Anexa 2a

Titlu proiect: *Influence of lead doped manganites of type $La(Ho,Nd)_{0.54}Sr(Ca,Ba)_{0.35-x}Pb_xMnO_3$ on the microstructural, magnetic and transport properties*
Categoria de proiect: proiect de cercetare
Contractul de finanţare: Pozitia nr.68 din Ordinul IUCN nr. 96/15.02.2016, Tema *04-4-1121-2015/2017* ,
Manager proiect: Conf. Dr. Nicoleta Cornei

Lista rezultate

Nr. crt.	NUME AUTORI	TITLUL ARTICOLULUI/ CĂRŢII / COMUNICĂRII ŞTIINŢIFICE	REVISTA / VOLUMUL/EDITURA IN CARE A APARUT / CONFERINTA LA CARE S-A COMUNICAT	ANUL PUBLICARII/ COMUNICARII
COMUNICARI STIINTIFICE INTERNATIONALE				
1				
1	M.-L. Craus, V. Dobrea, E. Anitas, R. Erhan, N. Cornei,	*Magnetic structure and transport phenomena in Pb low doped $LaMnO_3$ manganites*	The 11th edition of the EMSA Conference Torino, Italy, EU	12-15 iulie 2016
2	M.-L.Craus, E. M. Anitas, N. Cornei, V. Turchenko	*Magnetic Structure and Transport Phenomena in $La_{0.5}Pr_{0.2}Pb_{1-x}Sr_xMnO_3$manganites*	The 11th edition of the EMSA Conference Torino, Italy, EU	12-15 iulie 2016
3	N. Cornei, C. Mîţă, M.-L. Craus, I. A. Gorodea, V. Dobrea, A. Domocoş	*Synthesis, Structural and Catalytic Properties of $LaFe_{1-x}Co_xO_3$ perovskites.*	16th International Balkan Workshop on Applied Physics and Materials Science - IBWAP 2016	7-9 iulie 2016

Lista achiziţiilor realizate în cadrul proiectului

Denumire echipament	Categorie de achiziţii*: (numai mijloace fixe)	Valoarea (lei)	Locaţie
-			

Director proiect,
Conf. Dr. Nicoleta Cornei

The 11th edition of the EMSA Conference
Torino, Italy, EU, July 12 through July 15, 2016.

Magnetic structure and transport phenomena in Pb low doped $LaMnO_3$ manganites

M.-L. Craus[1,2], V. Dobrea[1], E. Anitas[2,3], R. Erhan[2,3], N. Cornei[4]

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The aim of this paper is to establish the influence of Pb substitution on magnetic/crystalline structure and transport properties of $LaMnO_3$ manganites

EXEPRIMENTAL DETAILS

Ceramic technology: The $La_{1-x}Pb_xMnO_3$ manganites were synthesized by ceramic technology at Laboratory of Neutron Physics, JINR, Dubna, Russia. The samples were finally treated at 1200°C in a closed vessel to prevent Pb evaporation.

X-ray Diffraction (XRD): X-ray diffraction (XRD) experiments were performed at room temperature in order to determine the phase composition and microstructural parameters by using Fullprof software. The space group and lattice constants were obtained by means of the CeckCell and proofed by FullProf software.

Magnetic measurements: Foner type magnetometer, between 77 and 400K.

Electric measurements: Four points method. Resistance measurements with temperature and magnetic field intensities were performed by using a closed cycle refrigerator and an electromagnet at JINR, Dubna, Russia.

RESULTS

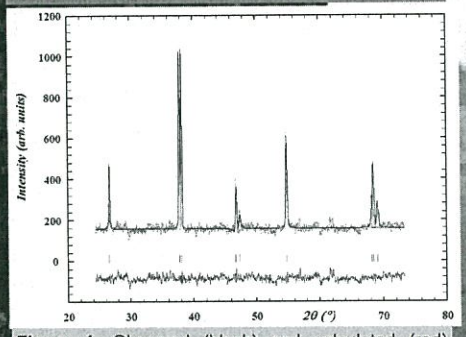


Figure 1. Observed (black) and calculated (red) diffractograms of $La_{0.94}Pb_{0.06}MnO_3$ using FullProf software; bottom (green) – the difference between the calculated and observed diffractograms

Table 1. Variation of lattice constants (a, b, c), unit cell volume (V_{uc}) and occupied by a molecule (V_{uc}/z) for $La_{1-x}Pb_xMnO_3$ manganites volume

x	a=b (Å)	c (Å)	V_{uc}(Å^3)
0.03	5.5320	13.3778	354.6
0.06	5.5272	13.3625	353.5
0.10	5.5273	13.3667	353.7
0.15	5.5297	13.3703	354.1
0.20	5.5256	13.3628	353.3

Structure The synthesized manganites contain only the perovskite phase: SG R - 3c, with La or Pb on (6a) sites (0, 0, 0.25), Mn on (6b) sites (0, 0, 0) and O on (18e) (X, 0, 0.25), for x = 0.00, 0.05, 0.10, 0.15 and x = 0.20. The cell parameters, average size of crystalline blocks and microstrains have been obtained through the profile matching stage of the Rietveld refinement (Fig. 1 and Tab. 1). Only a small variation of the unit cell volume was observed with the increase of the Pb concentration and we attribute this behaviour to the presence of a small concentration of Pb^{4+} and/or to a small amount of the vacancies on both type of sites (Tabs.1 and 2).

Table 2. Variation of the average size of mosaic blocks (D), microstrains (ε), space group (SG) and calculated tolerance factor (t) for $La_{1-x}Pb_xMnO_3$ manganites.

x	D (Å)	ε	t
0.03	1275	0.00006	0.967
0.06	1080	0.00031	1.000
0.10	1230	0.00014	1.000
0.15	1176	0.00005	0.995
0.20	1028	0.00001	0.995

•**Magnetic properties** We suppose that a part of the Mn^{3+} cations does not participate to the total magnetic moment or they are forming an antiferromagnetic compound, with the same chemical composition and the same structure as the main phase. The substitution of La with Pb, together with the oxygen non-stoichiometry contributes to the appearance of the ferromagnetic interactions, and implicitly to a metallic phase. The variation of magnetization vs. temperature at relatively small intensities magnetic fields is similar to that observed in the samples characterized by the spin glass state, which were cooled in magnetic field (Figs. 2, 3).

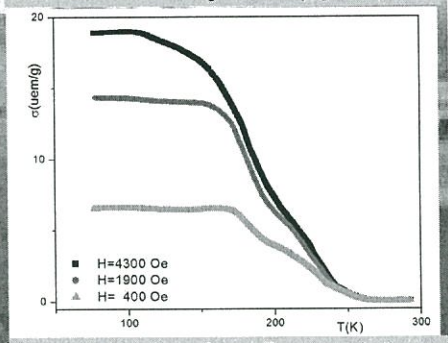
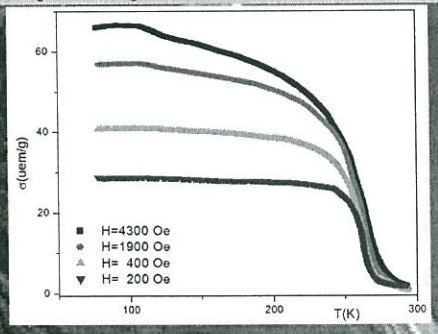


Figure 2 Variation of specific magnetization vs temperature and Pb concentration of LPMO (x=0.06) manganites, magnetic field cooled.



•**Figure 3** Variation of specific magnetization vs temperature and magnetic field intensity of $La_{1-x}Pb_xMnO_3$.

For all samples a spin glass transition was observed at temperatures apparently higher as 100 K. Examples were given in Figs. 2 and 3. The reasons for this behaviour is the decrease of the Pb^{4+} concentration and of the oxygen concentration, in the samples, with the increase of Pb concentration.

Transport characteristics The transport measurements were performed on field cooled and without field cooled samples, only on heating, with and without applied magnetic field (Figs. 4 and 5).

At low temperature the variation of the resistance can be described with relation:

$$R(T) = R_{4.5}T^{4.5}+R_2T^2+R_0$$

where the last term (R_0) represents the resistance due to the temperature-independent scattering processes, the second term (in T^2) corresponds to the electron– electron scattering processes, and the first term (in $T^{4.5}$) includes contribution from the electron–magnon scattering or spin wave scattering. These terms are more or less field dependent.

The larger values of resistance for the sample corresponding to x=0.06 is probably due to the appearance of a (nano)magnetic phase with a large resistivity, possibly as magnetic clusters based on Mn^{3+} or Mn^{4+} (s. Figs. 2 and 4).

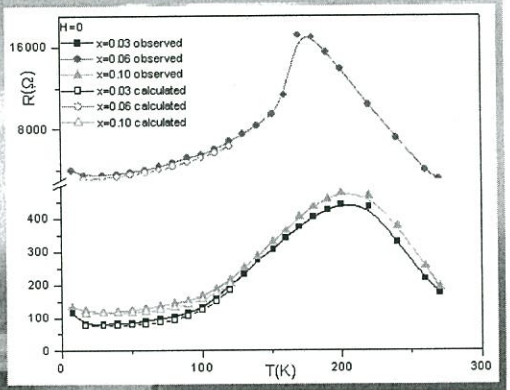


Figure 4 Variation of resistance vs temperature and Pb concentration, without magnetic field cooled; measurements were performed at H=0. For low temperature we observed a good agreement between the calculated and observed data.

CONCLUSIONS

1.We synthesized a set of pure $La_{1-x}Pb_xMnO_3$ manganites for various Pb concentrations (x = 0.03, 0.06, 0.10, 0.15 and 0.20).

2. All the samples have a rhombohedral structure (R-3c), with an almost constant unit cell volume. We observed a small variation of the lattice constants, despite the difference between the radii of La^{3+} (1.216 Å) and Pb^{2+} (1.35 Å), probably due to a change of oxygen concentration or/and an increase of Pb^{4+} concentration with total Pb concentration in the samples.

3.We have shown that they exhibit a spin glass state to metallic state transition at temperatures lower than 170 K.

4.There is a qualitative dependence between the presence of spin glass state and the observed large magnetoresistance.

We intend to perform more exact experiments concerning the dependence between the presence (concentration) of spin glass state and the variation of resistance at low temperature.

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Magnetic structure and transport phenomena in Pb low doped $LaMnO_3$ manganites

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The $La_{1-x}Pb_xMnO_3$ (x=0.03 - 0.10) manganites were obtained by ceramic technology, from oxides, mixed in corresponding ratio. The sintering was performed at 1100°C, in a closed quartz tube, to prevent Pb evaporation. X-ray diffraction data at room temperature indicated that the samples contain only a distorted R-3c rhombohedral phase (s. Fig. 1). The cell parameters, average size of crystalline blocks and microstrains have been obtained through the profile matching stage of the Rietveld refinement (s. Fig. 1). We observed a small variation of the lattice constants, despite the difference between the radii of La^{3+} (1.216 Å) and Pb^{2+} (1.35 Å), probably due to a change of oxygen concentration or/and an increase of Pb^{4+} concentration with total Pb concentration in the samples. The oxigen parameter (X), d_{Mn-O}(Å), d_{A-O}(Å) distances and ∠Mn-O-Mn(°) angles were determined by using Fullprof code.
Curie temperature and specific magnetization at low temperature, determined with a VSM remain practically independent on Pb concentration.

At low temperature the variation of the resistance can be described with relation [1]:

$$R(T) = R_{4.5}T^{4.5}+R_2T^2+R_0 \quad (1)$$

where R_0 represents the resistance due to the temperature-independent scattering processes, R_2 corresponds to the electron– electron scattering processes, and $R_{4.5}$ includes contribution from the electron–magnon scattering or spin wave scattering. The larger values of resistance for the sample corresponding to x=0.06 is probably due to the appearance of a (nano)magnetic phase with a large resistivity, possibly as magnetic clusters based on Mn^{3+} or Mn^{4+} (s. Fig.2).

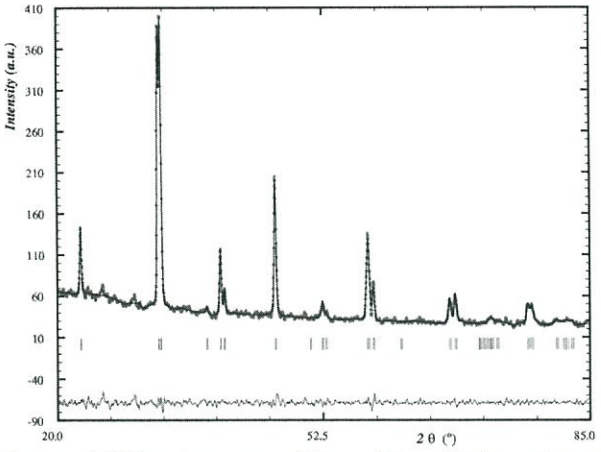

Figure 1 Diffractograms of $La_{0.97}Pb_{0.03}MnO_3$: at zero intensity - Bragg position of calculated maxima (vertical segment) and the difference between observed and calculated diffractograms, by using FullProf code.

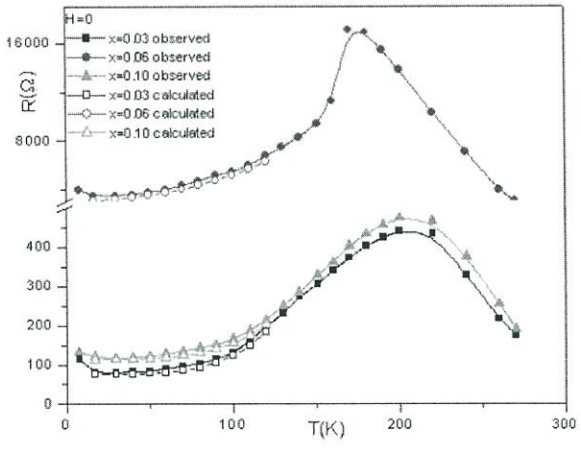

Figure 2 Variation of resistance with temperature for $La_{1-x}Pb_xMnO_3$ (H=0)

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16th International Balkan Workshop on Applied Physics and Materials Science - IBWAP 2016 (7-9, July, 2016)

SYNTHESIS, STRUCTURAL AND CATALYTIC PROPERTIES OF $LaFe_{1-x}Co_xO_3$ PEROVSKITES

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PURPOSE

The purpose of the present work is to obtain powders of $LaFe_{1-x}Co_xO_3$ perovskite by sol-gel method, with a good catalytic activity.

INTRODUCTION

- The perovskites oxides contain more than one metallic element in their lattice. Due to the different amount of metals, the perovskites play an important role as catalysts in various chemical reactions [1, 2]. It can be used in many reactions due to its different redox properties, high oxygen mobility and thermal stability [3,4].
- By replacement of B cations with cations of similar size but lower oxidation state can be generate the vacancies.
- The main application of perovskite as catalysts has been in the oxidation of hydrocarbons and carbon monoxide.
- Recently, the perovskites oxides have been studied in the Fischer-Tropsch synthesis [5, 6].

EXPERIMENTAL DETAILS

Sol-gel method:

- The mixed oxide $LaFe_{1-x}Co_xO_3$ (x =0; 0,05; 0,1; 0,2; 0,3) was prepared by sol-gel self-combustion method using nitrates as precursors and citric acid and ethylene glycol as chelating agent. The obtained powder was annealed at 750 °C for 6 hours in air atmosphere.
- *X-ray Diffraction (XRD):* was performed with a Shimadzu XRD 6000 at room temperature (Cu Kα.1 radiation and the step 0.02). Lattice constants and space group were determined and refined by using Powder cell and Celref programs.
- *FT-IR analysis:* JASCO 660 Plus spectrophotometer in wave number range 4000 cm^{-1}– 350 cm^{-1} , in atmospheric air, in KBr disks .
- *BET analysis:* Nova 2200e BET analyzer
- The H_2O_2 *catalytic decomposition experiments* were conducted in a batch reactor that was stirred at a speed to provide a uniform distribution of mixed oxide catalyst. The pH was adjusted by using a Na_2HPO_4 buffer solution. In the reaction vessel 2.5 mL H_2O_2 (30%), 5 mL buffer solution, 7.5 mL distilled water and 0.05 g catalyst were added. The temperature of reaction chamber was maintained at 25 °C (±0.1 °C) by using a Haake F4 pump. Oxygen evolution measurements were carried out with a water barometric system at normal pressure. All experiments were performed under the same conditions.

RESULTS AND DISSCUTION

XRD data:

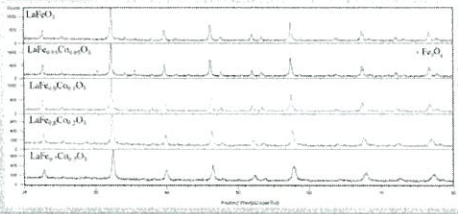
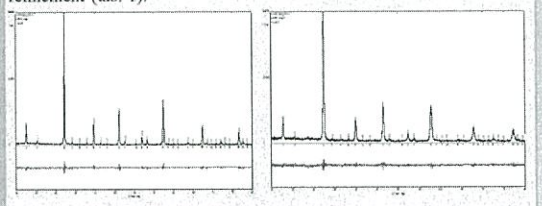


Figure 1. X-ray diffraction for $LaFe_{1-x}Co_xO_3$ perovskites annealed at 750 °C/6h

- The samples $LaFe_{1-x}Co_xO_3$ became almost pure after a treatement for 6 hours at 750°C (figs. 1 and 2).
- Structural phase identification was done using program's database X'Pert Plus High Score.
- The samples with x = 0.05 and 0.2 contain a small quantity of Fe_3O_4 (98-007-8086) and Co_3O_4 (98-002-6743)
- The results of X-ray diffraction indicated that $LaFe_{1-x}Co_xO_3$ had a orthorhombic structure (space group: Pbnm, according with cristallografic data (fig.2).

- The cell parameters, average size of mosaic blocks and microstrains, have been obtained through the profile matching stage of the Rietveld refinement (tab. 1).



a b

Figure 2. XRD powders of $LaFe_{1-x}Co_xO_3$ (calculated and observed), annealed at 750 °C: a) x = 0.0; b) x = 0.3

Table 1. The variation of cell parameters (a, b, c), unit cell volume (V), average size of mosaic blocks (D), microstrains (ε) for $LaFe_{1-x}Co_xO_3$ perovskites and BET surface area.

Chemical compozition	a(Å)	b(Å)	c(Å)	V(Å³)	D(Å)	ε	BET surface area (m^2/g)
$LaFeO_3$	5.5721	5.5537	7.8550	243.08	1075	0.000228	1.418
$LaFe_{0.95}Co_{0.05}O_3$	5.5686	5.5520	7.8531	242.79	1031	0.000247	1.285
$LaFe_{0.9}Co_{0.1}O_3$	5.5661	5.5504	7.8486	242.48	856	0.000122	2.179
$LaFe_{0.8}Co_{0.2}O_3$	5.5216	5.5468	7.8431	240.21	655	0.000910	1.227
$LaFe_{0.7}Co_{0.3}O_3$	5.5171	5.5242	7.8189	238.30	764	0.002235	1.583

- The D values decrease from $LaFeO_3$ to $LaFe_{0.7}Co_{0.3}O_3$ powders, that indicates that the doping with element cobalt in $LaFeO_3$ may prevent the grain growth during high temperature treatment.

IR data:

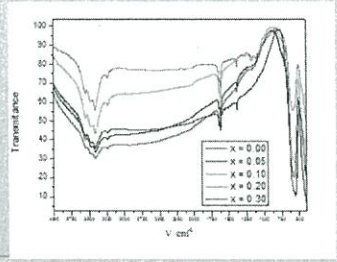
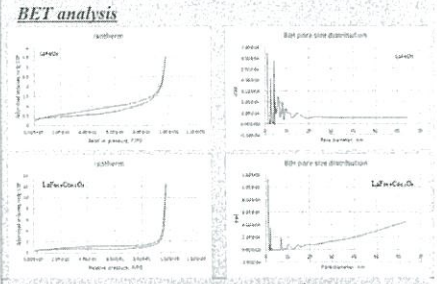


Figure 3. FTIR spectra of samples $LaFe_{1-x}Co_xO_3$ perovskites annealed at 750 °C

- The spectrum shows bands at 1640 and 1616 cm^{-1} assigned to the asymmetric and symmetric O–C–O stretching vibration modes of acid carbonate associated with the presence of the CO_2 and H_2O adsorbed on the oxide surface.
- The broad band in 3550-3300 cm^{-1} range is associated to the water's O–H bond due to exposure to air and environmental humidity for the studied perovskites.
- IR absorption spectra of all samples, in the 400-700 cm^{-1} show two intense absorption bands assigned to symmetric and asymmetric vibrations deformation of the Co-O-Co/Fe-O-Fe bonds, whose frequencies are centered at 603 ± 3 cm^{-1} and 556 ± 2 cm^{-1}

BET analysis



a b

Figure 4. BET analysis: a) Isotherm of adsorbtion; b) Pore size distribution.

- From BET isotherm we observe a variation of III type, specifi for nonporous samples. Because they present a hysteresis loop, w can say that the samples have a poor porosity.
- BET surface area is in table 1.

Catalytic Activity

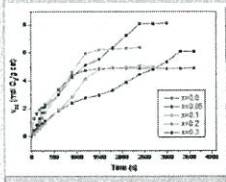


Figure 5. Variation of O_2 quantity with time in presence of $LaFe_{1-x}Co_xO_3$ as catalyst

Table 2.The rate constant for th H_2O_2/$LaFe_{1-x}Co_xO_3$ systems pH= 7.

x value	k_{obs}, s^{-1}
0.0	$5.885 \cdot 10^{-4}$
0.05	$2.155 \cdot 10^{-3}$ (0-1200 s) $1.620 \cdot 10^{-3}$ (1200-3200 s)
0.1	$3.282 \cdot 10^{-3}$
0.2	$4.938 \cdot 10^{-3}$
0.3	$7.120 \cdot 10^{-3}$ (0-400 s) $2.713 \cdot 10^{-3}$ (400-2400s)

- The decomposition of oxygen peroxide: $H_2O_2 = H_2O + 1/2O$ follows a pseudo-first kinetic order rate law $\log[H_2O_2]=\log[H_2O_2]_0$ $k_{obs}t/2.3$ at square correlation coefficient (R^2) >0.980, whe $[H_2O_2]_0$ and $[H_2O_2]$ are the concentrations of H_2O_2 in solution time zero and any time t, k_{obs} is observed rate law.
- The k_{obs} values and kinetic relationship indicates that the ra determining step in H_2O_2 decomposition could be diffusion chemicals to the surface, adsorption on the reactive sites, electr transfer, desorption of products or regeneration of the reactive site

CONCLUSION

- The samples present an orthorhombic structure
- The presence of CO_2 and H_2O adsorbed on the oxide surfa suggest that perovskites have hydrofilic properties and go catalytic activity
- The obtained samples have potential application as gas senzor

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▪**This work has been carried out with the financial support o JINR-IFIN-HH project no. 68 from IUCN order n 96/15.02.2016, theme no. 04-4-1121-2015/2017**
▪**The authors thanks to A. Pui for FT-IR analysis and Ignat for BET analysis.**

The 11th edition of the EMSA Conference
Torino, Italy, EU, July 12 through July 15, 2016.

Magnetic Structure and Transport Phenomena in $La_{0.5}Pr_{0.2}Pb_{1-x}Sr_xMnO_3$ manganites

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[3] Horia Hulubei National Institute of Physics and Nuclear Engeneering, Bucuresti-Magurele, Romania; [4] Department of Chemistry, "Al.I.Cuza" University, Iasi, Romania

The aim of this paper is to establish the influence of Pb substitution with Sr and of La with Pr on magnetic/crystalline structure and transport properties of $La_{0.5}Pr_{0.2}Pb_{0.3-x}Sr_xMnO_3$ manganites.

EXEPRIMENTAL DETAILS

Ceramic technology: The $La_{0.5}Pr_{0.2}Pb_{0.3-x}Sr_xMnO_3$ manganites were synthesized by ceramic technology at Laboratory of Neutron Physics, JINR, Dubna, Russia. The samples were finally treated at 1200°C in a closed vessel to prevent Pb evaporation.

X-ray Diffraction (XRD): X-ray diffraction (XRD) experiments were performed at room temperature in order to determine the phase composition and microstructural parameters by using Fullprof software. The space group and lattice constants were obtained by means of the CeckCell and proofed by FullProf software.

Magnetic measurements: Foner type magnetometer, between 77 and 400K.

Electric measurements: Four points method. Resistance measurements with temperature and magnetic field intensities were performed by using a closed cycle refrigerator and an electromagnet at JINR, Dubna, Russia.

RESULTS

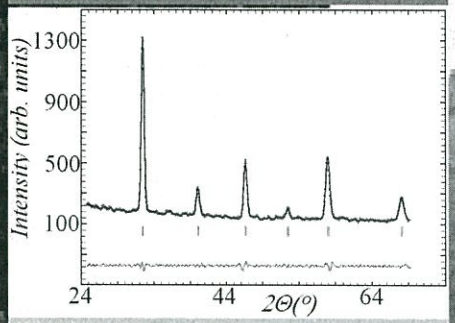

Figure 1. Observed (black) and calculated (red) diffractograms of $La_{0.5}Pr_{0.2}Pb_{0.3}MnO_3$ using FullProf software; bottom (blue) – the difference between the calculated and observed diffractograms

Table 1. Variation of lattice constants (a, b, c), unit cell volume (V_{uc}) and occupied by a molecule (V_{uc}/z) for $La_{0.5}Pr_{0.2}Pb_{0.3-x}Sr_xMnO_3$ manganites volume.

x	a=b (Å)	c (Å)	V_{uc}(Å^3)	V_{uc}/z(Å^3)
0.00	3.880	3.880	58.44	58.44
0.05	3.896	3.896	58.86	58.86
0.10	5.540	13.419	356.66	59.44
0.15	5.513	13.355	350.36	58.39
0.20	5.524	13.385	353.70	58.95

Structure The synthesized manganites contain only the perovskite phase: 1) SG Pm-3m with La/Pr/Sr or Pb on (1b) sites (1/2, 1/2, 1/2), Mn on (1a) sites (0, 0, 0) and O on (3d) sites (1/2, 1/2, 0) for x = 0 and 0.05 or 2) SG R - 3c, with La/Pr/Sr or Pb on (6a) sites (0, 0, 0.25), Mn on (6b) sites (0, 0, 0) and O on (18e) (X, 0, 0.25), for x = 0.10, 0.15 and x = 0.20. The cell parameters, average size of crystalline blocks and microstrains have been obtained through the profile matching stage of the Rietveld refinement (Fig. 1 and Tab. 1). We observed an increase of unit cell volume for each of the two types of structures separately and we attribute this behaviour to the presence of a small concentration of Pb^{4+} and/or to a small amount of the vacancies on both type of sites (Tabs.1 and 2).

Table 2. Variation of the average size of mosaic blocks (D), microstrains (ε), space group (SG) and calculated tolerance factor (t) for $La_{0.5}Pr_{0.2}Pb_{0.3-x}Sr_xMnO_3$ manganites.

x	D (Å)	ε	SG	t
0.00	315	0.0010	Pm-3m	1.000
0.05	551	0.0028	Pm-3m	1.000
0.10	845	0.0015	R-3c	0.963
0.15	600	0.0005	R-3c	0.995
0.20	480	0.0007	R-3c	0.963

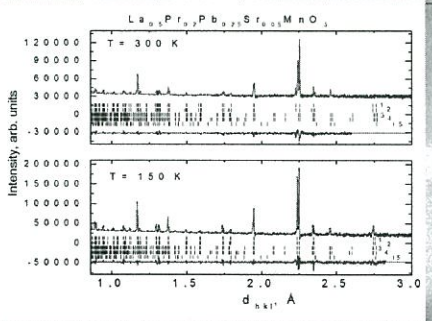

Figure 2 Observed (black), calculated (red) and the difference between the observed and calculated diffractogram (blue) for x=0.05.

In agreement with the obtained neutron data the LPPSMO samples contain two crystalline phases: an rhombohedral one (R-3c) (1) and an orthorhombic phase (Pnma) (3). There are two magnetic phases (2, 4) and a small contibution of hausmanite (5). We attributed the observed difference of the phase composition to a change in chemical composition at the surface comparing with the inner phase composition of the samples.

•Magnetic properties We suppose that a part of the Mn^{3+} cations does not participate to the total magnetic moment or they are forming an antiferromagnetic compound, with the same chemical composition and the same structure as the main phase. The substitution of La with Pb, together with the oxygen non-stoichiometry contributes to the appearance of the ferromagnetic interactions, and implicitly to a metallic phase. The variation of magnetization vs. temperature at relatively small intensities magnetic fields is similar to that observed in the samples characterized by the spin glass state .

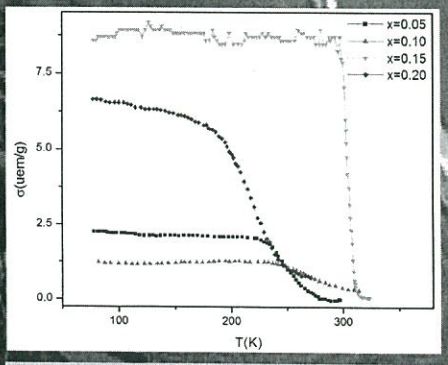

Figure 3 Variation of specific magnetization vs temperature and Pb concentration of LPPSMO manganites, zero magnetic field cooled; measurements were performed at H=0.

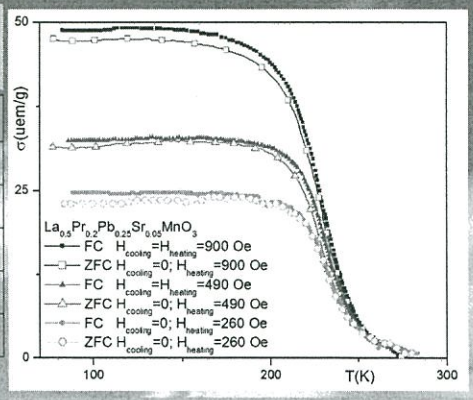

Figure 4 The transition from spin glass to ferromagnetic state for various magnetic field intensities. The spin glass transition was observed at T > 200 K (see Fig. 4).

There are two reasons for this behaviour: first, the decrease of the Pb^{4+} concentration and of the oxygen concentration, and second the increase of the Sr^{2+} concentration.

Transport characteristics The transport measurements were performed on field cooled and without field cooled samples, only on heating, with and without applied magnetic field (Fig. 5).

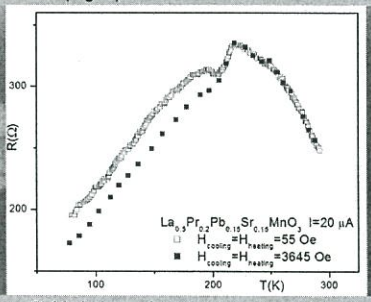

Figure 5 Variation of resistance vs temperature the applied magnetic field for the sample corresponding to x=0.15

CONCLUSIONS

1.We synthesized a set of $La_{0.5}Pr_{0.2}Pb_{0.3-x}Sr_xMnO_3$ manganites for various Sr concentrations (x = 0.0, 0.05, 0.10, 0.15 and 0.20). Its contain probably a small amount of hausmanite.

2.We have shown that they exhibit a spin glass state to metallic state transition at temperatures between 150 and 250 K.

3.At the sample surface a crystallographic transition from a cubic structure to a rhombohedral structure takes place at room temperature when x > 0.05.

4.There is a qualitative dependence between the presence of spin glass state and the observed large magnetoresistance

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Influence of spin-glass to ferromagnetic state transition on magnetoresistance in $La_{0.5}Pr_{0.2}Pb_{0.3-x}Sr_xMnO_3$ manganites

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The $La_{0.5}Pr_{0.2}Pb_{0.3-x}Sr_xMnO_3$ (x=0.05 - 0.20) manganites were obtained by ceramic technology, from oxides, mixed in corresponding ratio. X-ray diffraction data at room temperature indicated that the samples contain only a distorted phase: Pm-3m cubic, for x=0.05, and R-3c rhombohedral phase (s. Fig. 1) for x>0.05. Structure data obtained by neutron diffractometry (ToF method) showed a mixture of two phases: a rhombohedral and an orthorhombic phase. At 150 K neutronograms put in evidence the ferromagnetic phase. Magnetic measurements by VSM method between 77 and 350 K showed that at temperatures lower as 200 K a spin-glass state appeared (see Fig.2).

Curie temperature was determined as a minim of the first derivative of specific magnetization vs temperature and have a maximum for x=0.15, which corresponds to a minimum of the Mn-O distance of rhombohedral phase.

A variation of the concentration of oxygen and its influence on the ratio between Mn^{3+}/Mn^{4+} concentrations, implicitly on the magnetic structure of the samples, is discussed.

We put in evidence a strong dependence of the resistance not only on the ratio between Pb and Sr but also of the thermal history of the samples, which can influence the ratio between spin-glass state and ferromagnetic state concentrations at temperature lower as those corresponding transition.

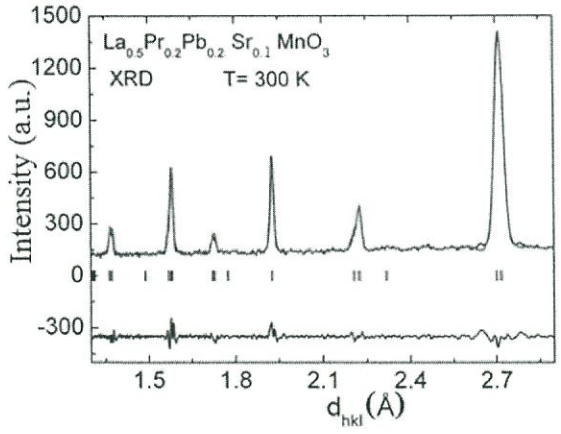

Figure 1 Observed and calculated diffractogram of $La_{0.5}Pr_{0.2}Pb_{0.25}Sr_{0.05}MnO_3$; at zero intensity - Bragg maxima; bottom - difference between the observed and calculated diffractograms

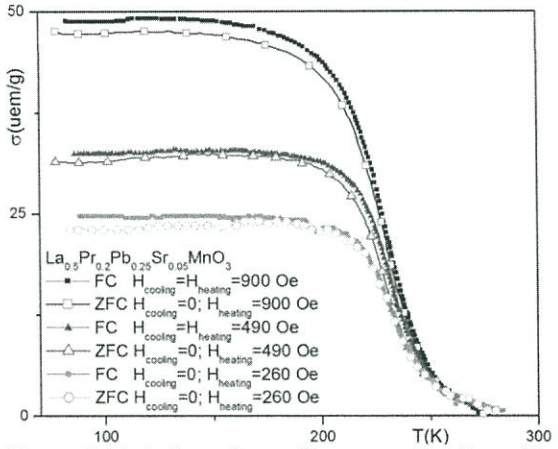

Figure 2 Variation of specific magnetization with temperature for $La_{0.5}Pr_{0.2}Pb_{0.25}Sr_{0.05}MnO_3$