First-Principles calculations of Material properties

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(22PPH101)

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Outline

- Objective
- First principles calculation – overview
- Software and codes used
- Computational Facilities
- Properties calculated
- Results
  - 2D Materials
  - Organic Materials
  - Inorganic Materials
  - Other Materials
- Further work

Objective

- To Understand the Theoretical framework of first principles calculations using density functional (DFT) theory.
- To develop optimized structure of materials.
- To calculate the various properties of materials.

First principles calculation – overview

Quantum mechanics $\hat{H}\psi = E\psi$ *Quantum calulations*

$$E = min_{\psi}\langle\psi|\hat{H}|\psi\rangle$$

$$\hat{H} = -\frac{1}{2}\left[\left(\sum_i \frac{\hbar^2}{m_e}\nabla_i^2 + \sum_\alpha \frac{\hbar^2}{M_\alpha}\nabla_\alpha^2\right) + \left(\sum_{i,\alpha}\frac{2z_\alpha e^2}{|\vec{r_i} - \vec{R_\alpha}|} - \sum_{i\neq j}\frac{e^2}{|\vec{r_i} - \vec{r_j}|} - \sum_{i,\alpha}\frac{z_\alpha z_\beta e^2}{|\vec{R_\alpha} - \vec{R_\beta}|}\right)\right]$$

$$\rho(\boldsymbol{r}) = \langle\psi|\hat{\rho}(\boldsymbol{r})|\psi\rangle$$

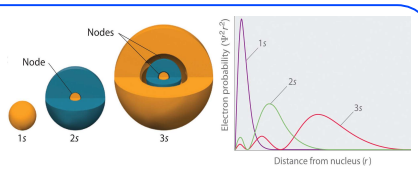
$$\hat{\rho}(\boldsymbol{r}) = \sum_{k=1}^{N} n_k|\varphi_k(\boldsymbol{r})|^2$$

$$\hat{\rho}(\boldsymbol{r}) = \sum_{k=1}^{N}\delta(r - r_i)$$

Slater determinant constructed from N orbitals, φ_k with corresponding n_k

Electron density is a +ve function integrating to total no. of electrons

Replacing the Hamiltonian by a function representing the **electron density** of the atom using **Hohenberg – Kohn Theorems**



Holding a single electron still in position r we sum over all possible arrangements of the other electrons.

The many body ground state problem can be mapped onto a single particle problem with the same electron density and a different effective potential. The electrons are not only affected by the nuclei in their lattice sites, but also by the other e. A functional is a function of a function. In DFT the functional is the electron density which is a function of space and time, usually time is kept constant and when time varies it is called as TDDFT.

Hohenburg-Kohn theorem asserts that the density of any system determines all ground-state properties of the system. In this case the total ground state energy of a many-electron system is a functional of the density. So, if we know the electron density functional, we know the total energy of our system.

Kohn-Sham equations are used to solve the system to obtain the total energy.

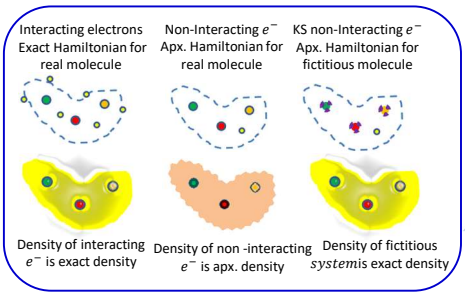
First principles calculation – overview

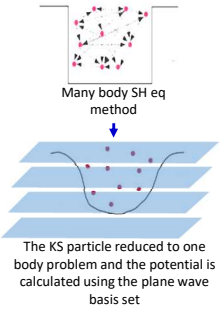
Total energy of our system in terms of which are all functionals of the charge density. These terms are: Ion-electron potential energy, Ion-ion potential energy, electron-electron energy, ***kinetic energy, exchange-correlation energy***.

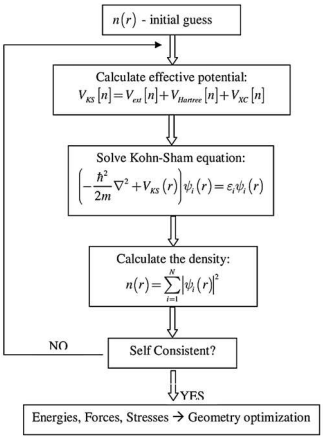
$$E[n] = E_{kin,KS}[n] + E_{Col}[n] + E_{ext}[n] + (E_{kin}[n] - E_{kin,KS}[n]) + E_{xc}[n]$$

$$E[n] = 2\sum_{i=1}^{\frac{N_{el}}{2}} \int \psi_i^*(r)\left(-\frac{1}{2}\nabla^2\right)\psi_i(r)dr + E_{Col}[n] + E_{ext}[n] + \mathrm{E}'_{\mathrm{xc}}[\mathrm{n}]$$

Approximations are sought for $\mathrm{E}'_{\mathrm{xc}}[\mathrm{n}]$ which even though it now contains also contributions from the kinetic energy, it is still just called "Exchange correlation functional







The properties of a system of 10 to 1000 atoms can be calculated using DFT theory

Software and codes

- Vesta
- XCrySDen
- Mercury
- Quantum ESPRESSO
- BURAI – QE GUI
- Elk Code - all-electron full-potential linearised augmented-plane wave (LAPW) code.
- Python and Fortran programming language.
- Gnuplot
- Origin

Computational Facilities

- Personal computer #Used for most of the calculations
  - Processor - 11th Gen Intel(R) Core(TM) i5-1135G7
  - RAM – 16GB (SSD)
  - Operating system – UBUNTU (Linux), Windows 11
  - Cores – 4
  - GPU – 2GB
- Workstation (remote access) - IITH (18 hrs per month)
  - Processor - Intel® Xeon® D-2700
  - RAM – 32 GB
  - Operating system - Red Hat Enterprise Linux
  - Cores – 8 to 20
  - GPU – 8 GB

Properties calculated

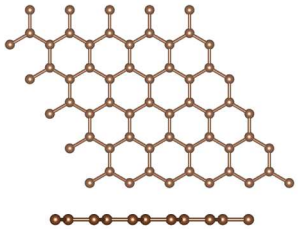
- Structural parameters*
- Bonding *
- Optimized structure*
- Powered XRD pattern*
- Fermi Energy*
- HOMO – LUMO
- Total magnetization
- Pressure and strain
- Total energy*
- Total enthalpy
- Density of states (DOS)*
- High symmetry k- points*
- Electronic band structure*
- Projected density of states (PDOS)
- Absorption spectra
- Linear optical properties
- Non – linear optical (NLO) properties

* Calculated for all the materials

Results – 2D materials

Graphene

Band structure and DOS



a = 2.47 Å
b = 2.47 Å
c = 7.80 Å

α = 90°
β = 90°
γ = 120°

Volume = 41.14 Å^3 Density = 1.93 gcm^{-3}

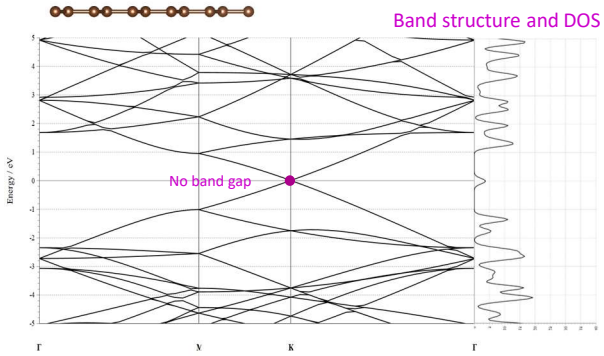
Three of the four outer-shell electrons of each atom in a graphene sheet occupy three sp^2 hybrid orbitals – a combination of orbitals s,p_x and p_y — that are shared with the three nearest atoms, forming σ-bonds.

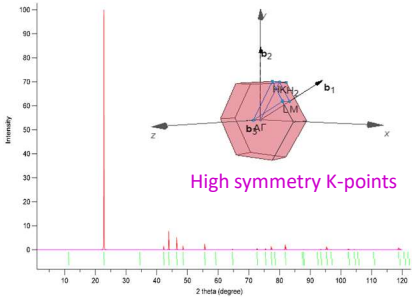
Space group = $P6_3/mmc$ Lattice system : Hexagonal

Fermi energy = 0.597 eV Total energy = -364.64762475 Ry

Band structure and DOS

Bulk modulus (Voigt) = 228 GPa

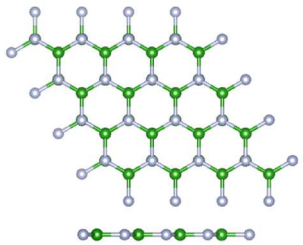




High symmetry K-points

Results – 2D materials

hBN - Boron Nitrate



a = 2.50 Å
b = 2.50 Å
c = 7.37 Å

α = 90°
β = 90°
γ = 120°

Volume = 39.97 Å^3 Density = 2.06 gcm^{-3}

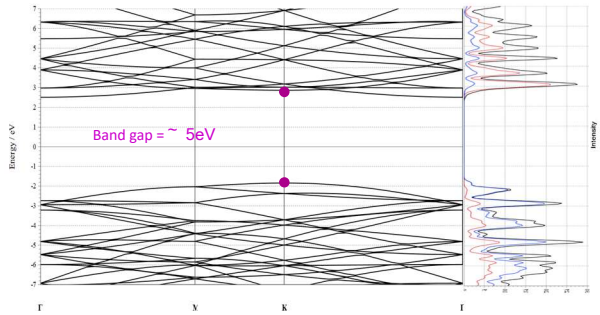
Hexagonal boron nitride has a layered structure similar to graphite. Within each layer, boron and nitrogen atoms are bound by strong covalent bonds, whereas the layers are held together by weak van der Waals forces.

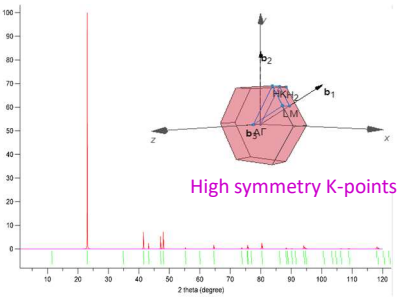
Space group = $P6_3/mmc$ Lattice system : Hexagonal

Fermi energy = 0.557 eV Total energy = -419.52929306 Ry

Band structure and DOS

Bulk modulus (Voigt) = 190 GPa

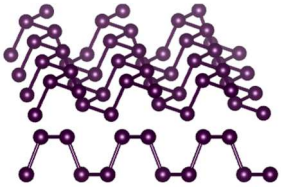


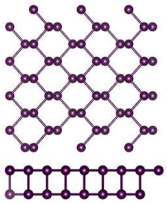


High symmetry K-points

Results – 2D materials

Phosphorene





a = 3.29 Å
b = 10.93 Å
c = 4.54 Å

α = 90°
β = 90°
γ = 90°

Volume = 163.66 Å^3 Density = 2.06 gcm^{-3}

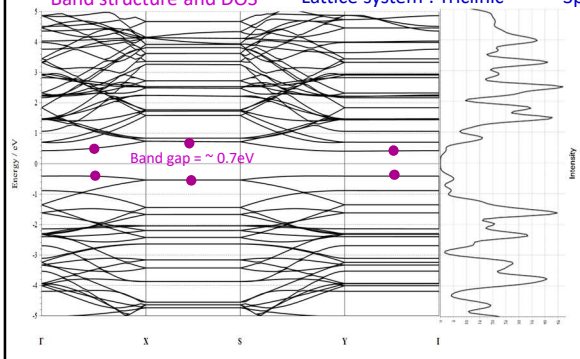
Each P atom in single layer phosphorene is coordinated to three neighboring atoms. The orbital hybridization is sp^3 like, yielding a crystal structure characterized by a puckered honeycomb lattice with a high level of structural anisotropy The edges of the valence and conduction bands are formed from p_z orbitals.

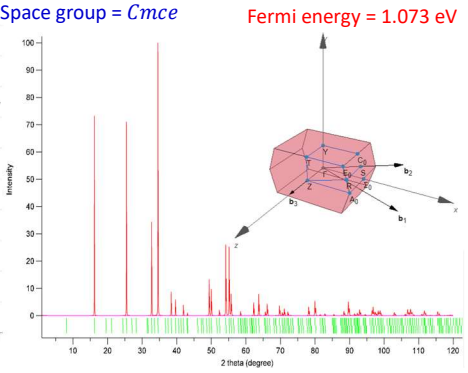
Band structure and DOS

Lattice system : Triclinic

Space group = $Cmce$

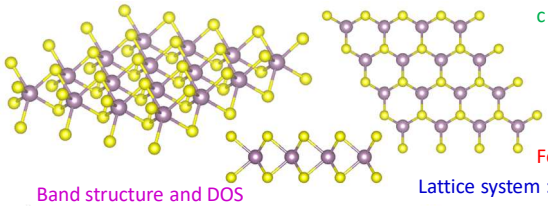
Fermi energy = 1.073 eV





Results – 2D materials

MoS_2 -Transition Metal Dichalcogenides
Molybdenum disulfide



a = 3.19 Å
b = 3.19 Å
c = 13.38 Å

α = 90°
β = 90°
γ = 120°

Volume = 118.07 Å^3 Density = 4.5 gcm^{-3}

A plane of molybdenum atoms is sandwiched by planes of sulfide ions. M atoms are ordered in a triangular lattice, each of them bonded covalently to six X atoms, three of them in the top and three in the bottom layer

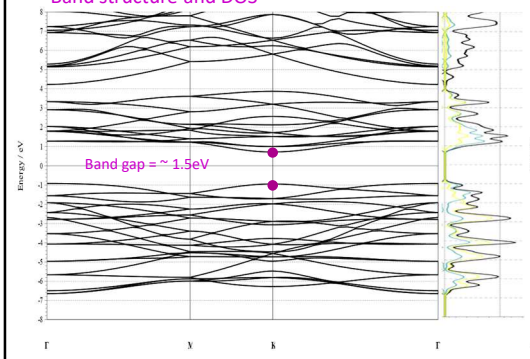
Fermi energy = 2.389 eV

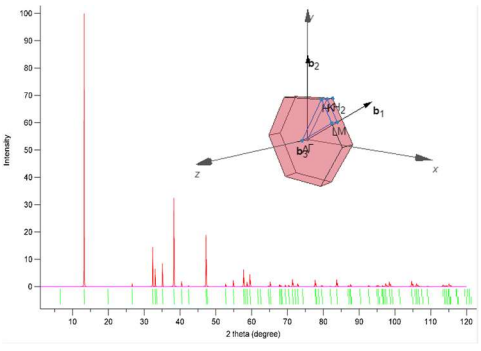
Space group = $P6_3/mmc$

Lattice system : Hexagonal

Bulk modulus (Voigt) = 50 GPa

Band structure and DOS

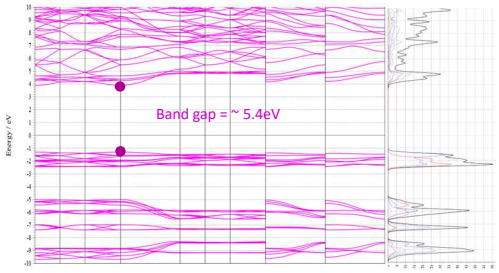


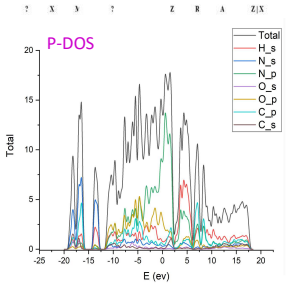


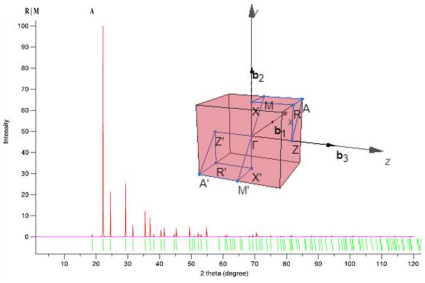
Results – Organic materials

Urea (H_4CN_2O)

Band structure and DOS



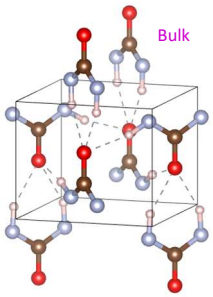




a = 5.56 Å α = 90°
b = 5.56 Å β = 90°
c = 4.65 Å γ = 143.4°

The structure is zero-dimensional and consists of two $CO(NH_2)_2$ clusters. C^{4+} is bonded in a trigonal planar geometry to two equivalent N^{3-} and one O^{2-} atom. Both C-N bond lengths are 1.34 Å. The C-O bond length is 1.27 Å. N^{3-} is bonded in a trigonal planar geometry to one C^{4+} and two H^{1+} atoms. Both N-H bond lengths are 1.01 Å.

Bulk



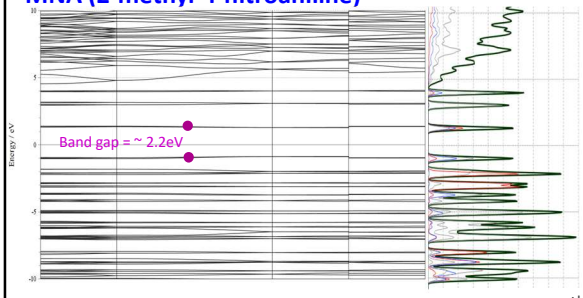
Lattice system : Tetragonal
Space group = $P-4\,2ab$
Volume = 143.40 Å^3
Density = 4.5 gcm^{-3}
Fermi energy = 1.7230 eV
Total energy = -713.21 Ry

Lowest occupied level = 0.2421eV
Highest occupied level = 0.6824 eV

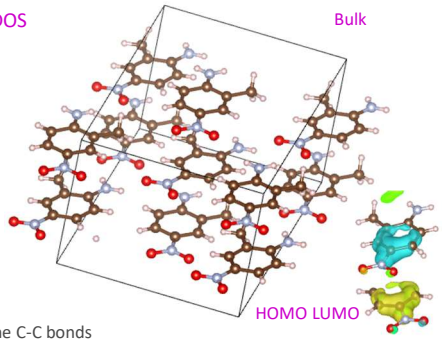
Results – Organic materials

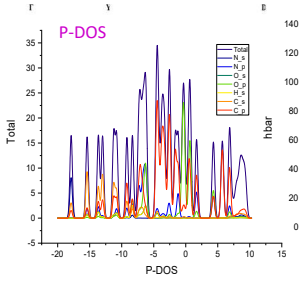
MNA (2-methyl-4-nitroaniline)

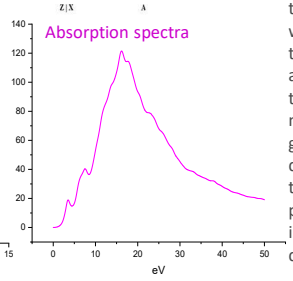
Band structure and DOS



Bulk







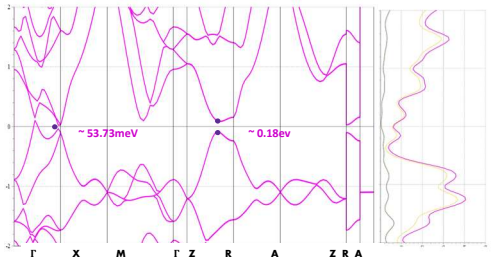
the C-C bonds which are near the amino-group are longer than those which are near the nitro-group .Such differences show that the benzene plays a major role in electron delocalization.

Lattice system : Monoclinic
Space group = Cc ($Unique\ axis\ b$)
a = 10.72 Å α = 90°
b = 11.57 Å β = 130.42°
c = 7.46 Å γ = 90°
Volume = 705.47 Å^3
Fermi energy = 2.1476 eV
Total energy = -785.58 Ry
Lowest occupied level = 4.2974eV
Highest occupied level = 1.6617 eV

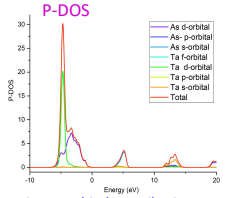
Results – Inorganic materials

TaAs (Tantalum Arsenide)

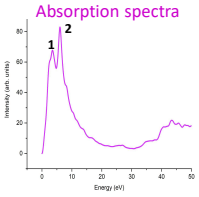
Band structure and DOS



P-DOS

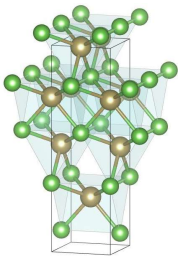


Absorption spectra

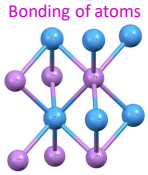


maximum orbital contributions to the band structure are provided by the d-orbital of As and d-orbital of Ta. From the absorption spectra it is seen that there are two distinct peaks at 6 eV (1) and 3.6eV (2), which shows that there is an electronic transition between those two states

Ta^{3+} is bonded to six equivalent As^{3-} atoms. As^{3-} is bonded to six equivalent Ta^{3+} atoms to form a mixture of distorted edge, corner, and face-sharing $TaAs_6$ and $AsTa_6$ pentagonal pyramids.



Bonding of atoms



Weyl semimetal

Total pressure = 218.21 kbar

Total density = 61.80720 $\frac{g}{cm^3}$

Total Bulk Modulus =175 Gpa.

Lattice system : Tetragonal

Space group = $I4_1md$

a = 3.44 Å α = 90°

b = 3.44 Å β = 90°

c = 711.75 Å γ = 90°

Volume = 139.17 $Å^3$

Enthalpy = 4964.33 Ry

Fermi energy = 23.4993 eV

Total energy = 4513.88 Ry

Total stress (Ry/$bohr^3$) =

$$\begin{matrix} -0.00821 & 0.000000 & 0.000000 \\ 0.000000 & -0.01100 & 0.000000 \\ 0.000000 & 0.000000 & 0.023672 \end{matrix}$$

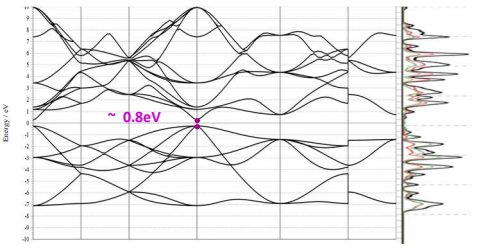
Total pressure (Kbar) =

$$\begin{matrix} -1208.26 & 0.000000 & 0.00000 \\ 0.000000 & -1619.48 & 0.00000 \\ 0.000000 & 0.000000 & 3482.37 \end{matrix}$$

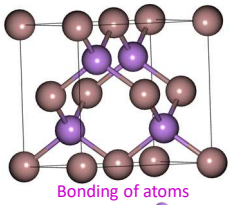
Results – Inorganic materials

GaAs

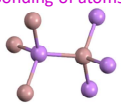
Band structure and DOS



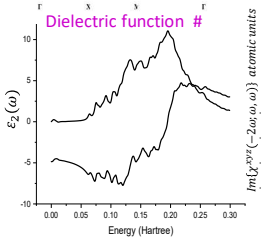
Ga^{3+} is bonded to four equivalent As^{3-} atoms to form corner-sharing $GaAs_4$ tetrahedra. All Ga-As bond lengths are 2.49 Å. As^{3-} is bonded to four equivalent Ga^{3+} atoms to form corner-sharing $AsGa_4$ tetrahedra.



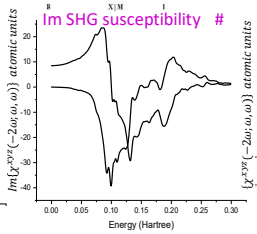
Bonding of atoms



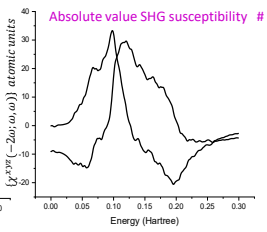
Dielectric function #



Im SHG susceptibility #



Absolute value SHG susceptibility #



Lattice system : Cubic

Space group = $F43m$

a = 5.75Å α = 90°

b = 5.75 Å β = 90 °

c = 5.75 Å γ = 90°

Volume = 190.13 $Å^3$

Total energy = -793.609 Ry

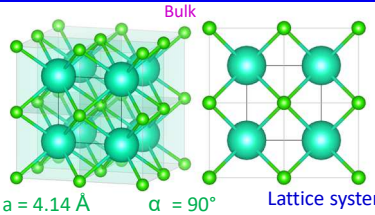
Fermi energy = 7.013 eV

Bulk modulus (Voigt) = 61 GPa

Need to be analysed and confirmed with experimental results

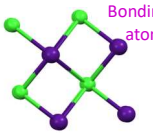
Results – Inorganic materials

Bulk

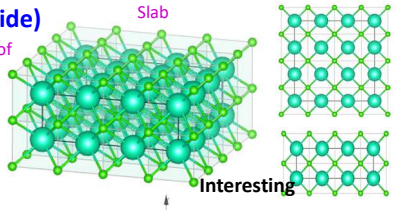


CsCl (Caesium chloride)

Bonding of atoms



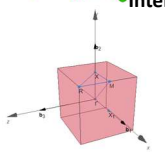
Slab

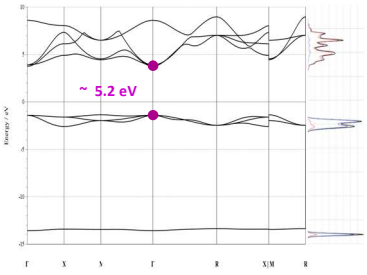


Interesting

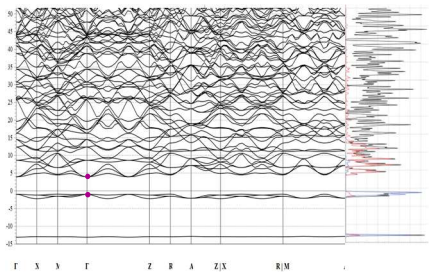
a = 4.14 Å α = 90°
b = 4.14 Å β = 90°
c = 4.14 Å γ = 90°
Volume = 71.15 Å^3

Lattice system : Cubic
Space group = $Pm3m$
Bulk modulus (Voigt) = 15 GPa
Total energy = -33.4510 Ry
Fermi energy = 0.122 eV



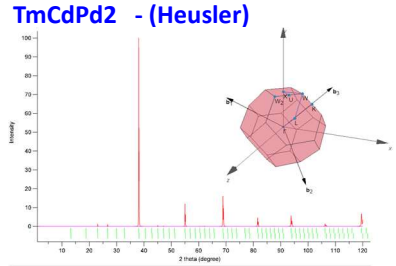


Cs^{1+} is bonded in a body-centered cubic geometry to eight equivalent Cl^{1-} atoms. All Cs-Cl bond lengths are 3.59 Å. Cl^{1-} is bonded in a body-centered cubic geometry to eight equivalent Cs^{1+} atoms.



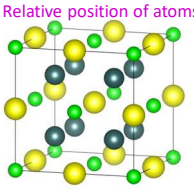
Results – Other materials

TmCdPd2 - (Heusler)

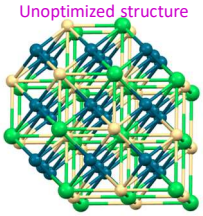


Tm is bonded in a body-centered cubic geometry to eight equivalent Pd atoms. All Tm-Pd bond lengths are 2.89 Å. Pd is bonded in a body-centered cubic geometry to four equivalent Tm and four equivalent Cd atoms. All Pd-Cd bond lengths are 2.89 Å. Cd is bonded in a distorted body-centered cubic geometry to eight equivalent Pd atoms.

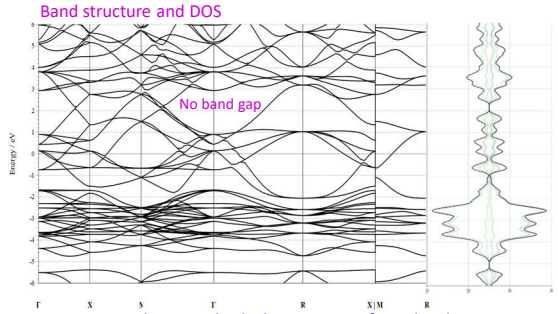
Relative position of atoms



Unoptimized structure

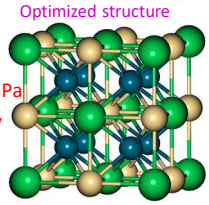


Band structure and DOS



a = 6.67 Å α = 90°
b = 6.67 Å β = 90°
c = 6.67 Å γ = 90°
Volume = 297.02 Å^3

Optimized structure



Lattice system : Cubic
Space group = $Fm3m$
Bulk modulus (Voigt) = 103GPa
Total energy = -1497.24 Ry
Fermi energy = 13.688 eV

NOTE: Just a theoretical calculation not confirmed with any resources

Further work

- To understand the SHG in the organic materials.
- To optimize the code and configure it to the system to perform calculation to avoid memory segmentation problem.
- To calculate the NLO properties (SHG susceptibility) of organic materials and other materials.