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# Magnetocaloric Effects of Barium-Strontium Ferrites for Magnetic Refrigeration System

Ummay Habiba [1], Sheikh Manjura Hoque [2], Samia Islam Liba [2], Hasan Khaled Rouf [1*]

[1] *Department of Electrical & Electronic Engineering, University of Chittagong, Chittagong – 4331, Bangladesh;*
[2] *Material Science Division, Bangladesh Atomic Energy Centre, Ramna, Dhaka, Bangladesh*

* Corresponding author. Tel.: +880 31 726311 4404. *E-mail*: hasan.rouf@cu.ac.bd

**Abstract**

A study of the magnetocaloric effect (MCE) of Barium-Strontium-Ferrites $BaO.SrO.xFe_2O_3$ and $BaO.SrO.xFe_3O_4$ ($x = 5.6, 5.8, 6$) is reported in this article. Using hematite of analytical grade and magnetite from Cox's Bazar beach sand mineral as ferrite contents, the hexaferrites were synthesized and their magnetic properties and MCE were systematically studied. The results indicate that the samples are strongly ferromagnetic and have high Curie temperature. All the samples are of second-ordered phase and exhibit large magnetic entropy changes. Among all the samples $BaO.SrO.5.8Fe_2O_3$ and $BaO.SrO.5.8Fe_3O_4$ exhibit the maximum entropy changes at the temperatures near and below the Curie temperature.

**Keywords**

Magnetocaloric effects; hexaferrites; ferromagnetism; magnetic entropy.



## Introduction

The development of the economical, durable and highly reliable cooling system has been an active field of research from the materials science as well as engineering perspectives. Conventional refrigeration systems use harmful gases such as chlorofluorocarbons (**CFCs**) and hydro-chlorofluorocarbons (**HCFCs**) as coolant materials which are detrimental to the Ozone layer of the atmosphere. In the evolution of cooling techniques energy-efficient and environment-friendly magnetic refrigeration can be a promising alternative to the conventional vapour-compression refrigeration techniques. Magnetic refrigeration is based on the magnetocaloric effect (MCE) [1, 2] and can be used in residential cooling, space science, medical applications etc. as well as to cool down computer microchip ICs with the use of microfluidic channels.

MCE is a magneto-thermodynamic phenomenon which refers to the cooling or heating of a magnetic material by exposing the material to a changing magnetic field. When exposed to a changing magnetic field, suitable materials undergo magnetic entropy as well as temperature changes [3]. At a temperature near the Curie point, a ferromagnetic material tends to become paramagnetic material and spins of the material become random. When an external magnetic field is applied, spins tend to become parallel to the applied magnetic field. If the system is adiabatic, the internal energy of the system decreases, and it creates a cooling effect [4]. Some rare earth metals and their alloys are ideal for producing the largest temperature change, although, the major concern is the cost.

Magnetic refrigeration technology has been applied in low temperatures. Materials used for magnetic refrigeration at low temperatures are mainly paramagnetic salts [6]. However there are some drawbacks of using salt materials because they are hydrated, which requires to be encapsulated in a hermetic container to prevent dehydration. The main requirement for magnetic refrigeration materials is to get large magnetic entropy change. The large magnetic entropy change can be obtained when the material has large Curie temperature. The main challenges for the application of MCE for magnetic refrigeration at high temperature are to reduce the requirement of applied magnetic fields and to enhance the magnetic refrigeration efficiency [6].

Due to the significant increase in the heat capacity near the ambient temperature, the heat transferred by each magnetizing-demagnetizing cycling of the refrigerator should be considerably large to guarantee refrigeration efficiency. As a result, most of the materials working at low temperatures cannot be directly utilized, and new materials with great entropy change around the ambient temperature must be explored. Brown in 1968 observed a large MCE of Gd ($T_C$ = 293 K) [7]. However, the entropy changes of magnetocaloric materials reported subsequently are much smaller than that of Gd. The entropy change of $Gd_5Si_2Ge_2$ with a fist order phase transition is ~18 J/kgK around $T_C$ =278 K for a field change of 0–5 *T*, which is significantly larger than that of Gd (~10 J/kgK) under a similar condition [8]. $La_{1-x}Ca_xMnO_3$ ($x$ = 0.2) has a large entropy change of 5.5 J/kgK at 230 K for a field change of 0–1.5 *T* [9]. Some new magnetocaloric materials with a first-order magnetic transition such as $LaFe_{13-x}Si_x$, $MnAs_{1-x}Sb_x$, and $MnFeP_{0.45}As_{0.55}$ were found to have entropy changes from 18 to 30 J/kgK [10–12]. These achievements aroused a new wave of MCE research.

In this work, we have successfully synthesized the $BaO.SrO.xFe_2O_3$ and $BaO.SrO.xFe_3O_4$ ($x$ = 5.6, 5.8, 6) hexaferrites by solid-state method using hematite of analytical grade and magnetite from Cox's Bazar beach sand mineral as ferrite contents. The magnetic properties and MCE in the intermetallic compounds were systematically studied. The results show that the samples are strong ferromagnetic materials and have high Curie temperature. All the samples are of second ordered phase and exhibits large magnetic entropy changes. Among all the samples $BaO.SrO.5.8Fe_2O_3$ and $BaO.SrO.5.8Fe_3O_4$ exhibit the maximum entropy changes at the temperatures near and below the Curie temperature and are promising candidates for magnetic refrigeration.

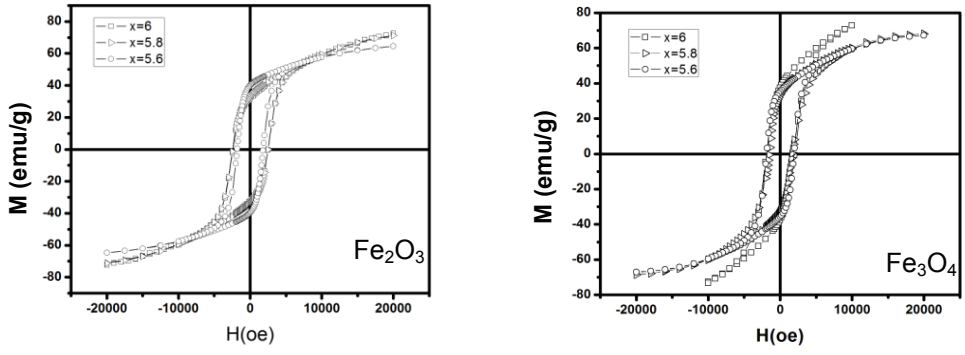
## Experimental procedure

Sample preparation technique is a vital part for ferrites processing which is explained in [13]. Here we used the solid state reaction method involving milling of reactions followed by sintering. $BaO.SrO.xFe_2O_3$ ($x$ = 5.6, 5.8, 6) were prepared from $BaCO_3$, $SrCO_3$ and hematite while $BaCO_3$, $SrCO_3$ and magnetite were used to prepare $BaO.SrO.xFe_3O_4$ ($x$ = 5.6, 5.8, 6). Agate mortar (hand milled) was used for intimate mixing of the materials for 4 hours for fine homogeneous mixing.Then the pre-sintering process was applied to the mixed samples at a temperature between 850 °C to 900 °C for 5 hours to form ferrite through chemical reaction. The pre-sintered materials were milled for another 4 hours in distilled water to reduce them to small crystallites of uniform size. The mixtures were then dried, and polyvinyl alcohol was added as a binder. The formed powders were pressed under a pressure of 15–20 $kN \cdot cm^{-2}$ in a stainless-steel die to make pellets, rods and toroids. Then the resulting pressed pellet, rod and toroid shaped samples were sintered at 1250 °C temperature for 4 hours and then cooled in the furnace. The phase pure characteristics of the samples were confirmed by the XRD patterns.

## Results and discussions

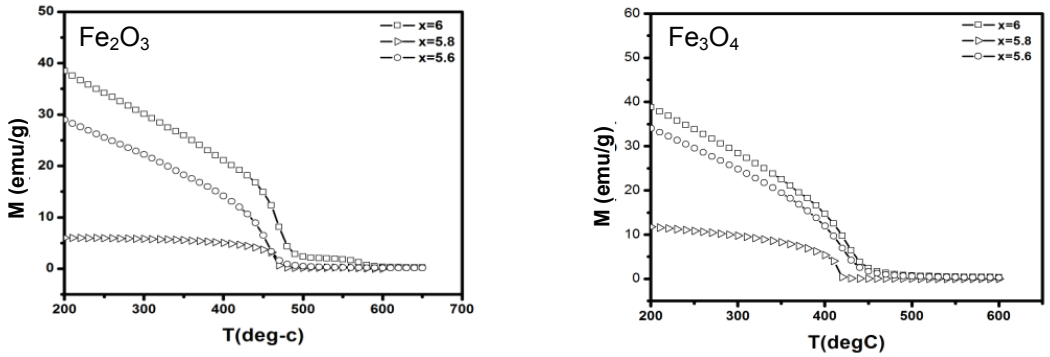
### *Magnetic properties*

Magnetic properties of $BaO.SrO.xFe_2O_3$ and $BaO.SrO.xFe_3O_4$ ($x$ = 5.6, 5.8, 6) were shown in our previous work [13]. The hysteresis loops for Ba–Sr-ferrites using hematite and magnetiteare shown in Fig. 1 while the variations of magnetic fields at different temperatures for all samples are given in Fig. 2. From these plots, we determined the Curie temperature of the samples. To determine the Curie temperature more precisely we also observed the $dM/dT$ versus $T$ curves for all the samples which are shown in Fig. 3.



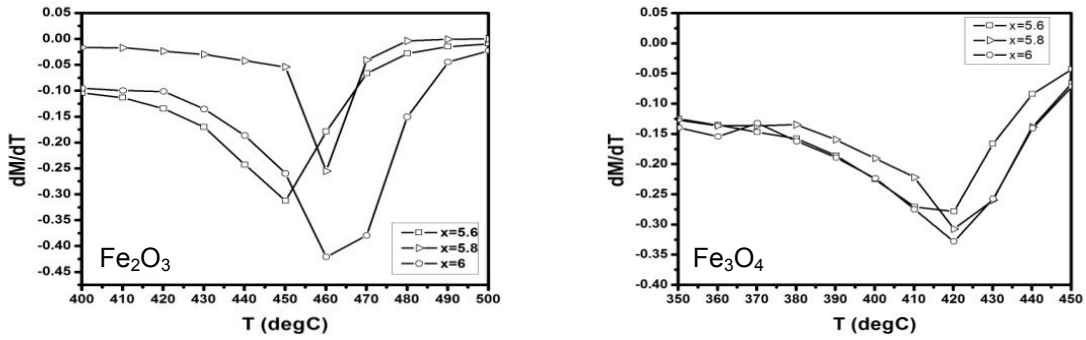

*a*) *b*)

**Fig. 1. Hysteresis loops of (*a*) $BaO.SrO.xFe_2O_3$ for $x$ = 5.6, 5.8, 6.0 and (*b*) $BaO.SrO.xFe_3O_4$ for $x$ = 5.6, 5.8, 6**




*a*) *b*)

**Fig. 2. M – T curves for (*a*) BaO.SrO.$x$Fe$_2$O$_3$ with $x$ = 5.6, 5.8, 6.0 and (*b*) BaO.SrO.$x$Fe$_3$O$_4$ with $x$ = 5.6, 5.8, 6**




*a*) *b*)

**Fig. 3. dM/dT – T curves for (*a*) BaO.SrO.$x$Fe$_2$O$_3$ with $x$ = 5.6, 5.8, 6.0 and (*b*) BaO.SrO.$x$Fe$_3$O$_4$ with $x$ = 5.6, 5.8, 6**

Table 1

**Saturation magnetization $M_s$, remanent magnetization $M_r$, coercive field $H_c$ for all samples**

| Samples | $X$ | $H_c$ (oe) | $M_r$ (emu) | $M_s$ (emu) |
|---|---|---|---|---|
| $Fe_2O_3$ | 6 | 2468.150 | 3.18E+01 | 7.25E+01 |
| | 5.8 | 2476.096 | 3.35E+01 | 7.13E+01 |
| | 5.6 | 1810.477 | 3.98E+01 | 6.46E+01 |
| $Fe_3O_4$ | 6 | 1897.688 | 3.55E+01 | 7.31E+01 |
| | 5.8 | 1931.297 | 3.76E+01 | 6.84E+01 |
| | 5.6 | 1588.256 | 3.31E+01 | 6.72E+01 |

Table 1 summarizes the magnetic parameters of the samples obtained from the Vibrating Sample Magnetometer. All the samples have very high coercive fields ($H_c$), remanent magnetizations ($M_r$), saturation magnetization ($M_s$) confirming their strong ferromagnetic nature. For both Ba-Sr-ferrites the saturation magnetization decreases with the decrease in the ferrite content concentration. Ferrites using hematite have higher Curie temperatures than those prepared using magnetite. These results menifest that BaO.SrO.$x$Fe$_2$O$_3$ is more ferromagneticthan BaO.SrO.$x$Fe$_3$O$_4$.

### *Magnetocaloric properties*

The magnetocaloric behavior of the samples is studied by observing themagnetic entropy change $\Delta S$ with temperature. The temperature regions, where the samples display a transition from a ferromagnetic to a paramagnetic state are observed carefully. Fig. 4 shows the isothermal magnetization curves for samples BaO.SrO.$x$Fe$_2$O$_3$ and BaO.SrO.$x$Fe$_3$O$_4$ ($x$ = 5.6, 5.8, 6). For each sample, among the isothermal curves, a large gap between two curves is obtained around the temperature at which magnetic entropy change due to magnetocaloric effect is maximum.

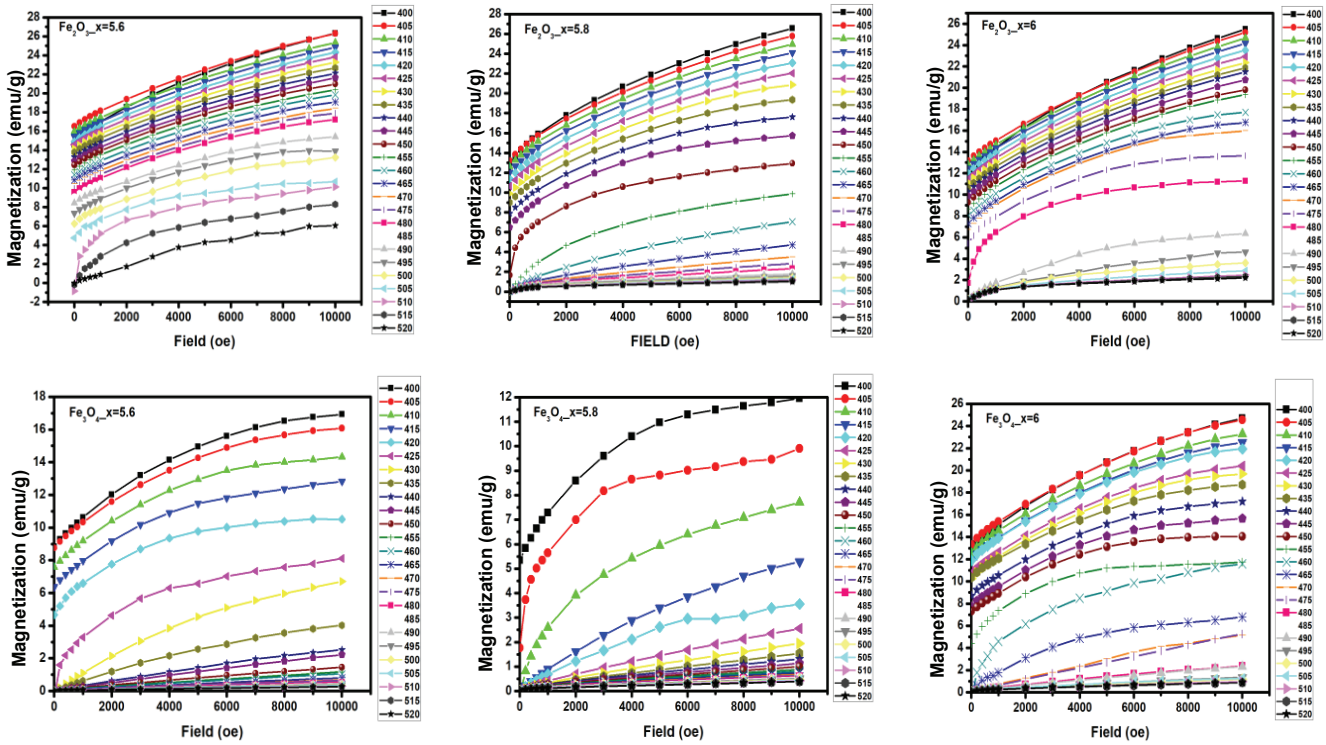



**Fig. 4. Isothermal magnetization curves at different temperature for BaO.SrO.$x$Fe$_2$O$_3$ ($x$ = 5.6, 5.8, 6) (*upper*) and BaO.SrO.$x$Fe$_3$O$_4$ ($x$ = 5.6, 5.8, 6) (*lower*)**

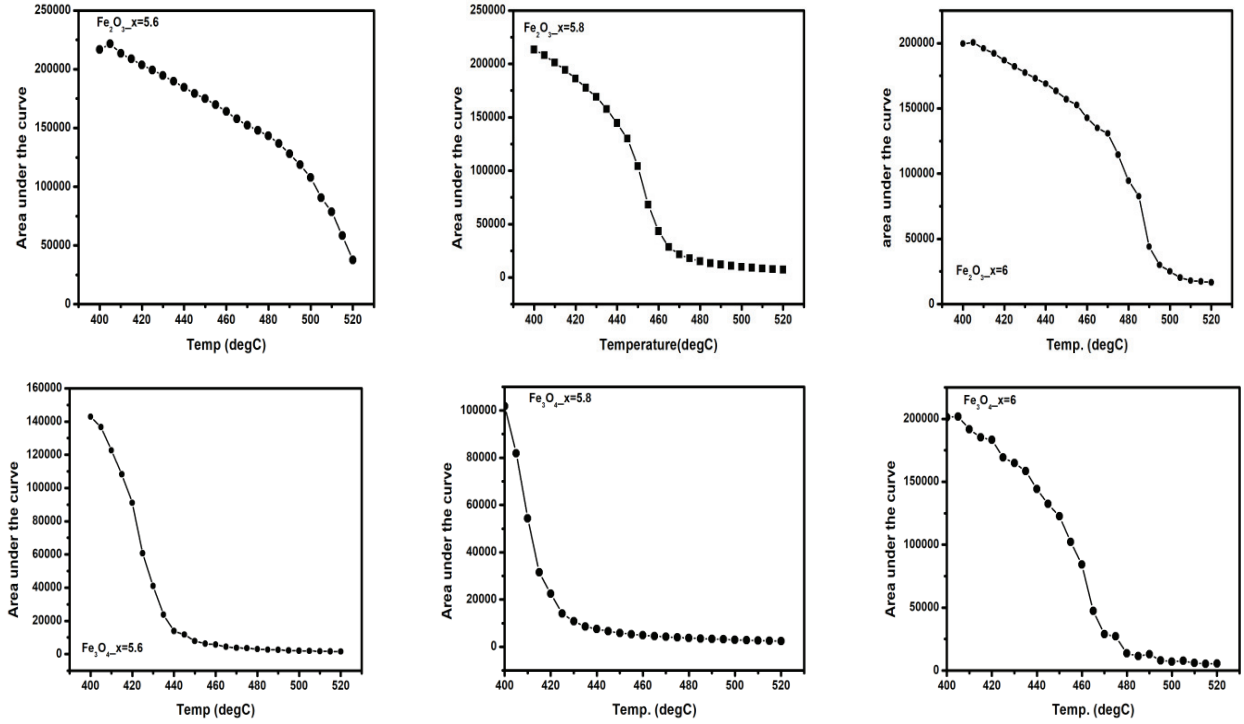



**Fig. 5. Area under the isothermal curve at various temperatures for BaO.SrO.$x$Fe$_2$O$_3$ ($x$ = 5.6, 5.8, 6) (*upper*) and BaO.SrO.$x$Fe$_3$O$_4$ ($x$ = 5.6, 5.8, 6) (*lower*)**

On the other hand, samples which show first-order phase transition exhibit a negative slope [4]. Fig. 6 shows the Arrott plots of BaO.SrO.xFe$_2$O$_3$ and BaO.SrO.$x$Fe$_3$O$_4$ ($x$ = 5.6, 5.8, 6) from which it is observed that slopes of all the six samples are positive indicating second-order phase transitions. The $T_c$ estimated from the $M$–$T$ curve and from the Arrott plots are close to each other. Fig. 7 plots the temperature

dependence of magnetic entropy change ($\Delta S$) for all the samples over a wide temperature range around their respective $T_c$. A broad maximum of $\Delta S$ around their respective $T_c$ are observed for all curves. As the ferrite content increases, the magnitude of $\Delta S$ increases under a given field strength. The Curie temperature, maximum entropy change and temperature for maximum entropy change for all the samples are given in the Table 2.

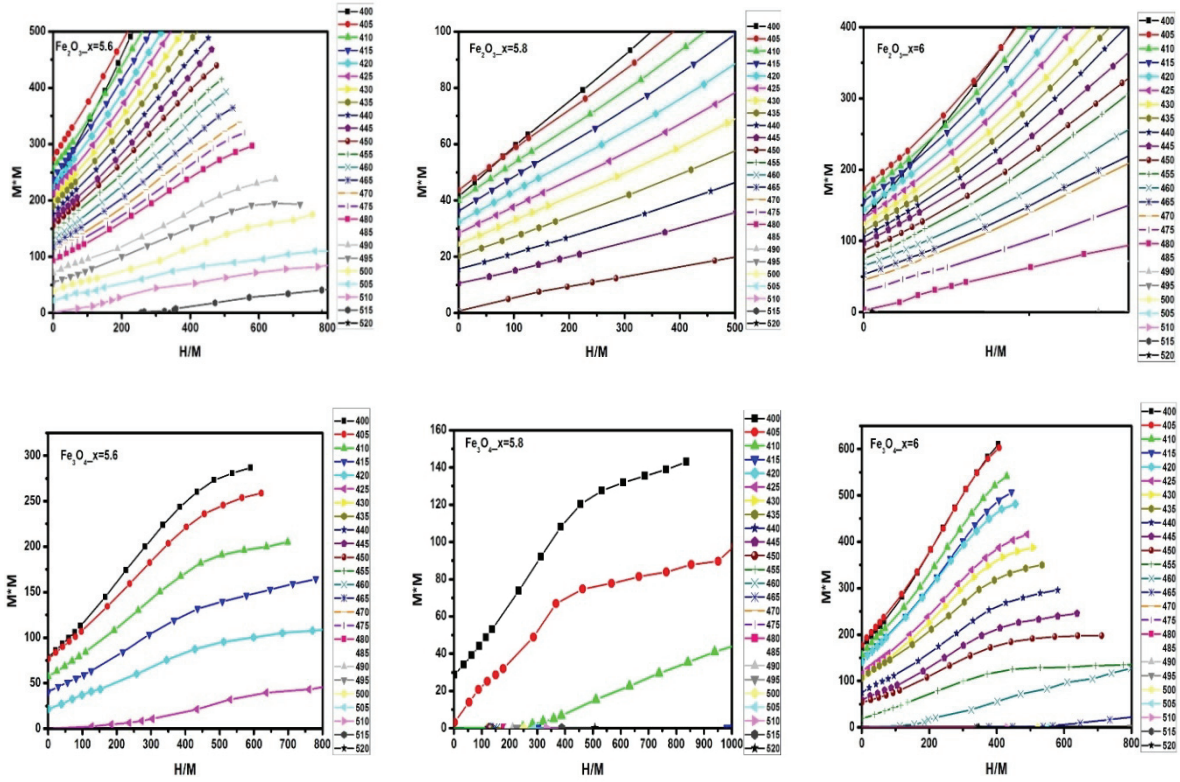



**Fig. 6. Arrot plots for BaO.SrO.$x$Fe$_2$O$_3$ ($x$ = 5.6, 5.8, 6) (*upper*) and BaO.SrO.$x$Fe$_3$O$_4$ ($x$ = 5.6, 5.8, 6) (*lower*)**

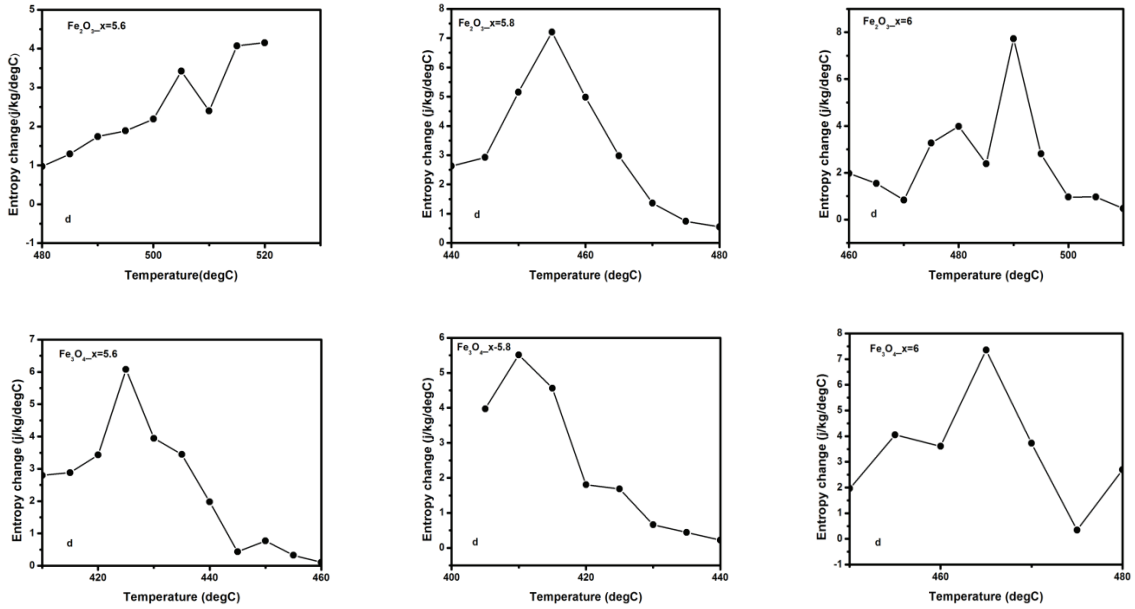



**Fig. 7. Temperature dependence magnetic entropy change ($\Delta S$) for BaO.SrO.$x$Fe$_2$O$_3$ ($x$ = 5.6, 5.8, 6) (*upper*) and BaO.SrO.$x$Fe$_3$O$_4$ ($x$ = 5.6, 5.8, 6) respectively (*lower*)**

Table 2

**Curie temperature, maximum entropy change and temperature for maximum entropy change for the samples**

| Samples | $T_c$, °C | Max. entropy change, j/kg/°C | Temp. for max. entropy change, °C |
|---|---|---|---|
| $BaO.SrO.5.6Fe_2O_3$ | 450 | 4.25 | 520 |
| $BaO.SrO.5.8Fe_2O_3$ | 460 | 7.5 | 455 |
| $BaO.SrO.6Fe_2O_3$ | 460 | 8 | 490 |
| $BaO.SrO.5.6Fe_3O_4$ | 420 | 6 | 425 |
| $BaO.SrO.5.8Fe_3O_4$ | 420 | 5.5 | 410 |
| $BaO.SrO.6Fe_3O_4$ | 420 | 7.5 | 465 |

It is observed that among the samples $BaO.SrO.5.8Fe_2O_3$ and $BaO.SrO.5.8Fe_3O_4$ exhibit the maximum entropy changes at the temperatures near and below the Curie temperature. Therefore, these two samples exhibit better magnetocaloric effects than other four. Materials used for magnetic refrigeration at low temperatures are mainly paramagnetic salts [6]. However there are some drawbacks of using salt materials because they are hydrated which require encapsulation in hermetic containers to prevent dehydration. Because of the demonstrated magnetocaloric effects, $BaO.SrO.xFe_2O_3$ and $BaO.SrO.xFe_3O_4$ can be promising for use in magnetic refrigeration.

## Conclusion

Magnetic and magnetocaloric properties of $BaO.SrO.xFe_2O_3$ and $BaO.SrO.xFe_3O_4$ ($x$ = 5.6, 5.8, 6) which were prepared using hematite of analytical grade and magnetite from Cox's bazaar beach sand mineral were studied in this work. The hysteresis loops for Ba-Sr-ferrites indicate that the samples are of ferromagnetic type. The Curie temperatures for ferrites using hematite are higher than those using magnetite. The results indicate that all the samples are of second ordered phase and exhibit large magnetic entropy changes. Among all the samples $BaO.SrO.5.8Fe_2O_3$ and $BaO.SrO.5.8Fe_3O_4$ exhibit the maximum entropy changes at the temperatures near and below the Curie temperature and are promising candidates for magnetic refrigeration.

## Disclosure

The authors declare no conflicts of interest.

## References


1. Warburg E., Magnetische Untersuchungen, Annalen der Physik, 1881, Vol. 249, Issue 5, pp. 141-164.

2. Giauque W.F. and MacDougall D.P., Attainment of Temperatures Below 1° Absolute by Demagnetization of $Gd_2(SO_4)_3 \cdot 8H_2O$, Physical Review, 1933, Vol. 43, Issue 9, 768 p.

3. Thanh T.D., Yen N.H., Dan N.H., Phan T.-L., and Yu S.-C., Magnetic Properties and Large Magnetocaloric Effect in Amorphous Fe-Ag-Ni-Zr for Room-Temperature Magnetic Refrigeration, IEEE Transactions on Magnetics, 2015, Vol.51, Issue 1.

4. Li L., Review of Magnetic Properties and Magnetocaloric Effect in theIntermetallic Compounds of Rare Earth with Low Boiling Point Metal(s), Chinese Physics B, 2015, Vol. 10, pp. 1-56.

5. Akhter S., Paul D.P., Hoque S.M., Hakim M.A., Hud M., Mathieu R., Nordblad P., Magnetic and Magnetocaloric Properties of $Cu_{1-x}$ $Zn_xFe_2O_4$ ($x$ ¼ 0.6, 0.7, 0.8) Ferrites, Journal of Magnetism and Magnetic Materials, 2014, Vol. 367, pp. 75-80.

6. Du J., Zheng Q., Li Y.B., Zhang Q., Li D., and Zhang Z.D., Large Magnetocaloric Effect and Enhanced Magnetic Refrigeration in Ternary Gd-based Bulk Metallic Glasses, Journal of Applied Physics, 2008, Vol. 103, 023918.

7. Brown G.V.,Magnetic Heat Pumping Near Room Temperature, Journal of Applied Physics, 1976, Vol. 47, p. 3673.

8. Pecharsky V.K. and Gschneidner Jr. K.A., Giant Magnetocaloric Effect in $Gd_5Si_2Ge_2$, Physical Review Letters, 1997, Vol. 78, p. 4494.

9. Guo Z.B., Du Y.W., Zhu J.S., Huang H., Ding W.P., and Feng D., Large Magnetic Entropy Change in Perovskite-Type Manganese Oxides, Physical Review Letters, 1997, Vol. 78, p. 1142.

10. Shen B.G., Sun J.R., Hu F.X., Zhang H.W., Cheng Z.H., Recent Progress in Exploring Magnetocaloric Materials, Advanced Materials, 2009, Vol. 21, Issue 45, pp. 4545-4564.

11. Wada H. and Tanabe Y., Giant magnetocaloric effect of $MnAs_{1-x}Sb_x$, Applied Physics Letters, 2001, Vol. 79, p. 3302.

12. Tegus O., Brück E., Buschow K.H.J., de Boer F.R. Transition-metal-based Magnetic Refrigerants for Room-Temperature Applications, Nature, 2002, Vol. 415, pp. 150-152.

13. Habiba U., Rouf H.K. and Hoque S.M., Structural and Magnetic Characterizations of Barium-Strontium-Ferrites using Hematite of Analytical Grade and Magnetite from Cox's Bazar Beach Sand Mineral, European Journal of Materials Science and Engineering, 2017, Vol. 2, pp. 41-50.