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SYNTHESIS AND CHARACTERIZATION OF NEW PRECURSORS FOR LANTHANUM NICKELATE PEROVSKITE

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Lucrarea prezintă sinteza şi caracterizarea unor noi precursori complecşi ai nichelitului de lantan, oxid mixt cu structura perovskitică. Precursorii au fost obtinuți prin procedeul sol-gel utilizând sistemele: $La(NO_3)_3 - Ni(NO_3)_2 - L$ *(unde L = sare cuaternară de amoniu a 2-amino-1-etanol, uree, sorbitol sau alanină). Precursorii au fost caracterizați prin analiză spectrală (UV-Vis şi IR) şi analiză termică, iar oxidul mixt prin analiză IR şi difracție de raze X.*

This paper presents the synthesis and characterization of new precursors for lanthanum nickelate, mixed oxide with perovskite structure. The precursors were obtained by sol-gel procedures using the systems: $La(NO_3)_3 - Ni(NO_3)_2 - L$ *(where L = quaternary ammonium salt of 2-amino-1-ethanol, urea, sorbitol or alanine). Precursors have been characterized by UV-Vis spectra, IR spectra and thermal analysis, while the lanthanum perovskite has been characterized by IR spectra and X-ray diffraction.*

Keywords: precursors for lanthanum nickelate, quaternary ammonium salts of 2-ammino-1-ethanol, urea, sorbitol, alanine

1. Introduction

Mixed metal oxides with perovskite-type structure are represented by ABO_3 general formula where A ions can be rare earth, alkaline earth and alkali metals that fit into dodecahedral site of the framework, and the B ions can be *3d*, *4d* or *5d* transitional metal ions which occupy the octahedral sites. [1, 2]

In the last years, theoretical and technological studies for mixed oxides with perovskite structure have developed, based on their physical (ferroelectric, piezoelectric, piroelectric, magnetic, electro-optic, dielectric, conducting and superconducting properties) and catalytic properties too. [3-5]

The perovskite type catalysts containing nickel, such as $LaNiO_3$, have a structure relatively stable when heated and a good activity for the steam

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reforming reaction which directs to obtaining CO_2 and H_2O under oxidative conditions [6, 7].

The use of these oxides for the purification of the volatile organic compounds (VOCs), total combustion of hydrocarbons for energetic conversion, reduction of NO_x, and automotive emission make them the catalysts of the future. [8] These systems are potential substitutes of catalysts containing platinic metals deposited on different supporting materials, like alumina, silica, asbestos, in the total oxidation reaction of the hydrocarbons.

This paper presents the synthesis and characterization of new precursors for lanthanum nickelate used as catalyst and it is a part of our large study about this subject. [10] The precursors have been prepared in the systems of metallic nitrates and organic compounds which act as ligands and “fuels” too. In this study we have researched the possibilities to obtain lanthanum nickelate perovskites by thermal decomposition of some polynuclear complex precursors obtained in the systems: $La(NO_3)_3 – Ni(NO_3)_2 – L$ – where L was quaternary ammonium nitrate of 2-amino-1-ethanol (choline nitrate), urea, sorbitol or alanine.

2. Experimental data

In an aqueous or alcoholic solution of $La(NO_3)_3 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$ and L (choline nitrate – alcoholic solution, urea, sorbitol or alanine – aqueous solution) with the molar ratio 1:1:2 ammonia (12.5 %) was added up to pH 7.5- 8. The solution was heated at boiling point until a gel (when using sorbitol) or a powder (when using choline, urea or alanine) was formed. The gel and powders were dried in air at 80ºC. The synthesized precursors have had different colours: light green (compounds with choline, urea, sorbitol) and light blue-mauve (compound with alanine).

The synthesized precursors were calcinated 3 hours at 700ºC and black $LaNiO_{3-\delta}$ perovskites were obtained.

The results of the elemental chemical analysis obtained by atomic absorption (AAS) are presented in Table 1.

Table 1

Results of the elemental chemical analysis

Compounds	Weight, %	
	La	Ni
Choline based complex precursor	16.75	3.71
Urea based complex precursor	22.09	3.88
Sorbitol based complex precursor	17.75	3.57
Alanine based complex precursor	21.11	4.77

Precursors have been characterized by UV-Vis and IR spectra, and thermal analysis. The lanthanum nickelate perovskite has been characterized by IR spectra and X-ray diffraction pattern.

Electronic reflectance spectra were recorded at room temperature using a Jasco V560 spectrophotometer.

IR spectra were recorded with a Perkin-Elmer spectrophotometer using pressed KBr pellets technique.

TG-DTG analyses were performed in air, between 25-800ºC on a Paulik-Erdey derivatograph (Al_2O_3 as standard material).

X-Ray diffraction patterns were performed on a Bruker AXS diffractometer D8 ADVANCE type.

3. Results and discussion

Electronic reflectance spectra of the precursors present absorbtion bands in similar wavelength domains (Figure 1), corresponding to a Ni^{2+} tetrahedral configuration. These spectra are characteristic for a D_{4h} symmetry pattern. The band in the ultra violet range is the ligand band (choline, urea, sorbitol or alanine) and the bands around 400 nm could be attributed to charge transfer (CT) bands.

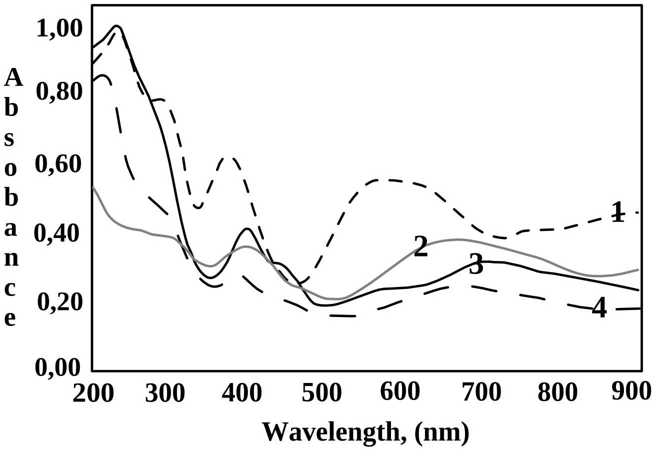

Fig. 1. Electronic reflectance spectra of the choline (3), alanine (1), urea (4), sorbitol (2) based precursor

The IR spectra of the used ligands and obtained precursors (Fig. 2) show some changes on the ligand (choline, urea, sorbitol or alanine) moiety determined by a possible coordination of the ligand with the metallic ions.

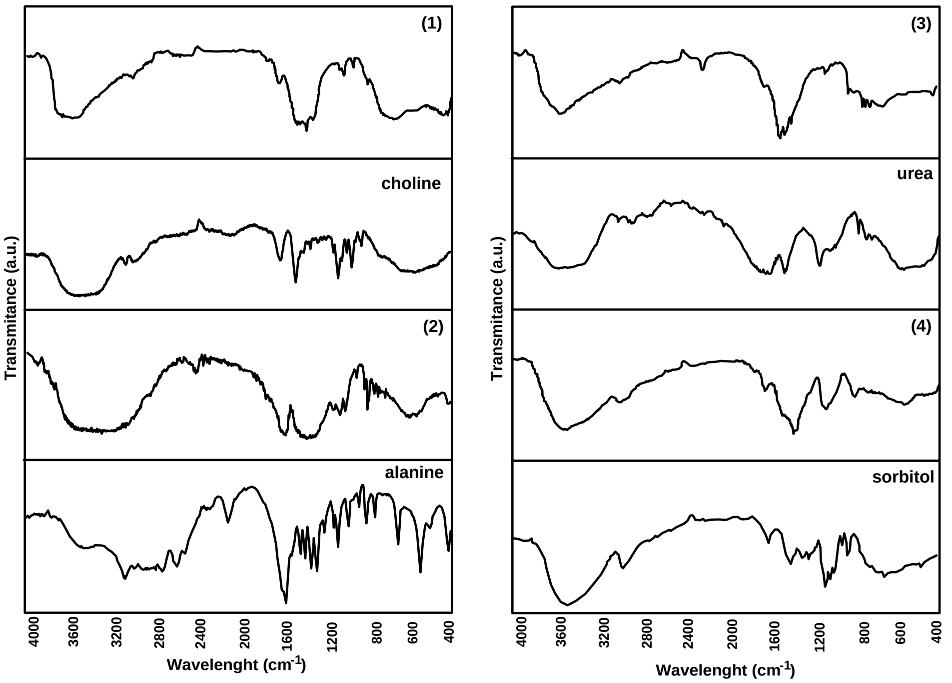

Fig. 2. IR spectra of the choline (1), alanine (2), urea (3), sorbitol (4) based precursors and their corresponding ligands

TG and DTG curves (Fig. 3a) for urea based precursor present three losses of weight at about 250ºC (19.9%), 350ºC (24.4%) and 500ºC (13.8%). Total decomposition took place at about 550ºC with the formation of a stable mixed oxide.

A unique loss of weight is observed on the TG/DTG curves of choline based precursor in 250 - 300ºC range (Fig. 3b). In this case the temperature of the precursor total decomposition and the formation of mixed oxide is 350ºC.

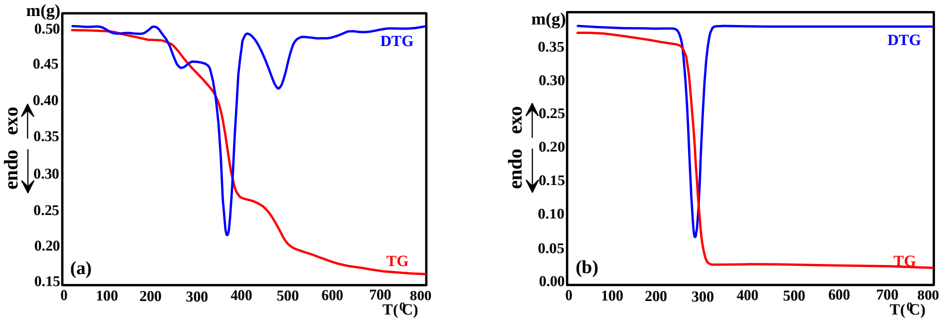

Fig. 3. Thermogravimetric analysis of the urea based precursor (a) and choline based precursor (b)

IR- spectra of the powders obtained by the calcinations of urea precursor at 500ºC/1 h (Fig. 4) and choline precursor at 350ºC/1h (Fig. 5) present bands only at about 600-650 cm^{-1} which may be assigned to Ni-O and La-O frequencies (the aspect of the IR spectra is characteristic for mixed oxides).

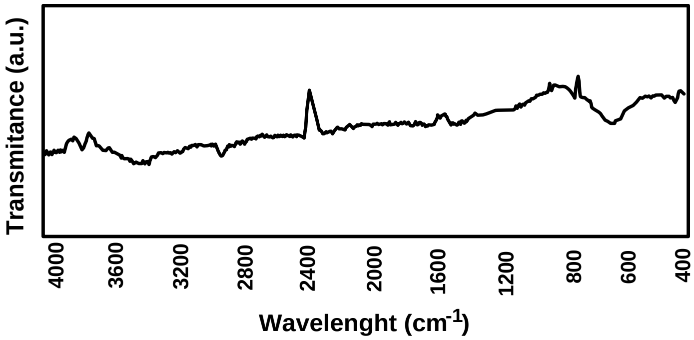

Fig.4. IR spectrum of lanthanum nickelate obtained by calcination of choline precursor

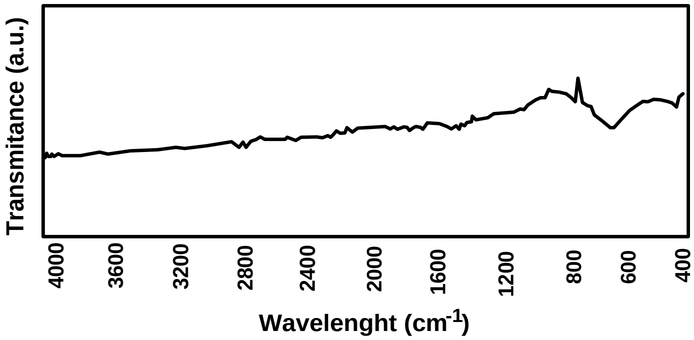

Fig.5. IR spectrum of lanthanum nickelate obtained by calcination of urea precursor

X-Ray diffraction pattern data for powders obtained by calcinations of choline, urea and sorbitol based precursors are presented in Figs 6. The XRD diagrams of these powders were compared with the diffractograms of $LaNiO_3$ [9] and $LaNiO_{3-\delta}$ patterns (Fig. 7).

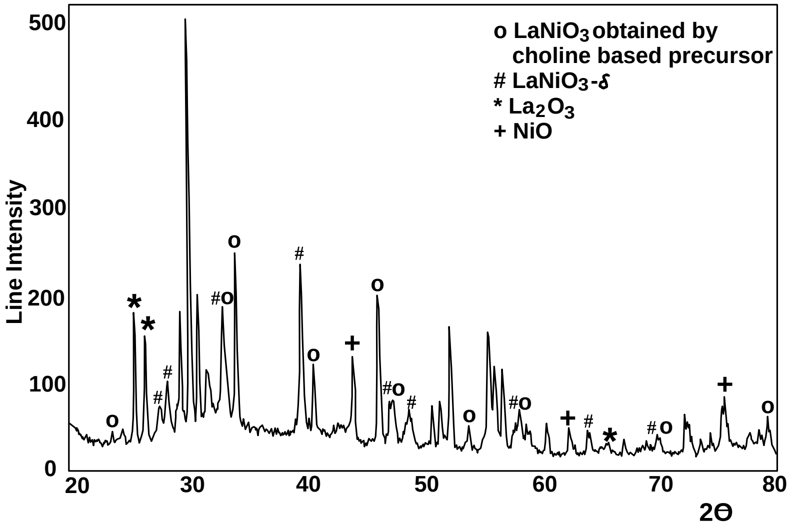

Fig. 6.a. X-ray power patterns of $LaNiO_3$ obtained by choline based precursor at 700ºC/3h

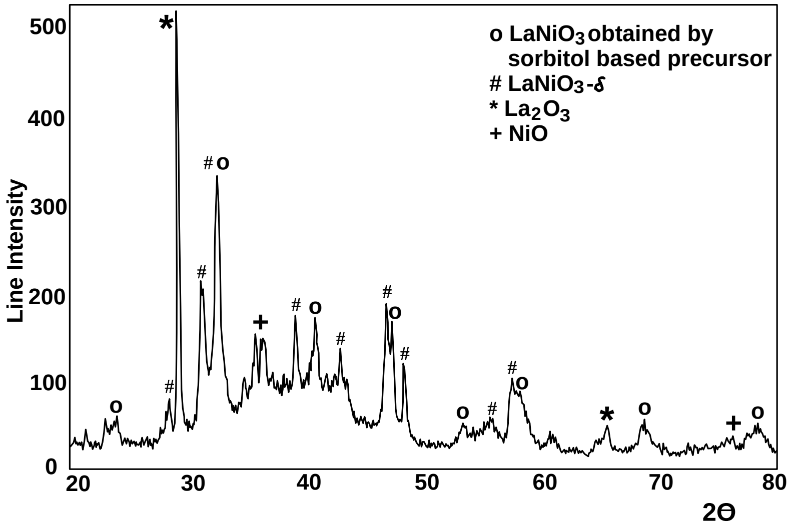

Fig. 6.b. X-ray power patterns of $LaNiO_3$ obtained by urea based precursor at 700ºC/3h

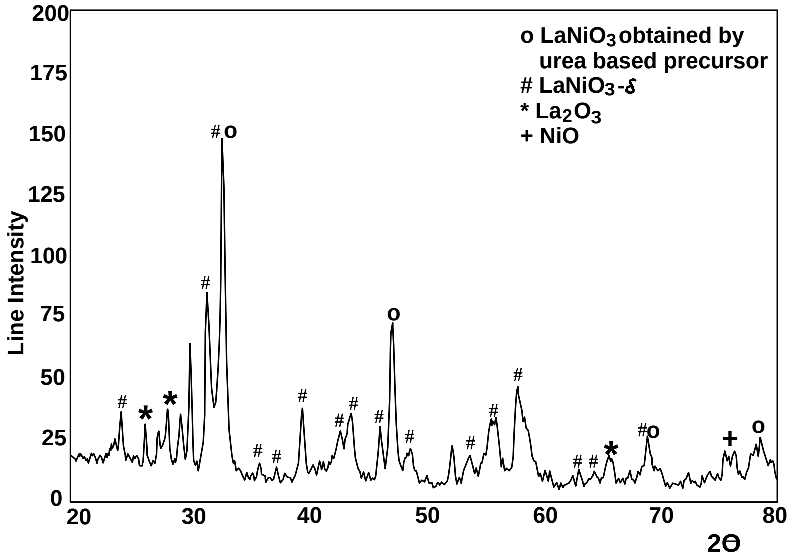

Fig. 6.c. X-ray power patterns of $LaNiO_3$ obtained by sorbitol based precursors at 700ºC/3h

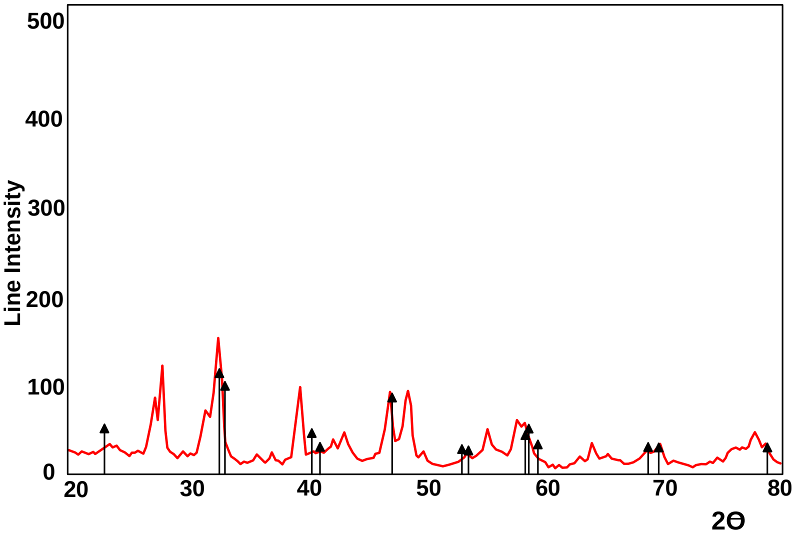

Fig. 7. Diffractograms of $LaNiO_3$ and $LaNiO_{3-\delta}$. The fleshes give the position and relative intensity patterns of the pure $LaNiO_3$ [9] and the continuous curve is the XRD diagrams of $LaNiO_{3-\delta}$.

In all cases the formation of lanthanum nickelate in the form $LaNiO_{3-\delta}$ (with oxygen deficiency) was confirmed. The picks of $LaNiO_3$ and $LaNiO_{3-\delta}$ in the synthesized compounds are slowly shifted to the left compared to the patterns of the stoichiometric mixed oxide and the picks of $LaNiO_{3-\delta}$.

NiO and La_2O_3 were also observed as impurities, especially in the case of lanthanum nickelate obtained from choline precursor. This fact could be a consequence of the forced formation of a mixed oxide at this lower temperature (350ºC).

The lanthanum nickelates obtained in this study have been used as catalyst in toluene oxidation [11] and we have demonstrated the importance of the nickelate nature (stoichiometric or with oxygen deficiency) on the catalysis result.

4. Conclusions

The precursors of lantahnum nickelate were prepared by calcination at 700ºC/3h of the complex precursors obtained in the systems: $La(NO_3)_3$ – $Ni(NO_3)_2$ – L (where L = choline, urea, sorbitol or alanine). The precursors were characterized by UV-Vis, IR spectra and thermal analysis. The lanthanum nickelates obtained by calcination were characterized by IR spectra and X-ray diffraction analysis.

The XRD analysis sustained the formation of $LaNiO_{3-\delta}$ mixed oxides with perovskite type structure in all cases.

REFERENCES

[1] *Sania Maria de Lima, José Mansur Assaf*, Mat. Res. **vol. 5**, no. 3, September 2002, p. 329-335

[2] *V.R. Choudhary, B.S. Uphade, A.A. Belhekar*, Journal of Catalysis, **vol. 163**, issue 2, October 1996, p. 312-318

[3] *A.Yu. Dobin, K.R. Nikolaev, A.M. Goldman*, Physical Review B, **vol. 68**, issue 11, October 2003, p. 113408-113411

[4] *T. Aytug, B.W. Kang, C. Cantoni, E.D. Specht, M. Paranthaman, A. Goyal, D.K. Christen, D.T. Verebelyi, J.Z. Wu, R.E. Ericson, C.L. Thomas, C-Y. Yang, S.E. Babcock*, J. Mater. Res., **vol. 16**, issue 9, September 2001, p. 2661-2669

[5] *G. Catalan, R.M. Bowman, J.M. Gregg*, Phys. Rev. B, **vol. 62**, issue 12, September 2000, p. 7892-7900

[6] *M.R. Goldwasser, E. Pietri, A. Barrios, O. González, M.J. Pérez-Zurita, M.L. Cubeiro,* Proceeding of the XVII Ibero-American Symposium of catalysts, Porto, Portugal, June 2000

[7] *F.T. Akin, J.Y.S. Lin,* J. Membrane. Sci. **vol. 231**, issue 1-2, March 2004, p. 133-146

[8] *V. Matei, D. Matei, L. Patron, C. Suciu, A. Borcea*, “The toluene oxidation study on mixed oxides perovskite type”, Scientific Communication Session, Ploiesti, Romania, November 2002

[9] JCPDS – Joint Committee on Powder Diffraction Standards, International Centre for Diffraction Data, Pennsylvania, USA, 1994

[10] *L.C. Chioaru, V. Matei, D. Matei, O. Mihai, M.G. Alexandru, C. Covaliu, I. Jitaru,* Proceeding of the International Symposium – SIMI 2007 „The environment and industry”, Bucharest, Romania, October 2007

[11] *L.C. Chioaru, I. Jitaru, V. Matei*, ”Perovskite oxides as catalysts for toluene oxidation”, J. Serb. Chem. Soc. (in press)