

Quantum chemical modeling of perovskite: An investigation of piezoelectricity in ferrite of yttrium

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Abstract In a previous article, we used Hartree-Fock (HF) theory to study the piezoelectricity in BaTiO₃. In this paper, we applied the Douglas-Kroll-Hess second order scalar relativistic method to investigate the possible piezoelectric properties in the perovskite YFeO₃ structure, which has not yet been studied experimentally. The 30s20p13d and 31s21p17d Gaussian basis sets for the Fe (⁵D) and Y (²D) atoms, respectively, were built with the Generator Coordinate HF method. After contraction to [13s7p5d] and [13s8p7d], in combination with the 20s14p/6s4p basis set for the O (³P) atom from literature, they had their quality evaluated using calculations of the total and the orbital energies for the ²FeO⁺¹ and ¹YO⁺¹ fragments. The dipole moment, the total energy, and the total atomic charges in YFeO₃ in C_s space group were calculated. The results and the analysis lead us to believe that the perovskite YFeO₃ does not present piezoelectric properties.

Keywords CGHF method · Douglas-Kroll-Hess method · Ferrite of yttrium · Modeling of perovskite · Piezoelectricity in YFeO₃

Introduction

The first perovskite structure developed for industrial aim, which has been widely used, was the Barium titanate (BaTiO₃). The polymorphic forms of BaTiO₃ have been grouped by Kay et al. [1] to a displacement of the central Ti⁴⁺ ion within its oxygen octahedron toward 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 the first useful approximation to understand the structure. For a review about the role of the perovskite structure in ceramic science and technology see Bhalla et al. [2].

If experimental information is not available in literature, experimentalist can use the results of the theory's application as guidance to facilitate a rational cost application and time reduction in the study of the system under investigation. The aim of this work is the study of the perovskite YFeO₃ model to offer, using theory, some insight into the investigation of piezoelectric effect in perovskites not yet investigated experimentally.

To adequately represent the polyatomic system using a very good description of the total and the orbital energies of the YFeO₃ system's constituent fragments, the CGHF method [3] was used to build 30s20p13d and 31s21p17d Gaussian basis sets for the Fe (⁵D) and Y (²D) atoms, which were contracted to [13s7p5d] and [13s8p7d], respectively. For the O (³P) atom, the 20s14p/[6s4p] basis set reported in literature [4] was used. Then, one d polarization function in the contracted

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Table 1 Total and orbital energies of the highest occupied molecular orbitals (hartree)

Fragment	Basis sets	Total energy	HOMO	HOMO-1
${}^2\text{FeO}^{+1}$	[13s7p5d] ^a /[5s3p] ^b	-1345.61753658	-0.24139	-0.70248
	(30s20p13d) ^c /(20s14p) ^d	-1345.61931522	-0.24904	-0.70672
${}^1\text{YO}^{+1}$	[13s8p7d] ^e /[5s3p] ^b	-3452.69815685	-0.55746	-0.58079
	(31s21p17d) ^f /(20s14p) ^d	-3452.69975805	-0.55782	-0.58211

^{a, c} Contracted and extended basis sets for the Fe (${}^5\text{D}$) atom

^{b, d} Contracted and extended basis sets for the O (${}^3\text{P}$) atom

^{e, f} Contracted and extended basis s sets for the Y (${}^2\text{D}$) atom

basis set for the O atom and one diffuse function by symmetry for the Fe and Y atoms was added. Finally, the [6s4p1d]/[14s8p6d]/[14s9p8d] basis set was used to calculate the dipole moment, the total energy, and the total atomic charges in the YFeO_3 in C_s space group which we used to verify the possible piezoelectric effect of this material.

Computational strategy

The basis sets to Fe (${}^5\text{D}$) and Y (${}^2\text{D}$) atoms were built with the GCHF method. Details about its formalism, as well the strategies used in the selection of the basis sets, are very well documented in Refs. [3, 5, 6]. In this section, we provide the description of the procedure used in the contraction of the basis sets. Concomitantly, we evaluate the quality of the basis sets in the calculations of constituent fragments of YFeO_3 , and the choice of the polarization functions used in contracted basis set for the O (${}^3\text{P}$) atom, and, as well as, we show the strategy adopted for choosing the diffuse functions used in the Fe (${}^5\text{D}$) and Y (${}^2\text{D}$) atoms.

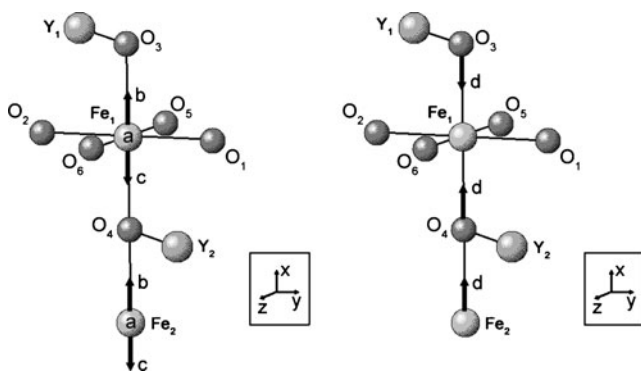


Fig. 1 The octahedral $[\text{YFeO}_3]_2$ fragment. **(1a)**: **(a)** represents the $[\text{YFeO}_3]_2$ fragment with the Fe atom fixed in the space; **(1b)** represents the $[\text{YFeO}_3]_2$ fragment being moved +0.005 Å in the symmetry X axis, while the Y and O atoms are maintained fixed; **(χ)** represents the $[\text{YFeO}_3]_2$ fragment in which the Fe atoms are moved -0.005 Å in the symmetry X axis and Y and O atoms are maintained fixed; **(2b)**: represents the $[\text{YFeO}_3]_2$ fragment with the bond lengths $\text{Fe}_1\text{-O}_3$, $\text{Fe}_1\text{-O}_4$ e $\text{Fe}_2\text{-O}_4$ shortened 0.005 Å

The contraction of the 30s20p13d/[13s7p5d] and 31s21p17d/[13s8p7d] was implemented by employing the segmented contraction scheme proposed by Dunning et al. [7]. For Fe (${}^5\text{D}$) atom, the 30s20p13d basis set was contracted to 13s7p5d through the contraction scheme 16, 1, 1, 2, 1, 2, 1, 1, 1, 1, 1, 1, 1, 1/12, 2, 1, 2, 1, 1, 1/8, 1, 2, 1, 1. For Y (${}^2\text{D}$) atom, the 31s21p17d basis set was contracted to 13s8p7d through the contraction scheme 14, 1, 2, 2, 2, 2, 2, 1, 1, 1, 1, 1, 1/10, 2, 2, 2, 1, 2, 1, 1/9, 2, 1, 2, 1, 1, 1.

In Table 1, the total and the orbital energies (HOMO and HOMO-1) for the ${}^2\text{FeO}^{+1}$ (${}^2\Sigma_g$) and ${}^1\text{YO}^{+1}$ (${}^1\Sigma_g$) fragments are shown. From this table, we can see that the total energies obtained with contracted basis sets are quite close to the corresponding values of 30s20p13d/20s14p and 31s21p17d/20s14p basis sets. The total energies differ by 1.78 and 1.60 milihartree for the ${}^2\text{FeO}^{+1}$ and ${}^1\text{YO}^{+1}$ fragments, respectively. The HOMO energies obtained from contracted basis sets are closer to those of the extended basis sets and differ by 7.65 and 1.36 milihartree for the ${}^2\text{FeO}^{+1}$ and ${}^1\text{YO}^{+1}$ fragments, respectively. The HOMO-1 energies obtained from contracted basis sets are also closer to the values of extended basis sets and present deviations of 3.76 and 1.32 milihartree.

In order to better describe the properties of YFeO_3 , polarization function for the O atom and diffuse functions for Fe and Y were include in the basis sets. The adequate polarization function was chosen through successive calculations for the $[\text{YFeO}_3]_2$ fragment by using different primitive functions, taking into account the minimum energy criterion. The diffuse functions were obtained through the total energy optimization of the ground state anions Fe^{1-} (${}^4\text{F}$) and Y^{1-} (${}^3\text{F}$) by HF method.

All molecular calculations in this work were performed by Hartree Fock method with inclusion of the Douglas-Koll-Hess (DKH) second-order scalar relativistic calculations [8–10] as implemented in the Gaussian 03 [11] program.

Results and discussion

In the study of the crystalline 3D periodic YFeO_3 system [12] it is necessary to choose a fragment (or a molecular model),

Table 2 Dipole moment (Debye) and total energy (hartree) of the $[\text{YFeO}_3]_2$ fragment

Fe atom position	μ_x	μ_y	μ_z	μ	Total energy
(a)	7.792	11.646	0.085	14.013	-9745.41089967
(b)	7.758	11.616	0.091	13.968	-9745.41244783
(c)	7.751	11.619	0.090	13.931	-9745.41181570
(d)	7.705	11.614	0.096	13.929	-9745.39118865

which represents adequately a physical property of the crystalline system as a whole. The model shown in Fig. 1 is the same used to simulate the necessary conditions to the existence of piezoelectricity in barium titanate (BaTiO_3) as full solid [2] and to investigate theoretically possible piezoelectric effect in samarium titanate (SmTiO_3) [13]. The $[\text{YFeO}_3]_2$ fragment was chosen because, after its optimization, the obtained structural parameters (interatomic distances) were close to experimental values with very good precision. The Fe atom is located in the center of the octahedron being wrapped up by six atoms, disposed in the reticular plane (200), and two Y atoms arranged in the reticular plane (100).

In the present study, the following strategy was used: (i) firstly, the geometry optimization of the $[\text{YFeO}_3]_2$ fragment in the C_s symmetry and electronic state $^1A'$ was performed. (ii) Secondly, single-point calculations were carried out with the optimized geometry according to the descriptions shown in Fig. 1.

With the aim of verifying possible piezoelectric properties of perovskite YFeO_3 , we considered that those properties in this structure type result from uncentrosymmetric characteristics presented by the central ion and the probable polarization of the crystal when submitted to mechanical stress. For the perovskite YFeO_3 , initially, we would like to call attention to the comparison of the calculated bond lengths and the experimental values [11]. For Y-O, Fe-O and Fe-Y our results are 1.999, 2.690 and 3.351 Å, while the experimental values are 1.903, 2.621 and 3.186 Å, respectively. The differences between the theoretical and the experimental values are 0.096, 0.069 and 0.155 Å. This shows a good performance of the molecular $[6s4p1d]/[14s8p6d]/[14s9p8d]$ basis set to describe the geometry of the $[\text{YFeO}_3]_2$ fragment studied.

Table 2 shows the dipole moment and the total energy of the $[\text{YFeO}_3]_2$ fragment. According to Table 2, we can see that the fragment with Fe^{+3} at (b) is 0.0260 hartree more stable than at (a). On the other hand, when the central ion is moved to the position (c), it can be verified that the fragment is less stable than at (a), indicating that the Fe^{+3} central ion is not centrosymmetric. That is corroborated by the increase of the dipole moment. Also, in that table, we can see the decrease of the $\text{Fe}_1\text{-O}_3$, $\text{Fe}_1\text{-O}_4$, and $\text{Fe}_2\text{-O}_4$ bond lengths (position d) does not provoke a migration of atomic charges in the atoms of the $[\text{YFeO}_3]_2$ fragment although increases the dipole moment at position (d). These

results suggest that there is not a probable polarization of the YFeO_3 crystal when submitted to mechanical stress.

Table 3 shows the atoms' total charges values in the $[\text{YFeO}_3]_2$ fragment with the Fe^{+3} central ion moving between the positions (a), (b), and (c) and the Fe-O bond length being shortened in 0.005 Å (position d). In this table, as we can see, the displacement of the Fe^{+3} between the positions (a), (b), and (c) occur with the distribution of the electronic density among the atoms so that it is not possible to verify a tendency in terms of migration of the atomic charges. This situation is due to the lack of uncentrosymmetric characteristics presented by the Fe^{+3} central ion. At atomic position (d), the decrease of $\text{Fe}_1\text{-O}_3$, $\text{Fe}_1\text{-O}_4$ and $\text{Fe}_2\text{-O}_4$ bond lengths, which could be caused by a mechanical stress, provokes a rearrangement of the atomic charges. However, it is not possible again to verify a tendency in the distribution of those charges. These results suggest that there is not a probable polarization of the YFeO_3 crystal when submitted to mechanical stress.

Thus, we suggest that Metal-O bonds in the $[\text{YFeO}_3]_2$ fragment are constituted by π -symmetry covalent bonds between the 3d orbital of Fe atom and the 3d orbital of Y atom to the p orbital of O atom in opposition to the BaTiO_3 crystal, where it was verified those bonds are ionic. The ionic characteristic between Metal-O bonds is a fundamental condition to occurrence of piezoelectric effect in our opinion, which is not observed in perovskite YFeO_3 .

Table 3 Total atomic charges of the $[\text{YFeO}_3]_2$ fragment

Atom	Atom position			
	(a)	(b)	(c)	(d)
Fe_1	2.300	2.306	2.304	2.281
Fe_2	0.197	0.191	0.192	0.194
Y_1	1.336	1.332	1.331	1.334
Y_2	0.998	1.000	0.991	0.995
O_1	-0.914	-0.915	-0.900	-0.908
O_2	0.401	0.403	-0.402	0.417
O_3	-0.991	-0.992	-0.991	-0.989
O_4	-1.153	-1.151	-1.156	-1.152
O_5	-1.019	-1.021	-1.016	-1.018
O_6	-1.155	-1.153	-1.157	-1.154

Conclusions

In the present report, the perovskite YFeO_3 in the C_s space group and $^1A'$ electronic state was modeled using the HF method. Our theoretical values to the bond lengths showed a very good concordance when compared with the corresponding experimental values from literature. The calculated dipole moment, the total energy and the total atomic charges show that it is reasonable to believe that the YFeO_3 does not present piezoelectric properties.

Full details about the wave function developed in this work are available by e-mailing to ciriaco@ufpa.br.

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