Electronic and structural properties of CuMO$_2$ (M = Al, Ga, In)

Venkatachalam Jayalakshmi, Ramaswamy Murugan, Balan Palanivel*

Department of Physics, Pondicherry Engineering College, Pondicherry 605 014, India

Abstract

The electronic and structural properties of delafossite transparent conducting oxides, namely CuMO$_2$ (M = Al, Ga, In), have been studied by means of self-consistent Tight Binding Linear Muffin-Tin Orbital (TB-LMTO) method. Electronic structure and hence total energies of these compounds have been computed as a function of reduced volumes and fitted with Birch Murnaghan equation.

The calculated equilibrium lattice parameters and bulk modulus are in good agreement with experimental and reported values. The energy band gap of 2H (hexagonal) and 3R (trigonal) CuMO$_2$ (M = Al, Ga, In) has been calculated and compared with available data. The stability of 2H and 3R polytypes has also been studied.
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1. Introduction

Solids with wide band gap usually exhibit insulating behavior but some of the metal oxides with wide gap are made to conduct. Such transition metal oxides are called transparent conducting oxides (TCO). Transparent conducting oxide materials are noble metal oxides of the form AMO$_2$ (A = Cu, Pd and M = Al, In, Fe, Ga, etc.) that crystallize in the simple delafossite structure. Many metallic oxides have a wide band gap because of the significant contribution of the ionic character to the chemical bonds between metallic cation and oxide ions. Wide-gap semiconductors are difficult to dope, particularly p-type.

More recently, efforts have been devoted to develop p-type wide gap materials using low-T [1], non-equilibrium [2] or surface processes [3] to avoid self-compensation while enhancing dopant solubility. According to the recently developed doping limit rule [4,5], the degree of self-compensation in a material correlates directly to its band-edge positions with respect to others. A compound with higher valence band maximum (VBM) is easier to dope p-type, while a compound with lower conduction band minimum (CBM) is easier to dope n-type.

TCO materials are widely used in flat panel displays, solar cells and touch displays. A large number of ternary noble metal oxides crystallize in the relatively simple delafossite structure CuMO$_2$ [6]. The variation in the chemical and physical properties of these delafossite TCOs is the origin of the diverse technological applications. The conductivity of TCO materials can be controlled across an extremely wide range such that they can behave as insulators, semiconductors or metals. Delafossites are currently being employed as catalyst. Recently, they have also been suggested for use in solar applications.

Mattheiss [7] performed calculation for the electronic structure of a compound with the delafossite structure, which concerned to the problem of oxygen doping in CuYO$_2$. Rogers et al. [8] proposed a qualitative band structure model and based on this, the experimental data on structural and electrical properties of delafossite can be interpreted. Weak closed shell d^{10}–d^{10} interaction normally plays an important role in the structural physical properties of organo-metallic compounds [9]. According to Kawazoe et al. [10], this interaction plays an important role in electro-optical properties. Three different motifs exist in the same delafossite crystal

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* Corresponding author.
E-mail address: bp_vel@yahoo.com (B. Palanivel).

structure (MO_6 octahedra, linear O–Cu–O units and hexagonal Cu layers). The coexistence of different structural units (MO_6 layers, O–Cu–O fragments and hexagonal Cu layers) in the same crystal structure makes an accurate prediction of the structural data very difficult [11].

Based on the LDA calculation of Nie et al. [12], the band structure of $3R$-$CuMO_2$ (M = Al, Ga, In) has been calculated. It was found that all materials had an indirect band gap between the Γ-F symmetry points. The indirect gap decreases from $CuAlO_2$ to $CuGaO_2$ and to $CuInO_2$ according to the calculations performed by Nie et al. [12]. The band structure calculation for the 3R and 2H structure of $CuAlO_2$ was calculated by Buljan et al. [11], but these authors found large discrepancy when compared with the experiment. The appearance of discrepancy was due to the inability of the Hartree–Fock method in the calculation of this property.

With the increase of computational power, ab initio calculations become a powerful tool in understanding the electronic band structure and structural phase stability of materials. This paper deals with electronic properties of 2H (hexagonal) and 3R (trigonal) $CuMO_2$ (M = Al, Ga, In) in delafossite structure. The space group of the 2H phase is $P6_3/mmc$ (no. 194) and for the 3R phase, it is R-3m (no. 166). The difference between these two structures is the stacking of successive layers of MO_6 octahedra, which results in two types of polytypes. In the present work, the electronic structure of $CuMO_2$ has been calculated by means of self-consistent Tight Binding Linear Muffin-Tin Orbital (TB-LMTO), which is used to calculate the ground state properties of the materials [13–15]. The energy band gap for the above delafossite compounds is calculated from the electronic structure and compared with available reported values.

2. Methodology

The energy band structure and electronic properties of the delafossite $CuMO_2$ have been obtained using TB-LMTO method within atomic sphere approximations [13–15]. The calculations are performed within the framework of local density approximation (LDA). The von Barth and Hedin exchange correlation potential [16] is employed in the present calculations. The relativistic mass–velocity variation is taken into account; however, the spin-orbit coupling is neglected. The densities of states are calculated by the tetrahedron method.

In the present work, the electronic band structures of the 2H and 3R-$CuMO_2$ at ambient as well as at high pressures have been studied. The equilibrium lattice parameter and bulk modulus of the two types of polytypes 2H and 3R at ambient condition are determined by a total energy calculation and fitted into the Birch–Murnaghan equation of state. The calculations have been performed on a grid of 72 k points in the entire Brillouin zone. The band gaps for the two polytypes have been calculated by the density of states.

3. Crystal structure

At ambient conditions, $CuMO_2$ oxides crystallize in a delafossite structure, which is a built of infinite one-octahedron-thick sheets of close-packed MO_6 octahedra. These layers are linked together by Cu atoms that form O–Cu–O units. The O–Cu–O fragment has a considerable covalent character, while the M–O bonds in MO_6 octahedra are strongly ionic.

The successive stacking of layers of MO_6 octahedra leads to different polytypes. The two most common polytypes are 2H and 3R delafossite. In the trigonal 3R structure, there are three layers per unit cell and the fourth layer coincides with the first one. The hexagonal 2H structure contains only two layers per unit cell. The atomic positions in 2H and 3R structures were all fixed by symmetry except the *u*-value of the oxygen atoms. The position of Cu for the 2H and 3R structure is at (2c) site at 0.333, 0.667, 0.25 and at (3a) site at 0, 0, 0. The position of Al is at (2a) site at 0, 0, 0 and at (3b) site at 0, 0, 0.5. The position of O for 2 H and 3 R is at (4f) site at 0.333, 0.667, *u* and at (6c) site at 0, 0, *u*. The experimental *u* values were taken for the present calculations from reference [11].

4. Results and discussion

The conductivity of the TCO materials can be controlled such that they exhibit insulating, conducting and semiconducting properties. The TCOs have variety of properties such as the optical and electronic behavior, optical transparency and electrical conductivity. The present work deals with electronic behavior property of the delafossites.

In the present study of $CuMO_2$, the 3d, 4s, 4p orbitals of Cu, the 3s, 3p, 3d orbitals of Al, the 3d, 4s, 4p orbitals of Ga, the 4d, 5s, 5p orbitals of In and the 2s, 2p, 3d for O have been treated as valence states. Empty spheres are included in the structures to obtain close packing, which is necessary to obtain accurate LMTO results. In the calculation, two types of empty spheres are included for complete overlapping. The percentage of overlap is ~8.5–10.2% for the different $CuMO_2$. The average Wigner–Seitz radius was scaled so that the total volume of the spheres is equal to the equilibrium volume of the primitive cell.

The calculated total energies are fitted with the Birch Murnaghan equation, to determine the equilibrium lattice parameter and bulk modulus. The calculated lattice parameters and bulk modulus of 2H and 3R-$CuMO_2$ are given in Table 1 along with the available experimental and reported values. It is found that the calculated lattice parameter increases from Al to In. However, the calculated bulk modulus for the 2H and 3R structure of $CuMO_2$ shows a linear decrease from Al to In.

The total energy is computed for all the three compounds by varying the molecular volume from 1.2 V_0 to 0.85 V_0, where $V_0 = V_{exp}$. The variation of the total energy versus the

Table 1
Calculated lattice parameters and bulk modulus for some delafossite type oxides with the available experimental and theoretical values for comparison

	a (Å)	c (Å)	Bulk modulus (GPa)
2H-CuAlO$_2$			
TB-LMTO	2.9099 (2.8630)[a]	11.4993 (11.3140)[a]	185.76 (211)[a]
3R-CuAlO$_2$			
TB-LMTO	2.8096 (2.8580)[a]	16.6708 (16.9580)[a]	294.20 (204)[a]
LAPW	2.816	16.978	
2H-CuGaO$_2$			
TB-LMTO	2.9730 (2.9730)[a]	11.5950 (11.5950)[a]	175.37 (192)[a]
3R-CuGaO$_2$			
TB-LMTO	2.9770 (2.9770)[a]	17.1710 (17.1710)[a]	180 (192)[a]
LAPW	2.963	17.172	
2H-CuInO$_2$			
TB-LMTO	3.4711	11.2245	146.06
3R-CuInO$_2$			
TB-LMTO	3.2920 (3.2920)[a]	17.3880 (17.3880)[a]	156.41
LAPW	3.285	17.270	

[a] Experimental and reported values: reference [11]; LAPW [12].

relative molecular volumes for CuMO$_2$ is given in Figs. 1–3. The energy difference is small between the two phases which is however at the limits of accuracy of our computational method and should be taken only as an indication that both the structures have similar stabilities, in accordance with the experimental observation at normal condition. However, the present work predicts that 3R phase of CuGaO$_2$ is more stable at around 13 GPa.

The densities of states have been calculated. Usually, the LDA calculation underestimates the band gap. The present study deals with the difference between the gaps of the 2H and 3R structure of the above compounds. The systematic LDA error has been expected to be largely canceled. All the above compounds have an indirect band gap with the valence band maximum on the Γ-L line and conduction band minimum at Γ. The calculated indirect gap decreases from Al to In and the gap values are found to be 1.85 eV, 0.85 eV and 0.4 eV,

respectively, for the 2 H structure of CuAlO$_2$, CuGaO$_2$ and CuInO$_2$.

In the 3R structure, the valence band maximum lies on the Γ-F line. The gap value for 3R-CuMO$_2$ decreases from Al to In similar as that of the 2H structure. The gaps' values decrease from 1.6 eV for CuAlO$_2$ to 0.6 eV for CuGaO$_2$, to 0.55 eV for CuInO$_2$. This 3R structure gap value agrees with the available reported values [12]. The reported values are 1.97 eV for CuAlO$_2$, 0.95 eV for CuGaO$_2$ and 0.41 for CuInO$_2$ which are based on the LDA calculation. The band gap of CuAlO$_2$ also agrees well with the experimental result of 1.65 eV [17].

The total density of states for the 2H and 3R polytypes is calculated by the tetrahedron method. The valence band is dominated by the Cu 3d states, while the contribution of the 4p states is practically zero. The 4s Cu states show a small contribution to the valence band which agrees with the
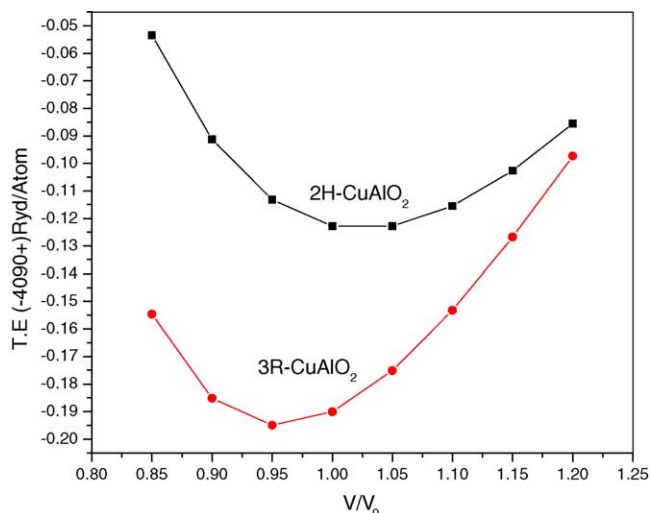
Fig. 1. Energy vs. volume curve for the 3R phase of CuAlO$_2$.
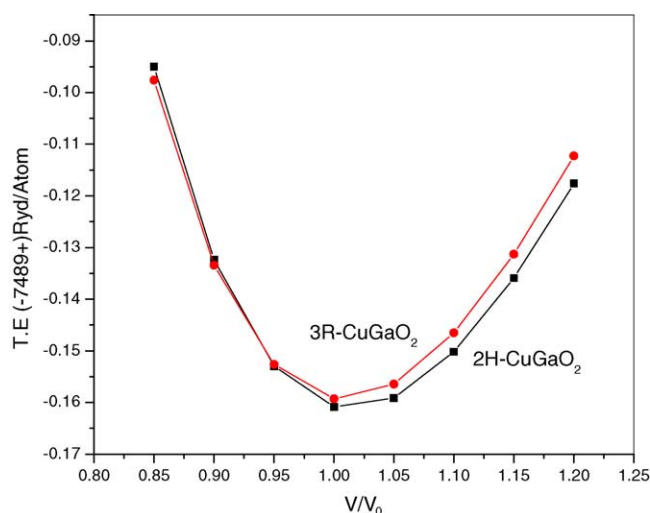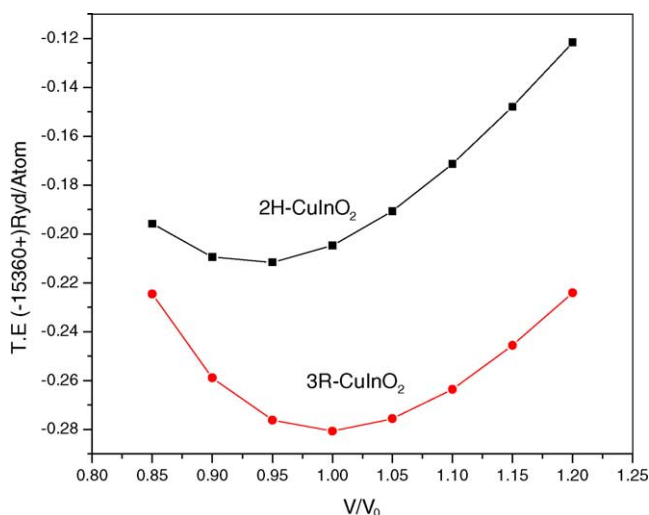

Fig. 2. Energy vs. volume curve of CuGaO$_2$.

Fig. 3. Energy vs. volume curve for $CuInO_2$.

and to In. In the case of the 3R structure, the band gap trend of the present work agrees well with the reported data [7]. In this calculation, it has been found that the 3R structure is more stable in the case of $CuAlO_2$ and $CuInO_2$. However, in the case of $CuGaO_2$, it has been found that the 3R structure is stable only at a pressure of about 13 GPa. Based on the experiment, it is indicated that both phases have a similar stability at normal conditions. It is proposed to extend a similar type of investigation to the other delafossite materials, so that one can obtain complete information about the electronic and structural properties of transparent conducting oxide materials.

Orgel model [18] that proposes an s–d_z^2 hybridization for linearly coordinated Cu^+ ions. The contribution of O atoms to the valence band comes from the 2p states, which appear overlapped with the sharp Cu 3d peak. Aluminum shows a negligible contribution to the valence band. A similar DOS have been found for 3R-$CuAlO_2$, 2H and 3R-$CuGaO_2$ and $CuInO_2$. The band structure calculation of $CuAlO_2$ agrees well with the calculation of Buljan et al. [11].

5. Conclusion

In this paper, the ground state properties of 2H and 3R structure of $CuMO_2$ delafossite have been reported. In both the polytypes, we found that the lattice parameters increase from Al to In. At the same time, we found that the bulk modulus decreases from Al to In. The lattice parameter and bulk modulus of the 2H structure of these delafossites also follow the same trend as the 3R structure. In the case of the 2H structure of $CuInO_2$, the calculated lattice parameters have been reported and experimental results are needed for comparison. The band gaps for the 2H and 3R structure of $CuMO_2$ are found to follow the trend of decreasing from Al to Ga

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