (PbTiO_3) was also found at about the same time to be ferroelectric at room temperature, with the same tetragonal structure, and many attempts have since been made to calculate the properties of both materials. Two treatments that have been particularly successful in calculating the basic ferroelectric properties are a thermodynamic treatment and a point-dipole treatment. Very recently, Dr. Donald C. Wunsch, now at the Air Force Weapons Laboratory, succeeded in extending the point-dipole model to calculate the electro-optic behavior of BaTiO_3 . Further verification of the model's ability to perform these calculations correctly is looked for here, with an application to PbTiO_3 .

I am indebted to Dr. Wunsch for sparking my interest in this field and for having established the necessary mathematical tools and guidelines to use in working with PbTiO_3 , also for the discussion and time spent in making little problems out of big ones. I thank my Thesis Advisor, LtCol John S. DeWitt for the 'unending' patience extended to me during this venture.

August S. Sanchez

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TESTING A POINT-DIPOLE ELECTRO-OPTIC MODEL

BY AN APPLICATION TO LEAD TITANATE

I. IntroductionBackground

In a doctoral dissertation entitled "Phenomenological Theory of Refractive Index and Electro-Optical Phenomena in Crystals of Perovskite Structure (With Application to Barium Titanate)", Wunsch (Ref 27) has proposed a point-dipole model for calculating electro-optic effects of ferroelectric materials having the perovskite crystal structure. The model describes the material in terms of its crystal lattice dimensions, relative positions of its ions within the lattice, internal electric fields, and ion polarizabilities. The model performs a self-consistent computer solution of the Lorentz formula for the crystal's electric fields and polarizabilities and uses the results in solving for those components of the dielectric tensor that lie along the crystal's axes.

Models of this type have been used by other investigators in attempts to calculate refractive indices, dielectric constants, and other basic electromagnetic material parameters (Ref 9, 14, 25). These efforts along with those using other models, such as the thermodynamic treatment of Devonshire (Ref 19:68) have met with mixed success, failing in many cases to calculate correctly basic crystal parameters such as the natural birefringence in barium titanate (BaTiO_3) and lead titanate (PbTiO_3). These materials are optically negative, whereas, calculations have shown them to be optically positive (Ref 11:349).

In his application to barium titanate, Wunsch used measured lattice parameters and varied slightly the approximate polarizabilities reported

in the literature to match the dielectric constants, refractive indices, and birefringence in a free-field environment. Then using the same basic parameters in a non-zero field, he successfully calculated the linear and quadratic electro-optic constants.

His success was due to two major differences incorporated in his model. The first and most important was to use an anisotropic field-dependent form of the polarizabilities. This form was obtained by a first order perturbation quantum mechanical calculation with the final result being expressed in terms of the isotropic zero -field polarizabilities. The second change was to depart from a pure ionic treatment by incorporating a numerical factor that simulates the degree of covalency of bonds between ions. This factor essentially reduces the charge at each ion site by the amount of electronic charge that is shared with the oppositely charged ion in bonding.

The interest in being able to theoretically determine the electro-optic behavior of linear or non-linear optical materials is due to their extensive use in laser applications. The most common of these uses include laser switching and amplitude or frequency modulation, with others being investigated, such as information storage and visual display.

Thesis Problem

The problem addressed here is to take the point-dipole model that Wunsch applied to BaTiO_3 and test it further by applying it to PbTiO_3 . PbTiO_3 appears to be an ideal material for further tests on the model for the following reasons: 1) PbTiO_3 and BaTiO_3 have been studied more than other perovskites because only these two materials, of the many belonging to the perovskite ferroelectrics, have the tetragonal crystal structure at room temperature. Although there are not as many experi-

mental measurements reported on PbTiO_3 as on BaTiO_3 , due to greater difficulty in growing crystals of it and in making measurements on it, there is sufficient data on it to make many of the necessary comparisons with the model's calculations. 2) The crystal structure characteristics that are chiefly responsible for the ferroelectricity exhibited are more pronounced in PbTiO_3 . Any failings or weaknesses of the model should therefore be more easily detected. And, 3) Although at room temperature the spontaneous polarization of PbTiO_3 is approximately four times larger than that of BaTiO_3 , its natural birefringence is approximately three times smaller (Ref 19:95). This is contrary to the theories relating these two properties. The behavior of the natural birefringence with temperature is also quite different for PbTiO_3 . Any success by the model in predicting these as yet unexplained behavior (Ref 19:96) can be considered as strong support for the model.

The goals to be accomplished and the approach to be used may be summarized in the following way: Using experimental crystal structure parameters, approximate ionic parameters are varied to match as closely as possible the experimental refractive indices, dielectric constants, and spontaneous polarizations. Then keeping the crystal structure and ionic parameters fixed, an external electric field is introduced into the calculations and the new values of refractive indices, dielectric constants, and polarizations are obtained. The additional anisotropy of these values over the zero-field values are then used to determine the appropriate electro-optic constants.

An additional goal was preparation of existing computer codes, capable of performing the above calculations, to run on the Air Force Weapons Laboratory's computer system.

II. Discussion of Model

Basic Equations

As mentioned in the introduction, the model that Wunsch extended in his dissertation to do electro-optic calculations is a point-dipole model. The point-dipole model requires that the crystal lattice dimensions and positions of the ions within that lattice be well known. It assumes that: 1) The ions have constant electric moments equal to the statistical expectation value, 2) The field-polarized ions interact as point-dipoles, and 3) An individual ionic and electronic polarizability can be assigned to each type of ion. The basic problem faced by the model is a solution for dielectric constants along the crystal's principal axes.

The i -th component of the dielectric constant for an anisotropic material is given by

$$\epsilon_{ii} E_i = E_i + 4\pi \sum_b P_i^b \quad (1)$$

where E_i is the external electric field in the i -th direction and P_i^b is the polarization in the i -th direction of each type of ion. The polarization of an ion type per unit volume is given by

$$P_i^b = N^b \alpha^b F_i^b \quad (2)$$

where N^b is the number of ions of each type per unit volume. Similarly, F_i^b is the local field at each ion and α^b is the polarizability of the ion in the i -th direction.

The local field at each ion is given by the Lorentz formula. For a non-cubic material composed of different ions, this formula is

$$F_i^a = E_i + 4\pi \sum_b \sum_j N^b L_{ij}^{ab} \alpha_j^b F_j^b \quad (3)$$

where: F_i^a = local field at the a-th ion in the i-th direction
 E_i = applied field in the i-th direction
 N^b = number of type 'b' ions per unit volume
 L_{ij}^{ab} = lorentz factors
 α_j^b = field-dependent polarizability of a type 'b' ion

Substituting for the polarization in equation (1) from equation (2) and solving for the dielectric constant along the principal axes, gives

$$\epsilon_i = 1 + \frac{4\pi}{\Delta} \sum_b \alpha^b \frac{F_i^b}{E_i}$$

where, for only one ion of each type per unit cell, $N = \frac{1}{\Delta}$ where Δ is the volume per unit cell. The $\frac{F_i^b}{E_i}$ (local field factors) are found by solving equation (3). Since the polarizabilities are defined as being field-dependent, a closed-form solution is difficult to obtain. A major goal of the model, then, is a self-consistent solution of this equation by computer techniques.

For a cubic lattice, each of the Lorentz factors is equal to $1/3$. Therefore, for a cubic lattice with one atom of each type per unit cell equation (3) can be written as

$$F_i^b = E_i + \frac{4\pi}{3\Delta} \sum_b \alpha_i^b F_i^b \quad (5)$$

Assuming very small local fields so that the polarizabilities can be taken as constants, equation (5) can be solved for the local field factors as

$$\frac{F_i^a}{E_i} = \frac{1}{1 - \frac{4\pi}{3\Delta} \sum_b \alpha^b} \quad (6)$$

Then substituting for the local factors in equation (4), the dielectric constant can be written as

$$\epsilon_i = 1 + \left(\frac{4\pi}{\Delta} \sum_b \alpha^b \right) \frac{1}{1 - \frac{4\pi}{3\Delta} \sum_b \alpha^b} \quad (7)$$

For a material that does not have a simple cubic lattice, the solution for any component of the dielectric constant differs from equation (7) in that the denominator of the local field factor does not involve a simple product of $1/3$ times the sum of polarizabilities. It involves a sum of the products of the proper Lorentz factors and polarizabilities.

The methods for calculating the Lorentz factors, field-dependent polarizabilities, Coulomb fields and other required parameters are treated in the following sections.

Polarizabilities

The polarizabilities of equation (3) are defined to be field-dependent, however, only a portion of the polarizability is given a field dependence. The polarizability is separated into an electronic and an ionic part as per basic assumption 3) of the point-dipole model. The electronic polarizability is defined as the tendency of the electronic charge cloud around an ion to be distorted by an electric field. The ionic polarizability is the tendency of an ion in a crystal to be displaced from its normal position with respect to other ions of different charge resulting in the formation of dipoles (Ref 12:164). The ionic polarizability is not an experimentally measurable value. It is determined instead by taking the difference between the total and the electronic polarizability. The total polarizability is defined and determined by the Clausius-Mossotti equation. This equation, which may be obtained by rewriting equation (7), is

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi}{3\Delta} \sum_b \alpha_+^b \quad (8)$$

In this equation α_+^b is the total polarizability (response to a static or a low frequency alternating electric field). For alternating electric fields of optical frequencies, the response would come from the electronic charge distributions of the ions, and at these frequencies,

equation (8) may be written as the Lorenz-Lorentz equation

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4\pi}{3\Delta} \sum_b \alpha_e^b \quad (9)$$

where the square of the refractive index is also known as the optical dielectric constant, and the α_e are the electronic polarizabilities.

The electronic polarizabilities that are obtained through equation (9) are isotropic. The anisotropic field-dependent polarizabilities required by the model are arrived at through a quantum-mechanical perturbation calculation. The resultant relation is

$$\alpha = \frac{\alpha_0}{[1 + 2\beta]^{1/2}} \quad (10)$$

where

$$\alpha_0 = \frac{4q^2 |z^2| m^2}{\hbar} \quad (11)$$

and

$$\beta = \frac{\alpha_0^{3/2} m^{1/2} F^2}{q\hbar} \quad (12)$$

In using equation (10), α_0 is replaced by the isotropic electronic polarizability determined by the Lorenz-Lorentz equation.

Lorentz Factors

The use of correct Lorentz factors for non-cubic crystals is a basic distinguishing characteristic of the model, and although a rigorous derivation is very long (Ref 27:155), some discussion is required to gain an appreciation for what the model involves. This discussion tries only to show, as briefly as possible, the conditions under which the form of the Lorentz factors is determined.

Consider a neutral crystal with a periodic charge distribution that can be expressed in a Fourier series

$$\rho = \sum_L \rho^L e^{i\vec{q}^L \cdot \vec{r}} \quad (13)$$

and in terms of the three-dimensional Dirac delta function as

$$\rho = \sum_k e_k \delta(\vec{r} - \vec{r}^k) \quad (14)$$

The electric potential of this crystal may also be written in a Fourier series

$$\phi = \sum_L C^L e^{i\vec{q}^L \cdot \vec{r}} \quad (15)$$

or given by Poisson's equation as

$$\nabla^2 \phi = -4\pi\rho \quad (16)$$

Having solved for the fourier coefficient ρ^L of equation (13) by using the expression for ρ from equation (14), the fourier coefficient C^L of equation (15) may be determined by substituting the expressions for ρ , equation (13), and for ϕ , equation (15), into equation (16). Having done so, equation (15) may be written as

$$\phi = \frac{4\pi}{\Delta} \sum_L \sum_k e_k \frac{e^{i\vec{q}^L \cdot (\vec{r} - \vec{r}^k)}}{|\vec{q}^L|^2} \quad (17)$$

or

$$\phi = \sum_k e_k \psi(\vec{r} - \vec{r}^k) \quad (18)$$

where

$$\psi = \frac{4\pi}{\Delta} \sum_L \frac{e^{i\vec{q}^L \cdot \vec{r}}}{|\vec{q}^L|^2} \quad (19)$$

A system of dipoles may be formed by placing a charge 'e' at the origin and an equal opposite charge very near it at $\delta\vec{r}$ and repeating the arrangement within each unit cell. The potential for this lattice of dipoles is then given by equation (18) as

$$\begin{aligned} \phi &= e\psi(\vec{r}) - e\psi(\vec{r} - \delta\vec{r}) \\ &\approx e\psi(\vec{r}) - e\psi(\vec{r}) + e\delta\vec{r} \cdot \nabla\psi \\ &\approx e\delta\vec{r} \cdot \nabla\psi = -\vec{\mu} \cdot \nabla\psi \end{aligned} \quad (20)$$

where $\vec{\mu} = -e\delta\vec{r}$ is the dipole moment.

The potential acting on the dipoles at the origin due to all other dipoles, with the exception of itself, is

$$\bar{\phi} = -\bar{\mu} \cdot \delta\bar{\psi} \quad (21)$$

where

$$\bar{\psi} = \psi - \frac{1}{r} \quad (22)$$

The local field \vec{F} at the origin in the presence of an applied field \vec{E} is now just the sum of the applied and the crystal's field, or

$$\begin{aligned} \vec{F} &= \vec{E} - (\nabla\bar{\phi})_0 \\ &= \vec{E} + \left(\nabla(\bar{\mu} \cdot \nabla\bar{\psi}) \right)_0 \end{aligned} \quad (23)$$

If $\bar{\mu}$ is assumed to be proportional the local field at the origin, then

$$\vec{F} = \vec{E} + \bar{\mu} \cdot (\nabla\nabla\bar{\psi})_0 \quad (24)$$

or

$$\vec{F} = \vec{E} + 4\pi P_i L_{ij} \quad (25)$$

where

$$P_i = \frac{\mu_i}{\Delta} \quad (26)$$

and the L_{ij} (Lorentz factors) are defined by

$$\begin{aligned} L_{ij} &= \frac{\Delta}{4\pi} (\nabla\nabla\bar{\psi}) \\ &= \frac{\Delta}{4\pi} \left(\frac{\partial^2 \bar{\psi}}{\partial_i \partial_j} \right) \end{aligned} \quad (27)$$

Coulomb Fields

The electric fields (coulomb) existing within the crystal at the different ion sites, due to the unsymmetrical distribution of the ions, are calculated in a manner similar to the calculation for the crystal dipole fields discussed in the preceding section. Once the electric potential ϕ for the lattice of charges is defined by equation (18), the field is given by

$$E = -\nabla\phi \quad (28)$$

For a non-cubic non-symmetric lattice, the lattice is broken down into a number of sub-lattices, each of which is cubic and meets the requirements of the model's development. For such a lattice, the field at an ion site is found by adding the field contributions from each of the different sub-lattices.

Spontaneous Polarization

The spontaneous polarization is equal to the sum of the electronic and the ionic polarizations. The electronic contribution by each ion is due to the deformation of its electronic charge distribution by the local field and is given by

$$p^a = \frac{\alpha^a F^a}{\Delta} \quad (29)$$

where α^a is the anisotropic field-dependent electronic polarizability.

The ionic polarizability has been defined within a crystal (page 7) in terms of the displacement of an ion with respect to other ions in the

lattice. The ionic spontaneous polarization is therefore calculated in terms of the ion shifts away from their symmetrical lattice positions. The equation for calculating the polarization of each ion type per unit cell, in the direction of its displacement Z , is

$$P_Z = \frac{NqZd}{\Delta} \quad (30)$$

where: N = number of ions per unit cell
 q = the electronic charge
 Z = degree of ionization of the ion
 d = the ion's shift from its symmetrical cubic position

Electro-optic Constants

When the perovskite crystal is subjected to an external electric field, the electronic charge distribution of the individual ions suffer a deformation in addition to any that may already exist due to internal coulomb fields. This deformation results in a change in the electronic polarizability in the direction of the applied field. In a manner identical with the natural birefringence, the induced anisotropy in electronic polarizabilities results in an induced birefringence. This induced birefringence can be expressed as a sum of a linear and quadratic term in the electric field strength, with the terms being called the Pockel and the Kerr effect, respectively.

In the crystal's cubic phase, the linear term is absent due to the crystal's symmetry (Ref 29:301). The constant for the quadratic effect can be expressed (Appendix A) as

$$R_{11} - R_{12} = \frac{2\Delta n}{n_o^3 E_z^2} \quad (31)$$

where Δn is the induced birefringence and n_0 is the zero-field refractive index along either of the principal axes. The above constant is also expressed in terms of the induced polarization, rather than the applied electric field. This relation is given by

$$g_{11} - g_{12} = \frac{2\Delta n}{n_0^3 P_z^2} \quad (32)$$

The induced polarization that goes into the above relation is calculated by equation (29), where the polarizability is now a sum of both the electronic and the ionic polarizability, and the field is the local field solution of equation (3) when an external electric field is present.

In the tetragonal phase, the linear effect is dominant and now the quadratic contribution is neglected to write the expression for the linear electro-optic constant (Appendix A) as

$$r_{33} - \left(\frac{n_o}{n_e}\right)^3 r_{13} = \frac{2(n_e - n'_z)}{n_e^3 E_z} \quad (33)$$

In this expression, n_o and n_e are the zero-field refractive indices along the 'a' axis and 'c' axis, respectively. n'_z is the refractive index along the 'c' axis in the presence of the applied field.

III. Perovskite Ferroelectrics

General Properties

The perovskite ferroelectrics are a large number of materials having the chemical formula ABO_3 , where generally A is a metal, B is a transition element, and O is oxygen. This family is a member of still a larger family entitled the oxygen-octahedra family, and is itself divided into smaller families. Barium titanate and lead titanate belong to one of the smaller families where the A atom is bi-valent and the B atom is tetra-valent. The perovskite ferroelectrics meet the additional requirement that their structures are similar to that of perovskite ($CaTiO_3$) at room temperature (Figure 1). This material from which the family took its name has since been shown to have a slightly distorted cubic structure at room temperature (Ref 15:10).

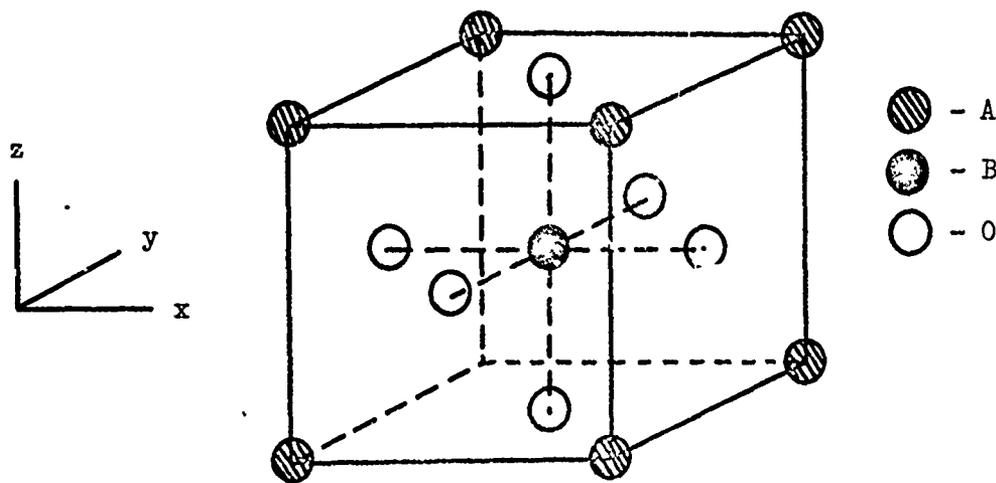


Fig. 1. Cubic Perovskite Structure

The materials must of course also satisfy the definition of a ferroelectric. Although at first this might seem a trivial matter, it is not, as has been shown by a number of attempts to clearly define the properties

of ferroelectrics. This problem continues even up to the present due to the difficulty of classifying the many new solutions and mixtures of these materials. However, the following definition discussed in length by Bogdanov (Ref 2:591) appears to be the most basic and clearest - "ferroelectric materials are those which in some range of temperature show spontaneous polarization, the direction of which may be changed by an external electric field."

The perovskites do not generally have the cubic structure of Figure 1, but their structures can be described in terms of the cubic structure as slight expansions or contractions along an axis or diagonal. For barium titanate, these structures are tetragonal, orthorhombic, and trigonal over different temperature ranges. The tetragonal structure is the simplest and consists of an expansion along one axis ('c' axis) and a contraction along the other two axes ('a' and 'b' axes). At high enough temperatures, these ferroelectrics do attain a cubic structure and lose their ferroelectric properties. This transition temperature is called the 'curie' temperature and the higher temperature phase is called the paraelectric phase in analogy with the ferromagnetic to paramagnetic transition.

In applying the point-dipole model to the perovskite crystal, the crystal lattice must be divided into sub-lattices which have the periodicity assumed in the development of the model. The sub-lattices required for the perovskite crystal are (see Figure 1):

1. Barium ion lattice
2. Titanium ion lattice
3. Oxygen I ion lattice (in yz plane)
4. Oxygen II ion lattice (in xz plane)
5. Oxygen III ion lattice (in xy plane)

Lead Titanate

Lead titanate exists in the cubic perovskite structure above 490°C and in a tetragonal structure below this temperature. This high curie temperature has been attributed to a higher polarizability of the lead ion than that of the barium ion (Ref 1:1433). Although some anomalies were seen in dielectric constant measurements at temperatures lower than room temperature (Ref 13), it has not been established that it goes through any additional transitions at lower temperatures.

The transition to the tetragonal structure involves more than the simple expansion and contraction along the crystallographic axes of the cubic structure as mentioned above. It also involves shifts of the ions away from their symmetrical lattice positions. No satisfactory explanation exists for the condition causing these shifts, but the situation does result in internal fields that are no longer zero at the various ion sites. The fields at the ion sites tend to polarize the ions, producing dipoles whose fields further affect the fields and ions at other lattice sites. Since the polarizabilities depend on the crystal's electric fields, it is these deviations from a cubic perovskite lattice that can be related to the ferroelectric properties of the barium titanate-type perovskites.

The basic PbTiO_3 crystal dimensions were determined by Shirane and Hoshino (Ref 22:268) in 1950 by x-ray diffraction analysis. Their results for crystal lattice dimensions versus temperature in the tetragonal and cubic phase are shown in Figure 2, and are listed along with other crystal physical properties in Table I.

The ion positions have been determined by Shirane and co-workers (ref 21:136) and the accepted model is shown in Figure 3.

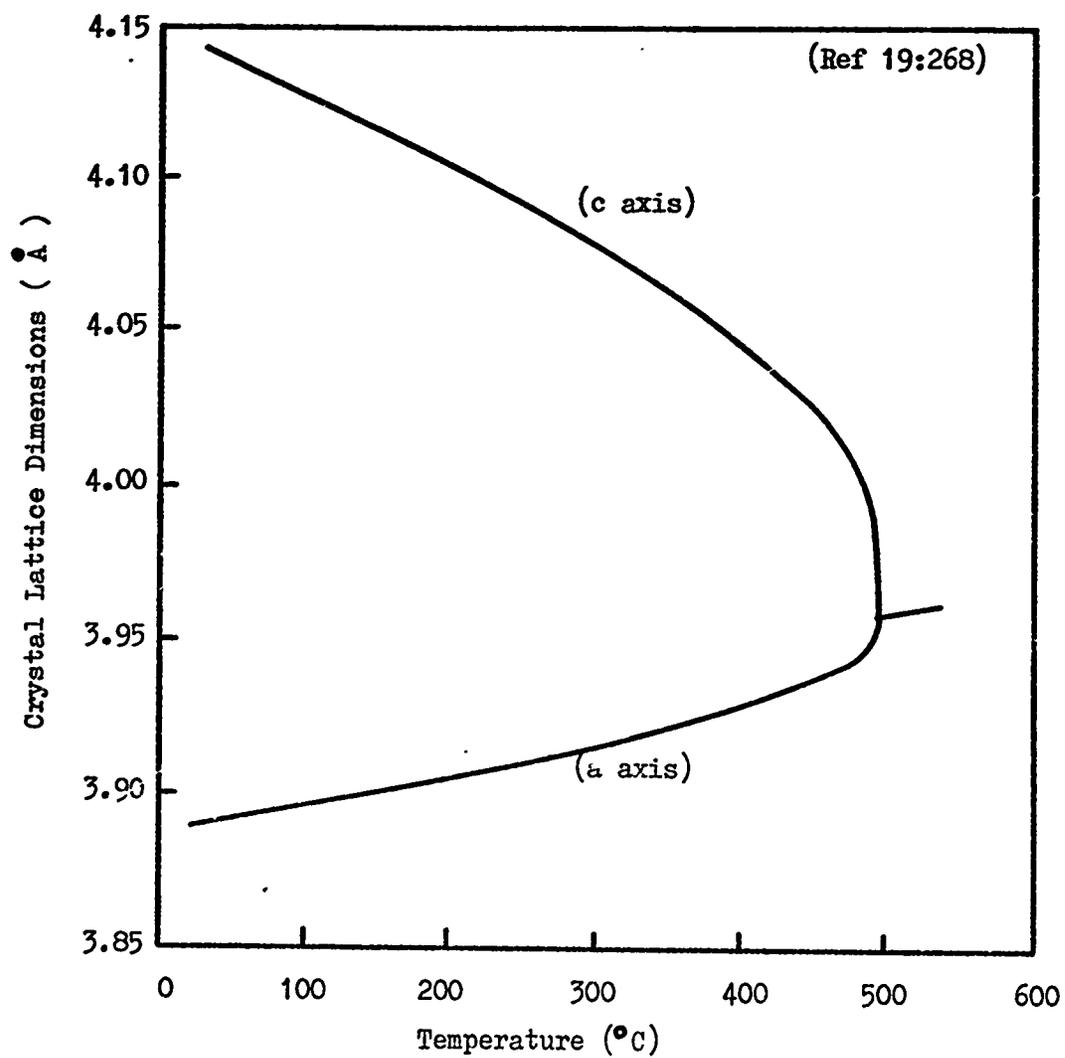


Fig. 2. PbTiO_3 Crystal Lattice Dimensions vs. Temperature
(Experimental)

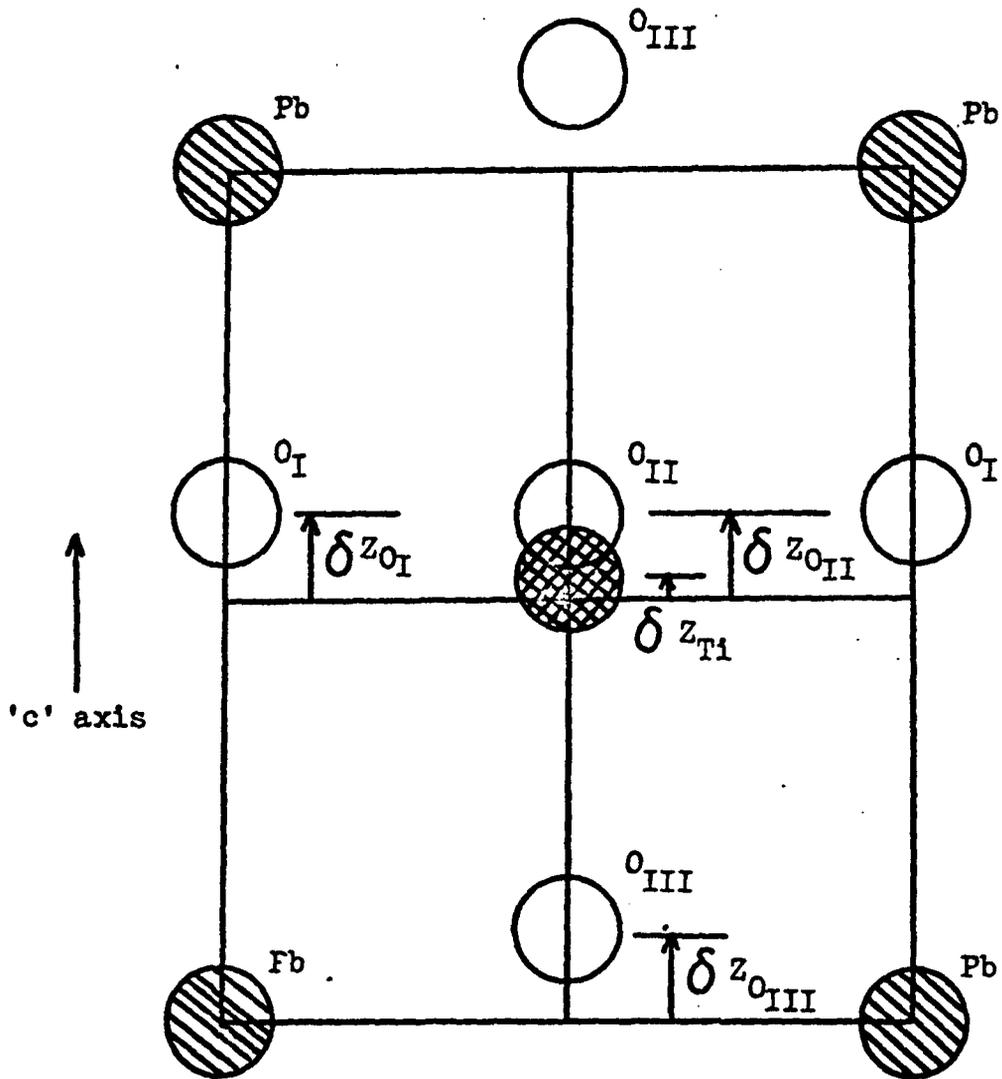
Table I.

PbTiO₃ Crystal Lattice Parameters

Temperature (°C)	c axis (Å)	a axis (Å)	c/a	Unit Cell Vol. (Å ³)
30	4.140	3.894	1.063	62.77
110	4.125	3.899	1.058	62.72
200	4.104	3.907	1.050	62.65
300	4.081	3.918	1.041	62.65
325	4.073	3.921	1.039	62.61
350	4.066	3.923	1.037	62.58
400	4.046	3.930	1.029	62.49
410	4.041	3.933	1.028	62.50
425	4.036	3.934	1.026	62.45
440	4.030	3.936	1.024	62.43
450	4.028	3.937	1.023	62.44
460	4.021	3.938	1.021	62.37
470	4.016	3.942	1.019	62.31
480	4.011	3.942	1.018	62.31
490	3.958	3.958	1.000	62.03
510	3.959	3.959	1.000	62.05
525	3.960	3.960	1.000	62.09
535	3.960	3.960	1.000	62.10
* 800	3.964	964	1.000	

* (Ref 4:65)

(Ref 22:267)



$$\delta z_{Ti} = + 0.040$$

$$\delta z_{O_I} = \delta z_{O_{II}} = \delta z_{O_{III}} = + 0.112$$

(Note: δz 's are ratio of the atom's shift distance to 'c' axis dimension)

Fig. 3. PbTiO_3 Tetragonal Crystal Lattice

A very distinguishing characteristic of PbTiO_3 among the perovskite ferroelectrics is the natural birefringence exhibited by the tetragonal phase. This natural birefringence has been measured by Shirane (Ref 21:140) and by Fesenko (Ref 5:55). Figure 4 shows the results obtained by Shirane for PbTiO_3 . To emphasize the distinguishing behavior, Figure 5 shows the natural birefringence exhibited by BaTiO_3 (Ref 19:95), which is more representative of other perovskite ferroelectrics. The sharp difference in values at room temperature and in the behavior with temperature can be easily seen.

It must be pointed out that it is more difficult to work experimentally with PbTiO_3 than with BaTiO_3 , due to greater difficulty in producing single-domain, or even multi-domain, single crystals of PbTiO_3 . Measurements are hampered by the higher fields required to reverse the polarization in PbTiO_3 and by conductivities large enough to influence dielectric hysteresis measurements. Because of these difficulties, some of the reported parameter values, needed for comparisons with the model's predictions, have involved approximations that reduce their credibility. This is true for the electro-optic constants. Other parameters, such as the natural birefringence and other basic properties are well established, however, and should provide a good test for the model.

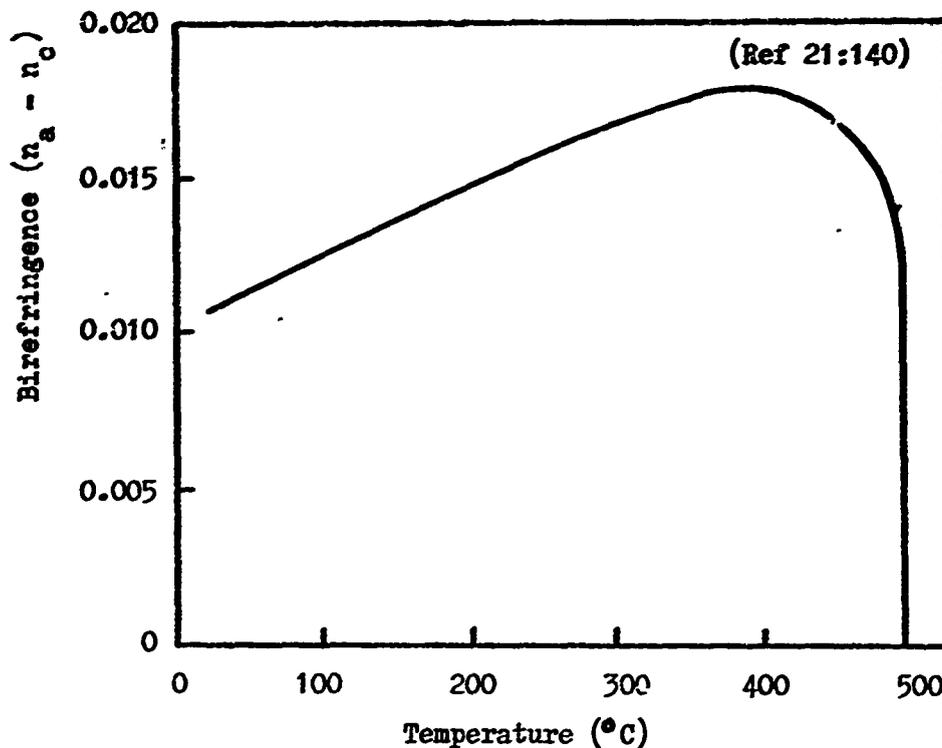


Fig. 4. Natural Birefringence in Tetragonal PbTiO₃ (Experimental)

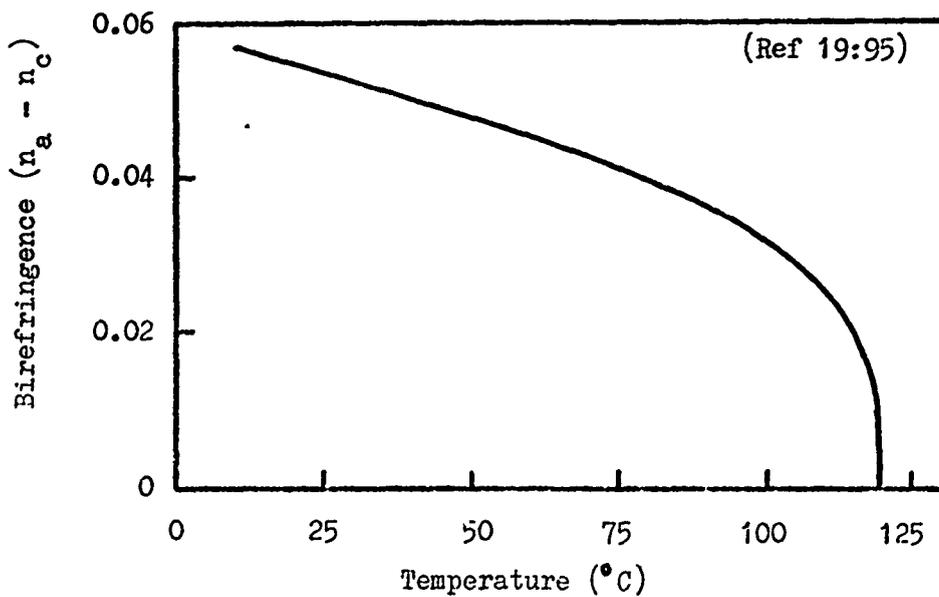


Fig. 5. Natural Birefringence of Tetragonal BaTiO₃ (Experimental)

IV. Lorentz Factors

As mentioned in discussing the model, the Lorentz factors for the perovskite crystal cannot be approximated by a value of $1/3$. The Lorentz factors must be calculated with every lattice change, with the exception of changes in the cubic phase. More specifically, in the tetragonal phase, where every change in temperature produces a change in the c/a ratio, new Lorentz factors must be calculated at each new temperature. In the cubic phase, the three crystal axes dimensions are equal and increase equally with temperature, therefore, once the Lorentz factors have been calculated at any temperature within the cubic phase, these same factors can be used at any temperature in that phase.

The crystal dimensions and ion shifts, used in calculating Lorentz factors at the different temperatures considered, were taken from Table I and Figure 3, respectively. The one exception was the value of the 'a' axis at room temperature, where a value of 3.899 \AA was used as an average of the values measured by various investigators.

The Lorentz factors for the tetragonal phase at room temperature and for the cubic phase at the Curie temperature are given in Table II and Table III, respectively. The cross-terms are not included because they are equal to zero due to the crystal lattice symmetry.

Table II.

Lorentz Factors L_{ij}^{ab} for Tetragonal Lead TitanateLattice Dimensions $a = 3.899 \text{ \AA}$ $b = 3.899 \text{ \AA}$ $c = 4.155 \text{ \AA}$

	Lead	Titanium	Oxygen I	Oxygen II	Oxygen III
'b' ions					
'a' ions					
Lorentz Factors - xx					
Pb	0.3649392396	0.3081119692	-0.3738510555	0.7530951459	0.6584880615
Ti	0.3081119692	0.3649392396	2.7140829244	-0.8734540645	-0.8565762191
Oxy I	-0.3738510555	2.7140829244	0.3649392396	0.7154441960	0.5855636166
Oxy II	0.7530951459	-0.8734540645	0.7154441960	0.3649392396	-0.3206924778
Oxy III	0.6584880615	-0.8565762191	0.5855636166	-0.3206924778	0.3649392396
Lorentz Factors - yy					
Pb	0.3649392396	0.3081119692	0.7530951459	-0.3738510555	0.6584880615
Ti	0.3081119692	0.3649392396	-0.8734540645	2.7140829244	-0.8565762191
Oxy I	0.7530951459	-0.8734540645	0.3649392396	0.7154441960	0.5855636166
Oxy II	-0.3738510555	2.7140829244	0.7154441960	0.3649392396	-0.3206924778
Oxy III	0.6584880615	-0.8565762191	-0.3206924778	0.5855636166	0.3649392396
Lorentz Factors - zz					
Pb	0.2701215208	0.3837760616	0.6207559095	0.6207559095	-0.3169761229
Ti	0.3837760616	0.2701215208	-0.8406288599	-0.8406288599	2.7131524382
Oxy I	0.6207559095	-0.8406288599	0.2701215208	-0.430883920	0.7351288613
Oxy II	0.6207559095	-0.8406288599	-0.430883920	0.2701215208	0.7351288613
Oxy III	-0.3169761229	2.7131524382	0.7351288613	0.7351288613	0.2701215208

Table III.

Lorentz Factors L_{ij}^{ab} For Cubic Lead Titanate

Lattice Dimensions $a = 3.958 \text{ \AA}$ $b = 3.958 \text{ \AA}$ $c = 3.958 \text{ \AA}$

'b' ions	Lead	Titanium	Oxygen I	Oxygen II	Oxygen III
'a' ions					
Lorentz Factors - xx					
Pb	0.3333333333	0.3333333333	-0.3564226842	0.6782113421	0.6782113421
Ti	0.3333333333	0.3333333333	2.7271864068	-0.8635932034	-0.8635932034
Oxy I	-0.3564226842	2.2771864068	0.3333333333	0.6782113421	0.6782113421
Oxy II	0.6782113421	-0.8635932034	0.6782113421	0.3333333333	-0.3564226842
Oxy III	0.6782113421	-0.8635932034	0.6782113421	-0.3564226842	0.3333333333
Lorentz Factors - yy					
Pb	0.3333333333	0.3333333333	0.6782113421	-0.3564226842	0.6782113421
Ti	0.3333333333	0.3333333333	-0.8635932034	2.7271864069	-0.8635932034
Oxy I	0.6782113421	-0.8635932034	0.3333333333	0.6782113421	0.6782113421
Oxy II	-0.3564226842	2.7271864069	0.6782113421	0.3333333333	-0.3564226842
Oxy III	0.6782113421	-0.8635932034	-0.3564226842	0.6782113421	0.3333333333
Lorentz Factors - zz					
Pb	0.3333333333	0.3333333333	0.6782113421	0.6782113421	-0.3564226842
Ti	0.3333333333	0.3333333333	-0.8635932034	-0.8635932034	2.7271864067
Oxy I	0.6782113421	-0.8635932034	0.3333333333	-0.3564226842	0.6782113421
Oxy II	0.6782113421	-0.8635932034	-0.3564226842	0.3333333333	0.6782113421
Oxy III	-0.3564226842	2.7271864067	0.6782113421	0.6782113421	0.3333333333

V. Refractive Index and Electronic Polarizabilities

Electronic polarizabilities reported in the literature have been determined by the requirement that they predict correct refractive indices through the Lorenz-Lorentz equation. The procedure is to consider a number of different materials containing different combinations of the ions whose polarizabilities are desired. By 'trial-and-error', electronic polarizabilities are assigned to the individual ions and then summed to satisfy the molecular compositions of the different materials. The correct polarizabilities are determined to be those that are most consistent in predicting the correct refractive indices for the materials considered. A study of this type has been done by Tessman, Kahn, and Schockley (Ref 26) for a number of atoms including lead, titanium, and oxygen. Polarizabilities obtained by this method, however, can be considered to be only approximately correct for two reasons. First, the Lorenz-Lorentz equation has been shown to hold for materials with a cubic lattice, but in the above study, many non-cubic materials were included. And second, an ion's electronic polarizability should not be expected to be a constant, it should depend on its environment (Ref 12:166). Slight variations of the reported values may therefore be necessary for good predictions of the refractive index for a particular material.

The approximate polarizabilities determined by the above method are here used and varied in equation 4, using correct Lorentz factors, to match the experimental cubic phase refractive index at the Curie temperature. The electronic polarizabilities of oxygen and titanium that satisfy the refractive index of BaTiO_3 have been determined by Wunsch. These values are 2.322 \AA^3 and 0.19 \AA^3 , respectively (Ref 27:30).

Since the environments of these ions are identical in the cubic phase of both materials, with the exception of replacing barium by lead, their electronic polarizabilities were held constant at the above values and the reported lead value was varied to satisfy a refractive index equal to 2.72 (Ref 24:4792) for cubic PbTiO_3 at its curie temperature.

Tessman (Ref 26:893) reports the electronic polarizability of lead to be 4.79 \AA^3 , while Fedulov (Ref 4:67) reports a value of 4.32 \AA^3 .

In doing the calculations, the lead value was varied from below 3.00 \AA^3 to 5.00 \AA^3 . The first set of calculations done for a lattice dimension of 3.960 \AA showed that the lead electronic polarizability had to be extended below 3.0 \AA^3 before the 2.72 refractive index value could be obtained (Figure 6). The other curves in the figure correspond to larger values of the lattice dimensions and give an idea of the error that may be expected in the calculated refractive index due to errors in the measured lattice dimensions. Since the measurement error is less than the difference between the lattice dimension corresponding to the upper and lower curve in the figure, the calculation error due to uncertainty in the lattice dimension should be small. The lead electronic polarizability required to match the refractive index at a lattice dimension of 3.958 \AA is 2.90 \AA^3 . Table IV summarizes these values, which will be used throughout the remaining calculations, both in the cubic and tetragonal phase. In the tetragonal phase, these values are the isotropic electronic polarizabilities that go into equation 10.

The 2.90 \AA^3 lead value is much lower than the two values reported in the literature. A close study of Tessman's value, however, shows that 2.90 \AA^3 may not be an unreasonable value. The original source of the 4.32 \AA^3 value was not available for further consideration.

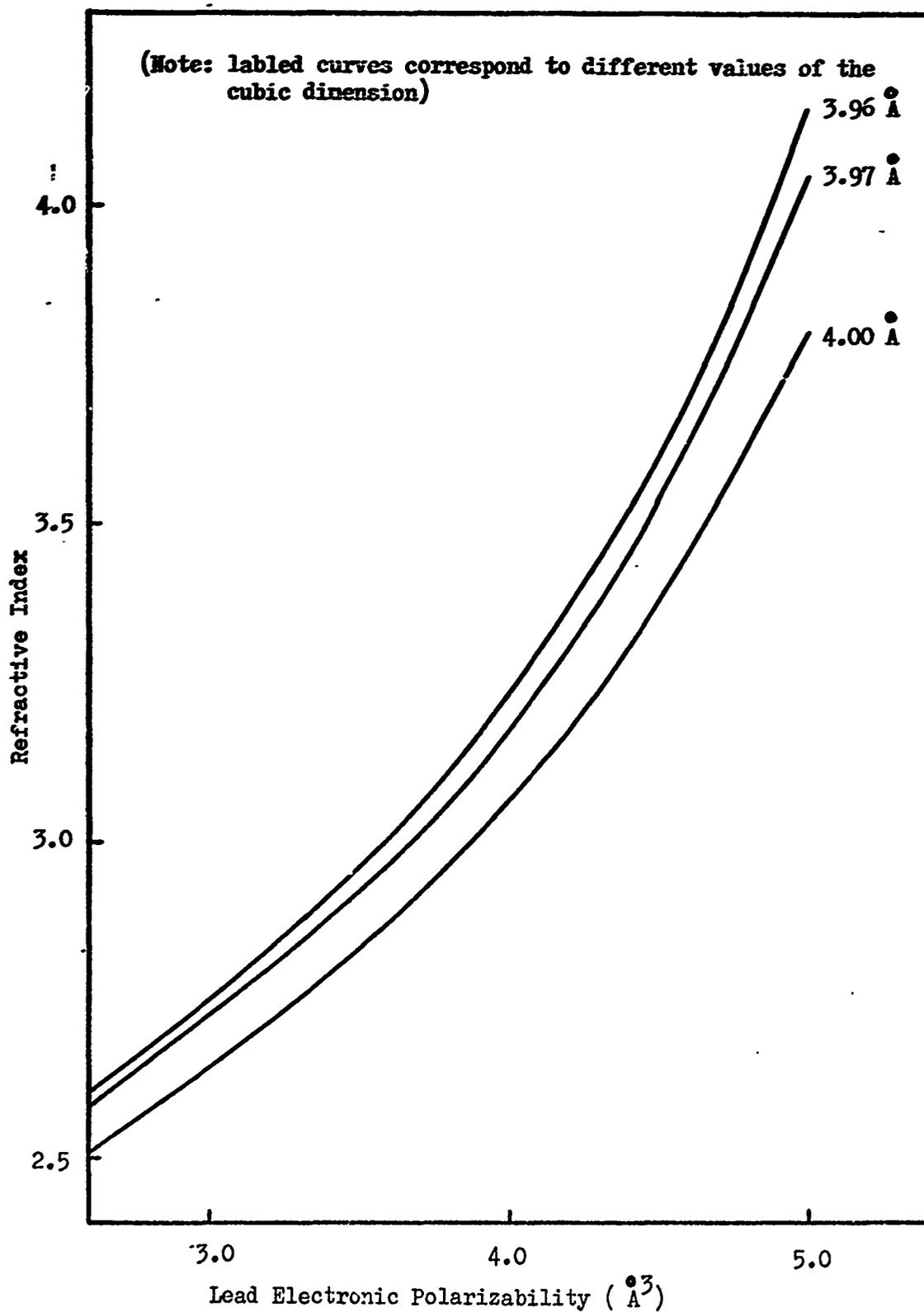


Fig. 6. Refractive Index vs. Lead Electronic Polarizability in Cubic PbTiO_3 (Theoretical)

Table IV.

Electronic Polarizabilities for Ions in PbTiO_3

Ion	Electronic Polarizability
Pb	2.90 \AA^3
Ti	0.19 \AA^3
O	2.322 \AA^3

VI. Dielectric Constants and Total Polarizabilities

The procedure used in determining the total polarizabilities that have been reported in the literature, is similar to the one for electronic polarizabilities from the previous section. By using the Clausius-Mossotti equation, total polarizabilities are established for a number of ions by requiring that they be consistent with the dielectric constants of a number of materials involving the ions. This has been done by Roberts (Ref 17, 18) .

Here, as with the electronic polarizabilities, total polarizabilities are established by equation 4 using correct Lorentz factors to match the dielectric constant of cubic PbTiO_3 at the Curie temperature and of tetragonal PbTiO_3 at room temperature. The experimental dielectric constants to be matched are 10,000 for the cubic phase (Ref 16:41) and 210 and 120 for the tetragonal 'a' and 'c' axis, respectively (Ref 7:549).

As with the electronic polarizabilities, Wunsch (Ref 27:87) has shown that total polarizabilities of 0.875 \AA^3 and 2.8518 \AA^3 for titanium and oxygen, respectively, satisfy the dielectric constant of cubic BaTiO_3 . An attempt, however, to match the dielectric constant of cubic PbTiO_3 at the Curie temperature by using the above values for titanium and oxygen and varying the lead's value around Roberts' value, 7.1 \AA^3 (Ref 17:866) resulted in negative dielectric constants.

The negative dielectric constants may be explained by considering equation 4 , where the presence of negative local field factors (summation term in equation 6, being larger than one) can result in negative dielectric constants. At any one temperature, the Lorentz factors and unit cell volume are fixed and therefore only the polarizabilities may

be varied to correct the situation. The Lorentz factors, however, contain both positive and negative terms and so it is not clear which polarizabilities should be increased or decreased to produce the desired results. It is necessary, therefore, to solve the complete set of equations for every variation, and this requires a very large number of calculations. To make this possible, the various computer programs responsible for the different parts of the model were combined into one program with the necessary modifications and additions to allow the variations to be done efficiently.

Once this was done, the polarizability variations consisted of two parts: 1) varying the values for lead from 4.5 \AA^3 to 7.7 \AA^3 and for oxygen from 2.672 \AA^3 to 2.852 \AA^3 while holding the titanium value constant at 0.19 \AA^3 , and 2) varying the lead and oxygen over the same range as in 1), but for values of titanium polarizabilities that were increased and decreased by 5, 10, and 50% of the ionic polarizability.

The results of the polarization variations were not as expected or hoped for. No variation was found that could simultaneously predict the experimental cubic and tetragonal dielectric constants. Instead, several variations were found to satisfy the cubic dielectric constant, and although only one region of polarizabilities satisfied simultaneously the tetragonal 'a' and 'c' axes, several satisfied the 'a' axis alone. Polarizabilities in the region that satisfied both tetragonal axes, however, resulted in mixed positive and negative local field factors, and this has been suggested as indicating antiferroelectric tendencies (Ref 28).

The promising polarizability combinations were used in extending the dielectric constant calculations with respect to temperature in

both the cubic and tetragonal phase. In the cubic phase, these polarizabilities were also used in calculating the electro-optic effects. It was hoped that these calculations, which are discussed in the following sections, would help to eliminate all but one combination.

VII: Calculations in the Cubic Phase

For the cubic PbTiO_3 crystal in the absence of external fields, the only interesting observations are the behavior of the refractive index and dielectric constant with temperature.

The calculated refractive index at different temperatures is shown in Figure 7. In this figure, the refractive index at the curie temperature is slightly smaller than the 2.72 value initially calculated. This is due to having reduced slightly the electronic polarizabilities in an attempt to reduce the quadratic electro-optic discussed in a later chapter. No experimental values of the refractive index were found for comparison at temperatures other than the curie temperature.

The dielectric constant's change with temperature is much larger than the refractive index's change. Calculations were done for the different combinations of total polarizabilities that satisfied the dielectric constant at the curie temperature. A few of the calculated curves that best show the effects of using different polarizabilities, are plotted in Figure 8. Since the experimental dielectric constant versus temperature has been shown to satisfy the Curie-Weiss law

$$\epsilon = \frac{C}{T - T_0} \quad (34)$$

for a Curie constant $C = 4.11 \cdot 10^5$ and a Curie-Weiss temperature $T_0 = 449^\circ\text{C}$ (Ref 16:41), the curve meeting these conditions is shown for comparison.

Comparison between the theoretical curves and the Curie-Weiss fit show that: If the theoretical curve (#3) is picked to fit at the curie temperature, then it falls far below at higher temperatures. And, if

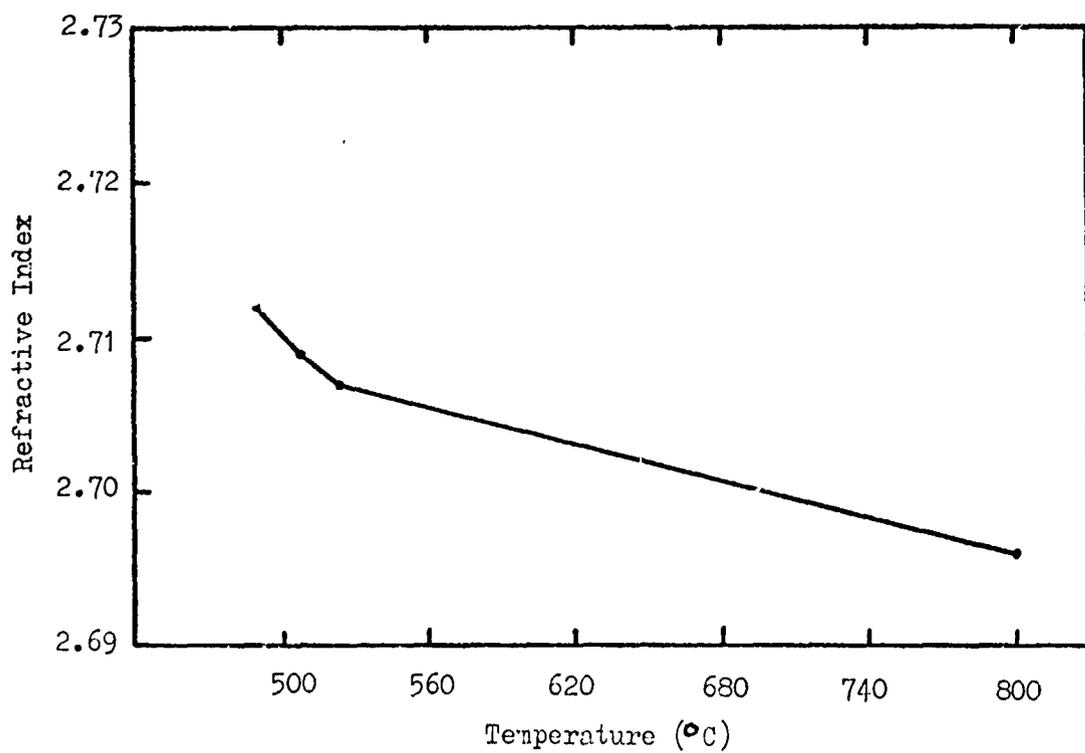


Fig. 7. Refractive Index vs. Temperature for Cubic PbTiO₃
(Theoretical)

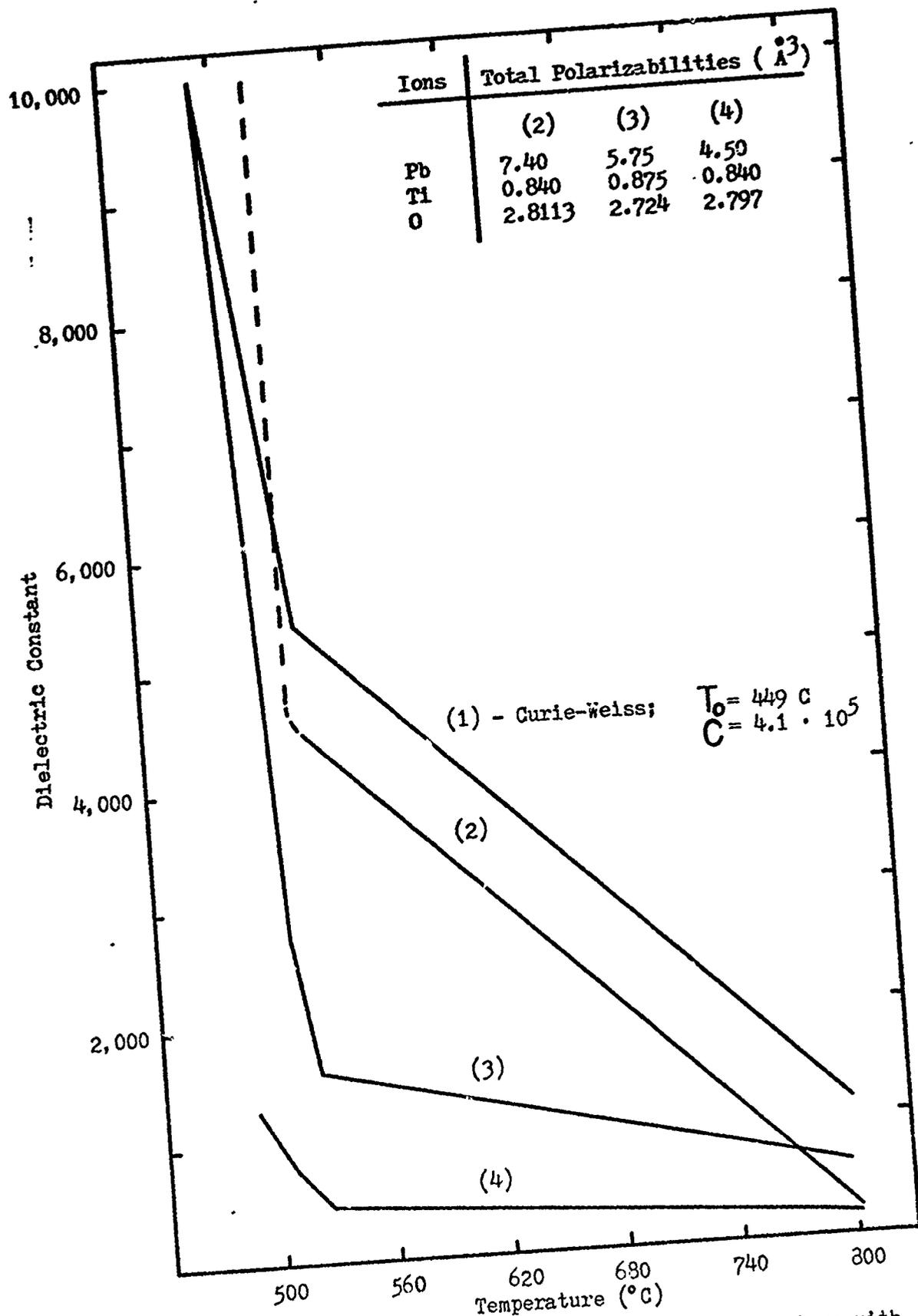


Fig. 8. Cubic PbTiO_3 Dielectric Constant vs. Temperature with Comparison to Curie-Weiss Fit (Theoretical - for various Polarizabilities)

the theoretical curve (#2) is raised towards the Curie-Weiss curve at higher temperatures. then it has gone to infinity at the curie temperature. Curve #3 was the most satisfactory and, as will be seen in a later chapter, the corresponding polarizabilities give the best results in the quadratic electro-optic calculations.

VIII. Calculations in the Tetragonal Phase

Dielectric Constants

As was discussed in Chapter VI, various combinations of total polarizabilities were found to produce the required dielectric constant along the 'a' axis at room temperature. Matching both the 'a' and 'c' axes experimental dielectric constant, however, could only be done for a combination that showed mixed positive and negative local field factors. A number of these combinations have been used to calculate the dielectric constant behavior with temperature in the tetragonal phase to help in selecting a unique set for this phase. The results of two calculations are presented here.

The dielectric constants, for the polarizabilities that matched both axes at room temperature, along both axes at various temperatures are given in Figure 9. The 'c' axis dielectric constant shows a gradual rise at low temperatures, then a more rapid rise and finally rises very steeply at temperatures approaching the transition temperature. This is the desired behavior for both axes (Ref 7). The 'a' axis is unsatisfactory, dropping throughout the temperature range with no increase even at temperatures approaching the transition temperature. The 'a' axis dielectric constant behavior wasn't too surprising, as the effect of the mixed negative and positive local field factors with temperature was difficult to predict.

The second set of results presented here are for polarizabilities with the same titanium value as above, but for lower lead and oxygen values. At these lower values, the local field factors are all positive and the results for the 'a' axis now show a satisfactory behavior while the 'c'

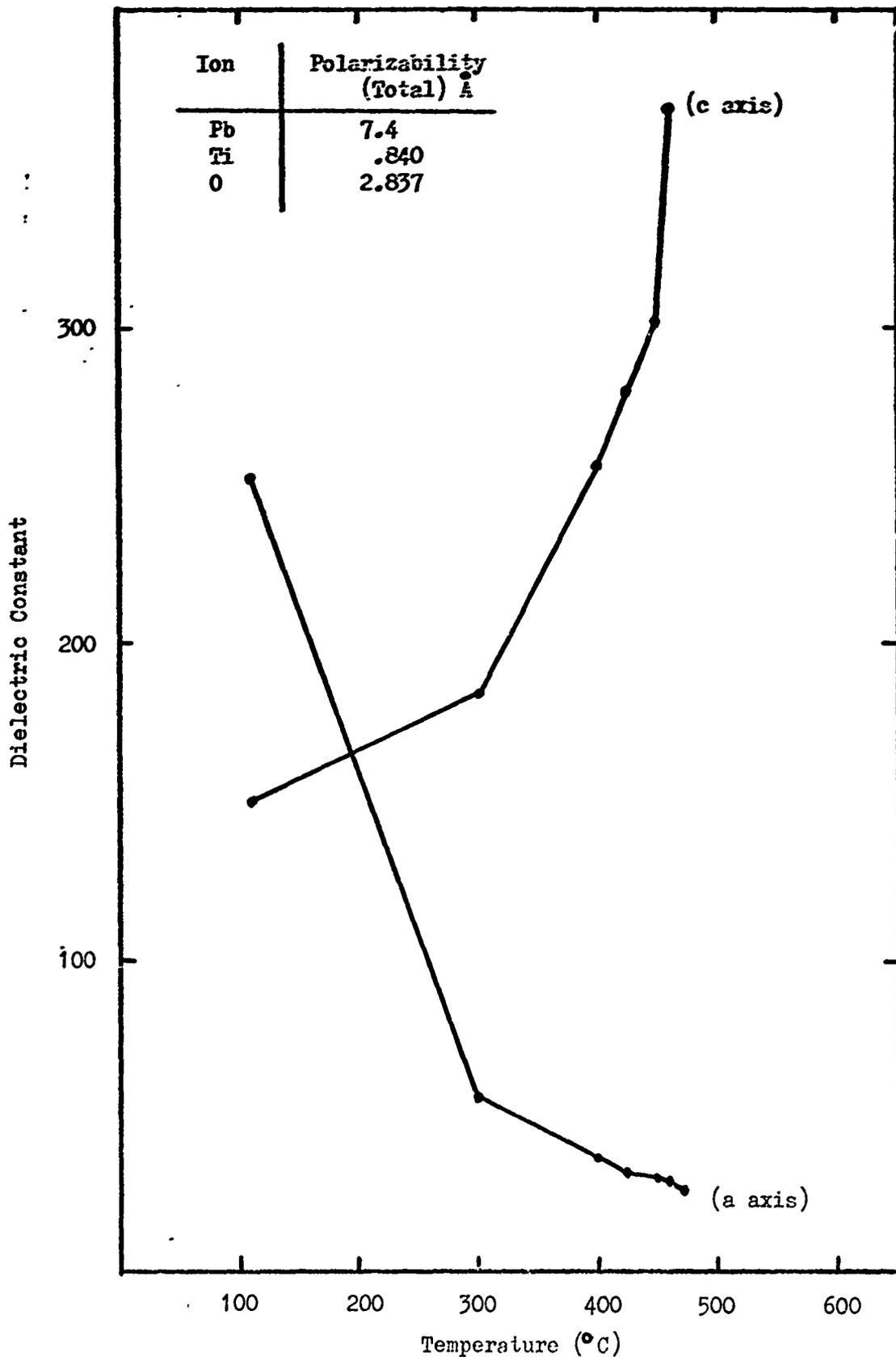


Fig. 9. Dielectric Constants vs. Temperature in Tetragonal PbTiO_3 - High Lead Polarizability (Theoretical)

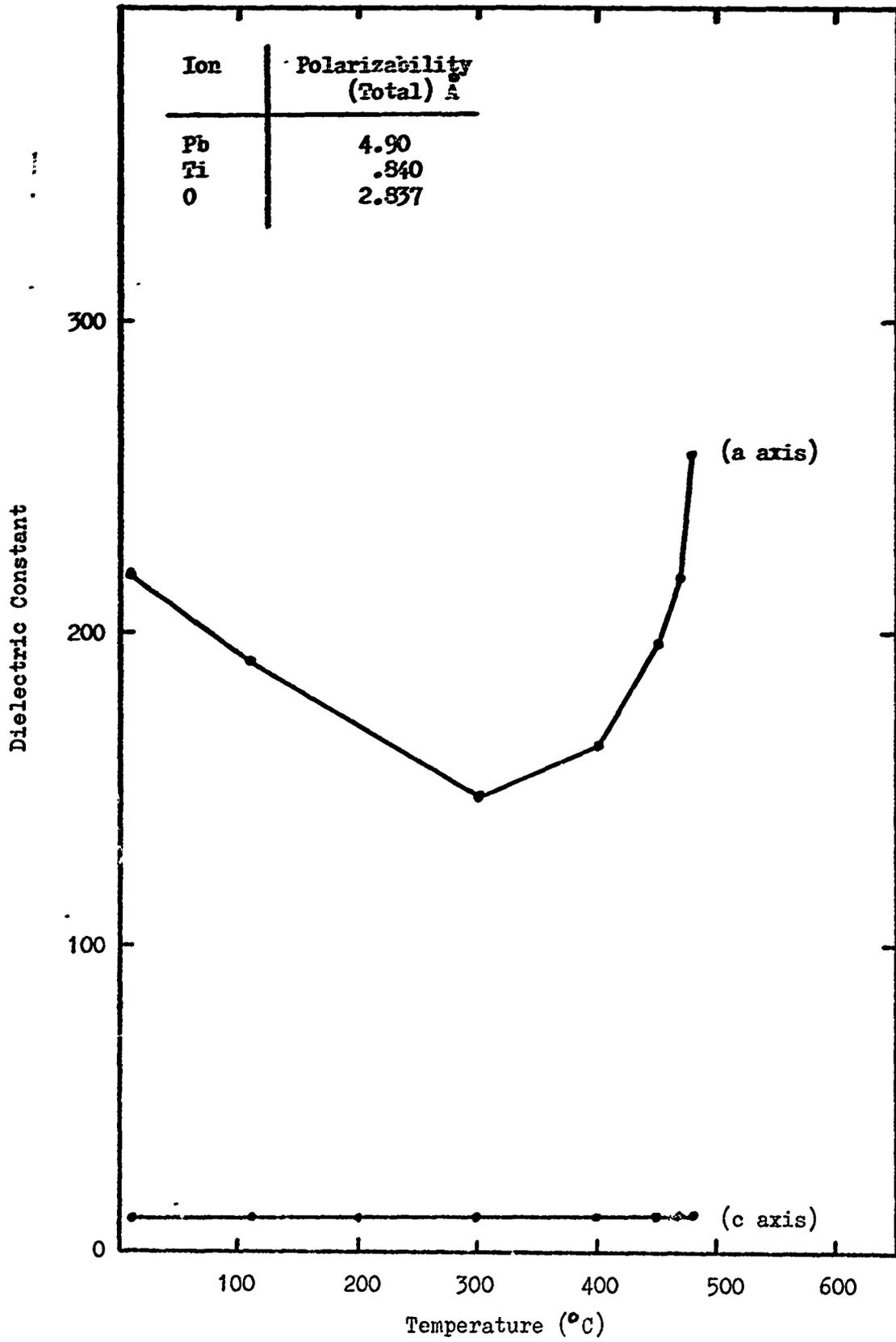


Fig. 10. Dielectric Constants vs. Temperature in Tetragonal $PbTiO_3$ - Low Lead Polarizability (Theoretical)

axis results remained very low throughout (Figure 10). The low value of the 'c' axis dielectric constant was characteristic of the calculations at other polarizabilities. It appears to be due to a very large effect of the local fields on the polarizabilities.

Covalent-ionic Bonding Factors

As was noted above, a very large anisotropy was exhibited by the dielectric constant in the tetragonal phase calculations. This large anisotropy which is partially produced by the crystal's internal electric fields via the field-dependent electronic polarizabilities, is also exhibited by the refractive index. At room temperature, the natural birefringence was calculated to be approximately 0.70 compared to the experimental value of approximately 0.01 . In this section, covalent-ionic bonding factors are established for reducing the local fields at the ion sites, in an effort to reduce the large anisotropies.

The covalent-ionic bonding factor was varied in two ways. The bonding factor was first given the same value at all bonds and varied from 0.0 to 1.0 . Then, the factor was given different values at the different bonds. The reason for treating the bonds individually was because Wunsch found that two different values of this factor were required to match the experimental values of natural birefringence and spontaneous polarization for BaTiO_3 . It was hoped that by allowing different values of covalent bonding at the different bonds (seemingly a truer physical situation), the correct birefringence and spontaneous polarization might be calculated for only one set of covalent bonding factors.

To understand how the bonding factors were determined, refer to

Figure 11, of a unit cell in the perovskite crystal. If within that unit cell, a smaller cell is considered, such as that outlined by the heavy lines with one full ion at each lattice point, then the proper number and types of ions and bonds have been accounted for. The different bonding factors were determined by considering Shuvaev's report (Ref 23: 553) that in BaTiO_3 the minimum charge of the titanium ion is 1.6 units of electronic charge equivalent. With this in mind, a charge of 1.0 was assigned to the titanium in PbTiO_3 based on the comment that the higher polarizable lead ion increases the bond covalency between titanium and oxygen (Ref 1:1433). The next step was to give one-half of the charge lost by the titanium to the oxygen III ion, because of its nearness in the tetragonal phase, and to share the other half between the oxygen I and oxygen II ions. The lead ion was left with its full charge of +2.0. The resulting charge distribution is shown in Figure 11. The covalent-ionic bonding factors are now simply equal to the ratio of the final charge of the ion to its original full ionic charge.

A second set of bonding factors was determined by assuming that in addition to the charge distribution described above, the lead ion now loses a fourth of its charge equally to the oxygen I and oxygen II ions. The two sets of bonding factors are listed in Table V.

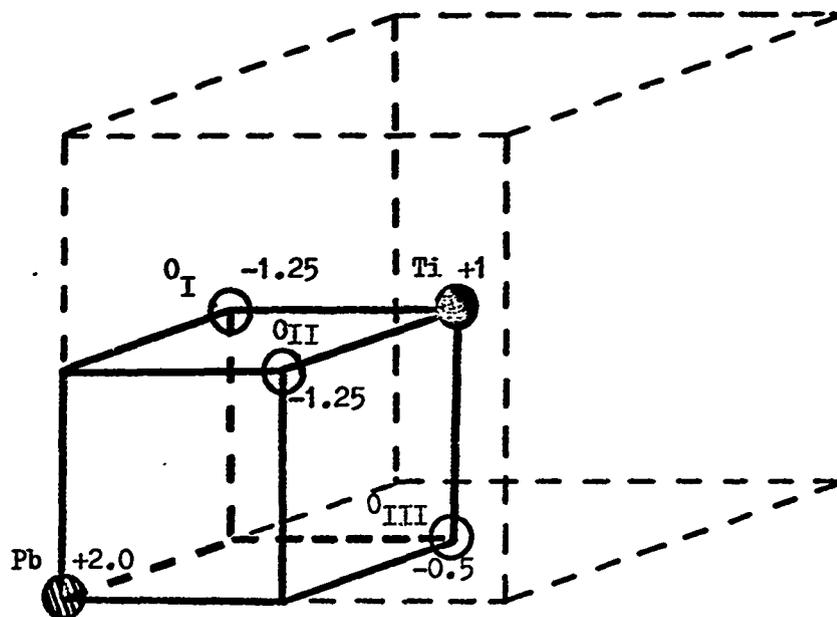


Fig. 11. 'Effective' Charges for Ions in Tetragonal PbTiO_3 (Arbitrary)

Table V.

Special Covalent-ionic Bonding Sets for PbTiO_3

Set	Pb	Ti	O_I	O_{II}	O_{III}
1	1.0	0.25	0.625	0.625	0.25
2	0.75	0.25	0.50	0.50	0.25

Natural Birefringence

As already mentioned in the previous section, the natural birefringence for the fully ionic crystal at room temperature was calculated to be approximately 0.70 ; a value almost 70 times larger than the experimental value of 0.01 from Figure 4 . In this section, the covalent-ionic bonding factor is employed in reducing the birefringence.

At room temperature, the natural birefringence was calculated for the various bonding factors discussed in the previous section: a simultaneous variation from 1.0 to 0.0 at all bonds and then the two sets from Table V . The results are shown in Figure 12 . The birefringence is seen to vary quite predictably from 0.198 to 0.68 for bonding factor values from 0.0 to 1.0 , respectively. The zero bonding factor may be physically unrealizable, but it does establish a minimum birefringence that may be calculated by the use of covalent-ionic bonding factors alone. The two X's in the figure correspond to the two special sets of factors from Table V .

The natural birefringence was also calculated as a function of temperature to determine if perhaps the qualitative behavior might be correct. The results (Figure 13) do not compare, as the birefringence continues to increase after 400°C , while the experimental curve (Figure 4) decreases above this temperature. This calculation corresponds to the fully ionic crystal.

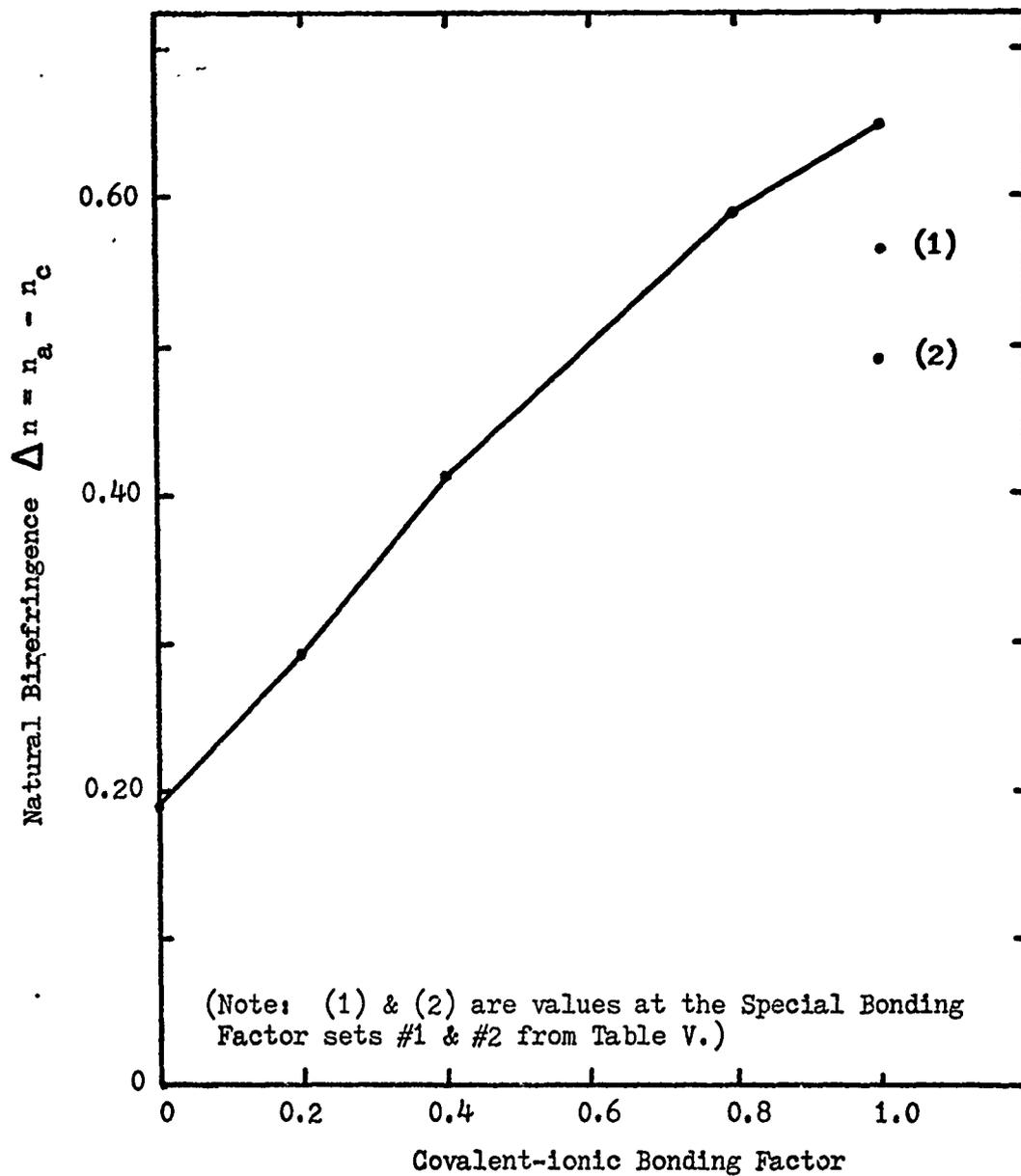


Fig. 12. Natural Birefringence vs. Covalent-ionic Bonding Factor for Room Temperature PbTiO_3 (Theoretical)

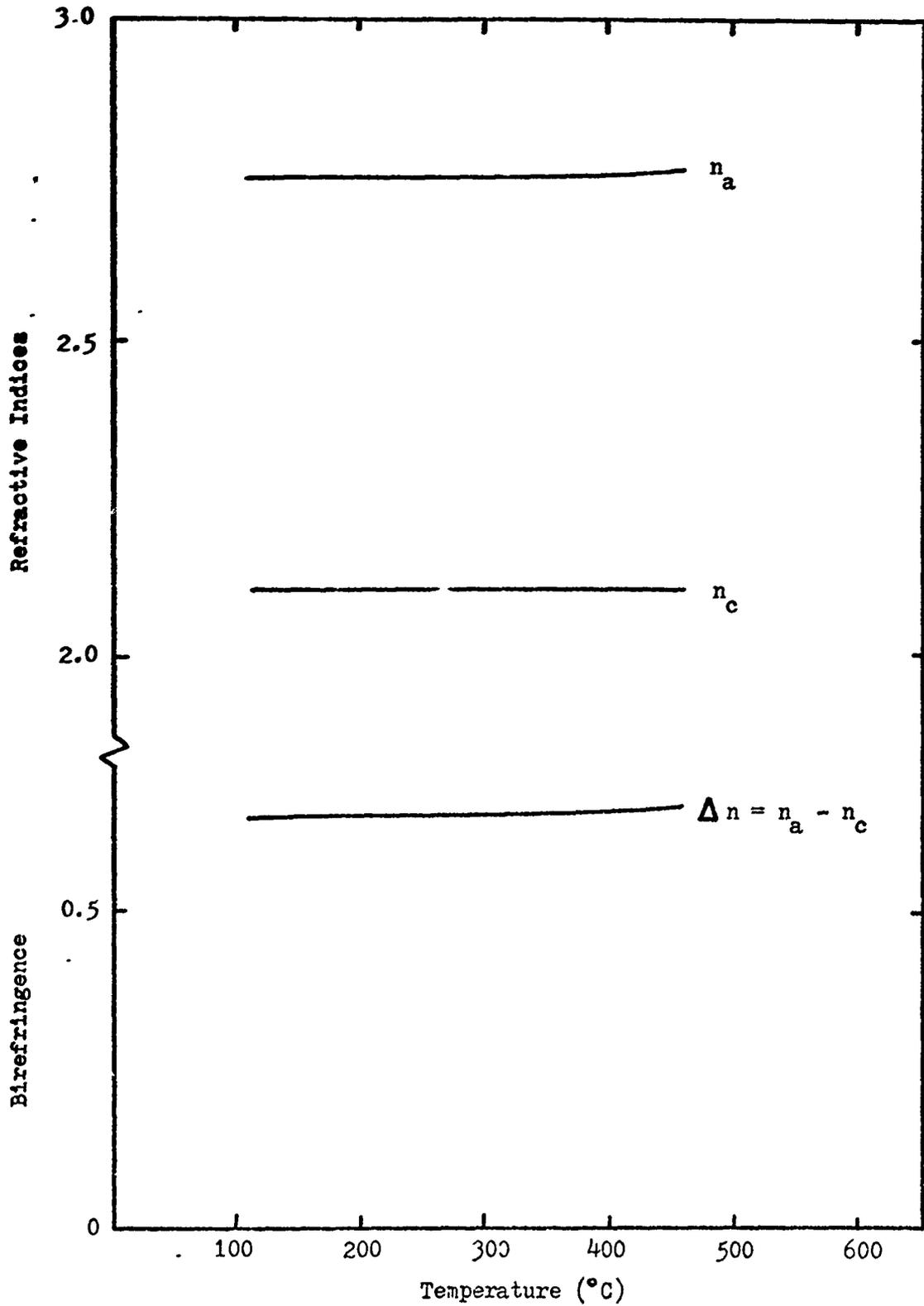


Fig. 13. Refractive Indices and Birefringence vs. Temperature for Full Ionic Tetragonal PbTiO₃ (Theoretical)

Spontaneous Polarization

The spontaneous polarization was calculated as a function of the covalent-ionic bonding factor at room temperature. In these calculations the experimental $75 \mu\text{C}/\text{cm}^2$ value (Ref 8:1230) was approximately matched by a covalent-ionic bonding factor equal to 0.7 and by special set #2 from Table V.

The spontaneous polarization was also calculated as a function of temperature for the full ionic crystal and is seen to increase from $85 \mu\text{C}/\text{cm}^2$ at room temperature to $88 \mu\text{C}/\text{cm}^2$ at 470°C , as compared to a reported value of $17 \mu\text{C}/\text{cm}^2$ at the transition temperature (Ref 16:44). No attempt has been made here to consider a possible decrease in the ratios of the ion shift distances to the 'c' axis dimension with increasing temperature, as exhibited by BaTiO_3 (Ref 19:163), since these measurements have not been reported for PbTiO_3 . Doing so, plus treating the crystal as only partially ionic, would result in a value closer to the reported value but would introduce undesired speculation at this point.

Discussion

Efforts to reduce the large natural birefringence and dielectric constant anisotropy via the covalent-ionic bonding factor have failed. An interesting result is that even for a covalent-ionic bonding factor equal to zero (removing all anisotropy in the polarizabilities), the natural birefringence is still approximately 0.20. Since under these conditions, only the physical structure, through the Lorentz factors is present to produce these results, it seems that this anisotropy can not be reduced further. In Chapter XI, this problem is considered by calculating the contribution from each individual mechanism in the model.

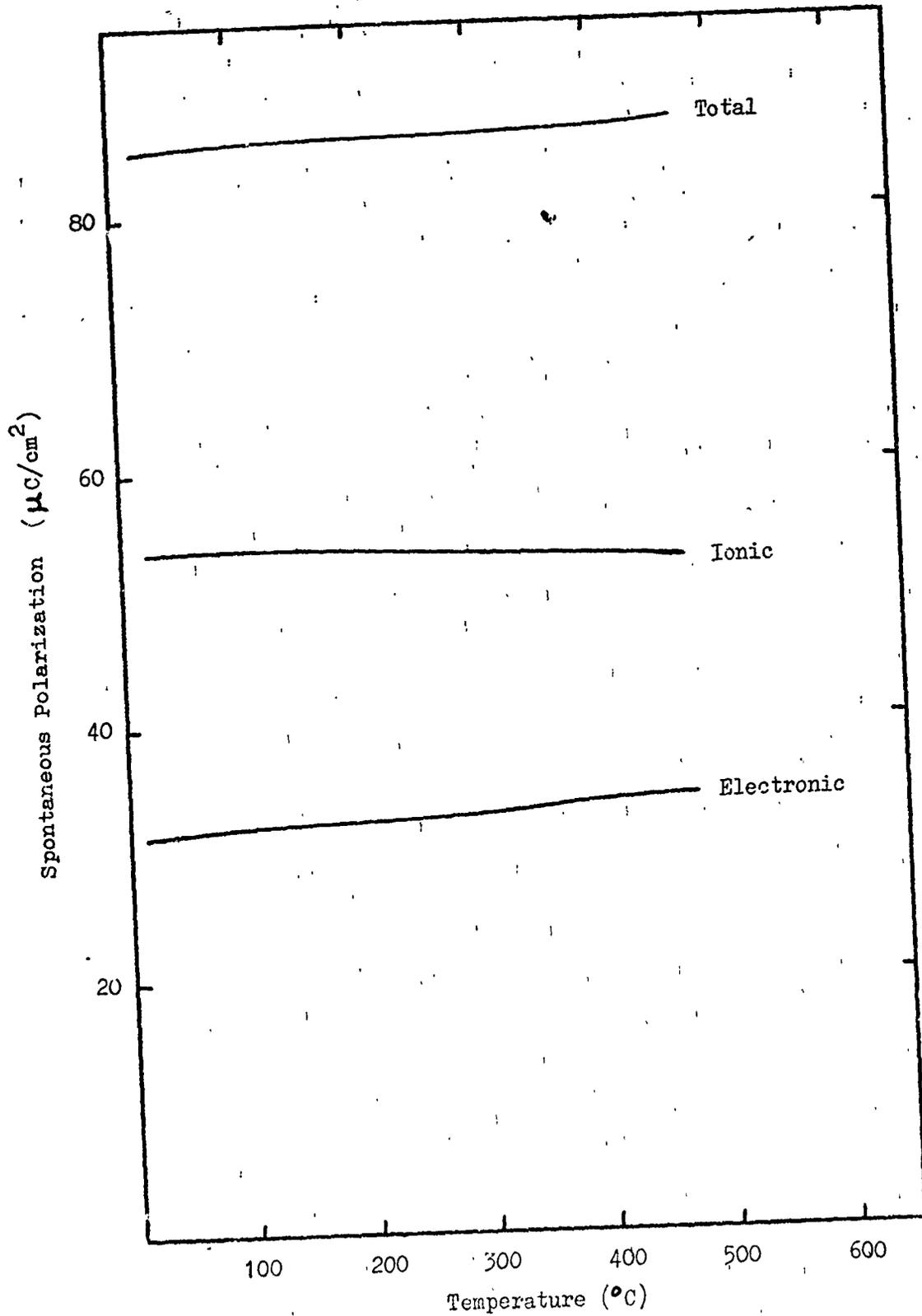


Fig. 14. Spontaneous Polarization vs. Temperature for Full Ionic Tetragonal PbTiO_3 (Theoretical)

IX. Electro-optic Calculations in the Cubic PhaseElectro-optic ($\epsilon_{11} - \epsilon_{12}$) Constant

Although the model has not been successful in calculating the values of the various parameters along the 'c' axis of tetragonal PbTiO_3 , it has been satisfactory in the cubic phase. The model is therefore used to calculate the anisotropy induced in the refractive index and dielectric constant by a 10^6 V/M electric field. The electro-optic constant discussed here is the quadratic ($\epsilon_{11} - \epsilon_{12}$) constant. This constant has been reported to have a value of approximately 0.01 for lead-containing perovskites (Ref 24:4790).

The electro-optic calculations were made for the different polarizabilities that predicted correct dielectric constants at the curie temperature. The results of these calculations are presented in Figure 15. A lead polarizability approximately equal to that of barium results in the lowest value of the quadratic electro-optic constant (curve #5). Going to lower or higher values of lead polarizability increased the constant. The lowest value (0.13), however, is an order of magnitude larger than the reported value, or approximately equal to the values for other barium titanate-type perovskites (Ref 24:4791). The high lead polarizability that had correctly predicted the 'c' axis dielectric constant at room temperature, resulted in the highest value for the electro-optic constant.

Other attempts were made to lower the calculated electro-optic constant. These attempts involved: 1) varying the oxygen total polarizability, and 2) varying the electronic polarizabilities of titanium and oxygen. No indications were seen that the 0.01 value could be

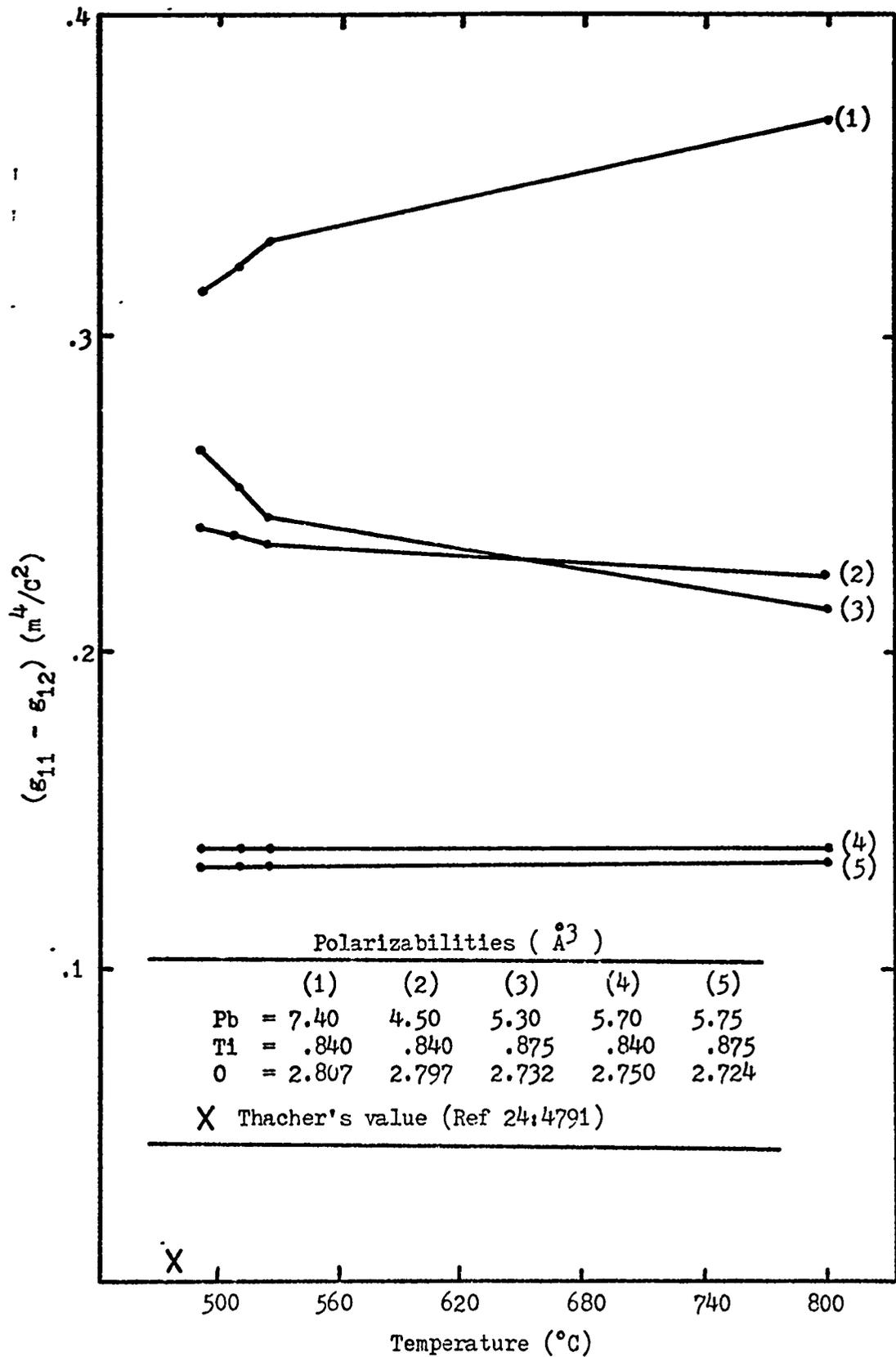


Fig. 15. PbTiO_3 Cubic Phase Electro-optic $(\epsilon_{11} - \epsilon_{12})$ Constant for Various Total Polarizabilities (Theoretical)

approached by this variations.

There is a strong possibility that the reported 0.01 value may be incorrect, because it has been calculated by using the tetragonal phase's natural birefringence and spontaneous polarization in the quadratic electro-optic relation. This assumes that such a relation, the so-called "spontaneous" Kerr Effect, holds in the tetragonal phase. The natural birefringence of PbTiO_3 , however, has not been shown to be proportional to the square of the spontaneous polarization as in BaTiO_3 (Ref 19:94), and this method may not be applicable to PbTiO_3 . Indeed, Remeika (Ref 16:41) has reported on the incremental change of the spontaneous polarization with respect to temperature and the spontaneous polarization curve that is implied, is not like the birefringence curve. It also seems improbable that cubic PbTiO_3 , with crystal conditions similar to those in cubic BaTiO_3 , should have a quadratic electro-optic effect so drastically different from BaTiO_3 and other perovskites of this family.

Dielectric Constant Anisotropy

The anisotropy induced in the dielectric constant for cubic PbTiO_3 has been calculated for an electric field strength of 10^6 V/M. At this field strength, the dielectric constant at the curie temperature, along the applied field, drops to a little less than half its unbiased value. Although no similar experimental measurements are available for PbTiO_3 , this may be compared with the results for BaTiO_3 (Ref 27:116) which showed a similar drop for a field strength of 10^5 V/M.

X. Electro-optic Calculations in the Tetragonal Phase

Since the model has not been successful in calculating the natural birefringence and dielectric constants in tetragonal PbTiO_3 , its use in calculating electro-optic effects in this phase is questionable. For this reason, although the calculations were done for their instructive value, no detailed discussion is given. It is sufficient to report, for future considerations, a value for $(r_{33} - (n_o/n_e)^3 r_{13})$ of $-1.03 \cdot 10^{-11} \text{M/V}$, at a field strength of 10^6V/M . In this calculations, the total polarizabilities used were 4.90 \AA^3 , 0.840 \AA^3 , and 2.837 \AA^3 for lead, titanium, and oxygen, respectively. The only value reported in the literature is a semi-empirical value equal to approximately $3 \cdot 10^{-10} \text{M/V}$ for $(r_{13} - r_{33})$, (Ref 20:116).

XI. Point-dipole Model Study

The model's failure to calculate correctly the properties for the tetragonal phase of lead titanate prompted a study of the contributions to natural birefringence from the different mechanisms in the model. The study consisted of looking at the individual contributions from tetragonality, ion shifts, and electric field dependence and combinations of the three. In doing the calculations, field effects were removed by simply neglecting the field dependence of the electronic polarizability, while the tetragonality and ion shifts were considered by setting one or the other equal to zero.

The results can be best summarized by Figure 16 showing the different contributions at different temperatures. Several statements can be made from the curves in the Figure. These are: a) Each individual contribution is larger than the experimental value., b) The individual contributions all add constructively at all temperatures., c) The ion shifts and field dependence contribution both increase with temperature., and d) Above the reference base line, curve #1 shows a behavior similar to that of the experimental curve; a behavior which is also evident in the other curves. The sharp increase in the topmost curve at temperatures approaching the transition temperature is due to the sharp decrease in the crystal's unit cell volume.

It is obvious from the results that both the tetragonality and ion shifts are so large in PbTiO_3 , that they alone can produce a birefringence much larger than the experimental value. One more thing is clear: the effects of tetragonality and ion shifts add constructively and do not subtract from each other as had been hoped for in explaining the anomalously low birefringence of PbTiO_3 .

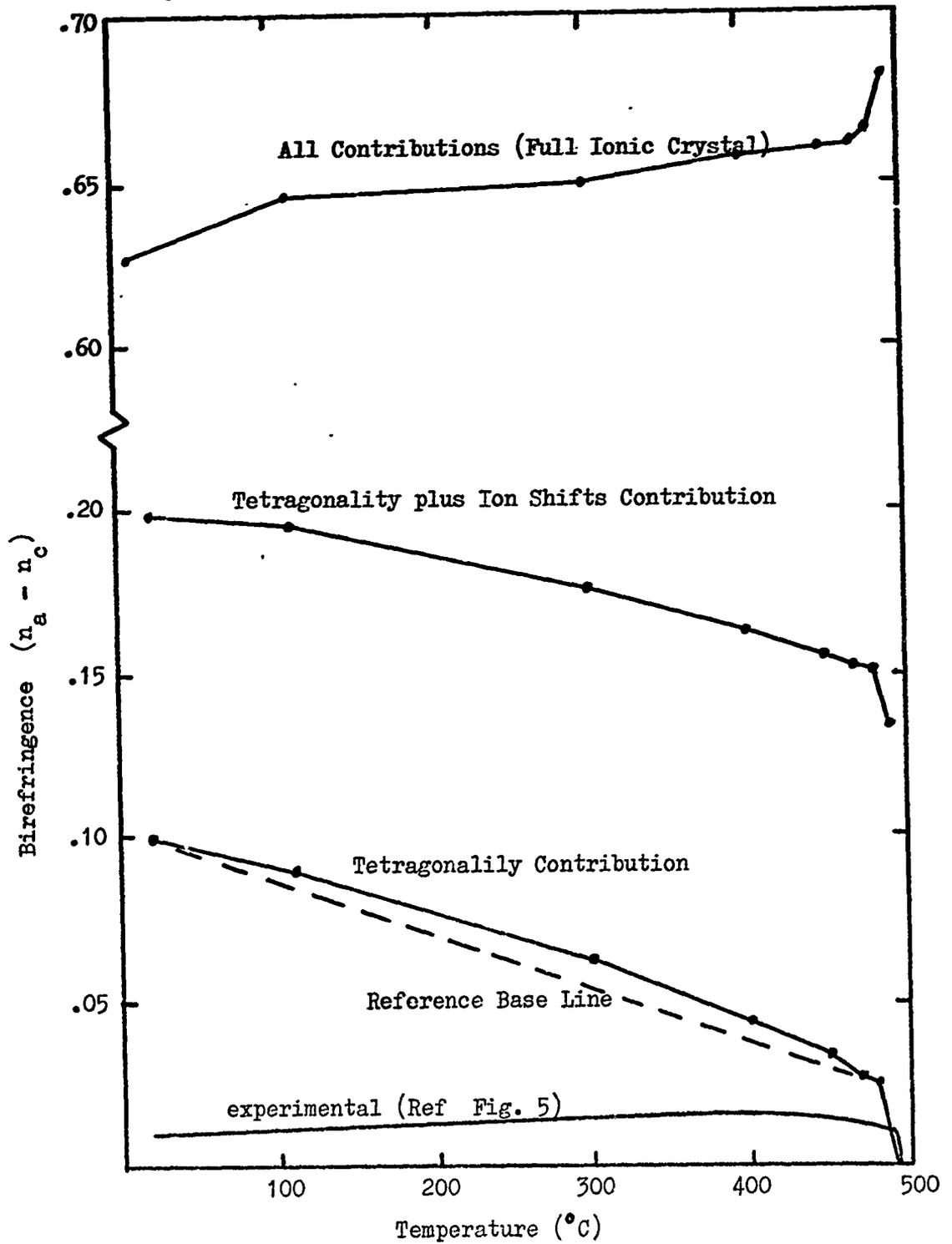


Fig. 16. Contribution to Natural Birefringence by Different Mechanisms in Point-Dipole Model

XII. Results, Conclusions, and Recommendations

Results

The application of a point-dipole model to calculate ferroelectric and electro-optic properties of PbTiO_3 has resulted in the following:

- a) Satisfactory refractive index and dielectric constant in the cubic phase at the curie temperature
- b) Satisfactory 'a' axis dielectric constant and spontaneous polarization in the tetragonal phase at room temperature
- c) Acceptable calculations of the dielectric temperature dependence in the cubic phase
- d) An electro-optic ($\epsilon_{11} - g_{12}$) constant, in the cubic phase, approximately equal to that of most barium titanate-type perovskites, in contrast to a reported semi-empirical value that is only one-tenth the magnitude
- e) An electro-optic ($r_{33} - (n_o/n_e)^3 r_{13}$) constant, in the tetragonal phase, equal to $-1.03 \cdot 10^{-11} \text{ M/V}$ for an electric field of 10^6 V/M
- f) An unsatisfactory value of the natural birefringence (large by a factor of 70) and of the anisotropy in the tetragonal dielectric constant
- g) A qualitative behavior of the temperature dependent birefringence in the tetragonal phase that is not unlike the experimentally measured behavior

A study was then made of the different mechanisms in the model, by calculating their individual contributions to the natural birefringence. The results showed that disregarding the effects of the crystal's fields, the crystal's physical structure alone, through the lorentz factors, produced a natural birefringence that was more than an order of magnitude larger than the experimental value.

Conclusions

The above results lead to the following general conclusion: The point-dipole model, in the form used by Wunsch, can be satisfactorily

applied to PbTiO_3 in its cubic phase to calculate ferroelectrics and electro-optic properties, and it can not be satisfactorily applied to PbTiO_3 in its tetragonal phase. The unsatisfactory behavior of the model in the tetragonal phase seems to be due to the dominating effect of the crystal's large c/a axis ratio and highly unsymmetrical ion positions.

Recommendations

Since the present form of the field-dependent electronic polarizability neglects effects in a direction perpendicular to the electric field, further efforts should consider the significance of including such an effect. Furthermore, since it is unlikely that the perpendicular effects alone, could correct the large anisotropy in refractive index and dielectric constant, further efforts should also consider the possibility of adding an explicit dependence of the polarizabilities on bond covalency.

In the present effort, a computer program was written to operate on the Air Force Weapons Laboratory's computer system. This program consists of the various programs used by Wunsch in doing the various basic calculations plus many added capabilities, such as temperature dependence and plotting capabilities. This program called FERROEL calculates all the desired calculations with a minimum number of inputs and should be used in further efforts to improve the point-dipole electro-optic model.

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Appendix A

Electro-optic Effects

The change in a crystal's refractive indices in the presence of an external electric field can be best explained by considering the equation for the crystal's field-free index ellipsoid in a non-principal coordinate system:

$$\left(\frac{1}{n^2}\right)_1 x^2 + \left(\frac{1}{n^2}\right)_2 y^2 + \left(\frac{1}{n^2}\right)_3 z^2 + 2\left(\frac{1}{n^2}\right)_4 yz + 2\left(\frac{1}{n^2}\right)_5 xz + 2\left(\frac{1}{n^2}\right)_6 xy = 1 \quad (35)$$

The presence of an electric field results in changing the coefficients of the different terms. The change in each coefficient can be expanded in powers of the electric field. In this expansion, the term that is proportional to the first power of the electric field defines the coefficients of the linear (Pockel) electro-optic effect. This defining equation is

$$\Delta\left(\frac{1}{n^2}\right)_i = r_{ij} E_j \quad (36)$$

where the r_{ij} (Pockel coefficients) are members of a second order tensor. The expansion term that is proportional to the square of the electric field defines the coefficients of the quadratic (Kerr) electro-optic effect. This defining equation is

$$\Delta\left(\frac{1}{n^2}\right)_{ij} = R_{ijkl} E_k E_L \quad (37)$$

where the R_{ijkl} (Kerr coefficients) are members of a fourth order tensor.

In the tetragonal phase of the perovskite ferroelectrics, the linear effect is much larger than the quadratic effect and so the quadratic effect is usually disregarded. In the cubic phase, the linear effect is not allowed because the crystal lattice has inversion symmetry.

In a crystal's principal coordinate system, the fourth, fifth, and sixth coefficients of equation (35) are zero, so that in the presence of an electric field, it may be written as

$$\left[\frac{1}{n_1^2} + \Delta \left(\frac{1}{n^2} \right)_1 \right] x^2 + \left[\frac{1}{n_2^2} + \Delta \left(\frac{1}{n^2} \right)_2 \right] y^2 + \left[\frac{1}{n_3^2} + \Delta \left(\frac{1}{n^2} \right)_3 \right] z^2 + 2\Delta \left(\frac{1}{n^2} \right)_4 yz + 2\Delta \left(\frac{1}{n^2} \right)_5 xz + 2\Delta \left(\frac{1}{n^2} \right)_6 xy = 1 \quad (38)$$

Writing the $\Delta \left(\frac{1}{n^2} \right)_i$ in terms of the Pockel coefficients for the tetragonal perovskite crystal (keeping only the non-zero terms), for an electric field in the z direction, equation (38) becomes (Ref 27:119)

$$\left[\frac{1}{n_1^2} + r_{13} E_3 \right] x^2 + \left[\frac{1}{n_2^2} + r_{13} E_3 \right] y^2 + \left[\frac{1}{n_3^2} + r_{33} E_3 \right] z^2 = 1 \quad (39)$$

where the new coefficients of the different terms define the new refractive indices along the crystal's principal axes.

Subtracting the refractive indices along the x and z directions from each other, results in the following equation for the linear

electro-optic constant

$$r_{33} - \left(\frac{n_1}{n_3}\right)^3 r_{13} = \frac{2(n_3 - n_3')}{n_3^3 E_3} \quad (40)$$

where the prime denotes values in the presence of the electric field.

Similarly, for the cubic phase, equation (38) becomes (Ref 27:100)

$$\left[\frac{1}{n_1^2} + R_{12} E_3\right] x^2 + \left[\frac{1}{n_2^2} + R_{12} E_3\right] y^2 + \left[\frac{1}{n_3^2} + R_{11} E_3\right] z^2 = 1 \quad (41)$$

In this case, subtracting the new refractive indices along the X and Z directions from each other results in the following equation for the quadratic electro-optic constant.

$$R_{11} - R_{12} = \frac{2\Delta n}{n_1^3 E_3^2} \quad (42)$$

where Δn is the induced birefringence in the presence of the electric field.

VITA

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