High performance magnetocaloric perovskites for magnetic refrigeration

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Mixed valence manganites have recently found use in applications due to the rich physics present in these. The applications range from colossal magneto-resistance\(^1\) to spintronics\(^2\) and thus these ceramic perovskite materials have been extensively studied.\(^3\) The magnetocaloric effect, which manifests itself as a temperature change of the material upon a change of the applied magnetic field, is maximised close to the magnetic phase transition. Numerous studies of the magnetocaloric properties of perovskite ceramics have been conducted, finding a strong dependence of both the magnetic transition temperature and the size of the magnetocaloric effect on stoichiometry and the level and type of various dopants.\(^4,5\) Among the most promising of the magnetocaloric effect on stoichiometry and the level and size of the magnetic transition temperature and the size of the magnetocaloric effect on stoichiometry and the level and type of various dopants.

We will show here how the ability of accurately tuning the Curie temperature by doping, coupled with the advantageous abilities of these materials to be shaped into fine structures, leads to high performance in magnetic refrigeration devices. This makes them promising materials for this technology, opening up yet another application for this class of materials. The high performance found in the experimental results is corroborated by numerical modelling results.

In the active magnetic regenerator (AMR) cycle, a porous magnetocaloric regenerator is alternately magnetised and demagnetised, e.g., by moving in and out of the magnet field source. After each movement, a heat transfer fluid is pushed through the void space in the regenerator in alternating directions. Upon performing this AMR cycle, a temperature gradient will build up across the regenerator, as heat is moved from the “cold end” to the “hot end”. The use of layered regenerators consisting of materials with different magnetic transition temperatures has been proposed and experimentally tested in a few devices.\(^7,9\) The regenerators are constructed so that each material along the temperature gradient is operating close to its optimal temperature, i.e., Curie temperature. Such a design relies heavily on the ability to tune the Curie temperature as well as the ability of constructing a multiple material regenerator in a practical way. We show how the materials series La\(_{2/3}\)(Ca,Sr)\(_{1/3}\)MnO\(_3\) and the processing route of tape casting are well suited to achieve this.

We have applied mixed valance manganite perovskites as magnetocaloric materials in a magnetic refrigeration device. Relying on exact control of the composition and a technique to process the materials into single adjoining pieces, we have observed temperature spans above 9 K with two materials. Reasonable correspondence is found between experiments and a 2D numerical model, using the measured magnetocaloric properties of the two materials as input. © 2012 American Institute of Physics.
The 28 plate stack was mounted as an active magnetic regenerator in a magnetic refrigeration test device at the Technical University of Denmark with a 1.1 T Halbach type permanent magnet assembly and a heat transfer fluid of water containing 20% commercial ethylene glycol being moved through the channels between the plates by way of a piston. The LCSM-2 parts of the plates are oriented toward the hot end, while the LCSM-1 parts of the plates are oriented toward the cold end. A heat exchanger in the hot reservoir of the device allows the hot end temperature to be controlled. Further details of this device and the operation of it can be found in Refs. 15 and 16 and a sketch of the device is given in Figure 1.

The utilization, $\phi$, of the AMR is conventionally defined as the ratio between the thermal mass of fluid pushed through the regenerator and the thermal mass of the regenerator:

$$\phi = \frac{m_f c_f}{M_s c_{H,s}},$$

(1)

where $m_f$ is the mass of the fluid pushed through in one direction, $c_f$ is the specific heat of the fluid, $M_s$ is the mass of the solid regenerator, and $c_{H,s}$ is the specific heat of the regenerator. As the regenerator consists of equal amounts of two materials, each with a temperature dependent specific heat, the value chosen for $c_{H,s}$ is the average of the peak values of the two materials, i.e., 765 J kg$^{-1}$ K$^{-1}$. Experiments were performed with the LCSM regenerator varying the mass flow rate, the utilization, and the hot end temperature. During operation, a steady state temperature span is reached between the set hot end temperature and the cold end temperature. Figure 2(a) shows the temperature spans achieved as a function of hot end temperature and utilization, keeping the fluid flow rate at a constant value of 1.32 gs$^{-1}$. The highest temperature span of 9.3 K was reached at a hot end temperature of 283.8 K and a utilization of 0.4, which results in a cycle time of 8.9 s. This is an exceptionally high span, more than 7.5 times the average maximum $\Delta T_{ad}$ of the two materials. Experiments were performed with the LCSM regenerator varying the mass flow rate, the utilization, and the hot end temperature. During operation, a steady state temperature span is reached between the set hot end temperature and the cold end temperature. Figure 2(a) shows the temperature spans achieved as a function of hot end temperature and utilization, keeping the fluid flow rate at a constant value of 1.32 gs$^{-1}$. The highest temperature span of 9.3 K was reached at a hot end temperature of 283.8 K and a utilization of 0.4, which results in a cycle time of 8.9 s. This is an exceptionally high span, more than 7.5 times the average maximum $\Delta T_{ad}$ of the two materials. For comparison, the highest temperature span obtained in this device with LCS of the benchmark magneto-caloric material Gd was 10.2 K, albeit with somewhat thicker flat plates of 0.9 mm. It is also seen that the temperature span decreases either side of the optimum utilization of 0.4, in good correspondence with previously obtained results. Doubling the mass flow rate while maintaining $\phi$ results in a lowering of the maximum temperature span to a value of 8.1 K, again at an optimum utilization of 0.4 and a optimum hot end temperature of 283.9 K. This is due to a reduction in the number of transfer units (NTU) with an increase of the mass flow rate, leading to a reduced temperature span.

A numerical 2D model of the AMR cycle has recently been developed. Using only the measured properties of the LCSM plates and physical properties of the heat transfer fluid, the no-load temperature span has been modelled as shown in Fig. 2(b). Comparing the curves in Fig. 2, it is evident that the trend and peak temperatures are the same, albeit with the predicted temperature span being a little higher and

### Table I. Measured magnetocaloric properties of the two materials. $\Delta T_{ad}$ and $\Delta s$ are reported upon magnetisation in an applied field of $\mu_0 H = 1$ T while $c_{H,s}$ is at zero applied field.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Peak temperature</th>
<th>Peak value</th>
</tr>
</thead>
<tbody>
<tr>
<td>LCSM-1</td>
<td>$\Delta T_{ad}$</td>
<td>277 K</td>
</tr>
<tr>
<td></td>
<td>$\Delta s$</td>
<td>275 K</td>
</tr>
<tr>
<td></td>
<td>$c_{H,s} (H = 0)$</td>
<td>273 K</td>
</tr>
<tr>
<td>LCSM-2</td>
<td>$\Delta T_{ad}$</td>
<td>282 K</td>
</tr>
<tr>
<td></td>
<td>$\Delta s$</td>
<td>282 K</td>
</tr>
<tr>
<td></td>
<td>$c_{H,s} (H = 0)$</td>
<td>278 K</td>
</tr>
</tbody>
</table>

![FIG. 1. Sketch of the experimental setup showing the different components.](image1)

![FIG. 2. (Color online) Temperature spans obtained at a mass flow rate of 1.32 gs$^{-1}$. (a) gives experimental results and (b) gives the predictions of the numerical model. The lines are guides to the eye.](image2)
the temperature span closer to the range where both LCSM favours the lower hot end temperature of 281 K as this brings the regenerator. Also, the lower span at high cooling power increased thermal capacity of the fluid being pushed through.

As expected, the model over-predicts the temperature span, but surprisingly the experimental zero span cooling powers are slightly above the predicted values. This may be caused by dissipation of some of the heater power through the walls of the device rather than into the regenerator. The extrapolated maximum zero-span cooling power of about 35 W kg\(^{-1}\) in the experiment is significantly larger than the highest measured value of 16 W kg\(^{-1}\) for Gd plates in the same device in similar conditions.\(^{19}\) Due to the lower parasitic loss of larger devices and the faster operation possible when using packed bed regenerators, significantly higher values are reported for such devices\(^{8,9}\) but at the cost of a significantly higher pumping pressure.

In conclusion, the results clearly show the potential value of the mixed valence manganese ceramics as magnetocaloric materials for application in devices. The strength of the materials lies in the ability to accurately tune the Curie temperature and process the materials into thin plates with adjacent regions of different Curie temperatures. Future regenerators will be constructed of numerous adjacent materials, leading to further improvements of the performance. The relatively low cost of materials and especially the processing route, compared to conventional materials and processing routes, reduces the price which is otherwise a major obstacle in the way of magnetocaloric applications.

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FIG. 3. (Color online) Cooling curves obtained at a mass flow rate of 2.63 gs\(^{-1}\) for both experiments and model predictions. Each curve is indexed by the hot end temperature and the utilization. The lines are guides to the eye.