Proceedings of the 16th Czech and Slovak Conference on Magnetism, Košice, Slovakia, June 13–17, 2016

Influence of Spark Plasma Sintering on Microstructure and Properties of Bulk LaCaSrMnO Magnetocaloric Materials

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Polycrystalline $La_{0.67}Ca_{0.33-x}Sr_xMnO_3$ (x = 0.33, 0.03, 0) (LCSM) perovskite samples treated by spark plasma sintering technique were investigated. This study proved influence of the sintering temperature on microstructure of these perovskite ceramics. The thermogravimetric measurements revealed the possibility of increase of oxygen content in studied LCSM samples by additional annealing under oxygen atmosphere and low temperature. Finally, the effect of this annealing on magnetic properties was demonstrated.

DOI: 10.12693/APhysPolA.131.804
PACS/topics: 75.47.Lx, 61.72.–y, 75.30.Kz, 77.80.B–, 81.70.Pg, 81.20.Ev, 81.30.Fb

1. Introduction

A wide range of different types of materials, from metals to ceramics, exhibit the magnetocaloric effect, such as also the polycrystalline Ca- and Sr-doped lanthanum manganites, $La_{0.67}Ca_{0.33-x}Sr_xMnO_3$ ($0 \leq x \leq 0.33$) with the perovskite structure. This compound belongs to the materials that exhibit the magnetocaloric effect in a temperature range around their respective Curie temperature. Depending on composition parameter x the Curie temperature can be adjusted between 260 K ($x = 0$) and 370 K ($x = 0.33$) [1, 2]. Therefore, this type of compound is very interesting and potential material for practical applications.

Technologically the most problematic step in preparation of these materials is sintering of the $La_{0.67}Ca_{0.33-x}Sr_xMnO_3$ samples. It requires temperatures higher than 1400 °C to decrease porosity into reasonable level [3]. At these temperatures the grain growth leads to development of big grains and consequently to cracking at cooling due to dilatation stresses induced by anisotropy of thermal expansion of $La_{0.67}Ca_{0.33-x}Sr_xMnO_3$ phase.

The spark plasma sintering (SPS) technique is considered as very suitable for sintering of powder materials at lower temperatures and for preventing of grain growth [4, 5].

In this contribution microstructure and magnetic properties of polycrystalline $La_{0.67}Ca_{0.33-x}Sr_xMnO_3$ (x = 0.33, 0.03, 0) perovskite samples prepared by SPS technique were investigated.

2. Experimental

Polycrystalline LCSM samples were prepared with the following compositions: sample A: $La_{0.67}Sr_{0.33}Mn_{1.05}O_3$, sample B: $La_{0.67}Sr_{0.33}Mn_{1.05}O_3$ + $La_{0.67}Ca_{0.3}Sr_{0.03}Mn_{1.05}O_3$ (1:1) and sample C: $La_{0.67}Sr_{0.33}Mn_{1.05}O_3$ + $La_{0.67}Ca_{0.3}Sr_{0.03}Mn_{1.05}O_3$ + $La_{0.67}Ca_{0.33}Mn_{1.05}O_3$ (1:1:1) with the aim to obtain material with broad temperature interval with magnetocaloric effect. The samples were treated by SPS.

Firstly, the stoichiometric amounts of the starting materials — La_2O_3, CaO, $SrCO_3$ and MnO_2, were mixed in a shaker for 30 min and then intensively milled for 15 min in a friction mill. The homogenized milled mixtures of powders were subsequently calcinated twice: the first time at the temperature of 1200 °C for 16 h and the second time at the temperature of 1300 °C for 6 h (with heating and cooling rates of 100 °C/h in both cases). After each calcination the powders were intensively milled for 15 min in the friction mill.

Finally, the samples were treated under dynamic vacuum by SPS (FCT Systeme GmbH, HD25, Rauenstein, Germany) in DC mode according to the following steps. In the first step, the powder was inserted into a graphite die (15 mm diameter), then placed into the working chamber. The samples were heating up at the rate of 100 °C/min to the sintering temperatures, dwell 20 min and then cooling to the room temperature with cooling rate of 100 °C/min. Three different sintering temperatures (TSPS) and uniaxial pressure of 50 MPa were applied. For sample A — TSPS = 1000 °C, sample B — TSPS = 1250 °C and for sample C — TSPS = 1150 °C.

Microstructural analysis of LCSM samples was performed on polished surfaces using a scanning electronic microscope (SEM — TESCAN MIRA 3). The energy dispersive spectrometer (EDS) analysis was used for determination of new type of phases in the samples.

The thermogravimetric (TG) analyses were carried out in the temperature range from 40 °C to 1000 °C using Netzsch STA 449 F1 Jupiter thermal analyzer. The experiments were performed with a heating and cooling rate of 5 K/min in high purity oxygen atmosphere. After SPS process a part of each sample for TG measurements was grinded into the powder and the other parts were measured as the small pieces. For each measurement we used a

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base line in order to subtract the signals from a sample holder and a crucible.

The magnetic properties of the samples were measured by the Quantum Design Magnetic Properties Measurement System (MPMS XL5) due to determination of changes in magnetic properties of the samples. The thermomagnetic dependences were measured in magnetic field of 8000 A/m and in temperature range from 5 K to 370 K. The isothermal magnetization curves were examined in magnetic fields up to ±5 T in different temperatures for each sample such that the sample was fully ferromagnetic at this temperature. These temperatures were estimated based on shape of thermomagnetic dependences.

3. Results and discussion

As we reported in previous work [3], the LCSM materials sintered by conventional solid state synthesis exhibit very low strength, high porosity and sintering temperature to obtain must be higher than 1400 °C. The SPS technique allows the preparation of the compact materials with high-density at a relatively low temperature and shorter treatment time compared to conventional sintering techniques [4].

The SEM micrographs of the LCSM samples after SPS sintering are present in Fig. 1a–c. The porosity was higher at the lowest temperature TSPS = 1000 °C (Fig. 1a). Higher TSPS = 1250 °C (sample B, Fig. 1b) and 1150 °C (sample C, Fig. 1c) leads to a lower porosity but allows the growth of the grains and formation of new phases in the samples.

The EDS analyses confirmed the formation of plate like particles: $La_{1.3}Ca_{0.35}Sr_{0.41}MnO_x$ (Fig. 1b, spectrum S1), globular particles: $Ca_{0.22}MnO_x$ (Fig. 1b, spectrum S2) and eutectic structure (Fig. 1b, spectrum S3) in the sample B.

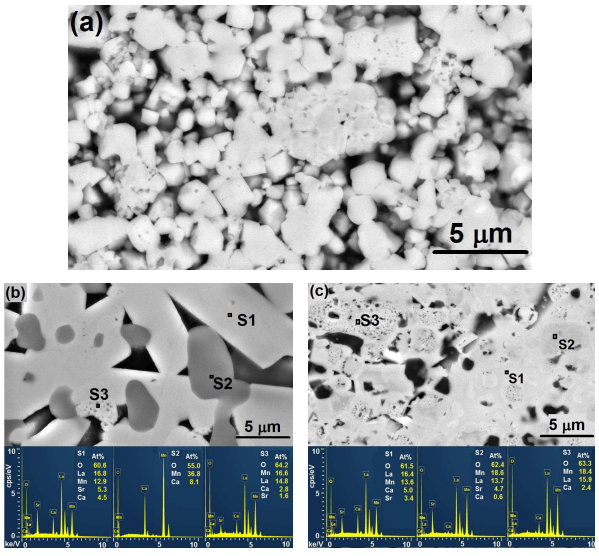

Fig. 1. SEM micrographs and EDX analyses of LCSM samples after SPS: sample A sintering at 1000 °C (a), sample B sintering at 1250 °C (b) and sample C sintering at 1150 °C (c).

In the case of the sample C there were detected particles with content of $La_{1.2}Ca_{0.37}Sr_{0.25}MnO_x$ (Fig. 1c, spectrum S1), $La_{0.74}Ca_{0.03}Sr_{0.25}MnO_x$ (Fig. 1c, spectrum S2) and eutectic structure (Fig. 1c, spectrum S3).

The samples processed by SPS in vacuum have low oxygen content. The oxygen (O_2) deficiency has an impact on the valence state of Mn and thereby on the physical properties of studied LCSM samples. Therefore, after SPS the samples must be annealed for increase of oxygen content.

For investigation of oxygen saturation in LCSM samples we used the thermogravimetric analysis and the results of TG measurements of powdered samples are shown in Fig. 2.

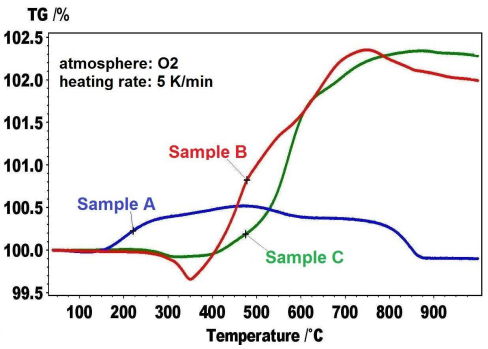

Fig. 2. TG analyses of powdered samples in flowing oxygen atmosphere with the heating rate of 5 K/min from 40 to 1000 °C.

From these results we determined the temperatures, where we have the maximum value of oxygen saturation for each sample. The maximum value of oxygen was reached for the sample A at about 450 °C and for the samples B and C at about 780 °C. As could be seen in Fig. 2, at higher temperatures as above mentioned we observe re-evolving of oxygen from the samples that is undesirable effect for us.

Subsequently, the weight changes of small pieces of each sintered sample were isothermally measured at determined temperatures and the results are presented in Fig. 3a for the sample A and 3b for the samples B–C. After reaching of 450 °C for the sample A (Fig. 3a) and 780 °C for the sample B–C (Fig. 3b), two-hour annealing process was applied in order to increase oxygen content in the samples. As can be seen in Fig. 3a in the sample A the oxygen content increased about 0.34%. Higher increment of the oxygen content was observed in the sample B (3.24%) and the sample C (2.15%) (Fig. 3b). It is important to note that all samples increased their oxygen content mainly during heating process. After two-hour annealing process at the highest temperatures followed cooling down and in Fig. 3a,b is clearly seen that oxygen content did not significantly change and remained more-less at the highest value after cooling process. Then, these samples were used for magnetization measurements.

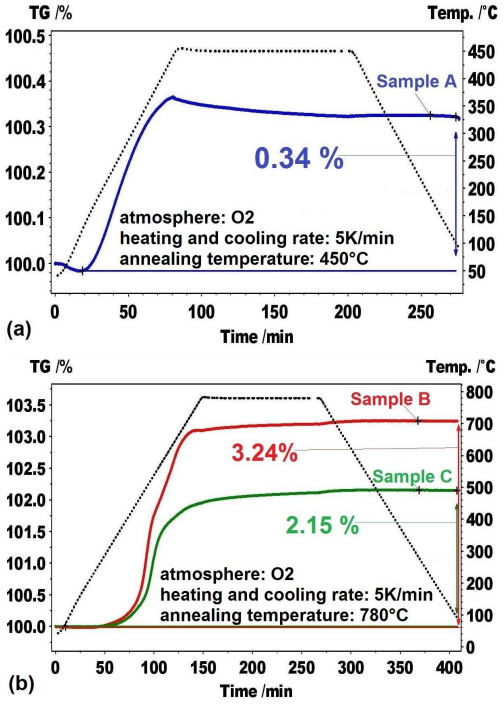

Fig. 3. TG measurements of the small pieces of the samples performed in O_2 atmosphere with two-hour annealing at 450 °C for the sample A (a) and at 780 °C for the samples B–C (b). The dashed line represents the measurement process.

The thermomagnetic curves of all samples after SPS process and annealing in O_2 atmosphere are shown in Fig. 4. The substantial changes in magnetic properties of all samples can be seen after annealing in O_2 atmosphere. The transition from ferro-ferrimagnetic to paramagnetic state is significantly shifted to higher temperatures.

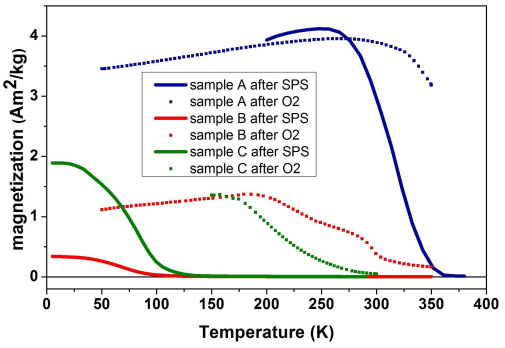

Fig. 4. Thermomagnetic dependences of the samples after SPS process and annealing in O_2 atmosphere.

The influence of oxygen atmosphere annealing is evident also on the shape of the isothermal magnetization curves, as it is visible in Fig. 5. These curves were measured at 200 K for the sample A and at 50 K for the samples B and C after SPS process and at 100 K for all samples after annealing in O_2 atmosphere. As it is shown in Fig. 5 after SPS process, the samples B and C contain the material with significant part of paramagnetic component. After annealing in pure oxygen atmosphere the shape of curves indicates increase of ferromagnetic phase in both samples. In sample A, which was ferromagnetic already after SPS process, the annealing in oxygen atmosphere induces the significant increase of saturation magnetization.

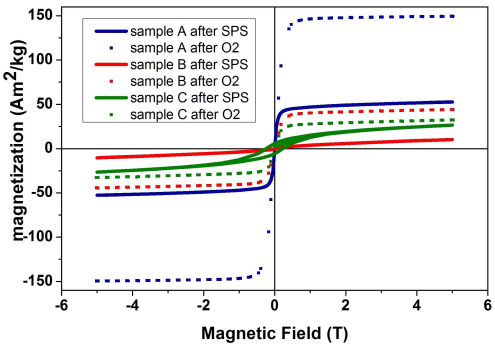

Fig. 5. Isotherm magnetization curves of the samples after SPS process and annealing in O_2 atmosphere.

From presented results it is evident that the additional annealing in a pure oxygen atmosphere affected magnetic properties of studied samples in such way that transient temperature from ferro-ferrimagnetic to paramagnetic state is shifted to higher temperatures and magnetization is increased.

4. Conclusion

The SPS process permits to prepare the LCSM ceramics with high density at lower temperature and shorter sintering time. SPS treatment in dynamic vacuum caused partial decomposition of originally single-phase materials as well as some deficiency in oxygen content. The thermogravimetric measurements showed that oxygen content could be changed by additional oxygenation after SPS process that has a significant impact on the magnetic behavior of studied samples.

Acknowledgments

This work was supported by the project: ITMS 26220120035, ITMS 26220220061, ITMS 26220220041, APVV No. 0330-12, VEGA 2/0121/16, VEGA 1/0377/16 and Stefanik Project SK-FR-2013-0025/PHC STEFANIK 2014-2015 (No. 31766RC).

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