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Magnetocaloric Effect in Half-Doped and Self-Doped Manganites: A Study to Green Refrigeration.

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Abstracts

Magnetic refrigeration has emerged as a promising and environmentally friendly technology due to its high efficiency and eco-friendly nature. It is becoming a strong competitor to traditional gas refrigeration and is often referred to as a green refrigeration technique. This technique utilizes the magnetocaloric effect (MCE) or inverse magnetocaloric effect (IMCE) to achieve a change in temperature after adiabatic demagnetization. Among various magnetocaloric materials, perovskite manganites have drawn significant attention due to their abundance and low field MCE. In this paper, a comparative study of MCE has been presented for two different types of manganites. The self-doped $La_{0.9}MnO_3$ shows a considerable amount of MCE (2.5 J/Kg-K) at an applied magnetic field of 10 kOe around 255 K. In contrast, $Pr_{0.5}Sr_{0.5}Mn_{0.98}Cr_{0.02}O_3$another manganite, shows a comparably lower value of MCE (0.55 J/Kg-K) around 220 K under the same magnetic field, but it exhibits a large IMCE (1.26 J/Kg-K) around 150 K. This comparative study provides insights into the magnetocaloric properties of these manganites, which could have potential applications in green refrigeration.

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Introduction

The refrigeration sectors have a significant and growing influence in the global economy, making substantial contributions to areas such as food preservation, healthcare, energy efficiency, and environmental protection, which policy makers need to thoroughly sunderst and and consider. Didier Coulomb *et. al* reported that there were approximately 3 billion refrigeration, air-conditioning, and heat pump systems in operation worldwide, including 1.5 billion domestic refrigerators and almost 17% of the world's total electricity usage has been consumed in this sector in the informatory note on refrigeration technology in November 2015.[1] One of the pressing environmental concerns related to refrigeration systems is their contribution to global warming. Approximately 20% of the environmental impact of these systems is attributed to direct emissions, such as release of fluorocarbons (CFCs, HCFCs, and HFCs). The remaining 80%

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of the impact stems from indirect emissions resulting from the electricity generation needed to power these systems, which is largely derived from fossil fuel power plants. Despite economic growth often taking precedence over environmental considerations in many developing countries, it is imperative to adopt eco-innovative approaches to achieve long-term environmental sustainability. This requires finding innovative solutions that balance economic growth with environmental protection and prioritizing sustainable practices in the refrigeration industry and beyond.[2,3]

The conventional method of refrigeration, the vapour compression method, uses refrigerants that contain chlorofluorocarbons (CFC) and hydrochlorofluorocarbons (HCFC) which produces ozone-depleting gases and also greenhouse gases. However, the use of CFCs, HCFCs, and other harmful refrigerants has been banned under the Montreal Protocol, which was implemented on September 16, 1987, to achieve zero ozone depletion effect. Additionally, the Kyoto Protocol, an international treaty set on December 11, 1997, in Kyoto, Japan, aims to reduce greenhouse gas emissions. This has led to the development of alternative sustainable methods of refrigeration that are environmentally friendly and have low global warming potential (GWP) and zero ozone depletion potential (ODP). One such method that has made significant progress in recent years is magnetic refrigeration, which offers several advantages.[4]

- use of solid refrigerant material with zero ODP
- less energy consumption with less GWP.
- higher efficiency (30-60%) compared to the vapour compression method (5-10%).

Magnetic refrigeration technology has been developed on the basis of magnetic solid materials which can be acted as a refrigerant by magneto-caloric effect (MCE). Advantages of this technique over the conventional one are :(i) no release of any kind of ODP/GWP gases and (ii) high energy efficiencies. The magneto caloric effect is an inherent characteristic of certain of specific magnetic materials like rare earth alloys and compounds.[5-10] These materials exhibit a temperature change when exposed to an external magnetic field, both during its application and subsequent removal.So, the essential requirements for a magnetic cooling machine are (i) a powerful magnetic source and (ii) a material with a significantly high refrigerant capacity. As the entropy as well as adiabatic temperature change increases with application of external magnetic field, a source to generate high value of magnetic field becomes the key parameter of a magnetic refrigerator. For a large value of magnetic field generation, we have to implement the superconducting magnet which can be utilized for industrial application but not for domestic purpose. So, fabrication of different functional materials with low-field (within 1T) MCE is mandatory for all purpose use of magnetic refrigeration. In addition to find materials with higher MCE, current research trends also prioritize other crucial properties, including thermal hysteresis, cost-effectiveness, aging resistance, low toxicity, and recyclability.[11]

From the beginning, gadolinium (Gd), has been widely considered as a promising magnetic refrigerant for magnetic refrigerators operating at room temperature.[12] However, its commercial application is somewhat constrained due to its high cost. As a result, research in the field of magnetic cooling has been concentrated on discovering alternative materials that are more affordable yet exhibit greater magnetic cooling effects (MCEs).[13-15] The unique magnetocaloric properties of rare-earth manganites were not reported until 1996, despite being known for over 50 years.[16] However, these materials offer advantages over previously studied materials due to their lack of thermal and field hysteresis and lower cost. Such a proposition was made over a decade ago by Zhang *et al.*, wherein magnetocaloric measurements were conducted on $La_{0.67}Ca_{0.33}MnO_3$ and $La_{0.60}\ Ca_{0.33}\ Y_{0.07}\ Mn_{O3}$.[17] For better adjustment of temperature region and value of MCE, three types of doping such as A-site, B-site and vacancy doping has been investigated.[18-20] Another interesting phenomenon that has been observed in some doped manganites is inverse magnetocaloric effect which also has drawn considerable attention as it can serve as a heat sink for dissipating heat generated when a conventional magnetocaloric material is magnetized prior to cooling through adiabatic demagnetization.[21-26] Therefore,the combination of conventional magnetocaloric materials with inverse magnetocaloric effect materials presents an exciting opportunity to enhance the efficiency of room-temperature refrigeration.

In this paper we will discuss about the temperature dependence of magnatocaloric effect for a self-doped manganite $La_{0.9}$ MnO_3 which shows a considerable conventional MCE with application of 1T field. In addition, with we will discuss the IMCE effect observed in 2% Cr doped $Pr_{0.5}$ $Sr_{0.5}$ MnO_3.

Experimental Details and Methods of Calculations

Both the samples $La_{0.9}$ MnO_3 and $Pr_{0.5}$ $Sr_{0.5}$ $Mn_{0.98}$ $Cr_{0.02}O_3$ was prepared by the chemicalroute as described our earlier report.[20,21] In order to calculate MCE, isothermal magnetization (M-H) curve has been measured at different temperatures from 0 to 10 kOe (1T) field using commercial superconducting quantum interference devicemagnetometer (Quantum Design).

The MCE can be measured through direct or indirect methods.[27] Direct measurement involves observing the change in temperature (ΔT) during the application or removal of a magnetic field, while indirect methods involve measuring either the heat capacity (C) or magnetization (M). In this study, we employed the conventional indirect method of measuring the MCE through magnetization measurement. Firstly, we generated the temperature-dependent magnetization curve by simulating the experimental data obtained from the isothermal M-H curve. Subsequently, we calculated the magnetic entropy change (ΔSM) due to variations in the magnetic field at constant temperature using the Maxwell equation of classical thermodynamics.

$$\Delta S_M=\int^0_H (\partial M/\partial T)_H \, dH \qquad ...(1)$$

Results and Discussions

Large MCE in Self-Doped $La_{0.9}$ Mno_3 with Low Field Change

From the isothermal M-H curve temperature dependent magnetization curve (M-T) has been drawn under different magnetic field. As shown in dashed line of figure 1 shows M-T curve for self-doped $La_{0.9}$ MnO_3 for 10 kOe field. A paramagnetic to ferromagnetic transition occurs at 252 K, which is similar to our earlier reported data. Figure 1 shows the temperature dependent MCE for the change in magnetic field from 0 to 10 kOe. Maximum MCE has been observed around T_C with value 2.5 J/Kg-K which is reasonably high value for such a low field.

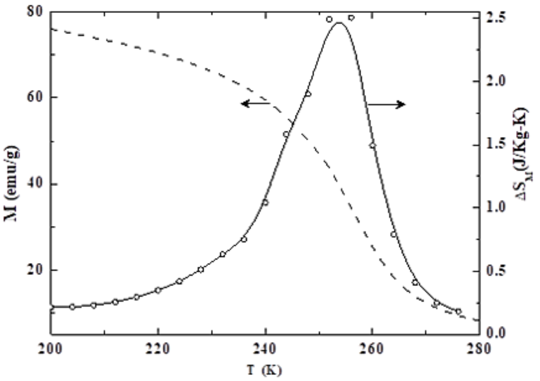

Fig. 1: Temperature dependence magnetization (dashed line) and magnetocaloric effect (MCE) for $La_{0.9}$ MnO_3.

Large IMCE in Half-Doped $Pr_{0.5}$ $Sr_{0.5}$ $Mn_{0.98}$ $Cr_{0.02}O_3$ with Low Field Change

The addition of a small amount of Chromium (Cr) to the Manganese (Mn) site has been observed to have a significant impact on the Magnetocaloric Effect (MCE) and Inverse Magnetocaloric Effect (IMCE) in $Pr_{0.5}$ $Sr_{0.5}$ MnO_3, as discussed in our earlier findings.[21] Out of various doping concentration we have found that maximum change in temperature happens when 2% Cr is doped. So here we have calculated the temperature dependence MCE and IMCE for $Pr_{0.5}$ $Sr_{0.5}$ $Mn_{0.98}$ $Cr_{0.02}$ O_3 in 10 kOe field. Figure 2 shows the M-T curve and ΔS_M-T curve for this sample. From the M-T curve two distinct magnetic transition

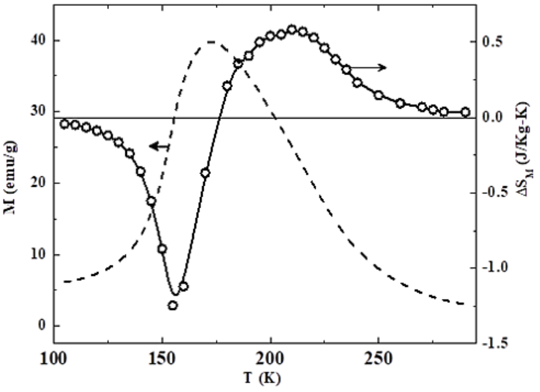

Fig. 2: Temperature dependence magnetization (dashed line) and magnetocaloric effect (MCE) for $Pr_{0.5}$ $Sr_{0.5}$ $Mn_{0.98}$ $Cr_{0.02}O_3$.

exists for the hole doped sample. A paramagnetic to ferromagnetic transition occurs around 220 K where we get a broad peak in conventional MCE with a comparatively peak value (0.55 J/Kg-K). And in the lower temperature region a sharp dip occurs for inverse magnetocaloric effect around 180 K i.e, the ferromagnetic to antiferromagnetic transition temperature with a value of 1.26 J/Kg-K.

Table 1: Calculated values of ΔS_{max} and RCP for these two materials with change of 10kOe field

Material	Transition temperature (K)	Type of MCE	ΔS_{max} (J/Kg-K)	RCP (J/Kg)
$La_{0.9}MnO_3$	252	MCE	2.5	56.2
$Pr_{0.5}Sr_{0.5}Mn_{0.98}Cr_{0.02}O_3$	220	MCE	0.55	26
	180	IMCE	1.26	42.2

So as shown in table 1, both samples exhibit considerable amount of RCP values to be used as a magnetocaloric materials. [28]

In order to assess the magnetocaloric effect and its potential viability in magnetic refrigeration applications, we have calculated the relative cooling power (RCP). The RCP is determined by multiplying the maximum value of entropy change (ΔS_{Max}) by the temperature change at half maximum (δT_{FWHM})i.e, RCP = $|\Delta S_{max} \times \delta T_{FWHM}|$. Table 1 shows the maximum magnetic entropy change and RCP of these two materials around transition temperatures.

Conclusion

In conclusion, to develop environment-friendly cooling technology, it is necessary to seek magnetocaloric materials that exhibit large MCE, no thermal hysteresis, nontoxicity, and cost-effectiveness. In this study, we calculated the temperature-dependent $-\Delta S_M$ and RCP around transition temperature for $La_{0.9}MnO_3$ and $Pr_{0.5}Sr_{0.5}Mn_{0.98}Cr_{0.02}O_3$. A comparatively large MCE in self-doped $La_{0.9}MnO_3$ has been observed with application or withdrawal of 10kOe magnetic field which can be generated by a reasonably lightweight and compact permanent magnet.We also observed a reasonable amount of IMCE (1.26J/Kg-K) in $Pr_{0.5}Sr_{0.5}Mn_{0.98}Cr_{0.02}O_3$ for the application or withdrawal of 10 kOe magnetic field. Both samples displayed significant MCE and RCP values without exhibiting any thermal hysteresis or aging effects. Furthermore, these samples are non-toxic, making them ideal for use in magnetic refrigeration applications. Among these samples, $Pr_{0.5}Sr_{0.5}Mn_{0.98}Cr_{0.02}O_3$, with its large MCE and IMCE, is suitable for cooling during both magnetization and demagnetization processes. Thus, this study is a crucial step to find a suitable refrigeration material which can contribute to sustainable practices and help reduce the negative impact of refrigeration on the environment.

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Conflict of Interest

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