THERMOELECTRIC PROPERTIES OF Ag DOPED $Na_{0.8}CoO_2$ SYNTHESIZED VIA CITRATE-NITRATE AUTO COMBUSTION REACTION

MUHAMMAD RADZI BIN MASURI
B051510015

UNIVERSITI TEKNIKAL MALAYSIA MELAKA
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This report is submitted in accordance with requirement of the University Teknikal Malaysia Melaka (UTeM) for Bachelor Degree of Manufacturing Engineering

by

MUHAMMAD RADZI BIN MASURI

B051510015

940622-01-5363

FACULTY OF MANUFACTURING ENGINEERING

2018

UNIVERSITI TEKNIKAL MALAYSIA MELAKA

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Tajuk: **THERMOELECTRIC PROPERTIES OF Ag DOPED $Na_{0.8}CoO_2$ SYNTHESIZED VIA CITRATE-NITRATE AUTO COMBUSTION REACTION**

Sesi Pengajian: **2017/2018 Semester 2**

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Author's Name : MUHAMMAD RADZI BIN MASURI

Date : 24 May 2018

APPROVAL

This report is submitted to the Faculty of Manufacturing Engineering of Universiti Teknikal Malaysia Melaka as a partial fulfilment of the requirement for Degree of Manufacturing (Hons). The members of the supervisory committee are as follow:

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(Dr. Mohd Shahadan Bin Mohd Suan)

……………………….................

(Dr. Mohd Shukor Bin Salleh)

ABSTRACT

This study focuses on the synthesis of Ag dope with thermoelectric ceramic oxide of Na_xCoO_2 via citrate-nitrate auto combustion reaction method. The reason of this study is to improve the present ceramic-based thermoelectric Na_xCoO_2 to achieve higher ZT its current conversion efficiency by material doping. The previous researches of synthesizing the thermoelectric were mostly used the solid state reaction where issues can be found as it has less control of stoichiometry, poor quality of material purity and its homogenous. Thus, in order to achieve a better stoichiometry of the compound and better homogenous also the compound purity, the auto combustion reaction method is highlighted. The concentration of Ag is controlled at 0.1, 0.3, 0.5, 0.7 and 0.9M of concentration in the mixed solution of $Ag(NO)_3$, $NaNO_3$ and $Co(NO_3)_2$ as the concentration of Na is at 0.8M of concentration. The mixture of solutions of $Ag(NO)_3$ and $Na_{0.8}CoO_2$ is then dried over 250°C under the UV light and turn into gel state. The combustion properties were observed by using TG-DTA to analyse the weight loss during the drying process. Precursor gels of $Na_{0.8}CoO_2$ Ag-doped were being heated until it achieves the auto combustion reaction which turned the precursor gels into ashes. The ashes from the combustion were calcined at 900°C. Then the powder was continued to be pelletized by using compressive machine at pressure of 14.2 MPa. The size of the pellet was fixed at about 10mm x 2mm diameter. The characterization of the $Na_{0.8}CoO_2$ Ag-doped was performed by using the XRD to study the crystallinity structure and the concentration of Ag in the $Na_{0.8}CoO_2$ Ag-doped. The surface morphology of $Na_{0.8}CoO_2$ Ag-doped was analysed by using SEM. At molarity x = 0.1, 0.3 and 0.5M shows the agglomerated surface structure while x=0.7 and 0.9M showed coarse structure regions. Thermogravitatiometric analysis and differential thermal analysis (TG-DTA) indicated that the precursor gels with molarity x=0.7 decomposed in a single-step reaction combusted at 270°C. Sample with molarity x=0.7 appeared in this work to be the electrically superconducting as measured by using standard four-probe technique.

ABSTRAK

Kajian ini memberi tumpuan kepada sintesis Ag bercampur dengan termoelektrik seramik oksida Na_xCoO_2 melalui kaedah tindak balas pembakaran auto sitrat-nitrat. Tujuan kajian ini adalah untuk memperbaiki termoelektrik Na_xCoO_2 yang sedia ada berasaskan seramik untuk mencapai lebih tinggi ZT kecekapan penukaran semasa dengan bahan campuran. Dalam penyelidikan terdahulu teknik sintesis termoelektrik yang kebanyakannya digunakan tindak balas pepejal di mana isu-isu boleh didapati kerana ia mempunyai kurang kawalan stoichiometri, menyebabkan kualiti material kesucian dan yang homogenus. Oleh itu, untuk mencapai sebuah stoichiometri lebih majmuk dan lebih homogenus juga keaslian kompaun, kaedah tindak balas pembakaran auto diserlahkan. Konsentrasi Ag dikawal pada 0.1, 0.3, 0.5, 0.7 dan 0.9 M penumpuan dalam penyelesaian bercampur daripada $Ag(NO)_3$, $NaNO_3$ dan $Co(NO_3)_2$ sebagai konsentrasi Na adalah sebanyak 0.8M penumpuan. Campuran daripada $Ag(NO)_3$ dan $Na_{0.8}CoO_2$ kemudian dikeringkan lebih 250° C di bawah lampu UV dan bertukar menjadi keadaan gel. Ciri-ciri pembakaran yang diperhatikan dengan menggunakan TG-DTA untuk menganalisis penurunan berat badan semasa proses pengeringan. Pelopor gel daripada $Na_{0.8}CoO_2$ bercampur Ag sedang dipanaskan sehingga ia mencapai auto pembakaran tindak balas yang bertukar gel pelopor menjadi abu. Abu dari pembakaran telah dibakar pada 900° C. Kemudian serbuk adalah terus dipelet dengan menggunakan mesin mampatan pada tekanan 14.2 MPa. Saiz pelet yang telah ditetapkan pada kira-kira 10 mm x 2 mm diameter. Pencirian $Na_{0.8}CoO_2$ bercampur Ag telah dilaksanakan dengan menggunakan XRD yang mengkaji struktur crystallinity dan konsentrasi Ag didalam $Na_{0.8}CoO_2$ bercampur Ag. Morfologi permukaan $Na_{0.8}CoO_2$ bercampur Ag dianalisis dengan menggunakan SEM. Pada molarity x=0.1, 0.3 dan 0.5M menunjukkan struktur permukaan diaglomerasi semasa x=0.7 dan 0.9M menunjukkan struktur kasar rantau. Thermogravitatiometric analisis dan pembezaan analisis terma (TG-DTA) menunjukkan bahawa gel pendahulu dengan molarity x=0.7 terurai dalam sebuah pembakaran satu langkah tindak balas pada 270° C. Sampel dengan molarity x=0.7 bermuncul dalam kerja-kerja ini perlu elektrik konduktor hebat diukur dengan menggunakan standard teknik empat-siasatan piawai.

DEDICATION

Dedicated to

My beloved father,

Masuri Bin Sahari

My appreciated mother,

Manisah Binti Belor

Most honoured supervisor,

Dr. Mohd Shahadan Bin Mohd Suan

My friends and team of FKP technicians in Engineering Material department
For giving me moral support, encouragement, cooperation and contribution to this research until this thesis is completely done.

ACKNOWLEDGEMENT

First, I would like to express my gratitude to Allah S.W.T. for His blessing throughout my journey in completing this final year project report. Therefore, I would like to take this opportunity to express my gratitude to all those who has helped me either directly or indirectly in completing this research.

A million awards to my supervisor, Dr Mohd Shahadan Bin Mohd Suan for his unfailing patience, concern, advice and encouragement throughout this research. Besides that, he has given guidance and support to me that enabled me to complete my final year project and as well as the report.

Finally, thanks also to all the parties involved in providing encouragement to me while completing this research, including both my parents and all FKP staff for giving me guidance to accomplish my research. Not forgotten, I would like to thank to all my friends especially Izzat Bin Mohd Yusuf and Nur Shuhadah Sahatim together with newly-made friends whom have worked at Engineering Material Laboratories that have helped me a lot by giving some ideas, suggestions and guidance to accomplish this final year project.

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LIST OF ABBREVIATIONS

Na_xCoO_2	-	Sodium cobalt oxide
PbTe	-	Lead telluride
Bi_2Te_3	-	Bismuth Telluride
Ag	-	Silver
Ca	-	Calcium
XRD	-	X-Ray Diffraction
TGA	-	Thermogravimetric Analysis
DTA	-	Differential Thermal Analysis
FESEM	-	Field Emission Scanning Electron Microscope
Na	-	Sodium
ZT	-	Figure of merit
SSR	-	Solid state reaction
PC	-	Polymerized Complex
CoO_2	-	Cobalt oxide
MSS	-	Molten salt synthesis
BDS	-	Broadband dielectric spectroscopy
CSD	-	Cambridge Structural Database
$Ag(NO)_3$	-	Silver Nitrate
$NaNO_3$	-	Sodium Nitrate
$Co(NO_3)_2$	-	Cobalt Nitrate
$C_6H_8O_7$	-	Citric Acid
NH_4OH	-	Ammonia solution

LIST OF SYMBOLS

S	-	Seebeck coefficient
ΔT	-	Temperature changes between the ends of the material
ΔV	-	Potential change
μV/K	-	Micrometer Voltage per Kelvin
TH	-	Temperatures at the hot side
TC	-	Temperatures at the cold side
σ	-	Electrical conductivity
λ	-	Thermal conductivity
g/mol	-	Gram per Mol
$\Omega.\text{cm}^2$	-	Ohm centimetre square

CHAPTER 1

INTRODUCTION

1.1 Background of study

Over a century of thermoelectric materials invention, it has received renewed attention for potential applications in power generation, waste heat harvesting and solid-state cooling or heating. Due to the urgency of our energy and environmental issues, a variety of cost-effective and pollution-free technologies have attracted considerable attention, among which thermoelectric technology has made enormous progress. A renewable resource is one of the best inventions to replace the resources depletion as these processes regenerate the finite energy produced by natural cause. As in heat energy waste produced from home boiler, motorized exhaust, and manufacturing developments, the heat energy produced can be converted into electrical energy via thermoelectric generator.

However, a revolution of courtesy in thermoelectric started popular in the middle of 1990s after theoretical estimates that thermoelectric effectiveness might be significantly improved over nanostructure engineering. Thus, the experimental hard work is done to show the proof-of-principle and high-efficiency materials (Chen, 2003). Therefore, this energy can be used to conduct the electricity by using the thermoelectric materials. In this study, the newly sample of thermoelectric ceramic oxide is used as the raw material which is Sodium Cobalt Oxide (Na_xCoO_2) will be doped with certain material which is silver (Ag) where it is known with its nanostructure that possess electrical conductivity. These materials show the behaviour of non-toxicity compared to the conventional thermoelectric material which using toxicity materials such as lead telluride (PbTe). The elimination of toxicity from using the conventional thermoelectric based of heavy metal such as such as Bi, Sb, Pb and Te contains dangerous toxic and unstable at high temperature (Das VD, 1998).

By considering the time and cost factors, suitable synthesis method is important to synthesis Na_xCoO_2 to dope with Ag. Thus, the suitable method that involve in this project is using the citrate-nitrate auto combustion reaction. One of the benefits of this technique were the materials have improved the limitation of stoichiometry compared to the solid state reaction method that had been usually used in the previous synthesis over the conventional thermoelectric material. Next, the final oxide results of crystalline dimensions are invariably in the nanometer range which having high contact of surface area. Characterisation of the Na_xCoO_2 materials is tested in variable type of characterisation machine such as X-Ray Diffraction (XRD), Thermogravimetric Analysis (TGA), Differential Thermal Analysis (DTA), and Scanning Electron Microscope (SEM). Therefore, the behaviours of Na_xCoO_2 doped with Ag will be justified.

1.2 Problem statement

Thermoelectric materials have attracted the attentions of the researcher due to its function of converting the thermal energy into electrical energy. The idea of thermoelectric meant to save the non-renewable resources that generate electrical energy by converting the wasted thermal energy that released for example from industrial processing combustion, vehicle engine fuel consumption, electrical devices heat release. As reported by (Rowe, 1995), about 34% of electrical energy used in power plant site, automobile, etc etc will produce about 66% of heat energy released and wasted left to be unused. These waste of heat energy should be recycle by using thermoelectric to conserve the energy.

This idea was lead to the result of the Peltier and Seebeck effects. The two physicists were the first introducing the thermoelectric by providing the conventional thermoelectric materials of bismuth telluride (Bi_2Te_3) and lead telluride (PbTe). However, both the conventional thermoelectric materials are not stable at high temperature and gives a negative influence as they are toxicity materials that could harm the environment and also human. Even more, most of the metals possess very high electrical and thermal conductivity but several heavy metals such as Bi, Sb, Pb and Te contains dangerous toxic and unstable at high temperature (Das VD, 1998). Plus, to continue operating thermoelectric with conventional toxicity material, it will cost a lot of money to cover the toxic material from endanger the human surrounding who works on that field to secure their lives and health. Nevertheless toxicity materials are hardly to incinerate and the toxic material produced will likely to be discarded into the environment such as lake or river by the irresponsible organization.

Thus, Sodium Cobalt Oxide (Na_xCoO_2) which is basically a ceramic oxide was invented and selected to continue the experimentation of a stable thermoelectric material as the harm of toxicity produced by previous experiment of Bi_2Te_3 and PbTe were eliminated. The ceramic based thermoelectric is a stable material which still can conduct electricity other than metals. Nonetheless, even though the ceramic thermoelectric able to eliminate the conventional thermoelectric toxicity problem, the current thermoelectric Sodium Cobalt Oxide (Na_xCoO_2) is still inefficient enough in converting the heat energy to electrical energy because the low figure of merit, Z and thermoelectric performance, T. However, in this study the current thermoelectric properties of Na_xCoO_2 will be doped with Silver (Ag) that possesses a highly thermal and electrical conductivity to achieve higher ZT. Hence, the suitable synthesis method needs to be employed to achieve Na_xCoO_2 doped with Ag in expected compositions. Therefore, an appropriate technique is required in controlling Ag compositions in Na_xCoO_2Ag-doped reaction to get better resistivity.

There are various methods that can be used to synthesize the Na_xCoO_2 Ag-doped such as solid state reaction (SSR), hydrothermal, sol-gel, polymerized complex (PC) and also the auto-combustion reaction. However, the conventional process such as solid state reaction is difficult to synthesize a sintered body with high crystallographic and orientation due to higher reaction temperature. Therefore, the advantage of using the auto-combustion reaction is low cost and low temperature process and attracted much attention. By using auto combustion reaction, it is believed that the material composition in aqueous solvent will achieve high quality of homogeneous. It's also have a better control of stoichiometry which is more purity compared to the others method.

1.3 Objectives

1. To synthesize the thermoelectric properties of sodium cobalt oxide ($Na_{0.8}CoO_2$) doped with silver (Ag) via citrate-nitrate auto combustion reaction.
2. To evaluate the thermal and electrical properties of $Na_{0.8}CoO_2$ doped with Ag.
3. To investigate the effects of Ag composition in $Na_{0.8}CoO_2$ Ag-doped towards thermoelectric properties.

1.4 Scope of the study

This research scope is to synthesize and characterizing the Sodium Cobalt Oxide (Na_xCoO_2) doped with the composition of Ag to improve the thermoelectric properties experimenting via citrate-nitrate auto combustion reaction method. The parameter of this experiment is the concentrations of the Ag , (i.e; 0.1, 0.3, 0.5, 0.7 and 0.9M) to dope with a sodium cobalt oxide (Na_xCoO_2) which have been prepared in solution form. The combustion reaction of the Ag dope with Sodium Cobalt oxide samples will be evaluated by thermal behaviour as the sample will turn into gel form at an increasing temperature.

The samples will be determined by using the Differential Thermal Analysis (DTA) and Thermogravitational Analysis (TGA) material test machine. Henceforth, the doped thermoelectric structural properties such as lattices constants, crystalline size, elements, microstructure and morphology will be characterized by using the Scanning Electron Microscope (SEM) and X-Ray Diffraction (XRD) will also be used to study the doped thermoelectric properties to investigate each parameter of the materials.

1.5 Significant of research

This research presents the method of synthesizing the thermoelectric materials. The method of citrate nitrate auto combustion reaction consumed less time and energy compared to the other conventional method of processing of composite and compound superconductor oxides. As for the consequences, the properties of the thermoelectric Na_xCoO_2 doped with Ag will be justified if it meets the expectation to have a better result in nanostructure doping method beside able to eliminate the impurity of the substances problem that can be caused from the outside factors and easier to be conduct since it is in the form of aqueous solution that gives multiple benefits in synthesizing the material in term of stoichiometry rather than the conventional non-aqueous method to gain the higher ZT as possible.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

In this chapter, the fundamental of Na_xCoO_2 thermoelectric doped with $Ag(NO)_3$ via citrate nitrate auto combustion process will be discussed. The chapter is divided into some subchapters that required in making the preparation of samples and other related processes involved in doping the thermoelectric using citrate nitrate auto combustion technique. This topic will elaborate more about the application of the thermoelectric in section 2.2 due to its application used in the industry and general application in real life and the contribution of thermoelectric semiconductor in the industry. In section 2.3, the properties of Na_xCoO_2 and Ag will be discussed and in section 2.4 will be discussed about the history of the Na_xCoO_2doped with transition metal element to improve the thermoelectric properties. In section 2.5 will be discussed about the application of the thermoelectric nanoparticle. Lastly, in section 2.6 will be covered about the synthesis methods can be done to carry the experiment and focusing on the auto combustion reaction synthesis method on the thermoelectric Na_xCoO_2 doped Ag.

2.2 Thermoelectric

The era of global industrialization has been claimed as a good start to the world in developing the modern technologies that helps the growth of both social and politically conflicts. However, this developing industry has also leaded the ecological effect of the worldwide global warming, weather changes and every kind of pollution producible which may be hazardous due to the combustion from the fossil fuel sources rapidly consumed. Thus, a new method to recover the non-renewable resources of power base is by over seeking the waste of unused heat energy produced in daily life application. A large amount of wasted and used heat releases from industrial processes, automotive exhaust, and other various electrical appliances that will produced heat can be recycle and regenerate the electrical energy by thermoelectric energy conversion. Through various approaches attempted in progress to change the alternator in automobiles with a thermoelectric maker focus on relating to the exhaust part so it could achieve the fuel effectiveness to conserve energy of heat continuously.

Developments in thermoelectric might also allow the restoration of compression-based refrigeration by solid-state Peltier coolers (DiSalvo, 1999). Thus, thermoelectric keeps on as well efficient to be useful in most applications (Rowe, 1995). In the middle of 1990's the attention of the thermoelectric makers changed after theoretic expectation recommended that thermoelectric effectiveness might be significantly improved completely by the nanostructure engineering of the material substances where it can related to experimental works to show the proof-of-principle and high-efficiency materials (Chen, 2003).

A simultaneously research of complex bulk materials has been found such as skutterudites (Uher,2001), clathrates (Nolas, 2006) and zintl phases (Kauzlarich, 2007). It has been discovered that high productivities can be achieved. Through analyses which have been done before, we confine that the new development on the rearrangement and complication solving in the unit cell together with the nanostructured materials can guide to improve the effectiveness of the material. Thus, this allows us to discover mutual