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Importance of the synthesis and sintering methods on the properties of manganite ceramics: The example of $La_{0.7}Ca_{0.3}MnO_3$

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The influence of the synthesis and sintering methods on the structural, microstructural, stoichiometry and thus the magnetocaloric properties of the $La_{0.7}Ca_{0.3}MnO_3$ compound has been thoroughly studied. Soft-chemistry (sol-gel and polyol) synthesis and spark plasma sintering (SPS) procedures, used to obtain nanostructured materials, were compared to the traditional ceramic ones. This work evidences that SPS treatment not only reduces the grain size but also leads to oxygen sub-stoichiometry. This entails a lower Mn^{4+} content in the manganite, and probably heterogeneity in the Mn^{4+} grain distribution, which have consequences on the magnetic and magnetocaloric properties: a lower maximum entropy variation which is compensated by a larger transition temperature range. The sample prepared by combining polyol soft-chemistry synthesis and SPS sintering displays a higher maximum relative cooling power value, equal to 70% of that of gadolinium, the most effective material for domestic magnetic refrigeration.

1. Introduction

Manganites are very interesting materials from both fundamental and technological points of view: for magnetic recording and magnetic refrigeration applications [1–7]. Magnetic refrigeration, based on the magnetocaloric effect (MCE), has recently brought a promising alternative to the conventional technique of gas compression: it is safer, quieter, more compact and more environmentally friendly as it does not use greenhouse gases. Gadolinium is the reference material for this application at ambient temperature. It presents high efficiency but also drawbacks: a high cost, limited supply and sensitivity to corrosion [8–10]. Manganites, of formula $Ln_{1-x}A_xMnO_3$ (*Ln*: a rare earth; *A*: alkaline or alkaline earth metal) do not present such drawbacks. This family of materials presents a large variety of structural, magnetic and electronic properties depending on the nature and concentration of the cations. Some compositions present magnetocaloric performances close to that of Gd; among them, the $La_{0.7}Ca_{0.3}MnO_3$ compound, which displays a Curie Temperature T_C, at which the magnetocaloric effect is maximum, close to ambient temperature (256 K) [11]. The properties vary with the structure, microstructure and stoichiometry and hence with the synthesis and sintering procedures as shown, for example, for p-doped manganites [12–15]. The most widely used method to obtain and densify these materials is the solid-solid (also called ceramic) route [16–19]. Modification of the experimental conditions, such as sintering and annealing temperature and atmosphere (partial oxygen pressure), has been used to tune their stoichiometry [20]. Depending on the cationic deficiency concentration, different crystallographic structures and magnetic behaviors were obtained. The Pechini method, a soft chemistry sol-gel procedure, was also used to prepare substituted manganites [13,14,21–26]. This method presents some advantages: it leads to pure, homogeneous and quite stoichiometric solid solutions, even complex, at low synthesis temperature within a short reaction time, allowing the preparation of nanostructured materials and reducing the associated cost. Nanostructuration has an impact on the magnetic properties. Indeed, surface disorder is taking more importance as the grain size decreases, leading to a slight decrease of the values of Curie temperature, saturation magnetization and magnetic entropy variation (ΔS_M). However, concomitantly, the magnetic transition may expand to a wider temperature range. These two effects can compensate each other

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and nanostructuration does not always have a negative impact on the relative cooling powder (RCP) value [24,25]: when superparamagnetic nanosclusters are formed above T_C, a higher RCP has been observed [23]. Changes in the nature of the magnetic transition can also be expected for nanostructured $La_{0.7}Ca_{0.3}MnO_3$ compound. The evolution of the para-to-ferromagnetic transition from a first order (corresponding to a sharp variation of the magnetization with temperature around T_C) to a second order (characterized by a lower maximum of entropy change but on a larger temperature range) contributes to the increase of the RCP value, which is valuable for magnetocaloric application.

More recently we used pulsed current sintering technology, also known as Spark Plasma Sintering (SPS) to produce dense nanostructured materials thanks to a quick thermal treatment under pressure [27,28]. We also prepared manganites from the parent oxides or hydroxides by reactive SPS (RSPS) route [12,29]. Effects on microstructure and on the oxygen stoichiometry, and thus on the magnetic properties were observed. However, an exhaustive study on a same composition is lacking to understand the exact influence of the synthesis and sintering conditions on the chemical and physical properties. Consequently, we report here the variations of stoichiometry, structure, microstructure, magnetic and magnetocaloric properties of the $La_{0.7}Ca_{0.3}MnO_3$ ceramic depending on the synthesis method (solid-solid, sol-gel and polyol soft chemistry routes or reactive SPS) and on the sintering technique (traditional furnace or SPS).

2. Experimental procedure

2.1. Chemicals

The solvents, ethylene glycol (EG, 99%) and diethylene glycol (DEG, 99%) were supplied by Acros. La_2O_3 (99.9%) and $La(OH)_3$ (99.95%) were purchased to Alfa Aesar. The other chemicals, $CaCO_3$ (≥ 99%), MnO_2 (99.99%), $La(NO_3)_3.6H_2O$ (99.9%), $Mn(NO_3)_2.4H_2O$(≥99.99%), $Ca(NO_3)_2.4H_2O$(≥ 99.0%), $Ca(OH)_2$ (≥ 96%), nitric acid (NA, 69%) and citric acid (CA, 99%) were from Sigma Aldrich.

2.2. Synthesis

The densified $La_{0.7}Ca_{0.3}MnO_3$compound was obtained by 6 different routes:

Ceramic.1300. La_2O_3, $CaCO_3$ and MnO_2 raw oxides were intimately mixed in stoichiometric ratio and then heated in a conventional oven in air at 1000 °C for 48 h. The obtained powder was subsequently pressed as a pellet (Ø = 13 mm) under an uniaxial pressure of 5 tons and heated in air at 1300 °C for 48 h, with intermediate grinding and annealing at 1100 and 1200 °C.

Sol-gel.1000 and Sol-gel.SPS800. Stoichiometric amounts of La_2O_3, $CaCO_3$, and MnO_2 were dissolved in nitric acid. Citric acid (CA) and ethylene glycol (EG) were added to the previous solution with the total metal:CA:EG molar ratio of 1:5:5. The resulting solution was left evaporating at 130 °C until a viscous gel-like product was formed, subsequently dried by additional heating under air up to 300 °C and then annealed at 500 °C for 1 h. The as-obtained powder was finally sintered either in a conventional oven at 1000 °C for 48 h (Sol-gel.1000) or by SPS at 800 °C for 10 min with upon rate 100 °C min^{-1}, under vacuum (~30 Pa) and applying continuously a uniaxial pressure of 100 MPa (Sol-gel.SPS800) [9,16]. Spark plasma sintering (SPS) was carried out using a Dr. Sinter 515S Syntex setup belonging to the “Plateforme de Frittage Ile de France” (Thiais, France).

Polyol.1000 and Polyol.SPS800. Stoichiometric amounts of La, Ca and Mn nitrate salts were dissolved in 125 mL of DEG. Typically, the concentrations of Mn nitrate was 7.339 mM. The reaction solution was heated up to 194 °C (heating rate of 6 °C.min^{-1}) for 2 h under reflux. During heating, the initially transparent solution turned out to dark brown. The reaction medium was then quenched in an ice bath. The black-brown precipitate formed was recovered by centrifugation and washed 3 times with ethanol through repeated sonication and centrifugation cycles. It was then dried at 50 °C overnight and subsequently annealed in air at 500 °C for 1 h. The two sintering procedures described here above were also used to prepare dense pellets: Polyol.1000 sample was obtained by heating under air in a conventional furnace at 1000 °C for 48 h and Polyol.SPS800 by SPS at 800 °C and 100 MPa for 10 min.

R-SPS.800. As-purchased $La(OH)_3$, $Ca(OH)_2$ and MnO_2, were carefully weighted and mixed in stoichiometric ratio in an oscillating milling machine (Retsch MM200) for 20 min. The mixture was then introduced into the SPS machine and treated, under vacuum (~30 Pa), at 500 °C for 2 min (heating rate of 100 °C min^{-1}) and then at 800 °C for 10 min (heating rate of 50 °C min^{-1}), applying a continuous uniaxial pressure of 100 MPa.

2.3. Material characterization

The X-Ray Diffraction (XRD) patterns of all the produced powders and pellets were recorded, at room temperature, on an Empyrean Panalytical diffractometer in the Bragg-Brentano reflexion configuration equipped with a Cu-Kα anode (λ = 1.5418 Å) in the 10–90° 2θ range using a step size of 0.0262°. Divergent and scattering slits of 1 and 2°, respectively, were placed in the incident beam path. The pellets were ground and introduced in a powder sampling plate. The patterns were analyzed with the Rietveld method [30] using FULLPROF software [31] to determine the main structural parameters of each studied phase. The global chemical composition was also checked by induced coupled plasma mass spectrometry (ICP-MS) at the CNRS French analytical facilities (Vernaison, France). The Mn^{4+}/Mn^{3+} ratio and oxygen content were determined by iodometric titration [27].

Finally, the microstructure of all the produced ceramics was studied by Scanning Electron Microscopy (SEM) using a Supra40 ZEISS FEG-SEM microscope working at 5 kV and equipped with a In Lens detector. It was also addressed by measuring the density of the pellets using a Micromeritics Accu-Pyc 1330 helium pycnometer.

2.4. Magnetic and magnetocaloric measurements

The variation of the magnetization M as a function of the temperature in the 10–300 K range under a magnetic field H of 0.05 T and its variation as a function of the magnetic field in the 0–5 T range for different temperatures were measured on all the produced ceramics, using a XL Quantum design SQUID magnetometer. One piece of the obtained pellets was powdered and placed in a plastic diamagnetic tube which was subsequently introduced into the magnetometer.

Using the collected M(H) data, the magnetic entropy change ΔS_M was deduced, for each temperature, from the discreet form of the following relationship, where H_{max} is the maximum value of the external applied field [32]:

$$\Delta S_M(T,H) = S_M(T,H) - S_M(T,0) = \int_0^{H_{max}} \left(\frac{\partial M}{\partial T}\right)_H dH$$