First principles investigation of structural, elastic, electronic and optical properties of Barium seleno-germanate, Ba_2GeSe_4

Abdu Barde [1,2] **and Daniel P Joubert**[1]

[1] The National Institute for Theoretical Physics, School of Physics and Mandelstam Institute for Theoretical Physics, University of the Witwatersrand, Johannesburg, Wits 2050, South Africa.

[2] College of Science and Technology, Jigawa state Polytechnic, Dutse - Jigawa state, Nigeria.

E-mail: `abdubarde@gmail.com`

Abstract. Ternary and quaternary chalco-germanates and stannates have a rich structural chemistry. Experimental studies of their non-linear optical properties have been reported, but there are few published computational studies on their structural, elastic, electronic and optical properties. In this work, we investigate the structural, elastic, electronic and optical properties of Ba_2GeSe_4 using Density Functional Theory (DFT) and post-DFT many body perturbation theory. The ground state energy and properties, including equilibrium lattice parameters, bulk modulus and band gap were calculated at the DFT level of approximation. The fundamental gap was determined at the post-DFT G_0W_0 level of approximation while optical absorption was determined with the Bether-Salpeter Equation approximation. The ground state energy and mechanical results show that Ba_2GeSe_4 is a stable compound while the caclulated optical absorption results and estimated optical band gap show that it is a wide band gap material that is well-situated for photon absorption in the high energy visible range with potential application in multi-junction solar cells.

1. Introduction

The ternary and quaternary compounds containing metal chalcogenides, chalco-germanates and thiostannates have received considerable attention due to their structural chemistry [1, 2], important physical and chemical properties for potential applications in non-linear optics (NLO) [3, 4], thin film for solar cell [5] and visible light response photocatalysts [6, 7]. Among the family of chalco-germanates is seleno-germanate earth alkali metal barium seleno-germanate Ba_2GeSe_4. The experimental synthesis of Ba_2GeSe_4 has been reported and the compound is found to crystallize in a monoclinic structure with space group p_12/m [8]. The thio/seleno-germanate and stannate compounds exhibit interesting physical properties due their isolated tetrahedral ortho-anion $[MQ_4]^{4-}$ corner shearing, were [M = Ge, Sn; Q = S, Se]. The compounds are well known to have a structure of type A_2MQ_4 [4]. Little has been reported on the structural, elastic, electronic and optical properties of Ba_2GeSe_4. We are only aware of the study of Assoud and Soheilnia [8], were the authors reported experimental data on the structure and lattice constants and theoretically investigated the electronic properties using density functional theory with the local density approximation (LDA). However, the authors did not measure the optical band

gap of this compound, but predicted it to lie within 2.6 - 3.0 eV. LDA is well known to give a less accurate description of electronic and optical properties of materials due to the omission of the contribution from quasiparticle renormalization of electronic band gaps and excitonic effect in the linear and non-linear optical absorption [9]. In view of this and the rich range of properties of the seleno-germanate family of compounds with potential practical applications, it is worthy here to investigate the structural, elastic, electronic and optical properties of Ba_2GeSe_4. We use two DFT exchange-correlation approximtations, the Perdew-Burke-Ernzerhof generalised gradient approximation (PBE) [10] and PBEsol [11] to determine the ground state energy and lattice structure. DFT band structure calculations were performed using two hybrid functionals, the modified Johnson Becke (MBJ) [12] and Heyd-Scuseria-Ernzerhof (HSE) [13], two approximations that normally improve on the band gap underestimation by local and semi-local DFT approximations. A Green's function (GW) calculation was used to determined the fundamental gap while optical absorption properties were determined within the Bether-Salpeter Equation (BSE) approximation, which is effective in reproducing the experimental band gap for semiconductors.

2. Computational details

The investigation of structural, elastic, electronic and optical properties of Ba_2GeSe_4 were carried out within the framework of density functional theory (DFT) as implemented in the Veinna Ab initio simulation package (VASP) [14, 15]. A projected-augmented-wave (PAW) [16] formulation was used for the description of electron-ion interactions. The groundstate energy was calculated within the Perdew-Burke-Ernzehof generalised gradient approximation (PBE) [10] and PBEsol [11] for the electron exchange correlation relations. Equilibrium structure optimization was performed on the primitive cell of the structure with cut-off energy of 520 eV and a $6 \times 6 \times 4$ Monkhorst-pack mesh for sampling the Brillouin zone. The k-point mesh sampling was chosen to achieve convergence energies within less then 1 meV/atom. The elastic tensor was calculated for the fully relaxed equilibrium geometry with PBE and PBEsol. DFT band structure calculations were performed for the PBEsol optimized structure using PBEsol and the modified Johnson-Becke potential (MBJ) [12]. The band gap was also estimated with the hybrid Heyd-Scuseria-Ernzerhof (HSE) [13] approximation. The MBJ and HSE approximations normally give a better estimate of the band gap at the DFT level when compared to conventional DFT calculations with local or semi-local exchange-correlation functions. Moreover, in this study we performed a post-DFT many-body Green's function G_0W_0, [17, 18] calculation to obtain an estimate of the quasi-particle excitations. We used a 180 eV energy cut-off for the response functions to determined the fundamental gap. Finally, the optical absorption spectrum was obtain by including excitonic effects using the $G_0W_0 + BSE$ approximation[19, 20, 21]. From the optical absorption spectra, the optical band gap were determined using a Tauc plot [22].

3. Result and discussion

3.1. Structural properties

X-ray powder diffractogram structural studies reveal that at room temperature the layered ternary Ba_2GeSe_4 compound contains isolated tetrahedral $GeSe_4$ that form the structure type of K_2ZnBr_4. The compound crystallises in a monoclinic structure, space group $p2_1/m$ [8], with a conventional unit cell made which contains two Ba_2GeSe_4 formula per units cell. Figure 1 shows the Ba_2GeSe_4 super cell showing the tetrahedral $GeSe_4$ arrangements.

Energy versus volume calculations for Ba_2GeSe_4 were performed with the PBE and PBesol approximations. A 3rd order Murnaghan equation of state (EOS) function [23] was fitted to the calcualted values and is shown in Fig.2(b). The results show that the PBEsol equilibrium volume is closer to the experimental value than the PBE value. Calculated equilibrium structural parameters and the available experimental data are given in Table.1. Compared to the
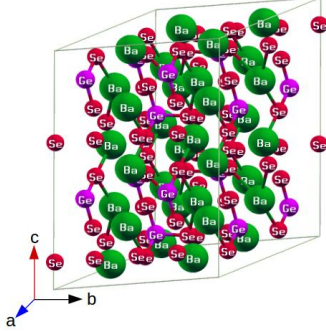
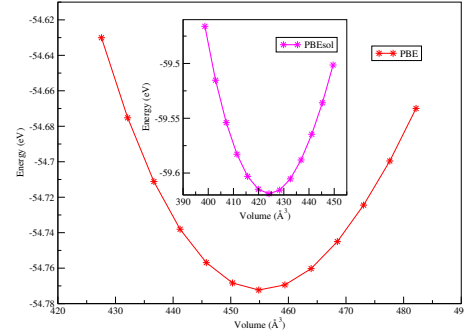**Figure 1.** Craystal structure of Ba_2GeSe_4.

Figure 2. Variation of total energy as a function of volume.

experimental data one can clearly see that the calculated lattice parameters (a, b and c), β, the angle between cell length a, b, and one of factors that defines the lattice plane spacing, and volume of the unit cell obtained by PBEsol, are very close to the experimentally measured values. The percentage difference of calculated lattice parameter and angle values from experimental values do not exceed 1.54%. Based on the consistent performance of the calculated PBEsol sructural parameters, this approximation was used to determine DFT electronic and optical properties and the orresponding calcualted structure was used for the GW and BSE calculations.

Table 1. Calculated and experimental structural parameters for Ba_2GeSe_4. Lattice parameters a, b and c in $\mathring{A}$. The angle between a and b, β, in degrees. Volume V, in $\mathring{A}^3$. E_{coh}, cohesive energy per atom, in eV.

	a	b	c	V	β	E_{coh}
PBE	7.204	7.240	9.292	454.96	108.52	-3.61
PBEsol	7.022	6.986	9.150	424.20	109.078	-3.95
Exp.[8]	6.9958	7.0938	9.1738	430.11	109.153	-

3.2. Elastic Properties

The elastic properties of a material provides important information about structural stability, binding characteristic, the anisotropy character, the link between mechanical and dynamical properties of a crystal. There are 13 independent elastic constants elastic stiffness constants C_{ij} for Ba_2GeSe_4, a monoclinic system. The calculated values of the elastic constants, for PBE and PBEsol, satisfy the stability criteria for monoclinic systems [24]. In Table 2 the bulk modulus B, the shear modulus G, Young's E modulus calcualted from the C_{ij} values using the Voigt-Reuss-Hill (VRH) approximation[25, 26] and the ratio B/G, A^U, the universal measure of anisotropy of a material, and the Poisson ratio ν of Ba_2GeSe_4 are shown. The bulk modulus is a measure of resistance to volume change in response to an applied pressure, while the shear modulus G is a measure of resistance to reversible deformation due to shear stress. Young's modulus is a measure of resistance to linear stress. Pugh [27] suggested the critical value of 1.75, for B/G >1.75 the

material behaves in ductile manner otherwise it is brittle. The Voigt and Reuss methods are known to define the upper and lower limits, respectively, of the machanical parameters. We therefore, use Hill's value which is an arithmetic average of Voigt and Reuss[28] for calculating the values of B/G and ν. The determined value of B/G from both PBE and PBEsol indicating that Ba_2GeSe_4 is ductile material. Similarly, ν provides an information of nature in bonding forces and volume compressibility of solid materials, ν takes values between $-1 < \nu < 0.5$[29]. The determined ν for both PBE and PBEsol indicated that Ba_2GeSe_4 is of good plasticity and have central inter-atomic forces. The calculated bulk modulus at zero pressure, B_0, from EOS fit, Table 2 and B from VRH approximation are in good agreement demonstrating the reliablity of this calculation. The relatively small value of the bulk modulus in Table 2 is evidence that Ba_2GeSe_4 is not very resistant to volume change with applied pressure. Similarly the values of Young's E is greater than bulk B modulus demonstrating that the title compound is soft material. The departure of A^U from zero defines the extent of single crystal anisotropy [30]. A^U and the Possion ratio ν were calculated using equations from Ref.[24, 30] which are depicted in Table 2.

Table 2. Calculated mechanical parameters. Bulk modulus B_0 and its derivative B_0' from EOS fitting, bulk B_V, shear G_H and Young's E_H from VRH-approximations modulus in GPa, universal anisotropy A^U, Poission's ratio ν and ratio B/G of Ba_2GeSe_4

	B_0	B_0'	B_H	G_H	E_H	A^U	ν	B/G
PBE	23.49	6.08	24.44	11.87	30.64	0.939	0.29	2.06
PBEsol	28.01	5.16	26.05	13.29	34.08	1.963	0.28	1.96

3.3. Electronic Properties

In Figure 3 and 4 the band structure along the high symmetry directions in the Brillouin zone are shown for PBEsol and the modified Becker Johnson potential (MBJ). MBJ normally gives a better estimation of the gap for large band gap semiconductors. From the band structures for PBEsol and MBJ, Figure 3 and 4 Ba_2GeSe_4 has a direct band gap of 1.46 eV and 2.26 eV located at Γ, respectively. It is also observed that from the projected density of states (PDOS) that the dominant contributions to the lower conduction band (CB) come from the hybridizations of Se(p), Ge(s) and Ba(d) orbitals, while the upper valency band (VB) is dominated by contributions from Se(p) with a limited contribution from Ba(d) orbitals. Band gaps calculated with PBE, PBEsol, MBJ, HSE and the fundamental gap at the G_0W_0 level of approximation, are listed in Table 3. The PBE and PBEsol gaps are smaller than the experimental gap, while the MBJ and HSE gaps are closer to the experimental range. The G_0W_0 estimate of the fundamental gap is smaller than the experimental gap, which is surprising since this estimate is frequently larger than the experimental optical gap.

3.4. Optical properties

The study of optical properties gives a better understanding of electronic structure and possible applications of a materials. The frequency dependent dielectric function $\varepsilon(\omega) = \varepsilon_1(\omega) + \varepsilon_2(\omega)$ fully described the optical properties of a materials [31]. The imaginary part $\varepsilon_2(\omega)$ is obtained from the momentum matrix element between the occupied electronic states relations, while the real part $\varepsilon_1(\omega)$ is determined from the imaginary part through the Kramers-Kroning relations using equations from Ref. [31]. From the calculated structural parameter $A^U = 1.963$, Ba_2GeSe_4 is anisotropic in nature. This is confirmed by the anisotropic nature of its optical properties
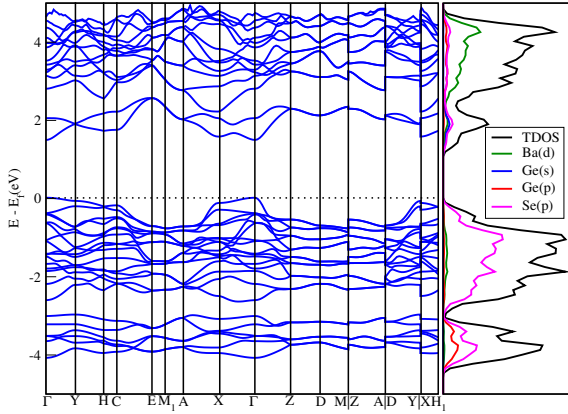
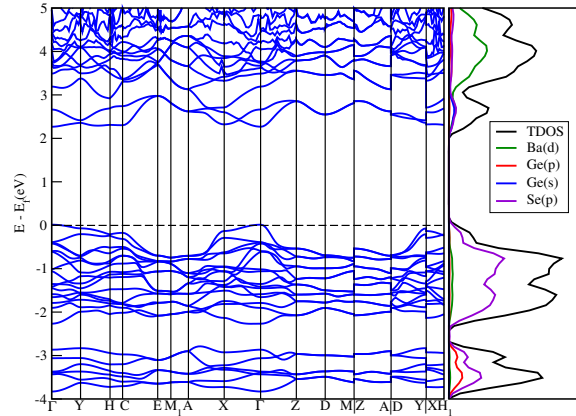**Figure 3.** PBEsol Electronic bands structure along high symmetry directions

Figure 4. MBJ Electronic bands structure along high symmetry directions

Table 3. Calculated and experimental band gaps, E_g, of Ba_2GeSe_4.

	PBE	PBEsol	MBJ	HSE	G_0W_0	Others (LDA)	Exp.
E_g(eV)	1.38	1.46	2.26	2.66	2.53	1.70[8]	2.6 - 3.0 [8]

determined using the $G_0W_0 + BSE$ calculations. The resolved optical spectra correspond to electric vector polarizations along the x, y and parallel to z directions, respectively. The imaginary part of the dielectric matrix, the optical absorption spectrum and corresponding Tauc plots in the x, y, z directions, are show in Figure 5 and 6. The optical band gap are estimated from Tauc plots with the onset of yy is at 2.05 eV, xx at 2.38 eV and zz at 2.58 eV, which agrees well with the experimental range of 2.6-3.0 eV.
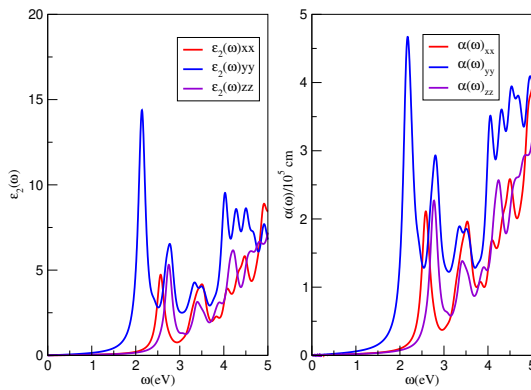

Figure 5. The calculated optical functions from left, the imaginary part of the dielectric function, the optical absorption spectra at G_0W_0+BSE level
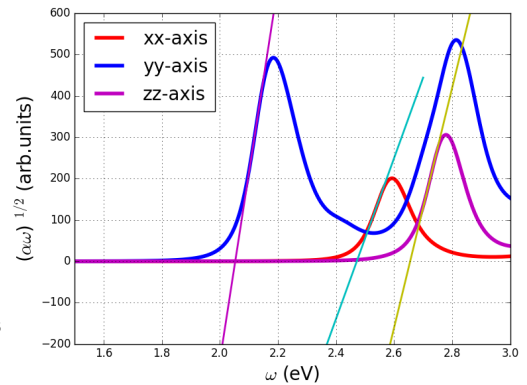

Figure 6. The Tauc plot of optical absorption spectra versus photon energy at G_0W_0+BSE level

3.5. Conclusion

Using first principle calculations, we investigate the structural, elastic, electronic and optical properties of the barium seleno-germanate Ba_2GeSe_4 compound. The calculated lattice parameters are in reasonable agreement with available experimental data. The electronic band structure calculations from MBJ which provide accurate band structure for most large band gap semiconductors shows an 2.26 eV direct band gap at $\Gamma - \Gamma$ points other energy gap calculation from HSE and G_0W_0 are within the predicted value. The significant hybridization of Ba(d), Ge(s) and Se(p) was observed from the PDOS analysis of conduction band indicating covalent character in addition to ionic character. The calculated optical properties shows anisotropy. The optical gap are in energetic order of yy<xx<zz, the onset of yy is at 2.05 eV, xx at 2.38 eV and zz at 2.58 eV, which agreed well with predicted value of 2.6-3.0 eV [8]. Our result shows that Ba_2GeSe_4 potential as wide band gap material [32] with potential applications in multi-junction solar cells. [33].

3.6. Acknowledgments

References

[1] Wachhold M and Kanatzidis M G 1999 *Inorg. Chem.* **38** 4178–4180
[2] Sheldrick W S and Wachhold M 1998 *Coord. Chem. Rev.* **176** 211–322
[3] Mei D, Yin W, Feng K, Lin Z, Bai L, Yao J and Wu Y 2011 *Inorg. Chem.* **51** 1035–1040
[4] Wu K, Su X, Yang Z and Pan S 2015 *Dalton Trans.* **44** 19856–19864
[5] Scragg J J et al 2013 *Chem. Mater.* **25** 3162–3171
[6] Regulacio M D and Han M Y 2016 *Acc. Chem. Res.* **49** 511–519
[7] Zhou M, Xiao K, Jiang J, Huang H, Lin Z, Yao J and Wu Y 2016 *Inorg. Chem.* **55** 12783–12790
[8] Assoud A, Soheilnia N and Kleinke H 2004 *Zeitschrift für Naturforschung B* **59** 975–979
[9] Yakovkin I and Dowben P A 2007 *Surf. Rev. Lett.* **14** 481–487
[10] Perdew J P, Burke K and Ernzerhof M 1996 *Phys. Rev. Lett.* **77** 3865
[11] Perdew J P et al 2008 *Phys. Rev. Lett.* **100** 136406
[12] Tran F and Blaha P 2009 *Phys. Rev. Lett.* **102** 226401
[13] Heyd J, Scuseria G E and Ernzerhof M 2003 *J. Chem. Phys.* **118** 8207–8215.
[14] Kresse G and Hafner J 1993 *Phys. Rev. B* **47** 558
[15] Kresse G and Furthmüller J 1996 *Comput. Mater. Sci.* **6** 15–50
[16] Kresse G and Joubert D 1999 *Phys. Rev. B* **59** 1758
[17] Hedin L 1965 *Phys. Rev.* **139** A796
[18] Hybertsen M S and Louie S G 1986 *Phys. Rev. B* **34** 5390
[19] Onida G, Reining L and Rubio A 2002 *Rev. Mod. Phys.* **74** 601
[20] Hanke W and Sham L J 1980 *Phys. Rev. B* **21** 4656
[21] Salpeter E E and Bethe H A 1951 *Phys. Rev.* **84** 1232
[22] Tauc J, Grigorovici R and Vancu A 1966 *phys. Stat. Sol. b* **30** 244–247
[23] Murnaghan F D 1944 *Proc. Natl. Acad. Sci.* **30** 244–247
[24] Wu Z, Zhao E, Xiang H, Hao X, Liu X and Meng J 2007 *Phys. Rev. B* **76** 054115
[25] Reuss A 1929 *J. Appl. Math. Mech.* **9** 49–58
[26] Hill R 1952 *Proc. Phys. Soc. Sec. A* **65** 349
[27] Pugh S F 1954 *Phil. Mag.* **45** 823–843
[28] Hirsekorn S 1990 *Text. Stress, Micro.* **12** 1–14
[29] Boucetta S 2014 *J. Mag. Allo.* **2** 59–63
[30] Ranganathan S I and Ostoja-Starzewski M 2008 *Phys. Rev. Lett.* **101** 055504
[31] Saha S, Sinha T P and Mookerjee A 2000 *Phys. Rev. B* **62** 8828
[32] Yoshikawa A, Matsunami H and Nanishi Y 2007 *Wide Bandgap Semiconductors* (Berlin: Springers)
[33] Green M A 2003 *Third generation concepts for photovoltaics* (IEEE: 3rd World Conference on Photovoltaic Energy Conversion, Proceedings of)