Electro-optical properties of tetragonal KNbO₃

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Abstract. Linear electro-optical tensor coefficients and optical susceptibility of tetragonal KNbO₃ are calculated using a formalism based on bond charge theory. Results are in close agreement with the experimental data. The covalent Nb–O bonding network comprising the distorted NbO₆ octahedral groups in the structure is found to be a major contributor to the electro-optic coefficients making these groups more sensitive to these properties than the KO₁₂ groups. The orientations of the chemical bonds play an important role in determining these properties.

Keywords. Electro-optic; bond charge; crystal structure; ferroelectrics.

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1. Introduction

Potassium niobate (KNbO₃) is one of the widely studied members of the perovskite class of ferroelectrics because of its promising nonlinear optical (NLO) and electro-optical (EO) properties. Like BaTiO₃, it undergoes three successive ferroelectric phase transitions [1]. It transforms from cubic (paraelectric) to tetragonal phase at 701 K, then to orthorhombic at 488 K and to rhombohedral phase at 210 K. Experiments showed [2,3] that both the room temperature orthorhombic as well as high temperature tetragonal phase exhibit larger electro-optic (EO) coefficients. On a structural point of view, the NLO properties of KNbO₃ were theoretically investigated [4]. Another study [5], based on a microscopic model, investigated the role of polarizability in the EO properties of tetragonal phase. Those calculations suggested larger shifts for Nb^{5+} ions than for K^+ ions. However, the structural origin of larger EO coefficients of the tetragonal phase is not examined. It is known [6–9] that the EO coefficients of a crystal can be estimated using the optical susceptibility of individual chemical bonds by dividing the molecular formula into various types of constituent chemical bonds in the structure. The amount of optical nonlinearity is determined by the relative magnitude of bond polarizabilities and mutual orientation, characterized by direction cosines of chemical bonds. The extent of polarizability of a bond depends on various factors such as the amount of mobile

charge located along the bonding region, the degree of covalency and the nature of constituting atoms [10]. Hence, a quantitative analysis based on these aspects enables one to locate the sensitive region of the crystal structure for these properties and it is helpful for their further improvement.

In this paper, the linear electro-optic coefficients (r_{ijk}) of tetragonal KNbO$_3$ are computed using a formalism [6] based on Phillips–Van Vetchen' dielectric theory of solids [11,12] and Levine's bond charge model [13]. Results are discussed.

2. Methodology

The EO coefficient (r^T) for an unclamped (stress free) crystal is given by

$$r^T = r^d + r^S, \tag{1}$$

where r^d is the contribution arising from piezo-optic effect and r^S is the coefficient for a clamped (strain-free) crystal. The piezo-optic contribution can be estimated using the components of piezo-electric and elasto-optic tensors whereas r^S can be estimated from the ionic and electronic components.

$$r^S = r^{\text{ion}} + r^{\text{e}}, \tag{2}$$

r^{e} is related to the coefficient (d_{ijk}) of second harmonic generation (SHG) as [14]

$$(r_{ijk})^{\text{e}} = -4d_{ijk}/\varepsilon_i\varepsilon_j \tag{3}$$

ε_i, ε_j being the optical permittivities.

The ionic component can be computed using the expression [6]

$$(r_{ijk})^{\text{ion}} = \left(\frac{A_k}{B_{ij}}\right) \sum \left(2\frac{\beta_{\text{on}}}{d_{\text{no}}}\right) [F_{ijk}], \tag{4}$$

where

$$A_k = \varepsilon_0(\varepsilon_{dck} - \varepsilon_k); \quad B_{ij} = NV(e_c)^*\varepsilon_i\varepsilon_j,$$
$$F_{ijk} = f\alpha_{ni}\alpha_{nj}\alpha_{nk} + \frac{1}{2}(\alpha_{ni}\delta_{jk} + \alpha_{nj}\delta_{ik}).$$

The summation is done over all bonds in one unit cell. $\alpha_{ni,j,k}$ are the direction cosines of the nth bond having a length d_0 and a bond susceptibility β_0 along the bond direction and f is the ionicity factor. ε_0 is the electric permittivity in vacuum, ε_{dc} is the low-frequency dielectric constant, $\varepsilon_{i,j,k}$ are the optical permittivities, $\delta_{i,j,k}$ are the Krönecker 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 related to the Szigeti effective charge $(e_S)^*$ by the relation [15]:

$$(e_c)^* = (e_S)^* \frac{(\varepsilon_\infty + 2)}{3\varepsilon_\infty}. \tag{5}$$

In this formalism, the fractional covalency (f_c) of the chemical bond can be estimated from the relation

$$f_c = \left(\frac{E_h}{E_g}\right)^2,\qquad(6)$$

where E_h is the symmetric part of average energy gap E_g and

$$E_h = 39.7(d_0)^{-2.48}.\qquad(7)$$

Further details on the formalism are discussed in [6–8].

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

$$\chi = \frac{\{(n_o)^2 - 1\}}{4\pi} = \sum F^\mu \chi^\mu = \sum (N_b)^\mu (\chi_b)^\mu\qquad(8)$$

in which χ^μ is the total macroscopic susceptibility of the crystal composed entirely of bonds of type μ, n_o is the refractive index at long wavelength, F^μ 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 μ per cm^3.

$$\chi^\mu = \left(\frac{1}{4\pi}\right)\left(\frac{\hbar\omega_p}{E_g}\right)^2 D^\mu A^\mu,\qquad(9)$$

where D^μ and A^μ are the correction factors [13]. The parameter β_0 is proportional to χ^μ. Using the above formalism, the bond parameters and the clamped electro-optic coefficients (r_{ijk}) of tetragonal KNbO$_3$ are estimated.
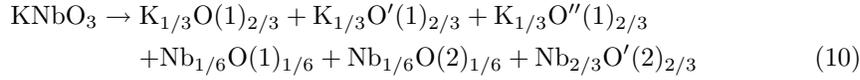
3. Results and discussion

The space group of tetragonal KNbO$_3$ is P4mm with cell dimensions $a_0 = 3.997$ Å and $c_0 = 4.063$ Å reported at 270°C [1]. According to Kleinman symmetry conditions [16], the nonzero components of r_{ijk} tensor for 4 mm point group symmetry are r_{13} ($= r_{23}$), r_{33} and r_{42} ($= r_{51}$). At 270°C, the measured EO coefficients r_c ($= r_{33} - (n_o/n_e)^3 r_{13}$), and r_{42} where n_o, n_e are the ordinary and extraordinary refractive indices, were reported [3,4]. Different coordinations of elements lead to different distributions of valence electrons among the chemical bonds. The structure consists of NbO$_6$ octahedra and KO$_{12}$ groups in which the oxygen atoms are connected to four potassium atoms and two niobium atoms. Hence, the coordination numbers of 6, 6 and 12 are used for O, Nb and K atoms respectively. The structural groups contain three types of K–O bonds (each type four in number) and three types of Nb–O bonds (one of them four and other two one each in number) [1]. Accordingly, the parameters are computed for these bonds based on the equation representing the number of types of bonds constituting a single molecule in the unit cell

Table 1. Bond parameters of tetragonal KNbO$_3$.

	K–O(1)	K–O$'$(1)	K–O$''$(1)	Nb–O(1)	Nb–O(2)	Nb–O$'$(2)
d (Å)	2.828	2.787	2.914	1.853	2.005	2.21
E_h (eV)	3.02	3.13	2.80	8.61	7.08	5.56
C (eV)	17.09	17.72	15.84	12.3	10.3	8.2
f_i	0.97	0.97	0.97	0.67	0.68	0.69
f_c	0.03	0.03	0.03	0.33	0.32	0.31
f	0.02	0.008	0.041	−0.177	−0.145	−0.102
k_s (Å)$^{-1}$	2.15	2.16	2.12	2.69	2.58	2.46
$4\pi\chi$	0.86	0.84	0.92	10.3	11.78	14.02
$(\chi_b)^\mu$ (Å)$^{-3}$	0.25	0.24	0.26	2.95	2.38	4.02
$\sum \alpha_3$	0.15	−2.79	2.91	−1.0	0.32	1.0
$\sum (\alpha_3)^3$	0.000	−1.35	1.54	−1.0	0.002	1.0
$\sum (\alpha_1)^2 \alpha_3$	0.075	−0.717	0.685	0.0	0.161	0.0
$f \sum (\alpha_3)^3 + \sum \alpha_3$	0.15	−2.80	2.97	−0.82	0.324	0.898
$f \sum (\alpha_2)^2 \alpha_3 + 1/2 \sum \alpha_3$	0.076	−1.4	1.48	−0.5	0.139	0.5

$(e_S)^*/e = 3.19 (e_c)^*/e = 1.45$ per formula unit

$$\text{KNbO}_3 \rightarrow \text{K}_{1/3}\text{O}(1)_{2/3} + \text{K}_{1/3}\text{O}'(1)_{2/3} + \text{K}_{1/3}\text{O}''(1)_{2/3}$$
$$+\text{Nb}_{1/6}\text{O}(1)_{1/6} + \text{Nb}_{1/6}\text{O}(2)_{1/6} + \text{Nb}_{2/3}\text{O}'(2)_{2/3} \quad (10)$$

and using the experimental refractive index (n_o) of 2.356 at 270°C [3,17]. The calculated bond parameters are listed in table 1. From the values of f_i, the K–O bonds are indicated to be highly ionic as compared to Nb–O bonds. This result is consistent with the formalism relating the ionicity of a chemical bond and the electronegativity of the constituent elements [18]. It also agrees with the earlier results [5,6] for compounds consisting of K–O bonds. Band structure calculations [19] on KNbO$_3$ established significant covalency for Nb–O bonds. From table 1, the dominating contribution from Nb–O bonds to the linear susceptibility χ with significantly higher $(\chi_b)^\mu$ values can also be noticed.

The ionic components of EO coefficients are computed using the expression (4), the crystal structure [1] and the dielectric constants [3,4] (table 2). Since the measured d_{ijk} values for tetragonal phase are not available, the electronic components $(r_{ijk})^{el}$ (eq. (3)) were not estimated. The errors in $(r_{ijk})^{ion}$ are evaluated from those in the structural [1] and the dielectric constant [3,4] data. From the experimental values of n_o, n_e and the calculated values of $(r_{33})^{ion}$ and $(r_{13})^{ion}$, the magnitude of $(r_c)^{ion}$ at 270°C is calculated. Within the errors, the calculated ionic components are closer to measured total ones [3,4] as shown in table 3. The differences obtained between the calculated and measured values could be due to the electronic components which are not included. However, the close agreement between ionic components and experimental total values (table 3) suggests that, like in the orthorhombic phase [20], the ionic components are major contributors to EO coefficients and the electronic components are not much significant in tetragonal KNbO$_3$.

Table 2. Experimental dielectric constants [3,4] and refractive indices [17] of tetragonal KNbO$_3$.

$\varepsilon_{11} = \varepsilon_{22} = 1365 \pm 205$	$\{(\varepsilon_{33} - \varepsilon_3)/(\varepsilon_3)^2\} = 12.33$
$\varepsilon_{33} = 306 \pm 46$	$\{(\varepsilon_{22} - \varepsilon_2)/(\varepsilon_3\varepsilon_2)\} = 49.18$
$n_o = 2.356$	
$n_e = 2.244$	

Table 3. Linear electro-optic coefficients (in pm/V) of tetragonal KNbO$_3$.

$(r_{33})^{\text{ion}} = 217.4 \pm 33$	$(r_{13})^{\text{ion}} = -6.9 \pm 1.0$
$(r_c)^{\text{ion}} = (225.4 \pm 32)^{\dagger}$	$(r_{42})^{\text{ion}} = -350.3 \pm 53$
$(r_c)_{\text{exp}} \approx 250^*$	$(r_{42})_{\text{exp}} = 420^*$

*Experimental values from [3,4]. †Calculated using the refractive indices from [17].

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

		NbO$_6$	KO$_{12}$
$(r_{33})^{\text{ion}}$	$=$	207.3	10.1
$(r_{13})^{\text{ion}}$	$=$	-7.3	0.4
$(r_{42})^{\text{ion}}$	$=$	330.3	20.0

From the values of individual chemical bonds, contributions from the two groups NbO$_6$ and KO$_{12}$ are evaluated and are listed in table 4. We can see that the linear EO behavior in tetragonal KNbO$_3$ is dominated by the distorted NbO$_6$ octahedra and not by KO$_{12}$ groups. This is due to higher values of the bond susceptibility $(\chi_b)^\mu$ for Nb–O than for K–O bonds (table 1). The Nb atoms, compared to K atoms, have more number of valence electrons (including the d-shell electrons) and a lower coordination number. These electrons are more delocalized (as evident from the higher f_c values for Nb–O) and are relatively more susceptible to applied field leading to a higher contribution to the EO coefficients, as described in the Introduction. Recently, linear EO coefficients of ABO$_3$ ferroelectrics were computed by first-principle density functional theory [21]. In the case of LiNbO$_3$ and tetragonal BaTiO$_3$, the EO tensors get dominating contributions by the ionic part of the optic modes. Additionally, atomic displacements along B–O bonding network make a prominent role in determining the EO coefficients. It is noteworthy that the finding of the preset calculations, namely the dominance of ionic contributions and major contributions from Nb–O bonds agree with the first first-principle calculations. In addition, in the present work, contributions from every individual type of bonds are worked out in detail.

Apart from the role of the nature of atoms and their coordination numbers, the importance of mutual orientation of the bonds towards the EO coefficients 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. (4) 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 the electronic structure. Since $\sum \alpha_3$ is present only for the coefficients r_{33} and r_{42} and is absent in the coefficient r_{13}, the value of the last one are much lower than the other two. The calculations show a better contribution but with opposite sign from the two K–O bonds of lengths 2.787 Å and 2.914 Å for r_{33} and r_{42}. Thus the net value is significantly lower due to cancellation of direction cosines (see the term $\sum \alpha_3$ for them in table 1) and hence of the individual contributions. Likewise, the net contribution from the two Nb–O bonds of lengths 1.853 Å and 2.21 Å is reduced due to the cancellations as described. The calculations also show that the value of the coefficient r_{13} arises significantly from the Nb–O bonds of length 2.005 Å.

4. Conclusions

The present study indicates that the clamped EO coefficients of tetragonal $KNbO_3$ originate from the NbO_6 octahedral groups in the crystal structure due to favourable coordinations and electronic configuration of Nb atoms and higher amount of electronic delocalization along the Nb–O bonds. The ionic components dominate over the electronic components of EO coefficients. Mutual orientations of chemical bonds are important in determining the EO properties of tetragonal $KNbO_3$.

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