Influence of higher sodium substitutions on magnetic entropy change and transition temperature in lanthanum manganites

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Abstract. Present investigation focuses on the variation of magnetic entropy change for higher sodium substitution above 50% in lanthanum manganites. Magnetic measurements indicated that all samples exhibit a ferromagnetic ordering near room temperature. Magnetic isotherms for different temperatures above and below 300 K were recorded and the magnetic entropy change for compositions belonging to $\text{La}_{1-x}\text{Na}_x\text{MnO}_3$ for $x = 0.6$ to 0.9 in steps of 0.1 was estimated for different applied magnetic fields. It has been found that the compositions having a Na substitution of 0.6 are having the largest entropy change, and the entropy change increases with applied magnetic field for all compositions. The change in entropy also decreases with increase in substitution of sodium. A notable change in transition temperature with Na concentration is also found in this sample series.

Keywords. Magnetic materials; manganites; magnetic entropy change.

1. Introduction

Manganites are perceived as interesting materials with strong correlation between charge and spin degrees of freedom. These classes of materials belong to the family of perovskites (ABO_3), possessing BO_6 octahedra with B and A sites occupied by divalent, trivalent or tetravalent ions. Manganites, especially rare-earth manganites (REMnO_3), attracted immense attention after the discovery of colossal magnetoresistance. They are characterized by having one type spin electrons dominating over the other and only energies of these particular spin electrons reach the Fermi level. These materials thus belong to a specific class called half metallic compounds, as the material acts as an insulator for one type of spins while for other type, it is a conductor. Spin-dependent transport is a unique feature of these class of materials, which has been exploited largely for developing spintronic devices, a concept of utilizing the spin of electrons in addition to charge.^{1,2} Manganites also possess large magnetic moments and exhibit a variety of magnetic phases, such as ferromagnetism (FM), antiferromagnetism (AFM), charge ordering, spin glass or canted AFM. Magnetic property is largely dependent on exchange interactions between mixed valence states of Mn and is also closely linked to the spin-dependent electron transfer. From a fundamental perspective, they serve as ideal templates for studying correlation between structure, magnetic and charge transport.^{3,4}

Properties of manganites are dependent on size and valence states of A or B site ions, their concentration, nature of substituting elements for A and B ions, valence states of Mn and the oxygen stoichiometry. Variation in any of these parameters can result in structural changes, resulting in distortion in the form of deformation of unit cell from the ideal cubic phase. Structural distortion in manganites is often associated with Jahn teller distortion, which is a deciding factor for inducing further changes in magnetoresistance and formation of magnetic phases. There exist reports in literature dealing with hole- or electron-doped manganite systems with a wide variety of structural, magnetic and electrical properties. They are also known to influence electron transport.^{5–8}

Magnetocaloric effect (MCE) is termed as the reversible change in temperature exhibited by materials with and without external magnetic field and such materials are called magnetocaloric materials. Manganites with large magnetic moments close to room temperature can serve as excellent candidates for magnetic refrigeration applications, which add to their multifunctionality.^{9,10} This phenomenon can be traced to the Maxwell's thermodynamic relations and adiabatic demagnetization. Magnetic refrigeration applications are characterized by magnetic entropy (ΔS_M) and adiabatic temperature change (ΔT). MCE is an intelligent substitute for the conventional cooling technology, as it does not make use of any refrigerant gases and is an ecofriendly refrigeration mechanism. Large magnetic entropy changes have been observed so far for Gd-based compounds, such as $\text{Gd}_5(\text{SiGe})_4$ and MnFe alloys close to the mark of $40 \text{ J kg}^{-1} \text{ K}^{-1}$.¹¹ Many other materials such as Laves phases

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(La(FeSi)), MnAs, heusler alloys and rare-earth manganites are also being increasingly investigated for magnetic refrigeration.^{12,13} Manganites have an advantage of tunable magnetic properties with respect to substituting elements and the potential of developing a near room temperature magnetic refrigerant.¹⁴

A survey of literature also reveals that though compositions having lower substitutions of sodium (Na) in LaMnO_3 (LMO) have been investigated and thoroughly studied, there exists no report on higher sodium substitution above 50%. For higher substitution levels of sodium, maintaining its exact stoichiometry in the compound is challenging as sodium is volatile. Thus sodium substitution in LaMnO_3 presents new challenges, especially from the sample preparation point of view because of the loss of Na during sintering or synthesis. As an initial study, the composition with 50% Na substitution (LNMO5) was prepared. Investigation carried out on LNMO5 for evaluating the ΔS_M was encouraging and it has been found that 50% Na-substituted LMO is a potential magnetic refrigerant.¹⁵ It could then be presumed that compositions with Na above 50%, i.e., $\text{La}_{1-x}\text{Na}_x\text{MnO}_3$ ($x = 0.6$ to 0.9), are also of interest. Present work is a systematic study on magnetic characteristics and entropy changes associated with LMO for Na compositions greater than 50%. Monovalent substitution at La sites can lead to the formation of twice the number of holes than divalent substitution, which can play a decisive role in the conversion of Mn^{3+} ions to Mn^{4+} ions, thereby in the magnetic property.¹⁶ Monovalent ions like K, Li have been substituted for A site rare-earth atoms and recently Na in PrSrMnO_3 has been reported to exhibit ΔS_M of $4.4 \text{ J kg}^{-1} \text{ K}^{-1}$ at 290 K at an applied external magnetic field of 7 T.¹⁷ Sodium substitution in LaBaMnO_3 has led to a ΔS_M of $4 \text{ J kg}^{-1} \text{ K}^{-1}$ at 280 K for 7 T external magnetic field.¹⁸ There are also reports to suggest that a magnetic entropy change of $3 \text{ J kg}^{-1} \text{ K}^{-1}$ was observed in lower sodium-substituted manganite, that is, $\text{La}_{0.65}\text{Ca}_{0.3}\text{Na}_{0.05}\text{MnO}_3$ below 300 K.¹⁹ Magnetocaloric studies carried out in $\text{La}_{0.799}\text{Na}_{0.199}\text{Mn}_{1.000}\text{O}_{2.97}$ by Zhong *et al* revealed a ΔS_M of $1.96 \text{ J kg}^{-1} \text{ K}^{-1}$ at 334 K. A magnetic entropy change within a range of $1\text{--}3 \text{ J kg}^{-1} \text{ K}^{-1}$ was observed for lower levels of monovalent ion substitutions (Na or K) in lanthanum manganites.^{20,21}

2. Experimental

Sodium ion (Na^+) is substituted for La^{3+} ion in LMO as ionic radii of Na^+ is comparable with La^{3+} thereby limiting structural distortion. Samples with Na concentration of 0.6 to 0.9 in steps of 0.1 (samples coded as LNMO6 to LNMO9 correspondingly, shortly as LNMO series) were synthesized using citrate gel method. Required amounts of lanthanum oxide, manganese nitrate and sodium carbonate were dissolved in de-ionized water. Adequate amount of citric acid and nitric acid was added to the solution and was heated to a temperature of 80°C with continuous stirring. The resultant dark powder was then

fired at a temperature of 1100°C for several hours. Structural studies were carried out using X-ray diffraction and magnetization studies were carried out using a Vibrating Sample Magnetometer (VSM) and a SQUID Magnetometer. Magnetization data were utilized to evaluate the magnetic entropy change.

3. Results and Discussion

All the four samples of substituted lanthanum manganite, namely, LNMO6, LNMO7, LNMO8 and LNMO9 exhibited distorted orthorhombic structure with a pbnm space group, which has been reported elsewhere.²² It has been reported that for Na substitutions ranging from 0.025 to 0.25 in LMO, samples exhibited rhombohedral structure with $R\bar{3}C$ space group.¹⁶ For Na substitutions in La and Mn sites in LMO system, rhombohedral structure was observed. A systematic decrease in rhombohedral distortion has been observed for sodium-substituted LMO system.^{23,24} Reports on sodium-substituted praseodymium manganites exhibiting orthorhombic structure with pbnm space group, showed an increase in orthorhombic distortion with decrease in Na ion concentration resulting in decrease of Mn–O–Mn bond angle and cell volume. Orthorhombic and rhombohedral phases have been observed in Na-substituted mixed manganites of praseodymium and lanthanum.²⁴ Roy *et al*³ have reported a change in characteristic peak as the Na concentration is increased in manganites, indicating the onset of orthorhombic phase. Shimura *et al*⁴ have also proposed a distorted perovskite structure for monovalent ion doping. Magnetization measurements carried out using VSM (figure 1) indicated that all samples show ferromagnetic ordering with negligible coercivity. It is also found that saturation magnetization (M_S) decreases with increase in Na concentration. Magnetic ordering in manganites is mainly attributed to exchange mechanism between mixed valence states of Mn; Mn^{3+} and Mn^{4+} . An X-ray photoelectron spectroscopy (XPS) profile of $\text{Mn}2p_{3/2}$ peak for LNMO sample series in figure 2 clearly indicates the presence of Mn^{3+} and Mn^{4+} ions and their variation with respect to Na concentration. It is found that as Na concentration increases, Mn^{4+} ions outnumber Mn^{3+} ions. Increase in Mn^{4+} ions result in a decreased double exchange interaction, which could lead to decrease in saturation magnetization. Reduced mobility of charge carriers owing to the presence of oxygen vacancies also has direct influence in magnetization decrease.^{25–27} Structural and magnetic studies of LNMO series do not form the objective of present article and have been discussed in another article of the same author.²² As part of a brief overview, two major results are indicated in figures 1 and 2. From figure 1 it is clear that samples are ferromagnetic at 300 K.^{15,22} Inset of figure 1 shows that all samples possess a nominal coercivity close to 10 Oe. Figure 2 indicates the $\text{Mn}2p_{3/2}$ XPS profile of LNMO series, which indicates the presence of $\text{Mn}^{3+}/\text{Mn}^{4+}$ ions and it is observed that as Na concentration increases, more Mn^{3+} ions are getting converted to Mn^{4+} ions.²²

Figure 1. Ferromagnetic behaviour of LNMO samples. Inset is the magnified graph for the magnetic field range -120 to $+120$ Oe, which shows that coercivity is close to 10 Oe.

Figure 2. $\text{Mn}2p_{3/2}$ XPS profile of LNMO samples.

$M-H$ (magnetization–magnetic field) isotherms with magnetization expressed in $\text{Am}^2 \text{kg}^{-1}$ for magnetic field variation $\mu_0 H$ up to 5 T in the temperature range 200–300 K in steps of 20 K for samples LNMO6, LNMO7, LNMO8 and LNMO9 are shown in figure 3.

Determination of magnetic entropy change from magnetic isotherms is a reliable technique, as it is difficult to determine the adiabatic temperature change directly in manganites. Area between $M-H$ isotherms is a measure of the entropy change and is governed by equation (1), which stems

Figure 3. M – H isotherms for LNMO samples: (a–d) LNMO6 to LNMO9.

out from Maxwell's thermodynamic relations,²⁸ where M is the magnetization at a particular temperature T and H the magnetic field. An alternate form of equation (1) is given by equation (2), where M_i and M_{i+1} are the magnetization values corresponding to temperatures T_i and T_{i+1} , respectively.

$$\Delta S_M(T, H) = \mu_0 \int_0^H \frac{\partial M(T, H)}{\partial T} dH \quad (1)$$

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

Thus as per equation (2), entropy change, ΔS_M can be evaluated by multiplying the reciprocal of temperature difference (ΔT) and area between two adjacent M – H curves.^{28,29} Area between 200 K and 220 K M – H curves with ΔT of 20 K yields ΔS_M value at 210 K.

From the isotherms in the temperature range of 200 to 300 K, it could be seen that all samples are ferromagnetic with a magnetic ordering temperature above 300 K. Calculated magnetic entropy change (ΔS_M) values as per equation (1) (absolute values, i.e., sign of entropy are not considered) for LNMO6 are shown in figure 4a. From figure 4a it is observed that ΔS_M increases with increase in temperature

reaching a maximum of $1 \text{ J kg}^{-1} \text{ K}^{-1}$ at 290 K and the entropy change increases with increase in external magnetic field. Entropy values for 0.5, 1, 2 and 5 T follow a decreasing trend for a particular temperature. For analysing entropy variation above 300 K, magnetic isotherms in the high temperature range of 303 to 393 K were also analysed and the magnetic entropy variation was estimated. For this set of isotherms small field variations are considered, as main focus is on variation of entropy with temperatures above 300 K.

Figure 4b shows entropy variation in the temperature range 303–393 K for 0.5, 1, 1.15, 1.25 and 1.35 T magnetic field ranges. It indicates that ΔS_M is found to be decreasing from 308 K and reaches a minimum at 388 K. Thus the entropy variation is maximum in the temperature range of 250 to 320 K. Entropy change at 308 K for 1.35 T magnetic field is found to be $0.082 \text{ J kg}^{-1} \text{ K}^{-1}$. Similarly, ΔS_M values for LNMO7 is also determined and shown in figure 5a for 0.5, 1, 2 and 5 T in the temperature range 200–300 K, which also showed a decreasing trend with increase in temperature, a maximum ΔS_M of $0.82 \text{ J kg}^{-1} \text{ K}^{-1}$ for 5 T magnetic field. For LNMO7, a maximum ΔS_M of $0.028 \text{ J kg}^{-1} \text{ K}^{-1}$ is observed for 1.35 T as analysed from isotherms in the high temperature range 303–393 K (figure 5b). LNMO8 and LNMO9 recorded a maximum ΔS_M of 0.55 and $0.32 \text{ J kg}^{-1} \text{ K}^{-1}$, respectively, for 5 T magnetic field (figures 6a and 7a) in the temperature range 200–300 K. In the high temperature range 303–393 K, LNMO8 and LNMO9 possessed a ΔS_M of 0.033 and

Figure 4. Magnetic entropy change (ΔS_M) for LNMO6 sample for the temperature range (a) 200–300 K and (b) 303–393 K.

Figure 5. Magnetic entropy change (ΔS_M) for LNMO7 sample for the temperature range (a) 200–300 K and (b) 303–393 K.

Figure 6. Magnetic entropy change (ΔS_M) for LNMO8 sample for the temperature range (a) 200–300 K and (b) 303–393 K.

$0.015 \text{ J kg}^{-1} \text{K}^{-1}$ for 1.35 T magnetic field, respectively (figures 6b and 7b).

Entropy variation in the range 200–300 K and 303–393 K is depicted in figures 8 and 9, respectively. Maximum

entropy variation is observed for LNMO6 and as Na content increases, value of entropy change decreases.

There are reports on magnetic entropy changes with respect to substituted lanthanum manganites. Zhong *et al.*³⁰

Figure 7. Magnetic entropy change (ΔS_M) for LNMO9 sample for the temperature range (a) 200–300 K and (b) 303–393 K.

Figure 8. Magnetic entropy change (ΔS_M) for LNMO6 to LNMO9 samples for the temperature range 200–300 K.

Figure 9. Magnetic entropy change (ΔS_M) for LNMO6 to LNMO9 samples for the temperature range 303–393 K.

reported a ΔS_M of 1.32 and 1.53 $\text{J kg}^{-1} \text{K}^{-1}$ at 195 and 218 K under 1 T magnetic field for $\text{La}_{0.925}\text{Na}_{0.075}\text{MnO}_3$ and $\text{La}_{0.9}\text{Na}_{0.1}\text{MnO}_3$, respectively. But in both cases, magnetic ordering temperature was much below room temperature. However it must be noted that in the present LNMO series, entropy change obtained is maximum within the temperature range of 250 and 320 K. In an earlier study conducted on $\text{La}_{0.83}\text{Li}_{0.17}\text{Ti}_{0.4}\text{Mn}_{0.6}\text{O}_3$ a ΔS_M of 0.9 $\text{J kg}^{-1} \text{K}^{-1}$ was observed at 3 T, while a ΔS_M of 1.1 $\text{J kg}^{-1} \text{K}^{-1}$ was recorded in $\text{La}_{0.85}\text{Li}_{0.15}\text{Ti}_{0.3}\text{Mn}_{0.7}\text{O}_3$ at 3 T magnetic field at 80 K.³¹ Thus major outcome of the present investigation is that entropy variation observed in all four samples belonging to the series $\text{La}_{1-x}\text{Na}_x\text{MnO}_3$ is near room temperature with lower hysteresis loss or lower coercivity. The low values observed in these samples could be attributed to (a) distortion of lattice from orthorhombic to rhombohedral along with change in space group, and (b) presence of first-order magnetic transition from AFM to FM in addition to dominant second-order transition from FM to paramagnetism. It could be interesting to study the magnetic properties and

MCE behaviour in managnite systems, where monovalent as well as divalent ions are substituted for La sites.

Magnetic isotherms in the case of sample series of LNMO were also utilized to generate Arrott plots, which plots second-order terms in Landau free energy terms, i.e., $\mu_0 H/M$ vs. M^2 . Positive slope of Arrott plots are indicative of second-order magnetic transition. Arrott plots for LNMO series are shown in figures 10a, b and 11a, b, which confirm that magnetic transition in them is of second order. In the Arrott plots, curve that can be extrapolated to origin corresponds to T_C . For determining T_C , a linear line from the origin that is 45° inclined to both x and y axes are taken as reference line and the curve from isotherms corresponding to a particular temperature that coincides with the reference line gives the T_C value. In case if the reference line does not coincide but pass between two temperature curves, only the range of T_C could be specified. In our case for LNMO6 (figure 10a), the reference line passes between the two curves 333 and 323 K and hence T_C range is 333–323 K. Also for LNMO7 sample (figure 10b), the reference line passes between the two curves

Figure 10. Determination of T_C range from Arrott plots: (a) for LNMO6 T_C range is between 333 and 323 K and (b) for LNMO7 T_C range is between 323 and 313 K.

Figure 11. Determination of T_C range from Arrott plots: (a) for LNMO8 T_C range is between 313 and 303 K and (b) for LNMO9 T_C is at 303 K.

Figure 12. (a) M vs. T measurement for LNMO6, which indicates T_C at 323 K. (b) M vs. T measurement for LNMO7, LNMO8 and LNMO9 with T_C at 314, 310 and 304 K, respectively.

323 and 313 K and T_C range can be defined between 313 and 323 K. In the case of LNMO8 (figure 11a) also, T_C range is between 313 and 303 K and in LNMO9 (figure 11b), T_C is found to be at around 303 K. Arrott plots for LNMO7 and LNMO8 (figures 10b and 11a, respectively) are linear, while for LNMO9 (figure 11b) curves are slightly deviated from linear behaviour in the temperature range 200 to 300 K indicative of a magnetic inhomogeneity.

Estimation of exact value of T_C from Arrott plots is difficult as the curves overlap at high temperatures, but it can be established that there is considerable variation in T_C with Na doping and it decreases with increase in Na doping. Such anomalous behaviour in T_C from divalent ion substitutions has been observed earlier. It has been proposed that many factors like competition between different structures like orthorhombic or rhombohedral phases, Hund's

coupling and oxygen vacancies could decide magnetic ordering mechanism and transition temperature.^{26,27} Magnetization vs. temperature measurements were also carried out on LNMO samples to determine transition temperature, T_C , and it matches well with that obtained from Arrott plots. Figure 12a shows magnetization vs. temperature (M vs. T) measurements on LNMO6, which indicates T_C at 323 K, while figure 12b shows M vs. T on LNMO7, LNMO8 and LNMO9 samples.

4. Conclusions

In conclusion, magnetic isotherms and the respective entropy change for samples belonging to the series of sodium-substituted lanthanum manganites LNMO6 to LNMO9 were evaluated. An appreciable change in magnetic entropy was observed for the samples and the entropy variation is dependent on magnetic field and temperature. From the entropy values of LNMO6 to LNMO9, it can be pointed out that entropy change increases with increase in magnetization while it exhibits maximum entropy change in the temperature range of 250 to 320 K. Maximum entropy variation is observed for sample with lower Na content, which is LNMO6. Magnetic isotherms were also utilized to generate Arrott plots to study the variation of transition temperature. It was found that there is decrease in T_C with increase in Na concentration, which was confirmed from the M vs. T measurements. Monovalent-substituted lanthanum manganites exhibit tunable magnetic properties and are potential candidates for magnetocaloric applications.

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