

Electronic and optical properties of β -HgS

J.O. Akinlami* and F.C. Onyeonu

Department of Physics, Federal University of Agriculture, Abeokuta, Ogun State, Nigeria

*Corresponding author e-mail: johnsonak2000@yahoo.co.uk

Abstract. Electronic and optical properties of β -HgS have been investigated using the density functional theory. The calculated lattice parameter is 6.043 Å, the bulk modulus is 57.17 GPa, the equilibrium volume is 55.25 Å³. From the band structure, a direct band gap of 0.00002 eV was obtained, which agreed well with other calculations. The plot of the dielectric constant against photon energy indicated several distinctive peaks. The imaginary part has a peak value of 34.99 at 0.47 eV and the real part has a peak value of 29.65 at 0.40 eV. The values obtained for electronic and optical properties of β -HgS are essentially important for applications in optoelectronics.

Keywords: mercury sulphide, electronic properties, optical properties, density functional theory, plane-wave pseudopotential method.

<https://doi.org/10.15407/spqeo22.02.150>

PACS 42.79.Pw

Manuscript received 24.01.19; revised version received 23.04.19; accepted for publication 19.06.19; published online 27.06.19.

1. Introduction

Mercury sulphide (HgS) belongs to the group II-VI compounds. HgS has an ionicity of 0.79, which is the borderline between the ionic rocksalt structure and the covalent zinc-blende structure of $A^N B^{8-N}$ (N = group number) compounds. According to the ionicity, it was defined by [1]. It exhibits two structural modifications in nature, α -HgS (cinnabar, red, trigonal structure) and β -HgS (metacinnabar, black, cubic structure) [2]. β -HgS is metastable and is known to transform to stable α -HgS even at room temperature [3, 4]. β -HgS can also be stabilized at ambient temperature through a couple of percent doping with a transition metal, for example Fe [5], and CdS/HgS/CdS heterostructures [6]. A small addition of Fe helps to crystallize HgS in the zinc-blende structure (β -HgS), both in nature ($\sim 1\%$ Fe), [7] and in the laboratory [8]. The zinc-blende variety of HgS (β -HgS, metacinnabar) is zero or near zero gap material [9]. The electronic structure of ZB mercury chalcogenides differs in a fundamental way from the electronic structure of the corresponding isoelectronic Zn and Cd systems [10-12]. Wei and Zunger (1988) have noted that the difference among Hg, Zn and Cd chalcogenides is due to the cation d band. The incomplete screening of the core by d electrons is thought to be the origin of the very different properties of the IIB-VI compounds relative to IIA-VI compounds. Mahapatra and Dash (2006) [13] synthesized well-separated HgS nanocrystals by a wet chemical route and found out that HgS nanocrystals are in cinnabar phase. Xu and Carraway (2012) [14] used

solven based approach for the synthesis of β -HgS nanocrystals. Khalilzabeh and Kangarlov (2015) [15] prepared thin layers of HgS by chemical bath deposition techniques. Patil *et al.* (2017) [16] studied HgS doped with chromium by using novel chemical route. β -HgS are useful in ultrasonic transducers, image sensors [17], electrostatic imaging materials [18], photoelectric conversion devices [19, 20] and low-power consumption electronic devices [21]. It is also known to be a technologically important material for its pronounced dichroism [22], birefringence [23] and acoustic-optic properties [24]. In this study, we present electronic and optical properties of β -HgS, namely: lattice parameter, bulk modulus, equilibrium volume, density of states (DOS), band structure, real and imaginary dielectric constant using the first principles method [25-29]. To the best of our knowledge, the plane-wave pseudopotential (PWPP) method [30] has not been used to calculate the electronic and optical properties of β -HgS. Hence, the aim of this study is to investigate electronic and optical properties of β -HgS by using PWPP method as implemented in ABINIT package for the first time.

2. Methods of calculations

The first-principles density functional theory (DFT) [25] within Plane-Wave Pseudopotential within the Generalized Gradient Approximation (GGA) [31] implemented in the ABINIT code [32] was used to calculate electronic and optical properties of β -HgS. The Brillouin zone was performed automatically with

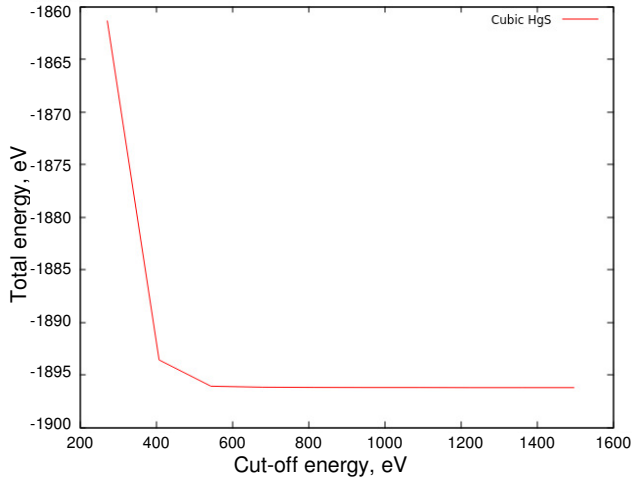


Fig. 1. Plot of total energy vs the cut-off energy (E_{cut}) for β -HgS.

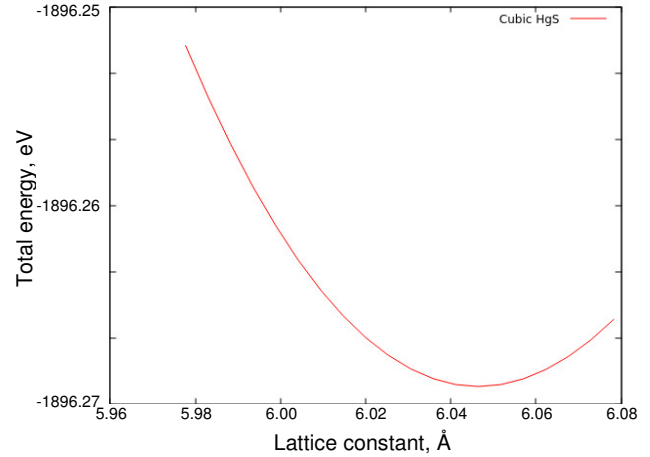


Fig. 3. Total energy vs lattice constant for β -HgS.

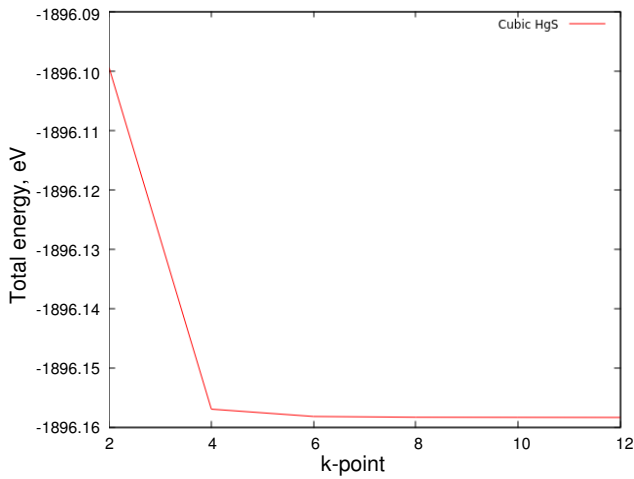


Fig. 2. Total energy vs k-point for β -HgS.

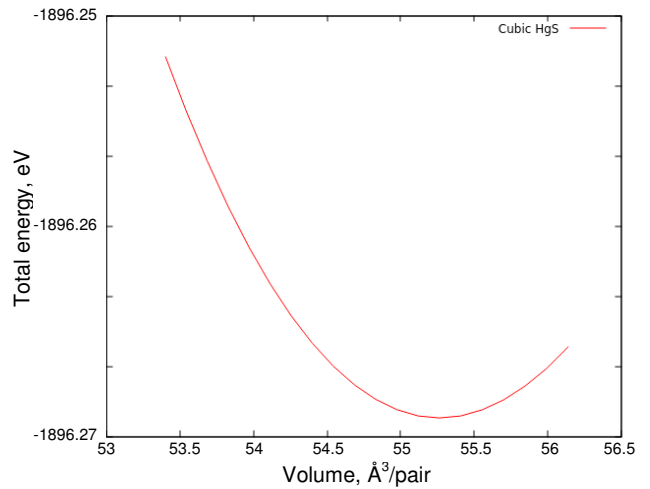


Fig. 4. Total energy – volume dependence for unit cells of β -HgS.

$6 \times 6 \times 6$ k-point mesh according to Monkhorst-pack scheme [33]. Equation of states that consists of mathematical relationship between two or more state functions such as pressure and volume was used to obtain the pressure-volume relationship that allowed us to obtain the equilibrium lattice parameter.

$$P(V) = \frac{B_0}{B_0'} \left[\left(\frac{V}{V_0} \right) - 1 \right]. \quad (1)$$

Later, we obtained the volume equation from the above pressure as follows:

$$V(P) = V_0 \left[1 + P \left(\frac{B_0'}{B_0} \right) \right], \quad (2)$$

where P is the pressure, V – volume, B_0 – bulk modulus, B_0' – pressure derivative of the bulk modulus and V_0 – equilibrium volume.

3. Results and discussion

3.1. Structural properties

The results obtained for electronic and optical properties of β -HgS are presented in Figs. 1–11 and Table. The plot of E_{tot} vs lattice constants for β -HgS yields a parabolic curve with the minimum energy of β -HgS at 6.043 Å as shown in Fig. 3, which is in good agreement with previous theoretical and experimental results for lattice parameters. Fig. 2 is the plot of E_{tot} vs its k-point sampling curve with monotonic minimum range between 4 and 12. The volume parameter was calculated to be 55.25 Å³ as shown in Fig. 4. Subsequently, the calculated results were used for calculation of all the physical properties of this compound. The total energy was investigated as a function of volume in Fig. 4 and as a function of pressure of unit cell for β -HgS crystal as seen in Fig. 5. The total energy vs volume curve is a mirror of total energy versus pressure curve. Fig. 1 is the plot of

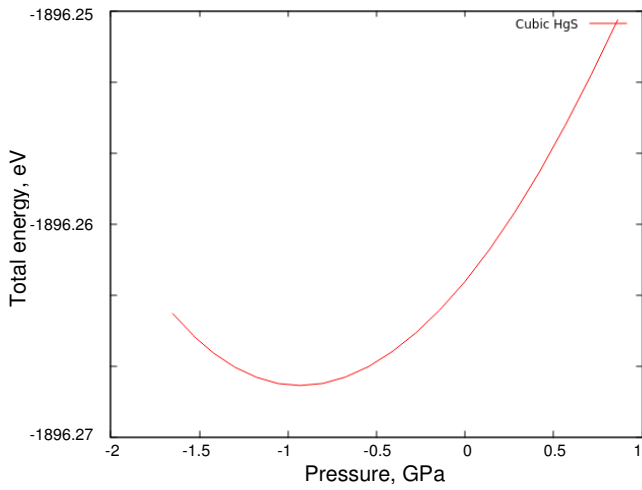


Fig. 5. Total energy – pressure dependence for unit cells of β -HgS.

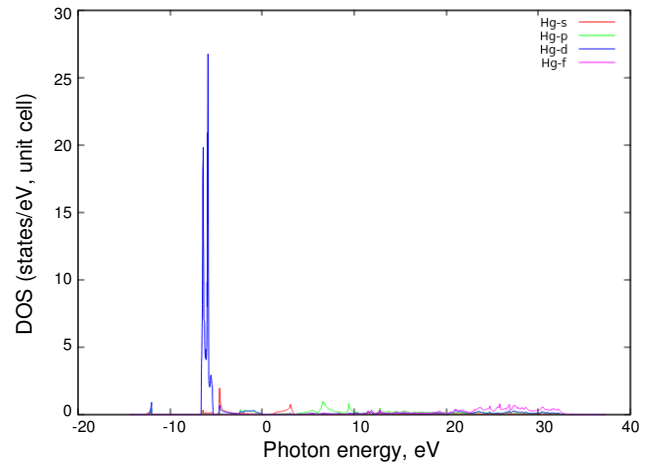


Fig. 8. Partial density of states of mercury sulphide (β -HgS) for Hg-constituent.

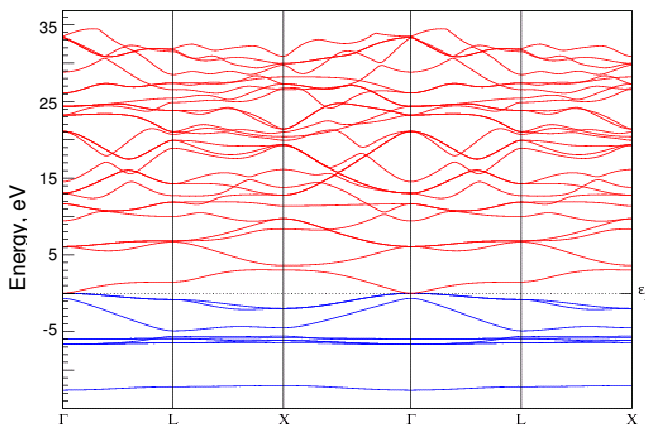


Fig. 6. Electronic band structure of β -HgS. The blue solid lines indicate the valence, and the red solid lines are the conduction bands, respectively. For β -HgS E_g (direct) = $2.0 \cdot 10^{-5}$ eV.

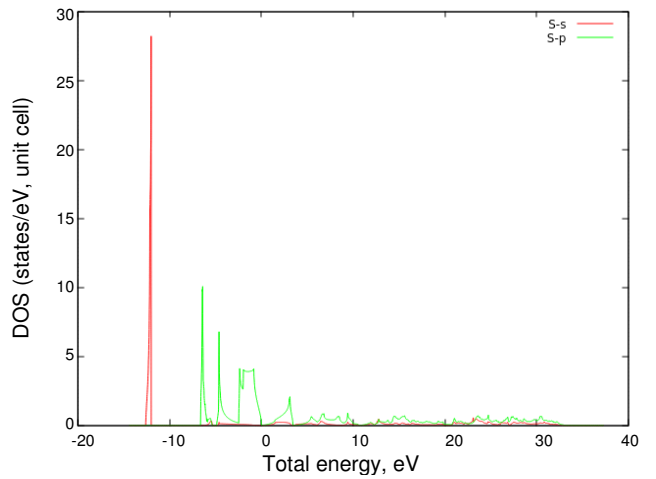


Fig. 9. Partial density of states of mercury sulphide (β -HgS) for S-constituent.

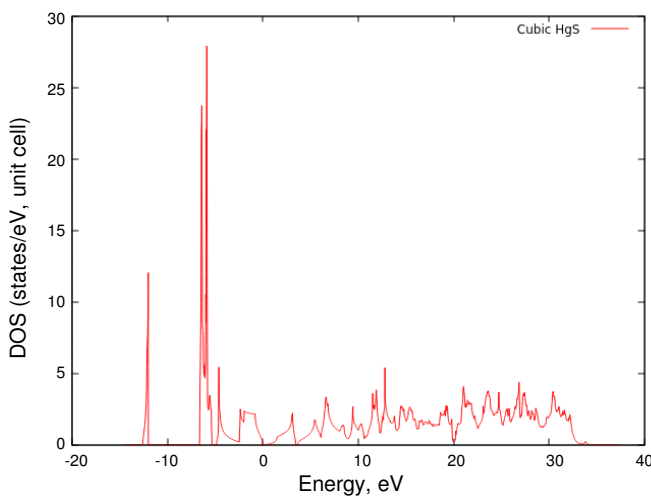


Fig. 7. Total density of states for cubic mercury sulphide (β -HgS).

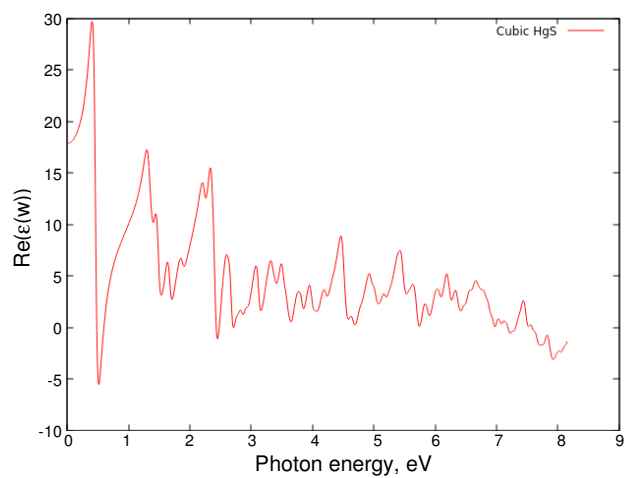


Fig. 10. Real part of dielectric function for cubic mercury sulphide (β -HgS).

Table of calculated GGA lattice constant a_0 , bulk modulus B , equilibrium volume V_0 and band gap E_g for β -HgS compared to other theoretical studies and experiment.

Physical parameter	This study GGA:PWPP	Theory	Experimental
Lattice constant a_0 (Å)	6.043	5.999 [9], 5.863 [34]	5.852 [36]
Bulk modulus B (GPa)	57.17	59.07 [36], 63.6 [34]	68.6 [36]
Equilibrium volume V_0 (Å ³)	55.25	54.8 [39]	50.1 [36]
Band gap E_g (eV)	0.00002	0 [34], 0.12 [35]	0.25 [9], 0.54 [38]

E_{tot} vs its kinetic energy cutoff (E_{cut}) curve with the monotonic minimum range between 600 and 1500 eV. In Fig. 3, it was observed that the minimum value of total energy is -1896.26 eV, and in Fig. 4, it was observed to be -1896.27 eV for this compound.

3.2. Electronic properties

The plane-wave pseudopotential based on density functional theory within the generalized gradient approximation (GGA) was used for electronic structure calculations of β -HgS. The electronic band structure of β -HgS was presented in Fig. 6. The plot displays the energy range between -12.8 and 34.8 eV versus the wave-vectors Γ , L, X, Γ , L and X.

From the electronic band structure of β -HgS, it was observed that it has a direct band gap at high symmetry gamma (Γ) point with the value of $2.0 \cdot 10^{-5}$ eV.

The DOS and partial density of states are presented in Figs. 7, 8, and 9. In Fig. 7, seven main features can distinctly be seen in DOS. Following detailed incite from PDOS of Figs. 8 and 9, the first one is in the energy range from -12.5 to -11.8 eV, which is mainly attributed to S s -states; the second one, -6.5 to -5.3 eV, is mainly attributed to the Hg d -states; the third one, -4.9 to -2.5 eV, is mainly attributed to the hybridization of Hg s -, Hg d -, and S p -states; the forth one, corresponding to the top valence bands, from -2.5 to 0.0 eV (Fermi level), is mainly due to the hybridization of Hg d - and S p -states; the fifth one, corresponding to the bottom of the conduction bands, from 0.4 to 3.5 eV, is mainly due to the hybridization of Hg s - and S p -states with small contribution from S s -state; the sixth one, 3.8 to 20.0 eV, is mainly due to the hybridization of Hg p - and S p -states. Whereas beyond 20 eV, Hg f - and S p -states contribute mainly.

3.3. Optical properties

β -HgS is an optic crystal that exhibits the symmetry of point group 216. The calculated real (ϵ_1) and imaginary (ϵ_2) parts of this compound are as presented in Figs. 10 and 11.

In Fig. 10, the real part of linear dielectric function, ϵ_1 , goes to its maximum value of 29.65 at 0.40 eV. It was observed that β -Hg has a static dielectric constant value 17.74 as shown in Fig. 11. The real part of the complex dielectric constant showed how much the speed of light in this material is slowed down, the imaginary part portrayed how a dielectric material absorbed energy from an electric field due to dipole motion. The real part of the complex dielectric constant obtained for β -HgS is in the photon energy range of 0.0 to 8.2 eV as shown in Fig. 10. Variations in the real part of the complex dielectric constant with photon energy showed several peaks at the energies: 0.40, 1.32, 2.34, 4.48, and 5.43 eV. The peaks are points of inter-band transitions along the high symmetry points in the Brillouin zone. This real part of the complex dielectric constant has the minimum value -5.60 at the photon energy 0.52 eV and also the maximum value 29.65 at the photon energy 0.40 eV. The regions above and below zero indicate that the material behaves as dielectric and semiconductor, respectively. The imaginary part of the complex dielectric constant for β -HgS is in the range 0.00 to 8.17 eV as seen in Fig. 11. Variations in the imaginary part of the complex dielectric constant with photon energy showed several peaks, at the energies: 0.47, 1.49, 2.40, 2.68, and 4.52 eV. The imaginary part of complex dielectric constant has the maximum value 34.99 at the photon energy 0.47 eV.

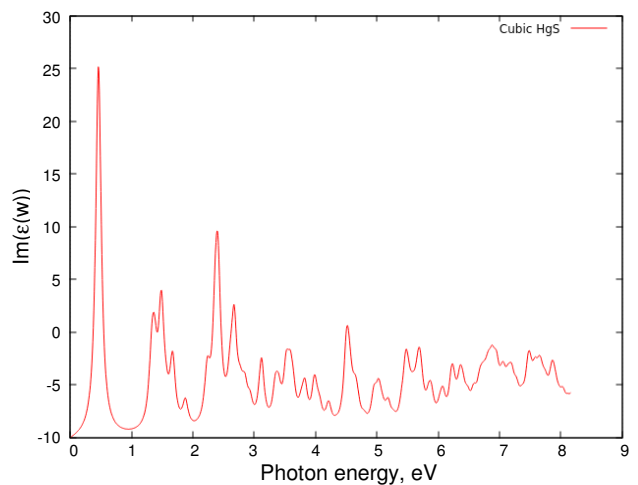


Fig. 11. Imaginary part of dielectric function of β -HgS.

4. Conclusion

The electronic and optical properties of β -HgS have been investigated using the plane-wave pseudopotential method for the first time. The density functional theory within the generalized gradient approximation was used as the exchange correlation. The ground state properties including equilibrium lattice parameter, pressure and volume derivative and minimized total energy were determined. The obtained results agree with other experimental and theoretical values. It was observed that β -HgS is semiconductor with a direct band gap of $2.0 \cdot 10^{-5}$ eV at the gamma (Γ) point.

The real and imaginary dielectric responses of the compound have been also determined. β -HgS is an optic crystal, the compound has a static dielectric constant of 17.74. The results obtained showed that β -HgS exhibits a semi-metallic properties at ambient temperature and pressure, which provides good application in optoelectronic materials.

References

- Bhushan S., Mukherjee M. and Bose P. Electro-optical studies in chemically deposited La/Nd doped (Cd-Pb)S films. *J. Mater. Sci: Mater. Electron.* 2002. **13**. P. 581–584. <https://doi.org/10.1023/A:1020196030287>.
- Phillips J.C. and Van Vechten J.A. Spectroscopic analysis of cohesive energies and heats of formation of tetrahedrally coordinated semiconductors. *Phys. Rev. B.* 1970. **2**, No 6. P. 2147. <https://doi.org/10.1103/PhysRevB.2.2147>.
- Qadri S.B., Kumo M., Feng C.R., Rath B.B. and Yousuf M. High temperature structural studies of HgS and HgSe quantum dots. *Appl. Phys. Lett.* 2003. **83**, No 19. P. 4011–4013. <https://doi.org/10.1063/1.1625433>.
- Kowalski B.J., Szuszkiewicz W., Orlowski B.A. et al. Photoemission study of β -HgS. *Journal of Electron Spectroscopy and related Phenomena.* 1997. **85**, No 1. P. 17–22. [https://doi.org/10.1016/S0368-2048\(97\)00020-0](https://doi.org/10.1016/S0368-2048(97)00020-0).
- Dybko K., Szuszkiewicz W. and Witkowska B. New semimagnetic semiconductors: HgS doped with transition metals. *Defect and Diffusion Forum.* 1995. **121/122**. P. 41-0. <https://doi.org/10.4028/www.scientific.net/DDF.121-122.41>.
- Mews A., Kadavanich A.V., Banin U. and Alivisatos A.P. Structural and spectroscopic investigation of CdS/HgS/CdS quantum-dots quantum wells. *Phys. Rev. B.* 1996. **53**, No 20. P. R13242-R13245. <https://doi.org/10.1103/PhysRevB.53.R13242>.
- Zallen R. and Slade M. Plasma edge and band structure of cubic HgS. *Solid State Commun.* 1970. **8**, No 16. P. 1291–1294. [https://doi.org/10.1016/0038-1098\(70\)90622-8](https://doi.org/10.1016/0038-1098(70)90622-8).
- Szuszkiewicz W., Witkowska B., Jouanne M., and Balkanski M. Raman spectroscopy of cubic $\text{Hg}_{1-x}\text{Fe}_x\text{S}$. *Mater. Sci. Forum.* 1995. **182-184**. P. 711–714.
- Cardona M., Kremer R.K., Lauck R., Siegle G., Munoz A. and Romero A.H. Electronic, vibrational, and thermodynamic properties of metacinnabar β -HgS, HgSe, and HgTe. *Phys. Rev. B.* 2009. **80**, No 19. P. 195204. <https://doi.org/10.1103/PhysRevB.80.195204>.
- Wei S.H. and Zunger A. Role of metal d states in II-VI semiconductors. *Phys. Rev. B.* 1988. **37**, No 15. P. 8958. <https://doi.org/10.1103/PhysRevB.37.8958>.
- Heda N.L., Mathur S., Ahuja B.L. and Sharma B.K. Compton profiles and band structure calculations of CdS and CdTe. *phys. status solidi (b)*. 2007. **244**, No 3. P. 1070–1081. <https://doi.org/10.1002/pssb.200642308>.
- Ahuja B.L. and Heda N.L. Electron momentum density in ZnSe: Theory and Experiment. *Radiation Physics and Chemistry.* 2007. **76**, No 6. P. 921–928. <https://doi.org/10.1016/j.radphyschem.2007.01.006>.
- Mahapatra A.K. and Dash A.K. α -HgS nanocrystals: synthesis, structure and optical properties. *Physica E.* 2006. **35**. P. 9–15.
- Xu X. and Carraway E.R. Sonication-assisted synthesis of β -mercuric sulphide nanoparticle. *Nanomaterials and Nanotechnology.* 2012. **2**, Art. 17. <https://doi.org/10.5772/55823>.
- Khalilzadeh M. and Kangarlou H. Optical properties determination of mercury sulfide biological composites. *International Journal of Biology, Pharmacy and Allied Science.* 2015. **4**, No 11. P. 187–193.
- Patil H.B., Borse S.V. and Ahire R.R. Structural, optical and thermoelectrical properties of mercury chromium sulfide thin film deposition by novel chemical route. *IOSR J. Appl. Phys.* 2017. **9**, No 3 Ver. II. P. 08-14. <https://doi.org/10.9790/4861-0903020814>.
- Kale S.S. and Lokhande C.D. Preparation and characterization of HgS films by chemical deposition. *Mater. Chem. Phys.* 1999. **59**, No 3. P. 242–246. [https://doi.org/10.1016/S0254-0584\(99\)00048-6](https://doi.org/10.1016/S0254-0584(99)00048-6).
- Kale S.S., Pathan H.M. and Lokhande C.D. Thickness dependent photoelectrochemical cells performance of CdSe and HgS thin film. *J. Mater. Sci.* 2005. **40**. P. 2635–2637.
- Kreingol'd F.I. *Sov. Phys. Solid State.* 1963. **4**. P. 1904.
- Robert C.G., Lind E.L. and Davis E.A. Photoelectronic properties of synthetic mercury sulphide crystals. *J. Phys. Chem. Solids.* 1969. **30**, No 4. 833–844. [https://doi.org/10.1016/0022-3697\(69\)90279-0](https://doi.org/10.1016/0022-3697(69)90279-0).
- Virost F., Hayn R., Richter M., van den Brink J. Metacinnabar (β -HgS): A strong 3D topological insulator with highly anisotropic surface states.

- Phys. Rev. Lett.* 2011. **106**, No 23. P. 236806-1-4. <https://doi.org/10.1103/PhysRevLett.106.236806>.
22. Zallan R. in: *II-IV Semiconducting Compounds*, D.G. Thomas (Ed.). W.A. Benjamin, Inc., New York, 1967.
 23. Bond W.L., Boyd G.D., and Carter H.L. Jr. Refractive Indices of HgS (Cinnabar) between 0.62 and 11 μ . *J. Appl. Phys.* 1967. **38**. P. 4090. <https://doi.org/10.1063/1.1709079>.
 24. Sapriel J. Cinnabar (α HgS), a promising acousto-optical material. *Appl. Phys. Lett.* 1971. **19**. P. 533. <https://doi.org/10.1063/1.1653802>.
 25. Eschrig H. *Fundamentals of Density Functional Theory* (Revised and extended version). 1996. P. 5. <https://doi.org/10.1007/978-3-322-97620-8>.
 26. Zein N.E. Density functional calculations of elastic moduli and phonon spectra of crystals. *Sov. Phys. Solid State.* 1984. **26**. P. 1825.
 27. Blat D.K., Zein N.E., and Zinenko V.I. Calculations of phonon frequencies and dielectric constants of alkali hydrides via the density functional method. *J. Phys.: Condensed Matter.* 1991. 3, No 29. P. 5515.
 28. Zein N.E. Ab initio calculations of phonon dispersion curves. Application to Nb and Mo. *Phys. Lett. A.* 1992. **161**, No 6. P. 526-530. [https://doi.org/10.1016/0375-9601\(92\)91086-7](https://doi.org/10.1016/0375-9601(92)91086-7).
 29. Baroni S., de Gironcoli S., Carso A. Dal and Giannozzi P. Phonons and related crystal properties from density-functional perturbation theory. *Rev. Mod. Phys.* 2001. **73**, No 2. P. 515. <https://doi.org/10.1103/RevModPhys.73.515>.
 30. Akinlami J.O., Odeyemi O.O. Electronic structure and optical properties of HgSe. *Semiconductor Physics, Quantum Electronics and Optoelectronics.* 2018. **21**, No 3. P. 288–293. <https://doi.org/10.15407/spqeo21.03.288>.
 31. Jones R.O. Introduction to Density Functional Theory and Exchange-Correlation Energy Functionals. *NIC Series.* 2006. **31**. P. 45–70. <https://www.fz-juelich.de/nic-series/volume31>.
 32. Gonze X., Beuken J.M., Caracas R. *et al.* First-principles computation of material properties: the ABINIT software project. *Comput. Mater. Sci.* 2002. **25**, No 3. P. 478–482.
 33. Monkhorst H.J. and Pack J.D. Special points for Brillouin-zone integrations. *Phys. Rev. B.* 1976. 13, No 12. P. 5188–5192. <https://doi.org/10.1103/PhysRevB.13.5188>.
 34. Shafaay B. Al, Hassan F. El Haj, Korek M. First principle investigation of mercury chalcogenides and their $\text{HgS}_x\text{Se}_{1-x}$ and $\text{HgS}_x\text{Te}_{1-x}$ ternary alloys. *Computat. Mater. Sci.* 2014. **83**. P. 107–113.
 35. Fleszar A. and Hanke W. Electronic structure of IIB-VI semiconductors in the GW approximation. *Phys. Rev. B.* 2005. **71**, No 4. P. 045207. <https://doi.org/10.1103/PhysRevB.71.045207>.
 36. Delin A., and Klüner T. Excitation spectra and ground-state properties from density-functional theory for the inverted band-structure systems β -HgS, HgSe, and HgTe. *Phys. Rev. B.* 2002. **66**, No 3. P. 035117. <https://doi.org/10.1103/PhysRevB.66.035117>.
 37. Kumar V., Shrivastava A.K. and Jha V. Bulk modulus and microhardness of tetrahedral semiconductors. *J. Phys. Chem. Solids.* 2010. **71**, No 11. P. 1513–1520. <https://doi.org/10.1016/j.jpcs.2010.07.012>.
 38. Madelung O. (Ed.). *Semiconductors: Data Handbook*, Third Edition. Springer-Verlag Berlin Heidelberg, 2003.
 39. Perdew J.P. Unified theory of exchange and correlation beyond the local density approximation. *Electronic Structure of Solids.* 1991. **17** (Physical Research). P. 11–20. Berlin, Akademie Verlag, 1991.

Authors and CV



Akinlami Johnson Oluwafemi, born in 1972, defended his Doctoral Dissertation in Physics (Theoretical Condensed Matter Physics) in 2011. Senior Lecturer at Federal University of Agriculture, Abeokuta, Ogun State, Nigeria. Authored over 30 publications. The area of his scientific interests includes optical properties of A^3B^5 and A^2B^6 compounds, photoemission study of the electronic structure of A^2B^6 compounds and layered oxysulfide (LaO)CuS, magneto-optical properties of solids.



Francis Chidubem Onyeanu born in 1980, defended his M Sc. dissertation “Investigations of the Structural and Opto-Electronic Properties of Mercury Sulphide” in 2017 at the Department of Physics, College of Physical Science, Federal University of Agriculture Abeokuta (FUNAAB), Ogun State, Nigeria. The area of his scientific interests includes the theoretical study of the structural, electronic and optical properties of novel materials using density functional theory.