Investigation of magnetocaloric effect in La$_{0.67}$Sr$_{0.33}$Mn$_{1-x}$Zr$_x$O$_3$

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Abstract. The influence of Zr-doping on the magnetocaloric effect of La$_{0.67}$Sr$_{0.33}$Mn$_{1-x}$Zr$_x$O$_3$ manganese perovskites in low magnetic field has been investigated. Using Hamad’s phenomenological model, we have estimated the important magnetocaloric properties, for example, the thermal magnetization, the change of magnetic entropy and the relative cooling power. We have shown that the magnetocaloric properties decrease as the increase of the dopant amount. Tunable magnetocaloric effect in these compounds is advantageous to magnetic refrigeration applications in wide temperature ranges. Therefore, these compounds are good candidates for working materials in magnetic refrigeration.

1. Introduction

Emerging technology of magnetic refrigeration exploiting the magnetocaloric effect (MCE) has received great interest, because of its great potential, inexpensive and environmentally friendly features compared with those of current refrigeration technology which uses greenhouse gases that are ozone-depleting and global warming [1–3].

The (La, A)MnO$_3$ manganese perovskites (A = Ca, Sr, and Ba) are considered as potential candidates for magnetic refrigeration. Especially, a series of La$_{1-x}$Sr$_x$MnO$_3$ magnetic perovskites has the rich physics and the technological applications such as the large colossal magnetoresistance effect and the MCE [4, 5]. Moreover, these magnetic perovskites are cheaper and more chemically stable than Gd metal which is the paradigmatic material for near-room-temperature magnetic refrigeration. This is the reason why many researchers have made enormous efforts in the past years to study the MCE in La$_{1-x}$Sr$_x$MnO$_3$ manganites. The Curie temperature ($T_C$) in this series, however, is too far from room temperature. In order to exploit the magnetocaloric effect in wide temperature ranges, it is necessary to tune the Curie temperature of this series to near and above room temperature by doping in the A- or the B-site. Characterization and enhancement of the MCE in magnetic materials are crucial for realization of great potential and environmentally friendly magnetic refrigeration.

In this work, theoretical investigation of magnetization variation with temperature for La$_{0.67}$Sr$_{0.33}$Mn$_{1-x}$Zr$_x$O$_3$ compounds in 1T magnetic field is presented. Hamad’s model [6] is applied for simulation of magnetization variation with temperature to estimate the magnetocaloric effect in the Zr-doped La$_{0.67}$Sr$_{0.33}$Mn$_{1-x}$Zr$_x$O$_3$ compounds. The advantage of this phenomenological model is that the only measurement of the magnetization variation with temperature in the applied magnetic field is...
necessary for the theoretical investigation of the MCE in the magnetocaloric materials. And the validity of this model has already been confirmed by many researchers.

2. Phenomenological model

By Hamad’s phenomenological model, the variation of magnetization with temperature is written as:

$$M = \left(\frac{M_i - M_f}{2}\right) \left(\tanh(A(T - T_C))\right) + BT + C.$$  

(1)

Here:

$$A = \frac{2(B - S_c)}{M_i - M_f}, \quad C = \frac{(M_i + M_f)}{2} - BT_C.$$  

(2)

As depicted in figure 1, $M_i$ and $M_f$ are magnetization values at initial and final states of the magnetic phase transition process, respectively.

![Figure 1. Variation of magnetization with temperature in magnetic field.](image)

$S_c$ and $B$ are the temperature derivatives of the magnetization $\frac{dM}{dT}$ at $T_C$ and the ferromagnetic state before magnetic phase transition, respectively.

The change in magnetic entropy ($\Delta S_M$) of the magnetic materials in the magnetic field is calculated using Maxwell’s relations:

$$\Delta S_M = \int_{0}^{H_{max}} \left(\tanh(\frac{M_i - M_f}{2})\right) \frac{\partial M}{\partial T} dH,$$

(3)

From equations (1) and (3),

$$\Delta S_M = \left\{ -A \left(\frac{M_i - M_f}{2}\right) \sec^2 (A(T - T_C)) + B \right\} H_{max}.$$  

(4)

Maximum change in magnetic entropy is given from equations (4) as follows:

$$\Delta S_{max} = H_{max} \left\{ -A \left(\frac{M_i - M_f}{2}\right) + B \right\}.$$  

(5)

As it is seen from equation (5), the maximum change of magnetic entropy ($-\Delta S_{max}$) increases with increasing of the magnetic field. The full-width at half-maximum ($\delta T_{FWHM}$), which is another important property of the $\Delta S_M$ to estimate the magnetic cooling efficiency, is given by

$$\delta T_{FWHM} = \frac{2}{A} \cosh^{-1} \left(\sqrt{\frac{2A(M_i - M_f)}{A(M_i - M_f) + 2B}}\right).$$  

(6)
A relative cooling power (RCP) of the magnetocaloric materials is a product of \(-\Delta S_{\text{max}}\) and \(\delta T_{\text{FWHM}}\) and it is given by
\[
RCP = -\Delta S_{\text{max}} \times \delta T_{\text{FWHM}} = \left( M_i - M_f - \frac{2B}{A} \right) H_{\text{max}} \times \cosh^{-1} \left( \frac{2A(M_i - M_f)}{A(M_i - M_f) + 2B} \right). \tag{7}
\]

The specific heat change related with magnetization is given by
\[
\Delta C_{\text{P},H} = T \frac{\delta \Delta S_{\text{M}}}{\delta T}. \tag{8}
\]

From equations (4) and (8), \(\Delta C_{\text{P},H}\) can be calculated as follows:
\[
\Delta C_{\text{P},H} = -TA^2(M_i - M_f)\sech^2(A(T_c - T))\times \tanh(A(T_c - T))H_{\text{max}}. \tag{9}
\]

Thus, the values of important properties for magnetocaloric materials can be easily calculated using Hamad’s phenomenological model.

### 3. Results and discussion

To adopt the phenomenological model in simulation of magnetization versus temperature, the parameters versus dopant amount were determined as shown in table 1. Variation of magnetization with temperature for \(\text{La}_{0.67}\text{Sr}_{0.33}\text{Mn}_{1-x}\text{Zr}_x\text{O}_3\) compounds in 1T magnetic field is shown in figure 2. The solid lines denote simulation curves generated by equation (1) using the model parameters, while the symbols denote the experimental data from [4]. This figure shows that experimental and simulated data are in agreement.

| Table 1. Parameters for \(\text{La}_{0.67}\text{Sr}_{0.33}\text{Mn}_{1-x}\text{Zr}_x\text{O}_3\) compounds in 1T magnetic field. |
|---|---|---|---|---|---|
| \(x\) | \(M_i\) (emu•g\(^{-1}\)) | \(M_f\) (emu•g\(^{-1}\)) | \(A\) (K\(^{-1}\)) | \(B\) (emu•g\(^{-1}\)•K\(^{-1}\)) | \(T_c\) (K) |
| 0 | 0.11 | 73.23 | 0.055 | -0.035 | 341 |
| 0.02 | 0.31 | 68.06 | 0.038 | -0.030 | 293 |
| 0.04 | 0.42 | 67.86 | 0.033 | -0.030 | 278 |

The change of magnetic entropy, \(\Delta S_{\text{M}}\) is one of the important parameters for estimation of the MCE. In order to understand the influence of Zr doping on the \(\Delta S_{\text{M}}\) in \(\text{La}_{0.67}\text{Sr}_{0.33}\text{Mn}_{1-x}\text{Zr}_x\text{O}_3\) compounds, we have calculated the variation of \(-\Delta S_{\text{M}}\) with temperature for this compounds by equation (4). The variation of \(-\Delta S_{\text{M}}\) with temperature for \(\text{La}_{0.67}\text{Sr}_{0.33}\text{Mn}_{1-x}\text{Zr}_x\text{O}_3\) compounds is shown in figure 3, which displays that \(T_c\) and \(-\Delta S_{\text{M}}\) decrease as the increase of dopant amount. As it is seen from the change of magnetic entropy for \(\text{La}_{0.67}\text{Sr}_{0.33}\text{Mn}_{1-x}\text{Zr}_x\text{O}_3\) compounds, the temperature ranges for using the MCE can be extended. Furthermore, it is well known that the \(-\Delta S_{\text{M}}\) increases with the increasing of the external magnetic field. These properties are useful for the magnetic refrigerator [7]. In addition, the tunable Curie temperature to around room temperature of these perovskites is favorable for magnetic refrigeration applications in various temperatures.

The values of \(\Delta S_{\text{max}}, \delta T_{\text{FWHM}}\) and the RCP at different dopant amount for \(\text{La}_{0.67}\text{Sr}_{0.33}\text{Mn}_{1-x}\text{Zr}_x\text{O}_3\) compounds are calculated using equations (5)–(7), respectively. They are tabulated in table 2.

| Table 2. Magnetocaloric properties for \(\text{La}_{0.67}\text{Sr}_{0.33}\text{Mn}_{1-x}\text{Zr}_x\text{O}_3\) compounds in 1T magnetic field. |
|---|---|---|---|---|---|
| \(x\) | \(\Delta S_{\text{max}}\) (J•K\(^{-1}\)•K\(^{-1}\)) | \(\delta T_{\text{FWHM}}\) (K) | RCP (J•Kg\(^{-1}\)) | \(\Delta C_{\text{P},(\text{min})}\) (J•Kg\(^{-1}\)•K\(^{-1}\)) | \(\Delta C_{\text{P},(\text{max})}\) (J•Kg\(^{-1}\)•K\(^{-1}\)) |
| 0.00 | -2.03 | 16.64 | 33.78 | -27.49 | 29.50 |
| 0.02 | -1.33 | 23.58 | 31.35 | -10.56 | 11.88 |
| 0.04 | -1.13 | 27.66 | 31.25 | -7.10 | 8.22 |
Figure 2. Variation of magnetization with temperature for the La$_{0.67}$Sr$_{0.33}$Mn$_{1-x}$Zr$_x$O$_3$ compounds in 1T magnetic field. Symbols denote experimental data from [4] and the solid lines denote simulated curves using the model parameters as shown in table 1.

Figure 3. Predicted change of magnetic entropy for La$_{0.67}$Sr$_{0.33}$Mn$_{1-x}$Zr$_x$O$_3$ compounds in 1T magnetic field.

With increasing Zr dopant amount, the magnetic entropy change decreases drastically. Nevertheless, the RCP is still considerable. The negative minimum and positive maximum of specific heat variation of all samples are obtained from figure 4.
The change of magnetic entropy in manganese perovskites generally has been considered to be associated with the remarkable change of magnetization around \( T_C \). The supplementary change of magnetic entropy in manganese perovskites is generated from the coupling between spin and lattice in the magnetic ordering process. The ferromagnetic phase transition at Curie temperature in manganese perovskites is accompanied by considerable lattice structural change originated from the strong spin-lattice coupling. The change of lattice structure in the bond angle of Mn-O-Mn and the bond length of Mn-O is favourable for the ordered arrangement of spin structure. Therefore, the reduction of magnetization around \( T_C \) becomes more drastic, which is accompanied by the considerable change of magnetic entropy. Thus, the simultaneous occurrence of magnetic phase transition and lattice structural change has a strong effect on the change of magnetic entropy. As a consequence, this is favorable for the magnetocaloric effect.

![Figure 4](image_url)

**Figure 4.** Predicted temperature dependence of specific heat change for La\(_{0.67}\)Sr\(_{0.33}\)Mn\(_{1-x}\)ZrxO\(_3\) compounds in 1T magnetic field.

### 4. Conclusion

We have investigated the MCE for the Zr-doped La\(_{0.67}\)Sr\(_{0.33}\)Mn\(_{1-x}\)ZrxO\(_3\) compounds using the phenomenological model. It is shown that the Zr doping makes magnetocaloric effect in compounds La\(_{0.67}\)Sr\(_{0.33}\)MnO\(_3\) tunable. The change of magnetic entropy decreases drastically when the Curie temperature of these compounds is tuned to near room temperature. Nevertheless, the RCP values are still considerable. Therefore, these compounds will be good candidates for working materials in magnetic refrigerator.

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