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Exploiting of magnetocaloric effect from manganese doped cobalt ferrite nanoparticles for low temperature applications

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ABSTRACT: *This paper reports on the magnetocaloric effect exploited from the manganese doped cobalt ferrite nanoparticles using indirect method. The optimum values of magnetic entropy change, adiabatic temperature change, refrigeration capacity and maximum specific cooling energy are found to be -0.37J $kg^{-1}K^{-1}$, 65.01K, 24.05 J $kg^{-1}$and 192.95J kg^{-1} under the magnetic field difference 0.2 T between 0.2 – 0.4 T below 200 K temperature range. As such the investigated materials are expected to be suitable for the applications in low temperature physics and also promising for space born applications.*

KEYWORD: *Magnetocaloric effect, Magnetic entropy, refrigeration capacity, maximum specific cooling energy*

I. INTRODUCTION

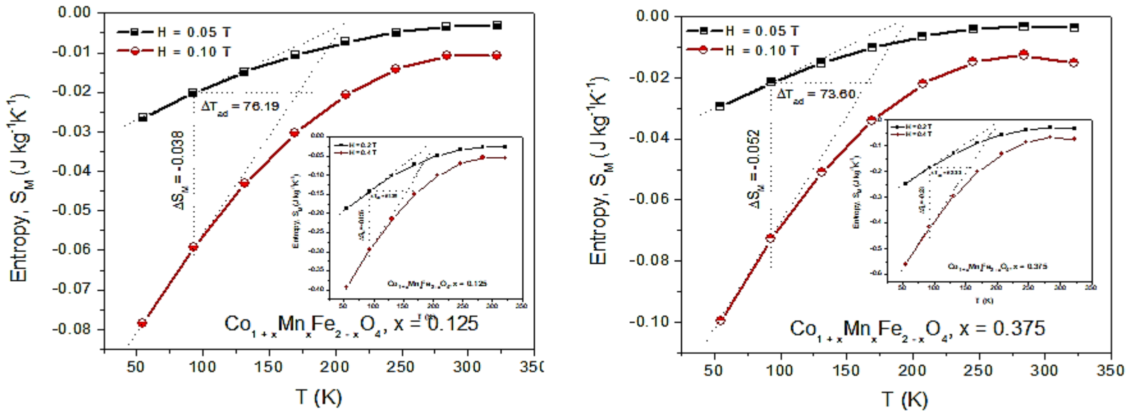
Magnetocaloric effect (MCE) is defined as the cooling or heating of a magnetic material when it is subjected to a varying magnetic field and characterized by an adiabatic change in temperature ΔT (or an isothermal change in entropy, ΔS) arising from the application of external magnetic field, H. The MCE was first discovered by the French and Swiss physicists Weiss and Piccard [1]. The first practical use of this MCE was suggested by Debye [2]and Giauque[3]to attain temperatures lower than that of liquid helium, which had been the lowest achievable experimental temperature. Magnetic refrigeration is relatively a new entrant to the list of application of magnetic materials [4, 5]. The use of magnetic material as a refrigerant relies on its magnetocaloric behavior. The magnetocaloric material usually of perovskite structure, where the rotational disorder of octahedrons is the origin of this magnetocaloric effect due to their spin-lattice (magnetoelastic) interactions [6].The disorderliness of octahedrons leads to possess the magnetic entropy $S_M$in the solids and therefore is one of the governing parameter of MCE. Almost all the magnetic materials can exhibit this magnetocaloric (MCE) effect. However, in general, the compounds exhibiting large change in magnetic entropy, adiabatic temperature and cooling power are considered as large MCE materials. Large MCE near room temperature is important for household purpose but for liquefaction of hydrogen, helium and space technology application, low temperature region is also very important. As such efforts have been made to synthesize materials of large magnetocaloric property, which are capable to operate in different temperature ranges, suitable for corresponding applications over the years.

The magnetocaloric effect can be exploited for cooling applications in various temperature regimes, the oldest being the adiabatic demagnetization which was used to achieve the temperatures below 1 K with the help of paramagnetic salts such as $Gd_2(SO_4)_3.8H_2O$. Apart from the paramagnetic salts, the paramagnetic alloys like $PrNi_5$ has also been used in the adiabatic demagnetization devices [6]. Recent studies are on intermetallic compound formed between different rare earths R and transition metals (TM=Fe, Co, Ni) in the cubic with $MgCu_2$-type structure [7]. They also form with nonmagnetic elements such as Al, Ga, Si, and Ge etc. The magnetic ordering temperatures of RFe_2 compounds being much above the room temperature, from the point of view of magnetic refrigeration application, they are not suitable. On the other hand, the compounds based on Co and Ni has their ordering temperatures below room temperature and has attracted several studies. The tunability of the magnetic ordering temperature of these compounds over a wide span with the help of substitutions at the Co/Ni site, without changes in the crystal structure, has prompted many researchers to carry out detailed magnetic and other related investigations [8-13]. Keeping the above in view, an effort is made to exploit MCE from the manganese doped cobalt ferrite nanoparticles in their spinel structure using indirect method and results are reported in this paper for their suitability in low temperature physics, detectors in astronomy and heat regenerator for space born applications.

II. EXPERIMENTAL

The sample for the present work has been prepared by the solid-state reaction route using the planetary ball milling technique. The powder of Co_2O_3, MnO_2 and Fe_2O_3 were mixed in desired proportionate (non-stoichiometric ratio) and hand milled for 2 hours before calcination. After calcination at 550^{0}C, again the mixer was ball milled for 12 hours. The composition formula of the prepared samples was $Co_{1+x}Mn_xFe_{2-x}O_4$, where $0 \leq x \leq 0.5$. The powders of these samples have been used to scaling the particle size using FESEM and the EDS spectrum used to confirm the presence of compositional elements at the laboratory of ceramic and glass engineering department of Bangladesh University of Engineering and Technology (BUET).The average particle size of all the samples are found to be in the nanometer rangeand the presence of Co, Mn, Fe and O in them are also confirmed [14]. The XRD was also performed for the investigated samples and the appearance of the peaks confirmed their crystallinity and single-phase inverse spinel structure as reported in the literature [15]. The sample powders were used to measure isothermal magnetization using homemade vibrating sample magnetometer (VSM) at the laboratory of physics department of BUET in the temperature range 77 K – 300 K (RT) by varying the magnetic field up to 0.4 T(4kOe). The magnetocaloric effect of the material was determined from the isothermal magnetization curves.

III. RESULT AND DISCUSSION



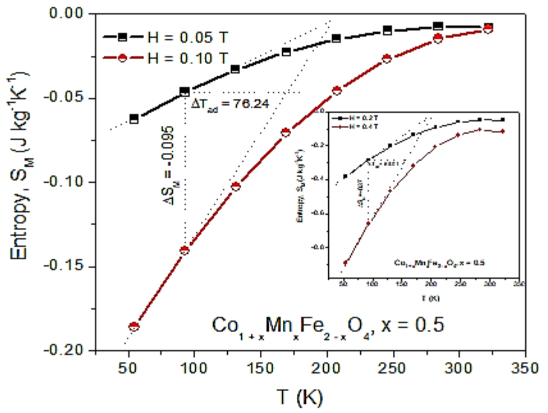


Table-1: MCE parameters for the samples of $Co_{1+x}Mn_xFe_{2-x}O_4$ in SI unit

x	ΔS_M Jkg^{-1}K-1	ΔT_{ad} (K)	RC Jkg^{-1}	qR_{max} Jkg^{-1}
$\Delta H = 0.05\,T$				
0.125	-0.038	76.19	2.89	20.86
0.375	-0.052	73.60	3.83	27.50
0.5	-0.095	76.24	7.24	50.07
$\Delta H = 0.2\,T$				
0.125	-0.16	61.39	9.82	86.67
0.375	-0.23	62.33	14.34	120.33
0.5	-0.37	65.01	24.05	192.95

Fig.1: Entropy S_M vs. T curves for the composition $Co_{1+x}Mn_xFe_{2-x}O_4$ at x = 0.125, 0.375 and 0.5

Magnetic entropy change ΔS_M and adiabatic temperature change ΔT_{ad} are the characteristic parameters or values, used to confirm the existence of magnetocaloric effect, MCE, in the material. Isothermal magnetization curves were used to determine the magnetic entropy, $\mathbf{S_M}$ by integrating the following Maxwell equation, which gives the relation between H, M and T to the MCE values $\Delta T_{ad}(T,\Delta H)$ and $\Delta S_M(T,\Delta H)$ [16]:

$$\left(\frac{\partial S(T,H)}{\partial H}\right)_T = \left(\frac{\partial M(T,H)}{\partial T}\right)_H \qquad (1)$$

Integrating this equation-(1) yields:

$$S_M(T,\Delta H) = \int_{H_1}^{H_2} \left(\frac{\partial M(T,H)}{\partial T}\right)_H dH \qquad (2)$$

This equation indicates that the magnetic entropy is proportional to both the derivative of magnetization with respect to temperature at constant field and to the field variation. Thus, the magnetic entropy $S_M$is evaluated for the magnetic field, H,0.05 T and0.1T and presented in fig.1 as a function of temperature for the sample of composition $Co_{1+x}Mn_xFe_{2-x}O_4$ at different Mn content i.e. x = 0.125, 0.375 and 0.5 respectively. From these graphs, the governing parameters ΔS_M and ΔT_{ad} of MCE have been calculated using the slope lines as shown in fig.1.Significantadiabatic temperature change, ΔT_{ad} and insignificant magnetic entropy change $\Delta S_M$are noticed from the graphs below the temperature 200 K for magnetic field difference $\Delta H = 0.05\,T$ between 0.05 – 0.1Tbut above this temperature, they are appear to be trivial for all three samples, those are listed in the table-1. Besides, the most meaningful figures of merit that provides a good measure of the effectiveness of materials for cooling applications is the refrigeration capacity (RC), which has been calculated by the following equation:

$$RC = \Delta S_M \times \Delta T_{ad} \qquad (3)$$

From table-1, it is seen that the absolute value of ΔS_M,ΔT_{ad},RC are found to increase with the Mn content. This increasing trend of the aforesaid parameters with the increase of Mn content may be attributed to theusual antiferromagnetic effect of Mn^{2+} in the B site. Furthermore, the maximum specific cooling energy is another important parameter needed to take in account in the design of active magnetic refrigerator and mathematically expressed [1] as:

$$qR_{max} = \frac{(2T_C + \Delta T_{ad})}{2} \times \Delta S_M \qquad (4)$$

Here, the symbols bear the usual meanings. The Curie temperature, T_C for the investigated sample are found to be 511 K at x = 0.125, 492K at x = 0.375 and 489 K at x = 0.5 as reported in the literature [21]. Using these values of T_C, the value of qR_{max}have been calculated by the equation-4 and tabulated (table-1) as well.

In the similar way, the MCE governing parametersΔS_M, ΔT_{ad} and RC have been evaluated for the magnetic field 0.2 T and 0.4 T(as shown in the inset of fig.1) and presented in the table-1to analyze the effect of magnetic field on MCE. The values of ΔS_M and RC for all three samples are found to be significantly high but ΔT_{ad} to be comparatively low for the magnetic field difference $\Delta H = 0.2\,T$ between 0.2 – 0.4 T. The increase of ΔS_M with the magnetic field may be attributed to the degeneracy in the ground state tend to be lifted causing frustrated magnetic moments to polarize in the field direction as explained in the literature [17]. However, the maximum values of $\Delta S_M$and ΔT_{ad}at x = 0.5for the magnetic field difference 0.2 T between 0.2 – 0.4 T may be correlated to the surface disorder originating from the broken exchange bonds and high anisotropy on the surface due to effects of nanosized particles that leading to non-colinearity of magnetic moments on their surface as explained in the literature [18, 19, 20].

IV. CONCLUSION

Indirect method is used to evaluate the governing parameters such as magnetic entropy change, ΔS_M and adiabatic temperature change, ΔT_{ad} from the isothermal magnetization curves of the investigated samples. The samples were prepared with the composition formula $Co_{1+x}Mn_xFe_{2-x}O_4$ at different weight percent of manganese $(0 \leq x \leq 0.5)$. The optimum value of the magnetic entropy changeΔS_M and adiabatic temperature change $\Delta T_{ad}$is obtained at weight percent of manganese 0.5 under both the magnetic field difference (0.05 T and 0.2 T) whereas the adiabatic temperature change is found to be maximum under the magnetic field difference 0.05 T at x = 0.5(Mn content) below the temperature 200 K. Above this temperature the magnetocaloric effect is insignificant. Since the high value of magnetic field is a challenge for practical application of magnetocaloric effect, so the material at weight percent of manganese 0.5 under the magnetic field difference 0.2T between 0.2 – 0.T, very much achievable by the permanent magnet, is expected to be suitable for the low temperature detector or sensor in space born applications because of large refrigeration capacity and the maximum specific cooling energy. However, the values of MCE are completely based on indirect method, so it is suggested to measure the same using direct method for further confirmation before of their practical implementation.

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