

UNIVERSITI TEKNOLOGI MARA

**FIRST-PRINCIPLES STUDY
OF THERMOELECTRIC
PERFORMANCE
OF PURE AND Ni-DOPED
Bi₂Se₃ AND Bi₂Te₃ USING
DENSITY FUNCTIONAL THEORY**

**MUHAMMAD ZAMIR BIN
MOHYEDIN**

Thesis submitted in fulfillment
of the requirements for the degree of
Master of Science
(Physics)

Faculty of Applied Sciences

February 2020

ABSTRACT

First principles study-based density functional theory on structural, electronic and thermoelectric properties of Bi_2Se_3 and Bi_2Te_3 materials was conducted using CASTEP and WIEN2K computer code within the exchange-correlation of local density approximation (LDA). Calculations of electronic properties were carried out with spin-orbit coupling (SOC). The thermoelectric properties were calculated using Boltzmann transport theory that implemented in BoltzTraP with the inclusion of SOC. The effect of SOC on electronic properties and thermoelectric properties were analysed and found that SOC gives a significant contribution. The band gap result showed that spin-orbit coupling is necessary for the calculation to show the true nature of Bi_2Se_3 and Bi_2Te_3 that verified by the experimental studies. Bi_2Se_3 depicts band gap 0.23 eV which is higher than Bi_2Te_3 with band gap 0.15 eV. Based on the calculated figure of merit, Bi_2Te_3 shows a better thermoelectric performance of 0.3 compared with the Bi_2Se_3 which has performance 0.07 at room temperature. The performance of Bi_2Se_3 increases from temperature 300K to 500K. While, the performance of Bi_2Te_3 decreases. Then, thermoelectric properties are calculated based on the Fermi level range from -1.0 eV to 1.0 eV to prove that tailoring Fermi level could optimize thermoelectric performance for both Bi_2Se_3 and Bi_2Te_3 . Thermal conductivity is undesirable for the performance, however it cannot be reduced without reducing electrical conductivity. Adjusting Fermi level could alter the performance of Bi_2Se_3 and Bi_2Te_3 . It is found that Bi_2Se_3 has higher ideal thermoelectric performance which possesses figure of merit 0.88, while Bi_2Te_3 has figure of merit of 0.66. Nickel has reduced band gap of both Bi_2Se_3 and Bi_2Te_3 , improving electrical conductivity. Ni-doped Bi_2Se_3 has a slightly better performance with figure of merit 0.335 at 300 K compared with the Ni-doped Bi_2Te_3 that has figure of merit 0.316.

ACKNOWLEDGEMENT

Firstly, I wish to thank God for giving me the opportunity to embark on my Master and for completing this long and challenging journey successfully. My gratitude and thanks go to my supervisor Dr. Mohamad Fariz bin Mohamad Taib. Also, thanks to Mr. Masnawi bin Mustaffa, Dr. Amiruddin bin Shaari and Prof. Dr. Muhd Zu Azhan bin Yahya.

My appreciation goes to the crewmembers of the Ionic, Materials & Devices (iMADE) Research Laboratory and Scientific Computation and Instrumentation (SCNI) research group who provided the facilities and assistance. Special thanks to my colleagues and friends for helping me with this project.

Finally, this thesis is dedicated to my very dear wife, father and mother for the vision and determination to educate me. This piece of victory is dedicated to all three of you. Alhamdulillah.

TABLE OF CONTENTS

	Page
CONFIRMATION BY PANEL OF EXAMINERS	ii
AUTHOR'S DECLARATION	iii
ABSTRACT	iv
ACKNOWLEDGEMENT	v
TABLE OF CONTENTS	vi
LIST OF TABLES	ix
LIST OF FIGURES	xi
LIST OF SYMBOLS	xiv
LIST OF ABBREVIATIONS	xv
CHAPTER ONE: INTRODUCTION	1
1.1 Research Background	1
1.2 Problems Statement	2
1.3 Objective of Study	3
1.4 Significance of Study	4
1.5 Scope of Study and Limitation	4
CHAPTER TWO: LITERATURE REVIEW	6
2.1 Introduction	6
2.2 Topological Insulator	6
2.3 Thermoelectric Material	8
2.4 Bismuth Selenide (Bi ₂ Se ₃)	11
2.5 Bismuth Telluride (Bi ₂ Te ₃)	13
2.6 Density Functional Theory	17
2.7 Spin-Orbit Coupling	23
2.8 Boltzmann Transport Theory	24
2.9 Software	26
CHAPTER THREE: METHODOLOGY	27
3.1 Introduction	27
3.2 Geometrical Optimization	27
3.3 Convergence Test	30

3.4	Calculation of Electronic Properties	35
3.5	Thermoelectric Properties Calculation	37
3.6	Computational Details for Ni-Doped Bi ₂ Se ₃ and Ni-Doped Bi ₂ Te ₃	39
CHAPTER FOUR: RESULT AND DISCUSSION		40
4.1	Introduction	40
4.2	Structural Properties of Bi ₂ Se ₃ and Bi ₂ Te ₃	40
4.2.1	Lattice Parameter of Bi ₂ Se ₃ and Bi ₂ Te ₃	40
4.2.2	Bond Length of Bi ₂ Se ₃ and Bi ₂ Te ₃	42
4.3	Electronic Properties of Bi ₂ Se ₃ and Bi ₂ Te ₃	45
4.3.1	Band Structure of Bi ₂ Se ₃ and Bi ₂ Te ₃	45
4.3.2	Density of States of Bi ₂ Se ₃ and Bi ₂ Te ₃	50
4.3.3	Chemical Bonding of Electron Charge Density of Bi ₂ Se ₃ and Bi ₂ Te ₃	54
4.4	Formation Energy of the Stable Position for Nickel Doping	56
4.5	Structural Properties of Ni-doped Bi ₂ Se ₃ and Ni-doped Bi ₂ Te ₃	58
4.5.1	Lattice Parameter of Ni-doped Bi ₂ Se ₃ and Ni-doped Bi ₂ Te ₃	58
4.5.2	Bond Length of Ni-doped Bi ₂ Se ₃ and Ni-doped Bi ₂ Te ₃	60
4.6	Electronic Properties of Ni-doped Bi ₂ Se ₃ and Ni-doped Bi ₂ Te ₃	62
4.7	The Effect of SOC on Thermoelectric Properties of Bi ₂ Se ₃ and Bi ₂ Te ₃	66
4.7.1	Thermopower of Bi ₂ Se ₃ and Bi ₂ Te ₃	66
4.7.2	Electrical Conductivity of Bi ₂ Se ₃ and Bi ₂ Te ₃	68
4.7.3	Thermal Conductivity of Bi ₂ Se ₃ and Bi ₂ Te ₃	71
4.7.4	Figure of Merit of Bi ₂ Se ₃ and Bi ₂ Te ₃	73
4.8	Thermoelectric Properties of Ni-doped Bi ₂ Se ₃ and Ni-doped Bi ₂ Te ₃	76
4.8.1	Thermopower of Ni-doped Bi ₂ Se ₃ and Ni-doped Bi ₂ Te ₃	77
4.8.2	Electrical Conductivity of Ni-doped Bi ₂ Se ₃ and Ni-doped Bi ₂ Te ₃	79
4.8.3	Thermal Conductivity of Ni-doped Bi ₂ Se ₃ and Ni-doped Bi ₂ Te ₃	81
4.8.4	Figure of Merit of Ni-doped Bi ₂ Se ₃ and Ni-doped Bi ₂ Te ₃	83
4.9	Thermoelectric Properties of Bi ₂ Se ₃ and Bi ₂ Te ₃ as a Function of Fermi Level	85
CHAPTER FIVE: CONCLUSIONS		91
5.1	Conclusions	91
5.2	Recommendations	92