

SYNTHESIS AND STUDIES ON THE STRUCTURAL AND ELECTRICAL PROPERTIES OF Sr DOPED LANTHANUM MANGANITES

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This work reports the synthesis of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ ($x=0;0.2;0.3;0.5$) doped perovskites via autocombustion method starting from an aqueous solution of metallic nitrates and urea as complexing and fuel agent. The complex precursors obtained have been characterized by electronic and IR spectra, as well as thermodifferential analysis. The oxide powders obtained by heat treatments of precursors at low temperature have been structural characterized by X-ray diffraction and a complete crystallization has been observed between 600^oC and 700^oC. The crystallite mean size was slightly influenced by the heating temperatures. The electrical and magnetic properties of the as-prepared oxide samples are also reported.

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1. Introduction

Electrical and magnetic properties make perovskite-type oxides, ABO_3 , attractive candidate materials for several important applications, including high-temperature superconductors, ferro- and piezoelectric or magnetoresistive materials, oxygen ion conductors, catalysts, etc. [1, 2, 3].

Doped perovskite lanthanum manganites, $\text{La}_{1-x}\text{A}_x\text{MnO}_3$, where A are divalent metallic ions which present today considerable attention due to their special electric and magnetic properties. Such materials display two characteristic transport phenomena: the first, the crossover from metallic conduction at low temperatures to semiconducting at high temperatures and the second, the colossal magnetoresistive effect near the transition temperature [3 -7].

Doped lanthanum manganites are used in high-temperature solid oxide fuel cells (SOFCs) as interconnect material, which provides the electrical contact between the fuel and air electrodes when single cells are stacked in series and separates the fuel and oxidant gases during operation. The requirements for interconnect materials are high electronic conductivity, negligible ionic conductivity, thermodynamic stability at SOFC operating temperature in both oxidizing and reducing ambient, high density and mechanical and chemical compatibility with other SOFC components [8 -10].

The electronic conductivity of the pure, stoichiometric lanthanum manganite is modified by the substitution with divalent ions on A site.

Like in the case of other mixed oxides, it is usually admitted that the morphology, physical

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properties and as a consequence the applications of these materials depend on their processing method.

Some processing methods are described in literature for the manganites preparation like: solid state reaction, sol-gel methods, heterodinuclear complexes decomposition or auto combustion methods [9, 10].

This paper reports on the synthesis of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ ($x=0; 0.2; 0.3; 0.5$) doped perovskites *via* autocombustion method starting from an aqueous solution of metallic nitrates and using urea as organic “fuel”. The advantage of this method is that manganites with a good crystallinity have been obtained at lower temperature and shorter time of heating than by ceramic procedure.

The paper is a part of our large study about the influence of organic “fuel” nature on the structure and properties of doped manganites [11].

The urea containing precursors and the manganites powders obtained by heat treatments of precursors at low temperature have been characterized by electronic and IR spectra, as well as thermodifferential analysis, X-ray diffraction and SEM analysis. The electrical properties of the prepared doped manganites samples are also reported.

2. Experimental data

Synthesis of precursors and $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ powders

The complex urea precursors were obtained in aqueous solution of metal nitrates and urea, at molar ratios of $\text{La} : \text{Mn} : \text{Sr} : \text{urea} = (1-x) : x : 1 : 5$.

The stoichiometric compositions of the redox mixture (oxidizer -metal nitrate and reducing agent - urea) were calculated using oxidizing valences of metal nitrates and reducing valence of urea used in the field of propellants and explosives [12].

A stoichiometric proportion of high-purity metal nitrates (Merck) were dissolved in a minimum volume of deionized water. The saturated aqueous solution of urea (Merck) was added, with stirring, to the aqueous solution of corresponding metal nitrates. The mixture was then heated at approximately 900C on a hot plate with stirring to evaporate the water until a pink-brown precipitate was obtained. The precursors were washed with ether and dried in air.

Sr doped lanthanum manganites powders, $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ ($x=0; 0.2; 0.3; 0.5$) were prepared by heating of isolated urea-containing precursors at 800⁰C/1h, in air.

The isolated urea containing precursors were characterized by AAS, electronic and IR spectra, as well as differential thermogravimetric analysis and powders and the oxide powders were investigated by XRD and SEM.

Elemental analysis

The metal content of the samples were determined on Pye Unicam atomic absorption spectrophotometer.

Reflectance electronic spectra were recorded on a VSU-2G spectrophotometer using MgO as a reference material.

IR spectra were performed on a Perkin Elmer spectrophotometer (KBr pellet technique).

TG-DTA analysis was performed in air in the temperature range 25 - 800⁰C, at a heating rate of 10⁰C/min using Paulik Paulik Erdey equipment.

XRD analysis

The oxide powders were investigated by XRD using a Bruker AXS diffractometer type D8 ADVANCE Cu anode tube.

Scanning electron micrographs of the doped lanthanum manganites were obtained using a JEOL JSM-5800 scanning electron microscope

Electrical conductivity of the samples were measured by means of the standard four probe technique in the temperature range 295 – 1273 K in air.

3. Results and Discussion

1. Characterization of urea precursors

Electronic spectra (Fig. 1) in visible range of urea complex precursors present a large, weak intensity band characteristic for Mn(II)(d⁵) ion in a square planar symmetry.

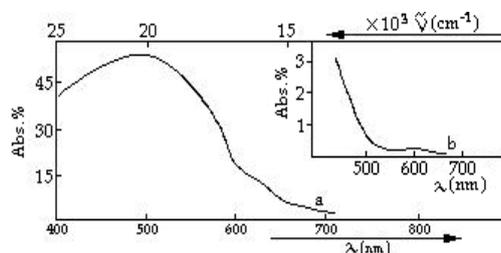


Fig.1. Electronic spectra of:
a. complex precursor; b. LaMnO_3 obtained from (a).

The data of IR spectra (Fig. 2) for urea containing precursors in comparison with that of urea can be summarized as following:

- the shifting of the intense band of urea at about 1670 cm^{-1} (ν_{CO}) to lower frequency (1640 cm^{-1}) in the spectra of complex precursors indicates the coordination of urea by oxygen atom; the oxygen coordination is also sustained by the presence of the band at approximately 510 cm^{-1} range that can be assigned to the frequency $\nu_{\text{M-O}}$

- the characteristic frequencies of ν_{sym} and ν_{asym} of NH_2 urea group at 3250 cm^{-1} and 3450 cm^{-1} respectively, appear at about the same values in the precursors spectra as in urea spectrum

- the spectra of all precursors also reveal two different bands characteristic for the NO_3^- anion, i.e. $\nu_3(\text{NO}_3^-)$ at 1380 cm^{-1} and $\nu_2(\text{NO}_3^-)$ at 830 cm^{-1} , respectively

- the presence of characteristic vibration mode $\nu_{\text{Mn-N}}$ in the precursors spectra sustains, very probable, the coordination of urea NH_2 group to Mn

- it is assumed that urea molecules are coordinated to lanthanum ions by oxygen atom and to manganese ions by nitrogen.

Table 1. Characteristic IR frequencies and their assignments of urea and urea containing complex precursor

Urea	Assignments	Precursor	Assignments
3450fi	ν (OH)	3450	ν (OH)
3347fi	$\nu_{\text{as}}(\text{NH}_2)$	3340	$\nu_{\text{as}}(\text{NH}_2)$
3250u	$\nu_{\text{s}}(\text{NH}_2)$	3250	$\nu_{\text{s}}(\text{NH}_2)$
1680fi	$\nu(\text{CO}) + \delta$ (NH_2)	1620	$\nu(\text{CO}) + \delta$ (NH_2)
1600		1600	
1470fi	$\nu(\text{CN}) + \delta$ (NH_2)	1470	$\nu(\text{CN}) + \delta$ (NH_2)
		1380	$\nu_3(\text{NO}_3^-)$
1155m	$\gamma_{\text{r}}(\text{NH}_2)$	1150	$\gamma_{\text{r}}(\text{NH}_2)$
1050s	$\delta_{\text{w}}(\text{NH}_2)$	1030	$\delta_{\text{w}}(\text{NH}_2)$
		820	$\nu_4(\text{NO}_3^-)$
785s	ρ (NH_2) out of plane	785	ρ (NH_2) out of plane
		490	ν (M - O)

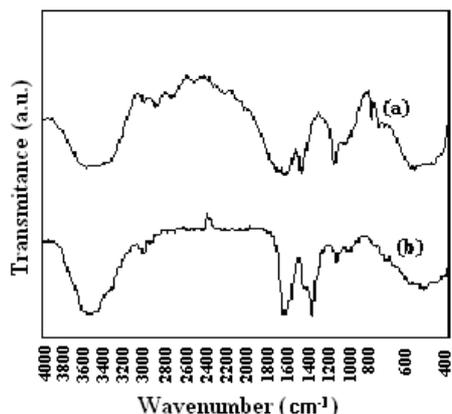


Fig. 2. IR spectra of:
(a) urea and (b) urea – based precursor

The thermal decomposition of complex precursors was studied in order to establish the best conditions for $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ synthesis. The decomposition of urea into gaseous products (HNCO and NH_3) occurs below 300°C . Metal nitrates decompose into nitrogen oxides and metal oxides as residue. During combustion, the urea containing precursors decompose with foaming due to gaseous decomposition products (a mixture of nitrogen oxides, NH_3 and HNCO). The foam is reported to be made up of polymers, such as cyanuric acid and polymeric nitrate [13]. The complex combustion of one mol of urea produces four moles of gases:



This large amount of formed gases during the decomposition of urea-based precursors dissipates the heat and thereby determines the formation of mixed oxides with fine particles.

The thermal decomposition curves (TG-DTG-DTA) of urea containing as- prepared precursor, presented in fig.3., show a complex decomposition in one step assigned to: dehydration (up to 90°C), coordination water molecules loss, melting of urea molecules (135°C), decomposition of urea molecules to give izocyanic acid and ammonia ($160 - 180^\circ\text{C}$), decomposition of nitrate ions to yield nitrogen oxides ($180-300^\circ\text{C}$), with $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ formation up to 300°C .

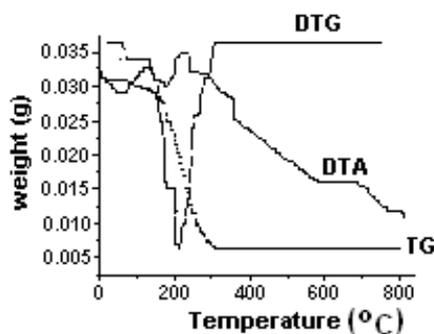


Fig. 3. Thermogravimetric curves of urea containing precursor

The first endothermic decomposition step with a minimum on the DTA curve at 90°C corresponds to the dehydration of the sample. The corresponding weight loss is about 2%. The steps of nitrates groups decomposition, as well as, urea molecules decomposition are overlapped and are accompanied by two exothermic peaks on the DTA curve. The experimental total weight loss is 80%.

2. $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ characterization

$\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ samples were characterized by XRD, SEM and electrical conductivities.

According to the X-ray powder diffraction patterns, $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ obtained by calcining the corresponding urea containing precursors are single phases with the orthorhombic structure at room temperature.

The lattice parameters and unit cell volumes, as well as the dimension of particles are summarized in Table 2.

The unit cell volume of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ decreases with Sr^{2+} content as a result of La^{3+} ($r_{\text{La}^{3+}} = 1.15 \text{ \AA}$) replacement with Sr^{2+} cations, having a larger ionic radius ($r_{\text{Sr}^{2+}} = 1.12 \text{ \AA}$).

Table 2. Crystallographic data of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ and relative densities of the samples

Sample	a [Å]	b [Å]	c [Å]	V [Å ³]	d [%]
LaMnO_3	5.5 4	5.55	7.84	241.80	75
$\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$	5.5 3	5.54	7.83	240.59	68. 5
$\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$	5.5 6	5.54	7.75	239.32	65. 6
$\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$	5.5 5	5.53	7.74	239.12	64. 5

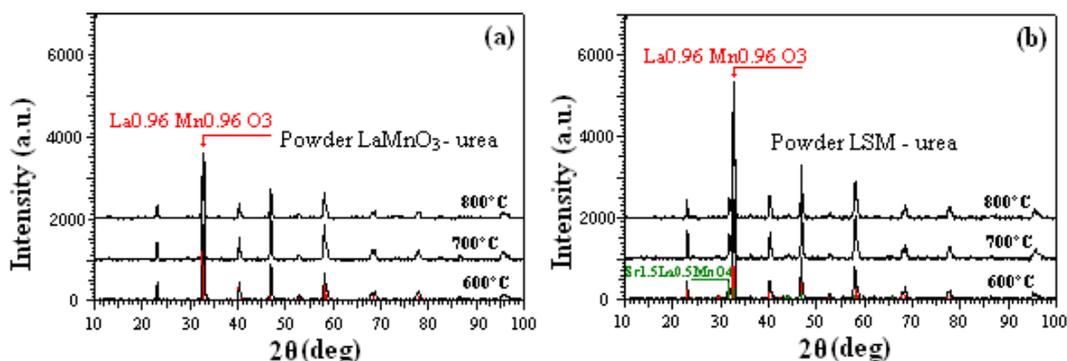


Fig.4. XRD patterns for $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ obtained from urea containing precursors by calcining at different temperatures for 1h (a) for $x=0$ and (b) for $x=0.3$

SEM examination of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ powders calcined in air at 800-900°C for one hour revealed that all the samples of lanthanum manganites produced by the urea-nitrate process have grain sizes smaller than 1 μm (between 55-65 nm as is determined from XRD analysis) with the tendency to growth and form agglomerates at higher temperature.

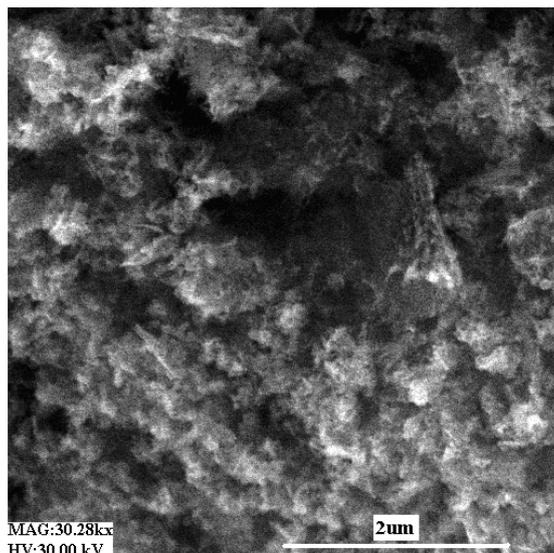


Fig. 5. SEM micrograph of $La_{1-x}Sr_xMnO_3$ obtained at $800^\circ C$ for one hour

The electrical conductivities of doped lanthanum manganites obtained by precursor calcining in air at $800^\circ C/1h$ are presented in Fig.6.

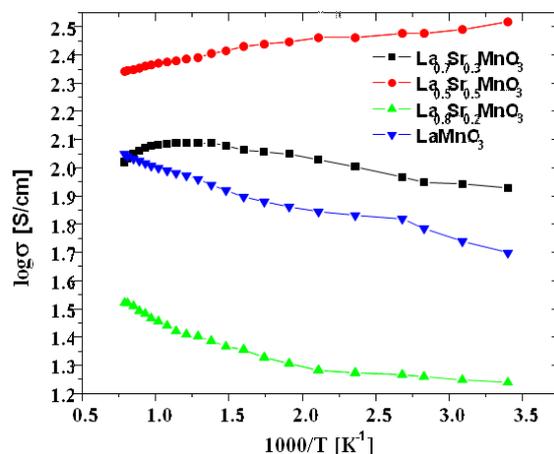


Fig .6. Temperature dependence of the electrical conductivity of $La_{1-x}Sr_xMnO_3$

There was observed that electrical conductivity of manganites is strongly depending on Sr content:

- at low temperature, $La_{0.5}Sr_{0.5}MnO_3$ has a conductivity of metallic type, but, $La_{0.8}Sr_{0.2}MnO_3$ is a semiconductor;
- $La_{0.7}Sr_{0.3}MnO_3$ presents metal-semiconductor transition at about $400^\circ C$ that can be assigned to ferromagnetic-paramagnetic transition.
- $La_{0.7}Sr_{0.3}MnO_3$ sample obtained by sintering at $1200^\circ C/5 h$ presents at $420^\circ C$ a metal-isolator transition.

The increasing of electrical conductivity with Sr content could be explained by the formation of electronic defects localized on Mn sites due to the substitution of trivalent ions (La^{3+}) with divalent ions (Sr^{2+}) in manganite lattice [14,15].

According to the Kroger -Vink point defect model, the substitution of a lower valence ion, such as Sr^{2+} leads to the formation of a tetravalent manganese ion (Mn^{4+}) for charge neutrality. A thermally activated small polaron-hopping conduction between Mn^{3+} and Mn^{4+} could be proposed

for Sr doped lanthanum manganite.

5. Conclusions

$\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ ($x=0; 0.2; 0.3; 0.5$) samples were prepared in air from urea-based precursors isolated in the $\text{La}(\text{NO}_3)_3 - \text{Sr}(\text{NO}_3)_2 - \text{Mn}(\text{NO}_3)_2 - \text{urea}$ systems. The isolated precursors were characterized by electronic and IR spectra, as well as, by thermal analysis. The weak intensity band characteristic for $\text{Mn}(\text{II})(d^5)$ ion in a square planar symmetry observed in the electronic reflectance spectrum of urea precursor disappears in oxide sample. IR spectra of precursors indicate the urea coordination (to lanthanum ions by oxygen atom and to manganese ions by nitrogen). The steps of thermal decomposition of nitrates groups, as well as, of biuret and cyanuric acid were not well resolved on the TG curve.

According to X-ray powder diffraction patterns, all solid solutions $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ obtained by urea precursors heating at $800^\circ\text{C}/1\text{h}$ were single phase with an orthorhombic perovskite-like structure.

The electrical properties of Sr doped manganites depend on the precursor sintering temperature and the Sr content. The sample with smaller Sr content ($x=0.2$) has semiconductor properties, but that with a higher Sr content ($x=0.5$) has metallic properties. $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ sample obtained by precursor sintering at $1200^\circ\text{C}/5\text{h}$ presents at 420°C a metal-insulator transition

References

- [1] N. Mannella, A. Rosenhahn, A. Nambub, B.C. Sella, B.S. Muna, S.-H. Yang, S. Marchesini, M. Watanabe, K. Ibrahime, S.B. Ritchey, Y. Tomiak, C.S. Fadley, *Journal of Electron Spectroscopy and Related Phenomena*, **153**, 37 (2006).
- [2] X. Wu, L. Xu, D. Weng, *Catalysis Today*, **90**, 199, (2004).
- [3] F. Krok, I. Abrahams, W. Wrobel, A. Kozanecka-Szmigiel, J. Dygas, *Materials Science - Poland*, **24**, 13 (2006).
- [4] J.H. Kuo, H.U. Anderson, *J. of Solid State Chem.*, **87**, 55 (1990).
- [5] V.E. Arkhipov, V.S. Gaviko, A.V. Korolyov, A.A. Arsenov, *J. Magn. Magn. Mater.*, **196**, 539 (1999).
- [6] M.R. Ibarra, J.M. De Teresa, *J. Magn. Magn. Mater.*, **177**, 846 (1998).
- [7] J. Rivas, L.E. Hueso, A. Fondado, F. Rivadulla, M.A. Lopez-Quintela, *J. Magn. Magn. Mater.*, **221**, 57 (2000).
- [8] Jun Zhang, Hidekazu Tanaka, Tomoji Kawai, *J. Appl. Phys.*, **12**, 75 (2001).
- [9] M. Garcia-Hernandez, J.L. Martinez, A. de Andres, E. Herrero, J.M. Alonso, L. Vazquez, *J. Magn. Magn. Mater.*, **196**, 530 (1999).
- [10] Ying Hai Li, Françoise Damay, Lesley F. Cohen, Kodankandath A. Thomas, Akther K.M. Hossain, Judith MacManus-Driscoll, *J. Am. Ceram. Soc.*, **84**, 47 (2001).
- [11] J. Neamtu, T. Malaeru, I. Jitaru, A. E. Patroi, G. Georgescu, *J. Optoelectron. Adv. Mater.*, **8**, 470 (2006).
- [12] S. Sundar Manoharan, K. C. Patil, *J. Solid State Chem.*, **267** (1993).
- [13] S. Sundar Manoharan, K. C. Patil, *J. Amer. Chem. Soc.*, **75**, 1012 (1992).
- [14] G. Brankovic, K. Duris, Z. Jaglicic, M. Jagodic, Z. Brancovik, *Adv. Appl. Ceram.*, **108**, 267 (2009).
- [15] S.P., Jiang, S. Zhang, Y.D. Zhen, *J. Mater. Res.*, **20**, 747 (2005).