The Effect of Fe and Mn Substitution on Structural and Electrical Properties of LaCoO₃ Nanoparticles

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Abstract: Pure and Fe, Mn doped LaCoO₃ nanoparticles are primed by sol gel ignition method, and their electrical properties are studied. All the materials were characterized to study the structure and morphology. The chemical composition of the samples was analysed by EDAX analysis revealing that La, Co, O (Mn, Fe) compounds were present. Electrical properties were identified in impedance analysis and the conductivity of the materials was calculated. And it is found that Fe doped LaCoO₃ possesses higher conductivity than all others.

Keywords: Sol-gel ignition method, LaCoO₃.

I. INTRODUCTION

To meet the future needs of power generation, high energy density technologies like fuel cells and batteries are considered as an efficient source to store energy. And the solid oxide fuel cell has been attracting the greatest attention as a promising technology for electrical power generation due to its high energy conversion and fuel efficiency. It has a potential for high energy conversion of greater than 70% with low emission of pollutants. But the main drawback in SOFC is its high operating temperature (800-1000 °C). The challenge in the development of solid oxide fuel cells is to lower the functional temperature to 500 – 700 °C [1].

To overcome the drawbacks in the performance of SOFC, new technical approaches have been in under consideration. Some of the major considerations are to improve the performance of SOFC cathodes that are catalytically active and electrically conductive [2]. In particular, Perovskite structure with rare earth metals (La) and transition metal cations (Mn, Fe, Co, Ni) meet the considerations of SOFC including high electrical conductivity and structural and chemical stability.

The Perovskite oxides are a known group in the universal formula of ABO_3, in which A represents rare earth or alkaline-earth metal and B transition metal oxide [3]. Suitable A and B site substitutions on perovskite oxides offer improved flexibility in redox active sites and oxygen vacancies and physical and chemical properties. Perovskite oxides have a range of applications in various fields as a result of their different compositions such as oxygen mobility, structure and excellent thermal stability, reduction-oxidation behaviour and electronic and ionic conductivity.

In the past two decades, Lanthanum Cobalt Oxide has been widely studied and it has many practical applications due to its unique electrical and thermoelectric properties.

In gas sensors and fuel cells Lanthanum Cobal Oxide can be used as an electrode material [4]. The properties of $LaCoO_3$ are strongly dependent on the preparation method, and it is vital to control the synthesis for highly pure, homogeneous, and high surface area particles. There are different types of methods opted to prepare $LaCoO_3$ nanoparticles such as co-precipitation method, sol gel combustion method, hydrothermal method, etc. The superior advantage of sol gel combustion method is its fast, exothermic and self-sustaining chemical reaction between the suitable organic fuel and metal nitrate. Sol gel combustion is a simple method and has been used to produce a homogeneous, crystalline method [5]. But the success of this method depends on the synthesis parameters.

In the present work pure and Mn, Fe doped $LaCoO_3$ nanoparticles were synthesized by sol gel combustion method and characterized.

II. MATERIALS AND METHOD

$LaCoO_3$ and Fe, Mn substituted $LaCoO_3$ was primed using sol-gel combustion method. High purity of nitrate compounds, Lanthanum nitrate, cobalt nitrate, Ferric nitrate and Manganese nitrate were taken in stoichiometric ratios to synthesis LCO, Fe-LCO, Mn-LCO. Ammonia solution was used to maintain pH throughout the synthesis (pH=7). The precursors were dissolved in de-ionized water. Citric acid was added to the dissolved solution. The solution was stirred continuously at 60°C for 1 hr. Then the solution was heated up to 70°C for formation of gel. On further heating gel started igniting and powder was formed. The obtained powder was ground and calcined at 650°C for 7 hrs in muffle furnace to achieve the perovskite type crystal.

A. Material Characterization

As prepared and doped $LaCoO_3$ powder was exposed to PANalytical X'pert PRO powder x-ray diffraction to interpret the structural analysis. The electrical properties of sintered samples were characterized by LCR meter (HIOKI 3532-50 LCR).

III. RESULT AND DISCUSSION

A. Structural Analysis

Fig.3.1. exhibits the XRD pattern of $LaCoO_3$ and Fe, Mn doped $LaCoO_3$. As observed, the diffracted peaks can be attributed to primitive cubic perovskite structure along with Pm3m space group. The XRD pattern clearly indicates the crystalline nature of pure and doped $LaCoO_3$ samples with preferred orientation (110) and it is exactly matched with JCPDS card no: 75-0279.

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Fig.1 it shows the invariance in structural characteristics due to the addition of foreign atom, which clearly indicates that the Fe, Mn atoms occupied the lattice structure. Their lattice parameters are calculated and are in good agreement with standard value. There is a small variation in cell volume, which may be due to the incorporation of dopant. XRD results reveal that the intensity of the peaks is relatively weak with addition of dopant and the shift in peak at lower angle side [6]. This fact can be explained due to point defect or electron density. As the Fe is doped with $LaCoO_3$ (ABO_3 perovskite type), the Co element is partially substituted by Fe., since Fe has higher ionic radii as compared to Co. Due to this intensity decreases and the peaks get broadened and widely similar for Mn dopant.
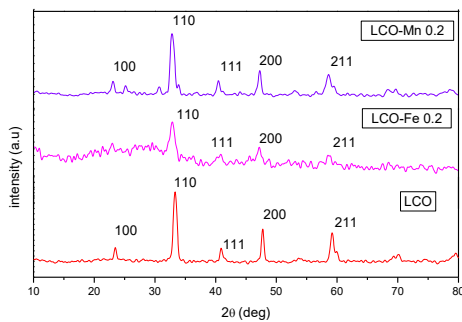

Fig. 1 XRD pattern of Pure and Fe, Mn doped $LaCoO_3$ nanoparticles

Table 1 Structural parameters

Sample	Grain size (nm)	Lattice parameter (a)	Volume (m³)
LaCoO₃	50.112	3.824	55.924
Fe-LaCoO₃	20.032	3.836	56.482
Mn-LaCoO₃	59.851	3.872	58.085

B. Surface Morphology

In furtherance of study the samples surface morphology prepared by sol gel citrate method is examined by a scanning electron microscope. The SEM images are shown in fig. (3.2a-c) for the samples. It is observed that all the samples are homogenous. All the samples show the presence of small grains along with a few larger grains. The formation of larger grains is correlated to the presence of agglomerate in the sample [7]. A significant improvement in the morphology of the samples is observed from the micrographs 3.2 a - 3.2 c. The decrease in agglomeration is observed when the dopant is added to the pure.
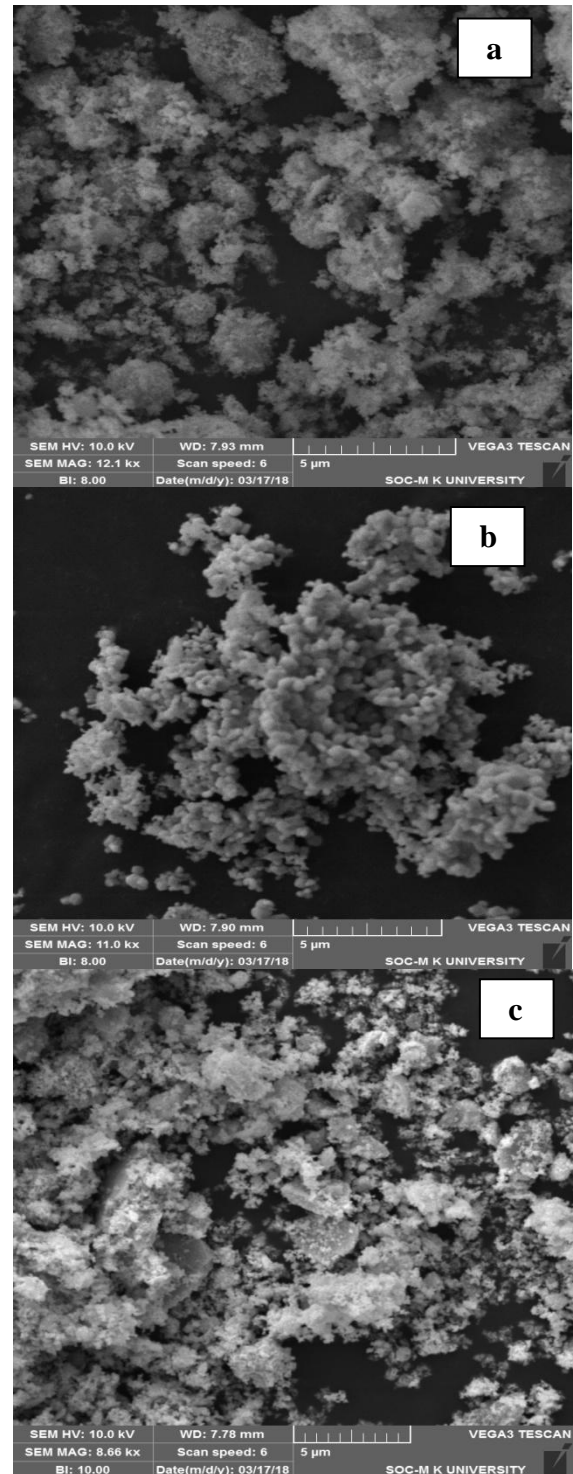

Fig. 2 (a-c) SEM images of LaCoO₃, Mn doped of LaCoO₃, Fe doped of LaCoO₃

C. Compositional Analysis

The elemental analysis of pure and doped $LaCoO_3$ samples has been calculated by EDAX. Fig. (3a-c) show the EDAX pattern for pure and doped samples. EDAX analysis indicates the presents of La, Co, Mn, Fe and O compounds for the corresponding samples. This confirms the homogenous mixing of La, Co, Mn, Fe and O.
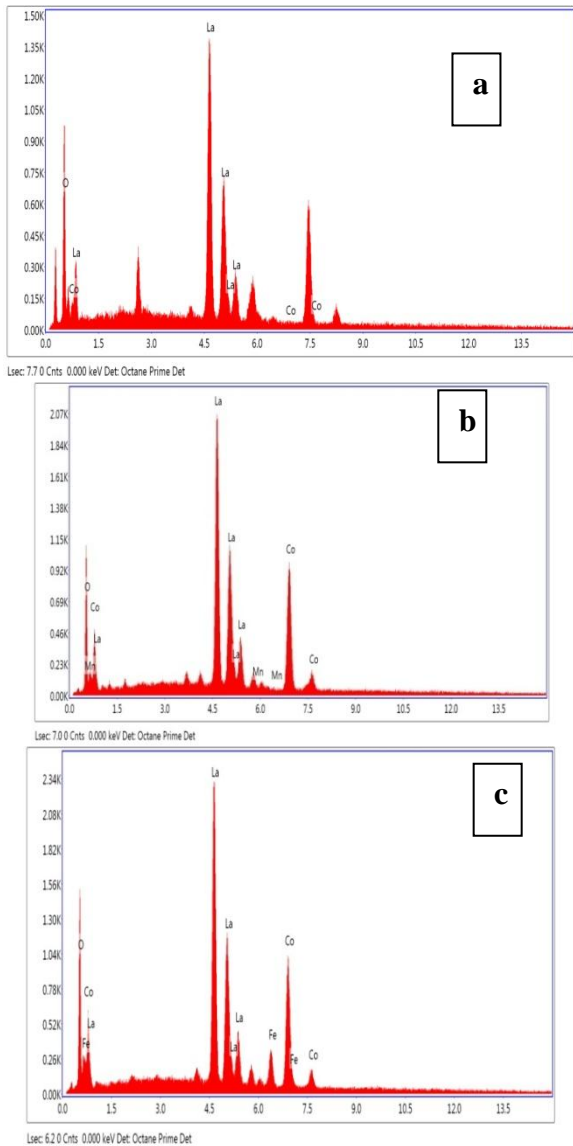
Fig. 3 (a-c) EDAX spectrum of LaCoO₃, Mn doped of LaCoO₃, Fe doped of LaCoO₃.

D. Impendence Analysis

The impedance spectroscopic analysis has been made to study the electrical transport properties of the prepared sample at different temperatures. Fig. 3.4 explains the Cole-cole plot of pure and Fe, Mn doped $LaCoO_3$ at different temperatures (313, 333, 353, 373 and 393 K). Cole-cole plot is a well-known tool used to study the electrical behaviour of the material when any changes are made in the sample like dopant or surface modification effects. The graph reveals the formation of single semicircle for all the temperatures [8]. The absence of grain boundary effect can be indentified from the development of single semi-circle that also indicates that the conductivity is mainly due the grain boundary effect [9]. The radius of the semi-circle is reduced when the temperature is increased, which shows a decrease in bulk resistance for all the samples, which implies the semi-conducting nature of the sample. The semi-circle is attributed to the parallel combination of bulk resistance R_b and bulk capacitance C_b. The capacitance value of the material can be calculated using $2\pi\gamma_{max}R_bC_b=1$ relation, and tabulated below (Table 2). The ionic conductivity of the material is also calculated using $\sigma =1/AR_b$ (Scm⁻¹) and the value is tabulated.
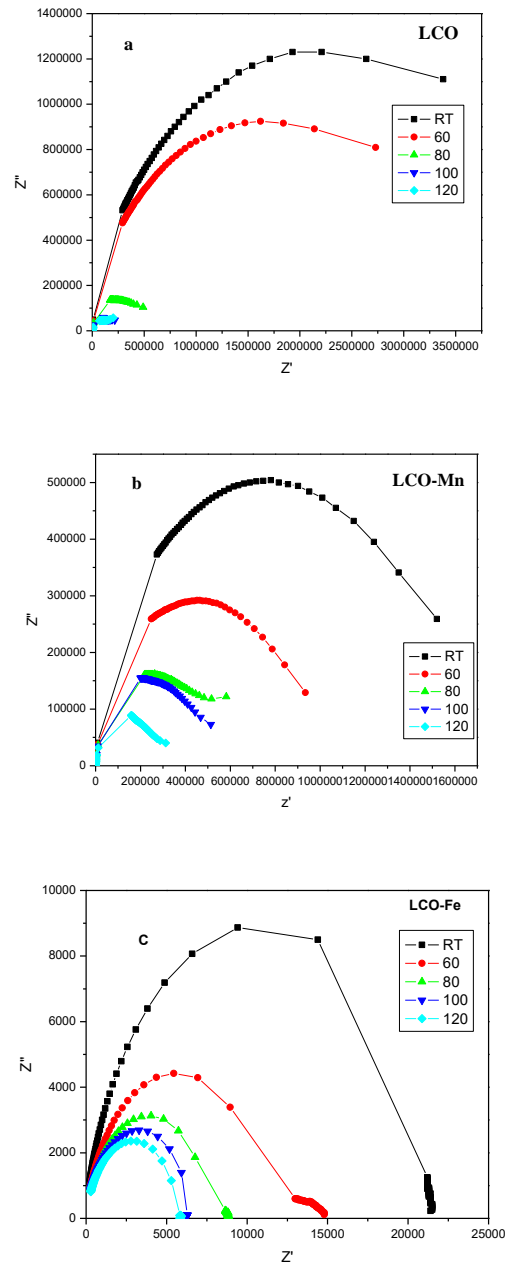

Fig. 4 Cole-cole plot of Pure LaCoO₃, Fe doped LaCoO₃ and Mn doped LaCoO₃ for different temperature.

Table 2 Electrical parameters of Pure LaCoO₃, Fe doped LaCoO₃ and Mn doped LaCoO₃ for different temperature.

Material	Temp	σ_dc (SCm⁻¹) 10⁻⁶		Diffusion Coefficient (D) x 10¹⁹ (Cm²S⁻¹)
		Cole cole	Conductance	
LCO	313	0.2286	0.2199	0.1608
	333	0.2838	0.2150	0.2211
	353	1.8513	2.3345	0.2266
	373	3.0708	2.6905	0.5873
	393	3.5230	3.0328	25.4158
LCO-Mn	313	0.2886	0.309	0.316
	333	0.4706	0.2706	0.402

353	0.7590	1.7207	0.461
373	1.8491	2.0768	1.127
393	14.102	18.130	7.014
313	6.21	6.13	7.321
333	14.80	10.15	11.775
LCO-Fe 353	22.23	16.13	20.568
373	24.39	22.36	25.485
393	26.57	23.96	28.167

E. Conductivity Spectra Analysis

The dc electrical conductivity spectrum of pure and Fe, Mn doped LaCoO₃ is shown in the figure 3.5. From the conductance spectra each curve consists of two different regions: low frequency flat terrain region corresponds to direct current component and high frequency dispersive region corresponds to alternating current conductivity. The conductivity of material found increases with increase in temperature and it could be due to the increase in thermally active hopping rate. When the temperature increases, there is a shift in hopping frequency towards the higher frequency. This behaviour reveals that the conduction in the material occurs via hopping mechanics governed by Jonscher's power equation [10]

$$\sigma(\omega) = \sigma_{ac} + A\omega^n$$

Whereas n indicates a frequency exponent, A and n are temperature-dependent parameters which represent the thermally activated conduction process. The conductivity increases for all the samples with increase in temperature. The maximum conductivity is observed for Fe doped LaCoO₃ (2.396×10^{-5} S Cm^{-1}) compared to LaCoO₃ (3.032×10^{-6}) and Mn doped LaCoO₃ (1.813×10^{-5} S Cm^{-1}) at 393 K. The diffusion constant of the samples was calculated using the relation $D = (\sigma K_B T)/Ne^2$ where D is diffusion, σ electrical conductivity (S Cm^{-1}) K_B Boltzmann constant.
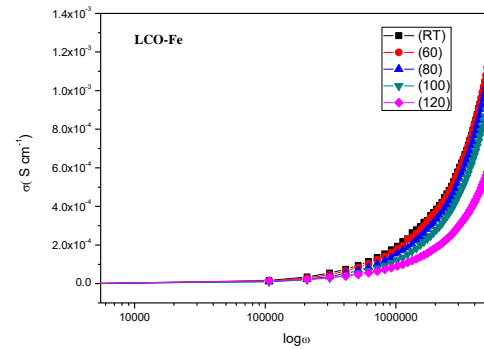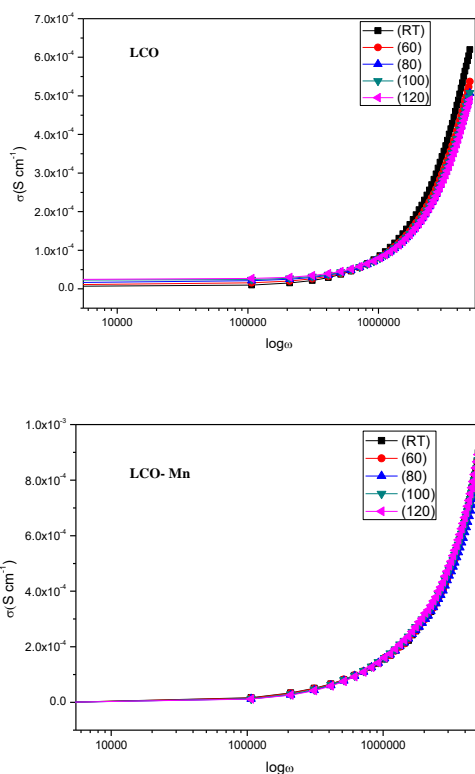

Fig. 5 Conductance spectra of Pure LaCoO₃, Fe doped LaCoO₃ and Mn doped LaCoO₃ for different temperature.

VI. CONCLUSION

Fe doped, Mn doped LaCoO₃ and undoped LaCoO₃ samples were synthesised by sol gel combustion method. The structural parameters were analysed by XRD revealing the formation of cubic structured LaCoO₃ with no impurity peaks, and the grain size of the samples was also calculated. Surface morphology reveals that some agglomeration is seen. The impedance analysis shows that the R_b value decreases when there is increase in temperature, showing the negative temperature coefficient effect. The maximum conductivity is obtained for Fe doped LaCoO₃ at 393K which shows the good conducting nature of the sample compared to other two samples.

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