

Research Article

Quantum Mechanical Study of YTiO_3 to the Investigation of Piezoelectricity

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In previous articles we reported through theoretical studies the piezoelectric effect in BaTiO_3 , SmTiO_3 , and YFeO_3 . In this paper, we used the Douglas-Kroll-Hess (DKH) second-order scalar relativistic method to investigate the piezoelectricity in YTiO_3 . In the calculations we used the [6s4p] and [10s5p4d] Gaussian basis sets for the O (³P) and Ti (⁵S) atoms, respectively, from the literature in combination with the (30s21p16d)/[15s9p6d] basis set for the Y (³D) atom, obtained by generator coordinate Hartree-Fock (GCHF) method, and they had their quality evaluated using calculations of total energy and orbital energies (HOMO and HOMO-1) of the $^2\text{TiO}^{+1}$ and $^1\text{YO}^{+1}$ fragments. The dipole moment, the total energy, and the total atomic charges in YTiO_3 in C_s space group were calculated. When we analyze those properties we verify that it is reasonable to believe that YTiO_3 does not present piezoelectric properties.

1. Introduction

Even today barium titanate (BaTiO_3), the first perovskite structure developed, is widely used in the industry. The polymorphic forms of BaTiO_3 have been likened by Kay and Vousden [1] to a displacement of the central Ti^{+4} ion within its oxygen octahedron towards one, two, and then three of the six adjacent oxygen ions as the temperature is lowered. This is a simplification of the actual atomic displacements, but it is a useful first approximation for understanding the structure. The piezoelectric properties in perovskite structure result from uncentrosymmetric characteristics [2]. The structure is a network of corner-linked oxygen octahedral holes and large cation filling the dodecahedral holes [3]. For a review about the role of the perovskite structure in ceramic science and technology see Bhalla et al. [4].

In previous reports [5–7], we performed Hartree-Fock (HF) studies to investigate the piezoelectric effect in BaTiO_3 ,

SmTiO_3 and YFeO_3 . The obtained results offered evidences that the piezoelectricity can be caused by electrostatic interactions. The purpose of this paper is to present a quantum mechanical study of the YTiO_3 and offer some insight into the investigation of this property in perovskites not experimentally investigated yet.

In our study of YTiO_3 we used the 6s4p and [10s5p4d] Gaussian basis sets for O (³P) and Ti (⁵S) atoms, respectively, from the literature [5]. For Y (³D) atom, we utilized the Generator Coordinate HF method [8] to obtain the (30s21p16d) Gaussian basis set which was contracted to [15s9p6d]. The quality of the contracted basis sets [6s4p]/[10s5p4d]/[15s9p6d] was evaluated in the study of the total energy and orbital energies for the $^2\text{TiO}^{+1}$ and $^1\text{YO}^{+1}$ fragments. Then it was done the addition of one d polarization function in the contracted basis set for the O atom and one diffuse function by symmetry for Ti and Y atoms. The [6s4p1d]/[11s6p5d]/[16s10p7d] molecular basis set was

used to model the dipole moments, total energy, and total atomic charges in YTiO_3 in C_s space group. In these work, we intend to investigate the possible piezoelectricity property of YTiO_3 using theoretical calculations.

2. Computational Procedure

2.1. The Development of the (30s21p16d) Basis Set to Y (3D) Atom. By the GCHF approach, we choose the one-electron as the continuous superposition

$$\Psi_i = \int \varphi_i(1, \alpha) f_i d\alpha, \quad i = 1, 2, \dots, n, \quad (1)$$

where φ_i are the generator functions (STFs and GTFs or other type of functions—in our case GTFs), the f_i are unknown weight functions, and α is the generator coordinate. The application of (1) to calculate expectation values using a Slater determinant leads to the Griffin-Wheeler-HF (GWHF) equations, which underlie the CGHF method

$$\int [F(\alpha, \beta) - \varepsilon_i S(\alpha, \beta)] f_i(\beta) d\beta = 0, \quad i = 1, 2, \dots, m, \quad (2)$$

where the ε_i are the HF eigenvalues, and the Fock, $F(\alpha, \beta)$, and overlap $S(\alpha, \beta)$, kernels are defined in [8].

In practical application the GWHF equations are solved through numerical integration. This is accomplished by discretization preserving the character of the CGHF method. This integration is implemented with a relabeling of the α space

$$\Omega = \frac{\ln \alpha}{A}, \quad A > 1, \quad (3)$$

where A is a scaling factor determined numerically.

The Ω space is discretized in an equally spaced mesh formed by Ω values so that

$$\Omega_m = \Omega_{\min} + (m - 1)\Delta\Omega, \quad m = 1, 2, \dots, N. \quad (4)$$

In (4), N corresponds to the number of discretization points defining the basis set size, Ω_{\min} is the initial point, and $\Delta\Omega$ the increment.

In the solution of the discretized form of (2), the (30s21p16d) basis set was used as defined by the mesh of (3). The discretization parameters (which define the exponents) for the basis set built to Y (3D) are $\Omega_{\min(s)} = -0.670$, $\Delta\Omega_{(s)} = 0.123$, and $N_{(s)} = 30$; $\Omega_{\min(p)} = -0.377$, $\Delta\Omega_{(p)} = 0.109$, and $N_{(p)} = 21$; $\Omega_{\min(d)} = -0.498$, $\Delta\Omega_{(d)} = 0.115$, and $N_{(d)} = 16$.

2.2. Building the [15s9p6d] Contracted Basis Set Y (3D) Atom and Evaluating the Quality of the [6s4p]/[10s5p4d]/[15s9p6d] Contracted Basis Set in Polyatomic Calculations. The contraction of the (30s21p16d) basis sets was implemented by employing the segmented contraction scheme proposed by Dunning and Hey [9]. The (30s21p16d) basis set was contracted to 15s9p6d through the following scheme: (14,2,1,1,1,1,1,1,1,1,1,2,1,1/9,3,1,1,1,3,1,1/8,1,1,1,4,1).

The (30s21p16d) and [15s9p6d] basis sets were obtained through a slightly modified version of the ATOMSCF program of Pavani and Clementi [10].

In order to evaluate the quality of the [6s4p], [10s5p4d], and [15s9p6d] basis sets in polyatomic study, we performed calculations of total energies, highest occupied molecular orbital (HOMO) energy, and the energy of one level below the highest occupied molecular orbital (HOMO-1) for the $^2\text{TiO}^{+1}$ and $^1\text{YO}^{+1}$ fragments. The results are compared with those obtained from the (24s14p), (30s19p14d), and (30s21p16d) basis sets.

Table 1 shows the HF total and orbital energies for $^2\text{TiO}^{+1}$ and $^1\text{YO}^{+1}$ fragments obtained with the uncontracted and contracted basis sets. From this table, one can see that the total energy obtained with [10s5p4d]/[6s4p] and [15s9p6d]/[6s4p] basis sets are close to the corresponding values of (30s19p14d)/(24s14p) and (30s21p16d)/(24s14p) basis sets. The total energies differ by 0.885 and 0.172 hartree for $^2\text{TiO}^{+1}$ and $^1\text{YO}^{+1}$ fragments, respectively. The HOMO energies obtained from contracted basis sets are closer to those of the uncontracted basis sets and differ by 0.00841 and 0.0138 hartree for the $^2\text{TiO}^{+1}$ and $^1\text{YO}^{+1}$ fragments, respectively. The HOMO-1 energies obtained from contracted basis sets are also close to the values of uncontracted basis sets and present deviations of 0.0128 and 0.00577 hartree.

To better describe the properties of the YTiO_3 in the implementation of the calculations it was necessary to include polarization function for the O (3P) atom. The polarization function value is $\alpha_d = 0.622507$ [5].

In *ab initio* calculations of the transition metal compounds, the role of the basis set is a crucial point, since the description of the configuration of the metal in the compound differs from the neutral state. The adequate diffuse functions were obtained through the total energy optimization of the ground state anion Ti^{-1} (4F) and Y^{-1} (3F) by HF method. The following diffuse functions for the [10s5p4d] and [15s9p6d] basis sets were determined for the Ti (5S) and Y (3D), respectively, using this strategy: $\alpha_s = 0.00177827$; $\alpha_p = 0.0537032$; $\alpha_d = 0.0263027$ and $\alpha_s = 0.0081283$; $\alpha_p = 0.0489779$; $\alpha_d = 0.0323594$.

The [6s5p1d]/[11s6p5d]/[16s10p7d] basis set was used in the modelling of dipole moment, total energy, and total atomic charges from $[\text{YTiO}_3]_2$ fragment.

2.3. The Representation of the Crystalline 3D Periodic YTiO_3 System. In previous papers [5–7], the fragment model shown in Figure 1 was used to simulate the necessary conditions to the existence of piezoelectricity in BaTiO_3 as full solid. In this paper, we used the same model to represent the crystalline 3D periodic YTiO_3 system. The Ti atom is located in the center of the octahedron, being wrapped up by six O atoms, disposed in the reticular plane (200), and two Y atoms arranged in the reticular plane (100).

To study the crystalline 3D periodic YTiO_3 system it is necessary to choose a fragment (or a molecular model), which represents adequately a physical property of the crystalline system as a whole. The fragment $[\text{YTiO}_3]_2$ was chosen because, after its optimization, the obtained structural parameters (interatomic distances) were closer to experimental values with good precision. The study was developed according to the following strategy: (i) first, it was carried out the

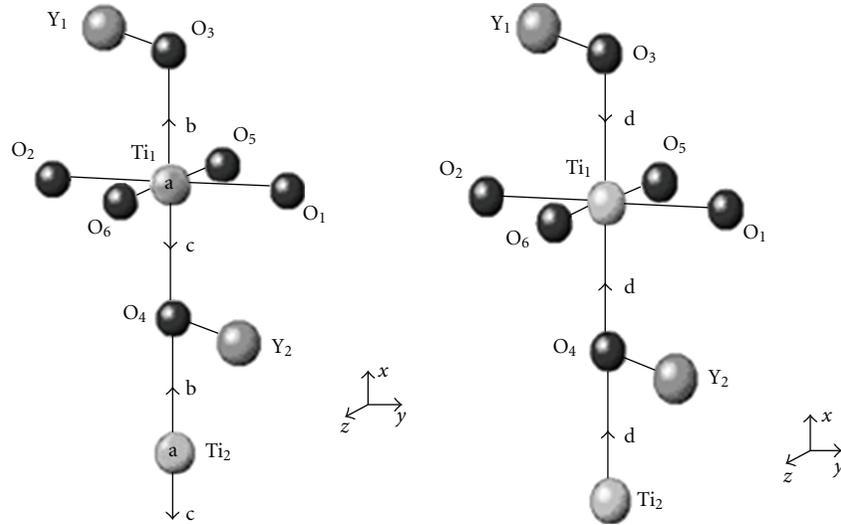


FIGURE 1: The octahedral $[YTiO_3]_2$ fragment. (Ia): (a) represents the $[YTiO_3]_2$ fragment with the Ti atoms fixed in the space; (b) represents the $[YTiO_3]_2$ being moved $+0.005 \text{ \AA}$ in the symmetry x axis, while the Y and O atoms are maintained fixed; (c) it presents the $[YTiO_3]_2$ fragment in which the Ti atoms are moved -0.005 \AA symmetry x axis, and Y and the O atoms are maintained fixed; (Ib), represents the $[YTiO_3]_2$ fragment with the bond lengths Ti_1-O_3 , Ti_1-O_4 , and Ti_2-O_4 shortened 0.005 \AA .

TABLE 1: Total and HOMO and HOMO-1 energies (hartree).

Fragment	Basis	Total energy	ϵ_{Homo}	$\epsilon_{\text{Homo-1}}$
$^2TiO^{+1}$	$[10s5p4d]^a/[6s4p]^b$	-922.0036930	-0.2860	-0.4573
	$(30s19p14d)^c/(20s14p)^d$	-992.8885441	-0.2944	-0.5857
$^1YO^{+1}$	$[15s9p6d]^e/[6s4p]^b$	-3406.227040	-0.4952	-0.5191
	$(30s21p16d)^f/(20s14p)^d$	-3406.3985754	-0.5090	-0.5249

^{a, c}Contracted and uncontracted basis for the Ti (3F) atom from [4].

^{b, d}Contracted and uncontracted basis for the O (3P) atom from [4].

^{e, f}Contracted and uncontracted basis for the Y (2D) atom from this paper.

geometry optimization of the $[YTiO_3]_2$ fragment in the C_s symmetry and $^1A'$ electronic state. (ii) Finally, calculations of single points were performed with the geometry optimized according to the descriptions shown in Figure 1.

In Figure 1 (I), (a) represents the $[YTiO_3]_2$ fragment with the Ti atoms fixed in the space. (b) represents the $[YTiO_3]_2$ fragment with the Ti atoms being moved $+0.005 \text{ \AA}$ in the x axis, while the Y and O atoms are maintained fixed. (c) represents the $[YTiO_3]_2$ fragment in which the Ti atoms are moved -0.005 \AA in the x axis, and Y and the O atoms are maintained fixed.

Figure 1 (II) represents the $[YTiO_3]_2$ fragment with the bond lengths Ti_1-O_3 , Ti_1-O_4 , and Ti_2-O_4 shortened 0.005 \AA .

All molecular calculations in this work were carried out by Hartree-Fock method with inclusion of the DKH second-order scalar relativistic calculations [11–13] as implemented in the Gaussian 03 program [14].

3. Results and Discussion

Aiming at the verification of possible piezoelectric properties of $YTiO_3$, the Ti^{+3} central ion, should be centric and the $[YTiO_3]_2$ fragment polarises when submitted to

mechanical stress. Firstly, we would like to call the attention for the comparison among the calculated bond lengths and the experimental values [15]. For Y–O and Ti–O bond lengths, our results are 2.009 and 2.421 \AA , while the experimental values are 2.077 and 2.508 \AA , respectively. The differences between the theoretical and experimental values are 0.0682 and 0.087 \AA . This shows a very good performance of our $6s5p1d/11s6p5d/16s10p7d$ basis set to model the geometry of the fragment studied.

In Table 2 are shown the dipole moment (in Debye) and the total energy (in hartree) from $[YTiO_3]_2$ fragment. In this table, one can see that the fragment with Ti^{+3} at (b) is 0.0111 hartree more stable when compared at (a); this evidence is confirmed by the decrease of the dipole moment. Also, when the central ion is moved to the position c, it can be verified that the fragment is 0.00813 hartree more stable than at (a). This indicates that the Ti^{+3} central ion is not centric. Still in Table 2 one can see that reducing the Ti_1-O_3 , Ti_2-O_4 , and Ti_2-O_4 bond lengths, the calculations in the atomic position d did not show either a deviation of atomic charges among the atoms of the $[YTiO_3]_2$ fragment, besides the decreasing of the dipole moment of the fragment. These results suggest that there is not a probable polarization of

TABLE 2: Dipole moment (Debye) and total energy (hartree) of the $[\text{YTiO}_3]_2$ fragment.

Ti atom position	μ_x	μ_y	μ_z	μ	Energy total
a	-7.817	6.546	0.463	10.21	-8807.601595
b	-1.200	5.861	2.878	6.639	-8807.612686
c	-3.485	2.419	3.515	5.510	-8807.609726
d	-3.620	-2.319	3.737	5.697	-8807.610393

TABLE 3: Total atomic charges from the $[\text{YTiO}_3]_2$ fragment.

Atom	Atom position			
	a	b	c	d
Ti(1)	2.1297	1.9474	1.9060	1.9082
Ti(2)	0.1786	0.2709	1.5778	0.1695
Y(1)	1.7391	1.6882	1.7362	1.7350
Y(2)	1.4534	1.4650	1.5351	1.5241
O(1)	-1.0417	-1.1458	-1.1290	-1.1296
O(2)	-0.992	-0.8898	-0.8994	-0.8967
O(3)	-0.5809	-0.3688	-0.3055	-0.2873
O(4)	-0.6715	-1.0558	-1.0715	-1.0788
O(5)	-1.1059	-0.7628	-0.8790	-0.8976
O(6)	-1.1015	-1.1484	-1.0504	-1.0467

YTiO_3 crystal when submitted to mechanical stress. Configurations b, c, and d show lower total energy compared to configuration a, as well as, lower values of total dipole moment μ and its individual components μ_x , μ_y , and μ_z . We suggest in this work that symmetric distribution of atomic charges provides a more stability of studied molecular fragment.

Table 3 shows the values of the total charges of the atoms in the $[\text{YTiO}_3]_2$ fragment with Ti^{+3} at a, b, and c positions and the Ti–O bond length reduced 0.005 Å. According to the table, when the Ti^{+3} central ion is deviated from the position a to b and c positions, it occurs the rearrangement of the electronic density, without being clearly established, however, a tendency in the migration of the atomic charges. On the other hand, in Table 3 one can see that when the $\text{Ti}_1\text{--O}_3$, $\text{Ti}_1\text{--O}_4$, and $\text{Ti}_2\text{--O}_4$ bond lengths are shortened, at atomic position (d), by a mechanical stress, it also occurs the rearrangement of the electronic density, without again verifying the clear tendency in the migration of the atomic charges in the material.

For the fragment a, which represents the probable configuration of this work, the HOMO and LUMO orbitals are $\text{HOMO} = -0.14 4s \text{ Ti}_1 - 0.27 2p_z \text{ O}_1 - 0.48 2p_z \text{ O}_4 + 0.82 2p_x \text{ O}_4 + 0.11 2s \text{ O}_6 - 0.27 2p_z \text{ O}_6 + 0.12 4d_{xz} \text{ Y}_1$; $\text{LUMO} = +0.17 4s \text{ Ti}_1 + 0.16 3p_x \text{ Ti}_1 + 0.14 2s \text{ O}_2 - 0.21 2p_y \text{ O}_2 + 0.16 2p_x \text{ O}_2 - 0.24 2p_x \text{ O}_3 + 0.24 4s \text{ Ti}_2 + 0.38 3p_x \text{ Ti}_2 + 0.43 3p_y \text{ Ti}_2 + 0.33 3d_{x^2-y^2} \text{ Ti}_2 + 0.10 3d_{xy} \text{ Ti}_2 + 0.10 3d_z^2 \text{ Ti}_2 - 0.20 5s \text{ Y}_2 + 0.16 4p_x \text{ Y}_2 + 0.274p_y \text{ Y}_2$.

Thus, we suggest that the metal–O distance in the $[\text{YTiO}_3]_2$ fragment is formed by π -symmetry covalent bonds between 3d and 4d orbitals of the Ti (^5S) and Y (^3D) atoms, respectively, to 2p orbital of the O (^3P) atom in opposition

to BaTiO_3 where it was verified that those bonds were ionic. The ionic characteristic between metal–O bonds is a fundamental condition to occurrence of piezoelectricity in our opinion, which is not observed in YTiO_3 . Therefore, previous theoretical studies of BaTiO_3 [5] have suggested that known piezoelectric properties are caused by electrostatic effects, and for SmTiO_3 [6] they have suggested the possible piezoelectric effect as well as electrostatic effects in its chemical bonds. On the other hand, for YFeO_3 [7] and YTiO_3 (this work), the theoretical calculations suggest absence of piezoelectric effect with covalent bonds between their atoms. For us, it seems that ionic bonds contribute to the occurrence of piezoelectric effect.

4. Conclusions

In the theoretical modeling of YTiO_3 in the C_s symmetry and $^1\text{A}'$ electronic state, the calculated results of the bond lengths showed a very good concordance with the experimental values from the literature. Obtained values of the moment of dipole, the total energy, and the total atomic charges showed that it is reasonable to believe that YTiO_3 does not present behavior of piezoelectric material.

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