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SYNTHESIS OF $LaCo_{1-x}Fe_xO_3(0.1 \leq x \leq 0.4)$ NANOCRYSTALLINE POWDER BY CITRATE SOL-GEL METHOD

Zar Chi Myat Mon[1], MyaTheingi[2], Cherry Ohnn[3]

Abstract

Lanthanum based pervoskite type oxides are attractive materials due to their interesting optical, electric and magnetic properties as well as their potential applications. $LaCo_{1-x}Fe_xO_3(0.1 \leq X \leq 0.4)$ nanocrystalline powders were prepared by the use of lanthanum nitrate, cobalt nitrate, ferric nitrate as starting materials, citric acid as chelating agent and ethylene glycol as a gelification agent by citrate sol-gel method. The prepared samples were designated as LCFO-SG-I for $LaCo_{0.6}Fe_{0.4}O_3$, LCFO-SG-II for $LaCo_{0.7}Fe_{0.3}O_3$, LCFO-SG-III for $LaCo_{0.8}Fe_{0.2}O_3$ and LCFO-SG-IV for $LaCo_{0.9}Fe_{0.1}O_3$. The prepared $LaCo_{1-x}Fe_xO_3(0.1 \leq X \leq 0.4)$ nanocrystalline powders were characterized by modern techniques (Thermogravimetry/Differential Thermal Analysis, X-ray Diffractometry, Fourier Transform Infrared Spectroscopy, Energy Dispersive X-ray Fluorescence and Scanning Electron Microscope). The effect of calcination temperatures was investigated on $LaCo_{0.6}Fe_{0.4}O_3$. From the XRD analysis, the single phase perovskite structure was obtained after the sample were calcined at 500 °C. It was found that $LaCo_{1-x}Fe_xO_3$ $(0.1 \leq X \leq 0.4)$ nanocrystalline powders were single pervoskite phase, good crystallinity and average crystallite sizes at 600 °C calcination temperature. From the TG-DTA thermogram of the prepared powders calcined at 600 °C, the weight loss percents of all prepared samples are very low and therefore they have thermal stability. Relative abundances of elements analyzed by EDXRF showed lanthanum, cobalt and iron as the major constituents in the prepared powders. From FT IR spectral data, as the organic groups were removed during calcination, the band observed between 1470 and 1390 cm^{-1} is due to C-H stretching of residual carbon. Only the stretching vibration of metal-oxygen bond in the frequency range between 599 and 406 cm^{-1}were observed. From the SEM micrographs, the $LaCo_{1-x}Fe_xO_3(0.1 \leq X \leq 0.4)$ nanocrystalline powders have highly porous nature and agglomerates depending on the calcination temperatures and Fe doping levels.

Keywords: perovskites, lanthanum cobalt iron oxide, nanocrystalline powders, citrate sol-gel method

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[1] 2PhD Candidate, Department of Chemistry, University of Yangon

[2] Lecturer, Department of Chemistry, University of Yangon

[3] Lecturer, Department of Chemistry, West Yangon University

Introduction

Recently, a number of mixed-metal oxides with a perovskite type structure and the overall formulation of ABO_3 have received considerable attentions due to their interesting optical, electric and magnetic properties as well as their potential applications. Their applications such as gas sensors, catalysis, thermoelectric materials, electrode materials in solid oxide fuel cells, provide a wide ranging interest in the synthesis and their structural analysis. For achieving optimum performances and functional properties well defined microsturctures are desirable, which in fact strongly depend on the method of synthesis (Unikoth *et al*., 2014).

Goldschmidt's tolerance factor is an indicator for the stability and distortion of crystal structures. It was originally only used to describe perovskite structure, but now tolerance factors are also used for ilmenite. Alternatively the tolerance factor can be used to calculate the compatibility of an ion with a crystal structure. The first description of the tolerance factor for perovskite was made by Victor Moritz Goldschmidt in 1926. Ideal perovskites have the ABO_3 stoichiometry and the ratio of bond length between A-O and B-O maintains a constant value which is equal to $\sqrt{2}$. The deviation from this is taken as the tolerance factor and in terms of ionic radii, it assumes:

$$\mathrm{t} = \frac{\mathrm{rA+rO}}{\sqrt{2}\,(\mathrm{r}\boldsymbol{B}+\mathrm{rO})}$$

where r_A, r_B and r_O are the ionic radii of A and B cations and oxygen, respectively. If $t > 1$ hexagonal or tetragonal, $0.9 < t < 1$ cubic, $0.71 < t < 0.9$ orthorhombic / rhombohedral, < 0.71 different structures, eg. trigonal (Liu *et al*., 2008).

Pervoskite is mixed oxide of transition metals with chemical formula ABO_3, where A is a transition metal or lanthanide series cation (Farhadi and Sepahvand, 2010). The structure of pervoskite is a face-centered cubic cell of cation A and anion O. In the unit cell, cation A locates at the cubic corner and B at the center of the lattice (Athayde *et al*., 2016). Several properties such as structures, electronic and magnetic properties of these compounds depends on the type of cations A and B.

The preparation of highly homogeneous and fine perovskite powders at lower temperature through other methods such as nitrate molten salts process, coprecipitation technique, citrate sol-gel method and glycine combustion method has attracted a great deal of interest. In some of the sol-gel processes, using expensive metal alkoxides that make it difficult to control the condition of the process led us toward employing the low-cost polymeric Pechini sol-gel technique which is based on using metal salts, a hydrocarboxylic acid which is mainly citric acid as a chelating agent and ethylene glycol to establish esterification reaction with citric acid (Zahra *et al.*, 2016). By this method, it is possible to control the particle size and can reduce the agglomeration of nanoparticles. In citrate sol-gel auto combustion route, at very low temperature excellent chemical homogeneity can be achieved. The nanopowders thus obtained have uniform particle size which allows sintering to give uniformly grained microstructures.

In the present work, the preparation of the perovskite base $LaCo_{0.6}Fe_{0.4}O_3$ nanocrystalline powders by citrate sol-gel method at different temperatures. The prepared calcined powders were characterized by XRD in order to investigate phase purification and structures. The characterization of the perovskite-based $LaCo_{1-x}Fe_xO_3$ ($0.1 \leq x \leq 0.4$) nanocrystalline powders were prepared at optimum temperature by citrate sol-gel method. The prepared nanocrystalline powders were also characterized by XRD, SEM, FT IR, EDXRF and TG-DTA techniques.

Materials and Methods

All of the chemicals used were analytical grade. $La(NO_3)_3.6H_2O$ was product from Leap Lab Chem Co.Ltd, China. $Fe(NO_3)_3.9H_2O$ and $Co(NO_3)_2.6H_2O$ were products from Oxford Lab Chem Co.Ltd and citric acid were products from Alpha Chemika Co.Ltd, India. Ethylene glycol was product from Dow Chemical Co.Ltd, Germany.

Various conventional and modern instruments techniques were used throughout the experimental procedure. These include Thermogravimetry /Differential Thermal Analysis (TG-DTA), X-ray Diffractometry (XRD), Energy Dispersive X-ray Fluorescence (EDXRF), Fourier Transform Infrared Spectroscopy (FT IR) and Scanning Electron Microscope (SEM).

Preparation of $LaCo_xFe_{1-x}O_3$ Nanocrystalline Powders

$LaCo_xFe_{1-x}O_3$ nanocrystalline powder was prepared by sol-gel method using $La(NO_3)_3.6H_2O$, $Fe(NO_3)_3.9H_2O$, $Co(NO_3)_2.6H_2O$, citric acid and ethylene glycol. The precursor solution was prepared by mixing metal nitrates, citric acid and deionized water. The solution was ultra-sonicated for complete dissolution of metal cations in solution. The molar ratio of citric acid to the metal cation was 2:1. The solution was well stirred using magnetic stirrer and heated to about 60 °C. Ethylene glycol was added to the above solution in the molar ratio as 3:1 with citric acid. The resultant solution was heated and stirred on the magnetic stirrer to about 90 °C and then transferred to oil bath at 120 °C in order to form gel and finally heated at 300 °C in the furnace. Dried gels were ground and then calcined at 400 to 700°C for 4 h in air. Finally the samples were ground smoothly in an agitate mortar. $LaCo_{0.6}Fe_{0.4}O_3$, $LaCo_{0.7}Fe_{0.3}O_3$, $LaCo_{0.8}Fe_{0.2}O_3$ and $LaCo_{0.9}Fe_{0.1}O_3$ samples were also prepared by the above same method (Zahra *et al.*, 2016).

Characterization Techniques

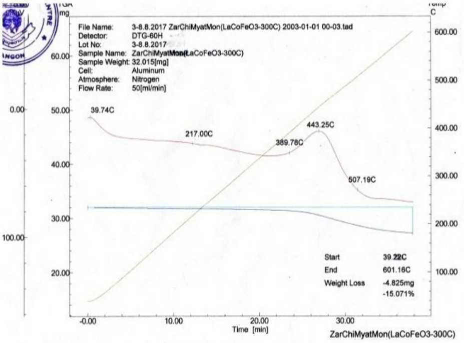
Crystal structure and phase analysis of prepared powders were performed by X-ray diffraction (XRD) using XRD-2000 diffractometer, Enraf Nonius Co., Bohemin NY, Physics Department, Yangon University. Morphology of the prepared powder was recorded by scanning electron microscope (SEM) EVO-18, ZEISS, Germany. FT IR transmission spectra in the region from 400-4000 cm^{-1} were measured by using Perkin Elmer GX system FT IR spectrophotometer. The thermal decomposition behaviours of the $LaCo_xFe_{1-x}O_3$ precursors were examined by means of thermogravimetric and differential thermal analysis (TG-DTA) by using Simultaneous TGA-DTA (DTG-6OH), Thermal analyzer, Shimadzu, Japan. Energy dispersive X-ray fluorescence (EDXRF) analysis confirms the elemental compositions of the prepared sample by using Shimadzu model EDX-8000, EDXRF spectrometer.

Results and Discussions

Characterization of the $LaCo_{0.6}Fe_{0.4}O_3$, $LaCo_{0.7}Fe_{0.3}O_3$, $LaCo_{0.8}Fe_{0.2}O_3$ and $LaCo_{0.9}Fe_{0.1}O_3$ Prepared Samples

TG-DTA analysis

Thermal decomposition of the prepared $LaCo_{1-x}Fe_xO_3$ precursor powders heated at 300°C are shown in Figures 1-4 and thermal stability of the prepared $LaCo_{1-x}Fe_xO_3$ nanocrystalline powders calcined at 600°C are shown in Figures 5-8 and their total weight loss are listed in Table 1. It was found that the prepared samples calcined at 300 °C, the temperature range between 38-140°C, an endothermic peak was observed and the weight loss was due to the removal of water and moisture. At the temperature range between 140-300°C, the weight loss is due to the degradation of organic matter. In the temperature range between 300-600, °C an exothermic peak was observed and the final weight loss is due to the burning of volatile materials and char. It was found that in the prepared samples calcined at 600°C, the weight loss percent of all sample was very low and therefore thermally stability of all prepared samples was observed above the temperature of 600 °C. So, the prepared samples are pure and have thermal stability.



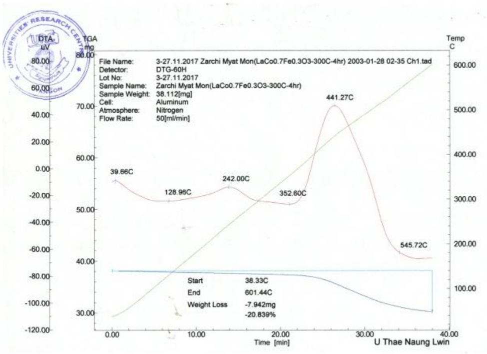


Figure 1: TG-DTA thermogram for the $LaCo_{0.6}Fe_{0.4}O_3$ heated at 300°C

Figure 2: TG-DTA thermogram for the $LaCo_{0.7}Fe_{0.3}O_3$ heated at 300 °C

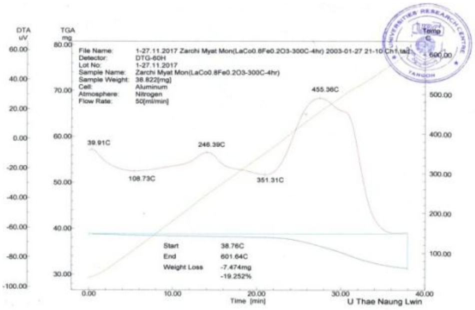


Figure 3: TG-DTA thermogram for the $LaCo_{0.8}Fe_{0.2}O_3$ heated at 300 °C

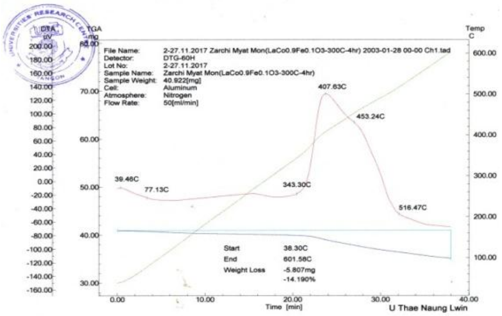


Figure 4: DTA thermogram for the $LaCo_{0.9}Fe_{0.1}O_3$ heated at 300 °C

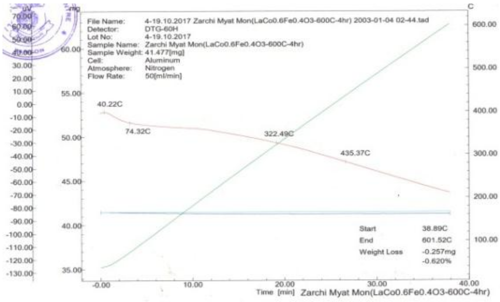


Figure 5: TG-DTA thermogram for the $LaCo_{0.6}Fe_{0.4}O_3$ calcined at 600 °C

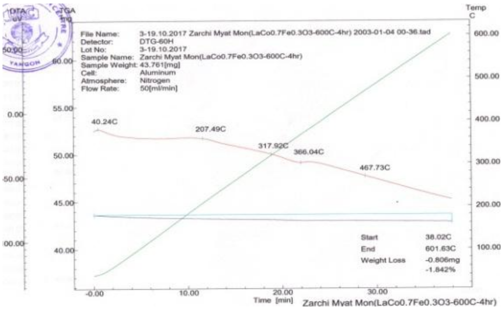


Figure 6: TG-DTA thermogram for theLaCo0.7Fe0.3O3calcined at 600 °C

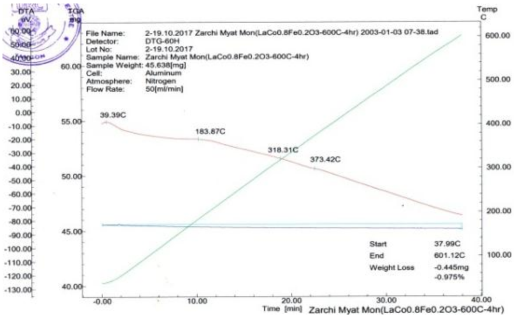


Figure 7: TG-DTA thermogram for the $LaCo_{0.8}Fe_{0.2}O_3$ calcined at 600 °C

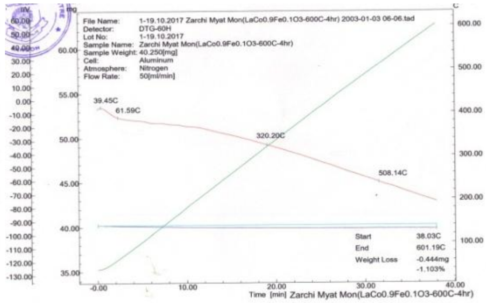


Figure 8: TG-DTA thermogram for the $LaCo_{0.9}Fe_{0.1}O_3$ calcined at 600 °C

Table 1: Thermal Analysis Data of $LaCo_{1-x}Fe_xO_3$ ($0.1 \leq X \leq 0.4$) Compounds calcined at 600 °C for 4 Hours

Sample	Weight loss (%)
$LaCo_{0.6}Fe_{0.4}O_3$	0.62
$LaCo_{0.7}Fe_{0.3}O_3$	1.84
$LaCo_{0.8}Fe_{0.2}O_3$	0.97
$LaCo_{0.9}Fe_{0.1}O_3$	1.10

XRD analysis

The XRD patterns of the prepared samples calcined at different temperatures are shown in Figure 9-12 and XRD patterns of $LaCo_{1-x}Fe_xO_3$ ($0.1 \leq X \leq 0.4$) powders calcined at 600°C are shown in Figures 10, 13-15 and their lattice parameters and average crystallite sizes are summarized in Table 3. LCFO-SG-I was found that single phase perovskite structure was obtained after calcination at 500 °C. LCFO-SG-I sample calcined at 600°C was selected as optimum temperature because at that temperature the sample showed high crystallinity and single phase with small average crystallite size. From XRD patterns, the prepared $LaCo_{1-x}Fe_xO_3$ powders calcined at 600 °C also showed single perovskite phase and good crystallinity. It was also found that crystal structure of the prepared samples were matched with those calculated from tolerance factor and they were found to have hexagonal crystal structure.

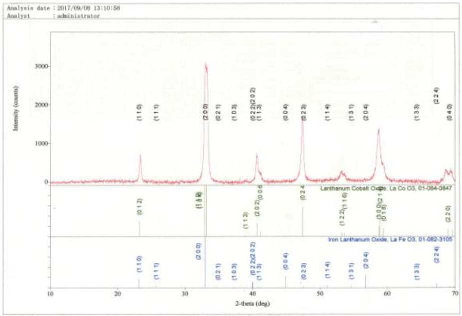


Figure 9: XRD patterns of LCFO-SG-I nanocrystalline powders calcined at 500 °C

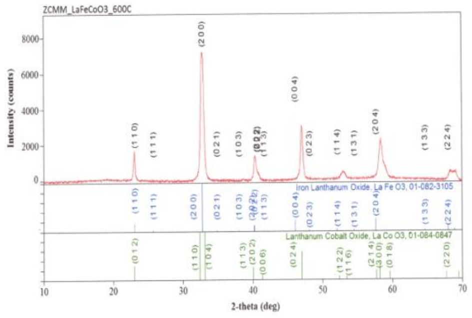


Figure 10: XRD patterns of LCFO-SG-I nanocrystalline powder calcined at 600

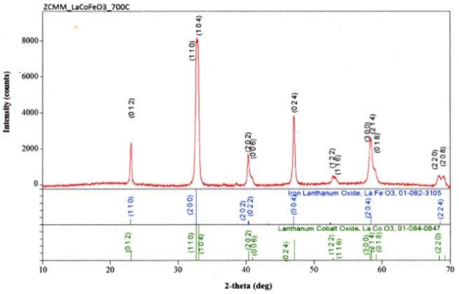


Figure 11: XRD patterns of LCFO-SG-I nanocrystalline powders calcined at 700 °C

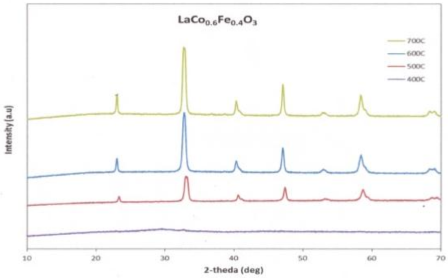


Figure 12: XRD patterns of LCFO-SG-I nanocrystalline powder calcined at different temperature

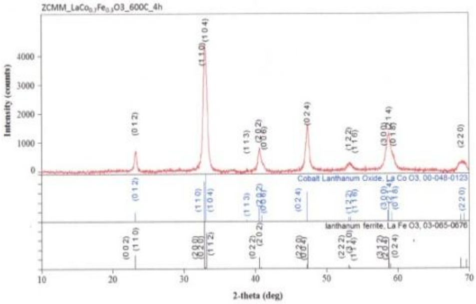


Figure 13: XRD patterns of $LaCo_{0.7}$ $Fe_{0.3}O_3$ nanocrystalline powder calcined at 600 °C

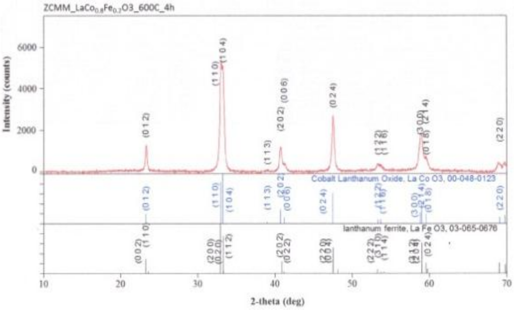


Figure 14: XRD patterns of $LaCo_{0.8}$ $Fe_{0.2}O_3$ nanocrystalline powder calcined at 600 °C

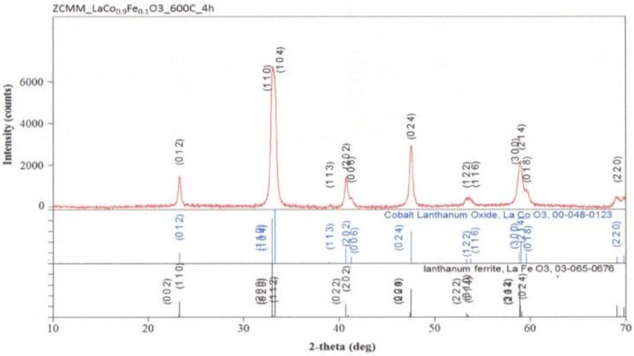


Figure 15: XRD patterns of $LaCo_{0.9}Fe_{0.1}O_3$nanocrystalline powder calcined at 600 °

Table 2: Lattice Parameters (a and c) and the Average Crystallite Size (D) of LCFO Powders Calcined at Different Temperatures

Calcined Temperature (° C)	Lattice Parameters		D / nm
	a / Å	c / Å	
400	-	-	-
500	5.4438	13.1682	22.20
600	5.5281	13.0971	20.60
700	5.4822	13.2132	25.46

Table 3: Lattice Parameters (a and c) and the Average Crystallite size (D) of LCFO Nanocrystalline Powders Calcined at 600 °C

Samples	Lattice Parameters		Crystal System		Average Crystallite Size/ nm
	a / Å	c / Å	XRD	Calculated tolerance factor	
LCFO-SG-I	5.5281	13.0971	Hexagonal	1.0244	20.6
LCFO-SG-II	5.4512	13.2319	Hexagonal	1.0266	15.7
LCFO-SG-III	5.4351	13.1401	Hexagonal	1.0288	24.2
LCFO-SG-IV	5.4343	13.1280	Hexagonal	1.0310	27.1

EDXRF analysis

The relative advance of the elements in $LaCo_{1-x}Fe_xO_3$ nanocrystalline powders are described in Figures 16 to 19 and their relative abundance of elements are listed in Table 4. According to the experimental results, La, Co and Fe are major constituents of the prepared sample and the stoichiometric ratio of the resulting compound are found to match with their relative abundance of elements.

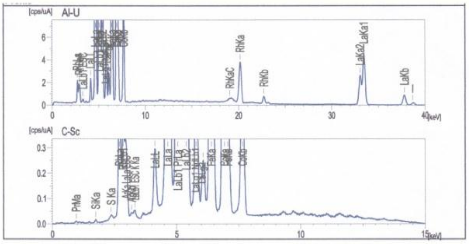


Figure 16: EDXRF spectrum of La $Co_{0.6}Fe_{0.4}O_3$ nanocrystalline powder

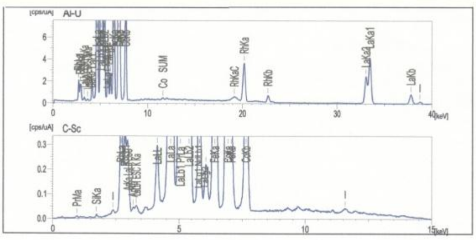


Figure 17: EDXRF spectrum of $LaCo_{0.7} Fe_{0.3}O_3$ nanocrystalline powder

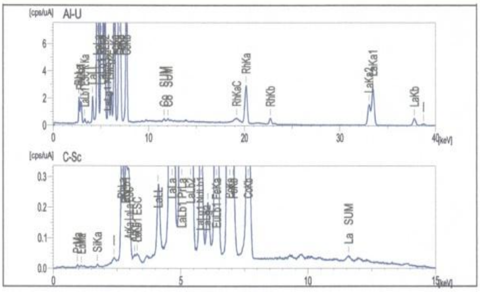


Figure 18: EDXRF spectrum of $LaCo_{0.8}Fe_{0.2}O_3$ nanocrystalline powder

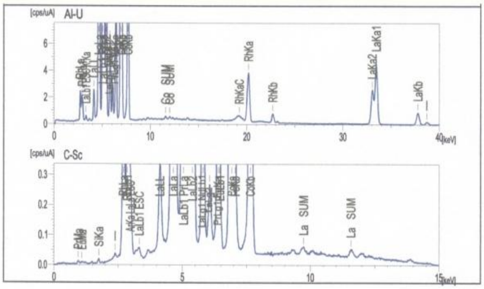


Figure 19: EDXRF spectrum of $LaCo_{0.9}Fe_{0.1}O_3$ nanocrystalline powder

Table 4: Relative Abundance of Elements in $LaCo_{1-x}Fe_xO_3$ Nanocrystalline Powders (EDXRF)

Elements	Relative Abundance of Elements in the Samples (%)			
	LCFO-SG-I	LCFO-SG-II	LCFO-SG-III	LCFO-SG-IV
La	60.818	61.657	61.336	61.510
Co	14.480	18.100	21.060	23.586
Fe	10.893	6.912	4.478	1.942

FT IR Analysis

FT IR spectrum of $LaCo_{1-x}Fe_xO_3$ nanocrystalline powders are presented in Figure 20. The small bands at 3400 and 3000 cm^{-1}are assigned to stretching vibration of O-H group. The small band observed between 1470 and 1390 cm^{-1} is due to C-H stretching of residual carbon. The bands around 650 and 400 cm^{-1}are characteristics of metal-oxygen bond stretching vibration.

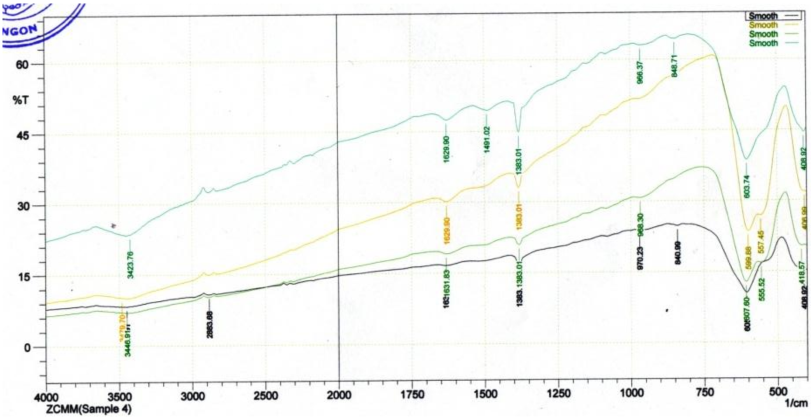


Figure 20: FT IR spectra of LaCoFeO$_3$ nanopowders (a) LaCo$_{0.6}$Fe$_{0.4}$O$_3$ (b) LaCo$_{0.7}$Fe$_{0.3}$O$_3$ (c) LaCo$_{0.8}$Fe$_{0.2}$O$_3$ and (d) LaCo$_{0.9}$Fe$_{0.1}$O$_3$

SEM Analysis

SEM micrographs of the LaCo$_{1-x}$Fe$_x$O$_3$ samples are shown in Figures 21 to 24. It was found that the prepared sample agglomeration of LCFO-SG-I is much less than other three compounds. It was observed that agglomeration decreased with increasing Fe doping levels. The LCFO-SG-IV was found to have higher porosity than other three compounds and it could be concluded that the porosity decreased with increasing Fe doping levels.

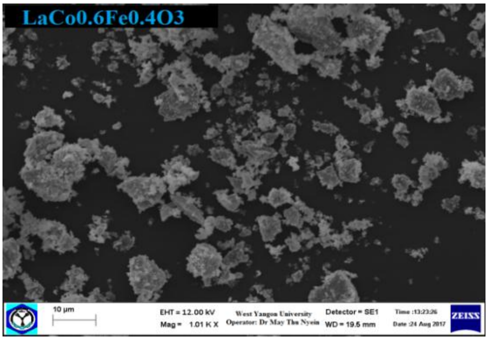


Figure 21: SEM micrograph of LaCo$_{0.6}$Fe$_{0.4}$O$_3$ nanocrystalline powder

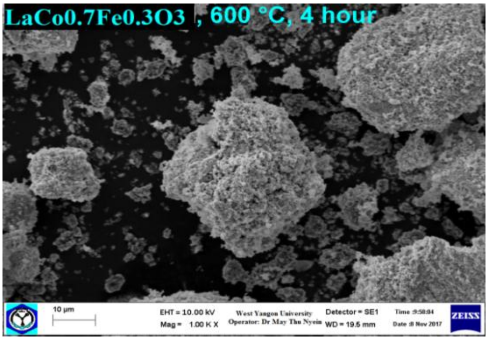


Figure 22: SEM micrograph of LaCo$_{0.7}$Fe$_{0.3}$O$_3$ nanocrystalline powder

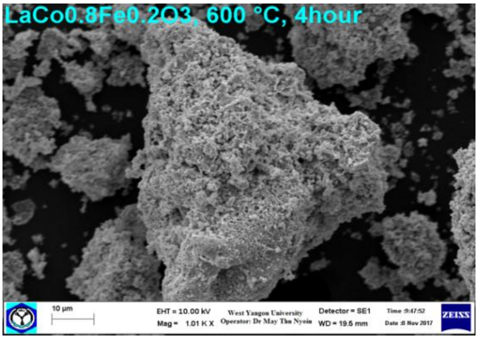


Figure 23: SEM micrograph of $LaCo_{0.8}Fe_{0.2}O_3$ nanocrystalline powder

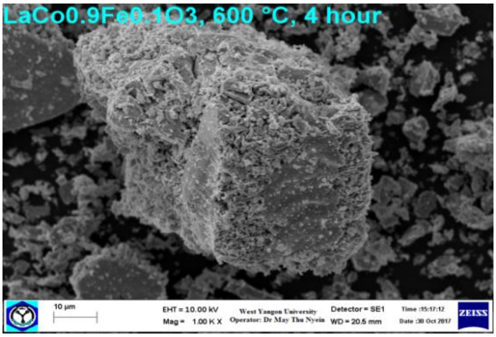


Figure 24: SEM micrograph of $LaCo_{0.9}Fe_{0.1}O_3$ nanocrystalline powder

Conclusion

$LaCo_{0.6}Fe_{0.4}O_3$nanocrystalline powder was prepared by citrate sol-gel method at different calcinations temperature. XRD confirms the formation of perovskite structure and the average particle size confirms their nanosized nature. The average crystallite sizes are 22.20 nm at 500 °C, 20.60 nm at 600°C and 25.46 nm at 700 °C. The calcination temperature 600 °C was selected as optimum temperature because it had high crystallinity and small crystallite size at that temperature. The samples $LaCo_{0.6}Fe_{0.4}O_3$, $LaCo_{0.7}Fe_{0.3}O_3$, $LaCo_{0.8}Fe_{0.2}O_3$ and $LaCo_{0.9}Fe_{0.1}O_3$ were also prepared at the selected temperature 600°C. Thermal analysis of the precursor powders heated at 300 °C revealed that crystallization temperature were around 500 °C. From FT IR analysis, only obvious stretching metal oxygen bond vibration were observed and the band observed between 1470 and 1390 cm^{-1} is due to C-H stretching of residual carbon. It indicated the purity of the prepared compounds. Relative abundances of elements analysed by EDXRF showed the presence of lanthanum, cobalt and iron as major elements in the prepared samples. Agglomeration of $LaCo_{0.6}Fe_{0.4}O_3$ was much lesser than other three compounds. The $LaCo_{0.9}Fe_{0.1}O_3$ had higher porosity than other three compounds and it could be concluded that the porosity decreased with increasing Fe doping levels. From above analyses, the prepared samples have desired phases, purity and structures. They will have potential for further applications.

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