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Freeze-casting to create micro-channels in La$_{0.66}$Ca$_{0.33-x}$Sr$_x$Mn$_{1.05}$O$_3$  

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Introduction  

The templating technique of freeze casting is utilized as a way of creating directional porosity in the form of micro-channels in La$_{0.66}$Ca$_{0.33-x}$Sr$_x$Mn$_{1.05}$O$_3$ (LCSM). LCSM is a magnetocaloric material in which the Curie temperature can be controlled by varying strontium doping (x), making it ideal for application as a regenerator material in magnetic refrigeration [1]. One way to increase the cooling performance of a magnetic regenerator is by optimizing its geometry: while maintaining a large surface area to increase heat exchange with the regenerator fluid, it must not provide too much resistance to flow. It has been proposed that a matrix of micro-channels with a width of 100 μm is an optimum geometry [2]. Freeze-casting results in channels of widths of 10 to 100 μm, where the porosity depends on the solid load while the size and homogeneity of the channels depends on freezing conditions [3][4]. The figure on the right shows solid magnetic regenerators made of magnetocaloric materials of packed irregular particles and stacked plate geometries. A geometry in between – such as a micro-channel matrix – would be optimum.

Materials and methods  
The standard freeze casting route is altered in two steps: Dynamic and static freezing. Samples were frozen either statically at −30° or dynamically at −10 °C/min. Drying freeze-casting: Gelatin was added at 0.3 wt% (of solids) and left to harden before freezing Powders were used as received from Cer-Po-Tech and characterized as follows:  

<table>
<thead>
<tr>
<th>Sample</th>
<th>Density [g/cm³]</th>
<th>Surface area [m²/g]</th>
<th>Particle size [μm]</th>
<th>X-ray point</th>
<th>Zeta potential [mV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>LCSM0%</td>
<td>0.96</td>
<td>6.061</td>
<td>10.12</td>
<td>30.48</td>
<td>8.76</td>
</tr>
<tr>
<td>LCSM70%</td>
<td>0.92</td>
<td>6.401</td>
<td>17.02</td>
<td>0.34</td>
<td>8.70</td>
</tr>
<tr>
<td>LCSM975</td>
<td>0.075</td>
<td>6.063</td>
<td>0.14</td>
<td>5.02</td>
<td>8.54</td>
</tr>
</tbody>
</table>

Results: Varying particle size  
SEM images showing the cross section perpendicular to the freezing direction of 14 vol% LCSM506 frozen with no control of temperature. Scale bar indicates 100 μm. The freezing front velocity decreases as the ice height increases due to increased thermal resistance. The lamellar pore size increases as the freezing front velocity decreases. Length and width of lamellar pores were determined by fitting an elliptical to individual pores in ImageJ. Pore size is here plotted as a function of height. Lamellar pore width is increased by a factor of 3, while the length is increased by a factor of 7.

Results: Dynamic and static (gelation) freezing  
Slimes of 14 vol% LCSM were freeze casted without control of temperature besides that of liquid N₂. Slip casted sample sintered in a diamat at 5K/min. LCSM starts densifying at 1000 °C. All samples were thus partially sintered at 1150 °C for 3h.

Results: Copper rod immersed directly in liquid N₂  
Slimes of 14 vol% LCSM were freeze casted without control of temperature besides that of liquid N₂. Copper rod immersed directly in liquid N₂.

Conclusions and outlook  
Anisotropic porosity in the form of lamellar channels where achieved in LCSM ceramics by freeze casting, with increased homogeneity and lower aspect ratios achieved by implementing dynamic freezing profiles and an additional gelation step, respectively. Thus, future work includes:  

- X-ray tomography to establish 3D structure (i.e. pore connectivity, quantification of gelation)  
- Increased control of freezing for homogenous macrostructure  
- Detailed quantification of microstructure to establish correlation between processing (specifically freezing and sintering) and structure  
- Structure of ceramics vs. performance as regenerator material in magnetocaloric refrigeration systems

References  
[1] J. Christiansen, S. Linderoth, and S. Markup, 2005, “Direct and indirect measurement of the freezing direction of 14 vol% LCSM506 frozen with no control of temperature. Scale bar indicates 100 μm. The freezing front velocity decreases as the ice height increases due to increased thermal resistance. The lamellar pore size increases as the freezing front velocity decreases. Length and width of lamellar pores were determined by fitting an elliptical to individual pores in ImageJ. Pore size is here plotted as a function of height. Lamellar pore width is increased by a factor of 3, while the length is increased by a factor of 7.

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