YANG NURHIDAYAH ASNIDA BINTI NORIZAN
MASTER OF SCIENCE (ELECTRICAL AND ELECTRONIC ENGINEERING)
UPNM 2021

EFFECT OF DIFFERENT HEAT TREATMENT ANNEALING AND SUBSTITUTION OF LANTHANUM (La) WITH YTTRIUM (Y) IN $La(Fe,Si)_{13}$ COMPOUNDS

YANG NURHIDAYAH ASNIDA BINTI NORIZAN

MASTER OF SCIENCE
(ELECTRICAL AND ELECTRONIC ENGINEERING)

UNIVERSITI PERTAHANAN NASIONAL MALAYSIA

2021

EFFECT OF DIFFERENT HEAT TREATMENT ANNEALING AND SUBSTITUTION OF LANTHANUM (La) WITH YTTRIUM (Y) IN $La(Fe,Si)_{13}$ COMPOUNDS

YANG NURHIDAYAH ASNIDA BINTI NORIZAN

Thesis submitted to the Centre for Graduate Studies, Universiti Pertahanan Nasional Malaysia, in fulfilment of the requirements for the Degree of Master of Science (Electrical and Electronic Engineering)

2021

ABSTRACT

The cubic $NaZn_{13}$-type $LaFe_{13}$-xSix based compounds have been studied systematically and have become one of the most interesting systems for exploring large magnetocaloric effects, MCE. Its magnetic properties are strongly doping dependent and provides many advantages compared to other as magnetic materials for magnetic refrigerator application. For the sample preparation, the study of ball milling treatment and properties in $La(FeSi)_{13}$ compound from raw materials of Lanthanum (La), Iron(Fe) and Silicon (Si) as refrigerant for magnetic refrigeration system have been conducted intensively. The compounds underwent the pellet press process. For the structural properties investigation, $LaFe_{11.5}Si_{1.5}$ compounds were annealed at two different heat treatment which are 1323 K for 14 days and 1523 K for 4 hour. The powder X-ray diffraction shows that high temperature annealing increase the main structure and decrease the impurity (α-Fe and LaFeSi). Rietveld refinement results indicate that the lattice parameter has increased at the high temperature annealing because of more cubic $NaZn_{13}$ is formed at higher temperature. In an effort to explore the effect of La substitution by Y in $NaZn_{13}$-type $La_{1-x}Y_xFe_{11.5}Si_{1.5}$ (x=0, 0.05, 0.1, 0.3) compound, the structural and magnetic properties of the heat treatment have been studied systematically. The permittivity measurements found that, for $La_{1-x}Y_xFe_{11.5}Si_{1.5}$ at Y=0.05, it shows high value of resistivity while at Y= 0.3 it has the lowest value of tan delta. On mechanical perspective,

the highest storage modulus and static stress are at Y=0.3 which are 3.8x10^9 Pa and 2.72x10^6 N/m^2respectively.

ABSTRAK

Sebatian $NaZn_{13}$ jenis $LaFe_{13-x}Si_x$ berbentuk kubik telah dikaji secara sistematik dan telah menjadi salah satu sistem yang paling menarik untuk meneroka kesan magnetokalorik (MCE) yang besar. Sifat magnetiknya sangat bergantung pada doping dan memberikan banyak kelebihan berbanding yang lain sebagai bahan magnet untuk penggunaan peti sejuk magnetik. Untuk penyediaan sampel, kajian secara menyeluruh berkaitan rawatan dan sifat penggilingan bola bagi sebatian La (FeSi) dari bahan mentah Lanthanum (La), Besi (Fe) dan Silikon (Si) sebagai bahan pendingin untuk sistem penyejukan magnetik telah dilakukan. Sebatian akan menjalani proses penekan pelet. Sifat struktur sebatian $LaFe_{11.5}Si_{1.5}$ dianil pada dua rawatan haba berbeza iaitu 1323 K selama 14 hari dan 1523 K selama 4 jam. Difraksi serbuk sinar-X menunjukkan bahawa penyepuhlindapan suhu tinggi meningkatkan struktur utama dan mengurangkan bendasing (α-Fe dan LaFeSi). Rietveld refinement menunjukkan bahawa parameter kisi meningkat pada suhu penyepuhlindapan kerana lebih banyak kubik $NaZn_{13}$ terbentuk pada suhu yang lebih tinggi. Dalam usaha untuk mengkaji kesan penggantian La oleh Y dalam sebatian $NaZn_{13}$-jenis $La_{1-x}Y_xFe_{11.5}Si_{1.5}$ (x = 0, 0.05, 0.1, 0.3), sifat struktur dan magnet rawatan haba telah dikaji secara sistematik. Pengukuran permitiviti mendapati bahawa, untuk $La_{1-x}Y_xFe_{11.5}Si_{1.5}$ pada Y = 0.05, ia menunjukkan nilai resistiviti yang tinggi sedangkan pada Y = 0.3 ia mempunyai nilai tan delta yang paling rendah. Pada

perspektif mekanikal, modulus penyimpanan tertinggi dan tekanan statik masing-masing adalah pada Y = 0.3 iaitu 3.8x10^9 Pa dan 2.72x10^6 N/m^2.

ACKNOWLEDGEMENTS

Bissmillahirrahmanirrahim,

Alhamdulillah. Thanks to Allah SWT, who with His willing give me the opportunity to accomplish this study in spite of the numerous constraints that I encountered.

Firstly, I would like to express my deepest thanks to, Associate Professor Dr. Muhamad Faiz Bin Md Din, my supervisor who had guided me a lot on this master study with his invaluable support, continual encouragement, and patience throughout this work. To be your student been a real pleasure for me. I also want to express my deepest gratitude to my co-supervisors, Associate Professor, Dr. Mohd Taufik Bin Jusoh for the cooperation and had given valuable information, suggestions and guidance in the compilation of this thesis.

I would like to thank the Malaysian Government, especially the Ministry of Education Malaysia for the scholarship support during my studies at the National Defence University of Malaysia. Deepest thanks and appreciation to my parents, Norizan Md. Zin and Samsiah Idris, my lovely husband, Nabil Fikri Pahrul Raji, family, and others for their cooperation, encouragement, constructive suggestion and full of support for the thesis completion, from the beginning till the end. Finally, thank you to all those involved directly and indirectly helping me out during my master study which I can’t state out every one of them. A special expression of gratitude is extended to everyone for their tolerance and patience. I must admit that they had enriched me in many ways and words alone are not enough to express my gratitude.

APPROVAL

The Examination Committee has met on **25th Mac 2021** to conduct the final examination of Yang Nurhidayah Asnida Binti Norizan on his degree thesis entitled **'Effect of Different Heat Treatment Annealing and Substitution of Lanthanum (La) with Yttrium (Y) in $La(FeSi)_{13}$ Compounds'**.

The committee recommends that the student be awarded the Master of Science (Electrical and Electronic Engineering).

Members of the Examination Committee were as follows.

Dr. Anis Shahida Niza Binti Mokhtar
Faculty of Engineering
Universiti Pertahanan Nasional Malaysia
(Chairman)

Prof. Madya Dr. Siti Nooraya Binti Mohd Tawil
Faculty of Engineering
Universiti Pertahanan Nasional Malaysia
(Internal Examiner)

Prof. Madya Dr. Mohd Hanafi Bin Ani
Kuliyyah of Engineering
International Islamic University Malaysia
(External Examiner)

APPROVAL

This thesis was submitted to the Senate of Universiti Pertahanan Nasional Malaysia and has been accepted as fulfilment of the requirements for the degree of **Master of Science (Electrical and Electronic Engineering)**. The members of the Supervisory Committee were as follows.

Associate Professor Dr. Muhamad Faiz bin Md Din
Faculty of Engineering
Universiti Pertahanan Nasional Malaysia
(Main Supervisor)

Associate Professor Dr. Mohd Taufik Bin Jusoh
Faculty of Engineering
Universiti Pertahanan Nasional Malaysia
(Co-supervisor)

UNIVERSITI PERTAHANAN NASIONAL MALAYSIA

DECLARATION OF THESIS

Student's full name : Yang Nurhidayah Asnida Binti Norizan

Date of birth : 6th May 1990

Title : Effect of Different Heat Treatment Annealing and Substitution of Lanthanum (La) with Yttrium (Y) in $La(FeSi)_{13}$ Compounds

Academic session : June 2016

I hereby declare that the work in this thesis is my own except for quotations and summaries which have been duly acknowledged.

☐ **CONFIDENTIAL** (Contains confidential information under the official Secret Act 1972)*

☐ **RESTRICTED** (Contains restricted information as specified by the organisation where research was done)*

☐ **OPEN ACCESS** I agree that my thesis to be published as online open access (full text)

I acknowledge that Universiti Pertahanan Nasional Malaysia reserves the right as follows.

1. The thesis is the property of Universiti Pertahanan Nasional Malaysia.
2. The library of Universiti Pertahanan Nasional Malaysia has the right to make copies for the purpose of research only.
3. The library has the right to make copies of the thesis for academic exchange.

Signature	**Signature of Supervisor / Dean of CGS/ Chief Librarian
IC/PassportNo.	**Name of Supervisor/Dean of CGS/ Chief Librarian
Date:	Date:

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

Al	Aluminium
CFCs	Chlorofluorocarbons
Co	Cobalt
CO_2	Cabon Dioxide
Cr	Chromium
Fe	Iron
FM	Ferromagnetic
FOMT	First Order Magnetic Transition
Ge	Germanium
HCFCs	Hydro chlorofluorocarbons
IEM	Itenerant Electron Metamagnetism
Gd	Gadolinium
Kpa	Kilopascal
La	Lanthanum
MCE	Magnetocaloric Effect
Mn	Manganese
MR	Magnetic Refrigeration
PM	Paramagnetic
PPMS	Physical Properties Measurement System
Pr	Praseodymium
SEM	Scanning Electron Microscopy

Si	Silicon
Tc	Curie Temperature
XRD	X-ray Diffraction
Y	Yttrium

CHAPTER 1

INTRODUCTION

1.1 General Introduction

Refrigeration is a major consumer of energy and thus an important cause of greenhouse gas emissions in modern society. To further developing the current vapour compression technology, scientist and engineer have begun to explore new refrigeration technologies, such as magnetic refrigeration. Modern society relies on cooling technology for food safety, comfort, and medical applications. For example, in the US about 34 % of the electricity is consumed by cooling appliances [1], and 15 % of total worldwide energy consumption involves the use of refrigeration (air conditioning, refrigeration, freezing, chilling, etc.) [2]. Nowadays, most cooling devices are based on vapour-compression technology, which was originally developed in the 19th century. Cooling systems are very important for food storage and transport, as well as air-conditioning in building and car. Without refrigeration, the food supply would still be seasonal and limited to locally produced or non-perishable items;

comfortable living condition would be impossible everywhere; certain medical advance such as organ transplantation, organ and tissue cryo-storage would be impossible. Conventional refrigerators have become omnipresent in a large number of cooling applications, but the use of chlorofluorocarbons (CFCs) and hydro chlorofluorocarbons (HCFCs) as working fluids has raised serious environmental concerns, mainly because of their contributions to destruction of the ozone layer and global warming [3, 4]. Replacement by fluid HFCs which contain no chlorine and therefore have no ozone depletion potential, is not without problems because HFCs are greenhouse gases [5] with higher global warming potential than CO_2. Thus, due to serious concerns for the environment, alternative technology should be a more attractive solution to the environmental problems.

Magnetic refrigeration based on the magnetocaloric effect (MCE) in magnetic materials has been demonstrated to be a promising alternative to conventional gas compression refrigeration [6,7]. By using solid magnetic materials as coolants instead of conventional gases, magnetic refrigeration avoids all harmful gases, including ozone-depleting gases, greenhouse-effect gases that contribute to global warming, and other hazardous gaseous refrigerants. A solid coolant can easily be recycled. Furthermore, it has been demonstrated that magnetic cooling is energetically more energy efficient than conventional gas-compression cooling. This is of particular interest in view of the global energy problems [6]. In addition, magnetic refrigerators make very little noise and may be built to be very compact. Therefore, magnetic refrigeration has attracted attention in recent years as a promising environmentally-friendly alternative to conventional gas-compression cooling.

1.2 Historical Development of Magnetic Refrigeration

Magnetic refrigeration is based on the concept of thermodynamic property of the magnetic materials where it is called the magnetocaloric effect. The study of magnetic refrigeration (MR) started with the discovery of the magnetocaloric effects a century ago. Warburg first discovered the thermal effect of iron metal when placing it in a varying magnetic field in 1881 [9]. In 1933, Giauque and MacDougall [10] put this idea into practice and experimentally demonstrated the use of the MCE to achieve temperature below 1K. From then on, the MCE has been successfully utilized to achieve ultra-low temperature by employing a process known as demagnetization. Giauque was awarded the Nobel Prizes in physics for his work in magnetic refrigeration in in 1949. An upsurge in research has occurred over the last few years.

The MCE is represented by the adiabatic temperature change ΔT_{ad} or the entropy ΔS_M change, which are intrinsic to all magnetic materials. The MCE is based on the facts that paramagnetic or soft ferromagnetic materials expel heat and their magnetic entropy decreases when a magnetic field is applied isothermally; or otherwise they absorb heat and their magnetic entropy increases when the magnetic field is reduced isothermally. The MCE reaches a peak in the vicinity of the magnetic ordering or Curie Temperature (T_c). Gadolinium (Gd) was used in a room temperature magnetic refrigerator in 1976, and since then, research on MR materials has been underway to increase the temperature range or capacity.

1.3 The Magnetocaloric Effect

Magnetic refrigeration is based on the magnetocaloric effect (MCE), which was discovered by Warburg in 1881 [7]. When a magnetic material is subjected to a sufficiently high magnetic field, the magnetic moments of the atoms become reoriented. If the magnetic field is applied adiabatically, the temperature of the materials rises, and if the magnetic field is subsequently removed, the temperature decreases. This warming and cooling in response to the application and removal of an external magnetic field is called the 'MCE'. The magnitude of the MCE in a magnetic material is defined by the isothermal magnetic entropy change (ΔS_M) or by the adiabatic temperature change (ΔT_{ad}) as the magnetic field is applied or removed. Both of these points are very important factors for ideal magnetic material selection to produce a high performance magnetic refrigerator.

Magnetic materials can order their magnetic moments in a variety of ways, such as ferromagnetic, ferromagnetic, and antiferromagnetic orderings, depending on the characteristics of the material. The moments of a magnetic material are aligned parallel to the magnetic field, as shown in Figure 1.1, when a magnetic field is applied to a magnetic material and affects the spin ordering, leading to lower entropy of the system as disorder decreases. To compensate for the aligned spins, the atoms of the material start to vibrate in an attempt to randomize the spin and lower the entropy of the system again, which contributes to increasing the temperature of the magnetic material. The opposite behaviour occurs when the material is removed from the magnetic field, which decreases the temperature of the magnetic material. All the moments may be aligned, and increasing the applied field will not yield a further increase in the magnetization at very low temperature and very high field. Magnetization is defined by how much the magnetic moment is aligned, and this behaviour occurs around the phase transition temperature of the material respectively.