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Electronic and Optical Studies of PbO with Oxygen Defect: A DFT Approach.

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ABSTRACT

The GGA exchange correlation with PBE functional has been taken to analyze PbO with and without oxygen defect. It was observed the structural stability and the density of states in the PbO super cell with oxygen defects -33537.19eV and 5.70eV. The HOMO-LUMO level of PbO was observed in DFT method, while oxygen defects in the super cell the energy level was reduced simultaneously -3.68 eV and -3.11 eV.
Keywords: PbO super cell; DFT; band structure; DOS; optical properties; HOMO-LUMO

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INTRODUCTION

The synthesis of PbO nanomaterial is an important research in various scientific and industrial fields due to their physical and chemical properties and also their potential application. Structure, Electrical, Optical properties of PbO nanoparticles depend on their sizes, shapes, and surface conditions. Lead dioxide is used as anode material in electrochemistry.Beta-PbO_2 is more attractive for this purpose than the alpha form because it has relatively low resistivity, good corrosion resistance even in low-pH medium, and a high overvoltage for the evolution of oxygen in sulfuric acid and nitric acid based electrolytes. It is mainly used as raw material in making lead glass for electronic elements, optical glass etc, and also used in industries such as antirust paint, and ceramics store battery.

The first-principles calculation is guaranteed by the physics theory [4]. The excess of PbO and oxygen vacancies act as pinning centers and have a strong pinning effect on the domains. When the poling voltage is not large enough, part of the domains can overcome the force of the pinning, and abnormal ferroelectric and C–V properties were observed [1].Toyobo developed the high performance of PbO fiber and also have a high tensile strength and thermal stability [2].

Ab initio calculation absorbs the oxygen vacancy affect the structure of the domain wall but not affect the thickness of the wall, it will broadened the domain wall and to study the both perfect and defective domain wall[3].DFT is a study of electronic ground state structure, in terms of electron density distribution. It is decided to optimize the PbO super cell with and without oxygen vacancy using Density Functional Theory (DFT) and to absorb the structural, electronic and optical properties of super cell by using DFT [4]. The present work studies and reports the different parameters such as Electronic structure, Density of States, Optical Property, HOMO and LUMO of the PbO cluster.

Computational Details

The different parameters are calculated and studied with the help of DFT implemented in SIESTA package. Generalize Gradient Approximation GGA exchange correlation is used with PBE as functional. The basis set is completely optimized the PbO cluster and studied all the parameters. Usually in DFT studies, the exchange correlation functional includes both the parameters namely the correlation of electrons and the exchange energy [5]. Density of states (DOS) spectrum and HOMO-LUMO gaps were calculated with SIESTA package [6]. The energy convergence is achieved in the order of $10-5eV$ in the present study.

RESULTS AND DISCUSSION

Structures of PbO, 1PbO, 2PbO and 3PbO for 36 atoms

The ground state energy of PbO cluster can be calculated by using DFT under basis set. Total energy of exciting structure of PbO, 1PbO, 2PbO, 3Pbo tabulated in table 1.The total energy of PbO cluster is -34410.12462eV. Electrostatic energy is used for to measure the potential energy in the cluster with and without of oxygen. Entropy is used to measure disorder term in the super cell, whether the process is reversible so it will be decreasing the entropy term. The removal of one oxygen (1PbO) from the cluster the total energy will be reduced -33537.19069 eV. Further removal of oxygen (2Pbo, 3Pbo) in the cluster the energy will be -33100.96844ev and -32664.84567ev. Due to defects of oxygen, the cluster position will be change so the kinetic energy will be reduced and also exchange correlation, electrostatic energy and entropy term will be reduced. Due to decrease of energy the stability of the cluster is decreased.

Band Structure of PbO, 1PbO, 2PbO and 3PbO

From the figure it is seen that all the structures have direct band gap. Fig 2(a) shows the band structure of pure PbO of 36 atoms. The band gap was observed as 2.37ev and is smaller than the experimental value. The reason is that the density functional theory method may usually underestimate the band gap because of the well-known problem in GGA approximation. It can optimize the electronic structure of with and without of oxygen in the cluster. Ionization potential (IP) and electron affinity (EA) gives clear information about the electronic properties of (PbO) clusters. The EA is an important parameter for the determination of chemically reactive substance as in the case of chemical sensors [7]. Removal of one oxygen atom from the

super cell changes valance band states-Fig2 (b). It will be overlapped and the band gap becomes narrowing. The band gap is observed as 5.70ev. If there is some dispersion in the conduction band due to the defects in super cell. The band gap observed for this structure is 4.60eV. Fig 2(c) shows two oxygen removed from PbO cluster. In this band structure, more number of oxygen is removed in the super cell, dispersion occurs in conduction band. However, some localized states are raised and narrowing the band gap further which has the value 4.79EeV. Further removal of O atom from the super cell, results more dispersion in the conduction band. The valance band has more localized states due the oxygen vacancy which further reduces the band gap. Removal of oxygen from the super cell, it will change the property of material. So the band gap will be changes due to the defects in the super cell.

Density of States

Normally in PbO clusters, the DOS arises due to 3d states of Pb and 2p states of O. For pure PbO super cell shown in Fig 3(a), only one major peak are observed below the Fermi level is in the range -25eV to 0eV with highest number of DOS 3500 eV. A strong peak is also observed above the Fermi level indicates that pure PbO super cell is having both valence and conduction band states equal. The creation of oxygen vacancy in the cluster the electronic structure and DOS will be affected. The presence of oxygen vacancy in the cluster it will reduce the Fermi level energy and both the band edges will be overlapped Fig 3(b). The density of state was reduced from 3500 to 250eV. So the energy region in the donor level increases. Fig 3(c) shows the DOS spectrum of PbO clusters with two oxygen vacancies. This results the increase in the donor level. The same number of states remains when one more oxygen atom is removed - Fig 3(d). Hence it is clear from this, when oxygen is removed from the PbO super cell form O vacancy site results raise in the donor level states. These results may leads to the formation of F centers.

Optical property

From the figure it is seen that the optical property of PbO super cell. The optical response of the dielectric function (DF) was computed employing the Generalize Gradient (GGA) approximation by the augmented plane wave. Red shift shows the maximum absorption of peak in pure PbO super cell. If there is an oxygen defects in the super cell the blue shift will occur, electromagnetic radiation move towards in a gravitational field [8]. Further removal of oxygen in the super cell the peak will be shifted and dielectric function is move towards higher wavelength region.

Electron density of HOMO and LUMO

From the figure shows the electronic structure of HOMO and LUMO energy level. In pure PbO super cell, the HOMO and LUMO energy level are -9.36 eV and 1.44 eV. The binding energy was large in between the HOMO-LUMO level, so that the energy level was reduced as shown in the given table [9]. The removal of atom from the crystal structure depends on the strength of the electronic interactions within the lattice [10]. Further removal of oxygen in the super cell, the Fermi energy level, band gap energy was reduced [11].

Table 1: Total Energy of exciting structure of PbO, 1PbO, 2PbO, 3PbO

System Name	Exchange Correlation (eV)	Kinetic Energy(eV)	Electrostatic Energy (eV)	Entropy-Term	Total energy(eV)
pbo	-21760.32245	10532.28675	-23182.08892	0	-34410.12462
1pbo	-21560.29259	9926.96052	-21903.85861	-0.00001	-33537.19069
2pbo	-21460.26959	9624.23146	-21264.93025	-0.00006	-33100.96844
3pbo	-21360.45732	9322.3602	-20626.74823	-0.00031	-32664.84567

Table 2: Band gap energy of PbO, 1PbO, 2PbO, 3PbO

System Name	Chemical potential(eV)	HOMO value(eV)	LUMO Value(eV)	Fermi energy(eV)	Band gap(eV)
pbo	-4.112586	-9.36E-01	1.44E+00	-4.11E+00	2.37E+00
1pbo	-3.390533	-3.68E+00	-3.11E+00	-3.39E+00	5.70E-01
2pbo	-3.465015	-2.74E-01	1.86E-01	-3.47E+00	4.60E-01
3pbo	-3.448788	-1.78E-01	3.01E-01	-3.45E+00	4.79E-01
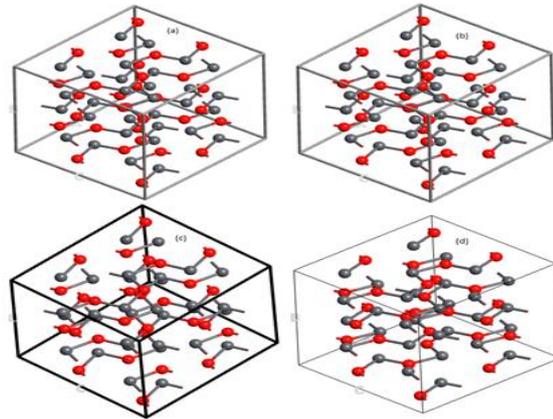
Figure 1: Optimized structures for a) PbO b) 1PbO c) 2PbO d) 3PbO
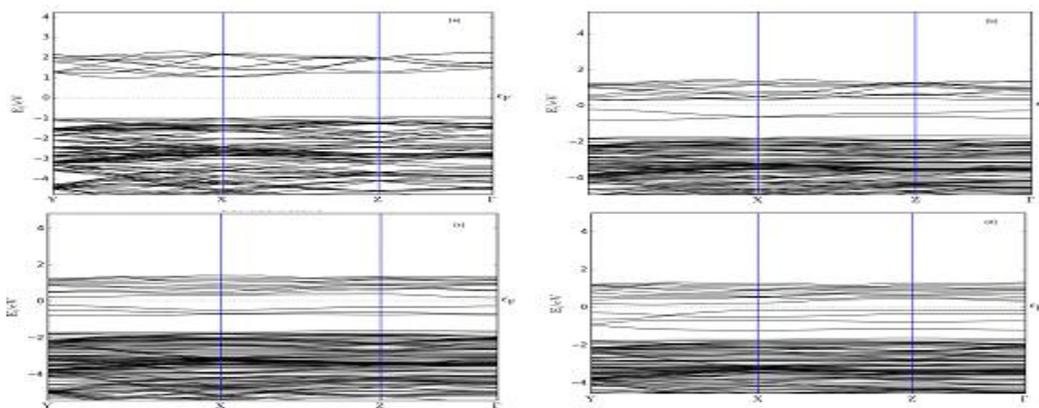
**Figure 2: Band structure of (a) PbO, (b) 1PbO, (c) 2PbO and (d) 3PbO**
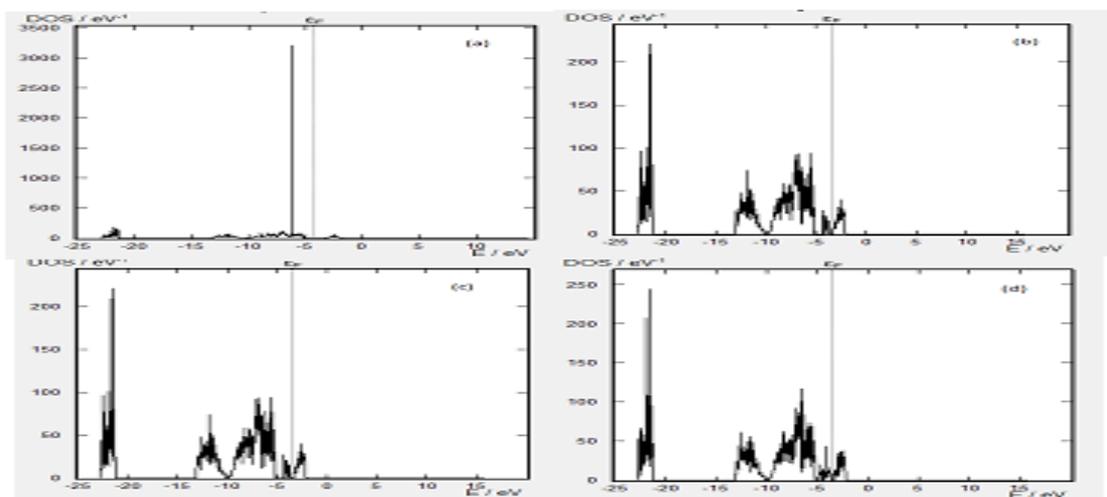
**Figure 3: Density of States (a) PbO, (b) 1PbO, (c) 2PbO and (d) 3PbO**
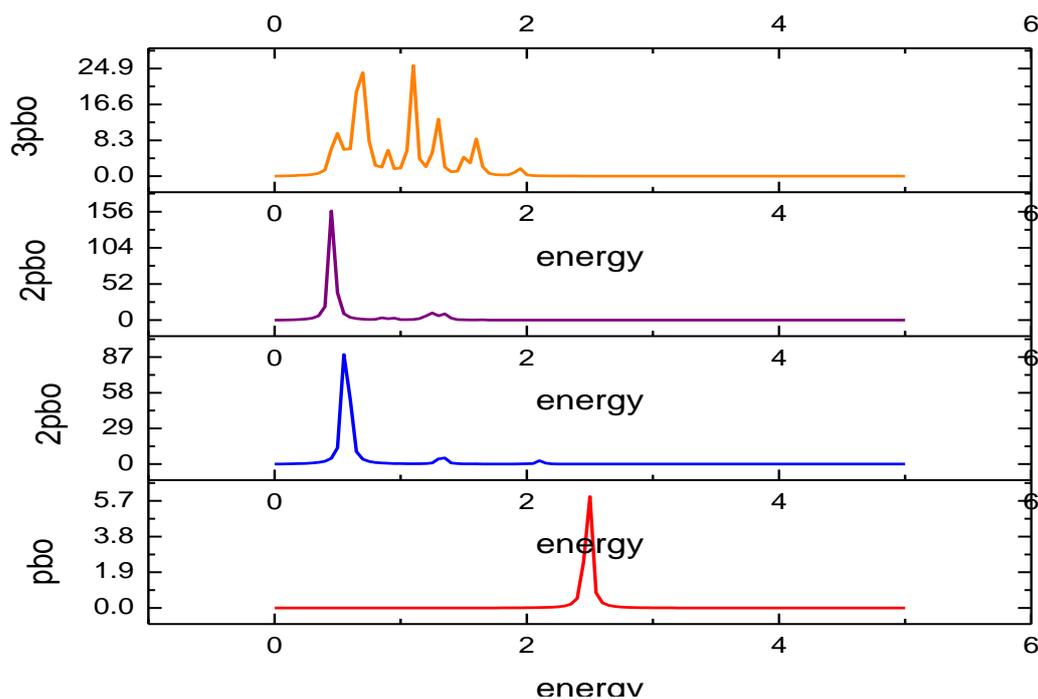
**Figure 4: optical property (a) PbO, (b) 1PbO, (c) 2PbO and (d) 3PbO**
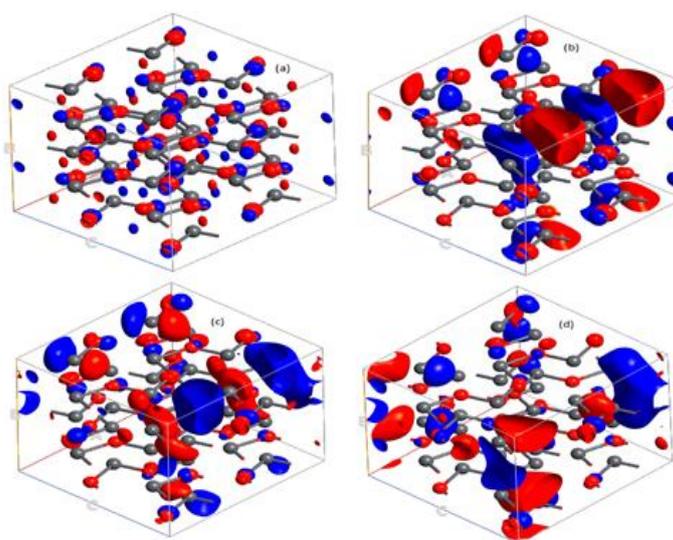
Figure 5: HOMO-LUMO of (a) PbO, (b) 1PbO, (c) 2PbO and (d) 3PbO

CONCLUSION

PbO can be completely optimized in DFT with the help of SIESTA package. The band structure analysis shows the removal of oxygen or vacancy of oxygen in the super cell increases more localized states in the conduction band which tends to decrease band gap. The density of states (DOS) spectrum reveals that the donor levels are increased when the super cell becomes oxygen deficient. The HOMO-LUMO gap is depends on the position of the element in the cluster.

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