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STRUCTURAL, ELECTRONIC AND MAGNETIC PROPERTIES OF VANADIUM DOPED DELAFOSSITE $CUGAO_2$: AN AB INITIO STUDY

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ABSTRACT

Delafossite copper gallium oxide ($CuGaO_2$) is one of the most important copper-based delafossite materials reported. It has variety of applications that include but are not limited to; photo catalysis, dye-sensitized solar cells. However, due to the wide band gap of this material, it appears very attractive as transparent conductive oxide (TCO). Thus, it is very important and applicable in optoelectronic device technologies. In this paper, the structural, electronic and magnetic properties of vanadium (V) doped delafossite $CuGaO_2$ are investigated using first principle study based on density functional theory (DFT) as implemented in the QUANTUM ESPRESSO simulation package. We used Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) exchange-correlation scheme for the undoped and vanadium (V) doped structures. There is no structural transition after the doping. The results indicated that the V doping reduced the band gap of the undoped delafossite $CuGaO_2$ by 0.8 eV. It also contributed more to the conduction band states. However, our results also revealed that the 50 % V doping induced significant changes to the magnetic properties of the undoped $CuGaO_2$. It was found that the undoped $CuGaO_2$ is slightly paramagnetic similar to the same group member $CuAlO_2$, whereas the V doped $CuGaO_2$ system is slightly ferromagnetic. This result is in agreement with previous literature concerning the effect of doping semiconductor material with magnetic metals. Thus, based on our results, V doped $CuGaO_2$ material may be considered as an important candidate for spintronics and other related applications.

Keywords: Delafossite, Doping, Ferromagnetic, Transparent conducting oxide, Spintronics, Paramagnetic

INTRODUCTION

After the first report of transparent conducting Cadmium Oxide (CdO) thin film by Badeker in 1907 (Badeker, 1907), a lot of works have been done in the field of Transparent Conducting Oxide (TCO) technology to prepare new types of TCOs with wide range of applications. However, the TCOs are being used extensively in various fields, which include: dye solar cells, flat panel displays (FPDs), low-emissivity ("low- e") windows (Renaud *et al*, 2012; Banerjee and Chattopadhyay, 2008) among others. Despite the fact that, TCOs have several ranges of applications as mentioned, very little work has been done on the active devices fabrication using TCOs (Banerjee and Chattopadhyay, 2008). This is because most of the known TCOs are n-type semiconductors. But the corresponding p-type transparent conducting oxide (p-TCO) which are needed for junction devices fabrication were missed for a long time, until in 1997, Kawazoe and co-researchers reported the p-type conductivity in a transparent thin film of $CuAlO_{2+x}$ (Kawazoe *et al*, 1997).

This has triggered many research interests especially on the copper-based delafossite family with the general formula $CuMO_2$ (M= Al, Ga, In). The idea is based on the observations that Cu has shallow, occupied 3d orbital that is close to the O 2p orbitals. The coupling between the Cu d-states and O p-states can lead to smaller ionization energies which is equivalent to the higher valence band maximum (VBM), there-by making them to be doped p-type easily. Apart from p-type conductivity of this group, they exhibit two uncommon physical properties which are increasing in optical band gap with increase in the atomic number (from M=Al, Ga to In) and bipolar doping in the largest band gap $CuInO_2$ (both n-type and p-type)) (Yanagi *et al*, 2002). The reason behind these two unique properties was explained based on first principle density functional theory study (DFT), that are the results of a large disparity between the fundamental band gap and the apparent optical band gap (Xiliang *et al*, 2002).

Delafossite $CuGaO_2$ being one of the most important copper-based delafossite materials reported. It has variety of applications. It can be used in photocatalytic applications in reducing carbon (IV) oxide (CO_2) to carbon monoxide (CO) (Jonathan, *et al*., 2012). It is also used as a photocathode in place of nickel oxide (NiO) for p-type dye-sensitized solar cells (Renaud *et al*, 2012). Their results indicated that both photovoltaic characteristics and flat band potentials of the delafossite $CuGaO_2$ suggested that it can be viewed as a promising substitute for NiO. However, due to the wide band gap of this material, it appears very attractive as transparent conductive oxide (TCO). Thus, it is very important and applicable in optoelectronic device technologies. But one major problem of this material that needs to be solved for more diverse applications especially in the fabrication of all-transparent junction devices is the low conductivity. The problem may be solved either by oxygen intercalation or substitutional doping with appropriate dopants. But oxygen intercalation in the delafossite p-TCOs only showed a small conductivity which is still quite less than that of commercially available n-TCOs (Banerjee and Chattopadhyay, 2008). Therefore, the next alternative is the substitutional doping.

Moreover, several works were reported in relation to the doping of delafossite $CuGaO_2$ using different dopants and methods. Tate, et al., reported a heavy doping (~ 50%) of $CuGaO_2$ by Fe^{3+} in Ga sites. Both the polycrystalline powder and thin film of $CuGa_{1-x}Fe_xO_2$ ($0 \leq x \leq 1$) have shown p-type conductivity (Tate, *et al*., 2002). Using sol-gel method, Meijie, et al., reported a substitutional doping of Cr atom in the Ga site of delafossite $CuGaO_2$ (Meijie, *et al*., 2012). It was found that the Cr-substituting induced the increase of the film's roughness, changed the film's internal structure and

made more crystal defects and grain boundaries. The effect of Mg doping on $CuGaO_2$ was reported using impedance spectroscopy (Isaac, *et al*., 2013). Aluminium doped $CuGaO_2$ has been synthesized by hydrothermal method and its properties has been investigated as cathode elements in ruthenium dye N719-sensitized solar cells (Ursu, *et al*., 2016). However, Chien and 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 (Chien and Ching, 2017). The Mg and Zn doped thin films exhibited improvement in the electrical properties, and the Zn-doped thin films had the highest mean carrier concentration of 3.49×10^{16} cm^{-3}. A theoretical study based on Density Functional Theory (DFT) was reported using manganese as dopant (Alhassan et al., 2019). To the best of our knowledge no theoretical study reported on the doped version of the delafossite $CuGaO_2$ using Vanadium atom as dopant. Therefore, the aim of this work is centred toward a theoretical study on the structural, electronic and magnetic properties of the vanadium doped $CuGaO_2$ using first principle study within the framework of Density Functional Theory (DFT).

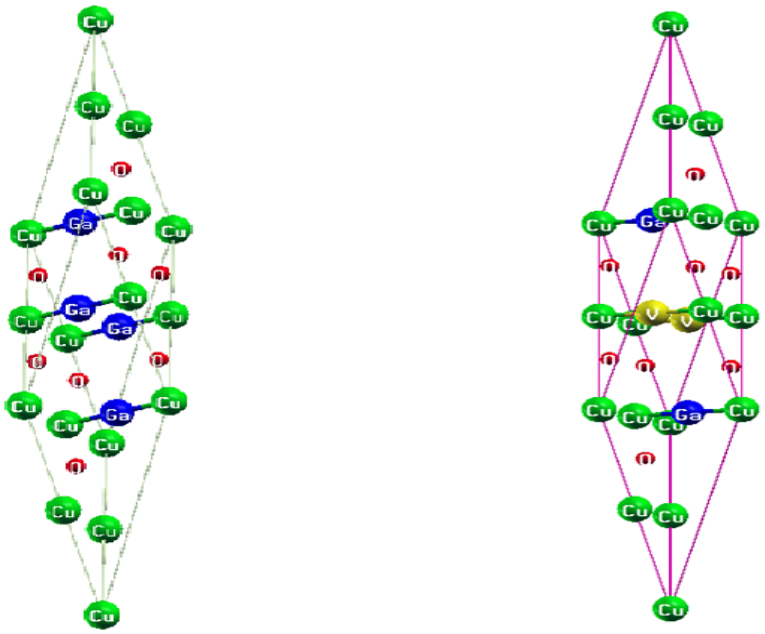
MATERIALS AND METHODS

We obtained the crystal parameters for the pure delafossite $CuGaO_2$ from references (Ong *et al*., 2008; Jain *et al*., 2013). The calculations were performed 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 (Paola *et al*., 2009). The Perdew-Burke-Ernzerhof Generalized Gradient Approximation (PBE-GGA) (Perdew, *et al*., 1996) scheme has been employed in approximating the exchange-correlation potential for both the pure and doped materials. The plane wave basis sets with the maximum kinetic energy cut-off of 340 eV has been used to expand the wavefunctions. The electron-ion core interaction is treated by ultrasoft pseudopotentials for Cu ($3d^{10}4s^1$), Ga ($3d^{10}4s^24p^1$), O ($2s^22p^4$) and V ($3d^34s^2$) valence orbitals. For integrals, smearing has been adopted and to be specific Maxfessel-Paxton smearing method with small Gaussian spreading of 0.02 Ry has been used. The brillouin zone integration is performed using Monkhorst-Pack scheme (Monkhorst and Pack, 1976) with $10 \times 10 \times 1$ k-points grids. The 2×2 supercell used consists of four Gallium (Ga) atoms, so during the substitutional doping, two atoms were substituted with two different atoms of Vanadium (V). That is to say, 50 % V doping in the Ga-atomic sites of the delafossite $CuGaO_2$ is performed. 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 electronic densities of states are found using denser k-point mesh.

RESULTS AND DISCUSSIONS

Structural Properties

The delafossite $CuGaO_2$ exhibits two different polytypes, the hexagonal crystal structure corresponding to conventional unit cell with space group $P6_3/mmc$ and rhombohedral crystal structure corresponding to the primitive unit cell with space group $R\bar{3}m$. The primitive unit cell was adopted in this work, but the simple primitive cell contains only one gallium atom, as such, substitutional doping cannot be performed on it, since the doping is going to be in the gallium atomic site. As such, 2×2 supercell relative to the primitive unit cell was constructed as shown in figure 1(a). The optimized crystal parameters of the supercell are a=b=12.06 Å, c=6.030 Å and $\alpha=\beta=\gamma=28.937^0$.



(a) (b)

Figure 1: (a) DFT-GGA optimized crystal structure of pure delafossite $CuGaO_2$. (b) DFT-GGA optimized crystal structure of 50% V doped $CuGaO_2$.

From table 1, for 50 % substitutional doping case, there are three symmetrically distinct ways for replacing the gallium (Ga) atom by vanadium (V) atom. In this particular work, D_3_0.50) was adopted, as shown in figure 1(b) above. The structure didn't change after the doping.

Table 1: Configurations for Substitutional Doping of Ga by V of $CuGaO_2$ Material

Pure	Ga	Ga	Ga	Ga
D_1_0.50	V	V	Ga	Ga
D_2_0.50	V	Ga	Ga	V
D_3_0.50	Ga	V	V	Ga

To find the stability of the structure after vanadium doping, the dopant formation energy of the vanadium atom was estimated using equation (1) (Zhang Chao, *et al*., 2007). The dopant formation energy is the energy needed to insert one vanadium atom with a chemical potential μ_V into the supercell after removing one gallium atom with chemical potential μ_{Ga} from the same position (Dorian, *et al*., 2012).

$$E_f = E_{doped} - E_{undoped} + \mu_{Ga} - \mu_V \quad (1)$$

Where,

E_{doped} is the DFT total energy of the $CuGa_{1-x}V_xO_2$ 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_V is the chemical potential per atom of vanadium bulk crystal.

The dopant formation energy of Vanadium doped $CuGaO_2$ calculated is 239.4 Ry.

Electronic Properties

The electronic properties of both the pure and doped $CuGaO_2$ systems are explained using the density of states (DOS) plots as shown in the figures below.

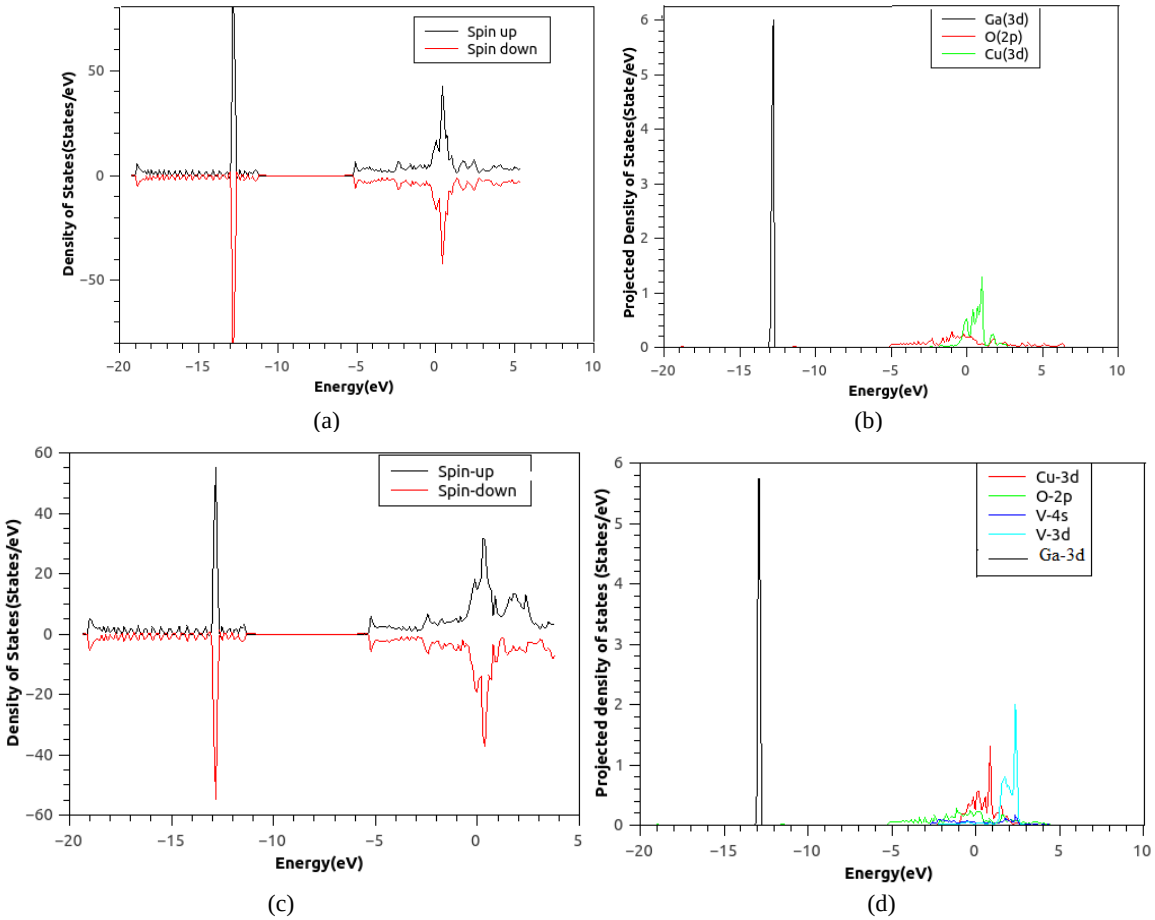


Figure 2: (a) The spin-polarized density of states for the pure delafossite $CuGaO_2$ (b) The projected density of states for the undoped $CuGaO_2$ (c) The spin- polarized density of states for the $CuGa_{1-x}V_xO_2$ (x=0.5) (d) The projected density of states for the $CuGa_{1-x}V_xO_2$ (x=0.5).

Figure 2(a) displays a sharp peak at the -12.85 eV in the valence band (VB) which translates to high states available for occupations at this particular energy level. From left of this sharp peak, are some small peaks with almost same height. Moving right to the sharp peak again, are some few peaks whose onsets disappear between -11.10 eV to -5.10 eV. The total DOS is zero between these intervals, meaning that no states available for occupation. Therefore, this may be regarded as the forbidden gap. The calculated value for this gap is 6 eV. The allowable conduction band states start at around 0.0 eV.

From figure 2(b), it can be deduced that the sharp peak seen in the DOS plot is a contribution from Ga 3d orbital. It can clearly be seen that 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 a Cu (I) oxide based compounds (David et al.,2009). 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 $CuBO_2$ (David et al., 2009; David et al., 2010). There is

also a strong hybridization between Cu 3d and O 2p states in the conduction band.

Figure 2(c) shows the density of states of the vanadium doped $CuGaO_2$. It displays a sharp peak almost similar to that of the pure system. The calculated value for the forbidden gap of the system is 5.2 eV. This is smaller than the one for the undoped $CuGaO_2$. The allowable conduction band states begin around 0.0 eV. For the spin up and spin down components, they are almost the same except for the conduction band states which differ for the two opposite spins.

However, figure 2(d) which is the plot for the projected density of state for the V doped $CuGaO_2$. It shows that, the sharp peak seen on the DOS plot (figure 2c) is the Ga 3d states. As such, the bottom of the valence band is dominated by the Ga 3d orbitals with minor contributions from O 2p states similar to the undoped material. The top of the valence band contains V 4s, V 3d, O 2p and Cu 3d states, but it is mainly dominated by Cu 3d and O 2p states. Whereas, the bottom of the conduction band is composed of Cu 3d states, O 2p states mix with minor contributions from V 4s and V 3d states. Also, there is a hybridization between Cu 3d and V 3d states in the conduction band. The middle of the conduction band is dominated by V 3d states with minor V 4s states. Therefore, it can be deduced that, V 3d and V 4s states contributed largely to the conduction band states for the V doped $CuGaO_2$ system.

Magnetic Properties

From figure 2(a), the spin up and spin down components are exactly the same. Meaning that, the density of states for the two opposite spins (majority and minority spins) is identical. The total magnetization of the pure $CuGaO_2$ calculated is 0.02 Bohr mag/cell. Thus, it can be predicted that the dominant magnetic interactions in the material are slightly paramagnetic (PM) in nature which is similar to the $CuAlO_2$ (Jean-Pierre et al., 1986). This may be the reason why delafossite $CuGaO_2$ itself cannot be regarded as a magnetic semiconductor (Ong et al., 2008). Because, materials that exhibit PM property usually considered as non-magnetic as their magnetism is very weak.

On the other hand, from the DOS plot of the $CuGa_{1-x}V_x\ O_2$ (x=0.5) material (fig. 2b), the two opposite spins contributions are not the same. In addition to this, the calculated total magnetization for the material is 6.98 Bohr mag/cell. This implies that the dominant magnetic interactions are slightly ferromagnetic (FM) in nature. This is consistent to many studies that doping semiconductor with magnetic metals induces significant changes to the magnetic properties of the system (Zhang et al., 2013).

CONCLUSION

The work was reported based on the first principle study within the framework of density functional theory on the structural, electronic and magnetic properties of vanadium doped delafossite $CuGaO_2$. It was found that the doped structure is stable against decomposition after vanadium doping. This is deduced from the value of the calculated dopant formation energy for the vanadium atom. The results revealed that, the V doping reduces the band gap of the pure delafossite $CuGaO_2$. Though, the DFT-GGA does not predict both the fundamental and optical band gaps accurately, but it is possible to make an effective statement regarding the effects of dopant (Aqeel and Ali, 2013; Mahmud and Daniel, 2014). So, 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 employed. However, the results also indicated that the V doping induces significant changes in terms of magnetic properties of the undoped $CuGaO_2$. This is deduced from the asymmetric nature of the majority and minority spins coupled with the high value of the total magnetization of the V doped system. As such, the V doped $CuGaO_2$ system may be considered as important candidate for spintronics and other related applications.

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