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Electronic and Optical Studies of CeO_2 with Oxygen Defect: A DFT Approach.

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ABSTRACT

Generalized gradient approximation (GGA) exchange correlation with PBE functional has been taken to analysis its structural, electrical and optical properties. It was observed the structural stability, density of states and HOMO and LUMO level of CeO_2 super cell with and without oxygen defects in density functional theory (DFT) method. The energy level was reduced because of decreasing oxygen in the super cell -21034.708 eV and -10215.76 eV.

Keywords: CeO_2 super cell, DFT, optical properties, band structure, DOS, HOMO-LUMO.

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INTRODUCTION

Ceria (CeO_2) has been extensively employed as an important component of automotive three-way catalysts (TWC) for reducing the exhaust populations. One of the most important groups of materials for heterogeneous catalysis is that of the metal oxides. Understanding the mechanisms of catalyzed reactions over metal oxide surfaces and the influence of different material characteristics on the performance of the catalyst is therefore of central importance for rational catalyst development. Cerium oxide (CeO_2) is commercially is important part both oil-refining catalyst and automotive exhaust gas converters [1]. Several supported and unsupported ceria-based mixed metal oxides have been investigated, the search for the second metal/metal oxide to improve both stability at high temperature and the chemical activity, by introducing oxygen vacancies. The enhanced capacity for storage and release of oxygen i.e., the oxygen mobility was proposed to be due to the presence of oxygen vacancies associated with terbium incorporation to ceria lattice. The Tb takes part in the catalyst defect generation and thereby oxygen vacancies are ceria host generating strain in the lattice. The structure, Electrical, Optical properties of CeO_2 depends on their size, shape and surface conditions. The first principles calculation is guaranteed by the physics theory. It can calculate the few hundreds of atom simultaneously and in easy manner.

Total-energy calculations have been performed using a plane-wave-based density functional theory. A CeO_2 super cell was used to low doping concentration case, where one oxygen atom is removed from a 36 atom 3 x 3 x 2super cell of pure CeO_2 shows the density of state (DOS) of CeO_2. The peak just below the Fermi level represents the localized f states, which are mainly on two Ce ions that are the nearest neighbor s on the oxygen vacancy. The gap between the O 2_p valence band edge and occupied f state is 1.4eV [2]. DFT is a study of electronic ground state structure, in terms of electron density distribution. It is described to optimize the CeO_2 super cell with and without oxygen vacancy using Density Functional Theory (DFT) and to absorb the structural, electrical and optical properties of super cell by using DFT.

Computational Details

Full geometry optimization of CeO_2 super cell of pure and oxygen deficient form is performed using density functional theory using SIESTA package. Generalized Gradient Approximation GGA exchange correlation is used with PBE as functional. Double zeta basis type has been used for Ce and O atoms. The convergence criteria of self-consistence field calculation are 10^{-5} on the total energy. For band structure calculation 3 x 3 x 2 monkhorst pack grid was used to simple the brilliance zone. Mesh cut of the SCF calculation was set to 140 Ry. The optical excitation calculation is performed with in the energy range of 0 to 5 hartees with 0.02eV broadening value. For optical calculation 1 x 1 x 1 optical mesh is used with .002eV optical broadening.

RESULTS AND DISCUSSION

Structures of CeO_2, CeO_2@Vo1,CeO_2@Vo2 and CeO_2@Vo3 for 36 atoms

Fig. 1 shows the structure of CeO_2 super cells used in this study. Table 1 shows the energy obtained for various CeO_2 super cells. The Exchange correlation is the interaction between electrons in the electronic structure. We attribute the improved calculation results to the convince of the direct method in implementing new exchange correlation [3]. The kinetic energy had a similar effect as a temperature, and it is believed that a higher ion kinetic energy also improves the surface diffusion of ad atoms [4]. For pure CeO_2 super cell, that energy obtained is-21034.70865 eV. This is majorly used to Ion electron exchange. However the removal of oxygen from the super cell (CeO_2@Vo1)makes a defect or oxygen vacancy which tends to decrease the stability of the structure. The calculated energy for this structure is -11096.53764 eV. When two oxygen vacancies are created from the structure (CeO_2@Vo2), it becomes more unstable by decreasing the energy level. Making of the super cell by more energy vacancy (CeO_2@Vo3) result the more F center is formed and the cluster becomes more unstable. The energy obtained for CeO_2@Vo2 and CeO_2@Vo2 are -10656.1398 eV and -10215.76429 eV respectively.

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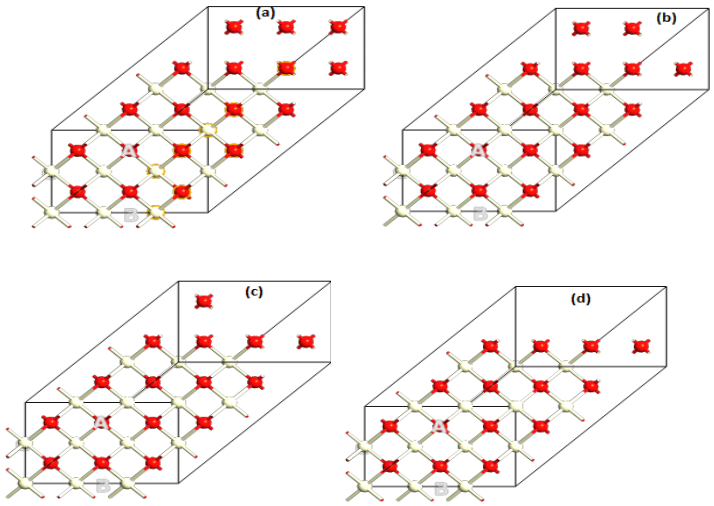

Figure 1: (a) Pure CeO_2 optimized structure super cell, (b) CeO_2@Vo1-one oxygen vacancy, (c) CeO_2@Vo2-two oxygen vacancy, (c) CeO_2@vo3-three oxygen vacancy

Band Structure of CeO_2, CeO_2@Vo1, CeO_2@Vo2 and CeO_2@Vo3

From the figure it is seen that all the structure have direct band gap. Fig 2(a) shows the direct band structure of pure CeO_2 of 36 atoms. Ce donates all its 6s and 5d valance electrons to the oxygen atoms, while the ground state of 4f orbital was established to be the mixed valance state of $4f^0$ and $4f^1v$ (v is ligand hole) configurations. This makes valance band top 0 2_p is character, with a contribution from 4f states. The lowest conduction band consists mainly of empty Ce5d starting at approximately 6 eV above the valance band edge [5]. Removal of one oxygen from the super cell changes valance band states-Fig 2(b). It will be overlapped and the band gap becomes narrowing. The band gap is observed as -5.80 eV. If there is some dispersion in the conduction band due to the defects in super cell. Fig 2(c) shows two oxygen removed from CeO_2 cluster. In the band structure, more number of oxygen is removed in the super cells, dispersion occurs conduction band. It may due to the domination of increasing in the number of oxygen vacancies. However, some localized states are raised and narrowing the band gap further which has the value -5.65 eV. Fig 2(d) further removal of oxygen from the super cell, resultant more dispersion in the conduction band. The valance band has more localized state due to the oxygen vacancy which further reduces the band gap -5.49 eV. Removal of oxygen from the super cell, it will change the property of material. So the band gap will be changed due to the defects in the super cell.

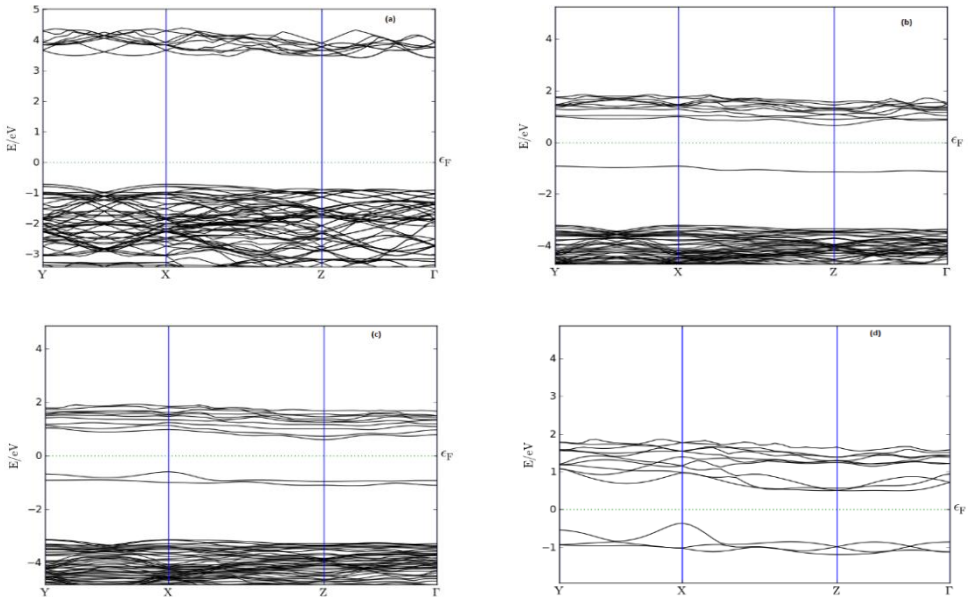

Figure 2: Band structure diagram (a) CeO_2, (b) CeO_2@Vo1, (C) CeO_2@Vo2, (d) CeO_2@Vo3

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Density of State

Normally in CeO_2 clusters, the DOS arises due to the 3d state of CeO_2 and 2p state of oxygen. For pure CeO_2 super cells shows in fig 3(a), the major peaks are observed below the Fermi level is in the range -14 eV to 0 eV with highest number of states per eV. A strong peak is also observed above the Fermi level indicates that that pure CeO_2 super cell is having both valance and conduction band states unequal. Fig 3(b) removal of oxygen from the cluster influences the decrease in the number stats in the valance band and also in the conduction band. This increases the energy region in the donor level. Fig 3(c) shows the DOS [6] spectrum of CeO_2 clusters with two oxygen vacancies. This results the increase the donor level. Fig 3(d) the same number of state remains two more oxygen atoms is removed. Hence it is clear from this, when oxygen removed from the CeO_2 super cell from oxygen vacancy site results raise in the donor level states. These results may leads to the formation of F center (Natural oxygen vacancy).

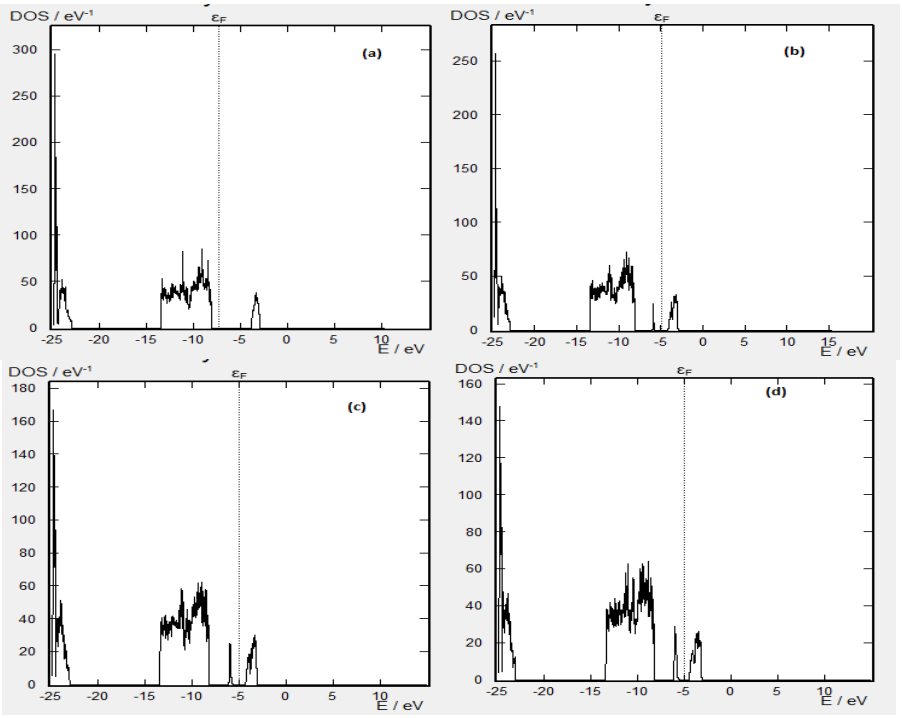

Figure 3: Density of States for (a) CeO_2, (b) CeO_2 @Vo1, (c) CeO_2@Vo2, (d) CeO_2@Vo3

Optical property

Fig. 4 shows a shift in the absorbance peaks as oxygen deficient increased in the CeO_2. This is because, CeO_2 is generally a p-type semiconductor and hence holes concentration increases as oxygen deficient increased. This can also be attributed in the reduction of electron concentration from 448 to 429. It also signifies an increase in energy band gap. In pure CeO_2 super cell major peak shift occur when the light move away from the observe materials. If there is oxygen defects in super cell the peak shift will occur move towards in a gravitational field. Further removal of oxygen in the super cell the deflected peak will be shifted and dielectric function move towards higher wavelength region [7].

Electron density and HOMO and LUMO

Electronic excitation is simulated by robust total-energy calculations for constrained states with atomic core holes or valence holes. The energy between HOMO and LUMO is Fermi energy level is determined by E_f. The ground state of defective ceria, the Ce-*f* majority band resides near the Fermi level. The surface structures and stabilities are determined by the chemical potentials [8] of the participating species at such temperature and oxygen chemical potential, and extend our DFT investigations to some Ce or O terminated surface. From the fig.5 it is seen that the electronic structure of HOMO and LUMO [9] level. From table 2 pure

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super cell contain the HOMO and LUMO energy levels are 3.41 eV and -7.25 eV respectively. First the electronic structure of the vacancy with an extra electron was calculated using DFT method. We found that the one electron state occupied by the additional electronic (HOMO) is slightly split from the bottom of the conduction bands represent by the (LUMO). One oxygen is removed from the pure CeO_2 it becomes CeO_2@Vo1, then the corresponding HOMO and LUMO energy values are changed. Such that a removal of one by one oxygen from the CeO_2 super cell the vacancies of oxygen atoms is increases in a clusters CeO_2@Vo2, CeO_2@Vo3 due to that both the HOMO and LUMO energy level will be decreasing, the values are -4.23 eV and -4.95 eV.

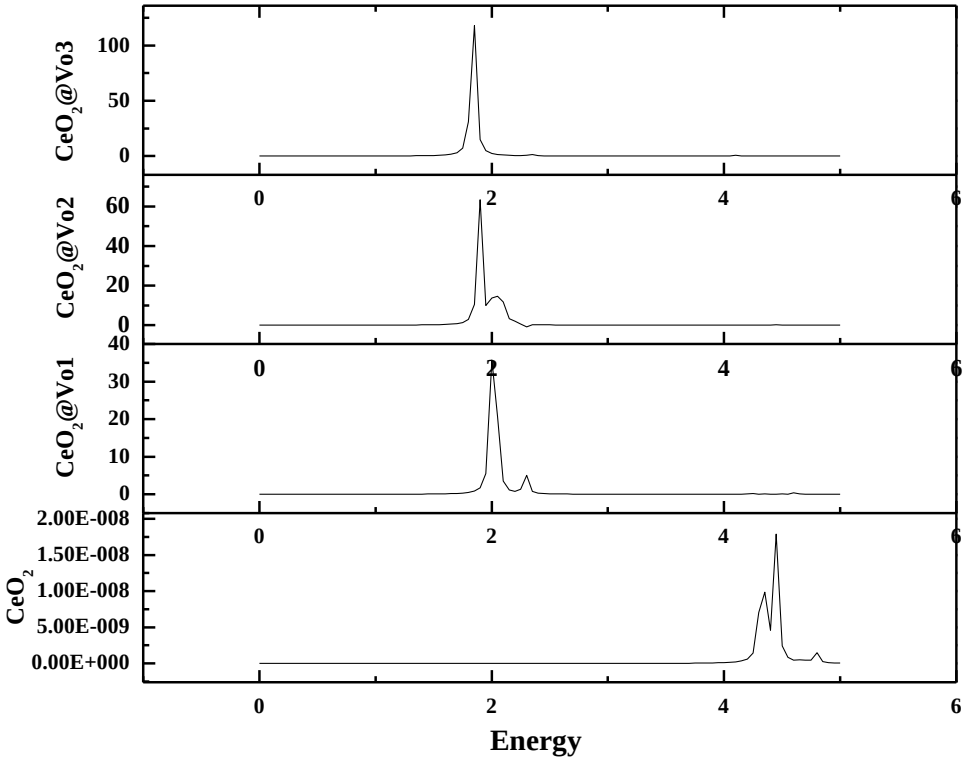

Figure 4: Optical property of CeO_2, CeO_2@Vo1, CeO_2@Vo2 and CeO_2@Vo3

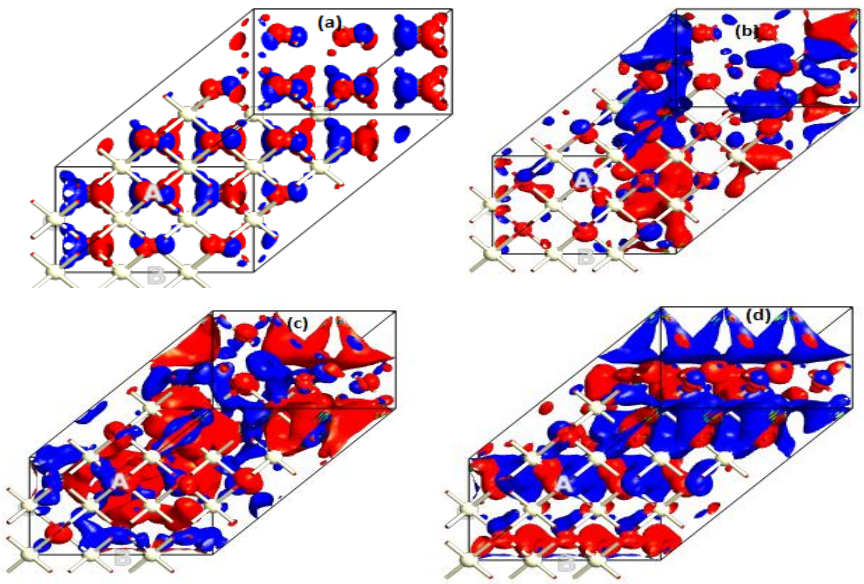

Figure 5: a HOMO and LUMO for (a) CeO_2, (b) CeO_2@Vo1, (C) CeO_2@Vo2 and (d) CeO_2@Vo3

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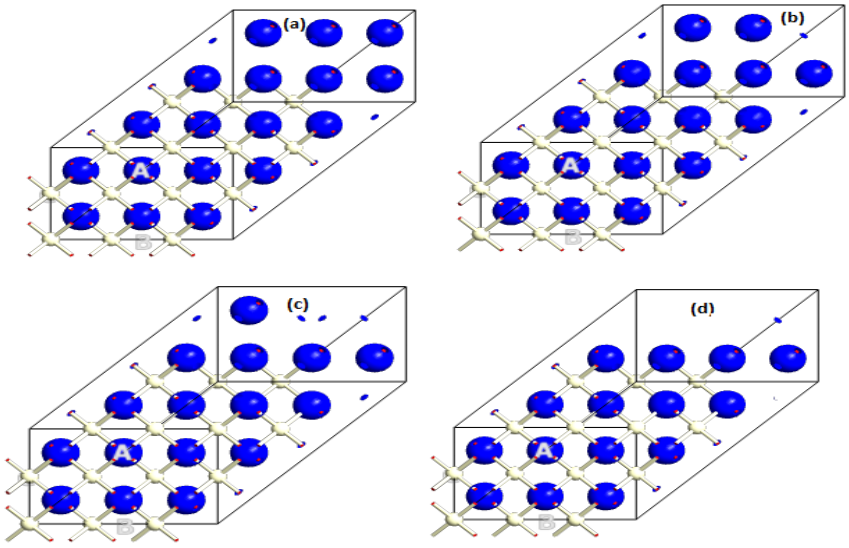

Figure 5: b Electron density for (a) CeO_2, (b) CeO_2@Vo1, (c) CeO_2@Vo2 and (d) CeO_2@Vo3

Table 1: Total energy of exciting structure of CeO_2, CeO_2@Vo1, CeO_2@Vo2 and CeO_2@Vo3

System Name	Exchange Correlation (eV)	Kinetic Energy (eV)	Electrostatic Energy (eV)	Entropy-Term	Total energy (eV)
CeO_2	-7637.34662	11128.94552	-24526.30755	0	-21034.70865
CeO2@Vo1	-5230.42365	5423.89402	-11290.00801	0	-11096.53764
CeO2@Vo2	-5130.72144	5123.63887	-10649.05724	0	-10656.1398
CeO2@Vo3	-5031.07549	4823.67911	-10008.36781	-0.0001	-10215.76429

Table 2: HOMO and LUMO band gap energy for CeO2

System Name	Chemical potential (eV)	HOMO value (eV)	LUMO Value (eV)	Fermi energy (eV)	Band gap (eV)
CeO_2	-9.19E-01	3.41E+00	-7.25E+00	4.33E+00	-7.251292
CeO2@Vo1	-5.95E+00	-3.95E+00	-4.81E+00	2.00E+00	-5.807875
CeO2@Vo2	-5.87E+00	-4.16E+00	c-4.94E+00	1.71E+00	-5.657436
CeO2@Vo3	-5.81E+00	-4.23E+00	-4.95E+00	1.57E+00	-5.49829

CONCLUSION

CeO2 super cell with 36 atoms are constructed in pure CeO_2, CeO_2@Vo1, CeO_2@Vo2 and CeO_2@Vo3 oxygen removed form to study about it structural, electronic and optical properties using density functional theory implemented in SIESTA package. The stability of the clusters decreased when the oxygen vacancy are created. The density of state (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 is the super cell increases more localized states in the conduction band which tends to decrease the band gap. The band gap narrowing property is absorbed. From the optical properties, calculated absorbance coefficient values of the clusters decreases when the oxygen vacancy are created and the structure becomes more transparent tends to form the F centers. The reflect ants spectra do not show anything sufficient vacancies.

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