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Dedicated to Professor Dr. Sorin Dan Anghel on His 65th Anniversary

MAGNETOCALORIC AND MAGNETIC PROPERTIES OF NANOCRYSTALLINE $La_{0.75}Pb_{0.25}MnO_3$ SYNTHESIZED BY HIGH ENERGY BALL MILLING

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ABSTRACT. Nanocrystalline $La_{0.75}Pb_{0.25}MnO_3$ powders were synthesized by grinding the constituent oxides in air at room temperature, using a high-energy planetary mill. The reaction process, evaluated by analyzing the evolution of the crystalline structure in the XRD patterns, is completed after about 12 h. The magnetic measurements indicate that the manganite nanoparticles with sizes smaller than 15 nm obtained by reacting milling have significant defects at the surface, leading to a serious decrease of the magnetic moments in comparison to the bulk material. A significant magnetocaloric effect was found at temperatures ranging from below to above room temperature, with the maximum entropy change located at temperatures near the magnetic transition one. The high RCP(S) values together with the broadened magnetic entropy curve suggest the possibility to use these materials for magnetic refrigeration devices.

Keywords: *nanoparticles; LPMO; high energy ball milling; magnetocaloric effect;*

INTRODUCTION

The doped manganese perovskites, with general composition $R_{1-x}A_xMnO_3$, where R is a La or a rare-earth ion and A is an alkaline-earth ion, have been intensively investigated in the last years due to their interesting and intriguing physical properties such as colossal magnetoresistance (CMR), phase separation (PS), charge ordering (CO), orbital ordering (OO) and spin glass (SG) behavior and for their potential technical

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applications [1–8]. Their rich electronic phase diagrams reflect the fine balance of interactions, which determine the electronic ground state. Many of the lanthanum manganite compounds, $La_{1-x}A_xMnO_3$, where A=Ca, Sr or Ba, were found to exhibit large or unusual magneto-caloric effect (MCE) values under moderate external magnetic field [9]. On the other hand, these materials display considerably small magnetic hysteresis and their Curie temperature can be tuned easily. $La_{1-x}Pb_xMnO_3$ (LPMO) manganites are also promising for applications, considering the ferromagnetic metallic (FMM) phase at room temperature along with large magnetoresistance and good MCE at temperatures ranging from below to above room temperature [10-13]. However, the investigation of polycrystalline LPMO manganites has been restricted due to evaporation of Pb at temperatures higher than 900°C which are required for the conventional powder solid-state reaction synthesis. Using a PbO atmosphere in the furnace is one approach to overcome PbO loss which obviously cannot impart perfect homogeneity and uniform microstructure to the final products [14]. Another approach to maintain better homogeneity and stoichiometry is lowering reaction temperature below the melting point of PbO by using sol-gel route [15], but the chemical solution methods they are generally complicated and the agents used can be very expensive. A satisfactory method for obtaining fine and homogeneous manganites powder may be mechanochemical synthesis, which is a powerful method for the production of novel, high performance and low cost materials such as ferrites or intermetallics. The mechanochemical synthesis can deliver the designed phases and structures by a single step of the high-energy ball milling conducted in an enclosed activation chamber at room temperature. In recent years, high-energy ball milling was used to the mechanosynthesis of stoichiometric $La_{0.8}Pb_{0.2}MnO_3$ manganites by grinding constituent oxides at room temperature [16].

In this paper we report the single step synthesis of nanocrystalline $La_{0.75}Pb_{0.25}MnO_3$ manganite powders via high-energy milling of oxide precursors and the investigation of the magnetic and magnetocaloric properties.

EXPERIMENTAL

$La_{0.75}Pb_{0.25}MnO_3$ nanoparticles were synthesized from 99.99% purity oxides of La_2O_3, PbO, MnO and MnO_2. The oxides were mixed in stoichiometric proportions and mechanically milled in air using a high-energy planetary mill (Fritsch Pulverisette 4) with 440C hardened steel balls and milling vial. The milling speed of the vial was 900 rpm and the ball-to-powder ratio of 10:1. The powder milling process was interrupted several times and small amounts of powder were taken out of the vial. In order to prevent the excessive overheating of the containers, the experiments were carried out by alternating 120 min of milling with 30 min of rest. For magnetic measurements the powders were pressed into pellets of 10 mm diameter under a pressure of 1 tonne/cm^2, heated in air to 600^{o}C for 12 h and slowly cooled to room temperature.

The crystallographic properties of the samples were investigated by X-ray diffraction (XRD) at room temperature by using a Bruker D8 Advance AXS diffractometer with Cu Kα radiation in the 2ϑ region 20^o-65^o. The crystallite-sizes were calculated using the Debye-Scherrer formula:

$$D = \frac{\mathrm{k}\lambda}{\beta \cos\theta} \tag{1}$$

where β is the peak full width at half maximum (in radians) at the observed peak angle ϑ, k is the crystallite shape factor (was considered 0.94) and λ is the X-ray wavelength (0.154 nm).

Magnetic measurements were carried out using a 12 T VSM from Cryogenics in the temperature range 4.2 – 350 K and external magnetic field up to 4 T. Both zero-field-cooled (ZFC) and field-cooled (FC) measurements were performed.

The magnetic entropy changes were determined from magnetization isotherms, between zero field and a maximum field (H0) using the thermodynamic relation:

$$\Delta S_m(T,H_0) = S_m(T,H_0) - S_m(T,0) = \frac{1}{\Delta T}\int_0^{H_0}\left[M(T+\Delta T,H) - M(T,H)\right]dT \tag{2}$$

where ΔT is the temperature increment between measured magnetization isotherms (ΔT = 5K). The magnetic cooling efficiency was evaluated by calculating the relative cooling power (RCP) based on the magnetic entropy change:

$$\mathrm{RCP}(S) = -\Delta S_m(T,H_0)\times \delta T_{FWHM} \tag{3}$$

where ΔS_m represents the maximum magnetic entropy change and δT_{FWHM} its full-width at half-maximum.

RESULTS AND DISCUSSION

Fig 1 shows the XRD patterns at room temperature of the powders milled for different periods of time (t_{mill} = 2 h, 5 h, 7 h, 9 h, 11 h, 12 h).

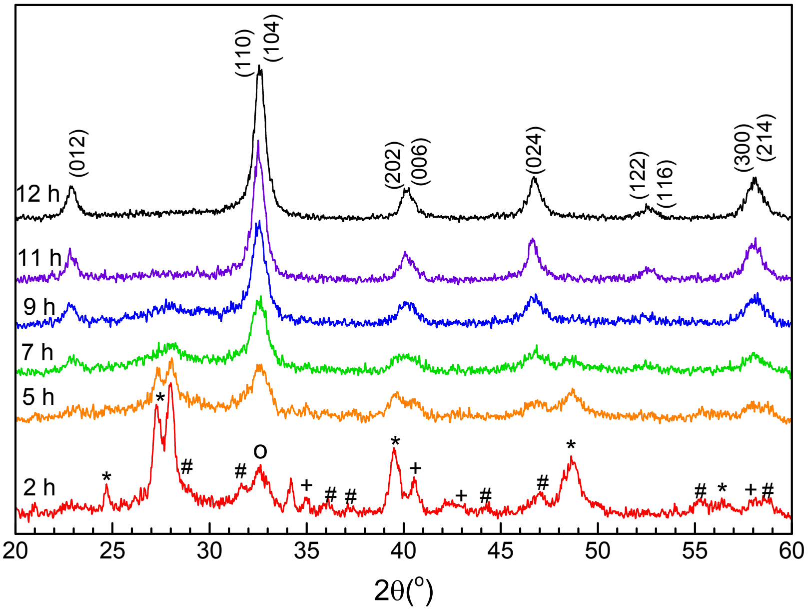

Fig. 1. XRD patterns of the mixture milled for different periods of time: (*) La_2O_3, (+)MnO/MnO_2, (#) PbO, (o) $La_{0.75}Pb_{0.25}MnO_3$

For milling time higher than 5 h the perovskite phase is preponderant and single phase $La_{0.75}Pb_{0.25}MnO_3$ powders were obtained after 12 h milling time. The profiles of the diffraction peaks in Fig 1 are broadened, suggesting that the synthesized powders are crystallites of nanoscale size. For milling time of 11 h and 12 h, for which the percentage of the LPMO phase is higher than 95 %, the lattice parameters, c/a ratios and crystallite-sizes (calculated using the Debye-Scherrer formula) were obtained from the XRD patterns and collected in Table 1. The values obtained from Rietveld refinement for the *a* lattice parameter and *c/a* ratio are clearly smaller than the values obtained previously for $La_{0.762}Pb_{0.238}Mn_{0.98}O_{3.04}$ synthesized by standard ceramic reaction (*c* = 13.351 Å, *c/a* = 2.418) [13], suggesting that for nanocrystalline LPMO powders the lattice contracts preferably in the *a*-direction rather than in the *c*-direction.

Table 1. Lattice parameters, c/a ratio and crystallite sizes estimated from XRD patterns

Milling time	a (Å)	c (Å)	c/a	χ^2	Crystallite size (nm)
11 h	5.51(2)	13.40(0)	2.43(1)	1.30	11
12 h	5.51(6)	13.40(7)	2.43(0)	1.18	14

The magnetization of the powder milled for 12 h and pressed into pellet, in zero field cooling (ZFC) and field cooling (FC) modes was measured. With decreasing temperature the magnetization shows an increase in the temperature range of 50 – 300 K, as shown in Fig 2a. The magnetic order temperature, defined as the temperature corresponding to the minimum of $\delta M/\delta T$ is about 255 K, smaller than for bulk LPMO, as it can be seen in the inset of Fig 2a. It has been shown that while synthesizing perovskite nanoparticles, the reactive milling technique creates significant defects not only at particles surface but also inside them that result the diminution of the exchange interaction strength. Fig 2b shows the *M(B)* curves at 5 K in magnetic fields up to 4 T. The saturation magnetization of our nanocrystalline sample, of about 2.6 μ_B/f.u. at 5 K, is smaller than the bulk value of 3.2 μ_B/f.u., which may be an effect of the small particles size. A model for the nanoparticles in which the inner part has the same properties as the bulk compound (oxygen

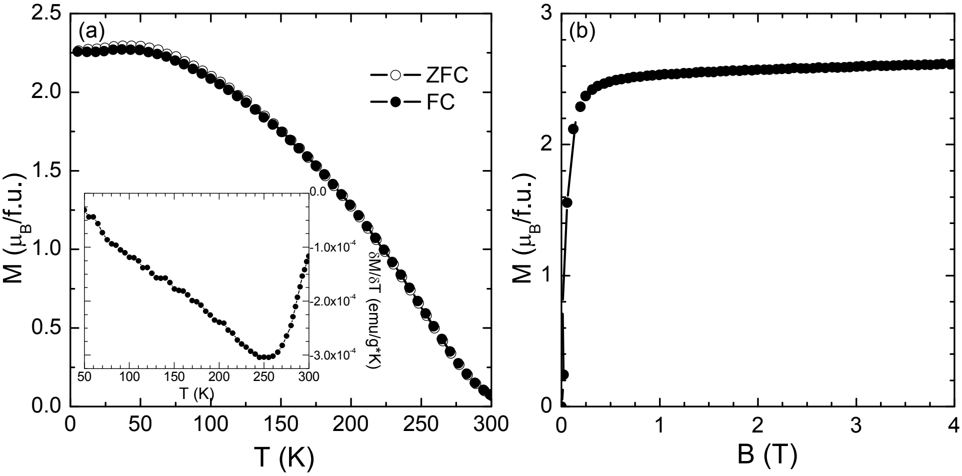

Fig 2. a) Temperature dependence of ZFC and FC magnetizations in 0.2 T; b) Magnetic field dependence of the magnetization at 5 K

stoichiometry, magnetic and transport properties), but the outer layer containing most of defects in the crystallographic structure shows a magnetically disordered state, is conceded widely to explain the size dependence of magnetization [17,18]. For nanoparticles of sizes lower than 15 nm the surface contribution is large and therefore leads to the diminution of the total magnetization.

The temperature dependence of the magnetic entropy change for $La_{0.75}Pb_{0.25}MnO_3$ in magnetic field of 4 T, determined from magnetization data, is plotted in Fig 3. The maximum value of $|\Delta S_m|$ is about 1.15 J/kgK, slightly smaller than the reported value of 1.3 J/kgK for bulk $La_{0.8}Pb_{0.2}MnO_3$ [10], which is expected considering the decreased value of the magnetization. The maximum value of the magnetic entropy change is located at about 250 K, close to the magnetic transition temperature and the peak is nearly symmetric around the maximum value. In order to evaluate the magnetic cooling efficiency, the RCP(S) values were calculated by using equation (3). The obtained value of about 200 J/kg is higher than for bulk LPMO (50-60 J/kg), due to the fact that the magnetic entropy change has a significant value over a broader temperature range. The RCP(S) value for our sample is comparable with those obtained in other oxide compounds, recommending nanocrystalline LPMO as good magnetic refrigerant materials operating at temperatures around room temperature.

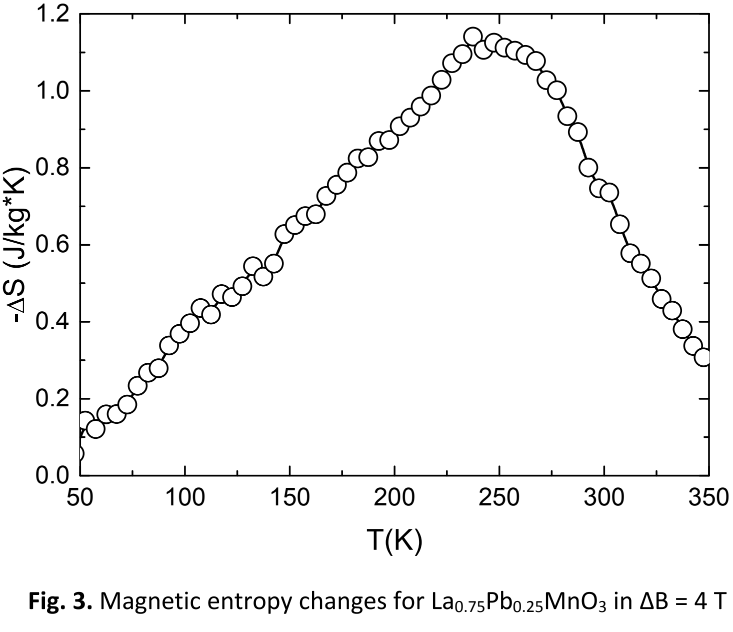

Fig. 3. Magnetic entropy changes for $La_{0.75}Pb_{0.25}MnO_3$ in ΔB = 4 T

CONCLUSIONS

We have shown that nanocrystalline $La_{0.75}Pb_{0.25}MnO_3$ manganite powders can be synthesized at room temperature by high-energy milling of oxide precursors in a single step process. The reaction increases rapidly with the milling time and is completed after 12 h. The obtained powder consists of nanocrystals with sizes smaller than 15 nm. The magnetic measurements indicate that the perovskite nanoparticles obtained by reacting milling have significant defects at the surface, leading to a serious decrease of the magnetic moments in comparison to the bulk material. Our sample shows a significant magnetocaloric effect at temperatures ranging from below to above room temperature. Considering the high RCP(S) value, nanocrystalline $La_{0.75}Pb_{0.25}MnO_3$ can be considered as good magnetic refrigerant material. The results recommend high-energy milling as an effective method to prepare nanosized LPMO manganites.

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