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Freeze-casting to create directional micro-channels in regenerators for magnetic refrigeration

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ABSTRACT

We present the engineering of directional porosity in the form of lamellar micro-channels in the magnetocaloric ceramic of $La_{0.66}Ca_{0.27}Sr_{0.06}Mn_{1.05}O_3$ (LCSM) by freeze-casting. Freeze-casting is a templating technique based on the anisotropic growth of ice crystals in aqueous suspensions upon directional freezing, which, when applied to a suspension of LCSM results in hierarchical structures of aligned porosity in the form of micro-channels with widths of 5 µm to 20 µm. Channel sizes and tortuosity are measured and calculated from analysis of SEM images obtained at cross sections perpendicular and parallel to the freezing direction, respectively, while freezing conditions are monitored by temperature measurements. We propose that freeze-casting demonstrate apparent applicability within processing of ceramic materials for application as regenerator for magnetic refrigeration.

Keywords: Freeze-casting, ice templating, micro-channels, porous ceramics, magnetocaloric, magnetic refrigeration, active magnetic regenerator.

1. INTRODUCTION

Magnetic refrigeration utilizing the active magnetic regenerator (AMR) cycle offers an alternative to conventional refrigeration using cfc-gasses. The latter poses an environmental risk, while AMR technology is based on a porous magnetic material through which an environmentally friendly fluid flows transferring heat. The efficiency of the AMR cycle strongly depends on the geometry of the regenerator material. Common geometries are packed beds of epoxy-bonded spherical or irregular particles and parallel plates of varying thickness. While the packed beds offer a high heat transfer rate they are limited by their resistance to flow and fixed porosity. The plate geometry offers a low pressure drop but also a low surface area resulting in a reduced heat transfer rate. A geometry of micro-channels might pose an alternative, exhibiting a lower resistance to flow while maintaining a larger surface area and thus a high heat transfer rate (Lei et al., 2017). Although, such a geometry is hard to achieve by conventional processing routes.

Freeze-casting, or ice templating, however, introduces a potential processing route to fabricate micro-channels in ceramics. Freeze-casting is a templating technique where a ceramic aqueous suspension is directionally frozen resulting in the growth of anisotropic ice crystals, which redistributes the ceramic particles. Following this, water is sublimated from the frozen body by freeze-drying, leaving voids where the ice crystals were and thereby creating macro-pores or channels in the green body. Subsequent sintering results in a structure with parallel, well-defined channels with widths in the range ~10 µm to ~100 µm, solid ceramic walls and tunable porosity (Deville et al., 2007; Lichtner et al., 2013). For a status on recent trends in freeze-casting, the reader is referred to (Deville, 2018).

The well-known $La_{0.66}Ca_{0.33-x}Sr_xMn_{1.05}O_3$ magnetocaloric ceramic, for which the Curie Temperature can be conveniently controlled around room temperature by varying x (Dinesen et al., 2005), is highly relevant for application as regenerator-material in magnetic refrigeration (Bahl et al., 2012). In this context, we present engineered structures with aligned, directional porosity in $La_{0.66}Ca_{0.27}Sr_{0.06}Mn_{1.05}O_3$ ceramics by freeze-casting.

2. MATERIALS & METHODS

2.1. Powder properties and preparation of ceramic suspension

Ceramic suspensions were prepared from 14 vol% powders of $La_{0.66}Ca_{0.27}Sr_{0.06}Mn_{1.05}O_3$ (LCSM, CerPoTech, Norway) in distilled water, with the addition of 2.5 w.t. % (in relation to powder) of polyvinylpyrrolidone (PVP K15, $M_w \sim 10{,}000$ g/mol, Sigma-Aldrich, Germany) as dispersing agent.

The specific surface area and density of the powder were determined by the BET method using a Nova 4000e (Quantachrome Instruments, United States), and by gas pycnometry using an AccuPyc II 1340 (Micromeritrics, United States), respectively. The particle size distribution (PSD) of both raw powders and milled suspensions was determined using a Laser Diffraction Particle Size Analyser (LS 13 320, Beckman Coulter). Powder properties are summarized in Table 1.

Table 1. Summarization of powder properties of $La_{0.66}Ca_{0.27}Sr_{0.06}Mn_{1.05}O_3$. The median of the particle size distribution is denoted d_{50}.

Density	Specific surface area	d_{50}
6.00 g/cm^3	10.12 m^2/g	2.6 μm

In order to achieve a sufficient dispersion of powders, slurries were upon mixing by stirring sonicated using a homogenizer (UP200St, Hielscher) for 60 seconds and subsequently homogenized using a low energy ball mill with zirconia balls (Ø = 10 mm) for 24 hours. 1.5 w.t. % (in relation to powder) of polyvinylpyrrolidone (PVP K30, $M_w \sim 30{,}000$ g/mol, Sigma-Aldrich, Germany) was added as binder and mixed for an additional 30 minutes before use. Suspensions were de-aired under low vacuum for a few minutes immediately before casting.

2.2. Freeze-casting procedure

Samples were frozen directionally with no other temperature control than that of liquid nitrogen. An acrylic cylindrical mould with an inner diameter of 16.5 mm, an outer diameter of 36 mm and with a detachable copper bottom containing approximately 5 mL of de-aired slurry was placed on top of a vertically positioned copper rod (Ø = 20 mm, l = 315 mm) directly immersed into a container of liquid nitrogen at 77 K. The mould was equipped with thermocouples (K-type, gauge 36, Omega) positioned at varying heights 6 mm apart by insets drilled radially inward in the mould leaving 750 μm mould wall between thermocouples and suspension. Thus, the temperature through the suspension could be monitored during freezing. The top of the mould was left open to ambient conditions and the suspension was frozen directionally due to the applied temperature gradient across the suspension in the vertical direction caused by the difference in temperature of the top of the copper rod and the ambient temperature.

Upon freeze-casting, samples were removed cautiously from their moulds and transferred to a freeze drier (Alpha 1-2 LD plus, Christ, Buch & Holm) where ice was removed from the samples by sublimation for at least 24 hours. Dry samples were subsequently sintered in air at 1150 °C for 3 hours (heating rate of 2 K/min) with an initial burnout of organic additives at 450 °C for 4 hours.

2.3. Structure characterization and quantification

Ceramic samples were prepared for mechanical handling and structural analysis by infiltration with epoxy (EpoFix, Struers Aps, Denmark). Samples were upon mounting cut in half parallel to the freezing direction and one-half of the sample was then cut in 4 mm slices perpendicular to the freezing direction. This procedure exposes parallel and perpendicular cross sections of the sample, which were then polished and coated with a ~12 nm thick carbon layer. Images of the cross sections were obtained using a scanning electron microscope (TM3000, Hitachi High-Technologies), and analysed using Matlab® (The MathWorks, Inc.). Three images at each sample height in the parallel cut samples and each slice cut in the perpendicular direction were obtained for statistical analysis. Channel widths were measured on perpendicular cross sections while tortuosity was calculated from parallel cross sections using a modified version of the TauFactor application (Cooper et al., 2016) in Matlab® (The MathWorks, Inc.). The software has been modified (De Angelis et al., 2018, 2017;

Jørgensen et al., 2015), for our purpose specifically for analysis in 2D, in order to calculate the tortuosity from SEM images. Tortuosity was calculated parallel to the freezing direction across cross sectional areas of 830 x 620 µm.

3. RESULTS & DISCUSSION

Freeze-casting a suspension of ceramic particles under the conditions described in the previous section results in hierarchical structures of aligned porosity in the form of micro-channels as shown in Figure 1. The channels are aligned and lamellar, but changes in morphology and size within one single sample are apparent.

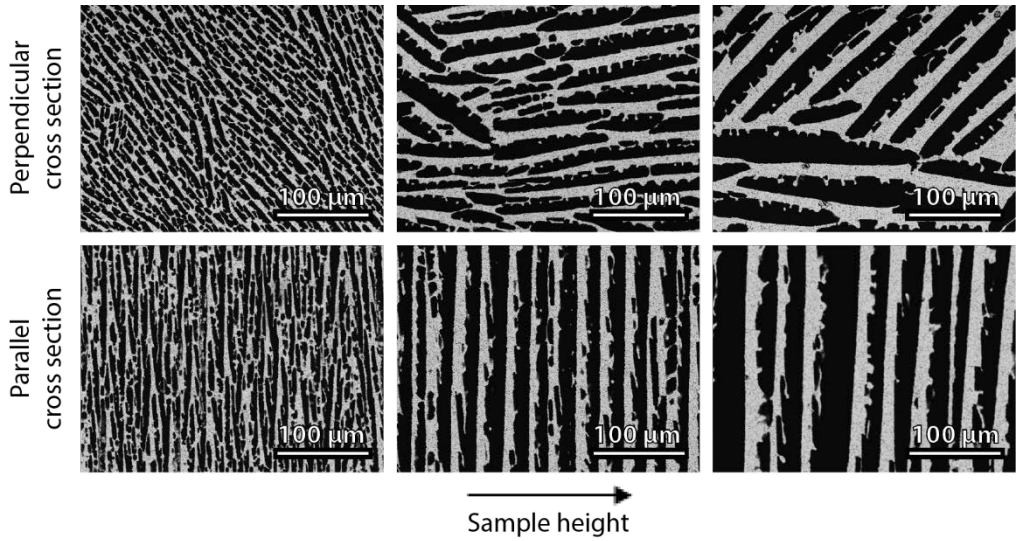

Figure 1: SEM images of cross sections perpendicular and parallel to the freezing direction, where the grey parts are ceramic walls while the black areas are voids or channels. Directional freezing thus results in a hierarchical, porous structure of lamellar micro-channels.

The structural properties of freeze-casted species can be quantified by the size, or width, of channels and tortuosity. From cross sections perpendicular and parallel to the freezing direction, it is evident that the channel size increases with increasing sample height. On the contrary, the tortuosity decreases with increasing sample height. Sample height is the vertical distance – parallel to the freezing direction – from the bottom of the sample and to the specific cross section of interest. The width of the lamellar channels at various heights in the sample are plotted in Figure 2a, while the calculated tortuosity at various heights in the sample are plotted in Figure 2b.

The calculated tortuosities of the channels drop drastically up through the sample. A tortuosity of $\tau = 1$ corresponds to a direct flow path, while the greater the tortuosity the greater the curviness of the channels. At the bottom of the sample, the calculated tortuosity was infinite, because no channels span across the entire analysed cross sections. The tortuosity can be directly correlated to the nature of ice crystal growth under the conditions described above. The growth of ice crystals in ceramic suspensions during freeze-casting has previously been observed by *in situ* x-ray (Bareggi et al., 2011; Deville et al., 2009). Upon freezing, rapid nucleation takes place at the bottom copper surface forming ice crystals growing in random directions. This is the isotropic region with no resulting directional porosity. Eventually, ice crystals growing along the direction of the temperature gradient are favoured, resulting in a region of aligned crystals. This region is referred to as the steady state region or the anisotropic region. In this region, aligned, lamellar ice crystals are arranged in domains of various orientations, as is also evident on the perpendicular cross sections in Figure 1 (top). The resulting channels are greater and more homogeneous in size, giving rise to a significant drop in calculated tortuosity.

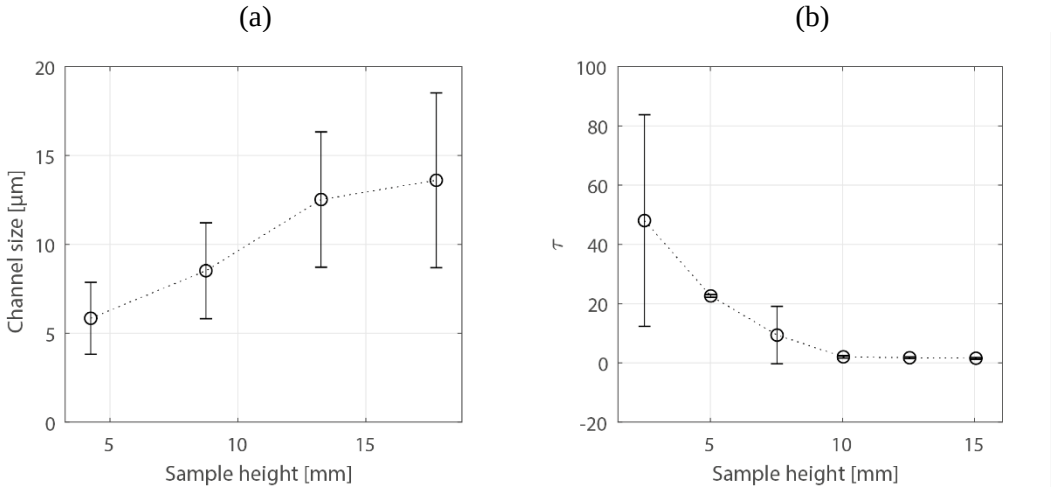

Figure 2: Structural properties of freeze-casted LCSM ceramics. (a) Channel size is measured as the width of lamellar pores on SEM images of perpendicular cross sections at various sample heights, while (b) tortuosity is calculated from SEM images obtained at various heights parallel to the freezing direction.

The channel size of freeze casted species has previously been correlated to the velocity of the freezing front, where the channel size increase with a decrease in freezing front velocity (Deville et al., 2007; Lichtner et al., 2013; Waschkies et al., 2009). The freezing front is the interface between the liquid ceramic suspension and the frozen sample of ice and ceramic phases. The freezing front in a ceramic suspension undergoing freeze-casting have previously been found, by *in situ* x-ray, to be a well-defined, slightly concave planar interface perpendicular to the freezing direction (Bareggi et al., 2011), and thus, it can often be tracked by visible inspection using a transparent mould.

However, due to the colour (or lack thereof) of LCSM, we found that it was not possible to visibly track the freezing front during casting for determination of the velocity of the freezing front. Instead, we installed thermocouples along the height of the casting mould in order to measure the temperature through the sample during freezing. This inevitably involves a thermal lag. The measured temperature of the copper mould bottom and at various positions in the mould during casting are shown in Figure 3a. These measurements allowed us to calculate the local freezing rate, i.e. the rate of temperature change. Assuming that the local freezing rate at the time of freezing (T = 0 °C) can be used as a measure to quantify the freezing conditions at the freezing front, a decrease of this quantity along the height of the sample is evident from Figure 3b.

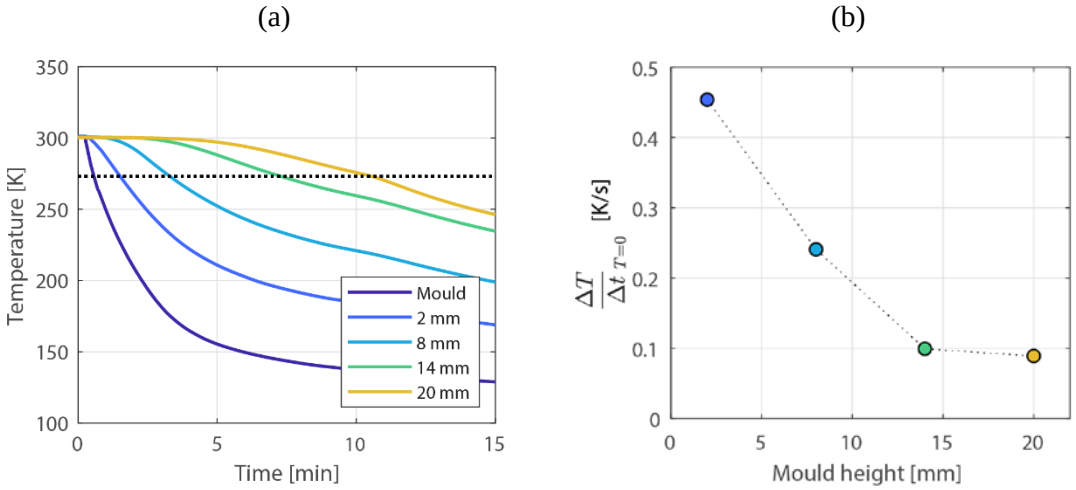

Figure 3: Freezing conditions for freeze-casted LCSM ceramics. (a) Temperature of mould bottom and at various positions along the height of the mould, the freezing point of water is indicated by the dashed line, and (b) the local freezing rates at the time of freezing.

The sample shrinkage in the direction of freezing upon sintering is approximately 25%, which means that Figure 2a-b and Figure 3b approximately span the same region of the sample. The structural properties of channel size and tortuosity is thus clearly correlated to the local freezing rate, where a decrease in local freezing rate increases the channel size and decreases tortuosity.

We found that these tendencies are true for various solid loads of 14-20 vol%, leading to ceramics of varying porosity, however, upon freeze-casting of an LCSM suspension of powders of larger particle size, we observed only vaguely defined channels:

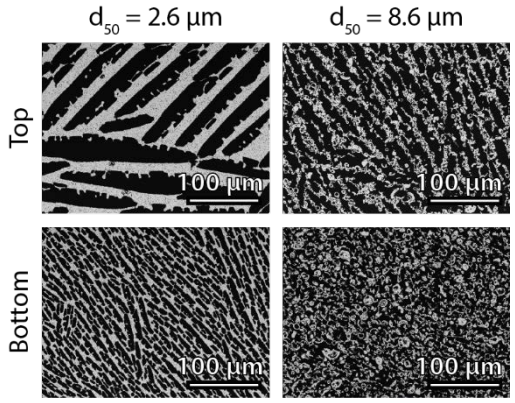

Figure 4: SEM images of cross sections perpendicular to the freezing front obtained at the top (sample height: 18 mm) and bottom (sample height: 4 mm) of samples prepared from ceramics of various particle size. d_{50} denote the median particle size of the particle size distribution of freeze-casted suspensions.

From Figure 4 it is evident that no channels have formed at the bottom of the sample freeze-casted from the suspension of larger particles. At the top of the sample, the wall thickness and particle sizes are in the same order of magnitude resulting in vaguely defined channels and walls, where the latter is varying in thickness and density. The lack of well-defined channels, specifically at the bottom, is presumably due to particle entrapment (Deville et al., 2007), the freezing rate simply resulted in a freezing front moving too fast thereby engulfing particles instead of ejecting them from the ice phase.

4. CONCLUSIONS

We show that freeze-casting a suspension of ceramic particles by directional freezing, applying no other temperature control than that of liquid nitrogen, results in hierarchical structures of anisotropic porosity in the form of micro-channels in the size range of 5 µm to 20 µm. The channels are aligned and lamellar. Structural properties such as channel size and tortuosity was determined from analysis of SEM images of cross sections obtained at various sample heights, revealing an increase in channel size and a decrease in tortuosity with increasing sample height. The micro-channels are shaped from the sublimated ice crystals and as such, the structural properties depend strongly on the morphology of the ice crystals, which is determined by the freezing conditions. We found that when freeze-casting ceramic suspensions using a set-up with no temperature control other than that of liquid nitrogen, the local freezing rate decreases as the freezing front moves further away from the copper rod, i.e. with increasing sample height.

Freeze-casting hold the promise of a processing route with the ability to tune and optimize channel size, tortuosity and also porosity, yielding high tunability of ceramics for energy application, specifically as regenerator-material for magnetic refrigeration. However, the applicability depend on implementation of enhanced control of freezing conditions in order to obtain more homogenous structures regarding channel size and tortuosity.

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REFERENCES

Bahl, C.R.H., Velzáquez, D., Nielsen, K.K., Engelbrecht, K., Andersen, K.B., Bulatova, R., Pryds, N., 2012. High performance magnetocaloric perovskites for magnetic refrigeration. Appl. Phys. Lett. 100. https://doi.org/10.1063/1.3695338

Bareggi, A., Maire, E., Lasalle, A., Deville, S., 2011. Dynamics of the freezing front during the solidification of a colloidal alumina aqueous suspension: In situ x-ray radiography, tomography, and modeling. J. Am. Ceram. Soc. 94, 3570–3578. https://doi.org/10.1111/j.1551-2916.2011.04572.x

Cooper, S.J., Bertei, A., Shearing, P.R., Kilner, J.A., Brandon, N.P., 2016. TauFactor: An open-source application for calculating tortuosity factors from tomographic data. SoftwareX 5, 203–210. https://doi.org/10.1016/j.softx.2016.09.002

De Angelis, S., Jørgensen, P.S., Esposito, V., Tsai, E.H.R., Holler, M., Kreka, K., Abdellahi, E., Bowen, J.R., 2017. Ex-situ tracking solid oxide cell electrode microstructural evolution in a redox cycle by high resolution ptychographic nanotomography. J. Power Sources 360, 520–527. https://doi.org/10.1016/j.jpowsour.2017.06.035

De Angelis, S., Jørgensen, P.S., Tsai, E.H.R., Holler, M., Kreka, K., Bowen, J.R., 2018. Three dimensional characterization of nickel coarsening in solid oxide cells via ex-situ ptychographic nano-tomography. J. Power Sources 383, 72–79. https://doi.org/10.1016/j.jpowsour.2018.02.031

Deville, S., 2018. The lure of ice-templating: Recent trends and opportunities for porous materials. Scr. Mater. 147, 119–124. https://doi.org/10.1016/j.scriptamat.2017.06.020

Deville, S., Maire, E., Lasalle, A., Bogner, A., Gauthier, C., Leloup, J., Guizard, C., 2009. In situ X-ray radiography and tomography observations of the solidification of aqueous alumina particle suspensions - Part I: Initial instants. J. Am. Ceram. Soc. 92, 2489–2496. https://doi.org/10.1111/j.1551-2916.2009.03163.x

Deville, S., Saiz, E., Tomsia, A.P., 2007. Ice-templated porous alumina structures. Acta Mater. 55, 1965–1974. https://doi.org/10.1016/j.actamat.2006.11.003

Dinesen, A., Linderoth, S., Mørup, S., 2005. Direct and indirect measurement of the magnetocaloric effect in La0.67Ca0.33−xSrxMnO3±δ. J. Phys. Condens. Matter 17, 6257–6269. https://doi.org/10.1088/0953-8984/17/39/011

Jørgensen, P.S., Ebbehøj, S.L., Hauch, A., 2015. Triple phase boundary specific pathway analysis for quantitative characterization of solid oxide cell electrode microstructure. J. Power Sources 279, 686–693. https://doi.org/10.1016/j.jpowsour.2015.01.054

Lei, T., Engelbrecht, K., Nielsen, K.K., Veje, C.T., 2017. Study of geometries of active magnetic regenerators for room temperature magnetocaloric refrigeration. Appl. Therm. Eng. 111, 1232–1243. https://doi.org/10.1016/j.applthermaleng.2015.11.113

Lichtner, A.Z., Jauffrès, D., Martin, C.L., Bordia, R.K., 2013. Processing of hierarchical and anisotropic porosity LSM-YSZ composites. J. Am. Ceram. Soc. 96, 2745–2753. https://doi.org/10.1111/jace.12478

Waschkies, T., Oberacker, R., Hoffmann, M.J., 2009. Control of lamellae spacing during freeze casting of ceramics using double-side cooling as a novel processing route. J. Am. Ceram. Soc. 92, 79–84. https://doi.org/10.1111/j.1551-2916.2008.02673.x