ISSN: 0975-833X

Available online at http://www.journalcra.com

International Journal of Current Research
Vol. 9, Issue, 03, pp.48349-48352, March, 2017

INTERNATIONAL JOURNAL OF CURRENT RESEARCH

RESEARCH ARTICLE

A DFT STUDY OF STRUCTURAL AND ELECTRONIC PROPERTIES OF PERVOSKITE SOLIDS

[1, 2,*]Madan Lal and [3]Shikha Kapila

[1]Department of Physics, Govt. Degree College Una, Himachal Pradesh-174303 (India)
[2]Research Scholar, I.K. Gujral Punjab Technical University, Jalandhar, Punjab -144603 (India)
[3]Department of Applied Science, Bahra Group of Institutions, Bhedpura, Patiala, Punjab -147001 (India)

ARTICLE INFO

Article History:
Received 25th December, 2016
Received in revised form
05th January, 2017
Accepted 16th February, 2017
Published online 31st March, 2017

Key words:

Lattice Constant, DFT,
Band Gap, Perovskite.

ABSTRACT

We have applied a potential approximation known as modified Becke-Johnson (mBJ) based on density functional theory (DFT) method to calculate structural and electronic properties of BaPaO3 and BaUO3 compounds is presented. The Types of chemical bonding is examined 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.

Citation: Madan Lal and Shikha Kapila, 2017. "A DFT study of structural and electronic properties of Pervoskite solids", *International Journal of Current Research*, 9, (03), 48349-48352.

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 (Verma and Kumar, 2012). The ternary oxides (ABO_3) are important materials as they have significant applications (Piskunov, 2004) in piezoelectricity, ferroelectricity colossal magneto-resistivity, and high temperature superconductivity (Verma and Kumar, 2012). Moreover, they are also promising candidates for solid-state devices, radiation detection devices, spintronic devices and optoelectronic devices as well (Verma, 2008 & 2013). $BaPaO_3$ 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 (ε_o=7) are classified as high dielectric constant materials (Homes *et al.,* 2001). $BaUO_3$ 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 (Williams, 1984; Matsui, 1995; Yamawaki, 1996). Moreover, thermo-physical and thermo chemical properties are also investigated (Chen *et al.,* 1996; Kurosaki *et al.,* 2001). However, on theoretical side, Huang *et al.* 2006 investigated vaporization properties by simulation method.

Corresponding author: Madan Lal,
Department of Physics, Govt. Degree College Una, Himachal Pradesh-174303 India.

On the other hand, $BaPaO_3$ compound is competing in scientific investigation (Radiochemie, 1965). 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 and electronic properties of $BaPaO_3$ and $BaUO_3$ cubic perovskites.

CALCULATION METHOD

The calculations were done using full potential linearized augmented plan wave (FP-LAPW) computational scheme (Madsen *et al.,* 2001; Schwarz *et al.,* 2002) as implemented in the WIEN2K code (Blaha *et al.,* 2001). 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) (Wu, 2006; Tran *et al.,* 2007) 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 (Kohn, 1965) and Perdew-Burke-Ernzerh of (PBE) (Perdew, 1996) 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) (Tran, 2009) as coupled with WC-GGA is used.

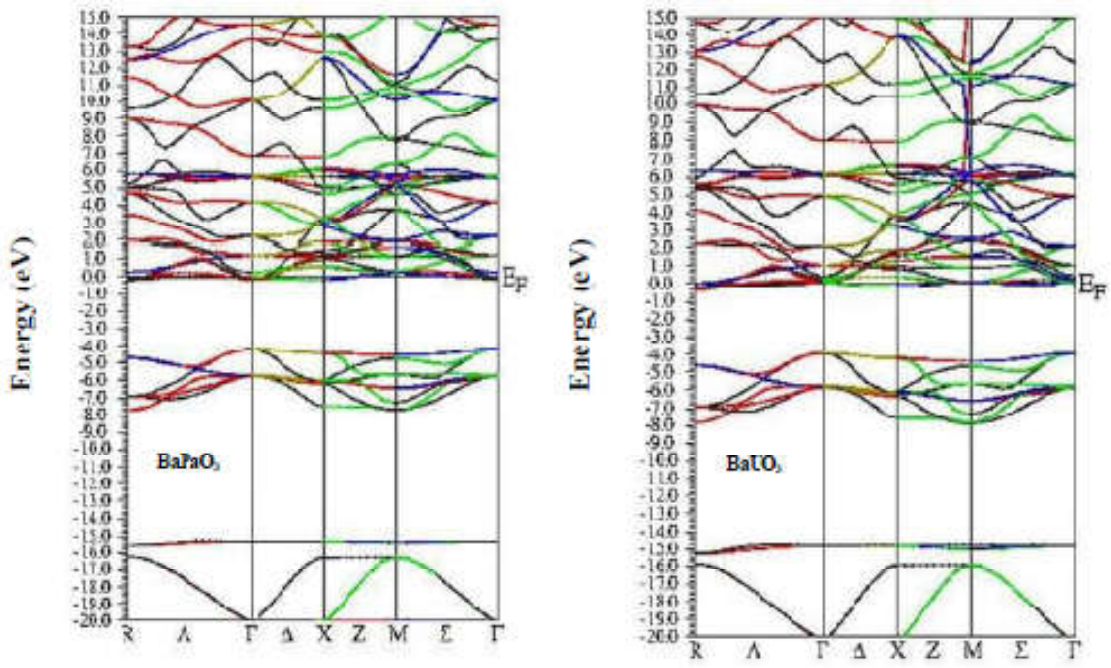


Figure 1. Band Structure of (a) $BaPaO_3$ and (b) $BaUO_3$

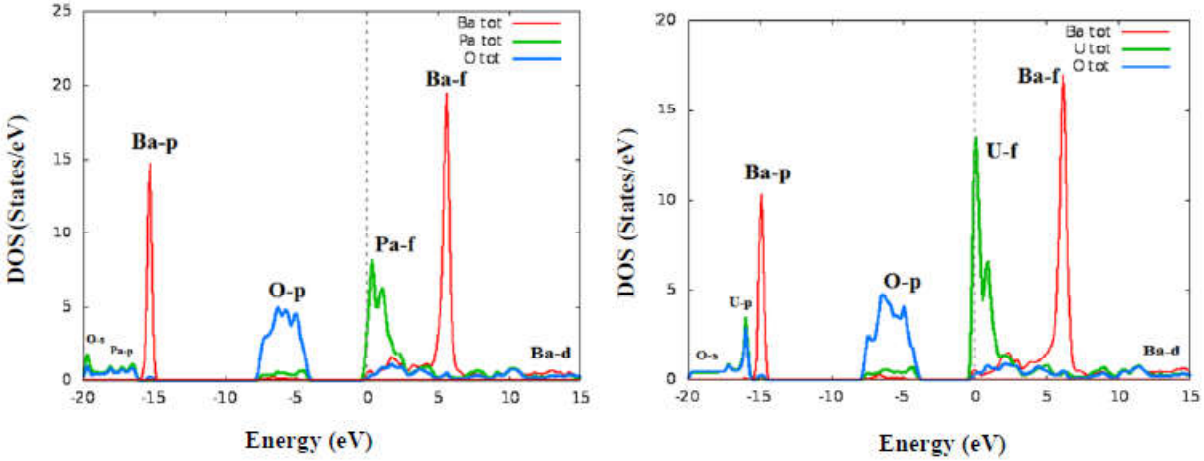


Figure 2. Total Density of States of (a) $BaPaO_3$ and (b) $BaUO_3$

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.

RESULTS AND DISCUSSION

Structural properties

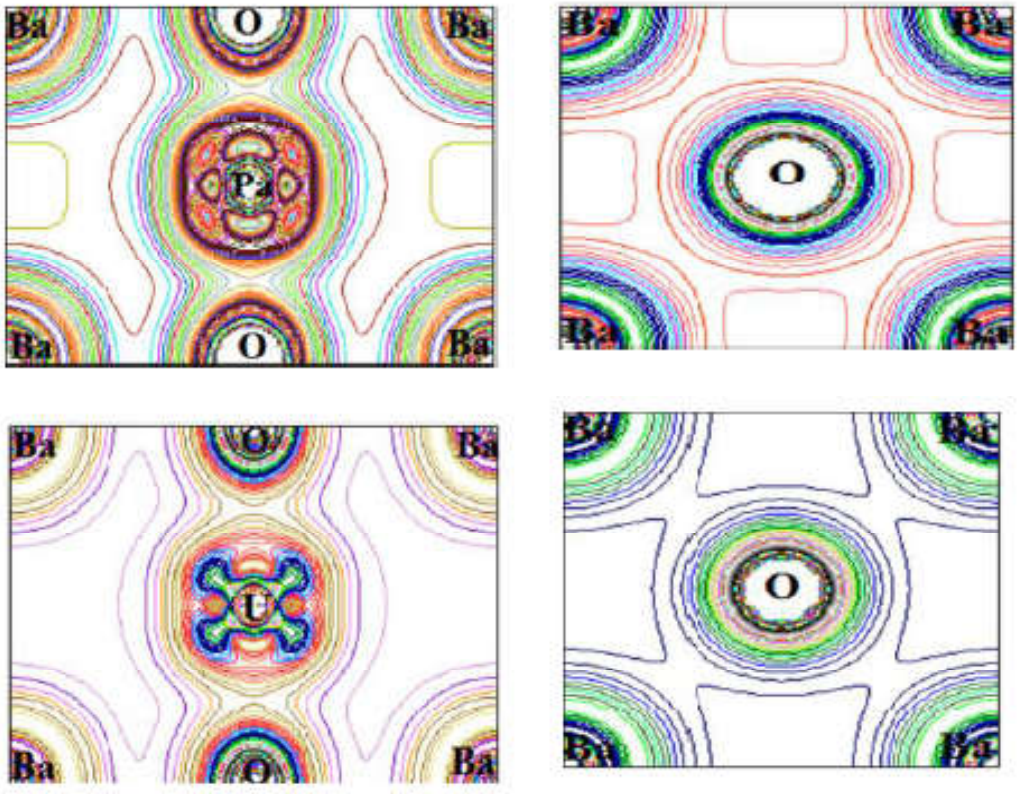
$BaPaO_3$ and $BaUO_3$ crystallize in cubic structure having space group Pm3m (#221). The Ba, X and O atoms are positioned at 1a (0 0 0), 1b (1/2, 1/2,1/2), 3c (1/2, 1/2, 0) sites of Wyckoff coordinates respectively.

Energy versus volume minimization process (Murnaghan Proc, 1944) 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.* (2012)

$$B\,(GPa) = S + V\frac{(Z_aZ_bZ_c)^{0.35}}{a^{3.5}} \quad \text{..... (1)}$$

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.



(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

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

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 (Kandpal *et al.,* 2007). 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 (Cuevas-Saavedraa *et al.,* 2016) 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 (Hoffman, 1988). 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_3octahedra. 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 (Murtaza *et al*., 2011).

Conclusion

In summary, Full Potential Linearized Augmented Plane Wave (FP-LAPW) method is used to investigate bonding nature, structural and electronic 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. Hence our calculations show good agreement with available experimental data and previous calculations.

Acknowledgements

The first author (Madan Lal) wishes to acknowledge I. K. Gujral Punjab Technical University, Jalandhar for providing the necessary facilities.

REFERENCES

Blaha, P., K. Schwarz, G. K. H. Madsen, D. Kvasnicka, J. Luitz: 2001."WIEN2k: An Augmented Plane Wave+Local Orbitals Program for Calculating Crystal Properties" (Karlheinz Schwarz/Techn. Universität Wien, Austria.

Chen, F., R C Ewing, S B Clark, 1999. "The thermodynamics and kinetics of uranophane dissolution in bicarbonate test solutions"Amer miner. Vol. 84 pp.650-666.

Cuevas-Saavedraa, R., V. N. Staroverov, 2016. "Exactexpressions for the Kohn-Shamexchange- correlation *Mol. Phys.,* Vol.114, Issue 7-8, pp.1050-1058.

Hoffman, R. 1988. "A chemical and theoretical way to look at bonding on surfaces", *Rev. Mod. Phys*. vol.60, Issue 3,pp. 601

Homes, C C., T Vogt, S M Shapiro, *et al,2001* "Optical response of high-dielectric-constant perovskite-related oxide", *Science,* vol.293 No. 5530, pp. 673-676.

Huang, Y H., R I Dass, Z L Xing *et al,*2006."Double Perovskites as Anode Materials for Solid-Oxide Fuel Cells"*Science* vol.312, Issue 57710, pp. 254-257.

Kandpal, H.C., G.H. Fecher, C. Felser, 2007. "Calulated electronic and magnetic properties of the half-metallic, transition metal based Heusler compounds", *J. Phys. D*. Vol. 40, No.6, pp.1507-1523.

Kohn, W. and L. J. Sham, 1965. "Self-Consistent Equations Including Exchange and Correlation Effects" Phys. Rev. No. 140 A1133.

Kurosaki, K., T Matsuda, M Uno *et al,* 2001, "Thermoelectric properties of $BaUO_3$"*J. Alloys and Compounds,* vol.319,Issue1-2,pp.271-275.

Madsen, G. K. H., P. Blaha, K. Schwarz, E. Sjöstedt, L. Nordström*, 2001.*"Efficient linearization of the augmented plane-wave method"*, Phys. Rev. B*vol. 64, Issue 19, pp.195134.

Matsui, T. 1995. "Thermodynamic properties of ternary barium oxides", *ThermochimActa,* vol.253, Issue 3, pp.155-165.

Murnaghan, F D. 1944. "The Compressibility of Media under Extreme Pressures", *Proc. Natl. Acad. Sci. USA* vol. 30, No.9, pp.244-247.

Murtaza, G., Iftikhar Ahmad, M. Maqbool, H. A. Rahnamaye Aliabad and A. Afaq, 2011. "Structural and Optoelectronic Properties of Cubic $CsPbF_3$ for Novel Applications",*Chin. Phys. Lett.* Vol.28, No.11, pp. 117803.

NaziaErum and Muhammad Azhar Iqbal, 2017. "*Ab initio* study of high dielectric constant oxide-perovskites: perspective for miniaturization technology" Materials Research Express, Volume 4, No.2 pp.025904.

Perdew, J. P., K. Burke, M. Ernzerhof, 1996. "Generalized Gradient Approximation Made Simple", Phys. Rev. Lett. **77,** Issue 18, pp. 3865.

Piskunov, S., E. Heifets, R.I. Eglitis and G. Borstel, 2004. "Bulk properties and electronic structure of $SrTiO_3$, $BaTiO_3$, $PbTiO_3$pervoskites: an ab initio HF/DFT study", *Computational Material Science*, vol.29, Issue 2, pp.165-178.

Schwarz, K., P. Blaha, G. K. H. Madsen, 2002. "Electronic structure calculations of solids using the WIEN2K package"*, Comput. Phys. Commun*. Vol.147 pp.71.

Tran, F., P. Blaha, 3 June, 2009. "Accurate Band Gaps of Semiconductors and Insulators with a Semilocal Exchange-Correlation Potential", *Phys. Rev. Lett.* Vol.102, Issue 22, pp.226401.

Tran, F., R. Laskowski, P. Blaha, K. Schwarz, 2007. "Performance on molecules, surfaces, and solids of the Wu-Cohen GGA exchange-correlation energy functional" *Phys.Rev. B.,* vol.75 , Issue 11, pp.115131.

Verma A. S. and A. Kumar, 2012. "Bulk modulas of cubic pervoskites", *J. Alloys and Compounds*, vol. 541, pp.210-214.

Verma A. S. and V. K. Jindal, 2009. "Lattice constants of cubic perovskite", *J. Alloys and Compounds*, vol.485, No.1-2, pp.514-518.

Verma, A. S. 2013. "Elastic moduli of orthorhombic pervoskites", *Solid State Communications*, Vol. 158 pp.34-37.

Verma, A. S., A. Kumar and S. R. Bhardwaj, 2008. "Correlation between ionic charge and the lattice constant of cubic perovskite solids" *Physica Status Solidi B*, vol. 245, Issue 8, pp.1520-1526.

Williams, C W., L R Morss, I K Choi, 1984."Stability of Tetravalent Actinides in Perovskites" *ACSSympSr. no*.246 chapter 20, pp.323-334.

Wu, Z. and R. E. Cohen, 2006. "More accurate generalized gradient approximation for solids". *Phys. Rev. B* vol.73, Issue 23, 235116.

Yamawaki, M., J Hang, K Yamaguchi *et al*, 1996. "Investigation of the vaporization of $BaUO_3$ by means of mass spectrometry", *J.Nucl. Mater*, Vol.231, Issue 3, pp. 199-203.

****