First principles calculation of structural and optical properties of $RaHfO_3$ perovskite semiconductor for solar cells

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Abstract – **An ab initio calculations were performed using the full potential linearized augmented plane waves (FP-LAPW) within the Angel-Vosko (EV) generalized gradient approximation (GGA) for the treatment of the exchange correlation potential in framework of the density functional theory (DFT) as implemented in wien2k code. In aims to predict the elastic, structural, electronic and optical properties of $RaHfO_3$ perovskite. Elastic properties confirm the stability for wide range and the electronic properties like DOS and band structure was studied in detail. The preliminary results of compound exhibit semiconductor behavior with gap energy around 1ev. On the other hand, an accurate calculation of linear optical function (refraction index and the dielectric function) was performed, these properties make it good candidates for solar cells applications.**

Keywords – DFT, EV- GGA, perovskites, gap energy.

I. INTRODUCTION

The perovskite compounds with chemical formula ABO_3 have been the subject of extensive investigation, due to their fascinating electrical, optical and magnetic properties which make them suitable for a host application in the solar cells.[1]

The perfect perovskite structure is very simple and has full cubic symmetry. It can be thought of as a lattice of corner sharing oxygen octahedral with interpenetrating simple cubic lattices of A and B cations. The B cations sit at the center of each oxygen octahdera while the A metal ions lie in 12-fold coordinated sits between the octahedral [2].

In our study, the structural, elastic, electronic and optic properties have been investigated using ab initio calculations within the Angel-Vosko (EV) generalized gradient approximation (GGA) of cubic $RaHfO_3$ perovskite.

The aim of this study is to have more insight on the behavior of perovskite compounds. The obtained results are considered as purely predictive since no data are available in the literature. This contribution enhances the understanding and broadens the database of optoelectronic properties of rare-earth. Which will benefit the emerging area of research concerning solar cells.

The paper is organized in the following way: section 2 deals with a description of the methods, as well as some details of calculations. The calculated structural and optical properties are presented and discussed in section 3. Finally, the conclusion is given in section4.

II. COMPUTATIONAL METHOD:

The first-principles calculations performed in this communication are based on the density functional theory (DFT). The total energies were calculated within the full potential linearized augmented plane wave (FPLAPW) +local orbitals (lo) method, implemented in the WIEN2K code [3]. In this code, the crystal structures were decided under the condition that the total energy is minimized from all atomic configurations. The exchange–correlation energy of electrons is described in generalized gradient approximation (GGA96) [4]. In order to increase the reliability and a reasonable comparison, we used the same radius of the muffin-tin sphere for the same kind of atom in all of the calculations. Within these spheres, the potential is expanded in the form and outside the sphere:

$V(r) = \sum_{bn} V_{bn}(r) Y_{bn}(\hat{r})$ (1)

$V(r) = \sum_{k} V_k \, e^{ikr}$ (2)

Where a linear combination of radial functions is times spherical harmonics. Within this calculational scheme, there are no shape approximations to the charge density or potential. The charge density was Fourier expanded up to Gmax = 14 (Ryd)1/2. The iteration process was repeated until the calculated total energy of the crystal converged to less than 0.1 mRy/unit cell. A mesh of 72 special was taken in the irreducible wedge of the Brillouin zone. Both the muffin-tin radius and the number of k-points were varied to ensure total energy convergence [5].

TABLE I

Lattice constant a, bulk modulus B, pressure derivative of bulk modulus B′, and elastic constants parameters of $RaHfO_3$ at zero pressure and zero temperature.

Size	$RaHfO_3$
A(Å)	4.52
B(GPa)	93.55
B′	4.16
C11(GPa)	91.17
C12(GPa)	87.91
C44(GPa)	36.53

III. RESULTS AND DISCUSSION:

A. Structural properties:

The calculated total energy versus volume are fitted to the Murnaghan's equation of state [6] to determine the ground state properties. The calculated total energy as a function of volume are plotted in figure.1 for the compound $RaHfO_3$ in Pm-3m structure. The optimized lattice parameter derived from the volume of minimum total energy is a = 4.52 Å. This value was used for the calculations reported in the next section. The accompanying bulk modulus for the compound is around 94 GPa of this compound. Until now, an experimental lattice constant value has not been reported.

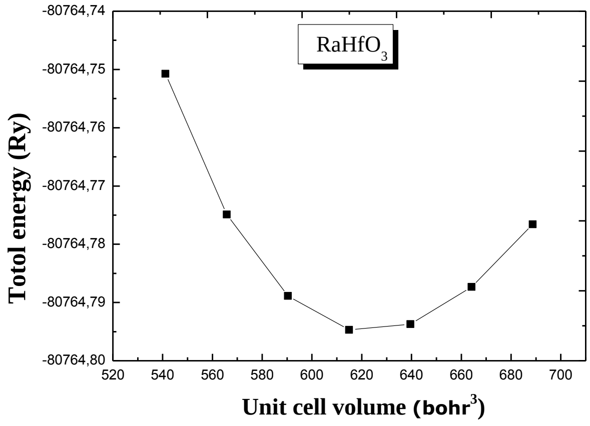


Fig.1: Total energy as a function of the volume for states of $RaHfO_3$ in the Pm-3m structure.

B. Electronic properties:

Density of states and electronic band structure often provide sufficient information for a through characterization of the electronic properties of a material. The energy band structure, total and partial density of states (DOS) of $RaHfO_3$ were calculated by FP-LAPW method. The results are presented in fig.2 and fig.3 of the compound respectively. Our calculation show that in fig.2 we can find that the DOS can be divided into two parts: (1) deep energies which represent the contribution of the majority spin of 2s orbital of Hf atom, (2) energies around the Fermi level where the 3d orbitals of Ra (eg, t2g) are dominated. In fig.3 there is a direct low gap for the $RaHfO_3$, where the valence band maximum is located at ʌ and the conduction band minimum at ʌ. The existence of a gap at the Fermi level for the compound confirms the semiconductor behaviour.

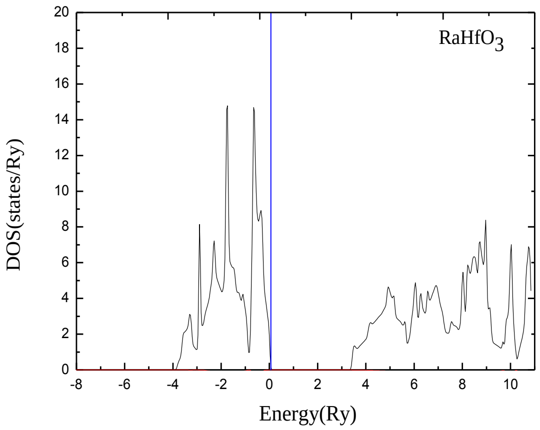


Fig.2: Electronic structure of cubic RaHfO3: the total density of states (DOS).

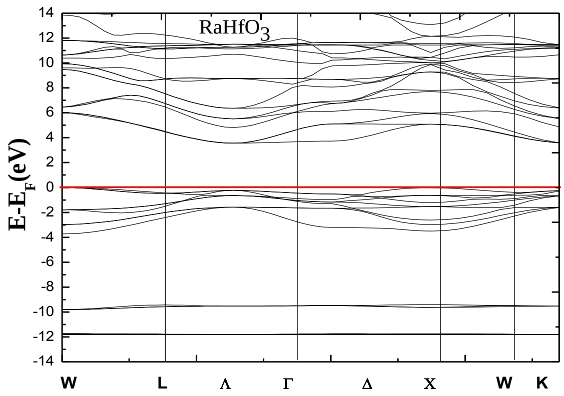


Fig.3: Electronic band structure of cubic $RaHfO_3$.

C. Optical properties

The linear response to an external electromagnetic field with a small wave vector is measured through the complex dielectric function:

$$\mathcal{E}(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega) \qquad (3)$$

which is related to the interaction of photons with electrons [7]. The imaginary part ε_2(w) of the dielectric function could be obtained from the momentum matrix elements between the occupied and unoccupied wave functions and is given by [8]

$$\varepsilon_2(\omega) = \frac{4\pi^2\ e^2}{Vm^2\omega^2}\sum\int\langle i|M|j\rangle f_i\ (1 - f_i\ ) \times \delta\big(E_f - E_i - \hbar\omega\big)d^3k. \qquad (4)$$

Where ω is the electromagnetic radiation impinging the crystal, V is the unit cell volume, e and m are the charge and mass of the electron, M is the momentum operator in bracket notation, i and j are the initial and final states respectively, f_i the Fermi distribution function for the ith state and condition for the conservation of total energy is represented by

$\delta(E_f - E_i - \hbar\omega)$ where E_f and E_i are the energies of the electron in the ith and jth state.

The real part $\varepsilon_1(\omega)$ can be evaluated from $\varepsilon_2(\omega)$ using the Kramers-Kronig relations and is given by [9]

$$\varepsilon_1(\omega) = 1 + \left(\frac{2}{\pi}\right) P \int_0^\infty \frac{\varepsilon_2(\omega)\omega' d\omega'}{\omega'^2 \omega^2} \qquad (5)$$

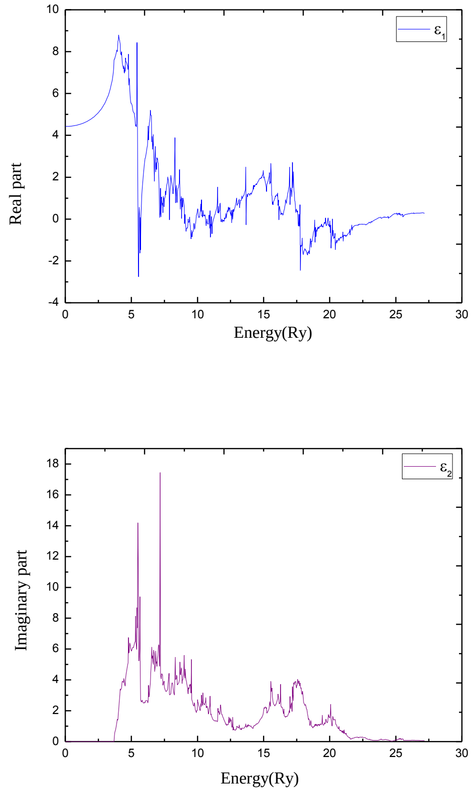
Where P represents the principal value of the integral. All of the other optical properties, including the absorption coefficient $\alpha(\omega)$, the refractive index $n(\omega)$, the extinction coefficient $k(\omega)$, and the energy-loss spectrum $L(\omega)$, can be directly calculated from $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ [10,12]

Fig.4 (a) displays the real and imaginary parts of the electronic dielectric function $\varepsilon(\omega)$ spectrum for the phonon energy ranging up to 30 Ry, respectively. The real dielectric function $\varepsilon_1(\omega)$ gives the static dielectric constant in the zero frequency limit, which has the value of 4.4. the main features of these curves are: a peak at 3.9 and the others present a transition probabilities. The imaginary part of the electronic dielectric function $\varepsilon_2(\omega)$ is the fundamental factor of the optical properties of material. Fig.4 (b) displays the imaginary (absorptive) part of the dielectric function $\varepsilon_2(\omega)$ up to 30 Ry. Our analysis shows that the critical points of the $\varepsilon_2(\omega)$ occurs at around 3.71Ry. this point correspond to splitting which gives the threshold for the direct optical transitions between the absolute valence band maximum and the first conduction band minimum. It is known as fundamental adsorption edge.

Fig.5 presents the refractive index $n(\omega)$ along with the extinction . The peak values of refractive indices are 2.2 at 3.0. The refractive index spectrum increases with respect to photon energy in the transparency region.

Fig.6 presents absorption coefficient which is the parameter indicates the fraction of light lost by the electromagnetic wave when it passes through a unit thickness of the material. It is clear that polarisation has a minor influence on the spectrum. From the absorption spectrum, we can easily find the absorption edges located at 3.6 eV.

Fig.7 the maximum reflectivity occurs in region 4.45-5.67 and from 6.29-9.84 and 17.51-24.12.



(a)

(b)

Fig.4 (a) the real part and (b) the imaginary part of the dielectric function for cubic $RaHfO_3$.

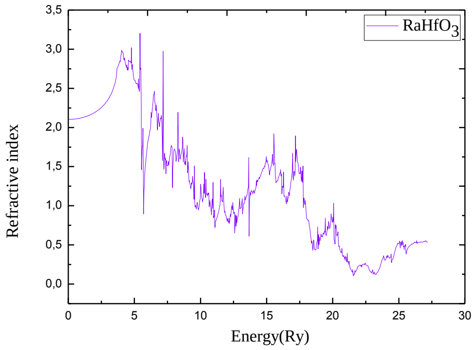


Fig.5: Calculated of refractive index of $RaHfO_3$.

(g)

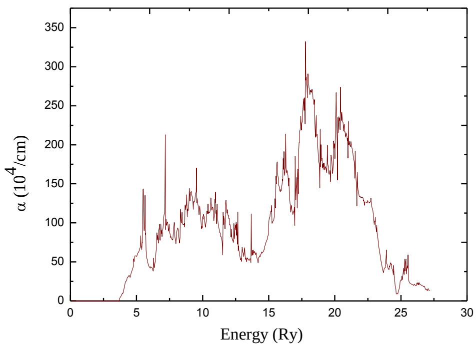


Fig.6: Calculated absorption coefficient (α(w))of $RaHfO_3$.

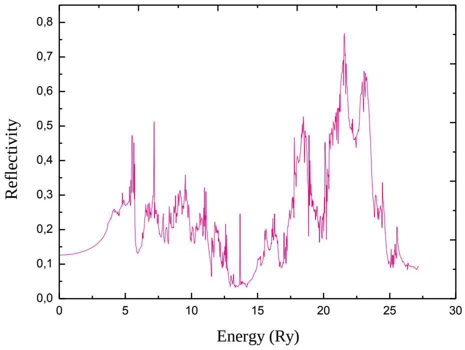


Fig.7: Calculated reflectivity (R(w)) for $RaHfO_3$.

D. Conclusion

In summary, the structural, elastic, electronic and optical properties of low-gap semiconductor $RaHfO_3$ at temperature T=0K were extensively studied using full-potential linearized augmented plane wave (FP-LAPW) method. The exchange-correlation potential was calculated within the Angel-Vosko (EV) with the frame of generalized gradient approximation (GGA). The ground-state parameters, such as lattice parameter, bulk modulus and its pressure derivative were predicted. We have additionally predicted the elastic constants. The partial contribution from each atom to the total density of states was calculated. From the band structures we find that the $RaHfO_3$ have direct gap at ʌ point. which make it good candidate for solar cell applications.

V. REFERENCES

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