Yangthaisong A.

ELECTRONIC STRUCTURE AND PREDICTION OF THERMOELECTRIC PROPERTIES OF $CuBO_2$

Yangthaisong A.
(Computational Materials and Device Physics Group, Department of Physics, Ubon Ratchathani University, Ubon Ratchathani 34190, Thailand)

- *Delafossite $CuBO_2$ has been discovered experimentally as a promising p-type transparent conducting oxide with a high intrinsic electrical conductivity and excellent transparency. In this work, the first-principles calculation based on density functional theory (DFT) has been performed to investigate the geometry and electronic structure of $CuBO_2$. In particular, the lattice parameters and the energy band structure were calculated. It was found that the lattice parameters of $CuBO_2$ are a = 2.539 Å, c = 16.936 Å. The $CuBO_2$ has an indirect band gap with the value of 2.06 eV and a direct gap value of 3.20 eV. Note that the experimental indirect (direct) gap of $CuBO_2$ is 2.20 (4.5) eV. In addition, the calculated energy band structures were then used to calculate the electrical transport coefficients of $CuBO_2$ and hence thermoelectric parameters can be derived. The present study is compared to our recent work on $CuAlO_2$.*

Introduction

Thermoelectric properties of delafossite materials $CuMO_2$ ($M = Al, Ga, In, Sc, Y, La$) as high potential thermoelectric materials have been extensively studied [1, 2]. The thermoelectric conversion performance of materials can be described by the dimensionless figure of merit ZT which is defined as $ZT = S^2\sigma T / \kappa$, where S is the Seebeck coefficient, σ is the electrical conductivity, and κ is the thermal conductivity. To achieve a high ZT, a high power factor ($S^2\sigma$) is required for example by changing the carrier concentration with doping, whilst the thermal conductivity is kept as low as possible. Since S, σ, κ are all functions of carrier concentration and are interrelated with each other [3], the optimization of the figure of merit can be considered as a challenging problem.

Recently, delafossite $CuBO_2$ has been discovered experimentally as a promising *p*-type transparent conducting oxide with a high intrinsic electrical conductivity and excellent transparency [4]. In particular, the electrical conductivity of $CuBO_2$ films was found to be 1.65 $S \cdot cm^{-1}$, which is 65 % higher than the corresponding value of $CuAlO_2$ reported by Kawazoe's group [5]. This may result in the enhancement of power factor of $CuBO_2$ and hence thermoelectric conversion performance. Apart from the experimental investigation, the calculations of electronic structures have also been used to investigate the electronic and optical conductivity of $CuBO_2$. However, a calculation reported in Ref. [6] questioned the validity of the experimental lattice parameters measured by Snure and Tiwari, as they were in disagreement by more than 10 % with the theoretical values obtained using either local density approximation (LDA) or hybrid HSE06 functionals. It is worthwhile to mention that DFT calculations using LDA or GGA usually give good estimations of the lattice parameters, within few percent, especially for delafossite materials.

In the present work, the first-principles calculation of the electronic structure has been performed. The calculated band structures are then used in combination with the Boltzmann transport equation solver under the constant relaxation time (τ) approximation to calculate the electrical transport quantities. The doping level dependence on the thermoelectric properties of delafossite material $CuBO_2$ has been investigated.

Computational details

The space group of $CuBO_2$ is *R-3m* with the hexagonal atom positions of *Cu* (0, 0, 0), *B* (0, 0, 0.5), *O* (0, 0, ± *u*). The electronic structures are calculated using the plane-wave pseudopotential method based on the density functional theory (DFT), as implemented in the CASTEP code [7]. The generalized gradient approximation (GGA) is used for the exchange and correlation potential. The presence of tightly bound core electrons was represented by norm-conserving pseudopotential as generated with OPIUM code [8]. The states *Cu*-$3p^6$ $3d^{10}$ $4s^1$, *Al*-$2s^2$ $2p^1$ and *O*-$2s^2$ $2p^4$ were treated as valence states. Plane wave cut-off energy of 880 eV and a 10 × 10 × 10 grid of Monkhorst-Pack points have been employed to ensure a good convergence of the computed structures and energies. Geometry optimization is determined using the Broyden-Fletcher Goldfarb-Shenno (BFGS) minimization technique, with the thresholds for converged structure: energy change per atom less than 10^{-5} eV / atom, residual force less than 0.03 eV/Å, stress below 0.05 GPa and the displacement of atoms during the geometry optimization less than 0.001 Å. The tolerance in the self-consistent field (SCF) calculation is 1.0×10^{-6} eV/atom. The doping level dependence on thermoelectric properties is then obtained in the rigid band approach and the constant τ approximation using the BoltzTraP program [9]. The results are based on electronic eigenvalues calculated on uniform 20 × 20 × 20 grid of *k*-point.

Results and discussion

The energy versus volume curve is obtained by using the third-order Birch-Murnaghan equation to find the optimized parameters. The lattice constants of the conventional cell $CuBO_2$ as shown in Fig. 1(*a*) are *a* = 2.539 Å, *c* = 16.936 Å. The lattice parameters *a* and *c* of this work are quite different from the experimental data *a* = 2.84 Å, *c* = 16.52 Å [4]. It is worthwhile to mention that DFT calculations using LDA or GGA usually give good estimations of the lattice parameters, within few percent, especially for delafossite materials [6, 10]. However, our calculations are consistent with the theoretical investigations reported recently [6].

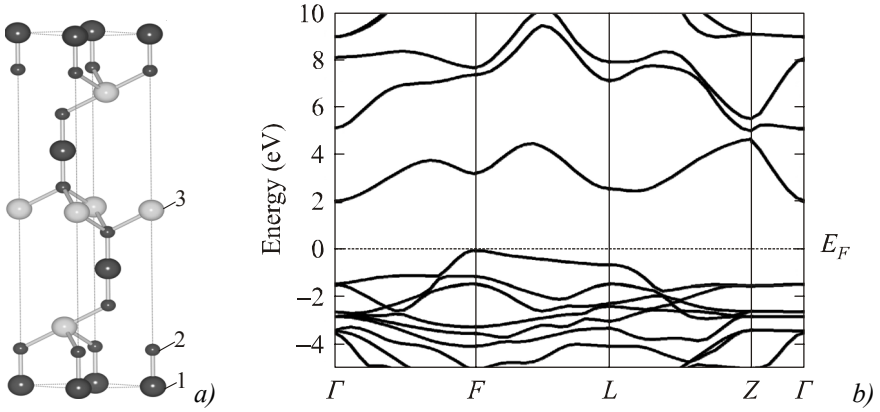


Fig. 1. (a) Structure of $CuBO_2$ belongs to the space group R-3m. The 1, 2, and 3 balls are copper, oxygen, and boron, respectively. (b) Calculated band structure of $CuBO_2$.

The calculated band structure, density of states (DOS), and partial density of states (PDOS) are illustrated in Fig. 1 and 2, respectively. From Fig. 1 (*b*) it can be seen that the bottom of the conduction band is at *Γ* – point, whereas the top of the valence band is located at *F* – point, resulting in an indirect gap of 2.06 eV. Note that the calculated direct gap at *Γ* – point of $CuBO_2$ is 3.2 eV. Our calculated energy gaps agree well with the recent theoretical results. For example, the investigations using GGA corrected for on-site Coulomb interactions (GGA + U) and a hybrid density functional

(HSE06) reported in Ref. [11] reveal the indirect fundamental band gap of about 3.1 eV and a direct optical band gap of 3.6 eV. In fact, the electronic band structure calculations of $CuBO_2$ were also performed using the GW (with a self-consistent Coulomb hole plus screened exchange calculation) correction to LDA calculation with the two experimental and theoretical configurations [6]. It was found that the indirect (direct) gap is 3.18 (3.52) eV for the LDA-optimized geometry, whilst the relevant values are 3.56 and 3.90 eV for indirect and direct gaps using the experimental geometry. Note that GW approaches, based on many-body perturbation theory, have proved to be an invaluable tool to compute accurate band gaps for a wide range of materials [12 – 14]. Hence, it is instructive to investigate the electronic structure of this material further both theoretically and experimentally.

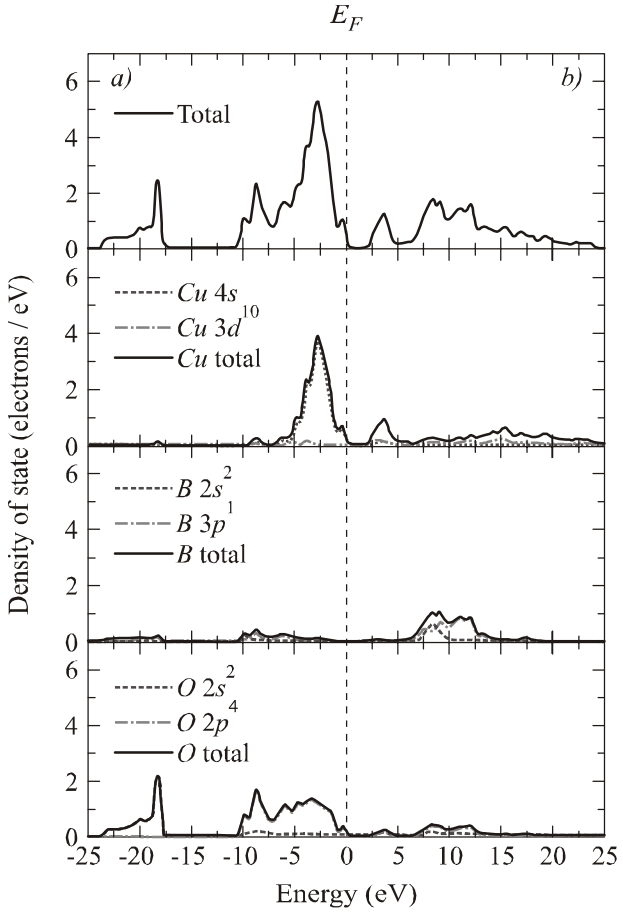


Fig. 2. Calculated (a) DOS and PDOS (b) of $CuBO_2$.

The calculated DOS and PDOS are shown in Fig. 2. The Fermi level (E_F) is chosen to be located at 0 eV. The electronic structure around E_F regions is considered, since the basic physical properties of materials depend mainly on these regions. As can be seen, the bottom of the conduction bands (below 10 eV) is dominated by *B*-2*s*, *O*-2*p* and *Cu*-3*d* states and the top of the valence bands (above – 5 eV) is derived from *Cu*-3*d* and *O*-2*p* states. These calculated results may provide a means to enhance the thermoelectric conversion performance of $CuBO_2$ due to the effect of doping [15 – 18].

The calculated band structures are used in combination with the Boltzmann transport equation solver under the constant relaxation time approximation (CRTA) to calculate the Seebeck coefficient, electrical conductivity and power factor of $CuBO_2$. Similar to our recent work on $CuAlO_2$, the effects of doping levels and temperatures can be considered in term of the different values of *p*-type acceptor-doping (A_d) levels in a gap by varying their values from 0.130 – 0.260 eV. Note that middle gap is

located at 1.03 eV above the top of valence band. According to the CRTA used, it is assumed that τ is isotropic and only depending on energy, so that τ can be cancelled in the expression for $S(T)$ for fixed temperature and doping level [1].

Our calculated $S(T)$ is shown in Fig. 3. It can be seen that when the A_d level is close to the middle gap level, $S(T)$ increases due to the decrease of the carrier density. This effect is the same as that found in common semiconductors [19]. The value of $S(T)$ in our calculation is of the same order of magnitude as those reported for $CuAlO_2$ in the literature. Nonetheless, our calculated values of $S(T)$ are two orders of magnitude greater than that reported experimentally [4]. Note the Fermi level E_F, is labeled as zero in the graph. The negative (positive) value of A_d level corresponding to it is below (above) the Fermi level in $CuBO_2$ material.

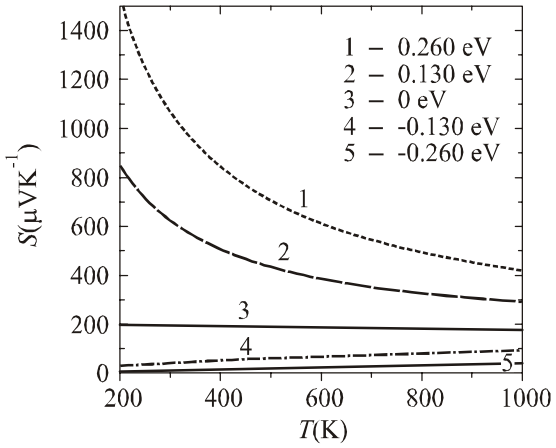
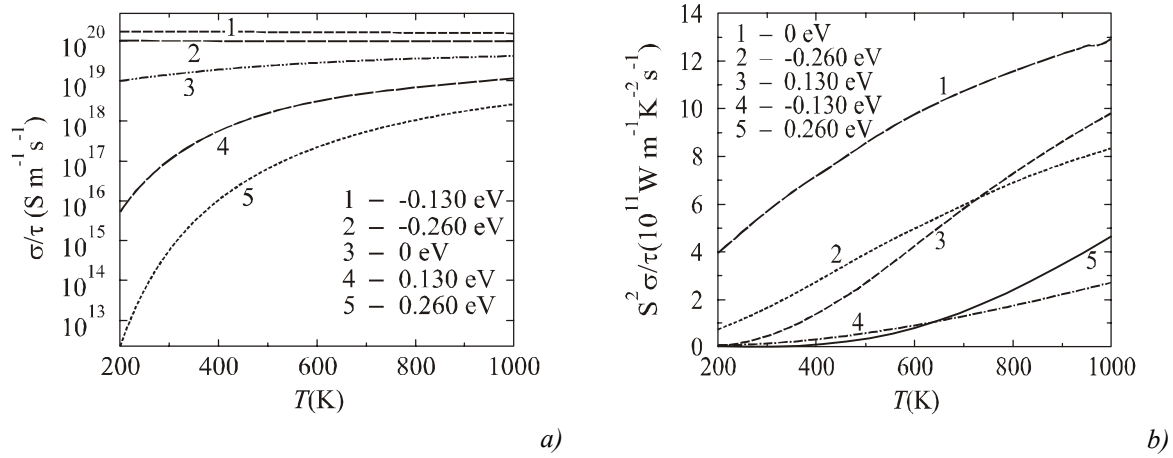


Fig. 3. Seebeck coefficient S(T) for various p-type doping levels.



a) *b)*

Fig. 4. (a) Electrical conductivity σ(T) (b) Power factor $S^2\sigma T$ for various p-type doping levels with relaxation time (τ) as a parameter.

In our recent work on $CuAlO_2$ the constant relaxation time is estimated by fitting our experimental Seebeck coefficient of $CuAlO_2$ to the electrical conductivity and the constant relaxation time is estimated to be 1×10^{-16} s. Note that our method used there is the same as that reported recently [20], in which the values of 2.2×10^{-14} s and 5.5×10^{-15} s were used for $n(p)$-doped Bi_2Te_3. In the case of $CuBO_2$, however, there is only a few experimental data of electrical conductivity available. Hence, temperature dependencies of $\sigma(T)$ with relaxation time τ as a parameter were calculated as illustrated in Fig. 4 (*a*). Note that the A_d level is close to the top of the valence band, $\sigma(T)$ increases since the carrier density is high. In addition, $\sigma(T)$ increases with increasing temperature, because

electrons can easily move into the acceptor level. However, this effect is less important at high temperature, since more electrons can be thermally excited to the acceptor level. Fig. 4 (*b*) shows the temperature dependence of power factor, it can be seen that the power factor increases with increasing temperature. Note that the power factor is large for non-doped material. This may be a consequence of a simplified model used here regarding constant relaxation time model or rigid band approach. Hence, $CuBO_2$ may become a good thermoelectric material at high temperatures, provided that the thermal conductivity is very low and the electrical conductivity can be enhanced. Therefore, it is instructive to investigate experimentally and theoretically the effect of heavy doping on conductivity while maintaining the high Seebeck coefficient of this material.

Conclusions

The lattice constants and electronic structures of delafossite $CuBO_2$ were calculated by first-principles method. The results of the lattice parameters are in favorable agreement with the other theoretical and experimental results. The energy band structure shows that $CuBO_2$ is an indirect band gap material with the gap value of 2.06 eV. Its direct energy gap value is 3.20 eV. The valence band is dominated by *Cu*-3*d* and *O*-2*p* states, whereas the conduction band is dominated by *B*-2*s*, *O*-2*p* and *Cu*-3*d* states. Based on the calculated electronic properties of $CuBO_2$, we were able to calculate the thermoelectric parameters by employing the Boltzmann theory and rigid-band approach. Our investigation revealed that the power factor of $CuBO_2$ increases with temperatures, but decreases with increasing doping levels. It is expected that our calculations combined with the experimental data may serve as a guide in designing high efficient thermoelectric device based on delafossite $CuBO_2$ and related compounds.

Acknowledgement. This work has been partially supported by the Human Resource Development in Science Project (Science Achievement Scholarship of Thailand, SAST), the National Nanotechnology Center (NANOTEC), National Science and Technology Development Agency (NSTDA), Ministry of Science and Technology, Thailand, through its Computational Nanoscience Consortium (CNC). Author is very grateful to Dr S.J. Clark of Durham University, UK for use of his codes.

References

1. D.J. Singh, Band Structure and Thermopower of Doped $CuYO_2$, Phys. Rev. B 77, 205126 (2008)
2. A.N. Banerjee, R. Maity, P.K. Ghosh, K.K. Chattopadhyay, Thermoelectric Properties and Electrical Characteristics of Sputter-Deposited *p*-$CuAlO_2$ Thin Films, Thin Solid Films 474, 261 (2005).
3. G.D. Mahan, J.O. Sofo, The Best Thermoelectric, Proc. Natl. Acad. Sci. USA 93, 7436 (1996).
4. M. Snure, A. Tiwari, $CuBO_2$: a *p*-type Transparent Oxide, Appl. Phys. Lett. 91, 092123 (2007).
5. H. Kawazoe, M. Yasukawa, H. Hyodo, M. Kurita, H. Yanagi, H. Hosono, *p*-type Electrical Conduction in Transparent Thin Films of $CuAlO_2$, Nature 389, 939(1997).
6. F. Trani, J. Vidal, S. Botti, M.A.L. Marques, Band Structures of Delafossite Transparent Conductive Oxides from a Self-Consistent GW Approach, Phys. Rev. B 82, 085115 (2010).
7. S.J. Clark et al., First Principles Methods Using CASTEP, Zeitschrift fur Kristallographie 567, 220 (2005).
8. http://opium.sourceforge.net
9. G.K.H. Madsen, D.J. Singh, BoltzTrap: A Code for Calculating Band-Structure Dependent Quantities, Comput. Phys. Commun. 175, 67 (2006).
10. P. Poopanya, A. Yangthaisong, C. Rattanapun, A. Wichainchai, Theoretical Study of Electronic

Structure and Thermoelectric Properties of Doped $CuAlO_2$, J. Elec. Mat. 40 (5), 987, 2011.

11. D.O. Scanlon, A. Walsh, G.W. Watson, Understanding the *p*-type Conduction Properties of the Transparent Conducting Oxide $CuBO_2$: A Density Functional Theory Analysis, Chem. Mater. 21, 4568 (2009).
12. W.G. Aulbur, L. Jönsson, J. Wilkins, Quasiparticle Calculations in Solids Solid State Phys. 54, 1, 1999.
13. M. van Schilfgaarde, T. Kotani, S. Faleev, Quasiparticle Self-Consistent GW Theory, Phys. Rev. Lett. 96, 226402 (2006).
14. T. Kotani, M. van Schilfgaarde, S. Faleev, Quasiparticle Self-Consistent GW Method: A Basis for the Independent-Particle Approximation, Phys. Rev. B 76, 165106 (2007).
15. B. Falabretti, J. Robertson, Electronic Structures and Doping of SnO_2, $CuAlO_2$, and $CuInO_2$, J. Appl. Phys. 102, 123703 (2007).
16. M.V. Lalic, J. Mestnik-Filho, A.W. Carbonari, R.N. Saxena, M.J. Moralles, Influence of *Cd* Impurity on the Electronic Properties of $CuAlO_2$ Delafossite: First-Principles Calculations, J. Phys: Condens. Matter. 14, 5517 (2002).
17. J. Robertson, K. Xiong, S.J. Clark, Band Gaps and Defect Levels in Functional Oxides, Thin Solid Films 496, 1 (2006).
18. D.O. Scanlon, A. Walsh, M.J. Morgan, G.W. Watson, Effect of *Cr* Substitution on the Electronic Structure of $CuAl_{1-x}Cr_xO_2$, Phys. Rev. B 79, 035101 (2009).
19. C.M. Bhandari, D.M. Rowe, CRC Handbook of Thermoelectrics (CRC Press, Boca Raton, 1995).
20. S. Lee, P. von Allmen, Tight-Binding Modeling of Thermoelectric Properties of Bismuth Telluride, Appl. Phys. Lett. 88, 022107 (2006).

Submitted 23.05.2011.