8.1. Introduction

Ceria, one of the most important rare earth metal oxides exhibit unique chemical and physical properties. As a result of its high thermal and mechanical stability, excellent oxygen storage capacity and enhanced redox properties\(^1\), it can find wide variety of applications in catalysis\(^2\), oxygen sensors\(^3\), UV-filters\(^4\), solid oxide fuel cell\(^5\), medicinal fields\(^6\), etc. It can perform as better promoters in Three Way Catalysts (TWC)\(^1\). Modification of properties of ceria was enabled by isomorphous substitution of Ce by other metals (such as Cu, Ni, La, Gd, Eu, Pt, Au, Ru, etc.) to form solid solutions. This solid solution can withstand the change in the cubic fluorite type structure of ceria up to the higher concentration of dopants in the range of 1-50%. Recently DFT investigations have given valuable qualitative and quantitative descriptions about the structure of ceria and its solid solutions. Using this approach many of the properties of the material can be explored by solving the Schrödinger equation for the electrons of the atom, molecule, and assemblies of atoms in solids or liquids. The combination of molecular dynamics and electronic structure methods called \textit{ab initio} molecular dynamics which can predict approximate solutions for the problems of many electron systems. The plane wave based \textit{ab initio} DFT package of VASP\(^7\) is now used for making solutions to the problems of many body problems. The calculations are based on Kohn-Sham equations\(^8\) using exchange correlation functional GGA\(^9\) or LDA\(^10\). In this approach, the employment of pseudo potentials are carried out by using relatively small set of plane waves. DFT method can simplify the problems of large experimental work
regarding which concentration of dopant can be effective for the best description of properties of ceria. Carlos et al. carried out both experimental and DFT studies regarding the addition of Ni and Cu to the ceria lattice and calculated the formation energies for a range of concentration of dopant. The effect of group IV (a & b) elements (C, Si, Ge, Sn, Pb, Ti, Zr, Hf) as dopants to the ceria lattice within the framework of DFT+U was carried out. This study revealed the change in formation energies of the solid solution Ce$_{1-x}$Z$_x$O$_2$ where 0 ≤ x ≤ 0.2 with respect to the concentrations of dopants. Effect of rare earth dopants (La, Pr, Nd, Pm, Sm, Eu and Gd) on the bulk properties of ceria was investigated within the framework of DFT+U and found that earlier rare earth elements are more suitable for promoting oxygen storage capacity and migration of oxygen ion vacancies. Adsorption of Cu, Ag and Au on the CeO$_2$ surface (110) is quantum mechanically predicted using the plane wave DFT code of VASP. While adsorption, Cu and Au are oxidized to Cu$^{2+}$ and Au$^{2+}$. $ab$ initio DFT calculations of the structural, electronic, and thermodynamic properties of cerium ortho vanadate, CeVO$_4$, were performed utilizing the LDA, GGA-PBE, LDA+U, and GGA-PBE+U functional. The LDA+U, GGA-PBE+U, LDA, and GGA-PBE methods show deviations of equilibrium volumes of about −2.4%, +3.6%, −7.4%, and −0.8% respectively from the experimental results. Jalborg et al. studied the electronic structure of super cells (2×2×2) CeO$_{2-δ}$ within the framework of DFT+GGA. The equilibrium properties of bulk ceria such as lattice constants, bulk moduli and magnetic moments of super cells were well characterized with exchange correlational GGA. At present a lot of computational studies are reported regarding the electronic structure and bulk
properties of ceria, studies on quantum mechanical predictions on the electronic structure of bulk ceria with single lattice containing 12 atoms and the substitution of one of its Ce by divalent Cu were carried out using plane wave based approach using DFT package of VASP 5.4.1.

In the present chapter, *ab initio* plane wave DFT package of VASP is used for the investigations of electronic structure of ceria \((1\times 1\times 1)\) unit cell and to find out solution for how the electronic properties are varied with respect to Cu in the lattice. Based on this structural examination, band structure, total density of states (TDOS), projected density of the states (PDOS) and charge density distribution of rare earth oxide ceria were established. The results were compared by utilizing both GGA and LDA exchange correlation functional.

**8.2. Computational methods**

DFT calculations were performed using Vienna ab initio simulation package (VASP 5.4.1)\(^{16, 7}\) choosing plane wave basis set with an energy cut off 180eV for accounting the valence electrons. In order to study the effect of core electron on the valence electron density, projected augmented wave approach (PAW) was employed. The interaction between the ions and valence electrons are accounted by the standard frozen-core potentials which are utilized in the PAW method. The exchange correlational functional was introduced by generalized gradient approximation (GGA) and local density approximation (LDA) of Perdew and Wang (PW91). In order to study the convergence calculation of bulk ceria \((1\times 1\times 1)\) unit cell, we have
computed volume and total energy of the bulk CeO$_2$ using plane wave cut off energies in the range of 170-450eV. The Brillouin-zone convergence calculations were performed using Monkhorst-Pack grids of (7×7×7), (8×8×8), (9×9×9), (10×10×10), (11×11×11), (12×12×12), (13×13×13), (14×14×14), (15×15×15), (16×16×16), (17×17×17) and (18×18×18). It was found that calculations are well converged for a $k$-point grid of (11×11×11) and energy cut off 180eV. Lattice convergence calculations show the lattice constant of 5.4Å for the cubic fluorite type structure of ceria. After the convergence calculations, electronic structure of bulk ceria (1×1×1) single lattice was investigated by calculating the band structure, total density of states and projected density of states and charge density distribution of the material. Further in this chapter, the effect of Cu-doping on the total energy, lattice constant, Brillouin zone and plane wave cut off energy were measured as same above for the bulk ceria. The volume of the defect unit cell was computed from the converged lattice parameter. The influence of dopant on the band structure, density of states and charge density of the state were also evaluated. DFT+$U$ (GGA) methodology with varying values of $U$ in the range of 3-5 eV was performed for the evaluation of the contribution of localized strongly correlated Ce 4f states.
8.3. Results and discussion

8.3.1. Convergence of lattice parameter, k-point grid, and energy cut off

The converged plane wave cut off energy, k-point grid and lattice constants were investigated. From the bulk convergence calculation, the total energy and equilibrium volume were calculated. Fig. 1 represents convergence of plane wave cut off (Fig. 1a), k-point grid (Fig. 1b) and lattice parameter (Fig. 1c) of bulk ceria. For this calculation, DFT based on GGA introduced by PW91 were used. Fig. 1a shows that the energy cut off for the bulk ceria unit cell (1×1×1) is 180eV. Brillouin zone grid is converged for (11×11×11) (Fig. 1b) and lattice parameter convergence of 5.4 Å (Fig. 1c).

![Fig. 1 Plots of convergence of Encut (a), k-point (b) and lattice parameter of bulk ceria (c) (calculated based on DFT+GGA).](image)

![Fig. 1 Plots of convergence of Encut (a), k-point (b) and lattice parameter of bulk ceria (c) (calculated based on DFT+GGA).](image)
The total ground state energy for the bulk ceria was found to be -112.94eV and the volume computed from the lattice parameter was 157.46Å³. The DFT calculation based on LDA introduced by PAW approach is also performed in order to make comparison with DFT+GGA.

**Fig. 2** The plots of convergence of Encut (a), Encut vs Total CPU time (b), k-point (c), k-point vs Total CPU time(d) and lattice parameter of bulk ceria(e) and lattice parameter vs Total CPU time(f) (calculated based on DFT+LDA).
Fig. 3 The comparison of total energy convergence plots made by DFT+GGA and DFT+LDA of bulk ceria

Fig. 2 shows the plots of convergence of energy cut off, k-point grid and lattice parameter and total CPU time needed for each convergence. The results show that these values are concomitant with those evaluated by GGA method. LDA chooses delocalized electron interaction while GGA account localized electron interaction. Literature reports that for studying bulk properties of materials, DFT with GGA is more profound than LDA. Fig. 2a corresponds to the convergence graph of plane wave cut off energy in the range of 175-350eV and total CPU time needed for the plane wave energy convergence (Fig. 2b). It was displayed that converged plane wave cut off energy is 180eV, which requires comparatively lesser CPU time than others. Fig. 2c represents the convergence of k-point grid and Fig. 2d exhibits that k-point grid of (12×12×12) requires lower time and energy for its convergence. Fig. 2e displays the convergence plot of lattice parameter and was found that the calculations were converged at lattice constant, a, at 5.4Å. Fig. 2f exhibits the time need for the lattice constant convergence and was observed that the factors, time and energy are the key component in determining the converged values of a bulk crystalline material. Fig. 3 represents the plots of total energy
convergence carried out by GGA and LDA exchange correlation functional. The converged total energy by LDA methods takes more iteration steps for the optimization and the value was found to be $-120.834\text{eV}$.

Fig. 4 represents the DFT+GGA calculation for the convergence of lattice parameter, k-point grid and plane wave cut off energy for the copper doped ceria. The presence of displacement of Ce with Cu has not made changes to the k-point grid ($11\times11\times11$) and lattice parameter ($5.38\ \text{Å}$). But the energy utilized for the plane wave basis set remains unchanged. The presence of Cu$^{2+}$ increases the total ground state energy of the bulk material to $-95.82\text{eV}$. Hence, the volume computed from the lattice parameter was found to be $155.72\text{Å}^3$. The decrease of volume occurs because of the prevailing lattice strain due to the introduction of copper.

![Graphs](image)

**Fig. 4** The plots of convergence of Encut, k-point and lattice parameter of Cu$^{2+}$-doped ceria (calculated based on DFT+GGA).
The same convergence calculations are repeated with exchange correlation functional LDA introduced by projected augmented wave approach. Fig. 5 shows the results of convergence calculation of copped doped ceria made by LDA method. The calculated converged values of copper doped ceria was found to be 210eV (Fig. 4a) for the Encut value of plane waves with Monkhorst pack grid of 20×20×20 (Fig. 4c). Figs. 4b&d respectively displays the total CPU time vs Encut and k-point grid. The introduction of copper to the ceria lattice markedly enhances the value of plane wave cut off and k-point grid. But the presence of copper made some lattice strain causing a decrease in lattice parameter. This has aroused the total ground state energy of the bulk ceria to -106.46eV.
**Fig. 5** The plots of convergence of Encut (a), Encut vs Total CPU time(b), k-point (c), k-point vs Total CPU time(d), lattice parameter of copper doped ceria (e) and lattice parameter vs Total CPU time (f) (based on DFT+LDA).
From the comparison of total energy convergence plots of doped ceria (Fig. 6), it has been found that LDA method takes more optimization steps than GGA method and hence lowers the convergence value of total ground state energy ($E_0$).

![Graph showing comparison of total energy convergence plots for DFT+GGA and DFT+LDA of Cu$^{2+}$ doped ceria.]

**Fig. 6** The comparison of total energy convergence plots made by DFT+GGA and DFT+LDA of Cu$^{2+}$ doped ceria

### 8.3.2. Band structure and density of states

CeO$_2$ has cubic fluorite type structure with four Ce atoms and 8 oxygen atoms per unit cell. Band structure of bulk ceria and Cu$^{2+}$ doped ceria were calculated by the non-self-consistent field energy calculation by DFT with exchange energy correlational brought out by GGA and LDA. Fig. 7 exhibits the band structure of CeO$_2$ described by DFT+GGA method. The low lying bands are not included in the plot. Fig. 8 represents the band structures of low lying Ce (5s) & Ce (5p), highest occupied valance band orbitals of Ce (5d) and lowest conduction bands of Ce (4f) orbitals. The low lying 5s orbitals of Ce are overlapped to form bands in the energy range of -32.05 - -32.65eV
Fig. 8a. Fig. 8b represents bands of 5p orbitals of Ce in the energy range of -11- -20eV (which are below the valence bands). The 5d atomic orbitals of Ce are overlapped to form valence band in the region of -0.5- -0.45eV (Fig. 8c). The narrow conduction band is formed from the overlapping of 4f atomic orbitals of cerium atom; these are above the Fermi level in the range of 2.1-2.5 eV (Fig. 8d).

![Band Structure](image)

**Fig. 7** The band structure of CeO$_2$ calculated from DFT+GGA method

Fig. 9a consists of bands constructed from the 2s atomic orbitals of oxygen atom of CeO$_2$. These bands are occupied just below the valence bands in the region of -11- -20eV. Besides, the Figs. 8b & 9a exposed that there exist interaction between 5p (Ce) and 2s orbitals of oxygen atom. Fig. 9b corresponds to the band structure of 2p atomic orbitals of oxygen atom in the region of -1.5 - -4.5eV. The valence band between -0.5 - 4.5eV are composed of O (2p) and small mixture of Ce 5d atomic orbitals. The nature of Ce active site is not well described yet since the 4f electrons are laying far above the Fermi level.
The width of the band increases as the electronic overlap increases. The interatomic orbitals or core orbitals (valence f or d orbitals) will tend to form narrow bands with high effective masses. The band structure of ceria (Fig. 7) shows non-zero Fermi energy. A Fermi level is the highest occupied electronic state, and now in the considered work, it is placed just below the zero energy. The range of forbidden energy between the energy bands are known as band gaps. The lower energy bands are formed from the core orbitals and form narrow bands and for most cases, they are treated as a set of localized atomic orbitals. This occurs due to the strong interaction of nuclei with these orbitals that prevent the overlapping of orbitals of neighboring nuclei. For small molecules, the greater overlap leads to greater energy difference between valence band and conduction band. Similarly, in continuous solids, the greater overlap causes to greater spread of energies called band width of the resulting band\textsuperscript{17}. 

![Graph of band structure showing energy levels and Fermi level placement.](image)
Fig. 8 The band structures of 5s (a), 5p (b), 5d (c) and 4f (d) orbitals of cerium atom
The qualitative description of an electronic conduction can be predicted for materials with band gaps. If the band gap value is lower than the 3eV, the material is semiconductor and if the band gap value is wider, it is said to be insulator. The direct band gap between highest occupied valence band and lowest region of conduction band indicates a band gap of 2.09eV. This value is comparable to the experimentally and theoretically observed band gap, 1.82eV, of bulk CeO\(_2\) crystals\(^{18}\). Hence the bulk CeO\(_2\) is a semiconductor material. For the metals, the forbidden region is also occupied with energy bands.

One important quantity which can be used to define electronic state of a material is the electronic density of the material. Electronic density of state \(\rho (E) \, dE = \text{number of electronic states with energies in interval } E, E+dE\). Plane wave DFT calculation expresses the electronic density in function of the form \(\exp (ik.r)\). Electron associated with plane wave has the energy \(E = \frac{hK^2}{2m}\). The electronic density is determined by integrating the resulting electron density in k-space.
**Fig. 9** The band structure of 2s (a) and 2p (b) atomic orbitals of oxygen atom

Fig. 10a shows the total density of states (TDOS) plot calculated by non-spin polarized method. As shown in Fig. 10, density of states (DOS) can be separated into two regions, valence band and conduction band. Valence band is the collection of all occupied electronic states while in conduction band; all the states are not occupied. From the density plot, the band gap is the region where valence band and conduction band have no density of states. The slope of the plot varies discontinuously in a number of places (hence indicates the presence of van Hove singularities). Fig. 10b represents
the electron density calculated by the spin polarized DFT method. But the marked difference in electron density calculated by with and without spin polarization was absent. This considered that no change in the total ground state energy of the bulk material. Calculation performing with considering spin of electron tends to lower the energy of the bulk material substantially. Moreover, the density of states of spin up and spin down were cancelled to each other giving non-magnetic ceria unit cell. TDOS calculated without spin of electron shows the non-zero Fermi energy, while TDOS performed with considering spin of electron indicates zero Fermi energy.

Fig. 10 The total electron density of the material (TDOS): calculated by non-spin polarization (a) and spin polarization (b) of CeO$_2$. 
In order to study the electronic structure of material, it is often important to study which state is important in the vicinity of atom. One standard method is to do is the calculation of projected density of states (PDOS). It is defined as the number of electronic states at a specified energy weighted by the fraction of the total electron density for these states that appears in a specified volume around the nuclei. For performing PDOS computation, need effective radii of atom. PDOS predicts the contribution of each band. Fig. 11 shows the PDOS for 5s (Fig. 11a), 5p (Fig. 11b), 5d (Fig. 11c) and 4f (Fig. 11d) atomic orbitals of Ce.

![Graphs of PDOS for 5s, 5p, 5d, and 4f orbitals of Ce](image)

**Fig. 11** The PDOS of the 5s (a), 5p (b), 5d (c) and 4f (d) of Ce.
The PDOS of 5s (Fig. 11a) and 5p (Fig. 11b) shows the low lying core electron density. The electron densities of these orbitals are also higher compared to other PDOS. Towards the valence band regions, the contributions of 5d electrons are predominant (Fig. 11c). A small contribution of 5d electrons are also found in the above Fermi energy level. The electron density of 4f orbitals is far above from the Fermi level (Fig. 11d). Fig. 12 shows the PDOS plots of 2s and 2p orbitals of oxygen atom in ceria. 2s bands are overlapped with 5p atomic orbitals of Ce in the region of -10 - -20eV, whereas 2p bands are overlapped with 5d bands of Ce in the valence band region. Fig. 13 shows the PDOS plots of 5s (Fig. 13a), 5p (Fig. 13b), 5d (Fig. 13c) and 4f (Fig. 13d) atomic orbitals of the copper doped ceria.

Fig. 12 The PDOS plots of the 2s and 2p orbitals of oxygen.
Density of states of localized atomic orbital 5s (Fig. 13a) was reduced in copper doped ceria, so that the peak became sharper. DOS of 5p atomic orbital remain unchanged in the Cu-Ce-O while significant change in the 5d orbital is seen (Fig. 13c). A similar broadening is observed for 4f orbital (Fig. 13d). These changes were occurred due to the overlapping of 3d and 2p atomic orbitals of copper.

The 2s atomic orbital of oxygen atom is retained its DOS, but 2p atomic orbitals (Fig. 14) experiences overlapping which led to increase in the Fermi energy of the doped ceria than the undoped ceria. Fig. 15
indicates that valence shell atomic orbitals (3d, 3p & 4s) and 2p atomic orbitals take part in the overlapping with valence shell orbital 5d of Ce. Hence the 5d peaks of doped ceria get broadened and increase the Fermi energy level of ceria. Besides, rather smaller overlapping of 4f orbital with 5d, 2p, 3p and 4s orbitals, the narrow peak of conduction band is get broadened. This led to reduction of the forbidden region. Hence the electron transport and conductance properties of copper doped ceria shows enhanced performance than the pure ceria. Fig. 16 displays the calculated TDOS plot of Cu-Ce-O calculated by non-spin polarized DFT with exchange correlation functional GGA.

Fig. 14 The PDOS plots of 2s and 2p atomic orbitals of Ce

Upon doping the density of the mixed oxide was decreased markedly as seen from Figs. 10a &b and Figs. 16a&b. Moreover, the ground state energy calculated by considering both spin of electron in the copper doped ceria shows lowering of the ground state energy by small fraction. Also, the DOS of spin up and down are unequal, imparting some un paired character in the single unit cell of ceria due to the overlapping of the orbitals of Cu$^{2+}$. The electronic state
concentrated in wider range of energies and higher electron density of un-occupied or partially occupied electronic states above the Fermi energy level specifies that Cu-Ce-O has gained enhanced chemical reactivity.\(^7\)

Fig. 15 The PDOS plots of 4s (a), 3p (b) and 3d (c) atomic orbitals of Cu\(^{2+}\) in ceria.

Fig. 16 TDOS plot of Cu-Ce-O non-spin polarized (a) and spin polarized (b)
Fig. 17 The total band structure of copper doped ceria

Fig. 17 exposes the total band structure of copper doped ceria unit cell. As indicated in figure, the valence bands are moved nearest to the conduction band. Hence energy of highest occupied energy levels increases, causing a decrease of band gap to 1.54eV. Presence of metal impurities in the ceria lattice can enhance the electron hole recombination rate since it enhances the electronic states within the band gap. This can generate increment in conducting properties of the ceria. Fig. 18 displays the significant changes in the band structures of Cu-Ce-O for the atomic orbitals of 5s, 5p, 5d, and 4f. Fig. 19 reminds the effect of copper doping on the individual bands of 2s and 2p atomic orbitals of oxygen atom of Cu-Ce-O. The band width of 2s (Fig. 19a) and 2p (Fig. 19b) orbital band were increased. The 2p bands were moved towards the forbidden region of ceria whereas the 2s bands to low lying energy region.
The band structures of 5s (a), 5p (b), 5d(c) and 4f (d) atomic orbitals of Ce of doped ceria.
The 4s orbital bands of copper lie in the region of energies of -3 to -5.25eV just below the valence band (Fig. 20a). The 3p orbital bands are spread out in the range of -0.9 to -4.5eV (Fig. 20b). The more electron dense 3d orbital bands are lying in the energy range of 0.75 - 4.25eV (Fig. 20c).

Fig. 19 The band structures of 2s (a) and 2p (b) atomic orbitals of oxygen
Fig. 20 The band structures of 4s (a), 3p (b) and 3d (c) atomic orbitals of Cu
The broadness of the band near Fermi energy level increased due to the presence of electronic contributions from the Cu 3d, 4s and 3p (Fig. 20) atomic orbitals with 5d orbitals of Ce. The core electron orbital 5s of Ce decreases its band width upon doping whereas; the band width of 4f orbital enhances which makes the oxide more chemically reactive.

![DOS plot of copper doped ceria: non-spin polarized (a) and spin-polarized (b) (DFT+LDA method)](image)

**Fig. 21** The DOS plot of copper doped ceria: non-spin polarized (a) and spin-polarized (b) (DFT+LDA method)

Density of states (Fig. 21) and band structure (Fig. 22) calculated by the DFT+LDA shows much difference compared to that
depicted by using GGA correlation functional. Fig. 21a expresses the DOS of non-polarized spin, while spin polarized DOS is expressed in Fig. 21b. LDA is best suitable for giving correction to the contribution to delocalized electrons, while GGA contribute gradient in density and more suitable for localized electron contribution. From the figures one can ensure that GGA correlation functional predict more accurately the DOS and band structure to an extent. For the purpose of studying bulk properties of a material, GGA provides more accurate predictions than LDA method.

Fig. 22 The band structure of copper doped ceria calculated by DFT+LDA

The calculated band gap between O-2p valence band and 4f conduction band is found to be 1.7eV, which is higher than that predicted by DFT+GGA method.

8.3.3. Charge density distribution

Figs. 23 & 24 explains the charge density distribution of ceria and copper doped ceria along (011) and (001) planes. There exists
significant change in the distribution of electron density along different crystalline planes. This indicates the absence of uniformity of charge density along different crystallographic directions. The charge density distribution of the doped ceria shows the marked influence of copper in the ceria lattice. It increases the charge densities of the bulk ceria, besides, the overlapping of Cu-3d with O-2p and Ce-5d atomic orbitals. In the charge density distribution plots, red region indicates more electron density, while that of blue for more electropositive region.

Fig. 23 The charge density distribution of bulk (1×1×1) ceria along (011) (a) and (001) (b) planes
Fig. 24 The charge density distribution of Cu-Ce-O (1×1×1) along (011) (a) and (001) (b) planes.

The existence of higher charge density in the defect ceria clarifies the possibility of bond formation of Cu with Ce and O atoms in the lattice. Hence the bulk energy was increased to -95.82eV. Therefore, the presence of copper in the ceria lattice can empower the performance of ceria to become an eventual material.

DFT method predicts the structure by considering the electron delocalization of the overall Ce atoms in the simulation cell. In order to demonstrate the most accurate ground state properties of ceria and defect ceria, the strongly correlated Ce 4f states in ceria were performed with DFT+U methodology. Coulomb parameter $U$ (Hubbard correction) varying in the range of 3-5eV is deployed in the GGA scheme. It was arrived at a conclusion that simulation does not
change the total ground state energy, band structure, and DOS. This happens because the corrections with $U$ effectively work with many-body system rather than single lattice structures. However, for single lattices, it was observed that variation of $U$ made change in the total CPU time needed for the simulation. In the concerned work, simulation with $U = 3.2$ eV required lesser time than other $U$ values.

8.4. Conclusion

The convergence of lattice parameter, k-point grid, and plane wave energy cut off for ceria and copper doped ceria was performed by DFT+GGA and DFT+LDA. DFT+GGA method is more accurate to predict the electronic structures which are comparable with both theoretical and experimental studies. The total ground state energy of the single cubic unit cell of ceria is $-112.94$ eV (DFT+GGA) and $-120.834$ eV (DFT+LDA) methods. The computed volume from the lattice parameter is $157.46\text{Å}^3$. For the copper doped ceria, the total ground state energy is increased to $-95.82$ eV (DFT+GGA) and $-106.46$ eV (DFT+LDA). The volume of the cell was reduced to $155.72\text{Å}^3$. The calculated direct band gap between highest occupied energy band (O2p band) and lowest unoccupied (4f band) was found to be $2.02$ eV. The presence of Cu$^{2+}$ in the crystal lattice of ceria caused to decrease the band gap to $1.54$ eV (GGA scheme). Simulation with DFT+$U$ (GGA) did not provide any change in the ground state properties of ceria and defect ceria single lattices. The charge density distribution plots along (011) and (001) planes confirmed the absence of uniformity of charge distribution along different crystallographic directions. The introduction of Cu$^{2+}$ increases the electronic charge density of the ceria lattice.
8.5. References


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