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# Microstructure and Magnetic Properties of La-Ca-Sr-Mn-O Perovskite Ceramics

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La<sub>0.67</sub>Ca<sub>0.33-x</sub>Sr<sub>x</sub>MnO<sub>3</sub> ( $x = 0.33; 0.03; 0$ ) (LCSM) perovskite magnetocaloric ceramics were prepared by solid state synthesis in air and sintering at 1520 °C. The phase composition was checked by x-ray powder diffraction. Microstructure analyses were done by scanning electron microscopy. The influence of high pressure oxygenation on magnetisation behaviour is shown.

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## 1. Introduction

A wide range of different types of materials, from metals to ceramics, exhibit the magnetocaloric effect [1]. Generally, the magnetocaloric effect manifests itself as a reversible increase in temperature when the magnetic material is placed in a magnetic field, and the maximum magnetocaloric effect occurs near the Curie temperature. Magnetic ceramics materials are very stable at room temperature, can be compositionally tuned to adjust the Curie temperature, and do not corrode in water. This makes them an attractive option for use as regenerators for magnetic refrigeration systems. Families of functional materials with a large magnetocaloric effect have been found in several perovskite type manganese oxides such as Ca- and Sr-doped lanthanum manganites, La<sub>0.67</sub>Ca<sub>0.33-x</sub>Sr<sub>x</sub>MnO<sub>3</sub> ( $x = 0; 0.33$ ) [2]. These samples show a substantial magnetocaloric effect in a temperature range around their respective Curie temperature, which makes the compounds suitable for air-conditioning and refrigeration applications. By varying the composition parameter  $x$  the Curie temperature can be adjusted between 267 K ( $x = 0$ ) and 369 K ( $x = 0.33$ ) [2].

In this contribution, the structure, microstructure and the influence of high pressure oxygenation on magnetisation behaviour of La<sub>0.67</sub>Ca<sub>0.33-x</sub>Sr<sub>x</sub>MnO<sub>3</sub>, prepared by solid state synthesis were investigated.

## 2. Experimental

The La<sub>0.67</sub>Ca<sub>0.33-x</sub>Sr<sub>x</sub>MnO<sub>3</sub> ( $x = 0.33$  (S1); 0.03 (S2); 0 (S3)) perovskite powders were prepared by conventional solid state synthesis in air from the starting materials: lanthanum oxide (La<sub>2</sub>O<sub>3</sub>), calcium oxide (CaO), strontium carbonate (SrCO<sub>3</sub>) and manganese oxide (MnO<sub>2</sub>). The powders were mixed in appropriate

amounts in a mixer for 30 min., and then calcined two times: first at the temperature of 1200 °C for 16 hours and the second at the temperature of 1300 °C for 6 hours (heating and cooling rate of 100 °C/h in both cases). After each calcination the powders were intensively milled for 15 min. in a friction mill. Then the powders were pressed into cylindrical pellets of 8 mm in diameter and sintered at 1520 °C by following temperature programme: heating the sample to sintering temperature with the heating rate 100 °C/h, dwell at sintering temperature for 2 hours, cooling down to room temperature at 100 °C/h.

The purity of calcined powders and sintered samples was checked by X-ray diffraction (XRD). The patterns were collected using the Cu K<sub>α</sub> (calcined powders) or Mo K<sub>α</sub> (sintered ceramics) wavelength by powder diffractometers. Microstructure analyses were done by scanning electron microscopy (SEM) on fractured surfaces of sintered ceramics.

Small samples, cut for magnetization measurements, were additionally treated by high pressure oxygenation (HPO) at following conditions: 700 °C for 1 hour, cooling to room temperature at 10 bar pressure of pure oxygen atmosphere.

The thermomagnetic curves were measured by a vibrating-sample magnetometer (VSM) in magnetic field of 200 kA/m and in temperature range from 140 K up to 400 K, for the determination of the Curie temperature of samples.

## 3. Results and discussion

The XRD patterns of LCSM powders after calcination and the sintered ceramics are presented in Fig. 1. It can be seen, that not all of the observed peaks can be attributed to the LaSrMnO<sub>3</sub> phase after the second calcination. About 16 mass % belongs to alpha-La<sub>2</sub>O<sub>3</sub> (6%) and La (MnO<sub>3</sub>) (10%) type secondary phases. These secondary phases disappeared after sintering at 1520 °C and all observed peaks were assigned to the single phase of crystalline perovskite (Fig. 1b). All three studied compositions behaved in the same manner.

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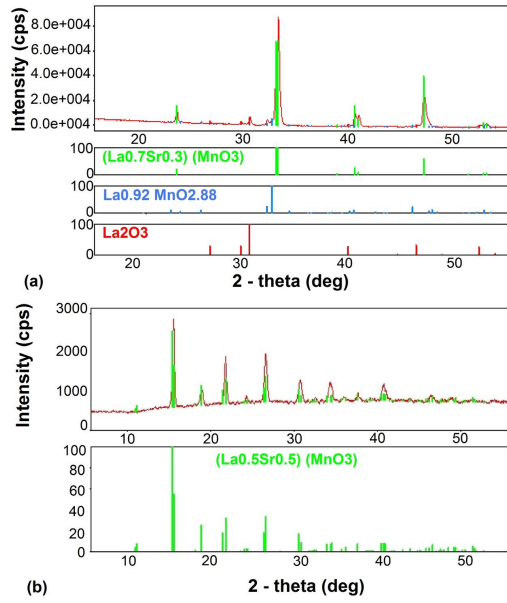


Fig. 1. XRD patterns of  $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$  sample (a) after second calcinations (b) after sintering at 1520.

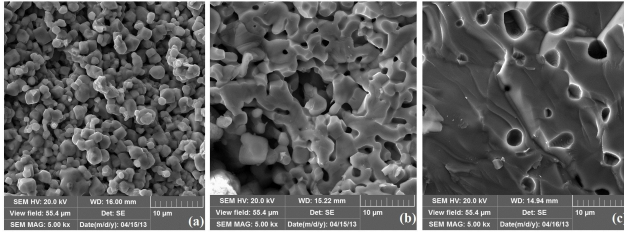


Fig. 2. Fracture surfaces observed by SEM for the samples S1 (a), S2 (b) and S3 (c), sintered at 1520.

After sintering both, the porosity and the grain size depend on the sample composition, as it is confirmed by observation of fractured surfaces of sintered ceramics by SEM (Fig. 2). From the Fig. 2(c) it can be seen that the sintering and grain growth are the most intensive for the sample S3, where the fracture surface is completely created by transgranular cleavage and exhibits the lowest porosity.

TABLE

$T_C$  of the samples S1, S2, S3 cooled in air and after HPO.

$T_C$ (50%)	S1	S2	S3
Cooled in air	356.5 K	255.6 K	161.9 K
HPO	353.5 K	253.9 K	165.1 K

The magnetization measurements of Curie temperature,  $T_C$ , for the samples with different compositions are shown in Fig. 3. We can see that the Curie temperature depends on the nominal composition of  $\text{La}_{0.67}\text{Ca}_{0.33-x}\text{Sr}_x\text{MnO}_3$ , as we expected [2], but also on HPO. The HPO leads to lower  $T_C$  for the samples S1 or S2 and to higher  $T_C$  for the sample S3 (Table).

Such different behaviour can be attributed to changes in oxygen stoichiometry and to consequent changes in the  $\text{Mn}^{3+}/\text{Mn}^{4+}$  ratio of  $\text{LaSrMnO}_3$  phase.

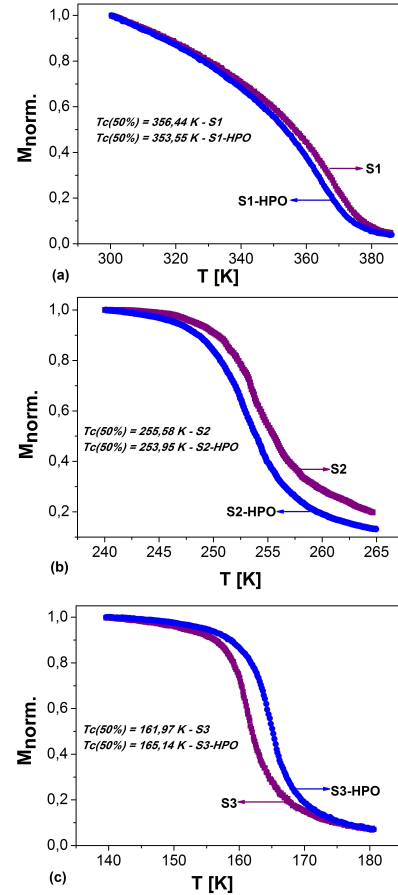


Fig. 3. Curie temperature of the samples (a) S1, (b) S2 and (c) S3 sintered at 1520 °C, cooled in air and after HPO.

#### 4. Conclusions

$\text{La}_{0.67}\text{Ca}_{0.33-x}\text{Sr}_x\text{MnO}_3$  ( $x = 0, 0.03, 0.33$ ) perovskite samples were prepared by solid state synthesis in air. It is shown that synthesised powders contain some impurity phases, which further react at sintering of ceramic bulk samples at higher temperatures. The magnetisation measurements confirmed expected behaviour of Curie temperature with Sr substitution and have shown the influence of high pressure oxygenation.

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