

Theoretical investigation of spontaneous polarization, electronic and optical properties of cubic perovskite BaHfO₃

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Abstract Electronic, optical properties and spontaneous polarization of cubic perovskite BaHfO₃ have been investigated using the Full Potential Linear Augmented Plane Wave method, implemented in the Wien2k code, in connection with the Generalized Gradient Approximation (GGA) and the Tran–Blaha modified Becke–Johnson exchange potential approximation (TB-mBJ). The calculation of band structure and density of state using TB-mBJ approach shows that the gap of BaHfO₃ is direct and equal to 5.9 eV which is in good agreement with the experiment data (6.0 eV), compared with GGA which gives 3.9 eV. The absorption coefficient $\alpha(\omega)$ and the complex dielectric function $\epsilon(\omega)$ are also investigated and predict that this compound can be effectively used in UV based optoelectronic devices. Furthermore, Using the PI approach, we can calculate the spontaneous polarization which is equal to 0.40 C/m² and predict that is in the same order as the Ps of other perovskite.

Keywords Perovskite BaHfO₃ · FP-LAPW · TB-mBJ · Electronic and optical properties · Spontaneous polarization · GGA

1 Introduction

Perovskite family contains a large number of compounds ranges from insulators to superconductors. It is also expected that these materials can be used for several spintronic applications, therefore the investigation of it physical properties is highly desirable. It

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reveals many fascinating properties from both theoretical as well as experimental point of view. The perovskite presents different characteristic as a high thermoelectric power (Okuda et al. 2001), ferroelectricity (Samantaray et al. 2004), charge ordering (Bednorz and Muller 1984), spin dependent transport (Frederikse et al. 1964), colossal magnetoresistance (Ramirez 1997) and the interplay of structural, magnetic and optical properties (Saha et al. 2000). It is frequently used as sensors, substrates, catalytic electrodes in fuel cells and are also promising candidates for optoelectronics (Ali et al. 2013).

Among the perovskite, we can distinguish the ferroelectric oxides which are more interesting in photovoltaic applications due to its large band gaps of 3.0 eV (Lee et al. 2012). The substitution of some parts of its crystal lattice allows obtaining materials functional characteristics tailored.

The perovskite type alkaline earth hafnates, BaHfO₃ and SrHfO₃ have been well known as high melting temperature materials (Jorba et al. 1964). In addition, these materials are useful as a superconducting films substrat (Zhang and Evetts 1994), while the polycrystalline films cubic BaHfO₃ can be also regarded as promising candidates for future memory storage capacitor applications (Abrutis et al. 2011; Dudek et al. 2011).

Pervious investigations of BaHfO₃ have been developed theoretically (Bouhemadou et al. 2008; Yangthaisong 2013; Vali 2008), using the CASTEP code with LDA (Bouhemadou et al. 2008), GGA approximation, and sX-LDA in order to calculate the structural, elastic, electronic and optical properties. Other studies were also interested on the electronic properties (Yangthaisong 2013; Vali 2008).

We note that there aren't many studies on the optical properties of BaHfO₃, the electrical properties such as the spontaneous polarization has not yet investigated.

In this paper, we are interested to study the electronic, optical properties of this system by using the Full-Potential Linearized Augmented Plane Wave (FP-LAPW) method; we essentially use the modified Becke–Johnson (TB-mBJ) approximation to more accurate results. We focus also on the study of the spontaneous polarization of cubic perovskite BaHfO₃, using the Berry phase which is implemented in the Wien2k code (Gonze et al. 2002; Ahmed et al. 2013).

Therefore, the band structure, density of states, imaginary and real part of dielectric function, absorption coefficient and the spontaneous polarization of BaHfO₃ are calculated.

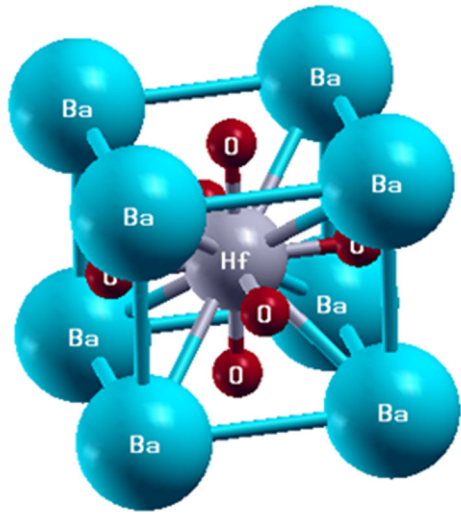
2 Calculation details

The calculations were carried out using (FP-LAPW) method as implemented in Wien2k code (Blaha et al. 2001). The electronic structure and optical properties were calculated with both the Generalized Gradient Approximation (GGA) of Perdew–Burke–Ernzerhof (PBE) (Perdew et al. 1996) and the modified Becke–Johnson (mBJ) (Tran and Blaha 2009) exchange–correlation potential. The latter approximation was recently proposed by Tran and Blaha introducing the parameter c into the original BJ exchange potential (Becke and Johnson 2006):

$$v_{\chi,\sigma}^{mBJ}(r) = cv_{\chi,\sigma}^{BR}(r) + (3c - 2) \frac{1}{\pi} \sqrt{\frac{5}{12}} \sqrt{\frac{2t_{\sigma}(r)}{n_{\sigma}(r)}} \quad (1)$$

where $n_{\sigma}(r)$ is the spin-dependent electron density and $t_{\sigma}(r)$ is the spin-dependent kinetic-energy density. The parameter $v_{\chi,\sigma}^{BR}(r)$ is the Becke–Roussel potential (Becke and Roussel

Fig. 1 The cubic structure of the perovskite-type BaHfO₃



1989). Within the modified Becke–Johnson (mBJ) potential, the parameter c was proposed to be determined self-consistently from the density by:

$$c = \alpha + \beta \left(\frac{1}{V_{cell}} \int_{cell} \frac{|\nabla n(r')|}{n(r')} d^3 r' \right)^{1/2} \quad (2)$$

The parameters α and β have been chosen to fit the band gaps in a broad range of solids.

The calculation was done with a scalar relativistic approach without spin–orbit coupling. The partial waves inside the atomic spheres are expanded up to the angular momentum $l_{max} = 10$ with the product $R_{MT}k_{max} = 7$, which determines the matrix size, where R_{MT} is the smallest muffin-tin radius (R_{MT}) and k_{max} is the maximum value of the wave vector. The radii of the atomic spheres of Ba, Hf and O are set to 2.50, 2.11 and 1.81 (atomic units) respectively. The self-consistency is obtained by 250 k-points in the irreducible symmetry wedge of the first Brillouin zone. The self-consistent calculations are considered to converge when the total energy of the system is stable within 10^{-5} Ryd.

At room temperature, BaHfO₃ crystallized in the cubic phase, where the Ba atom is located at (0, 0, 0), Hf at (0.5, 0.5, 0.5), and three O atoms takes place at face centered positions (0.5, 0.5, 0) (see Fig. 1). The optimized value of lattice parameter (4.16 Å) is close to the experimental one (4.171 Å) (Maekawa et al. 2006).

3 Results and discussion

3.1 Electronic properties

In order to describe the electronic properties, we have represented the band structure, the total and partial density of states using with both GGA and mBJ approach in Figs. 2 and 3 respectively.

The Fermi level E_F is set at 0 eV, it coincides with the top of the valence band. Using GGA calculations, the maximum of the valence band (VBM) and the minimum of the conduction band (CBM) are at the same point Γ and the gap is equal to 3.9 eV, which

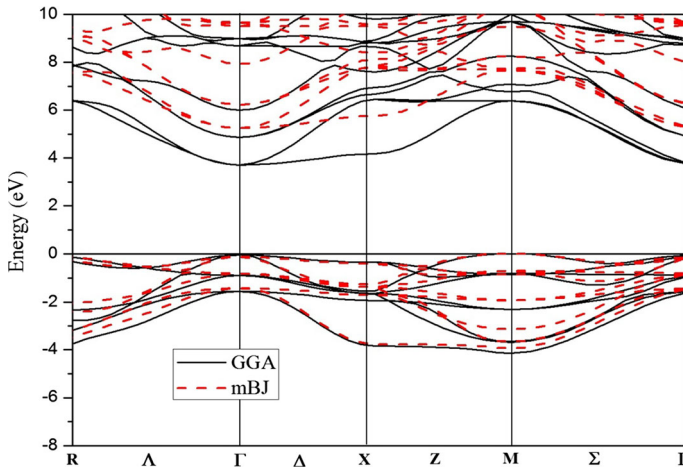


Fig. 2 The band structure of cubic perovskite BaHfO₃ along the high symmetry lines of the Brillouin zone, Fermi level $E_F = 0$ eV with GGA and mBJ approach

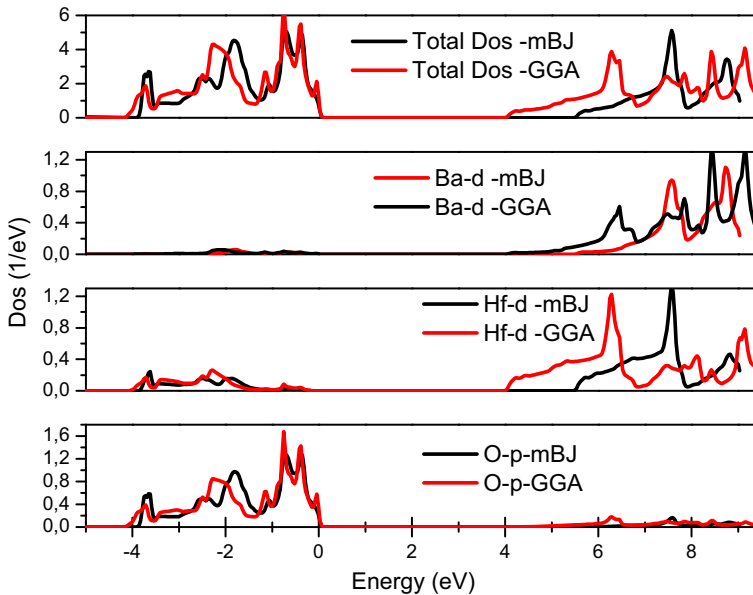


Fig. 3 Total and partial densities of states of BaHfO₃ with GGA and mBJ approach

means that this compound has a direct band gap (Γ - Γ), as shown the Fig. 2, the result is consistent with other calculations (Bouhemadou et al. 2008; Liu et al. 2010). The occupied Hf d-states and p-states of Oxygen are positioned mainly between -4 and -1 eV, at the very top of the valence band. On the other hand, the full Hf d-states and d-states of Ba in the conduction band are within a narrow band centered at approximately 4 eV, making the band gap of 3.9 eV which is in strong disagreement with the experimental measurements $E_g = 6$ eV (Vali 2008).

Table 1 Some direct band gaps (Γ - Γ , M-M, R-R, X-X), indirect band gap (Γ -M, Γ -R, Γ -X) for BaHfO₃

	Γ - Γ	M-M	R-R	X-X	Γ -M	Γ -R	Γ -X
E _g (eV)—GGA	3.9	6.2	6.1	4.3	4.1	6.2	6.18
E _g (eV)—mBJ	6.0	7.8	7.2	6	5.60	7.19	5.79

Table 2 Calculated Band gap of cubic BaHfO₃ crystal compared with others calculations

Band gap (eV)	Our works (mBJ)	Experimental value (Vali 2008)	Other calculations			
			SX-LDA (Yangthaisong 2013)	SX-LDA (Zhao et al. 2009a, b)	LDA (Bouhemadou et al. 2008)	GGA
	5.9	6.0	5.3	3.94	2.99	3.17

However with using the mBJ correction, the occupied Hf d-states are localized in the conduction band. We can show in the Figs. 2 and 3 that the top of conduction band shift of 2.0 eV than GGA approximation value (Table 1).

Finally, the present mBJ calculations seem to lead to the best agreement with known experimental facts. Obviously the O-2p states dominate the top of the valence band, the calculated gap is equal to 5.9 eV which is very close to the experimental data (6.0 eV) (Vali 2008). This value is more accurate than other works as shown in Table 2. It is found that with (sX-LDA) implemented in CASTEP code, that the band gap is 5.3 eV, some works (Yangthaisong 2013), predicted also smaller values as 3.94 and 3.17 eV (Zhao et al. 2009a, b), the value obtained with mBJ is the better compared with experimental data (Vali 2008).

3.2 Optical properties

In order to investigate the optical properties, we have computed the real part of the dielectric function $\epsilon_1(\omega)$, imaginary part $\epsilon_2(\omega)$ and the absorption spectrum using the GGA approximation and TB-mBJ approximation as represented in Figs. 4 and 5.

The $\epsilon_2(\omega)$ has a large peaks correspond to the interband transition, and we can see that the peaks of the imaginary part of the dielectric function using TB-mBJ are shifted to higher energies compared to GGA.

The same behavior for the real part of the dielectric function in both GGA and TB-mBJ. The absorptive part of the dielectric function $\epsilon_2(\omega)$ exhibits three structures labeled 1, 2, 3 and 4 as shown in Fig. 5.

1. Structure 1 originates mainly from transitions of O-2p into the lower conduction bands.
2. Structure 2 from transitions of O-2p into the anti bonding from Hf-5d T_{2g} (d_{xy} - d_{yz} , d_{xz}) conduction bands as well as O-2p into the Ba-5d conduction bands.
3. Structure 3 from transitions of O-2p into Hf-5d e.g. ($d_{x^2-y^2}$, d_z^2) conduction bands as well as O-2p into Ba-5d conduction bands.
4. Structure 4 from transitions of Ba-5p into conduction bands, and structure 5 from transitions of O-2p into Hf-6s and Hf-5p conduction bands. These results are in good agreement with (Bouhemadou et al. 2008; Liu et al. 2010).

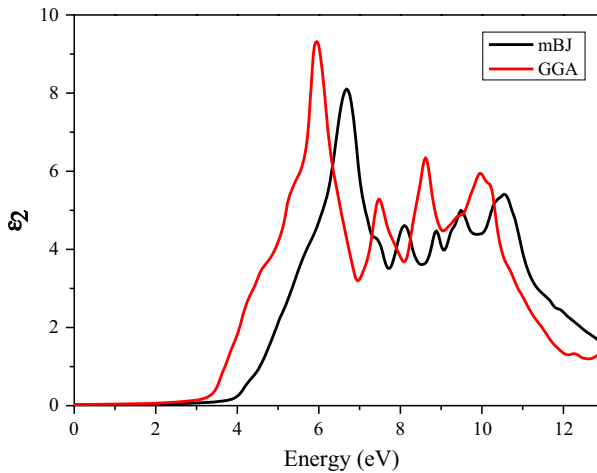


Fig. 4 The imaginary part of the dielectric function of BaHfO₃ using GGA and mBJ approach

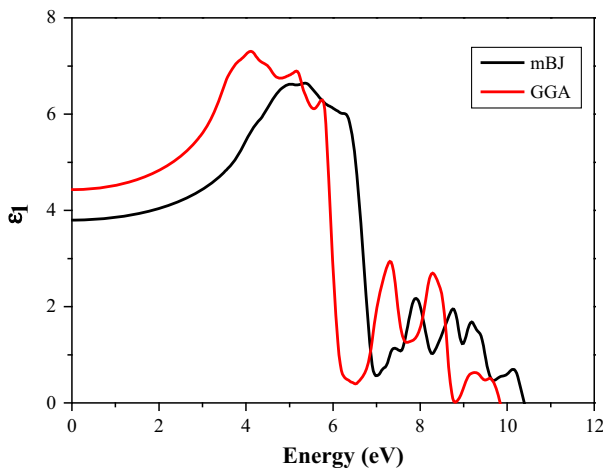


Fig. 5 The reel part of the dielectric function of BaHfO₃ using GGA and mBJ approach

The calculated static dielectric constant is $\epsilon(0) = 3.74$, with mBJ approach we have $\epsilon(0) = 4.44$ value closer to the some references $\epsilon(0) = 4.39$ (Bouhemadou et al. 2008), $\epsilon(0) = 6$ (Liu et al. 2010).

From the Fig. 6, we can see that the low absorption and the strong absorption occur in the visible and UV respectively, the absorption edge starts at 4.1 eV.

3.3 Spontaneous polarization

BaHfO₃ is a good ferroelectric material for the existence of a large spontaneous polarization; it is applied in the first field ferroelectricity. Spontaneous polarization P_s is one of the important characteristics for ferroelectric materials. It is defined as the change in

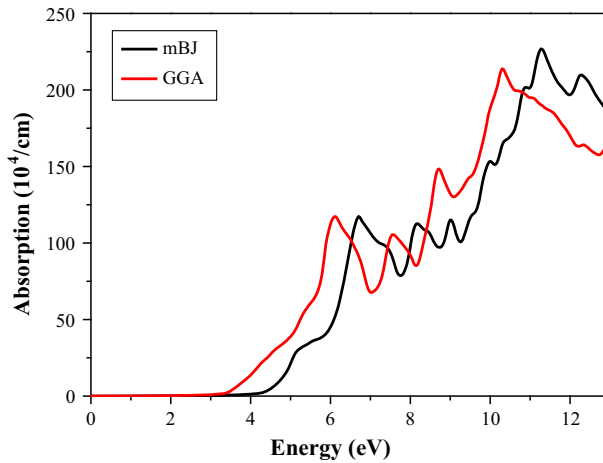


Fig. 6 Absorption spectra of BaHfO₃ by using GGA and mBJ approach

Table 3 The spontaneous polarization (C/m²) for different perovskite compounds

Compounds	Ps (theoretical values; Perdew et al. 1996)	Ps (Experiment values; Perdew et al. 1996)
BaHfO ₃ (the present work)	0.40	–
BaTiO ₃	0.31	0.26
KNbO ₃	0.36	0.37
PbTiO ₃	0.86	0.75

polarization that occurs when the crystal undergoes a phase change from the Centrosymmetric structure to a non centrosymmetric structure without inversion the symmetry.

The spontaneous polarization $P_s = P_{nc} - P_c$, with P_{nc} and P_c refer to the polarization values for non centrosymmetric and centrosymmetric structures, respectively.

It is known that there are not a reported experiment and theoretical results of spontaneous polarization for BaHfO₃. Using the Berry phase PI approach implemented in Wien2k code, we note that the value found for P_s is significant and in good agreement compared with other compound in the same family of perovskite (BaTiO₃), and with other perovskite as KNbO₃ and PbTiO₃ which the experiment values of P_s are respectively 0.26, 0.37, 0.57 C/m², Table 3 shows the P_s values of different perovskites (Perdew et al. 1996) compared with our calculation.

4 Conclusion

The merits of Tran–Blaha approach, which use the modified Becke–Johnson exchange potential for calculation of electronic structures, in the case of BaHfO₃ is the special emphasis to its optical properties. The calculated mBJ electronic structure and optical spectra are in good agreement with the known experimental facts, specially the calculation of band gap which is equal to 5.9 eV.

Additionally, it changes the character of electronic states near the valence band top. Namely, the separation of narrow band, we have also analyzed the interband contribution to the optical response functions. We have shown that O 2p states and Hf 5d states play a major role in these optical transitions as initial and final states, respectively. Finally, we calculated the spontaneous polarization using Berry phase approach for perovskite BaHfO₃ which is equal to 0.40 C/m².

The presented results are important in connection with the new findings about the proclivity of BaHfO₃ to act as a promising candidate in different application as in Dynamic Random Access Memory Storage Capacitor and optoelectronic applications.

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