

MAGNETOCALORIC MATERIALS FOR ROOM TEMPERATURE, MAGNETIC REFRIGERATION & BIOMEDICAL APPLICATIONS - A REVIEW

Abstract

In the past two decades, there has been a surge in research on the magnetocaloric response of materials mainly to the possibility of applying this effect for magnetic refrigeration close to room temperature. Magnetocaloric effect (MCE) has emerged as a more advantageous technique when compared to Conventional Gas Compression (CGC) technology. Apart from cooling, MCE has tremendous applications such as industrial heat pump, supermarket refrigeration, sugar refining, liquor distilling, gas liquefaction and chemical processing. In addition to this, MCE has biomedical applications too. Nowadays, a wide range of research is being done on drug delivery systems for accurate diagnosis and timely treatment. Drug delivery systems are currently the focus of important research in order to provide timely and accurate diagnosis and treatment. Delivering drugs with the highest therapeutic affect and the fewest side effects is the primary objective of these research. Another aim is to develop a hyperthermia method that allows internal heating mechanisms to destroy cancer cells. In this review paper, a detailed discussion about Magnetocaloric Materials for room temperature, magnetic refrigeration and its bio-medical applications have been done.

Keywords: Magnetocaloric effect, Magnetic Refrigeration, Hyperthermia, Magnetic drug delivery.

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I. INTRODUCTION

MCE refers to the Magnetocaloric effect which has a significant part in the field of magnetic refrigeration. The MCE technique is discovered before 1917 by French and Swiss physicist namely Weiss and Piccard [1]. The MCE is certain materials heat up, when brought into a magnetic field. Magnetocaloric materials are those that exhibit this effect. A magnetic cooling cycle near room temperature can be achieved by utilizing the magnetocaloric effect. The largest MCE value measured was shown by FeRh alloys, which have been discovered 26 years ago by Nikitin [1][2] till date. A milestone in the field of magnetocalorics was the discovery of the giant MCE, which was published by Pecharsky and Gschneidner [2]. Many researchers and industrialists attract their attention towards MCE because of its wide- range of practical applications. Since last two decades, the progress in new magnetocaloric materials development that provides the recent 'boom' in MCE studies. Even though that the MCE has been studied for more than hundred years, there is no large-scale practical application of the effect so far. High Cost of magnetic field sources, not- ready enough technologies for manufacturing of the MCE materials, the shapes to be used as working bodies in refrigerators and also difficulties to substantially increase the working cycle of frequency are the problems which needs to be overcome in the field of MCE. International institute of refrigeration (IIR) has done a numerous promising effort which have been performed on magnetic refrigeration leading to an optimistic view for the upcoming future of this technology. The large refrigeration market led to degrees of refrigerator costs which makes it challenging in an initial phase to enter refrigeration markets with new MCE based equipment. Magnetocaloric materials, embedded in heat pipes, are at the core of this technology, creating cooling systems without any harmful re-agents.

Previously, conventional gas compression (CGC) technology was used in cooling applications, which is based on mechanism of expanding and compressing process, of a gas in refrigerators. During this process harmful gases such as chlorofluorocarbons (CFC) and hydro fluorocarbons (HFC) are released and cause damage to the ozone layer. To overcome this, an environmentally friendly cooling technology was introduced in recent times i.e., magnetocaloric effect. The MCE has emerged as a more advantageous technique than CGC by reducing the release of a number of harmful gases such as CFC's and HFC's when compared to CGC's. This results in the minimization of depletion of ozone that protects the health of environment. When coming to the point of cooling efficiency, MCE can be marked up to 20 - 50% more than CGC[1]. MCE has brought as an alternative to the CGC depending upon the several advantages it shows. In simple words, it can be defined as the reversible change in temperature that accompanies the change of magnetization of a ferromagnetic or paramagnetic material.

Basically, for any given material at a constant pressure the characteristics of MCE are the functions of the absolute temperature and the magnetic field change ($\Delta H = H_f - H_i$) where H_f and H_i are the final and initial magnetic fields respectively experienced by the material. It is generally can also be referred as the isothermal change of entropy (ΔS) and adiabatic change of temperature (ΔT) upon the variation of magnetic field H . The value of ΔT is directly measured using a thermometer or indirectly measured from specific heat data while ΔS is calculated from magnetization of specific heat. It is noted that change in entropy is expressed by the following relation:[1]

$$\Delta S = \int \frac{\partial M}{\partial T} .dH$$

MCE provides better cooling and environment protection and also has various applications. In this article, we focused more on recent developments in RT MCE materials and their applications.

In addition to this, MCE has biomedical applications and can be used in the wherein treatment of hyperthermia and drug delivery[3]. Now-a-days research is being done on drug delivery to the tumor with minimal side effects than the conventional drug delivery system for prompt diagnosis and accurate treatment. Magnetic drug delivery system is to deliver a drug to its targeted tissue with help of external magnetic field which may overcome the problem associated with traditional drug delivery system like target selectivity. The dangerous and biggest drawback of the conventional drug delivery system is that the anti-cancer medicine given directly through veins can accumulate at tumor cells due to permeability and retention effects, which may have many leaky blood vessels. As a result of this accumulation, the drug may also negatively affect healthy tissues and exhibit numerous side effects. It can be prevented by using the magnetic drug delivery system in which the drug can be precisely regulated by external magnetic field and it acts only on the tumors doesn't harm healthy tissues. Apart from this the magnetic drug delivery system can be utilized to treat a variety of conditions, including gene therapy, hearing loss, nervous system problems, and tumors etc., In the present article focused on the materials (alloys and oxides) suitable for near room temperature applications and biomedical applications of MCE materials.

II. FUNDAMENTAL ASPECTS

The current research on the MCE can be divided into two groups: The first method is the characterization of new materials in which the research is mainly focused on investigation of conventional magnetic and magneto thermal properties of new MC materials. By using this method, we can observe a substantial temperature range. One best option is to use the series of materials with different amounts of magnetic component which is responsible for the MCE. Magnetic entropy change can't be the criterion to judge the MC's performance in real applications because the magnetic entropy is an indirect and a non-measurable parameter which allows performing on rough estimates of an MCE value. But there is a possibility in such case it is recommended to measure the adiabatic temperature change in order to get a direct result of the considered material's behavior.

The second direction in the studies of MC materials is the investigation of subtle effects which play a crucial role in understanding the Physics of the phenomena and as a result could then influence its practical applications in the near future. The investigations of conventional materials, but of higher chemical purity and perfectness of the crystal structures are the example for this type of method.

III. PRINCIPLE AND WORKING OF MAGNETIC REFRIGERATION

Magnetic refrigeration is mainly based on a fundamental thermodynamic property of magnetic materials nothing but MCE which causes a temperature change if the material is subjected to a magnetic field applied under adiabatic conditions. When they are exposed to a magnetic field, the temperature increases and decreases when they are removed from it that is the effect is reversible and almost instantaneous. The MCE has many advantages than the CGC technology. The magnetic cooling obtained via MCE resolves two main issues associated with the CGC system.

The environmental challenge via a gas free solution. The economic challenge by reducing energy consumption and increasing the efficiency.

PARIS AND STRASBOURG, France based world's leading magnetic refrigeration company, cooltech announced the availability of the first commercial magnetic cooling system for its magnetic refrigeration system (MRS), the MRS 400, boasts 400 w of cooling power, keeping the internal temperature between 35.6⁰ F - 41⁰ F (20C and 5⁰ C) which is within the recommended levels for safe food storage. The magnetic cooling system utilizes a glycol-water coolant instead of a refrigerant gas which is a major contributor to climate change also resulting in an eco-friendly solution that consumes a minimal energy. The magnetic unit operates at low pressure with the rotational speed virtually eliminating vibrations are cutting noise to less than 35 decibels reducing maintenance cost. The whole system enjoys a quasi- indefinite lifespan.

With cooling powers between 200 W and 700 W, it is optimized for a wide range of products in commercial refrigeration, including products like medical refrigerators display cabinets beverage dispensers, storage plugins and wine cellars, a market that is worth over 20 billion dollars a year.

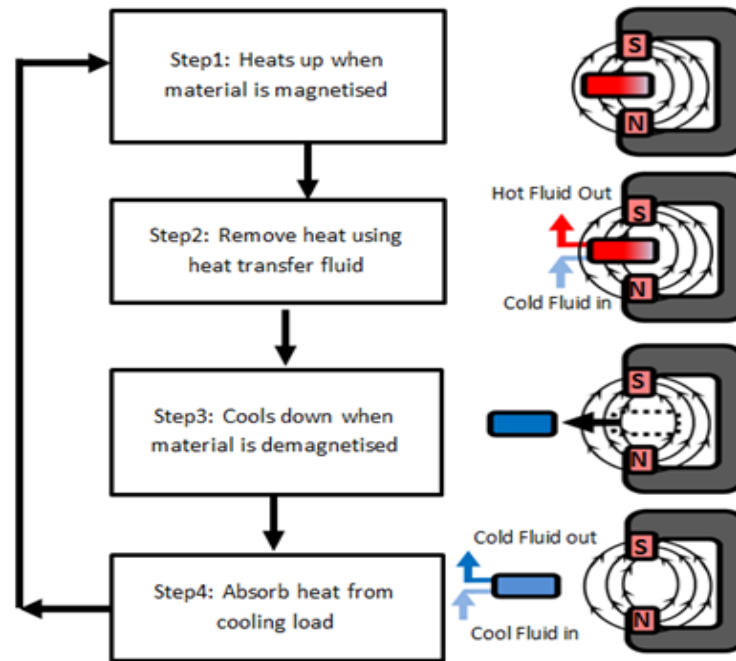


Figure1: Schematic showing basic working principle of magnetic refrigeration

Credit: Sirach's Metkel yebiyoo Cooltech applications

In a Magnetic refrigeration system, a controlled magnetic field applied a series of magnetization- demagnetization cycles to the magnetocaloric alloys. Each cycle creates a temperature gradient in the material and also the rapid succession of these cycles produces the final and stabilized hot and cold temperature in a refrigerated system.

IV. MAGNETOCALORIC MATERIALS FOR ROOM TEMPERATURE APPLICATIONS

The MCE has several applications at room temperature and the magnetocaloric materials whose transition temperatures are around the room temperature are discussed in details in this section listed in table 1. The well-known magnetocaloric material for room temperature commercial applications is Gd. The transition temperature of Gd is near to room temperature (294K) [2]. The isothermal entropy changes and adiabatic temperature changes of this rare earth metal are 10 J/kg-K and 11K at 5T magnetic field change. Among the various rare earth metals such as Gd[4], Tb[5], Dy[6], Er[7], Tm[8] etc., the Gd metal shows the transition at room temperature with high MCE parameters. Researchers alloyed the Gd metal with various other rare earths, but, the MCE values and transition temperatures were not much improved.

Table 1: Magnetocaloric effect of rare earth metals at room temperature

S.No	Sample/Composition	T _c (K)	$\Delta S_{\max}$ (J/Kg-K)	Ref
1	Gd	292	11.1 at 6 T	[4]
2	Tb	230	20 at 7.5 T	[5]
3	Dy	180	14.2 at 6.02 T	[6]
4	Ho	134	1.8 at 6.02 T	[7]
5	Er	85	1.2 at 6.02 T	[7]
6	Tm	56	-	[8]

In addition to the magnetocaloric rare-earth metals at room temperature alloys are also present and listed in table 2. The $-(\Delta S_M)_{\max}$ values are found to be 7.6 J/Kg-K for Gd₉₀Ga₁₀ at 5T magnetic field reported by Susilo et al.,[9]. According to Liu et al[10], when 5% of more Fe is added to the Gd₅₀Co₄₅ alloy, the isothermal entropy change drops from 4.6 J/Kg-K to 3.8 J/Kg-K and the transition temperature rises to room temperature i.e., from 268K to 289 K for a magnetic field change of 0-5T and RCP drops from 686 J/Kg and 673 J/Kg as well. The MCE properties of Gd replaced by Tb were reported by Ao et al.[11] that the isothermal entropy change of 5.15 J/Kg-K near room temperature 297 K with 2 Tesla magnetic field change. The characteristics of Gd₅Si₄ reported by Tishin et al.,[12] that the MCE values improved when Si was substituted with Gd instead of Tb wherein the transition temperature has increased to 336 K due to the substitution of Si, and the isothermal entropy change has increased to 9 J/Kg-K for a change in magnetic field of 0–5 Tesla. An additional significant development was made in the alloy Gd₅Si₂Ge₂ in which the T_c is 276K [13] with maximum $\Delta S_{\max}$ of 18.5 J/kg-K and $\Delta T_{\max}$ is 15K at 5T magnetic field change. Tishin et al.,[12] studied the properties of Gd₅Si₄ in which the substitution of Si to Gd than Tb has increased transition temperature to 336 K and also increased isothermal entropy change to 9 J/Kg-K for 0-5 Tesla magnetic field change. Furthermore, Gd₈₀Ge₁₅Si₅ has shown $\Delta S_{\max}$ 11.91 J/Kg-K at 260 K with RCP 164 J/Kg for 0-5 Tesla magnetic field change studied by Piotr Gebara et al[14]. It is more promising for the commercial application of magnetic refrigeration technology near room temperature because of the significantly high RC value of 351 J/kg and the maximum isothermal magnetic entropy change of 18.5 J/kg-K obtained in Gd₅Si₂Ge₂B_{0.075} at $\Delta H=0-5$ T [15]. The properties of Gd₅Si_{2.8}Sn_{1.2} which exhibits an isothermal magnetic entropy change 1.69 J/Kg-K for 1.8 T at the temperature of 301.5 K reported by Zhang et. al. [16]. The transition temperature and isothermal magnetic entropy value of Ge added to Gd₅Si_{2.06} have been improved obtained the values of $\Delta S_{\max}$ 9.5 J/Kg-K at 306 K for 0-5 Tesla magnetic field change reported by Tishin et al[12]. It is observed that the transition temperature of Mn₅Ge₃ is 297.5 K and isothermal entropy change is found to be 2.5 J/kg-K for 1T magnetic field change where the adiabatic temperature change value is 2.3 K for 2T magnetic field change[17]. The transition temperature of Mn_{0.7}Fe_{0.3}Co_{0.7}Fe_{0.3}Ge is 298 K the isothermal entropy change has found to be –3.91 J/kg-K, while the adiabatic temperature change value for 2.3 K for 2T magnetic field change[18]. The transition temperature of Ni₄₃Mn₄₇Sn_{10.5}B_{0.5} has the transition temperature of 283 K [19] and the adiabatic temperature change has found to be 17 J/kg-K. Both Ni₄₁Co₇Fe₂Mn₄₀Sn₁₀ and Ni₄₁Co_{6.5}Fe_{2.5}Mn₄₀Sn₁₀ showed a significant

change in entropy of 18.9 (22.4) J/Kg/K and 11.8 (16.8) J/Kg/K as well as refrigeration capacity of 128 (396) J/Kg and 99 (313) J/kg for a magnetic field change of 2 T (5 T)[20]. The La is doped with metals $\text{La}_{0.75}\text{Sr}_{0.25}\text{MnO}_3$ at room temperature, the isothermal entropy change of this rare earth metal is 9.23 J/Kg-K[21] at 6 T. $\text{Fe}_{85}\text{Co}_3\text{Zr}_5\text{B}_4\text{Nb}_3$ the isothermal entropy change of this rare earth metal is 3.55 J/Kg-K[22] at room temperature 336 K. For $\text{Tb}(\text{Co}_{0.94}\text{Fe}_{0.06})_2$ the isothermal entropy change of this rare earth metal is 4.3 J/Kg-K [23] at 304 K. According to Biswal et al.,[24] the transition temperature of $(\text{La}_{1-x}\text{Bi}_x)_{0.67}\text{Ba}_{0.33}\text{MnO}_3$ ($x=0-0.3$) in the range 336 K- 229 K which shifts towards low temperatures with increasing x and also entropy change ($\Delta S_{\max}$) decreases from 6.19 J/ Kg/K for $x = 0$ to 4.79 J/ Kg/K for $x = 0.3$ for a field change of 9 T. At 273K transition temperature $\text{La}(\text{Fe}_{0.94}\text{Co}_{0.06})_{11.83}\text{Al}_{1.17}$ has shown the entropy change $\Delta S_{\max} = 24$ J/Kg-K studied by Hu et al [25]. $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ has $\Delta S_{\max} = 2.75$ J/Kg-K at 260 K under the magnetic field change of 3T studied by Morelli et al [26]. According to Zhang et al [27] Na doped LaMnO_3 exhibited magnetic entropy change of 2.11 J/Kg-K with transition temperature 342 K with 63 J/Kg at 1 T. Zhong [28] investigated the MCE properties of $\text{La}_{0.813}\text{K}_{0.160}\text{Mn}_{0.987}\text{O}_3$ which has shown the magnetic entropy change of 2.10 J/Kg-K and transition temperature of 338 J/Kg with RCP 128 J/Kg under 1.5 T

Table 2: Magnetocaloric effect in alloys at room temperature

S.No	Sample/Composition	$\Delta S_{\max}$ (J/Kg-K)	T_c (K)	RCP (J/Kg)	H (T)	Ref
1	$\text{Gd}_{90}\text{Ga}_{10}$	7.6	285	392	5	[9]
2	$\text{Gd}_{50}\text{Co}_{50}$	4.6	268	686	5	[12]
3	$\text{Gd}_{50}\text{Co}_{45}\text{Fe}_5$	3.8	289	673	5	[10]
4	$\text{Gd}_{60}\text{Tb}_{40}$	5.15	297		2	[11]
5	Gd_5Si_4	9	336	-	5	[12]
6	$\text{Gd}_5\text{Si}_2\text{Ge}_2$	18.5	276		5	[13]
7	$\text{Gd}_{80}\text{Ge}_{15}\text{Si}_5$	11.91	260	164	3	[14]
8	$\text{Gd}_5\text{Si}_2\text{Ge}_2\text{B}_{0.075}$	18.5	272	351	5	[15]
9	$\text{Gd}_5\text{Si}_{2.8}\text{Sn}_{1.2}$	1.69	301.5	-	1.8	[16]
10	$\text{Gd}_5\text{Si}_{2.06}\text{Ge}_{1.94}$	9.5	306	-	5	[12]
11	Mn_5Ge_3	2.3	297.5		2	[17]
12	$\text{Mn}_{0.7}\text{Fe}_{0.3}\text{Co}_{0.7}\text{Fe}_{0.3}\text{Ge}$	-3.91	298		2	[18]
13	$\text{Ni}_{43}\text{Mn}_{47}\text{Sn}_{10.5}\text{B}_{0.5}$	17	283			[19]
14	$\text{Ni}_{41}\text{Co}_7\text{Fe}_2\text{Mn}_{40}\text{Sn}_{10}$	18.9 (22.4)		128 (396)	2(5)	[20]
15	$\text{Ni}_{41}\text{Co}_{6.5}\text{Fe}_{2.5}\text{Mn}_{40}\text{Sn}_{10}$	11.8 (16.8)		99 (313)	2(5)	[20]
16	$\text{La}_{0.75}\text{Sr}_{0.25}\text{MnO}_3$	9.23			6	[21]
17	$\text{Fe}_{85}\text{Co}_3\text{Zr}_5\text{B}_4\text{Nb}_3$	3.55	336			[22]
18	$\text{Tb}(\text{Co}_{0.94}\text{Fe}_{0.06})_2$	4.3	304			[23]
19	$(\text{La}_{1-x}\text{Bi}_x)_{0.67}\text{Ba}_{0.33}\text{MnO}_3$ ($x = 0 - 0.3$)	6.19($x=0$), 4.79($x=0.3$)	336($x=0$), 229($x=0.3$)			[24]
20	$\text{La}_{0.65}\text{Nd}_{0.05}\text{Ba}_{0.3}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3$ ($0 \leq x \leq 0.15$)	6.19($x=0$), 4.79($x=0.3$)	330($x=0$), 275($x=0.15$)		9	[24]
21	$\text{La}(\text{Fe}_{0.94}\text{Co}_{0.06})_{11.83}\text{Al}_{1.17}$	24	273		2	[25]
22	$\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_6$	2.75	260	-	3	[26]
23	$\text{La}_{0.835}\text{Na}_{0.165}\text{MnO}_3$	2.11	342	63	1	[27]
24	$\text{La}_{0.813}\text{K}_{0.160}\text{Mn}_{0.987}\text{O}_3$	2.10	338	128	1.5	[28]
25	$\text{La}_{0.78}\text{Ag}_{0.22}\text{MnO}_3$	2.90	306	38	1	[29]
26	$\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$	6.4	267	-	3	[30]
27	$\text{La}_{0.7}\text{Ba}_{0.3}\text{MnO}_3$	1.6	336	36	1	[31]

28	$\text{La}_{0.6}\text{Sr}_{0.2}\text{Ba}_{0.2}\text{MnO}_3$	2.26	354	67	1	[32]
29	$\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{0.98}\text{Ni}_{0.02}\text{O}_3$	7.65	350	459	7	[33]

magnetic field change. At the transition temperature 306 K, the $\text{La}_{0.78}\text{Ag}_{0.22}\text{MnO}_3$ [29] exhibited magnetic entropy change 2.9 J/Kg-K and RCP of 38 J/Kg has been observed under 1 T studied by Nguyen et al. J. Meera[30] reported that the transition temperature of $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$ is 370 K, with RCP 41 J/Kg, magnetic entropy change of 1.5 J/Kg-K at 1 T. Phan et al [31] reported that the transition temperature of $\text{La}_{0.7}\text{Ba}_{0.3}\text{MnO}_3$ is $T_c = 336$ K, and entropy change is $\Delta S_{\max} = 1.6$ J/Kg-K, with RCP = 36 J/Kg at 1 T field change. Ayadi reported the MCE properties of $\text{La}_{0.6}\text{Sr}_{0.2}\text{Ba}_{0.2}\text{MnO}_3$ [32]. The values are $T_c = 354$ K, $\Delta S_{\max} = 2.26$ J/Kg-K, with RCP=67 J/Kg under 1 T. Phan et al [33] studied the properties of $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{0.98}\text{Ni}_{0.02}\text{O}_3$ which shown the transition temperature 350 K, magnetic entropy change of 7.65 J/Kg-K with RCP of 459 J/Kg at 7 T.

The following MCE values are listed in the table 3. The magnetization, magnetic entropy change of $\text{Pr}_{0.58}\text{Sr}_{0.42}\text{MnO}_3$ [34], that the transition temperature is 300 K for a magnetic entropy change of 2.33 J/Kg-K at 5 T with RCP 65 J/Kg Investigated by D.V. Maheshwar repaka. Recently, with a magnetic field change of 9 T at 303 K, a gigantic magnetocaloric effect of $\Delta S_M = -81.8$ J/Kg-K has been reported in the $\text{Ni}_{50}\text{Mn}_{18.5}\text{Cu}_{6.5}\text{Ga}_{25}$ alloy during the reverse martensitic transformation (heating cycle)[35]. Mn rich alloys have a greater curie temperature than Ni rich alloys in the same series, such as $\text{Ni}_{50}\text{Mn}_{25-x}\text{Ga}_{25-x}$, when Zhou et al. [36] investigated the MCE characteristics of the $\text{Ni}_{50}\text{Mn}_{25-x}\text{Ga}_{25-x}$ series, he found that the magnetic transition temperature increased as the Mn content increased. The MCE values of $\text{Ni}_{50}\text{Mn}_{29}\text{Ga}_{21}$ are ΔS_M 9.56 J/Kg-K 396 K with 8 Tesla. Aliev et al[37] observed the magnetic and thermodynamic properties of $\text{Ni}_{2.19}\text{Mn}_{0.81}\text{Ga}$ alloy with coupled magnetic and structural phase transitions, in which he observed the magnetic entropy change of 4.5 J/Kg-K with curie temperature of 335 K at 1.5 T. With the replacement of In at Ga, increases the Curie temperature. The alloy is $\text{Ni}_{59.0}\text{Mn}_{23.5}\text{In}_{17.5}$, where a magnetic field change of 0–3 T causes the Curie temperature to drop to 246 K and $\Delta S_{\max}$ to drop to 2.01 J/Kg–K with RCP 120 J/Kg. According to Feng et al. (2011), the greatest value of $\Delta S_{\max}$ for the $\text{Ni}_{48}\text{Cu}_1\text{Mn}_{39}\text{Sb}_{12}$ alloy is $\Delta S_{\max} = 9.38$ J/Kg-K at 291K for a magnetic field change of 5 T.

The alloy has a refrigerant capacity of 25.9 J/kg[38]. The MCE values of $\text{Ni}_{45}\text{Co}_5\text{Mn}_{36.6}\text{In}_{13.4}$ are as $\Delta S_{\max} = 28.4$ J/Kg-K, $T_c = 292$ K at field $\Delta H = 7$ T investigated by Kainuma et al [39]. The magnetocaloric properties of $\text{Ni}_{59.0}\text{Mn}_{23.5}\text{In}_{17.5}$ have been studied by V. Zhukova et al.[40]. Under an external magnetic field of $\Delta H = 3$ T with RCP 120 J/kg, the estimated magnetocaloric parameters are $\Delta S_{\max} = 2.01$ J/Kg-K and $T_c = 246$ K. Wada et al. [41] investigated $\text{MnAs}_{0.9}\text{Sb}_{0.1}$, another alloy based on Mn. At the transition temperature (T_c) of 280K with a change of 5T magnetic field, $\text{MnAs}_{0.9}\text{Sb}_{0.1}$ exhibits the greatest magnetic entropy change of 35 J/Kg-K. Materials like $\text{Fe}_{88}\text{Zr}_8\text{B}_4$ that were studied by Liu et al. [10] show $\Delta S_{\max} = 3.3$ J/Kg-K, $T_c = 284$ K, and RCP = 646 at field $\Delta H = 5$ T. According to Sharma et al. [42], the magnetocaloric characteristics of $(\text{Fe}_{0.8}\text{Mn}_{0.2})_3\text{Al}$ are $\Delta S_{\max} = 0.96$ J/Kg-K, $T_c = 350$ K, with RCP 400 J/Kg at field $\Delta H = 5$ T. According to Thanveer et al. [43], the alloy $(\text{Fe}_{70}\text{Ni}_{30})_{97}\text{Mo}_3$ showed $\Delta S_{\max} 1.69$ J/Kg-k, $T_c = 320$ K, with RCP 440 J/Kg in a magnetic field of 5 T[43]. The MCE properties of $\text{Fe}_{17}\text{Pr}_2$ were examined by Chaudary et al. [44] under a magnetic field of 5 T. The magnetic entropy changed by 4.5 J/Kg-K, the transition temperature was 292 K, and the RCP was 573 J/Kg. According to J. L. Sanchez

Llamazares et al., the alloy Fe_{17}Y_2 showed ΔS_{max} 4.4 J/Kg-k, T_c 301 K, and RCP 533 J/Kg in a magnetic field of 5 T [45]. According to Chaudary et al. [44], the magnetic entropy change of $\text{Fe}_{65}\text{Cu}_{35}$ is 1.04 J/Kg-k, with a transition temperature of 360 K and an RCP of 234 J/Kg at magnetic field changes of 0–5 T. According to Tian et al. [46], the alloys $\text{Fe}_{77}\text{Ce}_1\text{Si}_4\text{Nb}_5\text{B}_{12}\text{Cu}_1$ MCE characteristics include $\Delta S_{\text{max}} = 2.18$ J/Kg-k, $T_c = 348$ K with RCP = 271 J/Kg, and magnetic field of 5 T. Table 3 lists the alloy compounds mentioned previously. According to reports by Sharma et al. [42] and Chaudary et al. [47], the Fe-based alloys $(\text{Fe}_{0.72}\text{Cr}_{0.28})_3\text{Al}$, $\text{Fe}_{79}\text{B}_{12}\text{Cr}_8\text{Gd}_1$, exhibit magnetic entropy changes of 1.16 J/Kg-K, 1.42 J/Kg-K, and transition temperatures are 330 K, 355 K with RCP 305,153 J/Kg under the external magnetic field of 5 T, 1.5 T. Another Fe-based alloy, $\text{Fe}_{79}\text{Ce}_{11}\text{B}_6$, was examined by Zhu-bai Li et al. [48]. Its magnetic entropy change was 3.90 J/Kg-K, and at 5 T magnetic field change, it had a transition temperature of 297 K and an RCP of 420 J/Kg. According to Chaudary et al. [47], the ferrite with the compositional formula $\text{Mn}_{0.3}\text{Zn}_{0.7}\text{Fe}_2\text{O}_4$ showed ΔS_{max} of 0.88 J/Kg-k and RCP of 174 J/Kg in a magnetic field of 5T at a broad temperature range of 30 K to 400 K. This broad temperature range indicates high RCP value which used for magnetic cooling applications, such as self-pumping fluids.

A large magnetic entropy change was found in CMR manganite-based oxides suggesting that these materials might be exploited for magnetic refrigeration applications. Moreover, additional advantage with these materials is that they are less expensive when compared with those of Gd based ones. Wang et al (2005) [49] studied the MCE properties of well-known oxide material $\text{La}_{0.7}\text{MnO}_{3-\delta}$, which has 1.32 J/Kg-K magnetic entropy change at 290 K with RCP of 37 J/Kg at 1 T. The effect of Ca doping in LaMnO_3 was studied by R. Vonhelmut et al [50]. They have found that Ca doped LaMnO_3 showed an increase in magnetic entropy of 6.4 J/Kg-K with increasing doping and the transition temperature decreased to 267K with 0-3 T magnetic field change. Another doped material $(\text{La}_{0.47}\text{Gd}_{0.2})\text{Sr}_{0.33}\text{MnO}_3$ has magnetic entropy change of 1.93 J/Kg-K which is lower than $\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$, and has transition temperature 289 K at 2 Tesla field [49]. Phan et al [51] has studied the magnetocaloric properties of the compound $\text{La}_{1.6}\text{Ca}_{1.4}\text{Mn}_2\text{O}_7$, and an entropy change of 17 J/Kg-K has been observed at 270 K under the magnetic field change of 5 T.

Table 3: Magnetocaloric effect in alloys at room temperature

S.No	Sample/Composition	ΔS_{max} (J/Kg-K)	T_c (K)	RCP (J/Kg)	H (T)	Ref
1	$\text{Pr}_{0.58}\text{Sr}_{0.42}\text{MnO}_3$	2.3	300	65	2	[34]
2	$\text{Ni}_{50}\text{Mn}_{18.5}\text{Cu}_{6.5}\text{Ga}_{25}$	81.8	303	-	9	[35]
3	$\text{Ni}_{2.19}\text{Mn}_{0.81}\text{Ga}$	4.5	335	-	1.5	[37]
4	$\text{Ni}_{50}\text{Mn}_{29}\text{Ga}_{21}$	9.56	396	-	8	[36]
5	$\text{Ni}_{48}\text{Cu}_1\text{Mn}_{39}\text{Sb}_{12}$	9.38	291	25.9	5	[38]
6	$\text{Ni}_{45}\text{Co}_5\text{Mn}_{36.6}\text{In}_{13.4}$	28.4	292	-	7	[40]
7	$\text{Ni}_{59.0}\text{Mn}_{23.5}\text{In}_{17.5}$	2.01	246	120	3	[40]
8	$\text{MnAs}_{0.9}\text{Sb}_{0.1}$	35	280	-	5	[41]
9	$\text{Fe}_{88}\text{Zr}_8\text{B}_4$	3.30	284	646	5	[10]
10	$(\text{Fe}_{0.8}\text{Mn}_{0.2})_3\text{Al}$	0.96	350	400	5	[42]
11	$(\text{Fe}_{70}\text{Ni}_{30})_{97}\text{Mo}_3$	1.69	320	440	5	[43]
12	$\text{Fe}_{17}\text{Pr}_2$	4.5	292	573	5	[44]
13	Fe_{17}Y_2	4.4	301	533	5	[45]

14	$\text{Fe}_{65}\text{Cu}_{35}$	1.04	360	234	5	[44]
15	$\text{Fe}_{77}\text{Ce}_1\text{Si}_4\text{Nb}_5\text{B}_{12}\text{Cu}_1$	2.39	348	271	5	[46]
16	$(\text{Fe}_{0.72}\text{Cr}_{0.28})_3\text{Al}$	1.16	330	305	5	[42]
17	$\text{Fe}_{79}\text{B}_{12}\text{Cr}_8\text{Gd}_1$	1.42	355	153	1.5	[42]
18	$\text{Fe}_{79}\text{Ce}_{11}\text{B}_6$	3.90	297	420.09	5	[47]
19	$\text{La}_{0.7}\text{MnO}_{3-\square}$	1.32	290	37	1	[49]
20	$\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$	6.4	267	-	3	[49]
21	$(\text{La}_{0.47}\text{Gd}_{0.2})\text{Sr}_{0.33}\text{MnO}_3$	1.93	285.9	-	2	[49]
22	$\text{La}_{1.6}\text{Ca}_{1.4}\text{Mn}_2\text{O}_7$	17	270	-	5	[51]

V. BIO-MEDICAL APPLICATIONS- MAGNETIC NANO PARTICLES

Magnetocaloric materials are well known for its room temperature magnetic refrigeration applications. Apart from that, researchers focus mainly on environmentally friendly magnetic materials and their applications in heating, refrigeration and magnetic energy conversion technologies. Recently, there are many increasing numbers of medical applications of MC materials as controllable delivery and release of drugs and biomedical substances to some of the defined locations in the human body i.e., magnetic drug delivery system and magnetic hyperthermia. The history of magnetic drug delivery system is, in 1956, Gilchrist published a lecture on the process of inductive heating of lymph nodes following the injection of particles that induce magnetism in lymph nodes close to surgically excised tumours. In 1963, Meyers describes how they used a horseshoe magnet to successfully direct and block tiny iron particles in the veins of dog legs[52]. In 1970 Magnetic nanoparticles were first postulated by Widder, Senyi, and colleagues[53]. Wu and colleagues, as well as Jones and Winter, were the first to employ magnetic drug delivery in the treatment of liver cancer[54]. In 1996, the first clinical trial using magnets to distribute medication was carried out. This magnetic drug delivery system has more advantages than the conventional drug delivery system which mentioned in table 4.

Table 4: Differences between magnetic drug delivery system and conventional drug delivery system

Magnetic drug delivery system	Conventional drug delivery system
Do not affect healthy tissues	Affect healthy tissues
Toxicity level is lower	Toxicity level is higher
Low dose is required	High dose is required
Lower side effects	Higher side effects
Target specific	Not target specific
It is not possible to diagnose and treat with a single agent.	Possible to diagnose and treat with a single agent.
High cost	Low cost

Apart from the above applications there are many uses for magnetocaloric materials, a few of them are mentioned here.

- Tetrahedral antibodies, chemotherapeutic drug, and magnetic nanoparticles conjugated as the carrier[55].
- GIT cancer therapy and target imaging using antibody-linked fluorescent magnetocaloric materials[56].
- Magnetocaloric materials coated in meso-2, 3-dimercaprosuccinic acid with a carboxylic acid group can be used to absorb DNA[57].
- These materials with an iron oxide gold core-shell were employed to detect *Escherichia coli*[58].
- The materials can be employed in tumor thermotherapy because they create heat effects when exposed to a changing magnetic field[59]. Hyperthermia and magnetofection are two applications of these materials.

Magnetic drug delivery and hyperthermia are covered in detail since these are two of the most useful uses nowadays.

1. **Magnetic Drug Delivery:** One of the problems with the artificial implants as joints, abdominal nets, stents, urinary and biliary ducts etc. is the rejection. Researchers proposed that applying a special type of coating to these implants consisting of several layers. The first thin film layer is a negative Magnetocaloric material that is cooled in an external magnetic field and the layer is covered with a polymer Matrix that absorbs the drug. The polymer matrix is in direct contact with the MCE material. The entire structure is placed in the body during the operation. Here, when the magnetic field lowers its temperature, the polymer changes into a liquid state and releases drug at the site of the implantation. In this technique of targeted drug delivery, the rest of the body will be unaffected as it only influences the source of inflammation. Some researchers have also proposed to use Magneto cal materials as drug delivery agents even during the surgeries. Aleksei S.Komlev [60], focused to use FeRh as MC Material with high magnetic entropy change for drug delivery because this material is nontoxic like other alloys of iron with platinum group metals. Poly-N-isopropyl-acrylamide (PNIP Am) is also an implantable element with a film containing a drug is biocompatible and widely used in the therapeutic practice of dental prosthetic.

Tishin [2] concentrated on the development of functional coatings for controlled release of bioactive compounds in an external magnetic field and methods of its application to the implants. Functional coating consists of a composite material with magnetocaloric properties. Changing the temperature of the magnetic component causes a transition of a biocompatible polymer (which is in thermal contact with the magnetic material) to the hydrophilic state. The composite coating also includes a thermal insulating layer in order to reduce heat transfer to the surrounding tissues. A proposed carrier for active substances combines the advantages of accurate delivery by using magnetic carriers with the convenience of controlling the retention/release rate of the active substance from the carrier using materials of varying characteristics under the influence of external conditions, such as temperature, magnetic field strength, etc.[61].

2. **Hyperthermia:** Hyperthermia is a process in which the treating of diseases is done by heating. This method was known since the ancient era. In this method, increasing the temperature of cell above 41°C is known to cause some effects in the membrane and interior part of the cell, such as Increasing the fluidity and permeability of the cell membrane
- Slowing down of the mechanism of synthesis of nucleic acid and protein
 - Including protein denaturation and agglomeration and damaging the tumor vasculature resulting in a decrease of blood flow [61][2].

Cancer therapy is the technique in which the intensive research has been conducted in the stream of electromagnetically excitable thermo seeds. In the whole-body hyperthermia heat is applied to the whole body in several ways such as using hot water blankets, electric blankets and hot wax. In the regional hyperthermia method, heat is applied to a whole organ or region of the body using external ways of the applicators and regional perfusion. In local hyperthermia heat is applied to small tumor regions using electromagnetic waves such as radio waves microwaves and ultrasound which are generated by applicators that are placed at the surface are under the skin of superficial cancer or implanted inside the targeted region.

Hyperthermia is the destruction of malignant cancer cells by an internal heating mechanism.

Following,[3] it is categorized by the obtained steady temperature level of the tumor

- Diathermia ($T < 41^{\circ}\text{C}$)
- Apoptosis (moderate hyperthermia with a final temperature of $42^{\circ} < T < 46^{\circ}$)
- Thermo ablation by necrosis ($T > 46^{\circ}$).

The conventional hyperthermia methods have problems to achieve sufficiently high heating rates. A numerical feasibility study by[3] demonstrates about this method that responds ideally to the demanded heating rate within the medical tolerated limit $H_0 \cdot f < 5 \cdot 10^8 \text{ Am}^{-1} \text{ s}^{-1}$, where H_0 and f denotes the applied external field and the rotation frequency of this field.

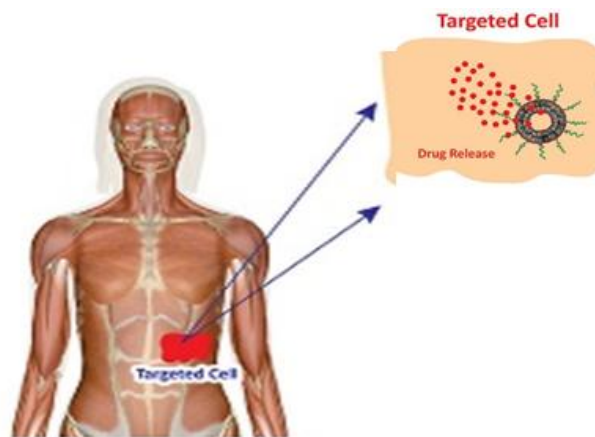


Figure 2: Schematic showing targeted drug delivery in cancer cells

There are two new inventions of magnetic hyperthermia methods in which first invention of the Russian authors[2] relates to magnetocaloric material physics and to medicine, in particular to magneto therapy (hyper thermal electromagnetic therapy) of malignant neoplasms. In this method, a high MCE exhibiting nanoparticles injected into a tumor, wherein the material has a magnetic ordering temperature close to human body temperature and it is selected from a group containing precious metals, rare-earth elements and the alloys for intermetallic compounds. A Low concentration of magnetocaloric material particles in the Nano size domain (e.g. 200 nm) is injected and uniformly distributed over the tumor that is assumed to be spherical. Approximately 42 °C in heating of tumor is demanded. The method will be applied several times and often in combination with other cancer defeating methods as radiotherapy, chemotherapy etc.

The second invention is substantially different to conventional magnetic hyperthermia methods which work by internal magnetic heating mechanism like a browns & Neels relaxation, hysteresis effect etc. In this new method, a large number of nanowires are homogeneously distributed in a biocompatible gel or fluid and then injected into the cancer tumor. A rotational magnetic field is applied, the rotating nanowires could be used as Nano scalpels to cut malignant tumor cells, but this kind of application is not evaluated. Instead, by fluid friction in the nano wire's fluid boundary layer, a strong heating effect is produced which finally leads to an elevated steady-state temperature of the tumor that destroyed the malignant cancer cells.

VI. FUTURE WORK IN MEDICAL FIELD

Using MCE for the treatment of hyperthermia can be enhanced by improving the heating rate to destroy cells by a simultaneous occurrence of several magnetic heating effects. It is also possible to design a magnetic field change in the interior of the nanowires and to induce the MCE. This has the additional advantage of temperature stabilization given by the magnetic phase transition with its elevated effective specific heat and related higher thermal capacity.

VII. CONCLUSIONS

Magnetocaloric materials provide better cooling and environment protection from various gases. Progress in magnetic refrigeration technology, especially in room-temperature magnetic refrigeration, has been recognized worldwide. This enabling technology will firmly replace the CGC technology in the near future. The discoveries of outstanding magnetocaloric materials have provided new opportunities to use them as alternative working materials in active magnetic refrigerators at various temperatures. Medical applications can be focused more as e.g., MCE materials consisting of thermo-sensitive polymers and magnetic materials with large MCE values. Such materials can perform local cooling inside the human body and release drugs, hormones, glues and other substances from the surface of the implant and also uses as drug delivery agents to the tumors under the guidance of external magnetic field which has more advantages than the conventional methods. It is still early in the field of magnetic drug delivery; thus, efforts are being made to move it from the bench to the clinic by creating improved magnetic drug delivery systems.

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