STRUCTURE, ELECTRONIC AND THERMOELECTRIC PROPERTIES OF XCuOTe (X: Bi, Ce, La) BY DENSITY FUNCTIONAL THEORY

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Dedicated to:

To my beloved mother, Aznida Binti Alias, and

father, Mohd Amin B. Mamat

and

my lovely supervisor, Dr Rashid Ahmed

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ABSTRACT

To lessen the energy crisis, one of the imperative ways out is to exploit the waste energy, in particular, waste heat. To make use of waste heat, among many ways the most appropriate and simplest one is the application of thermoelectric (TE) materials, as it does not require any appreciable changes in the industrial as well as domestic appliance technology. Although TE materials are recently investigated for refrigeration and power generation applications, the key issue of their limited applications is the development of high-performance TE materials. Oxytellurides are considered potential TE materials because of their aligned electronic bandgap energy. However, the exploration of a new and low cost material within a short period is very challenging. In this work, XCuOTe (X= Bi, Ce, and La) oxytellurides are investigated with a computational technique based on density functional theory (DFT) together with semi-empirical Boltzmann theory. Calculations are performed using the full potential linear augmented plane wave (FP-LAPW) method implemented in WIEN2k package and BoltzTraP package. The quality of the DFT results is comprehensively dependent on the chosen form of the exchange-correlation functionals. To obtain more precise results, different exchange-correlation functionals such as local density approximation (LDA), generalized gradient approximation (GGA), Wu-Cohen (WC-GGA) and modified Becke-Johnson (mBJ) potential are used. The obtained results for structural parameters are in good agreement with the available reported experimental and theoretical results in the literature. Based on the band structure calculations, BiCuOTe and LaCuOTe show their semiconducting behavior whereas CeCuOTe exhibits its metallic disposition. In line analysis of the obtained thermoelectric properties, results show that BiCuOTe and LaCuOTe are potential thermoelectric materials with higher Seebeck coefficients, electronic conductivities and power factor, $S^2\sigma$, values.

ABSTRAK

Bagi mengurangkan krisis tenaga, salah satu langkah yang seharusnya dilakukan adalah dengan mengeksploitasi sisa tenaga, khususnya sisa tenaga haba. Untuk memanfaatkan sisa tenaga haba, satu cara yang paling sesuai dan mudah antara banyak-banyak cara adalah penggunaan bahan termoelektrik (TE) yang tidak memerlukan perubahan ketara dalam industri serta teknologi peralatan domestik. Walaupun, bahan TE sekarang ini dikaji untuk sistem penyejukan dan aplikasi penjanaan kuasa, isu utama yang menghadkan penggunaannya adalah pembangunan bahan TE yang berkuasa tinggi. *Oxytellurides* dianggap sebagai bahan TE yang berpotensi kerana tenaga jurang jalur sejajarnya. Walau bagaimanapun, pencarian bahan baharu dan kos rendah dalam jangka masa yang singkat adalah sangat mencabar. Dalam kajian ini XCuOTe (X=Bi,Ce, dan La) *Oxytellurides* telah dikaji dengan teknik komputeran berlandaskan teori fungsian ketumpatan (DFT) bersama teori separa-empirikal Boltzmann. Pengiraan telah dijalankan menggunakan kaedah keupayaan penuh gelombang satah linear terimbuh (FP-LAPW) yang dilaksanakan dalam pakej WIEN2k dan BoltzTraP. Kualiti hasil DFT adalah bergantung kepada pemilihan bentuk fungsian pertukaran-kolerasi. Bagi memperoleh hasil yang lebih tepat, fungsian pertukaran-kolerasi yang berbeza seperti penghampiran ketumpatan tempatan (LDA), penghampiran kecerunan teritlak (GGA), Wu-Cohen (WC-GGA) keupayaan , dan Becke-Johnson terubah suai (mBJ) telah digunakan. Keputusan yang diperoleh bagi parameter struktur adalah berpadanan dengan hasil kajian eksperimen dan teori yang dilaporkan dalam literatur. Berdasarkan kepada pengiraan struktur jalur, BiCuOTe dan LaCuOTe menunjukkan tingkahlaku semikonduktor manakala CeCuOTe mempamerkan sifat logam. Sejajar dengan analisis termoelektrik, keputusan menunjukkan bahawa BiCuOTe dan LaCuOTe ialah bahan termoelektrik yang berpotensi dengan nilai pekali Seeback, konduktiviti elektronik dan faktor kuasa, $S^2\sigma$, yang tinggi.

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LIST OF ABBREVIATIONS

DFT	Density functional theory
PBE	Perdew Burke Ernzerhof
GGA	Generalized Gradient Approxiamtion
WC	Wu-Cohen
EV	Engel-Vosko
mBJ	modified Becke Johnson
FP-LAPW	Full Potential-Linearized Augmented Plane Wave
E_g	Energy gap
PF	Power factor
ZT	Figure of merit
XC	Exchange-correlation functional
TE	Thermoelectric
DOS	Density of States
TDOS	Total density of states
PDOS	Partial density of states
lo	Local orbital

LIST OF SYMBOLS

Bi	Bismuth
Ce	Cerium
La	Lanthanum
O	Oxygen
Te	Tellurium
Se	Selenium
eV	electron Volt
κ_e	Thermal conductivity (electronic)
κ_l	Thermal conductivity (lattice)
S	Seebeck coefficient
σ	Electrical conductivity
Sb	Antimony
T	Temperature
K	Kelvin
K	Potassium
Mg	Magnesium
Sr	Strontium
Ba	Barium
E	Energy
n	Carrier concentration
e	Electron charge
τ	Relaxation time
v	Group velocity
μ	Carrier mobility
L	Lorentz number
$S^2\sigma$	Power factor

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Since the past decades, a lot of disasters occurred due to the Greenhouse effect, resulting in global warming, causing thawing of ice at North and South Poles, along with the Ozone layer's depletion. These problems have triggered considerable debate among politicians, NGOs, environmental agencies, etc. globally. Commonly, green energy sources are referred to biomass, solar and wind energy, have a significant contribution to the people and also reduce the pollutions [1]. On the other hand, human activities such as open burning, illegal deforestation, and uncontrolled vehicles exhaust heat, are also appreciably contributing to the increase of world temperature. To overcome such issues and make useful of the waste heat, scientists came up with the idea to produce a green environment and better future energy known as thermoelectricity. The ability in the direct conversion of heat into the useful electricity is a very good application in the society nowadays. For example, the efficiency of a car is less than 40% and the remaining 60% is released in terms of waste heat. Therefore, researchers/scientists are trying to find suitable ways to convert the waste heat into electricity. Somehow the scientists already used of this principle in different applications like the application of the radioisotopes as the purpose of thermal power generators for drones (unmanned vehicles) and deep space satellites [2]. Besides that, with suitable materials thermoelectric (TE) generators can also be used for converting heat generated by many sources, such as automotive exhaust and industrial processes into electricity. Considering the extremely high reliability and useful role of the thermoelectric materials, efficient and cost effective TE materials and technologies are

widely studied concerning infrared sensors, exhaust waste heat recovery, computer chips, satellites, etc. [1]. The intent of this report is to find the better and cheaper alternatives for TE materials, which can convert heat energy into electricity directly, in particular, for the recovery of the waste heat. Hence, a potential candidate i.e. XCuOTe (X= Bi, Ce, La) compounds are selected as the materials for this study, which could be good thermoelectric materials.

Over the past few decades, researchers are working hard to look for the high-performance TE materials. By some aspect and factors, a lot of TE materials were found like skutterudites, clathrates, half-Heusler alloys, SiGe-based, PbTe based and etc. One of the potential class of TE materials is known as oxytellurides. It is because they have high ZT value such as BiCuOTe has shown ZT = 0.66 (experimentally) at 673 K [6]. Other than BiCuOTe, the rare earth element oxytellurides (LaCuOTe and CeCuOTe) also included in this study.

Various method has been used for investigating the thermoelectric properties whether through experimental and theoretical studies. Theoretical studies have been widely used in thermoelectric especially transport properties. In the past few years, researchers were looking hard for finding best method and approaches by introducing various of theories such density functional theory (DFT) [22], Diffusion Monte Carlo (DMC) [23] and Variational Monte Carlo (VMC) [24]. DFT has been employed in $CuGaTe_2$ compound for investigating the thermoelectric behavior. $CuGaTe_2$ compound which is belong to chalcopyrite group produced low lattice thermal conductivity due to the low sound velocities [66].

In addition, researchers from Florida has been introduced new structures of oxytellurides which is known as Ba_2TeO and $Ba_3Yb_2O_5Te$ compounds. Both these compounds were studied by using DFT approach with different exchange-correlation functional. Ba_2TeO compound with Perdew-Burke-Ernzerhof generalized gradient approximation (PBE-GGA) produced 1.9 eV direct band gap and $Ba_3Yb_2O_5Te$ compound with local spin density approximation (LSDA) produced 2.2 eV direct band

gap. Both band gap values also indicating semiconductor properties. Therefore, by using DFT which is preferable in producing good and small band gap, Ba_2TeO and $Ba_3Yb_2O_5Te$ compounds have potential to be one of the potential thermoelectric materials [67].

1.2 Problem Statement

Material sciences offering various type of study such as experimental and through simulation where a lots of theorem have been introduced. Density functional theory (DFT) became a tool in solving some problems especially bandstructure calculation, density of states (DOS) and so on. Previous study has mentioned various how good DFT in producing good and small band gap which is very preferable in calculating thermoelectric properties such as Seebeck coefficient (S), electronic conductivity (σ) and thermal conductivity (τ). Due to low cost of operation and time consuming, DFT with various exchange correlation functionals has been involved in this study. Various of exchange-correlation functionals have been introduced in previous study such as local density approximation (LDA), generalized gradient approximation (GGA), modified Becke-Johnson (mBJ) but looking for suitable and comparable one is hard. In addition, semi-empirical Boltzmann theory has been used along to solve and investigate the thermoelectric properties which is still lacking for oxychalcogenides. Moreover, DFT approaches do not require prior knowledge about the materials except basic parameters and are considered to be suitable for the atomic scale fundamental understanding of the properties which are not yet explored well. Due to unique structure and and layers which consist of "superlattice" layer and oxide layer make XCuOTe (X: Bi, Ce, La) one of promising thermoelectric materials. These two layers are contributing to high Seebeck coefficient (S) and low thermal conductivity (τ).

1.3 Objectives of Study

This study embarks on the following objectives:

1. To calculate the structural and electronic properties of XCuOTe (X= Bi, Ce, La) compounds using DFT methodology through variation of the exchange-correlation functional.
2. To analyze the accurate exchange-correlation functional for structural and electronic properties studies of XCuOTe (X= Bi, Ce, La) compounds.
3. To determine the thermoelectric and transport properties respect to the temperature (T) and chemical potential (μ).
4. To verify the difference between theoretical and experimental values of thermoelectric parameter with available records.

1.4 Scope of Study

In this project, XCuOTe (X= Bi, Ce, La) oxychalcogenides have been studied through DFT method. All these compounds are simulated using the unit cell approach. The investigation of the structural and electronic properties has been carried out based on a full potential linearized augmented plane wave (FP-LAPW) method implemented in WIEN2k package. Various exchange-correlation functional were used such as PBE-GGA, WC-GGA, LDA, mBJ, and EV-GGA.

In the light of aforementioned objectives, the following scope of this research work is chalked out:

i. Construction and optimization of the structural unit cell of XCuOTe (X= Bi, Ce, La) with XCrysden and WIEN2k package.
ii. Investigation of the structural properties of XCuOTe (X= Bi, Ce, La) by using DFT-based full potential linearized augmented plane wave (FP-LAPW) method with several different exchange-correlation functional focusing on local density approximation (LDA), Perdew Burke Ernzenhof-Generalized gradient approximation (PBE-GGA) and Wu Cohen-Generalized gradient approximation (WC-GGA) exchange-correlation functional.
iii. Investigation of electronic properties of the XCuOTe (X= Bi, Ce, La) consists of band gap calculations along with the partial and total density of states (PDOS & TDOS) focusing on modified Berke Johnson (mBJ), Engel Vosco- Generalized gradient approximation (EV-GGA) and WC-GGA exchange-correlation functional.
iv. Calculation of the thermoelectric properties and transport coefficient with semi-empirical Boltzmann theory implemented in BoltzTrap package.
v. Comparison between the calculated values of thermoelectric properties; Seebeck coefficient (S), electrical conductivity (σ), thermal conductivity (κ), power factor ($S^2\sigma$) and ZT figure of merit for XCuOTe (X= Bi, Ce, La) compounds with the previous available data in literature.

1.5 Significant of Study

This study is mainly a way forward to approach and improve the ongoing research on thermoelectric materials. The study of physical properties with various exchange-correlation potential provides an opportunity in opting for an appropriate

exchange-correlation potential to determine electronic properties. In addition, this work is conducted through the state of the art ab initio methods based on DFT. Hence, the prediction of thermoelectric properties of XCuOTe (X= Bi, Ce, La) material can be done in short time and low cost. This research plays an important role in the advancement of knowledge about conversion of waste heat to electrical power generation. In addition, this research also could be provide promising TE material that might be used as a strong footing to the experimentalist, academicians, and industrial scientists in the construction of TE technology with more economical and environmental friendly that are beneficial to the country and community.

1.6 Structure of Thesis

This thesis consists of 5 chapters and is describing the XCuOTe (X=Bi, Ce, La) compounds analysis related to structural, electronic, thermoelectric and transport properties with the first principles DFT approaches. This work was studied in compliance with WIEN2k code based on FP-LAPW. In addition, the thermoelectric and transport properties were studied using the semi-empirical Boltzmann theory implemented in BoltzTrap package. In Chapter 1, a general and brief introduction related to this study especially current issues about thermoelectric studies and materials are addressed. The problem statement and the objectives of this study were also defined in this chapter. Moreover, the scope of the study was listed accordingly in order to outline the direction of the work. The significance of this study also clearly elaborated through this chapter. In Chapter 2, the introduction and explanation of the concept of thermoelectric were stated. Several of thermoelectric materials were mentioned in this chapter for example tellurides based, selenides based, etc. Available experimental and theoretical results from previous studies were also stated in this chapter in order to compare with the obtained results of each compound. Chapter 3 describes the methodologies and computational details used throughout this study especially about Kohn-Sham theory, exchange-correlation functional and semiempirical Boltzmann theory. Chapter 4 is about the outcomes and results of the

investigations of structural, electronic, thermoelectric and transport properties of the XCuOTe (X: Bi, Ce, La). Various exchange-correlation functional were employed for calculating the structural and electronic properties. This chapter describes lattice parameter, band gap energy, and the density of states, Seebeck coefficient, figure of merit, ZT and electrical conductivity. Lastly, Chapter 5 is about conclusions drawn from this research work and recommendation for future works.

However, this work can be improved with some further studies theoretically and experimentally. Through this study, some recommendation could be applied due to the inconsistent output such as using different theory and method. Monte Carlo calculation is also one of the approaches has been used to study the behavior and properties of solid, semiconductor, etc. The techniques such as diffusion Monte Carlo (DMC) and variational Monte Carlo (VMC) could be used to further this works in the future. This study also does not include the discussion related to the contribution of thermoelectric from Hall coefficient and phonon scattering. Phonon scattering plays an important role in determining and calculating the electrical conductivity, which contributes most to the thermoelectric performance. In addition, it is believed that there will be better approaches for the improvement of ZT parameter by carefully control the stoichiometry and doping/alloying. A parallel study between theoretical and experimental is supposed to be implemented in getting better information. By using fabricating technique and various methods in producing thermoelectric materials, a huge bank of data could be collected. Therefore, a systematic and productive study will be implemented in looking for better thermoelectric materials.

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