International Journal of Technology (2016) 3: 493-499
ISSN 2086-9614

INFLUENCE OF Sn-DOPING ON MAGNETOCALORIC PROPERTIES OF $La_{0.7}Ca_{0.3}Mn_{1-x}Sn_xO_3$ (x = 0.0, x = 0.02 and x = 0.04) COMPOUNDS

Dwi Nanto[1,2], Wen-Zhe Nan[1], Suhk-Kun Oh[1], Seong-Cho Yu[1*]

[1] *Department of Physics, Chungbuk National University, Cheongju, 361-763, South Korea*
[2] *Dept. of Physics Education, Syarif Hidayatullah State Islamic University, Jakarta, 15412, Indonesia*

(Received: December 2015 / Revised: January 2016 / Accepted: February 2016)

ABSTRACT

Modern technology for refrigerators and coolers is based on the chemical gas Chlorofluorocarbon (CFC) compression method that is indicative of a high consumption of electricity. The CFC is also understood as a reason for global warming. One of the solutions to this issue is magnetic refrigeration technology, which is environmentally friendly because it does not use any hazardous chemicals or ozone depleting/greenhouse gases. Magnetic refrigeration technology is based on the magnetocaloric effect of magnetic refrigerant materials. Exploring the magnetocaloric effect of magnetic refrigerant materials is important because these contain many of the physical properties needed for magnetic refrigeration technology. Herein, the present work reports on the magnetocaloric effect of $La_{0.7}Ca_{0.3}Mn_{1-x}Sn_xO_3$ (x = 0.0, x = 0.02 and x = 0.04) compound samples produced with the solid state reaction technique. Curie temperature T_C obtained for the $La_{0.7}Ca_{0.3}Mn_{1-x}Sn_xO_3$ (x = 0.0, x = 0.02 and x = 0.04) are 260 K, 176 K and 170 K with $-\Delta S_{M\ \max}$ of 4.32 $J{\cdot}kg^{-1}{\cdot}K^{-1}$, 1.61 $J{\cdot}kg^{-1}{\cdot}K^{-1}$ and 1.24 $J{\cdot}kg^{-1}{\cdot}K^{-1}$ and a refrigerant capacity of 48 J/kg, 41.43 J/kg and 28.53 J/kg for x = 0.0, x = 0.02 and x = 0.04, respectively. A small addition of Sn-doped resulted in a significant decrease of more than 80 K on the Curie temperature scale compared to that of $La_{0.7}Ca_{0.3}MnO_3$. The large gap in the decreasing magnetic temperature phase transition might be useful as an option of metal/transition metal doped for tuning the Curie temperature of magnetic refrigerant materials.

Keywords: Magnetic refrigerant material; Magnetocaloric effect; Polycrystalline perovskite manganites; Refrigerant capacity; Sn-doped

1. INTRODUCTION

Magnetocaloric effect (MCE) has been studied widely for magnetic refrigeration technology in order to suppress emissions of pollution components, which are a problem while using conventional mechanical refrigeration technology. Due to the possibility of its promising application for magnetic refrigeration technology, a substantial number of works on polycrystalline perovskite ABO_3 (A = La, Sr, Nd.. rare earth material and B = manganese) have been reported. In the middle of 20th century, Zener proposed the famous theoretical explanation for the double-exchange (DE) mechanism, which is significant in understanding the Magnetocaloric Effect (MCE) (Zener, 1951). The theory described magnetic properties of manganite perovskite, which later was simply designated as a Double Exchange.

*Corresponding author's email: scyu@cbnu.ac.kr, Tel. +82-43-261-2269, Fax. +82-43-274-7811
Permalink/DOI: http://dx.doi.org/10.14716/ijtech.v7i3.2946

The DE mechanism successfully describes MCE as being electrons itinerant between Mn^{4+} and Mn^{3+} transferred through Oxygen. Curie temperature, T_C, is one crucial property in MCE because T_C demonstrated the magnetic phase transition from ferromagnetic to paramagnetic, which occurred mostly around T_C, thus it obtained a maximum magnetic entropy change, ΔS_M. One way for tuning T_C is a treatment in which the *A*-site or *B*-site is supplemented (doped) with other metal(s) (Al, Ga, Sn, and Bi) as reported by previous researchers (Kumar & Mahendiran, 2011; Omri et al., 2012; Dhahri et al., 2008; Gencer et al., 2005; Kammoun et al., 2008b). Therefore, introducing other doped metal(s) will influence the DE mechanism, which corresponds to the T_C and MCE properties.

The purposes of *A*-site doped or *B*-site doped in manganites perovskite are to achieve a mismatch effect (Rodriguez-Martinez & Attfield, 1996; Koubaa et al., 2011) and a polaron effect that exerts from the strong electron–phonon coupling arising from Jahn–Teller distortions. These distortions are due to a number of factors, such as vacancy (Millis et al., 1995), a decreased sintering temperature (Gencer et al., 2005), and to reduce the content of mobile e_g electrons when Mn^{3+} is substituted (Omri et al., 2012). This way, appropriate properties were obtained and thus proposed as suitable candidates for magnetic refrigeration materials at a designed temperature range. Another factor to consider besides the phase transition T_C, is an important property that is inherent to the magnetic refrigerant material. This property has a large magnetic entropy change characteristic, $|\Delta S_M|$. That is, the material should show a large spontaneous magnetization as well as a sharp decline in the magnetization associated with the ferromagnetic–paramagnetic phase transition around the T_C. Other important issue is inexpensive material (Tan et al., 2013); moreover, the material is lightweight. Other considerations for application include advantages, such as economic, non-critical and non-toxic materials with limited thermal/magnetic hysteresis that are also important (Yibole et al., 2014).

Recently, Dhahri et al. (2008) reported MCE in fine-grained perovskite manganites type $La_{0.67}Ba_{0.33}Mn_{1-x}Sn_xO_3$ (x = 0.05, 0.1 and 0.15) that achieved a phase transition (T_C) at 340 K, 325 K and 288 K for x = 0.05, 0.1 and 0.15, respectively and $-\Delta S_{M\ max}$ reached the highest value of 2.49 J/kg K for the sample x = 0.15, with H = 2 T (Dhahri et al., 2008). Another compound reported by Tka et al. (2013) indicated that $La_{0.57}Nd_{0.1}Sr_{0.33}Mn_{1-x}Sn_xO_3$ with ($0.05 \leq x \leq 0.30$) $-\Delta S_{M\ max}$ reaches the highest value of 3.22 J/kg K under a magnetic field change of 5 T with a refrigerant capacity (RC), at a value of 56 J/kg for x = 0.10 (Tka et al., 2013). Both reported works by Dhahri et al. (2008) and Tka et al. (2013) gave interesting information that indicated the Sn-doped reached ΔS_M without a trend either by low or high for the Sn-doped. This means there is no tendency that increasing Sn-doped will optimize to reach maximum magnetic entropy change. Sn-doped manganite perovskite showed an opposite trend in magnetic entropy change. Although the Curie temperature decreases as the Sn-doped increased, the magnetic entropy change also increased (Dhahri et al., 2008). Meanwhile, other metals or transition metals will experience a decrease in both Curie temperature and magnetic entropy change as found in Ga-doped (Omri et al., 2012) and Fe-doped conditions (Lampen et al., 2012).

The current work reports the influence of slight Sn-doped in a *B*-site on the MCE for a polycrystalline $La_{0.7}Ca_{0.3}MnO_3$ sample. Interestingly enough, it was found that the T_C decreases significantly to larger than 80 K. On the other hand, the maximum magnetic entropy changes as well as the T_C which is lowered by increasing the Sn-doped followed by a reduction in the Refrigeration Capacity (RC).

2. EXPERIMENTAL

The $La_{0.7}Ca_{0.3}Mn_{1-x}Sn_xO_3$ (x = 0.0, x = 0.02 and x = 0.04) samples were prepared by the standard method of solid-state phase reactions with the precursors of high purity La_2O_3, CaO, pure Mn powder and pure Sn powder. After synthesizing at 900°C for 24 hours, the samples were grounded, pressed and then, annealed again at 1350°C for 24 hours, finally followed by slowly cooling to room temperature. The crystal structure of sample was characterized by a XRD diffractometer (Brucker AXS, D8 Discover) using Cu-$K\alpha$ radiation at room temperature. Magnetization characteristics were investigated by means of a temperature-dependent vibrating sample magnetometer.

3. RESULTS AND DISCUSSION

Before investigating the MCE properties the sample were characterized by means of XRD as one could see in Figure 1. The XRD pattern of $La_{0.7}Ca_{0.3}Mn_{1-x}Sn_xO_3$ (x = 0.0, x = 0.02 and x = 0.04) was within the angle range of 20°–90° which was measured at room temperature. It appears that the XRD patterns from all of the samples have the same features. There are no obvious additional peaks implying that Mn site has been completely substituted by Sn. Moreover, those XRD patterns have similar properties with the parent composition $La_{0.7}Ca_{0.3}MnO_3$ (Lampen et al., 2012).

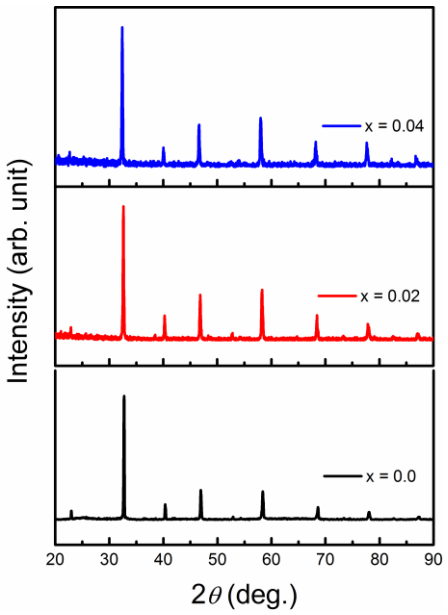

Figure 1 XRD pattern of $La_{0.7}Ca_{0.3}Mn_{1-x}Sn_xMnO_3$ (x = 0.0, x = 0.02 and x = 0.04) at room temperature

In Figure 2, the magnetization curve with respect to the temperature for the samples of $La_{0.7}Ca_{0.3}Mn_{1-x}Sn_xO_3$ (x = 0.0, x = 0.02 and x = 0.04) are shown. It was observed that at 100 K under an applied field of 100 Oe the sample $La_{0.7}Ca_{0.3}Mn_{0.98}Sn_{0.02}O_3$ has a higher magnetization than $La_{0.7}Ca_{0.3}Mn_{0.96}Sn_{0.04}O_3$. In this condition, a slight increase in Sn-doped showed a tendency of weakening magnetization. In $La_{0.7}Ca_{0.3}MnO_3$ the $M(T)$ curve shows a sharp drop of magnetization as a characteristic of first order magnetic transition, while $La_{0.7}Ca_{0.3}Mn_{0.96}Sn_{0.02}O_3$ and $La_{0.7}Ca_{0.3}Mn_{0.96}Sn_{0.04}O_3$ does not. Moreover, the inset of Figure 2 shows the small addition of Sn-doped tends to be in the second order magnetic phase transition of $La_{0.7}Ca_{0.3}MnO_3$ because dM/dT shows a continuous curve. Current work used a simple method to find T_C by computing the first derivative of the $M(T)$ curve. T_C is defined as an

extreme value of the dM/dT obtained value of 260 K, 176 K and 170 K for x = 0.0, x =0.02 and x = 0.04, respectively. Lampen et al. (2012) reported the sample $La_{0.7}Ca_{0.3}MnO_3$ without any doped, obtained T_C of 263 K. Therefore, slight Sn-doped on $La_{0.7}Ca_{0.3}MnO_3$ will obtain a significant decrease of larger than 80 K in the Curie temperature compared to $La_{0.7}Ca_{0.3}MnO_3$. In detail, comparing the 2 % Fe-doped result in decreasing T_C of 30 K to 2 % Sn-doped result revealed a decrease in the T_C of more than 80 K on $La_{0.7}Ca_{0.3}MnO_3$. Thus, Sn-doped is more effective in decreasing T_C when compared to the Fe-doped (Lampen et al., 2012).

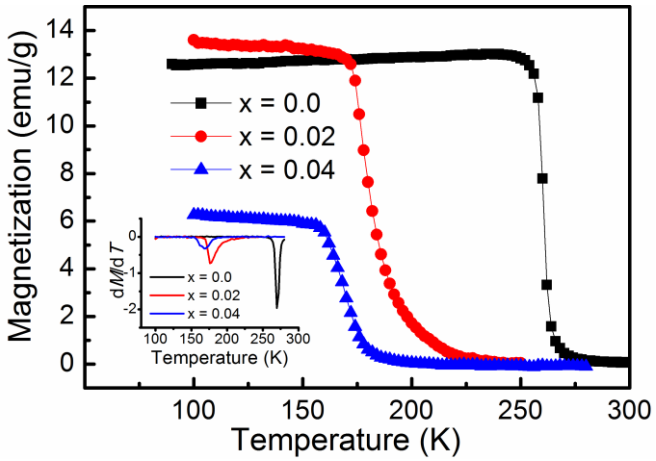

Figure 2 $M(T)$ curve for polycrystalline $La_{0.7}Ca_{0.3}Mn_{1-x}Sn_xO_3$ (x = 0.0, x = 0.02 and x = 0.04) under an applied field of 100 Oe. Insets are the first derivative of the $M(T)$ curve

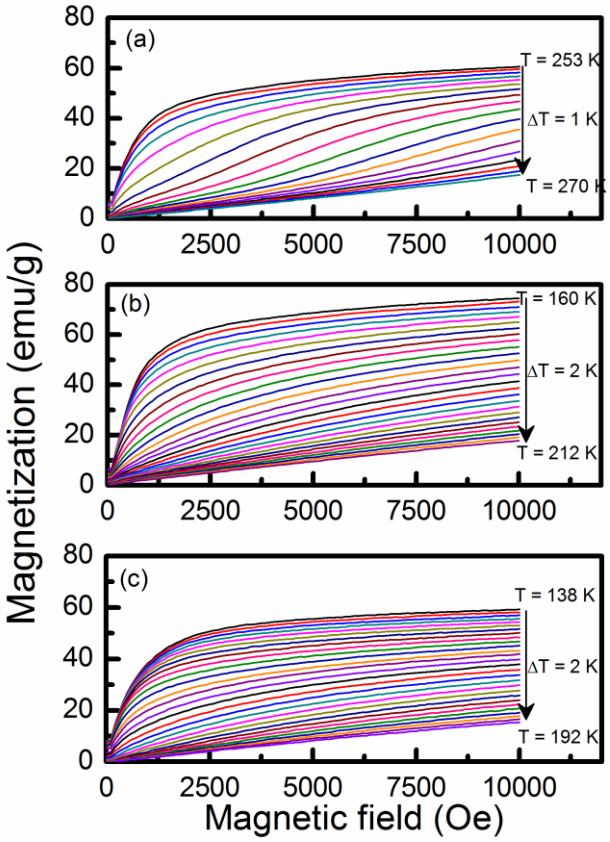

Figure 3 Isothermal magnetization of polycrystalline $La_{0.7}Ca_{0.3}Mn_{1-x}Sn_xO_3$ for: (a) x = 0.0; (b) x = 0.02; and (c) x = 0.04 under an applied field of 10 kOe

In order to explore MCE, isothermal magnetic measurements were carried out and the MCE properties of the samples were computed. The isothermal magnetic measurement $La_{0.7}Ca_{0.3}Mn_{1-x}Sn_xO_3$ for (x = 0.0, x = 0.02 and x = 0.04) are depicted in Figure 3. During the ferromagnetic regime, the magnetization curve had not reached a saturation level below 10 kOe indicating a tendency of increasing magnetic saturation at the incidence of an increasing external magnetic field. However, at the paramagnetic regime, the magnetic saturation increased almost linearly as external magnetic field increased. As demonstrated in Figure 3, it is observed that the scale of magnetic saturation was set up with the same value under an applied field of 10 kOe. The gap of magnetic saturation between one isothermal and another isothermal magnetization has been set at the same scale. In detail, about a 60 K wide range of working temperature, the magnetization of x = 0.02 shows a larger isothermal magnetization gap than x = 0.04. From this point of view, it might influence the value of maximum magnetic entropy change as well as refrigerant capacity.

$$\Delta S_M = \int_0^{H\max} \left(\frac{\partial S}{\partial H}\right)_T dH. \tag{1}$$

The magnetic entropy change versus temperature is depicted for both samples in Figure 4. Under a field of 10 kOe, the $La_{0.7}Ca_{0.3}Mn_{1-x}Sn_xO_3$ samples have a maximum entropy change of $-\Delta S_{M\,\max}$= 4.32 J·kg^{-1}·K^{-1}, $-\Delta S_{M\,\max}$= 1.61 J·kg^{-1}·K^{-1} and $-\Delta S_{M\,\max}$ = 1.24 J·kg^{-1}·K^{-1} for x = 0.0, x = 0.02 and x = 0.04, respectively. The decrease in the entropy change is expected from Figure 2 and Figure 3 as well. As the Sn-doped increased, it would result in shift of the Mn^{3+}/Mn^{4+} ratio to other ratio. The transition to the lower temperature produces a reduction of only magnetic entropy change in common. This phenomenon could be described as a weakening of the spin-lattice coupling in the matrix sample which affected ferromagnetic behavior (Phan et al., 2004). This weakening of the ferromagnetic regime corresponds to the weakening in the Double-Exchange (DE) mechanism as is also found in other metals Bi-doped (Kammoun et al., 2008a, Kammoun et al., 2008b), Sn-doped (Dhahri et al., 2008), and Ga-doped (Omri et al., 2012) in *B*-site atomic position.

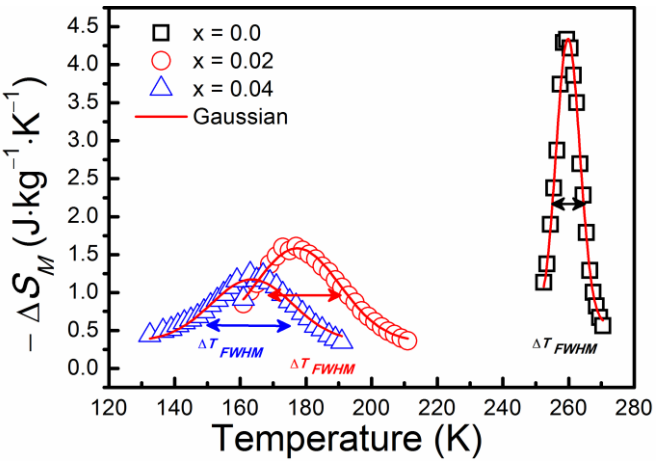

Figure 4 Entropy change for polycrystalline $La_{0.7}Ca_{0.3}Mn_{1-x}Sn_xO_3$ (x=0.0, x=0.02 and x = 0.04 under an applied field of 10 kOe. The dashed line is the Gaussian fit to find out the temperature span of T_{cold} and T_{hot} of ΔT_{FWHM} for refrigerant capacity calculation

Another important magnetocaloric property is RC formulated as:

$$RC = -\int_{T_1}^{T_2} \Delta S_M(T)dT \quad (2)$$

which describes how much heat can be delivered from the cold end (at T_1) to the hot end (at T_2) of a refrigerator in an ideal thermodynamic cycle. The RC value of $La_{0.7}Ca_{0.3}Mn_{1-x}Sn_xO_3$ are 48 J/kg, 41.43 J/kg and 28.53 J/kg for x = 0.02 and x = 0.04, respectively. Again, the decreasing of the RC is expected from Figure 2 and Figure 3 as well.

The solid state reaction will probably produce Sn^{4+} from a pure Sn powder; while pure Mn powder will produce Mn^{3+} and Mn^{4+}. Taking charge neutrality into account, the sample will have a chemical distribution of $La_{0.7}{}^{3+}Ca_{0.3}{}^{2+}Mn_{0.7}{}^{3+}Mn_{0.3-x}{}^{4+}Sn_x{}^{4+}O_3{}^{2-}$. Then, Sn^{4+} is chemically expected to shift the average valence state of Mn to become Mn^{3+}. The decrease in the density of Mn^{4+} ions mainly causes a reduction in the population of hopping electrons (e_g) leading to a weakening of the ferromagnetic behavior. Increasing Sn^{4+} ($r_{Sn}{}^{4+}$ = 0.69Å) to substitute Mn^{4+} ($r_{Mn}{}^{4+}$ = 0.53Å) will introduce a mismatch in the structure, due to difference of the ionic radius (Dhahri et al., 2008). Thus, it could cause a considerable change in the structural lattice parameters, such as the bond length of Mn–O and the bond angle of Mn–O–Mn. Therefore, the DE mechanism would be suppressed that implied in weakening of ferromagnetism.

4. CONCLUSION

Present work has successfully synthesized $La_{0.7}Ca_{0.3}Mn_{1-x}Sn_xO_3$ (x = 0.0, x = 0.02 and x = 0.04) samples. This research offers a study of the magnetocaloric effect in detail and found that the Curie temperature decreases significantly by the small addition of Sn-doped. The small addition of Sn-doped tends to be a second order magnetic phase transition of $La_{0.7}Ca_{0.3}MnO_3$. It proposes that Sn-doped may be useful for effective tuning of decreasing T_C for magnetic refrigerant materials. The refrigerant capacity of $La_{0.7}Ca_{0.3}MnO_3$ Sn-doped shows a negative result.

5. ACKNOWLEDGMENT

This research was supported by the Converging Research Center Program funded by the Ministry of Science, ICT and Future Planning Korea (2015055808), South Korea. This work also partially funded by Syarif Hidayatullah State Islamic University and Directorate Islamic Higher Education, Ministry of Religious Affair, **(**PPNDT/19/2015), Indonesia.

6. REFERENCES

Dhahri, J., Dhahri, A., Oumezzine, M., Dhahri, E, 2008. Effect of Sn-doping on the Structural, Magnetic and Magnetocaloric Properties of $La_{0.67}Ba_{0.33}Mn_{1-x}Sn_xO_3$ Compounds. *J. Magn. Magn. Mater.*, Volume 320, pp. 2613–2617

Gencer, H., Atalay, S., Adiguzel, H.I., Kolat, V.S., 2005. Magnetocaloric Effect in the $La_{0.62}Bi_{0.05}Ca_{0.33}MnO_3$ Compound. *Physica B*, Volume 357, pp. 326–333

Kammoun, I., Cheikhrouhou-Koubaa, W., Boujelben, W., Cheikhrouhou, A., 2008a. Bi Doping Effects on the Physical Properties of $Pr_{0.6}Sr_{0.4}Mn_{1-x}Bi_xO3$ ($0 \leq x \leq 0.2$) Manganese Oxides. *J. Alloys Comp.*, Volume 452, pp. 195–199

Kammoun, I., Cheikhrouhou-Koubaa, W., Boujelben, W., Cheikhrouhou, A., 2008b. Structural and Magnetic Properties of Bi Doped in the A-site of $(Pr_{1-x}Bi_x)_{0.6}Sr_{0.4}MnO_3$ ($0 \leq x \leq 0.4$) Perovskite Manganites. *J. Mater. Sci.*, Volume 43, pp. 960–966

Koubaa, M., Regaieg, Y., Cheikhrouhou Koubaa, W., Cheikhrouhou, A., Ammar-Merah, S., Herbst, F., 2011. Magnetic and Magnetocaloric Properties of Lanthanum Manganites with Monovalent Elements Doping at A-site. *J. Magn. Magn. Mater.*, Volume 323, pp. 252–257

Kumar, V.S., Mahendiran, R., 2011. Effect of Impurity Doping at the Mn-site on Magnetocaloric Effect in $Pr_{0.6}Ca_{0.4}Mn_{0.96}B_{0.04}O_3$ (B=Al, Fe, Cr, Ni, Co, and Ru). *J. Appl. Phys.*, Volume 109(2), pp. pp. 023903-1–023903-7

Lampen, P.J., Zhang, Y., Phan, T.-L., Zhang, P., Yu, S.-C., Srikanth, H., Phan, M.-H., 2012. Magnetic Phase Transitions and Magnetocaloric Effect in $La_{0.7}Ca_{0.3}Mn_{1-x}Fe_xO_3$ $0.00 \leq x \leq 0.07$ Manganites. *J. Appl. Phys.*, Volume 112(11), pp. 113901-1–113901-6

Millis, A.J., Littlewood, P.B., Shraiman, B.I., 1995. Double Exchange Alone does not Explain the Resistivity of $La_{1-x}Sr_xMnO_3$. *Phys. Rev. Lett.*, Volume 74, pp. 5144–5147

Omri, A., Bejar, M., Sajieddine, M., Dhahri, E., Hlil, E.K., Es-Souni, M., 2012. Structural, Magnetic and Magnetocaloric Properties of $AMn_{1-x}Ga_xO3$ Compounds with $0 \leq x \leq 0.2$. *Physica B*, Volume 407, pp. 2566–2572

Phan, M. H., Pham, V. T., Yu, S. C., Rhee, J. R., Hur, N. H. 2004. Large magnetic entropy change in a $La_{0.8}Ca_{0.2}MnO_3$ single crystal. *J. Magn. Magn. Mater.*, Volume 272–276, Part 3, pp. 2337–2339

Rodriguez-Martinez, L.M., Attfield, J.P., 1996. Cation Disorder and Size Effects in Magnetoresistive Manganese Oxide Perovskites. *Phys. Rev. B*, Volume 54, R15622–R15625

Tan, X., Chai, P., Thompson, C.M., Shatruk, M., 2013. Magnetocaloric Effect in $AlFe_2B_2$: toward Magnetic Refrigerants from Earth-Abundant Elements. *J. American Chem. Soc.*, Volume 135, pp. 9553–9557

Tka, E., Cherif, K., Dhahri, J., 2013. Evolution of Structural, Magnetic and Magnetocaloric Properties in Sn-doped Manganites $La_{0.57}Nd_{0.1}Sr_{0.33}Mn_{1-x}Sn_xO_3$ (x = 0.05–0.3). *Appl. Phys. A*, Volume 116(3), pp. 1181-1191

Yibole, H., Guillou, F., Zhang, L., Dijk, N.H.V., Brűck, E., 2014. Direct Measurement of the Magnetocaloric Effect in MnFe(P, X)(X=As, Ge, Si) Materials. *J. Phys. D: Appl. Phys.*, Volume 47(7), pp. 1–9

Zener, C., 1951. Interaction between the *d*-Shells in the Transition Metals. II. Ferromagnetic Compounds of Manganese with Perovskite Structure. *Phys. Rev.*, Volume 82, pp. 403–405