SYNTHESIS OF PURE AND DOPED LANTHANUM COBALTITE BY THE COMBUSTION METHOD

D. Berger[a*], Nitte van Landschoot[c], C. Ionica[a,b], F. Papa[b], V. Fruth[b]

[a]"Politehnica" University Bucharest, Department of Inorganic Chemistry, 1 Polizu street, 78126-Bucharest, Romania
[b]Romanian Academy, Institute of Physical Chemistry, Bucharest, Romania
[c]Delft University of Technology, Laboratory for Inorganic Chemistry, Julianalaan 136, 2628 BL, Delft, The Netherlands

The paper presents structural and morphological investigation on pure and doped lanthanum cobaltite, $La_{1-x}M_xCoO_3$ (M=Sr, Ca; x=0, 0.1). High specific–surface area perovskites (36 – 86 m^2/g) have been synthesised by the combustion synthesis method using the corresponding metal nitrates and α-alanine as fuel The isolated complex precursors were characterised by chemical analysis, electronic and FT-IR spectra, as well as DTA-TG analysis. $La_{1-x}M_xCoO_3$ (x=0, 0.1) powders were characterised by XRD, IR, SEM-EDX, and specific surface area measurements. The XRD data for $La_{1-x}M_xCoO_3$, support the rhombohedral perovskite structure. $La_{1-x}M_xCoO_3$ powders are characterized by crystallites of size 31-45 nm and large values of the specific surface area.

1. Introduction

Recently, lanthanum-based perovskite have attracted much attention due to their electrical, magnetic, structural and catalytic properties [1]. Pure and doped lanthanum cobaltites have been studied due to their potential application as a catalysts for hydrocarbons oxidation [2], for the control of automobile emission [3], cathode material for solid oxide fuel cells (SOFCs) [4], as well as gas detection sensors [5]. In recent years, a lot of research efforts have been devoted to the study of perovskite-type oxides in catalytic combustion. Nevertheless, the application of perovskite is still limited by their low surface area and strong tendency to sintering. A deeper insight into their physicochemical properties and their dependence on the synthetic routes can lead to optimisation of the material performance. In this regard, nanostructured materials with large surface area and high defect content are expected to show enhanced properties with respect to materials prepared by conventional methods. Wet chemical routes have been applied to lower the synthesis temperature and to obtain nanopowders of desired compositions [6-10]. The combustion method is an attractive synthetic route for preparation of multicomponent oxide materials and leads to uniform, fine particle size [8-10].

This paper deals with the synthesis of fine particles of pure and alkaline-earth doped lanthanum cobaltites via thermal decomposition of complex precursors isolated in the following system: $La(NO_3)_3 \cdot 6H_2O – Co(NO_3)_2 \cdot 6H_2O – M(NO_3)_2$ (M=Sr, Ca) – α-alanine.

---

* Corresponding author: danaberger01@yahoo.com

2. Experimental

The $La_{1-x}M_xCoO_3$ (M = Sr, Ca; x = 0; 0.1) samples were prepared by calcining of isolated α-alanine containing precursors. The complex precursors were synthesized in aqueous solution from metal nitrates and α-alanine, at molar ratios of La : Co : M(II) : α-alanine = (1-x) : 1 : x : 1.7 (M = Ca, Sr; x = 0; 0.1). Oxidizer (metal nitrates)-fuel (α-alanine) compositions were calculated using oxidizing valences of metal nitrates and reducing valence of organic ligand used in the field of propellants and explosives [9]. The stoichiometric composition of the redox mixture was established on the basis of a simple valence balance of the contained elements in the oxidizer and fuel components of the mixture. The high purity metal nitrates (Merck) were dissolved in a minimum volume of deionized water. The saturated aqueous solution of α-alanine (Merck) was added with stirring to the aqueous solution of corresponding metal nitrates. Then, the mixture was heated at ~110 °C on a hot plate with stirring to evaporate the water until a violet precipitate was obtained. The precursor was washed with ether, dried and kept on P_4O_{10}.

The isolated complex precursors were characterised by chemical analysis, electronic and FT-IR spectra, as well as DTA-TG analysis. The metals content of the samples were determined on Pye Unicam atomic absorption spectrophotometer. The reflection electronic spectra were recorded on a VSU-2G spectrophotometer using MgO as a reference material. IR spectra were performed on a Specord M80 Carl Zeis Yena spectrometer (KBr-pellet technique). Thermal analysis was performed in air in 25 °-1000 °C temperature range using a Paulik Paulik-Erdey equipment.

The $La_{1-x}M_xCoO_3$ (M=Sr, Ca; x = 0; 0.1) powders were prepared by calcining the isolated complex precursors at 800 °C, 3h for $LaCoO_3$, 1000 C, 4h for $La_{0.9}M_{0.1}CoO_3$. $La_{1-x}M_xCoO_3$ samples were characterised by infrared spectroscopy, X-ray diffraction patterns (XRD), scanning electron microscopy – energy dispersive X-ray spectroscopy (SEM-EDX), as well as specific surface area measurements. X-ray diffraction data were collected using a Bruker AXS D8 Advance diffractometer with Cu$K\alpha$ radiation at a step of 0.02°/s in the range 2θ = 10 to 90 °. Lattice parameters were calculated using the software Powder X. Particles sizes (D) were calculated by means of the Scherrer equation, $D = K\lambda/\beta\cos\theta$, where K is a constant equal to 0.9, λ, the wavelength of the X-ray used, β, the full width at half-maximum (FWHM) of the X-ray reflection. Scanning electron micrographs of the $La_{1-x}M_xCoO_3$ (x = 0; 0.1) powders were obtained using a JEOL JSM-5800 scanning electron microscope. Specific surface areas were measured by nitrogen adsorption-desorption at liquid nitrogen temperature (BET method).

3. Results and discussion

3.1. Precursor characterisation

The *electronic reflection spectrum* of the $LaCoO_3$ precursor shows the characteristic bands of Co(II) ion in octahedral coordination, one at 540 nm (18,5 kK) assigned to $^4T_{1g} \rightarrow {}^4T_{1g}(P)$ (ν_3) and another one in the near infrared assigned to $^4T_{1g}\rightarrow{}^4T_{1g}$ (ν_1). The electronic spectrum of $LaCoO_3$ alanine-based precursor presents a charge transfer band at 360 nm (27.8 kK) (Fig. 1) [11].

The *FT-IR spectra* were recorded in order to obtain more data about the structure of prepared complex precursors.
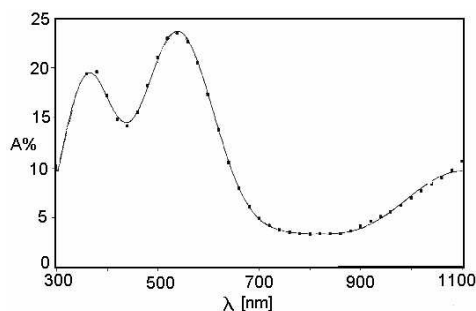

Fig.1. Electronic spectrum of $LaCoO_3$ precursor.

The IR frequencies and their assignments for α-alanine containing precursor of LaCoO$_3$ in comparison with those of free α-alanine [12,13] are gathered in Table 1. The shift of the very intense band from 1597 cm^{-1} (ν_{as}(CO) of α-alanine) to a higher frequency (1632 cm^{-1}) in the spectra of the complex precursors indicates the coordination of alanine by oxygen atoms. The coordination of alanine molecules by nitrogen is sustained by the shift of ρ_r(NH$_2$) vibration mode and the presence of the band at 354 cm^{-1} that can be assigned to the ν(Co-N) vibration mode. The FT-IR spectrum of [LaCo(C$_3$H$_7$NO$_2$)$_2$(H$_2$O)$_9$](NO$_3$)$_5$·xH$_2$O also reveals the characteristic bands for NO$_3^-$ anion: ν_1=1046 cm^{-1}, ν_2=837 cm^{-1}, ν_2=746 cm^{-1}. The frequencies of coordinated water (542 cm^{-1}, 668 cm^{-1}, 3430 cm^{-1}) are also present in the IR spectrum.

Table 1. IR frequencies and their assignments of α-alanine and LaCoO$_3$ alanine-based precursor.

α-alanine [cm^{-1}]	Assignments	LaCoO$_3$ precursor [cm^{-1}]	Assignments
		3430	ν_{as}(NH)
		3200	ν_s(NH)
1623	δ_d(NH$_3^+$)		
1597	ν_{as}(CO)	1632	ν_{as}(CO)
		1482	ρ(HOH)
1455	δ_d(CH$_3$)	1468, 1432	δ_d(CH$_3$)
1412	ν_s(CO)	1385	ν_s(CO), ν_2(NO$_3^-$)
1355	δ_s(CH$_3$)	1352	δ_s(CH$_3$)
1237, 1113	ρ_r(NH$_3^+$)	1204,	ρ_r(NH$_2$)
1148	ν_{as}(CCN)	1116	ν_{as}(CCN)
		1046	ν_1(NO$_3^-$)
1026, 1015	ρ_r(CH$_3$)	976	ρ_r(CH$_3$)
918, 852	ν_s(CCN)	930	ν_s(CCN)
		837	ν_2(NO$_3^-$)
771	δ(COO$^-$)	770	δ(COO$^-$)
		746	ν_4(NO$_3^-$)
648	ρ_w(COO$^-$)	668	ρ(C=O), ρ_r(HOH)
540	ρ_r(COO$^-$)	542	ρ_r(COO$^-$), ρ_w(HOH)
492	ρ_t(NH$_3^+$)	400	ν(Co-O) (Co-OH$_2$)
		354	ν(Co-N)
		284	CCCN def.

It is known that the lanthanoides are oxofiles. It is assumed that α-alanine molecules are coordinated to lanthanum by oxygen and to cobalt by nitrogen.
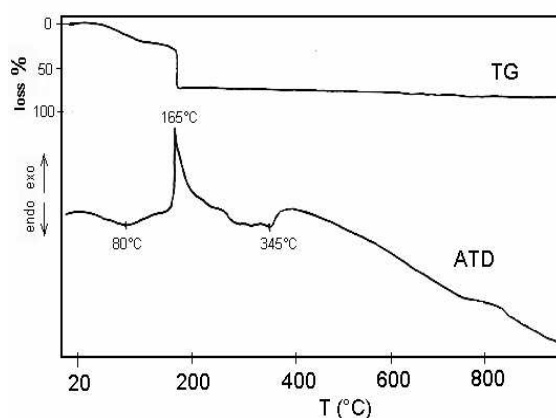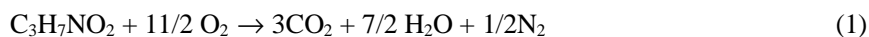

Fig. 2. DTA-TG curves of LaCoO$_3$ alanine-based precursor.

The temperature of perovskite-phase formation has been studied using *thermal analysis* (DTA-TG) on the alanine-based precursors. The endothermic peak observed at $60°-110°C$ temperature range ($T_{max}=80°C$) is accompanied by a noticeable weight loss (18.5%) in the TG curve. It is assigned to hydration water loss. The endothermic noticed in $110°-150°C$ temperature range and accompanied by a 5.2% weight loss is assigned to a part of coordination water loss. The DTA curve presents three exothermic effects, a big one at $150°-185°C$ ($T_{max}=165°C$) temperature range that could be assigned to the rest of coordination water loss and decomposition of organic molecules and other two effects, not well defined, at $185°-340°C$ temperature range assigned to decomposition of nitrate ions into nitrogen oxides. These exothermic effects are accompanied by a 47.5% weight loss. In the Fig. 2 it can be noticed an endothermic effect at $345°C$. This effect could be assigned to crystallisation process of lanthanum coblatite. At $T>350°C$ the weight loss is very small and it could be assigned to superficial OH groups loss and formation of lanthanum cobaltite. During combustion, the α-alanine-based precursors decompose with foaming due to gaseous decomposition products. The complete combustion of 1 mol of α-alanine produces 4 mol of gases as (Eq. 1).

$$C_3H_7NO_2 + 11/2\ O_2 \rightarrow 3CO_2 + 7/2\ H_2O + 1/2N_2 \qquad (1)$$

The total experimental weight loss of $LaCoO_3$ alanine - based precursor is 77.7% and the theoretical one, 76.5%.

3.2. The characterisation of pure and doped lanthanum cobaltites

The *XRD data* for $La_{1-x}M_xCoO_3$ (M=Sr, Ca; x = 0; 0.1) obtained by thermal treatment of alanine-based precursors at $800°C$, 3h for $LaCoO_3$ and $1000°C$, 4h for $La_{0.9}Sr_{0.1}CoO_3$ and $La_{0.9}Ca_{0.1}CoO_3$ show that the powders are single phase with rhombohedral distorted perovskite structure, space group $R\overline{3}m$ (Fig. 3). No secondary phase was observed in the calcined samples. The refined lattice parameters are presented in Table 2. The substitution of La^{3+} ions with Sr^{2+} ions causes an increasing of lattice parameters because of the larger ionic radius of Sr^{2+} ($r_{La^{3+}} = 1.23\,\text{Å}$, $r_{Sr^{2+}} = 1.25\,\text{Å}$ in dodecahedral coordination). The substitution of La^{3+} ions with Ca^{2+} causes a decreasing of the lattice parameters that could be explained by smaller radius of calcium cations (1.07 Å). Unit cell parameters are in good agreement with JCPDS 84-0846, 84-0847, 36-1392 and 28-1229.
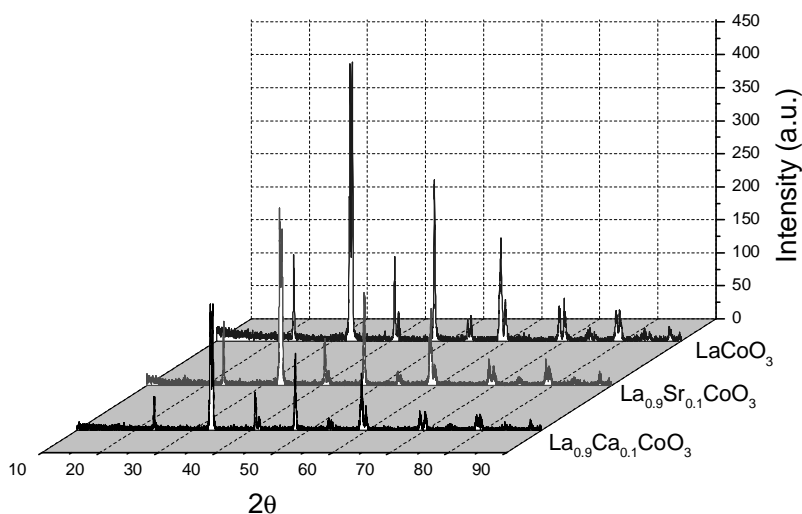

Fig. 3. XRD patterns of $La_{1-x}M_xCoO_3$ powders.

Table 2. Some properties of pure and doped lanthanum cobaltite samples.

Sample	a^* [Å]	c [Å]	σ	R [%]	D_{012} [nm]	S [m^2/g]
LaCoO$_3$	5.4452	13.1032	0.066	0.024	31	86.9
La$_{0.9}$Sr$_{0.1}$CoO$_3$	5.4492	13.1411	0.090	0.040	41	42.7
La$_{0.9}$Ca$_{0.1}$CoO$_3$	5.4377	13.0910	0.086	0.035	44	36.6

$*a = b$; σ is the standard deviation and R, the residuals for the Powder X refinement.
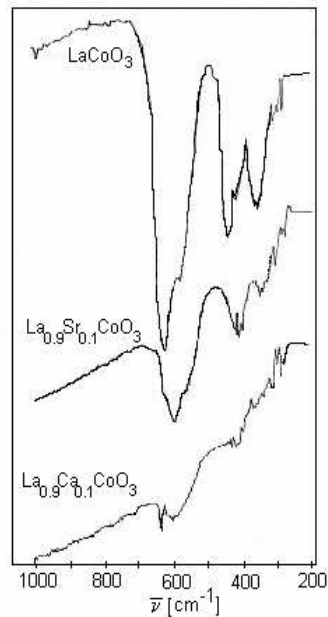

Fig. 4. IR spectra of La$_{1-x}$M$_x$CoO$_3$.

Fig. 4 presents the IR spectra of La$_{1-x}$M$_x$CoO$_3$ samples. The IR spectrum of LaCoO$_3$ presents an intense band around 605 cm^{-1} that could be assigned to vibration of Co-O bond in octahedral coordination and a band from 420 cm^{-1} assigned to vibration of La-O bond in dodecahedral coordination [14]. In the IR spectra of doped samples appears a shoulder at around 670 cm^{-1} maybe due to Co^{4+} ions formation. The appearance of this band at higher frequencies could be explained by the increasing of constant force of Co-O as result of increasing of cobalt ions electrical charge. It can be noticed also the splitting of characteristic vibration of ν_{La-O} that might be assigned to the presence of doping ions.
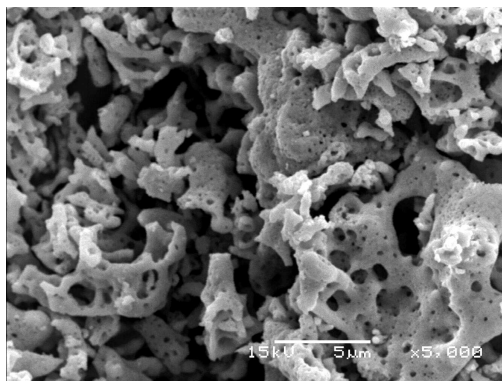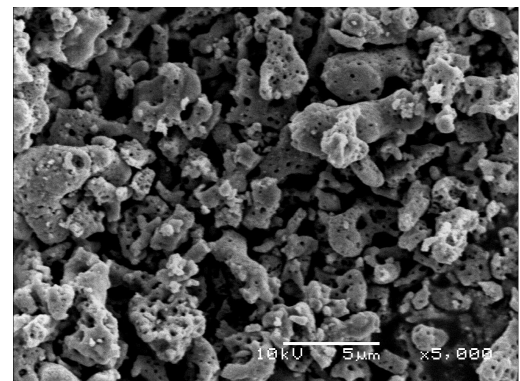

Fig. 5. SEM picture of La$_{0.9}$Sr$_{0.1}$CoO$_3$

Fig. 6. SEM picture of La$_{0.9}$Ca$_{0.1}$CoO$_3$

Table 2 lists the crystallite sizes (D_{012}), determined from FWHM of the (012) diffraction peak using Scherrer's equation and the specific surface area values for $La_{1-x}M_xCoO_3$ (M=Sr, Ca; x=0; 0.1) determined by BET method. From Table 2 it can notice that $La_{1-x}M_xCoO_3$ samples have large surface area values and the presence of M^{2+} ion determines a decrease of it. The chemical analysis results by EDX for lanthanum cobaltite samples show a homogenous distribution of metallic cations.

SEM examination of the $La_{1-x}M_xCoO_3$ powder surfaces show that the oxides have fine particles with a small tendency of agglomerates formation with different shapes and spongy appearance, more markedly for strontium-doped sample (Figs. 5 and 6).

4. Conclusions

To our knowledge, this is the first report of the preparation of the cobaltite compounds $La_{1-x}M_xCoO_3$ (M = Sr, Ca; x = 0; 0.1) from thermal decomposition of alanine-based precursors, which has been successfully used to get nanopowders with very large specific surface area values.The isolated alanine-based precursors were characterized by chemical analysis, electronic and IR spectra, as well as thermal analysis. The oxide powders obtained by calcining of complex precursors were investigated by XRD, IR spectroscopy, SEM-EDX and specific surface area measurements. The XRD data for $La_{1-x}M_xCoO_3$ show that the samples are single phase with rhombohedral distorted perovskite structure. SEM pictures of $La_{1-x}M_xCoO_3$ powders showed that all the samples have primary fine with a small tendency to form agglomerates and exhibiting high porosity. All $La_{1-x}M_xCoO_3$ samples have the crystallite sizes in 30-45 nm range and very large specific surface area for perovskite oxides. This preparation method is a simple route and the powders are suggested for application as catalysts.

References

[1] H. Hayashi, H. Inaba, M. Matsuyama, N. G. Lan, M. Dokiya, H.Tagawa, Solid State Ionics, **122**, 1(1999).
[2] M. O'Connell, A. K. Norman, C. F. Hüttermann, M. A. Morris, Catalysis Today **47**, 123(1999).
[3] H. Tanaka, N. Mizuno, M. Misono, Appl. Catal. A: General **244**, 371(2003).
[4] E. Maguire, B. Gharbage, F. M. B. Marques, J. A. Labrincha, Solid State Ionics **127**, 329(2000).
[5] E. Di Bartolomeo, E. Traversa, M. Baroncini, V. Kotzeva, R. V. Kumar, J. Europ. Ceram. Soc. **20,** 2691(2000).
[6] H. Taguchi, S. Yamada, M. Nagao, Y. Ichikawa, K. Tabata, Materials Research Bulletin **37,** 69(2002).
[7] L. Amelao, G. Bandoli, D. Barreca, M. Bettinelli, G. Bottaro, A. Caneschi, Surface and Interface Analysis **34,** 112(2002).
[8] S. T. Aruna, M. Muthuraman, K. C. Patil, Materials Research Bulletin **35**, 289(2000)
[9] S. Sundar Manoharan, K. C. Patil, J. Solid State Chem. **75**, 267(1993).
[10] M. T. Colomer, D. A. Fumo, J. R. Jurado, A. M. Segadaes, J. Mater. Chem. **9**, 2505(1999).
[11] B. P. Lever, Inorganic Electronic Spectroscopy, Elsevier, Amsterdam, London, New York (1984).
[12] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, Wiley, New York (1986).
[13] J. F. Jackovitz, J. A. Durkin, J. L. Walter, Spectrochimica Acta **23A**, 67(1966).
[14] P. Ganguly, Y. Vasanthacharya, J. Solid State Chem. 61, 164(1986).