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Synthesis of Mg doped $LaCrO_3$ Nano Powders by Sol-Gel Process for Solid Oxide Fuel Cell (SOFC) Application*

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Abstract: Magnesium doped lanthanum chromate ($LaCrO_3$) nano ceramic powders were prepared using Sol-Gel process for solid oxide fuel cell (SOFC) applications. This powder is considered as interconnect material for SOFC application. This interconnect powder was prepared using $La(NO_3)_3{\cdot}6H_2O$, $4MgCO_3{\cdot}Mg(OH)_2{\cdot}5H_2O$, $(NH_4)_2Cr_2O_7$ and $Cr(NO_3)_3{\cdot}9H_2O$ chemicals in which the chelating agent was citric acid and the dispersant agent was ethylene glycol. While physical Characterization for the powders was carried out using SEM / EDS, XRD techniques, TGA and DTA techniques were used for thermal characterization. The SEM images reveal that the particle size of $La_{0.7}Mg_{0.3}CrO_3$ powders achieved by Sol-Gel process is in the range of ~50-200nm. The EDS study indicates that the carbon content is high in the as prepared powders comparing to the calcined powders. The powders prepared using $(NH_4)_2Cr_2O_7$ is more cost effective than using $Cr(NO_3)_3{\cdot}9H_2O$ since it also acts as fuel. The XRD analysis reveal the presence of $La_{0.7}Mg_{0.3}CrO_3$ and $MgCr_2O_4$ phases. The TGA plots depict that there is no further weight loss after reaching the temperatures 350°C and 575°C for the LMC gels prepared using AD and Cr-N respectively indicating the complete combustion and obtaining oxide phases.

Keywords: Sol-Gel, Ammonium dichromate (AD) , Chromium nitrate (Cr-N), Interconnect, XRD, TGA and DTA.

1. INTRODUCTION

Solid oxide fuel cells (SOFCs) have attracted a considerable attention because of their high–energy-conversion efficiency, environment amity, and fuel flexibility [1,2]. The current status of the development of a cell unit is based on yttria-stabilized zirconia (YSZ) solid electrolyte and electrodes consisting of Sr-doped $LaMnO_3$ (Cathode) and Ni-YSZ cermet (Anode). A suitable material to be used to interconnect the air and fuel electrodes of adjacent cells is an alkaline earth metal doped $LaCrO_3$ [3]. To achieve the desired higher power output, single cells are connected in series and parallel using interconnect materials. The interconnect materials should meet the requirement such as : chemical stability in both oxidizing and reducing atmosphere, high electronic conductivity, chemical and mechanical compatibility with other components, and sufficient mechanical strength. Also interconnects for SOFC should be dense to avoid cross leakage of fuel and oxidant gases [4]. For this, a very few oxide materials are considered as interconnects. The Sol-Gel process was successfully applied for the preparation of the fine nano size powders to make SOFC components and interconnect as it is a simple and more economical. Some of them are alkaline earth metals like Ca, Sr and Mg doped $LaCrO_3$ materials reported in the literature using Sol-Gel process [5-11].

The Sol-Gel process [12] is a versatile solution process for making ceramic and glass materials in to various forms such as: ultrafine/special shaped powders, thin films coatings, ceramic fibers, microporous inorganic membranes, monolithic ceramic/glass and extremely porous aerogel materials. In a typical sol-gel process the precursor is subjected to a series of hydrolysis/polymerization reactions to form a colloidal suspension or a sol. Further processing of the “sol” enables one to make ceramic materials in different forms. Usually starting materials include inorganic metal salts or metal organic compounds/metal alkoxides. The main steps of sol-gel process include, mixing, gelling, shaping, drying and densification. The advantages of sol-gel process are : simplicity, flexibility, low temperatures, small capital investment and the results in highly pure, uniform, nanostructures.

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Table 1. Suitable Materials for SOFC Components [15]

Component	Requirements	Preferred Materials	Possible Alternatives
Electrolyte	$\sigma_i > 0.05$ S.cm^{-1}	ZrO_2-Y_2O_3 (3-10mol%)	ZrO_2-Sc_2O_3, CeO_2 -Gd_2O_3, (Sm_2O_3)
Cathode	> 100 S.cm^{-1} (electronic/mixed)	La $_{1-x}$ Sr$_x$ MnO$_3$	(La $_{1-x}$ Sr$_x$)Co, FeO$_3$
Anode	> 100 S.cm^{-1} (electronic/mixed)	Ni /ZrO_2-Y_2O_3	Ru / ZrO_2-Y_2O_3 Ni /CeO_2- ZrO_2-M_2O_3 cermets
Interconnect	Inert material, high temp. stability	High temp. alloys La $_{1-x}$ (Sr ,Ca, Mg)$_x$ CrO$_3$	–
Manifold	Non-volatile, inert	Ceramics, metals	–
Seal	Non-volatile, inert	Glass, glass-ceramic, Metal/ceramic	–

Table 2. Samples of Nano $La_{0.7}Mg_{0.3}CrO_3$ **(**LMC) by Sol-Gel process

Samples ID	La $_{0.7}$ Mg $_{0.3}$ CrO$_3$ (LMC) Nano powder	La $_{0.7}$ Mg $_{0.3}$ CrO$_3$ (LMC) Nano powder
41,58, 61	With Ammonium dichromate (AD)	–
49, 57, 60	–	With Chromium Nitrate (Cr-N)

a: as prepared, b: calcined at 650ºC/6hrs and c: calcined at 900ºC/3hrs

Ishihara et al [13] have reported that the high oxide ion conductivity in the perovskite system $LaGaO_3$ doped with Sr, on the La site and Mg on the Ga site [14].The oxide ion conductivity at 850ºC for $La_{0.9}S_{r0.1}Ga_{0.8}MgO_{2.85}$ is similar to YSZ at 1000ºC.

The material requirements for SOFC fuel cell components [15] are summarized in the Table 1.

Several Researchers have reported [16-21] the preparation of Mg doped interconnect materials using various combinations of elements for SOFC application with different techniques.

In the present investigation super fine particles of Magnesium doped lanthanum chromate powders were prepared by the Sol-Gel process in which the chelating agent was citric Acid and the dispersant agent was ethylene glycol using lanthanum nitrates, magnesium carbonate and chromium nitrates/ammonium dichromate. This technique was successfully applied for synthesis of the fine nano size (~50-200nm) powders to make SOFC components like interconnect. The physical characterization of the powders were carried out using SEM/EDS, XRD techniques and the thermal properties of gel samples were carried out using TGA/DTA techniques.

2. EXPERIMENTAL

2.1. Preparation of Powders:

The $La_{0.7}Mg_{0.3}CrO_3$ Powder was prepared by modified Sol-Gel Process [5-11] using $La(NO_3)_3.6H_2O$ (BDH), $MgCO_3.Mg(OH)_2.5H_2O$ (BDH), $(NH_4)_2Cr_2O_7$ (Fluka), $Cr(NO)_3.9H_2O$ (Fluka), citric acid (BDH) and ethylene glycol (BDH).The precursor solution was prepared by mixing individual aqueous solution of the above chemicals in a molar ratio of 0.7:0.3:1.0. To the mixed solution, required citric acid, ammonia solution and ethylene glycol was added. The solution was taken in a pyrex glass beaker and heated to evaporate on a hotplate using magnetic stirrer until a greenish gel was formed. When the heating was continued further, the gel gets completely burnt on its own and becomes light, and fragile ash. The ash was calcined at 650ºC/6hrs and 900ºC/2hrs in air in a Barnstead Thermolyne 47900 Furnace (USA). Table 2 shows sample preparation using Ammonium dichromate (AD) and Chromium nitrate (Cr-N) Figure 1. shows the flow Sheet for the preparation of $La_{0.7}Mg_{0.3}CrO_3$ Powder by Sol-Gel Process.

2.2. Physical Characterization:

2.2.1. SEM / EDS :

Small amounts of the samples were examined with both the Scanning Electron Microscopes (JEOL 5800LV) and FEI, Holland. Imaging was performed in Secondary Electron (SEI) mode only using an accelerating voltage of 20keV. Energy Dispersive Spectroscopy (EDS) was used to determine the elemental compositions at the spot and area of the Mg doped $LaCrO_3$ (LMC) powder samples.

2.2.2. XRD:

X-ray Diffractometry (XRD) Model XRD 8030, Jeol, Japan with a Cu-Kα radiation at 35kV and 20mA was used for phase analysis within diffraction angle 2θ range of 10-80º.

2.2.3. TGA/DTA

For Thermal Gravimetric Analysis (TGA) and Differential Thermal analysis (DTA) around 7-8mg of the LMC Gel samples (prepared by using Ammonium dichromate and Chromium nitrate as a source for Cr) were loaded in a alumina crucible and put inside the thermo balance of TG machine (Perkin-Elmer Thermal Analysis Contoroller TAC 7/DX, USA). The thermal decomposition behavior was studied up to 850ºC that was raised at a rate of ~10ºC per minute.

3. RESULTS AND DISCUSSION

3.1 SEM / EDS :

Figures 2-3 show the nano-sized particles observed by Scanning electron microscopy from the $La_{0.7}Mg_{0.3}CrO_3$ powder samples calcined under oxygen atmosphere at 650ºC and 900ºC which were

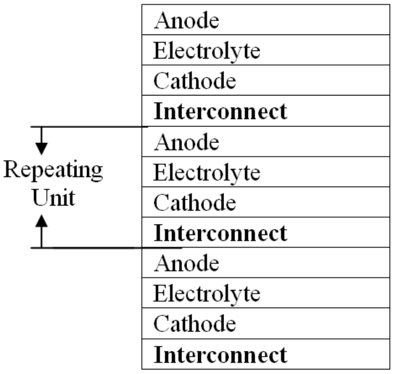


Figure 1a. Schematic illustrating the stack of 3 individual fuel cell for the flat SOFC design [16].

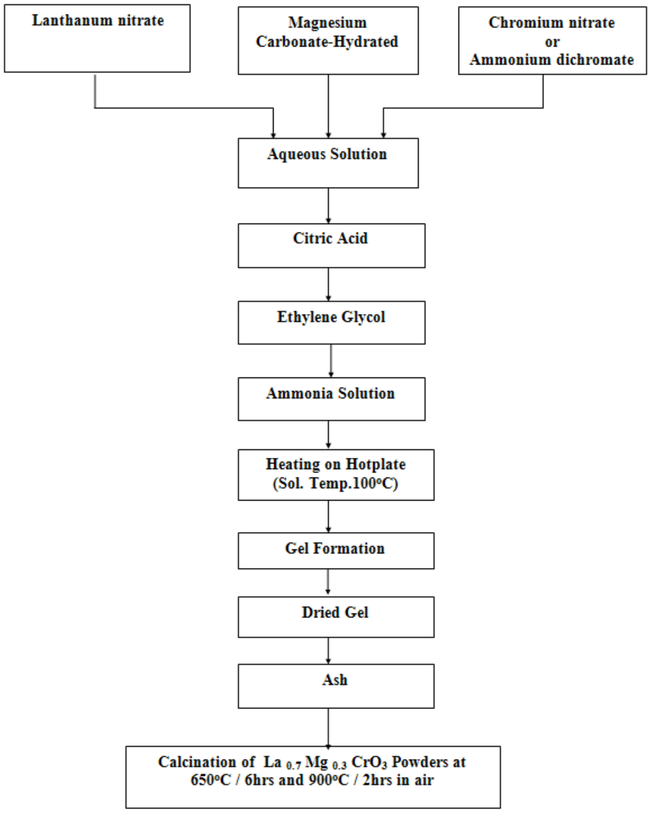


Figure 1b. Flow Sheet for the preparation of $La_{0.7}Mg_{0.3}CrO_3$ (LMC) powder by Sol-Gel Process [22-24].

prepared by Sol-Gel process using Chromium nitrate and Ammonium dichromate respectively as source for chromium. It is seen in the SEM images that the particles are homogeneous with the presence of highly porous spherical particles with approximate particle size between 50-200nm. It is noted from the figures that the particle size of the calcined powders at 900ºC are larger than the as prepared and calcined at 650ºC as per expectation. It is seen that the powders prepared using AD are slightly smaller than the powders prepared using Cr-N . This is in agreement with the other au-

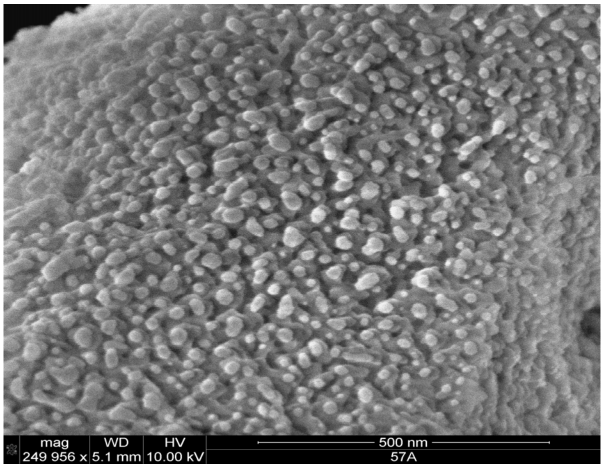


Figure 2a. SEM of the $La_{0.7}Mg_{0.3}CrO_3$ powder (As prepared) –Cr-N # 57a

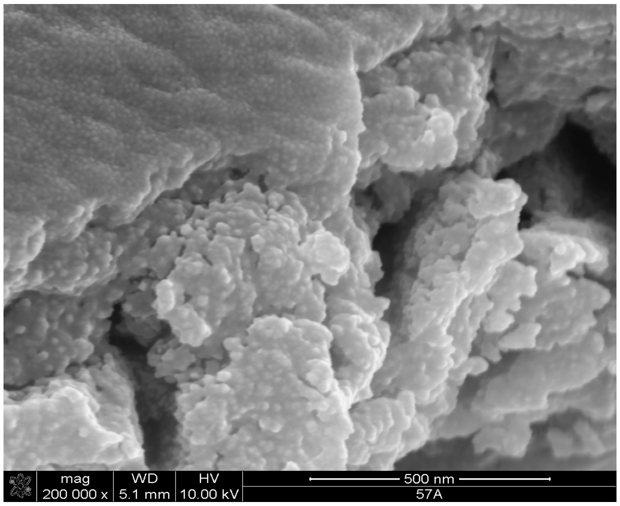


Figure 2b. SEM of the $La_{0.7}Mg_{0.3}CrO_3$ powder (As prepared)-Cr-N # 57a.

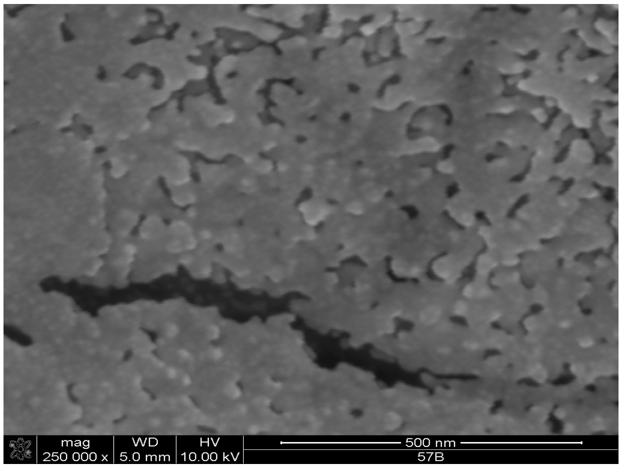


Figure 2c. SEM of the $La_{0.7}Mg_{0.3}CrO_3$ powder (Calcined at 650°C/6hrs) Cr-N#57b

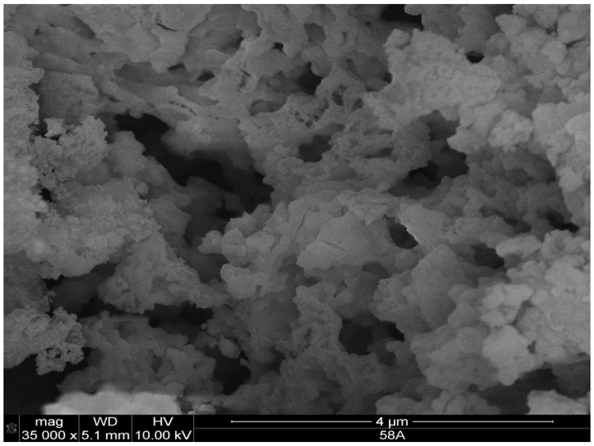


Figure 3a. SEM of the $La_{0.7}Mg_{0.3}CrO_3$ powder (As prepared)-AD# 58a.

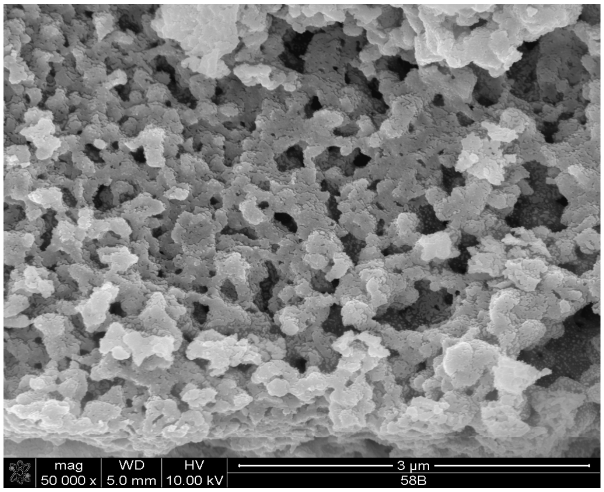


Figure 3b. SEM of the $La_{0.7}Mg_{0.3}CrO_3$ powder (Calcined at 650°C/6hrs)-AD #58b

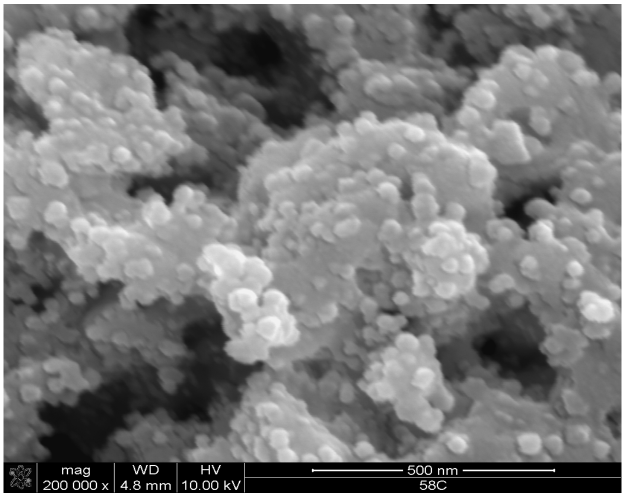


Figure 3c. SEM of the $La_{0.7}Mg_{0.3}CrO_3$ powder (Calcined at 900°C/6hrs) AD#58c

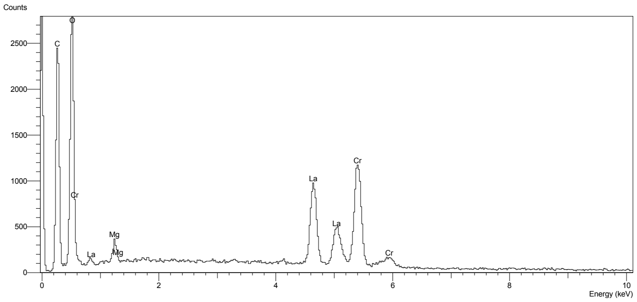


Figure 4a. EDS of the $La_{0.7}Mg_{0.3}CrO_3$ powder (As prepared)

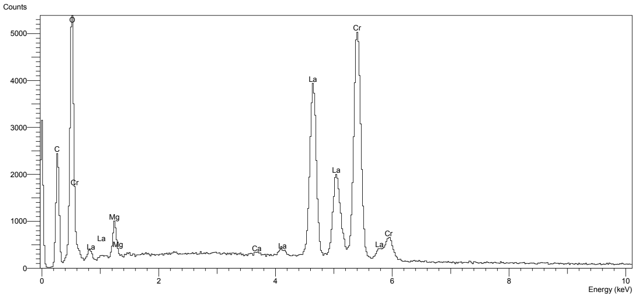


Figure 4b. EDS of the $La_{0.7}Mg_{0.3}CrO_3$ powder (Calcined at 650°C)

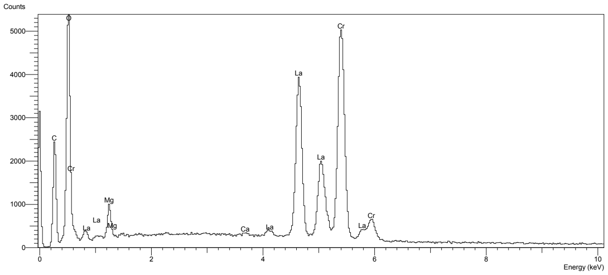


Figure 4c. EDS of the $La_{0.7}Mg_{0.3}CrO_3$ powder (As prepared)

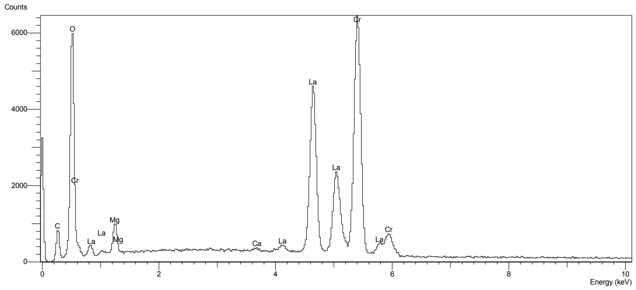
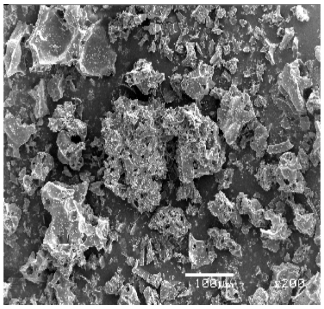


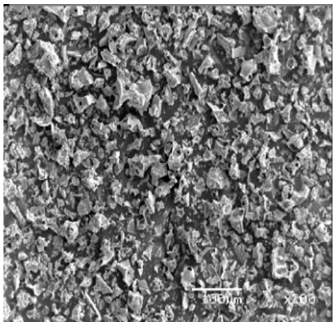
Figure 4d. EDS of the $La_{0.7}Mg_{0.3}CrO_3$ powder (Calcined at 650°C)

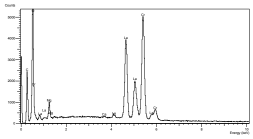


60A (As prepared)

Elmt	Spect. Type	Element %	Atomic %
C K	ED	29.81	45.73
O K	ED	41.62	47.93
Mg K	ED	1.12	0.85
Cr K	ED	8.33	2.95
La L	ED	19.12	2.54
Total		100.00	100.00

Figure 4e. SEM with elemental analysis of LMC powder by EDS (As prepared)-Cr-N#60A

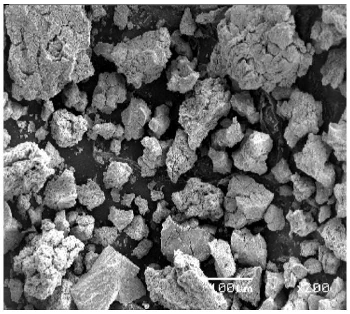




60B (Calcined at 650 C /6 hrs)

Elmt	Spect. Type	Element %	Atomic %
C K	ED	15.72	34.36
O K	ED	29.39	48.21
Mg K	ED	2.04	2.20
Ca K	ED	0.12	0.08
Cr K	ED	16.44	8.30
La L	ED	36.29	6.86
Total		100.00	100.00

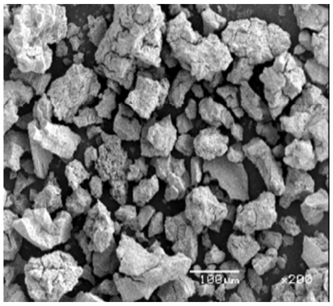
Figure 4f. with elemental analysis of LMC powder by EDS (Calcined at 650ºC)- Cr-N #60B

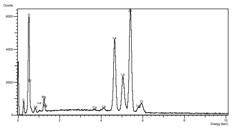


61A (As prepared)

Elmt	Spect. Type	Element %	Atomic %
C K	ED	7.71	18.59
O K	ED	33.32	60.30
Mg K	ED	2.39	2.85
Cr K	ED	18.56	10.33
La L	ED	38.01	7.92
Total		100.00	100.00

Figure 4g. SEM with elemental analysis of LMC powder by EDS (As prepared)-AD#61A





61B (Calcined at 650 C /6 hrs)

Elmt	Spect. Type	Element %	Atomic %
C K	ED	5.54	15.31
O K	ED	27.68	57.45
Mg K	ED	2.47	3.37
Ca K	ED	0.13	0.11
Cr K	ED	21.06	13.45
La L	ED	43.12	10.31
Total		100.00	100.00

Figure 4h. SEM with elemental analysis of LMC powder by EDS (Calcined at 650ºC)-AD #61B

thors reported elsewhere [25] for $La_{0.7}Ca_{0.3}CrO_3$ powder prepared by auto-ignition method .Figures 4a , 4b and 4c, 4d show the EDS patterns of $La_{0.7}Mg_{0.3}CrO_3$ powders using Chromium nitrate and Ammonium dichromate respectively as a source for chromium. The figures show the presence of La, Cr, Mg, O peaks. The residual C element from the citric acid probably that had not been combusted yet is shown in EDS in the as prepared powder. However, C content has been reduced in the calcined powders. By increasing the calcination temperature, Carbon content is reduced further.

3.2. XRD

Figures 5a-5c show the XRD patterns for as prepared and calcined at 650ºC/6hrs and 900ºC/2hrs respectively. The as prepared XRD pattern shows the amorphous in nature where as the calcined powders (at 900ºC) are well crystallined. It is seen that the powders have well crystalline perovskite phases of $La_{0.7}Mg_{0.3}CrO_3$ and $MgCr_2O_4$ peaks. Figure 5b indicates that the presence of certain amount of amorphous material calcined at 650ºC that the reaction for the formation of the chromate phase was not completed. Free oxides or other secondary phases were not detected at this temperature. At 900ºC for 2hrs, a well crystallized chromate phase was formed .Also it is seen that the XRD analysis on powders calcined at 900ºC for 2hrs indicated the formation of clear perovskite solid solution. In addition to such perovskite phase, a minority second phase was also present and it seems to correspond to a residual of $MgCr_2O_4$ phase. However further investigation is required to have clear conclusion of formation of phases.

In the case of $La_{0.7}Mg_{0.3}CrO_3$ and $MgCr_2O_4$ phases spinal phase was detected in addition to the perovskite phase, probably due to the small ionic size of Mg. The ionic radius of Mg with a coordination no (CN) of 8 is 0.89Å [26] i.e. about 23.3% smaller than La^{3+} with the same CN (r, 1.16Å). It is reported in the literature that Mg^{2+} is often chosen to dope the B-site [13, 21, 27]. Hence doping Mg results in a deficiency of A-site cations. Although the perovskite structure is known to be able to accommodate cation or anion deficiency to some extent, the extra B-site cations dissolve from the perovskite lattice, to form a $MgCr_2O_4$ secondary phase.

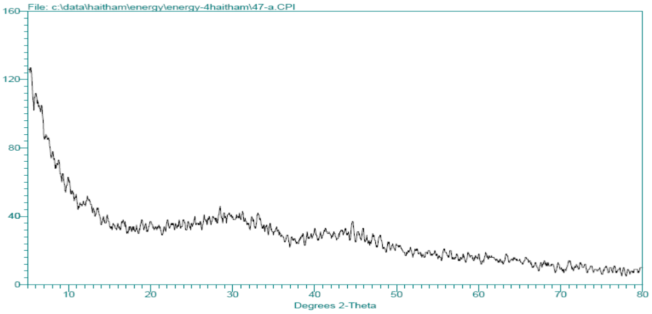


Figure 5a. XRD Pattern of the $La_{0.7}Mg_{0.3}CrO_3$ powders (as prepared) -AD

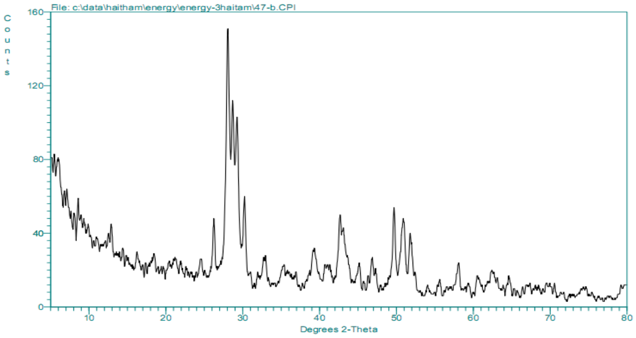


Figure 5b. XRD Pattern of the $La_{0.7}Mg_{0.3}CrO_3$ powders (calcined at 650°C)-AD

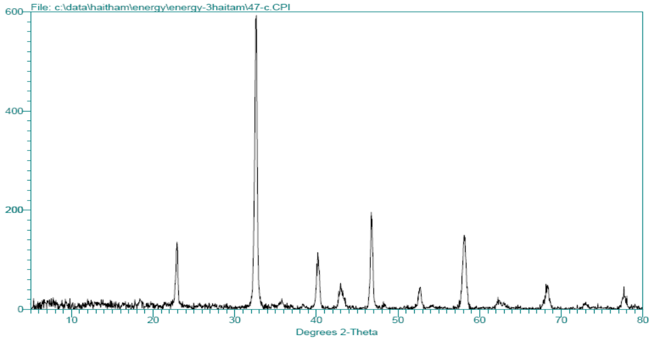


Figure 5c. XRD Pattern of the $La_{0.7}Mg_{0.3}CrO_3$ powders (calcined at 900ºC) –AD

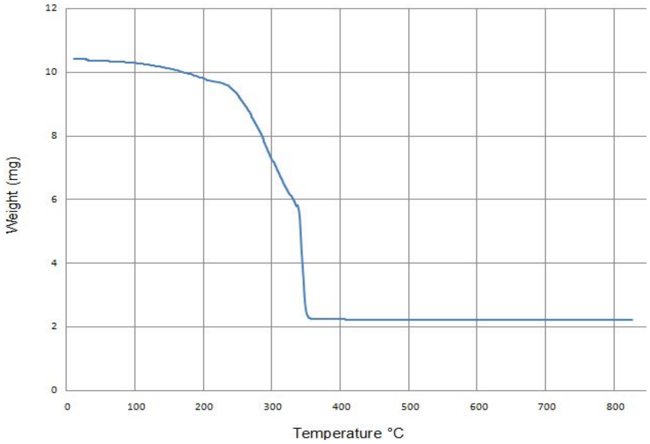


Figure 6a. TGA Plot of $La_{0.7}Mg_{0.3}CrO_3$ Gel (# 41)

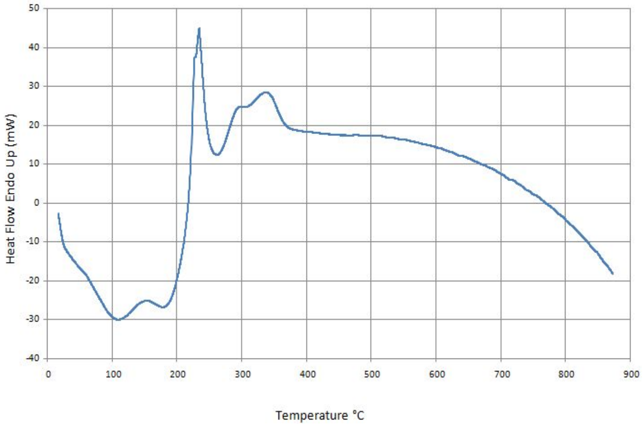


Figure 6b. DTA Plot of $La_{0.7}Mg_{0.3}CrO_3$ Gel (# 41)

3.3. TGA / DTA:

Figures 6a and 6b show the TGA and DTA plots of Interconnect (LMC) gels prepared (using Ammonium dichromate-AD as a source for Chromium) in the temperature range of 30-800ºC for the samples #41. It is seen that the endothermic peak observed at 120ºC in the DTA curve is due to the evaporation of water. The drastic weight loss in the TGA curve occurs at ~250ºC and corresponding exothermic peak at 230ºC in the DTA indicates a sharp 3 step decomposition of La-citric acid and Mg-citric acid complexes. From 230-340ºC three exothermic peaks were observed which seemed to be associated with the decomposition/oxidation of the metal-chelates producing oxide phases. The weight loss steps in the TG curve indicate that the thermal decomposition of the gel occurred gradually. The larger exothermic peak at 340ºC is associated with the combustion of remaining components. No further weight loss after ~350ºC in the TGA indicates complete combustion manifested by an exothermic peak in the DTA curve at ~340ºC. Similar trend is observed in the other TGA and DTA plots (Figures 7a and 7b) for the sample #49 for $La_{0.7}Mg_{0.3}CrO_3$ gel prepared using Chromium nitrate. It is seen that the water removal took place at an endothermic peak of slightly higher temperature of 180ºC. In this case there are 4 step decompositions to complete reactions. It is seen that no further weight loss after 575ºC indicating completion of combustion. In the case Ammonium dichromate used gels of LMC the temperature reached fast since it also acts as a fuel. This may be one of the reasons to have low temperature (350ºC) to reach complete combustion.

4. CONCLUSIONS

The following conclusions are drawn from the present investigation:

- The $La_{0.7}Mg_{0.3}CrO_3$ Powders prepared by Sol-Gel process

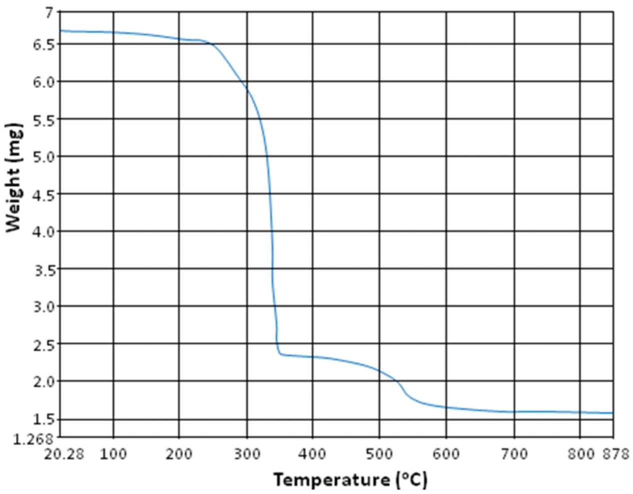


Figure 7a. TGA Plot of $La_{0.7}Mg_{0.3}CrO_3$ Gel (# 49)-Cr-N

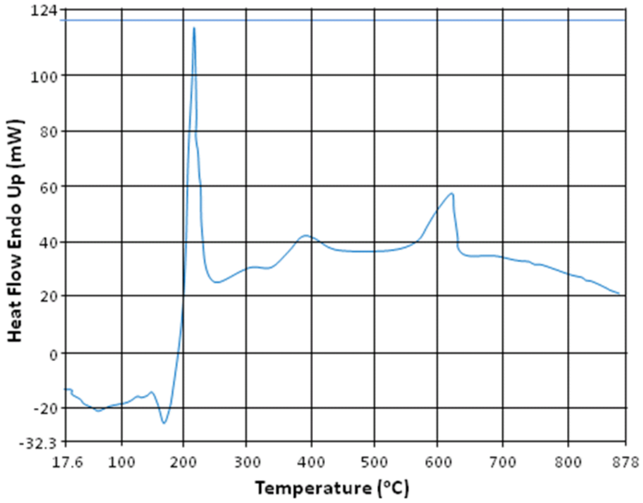


Figure 7b. DTA Plot of $La_{0.7}Mg_{0.3}CrO_3$ Gel (# 49)-Cr-N

have nano range from 50-200nm.

- Powder prepared using $(NH_4)_2Cr_2O_7$ is more cost effective than using $Cr(NO_3)_3{\cdot}9H_2O$.
- XRD patterns show the presence of $La_{0.7}Mg_{0.3}CrO_3$ and $MgCr_2O_4$ phases.
- EDS study indicates that the carbon content in the high temperature calcined powders is low.
- TGA and DTA plots show that there is no further weight loss after 350ºC indicating complete combustion for the gel prepared using Ammonium dichromate. But for the gels prepared using chromium nitrate, the weight is constant after reaching a temperature of 575ºC.

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