CHARACTERISATION OF NOVEL MAGNETOCALORIC MATERIALS (MnCoGe) FOR MAGNETIC REFRIGERATION APPLICATION

ABDUL RASHID ABDUL RAHMAN

DOCTOR OF PHILOSOPHY (ELECTRICAL AND ELECTRONICS ENGINEERING)

UNIVERSITI PERTAHANAN NASIONAL MALAYSIA

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ABSTRACT

Conventional vapour compressor-based refrigeration systems are less energy-efficient and harmful to the environment due to chlorofluorocarbon (CFC), which can deplete the ozone layer and contribute to global warming. Therefore, an alternative solution that is both energy-efficient and environmentally friendly is desirable. Studies on magnetocaloric materials (MCMs) with excellent properties are important to demonstrate their suitability and potential use in refrigeration. This work has focus on MnCoGe-based compound for magnetic cooling, which does not contain high-cost rare earth elements and can provide a favourable working temperature range near room temperature. MnCoGe has unique properties where it exhibits two stable crystallographic structures which can manipulate the magneto-structural transition by adjusting the composition. The magnetic behaviour was analysed through its structural properties, magnetic measurement, and magnetic entropy change ($-\Delta S_M$) for $MnCoGe_{1-x}Al_x$ and $MnCoGe_{1-x}Si_x$. The neutron diffraction is employed to study the magnetic structure and the moment of material. This measurement focus on $MnCoGe_{0.97}Al_{0.03}$ only due to the Echidna and Wombat neutron beam instruments offer very limited beam time. The room temperature x-ray diffraction shows that the $MnCoGe_{1-x}Al_x$ (x=0, 0.05, 0.1, 0.15 and 0.2) alloys have a major phase consisting of TiNiSi-type structure for $x \leq 0.03$ and the Ni_2In-type structure for $x > 0.03$. For $MnCoGe_{1-x}Si_x$ (x=0, 0.05, 0.1, 0.15 and 0.2) alloys, the results indicate that the compounds have a major phase consisting of orthorhombic TiNiSi-type structure with increasing lattice parameter *b* and decreased others (*a* and *c*) with the increase of Si concentration. The $-\Delta S_M$ maximal value increased with the increase of Al content from

8.36 to 9.57 $J \cdot kg^{-1}K^{-1}$ for x = 0.00 to 0.15. On the other hand, the $MnCoGe_{1-x}Si_x$ compounds shows decreasing pattern from $-\Delta S_M$~8.36 J kg^{-1} K^{-1} at x=0 to $-\Delta S_M$~5.49 J kg^{-1} K^{-1} at x=0.2 with 5 T applied field. The theoretical study mainly focuses on the $MnCoGe_{0.97}Al_{0.03}$ compound, as the compound shows that TiNiSi-type and Ni_2In-type structures start to coexist together which given the best interest to further study the nature of FM - PM transition. The obtained critical parameters concluded the compound having long-range ferromagnetic order, which is second-order type magnetic transition, thus, verified the experimental studies and confirmed the reliability of the compounds for magnetic refrigeration application.

ABSTRAK

Sistem penyejukan berasaskan pemampat wap konvensional kurang cekap tenaga dan berbahaya kepada alam sekitar disebabkan oleh klorofluorokarbon (CFC), yang boleh menipiskan lapisan ozon dan menyumbang kepada pemanasan global. Oleh itu, penyelesaian alternatif yang cekap tenaga dan mesra alam adalah wajar. Kajian tentang bahan magnetocaloric (MCM) dengan sifat yang sangat baik adalah penting untuk menunjukkan kesesuaian dan potensi penggunaannya dalam penyejukan. Kajian ini memberi tumpuan kepada sebatian berasaskan MnCoGe untuk magnet penyejukan, yang tidak mengandungi unsur nadir bumi yang berkos tinggi dan boleh memberikan julat suhu kerja yang baik berhampiran suhu bilik. MnCoGe mempunyai sifat unik di mana ia mempamerkan dua struktur kristalografi yang stabil dan boleh memanipulasi peralihan magneto-struktur. Kajian ini dianalisis melalui sifat strukturnya, pengukuran magnetik dan perubahan entropi magnetik ($-\Delta S_M$) untuk $MnCoGe_{1-x}Al_x$ dan $MnCoGe_{1-x}Si_x$. Difraksi neutron digunakan untuk mengkaji struktur magnet dan momen bahan. Pengukuran ini memfokuskan pada $MnCoGe_{0.97}Al_{0.03}$ sahaja kerana instrumen pancaran neutron Echidna dan Wombat menawarkan masa pancaran yang sangat terhad. Difraksi sinar-x menunjukkan bahawa aloi $MnCoGe_{1-x}Al_x$ (x=0, 0.05, 0.1, 0.15 dan 0.2) mempunyai fasa utama yang terdiri daripada struktur jenis TiNiSi untuk $x \leq 0.03$ dan struktur jenis Ni_2In untuk $x > 0.03$. Bagi aloi $MnCoGe_{1-x}Si_x$ (x=0, 0.05, 0.1, 0.15 dan 0.2), sebatian menunjukkan fasa utama yang terdiri daripada struktur jenis TiNiSi ortorombik dengan parameter kekisi *b* yang meningkat dan yang lain menurun (*a* dan *c*) dengan peningkatan Si. Nilai maksimum $-\Delta S_M$ meningkat dengan peningkatan kandungan Al daripada 8.36 kepada

9.57 J $kg^{-1}K^{-1}$ untuk x = 0.00 kepada 0.15. Sebaliknya, sebatian $MnCoGe_{1-x}Si_x$ menunjukkan corak penurunan dari $-\Delta S_M$~8.36 J kg^{-1} K^{-1} pada x=0 kepada $-\Delta S_M$~5.49 J kg^{-1} K^{-1} pada x=0.2 dengan medan 5 T digunakan. Kajian teoretikal tertumpu kepada sebatian $MnCoGe_{0.97}Al_{0.03}$, kerana sebatian itu menunjukkan struktur jenis TiNiSi dan Ni_2In mula wujud bersama dan memberikan minat untuk mengkaji lebih lanjut sifat peralihan FM - PM. Parameter kritikal yang diperoleh menyimpulkan sebatian mempunyai susunan feromagnetik jarak jauh, iaitu peralihan magnet jenis tertib kedua, oleh itu, mengesahkan kajian eksperimen dan mengesahkan kebolehpercayaan sebatian untuk aplikasi penyejukan magnet.

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APPROVAL

The Examination Committee has met on **16 November 2022** to conduct the final examination of **Abdul Rashid Abdul Rahman** on his degree thesis entitled **Characterisation of Novel Magnetocaloric Materials (MnCoGe) For Magnetic Refrigeration Application.**

The committee recommends that the student be awarded the of Doctor of Philosophy (Electric and Electronics Engineering).

Members of the Examination Committee were as follows.

Prof. Dr. Mohd Taufik bin Ishak
Faculty of Engineering
Universiti Pertahanan Nasional Malaysia
(Chairman)

Dr. Khadijah binti Ismail
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Assoc. Prof. Ir. Dr. Irni Hamiza Hamzah
Centre of Electrical Engineering Studies
Universiti Teknologi Mara Pulau Pinang
(External Examiner)

Prof. Dr. Ab Malik Marwan bin Ali
Faculty of Applied Science
Universiti Teknologi Mara Shah Alam
(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 **Doctor of Philosophy (Electric and Electronics Engineering)**. The members of the Supervisory Committee were as follows.

Assoc. Prof. Dr. Muhamad Faiz Md Din
Faculty of Engineering
Universiti Pertahanan Nasional Malaysia
(Main Supervisor)

Assoc. Prof. Dr. Siti Nooraya Mohd Tawil
Faculty of Engineering
Universiti Pertahanan Nasional Malaysia
(Co-Supervisor)

Assoc. Prof. Ts. Dr. Norinsan Kamil Othman
Faculty of Science and Technology
Universiti Kebangsaan Malaysia
(Co-Supervisor)

UNIVERSITI PERTAHANAN NASIONAL MALAYSIA

DECLARATION OF THESIS

Student's full name : Abdul Rashid Abdul Rahman

Date of birth : 22 January 1991

Title : Characterisation of Novel Magnetocaloric Materials (MnCoGe) For Magnetic Refrigeration Application

Academic session : 2018/2022

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LIST OF ABBREVIATIONS

DSC	-	Differential scanning calorimetry
FM	-	Ferromagnetic
FOMT	-	First order magnetic transition
GMCE	-	Giant magnetocaloric effect
HTMO	-	Hybrid thermomagnetic oscillator
MCE	-	Magnetocaloric effect
MCM	-	Magnetocaloric material
PM	-	Paramagnetic
PPMS	-	Physical property measurement system
RC	-	Refrigeration capacity
SOMT	-	Second order magnetic transition
STMO	-	Single thermomagnetic oscillator
VSM	-	Vibrating sample magnetometry
XRD	-	X-Ray diffraction
CFC	-	Chlorofluorocarbon
FWHM	-	Full width at half maximum
HFC	-	Hydrofluorocarbon
HCFC	-	Hydrochlorofluorocarbon
ICSD	-	Inorganic Crystal Structure Database
IEA	-	International Energy Agency
LP	-	Lorentz and Polarization
MM’X	-	M, M' = transition metals, X = carbon or boron group elements)

LIST OF SYMBOLS

θ	-	Theta (Angle)
T	-	Temperature
T_C	-	Curie temperature
T_{str}	-	Structural transformation temperatures
$-\Delta S_M$	-	Magnetic entropy change
E′	-	Storage modulus
E″	-	Loss modulus
α	-	Alpha
β	-	Betha
δ	-	Delta
γ	-	Gamma
M	-	Magnetic moment
B	-	Magnetic field
Mn	-	Manganese
Co	-	Cobalt
Ge	-	Germanium
Al	-	Aluminium
Si	-	Silicon
H	-	Hydrogen
S_M	-	Magnetic entropy
S_{lat}	-	Lattice entropy
T_{ad}	-	Adiabatic temperature
T_C^A	-	Austenite transition temperature
T_C^M	-	Martensite transition temperature
T_C^{orth}	-	Orthorhombic phase curie temperature
T_C^{hex}	-	Hexagonal phase curie temperature
T_M	-	Martensitic transformation
La	-	Lanthanum
Gd	-	Gadolinium

Fe	-	Iron
Cu	-	Copper
Ni	-	Nickel
Ga	-	Galium
C	-	Carbon
P	-	Steel group materials
Cr	-	Chromium
Zn	-	Zinc
E’	-	Elastic modulus
E”	-	Imaginary loss modulus
T_g	-	Glass transition temperature
V	-	Volume
V	-	Elements in Nitrogen group
R_{wp}	-	Weight residual
R_{bragg}	-	Bragg R factor

CHAPTER 1

INTRODUCTION

There is a rising demand for energy-efficient, environmentally sustainable materials and technologies in today's world. Because conventional refrigerator are harmful to the environment, magnetic refrigerator, which employs magnetocaloric materials' thermomagnetic response, have gained great demand due to their eco-friendly technology and energy-efficient cooling. This chapter provides an overview of magnetic refrigeration as well as the problem statement of this thesis, followed by the objective and organisation of this research.

1.1 Overview of Magnetic Refrigeration

Refrigeration systems used in commercial and residential buildings cooling contribute 700 million metric tons of CO_2 globally every year (~10% of all greenhouse gas emissions) and are responsible for nearly 15% of total energy consumption worldwide; total localized energy consumption in peak areas and at times can reach as high as 70% [1]. According to a 2018 report on cooling prepared by the International Energy Agency (IEA), only ~8% of the 2.8 billion residents own AC units in the world's hottest regions. This percentage will rise in tandem with their rapidly developing economies, resulting in a substantial increase in total energy consumption and CO_2 emissions [2]–[4]. Magnetic refrigerator (MR) provides an energy-efficient and environmentally friendly alternative to such conventional techniques as the conventional vapour compressor-based refrigerator uses harmful chlorofluorocarbons (CFCs) that can deplete the ozone layer and increases the rate of global warming [1], [3].

MR is a relatively novel technique that employs magnetically ordered materials and is based on the magnetocaloric effect (MCE), which results from the coupling of a system of magnetic moments with an external magnetic field resulting in the cooling or heating of a system. The critical phenomenon of a refrigeration system is a constriction of the degree of freedom, which increases the temperature. In the conventional gas compression (vapour cycle) refrigerator, the constriction is realised by a volume compression of the atom gas, whereas the magnetic refrigerator is realised by a constriction of the magnetic spins in magnetocaloric materials. Both magnetic and conventional vapour cycles are based on the four following steps, as illustrated in Figure 1.1. The first stage indicated the adiabatic compression or magnetisation, where

the temperature of the refrigerant increases due to the application of compression or the magnetic field. The second stage is iso-volume or iso-field cooling, where the surroundings extract the added heat. The third stage is the adiabatic expansion or demagnetisation, where the temperature of the refrigerant decreases due to an increased volume or the removal of the magnetic field. The last stage is iso-volume or iso-field heating, where the heat is loaded from the inside of the fridge.

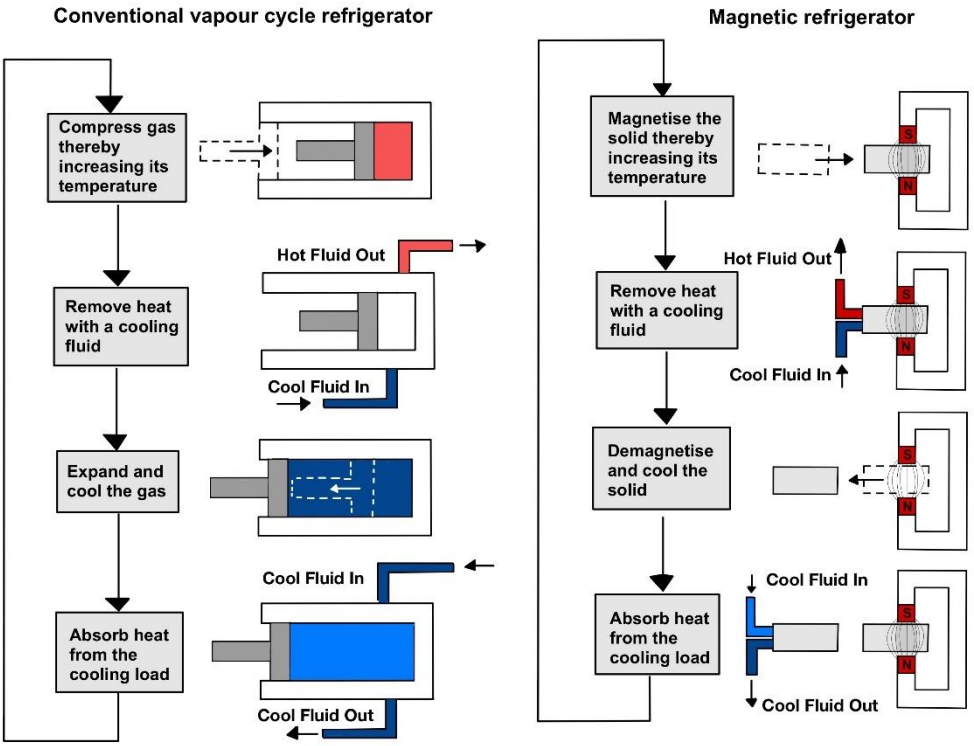

Figure 1.1 Comparison between gas compression and magnetic refrigeration cycles [5].

This magnetocaloric phenomenon was discovered in pure iron in 1881 by Emil Warburg [6]. A notable achievement in magnetic refrigeration was then made in 1976 by Brown, who proved magnetic refrigeration could work at ambient temperatures by generating a temperature difference of 47 K with a ferromagnetic refrigerant [7]. In 1997, there was a significant breakthrough at Ames laboratory/Astronautics Corporation of America with Profs. Karl A. Gschneider, Jr and V.K. Percharsky