Faculty of Industrial and Manufacturing Technology and Engineering

THE EFFECT OF BLACK PHOSPHORUS ADDITIONS ON THE STRUCTURAL AND MECHANICAL PROPERTIES OF Na_XCoO_2 THERMOELECTRIC

Parveen Kaur A/P Harjinder Singh

Master of Manufacturing Engineering (Quality System Engineering)

2024

THE EFFECT OF BLACK PHOSPHORUS ADDITIONS ON THE STRUCTURAL AND MECHANICAL PROPERTIES OF Na_XCoO_2 THERMOELECTRIC

PARVEEN KAUR A/P HARJINDER SINGH

A thesis submitted in fulfilment of the requirements for the Master of Manufacturing Engineering (Quality System Engineering)

Faculty of Industrial and Manufacturing Technology and Engineering

UNIVERSITY TEKNIKAL MALAYSIA MELAKA

2024

DECLARATION

I declare that this thesis entitle "The Effect of Black Phosphorus Additions on the Mechanical and Structural Properties of Na_xCoO_2/Black Phosphorus Thermoelectric" is the result of my own research except as cited in the references. The thesis has not been accepted for any master and is not concurrently submitted in candidature of any other master.

Signature : *Parveen Kaur*

Name : Parveen Kaur A/P Harjinder Singh

Date : 13 January 2024

APPROVAL

I hereby declare that I have read this master project and in my opinion this master project is sufficient in terms of scope and quality as a partial fulfillment of Master of Manufacturing Engineering (Quality System Engineering)

Signature :...

Supervisor Name :...

Date :...

ABSTRACT

In recent years, condensed matter physics and materials research have focused on sodium cobaltate (Na_xCoO_2). Its thermoelectric qualities make it a promising component in many energy conversion applications. Sodium cobaltate was doped with different compounds to improve its thermoelectric characteristics. Conventional thermoelectric materials are unstable at high temperatures and toxic which can harm individuals and the environment. Due to the toxicity of BiTe and PbTe, this experiment uses Sodium Cobaltate, a ceramic oxide, to continue researching a stable thermoelectric material. Despite eliminating the toxicity concern of traditional thermoelectric, ceramic thermoelectric are poor in converting heat to electricity. In this work, $Na_{0.7}CoO_2$ with varied black phosphorus compositions (x = 0.1–1.0) is tested for enhanced performance and thermoelectric qualities. Its adjustable band gap and great carrier mobility make Black Phosphorus a semiconducting and metallic gadget. Black phosphorus, a transition metal, has a nanostructure with electrical conductivity, which increases Na_xCoO_2 ZT value when added. To eliminate contaminants, Na_xCoO_2 is produced by auto combustion. The gel samples' TG/DT analysis shows that the Na and Co nitrates decomposed in a highly exothermic single-step reaction at 250–280 °C, leaving the desired mass. XRD and FESEM indicate a well crystalline and denser sample of $Na_{0.7}CoO_2$ added with Black Phosphorus. Sample with x=1.0 had the maximum Vickers hardness of 428Mpa. The four-point probe method is used to investigate the thermoelectric material's electrical performance. The material has a high conductivity of 598 S·cm-1 at 330K with x=1.0 due to the high mobility of BP, which increases electron movement and electrical conductivity.

ABSTRAK

Dalam tahun-tahun kebelakangan ini, sebatian yang menarik yang dikenali sebagai natrium kobaltat (Na_xCoO_2) dan fosfor hitam (BP) telah menarik perhatian yang signifikan dalam disiplin fisika bahan kondensat dan penyelidikan bahan. Oleh kerana sifat-sifat termoelektrik yang ia mempunyai, natrium kobaltat mempunyai potensi untuk menjadi komponen yang menguntungkan dalam pelbagai aplikasi yang melibatkan proses penukaran tenaga. Fosfor hitam, sebaliknya, mempunyai jurang band yang boleh disesuaikan di samping mobiliti pembawa yang tinggi, yang semua membolehkan ia bertindak sebagai peranti semikonduktor selain daripada logam. Ini kerana fosfor hitam adalah logam transisi. Di masa lalu, beberapa bahan telah dimodifikasi ke dalam natrium kobaltat untuk meningkatkan sifat-sifat termoelektrik senyawa. Ini dilakukan dalam usaha untuk menjadikan natrium kobaltat lebih berguna. Temuan-temuan ini dipelajari lebih terperinci dalam bahagian laporan yang didedikasikan untuk mengkaji literatur yang berkaitan. Dalam penyelidikan semasa, campuran natrium kobaltat dan fosfor hitam sedang disiasat untuk menyiasat kebarangkalian peningkatan prestasi dan sifat termoelektrik. Ia disyorkan bahawa teknologi tertentu digunakan untuk mencapai matlamat pengurangan kos. Salah satu teknologi tersebut ialah reaksi pembakaran kenderaan. Di samping itu, beberapa kaedah karakterisasi tambahan telah disyorkan, seperti XRD dan FESEM, untuk mengkaji sifat struktural dan mekanikal natrium kobaltat yang mempunyai fosfor hitam ditambahkannya. Ini dilakukan untuk mengetahui lebih lanjut tentang mikrostruktur bahan ini. Selepas ini, pendekatan probe empat titik disyorkan sebagai cara tambahan untuk mengkaji lebih lanjut prestasi elektrik bahan termoelektrik. Perbincangan yang lebih mendalam mengenai butiran ini boleh didapati dalam bab laporan yang didedikasikan kepada metodologi.

ACKNOWLEDGEMENT

The opportunity to start and complete my master project 2 in the past trimester was a very challenging yet exciting moment for myself that I am truly grateful and blessed to be able to fulfil this part of my academics for my master's degree. Throughout the 14 weeks of this trimesters, I have given my upmost effort and contribution towards the completion of this master project 2 report, and to this I would like to say that I am absolutely thankful to a number of people as without them, the chance in completing this research may never have been taken. First of all, I would like to give thanks to the coordinator of the final year project of this trimester who have helped in the registration of this subject and has always informed us timely on the important announcements and events that are very important in meeting the requirements of this project report. Furthermore, I would like to give special thanks to the supervisor of this project, Dr. Mohd Shahadan Bin Mohd Suan for his unlimited guidance and supervision during this entire trimester. His continuous assistance has indeed help me to be well prepared and knowledgeable about the necessities and requirements in completing this final year project report. Finally, I would like to make an acknowledgement to my wonderful parents, family and friends and thank them for their constant encouragement, supportiveness, and confidence of me throughout the weeks in this trimester 2 as I was completing this project report.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

Na_xCoO_2	-	Sodium Cobalt Oxide/Sodium Cobaltate
PbTe	-	Lead Telluride
Bi_2Te_3	-	Bismuth Telluride
Ca	-	Calcium
XRD	-	X-Ray Diffraction
TGA	-	Thermogravimetric Analysis
DTA	-	Differential Thermal Analysis
FESEM	-	Field Emissions Scanning Electron Microscope
Na	-	Sodium
ZT	-	Figure of Merit
SSR	-	Solid State Reaction
PC	-	Polymerized Complex
CoO_2	-	Cobalt Oxide
MSS	-	Molten Salt Synthesis

CHAPTER 1

INTRODUCTION

1.1 Background

Since the invention of thermoelectric materials, a century ago, there has been a resurgence of interest in the material due to its possible applications in power generation, the harvesting of waste heat, and the cooling or heating of solid-state devices. The importance of the problems we face with our energy supply and the environment has resulted in a significant amount of focus being placed on the development of a wide range of technologies that are both inexpensive and free of pollution. One of these technologies, thermoelectric technology, has made significant headway in recent years. Because these processes regenerate the limited amount of energy that is produced by natural causes, a renewable resource is one of the best inventions that has been made to replace the resources that have been depleted. Using a thermoelectric generator, the heat energy that is produced can be converted into electrical energy. This is possible in situations where heat energy is wasted, such as when it is produced by a home boiler, an automobile's exhaust, or developments in manufacturing.

Nevertheless, a revolution of courtesy in thermoelectric began gaining popularity in the middle of the 1990s after theoretical estimates that thermoelectric effectiveness might be significantly improved through nanostructure engineering. This revolution is credited with starting the popularisation of the term "thermoelectric revolution." As a result, a significant amount of laborious experimental effort has been completed in order to demonstrate high-efficiency materials (Chen, 2003). Because of this, the energy can be converted into a form that can conduct electricity through the use of thermoelectric materials. In this work, a freshly obtained sample of thermoelectric ceramic oxide is used as the raw material. This material, which is Sodium Cobalt Oxide (Na_xCo0_2), is added with a particular substance recognised for its nanostructure that possesses electrical conductivity. This material is Black Phosphorus. In comparison to traditional thermoelectric materials, which make use of toxic substances like lead telluride (PbTe), these materials exhibit a non-toxic behaviour, demonstrating their superiority as a non-toxic alternative. The elimination of toxicity caused by the use of conventional thermoelectric technology, which is based on heavy metals such as Bi, Sb, Pb, and Te, which are harmful, toxic, and unstable when heated to high temperatures (Das VD, 1998).

To synthesise Na_xCoO_2, added together with black phosphorus, the most appropriate synthesis method is essential, and this must be done with consideration for both time and cost. Consequently, utilising the citrate-nitrate auto combustion reaction is the most appropriate method that can be involved in this project considering it is time and cost saving. One of the advantages of using this method is that the materials have enhanced their limitation of stoichiometry in comparison to the solid-state reaction method, which was typically utilised in the conventional synthesis of thermoelectric material. This is one of the benefits of using this method. After that, the crystalline dimensions of the final oxide products are invariably in the nanometre range, having a high contact of surface area.

The Na_xCoO_2 material undergoes characterization testing using a variety of machines, including X-ray diffraction (XRD), thermo-gravimetric analysis (TGA), differential thermal analysis (DTA), and scanning electron microscopy (SEM), among others. As a result, the actions of Na_xCoO_2 while under the influence of black phosphorus is deemed acceptable when it goes through several characterization testing.

1.2 Problem Statement

The ability of thermoelectric materials to transform thermal energy into electrical energy has piqued the interest of researchers in recent years. The concept of thermoelectric meant to save the non-renewable resources that provide electrical energy by converting the lost thermal energy that was released for example from industrial processing combustion, car engine fuel consumption, and electrical device heat release. This was accomplished through the use of thermoelectric. According to Rowe (1995), approximately 34% of the electrical energy used in power plant sites, automobiles, and other such places will produce approximately 66% of the thermal energy that will be produced and squandered, leaving very little of it to be utilised. In order to prevent the waste of energy caused by heat, it is necessary to recycle it through the use of thermoelectric.

The Peltier and Seebeck effects were the driving force for the development of this concept. Bismuth telluride (BiTe) and lead telluride (PbTe) are two examples of traditional thermoelectric materials. The two physicists were the first to introduce the thermoelectric by giving these materials. Both of the conventional thermoelectric materials, however, are unstable at high temperatures and have a negative impact due to the fact that they are toxic materials that have the potential to cause harm to humans as well as the environment. In addition, the majority of metals have very high electrical and thermal conductivities, but certain heavy metals, such as Bi, Sb, Pb, and Te, contain harmful toxins and are unstable when heated to high temperatures (Das VD, 1998). In addition, in order to continue operating thermoelectric with traditional toxicity material, a significant amount of money will be required. This is because it will be necessary to prevent the poisonous material from putting the lives and health of the people who operate in that sector in danger. However, toxicity materials are difficult to incinerate, and the toxic material that is produced as a result is likely to be discarded into the environment, such as a lake or river, by an organisation that is irresponsible.

As a result, Sodium Cobalt Oxide (Na_xCoO_2), which is fundamentally a ceramic oxide, was designed and chosen to continue the research of a stable thermoelectric material once the danger of toxicity produced by prior experiments with BiTe and PbTe was eliminated. The thermoelectric material that is based on ceramic is a durable substance that, in addition to metals, can still conduct electricity. The current thermoelectric Sodium Cobalt Oxide (Na_XCoO_2) is still inefficient enough in converting the heat energy to electrical energy because of the low figure of merit, Z, and thermoelectric performance, T. Despite the fact that the ceramic thermoelectric is able to eliminate the conventional thermoelectric toxicity problem, the ceramic thermoelectric is still inefficient enough in converting heat energy to electrical energy. This is because the thermoelectric characteristics of this oxide are significantly influenced by the quantity of sodium. This is due to the fact that sodium plays a function in regulating the concentration of electrons in the CoO_2 layer and also serves as a phonon scattering centre. At a temperature of 650 degrees Kelvin, the ZT of Na_xCoO_2 with a concentration ratio of Na/Co = 0.5 and Na/Co = 0.8 is reported by (Ito M and Furumoto D, 2008) to be 0.02 and 0.4, respectively. The traditional sintering process also causes significant exfoliation and cracking (Schneider C, Schichtel P, Rohnke M, 2016). Consequently, the synthesis process is critical for obtaining the desired Na concentration in the NaxCoO2 molecule with enhanced thermoelectric characteristics. This is the reason why citrate nitrate combustion process is used as it has been used to effectively synthesise different ceramic oxides, such as Al_2O_3, $YB_{a2}Cu_3O_{7-\delta}$, ZrO_2 and TiO_2, with the concentration being easily regulated (Singh K A, Pathak L C, and Roy S K, 2007). This is due to it is a very exothermic combustion process to vaporise the contaminants and can provide extremely clean samples without impurities.

To produce a greater ZT, the present thermoelectric characteristics of Na_XCo0_2, for the purposes of this research, is added with Black Phosphorus, which has a high thermal and electrical conductivity and is extremely conductive. In addition to its high carrier mobility and thickness-dependent bandgap, BP's distinctive electrical, thermal, optical, and other features are due to its puckered honeycomb layer structure with in-plane anisotropy (Wan, B., Guo, S., Sun, J., Zhang, Y, 2019). As a result, the appropriate synthesis process must be utilised in order to provide Na_xCoO_2 that has been added with black phosphorus in the desired compositions.

Synthesising Na_xCoO_2 that has been added with black phosphorus can be done in a number of different ways, including by using the solid-state reaction (SSR), the hydrothermal approach, the sol-gel method, the polymerized complex (PC) method, and also the auto-combustion process. Due to the increased reaction temperature, however, the traditional processes, such as solid-state reaction, make it impossible to synthesise a sintered body with excellent crystallographic and orientation quality (Tubtim Khajadmontin, 2020). Because of this, adopting an auto-combustion reaction has the advantage of being a low-cost and low-temperature technique, both of which have received a lot of attention. It is believed that by applying an auto combustion reaction, the material composition in the aqueous solvent will attain a high quality of homogenous. In comparison to the other methods, it possesses a superior control of stoichiometry, which results in a higher level of purity (Singh K A, Pathak L C, and Roy S K, 2007).

1.3 Project Scope

The purpose of this study is to synthesise and characterise Sodium Cobalt Oxide ($Na_{0.7}CoO_2$) that has been added with a composition of black phosphorus in order to enhance the thermoelectric properties by conducting experiments using the citrate-nitrate auto combustion reaction method. The amount of sodium cobalt oxide ($Na_{0.7}CoO_2$) that is added together in the various concentrations of black phosphorus (i.e., 0.1, 0.3, 0.5, 0.7, and 1.0) in this experiment is the variable that is referred to as the parameter. The thermal behaviour of the sample, which is changed into gel form as the temperature rises, is used to analyse the combustion reaction of the black phosphorus added with samples of Sodium Cobalt oxide. Differential Thermal Analysis (DTA) and Thermogravitational Analysis (TGA) are two types of material testing machines that are utilised in the process of analysing the samples. The black phosphorus added thermoelectric structural properties, such as lattices constants, crystalline size, elements, microstructure, and morphology, are characterised by using the Field-Emission Scanning Electron Microscope (SEM). In addition, X-Ray Diffraction (XRD) is also used to study the black phosphorus added thermoelectric properties in order to investigate each parameter of the materials.

1.4 Objectives

Objectives of the project are:

i. To use a citrate nitrate combustion reaction to synthesize a series of impurities free $Na_{0.7}CoO_2$ compounds to which black phosphorus is added.

ii. To investigate the structural and mechanical properties of the $Na_{0.7}CoO_2$/BP by using XRD, FESEM, EDX and Vickers microhardness test.

iii. To correlate between structural and electrical properties of the thermoelectric compound using electrical conductivity measurement.

1.5 Significance of Project

The process of synthesizing thermoelectric materials is presented in this research. When compared to the other conventional method of processing composite and compound superconductor oxides, the citrate nitrate auto combustion reaction method required a lower amount of time and energy to complete the process. As for the repercussions, the properties of the thermoelectric $Na_{0.7}CoO_2$ added with Black Phosphorus is justified if it meets the expectation to have a better result in its structural, mechanical and electrical properties in addition to being able to eliminate the impurity of the substances problem that can be caused from the outside factors and easier to be conducted because it is in the form of an aqueous solution that gives multiple benefits in synthesizing the material in terms of stoichiometry rather than the conventional method.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

In this chapter, the discussion is about the fundamentals of Na_xCoO_2, a thermoelectric material that has been added with Black Phosphorus using a method called citrate nitrate auto combustion. This chapter is divided into several subchapters that cover the necessary steps involved in the preparation of samples and other connected procedures that are necessary for adding thermoelectric materials with citrate nitrate auto combustion method. Due to the fact that its application is utilised in industry as well as general application in real life and the contribution of thermoelectric semiconductors to the industry, this item is elaborated further on the use of the thermoelectric in section 2.2. In part 2.3, it is discussed about the properties of Na_xCoO_2 and Black Phosphorus. In section 2.4, further elaboration about the history of the Na_xCoO_2, which has been added with transition metal element to increase its thermoelectric capabilities is done. In the following section, section 2.5, it is discussed about the applications of the thermoelectric nanoparticle. In the end, the topic of synthesis methods that can be used to carry out the experiment is discussed in section 2.6, with a particular emphasis placed on the auto combustion reaction synthesis method for the thermoelectric Na_xCoO_2 added with Black Phosphorus.