Structural, electronic, optical and mechanical properties of BaPaO₃ and BaUO₃ cubic perovskites

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Abstract

In this paper, we have applied a potential approximation known as modified Becke-Johnson (mBJ) based on density functional theory method to compute structural, electronic, optical and mechanical properties of $BaPaO_3$ and $BaUO_3$ compounds. Type of chemical bonding is analyzed with the help of variations in electron density difference distribution that is induced due to changes of second cation. Results reveal (Γ-Γ) direct band gap semiconducting nature. We have also investigated the band gap dependent optical properties such as complex dielectric function $\mathcal{E}(\omega)$, optical conductivity $\sigma(\omega)$, refractive index $n(\omega)$, reflectivity $R(\omega)$.

Keywords: lattice constants, bulk modulus, band gap, perovskites

1. INTRODUCTION

Compounds having ABO_3 stoichiometry is known as Oxide-perovskites. Here A is usually alkaline earth metals while B is to be transition or non-transition metals and anion is represented by O that are oxides [1]. The ternary oxides (ABO_3) are important materials as they have significant applications in piezoelectricity,

ferroelectricity colossal magnetoresistivity, and high temperature superconductivity [2]. Moreover they are also promising candidates for solid-state devices, radiation detection devices, spintronic devices and optoelectronic devices as well [3-4]. $BaPaO_3$ and $BaUO_3$ are characterized by their high value of static dielectric constant (ε_o) which can decide about degree of miniaturization of material that can ultimately use for device synthesis because materials having static dielectric constant (ε_o) greater than that of silicon nitride ($\varepsilon_o=7$) are classified as high dielectric constant materials [5]. $BaUO_3$ has been quite successfully explored by experimental studies such as molar Gibbs energy of formation and enthalpies of formation are measured by solution calorimetric method [6-8]. Moreover, thermo-physical and thermochemical properties are also investigated [9, 10]. However, on theoretical side, Huang et al. [11] investigated vaporization properties by simulation method. On the other hand, $BaPaO_3$ compound is competing in scientific investigation [12]. Moreover, neither experimental nor theoretical efforts have been made to explore electronic and optical properties of these ternary oxides. With this motivation, we perform density functional theory (DFT) calculations to probe structural, electronic optical and mechanical properties of $BaPaO_3$ and $BaUO_3$ cubic perovskites.

2. COMPUTATIONAL METHODS

The calculations were done using FP-LAPW computational scheme [13,14] as implemented in the WIEN2K code [15]. The FP-LAPW method expands the Kohn-Sham orbitals in atomic like orbitals inside the muffin-tin (MT) atomic spheres and plane waves in the interstitial region. The Kohn-Sham equations were solved using the recently developed Wu-Cohen generalized gradient approximation (WC-GGA) [16, 17] for the exchange-correlation (XC) potential. It has been shown that this new functional is more accurate for solids than any existing GGA and meta-GGA forms. For a variety of materials, it improves the equilibrium lattice constants and bulk moduli significantly over local-density approximation [18] and Perdew-Burke-Ernzerhof (PBE) [19] and therefore is a better choice. For this reason we adopted the new WC approximation for the XC potential in studying the present systems. Further for electronic structure calculations modified Becke–Johnson potential (mBJ) [20] as coupled with WC-GGA is used.

The valence wave functions inside the atomic spheres were expanded up to $l=10$ partial waves. In the interstitial region, a plane wave expansion with $R_{MT}K_{max}$ equal to seven was used for all the investigated systems, where R_{MT} is the minimum radius of the muffin-tin spheres and K_{max} gives the magnitude of the largest K vector in the plane wave expansion. The potential and the charge density were Fourier expanded up

to $G_{max} = 12$. We carried out convergence tests for the charge-density Fourier expansion using higher G_{max} values. The modified tetrahedron method [20] was applied to integrate inside the Brillouin zone (BZ) with a dense mesh of 5000 uniformly distributed k-points (equivalent to 405 in irreducible BZ) where the total energy converges to less than 10^{-6} Ry.

3. RESULTS AND DISCUSSION

3.1 Structural properties

$BaPaO_3$ and $BaUO_3$ crystallize in cubic structure having space group Pm3m (#221). The Ba, X and O atoms are positioned at 1a (0 0 0), 1b (1/2, 1/2,1/2), 3c (1/2, 1/2, 0) sites of Wyckoff coordinates respectively. Energy versus volume minimization process [21] is used to calculate equilibrium lattice parameters such as lattice constants (a_o), ground state energy (E_o), bulk modulus (B), and its pressure derivative (B') by LDA and GGA exchange correlation schemes as shown in Table (1). In addition to it, we use lattice parameters calculated by generalized gradient approximation (GGA) for investigating electronic and optical properties. The value of bulk modulus represents that $BaUO_3$ have highest value of bulk modulus that represents good crystal rigidity regarding to $BaPaO_3$.

We can also provide a prediction of the bulk modulus by using the semi-empirical equation developed by Verma et al [1]

$$B\,(GPa) = S + V\frac{(Z_aZ_bZ_c)^{0.35}}{a^{3.5}}$$

(1)

where Z_a, Z_b and Z_c are the ionic charges on the A, B and O, respectively and a is lattice parameter in Å. The S and V are constants and the values are 1.79 and 5505.785 respectively.

3.2 Electronic Properties

The electronic properties of herein investigated perovskite oxides are based on energy band structure and total as well as partial density of states (TDOS and PDOS) while influence of bonding nature is discussed in terms of charge density distribution. Graphically, we have highlight recently improved Trans-Blaha modified Becke–Johnson (TB-mBJ) potential, which removes wrong interpretation of the true unoccupied states of the system which causes underestimation of electronic band gap [22].The calculated band structures are shown in Fig. (1). It is observed that overall trend of band dispersion curves are almost same but conduction band minimum (CBM) and valence band maximum (VBM) lies at Γ symmetry point of brillouin zone (BZ) revealing (Γ-Γ) direct band gap of 4.18 eV and 4.03 eV for $BaPaO_3$ and $BaUO_3$

compounds respectively. Valence band of both compounds are well below Fermi level while conduction band passes from Fermi level so compound tend towards metallic in nature. However, materials with band gaps larger than 3.1 eV can work well in the ultraviolet region of electromagnetic spectrum [23] so these compounds can work well in this region. According to figure (2) states of energy density distribution can be splitted into four regions ranging from (EF – 20eV) upto (EF + 15eV). The core state region between -20 to -14.4 eV is occupied by X-6p states. Then a sharp peak of Ba-4p state is observed at -15 eV while O-2p state occupies maxima of valence band from -7 to -4.2 eV. In conduction band X-5f states play a prominent role in overall physical properties along with some Ba hybridized (f and d) states. In crystalline materials, nature of chemical bond can be analyzed through contour plots of electronic charge density [24]. The density distribution of contour maps are calculated along (100) and (110) planes as shown in Fig. (3). It can be observed that there is uniform distribution of charge between X cation and O anion, which explores covalent nature in XO_3 octahedra. On the other hand, non-uniform distribution of charge is observed between Ba cation and O anion, which reveals ionic nature in them. The similar bonding nature has been predicted for other perovskites as mentioned in Refs. [25]

3.3 Optical properties

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

$$\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega) \tag{2}$$

which is related to the interaction of photons with electrons [26]. The imaginary part $\varepsilon_2(\omega)$ of the dielectric function could be obtained from the momentum matrix elements between the occupied and unoccupied wave functions and is given by [27]

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

The real part $\varepsilon_1(\omega)$ can be evaluated from $\varepsilon_2(\omega)$ using the Kramer-Kronig relations and is given by [28]

$$\varepsilon_1(\omega) = 1 + \left(\frac{2}{\pi}\right) \int_0^\infty \frac{\omega' \, \varepsilon_2(\omega')}{\omega'^2 - \omega^2} d\omega'. \tag{4}$$

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 $\varepsilon_2(\omega)$ [26,28].

As shown in Fig. (4a) the threshold point in $\mathcal{E}_2(\omega)$ occurs at about origin while major peaks are located at about 0.29- 0.39 eV for both compounds that corresponds to transition of occupied valence band states to unoccupied conduction band states. These peaks are majorly due to X- 5f states, which play a significant role in overall internal optical response. After that, steady peaks are observed till 15eV. It is obvious from Fig. 4 that $BaPaO_3$ and $BaUO_3$ compounds possess strong absorption in region from 0 to 2 eV. Absorption in this energy range is might be due to collective excitations of large effective mass in the interfaces, which is induced by the electric field [29]. Polarizability of material is analyzed with the help of real part of dielectric function $\mathcal{E}_1(\omega)$ as shown in Fig. (4b). The peak value of the static dielectric constant $\mathcal{E}_1(0)$ for $BaPaO_3$ is 41 and for $BaUO_3$ is 71. This high value classifies high degree of miniaturization in both compounds. Then an abrupt decrease is seen which reaches to minimum negative value at about 0.29 - 0.39 eV for both compounds. After that, an overall narrow band gap semiconducting nature is observed for both compounds till 14 eV. The plots of optical conductivity $\sigma(\omega)$ for $BaXO_3$ (X= Pa, U) compounds are shown in Fig. (5a). It can be observed that phenomenon of optical conductivity starts from origin which eventually reaches to its maxima at about 0.29 - 0.39 eV for $BaXO_3$ (X= Pa, U) compounds, then decreases with certain oscillations. The spectrum of refractive index n(w) follows trend of real part of dielectric function $\mathcal{E}_1(\omega)$ having a close relationship. The static part of refractive index n(0) represents an important quantity which is 6.31 and 8.49 for $BaPaO_3$ and $BaUO_3$ respectively as shown in Fig. (5b). The vanishing of curves in the high energies reflects that beyond certain energy limit, the studied material loses transparency and absorbs photons which possess high energy. The calculated spectrum of reflectivity as a function of electromagnetic energy is shown in Fig. (5c). It can be observed that investigated material starts reflectivity highly from origin in accordance with $\mathcal{E}_2(\omega)$ which is more for $BaUO_3$ rather than $BaPaO_3$. After the incent of optimum reflectivity peak it again going to decrease suffering trivial variations following other maxima in curve within 7.5 eV – 8.5 eV. Hence, these materials remain highly transparent in infrared (IR) regions of electromagnetic spectrum (EM).

4. CONCLUSIONS

In summary, Full Potential Linearized Augmented Plane Wave (FP-LAPW) method is used to investigate bonding nature, structural, electronic, and optical properties of $BaXO_3$ (X= Pa, U) compounds within LDA, GGA approximation and TBmBJ potential. Evaluation of structural properties is also done with analytical techniques. Detailed analysis of electronic properties authenticates that $BaPaO_3$ and $BaUO_3$ are narrow band gap semiconductors with mixed nature of ionic and covalent bonding. Finally particulars of optical properties are discussed in terms of complex dielectric

function $\mathcal{E}(\omega)$, optical conductivity $\sigma(\omega)$, refractive index $n(\omega)$, reflectivity $R(\omega)$, and effective number of electrons neff via sum rules. The prominent value of static dielectric constant of herein studied materials suggests that $BaPaO_3$ and $BaUO_3$ can play a significant role in miniaturization technology.
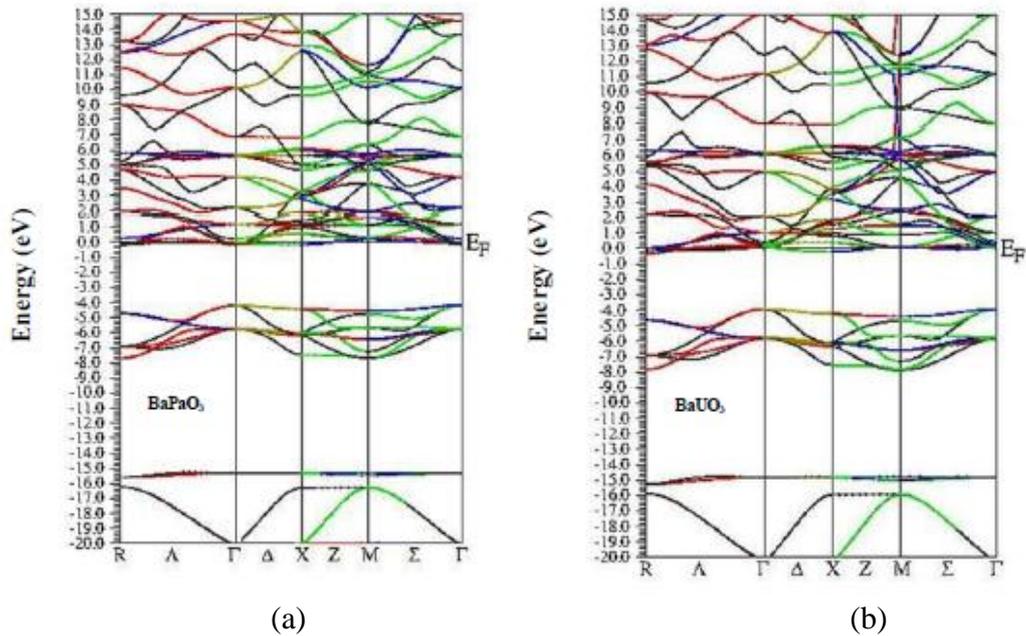

(a)   (b)
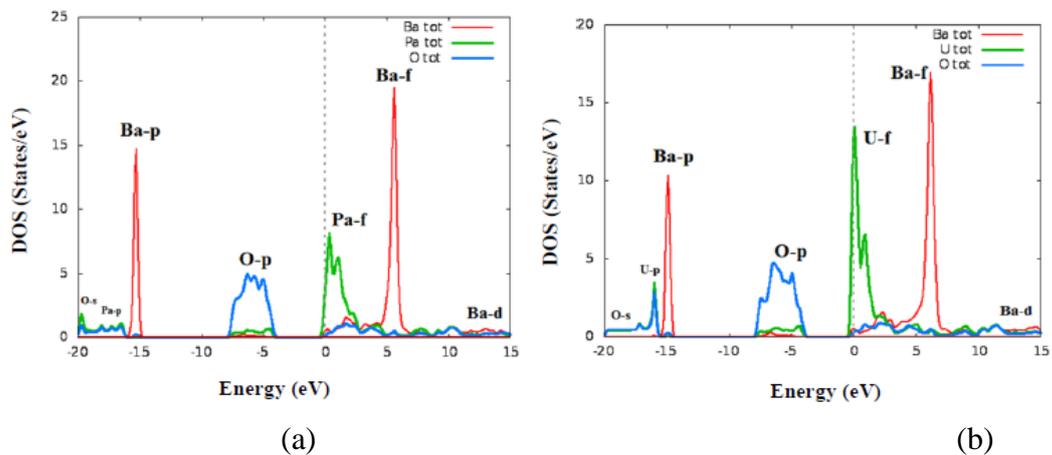
Figure 1. Band Structure of (a) $BaPaO_3$ and (b) $BaUO_3$.

(a)   (b)

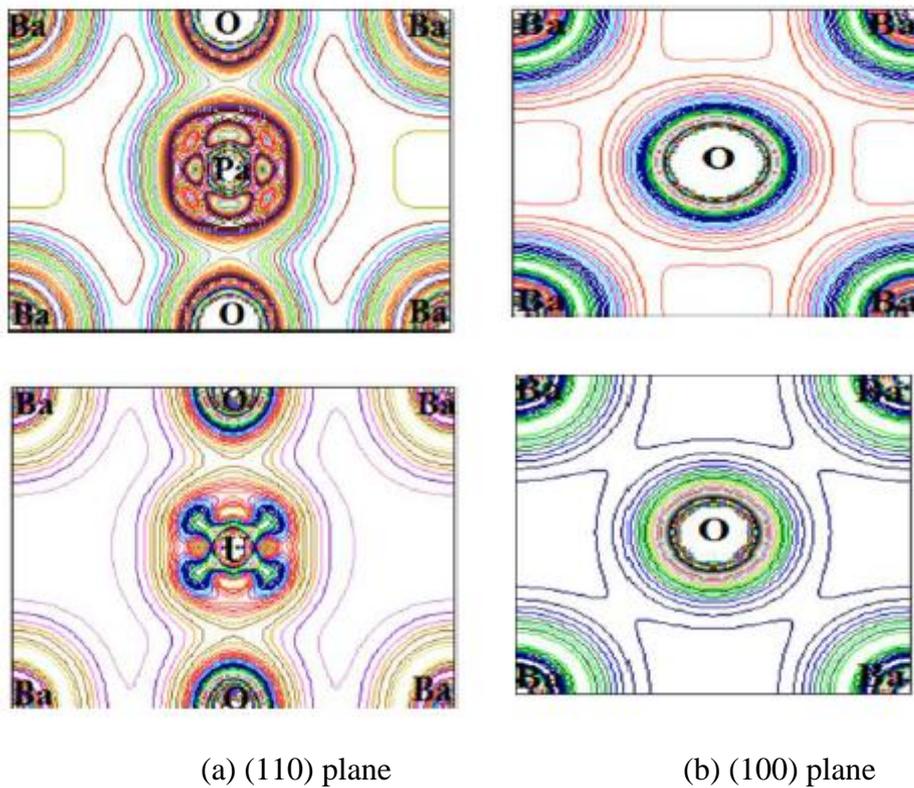**Figure 2.** Total Density of States of (a) $BaPaO_3$ and (b) $BaUO_3$.

(a) (110) plane   (b) (100) plane

Figure 3. Three dimensional electronic charge densities of (a) $BaPaO_3$ and (b) $BaUO_3$ in the (110) and (100) plane.
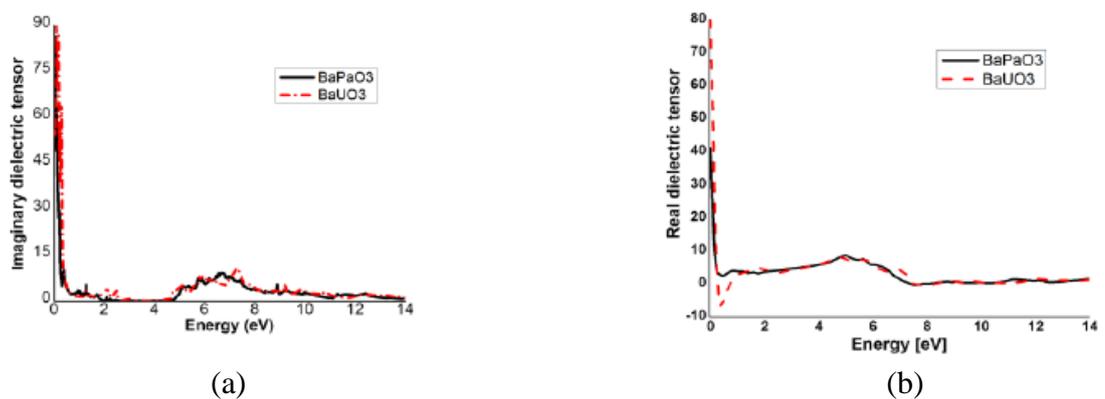

(a)   (b)

Figure 4. The calculated (a) imaginary $\varepsilon_2(\omega)$ and (b) real $\varepsilon_1(\omega)$ parts of complex dielectric constant of $BaXO_3$ (Pa, U) perovskites.
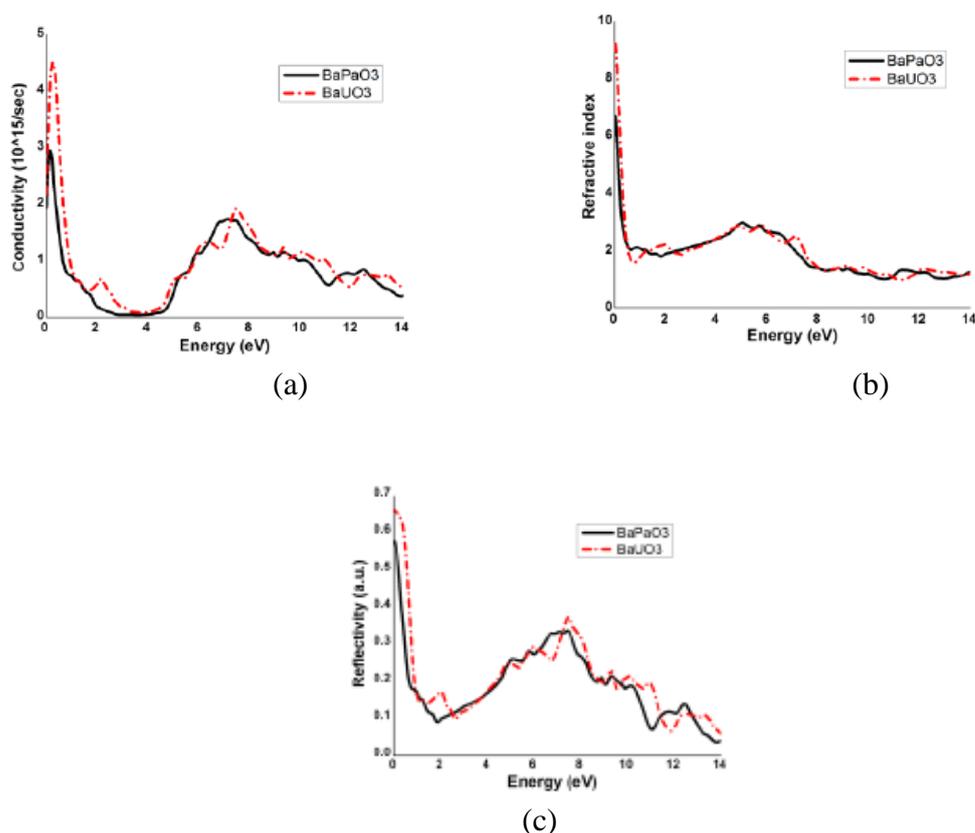
(a)

(b)

(c)

Figure 5. The calculated (a) photoconductivity ($\sigma(\omega)$) (b) refractive index (n) and (c) reflectivity (R (ω)) of $BaXO_3$ (Pa, U) perovskites.

Table 1. Structural parameters, lattice constants a (Å), ground state energies E_o (Ry) bulk modulus B (GPa) and its pressure derivative B′ (GPa) with experimental and other theoretical values of $BaXO_3$ (X = Pa and U) cubic perovskites.

Structural analysis	a (Å)	a (Å) exp. [1]	E_o (Ry)	B′	B (GPa)	B (GPa) [1]
$BaPaO_3$	4.40 (GGA), 4.45 (LDA)	4.45	-71328.522 (GGA), -71328.545 (LDA)	4.34 (GGA), 4.30 (LDA)	125 (GGA), 123 (LDA)	115
$BaUO_3$	4.38 (GGA), 4.35 (LDA)	4.39	-72843.521 (GGA), -72843.535 (LDA)	3.95 (GGA), 3.89 (LDA)	135 (GGA), 133 (LDA)	121

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