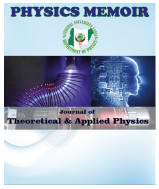

PHYSICS MEMOIR
Available online @ http://jtap.physicsmemoir.com.ng

Phys. Memoir 1 (2019) 106–112

Journal of Theoretical & Applied Physics

Original Research

Structural and Electronic Properties of Delafossite $CuGa_{1-x}Mn_xO_2$(X=0.5) Nanocomposite: A First Principle Study

S. S. Alhassan[a,*], A. Shuaibu[b], M. Y. Onimisi[c]

[a]*Department of Physics, Umaru Musa Yaradua University, Katsina State, Nigeria*
[b]*Department of Physics, Kaduna State University, Kaduna State, Nigeria*
[c]*Department of Physics, Nigerian Defence Academy, Kaduna State, Nigeria*

Abstract

In this paper, we investigate the structural and electronic properties of manganese doped delafossite $CuGaO_2$ nanocomposite using first principle study based on density functional theory (DFT). The generalised gradient approximation (GGA) as parameterized by Perdew-Burke-Ernzerhof (PBE) has been used for both the undoped and doped systems. The crystal structure of the material does not change after manganese doping. Our calculation shows that the doped structure is stable. However, the results reveal that the 50% Mn doping decreases the band gap of the delafossite $CuGaO_2$ system by 0.5 eV. The charge density distributions for the undoped $CuGaO_2$ and $CuGa_{1-x}Mn_xO_2$(X=0.5) are almost the same.

Keywords: Delafossite, Density Functional Theory, Electronic Properties, Doping, Manganese, Nanocomposite

Article History:
Received 5 March 2019
Received in revised form 23 April 2019
Accepted for publication 25 April 2019
Published 19 May 2019

1. Introduction

The fundamental aspects and applications of Transparent conducting oxide (TCO) have become an important field of research in material sciences and solid state physics. Because,these materials have variety of applications that include, but are not limited to: dye solar cells,flat panel displays (FPDs), low-emissivity (low-e) windows [1, 2]. But, little works have been done especially in the fabrication of junction devices. This is because most of the reported TCOs are n-type semiconductors, the p-type counterpart that are necessary in fabricating the active devices were missed for a long time. It was in 1997, when Kawazoe and co-researchers reported the p-type conductivity in

*Corresponding author tel. no: +2347035265877
Email address: danmaigauta39@gmail.com (S. S. Alhassan)

a transparent thin film of $CuAlO_2$ [3]. This has resulted in many research interests on the copper-based delafossite group which have a general formula $CuMO_2$ (M = Al, Ga, In). The family exhibits an intrinsic p-type conductivity and wide band gap.

Delafossite $CuGaO_2$ is one of the most important copper-based delafossite materials. But one major challenge facing this material that need to be solved before it can be used for more diverse applications is the low concentration of the charge carriers. Substitutional doping has been reported to be the best way of solving the problem [1]. In view of this, a lot of works were reported using different dopants and methods. Tate and his co-researchers reported a heavy doping of $CuGaO_2$ by Fe^{3+} in Ga sites [6]. Both the polycrystalline powder and thin film of $CuGa_{1-x}Fe_xO_2(0\leq x\leq 1)$ have shown p-type conductivity and the Fe doping has increased the conductivity of the film. Moreover, a substitutional doping of Cr atom in the Ga site of delafossite $CuGaO_2$ was reported using sol gel method [7]. It was found that the Cr-substituting induced the increase of the films roughness, changed the films internal structure and made more crystal defects and grain boundaries. The effect of Mg doping was reported [8], their results showed that after Mg doping, the optical band gap is red-shifted 0.15 eV and the conductivity was increased one order of magnitude, indicating the real p-type doping of the material. However, Al-doped $CuGaO_2$ has been synthesized by hydrothermal method and its properties have been investigated as cathode elements in ruthenium dye N719-sensitized solar cells [9]. Recently, T. Y. Chien and C. L. Ching investigated the effects of the two dopants (Mg and Zn) on the structural features and electrical properties of the $CuGaO_2$-based thin films using sol-gel spin coating method [10]. The Zn-doped thin films had the highest mean carrier concentration of $3.49 \times 10^{16} cm^{-3}$.

Most of the works reported in relation to the doping of this material are experimental based; the theoretical studies are very scarce. But many theoretical works were reported all trying to explain some important properties of the delafossite $CuGaO_2$ [11, 12, 13, 14]. Therefore, the main aim of this work is to carry out a theoretical investigation on the structural and electronic properties of the manganese doped $CuGaO_2$ using first principle study within the framework of Density Functional Theory (DFT).

2. Computational Methods

We performed the calculations on the 2×2 supercell relative to the primitive cell of delafossite $CuGaO_2$ using first principle calculation based on density functional theory (DFT), as implemented in the QUANTUM ESPRESSO code [15]. The generalized gradient approximation (GGA) as parameterized by Perdew-Burke-Ernzerhof [16] scheme has been employed in approximating the exchange-correlation potential for the undoped and Manganese doped $CuGaO_2$ materials. The plane wave basis sets with the maximum kinetic energy cut-off of 340 eV has been used in expanding the wave functions. The electron-ion core interaction is treated by ultrasoft pseudo potentials for Cu($3d^{10}4s^1$), Ga($3d^{10}4s^24p^1$), O($2s^22p^4$) and Mn($3s^23p^63d^54s^2$) valence orbitals as all in the pseudo potential files. For integrals, smearing has been adopted and specifically Maxfessel-Paxton smearing method with small Gaussian spreading of 0.02Ry has been used. The brillouin zone integration is performed using Monkhorst-Pack scheme [17] with $10\times10\times1$ k-points grids.

The 2×2 supercell used contains four Gallium (Ga) atoms, in such a way that, during the substitutional doping, two Ga atoms were replaced by two different atoms of manganese (Mn) and this corresponds to 50% Mn doping in the Ga-atomic sites of the delafossite $CuGaO_2$. The supercell dimensions are kept fixed throughout the calculations, while the atomic positions are fully relaxed for all calculations using Broyden-Fletcher-Golfarb-Shannon (BFGS) algorithm, until the forces acting on the atoms are below 0.001 eV/Å. The calculated charge density and electronic densities of states are found using denser k-point mesh.

3. Results and Discussions

3.1. Structural Propersties

The primitive unit cell of the delafossite $CuGaO_2$ has a rhombohedral crystal structure as shown in Figure 1 with space group of $R\bar{3}$ m. The simple primitive cell contains only one gallium atom, this means that substitutional doping cannot be performed on it, since the doping is going to be in the gallium atomic site. That is why; a 2×2 supercell relative to the primitive unit cell was constructed as shown in Figure 1(a). The supercell consists of four gallium atoms. The optimized crystal parameters of the supercell are a = 12.06Å, b = 12.06Å, c = 6.030Å, and $\alpha = \beta = \gamma = 28.937^o$.

However, after the manganese doping, there was no structural transition, this is because the arrangement of the atoms in the crystal lattice of the undoped material is not altered as a result of the substitutional doping performed, therefore the structure was still delafossite and as such the crystal parameters remained the same as that for the undoped system.To find the stability of the doped structure, the dopant formation energy of the manganese atom is estimated using equation (1.0) [18]. The dopant formation energy here simply refers to the energy required to insert one manganese atom with a chemical potential μ_{Mn} into the supercell after removing one gallium atom from the same position [19].

$$E_f = E_{doped} - E_{undoped} + \mu_{Ga} - \mu_{Mn}, \tag{1}$$

where, E_{doped} is the DFT total energy of the $CuGa_{1-x}Mn_xO_2$ material, $E_{undoped}$ is the DFT total energy of the undoped $CuGaO_2$ system, μ_{Ga} is the chemical potential per atom of gallium bulk crystal, μ_{Mn} is the chemical potential per atom of manganese bulk crystal. The chemical potentials are calculated as the DFT total energy per atom in the bulk systems [18, 20]. The dopant formation energy of manganese is calculated to be 57.22Ry. Moreover, the formation energy serves as the measure of the stability of the doped structure; the lower value of the formation energy signifies the most stable structures [19]. From this value of dopant formation energy, it can be stated that the manganese doped $CuGaO_2$ is stable.

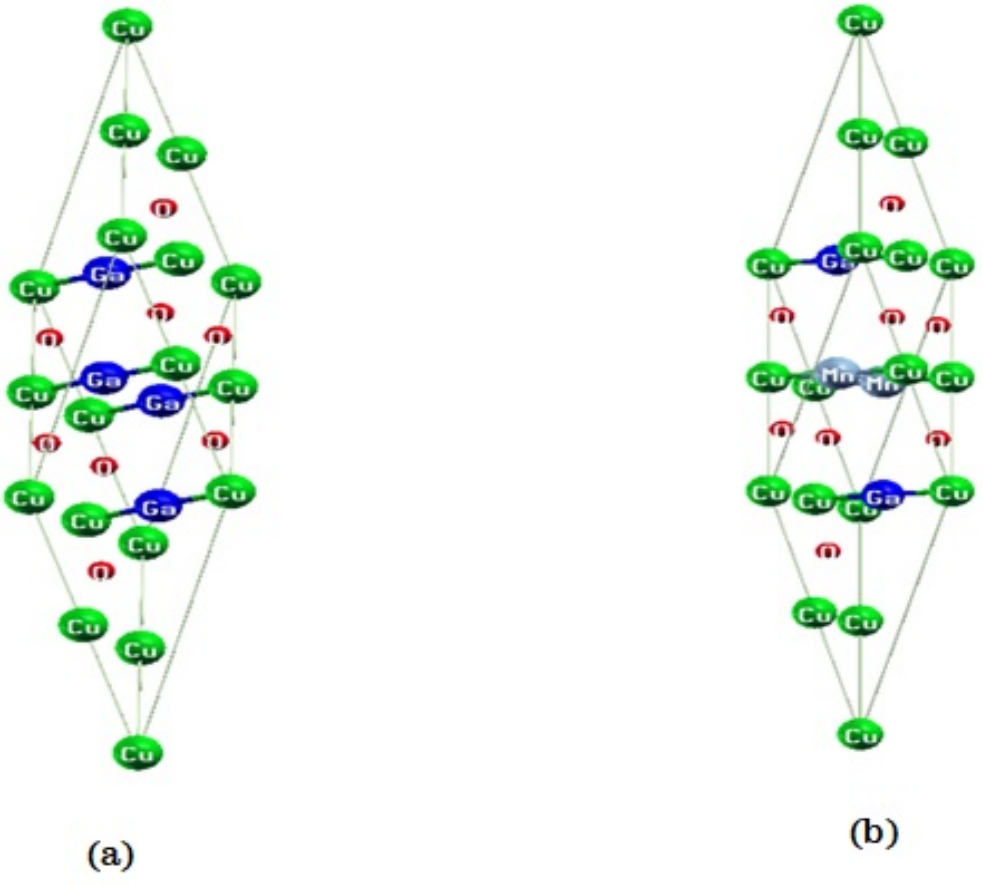

Figure 1. (a) The 2×2 supercell relative to primitive cell DFT-GGA optimized crystal structure of delafossite $CuGaO_2$. (b) The 2×2 supercell relative to primitive cell DFT-GGA optimized crystal structure of $CuGa_{1-x}Mn_xO_2$(X=0.5)

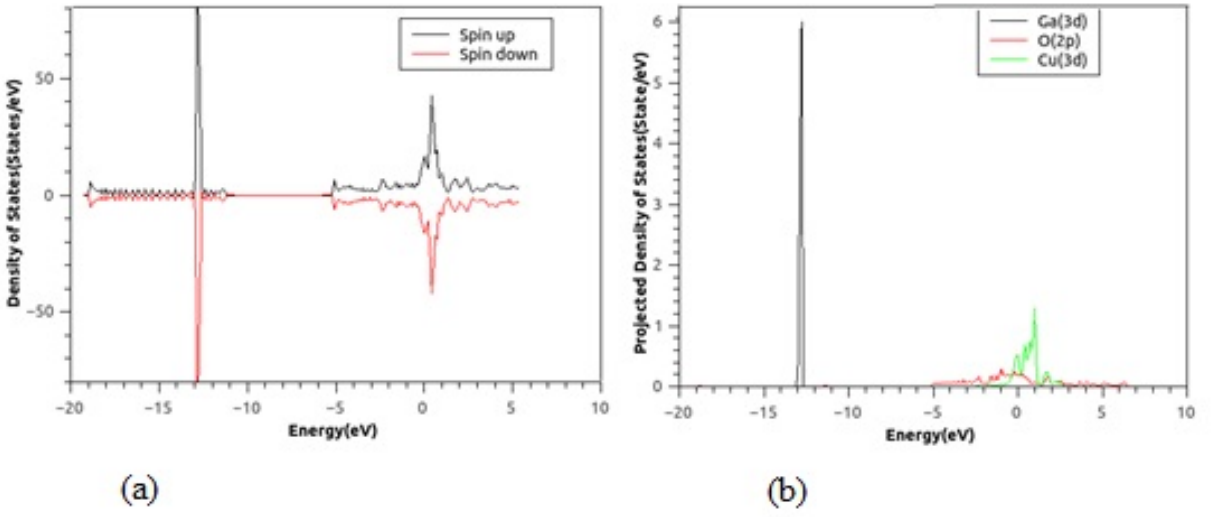

Figure 2. (a) The spin-polarized density of states for the undoped delafossite $CuGaO_2$ (b) The projected density of states for the undoped $CuGaO_2$

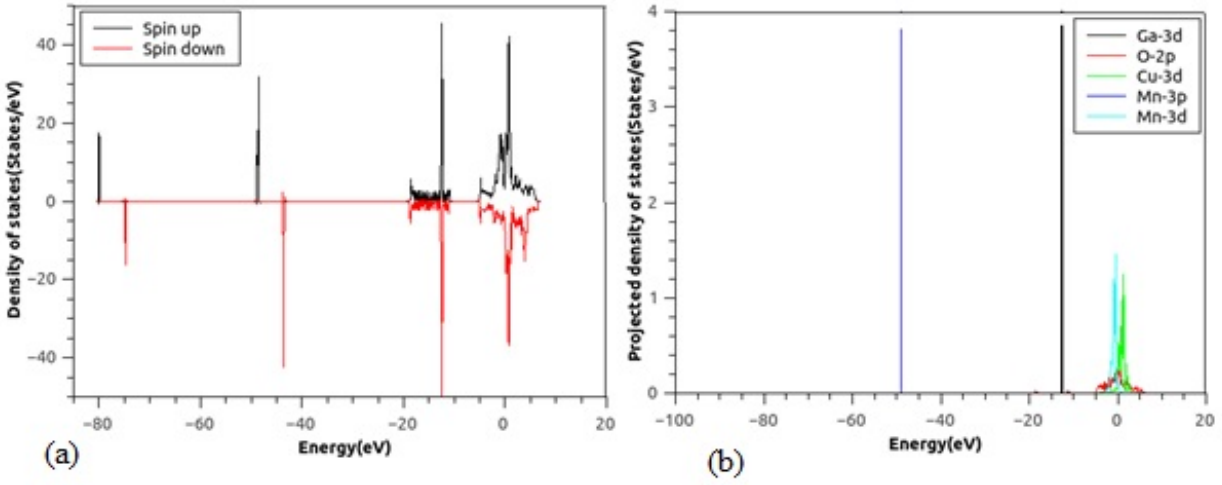

Figure 3. (a) The spin-polarized density of states for the $CuGa_{1-x}Mn_xO_2$(X=0.5) (b) The projected density of states for the $CuGa_{1-x}Mn_xO_2$(X=0.5)

3.2. Electronic Properties

The electronic properties of delafossite $CuGaO_2$ and $CuGa_{1-x}Mn_xO_2$(x=0.5) are explained based on the density of states, projected density of states and charge density distribution. From Figure 2(a), the DOS plot clearly explained the number of states per each energy level available for occupation of the undoped delafossite $CuGaO_2$. It also indicates that there is a sharp peak at the -12.85 eV in the valence band which translates to very high states available for occupations at this particular energy.

From left of this sharp peak, are some small peaks with almost same states. Moving right to this sharp peak again, are some few peaks whose onsets disappear between -11.10 eV and -5.10 eV. The total DOS is zero between these intervals, meaning that there are no available states for occupation. This is regarded as the forbidden gap. The

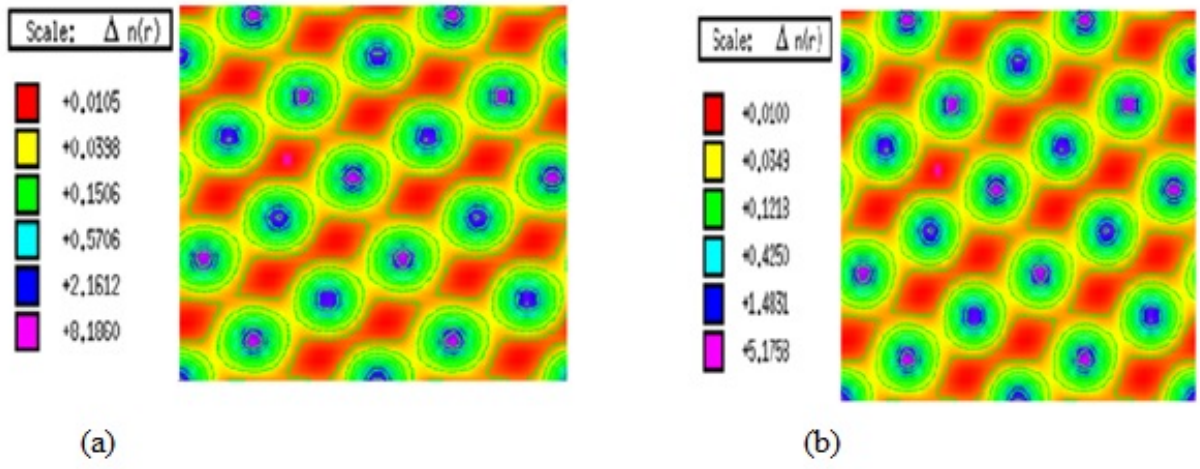

Figure 4. (a) The charge density plots for the undoped delafossite $CuGaO_2$ showing oxygen, copper and gallium atoms in red, green and purple colours respectively. The scale n(r) signifying ranges of isodensity values in atomic unit (a.u) (b) The charge density plots for the $CuGa_{1-x}Mn_xO_2$(X=0.5) showing oxygen (red), copper (green), gallium (purple) and manganese (light blue) atoms

calculated value for this gap is 6 eV. The onset of some peaks appears close to the top of the valence band. The allowable conduction band states start at around 0.0 eV.

However, from Figure 2(b), it can be deduced that the sharp peak in the valence band seen in the DOS plot is a contribution from Ga 3d orbital. The bottom of the valence band is dominated by Ga 3d states with a minor contribution from O 2p states. At the top of the valence band, Cu 3d states are dominant with some mixing O 2p states, as it is expected from Cu (I) oxide based compounds [21]. The bottom of the conduction band consists of a mixture of Cu 3d states and O 2p states which is similar to that of the $CuAlO_2$ and $CuBO_2$ [21, 22]. There is a strong hybridization between Cu 3d and O 2p states in the conduction band.

From Figure 3(a), it is seen that the DOS plot for Mn doped $CuGaO_2$ contains three sharp peaks (all at the bottom of the valence band) at various energies values of -80 eV, -44 eV and -12.9 eV, meaning that there are more states available for occupation at these energies. The one at -12.9 eV is similar to the one seen in the undoped $CuGaO_2$ states. Moving by the right side of the third sharp peak, are short peaks whose onset disappears between -10.5 eV to -5.0 eV which implies that no available states for occupation at this interval. The calculated value for the band gap is 5.5 eV. Another sharp peak is observed at 1.5 eV in the conduction band.

In Figure 3(b), the projected density of states plot of Mn doped $CuGaO_2$, it can be understood that the additional sharp peaks seen in the DOS plot (Figure 3(a)), are due to the Mn 3p states. There are minor contributions from O 2p states around the sharp peak (third one). The top of the valence band is dominated by Mn 3d and O 2p states with minor contributions from Cu 3d states. There is also strong hybridization between Mn 3d and O 2p states and similarly between Cu 3d and O 2p states at this stage. Whereas, the bottom of the conduction band is mainly dominated by Cu 3d states and O 2p states with minor contribution from Mn 3d states. It can be deduced that, the manganese states largely contribute to the valence band states.

However, Figure 4(a) shows the mixed p and s orbitals on the Cu ions and the p-like nature of the density on the oxygen atoms, with the Ga s-orbital just visible. So, Ga-O makes ionic bonding due to the transfer of charge from Ga to O atoms. It can be seen that, oxygen atom has a weaker charge density; this is deduced from the charge density colour scale. Again, from the charge density scale, it is clear that, the purple colour corresponds to the maximum charge accumulating site, as such; gallium atoms have the greater charge density than other atoms. Figure 4(b) is similar to the Figure 4(a), only that Mn states are also visible on some of the contours.

4. Conclusion

First principle study was reported within the framework of density functional theory implemented in the QUANTUM ESPRESSO simulation package on the structural and electronic properties of manganese doped delafossite $CuGaO_2$.

First of all, about the structure of the doped system, it was found that the structure is stable against decomposition after manganese doping. This is deduced from the value of the calculated dopant formation energy for the manganese atom.

Also, on the electronic properties of the doped material, it was found that, there is a decrease in the band gap of the doped system. That is to say, the Mn doping reduces the band gap of the undoped delafossite $CuGaO_2$. Reducing band gap simply leads to the increase in the conductivity of the material. Even though, the DFT-GGA is not a good predictorof both fundamental and optical band gaps, but it is possible to make a qualitative statement regarding the effects of dopant [23, 24]. Therefore, the general trend is that, doping decreases the band gaps and it is expected to be maintained even when more powerful methods (such as GW) are used. However, the results revealed that, the Mn doping contributes more to the valence band states. The charge density distributions for the undoped $CuGaO_2$ and $CuGa_{1-x}Mn_xO_2$(x=0.5) are almost the same, except for the doped system which includes additional charges from Mn atom. The gallium atom was found to have the highest charge density when compared with the other elements in the materials while oxygen has the least charge density.

Conclusively, based on our results, it can be predicted that the Mn doping is feasible and will considerably increase the conductivity of the delafossite $CuGaO_2$.

Acknowledgment

The support of Umaru Musa Yaradua University, Katsina is hereby acknowledged. All the figures showing crystal structures were generated using the XCrySDen Program. We thank the referees for the positive enlightening comments and suggestions, which have greatly helped us in making improvements to this paper.

References

[1] A. N. Banerjee & K. K. Chattopadhyay, "P-type Transparent Semiconducting Delafossite $CuAlO_{2+x}$ Thin Film: Promising Material for Optoelectronic Devices and Field-Emission Displays", Materials Science Research Trends (2008) 1.

[2] A. Renaud, B. Chavillon, L. Le Pleux, Y. Pellegrin, E. Blart, A. Boujtita, T. Pauport, L. Cario, S. Jobic & F. Odobel, "$CuGaO_2$: A Promising Alternative for NiO in p-type Dye Solar Cells", Journal of Material Chemistry **22** (2012) 14353.

[3] H. Kawazoe, M. Yasukawa, H. Hyodo, M. Kurita, H. Yanagi & H. Hosono, "P-ype Electrical Conduction in Transparent Thin Films of $CuAlO_2$", Nature (London) **389** (1997) 939.

[4] H. Yanagi, T. Hase, S. Ibuki, K. Ueda & H. Hosono, "Bipolarity in Electrical Conduction of Transparent Oxide Semiconductor $CuInO_2$ with Delafossite Structure", Journal of Applied Physics **88** (2000) 4159.

[5] N. Xiliang, W. Su-Hui & S. B. Zhang, "First Principles Study of Doping and Bandgap Anomalies in Delafossite Transparent Conductive Oxides", Annual APS March Meeting (2002) 18.

[6] J. Tate, M. K. Jayaraj, A. D. Draeseke, T. Ulbrich, A. W. Sleight, K. A. Vanaja, R. Nagrajan, J. F. Wager & R. L. Hoffman, "P-type Conductivity in the Delafossite Structure", Thin Solid Films **411** (2002) 119.

[7] H. Meijie, J. Kai, Z. Jinzhong, Y. Wenlei, L. Yawei, H. Zhigao & C. Junhao, "Structural, Electronic Band Transition and Optoelectronic Properties of Delafossite $CuGa_{1-x}Cr_xO_2$ ($0 \leq x \leq 1$) Solid Solution Films Grown by Sol-gel Method", Journal of Material Chemistry **22** (2012) 18463.

[8] H. C. Isaac, F. S. Franscisco, R. Adele, J. L. Beatriz, O. Fabrice, C. Laurent, S. Jobic & G. Sixto, "Hole Conductivity and Acceptor Density of P-type $CuGaO_2$ Nanoparticles Determined by Impedance Spectroscopy: The Effect of Mg Doping", Electrochimica Acta **113** (2013) 570.

[9] D. Ursu, N. Vaszilcsin, R. Banica & M. Miclau, "Effect of Al Doping on Performance of $CuGaO_2$ p-type Dye-sensitized Solar Cells", Journal of Material Engineering and Performance **25** (2016) 59.

[10] T. Y. Chien & C. L. Ching, "Improved Electrical Properties of P-type $CuGaO_2$ Semiconductor Thin Films through Mg and Zn Doping", Ceramics International **43** (2007) 2563.

[11] N. H. Muhammad, Y. Yanfa, W. Aron, W. Su-Huai & M. A. Mowafak, "Group-IIIA Versus IIIB Delafossites: Electronic Structure Study", Physical Review B **80** (2009) 035205.

[12] Q. J. Liu, Z. T. Liu, J. C. Chen, L. P. Feng & Tian, "First Principles Study of Structural, Mechanical, Electronic and Optical Properties of 3R-and 2H-$CuGaO_2$" Physica B **406** (2011) 3377.

[13] P. Poopanya, R. Nakowong, A. Yanthaisong & T. Seetwan, "Theoretical Calculations of Electronic Structure and Thermoelectric Properties of $CuGaO_2$", Proceedings-Science and Engineering (2003) 570.

[14] S. Issei, N. Hiraku, K. Masao, I. Yuki, S. Chiyaki, Y. Hiroshi, O. Naoki & O. Takahisa, "First Principle Study of $CuGaO_2$ Polmorphs; Delafossite α- $CuGaO_2$ and Wurtzite β- $CuGaO_2$", Inorganic Chemistry **55** (2016) 7610.

[15] G. Paola, B. Stefano, B. Nicola, C. Matteo, C. Roberto, C. Carlo, C. Davide, L. C. Guido, C. Matteo & D. Ismail, "Quantum ESPRESSO: A Modular and Open-source Software Project for Quantum Simulations of Materials" Journal of Physics: Condensed Matter **21** (2009) 395502.
[16] J. P. Perdew, K. Burke & M. Ernzerhof, "Generalized Gradient Approximation Made Simple", Physical Review Letters **77** (1996) 3865.
[17] H. J. Monkhorst & J. D. Pack, "Special Points for Brillouin-zone Integrations", Physical Review B **13** (1976) 5188.
[18] C. Zhang, C. L. Wang, J. C. Li & K. Yang, "Structural and Electronic Properties of Fe-doped $BaTiO_3$ and $SrTiO_3$", International Research Journal of Pure and Applied Chemistry **16** (2007) 1422.
[19] A. H. Dorian, H. N. Mohammed, L. Sean, Y. Aibing & C. S. Charles, "Ab Initio Study of Phase Stability in Doped TiO", Computational Mechanics **50** (2012) 185.
[20] A. Fazzio, R. J. Baierle, S. B. Fagan, R. Mota & J. R. Antonio, "Ab Initio Study of Si Doped Carbon Nanotubes: Electronic and Structural Properties", Materials Research Society Symposium Proceedings (2001) 675.
[21] O. S. David, G. G. Kate, J. M. Benjamin & W. W. Graeme, "Understanding Conductivity Anomalies in CuI^I-based Delafossite Transparent Conducting Oxides: Theoretical Insights", Journal of Chemical Physics **132** (2010) 024707.
[22] O. S. David, W. Aron & W. W. Graeme, "Understanding the P-type Conduction Properties of the Transparent Conducting Oxide $CuBO_2$: A Density Functional Theory Analysis", Chemistry of Materials **21** (2009) 4568.
[23] M. A. Aqeel & H. A. Ali, "Doping, Vacancy Formation and Substitutional Effects on Semiconductor Selection of Rutile TiO_2 Crystal", Chemistry and Material Research **3** (2013) 22.
[24] A. Mahmud & P. J. Daniel, "Structural and Electronic Properties of Iron Doped Technetium Sulphide", Proceedings of SAIP (2014) 558.