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Novel magnetocaloric materials and room temperature magnetic refrigeration

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NOVEL MAGNETOCALORIC MATERIALS
AND ROOM TEMPERATURE MAGNETIC
REFRIGERATION

A thesis submitted in fulfilment of the requirement
for the award of the degree of

DOCTOR OF PHILOSOPHY

from the

UNIVERSITY OF WOLLONGONG

by

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August 2011
I, Jyotish Chandra Debnath, declare that this thesis, submitted in fulfilment of the requirements for the award of Doctor of Philosophy, in the Institute for Superconducting & Electronic Materials, Faculty of Engineering, University of Wollongong, is wholly my own work unless otherwise referenced or acknowledged. This document has not been submitted for qualifications at any other institution.

Jyotish Chandra Debnath
29 August 2011
DEDICATION

To my late parents, parents in law, siblings, my beloved wife,

Jui Moni Das, and my delightful sons, Adrita, Joydeep and

Shammya Debnath, who wonder what I do all day
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ABSTRACT

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 and 15% of the total worldwide energy consumption involves the use of refrigeration (air conditioning, refrigeration, freezing, chilling, etc.). Nowadays, most cooling devices are based on vapour-compression technology, which uses strong greenhouse gases and the energy efficiency has reached its limit, the increased international concerns over global warming due to ever increasing energy consumption calls for a change. Currently, several solid-sate cooling technologies, such as optical refrigeration, thermoelectric refrigeration, electric refrigeration, and magnetic refrigeration, are being considered as viable alternative techniques because they are becoming increasingly efficient and affordable. However, for a technique to become a fully mature alternative, clever engineering and more detailed studies on the fundamental physical properties are needed. Room-temperature magnetic cooling has attracted attention in recent years as a promising environmentally friendly alternative to conventional gas-compression cooling. Using solid magnetic materials as coolant, magnetic cooling does not involve any gases that cause ozone-depletion or global warming, which can help to meet the demands of the recently implemented Kyoto treaty. Furthermore, it has been demonstrated that magnetic cooling is energetically 20% more efficient than gas-compression cooling, which is of particular interest in view of the global energy shortage.
The working materials for room-temperature magnetic cooling are required to possess Curie temperatures around room temperature. Having large magnetization is a prerequisite for achieving a large magnetocaloric effect (MCE). For a long time, Gd was the best room temperature magnetic cooling material with a Curie temperature of 293 K. In comparison with rare-earth-based compounds that exhibit large MCE but are expensive, perovskite manganites exhibit smaller magnetic moments but are far less expensive. The magnetic properties of manganites, the Curie temperature, and the saturation magnetization are strongly doping-dependent. Perovskite manganites are more convenient to prepare and exhibit higher chemical stability, as well as the higher resistivity that is favorable for lowering eddy current heating. In addition, the manganites possess much smaller thermal and field hysteresis than any rare earth and 3d-transition metal based alloy. So, these materials may be good candidates for MR at various temperatures. Many investigations have therefore concentrated on perovskite manganites. The work presented in my thesis is a study of various perovskite manganites magnetocaloric materials for refrigeration applications. We also investigated the MCE of alloys.

The structural, magnetic, and magnetocaloric properties of the manganite La_{0.7}Ca_{0.3}MnO_3 have been studied. Significant magnetic entropy change of 5.27 J/kg K was observed at 251 K under the magnetic field of 1.5 T with out noticeable magnetic hysteresis and tiny thermal hysteresis loss. This value is about twice as large as those for other perovskite manganites and is even larger than for Gd-based magnetic materials at low fields.
The influence of first and second order magnetic phase transitions on the magnetocaloric effect (MCE) and refrigerant capacity or relative cooling power (RCP) of $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ and $\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{0.95}\text{Co}_{0.05}\text{O}_3$ materials has been investigated. The $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ material experiences a large entropy change with the first-order magnetic phase transition at the Curie temperature, $T_C$. On the other hand, $\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{0.95}\text{Co}_{0.05}\text{O}_3$ displays a smaller entropy change with a second order phase transition. While the first-order magnetic transition material induces a larger MCE (7.528 J/kg K at 5 T) at $T_C$, which is limited to a narrow temperature range, resulting in a relatively small RCP (218 J/kg), while the Co-doped second-order magnetic transition material induces a smaller MCE (7.14 J/kg K for 5 T), but it is spread over a broader temperature range, resulting in a larger RCP (308 J/kg). The maximum magnetoresistance under a field of 5 T is about 206% and 333% for $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ and $\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{0.95}\text{Co}_{0.05}\text{O}_3$, respectively. The refrigeration capacity (RCP) is enhanced in $\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{0.95}\text{Co}_{0.05}\text{O}_3$ (by about 41%) due to small changes from Co doping. The magnetocaloric features of these materials at lower magnetic fields (MCE = 3.163 J/kg K for $\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{0.95}\text{Co}_{0.05}\text{O}_3$ and 4.63 J/kg K for $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ at 1 T), and the high RCP and MR can provide some ideas for exploring novel magnetic refrigerants that can be operated with permanent magnets rather than superconducting ones as the magnetic field source.

The magnetic properties and magnetocaloric effect of $\text{La}_{0.7}(\text{Ca}_{1-x}\text{Ag}_x)_{0.3}\text{MnO}_3$ ($x = 0, 0.1, 0.2, 0.7, \text{and} 1$) powder samples were studied. The Curie temperature, $T_C$, has been found to increase from $\sim250$ K for $x = 0$ to $\sim270$ K for $x = 1$. Ag doping weakens the first order phase transition, and at higher Ag doping, the phase transition is of second order. For the $\text{La}_{0.7}(\text{Ca}_{0.27}\text{Ag}_{0.03})\text{MnO}_3$ composition, the maximum
magnetic entropy change (|ΔSM|) from change in the applied magnetic field of 0-2 T and 0-5 T is about 4.5 and 7.75 J/kgK, respectively, at the Curie temperature of ∼263 K. The relative cooling power (RCP) values without hysteresis loss are about 102 and 271 J/kg for applied field change of 0-2 T and 0-5 T, respectively. Due to the large ΔSM, large RCP, and high Curie temperature, La0.7(Ca0.27Ag0.03)MnO3 may be a promising candidate for application in potential magnetic refrigeration near room temperature.

Magnetic properties and the magnetocaloric effect have been investigated in La0.7Ca0.3MnO3 single crystal. Upon application of a 0-5 T field change, the magnitude of the magnetic entropy changes, reaching values of 7.668 J/kg K and 6.412 J/kgK for both the ab-plane and the c-direction, respectively. A magnetic entropy change of 3.3 J/kgK was achieved for a magnetic field change of 1.5 T at the Curie temperature, TC = 245 K. Due to the absence of grains in the single crystal, the ΔSM distribution here is much more uniform than for gadolinium (Gd) and other polycrystalline manganites, which is desirable for an Ericsson-cycle magnetic refrigerator. For a field change of 0-5 T, the relative cooling power, RCP, reached 358.17 J/kg, while a maximum adiabatic temperature change of 5.33 K and a magnetoresistance (MR) ratio of 507.88% at TC were observed. The spin fluctuation parameters were estimated by adapting Takahashi’s developed spin-fluctuation theory, and the reciprocal susceptibility was calculated. Evidence is presented that the magnetic property of La0.7Ca0.3MnO3 is weakly itinerant ferromagnetic. The large reversible MCE and lack of any hysteresis loss, combined with a considerable value of refrigerant capacity, indicate that La0.7Ca0.3MnO3 single crystal is a potential candidate as a magnetic refrigerant.
Epitaxial grown La$_{0.8}$Ca$_{0.2}$MnO$_3$/LaAlO$_3$ (LCMO/LAO) thin film exhibited a paramagnetic-to-ferromagnetic second order phase transition at 249 K. The lack of any hysteresis loss also confirmed that the material is intrinsically reversible. In addition, the large magnetization of the thin film results in a total entropy change larger than those of all other perovskite type materials and the same as that of Gd. Consequently, the relative cooling power is significantly enhanced. Improved film morphology would be the main reason for the remarkable values of entropy change and relative cooling power of the film. This indicates that thin film processing might provide an alternative pathway in searching for efficient magnetic refrigerators for microscale systems.

The effect of frozen spin on the magnetocaloric properties of La$_{0.7}$Ca$_{0.3}$CoO$_3$ polycrystalline and single crystal samples has been studied. Interestingly, an anomalous magnetic field memory effect, an exchange-bias-like effect, and a large inverse irreversible magnetocaloric effect have been observed in this system. It is found that the frozen spins have a significant influence on the $\Delta S_M$. The $\Delta S_M$ – $T$ curves in the low temperature range show totally different features between the ZFC and FC cooling procedures. The $\Delta S_M$ shows a very large inverse irreversibility value for the ZFC process, since there are a large amount of unfrozen spins aligned under the external field in the low temperature range, while the $\Delta S_M$ shows a normal positive value and a slightly larger $\Delta S_M$ value, which indicates that a small amount of unfrozen spins still exist. It is proposed that compositional inhomogeneity is the predominant source of the magnetic properties and the magnetocaloric effect.
Reduction of hysteresis loss in LaFe$_{11.7}$Si$_{1.3}$H$_x$ hydrides with significant magnetocaloric effect has been investigated. The influence of hydrogen absorption on the MCE and especially on the magnetic hysteresis in LaFe$_{11.7}$Si$_{1.3}$H$_x$ ($x=0$, 1.37, and 2.07) compounds is discussed from the viewpoint of magnetic refrigerants, and a large MCE which is still higher than for Gd and a small hysteresis loss are achieved near room temperature are favourable for the practical application of these materials near room temperature.
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**NOMENCLATURE**

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<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full name</th>
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<tbody>
<tr>
<td>MR</td>
<td>Magnetic refrigeration</td>
</tr>
<tr>
<td>a.u.</td>
<td>Arbitrary unit</td>
</tr>
<tr>
<td>MCE</td>
<td>Magnetocaloric effect</td>
</tr>
<tr>
<td>ODS</td>
<td>Ozone depletion substance</td>
</tr>
<tr>
<td>CFC</td>
<td>Chlorofluorocarbons</td>
</tr>
<tr>
<td>HCFC</td>
<td>Hydro chlorofluorocarbons</td>
</tr>
<tr>
<td>HFC</td>
<td>Hydro fluorocarbons</td>
</tr>
<tr>
<td>PLD</td>
<td>Pulsed-laser deposition</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
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<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
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<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
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<tr>
<td>EDS</td>
<td>Energy dispersive spectroscopy</td>
</tr>
<tr>
<td>PPMS</td>
<td>Physical properties measurement system</td>
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<tr>
<td>FWHM</td>
<td>Full width at half maximum</td>
</tr>
<tr>
<td>ISEM</td>
<td>Institute for Superconducting &amp; Electronic Materials</td>
</tr>
<tr>
<td>IEM</td>
<td>Itinerant electron metamagnetism</td>
</tr>
<tr>
<td>MR</td>
<td>Magnetoresistance</td>
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<tr>
<td>RCP</td>
<td>Relative cooling power</td>
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<tr>
<td>RC$_{eff}$</td>
<td>Effective refrigeration capacity</td>
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<tr>
<td>Acronym</td>
<td>Description</td>
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<tr>
<td>WIF</td>
<td>Weakly itinerant ferromagnetic</td>
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<tr>
<td>FFT</td>
<td>Fast Fourier transform</td>
</tr>
<tr>
<td>BF</td>
<td>Bright field</td>
</tr>
<tr>
<td>MI</td>
<td>Metal-insulator</td>
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<td>Zero-field cooling</td>
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<td>Cluster spin glass</td>
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<tr>
<td>$B_c$</td>
<td>Critical field</td>
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CHAPTER 1 INTRODUCTION

1.1 General Background

Although the Montreal protocol has been restricting the harm to the environment from ozone depletion substance (ODS) to a great extent, the greenhouse effect problem is not solved yet. Refrigeration is a major consumer of energy and thus an important cause of greenhouse gas emissions in modern society. So, in addition to further developing the current vapour compression technology, scientists and engineers have begun to explore new refrigeration technologies, such as magnetic refrigeration. Our modern society relies very heavily on readily available cooling technology. Nowadays, there is not very much interest in conventional refrigeration systems. Instead of the ozone-depleting refrigerants and energy consuming compressors found in conventional vapour cycle refrigerators, we need to try a new approach. Without refrigeration, the food supply would still be seasonal and limited to locally produced or non-perishable items; comfortable living conditions would be impossible everywhere; certain medical advances, e.g. organ transplantation, organ and tissue cryo-storage, and cryo-surgery would be impossible. So, cooling systems are very important for food storage and transport, as well as air conditioning in buildings and cars. In the near future widespread superconducting electronics may also be operated at liquid-nitrogen temperatures. These developments call for energy-efficient and versatile refrigeration technology. 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 with respect to the destruction of the ozone layer and global warming [1, 2], which is a prime headache for the environmentalist. Replacement by fluid hydro-fluorocarbons (HFCs), which contain no chlorine and therefore have no ozone depletion potential, is not without problems, because HFCs are greenhouse gases [3] with higher global warming potential than CO₂. Thus, due to serious concern for the environment, alternative technologies should provide more attractive solutions 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 [4-6]. The cooling efficiency of a proof-of-principle magnetic refrigerator based on Gd has reached 60 % of the theoretical limit [7], whereas the best gas compression refrigerator reaches only 40 %. Meanwhile, magnetic refrigeration (MR) is an environmentally friendly and cost effective technology with considerable energy saving, up to 30 % in comparison with conventional gas compression technology. The use of highly energy efficient MR will reduce consumption of fossil fuels, hence reducing CO₂ emissions. It also avoids the use of ozone depleting chemicals (CFCs), Greenhouse gases, and hazardous chemicals (NH₃). Magnetic refrigeration also offers considerable advantages such as small volume, chemical stability, low-cost, non-toxicity and lack of noise pollution.

Magnetic refrigeration has been in use in scientific applications for a long time for cooling below 1 K. However, there are no commercial applications around room temperature, due to the fact that the magnetocaloric effect (MCE) is relatively weak in most ferromagnetic materials at room temperature. Nevertheless, many good materials are currently showing large MCE effects, including elemental Gd and alloys [8-11], particularly Mn alloys [12, 13], manganese oxide materials [14-17],
etc. Among them, the manganese oxide materials are providing themselves to be more suitable candidates for magnetic refrigeration at various temperatures because their magnetic properties, first-order phase transition temperature \[18\], and saturation magnetization (Ms) are strongly doping dependent. Nevertheless, the major focus in magnetic refrigeration is still to find working materials with a large MCE in different temperature ranges. A large number of materials have been reported as candidate materials for magnetic cooling, but considerable success has been achieved in developing magnetic refrigerants based on the search for novel working materials, in particular, in order to develop suitable materials for room-temperature applications in lower fields, which can be generated by permanent magnets \[19, 20\]. The motivation of this research program, namely to explore new materials for magnetic cooling. From the applications point of view, we have focused on finding potential refrigerants, specifically among the manganite materials and other alloys, in order to develop novel giant magnetocaloric materials for fulfilling the operational demands of magnetic refrigeration at room temperature. From the fundamental point of view, our motivation was to gain a deeper insight into the fundamental relations between the MCE and magnetic phase transition, and the magneto-thermal behaviour of magnetic materials. This insight may serve as a guide in the search for new materials suitable for application.

1.2 Historical Development of Magnetic Refrigeration

The study of magnetic refrigeration (MR) started with the discovery of the magnetocaloric effect a century ago. Warburg first discovered the thermal effect of iron metal when placing it in a varying magnetic field in 1881 \[21\]. He discovered that when iron was placed in a magnetic field, it was immediately warmed, and on
removal of the magnetic field, the iron sample cooled down, with the cooling effect varying between 0.5 to 2 K/T. In 1926, Debye and Giauque [22, 23] explained the nature of MCE and suggested that it would be able to achieve ultra-low temperatures using adiabatic demagnetization cooling. They independently proposed the principle of adiabatic magnetic cooling, which utilizes the MCE of paramagnetic salts, as a means of reaching temperatures below the boiling point of liquid helium. In 1933, Giauque and MacDougall [24] put this idea into practice and experimentally demonstrated the use of the MCE to achieve temperatures below 1 K. From then on, the MCE has been successfully utilized to achieve ultra-low temperatures by employing a process known as demagnetization. Giauque was awarded the Nobel Prize in physics for his work on magnetic refrigeration in 1949. In 1976, Brown [8] reported a prototype of a room-temperature magnetic refrigerator and demonstrated that magnetic refrigeration can be realized in the room temperature region. In 2001, the Astronautics Corporation of America [25] realized the world’s first successful room-temperature magnetic refrigerator, in which permanent magnets were used to generate the magnetic field. This achievement has moved the magnetic refrigerator a step closer to commercial application. An upsurge in research has occurred over the last few years. The MCE is represented by the adiabatic temperature change ($\Delta T_{\text{ad}}$) or the entropy ($\Delta S_M$) change, which are intrinsic to all magnetic materials. The MCE is based on the fact 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. Recently, magnetocaloric materials undergoing first-order magnetic transitions have been the centre of attention. In particular, numerous efforts over the last few years have been directed towards understanding the nature of the intrinsic relationships between the composition, structure and magneto-thermal properties and towards improving MCE effects [10, 13, 26-28].

1.3 The magnetocaloric effect

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 material 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”. It was discovered by Warburg [21] in 1881 and is intrinsic to all magnetic materials. In the case of a ferromagnetic material, the material heats up when it is magnetized and cools down when it is removed from the magnetic field. The magnitude of the MCE of a magnetic material is characterized by the isothermal magnetic-entropy ($\Delta S_M$) change, or by the adiabatic temperature ($\Delta T_{ad}$) change due to a varying magnetic field. The nature of the MCE in a solid is the result of the entropy variation due to the coupling of the magnetic spin system with the magnetic field. Since the MCE is directly related to the magnetic entropy change and the adiabatic temperature change, these are the important factors for the selection of ideal magnetic materials for magnetic refrigeration. For the various aspects of the MCE and magnetic refrigeration, we refer to Tishin [5] and Gschneidner and
Pecharsky [6]. Magnetic materials can order their magnetic moments in a variety of ways, as shown in Figure 1.1, with the simplest being the so-called ferromagnetic order, in which the interactions between the moments act to align them. These interactions have a much larger effect on the alignment than the magnetic fields we apply.

Fig. 1.1 Examples of magnetic order. Arrows represent the magnetic moments of atoms in a cubic lattice. Left: ferromagnetic order, where all the spins align in the same direction. Right: antiferromagnetic order, where all the spins align opposite to each other [21].

Fig. 1.2 Illustration of the effect of applying an external magnetic field $H$ to a ferromagnetic spin system [29].
When a magnetic field is applied to a magnetic material, the unpaired spins partially comprising the material’s magnetic moment are aligned parallel to the magnetic field, as shown in Figure 1.2. This spin ordering lowers the entropy of the system since disorder has decreased. To compensate for the aligned spins, the atoms of the material begin to vibrate in attempt to randomize the spins and lower the entropy of the system again. In doing so, the temperature of the material increases. An opposite effect occurs on removal of the applied magnetic field. At very low temperatures or very high fields, all the moments may be aligned and an increase in field will not yield a further increase in the magnetization. The magnetization is a measure of how much the magnetic moments are aligned. All magnetic materials have a phase transition temperature below which the moments are ordered and above which the moments are disordered. In the disordered state, the magnetic materials are said to be paramagnetic. Near the transition temperature, the magnetization, M, changes rapidly, whereas the changes at other temperatures are small.

1.4 Basic Concepts of Conventional Refrigeration and Magnetic Refrigeration

1.4.1 Conventional Refrigeration

Refrigeration is defined as “the transfer of heat from a lower temperature region to a higher temperature one”. Most current refrigeration devices operate using the vapour-compression cycle (reverse Carnot cycle). Some examples of refrigeration devices are heat pumps, refrigerators, automotive air-conditioners, and residential/commercial air-conditioners. All of these devices have one thing in common: they reduce the temperature of an enclosed environment. The ideal vapour-
Domestic refrigeration is accomplished by using a system similar to the one shown above. The four main parts of the refrigerator are 1) The compressor, 2) The condenser, 3) The expansion valve, and 4) The evaporator. In the ideal vapour-compression cycle, refrigerant enters the compressor as a saturated vapour (Figure 1.3). As the refrigerant is compressed, it increases in temperature and pressure (points 1-2). After leaving the compressor, the refrigerant passes through the condenser. Heat energy is exchanged with the surrounding environment causing the refrigerant to cool and become a saturated liquid (points 2-3). Next, the refrigerant passes through the expansion valve, causing the temperature and pressure to decrease (points 3-4). Because of the reduction in temperature and pressure, the refrigerant
enters the evaporator as a saturated mixture. As the refrigerant passes through the evaporator, it absorbs heat energy from the environment that it is trying to cool. The refrigerant exits the evaporator as a saturated vapour and returns to the compressor to begin the process all over again (points 4-1).

1.4.2 Magnetic Refrigeration

Magnetic refrigeration is an emerging technology that has the potential for high energy efficiency [6, 31-33]. The high efficiency arises because the analogues to the compression and expansion parts of the vapour cycle are accomplished by the magnetization and demagnetization, respectively, of a magnetic material [8].

![Fig. 1.4](image)

Fig. 1.4 (a) Gadolinium alloy heats up inside the magnetic field and loses thermal energy by irradiation, so it exits the field cooler than when it entered. (b) Analogy between magnetic refrigeration and vapour cycle or conventional refrigeration [34].
In a magnetically soft ferromagnetic compound, these magnetic processes can be essentially dissipation free, thus approaching 100% of Carnot efficiency. Furthermore, the magnetic refrigerant is a solid and will generally present a negligible environmental hazard. Magnetic refrigeration is based on the magnetocaloric effect (MCE). Originating from coupling of a magnetic field with magnetic moments carried by itinerant or localized electrons and quantified in terms of temperature and/or entropy changes, the MCE reflects field-induced, reversible variations of internal energy, and the effect itself represents one of the most basic properties of magnetic solids. [21-23]. Magnetic refrigeration is a method of cooling based on the MCE. The heating and cooling caused by a changing magnetic field are similar to the heating and cooling of a gaseous medium in response to compression and expansion. A schematic representation of the magnetic-refrigeration cycle is depicted in Figure 1.5.

**Fig. 1.5** Schematic representation of a magnetic-refrigeration cycle, which transports heat from the heat load to the ambient. Left and right sides depict the material in low and high magnetic field, respectively [35].
When a ferromagnetic material is placed in an external magnetic field, the field forces the magnetic moments to align, reducing the magnetic entropy. Since the total entropy is constant under adiabatic condition, the reduced part of the magnetic entropy is transferred from the spin subsystem to the lattice subsystem via spin and lattice coupling. This causes an increase in the lattice entropy, which makes the atoms vibrate more rapidly, and results in an increase in the temperature of the material. Conversely, when the material is taken out of the magnetic field, the moments randomize again and remove entropy from the lattice, creating a cooling effect. Throughout its 120 years of history, counting from the discovery of the magnetocaloric effect in iron by Warburg, experimental measurements of MCE were combined with a general thermodynamic theory, or the Landau theory of phase transition, or the mean field approximation, which resulted in the notion that both the rate of change of the magnetization with temperature at constant field $|\frac{\delta M}{\delta T}_H|$, and / or the magnetic field change, $\Delta H$, must be maximized in order to maximize the MCE [36]. Therefore, maximizing $|\frac{\delta M}{\delta T}_H|$ via the proper design of a magnetocaloric material is the only rational approach to improve performance of a magnetic refrigerant. The response of a magnetocaloric material to a magnetic field is similar to the response of a gas to compression and expansion. This analogy between the vapor compression refrigeration cycle and the magnetic refrigeration cycle is depicted in Fig. 1.4. In a vapor cycle refrigerator, the refrigerant gas is compressed, increasing its temperature. The compressed gas then rejects heat to the environment or hot sink, the refrigerant gas is then expanded decreasing its temperature, the expanded gas then absorbs heat from the source or space to be cooled, and the cycle begins again. In a magnetic refrigerator the magnetocaloric material is magnetized, increasing its temperature, the magnetized magnetocaloric
material then rejects heat to the environment or hot sink. The magnetocaloric material is then demagnetized, decreasing its temperature, the demagnetized magnetocaloric material then absorbs heat from the source or space to be cooled, and the cycle begins again.

Fig. 1.6 Analogy to vapor compression [38].

Since the refrigerant in a magnetic refrigerator is a solid, for example, in the form of spherical particles, the heat transfer must be facilitated by a fluid, such as water or aqueous anti-freeze, depending on the operating temperature. The repeated cycling of the magnetocaloric material into and out of the magnetic field, along with appropriately phased fluid flow, replaces the function of the compressor found in conventional vapor cycle systems.
1.5 Magnetocaloric Materials

The prototype magnetic material available for room temperature magnetic refrigeration is the lanthanide metal gadolinium (Gd). At the Curie temperature of 294 K, Gd undergoes a second-order paramagnetic to ferromagnetic phase transition. The MCE [16, 38-42] and the heat capacity [43, 44] of Gd have been studied in many research activities. Being a metal, its thermal conductivity and easy-gain are both favourable. It would be the first choice for laboratory research on room temperature magnetic refrigerators, so long as the problem of easy oxidization is settled. Some Gd-based intermetallic compounds have been shown to possess large MCE [45, 46]. These are favourable to be used in the magnetic Ericsson cycle because the adiabatic temperature change is almost constant in the room temperature range. It was considered to be a milestone of magnetic material research that the reversible giant magnetocaloric effect in a series of GdSiGe alloys was observed in Ames Laboratory [9, 47, 48]. Subsequently, plenty of effort has been devoted to the research on this series [49-52]. These alloys, which have a first-order magnetic transition between 30 and 275 K and have peak values 2-10 times larger than those of other known prototype magnetic refrigerant materials. The non-rare-earth based Heusler alloys, Ni-Mn-Ga, undergo a first order transition, which brings about a great magnetic entropy change [11, 53]. This has attracted considerable interest. However, the width of the peak is only several K, and there is a 6 K thermal hysteresis accompanying the transition, which makes the alloys unfavourable for applications. Of the transition-metal-based compounds, MnAs shows a giant MCE, however, the magnetic transition is accompanied by a large thermal hysteresis [12]. Another compound MnFeP$_{0.45}$As$_{0.55}$ exhibits a giant magnetic entropy change of
similar magnitude to that of the giant MCE material Gd$_5$Ge$_2$Si$_2$. Variation of the P/As ratio between 3/2 and 1/2 makes it possible to tune $T_C$ and the optimal operating temperature between 200 and 350 K, without losing the giant MCE [13]. LaFe$_{13-x}$Si$_x$ compounds with a low Si content show an itinerant electron metamagnetic transition above $T_C$ and a negative lattice expansion at the $T_C$ [54], which results in a sharp change in the magnetization. The simultaneous sharp changes in the lattice parameter and in the magnetization at the transition temperature should strongly influence the magnetic entropy change. In recent years, large magnetic entropy has been found in the perovskite manganese oxides [55-64]. The main advantages of this series of compounds over GdSiGe alloys are their low cost, inert chemical properties, small coercive force, and high electrical resistance. Their $T_C$ also can be easily tuned to the required range by introducing other elements into the lattice.

1.6 Criteria for Selecting Magnetic Materials

In terms of the theoretical analyses and the magnetocaloric nature of existing materials [33, 36], the criteria for selecting magnetic refrigerants for active magnetic refrigerators are given as follows:

a. Large magnetic entropy change and large adiabatic temperature change (i.e., large MCE).

b. Large density of magnetic entropy.

c. Small lattice entropy.

d. Nearly zero magnetic hysteresis (related to the working efficiency of a magnetic refrigerant material).
e. Very small thermal hysteresis (related to the reversibility of the MCE of a magnetic refrigerant material).

f. Small specific heat and large thermal conductivity (as these ensure remarkable temperature change and rapid heat exchange).

g. Large electric resistance (i.e., low eddy current heating or small eddy current loss).

h. High chemical stability, low cost, availability, and simple sample synthesis route.

1.7 Advantages of Magnetic Refrigerator

Magnetic refrigeration based on the magnetocaloric effect (MCE) in magnetic materials has been demonstrated to be a promising alternative to conventional gas compression refrigeration because:

a. The cooling efficiency of a proof-of-principle magnetic refrigerator working with Gd reaches 60% of the theoretical limit, whereas the best gas compression refrigerator reaches only 40%.

b. Magnetic refrigeration (MR) is an environmentally friendly and cost effective technology with considerable energy saving, up to 30% in comparison with conventional gas compression technology.

c. The use of highly energy efficient MR will reduce consumption of fossil fuels, hence reducing CO₂ emissions.

d. It also avoids the use of ozone depleting chemicals such as chlorofluorocarbons (CFCs), Greenhouse gases, and hazardous chemicals (NH₃).
In addition, magnetic refrigeration offers considerable advantages such as small volume, chemically stability, low-cost, non-toxicity, and lack of noise pollution.

1.8 Why Manganite Magnetocaloric Materials are Suitable MR candidates

There are two key requirements for a magnetic material to possess a large MCE. One is a large enough spontaneous magnetization, which is characteristic of a class of heavy rare-earth metals. The second is that it exhibit sharp drop in magnetization, which is associated with the ferromagnetic-paramagnetic transition at the Curie temperature, as was found in perovskite manganites. The magnetic properties of manganites, the Curie temperature, and the saturation magnetization are strongly doping-dependent. So, these materials may be good candidates for MR at various temperatures. Manganite magnetocaloric materials can be promising candidates for active magnetic regenerative (AMR) refrigeration, because they show large MCEs that are comparable to those of Gd and other magnetic refrigerant candidate materials. It is interesting to note that, when compared with Gd and other candidate materials, such perovskite manganites are more convenient to prepare and exhibit higher chemical stability, as well as the higher resistivity that is favorable for lowering eddy current heating. In addition, the manganites possess much smaller thermal and field hysteresis than any rare earth and 3d-transition metal based alloy. The MCE peak temperature can be easily tuned within the wide temperature range of 100–375 K, which is beneficial for AMR at various temperatures. In addition, the manganite materials are the cheapest among the existing magnetic refrigerants. These superior features may make them more promising for future MR technology.
One disadvantage of this typical material is that the adiabatic temperature change is not very large, due to the relatively high heat capacity. This may somewhat limit the utility of such manganites for AMR technology. However, this drawback is very likely to be overcome by the rapid development that is currently ongoing in magnetic cooling technology.

1.9 Objectives of Thesis Research

a. Develop new magnetocaloric materials for room temperature refrigeration.
b. Understand the phase transitions of magnetic materials and achieve the required magnetic refrigeration efficiency.
c. Characterize the MCE by magnetic measurements (isothermal magnetic entropy change, $\Delta S_M$) and magnetic thermal measurements (adiabatic temperature change, $\Delta T_{ad}$).
d. Explore the crystallographic/magnetic phase structure and transitions induced in these MCE materials by changing composition, applied fields, temperature, and pressure, and investigate the thermal properties (thermal conductivity, heat capacity, etc.) of these materials.

2.0 Thesis Structure

The present work is aimed at studying the magnetocaloric effect (MCE) in various perovskite manganites and alloys. The discovery of giant MCE in these compounds has renewed interest in magnetic refrigeration, which is an energy efficient and environmentally friendly alternative to the conventional vapour-cycle refrigeration.
This PhD thesis is devoted to the understanding of the MCE of perovskite manganites and alloys.

In Chapter 1, we provide a general introduction to the MCE and to some of the materials showing this effect, while Chapter 2 reviews the most relevant properties of perovskite manganites and alloy compounds. After this overview of the state-of-the-art in this field, Chapter 3 is devoted to the sample synthesis and annealing strategies used in the present work, as well as to the characterisation of the samples using conventional experimental techniques. Chapter 4 analyses the giant magnetic entropy change in colossal magnetoresistance La$_{0.7}$Ca$_{0.3}$MnO$_3$ material in low field. The isothermal magnetic entropy change of La$_{0.7}$Ca$_{0.3}$MnO$_3$ was determined by means of both magnetization and specific-heat measurements, which are in good agreement at low field. Improvement of the refrigerant capacity of La$_{0.7}$Ca$_{0.3}$MnO$_3$ material by a few percent Co doping is presented in Chapter 5, while the large magnetic entropy change near room temperature in La$_{0.7}$(Ca$_{0.27}$Ag$_{0.03}$)MnO$_3$ perovskite is studied in Chapter 6. We have also grown a single crystal of La$_{0.7}$Ca$_{0.3}$MnO$_3$ and have studied the anisotropic and large magnetocaloric effect in La$_{0.7}$Ca$_{0.3}$MnO$_3$ single crystal with anomalous magnetization, which is presented in Chapter 7. Chapter 8 is devoted to the strong correlation between structural parameters and the magnetocaloric effect in epitaxial La$_{0.8}$Ca$_{0.2}$MnO$_3$/LaAlO$_3$ thin film, which shows large MCE that had not been previously reported in the literature. The effect of frozen spin on the magnetocaloric properties of La$_{0.7}$Ca$_{0.3}$CoO$_3$ polycrystalline and single crystal samples is studied in Chapter 9. A study of the reduction of hysteresis loss in LaFe$_{11.7}$Si$_{1.3}$H$_x$ hydrides with significant magnetocaloric effect is detailed in Chapter 10 and finally, the outlook of the thesis is presented in Chapter 11.
References:


[34] Magnetic refrigeration – Wikipedia, the free encyclopedia.


2.1 Materials for MR

The interest in magnetic refrigeration as a new solid state cooling technology competitive with the conventional vapour compression approach has grown considerably over the past 20 years, coinciding with rising international concerns about global warming due to ever increasing energy consumption. As pointed out by Coulomb (2007) in his introductory talk at the Second International Conference on Magnetic Refrigeration at Room Temperature (Thermag II), 15% of total worldwide energy consumption involves the use of refrigeration (air conditioning, refrigeration, freezing, chilling, etc.). The potential of magnetic cooling has not gone unnoticed by fundamental science as well. As shown in Figure 2.1, the number of published papers per annum on the magnetocaloric effect has grown at an exponential rate in the past 10 years. It has been estimated, based on the number of papers published in the first three quarters of 2007, that on average a paper on the magnetocaloric effect appears in print every working day (5 days per week) [1]. Although the roots of magnetic cooling can be traced back to Warburg’s discovery of the magnetocaloric effect in 1881, the true beginning of near room temperature cooling has its origin in the seminal paper by Brown (1976). Between 1881 and 1976 a number of important papers were published on magnetic cooling, but most were concerned with cooling below 20 K. Yet in spite of this large number of publications, magnetic cooling technology is in its earliest stages: there was an initial infinitesimally slow growth in the first 50 years after the discovery of the effect from 1881 to 1930, to a slightly
greater growth rate in the ensuing 45 years (1930–1975). In the following 35 years (1975–to date), the growth rate has been increasing more rapidly perhaps signalling the initial stages of an exponential increase, but it still has a way to go before it will reach its maximum growth rate – this is to be realized in the future.

![Graph showing the number of research papers published annually over the past 80 years containing the word “magnetocaloric” in the title, abstract, or among the keywords. The values for 2007 (triangles) are based on the number of papers abstracted during the first three-fourths of the year [1].](image)

**Fig. 2.1** The number of research papers published annually over the past 80 years containing the word “magnetocaloric” in the title, abstract, or among the keywords. The values for 2007 (triangles) are based on the number of papers abstracted during the first three-fourths of the year [1].

Through the MCE was first discovered in pure iron [2], for years, research on magnetocaloric materials was concentrated on certain types of materials. The prototype magnetic material available for room temperature magnetic refrigeration is the lanthanide metal gadolinium (Gd). Some Gd-based intermetallic compounds have been shown to possess large MCE. These are favourable to be used in the magnetic Ericsson cycle because the adiabatic temperature change is almost constant in the room temperature range. It was considered to be a milestone of magnetic material
research that the reversible giant magnetocaloric effect in a series of GdSiGe alloys was first observed in the Ames Laboratory. Subsequently, great efforts have been devoted to the research on this series. The non-rare-earth based Heusler alloys Ni-Mn-Ga undergo a first order transition which brings about a great magnetic entropy change. Of the transition-metal-based compounds, MnAs shows a giant MCE, however, the magnetic transition is accompanied by a large thermal hysteresis. Another compound, MnFeP, exhibits a giant magnetic entropy change of similar magnitude to that of the giant MCE material Gd₅Ge₂Si₂. LaFe₁₃₋₈Si₆ compounds with a low Si content show an itinerant electron metamagnetic transition above Tc and a negative lattice expansion at the Tc, which results in a sharp change in the magnetization. In recent years, large magnetic entropy had been found in the perovskite manganese oxides. The main advantages of this series of compounds over GdSiGe alloys are their low cost, inert chemical properties, small coercive force, and high electrical resistance. Their Tc also can be easily tuned to the required range by introducing other elements into the lattice.

2.1.1 Gd and Gd-based Intermetallic Compounds

The prototype magnetic material available for room temperature magnetic refrigeration is the lanthanide metal gadolinium (Gd). At its Curie temperature of 294 K, Gd undergoes a second-order paramagnetic ↔ ferromagnetic phase transition. The MCE [3-8] and the heat capacity [9, 10] of Gd have been studied in many research activities. Its ΔT_{ad} values at Tc are ~6, 12, 16, and 20 K for ΔH = 2, 5, 7.5, and 10 T, respectively; its |ΔSM| is about 4.2 J kg⁻¹ K⁻¹ and 10.2 J kg⁻¹ K⁻¹ for ΔH = 1.5 T and 5 T at Tc, respectively. Being a metal, its thermal conductivity and easy-
gain are both favorable. It would be the first choice for laboratory research into room temperature magnetic refrigeration, so long as the problem of easy oxidization is settled. Some Gd-based intermetallic compounds have also been proved to possess large MCE. Gschneidner et al. [11] and Dai et al. [12] reported that both Gd$_{0.74}$Tb$_{0.26}$ and Gd$_{0.5}$Dy$_{0.5}$ present MCE equivalent to Gd at ~280 K and at ~265 K, respectively. The $\Delta T_{ad}$ values of Gd$_{91.8}$Dy$_{8.2}$ and Gd$_{89.9}$Er$_{10.1}$ for a 0.45 T low field are ~1.4 K and ~1.5 K (at 280 K), respectively, somewhat lower than that of Gd, ~2.0 K [7]. Eutectic Gd$_{76}$Pd$_{24}$ was found to have two $\Delta T_{ad}$ peaks of 8.4 K and 9.4 K at 294 K and 323 K, respectively, and it is favourable to be used in the magnetic Ericsson cycle because the adiabatic temperature change is almost constant in the room temperature range [13]. Concerning Gd$_4$(Bi$_x$Sb$_{1-x}$)$_3$ alloys, although the maximum MCE is nearly 50% of that of pure Gd for a 10 T field change, the width of the peaks at half maximum reaches 60–100 K, which is comparable with that of Gd. So, they can provide considerable cooling power over a wide temperature range from ~240 to ~360 K [14].

### 2.1.2 Gd$_5$(Ge,Si)$_4$ and Related Compounds

Though the MCE was first discovered in pure iron [2], for years, research on magnetocaloric materials was concentrated on rare earths and their compounds. It was considered to be a milestone of magnetic material research when the reversible giant magnetocaloric effect in a series of GdSiGe alloys was observed in the Ames Laboratory [15, 16]. Its $|\Delta S_m|$ is about 18.4 J kg$^{-1}$ K$^{-1}$ for $\Delta H = 5$ T at $T_C = 276$ K, which is larger than for Gd by 70%-80%. Following the discovery of a sub-room-temperature giant-MCE in the ternary compound Gd$_5$(Ge$_{1-x}$Si$_x$)$_4$ (0.3 $\leq x \leq 0.5$) [16],
there has been strongly increased interest from both fundamental and practical points of view in studying the MCE in these materials [17, 18]. The most prominent feature of these compounds is that they undergo a first-order structural and magnetic phase transition, which leads to a giant magnetic field-induced entropy change across their ordering temperature. Pecharsky et al. 2002 [19] reported that at low temperatures for all x, Gd₅(Ge₁₋ₓSiₓ)₄ adopts an orthorhombic Gd₅Si₄-type structure (Pnma) and the ground state is ferromagnetic. However, at room temperature, three different crystallographic phases are observed depending on x. For x > 0.55, the aforementioned Gd₅Si₄ structure is stable, for x < 0.3 the materials adopt the Sm₅Ge₄-type structure with the same space group (Pnma), but a different atomic arrangement and a somewhat larger volume, and finally, in between these two structure types, the monoclinic Gd₅Si₂Ge₂ type with space group (P112₁/a) is formed, which has an intermediate volume. The latter structure type is stable only below about 570 K, where again the orthorhombic Gd₅Si₄-type structure is formed in a first order phase transition [20]. Pecharsky et al. (1997) reported that the unit cells always contain four formula units and essentially only differ in the mutual arrangement of identical building blocks, which are either connected by two, one, or no covalent-like Si–Ge bond, resulting in successively increasing unit-cell volumes [21]. The giant MCE is observed for the compounds that exhibit a simultaneous paramagnetic to ferromagnetic and structural phase transition that can be induced by a change in temperature, applied magnetic field, or applied pressure [22, 23]. The fact that the structural and magnetic transitions are simultaneous is somewhat accidental, as the exchange energy is of the same order of magnitude as the thermal energy at the structural phase transition. The electrical resistivity and magneto-resistance of Gd₅Si₂Ge₂ also shows unusual behaviour, indicating a strong coupling between the
electronic structure and the lattice. For several compounds of the series, a very large magneto-resistance effect is reported next to a cusp-like anomaly in the temperature dependence of the resistivity [24, 25]. So, in view of building a refrigerator based on Gd$_5$(Ge$_{1-x}$Si$_x$)$_4$, there are a few points to consider. The largest MCE is observed considerably below room temperature, while a real refrigerator should expel heat at least at about 320 K. Because the structural transition is connected with sliding of building blocks, impurities, especially at the sliding interface, can play an important role. The thermal hysteresis and the size of the MCE connected with the first-order phase transition strongly depend on the quality of the starting materials and the sample preparation [26]. For the compounds Gd$_5$(Ge$_{1-x}$Si$_x$)$_4$, with $x$ around 0.5, small amounts of impurities such as Al, Bi, C, Co, Cu, Ga, Mn, O, or Sn may suppress the formation of the monoclinic structure near room temperature. These alloys then show only a phase transition of second order at somewhat higher temperature, but with a lower MCE [20, 27-28]. The only impurity that appears to enhance the MCE and increases the magnetic ordering temperature is so far Pb [29]. This sensitivity to impurities such as carbon, oxygen, and iron strongly influences the production costs of the materials, which may hamper broad-scale application. Compared to the thermal and field hysteresis, the magneto-structural transition in Gd$_5$(Ge$_{1-x}$Si$_x$)$_4$ appears to be rather sluggish [30, 31]. This will also influence the optimal operation frequency of a magnetic refrigerator and the efficiency. Therefore, this series of alloys meet the requirements of room temperature magnetic refrigeration. However, many urgent problems such as easy oxidation, difficult preparation, and high price, need to be settled before they are actually applied in room temperature magnetic refrigeration [32].
Yucel et al. [33] investigated the effect of alloying $\text{Gd}_5(\text{Si}_{2-x}\text{Ge}_{2-x}\text{R}_x)$ compounds with 3d (Co and Mn) and p (Ga and B) orbits. They found that the substitution of Si and Ge could adjust $T_C$ of the compound between 20 and 286 K, with $\Delta S_M$ variation in this process. For $R = \text{Mn}$, the maximum $|\Delta S_M|$ is decreased by up to 17% as the Mn content increases from $z = 0.01$ to 0.1. When $R$ denotes Co and $z$ is above 0.04, the increase in Co content causes strong reduction of $T_C$ down to 260 K, with a 13% increase of $|\Delta S_M|$. For $R = \text{Ga}$ or B, the magnetic entropy is slightly reduced by 12% with increasing R content. Chen et al. [34] studied the magnetic properties of $\text{Gd}_5\text{Si}_{2-x}\text{Ge}_{2-x}\text{Sn}_{2x}$ ($x = 0.05$, 0.10, 0.15, 0.20, 0.25, and 0.50). They reported that $|\Delta S_M|$ of the $\text{Gd}_5\text{Si}_{2-x}\text{Ge}_{2-x}\text{Sn}_{2x}$ alloys gradually increases with increasing Sn content from $x = 0$ to $x = 0.25$. For $x \leq 0.2$, the alloys have a dominant phase of monoclinic $\text{Gd}_5\text{Si}_2\text{Ge}_2$-type crystal structure and a small quantity of $\text{Gd}_5\text{Si}_4$-type phase at room temperature, and the latter decreases with increasing Sn content. The maximum $|\Delta S_M|$ of $\text{Gd}_5\text{Si}_{1.75}\text{Ge}_{1.75}\text{Sn}_{0.5}$, which has only one paramagnetic-ferromagnetic phase transition, is as large as 16.7 J kg$^{-1}$K$^{-1}$ under a magnetic field change of 1.8 T at its $T_C$ of 269 K. Its MCE exceeds that of Gd by about two times. When Dy replaces Gd in $\text{Gd}_5\text{Si}_4$, Xie et al. [35] found that $T_C$ decreases in a linear fashion from $\text{Gd}_5\text{Si}_4$ ($T_C = 338$ K) to $\text{Dy}_5\text{Si}_4$ ($T_C = 140$ K), but $|\Delta S_M|$ is only slightly reduced, by about 8% for $(\text{Gd}_{2.5}\text{Dy}_{2.5})\text{Si}_4$.

2.1.3 Transition Metal Compounds

Oesterreicher et al. (1984) [36] reported the magnetocaloric effect in rare-earth transition metal compounds whose Curie temperatures are in the vicinity of room temperature, and suggested that it is possible for the series of $\text{Y}_2\text{Fe}_{17-x}\text{Co}_x$ and
Y$_2$Fe$_{17-x}$Ni$_x$ compounds to be room temperature magnetic refrigerants. Later investigations showed that some other rare-earth transition metal compounds besides the GdSiGe alloys mentioned above also exhibit great magnetic entropy change, and their Curie temperatures can easily be tuned by ion doping. The research on Ce$_{2-x}$Dy$_x$Fe$_{17}$ alloys showed that $|\Delta S_M|$ (in a 1.4 T magnetic field) is ~1.67, 1.41, and 1.18 J kg$^{-1}$K$^{-1}$, where $x = 0.0$, 0.3, and 0.5, and the corresponding temperatures are ~234, ~267, and ~286 K, respectively [37]. Wang et al. reported that the maximum $\Delta T_{ad}$ in the series of Ce$_2$Fe$_{17-x}$Co$_x$ and Er$_2$Fe$_{17-x}$Ni$_x$ ($x = 0.3–2.0$) compounds are 4.75 and 4.51 K (in a 2 T magnetic field), and their corresponding Curie temperature values are 294.2 K and 293.5 K, respectively, near that of Gd metal, but much less expensive than for Gd [38]. Hence, this series of compounds are benign choices from the point of view of practical application.

2.1.4 Heusler Alloys

The non-rare-earth based Heusler alloys Ni-Mn-Ga undergo a first order transition, which is responsible for a great magnetic entropy change and has attracted considerable interest [39, 40]. Hu et al. (2000) reported that the magnetic entropy change of Ni$_{52.6}$Mn$_{23.1}$Ga$_{24.3}$ at 300 K is ~18.0 J kg$^{-1}$K$^{-1}$, roughly comparable with that of Gd$_5$Si$_2$Ge$_2$ and notably exceeding that of Gd near room temperature [39]. However, the width of the peak is only several K, and there is a 6 K thermal hysteresis accompanying the transition, both of which make this alloy unfavourable. Heusler alloys frequently undergo a martensitic transition between the martensitic and the austenitic phase, which is generally temperature induced and of first order. Webster et al. (1984) reported that the Heusler alloy Ni$_2$MnGa orders
ferromagnetically with a Curie temperature of 376 K and a magnetic moment of 4.17 \( \mu_B \), which is largely confined to the Mn atoms, and with a small moment of about 0.3\( \mu_B \) associated with the Ni atoms [41]. In the martensitic phase the compound exhibits a much larger anisotropy. The martensitic transformation temperature is near 220 K. This martensitic transformation temperature can be easily varied to around room temperature by modifying the composition of the alloy from the stoichiometric. Krenke et al. (2005) reported that they had found a large inverse MCE in the Heusler alloy NiMnSn, which was related in the increase in magnetization with increasing temperature over the martensitic transition temperature. Substitution of Co for Ni leads to an increase in the transition temperature to close to room temperature [42]. Bao et al. [43] reported that substitution of Co for Mn gives rise to a non-modulated tetragonal martensitic structure at room temperature. According to the experimental results, NiMnCoGa alloys undergo a magnetostructural phase transition on heating when the electron concentration is in the range from 7.633 to 7.643. The alloys also show large magnetic entropy changes. With increasing Co content, the magnetic entropy change decreases. Nayak et al. showed that substitution of Co for Ni decreases the transition temperature monotonically with Co concentration. The maximum magnetic entropy change of 34 J kg\(^{-1}\)K\(^{-1}\) was achieved for \( x = 5 \) at 262 K for a field change of 5 kOe, and a value of 29 J kg\(^{-1}\)K\(^{-1}\) was found near room temperature [44]. Passamani et al. reported the influence of Fe substitution for Mn in NiMn-Sn Heusler-type compound and showed that the insertion of Fe atoms reduces the Mn-Mn antiferromagnetic (AF) interactions, resulting in a systematic decrease in the martensitic transition temperature, down to its disappearance at 15 at. % of Fe, and a monotonic increase in the L2\(_1\)-type phase Curie temperature. The maximum inverse magnetic entropy change, for a field variation of 5 T, is about 12 J kg\(^{-1}\)K\(^{-1}\),
and it is nearly constant for Fe content up to 7 at.% [45]. Hu et al. measured the MCE properties of Ni$_{51}$Mn$_{49-x}$In$_x$ and found that all alloys show a very small thermal hysteresis, < 2 K, around the martensitic transition. An increase in magnetic field does not enlarge the hysteresis for all samples. The maximum values of entropy change reach 33, 20, and 19 J kg$^{-1}$K$^{-1}$ at 308, 262, and 253 K for compositions x = 15.6, 16.0, and 16.2 respectively [46].

2.1.5 MnAs-based Compounds

Of the transition-metal-based compounds, MnAs shows a giant MCE. Similar to Gd$_5$Ge$_2$Si$_2$, MnAs exists in two distinct crystallographic structures [47]. At low and high temperature, the hexagonal NiAs structure is found, and for a narrow temperature range 307–393 K, the orthorhombic MnP structure exists. The high-temperature transition in the paramagnetic region is of second order. The low-temperature transition is a combined structural and ferro-paramagnetic transition of first order with large thermal hysteresis. The change in volume at this transition amounts to 2.2% [48]. The transition from paramagnetic to ferromagnetic occurs at 307 K, while the reverse transition from ferromagnetic to paramagnetic occurs at 317 K. Very large magnetic entropy changes are observed in this transition [49]. Wada et al. (2001) showed that MnAs compound undergoes a first-order ferromagnetic to paramagnetic transition at 318 K and that the magnetic entropy change induced by a 5 T magnetic field is 30 J kg$^{-1}$K$^{-1}$ at the maximum, which exceeds that of Gd$_5$Si$_2$Ge$_2$ by a factor of 2. However, the magnetic transition is accompanied by a large thermal hysteresis [50].
Similar to the application of pressure [51, 52], substitution of Sb for As leads to reduced \(T_c\) [53]; 25% Sb gives a transition temperature of 225 K. However, the thermal hysteresis is affected quite differently by hydrostatic pressure and by Sb substitution. In Mn(As,Sb), the hysteresis is strongly reduced, and at 5% Sb, it is reduced to about 1 K. In the concentration range of 5–40% Sb, \(T_c\) can be tuned between 220 and 320 K without losing much of its magnetic entropy change [54, 55]. Wada et al. (2002) reported that \(|\Delta S_m|\) of MnAs\(_{1-x}\) Sb\(_x\) for \(0 \leq x \leq 0.3\) in a 5 T field reaches 25–30 J kg\(^{-1}\)K\(^{-1}\), and the substitution of Sb for As can tune the Curie temperature between 230 K and 315 K without significant reduction of \(|\Delta S_m|\). Moreover, there is no hysteresis behavior for \(0.05 \leq x \) [56]. Direct measurements of the temperature change confirm a \(\Delta T\) of 2 K/T [57]. On the other hand, Gama et al. (2004) showed that MnAs under pressure experiences an extremely large magnetic entropy change [58] in conjunction with large hysteresis. The material costs of MnAs are quite low, but processing of As containing alloys is, however, complicated due to the biological activity of As. In the MnAs alloy, the As is covalently bound to the Mn and would not be easily released into the environment. However, this should be experimentally verified, especially because in an alloy, second phases frequently form that may be less stable. The change in volume in Mn(As,Sb) is still 0.7%, which may result in aging after frequent cycling of the material.

### 2.1.6 Fe\(_2\)P-based Compounds

Beckmann et al. (1991) [59] reported that the magnetic phase diagram for the system MnFeP–MnFeAs shows a rich variety of crystallographic and magnetic phases. The most striking feature is the fact that for As concentrations between 30% and 65%, the
hexagonal Fe$_2$P type of structure is stable and the ferromagnetic order is accompanied by a discontinuous change of volume. While the total magnetic moment is not affected by changes in the composition, the Curie temperature increases from about 150 K to well above room temperature. From the magnetization curve at 5 K, the saturation magnetisation was determined as 3.9 $\mu_B$/f.u. This high magnetization originates from the parallel alignment of the Mn and Fe moments, although the moments of Mn are much larger than those of Fe. Surprisingly large MCE is observed in the compound MnFeP$_{0.45}$As$_{0.55}$ at room temperature, as reported by Tegus et al. [60]. It was found that at room temperature, 300 K, the entropy change value is 18 and 28 J kg$^{-1}$K$^{-1}$ for field changes of 1.5 and 5 T, respectively. After replacing all the As, a quite large MCE is still observed for MnFe(P,Si,Ge) [61]. The magnetic-entropy changes of different MnFe(P,As, Si,Ge) alloys is shown in Figure 2.2. The origin of the large magnetic-entropy change should be attributed to the comparatively high 3d moments and the rapid change in the magnetisation in the field-induced magnetic phase transition.

![Fig. 2.2 Magnetic entropy changes of Fe$_2$P-type compounds for magnetic field changes of 2 T [60-62].](image-url)
The large MCE observed in Fe$_2$P-based compounds originates from a field-induced first-order magnetic phase transition. The magnetisation is reversible in temperature and in alternating magnetic field. The magnetic ordering temperature of these compounds is tuneable over a wide temperature interval (200–450 K). The excellent magnetocaloric features of compounds of the type MnFe(P,Si,Ge,As), in addition to the very low material costs, make them attractive candidate materials for a commercial magnetic refrigerator. Tegus et al. [62] studied the effects of Cr and Co substitution for Fe in MnFe(P$_{1-x}$As$_x$). For the Mn(Fe$_{1-x}$Cr$_x$)P$_{0.47}$As$_{0.53}$ alloy ($T_C = 305$ K), Cr lowers both $T_C$ and $|\Delta S_M|$, and the first order magnetic transition changes to a second order transition at $x = 0.02$. $T_C = 275$ K, and $|\Delta S_M|$ is reduced by 25% for a 2 kOe field, while for $x = 0.09$, $T_C = 190$ K, and $|\Delta S_M|$ is reduced by 65% for the same field. For the alloy Mn(Fe$_{1-x}$Co$_x$)P$_{0.5}$As$_{0.5}$, a 10% substitution of Co for Fe ($x = 0.1$) reduces $T_C$ from 282 to 260 K and reduces the $|\Delta S_M|$ value by 55% for the same field.

Liu et al. [63] measured the MCE of Mn$_{1.1}$Fe$_{0.9}$(P$_{0.8}$Ge$_{0.2}$) and showed that for this material, it has a similar shape for both increasing and decreasing field, with maximum entropy change of 74 and 78 J kg$^{-1}$K$^{-1}$ on increasing and decreasing field, respectively, for a field change of 5 T at about 257 K. The MCE of MnFe(P,Ge) was studied by Trung et al. [64]. They showed that the critical behaviour of the phase transition can be controlled by changing either the composition or the annealing conditions. The thermal hysteresis is found to be tuneable. It can reach very small values, while maintaining a large magnetocaloric effect over a large range of working temperatures and under field changes that may be produced by conventional permanent magnets.
The fact that the magneto-elastic phase transition is a change of c/a rather than a change of volume makes it feasible that this alloy, even in polycrystalline form, will not experience severe aging effects after frequent magnetic cycling.

### 2.1.7 Composite Material

Single materials, whose temperature range is not wide enough to be useful, cannot meet the needs of an ideal magnetic Ericsson cycle. As a solution, a method of composition was first raised by Brown GV, 1977 [65]. A few ferromagnetic materials with different magnetic phase transition temperatures $T_C$ are combined into one new material composite whose $|\Delta S_M|$ is within a suitable range of refrigeration temperatures. Hashimoto et al. (1987) [66, 67] have made experimental trials to construct layer structured sintered material composed of ErAl, HoAl, (DyHo)Al, and DyAl alloys in the low temperature range, which confirmed that the composition of magnetic materials is a future method likely to be suitable for the magnetic Ericsson cycle. In another investigation, Smaïli et al. (1997) [68] have obtained two sets of composite materials over the temperature ranges of 240–290 and 210–290 K, respectively, from among the GdDy alloys and showed that the resultant $|\Delta S_M|$ is practically constant in the required temperature range, amounting to 8.0 and 7.3 J kg$^{-1}$K$^{-1}$ for the two respective sets. Zhang et al. [69] measured the MCE of DyCo$_2$ and TbCo$_2$, and found that the $|\Delta S_M|$ was 11 and 6.5 J kg$^{-1}$K$^{-1}$ at 140 and 227 K, respectively.
2.1.8 La (Fe,Si)$_{13}$ and Related Compounds

The rare-earth transition-metal compounds crystallizing in the cubic NaZn$_{13}$ type of structure are another interesting type of material for MR. Kripyakevich et al. [70] reported that with an addition of at least 10% Si or Al, this structure can also be stabilized with iron and nickel. The NaZn$_{13}$ structure contains two different Zn sites. In La (Fe,Si)$_{13}$, La goes on the 8a site, the 8b site is fully occupied by Fe, and the 96i site is shared by Fe and Si.

![Fig. 2.3 Magnetic-entropy change for LaFe$_{13}$ based samples for a field change of 2T [75, 90].](image)

The iron-rich compounds La(Fe,Si)$_{13}$ show typical Invar behaviour, with magnetic ordering temperatures around 200 K that increase to 262 K with lower iron content [71]. Thus, although the magnetic moment is diluted and also decreases per Fe atom, the magnetic ordering temperature increases. Around 200 K, the magnetic-ordering transition is found to be also distinctly visible in the electrical resistivity, where a chromium-like cusp in the temperature dependence is observed.
In contrast to Gd$_3$Ge$_2$Si$_2$, this phase transition is not accompanied by a structural change, thus above and below $T_C$, the material is cubic. Recently, because of the extremely sharp magnetic ordering transition, the (La,Fe,-Si,Al) system was reinvestigated by several research groups, and a large MCE was reported. Although the magnetic properties of LaFe$_{13-x}$Si$_x$ had been intensively studied before, the magnetocaloric property did not come into the focus until the work done by Hu et al. [72]. They observed an entropy change as high as $\sim$20 J kg$^{-1}$K$^{-1}$, for a field change of 0-5 T, in LaFe$_{13-x}$Si$_x$ with lower Si concentrations. Further study by Hu et al. [73] found that the large entropy change in LaFe$_{13-x}$Si$_x$ is associated with negative lattice expansion and metamagnetic transition behaviour. They showed that for LaFe$_{11.4}$Si$_{1.6}$, the maximal values of $\Delta S_M$ under fields of 1, 2, and 5 T are 10.5, 14.3, and 19.4 J kg$^{-1}$K$^{-1}$, respectively. In view of shifting $T_C$ toward high temperatures without significantly affecting $\Delta S_M$ Hu et al. [72, 74] showed that the best effect could be obtainable by replacing Fe with an appropriate amount of Co. An entropy change of 11.5 J kg$^{-1}$K$^{-1}$ in LaFe$_{10.98}$Co$_{0.22}$Si$_{1.8}$ at 242 K for a field change of 5 T was observed [72]. Further study [74] on LaFe$_{11.2}$Co$_{0.7}$Si$_{1.1}$ showed that the maximal value of $|\Delta S_M|$ near the Curie temperature $T_C$ of 274 K for a field change of 0–5 T is 20.3 J kg$^{-1}$K$^{-1}$, which exceeds the value for Gd by a factor of 2 and is nearly as large as that for Gd$_3$Si$_2$Ge$_2$ and MnFeP$_{0.45}$As$_{0.55}$. Again, the same authors showed that in La(Fe$_{1-x}$Co$_x$)$_{11.9}$Si$_{1.1}$ ($x = 0.04, 0.06, \text{and} 0.08$), the Curie temperature increases from 243 to 301 K as $x$ increases from 0.04 to 0.08, while $|\Delta S_M|$ only slowly decreases from $\sim$23 to $\sim$15.6 J kg$^{-1}$K$^{-1}$ for a field change of 0–5 T [75]. A study on the MCE of La$_{0.5}$Pr$_{0.5}$Fe$_{11.5-x}$Co$_x$Si$_{1.5}$ ($0 \leq x \leq 1.0$) was performed by Shen et al. [76]. The substitution of Co in La$_{0.5}$Pr$_{0.5}$Fe$_{11.5}$Si$_{1.5}$ causes the phase transition at $T_C$ to change from first-order to second-order at $x = 0.6$. Although the magnetic entropy change
decreases with increasing Co concentration, $T_C$ increases from 181 K for $x = 0$ to 295 K for $x = 1.0$. For the sample with $x = 1.0$, it is noteworthy that the maximum values of $|\Delta S_M|$ at $T_C = 295$ K for magnetic field changes of 0–2 T and 0–5 T, respectively, are 6.0 and 11.7 J kg$^{-1}$K$^{-1}$, which are 20% higher than those of Gd. The MCE of La$_{1-x}$Pr$_x$Fe$_{10.7}$Co$_{0.8}$Si$_{1.5}$ was also studied [77] by the same authors. As $x$ grows from 0 to 0.5, the maximum value of entropy change increases from 13.5 to 14.6 J kg$^{-1}$K$^{-1}$ for a field change of 0–5 T, while $T_C$, which is near room temperature, exhibits only a small change. The effects of replacing Fe by Co on the MCE in LaFe$_{11.7-x}$Co$_x$Si$_{1.3}$ [78], LaFe$_{11.9-x}$Co$_x$Si$_{1.1}$ [78], LaFe$_{11.8-x}$Co$_x$Si$_{1.2}$ [79], and LaFe$_{11.4-x}$Co$_x$Si$_{1.6}$ [80] were also studied, and similar effects to those described above were observed. The MCE of La$_{0.7}$Pr$_{0.3}$Fe$_{13-x}$Si$_x$ ($x = 1.5, 1.6, 1.8$, and $2.0$) exhibited an increase in $T_C$ and a reduction in $|\Delta S_M|$ due to the substitution of Si for Fe [81], which is similar to the case of LaFe$_{13-x}$Si$_x$. Although both the Si-doping and the Co-doping drive $T_C$ to higher temperatures, the reduction of $|\Delta S_M|$ is much slower in the latter case. The maximum $\Delta S_M$ is $\sim 24$ J kg$^{-1}$K$^{-1}$ ($\Delta H = 5$ T) for La$_{0.5}$Pr$_{0.5}$Fe$_{11.5-x}$Co$_x$Si$_{1.5}$ ($x = 0.3$) and $\sim 11$ J kg$^{-1}$K$^{-1}$ ($\Delta H = 5$ T) for La$_{0.7}$Pr$_{0.3}$Fe$_{13-x}$Si$_x$ ($x = 2.0$), while $T_C$ takes on nearly the same value of $\sim 218$ K. Therefore, reducing the Si content in LaFe$_{13-x}$Si$_x$ and partial replacing Fe by Co is a promising way to get room-temperature giant MCE. Wang et al. [82, 83] studied the effects of substituting Mn for Fe, on La(Fe$_{1-x}$Mn$_x$)$_{11.7}$Si$_{1.3}$ ($x = 0, 0.01, 0.02$, and $0.03$) [83]. The Curie temperature was found to decrease at a rate of $\sim 174$ K for 1% Mn. A large $|\Delta S_M|$ was obtained over a wide temperature range, although a tendency toward degeneration appears as $x$ increases, and its values were $\sim 17$ J kg$^{-1}$K$^{-1}$ for $T_C = 130$ K and $\sim 25$ J kg$^{-1}$K$^{-1}$ for $T_C = 188$ K respectively, for a field change of 0–5 T.
The effects of Nd substitution on MCE were studied by Anh et al. [84], who reported an increase in Tc and a decrease in MCE in La$_{1-x}$Nd$_x$Fe$_{11.44}$Si$_{1.56}$ ($x = 0–0.4$) with the incorporation of Nd. Fujieda et al. [85, 86] performed a systematic study on the effects of Ce-doping for the compounds LaFe$_{13-x}$Si$_x$ with $x = 1.3$, 1.56, and 1.82. It was observed that the substitution of Ce caused Tc to be reduced, and the entropy and adiabatic temperature changes to be increased. Shen et al. [87] systematically studied the effects of substituting R for Fe on magnetic properties and MCEs of La$_{1-x}$RxFe$_{13-x}$Si$_x$. It was found that the substitution of R for La in La$_{1-x}$RxFe$_{11.5}$Si$_{1.5}$ (R = Ce, Pr, and Nd) leads to a monotonic reduction in Tc. The $|\Delta S_M|$ for a field change of 0–5 T varies from 23.7 J kg$^{-1}$K$^{-1}$ for $x = 0$ to 32.4 J kg$^{-1}$K$^{-1}$ for La$_{1-x}$Pr$_x$Fe$_{11.5}$Si$_{1.5}$ ($x = 0.5$) and 32.0 J kg$^{-1}$K$^{-1}$ for La$_{1-x}$Nd$_x$Fe$_{11.5}$Si$_{1.5}$ ($x = 0.3$), but remains at 24 Jkg$^{-1}$K$^{-1}$ for La$_{1-x}$Ce$_x$Fe$_{11.5}$Si$_{1.5}$ ($x = 0–0.3$). The effects of hydrogenation on MCE were studied by Chen et al. [88] and Fujita et al. [89] independently. They found that the incorporation of interstitial hydrogen into LaFe$_{13-x}$Si$_x$ shifts Tc to higher temperatures, while a large MCE still appears. The entropy change is as large as 17 Jkg$^{-1}$K$^{-1}$ ($\Delta H = 5$ T) in LaFe$_{11.5}$Si$_{1.5}$H$_{1.3}$, even at a temperature of 288 K [88]. By changing either the hydrogen pressure or the annealing temperature under which the sample was processed, Fujieda et al. [90] controlled the concentration of interstitial hydrogen. In contrast, Chen et al. [88, 91] tuned the content of hydrogen by carefully regulating the desorption of absorbed hydrogen. The Curie temperature Tc of LaFe$_{13-x}$Si$_x$H$_{\delta}$ was found to increase linearly with increasing hydrogen content $\delta$, while the magnetic transition remains the first order. The entropy changes of LaFe$_{11.5}$Si$_{1.5}$H$_{\delta}$ ($\delta = 0–1.8$) are 24.6 and 20.5 J kg$^{-1}$K$^{-1}$ ($\Delta H = 5$ T) at 195 and 340 K, respectively. Wang et al. [92] studied the MCE of the hydrides La(Fe$_{1-x}$Mnx)$_{11.7}$Si$_{1.3}$H$_y$. They showed that it is possible to tune the Tc.
around room temperature by controlling the hydrogen absorption. The maximal values of $\Delta S_M$ are 23.4, 17.7 and 15.9 $\text{J kg}^{-1}\text{K}^{-1}$ under a magnetic field change of 0–5 T for $x = 0.01$, 0.02, and 0.03, at 287, 312, and 337 K respectively. Chen et al. [93, 94] studied the effects of interstitial carbon on the LaFe$_{13-x}$Si$_x$C$_{\delta}$ carbides, which are stable up to the melting point. For LaFe$_{11.6}$Si$_{1.4}$C$_{\delta}$ ($\delta = 0$, 0.2, 0.4, and 0.6) the entropy change is nearly constant when $\delta$ is below 0.2, but decreases rapidly for $\delta > 0.4$. The maximal values of $|\Delta S_M|$, for a field change of 0–5 T, are 24.2 $\text{J kg}^{-1}\text{K}^{-1}$ for $\delta = 0.2$, 18.8 $\text{J kg}^{-1}\text{K}^{-1}$ for $\delta = 0.4$, and 12.1 $\text{J kg}^{-1}\text{K}^{-1}$ for $\delta = 0.6$, respectively. Slightly different carbides in the form LaFe$_{11.5}$Si$_{1.5}$C$_{\delta}$ were also studied by the same authors and similar effects were observed [94]. Gao et al. [95] also investigated the entropy change and hysteresis loss in LaFe$_{11.7}(\text{Si}_{1-x}\text{Cu}_x)_{1.3}$. With Cu content increasing from $x = 0$ to 0.2, $T_C$ increased from 185 to 200 K, and the magnetic entropy change $|\Delta S_M|$ drops off. However, $|\Delta S_M|$ remains large, ~20 $\text{J kg}^{-1}\text{K}^{-1}$, when $x$ reaches 0.2. Both thermal and magnetic hystereses are reduced by introducing Cu. The maximum hysteresis loss at $T_C$ drops off from 74.1 $\text{J kg}^{-1}\text{K}^{-1}$ to zero when the Cu content $x$ increases from 0 to 0.2. LaFe$_{1-x}$Al$_x$ compounds posses rich magnetic properties compared with LaFe$_{1-x}$Si$_x$ compounds. By substituting Al for Fe atoms, the concentration region becomes much wider, $1.0 < x < 7.0$, and the stabilized LaFe$_{1-x}$Al$_x$ compounds exhibit complicated magnetic properties [96]. Hu et al. [97] tuned the Al content from $x = 1.82$ to 1.43 in LaFe$_{1-x}$Al$_x$ and observed a gradual change from the ferromagnetic (FM) to a weak antiferromagnetic (AFM) state. A completely FM ground state at $x = 1.82$ is followed by the emergence of AFM coupling at $x = 1.69$ and 1.56, in which two spaced transitions appear, one at $T_0$, from FM to AFM, and the other at the Néel temperature, $T_N$, from AFM to the paramagnetic state. The natures of the transitions at $T_0$ and $T_N$ are of first and
second-order, respectively. Continuously reducing Al to \( x = 1.43 \) results in a completely AFM ground state. The magnetic entropy change for \( \text{LaFe}_{1-x}\text{Al}_x \) (\( x = 1.82, 1.69, 1.56, \) and 1.43) compounds showed that the \( |\Delta S_M| \) profile evolves from a single-peak shape at \( x = 1.82 \) to a nearly constant-peak shape at \( x = 1.69 \) and 1.56, and then to a two-peak shape at 1.43.

Hu et al. [98] firstly studied magnetic entropy change in Co-doped \( \text{La(Fe,Al)}_{13} \). \( \text{La(Fe}_{0.98}\text{Co}_{0.02})_{11.7}\text{Al}_{1.3} \) and \( \text{LaFe}_{11.12}\text{Co}_{0.71}\text{Al}_{1.17} \) exhibit ferromagnetic behavior with a second-order magnetic transition at \( T_C \sim 198 \) and \( \sim 279 \) K, respectively. The magnetic entropy changes are about 5.9 and 10.6 J kg\(^{-1}\) K\(^{-1}\) for \( \text{La(Fe}_{0.98}\text{Co}_{0.02})_{11.7}\text{Al}_{1.3} \), and 4.6 and 9.1 J kg\(^{-1}\) K\(^{-1}\) for \( \text{LaFe}_{11.12}\text{Co}_{0.71}\text{Al}_{1.17} \) under field changes of 0–2 and 0–5 T, respectively. They found that Co doping can convert the antiferromagnetic coupling to ferromagnetic. \( T_C \) shifts toward higher temperatures with increasing Co content. [99]. The \( \Delta S_M \) of \( \text{La(Fe}_{1-x}\text{Co}_x)_{11.83}\text{Al}_{1.17} \) has nearly the same magnitude as that of Gd near room temperature. Wang et al. [100] investigated interstitial effects on the magnetic properties and the magnetic entropy change in \( \text{La(Fe,Al)}_{13} \) alloys. In \( \text{LaFe}_{11.5}\text{Al}_{1.5} \), a considerable increase of the Curie temperature from 191 to 262 K was observed as the carbon concentration increased from 0.1 to 0.5; however, this was accompanied by only a slight increase in the saturation magnetization. The magnetic transition is of second-order in nature and, thus, the magnetization is fully reversible with temperature and magnetic field. One can find that all the \( \text{LaFe}_{11.5}\text{Al}_{1.5} \) carbides exhibit considerable magnetic entropy change, comparable with that in Gd, around the Curie temperature. Thus, one can get a large reversible magnetic entropy change over a wide temperature range by controlling the carbon concentration. From the material cost point of view, the \( \text{La(Fe,Si)}_{13} \) type of alloys appear to be very
attractive. La is the cheapest element from the rare-earth series, and both Fe and Si are available in large amounts. However, La(Fe, Si, Al)\textsubscript{13} material is brittle and easily pulverized. The poor corrosion resistance of the compounds also restricts their potential applications.

Table 2.1

Magnetic entropy change of some near room temperature magnetic materials

<table>
<thead>
<tr>
<th>Magnetic material</th>
<th>T\textsubscript{c} (K)</th>
<th>(\Delta H) (K)</th>
<th>(\Delta S\textsubscript{M}) (J kg\textsuperscript{-1} K\textsuperscript{-1})</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gd</td>
<td>294</td>
<td>5.0</td>
<td>(\sim 10.2)</td>
<td>7</td>
</tr>
<tr>
<td>Gd\textsubscript{0.5}Dy\textsubscript{0.5}</td>
<td>230</td>
<td>5.0</td>
<td>10.2</td>
<td>12</td>
</tr>
<tr>
<td>Gd\textsubscript{0.74}Tb\textsubscript{0.26}</td>
<td>280</td>
<td>5.0</td>
<td>11.5</td>
<td>11</td>
</tr>
<tr>
<td>Gd\textsubscript{0}(Si\textsubscript{x}Ge\textsubscript{1-x})\textsubscript{4}</td>
<td>x = 0.43</td>
<td>247</td>
<td>5.0</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(\sim 39.0)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(\sim 11.7)</td>
<td>19</td>
</tr>
<tr>
<td>Ni\textsubscript{52.6}Mn\textsubscript{23.1}Ga\textsubscript{24.3}</td>
<td>300</td>
<td>5.0</td>
<td>(\sim 18.0)</td>
<td>39</td>
</tr>
<tr>
<td>MnAs</td>
<td>318</td>
<td>5.0</td>
<td>30.0</td>
<td>50</td>
</tr>
<tr>
<td>MnAs\textsubscript{0.9}Sb\textsubscript{0.1}</td>
<td>(\sim 286)</td>
<td>5.0</td>
<td>(\sim 30)</td>
<td>56</td>
</tr>
<tr>
<td>MnFeP\textsubscript{0.45}As\textsubscript{0.55}</td>
<td>300</td>
<td>5.0</td>
<td>18.0</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.5</td>
<td>(\sim 3.8)</td>
<td></td>
</tr>
</tbody>
</table>
In 1950, Jonker and Van Santen [101] were the first to synthesize the distorted perovskite-type structure of manganites (or the so-called manganese oxides) whose general formula is \( R_{1-x}M_xMnO_3 \), where \( R \) stands for trivalent rare-earth elements such as La, Pr, Nd, Sm, Eu, Gd, Ho, Tb, Y, etc., and \( M \) stands for divalent alkaline earth ions such as Sr, Ca, Ba, and Pb, or for Na\(^{1+}\), K\(^{1+}\), Ag\(^{1+}\), etc. The (\( R, M \)) site (i.e., the so-called perovskite A-site) can be in most cases formed from a homogeneous solid solution. In general, the conventional solid-state reaction method has been used to synthesize polycrystalline manganite materials. Stoichiometric samples are usually pre-sintered in the temperature range of 700–900°C for 10–20 h, followed by grinding into compound powders. The compound powders are then pressed into pellets and sintered at 900–1300°C for 15–30 h to give the finished samples. The sol–gel method has recently been used to synthesize such ceramic materials. Large magnetic entropy change has been found in the perovskite manganese oxides in recent years, so that these materials have been attracting more and more attention. The main advantages of this series of compounds over Gd and GdSiGe alloys are low cost, good chemical stability, and small coercive force, as well as large electrical resistivity. Their Curie temperature also can be easily tuned to the needed range by introducing some kinds of metal additions, which means that they are strongly doping-dependent. So, these materials may be good candidates for MR at room temperature. However, \(|\Delta S_M|\) will decrease significantly with increased doping level, lowering their practicability. For instance, \(|\Delta S_M|\) of La\(_{0.8}\)Ca\(_{0.2}\)MnO\(_3\) [102] with 1.5 T magnetic field change reaches 5.5 J kg\(^{-1}\)K\(^{-1}\), about 1.5 times that of Gd, but its Curie temperature is only 230 K. After adjusting the Ca ratio to
La$_{0.6}$Ca$_{0.4}$MnO$_3$, the Curie temperature increases to 263 K, but $|\Delta S_M|$ decreases to 70% of the Gd value at 3.0 T [103]. On improving the Curie temperature by adding Sr and Pb, the Curie temperatures reach 327 and 296 K, respectively, but $|\Delta S_M|$ decreases significantly. In addition, the heat transfer behavior of these compounds is inadequate because they are oxides.

2.1.9.1.1 (La$_{1-x}$M$_x$)MnO$_3$ group where M = Ca, Sr, Ba, Cd, and Pb

2.1.9.1.1 (La$_{1-x}$Ca$_x$)MnO$_3$

The MCE of the (La$_{1-x}$Ca$_x$)MnO$_3$ phases has been extensively studied, and this is probably the most thoroughly investigated manganite family. Morelli et al. [104] first reported the MCEs of (La$_{1-x}$M$_x$)MnO$_3$ (M = Ca, Sr, Ba) manganite films. However, the obtained $|\Delta S_M|$ values were not very large, except that the MCE peak temperature could be tuned in the temperature range of 250–350 K by varying the doping concentration. More interestingly, Guo et al. [102,105] found large MCEs in (La$_{1-x}$Ca$_x$)MnO$_3$ polycrystalline samples with $0.20 \leq x \leq 0.33$. It was shown that, for $\Delta H = 1.5$ T, the $|\Delta S_M|$ reached a maximum of about 5.5 J kg$^{-1}$K$^{-1}$ at 230 K, 4.7 J kg$^{-1}$K$^{-1}$ at 224 K, and 4.3 J kg$^{-1}$K$^{-1}$ at 260 K, for the x = 0.2, 0.25, and 0.33 compositions, respectively [102]. These values are larger than that of Gd, $\Delta S_M = 4.2$ J kg$^{-1}$K$^{-1}$, for the same field change of 1.5 T [106]. In contrast, Zhang et al. [107] found a smaller value of $|\Delta S_M|$ of 0.6 J kg$^{-1}$K$^{-1}$ for $\Delta H = 1$ T and a wider breadth of the MCE peak, $\delta T_{FWHM} = 62$ K, in La$_{0.67}$Ca$_{0.33}$MnO$_3$ (x = 0.33) than what Guo et al. [102] reported. This discrepancy could arise from the differences in the sample processing routes and/or from the different chemical composition. On the other hand,
Ulyanov et al. [108] found a larger value of $\Delta S_M$ of 5.04 and 6.25 J kg$^{-1}$ K$^{-1}$ for $\Delta H = 0.5$ and 1 T, respectively. The effect of hydrostatic pressure on the Curie temperature, the critical exponents, and the entropy change in $\text{La}_0.7\text{Ca}_0.3\text{MnO}_3$ were determined by Szymczak et al. [109], and they showed that the applied pressure itself can be used to change the entropy of a solid in a significant way, without the need for magnetic variation. The obtained results suggest that the combined effects of magnetic field and applied hydrostatic pressure on the caloric properties of manganites are very promising for refrigerators. In fact, $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ was found to show the largest MCE among the compositions investigated [110-112]. Lin et al. [112] measured the MCE of $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ and found a $\Delta T_{ad}$ of 2.4 K for $\Delta H = 2.02$ T. This value of $\Delta T_{ad}$ is smaller than that of Gd. It was suggested that the large magnetic entropy change was produced by the abrupt jump in magnetization that is associated with a first-order magnetic phase transition [110,111]. Note that, while the MCE decreased significantly, the MCE transition became more broadened when the material transformed from a first-order phase magnetic transition to a second-order one, which is beneficial for MR [113]. MCEs were also reported in several deficient manganites [114-119]. Biswas et al. [114] reporteded that some recent experimental studies do not show any antiferromagnetic transition in some cases where the manganite particle size is reduced to the nanometer scale. In complete contrast to these cases, they have observed the signature of an antiferromagnetic transition in the magnetocaloric properties of nanocrystalline $\text{La}_{0.125}\text{Ca}_{0.875}\text{MnO}_3$, with average particle sizes of 70 and 60 nm, that is similar to what occurs in its polycrystalline bulk form. This system exhibits an inverse magnetocaloric effect in its polycrystalline and nanocrystalline forms. An extra ferromagnetic phase is stabilized at low temperature for the sample with particle size of ~60 nm. Xu et al. [115]
showed that the La$_{0.54}$Ca$_{0.32}$MnO$_{3-\delta}$ deficient manganite had a large $|\Delta S_M|$ of 2.9 J kg$^{-1}$K$^{-1}$ for $\Delta H = 0.9$ T. Interestingly, the Curie temperature of this sample is $\sim 272$ K, about 10 K higher than that of the La$_{0.67}$Ca$_{0.33}$MnO$_3$ compound. This indicates that La$_{0.54}$Ca$_{0.32}$MnO$_{3-\delta}$ compound could be used as active magnetic refrigerants in sub-room-temperature magnetic refrigerators. In another investigation, Hueso et al. [116] revealed the possibility of tuning the MCE peak temperature without suppressing the large MCE values of La$_{0.67}$Ca$_{0.33}$MnO$_{3-\delta}$ nanoparticles synthesized by sol–gel techniques. It should be, however, noted that the magnitude of $\Delta S_M$ was found to be inversely proportional to the grain size. Phan et al. [117,118] also investigated the magnetic and magnetocaloric properties of (La$_{1-x}$)$_{0.8}$Ca$_{0.2}$MnO$_3$ (x = 0.05, 0.10, 0.20, and 0.30) with deficient La-site vacancies. It is interesting that the increase in La-deficiency favoured not only the MCE but also lifted the Curie temperature up to higher values, which is beneficial for MR at various temperatures. Recently, Hou et al. [119] also investigated the MCEs of La$_{0.67-x}$Ca$_{0.33}$MnO$_3$ (x = 0, 0.02, 0.06, and 0.1) deficient samples. The largest $\Delta S_M$ value was obtained to be 2.78 J kg$^{-1}$K$^{-1}$ at 277 K for $\Delta H = 1$ T for the x = 0.02 sample, which is good for sub-room-temperature MR.

2.1.9.1.2 (La$_{1-x}$Sr$_x$)MnO$_3$

In order to tailor MCEs in the room-temperature range, several efforts were made to explore the MCEs of (La$_{1-x}$Sr$_x$)MnO$_3$ manganites. Szewczyk et al. [120] first reported the MCE of a La$_{0.845}$Sr$_{0.155}$MnO$_3$ polycrystalline manganite, which underwent a magnetic phase transition at 234 K. The $|\Delta S_M|$ and $\Delta T_{ad}$ reached, respectively, 6.6 J kg$^{-1}$K$^{-1}$ and 3.3 K for $\Delta H = 7$ T. Later on, these authors [121] measured
systematically the MCEs of \((\text{La}_{1-x}\text{Sr}_x)\text{MnO}_3\) (\(x = 0.120, 0.135, 0.155, 0.185,\) and \(0.200\)) manganites. It was shown that the MCE increased with increasing Sr doping, except for the \(x = 0.12\) composition. The \(\Delta T_{ad}\) reached the highest value of 4.15 K for \(\Delta H = 7\ T\) for the \(x = 0.20\) composition \([121]\). In an analogous manner, Demin et al. \([122]\) also found that the MCE increased in \((\text{La}_{1-x}\text{Sr}_x)\text{MnO}_3\) \((0.1 < x < 0.3)\) single crystals with Sr addition. For \(\Delta H = 0.82\ T\), the obtained \(\Delta T_{ad}\) values were 0.2 K at 175 K for \(x = 0.1\), 0.37 K at 180 K for \(x = 0.125\), 0.7 K at 160 K for \(x = 0.175\), and 0.78 K at 346 K for \(x = 0.3\). Mira et al. \([111]\) found a \(|\Delta S_M|\) of 1.5 J kg\(^{-1}\)K\(^{-1}\) at 370 K for \(\Delta T_{ad} = 1\ T\) in a \(\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3\) polycrystalline sample. This result is quite similar to that of Xu et al. \([123]\). Most interestingly, a large \(|\Delta S_M|\) value of 2.12 J kg\(^{-1}\)K\(^{-1}\) at 305 K for \(\Delta H = 1\ T\) was reported by Phan et al. \([124]\) in \(\text{La}_{0.63}\text{Sr}_{0.35}\text{MnO}_3\). Later on, Pekala et al. \([125]\) measured the MCE of \(\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3\) that was synthesized by the carbonate precursor method. They reported a \(|\Delta S_M|\) value of 1.7 J kg\(^{-1}\)K\(^{-1}\) at 275 K for \(\Delta H = 2\ T\). After that, the same authors \([126]\) measured the MCE in nanosize and polycrystalline forms of \(\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3\) that were prepared by the sol-gel process and showed that the Curie temperature were about 295 and 301 K, respectively. The \(|\Delta S_M|\) values are about 0.5 and 2.2 J kg\(^{-1}\)K\(^{-1}\) for \(\Delta H = 2\ T\). In 2010, Pakela et al. \([127]\) again measured the same manganite prepared by the carbonate precipitation route and showed that the \(|\Delta S_M|\) value was 2.0 J kg\(^{-1}\)K\(^{-1}\) at 331 K for \(\Delta H = 2\ T\). This material has the potential for room temperature MR.

2.1.9.1.3 \((\text{La}_{1-x}\text{Ba}_x)\text{MnO}_3\)

The MCE properties of \(\text{La}_{1-x}\text{Ba}_x\text{MnO}_3\) have been reported by Phan et al., Zhong et al., and Xu et al. \([123, 128-129]\). The MCE of a \(\text{La}_{0.7}\text{Ba}_{0.3}\text{MnO}_3\) polycrystalline
manganite was first measured by Phan et al. [128], and they found a $|\Delta S_M|$ of 1.6 J kg$^{-1}$ K$^{-1}$ at 336 K for $\Delta H = 1$ T. Zhong et al. (2003), [129], studied the effects of oxygen stoichiometry on the magnetic and magnetocaloric properties of $\text{La}_{2/3}\text{Ba}_{1/3}\text{MnO}_3-\delta$ ($\delta = 0, 0.02, 0.05, 0.08,$ and 0.1) samples. They observed a considerable reduction of the MCE in the samples with oxygen deficiency. It is interesting to note that the $\text{La}_{2/3}\text{Ba}_{1/3}\text{MnO}_3-\delta$ ($\delta = 0.0)$ sample exhibited a large $|\Delta S_M|$ of 2.7 J kg$^{-1}$ K$^{-1}$ at 350 K for $\Delta H = 1$ T [129]. This result is quite different from that reported by Xu et al. [123] for the $\text{La}_{0.67}\text{Ba}_{0.33}\text{MnO}_3$ composition. This discrepancy could be caused by the differences in the sample preparation and the chemical composition [123,129]. Recently Koubaa et al. [130] studied the MCE of $\text{La}_{0.65}\text{Ba}_{0.3}\text{M}_0.05\text{MnO}_3$ ($\text{M} = \text{Na}, \text{Ag}, \text{K}$) and showed that the maximum $|\Delta S_M|$ values were 2.65, 2.82, and 2.66 J kg$^{-1}$ K$^{-1}$ for $\text{M} = \text{Na}, \text{Ag},$ and $\text{K}$, at 310, 300, and 290 K, respectively. Dhahri et al. [131] measured the MCE of $\text{La}_{0.7-x}\text{Eu}_x\text{Ba}_{0.3}\text{MnO}_3$ ($x = 0.05, 0.1,$ and 0.15) and showed that $x = 0.15$ had the highest MCE at 298 K, with a $|\Delta S_M|$ of about 2.3 J kg$^{-1}$ K$^{-1}$ for a 1 T field. In general, $\text{La}_{2/3}\text{Ba}_{1/3}\text{MnO}_3$ material is suitable for room-temperature MR.

### 2.1.9.1.4 (La$_{1-x}$Pb$_x$)MnO$_3$

Several efforts were made to explore the MCEs of (La$_{1-x}$Pb$_x$)MnO$_3$ manganites. Chau et al. [132] investigated the magnetocaloric properties of La$_{1-x}$Pb$_x$MnO$_3$ ($x = 0.1, 0.2, 0.3, 0.4,$ and 0.5) manganites and observed that the $|\Delta S_M|$ increased with increasing Pb concentration up to $x = 0.3$ and then decreased for higher Pb-doping levels. The largest $|\Delta S_M|$ was 1.53 J kg$^{-1}$ K$^{-1}$ at 358 K for $\Delta H = 1.35$ T for $\text{La}_{0.7}\text{Pb}_{0.3}\text{MnO}_3$. In addition, Min et al. [133] measured both $\Delta H$ and $\Delta T_{ad}$ of La$_{1-x}$Pb$_x$MnO$_3$ ($x = 0.1, 0.2,$
and 0.3) samples and showed that the largest $|\Delta S_M|$ value was obtained for the $x = 0.2$ composition. However, for $\Delta H = 1.5$ T, $\Delta T_{ad}$ was obtained to be about 0.68 and 1 K for $x = 0.2$ and 0.3 at 292 and 349 K, respectively. Later, Tozri et al. [134] measured the MCEs of La$_{0.8}$Pb$_{0.1}$MnO$_3$ and La$_{0.8}$Pb$_{0.1}$Na$_{0.1}$MnO$_3$, and showed that $|\Delta S_M|$ values were considerably lower than for the previously discussed samples (0.43 and 0.68 J kg$^{-1}$K$^{-1}$ at 201 and 247 K for $\Delta H = 1$ T). It is clear that, although the $|\Delta S_M|$ and $\Delta T_{ad}$ could be obtainable in the room-temperature range, these values were quite small and therefore not desirable for room-temperature AMR.

2.1.9.2. (La$_{1-x}$M$_x$)MnO$_3$ group where M = Na, K, and Ag

In the mean-time, many studies were completed on compounds from the (La$_{1-x}$M$_x$)MnO$_3$ group, where M = Na, K, and Ag. First, Zhong et al. [135-137] showed that the MCE peak temperature could be tuned in the temperature range of 195–334 K for La$_{1-x}$Na$_x$MnO$_3$ compounds and in the temperature range of 230–334 K for La$_{1-x}$K$_x$MnO$_3$ compounds. The maximum $|\Delta S_M|$ of La$_{1-x}$Na$_x$MnO$_3$ [135] for $\Delta H = 1$ T is 1.32, 1.53, 2.11, and 1.96 J kg$^{-1}$K$^{-1}$ for $x = 0.075$, 0.10, 0.165, and 0.20, respectively. Das et al. [138] later studied the MCEs of La$_{1-x}$K$_x$MnO$_3$ ($x = 0.05$, 0.1, 0.15) prepared by the pyrophoric method. They showed that potassium addition in lanthanum manganite enhances the Curie temperature of the system from 264 K ($x = 0.05$) to 310 K ($x = 0.15$) and that La$_{0.85}$K$_{0.15}$MnO$_3$ shows the largest value of $|\Delta S_M|$ (3 J kg$^{-1}$K$^{-1}$ at 310 K for application of a 1 T field). After that in 2011, Juan et al. [139] studied the relationship between the magnetocaloric properties and the calcination temperature of La$_{1-x}$K$_x$MnO$_3$ nanoparticles and showed that for the La$_{0.85}$K$_{0.15}$MnO$_3$ sample the maximum $|\Delta S_M|$ for samples calcined at 600°C, 800°C,
and 1000°C are 2.02, 3.06, and 3.56 J/kg K at 274 K for field change of 2 T, respectively. Tang et al. [140] found the large MCEs in La$_{1-x}$Ag$_x$MnO$_3$ ($0 \leq x \leq 0.3$) manganites. They showed that for $\Delta H = 1$ T, $|\Delta S_M|$ reached a maximum of 3.4 J kg$^{-1}$ K$^{-1}$ for La$_{0.8}$Ag$_{0.2}$MnO$_3$; this value is obviously larger than that observed in Gd. By varying Ag the concentration of La$_{1-x}$Ag$_x$MnO$_3$, Hien et al. [141] revealed that the MCE peak temperature could be tuned in the room-temperature range and that the $|\Delta S_M|$ value was the highest for the $x = 0.22$ composition. Gamzatov et al. [142] investigated the MCEs of La$_{0.9}$Ag$_{0.1}$MnO$_3$, La$_{0.8}$Ag$_{0.2}$MnO$_3$, and La$_{0.8}$Ag$_{0.15}$MnO$_3$ manganites. It was shown that, for $\Delta H = 2.6$ T, the $|\Delta S_M|$ reached 2.8 J kg$^{-1}$ K$^{-1}$ at 270 K for the La$_{0.8}$Ag$_{0.15}$MnO$_3$ sample when it was sintered at 1373 K and $P_{O_2} = 1$ bar. However, when a sample of the same composition was sintered at a higher partial pressure of oxygen ($P_{O_2} = 5$ bar), it showed lower MCE with higher Curie temperature ($T = 310$ K). This indicates that La$_{1-x}$Ag$_x$MnO$_3$ ($x = 0.2, 0.22$) materials have the potential for room temperature MR.

2.1.9.3. (La–Ca–M)MnO$_3$ where $M =$ Sr, Ba, Pb, K, Na, and Ag

La$_{1-x}$Ca$_x$MnO$_3$ phases [102, 104-105, 107, 110-113, 115-119] exhibit the largest MCEs among the existing manganites, but their Curie temperatures are far below room temperature, which probably limits the usage of La$_{1-x}$Ca$_x$MnO$_3$ materials for AMR in the room-temperature range. In this context, substitution of Ca by other elements, such as Sr, Ba, Pb, K, Na, and Ag could be of significant importance, because this could allow increasing $T_C$ while still retaining relatively large MCE values. Phan et al. [113,143] reported the room-temperature large MCEs of La$_{0.7}$Ca$_{0.3-x}$Sr$_x$MnO$_3$ ($x = 0.05$, 0.10, 0.20, and 0.25) single crystals. For $\Delta H = 5$ T,
the $|\Delta S_M|$ reached a maximum value of 10.5 J kg$^{-1}$K$^{-1}$ at 275 K for the $x = 0.05$ composition, which is larger than that of Gd, with $|\Delta S_M| = 10.2$ J kg$^{-1}$K$^{-1}$ at 294 K. Therefore, these single crystals are attractive candidate materials for room-temperature AMR. For the case of La$_{2/3}$(Ca$_{1-x}$Sr$_x$)$_{1/3}$MnO$_3$ ($x = 0, 0.05, 0.15, 0.25, 0.50, 0.75, and 1$) polycrystalline samples, a drop in the MCE value was observed as the Sr-substitution was increased [111]. Sun et al. [144] measured the MCE of La$_{0.7}$Ca$_{0.2}$Sr$_{0.1}$MnO$_3$ and showed that the $|\Delta S_M|$ was 2.85 J kg$^{-1}$K$^{-1}$ at 315 K for application of a 2 T field. Again, Li et al. [145] measured the $|\Delta S_M|$ of La$_{0.5}$Ca$_{0.3}$Sr$_{0.2}$MnO$_3$ and found it to be 1.52 J kg$^{-1}$K$^{-1}$ at 317 K for $\Delta H = 2$ T. In order to elucidate the effect of lattice structure on the MCE, Kim et al [146] studied $\Delta S_M$ in La$_{0.7}$Ca$_{0.3-x}$Sr$_x$MnO$_3$ ($x = 0.120, 0.135, and 0.150$) ferromagnetics. The samples with $x = 0.120$ and 0.150 showed the usual M-T behavior with $T_C$ of 300 and 323 K, respectively. The composition with $x = 0.135$ displayed a two-step dependence, with inflection points at 309 and 320 K, which correspond to the $T_C$ values of orthorhombic and rhombohedral phases, respectively. Moreover, the maximum values of $|\Delta S_M|$ are 1.87, 1.72, and 1.7 J kg$^{-1}$K$^{-1}$ for the samples with $x = 0.120, 0.135, and 0.150$, respectively. When substituting Ba partially for Ca, Phan et al. [128] found large magnetic entropy changes above 300 K in La$_{0.7}$Ca$_{0.3-x}$Ba$_x$MnO$_3$ ($x = 0.12, 0.24, and 0.3$) compounds. It was found that the $|\Delta S_M|$ decreased with increasing Ba-doping level. For $\Delta H = 1$ T, the $|\Delta S_M|$ was 1.85 J kg$^{-1}$K$^{-1}$ at 298 K for $x = 0.12, 1.72$ J kg$^{-1}$K$^{-1}$ at 320 K for $x = 0.24, and 1.6$ J kg$^{-1}$K$^{-1}$ at 336 K for $x = 0.3$. These materials are suitable for room-temperature MR. Sun et al. [147] investigated the MCE of La$_{2/3}$(Ca,Pb)$_{1/3}$MnO$_3$, which underwent a transition from paramagnetic insulator to ferromagnetic metal, at around 290 K. They found that $|\Delta S_M| = 7.5$ J kg$^{-1}$K$^{-1}$ and $\Delta T_{ad} = 5.6$ K for $\Delta H = 7$ T. This $|\Delta S_M|$ value is smaller than that of
La$_{2/3}$Ca$_{1/3}$MnO$_3$ for the same magnetic field change [106,146]. More interestingly, Phan et al. [148] investigated the MCEs of La$_{0.6}$Ca$_{0.3}$Pb$_{0.1}$MnO$_3$, La$_{0.7}$Ca$_{0.2}$Pb$_{0.1}$MnO$_3$, and La$_{0.7}$Ca$_{0.1}$Pb$_{0.2}$MnO$_3$ samples and found the largest $|\Delta S_M|$ of 3.72 J kg$^{-1}$ K$^{-1}$ at 337 K for $\Delta H = 1.35$ T for the third sample. Hanh et al. [149] also measured the MCE of La$_{0.7}$Ca$_{0.3-x}$Pb$_x$MnO$_3$ ($x = 0.05, 0.01, 0.15,$ and 0.2). For the first and fourth samples they obtained the same 3.72 J kg$^{-1}$K$^{-1}$, $|\Delta S_M|$ value for application of 1.35 T field at 270 and 337 K, respectively. Polycrystalline perovskite samples of La$_{0.7}$Ca$_{0.3-x}$K$_x$MnO$_3$ ($x = 0.05, 0.075,$ and 0.01) were investigated by Bejar et al. [150]. They found the largest $|\Delta S_M|$ of 3.95, 3.75, and 3.49 J kg$^{-1}$ K$^{-1}$ at 270, 281, and 272 K, respectively, for $\Delta H = 2$ T. Koubaa et al. [151] again measured the MCEs of La$_{0.65}$Ca$_{0.35-x}$K$_x$MnO$_3$ and found the largest $|\Delta S_M|$ of 3.18, 4.16, and 7.09 J kg$^{-1}$K$^{-1}$ at 310 K for field changes of 2, 3, and 5 T, respectively. These values are less than the previous ones. Koubaa et al. [152] investigated the MCEs of La$_{0.65}$Ca$_{0.35-x}$Na$_x$MnO$_3$ and showed that with increasing Na content, the Curie temperature increases from 248 K for $x = 0$ to 315 K for $x = 0.2$. The highest value of $|\Delta S_M|$ reaches 3 and 5.8 J kg$^{-1}$K$^{-1}$ for a magnetic field change of 5 T for $x = 0.05$ and 0.2, respectively. Mehri et al. [153] also investigated MCEs of La$_{0.5}$Ca$_{0.5-x}$Na$_x$MnO$_3$ and found that with increasing Na content, the Curie temperature decreases, but $|\Delta S_M|$ increases, which is still lower than for the previous one. The same authors [154] also measured the MCEs of La$_{0.5}$Ca$_{0.5-x}$Ag$_x$MnO$_3$ and found the same characteristics as for the Na doped compounds. It is well known that any substitution of M (M = Sr, Ba, Pb, K, Na, and Ag) for Ca in (La–Ca–M)MnO$_3$ manganites usually leads to an increase in $T_C$, but to a reduction in the MCE. However, a proper combination of both the MCE and the Curie temperature can
produce appropriate magnetic refrigerants for room-temperature magnetic refrigerators.

2.1.9.4. \((\text{La–Sr–M})\text{MnO}_3\) where \(M = \text{Ba}, \text{Ag}, \text{and K}\)

Phan et al. observed the large \(|\Delta S_M|\) of 2.26 J kg\(^{-1}\)K\(^{-1}\) at 354 K for \(\Delta H = 1\) T for \(\text{La}_{0.6}\text{Sr}_{0.2}\text{Ba}_{0.2}\text{MnO}_3\) [124]. Koubaa et al [155, 156] also measured the \(\Delta S_M\) of \(\text{La}_{0.7}\text{Sr}_{0.3-x}\text{Ag}_x\text{MnO}_3\) and \(\text{La}_{0.7}\text{Sr}_{0.3-x}\text{K}_x\text{MnO}_3\) \((x = 0.05, 0.1, 0.15\) and 0.2\) and showed that with increasing Ag content from 0 to 0.2 the Curie temperature decreases from 365 K to 286 K. The maximum \(|\Delta S_M|\) values were obtained for \(\text{La}_{0.7}\text{Sr}_{0.2}\text{Ag}_0.1\text{MnO}_3\), and these are 0.9 and 4.5 J kg\(^{-1}\)K\(^{-1}\) for 1 and 7 T field changes. The Curie temperature for this compound also decreases from 365 K for \(x = 0\) to 328 K for \(x = 0.2\). The maximum \(|\Delta S_M|\) of \(\text{La}_{0.7}\text{Sr}_{0.3-x}\text{K}_x\text{MnO}_3\) for \(x = 0.05\) and 0.15 is found to be 1.37 and 1.2 J kg\(^{-1}\)K\(^{-1}\), respectively, under a magnetic field change of 1 T. Such materials are promising for room temperature AMR.

2.1.9.5 \((\text{La–M–Ca})\text{MnO}_3\) group where \(M = \text{Nd, Bi, Tb, Dy, Gd, Ce, and Y}\)

Several studies have been conducted on this group of materials and have shown that MCE could be improved in \((\text{La–M–Ca})\text{MnO}_3\) manganites with substitution for La by other elements such as \(M = \text{Nd, Bi, Tb, Gd, and Ce}\). Wang et al. [157] investigated the MCEs of \(\text{La}_{0.7-x}\text{Nd}_x\text{Ca}_{0.3}\text{MnO}_3\) \((x = 0, 0.05, 0.1, 0.15\) and 0.20\) compounds with Nd substitution for La. The largest \(|\Delta S_M|\) value was obtained to be 2.31 J kg\(^{-1}\)K\(^{-1}\) at 213 K for \(\Delta H = 1\) T for the \(x = 0.2\) composition. The Nd addition in the precursor \(\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3\) sample shifted the MCE peak towards lower temperatures, which are
well below room temperature. This perhaps limits the usage of La_{0.7-x}Nd_xCa_{0.3}MnO_3 materials for the purpose of room-temperature MR, although these materials are good for MR in the temperature range of 210-270 K. The substitution of Bi (5 at \%) for La in La_{0.67}Ca_{0.33}MnO_3 was found to significantly improve the MCE, as was investigated by Gencer et al. [158]. They showed that for ΔH = 1 T, the La_{0.62}Bi_{0.05}Ca_{0.33}MnO_3 (x = 0.05) sample exhibited a large \(|\Delta S_M|\) of 3.5 J kg\(^{-1}\) K\(^{-1}\) at 248 K. This value of \(|\Delta S_M|\) is slightly larger than that of the precursor sample of La_{0.67}Ca_{0.33}MnO_3. In this case, it should be noted that though the MCE was enhanced, the remarkable drop in \(T_C\) could make it difficult to use in room-temperature magnetic refrigerators. Chen et al. (2003) [159] reported the magnetocaloric properties of (La_{1-x}R_x)_{2/3}Ca_{1/3}MnO_3 (R = Gd, Dy, Tb, x = 0–0.2) and La_{0.7-x}Ce_{x}Ca_{0.3}MnO_3 (x = 0–0.3) compounds, and showed that partial substitution of La by rare-earth elements caused a decrease in \(T_C\). The highest \(|\Delta S_M|\) values were obtained for all x = 0.1 rare-earth dopants. The maximum magnetic entropy change \(|\Delta S_M|\) for a 1.5 T magnetic field change is 6.06 J kg\(^{-1}\) K\(^{-1}\) for (La_{0.9}Dy_{0.1})_{2/3}Ca_{1/3}MnO_3 around its Curie temperature of 176 K. In another work, Zhang et al. [160] revealed that the partial replacement of La by Y in the La_{0.60}Y_{0.07}Ca_{0.33}MnO_5 sample resulted in a decrease in both the MCE and the Curie temperature. Its value of \(|\Delta S_M|\) is 1.46 J kg\(^{-1}\) K\(^{-1}\) at 230 K for 3 T field change.

2.1.9.6 (La–M) (Mn–M')O_3 group where M = (Ca, Li, Sr) and M' = (Ni, Cu, Co, Ti, Al, Fe, and Cr)

Choudhury et al. investigated [161] the influence of Ni partial substitution for Mn on the MCE of La_{0.7}Sr_{0.3}Mn_{1-x}Ni_xO_3 (x = 0.01, 0.02, 0.03, and 0.05) manganites and
experimentally observed that for 1.35 T field change, the $|\Delta S_M|$ values were 2.67, 3.54, 3.15, and 2.33 J kg$^{-1}$ K$^{-1}$ for $x = 0.01, 0.02, 0.03,$ and $0.05,$ respectively. The $x = 0.02$ sample exhibited the highest $|\Delta S_M|$ of 3.54 J kg$^{-1}$K$^{-1}$ at 320 K, which is potentially useful for room temperature AMR. In a more detailed investigation, Phan et al. [162] studied the $|\Delta S_M|$ of La$_{0.7}$Sr$_{0.3}$Mn$_{1-x}$Ni$_x$O$_3$. The magnetic entropy changes reach values of 2.25, 5.20, 6.52, and 7.65 J kg$^{-1}$K$^{-1}$ for field changes of 1, 3, 5, and 7 T, respectively. The ($x = 0.02$) sample reached a value as high as 7.65 J kg$^{-1}$K$^{-1}$ at 350 K for a 7 T field change. The $\Delta S_M$ distribution of this material was much more uniform than that of Gd and of several other polycrystalline perovskite manganites which have desirable properties for an Ericson-cycle magnetic refrigerator. Chau et al. [163] investigated the influence of Cu partial substitution for Mn on the MCE of La$_{0.7}$Sr$_{0.3}$Mn$_{1-x}$Cu$_x$O$_3$ ($x = 0.05, 0.1$) manganites. They showed that, for $\Delta H = 1.35$ T, the $|\Delta S_M|$ reached values of 1.96 and 2.07 J kg$^{-1}$K$^{-1}$ for $x = 0.05$ and 0.1 compositions, respectively. Later on, Phan et al. [164] significantly improved the MCE of these samples by optimizing the annealing conditions. For 1 T field change, the maximum $|\Delta S_M|$ values of the Cu-doped samples were found to be 3.05 and 3.24 J kg$^{-1}$K$^{-1}$ at 345 and 347 K for $x = 0.05$ and 0.10, respectively, which are higher than for Gd (2.8 J/kgK at 294 K) [106]. These materials are promising for AMR above room temperature. In another work, the same authors [165] also found large magnetic entropy changes in La$_{0.845}$Sr$_{0.155}$Mn$_{1-x}$M$_x$O$_3$ ($M = \text{Cu, Co}$) manganites. However, the Curie temperatures of these samples were reduced well below room temperature, which is not desirable for room-temperature AMR. Bau et al. [166] also measured the MCE of La$_{0.7}$Sr$_{0.3}$Co$_{0.95}$Mn$_{0.05}$O$_3$ and showed that the maximum $|\Delta S_M|$ was 1.41 J kg$^{-1}$K$^{-1}$ at 191 K for 5 T field change.
Bohigas et al. (1998) [167] first showed that the MCE peak temperature could be tuned in the wide temperature range of 35–263 K by partially substituting Ti for Mn in the La$_{0.65}$Ca$_{0.35}$Ti$_{1-x}$Mn$_x$O$_3$ and La$_{0.5+x+y}$Li$_{0.5-3y}$Ti$_{1-3x}$Mn$_{3x}$O$_{3-y}$ systems. For the La$_{0.65}$Ca$_{0.35}$Mn$_{0.9}$Ti$_{0.1}$O$_3$ sample, $|\Delta S_M|$ reached value of 1.3 J kg$^{-1}$K$^{-1}$ at 103 K for a field change of 3 T. Sun et al. [168] found a decrease in both MCE and $T_C$ in La$_{0.67}$Sr$_{0.33}$Mn$_{1-x}$Cr$_x$O$_3$ (x = 0, 0.1) manganites with Cr partial substitution for Mn. For a 5 T field change, La$_{0.67}$Sr$_{0.33}$Mn$_{0.9}$Cr$_{0.1}$O$_3$ has the maximum $|\Delta S_M|$ of 5.0 J kg$^{-1}$K$^{-1}$ at 328 K. Magnetic entropy changes in and above the room-temperature region have been measured by Nam et al. [169] for La$_{0.7}$Sr$_{0.3}$Mn$_{1-x}$M$_x'O_3$ (M$'=\text{Al, Ti}$). The magnetocaloric effect becomes largest at $T_C$, which is tuned from 364.5 K for x= 0 to ~300 K by the substitution of Al or Ti for Mn, while the substitution of Al for Mn drastically reduces the maximum magnetic entropy change. Under a magnetic field change $\Delta H = 2$ T, $|\Delta S_M|$ of La$_{0.7}$Sr$_{0.3}$Mn$_{1-x}$Al$_x$O$_3$ decreases from 2.66 J kg$^{-1}$K$^{-1}$ for x = 0 to 1.18 J kg$^{-1}$K$^{-1}$ for x =0.1. While $T_C$ is largely suppressed, the magnetocaloric effect is only slightly affected by the Ti substitution. With $\Delta H = 2$ T, the La$_{0.7}$Sr$_{0.3}$Mn$_{0.95}$Ti$_{0.05}$O$_3$ sample exhibits $|\Delta S_M|$ = 2.44 J kg$^{-1}$K$^{-1}$. Barik et al. [170] studied the effects of Fe substitution on the magnetic and magnetocaloric properties of La$_{0.7}$Sr$_{0.3}$Mn$_{1-x}$Fe$_x$O$_3$ (x = 0.05, 0.07, 0.10, 0.15, and 0.20) over a wide temperature range (T = 10–400 K). It was shown that substitution by Fe gradually decreases the ferromagnetic Curie temperature $T_C$ up to x = 0.15 but a dramatic change occurs for x = 0.2. The magnetic entropy change $|\Delta S_M|$ was estimated from isothermal magnetization curves, and it decreases with increasing Fe content from 4.4 J kg$^{-1}$K$^{-1}$ at 343 K (x = 0.05) to 1.3 J/kg K at 105 K (x = 0.2), under $\Delta H = 5$ T. Kallet et al. [171] also studied the magnetocaloric effect in a series of single-phase polycrystalline samples of La$_{0.7}$Sr$_{0.3}$Mn$_{1-x}$Cr$_x$O$_3$ with nominal composition of x =
0.00, 0.20, 0.40, and 0.50. Near room temperature (280 K), the La$_{0.7}$Sr$_{0.3}$Mn$_{0.8}$Cr$_{0.2}$O$_3$ sample displayed a large value of maximum entropy change of 1.203 J kg$^{-1}$K$^{-1}$ under a modest magnetic field of 2 T.

2.1.9.7 (La–M–Sr)MnO$_3$ group where M = Er, Eu, Gd, and Ce

Amaral et al. [172] measured the MCEs of La$_{0.7-x}$Er$_x$Sr$_{0.3}$MnO$_3$ (x = 0.014, 0.035, 0.14, and 0.21) and La$_{0.7-x}$Eu$_x$Sr$_{0.3}$MnO$_3$ (x = 0.035, 0.14, and 0.21), and showed that $T_C$ is effectively reduced to near room temperature when La ions are replaced by Er or Eu ions, while $|\Delta S_M|$ remains constant in this process. The $|\Delta S_M|$ value for 1 T field change is about 1.6 J kg$^{-1}$K$^{-1}$. MCE in nanoparticle perovskite manganites of the type (La$_{0.67-x}$Gdx)Sr$_{0.33}$MnO$_3$ (x = 0.10, 0.15, 0.20) were studied by Juan et al. [173]. They have discovered that the Curie temperature ($T_C$) of the prepared samples was strongly dependent on Gd content. The Curie temperature of the samples are 358.4, 343.2, and 285.9 K for x = 0.1, 0.15, and 0.2, respectively. A large magnetocaloric effect close to $T_C$ has been observed with a maximum magneto-entropy change in all the samples, $|\Delta S_M|$, of 1.96 and 4.90 J kg$^{-1}$K$^{-1}$ for 2 and 5 T field change, respectively, for a x = 0.15. A large magnetic entropy change $|\Delta S_M|$ in Ce-doped La$_{0.7}$Sr$_{0.3}$MnO$_3$ material has been observed by Kallel et al. [174]. It was shown for (La$_{0.56}$Ce$_{0.14}$)Sr$_{0.3}$MnO$_3$ composition at the Curie temperature of 357 K, that the maxima of the magnetic entropy changes $\Delta S_M$ upon variations of the applied magnetic field of 1 and 5 T are about 1.55 and 4.78 J kg$^{-1}$K$^{-1}$, respectively.
2.1.9.8 \((\text{Nd}_{1-x}\text{M}_x)\text{MnO}_3\) group where \(\text{M} = \text{Ca and Sr}\)

The MCE of Nd\(_{0.5}\)Sr\(_{0.5}\)MnO\(_3\) was first observed by Sande et al. [175]. They observed a large \(|\Delta S_M|\) of 2.8 J kg\(^{-1}\)K\(^{-1}\) at the charge-ordering temperature of 155 K for 1 T field change. They also confirmed that the magnitude of \(\Delta S_M\) obtained around the first-order transition is about three times larger than that obtained around the second order one. Chen et al. [176] reported a larger MCE value at the same composition and showed that the \(|\Delta S_M|\) reached a value as high as 7.5 J kg\(^{-1}\)K\(^{-1}\) at 183 K for 1 T. This value of \(\Delta S_M\) is much larger than that of Gd. Later on, Si et al. [177] measured the MCE of Nd\(_{2/3}\)Sr\(_{1/3}\)MnO\(_3\) and found a \(|\Delta S_M|\) value of 3.25 J kg\(^{-1}\)K\(^{-1}\) with an applied field change of 1 T at the Curie temperature of 257.5 K, which equals that of Gd. In contrast to previous works [175,176], Chau et al. [178] reported a much smaller value of \(\Delta S_M\) of 1.9 J kg\(^{-1}\)K\(^{-1}\) at 155 K for 1.35 T field change in the same composition of Nd\(_{0.5}\)Sr\(_{0.5}\)MnO\(_3\). This discrepancy could arise from the different sample preparation methods. In fact, it should be noted that the change in magnetization with respect to temperature occurred much more sharply in the cases of Refs. [175,176] than in the case of Ref. [178], and this is the reason for the larger variation in the \(\Delta S_M\) [175,176]. The authors [178] also found a significant decrease in the MCE of Nd\(_{0.5}\)Sr\(_{0.5}\)Mn\(_{1-x}\)Cu\(_x\)O\(_3\) (\(x = 0.02, 0.1\)) manganites with Cu substitution for Mn. This could be understood from the fact that the charge-ordering behavior was drastically modified by Cu doping. In 2010, Fan et al. [179] measured the MCE of half-doped manganite Nd\(_{0.5}\)Ca\(_{0.25}\)Sr\(_{0.25}\)MnO\(_3\) and also found a significance decrease in MCE and the Curie temperature. They found \(|\Delta S_M|\) of 0.77 J kg\(^{-1}\)K\(^{-1}\) at 175 T for 1 T field change. The same authors [180] also measured the MCE of Nd\(_{0.6}\)La\(_{0.1}\)Sr\(_{0.3}\)MnO\(_3\) and observed \(|\Delta S_M|\) of 3.14 J kg\(^{-1}\)K\(^{-1}\) at 175 T for 1.5 T magnetic
field change. It should be noted that, although this charge-ordering manganite has large $|\Delta S_M|$ induced by only a low magnetic field change, this charge-ordering state is strongly dependent on doping and magnetic field [175-176, 178]. When an applied magnetic field is sufficiently high, the charge-ordered state will be melted and an insulator–metal transition is induced. In addition, even if the charge-order transition temperature of the material is tuned by doping, a sharp charge-ordering magnetic transition will be modified thereby, leading to a considerable reduction in the MCE [178]. Another disadvantage is that the FWHM of the MCE peak is only several K, accompanied by large thermal and field hysteresis, which is not beneficial for AMR.

2.1.9.9 (Pr$_{1-x}$M$_x$)MnO$_3$ group, (M = Ca, Sr, and Pb) and (Sm$_{1-x}$Sr$_x$)MnO$_3$

A studies were conducted on Pr$_{1-x}$M$_x$MnO$_3$ (M = Ca, Sr, and Pb). The MCEs of Pr$_{1-x}$Sr$_x$MnO$_3$ (x = 0.3, 0.4, and 0.5) polycrystalline manganites were investigated by Chen et al. [181], who found the largest $|\Delta S_M|$ of 7.1 J kg$^{-1}$K$^{-1}$ at 160 K with a 1 T field change for the x = 0.5 sample. This value of $|\Delta S_M|$ is much larger than that of Gd ($|\Delta S_M| = 2.8$ J kg$^{-1}$K$^{-1}$ for $\Delta H = 1$ T). Of these three compositions, only the Pr$_{0.5}$M$_{0.5}$MnO$_3$ phase exhibited charge ordering at the charge ordering temperature, $T_{CO} = 161$ K. Chen and Du [182] found that when Nd is substituted for Pr in (Pr$_{1-y}$Nd$_y$)$_{0.5}$Sr$_{0.5}$MnO$_3$ (y = 0, 0.3, 0.5, 0.7 and 1.0), $T_C$ and $T_{CO}$ are increased from 205 to 267 K for $T_C$ and from 161 to 183 K for $T_{CO}$, but $|\Delta S_M|$ seems to be approximately constant (6.5-8 J kg$^{-1}$K$^{-1}$) under a change of 1 T for the five samples. This exceeds the magnetic entropy change (3.1 J kg$^{-1}$K$^{-1}$) in Gd at 294 K by a factor of two under the same conditions. In another work, Gomes et al. [183] investigated the MCEs of Pr$_{1-x}$Ca$_x$MnO$_3$ (0.3 $\leq$ x $\leq$ 0.45) manganites and reported large positive
and negative changes of $|\Delta S_M|$. It was experimentally observed that $\text{Pr}_{0.68}\text{Ca}_{0.32}\text{MnO}_3$ exhibited, respectively, positive and negative $\Delta S_M$ of $24 \text{ J kg}^{-1}\text{K}^{-1}$ at 21.5 K and $27 \text{ J kg}^{-1}\text{K}^{-1}$ at 31 K for $\Delta H = 5 \text{ T}$. This material could be good for MR at low temperatures. In addition, these authors [184] studied the charge-ordering contribution to the magnetic entropy change of $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ ($0.2 \leq x \leq 0.95$) manganites. They suggested that the $\Delta S_M$ of $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ ($0.3 < x < 0.90$) charge-ordered manganites around the charge-ordering temperature was related to a negative contribution from the change in entropy due to spin ordering, $\Delta S_{\text{spin}}$, which was superimposed on a positive contribution due to the change in entropy due to charge-ordering, $\Delta S_{\text{CO}}$. After that, Phan et al. [185] found a large MCE in a single crystal of $\text{Pr}_{0.63}\text{Sr}_{0.37}\text{MnO}_3$. A $|\Delta S_M|$ of $8.52 \text{ J kg}^{-1}\text{K}^{-1}$ for a $5 \text{ T}$ field change was found to occur around 300 K, thereby allowing water to be used as a heat transfer fluid in the room-temperature MR regime. The large magnetic entropy change induced by a relatively low magnetic field change is beneficial for household application of active magnetic refrigerant materials. To evaluate the $\text{Pr}_{0.63}\text{Sr}_{0.37}\text{MnO}_3$ single crystal as a competitive candidate for commercial applications of room-temperature MR, $\text{Pr}_{1-x}\text{Pb}_x\text{MnO}_3$ ($0.1 \leq x \leq 0.5$) manganites were investigated by the same authors, Phan et al. [186]. It was shown that, for $1.35 \text{ T}$ field change, the $|\Delta S_M|$ reached values of 3.91, 3.68, and $3.34 \text{ J kg}^{-1}\text{K}^{-1}$ for the $x = 0.1$, 0.4, and 0.5 compositions, respectively. These values are larger than that of Gd ($3.32 \text{ J kg}^{-1}\text{K}^{-1}$) and were attained by a low applied magnetic field that can be generated by permanent magnets. Recently, Bingham et al. [187] measured the MCE of charge-ordered $\text{Pr}_{0.5}\text{M}_{0.5}\text{MnO}_3$. The system undergoes a paramagnetic to ferromagnetic transition at $T_C \sim 255 \text{ K}$, which is followed by a ferromagnetic charge-disordered to antiferromagnetic charge-ordered transition at $T_{\text{CO}} = 165 \text{ K}$. However, the $|\Delta S_M|$ ($7.5 \text{ J kg}^{-1}\text{K}^{-1}$) at $T_{\text{CO}}$ is about twice as large as that
63

(3.2 J kg\(^{-1}\)K\(^{-1}\)) at T\(_C\) for a 5 T field change. Sarkar et al. [188] investigated the MCE of Sm\(_{0.52}\)Sr\(_{0.48}\)MnO\(_3\) single crystal and found that a magnetic field change of only 1 T yields a change in the magnetic entropy of 5.9 J kg\(^{-1}\)K\(^{-1}\) at T\(_C\) = 125 K, which is higher than those observed in several other perovskite manganites and rare earth alloys of comparable T\(_C\). In another investigation, Rebello et al. [189] showed that for the Sm\(_{1-x}\)Sr\(_x\)MnO\(_3\) (x = 0.3-0.5) system, there are a magnetic-field-driven first-order metamagnetic transition in the paramagnetic state in the x = 0.4 and 0.5 compounds and a second-order transition in the x = 0.3 compound. The highest magnetic entropy of 1.41 J/molK at 125 K for a 5 T field change occurs for x = 0.4.

2.1.9.9 (La\(_{1-x}\)M\(_x\))\(_3\)Mn\(_2\)O\(_7\) group where M = Ca and K

Giant MCEs were first discovered by Zhou et al. and Zhu et al. [190, 191] in new two-layered manganites, La\(_{1.6}\)Ca\(_{1.4}\)Mn\(_2\)O\(_7\) prepared by the sol-gel method and La\(_{1.4}\)Ca\(_{1.6}\)Mn\(_2\)O\(_7\) prepared by the standard ceramic method. Zhou et al. [190] showed that, for ΔH = 1.5 T, the |ΔSM| of La\(_{1.6}\)Ca\(_{1.4}\)Mn\(_2\)O\(_7\) reached a maximum of 3.8 J kg\(^{-1}\)K\(^{-1}\) at 168 K, which is comparable to the performance of Gd. More interestingly, Zhu et al. [191] found a large |ΔSM| of 11.3 and 16.8 J kg\(^{-1}\)K\(^{-1}\) at 270 K for ΔH = 2 and 5 T, respectively in the La\(_{1.4}\)Ca\(_{1.6}\)Mn\(_2\)O\(_7\) compound. This value of |ΔSM| is much larger than that of Gd (~10.2 J kg\(^{-1}\)K\(^{-1}\)) and is close to that of Gd\(_8\)Si\(_2\)Ge\(_2\) (~18.4 J/kgK) or MnFeP\(_{0.45}\)As\(_{0.55}\) (~18 J kg\(^{-1}\)K\(^{-1}\)) for ΔH = 5 T. Another advantage is that the two-layered manganites have a broad FWHM of the MCE peak, resulting in high cooling capacity. In 2011, Tasarkuya et al. [192] investigated the effect of high temperature sintering on the structural and the magnetic properties of La\(_{1.4}\)Ca\(_{1.6}\)Mn\(_2\)O\(_7\) and found that as the sintering temperature increases from 1273 K to
1673 K, the Curie temperature increases from 225 to 268 K and the $|\Delta S_M|$ increases from 0.58 to 3.1 J kg$^{-1}$ K$^{-1}$ under an applied magnetic field change of 1 T. However, this value is very small compared to that observed in La$_{1.4}$Ca$_{1.6}$Mn$_2$O$_7$ [191]. The magnetocaloric effect in the bilayered Ruddlesden-Popper perovskites La$_{1.4}$(Sr$_{1-x}$Ba$_x$)$_{1.6}$Mn$_2$O$_7$ ($0 \leq x \leq 0.6$) prepared by sol-gel methods has been investigated by Cherif et al. [193]. They showed that the Curie temperature decreases from 161 K to 94 K with increasing Ba substitution. With increasing Ba concentration, an increase in the magnitude of the magnetic entropy is observed (1.95 to 2.84 J kg$^{-1}$K$^{-1}$) at $\Delta H = 2$ T. This value is also very small compared to that observed in La$_{1.4}$Ca$_{1.6}$Mn$_2$O$_7$ [191]. These materials could be ideal for sub room-temperature MR. MCE of the double layered manganites, La$_{1.4-x}$ R$_x$Ca$_{1.6}$Mn$_2$O$_7$, where R = Ho or Yb and x = 0 or 0.2, were investigated by Tetean et al. [194]. They showed that the Curie temperature decreases from 246 K (x = 0) to 211 K (x = 0.2) for R = Yb and 221 K (x = 0.2) for R = Ho. The maximum $|\Delta S_M|$ values are 2.85 J kg$^{-1}$K$^{-1}$ for the compound with x = 0, 2.1 J kg$^{-1}$K$^{-1}$ for the compound with Yb, and 1.87 J kg$^{-1}$K$^{-1}$ for the compound with Ho in 2 T magnetic field.
Fig. 2.4 The magnetic entropy change, $\Delta S_M$, is plotted against the Curie temperature ($T_C$) for $\Delta H = 5$ T for the potential magnetocaloric candidate materials for magnetic refrigeration in the sub-room and room-temperature range. The material compositions are MnAs$_{1-x}$Sbx ($x = 0, 0.1, 0.15, 0.25, 0.3$) [195], La(Fe$_{1-x}$Cox)$_{11.2}$Si$_{1.8}$ ($x = 0, 0.02, 0.07, 0.08$) [196], La$_{0.7}$Ca$_{0.3-x}$Sr$_x$MnO$_3$ ($x = 0.05, 0.10, 0.15, 0.25$) [113], Gd$_5$(Si$_x$Ge$_{1-x}$)$_4$ ($x = 0.43, 0.50, 0.515, 1$) [197], and MnFeP$_{1-x}$As$_x$ ($x = 0.45, 0.50, 0.55, 0.65$) [198].
<table>
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<th>Gd</th>
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<th>RMnO$_3$</th>
<th>LaFeSi</th>
<th>MnAs</th>
<th>FeMn</th>
<th>Ni$_2$M</th>
<th>PAs</th>
<th>nGa</th>
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<td>++</td>
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<td>0</td>
<td>-</td>
<td>-</td>
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<tr>
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<td>-</td>
<td>-</td>
<td>-</td>
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<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MCE, $\Delta S_M$</td>
<td>0</td>
<td>++</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MCE, $\Delta T_{ad}$</td>
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<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>?</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Refrigeration Capacity</td>
<td>0</td>
<td>+</td>
<td>?</td>
<td>+</td>
<td>?</td>
<td>+</td>
<td>?</td>
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<td>-</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>_</td>
<td>-</td>
<td>-</td>
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<tr>
<td>Time dependence of $\Delta T_{ad}$</td>
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<td>?</td>
<td>-</td>
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<td>?</td>
<td>?</td>
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</table>

Note: “a” represents zero for second order magnetic transition (SOMT) manganites; for the few first order magnetic transition (FOMT) manganites, the zero becomes a minus.
From the above discussion it should be noted that Gd, Gd-Si-Ge, La(Fe,M)\textsubscript{13} based compounds, and other compounds showing higher MCE with narrow applicable temperature region are all first order phase transition materials. Due to the first order transition, all of them show high magnetic and thermal hysteresis, which is not beneficial for MR application. So the connection between the MCE and the magnetic-phase transformation needs to be emphasized in the study of MCE materials. On the other hand, all these materials show a low Curie temperature, even though it can be tuned to room temperature by hydrogenation, although the stability of the hydrogen is questionable indeed. The preparation route and time, as well as the material cost, are all important factors for practical application, and these are not suitable for those materials. On the other hand it can be seen from the literature review that manganite magnetocaloric materials can be promising candidates for AMR due to large MCEs that are comparable to those of Gd and other magnetic refrigerant candidate materials. One disadvantage of typical manganite material is that the adiabatic temperature change is not very large, due to the relatively high heat capacity. This may somewhat limit such manganites for AMR technology. However, this task is very likely to be overcome because of the current rapid development of magnetic cooling technology. It is interesting to note that, when compared with Gd and other candidate materials, such perovskite manganites are more convenient to prepare and exhibit higher chemical stability, as well as the higher resistivity that is favourable for lowering eddy current heating. In addition, the manganites feature much smaller thermal and magnetic hysteresis than any rare earth and 3d-transition metal based alloys. The Curie temperature can be easily tuned in the wide temperature range of 100-375 K. In addition, the manganite materials are the cheapest and the most available among the existing magnetic refrigerants.
These superior features make them more promising for future technology. Considering all of these above-mentioned points relating to the discoveries of better manganite materials for practical application of MR, this thesis is mainly devoted to an investigation of manganite materials and also an alloy compound.
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CHAPTER 3  THEORETICAL ASPECTS AND EXPERIMENTAL

Theoretical Aspects

Certain magnetic materials are known to exhibit significant temperature changes during magnetization and demagnetization. That is to say, changing the applied field changes the temperature of an insulated piece of magnetic material. This phenomenon is called the magnetic heat quantity effect. In a physical sense, the degree of freedom of magnetic spins inside the magnetic material is changed by the magnetic field. This in turn changes the entropy of a magnetic spin system. The entropy change instantaneously transfers energy between the electron system and the lattice system. This changes the temperature of the magnetic material. Magnetic refrigeration utilizes the magnetic heat quantity effect to perform refrigerating operations. The magnetocaloric effect (MCE) of a magnetic material is associated with the magnetic-entropy change of the material. According to the thermodynamics, the MCE is proportional to $\delta M/\delta T$ at constant field and inversely proportional to the field dependence of the specific heat $c_p (T, B)$. In the temperature region of a magnetic phase transition, the magnetization changes rapidly and, therefore, a large MCE is expected in this region [1, 2]. However the critical behaviour of the physical quantities in the phase transition region is so complicated that there is no unified theory. Therefore, the adiabatic temperature change $\Delta T_{ad}$ of a given material can only be determined by using experimental methods. Achieving an understanding of magnetic phase transitions and the evaluation of the entropy change associated with the magnetic phase transitions, therefore, form an important part of this thesis. So, we will first introduce the theoretical background of the MCE.
3.1 Gibbs Free Energy

The greatest amount of mechanical work which can be obtained from a given quantity of a certain substance in a given initial state, without increasing its total volume or allowing heat to pass to or from external bodies, except such as at the close of the process are left in their initial condition. Technically, the Gibbs free energy is the maximum amount of non-expansion work which can be extracted from a closed system, and this maximum can be attained only in a completely reversible process. The thermodynamic properties of a system are fully determined by the Gibbs free energy or free enthalpy of the system. The system we consider here consists of a magnetic material in a magnetic field \( B \) at a temperature \( T \) under a pressure \( p \). The Gibbs free energy \( G \) of the system is given by

\[
G = U - TS + pV - MB
\]  

(3.1)

Where \( U \) is the internal energy of the system, \( S \) the entropy of the system, and \( M \) the magnetization of the magnetic material. The volume \( V \), magnetization \( M \), and entropy \( S \) of the material are given by the first derivatives of the Gibbs free energy as follows:

\[
V(T, B, p) = - \frac{\partial G}{\partial p}_{T,B}
\]

\[
M(T, B, p) = - \frac{\partial G}{\partial B}_{T,p}
\]

(3.2)

\[
S(T, B, p) = - \frac{\partial G}{\partial T}_{B,p}
\]

The specific heat of the material is given by the second derivative of the Gibbs free energy with respect to temperature.
By definition, if the first derivative of the Gibbs free energy is discontinuous at the phase transition, then the phase transition is of the first order. Therefore, the volume, magnetization, and entropy of the magnetic material are discontinuous at a first-order phase transition. If the first derivative of the Gibbs free energy is continuous at the phase transition, but the second derivative is discontinuous, then the phase transition is of second order.

3.2 Magnetic Entropy

Entropy measures the spontaneous dispersal of energy; how much energy is spread out in a process or how widely spread out it becomes—at a specific temperature. It also describes the tendency for systems to go from a state of higher organization to a state of lowest organization on the molecular level. In physics, entropy is a mathematical measurement of a change from greater to lesser potential energy, which is related to the second law of thermodynamics. The total entropy of a magnetic material in which the magnetism is due to localized magnetic moments is expressed by

\[ S(T, B, p) = S_l(T, B, p) + S_c(T, B, p) + S_M(T, B, p) \] (3.4)

Where \( S_l \) represents the entropy of the lattice subsystem, \( S_c \) the entropy of the conduction-electron subsystem, and \( S_M \) the magnetic entropy, i.e. the entropy of the subsystem of the magnetic moments. In magnetic solids exhibiting itinerant-electron magnetism, separation of these three contributions to the total entropy is, in general,
not straightforward, because the 3d electrons give rise to the itinerant-electron magnetism, but also participate in the conduction. Separation of the lattice entropy is possible only if electron-phonon interaction is not taken into account. Since the entropy is a state function, the full differential of the total entropy of a closed system is given by

\[ dS = \left( \frac{\partial S}{\partial T} \right)_{p,B} dT + \left( \frac{\partial S}{\partial p} \right)_{T,B} dp + \left( \frac{\partial S}{\partial B} \right)_{T,p} dB \]  

(3.5)

Among these three contributions, the magnetic entropy is strongly field dependent, and the electron and lattice entropies are much less field dependent. Therefore, for an isobaric-isothermal \((dp = 0; dT = 0)\) process, the differential of the total entropy can be represented by

\[ dS = \left( \frac{\partial S_M}{\partial B} \right)_{T,p} dB \]  

(3.6)

For a field change from the initial field \(B_i\) to the final field \(B_f\), integration of Eq. (3.6) yields the total entropy change

\[ \Delta S (T, \Delta B) = S (T, B_f) - S (T, B_i) = \Delta S_M (T, \Delta B) \]  

(3.7)

Where \(\Delta B = B_f - B_i\). This means that the isothermal-isobaric total entropy change of a magnetic material in response to a field change \(\Delta B\) is also expressed by the isothermal-isobaric magnetic-entropy change.

The magnetic-entropy change is related to the bulk magnetization, the magnetic field, and the temperature through the Maxwell relation
\[
\left( \frac{\delta S_M(T, B)}{\delta B} \right)_{T, p} = \left( \frac{\delta M(T, B)}{\delta T} \right)_{B, p}
\] (3.8)

Integration yields
\[
\Delta S_M(T, \Delta B) = \int_{B_i}^{B_f} \left( \frac{\delta M(T, B)}{\delta T} \right)_{B, p} dB
\] (3.9)

On the other hand, according to the second law of thermodynamics
\[
\left( \frac{dS}{dT} \right)_{B, p} = \frac{c_p(T, B)}{T}.
\] (3.10)

Integration yields
\[
S(T, B) = S_0 + \int_{0}^{T} \frac{c_p(T', B)}{T'}dT'
\] (3.11)

In the absence of configuration entropy, the entropy will be zero at \( T = 0 \) K, so that the value of \( S_0 \) is usually chosen to be zero. Therefore, the entropy change in response to a field change \( \Delta B \) is given by
\[
\Delta S(T, \Delta B) = \int_{0}^{T} \frac{c_p(T', B_f) - c_p(T', B_i)}{T'}dT'
\] (3.12)

Where \( c_p(T', B_f) \) and \( c_p(T', B_i) \) represent the specific heat at constant pressure \( p \) and in the magnetic field \( B_f \) and \( B_i \), respectively.
Experimental

3.3 Sample Preparation

3.3.1 Solid State Method

Generally, perovskite materials are prepared by the standard solid-state reaction method. The perovskite materials investigated in this present thesis were also prepared in this way. Powder samples were synthesized using the standard solid-state reaction method at high temperature, by mixing La$_2$O$_3$, CaCO$_3$, Ag$_2$CO$_3$, Co$_3$O$_4$, and MnO$_2$ up to 99.9% purity in the desired proportions. The starting materials were intimately mixed in an agate mortar and first fired at 700°C for 12 h. Then, the mixture was reground and again fired at 900°C for 12 h. The mixture was ground again for a third time, pressed into pellets, and fired at 1100°C for 12 h to obtain better crystallization. Finally, the sample was again reground, pressed into pellets, and sintered at 1350°C for 24 h.

3.3.2 Crystal Growth

Single crystals of La$_{0.7}$Ca$_{0.3}$MnO$_3$ and La$_{0.7}$Ca$_{0.3}$CoO$_3$ were prepared by the travelling-zone method in an adapted NEC double-ellipsoidal-type image furnace. The furnace consists of two mirrors, which are plated with gold for enhanced reflectivity and corrosion resistance. The heat sources are two halogen lamps. The filaments of the two halogen lamps are positioned in the focus of each of the mirrors, and are projected on the common focal point of the two mirrors. In this way, the input power is concentrated on the molten zone between the feed and the seed rods.
The temperature of the molten zone is controlled by controlling the dc-voltage of the two lamps. Feed rods were prepared by the solid state reaction method. The pure starting materials were cast into a cylindrical rod about 5 mm in diameter. A quartz tube served as the growth chamber. Before the growth, the chamber was evacuated to a pressure of $10^{-6}$ mbar, and then filled with about 900 mbar Ar gas. During the growth, the Ar atmosphere was continuously purified with Ti-Zr getter. The feed and seed rods were counter rotated at a speed of 20 rpm. After the growth, the sample was slowly cooled down to room temperature. In this way, single crystals of the samples were obtained.

3.3.3 Thin Film Growth

La$_{0.8}$Ca$_{0.2}$MnO$_3$ (LCMO) thin film (~200 nm) was grown on a (100) LaAlO$_3$ substrate by pulsed-laser deposition (PLD). A short pulse excimer laser ($\lambda = 248$ nm) was focused onto a stoichiometric LCMO target with an estimated energy density of ~3.2 J/cm$^2$, with a repetition rate of 5 Hz. The oxygen pressure in the deposition chamber was kept at 300 mTorr, while the temperature of the substrate was maintained at 800°C during the preparation process. The film thickness was controlled by deposition time, with deposition at the rate of 50 nm/m. Following the deposition, the film was cooled to room temperature over two hours in an oxygen atmosphere without any further thermal treatment.
3.4 Sample Characterization

Powder x-ray diffraction (XRD) patterns were collected at room temperature by means of a Philips diffractometer with Cu Kα radiation. In this way, the main phase as well as the impurity phases could be detected. Scanning electron microscopy (SEM) was used to check the homogeneity and the stoichiometry of the samples. For transmission electron microscopy (TEM), thin film sample was prepared by ion milling in a JEOL JEM-9320FIB. The sample was deposited on silicon substrate. Thin film sample was observed in TEM (JEOL JEM-2100F) equipped with energy dispersive spectroscopy (EDS). The epitaxy and lattice parameters of the film were examined and calculated from the data obtained using a four-circle X-ray diffractometer.

3.5 Magnetic, Specific-heat, and Resistance Measurements

Magnetization and specific heat measurements were performed using a physical properties measurement system (PPMS) with a 14 T magnetometer. This magnetometer is capable of measuring magnetization with an accuracy of 0.5% in the temperature range from 2 to 400 K and in the field range of -14 to 14 T. The samples used for magnetization measurements in the magnetometer were single crystals, thin film, polycrystalline bulk pieces, and powders. Resistance and magnetoresistance were measured by the conventional four-probe technique.
3.6 Determination of the Magnetocaloric Effect

There are several ways to determine the MCE in a magnetic material experimentally. Clark and Callen [3], Kuhrt et al. [4], and Ponomarev [5] have directly measured the temperature of samples with a thermocouple during the application or removal of a magnetic field. For the principal scheme of these direct measurement methods and set-ups, we refer to Dan’kov et al. [6, 7]. The accuracy of the direct measurements depends on the errors in thermometry, the errors in field setting rates, the quality of thermal isolation of the samples, and the quality of the compensation circuitry to eliminate the effect of the changing magnetic field on the temperature sensors. As Pecharsky and Gschneidner [8] have pointed out, the accuracy is claimed to be in the 5 to 10% range. Larger error will occur if one of the above-mentioned issues affecting the accuracy is not resolved properly. Other techniques for determining the MCE are indirect. Indirect methods that are often used include the ones based on magnetization measurements and on specific-heat measurements in a constant magnetic field.

3.6.1 Determination of Magnetocaloric Effect from Magnetization Measurements

For magnetization measurements made at discrete temperatures, the integral in Eq. (3.9) can be numerically evaluated by

\[
\Delta S_M(T, \Delta B) = \sum_i \frac{M_i(T_i, B_i) - M_i(T'_i, B_i)}{T'_i - T_i} \Delta B_i,
\]  

(3.13)
Where $M (T'_i, B_i)$ and $M (T'_i, B_i)$ represent the values of magnetization at a magnetic field $B_i$ at the temperatures $T'_i$ and $T'_i$, respectively. $T$ is the mean value of $T'_i$ and $T'_i$. $\Delta B_i$ is the step size of the field increase, and $\Delta B = B_f - B_0$. In the experiments that we have conducted, the field was varied from $B_0 = 0$ to $B = B_f$. The accumulation of experimental errors in the determination of $\Delta S_M (T, \Delta B)$ has been analysed by Pecharsky and Gschneidner [9], and the validity of using the method, even for a first-order magnetic phase transition, is discussed in Refs. [10] and [11]. Although a magnetization measurement by magnetometer is the most accurate method to determine the bulk magnetization of a magnetic material, the accumulated errors in the determination of the magnetic-entropy change $\Delta S_M (T, \Delta B)$ can be as high as 20 to 30%, mainly because of the poor thermal contact between the sample and the thermocouple. Nevertheless, this method is often used to quickly establish the potential magnetocaloric properties of a magnetic material.

### 3.6.2 Determination of the Magnetocaloric Effect from Specific-heat Measurements

Specific-heat measurement is the most accurate method of determining heat effects in a material. The total entropy change of a magnetic material can be derived from the specific heat by using Eq. (3.12). According to Eq. (3.7), this entropy change is equal to the magnetic-entropy change for an isobaric-isothermal process. This means that we can also obtain the magnetic-entropy change from the field dependence of the specific-heat measurements by using Eq. (3.12). The determination of the absolute value of the adiabatic temperature change in different magnetic materials is a rather complicated task. By combining Eqs. (3.6), (3.8), and (3.10), the
infinitesimal adiabatic temperature change for the adiabatic-isobaric process is found to be

\[ \text{d}T (T, B) = - \frac{T}{c_p(T, B)} \left( \frac{dM}{dT} \right)_{B, p} dB \]  

(3.14)

By integration of Eq. (3.14), the adiabatic temperature change for a field change from \( B_i \) to \( B_f \) is given by

\[ \Delta T_{ad} (T, \Delta B) = - \int_{B_i}^{B_f} \frac{T}{c_p(T, B)} \left( \frac{dM}{dT} \right)_{B, p} dB \]  

(3.15)

Analytical integration of Eq. (3.15) is actually possible since both the magnetization and the specific heat are material dependent and generally unknown functions of temperature and magnetic field in the vicinity of the phase transition. Above the Debye temperature, the lattice specific heat of solids approaches the Dulong-Petie limit of 3R. Therefore, at higher temperatures, if the specific heat can be considered to be only weakly dependent on temperature and the variation of \( T/c_p (T, B) \) with temperature is slow compared with the variation of the magnetization with temperature, then, Eq. (3.15) can be simplified to

\[ \Delta T_{ad} (T, \Delta B) = - \frac{T}{c_p(T, B)} \Delta S_M (T, \Delta B) \]  

(3.16)

Obviously, the MCE is large when \( (dM / dT)_{B, p} \) is larger and \( c_p (T, B) \) is small at the small temperature. Since \( (dM / dT)_{B, p} \) peaks around the magnetic ordering temperature, a large MCE is expected in the vicinity of the temperature of the magnetic phase transition. The determination of the MCE from magnetization, specific heat or the combined magnetization and specific-heat data can be used to characterize the magnetocaloric properties of magnetic refrigerant materials. Magnetization data provides the magnetic-entropy change \( \Delta S_M (T, \Delta B) \). Specific heat
at constant field provides both the magnetic-entropy change $\Delta S_M (T, \Delta B)$ and the adiabatic temperature change $\Delta T_{ad} (T, \Delta B)$. However, an analysis of experimental errors in the MCE as derived from magnetization measurements and specific-heat measurements has shown that the accumulation of experimental errors may be as high as 20% to 30% near room temperature [9].

### 3.6.3 Determination of the Magnetocaloric Effect from Resistivity Measurements

The electrical resistivity $\rho$ is obtained from the electrical resistance by

$$\rho = R \frac{A}{l} \quad (3.17)$$

Where $R$ is the electrical resistance, $A$ the cross section of the sample perpendicular to the current direction, and $l$ is the distance between the voltage contacts.

The entropy changes determined by the resistivity measurement is

$$\Delta S_M = - \alpha \int_0^H \left[ \frac{\delta \ln(\rho)}{\delta T} \right]_H dH \quad (3.18)$$

Where $\alpha$ is a fitting parameter and $H$ is the applied field.
Fig. 3.1 S-T diagram of MCE [12].

Figure 3.1 is an S-T diagram for a ferromagnetic solid, showing the total entropy in magnetic fields $H_0$ and $H_1$ ($H_1 > H_0$). The diagram also illustrates the MCE (inset), which is represented by $\Delta T_{ad}$ or $\Delta S_M$ in the vicinity of the magnetic ordering temperature (Curie temperature, $T_C$). The vertical arrow shows the isothermal magnetic entropy change, $\Delta S_M$, whilst the horizontal arrow shows the adiabatic temperature change, $\Delta T_{ad}$ [12].
References


CHAPTER 4

GIANT MAGNETIC ENTROPY CHANGE OF COLOSSAL MAGNETORESISTANCE IN \( \text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3 \) MATERIAL IN LOW FIELD

4.1 Introduction

Interest in the rare-earth manganites has been considerable, due to the occurrence of colossal magnetoresistance (CMR) in these materials. The magnetocaloric effect (MCE) that is present in some of these materials is a crucial factor for practical application in magnetic refrigeration. So far, Gd-based magnetic materials have been primarily considered because of their large MCE property near room temperature. Doping can be used to modify the relevant intrinsic properties, however, i.e., for a CMR material, the Curie temperature (\( T_C \)) and the saturation magnetization properties. Even so, much more effort and attention are still needed to find candidates for application in energy-efficient refrigeration. Recently, some promising new candidates have been suggested, such as \( \text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4 \) [1], \( \text{Gd}_2\text{PdSi}_3 \) [2], \( \text{Ni}_{51.5}\text{Mn}_{22.7}\text{Ga}_{25.8} \) [3], \( (\text{Tb}_{1-x}\text{Gd}_x)\text{Al}_2 \) [4], and the hole-doped perovskite manganites [5]. Large magnetoresistance (MR) is the phenomenon where resistance of a material drops drastically on application of magnetic field. It is described as large when the effect is much larger than in metals, and it has tremendous applications in recording information on hard disks, magnetic sensors, and spin-electronic devices [6, 7] [1, 2]. On the other hand, materials with a large magnetocaloric effect (MCE) have been recognized as a promising alternative to conventional gas refrigeration [8, 9] [3, 4].
The coexistence of large magnetoresistance (MR) and a large magnetocaloric effect in a compound should attract considerable attention for promising technological applications. According to the double exchange theory, electrons tend to hop between Mn ions of different valences while keeping their spins unchanged. Therefore, when the arrangement of the spins of the Mn ions is modified by external field, the resistivity changes simultaneously. In this picture, the colossal magnetoresistance in the manganites can be qualitatively understood [10-13] [5-8]. This explanation actually suggests a magnetic-resistive interplay in the manganites. Mills et al. have suggested the presence of electron-phonon interaction, which leads to the formation of lattice polarons that influence the magnetoresistive property of the oxides [14, 15] [9, 10]. There are also arguments for the presence of magnetic polarons, and the appearance of MR has been ascribed to the depression of magnetic polarons by magnetic field [11]. In the literature, most of the previous studies have concentrated on indirect calculation of the isothermal magnetic entropy change. However, it can be directly determined by using the heat capacity method. In this study, therefore, we evaluated the calculation of entropy change in La$_{0.7}$Ca$_{0.3}$MnO$_3$ on the basis of magnetization and heat capacity measurements. The aim of this study is to find correlations between different methods and provide a quantitative description. In this chapter, we report large MCE and MR in La$_{0.7}$Ca$_{0.3}$MnO$_3$, where MCE and MR are observed at the Curie temperature ($T_C$) associated with the first order transition. We also report the correlation between resistivity and change in the magnetic entropy ($\Delta S_M$) in a specific region around $T_C$. 
4.2 Experimental

The manganite La$_{0.7}$Ca$_{0.3}$MnO$_3$ was prepared by the conventional solid state reaction method. Stoichiometric proportions of La$_2$O$_3$, CaCO$_3$, and MnO$_2$ were mixed and first fired at 700°C for 12 h. Then, the mixture was reground and again fired at 900°C for 12 h. The mixture was then ground for a third time, pressed into pellets, and fired at 1100°C for 12 h to obtain better crystallization. Finally, the sample was again reground, pressed into pellets, and sintered at 1350°C for 24 h. Powder X-ray diffraction (XRD) patterns, obtained with Cu Kα radiation at room temperature, revealed the single-phase orthorhombic perovskite structure. The XRD data was analysed by using Rietveld refinement with the Fullprof program. The results show a very good single phase sample. Magnetization and resistivity measurements were performed using a physical properties measurement system (PPMS) 14 T magnetometer in the temperature range from 0-300 K and magnetic fields up to 5 T. To measure the magnetic entropy change, ΔS$_M$, we used a sweep rate of 50 Oe/s.

4.3 Results and Discussion

Figure 4.1 shows the XRD pattern of the La$_{0.7}$Ca$_{0.3}$MnO$_3$ sample. The X-ray diffraction analysis shows that the perovskite is of single phase with orthorhombic structure. The lattice parameters of the sample are given in Table 4.1.

Table 4.1: Lattice parameters determined by means of XRD at room temperature.

<table>
<thead>
<tr>
<th>Sample</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>V (Å$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>La$<em>{0.7}$Ca$</em>{0.3}$MnO$_3$</td>
<td>5.48347</td>
<td>5.47520</td>
<td>7.73256</td>
<td>232.155</td>
</tr>
</tbody>
</table>

100
Figure 4.2 shows the low field magnetization in zero-field cooled (ZFC), and field cooled cooling (FCC), and field cooled warming (FCW) processes. We estimated the Curie temperature \( T_C \) to be 251 K. It can be clearly seen that there is a drastic change in the magnetization around \( T_C \). Under ZFC, magnetic domain wall pinning causes low magnetization, and a small part of the particle surface shows spin-glass behaviour, which may be the reason for the separation of the curves at low temperature. It can be seen that the FCC and FCW curves follow different paths at the transition temperature, which is one of the features of a first order transition. So, we think that the thermal hysteresis at the transition temperature is due to the first order phase transition. At and near \( T_C \), however, the magnetization also shows an S-shape, which is unusual for the lanthanum manganites, indicating a large magnetic entropy change.
Magnetization as a function of temperature in the ZFC, FCC, and FCW processes with applied field of 500 Oe, for La$_{0.7}$Ca$_{0.3}$MnO$_3$.

Figure 4.3 shows isothermal magnetization measurements at different temperatures between 230 and 280 K, and magnetic field up to 5 T. It can be seen clearly from the figure that there is a drastic change in the magnetization around $T_C$, as well as an S shape at and after $T_C$, which is unusual for the lanthanum manganites, indicating a large magnetic entropy change. This also coincides with the rapid reduction of magnetization at $T_C$ (Fig. 4.2). Another important feature to be noted is that a large proportion of the changes in the magnetization occurs in a relatively low field range (up to 2.5 T), which is also beneficial for the household application of MCE materials.
Fig. 4.3 Isothermal M-H curves of the La$_{0.7}$Ca$_{0.3}$MnO$_3$ sample at different temperatures between 230 and 280 K.

[Graph of M-H curves]

Fig. 4.4 The $M^2$ vs H/M plots for the isotherms of the La$_{0.7}$Ca$_{0.3}$MnO$_3$ sample.

Arrott plots derived from M (H) in a broad temperature range around $T_C$ are displayed in Figure 4.4. The Arrott plots derived from M (H) provide evidence that
the slopes of the $H/M$ vs. $M^2$ curves are negative over the complete $M^2$ range. According to the Banerjee criterion [16], the transition is confirmed as first order and is also an indication of a large magnetic entropy change.

Magnetic entropy change versus temperature at various applied fields (1-5 T) is presented in Figure 4.5. At or near the Curie temperature ($T_C$), the maximum entropy changes were about 4.63, 5.27, 5.71, 6.42, 7.03, and 7.53 $\text{J kg}^{-1}\text{K}^{-1}$ for field changes from 0 to 1, 1.5, 2, 3, 4, and 5 T, respectively. It should be noted that these values are about two times larger than those reported for other perovskite manganites [17-19], and even larger than for Gd-based magnetic materials at low fields [20].

![Figure 4.5](image)

**Fig. 4.5** Magnetic entropy change in $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ as a function of temperature under magnetic field changes from 0 to 1, 1.5, 2, 3, 4, and 5 T, respectively.

From the results, the material studied in this work is characterized by large magnetic entropy changes induced by low magnetic field change, which is also beneficial for
the household application of active magnetic refrigerant (AMR) materials. One of the most important criteria for the magnetic refrigerant materials is the temperature at which large MCE is observed for the application. This should be either in the range of 10-80 K or higher than 250 K. Here, the peak is observed at 251 K.

**Table 4.2** Magnetic entropy changes and temperature changes for several lanthanum manganites and for elemental Gd at their Curie temperature in low magnetic field.

| Composition           | $\Delta H$ (T) | $T_C$ (K) | $|\Delta S_M|$ (J·K$^{-1}$·kg$^{-1}$) | $\Delta T$ (K) | Reference |
|-----------------------|----------------|-----------|--------------------------------------|----------------|-----------|
| $La_{0.7}Ca_{0.3}MnO_3$ | 1              | 251       | 4.63                                 | 2.02           | present   |
| $La_{0.7}Ca_{0.3}MnO_3$ | 1              | 227       | 1.95                                 | 1.3            | 17        |
| $La_{0.7}Ca_{0.3}MnO_3$ | 1              | 256       | 1.38                                 | -              | 18        |
| $La_{0.8}Ca_{0.2}MnO_3$ | 1              | 176       | 2.75                                 | -              | 19        |
| $La_{0.67}Sr_{0.33}MnO_3$ | 1              | 370       | 1.50                                 | -              | 30        |
| Gd                    | 1              | 294       | 2.8                                  | 2.6            | 20        |
| $La_{0.7}Ca_{0.3}MnO_3$ | 2              | 251       | 5.71                                 | 2.69           | present   |
| $La_{0.7}Ca_{0.3}MnO_3$ | 2              | 227       | 3.4                                  | 2.3            | 17        |
| $La_{0.8}Ca_{0.2}MnO_3$ | 2              | 176       | 4.2                                  | -              | 19        |
| Gd                    | 2              | 294       | 5.0                                  | 5.0            | 20        |

As mentioned above, the entropy change was also determined by using the heat capacity method. The heat capacity of the sample at different fields (0 and 1.5 T) is plotted against temperature and is shown in Figure 4.6. The entropy changes determined from the heat capacity and the Maxwell relation are shown in Figure 4.7.
Fig. 4.6 Temperature dependence of the heat capacity of the La$_{0.7}$Ca$_{0.3}$MnO$_3$ sample for zero and 1.5 T field.

Fig. 4.7 The temperature dependence of the entropy changes of the sample calculated from the heat capacity and the Maxwell relation.
Quite interestingly, the entropy change determined by using the heat capacity method almost dovetails with that from the Maxwell relation. The quantitative value from the heat capacity is also in good agreement with that from the magnetization.

The adiabatic temperature change ($\Delta T_{\text{ad}}$) for the temperature range of 230-275 K is shown in Figure 4.8. The estimated $\Delta T_{\text{ad}}$ values are 2.02, 2.69, and 3.62 K for field changes from 0 to 1, 2, and 5 T, respectively. The $\Delta T_{\text{ad}}$ value for 1 T is 1.5 times larger that those reported in Reference [18] and is nearly same as for Gd.

![Fig. 4.8 Temperature dependence of the adiabatic temperature change of the sample for a field change from 0 to 1, 2, and 5 T.](image)

It is well known that the presence of either no or low hysteresis is an important criterion for magnetic refrigeration without loss. The magnetic isotherms of the sample at the temperatures of 200, 260, and 300 K were measured in both an increasing and a decreasing field from 5 T to -5 T, as respectively shown in Figure
Almost no magnetic hysteresis was observed, which indicates that the MCE is fully reversible. The magnetization of the sample, when measured in cooling and then heating cycles at 500 Oe (Figure 4.2), shows a small thermal hysteresis of about 6 K, which is consistent with the Arrott plot, indicating a first order transition near $T_C$.

![Graph showing magnetic field dependence of magnetization](image)

**Fig. 4.9** The magnetic field dependence of the magnetization of the sample.

The magnetization isotherms of $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ at and above $T_C$ appear to exhibit an unusual dependence for lanthanum manganites, which is evidenced by the S-shaped magnetization curves, as mentioned above. It is believed that a large low-field value of $(\delta M/\delta T)$, which is caused by the S-shape of the magnetization, gives rise to the giant low-field magnetic entropy change. It is well known that itinerant electron metamagnetism (IEM) materials show the S magnetization shape [21, 22]. The properties are well described by the Landau energy expansion, $\Delta F = aM^2 + bM^4 + cM^6 - HM$, with a negative $M^4$ prefactor [23]. Due to the peculiarity of the exchange
interaction and the magnetoelastic coupling, the $b$ prefactor in the Landau expansion can, in fact, be negative, and phenomena similar to itinerant electron metamagnetism are possible. Again, in Nagaev [24], it is mentioned that metamagnetism is possible in magnetic systems, which include giant magnetoresistance manganites, as a result of both the spin–phonon interaction and the influence on spin exchange due to the Jahn–Teller ordering of the electron orbits. This S-shaped magnetization was recently observed in the manganite $\text{La}_{0.7}\text{Y}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ [25] as well and was clearly explained by the magnetoelastic contribution to the magnetic part of the free energy. Therefore, we can conclude that the observed giant magnetic entropy changes, following the strong manifestation of S-shaped magnetization, are caused by a metamagnetic transition. A change in the nature of the magnetic transition suggests a variation in the nature of the magnetic coupling. Goodenough has suggested that in manganites, the static-cooperative Jahn-Teller (JT) distortions are replaced in the ferromagnetic phase by dynamic JT distortions that introduce vibrational modes into the spin-spin interaction, giving rise to an extra superexchange term [25, 26]. That is, in our case, there is a strong influence of lattice effects in the sample, which is reflected in strong variations in several physical properties [27]. The anomalous volume change at $T_C$ in the sample supports the first-order character of the transition. In addition, giant magnetoelastic coupling (MEC) may exist in our sample. This MEC phenomenon has been found in other manganites [28], which again confirm the lack of any noticeable magnetic hysteresis with a field-induced first order transition.

Resistance was measured using the conventional four-probe method. Figure 4.10 illustrates the temperature dependence of the resistivity under different magnetic fields. The sample is metallic at low temperatures and insulating at high temperatures.
The metal-insulator (MI) transition takes place at $T_C$ for zero field, but shifts to higher temperature with applied field. Due to the instability of magnetic polarons in an external magnetic field, the resistivity peak shifts to higher temperatures, and its magnitude drastically diminishes as one applies magnetic field, which also can be explained by the double exchange model. When field is applied, the angle between the Mn$^{3+}$-O-Mn$^{4+}$ bonds is flattened, which is favourable for hopping. In addition to driving the MI transition to higher temperatures, an external field greatly depresses the resistivity.

**Fig. 4.10** Temperature dependence of the resistivity, $\rho$, measured under different magnetic fields.

The MR ratio, defined as $\text{MR} = (\rho(0) / \rho(H) - 1)$, exhibits a maximum of ~206% at $T_C$ under magnetic field of 5 T, as shown in Figure 4.11. This value is higher than for many other manganite perovskites. Based on the Maxwell formula, $\Delta S_M (T, \Delta H) =$
magnetic entropy change has been calculated from the magnetic data and is shown in Figure 4.5. As expected, the effect of external field on magnetic order is strongly temperature dependent, and the maximum variation of magnetic entropy occurs near $T_C$, where $\Delta S_M$ shows a rapid decrease, resulting in an asymmetric peak. It is well known that the MR of La$_{0.7}$Ca$_{0.3}$MnO$_3$ also undergoes a great change near the magnetic transition temperature due to the magnetic ordering. So, it is an interesting question whether a quantitative relation can be found between $\Delta S_M$ and MR. As expected, the MR and $\Delta S_M$ peaks appear simultaneously (inset in Fig. 4.11). However, the detailed temperature dependences of MR and $\Delta S_M$ are apparently different. This result reveals the absence of a simple relation between these two quantities.

Fig. 4.11 Magnetoresistance (MR) plotted vs. temperature. The MR and magnetic entropy changes under a field of 5 T are shown in the inset.
The entropy changes determined by the resistivity measurement, $\Delta S_M = -\alpha \int_0^H \left[ \frac{\delta \ln(\rho)}{\delta T} \right] \, dH$, and the Maxwell relation, $\Delta S_M (T, \Delta H) = \int_0^H \left( \frac{\delta M}{\delta T} \right)_H \, dH$, are shown in Figure 4.12, where the resistivity results agree quite well with the fitting parameter $\alpha = 9.98 \text{ emu/g}$ in the intermediate temperature range.

![Fig. 4.12 Comparison of the magnetic entropy change vs. temperature ($\Delta S_M - T$ relation) calculated from the magnetic data (Maxwell relation) and the resistivity data.](image-url)

It can be seen that deviation of the magnetic results from the resistivity measurements occurs in the temperature range below 245 K, where the system is in a nearly complete ferromagnetic state, and above 270 K, where the paramagnetic state prevails. This result implies that the resistivity measurements are in agreement with the magnetic data only in the intermediate temperature range, i.e., during the establishment of perfect ferromagnetic order. This also remind us of magnetic
polarons, which prevail when magnetic disorder exists. It is obvious that magnetic disorder, characterized by $\Delta S_M$, affects the magnetic polarons, while the magnetic polarons influence the electronic transport properties, which may be the underlying reason for the occurrence of the $\Delta S_M - \rho$ relation. In the low temperature region, where the system is in a relatively ordered magnetic state, the magnetic polarons are depressed significantly, which causes the deviation from the resistivity measurements. It is obvious that a larger fitting parameter $\alpha$ means a more sensitive dependence of $\Delta S_M$ on $\rho$. On the other hand, the stronger the magnetic scattering is, the smaller the $\alpha$ will be. In this picture, it is expected that $\alpha$ could be small in a compound with a low Curie temperature or a large Hund’s rule coupling. So, it can be expected that the smaller value of $\alpha$ in the present compound is due to the stronger magnetic scattering. It should be noted that Xiong et al. [29] have obtained a close relation between the temperature derivative of the resistivity and the magnetic entropy. The $\alpha$ value given by them is 21.74 emu/g, which is higher than the present one, but the Curie temperature of their compound is 265 K, whereas in our case it is 251 K. In this picture, it is again expected that the lower $\alpha$ value of our compound is due to the low Curie temperature.

4.4 Conclusions

A large magnetocaloric effect (MCE) and large magnetoresistance (MR) are observed in La$_{0.7}$Ca$_{0.3}$MnO$_3$. The maximum MCE and MR are, in magnetic field of 5 T, $\sim$7.54 J/kgK and 206 %, respectively. A strong correlation between $\Delta S_M$ and $\rho$ is observed in the intermediate temperature range around $T_C$. The lack of any noticeable magnetic hysteresis loss confirms the reversibility of the compound,
which is desirable for magnetic refrigeration. The exhibition of large MR and MCE near room temperature suggests the utility of the compound for multiple applications in magnetic refrigeration, as well as magnetoresistive devices. Magnetic materials which show a first order magnetic phase transition, especially at the low fields that are obtainable from a permanent magnet, are also good candidates for magnetic refrigeration.
References


CHAPTER 5

IMPROVEMENT OF REFRIGERANT CAPACITY OF La$_{0.7}$Ca$_{0.3}$MnO$_3$
MATERIAL WITH A FEW PERCENT Co DOPING

5.1 Introduction

The magnetocaloric effect (MCE) is the basis of the magnetic refrigeration process, which is expected to be competitive with traditional gas compression technology because of its higher energy efficiency and environmental friendliness [1-3]. For a long time, a rare earth element, Gd, was considered to be the only usable material that exhibits a large MCE near room temperature. However, large values of magnetic entropy change also have been found in a number of compounds, such as Gd$_5$ (Si$_{6}$Ge$_{1-x}$)$_4$ [4, 5], Gd$_2$PdSi$_3$ [6], Ni$_{51.5}$Mn$_{22.7}$Ga$_{25.8}$ [7], (Tb$_{1-x}$Gd$_x$) Al$_2$ [8], ErCo$_2$ [9], and the hole-doped perovskite manganites [10, 11]. Since the magnetic properties of perovskite manganites, including the colossal magnetoresistance effect, the Curie temperature ($T_C$), and the saturation magnetization, are strongly doping dependent, these materials are believed to be good candidates for magnetic refrigeration over various temperature ranges. Therefore, there have been an increased number of studies of the MCE of perovskite manganites [12-14]. In assessing the usefulness of a magnetic refrigerant material, the refrigerant capacity or relative cooling power (RCP), which is a measure of the amount of heat transfer between the cold and hot sinks in an ideal refrigeration cycle, is considered to be the most important factor [15-17]. The RCP depends not only on the magnitude of the entropy change, $\Delta S_M$, but also on the temperature dependence of $\Delta S_M$ (e.g., the full
width at half maximum (FWHM) of the $\Delta S_M$ peak) [15, 17]. In this context, a good magnetic refrigerant material with large RCP requires both a large magnitude of $\Delta S_M$ and a broad width of the $\Delta S_M$ curve. Most previous studies on manganites were focused mainly on exploring large MCE and did not consider the issue of RCP. Thus, from fundamental and practical perspectives, it is essential to understand the influence of magnetic phase transitions on both the MCE and the RCP. In this chapter, we present systematic studies of the influence of the first order magnetic transition (FOMT) and the second order magnetic transition (SOMT) on the MCE and RCP. Our results reveal that while the FOMT at $T_C$ induces a larger MCE, it is restricted to a narrow temperature range, resulting in a smaller RCP. However, the SOMT at $T_C$ induces a smaller MCE, but with a distribution over a broader temperature range, thus resulting in a larger RCP. A large low-field-induced magnetic entropy change was also achieved with larger magnetoresistance (MR).

5.2 Theoretical Considerations

When a material is magnetized by the application of a magnetic field, the entropy associated with the magnetic degrees of freedom, called the magnetic entropy, $S_M$, is changed as the field changes the magnetic order of the material. Under adiabatic conditions, $\Delta S_M$ must be compensated by an equal but opposite change of the entropy associated with the lattice, resulting in a change in temperature of the material. This adiabatic temperature change, $\Delta T_{ad}$, is usually called the MCE. The magnetic-entropy change is related to the bulk magnetization, the magnetic field, and the temperature through the Maxwell relation
\[
\left( \frac{\partial S_M(T, B)}{\partial B} \right)_{T,p} = \left( \frac{\partial M(T, B)}{\partial T} \right)_{B,p}
\]  

(5.1)

Integration yields

\[
\Delta S_M (T, \Delta B) = \int_{B_i}^{B_f} \left( \frac{\partial M(T, B)}{\partial T} \right)_{B,p} dB
\]  

(5.2)

In order to evaluate the magnetic entropy change, \( \Delta S_M \), one needs to make a numerical approximation to the integral in Eq. (5.2). The usual method is to use isothermal magnetization measurements. In the case of magnetization measurements at small discrete field and temperature intervals, \( \Delta S_M \) can be approximated from Eq. (5.2) by

\[
\Delta S_M (T, \Delta B) = \sum_i \frac{M_i(T_i', B_i) - M_i(T_i, B_i)}{T_i' - T_i} \Delta B_i,
\]  

(5.3)

where \( M(T_i', B_i) \) and \( M(T_i, B_i) \) represent the values of magnetization at a magnetic field \( B_i \) at the temperatures \( T_i' \) and \( T_i \) respectively. \( T \) is the mean value of \( T_i' \) and \( T_i \). \( \Delta B_i \) is the step size of the field increase, and \( \Delta B = B_f - B_0 \) is the difference between the final and initial fields. In the experiments conducted here, the field was varied from \( B_0 = 0 \) to a field \( B = B_f \). Using Eq. (5.3), by measuring the M–H curve at various temperatures, one can calculate the magnetic entropy change associated with the magnetic field variation. The refrigerant capacity or cooling power is one of the most important parameters for magnetic refrigeration. It is defined as the product of the maximum magnetic entropy change, \( -\Delta S_{M_{\text{max}}} \), and the full width at half maximum of the incremental temperature change, \( \delta T_{\text{FWHM}} \).

\[
\text{RCP} = -\Delta S_{M_{\text{max}}} \delta T_{\text{FWHM}}
\]  

(5.4)
5.3 Experimental

The manganites La$_{0.7}$Ca$_{0.3}$MnO$_3$ (LCMO) and La$_{0.7}$Ca$_{0.3}$Mn$_{0.95}$Co$_{0.05}$O$_3$ (LCMCO) were prepared by the conventional solid state reaction method. Stoichiometric proportions of La$_2$O$_3$, CaCO$_3$, MnO$_2$, and Co$_3$O$_4$ were mixed and first fired at 700°C for 12 h. Then, the mixture was reground and again fired at 900°C for 12 h. The mixture was then ground for a third time, pressed into pellets, and fired at 1100°C for 12 h to obtain better crystallization. Finally, the sample was again reground, pressed into pellets, and sintered at 1350°C for 24 h. Powder X-ray diffraction (XRD) patterns, obtained with Cu Kα radiation at room temperature, revealed the single-phase orthorhombic perovskite structure. The XRD data were analysed by using Rietveld refinement with the Fullprof program. The results show very good single phase samples. The magnetization measurements were performed using a physical properties measurement system (PPMS) 14 T magnetometer in the temperature range from 5-300 K and magnetic fields up to 5 T.

5.4 Results and Discussion

Figure 5.1 shows XRD traces of the La$_{0.7}$Ca$_{0.3}$MnO$_3$ and La$_{0.7}$Ca$_{0.3}$Mn$_{0.95}$Co$_{0.05}$O$_3$ samples. The X-ray diffraction analysis shows that the perovskites are of single phase with orthorhombic structure. The lattice parameters of the samples are shown in Table 5.1. The lattice parameters decrease slightly with Co doping. The decrease of the unit cell volume with Co content indicates a random distribution of the Mn and Co ions in the lattice, i.e., no long range Co/Mn order [18].
Table 5.1 Lattice parameters of the samples.

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<th>c (Å)</th>
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![XRD patterns of La0.7Ca0.3MnO3 and La0.7Ca0.3Mn0.95Co0.05O3 samples.](image)

**Fig. 5.1** XRD patterns of La$_{0.7}$Ca$_{0.3}$MnO$_3$ and La$_{0.7}$Ca$_{0.3}$Mn$_{0.95}$Co$_{0.05}$O$_3$ samples.

Figure 5.2 shows the low-field (0.5 T) magnetization as a function of temperature in the field-cooled (FC) process for La$_{0.7}$Ca$_{0.3}$MnO$_3$ and La$_{0.7}$Ca$_{0.3}$Mn$_{0.95}$Co$_{0.05}$O$_3$.

The Curie temperature, $T_C$, for La$_{0.7}$Ca$_{0.3}$MnO$_3$ is 251 K and for La$_{0.7}$Ca$_{0.3}$Mn$_{0.95}$Co$_{0.05}$O$_3$ is 195 K is shown in Figure 5.2. In La$_{1-x}$Ca$_x$MnO$_3$ perovskite, the Curie temperature is determined by the double exchange interaction between Mn$^{3+}$ and Mn$^{4+}$ ions. The substitution of Co for Mn weakens the double
exchange interaction between Mn$^{3+}$ and Mn$^{4+}$ ions and consequently decreases the Curie temperature [19].

Fig. 5.2 Magnetization as a function of temperature in the field cooling (FC) process with applied field of 0.5 T for La$_{0.7}$Ca$_{0.3}$MnO$_3$ and La$_{0.7}$Ca$_{0.3}$Mn$_{0.95}$Co$_{0.05}$O$_3$.

In order to evaluate the MCE, the isothermal magnetization curves of the samples were measured with a field step of 0.05 mT in the magnetic field range of 0-5 T and over a range of temperatures around T$_C$. Such families of M (H) curves are shown in Figure 5.3. It is worth mentioning that around the T$_C$, both samples shows S-shaped magnetization, which is typical for metamagnetic materials [20]. It is worth noting that a large proportion of the changes in the magnetization occur in the relatively low field range (< 2.5 T), which is beneficial for the application of MCE materials.
Fig. 5.3 Isothermal M-H curves at different temperatures for (a) La$_{0.7}$Ca$_{0.3}$Mn$_{0.95}$Co$_{0.05}$O$_3$ and (b) La$_{0.7}$Ca$_{0.3}$MnO$_3$.

The Inoue–Shimizu model, which involves a Landau expansion of the magnetic free energy up to the sixth power of the total magnetization, $M$, can be used to determine the transition type [21].

$$F(M,T) = \frac{c_1(T)}{2} M^2 + \frac{c_2(T)}{4} M^4 + \frac{c_3(M)}{6} M^6 + \cdots - BM$$  \hspace{1cm} (5.5)

The parameters $c_1(T)$, $c_2(T)$, and $c_3(T)$ represent the Landau coefficients, and it has been reported that the order of a magnetic transition is related to the sign of the Landau coefficient $c_2(T)$ at the Curie temperature, $c_2(T_C)$. A transition is expected to
be first order when $c_2(T_C)$ is negative, whereas it will be second order for a positive $c_2(T_C)$. The sign of $c_2(T_C)$ can be determined by means of an Arrott plot [22, 23]. If the Arrott plot is S-shaped near $T_C$, $c_2(T_C)$ is negative; otherwise, it is positive.

To understand the nature of the magnetic transition in $\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{0.95}\text{Co}_{0.05}\text{O}_3$ and $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$, Arrott plots of $M^2$ versus $H/M$ over a broad temperature range around $T_C$ are plotted in Figure 5.4. Neither an inflection point nor negative slopes are observed in Figure 5.4(a), proving the occurrence of a second order magnetic transition for $\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{0.95}\text{Co}_{0.05}\text{O}_3$. However, for $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ in Figure 5.4(b), negative slopes are clearly observed, indicating the occurrence of a first order magnetic transition. Therefore, it is expected that the different types of magnetic phase transformation in LCMCO and LCMO determine the different MCE behaviour in response to temperature and magnetic field. A change in the nature of the magnetic transition suggests a variation in the nature of the magnetic coupling. Zhou and Goodenough have suggested [24, 25] that in manganites, the static-cooperative Jahn-Teller (JT) distortions are replaced in the ferromagnetic phase by dynamic JT distortions that introduce vibrational modes into the spin-spin interaction, giving rise to an extra superexchange term. That is, in our case, there is a strong influence of lattice effects in the sample at $x = 0$, which is reflected in strong variations in several physical properties supporting the first order character [26]. The decrease in the unit cell volume may have depressed the anomalous volume change at $T_C$ in the $x = 0.05$ sample, supporting the second-order character.
Figure 5.4 $M^2$ vs. H/M plots for the isotherms of (a) La$_{0.7}$Ca$_{0.3}$Mn$_{0.95}$Co$_{0.05}$O$_3$ and (b) La$_{0.7}$Ca$_{0.3}$MnO$_3$.

Figure 5.5 shows the entropy change as a function of temperature in different magnetic fields ranging from 0 to 5 T for (a) La$_{0.7}$Ca$_{0.3}$Mn$_{0.95}$Co$_{0.05}$O$_3$ and (b) La$_{0.7}$Ca$_{0.3}$MnO$_3$. The maximum values of $|\Delta S_M|$ corresponding to external field changes of 1 T and 5 T for LCMCO and LCMO reach about 3.16 J/kgK and 4.63 J/kg K, and 7.14 J/kgK and 7.528 J/kgK, respectively. An abrupt variation in the magnetization and a sharp volume change at $T_C$ are two of the key conditions required for a large $\Delta S_M$. For the sample with $x = 0.05$, the transition is of second
order, so the above-mentioned conditions are not present, and therefore, $|\Delta S_m|$ falls considerably. The giant magnetic entropy changes in these magnetic materials suggest that they could be potential candidates for magnetic refrigerants. However, before magnetic refrigeration becomes a viable cooling technology, one must reduce the applied magnetic field so as to allow the use of permanent magnets instead of superconducting magnets as the magnetic-field source. Therefore, a very important task is to search for novel magnetic materials possessing giant low-field induced MCEs. Our results provide a possibility for the development of magnetic refrigerant substances that are operable with a permanent magnet rather than a superconducting one as the magnetic field source.

**Fig. 5.5** Temperature dependence of magnetic entropy change for different applied field changes of up to 5 T for (a) La$_{0.7}$Ca$_{0.3}$Mn$_{0.95}$Co$_{0.05}$O$_3$ and (b) La$_{0.7}$Ca$_{0.3}$MnO$_3$. 

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As shown in Figure 5.5(a), for the $\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{0.95}\text{Co}_{0.05}\text{O}_3$ sample, $|\Delta S_M|$ decreases gradually below the transition temperature, an indication of a spreading distribution of $|\Delta S_M|$. Therefore, despite the smaller magnitude of $|\Delta S_M|$ for the $\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{0.95}\text{Co}_{0.05}\text{O}_3$ compound, its $|\Delta S_M|$ versus $T$ curve is significantly broader, compared to those of the $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ sample, as shown in Figure 5.5(b), and of some first order transition materials, which is important for active magnetic regenerative (AMR) refrigeration.

Although the maximum value of $|\Delta S_M|$ in LCMCO is slightly decreased compared with that of LCNO, the half height width of the $|\Delta S_M|$ peak is increased by Co doping. Figure 5.6(a) shows the magnetic field dependence of the full-width-at-half-maximum temperature interval, $\delta T_{\text{FWHM}}$, of the LCNO and LCMCO samples for field change from 1 to 5 T. The $\delta T_{\text{FWHM}}$ increases almost linearly with the field change. It should be noted that the $\delta T_{\text{FWHM}}$ value of the $\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{0.95}\text{Co}_{0.05}\text{O}_3$ is approximately double that of the $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$. Figure 5.6(b) shows the dependence of the refrigerant capacity of the sample on the field change from 1 to 5 T. The RCP also increases almost linearly with field change up to 5 T. The RCP value of $\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{0.95}\text{Co}_{0.05}\text{O}_3$ (308 J/kg for a field change of 5 T) is about 1.5 times that of $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ (218 J/kg for 5 T change). The RCP value in LCMCO is enhanced from 218 J/kg to 308 J/kg by 5% Co doping under a magnetic field of 5 T. The relatively high RCP arises from the strongly asymmetric distribution of $|\Delta S_M|$ and the large $\delta T_{\text{FWHM}}$. In addition, the composition inhomogeneity and/or non-stoichiometry of the phase may also contribute to the large $\delta T_{\text{FWHM}}$. This suggests that the magnetic entropy change alone is insufficient to justify the potential for practical application of a magnetic refrigerant.
Fig. 5.6 (a) Magnetic field dependence of full width at half maximum of $\delta T$ ($\delta T_{\text{FWHM}}$) for $\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{0.95}\text{Co}_{0.05}\text{O}_3$ and $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$. (b) Magnetic field dependence of relative cooling power (RCP) for $\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{0.95}\text{Co}_{0.05}\text{O}_3$ and $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$.

For a material to be suitable as a magnetic refrigerant, it should show a large adiabatic temperature change, $\Delta T_{\text{ad}}$ which is calculated by the equation

$$\Delta T_{\text{ad}}(T, \Delta B) = -\frac{T}{c_p(T, B)} \Delta S_M(T, \Delta B)$$  \hspace{1cm} (5.6)

This change depends on the magnetic entropy change as well as the specific heat. Figure 5.7 shows the adiabatic temperature change of $\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{0.95}\text{Co}_{0.05}\text{O}_3$. The estimated $\Delta T_{\text{ad}}$ values are 1.42, 2.18, and 3.20 K for field change from 0 to 1, 2, and
5 T, respectively. The maximum adiabatic temperature change is about 40% of that for Gd, but close to the values of some manganite perovskites [27].

Fig. 5.7 Temperature dependence of the adiabatic temperature change of the La$_{0.7}$Ca$_{0.3}$Mn$_{0.95}$Co$_{0.05}$O$_3$ sample for a field change from 0 to 1, 2, and 5 T.

Resistance was measured using the conventional four-probe method. Figure 5.8 presents the temperature dependence of the resistivity under different magnetic fields for the two La$_{0.7}$Ca$_{0.3}$Mn$_{0.95}$Co$_{0.05}$O$_3$ and La$_{0.7}$Ca$_{0.3}$MnO$_3$ samples.
Fig. 5.8 Temperature dependence of the resistivity ($\rho$) measured under different magnetic fields for La$_{0.7}$Ca$_{0.3}$Mn$_{0.95}$Co$_{0.05}$O$_3$ (a) and La$_{0.7}$Ca$_{0.3}$MnO$_3$ (b).

The MR ratio, defined as MR = ($\rho(0)/\rho(H)$ $-$ 1), exhibits a maximum of ~65.03 % and 82.5%, respectively, for the La$_{0.7}$Ca$_{0.3}$Mn$_{0.95}$Co$_{0.05}$O$_3$ and La$_{0.7}$Ca$_{0.3}$MnO$_3$ samples at $T_C$ under magnetic field of 1 T, as shown in Figure 5.9. This value is higher than those of many other manganite perovskites.
5.5 Conclusions

We have studied the influence of first and second order magnetic phase transitions on the MCE and the relative cooling power (RCP) of LCMO and LCMCO samples. It is shown that the first order magnetic transition material LCMO has a larger MCE in terms of magnitude, but the peak is confined to a narrow temperature region. The LCMCO yields a slightly smaller MCE at \( T_C \), with a broader peak spanning a wider temperature range. This results in a larger value of the RCP around \( T_C \). The refrigeration capacity (RCP) is enhanced in LCMCO by about 41\% due to small changes resulting from Co doping, which makes LCMCO more useful for practical application. A higher RCP and a magnetic entropy change that can be induced at low field make LCMCO a potential candidate material in magnetic refrigeration technology.
References


CHAPTER 6

LARGE MAGNETIC ENTROPY CHANGE NEAR ROOM TEMPERATURE
IN La0.7(Ca0.27Ag0.03)MnO3 PEROVSKITE

6.1 Introduction

Doped manganites with the general formula of $R_{1-x}M_xMnO_3$ ($R$ = La, Pr, Nd, etc., and $M$ = Sr, Ca, Ba, etc.) exhibit a rich variety of phenomena such as colossal magnetoresistance [1] and a large magnetocaloric effect (MCE) [2]. The latter effect, which is represented by an isothermal change in the magnetic entropy or an adiabatic change in the temperature in magnetic field, forms the basis for magnetic refrigeration [3]. Manganites are relatively easy to synthesize, are tunable by adjustment of the doping concentration, and are considered promising candidates for magnetic refrigeration at various temperatures, as reviewed by Phan and Yu [2]. The main requirements for a magnetic material to possess a large change in magnetic entropy, $|\Delta S_M|$, are a large spontaneous magnetization as well as a sharp drop in the magnetization associated with the ferromagnetic (FM) to paramagnetic (PM) transition at the Curie temperature, $T_C$ [4, 5]. It should be noted that the magnitude of the MCE in compounds which undergo a structural transition in conjunction with the magnetic transition is increased due to the additional lattice entropy contribution [6]. Phan and Yu have provided an overview of magnetocaloric properties in perovskite manganese oxides [2]. The largest reported value of $|\Delta S_M|$ in the La$_{1-x}$Ca$_x$MnO$_3$ manganites is found to be 6.25 J/kgK at 216 K upon a magnetic field change of 1 T.
for $x = 0.3$, a compound which exhibits a first order paramagnetic to ferromagnetic transition \[7\]. According to previous reports, the $La_{0.7}Ca_{0.3}MnO_3$ compound exhibits different $|\Delta S_M|$ values, depending on the elaborating technique and the oxygen stoichiometry. In fact, under a magnetic field change of 1 T, Phan et al. \[8\] found that $|\Delta S_M|_{\text{max}}$ is 1.38 J/kgK at 256 K, while the maximum value of the magnetic entropy $|\Delta S_M|_{\text{max}}$ observed by Ulyanov et al. \[9\] reaches 7 J/kgK at 242 K. Similarly to the doping at A sites with divalent elements, monovalent substitution is expected to introduce large potential fluctuations leading to large magnetocaloric effects. Tang et al. \[10\] measured the MCE in $La_{0.7}Ag_{0.3}MnO_3$ compound. The $|\Delta S_M|_{\text{max}}$ was found to be 1.35 J/kgK around room temperature for a magnetic field variation, $\Delta H$, of 1 T, while for a $La_{0.8}Na_{0.2}MnO_3$ sample, the $|\Delta S_M|_{\text{max}}$ value observed by Hou et al. \[11\] was found to be 0.43 J/kgK at 333 K for an applied magnetic field change of 1 T. Bejar et al. \[12\] measured the MCE in $La_{0.7}Ca_{0.3-x}K_xMnO_3$, and the $|\Delta S_M|_{\text{max}}$ was found to be 3.95 J/kgK at 270 K upon a magnetic field change of 2 T for $x = 0.05$, while for $La_{0.65}Ca_{0.35-x}K_xMnO_3$, the entropy change value observed by Koubaa et al. \[13\] was found to be 3.18 J/kgK at 310 K upon a magnetic field change of 2 T for $x = 0.2$. For their $La_{0.7}Sr_{0.3-x}K_xMnO_3$ sample, Koubaa et al. \[14\] showed that the $|\Delta S_M|_{\text{max}}$ was about 2.15 J/kgK upon a magnetic field change of 2 T for $x = 0.15$. The entropy change value measured by the same author \[15\] for $La_{0.7}Sr_{0.3-x}Na_xMnO_3$ was found to be 2.04 J/kgK under a magnetic field change of 2 T. Again, they \[16\] measured the MCE in $La_{0.65}Ba_{0.3}MnO_3$, and the $|\Delta S_M|_{\text{max}}$ was found to be 1.3, 1.43, and 1.34 J/kgK upon a magnetic field change of 2 T for $M = Na$, Ag, and K, respectively, while they also showed the entropy change value to be about 1.6 J/kgK for $La_{0.7}Sr_{0.1}Ag_{0.2}MnO_3$ at 315 K \[17\]. Finally, they \[18\] measured the MCE in $La_{0.65}Ca_{0.35-x}Ag_xMnO_3$, and the maximum entropy change, $|\Delta S_M|_{\text{max}}$, corresponding to
a magnetic field variation of 1 T, was found to be 1.65, 1.14, 1.01, and 0.89 J/kgK for \( x = 0.05, 0.1, 0.15, \) and 0.2, respectively. It has been generally shown that the most prominent magnetic and magneto-transport properties in substituted manganites are obtained for samples having Mn\(^{4+}\) amounts of around 33\% [19]. In assessing the usefulness of a magnetic refrigerant material, the refrigerant capacity or relative cooling power (RCP), which is a measure of the amount of heat transfer between the cold and hot sinks in an ideal refrigeration cycle, is considered to be the most important factor, however, not the magnetic entropy change alone [20-22]. The RCP depends not only on the magnitude of \( \Delta S_M \), but also on the temperature dependence of \( \Delta S_M \) (e.g., the full width at half maximum of the \( \Delta S_M \) (T) peak) [20, 22]. In this context, a good magnetic refrigerant material with large RCP requires both a large magnitude of \( \Delta S_M \) and a broad width of the \( \Delta S_M \) (T) curve. Most previous studies on monovalent substitution were focused mainly on exploring large MCE (large magnitudes of \( \Delta S_M \)) and did not consider in detail the issues of RCP and hysteretic losses. Thus, from fundamental and practical perspectives, it is essential to understand the influence of the magnetic phase transitions on both the MCE and the RCP in these materials. In the present chapter, we investigate the MCE related to the effects of Ag doping in La\(_{0.7}(\text{Ca}_{1-x}\text{Ag}_x)_{0.3}\)MnO\(_3\), which can be a suitable candidate as a working substance in magnetic refrigeration near room temperature.

### 6.2 Experimental

Powder samples of La\(_{0.7}(\text{Ca}_{1-x}\text{Ag}_x)_{0.3}\)MnO\(_3\) were synthesized using the standard solid-state reaction method at high temperature, by mixing La\(_2\)O\(_3\), CaCO\(_3\), Ag\(_2\)CO\(_3\), and MnO\(_2\) of up to 99.9\% purity in the desired proportions. The starting materials
were intimately mixed in an agate mortar and first fired at 700°C for 12 h. Then, the mixture was reground and again fired at 900°C for 12 h. The mixture was ground again for a third time, pressed into pellets, and fired at 1100°C for 12 h to obtain better crystallization. Finally, the sample was again reground, pressed into pellets, and sintered at 1350°C for 24 h. Powder X-ray diffraction (XRD) patterns were obtained with Cu Kα radiation at room temperature. Structural analysis was carried out using the standard Rietveld method [23, 24]. Magnetization measurements versus temperature in the range of 5–300 K and versus applied magnetic field up to 5 T were carried out using a physical properties measurement system (PPMS). MCE results were deduced from the magnetization measurements versus magnetic applied field up to 5 T at several temperatures.

6.3 Results

6.3.1 Structural and magnetic properties

The phase composition and crystal structure of the samples were characterized by X-ray diffraction (XRD). The XRD patterns of the La$_{0.7}$(Ca$_{1-x}$Ag$_x$)$_{0.3}$MnO$_3$ samples are shown in Figure 6.1. The X-ray diffraction analysis shows that the samples with $x \leq 0.2$ are mainly composed of orthorhombic perovskite structure phases. The sample with $x = 0.7$ has two phases (perovskite structure and Ag metal phase), and the one with $x = 1.0$ has three phases (perovskite structure, Ag metal, and Mn$_3$O$_4$ phase). As might be expected, the lattice parameters, as well as volume of the unit cell, are continuously increased with increasing $x$ due to the substitution of large Ag$^+$ (1.28 Å) ions for smaller Ca$^{2+}$ (1.18 Å) ions. Our results agree well with those obtained on the
effects of K$^+$ doping on the physical properties of $\text{La}_{0.65}\text{Ca}_{0.35-x}\text{K}_x\text{MnO}_3$ by Koubaa et al. [13], but differ from those obtained for the effects of Ag$^+$ doping on the physical properties of $\text{La}_{0.65}\text{Ca}_{0.35-x}\text{Ag}_x\text{MnO}_3$ by Koubaa et al. [18]. Lattice parameters and unit cell volumes are listed in Table 6.1.

**Table 6.1** Lattice parameters of the $\text{La}_{0.7}(\text{Ca}_{1-x}\text{Ag}_x)_{0.3}\text{MnO}_3$ samples.

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<td>$x = 0.7$</td>
<td>5.52073</td>
<td>5.47321</td>
<td>7.77363</td>
<td>234.889</td>
</tr>
<tr>
<td>$x = 1.0$</td>
<td>5.54087</td>
<td>5.47698</td>
<td>7.78994</td>
<td>236.403</td>
</tr>
</tbody>
</table>

**Fig. 6.1** XRD patterns for $\text{La}_{0.7}(\text{Ca}_{1-x}\text{Ag}_x)_{0.3}\text{MnO}_3$ samples.
Magnetization measurements as a function of temperature in an applied magnetic field of 200 Oe (Figure 6.2) showed that all our synthesized samples exhibited a paramagnetic to ferromagnetic transition with decreasing temperature. With increasing Ag content, the Curie temperature $T_C$ increases from 250 K for $x = 0$ to 270 K for $x = 1$. As a result of increasing average ionic radius in the A site, $<r_A>$, the values of $T_C$ shifted to higher temperature with increased Ag doping content. The increasing $T_C$ (or magnetic coupling versus double exchange interaction) can be due to increasing $<r_A>$ or an increasing Mn$^{4+}$/Mn$^{3+}$ ratio. In this case, the increasing $T_C$ is due to the first former [25].

![Fig. 6.2 Temperature dependence of magnetization at 200 Oe for La$_{0.7}$(Ca$_{1-x}$Ag$_x$)$_{0.3}$MnO$_3$ samples.](image)

In order to evaluate the MCE, the isothermal magnetization curves of the samples were measured with a field step of 0.05 mT in the magnetic field range of 0-5 T and over a range of temperatures around $T_C$. Such families of $M$ ($H$) curves are shown in Figure 6.3(a-d).
It is worth mentioning that around the $T_C$, the samples shown in both (a) and (b) feature S-shaped magnetization, which is typical for metamagnetic materials [26], whereas this property is absent for the (c) and (d) samples.

**Fig. 6.3** Magnetization evolution vs. magnetic applied field at several temperatures for $\text{La}_0.7(\text{Ca}_{1-x}\text{Ag}_x)_{0.3}\text{MnO}_3$ samples: (a) $x = 0$, (b) $x = 0.1$, (c) $x = 0.7$, and (d) $x = 1$.

It is also worth noting that a large proportion of the changes in the magnetization occur in the relatively low field range ($< 2.0$ T), which is beneficial for the application of MCE materials. For the samples in (a) and (b), the curves reveal a strong variation in the magnetization around the Curie temperature, indicating that there is a possibility of obtaining a large magnetic entropy change associated with the FM-PM transition occurring at $T_C$. 

140
To understand the nature of the magnetic transition of the samples, Arrott plots of $M^2$ versus $H/M$, covering a broad temperature range around $T_C$, are plotted in Figure 6.4. Clearly, an inflection point and negative slopes are observed in Figure 6.4(a) and (b), indicating the occurrence of a first order magnetic transition.

Neither an inflection point nor negative slopes are observed in Figure 4(c) and (d), proving the occurrence of a second order magnetic transition. Therefore, it is expected that doping with Ag weakens the first order magnetic phase transition and that at higher Ag doping, the nature of the phase transition is second order.
6.3.2 Magnetocaloric properties

The entropy change as a function of temperature in different magnetic fields ranging from 0 to 5 T for the samples x = 0.0, 0.1, 0.7, and 1 are shown in Figure 6.5. The maximum values of $|\Delta S_M|$ corresponding to an external field change of 2 T for those samples are about 5.71, 4.5, 2.47, and 2.59 J/kgK, respectively, and 7.528, 7.63, 5.04, and 4.83 J/kgK, respectively, for a 5 T magnetic field. $|\Delta S_M|$ exhibits a linear rise with increasing field, as shown in Figure 6.5, which indicates that a much larger entropy change is to be expected at higher magnetic field, satisfying thereby the effects of spin-lattice coupling associated with the changes in the magnetic ordering process in the samples [27]. Besides this, we note that for the La$_{0.7}$(Ca$_{0.3}$)MnO$_3$ and La$_{0.7}$(Ca$_{0.27}$Ag$_{0.03}$)MnO$_3$ samples, the maximum magnetic entropy change (5.71 J/kgK at 251 K and 4.5 J/kgK at 263 K for a 2 T field change) is larger, about 90% of that for pure Gd for a 2 T field change [28], and also larger than for many other perovskite materials [14-16, 18, 25, 29-31], but smaller than for the most conspicuous magnetocaloric material, Gd$_5$(Si$_2$Ge$_2$) [28]. In particular, these values are larger than the values reported by Koubaa et al. (14-16, 18). An abrupt variation in the magnetization and a sharp volume change at $T_C$ are two of the key conditions required for a large $|\Delta S_M|$. For the samples with x = 0.7 and 1.0, the transitions are of second order, so the above-mentioned conditions are not present, and therefore, $|\Delta S_M|$ falls considerably. The giant magnetic entropy changes in these magnetic materials suggest that they could be potential candidates for magnetic refrigeration. However, before magnetic refrigeration becomes a viable cooling technology, one must reduce the applied magnetic field, so as to allow the use of permanent magnets instead of superconducting magnets as the magnetic-field source. Therefore, a very important
task is to search for novel magnetic materials possessing giant low-field induced MCEs. Our results provide a possibility for the development of magnetic refrigerant substances that are operable with a permanent magnet rather than a superconducting one as the magnetic field source.

Fig. 6.5 Magnetic entropy change of La_{0.7}(Ca_{1-x}Ag_x)_{0.3}MnO_3 samples: (a) x = 0, (b) x = 0.1, (c) x = 0.7, and (d) x = 1 samples as a function of temperature for different magnetic field intervals.

On the other hand, the cooling efficiency of magnetic refrigerants is evaluated by means of the so-called relative cooling power (RCP), which corresponds to the amount of heat transferred between the cold and the hot sinks in the ideal refrigeration cycle defined by \( \text{RCP} = |\Delta S_M| \times \delta T_{\text{FWHM}} \), where \( \delta T_{\text{FWHM}} \) means the full width at half-maximum of the magnetic entropy change curve. The RCP values for
the La$_{0.7}$Ca$_{0.3}$MnO$_3$, La$_{0.7}$Ca$_{0.27}$Ag$_{0.03}$MnO$_3$ and the La$_{0.7}$Ag$_{0.3}$MnO$_3$ samples exhibit
an almost linear rise with increasing field, as shown in Figure 6.6. The RCP values of
La$_{0.7}$Ca$_{0.27}$Ag$_{0.03}$MnO$_3$ and La$_{0.7}$Ca$_{0.3}$MnO$_3$ are 270.8 J/kg and 218 J/kg for a 5 T field
change. These values are, however, lower than the RCP value reported for Gd,
although they are high enough compared with many perovskite materials.

![Figure 6.6](image)

**Fig. 6.6** Relative cooling power values (RCP) vs. applied magnetic field for the
La$_{0.7}$Ca$_{0.3}$MnO$_3$, La$_{0.7}$Ca$_{0.27}$Ag$_{0.03}$MnO$_3$, and La$_{0.7}$Ag$_{0.3}$MnO$_3$ samples.

From Fig. 6.6, we can conclude that even though at low field the $|\Delta S_M|$ value of
La$_{0.7}$Ca$_{0.3}$MnO$_3$ is slightly higher than that of La$_{0.7}$Ca$_{0.27}$Ag$_{0.03}$MnO$_3$, the value of
RCP for the La$_{0.7}$Ca$_{0.27}$Ag$_{0.03}$MnO$_3$ is much higher than for the La$_{0.7}$Ca$_{0.3}$MnO$_3$, and
this is only due to the uniform distribution of the $|\Delta S_M|$, which is desirable for an
Ericsson-cycle magnetic refrigerator.
Furthermore, we recall that hysteretic losses (magnetic and thermal hysteresis) are often involved in first order magnetic phase transitions [26], which would again justify the calculated RCP values. Because these hysteretic losses are the costs in energy to drive one cycle of the magnetic field, they must be considered when calculating the usefulness of a magnetic refrigerant material being subjected to field cycling [21].

Fig. 6.7 Isothermal magnetization for La\(_{0.7}(\text{Ca}_{1-x}\text{Ag}_x)_{0.3}\text{MnO}_3\) samples measured at 260 K.

To evaluate possible hysteretic losses involved in the magnetic phase transitions in the La\(_{0.7}\text{Ca}_{0.3}\text{MnO}_3\), La\(_{0.7}\text{Ca}_{0.27}\text{Ag}_{0.03}\text{MnO}_3\), and La\(_{0.7}\text{Ag}_{0.3}\text{MnO}_3\) samples, we measured the M-H curves at temperatures around \(T_C\). Figure 6.7 shows, for example, the M (H) curves measured at 260 K (near \(T_C\)). Interestingly it can be seen that even though La\(_{0.7}\text{Ca}_{0.3}\text{MnO}_3\) and La\(_{0.7}\text{Ca}_{0.27}\text{Ag}_{0.03}\text{MnO}_3\) show a first order phase transition, the hysteresis loss is almost negligible, so the effective refrigeration capacity (RCP\(_{\text{eff}}\))
is the same as the RCP value, which is desirable for an efficient magnetic refrigerant cycle. The lack of any hysteresis loss indicates that the MCE is fully reversible. This also means that strong magnetoelastic coupling is present, while there is no magnetoplastic coupling in these materials. So, there should be no potential work hardening of these materials as a result of cycling over the first order transition. The heat flow through the cooling engine is the mass of working medium times the cycle frequency times the Curie temperature times the entropy change. We know that Ag has the highest thermal conductivity of any metal. So, we expect that the heat conductivity of the substance should be increased.

6.4. Discussion

A change in the nature of the magnetic transition suggests a variation in the nature of the magnetic coupling. Goodenough has suggested that in manganites, the static-cooperative Jahn-Teller (JT) distortions are replaced in the ferromagnetic phase by dynamic JT distortions that introduce vibrational modes into the spin-spin interaction, giving rise to an extra superexchange term [32, 33]. That is, in our case, there is a strong influence of lattice effects in the samples at $x = 0$ and 0.1, which is reflected in strong variations in several physical properties supporting the first order character of the transition [34]. The large magnetic entropy change in perovskite manganites is believed to originate from the role of spin–lattice coupling in the magnetic ordering process [35]. Due to strong coupling between spin and lattice, significant lattice change accompanying the magnetic transition in perovskite manganites has been observed [36, 37]. The lattice structural change in the Mn–O bond distances and Mn–O–Mn bond angles would in turn favour the spin ordering.
Therefore, a more abrupt change in magnetization near $T_C$ occurs and results in a large magnetic entropy change. From the observation of large magnetic entropy change and the fact that a strong spin–lattice coupling exists in perovskite manganites, a conclusion can be drawn that a strong spin–lattice coupling in the magnetic transition process would lead to an additional magnetic entropy change near $T_C$ and consequently favour the MCE.

Again the larger size of the Ag ion compared to the Ca ion causes the A-site average ionic radius $<r_A>$ to increase. This leads to a change in the Mn–O bond length and the Mn–O–Mn bond angle. Consequently, it increases the tolerance factor, $t$, and the electron bandwidth, $W$, which both contribute to the increase in the transition temperature and have a strong influence on the high-field magnetic entropy change. The larger internal stress caused by the larger $<r_A>$ may result in a lower rotation of MnO$_6$ and a smaller volume of thermal expansion, accompanied by an increase in the magnetization at $T_C$. A larger MCE is consequently observed. The large low-field induced MCEs with negligible hysteresis loss in these materials provide a possibility for the development of magnetic refrigerant substances that are operable with a permanent magnet rather than a superconducting one as the magnetic field source.
6.5 Conclusions

In this work, we have studied the MCE for La$_{0.7}$(Ca$_{1-x}$Ag$_x$)$_{0.3}$MnO$_3$ compounds. Doping with monovalent Ag increases the Curie temperature and weakens the first order phase transition, so that at higher Ag doping levels, the nature of the phase transition is second order. The Ag doped La$_{0.7}$Ca$_{0.27}$Ag$_{0.03}$MnO$_3$ compound showed an increase in $|\Delta S_M|$ of 4.5 J/kgK for a 2 T field change and of 7.63 J/kgK for a 5 T field change, respectively, at the Curie temperature of 263 K, as well as a higher RCP value (270.8 J/kg) without any hysteresis loss. These results indicate that La$_{0.7}$Ca$_{0.27}$Ag$_{0.03}$MnO$_3$ may be a good candidate for magnetic refrigeration.
References


CHAPTER 7

ANISOTROPIC AND LARGE MAGNETOCALORIC EFFECT IN 
La$_{0.7}$Ca$_{0.3}$MnO$_3$ SINGLE CRYSTAL WITH ANOMALOUS 
MAGNETIZATION

7.1 Introduction

The magnetocaloric effect (MCE) is a basic characteristic of magnetic materials and is understood as an isothermal magnetic entropy change or an adiabatic temperature change of a magnetic material upon the application of a magnetic field. It has been shown that the heating and cooling in the magnetic refrigeration process are proportional to the size of the magnetic moments and to the applied magnetic field. That is why research on magnetic refrigeration has been exclusively conducted on heavy rare-earth elements and their compounds [1, 2]. Among the rare-earth metals, gadolinium was found to show the highest MCE [2]. Nonetheless, the cost of gadolinium as a magnetic refrigerant is quite expensive (~$4000/kg), and this actually limits the usage of it as an active magnetic refrigerant (AMR) in magnetic refrigerators. Since the discovery of the giant MCE phenomenon, a giant MCE has been found in a large variety of magnetic materials, including Gd$_5$(Si$_{1-x}$Ge$_x$)$_4$, MnAs$_{1-x}$Sb$_x$, MnFe(P$_{1-x}$As$_x$), La(Fe$_{13-x}$Si$_x$), and RM$_2$ (where R = rare earth, M = Al, Co, Ni) [3-8]. Further efforts to discover new materials, especially materials without rare-earth elements and exhibiting large MCE in response to low applied field, are of significant importance. Among them, perovskite-type manganese oxide materials
[9-13] having large MCEs are believed to be good candidates for magnetic refrigeration at various temperatures. In view of the AMR requirements, note that besides the requirement that an AMR material should have a large magnetic entropy change ($\Delta S_M$) induced by a low magnetic field change, the $\Delta S_M$ distribution also plays an important role in achieving magnetic cooling efficiency. [14, 15] Unfortunately, a non-uniform $\Delta S_M$ distribution, which is not beneficial for an Ericsson-cycle magnetic refrigerator, has been found for several AMR materials, such as gadolinium [1] and polycrystalline perovskite manganites, due to structural inhomogeneity [11, 12]. In this context, study of the MCE in lanthanum manganite single crystals can be of great interest, because the absence of grains in these materials would be expected to allow a uniform $\Delta S_M$ distribution, which is desirable for an Ericsson-cycle magnetic refrigerator. In this chapter, we report on the excellent magnetocaloric properties of $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ single crystal, with which the requirements for an AMR material can be fulfilled. We estimated the spin fluctuation parameters by adopting Takahashi’s developed spin-fluctuation theory and calculated $1/\chi$. It was observed that the magnetic property of $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ is weakly itinerant ferromagnetic (WIF).

7.2. Experimental

A high-quality single crystal of $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ was prepared by the floating zone method, using an infrared radiation convergence-type image furnace that consists of four mirrors and a halogen lamp. The starting ceramic rods were synthesized by the standard methods of solid-state reaction of a stoichiometric mixture of $\text{La}_2\text{O}_3$, $\text{CaCO}_3$, and $\text{MnO}_2$. X-ray diffraction data confirmed the quality of the single crystal.
The magnetic measurements were performed using a physical properties measurement system 14 T (PPMS-14T) magnetometer.

7.3. Results and Discussion

The phase composition and crystal structure of the sample was characterized by X-ray diffraction (XRD), and high purity and perovskite structure were confirmed. The XRD pattern of the sample is shown in Figure 7.1. A single-phase diffraction pattern was obtained, yielding an orthorhombic structure with the Pnma space group.

![XRD pattern of the La$_{0.7}$Ca$_{0.3}$MnO$_3$ single crystal.](image)

**Fig. 7.1** XRD pattern of the La$_{0.7}$Ca$_{0.3}$MnO$_3$ single crystal.

Figure 7.2 shows the temperature dependence of the magnetization (M-T curves) in a 200 Oe field with the direction of the magnetic field along both the $ab$-plane and the $c$-direction of the La$_{0.7}$Ca$_{0.3}$MnO$_3$ single crystal. The Curie temperature ($T_C$), defined by the maximum in the absolute value of $dM/dT$, has been determined from the M-T
curve to be about 245 K. The magnetization in the $ab$-plane is much bigger than that in the $c$-direction, suggesting that the magnetic easy axis lies in the $ab$-plane of the crystal. A steep change in the magnetization occurs at $T_C$, implying a first-order transition, leading to expectations that the material will show a large MCE near the Curie temperature.

![Graph of magnetization vs. temperature](image)

**Fig. 7.2** Temperature dependence of magnetization along the $ab$-plane and the $c$-direction of La$_{0.7}$Ca$_{0.3}$MnO$_3$ single crystal. Inset: hysteresis curve of the sample at 265 K.

In order to confirm this, the isothermal magnetization of the sample was measured in the range of 0-5 T for a range of temperatures around $T_C$. To ensure the readability of the figure, only some of isothermals are presented in Fig. 7.3. It can be seen from Figure 7.3 that there is a drastic change in the magnetization around $T_C$, indicating a large magnetic entropy change.
In order to evaluate the MCE of the present material, we calculated the changes in the magnetic entropy $\Delta S_M$ caused by the application of external magnetic fields from the isothermal curves of magnetization versus applied field. Figure 7.4 shows the magnetic entropy change as a function of temperature in different magnetic fields ranging from 0 to 5 T for (a) the $ab$-plane and (b) the $c$-direction.
Fig. 7.4 Magnetic entropy change $|\Delta S_M|$ as a function of temperature for the magnetic field along (a) the $ab$-plane and (b) the $c$-direction of the La$_{0.7}$Ca$_{0.3}$MnO$_3$ single crystal.

The maximum value of $|\Delta S_M|$, corresponding to external field changes of 1.5 T and 5 T for both the $ab$-plane and the $c$-direction reaches about 3.33 and 2.364 J/kgK, and 7.668 and 6.412 J/kgK, respectively. These values are higher than the result found by Phan et al. [16] and Tian et al. [17] for the same single crystal La$_{0.7}$Ca$_{0.3}$MnO$_3$. We have compared the peak values of $|\Delta S_M|$ between the $ab$-plane and $c$-direction as a function of magnetic field. In the whole field range from 0 to 5 T, $|\Delta S_M|$ in the $ab$-plane is larger than along the $c$-direction. The maximum differences at 1.5 T and 5 T
are about 1 and 1.37 J/kgK, respectively. It is apparent that the magnetic entropy change is anisotropic with a larger value in the $ab$-plane. The large anisotropic magnetic entropy change in La$_{0.7}$Ca$_{0.3}$MnO$_3$ single crystal is ascribed to the strong magnetocrystalline anisotropy. Another interesting result is that the magnitude of the large low-field magnetic entropy change along the $ab$-plane of the single crystal is 3.3 J/kgK for a magnetic field change of 1.5 T. This value of $|\Delta S_M|$ is of the same magnitude as that of Gd [2] and also is larger than for many cubic perovskite manganites [18-19]. This low-field MCE is beneficial for the practical application of MCE because the low field can be directly supplied by Nd$_2$Fe$_{14}$B or other permanent magnets. This low-field large magnetic entropy change in the La$_{0.7}$Ca$_{0.3}$MnO$_3$ single crystal is due to the rapid change in the magnetization near the Curie temperature in the easy magnetizing plane. The symmetrical and uniform distribution of $\Delta S_M$ is observed for single crystal, even in high fields, and is much more uniform than for gadolinium and polycrystalline manganites [12, 20-23]. This is ascribed to the absence of grains in such a single-crystalline material, where there was a symmetric and uniform distribution of the temperature dependence of magneto-resistance [24, 25]. In contrast to the single crystalline manganite, considerable and asymmetrical variations in the $\Delta S_M$ curves with external magnetic field, particularly under high magnetic fields, for the polycrystalline manganites were observed and are likely due to the grain boundary effects [24-26]. The non-uniform distribution of $\Delta S_M$ in polycrystalline perovskite manganites is also believe to be attributable to a spread of the ferromagnetic clusters caused by the inhomogeneity of structure and stoichiometry [21, 22].
A first-order magnetic transition is of particular importance for giant MCE. The first order nature of the phase transition of the single crystal can be confirmed by the Banerjee criterion [27]. According to the Banerjee criterion, a negative slope in a relatively small $M^2$ region above $T_C$ indicates that the magnetic phase transition is first order, as is shown in Figure 7.5. The curves have negative slopes or inflection points above $T_C$, also indicating a metamagnetic transition from a paramagnetic to a ferromagnetic state [28].

**Fig. 7.5** Arrott plots of the La$_{0.7}$Ca$_{0.3}$MnO$_3$ single crystal with the direction of the magnetic field along (a) the $ab$-plane and (b) the $c$-direction.
To gain more insight into the magnetic transition, the Landau coefficients $c_1(T_C)$, $c_3(T_C)$, and $c_5(T_C)$ were determined by fitting the magnetic field against magnetization using the equation

\[
\mu_0 H = c_1(T)M + c_3(T)M^3 + c_5(T)M^5
\]

(7.1)

Fig. 7.6 Temperature dependence of Landau coefficients for La$_{0.7}$Ca$_{0.3}$MnO$_3$ single crystal along (left) the $ab$-plane and (right) the $c$-direction. The units of $c_1(T)$, $c_3(T)$, and $c_5(T)$ are $T^2$ gm/emu, $T^4$ gm$^3$/emu$^3$, and $T^6$ gm$^5$/emu$^5$, respectively.
The details of the fitting method have been reported elsewhere [29]. The temperature
dependence of the Landau coefficients derived from these fitting results is shown in
Figure 7.6. The value of $c_3(T_C)$ at $T_C$ is negative for both field directions, again
confirming that the magnetic phase transition is first-order.

In Figure 7.5, $M^2$ does not show a linear relation, but does have a convex curvature
against $H/M$ for every temperature. The convex curvature of $M^2$ against $H/M$
reminds us of typical weakly itinerant ferromagnet (WIF) property of the
magnetization which is found in MnSi [30]. To the best of our knowledge, the
convex curvature of $M^2$ against $H/M$ has been reproduced only by Takahashi’s
developed spin-fluctuation theory so far [31]. In this theory, it is assumed that the
sum of the zero point and thermal spin fluctuations is conserved against $T$, and as a
consequence of this assumption, he argued the importance of the sixth coefficient of
the free energy when the system has a relatively large $\eta = (T_C/T_0)^{1/3}$ value. Here, $T_0$
characterizes the energy width of the dynamical spin-fluctuation spectrum. In such a
case, the magnetization obeys the following relation at $T_C$ because the fourth
coefficient becomes zero:

$$H^* = \frac{TA}{3(2+\sqrt{5}) T_C^2} p^5 \quad (7.2)$$

where $H^* = H/2\mu_B$ and $p$ are the magnetic field and the magnetization respectively.
The parameter $T_A$ characterizes the dispersion of the static magnetic susceptibility in
wave vector ($q$) space. We plotted the isothermal magnetization curves in the form
of $M^4$ vs. $H/M$, as shown in Figure 7.7. Here, $M^4$ is almost linear against $H/M$ around
$T_C \approx 245$ K. Strictly speaking, $M^4$ is not completely linear with respect to $H/M$
around $T_C$, as seen in Figures 7.7 and 7.8(b). However, most itinerant ferromagnets
show concave behaviour when plotted in the form of $M^4$ vs. $H/M$ [32].
Furthermore, $M^4$ of the typical itinerant ferromagnetic compound MnSi is also not exactly linear with respect to $H/M$ [30]. According to Takahashi’s theory, in the case of the coefficient of $M^4$ in the Landau expansion of free energy being zero, $M^4$ becomes linear against $H/M$. Thus, complete linearity is only obtained in a delicate condition. $La_{0.7}Ca_{0.3}MnO_3$ is not just on this condition, but seems to be very near it, as well as having a quantum critical point due to spin fluctuations.

![Fig. 7.7](image)

**Fig. 7.7** $M^4$ versus $H/M$ for $La_{0.7}Ca_{0.3}MnO_3$ single crystal, along the $ab$-plane at various temperatures. Around $T_C$, $M^4$ is almost linear against $H/M$.

We show the results of linear fitting to $M^2$ and $M^4$ plotted against $H/M$ in Figure 7.8. This figure clearly shows that at $T_C \approx 245$ K, the $M^4$ curve shows higher linearity against $H/M$ than the $M^2$ curve against $H/M$. Equation (7.2) can be transformed to the relation of $M^4$ vs. $H/M$ as

$$M^4 = 1.17 \times 10^{19} \left( \frac{T^2_C}{T^3_A} \right)(H/M) \quad (7.3)$$
where \( M \) and \( H \) are in units of emu/g and Oe, respectively. By putting the value of the slope at \( T_C \approx 245 \) K into Eq. (7.3), we obtained \( T_A \) as \( 2.5 \times 10^6 \) K.

According to the SCR (self-consistent renormalization) theory for WIF materials [33-35], \( T_C \) is related to \( P_s, T_A, \) and \( T_0 \) by the following relation:

\[
T_C = (60c)^{3/4} P_s^{3/2} T_A^{3/4} T_0^{1/4}
\]  

(7.4)

where \( c \) and \( P_s \) are constants equals to 0.335 and 2.76. By putting the value of \( T_A \) determined by Takahashi’s theory into Eq. (7.4), we obtained \( T_0 \) as \( 6 \times 10^{-4} \) K.

**Fig. 7.8** Linear fitting for (a) \( M^2 \) versus \( H/M \) and (b) \( M^4 \) versus \( H/M \) for La_{0.7}Ca_{0.3}MnO_{3} single crystal along the \( ab \)-plane at \( T = 245 \) K. Straight lines are the results of linear fitting to the data.
We estimated the saturation magnetization, $M_S(T)$, below $T_C$ and the reciprocal magnetic susceptibility, $1/\chi$ ($= \lim_{H \to 0} H/M$) above $T_C$ from Figures 7.5(a) and 7.7, respectively. The $M_S$ and $1/\chi$ are estimated as the values of the intersections of natural extrapolations of the $M^2$ ($M^4$) curves with the vertical and horizontal axes, respectively. The values estimated from the $M^2$ and the $M^4$ curves were almost the same, so we only show the values estimated from the $M^2$ curves. The obtained $M_S$ and $1/\chi$ are shown in Figure 7.9(a).

![Graphs showing $M_S(T)$ and $1/\chi(T)$ for La$_{0.7}$Ca$_{0.3}$MnO$_3$ single crystal along the $ab$-plane estimated from the Arrott plot. $M_S^2$ and $1/\chi$ plotted against $T^{4/3}$.

**Fig. 7.9** $M_S(T)$ and $1/\chi(T)$ of La$_{0.7}$Ca$_{0.3}$MnO$_3$ single crystal along the $ab$-plane estimated from the Arrott plot (a). $M_S^2$ and $1/\chi$ plotted against $T^{4/3}$ (b).
We also show the $M_s^2$ and $1/\chi$ vs. $T^{4/3}$ plots in Figure 7.9(b), since the $M_s^2$ and $1/\chi$ of WIFs are predicted to show non-Fermi-liquid behaviour and to obey a $T^{4/3}$ relation according to the SCR theory of spin fluctuations. $M_s^2$ and $1/\chi$ show linear relations against $T^{4/3}$ over a relatively wide temperature range, in good agreement with the SCR theory around $T_C$.

![Graphs showing adiabatic temperature change and magnetoresistance](image)

**Fig. 7.10** Adiabatic temperature change $\Delta T_{ad}$ as a function of temperature under field change of 1.5 and 5 T, respectively (a). Magnetoresistance plotted against temperature (b).

In order to further make sure of the great potential of the present La$_{0.7}$Ca$_{0.3}$MnO$_3$ single crystal along the $ab$-plane as a candidate for magnetic refrigerant, we have
measured the adiabatic temperature change, $\Delta T_{ad}$, by the equation $\Delta T_{ad} (T, \Delta B) = -\frac{T}{c_p(T, B)} \Delta S_M (T, \Delta B)$ for magnetic field change up to 5 T. Figure 7.10(a) displays the temperature dependence of $\Delta T_{ad}$. The estimated $\Delta T_{ad}$ value is 5.53 K for a field change from 0 to 5 T. This value is about 70% of that of Gd and higher than for many manganese oxides [19]. Large magnetoresistance (MR) is the phenomenon where resistance of a material drops drastically on application of magnetic field. It has tremendous applications in recording information on hard disks, magnetic sensors, and spin-electronic devices [36-37]. The MR ratio, defined as $\text{MR} = \frac{\rho(0)}{\rho(H)} - 1$, exhibits a maximum value of 507.88 % at $T_C$ under a magnetic field of 5 T, as shown in Figure 7.10(b).

The value of the refrigerant capacity or relative cooling power (RCP) of La$_{0.7}$Ca$_{0.3}$MnO$_3$ single crystal along the $ab$-plane is calculated by numerically integrating the area under the corresponding $\Delta S - T$ curve, with the temperature difference for the full width at half maximum (FWHM) of the peak, $\delta T_{\text{FWHM}}$, used for the integration limits, as shown in Figure 7.11. The maximum value of RCP is found to be 358.17 J/kg under a magnetic field change from 0 to 5 T. For the RCP value, however, it is necessary to take into account the hysteresis loss. We have also noted a very small (almost negligible) hysteresis loop exhibited by the M-(H) curve (inset to Figure 7.2). Small magnetic losses are beneficial to the magnetic cooling efficiency. Large hysteretic losses reduce the magnetic refrigeration effect by about 23% in Gd$_5$Ge$_2$Si$_2$ [38, 39], in which the magnetic loops exceed those of perovskite like magnetic refrigerants by a factor of about 40. The large magnetic loops in Gd$_5$Ge$_2$Si$_2$ are caused by a first order structural phase transition, induced by magnetic
field. The structural transition shows large hysteresis with field, which, in turn, causes the high magnetic loop and large hysteretic losses. Magnetization-demagnetization processes in La$_{0.7}$Ca$_{0.3}$MnO$_3$ single crystal lanthanum manganites are not accompanied by any structural transition, and because of this, the hysteresis loops are very small.

![Fig. 7.11](image)

**Fig. 7.11** Relative cooling power values (RCP) versus applied magnetic field for La$_{0.7}$Ca$_{0.3}$MnO$_3$ single crystal along the $ab$-plane and the $c$-direction.

In our case, the hysteresis loss is almost negligible, so the effective refrigerant capacity or relative cooling power ($RCP_{eff}$) is the same as the RCP. For our sample, the value of $RCP_{eff}$ at 358.17 K is comparable to that of Gd$_5$Ge$_{1.9}$Si$_2$Fe$_{0.1}$ (about 355 J/kg) [39]. This value is also much larger than those of some other magnetocaloric materials for a field change of 0–5 T, such as Gd$_5$Si$_2$Ge$_2$ (about 240 J/kg) [39], Ni$_{50}$Mn$_{34}$In$_{16}$ (about 181 J/kg) [40], LaFe$_{11.0}$Co$_{0.9}$Si$_{1.1}$ (about 275 J/kg) [41], and LaFe$_{11.2}$Co$_{0.7}$Si$_{1.1}$C$_{0.1}$ (about 320 J/kg) [42]. Our study shows that the large values of
RCP$_{eff}$ and the lack of magnetic hysteresis in La$_{0.7}$Ca$_{0.3}$MnO$_3$ single crystal favours practical application of the material near room temperature. This relatively high RCP arises from the strongly asymmetric distribution of $|\Delta S_M|$ and the large $\delta T_{FWHM}$. In addition, the composition inhomogeneity and/or non-stoichiometry of the phase may also contribute to the large $\delta T_{FWHM}$.

7.4 Conclusions

We have studied the MCE in La$_{0.7}$Ca$_{0.3}$MnO$_3$ single crystal. Due to the strong magnetocrystalline anisotropy, the crystal shows anisotropic magnetic entropy change. The uniformity of the $\Delta S_M$ distribution and the lack of any hysteresis loss are desirable for an Ericsson-cycle magnetic refrigerator and for high magnetic cooling efficiency. The nature of the magnetic transition is confirmed by the Landau coefficients. By adopting Takahashi’s spin-fluctuation theory, we estimated the spin fluctuation parameters and calculated $1/\chi$. The convex curvature of $M^2$ against $H/M$ in the form of an Arrott plot indicates that La$_{0.7}$Ca$_{0.3}$MnO$_3$ is WIF, and the characteristics of its spin fluctuations can be understood within three-dimensional SCR and Takahashi’s spin-fluctuation theories, at least around $T_C$. 
References


CHAPTER 8

STRONG CORRELATION BETWEEN STRUCTURAL PARAMETERS AND THE MAGNETOCALORIC EFFECT IN EPITAXIAL La_{0.8}Ca_{0.2}MnO_{3}/LaAlO_{3} THIN FILM

8.1 Introduction

Magnetic refrigeration, based on the change in isothermal magnetic entropy, is an important development in the quest for energy-efficient and environmentally friendly technologies. Materials exhibiting the giant magnetocaloric effect (MCE) have demonstrated potential for advancing magnetic refrigeration, an energy-efficient and environmentally friendly alternative to conventional refrigeration [1, 2]. Since the discovery of the giant MCE phenomenon, giant MCE has been found in a large variety of magnetic materials, including Gd, Gd_{5}(Si_{x}Ge_{1-x})_{4}, MnAs_{1-x}Sb_{x}, MnFe(P_{1-x}As_{x}), La(Fe_{13-x}Si_{x}), and RM_{2} (where R = rare earth, M = Al, Co, Ni) [3-6]. Further efforts to discover new materials, especially materials without rare-earth elements and exhibiting large MCE in response to low applied field, are of significant importance. Among them, perovskite-type manganese oxide materials having large MCE are believed to be potential candidates for magnetic refrigeration applications [7-14]. In particular, the lanthanum manganite (LaMnO_{3}) family shows the perovskite structure and consists of typical semiconductor materials. Here, the transition metal atoms of pure lanthanum manganite are predominantly in the state Mn^{3+}. Upon substitution of a divalent ion (such as Ca^{2+}, Ba^{2+}, or Sr^{2+}) on the rare
earth site, an equal number of Mn$^{4+}$ ions are created at the expense of Mn$^{3+}$. The resulting compound can then be written, for instance in the case of Ca substitution, as $(\text{La}_{1-x})^{3+} (\text{Ca}_x)^{2+} (\text{Mn}_{1-x})^{3+} (\text{Mn}_x)^{4+}$. The intricate magnetic behavior of this compound is determined by the nature of the magnetic interactions between the mixed valence Mn ions. Very recently, the thin film structure has been receiving increased attention because it is easy to integrate into electronic structures for applications. Interest in lanthanum manganite has been rekindled in the last few years due to the observation of large magnetoresistance in films deposited by pulsed laser deposition. Thin films of La-Ca-Mn-O [15-18], La-Ba-Mn-O [19], La-(Ca,Pb)-Mn-O [20], La-Ce-Mn-O [21], and La-Sr-Mn-O [22] exhibit magnetoresistance in the range of 5%–150%, which is comparable to that obtained in giant magnetoresistance (GMR) metal multilayers. Jin et al. and McCormack et al. reported [23, 24] a “colossal” magnetoresistance of more than 100000% for epitaxial La-Ca-Mn-O films on LaAlO$_3$. The origin of these enormous magnetoresistance values is unknown, although they evidently are related to the magnetic state of the system. The very large magnetization obtainable in this system near room temperature has also led us to study the magnetocaloric behavior of doped LaMnO$_3$ films. It should be mentioned that most of today’s research activity in this field is limited to bulk and single crystal perovskite-type manganese oxide materials, but studies on thin film for MCE are very limited. Recently, scientists have started doing research on the MCE properties of thin films, but only a few reports are currently available [25-31], although in principle, such films will be easier to integrate into electronic structures for applications. However, with the currently available magnetic materials, this high efficiency is only realized in high magnetic fields. Nanostructuring is a promising route to perturb properties, and may lead to novel and advantageous magnetocaloric
properties using existing materials. As LCMO is traditionally the standard by which all perovskite-type manganese oxide materials are measured, we have begun investigating the impact of nanostructuring using La$_{0.8}$Ca$_{0.2}$MnO$_3$ thin film with a simple monoclinic structure.

In this work, we fabricated an epitaxial La$_{0.8}$Ca$_{0.2}$MnO$_3$ / LaAlO$_3$ (LCMO/ LAO) thin film by pulsed laser deposition (PLD). This structure would help to improve the performance of the materials by maximizing the entropy change, suppressing hysteresis losses, adjusting the operation temperature, and reducing the required magnetic field. In addition, thin films show phase diagrams that are much richer than those for the corresponding bulk materials. This is because thin films emerge with two additional external variables, i.e., the film thickness and the epitaxial stress caused by lattice mismatch between the film and the substrate. The epitaxial strain in thin films can change the Jahn-Teller (JT) distortions of Mn$^{3+}$O$_6$ octahedra, leading to strong electron-phonon coupling, which may produce substantial effects that act on various aspects of the film, including the growth mode, imperfections, and the associated structural and physical properties [32, 33]. Therefore, it is necessary to evaluate the correlation between the MCE and the microstructure in detail.

While a wide range of materials have been studied thus far, magnetocaloric materials have been largely unexplored on the nanoscale. Because nanostructuring is a well known approach used to perturb and tune structure-property relationships [34], associated techniques are being applied to study the MCE in nanoparticles and thin films [35-36]. In this sense, the study of MCE in LCMO thin film is of great interest for testing the viability of LCMO as the nucleus of refrigeration systems.
8.2 Experimental

The epitaxial La$_{0.8}$Ca$_{0.2}$MnO$_3$ (LCMO) film (~200 nm) was grown on a (100) LaAlO$_3$ substrate by pulsed-laser deposition (PLD). A short pulse excimer laser ($\lambda = 248$ nm) was focused onto a stoichiometric LCMO target with an estimated energy density of ~ 3.2 J/cm$^2$ and a repetition rate of 5 Hz. The oxygen pressure in the deposition chamber was kept at 300 mTorr, while the temperature of the substrate was maintained at 800°C during the preparation process. The film thickness was controlled by the deposition time, which was at a rate of 50 nm/min. Following the deposition, the film was cooled to room temperature over two hours in an oxygen atmosphere without any further thermal treatment. For transmission electron microscopy (TEM), a thin sample was prepared by ion milling in a JEOL JEM-9320FIB. The sample was attached to a molybdenum TEM grid. This film was observed in a transmission electron microscope (JEOL JEM-2100F) equipped with energy dispersive spectroscopy (EDS). The epitaxial and lattice parameters of the film were examined and calculated from the data obtained using X-ray diffraction. Magnetization measurements were performed using a physical properties measurement system (PPMS) with a 14 T magnetometer in the temperature range from 5-300 K and magnetic fields up to 5 T. To measure the magnetic entropy change, $\Delta S_M$, we used a sweep rate of 50 Oe/s.

8.3 Results and Discussion

Figure 8.1(a) shows the X-ray diffraction pattern of a La$_{0.8}$Ca$_{0.2}$MnO$_3$ film deposited on LaAlO$_3$ substrate. It appears to have a strong out-of-plane texture, reflecting (00$l$).
It is well known that thin film quality can be basically evaluated by the full-width at half maximum (FWHM) of important peaks. The corresponding FWHMs of the (002) and (004) peaks were $0.1340^\circ$ and $0.2620^\circ$, respectively, for $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3$ thin film on the $\text{LaAlO}_3$ substrate ($a = 3.79$ Å), indicating the excellent $c$-axis orientation of all the films.

Fig. 8.1 (a) XRD pattern of the film grown on LAO showing (00$l$) peaks of the orthorhombic structure. (b) Cross-sectional SEM image of the film showing the epitaxial nature and columnar grain growth.
In addition, the crystal structure of our sample is exactly matched with the monoclinic structure \((a = 7.75 \text{ Å}, b = 7.745 \text{ Å}, c = 7.75 \text{ Å})\) from X-ray refinement analysis. A cross-sectional view is also shown in Figure 8.1(b). We observe that the interface between the substrate and the film is uniform and sharp. To further clarify, there still needs to be deeper insight from the viewpoint of microstructure. Figure 8.2(a) shows a TEM bright field image of a \(\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3/\text{LaAlO}_3\) thin film. Electron diffraction patterns were acquired from the \(\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3\), the \(\text{LaAlO}_3\), and the interface area, and the results are displayed in Figure 8.2(b), (c), and (d), respectively. Comparing the image in Fig. 8.2(a) and the electron diffraction pattern in Figure 8.2(b), it is clear that the \(\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3\) layer grew in the [001] direction. Here, an orientation relationship between \(\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3\) and \(\text{LaAlO}_3\) exists and is given by

\[
[100]_{\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3} // [100]_{\text{LaAlO}_3},
\]

\[
(010)_{\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3} // (010)_{\text{LaAlO}_3},
\]

and \((001)_{\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3} // (001)_{\text{LaAlO}_3}\).

The lattice parameters of \(\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3\) are almost double those of the \(\text{LaAlO}_3\) substrate, as mentioned above. However, lattice misfit between the two phases exists, and this is responsible for the elongated diffraction spots in Figure 8.2(d). The actual intensity profiles of the white and red dashed lines in Figure 8.2(d) are displayed in Figure 8.2(e). The profiles have two maximum points, as indicated by the red arrows. Because this diffraction pattern was taken from the interface of two phases, one of the maximum points comes from \(\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3\), and the other comes from \(\text{LaAlO}_3\). We calculated lattice misfit at the \(\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3 / \text{LaAlO}_3\) interface from the distances \((R)\) of peaks in Fig. 8.2(e).
Fig. 8.2 (a) TEM bright field image of La$_{0.8}$Ca$_{0.2}$MnO$_3$/LaAlO$_3$ thin film, with red arrows marking areas of dark contrast in the substrate where strain is present around misfit dislocations. Electron diffraction patterns of (b) La$_{0.8}$Ca$_{0.2}$MnO$_3$, (c) LaAlO$_3$, and (d) an interface area, respectively. The actual intensity profiles of the white and red dashed lines in (d) are displayed in (e).
Lattice misfit can be calculated by \((D_{\text{film}} - D_{\text{substrate}}) / D_{\text{substrate}} \times 100 = (1/R_{\text{film}} - 1/R_{\text{substrate}}) / (1/R_{\text{substrate}}) \times 100 = ((R_{\text{substrate}} / R_{\text{film}}) - 1) \times 100\), where D is the interplanar distance. The calculated value is about 1.9%. We calculated lattice misfit at the \(La_{0.8}Ca_{0.2}MnO_3 / LaAlO_3\) interface from the distances (R) of peaks in Figure 8.2(e). This large lattice misfit is responsible for the misfit dislocation at the \(La_{0.8}Ca_{0.2}MnO_3 / LaAlO_3\) interface. The existence of misfit dislocations at the \(La_{0.8}Ca_{0.2}MnO_3 / LaAlO_3\) interface was reported by K. Daoudi et al. [37]. It was explained that the misfit dislocation releases the lattice misfit strain at the interface. Even though a misfit dislocation releases misfit strain, there is a strain field in the areas around the misfit dislocations. In the bright field TEM image, we can find these contrasts. When we compare the \(La_{0.8}Ca_{0.2}MnO_3 / LaAlO_3\) interface image in Figure 8.2(a) with that of Figure 8.1(b), irregular contrast at the interface in Figure 8.2(a) is attributable to the strain field around interface. Interestingly, the dark contrasts show up in the LaAlO_3 substrate, as marked with red arrows.

The magnified columnar structure of the \(La_{0.8}Ca_{0.2}MnO_3\) thin film is shown in Figure 8.3. The size of each column was estimated to be about 30 nm. The annular dark field scanning TEM (ADF-STEM) image in Figure 8.3(b) clearly reveals the existence of dislocations around \(La_{0.8}Ca_{0.2}MnO_3 / LaAlO_3\) interface where there are areas of dark contrast in Figure 8.2(a). Interestingly, it is clear that all the dislocations are located in the LaAlO_3 substrate region. This suggests that the LaAlO_3 substrate accommodates lattice misfit strain between \(La_{0.8}Ca_{0.2}MnO_3\) and LaAlO_3.
Fig. 8.3 (a) High magnification TEM image of La₀.₈Ca₀.₂MnO₃/LaAlO₃ thin film. (b) ADF-STEM image; dislocations are generated in the LaAlO₃ substrate.
Fig. 8.4 (a) Bright field image of La$_{0.8}$Ca$_{0.2}$MnO$_3$/LaAlO$_3$ thin film. (b) High resolution image of the interface between two neighboring columns is denoted by the rectangle in (a). The FFT patterns of selected areas 1 and 2 are displayed in (c) and (d), respectively. Beam diffraction patterns of two adjacent columns (e) and (f).
Figure 8.4(a) shows a bright field (BF) image of a La$_{0.8}$Ca$_{0.2}$MnO$_3$/LaAlO$_3$ thin film. There are many columns in the La$_{0.8}$Ca$_{0.2}$MnO$_3$ thin film layer. We investigated a high resolution image of the interface, which is denoted by the rectangle in Figure 8.4(a), between two neighboring columns (Figure 8.4(b)). The fast Fourier transform (FFT) patterns of selected areas 1 and 2 are displayed in Figure 8.4(c) and (d), respectively. These two patterns clearly show that these two areas are not different grains but different domains. The domains are ordered perpendicular each other. Therefore, each column in the La$_{0.8}$Ca$_{0.2}$MnO$_3$ thin film layer is a domain which has a different ordering direction. The existence of domain structures in La$_{0.8}$Ca$_{0.2}$MnO$_3$ thin film has been previously reported [38]. To confirm the domain structure, we analyzed two adjacent columns by the nano-beam diffraction method. The beam size was 1.6 nm, so that the size was sufficient to acquire information from only one column. Figure 8.4(e) and (f) shows the results. These results are in agreement with those of the high resolution analysis in Figure 8.4(c) and (d).

Figure 8.5(a) shows the temperature dependence of the magnetization (M-T) for different field directions. The Curie temperature (T$_C$) was estimated to be 249 K. In the literature, the T$_C$ values of bulk specimens and single crystals with the same composition were around 230 and 176 K, respectively [39-40]. It is noteworthy that there is a drastic change in the magnetization around T$_C$ in the $ab$ plane (H//ab). However, the magnetization along the $c$-axis (H//c) seems to be insensitive to increasing temperature. This is mainly due to the columnar structure of $c$-axis alignment observed in the TEM. Hysteresis loops (M-H) of the thin film are also shown in Figure 8.5(b). Interestingly, there is no magnetic hysteresis, which indicates that the magnetocaloric effect (MCE) is fully reversible and confirms the second-order character of the ferromagnetic-paramagnetic (FM-PM) transition.
Fig. 8.5 (a) Temperature dependence of the magnetization (M-T curves) along the \( ab \)-plane, at a \( 45^\circ \) angle to the \( ab \)-plane, and in the \( c \)-direction for the La\(_{0.8}\)Ca\(_{0.2}\)MnO\(_3\) thin film. (b) M-H hysteresis loops measured at a temperature of 259 K for all directions.

We also collected initial magnetization isotherms in the vicinity of \( T_C \). From the Banerjee criterion [41], the phase transition of our thin film appears typically second order. We also confirmed that \( T_C \) is approximately 249 K from Arrott plots. This is quite comparable with the results shown in Figure 8.5(a).
Fig. 8.6 Magnetic entropy change as a function of temperature and change in magnetic field $\Delta H$, as indicated in the legend, with different field directions.

The magnetic entropy changes in the La$_{0.8}$Ca$_{0.2}$MnO$_3$ thin film for different magnetic field directions are shown in Figure 8.6. $|\Delta S_M|$ shows a peak with its maximum around
247 K near $T_C$. The maximum values of $|\Delta S_M|$ were estimated to be 35.90, 27.50, and 24.97 mJ/cm$^3$K under a field change of 1 T for the different field directions, $H//ab$, $H//45^\circ$, and $H//c$, respectively. Corresponding values were 112.9, 102.6, and 101 mJ/cm$^3$K under a 5 T magnetic field change. What is interesting is that a large low-field magnetic entropy change along the $ab$-plane is observed. The maximum values of $|\Delta S_M|$ are about 35.9 and 61.18 mJ/cm$^3$K for a magnetic field change of 1 T and 2 T, respectively. These values of $|\Delta S_M|$ are on the same order of magnitude as that of Gd [42] and are even higher than in many perovskite manganites [39-40]. These low-field large magnetic entropy changes in the thin film are mainly due to the rapid change in the magnetization near the transition temperature in the easy magnetizing plane. In the La$_{0.8}$Ca$_{0.2}$MnO$_3$ thin film, there are two exchange interactions, i.e., the intralayer exchange interaction, $J_{ab}$, and the interlayer exchange interaction, $J_c$. Because $J_{ab}$ is much stronger than $J_c$, the magnetic moments tend to lie in the $ab$-plane. In the vicinity of $T_C$, a small magnetic field along the $ab$-plane can easily promote the paramagnetic to ferromagnetic transition, which causes a rapid change in the magnetization. As a result, a low magnetic field can induce considerable magnetic entropy change.

Relative cooling power (RCP) of the thin film is shown in Figure 8.7. It shows large RCP values (i.e., $\sim$1000 mJ/cm$^3$ for the $ab$ plane and $\sim$780 mJ/cm$^3$ for the $c$-direction), which are higher than those observed in several other perovskite manganites and rare earth alloys. One of the interesting features of Figure 8.6 is that the $|\Delta S_M|$ peaks in all directions are significantly broadened over a wider temperature region than in the corresponding polycrystalline LCMO, due to higher nanostructural disorder [30-31].
In fact, the observed larger temperature FWHM, $T_{\text{FWHM}}$, for the peak at low field may indicate that nanostructuring is a potential route for developing magnetic refrigerants with large useful temperature ranges.

Resistance was measured using the conventional four-probe method. Figure 8.8(a) presents the temperature dependence of the resistivity along both the $ab$-plane and the $c$-direction of the film with and without an applied magnetic field of 5 T. It can be seen that for both directions of the film, the metal-insulator (MI) transition at the peak temperature, $T_p$, is lower than the corresponding Curie point and can be understood from the percolation nature of the MI transition [43]. The MR value, defined as $\text{MR} = (\rho(0)/\rho(H) - 1) \times 100\%$, exhibits a maximum of $\sim 798\%$ and $504\%$, respectively, for both the $ab$-plane and the $c$-direction at $T_C$ under a magnetic field of
5 T, as shown in Figure 8.8(b). These values are higher than many other manganite perovskites.

**Fig. 8.8** (a) Temperature dependence of the resistivity for the \(ab\)-plane and \(c\)-direction with and without an applied magnetic field of 5 T. (b) Temperature dependence of MR ratios.
8.4 Conclusions

In this study, we have investigated epitaxial La\textsubscript{0.8}Ca\textsubscript{0.2}MnO\textsubscript{3} / LaAlO\textsubscript{3} thin film for MCE. The magnetic anisotropy and the texture of the material greatly affect the MCE. Improved film morphology may be related to the different MCE behavior in the thin film from that in the bulk material. It is clear that this thin film form has a significant impact on the behaviour of this material relative to bulk La\textsubscript{0.8}Ca\textsubscript{0.2}MnO\textsubscript{3} and other perovskites, as well as other rare earth materials. The La\textsubscript{0.8}Ca\textsubscript{0.2}MnO\textsubscript{3} thin film shows an anisotropic entropy change of 35.9 and 24.97 mJ/cm\textsuperscript{3}K under 1 T magnetic field change for the \textit{ab}-plane and the \textit{c}-direction, respectively. This larger entropy change value and the enhanced entropy change FWHM is ideal for electronic device cooling. The higher entropy change value and higher RCP with no noticeable hysteresis loss may also make it more convenient for use as a magnetic refrigerant. This indicates that thin film processing might provide an alternative pathway in searching for efficient magnetic refrigerators for microscale systems.
References


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CHAPTER 9

EFFECT OF FROZEN SPIN ON THE MAGNETOCALORIC PROPERTY OF La$_{0.7}$Ca$_{0.3}$CoO$_3$ POLYCRYSTALLINE AND SINGLE CRYSTAL SAMPLES

9.1 Introduction

Rare-earth manganates of the general formula Ln$_{1-x}$A$_x$MnO$_3$ (Ln = rare earth, A = alkaline earth), possessing the perovskite structure, exhibit interesting properties such as colossal magnetoresistance, charge ordering, and electronic phase separation [1-5]. These properties of the manganates are strongly influenced by the average radius of the A-site cations, $<r_A>$. Perovskite cobaltates of the type Ln$_{1-x}$A$_x$CoO$_3$ (Ln = rare earth, A = alkaline earth) are somewhat similar to the manganates [6-8]. Accordingly, many of the cobaltates show ferromagnetism and metallicity, depending on the composition and the size of the A-site cations. The cobaltates also show some unusual features in their magnetic properties. Currently, there is an ongoing debate and increased research intensity on the magnetism of the LaCoO$_3$ system, due to the fascinating properties of compounds in this family and possible multifunctional applications [9-16]. The main controversial points are concerned with the spin states (low to intermediate/high spin), magnetic behavior (phase separation and spin glass (SG) state), and transitions between them. It is commonly accepted that the ground state of LaCoO$_3$ is a non-magnetic insulator. It is commonly
considered that with increasing temperature, a paramagnetic insulating state continuously develops above 50 K, and an insulator-to-metal transition is observed around 500 K [15]. There has been controversy over the nature of the high-temperature spin state, namely, whether it is high-spin (HS), intermediate-spin (IS), or even a mixture of both [16].

The La$_{1-x}$Ca$_x$CoO$_3$ system has been studied by many groups [16-25]. The substitution of Ca$^{2+}$ on La$^{3+}$ sites oxidizes part of the Co$^{3+}$ into Co$^{4+}$. The spin configuration of Co$^{4+}$ has been proposed by different investigators to be low spin (LS) ($t_{2g}^5 e_g^0$, $S = 1/2$), HS ($t_{2g}^3 e_g^2$, $S = 5/2$), and even IS ($t_{2g}^4 e_g^1$, $S = 3/2$), depending on the Ca content and temperature [14, 16]. The theoretical effective magnetic moment ($\mu_{\text{eff}}$) of Co$^{3+}$ and Co$^{4+}$ in the LS, IS, and HS states are 0, 2.83, and 4.90 $\mu_B$, and 1.73, 3.87, and 5.92 $\mu_B$, respectively [19-25]. Since the magnetic and electrical properties of rare earth transition metal oxides with perovskite structure are strongly dependent on the valence state and spin state of the metal ions, and on the defects, these make the material’s magnetic properties very sensitive to sample preparation conditions and processing. It will be worthwhile to compare the properties of a single crystalline (SC) sample with those of a bulk polycrystalline (PC) sample prepared by the conventional solid-state reaction method. In the present work, we have prepared PC and SC La$_{1-x}$Ca$_x$CoO$_3$ (LCCO) samples with the same composition of starting raw powders, determined the magnetic properties, and analyzed the differences between these two types of samples. Interestingly, an anomalous magnetic field memory effect, an exchange-bias-like effect, and a large inverse irreversible magnetocaloric effect have been observed in this system. We
propose that compositional inhomogeneity is the predominant source of the magnetic properties and magnetocaloric effect.

9.2 Experimental

PC and SC \( \text{La}_{0.7}\text{Ca}_{0.3}\text{CoO}_3 \) (LCCO) samples with the perovskite structure were synthesized by conventional solid-state reaction and the floating-zone growth method. Powder samples of \( \text{La}_{0.7}\text{Ca}_{0.3}\text{CoO}_3 \) were synthesized using the standard solid-state reaction method at high temperature, by mixing \( \text{La}_2\text{O}_3, \text{CaCO}_3, \) and \( \text{Co}_3\text{O}_4 \) with up to 99.9% purity in the desired proportions. The starting materials were intimately mixed in an agate mortar and first fired at 700°C for 12 h. Then, the mixture was reground and again fired at 900°C for 12 h. Finally, the sample was again reground, pressed into pellets, and sintered at 1100°C for 24 h. For the SC sample, as-grown single phase powders were then hydrostatically pressed into feed and seed rods with a diameter of 6 mm and a length of about 90 mm. The rods were sintered at 1200 °C for 6 h. The crystal growth was performed in an infrared furnace equipped with four 1000 W halogen lamps, and a single crystal was grown in 30 cc/min oxygen flow rate. To avoid Co evaporation during the growth, we used oxygen flow in the synthesis process for the SC sample. Crystal wafers were cut perpendicular to the growth direction and polished to a mirror finish to allow us to examine them for the existence of macroscopic defects such as cracks, twins, or grain boundaries and inclusions under a polarized microscope. X-ray diffraction (XRD) with Cu K\( \alpha \) wavelength \( \lambda = 1.540562\text{Å} \) was used for XRD measurements to check the phase purity and the crystal structure. Single crystal X-ray diffraction was carried out on the polished surface of the rectangular crystal samples to examine the crystal quality and orientation of the crystal growth. The measurements were
conducted in a θ-2θ scan mode in a 2θ range of 10-60° for single crystal measurements. Cu Kα radiation was used as the X-ray source. The typical XRD patterns obtained from the single crystal are shown in Fig. 1(b). All the peaks of each pattern can be indexed by the (h00) diffraction peaks of La$_{0.7}$Ca$_{0.3}$CoO$_3$. No traces of impurities or inclusions were obtained in our crystal sample. The composition was checked using energy dispersive x-ray analysis (EDX), and Raman spectra. The results confirm the composition within experimental errors. A rectangular piece of the crystal was cut, and magnetization measurements were performed using a physical properties measurement system (PPMS, 14 T) in the temperature range of 5–300 K. To restore the sample to the same demagnetized initial state, the sample was warmed up to 300 K after the measurement of each hysteresis loop. The entropy change was evaluated from the magnetization isotherms.

9.3 Results and Discussion

The phase composition and crystal structure of the samples were characterized by X-ray diffraction (XRD), and their high purity and perovskite structure were confirmed. The XRD patterns of the PC and SC La$_{0.7}$Ca$_{0.3}$CoO$_3$ (LCCO) samples are shown in Figure 9.1. XRD results on these LCCO samples (Figure 9.1) indicate that the PC sample is of orthorhombic (space group: P n m a) phase (O phase), while for the SC sample, a single-phase diffraction pattern was obtained, yielding a rhombohedral structure with the R-3C space group [26]. The suitable structure for x > 0.2 may be orthorhombic, as given in Ref. [14]. However, our x-ray analysis could not distinguish between the here used rhombohedral distortion from a slightly more distorted orthorhombic structure.
Fig. 9.1  XRD patterns for both polycrystalline (a) and single crystal (b) samples of La_{0.7}Ca_{0.3}CoO_3.

Fig. 9.2  EDX spectrum (a) and Raman spectra of La_{0.7}Ca_{0.3}CoO_3.
The EDX and Raman spectra are shown in Figure 9.2. EDS (9.2(a)) shows that the products are composed of La, Ca, Co and O and it confirms the composition within experimental errors. The C peak in the spectrum is attributed to the carbon tape of the sample holder. The Raman scattering of pure La$_{0.7}$Ca$_{0.3}$CoO$_3$ is shown in Figure 2(b). Four bands belonging to the cobaltite structure are observed at 156, 462, 551, and 672 cm$^{-1}$ (~156 cm$^{-1}$- rare earth internal vibration mode; ~ 462 cm$^{-1}$- O-O octahedral rotation; ~ 551 cm$^{-1}$- Co-O bending vibration; ~ 672 cm$^{-1}$- Co-O stretching vibration) and ~299, ~406, and 626 cm$^{-1}$ are for CaCoO$_2$ [27-29].

The temperature dependence of the zero-field-cooled (ZFC) and field-cooled (FC) magnetization was measured for both the PC powder and the single crystal (SC) samples. For all the results on the present SC sample, the applied fields were parallel to the $c$-axis.

**Fig. 9.3** DC and inverse susceptibility ($\chi$ and $1/\chi$) vs. $T$ curves under zero-field cooling (ZFC) and after field cooling (FC) at a field of 1 kOe: PC sample (a) and SC sample (b). The blue dashed-dotted lines mark the peak positions.

The results are replotted as DC susceptibility and inverse susceptibility in Figure 9.3 (a-b). A sharp increase in the magnetization occurs in the low-field FC data around
the Curie temperature, $T_C \approx 102$ K for the poly-crystal and $\approx 104$ K for the single-crystal samples, indicating that the system has become ordered and attained a spontaneous magnetization. A characteristic strong irreversibility between the low-field ZFC and FC magnetization curves appears just below the transition temperature. It is suggested that this irreversibility possibly arises due to the canted nature of the spins or due to the random freezing of spins. The peculiar shape of the $\chi$-$T$ curves suggests a complex magnetic structure below $T_C$. The ZFC curve of the PC sample shows two small peaks, one at 80 K and a second anomaly around 35 K as a relatively sharp maximum, accompanied by a change in the slope of the FC magnetization curve, indicating a transition in the ordered spin structure. The single-crystal sample shows much simpler transitions compared to the PC ones, whilst the ZFC curve shows only one similar peak around 90 K (Figure 9.3(b)). At high temperatures (higher than $T_C$), there may be a first order structural phase transition at temperature $T_{ST} \approx 250$ K (Figure 9.3(a)) for the PC sample and $T_{ST} \approx 160$ K (Figure 9.3(b)) for the single-crystal sample, which are induced by spin state changes (from lower spin state to higher spin state), since the slope of the $1/\chi$ - $T$ curves is changed and the effective magnetic moment ($\mu_{\text{eff}}$) increases after the transition (Figure 9.3(a) and (b)). Above the transition temperature, both samples show Curie-Weiss behaviour, and a fit to the Curie-Weiss law yields a ferromagnetic (FM) $\mu_{\text{eff}}$, the values of which are listed in Figure 9.3(a) and (b). The values of $\mu_{\text{eff}}$ below and above $T_{ST}$ are 3.01 $\mu_B$ and 3.32 $\mu_B$ for PC and 2.66 $\mu_B$ and 3.06 $\mu_B$ for the SC samples, respectively. For both samples the effective magnetic moment ($\mu_{\text{eff}}$) above the structural phase transition temperature ($T_{ST}$) is higher than the magnetic moment which is measured below the $T_{ST}$, indicating that the spin state changes are from lower spin state to higher spin state.
Figure 9.4 shows the difference in the magnetization between the ZFC and FC processes for the both the polycrystalline and single crystal samples. In the low temperature range, the difference in the magnetization is obvious, which may be due to the effects of exchange bias behaviour in this material.

![Magnetization difference between ZFC and FC processes](image)

**Fig. 9.4** The magnetization difference between ZFC and FC processes for the polycrystalline (a) and single crystal (b) samples.

We have conducted AC susceptibility measurements on the PC sample in the temperature range of 5 to 150 K. The in-phase and out-of-phase susceptibility versus temperature curves are shown in Figure 9.5(a) and (b). The AC susceptibility shows more complex spin states and phase transitions, and we can detect 6 significant transition temperatures, as is shown in Figure 9.5(b): $T_1 = 124$ K, $T_2 = 106$ K, $T_3 = 93$ K, $T_4 \approx 53.6$ to 58 K, $T_5 \approx 31$ to 34 K, and $T_6 = 20.5$ K. We suggest that $T_1$ may be another structural phase transition temperature (for lower Ca$^{2+}$ concentration). $T_2$ is the Curie temperature, $T_C$. The $T_4$ temperature range represents the temperature for the appearance of spin glass (SG), since it is strongly dependent on the AC frequency. $T_3$ and $T_5$ relate to the two peaks in Figure 9.3(a): these are the
temperatures at which antiferromagnetic (AFM) interactions appear due to the high spin (HS) or intermediate spin (IS) to low spin (LS) transitions. $T_6$ is the low spin transition temperature. It should be noted that $T_5$ has an AC frequency dependence, since it coexists with spin glass in this temperature range.

Fig. 9.5 In-phase $\chi'$ and out-of-phase $\chi''$ AC susceptibility vs. $T$ curves at different frequencies over a temperature range of 5 – 150 K for the PC sample: (a) $\chi'$– $T$ curves and (b) $\chi''$– $T$ curves.

Although ferromagnetic (FM) interactions dominate the magnetic transitions, AFM interactions also exist between Co ions. This is because the system phase may separate into hole-rich FM clusters dominated by the FM double exchange interaction between Co$^{3+}$ and Co$^{4+}$, with the clusters embedded in a hole-poor non-FM matrix. This matrix is dominated by the Co$^{3+}$–Co$^{3+}$ interaction, which is known to be AFM superexchange, as with the Co$^{4+}$–Co$^{4+}$ interaction (However, Co-Co
magnetic interaction depends on the spin state, e.g. Co$^{3+}$ IS-IS is FM, while Co$^{3+}$ HS-HS is AFM). The coexistence of and competition between FM and AFM interactions could lead to SG-like behaviour. Crystallographic inhomogeneity, stoichiometric inhomogeneities, and the Co ion spin-state transitions heighten the coexistence of the FM and AFM interactions, and bring about magnetic phase separation in the samples, which is similar to the situation in the Sr-doped system [25]. It is highly probable that the crystallographic homogeneity and the stoichiometric homogeneity in the PC sample are much lower than in the SC sample, which leads to much more complex magnetic behaviour in the PC sample.

M-H loops were collected at different temperatures under ZFC and FC conditions with different sweep fields. A large hysteresis loop develops below $T_C$ and attains a larger remanence value ($M_R$) and higher coercive force ($H_C$) at the lowest temperature. The material becomes harder with decreasing temperature, with the coercive field increasing monotonically with decreasing temperature. The difference between the PC and the SC samples is that the loops or curves of the SC sample appear straighter and show sharp changes in all the M-H loops, while all the values of $M_R$ and $H_C$ for the SC are larger than the corresponding PC ones. For clarification we have selected the 10 kOe and 20 kOe sweep field loops as examples, which are shown in Figure 9.6. It is interesting to note that, in the left panels, Figure 9.6(a) and (c), for sweep field of 1 T, less than the field cooling field of 1.5 T, the ZFC M-H loops are closed, while the FC M-H loops are not closed and are also upshifted. The non-closed loop phenomenon is typical SG relaxation behaviour, while the upshifts are mainly due to the FM $M_R$ behaviour. We suggest that the SG, or more likely
here, the cluster spin glass (CSG), has also significantly contributed to the up- or downshifts.

Fig. 9.6 M - H loops of La_{0.7}Ca_{0.3}CoO_3 PC ((a) and (b)) and single-crystal ((c) and (d)) samples after ZFC and 1.5 T FC to 5 K. Different sweep fields were used, lower or higher than the cooling field of 1.5 T, and they revealed different loop shifting features.

In the right panels, Figure 9.6(b) and (d), for a sweep field of 2 T, greater than the field cooling field of 1.5 T, both the FC and ZFC M-H loops are closed, but the M-H loops are still up-/downshifted, with the values lower than for the left panel ones. The up-/downshifts of the M-H loops are attributed to exchange bias – like behaviour (M_{EB}), and the values of M_{EB} are listed in Figure 9.6. Moreover, the left-/right-shifts of the M-H loops are attributed to exchange bias (H_{EB}), and the values of H_{EB} are
listed in Figure 9.6(b) and (d). For the origin of the exchange bias, we note that Luo et al. [30] have observed similar shifts on both axes, representing exchange bias – like phenomena, and there are later arguments on it [31], however, our results suggest that, excepting the minor hysteresis loops, the freezing properties of local anisotropy in a CSG system make a significant contribution to both shifts. Moreover, the grain boundaries in PC samples can enhance the exchange bias, so that the $H_{EB}$ in the PC sample (in Figure 9.6(b)) > $H_{EB}$ in the single-crystal sample (in Figure 9.6(d)), even though the $H_C$ of the PC sample is less than the $H_C$ of the SC sample.

The magnetization (M-H) curves of the PC and SC samples measured with different sweep fields after ZFC and 1.5 T FC to 5 K is shown in Figure 9.7. Different magnetic field-memory effects were observed after ZFC and 1.5 T field cooling. It should be noted that all the M-H curves exhibit a kink or step, where the field position is the same as the maximum field value of the last sweep field. For the ZFC M-H curves in the left panels of Figure 9.7(a) and (c), the kinks or the steps are increased step by step with increasing sweep field. For the M-H curves after 1.5 T FC in the right panels of Figure 9.7(b) and (d), the kinks are increased step by step with increasing sweep field, although the steps go down when the sweep field is less than the 1.5 T FC field, but increase back up to the first field sweep $M_R$ level when the sweep field is greater than the 1.5 T FC field. These demonstrate the feature that the kink value (field value) always coincides with (remembers) the last front maximum sweep field value – we define it as the magnetic field memory effect. This effect is possibly due to a combination of hard FM typical clusters showing SG behavior and frozen spin behavior.
Fig. 9.7 M-H curves of La$_{0.7}$Ca$_{0.3}$CoO$_3$ polycrystalline ((a) ZFC, (b) FC) and single-crystal ((c) ZFC, (d) FC) samples with different sweep fields after ZFC and 1.5 T FC to 5 K. Different magnetic field-memory effects were observed after ZFC and 1.5 T field cooling.

In order to obtain more information on properties of the magnetic clusters, we have measured the magnetization in the polycrystalline (PC) and single crystalline (SC) samples as a function of magnetic field in the ZFC regime over a wide range of temperatures. Figure 9.8 shows, as an example, the M-(H) dependences measured at 50–110 K for the PC and SC samples. According to the procedure proposed by Yamaguchi et al. [21] and Sun et al. [32], the results were fitted to the following functional dependence obtained in the molecular field approximation:

\[ M(H) = NgS\beta B_s (g\beta S (H + \lambda M)/kT) + \lambda_0 H, \]  

(9.1)
where $N$ is the number of clusters with effective spin $S$ per formula unit, $B_s$ is the Brillouin function, $\beta$ the Bohr magneton, and $\lambda$ is a molecular field constant. Unfortunately, no good fittings were obtained while assuming that the effective spin $S$ does not depend on the magnetic field value $H$.

![Magnetization curves](image)

**Fig. 9.8** Magnetization curves at 50, 80, 95, 100, 105, and 110 K for PC and SC La$_{0.7}$Ca$_{0.3}$CoO$_3$ samples.

To describe the experimental data, one needs to assume that $S$ increases with increasing $H$. This view confirms the concept of electronic-phase separation based on the presence of small clusters with mobile phase boundaries [33]. Nevertheless, another scenario is possible, namely, an increase in $S$ due to the field-induced spin state transition from the LS state to the IS, and/or from the IS to the HS state. Using magnetic methods, it is impossible to decide which mechanism is responsible for the observed increase in the effective spin $S$ in the enlarged magnetic field. In this scenario, it is expected that ferromagnetic/metallic states could be established as a result of percolation of ferromagnetic clusters.
In order to evaluate the magnetocaloric effect (MCE), isothermal magnetization curves of the PC and SC samples were collected with a field step of 0.05 mT in the magnetic field range of 0 - 1.5 T and over the large temperature range of 20 - 140 K. Such families of M-H curves are shown in Figure 9.9.

**Fig. 9.9** Magnetization evolution versus applied magnetic field at several temperatures for PC and SC La$_{0.7}$Ca$_{0.3}$CoO$_3$ samples.

The curves reveal slight variation in the magnetization around the Curie temperature for both samples, indicating that there is little possibility of obtaining a large magnetic entropy change associated with the ferromagnetic to paramagnetic transition occurring at $T_C$.

To understand the nature of the magnetic transition in the samples, Arrott plots of $M^2$ versus $H/M$, covering a broad temperature range around $T_C$, have indicated that the transition is second order.
The magnetic entropy change $\Delta S_M$ versus temperature under ZFC and FC conditions down to 2.8 K in 1.5 T field was derived for both samples from the calculated isothermal magnetic entropy change from the isothermal magnetization curves, according to the Maxwell equation. We found that the frozen spins have a significant influence on the $\Delta S_M$. An interesting result is presented in Figure 9.10, where the $\Delta S_M - T$ curves in the low temperature range show totally different features between the ZFC and FC cooling procedures.

**Fig. 9.10** Magnetic entropy changes ($\Delta S_M$) versus temperature curves for 0 to 1.5 T field change for PC (a) and SC (b) samples. Insets: M - H loops of La$_{0.7}$Ca$_{0.3}$CoO$_3$ PC and SC samples at 2.6 K and 3.0 K, respectively.

The $\Delta S_M$ shows a very large inverse irreversibility value for the ZFC process, since there are a large amount of unfrozen spins aligned under the external field in the low temperature range, while the $\Delta S_M$ shows a normal positive value and a slightly larger $\Delta S_M$ value at 2.8 K, which indicates that a small amount of unfrozen spins still exist. The most interesting feature is that at 2.8 K, both the PC and the SC samples show a very large inverse irreversibility value for the ZFC process, which is about 8.1 J/kgK.
and 9.8 J/kgK, respectively, whereas for the FC process, this value is very small, about 1 J/kgK for both samples. Another feature is that at or near $T_c$, this entropy change value is negligible, even compared to the low temperature value. We assume that the higher entropy change value at lower temperature is due to the significant influence of the frozen spins on the $\Delta S_M$.

To determine the behavior of the samples at lower temperatures, we have measured the entropy change values at 2.8 K, 4 K, 6 K, and 8 K under field changes of 0 to 2 T after ZFC to 2.8 K, which are shown in Figure 9.11.

**Fig. 9.11** $\Delta S_M$ – H curves at 2.8 K, 4 K, 6 K, and 8 K under field changes of 0 to 2 T after ZFC and 2 T field cooling to 2.8 K for the PC sample ((a) and (b)) and for the SC sample ((c) and (d)).
These ΔSM – H curves after ZFC to 2.8 K show more complex behavior than the FC ones. In the ZFC process, the PC bulk sample shows pronounced curvature in its ΔSM – H curves at the temperatures of 4 K, 6 K, and 8 K, whereas for the single crystal, no curvature behavior is observed at these temperatures. So, we think that further detailed investigation is necessary to explain these peculiar properties. Our results suggest that the cluster spin glass system confirms the presence and contribution of the freezing properties of local anisotropy of the material on MCE. So, we can draw the conclusion that this interesting MCE property is influenced by the effect of frozen spins in this material.

9.4 Conclusions

We have demonstrated several types of complex and fascinating magnetic behavior in the LCCO system, which will possibly be useful for multifunctional applications. The magnetic properties in this system strongly depend on the sample preparation processing and conditions. From comparing the magnetic behavior in PC and SC samples, we propose that compositional inhomogeneity (mainly Ca^{2+} content) leads to complex variations in the Co ion valence and spin states, which then lead to the strong spin-glass/cluster-spin-glass behavior which significantly influences the magnetic properties of this system. We also have measured the magnetic entropy change (ΔSM) under ZFC and FC processes. An interesting result is obtained at low temperature, where the ΔSM shows a very large inverse irreversibility value for the ZFC process, while the ΔSM shows a normal positive value and a slightly larger ΔSM value at 2.8 K for the FC process.
References


CHAPTER 10

REDUCTION OF HYSTERESIS LOSS IN LaFe_{11.7}Si_{1.3}H_x HYDRIDES WITH SIGNIFICANT MAGNETOCALORIC EFFECT

10.1 Introduction

Materials having large magnetocaloric effects (MCEs) are utilized as magnetic refrigerants because of their energy efficiency and environmental friendliness. To obtain high performance in magnetic refrigeration, it is necessary to investigate magnetic refrigerants having large MCEs in relatively low magnetic fields. Large MCEs in some magnetic materials have been reported. The rare earth elements and their compounds such as Gd [1] and (Dy_{0.3}Er_{0.7})Al_{12} [2] that have a second-order transition exhibit large MCEs. On changing the magnetic field from 0 to 5 T, Gd exhibits the isothermal entropy change $\Delta S_M = 10.2$ J/kg K at the second-order magnetic transition temperature of 294 K. Recently, large MCEs have been observed in compounds having a first order transition, such as ErCo$_2$ [3] and Gd$_5$(Si$_2$Ge$_2$) [4]. For example, Gd$_5$(Si$_2$Ge$_2$) exhibits $\Delta S_M = 18$ J/kg K for a magnetic field change from 0 to 5 T at the first-order crystallographic transition temperature of 278 K. This value is larger than that of Gd at its second order transition. Such large MCEs have also been observed in transition-metal compounds having a first-order crystallographic transition, such as MnAs [5] and Fe$_{49}$Rh$_{51}$ [6-7]. Furthermore, large values of $|\Delta S_M|$ have been reported for La(Fe$_{0.86}$Si$_{0.09}$Co$_{0.05}$)$_{13}$ [8] and MnFeP$_{0.45}$As$_{0.55}$ [9]. Therefore, materials having a first-order transition are attractive prospects for magnetic...
refrigeration. A large value of $\Delta S_M = 14 \text{ J/kg K}$ for a magnetic field change from 0 to 2 T has been observed from a magnetic measurement on La(Fe$_{0.877}$Si$_{0.123}$)$_{13}$ compound containing $\alpha$-Fe impurity of 8 wt% around $T_C = 208 \text{ K}$ [10]. However, the magnetic transition characteristics of the La(Fe$_{x}$Si$_{1-x}$)$_{13}$ compounds are sensitive to $x$ [11-14], and hence, the itinerant-electron metamagnetic (IEM) transition becomes obscured by compositional heterogeneity [15]. However, along with the large MCEs, a concomitant hysteresis loss inevitably occurs because of the nature of the first-order phase transition. The large hysteresis losses make magnetic entropy less efficient [16]. Many efforts have been made to increase the MCE and to reduce or even eliminate the hysteretic loss for the La(Fe$_{x}$Si$_{1-x}$)$_{13}$ compounds by the addition of substitutional or interstitial atoms. Partially replacing La with Pr [17] or Nd [18] in La(Fe$_{x}$Si$_{1-x}$)$_{13}$ can increase MCE, but leads also to an increase in hysteresis loss in the IEM transition process, which has the same effect as a decrease in Si [19] for the strengthened first-order phase transition. The substitution of Cu [20] and Co [18, 21] for Fe can lead to an obvious reduction in the hysteresis loss and an increase in the Curie temperature, $T_C$, but results in a decrease in the magnetic entropy change, because the magnetic transition itself changes from first-order to second-order. In addition, interstitial carbon addition in La(Fe$_{x}$Si$_{1-x}$)$_{13}$ can also increase the $T_C$ and depress the hysteresis [22]. However, the extent of the increase in $T_C$ is limited to about 50 K with less than 0.5 wt% carbon concentration and leads to an obvious decrease in MCE [23]. In contrast to carbon insertion, interstitial hydrogen addition [24-27] leads to a rapid increase in the Curie temperature and preserves the large magnetic entropy change, as well as maintaining the first-order transition. In the present chapter, the influence of hydrogen absorption on the MCE and especially on the magnetic hysteresis in LaFe$_{11.7}$Si$_{1.3}$H$_x$ ($x = 0$, 1.37, and 2.07) compounds are
discussed from the viewpoint of magnetic refrigeration, and a large MCE and a small hysteresis loss are achieved near room temperature.

10.1 Experimental

A LaFe_{11.7}Si_{1.3} sample was prepared by arc melting in high-purity argon gas atmosphere. The purities of the starting materials were 99.9% for La and Fe, and 99.999% for Si. To obtain NaZn13-type single phase, heat treatment was conducted in a quartz tube under vacuum at 1323 K for two weeks. The hydrogen absorption in the compound was conducted in a Sieverts apparatus (Advanced Materials Corporation, USA), where the temperatures and pressures of the sample and the gas reservoirs were monitored and recorded by GrcLV-LabVIEW-based control program software during the absorption process. Hydrogen absorption in the compound was accomplished by annealing in a hydrogen atmosphere in a sealed chamber at different pressures and temperatures. The hydrogen contents in the compounds can be determined from the ideal gas law \( PV = nRT \), where \( P \) is the hydrogen pressure, \( V \) is the volume of the sealed chamber, \( n \) is the mole quantity of the hydrogen in the chamber, \( R \) is the ideal gas constant, equal to 8.3145 J/mol K, and \( T \) is the temperature at which the initial compounds are annealed in the hydrogen. After hydrogenation, we deduced the change in hydrogen content from the change in hydrogen pressure in the sealed chamber, which also corresponds to the concentration of hydrogen in the compounds. X-ray diffraction (XRD) measurements on powder samples were performed with Cu K\(_\alpha\) radiation to identify the phase purity and crystal structure. It was shown that all the samples are single-phase compounds with cubic NaZn\(_{13}\)-type structure. The magnetization was measured as a function of
temperature and magnetic field around the Curie temperature by using a physical properties measurement system (PPMS). By using the Maxwell relation, the magnetic entropy change was calculated based on the isothermal magnetization data.

10.2 Results and Discussion

The x-ray powder diffraction patterns of LaFe$_{11.7}$Si$_{1.3}$H$_x$ compounds with $x = 0$, 1.37, and 2.07 are shown in Figure 10.1(a). The XRD patterns confirmed the NaZn13-type structure for all the samples. In LaFe$_{11.7}$Si$_{1.3}$, additional $\alpha$-Fe and La-Fe-Si are observed (total amount of about 7%), where as in the hydrides only a small amount of $\alpha$-Fe (less than 5%) is present as an impurity phase. The peaks in the hydride samples are shifted towards lower angles (Figure 10.1(b)) compared to the parent compound, indicating an increase in the lattice constant (11.446 to 11.567 Å) due to the incorporation of hydrogen atoms in the lattice structure, and the increase is ~1.06% for the sample with maximum H content ($x = 2.37$) [27]. Previous studies have demonstrated that the introduction of interstitial hydrogen or carbon atoms into La(Fe,Si)$_{13}$ compounds can cause $T_C$ to increase due to lattice expansion [24,26,28-30], while the application of a static pressure leads $T_C$ to decrease due to lattice contraction [31]. The lattice expansion generally enhances the magnetic coupling in the La(Fe,Si)$_{13}$ system. Thus, the increase in $T_C$ with increasing $x$ for LaFe$_{11.7}$Si$_{1.3}$H$_x$ can be attributed to the lattice expansion caused by the introduction of interstitial hydrogen atoms. In the series of 1:13 compounds, the insertion of a light element such as H does not affect the crystal structure type, but it leads to an increased unit cell parameter. It should be noted that after hydrogenation, the XRD peaks are
shifted towards lower angles (shown in Figure 10.1(b)), as is consistent with the increase in the lattice parameter.

![Room-temperature powder XRD patterns](image)

**Fig. 10.1** (a) Room-temperature powder XRD patterns for LaFe_{11.7}Si_{1.3} and its hydrides LaFe_{11.7}Si_{1.3}H_x (x = 1.37, 2.07). (b) Expanded XRD showing shifting of peaks towards lower angles.

Figure 10.2 shows the temperature dependence of the magnetization for LaFe_{11.7}Si_{1.3}H_x measured in the field-cooled (FC) process under a magnetic field of 200 Oe. The Curie temperature, T_C, defined as the temperature at which the dM/dT
of the M-T curve is maximal, is found to increase with the hydrogen content from 192 K for $x = 0$ to 338 K for $x = 2.07$.

![Figure 10.2](image)

**Fig. 10.2** Magnetization as a function of temperature in the field cooling process.

The Curie temperatures of Fe-rich rare-earth (R) iron compounds are determined by the Fe–Fe, the R–Fe, and the R–R interactions. Generally, the Fe–Fe interaction is dominant, whereas the R–R interaction is negligible. The increase in $T_C$ with increasing $x$ in LaFe$_{11.7}$Si$_{1.3}$H$_x$ compounds can be attributed to the lattice expansion caused by the introduction of interstitial hydrogen atoms. The Fe–Fe interaction is the key factor that influences the Curie temperature [32]. The interstitial H-atoms increase the lattice constants and reduce the overlap of 3d wave functions of Fe. The 3d electrons become more localized in the hydrides, increasing the $T_C$ of the hydrogenated samples. The thermomagnetic curves still exhibit a rapid decrease in magnetization with increasing temperature around $T_C$, revealing that the thermally induced first order magnetic transition is maintained after hydrogen absorption and

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that the significant change in magnetization around $T_C$ will reasonably induce a considerable magnetic entropy change.

**Fig. 10.3** Magnetization isotherms of LaFe$_{11.7}$Si$_{1.3}$H$_x$: $x =$ (a) 0, (b) 1.37, and (c) 2.07, measured under increasing and decreasing field.

Figure 10.3 shows the magnetization isotherms of LaFe$_{11.7}$Si$_{1.3}$H$_x$ measured under ascending and descending fields over a wide range of temperature around $T_C$. A large
The hysteresis effect in the M-H curve is observed in the case of the parent compound. The hysteresis effect is much less in the case of hydrogenated samples. A remarkable IEM transition from the paramagnetic (PM) to the ferromagnetic (FM) state above $T_C$ is observed. It can be seen from Fig. 10.3 that the magnetization curves measured under increasing and decreasing fields for $\text{LaFe}_{11.7}\text{Si}_{1.3}\text{H}_x$ exhibit an obvious magnetic hysteresis loop and a sharp change in magnetization at a critical field $B_C$, indicating a characteristic of the first-order magnetic transition above $T_C$, as observed in $\text{LaFe}_{11.7}\text{Si}_{1.3}$ [33].

The Arrott plots of $\text{LaFe}_{11.7}\text{Si}_{1.3}\text{H}_x$, as shown in Figure 10.4, exhibit obvious negative slopes, confirming further the first-order magnetic transition. However, with increasing hydrogen content, the negative slopes decrease almost monotonically, indicating that this feature of the first-order magnetic transition becomes weak after hydrogenation. Therefore, the introduction of hydrogen atoms into $\text{LaFe}_{11.7}\text{Si}_{1.3}\text{H}_x$ leads to a reduction in hysteresis.

![Arrott plots of $\text{LaFe}_{11.7}\text{Si}_{1.3}\text{H}_x$](image)

**Fig. 10.4** Arrott plots of $\text{LaFe}_{11.7}\text{Si}_{1.3}\text{H}_x$ ($x = 0, 1.37, \text{and} 2.07$).
Previous studies indicate that the IEM is the cause of the giant magnetocaloric effect observed in some materials [26, 34]. The variation in the magnetic transition after hydrogenation may be interpreted by the renormalization effect of spin fluctuations, based on the Landau–Ginzburg theory [26] discussed as follows.

**Fig. 10.5** Critical field $B_C$ of the IEM transition as a function of temperature for LaFe$_{11.7}$Si$_{1.3}$H$_x$: $x = (a)$ 0, (b) 1.37, and (c) 2.07.
Figure 10.5 shows the temperature dependence of the critical field $B_C$ of the IEM transition for the $\text{LaFe}_{11.7}\text{Si}_{1.3}H_x$ compounds with $x = 0$, 1.37, and 2.07, and it can be written as a function of $T$, using the amplitude of spin fluctuations, as [26, 35]

$$B_C(T) = A M_{T_c}^3 [\xi(T)^2 - \xi(T_c)^2] \quad (10.1)$$

where $A$ is a constant obtained from the curve of the density of states around the Fermi level in the ground state, $M_{T_c}$ is the thermally-induced magnetic moment at $T_c$, and $\xi(T)^2$, where $\xi(T)$ is the amplitude of spin fluctuations, is proportional to $T^2$ at low temperatures, but gradually becomes proportional to $T$ with increasing temperature. The critical field $B_C$ increases linearly with temperature at almost the same rate of $dB_C/dT \approx 0.19 \text{ T/K}$ for the samples with $x = 0$, 1.37, and 2.07, as shown in Fig. 10.5. The rise in the critical field $B_C$ with increasing temperature above $T_C$ is a typical characteristic of a field-induced first-order magnetic phase transition from the PM to the FM state. It is thus confirmed that the compounds after hydrogenation still exhibit their first-order transition. On the other hand, the difference in $B_C$ is due to the different amplitudes of the spin fluctuation $\xi(T_C)$ in $\text{LaFe}_{11.7}\text{Si}_{1.3}H_x$ compounds with $x = 0$, 1.37, and 2.07. The spin fluctuation at the transition temperature may be modified by interstitial site H, which leads to a lower energy barrier separating the PM from the FM state in the free energy curve due to the renormalization effect. Thus, the reduction in the energy barrier after hydrogenation leads to weakness in the first-order magnetic transition and a decrease in hysteresis loss [36].

The MCE of the samples was determined by calculating the change in magnetic entropy $\Delta S_M$ under a magnetic field change of 0-5 T using the Maxwell’s thermodynamic relation.
\[ \Delta S_M (T, \Delta B) = \int_{B}^{B_p} \left( \frac{\partial M(T, B)}{\partial T} \right)_{B, p} dB \]  

Figure 10.6 shows the entropy change as a function of temperature for different increasing and decreasing magnetic field changes from 0 to 5 T, for LaFe_{11.7}Si_{1.3}H_x. For the samples with \( x = 0, 1.37, \) and 2.07, the maximum values of \( |\Delta S_M| \) are found to be 20.9, 15.1, and 15.83 J/kg for an increasing field change of 0-5 T, and 20.76 J/kg K, 14.53 J/kgK, and 15.61 J/kgK for a decreasing field change of 0-5 T, respectively, which is still higher than for Gd [1]. It is apparent that the large \( |\Delta S_M| \) in LaFe_{11.7}Si_{1.3}H_x is due to a field-induced IEM transition from the PM to the FM state above \( T_C \). The introduction of interstitial hydrogen atoms into LaFe_{11.7}Si_{1.3}H_x can weaken the IEM transition and result in a small decrease in \( |\Delta S_M| \).

![Figure 10.6](image_url)

**Fig. 10.6** Magnetic entropy change \( \Delta S_M \) for increasing and decreasing magnetic field changes of 0-5 T.
It should also be noted that Fujita et al. [26] showed almost same entropy change value after hydrogenation, whereas Mandal et al. and Lyubina et al. [24, 37] reported a decreased magnetocaloric effect after hydrogenation. Our result is consistent with the latter two. According to Ref. [17], the $\Delta S_M$ value estimated by the Maxwell relation could yield an error in the vicinity of $T_C$ due to the magnetic hysteresis caused by the field-induced first-order metamagnetic transition. In order to properly estimate the $|\Delta S_M|$ value, we have calculated the $|\Delta S_M|$ of LaFe$_{11.7}$Si$_{1.3}$H$_x$ based on the isothermal magnetization data under ascending and descending fields around $T_C$ by using the Maxwell relation. In general, the computed $|\Delta S_M|$ values should be applicable if the $|\Delta S_M|$ values are almost same as those from the magnetization data in the increasing and decreasing fields. It is observed that the maximal values of $\Delta S_M$ obtained in the increasing field for $x = 0, 1.37$, and 2.07 (20.9, 15.1, and 15.83 J/kg K, respectively), are very close to those obtained in the decreasing field (20.76, 14.53, and 15.61 J/kgK, respectively). We thus draw the conclusion that these $\Delta S_M$ values are suitable for magnetic refrigeration.

Figure 10.7 shows the temperature dependence of the hysteresis loss, which is defined as the enclosed area between the ascending and descending magnetization curves. The hysteresis loss is found to have a maximum at $T_C$, and it decreases with increasing temperature above $T_C$. The maximum values of hysteresis loss are 33.4, 17.0, and 8.8 J/kg for the samples with $x = 0, 1.37$, and 2.07, respectively. For the compound with $x = 2.07$, a small hysteresis loss is observed. This indicates that the first-order magnetic transition has become weak or is restrained by the introduction of hydrogen atoms, which is very useful for magnetic refrigeration applications.
Fig. 10.7 Hysteresis loss as a function of temperature for LaFe$_{11.7}$Si$_{1.3}$H$_x$ (x = 0, 1.37, and 2.07).

It can be seen clearly from Figs. 10.6 and 10.7 that both the $\Delta S_M$ peak and the hysteresis loss peak broaden asymmetrically toward higher temperatures with increasing magnetic field change. This is a typical characteristic of the field induced metamagnetic transition above $T_C$. The magnitude of the broadening above $T_C$ is obviously larger than that below $T_C$, which is associated with the increase in the critical field $B_C$ for the IEM transition with increasing temperature, as shown in Fig. 10.5. A large $\Delta S_M$ can only result from the IEM transition, with a concomitant hysteresis loss above $T_C$, but the $\Delta S_M$ value of LaFe$_{11.7}$Si$_{1.3}$H$_x$ is very small, and no hysteresis loss is observed below $T_C$. Thus, the temperature dependence curves of both the $\Delta S_M$ and the hysteresis loss exhibit a sharp rise at $T_C$. The maximum value of hysteresis loss is 8.8 J/kg for the sample with $x = 2.07$. This value is much smaller than those of some other magnetocaloric materials, such as La$_{0.5}$Pr$_{0.5}$Fe$_{11.5}$Si$_{1.5}$C$_{0.3}$ (23.1 J/kg) [22], La$_{0.5}$Pr$_{0.5}$Fe$_{11.5}$Si$_{1.5}$ (94.8 J/kg) [22], LaFe$_{11.5}$Si$_{1.5}$ (20 J/kg) [38], La$_{0.7}$Pr$_{0.3}$Fe$_{11.5}$Si$_{1.5}$ (70 J/kg) [38], LaFe$_{11.7}$Si$_{1.3}$ (71.1 J/kg) [20], La$_{0.5}$Pr$_{0.5}$Fe$_{11.4}$Si$_{1.6}$...
(17.8 J/kg) [36], \(\text{La}_{0.5}\text{Pr}_{0.5}\text{Fe}_{11.4}\text{Si}_{1.6}\text{H}_{0.9}\) (11.7 J/kg) [36] but higher than that of \(\text{LaFe}_{11.7}(\text{Si}_{0.7}\text{Cu}_{0.3})_{1.3}\) (0.0 J/kg) [20] and \(\text{La}_{0.5}\text{Pr}_{0.5}\text{Fe}_{11.4}\text{Si}_{1.6}\text{H}_{1.6}\) (2.3 J/kg) [36], respectively.

The values of the refrigerant capacity or relative cooling power (RCP) of \(\text{LaFe}_{11.7}\text{Si}_{1.3}\text{H}_x\) are calculated by numerically integrating the area under the corresponding \(\Delta S_M-T\) curve, with the temperature at the half maximum of the peak used as the integration limit [39], as shown in Figure 10.8. The maximum values of RCP are found to be 473, 347, and 313 J/kg for the samples with \(x = 0, 1.37, \) and 2.07 under a magnetic field change from 0 to 5 T, respectively. Besides the RCP value, however, it is necessary to take into account the hysteresis loss. The effective refrigeration capacity (RCP_{eff}) is the RCP value obtained after subtracting the hysteresis loss [16].

![Fig. 10.8](image_url) The relative cooling power of the samples under a field change of 0-5 T.
The values of $R_{CP_{\text{eff}}}$ for LaFe$_{11.7}$Si$_{1.3}$H$_x$ ($x = 0$, 1.37, and 2.07) were determined to be 439.6, 330, and 304 J/kg under a field change of 0–5 T, respectively. For the sample with $x = 1.37$, the value of $R_{CP_{\text{eff}}}$ at 330 J/kg is comparable to that of Gd$_5$Ge$_{1.9}$Si$_2$Fe$_{0.1}$ (about 355 J/kg at 305 K) [16]. This $R_{CP_{\text{eff}}}$ value is also much larger than those of some other magnetocaloric materials for a field change of 0–5 T, such as Gd$_5$Si$_2$Ge$_2$ (about 240 J/kg at 275 K) [16], Ni$_{50}$Mn$_{34}$In$_{16}$ (about 181 J/kg at 304 K) [40], LaFe$_{11.0}$Co$_{0.9}$Si$_{1.1}$ (about 275 J/kg at 294 K) [41], and LaFe$_{11.2}$Co$_{0.7}$Si$_{1.1}$C$_{0.1}$ (about 320 J/kg at 290 K) [42]. Our study shows that the large values of $\Delta S_M$ and $R_{CP_{\text{eff}}}$, as well as the small magnetic hysteresis, in LaFe$_{11.7}$Si$_{1.3}$H$_{1.37}$ around room temperature are favourable for the practical application of these materials near room temperature.

10.4. Conclusions

By introduction of interstitial hydrogen atoms, the Curie temperature $T_C$ can be tuned to around room temperature without altering the magnetocaloric effect significantly. The first-order nature of the phase transition is weakened after hydrogenation, which leads to a reduction in thermal hysteresis and magnetic hysteresis. It is found that the maximum hysteresis loss drops from 33.4 to 8.8 J/kg for LaFe$_{11.7}$Si$_{1.3}$H$_x$, with $x$ varying from 0 to 2.07, while the magnetic entropy change remains at the comparatively large value of 15.83 J/kgK for a field change of 0–5 T. Considerable effective refrigerant capacity, 330 J/kg and 303 J/kg, are obtained for $x = 1.37$ and 2.07 under a field change of 0–5 T, respectively. This material system also exhibits almost the same entropy change values in increasing and decreasing field, which makes it more applicable for magnetic refrigeration. The LaFe$_{11.7}$Si$_{1.3}$H$_x$ hydrides are
promising candidates as high performance magnetic refrigerants working in a wide range of temperature, including room temperature. In other words, the efficiency of magnetic refrigeration is greatly improved by introducing interstitial hydrogen atoms into the LaFe$_{11.7}$Si$_{1.3}$ compound.
References


CHAPTER 11

OUTLOOK

This thesis presents a study of the magnetocaloric effect (MCE) and related physical properties of various perovskite manganites and La(FeSi)$_{13}$H$_x$ alloy. After a brief overview of conventional refrigeration techniques, the significance of developing magnetic refrigeration and the motivation for this study are pointed out in Chapter 1. Chapter 2 provides a thorough literature review on these materials. Isothermal magnetic-entropy change and adiabatic temperature change are the two characteristic parameters for evaluating the magnetocaloric properties of a magnetic material. The theoretical aspects of the MCE and the experimental procedure are presented in Chapter 3. Since a large MCE may be expected in the vicinity of a magnetic phase transition, this study is focused on the MCE associated with such transitions.

For the determination of the MCE, I have used both magnetic and specific-heat measurements. Therefore, in Chapter 4, the characterization and methods to determine the MCE were tested by studying the MCE in La$_{0.7}$Ca$_{0.3}$MnO$_3$. The results of this study show that the isothermal magnetic-entropy change derived from magnetization measurements is in good agreement with the values obtained by means of specific-heat measurements in magnetic field, thus confirming that it is reliable to investigate the MCE in new materials by means of simple magnetization measurements. In Chapter 4 large MCE and magnetoresistance (MR) in La$_{0.7}$Ca$_{0.3}$MnO$_3$ are reported, where MCE and MR were observed at the Curie
temperature ($T_C$) associated with the first order transition. The correlation between resistivity and change in the magnetic entropy ($\Delta S_M$) in a specific region around $T_C$ is also discussed. The lack of any noticeable magnetic hysteresis loss confirmed the reversibility of the compound, which is desirable for magnetic refrigeration. It should be noted that the obtained values are about two times larger than those reported for other perovskite manganites, and even larger than for Gd-based magnetic materials at low fields.

Chapter 5 presents systematic studies of the influence of the first order magnetic transition (FOMT) and the second order magnetic transition (SOMT) on the MCE and relative cooling power (RCP) in La$_{0.7}$Ca$_{0.3}$MnO$_3$ with a few percent Co doping. The results reveal that while a FOMT at $T_C$ induces a larger MCE, it is restricted to a narrow temperature range, resulting in a smaller RCP. However, a SOMT at $T_C$ induces a smaller MCE, but with a distribution over a broader temperature range, thus resulting in a larger RCP. A large low-field-induced magnetic entropy change was also achieved with larger magnetoresistance.

The MCE related to the effects of Ag doping in La$_{0.7}$Ca$_{0.3}$MnO$_3$ is discussed in Chapter 6. Doping with monovalent Ag increases the Curie temperature and weakens the first order phase transition, so that at higher Ag doping levels, the nature of the phase transition is second order. Ag doped La$_{0.7}$Ca$_{0.27}$Ag$_{0.03}$MnO$_3$ compound showed large $\Delta S_M$ (7.63 J/kgK for 5 T field change) at the Curie temperature of 263 K, as well as a high RCP value (270.8 J/kg) without any hysteresis loss. These results indicate that La$_{0.7}$Ca$_{0.27}$Ag$_{0.03}$MnO$_3$ may be a good candidate as a potential working material for magnetic refrigeration.
Chapter 7 presents the results of a study of the MCE and of related physical properties of a single crystal of La$_{0.7}$Ca$_{0.3}$MnO$_3$. The spin fluctuation parameters were estimated by adapting Takahashi’s developed spin-fluctuation theory, and $1/\chi$ was calculated. Evidence is presented that the magnetic property of La$_{0.7}$Ca$_{0.3}$MnO$_3$ is weakly itinerant ferromagnetic (WIF). The maximum value of $\Delta S_M$, corresponding to external field changes of 1.5 T and 5 T for both the $ab$-plane and the $c$-direction reaches about 3.33 and 2.364 J/kgK, and 7.668 and 6.412 J/kgK, respectively. These values are higher than the result found by Phan et al. and Tian et al. for the same single crystal La$_{0.7}$Ca$_{0.3}$MnO$_3$.

It should be mentioned that most of today’s research activity in this field is limited to bulk and single crystal perovskite-type manganese oxide materials, but studies on thin film for MCE are very limited. While a wide range of materials have been studied thus far, magnetocaloric materials have been largely unexplored on the nanoscale. Because nanostructuring is a well known approach used to perturb and tune structure-property relationships, associated techniques are being applied to study the MCE in nanoparticles and thin films. In this sense, the study of MCE in LCMO thin film is of great interest for testing the viability of LCMO as the nucleus of refrigeration systems.

Chapter 8 is focused on the strong correlation between structural parameters and the magnetocaloric effect in epitaxial La$_{0.8}$Ca$_{0.2}$MnO$_3$/LaAlO$_3$ thin film, which shows a large MCE that has not been previously reported in the literature. The magnetic anisotropy and the texture of the material greatly affect the MCE. Improved film
The effect of frozen spin on the magnetocaloric properties of La$_{0.7}$Ca$_{0.3}$CoO$_3$ polycrystalline and single crystal samples is studied in Chapter 9. Interestingly, an anomalous magnetic field memory effect, an exchange-bias-like effect, and a large inverse irreversible magnetocaloric effect have been observed in this system. It is found that the frozen spins have a significant influence on the $\Delta S_M$. The $\Delta S_M - T$ curves in the low temperature range show totally different features between the ZFC and FC cooling procedures. The $\Delta S_M$ shows a very large inverse irreversibility value for the ZFC process, since there are a large amount of unfrozen spins aligned under the external field in the low temperature range, while the $\Delta S_M$ shows a normal positive value and a slightly larger $\Delta S_M$ value, which indicates that a small amount of unfrozen spins still exist. It is proposed that compositional inhomogeneity is the predominant source of the magnetic properties and the magnetocaloric effect.
Finally, a study of the reduction of hysteresis loss in LaFe$_{11.7}$Si$_{1.3}$H$_x$ hydrides with significant magnetocaloric effect is detailed in Chapter 10. The influence of hydrogen absorption on the MCE and especially on the magnetic hysteresis in LaFe$_{11.7}$Si$_{1.3}$H$_x$ ($x = 0, 1.37, \text{ and } 2.07$) compounds is discussed from the viewpoint of magnetic refrigerants, and a large MCE which is still higher than for Gd and a small hysteresis loss are achieved near room temperature are favourable for the practical application of these materials near room temperature.

Finally, I would like to remark that the MCE can be studied in a large variety of materials. I hope that the present thesis has helped, to at least a small extent, to unveil and elucidate the properties of these present systems.
APPENDIX A: LIST OF PUBLICATIONS

1. Debnath, J.C., Zeng, R., Kim, J. H. & Dou, S. X., “Giant magnetic entropy change in colossal magnetoresistance in La_{0.7}Ca_{0.3}MnO_{3} material in low field”. Journal of Applied Physics, 107, 09A916 (2010). (JR: A).

2. Debnath, J.C., Zeng, R., Kim, J. H. & Dou, S. X., “Large magnetic entropy change near room temperature in La_{0.7}(Ca_{0.27}Ag_{0.03})MnO_{3} perovskite”. Journal of alloys and Compounds, 509, 3699-3704 (2011). (JR: A).


7. **Debnath, J.C., Zeng, R., Kim, J. H. & Dou, S. X.**, “Improvement of refrigerant capacity of La$_{0.7}$Ca$_{0.3}$MnO$_3$ material with a few percent Co doping”. *Journal of Magnetism and Magnetic Materials*, 323, 139-144 (2011). (JR: B).


11. **Debnath, J.C., Zeng, R., Kim, J. H. & Dou, S. X.** (2012). “Ideal ericsson cycle magnetocaloric effect in (La$_{0.9}$Gd$_{0.1}$)$_{0.67}$Sr$_{0.33}$MnO$_3$ single crystalline nanoparticles”. *(Manuscript ready for submission).*

APPENDIX B: RECEIVED AWARDS

1. University Postgraduate Award (UPA), University of Wollongong, Australia (2008-2011)

2. International Postgraduate Tuition Award (IPTA), University of Wollongong, Australia (2008-2011)

3. Excellent research Top Up award-2010, ISEM, University of Wollongong, Australia.

4. AINSE (Australian Institute of Nuclear Science and Engineering) research fellowship (2009)

5. Student Travel grant to attend International Conference-2010

6. Award of MMM/Intermag 2010 Conference Student Travel grant

7. Merit Scholarship (General), Dhaka University, Dhaka 1000, Bangladesh-1994

8. Merit Scholarship (General), Dhaka University, Dhaka 1000, Bangladesh-1992

9. Bangladesh Government Talent-Pool Scholarship at Secondary and Higher Secondary level