



Magnetic and magnetocaloric properties of $0.5\text{La}_{0.7}\text{Ca}_{0.2}\text{Sr}_{0.1}\text{MnO}_3/0.5\text{La}_{0.7}\text{Te}_{0.3}\text{MnO}_3$ composite

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Abstract

In this work, the magnetic and magnetocaloric properties of $0.5\text{La}_{0.7}\text{Ca}_{0.2}\text{Sr}_{0.1}\text{MnO}_3/0.5\text{La}_{0.7}\text{Te}_{0.3}\text{MnO}_3$ (0.5LCSM/0.5LTM) composite have been investigated. The 0.5LCSM/0.5LTM composite has been obtained by mixing the $\text{La}_{0.7}\text{Ca}_{0.2}\text{Sr}_{0.1}\text{MnO}_3$ and $\text{La}_{0.7}\text{Te}_{0.3}\text{MnO}_3$ manganites with a ratio of 0.5:0.5. All samples have been synthesized by using the standard solid state method. In order to investigate the magnetic and magnetocaloric properties of the samples, magnetization measurements dependence on temperature and magnetic field have been performed by using physical property measurement system. The nature of the magnetic phase transition for all materials has been identified by using Banerjee criterion and Landau theory and according to both methods the magnetic phase transition is second order. Magnetic entropy change values have been calculated by using Maxwell relation and Landau theory. Based on Maxwell relation, the maximum magnetic entropy change value of the composite has been calculated as 3.70 $\text{Jkg}^{-1}\text{K}^{-1}$ for 5 T.

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1. Introduction

Magnetic refrigeration (MR) systems are foreseen for near future as the best cooling technology because of their beneficial features such as large energy efficiency, small volume, and energy saving when compared to conventional gas compression cooling systems [1-2]. MR devices do not contain toxic refrigerant gases such as chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) [3]. For this reason, these cooling systems do not affect negatively our living areas. The basic principle of MR systems is magnetocaloric effect (MCE) described as thermal change of a material when an external magnetic field applied to this material [4]. The change observed in adiabatic temperature (ΔT_{ad}) and magnetic entropy (ΔS_M) of the material is two important parameters of MCE [5]. For the evaluating of a material as a cooling element in MR systems, the precondition is the showing large magnetocaloric property under low magnetic field change near room temperature [3]. Comprehensive studies have been made by different searching groups for this aim. Gd and its alloys have been used as a cooling material in prototype MR systems [3, 6-8]. However, some factors such as the cost of Gd and hard preparing methods limit usage of

Gd and Gd-based alloys [3]. Because of these limitations, many researchers have been tending toward perovskite manganites [9-13] symbolized with the general formula $\text{R}_{1-x}\text{A}_x\text{MnO}_3$ (R=rare earth elements, A: monovalent and divalent elements) which have advantages such as simple preparation methods, chemical stability and low cost [14]. The ΔS_M values which are comparable with Gd have been reported for doped manganites [15-18].

Recently, in the presence of magnetic multiphase in a system, it is reported that the $\Delta S_M(T)$ curves expand and correspondingly relative cooling power (RCP) values enlarge [19]. The new trend in the scope of MCE is to compose the composite samples which show the high ΔS_M with a high RCP. With single-phase systems, to obtain this is not simple and easy. For this reason, composite materials are being formed by using different material groups [20-23]. In the present work, we have selected $\text{La}_{0.7}\text{Ca}_{0.2}\text{Sr}_{0.1}\text{MnO}_3$ and $\text{La}_{0.7}\text{Te}_{0.3}\text{MnO}_3$ manganites. Because the magnetic phase transition of $\text{La}_{0.7}\text{Ca}_{0.2}\text{Sr}_{0.1}\text{MnO}_3$ manganite is near room temperature and both manganites show acceptable magnetic entropy change at low magnetic field changes [3, 24]. Both manganites have been investigated intensively but their composite has not composed yet. Therefore, we

have obtained the 0.5LCSM/0.5LTM composite sample by using these manganites at 0.5:0.5 mass fractions and investigated the magnetic and magnetocaloric properties of the 0.5LCSM/0.5LTM.

2. Experimental Procedure

Polycrystalline $\text{La}_{0.7}\text{Ca}_{0.2}\text{Sr}_{0.1}\text{MnO}_3$ and $\text{La}_{0.7}\text{Te}_{0.3}\text{MnO}_3$ samples labeled as LCSM and LTM were synthesized by using solid state technique. For LCSM sample, La_2O_3 , CaO , SrCO_3 and MnO_2 starting materials with higher purity than 99.9% in stoichiometric amounts were mixed in an agate mortar for 90 minutes. For calcination, the powder sample was heated in air at 800 and 950 °C, respectively for 12 h. The pelleted sample was sintered at 1400 °C for 24 h in air. The La_2O_3 , TeO_2 and MnO_2 starting materials were used in convenient amounts to obtain LTM sample. By using agate mortar, the powder mixture was stirred for 90 minutes as like LCSM sample. Then, in air at 500 °C for 12 h heat process was applied to the sample. Finally, the sample formed as pellets was sintered at 1000 °C for 24 h. The obtained pellets of LCSM and LTM samples were reground. By mixing the LCSM and LTM samples with a ratio 0.5:0.5, the $0.5\text{La}_{0.7}\text{Ca}_{0.2}\text{Sr}_{0.1}\text{MnO}_3/0.5\text{La}_{0.7}\text{Te}_{0.3}\text{MnO}_3$ (0.5LCSM/0.5LTM) composite was obtained. Finally, the composite were sintered at 900 °C during 24 h. By using physical property measurement system (PPMS; Quantum Design PPMS DynaCool-9), the temperature and magnetic field dependence of magnetization ($M(T)$ and $M(H)$, respectively) were

measured to analyze the magnetic and magnetocaloric properties.

3. Results and Discussion

The $M(T)$ measurements have been performed in order to investigate the magnetic properties of the LCSM and LTM manganites and their composite form with ratio 0.5:0.5. All measurements have been made at zero field cooled (ZFC) and field cooled (FC) modes, under 100 Oe magnetic fields and between 5-350 K temperature ranges. Figure 1a shows the $M(T)$ curves of the LCSM and LTM manganites. It is seen from Fig.1a that the LCSM and LTM manganites show a sharp ferromagnetic (FM)-paramagnetic (PM) magnetic phase transition with increasing temperature. The $M(T)$ curves of the LCSM and LTM manganites show similar tendency with change temperature. Curie temperature (T_c) which is corresponding to the minimum point of $dM/dT-T$ curve [25] has been determined as 286 and 238 K for LCSM and LTM samples, respectively. The $M(T)$ curves of the 0.5LCSM/0.5LTM composite shown in Fig. 1b have two magnetic phase transitions which are in accordance with the LCSM and LTM phase transition. At low temperatures when compared to the magnetization values of the LCSM and LTM manganites, the magnetization value of the composite is smaller than that of individual phases. This decrease caused by interactions between different magnetic phases with different T_c [26].

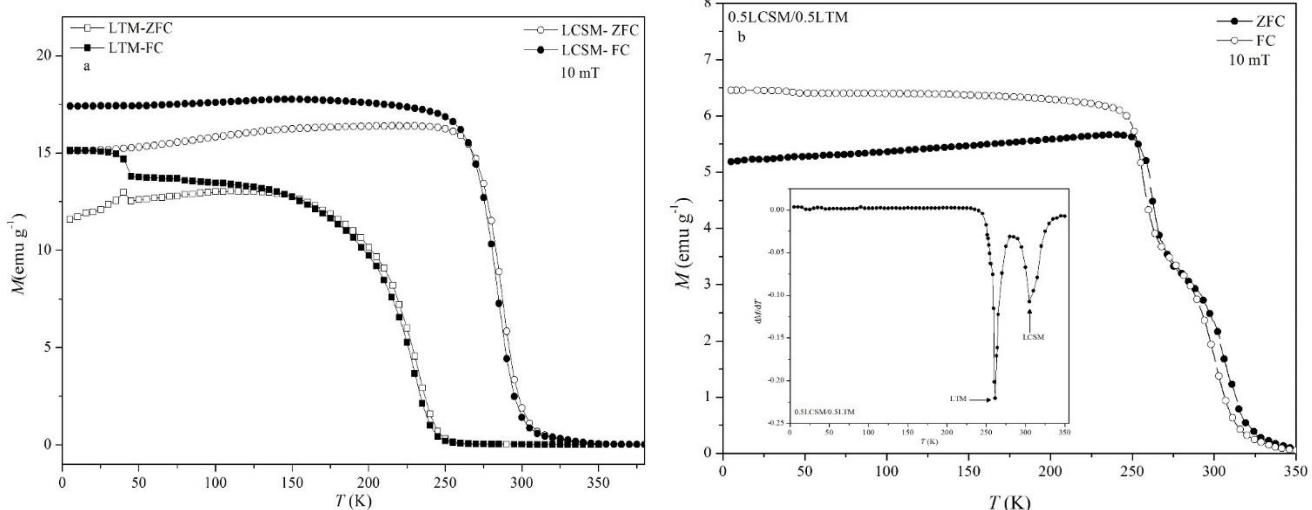


Figure 1a-b. The $M(T)$ curves at ZFC and FC modes under 100 Oe magnetic field for (a) the LCSM and LTM manganites and (b) 0.5LCSM/0.5LTM composite.

In order to obtain further information about the magnetic behavior of the samples and calculate the

magnetic entropy change for the samples, we have performed the $M(H)$ measurements up to 5 T around

T_C . Figure 2 exhibits the $M(H)$ curves of 0.5LCSM/0.5LTM composite in the range 240–352 K temperature. The $M(H)$ curves show a sharp increment with increasing magnetic field at low temperatures while they nearly reach up saturation at higher field values. Also, the $M(H)$ curves exhibit a linear change with increasing magnetic field above T_C . This behavior observed below and above T_C verifies that the samples show PM-FM phase transition.

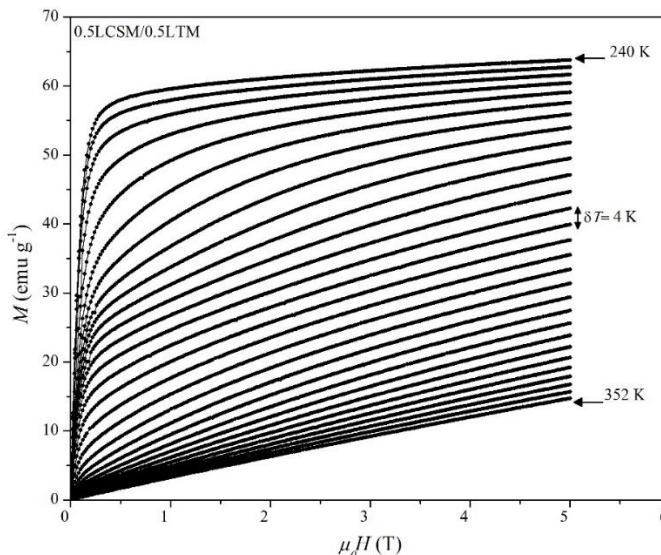


Figure 2. The $M(H)$ curves of the 0.5LCSM/0.5LTM composite.

The nature of the magnetic phase transition is important parameter for defining the usability of the magnetic material to be used in MR systems and it defines the cooling efficiency of a magnetic refrigerant [3]. Even though the ferromagnetic material showing the first-order phase transition presents a large magnetocaloric property around its phase transition temperature, thermal and magnetic hysteresis resulting from this magnetic phase transition affect negatively the usage of this type material as refrigerant material in MR applications [27]. For determination of the nature of the magnetic phase transition, Arrott plots proposed by Banerjee are generally used [28]. If the slope of these plots is negative around magnetic phase transition temperature, the type of magnetic phase transition is the first order. Otherwise, when the slope is positive, the phase transition is second order. To classify the magnetic phase transition for the studied materials, we have constructed the Arrott plots (Figs.3a-c). The Arrott plots of all samples have positive slope around phase transition temperatures. This confirms that FM-PM phase transition is second order for all samples.

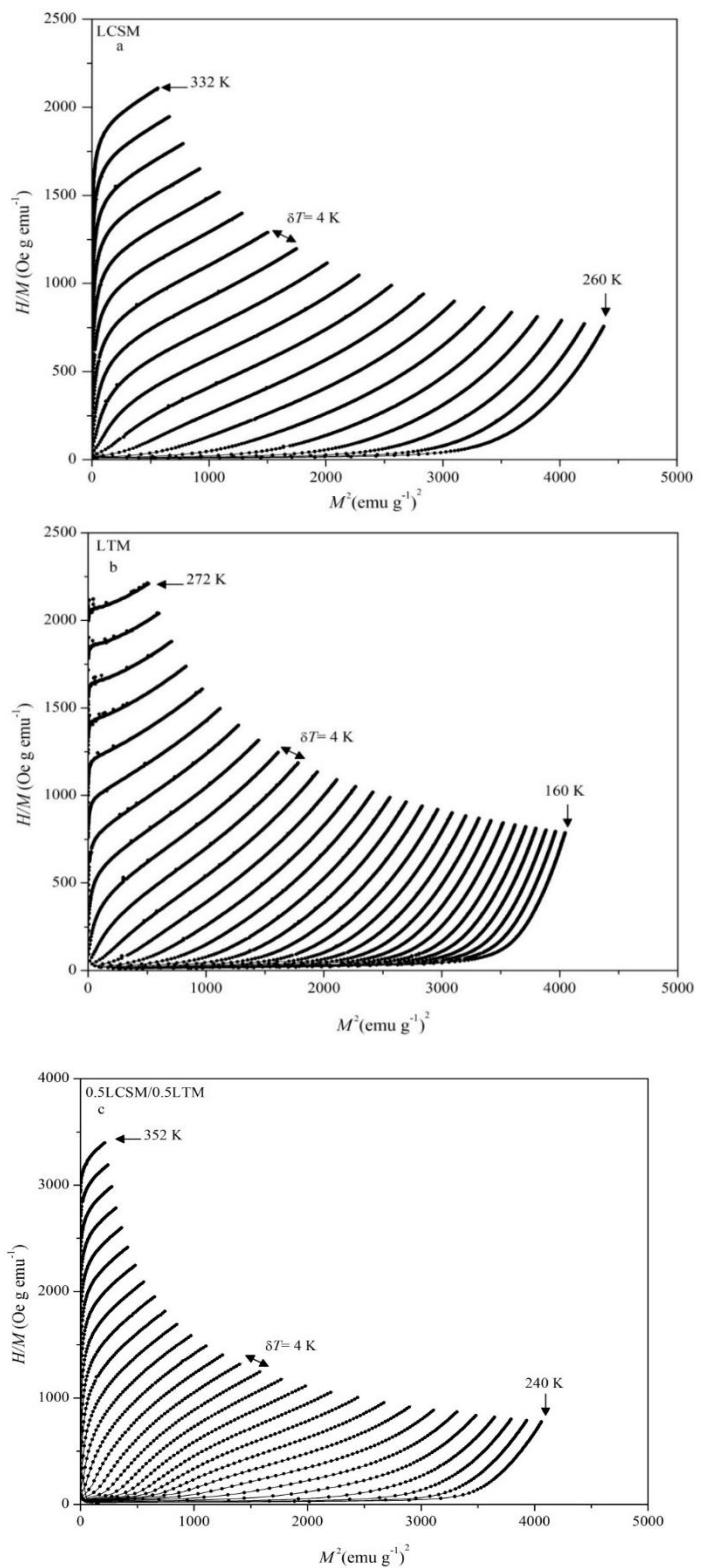


Figure 3a-c. Arrott plots of the studied materials for (a) LCSM, (b) LTM and (c) 0.5LCSM/0.5LTM composite.

Direct and indirect methods are used in the literature to determine the magnetocaloric effect values of a material [29]. But, the indirect methods generally are preferred to determine the magnetocaloric effect value by calculating $-\Delta S_M$ value. From the isothermal

$M(H)$ curve, we have calculated indirectly the $-\Delta S_M$ value by using the following equation:

$$-\Delta S_M(H, T) = \sum \frac{M_i - M_{i+1}}{T_{i+1} - T_i} \Delta H_i. \quad (1)$$

In the Eq. (1), M_i and M_{i+1} terms are the magnetization values at T_i and T_{i+1} temperature, respectively, under a magnetic field of H_i . For LCSM, LTM and 0.5LCSM/0.5LTM samples, the $-\Delta S_M$ values have been calculated at different magnetic field change values depending on temperature and shown in Figs.4a-b. In the $-\Delta S_M(T)$ curves of the LCSM and LTM manganite a maximum peak known as

maximum magnetic entropy change ($-\Delta S_M^{max}$) near T_C has been observed. It is seen that the $(-\Delta S_M^{max})$ values increase with increasing applied magnetic field. For the LCSM and LTM samples, the $-\Delta S_M^{max}$ value has been calculated as 4.96 and 3.68 $\text{Jkg}^{-1}\text{K}^{-1}$ in magnetic field change of 5T. Figure 4c displays the $-\Delta S_M(T)$ curves of 0.5LCSM/0.5LTM composite. It is seen that from this figure that $-\Delta S_M(T)$ curves show two peak shapes. This is due to the fact that the composite comprises two magnetic phases with different magnetic phase transition temperatures [30]. For 0.5LCSM/0.5LTM composite, the $-\Delta S_M^{max}$ value has been calculated as 3.70 $\text{Jkg}^{-1}\text{K}^{-1}$ at 5 T magnetic fields.

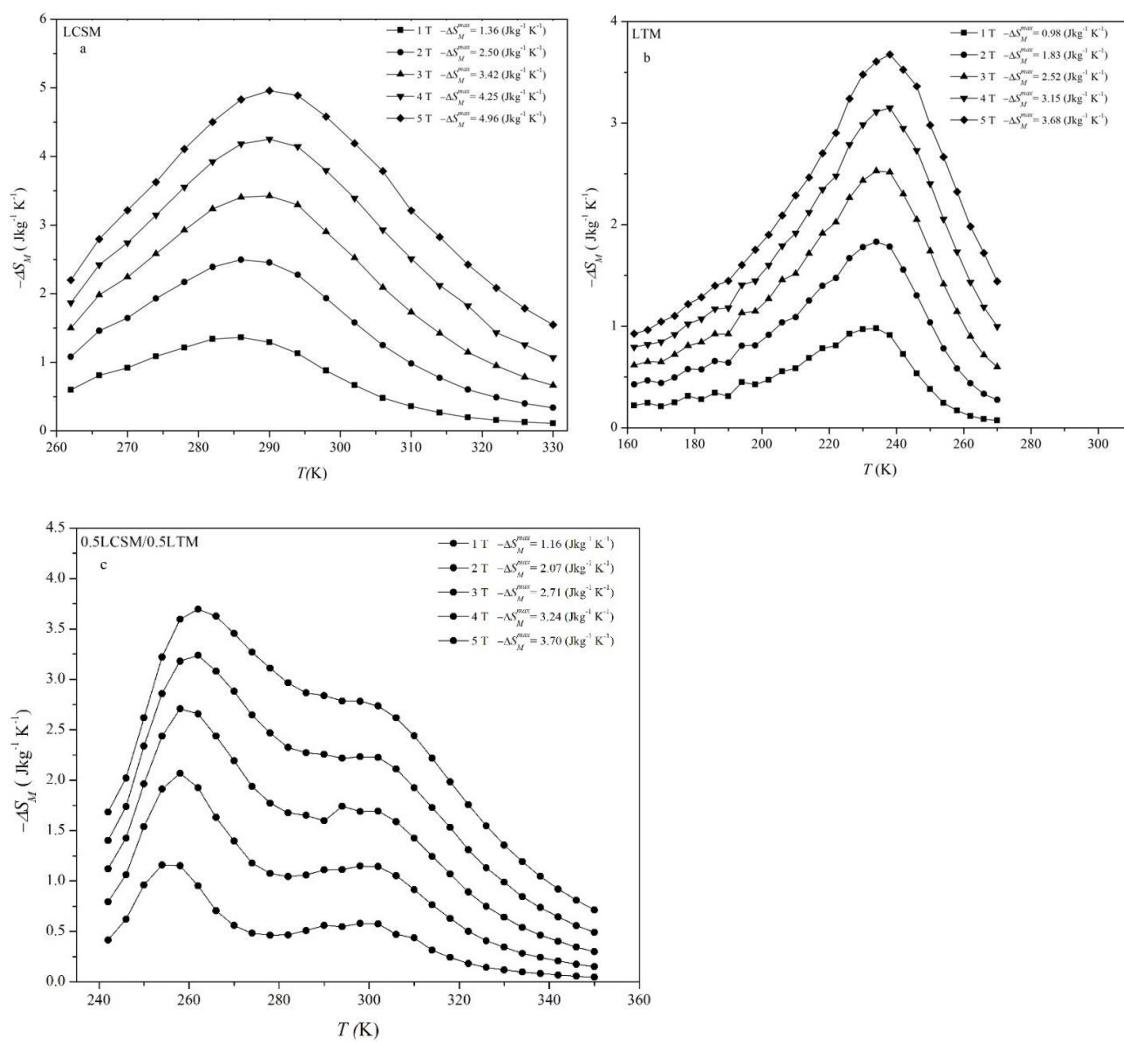


Figure 4a-c. The $-\Delta S_M(T)$ curves of the studied materials under different magnetic fields. (a) For the LCSM, (b) for the LTM, and (c) for the 0.5LCSM/0.5LTM composite

One important parameter in deciding about applicability of magnetic material in MR systems is also Relative Cooling Power (RCP) described as the

amount of heat transferred between hot and cold sink in an ideal refrigeration cycle [31, 32]. RCP values can be calculated from the following equation.

$$RCP = |-\Delta S_M^{max}| \times \delta T_{FWHM}. \quad (2)$$

The δT_{FWHM} term given in Eq.(2) is so-called as the full width at half maximum of the $-\Delta S_M(T)$ curve. We have calculated the RCP values of the LCSM and LTM manganite and 0.5LCSM/0.5LTM composite are 266.4, 235.6 and 282.4 Jkg^{-1} for 5T, respectively. The values display that RCP value of the composite is

increased by 6% and 19% when compared to those of LCSM and LTM manganites. Moreover, the RCP value of the 0.5LCSM/0.5LTM composite is around 68.9% of pure Gd [33]. This result emphasizes that composites have notable advantages for MR applications [34]. Our results obtained in the present work are comparable to several manganites and composites [11, 20-23, 30-32] and the results of our and some samples are summarized in Table 1

Table 1. Comparison of the obtained results with the other perovskite samples and composites reported in the literature.

Sample	$\mu_0 H(\text{T})$	$-\Delta S_M^{max}(\text{Jkg}^{-1}\text{K}^{-1})$	$RCP(\text{Jkg}^{-1})$	Refs.
LCSM	5	4.96	266.40	Present work
LTM	5	3.68	235.59	Present work
0.5LCSM/0.5LTM	5	4.54	223.76	Present work
$\text{La}_{0.65}\text{Ca}_{0.35}\text{MnO}_3/\text{Pr}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$	5	1.8	250.0	[20]
$\text{La}_{1.4}\text{Ca}_{1.6}\text{Mn}_2\text{O}_7-\text{La}_{1.3}\text{Eu}_{0.1}\text{Ca}_{1.6}\text{Mn}_2\text{O}_7$	5	4.07	232.85	[21]
$\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3/\text{La}_{0.8}\text{K}_{0.2}\text{MnO}_3$	5	3.10	217	[33]
0.5La _{0.7} Ca _{0.2} Sr _{0.1} MnO ₃ /0.5 La _{0.7} Ca _{0.15} Sr _{0.15} MnO ₃	5	3.02	245	[34]

Landau theory proposed by Amaral *et al.* [35, 36], interpret the contribution of magnetoelastic interaction between electrons on the magnetic entropy change. The Gibbs free energy state with the following equation;

$$G(M, T) = \frac{a(T)}{2} M^2 + \frac{b(T)}{4} M^4 + \frac{c(T)}{6} M^6 + \dots - \mu_0 H. \quad (3)$$

The terms $a(T)$, $b(T)$ and $c(T)$ in the given Eq.(3) are Landau coefficients. The magnetic equation of state can be written as based on energy minimization:

$$\frac{\partial G}{\partial M} = a(T) + b(T)M^2 + c(T)M^4. \quad (4)$$

From differentiation of the magnetic part of the free energy from the following equation, the $-\Delta S_M$ value of the ferromagnetic materials is calculated theoretically;

$$-\Delta S_M = \left(\frac{\partial G}{\partial T} \right)_H = \frac{1}{2} a'(T)M^2 + \frac{1}{4} b'(T)M^4 + \frac{1}{6} c'(T)M^6. \quad (5)$$

In equation, $a'(T)$, $b'(T)$ and $c'(T)$ parameters are the derivatives of the Landau coefficients. Theoretical $-\Delta S_M$ values have been calculated and the temperature dependencies for 5 T have been represented in Figure 5. According to our findings, the temperature dependence of the theoretical and experimental $-\Delta S_M$ value for LCSM and LTM manganites and the 0.5LCSM/0.5LTM composite are corresponding with each other. This refers that $-\Delta S_M$ and its temperature dependency can change with both the magnetoelastic coupling and electron interaction [37, 38].

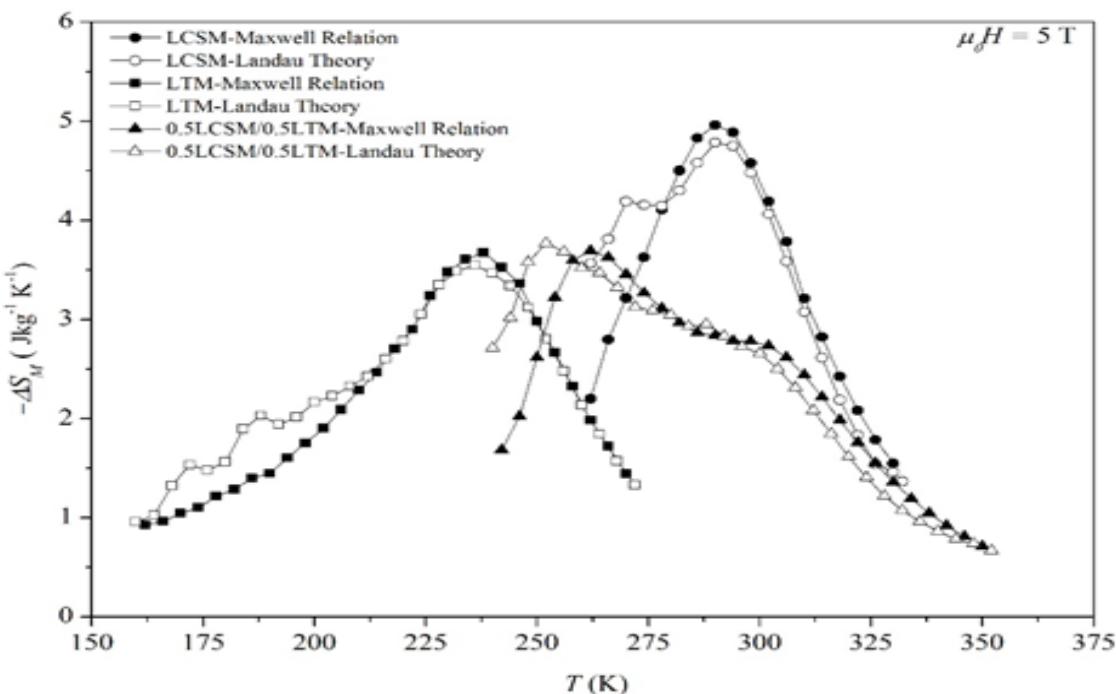


Figure 5. The experimental and theoretical $-\Delta S_M(T)$ curves of the studied materials under magnetic field of 5 T.

4. Conclusion

Summary, the 0.5LCSM/0.5LTM composite has been obtained by the mixture of the LCSM and LTM manganites in the mass ratio of 0.5:0.5. All materials studied in the present work show PM-FM phase transition with decreasing temperature. The magnetic phase transition of the materials has been determined as second order by using Banerjee criterion. The $-\Delta S_M^{max}$ and RCP value for the 0.5LCSM/0.5LTM composite under 5 T magnetic fields have been calculated as $3.70 \text{ J kg}^{-1}\text{K}^{-1}$ and 282.4 J kg^{-1} , respectively. Besides, the $-\Delta S_M^{max}$ values calculated based on Maxwell relation and Landau theory are in agreement with each other. The acceptable magnetocaloric properties of the 0.5LCSM/0.5LTM indicate that this composite may be a candidate cooling material for MR technology.

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