



Research Journal of Pharmaceutical, Biological and Chemical Sciences

DFT Studies of the Oxygen Vacancy in MgO Super Cell.

R Ayyappa¹, S Sriram², S Nisatharaju¹, and D Balamurugan*²

¹Centre for Nanotechnology & Advanced Biomaterial (CeNTAB), School of Electrical and Electronics Engineering, SASTRA University, Tirumalaisamudram, Thanjavur 613401, India

²School of Electrical and Electronics Engineering, SASTRA University, Tirumalaisamudram, Thanjavur 613401, India

ABSTRACT

MgO super cell with and without oxygen defects have been constructed. The GGA exchange correlation with PBE functional has been taken to analyse its structural, electrical and optical properties. It was observed that the structural stability is decreased with increasing the oxygen vacancy. The density of states (DOS) studies shows the acceptor levels are increased when the super cell becomes oxygen deficient. The band structure analysis shows the removal of oxygen or oxygen defect in the super cell tends to decrease the band gap. The calculated absorption coefficient values of the super cell decreases when the O vacancies are increased.

Keywords: MgO supercell, DFT, optical properties, band structure, DOS

**Corresponding author*



INTRODUCTION

Among the various intrinsic defects of MgO the oxygen vacancy at the surface has received particular attention both from experimentalists and theoreticians because it is a relatively common defect which has interesting properties in spite of its simplicity. According to the number of electrons trapped in the vacancy (2, 1, or 0) this defect is called F_s , F_s^+ or F_s^{2+} center, F standing for Farbe, the German word for color, because of its optical activity, and the s subscript recalling its location at the surface. First-principles computational studies on metal oxide surfaces are best tool for tailoring new kind of material effectively [1, 2]. In particular, defected metal oxide surface analysis such as voids or substitutional atoms as impurities at interstitial positions will change the entire behaviour of the surface which leads to electronic structure adjustment, structural distorted and some changes in their physiochemical properties [3]. Oxygen vacancies on metal oxide surfaces have been one of the subjects of different theoretical investigations [4]. Due to oxygen vacancies in metal oxides, some of its characteristics such as variation in total energy, change in Fermi level, density of states in valance band distortion and reduction in band gap may occur. [5]

MgO is one of the simplest metal oxide with rock salt cubic structure [6], having wider band gap of 7.8eV [7]. It is used in the fields of refractory [8], coating materials [9] substrates and catalysts [10]. Bulk MgO could be very efficient substrate for growing thin films. Simple clusters with small number of atoms (super cell) will cause substantial deviations of physical and chemical properties with molecules and bulk phase. Hence it decided to investigate on MgO supercell [11] with and without oxygen vacancies using Density functional theory (DFT). DFT is one of the widely used theories to study the electronic ground state structure, in terms of electronic density distributions [12]. In this present study MgO super cell with 36 atoms has been constructed in pure (MgO) and with oxygen vacancies MgO@Vo1, MgO@Vo2 and MgO@Vo3 to study its structural, electronic and optical properties using density functional theory.

Computational Details

Full geometry optimization of MgO super cell of pure and oxygen deficient forms is performed using density functional theory implemented in SIESTA [13,14] package. Generalize Gradient Approximation GGA [15] exchange correlation is used with PBE [16] as functional. Double zeta basis type has been used for Mg and O atoms. The convergence criteria for self consistent field calculation [17] are 10^{-5} on the total energy. For band structure calculation $3 \times 3 \times 2$ monkhorst pack grid was used to sample the brillouine zone [18]. Meshcut off for the SCF calculation [19] was set to 140 Ry. The optical excitation calculation is performed within the energy range of 0 to 5 hartrees with 0.02eV broadening value. For optical calculation $1 \times 1 \times 1$ optical mesh is used with 0.02 eV optical broadening.

RESULTS AND DISCUSSION

Structures of MgO, MgO@Vo1, MgO@Vo2 and MgO@Vo3 for 36 atoms

Fig. 1 shows the structures of MgO super cells used in this study. Table 1 shows the energy obtained for various MgO supercells. For pure MgO super cell, the energy obtained is -9669.839 eV. This is majorly due to Ion electron exchange. However, the removal of oxygen from the super cell (MgO@V_{o1}) makes a defect or oxygen vacancy which tends to decrease the stability of the structure. The calculated energy for this structure is -9215.23 eV. When two oxygen vacancies are created from the structure (MgO@V_{o2}), it becomes more unstable by increase in energy. Making of the supercell by more oxygen vacancies (MgO@V_{o3}) results that more F centers are formed and the cluster becomes more unstable. The energy obtained for MgO@VO2 and MgO@VO3 are -8760.14 eV and -8306.61 eV respectively.

Table 1: Total energy of Exciting Structure of MgO, MgO@Vo1, MgO@Vo2 and MgO@Vo3

Structure	Energy(eV)
MgO	-9669.83921
MgO@Vo1	-9215.23321
MgO@Vo2	-8760.14710
MgO@Vo3	-8306.61113

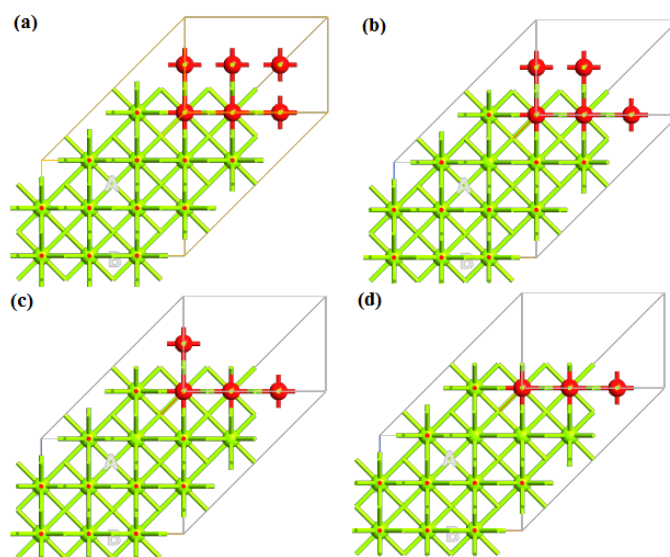


Figure 1: (a) Pure MgO optimized structure super cell (b) MgO@Vo1- one oxygen vacancy (c) MgO@Vo2- two oxygen vacancy, (d) MgO@Vo3 – three oxygen vacancy.

Band Structure of MgO, MgO@Vo1, MgO@Vo2 and MgO@Vo3

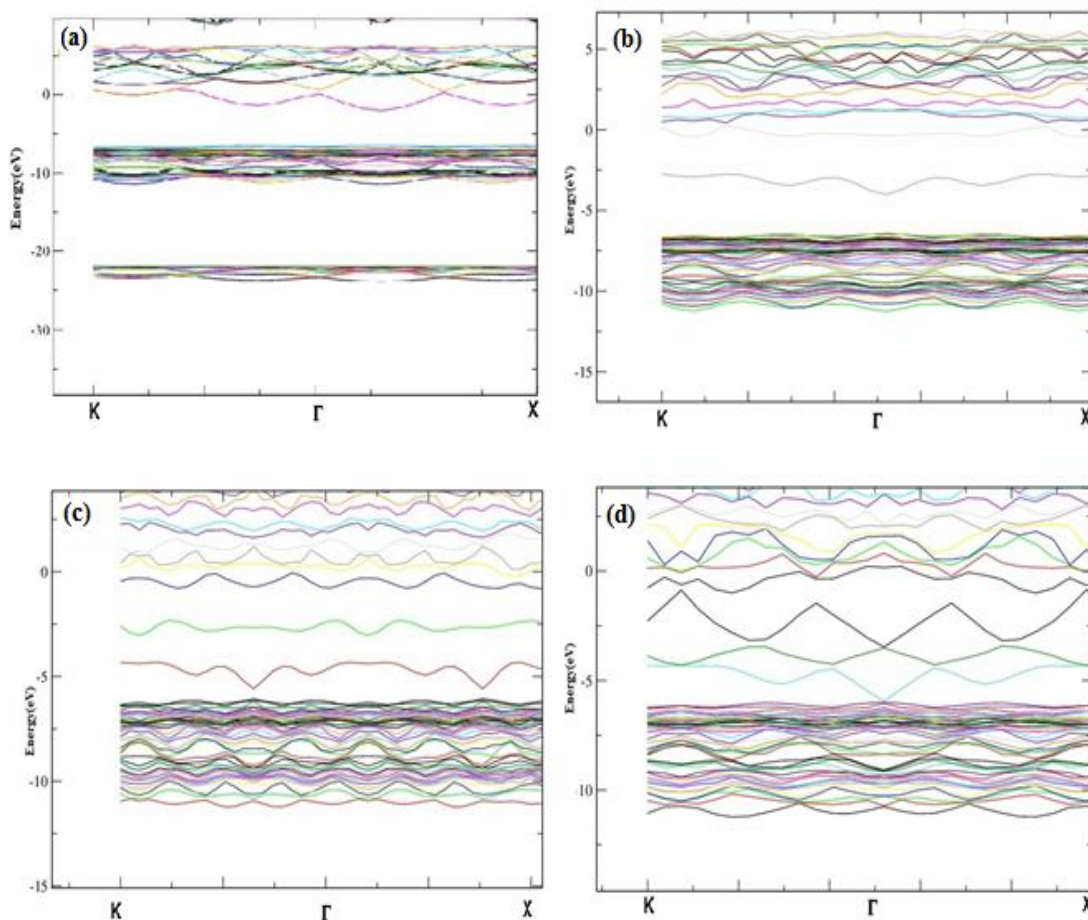


Figure 2: Band Structure diagram (a) MgO, (b) MgO@Vo1, (c) MgO@Vo2 and (d)MgO@Vo3

From the figure it is seen that all the structures have direct band gap. Fig 2(a) shows the band structure of pure MgO of 36 atoms. It is very clear from that the valance bands consists of O2p states. The O2s states are observed below the O2p states which are not interacted with O2p states. In the conduction band, due to Mg3d states are dominating and they are not very much dispersed. The band gap is observed as 5.21eV. Removal of one oxygen atom from the super cell changes valance band states-Fig 2(b). The O2p and O2s states are overlapped and the band gap becomes narrowing. A non interacting single energy state is hoisted due O2p in the valance band and results some dispersion of states in the conduction band due to the defect. The band gap observed for this structure is 4.84 eV. Fig 2(c) shows two oxygen removed MgO cluster. In this band structure, dispersion of Mg3d states in the conduction band occurs may due to the domination of increase in the number of O vacancies. However, some localised states are raised and narrowing the band gap further which has the value 3.94eV. 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.

Density of States

Normally in MgO clusters, the DOS arises due to 3d states of Mg and 2p states of O. For pure MgO super cell shown in Fig 3(a), two major peaks are observed below the Fermi level in the range -30eV to 0eV with highest number of states per eV. A strong peak is also observed above the Fermi level indicates that pure MgO super cell is having both valance and conduction band states equal. When removal of Oxygen - Fig 3(b) from the cluster influences the decrease in the number of states in the valance band and also in the conduction band. This increases the energy region in the acceptor level. Fig 3(c) shows the DOS spectrum of MgO clusters with two oxygen vacancies. This results the increase in the acceptor 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 MgO super cell form O vacancy site results raise in the acceptor level states. These results may leads to the formation of F centers.

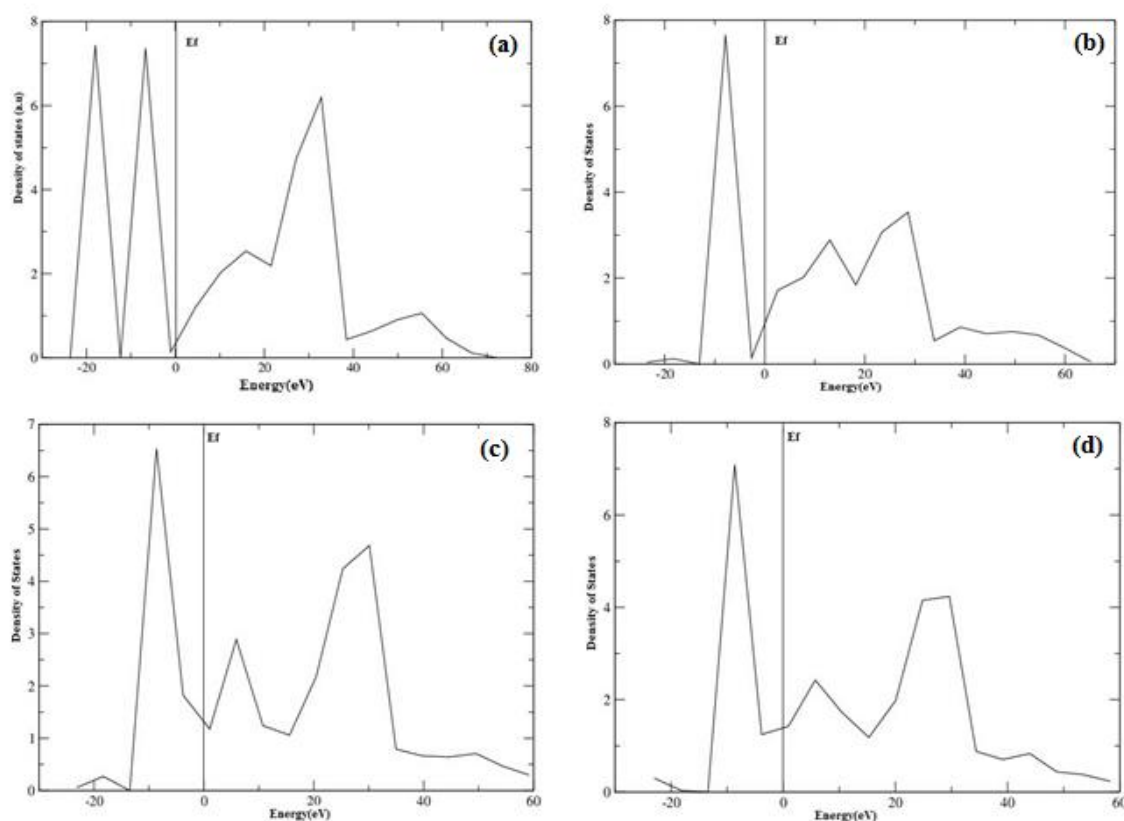


Figure 3: Density of States (a) MgO, (b)MgO@Vo1, (c) MgO@Vo2 and (d) MgO@Vo3

Optical property

Fig 4 and Fig 5 shows the imaginary and real part of dielectric constant of MgO, and oxygen removed MgO clusters. The imaginary part shows that the shift in the dielectric imaginary is towards higher wavelength region. This may due to the number increase in number of oxygen vacancies. The real part of dielectric shows the same trend.

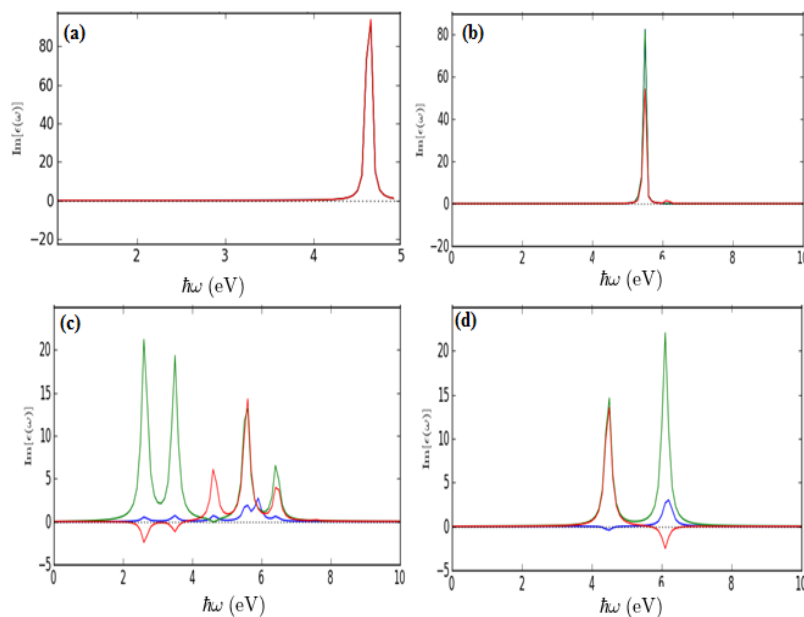


Figure 4: Dielectric Imaginary (a) MgO, (b)MgO@Vo1, (c) MgO@Vo2 and (d) MgO@Vo3

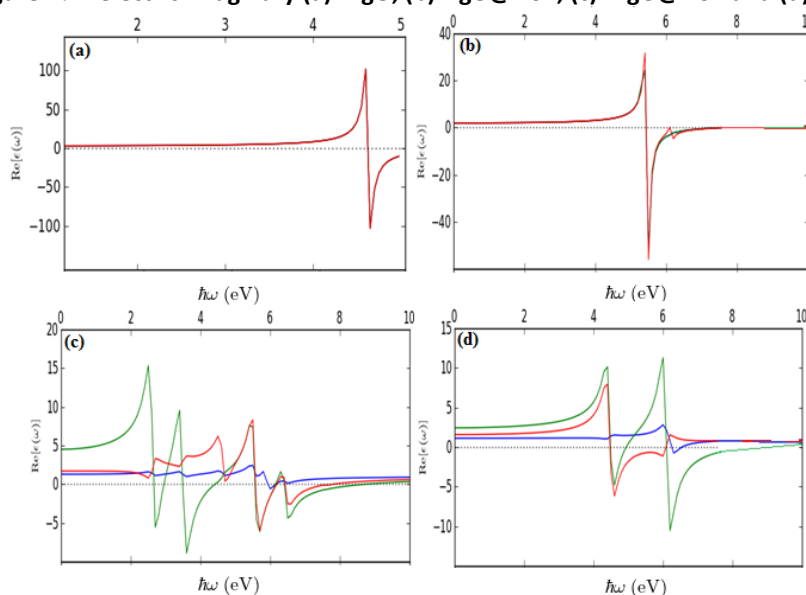


Figure 5: Dielectric Real (a) MgO, (b)MgO@Vo1, (c) MgO@Vo2 and (d) MgO@Vo3

CONCLUSION

MgO super cell with 36 atoms are constructed in pure MgO, MgO@Vo1, MgO@Vo2 and MgO@Vo3 oxygen removed forms to study about its structural, electronic and optical properties using density functional theory implemented in SIESTA package. The stability of the cluster is decreased when the oxygen vacancies are created. The density of states (DOS) spectrum reveals that the acceptor levels are increased when the super cell becomes oxygen deficient. The band structure analysis shows the removal of oxygen or vacancy of oxygen in the super cell increases more localised states in the conduction band which tends to decrease the

band gap. The band gap narrowing property is observed. From the optical properties, calculated absorption coefficient values of the clusters decreases when the O vacancies are created and the structures becomes more transparent tends to form the F centers. The reflectance spectra do not show any significant variance.

REFERENCES

- [1] S Krischok, P Stracke, O Hoff, V Kempter, YuF Zhukovskii, EA Kotomin. Surf Sci 2006; 600: 3815–3820.
- [2] Claudine Noguera, Fabio Finocchi and Jacek Goniakowski. J Phys Condens Matter 2004; 16: S2509–S2537.
- [3] Isao Tanaka, Fumiyasu Obu, Kazuyoshi Tatsumi, Masahiro Kunisu, Masanobu Nakano and Hirohiko Adachi. Mater Trans 2002;43(7):1426-1429.
- [4] S Picozzi, C Ma, Z Yang, R Bertacco, M Cantoni, A Cattoni, D Petti, S Brivio and F Ciccacci. Physical Review B 2007; 75: 094418.
- [5] E Castanier, C Noguera. Surf Sci 1996; 364: 1–16.
- [6] S Valeri, S Benedetti and P Luches. J Phys Condens Matter 2007;24:225002.
- [7] Jeffrey W. Bullard, Zhengkui Xu, Mohan Menon. J Crystal Growth 2001; 233 : 389–398.
- [8] Angeles G. De la Torre, Francisco Jose Valle, Antonio H. De Aza. J European Ceramic Soc 2006; 26: 2587–2592.
- [9] Ho-Jin Kweon, Sue Joo Kim, Dong Gon Park. J Power Sources 2000; 88: 255–261.
- [10] Li-Piin Sung, Stephanie Scierka, Mana Baghai-Anaraki, and Derek L. Ho, Mat. Res. Soc. Symp. Proc. Vol. Mater Res Soc 2003; 740: I5.4.1-I5.4.6.
- [11] GE GuiXian, JING Qun & LUO YouHua, Sci China Ser G-Phys Mech Astron, May 2009 ;52 : 734-741.
- [12] W Kohn, AD Becke, and RG Parr. J Phys Chem 1996; 100: 12974-12980.
- [13] José M. Soler, Emilio Artacho, Julian D. Gale, Alberto García, Javier Junquera, Pablo Ordejón, and Daniel Sánchez-Portal. J Phys Condens Matter 2002; 14: 2745-2779.
- [14] Lin Lin , Jianfeng Lu , Lexing Ying , Weinan E. J Compl Physics 2012;231: 4515–4529.
- [15] RO Jones. Eur Phys J D 1999;9: 81-84
- [16] Juliano B. Francisco, José Mario Martínez, Leandro Martínez. J Chem Physics 2004; 121: 10863-10878.
- [17] Zhang Shuai, Jiang Hua-Long, Wang Ping, Lu Cheng, Li Gen-Quan, and Zhang Ping. Chin Phys B 2013; 22: 123601.
- [18] V Ongun Özçelik and S Ciraci. J Phys Chem C 2013; 117:15327 – 15334.
- [19] Ravindra Shinde and Meenakshi Tayade, AIP Conf Proc 2013; 1512: 844-845.