First principle calculations of electronic structure and experimental determination of bandgap of $CaWO_4$

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Abstract— The optical properties of CaWO4 were studied in terms of Band Gap, adopting another method. The DFT method showed that the Band Gap was influenced by ionic radii and the electronic configuration of the divalent metal and conventional DFT + U method do not affect the structure of VB and CB, but increases Band Gap. The scheelite structured compounds, having point group symmetry show luminescence with greater energy gap. In this work, the change in the VB and CB levels with an effective variation in the Eg value has been observed. The charge density maps of VB clearly depict the localization of electron clouds with an increase in Hubbard U potential. The correct value of Eg (4.38eV) has been obtained for U_W=7 eV and U_O=3eV, which is supported by Uv-Vis data (Eg= 4.33eV).

Index Terms—Bandgap,$CaWO_4$, DFT, DRS,FMO,HOMO,LUMO and Uv-Vis.

1 INTRODUCTION

Luminescence diverted the attention of researchers for its determinate properties in terms of structure, bandgap, symmetry etc., confirmed with experimental [1-3] and theoretical studies[4-6]. DFT studies revealed the bandgap is sensitive to the ionic radii and the electronic configuration of the divalent metal. The application of the Hubbard U parameter leads to an opening ofa bandgap between VB and CB by localizing the electrons [7].

In particular structures with scheelite configuration and point group symmetry exhibit luminescent properties with a wide energy gap. The focus of work is to estimate the effect of Hubbard parameter U in obtaining correct Eg value.

CaWO4 exhibits tetragonal structure [8] and is a wide band-gap semiconductor with Eg values in the range of 4.1 to 4.5 eV. The structure of calcium tungstate with respective atoms is illustrated in figure 1.

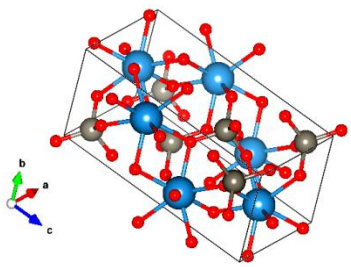


Fig.1.Structure of $CaWO_4$

2 METHODOLOGY

2.1Experimental method

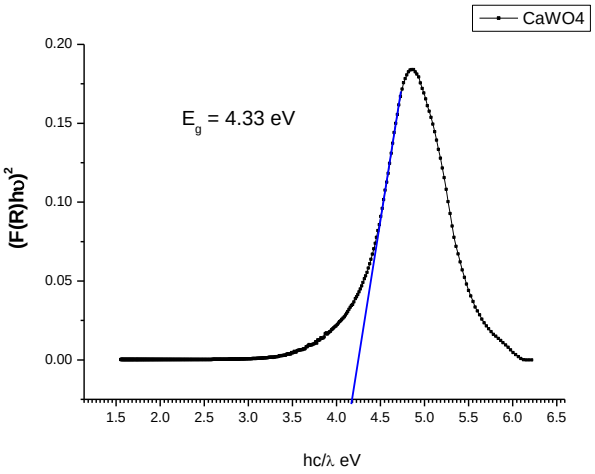
Uv-Vis spectra:

UV-vis (DRS) spectrum of CaWO4is examinedwith the help ofthe Perkin Elmer LAMBDA 950 UV-VIS-NIR Spectrophotometer. Eg has been determined from the Uv-Vis spectrumusing Kubelka and Munk method [9]. The Kubelka–Munk equation is given by

$$F(R_\infty) = \frac{(1-R_\infty)^2}{2R_\infty}$$

where $F(R_\infty)$ is the Kubelka–Munk function or absolute reflectance of the sample.

$CaWO_4$ having scheelitestructureexhibitsa direct bandgap. Therefore in the present case plottinga graph of $[F(R_\infty)h\upsilon]^2$ verses $h\upsilon$ and usingmodifiedKubelka–Munkequation $[F(R_\infty)h\upsilon]^2 = C_2(h\upsilon - E_g)$,E_g of $CaWO_4$ has been determined.



2.2 Computational Method

Computational studies were performed with DFT using a plane-wave method with the selection of Hubbard potential U implemented with Quantum Espresso [10-11].

Density functionals based on the generalized gradient approximation of ultrasoft, PAW based PBE [12] functional optimized for solids and Perdew-Wang (PW) [13] ultra-soft exchange-correlation functional have been considered to estimate the Eg of $CaWO_4$.

An energy cut-off of 680eV, Monkhorst-Pack grids with a 4x4x2 k-point mesh for SCF with occupations = 'smearing' and 8x8x6 k-point mesh for NSCF calculations with occupations = 'tetrahedra' respectively have beenutilized. For band structure calculation 8 special K points along Z-A-M-Γ-Z-R-X-Γ have been chosen.

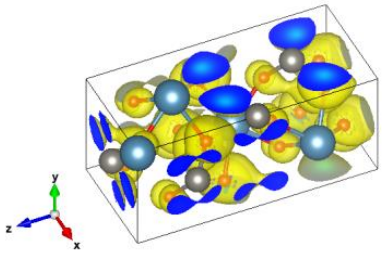
3 Results and Discussion

3.1. Computational studies for Band structure

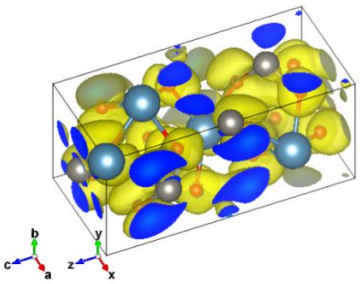
Luminescence diverted the attention of researchers for its determinate properties in terms of structure, bandgap, symmetry, etc., confirmed with experimental [1-3] and theoretical studies [4-6]. DFT studies revealed the bandgap is sensitive to the ionic radii and the electronic configuration of the divalent metal. Conventional DFT+U methods retain the structure of the VB and CB but the bandgap increases [7]. In particular structures with scheelite configuration and point group symmetry exhibit luminescent properties with a wide energy gap. The focus of work is to regulate bandgap with a selection of the Hubbard parameter U within certain limits (usually 4-7 eV).

On observation of geometry, it corresponds to scheelite structure with dense participation of oxygen atoms responsible for optical phenomena resulting in variation in charge distribution.

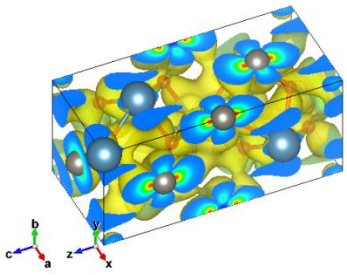
The study of these charge distributions corresponds to the transit of electrons in localized contours specified as Frontier Molecular Orbital's (FMO) contours. These contours are signifying HOMO-electron donation (Blue region) and LUMO- electron acceptance capacity (yellow region) as illustrated in figure 2 for different Hubbard potentials of tungsten with computed parameters listed in table 1.



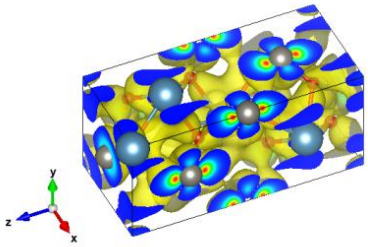
HOMO (pbesol)



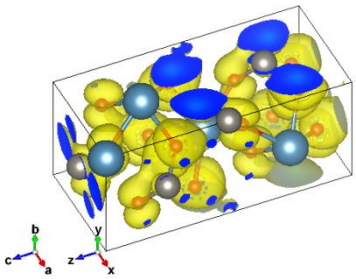
LUMO (pbesol)



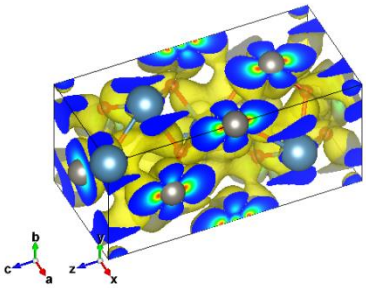
HOMO (pw91, U=0eV)



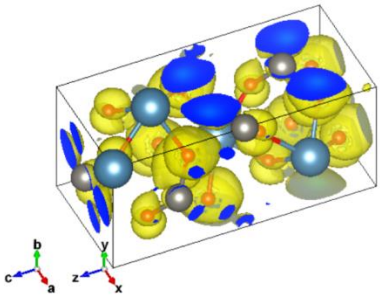
LUMO(pw91, U=0eV)



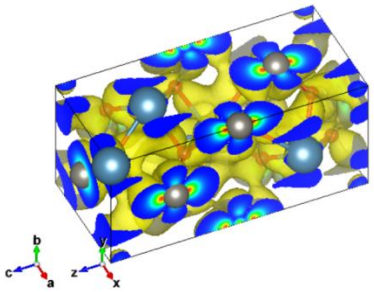
HOMO (pw91 UO=3eV, Uw = 5eV)



LUMO(UO=3eV, Uw = 5eV)



HOMO (pw91 UO=3eV, Uw = 7eV)



LUMO (pw91 UO=3eV, Uw = 7eV)

Fig.2: FMO Contours of CaWO 4

Computational studies are attributed to Hubbard's potential relative to oxygen and tungsten atoms. With no potential to these atoms, charge distribution is not affected attributed to a similar trend in its ionization potential and electron affinities of respective atoms.

The gradient of contours results in charge distribution associating energies E_{HOMO} signifying electron-donating capacity in blue regions and E_{LUMO} to electron acceptor regions in yellow. On observation on contours, there are greater tendency tungsten atoms responsible for energy gap (ΔE).

Changes in Hubbard's potential of respective atoms confirm a slight reduction in the Fermi level with a large change in the energy gap. The change in Hubbard potential of tungsten with 2eV affected charge distribution resulting in electron transfer from occupied states to unoccupied states.

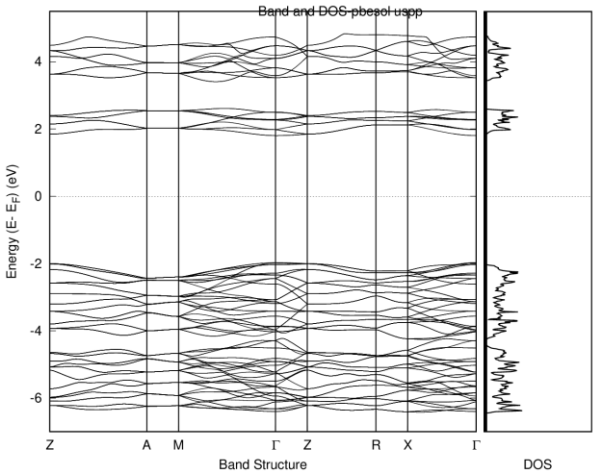


Figure3a $CaWO_4$ Band structure and DOS using pbesol PP without Hubbard U potential

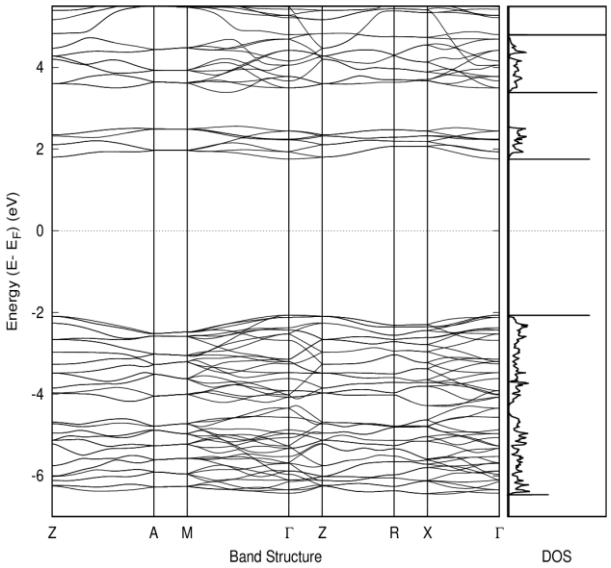


Figure 3b CaWO4 Band structure and DOS using pw91 PP without Hubbard U potential

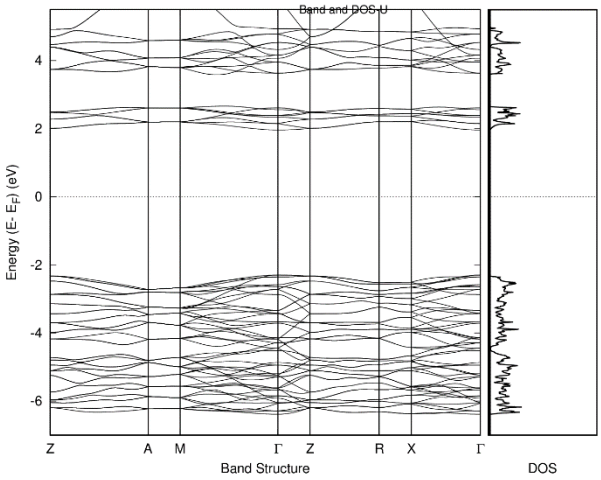
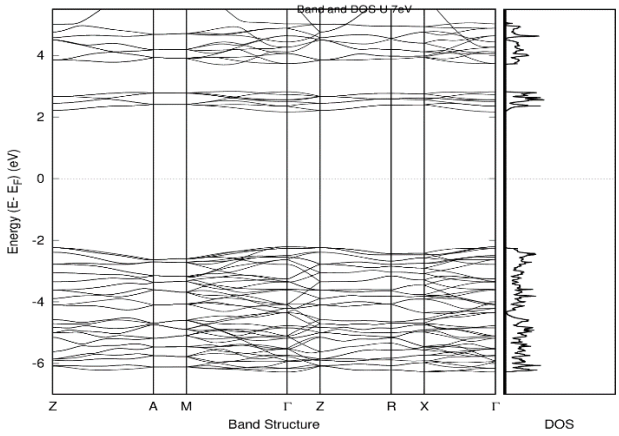


Figure 3c CaWO4 Band structure and DOS using pw91 PP with Hubbard U potential U_O = 3eV and U_W = 5eV

Figure 3d CaWO4 Band structure and DOS using pw91 PPwith Hubbard U potential U_O = 3eV and U_W = 7eV

An increase in energy gap (figures 3a-3d) results with high kinetic



stability and less reactive signify greater participation of oxygen atoms without altering scheelite structure.

Table 1: Computed parameters of CaWO4 for luminescence

S.No	Pseudo potential type	Hubbar U eV		Fermi level (eV)	E_{HOMO} (eV)	E_{LUMO} (eV)	ΔE (eV)
		O	W				
1	pbesol_v1.uspp.F	0	0	8.647	6.641	10.4487	3.8077
2	pw91-nsp-van	0	0	8.4749	6.6864	10.5123	3.8259
3	pw91-nsp-van	3	5	8.3919	6.0918	10.3528	4.261
4	pw91-nsp-van	3	7	8.3441	6.1282	10.5088	4.3806

These studies infer possible changes in charge distribution with bandgap without altering the geometrical structure as illustrated in figure 2 with and without Hubbard potential.

4 Conclusion

The bandgap studies were performed to investigate the optical properties of calcium tungstate compound by using UV-Vis spectra and Diffuse Reflectance Spectroscopy. This work clearly presents that CaWO4 exhibits a direct bandgap.

The investigation of charge distribution can be attributed to the transit of electrons in localized contours, regarded as specified Frontier Molecular orbital s contours which explain HOMO - electron donation contour (Blue Region)and LUMO - electron acceptance contour (yellow region) for different Hubbard potentials. The studies are based on Hubbard potential, relative to O2 and WO4 atoms.

The changes in Hubbard's potential of respective atoms corroborate a slight reduction in Fermi level and large change in energy gap, describing alteration of charge distribution and transfer of electrons from occupied to unoccupied states. The increase in the energy gap

reveals the O_2 atom's participation without affecting the scheelite structure. This study also shows that tungsten atoms are responsible for charge distribution with oxygen atoms responsible for the energy gap confirmed experimentally with UV spectra with less reactivity without altering the structure. These studies point to possible changes in charge distribution in terms of bandgap without any modification in geometrical structure in the presence and absence of Hubbard potential.

ACKNOWLEDGMENT

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