International Research Journal of Engineering and Technology (IRJET) e-ISSN: 2395-0056
Volume: 04 Issue: 12 | Dec-2017 www.irjet.net p-ISSN: 2395-0072

Theoretical Investigation on $Cu_xV_{2-x}O_5$ where x=0, 0.5 Using Density Functional Theory

D. Bala Abarna[1], P. Arun Chakkaravarthi[2], N.Soundarajan[3]

[1]*Assistant Professor of Physics, Department of Chemistry & Physics, Nadar Saraswathi College of Arts & Science, Theni, Tamilnadu, India.*
[2]*Lecturer of Physics, Department of Basic Engineering, Sri Andal Natchiyar Polytechnic College, Cholapuram, Tamilnadu, India.*
[3] *Professor, School of Physics, Madurai Kamaraj University, Madurai, Tamilnadu, India.*

Abstract - *In the present work orthorhombic structured compounds vanadium pentoxide and $Cu_{0.5}V_{1.5}O_5$ were investigated in terms of geometrical and electronic structure. The calculations are based on density functional theory using computational technique Vienna Ab-initio Simulation Package (VASP). The Ultrasoft-Pseudopotential (USPP) with Local Density Approximation (LDA) is used in this work. The minimized energy and lattice parameters are obtained by ionic and volume relaxation. The geometry of V_2O_5 and $Cu_{0.5}V_{1.5}O_5$ is obtained from total energy optimization. The bulk modulus, band gap and cohesive energy of the compounds are also calculated. The lattice parameters are underestimated by approximately 1.26% and the bulk moduli are overestimated. The cohesive energy of $Cu_{0.5}V_{1.5}O_5$ is smaller than V_2O_5 because V_2O_5 is more stable than $Cu_{0.5}V_{1.5}O_5$. The band gap of the material vanished for $Cu_xV_{2-x}O_5$ when x=0.5.*

Key Words: V_2O_5, DFT, LDA, VASP, Bulk modulus, Band gap, cohesive energy.

1. INTRODUCTION

Transition metal oxide materials are eminent for its scientific and technological applications. In particular, vanadium pentoxide has vast applications in many areas and diverse structural, physical and chemical properties. For instance, vanadium pentoxide materials can be widely used as a catalyst in many oxidation reactions [1], due to its high energy density it can be used as a cathode material for lithium ion batteries [2,3] and also used as energy storage devices. Because of its high coefficient of thermal resistance, it is used as a detector material in bolometer. V_2O_5 has been used in several purposes such as gas sensors, electrochromic devices, optical switching devices etc. Because of the massive applications of V_2O_5, many macroscopic and microscopic properties are still under study. Theoretical studies on V_2O_5 include those on its bulk structure using various techniques such as semi-emprical and *ab-initio* methods [4].

Understanding and controlling the properties of matter at the level of individual atoms and molecules is a successful key to scientific progress. Density functional theory (DFT) has proved to be highly successful to predict and describe the structural and electronic properties in vast class of materials ranging from atoms and molecules to simple crystal to complex extended systems. DFT is computationally very simple. Furthermore, DFT is one of the most accuracy and widespread methods for both macroscopic and microscopic levels computational studies of the structural and electronic properties of material [5]. For these reasons, DFT is the most widely used method to calculate many properties of a material. There are many computational packages such as VASP, Quantum Espresso, Gaussian, ABINT, CASTEP etc are available to perform DFT calculations. The VASP (Vienna Abinitio Simulation Package) is a complex package based on DFT of solids. It is used to obtain the structural and electronic properties of small atomic systems. It is also used to calculate total energy, geometry optimization, forces, and optical properties and so on. Reason for choosing the VASP package is it has much capable of yielding very high accuracy for band structure calculations.

Due to the various applications of vanadium pentoxide, many researchers carried out a large number of experimental and theoretical works on the compound V_2O_5 using tight binding method, *ab-initio* full potential linear augmented plane wave method, DFT-HF method with PBE exchange correlation functional, pseudopotential periodic Hartree-Fock method, *ab-initio* in density functional perturbation theory (DFPT) and based on density functional theory within local density approximation (LDA), the energy band, cohesive energy, electronic structure, vibrational numbers and bulk modulus are calculated[4,6-14].

2. STRUCTURAL DETAILS AND COMPUTATIONAL METHODS

V_2O_5 is a layered structure compound. The crystal structure of V_2O_5 orthorhombic i.e. $a \neq b \neq c$ and $\alpha = \beta = \gamma = 90^o$. The unit cell of vanadium pentoxide contains two formula units. The crystal structure of V_2O_5 is shown in the following Figure 1:

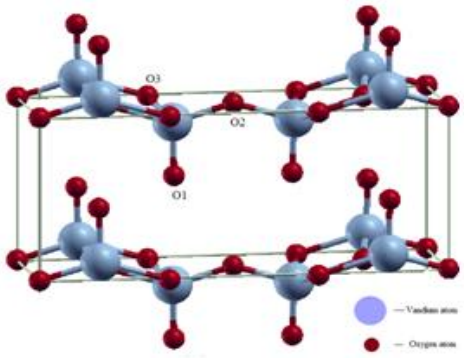

Figure- 1: Crystal structure of vanadium pentoxide

There are three distinct oxygen atoms in V_2O_5 molecule. The oxygen O1 is linked to one vandyl atom only; oxygen O2 links between two vandyl atoms and oxygen O3 is linked to another V_2O_5 molecule. Three types of V-O bonds are recognized. They are covalent vanadyl bond, ionic bond connecting the central vanadium to the chain oxygen and electrostatic Vanderwaals bond which ensures the stacking of the layers [15].

Static minimization is the initial step in the VASP calculation. From this calculation, the total energy can be minimized and the charge density can be calculated. The WAVECAR file produced from this calculation is used for further calculations. To calculate the equilibrium volume (V_0), bulk modulus (B_0) and derivative of the bulk modulus (B_0') with respect to pressure, volume relaxation is used. Before doing volume relaxation, ionic relaxation should carried out. The ionic relaxation and volume relaxation are performed to relax the ions to obtain minimized energy and the optimized lattice parameters can be determined. The bulk modulus can be calculated using the following formula,

$$B_0 = V\frac{d^2E}{dV^2} \quad \text{at } V = V_0$$

The Birch Murunaghan equation of state is used to fit the energy-volume data. The Birch Murunaghan equation is given by,

$$E(V) = E_0 + B_0V_0\left[\frac{1}{B_0'(B_0'-1)}\left(\frac{V_0}{V}\right)^{B_0'-1} + \frac{V}{B_0'V_0} - \frac{1}{(B_0'-1)}\right]$$

By fitting the energy-volume curve, the bulk modulus (B_0) and derivative of the bulk modulus (B_0') can be obtained.

The KPOINT and ENCUT convergences are used to obtain the converged minimized energy. K-point convergence is used to determine the k-point grid which yields the converged total energy. In this work, 4x8x8 k-point grid was chosen. Similarly, encut convergence is used to calculate the cutoff energy which is used to give converged energy which is done by changing the ENCUT value in the INCAR file. A cutoff energy of 400eV was used in this calculation. The self consistent (SC) calculations are used to solve the Kohn-Sham equations. In this calculation, the charge density and the wavefuctions are updated iteratively. The self consistent run is necessary to plot the density of states (DOS) and band structure. The non-self consistent (NSC) run is used for density of states plot and band structure calculation. One of the primary quantities used to describe the electronic state of a material is the electronic density of states DOS. The electronic DOS can be determined by integrating the resulting electron density in k space. For DOS calculation, a large number of k-points are necessary because the details of DOS come from the integrals in k space. For band structure calculation, high symmetry points are used. The high symmetry points along the brillouin zone of the simple orthorhombic lattice are shown in the following Figure 2

The coordinates of high symmetry points are as follows:

Γ:(0,0,0),X:(0.5,0,0),Y:(0,0.5,0), Z:(0,0,0.5),
T:(0,0.5,0.5),U:(0.5,0,0.5), S:(0.5,0.5,0),R: (0.5,0.5,0.5)

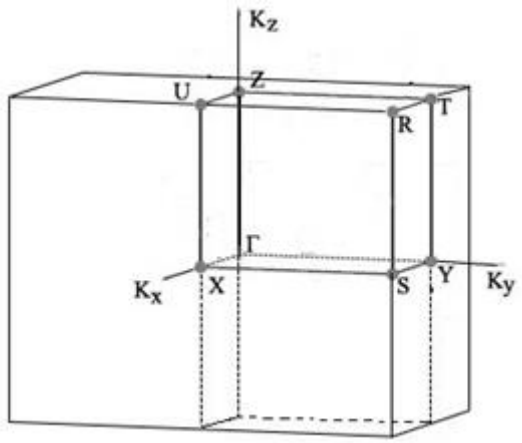

Figure- 2: High symmetry points along brillouin zone of simple orthorhombic lattice

The cohesive energy of a molecule can be determined using the formula,

$$E_{cohesive} = \frac{1}{N_A + N_B}\left\{\left[N_AE_A + N_BE_B\right] - E_{molecule}\right\}$$

Where, N_A and N_B is the number of A atoms and number of B atoms present in the molecule respectively. E_A and E_B is the ground state energy of atom A and B respectively. $E_{molecule}$ is the ground state energy of the molecule.

The crystal structure of V_2O_5 can be visualized using Visualization for Electronic and Structural Analysis (VESTA). The distance between atoms, bond length, bond angle, dihedral angle and interfacial angle can be determined from VESTA. The crystal structure of V_2O_5 visualized using VESTA is shown in Figure 3

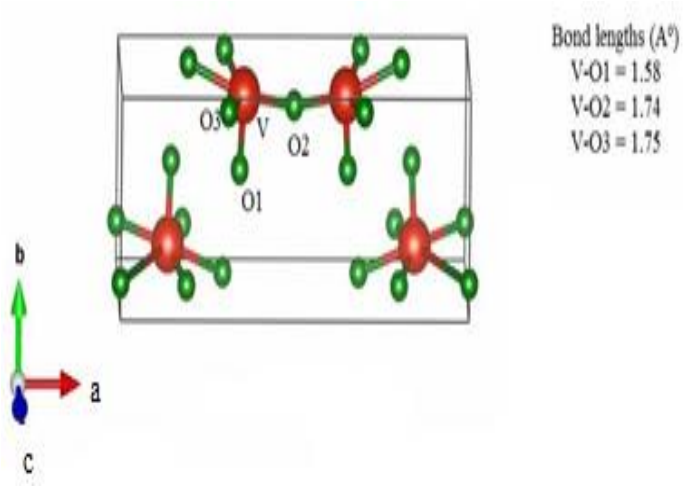

Figure- 3: Crystal structure of V_2O_5

3. RESULT AND DISCUSSION

3.1 INVESTIGATION ON V_2O_5

From the static minimization, the energy of vanadium pentoxide is -120.99 eV. After relaxation, the energy further reduced to -127.16 eV. The following Table 1 compares the calculated cell parameters with theoretical and experimental data.

Table 1: The result compared with experimental and theoretical values.

Cell Parameter	Present work	LDA[16]	GGA[17]	Experiment[18]
a (Å)	11.36	11.70	11.56	11.51
b (Å)	4.31	3.93	4.86	4.37
c (Å)	3.52	3.54	3.58	3.56
V ($Å^3$)	172.19	169.7	201.13	179.06

The lattice constant a is underestimated by 1.3%, b is underestimated by 1.37% and c is underestimated by 1.12%. From the above table, it is concluded that the lattice parameters are underestimated by LDA.

The bulk moduli of V_2O_5 per atom are 34GPa, 35Gpa and 29GPa respectively. These values are overestimated when compared with experimental result of the bulk modulus of V_2O_5 is 18.828GPa per atom [19].

The density of states (DOS) plot for V_2O_5 is shown in fig 4. A very sharp DOS line represents that the atomic orbital does not overlap much with neighboring orbital. Thus the sharp DOS in the left of the figure represents the core states. The density of states near the Fermi level is more important.

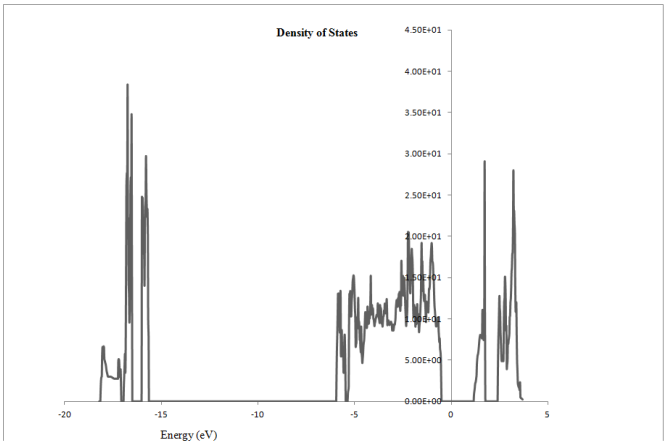

Figure- 4: Total Density of States of V_2O_5

The band structure of vanadium pentoxide is shown in the Figure5

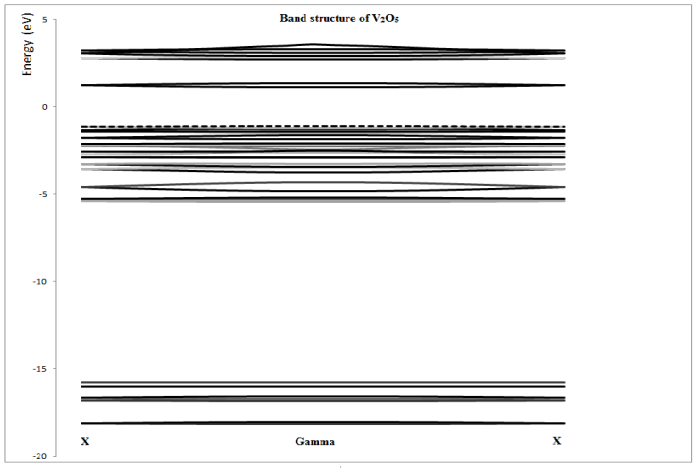

Figure- 5: Band structure of V_2O_5 for the high symmetry point X-Γ-X

In the above figure, the dotted line represents the Fermi level. There is a split in conduction above the Fermi level. These are characteristics of V_2O_5. The widths of these bands are smaller and thus it corresponds to large effective electron masses.

Along this high symmetry path, V_2O_5 exhibits direct band gap of 2.28 eV at Γ. Thus, the obtained band gap value is well agreed with experimental value and previous work.

The obtained cohesive energy for vanadium pentoxide is 8.67eV. It agreed with the experimental value. In formula units, the cohesive energy of V_2O_5 is 58.87eV/fu [12] is agreed with the calculated the cohesive energy of vanadium pentoxide is 59.09eV/fu. Thus, the calculated cohesive energy is agreed with previous work. The experimental value of the cohesive energy of V_2O_5 is 7.94 eV. The calculated values are smaller than the experimental value.

3.2 INVESTIGATION ON $Cu_{0.5}V_{1.5}O_5$

From the static minimization, the energy of $Cu_{0.5}V_{1.5}O_5$ is -111.42 eV. After volume relaxation, the energy further reduced to -111.96 eV. When compared with vanadium pentoxide, the energy of $Cu_{0.5}V_{1.5}O_5$ is high because V_2O_5 is more stable than $Cu_{0.5}V_{1.5}O_5$. The lattice parameters of $Cu_{0.5}V_{1.5}O_5$ are slightly varied from that of vanadium pentoxide which is shown in the Table 2:

Table- 2: comparison of results obtained from V_2O_5 & $Cu_{0.5}V_{1.5}O_5$

Parameters	$Cu_{0.5}V_{1.5}O_5$	V_2O_5
a (Å)	11.37	11.36
b (Å)	4.28	4.31
c (Å)	3.52	3.52
V (Å^3)	171.3	172.19
E (eV)	-111.96	-127.16

The bulk modulus obtained for $Cu_{0.5}V_{1.5}O_5$ by varying a, b and c values are 388GPa, 416GPa, 352GPa respectively.

The density of states (DOS) plot for $Cu_{0.5}V_{1.5}O_5$ is shown in Figure 6.

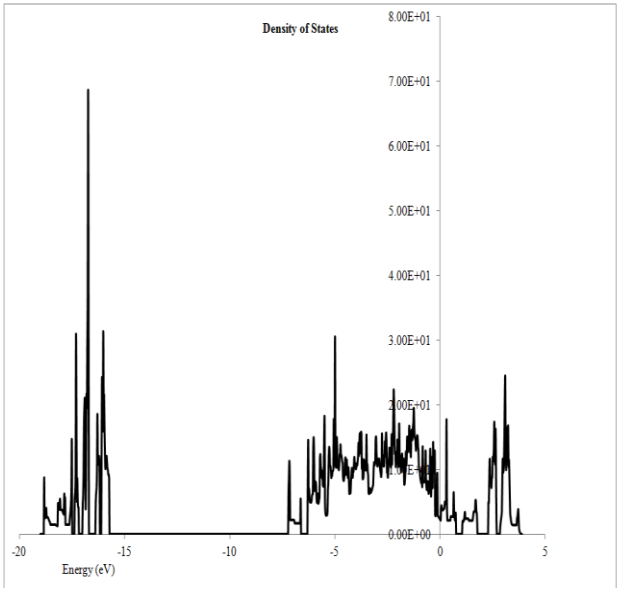

Figure- 6: Total DOS plot of $Cu_{0.5}V_{1.5}O_5$

The very sharp line in the left of DOS plot represents the core electrons. For $Cu_{0.5}V_{1.5}O_5$ there is no gap between the valence band and conduction band. When the composite Cu atom replace vanadium atom in vanadium pentoxide, the band gap destroyed and it becomes conductor.

The band structure of $Cu_{0.5}V_{1.5}O_5$ is plotted in the following Figure 7.

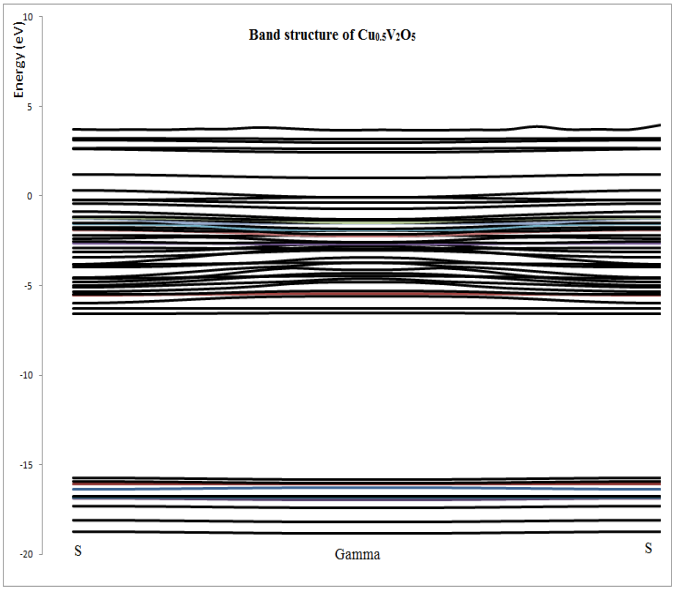

Figure- 7: Band structure of $Cu_{0.5}V_{1.5}O_5$ for the high symmetry point S-Γ-S

The band structure of $Cu_{0.5}V_2O_5$ along the body diagonal direction in the brillouin zone S-Γ-S is shown the figure. In $Cu_{0.5}V_{1.5}O_5$ band structure, the valence band and conduction band are not separated shown in figure. The band gap of $Cu_{0.5}V_2O_5$ is destroyed. There is an overlap of valence band and conduction band which results in high conductivity.

The calculated cohesive energy for $Cu_{0.5}V_{1.5}O_5$ is 7.5897eV. The cohesive energy for vanadium pentoxide is 8.67eV. Thus, vanadium pentoxide is more stable than $Cu_{0.5}V_2O_5$ because V_2O_5 required more energy to break the molecule than that of $Cu_{0.5}V_2O_5$.

4. CONCLUSIONS

The geometrical and electronic properties of orthorhombic structured compound vanadium pentoxide and $Cu_{0.5}V_2O_5$ were investigated using density functional theory local density approximation. The lattice parameters of the material were determined and compared with theoretical and experimental results. The bulk modulus of the compounds were calculated and compared with previous work. The cohesive energy of the V_2O_5 and $Cu_{0.5}V_2O_5$ were estimated and compared with experimental values and previous results. The calculate values reveals that the lattice parameters are underestimate, the bulk modulus is overestimated by LDA and yields approximately accurate results for band gap and cohesive energy.

ACKNOWLEDGEMENT

Valuable guidance and discussions from Prof. Dr.N.Soundarajan and Ms.M.Suganya are gratefully acknowledged.

REFERENCES

[1] Gellings P J G Webb and G C Bond, London: The Royal Society of Chemistry, Catalysis vol 7, ed, 1985.

[2] Guicun Li, Shuping Pang,Li Jiang,Zhiyan Guo, and Zhikun Zhang, J. Phys. Chem. *B*, 110 (19), pp 9383–9386, 2006.

[3] An-Min Cao, Jin-Song Hu, Han-Pu Liang and Li-Jun Wan Prof. Dr. , Angewandte Chemie International Edition, Volume 44, Issue 28, pages 4391–4395, July 11, 2005.

[4] Chakrabarti, K.Hermann, R. Druzinic, M.Witko, F.Wagner and M.Peterson, Physical review B, 59, 16, 1999.

[5] Elisa Londero and Elsebeth Schröder, Computer Physics Communications 182, 1805–1809, 2011.

[6] W. Lambecht, J.Phys. C: Solid State Phys. 13, 2485-501 1980.

[7] V. Eyert, K.H.Hock, Physical review B 57, 12727 1998.

[8] Thomas Reeswinkel, Denis Music and Jochen M Schneider, Journal of Physics: Condensed matter, 21, 145404 2009.

[9] Vitaly V. Porsev, Anderi V. Bandura, Robert A. Evarestor, Acta materialia, 75, 246-258 2014.

[10] W. Lambecht, J.Phys. C: Solid State Phys. 13, 2503-17 1980.

[11] P. Hejduk, M. Witko and K.Hermann, springer, 10, 2009.

[12] Xavier Rocquefelte, Florent Boucher, Pascal Gressier and Guy Ouvrard, Chem.Matter, 15, 1812-1819 2003.

[13] Bo Zhou, Su Qing and DeYan He, Chinese Physics B 39, 1475-1481 2008.

[14] D.K. Chakarabarthy, Dipak Guha and A.B. Biswas, Journal of Material Science, 11**,** 1347-1353 1976.

[15] J.Y. Kempf, B.Silvi, A.Dietrich, C.R.A.Catlow and B.Maigret, Chem.Matter, 5, 641-647, 1993.

[16] L.F. Da Silva, V. Ganduglia-Pirovano, J.Sauer Physical Review B, 76**,**125117 2007.

[17] T. Bucko, J.Hafner, S.Lebegue, J.Anryan, J.Phys. Chem. A, 114**,** 11814 2010.

[18] R. Enjalbert, J. Galy, Acta Crystallogr. Sect. C: Cryst.Struct. Commun. 42, 1467 1986.

[19] J.M. Gallardo Amores, N. Biskup, K Pearson, G. Ceder and E. Morian, chem.Matter, 19, 5262, 2007.

BIOGRAPHIES

D.Bala Abarna, Assistant Professor of Physics, Department of Chemistry & Physics, Nadar Saraswathi College of Arts & Science, Theni, Tamilnadu, India.

P.Arun Chakkaravarthi, Lecturer of Physics, Department of Basic Engineering, Sri Andal Natchiyar Polytechnic College, Cholapuram, Tamilnadu, India.