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Electronic and optical studies of CaO with oxygen defects: A DFT approach

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ABSTRACT

CaO super cell with and without oxygen defects have been constructed. The Generalized Gradient Approximation (GGA) exchange correlation with PBE functional has been taken to analyze its structural, electrical and optical properties. It was observed that with the increase of oxygen vacancy decreases the stability. The density of states (DOS) reveals that the donor level was increased with increase of oxygen vacancy in the super cell. The band structure analysis shows that the removal of oxygen or oxygen defect in the super cell tends to decrease the band gap. The optical absorption coefficient values of super cell decreases with the increase of oxygen vacancies. The electronic properties are discussed in terms of HOMO-LUMO energy gap, ionization potential and electron affinity.

Keywords: Super cell; Density functional theory; Band structure; Density of state; HOMO-LUMO

INTRODUCTION

The light alkaline - earth oxides (AEOs) form a chemically interesting series of metal oxides. Calcium oxide is the heaviest one in this group of light AEO and considered to be a purely ionic solid. Knowledge of the electronic properties of AEO is essential due to their rapidly increasing technological importance for production of new materials [1]. Among the various intrinsic defects of CaO the oxygen vacancy at the surface has received particular attention both from experimentalists and theoreticians because it is a relatively common defects which has interesting properties in spite of its simplicity. Structural, electrical and optical properties of CaO nanoparticles depend on their sizes, shapes, and surface conditions. First-principles computational studies on metal oxide surfaces are best tool for tailoring new kind of material effectively [2, 3]. According to the number of electrons trapped in the vacancy (2, 1 or 0) this defect is called Fs, Fs^+ or Fs^{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. In particular, defected metal oxide surface analysis such as voids or substitution atoms as impurities are at interstitial positions will change the entire behavior of the surface which leads to electronic structure adjustment, structural distorted and some changes in their physiochemical properties [4]. Oxygen vacancies on alkali oxide surfaces have been one of the subjects for different theoretical investigations [5]. Due to oxygen vacancies in alkaline 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 [6].

AOE has wide applications in microelectronics and heterogeneous catalysis. They are also geophysical interest, MgO and CaO are present in significant in the lower mantle of the earth [7]. This compound exhibits properties typical of an insulator with a wide band gap of 7.7 eV [1] and also a semiconductor with a high dielectric constant of 11.8. Bulk CaO could be very efficient substrate for growing thin films [8]. Simple clusters have small number of atoms (super cell) which causes substantial deviations of physical and chemical properties with molecules and bulk phase. In the present work investigated about the properties of CaO super cell 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. In the present work, CaO super cell with 36 atoms has been constructed without oxygen vacancies (CaO) and with oxygen vacancies (CaO@VO1, CaO@VO2 and CaO@VO3) and to study its structural, electronic and optical properties using density functional theory.

MATERIALS AND METHODS

Computational Details

Full geometry optimization of CaO super cell of pure and oxygen deficient forms was performed using density functional theory implemented in SIESTA [9,10] package. Generalized Gradient Approximation (GGA) [11] exchange correlation is used with PBE [12] as functional. Double zeta basis type has been used for Ca and O atoms. The convergence criteria for self-consistent field calculation [13] are 10^{-5} on the total energy. For band structure calculation, 3 x 3 x 2 monk horst pack grid was used to sample the Brillouin zone [14]. Meshcut off for the SCF calculation [15] was set to 140 Ry. The optical excitation calculation is performed within the energy range of 0 to 5 hartrees with 0.02 eV broadening value. For optical calculation 1 x 1 x 1 optical mesh is used with 0.02 eV optical broadening.

RESULTS AND DISCUSSION

3.1. Structures of CaO, CaO@VO1, CaO@VO2 and CaO@VO3 for 36 atoms

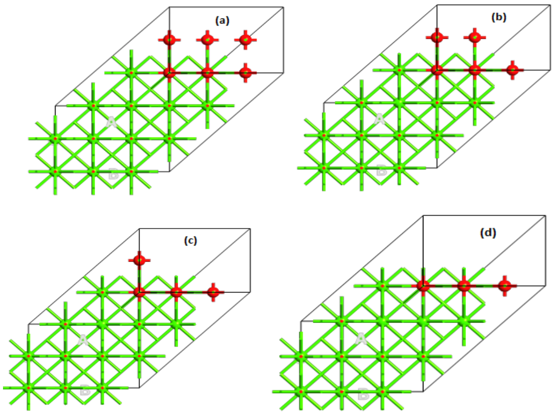

Figure 1. Optimized structures for (a) CaO (b)CaO@VO1 (c) CaO@VO2(d) CaO@VO3

Figure 1. shows the structures of CaO supercell which is used in this study. Table 1. shows the different energy values obtained for various CaO super cells. Without any oxygen defect in the CaO super cell obtained energy was -11536.941 eV. However, the removal of oxygen from the super cell (CaO@VO1) makes a defect or oxygen vacancy which tends to decrease the stability of the structure. The calculated energy for the removal oxygen structure was -11096.53764 eV. When two oxygen vacancies are created from the structure (CaO@VO2), it becomes more unstable by decrease in energy. Making the super cell by three oxygen vacancies (CaO@VO3) results that more F centers are formed and the cluster becomes more unstable. The energy obtained for CaO@VO2 and CaO@VO3 are -10656.1398 eV and -10215.76429 eV respectively. The ionizations potential (IP) and electron affinity (EA) provide a perception for the electronic properties of the nanoclusters [16]. The large value of EA is more suitable for gas sensing applications [17]. The electrostatic force that gives rise to the ionic bond is the electrical attraction existing between a Ca ion and an O ion. Chemical bonding results when the energy of two interacting atoms (or ions) is lowered. With the increasing defects of oxygen in the super cell, the cluster position will be altered and so the kinetic energy will decreases along with electrostatic energy and entropy [18].

Table 1. Total energy for exciting structure of CaO,CaO@VO1,CaO@VO2,CaO@VO3

System Name	Exchange correlation (eV)	Kinetic energy (eV)	Electrostatic energy (eV)	Entropy term	Total energy (eV)
CaO	-5330.19827	5724.58003	-11931.32314	0	-11536.94139
CaO@VO1	-5230.42365	5423.89402	-11290.00801	0	-11096.53764
CaO@VO2	-5130.72144	5123.63887	-10649.05724	0	-10656.1398
CaO@VO3	-5031.07549	4823.67911	-10008.36781	-0.0001	-10215.76429

3.2 Band structure of CaO, CaO@VO1, CaO@VO2 and CaO@VO3

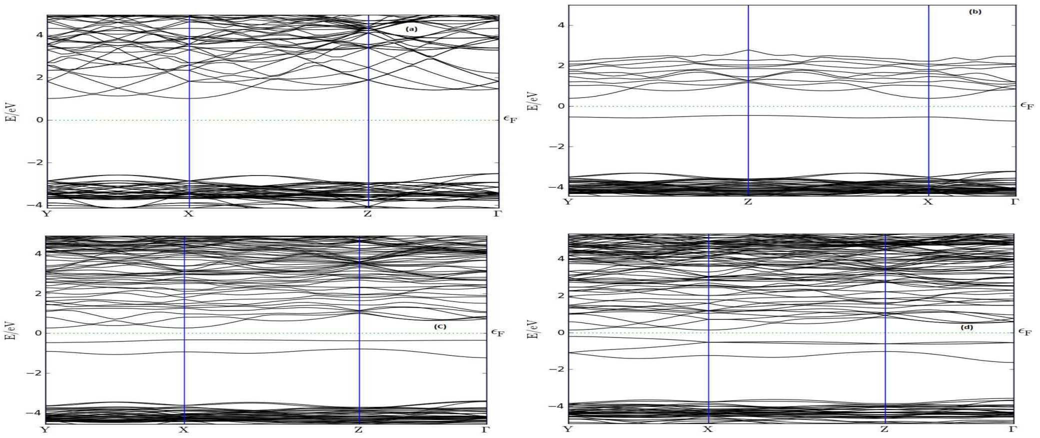

Figure 2. Band structure for (a) CaO (b)CaO@VO1 (c) CaO@VO2 (d) CaO@VO3

From the Figure 2. it is observed that all the structures are having indirect band gap. Figure 2 (a) shows the band structure of pure CaO which is having 36 atoms. The band gap was observed as 3.99 eV. Figure 2 (b) and (c) shows the removal of one and two oxygen atoms from the super cell changes valance band states, it will be dispersed and the band gap will be reduced. The band gap was observed as 3.99 eV. A non-interacting single energy state is hoisted 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 1.07 eV. Figure 2 (d) shows two oxygen atoms removed from CaO cluster. In this band structure, dispersion in the conduction band occurs due to the domination of increase in the number of oxygen vacancies in the cluster. The obtained band gap for this structure is 1.12 eV. One can see that removal of oxygen atoms leads to the formation of a filled defect state in the band gap. The calculations of total electron density also evidence the appearance of empty states close to the conduction band bottom which reduces the band gap.

3.3 Density of States

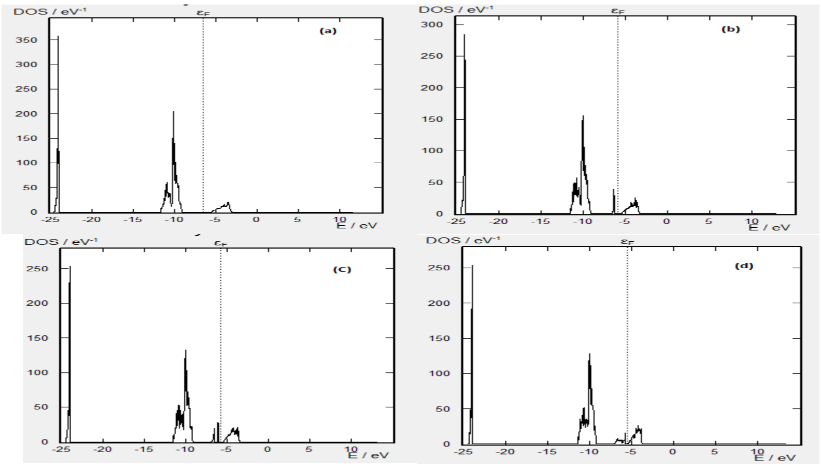

Figure 3. Density of States for (a) CaO (b)CaO@VO1 (c) CaO@VO2 (d) CaO@VO3

For pure CaO super cell shown in Figure 3 (a), two major peaks are observed below the Fermi level within the range of -25 eV to 0 eV. With removal of oxygen from the super cell (from Figure 3(b)) influences the number of states in both the valence and conduction band. The conduction band energy decreases from 360 eV to 280 eV. Figure 3 (c) shows the DOS spectrum of CaO clusters with two oxygen vacancies here the energy is decreased to 250 eV. The same number of states remains when one more oxygen atom is removed as shown in Figure 3 (d). It was observed that, when an oxygen atom is removed from the CaO super cell form oxygen vacancy site resulted raise in donor level states. These results may leads to the formation of F centers.

3.4. Optical studies

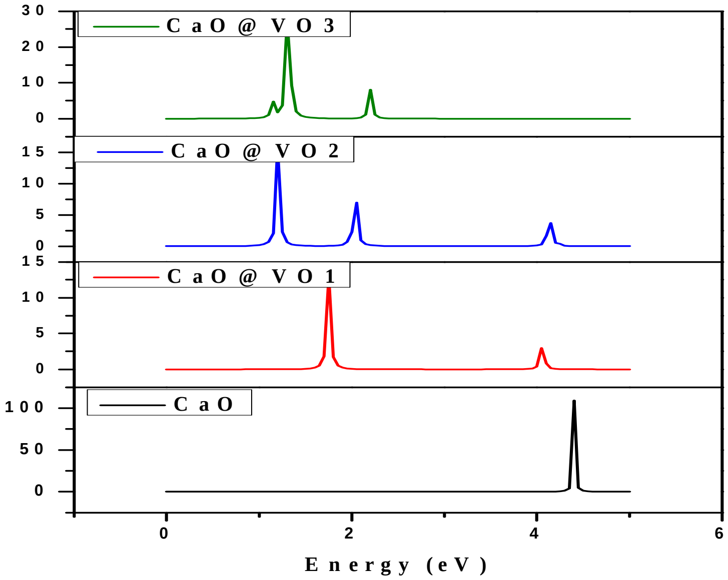

Figure 4. Optical spectra of CaO super cell (a) CaO (b)CaO@VO1 (c) CaO@VO2 (d) CaO@VO3

Figure 4. shows the optical spectra of CaO super without and with oxygen defects. The optical response of the dielectric function (DF), is computed employing the Generalize Gradient Approximation (GGA) by the augmented plane wave. Figure 4. shows the variation in dielectric function using spin-polarized calculations. Further removal of oxygen in the super cell the peak was shifted and dielectric function was shift towards higher wavelength region.

3.5 Electron density and HOMO and LUMO

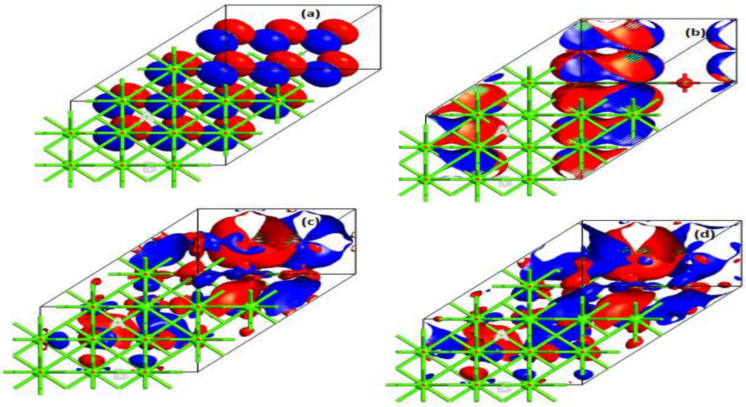

Figure 5. HOMO and LUMO for (a) CaO (b)CaO@VO1 (c) CaO@VO2 (d) CaO@VO3

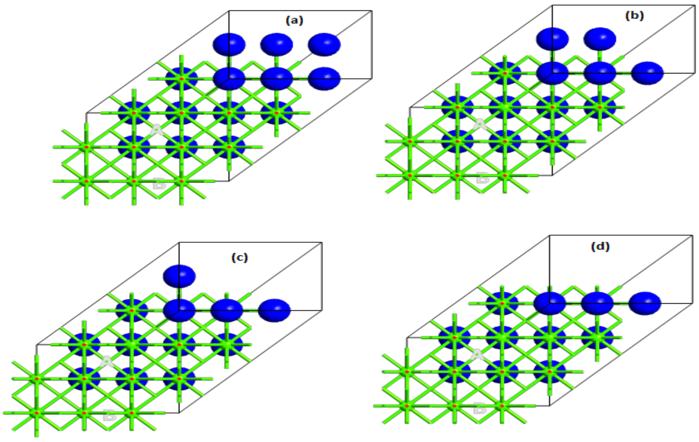

Figure 6. Electron density for (a)CaO (b)CaO@VO1 (c) CaO @VO2(d) CaO@VO3

Table 2. HOMO-LUMO energy for exciting structure of CaO,CaO@VO1, CaO@VO2, CaO@VO3

System name	Chemical potential (eV)	HOMO value (eV)	LUMO value (eV)	Fermienergy (eV)	Band gap (eV)
CaO	-6.450434	-8.98E+00	-4.99E+00	-6.45E+00	3.99E+00
CaO@VO1	-5.807875	-6.54E+00	-4.96E+00	-5.81E+00	1.58E+00
CaO@VO2	-5.657436	-6.01E+00	-4.94E+00	-5.66E+00	1.07E+00
CaO@VO3	-5.49829	-6.05E+00	-4.93E+00	-5.50E+00	1.12E+00

Figure 5. shows the HOMO-LUMO energy for (a) CaO (b) CaO@VO1 (c) CaO@VO2 (d) CaO@VO3. HOMO and LUMO energy is -8.98 eV and 4.99 eV respectively, presence of oxygen vacancies on the CaO surface modifies its electronic structure by generation of electronic states in the gap between the valence and conduction energy bands. The increase in number of atoms resulted that more number of molecular orbitals to overlap one another. Due to valence electrons of s and p orbitals of Ca and p orbitals of O, it changes the surface passivation of the cluster and results in decreased energy gap [19]. Defects with one electron in the cavity of the vacancy Fs reduce the band gap to 1.58 eV, and the electronic density is less localized than defects with two electrons which reduce the band gap to 1.07 eV. From the Table 2. We observed that removal of oxygen atoms from the super cell decreases the HOMO-LUMO energy level.

CONCLUSION

The oxygen deficiency defects in CaO were investigated using density functional theory implemented in SIESTA package. From band structure analysis results that stability of the cluster was decreases and band gap becomes narrower with the increase of oxygen vacancy in the super cell due to more localized states in the conduction band. From the density of states (DOS) spectrum points out, donor level is increases with increasing the oxygen vacancies. Moreover, the HOMO-LUMO energy levels were decreases as oxygen vacancies increases in super cell.

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