Structural and Electronic Properties of CeO_2: A First- Principles Study

Presented by-

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INTRODUCTION

- Density Functional Theory (DFT) is a powerful quantum mechanical modelling method widely used to investigate the electronic structure of many-body systems.
- The concept behind DFT is that all properties of a system can be determined from its electron density rather than the many body wave functions.
- DFT enables detailed understanding of: structural stability, electronic band structure, density of states, charge distribution, optical response, and magnetic properties.
- Recent works also indicates that DFT-based computational analysis is an effective approach for designing advanced multifunctional materials with improved efficiency and stability for modern technological applications.

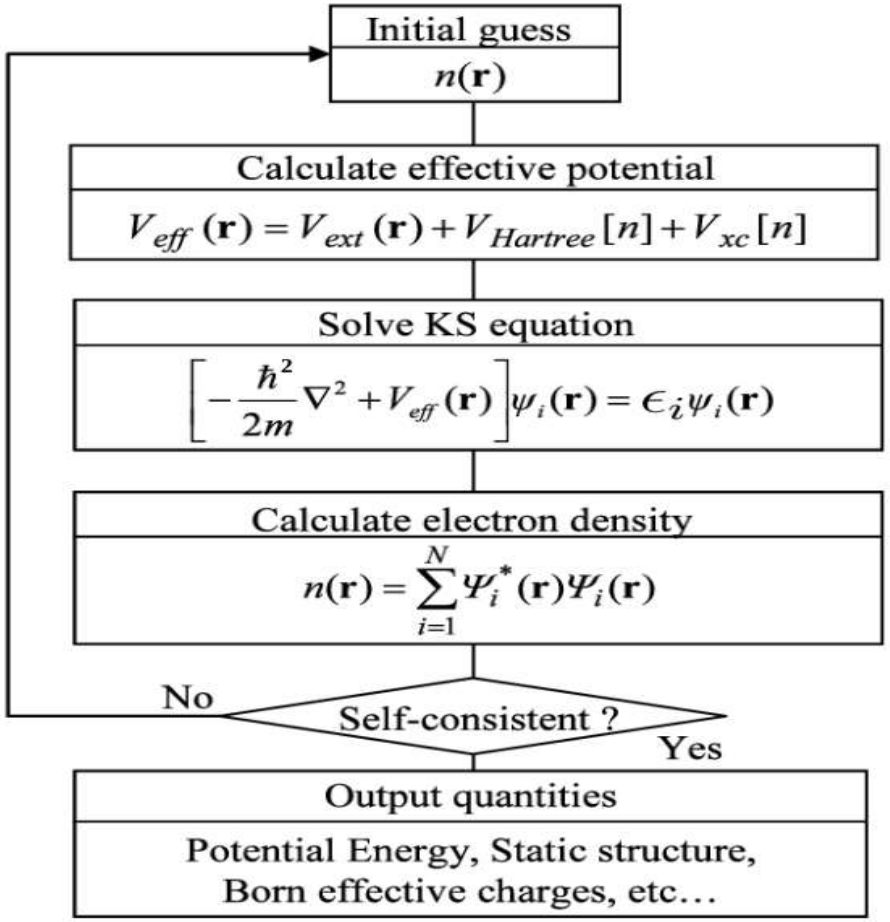
FOUNDATIONS OF DFT

- **The Hohenberg–Kohn Theorems** are the foundational theorems of Density Functional Theory (DFT), introduced in 1964 by Pierre Hohenberg and Walter Kohn.
- **FIRST THEOREM**: The ground-state electron density and the external potential correspond in a one-to-one manner
- **SECOND THEOREM:** For any trial electron density, the energy functional will yield a value that is greater than or equal to the ground-state energy
- The theorems prove DFT works, but they do not provide a practical equation to calculate electron density. That problem was solved by the **Kohn–Sham method**.

KOHN-SHAM EQUATION

- It reformulates the complex many-body problem into a set of simpler, non-interacting single-particle equations, making it more tractable for computational purposes
- The idea behind this equation is to replace interacting electrons with non-interacting electrons in an effective potential.
- the Kohn-Sham equations is expressed as:

$$\left(-\frac{\hbar^2}{2m_e}\nabla^2 + V_{eff}(r)\right)\psi_i(r) = \epsilon_i\,\psi_i(r)$$



METHODOLOGY

- The study of materials was carried out using Quantum ESPRESSO, an open-source integrated suite of computer codes based on plane-wave basis sets and pseudopotential methods.

- To simplify input generation, visualization, and post-processing of simulation data, BURAI was used as a graphical user interface (GUI) for Quantum ESPRESSO.

- The exchange–correlation interactions between electrons was treated using the Generalized Gradient Approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) functional.

- Ultrasoft pseudopotentials from standard pseudopotential libraries was employed to represent ion–electron interactions.

METHODOLOGY

1. The crystal structure of the CeO_2 was obtained from Materials Project in the form of a Crystallographic Information File (CIF) and imported into BURAI for visualization and structural modification.
2. The crystal structure was then optimized to obtain the minimum-energy configuration and then converted into a suitable supercell (2x1x1) to accommodate dopant atoms and defect structures.
3. Self-consistent field (SCF) calculations was performed to achieve electronic convergence for plane-wave cut-off energy, charge density cut-off, K-point mesh sampling, and total energy convergence threshold, followed by geometry relaxation of atomic positions and lattice parameters.
4. The optimized computational parameters was then used to determine band gap and Density of States.

OBSERVATIONS

- Supercell size 2x1x1
- No. of atoms= 24
- Optimized lattice parameters,

  a = 10.984011 Å

  b = 5.492003 Å

  c = 5.492003 Å
- Cut off for work function= 220 Ry
- Cut off for charge= 880 Ry
- K-points= 3 6 6
- Hubbard parameter (U) for Ce= 5eV

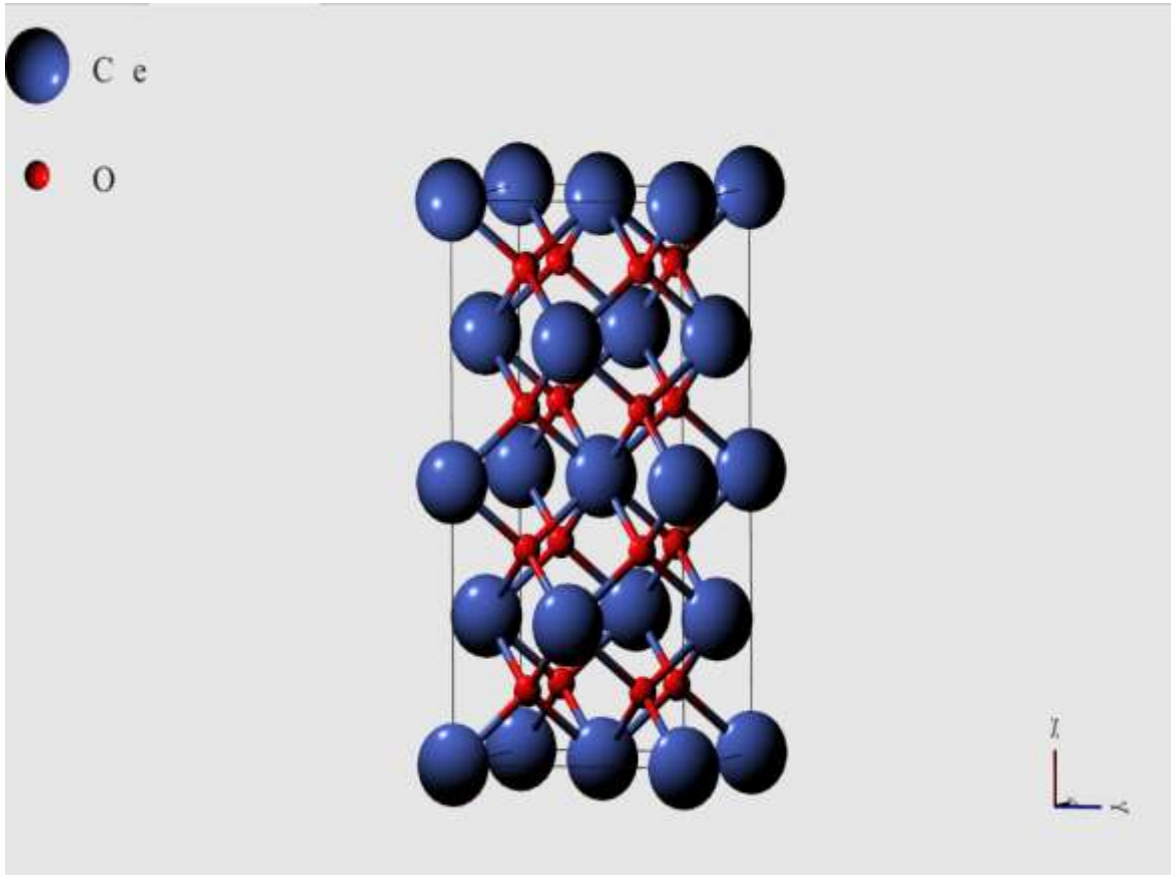


Fig 1 : Optimized structure of pristine CeO_2

BAND GAP

Highest occupied level = 12.1425 eV

Lowest occupied level = 14.3134 eV

Therefore band gap = 2.1709 eV

file:///C:\Users\deepa\.burai\bandgap\espresso.log.scf

```
1512        20.1667  20.1668  20.1668  20.1668  20.3679  20.3679  20.3679  20.3679
1513        21.4510  21.4510  21.4511  21.4511  21.5653  21.5653  21.5653  21.5653
1514        22.4771  22.4771  22.4771  22.4771  22.4830  22.4830  22.4830  22.4830
1515        22.5551  22.5551  22.5551  22.5551  23.1405  23.1405  23.1405  23.1405
1516        26.5768  26.5768  26.5769  26.5769  26.6589  26.6589  26.6589  26.6589
1517        29.2746  29.2746  29.2746  29.2746  30.6634  30.6634  30.6634  30.6634
1518        31.2938  31.2938  31.2939  31.2939  31.8027  31.8028  31.8028  31.8029
1519
1520         highest occupied, lowest unoccupied level (ev):    12.1425   14.3134
1521
1522    !    total energy              =   -4009.02197992 Ry
1523         Harris-Foulkes estimate   =   -4009.02198021 Ry
1524         estimated scf accuracy    <       0.00000039 Ry
1525
1526         The total energy is the sum of the following terms:
1527
1528         one-electron contribution =   -2195.48658631 Ry
1529         hartree contribution      =    1102.02520575 Ry
1530         xc contribution           =    -554.24991757 Ry
1531         ewald contribution        =   -2362.42450666 Ry
1532         Hubbard energy            =       1.11382488 Ry
1533
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GEOMETRIC OPTIMIZATION

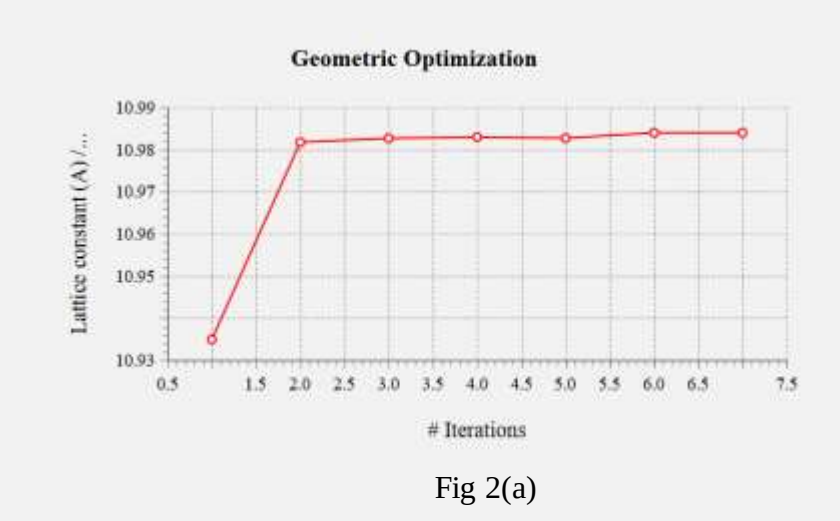


Fig 2(a)

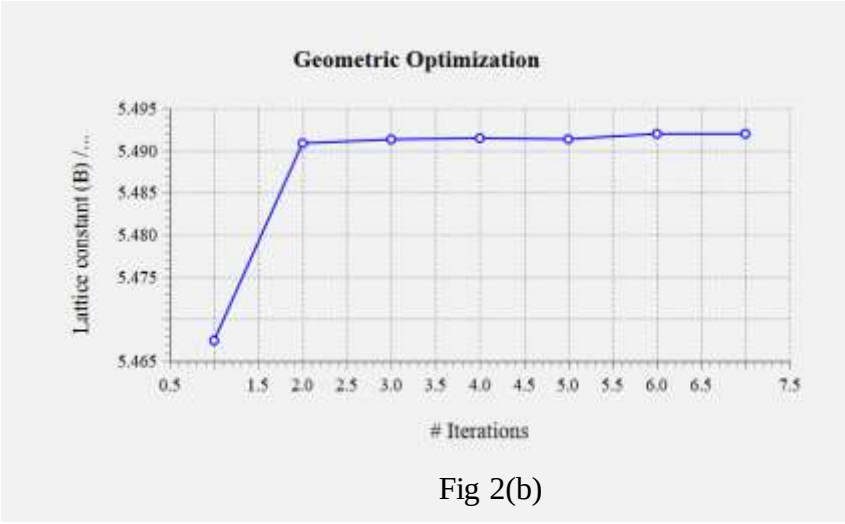


Fig 2(b)

Fig 2: Variation of lattice constants (a,b and c) with optimization iterations during the vc-relax of pristine CeO_2

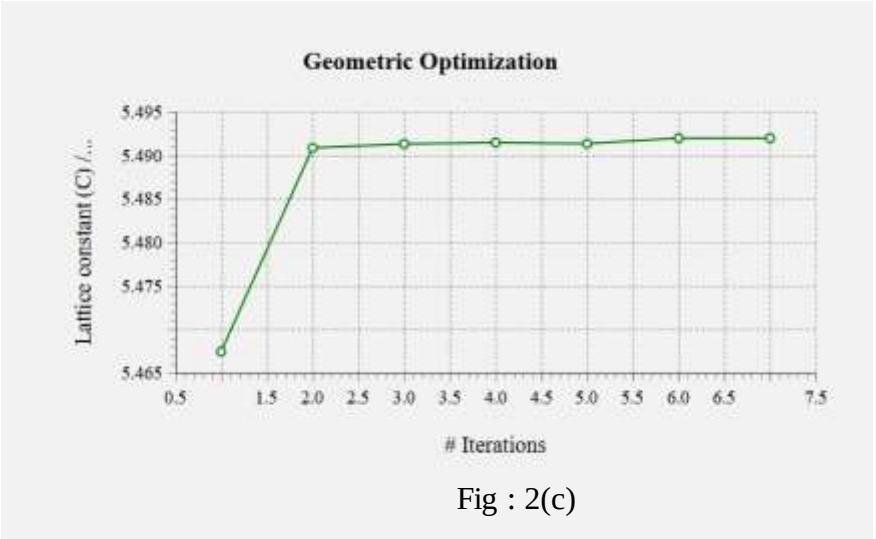


Fig : 2(c)

GEOMETRIC OPTIMIZATION

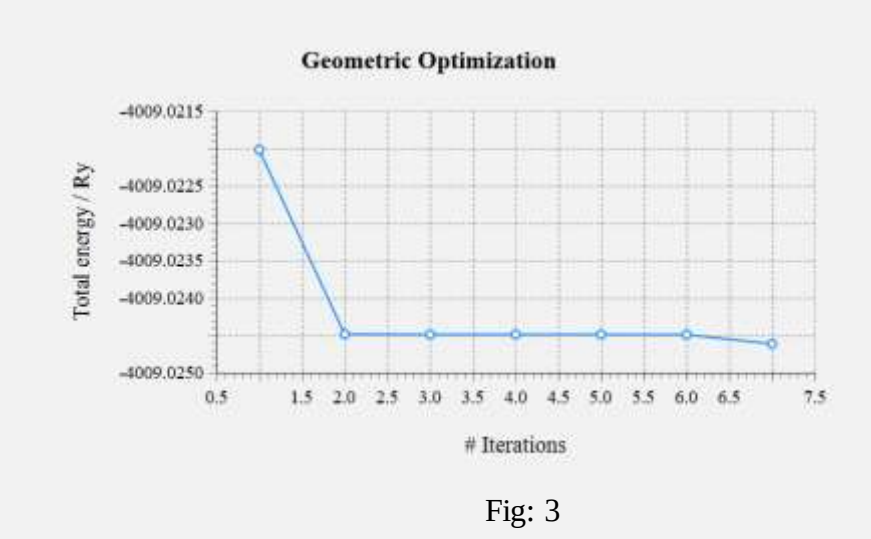


Fig: 3

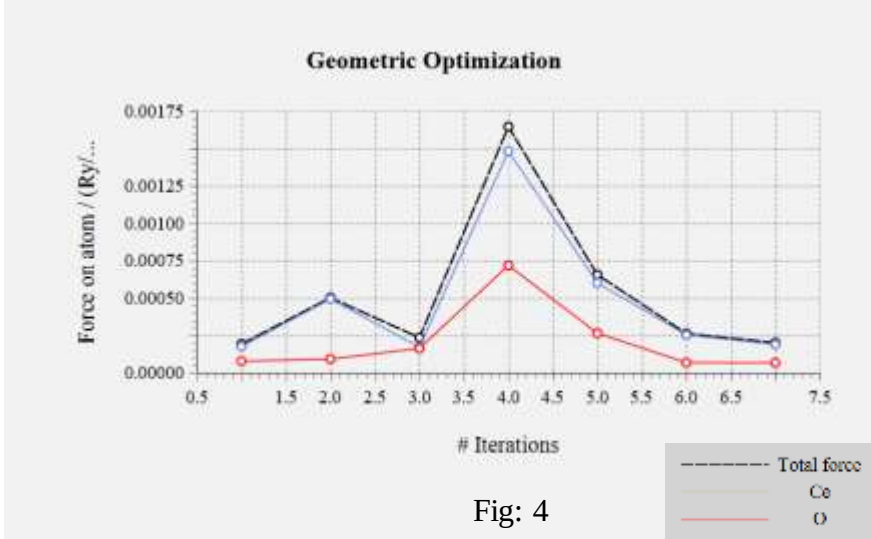


Fig: 4

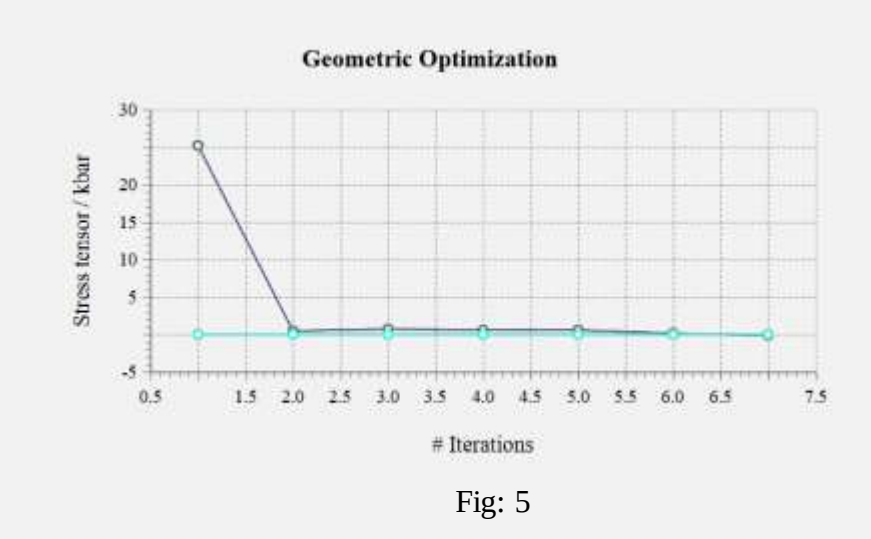


Fig: 5

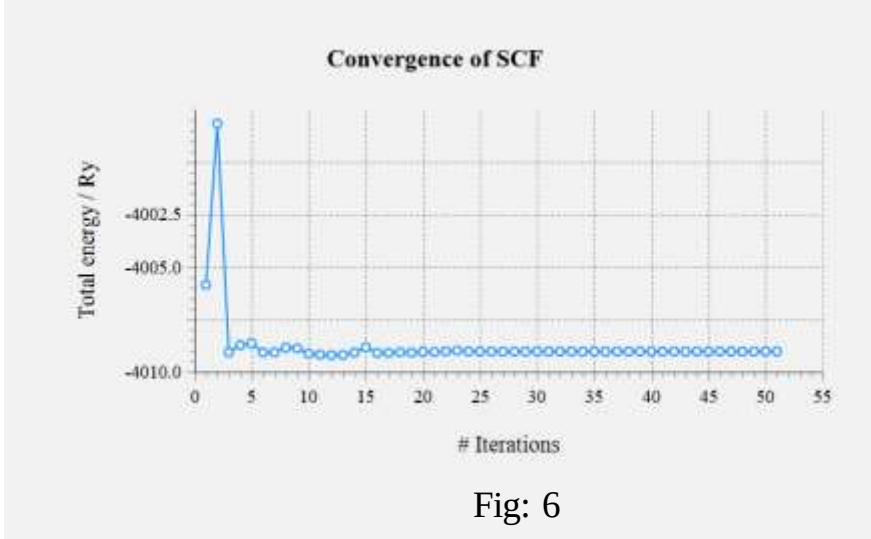
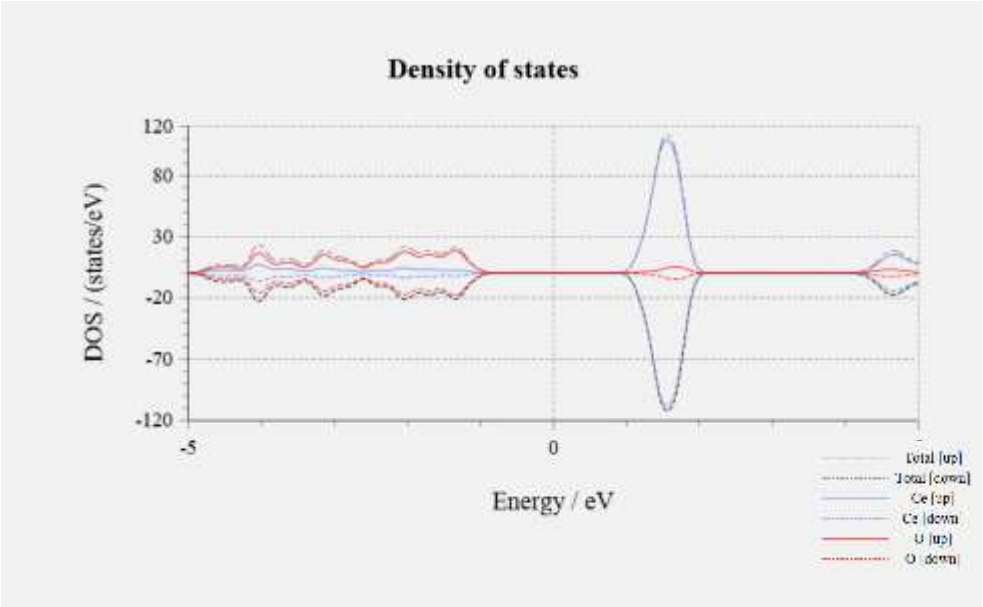
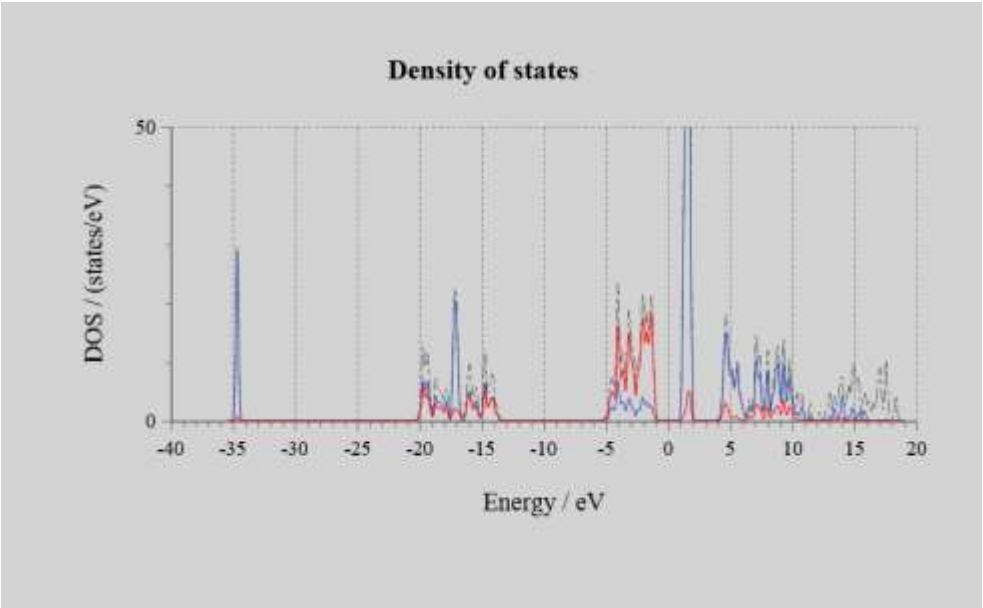


Fig: 6

DENSITY OF SATES (DOS)

- No states at the Fermi Level as the DOS is flat between about -1ev and +1.5 eV indicating the non-metallic behaviour of the material.
- Non-uniform distribution of electronic states is found.
- The spin up and spin down channels mirror each other, and there is nothing inside the gap. Hence it is non-magnetic and no defect states





CONCLUSION

- Structural optimization and optimized lattice parameters have been obtained.
- The calculated band gap was found to be 2.1709 eV.
- Total density of states has been calculated to investigate the electronic structure.
- The symmetric spin up and spin down DOS indicates negligible energy range.
- Further calculations are required to obtain a complete understanding of the electronic properties.
- It can be doped with various transition metals to study its changes in structural, electronic, magnetic and optical properties.

THANK YOU