IOSR Journal of Applied Physics (IOSR-JAP)
e-ISSN: 2278-4861.Volume 8, Issue 1 Ver. III (Jan. - Feb. 2016), PP 54-58
www.iosrjournals

Ab Initio Simulation Of Materials Properties

George S. Manyali*
Computational and Theoretical Physics Group (CTheP), Physics Department, Masinde Muliro University of Science and Technology, P.O Box, 190-50100, Kakamega, Kenya

***Abstract**: Ab initio simulation of materials properties is carried out by performing a systematic comparison of the structural and elastic properties of Perovskite oxide $BiGaO_3$, predicted by four well-known exchange-correlation functionals and pseudo-potentials for total energy calculations. The performance of the functionals in reproducing the zero temperature lattice parameters, volumes and bulk moduli was then evaluated. The PW91 and PBE functionals predict similar result, whereas WC and REVPBE respectively yield smaller and larger values of lattice parameter and volume. Very minimal variations in bulk modulus are noted when the ultra-soft and projector augmented wave pseudo-potentials are employed.*
***Keywords:** $BiGaO_3$, bulk modulus, DFT*

I. INTRODUCTION

Discovery and the urge for deeper understanding of new properties of materials have escalated in the recent years due to advancements in numerical techniques, computers and other laboratory equipment for running experiments. Numerical technique such as density functional theory (DFT) is currently a very useful tool employed in studies of several thousands of materials properties and their possible technological applications [1] and [2]. DFT is an exact theory, which states that ground-state properties of a material can be obtained from functionals of the charge density alone [3]. DFT is based on the complex Schrodinger equation that describes the many-body problem of the solid. Finding a solution to a many-body problem is numerically complicated. To simplify the process, exchange-correlation functional describing the many-body electron interactions are approximated. As a result of this, many ground-state properties of solids like structural and elastic properties can be determined with high level of accuracy.

Clear and systematic presentation of information on materials and their ground-state properties such as lattice parameter and bulk modulus is an interesting field that will continuously attract attention as long as exploration of new materials does not come to an abrupt end. The efforts made so far by material scientist in bringing deeper understanding to some basic properties of solids, is by the development of materials databases. Databases are a collection of crystal structure and properties (electronic, elastic, optical etc) of organic, inorganic, metal-organic compounds and minerals. While several of these databases developed by material scientist require subscription, most of new databases have open-access policy. Some of these databases include: Crystallography Open Database – an open-access collection of crystal structures [4], International Crystallographic Structural Database [5] and Materials project [2]. Therefore, databases are analogous to shopping-malls where materials scientists (both experimentalist and theoreticians) would deposit small/big data from their experiments, which is then accessed by scientific community worldwide for further processing. The processing here may entail tuning crystal structures either through straining or causing any form of deformation to the unit cell to bear desired material properties for the earmarked technological applications. In absence of such information, one has to utilize searching tools devised to predict unknown structures with very little knowledge of a material's elemental composition, unit cell dimensions, external conditions and some hints of its structure [6]. In this work, we demonstrate the usefulness of the databases and DFT in study of structural and elastic properties of perovskite oxide of type ABO_3. A family of Perovskite oxides are widely studied compounds because of their potential applications such as piezoelectricity, ferroelectricity, (anti-)ferromagnetism, metal- insulating transitions, multi-ferroic behavior and super- conductivity [7]. All these mentioned applications are anchored on the choice of the crystal structure. This is so, since each element in ABO_3 formular has different properties which can vary depending on the arrangement of the atoms in the unit cell.

In this paper, we calculate ground-state properties of bismuth gallate ($BiGaO_3$), with a simple cubic structure at zero temperature and ambient pressure. We also carefully investigate the effects of various exchange-correlation functionals and pseudo potential on the equation of states (EOS) and we analyze the variations of bulk modulus as a function of strain.

The paper is organized as follows: In section II, we give the computational details based on the density functional theory as implemented in QUANTUM-ESPRESSO[8] package for first-principles simulations. Our results are discussed in section III, while summary and major conclusions of this paper are presented in section IV. Section V is acknowledgement for financial support of this research work.

II. COMPUTATIONAL DETAILS

The simple cubic structure of $BiGaO_3$ was obtained from materials project database, see FIG. 1. The structure ID is *mp-22979*, space group (*Pm3m)* and space group number (*221)*. The cubic unit cell consists of unit formula with Wyckoff positions of the atoms O:3c(0.5,0.5,0), Ga:1a(0,0,0),and Bi:1b(0.5,0.5,0.5).

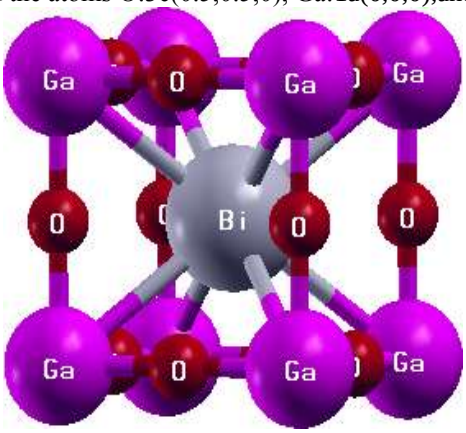

Figure 1. (color on line) the unit cell of simple cubic structure of $BiGaO_3$

We carried out calculations with four well-known ex-change-correlation (XC) functionals implemented in the open source QUANTUM-ESPRESSO distribution. The Perdew-Burke-Ernzerhof (PBE) [9] functional acted as the baseline which we compared against the Wu-Cohen functional (WC) [10], revised Perdew-Burke-Ernzerhof (REVPBE) [11] and Perdew-Wang-91 functional (PW91) [12]. We picked on these functionals since they are generalized gradient (GGA) functionals, which are computationally efficient and does not contain any adjustable parameter. Ultra-soft (US) and projector augmented wave (PAW) pseudo-potentials [13] from the 0.3.1 version of the library of Dal Corso et al. [14] were used throughout this work. The energy cut-off of 38 rydbergs, and a kpoint-grid of 6x6x6 were considered in the calculations of all ground-state properties.

III. RESULTS AND DISCUSSIONS

In this section, we present results obtained from fitting the energy-volume data to Murnaghan equation of state [15]. The energy-volume data were obtained as follows; the volume of simple cubic structure of $BiGaO_3$ was deformed by single parameter ϵ such that the lattice spacing is defined as $\alpha=\alpha_0 (1+ \epsilon)$ where α_0 is the theoretical equilibrium parameter that was extracted from Materials project. We then fitted Murnaghan equation of state to a series of total energy values for 21 set of volumes with ϵ ranging from -0.05 to +0.05 in steps of +0.005. The equation of state as a function of percentage volume change with respect to theoretical equilibrium configurations for some pseudo-potential is shown in FiG. 2. For these particular pseudo-potentials, no anomaly is observed for the given percentage volumes, an indication that the system is still within the thermodynamic regime. We also observe that the equation of state calculated with different functionals have very similar curvature especially in the region close to the equilibrium percentage volume.

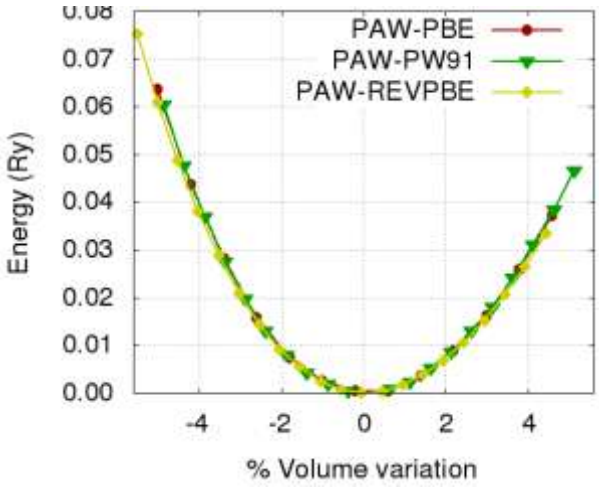

Figure 2. (color on line) Equation of state as a function of percent volume change with respect to theoretical equilibrium configurations for three selected pseudo-potentials. Between -2 and +2, the curves fit each other but small deviations in curves start appearing for higher percentage volumes.

Our calculated values of lattice parameter α_0, equilibrium volume V_0 and bulk modulus B_0 are presented in Table I. The smaller equilibrium lattice parameter α_0 and hence smaller volume lead to larger bulk moduli, which explain the fact that compact materials have higher resistance to deformation. The variation in the moduli obtained from the eight types of the pseudo-potentials is more pronounced than that in the equilibrium volume and lattice parameter. The WC functional predicts the smallest lattice parameter and equilibrium volume, whereas REVPBE yield the highest results. PW91 and PBE, predict very similar results which are intermediate between the two extremes. Highest values of bulk moduli are observed for the WC functional, which is about 20% over that of REVPBE functional. The comparison with previous DFT results is very good [16].

Table 1. Calculated equilibrium volume V_0(Å^3), lattice constant α_0(Å) and bulk modulus B_0 (GPa) for different exchange-correlation functionals and pseudo-potentials.

XC Functional	α_0(Å)	V_0(Å^3)	B_0 (GPa)
PAW-PBE	3.908	59.66	168.1
US-PBE	3.909	59.74	169.9
PAW-PW91	3.901	59.38	171.0
US-PW91	3.904	59.51	172.1
PAW-REVPBE	3.928	60.62	158.5
US-REVPBE	3.933	60.83	161.6
PAW-WC	3.853	57.19	189.4
US-WC	3.862	57.58	187.8
Others [16]	3.899	-	170.99

Generally, the WC and REVPBE functionals predicts ground-state properties which are extremely lower or higher respectively, as compared with values yielded by PW91 and PBE, see FIG.3 and FIG.4.

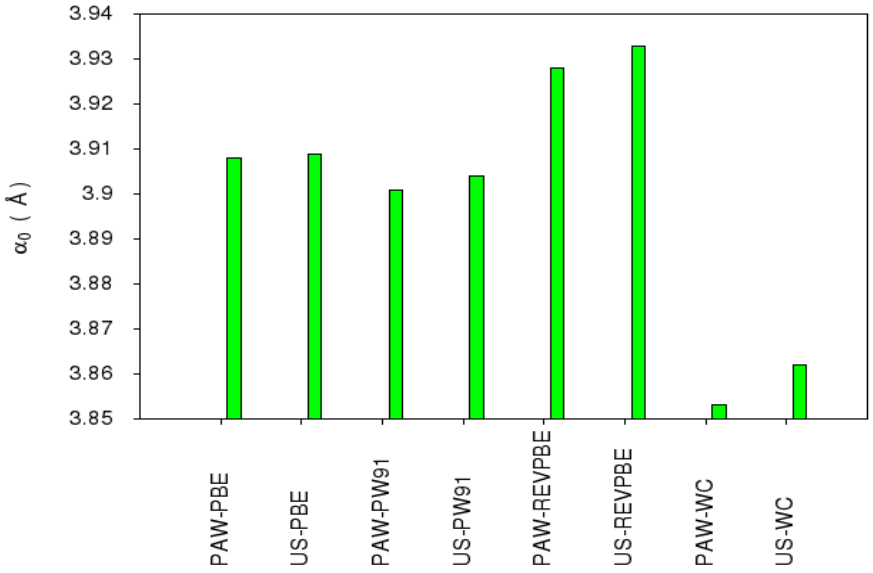

Figure 3: (Color online) The Equilibrium lattice parameter at 0 K (without zero point-energy included) for the different Bi, Ga and O pseudo-potentials employed in this work. We extracted this data from the Murnaghan fit.

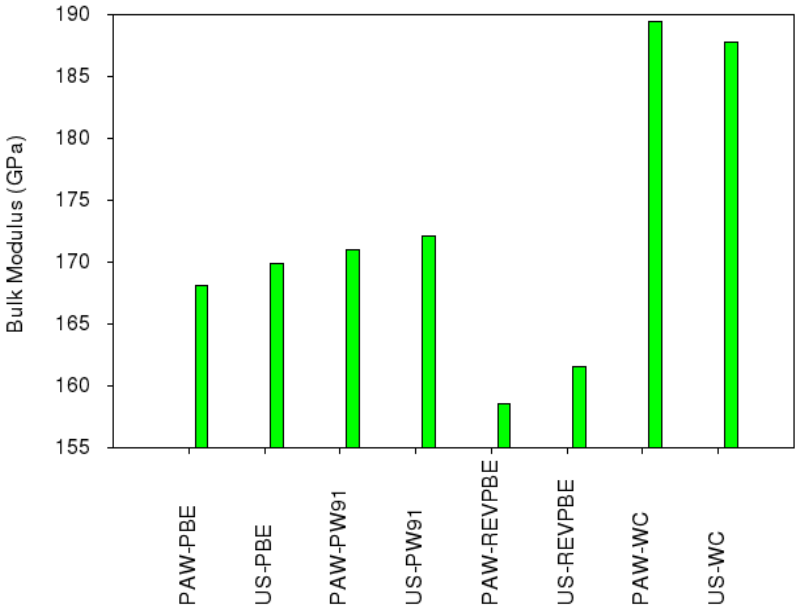

Figure 4. (Color online) The Equilibrium bulk moduli at 0 K (without zero point-energy included) for the different Bi, Ga and O pseudo-potentials employed in this work. We extracted this data from the Murnaghan fit.

In Fig. 5 we display the value of the bulk modulus obtained using the Murnaghan equation-of-state. The converged values of the bulk modulus for the 6th order polynomial fit are denoted by the flat part of curves in Fig. 5. The trend is almost similar for all pseudo potentials considered in this paper.

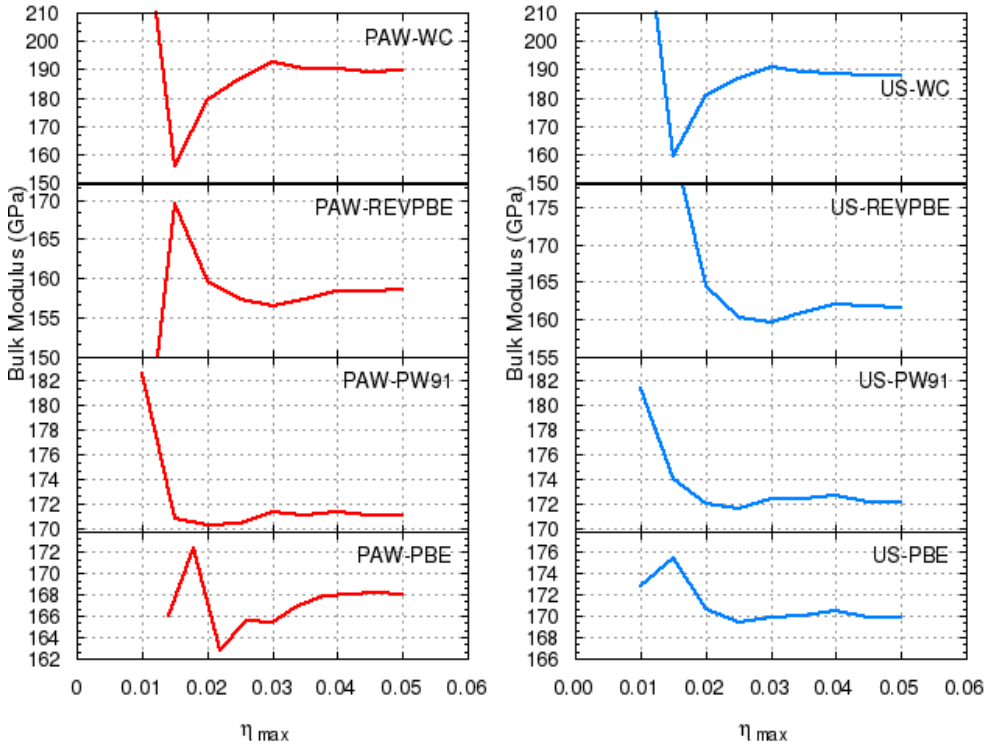

Figure 5. (color on line) Bulk modulus as a function of the maximum absolute value of deformation (η_{max}) obtained for eight different pseudo potentials. The Murnaghan equation of state and 6th order polynomial fit was applied throughout to produce the above curves.

IV. CONCLUSION

We have performed a quantitative comparison of equilibrium volume, lattice parameter and bulk moduli of the Perovskite oxide BiGaO3 from first principles calculations of total energy using different pseudo-potentials based on the open source QUANTUM-ESPRESSO distribution. The DFT functionals; PW91 and PBE produce almost similar results. However, the WC and REVPBE yield results at the two extreme ends. The WC predicts quite small volumes which in turn produces larger bulk moduli, whereas the REVPBE predict expanded volumes and smaller bulk moduli. In the interest of the future benchmarking studies, we recommend expansion of existing database of properties of materials obtained from state-of-the-art theoretical techniques. This will provide a baseline against which the old and new functionals and pseudo-potentials could be quantitatively evaluated

Acknowledgements

We acknowledge funding from the African-German Network of Excellence in Science (AGNES) Grant for Junior Researchers 2015. Discussions with Victor Odari are highly appreciated.

References

[1]. Driver, K. P., R. E. Cohen, Zhigang Wu, B. Militzer, P. López Ríos, M. D. Towler, R. J. Needs, and J. W. Wilkins. "Quantum Monte Carlo computations of phase stability, equations of state, and elasticity of high-pressure silica." Proceedings of the National Academy of Sciences 107, no. 21 (2010): 9519-9524.

[2]. Jain A, Ong SP, Hautier G, Chen W, Richards WD, Dacek S, Cholia S, Gunter D, Skinner D, Ceder G, Persson KA. Commentary: The Materials Project: A materials genome approach to accelerating materials innovation. Apl Materials. 2013 Jul 1;1(1):011002.

[3]. Kohn W, Sham LJ. Self-consistent equations including exchange and correlation effects. Physical review. 1965 Nov 15;140(4A):A1133.

[4]. Gražulis S, Chateigner D, Downs RT, Yokochi AF, Quirós M, Lutterotti L, Manakova E, Butkus J, Moeck P, Le Bail A. Crystallography Open Database–an open-access collection of crystal structures. Journal of Applied Crystallography. 2009 Aug 1;42(4):726-9

[5]. Belsky A, Hellenbrandt M, Karen VL, Luksch P. New developments in the Inorganic Crystal Structure Database (ICSD): accessibility in support of materials research and design. Acta Crystallographica Section B: Structural Science. 2002 Jun 1;58(3):364-9.

[6]. Manyali, George S., Robert Warmbier, and Alexander Quandt. "First-principles studies of the structural, electronic and optical properties of dinitrides CN 2, SiN 2 and GeN 2." Computational Materials Science 95 (2014): 706-711.

[7]. Zubko, Pavlo, Stefano Gariglio, Marc Gabay, Philippe Ghosez, and Jean-Marc Triscone. "Interface physics in complex oxide heterostructures." Annu. Rev. Condens. Matter Phys. 2, no. 1 (2011): 141-165.

[8]. Giannozzi, Paolo, et al. "QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials." Journal of Physics: Condensed Matter 21.39 (2009): 395502.

[9]. Perdew, John P., Kieron Burke, and Matthias Ernzerhof. "Generalized gradient approximation made simple." Physical review letters 77, no. 18 (1996): 3865.

[10]. Wu, Zhigang, and Ronald E. Cohen. "More accurate generalized gradient approximation for solids." Physical Review B 73, no. 23 (2006): 235116.

[11]. Zhang, Yingkai, and Weitao Yang. "Comment on "Generalized gradient approximation made simple"." Physical Review Letters 80, no. 4 (1998): 890.

[12]. Wang, Yue, and John P. Perdew. "Correlation hole of the spin-polarized electron gas, with exact small-wave-vector and high-density scaling." Physical Review B 44, no. 24 (1991): 13298.

[13]. Kresse, Georg, and D. Joubert. "From ultrasoft pseudopotentials to the projector augmented-wave method." Physical Review B 59, no. 3 (1999): 1758.

[14]. Corso, A. D. (n.d.). Pslibrary version 0.3.1, http://qe- forge.org/projects/pslibrary.

[15]. Murnaghan, F. D. "The compressibility of media under extreme pressures." Proceedings of the National Academy of Sciences 30, no. 9 (1944): 244-247.

[16]. Behram, Rasul Bakhsh, M. A. Iqbal, S. M. Alay-e-Abbas, M. Sajjad, M. Yaseen, M. Imran Arshad, and G. Murtaza. "Theoretical investigation of mechanical, optoelectronic and thermoelectric properties of BiGaO 3 and BiInO 3 compounds." Materials Science in Semiconductor Processing 41 (2016): 297-303.