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Low-field magnetoresistance of $La_{0.7}Sr_{0.3}MnO_3$ nanoceramics processed by different precursor approaches and powder compaction techniques

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Effect of the precursor approach, the method of nanosized powders pressing, and the sintering temperature of ceramic samples on the low-field magnetoresistance of nanosized $La_{0.7}Sr_{0.3}MnO_3$ ceramics was studied.

The discovery of a ‘colossal’ magnetoresistance in doped perovskite manganites with the general formula $R_{1-x}A_xMnO_3$ (R is La, Pr or Nd; A is Ca, Sr, Ba or Pb) caused interest in this class of magnetosensitive materials.[1–4] Although no clear theory is available, an attempt was made to explain the magnetotransport properties of these complex oxides in terms of a double-exchange mechanism between Mn^{3+} and Mn^{4+} ions.[5] The large negative magnetoresistance of the doped manganites near the Curie temperature results from the suppression of spin fluctuations by a magnetic field and may be associated with both fundamental processes (colossal magnetoresistance in strong fields) and the influence of grain boundaries (tunneling effect in low fields). In low magnetic fields (~0.1 T), the magnetoresistance of polycrystalline doped manganites depends on the grain size.[2–4] Therefore, the preparation of nanostructural ceramics with a grain size smaller than 100 nm is a topical problem from the point of view of practical application. For this purpose, a wide variety of solution-phase approaches have been proposed.[6]

The synthesis of nanostructural ceramics met the problem of controlling the recrystallization process when approaching the theoretical limit of density.[7,8] The low ability of nanosized powders to compaction additionally complicates this problem. Thus, the preferred routes of nanostructural ceramics preparation are high-energy methods of compaction, since the application of these methods significantly decreases the temperature and duration of sintering.[9,10] The method of pulsed magnetic compaction (PMC) makes it possible not only to reach a high relative density of samples (0.7–0.8) using nanopowders but also to mechanically activate particles by producing a variety of point and extended defects.

Here we describe the synthesis of $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) nanoparticles *via* the thermal decomposition of precursors at a relatively low temperature (700 °C). This work is also focused on the investigation of how the chosen precursor approach, different methods of nanosized powders compaction, and sintering temperature affect the low-field magnetoresistance (LFMR) of corresponding LSMO nanoceramics.

A solution of La, Sr and Mn chelates was obtained using pure-grade diethylenetriaminepentaacetic acid (H_5L) and analytical-grade $Mn(MeCOO)_2\cdot 4H_2O$, La_2O_3 and $SrCO_3$. First of all solutions of heterobimetallic lanthanum–manganese chelate LaMnL and strontium–manganese chelate HSrMnL were prepared by refluxing the suspensions of corresponding reagents in water. After that the polynuclear solution with the molar ratio $[La^{3+}]:[Sr^{2+}]:[Mn^{2+}] = 0.7:0.3:1$ was prepared by mixing solutions of LaMnL and HSrMnL in an appropriate stoichiometry. The concentration of the resultant solution was 0.44 mol dm^{-3} in terms of Mn^{2+}, pH 4. In the gelation process, we used acrylamide, *N*,*N*′-methylenebisacrylamide and α,α′-azoisobutyronitrile (Merck). We obtained solid precursors from the chelate solution by two approaches:[11] (i) gelation of solution followed by dehydration at 90 °C in air (‘GEL’ samples) and (ii) microwave dehydration of solution (‘MW’ samples). By both procedures we obtained solid foams, which were then heat-treated at 700 °C (oxygen atmosphere, 10 h) to form phase-pure perovskite-like LSMO, as established by X-ray diffraction (XRD).[12] The resultant powders were compacted into pellets, which were air-annealed at 700, 800, 900, 1000 and 1100 °C for 15 h to produce ceramics with different grain sizes.

The phase composition of complex oxides was detected by XRD (a DRON-3M automated diffractometer). The average grain size in powders was determined by the Debye–Scherrer equation using a reflection in the 2θ range from 45 to 48°. The powders were converted into pellets using normal pressing (~400 MPa) and the PMC (with an amplitude of pressure pulses of 1.5 GPa and a pulse duration of 300–500 μs). Density measurements were carried out by a geometrical method. The mole ratio $Mn^{4+}/(Mn^{4+} + Mn^{3+})$ and the oxygen non-stoichiometry index δ of ceramic samples obtained were determined by iodometric titration [the relative error in calculation of the $Mn^{4+}/(Mn^{4+} + Mn^{3+})$ ratio was 3%]. The grain size of nanopowders and the microstructure of ceramics were examined on a JEOL JEM-2000FX II electron microscope (accelerating voltage of 200 kV). Transition electron microscopy (TEM) and scanning electron microscopy (SEM) images were obtained

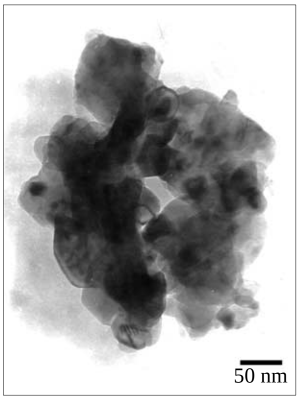

Figure 1 TEM image of LSMO powder prepared by microwave treatment of the initial solution.

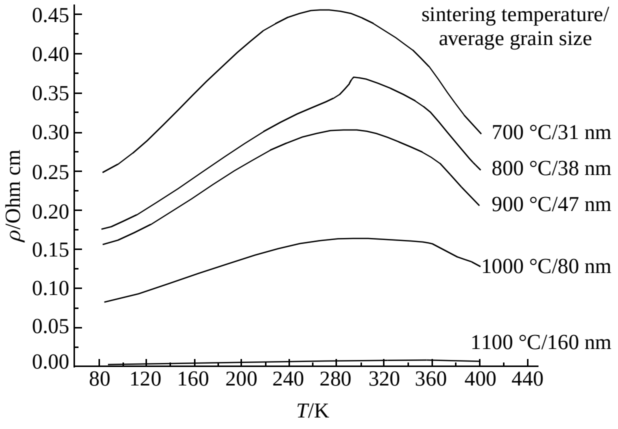

Figure 2 Resistivity *vs.* temperature for LSMO ceramic samples.

at magnifications of 200000 and 100000, respectively. Resistivity measurements were performed for samples approximately 5×1×1 mm in size by a standard four-probe technique using a Keithly-2700 unit (resistivity curves were obtained by heating the samples from liquid nitrogen temperature to 400 K). LFMR at the liquid-nitrogen temperature was defined as MR = $[R(B) - R(0)]/R(0)] \times 100\%$, where $R(B)$ and $R(0)$ are the resistances in the applied magnetic field B and in the zero field, respectively.

To transform the solution of polynuclear La, Sr, and Mn diethylenetriaminepentaacetates into a solid precursor, two approaches were used: (i) gelation by acrylamide polymerization and (ii) microwave treatment. After annealing the precursors in an oxygen flow at 700 °C, LSMO nanopowders were produced, and the average grain size of about 30 nm was in both cases according to calculations by the Debye–Scherrer equation and TEM images (Figure 1). To obtain ceramic samples with different densities, the resultant powders were converted into pellets by normal pressing and PMC (relative densities of compacts were about 45 and 70%, respectively).

Table 1 summarises the characteristics of LSMO ceramics processed by microwave treatment and normal pressing. Iodometric titration demonstrates that ceramic sample no. 1 is ‘over-oxidised’ and characterised by a positive oxygen nonstoichiometry index δ. This indicates that a cationic sub-lattice of the perovskite-like structure of the sample contains vacancies. At the same time, sample nos. 3–5 have negative δ values, which point to the existence of oxygen vacancies in the anionic sub-lattice. Thus, an increase in the sintering temperature from 700 to 1100 °C leads, as established by iodometric titration, to an increase in the number of vacancies in the anionic sub-lattice of the perovskite-like structure, which is caused by elimination of oxygen by the following quasi-chemical reaction:

$$O_o^x \rightarrow 0.5O_2\uparrow + V_o^{\bullet\bullet} + 2\bar{e},$$

where O_o^x are oxygen atoms in the perovskite-like structure, $V_o^{\bullet\bullet}$ are oxygen vacancies, and $\bar{e}$ are electrons.

As follows from Table 1, the increase in sintering temperature of the initial powder from 700 to 1100 °C leads to an approximately fivefold increase in the average grain size.

The resistive properties of ceramic sample nos. 1–5 are presented in Figure 2. It is shown that an increase in the sintering temperature from 700 to 1100 °C leads to a decrease in resistivity by a factor of 45. This is reasonable, since the total resistance of a sample is the sum of resistances of grains and their boundaries. The sum resistance of sample no. 1 (Table 1), obtained at the lowest sintering temperature (700 °C), is dominated by the resistance of grain boundaries, which is reflected by the existence of a broad peak in the resistivity curve at $T = 272$ K. This temperature is significantly below the Curie point and is unrelated to ferromagnetic ordering in LSMO. With an increase in the sintering temperature, the internal surface of a ceramic sample decreases and contacts between grains become ordered, which results in a decrease of the resistance. In sample no. 5 obtained at the highest sintering temperature (1100 °C), the overall resistance of grain boundaries becomes smaller than the overall resistance of the grains. As a result, the plot of resistance versus temperature shows an extra peak at $T = 368$ K corresponding to the Curie point.

Table 1 Characteristics of $La_{0.7}Sr_{0.3}MnO_{3+\delta}$ ceramic samples produced by the sintering of the initial powder with an average grain size of 31 nm.

Sample no.	Sintering temperature/ °C	Mole ratio $Mn^{4+}/(Mn^{4+} + Mn^{3+})$ (%)	Oxygen non-stoichiometry index, δ	Grain size/nm
1	700	32.0	0.010	31
2	800	30.2	0.001	38
3	900	28.4	–0.008	47
4	1000	28.3	–0.009	80
5	1100	26.3	–0.019	160

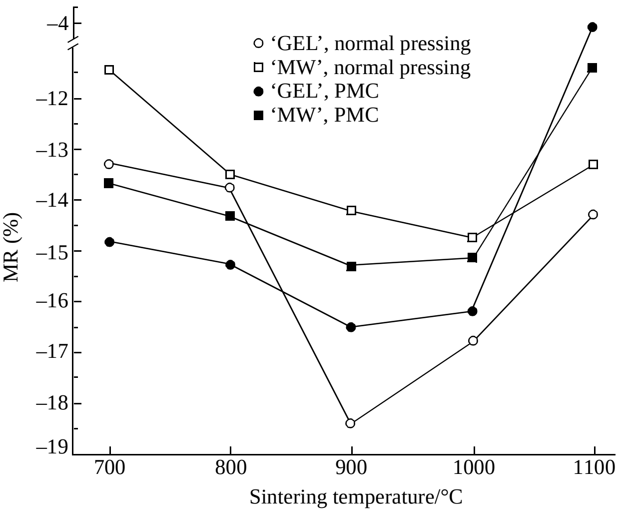

Figure 3 LFMR effect on sintering temperature for LSMO ceramics (in the applied magnetic field of 0.1 T).

The dependence of the LFMR (magnetic field of 0.1 T) on the sintering temperature of LSMO ceramic samples is illustrated in Figure 3. Note that the character of the sintering temperature change in the LFMR is the same for all kinds of ceramic samples. Figure 3 demonstrates that an increase in grain size while the temperature of sintering gradually increased from 700 to 900 or 1000 °C (in the case of ceramics processed by microwave treatment and normal pressing) leads to an increase in the LFMR. A further increase in the sintering temperature up to 1100 °C and, hence, in grain size brings about a certain decrease in the effect magnitude. In our opinion, this non-monotonic dependence of the LFMR on the sintering temperature of ceramic samples is determined not only by the size of nascent grains but also by the degree of their magnetic ‘ordering’. In all probability, grains and their boundaries in ceramic samples obtained at lower sintering temperatures (700–900 °C) are poorly formed domains in terms of magnetic ordering with a high concentration of defects on which the parasitic scattering of charge carriers takes place. An increase in the sintering temperature intensifies the formation of ferromagnetic domains and improves the quality of boundaries, on the one hand, and leads to an increase in grain size, on the other hand. These phenomena produce opposite actions on LFMR, which is resulted in the emergence of an extreme point on the curve of LFMR versus sintering temperature. In samples obtained at the highest sintering temperature (1100 °C), the target effect is most likely dominated by the contribution of grains resistance, which is manifested in a decrease in the LFMR. As shown in Figure 3, the applying of PMC to initial nanosized LSMO powders with pressure pulses of 1.5 GPa causes an increase in the LFMR (at sintering temperatures of 700 and 800 °C for the ceramics ‘GEL’, and at 700, 800, 900 and 1000 °C for the ceramics ‘MW’) in comparison with normal pressing (~400 MPa). This result can be explained from the point of view that PMC provides the formation of dense nanostructural ceramics with a big number of grain boundaries and point defects. The quality of as-prepared nanoceramics in terms of magnetic ordering of grain boundaries is kept while sintering at a low temperature. At the same time, when samples produced by PMC are sintered at higher temperatures (up to 1100 °C), the LFMR decreases in comparison with the normal pressing in both cases of the chosen precursor approach. It is caused by the intense diffusion between dense connected grains and their active sintering at higher temperatures, which is accompanied by a decrease in grain boundaries contribution in the ceramics, processed by such a powerful method as PMC.

Comparing the magnetoresistive properties of ceramic samples ‘GEL’ and ‘MW’, we note that the method of initial solution transformation to the solid precursor influences quite definitely on the LFMR. As follows from Figure 3, ceramics ‘GEL’ demonstrates higher values of LFMR than samples ‘MW’ in the entire range of sintering temperatures while the same method of nanopowders compaction is applied. In all probability, the gelation of the solution of polynuclear diethylenetriaminepentaacetates creates the precursor that provides the formation of

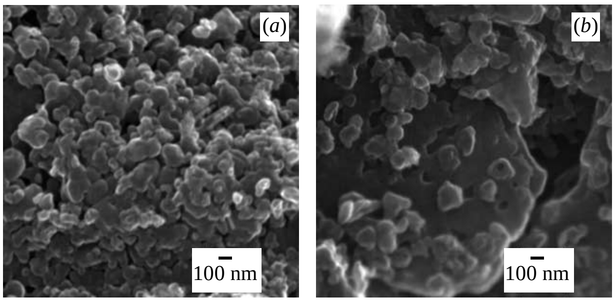

Figure 4 SEM images of LSMO ceramics produced by normal pressing and sintered at 700 °C: (*a*) 'GEL' and (*b*) 'MW'.

nanostructural LSMO ceramics with the more uniform grain size and fine grain boundaries in comparison with the ceramics produced by microwave treatment (Figure 4). As shown in Figure 3, the ceramics 'GEL', processed by normal pressing and heat-treated at 900 °C is a more interesting object from the point of view of possible practical application due to the highest value of magnetoresistance (about –18.5% in an applied magnetic field of 0.1 T) among the test samples.

In conclusion, we found that the nanosized powders of LSMO with an average grain size of 30 nm can be successfully synthesised by polynuclear chelate homogenization in water solution followed by the use of different precursor approaches and the annealing of precursors in an oxygen flow at a low temperature (700 °C).

The non-monotonic dependence of LFMR on sintering temperature is presumably caused by the interplay of two factors: the grain size, on the one hand, and the degree of magnetic ordering of grains and their boundaries, on the other hand. The grain growth and formation of ferromagnetic domains and fine boundaries, which take place while the temperature of sintering increases, produce opposite actions on magnetoresistance, so that its dependence on the sintering temperature of the initial nanosized powder has an extreme point.

More importantly, we also demonstrated that differences in the 'prehistory' of the final ceramics can result in different LFMR values. Thus, the application of PMC to initial nanosized LSMO powders in combination with relatively low sintering temperatures leads to an increase in the LFMR in comparison with normal pressing. Moreover, ceramics 'GEL' shows higher values of LFMR than samples 'MW' that can be explained due to formation of nanostructural LSMO ceramics with a more uniform grain size and fine grain boundaries. A very large LFMR (about –18.5%) was achieved for the LSMO ceramics 'GEL' processed by normal pressing and sintered at 900 °C.

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