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Magnetocaloric effect and improved relative cooling power in (La$_{0.7}$Sr$_{0.3}$MnO$_3$/SrRuO$_3$) superlattices

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Abstract
Magnetic properties of a series of (La$_{0.7}$Sr$_{0.3}$MnO$_3$/SrRuO$_3$) superlattices, where the SrRuO$_3$ layer thickness is varying, are examined. A room-temperature magnetocaloric effect is obtained owing to the finite size effect which reduces the $T_C$ of La$_{0.7}$Sr$_{0.3}$MnO$_3$ layers. While the working temperature ranges are enlarged, $-\Delta S_{\text{max}}$ values remain similar to the values in polycrystalline La$_{0.7}$Sr$_{0.3}$MnO$_3$. Consequently, the relative cooling powers are significantly improved, the microscopic mechanism of which is related to the effect of the interfaces at La$_{0.7}$Sr$_{0.3}$MnO$_3$/SrRuO$_3$ and higher nanostructural disorder. This study indicates that artificial oxide superlattices/multilayers might provide an alternative pathway in searching for efficient room-temperature magnetic refrigerators for (nano) micro-scale systems.

(Some figures in this article are in colour only in the electronic version)
entropy changes and RCP values. Thus, it is interesting to study the MCE in multilayers or superlattices, especially consisting of materials with second-order transitions, i.e. without the magneto-structural couplings. Furthermore, although attempts to study the MCE in metallic Gd/W [11] multilayers showed a reduced magnetic entropy change and decreased RCP, it is well known that the synthesis of smooth and sharp (at an atomic-scale level of the order of a few angstroms) layer interfaces in perovskite oxide magnetic multilayer structures can significantly influence the magnetic properties [12, 13]. For these reasons, we have investigated the magnetocaloric properties of (La0.7Sr0.3MnO3/SrRuO3) superlattices, consisting of two perovskite systems with second-order transitions, namely La0.7Sr0.3MnO3 (LSMO) and SrRuO3 (SRO). Interestingly, when comparing with the polycrystalline La0.7Sr0.3MnO3 compound, (La0.7Sr0.3MnO3/SrRuO3) superlattices exhibit a comparable magnetic entropy change but a significantly improved relative cooling power. These results are discussed and solutions to overcome the intrinsic limitations of film forms are also proposed.

The (La0.7Sr0.3MnO3/SrRuO3) superlattices were grown on [001]-oriented SrTiO3 (STO) substrates using a multitarget pulsed laser (KrF, λ = 248 nm) deposition system. The bottom layer LSMO, directly grown on the STO substrate, is fixed to be 20 unit cells while the SRO layer thickness varies with different n unit cells (n = 1, 3 and 6). The above bilayer is repeated 15 times and finally covered with an extra LSMO layer with a 20 unit cell thick LSMO layer, i.e. LSMO layer termination at both ends. The preparation method and structural details have been published elsewhere [14]. To calculate the thickness of LSMO and SRO layers, we have carried out quantitative refinement of the θ–2θ scan of the trilayer structures using the DIFFAX program [12, 14]. The high quality of the samples is also confirmed by the good agreement between the intense satellite peak positions in the θ–2θ x-ray diffraction patterns and the simulation profiles. Since in the literature, the −ΔSM values are most often in units of J kg−1 K−1, we also used this unit in the present work for the sake of comparison. Note that theoretical density values of LSMO and SRO are close to each other (6.42 and 6.39 g cm−3, respectively). Moreover, the density value in film form is larger than the experimental density value in polycrystalline La0.7Sr0.33MnO3 compound (6.23 g cm−3) [15]. Thus, to avoid any overestimation of the magnetocaloric properties caused by the introduction of density, we adopted the largest theoretical density value of 6.42 g cm−3 for calculating the magnetic entropy changes with a unit of J kg−1 K−1. The magnetic properties were measured by applying a field along the [100] in-plane direction in a superconducting quantum interference device magnetometer (Quantum Design MPMS).

The temperature dependences of the zero-field-cooled (ZFC) and the field-cooled (FC) magnetization of the (LSMO/SRO) superlattices with n = 1 (squares), 3 (triangles) and 6 (circles) in a field of 50 Oe.

Figure 1. Temperature dependences of the ZFC (open symbols) and FC (solid symbols) in-plane magnetization of (LSMO/SRO) superlattices with n = 1 (squares), 3 (triangles) and 6 (circles) in a field of 50 Oe.
follows:

\[
\Delta S_{M}(T, H) = \int_{0}^{H} \left( \frac{\partial S}{\partial H} \right)_{T} dH = \int_{0}^{H} \left( \frac{\partial M}{\partial T} \right)_{H} dH.
\]

(1)

Figures 3(a) and (b) show the \(-\Delta S_{M}(T)\) curves of the superlattices with different numbers \(n\) of SrRuO\(_3\) unit cells for a magnetic-field change \((\Delta H)\) of 50 kOe and 20 kOe, respectively. For \(\Delta H = 50\) kOe, \(-\Delta S_{M}^{\text{max}}\) values are found to be 4.45, 4.3 and 3.07 J kg\(^{-1}\) K\(^{-1}\) around 330 K, for \(n\) of 1, 3 and 6, respectively. To further evaluate the performance in terms of refrigeration efficiency, we have computed the RCP value, which depends not only on \(-\Delta S_{M}^{\text{max}}\), but also on the overall profile of \(-\Delta S_{M}(T)\). RCP can be calculated [3] by

\[
\text{RCP} = -\Delta S_{M}^{\text{max}} \delta_{\text{FWHM}},
\]

where \(\delta_{\text{FWHM}}\) is the full width at half maximum of the \(-\Delta S\) versus \(T\) curve.

From the viewpoint of applications, it is very beneficial to obtain a large magnetic entropy change and a high RCP for \(\Delta H = 20\) kOe since such a low field can be realized by using a NdFeB permanent magnet. For comparison, table 1 summarizes for \(\Delta H = 20\) kOe, the main parameters of our superlattices and polycrystalline La\(_{0.7}\)Sr\(_{0.3}\)MnO\(_3\) as well as another polycrystalline La\(_{0.67}\)Sr\(_{0.33}\)MnO\(_3\) with very close composition. Note that the RCP values are not sensitive to a La/Sr ratio of around 7/3. One of the interesting features of figure 3 and table 1 is that the \(-\Delta S_{M}(T)\) peaks in all investigated superlattices are significantly broadened over a wider temperature region than in the corresponding polycrystalline LSMO, due to higher nanostructural disorder [5, 11]. This is related to the previously noted increase in \(\delta T_{\text{C}}\). For \(\Delta H = 20\) kOe, the \(\delta_{\text{FWHM}}\) values are around 54 K when \(n\) is 1 and 3, and \(\delta_{\text{FWHM}}\) further increases significantly to 66 K for the \(n = 6\) superlattice. More importantly, while the working temperature ranges are enlarged, \(-\Delta S_{M}^{\text{max}}\) values are still kept to be comparable with the values in polycrystalline La\(_{0.7}\)Sr\(_{0.3}\)MnO\(_3\). It must be pointed out that thinner SRO layers (\(n = 1\) and 3) exhibit a higher value for \(-\Delta S_{M}^{\text{max}}\) compared to \(n = 6\). The RCP values derived from equation (2) in the superlattices are found to be significantly larger than those reported in polycrystalline LSMO.

Let us now investigate microscopic mechanisms to explore the origin of the improved RCP values in SRO-modulated (LSMO/SRO) superlattices. Assuming that only LSMO layers contribute to the magnetic entropy changes since the ordering temperature of SRO (around 150 K) is far below the investigated MCE temperature region, the maximum magnetic entropy changes \(-\Delta S_{M}^{\text{max}}\) (after normalizing to the LSMO mass only) should be almost the same. However, the
Table 1. Comparison of the main parameters of (LSMO/SRO) superlattices with those of the polycrystalline $La_0.7Sr_{0.3}MnO_3$ and $La_{0.67}Sr_{0.33}MnO_3$ for $\Delta H = 20$ kOe. N1, N3 and N6 denote the (LSMO/SRO) superlattices with $n = 1$, 3 and 6, respectively.

<table>
<thead>
<tr>
<th>Material</th>
<th>$-\Delta S_{\text{norm}}^{\text{max}}$ (J kg$^{-1}$ K$^{-1}$)</th>
<th>$\delta T_{\text{FWHM}}$ (K)</th>
<th>RCP (J kg$^{-1}$)</th>
<th>Volume ratio of LSMO (%)</th>
<th>Normalized $-\Delta S_{\text{norm}}^{\text{max}}$ (J kg$^{-1}$ K$^{-1}$)</th>
<th>$T_C$ (K)</th>
<th>$M(T_C, H = 20$ kOe) (emu g$^{-1}$)</th>
<th>Evaluated from references</th>
</tr>
</thead>
<tbody>
<tr>
<td>N1</td>
<td>2.35</td>
<td>53</td>
<td>125</td>
<td>93.5</td>
<td>2.51</td>
<td>325</td>
<td>41.6</td>
<td>This work</td>
</tr>
<tr>
<td>N3</td>
<td>2.2</td>
<td>54</td>
<td>119</td>
<td>87.6</td>
<td>2.51</td>
<td>325</td>
<td>42.7</td>
<td>This work</td>
</tr>
<tr>
<td>N6</td>
<td>1.52</td>
<td>66</td>
<td>100</td>
<td>77.9</td>
<td>1.95</td>
<td>325</td>
<td>33.8</td>
<td>This work</td>
</tr>
<tr>
<td>$La_0.7Sr_{0.3}MnO_3$</td>
<td>2.66</td>
<td>26</td>
<td>69</td>
<td></td>
<td></td>
<td>365</td>
<td>34</td>
<td>[16]</td>
</tr>
<tr>
<td>$La_{0.7}Sr_{0.3}MnO_3$</td>
<td>1.78</td>
<td>43</td>
<td>77</td>
<td></td>
<td></td>
<td>374</td>
<td>[22]</td>
<td></td>
</tr>
<tr>
<td>$La_{0.7}Sr_{0.3}MnO_3$</td>
<td>1.27</td>
<td>22.8</td>
<td>29</td>
<td></td>
<td></td>
<td>370</td>
<td>[23]</td>
<td></td>
</tr>
<tr>
<td>$La_{0.67}Sr_{0.33}MnO_3$</td>
<td>2.02</td>
<td>40</td>
<td>80</td>
<td></td>
<td></td>
<td>370</td>
<td>33</td>
<td>[24]</td>
</tr>
</tbody>
</table>

normalized $-\Delta S_{\text{norm}}^{\text{max}}$ values for a relatively low field change of 20 kOe are 2.51, 2.51 and 1.95 J kg$^{-1}$ K$^{-1}$ for $n = 1$, 3 and 6 superlattices, respectively. There is no difference in the normalized $-\Delta S_{\text{norm}}^{\text{max}}$ values for $n = 1$ and 3, but the difference becomes obvious when $n$ is increased to 6. Consequently, the volume ratio between LSMO and SRO is not the sole parameter that could influence the $-\Delta S_{\text{norm}}^{\text{max}}$ of the (LSMO/SRO) superlattices around $T_C$ and other factors must be considered.

Equation (1) shows that the magnitude of $\Delta S_M$ is strongly dependent on the magnitude of $|\text{d}M/\text{dT}|$ around the magnetic transition temperature, suggesting that a MCE is generally related to two factors: the magnetization values and the temperature interval $\delta T_C$ between PM and FM states around the magnetic phase transition [18]. In a previous report on the MCE in all types of thin films, the transition is spread out dependent on the magnitude of $|\text{d}M/\text{dT}|$ values. This smoothing of the transition (i.e. smaller $|\text{d}M/\text{dT}|$ values) leads to a strong decrease of the total entropy changes in Ni–Mn–Ga [5] and MnAs [6] monolayers involving the magneto-structural coupling and also a decrease of single magnetic entropy changes in the case of $La_{0.7}Sr_{0.3}MnO_3$ [8], $La_{0.67}Sr_{0.33}MnO_3$ (A = Ca, Sr or Ba) [9], Gd$_{1-x}$W$_x$ [10] monolayer and Gd/W [11] multilayers without the magneto-structural coupling. In our (LSMO/SRO) superlattices, although $\delta T_C$ values are also increased, the situation is different because an additional effect comes into play. It has already been pointed out [14] that the total magnetization of (LSMO/SRO) superlattices is found to be much higher than that of polycrystalline LSMO [14]. At $T_C$, the magnetization values of superlattices with thin SRO layers ($n = 1$ and 3) in a field of 20 kOe are also larger than those in the polycrystalline $La_{0.7}Sr_{0.3}MnO_3$ ($x = 0$ and 0.03), as shown in table 1. For these $n = 1$ and 3 superlattices, the stoichiometric SRO layers are not formed fully. The effect of roughness and the modification of the charge states of the Mn and Ru ions at the LSMO/SRO interfaces can probably induce such an enhanced total magnetization [13, 14, 19, 20] regardless of whether the coupled SRO layer is in the FM or PM state. On the other hand, the $\delta T_C$ values in superlattices with $n = 1$ and 3 are larger compared to polycrystalline $La_{0.7}Sr_{0.3}MnO_3$. As a result, the $-\Delta S_{\text{norm}}^{\text{max}}$ values derived from equation (1) are comparable with the largest $-\Delta S_{\text{norm}}^{\text{max}}$ values of $La_{0.7}Sr_{0.3}MnO_3$ reported in [16]. In consideration of the larger $|\text{d}M/\text{dT}|$ values, it is understood that the RCP values derived from equation (2) for superlattices with $n = 1$ and 3 are significantly improved with respect to the polycrystalline LSMO. For superlattices with a thicker SRO layer ($n = 6$ in our study), the stoichiometric SRO layer starts to form and suppresses the interfacial magnetic roughness, leading to a reduced magnetization around $T_C$ relative to thinner SRO layers, as can be seen from figure 2 and also in table 1. Thus, compared with $n = 1$ and 3 superlattices, the decreased magnetization and a slightly increased $\delta T_C$ around $T_C$ for the $n = 6$ superlattice, lead to a smaller $-\Delta S_{\text{norm}}^{\text{max}}$ value, but the RCP is mostly compensated by a larger $|\text{d}M/\text{dT}|$, also resulting in an improved RCP relative to polycrystalline LSMO.

In conclusion, we reported different magnetic and magnetocaloric effects in ($La_{0.7}Sr_{0.3}MnO_3$/$SrRuO_3$) superlattices with respect to polycrystalline $La_{0.7}Sr_{0.3}MnO_3$ compound. The transition from PM to FM states in all superlattices occurs in a wider temperature region, resulting in an enlarged working temperature region. However, the modification of the charge states of the Mn and Ru ions at the LSMO/SRO interfaces enhanced the magnetization around $T_C$, which counterbalances the negative effect of the transition broadening and leads to comparable $-\Delta S_{\text{norm}}^{\text{max}}$ values. The RCP values are found to be improved significantly due to the comparable $-\Delta S_{\text{norm}}^{\text{max}}$ values.
and increased $\delta T_{FWMH}$ values. With the increase of $n$ from 1 to 3, the reversible $-\Delta S_{\text{max}}^M$, the large $\delta T_{FWMH}$ and the high RCP value for $\Delta H = 20$ kOe are changed slightly and found to be around 2.3 J kg$^{-1}$, 53 K and 120 J kg$^{-1}$, respectively. When $n$ increased to 6, the reversible $-\Delta S_{\text{max}}^M$ decreased to be 1.52 J kg$^{-1}$ K$^{-1}$, whereas $\delta T_{FWMH}$ is increased to be 66 K, also resulting in a large RCP of 100 J kg$^{-1}$.

The study on $(La_{0.7}Sr_{0.3}MnO_3/SrRuO_3)$ superlattices, might be a stimulus to search for suitable materials with significantly improved relative cooling power in perovskite multilayers or superlattices by adjusting the interfaces and nanostructure for the RT magnetic refrigerant in (nano) microsystems.

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References