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Influence of non-magnetic and magnetic ions on the MagnetoCaloric properties of La_{0.7}Sr_{0.3}Mn_{0.9}M_{0.1}O_3 doped in the Mn sites by M=Cr, Sn, Ti

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A B S T R A C T

We have studied the MagnetoCaloric Effect (MCE) in La_{0.7}Sr_{0.3}Mn_{0.9}M_{0.1}O_3, M=Cr, Sn and Ti, prepared by a conventional solid state reaction. The temperature dependence of magnetization reveals that all compositions exhibit a ferromagnetic (FM) to paramagnetic (PM) transition at T_C temperatures of 369, 326, 228 and 210 K, respectively for La_{0.7}Sr_{0.3}MnO_3 (LSMO), La_{0.7}Sr_{0.3}Mn_{0.9}Cr_{0.1}O_3 (LSMO-Cr), La_{0.7}Sr_{0.3}Mn_{0.9}Sn_{0.1}O_3 (LSMO-Sn), and La_{0.7}Sr_{0.3}Mn_{0.9}Ti_{0.1}O_3 (LSMO-Ti). Using Arrott plots, the phase transition from FM to PM is found to be of second order. The maximum magnetic entropy change (−ΔS_M), at the applied magnetic field of 2 T, is found to be 1.27, 1.76, 0.47 and 1.45 J kg\(^{-1}\) K\(^{-1}\), respectively for LSMO, LSMO-Cr, LSMO-Sn and LSMO-Ti. The relative cooling power (RCP) for LSMO-Cr, LSMO-Sn and LSMO-Ti is in the order of 50%, 26% and 71%, respectively, compared to gadolinium (Gd).

As a result, the LSMO-Cr and LSMO-Ti compounds can be considered as promising materials in magnetic refrigeration technology.

1. Introduction

In recent years, magnetic refrigeration has received considerable attention because it is considered to be more energy-efficient and environmentally friendlier compared to the conventional refrigeration based on the compression-expansion of greenhouse gases, CFC (ChloroFluoroCarbons) and HCFC (Hydro-ChloroFluoroCarbons) [1,2]. The renewed interest in MagnetoCaloric materials is partly due to the discovery of a giant magnetic entropy change in Gd_{2}Si_{2}Ge_{2} and Gd alloys in the late 1990s and early 2000s [3–5]. The magnetic refrigeration is based on the MagnetoCaloric Effect (MCE) [6], which depends on the fact that the spin entropy of a magnetic material decreases upon application of an external magnetic field and this reduction in magnetic entropy is compensated by an increase in the lattice entropy resulting in an increase in the temperature of the sample. Conversely, when the magnetic field is removed adiabatically, magnetic spins tend to randomize which leads to an increase in the magnetic entropy and a decrease in the lattice entropy and hence lowering the temperature of the sample.

In this context, gadolinium (Gd) is the reference material for magnetic refrigeration at room temperature. This is the first material that has validated the principle of magnetic refrigeration at room temperature, and it is still used to test prototypes with a Curie temperature (T_C = 293 K) close to room temperature [7]. However, because of its very expensive price and limited resources, the studies on manganite-based materials have been accelerated these last years. Among these materials, perovskites of general formula R \(_{1}\)\_A\_MnO\(_{3}\) (R – rare-earth, A – alkali earth) have been studied in detail due to their interesting magnetic properties [8,9]. Among them, La\(_{1}\_x\)Sr\(_{x}\)MnO\(_{3}\) compounds are given particular attention because of their interesting magnetic properties such as Colossal MagnetoResistance (CMR) and MCE [10,11]. In addition, the presence of Mn\(^{2+}\) and Mn\(^{4+}\) cations (promoted by the inclusion of divalent cations such as Sr\(^{2+}\)) induces mobile holes in the e\(_{g}\) band near the Fermi energy, which affect the electronic conduction and the SuperExchange (SE) interaction. The SE interaction causes antiferromagnetic (AFM) coupling between magnetic moments in manganites and thus, moderate-to-low values for the magnetic moment per unit formula. This AFM ordering can be progressively suppressed by the increment of the number of Mn\(^{3+}\)–Mn\(^{4+}\) pairs, which favors the Double Exchange (DE) interaction and hence, the enhancement of the magnetic moment and Curie temperature (T_C). On the other hand, doping at the Mn-site is of great importance in modifying the DE strength between Mn\(^{3+}\) and Mn\(^{4+}\) via oxygen. This alters the magnetic and MagnetoCaloric behavior in doped manganites.

La\(_{0.7}\)Sr\(_{0.3}\)MnO\(_{3}\) (LSMO) is one of the extensively studied manganites which undergoes a paramagnetic (PM) to a ferromagnetic...
(FM) transition above room temperature. The ferromagnetic transition of this compound can be brought down to room temperature either by partial replacement of La$^{3+}$, of big ionic size, by Pr$^{3+}$ or Nd$^{3+}$, of smaller size, or by partial substitution of Mn ions by other transition metals such as Mn = Cr, Ni, Cu, Fe, Zn, Co, Al, etc. [12–22]. The influence of substitution of magnetic and non-magnetic elements at Mn-site on the MCE has been reported in the literature [23–25].

In this work, we present the MCE of La$_{0.7}$Sr$_{0.3}$Mn$_{0.9}$M$_{0.1}$O$_{3}$ manganites substituted at the Mn site by Mn = Cr, Sn and Ti. The Cr substitution deserves particular attention due to the magnetic nature of the Cr ion compared to non-magnetic Sn and Ti ions. It is noticed that both Sn$^{4+}$ ([Ar]3d$^{10}$5s$^{2}$5p$^{0}$) and Ti$^{4+}$ ([Ar]3d$^{2}$4s$^{0}$) are bigger than Mn$^{4+}$ (r$_{Mn}^{2+}$ = 0.530 Å, r$_{Sn}^{2+}$ = 0.690 Å and r$_{Ti}^{2+}$ = 0.605 Å), whereas Cr$^{3+}$ (3d$^{4}$4s$^{0}$ = $t_{2g}^{2}$e$_{g}^{0}$) is smaller than Mn$^{3+}$ (r$_{Mn}^{3+}$ = 0.650 Å and r$_{Cr}^{3+}$ = 0.615 Å).

2. Experimental

La$_{0.7}$Sr$_{0.3}$Mn$_{0.9}$M$_{0.1}$O$_{3}$ (M = Cr, Sn and Ti) polycrystalline compounds were prepared by a conventional solid-state reaction method in air. Magnetization (M) versus temperature (T) and magnetization versus magnetic field (μ0H) were measured using a Quantum Design MPMS-XL5 SQUID magnetometer. Isothermal M(μ0H) data were measured at different temperatures and an applied magnetic field varying from 0 to 5 T.

3. Results and discussion

3.1. Structural characteristics

Identification of the phase and structural analysis by X-ray diffraction technique are reported elsewhere [26–28]. These results show that the compounds La$_{0.7}$Sr$_{0.3}$Mn$_{0.9}$M$_{0.1}$O$_{3}$ (M = Cr, Sn, Ti) crystallize in the rhombohedral system with the $R$$3$$c$ space group. Lattice parameters and unit cell volumes are listed in Table 1.

3.2. Magnetic properties

The temperature dependence of magnetization M(T) for La$_{0.7}$Sr$_{0.3}$Mn$_{0.9}$O$_{3}$ (LSMO), La$_{0.7}$Sr$_{0.3}$Mn$_{0.9}$Cr$_{0.1}$O$_{3}$ (LSMO-Cr), La$_{0.7}$Sr$_{0.3}$Mn$_{0.9}$Sn$_{0.1}$O$_{3}$ (LSMO-Sn) and La$_{0.7}$Sr$_{0.3}$Mn$_{0.9}$Ti$_{0.1}$O$_{3}$ (LSMO-Ti) samples, measured under an applied magnetic field of 0.05 T, is shown in Fig. 1. All compositions exhibit a FM to PM transition at approximately 369, 326, 228 and 210 K, respectively for LSMO, LSMO-Cr, LSMO-Sn and LSMO-Ti. The inset indicates the dM/dT curve used to determine Tc.

The inset indicates the dM/dT curve used to determine Tc.

![Graph showing dM/dT curve](image-url)

**Table 1**

<table>
<thead>
<tr>
<th></th>
<th>LSMO</th>
<th>LSMO-Cr</th>
<th>LSMO-Sn</th>
<th>LSMO-Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice parameters (Å)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>5.5023</td>
<td>5.5018</td>
<td>5.5437</td>
<td>5.5255</td>
</tr>
<tr>
<td>Volume (Å$^3$)</td>
<td>350.210</td>
<td>349.80</td>
<td>357.340</td>
<td>354.040</td>
</tr>
<tr>
<td>(Mn, M)–O–(Mn, M)</td>
<td>165.60</td>
<td>166.470</td>
<td>164.960</td>
<td>166.360</td>
</tr>
<tr>
<td>W (a.u.)</td>
<td>0.0958</td>
<td>0.0955</td>
<td>0.0923</td>
<td>0.0940</td>
</tr>
</tbody>
</table>
we obtain

\[ \frac{\mu_0 H}{M} = A(T) + B(T)M^2 \]  

(2)

In order to get a deeper insight of the nature of magnetic phase transition, Arrott plots (\(\mu_0 H/M\) versus \(M^2\)) are shown in Fig. 3 for the LSMO-Cr compound. According to Banerjee’s criterion [35], a negative or positive sign of the slope of Arrott curves corresponds to a first-order or second-order magnetic phase transition, respectively. The results obtained from \(\mu_0 H/M\) versus \(M^2\) plots of all compounds studied in this work, LSMO, LSMO-Cr, LSMO-Sn and LSMO-Ti, show that a positive slope in all cases in the complete \(M^2\) range, confirming that a second-order FM to PM phase transition has occurred.

Thus, the temperature dependence of parameter \(A\), Eq. (2), can be extracted from the linear region of Arrott plots (Fig. 3), as shown in Fig. 4. It is found that parameter \(A\) varies from negative to positive with increasing temperature. It is noticed that the temperature corresponding to the intercept (zero-value of parameter \(A\)) correlates well with the value of the transition temperature \(T_C\).

Fig. 4. Temperature dependence of coefficient \(A\) for LSMO, LSMO-Cr, LSMO-Sn and LSMO-Ti deduced from the Arrott plots, using Eq. (2).

\[ \Delta S_{SM}(T,\mu_0 H) = S(T,\mu_0 H) - S(T, 0) = \int_0^{\mu_0 H} \left( \frac{\partial M}{\partial T} \right)_H \mu_0 dH \]  

(3)

where \(\mu_0 H\) is the external magnetic field.

In order to evaluate the magnetic entropy change (\(\Delta S_{SM}\)), one needs to make a numerical approximation for the integral in Eq. (3). The method consists of using the magnetization curves at various temperatures. Then, for given intervals of temperature \((\Delta T = T_2 - T_1)\), the magnetization measurements at small discrete fields lead to a magnetic entropy change \(\Delta S_{SM}\) approximated by

\[ \Delta S_{SM} \left( \frac{T_1 + T_2}{2} \right) = \frac{1}{T_2 - T_1} \left[ \int_0^{\mu_0 H} M(T_2,\mu_0 H)\mu_0 dH - \int_0^{\mu_0 H} M(T_1,\mu_0 H)\mu_0 dH \right] \]  

(4)

Fig. 5 shows the temperature dependence of the magnetic entropy change (\(-\Delta S_{SM}\)) at various intervals of the applied field from \(\mu_0 H\) of 1 T to 5 T, for LSMO, LSMO-Cr, LSMO-Sn and LSMO-Ti. It is clear that the magnetic entropy change depends on the magnetic field interval; also the largest changes in magnetic entropy take place near \(T_C\), which is a property of simple ferromagnets due to the efficient ordering of magnetic moments induced by the magnetic field at the ordering temperature. For each composition, the peak position is nearly unaffected because of the second-order nature of the FM–PM transition for these compounds. These peaks are situated at about 364 K, 325 K, 229 K and 212 K, respectively for LSMO, LSMO-Cr, LSMO-Sn and LSMO-Ti. Under a variation in the applied magnetic field \(\mu_0 H\) of 2 T, the \(\Delta S_{SM}^{max}\) values are on the order of 1.27, 1.76, 0.47 and 1.45 J kg\(^{-1}\) K\(^{-1}\), respectively for LSMO, LSMO-Cr, LSMO-Sn and LSMO-Ti.

In Table 1 we have compared the MCE of Cr, Sn and Ti with other B-site multi-element doping effect like Al, Co, Ni and Fe in \(La_{0.7}Sr_{0.3}Mn_{1-x}M_{x}O_3\) system. Phan et al. [15] studied MCE in \(La_{0.7}Sr_{0.3}Mn_{0.88}Ni_{0.12}O_3\) and found a maximum entropy change of...
2.25 J kg\(^{-1}\) K\(^{-1}\) under \(\mu_0 \Delta H = 1\) T. A large MCE \((\Delta S_M = 5.51\) J kg\(^{-1}\) K\(^{-1}\) under \(\mu_0 \Delta H = 1.5\) T) was found in La\(_{0.7}\)Sr\(_{0.3}\)Mn\(_{0.9}\)Cu\(_{0.1}\)O\(_3\) [17]. In the series La\(_{0.8}\)Sr\(_{0.2}\)Mn\(_{1-x}\)M\(_x\)O\(_3\) \((M = \text{Mn, Cu, and Co})\), the largest MCE \((\Delta S_M = 2.67\) J kg\(^{-1}\) K\(^{-1}\) under \(\mu_0 \Delta H = 1.35\) T) was also found for \(x = 0.1\) of Cu [20]. All these studies indicate that the large MCE in the perovskite manganites can originate from the spin–lattice coupling related to the magnetic ordering process [38,39]. This strong coupling is evidenced by the lattice changes accompanying the magnetic transitions in these manganites; the lattice structural change in \((\text{Mn, M})-\text{O}\) bond distances and \((\text{Mn}, \text{M})-\text{O}\) bond angles with temperature, which results in a variation of the volume, can cause an additional change in the magnetic properties of the material [40].

The influence of structural changes on the magnetism and MCE in these systems is related to the electronic bandwidth \(W\) [41] (see Table 1). The decrease in the values of \(W\) with different elements doping reduces the double-exchange (DE) interaction. The empirical formula of bandwidth \(W\) for ABO\(_3\)-type perovskites using the tight binding approach [42] is \(W \propto \cos \theta /d_{\text{Mn-O}}\), where \(\theta = (1/2) (\pi - (\text{Mn-O-Mn}))\) and \(d_{\text{Mn-O}}\) is the Mn–O length. The decrease in bandwidth \(W\) reduces the overlap between the O 2p and the Mn 3d orbital, which in turn decreases the exchange coupling of Mn\(^{3+}\)-Mn\(^{4+}\) resulting in a decrease in the magnetic ordering [43,44].

On the other hand, the oxygen deficiency could play an important role in the physical properties of this kind of materials, especially the structural transition that may appear in the magnetic, MCE and electrical properties [45,46].

The change of specific heat \((\Delta C_p)\) associated with a magnetic field variation from 0 to \(\mu_0 H\) is given by [47,48]

\[
\Delta C_p(T, \mu_0 H) = C_p(T, 0) - C_p(T, \mu_0 H) = \frac{T \Delta S_M(T, \mu_0 H)}{\Delta T} \cdot (5)
\]

Using Eq. (5), \(\Delta C_p\) of all samples versus temperature under different variations of the applied magnetic field \(\mu_0 H\) is displayed in Fig. 6. Here, we can see that \(\Delta C_p\) undergoes a sudden change of sign around \(T_c\) with a positive value above \(T_c\) and a negative value below \(T_c\). In addition, the maximum/minimum values of \(\Delta C_p\) exhibit an increasing trend with the applied field and are observed at temperatures 385/350, 337/317, 242/169 and 230/190 K, respectively for LSMO, LSMO-Cr, LSMO-Sn and LSMO-Ti. The values of \(\Delta C_p^{\text{max}}/\Delta C_p^{\text{min}}\) under the applied magnetic field of 2 T are listed in Table 2.

Generally, an important criterion for selecting magnetic refrigerants is the cooling power per unit volume, namely, the relative cooling power RCP [1,49,50], which corresponds to the amount of heat transferred between the cold and the hot sinks in the ideal refrigeration cycle. RCP has been defined as

\[
\text{RCP} = \left| \Delta S_M \right| \times \delta T_{\text{FWHM}}
\]

where \(\left| \Delta S_M \right|\) is the maximum entropy change at \(T_c\) and is equal to \(\delta T_{\text{FWHM}} = (T_2 - T_1)\), the full-width temperature span of the \(\left| -\Delta S_M \right|\) versus temperature plots at their half-maxima.

The magnetic field dependence of the RCP is shown in Fig. 7. RCP values increase linearly with the applied magnetic field \(\mu_0 H\). RCP values under an applied field of 2 T are about 29, 74, 40 and 113 J kg\(^{-1}\), respectively for LSMO, LSMO-Cr, LSMO-Sn and LSMO-Ti samples. To evaluate the applicability of LSMO-Cr, LSMO-Sn and LSMO-Ti compounds as magnetic refrigerants, the values of \(\Delta C_p^{\text{max}}\) and RCP obtained in our study were compared with those reported in the literature for several other magnetic materials (Table 2). For LSMO-Cr, LSMO-Sn and LSMO-Ti our values are in the order of 50%, 26% and 71% compared with gadolinium (Gd), while they are quite comparable to those reported for other manganites (Table 2). Hence, LSMO-Cr and LSMO-Ti compounds, in particular, are suitable candidates to be used in magnetic refrigeration; among these two, the value of RCP for LSMO-Ti is higher than the one for LSMO-Cr, the Curie temperature for the
Numerous works have been done concerning the field dependence of the magnetic entropy change \(\Delta S_M\) of manganites at the FM–PM transition \(T_c\). According to Oesterreicher et al. \cite{51}, the magnetic field dependence of the magnetic entropy change \(\Delta S_M\) at a temperature \(T\) for materials obeying a second-order phase transition follows an exponent power law of the type
\[
\Delta S_M(H) = a(\mu_0H)^n
\]
where \(a\) is a constant and the \(n\) exponent depends on the magnetic state of the sample. In a mean field approach, the value of \(n\) at the Curie temperature is predicted to be 2/3 \cite{51}. It is well known that in manganites the exponent is roughly field-independent and approaches approximate values of 1 and 2, far below and above the transition temperature, respectively \cite{52}.

By fitting the data of \(\Delta S_M\) versus \(\mu_0H\) to Eq. \(7\), we obtain the value of \(n\) as a function of temperature, as depicted on a log–log scale in Fig. \(8\). The \(n\) exponent is close to 1 in the FM regime and increases to 2 in the PM region. The \(n\) exponent exhibits a moderate decrease with increasing temperature, with a minimum value in the vicinity of the transition temperature, sharply increasing above \(T_c\). The \(n\) values around \(T_c\) are 0.556, 0.654, 0.794, and 0.807, respectively for LSMO, LSMO-Cr, LSMO-Sn and LSMO-Ti. These values are similar to those obtained for soft magnetic alloys, gadolinium (Gd) and other magnetic materials containing rare earth metals \cite{52–56}.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(T_c) (K)</th>
<th>(\Delta S_M^{max}) (J kg(^{-1}) K(^{-1}))</th>
<th>(\frac{\Delta S_M^{max}}{\Delta S_M^{min}}) (J kg(^{-1}) K(^{-1}))</th>
<th>RCP (J kg(^{-1}) K(^{-1}))</th>
<th>(\mu_0\Delta M) (T)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>La(<em>{0.7})Sr(</em>{0.3})MnO(_3) (LSMO)</td>
<td>369</td>
<td>1.27</td>
<td>15.4/−10.6</td>
<td>29</td>
<td>2</td>
<td>This work</td>
</tr>
<tr>
<td>La(<em>{0.7})Sr(</em>{0.3})Mn(<em>{0.9})Fe(</em>{0.1})O(_3)</td>
<td>326</td>
<td>1.76</td>
<td>21.5/−11.4</td>
<td>74</td>
<td>2</td>
<td>This work</td>
</tr>
<tr>
<td>La(<em>{0.7})Sr(</em>{0.3})Mn(<em>{0.9})Sn(</em>{0.1})O(_3) (LSMO-Sn)</td>
<td>228</td>
<td>0.47</td>
<td>1.82/−0.72</td>
<td>40</td>
<td>2</td>
<td>This work</td>
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<tr>
<td>La(<em>{0.7})Sr(</em>{0.3})Mn(<em>{0.9})Co(</em>{0.1})O(_3)</td>
<td>210</td>
<td>1.49</td>
<td>6.2/−4.2</td>
<td>113</td>
<td>2</td>
<td>This work</td>
</tr>
<tr>
<td>La(<em>{0.7})Sr(</em>{0.3})Mn(<em>{0.9})Al(</em>{0.1})O(_3)</td>
<td>370</td>
<td>1.53</td>
<td>40.5/−18.7</td>
<td>42</td>
<td>1</td>
<td>[47]</td>
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<tr>
<td>La(<em>{0.7})Sr(</em>{0.3})Mn(<em>{0.9})Ga(</em>{0.1})O(_3)</td>
<td>267</td>
<td>0.91</td>
<td>13.2/−5.2</td>
<td>35</td>
<td>1.10</td>
<td>[48]</td>
</tr>
<tr>
<td>La(<em>{0.7})Sr(</em>{0.3})Mn(<em>{0.9})Sn(</em>{0.1})Ga(_{0.1})O(_3)</td>
<td>301</td>
<td>2.2</td>
<td>–</td>
<td>90</td>
<td>2</td>
<td>[22]</td>
</tr>
<tr>
<td>La(<em>{0.7})Sr(</em>{0.3})Mn(<em>{0.9})Al(</em>{0.1})O(_3)</td>
<td>310</td>
<td>0.67</td>
<td>–</td>
<td>51</td>
<td>1</td>
<td>[22]</td>
</tr>
<tr>
<td>La(<em>{0.7})Sr(</em>{0.3})Mn(<em>{0.9})Fe(</em>{0.1})O(_3)</td>
<td>260</td>
<td>1.7</td>
<td>–</td>
<td>83</td>
<td>2</td>
<td>[21]</td>
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<tr>
<td>La(<em>{0.7})Sr(</em>{0.3})Mn(<em>{0.9})Cu(</em>{0.1})O(_3)</td>
<td>348</td>
<td>5.51</td>
<td>–</td>
<td>1.5</td>
<td>[17]</td>
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</tr>
<tr>
<td>La(<em>{0.7})Sr(</em>{0.3})Mn(<em>{0.9})Sn(</em>{0.1})O(_3)</td>
<td>328</td>
<td>5</td>
<td>–</td>
<td>5</td>
<td>[30]</td>
<td></td>
</tr>
<tr>
<td>La(<em>{0.7})Sr(</em>{0.3})Mn(<em>{0.9})Sn(</em>{0.1})O(_3)</td>
<td>350</td>
<td>2.25</td>
<td>–</td>
<td>1</td>
<td>[15]</td>
<td></td>
</tr>
<tr>
<td>La(<em>{0.7})Sr(</em>{0.3})Mn(<em>{0.9})Sn(</em>{0.1})Sn(_{0.1})O(_3)</td>
<td>220</td>
<td>2.60</td>
<td>–</td>
<td>1.35</td>
<td>[20]</td>
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<tr>
<td>La(<em>{0.7})Sr(</em>{0.3})Mn(<em>{0.9})Sn(</em>{0.1})Sn(_{0.1})O(_3)</td>
<td>267</td>
<td>2.67</td>
<td>–</td>
<td>1.35</td>
<td>[20]</td>
<td></td>
</tr>
<tr>
<td>La(<em>{0.7})Sr(</em>{0.3})Mn(<em>{0.9})Sn(</em>{0.1})Sn(_{0.1})O(_3)</td>
<td>293</td>
<td>5</td>
<td>–</td>
<td>153</td>
<td>2</td>
<td>[7]</td>
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</table>

Fig. 6. Temperature dependence of the specific heat \(\Delta C_p\) as evaluated from Eq. \((5)\), under given variations of the applied magnetic field \((\mu_0H)\) for LSMO, LSMO-Cr, LSMO-Sn and LSMO-Ti.
4. Conclusions

We have studied the MagnetoCaloric Effect (MCE) in La$_{0.7}$Sr$_{0.3}$MnO$_3$ (LSMO) manganites partly substituted at the Mn site by 10 at\% of Cr, Sn and Ti. LSMO, LSMO-Cr, LSMO-Sn and LSMO-Ti prepared by standard solid-state reaction methods. Magnetic measurements show that all compounds exhibit a FM–PM second order transition. A large MCE is observed near $T_C$. The maximum of the magnetic entropy change ($\Delta S_m$ observed for LSMO-Cr, LSMO-Sn and LSMO-Ti is found to be 1.27, 1.76, 0.47 and 1.45 J kg$^{-1}$ K$^{-1}$, respectively, under a magnetic field change ($\mu_0\Delta H$) of 2 T. The relative cooling power (RCP) for LSMO-Cr, LSMO-Sn and LSMO-Ti is on the order of 50%, 26% and 71%, respectively, compared to gadolinium (Gd). Our results indicate that both LSMO compounds substituted with Ti and Cr constitute potential candidates for magnetic refrigeration, with a relatively large change in entropy. The field dependence of the magnetic entropy variation shows a power law dependence ($\Delta S_m \propto (\mu_0\Delta H)^n$), with $n = 0.556$, 0.654, 0.794 and 0.706, respectively for LSMO, LSMO-Cr, LSMO-Sn and LSMO-Ti.

References