



Large magnetocaloric effect in geometrically frustrated polycrystalline ErMnO₃ compound at cryogenic temperature



Kalipada Das^{a,*}, Sanjib Banik^b, I. Das^b

^a Department of Physics, Seth Anandram Jaipuria College, 10 Raja Naba Krishna Street, Kolkata 700005, India

^b CMP Division, Saha Institute of Nuclear Physics, 1/AF, Bidhannagar, Kolkata 700064, India

ARTICLE INFO

Keywords:
Manganite
Magnetocaloric effect

ABSTRACT

In this manuscript we report significantly large magnetocaloric effect in the cryogenic temperature region for the chemically stable polycrystalline ErMnO₃ compound. For this compound, the antiferromagnetic transition temperature of the Mn³⁺ ions is nearly $T \sim 75$ K. However, the large non saturating magnetization and magnetocaloric effect are found at a temperature lower than 20 K. Such non saturating nature of magnetization and magnetic entropy changes for the application of external magnetic field is addressed by considering the gradual alignments of dominant paramagnetic moments caused by Er³⁺ ions.

1. Introduction

During previous few decades, the search for energy materials gets an utmost importance from the technological as well as fundamental point of view [1–20]. Among the several properties of the materials, multi-ferroic, magnetoresistive properties, magnetocaloric effect (MCE) *etc.*, were extensively studied [1,2,12,21–24]. MCE of a materials is generally described by the isothermal magnetic entropy changes or adiabatic temperature changes due to the application of external magnetic fields. Since magnetocaloric effect is directly related with the suppression of the magnetic randomness in the presence of external magnetic fields, initially the materials having high magnetic moment namely Gd, and Gd-based intermetallic compounds were considered to be giant magnetocaloric materials [1]. However, due to the lower production cost, high chemical stability, significantly larger resistivity, the oxide based perovskite manganites also get a noticeable attention during previous two decades [12]. Additionally, another beneficial aspect is the tunability of operating region of manganites. From the application point of view, magnetocaloric materials broadly categorize into two different operating regions: cryogenic temperature and near room temperature region. There are a numerous studies of MCE at low temperature on the intermetallic compounds and that on oxide based materials, near room temperature [1,12]. However, a few studies related to the large magnetocaloric effect at the cryogenic temperature range for stable oxide

based compounds were also reported earlier [12,16].

According to the earlier reports, maximum value of the magnetic entropy changes generally occur near the vicinity of the disorder to order (paramagnetic to ferromagnetic/antiferromagnetic) transition [1,12]. However, in some special cases the large magnetic entropy changes also appears in the relatively lower temperature region [16].

To concentrate on perovskite manganites, the general formula is RMnO₃ where R is trivalent element. In most of the cases cubical crystallographic symmetry and antiferromagnetic (A-type) insulating ground state was found. However slight distortion of this crystallographic symmetry gives rise to several interesting properties due to the strong correlation between the spin, lattice and charge degrees of freedom. The large magnetocaloric effect associated with the orientation of the trivalent rare earth ions having large magnetic moment was reported earlier [16]. Regarding this context it is important to mention that in case of the geometrically frustrated magnetic materials large value of the relative cooling power (RCP) which is the product of the maximum value of the entropy change and its temperature span at half maxima can be observed due to higher magnetic randomness. The large value of RCP due to similar fact is also reported recently in intermetallic compounds [25].

In the present study we report the magnetic and magnetocaloric properties of geometrically frustrated polycrystalline ErMnO₃ compound. According to the previous studies this compound form in hexag-

* Corresponding author.

E-mail address: kalipadadasphysics@gmail.com (K. Das).

onal crystal structure with space group $P6_3CM^{23}$. The $ErMnO_3$ compound also known to show multiferroic properties as mentioned in earlier works [21–23]. Our study indicates that the magnetization of this compound increases with decreasing temperature without any signature of saturation down to 5 K. The compound also exhibits significantly large non saturating magnetocaloric effect at low temperature region. Because of such magnetocaloric properties along with the other added advantages this compound can be important from the technological perspectives at the cryogenic temperature region.

2. Sample preparation, characterizations and measurements

The polycrystalline $ErMnO_3$ compound was prepared by the sol-gel route. Starting materials were preheated Er_2O_3 and MnO_2 . Er_2O_3 was converted to its nitrate forms by adding nitric acid and dissolved into millipore water. Since MnO_2 is directly not converted into its nitrates form, hence first its converted to its oxalate form by using appropriate amount of oxalic acid and millipore water and finally dissolved into the millipore water after adding the nitric acid.

After dissolving the constituent elements, next stage of this process is gel formation. For this part, individual clear solutions were mixed-up in a beaker and stirrer some time for proper homogeneity of the solution and appropriate citric acid was mixed. The beaker, containing the homogeneous precursor solution was kept in a water bath at $\sim 80^\circ C$ for slow evaporation of the extra water. After evaporation of water the gel was formed and it was decomposed at slightly higher temperature ($\sim 200^\circ C$) to get black porous powder. The powder was pelletized and finally annealed at $1300^\circ C$ for 36 h and crystalline compound was formed.

Room temperature x-ray diffraction study have been performed in a Rigaku-TTRAX-III diffractometer. To study the magnetic and magnetocaloric effect, a Super conducting Quantum Interference Device (SQUID) (Quantum Design) magnetometer was employed.

3. Results and discussion

X-ray diffraction study indicates the chemically single phase nature of the compound. The Rietveld refinement (profile fitting) indicates that the space group symmetry of that compound is $P6_3CM$ (hexagonal structure) which is similar as reported earlier [23].

Magnetization as a function of temperature in the presence of external magnetic field $H = 100$ Oe was measured and shown in Fig. 1. Magnetization of the compound was measured in two different protocols which are denoted by ZFC (Zero Field Cooled) and FC (Field Cooled). In case of ZFC method, sample was first cooled down from the room temperature in the absence of any external magnetic field and after stabilizing the temperature ($T = 5$ K), magnetic field of 100 Oe was applied and magnetization (as a function of temperature) in the warming cycle was measured from $T = 5$ –300 K. Whereas, for FC protocol, sample was cooled down in the presence of 100 Oe external magnetic field and temperature dependence magnetization was measured during warming cycle from $T = 5$ –300 K.

The temperature dependence of the magnetization (shown in Fig. 1) exhibits similar nature with decrease of temperature except slightly greater value of magnetization in FC protocol (at low temperature region). The greater value of FC magnetization compared to ZFC inhibits the anisotropic behavior of the sample. The origin of the anisotropic behavior is not the subject matter of this manuscript. It can be only mention that the value of anisotropy is very small. The inverse susceptibility ($1/\chi$) of this compound calculated from the FC data and given in Fig. 1, indicates almost linear in nature.

For further investigation about the nature of the magnetic ground state of the compound, magnetic field dependence of the magnetization was measured at $T = 5$ K and given in Fig. 2. Before starting the measurement, initially the sample was cooled down to $T = 5$ K from room temperature ($T = 300$ K) in the absence of any magnetic field. The

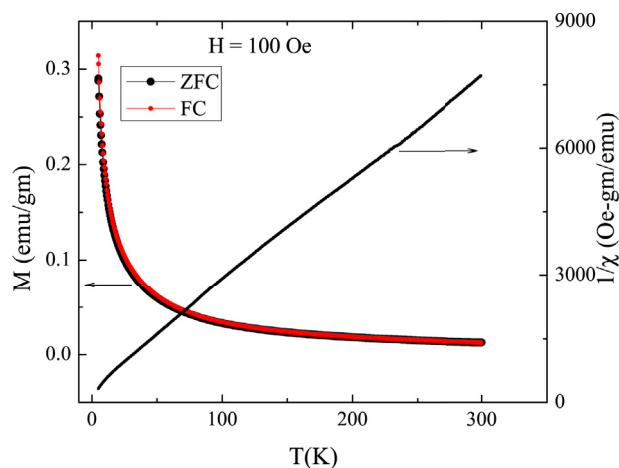


Fig. 1. Magnetization in ZFC and FC protocols (both coincide each other) and inverse susceptibility (calculated from FC data) as a function of temperatures for $H = 100$ Oe external magnetic field.

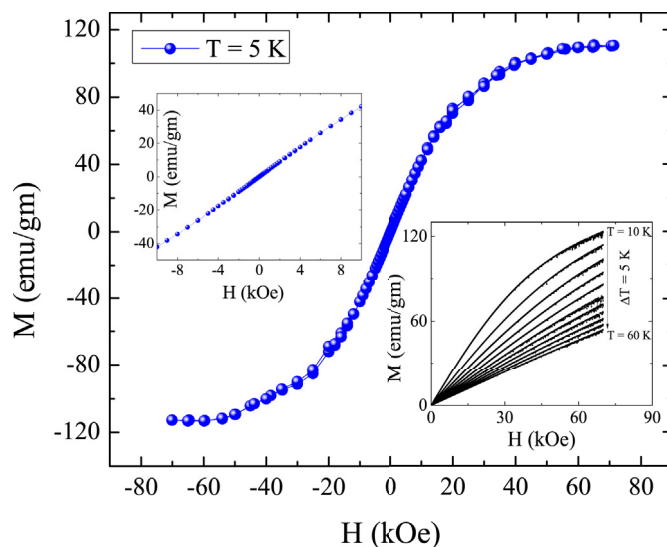


Fig. 2. Magnetization as a function of external magnetic field at $T = 5$ K. Upper inset is the enlarge view at the lower magnetic field region and lower inset is the some representatives magnetic isotherms at different temperature.

experimental data of magnetization as a function of magnetic field indicates that the magnetization value almost saturates at 70 kOe magnetic field value. Such nature again indicates negligible magnetic anisotropy in the system. Another important fact from the application point of view is even at low temperature region, there is negligible hysteresis loop in magnetization data (enlarged view is given in upper inset of Fig. 2). Some selected magnetic isotherms at different temperatures are given in lower inset of Fig. 2.

As mentioned in the introduction part, the multiferroicity in this compound was reported earlier [21]. In this present study, magnetic properties indicates that the saturation of the magnetization appears for $H = 70$ kOe at $T = 5$ K. Additionally no hysteretic nature (another beneficial aspect of refrigerant materials) even at the low temperature region motivated us to study the magnetocaloric responses of this material. The magnetocaloric properties (isothermal magnetic entropy change) of this materials were estimated from the magnetic isotherms data using Maxwell's thermodynamic relation which is given below

$$\Delta S = \int_0^H (\partial M / \partial T) dH \quad (1)$$

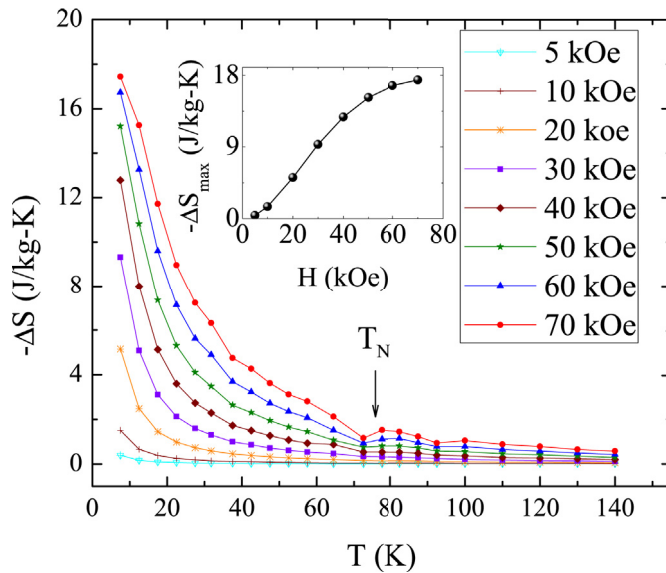


Fig. 3. Magnetic entropy changes as a function of temperatures for different external magnetic field. Inset indicates the variation of the maximum changes of entropy as a function of external magnetic field. The arrow represents antiferromagnetic ordering temperature.

Temperature dependence magnetic entropy change at different external magnetic field is given in Fig. 3. From the plotted data of temperature dependence of magnetic entropy change, the inflection point at the vicinity of the antiferromagnetic ordering of Mn^{3+} ions (which was not clear from the magnetization data) is clearly reflected at $T \sim 75$ K (indicated by arrow). This transition temperature also matches with the previously reported study for single crystalline compound [26]. Generally due to the oxygen non stoichiometry, the ordering temperature shifted drastically. However, in our present study the same ordering temperature ruled out such possibility.

In addition to that large magnetic entropy change appears especially below $T = 20$ K (adiabatic temperature change is ~ 1.2 K for 10 kOe magnetic field). The calculated temperature dependent magnetic entropy change is non saturating in nature with the reduction of temperature. Such significantly large magnetocaloric effect of this stable polycrystalline compound may have interests as a potential refrigerant material having working range at cryogenic temperature region. The variation of the maximum changes of entropy as a function of external magnetic field is given in inset of Fig. 3. There are several studies where large magnetocaloric entropy change were reported at the cryogenic temperature range [27–29]. In Table 1 the magnetic entropy change for several materials at the cryogenic temperature region is given.

To explain the physical origin of such magnetocaloric responses of this material, a schematic diagram of different atomic spin orientations below the Neel temperature ($T_N \sim 75$ K) is shown in Fig. 4. According to the earlier report on the magnetic properties of this compound, the paramagnetic to antiferromagnetic transition appears at $T \sim 75$ K. However, below this temperature (T_N), though the Mn^{3+} ions are ori-

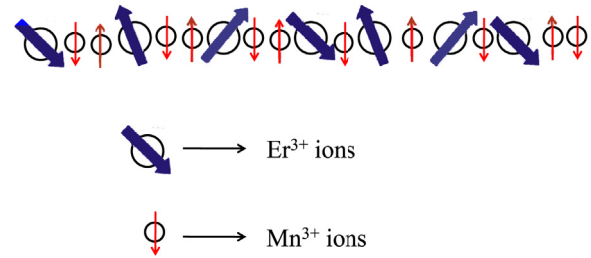


Fig. 4. Schematic representation of the arrangement of Er^{3+} and Mn^{3+} ions below the antiferromagnetic ordering of Mn^{3+} ions.

ents antiferromagnetically, the magnetic moments of Er^{3+} ions remains randomly oriented (paramagnetic in nature). For such magnetic configuration, in the presence of external magnetic field, due to the reduction of the temperature suppression of the magnetic randomness of Er^{3+} ions induced a large change of the magnetic entropy at the cryogenic temperature region. Regarding this context it is worth mentioning that for the higher values of the magnetic field, a saturation tendency of the magnetic entropy change was observed. Such behavior can be explained considering the modulated magnetic ground state of the compound. The magnetization as a function of the external magnetic field data (shown in Fig. 2) also exhibits saturation tendency at the higher field region which clearly reflects in magnetocaloric response of the compound. Moreover, recently Balli et al. also pointed out that the exchange interaction between manganese ions and rare-earth ions also played the important role for the large magnetocaloric effect of several manganite compounds [30].

4. Conclusions

To summarize, significant large magnetic entropy change is observed for the geometrically frustrated ErMnO_3 polycrystalline compound. In addition to that, present study reveals negligible magnetic hysteresis and magnetic anisotropy in this compound. The gradual alignment of Er^{3+} ions with reduction of the temperature in the presence of the magnetic field corroborates such large magnetic entropy change at the low temperature region. From the technological point of view, large magnetocaloric effect in this compound having insulating ground state and without magnetic hysteresis effect at the cryogenic temperature region may be important as a good refrigerant material.

Acknowledgements

The work was supported by Department of Atomic Energy (DAE), Govt. of India. Authors thank to Santanu Pakhira for helping in manuscript preparation and discussions.

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Table 1
Comparison of $-\Delta S$ of several compounds.

Compound	Magnetic field (kOe)	$-\Delta S$ (J/kg-K)	Reference
$\text{Gd}_3\text{Fe}_5\text{O}_{12}$ (bulk)	30	2.5	[29]
$\text{Gd}_3\text{Fe}_5\text{O}_{12}$ (~ 50 nm)	30	1.6	[29]
$\text{Gd}_3\text{Fe}_5\text{O}_{12}$ (~ 35 nm)	30	3.5	[29]
$\text{Gd}_2\text{O}_3 + \text{SiO}_2$	50	40	[28]
$\text{Eu}_8\text{Ga}_{16}\text{Ge}_{30}$	30	11.4	[27]
ErMnO_3	30	9.4	Present study

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