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# Near fifty percent sodium substituted lanthanum manganites—A potential magnetic refrigerant for room temperature applications

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Nearly half of lanthanum sites in lanthanum manganites were substituted with monovalent ion-sodium and the compound possessed distorted orthorhombic structure. Ferromagnetic ordering at 300 K and the magnetic isotherms at different temperature ranges were analyzed for estimating magnetic entropy variation. Magnetic entropy change of $1.5 \, \text{J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$ was observed near 300 K. An appreciable magnetocaloric effect was also observed for a wide range of temperatures near 300 K for small magnetic field variation. Heat capacity was measured for temperatures lower than 300 K and the adiabatic temperature change increases with increase in temperature with a maximum of 0.62 K at 280 K. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4867528]

Magnetic refrigeration based on magnetocaloric effect (MCE) is a promising cooling technology preferred over conventional thermomechanical cooling owing to its eco friendliness. Currently, pursued as most effective, easily accessible, and highly economical cooling technology, magnetic refrigeration is solely attributed to magnetic materials and derives its strength from the coupling of magnetic domains with material lattice. An ideal magnetocaloric material operating at room temperature exhibits an appreciable change in magnetic entropy near room temperature and can effectively contribute to lowering the energy consumption up to a level of 20%–30%. The change in magnetic entropy of a material with respect to magnetic field variations forms the basis of MCE. It is perceived that change in entropy under adiabatic conditions can induce an equal but opposite change in the entropy of lattice, which in turn is manifested as change in temperature of the material.[1,2] Such a type of magnetic cooling can be effectively utilized for refrigeration and materials exhibiting a large entropy change at low magnetic field with transition temperatures close to room temperature are considered as promising materials for magnetic refrigeration.

Major investigations on MCE behaviour were carried out on Gd and Yb based alloys, gadolinium germanium silicides, and La (Fe,Si) alloys. Giant MCE (GMCE) with an adiabatic temperature change ($\Delta T_{ad}$ or $|\Delta T_{ad}|$) of 15 K and magnetic entropy change ($\Delta S_M$ or $|\Delta S_M|$) of $18.5 \, \text{J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$ have been observed in $Gd_5Ge_2Si_2$ at 276 K for a magnetic field of 5 T.[3,4] These silicides are prototype materials for magnetic refrigeration and various elemental substitutions like Cu, Ga, Mn, and Nb for Ge and Si has led to varied entropy and adiabatic temperature changes.[5] Later, GMCE have been reported in $LaFe_{11.4}Si_{1.6}$ at 210 K with a $|\Delta S_M|$ of $20 \, \text{J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$ at a magnetic field of 5 T comparable with Gd compounds.[6] In parallel, materials like hydrogen-added $YFe_2$ [$YFe_2(H_{1-y}D_y)_{4.2}$] with $AB_2$ stoichiometry have also been

studied, which exhibited a $|\Delta S_M|$ of $10 \, \text{J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$ and similar compounds like $Ho_2Co$ and $HoCoSi$ also reported entropy values of 11 and $30 \, \text{J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$, respectively, at 5 T in the low temperature range below 130 K.[7–9] Superparamagnetic ferrites are also investigated for which the blocking temperature ($T_B$) can modulate the entropy change.[10] Other materials of interest in the area of MCE are MnAs, MnFe compounds, Heusler alloys, intermetallics with rare earth metals, and ferromagnetic (FM) lanthanum manganites.[1,11]

Manganites are perceived as interesting materials, since their physical, magnetic, or electrical properties are tunable with the substituting elements, their concentration, ionic radii, and also possibly by oxygen stoichiometry. Colossal magnetoresistance, charge ordering, ferro/antiferro magnetism, and metal insulator transition near room temperature render multifunctionality to manganites. Among them, lanthanum manganites (LMO) with $ABO_3$ structure and its derivatives have secured a prominent position in the MCE phenomenon as they possess high magnetic moments. Magnetism in manganites is based on double exchange/super exchange mechanism between mixed valence states of Mn ions. FM to paramagnetic (PM) transition at high temperatures often coupled with metal-insulator transition in doped manganites directed the focus towards magnetic entropy studies.[11,12] $\Delta S_M$ of $1 \, \text{J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$ and $2 \, \text{J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$ was observed in $La_{0.67}Ca_{0.33}MnO_3$ and $La_{0.87}Sr_{0.13}MnO_3$, respectively, under a magnetic field of 10 kOe.[13,14] Highest $\Delta S_M$ of $8 \, \text{J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$ around 250 K was found in $La_{0.7}Ca_{0.3}MnO_3$ under 2 T magnetic field.[15] Recently, a $\Delta S_M$ of $5.15 \, \text{J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$ corresponding to a magnetic field of 5 T was reported for $La_{0.67}Sr_{0.33}MnO_3$ at 370 K.[16] Efforts are on to effectively utilize the tunability of magnetic properties of doped manganites in MCE for developing manganites with high entropy values near room temperature. A possible concern in manganites is that their specific heat is higher and hence adiabatic temperature variation is smaller, but higher Curie temperature well above room temperatures can be of help as the adiabatic temperature change is proportional to temperature.[16]

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MCE behaviour for divalent and trivalent substitutions in manganites have already been discussed and reported. But monovalent doping for A sites in manganites is an effective way of introducing mixed valence states of $Mn^{3+}/Mn^{4+}$ pairs, which contributes to ferromagnetism in manganites and $Mn^{3+}$ to $Mn^{4+}$ conversion rate for monovalent doping is twice that for the equivalent concentration of divalent doping.[17,18] Reports dealing with monovalent doping are scarce in literature. Another important feature of monovalent substitution is the role of vacancies in deciding the material characteristic especially magnetic ordering. The present communication deals with 50% monovalent ion sodium $(Na^+)$ substitution for $La^{3+}$ sites in LMO as no reports could be found pertaining to higher concentrations of Na at La sites possibly due to loss of Na during sintering process. Thus, sodium doped lanthanum manganites (LNMO) are virgin compounds and hence evaluation of magnetic entropy change and associated adiabatic temperature change are of interest to scientific community. Fifty percent sodium substituted LMO was synthesized using a modified citrate gel method. Composition analysis using X-ray Photoelectron Spectroscopy (XPS) showed that La:Na ratio is 1:1, but it cannot be verified whether Na is fully replacing La ions and in the earlier reports of Tovstolytkin *et al.*,[19] it has been mentioned that with higher Na substitution, vacancies are induced in La or O sites and these vacancies also play a role in magnetic ordering in manganites. So, 50% substitution leads to magnetic interactions from double exchange as well as from vacancies but for an easy interpretation sample is referred as LNMO5. LNMO5 sample was subjected to structural characterization using X-ray diffraction (XRD) and Rietveld refinement, magnetic characterization such as M-H curves at different temperatures (magnetic isotherms) using SQUID magnetometer. These isotherms were analyzed and the magnetic entropy was evaluated. Heat capacity measurements of LNMO5 were also carried out using physical property measurement system (PPMS), and the adiabatic temperature change was also determined.

Magnetic entropy change $(\Delta S_M)$ can be evaluated either from the variation of adiabatic temperature in the presence of magnetic field or from the M-H isotherms at different temperatures. In the present paper, second method using M-H isotherms is employed as adiabatic temperature measurement in manganites is rather difficult as stated earlier. Based on the theory of thermodynamics, the entropy change can be given using Maxwell relation[20,21]

$$\left(\frac{\partial S}{\partial H}\right)_T = \mu_0 \left(\frac{\partial M}{\partial T}\right)_H.$$ (1)

The entropy change $\Delta S_M$ determining the MCE behaviour can be calculated from the area between the M-H curves multiplied by the reciprocal of the temperature difference between the curves as given by

$$\Delta S_M = \frac{\mu_0}{\Delta T}\left[\int_0^H M_{i+1}(T_{i+1}, H)dH - \int_0^H M_i(T_i, H)dH\right].$$ (2)

The adiabatic temperature change associated with the entropy change can be given by

$$\Delta T_{ad} = -\mu_0 \int_0^H \frac{T}{C_p}\left(\frac{\partial M}{\partial T}\right)_H dH,$$ (3)

where $C_p$ denotes specific heat capacity, which is considered as independent of magnetic field variations. Magnetic field dependence of $C_p$ for second order phase transition (SOPT) materials is lower than that of first order phase transition (FOPT) materials.[1] Considering the insignificant magnetic field dependence of $C_p$ for SOPT materials, Eq. (3) can be further written in the form

$$\Delta T_{ad} = \frac{T}{C_p}\Delta S_M.$$ (4)

Equation (4) provides approximate values for the indirect estimation of adiabatic temperature change, $\Delta T_{ad}$ for different temperatures from the magnetic entropy change and specific heat capacity.

In the present work, sample with a composition LNMO5 was synthesized using citrate gel method. For this, stoichiometric amounts of the precursors, such as lanthanum oxide, manganese nitrate, and sodium carbonate, were dissolved in deionized water, and an adequate amount of citric acid was added. The solution was then heated at $80\,^\circ C$ with continuous stirring; it boiled, frothed, turned dark, and caught fire giving a spongy dark powder. This powder was then fired at high temperature of $1100\,^\circ C$ for 12 h.

Structural analysis from XRD pattern confirmed that LNMO5 peaks correspond to a distorted orthorhombic structure. The XRD peaks are indexed as per JCPDS file No. 86-132 in Figure 1. Crystal structure of lanthanum manganites undergoes a transition from orthorhombic to pseudo cubic through rhombohedral phase with the substitution at La or Mn sites. Literature reports suggest onset of orthorhombic phase for heavily doped samples of $LaMnO_3$ which are in good conformity with our XRD analysis on LNMO5.[17,22] Rietveld refinement confirmed orthorhombic phase of LNMO5 with *pbnm* space group and is shown in Figure 2.
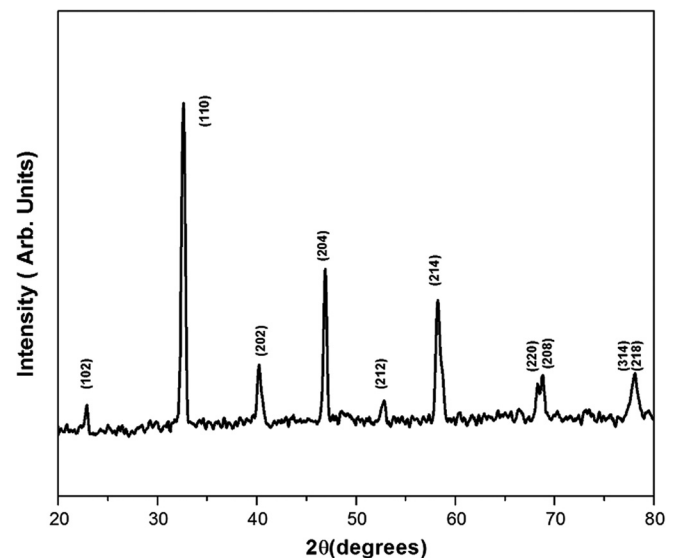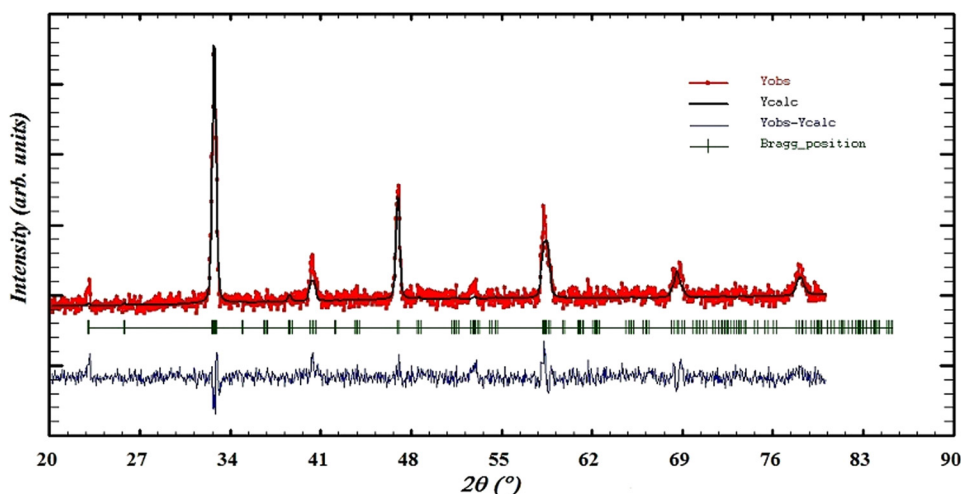


FIG. 1. XRD pattern of LNMO5.

FIG. 2. Rietveld refinement of LNMO5.

Reported values for lattice parameters of the orthorhombic cell for undoped lanthanum manganites with *pbnm* space group are a = 5.5367 Å, b = 5.7473 Å, and c = 7.6929 Å.[23] LNMO5 sample in the present investigation has lattice parameters, a = 5.4976 ± 0.0025 Å, b = 5.4436 ± 0.0025 Å, and c = 7.7385 ± 0.0039 Å, which when compared to undoped samples has a compression of a and b axes compensated by an elongation along c axis. Magnetic characterization using Vibrating Sample Magnetometer (VSM) shows a ferromagnetic behaviour for the sample at 300 K with a coercivity of 10 Oe; the hysteresis loop is shown in Figure 3. Detailed analysis of magnetic characteristic in LNMO5 by employing XPS is discussed in another article of the same author which is already communicated. M-H isotherms with magnetization expressed in A m²/kg for magnetic field variation ($\mu_0 H$) up to 5 T for the temperature range of 200 K to 300 K with a step of 20 K is shown in Figure 4. A saturation magnetization ($M_s$) of 54 emu/g is observed at 200 K and on increasing temperature to 300 K, $M_s$ decreases steadily to 34 emu/g. From M-H isotherms, Banerjee's criterion has been utilized to determine the nature of magnetic transition in LNMO5. Thermodynamic theory for phase transitions first developed by Landau and Lifshitz[24,25] was later applied in ferromagnets for magnetic transitions near Curie point by Ginzburg as

governed by the equation: $\alpha M + \beta M^3 = H$, where $\alpha$ and $\beta$ are constants incorporating thermodynamic variables and magnetization.[26] Bean and Rodbell[27] suggested a theory for FOPT and later Banerjee combined all these existing theories into one and proposed a criterion for distinguishing between FOPT and SOPT. In order to test this criterion, Arrott plots are adopted with $\mu_0 H/M$ versus $M^2$ as indicated in Figure 5. Figure 5(a) shows Arrott plots in the temperature range of 200 K to 300 K within magnetic field range of 5 T. A linear behaviour of curves at different temperatures is indicative of second order transition.[28] It is observed that Arrott plots are approaching a linear behaviour parallel to one another with the increase in temperature. Thus, positive slope of the curves confirms that the magnetic transition is of second order and the magnetic transition is above 300 K. For the detailed investigation of the magnetic phase in manganites, M-H isotherms for the temperature range of 303 K to 393 K with small steps of 10 K are analyzed for the maximum magnetic field of 1.35 T, and Arrott plots plotted from these isotherms shows a parallel behaviour as observed in Figure 5(b). Magnetization vs temperature measurements confirm a magnetic ordering at around 334 K which is shown in Figure 6.

Two sets of M-H isotherms, first one in the low temperature range of 200 K to 300 K and the second within the range
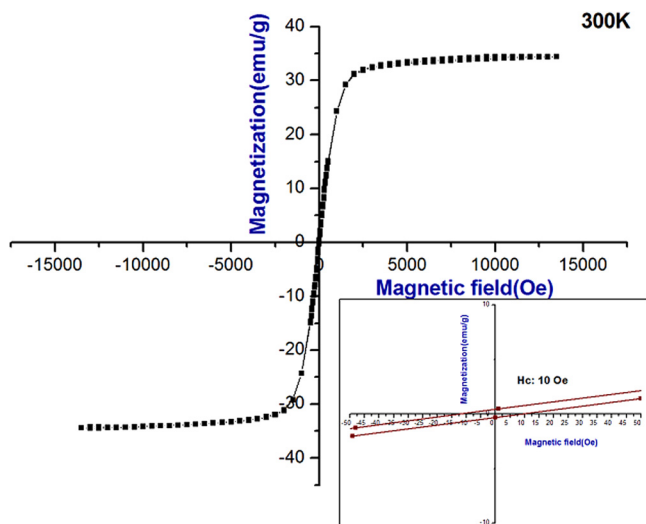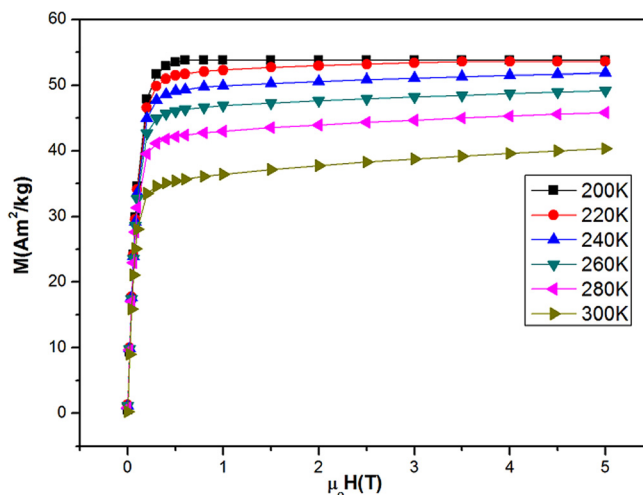


FIG. 3. M vs H loop of LNMO5 at 300 K.



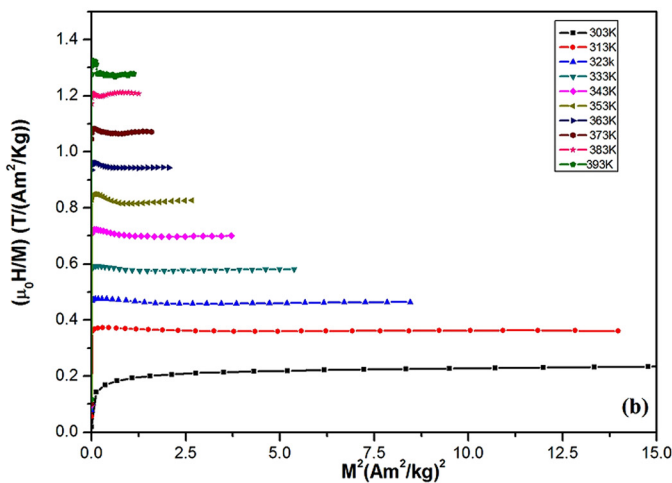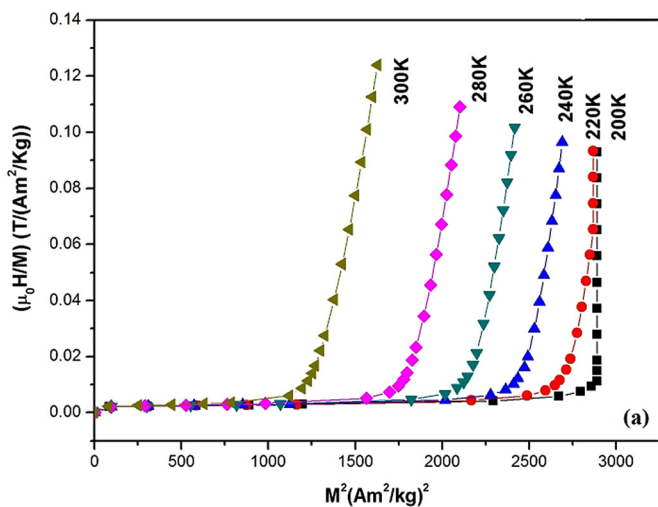FIG. 4. M-H isotherms of LNMO5 in the temperature range of 200 K to 300 K.

FIG. 5. Arrott plots of LNMO5 (a) in the temperature range of 200 K to 300 K (b) in the temperature range of 303 K to 393 K.

of 303 K to 393 K, are utilized for calculating magnetic entropy. After determining area between the adjacent curves from isotherms, magnetic entropy change, $\Delta S_M$ is evaluated using Eq. (2) [negative sign of entropy is excluded]. $\Delta S_M$ evaluated for dH (or $\Delta H$) values of 0.5 T, 1 T, 2 T, and 5 T from 200 K to 300 K is depicted in inset of Figure 7. It is observed that magnetic entropy increases with increase in dH, thus establishing the linear dependence of entropy with magnetic field and maximum entropy change of 1.5 J·kg$^{-1}$·K$^{-1}$ is found at 290 K for a field of 5 T. $\Delta S_M$ is also found to be increasing with increase in temperature in the range of 200 K to 300 K. In order to determine the temperature range within which $\Delta S_M$ is maximum, second set of isotherms in the temperature range of 303 K to 393 K dealing with small magnetic fields is considered. Also small steps of 10 K give more precise values of $\Delta S_M$ near transition temperature. Entropy values corresponding to magnetic fields of 0.5 T, 1 T, 1.15 T, 1.25 T, and 1.35 T has been plotted and the maximum entropy change of 0.12 J·kg$^{-1}$·K$^{-1}$ is observed for 1.35 T for a temperature of 308 K. Further, $\Delta S_M$ decreases with increase in temperature as evident from Figure 7. Although two sets of isotherms consider two different field

variations, it can be confirmed that the entropy approaches maximum values in the room temperature range.

Heat capacity ($C_p$) measurement in manganites assumes importance and can be utilized for the estimation of $\Delta T_{ad}$. Evaluation of $\Delta T_{ad}$ from measured $C_p$ values are more accurate rather than relying on the earlier reported results of $C_p$. Heat capacity of LNMO5 is plotted as a function of temperature, and the measurement have been carried out for temperatures below 300 K as indicated in Figure 8. It is also observed that variation of $C_p$ with and without magnetic fields is similar. Heat capacity is found to have direct dependence on temperature and $C_p$ approached highest value of 660 J·kg$^{-1}$·K$^{-1}$ at 300 K. $C_p$ values are then used to evaluate the adiabatic temperature change ($\Delta T_{ad}$) associated with manganite system as given by Eq. (4) and $\Delta T_{ad}$ values are plotted with respect to temperature. It is found that $\Delta T_{ad}$ increases with increase in temperature and a maximum temperature change of 0.62 K is observed at 280 K as indicated in Figure 9. Variation of $\Delta T_{ad}$ against temperature plot is linear, which is a promising result as far as MCE applications are concerned. Increase in $\Delta T_{ad}$ close to room temperatures
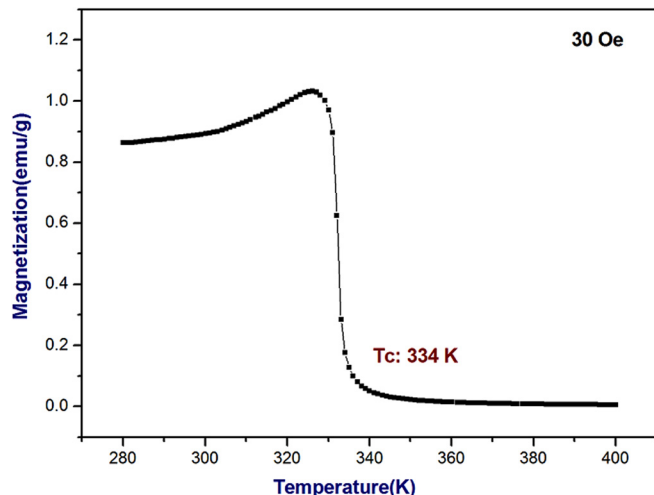


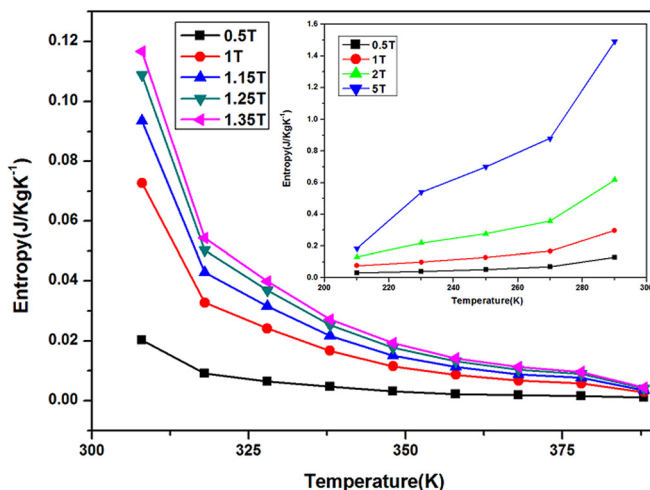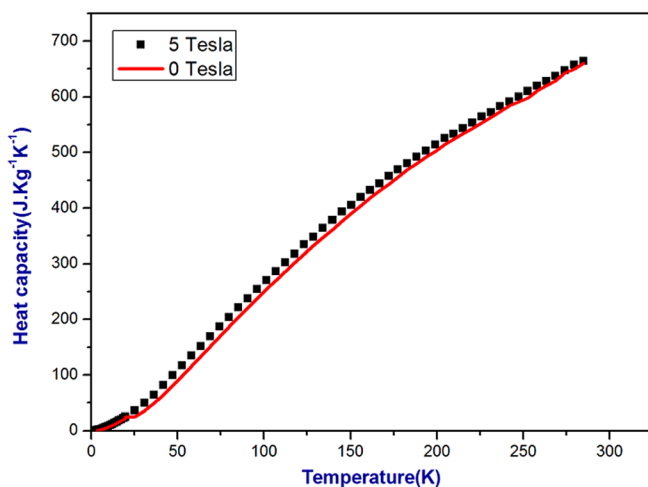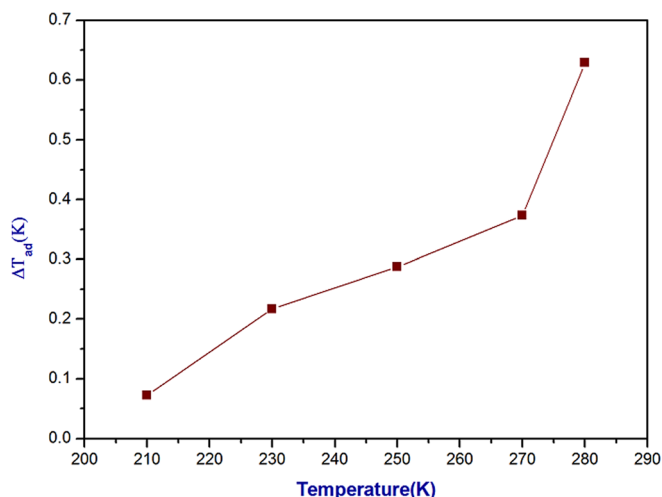FIG. 6. M vs T behaviour of LNMO5 in the temperature range of 280 K to 400 K.



FIG. 7. Magnetic entropy change ($\Delta S$) in LNMO 5 at different magnetic fields for T > 300 K. Inset figure shows magnetic entropy change at different field magnetic fields for T < 300 K.

FIG. 8. Heat capacity ($C_p$) vs temperature of LNMO5 sample for T < 300 K.



FIG. 9. Adiabatic temperature change ($\Delta T_{ad}$) of LNMO5 sample.

and preferably near transition temperature is indicative of the potential of the material for refrigeration mechanism at near room temperature.

In conclusion, nearly half sodium substituted lanthanum manganites synthesized using modified citrate gel method were subjected to X-ray diffraction studies and Rietveld refinement, which showed a distorted orthorhombic structure. The magnetic measurements confirmed that sample exhibited ferromagnetic ordering at room temperature. Two types of isotherms, below 300 K and above 300 K, were analyzed and were utilized for the estimation of magnetic entropy of the material. Magnetic entropy change of $1.5 \, \text{J·kg}^{-1}\text{·K}^{-1}$ was observed at 290 K for $\Delta H$ of 5 T, while $0.12 \, \text{J·kg}^{-1}\text{·K}^{-1}$ was observed for 1.35 T at 308 K. Heat capacity of the samples were also determined and $C_p$ was evaluated to be $660 \, \text{J·kg}^{-1}\text{·K}^{-1}$ at 300 K. Adiabatic temperature change was evaluated from $C_P$ and $\Delta S_M$ values and was found to be increasing with increase in temperature with a maximum of 0.62 K at 280 K. The magnetic entropy studies

on monovalent sodium doped lanthanum manganites provide higher values of entropy for a wide range of temperature close to room temperature and are highly beneficial from an applied perspective.

[1]V. Franco, J. S. Blazquez, B. Ingale, and A. Conde, Annu. Rev. Mater. Res. **42**, 305–342(2012).
[2]S. Das and T. K. Dey, J. Phys.: Condens. Matter **18**, 7629–7641 (2006).
[3]H. Zeng, C. Kuang, J. Zhang, and M. Yue, Bull. Mater. Sci. **34**(4),825–828 (2011).
[4]V. K. Pecharsky and K. A. Gschneidner, Jr., Phys. Rev. Lett. **78**, 4494 (1997).
[5]R. D. Shull, V. Provenzano, A. J. Shapiro, A. Fu, M. W. Lufaso, J. Karapetrova, G. Kletetschka, and V. Mikula, J. Appl. Phys. **99**, 08K908 (2006).
[6]F.-x. Hu, B.-g. Shen, J.-r. Sun, Z.-h. Cheng, G.-h. Rao and X.-X. Zhang, Appl. Phys. Lett. **78**(23), 3675–3677 (2001).
[7]J. Chen, B. G. Shen, Q. Y. Dong, F. X. Hu, and J. R. Sun, Appl. Phys. Lett. **96**, 152501 (2010).
[8]Q. Zhang, J. H. Cho, B. Li, W. J. Hu, and Z. D. Zhang, Appl. Phys. Lett. **94**, 182501 (2009).
[9]V. Paul-Boncour and T. Mazet, J. Appl. Phys. **105**, 013914 (2009).
[10]P. Poddar, J. Gass, D. J. Rebar, S. Srinath, H. Srikanth, S. A. Morrison, and E. E. Carpenter, J. Magn. Magn. Mater. **307**, 227–231 (2006).
[11]M.-H. Phan and S.-C. Yu, J. Magn. Magn. Mater. **308**, 325–340 (2007).
[12]K. A. Gschneidner, Jr. and V. K. Pecharsky, Annu. Rev. Mater. Sci. **30**, 387–429 (2000).
[13]X. X. Zhang, J. Tejada, Y. Xin, G. F. Sun, K. W. Wong, and X. Bohigas, Appl. Phys. Lett. **69**, 3596 (1996).
[14]A. Szewczyk, H. Szymczak, A. Wisniewski, K. Piotrowski, R. Kartaszyn-ski, B. Dabrowski, S. Kolesnik, and Z. Bukowski, Appl. Phys. Lett. **77**, 1026 (2000).
[15]R. Szymczak, R. Kolano, A. Kolano-Burian, V. P. Dyakonova, and H. Szymczak, Acta Phys. Pol. A **117**, 203 (2010), http://przyrbwn.icm.edu.pl/APP/PDF/117/a117z141.pdf.
[16]A. Rostamnejadi, M. Venkatesan, P. Kameli, H. Salamati, and J. M. D. Coey, J. Magn. Magn. Mater. **323**, 2214–2218 (2011).
[17]S. Roy, Y. Q. Guo, S. Venkatesh, and N. Ali, J. Phys.: Condens. Matter **13**, 9547 (2001).
[18]A. Das, M. Sahana, S. M. Yusuf, L. Madhav Rao, C. Shivakumara, and M. S. Hegde, Mater. Res. Bull. **35**, 651–659 (2000).
[19]A. I. Tovstolytkin, A. M. Pogorily, D. I. Podyalovskii, V. M. Kalita, A. F. Lozenko, P. O. Trotsenko, S. M. Ryabchenko, A. G. Belous, O. I. V'yunov, and O. Z. Yanchevskii, J. Appl. Phys. **102**, 063902 (2007).
[20]A. H. Morrish, *The Physical Principles of Magnetism* (Wiley, New York, 1965), Chap. 3.
[21]E. Veena Gopalan, I. A. Al-Omari, D. Sakthi Kumar, Y. Yoshida, P. A. Joy, and M. R. Anantharaman, Appl. Phys. A **99**, 497–503 (2010).
[22]Y. Kalyana Lakshmi, G. Venkataiah, and P. Venugopal Reddy, J. Appl. Phys. **106**, 023707(2009).
[23]J. Rodríguez-Carvajal, M. Hennion, F. Moussa, and A. H. Moudden, Phys. Rev. B **57**(6), R3189 (1998).
[24]L. D. Landau, Zh. Eksp. Teor. Fiz. (JETP) **7**, 19 (1937); **7**, 627 (1937).
[25]E. M. Lifshitz, Zh. Eksp. Toer. Fiz. **11**, 269 (1941).
[26]V. L. Ginzburg, Zh. Eksp. Teor. Fiz. **17**, 833 (1947).
[27]C. P. Bean and D. S. Rodbell, Phys. Rev. **126**, 104 (1962).
[28]S. K. Banerjee, Phys. Lett. **12**, 16 (1964).