

# Magnetic Properties of $\text{La}_{0.85}\text{Ag}_{0.15}\text{MnO}_3$ Nano-Powders Under Pressure

M. ANTOŇÁK<sup>a,\*</sup>, M. MIHALIK<sup>a</sup>, M. ZENTKOVÁ<sup>a</sup>, M. MIHALIK JR.<sup>a,b</sup>, M. VAVRA<sup>a</sup>,  
J. LAZÚROVÁ<sup>a</sup>, M. FITTA<sup>c</sup>, M. BALANDA<sup>c</sup>

<sup>a</sup>Institute of Experimental Physics SAS, Watsonova 47, 040 01 Košice, Slovakia

<sup>b</sup>Institute of Chemistry, Faculty of Science, P. J. Šafárik University, Moyzesova 11, 041 54 Košice, Slovakia

<sup>c</sup>Polish Academy of Sciences, Radzikowskiego 152, Kraków, Poland

In our paper we present effect of pressure on magnetic properties of  $\text{La}_{0.85}\text{Ag}_{0.15}\text{MnO}_3$  nanopowders prepared by glycine-nitrate method. The particle size and crystal structure were modified by heat treatment. The average size of particle varies from about 25 nm for as prepared sample to 60 nm for annealed sample. Crystal structure changes from orthorhombic to rhombohedral after annealing at 600 °C/2 hours. The Curie temperature increases with annealing and is more than doubled after annealing at 600 °C/2 hours. The exchange bias phenomenon was observed in samples with orthorhombic crystal structure with average particle size of about 25 nm. Pressure effect on the Curie temperature  $T_C$ , saturated magnetization  $\mu_s$  and exchange bias field  $H_E$  is negligible in this case. In the case of the samples with rhombohedral structure,  $T_C$ ,  $\mu_s$  and remnant magnetization  $\mu_r$  increase with pressure; the coercive field decreases with pressure.

DOI: [10.12693/APhysPolA.126.296](https://doi.org/10.12693/APhysPolA.126.296)

PACS: 75.50.-y, 75.50.Tt, 75.47.Lx, 75.30Kz

The mixed-valence manganese oxides of the general formula  $\text{La}_{1-x}\text{A}_x\text{MnO}_3$  (A is a divalent ion like Ca, Sr, Ba and Pb) are a subject of interest due to a desire to understand and exploit the large negative magnetoresistance and magnetocaloric effects [1]. The ratio of  $\text{Mn}^{3+}/\text{Mn}^{4+}$  is an important factor to show insulator-to-metal (I-M) transition and ferromagnetic phase transition in manganites. It is possible to achieve an equal amount of hole-doping with just half the quantity of monovalent ions such  $\text{Ag}^+$ . Group of  $\text{La}_{1-x}\text{Ag}_x\text{MnO}_3$  manganites provides a series of new oxides to study magnetocaloric effect [2] insulator-to-metal transition and colossal magnetoresistance [3] at room temperature. Recently exchange bias (EB) phenomena were first observed in the  $\text{La}_{1-x}\text{Ag}_x\text{MnO}_3$  as prepared and heat treated (300 °C/2 hours) nanopowders ( $x = 0.10, 0.15$  and  $0.20$ ) which were synthesized by self-combustion glycine-nitrate method [4]. In our paper we study pressure effect on magnetic properties of  $\text{La}_{0.85}\text{Ag}_{0.15}\text{MnO}_3$  nanopowders.

Preparation of nanopowders followed the glycine-nitrate method, where glycine was used as fuel and nitrates as oxidants [5]. The X-ray powder diffraction (XRD) measurements have been carried out on the X'Pert PRO diffractometer with Cu- $K_\alpha$  radiation ( $\lambda_1 = 1.54056$  Å,  $\lambda_2 = 1.54440$  Å) and the XRD patterns were identified with the FullProf program based on the Rietveld method [6]. Annealed sample at 300 °C (sample 1) crystallizes in orthorhombic crystal structure (space group  $Pnma$ ) with lattice parameters:  $a = 0.5611(3)$  nm;

$b = 0.7755(4)$  nm;  $c = 0.5530(3)$  nm;  $\text{MnO}_6$ -building blocks of crystal structure are distorted and tilted. The average size of nanoparticles for sample 1 is about 25 nm. Traces of segregated silver were observed. Silver content increases with increasing temperature of annealing. Samples annealed at 600 °C (sample 2) adopt rhombohedral structure (space group  $R\bar{3}c$ ) with lattice parameters  $a = 0.5502(2)$  nm;  $c = 1.3361(3)$  nm and average size of nanoparticles of about 60 nm. All magnetization measurements were performed in a SQUID magnetometer MPMS XL-5. The sample was placed in a pressure cell during all magnetization measurements. A piston cylinder type of the CuBe pressure cell was filled up by a mixture of mineral oils serving as hydrostatic pressure transmitting medium and operating up to 1.2 GPa [7].

Our measurements indicate [4] that both samples undergo a paramagnetic (PM) to ferromagnetic (FM) transition at the Curie temperature  $T_C$ , which increases with annealing temperature, indicating gain of ferromagnetic interactions. The hysteretic behavior between magnetization measurements performed in ZFC and FC regimes, for low applied magnetic fields, is a typical feature of both samples (Fig. 2, Fig. 3). The applied pressure does not change  $T_C$  for sample 1 (Fig. 2) and increases  $T_C$  with coefficient  $dT_C/dP = 12.15$  K/GPa for sample 2 (Fig. 3), indicating dominant superexchange interaction for sample 1 and dominant double exchange interaction for sample 2. The increase of  $T_C$  with pressure can be attributed to increasing value of the electronic band width  $W$  related with increasing value of Mn-O-Mn bond angle by pressure.

The exchange bias effect (EB) was observed on sample 1 with average particle size of 25 nm. It can be explained by the core shell model [4]. The tiny effect of pressure on vertical and horizontal shift of hysteresis loop after

\*corresponding author; e-mail: [antonak@saske.sk](mailto:antonak@saske.sk)

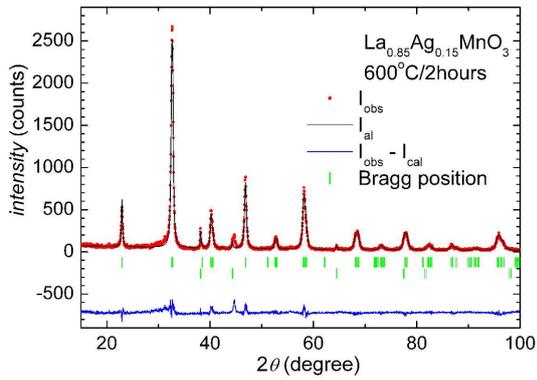


Fig. 1. X-ray powder diffraction pattern taken from sample annealed at 600 °C/2 hours.

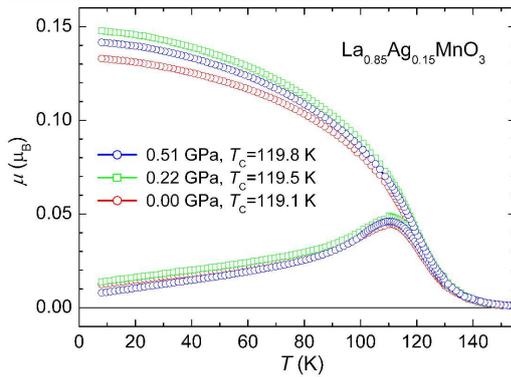


Fig. 2. Magnetization curves at different pressure for  $\text{La}_{0.85}\text{Ag}_{0.15}\text{MnO}_3$  sample annealed at 300 °C in air.

cooling in field  $\mu_0 H_{cf} = 1$  T is shown in Fig. 4. Only remnant magnetization is changing with pressure. Much more pronounced effect of pressure on hysteresis loop was observed for sample 2 (Fig. 5). In this case  $T_C$ ,  $\mu_s$  and remnant magnetization  $\mu_r$  increase with pressure; the coercive force decreases with pressure.

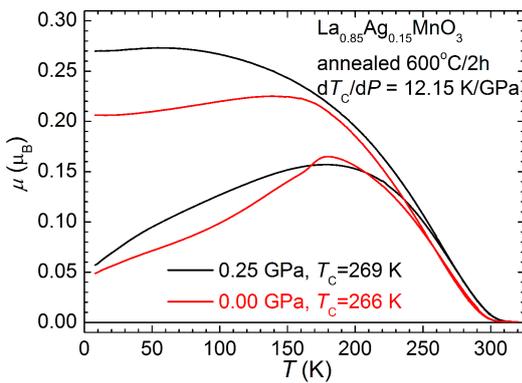


Fig. 3. Magnetization curves at different pressure for  $\text{La}_{0.85}\text{Ag}_{0.15}\text{MnO}_3$  sample annealed at 600 °C in air.

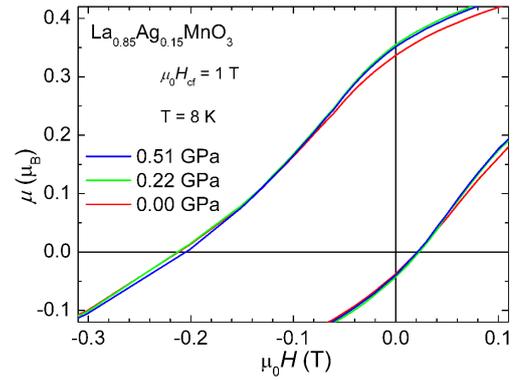


Fig. 4. Effect of pressure on bias exchange phenomenon for  $\text{La}_{0.85}\text{Ag}_{0.15}\text{MnO}_3$  sample annealed at 300 °C in air.

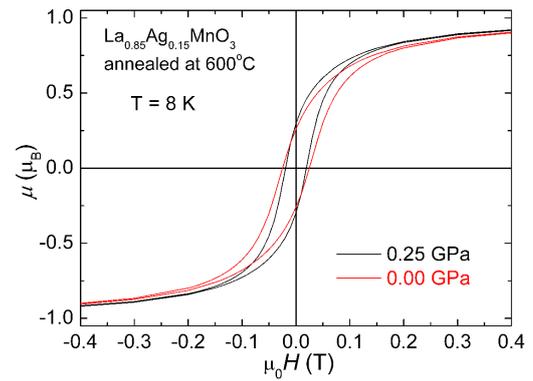


Fig. 5. Effect of pressure on hysteresis loops for  $\text{La}_{0.85}\text{Ag}_{0.15}\text{MnO}_3$  sample annealed at 600 °C in air.

### Acknowledgments

This work was supported by VEGA2/0178/13, APVV-0132-11, ERDF EU: No. ITMS26220120005 and ESF EU No. ITMS26220120034.

### References

- [1] J.M.D. Coey, T. Venkatesan, A.J. Millis, J.R. Cooper, P.C. Riedi, P.B. Littlewood, *Philos. Trans.: Math., Phys. Eng. Sci.* **365**, 1519 (1998).
- [2] N.T. Hiena, N.P. Thuya, *Physica B* **319**, 168 (2002).
- [3] Y. Kalyana Lakshmi, P. Venugopa Reddy, *J. Mag. Mag. Mater.* **321**, 1240 (2009).
- [4] M. Mihalik, M. Antonak, K. Csach, M. Fitta, M. Mihalik jr., M. Vavra, M. Zentková, *EPJ Web Conf.* **40**, 15006 (2013).
- [5] D. Markovic, V. Kusigerski, M. Tadic, J. Blanusa, M.V. Antisari, V. Spasojevic, *Scr Mater* **59**, 35 (2008).
- [6] M.H. Rietveld, *J. Appl. Cryst.* **2**, (1969).
- [7] J. Kamarád, Z. Machátová, Z. Arnold, *Rev. Sci. Instruments* **75**, 5022 (2004).