

## Linear electro-optical properties of tetragonal BaTiO<sub>3</sub>

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**Abstract.** Linear optical susceptibility and clamped linear electro-optical tensor coefficients of tetragonal BaTiO<sub>3</sub> are calculated using a formalism based on bond charge theory. Calculated values are in close agreement with experimental data. The covalent Ti–O bonds constituting distorted TiO<sub>6</sub> octahedral groups are found to be major contributors to the electro-optic coefficients making them more sensitive than the BaO<sub>12</sub> groups for these properties. Orientations of chemical bonds play an important role in determining these properties.

**Keywords.** Ferroelectrics; crystal structure; electro-optical; bond charge.

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### 1. Introduction

Perovskite ferroelectrics having oxygen octahedral groups are important for their electro-optical, nonlinear optical, acousto-optical and photorefractive applications. Of these, BaTiO<sub>3</sub> exhibits larger values of spontaneous strain and electro-optic (EO) coefficients. It undergoes successive ferroelectric phase transitions; from a high-temperature cubic phase (paraelectric) to a tetragonal, orthorhombic to a low-temperature rhombohedral phase. In its tetragonal phase, the magnitude of the EO  $r_{42}$  coefficient is significantly higher than the rest [1]. A few studies towards understanding the origin of their EO coefficients were reported in literature. Recent theoretical study [2] suggested the importance of ionic contribution to its EO properties. The ionic polarization associated with relaxation process occurring at higher frequency (of about 200 MHz) is suggested to be responsible for larger value of  $r_{42}$  coefficient.

The values of EO coefficients of a crystal can be estimated using the optical susceptibility of individual chemical bonds comprising its crystal structure [3–5]. The amount of optical nonlinearity is determined by the relative magnitudes of bond polarizabilities and mutual orientations, characterized by direction cosines of chemical bonds. Such type of bonds, involving polarizable electrons which are also influenced by an anharmonic potential arising from asymmetrically oriented bonding network, are likely to be the major contributors to EO and NLO properties [6]. A detailed analysis based on these aspects enables us to locate the sensitive region of the crystal structure for these properties which is helpful for their further improvement.

In this paper, linear optical susceptibility ( $\chi$ ) and linear clamped EO coefficients ( $r_{ijk}$ ) of tetragonal BaTiO<sub>3</sub> are computed using a formalism [3] based on Phillips–Van Vechters’ dielectric theory of solids [7,8] and Levine’s bond charge model [9]. Results are discussed.

## 2. Theory

The clamped EO coefficient ( $r_{ijk}$ )<sup>s</sup> comprises ionic and electronic components. The value of the electronic component ( $r_{ijk}$ )<sup>e</sup> can be estimated from the coefficient ( $d_{ijk}$ ) of second harmonic generation (SHG) as [10]

$$(r_{ijk})^e = -4d_{ijk}/\epsilon_i\epsilon_j \quad (1)$$

$\epsilon_i, \epsilon_j$  being the optical permittivities.

The ionic component can be computed using the expression [3]

$$(r_{ijk})^{\text{ion}} = (A_k/B_{ij}) \sum (2\beta_{on}/d_{no}) [F_{ijk}] \quad (2)$$

where

$$A_k = \epsilon_0(\epsilon_{dck} - \epsilon_k); \quad B_{ij} = NV(e_C)^* \epsilon_i\epsilon_j$$

$$F_{ijk} = f\alpha_{ni}\alpha_{nj}\alpha_{nk} + 1/2(\alpha_{ni}\delta_{jk} + \alpha_{nj}\delta_{ik}).$$

The summation is done over all bonds in one unit cell.  $\alpha_{ni,j,k}$  are the direction cosines of the  $n$ th bond having a length  $d_0$  and a bond susceptibility  $\beta_0$  along the bond direction.  $\epsilon_0$  is the electric permittivity in vacuum,  $\epsilon_{dc}$  is the low-frequency dielectric constant,  $\epsilon_{i,j,k}$  are the optical permittivities,  $\delta_{i,j,k}$  are the Kronecker delta functions,  $N$  is the number of pairs of atoms in the unit cell,  $V$  is the volume of one unit cell,  $(e_C)^*$  is the Callen effective ionic charge, the value of which can be estimated from that of the Szigeti effective charge  $(e_S)^*$  [11]. The expressions for various bond parameters are described in literature [3,9] in detail.

If the crystal is composed of different types (according to their lengths, nature of constituting elements etc.) of chemical bonds labeled  $\mu$ , then its total linear macroscopic susceptibility ( $\chi$ ) can be estimated from those ( $\chi^\mu$ ) for the individual bonds from the relation

$$\chi = \{(n_0)^2 - 1\}/4\pi = \sum F^\mu \chi^\mu = \sum (N_b)^\mu (\chi_b)^\mu \quad (3)$$

in which  $\chi^\mu$  is the total macroscopic susceptibility of the crystal composed entirely of bonds of type  $\mu$ ,  $n_0$  is the refractive index at long wavelength,  $F^\mu$  is the fraction of number of bonds,  $(\chi_b)^\mu$  is the susceptibility of a single bond and  $(N_b)^\mu$  is the number of bonds of type  $\mu$  per cm<sup>3</sup>.

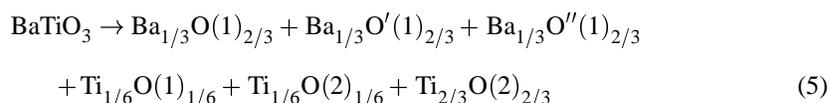
$$\chi^\mu = (1/4\pi)(\hbar\omega_p/E_g)^2 D^\mu A^\mu \quad (4)$$

where  $D^\mu$  and  $A^\mu$  are the correction factors [9]. The parameter  $\beta_0$  is proportional to  $\chi^\mu$ .

Using the above formalism, bond parameters and clamped electro-optic coefficients ( $r_{ijk}$ )<sup>s</sup> of BaTiO<sub>3</sub> are estimated.

### 3. Results and discussion

The space group of tetragonal BaTiO<sub>3</sub> is P4mm with cell dimensions  $a_0 = 3.9945 \text{ \AA}$  and  $c_0 = 4.0335 \text{ \AA}$  [12]. According to Kleinman symmetry conditions [13], the non-zero components of  $r_{ijk}$  tensor for 4 mm point group symmetry are  $r_{13}(=r_{23}), r_{33}$  and  $r_{42}(=r_{51})$ . At room temperature, measured [1] values of  $(r_{33})^s$  and  $(r_{42})^s$  are larger than that of  $(r_{13})^s$ . Different coordinations of elements lead to different distributions of valence electrons among the chemical bonds. The structure consists of TiO<sub>6</sub> octahedral and BaO<sub>12</sub> groups in which oxygen atoms are connected to four barium atoms and two titanium atoms. Hence, coordination numbers of 6, 6 and 12 are used for O, Ti and Ba atoms respectively. The structural groups contain three types of Ba–O bonds (each type four in number) and three types of Ti–O bonds (one of them four and other two one each in number) [12]. Accordingly, bond parameters are estimated for them based on the equation representing the number of types of bonds constituting a single molecule in the unit cell:



using the average value ( $n_0$ ) of experimental principal refractive indices 2.412 ( $n_1$ ) and 2.36 ( $n_3$ ) [1] at a wavelength of 633 nm. Such a way of division of a molecule in terms of all types of constituting chemical bonds is also discussed in literature [14]. The calculated bond parameters are listed in table 1. From the values of  $f_i$ , Ba–O bonds are indicated to be highly ionic as compared to Ti–O bonds. This result is supported by the known formalism relating ionicity of a chemical bond and electronegativity of its constituent elements [15]. It is also consistent with earlier results reported [16] for compounds consisting of Ba–O bonds. From table 1, the dominating contribution from Ti–O bonds to the linear susceptibility  $\chi$  with significantly higher  $(\chi_b)^\mu$  values can also be noticed.

**Table 1.** Bond parameters of tetragonal BaTiO<sub>3</sub>.

	Ba–O(1)	Ba–O(1)	Ba–O(1)	Ti–O(1)	Ti–O(2)	Ti–O(2)
$d$ (Å)	2.796	2.826	2.882	1.862	2.001	2.172
$E_h$ (eV)	3.10	3.02	2.88	8.51	7.12	5.80
$C$ (eV)	11.72	11.40	10.85	13.1	11.1	9.1
$f_i$	0.93	0.93	0.93	0.70	0.71	0.71
$f_c$	0.07	0.07	0.07	0.30	0.29	0.29
$f$	0.026	0.034	0.048	–0.163	–0.131	–0.092
$k_s$ (Å) <sup>–1</sup>	2.19	2.18	2.15	2.74	2.64	2.54
$4\pi\chi$	2.55	2.61	2.72	7.84	8.89	10.32
$(\chi_b)^\mu$ (Å) <sup>–3</sup>	0.72	0.74	0.77	2.23	2.53	2.94
$\Sigma\alpha_3$	2.80	–0.14	–2.88	1.0	–0.23	–1.0
$\Sigma(\alpha_3)^3$	1.37	–0.0002	–1.5	1.0	–0.0008	–1.0
$\Sigma(\alpha_1)^2\alpha_3$	0.71	–0.071	–0.693	0.0	–0.115	0.0
$f\Sigma(\alpha_3)^3 + \Sigma\alpha_3$	2.83	–0.143	–2.95	0.84	–0.23	–0.907
$f\Sigma(\alpha_2)^2\alpha_3 + 1/2\Sigma\alpha_3$	1.42	–0.074	–1.47	0.5	–0.1	–0.5
$(e_S)^*/e = 2.90$	$(e_C)^*/e = 1.30$ per formula unit					

The ionic components of EO coefficients are computed using eq. (2), crystal structural parameters [12] and clamped dielectric constants at high frequency (exact value of the frequency is not available) [1] (table 2). Since the values of  $d_{ijk}$  measured at 633 nm are not available, the electronic components  $(r_{ijk})^{\text{el}}$  (eq. (1)) are estimated using the available [17]  $d_{ijk}$  values measured at about 1064 nm. The errors in  $(r_{ijk})^{\text{ion}}$  are estimated from those in structural [12] and dielectric constant [1] data. The large difference between the calculated and reported [1] value of  $r_{42}$  is mainly due to the error in the reported value of  $(\epsilon_{11})^s$  which is used in the present calculations. It is also partly due to the difference in the wavelength at which the electronic component and ionic components are estimated. However, within the errors, the calculated  $(r_{ijk})^s$  are in close agreement with the reported ones [1], as shown in table 3. From these results, it is evident that, like in  $\text{KNbO}_3$  [18], the ionic components are major contributors to EO coefficients and electronic components are not much significant in tetragonal  $\text{BaTiO}_3$ . This result is supported by the earlier theoretical study [2] on  $\text{BaTiO}_3$ .

From the values of individual chemical bonds, contributions from  $\text{TiO}_6$  and  $\text{BaO}_{12}$  groups are estimated and are listed in table 4. We can see that linear EO behavior in tetragonal  $\text{BaTiO}_3$  is dominated by distorted  $\text{TiO}_6$  octahedral and not by  $\text{BaO}_{12}$  groups. This is due to higher values of bond susceptibility  $(\chi_b)^\mu$  for Ti–O than for Ba–O bonds (table 1). The Ti atoms have more number of valence electrons (including the d-shell electrons) and a lower coordination number as compared to K atoms. These electrons are more delocalized (as evident from the higher  $f_c$  values for Ti–O) and are relatively more susceptible to applied field leading to a higher contribution to EO coefficients, as described in the Introduction. In  $\text{BaTiO}_3$ , the movement (or response) of  $\text{Ba}^{2+}$  ions with respect to oxygen octahedral network due to applied field is known [19] to be much less than that of  $\text{Ti}^{4+}$  ions. Thus, most of the polarization and other optical properties arise due to the network involving  $\text{Ti}^{4+}$  ions. Covalent nature of Ti–O bonds was indicated also in other  $\text{TiO}_6$  octahedral ferroelectrics [4].

**Table 2.** Experimental clamped dielectric constants and refractive indices [1] of tetragonal  $\text{BaTiO}_3$  at 633 nm.

$\epsilon_{11} = \epsilon_{22} = 2180 \pm 300$	$\{(\epsilon_{33} - \epsilon_3)/(\epsilon_3)^2\} = 1.626$
$\epsilon_{33} = 56 \pm 3$	$\{(\epsilon_{22} - \epsilon_2)/(\epsilon_3 \epsilon_2)\} = 67.1$
$n_1 = 2.412$	
$n_3 = 2.360$	

**Table 3.** Clamped linear electro-optic coefficients (in pm/V) of tetragonal  $\text{BaTiO}_3$ .

$(r_{33})^{\text{ion}} = 37.85 \pm 2.2 \diamond$	$(r_{33})^{\text{el}} = 0.85 \clubsuit$
$(r_{33})^{\text{cal}} \approx 38.7 \pm 2.2$	$(r_{33})^{\text{exp}} = 40.6 \pm 2.5^*$
$(r_{42})^{\text{ion}} = 641.6 \pm 88.5 \diamond$	$(r_{42})^{\text{el}} = 2.2 \clubsuit$
$(r_{42})^{\text{cal}} \approx 643.8 \pm 88.5$	$(r_{42})^{\text{exp}} = 730 \pm 100^*$

\*Reported [1] values at 633 nm determined using experimental data.  $\clubsuit$  Electronic component calculated using reported [17] measured SHG coefficients at 1064 nm.  $\diamond$  Calculated values of the ionic components at 633 nm.

**Table 4.** Contributions (in pm/V) from structural groups to clamped electro-optic coefficients.

	TiO <sub>6</sub>	BaO <sub>12</sub>
$(r_{33})^{\text{ion}}$	31.85	6.0
$(r_{42})^{\text{ion}}$	518.6	123.0

Apart from the role of the nature of atoms and their coordination numbers, the importance of mutual orientation of chemical bonds in EO properties can be noticed from the terms  $(f \sum (\alpha_3)^3 + \sum \alpha_3)$  and  $(f \sum (\alpha_2)^2 \alpha_3 + 1/2 \sum \alpha_3)$  in eq. (2) for the ionic components of  $r_{33}$  and  $r_{42}$  respectively. As the values of the magnitudes  $f$  are small ( $< 0.2$ ), the term  $\sum \alpha_3$  dominates over the term containing  $f$  (see table 1) which is related to electronic structure. Since  $\sum \alpha_3$  is present only for  $r_{33}$  and  $r_{42}$  coefficients and is absent in the formula of the coefficient  $r_{13}$ , the value of the latter is much lower than those of former two. Calculations show a better contribution, of nearly the same magnitude but with opposite sign, from the two Ba–O bonds of lengths 2.796 Å and 2.882 Å and a negligible contribution from the third type of Ba–O bonds for  $r_{33}$  and  $r_{42}$ . Thus the net value is significantly lower due to cancellation of direction cosines (see the values of  $\sum \alpha_3$  for them in table 1) and hence of individual contributions. Likewise, net contribution from the two Ti–O bonds of lengths 1.862 Å and 2.172 Å is reduced due to cancellations as described. Calculations also show that the value of the coefficient  $r_{13}$  is maximum for Ti–O bonds of length 2.001 Å.

Observed anisotropy in the values of  $r_{ijk}$ , namely much higher value for  $r_{42}$  than that of  $r_{33}$  is indicated to be mainly due to the corresponding anisotropy in measured dielectric constant [1] than due to orientations of chemical bonds (as suggested from nearly the same values for the factors  $(f \sum (\alpha_3)^3 + \sum \alpha_3)$  and  $(f \sum (\alpha_2)^2 \alpha_3 + 1/2 \sum \alpha_3)$  involving the direction cosines in table 1).

#### 4. Conclusions

Present study indicates that the clamped EO coefficients of tetragonal BaTiO<sub>3</sub> originate from TiO<sub>6</sub> octahedral groups in its crystal structure due to favorable coordinations and electronic configuration of Ti atoms which leads to higher amount of electronic delocalization along the Ti–O bonds. Ionic components dominate over the electronic components of EO coefficients. Geometrical orientations of chemical bonds play an important role in determining its EO properties.

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