

Thermal evolution of nitrate precursors for processing of lanthanide perovskites

V. S. KOZHUKHAROV, M. S. MACHKOVA AND N. V. BRASHKOVA

University of Chemical Technology and Metallurgy- Sofia, 8 Kl. Okhridski blvd., Sofia-1756, Bulgaria

Studies on thermal decomposition of ceramic powder with a general formula of $(La_{1-x}Ba_x)(Co_{0.8}Fe_{0.2})O_3$ have been achieved. Precursors as nitrate solutions with additive of EDTA as complexing agent are used for powder processing. The black powders obtained are dried and their thermal evolution up to 1000°C has been investigated by Differential Thermal Analysis. The powders were analyzed by EDX and ICP-AES, as well. It was established that the powder compositions are very close to the nominal one. The resulting DTA, TA, TG and DTG curves are analyzed as function of the composition and heating rate applied. At polythermal scanning regime three regions the powder thermal evolution are discussed. The correlation dependence has been examined for both Sr- and Ba- doped multicomponent lanthanide samples. The multicomponent nature of the samples have been shown on the base of the thermal treatment applied and XRD phase control carried out.

Key words: thermal decomposition, lanthanum perovskites

Evolución térmica de precursores de nitratos para el procesado de perovskitas de lantánidos

Se han realizado estudios sobre la descomposición térmica de polvos cerámicos de fórmula general $(La_{1-x}Ba_x)(Co_{0.8}Fe_{0.2})O_3$. Se utilizaron como precursores soluciones de nitratos con EDTA como agente complejante. La evolución térmica de el polvo negro obtenido se estudió hasta la temperatura de 1000 °C por medio de análisis térmico diferencial. Los polvos se analizaron así mismo por EDX e ICP-AES. Se estableció que la composición de los polvos esta muy próxima a la composición nominal. Se distingue tres regimenes en la evolución térmica. Se examina la dependencia con el contenido en lantánidos multicomponentes de pulsos con Sr y Ba. La naturaleza multicomponente se ha mostrado sobre la base de el tratamiento térmico empleado y el análisis de las fases cristalinas.

Palabras clave: descomposición térmica, perovskitas de lantánidos.

1. INTRODUCTION

In an electrochemical reactor which facilitates the transfer of oxygen, a very important element is the mixed- conductive oxide membrane. In that element the oxygen is driven across the membrane from an oxygen containing gas (for example air) to an oxygen consuming gas (i.e. methane as a reactant gas). According to (1) the function of a such electrochemical process generally comprises:

- providing an electrochemical cell comprising a first zone and a second one separated from the first by the solid multicomponent membrane;
- raising the temperature of the electrochemical cell from 300°C to 1400°C;
- passing the oxygen-containing gas in surface contact with the membrane;
- passing methane in contact with the membrane surface in the second zone.

Undoubtedly at high temperature working regime both the oxygen permeability and the membrane parameters are very important. It was reported (2-6) that the lanthanide perovskites are thought to be potential high powerful materials for the discussed process.

However, for the final working characteristics of the membranes very important are the technological steps of preparation. Generally there are two, first concerning powder processing and second the membrane development. There are few

methods for ceramic powder processing that start separately from liquid and gas mixture phases. An update on activity about the technological methods used is presented in ref. (7). Perovskite- type $LaFeO_3$ powders prepared by drop co- precipitation method is reported (8) too. There are some advantages (9) if we start from nitrate precursors using EDTA route (10).

The aim of the present work is to study the thermal evolution of the precursors to obtain ceramic powders of type $(La_{1-x}Sr(Ba)_x)(Co_{0.8}Fe_{0.2})O_3$ base. Nitrate solutions with additive of EDTA as complexing agent, has been used for powders preparation. The evolution of the powders obtained as a function of the composition, applied temperature and heating rate has been studied.

The investigation of the thermal evolution of the powders obtained is very important for both calcination and sintering processes. Undoubtedly, the thermal treatment of the powders affect on the crystal phase formation processes at the final dense samples.

2. EXPERIMENTAL PROCEDURE

2.1. Powders processing to membrane preparation track

Samples according to the general formula $(La_{1-x}$

$x\text{Sr}(\text{Ba})_x(\text{Co}_{0.8}\text{Fe}_{0.2})\text{O}_3$ have been prepared, where x values are 0.6, 0.4 and 0.2 respectively. The starting materials used are $\text{Sr}(\text{NO}_3)_2$, $\text{Ba}(\text{NO}_3)_2$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Merck) of AnalaR grade. Only $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ has been used starting from La_2O_3 "reagent grade" and completely dissolved in HNO_3 acid. Following the procedure for the preparation of disperse and homogeneous powders the NH_4 -EDTA solution has been added (1.5 mole per mole of metal in the solution) to the clear nitrate solutions (pH values 8-8.5) containing stoichiometric amounts of the reagents.

A pyrolysis at 280 °C for 2 h) of the solution decanted in few portions into special quartz dishes was done. The so obtained high dispersive black powder is referred as complex uncalcined product. The procedure for ceramic powder processing and following heat treatment is presented in Figure 1. The powder compositions are given in the Table I.

Later the resulting black mass has been calcined in an electric furnace at 925°C / 12 h using Pt dishes covered by quartz ones. A gradual cooling procedure to room temperature has

been applied. The obtained final powder product is referred as calcined powder sample. Thermal treatment was performed in an electrical furnace (Naber, Germany) using constant heating rates. The calcined powder is ball milled using polyethylene mortar and agate balls (Pulverize 6, Fritsch, Germany). The powder granulometry was controlled periodically by using scanning electron microscope.

TABLE I
COMPOSITION OF ALKALI EARTH A-SITE DOPED LANTHANUM- PEROVSKITE POWDERS

No	Index	Perovskite composition (nominal)
	Sr- doped	
1	I - 4 (4LSCF)	$\text{La}_{0.4}\text{Sr}_{0.6}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$
2	I - 6 (6LSCF)	$\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$
3	I - 8 (8LSCF)	$\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$
	Ba- doped	
4	II - 4 (4LBCF)	$\text{La}_{0.4}\text{Ba}_{0.6}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$
5	II - 6 (6LBCF)	$\text{La}_{0.6}\text{Ba}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$
6	II - 8 (8LBCF)	$\text{La}_{0.8}\text{Ba}_{0.2}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$

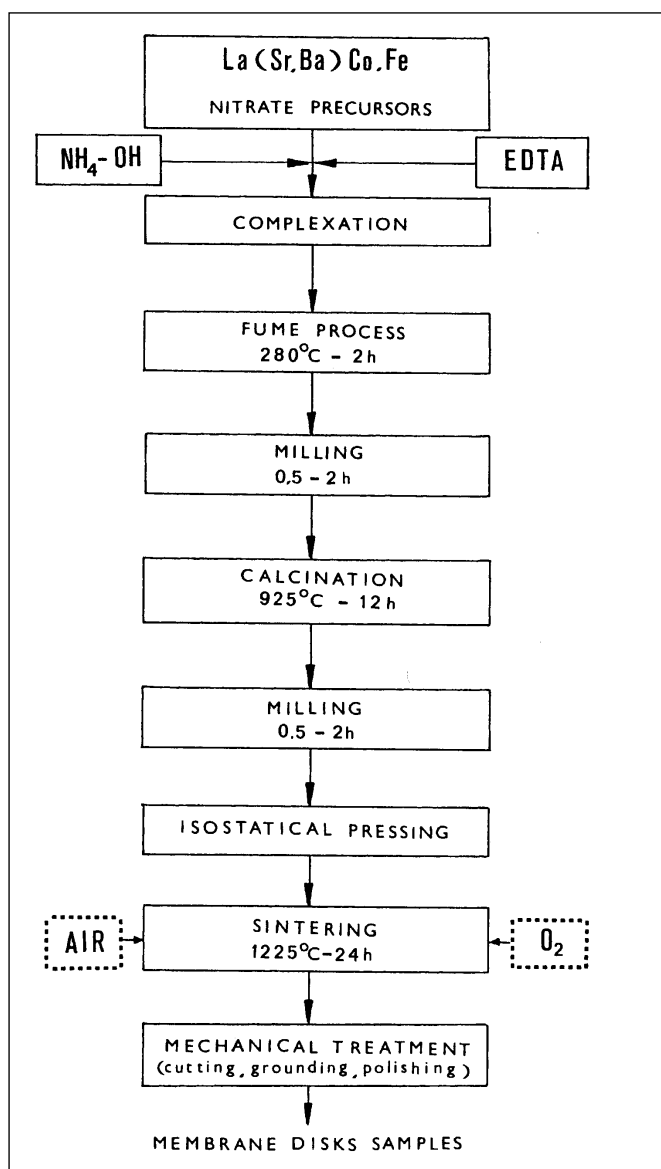


Figure 1 Flow chart of preparation of mixed-conducting oxide perovskite membranes using EDTA-modifier nitrate precursor method.

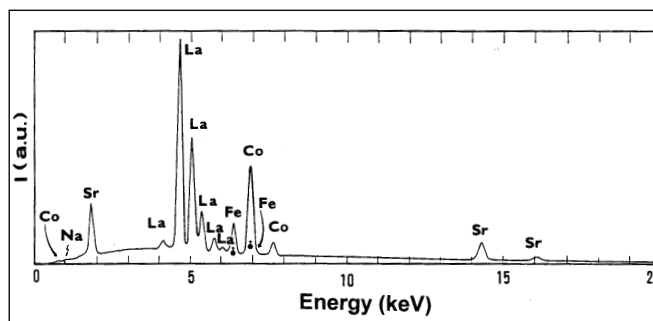


Figure 2 EDX analysis of I-4 powder sample, Fe Ka and Co Ka peaks are marked by (I).

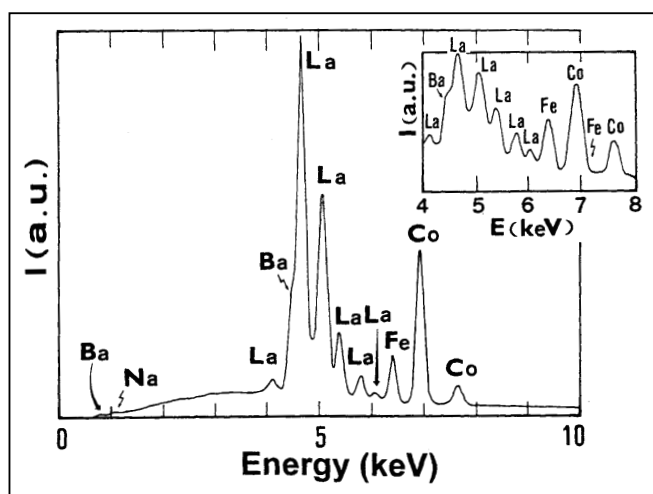


Figure 3 EDX spectra of II-4 powder sample

2.2. Methods of analysis and composition control

The thermal decomposition of the powders obtained was determined by a MOM derivatograph Pertlik- Erdey system. Heating rate was 10°C/ min. with ±5°C accuracy of the temperature measured. A calibrated Pt- PtRh thermocouple was used. Aluminium oxide heated up to 1200°C was adopted as a standard during the experiments.

Energy dispersive X-ray analysis (EDX) has been performed by ESCA- XPS using MICROLAB VG Scientific equipment were X- ray Al- K_α source at 20 eV per chain was specified.

Chemical analysis, before and after calcination process, was performed by means of inductively coupled plasma atomic emission spectrometry (ICP- AES), used SPECTROFLAME spectrophotometer- Kleve, Germany.

Powder X-ray characterization was carried out on a SIEMENS D-500 diffractometer in 2θ range from 6 to 80 degree by the diffracted beam using Cu- K_α (λ= 1.5418 Å) radiation and silicon as an internal standard. Phase identification has been realized by DIFFRAK 11 software (IDR, EVAL and JCPSEA program products) using JCPDS Mineral powder diffraction file (11).

3. RESULTS AND DISCUSSION

3.1 Composition control

Figure 2 shows EDX semiquantitative microanalysis of I-4

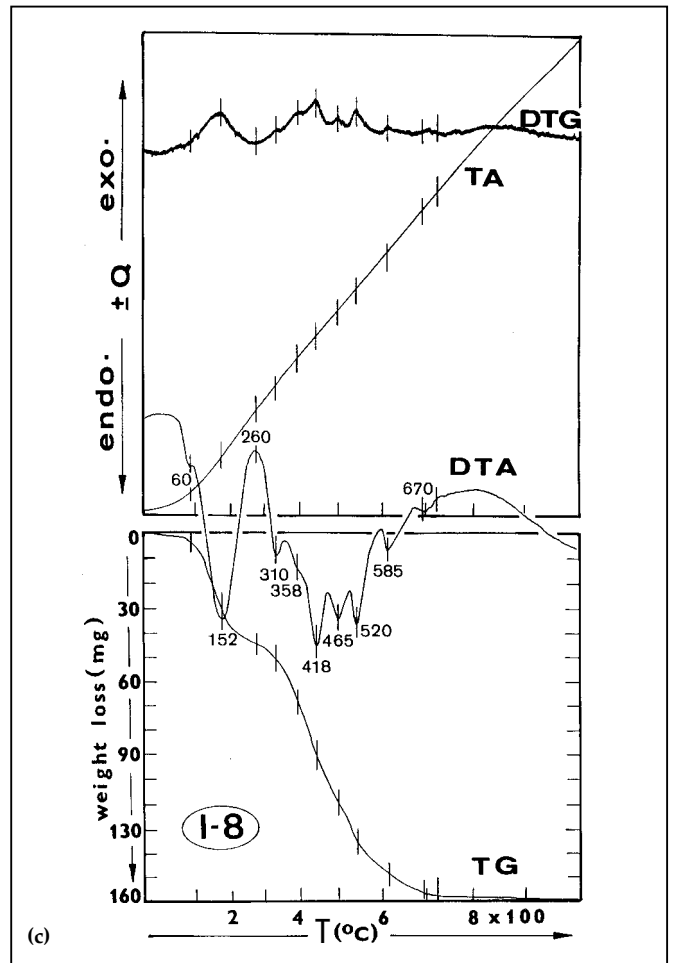
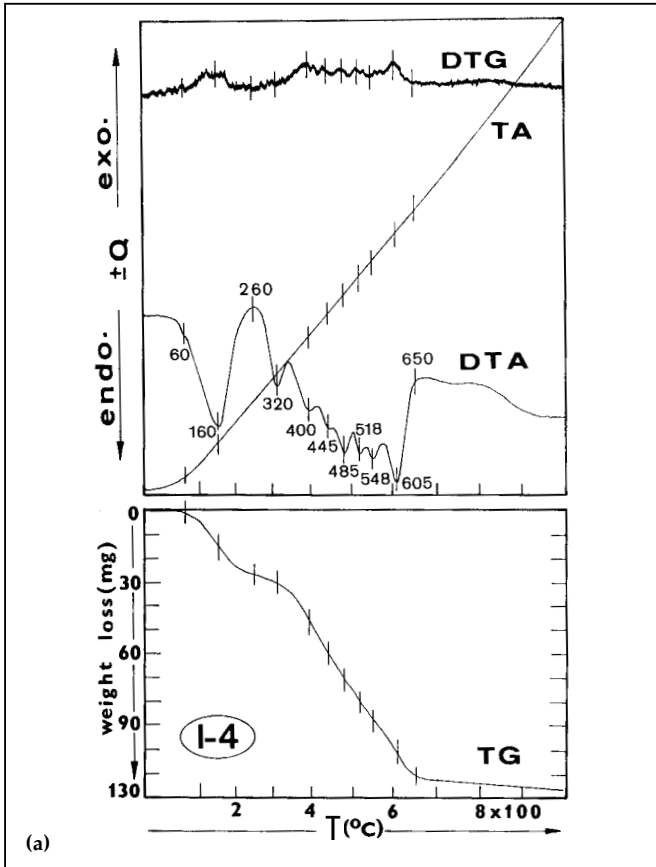
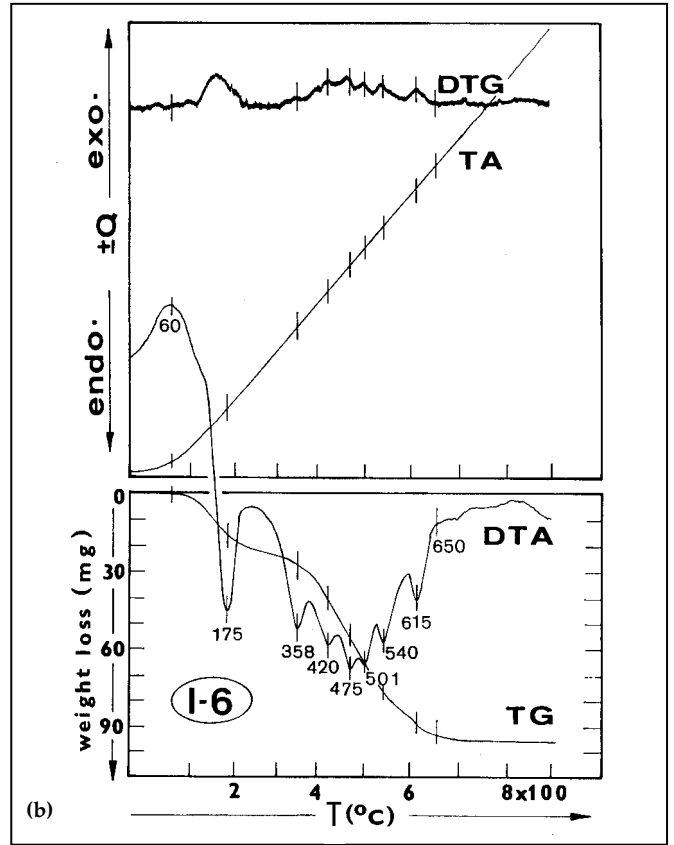


Figure 4 Heating curves (TA, DTA, TG and DTG) for (a)I- 4, (b)I- 6 and (c)I-8 in air; sample weight 266 mg, 235 mg and 363 mg, respectively

powder sample. It can be seen that the powder constituents are La (six lines, the highest one is a contribution of La $L_{\alpha 1}$), Sr (three lines), Co (three lines), Fe (two lines, as the second one Fe K_{β} is not well resolved). A fluctuation on the curve as a contribution of Na K_{α} at about 1 keV can be checked. The ratio of the surface peak area of Co K_{α} ($A=199\,230$ pulses) to Fe K_{α} ($A=53\,049$ pulses) is checked as 3.76 which value is close to nominal one. Actually, after a correlation procedure it was established that the microanalytical data of I-6 and I-8 powder samples are equivalent.

As a comparison, Figure 3 shows EDX semiquantitative microanalysis of II - 4 powder sample. Except well express La lines there are Fe, Co and Ba lines as contributions, too. It can be seen that the Ba lines are not intensive and a covering effect is registered. The ratio of the peak area of Co K_{α} (222300 pulses) to Fe K_{α} (56653 pulses) is 3.92 i.e. close to nominal, one.

ICP - AES analysis has been applied as a second analytical technique for composition control of the powder and membrane samples. Both major and minor constituents have been analyzed. In general, the results obtained are in good correlation with EDX data. We like only to mention that the amount of iron obtained by ICP-AES is little bit higher than nominal one. There is a small amount of Ca content (app. 1.05 w.%, according to ICP - AES analysis only) which is registered before and after the calcination process.

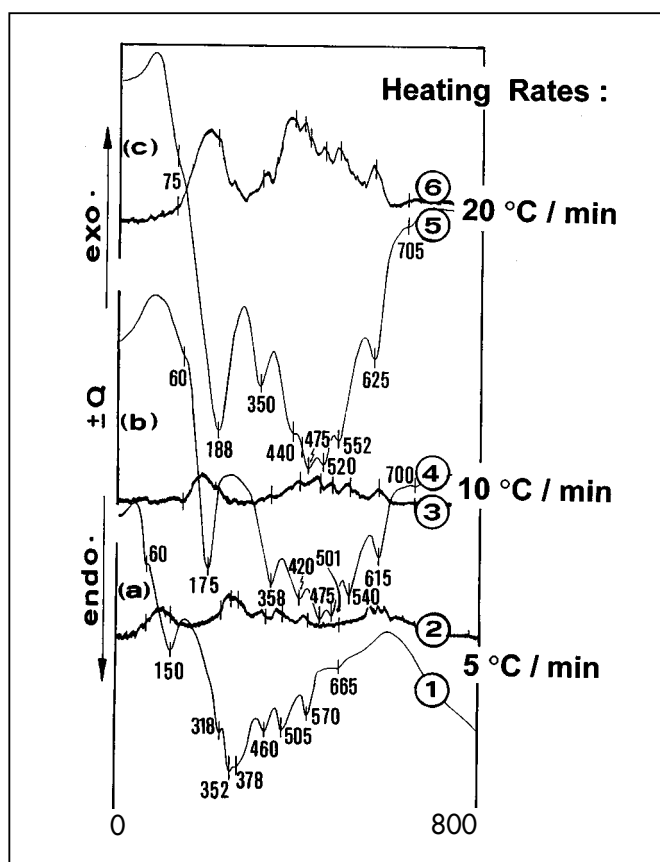


Figure 5 Heating curves for Sample I-6 at different heating rates: a) heating rate 5°C/ min.; b) heating rate 10°C /min.; and c) heating rate 20°C /min.; curves 1, 3 and 5- are DTA- and curves 2,4 and 6 DTG effects respectively. The exact temperature checked is presented on curves

3.2. Thermal decomposition of Sr-doped lanthanide perovskite powders

In order to optimize the process of thermal decomposition the samples obtained have been analyzed by DTA up to 1000°C. At polythermal scanning regime the powder samples with I-4, I-6 and I-8 indexes show identical behavior as shown in Figure 4. The thermal reaction curves can be grouped generally into three regions following the curve behaviour.

The first one is from room temperature up to 260°C- 270°C where a well- expressed endothermic effect at 160°C $\pm 10^\circ\text{C}$ is registered. Undoubtedly, this is a contribution of the dehydration process. The weight loss checked is about 25 mg that is 8.97% of the sample weight.

In the second region up to 670°C there are set of 6-7 endothermic peaks on DTA curve. It is seen that these peaks are variable in relation of their position and depth profile. This is well express following DTA curve behaviour in Figure 4 (a, b & c). Namely, in this region during the heating process both TG and DTG curves indicate a very sharp weight loss. The endothermic peaks at 420 $\pm 10^\circ\text{C}$ and 500 $\pm 20^\circ\text{C}$ should corresponds to the decomposition of nitrate ions. The peak at 710 $\pm 10^\circ\text{C}$ arises from deoxidizing and phase transition to form stable alkali earth- and Fe- doped lanthanum cobalt compounds. The other endothermic effects can be attributed to the processes of degradation of the organic groups introduced mainly by EDTA and simultaneously crystallization rearrangement process. Evidently, the last process is highly effective above 550°C up to 720°C following the thermal behaviour of the curves. Formation of metastable perovskite phase can be attributed to plateau presence on the curves. It is well illustrated above 700°C on the TG curves.

There is not any thermal effect exist above 670°C in the third temperature region. In this range the weight loss (please see DG and DTG curves) is constant. This indicates that the solid state reactions are complete. The same conclusion can be drawn from DTA and DTG curves behaviour where only a thermal influence from the furnace heating process can be checked.

In the present study any exothermic effect has not been registered as reported before (12). Namely, existing effects for 3- LSC powder sample at 390°C, 416°C (13) and for 6-LBSF powder sample at 298°C, 330°C (12). It is interesting to mention that the results reported for existence of the exo- thermal effects at 220°C, 320°C and 350°C of polyethylene glycol (PEG) and at 322°C and 364°C of citric acid (CTA) methods (14) are not confirm at the present method used. The precursor nature in the present study is a protonic EDTA- modifier nitrate solution.

It is attractive to follow the thermal decomposition of the powder samples as a function of the heating rate. This is well illustrated by heating of powder sample of composition I- 6 (6LSCF). Figure 5 summarized the kinetic behaviour of the thermal decomposition for this composition. Evidently, the dehydration process is a function of the heating rate. The endothermic dehydration effect at 150°C (curve 1) is shifted to 188°C as is seen on curve 5. A deeper endothermic effect is recorded at low heating rate at 352°C (curve 1) in comparison to 475°C and 520°C endo- doublets registered at curves 4 and 5. There is no clear difference checked in the exo- thermal effects between 300°C and 700°C for heating rates at 10°C and 20°C /min. We like only to mention that high heating rates stimulate a better appearance of endo- thermal effects as this is well illustrated in Figure 5, curve 5.

3.2. Thermal decomposition of Ba-doped lanthanide perovskite powders

For correlation with the results obtained for Sr-doped samples the Ba-doped ones have been analyzed thermogravimetrically up to 1000°C. In this high temperature region the solid solution must be stable. A single phase is aimed. The same behavior, as is shown in Figure 4, has been registered for samples after Ba-substitution. It is well presented in Figure 6. By analogy of the Sr-doped samples three regions of heat transitions can be accepted and confirmed.

The first (dehydration) region took place before 280°C. The dehydration process is not sensitive so composition sensitive. In the present study any exothermic peak not has been checked in the dehydration region as reported by Furusaki et al. (15) for La(III)-Cr(VI) precursors. On the other hand, the authors do not assign any explanation for the registered exothermic peak at 250°C.

There are lot of peaks which exist in the second region marked from 280°C to 700°C. The peak at 325°C is present in all samples. The deeper peak at 435°C is well seen at II-6 sample. The next sharp endothermic effect which is observed on the DTA curves is located at 625°C. In the high temperature region above 700°C a small endothermic effect has been registered at 820°C on all DTA curves. Not any influence is established on TG and DTG curves in this region. Following the temperature behavior of the powder ceramics it may be concluded that the II-6 sample is more temperature stable in comparison with II-4 and II-8.

Details about phase distribution using IR, XRD and Neutron diffraction analyses will be published separately. In short only part of the XRD data will be reported at present. Figure 7 shows X-ray diffraction powder patterns of lanthanum samples doped with Sr- and Ba- oxides at level one of heat treatment (280°C / 2h). Evidently the samples are multicomponent with many phases in an intermediate state and with diffraction intensities not well expressed. There are complex binary phases checked as lanthanum ferrate (15-0148) [16], Ba₃Fe₂O₆ (25-

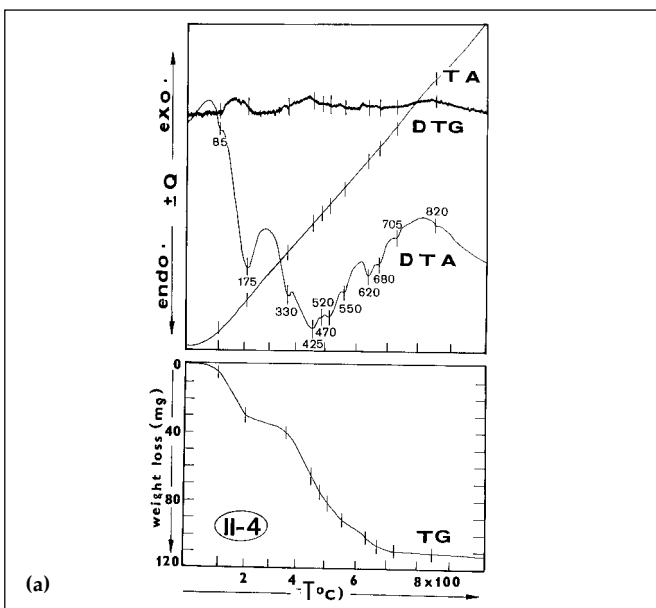
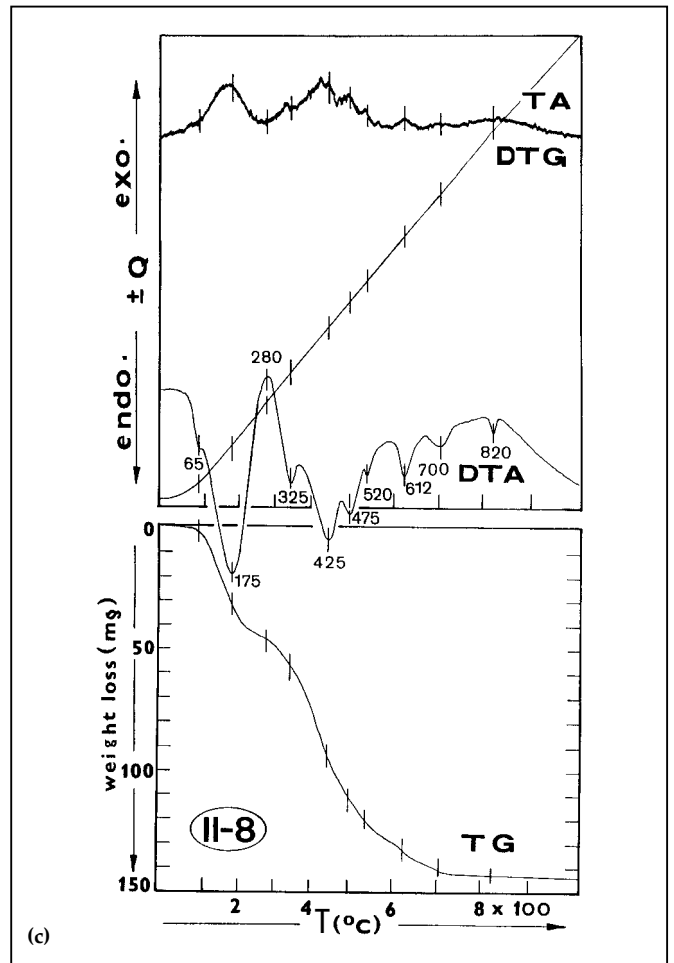
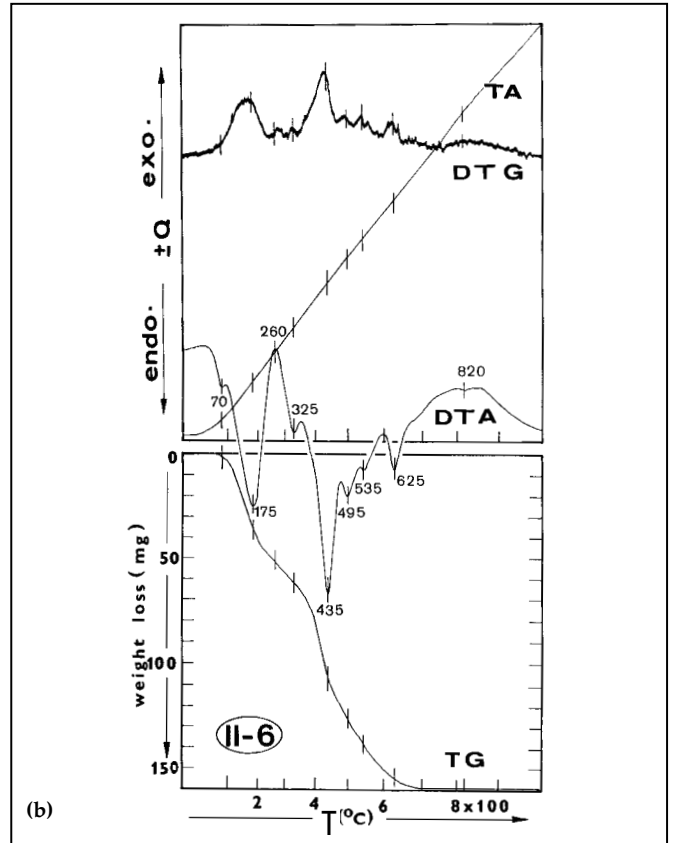


Figure 6 Heating curves (TA, DTA, TG and DTG) for (a) II-4, (b) II-6 and (c) II-8 in air; sample weight 259 mg, 413 mg and 319 mg, respectively.

1477) (16), not well displayed ternary compound $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ (17), $\text{La}_{0.5}\text{Ba}_{0.5}\text{CoO}_3$ (32- 0480) (16) as well as a simple phase- $\text{Ba}(\text{NO}_3)_2$ (16) coexists.

As is shown in Figure 8 Sr-doped powder samples are not monophasic product even after calcination at $950^\circ\text{C}/12\text{h}$ in air. Except the hexagonal phase $\text{SrCoO}_{2.5}$ (17) there is a tetragonal phase of $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ (17). Some of the peaks position are slightly shifted to low d-values (e.g. 2.703, 2.039, 1.6171, 1.578 Å). We accepted that this is due of the iron influence of B- type isomorphous substitution in the cobalt ion positions. As a comparison the characteristic d-values of the perovskite cubic unit cell are 3.82, 2.717, 2.218, 1.911, 1.520, 1.391 Å, respectively.

4. CONCLUSIONS

It was confirmed that the procedure applied for ceramic powders processing, starting from nitrate precursors and NH_4 - EDTA solution, is effective one. A complex uncalcined product of high homogeneity is possible to be obtained. It was established that the compositions of the powders obtained are very close to the nominal. It was well illustrated from EDX and ICP- AES analytical data. There is a small amount of Na checked with origin from EDTA and Ca- which appear from liquids powder preparation procedure.

The thermal analysis carried out shows that only endothermic effects are registered. According to the data it was established that a more clear phase transition for I-8, II-6 and II-8 exist. Namely, there are those compositions with high amount of lanthanum oxide. At polythermal scanning regime three regions of thermal evolution can be accepted. The first one is from room temperature up to 270°C which is due of the dehydration process. The second region is checked up to 670°C where a very sharp weight loss is registered. In this region process of decomposition of nitrate ions and degradation of organic groups (EDTA influence) can be adopted. In the third high temperature region (up to $650/700^\circ\text{C}$) the solid state reactions are complete and the weight loss is a constant. The low heating rate at $5^\circ\text{C}/\text{min}$. is better to accept for a next calcination procedure. It was established that the processes of thermal decomposition of the powders running well and complete at relatively low temperatures. In correlation with Sr- the Ba- substituted samples are characterized with higher temperatures' transitions (marked at 820°C on DTA curves). Undoubtedly, in the next sintering process a high temperature treatment and an extended time is needed. The thermal treatment and phase control carried out show a multicomponent nature of the samples.

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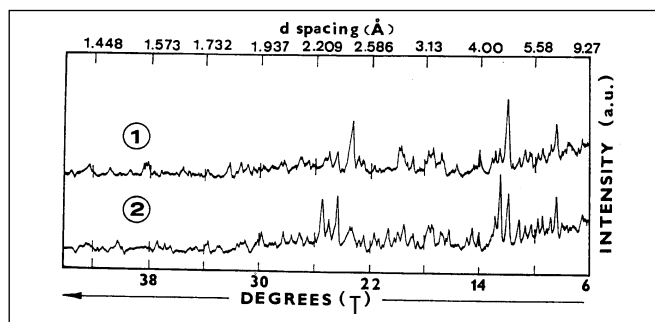


Figure 7 Powder X-ray diffraction pattern of II-6 sample (curve 1) and for I-6 sample (curve 2) after fume but before the calcination process.

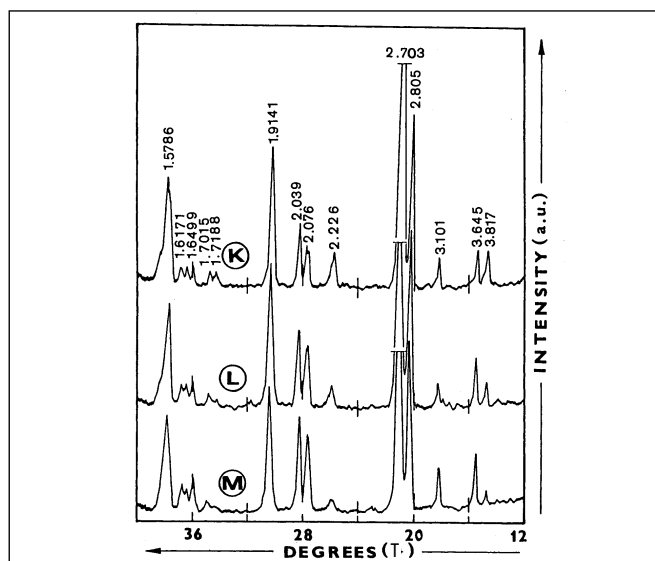


Figure 8 XRD pattern of Sr-doped lanthanum samples as function of the composition; curve K- sample I-8, curve L- sample I-6 and curve M- sample I-4, heat treatment $950^\circ\text{C}/12\text{h}$.

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