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Optical Anisotropy of Tetragonal Barium Titanate*

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The optical dielectric constants and the anisotropy of tetragonal barium titanate were calculated by assuming spherical symmetry for the electron clouds of its constituent atoms. An analogous calculation was carried out for lead titanate. The calculated birefringences are positive in both crystals, in contrast to the observed ones. The results are discussed.

OPTICAL refractivity shows directly the electronic response of atoms in a crystal to an electromagnetic field of optical frequency where the contributions of the ionic displacements due to the applied field are of no importance. Therefore studies on refractivities and their anisotropy in ferroelectrics will be useful in understanding the behavior of the electrons of the constituent atoms.

The present investigation was undertaken with the aim of obtaining the optical dielectric constants and their anisotropy in barium titanate theoretically, with due regard to its well-known lattice spacings[1] but with the assumption of spherical symmetry for the electronic configuration of the atoms.

When we modify the usual Lorentz field for barium titanate, taking account of the orthorhombic deformation of the crystal, the local field on each ion can be written as[2–4]

$$E_{\mathrm{Ti}}=P_{\mathrm{Ti}}/\alpha_{\mathrm{Ti}}=E+\frac{1}{v}\Bigg[\left\{\frac{4\pi}{3}+(-12\Delta_1+6\Delta_2+6\Delta_3)\right\}P_{\mathrm{Ti}}+\left\{\frac{4\pi}{3}+\left(\frac{512}{9\sqrt{3}}\Delta_1-\frac{256}{9\sqrt{3}}\Delta_2-\frac{256}{9\sqrt{3}}\Delta_3\right)\right\}P_{\mathrm{Ba}}$$
$$+\left\{\frac{4\pi}{3}+q-96\Delta_1\right\}P_{\mathrm{O}1}+\left\{\frac{4\pi}{3}-\frac{q}{2}+48\Delta_2\right\}P_{\mathrm{O}2}+\left\{\frac{4\pi}{3}-\frac{q}{2}+48\Delta_3\right\}P_{\mathrm{O}3}\Bigg]\cdots, \quad \text{(1a)}$$

$$E_{\mathrm{Ba}}=P_{\mathrm{Ba}}/\alpha_{\mathrm{Ba}}=E+\frac{1}{v}\Bigg[\left\{\frac{4\pi}{3}+\left(\frac{512}{9\sqrt{3}}\Delta_1-\frac{256}{9\sqrt{3}}\Delta_2-\frac{256}{9\sqrt{3}}\Delta_3\right)\right\}P_{\mathrm{Ti}}+\left\{\frac{4\pi}{3}+(-12\Delta_1+6\Delta_2+6\Delta_3)\right\}P_{\mathrm{Ba}}$$
$$+\left\{\frac{4\pi}{3}-p+24\sqrt{2}(\Delta_2+\Delta_3)\right\}P_{\mathrm{O}1}+\left\{\frac{4\pi}{3}+\frac{p}{2}+(12\sqrt{2}\Delta_1-36\sqrt{2}\Delta_3)\right\}P_{\mathrm{O}2}$$
$$+\left\{\frac{4\pi}{3}+\frac{p}{2}+(12\sqrt{2}\Delta_1-36\sqrt{2}\Delta_2)\right\}P_{\mathrm{O}3}\Bigg]\cdots, \quad \text{(1b)}$$

$$E_{\mathrm{O}1}=P_{\mathrm{O}1}/\alpha_{\mathrm{O}}=E+\frac{1}{v}\Bigg[\left\{\frac{4\pi}{3}+q-96\Delta_1\right\}P_{\mathrm{Ti}}+\left\{\frac{4\pi}{3}-p+24\sqrt{2}(\Delta_2+\Delta_3)\right\}P_{\mathrm{Ba}}+\left\{\frac{4\pi}{3}+(-12\Delta_1+6\Delta_2+6\Delta_3)\right\}P_{\mathrm{O}1}$$
$$+\left\{\frac{4\pi}{3}+\frac{p}{2}+(12\sqrt{2}\Delta_1-36\sqrt{2}\Delta_2)\right\}P_{\mathrm{O}2}+\left\{\frac{4\pi}{3}+\frac{p}{2}+(12\sqrt{2}\Delta_1-36\sqrt{2}\Delta_3)\right\}P_{\mathrm{O}3}\Bigg]\cdots, \quad \text{(1c)}$$

$$E_{\mathrm{O}2}=P_{\mathrm{O}2}/\alpha_{\mathrm{O}}=E+\frac{1}{v}\Bigg[\left\{\frac{4\pi}{3}-\frac{q}{2}+48\Delta_2\right\}P_{\mathrm{Ti}}+\left\{\frac{4\pi}{3}+\frac{p}{2}(12\sqrt{2}\Delta_1-36\sqrt{2}\Delta_3)\right\}P_{\mathrm{Ba}}+\left\{\frac{4\pi}{3}+\frac{p}{2}(12\sqrt{2}\Delta_1-36\sqrt{2}\Delta_2)\right\}P_{\mathrm{O}1}$$
$$+\left\{\frac{4\pi}{3}+(-12\Delta_1+6\Delta_2+6\Delta_3)\right\}P_{\mathrm{O}2}+\left\{\frac{4\pi}{3}-p+24\sqrt{2}(\Delta_2+\Delta_3)\right\}P_{\mathrm{O}3}\Bigg]\cdots, \quad \text{(1d)}$$

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[1] H. F. Kay and P. Vousden, Phil. Mag. **40**, 1019 (1949).

[2] In these corrections only the nearest neighbor ions of each ion in question are taken into account.

[3] J. C. Slater, Phys. Rev. **78**, 748 (1950).

[4] W. Kinase and H. Takahasi, J. Phys. Soc. Japan **10**, 942 (1955); **12**, 464 (1957).

$$E_{\mathrm{O3}}=P_{\mathrm{O3}}/\alpha_{\mathrm{O}}=E+\frac{1}{v}\left[\left\{\frac{4\pi}{3}-\frac{q}{2}+48\Delta_3\right\}P_{\mathrm{Ti}}+\left\{\frac{4\pi}{3}+\frac{p}{2}+(12\sqrt{2}\Delta_1-36\sqrt{2}\Delta_2)\right\}P_{\mathrm{Ba}}+\left\{\frac{4\pi}{3}+\frac{p}{2}(12\sqrt{2}\Delta_1-36\sqrt{2}\Delta_3)\right\}P_{\mathrm{O1}}\right.$$
$$\left.+\left\{\frac{4\pi}{3}-p+24\sqrt{2}(\Delta_2+\Delta_3)\right\}P_{\mathrm{O2}}+\left\{\frac{4\pi}{3}+(-12\Delta_1+6\Delta_2+6\Delta_3)\right\}P_{\mathrm{O3}}\right]\cdots. \quad (1e)$$

The symbols used in the above equations are as follows: E_{Ti}, the local field acting on the Ti ion, and similarly for E_{Ba} and E_{O}; E, the applied field; v, the lattice volume $(4A)^3$; P_{Ti}, the electronic dipole moment of the Ti ion, and so on; α_{Ti}, the electronic polarizability of the Ti ion, and so on [here we use the values[5] $\alpha_{\mathrm{Ti}}=(0.0365/4\pi)v$, $\alpha_{\mathrm{Ba}}=(0.382/4\pi)v$, and $\alpha_{\mathrm{O}}=(0.470/4\pi)v$]; O_1, oxygen which lies along the same line parallel to the applied field; O_2 and O_3, oxygens which lie on a plane perpendicular to the applied field; Δ_1, the elongation of the unit cell in the direction of the Ti and O_1 chain, relative to the basic lattice side, i.e., 4A, and so on; p and q, the corrections to the Lorentz factor (here we use the values[6,7] $p=8.668$ and $q=30.080$).

The solution of these simultaneous equations are

$$P_{\mathrm{Ti}}=\frac{vE}{4\pi}(0.1185-0.4279\Delta_1+0.0319\Delta_2+0.0319\Delta_3)\cdots, \quad (2a)$$

$$P_{\mathrm{Ba}}=\frac{vE}{4\pi}(0.9197+2.1206\Delta_1-0.6443\Delta_2-0.6443\Delta_3)\cdots, \quad (2b)$$

$$P_{\mathrm{O1}}=\frac{vE}{4\pi}(1.4305-0.2462\Delta_1-1.4930\Delta_2-1.4930\Delta_3)\cdots, \quad (2c)$$

$$P_{\mathrm{O2}}=\frac{vE}{4\pi}(1.1585+1.7242\Delta_1-1.6453\Delta_2-0.5208\Delta_3)\cdots, \quad (2d)$$

$$P_{\mathrm{O3}}=\frac{vE}{4\pi}(1.1585+1.7242\Delta_1-0.5208\Delta_2-1.6453\Delta_3)\cdots. \quad (2e)$$

The total electronic dipole moment of the unit cell is obtained by summing the P's;

$$\mu=\sum_i P_i=\frac{vE}{4\pi}(4.7857+4.8949\Delta_1-4.2715\Delta_2-4.2715\Delta_3)\cdots. \quad (3)$$

Dividing μ by the true volume $v(1+\Delta_1)(1+\Delta_2)(1+\Delta_3)$, we obtain the total electronic polarization P:

$$P=\frac{E}{4\pi}\times 4.7857(1+0.02282\Delta_1-1.89255\Delta_2-1.89255\Delta_3)\cdots. \quad (4)$$

Then the optical dielectric constant is obtained as

$$\epsilon=1+\frac{4\pi P}{E}=5.7857+0.1092\Delta_1-9.0572\Delta_2-9.0572\Delta_3\cdots. \quad (5)$$

Equation (5) generally gives the dielectric constants of orthorhombic $\mathrm{BaTiO_3}$, which is deformed slightly from a cubic lattice, by inserting the observed Δ's. Actually, by using the observed values[1] of the tetragonal phase at room temperature, i.e.,

$$\Delta_1=\Delta_2=-0.0025,\quad \Delta_3=0.0075,\quad \text{for } \epsilon_a,$$

and

$$\Delta_1=0.0075,\quad \Delta_2=\Delta_3=-0.0025,\quad \text{for } \epsilon_c;$$

we obtain

$$\epsilon_a=5.7401, \quad (6a)$$

and

$$\epsilon_c=5.8318. \quad (6b)$$

According to the relation $n=\sqrt{\epsilon}$ (n is a refractive index), the refractive indices are about 2.40; and as a calculated birefringence, we get

$$\Delta n=n_c-n_a=0.0191. \quad (7)$$

This result means that barium titanate is "optically positive" in a case where the electron clouds are of spherical symmetry and the electro-optic coefficients are left out of consideration.

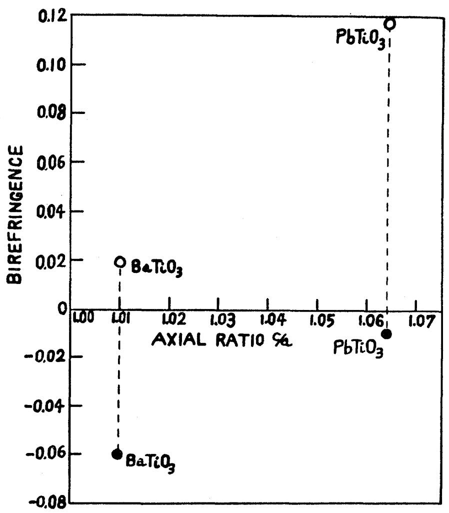

FIG. 1. The relation between the crystallographic and optical anisotropies. ○ calculated values; ● observed values.

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[5] P. W. Anderson and W. Shockley (unpublished).

[6] L. W. McKeehan, Phys. Rev. 43, 913 (1933); 72, 78 (1947).

[7] J. M. Luttinger and L. Tisza, Phys. Rev. 70, 954 (1946); 72, 257 (1947).

Similar calculations in the case of lead titanate were carried out by assuming that the electronic polarizability of Pb ions is identical with that of Ba ions. If we substitute the following values[8] into Eq. (5):

$$\Delta_1=\Delta_2=-0.025, \quad \Delta_3=0.0375, \quad \text{for} \quad \epsilon_a,$$

and

$$\Delta_1=0.0375, \quad \Delta_2=\Delta_3=-0.025, \quad \text{for} \quad \epsilon_c,$$

we obtain

$$\epsilon_a=5.6698, \tag{8a}$$

and

$$\epsilon_c=6.2427. \tag{8b}$$

So we get

$$\Delta n=n_c-n_a=0.1174. \tag{9}$$

Recently it has been found that the relationship of the crystallographic and optical anisotropies are not similar in lead titanate and barium titanate[8]: Lead titanate has a much larger tetragonality than that of barium titanate, whereas the former shows a smaller birefringence than the latter. This phenomenon appears strange, and so it will be worth while to examine it thoroughly.

Figure 1 shows the relations between the calculated Δn's and the observed Δn's[8,9] with respect to the lattice anisotropies of $BaTiO_3$ and $PbTiO_3$. Here it is noteworthy that the observed Δn's are negative and the calculated Δn's are positive.

This discrepancy is due to the fact that we have calculated Δn's leaving the electro-optic effects out of consideration. In other words, the values calculated above are the so-called natural birefringences of $BaTiO_3$ and $PbTiO_3$. The contribution of the electro-optic effect to Δn will be $-0.06-0.02=-0.08$ in $BaTiO_3$, the value -0.06 being given in Merz's article.[9]

For $PbTiO_3$, however, we cannot give a definite conclusion, because precise knowledge about the electronic polarizability of the Pb ions and the behavior of their surrounding electron clouds is not available at present. The investigation of this problem is in progress.

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[8] H. H. Rogers, Massachusetts Institute of Technology Report MIT-52, Dec. 1952 (unpublished); Shirane, Pepinsky, and Frazer, Acta Cryst. **9**, 131 (1956); J. Kobayashi and N. Yamada (unpublished).

[9] W. Merz, Phys. Rev. **76**, 1221 (1949).