ISSN 1996-3343

Asian Journal of Applied Sciences

http://knowledgiascientific.com

Knowledgia SCIENTIFIC
A Place to Publish Outstanding Research

Asian Journal of Applied Sciences 7 (8): 774-779, 2014
ISSN 1996-3343 / DOI: 10.3923/ajaps.2014.774.779

First-principle Studies on Electronic Properties of PbO Structures

S. Sriram, R. Chandiramouli and P. Gopinath
School of Electrical and Electronics Engineering, SASTRA University, Tirumalaisamudram, Thanjavur, 613 401, India

Corresponding Author: R. Chandiramouli, School of Electrical and Electronics Engineering, SASTRA University, Tirumalaisamudram, Thanjavur, 613 401, India

ABSTRACT

The different structures of PbO such as hexagonal sheet, tubular, bucky ball and cone super cells were constructed and optimized using density functional theory. The total energy of PbO super cells were calculated and it is inferred that the stability of the super cells depends on the number of atoms, more number of atoms increases the stability of the super cell. The bonding capability depends on the electronic charge of the molecule. The molecular electronic configurations were analyzed using Mulliken population analysis. The electronic properties of PbO super cells were discussed in terms of density of states. The reported results will provide the information about the realistic structures of PbO super cells which helps in the synthesis of new nanomaterial.

Key words: Mulliken population, electronic properties, super cells, density of states

INTRODUCTION

Metal oxides play an important role in industrial applications due to their novel physical and chemical properties. The recent advancement in technology leads to applications of nano dimensional material clusters for gas sensing (Gupta *et al*., 2010; Srivastava *et al*., 2011), fuel cell electrodes (Suffredini *et al*., 2007), catalysts (Romantsova *et al*., 2013), photovoltaics (Burnside *et al*., 2000), optoelectronics (Yin *et al*., 2011) etc. Apart from these metal oxides clusters, new inorganic-organic hybrid nanostructures (Sergeev-Cherenkov *et al*., 2004), metal clusters (Janssens *et al*., 2004), chemical doping in clusters (Ding *et al*., 2010) and ligand capping (Braunstein *et al*., 1997) are possible which can be tailored with metal oxide nanomaterials to improve their properties and application. Lead (Pb) is the heaviest group 14 element which finds its potential applications in lead-acid batteries and integrated circuits (Rochliadi and De Marco, 2002; Rezaei, 2006). PbO exists in different phases such as α-PbO (litharge) which is a low temperature phase and the other is a high temperature phase which is called as β-PbO (massicot). Even though lead has its importance it is biologically toxic. The electronic and chemical properties of lead oxides (PbO) can be fine-tuned by incorporating the dopants (Plucinski *et al*., 2003; Hussain *et al*., 2002), preparatory conditions (Haddadian *et al*., 2009; Li *et al*., 2005) etc. The morphology of lead oxide can be varied by synthesis process of lead oxide such as nanorod (Jia and Gao, 2006), nanostars, nanoflake, nanoneedles and multibranched nanostructure (Chen *et al*., 2011; Zeng *et al*., 2012). There are many techniques used for the synthesis of PbO, among the vapour phase technique, thermal evaporation (Wiechert *et al*., 2005), laser ablation (Sajjadi *et al*., 1992), RF sputtering (Wu *et al*., 2008) are used for synthesis. Among the liquid phase techniques, some of the methods are sol-gel (Zhu *et al*., 2005), spray

pyrolysis (Cruz *et al.*, 2002) and electro deposition (Gonzalez-Garcia *et al.*, 2002). Since the electronic properties can be altered by different ways to get a proper nanostructure, keeping this as motivation, literature survey was conducted. From the survey it is inferred that not much work has been reported in the density functional theory approach for PbO clusters. In recent years, investigations are carried out in lead oxide clusters (Liu *et al.*, 2012; Wu, 2003; Walsh and Watson, 2005), even though there are some reports in the PbO clusters, in the present study some of the realisticpossible geometrical structures were constructed and optimized using density functional theory (Hu and Dai, 2012).

COMPUTATIONAL METHODS

Four different realistic structures of PbO supercells with different geometries are constructed and optimized. The total energy calculations are done based on plane wave basis sets using ABINIT (Gonze *et al.*, 2002) package. The electron exchange and correlation are treated with GGAby using Pedrew-Burke-Ernzerhof (Perdew *et al.*, 1996) functional. The plane wave cut off energy of the wave functions was set to 400 eV. A 4×4×4 k grid was used to integrate over the Brillouin zone. The 5d, 6s and 6p shells of Pb and 2s, 2p shells of O are treated as valance states. The pulay density matrix schemeis used to compute the self-consistent cycle to obtain the total energy. The energy convergence for SCF cycle is fixed to 10^{-6} eV.

RESULTS AND DISCUSSION

Structures of PbO: The different geometries of PbO super cells are constructed which has the form of hexagonal sheet, tubular, bucky ball and cone having 14, 30, 20 and 21 atoms, respectively. In hexagonal sheet structure, the lead and oxygen atom are arranged alternatively which forms a bees hive like structure. In tubular structure all the lead and oxygen atoms forms a nanotube like structure. In the case of bucky ball structure the lead and oxygen atoms forms a three dimensional ball structure with alternative lead and oxygen atoms. The nano cone structure has lead and oxygen atoms arranged in three dimensional cone one over the other. All the realistic possible structure of hexagonal sheet, tubular, bucky ball and cone are optimized and the results are reported. Figure 1a-d shows the constructed super cells of hexagonal sheet, tubular, bucky ball and cone structures of PbO, respectively.

Total energy calculations are calculated using GGA-PBE scheme and the calculated energy for different structures of PbO are listed in Table 1.

From the values it is observed that when the number of atoms increases the super cell stability is increased. This may be due to the dependence of number of atoms. Initially the super cells are in the premature state; upon addition of atoms to the super cells will leads to its stability.

Mulliken population analysis: The bonding capability of a molecule depends upon the electronic charge of the molecule. The charge distribution is dependent onspin and transformation of electrons

Table 1: Total energies obtained by GGA-PBE for different PbO clusters

Structure	Atoms	Total energy (eV)
Hexagonal sheet	14	-7424.36
Tubular	30	-15904.8
Bucky ball	20	-10191.3
Cone	21	-10634.1

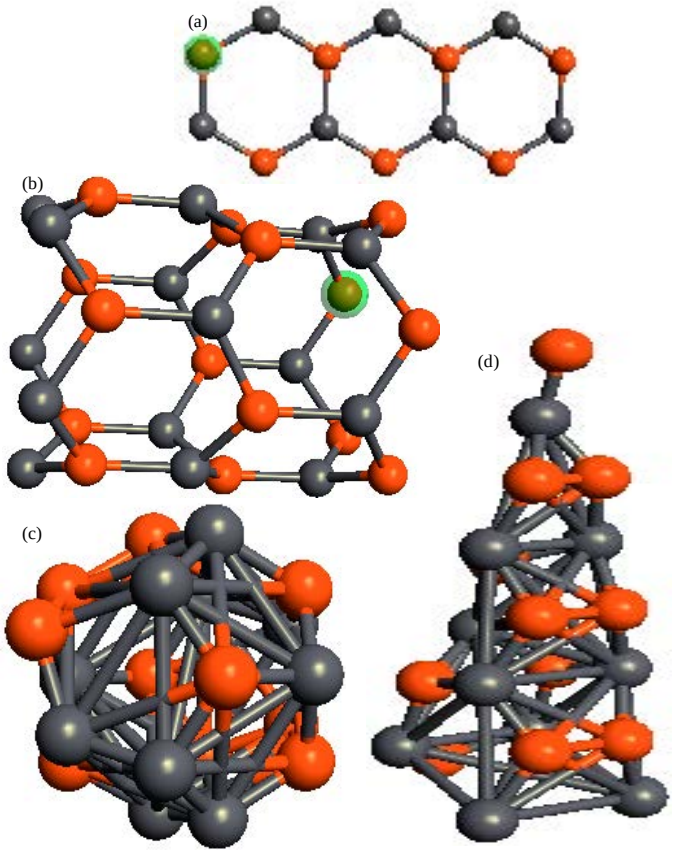

Fig. 1(a-d): Structures of PbO, (a) Hexagonal sheet, (b) Tubular, (c) Bucky ball and (d) Cone

in the atoms of the molecule. The molecular electronic configuration can be acquired by analyzing the charge distribution. The atomic charge values are obtained by Mulliken population analysis. The charge distribution on hexagonal sheet shows that the contribution of charges on O atom is more than the charge contribution of Pb atoms. In particular, the s orbital and p orbital of the O atom plays significant contribution in the overall charge of the molecule. While analyzing the charge distribution in the tubular super cell, same trend is seen as in the case of hexagonal sheet. It is noted that the d orbital of the Pb atom possess a small amount of charge in the total charge distribution since the super cell is in nano tube form. In the case of bucky ball, most of the s orbitals of O and Pb have the influence of anti-bonding charges, whereas d orbital in the Pb atom have the influence of bonding charges. Cone super cell possess same behavior in charge distribution as bucky ball due to more or less equal number of atoms in both super cells even they have different geometry.

Electronic properties: The Density of States (DOS) of different PbO super cells will give the insight for the electronic properties of different super cell. Figure 2a-d shows the density of states of hexagonal sheet, tubular, bucky ball and cone structures of PbO structures.

For hexagonal sheet, the DOS profile shows that there is a peak with the magnitude of nearly 38 eV is seen in the conduction band whereas in the valance band the maximum peak is observed

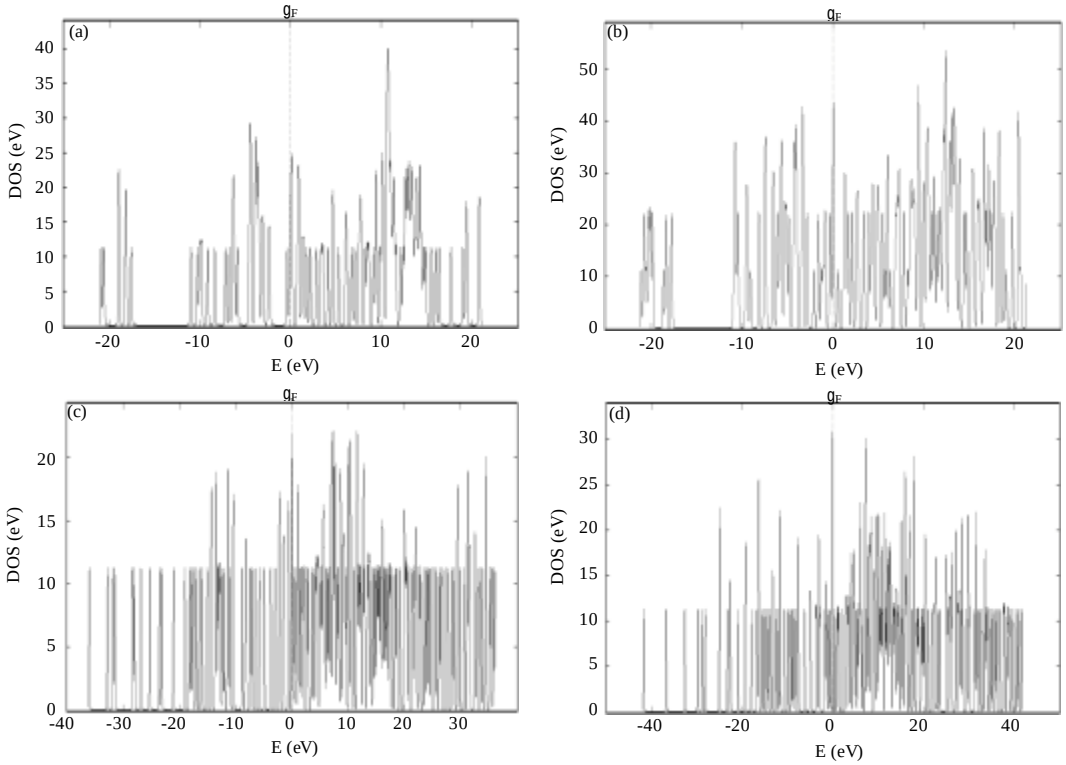

Fig. 2(a-d): Variation in Density of States (DOS) of PbO, (a) Hexagonal sheet, (b) Tubular, (c) Bucky ball and (d) Cone

around 30 eV. The Fermi level energy is calculated for this structure as -2.847 eV. The s orbital of Pb and O contributes much in the acceptor level. However, p orbitals of both Pb and O dominate in acceptor and donor levels. The d orbital of Pb contributes more density in the donor level. The addition of p and d orbitals gives rise to the energy of about 38 eV in the donor level. A broad gap is observed in the acceptor level of about 7 eV due to the sigma bonding of s orbitals in Pb and O. While analyzing the tubular DOS profile, the Fermi energy is about -3.508 eV. The contribution of s orbital lies almost in the acceptor level. The p orbital of Pb influences both acceptor and donor level. The maximum peak value is observed for this super cell which lies in the donor level of about 50 eV due to the fusion of p and d orbitals of Pb. As in hexagonal sheet DOS profile, a broad gap is observed in the acceptor level of about 7 eV. A prominent peak is observed near the Fermi level shows that allowed states are present near the Fermi level. In the case of bucky ball clumsy of states are observed on both acceptor and donor level. Compared to acceptor level, the donor level has more states and more prominent peaks. The Fermi energy level observed for this level is about -2.3145 eV. The s orbital of O constitutes an acceptor level state which lies between -40-30 eV above the Fermi level. A prominent peak is observed near the Fermi level of about 20 eV. There is no wide gap in the energy is observed in this type of super cell. While p and d orbital constraints themselves within the donor level. In the cone DOS profile, there are not much clumsy of states compared to bucky ball even they have almost same number of atoms. This may due to its geometry of the structure. The Fermi energy for this super cell observed is about -3.1131 eV. A prominent peak with density magnitude of 21 eV is observed near the Fermi level due to p orbital of Pb. When p and d orbital combines the prominent peak value is raised and it is shifted towards the donor level. Almost

all the DOS for this super cell are having an equal energy value of 12 eV. Among the four PbO super cell with different number of atoms, hexagonal sheet and tubular have a greater gap in the acceptor level, whereas the other two structures do not possess that much gap. The structure with wide energy gap is chemically inert whereas the structure with fewer gaps is highly reactive.

CONCLUSION

The realistic possible structures of PbO super cells were constructed and optimized using density functional theory. From the results, when there is increase in the number of atoms in the super cell it leads to the increase in the stability which is discussed in terms of total energy. The bonding capability and electronic configurations are analyzed using Mulliken population analysis. The electronic properties of different super cells are highlighted using density of states. In all the PbO super cells, the contribution to the electronic properties is due to s and p orbitals of both Pb and O atoms. However, the d orbital of Pb atom influences a small amount which gives rise to the energy value in DOS. The reported results of PbO super cells will help the experimentalists to synthesis a new material with improved electronic properties which will well suit for the engineering applications.

REFERENCES

Braunstein, P., C. Graiff, X. Morise and A. Tiripicchio, 1997. Carbonyl clusters with a capping methylidyne phosphonate ligand crystal structure of $[CO_3(CO)_9\{\eta^1\text{-}\mu_3\text{-}[CP(O)(Oet)_2]\}]$. J. Organometallic Chem., 541: 417-422.

Burnside, S., S. Winkel, K. Brooks, V. Shklover and M. Gra *et al.*, 2000. Deposition and characterization of screen-printed porous multi-layer thick film structures from semiconducting and conducting nanomaterials for use in photovoltaic devices. J. Mater. Sci.: Mater. Electron., 11: 355-362.

Chen, K.C., C.W. Wang, Y.I. Lee and H.G. Liu, 2011. Nanoplates and nanostars of â-PbO formed at the air/water interface. Colloids Surf. A: Physicochem. Eng. Aspects, 373: 124-129.

Cruz, M., L. Hernan, J. Morales and L. Sanchez, 2002. Spray pyrolysis as a method for preparing PbO coatings amenable to use in lead-acid batteries. J. Power Sour., 108: 35-40.

Ding, X., D. Zeng and C. Xie, 2010. Controlled growth of SnO_2 nanorods clusters via Zn doping and its influence on gas-sensing properties. Sensors Actuators B: Chem., 149: 336-344.

Gonzalez-Garcia, J., V. Saez, J. Iniesta, V. Montiel and A. Aldaz, 2002. Electrodeposition of PbO_2 on glassy carbon electrodes: Influence of ultrasound power. Electrochem. Commun., 4: 370-373.

Gonze, X., J.M. Beuken, R. Caracas, F. Detraux and M. Fuchs *et al.*, 2002. First-principles computation of material properties: The ABINIT software project. Comput. Mater. Sci., 25: 478-492.

Gupta, S.K., A. Joshi and M. Kaur, 2010. Development of gas sensors using ZnO nanostructures. J. Chem. Sci., 122: 57-62.

Haddadian, H., A. Aslani and A. Morsali, 2009. Syntheses of PbO nano-powders using new nano-structured lead (II) coordination polymers. Inorg. Chim. Acta, 362: 1805-1809.

Hu, P. and W. Dai, 2012. Computer simulation and density functional theory study on relationship between structure of amino acid and inhibition performance. Mater. Res. Innov., 16: 67-72.

Hussain, N.S., Y.P. Reddy and S. Buddhudu, 2002. Luminescence properties of Tb^{3+}-doped PbO-Bi_2O_3-GeO_2 glasses. Mater. Lett., 53: 25-29.

Janssens, E., S. Neukermans and P. Lievens, 2004. Shells of electrons in metal doped simple metal clusters. Curr. Opin. Solid State Mater. Sci., 8: 185-193.

Jia, B. and L. Gao, 2006. Synthesis and characterization of single crystalline PbO nanorods via a facile hydrothermal method. Mater. Chem. Phys., 100: 351-354.

Li, S., W. Yang, M. Chen, J. Gao, J. Kang and Y. Qi, 2005. Preparation of PbO nanoparticles by microwave irradiation and their application to Pb (II)-selective electrode based on cellulose acetate. Mater. Chem. Phys., 90: 262-269.

Liu, H., X. Zou, C. Wang, J. Yan and W. Duan, 2012. Structural transition of large lead monoxide clusters. Comput. Theor. Chem., 983: 61-64.

Perdew, J.P., K. Burke and M. Ernzerhof, 1996. Generalized gradient approximation made simple. Phys. Rev. Lett., 77: 3865-3868.

Plucinski, K.J., W. Gruhn, J. Wasylak, J. Ebothe, D. Dorosz, J. Kucharski and I.V. Kityk, 2003. Luminescence of the Yb-doped PbO-Bi_2O_3-Ga_2O_3-BaO glasses. Optical Mater., 22: 13-19.

Rezaei, B., 2006. Effects of casting temperature of Pb-Sb-Sn grid alloy on the polarization potential of oxygen evolution of lead acid batteries. Russ. J. Electrochem., 42: 350-354.

Rochliadi, A. and R. De Marco, 2002. Synergistic effects of novel battery manufacturing processes for lead-acid batteries. Part I: Charge/discharge cycling of batteries. J. Applied Electrochem., 32: 1039-1042.

Romantsova, I.V., Z.A. Mikhaleva and A.G. Tkachev, 2013. Sol-gel synthesis and investigation of metal-oxide catalysts for the preparation of carbon nanomaterials. Glass Phys. Chem., 39: 89-93.

Sajjadi, A., M.K. Yau, F. Saba, F Beech and I.W. Boyd, 1992. Laser ablation deposition of PbO/BiPbSrCaCuO. Applied Surf. Sci., 54: 154-159.

Sergeev-Cherenkov, A.N., M.N. Antipina, T.V. Yurova, A.A. Rakhnyanskaya and R.V. Gainutdinov *et al.*, 2004. Low-dimensional hybrid organic-inorganic nanostructures via planar DNA-amphiphilic polycation complexes. Surf. Sci., 566: 659-663.

Srivastava, J.K., P. Pandey, V.N. Mishra and R. Dwivedi, 2011. Structural and micro structural studies of PbO-doped SnO_2 sensor for detection of methanol, propanol and acetone. J. Nat. Gas Chem., 20: 179-183.

Suffredini, H.B., G.R. Salazar-Banda and L.A. Avaca, 2007. Enhanced ethanol oxidation on PbO_x-containing electrode materials for fuel cell applications. J. Power Sour., 171: 355-362.

Walsh, A. and G.W. Watson, 2005. The origin of the stereochemically active Pb (II) lone pair: DFT calculations on PbO and PbS. J. Solid State Chem., 178: 1422-1428.

Wiechert, D.U., S.P Grabowski and M. Simon, 2005. Raman spectroscopic investigation of evaporated PbO layers. Thin Solid Films, 484: 73-82.

Wu, J., D. Xiao, J. Zhu, J. Zhu and J. Tan, 2008. Effect of the PbO_x thickness on the microstructure and electrical properties of PLT thin films prepared by RF magnetron sputtering. Surf. Coatings Technol., 202: 2080-2084.

Wu, Z.J., 2003. Theoretical study on PbS, PbO and their anions. Chem. Phys. Lett., 370: 39-43.

Yin, Z., B. Wang, G. Chen and M. Zhan, 2011. One-dimensional 8-hydroxyquinoline metal complex nanomaterials: Synthesis, optoelectronic properties and applications. J. Mater. Sci., 46: 2397-2409.

Zeng, S., Y. Liang, H. Lu, L. Wang and X.Q. Dinh *et al.*, 2012. Synthesis of symmetrical hexagonal-shape PbO nanosheets using gold nanoparticles. Mater. Lett., 67: 74-77.

Zhu, C., Z. Yong, Y. Chentao and Y. Bangchao, 2005. PbO volatilization and annealing conditions investigation of Pb $(Zr_{0.52}Ti_{0.48})O_3$ thin films fabricated by sol-gel method. Mater. Sci. Eng. B Solid-State Mat. Adv. Technol., 123: 143-148.