Jurnal Teknologi

Full Paper

INVESTIGATION OF STRUCTURAL, ELECTRONIC AND THERMOELECTRIC PROPERTIES OF XCUOTE (X: BI, CE, LE) WITH GGA-WC EXCHANGE CORRELATION FUNCTIONAL

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Article history
Received
15 August 2015
Received in revised form
15 November 2015
Accepted
30 December 2015

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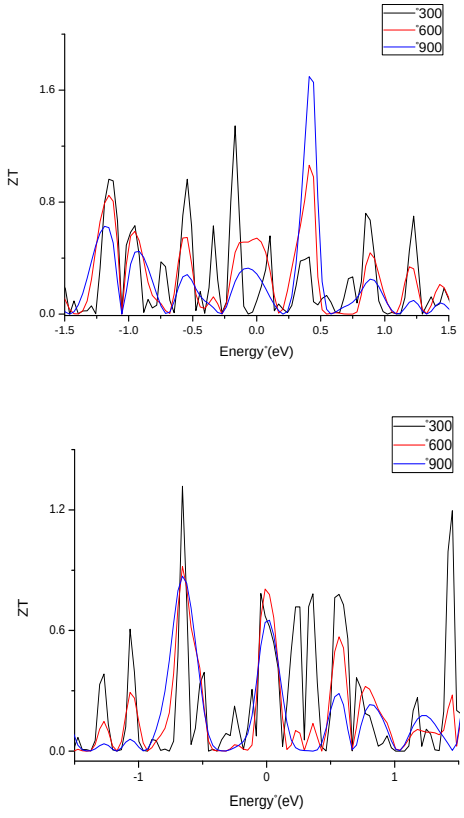
Graphical abstract



Abstract

Linearized augmented plane wave plus local orbitals (LAPW + lo) method designed within density functional theory (DFT) has been used in this study to calculate the structural, electronic and thermoelectric properties of XCuOTe (X=Bi, Ce, La). Generalized gradient approximation, Wu-Cohen (GGA-WC) parameterized exchange correlation functional, was used. The structural and electronic calculations have a good agreement with previous study. For thermoelectric calculation, semi empirical Boltzmann approach implemented in BoltzTraP package was used to calculate Seebeck coefficient, electronic conductivity as well as thermal conductivity. By referring to previous studies, the results have good agreement with them. In addition, the Seebeck coefficient of these materials was calculated as a function of the chemical potential at temperatures 300K, 600K, and 900K. Our calculations highlight suitability of these materials for applications in thermoelectric devices.

Keywords: Density functional theory, generalized gradient functional, Seebeck coefficient, thermal conductivity, Oxytellurides

Abstrak

Kaedah potensi penuh gelombang satah linear (LAPW) bersama dengan teori berfungsikan ketumpatan (DFT) telah digunakan dalam pembelajaran ini untuk mengira sifat-sifat struktur, elektronic dan termoelektrik bagi XCuOTe (X: Bi, Ce, La). Fungsi kecerunan teritlak berfungsi Wu-Cohen (GGA-WC) telah digunakan dalam kajian ini. Pengiraan struktur dan electronic mempunyai persetujuan dengan kajian sebelum ini. Untuk pengiraan termoelektrik, teori semi-empirikal Boltzmann dalam pakej Boltztrap adalah untu mengira pekali Seebeck, kekonduksian elektrik dan kekonduksian terma. Dengan merujuk kajian sebelum ini, corak lakaran mempunyai persamaan dengan kajian yang sedang dijalankan. Tambahan pula, pekali Seebeck untuk bahan-bahan ini dikira berfungsikan pada fungsi keupayaan kimia pada beberapa suhu (300K, 600K, 900K). Perkiraan kami bagi bahan-bahan ini sangat sesuai untuk diaplikasikan kepada peranti termoelectrik.

Kata kunci: Teori berfungsikan ketumpatan, fungsi kecerunan teritlak, pekali Seebeck, kekonduksian termal, Oxytellurides

1.0 INTRODUCTION

Presently, oxytellurides based XCuOTe has become a demand in thermoelectric materials. The ability of these materials to convert the waste heat to electricity is getting serious attention among researchers since the energy supplying resources like charcoal, petroleum, natural gases are depleting day by day [1]. Oxytellurides has become one of the good materials because having narrow band gap. The effectiveness of thermoelectric materials is described by ZT parameter (called figure of merit), and is related to Seebeck coefficient (S), electrical conductivity (σ) and thermal conductivity (κ) of the material as; $ZT = \frac{S^2\sigma T}{\kappa}$ [2].

A good and better thermoelectric material can be achieved by increasing the Seebeck coefficient (S), electronic conductivity (σ) and decreasing the thermal conductivity (κ) but to decrease the thermal conductivity that consists of two part (thermal conductivity due to electron transport) and (thermal conductivity due to lattice phonon) is challenging [3]. Therefore, power factor, $PF = S^2\sigma$ was introduced that exclude the factor of thermal conductivity [4] and more focuses on the structural, electronic, optical and transport properties of these materials. Early 90s, the best ZT achieved was about 1 (ZT ≈ 1) from a material called lead telluride PbTe [6]. In this paper, we have been adopted density functional theory (DFT) in order to investigate physical properties of XCuOTe (X: Bi, Ce, La).

2.0 COMPUTATIONAL DETAILS

In this study, we are using a package known as WIEN2k [5] integrated with full-potential linearized-augmented plane-wave method (FP-LAPW) based on DFT theory [6]. In our calculations, a fully relativistic description has been used for the core states, and for valences states, the scalar-relativistic descriptions have been used by neglecting the spin-orbital coupling. For studying the structural, electronic and optical properties, GGA-WC approach is used as exchange correlation functional.

In this method, unit cell is divided into two sections which are interstitial region (IR) and non-overlapping muffin-tin (MT) spheres centered at the atomic sites. In interstitial region, plane wave basis set is used, while inside the muffin-tin region, the basis set is described by a linear combination of the atomic like wave functions times the spherical harmonics. For achieving the energy eigenvalues convergence, a cutoff of K_{max} = 6 is used in the IR to expand wave functions in terms of the plane waves. The experimental lattice constants of BiCuOTe (a=b= 4.042, c = 9.5324), CeCuOTe (a=b=4.1497, c= 9.3090) and LaCuOTe (a=b= 4.1775, c= 9.3260) respectively [7], [8], are used as input variables to calculate theoretical lattice constant for both materials.

After the calculation of electronic structure, the thermoelectric properties of XCuOTe were calculated like Seebeck coefficient, thermal conductivities and electronic conductivity by using BoltzTraP package [8].

3.0 RESULTS AND DISCUSSION

3.1 Structural Properties

By refer to the Figure 1, the crystal structures of: A) BiCuOTe, B) CeCuOTe and C) LaCuOTe are corresponding to the tetragonal type crystal structure with space group F4/nmm (129), and the Wyckoff positions X, Y and Z are 2a(0.75, 0.25, 0.0), 2b(0.75, 0.75, 0.25), 2c(0.25, 025, 0.14829), and 2c(0.25, 0.25, 0.6710) respectively.

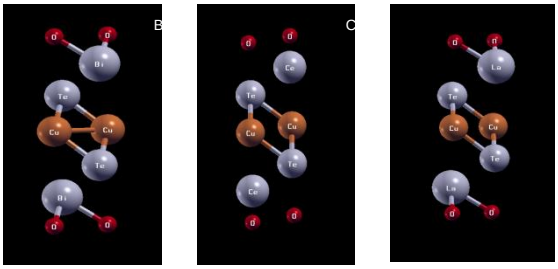


Figure 1 The crystal structure for XCuOTe A) BiCuOTe, B) CeCuOTe and C) LaCuOTe

3.2 Electronic Properties

Energy bandstructure provides valuable information for electronic industry especially fabricating electronic devices and to study transport properties of the semiconductors. Since oxytellurides is one of the promising thermoelectric materials group, precise and accurate knowledge about the bandstructure is essential. The calculation by DFT is famous especially structural calculation with GGA and LDA. However, these both exchange correlations usually give an underestimated energy bandgap [13]. It is because that the standard form of the GGA and LDA is simple that are not sufficiently flexible to accurately reproduce both exchange-correlation energy and its derivative [10]. Therefore, in this study GGA-WC is used.

In this study, as can be seen from Figure 2; A) BiCuOTe and C) LaCuOTe have semiconductor behavior with indirect gap for BiCuOTe and direct gap for LaCuOTe. But for the B) CeCuOTe, it has shown metallic behavior at Fermi level (E_f = 0), however conduction-band minimum (CBM) is dense with hole carriers. For BiCuOTe, the valence-band maximum (VBM) and conduction-band minimum (CBM) are located at different point which is at X and M. For LaCuOTe, the VBM and CBM are both located at Γ and is in contradiction with previous study by K. Ueda *et al*. which states the LaCuOTe is

an indirect gap semiconductor [14]. Whereas our results for LaCuOTe has good agreement with M. Ling Liu *et al.* [12].

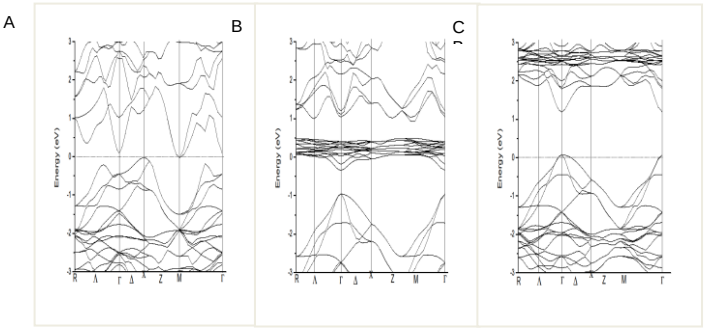


Figure 2 The electronic bandstructure of XCuOTe

The calculated total density of states (TDOS) for all the materials, A) BiCuOTe, B) CeCuOTe and C) LaCuOTe can be seen from Figure 3. In BiCuOTe compound, the conduction band (CB) is mainly occupied by Bi atoms at 2 eV including a small contribution from O and Te atoms. Whereas, in the valence band (VB), the major contribution is from Cu and O atoms at 2.5 eV along with a small contribution in valence band (VB) from Te atoms. For CeCuOTe compound, near to the Fermi energy level, the conduction band (CB) is mainly occupied with Ce atoms compare to the Cu, O, and Te atoms but for valence band (VB), it is mainly built up with Cu atoms at 0.75 eV, however Ce, O and Te atoms have small contribution. In LaCuOTe compound, the conduction band (CB) of LaCuOTe is mainly composed by La atoms at 2 eV. In valence band (VB), majority of states are occupied with Cu and O atoms at 3 eV.

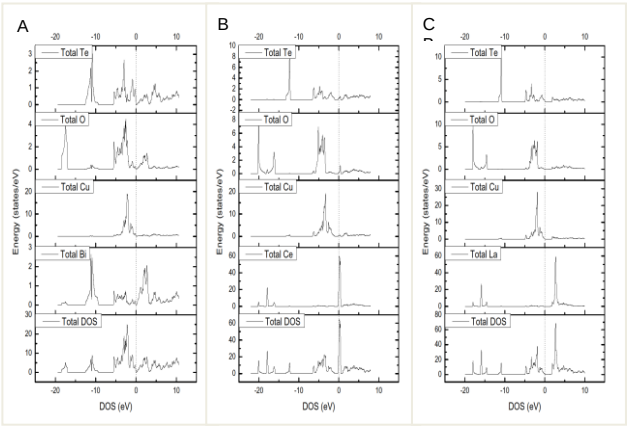


Figure 3 Density of state of XCuOTe

3.3 Optical Properties

The optical properties can be obtained by the determination of dielectric function. The complex dielectric function is given by $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$. ε_1 represents as the real parts while ε_2 represents as the imaginary part, and both of these describe the propagation properties and optical absorption in a medium respectively. This function is mainly used to understand optical properties of the materials. Kramer-Kronig relation was used to calculate the real part $\varepsilon_1(\omega)$, where $\varepsilon_1(\omega)$ was obtained from the imaginary part of dielectric function $\varepsilon_2(\omega)$. To calculate the imaginary part, $\varepsilon_2(\omega)$ is calculated from the momentum matrix elements between the occupied states of valence band and unoccupied conduction band states wave functions.

The optical parameters that are focused in this work, are dielectric function, absorption coefficient, $\alpha(\omega)$, energy loss spectrum, $L(\omega)$ reflectivity, $R(\omega)$ and refractive coefficient that can be obtained from $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$. All the calculations of BiCuOTe and LaCuOTe can be referred at Figure 4 for dielectric function, Figure 5 for loss function, Figure 6 for absorption spectra, Figure 7 for reflectivity and Figure 8 for refractive coefficient.

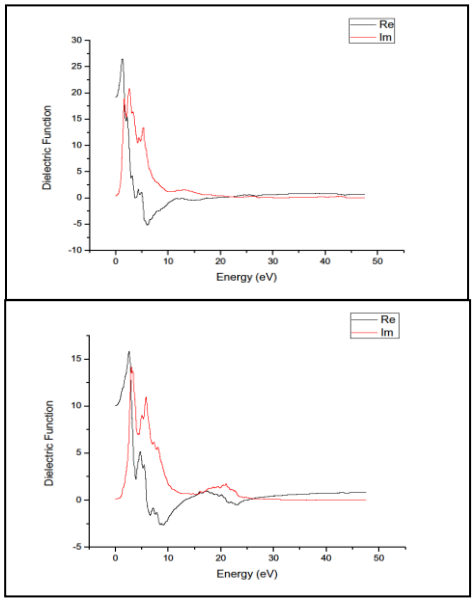


Figure 4 Dielectric function of a)BiCuOTe, and b)LaCuOTe

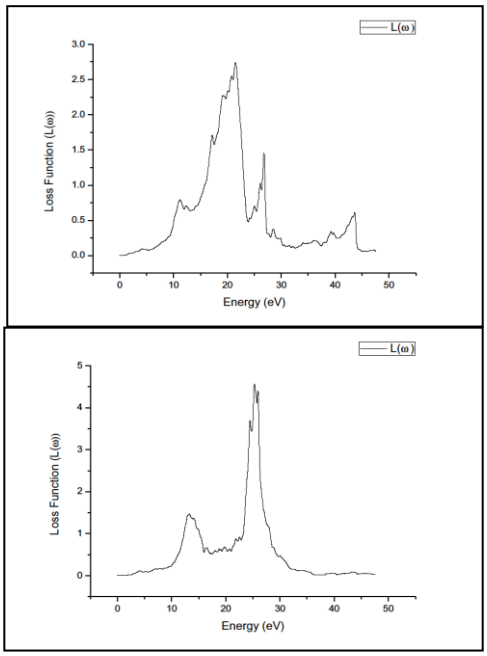


Figure 5 Loss function, L(ω) of a)BiCuOTe, and b)LaCuOTe

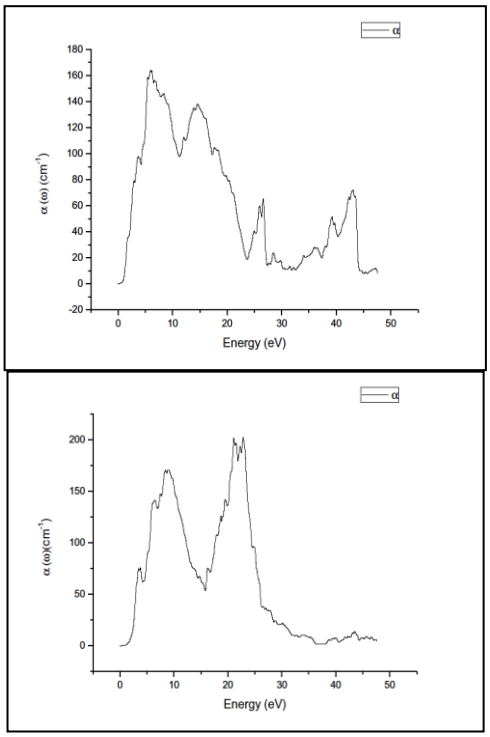


Figure 6 Absorption spectra, α(ω) of a)BiCuOTe, and b)LaCuOTe

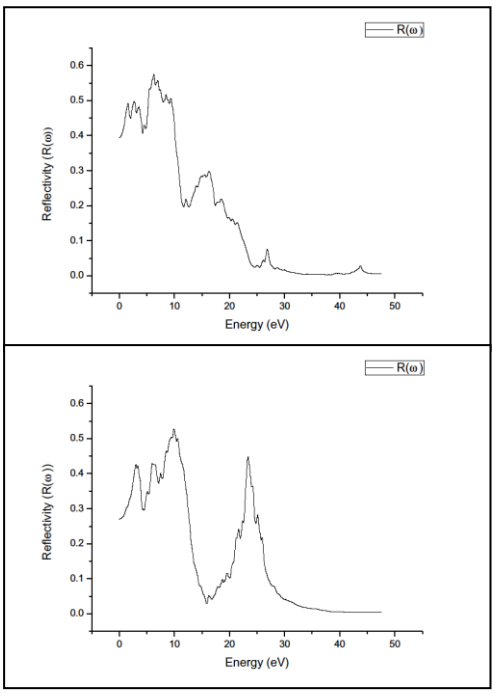


Figure 7 Reflectivity, R(ω) of a)BiCuOTe, and b)LaCuOTe

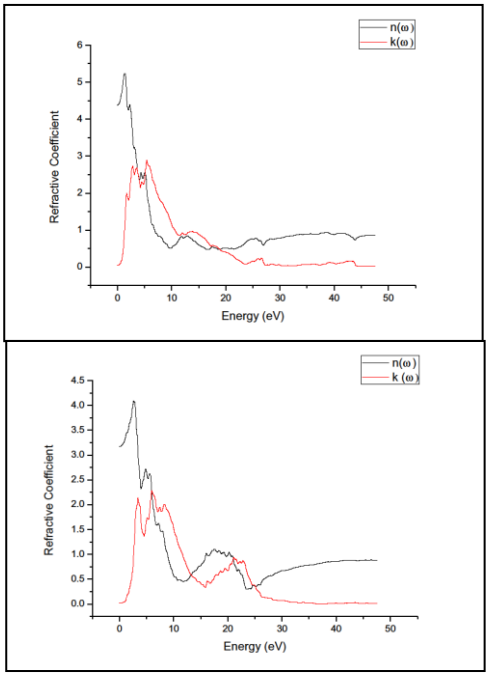


Figure 8 Refractive coefficient of a)BiCuOTe, and b)LaCuOTe

3.4 Thermoelectric Properties

3.4.1 Seebeck Coefficient

In this section, we show and explain about the calculated thermoelectric properties determined within the constant relaxation-time of electrons τ (independent of the energy levels and k-points). Although this constitutes a weak approximation, we have not found in the any reference or in literature study related to τ of BiCuOTe and LaCuOTe. We are excluding CeCuOTe since it showed metallic character. According to Ali Shakouri *et al.*, the best ZT materials are found in semiconductors. It is because metals have relatively low Seebeck coefficient and high thermal conductivity as compare to semiconductors [2].

In this section, we just focus on two thermoelectric properties which are Seebeck coefficient and electronic conductivity (σ). These two properties are very important to investigate the best TE materials. Therefore, in the following only $\frac{\sigma}{\tau}$ and $\frac{PF}{\tau}$ values, where PF = $S^2\sigma$ the power factor, are presented.

By referring to Figure 9, the Seebeck coefficient of BiCuOTe and LaCuOTe show same pattern with previous study by Manoj K. Yadav and Biplab Sanyal [7], G. Murtaza *et al.* [15], M. Bilal *et al.* [16], and H. Balout *et al.* [17]. In this study, the Seebeck coefficient, S is depicted at different temperature values of 300K, 600K and 900K with respect to the energy. At 300K, from the plot in (A), n-type region is more dominant compare to p-type region between -2.5eV and 2.5eV. Near to the Fermi energy, E_f, on the right side the highest value is 237.5μV/K represent for n-type region. For the p-type region, the highest point is 181.3μV/K at 2.3eV.

For LaCuOTe semiconductor in B) plot, p-type region shows dominant character compare to n-type region that means this material is dominated with positive carriers. The highest point at the p-type region is 287.5μV/K at -1.2eV and at n-type region is 193.8eV at 0.85eV. The values mentioned above is at 300K. For 600K and 900K, the plots show the value of Seebeck coefficients is getting lesser compare to 300K. Therefore, we can say the Seebeck coefficient decreases with increasing of temperature.

3.4.2 Thermal Conductivity

In this section, another contributor to understand good TE materials is explained. F good and best ZT materials, electronic conductivity, σ must be high value. There is significant number of carriers and states available for conduction in metals, typically n ≈ 10^{22} carriers/cm^3. Therefore, in metals, the electrical conductivity is higher compare with semiconductor and insulator but there is another factor known as thermal conductivity, κ that make metals less effective compare to semiconductors [11]. Therefore, for semiconductor the carriers must be thermally excited across a gap. The derivation of temperature-dependence of electrical conductivity is $\sigma \approx \sigma_0 e^{\frac{-E_g}{k_B T}}$. To achieve a good value of electrical conductivity, there is two ways: 1) by having a very small gap to excite the carries across ($\frac{E_g}{k_B T}$) and 2) by having very highly mobility of carriers [18].

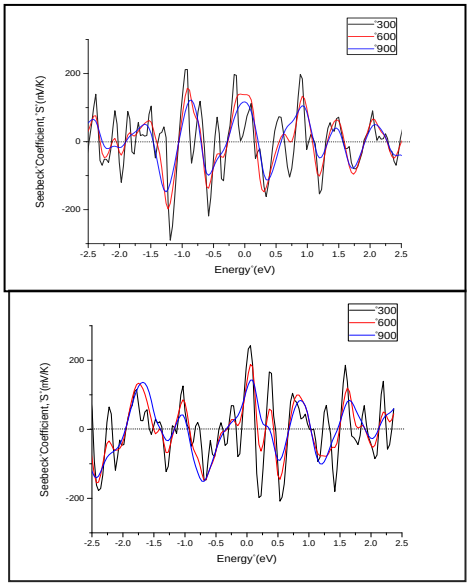


Figure 9 Seebeck coefficient of a)BiCuOTe, and b)LaCuOTe

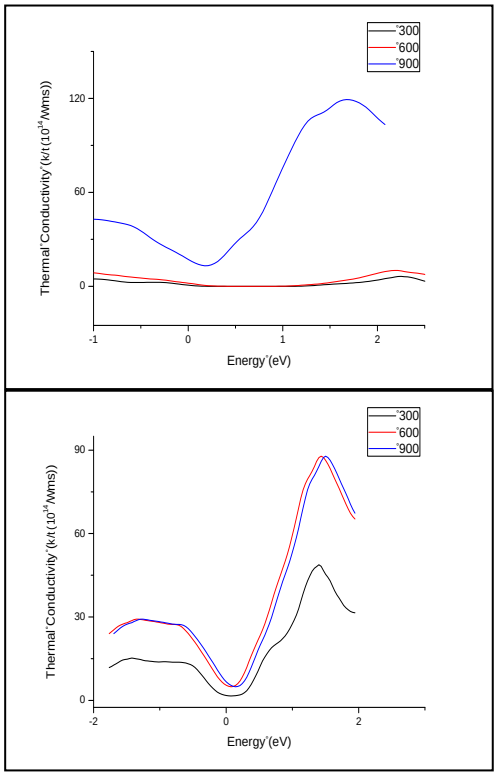


Figure 10 Thermal conductivity of a)BiCuOTe, and b)LaCuOTe

From the Figure 10, the electronic conductivity of BiCuOTe and LaCuOTe are relative to relaxation-time. By refer to the both plot A and plot B, electronic conductivity in BiCuOTe is lower compare to electronic conductivity in LaCuOTe. The highest value for BiCuOTe is 1034.9×10^{20} σ/τ at 1.5eV and for LaCuOTe has a highest value 2600.0×10^{20} σ/τ at 0.5eV. For this property, it has shown that LaCuOTe has good electronic conductivity compare to BiCuOTe. By comparing both materials with temperature, the values of electrical conductivity are the highest and the lowest at room temperature 300K. For 600K and 900K, the values of electrical conductivity became lesser. Therefore, we can conclude that the electrical conductivity is decreasing when temperature increasing.

4.0 CONCLUSION

The structural, electronic and thermoelectric properties of XCuOTe (X: Bi, Ce, La) were computed using full-potential linear-augmented plane wave (FP-LAPW) method formed within DFT. Generalized gradient approximation with the Wu-Cohen (WC) parameterization was used to calculate the exchange correlation energy potential. We have compared our results with the already done experimental and theoretical works. Our results are matching with the previous calculations with different exchange correlation approximations. Thus, the DFT approaches show its ability to solve the complex equation in more easy way. In addition, the calculations have good agreement in term of patterns of plotting for Seebeck coefficient and electronic conductivity. These materials show good values of TE properties at low temperature (T=300K) compare to higher temperature 600K and 900K.

Acknowledgement

The authors (Muhammad Azim Izzuddin Mohd Amin, Dr. Rashid Ahmed, etc.) greatly acknowledge to financial support by the Ministry of Higher Education (MOHE), Universiti Teknologi Malaysia (UTM) for the grant projects Q.J130000.2526.12H52 & Q.J130000.2526.06H15, and Physics Department of Faculty of Science. Finally, I want to greet and thankful to people who involve and contributed ideas in this study.

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